Supporting Information

Revealing the Metal-like Behavior of Iodine: An Iodide-Catalyzed Radical Oxidative Alkenylation

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General information
General procedure for the iodide-catalysed Heck-type alkenylationS2
General procedure for cyclic voltammetry (CV)S2
Table S1S3
Detail descriptions for products
References
Copies of product ¹ H NMR, ¹³ C NMR and ¹⁹ F NMR

General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Sulfonyl hydrozins^[1] and 1-(4-bromophenyl)-2-tosylethanol (**5b**)^[2] were prepared following literature procedures. KI was dried over 200 °C for 1 h. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and naphthalene was added as internal standard. For the ReactIR kinetic experiments, the reaction spectra were recorded using an IC 15 from Mettler-Toledo AutoChem. ¹H and ¹³C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

General procedure for the iodide-catalysed Heck-type alkenylation

In a clean tube equipped with a stir bar, KI (19.9 mg, 0.12 mmol) and sulfonyl hydrazine **1** (0.33 mmol) were combined and sealed. An N₂ balloon was fixed and purged for 3 times. DMSO (0.15 mL), HOAc (0.15 mL) and alkene **2** (0.30 mmol) was injected into the tube via syringe. Subsequently, TBHP (77.0 mg, 70% in aqueous solution, 0.60 mmol) was slowly injected into the reaction tube. The reaction was then stirred at 25-30 °C for 10 h. After completion, the reaction was quenched with water. After extraction with ethyl ether (3 x 10 mL), the organic layers were combined and dried over anhydrous Na₂SO₄, the pure product was obtained by flash column chromatography on silica gel (petroleum: ethyl acetate = 20:1).

General procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under Nitrogen at room temperature. The working electrode was a steady gold disk (d = 3 mm), the counter electrode a platinum wire. The reference was a Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 10 mL of DMSO containing 0.1 M $^{n}Bu_{4}NBF_{4}$ were poured into the electrochemical cell in all experiments.

Table S1

	\sim	40 mol% KI 2 equiv TBHP	0,0	
<i>p</i> -Tol	S ⁻ NHNH ₂ P-Tol 1a 2a	DMSO / HOAc = 1:1 r.t., 10 h	p-Tol p-Tol 3a	
Entry	Entry Variation from the "standard conditions"			
1		none		
2		no Kl		
3	20 mol%	20 mol% KI, instead of 40 mol% KI		
4		only DMSO		
5		only HOAc		
6		only DMSO, 80 °C		
7	20 mol% CuBr	20 mol% CuBr or FeBr ₂ , instead of 40 mol% KI		
8		open to air		
9		1 equiv tempo		

Effects of reaction parameters.^[a]

[a] The reactions were carried out with **1a** (0.33 mmol), **2** (0.30 mmol), KI (40 mol%), TBHP (0.60 mmol, 70% in aqueous solution), DMSO (0.15 mL), HOAc (0.15 mL), 20 °C, 10 h. [b] Yields are determined by GC analysis with naphthalin as the internal standard. n.d. = not detected.

The presense and amount of KI were both crucial for the reaction (Table S1, entry 2-3). It's worth noting that both of the solvents are fatal for the successful alkenylation since the yield decreased dramatically with only one solvent (Table S1, entry 4-5). Indeed, a moderate yield could be observed only with DMSO but an increased temperature is need (Table S1 entry 6). Copper and iron catalysts have been reported to initiate radicals from sulfonyl hydrazines under oxidative conditions.^[3] However, they were ineffective in this transformation, which indicated that iodine might involeved in the radical elimination process (Table S1, entry 7). To our pleasure, the reaction was

not sensitive to moisture and air since it still proceeded well when conducted open to air (Table S1, entry 8). Addition of tempo totally shut the reaction down, which indicated a radical involvement in this reaction (Table S1, entry 9).

Since β -hydroxysulfones could be generated for some electron-neutral and electron-rich olefins at 20 °C, the substrate scope was conducted under a slightly increase temperature of 25 – 30 °C to ensure the selectivity.

Detail descriptions for products



(*E*)-1-Methyl-4-((4-methylstyryl)sulfonyl)benzene (3a)^[4]: ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.08, 141.79, 141.52, 137.72, 129.75, 129.59, 129.45, 128.35, 127.42, 126.19, 21.42, 21.33.



(*E*)-1-Methoxy-4-((4-methylstyryl)sulfonyl)benzene (3b):^[5] ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.83 (m, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.10 – 6.98 (m, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 3.88 (s, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.97, 144.14, 141.75, 138.16, 130.32, 129.91, 127.58, 125.06, 124.78, 114.49, 55.45, 21.62.

(*E*)-1-Fluoro-4-((4-methylstyryl)sulfonyl)benzene (3c): ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.16 (m, 4H), 6.80 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.45 (d, *J* = 255.8 Hz), 142.67, 141.95, 136.91 (d, *J* = 3.1 Hz), 130.36 (d, *J* = 9.6 Hz), 129.77, 129.37, 128.55, 125.75, 116.52 (d, J = 22.6 Hz), 21.47. ¹⁹F NMR (376 MHz, CDCl₃) δ -104.14. HRMS (ESI) calcd for C₁₅H₁₃FO₂S [M+H]⁺: 277.0693; found: 277.0693



(*E*)-1-Chloro-4-((4-methylstyryl)sulfonyl)benzene (3d): ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.84 (m, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.03, 142.02, 139.82, 139.33, 129.76, 129.52, 129.30, 128.99, 128.57, 125.45, 21.47. HRMS (ESI) calcd for C₁₅H₁₃ClO₂S [M+H]⁺: 293.0398; found: 293.0396.



(*E*)-1-Bromo-4-((4-methylstyryl)sulfonyl)benzene (3e): ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.75 (m, 2H), 7.70 – 7.63 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.09, 142.05, 139.87, 132.51, 129.78, 129.30, 129.07, 128.59, 128.41, 125.40, 21.49. HRMS (ESI) calcd for C₁₅H₁₃BrO₂S [M+H]⁺: 336.9892; found: 336.9893.



(*E*)-1-Methyl-4-(2-((4-(trifluoromethyl)phenyl)sulfonyl)vinyl)benzene (3f): ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 15.4 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.56, 144.15, 142.42, 134.92 (*J* = 23.1 Hz), 129.92, 129.27, 128.78, 128.19, 126.46 (*J* = 3.7 Hz), 123.18 (*J* = 274.0 Hz), 124.95, 21.59. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.14. HRMS (ESI) calcd for C₁₆H₁₃F₃O₂S [M+H]⁺: 327.0661; found: 327.0660.



(*E*)-1-Chloro-2-fluoro-3-((4-methylstyryl)sulfonyl)benzene (3g): ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.87 (m, 1H), 7.76 (d, *J* = 15.3 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 15.3 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.11 (*J* = 259.0 Hz), 145.69, 142.51, 135.99, 130.68 (*J* = 14.4 Hz), 129.92, 129.34, 128.90, 127.77, 124.97 (*J* = 4.9 Hz), 124.33 (*J* = 17.9 Hz), 122.97 (*J* = 17.9 Hz), 21.62. ¹⁹F NMR (376 MHz, CDCl₃) δ -110.53. HRMS (ESI) calcd for C₁₅H₁₂ClFO₂S [M+H]⁺: 311.0303; found: 311.0305.



(*E*)-1-Methyl-4-(2-(octylsulfonyl)vinyl)benzene (3h): ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 15.5 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 15.5 Hz, 1H), 3.16 – 2.98 (m, 2H), 2.41 (s, 3H), 1.90 – 1.74 (m, 2H), 1.46 – 1.33 (m, 2H), 1.36 – 1.24 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.68, 141.91, 129.79, 129.44, 128.50, 123.38, 55.18, 31.61, 28.96, 28.87, 28.32, 22.51, 21.49, 14.00. HRMS (ESI) calcd for C₁₇H₂₆O₂S [M+H]⁺: 295.1726; found: 295.1723.



(*E*)-1-(*tert*-Butyl)-4-(2-tosylvinyl)benzene (3i): ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.41 (d, *J* = 0.9 Hz, 4H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H), 1.30 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 154.84, 144.27, 141.93, 137.95, 129.95, 129.67, 128.44, 127.64, 126.61, 126.07, 34.98, 31.11, 21.64. HRMS (ESI) calcd for C₁₉H₂₂O₂S [M+H]⁺: 315.1413; found: 315.1411.



(*E*)-1-Fluoro-4-(2-tosylvinyl)benzene (3j):^{[5] 1}H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 15.4 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 (d, J = 8.1 Hz,

2H), 6.81 (d, J = 15.4 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.28 (J = 253.7 Hz), 144.50, 140.61, 137.63, 130.57 (J = 8.7 Hz), 130.02, 128.71 (J = 3.4 Hz), 127.70, 127.39 (J = 2.4 Hz), 116.30 (J = 22.1 Hz), 21.64. ¹⁹F NMR (376 MHz, CDCl₃) δ -107.92.



(*E*)-1-Chloro-4-(2-tosylvinyl)benzene (3k):^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.81 (m, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 4H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.60, 140.43, 137.46, 137.11, 130.93, 130.05, 129.71, 129.37, 128.22, 127.76, 21.66.



(*E*)-1-Bromo-4-(2-tosylvinyl)benzene (31):^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 15.4 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.39 - 7.31 (m, 4H), 6.88 (d, J = 15.4 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.52, 140.40, 137.31, 132.23, 131.26, 129.96, 129.80, 129.65, 128.23, 127.67, 125.41, 21.58.



(*E*)-1-Methyl-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (3m): ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.60 (m, 5H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 15.4 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.75, 139.81, 137.09, 35.82, 132.40 (t, *J* = 32.8 Hz), 130.34, 130.04, 128.63, 127.79, 125.94 (t, *J* = 3.7 Hz), 123.56 (t, *J* = 273.4 Hz), 21.55. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.96. HRMS (ESI) calcd for C₁₆H₁₃F₃O₂S [M+H]⁺: 327.0661; found: 327.0666.



(*E*)-1-Methyl-2-(2-tosylvinyl)benzene (3n): ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 15.3 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H),

7.31 – 7.24 (m, 1H), 7.23 – 7.14 (m, 2H), 6.78 (d, J = 15.3 Hz, 1H), 2.44 (d, J = 2.8 Hz, 3H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.28, 139.48, 138.04, 137.61, 131.22, 130.93, 130.76, 129.89, 128.39, 127.61, 126.73, 126.38, 21.55, 19.69. HRMS (ESI) calcd for C₁₆H₁₆O₂S [M+H]⁺: 273.0944; found: 273.0945.



(*E*)-1-Bromo-3-(2-tosylvinyl)benzene (3o): ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.28 – 7.23 (m, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 144.58, 139.96, 137.26, 134.43, 133.74, 130.97, 130.48, 129.97, 129.21, 127.72, 127.11, 123.04, 21.56. HRMS (ESI) calcd for C₁₅H₁₃BrO₂S [M+H]⁺: 336.9892; found: 336.9899

(*E*)-Butyl 3-tosylacrylate (3p):^[4] ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 15.2 Hz, 1H), 6.80 (d, *J* = 15.2 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.46 (s, 3H), 1.71 – 1.57 (m, 2H), 1.44 – 1.30 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.54, 145.59, 143.30, 135.32, 130.43, 130.19, 128.30, 65.76, 30.32, 21.65, 18.94, 13.55.

(*E*)-1-Methyl-4-(oct-1-en-1-ylsulfonyl)benzene (3q):^{[6] 1}H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.96 (dt, *J* = 14.7, 6.8 Hz, 1H), 6.29 (d, *J* = 15.1 Hz, 1H), 2.44 (s, 3H), 2.22 (m, 2H), 1.51 – 1.40 (m, 2H), 1.33 – 1.21 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 146.70, 144.10, 137.70, 130.44, 129.80, 127.53, 31.42, 31.40, 28.65, 27.50, 22.43, 21.56, 13.96.

1-((2-Iodooctyl)sulfonyl)-4-methylbenzene (5):^{[7] 1}H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 4.48 – 4.36 (m, 1H), 3.83 – 3.66 (m, 2H), 2.47 (s, 3H), 2.04 – 1.89 (m, 1H), 1.89 – 1.74 (m, 1H), 1.55 – 1.42 (m, 1H), 1.33 – 1.22 (m, 7H), 0.89 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.28, 136.36, 130.16, 128.04, 65.88, 39.13, 31.59, 29.46, 28.14, 22.64, 22.59, 21.73, 14.09.

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Copies of product ¹H NMR, ¹³C NMR and ¹⁹F NMR













3d











3h

3k

3q

5