CuI/TBAB as a novel efficent catalytic system for Heck reaction in water

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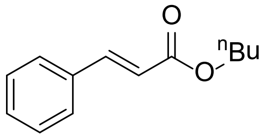
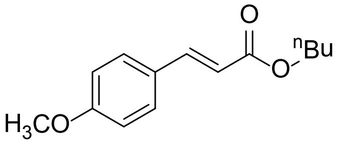
Procedures for the Heck reaction: all reactions were carried out under air.

Aryl halide (1.0 mmol), olefins (1.2 mmol), CuI (10 mol%), NaOH (1.0 mmol), TBAB(1.0 mmol) and 3 mL H_2O were continuously added to a sealed tube. The reaction mixture was stirred at 100℃ for 20 h. The progress of the reaction was monitored by GC. After completion of the reaction, the catalyst was filtered easily and the product was extracted with EtOAc, The combined organic layers was dried over $MgSO_4$ for 12h. The solvent was evaporated under reduced pressure and the desired product purified by flash chromatography on a silica gel column using hexane/ethyl acetate (5:1).

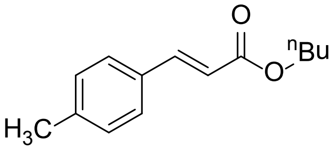
^{1}H NMR and ^{13}C NMR spectra of Heck products



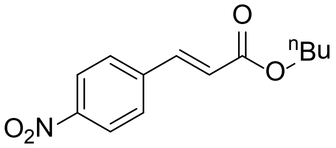
(E)-n-Butyl cinnamate[1-6].Table2, entry1,5; ^{1}HNMR($CDCl_3$, 300MHz, ppm) δ 7.68 (d, J = 16.0Hz, 1H), 7.52–7.50 (m, 2H), 7.38–7.36 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 4.21 (t, J = 6.6 Hz, 2H), 1.74–1.64 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}CNMR ($CDCl_3$, 75MHz, ppm) δ 167.0, 144.4, 134.5, 130.2, 128.9, 128.1, 118.3, 64.5, 30.8, 19.2, 13.7.



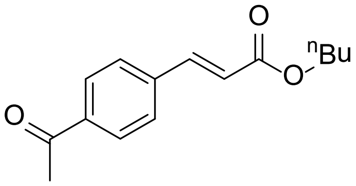
(E)-4-Methoxycinnamic acid *n*-butyl ester[1-4].Table2, entry2,7; ^{1}HNMR($CDCl_3$, 300MHz, ppm) δ:7.62(d, J =16.0Hz, 1H), 7.45 (d, J =8.3Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 6.29 (d, J = 16.0 Hz, 1H), 4.18 (t, J = 6.6 Hz, 2H), 3.79 (s, 3H), 1.71–1.62 (m, 2H), 1.46–1.38 (m, 2H), 0.95 (t, J=7.3 Hz, 3H); ^{13}CNMR($CDCl_3$,75MHz, ppm) δ167.3, 161.3, 144.2, 129.6, 127.1, 115.7, 114.3, 64.2, 55.3, 30.8, 19.2, 13.7.



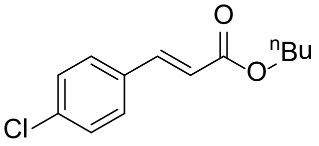
(E)-Butyl 3-p-tolylacrylate[1-5]. Table2, entry3,9; ^{1}HNMR($CDCl_3$, 300MHz, ppm) δ 7.66(d, J = 16.0 Hz, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 6.41(d, J = 16.0 Hz, 1H), 4.32 (t, J = 6.6 Hz, 2H), 2.36 (s, 3H), 1.74–1.65 (m, 2H), 1.50–1.40 (m, 2H), 0.97 (t, J=7.3 Hz, 3H); ^{13}CNMR($CDCl_3$,75MHz, ppm) δ 167.3, 144.6, 140.6, 129.7, 128.8, 128.1, 117.2, 64.4, 30.8, 21.5, 19.1, 13.8.



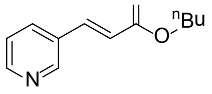
(E)-Butyl-3-(4-nitrophenyl)acrylate[1-5].Table2, entry4,8,12; ^{1}HNMR($CDCl_3$, 300MHz, ppm) δ 8.25(d, J =8.6Hz, 2H), 7.70 (d, J =16.0Hz,1H), 7.66 (d, J = 8.6 Hz, 2H), 6.57 (d, J = 16.0 Hz, 1H), 4.24 (t, J = 6.6 Hz, 2H), 1.75–1.66 (m, 2H), 1.48–1.38 (m, 2H), 0.96 (t, J=7.2 Hz, 3H); ^{13}CNMR($CDCl_3$, 75MHz, ppm) δ 166.1, 146.6, 141.5, 140.6, 128.6, 124.1, 122.7, 64.9, 30.7, 19.1, 13.7.



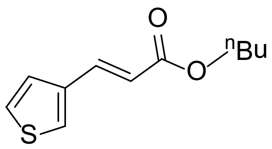
(E)-4-Acetylcinnamic acid butyl ester[2-4].Table2, entry6; ^{1}HNMR ($CDCl_3$, 300MHz, ppm): δ 8.11 (d, J = 8.5 Hz, 2 H), 7.89 (d, J = 15.5 Hz, 1 H), 7.72 (d, J = 8.5 Hz, 2 H), 6.92 (d, J = 16 Hz, 1 H), 5.35 (t, J = 7.5 Hz, 2 H), 3.98 (s, 3 H), 2.56 (m, J = 7.5 Hz, 2 H), 1.98 (m, J = 7.5 Hz, 2 H), 1.06 (t, J = 7.3 Hz, 3 H). ^{13}CNMR ($CDCl_3$, 75MHz, ppm) δ 195.5, 172.5, 155.0, 146.5, 141.5, 132.6, 130.8, 125.5, 88.3, 45.0, 33.4, 23.4, 16.0.



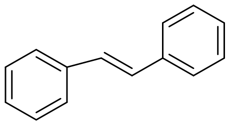
Butyl trans-4-chlorocinnamate[3,4]. Table2 entry10; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.09 (t, J =7.4 Hz, 3H), 1.44–1.51 (m, 2H), 1.70–1.85 (m, 2H), 3.99 (t, J=6.7 Hz, 2H), 5.87 (d, J=16.0 Hz, 1H), 7.43–7.50 (m, 2H), 7.54–7.78 (m, 2H), 7.89 (d, J=16.0 Hz, 1H).^{13}CNMR ($CDCl_3$, 75MHz, ppm): δ 175.88, 152.13, 134.40, 130.14, 127.75, 125.50, 108.82, 74.66, 47.55, 25.15, 15.55.



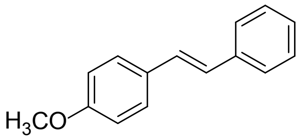
(E)-3-(3-Pyridinyl)acrylic acid butyl ester[3].Table2, entry13; ^{1}HNMR ($CDCl_3$, 300MHz, ppm): δ 8.85 (s, 1 H), 8.72 (m, 1 H), 7.75 (d, *J* = 8.5 Hz, 1 H), 7.57 (d, *J* = 16 Hz, 1 H), 7.24 (m,1 H), 6.79 (d, *J* = 16.5 Hz, 1 H), 5.09 (t, *J* = 6.5 Hz, 2 H), 2.23 (m, *J* = 7.3 Hz, 2 H), 1.78 (m, *J* = 7.3 Hz, 2 H), 1.04 (t, *J* = 7.3 Hz, 3 H). ^{13}CNMR ($CDCl_3$, 75MHz, ppm): δ 187.5, 172.2, 159.9, 138.8, 135.5, 128.5, 123.3, 111.4, 89.9, 56.6, 39.9, 28.4, 15.0.



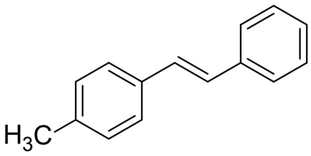
1-Thiophen-3-yl-hept-1-en-3-one[3].Table2, entry14; ^{1}HNMR (CDCl$_3$, 300MHz, ppm): δ 7.57 (d, J=17.5 Hz, 1H), 7.41 (d, J=8.2 Hz, 1H), 7.27–7.18 (m, 2H), 6.17 (d, J=17.5 Hz, 1H), 4.11 (t, J=7.5 Hz, 2H), 1.62–1.54 (m, 2H), 1.42–1.31 (m, 2H), 0.87 (t, J=7.5 Hz, 3H). ^{13}CNMR (CDCl$_3$, 75MHz, ppm): δ 166.2, 136.9, 136.5, 127.7, 126.9, 125.8, 116.9, 63.3, 29.7, 18.1, 12.7.



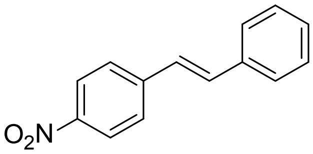
(E)-1,2-Diphenylethene[1-7]. Table3, entry1,5; ^{1}HNMR (CDCl$_3$, 300MHz, ppm) δ 7.61(d, J = 7.2 Hz, 4H), 7.46 (t, J = 7.2 Hz, 4H), 7.37 (t, J = 7.2 Hz, 2H), 7.20 (s, 2H); ^{13}CNMR (CDCl$_{3,}$ 75MHz, ppm) δ 137.4, 128.9, 128.6, 127.6, 126.8.



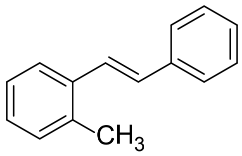
4-Methoxy-*trans*-stilbene[2-5,7].Table3, entry2,6; ^{1}HNMR (CDCl$_3$, 300MHz, ppm): δ 7.42 (d, *J* = 7.5 Hz, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H), 7.28 (t, *J* = 7.5 Hz, 2 H), 7.18 (t, *J* = 6.5 Hz, 1 H), 6.99 (d, *J* = 16.0 Hz, 1 H), 6.89 (d, *J* = 16.5 Hz, 1 H), 6.80 (d, *J* = 8.5 Hz, 2 H), 3.77 (s, 3 H). ^{13}CNMR (CDCl$_3$, 75MHz, ppm): δ 160.5, 138.8, 130.9, 129.5, 128.0, 127.5, 127.0, 126.5, 126.0, 116.5, 57.5.



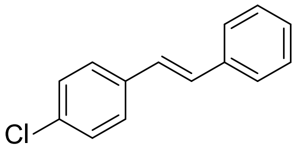
4-Methyl-trans-stilbene[3,4].Table3, entry3,8;^{1}H NMR (CDCl$_3$, 300MHz, ppm): δ 7.42 (d, J=8.5 Hz, 2H), 7.31 (d, J=8.0 Hz, 2H), 7.20 (t, J=7.5 Hz, 2H), 7.15 (t, J=6.5 Hz, 1H), 7.05 (d, J=8.0 Hz, 2H), 6.96 (d, J=16.5 Hz, 1H), 6.90 (d, J=16.5 Hz, 1H), 2.30 (s, 3H). ^{13}CNMR (CDCl$_3$, 75MHz, ppm): δ 136.7, 136.3, 134.2, 130.5, 129.8, 128.7,127.8, 127.2, 126.0, 126.0, 23.0



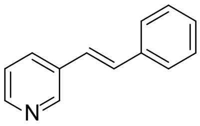
4-Nitro-trans-stilbene[3,4]. Table3, entry4,7,14; ^{1}HNMR (CDCl$_3$, 300MHz, ppm): δ 8.40 (d, J=9.3 Hz, 2H), 7.80(d, J=9.3 Hz, 2H), 7.71 (d, J=7.3 Hz, 2H), 7.45–7.55 (m, 3H), 7.37 (d, J=16 Hz, 1H), 7.23 (d, J=16.5 Hz, 1H). ^{13}CNMR (CDCl$_3$, 75MHz, ppm): δ 152.2, 149.9, 140.5, 135.5, 130.1, 129.0, 128.5, 128.0, 127.0, 125.5.



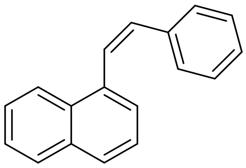
4-Methyl-trans-stilbene[3,4]. Table3, entry9; ^{1}HNMR (CDCl$_3$, 300MHz, ppm) δ 2.43 (s, 3H, Me), 7.00 (d, J=16.5 Hz, 1H), 7.05-7.38 m, 7H), 7.52 (d, J=7.5 Hz, 2H, Ar), 7.59 (d, J=7.5 Hz, 1H, Ar). ^{13}CNMR(CDCl$_3$,75MHz, ppm) δ 19.9, 125.4, 126.2, 126.55, 126.57, 127.5, 127.6, 128.7, 130.0, 130.4, 135.8, 136.4, 137.7.



4-Chloro-trans–stilbene[3]. Table3, entry11. ^{1}HNMR (CDCl$_3$, 300MHz, ppm): δ 7.80 (d, J=7.3 Hz, 2H), 7.65 (d, J=8.5 Hz, 2H), 7.30–7.44 (m, 5H), 7.20 (s, 2H). ^{13}CNMR (CDCl$_3$, 75MHz, ppm): δ 140.0, 137.9, 135.5, 131.3, 129.9, 129.5, 128.2, 127.5, 127.0, 125.5.



(E)-3-Styrylpyridine[3,6].Table3, entry12; ^{1}HNMR (CDCl$_3$, 300MHz, ppm): δ 8.70 (s, 1 H), 8.50 (d, J = 4.8 Hz, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.65 (d, J = 7.3 Hz, 2 H), 7.30 (t, J = 7.3 Hz, 2 H), 7.15–7.25 (m, 2 H), 7.08 (d, J = 16.5 Hz, 1 H), 6.90 (d, J = 16.0 Hz, 1 H) ppm. ^{13}C-NMR (CDCl$_{3,}$ 75MHz, ppm): δ 150.5, 149.5, 138.8, 135.0, 133.3, 130.0, 129.7, 127.6, 126.0, 125.0, 121.0.



E-1-Styryl-naphthalene[8].Table3, entry13; ^{1}HNMR (CDCl$_3$, 300MHz, ppm) δ 8.19 (d, J=8.3 Hz, 1H), 7.88–7.69 (m, 4H), 7.58–7.32 (m, 7H), 7.25 (q, J=7.6 Hz, 1H), 7.07 (d, J=10.4 Hz, 1H). ^{13}CNMR (CDCl$_3$,75 MHz,, ppm) δ 137.6; 135.0; 133.7; 131.7; 131.4; 129.2; 128.7;128.6; 128.0; 127.7; 127.5; 126.7; 126.4; 126.0; 125.8;125.7; 123.8; 123.6..

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