Supporting Information

Indium-Catalyzed 2-Alkenylation of 1,3-Dicarbonyl

Compounds with Unactivated Alkynes

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General: All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Thin layer chromatography plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at c.a. 30 mmHg. Flash column chromatography was performed on Kanto Silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still et al.¹

Instrumentation: Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded with a JEOL ECX-400 (400 MHz) or ECA-500 (500 MHz) NMR spectrometer. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of CDCl₃ (δ 7.26). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl₃ (δ 77.0). Data are presented as following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers, assignment (*italic*). IR spectra recorded on a React IR 1000 Reaction Analysis System equipped with DuraSample IR (ASI Applied System) are reported in cm⁻¹. High-resolution mass spectra are taken with EI (electron impact) method at a JEOL GC-mate II, APCI (atmosphere pressure chemical ionization) or ESI (electron spray ionization) method at a JEOL JMS-T100LC. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials: Unless otherwise noted, materials were purchased from Tokyo Kasei Co.,

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¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

Aldrich Inc., and other commercial suppliers and were used after appropriate purification before use. In(OTf)₃ was purchased from Aldrich Inc.

A representative procedure of the alkenylation of β -ketoesters (4.0 mmol scale) and physical properties of the alkenylated β -ketoesters

Ethyl 2-methyl-2-(1-oxoethyl)-3-phenyl-3-butenolate (5)

A CH₃CN solution of In(OTf)₃ (0.1 M, 20 μ L, 0.05 mol%) was introduced into a dried reaction vessel under argon atmosphere. Then CH₃CN was removed under reduced pressure (130 Pa) at room temperature for 1 h. Ethyl 2-methyl-3-oxobutanoate (4.0 mmol, 576 μ L, 576 mg) and phenylacetylene (4.8 mmol, 527 μ L, 490 mg, 1.2 equiv) were introduced into the reaction vessel. The reaction mixture was stirred at 140 °C for 90 minutes and then cooled to room temperature. Flash column chromatography (silica gel 10 g, eluent; hexane/Et₂O = 95/5) of the reaction mixture gave title compound in 99 % yield (973 mg); ¹H NMR (400 MHz, CDCl₃) δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.52 (s, 3H), 2.29 (s, 3H), 4.18 (q, *J* = 7.2 Hz, 2H), 5.28 (s, 1H), 5.44 (s, 1H) 7.18–7.31 (m, 5H, arom); ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 21.8, 27.2, 61.5, 65.8, 118.7, 127.5, 127.7 (2C), 128.0 (2C), 140.3, 147.9, 171.7, 205.2; IR (cm⁻¹) 2987, 1710, 1239, 1092, 1021, 915; Anal. Calcd. for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.32; H, 7.46.

Ethyl 2-methyl-3-(4-bromophenyl)-2-(1-oxoethyl)-3-butenolate (9)

¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, *J* = 5.6 Hz, 3H), 1.52 (s, 3H), 2.27 (s, 3H), 4.15–4.19 (m, 2H), 5.30 (s, 1H), 5.42 (s, 1H), 7.07–7.09 (m, 2H, arom), 7.41–7.43 (m, 2H, arom); ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 21.1, 27.1, 61.6, 65.5, 119.3, 121.6, 129.5 (2C), 131.1 (2C), 139.2, 146.8, 171.5, 204.9; IR (cm⁻¹) 2985, 1735, 1711, 1480, 1391, 1374, 1355, 1239, 1111, 1092, 1081, 1008, 918, 833, 731; Anal. Calcd. for C₁₅H₁₇BrO₃: C, 55.40; H, 5.27. Found: C, 55.34; H, 5.36.

Ethyl 2-methyl-3-(2-bromophenyl)-2-(1-oxoethyl)-3-butenolate (11)

^1H NMR (500 MHz, CDCl_3) δ 1.24 (t, $J = 7.2$ Hz, 3H), 1.43 (s, 3H), 2.37 (s, 3H), 4.17–4.22 (m, 2H), 5.39 (s, 1H), 5.50 (s, 1H), 7.13–7.18 (m, 2H, arom), 7.23–7.27 (m, 1H, arom), 7.58–7.60 (m, 1H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 20.1, 26.6, 61.7, 65.9, 122.7, 123.7, 126.9, 128.9, 130.1, 132.8, 141.2, 144.4, 171.3, 204.7; IR (cm^{-1}) 2983, 1733, 1710, 1470, 1428, 1355, 1239, 1117, 1096, 1025, 916, 760, 731; Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{BrO}_3$: C, 55.40; H, 5.27. Found: C, 55.40; H, 5.38.

Ethyl 2-methyl-3-(2-methoxycarbonylphenyl)-2-(oxoethyl)-3-butenolate (15)

^1H NMR (500 MHz, CDCl_3) δ 1.22 (t, $J = 6.9$ Hz, 3H), 1.45 (s, 3H), 2.36 (s, 3H), 3.83 (s, 3H), 4.14–4.23 (m, 2H), 5.23 (s, 1H), 5.35 (s, 1H), 7.20–7.21 (m, 1H, arom), 7.33–7.37 (m, 1H, arom), 7.40–7.42 (m, 1H, arom), 7.80–7.82 (m, 1H, arom); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 20.4, 26.4, 52.1, 61.5, 66.0, 119.8, 127.4, 129.67, 129.72, 131.0, 131.1, 141.3, 145.5, 168.1, 171.7, 205.2; IR (cm^{-1}) 2987, 1710, 1607, 1511, 1241, 1181, 1092, 1028, 835; Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_5$: C, 67.09; H, 6.62; Found: C, 67.03, H, 6.86.

Ethyl 3-[2-(2-methoxycarbonyl)ethenyl]phenyl]-2-methyl-2-(1-oxoethyl)-3-butenolate (17)

^1H NMR (500 MHz, CDCl_3) δ 1.23 (t, $J = 6.9$ Hz, 3H), 1.38 (s, 3H), 2.36 (s, 3H), 3.80 (s, 3H), 4.15–4.20 (m, 2H), 5.30 (s, 1H), 5.57 (s, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 7.12–7.14 (m, 1H), 7.30–7.32 (m, 2H), 7.65–7.67 (m, 1H), 7.98 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 20.7, 26.8, 51.7, 61.7, 66.1, 118.7, 122.9, 126.2, 127.9, 128.9, 129.5, 133.2, 141.2, 143.3, 143.6, 167.2, 171.5, 204.3; IR (cm^{-1}) 2989, 1710, 1632, 1480, 1447, 1436, 1355, 1316, 1273, 1241, 1198, 1171, 1144, 1090, 1069, 1017, 986, 862, 764; Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_5$: C, 69.07; H, 6.71. Found: C, 68.96; H, 6.93.

Ethyl 3-(2-methoxyphenyl)-2-methyl-2-(1-oxoethyl)-3-butenolate (21)

^1H NMR (400 MHz, CDCl_3) δ 1.25 (t, $J = 6$ Hz, 3H), 1.27 (s, 3H), 2.36 (s, 3H), 3.68 (s, 3H), 4.18 (q, $J = 6$ Hz, 2H), 5.35 (s, 1H), 5.42 (s, 1H), 6.80–6.82 (m, 1H, arom), 6.92–6.96 (m, 1H, arom), 7.16–7.17 (m, 1H, arom), 7.18–7.30 (m, 1H, arom); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 19.9, 26.6, 54.4, 61.3, 64.9, 109.9, 120.7, 120.9, 129.2, 129.7, 130.8, 146.4, 156.1, 172.2, 205.2; IR (cm^{-1}) 2983, 2943, 1736, 1710, 1598, 1492, 1430, 1374, 1353, 1297, 1235, 1111, 1094, 1040, 1023, 916, 762; Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.54; H, 7.30. Found: C, 69.41; H, 7.35.

Ethyl 2-methyl-3-methylene-2-(1-oxoethyl)-7-*N*-phthaloylaminoheptanoate (30)

^1H NMR (500 MHz, CDCl_3) δ 1.27 (t, $J = 6.9$ Hz, 3H), 1.50 (s, 3H), 1.51–1.58 (m, 2H), 1.71 (quint, $J = 7.5$ Hz, 2H), 2.01–2.09 (m, 2H), 2.21 (s, 3H), 3.69 (t, $J = 7.5$ Hz, 2H), 4.19 (q, $J = 6.9$ Hz, 2H), 4.99 (s, 1H), 5.11 (brs, 1H), 7.70–7.72 (m, 2H, arom), 7.83–7.85 (m, 2H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 19.5, 25.3, 26.8, 28.2, 31.9, 37.5, 61.2, 66.0, 113.2, 122.9 (2C), 131.9, 133.7 (2C), 146.4 (2C), 168.2 (2C), 171.5, 205.1; IR (cm^{-1}) 2943, 1771, 1704, 1638, 1466, 1437, 1395, 1245, 1189, 1119, 1090, 1030, 1021, 903, 861, 795, 718; Anal. Calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_5$: C, 67.91; H, 6.78; N, 3.77. Found: C, 67.72; H, 6.83; N, 3.59.

Ethyl 2-methyl-3-(4-octylfuryl)-2-(1-oxoethyl)-3-butenolate (34)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.24–1.33 (m, 10H), 1.25 (t, $J = 7.5$ Hz, 3H), 1.58–1.62 (m, 2H), 1.63 (s, 3H), 2.26 (s, 3H), 2.57 (t, $J = 7.5$ Hz, 2H), 4.21 (q, $J = 7.5$ Hz, 2H), 5.06 (s, 1H), 5.71 (s, 1H), 5.93 (d, $J = 3.5$ Hz, 1H), 6.17 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 13.9, 20.4, 22.5, 27.3, 27.8, 27.9, 28.9, 29.1, 29.2, 31.7, 61.4, 64.0, 106.4, 108.5, 111.8, 137.7, 150.2, 156.1, 171.1, 205.0; IR

(cm⁻¹) 2927, 2856, 1740, 1716, 1528, 1465, 1355, 1241, 1121, 1092, 1021, 969, 893, 859, 785; Anal. Calcd. for C₂₁H₃₂O₄: C, 72.38; H, 9.26. Found: C, 72.23; H, 9.21.

Ethyl 2-methyl-3-(4-octylthienyl)-2-(1-oxoethyl)-3-butenolate (36)

¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.24–1.37 (m, 10H), 1.62–1.64 (m, 2H), 1.64 (s, 3H), 2.27 (s, 3H), 2.73 (t, *J* = 7.5 Hz, 2H), 4.22 (q, *J* = 7.5 Hz, 2H), 5.12 (s, 1H), 5.57 (s, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 6.63 (d, *J* = 3.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.7, 13.9, 20.7, 22.5, 27.3, 28.9, 29.1, 29.2, 29.8, 31.4, 31.7, 61.4, 65.6, 115.9, 124.0, 125.4, 139.2, 141.5, 145.5, 171.2, 205.1; IR (cm⁻¹) 2954, 2925, 2856, 1739, 1715, 1607, 1465, 1376, 1355, 1239, 1111, 1092, 1021, 891, 858, 803, 723; Anal. Calcd. for C₂₁H₃₂O₃S: C, 69.19; H, 8.85. Found: C, 68.90; H, 8.82.

A representative procedure of the addition of ethyl 2-methyl-3-oxobutanoate to 1,3-decadiyne²

Ethyl 2-methyl-3-methylene-2-(1-oxoethyl)-4-undecynoate (38)

In a flame dried reaction vessel, In(NTf₂)₃ was dried at 140 °C under reduced pressure (26 Pa) for 10 h. After the In-containing vessel was flushed with argon at room temperature, a mixture of ethyl 2-methyl-3-oxobutanoate (151 mg, 1.05 mmol) and 1,3-decadiyne (147 mg, 1.10 mmol, 1.05 equiv), In(NTf₂)₃ (10.0 mg, 10.5 μmol, 1 mol%) was heated at 60 °C in the dark for 48 h. The resulting reaction mixture was filtered through a pad of silica gel with ether eluent to give a crude product. Purification by silica gel column chromatography (2% EtOAc/hexane) gave the title compound in 98% yield (286 mg, 1.03 mmol); ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.24–1.32 (m, 4H), 1.28 (t, *J* = 6.9 Hz, 3H), 1.33–1.40 (m, 2H), 1.50 (quint, *J* = 6.9 Hz, 2H), 1.56 (s, 3H), 2.28 (t, *J* = 6.9 Hz, 2H), 2.32 (s, 3H), 4.23 (dq, *J* = 1.7, 6.9 Hz, 2H), 5.37 (s, 1H), 5.59 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.8, 13.9, 19.1, 19.9, 22.4, 27.3, 28.3, 28.4, 31.2, 61.4, 64.9, 78.6, 92.8, 122.3, 130.7, 170.8, 203.9; IR (cm⁻¹) 2934, 2860, 2223, 1718, 1606, 1451, 1355, 1239, 1112, 1023, 907; Anal. Calcd. for C₁₇H₂₆O₃:

² Addition to 1,3-diynes and tandem [4+2] annulation reaction, see: Nakamura, M.; Endo, K.; Nakamura, E. *Adv. Synth. Catal.* **2005**, *347*, 1681–1686.

C, 73.34; H, 9.41. Found: C, 73.59; H, 9.60.

Ethyl 2-(3-hexyl-4-phenylethynyl-5-biphenyl)-2-(1-oxoethyl)propanoate (42)

To a resultant mixture after the addition reaction of ethyl 2-methyl-3-oxobutanoate (0.5 mmol) to 1,3-decadiyne (0.53 mmol, 1.05 equiv) in the presence of $\text{In}(\text{NTf}_2)_3$ (1 mol%), MS 3A (inactivated, 500 mg) 1,4-diphenyl-1,3-butadiyne (121 mg, 0.6 mmol, 1.2 eq), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (13 mg, 0.0125 mmol, 2.5 mol%), and $\text{P}(o\text{-tol})_3$ (15 mg, 0.05 mmol, 10 mol%) was added. The reaction mixture in degassed toluene (0.5 mL) was stirred at 25 °C for 20 h. The resulted reaction mixture was filtered through a pad of silica gel with ether eluent to give a crude product. Purification by silica gel column chromatography (2% EtOAc/hexane) gave the title compound in 98% yield (236 mg, 0.49 mmol); ^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, J = 6.9 Hz, 3H), 1.30–1.36 (m, 4 H), 1.31 (t, J = 6.9 Hz, 3H), 1.37–1.56 (m, 2H), 1.73 (quint, J = 7.5 Hz, 2H), 1.79 (s, 3H), 2.17 (s, 3H), 2.93 (m, 2H), 4.28 (q, J = 6.9 Hz, 2H), 7.14 (aromatic, s, 1H), 7.18 (aromatic, s, 1H), 7.28 (aromatic, 5H), 7.39–7.41 (aromatic, 1H), 7.44–7.47 (aromatic, 2H), 7.61–7.63 (aromatic, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.00, 14.05, 21.2, 22.6, 27.2, 29.3, 30.7, 31.7, 35.5, 61.7, 64.6, 87.4, 96.6, 120.6, 123.5, 125.9, 126.8, 127.5, 127.7 (2C), 128.1, 128.2 (2C), 129.5 (2C), 131.1 (2C), 138.1, 140.8, 144.6, 145.9, 171.6, 204.5; IR (cm^{-1}) 2930, 2856, 1714, 1598, 1494, 1459, 1355, 1243, 1193, 1092, 1023, 911, 884, 861, 776, 767; Anal. Calcd. For $\text{C}_{33}\text{H}_{36}\text{O}_3$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.65.

A representative procedure of the vinylation of ethyl 2-ethenyl-2-(1-oxoethyl)decanoate (41)³

$\text{In}(\text{OTf})_3$ (3.12 g, hydrated $\text{In}(\text{OTf})_3$) was put into a weighed 50 mL 2-necked round bottomed flask equipped with stirring bar filled with argon gas after flame-drying under reduced pressure. The white powder in the vessel was dried under reduced pressure at less than 6 Pa. The oil bath temperature gradually increased to 180 °C for 1 hour. After 1 hour at 180 °C under 6 Pa, the vessel was filled with argon gas. The reaction vessel was weighed to determine the amount of $\text{In}(\text{OTf})_3$, which is equivalent to 5 mol% catalyst (2.81 g, 5.0 mmol). Ketoester (25.5 g, 100 mmol) and MS 3A (2.81 g) were added to the reaction vessel. Substantial substitution of inert gas to acetylene was

³ Addition to acetylene: Nakamura, M.; Endo, K.; Nakamura, E. *Org. Lett.* **2005**, 7, 3279–3281.

carried out, followed by the reaction mixture was stirred at 100 °C for 48 hours equipped with acetylene gas balloon. The mixture was filtered through a pad of silica gel with ether to give a crude product (28.04 g, 99.5%, 93% GC area ratio). Distillation at 96 °C/6 Pa gave the title compound in 90% yield (25.1 g, >96% GC area ratio); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) δ 4.0, 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, 2925, 2856, 1742, 1715, 1466, 1355, 1248, 1229, 1173, 1133, 996, 924, 858, 723; Anal. Calcd. for C₁₆H₂₈O₃: C, 71.60; H, 10.52. Found C, 71.85; H, 10.70.

2-Propenyl 2-methyl-2-(1-oxoethyl)-3-phenyl-3-butenate (47)

¹H NMR (500 MHz, CDCl₃) δ 1.52 (s, 3H), 2.29 (s, 3H), 4.62 (brd, *J* = 5.2 Hz, 2H), 5.21–5.24 (m, 1H), 5.28 (s, 1H), 5.28–5.33 (m, 1H), 5.44 (s, 1H), 5.81–5.88 (m, 1H), 7.18–7.20 (m, 2H, arom), 7.26–7.30 (m, 3H, arom); ¹³C NMR (125 MHz, CDCl₃) δ 21.2, 27.3, 65.9, 66.1, 118.8, 118.9, 127.6, 127.7, 128.1 (2C), 131.4 (2C), 140.2, 147.8, 171.5, 205.2; IR (cm⁻¹) 2993, 1735, 1710, 1493, 1453, 1424, 1378, 1355, 1233, 1117, 1092, 974, 916, 777, 702; Anal. Calcd. for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.29; H, 7.16.

2-Propenyl 2-methyl-3-methylene-2-(1-oxoethyl)nonanoate (48)

¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.25–1.33 (m, 6H), 1.43–1.50 (m, 2H), 1.53 (s, 3H), 1.95–2.02 (m, 2H), 2.22 (s, 3H), 4.63–4.66 (m, 2H), 4.99 (s, 1H), 5.14 (distorted t, *J* = 1.7 Hz, 1H), 5.24–5.27 (m, 1H), 5.31–5.36 (m, 1H), 5.87–5.95 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 19.6, 22.6, 27.1, 28.3, 29.1, 31.7, 32.8, 65.9, 66.4, 113.1, 118.9, 131.5, 147.2, 171.6, 205.5; IR (cm⁻¹) 2929, 2866, 1713, 1640, 1455, 1376, 1355, 1233, 1119, 1090, 1013, 980, 932, 903; Anal. Calcd. for C₁₆H₂₆O₃: C, 72.14; H, 9.84. Found: C, 71.98; H, 10.09.

2-Propenyl 7-methoxy-2-methyl-3-methylene-2-(1-oxoethyl)heptanoate (49)

^1H NMR (500 MHz, CDCl_3) δ 1.55 (s, 3H), 1.55–1.61 (m, 4H), 2.00–2.05 (m, 2H), 2.22 (s, 3H), 3.32 (s, 3H), 3.38 (t, J = 6.3 Hz, 2H), 4.64 (m, 2H), 5.01 (s, 1H), 5.15 (distorted t, J = 1.8 Hz, 1H), 5.24–5.27 (m, 1H), 5.31–5.36 (m, 1H), 5.88–5.95 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.6, 24.9, 26.9, 29.4, 32.4, 58.5, 65.9, 66.3, 72.5, 113.3, 118.9, 131.4, 146.8, 171.5, 205.3; IR (cm^{-1}) 2941, 2867, 1713, 1640, 1453, 1355, 1237, 1115, 1092, 978, 912, 733; Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_4$: C, 67.14; H, 9.01; Found: C, 66.98; H, 9.26.

Ethyl 2-benzyl-2-(1-oxoethyl)-3-phenyl-3-butenolate (51)

^1H NMR (500 MHz, CDCl_3) δ 1.04 (t, J = 7.2 Hz, 3H), 2.23 (s, 3H), 3.18 (d, J = 13.8 Hz, 1H), 3.54 (d, J = 13.8 Hz, 1H), 3.92–3.99 (m, 2H), 5.39 (s, 1H), 5.48 (s, 1H), 7.12–7.18 (m, 7H, arom), 7.26–7.29 (m, 3H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.5, 28.6, 40.5, 61.2, 71.3, 121.2, 126.6, 127.5, 127.9 (4C), 128.0 (2C), 130.6 (2C), 136.9, 140.8, 146.1, 170.2, 203.9; IR (cm^{-1}) 2981, 2954, 1711, 1643, 1443, 1355, 1254, 1219, 1181, 1154, 1082, 1030, 914, 860, 775, 760, 698; Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_3$: C, 78.23; H, 6.88. Found: C, 78.10; H, 7.09.

Ethyl 2-benzyl-3-methylene-2-(1-oxoethyl)nonanoate (52)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, J = 6.9 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H), 1.24–1.32 (m, 6H), 1.35–1.52 (m, 2H), 1.80–1.87 (m, 1H), 2.03–2.11 (m, 1H), 2.17 (s, 3H), 3.10 (d, J = 13.8 Hz, 1H), 3.59 (d, J = 13.8 Hz, 1H), 3.98–4.05 (m, 2H), 5.20 (s, 2H), 7.15–7.21 (m, 5H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 14.0, 22.6, 28.1, 29.1 (2C), 31.7, 32.7, 39.5, 61.0, 71.9, 114.9, 126.6, 127.9 (2C), 130.3 (2C), 137.2, 145.8, 170.3, 203.7; IR (cm^{-1}) 2931, 2860, 1711, 1455, 1355, 1260, 1221, 1177, 1154, 1082, 1054, 1034, 904, 856, 739, 700; Anal. Calcd. for $\text{C}_{21}\text{H}_{30}\text{O}_3$: C, 76.33; H, 9.15. Found: C, 76.16; H, 9.24.

Ethyl 2-(1-oxoethyl)-3-phenyl-2-(2-propenyl)-3-butenolate (55)

^1H NMR (500 MHz, CDCl_3) δ 1.21 (t, $J = 7.2$ Hz, 3H), 2.30 (s, 3H), 2.60–2.65 (m, 1H), 2.68–2.74 (m, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 4.94–5.00 (m, 2H), 5.44 (s, 1H), 5.48 (s, 1H), 5.73–5.80 (m, 1H), 7.15–7.18 (m, 2H, arom), 7.26–7.30 (m, 3H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 28.1, 39.0, 61.4, 69.7, 118.3, 120.7, 127.6, 127.8 (2C), 128.1 (2C), 133.7, 140.4, 146.2, 170.7, 204.1; IR (cm^{-1}) 2981, 1711, 1443, 1355, 1277, 1218, 1135, 1028, 914, 775, 731, 700; Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97; H, 7.40. Found: C, 75.07; H, 7.57.

Ethyl 3-methylene-2-(1-oxoethyl)-2-(2-propenyl) nonanoate (56)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.24–1.32 (m, 6H), 1.41–1.46 (m, 2H), 1.85–1.93 (m, 1H), 1.7–2.04 (m, 1H), 2.22 (s, 3H), 2.59–2.65 (m, 1H), 2.78–2.83 (m, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 5.01–5.09 (m, 2H), 5.15 (s, 1H), 5.19 (brs, 1H), 5.74–5.82 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 14.1, 22.6, 27.6, 28.0, 29.1, 31.7, 32.5, 37.7, 61.1, 70.4, 114.6, 117.9, 133.9, 145.4, 170.6, 204.1; IR (cm^{-1}) 2958, 2929, 2860, 1713, 1638, 1466, 1445, 1355, 1210, 1131, 1030, 914, 856, 725; Anal. Calcd. for $\text{C}_{14}\text{H}_{25}\text{O}_4$: C, 72.82; H, 10.06; Found: C, 73.08; H, 10.28.

Ethyl 1-(1-methyleneheptanyl)-2-oxocyclopentanecarboxylate (59)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (m, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.23–1.33 (m, 6H), 1.43–1.50 (m, 2H), 1.83–1.96 (m, 2H), 1.99–2.06 (m, 2H), 2.21–2.27 (m, 1H), 2.31–2.36 (m, 2H), 2.53–2.59 (m, 1H), 4.15–4.23 (m, 2H), 4.93 (s, 1H), 5.08 (distorted t, $J = 1.7$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 14.1, 19.2, 22.5, 28.1, 29.1, 31.7, 32.7, 33.1, 37.8, 61.6, 67.4, 112.9, 144.5, 170.4, 212.5; IR (cm^{-1}) 2958, 2929, 2858, 1750, 1721, 1638, 1466, 1407, 1366, 1241, 1158, 1133, 1090, 1025, 957, 903, 860, 825, 731; Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_3$: C, 72.14; H, 9.84; Found: C, 71.98; H, 9.91.

Ethyl 2-methyl-3-phenyl-2-phenylcarbonyl-3-butenolate (63)

^1H NMR (500 MHz, CDCl_3) δ 1.10 (t, $J = 7.2$ Hz, 3H), 1.72 (s, 3H), 4.16 (q, $J = 7.2$ Hz, 2H), 5.46 (s, 1H), 5.49 (s, 1H), 7.22–7.26 (m, 5H, arom), 7.36–7.39 (m, 2H, arom), 7.46–7.48 (m, 1H, arom), 7.89–7.91 (m, 2H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.7, 23.8, 61.6, 63.9, 120.2, 127.4, 127.9 (2C), 128.0 (2C), 128.4 (2C), 129.6 (2C), 132.4, 135.6, 140.7, 148.3, 172.2, 197.8; IR (cm^{-1}) 2983, 1733, 1678, 1598, 1447, 1243, 1111, 1082, 1028, 1019, 966, 914, 775, 700; Anal. Calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_3$: C, 77.90; H, 6.54; Found: C, 77.85; H, 6.67.

Ethyl 2-methyl-3-methylene-2-phenyl-3-oxononanoate (64)

^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.10 (t, $J = 7.2$ Hz, 3H), 1.21–1.30 (m, 6H), 1.44–1.52 (m, 2H), 1.70 (s, 3H), 2.10–2.15 (m, 2H), 4.07–4.16 (m, 2H), 5.17 (distorted t, $J = 1.7$ Hz, 1H), 5.22 (s, 1H), 7.36–7.39 (m, 2H, arom), 7.47–7.51 (m, 1H, arom), 7.88–7.91 (m, 2H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.7, 14.0, 22.5, 22.6, 28.5, 29.1, 31.7, 33.1, 61.2, 64.4, 113.1, 128.1 (2C), 129.2 (2C), 132.4, 136.3, 148.6, 172.2, 198.2; IR (cm^{-1}) 2929, 2858, 1737, 1686, 1447, 1372, 1246, 1109, 1021, 966, 903, 708, 692, 669; Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_3$: C, 75.91; H, 8.92. Found: C, 75.73; H, 9.03.

Ethyl 1-oxo-2-(1-phenylethenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (67)

^1H NMR (500 MHz, CDCl_3) δ 1.26 (t, $J = 6.9$ Hz, 3H), 2.38 (ddd, $J = 14.4$ Hz, 4.6 Hz, 4.2 Hz, 1H), 2.69–2.84 (m, 3H), 4.31 (dq, $J = 6.9$ Hz, 1.7 Hz, 2H), 5.12 (s, 1H), 5.47 (s, 1H), 7.16 (d, $J = 7.4$ Hz, 1H), 7.25–7.33 (m, 6H), 7.46 (ddd, $J = 7.5$ Hz, 7.5 Hz, 1.2 Hz, 1H), 8.08 (dd, $J = 7.5$ Hz, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 25.5, 30.6, 61.8, 64.4, 120.7, 126.8, 127.7, 127.9 (2C), 128.1, 128.2 (2C), 128.6, 131.7, 133.5, 140.1, 142.8, 145.0, 171.3, 194.7; IR (cm^{-1}) 2987, 1710, 1607, 1511, 1241, 1181, 1092, 1028, 835; Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_3$: C, 78.73; H, 6.29; Found: C, 78.55; H, 6.46.

Ethyl 2-fluoro-2-(1-oxoethyl)-3-phenyl-3-butenolate (69)

^1H NMR (500 MHz, CDCl_3) δ 1.24 (t, $J = 6.9$ Hz, 3H), 2.35 (d, $J = 4.6$ Hz, 3H), 4.28 (dq, $J = 1.2, 7.2$ Hz, 2H), 5.48 (d, $J = 3.5$ Hz, 1H), 5.66 (s, 1H), 7.31–7.33 (m, 5H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 26.2, 62.7, 99.6 (d, $^1J_{\text{C-F}} = 195.5$ Hz, 1C), 120.8 (d, $^3J_{\text{C-F}} = 7.2$ Hz, 1C), 127.7 (2C), 128.2 (2C), 128.3, 136.9, 142.3 (d, $^2J_{\text{C-F}} = 20.3$ Hz, 1C), 165.3 (d, $^2J_{\text{C-F}} = 27.4$ Hz, 1C), 200.0 (d, $^2J_{\text{C-F}} = 26.2$ Hz, 1C); IR (cm^{-1}) 2985, 1754, 1731, 1445, 1358, 1299, 1254, 1202, 1094, 1075, 1019, 934, 776, 702; Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{FO}_3$: C, 67.19; H, 6.04. Found: C, 67.08; H, 6.12.

Ethyl 2-fluoro-3-methylene-2-(1-oxoethyl)nonanoate (70)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.25–1.33 (m, 6H), 1.32 (t, $J = 7.5$ Hz, 3H), 1.45 (quint, $J = 6.9$ Hz, 2H), 2.07–2.14 (m, 2H), 2.31 (d, $J = 4.6$ Hz, 3H), 4.29 (q, $J = 7.5$ Hz, 2H), 5.24–5.26 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 13.9, 22.4, 25.5, 27.6, 28.8, 30.8 (d, $^3J_{\text{C-F}} = 3.6$ Hz, 1C), 31.5, 62.5, 100.2 (d, $^1J_{\text{C-F}} = 194.3$ Hz, 1C), 115.0 (d, $^3J_{\text{C-F}} = 8.4$ Hz, 1C), 141.8 (d, $^2J_{\text{C-F}} = 21.5$ Hz, 1C), 165.3 (d, $^2J_{\text{C-F}} = 25.0$ Hz, 1C), 200.1 (d, $^2J_{\text{C-F}} = 26.2$ Hz, 1C); IR (cm^{-1}) 2953, 2931, 2860, 1756, 1731, 1466, 1356, 1254, 1206, 1082, 1069, 1019, 914, 859; Anal. Calcd. for $\text{C}_{14}\text{H}_{23}\text{FO}_3$: C, 65.09; H, 8.97. Found: C, 64.99; H, 9.05.

Ethyl 2-chloro-2-(1-oxoethyl)-3-phenyl-3-butenate (72)

^1H NMR (500 MHz, CDCl_3) δ 1.23 (t, $J = 6.9$ Hz, 3H), 2.42 (s, 3H), 4.22–4.29 (m, 2H), 5.54 (s, 1H), 5.65 (s, 1H), 7.28–7.32 (m, 5H, arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.5, 26.2, 63.1, 77.7, 120.9, 127.9 (2C), 128.0, 128.1 (2C), 138.1, 143.9, 166.5, 197.5; IR (cm^{-1}) 2983, 1721, 1493, 1445, 1350, 1229, 1183, 1054, 1028, 919, 849, 774, 700; Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{ClO}_3$: C, 63.04; H, 5.67. Found: C, 62.95; H, 5.65.

Ethyl 2-chloro-3-methylene-2-(1-oxoethyl)nonanoate (73)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.26–1.34 (m, 6H), 1.31 (t, $J = 6.9$ Hz, 3H), 1.51 (quint, $J = 7.5$ Hz, 2H), 2.12 (t, $J = 8$ Hz, 2H), 2.38 (s, 3H), 4.29 (q, $J = 6.9$ Hz, 2H), 5.24 (s, 1H), 5.30 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 13.9, 22.5, 26.0, 28.2, 28.9, 31.6, 32.1, 62.9, 79.3, 115.8, 143.2, 166.6, 198.0; IR (cm^{-1}) 2958, 2931, 2866, 1746, 1723, 1640, 1619, 1466, 1445, 1350, 1239, 1181, 1096, 1059, 1025, 910, 847, 726; Anal. Calcd. for $\text{C}_{14}\text{H}_{23}\text{ClO}_3$: C, 61.19; H, 8.44. Found: C, 61.30; H, 8.67.

Diethyl 2-methyl-2-(1-phenylethenyl)malonate (75)

^1H NMR (500 MHz, CDCl_3) δ 1.21 (t, $J = 7.5$ Hz, 6H), 1.59 (s, 3H), 4.16–4.21 (m, 4H), 5.34 (s, 1H), 5.35 (s, 1H), 7.26–7.27 (m, 5H arom); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8 (2C), 22.2, 59.9, 61.6 (2C), 117.9 (2C), 127.3, 127.8 (2C), 128.2, 140.7, 147.7, 171.3 (2C); IR (cm^{-1}) 2983, 1727, 1493, 1445, 1376, 1246, 1219, 1104, 1019, 915, 862, 776, 700; Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.54; H, 7.30. Found: C, 69.47; H, 7.39.

Diethyl 2-methyl-2-(1-methyleneheptyl)malonate (76)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (m, 3H), 1.27 (t, $J = 7.5$ Hz, 6H), 1.25–1.35 (m, 4H), 1.45–1.52 (m, 4H), 1.59 (s, 3H), 2.08 (t, $J = 7.5$ Hz, 2H), 4.21 (q, $J = 7.5$ Hz, 4H), 4.99 (s, 1H), 5.07 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 14.0 (2C), 20.8, 22.6, 28.5, 29.2, 31.7, 32.7, 60.5, 61.3 (2C), 111.9, 147.0, 171.3 (2C); IR (cm^{-1}) 2956, 2931, 2860, 1729, 1642, 1465, 1376, 1250, 1100, 1021, 901, 862, 723; Anal. Calcd. for $\text{C}_{14}\text{H}_{25}\text{O}_4$: C, 67.57; H, 9.92; Found: C, 67.37; H, 9.89.

A representative procedure of the alkenylation of α -diketones (1.0 mmol scale) and physical properties of the alkenylated compounds

4-Hydroxy-3-(1-phenylethenyl)-3-penten-2-one (3)⁴

⁴ (a) Schulte, K. E.; Rucker, G.; Feldkamp, J. *Chem. Ber.* **1972**, *105*, 24–33. (b) Dybova, T. N.; Yurchenko, O. I.; Gritsai, N. V.; Buikliskii, V. D.; Mel'nikova, *Russ. J. Org.*

To phenylacetylene (5 mmol, 549 μ L, 511 mg, 5 equiv), *n*-BuLi (0.025 mmol, 1.51 M in hexane, 17 μ L, 2.5 mol%) was added at 0 °C. After 30 minutes, In(OTf)₃ (0.025 mmol, 14 mg, 2.5 mol%) and Et₃N (0.025 mmol, 3.5 μ L, 2.5 mol%) were added. Then 2,4-pentanedione (1 mmol, 103 μ L, 100 mg) was added at room temperature. The reaction mixture was stirred at 100 °C for 24 hours and then quenched with a pH 6.88 phosphate buffer solution. The aqueous layer was extracted with ether (3 times, 10 mL). The combined organic layers were dried over Na₂SO₄. Removal of solvent and following flash column chromatography (silica gel 10 g, eluent; hexane/ethyl acetate = 95/5) gave the alkenylated compound in 97 % yield (197 mg); ¹H NMR (400 MHz, CDCl₃) δ 1.98 (s, 6H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.90 (d, *J* = 1.6 Hz, 1H), 7.29–7.44 (m, 5H, arom); ¹³C NMR (100 MHz, CDCl₃) δ 23.5 (2C), 113.8, 118.3, 125.8 (2C), 128.3, 128.7 (2C), 139.6, 143.5, 191.2 (2C); IR (cm⁻¹) 3083, 1598, 1574, 1493, 1391, 1243, 910.

3-Methyl-4-methylene-3-(1-oxoethyl)-2-decanone (79)

¹H NMR (CDCl₃, 500 MHz) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.24–1.31 (m, 6H), 1.42–1.48 (m, 2H), 1.47 (s, 3H), 1.93 (brt, *J* = 7.4 Hz, 2H), 2.18 (s, 6H), 4.97 (s, 1H), 5.21 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 14.0, 18.3, 22.6, 27.3 (2C), 28.0, 29.1, 31.6, 32.7, 71.8, 114.3, 147.3, 208.0 (2C); IR (cm⁻¹) 2987, 1710, 1607, 1511, 1241, 1181, 1092, 1028, 835; Anal. Calcd. for C₁₄H₂₄O₂: C, 74.95; H, 10.78. Found: C, 74.78; H, 10.77.

2-(1-Oxoethyl)-2-(1-phenylethenyl)cyclopentanone (81)

¹H NMR (500 MHz, CDCl₃) δ 1.68–1.77 (m, 1H), 1.82–1.88 (m, 1H), 1.90–1.96 (m, 1H), 2.26–2.35 (m, 1H), 2.35 (s, 3H), 2.38–2.44 (m, 1H), 2.76 (ddd, *J* = 6.8 Hz, 8.8 Hz, 13.2 Hz, 1H), 5.43 (s, 1H), 5.58 (s, 1H), 7.15–7.17 (m, 2H), 7.29–7.32 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 18.6, 27.6, 32.2, 38.4, 73.6, 118.9, 127.1 (2C), 128.0, 128.5 (2C), 139.5, 145.9, 205.1, 213.2; IR (cm⁻¹) 2987, 1710, 1607, 1511, 1241, 1181, 1092, 1028, 835; Anal. Calcd. for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found: C, 78.86; H, 7.33.

2-(1-Oxoethyl)-2-(1-phenylethenyl)cyclohexanone (83)

Colorless solid, recrystallized from CHCl_3 . mp 99 °C; ^1H NMR (500 MHz, CDCl_3) δ 1.45–1.52 (m, 2H), 1.71–1.78 (m, 1H), 1.80–1.94 (m, 1H), 2.03–2.09 (m, 1H), 2.15–2.21 (m, 1H), 2.34 (s, 3H), 2.43 (ddd, $J = 5.2$ Hz, 5.2 Hz, 13.8 Hz, 1H), 2.81 (ddd, $J = 6.8$ Hz, 10.9 Hz, 13.8 Hz, 1H), 5.26 (s, 1H), 5.61 (s, 1H), 7.11–7.13 (m, 2H), 7.29–7.32 (m, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.0, 27.5, 28.0, 33.0, 40.3, 72.7, 121.5, 127.6 (2C), 127.8, 128.2 (2C), 139.6, 147.6, 207.8, 210.4; IR (cm^{-1}) 2987, 1710, 1607, 1511, 1241, 1181, 1092, 1028, 835; Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.31; H, 7.49. Found: C, 79.10; H, 7.46.

The physical properties of compounds **7**, **13**, **19**, **24**, **26**, **28**, **32**, **45**, **53**, **58**, **61**, **65**, and **78** have been described.⁵

⁵ Nakamura, M.; Endo, K.; Nakamura, E. *J. Am. Chem. Soc.* **2003**, *125*, 13002–13003.

2. Computational details

Methods.

All calculations were performed with a Gaussian 03 package.⁶ The density functional theory (DFT) method was employed using the B3LYP hybrid functional.⁷ Structures were optimized with a basis set consisting of the LANL2DZ basis set including a double-zeta valence basis set with the Hay and Wadt effective core potential (ECP) for indium and 6-31G(d) for the rest.^{8,9} Each stationary point was adequately characterized by normal coordinate analysis (no imaginary frequencies for an equilibrium structure and one imaginary frequency for a transition structure). The intrinsic reaction coordinate (IRC) analysis¹⁰ was carried out to confirm that stationary points are smoothly connected to each other.

⁶ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

⁷ (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G.; *Phys. Rev. B* **1988**, *37*, 785–789.

⁸ Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 299–310.

⁹ Hehre, W. J.; Radom, L.; Schleyer, P. v R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons, Inc.: New York, 1986. References cited therein.

¹⁰ (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363–368. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161. (c) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523–5527.

Model Reaction.

Figure S1 shows a reaction pathway of the conversion of an indium enolate-acetylene π -complex to a vinyndium product via a concerted transition structure. The π -complex, **CP**, consists of one molecule of acetylene and indium acetylacetonate possessing two fluorosulfonate ligands, a simplified model of trifluoromethanesulfonate ligand in the real system. The transition structure of the C–In and the C–C bond formation was located as **TS** (shown as A in the text) and confirmed by the normal coordinate analysis to have one adequate imaginary frequency. The structure of vinyl indium product was optimized as **PD**, where two carbonyl groups of the 1,3-diketone coordinate to the indium center. The smooth connection of these three stationary points was confirmed by the intrinsic reaction coordinate analysis.

Figure S1. Reaction coordinate and energy diagram of the addition of indium enolate to acetylene.

Energies and Cartesian coordinates of stationary points.

Indium enolate–Acetylene π -complex (CP).

SCF Done: E(RB+HF–LYP) = -1871.82463750 A.U. after 7 cycles

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	1.971387	0.810710	0.635976
2	6	0	2.408873	1.962043	0.250836
3	49	0	0.168011	-0.057783	0.182210
4	8	0	-0.355917	1.676832	-0.738760
5	6	0	0.361247	2.725897	-0.949272
6	6	0	1.680393	2.896688	-0.498842
7	6	0	3.821719	2.269468	0.674544
8	1	0	3.895909	2.208219	1.766345
9	1	0	4.152390	3.256657	0.345280
10	1	0	4.493877	1.506562	0.265233
11	6	0	-0.324141	3.807823	-1.738171

12	1	0	0.311320	4.682693	-1.890251
13	1	0	-1.241372	4.104976	-1.217172
14	1	0	-0.630677	3.403418	-2.709594
15	1	0	2.174325	3.826992	-0.749607
16	6	0	0.232036	0.212864	2.946318
17	6	0	-0.881437	0.591233	2.653343
18	1	0	1.209906	-0.120518	3.219988
19	1	0	-1.877580	0.897328	2.375679
20	9	0	-3.998520	-1.309046	0.391495
21	16	0	-3.067705	-0.107114	-0.129100
22	8	0	-3.414019	0.103974	-1.516440
23	8	0	-1.705242	-0.803343	0.060115
24	8	0	-3.248873	0.968280	0.844173
25	9	0	3.010704	-2.304298	-0.497147
26	16	0	1.413195	-2.436946	-0.555207
27	8	0	0.998943	-1.288436	-1.443994
28	8	0	0.977801	-1.997695	0.825922
29	8	0	1.132137	-3.783570	-0.975358

Transition structure of the carboindation (TS).

SCF Done: E(RB+HF-LYP) = -1871.79557402 A.U. after 1 cycles
 NImag=1 (-307.5639 cm⁻¹)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	1.459011	1.695103	0.096675
2	6	0	0.954904	2.846866	0.250751
3	49	0	0.235286	-0.027217	-0.069431
4	8	0	-0.837801	1.199606	-1.359114
5	6	0	-1.161691	2.376916	-1.016355
6	6	0	-0.400438	3.151749	-0.084534
7	6	0	1.849417	3.912412	0.829942
8	1	0	2.324224	3.533778	1.740899
9	1	0	1.315724	4.840957	1.045721
10	1	0	2.652752	4.125407	0.114555
11	6	0	-2.421619	2.928453	-1.623220
12	1	0	-2.631138	3.954958	-1.314227
13	1	0	-3.251193	2.271416	-1.335755
14	1	0	-2.343933	2.884198	-2.715092
15	1	0	-0.733740	4.169074	0.089243
16	6	0	-1.218285	2.017724	1.832370
17	6	0	-0.901338	0.809575	1.816706
18	1	0	-1.636821	2.963257	2.104704
19	1	0	-1.115245	-0.036558	2.461018
20	9	0	-2.363178	-2.008633	1.636581
21	16	0	-2.486976	-1.753670	0.024890
22	8	0	-3.075924	-2.955538	-0.517409
23	8	0	-0.990449	-1.647687	-0.308352
24	8	0	-3.164984	-0.468074	-0.074878
25	9	0	3.865170	-0.679033	-0.112363
26	16	0	2.542240	-1.582245	-0.184394
27	8	0	1.759136	-0.960032	-1.319542
28	8	0	1.773100	-1.178289	1.050657
29	8	0	2.988224	-2.944009	-0.316637

Cyclized product (PD).

SCF Done: E(RB+HF-LYP) = -1871.83778199 A.U. after 17 cycles

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-2.283768	-0.523564	-0.007743
2	6	0	-2.523593	-1.722104	0.111121
3	49	0	-0.050580	0.220509	0.282861
4	8	0	0.037133	-1.440582	-1.223663
5	6	0	-0.399243	-2.554915	-0.930682
6	6	0	-1.377282	-2.725632	0.229913
7	6	0	-3.932343	-2.236429	0.184923
8	1	0	-4.640868	-1.408519	0.130582
9	1	0	-4.072765	-2.788484	1.123168
10	1	0	-4.119593	-2.943854	-0.632896
11	6	0	0.045412	-3.773604	-1.679870
12	1	0	-0.817186	-4.311920	-2.091267
13	1	0	0.547891	-4.453709	-0.979294
14	1	0	0.737585	-3.494805	-2.475359
15	1	0	-1.768700	-3.744903	0.232645
16	6	0	-0.636590	-2.443329	1.567982
17	6	0	-0.063106	-1.268156	1.825555
18	1	0	-0.633424	-3.292116	2.251316
19	1	0	0.444946	-1.150519	2.781215
20	9	0	3.687642	0.517980	1.294327
21	16	0	3.092490	-0.017826	-0.112889
22	8	0	4.073250	0.330838	-1.116245
23	8	0	1.832556	0.860276	-0.202362
24	8	0	2.744940	-1.413047	0.139806
25	9	0	-2.792664	2.666019	-0.241279
26	16	0	-1.187609	2.715816	-0.274617
27	8	0	-0.821245	1.628167	-1.250880
28	8	0	-0.799256	2.142384	1.070663
29	8	0	-0.835099	4.078658	-0.575988