Supplementary Information

Synthesis of α-Keto Esters by the Rhodium-Catalysed Reaction of Cyanoformate with Arylboronic Acids

Hiroshi Shimizu and Masahiro Murakami*

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

General. 1H- and 13C-NMR spectra were recorded on a Varian Gemini 2000 (1H at 300 MHz and 13C at 75 MHz) spectrometer using CHCl₃ (1H, δ = 7.26) and CDCl₃ (13C, δ = 77.16) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck).

Materials. 1,4-Dioxane was freshly distilled from sodium benzenophene ketyl. [Rh(OH)(cod)₂]₂ was prepared according to the reported procedure. Boric acid and all arylboronic acids were purchased from commercial sources and used without further purification. Ethyl cyanofomrate was purchased from TCI and used after distillation. Phenylboroxine were prepared from the commercially available phenylboronic acids by azeotropic removal of water from its toluene solution and purified by washing the crude boroxines repeatedly with hexane.

General procedure for rhodium-catalysed reaction of cyanoformate with arylboronic acids
A mixture of arylboronic acid 2 (0.6 mmol, 1.2 equiv), H₃BO₃ (1.0 mmol, 2.0 equiv), [Rh(OH)(cod)₂]₂ (0.0125 mmol, 2.5 mol%) and ethyl cyanofomrate (1, 0.5 mmol, 1.0 equiv) in 1,4-dioxane (1 ml) was stirred for 30 min at room temperature and then at 60 °C for 3 h under an Ar atmosphere. Then the reaction mixture was cooled and diluted with AcOEt (10 ml) and citric acid (10% aq. 5 ml). The organic layer was separated and the aqueous layer was extracted with AcOEt (5 ml x 3). The combined extracts were washed with water and brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:AcOEt) to give the product 3, which were characterized by 1H and 13C NMR spectra.

Ethyl benzoylformate (3a)
According to general procedure, 3a (73.7 mg, 83%) was prepared from 1 (49.5mg, 0.5 mmol) and 2a (73.2 mg, 0.6 mmol). 1H NMR: δ = 1.43 (t, J = 7.2 Hz, 3H), 4.46 (q, J = 7.2 Hz, 2H), 7.49-7.55 (m, 2H), 7.63-7.69 (m, 1H), 8.00-8.03 (m, 2H); 13C NMR: δ = 14.2, 62.4, 128.9, 130.0, 132.4, 135.0, 163.8, 186.4

Ethyl 4-methoxybenzoylformate (3b)$^4$
According to general procedure, 3b (83.6 mg, 80%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2b (91.2 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.42 (t, $J$ = 7.2 Hz, 3H), 3.90 (s, 3H), 4.43 (q, $J$ = 7.2 Hz, 2H), 6.96-6.99 (m, 2H), 7.99-8.02 (m, 2H); $^{13}$C NMR: $\delta$ = 14.2, 55.7, 62.3, 114.3, 125.5, 132.6, 164.2, 165.0, 184.9

Ethyl 3-methoxybenzoylformate (3c)$^5$
According to general procedure, 3c (77.5 mg, 74%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2c (91.2 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.43 (t, $J$ = 7.2 Hz, 3H), 3.87 (s, 3H), 4.45 (q, $J$ = 7.2 Hz, 2H), 7.20 (ddd, $J$=0.9Hz, 2.7Hz, 8.1Hz, 1H), 7.42 (t, $J$=8.1Hz, 1H), 7.51-7.59 (m, 2H); $^{13}$C NMR: $\delta$ = 14.2, 55.6, 62.5, 113.3, 121.9, 123.2, 130.0, 133.7, 160.0, 163.9, 186.4

Ethyl 2-methoxybenzoylformate (3d)$^6$
According to general procedure, 3d (90.1 mg, 87%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2d (91.2 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.40 (t, $J$ = 7.2 Hz, 3H), 3.87 (s, 3H), 4.49 (q, $J$ = 7.2 Hz, 2H), 6.99 (d, $J$=6.6Hz, 1H), 7.04-7.11 (m, 1H), 7.55-7.63 (m, 1H), 7.88 (dd, $J$=1.8Hz, 7.8Hz, 1H); $^{13}$C NMR: $\delta$ = 14.2, 56.1, 61.9, 112.1, 121.3, 122.7, 130.7, 136.4, 160.3, 165.3, 186.6

Ethyl 4-bromobenzoylformate (3e)$^4$
According to general procedure, 3e (105.2 mg, 82%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2e (120.5 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.43 (t, $J$ = 6.9 Hz, 3H), 4.45 (q, $J$ = 6.9 Hz, 2H), 7.64-7.68 (m, 2H), 7.88-7.92 (m, 2H); $^{13}$C NMR: $\delta$ = 14.2, 62.7, 130.6, 131.3, 131.5, 132.3, 163.2, 185.1

Ethyl 4-fluorobenzoylformate (3f)$^4$
According to general procedure, 3f (71.3 mg, 73%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2f (84.0 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.43 (t, $J$ = 6.9 Hz, 3H), 4.45 (q, $J$ = 6.9 Hz, 2H), 7.64-7.68 (m, 2H), 7.88-7.92 (m, 2H); $^{13}$C NMR: $\delta$ = 14.2, 62.7, 130.6, 131.3, 131.5, 132.3, 163.2, 185.1

Ethyl 4-methoxybenzoylformate (3h)$^7$
According to general procedure, 3h (48.6 mg, 46%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2h (93.8 mg, 0.6 mmol). $^1$H NMR: $\delta$ = 1.41 (t, $J$ = 6.9 Hz, 3H), 4.43 (q, $J$ = 6.9 Hz, 2H), 7.37-7.45

---

7 J-F. Carpentier and A. Mortreux, Tetrahedron: Asymmetry, 1997, 18, 1083
(m, 2H), 7.50-7.57 (m, 1H), 7.77 (dd, J=1.8Hz, 7.8Hz, 1H); 13C NMR: δ = 14.0, 63.0, 127.4, 130.6, 131.7, 133.4, 133.9, 134.4, 163.2, 186.7

**Ethyl 2-methylbenzoylformate (3i)**
According to general procedure, 3i (79.7 mg, 83%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2i (81.2 mg, 0.6 mmol). : 1H NMR: δ = 1.42 (t, J = 7.2 Hz, 3H), 2.61 (s, 3H), 4.43 (q, J = 7.2 Hz, 2H), 7.32 (t, J=7.5Hz, 2H), 7.45-7.53 (m, 1H), 7.69 (d, J=7.5Hz, 1H); 13C NMR: δ = 14.2, 21.6, 62.3, 126.0, 131.2, 132.3, 132.4, 133.7, 141.3, 164.7, 188.8

**Ethyl 2-phenylbenzoylformate (3j)**
According to general procedure, 3j (63.5 mg, 50%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2j (118.8 mg, 0.6 mmol). : 1H NMR: δ = 1.04 (t, J = 6.9 Hz, 3H), 3.72 (q, J = 6.9 Hz, 2H), 7.29-7.38 (m, 2H), 7.38-7.54 (m, 5H), 7.65 (dt, J=1.5Hz, 7.5Hz, 1H), 7.82 (dd, J=1.2Hz, 7.8Hz, 1H); 13C NMR: δ = 13.7, 62.2, 127.7, 128.3, 128.8, 129.6, 130.2, 130.4, 132.9, 134.5, 139.4, 143.1, 162.6, 189.7; HRMS (FAB+): Calcd for C_{16}H_{14}O_3, M^+ 254.0943. Found m/z 254.0945.

**Ethyl 4-methoxycarbonylbenzoylformate (3k)**
According to general procedure, 3k (68.6 mg, 58%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2k (108.0 mg, 0.6 mmol). : 1H NMR: δ = 1.44 (t, J = 7.2 Hz, 3H), 3.97 (s, 3H), 4.47 (q, J = 6.9 Hz, 2H), 8.06-8.12 (m, 2H), 8.14-8.20 (m, 2H); 13C NMR: δ = 14.3, 52.8, 62.8, 130.05, 130.10, 135.4, 135.7, 163.2, 166.0, 185.7; HRMS (FAB+): Calcd for C_{12}H_{13}O_5, (M+H)+ 237.0763. Found m/z 237.0770.

**Ethyl 3-formylbenzoylformate (3l)**
According to general procedure, 3l (51.7 mg, 50%) was prepared from 1 (49.5 mg, 0.5 mmol) and 2l (90.0 mg, 0.6 mmol). : 1H NMR: δ = 1.45 (t, J = 6.9 Hz, 3H), 4.49 (q, J = 6.9 Hz, 2H), 7.72 (t, J=7.8 Hz, 1H), 8.19 (dt, J=1.5Hz, 7.8Hz, 1H), 8.32 (dt, J=1.5Hz, 7.8Hz, 1H), 8.53 (t, J=1.5Hz, 1H), 10.10 (s, 1H); 13C NMR: δ = 14.2, 62.9, 129.9, 131.7, 133.5, 134.8, 135.4, 136.8, 162.9, 185.0, 191.0; HRMS (FAB+): Calcd for C_{11}H_{11}O_4, (M+H)^+ 207.0657. Found m/z 207.0668.

---

Supplementary Material (ESI) for Chemical Communications

This journal is © The Royal Society of Chemistry 2007
Pulse sequence: al2p1l
Solvent: C6D6
Ambient temperature: 298K
"varied"

Pulse delay 1.129 ms
Pulse 45.3 degrees
Acq. time 1.640 sec
MDA 1000 Hz on
305 repetitions

DATA PROCESSING
Zero filling 3.0 Hz
PT size 2048
Total time 49 min, 48 sec

\[
\text{3h}
\]
Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2007