

Supporting Information

A Palladium Catalyzed Regio- and Stereoselective Four-Component Coupling Reaction

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General Methods: Benzene, toluene, xylenes and anisole were distilled under nitrogen from sodium. Methylene chloride, acetonitrile, diethylamine, *N,N*-dimethyltrimethylsilylamine and pyridine were distilled under nitrogen from calcium hydride. All transition metal catalysts were commercially obtained and stored in a nitrogen filled glovebox. Carbon monoxide and diphenyl diselenide were purchased and used without further purification. Diphenyl disulfide was recrystallized from methanol and dried at 30 °C under vacuum. Acetylenes were commercially obtained, dried under nitrogen with CaH₂, P₂O₅ or molecular sieves, and distilled prior to use. Chemical shifts were referenced to residual ¹H or ¹³C signals in deuterated solvents. Column chromatography was performed using Sorbent 60 32-60 standard grade silica gel and/or activated neutral Brockmann I alumina standard grade gel

General Procedure for the Preparation of Sulfenamides. According to the method of Davis et al.,¹ in a 250 mL round bottom flask was placed silver nitrate (780.0 mg, 4.60 mmol) in 70 mL of methanol. After dissolution had taken place, an equivalent of (PhS)₂ was added, and the reaction mixture was immediately cooled in an ice bath. Five equivalents of the appropriate amine were added, and the reaction was stirred overnight. The silver mercaptide salt was filtered off, and the solvent removed *in vacuo*. The resulting residue was dissolved in ether, washed with water (4 x 50 mL), dried over MgSO₄, and the solvent removed *in vacuo*. The sulfenamide was then purified by either vacuum distillation or column chromatography on alumina (5% ethyl acetate/hexanes).

General Procedure for the Preparation of the (Z)-1,2-Bis(arylchalcogeno)-1-

Alkenes: According to the method of Kuniyasu et al.,² to a glass bomb in a nitrogen filled glovebox were added an equivalent of diphenyl dichalcogenide (**2** or **31**), alkyne and 5% catalyst **3**. The reaction was heated for 24 h at 85 °C with stirring. The resultant solutions were filtered through celite, reduced *in vacuo*, and used without further purification.

General Procedure for the Preparation of (Z)-1,3-Bis(Arylchalcogeno)-2-Alken-1-

ones: Based on the method of Kuniyasu et al.,² to a glass bomb in a nitrogen filled glovebox were added an equivalent of diphenyl dichalcogenide (**2** or **31**), alkyne, and 4.5% catalyst **3**. The reaction was charged with 0.5 atm of CO gas and heated for 24 h for the sulfur derivatives and 72 h for the selenium derivatives at 85 °C with stirring. The resultant solutions were filtered through celite, reduced *in vacuo*, and used without further purification.

References:

- (1) Davis, F. A.; Friedman, A. J.; Kluger, E. W.; Skibo, E. B.; Fretz, E. R.; Milicia, A. P.; LeMasters, W. C.; Bentley, M. D.; Lacadie, J. A.; Douglass, I. B. *J. Org. Chem.* **1977**, *42*, 967.
- (2) Kuniyasu, H.; Ogawa, A.; Miyazaki, S.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.