Electronic Supplementary Information

Insertion of carbon monoxide into an aldehyde C=O double bond induced by an (η^3-α-silabenzyl)carbonylmolybdenum complex

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Synthetic procedures and characterisation data

General procedures. All manipulations were carried out under argon in a glovebox. Hexane was dried using a Glass Contour solvent purification system (Nikko Hansen & Co., Ltd.) and degassed by three freeze-pump-thaw cycles. Toluene was dried using an MBRAUN solvent purification system, then was further dried over CaH_2 and vacuum transferred. Pentane, benzene-*d*$_6$ and dichloromethane-*d*$_2$ were dried over CaH_2 and vacuum transferred. 2-Methylpropanal and 2,2-dimethylpropanal were dried over Na_2CO_3 and distilled under argon. All solvents and reagents were stored under argon over 4 Å molecular sieves in a glovebox. Cp*Mo(CO)$_2${η^3(*Si,C,C*)-Si(*p*-Tol)$_3$} (**1**) was prepared according to the literature method.[S1]

Physical measurements. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker AVANCE III 400 Fourier transform spectrometer. Chemical shifts were reported in parts per million. Coupling constants (*J*) were given in Hz. ^{29}Si{^{1}H} NMR measurements were performed using the DEPT pulse sequence. The residual proton (C_6D_5H, 7.15 ppm; $CDHCl_2$, 5.32 ppm) and the carbon resonances (C_6D_6, 128.0 ppm; CD_2Cl_2, 53.8 ppm) of deuterated solvents were used as internal references for ^{1}H and ^{13}C NMR chemical shifts, respectively. Aromatic proton and carbon are abbreviated as ArH and ArC, respectively. ^{29}Si{^{1}H} NMR chemical shifts were referenced to $SiMe_4$ (0 ppm) as an external standard.

The NMR data were collected at room temperature unless indicated otherwise. Infrared spectra were measured on a KBr pellet sample using a Horiba FT-720 spectrometer. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics solariX 9.4T spectrometer operating in the electrospray ionization (ESI) mode. Elemental analyses were carried out using a J-Science Lab JM11 microanalyzer. Measurement of mass spectra and elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

Synthesis of Cp*Mo(CO)$_2${η^2(*C,O*)-CH(*i*-Pr)OSi(*p*-Tol)$_3$} (2). Complex **1** (25 mg, 0.042 mmol) was dissolved in toluene (0.5 mL) in a Schlenk tube. To the dark purple solution, 2-methylpropanal (4 mg, 0.05 mmol) was added by a syringe. The mixture was stirred at room temperature for 1 min. The colour of the solution changed to orange. After evaporation of volatiles, the residual oil was washed with hexane (2 mL) and was evaporated to dryness. Complex **2** (a 5 : 1 mixture of two diastereomers **2a** and **2b** in CD_2Cl_2) was obtained as an orange powder in 83% yield (23 mg, 0.035 mmol); (found: C, 67.49; H, 6.84. $C_{37}H_{44}O_3SiMo$ requires C, 67.25; H, 6.71%); $\nu_{\max}$/cm^{-1} 1909 s (CO$_{\mathrm{sym}}$), 1805 s (CO$_{\mathrm{asym}}$); *m*/*z* (ESI, positive mode) 662.2106 (M$^+$. $[C_{37}H_{44}O_3SiMo]^+$ requires 662.2108); NMR data for **2a**: δ_{H} (400 MHz, C_6D_6, r.t.) 7.70 (d, 6H, J_{HH} 7.8, ArH), 7.03 (6H, d, J_{HH} 7.8, ArH), 3.49 (1H, d, J_{HH} 8.7, C(*H*)CHMe$_2$), 2.23–2.36 (1H, m, C(H)C*H*Me$_2$), 2.05 (s, 9H, C_6H_4*Me*), 1.68 (15H, s, Cp*), 1.22 (3H, d, J_{HH} 6.6, C(H)CHMe_AMe$_{\mathrm{B}}$), 0.92 (3H, d, J_{HH} 6.4, C(H)CHMe$_{\mathrm{A}}$$\mathit{Me}_B$); δ_{H} (400 MHz, CD_2Cl_2, 240 K) 7.34 (6H, d, J_{HH} 7.6, ArH), 7.20 (6H, d, J_{HH} 7.6, ArH), 3.16 (1H, d, J_{HH} 9.2, C(*H*)(CHMe$_2$)), 2.34 (9H, s, C_6H_4*Me*), 1.65 (15H, s, Cp*), 0.95 (3H, d, J_{HH} 6.4, C(H)CHMe_AMe$_{\mathrm{B}}$), 0.53 (3H, d, J_{HH} 6.4, C(H)CHMe$_{\mathrm{A}}$$\mathit{Me}_B$), the signal of C(H)C*H*Me$_2$ could not be assigned possibly due to the overlap with the Cp* signal (δ 1.68) of **2a**; δ_{C} (101 MHz, CD_2Cl_2, 240 K) 263.9, 252.5 (CO), 140.7, 135.6, 129.2, 128.6 (ArC), 104.5 (C_5Me$_5$), 87.5 (*C*(H)CHMe$_2$), 38.1 (C(H)*C*HCMe$_2$), 25.2 (C(H)CHMe_AMe$_{\mathrm{B}}$), 21.4 (C_6H_4*Me*), 19.4 (C(H)CHMe$_{\mathrm{A}}$$\mathit{Me}_B$), 10.8 ($C_5\mathit{Me}_5$); δ_{Si} (79.5 Hz, CD_2Cl_2, 240 K) –0.2; NMR data for **2b**: δ_{H} (400 MHz, C_6D_6, r.t.)

7.77 (6H, d, J_{HH} 7.8, ArH), 7.06 (6H, d, J_{HH} 7.8, ArH), 4.12 (1H, d, J_{HH} 9.6, C(*H*)CHMe$_2$), 1.78 (15H, s, Cp*), 1.09 (3H, d, J_{HH} 6.8, C(H)CH$\mathit{Me_A}$Me$_\mathrm{B}$), 0.99 (3H, d, J_{HH} 6.1, C(H)CHMe$_\mathrm{A}$$\mathit{Me_B}$), the C$_6H_4$*Me* and C(H)C*H*Me$_2$ signals could not be assigned possibly due to overlap with ^{1}H signals of **2a**; δ_H (400 MHz, CD$_2$Cl$_2$, 240 K) 7.41 (6H, d, J_{HH} 7.6, ArH), 7.21 (6H, d, J_{HH} 7.6, ArH), 3.44 (1H, d, J_{HH} 9.6, C(*H*)CHMe$_2$), 2.35 (9H, s, C$_6$H$_4$*Me*), 1.79 (15H, s, Cp*), 0.92 (3H, d, J_{HH} 6.4, C(H)CH$\mathit{Me_A}$Me$_\mathrm{B}$), 0.73 (3H, d, J_{HH} 6.4, C(H)CHMe$_\mathrm{A}$$\mathit{Me_B}$), the signal of C(H)C*H*Me$_2$ could not be assigned possibly due to overlap with other ^{1}H signals of **2a** or **2b**; δ_C (101 MHz, CD$_2$Cl$_2$, 240 K) 136.0 (ArC), 105.9 (C$_6$H$_4$*Me*), 11.0 (C$_5$$\mathit{Me_5}$), other signals for **2b** were not observed because their intensities were too weak; assignments of ^{1}H and ^{13}C signals were confirmed by ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC NMR spectra in CD$_2$Cl$_2$ at 240 K.

Synthesis of Cp*Mo(CO)$_2${η^2(*C*,*O*)-CH(*t*-Bu)OSi(*p*-Tol)$_3$} (3). In a Schlenk tube, **1** (24 mg, 0.041 mmol) was dissolved in toluene (0.5 mL), and then 2,2-dimethylpropanal (5 mg, 0.06 mmol) was added. After the mixture was stirred at room temperature for 1 min, the resulting orange solution was evaporated to dryness. Recrystallization of the residual orange oil from hexane (2 mL) at –35 ºC afforded **3** in 76% yield (21 mg, 0.031 mmol) as an orange powder; (found: C, 67.96; H, 6.87. C$_{38}$H$_{46}$O$_3$SiMo requires C, 67.64; H, 6.87%); ν_max/cm^{-1} 1927 s (CO$_\mathrm{sym}$), 1803 s (CO$_\mathrm{asym}$); δ_H (400 MHz, C$_6$D$_6$, r.t.) 7.77 (6H, d, J_{HH} 8.0, ArH), 7.02 (6H, d, J_{HH} 8.0, ArH), 3.94 (1H, s, C(*H*)CMe$_3$), 2.05 (9H, s, C$_6$H$_4$*Me*), 1.67 (15H, s, Cp*), 1.12 (9H, s, C(H)C$\mathit{Me_3}$); δ_H (400 MHz, CD$_2$Cl$_2$, 240 K) 7.44 (6H, d, J_{HH} 8.0, ArH), 7.21 (6H, d, J_{HH} 8.0, ArH), 3.62 (1H, s, C(*H*)CMe$_3$), 2.35 (9H, s, C$_6$H$_4$*Me*), 1.60 (15H, s, Cp*), 0.71 (9H, s, C(H)C$\mathit{Me_3}$); δ_C (101 MHz, CD$_2$Cl$_2$, 240 K) 265.2, 254.9 (CO), 140.8, 136.2, 129.1, 128.6 (ArC), 104.7 ($\mathit{C_5}$Me$_5$), 93.8 (*C*(H)CMe$_3$), 36.7 (C(H)*C*Me$_3$), 28.2 (C(H)C$\mathit{Me_3}$), 21.4 (C$_6$H$_4$*Me*), 10.7 (C$_5$$\mathit{Me_5}$); assignments of ^{1}H and ^{13}C signals were confirmed by ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC NMR spectra in CD$_2$Cl$_2$ at 240 K; δ_Si (79.5 MHz, CD$_2$Cl$_2$, 240 K) –2.5; *m*/*z* (ESI, positive mode) 676.2265 (M$^+$. [C$_{38}$H$_{46}$O$_3$SiMo]$^+$ requires 676.2265).

NMR monitoring of a thermal reaction of 1 with 2,2-dimethylpropanal: formation of η^3-oxaallyl complex 4. Complex **1** (5 mg, 9 μmol) and Cp_2Fe (internal standard, less than 1 mg; Cp = η^5-C_5H_5) were dissolved in benzene-d_6 (0.6 mL). The solution was transferred into an NMR tube with a J-Young Teflon valve (5 mm o.d.). A ^{1}H NMR spectrum of the mixture was measured to determine the intensity ratio of the signals of **1** and Cp_2Fe. 2,2-Dimethylpropanal (1 mL, *d* = 0.793 g/mL, 9 μmol) was added to the solution. The colour of the mixture changed from dark-purple to orange instantaneously. The reaction was monitored by ^{1}H NMR spectroscopy at room temperature. After 10 min, complex **1** was completely consumed, and three-membered-ring complex **3** and η^3-oxaallyl complex **4** were formed in the NMR yields of 68% and 11%, respectively. At this stage, the colour of the mixture was orange. Then, the intensities of the signals of **3** decreased slowly, and those of the signals of **4** increased concurrently. After 4 h, **3** completely disappeared and **4** was formed in 40% NMR yield as the main product. The colour of the reaction mixture changed to dark red. The products **3** and **4** were identified by comparing the ^{1}H NMR spectra with those of the authentic samples synthesised by the above-mentioned (for **3**) and after-mentioned (for **4**) procedures.

NMR monitoring of a thermal reaction of 3: formation of η^3-oxaallyl complex 4. A solution of isolated **3** (5 mg, 7 μmol) and Cp_2Fe (internal standard, less than 1 mg) in benzene-d_6 (0.5 mL) was transferred into an NMR tube with a J-Young Teflon valve (5 mm o.d.). After 15 min, a ^{1}H NMR spectrum of the mixture was measured to determine the intensity ratio of the signals of **3** and Cp_2Fe. At this stage, the signals of complex **4** were observed besides those of **3** (**3** : **4** = 1 : 0.25). The reaction was monitored by ^{1}H NMR spectroscopy at room temperature. As the intensities of the signals of **4** increased, those of **3** decreased. After 5 h, the signals of complex **3** disappeared, and reaction was completed. Complex **4** was formed in 41% NMR yield based on the conversion of complex **3** in the reaction mixture after 15 min. The product **4** was identified by comparing the ^{1}H and

$^{29}Si\{^1H\}$ NMR spectra with those of the authentic sample synthesised by the aftermentioned procedure.

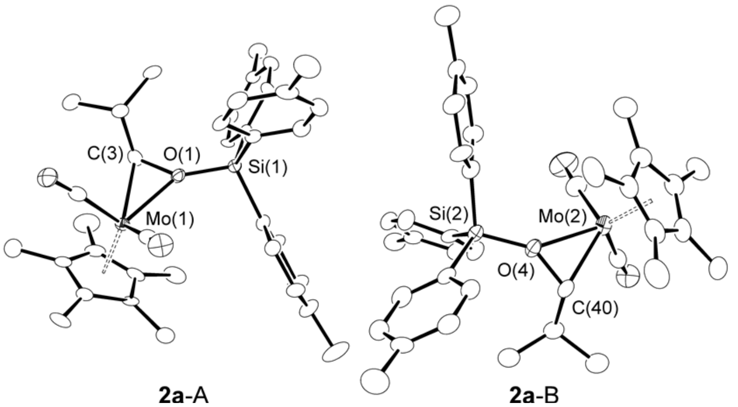
Synthesis of Cp*Mo(CO)$_2$[η^3(*O,C,C*)-OC{OSi(*p*-Tol)$_3$}CH(*t*-Bu)] (4). To a toluene (2.5 mL) solution of **1** (25 mg, 0.042 mmol) in a Schlenk tube was added 2,2-dimethylpropanal (4 mg, 0.05 mmol). The mixture was stirred at room temperature for 5 h, and then the resulting dark red solution was evaporated under vacuum. After the residual dark red oil was dissolved in pentane (0.5 mL), the solution was cooled at –35 ºC. Complex **4** was obtained as reddish purple crystals in 40% yield (12 mg, 0.017 mmol); (Found: C, 66.86; H, 6.73. $C_{39}H_{46}O_4SiMo$ requires C, 66.65; H, 6.60%); ν_{max}/cm^{-1} 1932 s (CO_{sym}), 1844 s (CO_{asym}); δ_H (400 MHz, C_6D_6) 7.82 (6H, d, J_{HH} 8.0, ArH), 7.08 (6H, d, J_{HH} 8.0, ArH), 2.30 (1H, s, OC{OSi(*p*-Tol)$_3$}C(*H*)CMe$_3$), 2.08 (9H, s, C_6H_4*Me*), 1.55 [9H, s, OC{OSi(*p*-Tol)$_3$}C(H)C*Me$_3$*], 1.54 (15H, s, Cp*); δ_C (101 MHz, C_6D_6) 257.7, 251.0 (CO), 155.0 [O*C*{OSi(*p*-Tol)$_3$}C(H)CMe$_3$], 140.3, 136.6, 130.2, 128.9 (ArC), 106.6 (*C$_5$*Me$_5$), 63.7 [OC{OSi(*p*-Tol)$_3$}*C*(H)CMe$_3$], 34.4 [OC{OSi(*p*-Tol)$_3$}C(H)*C*Me$_3$], 31.4 [OC{OSi(*p*-Tol)$_3$}C(H)C*Me$_3$*], 21.5 (C_6H_4*Me*), 10.2 (C$_5$*Me$_5$*); assignments of ^1H and ^{13}C signals were confirmed by ^1H–^{13}C HSQC and ^1H–^{13}C HMBC NMR spectra; δ_{Si} (79.5 MHz, C_6D_6) –8.1; *m*/*z* (ESI, positive mode) 704.2214 (M^+. $[C_{39}H_{46}O_4SiMo]^+$ requires 704.2214).

NMR monitoring of a reaction of 1 with 2,2-dimethylpropanal under a CO atmosphare. Complex **1** (5 mg, 9 μmol) and Cp_2Fe (internal standard, less than 1 mg) were dissolved in benzene-*d$_6$* (0.6 mL). The solution was transferred into an NMR tube with a J-Young Teflon valve (5 mm o.d.). A ^1H NMR spectrum of the mixture was measured to determine the intensity ratio of the signals of **1** and Cp_2Fe. 2,2-Dimethylpropanal (1 μL, *d* = 0.793 g/mL, 9 μmol) was added to the solution. The colour of the mixture changed to orange instantaneously. After standing the tube for 5 min at room temperature, the ^1H NMR signals of **3** were observed (78% NMR yield based on **1**). The NMR tube was then evacuated briefly to degas and was charged with 1 atm of CO gas. This procedure was repeated three times, and then the tube was shaken well. Conversion of **3** at room temperature was monitored by ^{1}H NMR spectroscopy. Complex **3** was completely consumed in the course of 13 h, and the colour of the solution changed to dark red. Complex **4** was formed as the main product in 75% NMR yield based on **1**. The NMR yields of **3** and **4** were determined by comparison of the intensities of the Cp* signals of these complexes with that of the signal of Cp_2Fe. The products **3** and **4** were identified by comparing the corresponding ^{1}H NMR spectra with those of the authentic samples synthesised by the above-mentioned procedures.

X-ray crystal structure determination. X-ray quality single crystals of **2a** (an orange plate) and **4** (a reddish-purple plate) were obtained from hexane (for **2a**) or pentane (for **4**) at –35 ºC. Intensity data for the analysis were collected on a Bruker SMART APEXII CCD diffractometer with Cu Kα radiation (λ = 1.54178 Å) using Bruker Helios multilayered confocal mirror monochromator under a cold nitrogen stream (T = 90 K) (for **2a**) or on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) under a cold nitrogen stream (T = 150 K) (for **4**). An empirical absorption correction (for **2a**) or a numerical absorption correction (for **4**) was applied to the collected reflections. We could not obtain a sufficient amount of reflections for **2a**: Data completeness to 2θ = 139.42º is 88.0%. This is caused by the gradual degradation of crystallinity of the sample under X-ray irradiation. The structure of **4** was solved as a racemic twin [Flack parameter: 0.22(3)] in the acentric space group $P2_1$. The structures were solved by direct methods using the SHELXS-97 program[S2] and refined by full matrix least-squares techniques on all F^2 data with SHELXL-97.[S2] Anisotropic refinement was applied to all non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. All calculations were carried out using Yadokari-XG 2009.[S3] Selected crystallographic data for **2a** and **4** are listed in Table S1. ORTEP drawings of two crystallographically independent molecules of each of **2a** and **4** are depicted in Figs. S1 and S2, respectively. CCDC reference numbers: 990556 (**2a**) and 990557 (**4**).

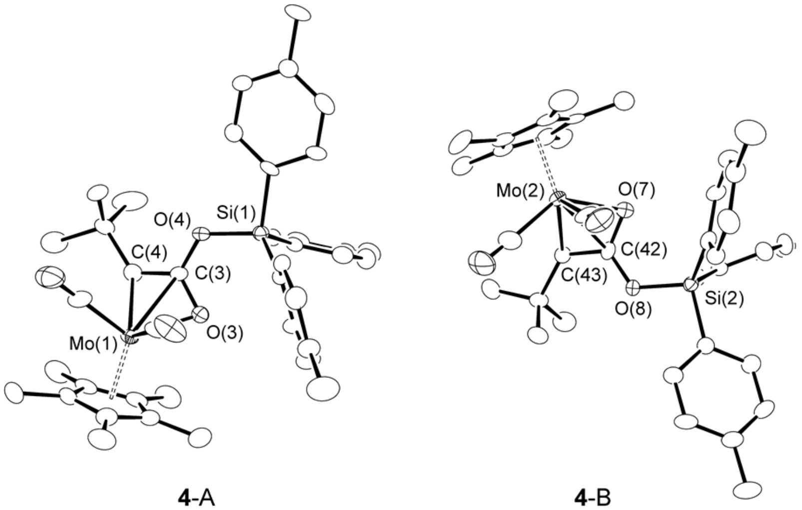
Table S1 Crystallographic data for $Cp^*Mo(CO)_2\{\eta^2(C,O)\text{-}CH(i\text{-}Pr)OSi(p\text{-}Tol)_3\}$ (**2a**) and $Cp^*Mo(CO)_2[\eta^3(O,C,C)\text{-}OC\{OSi(p\text{-}Tol)_3\}CH(t\text{-}Bu)]$ (**4**).

compound	**2a**	**4**
formula	$C_{37}H_{44}O_3SiMo$	$C_{39}H_{46}O_4SiMo$
formula weight	660.75	702.79
crystal system	triclinic	monoclinic
crystal size/mm^3	0.11 × 0.06 × 0.04	0.20 × 0.15 × 0.08
space group	P (No. 2)	$P2_1$ (No. 4)
a/Å	8.6566(3)	12.8069(3)
b/Å	10.9696(4)	13.1036(4)
c/Å	35.7255(11)	21.5568(7)
α/°	95.4889(13)	
β/°	92.2032(14)	90.7174(4)
γ/°	97.1362(15)	
V/Å^3	3346.4(2)	3617.30(18)
Z	4	4
D_{calcd}/g cm^{-3}	1.312	1.290
F(000)	1384	1472
μ(Cu-Kα or Mo-Kα)/mm^{-1}	3.806	0.433
reflections collected	31297	51709
unique reflections (R_{int})	11121 (0.0239)	15836 (0.1025)
refined parameters	777	834
$R1$, $wR2$ (all data)	0.0740, 0.1674	0.0853, 0.1364
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0732, 0.1671	0.0681, 0.1279
GOF	1.361	1.147
Largest residual peak, hole/e Å^{-3}	1.863, –1.573	0.709, –0.986



2a-A **2a**-B

Fig. S1 ORTEP drawing of two crystallographically independent molecules of Cp*Mo$(CO)_2$\{η^2(*C,O*)-CH(*i*-Pr)OSi(*p*-Tol)$_3$\} (**2a**), i.e., molecules **2a**-A and **2a**-B, in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (º) for molecule **2a**-A: Mo(1)–O(1) 2.175(4), Mo(1)–C(3) 2.167(6), O(1)–C(3) 1.434(7), O(1)–Mo(1)–C(3) 38.56(19); for molecule **2a**-B: Mo(2)–O(4) 2.169(4), Mo(2)–C(40) 2.160(7), O(4)–C(40) 1.450(8), O(4)–Mo(2)–C(40) 39.1(2).



4-A **4**-B

Fig. S2 ORTEP drawing of two crystallographically independent molecules of Cp*Mo$(CO)_2$[η^3(*O,C,C*)-OC\{OSi(*p*-Tol)$_3$\}CH(*t*-Bu)] (**4**), i.e., molecules **4**-A and **4**-B, in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (º) for molecule **4**-A: Mo(1)–O(3) 2.186(4), Mo(1)–C(3) 2.396(5), Mo(1)–C(4) 2.343(6), O(3)–C(3) 1.284(7), O(4)–C(3) 1.355(7), C(3)–C(4) 1.403(9), O(3)–Mo(1)–C(4) 61.27(18); for molecule **4**-B: Mo(2)–O(7) 2.185(4), Mo(2)–C(42) 2.402(5), Mo(2)–C(43) 2.370(6), O(7)–C(42) 1.277(7), O(8)–C(42) 1.333(7), C(42)–C(43) 1.420(8), O(7)–Mo(2)–C(43) 61.23(17).

References

S1 T. Komuro, Y. Kanno and H. Tobita, *Organometallics*, 2013, **32**, 2795.

S2 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

S3 (*a*) K. Wakita, *Yadokari-XG*, *Software for Crystal Structure Analyses*, 2001; (*b*) *Yadokari-XG 2009*, *Software for Crystal Structure Analyses*. See: C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.