Supporting Information for the article

Palladium-catalyzed addition of disulfides and diselenides to alkynes under solvent free conditions

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CONTENTS

1. Typical solvent free synthetic procedure

Ar_2E_2 ($1.0\cdot10^{-3}$ mol) and PPh_3 (39.3 mg, $1.5\cdot10^{-4}$ mol) were shaken at 100°C for 1-2 min until homogeneous yellow or light orange melt was formed. The $Pd(PPh_3)_4$ (1.2 mg, $1.0\cdot10^{-5}$ mol) was added to the melt followed by shaking reaction mixture for 1-2 min until homogeneous dark brown melt was obtained. The alkyne ($1.5\cdot10^{-3}$ mol) was added and reaction mixture was shaken for 1 min. The reaction was carried out in a sealed tube or in a screw-capped vessel in external bath at 100°C for 2h (depending on alkyne stability and reactivity 1.0-0.01 mol% of the catalyst may be used at 80-140°C).

2. Compounds separation and purification

After completing the reaction unreacted alkyne was removed on rotary evaporator and the crude product was pre-adsorbed on silica (15-40μm). Flash chromatography using dry vacuum column technique was used for product separation (see footnote 11a). Silica with pre-adsorbed product was placed on top of firmly pressed silica column of 5cm height and 2cm diameter. The solvent fractions of 10 ml were collected with Hexane:EtOAc used for gradient elution (0.1-1% increments).

For the products of Ar_2E_2 addition to **1-A**, **1-B** and **1-E** the unreacted Ar_2E_2 and PPh_3 were eluted first followed by the product. The products were isolated in 98+% purity as determined by NMR. The product of Ph_2S_2 addition to **1-D** overlaps with PPh_3 upon elution and was isolated as 90+% pure sample, which can be further purified to 98+% using conventional column chromatography. All the products were dried in vacuum.

For catalyst recycling: palladium complexes were separated as the last fraction after eluting Ar_2E_2, PPh_3 and the product. A 1:1 mixture of Hexane:EtOAc was used for eluting palladium complexes, followed by drying in vacuum. Brown oil, estimated yield 90-95% based on initial palladium complex.

For the products of Ph_2E_2 addition to **1-C** more easy alternative separation procedure was used. After completing the reaction and removing unreacted alkyne on rotor evaporator the crude was dissolved in 3 ml of toluene. The solution of HOOC-COOH in 2 ml of THF ($C_2O_4H_2$: Ph_2S_2

= 1:1) was added under stirring resulting in immediate white precipitate formation. The solid was washed with toluene, THF, extracted with methanol and dried in vacuum. The amine can be easily recovered from the salt by treating with aqueous base (3M NaOH) and extracting with CH_2Cl_2 (>95% yield).

3. Details of NMR studies

$^{31}P\{^{1}H\}$ NMR study under solvent free conditions. The sample was prepared directly in NMR tube in external bath at 80°C, placed into thermostated spectrometer probehead and kept for 30 min (80°C). The study was performed at 202.5 MHz on Bruker DRX-500 spectrometer using H_3PO_4/H_2O (capillary) as ^{31}P chemical shift reference.

Conversions measurement with ^{1}H NMR. The spectra were collected with ^{1}H 30° pulses of 4.0 μs and relaxation delay of 5 s (further increase of relaxation delay does not lead to noticeable integrals change). A 5000 Hz spectral window and 32k time domain points were used. For each spectrum 32 transients were collected. The data was zero filled to 64k size and processed with GM window function (LB=-0.5..-1.0, GB=0.1-0.3).

4. Kinetic measurements

The kinetic measurements were performed for studying reaction rate acceleration under solvent free conditions (see Table 2). Typical experimental setup was used to run the solvent free reaction (see footnote 13). An additional amount of toluene (1.4 and 4.4 ml) was added followed by shaking in the case of the reactions in solvent. The mixtures were heated in external bath at 80°C and 10μl samples were periodically taken for NMR analysis. The kinetic curves are shown on Figure S1; $t_{1/2}$ values (Table 2) were calculated based on linear regression analysis on initial concentration region. Kinetic measurement repeated in triplicate has shown good accuracy with the experimental errors below 5%.

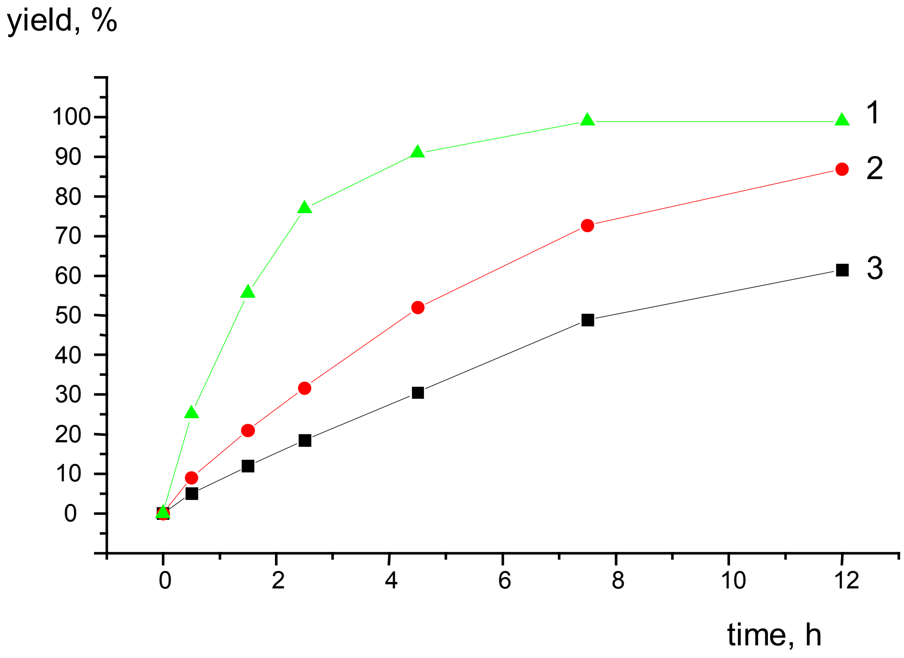

Figure S1. The yield of the product (**2-B**) of the catalytic Ph_2S_2 addition to **1-B**: 1 – under solvent free condition (reaction volume 0.6 ml); 2 and 3 – reactions in solvent (reaction volumes 2.0 and 5.0 ml, respectively).

5. Compounds characterization

In this section NMR, MS and microanalysis data is given for the prepared compounds (see also refs. 7, 10). The stereochemistry of each compound was confirmed with two-dimensional NOESY experiment. X-ray structures of both products of Ph_2E_2 (E=S, Se) addition to **1-C** were published separately (see ref. 10).

Ph_2S_2 addition to **1-A**, **1-B**, **1-C**, **1-D**, and **1-E**

Z-HC(SPh)=C(SPh)-C_6H_{10}(OH). Yellow oil. ^{1}H ($CDCl_3$; δ, ppm): 7.39 (m, 2H, Ph), 7.34 (s, 1H, HC=), 7.33-7.21 (m, 7H, Ph), 7.13 (m, 1H, Ph), 1.80-1.50 (m, 9H, CH_2), 1.64 (m, 1H, $^{1/2}CH_2$). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 138.2, 135.5, 135.1, 130.5, 129.1, 128.9, 127.3, 126.8, 125.4, 75.8, 36.3, 25.2, 21.8. Found, %: C 70.20; H 6.76; S 18.53. $C_{20}H_{22}OS_2$ Calc., %: C 70.13; H 6.47; S 18.72. MS (EI), m/e 342 (M^+).

Z-HC(SPh)=C(SPh)-CH_2-CH_2OH. Yellow oil. ^{1}H ($CDCl_3$; δ, ppm): 7.42 (m, 2H, Ph), 7.37 (m, 2H, Ph), 7.34-7.20 (m, 6H, Ph), 6.71 (s, 1H, HC=), 3.70 (t, 2H, J=6.2 Hz, CH_2OH), 2.48 (t, 2H, J=6.2 Hz, CH_2). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 135.2, 133.3, 132.9, 130.3, 130.0, 129.1, 129.0, 127.1, 127.0, 60.8, 40.0. Found, %: C 66.64; H 5.67; S 22.20. $C_{16}H_{16}OS_2$ Calc., %: C 66.63; H 5.59; S 22.23. MS (EI), m/e 288 (M^+).

Z-HC(SPh)=C(SPh)-CH_2-NMe_2·HOOC-COOH. White solid. ^{1}H (CD_3OD; δ, ppm): 7.62 (s, 1H, HC=), 7.52 (m, 2H, Ph), 7.44-7.27 (m, 8H, Ph), 3.87 (s, 2H, -CH_2-), 2.83 (s, 6H, CH_3-). $^{13}C\{^1H\}$ (CD_3OD; δ, ppm): 166.2, 149.9, 134.7, 133.2, 131.9, 130.8, 130.7, 130.6, 129.4, 128.8, 118.9, 62.1, 43.1. Found, %: C 58.11; H 5.46; N 3.53; S 16.16. $C_{19}H_{21}NO_4S_2$ Calc., % : C 58.29; H 5.41; N 3.58; S 16.38. MS (EI), m/e 301 (M^+-HOOC-COOH).

Z-HC(SPh)=C(SPh)-$^{\alpha}CH_2$-$^{\beta}CH_2$-$^{\gamma}CH_2$-$^{\delta}CH_3$. Light oil. ^{1}H ($CDCl_3$; δ, ppm): 7.41 (m, 2H, Ph), 7.37 (m, 2H, Ph), 7.34-7.18 (m, 6H, Ph), 6.56 (s, 1H, HC=), 2.25 (t, 2H, J=7.7 Hz, -$^{\alpha}CH_2$-), 1.48 (tt, 2H, J_1=7.7 Hz, J_2=7.5 Hz, -$^{\beta}CH_2$-), 1.25 (tq, 2H, J_1=7.3 Hz, J_2=7.5 Hz, -$^{\gamma}CH_2$-), 0.83 (t, 3H, J=7.3 Hz, -$^{\delta}CH_3$). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 135.9, 134.3, 133.8, 130.5, 129.7, 129.1, 129.0, 128.9, 126.8, 126.7, 36.8, 30.7, 21.9, 13.8. Found, %: C 71.99; H 6.68; S 21.08. $C_{18}H_{20}S_2$ Calc., % : C 71.95; H 6.71; S 21.34. MS (EI), m/e 300 (M^+).

Z,Z-HC(SPh)=C(SPh)-$^{\alpha}CH_2$-$^{\beta}CH_2$-$^{\alpha}CH_2$-(SPh)C=CH(SPh). Yellow oil. ^{1}H ($CDCl_3$; δ, ppm): 7.36 (m, 4H, Ph), 7.33-7.15 (m, 16H, Ph), 6.49 (s, 2H, HC=), 2.18 (t, 4H, J=7.3 Hz, -$^{\alpha}CH_2$-), 1.70 (m, 2H, J=7.3 Hz, -$^{\beta}CH_2$-). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 135.6, 133.5, 133.2, 130.5, 130.0, 129.7, 129.0, 128.9, 126.9, 126.8, 36.0, 27.3. Found, %: C 70.30; H 5.32; S 24.18. $C_{31}H_{28}S_4$ Calc., % : C 70.41; H 5.34; S 24.25. MS (EI), m/e 528 (M^+).

Ph_2Se_2 addition to **1-B** and **1-C**

HC(SePh)=C(SePh)-CH_2-CH_2OH. Yellow oil. ^{1}H ($CDCl_3$; δ, ppm): 7.54 (m, 4H, Ph), 7.29 (m, 6H, Ph), 7.09 (s, 1H, HC=), 3.69 (t, 2H, J=6.0 Hz, CH_2OH), 2.52 (t, 2H, J=6.0 Hz, CH_2). ^{77}Se ($CDCl_3$; δ, ppm): 403.6, 382.3. Found, %: C 50.37; H 4.28; Se 41.55. $C_{16}H_{16}OSe_2$ Calc., %: C 50.28; H 4.22; Se 41.32. MS (EI), m/e 384 (M^+).

Z-HC(SePh)=C(SePh)-CH_2-NMe_2·HOOC-COOH. White solid. ^{1}H (CD_3OD; δ, ppm): 7.99 (s, 1H, HC=), 7.62 (m, 2H, Ph), 7.55 (m, 2H, Ph), 7.36 (m, 6H, Ph), 3.87 (s, 2H, -CH_2), 2.82 (s, 6H, CH_3-). $^{13}C\{^1H\}$ (CD_3OD; δ, ppm): 166.6, 149.3, 134.4, 133.5, 131.0, 130.8, 129.5, 129.4, 130.76, 129.1, 120.6, 64.3, 43.2. ^{77}Se (CD_3OD; δ, ppm): 435.6; 364.2. Found, %: C 47.45; H 4.57; N 2.89; Se 32.76. $C_{19}H_{21}NO_4Se_2$ Calc., % : C 47.02; H 4.36; N 2.89; Se 32.54. MS (EI), m/e 397 (M^+-HOOC-COOH).

$(p\text{-}MePh)_2Se_2$ and $(p\text{-}F\ Ph)_2Se_2$ addition to **1-B**

Z-(p-MePhSe)HC=C(p-MePhSe)-CH_2-CH_2OH. Yellow oil, solidified on cooling. ^{1}H ($CDCl_3$; δ, ppm): 7.44 (m, 4H, Ar), 7.10 (m, 4H, Ar), 6.99 (s, 1H, HC=), 3.66 (t, 2H, J=6.2 Hz, CH_2OH), 2.47 (t, 2H, J=6.0 Hz, CH_2), 2.33 (s, 3H, CH_3), 2.32 (s, 3H, CH_3). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 137.7, 137.6, 133.4, 133.1, 131.1, 131.0, 130.1, 130.0, 61.0, 42.5, 21.1, 21.0. ^{77}Se ($CDCl_3$; δ, ppm): 395.3, 374.0. Found, %: C 52.72; H 4.98; Se 38.42. $C_{18}H_{20}OSe_2$ Calc., %: C 52.70; H 4.91; Se 38.49. MS (EI), m/e 412 (M^+).

Z-(p-F PhSe)HC=C(p-F PhSe)-CH_2-CH_2OH. Yellow oil, solidified on cooling. ^{1}H ($CDCl_3$; δ, ppm): 7.53 (m, 4H, Ar), 6.99 (m, 4H, Ar), 6.97 (s, 1H, HC=), 3.69 (t, 2H, J=6.2 Hz, CH_2OH), 2.48 (t, 2H, J=6.0 Hz, CH_2). $^{13}C\{^1H\}$ ($CDCl_3$; δ, ppm): 163.6, 161.7, 135.3, 135.2, 135.1, 131.4, 131.3, 125.1, 125.0, 123.5, 123.4, 116.7, 116.6, 116.5, 116.4, 61.0, 42.5. ^{77}Se ($CDCl_3$; δ, ppm): 398.5, 375.6. Found, %: C 46.23; H 3.45; Se 37.85. $C_{16}H_{14}F_2OSe_2$ Calc., %: C 45.95; H 3.37; Se 37.76. MS (EI), m/e 420 (M^+).