

Supporting Information

for the Communication Entitled

A Stable Neutral Stannaaromatic Compound: Synthesis, Structure and Complexation of a Kinetically Stabilized 2-Stannanaphthalene

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General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (GlassContour Company).¹ ¹H NMR (300 MHz), ¹³C NMR (76 MHz), and ¹¹⁹Sn NMR (111 MHz) spectra were measured in CDCl₃ or C₆D₆ with a JEOL JNM-AL300 spectrometer. In ¹H NMR signals due to CHCl₃ (7.25 ppm) and C₆D₅H (7.15 ppm) were used as references, and those due to CDCl₃ (77 ppm) and C₆D₆ (128 ppm) were used in ¹³C NMR. ¹¹⁹Sn NMR was measured with NNE technique using SnMe₄ as an external standard. Multiplicity of signals in ¹³C NMR spectra was determined by DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-SX102GC/MS spectrometer. WCC (wet column chromatography) was performed on Wakogel C-200. PTLC (preparative thin-layer chromatography) was performed with Merck Kieselgel 60 PF254 (Art. No. 7747). GLPC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. TbtSnX₃ was prepared according to the reported procedures of TbtSnCl₃² and used without sublimation.

Synthesis of 4 via 3. To a THF solution (16 mL) of **2** (493 mg, 1.64 mmol) was added *n*-butyllithium (1.5 M in hexane, 2.2 mL, 3.3 mmol) at –78 °C. After stirring at the same temperature for 10 min, THF solution (33 mL) of TbtSnX₃ (X = Cl or Br, ca. 75% purity; 1.63 g, ca 1.6 mmol as X = Cl) was added to the mixture. After stirring for 3 h at –78 °C, the reaction mixture was warmed to room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. The residue was separated by GLPC (CHCl₃) to afford 3-*t*-Bu-2-Tbt-2-X-1,2-dihydro-2-stannanaphthalene **A** (567 mg, X: Cl/Br = 7/3). To a THF solution (10 mL) of **A** was added lithium aluminum hydride (88.5 mg, 2.33 mmol) at 0 °C. After stirring for 1 h at the same temperature, ethyl acetate was added to the reaction mixture at 0 °C. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. This crude product was separated by WCC

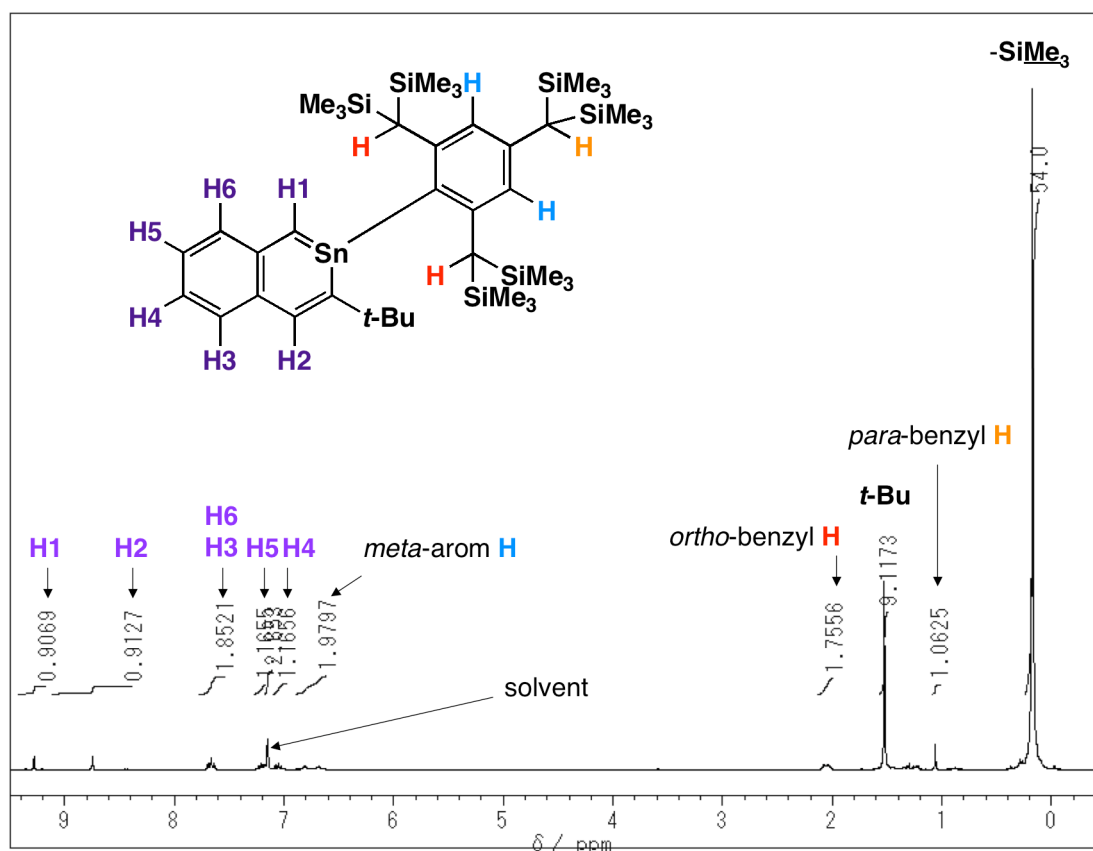
(hexane) to afford **4** (509 mg, 0.603 mmol, 37%, from **2**). **4**: colorless crystals; m.p. 179-181 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 0.05 (s, 9H), 0.10 (s, 9H), 0.137 (s, 9H), 0.144 (s, 9H), 0.16 (s, 9H), 0.21 (s, 9H), 1.39 (s, 9H), 1.44 (s, 1H), 1.65 (br s, 1H), 2.34 (br s, 1H), 2.58 (d, ²J = 15.0 Hz, 1H), 2.78 (dd, ²J = 15.0 Hz, ³J = 0.9 Hz, 1H), 5.95 (d, ³J = 0.9 Hz, 1H), 6.52 (br s, 1H), 6.67 (br s, 1H), 6.91-7.10 (m, 5H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 0.96 (q), 1.00 (q), 1.18 (q), 17.21 (t), 30.63 (d), 32.12 (d), 32.24 (q), 32.88 (d), 37.81 (s), 122.29 (d), 125.98 (d), 127.12 (d), 127.35 (d), 132.95 (d), 133.50 (d), 135.91 (s), 135.95 (s), 139.61 (d), 143.92 (s), 151.79 (s×2), 158.66 (s); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ -293.3; High resolution FAB-MS *m/z* calcd for C₄₀H₇₆Si₆¹²⁰Sn ([M]⁺): 844.3585, found: 844.3589. Anal. Calcd for C₄₀H₇₆Si₆Sn: C, 56.91; H, 9.07. Found: C, 56.93; H, 9.23.

Synthesis of 5. A benzene (50 mL) solution of **4** (509 mg, 0.603 mmol) and *N*-bromosuccinimide (118 mg, 0.663 mmol) was stirred for 1 h at room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed to afford **5** (509 mg, 0.552 mmol, 91%). **5**: colorless crystals; m.p. 162-165 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ -0.13 (s, 9H), -0.03 (s, 9H), -0.01 (s, 9H), 0.04 (s, 18H), 0.11 (s, 9H), 1.25 (s, 1H), 1.39 (s, 9H), 1.59 (br s, 1H), 2.42 (s, 1H), 3.02 (d, *J* = 15.0 Hz, 1H), 3.24 (d, *J* = 15.0 Hz, 1H), 6.29 (br s, 1H), 6.44 (br s, 1H), 7.01-7.11 (m, 5H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 0.96 (q), 0.98 (q), 1.21 (q), 30.44 (t), 30.83 (d), 31.24 (d), 31.75 (d), 33.09 (q), 38.51 (s), 123.46 (d), 126.41 (d), 127.48 (d), 128.00 (d), 132.55 (d), 133.65 (d), 134.02 (s), 135.81 (s), 136.10 (s), 142.01 (d), 145.42 (s), 151.13 (s), 152.35 (s), 160.65 (s); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ -93.0; High resolution FAB-MS *m/z* calcd for C₄₀H₇₅⁷⁹BrSi₆¹²⁰Sn ([M]⁺): 922.2690, found: 922.2695. Anal. Calcd for C₄₀H₇₅BrSi₆Sn: C, 52.04; H, 8.19. Found: C, 52.31; H, 8.44.

Synthesis of 1a. In a glovebox filled with argon, **5** (46.2 mg, 0.0500 mmol) was dissolved in hexane (2 mL, dried over K mirror and distilled by trap-to-trap method), and LDA (2.0 M in heptane/THF/ethylbenzene, 0.0300 mL, 0.0600 mmol) was added to the solution at -40 °C. After stirring for 1 h at room temperature, the solvents were removed under reduced pressure and hexane

was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. The residue was recrystallized from hexane to give **1a** (26.7 mg, 0.0317 mmol, 63%). **1a**: yellow crystals; m.p. 144-147 °C (dec.); ¹H NMR (300 MHz, C₆D₆, rt): δ 0.18 (br s, 54H), 1.06 (s, 1H), 1.53 (s, 9H), 2.04 (br s, 1H), 2.08 (s, 1H), 6.68 (br s, 1H), 6.81 (br s, 1H), 7.05 (dd, ³J = 9 Hz, ³J = 7 Hz, 1H), 7.21 (dd, ³J = 9 Hz, ³J = 7 Hz, 1H), 7.65 (d, ³J = 9 Hz, 1H), 7.68 (d, ³J = 9 Hz, 1H), 8.75 (s, 1H), 9.28 (s, 1H); ¹³C NMR (75 MHz, C₆D₆, rt): δ 0.91 (q), 1.55 (q), 30.84 (d), 34.93 (q), 39.36 (d), 39.72 (s), 39.90 (q), 119.97 (d), 122.12 (d), 125.30 (d), 125.92 (s), 126.76 (d), 127.93 (d), 135.39 (d), 141.58 (s), 142.22 (d), 146.02 (s), 147.26 (s), 147.38 (d), 150.92 (s×2), 174.03 (s); ¹¹⁹Sn NMR (111 MHz, C₆D₆, rt): δ 264; High resolution FAB-MS *m/z* calcd for C₄₀H₇₅Si₆¹²⁰Sn ([M+H]⁺): 843.3506, found: 843.3531. Since it was difficult to obtain the satisfactory data of the elemental analysis due to the extremely high air- and moisture-sensitivity, the purity was confirmed by the ¹H NMR spectrum as shown below.

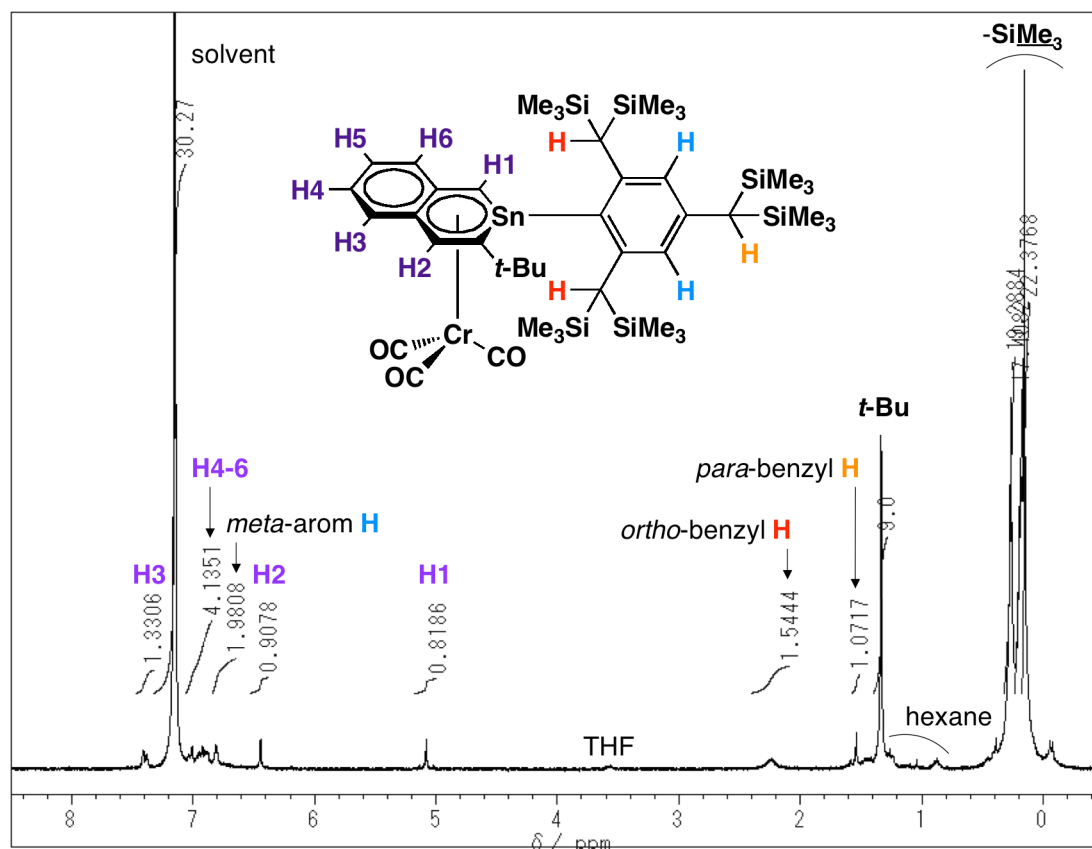
¹H NMR (300 MHz, C₆D₆, 298 K) spectrum of **1a**.



Crystal data for 1a. $C_{40}H_{74}Si_6Sn$ $MW = 842.22$; *triclinic*; space group $P\bar{1}$ (#2); $a = 12.4261(3)$, $b = 13.0149(3)$ Å, $c = 17.3641(6)$ Å; $\alpha = 73.4934(10)^\circ$, $\beta = 74.3341(12)^\circ$, $\gamma = 65.548(2)^\circ$; $V = 2376.69(11)$ Å³; $Z = 2$; $D_{\text{calcd}} = 1.177$ g/cm³; $\mu = 0.713$ mm⁻¹; $2\theta_{\text{max}} = 50^\circ$; $T = 103$ K; $R_1(I > 2\sigma(I)) = 0.0655$; wR_2 (all data) = 0.1534; GOF = 1.066 for 24587 reflections and 445 parameters.

Synthesis of 6a. In a glovebox filled with argon, **1a** (34.2 mg, 0.0406 mmol) and $[Cr(CH_3CN)_3(CO)_3]^3$ (14.6 mg, 0.0563 mmol) were dissolved in THF (1 mL, dried over K mirror and distilled by trap-to-trap method) at room temperature. After stirring for 4 h, the solvents were removed under reduced pressure and hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed to give almost pure **6a** (35.5 mg, 0.0363 mmol, 89%). **6a**: brown crystals; m.p. 154 °C (dec.); ¹H NMR (300 MHz, C₆D₆, 70 °C) δ 0.16 (s, 18H), 0.18 (s, 18H), 0.27 (s, 18H), 1.33 (s, 9H), 1.58 (s, 1H), 2.24 (s, 2H), 5.07 (s, 1H), 6.44 (s, 1H), 6.81 (br s, 2H), 6.90-7.01 (m, 3H), 7.38-7.41 (d, ³ $J = 8$ Hz, 1H); ¹³C NMR (75 MHz, C₆D₆, 50 °C) δ 0.86 (q), 0.95 (q), 1.34 (q), 31.42 (d), 34.31 (q), 38.40 (s), 39.79 (d), 40.27 (d), 88.37 (d), 96.41 (s), 102.75 (d), 116.84 (s), 122.70 (d), 125.19 (d), 125.70 (d), 128.68 (d), 131.31 (s), 132.89 (d), 134.59 (d), 134.91 (s), 147.69 (s), 151.87 (s×2), 233.77 (s, C=O); ¹¹⁹Sn NMR (111 MHz, 50 °C, C₆D₆) δ 106. High resolution FAB-MS m/z calcd for $C_{43}H_{74}O_3CrSi_6^{120}Sn$ ($[M]^+$): 978.2681, found: 978.2675. Since it was difficult to obtain the satisfactory data of the elemental analysis due to the extremely high air- and moisture-sensitivity, the purity was confirmed by the ¹H NMR spectrum as shown below.

^1H NMR (300 MHz, C_6D_6 , 343 K) spectrum of **6a**.



Crystal data for 6a. $\text{C}_{43}\text{H}_{74}\text{CrO}_3\text{Si}_6\text{Sn}$ $MW = 978.25$; *triclinic*; space group $P\bar{1}$ (#2); $a = 9.5178(4)$, $b = 13.1280(7)$ Å, $c = 22.1764(8)$ Å; $\alpha = 79.6768(18)^\circ$, $\beta = 82.5522(15)^\circ$, $\gamma = 82.2722(18)^\circ$; $V = 2685.5(2)$ Å³; $Z = 2$; $D_{\text{calcd}} = 1.210$ g/cm³; $\mu = 0.833$ mm⁻¹; $2\theta_{\text{max}} = 50^\circ$; $T = 173$ K; $R_1(I > 2\sigma(I)) = 0.0493$; wR_2 (all data) = 0.1052; GOF = 1.107 for 22659 reflections and 650 parameters.

References

- 1 Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- 2 Matsushashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351.
- 3 Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

Table S1. Observed and calculated bond lengths (Å) for 2-stannanaphthalenes^a

bond	1a (obsd)	1b (calcd)	1c (calcd)	1d (calcd)
C1–C8	1.394(8)	1.423	1.424	1.422
C1–Sn	2.029(6)	1.985	1.988	1.993
Sn–C2	2.081(6)	2.067	2.073	2.066
C2–C3	1.372(9)	1.374	1.374	1.380
C3–C9	1.443(9)	1.445	1.445	1.440
C4–C9	1.417(9)	1.423	1.423	1.425
C4–C5	1.356(9)	1.378	1.378	1.377
C5–C6	1.415(10)	1.411	1.411	1.413
C5–C7	1.361(9)	1.375	1.375	1.375
C7–C8	1.419(9)	1.431	1.431	1.432
C8–C9	1.436(9)	1.447	1.447	1.449
C2–C10	1.522(9)	1.535	1.535	1.541

^a calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level.**Table S2.** Observed and calculated ¹¹⁹Sn, ¹H, and ¹³C NMR chemical shifts (ppm) for 2-stannanaphthalenes

atom	1a (obsd) ^a	1b (calcd) ^b	1c (calcd) ^b	1d (calcd) ^c
Sn	264	123	273	150
H1	9.28	9.25	8.58	8.42
H2	8.75	8.79	8.57	8.91
H3	7.65	7.88	7.71	7.80
H4	7.05	7.38	7.01	7.17
H5	7.21	7.31	7.25	7.35
H6	7.68	7.64	7.59	7.66
C1	147.4	147.9	139.4	136.5
C2	174.0	175.4	173.8	169.9
C3	142.2	143.4	143.2	149.6
C4	135.4	137.0	136.9	136.6
C5	120.0	121.9	120.4	119.4
C6	125.3	125.3	126.0	125.4
C7	128.0	129.1	128.7	128.8
C8	147.3	149.9	148.8	151.0
C9	125.9	129.2	127.1	126.9
C10	39.7	42.5	41.2	41.8

^a measured in benzene-*d*₆. ^b calculated at the GIAO-B3LYP/6-311+(2d,p) (TZV on Sn)//B3LYP/6-31G(d) (LANL2DZ on Sn) level. ^c calculated at the GIAO-B3LYP/6-311+(2d,p) (TZV on Sn)//B3LYP/6-31G(d) [TZ(2d) on Sn] level.

Table S3. Coordinates (Å) of the optimized structure for **1b** calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level.

atom	x	y	z
C	-0.981222	0.577512	-0.000107
C	0.192435	1.292341	-0.000116
C	1.581429	0.892226	-0.000074
C	2.096791	-0.459829	0.000002
H	2.133866	2.97636	-0.000114
H	0.087735	2.377432	-0.000158
C	2.521344	1.959932	-0.000069
C	3.517964	-0.623732	0.000067
H	1.818068	-2.585674	0.000083
H	-1.836094	-2.715909	-0.000014
C	4.388118	0.441133	0.000058
C	3.884472	1.759018	-0.000008
H	3.905288	-1.639758	0.000123
H	5.461114	0.266934	0.00011
H	4.56341	2.60705	-0.000006
C	-2.369454	1.23156	0.000018
C	-2.309765	2.772924	-0.001338
H	-3.326541	3.181726	-0.001485
H	-1.797459	3.160732	0.886113
H	-1.797811	3.15914	-0.889688
C	-3.149422	0.779684	-1.257582
H	-3.274201	-0.310024	-1.284747
H	-4.151277	1.226312	-1.272895
H	-2.626491	1.078806	-2.172628
C	-3.148099	0.781767	1.259208
H	-2.624223	1.082462	2.173193
H	-4.149977	1.228338	1.274814
H	-3.272695	-0.30791	1.288333
C	1.293434	-1.634449	-0.000001
Sn	-0.684417	-1.468131	-0.000028

Table S4. Coordinates (Å) of the optimized structure for **1c** calculated at the B3LYP/6-31G(d) (LANL2DZ on Sn) level.

atom	x	y	z
C	4.548815	-0.011154	0.000022
C	3.541398	-0.947476	0.000004
C	2.155213	-0.592738	-0.000036
C	1.831022	0.817508	-0.000033
C	2.907711	1.747229	-0.000004
C	4.231033	1.363573	0.000017
H	1.588741	-2.659123	0.000001
H	5.587951	-0.330967	0.000048
H	3.787294	-2.006843	0.000018
C	1.196655	-1.645157	-0.000072
C	0.509803	1.403223	-0.000002
H	2.661261	2.806962	0.000005
H	5.019401	2.110994	0.000038
C	-0.751386	0.857283	-0.000005
H	0.556606	2.492563	-0.000028
Sn	-0.744438	-1.216017	0.000016
C	-2.380452	-2.596538	-0.000017
H	-3.001025	-2.45991	-0.889127
H	-1.983962	-3.615403	-0.000145
H	-3.000939	-2.460102	0.889184
C	-2.032263	1.703962	-0.000001
C	-2.867402	1.370333	1.258672
H	-3.796222	1.954151	1.275733
H	-3.145384	0.309315	1.28835
H	-2.305089	1.593291	2.172033
C	-2.867487	1.370212	-1.258575
H	-3.145496	0.309197	-1.288127
H	-3.7963	1.954041	-1.275639
H	-2.305238	1.593066	-2.172002
C	-1.756546	3.221937	-0.000088
H	-1.195129	3.533589	0.887644
H	-1.195198	3.533495	-0.887897
H	-2.706059	3.769331	-0.000076

Table S5. Coordinates (Å) of the optimized structure for **1d** calculated at the B3LYP/6-31G(d) [TZ(2d) on Sn] level.

atom	x	y	z
C	4.831404	-2.354805	0.019996
C	5.347505	-1.039438	0.015774
C	4.473385	0.024202	0.00803
C	3.057759	-0.135506	0.004083
C	2.526892	-1.483425	0.008797
C	3.472165	-2.559769	0.016514
C	2.295739	1.08676	-0.0049
C	0.943099	1.358676	-0.012638
Sn	-0.217183	-0.350466	-0.007723
C	1.142603	-1.806975	0.007689
C	0.456482	2.820659	-0.019599
C	0.938529	3.542458	1.261802
C	1.006039	3.559693	-1.263443
C	-1.080766	2.899352	-0.061992
C	-2.343912	-0.600865	0.004351
C	-3.03748	-0.664074	1.233737
C	-4.427381	-0.842432	1.222987
C	-5.123515	-0.956557	0.022247
C	-4.436188	-0.895008	-1.187402
C	-3.046453	-0.717575	-1.215859
C	-2.340972	-0.654851	-2.554585
C	-2.322816	-0.542473	2.563562
H	5.50868	-3.205354	0.025899
H	6.420414	-0.869447	0.018437
H	4.867478	1.038356	0.004446
H	3.077452	-3.573152	0.019765
H	2.946638	1.965264	-0.005542
H	0.887554	-2.863918	0.012593
H	0.549576	3.046942	2.15902
H	0.592445	4.583903	1.270112
H	2.030982	3.552128	1.334916
H	0.674253	3.070482	-2.186538
H	2.100584	3.581788	-1.273926
H	0.651096	4.597973	-1.280755
H	-1.484452	2.426139	-0.965805
H	-1.413232	3.944137	-0.062014
H	-1.535583	2.410565	0.808527

H	-4.964465	-0.892625	2.16699
H	-6.201514	-1.095033	0.029259
H	-4.980042	-0.986002	-2.124428
H	-3.047117	-0.789879	-3.379977
H	-1.572227	-1.432378	-2.647707
H	-1.842092	0.311569	-2.706917
H	-1.545607	-1.308215	2.681042
H	-3.021647	-0.652273	3.398861
H	-1.832726	0.434064	2.674993

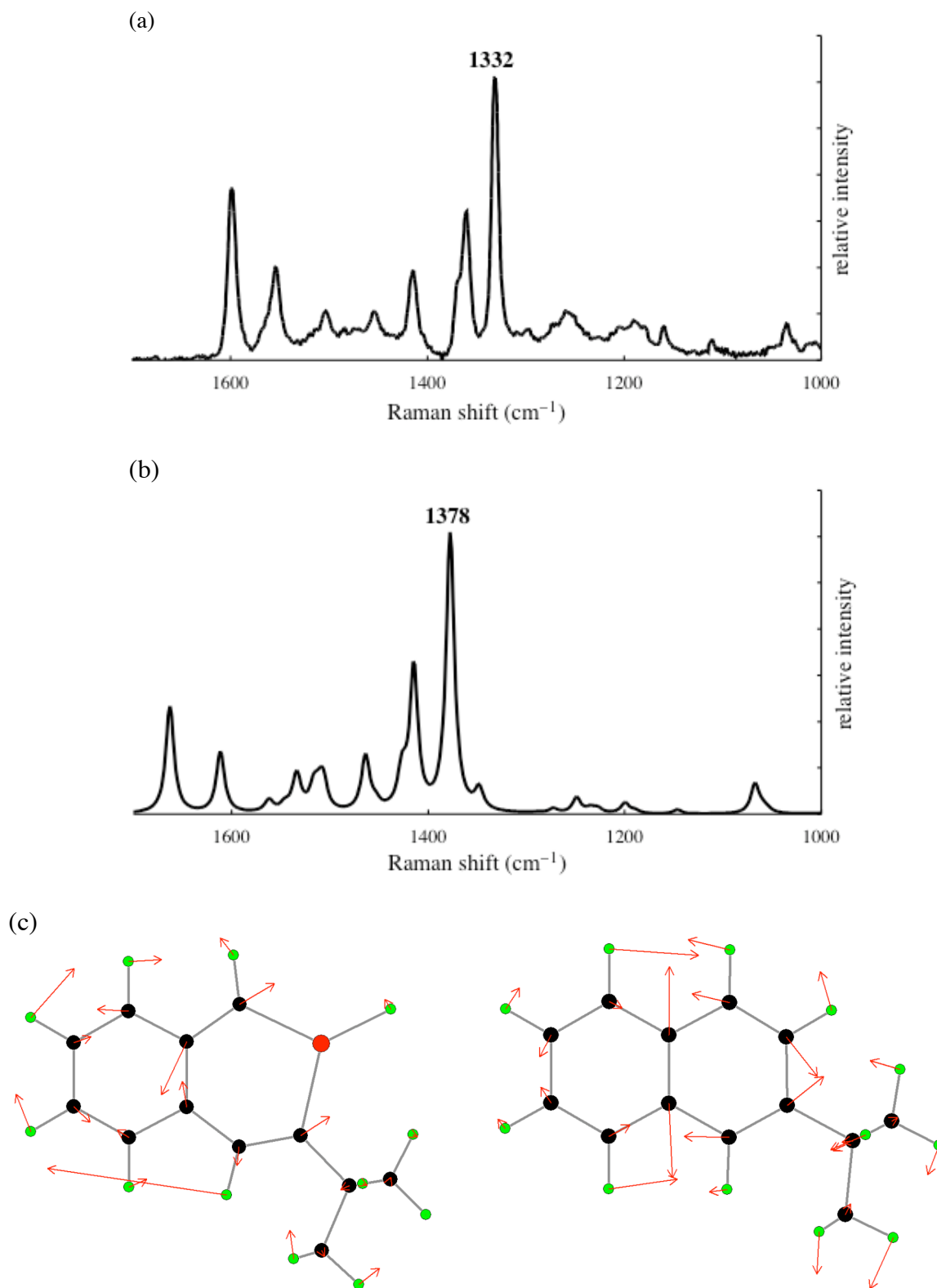


Figure S1. Raman spectra of 2-stannanaphthalenes measured by Prof. Furukawa at Waseda University. (a) FT-Raman spectrum of **1a** measured with the excitation by He-Ne laser (532 nm). (b) Spectrum of **1b** simulated by the theoretical calculation at the B3LYP/6-31G(d) (LANL2DZ on Sn) level. (c) Calculated vibration modes of **1b** (1378 cm^{-1} , left) and 2-*tert*-butyl-naphthalene (1424 cm^{-1} , right).

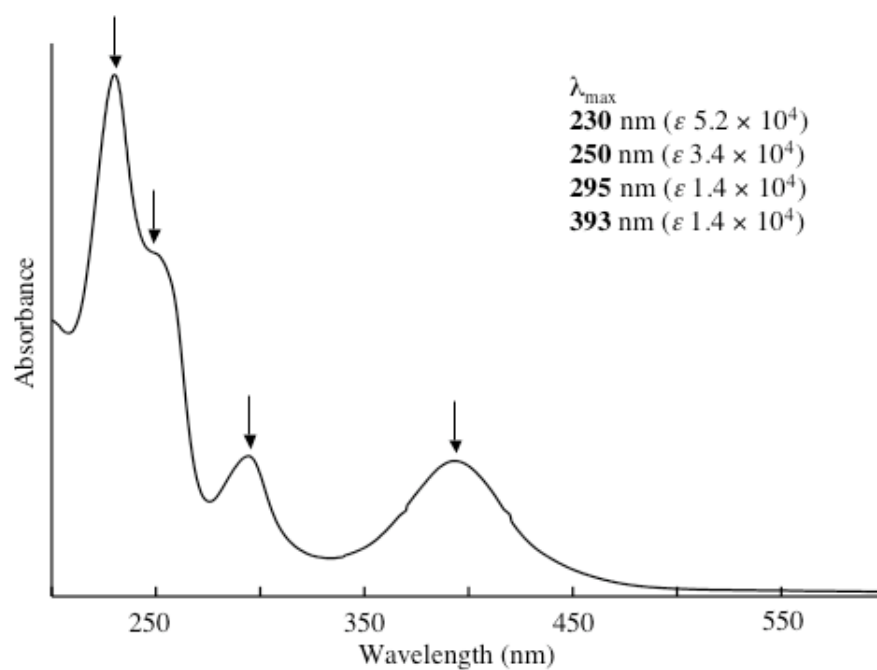


Figure S2. UV/vis spectrum of 2-stannanaphthalene **1a** in hexane at room temperature.