Supporting Information For:
Indium Triflate-Catalyzed Vinylation of β -Ketoesters
with Acetylene Gas

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General: All reactions were carried out in dry reaction vessels under argon or nitrogen atmosphere unless otherwise noted. Flash column chromatography was performed with silica gel 60 (spherical, neutral, 140–325 mesh). All ^1H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz) were measured on a JEOL ECA-500 for a CDCl_3 solution in the presence of tetramethylsilane as an internal standard and reported in ppm (δ). IR spectra recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) are reported in cm^{-1} . Anhydrous toluene was distilled in the presence of CaH_2 and stored over molecular sieves in a storage flask. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 10 ppm.

Materials: Acetylene (welding grade) was purchased from Tomoe Shokai Co., LTD and was used without further purification. Pure acetylene gas (analyzed as 100% purity by the supplier) was also purchased from the same company. $\text{In}(\text{OTf})_3$ was purchased from Aldrich Inc., stored under argon atmosphere in a storage flask. Prior to the vinylation reaction, $\text{In}(\text{OTf})_3$ was dried in reaction vessels. Because of the thermal instability of hydrated $\text{In}(\text{OTf})_3$, the reduced-pressure drying was performed carefully: $\text{In}(\text{OTf})_3$ was transferred to a flame-dried reaction vessel under Ar and was dried first at 60 °C under reduced pressure (26 Pa). After gradual increment of the temperature from 60 to 160 °C, the reduced-pressure drying was continued at 160 °C for 10 h. Molecular sieves in powder form were purchased from Nacalai tesque Inc., and used without further activation. Unless

otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification prior to use.

A Large-Scale Procedure for Catalytic Addition Reaction of β -Dicarbonyl Compounds to Acetylene

Ethyl 2-acetyl-2-ethenyldecanoate (**2**)

To the reaction vessel containing the dried $\text{In}(\text{OTf})_3$ (2.95 g, 5.18 mmol, 5 mol%), ketoester (**1**) (25.4 g, 105 mmol) and molecular sieves 3A (2.95 g) were added under atmospheric conditions. Acetylene was introduced to the vessel by attaching a balloon filled with 1-atm pressure of the welding-grade acetylene gas. The mixture was, then, heated at 100 °C for 36 h under the acetylene atmosphere (1 atm, welding grade). The resulting reaction mixture was filtrated through a pad of silica gel with ether eluent to obtain a crude product. Distillation of the crude product at 96 °C/9.3 Pa gave the titled product (**2**) in 90% yield (25.1 g, >96% GC area ratio).

A Representative Procedure for Catalytic Addition Reaction of β -Dicarbonyl Compounds to Acetylene

Condition A

To the reaction vessel containing the dried $\text{In}(\text{OTf})_3$ (109 mg, 0.194 mmol, 5 mol%), ketoester (**1**) (235 mg, 0.969 mmol) and molecular sieves 3A (109 mg) were added under argon atmosphere. The reaction vessel was evacuated and refilled with acetylene (welding grade). The reaction mixture was heated at 100 °C for 8 h under the acetylene atmosphere (1 atm). The resulting reaction mixture was filtrated through a pad of silica gel with ether eluent to obtain a crude product. The yield of product (**2**) was determined as 95% based on ^1H NMR analysis by using dibromomethane as an internal standard. The analytically pure product was obtained after silica gel column chromatography (10 g, 3% ether/pentane) in 86% yield (224.8 mg, 0.84 mmol). ^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, J = 6.9 Hz, 3H), 1.10–1.29 (m, 12H), 1.26 (t, J = 6.9 Hz, 3H), 1.91 (ddd, J = 4.6, 12.0, 13.8 Hz, 1H), 2.02 (ddd, J = 4.6, 12.0, 13.8 Hz, 1H), 2.11 (s, 3H), 4.23 (q, J = 6.9 Hz, 2H), 5.09 (d, J = 17.8 Hz, 1H), 5.32 (d, J = 10.9 Hz, 1H), 6.39 (dd, J = 10.9, 17.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 14.1, 22.6, 24.0, 26.8, 29.1, 29.2, 29.9, 31.8, 34.4, 61.4, 66.2, 117.5, 134.8, 171.3, 202.5; IR (cm^{-1}) 2956 (w), 2925 (w), 2856 (m), 1742 (m), 1715 (s), 1466 (w), 1355 (w), 1248 (m), 1229 (m), 1173 (m), 1133 (m), 996 (m), 924 (m), 858 (w), 723 (w); Anal. Calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_3$: C, 71.60; H, 10.52. Found: C, 71.85; H, 10.70.

Condition B

Prop-2-enyl 2-acetyl-2-ethenyldecanoate (**4**)

To the reaction vessel containing the dried $\text{In}(\text{OTf})_3$ (116.9 mg, 0.208 mmol, 5 mol%), ketoester (**3**) (254.4 mg, 1.04 mmol), molecular sieves 3A (116.9 mg) and toluene (1 mL) were added under argon atmosphere. The reaction vessel was evacuated and refilled with acetylene (welding grade). The reaction mixture was heated at 100 °C for 16 h under the acetylene atmosphere (1 atm, welding grade). The resulting reaction mixture was filtrated through a pad of silica gel with ether eluent to give a crude product. The purification by silica gel column chromatography (10 g, 3% ether/pentane) gave the product (**4**) in 74% yield (215.3 mg, 0.77 mmol). ^1H NMR (500 MHz,

CDCl₃) δ 0.87 (t, J = 6.9 Hz, 3H), 1.05–1.29 (m, 12H), 1.92 (ddd, J = 4.6, 12.0, 13.8 Hz, 1H), 2.03 (ddd, J = 4.6, 12.0, 13.8 Hz, 1H), 2.11 (s, 3H), 4.66 (d, J = 5.8 Hz, 2H), 5.12 (d, J = 17.8 Hz, 1H), 5.25–5.28 (m, 1H), 5.32–5.36 (m, 1H), 5.33 (d, J = 10.9 Hz, 1H), 5.86–5.94 (m, 1H), 6.39 (dd, J = 10.9, 17.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 14.1, 22.6, 24.1, 26.9, 29.1, 29.2, 29.9, 31.8, 34.4, 65.9, 66.3, 117.6, 119.2, 131.3, 134.6, 170.9, 202.3; IR (cm⁻¹) 2956 (w), 2925 (m), 2856 (w), 1744 (m), 1715 (s), 1457 (w), 1355 (w), 1227 (m), 1169 (m), 1129 (m), 988 (m), 926 (m), 723 (w); Anal. Calcd. for C₁₇H₂₈O₃: C, 72.82; H, 10.06. Found: C, 72.97; H, 10.29.

Methyl 2-acetyl-2-ethenyl-6-heptenoate (**6**)

¹H NMR (500 MHz, CDCl₃) δ 1.18–1.34 (m, 2H), 1.93 (ddd, J = 4.6, 12.6, 13.8 Hz, 1H), 2.00–2.09 (m, 3H), 2.11 (s, 3H), 3.77 (s, 3H), 4.94–5.03 (m, 2H), 5.11 (d, J = 17.8 Hz, 1H), 5.34 (d, J = 10.9 Hz, 1H), 5.71–5.80 (m, 1H), 6.38 (dd, J = 10.9, 17.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 23.5, 26.9, 33.7, 33.8, 52.5, 66.1, 114.9, 117.7, 134.5, 137.9, 171.7, 202.2; IR (cm⁻¹) 2954 (w), 1744 (m), 1713 (s), 1640 (w), 1436 (m), 1356 (m), 1289 (w), 1250 (m), 1239 (m), 1196 (m), 1173 (m), 1135 (m), 1082 (w), 993 (m), 912 (m), 793 (w); Anal. Calcd. for C₁₂H₁₈O₃: C, 68.54; H, 8.63. Found: C, 68.33; H, 8.69.

Ethyl 2-acetyl-2-ethenyl-7-octenoate (**8**)

¹H NMR (500 MHz, CDCl₃) δ 1.11–1.25 (m, 2H), 1.27 (t, J = 6.9 Hz, 3H), 1.38, (quint, J = 7.5 Hz, 2H), 1.92 (ddd, J = 4.6, 12.6, 13.8 Hz, 1H), 1.99–2.06 (m, 3H), 2.11 (s, 3H), 4.23 (q, J = 6.9

Hz, 2H), 4.94 (ddd, $J = 1.8, 17.2, 29.2$ Hz, 2H), 5.10 (d, $J = 17.8$ Hz, 1H), 5.32 (d, $J = 11.5$ Hz, 1H), 5.72–5.81 (m, 1H), 6.40 (dd, $J = 11.5, 17.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 23.4, 26.7, 29.0, 33.2, 34.2, 61.4, 66.1, 114.4, 117.5, 134.7, 138.4, 171.1, 202.2; IR (cm^{-1}) 2979 (w), 2931 (w), 1742 (m), 1713 (s), 1640 (w), 1447 (w), 1355 (w), 1301 (w), 1272 (w), 1237 (m), 1175 (m), 1135 (m), 1096 (m), 1019 (m), 993 (m), 911 (m), 859 (w); Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_3$: C, 71.56; H, 9.30. Found: C, 71.73; H, 9.30.

Ethyl 2-ethenyl-2-methyl-3-oxobenzenepropanoate (**10**)

^1H NMR (500 MHz, CDCl_3) δ 0.98 (t, $J = 6.9$ Hz, 3H), 1.65 (s, 3H), 4.04–4.12 (m, 2H), 5.06 (d, $J = 17.8$ Hz, 1H), 5.25 (d, $J = 10.9$ Hz, 1H), 6.73 (dd, $J = 10.9, 17.8$ Hz, 1H), 7.39 (aromatic, 2H), 7.50 (aromatic, 1H), 7.83 (aromatic, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.6, 23.3, 59.5, 61.5, 116.9, 128.3 (2C), 128.9 (2C), 132.6, 135.1, 137.4, 173.1, 195.4; IR (cm^{-1}) 2985 (w), 2937 (w), 1737 (s), 1686 (s), 1598 (w), 1447 (m), 1372 (m), 1254 (s), 1223 (s), 1183 (m), 1117 (s), 1019 (m), 961 (m), 926 (m), 864 (w), 793 (w), 751 (w), 702 (s), 691 (s); Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_3$: C, 72.39; H, 6.94. Found: C, 72.17; H, 7.04.

Condition C

Ethyl 1-oxo-2-ethenyl-indane-2-carboxylate (**12**)

To the reaction vessel containing the dried $\text{In}(\text{OTf})_3$ (118.0 mg, 0.209 mmol, 5 mol%), ketoester (**11**) (216.5 g, 1.06 mmol), molecular sieves 3A (118 mg), DBU (32 mg, 0.209 mmol, 5 mol%) and

toluene (1 mL) were added under argon atmosphere. The reaction vessel was evacuated and refilled with acetylene (welding grade). The reaction mixture was heated at 100 °C for 16 h under the acetylene atmosphere (1 atm, welding grade). The resulting reaction mixture was filtrated through a pad of silica gel with ether eluent to obtain a crude product. The purification by silica gel column chromatography (10 g, 3% ether/pentane) gave the product (**12**) in 75% yield (183.4 mg, 0.80 mmol). ¹H NMR (500 MHz, CDCl₃) δ 1.24 (t, *J* = 6.9 Hz, 3H), 3.38 (d, *J* = 17.2 Hz, 1H), 3.81 (d, *J* = 17.2 Hz, 1H), 4.20 (q, *J* = 6.9 Hz, 2H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H), 6.42 (dd, *J* = 10.9, 17.2 Hz, 1H), 7.40 (aromatic, 1H), 7.50 (aromatic, 1H), 7.63 (aromatic, 1H), 7.77 (aromatic, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 36.7, 61.9, 63.3, 115.9, 125.1, 126.2, 127.8, 134.1, 135.0, 135.4, 152.5, 170.1, 199.9; IR (cm⁻¹) 2983 (w), 1737 (s), 1710 (s), 1634 (w), 1605 (m), 1590 (w), 1465 (m), 1443 (w), 1270 (s), 1250 (s), 1210 (s), 1189 (s), 1154 (s), 1096 (m), 1061 (s), 996 (m), 903 (s), 859 (m), 793 (m), 750 (s), 697 (s); Anal. Calcd. for C₁₄H₁₄O₃: C, 73.03; H, 6.13. Found: C, 72.97; H, 6.27.

Ethyl 1,2,3,4-tetrahydro-1-oxo-2-ethenyl-naphthalene-2-carboxylate (**14**)

¹H NMR (500 MHz, CDCl₃) δ 1.19 (t, *J* = 6.9 Hz, 3H), 2.23 (ddd, 5.2, 8.0, 13.8 Hz, 1H), 2.75 (ddd, *J* = 5.2, 8.0, 13.8 Hz, 1H), 2.96–3.08 (m, 2H), 4.18 (q, *J* = 6.9 Hz, 2H), 5.16 (d, *J* = 17.8 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H), 6.27 (dd, *J* = 10.9, 17.8 Hz, 1H), 7.30 (aromatic, 1H), 7.32 (aromatic, 1H), 7.48 (aromatic, 1H), 8.08 (aromatic, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 25.6, 31.3, 60.5, 61.7, 117.5, 126.8, 128.0, 128.7, 131.8, 133.6, 134.9, 143.0, 170.5, 193.9; IR (cm⁻¹) 2983 (w), 2937 (w), 1729 (s), 1683 (s), 1636 (w), 1600 (m), 1455 (m), 1353 (w), 1293 (m), 1223 (s), 1191 (s), 1177 (s), 1067 (m), 1015 (m), 909 (s), 743 (s), 664 (m); Anal. Calcd. for C₁₅H₁₆O₃: C, 73.75; H, 6.60. Found: C, 73.76; H, 6.65.

Benzyl 1-ethenyl-2-oxocyclohexanecarboxylate (**16**)

¹H NMR (500 MHz, CDCl₃) δ 1.62–1.72 (m, 3H), 1.73–1.80 (m, 1H), 1.79–2.00 (m, 1H), 2.31–2.37 (m, 1H), 2.44–2.48 (m, 1H), 2.61–2.65 (m, 1H), 5.11 (d, *J* = 17.8 Hz, 1H), 5.14 (d, *J* = 12.6 Hz, 1H), 5.23 (d, *J* = 12.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 6.22 (dd, *J* = 10.9, 17.8 Hz, 1H), 7.31–7.37 (aromatic, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 22.3, 27.2, 35.5, 40.7, 63.3, 67.2, 116.8, 128.1, 128.4 (2C), 128.5 (2C), 135.2, 135.5, 169.9, 206.0; IR (cm⁻¹) 2943 (w), 2867 (w), 1740 (m), 1711 (s), 1453 (m), 1310 (w), 1239 (m), 1202 (m), 1173 (m), 1131 (m), 1086 (m), 965 (m), 926 (m), 737 (m), 697 (s); Anal. Calcd. for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.19; H, 7.12.

Ethyl 1-ethenyl-2-oxocyclododecanecarboxylate (**18**)

¹H NMR (500 MHz, CDCl₃) δ 1.17–1.41 (m, 15 H), 1.24 (t, *J* = 6.9 Hz, 3H), 1.99 (dt, *J* = 4.6, 13.7 Hz, 1H), 2.00–2.06 (m, 1H), 2.15–2.21 (m, 1H), 2.33 (ddd, *J* = 3.5, 5.8, 18.3 Hz, 1H), 2.81 (ddd, *J* = 2.9, 11.5, 18.3 Hz, 1H), 4.15–4.22 (m, 2H), 5.13 (d, *J* = 17.8 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 6.42 (dd, *J* = 10.9, 17.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 19.3, 21.5, 22.1, 22.2, 22.7, 23.5, 26.4, 26.8, 32.2, 34.2, 61.3, 65.6, 116.3, 134.9, 171.3, 205.9; IR (cm⁻¹) 2935 (w), 2867 (w), 1742 (m), 1710 (s), 1468 (m), 1219 (s), 1189 (s), 1127 (w), 1065 (m), 1032 (m), 994 (m), 967 (m), 928 (m), 859 (w), 727 (m), 706 (m); Anal. Calcd. for C₁₇H₂₈O₃: C, 72.82; H, 10.06. Found: C, 73.01; H, 10.09.