Aryl Sulfoxides via Palladium-Catalyzed Arylation of Sulfenate Anions

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(I) General remarks

Dichloromethane was distilled from CaH_2 . All other reagents and solvents were used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Brüker ARX-400 spectrometer using the residual peak of chloroform-*d* as internal standard. Chemical shifts are reported in ppm. IR spectra were recorded on a Brüker Tensor 27 (pike) instrument and only the strongest or structurally most important peaks were listed. Chromatographic purifications were conducted using 40-63 μm silica gel and analytical TLC were performed on Merck precoated silica 60-F₂₅₄ plates.

(II) Experimental procedure and characterization data for β -sulfinyl ester 1c

According to Maitro, G.; Prestat, G.; Madec, D.; Poli, G. *J. Org. Chem.* **2006**, 71, 7449-7454.

To a solution of thiol (20 mmol) and potassium carbonate (5 mol%) in dichloromethane (5 mL) was added rapidly *tert*-butyl acrylate (3.2 mL, 22 mmol). After stirring for 20 h at room temperature, water was added to the mixture and the organic layer was washed with successively water (2 x 30 mL) and brine (2 x 30 mL), dried over anhydrous MgSO_4 and evaporated under reduced pressure. The product was obtained as a colorless oil with 94% yield and was used without further purification.

3-benzylsulfanyl-propionic acid *tert*-butyl ester:

^1H NMR (CDCl_3 , 400 MHz): δ 7.35-7.30 (m, 4H), 7.28-7.24 (m, 1H), 3.74 (s, 2H), 2.67 (t, J = 7.1 Hz, 2H), 2.48 (t, J = 7.3 Hz, 2H), 1.47 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 171.1, 138.2, 128.8, 128.5, 127.0, 80.6, 36.2, 35.6, 28.0, 26.4.

IR (neat): ν 2977, 1725, 1366, 1250, 1147, 845, 698 cm^{-1} .

MS (CI/ NH_3): m/z 270 (MNH_4^+), 253 (MH^+), 214 [$(\text{MNH}_4^+)-(t\text{-Bu})$], 197 [$(\text{MH}^+)-(t\text{-Bu})$].

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{S}$: C, 66.63; H, 7.99. Found: C, 66.29; H, 8.31.

According to R. P. Greenhalgh, *Synlett* **1992**, 235-236.

A dry dichloromethane solution (25 mL) of preceding thioether (10 mmol) was added to a suspension of wet neutral alumine oxide (10 g, ratio alumina oxide/water: 5 g for 1 mL) and Oxone[®] in dry dichloromethane (25 mL) at room temperature. The reaction mixture was refluxed for 3 h, then cooled to room temperature, filtered and evaporated under reduced pressure. Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 3:2 → 1:1 → 3:7) followed by recrystallization from *n*-hexane to afford the product as a white solid (81% yield).

3-phenylmethylsulfinyl-propionic acid *tert*-butyl ester **1c**:

¹H NMR (CDCl₃, 400 MHz): δ 7.34-7.24 (m, 5H), 3.94 (AB, J = 12.9 Hz, 2H), 2.91-2.81 (m, 1H), 2.71-2.63 (m, 3H), 1.38 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 170.3, 129.9, 129.5, 128.9, 128.3, 81.3, 58.3, 45.6, 27.9 (2C).

IR (powder): ν 2963, 1727, 1364, 1235, 1156, 1037, 774 cm⁻¹.

MS (CI/NH₃): m/z 269 (MH⁺), 213 [(MH⁺)-(*t*-Bu)].

Anal. Calcd for C₁₄H₂₀O₃S: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.55; H, 7.79; S, 12.12.

M.p. 64-66 °C.

(III) General procedure for palladium-catalyzed arylation of sulfenate anions under biphasic conditions

To a solution of tris(dibenzylideneacetone)dipalladium (5 mol%) in toluene (500 μ L) was added xantphos (10 mol%). The solution was stirred at room temperature for 5 min. Then, a solution of iodide substrate (0.6 mmol in 1.5 mL of toluene), β -sulfinylester (0.5 mmol in 1.5 mL of toluene), 3.5 mL of distilled water and 50% aqueous KOH solution (10 mmol) were successively added. The resulting biphasic system was stirred vigorously at 70 °C for 2 h. Then, after cooling to room temperature, the aqueous phase was extracted twice with dichloromethane, the collected organic layers were dried over anhydrous MgSO₄ and the

solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

(IV) Characterization data for aromatic sulfoxides starting from 1a

***p*-anisyl-*p*-tolyl sulfoxide 2a:**

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 → 85:15) to afford the product as a pale yellow solid (70% yield).

¹H NMR (CDCl₃, 400 MHz): δ 7.58-7.55 (m, 2H), 7.52-7.50 (m, 2H), 7.26 (d, J = 8.1 Hz, 2H), 6.98-6.94 (m, 2H), 3.82 (s, 3H), 2.38 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 161.9, 142.7, 141.3, 137.0, 130.0, 127.1, 124.8, 114.8, 55.5, 21.4.

IR (powder): ν 2921, 1592, 1493, 1248, 1036, 809 cm⁻¹.

MS (CI/NH₃): m/z 247 (MH⁺).

HRMS m/z calculated for C₁₄H₁₄O₂S (M⁺): 246.0715. Found: 246.0729.

M.p. 50-52 °C.

bis(*p*-tolyl) sulfoxide 3a:

Purification by silica gel chromatography (cyclohexane/ethyl acetate, 9:1 → 85:15) to give a white solid (81% yield).

Spectral data in agreement with those already reported by Laali, K. K.; Nagvekar, D. S. *J. Org. Chem.* **1991**, 56, 1867-1874 (and commercially available).

^1H NMR (CDCl_3 , 400 MHz): δ 7.53 (d, J = 8.1 Hz, 4H), 7.26 (d, J = 8.1 Hz, 4H), 2.38 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 142.8, 141.5, 130.1, 125.0, 21.5.

IR (neat): ν 2920, 1492, 1088, 1038, 1014, 805 cm^{-1} .

MS (CI/NH_3): m/z 461, 248 (MNH_4^+), 231 (MH^+).

***m*-anisyl-*p*-tolyl sulfoxide 4a:**

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 85:15) to afford a brown oil (63% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.56-7.54 (m, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.26-7.24 (m, 3H), 7.17-7.14 (m, 1H), 6.97-6.94 (m, 1H), 3.84 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 160.4, 147.2, 142.5, 141.8, 130.3, 130.1, 125.1, 117.3, 116.9, 109.0, 55.6, 21.5.

IR (neat): ν 2923, 1593, 1479, 1232, 1035, 684 cm^{-1} .

HRMS m/z calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$ (M^+): 246.0715. Found: 246.0729.

***o*-anisyl-*p*-tolyl sulfoxide 5a:**

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate 9:1 $\rightarrow$ 85:15) followed by recrystallization from *n*-hexane to give colourless crystals (79% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.93 (dd, J = 7.8, 1.8 Hz, 1H), 7.60 (d, J = 8.1 Hz, 2H), 7.41 (ddd, J = 8.1, 7.6, 1.8 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.17 (ddd, J = 7.8, 7.6, 1.0 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 3.81 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 155.7, 142.4, 141.4, 133.4, 132.1, 129.8, 125.5, 124.7, 121.7, 111.1, 55.8, 21.6.

IR (powder): ν 2921, 1477, 1273, 1030, 762 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$: C, 68.26; H, 5.73; S, 13.02. Found: C, 67.86; H, 5.77; S, 13.32.

M.p. 88-90 $^\circ\text{C}$.

***p*-acetophenyl-*p*-tolyl sulfoxide 6a:**

Purification by silica gel chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 85:15) to afford the product as a pale yellow solid (58% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 8.01 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 2.60 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 197.2, 150.9, 142.4, 141.9, 138.8, 130.3, 129.1, 125.2, 124.6, 26.9, 21.5

IR (powder): ν 2922, 1681, 1257, 1049, 806, 615 cm^{-1} .

MS (CI/ NH_3): m/z 276 (MNH_4^+), 259 (MH^+), 243.

HRMS m/z calculated for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$ (M^+): 258.0715. Found: 258.0712.

M.p. 102-104 $^\circ\text{C}$.

***p*-nitrophenyl-*p*-tolyl sulfoxide 7a:**

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 85:15) to afford the product as a pale yellow solid (82% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 8.32 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 9.1 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 153.3, 149.2, 143.0, 141.3, 130.6, 125.3, 125.2, 124.5, 21.6.

IR (powder): ν 3097, 1527, 1342, 1047, 851, 722 cm^{-1} .

MS (CI/NH_3): m/z 279 (MNH_4^+), 262 (MH^+).

HRMS m/z calculated for $\text{C}_{13}\text{H}_{11}\text{NO}_3\text{S}$ (M^+): 261.0460. Found: 261.0441.

Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3\text{S}$: C, 59.76; H, 4.24; N, 5.36. Found: C, 59.77; H, 4.22; N, 5.25.

M.p. 119-121 $^\circ\text{C}$.

***p*-trifluoromethylphenyl-*p*-tolyl sulfoxide 8a:**

Purification by silica gel flash chromatography (cyclohexane/ ethyl acetate, 9:1 $\rightarrow$ 85:15) to give a pale yellow oil (96% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.77 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 150.3 (C_{Ar}), 142.5 (C_{Ar}), 141.9 (C_{Ar}), 133.5 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 133.1 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 132.9 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 132.6 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 130.4 (CH_{Ar}), 127.6 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 127.0 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 126.3 and 126.2 (CH_{Ar}), 125.4 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 125.2 (CH_{Ar}), 124.9 (CH_{Ar}), 122.2 ($\text{C}_{\text{Ar}}/\text{CF}_3$), 21.5.

IR (neat): ν 2924, 1321, 1127, 1056, 808, 698 cm^{-1} .

HRMS m/z calculated for $\text{C}_{14}\text{H}_{11}\text{OF}_3\text{S}$ (M^+): 284.0483. Found: 284.0463.

2-thiophenyl-*p*-tolyl sulfoxide 9a:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1) to afford a brown oil (82% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.61-7.55 (m, 4H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.06 (dd, $J = 5.1$, 3.8 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 148.5, 142.0, 141.9, 132.3, 131.2, 130.0, 127.4, 124.5, 21.6.

IR (neat): ν 2921, 1402, 1082, 1042, 808, 712 cm^{-1} .

HRMS m/z calculated for $\text{C}_{11}\text{H}_{10}\text{OS}_2$ (M^+): 222.0173. Found: 222.0183.

***p*-bromophenyl-*p*-tolyl sulfoxide 10a:**

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate 9:1 $\rightarrow$ 85:15) to afford the product as a brown solid (61% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.60-7.57 (m, 2H), 7.53-7.48 (m, 4H), 7.27 (d, $J = 8.1$ Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 145.1, 142.1, 142.0, 132.5, 130.3, 126.2, 125.4, 125.0, 21.5.

IR (powder): ν 2921, 1471, 1089, 1048, 1006, 821, 805, 722 cm^{-1} .

MS (CI/NH_3): m/z 591, 314 (MNH_4^+), 297 (MH^+).

HRMS m/z calculated for $\text{C}_{13}\text{H}_{11}^{79}\text{BrOS}$ (M^+): 293.9714. Found: 293.9731.

M.p. 60-62 $^\circ\text{C}$.

1,2-(bis-*p*-tolylsulfinyl)benzene 11a:

The reaction was performed with 0.5 equiv. of 1,2-diiodobenzene for 16 h.

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 95:5 $\rightarrow$ 9:1 $\rightarrow$ 85:15 $\rightarrow$ 8:2 $\rightarrow$ 7:3) to afford a pale yellow solid in a quantitative yield.

Spectral data in agreement with those already reported by Tokunoh, R.; Sodeoka, M.; Aoe, K. I.; Shibasaki, M. *Tetrahedron Lett.* **1995**, 36, 8035-8038.

^1H NMR (CDCl_3 , 400 MHz): δ 8.02-7.98 (m, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.62 (dd, $J = 5.8$, 3.3 Hz, 4H), 7.30 (d, $J = 7.8$ Hz, 4H), 2.40 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 143.9, 142.6, 140.9, 132.4, 130.5, 125.8, 124.5, 21.6.

IR (powder): ν 2922, 1433, 1397, 1082, 1055, 1008, 808, 697 cm^{-1} .

(*meso*) 1,2-(bis-*p*-tolylsulfinyl)benzene 11a':

This product is obtained by treating **12** with wet neutral alumina and 2 equiv. of oxone[®] followed by purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 8:2 $\rightarrow$ 7:3) to give **11a'** as a white solid (40% overall yield, starting from **1a**).

^1H NMR (CDCl_3 , 400 MHz): δ 7.94-7.92 (m, 2H), 7.63-7.61 (m, 2H), 7.23 (d, $J = 8.1$ Hz, 4H), 7.13 (d, $J = 8.1$ Hz, 4H), 2.32 (s, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 144.5, 141.9, 141.1, 132.4, 130.0, 126.1, 125.9, 21.4.

IR (powder): ν 2923, 1445, 1048, 1026, 803, 756, 620 cm^{-1} .

MS (ESI^+): m/z 747 ($2\text{M}+\text{K}^+$), 731 ($2\text{M}+\text{Na}^+$), 393 (MK^+), 377 (MNa^+), 355 (MH^+).

HRMS m/z calculated for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{S}_2$ (M^+): 355.0821. Found: 355.0821.

M.p. 123-125 $^\circ\text{C}$.

(*Z*)-1-(hex-1-ene-1-sulfinyl)-4-methyl-benzene 15a:

Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 9:1 $\rightarrow$ 85:15 $\rightarrow$ 8:2) to afford the product as a colorless oil (33% yield).

Spectral data in agreement with those already reported by Maezaki, N.; Izumi, M.; Yuyama, S.; Sawamoto, H.; Iwata, C.; Tanaka, T. *Tetrahedron* **2000**, 56, 7927-7945.

^1H NMR (CDCl_3 , 400 MHz): δ 7.51 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 6.24-6.16 (m, 2H), 2.68-2.61 (dt, $J = 14.1, 6.6$ Hz, 1H), 2.58-2.51 (dt, $J = 14.1, 6.6$ Hz, 1H), 2.42 (s, 3H), 1.51-1.40 (m, 2H), 1.31-1.27 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 142.1, 141.5, 141.2, 137.1, 130.1, 124.2, 31.3, 29.2, 22.4, 21.5, 14.0.

(V) Characterization data for aromatic sulfoxides starting from 1b

2-naphthyl-*p*-tolyl sulfoxide 13b:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 8:2) to afford a pale brown solid (79% yield).

Spectral data in agreement with those already reported by Furukawa, N.; Ogawa, S.; Matsumura, K.; Fujihara, H. *J. Org. Chem.* **1991**, 56, 6341-6348.

^1H NMR (CDCl_3 , 400 MHz): δ 8.33-8.32 (m, 1H), 7.98-7.26 (m, 10H), 2.38 (s, 3H).

M.p. 82-84 °C.

2-naphthyl-*p*-anisyl sulfoxide 14b:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 8:2 $\rightarrow$ 7:3) to afford a pale brown solid (45% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 8.33 (s, 1H), 7.98-7.95 (m, 1H), 7.88-7.85 (m, 2H), 7.64-7.57 (m, 4H), 7.46-7.43 (m, 1H), 6.96 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 162.2, 142.8, 136.6, 134.3, 132.9, 129.6, 128.7, 128.1, 127.9, 127.6, 127.3, 125.0, 120.8, 115.0, 55.6.

IR (powder): ν 2964, 1592, 1494, 1252, 1039, 816 cm^{-1} .

MS (CI/NH_3): m/z 300 (MNH_4^+), 283 (M^+).

HRMS m/z calculated for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$ (M^+): 282.0715. Found: 282.0719.

M.p. 92-94 $^\circ\text{C}$.

(VI) Characterization data for aromatic sulfoxides starting from 1c

benzyl-*p*-tolyl sulfoxide 13c:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 9:1 $\rightarrow$ 85:15 $\rightarrow$ 8:2 $\rightarrow$ 7:3) followed by recrystallization from *n*-hexane/toluene (2:1) to afford colourless needles (70% yield).

Spectral data in agreement with those already reported by Katritzky, A. R.; Yang, B.; Qian, Y. *Synlett* **1996**, 701-702.

^1H NMR (CDCl_3 , 400 MHz): δ 7.33-7.23 (m, 7H), 7.02-6.99 (m, 2H), 4.05 (AB, J = 12.4 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 142.8, 141.7, 130.4, 129.6, 128.9, 128.5, 128.3, 124.5, 63.8, 21.5.

benzyl-*p*-anisyl sulfoxide 14c:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 95:5 → 9:1 → 85:15 → 8:2 → 7:3) to afford the product as a pale brown solid (46% yield).

Spectral data in agreement with those already reported by Donnoli, M. I.; Superchi, S.; Rosini, C. *J. Org. Chem.* **1998**, *63*, 9392-9395.

^1H NMR (CDCl_3 , 400 MHz): δ 7.33-7.24 (m, 5H), 7.01-6.92 (m, 4H), 4.04 (AB, J = 12.4 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 162.1, 133.7, 130.5, 129.4, 128.6, 128.3, 126.5, 114.4, 63.8, 55.6.

(VII) Characterization data for aromatic sulfoxides starting from 1d

isopropyl-*p*-tolyl sulfoxide 13d:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 8:2 → 7:3) to afford the product as a pale yellow oil (41% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.47 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 2.82 (hept, J = 6.8 Hz, 1H), 2.42 (s, 3H), 1.20 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 141.5, 138.5, 129.7, 125.1, 54.6, 21.5, 15.8, 14.2.

IR (neat): ν 2925, 1462, 1085, 1041, 1022, 811 cm^{-1} .

HRMS m/z calculated for $\text{C}_{10}\text{H}_{14}\text{OS}$ (M^+): 182.0765. Found: 182.0752.

isopropyl-*p*-anisyl sulfoxide 14d:

Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 8:2 → 75:25) to give the product as a pale brown oil (35% yield).

^1H NMR (CDCl_3 , 400 MHz): δ 7.54 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.82 (hept, J = 6.8 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 162.1, 132.7, 127.0, 114.5, 55.6, 54.7, 15.6, 14.6.

IR (neat): ν 2925, 1596, 1496, 1251, 1025, 738 cm^{-1} .

HRMS m/z calculated for $\text{C}_{10}\text{H}_{14}\text{O}_2\text{S}$ (M^+): 198.0715. Found: 198.0702.

(VIII) Experimental procedure for the *pseudo-domino* arylation/Mizoroki-Heck sequence and characterization data for compound **16**

To a solution of tris(dibenzylideneacetone)dipalladium (5 mol%) in DMF (500 μL) was added xantphos (10 mol%). The solution was stirred at room temperature for 5 min. Then, a solution of *p*-iodo-bromobenzene (0.373 mmol in 1.5 mL of DMF), 3-*p*-tolylsulfanyl-propionic acid *tert*-butyl ester **1a** (0.373 mmol in 1.5 mL of DMF), and Cs_2CO_3 (1.87 mmol, 5 equiv.) were successively added. The resulting system was stirred vigorously at 130 $^\circ\text{C}$ for 72 h. Then, after cooling to room temperature, water (5 mL) was added and the aqueous phase was extracted two times with dichloromethane. The collected organic layers were dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. The crude material was purified by flash column chromatography (cyclohexane/ethyl acetate, 9:1 → 8:2 → 7:3) to afford **16** (41 mg, 32% yield) as a white solid.

(*E*)-3-[4-(tolyl-4-sulfinyl)-phenyl]-acrylic acid *tert*-butyl ester **16**:

^1H NMR (CDCl_3 , 400 MHz): δ 7.65-7.63 (m, 2H), 7.59-7.53 (m, 5H), 7.28 (d, J = 7.8 Hz, 2H), 6.40 (d, J = 15.9 Hz, 1H), 2.38 (s, 3H), 1.53 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 165.9, 147.3, 142.2, 142.1, 142.0, 137.3, 130.3, 128.7, 125.2, 125.1, 122.3, 81.0, 28.2, 21.5.

IR (powder): ν 2977, 1704, 1635, 1320, 1144, 1045, 804 cm^{-1} .

MS (CI/ NH_3): m/z 343 (MH^+).

HRMS m/z calculated for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$ (M^+): 342.1290. Found: 342.1289.

M.p. 82-84 $^\circ\text{C}$.