SUPPORTING INFORMATION FOR:

Oxidative Addition of Pd(0) to Ar-SO_2R bonds: Heck Type Reactions of Sulfones

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General Methods.

^{1}H NMR spectra were acquired at 200 or 300 MHz and ^{13}C NMR were acquired at 50 or 75 MHz (unless otherwise indicated). Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass spectra (MS) were determined at ionizing voltage of 70 eV. All reactions were carried out in anhydrous solvents and under argon atmosphere. THF and Et_2O were distilled from sodium-benzophenone under argon. CH_2Cl_2 was distilled from P_2O_5. Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). *n*-BuLi (2.5 M solution in hexane) and compounds **6**, **7**, **8f** and **11** were purchased from Aldrich.

Starting materials

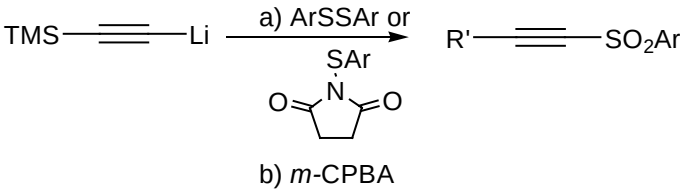
Diphenyl[(phenylsulfonyl)methyl]phosphine (10)[1]

To a solution of methylphenylsulfone (234 mg, 1.5 mmol) in 5 mL of THF, was added a 2.3M solution of *n*-BuLi in hexane (0.739 mL, 1.7 mmol) at -78 ºC. After 0.5 h chlorodiphenylphophine (1.7 mmol) was added at – 78 ºC and the temperature warmed to room temperature. Once the material was consumed (monitored by TLC), the mixture was treated with 10 mL of saturated solution of NH_4Cl and extrated with 10 mL of CH_2Cl_2. The organic phase was washed with a saturated solution of NaCl, and dried over anhydrous Na_2SO_4. After concentration under reduce pressure, the crude mixture was purified by flash-column chromatography (*n*-hexane-AcOEt 7:3), obtaining **10** as a white solid (188 mg). Yield: 40%. IR (KBr): 2897, 1590, 1490, 1309 cm^{-1}; ^{1}H-NMR (300

[1] Bordwell, F. G.; Mtthews, W. S.; Vanier, N. *J. Am. Chem. Soc*. **1975**, *97*, 442.

MHz) δ: 8.02 (dd, J = 7.2, 1.2 Hz, 2H), 7.62 (t, J = 4.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.2 (m, 10H), 4.06 (d, $J_{H\text{-}P}$ = 17 Hz, 2H); ^{13}C-NMR (75 MHz) δ: 149.5 (d, $J_{C\text{-}P}$ = 33Hz), 139.6, 134.2, 129.7, 129.1, 128.3, 125.6, 120.4, 120.3, 53.0 (d, $J_{C\text{-}P}$ = 140 Hz).

General method for the synthesis of alkynes 8 and 9



To a solution of trimethylsilylacetylene (1.5 g, 0.015 mmol) in anhydrous THF (20 mL) under argon atmosphere was added a 2.3M solution of *n*-BuLi in hexane (6.7 mL, 0.016 mmol) at –78 ºC. After 10 min., a solution of the disulfide or arylthiosuccinimide (0.015 mmol) in THF (10 mL) was added at –78 ºC.[2] Once the material was consumed (monitored by TLC), the reaction mixture was treated with 5 mL of saturated solution of NH_4Cl. Then, the mixture was diluted with 40 mL of Et_2O, dried with anhydrous $MgSO_4$ and solvent was concentrated to dryness. To this crude mixture diluted in CH_2Cl_2 (20 mL) was added dried *m*-CPBA (0.040 mmol) in 10 mL of CH_2Cl_2. Once the material was consumed (monitored by TLC), the crude mixture was treated with 10 mL of saturated solution of Na_2SO_3, washed with a saturated solution of Na_2CO_3 (3x15 mL), and solvent was concentrated to dryness. The purification it is indicated in each case.

[2] The thioalkynes derivates were prepared following the procedure described at: Savarin, C.; Srogl, J.; Liebeskind L. S. *Org. Lett.* **2001**, *3*, 91.

Phenylsulfonylethynyltrimetilsilane (9a)[3]

Following the general procedure the compound **9a** was obtained as colorless oil starting from phenyldisulfide. The product **9a** was used without further purification for the Heck reaction. Yield: 90%. ^{1}H-NMR (300 MHz) δ: 7.97 (d, *J* = 7.8 Hz, 2H), 7.70-7.50 (m, 3H), 0.17 (s, 9H); ^{13}C-NMR (75 MHz) δ: 141.1, 134.1, 129.2, 127.2, 101.9, 97.9, -1.3.

1-Ethynylsulfonyl-4-trifluoromethylbenzene (8e)

Following the general procedure the compound **8a** was obtained as a brown solid starting from trifluoromethylphenyldisulfide. The product **8a** was purified by column chromatography (hexane/AcOEt: 2/1). Yield: 85%. Brown solid; m.p.: 56.7-57.2 ºC; IR (film): 3185, 2039, 1604, 1403 cm^{-1}; ^{1}H-NMR (300 MHz) δ: 7.90 and 7.80 (AA´BB´ system *J* = 8.2 Hz, 4H), 3.82 (s, 1H); ^{13}C-NMR (75 MHz) δ: 147.0, 133.0 (q, J_{C-F} = 33.5 Hz), 123.0 (q, J_{C-F} = 271.7 Hz), 126.5, 125.0, 91.3, 80.9.

(4-Methoxybenzenesulfonylethynyl)trimethylsilane (9b) [4]

Following the general procedure the compound **9b** was obtained as white solid starting from 4-methoxyphenyldisulfide. The product **9b** was used without further purification for the Heck reaction. Yield: 81%; ^{1}H-NMR (300 MHz) δ: 7.90 and 7.01 (AA´XX´ system, *J* = 9.0 Hz, 4H), 3.86 (s, 3H), 0.18 (s, 9H); ^{13}C-NMR (75 MHz) δ: 164.1, 132.6, 129.8, 114.4, 100.6, 98.5, 55.6, -1.2.

[3] Zhang, C.; Balley, C. J.; Trudell, M. *J. Chem., Perkin Trans 1*, **1999**, 675.
[4] Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organometall. Chem. Syn.* **1971,** *1*, 145.

(4-Chlorobenzenesulfonylethynyl)trimethylsilane (9d)

Following the general procedure the compound **9d** was obtained as colorless oil starting from 4-chlorophenyldisulfide. The product **9d** was used without further purification for the Heck reaction. Yield: 99%. ^{1}H-NMR (200 MHz) δ: 7.94 and 7.55 (AA´BB´, J = 8.6 Hz, 4H), 0.20 (s, 9H); ^{13}C-NMR (75 MHz) δ: 142.3, 139.9, 130.9, 129.9, 92.5, 85.2, -1.9.

4-Ethynylsulfonyl(4-chlorobenzene) (8d)

Following the general procedure the compound **8d** was obtained as white solid starting from 1-chlorophenyldisulfide. The product **8d** was purified by column chromatography (hexane/AcOEt: 5/1). Yield: 68%; white solid; m.p.: 75-77 ºC; IR (film): 3233, 3089, 2064, 1823, 1655, 1573, 1337 cm^{-1}; ^{1}H-NMR (300 MHz) δ: 7.92 and 7.55 (AA´BB´ system, J = 5.7 Hz, 4H), 3.63 (s, 1H); ^{13}C-NMR (75 MHz) δ: 141.3, 138.9, 129.7, 128.9, 92.5, 79.5; Anal. Calcd for $C_8H_5O_2S$; C, 47.89; H, 2.51; S, 15.98; Found: C, 47.84; H, 2.46; S: 15.94.

1-Ethynylsulfonyl-4-nitrobenzene (9c)

Following the general procedure, the compound **9c** was obtained as yellow oil starting from 4-nitrophenyldisulfide. The product **9c** was purified by column chromatography (hexane/AcOEt: 15/1) as a yellow oil. Yield: 50%; ^{1}H-NMR (300 MHz) δ: 8.41 and 8.19 (AA´BB´ system, J = 5.9 Hz, 4H), 3.66 (s, 1H); ^{13}C-NMR (75 MHz) δ: 151.1, 145.8,

129.0, 124.6, 83.8, 78.9. Anal. Calcd for $C_8H_5NO_2S$: C, 45.50; H, 2.39; S, 15.18; Found: C, 45.40; H, 2.41; S: 15.29.

General method for Mizoroki-Heck reaction

In a sealed tube the correspoding sulfone (0.55 mmol, 1 equiv), $Pd(AcO)_2$ (5 mol%), Ag_2CO_3 (2 equiv) and PCy_3 (10 mol%) in anhydrous DMF (2 mL) was heated at 120 °C under argon atmosphere. Once the material was consumed (monitored by TLC), the crude mixture was diluted with Et_2O (5 mL), and the organic phase was washed with HCl (5%). Finally, the organic phase was dried with anhydrous $MgSO_4$ and solvent was concentrated to dryness. The residue was purified by flash-column chromatograph (eluent is indicated in each case).

(*E*)-1-(Phenylsulfonyl)-2-phenylethene (5)

Following the general procedure for Mizoroki-Heck reaction without PCy_3, the compound **5** was obtained as white solid starting from the comercial available phenylvinylsulfone. The product **5** was purified by flash-column chromatography: *n*-hexane-AcOEt 6:1; yield: 59%; white solid; mp. = 72-73 ºC; IR (KBr): 3000, 1605, 1480, 1325, 1175, 750 cm^{-1}; ^1H NMR (200 MHz): δ 7.93 (dd, *J* = 7.5, 1.0 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.20-7.40 (m, 8H), 6.85 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (75 MHz): δ 142.3, 140.4, 133.2, 132.0, 131.0, 129.1, 128.8, 128.3, 127.3; MS (EI): *m/z* 244 (M+, 58), 125 (22), 119 (56), 103 (66), 102 (93), 91 (100), 77 (99).

(*E*)- 1-(Phenylsulfinyl)-2-phenylethene (2)[5]

Following the general procedure for Mizoroki-Heck reaction without PCy_3, the compound **2** was obtained as yellow oil starting from comercial availabe phenylvinylsulfoxide. The product **2** was purified by flash-column chromatography: *n*-hexane-AcOEt 3:1; yield: 57%; yellow oil; ^{1}H NMR (200 MHz): δ 7.72-7.29 (m, 11H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H).

***(E)*-Ethyl cinnamate (12a)**[6]

Following the general procedure for Mizoroki-Heck reaction with ethyl acrylate (2 equiv) starting from different sulfones (see Table 2 and 3 of the manuscript), the compound **12a** was obtained as colorless oil. The product **12a** was purified by flash-column chromatography: *n*-hexane-AcOEt 15:1; colorless oil. Yield: 25-55%; ^{1}H-NMR (300 MHz) δ: 7.67 (d, *J* = 16.0 Hz, 1H), 7.53 (m, 2H), 7.50 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).

***(E)*-Butyl cinnamate (13a)**[7]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (2 equiv) starting from different sulfones (see manuscript), the compound **13a** was obtained as yellow oil. The product **13a** was purified by flash-column chromatography: *n*-hexane-AcOEt 15:1; yellow oil. Yield: 25-68 %. ^{1}H-NMR (200 MHz) δ: 7.75 (d, *J* = 16.1 Hz,

[5] Mikolajczyk, M.; Perlikowska, W.; Omelanczuk, J.; Cristau, H.-J.; Darcy, A.-P. *J. Org. Chem.* **1998,** *63*, 9716.
[6] Product commercial available from Aldrich.
[7] Product commercial available from Lancaster Synthesis.

1H), 7.70-7.38 (m, 5H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 1.69 (m, 2H), 1.60 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H).

***(E)*-Butyl-3-*p*-tolylacrylate (13f)** [8]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (3 equiv) starting from commercial available ethinylphenylsulfone (100 mg, 0.55 mmol), the compound **13f** was obtained as yellow oil. The product **13f** was purified by flash-column chromatography: *n*-hexane-AcOEt 15:1; yellow oil. Yield: 41%; ^{1}H-NMR (200 MHz) δ: 7.66 (d, 1H, *J* = 15.5 Hz), 7.42 and 7.25 (AA´XX´, *J* = 8.3 Hz, 4H), 6.42 (d, *J* = 15.5 Hz, 1H), 4.20 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 1.69 (m, 2H), 1.45 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (75 MHz) δ: 167.2, 144.4, 140.5, 131.7, 129.5, 128.0, 117.1, 64.2, 30.7, 21.3, 19.1, 13.7.

***(E)*-Butyl-3-(4-methoxyphenyl)acrylate (13b)**[9]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (3 equiv) starting from **9b** (100 mg, 0.40 mmol), the compound **13b** was obtained as yellow oil. The product **13b** was purified by flash-column chromatography: *n*-hexane-AcOEt 15:1; yellow oil. Yield: 30 %. ^{1}H-NMR (300 MHz) δ: 7.55 (d, *J* = 16.0 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.21 (d, *J* = 16.0 Hz, 1H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.69 (s, 3H), 1.60 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.33 (qt, *J* = 7.3, 6.8 Hz, 2H), 0.87 (q, *J* =7.3 Hz, 3H).

[8] Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511.
[9] Feuerstein, M.; Doucet, H.; Santelli, M.; *J. Org. Chem*. **2001**, *66*, 5923.

***(E)*-Butyl-3-[4-(trifluoromethyl)phenyl]acrylate (13e)**[10]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (3 equiv) starting from **8e** (100 mg, 0.45 mmol), the compound **13e** was obtained as yellow oil. The product **13e** was purified by flash-column chromatography: *n*-hexane-AcOEt 9:1; yellow oil (57 mg). Yield: 47%. ^{1}H-NMR (300 MHz) δ: 7.60 (d, *J* = 16.1 Hz, 1H), 7.55 (m, 4H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.43 (d, *J* = 16.1 Hz, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.62 (tt, *J* = 6.8, 6.8 Hz, 2H), 1.36 (qt, *J* = 6.8, 7.3 Hz, 2H), 0.89 (q, *J* = 7.3 Hz, 3H).

***(E)*-Butyl-3-(4-chlorophenyl)acrylate (13d)** [11]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (3 equiv) starting from the compound **9d** (100 mg, 0.45 mmol), the compound **13d** was obtained as yellow oil. The product **13d** was purified by flash-column chromatography: *n*-hexane-AcOEt 9:1; yellow oil (37 mg). Yield: 30%. ^{1}H-NMR (300 MHz) δ: 7.61 (d, 1H, *J* = 15.9 Hz), 7.43 (d, 2H, *J* = 8.6 Hz), 7.33 (d, 2H, *J* = 8.6 Hz), 6.38 (d, 1H, *J* = 15.9 Hz), 4.21 (t, 2H, *J* = 6.8 Hz), 1.60 (tt, 2H, *J* = 6.8, 6.8 Hz), 1.33 (qt, 2H, *J* = 7.3, 6.8 Hz), 0.87 (q, 3H, *J* =7.3 Hz).

***(E)*-Butyl -3-(4-nitrophenyl)acrylate (13c)**[12]

Following the general procedure for Mizoroki-Heck reaction with butyl acrylate (3 equiv) starting from the compound **8c** (122 mg, 0.49 mmol), the compound **13c** was obtained as yellow oil. The product **13c** was purified by flash-column chromatography: *n*-hexane-

[10] Hirabayashi, K.:; Ando, J.–I.; Nishihara, Y.; Mori, A.; Hiyama, T. *Synlett*. **1999**, 99.
[11] Du, X.; Suguro, M.; Hirabayashi, K.; Mori, A. *Org. Lett.* **2001**, *21*, 3313.
[12] (a) Gruber, A.; Zim, D.; Ebeling, G.; Monteiro, A.; Dupont J. *Org. Lett.* **2000**, *9*, 1287. (b) Feuerstein, M.; Docet, H.; Santelli, M. *J. Org. Chem*. **2001**, 5923.

AcOEt 9:1; yellow oil (67 mg). Yield: 55%; ^{1}H-NMR (300 MHz) δ: 8.18 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 16.0 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 7.3 Hz, 2H), 1.80-1.20 (m, 4H) 0.92 (t, *J* = 7.3 Hz, 3H).