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Supporting Information

Mn(III)-Mediated Regioselective Synthesis of (E)-Vinyl Sulfones

from Sodium Sulfinates and Nitro-olefins

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I. General Methods and materials:

All of the reactions were carried out in 25mL round-bottom flasks with air condensers. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on Varian 600 MHz and 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (TMS) (0.00 ppm) or CDCl₃ (7.26 ppm) for ¹H, CDCl₃ (77.0 ppm) for ¹³C. Flash column chromatography was performed on 200-300 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250µ) and visualized by fluorescence. MS were measured on a Bruker Apex IV FTMS spectrometer. Melting points were measured on a melting point tester RY-1G apparatus and uncorrected.

II. Experimental

The nitrostyrenes were synthesized according to the literatures as below:

- 1. M.-Y. Wu, M.-Q. Wang, K. Li, X.-W. Feng, T. He, N. Wang, X.-Q. Yu, *Tetrahedron Lett.* 2011, *52*, 679-683.
- 2. B. Quiclet-Sire, S. Z. Zard, Synthesis. 2005, 19, 3319-3326.

General experimental procedure for synthesis of (E)-Vinyl Sulfones



To a solution of nitro-olefin **1a** (1mmol) and sodium sulfinates **2a** (2 mmol, 2 equiv) in the DMF, was added Mn(OAc)₃ (447mg, 3 equiv), the mixture was stirring at 100 $^{\circ}$ C under the air atmosphere (1atm). The reaction was checked by TLC (thin layer chromatography). After the completion of the reaction, the mixture was poured into water, and extracted by ethyl acetate, washed with NaCl(aq), dried with anhydrous Na₂SO₄, then the solvent was removed under reduced pressure to obtain crude product, further purification by column chromatography on silica gel gave (E)-Vinyl Sulfones.

III. Compounds Characterization

(E)-(2-(phenylsulfonyl)vinyl)benzene $(3a)^1$



¹H NMR (600 MHz,CDCl₃, ppm) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 8.4 Hz, 3H), 6.87 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz,CDCl₃, ppm) δ 142.5, 140.7, 133.4, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.2.

(E)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3b)¹



H₃C⁷ ¹H NMR (600 MHz, CDCl₃, ppm

¹H NMR (600 MHz, CDCl₃, ppm) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 15.6 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 142.5, 141.8, 140.9, 133.2, 129.8, 129.6, 129.3, 128.5, 127.5, 126.0, 21.5.

(E)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene $(3c)^1$



MeO

¹H NMR (600 MHz, CDCl₃, ppm) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 15.6 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J*=7.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 162.1, 142.3, 141.1, 133.1, 130.4, 129.2, 127.4, 124.9, 124.4, 114.5, 55.4.

(E)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3d)¹



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.94 (d, *J* = 8.4, 2H), 7.64 (d, *J* = 9.6 Hz, 1H), 7.62 (s, 1H), 7.57-7.54 (m, 2H), 7.44-7.39 (m, 2H), 7.38-7.34 (m, 2H), 6.84 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 140.9, 140.4, 137.2, 133.5, 130.8, 129.7, 129.4, 129.2, 127.9, 127.6.

(E)-1-bromo-4-(2-(phenylsulfonyl)vinyl)benzene (3e)¹



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.63-7.60 (m, 2H), 7.55 (t, *J*=7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 141.0, 140.4, 133.5, 132.3, 131.3, 129.9, 129.4, 128.0, 127.7, 125.6.

(E)-1-bromo-2-(2-(phenylsulfonyl)vinyl)benzene $(3f)^2$



¹H NMR (600 MHz, CDCl₃, ppm) δ 8.08 (d, *J* = 15.6 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.69-7.62 (m, 2H), 7.59 (t, *J*=7.8 Hz 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J*=7.8 Hz 1H), 7.28 (s, 1H), 6.86 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 141.0, 140.3, 133.6,133.5, 132.5, 132.0, 130.2, 129.4, 128.2, 127.8, 127.8, 125.5.

(E)-1-bromo-2-(2-tosylvinyl)benzene (**3g**)



Yellow solid, mp 98-100°C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.03 (d, J = 15.6 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.34-7.21 (m, 3H), 6.83 (d, J = 15.6 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 144.6, 140.4, 137.3, 133.6, 132.6, 131.9, 130.5, 130.0, 128.2, 127.9,127.8, 125.5, 21.6. HRMS Calculated for C₁₅H₁₃BrO₂S [M+Na]⁺ 358.9712, found 358.9720.

(E)-1-bromo-2-(2-((4-chlorophenyl)sulfonyl)vinyl)benzene (**3h**)



White solid, mp 125-128°C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 8.05 (d, *J* = 15.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 3.3 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 141.5, 140.3, 138.8, 133.7, 132.3, 132.2, 129.8, 129.7, 129.3, 128.2, 127.8, 125.6. HRMS Calculated for C₁₄H₁₀BrClO₂S [M+H]⁺ 356.9346, found 356.9355.

(E)-1-chloro-4-(styrylsulfonyl)benzene(3i)¹



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.43-7.40 (m, 3H), 6.83 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ .143.0, 140.1, 139.2, 132.1, 131.4, 129.6, 129.1, 128.6, 126.8.

(E)-1-chloro-4-((4-methylstyryl)sulfonyl)benzene (3j)



H₃C

Yellow solid, mp 100-102°C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 7.88 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 15.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.77 (d, J = 15.6 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 143.1, 142.1, 139.9, 139.4, 129.8, 129.6, 129.4, 129.0, 128.6, 125.6, 21.5. HRMS Calculated for $C_{15}H_{13}CIO_2S$ [M+H]⁺ 293.0396, found 293.0403.

(E)-1-chloro-4-((4-methoxystyryl)sulfonyl)benzene(3k)



Yellow solid, mp 104-107°C. ¹H NMR (600 MHz, CDCl₃, ppm) δ 7.87 (d, J = 8.4 Hz, 2H), 7.63 (d, J =

15.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.68 (d, J = 15.6 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 162.2, 142.8, 139.8, 139.7, 130.4, 129.6, 129.0, 124.8, 124.0, 114.6, 55.5. HRMS Calculated for C15H13CIO3S [M+H]+ 309.0347, found 309.0352.

(E)-1-chloro-4-(2-((4-chlorophenyl)sulfonyl)vinyl)benzene(31)³



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 15.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 15.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃,ppm) δ 141.5, 140.3, 139.0, 137.5, 130.7, 129.8, 129.7, 129.5, 129.2, 127.5. (E)-1-methyl-4-(styrylsulfonyl)benzene $(3m)^1$



¹H NMR (400 MHz, CDCl₃, ppm) δ 7.83 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 15.6 Hz, 1H), 7.51-7.43 (m, 2H), 7.39 (d, J = 6.6 Hz, 3H), 7.34 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 15.6 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 144.4, 141.9, 137.7, 132.4, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.6.

(E)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (**3n**)⁴



¹H NMR (400 MHz, CDCl₃, ppm) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 15.6 Hz, 1H), 7.37-7.32 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 15.6 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 144.2, 142.0, 141.7, 138.0, 129.9, 129.7, 129.7 128.5, 127.6, 126.4, 21.5, 21.4. *(E)-1-methoxy-4-(2-tosylvinyl)benzene* (**3**0)⁴



MeO

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 161.9, 144.1, 141.7, 138.2, 130.3, 129.9, 127.5, 125.0, 124.8, 114.4, 55.4, 21.5.

(E)-1-chloro-4-(2-tosylvinyl)benzene (**3p**)⁴



¹H NMR (400 MHz, CDCl₃, ppm) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 3H), 7.18 (s, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 144.5, 140.4, 137.5, 137.1, 130.9, 129.9, 129.6, 129.3, 128.2, 127.7, 21.6. *(E)-1-bromo-4-(2-tosylvinyl)benzene*(**3q**)⁴



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J*=8.4 Hz 4H), 6.83 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃, ppm) δ 144.6, 140.5, 137.5, 132.3, 131.4, 130.0, 129.8, 128.4, 127.7, 125.5, 21.6. *(E)-2-(2-tosylvinyl)phenol*(**3r**)⁵



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.83 (t, J=9.9 Hz, 2H), 7.37 (d, J = 15.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.24 (s, 2H), 7.20 (d, J = 15.6 Hz, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 15.6 Hz, 1H), 6.58 (s, 1H), 2.43 (s, 3H); ¹³C NMR (150 MHz, CDCl₃, ppm) δ 155.7, 144.1, 138.3, 137.9, 132.2, 131.0, 129.9, 128.1, 127.6, 120.9, 119.7, 116.5, 21.6.

(E)-2-(2-tosylvinyl)furan $(3s)^6$

¹H NMR (600 MHz, CDCl₃, ppm) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.47 (s, 1H), 7.41 (d, *J* = 15.0 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 15.0 Hz, 1H), 6.69 (d, *J* = 3 Hz, 1H), 6.48 (s, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 145.5, 129.9, 128.4, 127.6, 125.1, 116.6, 112.5, 21.5. *(E)-1-fluoro-4-((4-methoxystyryl)sulfonyl)benzene*(**3**t)



White solid, mp 114-116°C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.00-7.88 (m, 2H), 7.62 (d, *J* = 15.6 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 15.6Hz, 1H), 3.83 (s, 3H); ¹³C NMR (150 MHz, CDCl₃, ppm) δ 166.3 , 164.6, 162.2, 142.4, 137.2 (d, *J* = 3.0 Hz), 130.5 – 130.2 (m), 124.8, 124.2, 116.7, 116.4, 114.5, 55.4. HRMS Calculated for C₁₅H₁₃FO₃S [M+H]⁺ 393.0631, found 393.0635.

(E)-1-methoxy-4-((4-methylstyryl)sulfonyl)benzene(3u)



White solid, mp 109-112°C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.86 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 15.6 Hz, 1H), 7.36 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 163.4, 141.5, 141.4, 132.4, 129.8, 129.7, 128.4, 126.7, 114.5, 55.6, 21.4. HRMS Calculated for C₁₆H₁₆O₃S [M+Na]⁺ 311.0712, found 311.0717.

(*E*)-1-methoxy-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene(**3v**)



Yellow solid, mp 110-114°C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.86 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 15.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 163.4, 161.9, 141.1, 132.7, 130.2, 129.7, 125.1, 125.1, 114.4, 55.6, 55.4. HRMS Calculated for C₁₆H₁₆O₄S [M+H]⁺ 305.0842, found 305.0848.

(E)-1-methoxy-2-(2-(phenylsulfonyl)vinyl)benzene(**3w**)⁷



¹H NMR (600 MHz, CDCl₃, ppm) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 15.6 Hz, 1H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.44-7.35 (m, 2H), 7.08 (d, *J* = 15.6 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 3.88 (s, 3H).¹³C NMR (100 MHz, CDCl₃, ppm) δ 158.8, 141.2, 138.5, 133.1, 132.5, 130.8, 129.2, 127.8, 127.6, 121.1, 120.8, 111.2, 55.5.

IV NMR spectra data











190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)



















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)

















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