Supporting Information

Halide Ions as a Highly Efficient Promoter in the Ru-Catalyzed Hydroesterification of Alkenes and Alkynes

Eun Ju Park, Ji Min Lee, Hoon Han, and Sukbok Chang*

*Center for Molecular Design and Synthesis (CMDs), Department of Chemistry and
School of Molecular Science (BK21), Korea Advanced Institute of Science and
Technology, Daejeon 305-701, Republic of Korea*

General Methods. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F₂₅₄ plates. Visualization on TLC was achieved by use of UV light (254 nm) and treatment with phosphomolybdic acid and anisaldehyde stain followed by heating. Flash column chromatography was undertaken on silica gel (F₂₅₄ 400-630 mesh). ¹H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ¹³C NMR was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance is reported. High resolution

mass spectra were recorded by using FAB method.

Experimental Procedure for the Screening of Additives. To a solution of 2-pyridylmethyl formate (**1**, 54.9 mg, 0.4 mmol), 3,3-dimethyl-1-butene (100.1 mg, 1.2 mmol), $\text{Ru}_3(\text{CO})_{12}$ (12.8 mg, 0.02 mmol) in DMF (0.2 mL) was added an additive (0.06 mmol). The reaction mixture was stirred at 70 °C for 12 h in a screw-capped vial. The crude product was extracted with ethyl acetate, washed with water, and dried over MgSO_4 . The organic layer was filtered and concentrated *in vacuo*. NMR yield of the desired product, (2-pyridylmethyl)-4,4-dimethyl pentanoate, was determined by comparing the integration of the pyridyl proton relative to an internal standard (anisole).

Experimental Procedure for the IR Studies. To a stirred solution of $\text{Ru}_3(\text{CO})_{12}$ (64.0 mg, 0.1 mmol) in THF (19 mL) a solution of an additive (0.3 mmol) in THF (1 mL) was added at 60 °C. An aliquot was taken from the reaction mixture at the indicated time interval and then dropped to a sodium chloride cell to record the infrared spectroscopy.

Figure S1. IR spectra of (a) $\text{Ru}_3(\text{CO})_{12}$ and NH_4PF_6 (3 equiv) in THF at 60 °C. (b) $\text{Ru}_3(\text{CO})_{12}$ and LiI (3 equiv) in THF at 60 °C.

Experimental Procedure for the ^1H NMR Study of the Hydroesterification of Alkenes.

To a solution of $\text{Ru}_3(\text{CO})_{12}$ (128 mg, 0.2 mmol) in $\text{DMF-}d_7$ (0.2 mL), tetrabutylammonium iodide (73.9 mg, 0.2 mmol) was added. After stirring the reaction mixture at 70 °C for 10 min, 2-pyridylmethyl formate (**1**, 27.4 mg, 0.2 mmol) and 3,3-dimethyl-1-butene (0.077 mL, 0.6 mmol) was added. An aliquot was taken from the reaction mixture (maintained at 70 °C) at the indicated time interval and then ^1H -NMR spectra were obtained.

Figure S2. ^1H -NMR Spectra of the reaction mixture of $\text{Ru}_3(\text{CO})_{12}$, $(n\text{-Bu})_4\text{NI}$, 2-pyridylmethyl formate and 3,3-dimethyl-1-butene in $\text{DMF-}d_7$ at 70 °C.

Representative Experimental Procedure for the Hydroesterification of Olefins. To a solution of 2-pyridylmethyl formate (**1**, 54.9 mg, 0.4 mmol), 3,3-dimethyl-1-butene (40.4 mg,

0.48 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (12.8 mg, 0.02 mmol) in DMF (0.2 mL) was added tetrabutylammonium iodide (22.2 mg, 0.06 mmol). The reaction mixture was stirred at 70 °C for 12 h in a screw-capped vial. The crude product was extracted with ethyl acetate, washed with water, and dried over MgSO_4 . The organic layer was filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography with ethyl acetate/*n*-hexane 1:5 to give the desired product, (2-pyridylmethyl)-4,4-dimethyl pentanoate (82 mg, 99%).

Representative Experimental Procedure for the Hydroesterification of Dienes. To a solution of 2-pyridylmethyl formate (**1**, 54.9 mg, 0.4 mmol) in the indicated solvent (0.2 mL) was sequentially added 4-vinylcyclohexene (129.8 mg, 1.2 mmol), $\text{Ru}_3(\text{CO})_{12}$ (12.8 mg, 0.02 mmol) and (*n*-Bu) $_4$ NI (22.2 mg, 0.06 mmol). The reaction mixture was stirred for 12 h in a screw-capped vial at 70 or 90 °C depending on the substrates employed. The crude product was extracted with ethyl acetate, washed with water, and dried over MgSO_4 . The organic layer was filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography with ethyl acetate/*n*-hexane (1:5) to give the desired product, (2-pyridylmethyl)-3-(3-cyclohexenyl) propanoate (96 mg, 98%) as a yellowish liquid. The solvent and reaction temperatures were dependent on the substrates employed as shown in Table 3.

Representative Experimental Procedure for the Hydroesterification of Alkynes. To a solution of 2-pyridylmethyl formate (**1**, 54.9 mg, 0.4 mmol) in DMSO (0.2 mL) was added 4-octyne (132.2 mg, 1.2 mmol), $\text{Ru}_3(\text{CO})_{12}$ (12.8 mg, 0.02 mmol) and then (*n*-Bu) $_4$ NI (22.2 mg, 0.06 mmol). The reaction mixture was stirred at 110 °C for 12 h in a screw-capped vial. The crude product was extracted with ethyl acetate, washed with water, and dried over MgSO_4 .

The organic layer was filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography with ethyl acetate/n-hexane (1:5) to give the desired product, (2-pyridylmethyl)-2-propyl-2-pentenoate (82 mg, 83%) as a yellowish liquid.

(2-Pyridylmethyl)-3-(trimethylsilyl)propanoate (Table 2, entry 7).

Yellowish liquid; ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, $J = 4.8$ Hz, 1H), 7.66 (td, $J = 7.7$, 1.8 Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 7.19 (dd, $J = 7.0$, 5.1 Hz, 1H), 5.19 (s, 2H), 2.36 (m, 2H), 0.84 (m, 2H), -0.021 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 155.7, 149.4, 136.7, 122.8, 121.8, 66.8, 29.8, 11.6, -2.0; IR (NaCl) 2954, 1742, 1594, 1438, 1375, 1197, 1046, 750 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{Si}$ $[M+H]^+$: 238.1263, found: 238.1263.

(2-Pyridylmethyl)-2-[(1S,5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]acetate (Table 2, entry 15)

Light yellowish liquid; ^1H NMR (400MHz, CDCl_3) δ 8.54 (d, $J = 4.4$ Hz, 1H), 7.64 (td, $J = 7.7$, 1.5 Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.18 (dd, $J = 7.2$, 5.0 Hz, 1H), 5.17 (s, 2H), 2.52-2.45 (m, 2H), 2.29-2.26 (m, 1H), 2.10-1.95 (m, 1H), 1.86-1.79 (m, 1H), 1.78-1.70 (m, 1H), 1.45-1.30 (m, 1H), 1.27 (d, $J = 10$ Hz, 1H), 1.14 (s, 3H), 0.97 (s, 2H), 0.90 (d, $J = 9.6$ Hz, 1H), 0.80 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.8, 156.0, 149.4, 136.6, 122.7, 121.7, 66.5, 46.1, 41.9, 41.0, 38.5, 37.4, 33.2, 27.9, 26.02, 23.1, 21.6; IR (NaCl) 2983,

1739, 1573, 1475, 1367, 1248, 1142, 1097, 1009 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{17}\text{H}_{24}\text{NO}_2$ $[M+H]^+$: 274.1807, found: 274.1811.

(2-Pyridylmethyl)-3-phenylbutanoate (Table 2, entry 17)

Yellowish liquid; ^1H NMR (400MHz, CDCl_3) δ 8.53 (d, $J = 4.7$ Hz, 1H), 7.57 (td, $J = 7.7$, 1.6 Hz, 1H), 7.28–7.14 (m, 6H), 7.3 (d, $J = 7.8$ Hz, 1H), 5.15 (dd, $J = 17.0$, 13.4 Hz, 2H), 3.31 (m, 1H), 2.70 (m, 2H), 1.30 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 155.7, 149.2, 145.4, 136.6, 128.4, 126.7, 126.3, 122.6, 121.4, 66.5, 42.6, 36.4, 21.9; IR(NaCl) 3028, 2965, 1738, 1594, 1438, 1049, 761 cm^{-1} ; HRMS (FAB) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{NO}_2$ $[M+H]^+$: 256.1338, found: 256.1337.

(2-Pyridylmethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (Table 2, entry 21)

Yellowish liquid; ^1H NMR (400MHz, CDCl_3) δ 8.58 (d, $J = 4.4$ Hz, 1H), 7.66 (m, 1H), 7.30 (d, $J = 7.8$ Hz, 4H), 7.22 (m, 1H), 7.08 (m, 4H), 5.27 (s, 2H), 3.06 (d, $J = 7.9$ Hz, 2H), 2.89–2.84 (m, 3H), 2.27–2.23 (m, 1H), 1.94–1.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 155.9, 149.4, 136.7, 135.6, 134.7, 129.0, 128.8, 125.9, 125.8, 122.8, 121.6, 66.8, 39.9, 31.6, 28.4, 25.9; IR(NaCl) 3061, 2935, 1736, 1573, 1476, 1263, 994 cm^{-1} ; HRMS(FAB) m/z calcd. for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ $[M+H]^+$: 268.1338, found: 268.1339.

Appendix I

Copies of ^1H and ^{13}C -NMR Spectra Obtained in this Study

(New Compounds)

(2-Pyridylmethyl)-3-(trimethylsilyl)propanoate (Table 2, entry 7)

(2-Pyridylmethyl)-2-[(1*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]acetate (Table 2, entry 15)

(2-Pyridylmethyl)-3-phenylbutanoate (Table 2, entry 17)

(2-Pyridylmethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (Table 2, entry 21)

Appendix II

Copies of ^1H and ^{13}C -NMR Spectra Obtained in this Study

(Known Compounds)

(2-Pyridylmethyl)-4,4-dimethylpentanoate (Table 2, entry 1)

(2-Pyridylmethyl)-heptanoate (Table 2, entry 3)

(2-Pyridylmethyl)-3-cyclohexylpropanoate (Table 2, entry 5)

exo-(2-Pyridylmethyl)-bicyclo[2.2.1]heptane-2-carboxylate (Table 2, entry 9)

(2-Pyridylmethyl)-cyclohexanecarboxylate (Table 2, entry 11)

(2-Pyridylmethyl)-3-methyl-6-oxo-heptanoate (Table 2, entry 13)

(2-Pyridylmethyl)-tetrahydro-2H-pyran-2-carboxylate (Table 2, entry 19)

(2-Pyridylmethyl)-3-(cyclohex-3-enyl)propanoate (Table 3, entry 1)

(R, S)-(2-Pyridylmethyl)-3-((S)-4-methylcyclohex-3-enyl)butanoate (Table 3, entry 3)

(2-Pyridylmethyl)-(3-isopropenylbenzenyl)butanoate (Table 3, entry 5)

(E)- (2-Pyridylmethyl)-2-propylhex-2-enoate (Table 3, entry 7)

(*E*)-(2-Pyridylmethyl)-2-ethylidenepentanoate and (*E*)-(2-Pyridylmethyl)-2-methylhex-2-enoate (Table 3, entry 9)