$GaCl_3$-Promoted Ethenylation of Silylated β-Dicarbonyl Compound with Silylethyne. Synthesis of Ethenylmalonate

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Supplementary Materials

^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Varian Mercury (400 MHz). Chemical shift values are given in ppm relative to internal Me_4Si. IR spectra were recorded on a JASCO FT/IR-410. MS spectra were taken with a JEOL JMS-DX303 or a JEOL JMS-AX500.

Ethyl 2-Ethenyl-2-methyl-3-oxohexanoate. Under an argon atmosphere, a solution of $GaCl_3$ (1.0 M, 2.0 mmol) in methylcyclohexane (2.0 mL) was added to a mixture of ethyl (*E*)-2-methyl-3-trimethylsilyloxy-2-hexenoate (122 mg, 0.5 mmol), trimethylsilylethyne (0.14 mL, 1.0 mmol), and *t*-butanol (0.25 mmol, 0.024 mL) in methylcyclohexane (2.0 mL) at room temperature. The mixture was stirred at 0 °C for 15 sec, when THF (5.0 mL) was added to dissolve the insoluble materials. Sulfuric acid (6 M, 5.0 mL) was added, and stirring was continued for 3 min at 40 °C. Then, the acid layer was removed, dried over $MgSO_4$, and concentrated. Then, the residue was dissolved in ether (2.0 mL), and conc. sulfuric acid (two drops) was added. Stirring was continued for 4 h at 35 °C to desilylate small amount of β-silylethenylated product formed. The solvent was removed, and the residue was purified by flash column chromatography to give ethyl 2-ethenyl-2-methyl-3-oxohexanoate (73 mg, 74%). Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.6 Hz), 1.27 (3H, t, J = 7.6 Hz), 1.47 (3H, s), 1.60 (2H, sixtet, J = 7.6 Hz), 2.44 (2H, t, J = 7.6 Hz), 4.21 (2H, q, J = 7.6 Hz), 5.17 (1H, d, J = 17.6 Hz), 5.30 (1H, d, J = 10.8 Hz), 6.35 (1H, dd, J = 17.6, 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.7, 14.1, 17.5, 19.0, 40.7, 61.6, 62.3, 116.7, 136.0, 171.5,

205.2. IR (neat) 2966, 1743, 1716, 1635, 1372, 1022, 928 cm^{-1}. MS (EI) m/z 198 (M^+, 0.4%), 128 (M^+-70, 77%), 71 (M^+-127, 100%). HRMS Calcd for $C_{11}H_{18}O_3$: 198.1256. Found: 198.1233.

Ethyl 2-Ethenyl-2-ethyl-3-oxohexanoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.80 (3H, t, *J* = 7.6 Hz), 0.87(3H, t, *J* =7.4 Hz), 1.27 (3H, t, *J* = 7.2 Hz), 1.59 (2H, m), 2.04 (2H, m), 2.37 (2H, m), 4.22 (2H, m), 5.10 (1H, d, *J* = 17.6 Hz), 5.33 (1H, d, *J* = 11.2 Hz), 6.39 (1H, dd, *J* = 17.6, 11.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 8.7, 13.7, 14.2, 17.5, 27.5, 41.4, 61.4, 66.6, 117.5, 134.4, 171.1, 204.2. IR (neat) 2970, 1742, 1715, 1632, 1233, 1127, 926 cm^{-1}. MS (EI) m/z 212 (M^+, 0.3%), 142 (M^+-70, 65%), 71 (M^+-141, 100%). HRMS Calcd for $C_{12}H_{20}O_3$: 212.1412. Found: 212.1420.

Ethyl 2-Ethenyl-3-oxo-2-propylhexanoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, m), 1.18 (5H, m), 1.58 (2H, m), 1.96 (2H, m), 2.36 (2H, m), 4.21 (2H, m), 5.09 (1H, d, *J* = 18.4 Hz), 5.31 (1H, d, *J* = 11.2 Hz), 6.35 (1H, dd, *J* = 18.4, 11.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.8, 14.2, 14.6, 17.6, 17.7, 36.7, 41.3, 61.4, 66.2, 117.3, 134.8, 171.2, 204.2. IR (neat) 2963, 1742, 1715, 1632, 1366, 1030, 926 cm^{-1}. MS (EI) m/z 226 (M^+, 5%), 71 (M^+- 155, 100%). HRMS Calcd for $C_{13}H_{22}O_3$: 226.1569. Found: 226.1575.

Ethyl 2-Butyl-2-ethenyl-3-oxooctanoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (6H,m), 1.10 (11H,m), 1.56 (3H, m), 1.98 (2H, ddt , *J* = 29.6, 4.8, 12.0 Hz), 2.37 (2H, m), 4.22 (2H, m), 5.09 (1H, d, *J* = 17.6 Hz), 5.31 (1H, d, *J* = 10.4 Hz), 6.40 (1H, dd, *J* = 17.6, 10.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 14.0, 14.2, 22.5, 23.2, 23.8, 26.4, 31.3, 34.2, 39.4, 61.4, 66.2, 117.3, 134.8, 171.2, 204.4. IR (neat) 2958, 1743, 1715, 1632, 925 cm^{-1}. MS (EI) m/z 268 (M^+, 0.3%), 170 (M^+-98, 90%), 99 (M^+-169, 100%). HRMS Calcd for $C_{16}H_{28}O_3$: 268.2038. Found: 268.2030.

Ethyl 2-Benzoyl-2-methyl-3-butenoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, d, *J* = 7.0 Hz), 1.65 (3H, s), 4.08 (2H, m), 4.80 (2H, m), 5.07 (1H, d, *J* = 17.6 Hz), 5.26 (1H, d, *J* = 10.4 Hz), 6.73 (1H, dd, *J* = 17.6, 10.4 Hz), 7.39 (2H, d), 7.50 (1H, m), 7.83 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.8, 23.4, 59.6, 61.6, 116.8, 128.2, 128.9, 132.5, 135.1, 137.3, 172.8. 195.1. IR (neat) 2984, 1738, 1688, 1598, 1448, 1259, 1120, 1019, 929 cm^{-1}. MS (EI) m/z 232 (M^+, 0.2%), 77 (M^+-155, 100%). HRMS Calcd for $C_{14}H_{16}O_3$: 232.1099. Found: 232.1093.

Ethyl 2-Methyl-2-(4-methylbenzoyl)-3-butenoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01 (3H, d, *J* = 7.2 Hz), 1.64 (3H, s), 2.38(3H, s), 4.09 (2H, q, *J* = 7.2 Hz), 5.05 (1H, d, *J* = 18.4 Hz), 5.24 (1H, d, *J* = 11.2 Hz), 6.72 (1H, dd, *J* = 18.4, 11.2 Hz) , 7.19 (2H, d, *J* = 8.0 Hz) , 7.73 (2H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.8, 21.7, 23.4, 59.5, 61.5, 116.6, 128.9, 129.0, 132.4, 137.5, 143.3, 173.0, 194.6. IR (neat) 2983, 1737, 1685, 1633, 1607, 1262, 1228, 1184, 1120, 928, 833 cm^{-1}. MS (EI) m/z 246 (M^+, 0.1%), 119 (M^+-127, 100%). HRMS Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1247.

Ethyl 2-(4-Fluorobenzoyl)-2-methyl-3-butenoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.01 (3H, t, *J* = 7.4 Hz), 1.64 (3H, s), 4.09 (2H, m), 5.04 (1H, d, *J* = 17.6 Hz), 5.26 (1H, d, *J* = 11.2 Hz), 6.72 (1H, dd, *J* = 17.6, 11.2 Hz), 7.07 (2H, m), 7.87 (2H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.5, 23.3, 59.4, 61.5, 115.5 (d, *J* = 21.6 Hz), 117.1, 131.6 (d, *J* = 3.5 Hz), 131.7 (d, *J* = 9.1 Hz), 137.5, 165.4 (d, *J* = 253.9 Hz), 173.1, 193.9. IR (neat) 2985, 1738, 1688, 1599, 1507, 1449, 1260, 1237, 1160, 1121, 930, 849 cm^{-1}. MS (EI) m/z 250 (M^+, 0.1%), 123 (M^+-127, 100%). HRMS Calcd for $C_{14}H_{15}O_3F$: 250.1005. Found: 250.1013.

Ethyl 2-Ethenyl-2,4-dimethyl-3-oxopentanoate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.08 (6H,d, *J* = 6.8 Hz), 1.28 (3H,t, *J* = 7.4 Hz), 1.49 (3H, s), 2.89 (1H, septet, *J* = 6.8 Hz), 4.21 (2H, m), 5.20 (1H, d, *J* = 17.6 Hz), 5.32 (1H, d, *J* = 11.2 Hz), 6.39 (1H, dd, *J* = 17.6, 11.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.2, 18.9, 20.3, 20.8, 37.5, 61.6, 62.6, 117.0, 135.6, 171.5, 209.8. IR (neat) 2979, 1743, 1716, 1634, 928 cm^{-1}. MS (EI) m/z 198 (M^+, 0.4%), 71 (M^+-127, 79%), 43 (M^+-155, 100%). HRMS Calcd for $C_{11}H_{18}O_3$: 198.1256. Found: 198.1261.

Ethyl 2-Ethenyl-3-oxo-2-cyclododecanecarboxylate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (2H, m), 1.27 (3H, m), 2.09 (2H, m), 1.60 (2H, sixtet, *J* = 7.6 Hz), 2.44 (2H, t, *J* = 7.6 Hz), 4.21 (2H, q, *J* = 7.6 Hz), 5.17 (1H, d, *J* = 17.6 Hz), 5.30 (1H, d, *J* = 10.8 Hz), 6.35 (1H, dd, *J* = 17.6, 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 19.5, 21.7, 22.3, 22.4, 22.8, 23.7, 26.6, 27.0, 32.4, 34.4, 61.4, 65.7, 116.2, 134.9, 171.1, 205.6. IR (neat) 2931, 1742, 1712, 1633, 1365, 1031, 922 cm^{-1}. MS (EI) m/z 280 (M^+, 35%), 124 (M^+-156, 100%). HRMS Calcd for $C_{17}H_{28}O_3$: 280.2038.

Found: 280.2030.

Diethyl Butylethenylmalonate. Under an argon atmosphere, a solution of $GaCl_3$ (1.0 M, 2.0 mmol) in methylcyclohexane (2.0 mL) was added to a mixture of diethyl butylmalonate (*E*)-silyl enol ether (144 mg, 0.5 mmol) and trimethylsilylethyne (0.14 mL, 1.0 mmol) in methylcyclohexane (2.0 mL) at room temperature. The mixture was stirred at room temperature for 5 min, when THF (5.0 mL) was added to dissolve the insoluble materials. Sulfuric acid (6 M, 5.0 mL) was added, and stirring was continued at r. t. for 5 min. Then, the acid layer was removed, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography to give diethyl butylethenylmalonate (111 mg, 92%). Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.4 Hz), 1.25 (10H, m), 2.03 (2H, m), 4.02 (2H, m), 5.17 (1H, d, *J* = 18.0 Hz), 5.29 (1H, d, *J* = 10.8 Hz), 6.34 (1H, dd, *J* = 18.0, 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 14.2, 23.1, 26.4, 34.7, 60.1, 61.4, 116.3, 134.8, 170.3. IR (neat) 2961, 1733, 1636, 926 cm^{-1}. MS (EI) m/z 242 (M^+, 1%), 169 (M^+-73, 100%). HRMS Calcd for $C_{13}H_{22}O_4$: 242.1518. Found: 242.1510.

Diethyl *i*-Butylethenylmalonate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (6H, d, *J* = 6.8 Hz), 1.25 (6H, t, *J* = 7.0 Hz), 1.66 (1H, 7tet, *J* = 6.8 Hz), 2.04 (2H, d, *J* = 6.0 Hz), 4.19 (2H, q, *J* = 7.0 Hz), 5.15 (1H, d, *J* = 17.2 Hz), 5.28 (3H, d, *J* = 10.8 Hz), 6.44 (1H, dd, *J* = 17.2, 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 23.8, 24.6, 44.0, 59.5, 61.3, 116.2, 135.3, 170.6. IR (neat) 2960, 1733, 1041, 924 cm^{-1}. MS (EI) m/z 242 (M^+, 0.3%), 169 (M^+-73, 100%). HRMS Calcd for $C_{13}H_{22}O_4$: 242.1518. Found: 242.1511.

Diethyl *sec*-Butylethenylmalonate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.93 (3H, t, *J* = 7.0 Hz), 0.96 (3H, d, *J* = 7.2 Hz), 1.26 (6H, t, *J* = 7.0 Hz), 1.68 (1H, m), 2.15 (1H, m), 4.21 (4H, dq, *J* = 7.0, 1.4 Hz), 5.10 (1H, d, *J* = 17.6 Hz), 5.30 (1H, d, *J* = 10.8 Hz), 6.24 (1H, dd, *J* = 17.6, 10.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.7, 14.2, 14.9, 25.8, 40.8, 61.2, 65.1, 116.8, 134.1, 170.0. IR (neat) 2974, 1733, 1050, 923 cm^{-1}. MS (EI) m/z 242 (M^+, 0.1%), 140 (M^+-102, 100%). HRMS Calcd for $C_{13}H_{22}O_4$: 242.1518. Found: 242.1479.

Dipropyl Ethenylmalonate. See reference 7 for the reaction conditions. Pale yellow oil. ^{1}H-NMR

(400MHz, $CDCl_3$) δ 0.94 (6H, t, J = 7.8 Hz), 1.67 (4H, sixtet, J = 7.2 Hz), 4.05 (1H, d, J = 8.8 Hz), 4.12 (4H, m), 5.29 (1H, d, J = 16.0 Hz), 5.32 (1H, d, J = 10.4 Hz), 6.07 (1H, ddd, J = 16.0, 10.4, 8.8 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ 10.4, 22.0, 56.6, 67.2, 120.1, 129.8, 167.8. IR (neat) 2970, 1737, 1643, 1293, 1194, 931 cm^{-1}. MS (EI) m/z 214 (M^+, 1%), 86 (M^+-128, 100%). HRMS Calcd for $C_{11}H_{18}O_4$: 214.1205. Found: 214.1198.

Dipropyl (*E*)-(2-Trimethylsilylethenyl)malonate. Pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.08 (9H, s), 0.93 (6H, t, *J* = 7.2 Hz), 1.66 (4H, sixtet, *J* = 7.2 Hz), 4.06 (1H, d, *J* = 8.0 Hz), 4.11 (4H, dt, *J* = 7.2, 2.8 Hz), 5.93 (1H, d, *J* = 18.4 Hz), 6.19 (1H, dd, *J* = 18.4, 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ -1.3, 14.2, 59.0, 61.6, 136.0, 137.0, 167.7. IR (neat) 2967, 1737, 1250, 1147, 1059, 991, 930 cm^{-1}. MS (EI) m/z 286 (M^+, 0.3%), 73 (M^+-243, 100%). HRMS Calcd for $C_{14}H_{26}O_4Si$: 286.1600. Found: 286.1606.

Dibutyl Ethenylmalonate. Pale yellow oil. ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.93 (6H, t, J = 7.4 Hz), 1.37 (4H, m), 1.63 (4H. m), 4.03 (1H, d, J = 8.0 Hz), 4.15 (4H, m), 5.28 (1H, d, J = 16.8 Hz), 5.32 (1H, d, J = 10.0 Hz), 6.06 (1H, ddd, J = 16.8, 10.0, 8.0 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ 13.8, 19.1, 30.6, 56.6, 65.5, 120.1, 129.8, 167.7. IR (neat) 2961, 1734, 1307, 1253, 1217, 1192, 1157 cm^{-1}. MS (EI) m/z 242 (M^+, 1%), 86 (M^+-156, 100%). HRMS Calcd for $C_{13}H_{22}O_4$: 242.1518. Found: 242.1557.

Dibutyl (*E*)-(2-Trimethylsilylethenyl)malonate. Pale yellow oil. ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.08 (9H, s), 0.93 (6H, t, J = 7.2 Hz), 1.37 (4H, m), 1.62 (4H, m), 4.05 (1H, dd, J = 8.0, 1.2 Hz), 4.15 (4H, m), 5.93 (1H, d, J = 17.6 Hz), 6.19 (1H, dd, J = 17.6, 8.0 Hz). ^{13}C-NMR (100MHz, $CDCl_3$) δ -1.3, 13.8, 19.1, 30.6, 59.1, 65.4, 136.1, 137.0, 167.8. IR (neat) 2959, 1736, 1250, 1147, 1023, 988 cm^{-1}. MS (EI) m/z 314 (M^+, 1%), 213 (M^+-101, 100%). HRMS Calcd for $C_{16}H_{30}O_4Si_1$: 314.1913. Found: 314.1900.

Deuteration experiment. Under an argon atmosphere, 1.0 M $GaCl_3$ (2.0 mmol) in methylcyclohexane (2.0 mL) was added to a methylcyclohexane (2.0 mL) solution of ethyl (*E*)-2-ethyl-3-trimethylsilyloxy-2-hexanoate (129 mg, 0.5 mmol), trimethylsilylethyne (0.14 mL, 1.0

mmol), and THF (20 μL, 0.25 mmol) at room temperature. After stirred for 15 sec at 0 °C, THF (2.0 mL) was added, and stirring was continued for another 5 min. Then, 12 M DCl in D_2O was added, and the mixture was stirred for 10 min at the temperature. The acid layer was removed, and the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography to give ethyl 2-ethenyl-2-ethyl-3-oxohexanoate (81 mg, 81%, *cis*-proton: 98%-*d*, *trans*-proton: 83%-*d*), and ethyl 2-(2-trimethylsilylethenyl)-2-ethyl-3-oxohexanoate (16 mg, 11%, 100%-*d*). The deuteration ratio was determined by ^{1}H-NMR.