Barbier Reaction in the Regime of Metal-Oxide: The First Example of Carbonyl Allylation Mediated by Tetragonal Tin(II)Oxide

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SUPPORTING INFORMATION: CONTENTS
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1. Methods.

General Methods.

All reactions were performed under an inert atmosphere of argon. Substituted allyl bromides were prepared from the corresponding alcohols (Lancaster) using standard protocol. β-tin(II)oxide, copper(I)oxide, copper(I)chloride, $PtCl_2(PPh_3)_3$, $Pd_2(dba)_3$, $Pd_2(dba)_3.CHCl_3$, $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$ and $NiCl_2(PPh_3)_2$ catalysts were prepared rather easily according to literature procedure[1-4]. All the starting materials were >98% pure vide NMR. Pre-coated silica gel $60F_{254}$, Merck was used for thin layer chromatography and silica gel 60-120 mesh, SRL was used for column chromatography.

^1H NMR spectra were taken in $CDCl_3$ or DMSO-d_6 on Brucker-300 spectrometer. EIMS (70 eV) spectra were recorded using VG Autospec M mass spectrometer. GC analysis was carried out in a Chemito-8610 instrument using Supelcowax-10 30, capillary column. X-ray photoelectron spectra were recorded by VG Escalab MKII spectrometer. X-ray powder diffraction data was obtained using Phillips PW-1840 instrument using a Mo-Kα target at 40 KV.

Typical Procedure for the Synthesis of Homoallylic Alcohols using β-SnO and $PtCl_2(PPh_3)_2$ as catalyst.

A mixture of 4-chlorobenzaldehyde (140 mg, 1 mM) and 1-bromobut-2-en (270 mg, 2 mM) in tetrahydrofuran (2 mL) was added slowly to a refluxing solution containing β-SnO (202 mg, 1.5 mM) and dichlorobistriphenylphosphine-platinum(II) (8 mg, 0.01 mM) in tetrahydrofuran-water (2.5 mL-0.5 mL) and under argon. The mixture was further refluxed for 2.5 h. (TLC monitoring on silica gel, eluent: n-hexane: ethyl acetate 9:1). An aqueous solution of ammonium fluoride (15%, 10 mL) was added to the reaction mixture and organic layer was extracted with diethyl ether (3 x 10 mL), washed with water (2 x 10 mL), brine (2 x 10 mL) and dried over magnesium sulfate. Solvent removal followed by column chromatography (eluent n-hexane: ethyl acetate 9:1) afforded pure 1-(4-chlorophenyl)-2-methylbut-3-en-1-ol (161 mg, 82% w.r.t. aldehyde).

Synthesis of Homoallylic Alcohols using β-SnO and Cu_2O as catalyst.

Similar procedure as above was followed for the synthesis of homoallylic alcohols using copper(I) oxide as catalyst (14 mg, 0.1 mM), the solvent used was dichloromethane-water (4.5 mL-0.5 mL).

Details of NMR Experiments.

A mixture of β-SnO (269 mg, 2 mM) and palladium(0)dibenzylideneacetone (18 mg, 0.02 mM) in tetrahydrofuran (3 mL) under argon atmosphere was refluxed for 0.5 h. Allyl bromide (484 mg, 4 mM) was added to the mixture dropwise. The mixture was further refluxed for 10 h. The excess tin oxide was filtered off under argon and solvent was removed under vaccuo. The residue was dissolved in DMSO-d_6 and examined by ^1H NMR, the resulting spectrum is shown in Figure 1 (c).

Details of XRD Experiments.

In a typical procedure β-SnO (269 mg, 2 mM) and $PtCl_2(PPh_3)_2$ (7 mg, 0.01 mM) were taken up in tetrahydrofuran-water (2.4 mL-0.6 mL) under argon atmosphere. After the mixture was refluxed for 0.5 h, a mixture of allyl bromide (484 mg, 4 mM) and 4-chlorobenzaldehyde (280 mg, 2 mM) in tetrahydrofuran (3 mL) was added dropwise. The mixture was reflxed for 7 h. The solvent was removed under reduced pressure. The solid after drying under vaccuo was subjected to XRD analysis.

All XRD spectra are shown in Figure S1 (β-SnO), S2 (β-SnO in THF-H_2O), S3 (Cu_2O), S4 (β-SnO+ Cu_2O in THF-H_2O) and S5 (β-SnO+ $PtCl_2(PPh_3)_3$+ allyl bromide in THF-H_2O).

Details of XPS Experiments.

A mixture of β-SnO (606 mg, 4.5 mM) and copper(I) oxide (86 mg, 0.6 mM) in dicholoromethane-water (12.6 mL-1.4 mL) under argon atmosphere was refluxed for 0.5 h. Allyl bromide (968 mg, 8 mM) was added to the mixture dropwise. The mixture was further reflxed for 7 h. The solvent was removed under reduced pressure. The solid after drying under vaccuo was subjected to XPS analysis.

Another sample was prepared under identical condition as above but in absence of allyl bromide.

Details of in-situ EIMS Experiments.

A mixture of β-SnO (269 mg, 2 mM) and palladium(0)dibenzylideneacetone (18 mg, 0.02 mM) in tetrahydrofuran (3 mL) under argon atmosphere was refluxed for 0.5 h. Allyl bromide (484 mg, 4 mM) was added to the mixture dropwise. The mixture was further refluxed for 10 h. The excess halide was removed under vaccum and the upper solution was directly injected into the mass spectrometer probe, the resulting spectrum is shown in Figure S6.

2. List of ^{1}H NMR, ^{13}C NMR , EIMS and analytical data of the homoallylic alcohols

Compd 3a: (syn:anti=55:45) ^{1}H NMR ($CDCl_3$): δ (anti isomer) 0.88 (d, 3H, J= 5.0 Hz), 2.19 (br s, 1H, -OH), 2.35-2.60 (m, 1H), 4.33 (m, 1H), 5.00-5.24 (m, 2H), 5.65-5.77 (m, 1H), 7.22-7.34 (m, 4H); δ (syn isomer) 0.99 (d, 3H, J= 5.0 Hz), 1.92 (br s, 1H, -OH), 2.35-2.60 (m, 1H), 4.59 (m, 1H), 5.00-5.24 (m, 2H), 5.65-5.77 (m, 1H), 7.22-7.34 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 14.02, 16.38 (anti+syn), 38.00, 44.76, 46.24 (anti+syn), 115.82, 117.00 (anti+syn), 127.21, 127.87, 128.35, 133.39, 141.07, 140.15 (anti+syn); EIMS m/z (rel abundance): 196 ($M^{\cdot+}$, <1), 178 [$(M-H_2O)^+$, <1], 163 (<1), 143 (31), 141 (100), 113(14), 77 (41), 55 (8); Anal. ($C_{11}H_{13}OCl$) calcd, C: 67.35, H: 6.63; found, C: 66.95, H: 6.29.

Compd 3b: ^{1}H NMR ($CDCl_3$): δ 0.92 (s, 3H), 0.96 (s, 3H), 2.15 (br s, 1H, -OH), 4.00 (s, 1H), 4.19 (s, 9H), 4.92-5.04 (m, 2H), 5.79-5.93 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 22.15, 23.76, 41.37, 65.67, 67.61, 68.34, 69.79, 112.35, 145.39; EIMS m/z (rel abundance): 284 (M.+, 29), 215 (82), 186 (100), 121 (47), 56 (19); Anal. ($C_{16}H_{20}OFe$) calcd, C: 67.61, H: 7.04; found, C: 67.35, H: 6.79.

Compd 3c: ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 3H), 1.08 (s, 3H), 2.16 (br s, 1H, -OH), 4.71 (s, 1H), 5.08-5.20 (m, 2H), 5.90-6.04 (m, 1H), 6.93-6.98 (m, 2H), 7.19-7.26 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 0.96, 21.58, 24.24, 42.22, 114.26, 124.34, 125.41, 125.99, 128.24, 144.49; EIMS m/z (rel abundance): 165 [$(M-H_2O)^+$,(9)], 113 (100), 85 (24), 41 (21); Anal. ($C_{10}H_{14}O_5$) calcd, C: 65.93, H: 7.64; found, C: 65.80, H: 7.47.

Compd 3d: ^{1}H NMR ($CDCl_3$): δ 1.03 (d, 3H, J= 5.9 Hz), 1.35-1.69 (m, 5H), 2.14-2.25 (m, 1H), 3.09 (br s, 1H, -OH), 3.37-3.50 (m, 1H), 5.01-5.11 (m, 2H), 5.65-5.86 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.37, 16.20, 18.01, 21.92, 33.93, 74.60, 115.09, 140.99, 178.02; EIMS m/z (rel abundance): 157 ($M^{\cdot+}$, 20), 139 [$(M-H_2O)^+$, 44), 121 (60), 95 (72), 79 (44), 69 (68), 55 (100), 43 (62); Anal. ($C_9H_{16}O_2$) calcd, C: 69.23, H: 10.26; found, C: 68.62, H: 9.71.

Compd 3e: ^{1}H NMR ($CDCl_3$): δ (anti & syn isomer) 0.89 (m, 3H), 1.26-1.47 (m, 2H), 1.59-1.65 (m, 2H), 2.1 (m, 1H), 2.46-2.90 (m, 2H), 3.70-3.77 (m, 1H), 5.05-5.23 (m, 2H), 5.60-5.79 (m, 1H), 7.24-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.10, 20.41, 32.23, 33.25 (anti+syn), 40.94 41.42 (anti+syn), 50.06, 74.79, 75.25 (anti+syn), 117.05,117.63 (anti+syn), 126.36, 128.37, 129.37, 138.51, 139.01, 139.22 (anti+syn); EIMS m/z (rel abundance): 205 ($M^{\cdot+}$, 6), 186 [$(M-H_2O)^+$, 20], 143 (50), 121 (78), 92 (100), 91 (82), 84 (38), 77 (14), 55 (26); Anal. ($C_{14}H_{20}O$) calcd, C: 82.35, H: 9.80; found, C: 82.16, H: 9.61.

Compd 3f: ^{1}H NMR (syn:anti=42:58) ($CDCl_3$): δ (anti isomer) 0.83 (t, 3H, J= 6.5 Hz), 1.22-1.41 (m, 4H), 2.15 (d, 1H, J= 5 Hz, -OH), 2.31-2.36 (m, 1H), 4.94-5.07 (m, 2H), 5.17 (d, 1H, J= 3.2 Hz), 5.58-5.76 (m, 1H), 7.23-7.46 (m, 3H); δ (syn isomer) 0.83 (t, 3H, J= 6.5 Hz), 1.22-1.41 (m, 4H), 2.02 (d, 1H, J= 5 Hz, -OH), 2.31-2.36 (m, 1H), 4.94-5.07 (m, 2H), 5.22 (d, 1H, J= 3.2 Hz), 5.58-5.76 (m, 1H), 7.23-7.46 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 13.66, 20.28, 30.39, 32.77, 49.79, 50.76 (anti+syn), 117.02, 118.71 (anti+syn), 126.90, 128.83, 128.89, 129.35, 132.18, 132.92, 137.78, 138.58 (anti+syn); Anal. ($C_{13}H_{16}OCl_2$) calcd, C: 60.46, H: 6.20; found, C: 60.18, H: 5.87.

Compd 3g: (syn:anti=26:74) ^{1}H NMR ($CDCl_3$): δ (anti isomer) 0.87 (d, 3H, J= 5.3 Hz), 2.17 (br s, 1H, -OH) 2.43-2.61 (m, 1H), 4.38 (d, 1H, J=5.3 Hz), 5.16-5.25 (m, 2H), 5.71-5.91 (m, 1H), 7.26-7.39 (m, 5H); δ (syn isomer) 0.99 (d, 3H, J= 5.3 Hz), 1.62 (br s, 1H, -OH) 2.43-2.61 (m, 1H), 4.63 (d, 1H, J=5.3 Hz), 5.16-5.25 (m, 2H), 5.71-5.91 (m, 1H), 7.26-7.39 (m, 5H); EIMS m/z (rel abundance): 162 (M^+, <1), 144 [$(M-H_2O)^+$,(2)], 129 (3), 107 (100), 79 (21), 56 (3).

Compd 3h: (syn:anti=50:50) ^{1}H NMR ($CDCl_3$): δ (anti isomer) 0.88 (m, 3H), 1.02 (d, 3H, J= 3.13 Hz), 1.25-1.35 (m, 16H), 2.15-2.21 (m, 1H), 3.35-3.44 (m, 1H), 4.99-5.10 (m, 2H), 5.64-5.81 (m, 1H); δ (syn isomer) 0.88 (m, 3H), 1.09 (d, 3H, J= 3.13 Hz), 1.25-1.35 (m, 16H), 2.15-2.21 (m, 1H), 3.35-3.44 (m, 1H), 4.99-5.10 (m, 2H), 5.64-5.81 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.14, 16.31 (anti+syn), 22.71, 25.81, 26.13, 28.98, 29.64, 31.95, 34.12, 34.31, 43.54, 44.14 (anti+syn), 74.68, 115.08, 116.09 (anti+syn), 140.39, 141.19 (anti+syn); EIMS m/z (rel abundance): 212 ($M^{\cdot+}$, 14), 194 [$(M-H_2O)^+$, 12], 157 (20), 97 (52), 83 (84), 69 (70), 56 (100); Anal. ($C_{14}H_{28}O$) calcd, C: 79.25, H: 13.21; found, C: 78.65, H: 12.82.

Compd 3i: ^{1}H NMR ($CDCl_3$): δ 1.23-1.37 (m, 6H), 2.26 (m, 2H) 2.42 (m, 2H), 3.61 (br s, 1H, -OH), 4.18 (m, 2H), 5.02-5.12 (m, 2H), 5.73-5.90 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.09, 26.75, 44.23, 46.43, 60.45, 70.57, 118.40, 133.61, 172.75; EIMS m/z (rel abundance): 131 (76), 127 (12), 118 (20), 103 (20), 85 (100), 82 (48), 70 (16), 55 (22), 50 (42); Anal. ($C_9H_{16}O_3$) calcd, C: 62.79, H: 9.30; found, C: 61.92, H: 8.92.

Compd 3j: ^{1}H NMR ($CDCl_3$): δ 1.55 (s, 1H, -OH), 2.89-3.19 (m, 2H) 4.97-5.14 (m, 2H), 5.63-5.84 (m, 1H), 7.26-7.75 (m, 10H); ^{13}C NMR ($CDCl_3$): δ 44.06, 81.39, 120.38, 125.62, 128.06, 128.89, 130.17, 132.37, 132.70, 134.61, 141.82, 200.68; EIMS m/z (rel abundance): 252 ($M^{\cdot+}$, 4), 234 [$(M-H_2O)^+$,14], 211 (52), 147 (54), 105 (100), 77 (62), 51 (12); Anal. ($C_{17}H_{16}O_2$) calcd, C: 80.95, H: 6.35; found, C: 80.32, H: 5.89.

3. Table S1. Table containing XRD data.[$]

Fig.	Compound	Observed d-values
S1	β-SnO	3.208, 2.717, 2.437, 1.799
S2	β-SnO in THF-H_2O	3.028, 2.717,2.437, 1.799
S3	Cu_2O	2.478, 2.126, 1.507, 1.289
S4	β-SnO+Cu_2O	3.028, 2.478, 2.126
S5	Inorganic Residue from the reaction of [β-SnO + $PtCl_2(PPh_3)_3$ + 4-chlorobenzaldehyde + allylbromide in THF-H_2O] after work up.	3.446, 3.321, 2.666, 1.799

$ JCPDS references: β-SnO: 6-0395; SnO_2: 21-1250; Cu_2O: 5-0667

4. Table S2. Table containing XPS data of (β-SnO+Cu_2O) (for details see text)

Element	Treatment	Binding Energy (eV)
C (1s)	Nil	284.5, 287.6
C (1s)	Refluxed with allyl bromide	280.80, 283.2, 284.5, 287.6
Sn ($3d_{5/2}$)	Nil	486.9
Sn ($3d_{5/2}$)	Refluxed with allyl bromide	478.2
Cu ($2p_{3/2}$)	Nil	932.1
Cu ($2p_{3/2}$)	Refluxed with allyl bromide	923.7
O (1s)	Nil	531
O (1s)	Refluxed with allyl bromide	525.3, 529.3

5. Reference:

1. Brauer, G.(ed.) *Handbook of Preparative Inorganic Chemistry* **Vol 1**; Academic Press: New York, 1963.
2. Brauer, G.(ed.) *Handbook of Preparative Inorganic Chemistry* **Vol 2***;* Academic Press: New York, 1965.
3. Bailar, J. C. (Jr.), Itatori, H. *Inorg*. Chem. **1965**, 4, 1618.
4. Herrmann, W. A.; Salzer, A.(ed.) *Synthetic Methods of Organometallic and Inorganic Chemistry* **Vol 1**; George Thieme Verlag: New York, 1996.

Figure S1 XRD spectra of β-SnO

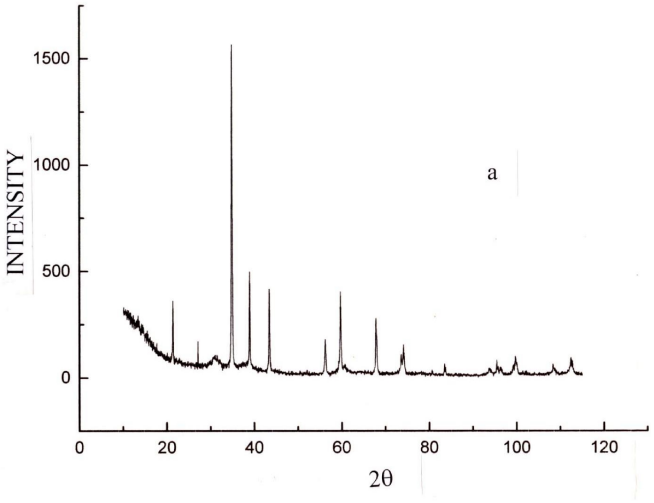

Figure S2. XRD spectra of β-SnO in THF-H_2O

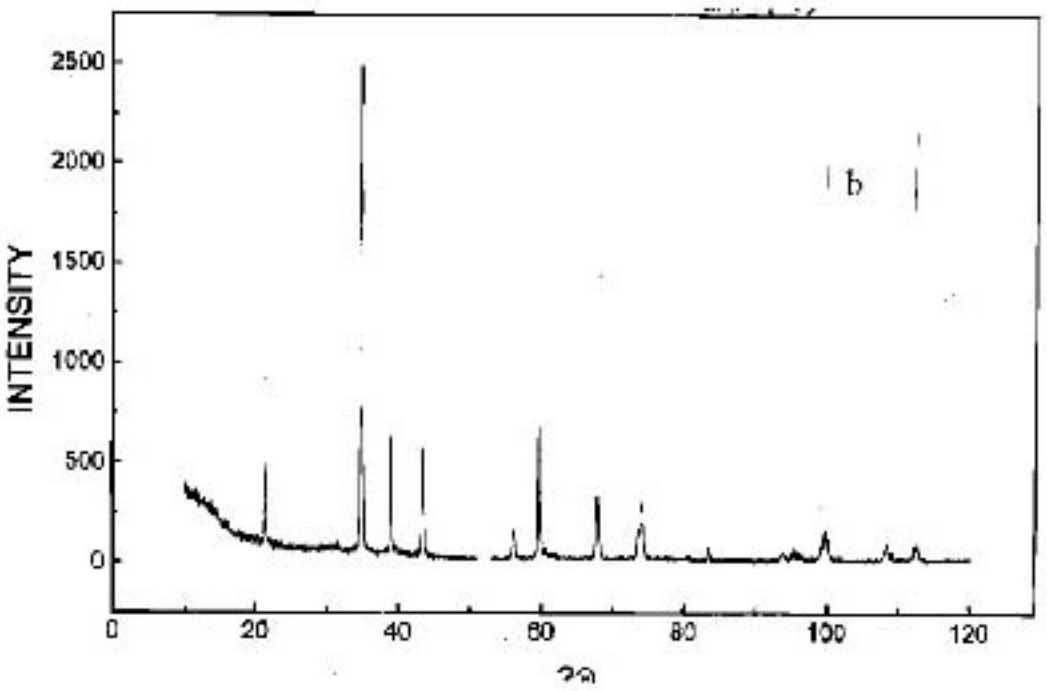

Figure S3. XRD spectra of Cu_2O

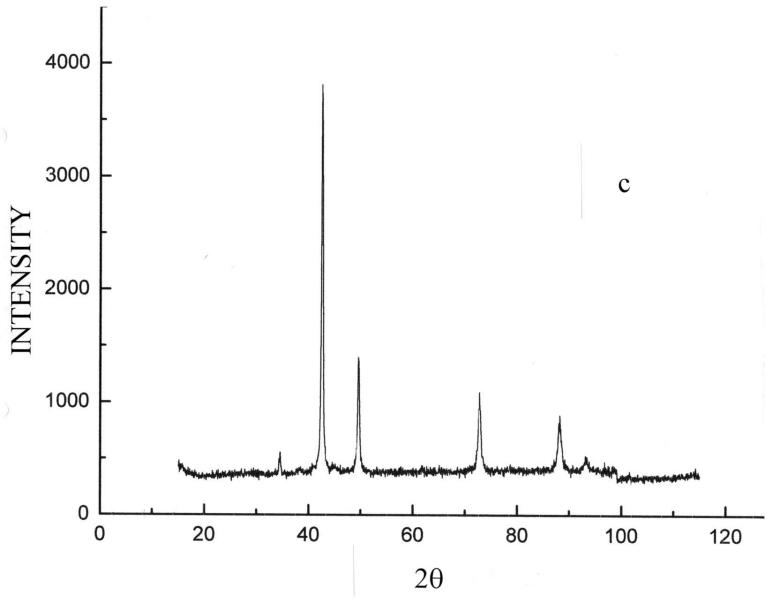

Figure S4. XRD spectra of β-SnO+Cu_2O

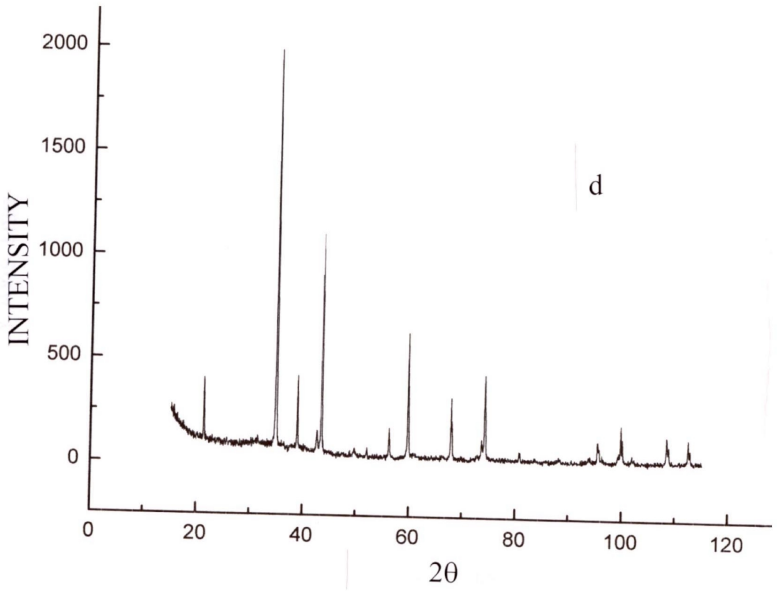

Figure S5. XRD spectra of Inorganic Residue from the reaction of

[β-SnO + $PtCl_2(PPh_3)_3$ + 4-chlorobenzaldehyde + allylbromide in THF-H_2O] after work up.

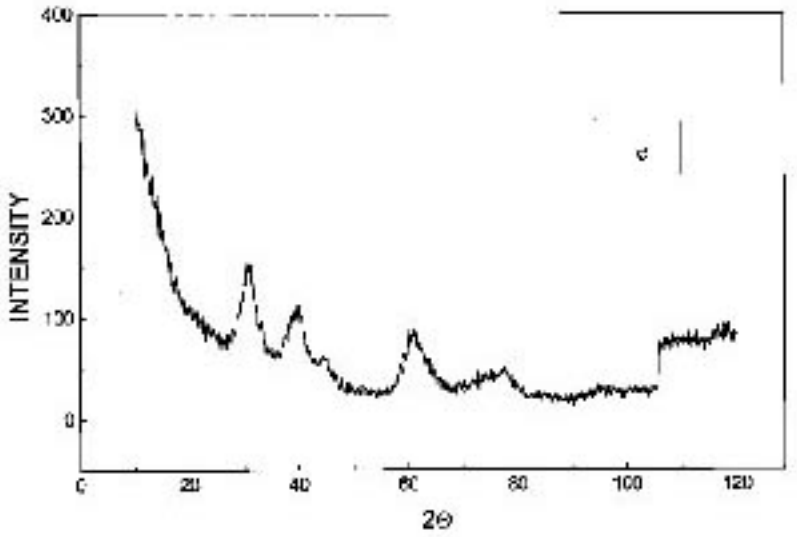

Figure S6. In-situ EIMS spectra of the reaction between β-SnO, $Pd_2(dba)_3$ and allyl bromide