Electrochemically Assisted Heck Reactions

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Supporting Information

1. Experimental Section

General Chemical and Electrochemical Reactions were Compared Using the Following Conditions:

General Chemical Procedure for Heck Reaction of Aryl Halides (Aryl Iodides and Aryl Bromides) and Olefins:

To a 50 mL round bottom flask with a mixture of aryl halide (1.0 mmol), olefin (1.2 mmol), Pd(OAc)₂ (67.3 mg, 0.3 mmol) and tetrabutylammonium bromide (644.8 mg, 2.0 mmol), a solution of 9 mL of DMF, 1 mL of water and 1 mL of triethyl amine was added. The resulting brown solution was stirred at room temperature under an argon atmosphere until aryl halide was consumed in 12-20 h. 1 M HCl was then added to the reaction mixture until pH<5. The resulting suspension was extracted with CH₂Cl₂ (3 × 20mL). The combined organic layers was first washed with water and brine, and then poured into a short pad column with silica gel eluting with CH₂Cl₂. The CH₂Cl₂ elute was concentrated under reduced pressure. The residue provided the Heck reaction products with sufficient purity for NMR determination.

General Electrochemical Procedure for Heck Reaction of Aryl Halides (Aryl Iodides and Aryl Bromides) and Olefins:

To a 25 mL 3-neck flask with a mixture of aryl halide (1.0 mmol), olefin (1.2 mmol), Pd(OAc)₂ (67.3 mg, 0.3 mmol) and tetrabutylammonium bromide (644.8 mg, 2.0 mmol), a solution of 9 mL of DMF, 1 mL of water and 1 mL of triethyl amine was added. The resulting brown solution was electrolyzed with constant current (15.0 mA) on Reticulate Vitreous Carbon (RVC) electrodes at room temperature under an argon atmosphere until aryl halide was consumed in 2-6 h. 1 M HCl was then added to the reaction mixture until pH<5. The resulting suspension was extracted with CH₂Cl₂ (3 × 20mL). The combined organic layers were first washed with water and brine, and then poured into a short pad column with silica gel eluting with CH₂Cl₂. The CH₂Cl₂ elute was concentrated under reduced pressure. The residue provided the Heck products with sufficient purity for NMR determination.

2. Spectral Data for Heck Reaction Products (New compounds are reported as being greater than 95% pure as evidenced by proton and carbon NMR. The spectra for these compounds is included at the end.)

(E)- Methyl-cinnamate (Table 1 – entry 1):

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, J = 16.2 Hz, 1H), 7.48-7.51 (m, 2H), 7.34-7.37 (m, 3H), 6.43 (d, J = 16.2 Hz, 1H), 3.78 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.6, 145.1, 134.6, 130.5, 129.1, 128.3, 118.0, 51.9. Reference: Yang, D.; Chen, Y. C.; Zhu, N. Y. *Org. Lett.* **2004**, 6, 1577.

Styrene (Table 1 – entry 2):

Colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, J = 6.6 Hz, 4H), 7.39 (t, J = 6.6 Hz, 4H), 7.31 (d, J = 6.6 Hz, 2H), 7.14 (s, 2H). Reference: Yang, D.; Chen, Y. C.; Zhu, N. Y. *Org. Lett.* **2004**, 6, 1577.

3-Phenyl-(2E)-propenamide (Table 1 – entry 3):

White solid; ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.67 (m, 2H), 7.56 (d, J = 15.6 Hz, 1H), 7.36-7.43 (m, 3H), 7.17 (brs, 1H), 6.76 (d, J = 15.6 Hz, 1H),

6.63 (brs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.2, 140.3, 135.5, 129.6, 129.1, 127.9, 121.9. Reference: Bayer, A.; Maier, M. E. *Tetrahedron*, **2004**, 60, 6665.

(E)-Methyl-11-phenylundec-10-enoate (Table 1 – entry 4, *trans/cis* = 5.2/1):

Colorless oil; IR (NaCl, cm^{-1}) ν 2927, 2854, 1740, 1494, 1435, 1172, 965, 745, 694; UV (λ nm) 209, 326. EIMS (m/z) 274 $[\text{M}]^+$; HREIMS calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_2$ (274.1933) $[\text{M}]^+$, found 274.1922. ^1H NMR (300 MHz, CDCl_3) δ 7.18-7.42 (m, 5H), 7.00 (dt, J = 11.4, 6.6 Hz, 0.16H), 6.40 (d, J = 15.9 Hz, 0.84H), 6.26 (dt, J = 15.9, 6.6 Hz, 0.84H), 5.84 (d, J = 11.4 Hz, 0.16H), 3.74 (s, 0.48H), 3.68 (s, 2.52H), 1.26-2.66 (m, 16H); ^{13}C NMR (75 MHz, CDCl_3) δ 174.4, 138.2, 131.3, 128.7, 128.5, 127.0, 126.2, 51.6, 34.3, 33.3, 29.6, 29.6, 29.5, 29.4, 29.4, 25.2 (*trans*).

(2E)-3-phenyl-2-propenenitrile (Table 1 – entry 5, *trans/cis* = 3.4/1):

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.46 (m, 5H), 7.38 (d, J = 16.8 Hz, 0.77H), 7.13 (d, J = 12.0 Hz, 0.23H), 5.87 (d, J = 16.8 Hz, 0.77H), 5.45 (d, J = 12.0 Hz, 0.23H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.8, 149.0, 133.9, 133.8, 131.5, 131.2, 129.4, 129.3, 129.2, 127.6, 118.4, 117.6, 96.6, 95.3. Reference: Krishna, T. R.; Jayaraman, N. *Tetrahedron* **2004**, 60, 10325.

***trans*-2-Ethoxystyrene (Table 1 – entry 6, *trans/cis* = 4.0/1):**

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.11-7.62 (m, 5H), 7.00 (d, J = 13.2 Hz, 0.8H), 6.22 (d, J = 7.2 Hz, 0.2H), 5.85 (d, J = 13.2 Hz, 0.8H), 5.23 (d, J = 7.2 Hz, 0.2H), 3.99 (q, J = 7.2 Hz, 0.2H), 3.91 (q, J = 7.2 Hz, 0.8H), 1.38 (q, J = 7.2 Hz, 0.2H), 1.36 (q, J = 7.2 Hz, 0.8H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.1, 146.8, 141.5, 136.8, 129.0, 128.8, 128.4, 127.5, 127.4, 125.8, 125.3, 106.2, 69.2, 65.7, 15.7, 15.1. Reference: Bolger, D. L.; Curran, T. T. *J. Org. Chem.* **1990**, 55, 5439.

(E)-Methyl-11-phenylundec-10-enoate (Table 1 – entry 7, *trans/cis* = 12/1):

Off-white solid; IR (NaCl, cm^{-1}) ν 2949, 1718, 1709, 1642, 1430, 1285, 1271, 1178, 1103, 848, 840, 736; UV (λ nm) 209, 327, 343. EIMS (m/z) 420 $[\text{M}]^+$; HREIMS calcd. for $\text{C}_{28}\text{H}_{20}\text{O}_4$ (420.1362) $[\text{M}]^+$, found 420.1377. ^1H NMR (300 MHz, CDCl_3) δ 8.02-8.37 (m, 9H), 8.00 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz,

0.08H), 7.74 (d, $J = 15.9$ Hz, 0.92H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 0.08H), 6.57 (d, $J = 8.4$ Hz, 2H), 5.98 (s, 1.84 H), 5.81 (s, 0.16H), 3.91 (s, 2.76H), 5.81 (s, 0.24H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 166.6, 144.0, 138.7, 132.0, 131.6, 131.4, 130.9, 130.3, 129.8, 128.9, 128.5, 128.1, 128.0, 127.6, 126.3, 125.8, 125.7, 125.1, 124.9, 123.1, 120.5, 115.7, 95.1, 65.3, 52.5 (*trans*).

***E*-Methyl-4-[3-amino-3-oxoprop-1-enyl] benzoate (Table 1 – entry 8):**

White solid; ^1H NMR (300 MHz, DMSO-d_6) δ 7.95 (d, $J = 8.4$ Hz, 1H), 7.75 (brs, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 15.9$ Hz, 1H), 7.24 (brs, 1H), 6.78 (d, $J = 15.9$ Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.0, 166.5, 140.2, 138.5, 130.6, 130.4, 128.4, 125.8, 52.9. Reference: Cai, M. Z.; Xu, Q.; Sheng, S. R.; Song, C. S. *Gaofenzi Xuebao*, **1999**, 5, 636.

***(E)*-Methyl-4-styrylbenzoate (Table 1 – entry 9):**

Pale yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.38 (t, $J = 8.4$ Hz, 2H), 7.30 (t, $J = 8.4$ Hz, 1H), 7.23 (d, $J = 16.5$ Hz, 1H), 7.12 (d, $J = 16.5$ Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 167.1, 142.1, 137.0, 131.5, 130.3, 129.1, 129.0, 128.5, 127.8, 127.0, 126.6, 52.3. Reference: Cai, M. Z.; Song, C. S.; Huang, X. *Synthesis*, **1997**, 521.

***(E)*-Ethyl-4-styrylbenzoate (Table 2 – entry 2):**

Pale yellow solid; ^1H NMR (300 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.39 (t, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 16.5$ Hz, 1H), 7.11 (d, $J = 16.5$ Hz, 1H), 4.40 (q, $J = 7.2$ Hz, 2H), 1.42 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.6, 141.9, 137.0, 131.4, 130.2, 129.5, 128.5, 127.8, 127.1, 126.5, 61.2, 14.6. Reference: Inoue, A.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2003**, 125, 1484.

***E*-Ethyl-4-[3-amino-3-oxoprop-1-enyl] benzoate (Table 2 – entry 3):**

White solid; IR (NaCl, cm^{-1}) ν 3375, 3157, 2978, 1707, 1669, 1615, 1606, 1389, 1281, 1114, 711; UV (λ nm) 209, 326. EIMS (m/z) 219 $[\text{M}]^+$; HREIMS calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_3$ (219.0895) $[\text{M}]^+$, found

219.0893. ^1H NMR (300 MHz, DMSO- d_6) δ 7.96 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.63 (brs, 1H), 7.45 (d, J = 15.9 Hz, 1H), 7.22 (brs, 1H), 6.73 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 6.6 Hz, 2H), 1.31 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 166.9, 166.0, 140.1, 138.5, 130.9, 130.4, 128.4, 125.6, 61.5, 14.8.

***trans*-4-Nitrostilbene (Table 2 – entry 4):**

Yellow powder; ^1H NMR (300 MHz, CDCl_3) δ 8.22 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.0, 144.1, 136.4, 133.5, 129.1, 129.1, 127.3, 127.1, 126.5, 124.4. Reference: Hamza, K.; Abu-Reziq, R.; Avnir, D.; Blum, J. *Org. Lett.* **2004**, 6, 925.

***(E)*-Methyl-4-[4-nitrostyryl]benzoate (Table 2 – entry 5):**

Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 8.22 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 16.2 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 6.54 (d, J = 16.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 148.7, 142.1, 140.7, 128.9, 124.4, 122.3, 52.3. Reference: Dai, M. J.; Liang, B.; Wang, C. H.; Chen, J. H.; Yang, Z. *Org. Lett.* **2004**, 6, 221.