# Synthesis of Surface Organopalladium Intermediates in Coupling

## **Reactions: The Mechanistic Insight**

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### **Supporting Online Material**

**General:** <sup>1</sup>H NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. The chemical shifts ( $\delta$ ) are reported in ppm, using TMS as an internal standard and CDCl<sub>3</sub> as solvent. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K $\alpha$  anode. The pressure in the spectrometer was about 10<sup>-9</sup> Torr. For energy calibration we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 284.6 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ± 0.1 eV. TGA-MS thermograms were

recorded on Mettler-Toledo TGA/SDTA 821<sup>e</sup> instrument coupled to Balzers Thermostar GSD 300T in the temperature range 25 - 1000°C with a heating rate of 10°C/min in nitrogen atmosphere.

EXAFS spectra at Pd K-edge were measured in a transmission mode at room temperature at the BL-10B station of the photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The energy and current of electrons in the storage ring were 2.5 GeV and 250-400 mA, respectively. X-rays from the storage ring were monochromatized by a Si(311) channel cut crystal. Ionization chambers filled with pure Ar and Kr gas were used to monitor the incident and transmitted X-rays, respectively. The EXAFS spectra were analyzed with the UWXAFS package. The threshold energy  $E_0$  was tentatively set at the inflection point of the absorption edge. The background was subtracted by the AUTOBK program. The  $k^3$ -weighted EXAFS data were Fourier transformed into R-space. The curve-fitting analysis was carried out using the FEFFIT program in the R-space. The k-range and Rspace were 30-130 or 30-160 nm<sup>-1</sup> and 0.1-0.3 nm, respectively. The number of independent parameters  $(N_{idp})$  in the curve-fitting of the Pd catalysts was evaluated to be 14 or 18 from Nyquist's law:  $N_{idp} = 2\Delta k \Delta R \pi^{-1} + 2$ . The fitting parameters were coordination numbers (CN), interatomic distances (R), Debye-Waller factors ( $\sigma$ ), and a correction-of-edge energy ( $\Delta E_0$ ). The same  $\Delta E_0$  was used for all the shells in a sample. The phase shifts and backscattering amplitudes were calculated by the FEFF8 code. The coefficient of the multiphoton effect  $(S_0^2)$  was fixed as 1.0 for the fitting.

Tetra-n-butyl ammonium bromide, NAIL purchased from CDH was dried and degassed by exposing the melt to vacuum/nitrogen for at least 2 h prior to use. MgCl<sub>2</sub>.6H<sub>2</sub>O and AlCl<sub>3</sub>.6H<sub>2</sub>O were purchased from Aldrich. Styrene, phenylboronic acid, phenylacetylene and tin reagents were purchased from Fluka. 4-chloroanisole was purchased from Merck and used as received. All the other solvents and chemicals were obtained from commercial sources and used as such without further purification. All the reactions were carried out under nitrogen atmosphere.

#### **Preparation of the catalyst:**

LDH (Mg-Al-Cl) preparation was based on literature procedure.<sup>1</sup> A mixture of MgCl<sub>2</sub>.6H<sub>2</sub>O (30.49 g, 0.15 mmol) and AlCl<sub>3</sub>.6H<sub>2</sub>O (12.07 g, 0.05 mmol) was dissolved in 200 mL of deionised water. To this aqueous solution, 100 mL of NaOH (2M) solution was slowly added at 25 °C and a further amount of 2M NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resulting suspension was stirred overnight at 70 °C. The solid product was isolated by filtration, washed thoroughly with deionised water and dried overnight at 80 °C. All the synthetic steps were carried out using decarbonated water.

 $Na_2PdCl_4$ :  $Na_2PdCl_4$  was prepared<sup>2</sup> by refluxing PdCl<sub>2</sub> (1.77 g, 10 mmol) and sodium chloride (0.58 g, 10 mmol) in 50 mL for 4 h. The solution was filtered in hot condition to avoid NaCl contamination. Evaporation of the filtrate gave dark brown flakes (2.88 g, 98%). **LDH-PdCl<sub>4</sub>:** Mg-Al-Cl (1.5 g) was suspended in 150 mL of aqueous Na<sub>2</sub>PdCl<sub>4</sub> (0.441 g, 1.5 mmol) solution and stirred at 25 °C for 12 h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water and vacuum-dried to obtain 1.752 g of LDH-PdCl<sub>4</sub> (0.86 mmol of Pd per gram).<sup>3</sup>

**LDH-Pd<sup>0</sup>:** LDH-PdCl<sub>4</sub> (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h at room temperature, filtered and washed with ethanol to give an air stable black powder (0.95 mmol of Pd per gram).<sup>3</sup>

#### Synthesis of Surface Transient Organometallic (STO) intermediates:

**LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1):** In a 100 mL Schlenk flask, the NAIL (3.23 g, 10 mmol) was heated to melt (130 °C) and degassed with nitrogen and vacuum prior to the addition of other reagents. After cooling the NAIL to room temperature, LDH-Pd<sup>0</sup> (105 mg, 10 mol%), 4-chloroanisole (28.2 mg, 0.2 mmol) were then added and the reaction was heated to 130 °C and stirred for 40 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain surface transient organometallic (STO) intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1) in good yield.

**LDH-PhPdCl (OA1'):** In a 100 mL Schlenk flask, the NAIL (3.23 g, 10 mmol) was heated to melt (130 °C) and degassed with nitrogen and vacuum prior to the addition of other reagents. After cooling the NAIL to room temperature, LDH-Pd<sup>0</sup> (105 mg, 10 mol%), chlorobenzene (23 mg, 0.2 mmol) were then added and the reaction was heated to 130 °C and stirred for 30 h under nitrogen atmosphere. After completion of the reaction,

the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-PhPdCl (OA1') in good yield.

Scheme S1. Oxidative Addition of Haloarenes

PhX + Pd(L)<sub>4</sub> 
$$\longrightarrow$$
 Ph L + 2L L X

#### Heck coupling

**HK2** ( $\sigma$ -complex): The STO intermediate, LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1), styrene (52 mg, 0.5 mmol), tri-*n*-butylamine (111 mg, 0.6 mmol), and *N*-methyl pyrrolidinone (5 mL) were charged in a round-bottomed flask. Reaction was carried out at 100 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate (**HK2**) in quantitative yield.

#### Synthesis of trans-4-methoxystilbene from HK2 intermediate:

The vacuum dried STO intermediate (HK2, 616 mg) on heating at 100 °C in NMP for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (592 mg) and *trans*-4-methoxystilbene (20 mg) in 88% isolated yield of the theoretical yield, which is calculated based on weight difference between HK2 and LDH-Pd<sup>0</sup>.

**HK2'** ( $\sigma$ -complex): The STO intermediate, LDH-PhPdCl (OA1'), styrene (52 mg, 0.5 mmol), tri-*n*-butylamine (111 mg, 0.6 mmol), and NMP (5 mL) were charged in a round-bottomed flask. Reaction was carried out at 100 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with

water and dichloromethane to obtain STO intermediate (HK2') in quantitative yield.

#### Synthesis of *trans*-stilbene from HK2' intermediate:

The vacuum dried STO intermediate (HK2', 641 mg), on heating at 100 °C in NMP for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (594 mg) and *trans*-stilbene (36 mg) in 92% isolated yield of the theoretical yield, which is calculated based on weight difference between HK2' and LDH-Pd<sup>0</sup>.

Our objective is to elucidate mechanism for coupling reactions by the isolation and identification of the reactive intermediates unambiguously on the solid support. We opted Stille-type reaction facilitated by KOAc, which is easily detectable by ESCA and TGA-MS and Suzuki cross coupling coaxed by easily discernable KF by ESCA to provide a strong evidence for the exchange of anion of the base with the Cl of the ArPdCl complex followed by metalation both in the Suzuki and Stille-type reactions.

#### Suzuki coupling

The use of KF in the Suzuki cross coupling reactions is well established.<sup>4-8</sup> Various bases (organic and inorganic) have been used in our studies in the present coupling reaction. We obtained optimum yields using KF as a base. We have reported the Suzuki cross coupling of deactivated chloroarenes using LDH-Pd<sup>0</sup> catalyst. The basic LDH surface in conjunction with a KF increases the electron density of the Pd center to promote metalation, which is responsible for higher activity. In view of the above and the easier identification of STO intermediates (SZ) by ESCA with KF (F 1s line at 685.3 eV) base prompted us to undertake studies with KF.

LDH-MeOC<sub>6</sub>H<sub>4</sub>PdF (SZ2) with 2 equiv. of potassium fluoride: The STO intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1), potassium fluoride (23 mg, 0.4 mmol) and acetonitrile (5 mL) were charged in a round-bottomed flask. Reaction was carried out at 80 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PdF (SZ2) in good yield.

LDH-MeOC<sub>6</sub>H<sub>4</sub>PdF (SZ2) with 0.5 equiv. of potassium fluoride: The STO intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1), potassium fluoride (3 mg, 0.05 mmol) and acetonitrile (5 mL) were charged in a round-bottomed flask. Reaction was carried out at 80 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediates LDH-MeOC<sub>6</sub>H<sub>4</sub>PdCl (OA1) and LDH-MeOC<sub>6</sub>H<sub>4</sub>PdF (SZ2).

**LDH-PhPdF (SZ2'):** The STO intermediate LDH-PhPdCl (**OA2**), potassium fluoride (23 mg, 0.4 mmol) and acetonitrile (5 mL) were charged in a round-bottomed flask. Reaction was carried out at 80 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate, LDH-PhPdF (**SZ2'**) in good yield.

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LDH-MeOC<sub>6</sub>H<sub>4</sub>PhPdB(OH)<sub>2</sub> (SZ3): The STO intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PdF (SZ2), phenylboronic acid (25 mg, 0.2 mmol) and 1,4-dioxane/water (5:1, 5 mL) were charged in a round-bottomed flask. Reaction was carried out at 100 °C for 10 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-MeOC<sub>6</sub>H<sub>4</sub>PhPdB(OH)<sub>2</sub> (SZ3) in good yield.

#### Synthesis of 4-methoxybiphenyl from SZ3 intermediate:

The vacuum dried STO intermediate (SZ3, 611 mg) on heating at 100 °C at in 1,4-dioxane/water (5:1, 5 mL) for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (597 mg) and 4-methoxybiphenyl (13 mg) in 94% isolated yield of the theoretical yield, which is calculated based on weight difference between SZ3 and LDH-Pd<sup>0</sup>.

LDH-PhPhPdB(OH)<sub>2</sub> (SZ3'): The STO intermediate LDH-PhPdF (SZ2), phenylboronic acid (25 mg, 0.2 mmol) and 1,4-dioxane/water (5:1, 5 mL) were charged in a round-bottomed flask. Reaction was carried out at 100 °C for 10 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-PhPhPdB(OH)<sub>2</sub> (SZ3') in quantitative yield.

#### Synthesis of biphenyl from SZ3' intermediate:

The vacuum dried STO intermediate (SZ3', 617 mg) on heating at 100 °C in 1,4dioxane/water (5:1, 5 mL) for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (598 mg)

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and biphenyl (18 mg) in 90% isolated yield of the theoretical yield, which is calculated based on weight difference between SZ3' and LDH-Pd<sup>0</sup>.

#### Sonogashira coupling

LDH-PhPdCCPh (SG2): The STO intermediate, LDH-PhPdCl (OA1'), phenylacetylene (51 mg, 0.5 mmol) and cuprous iodide (4 mg, 0.02 mmol), and THFwater (1:2, 6 mL) were charged in a round-bottomed flask. Reaction was carried out at 80 °C for 12 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-PhPdC=CPh (SG2) in good yield.

#### Synthesis of diphenylacetylene from SG2 intermediate:

The vacuum dried STO intermediate (SG2, 610 mg) on heating at 80 °C at in THF/water (1:2, 6 mL) for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (596 mg) and diphenylacetylene (13 mg) in 95% isolated yield of the theoretical yield, which is calculated based on weight difference between SG2 and LDH-Pd<sup>0</sup>.

#### Stille-type coupling

The reductive elimination products of the Suzuki and Stille<sup>12,13</sup> cross coupling reaction are the same (Ar-Ar'), while Suzuki and Stille-type<sup>3,13,14</sup> cross coupling reactions yield different products (Ar-Ar' and Ar- SnR<sub>3</sub>). In view of this it was felt to opt for Stille-type reaction. Since our interest is to isolate and study the transient organometallic intermediates primarily by XPS, Sn (stannane), which gives easily discernable lines at 485.7 eV and 494.1 eV for its  $3d_{5/2}$  and  $3d_{3/2}$ , respectively, is the best option. The base drives to yield Stille-type product ArSnR<sub>3</sub> via the exchange of anion of the base with the

chloride of the ArPdCl to give ArPdOAc and followed by metalation, ArPdSnR<sub>3</sub>.<sup>14</sup> Stilletype product has wide synthetic applications.<sup>15-21</sup>

**LDH-PhPdOAc (ST2):** The STO intermediate LDH-PhPdCl (**OA1'**), potassium acetate (40 mg, 0.4 mmol) and NMP (4 mL) were charged in a round-bottomed flask. Reaction was carried out at 50 °C for 5 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-PhPdOAc (ST2) in quantitative yields.

LDH-PhPdSnBu<sub>3</sub> (ST3): The STO intermediate LDH-PhPdOAc (ST2), tributyltin hydride (58 mg, 0.2 mmol) and NMP (5 mL) were charged in a roundbottomed flask. Reaction was carried out at 50 °C for 10 h under nitrogen atmosphere. After completion of the reaction, the solution was filtered and washed with water and dichloromethane to obtain STO intermediate LDH-PhPdSnBu<sub>3</sub> (ST3) in quantitative yield.

#### Synthesis of tributylarylstannane from ST3 intermediate:

The vacuum dried STO intermediate (ST3, 640 mg) on heating at 50 °C in NMP for 5 h under nitrogen atmosphere gave LDH-Pd<sup>0</sup> (599 mg) and tributylarylstannane (35 mg) in 85% isolated yield of the theoretical yield, which is calculated based on weight difference between ST3 and LDH-Pd<sup>0</sup>.

The final coupling products obtained in all the reactions are subjected for NMR, GC and mass spectroscopy, and the spectra are in accordance with those reported in the literature.

#### References

- 1. Miyata, S. Clays Clay Miner. 23, 369 (1975).
- Encyclopedia of Reagents for Organic Synthesis; John Wiley & Sons: Chichester, U. K., 1992; Vol. 4, p 2301.
- Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. J. Am. Chem. Soc. 2002; 124, 14127.
- 4. Wolfe J. P.; Buchwald, S. L. Angew. Chem. Int. Ed. 1999, 38, 2413.
- 5. Wolfe, J. P.; Stinger, R. A.; Yang, B. H.; Buchwald, S. L. J. Am. Chem. Soc. 1999, 121, 9550.
- Kabalka, G. W.; Wang, L.; Pagni, R. M.; Hair, C. M.; Namboodiri. V. Synthesis 2003, 2, 217.
- 7. Basu, B.; Das, P.; Bhuiyan, Md. M. H.; Jha, S. Tetahedron Lett. 2003, 44, 3817.
- 8. Wright, S. W.; Hageman, D. L.; McClure. L. D. J. Org. Chem. 1994, 59, 6095.
- Miyaura, N.; Yamada, K.; Suginome H.; Suzuki, A. J. Am. Chem. Soc., 1985, 107, 972.
- 10. Miyaura N.; Suzuki. A. Chem. Rev. 1995, 95, 24571.
- 11. Zhang, H.; Kwong, F. Y.; Tian, Y.; Chan. K. S. J. Org. Chem., 1998, 63, 6886.
- 12. Mitchell T. N. Synthesis 1991, 803.
- 13. Stille, J. K. Angew. Chem., Int. Ed. Engl. 1986, 25, 508.
- 14. Murata, M.; Watanabe, S.; Masuda, Y. Synlett 2000, 1043.
- 15. Corsico, E. F.; Postigo, A.; Rossi, R. A. Molecules 2000, 5, 1068.

- Yoon, C. H.; Chong, B, D.; Dueno, E.; Jung, K. W. ACS 221<sup>st</sup> national meeting in San Diego, CA, April, 2001.
- 17. Hunter, D. H.; Zhu, X. Journal of labelled compounds and radiopharmaceuticals 1999, 42, 653.
- Katisifis, A. G.; McPhee, M. E.; Mattner, F.; Ridley, D. D. Australian Journal of Chemistry 1999, 52, 1061.
- 19. Neumann, W. P. The Organic Chemistry of Tin, Wiley-Interscience, New York 1970.
- 20. Gielen, M.; de Poorter, B. Rev. Silicon Germanium Tin Lead Compd. 1977, 3, 9.
- 21. Gielen, M. Rev. Silicon Germanium Tin Lead Compd. 1981, 5, 6.

Table S-1. Measured binding energies (XPS) and m/z values (TGA-MS) for STO intermediates formed in the coupling reactions.

	Transient species	Binding Energy (eV)	Mass fragments (a.m.u)
Oxidative addition	OA1	Cl 2p 197.6; 198.4; 199.6; C 1s 288.8; 292.4; Pd 3d 337.1; 342. 3	15 (Me); 31(OMe) 76 (C <sub>6</sub> H <sub>4</sub> ) 107 (MeOC <sub>6</sub> H <sub>4</sub> )
	OA1'	Cl 2p 197.6; 198.4; 199.6; C 1s 288.8; Pd 3d 337.1;342.3	51 (C <sub>4</sub> H <sub>3</sub> ); 77 (C <sub>6</sub> H <sub>5</sub> )
Heck	НК2	Cl 2p 197.6;198.4;199.6 C 1s 284.2; 285.3; 288.8; 292.0 Pd 3d 336.4; 342.2 <sup>a</sup>	15 (Me); 30 (Cl) 36 (CH <sub>2</sub> O); 51 (C <sub>4</sub> H <sub>3</sub> ) 90 (C <sub>7</sub> H <sub>6</sub> ); 91 (C <sub>7</sub> H <sub>7</sub> )
			$\frac{103 (C_8H_7); 104 (C_8H_8)}{107 (MeOC_6H_4)}$
	НК2'	Cl 2p 197.6; 198.4; 199.6 C 1s 285.3; 287.1; 289.0 Pd 3d 336.3; 342.4	$51 (C_4H_3);77 (C_6H_5)$ $91 (C_7H_7); 104 (C_8H_8)$
Suzuki	SZ2	Pd 3d 339.0;345.6; F 1s 685.3 C 1s 283.9; 285.5; 287.6	19 (F); 51 (C <sub>4</sub> H <sub>3</sub> )
	SZ3	B 1s 192.6; O 1s 531.7; 532.6 C 1s 284.4; 285.5; 286.5; 287.3; 292.3	$\begin{array}{c} 15 \text{ (Me);} 17 \text{ (OH)19 (F);} \\ 26(C_2H_2)31 \text{ (OMe);} 45 \\ B(OH)_251 \text{ (C}_4H_3) \end{array}$
	SZ3'	Pd 3d 337.3, 342.3   B 1s 192.6; O 1s 532.6   C 1s 283.8; 285.2; 287.2   Pd 3d 337.5; 342.3	45 B(OH) <sub>2</sub> 51 (C <sub>4</sub> H <sub>3</sub> ) 77 (C <sub>6</sub> H <sub>5</sub> )
Sonogashira	SG2	C 1s 284.4; 285.3; 286.5 288.1; 289.1;Pd 3d 337.5; 341.8	51 (C <sub>4</sub> H <sub>3</sub> ); 77 (C <sub>6</sub> H <sub>5</sub> )
Stille-type	ST2	O 1s 531.1; 532.0 C 1s 284.2; 285.0; 288.9 Pd 3d 337.2; 341.3	43 (OAc); 44 (CO <sub>2</sub> )
	ST3	Sn 3d 485.7; 494.1; C 1s 284.2; 285.0; 286.3; 288.7; Pd 3d 336.9; 339.4	$\begin{array}{c} \hline 15 \ (\text{Me});26 \ (\text{C}_2\text{H}_2) \\ 29 \ (\text{C}_2\text{H}_5);43 \ (\text{C}_3\text{H}_7) \\ 51 \ (\text{C}_4\text{H}_3);54 \ (\text{C}_4\text{H}_6) \\ 56 \ (\text{C}_4\text{H}_8);57 \ (\text{C}_4\text{H}_9) \\ 77 \ (\text{C}_6\text{H}_5) \end{array}$

<sup>a</sup> The narrow scans of XPS spectra of Pd 3d shows 335.0 eV (3d<sub>5/2</sub>), 340.2 eV (3d<sub>3/2</sub>) lines in all the STO intermediates which are not presented here for clarity sake.



Figure S1. Deconvoluted XPS spectral lines for the STO intermediates formed in the coupling reactions.



Figure S2. TGA-MS fragments for STO intermediates formed in the Heck coupling reaction.

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**Figure S3.** EXAFS analysis of the Pd K-edge of fresh and used LDH-Pd(O) catalyst S16



**Figure S4.** TGA-MS fragments for STO intermediates formed in the Suzuki coupling reaction. S17

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Figure S5. TGA-MS fragments for STO intermediates formed in the Sonogashira coupling reaction.



Figure S6. TGA-MS fragments for STO intermediates formed in the Stille-type coupling reaction. S19