One-Step Ethynylation of Silyl Enol Ether with Chlorosilylethyne

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Supplementary Materials

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury NMR (400 MHz) with Me_4Si as an internal standard. IR spectra were measured on a JASCO FT/IR-400. Mass spectra were recorded on a JEOL JMS-DX-303 or a JEOL JMS-AX-500.

2,2-Dimetyl-1-phenyl-3-butyn-1-one Under an argon atmosphere, a solution of 1.0 M $GaCl_3$ (4 mmol) in methylcyclohexane (4 mL) was added to a mixture of 2-methyl-1-phenyl-1-trimethylsilyloxy-1-propene (220 mg, 1.0 mmol) and chlorotrimethylsilylethyne (132 mg, 1.0 mmol) in methylcyclohexane (4 mL) at –40 °C. The mixture was stirred for 5 min at –40 °C, when MeOH (2 mL) was added. After being stirred 5 min at the temperature, 6 M sulfuric acid (14 mL) was added, and stirring was continued for 5 h at room temperature. The organic materials were extracted twice with diethyl ether. The combined organic layers were washed with brine, and dried over $MgSO_4$. The extract was passed through short silica gel column (hexane/diethyl ether = 10), and concentrated. The residue was purified by flash column chromatography (hexane / ethyl acetate = 400) to give 2,2-dimetyl-1-phenyl-3-butyn-1-one (126 mg, 73%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.59 (6H, s), 2.45 (1H, s), 7.43 (2H, t, *J* = 7.2 Hz), 7.53 (1H, t, *J* = 7.2 Hz), 8.27 (2H, d, *J* = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.0, 41.5, 73.1, 87.8, 128.9, 129.7, 132.5, 134.7, 198.4. IR (neat) 3298, 3069, 2988, 2936, 2874, 2108, 1685 cm^{-1}. MS (EI) *m/z* 172 (M^+, 13%), 105 (M^+–C_5H_7, 100%). HRMS Calcd for $C_{12}H_{12}O$: 172.0889. Found: 172.0881.

2-Butyl-2-ethyl-1-phenyl-3-butyn-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 0.98 (3H, t, *J* = 7.6 Hz), 1.24-1.42 (4H, m), 1.52-1.88 (2H, m), 1.88-1.94 (2H, m), 2.46 (1H, s), 7.41 (2H, t, *J* = 8.0 Hz), 7.51 (1H, t, *J* = 9.6 Hz), 8.15 (2H, t, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 9.5, 14.1, 23.1, 27.1, 31.9, 38.2, 51.7, 75.2, 86.3, 127.7, 129.2, 132.1, 136.8, 200.2. IR (neat) 3305, 3060, 2959, 2931, 2873, 2108, 1682, 1597, 1579 cm^{-1}. MS (EI) *m/z* 228 (M^+, 0.4%), 213 (M^+–CH_3, 2%), 199 (M^+–C_2H_5, 2%) 171 (M^+–C_4H_9, 2%) 105 (M^+–C_9H_{15}, 100%). HRMS Calcd for $C_{16}H_{20}O$: 228.1513. Found: 228.1492.

2,4,4-Trimethyl-5-hexyn-3-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.14 (6H, d, *J* = 6.8 Hz), 1.38 (6H, s), 2.31 (1H, s), 3.44 (1H, septet, *J* = 6.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.3, 26.2, 36.3, 43.6, 71.2, 87.1. IR ($CDCl_3$) 3305, 2980, 2936, 2875, 2110, 1715 cm^{-1}. MS (EI) *m/z* 138 (M^+, 1.4%), 123 (M^+–CH_3, 3.8%), 95 (M^+–C_3H_7, 2%) 71 (M^+–C_5H_7, 85%) 43 (M^+–C_6H_7O, 100%). HRMS Calcd for C_9H_7O: 138.1045. Found: 138.1011.

3,3,5-Tributyl-1-nonyn-4-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.85-0.92 (12H, m), 1.18-1.40 (20H, m), 1.63-1.78 (4H, m), 2.38 (1H, s) 3.12 (1H, quintet, 5.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 23.0, 27.2, 29.6, 30.6, 37.5, 48.5, 52.8, 75.6, 85.8, 212.2. IR (neat) 3301, 3266, 2957, 2932, 2861, 2112, 1710, 1466 cm^{-1}. MS (EI) *m/z* 306 (M^+, 3%), 263 (M^+–C_3H_7, 3%) 180 (M^+-C_9H_{18}, 16%) 155 (M^+–$C_{11}H_{19}$, 15%) 127 (M^+–$C_{12}H_{19}O$ 43%) 85 (M^+–$C_{16}H_{29}$, 63%) 71 (M^+–$C_{17}H_{31}$, 100%). HRMS Calcd for $C_{21}H_{38}O$: 306.2923. Found: 306.2931.

2-Ethynyl-2,2,6-trimethylcyclohexanone ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.35 (3H, s),

1.41 (3H, s), 1.53-1.69 (3H, m), 1.79-1.86 (1H, m), 2.12-2.27 (2H, m), 2.28 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.0, 25.9, 27.5, 28.4, 41.1, 41.5, 43.6, 46.5, 71.5, 87.0, 211.3. IR (neat) 3306, 2976, 2935, 2869. 2110, 1710, 1454 cm^{-1}. MS (EI) *m/z* 164 (M^+, 10%), 149 (M^+–CH_3, 41%), 121 (M^+–C_3H_7, 100%) HRMS Calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1199.

Cyclohexyl 1-ethynylcyclohexyl ketone ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.35 (3H, s), 1.41 (3H, s), 1.53-1.69 (3H, m), 1.79-1.86 (1H, m), 2.12-2.27 (2H, m), 2.28 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.0, 25.9, 27.5, 28.4, 41.1, 41.5, 43.6, 46.5, 71.5, 87.0, 211.3. IR (neat) 3306, 2976, 2935, 2869. 2110, 1710, 1454 cm^{-1}. MS (EI) *m/z* 164 (M^+, 10%), 149 (M^+–CH_3, 41%), 121 (M^+–C_3H_7, 100%) HRMS Calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1199.

2-Pentyl-1-phenyl-3-butyn-1-one[1] Under an argon atmosphere, a solution of 1.0 M $GaCl_3$ (2 mmol) in methylcyclohexane (2 mL) was added to a mixture of (*Z*)-1-phenyl-1-trimethylsilyloxy-1-heptene (131 mg, 0.5 mmol) and chlorotrimethylsilylethyne (132 mg, 1.0 mmol) in a mixed solvent of methylcyclohexane (18 mL) and chlorobenzene (2 mL) at –40 °C. The mixture was stirred for 30 sec, when MeOH (2 mL) was added. After being stirred for 5 min at –40 °C, 6 M sulfuric acid (7 mL) was added, and the solution was warmed to room temperature. Stirring was continued for 1 h, and the organic materials were extracted twice with diethyl ether. The combined organic layers were washed with brine, and dried over $MgSO_4$. The extract was passed through short silica gel column (hexane/diethyl ether = 10), and concentrated. The residue was purified by flash column chromatography (Kanto Chemical, silica gel 60 N (spherical, neutral), 40-100 μm, hexane/ethyl acetate = 400) at -78 °C to give 2-pentyl-1-phenyl-3-butyn-1-one (91 mg, 85%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.2 Hz), 1.29-1.39 (4H, m), 1.40-1.50 (1H, m), 1.50-1.60 (1H, m), 1.80-1.90 (2H, m), 2.29 (1H, d, *J* = 2.8 Hz), 4.13 (1H, ddd, *J* = 2.8, 6.0, 8.4 Hz), 7.48 (2H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 6.8 Hz), 8.05 (2H, d, *J* = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.0, 31.5, 31.6, 40.2, 73.2, 81.7, 128.5, 158.7, 133.2, 135.3, 195.4. IR (neat) 3303, 2954, 2925, 2855, 2236, 1696 cm^{-1}. MS (EI) *m/z* 214 (M^+, 1%), 229 (M^+–C_4H_9, 4%), 105 (M^+–C_8H_{13}, 100%). HRMS Calcd for $C_{15}H_{18}O$: 214.1357. Found: 214.1331.

2-Octyl-1-phenyl-3-butyn-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.20-1.60 (12H, m), 1.80-1.96 (2H, m), 2.29 (1H, d, *J* = 2.8 Hz), 4.13 (1H, ddd, *J* = 2.8, 6.0, 8.4 Hz), 7.48 (2H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 8.4 Hz), 8.05 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 27.3, 29.3, 29.4, 29.5, 31.6, 31.9, 40.2, 73.2, 81.7, 128.5, 128.7, 133.2, 135.3, 195.4. IR (neat) 3309, 2953, 2925, 2855, 2114, 1696, 1596, 1448 cm^{-1}. MS (EI) *m/z* 256 (M^+, 0.4%), 157 (M^+–C_7H_{15}, 5%), 105 (M^+–$C_{11}H_{19}$, 100%) HRMS Calcd for $C_{18}H_{24}O$: 256.1827. Found: 256.1819.

2-Hexyl-1-(4-methylphenyl)-3-butyn-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 6.8 Hz), 1.20-1.60 (10H, m), 1.78-1.86 (2H, m), 2.27 (1H, d, *J* = 2.4Hz), 2.42 (3H, s), 4.1 (1H, ddd, *J* = 2.8, 6.4, 8.8 Hz), 7.27 (2H, d, *J* = 8.8 Hz), 7.94 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.2, 21.8, 22.8, 27.3, 29.2, 29.4, 31.6, 31.9, 40.0, 73.0, 81.9, 128.8, 129.2, 132.7, 144.1, 195.0. IR (neat) 3309, 2954, 2927, 2856, 2116, 1691, 1607, 1458 cm^{-1}. MS (EI) *m/z* 256 (M^+, 0.6%), 171 (M^+–C_6H_{13}, 1.3%), 119 (M^+–$C_{10}H_{17}$, 100%) HRMS Calcd for $C_{18}H_{24}O$: 270.1827. Found: 270.1737.

2-Methyl-1-phenyl-3-butyn-1-one[2] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.51 (3H, d, *J* = 7.2 Hz), 2.28 (1H, d, *J* = 2.4 Hz), 4.20 (1H, dq, *J* = 2.8, 6.8 Hz), 7.48 (2H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 7.2 Hz), 8.07 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.1, 34.3, 72.8, 82.8, 128.5, 128.9, 133.4, 135.0, 195.3. IR (neat) 3295, 3063, 2990, 2938, 2875, 2112, 1694, 1596, 1583, 1491 cm^{-1}. MS (EI) *m/z* 158 (M^+, 6%), 105 (M^+–C_4H_5, 100%), 77 (M^+–C_5H_5O, 100%) HRMS Calcd for $C_{11}H_{10}O$: 158.0732. Found: 158.0735.

1-(4-Methoxyphenyl)-2-methyl-3-butyn-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.49 (3H, d, *J* = 7.2 Hz), 2.26 (1H, d, *J* = 2.8 Hz), 3.88 (3H, s), 4.16 (1H, dq, *J* = 2.8, 6.8 Hz), 6.95 (2H, d, *J* = 8.8 Hz), 8.06 (2H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.1, 33.9, 55.5, 72.3, 83.1, 113.7, 127.9, 131.1, 163.5, 193.7 IR (neat) 3291, 2987, 2938, 2841, 2108, 1684, 1601, 1575, 1510, 1455 cm^{-1}. MS (EI) *m/z* 188 (M^+, 2.3%), 135 (M^+–C_4H_5, 100%), 107 (M^+–C_5H_5O, 10%). HRMS Calcd for $C_{12}H_{12}O_2$: 188.0837. Found: 188.0820.

1-(4-Fluorophenyl)-2-methyl-3-butyn-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.50 (3H, d, *J* = 6.8 Hz), 2.30 (1H, d, *J* = 2.8 Hz), 4.15 (1H, dq, *J* = 2.8, 6.8 Hz), 7.15 (2H, d, *J* = 8.8 Hz), 8.11 (2H, d, *J* = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.8, 34.2, 72.9, 82.5, 115.6 (*J* = 88 Hz), 131.2, 131.5 (*J* = 36 Hz), 165.6 (*J* = 212 Hz), 193.6. IR (neat) 3303, 3081, 2991, 2941, 2118, 1694, 1599, 1509 cm^{-1}. MS (EI) *m/z* 176 (M^+, 42%), 123 (M^+–C_4H_5, 100%). HRMS Calcd for $C_{11}H_9OF$: 176.0637. Found: 176.0669.

3-Chloro-2-pentyl-1-phenyl-3-buten-1-one Under an argon atmosphere, a solution of 1.0 M $GaCl_3$ (2 mmol) in methylcyclohexane (2 mL) was added to a mixture of (*Z*)-1-phenyl-1-trimethylsilyloxy-1-heptene (131 mg, 0.5 mmol) and chlorotrimethylsilylethyne (132 mg, 1.0 mmol) in methylcyclohexane (2 mL) at –40 °C. The mixture was stirred for 5 min at –40 °C, when 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added, and stirring was continued for 5 min at room temperature to dissolve the insoluble materials. The mixture was cooled to –40 °C, and 6 M sulfuric acid (7 mL) was added. After warmed to room temperature, the mixture was stirred for 1 h. The organic materials were extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate = 400) to give 3-chloro-2-pentyl-1-phenyl-3-buten-1-one (63 mg, 50%), 2-Pentyl-1-phenyl-3-butyn-1-one (9 mg, 8%) and 3-Methylene-2,4-dipentyl-1,5-diphenyl-1,5-pentanedione (5 mg, 5%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.4 Hz), 1.24-1.36 (6H, m), 1.84-1.90 (1H, m), 1.92-2.00 (1H, m), 4.24 (1H, t, *J* = 3.2 Hz), 5.32 (1H, d, *J* = 2.0 Hz), 5.36 (1H, d, *J* = 2.0 Hz), 7.47 (2H, t, *J* = 6.4 Hz), 7.58 (1H, t, *J* = 7.6 Hz), 7.99 (2H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.1, 30.6, 31.8, 55.7, 115.2, 128.3, 128.4, 133.1, 136.3, 140.1, 197.3. IR (neat) 3357, 2955, 2927, 2857, 1687, 1625, 1448 cm^{-1}. MS (EI) *m/z* 250 (M^+, 1%), 215 (M^+–Cl, 3%), 105 (M^+–$C_6H_{14}Cl$, 100%). HRMS Calcd for $C_{15}H_{19}OCl$: 250.1124. Found: 252.1128.

3-Chloro-2-octyl-1-phenyl-3-buten-1-one ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 6.8 Hz), 1.15-1.36 (12H, m), 1.80-1.92 (1H, m), 1.92-2.40 (1H, m), 4.24 (1H, t, *J* = 6.8 Hz), 5.32 (1H, d, *J* = 2.0 Hz), 5.37 (1H, d, *J* = 2.0 Hz), 7.47 (2H, t, *J* = 7.6 Hz), 7.58 (1H, t, *J* = 7.6 Hz), 7.99 (2H, d, *J* = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 27.4, 29.3, 29.5, 29.6, 30.5, 30.6, 31.9, 55.7, 115.3, 128.4, 128.5, 133.1, 136.4, 140.1, 197.3. IR (neat) 3062, 2925, 2855, 1687, 1625, 1597, 1580, 1448 cm^{-1}. MS (EI) *m/z* 292 (M^+, 0.2%), 257 (M^+–Cl, 1.8%), 105 (M^+–$C_{11}H_{20}Cl$, 100%). HRMS Calcd for $C_{18}H_{25}OCl$: 292.1594. Found: 292.1599.

3-Methylene-2,4-dipentyl-1,5-diphenyl-1,5-pentanedione Under an argon atmosphere, a solution of 1.0 M $GaCl_3$ (2 mmol) in methylcyclohexane (2 mL) was added to a mixture of 1-phenyl-1-trimethylsilyloxy-1-heptene (131 mg, 0.5 mmol) and chlorotriethylsilylethyne (174 mg, 1.0 mmol) in methylcyclohexane (2 mL) at 0 °C. The mixture was stirred for 5 min at room temperature, when MeOH (2 mL) was added to dissolve the insoluble materials. Then 6 M sulfuric acid (14 mL) was added. After warmed to room temperature, the mixture was stirred for 1 h. The organic materials were extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (hexane/ethyl acetate = 300) to give (2*RS*,4*RS*)-3-methylene-2,4-dipentyl-1,5-diphenyl-1,5-pentanedione (35 mg,

36%) and the (2*RS*,4*SR*)-isomer (27 mg, 27%). The former isomer gave two peaks in 1 : 1 ratio by chiral HPLC (chiralcel OD, hexane/*i*-PrOH = 99). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.65 (6H, t, *J* = 6.8 Hz), 1.03-1.13 (12H, m), 1.41-1.47 (2H, m), 1.76-1.85 (2H, m), 4.17 (2H, t, *J* = 7.6 Hz), 5.27 (2H, s), 7.44 (4H, t, *J* = 7.6 Hz), 7.55 (2H, t, *J* = 7.2 Hz), 7.93 (4H, d, *J* = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.4, 27.5, 31.7, 32.3, 52.1, 117.6, 128.3, 128.5, 132.8, 137.2, 144.2, 200.5. IR (neat) 3346, 2955, 2928, 2857, 1681, 1596, 1580, 1447 cm^{-1}. MS (EI) *m/z* 404 (M^+, 1%), 333 (M^+–C_5H_{11}, 3%), 299 (M^+–$C_{13}H_{17}O$, 18%), 105 (M^+–$C_{21}H_{31}O$, 100%). HRMS Calcd for $C_{28}H_{36}O_2$: 404.2715. Found: 404.2762.

(2*RS*,4*SR*)-3-Methylene-2,4-dipentyl-1,5-diphenyl-1,5-pentanedione ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.84 (6H, t, *J* = 6.4 Hz), 1.20-1.30 (12H, m), 1.57-1.66 (2H, m), 1.92-2.20 (2H, m), 4.11 (2H, dd, *J* = 6.0, 8.0 Hz), 5.29 (2H, s), 7.51 (4H, t, *J* = 7.6 Hz), 7.62 (2H, t, *J* = 7.2 Hz), 8.00 (4H, d, *J* = 7.6). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 27.8, 31.9, 32.5, 52.6, 117.5, 128.2, 132.6, 137.2, 144.2, 200.5. IR (neat) 3343, 2955, 2928, 2857, 1681, 1596, 1580, 1447 cm^{-1}. MS (EI) *m/z* 404 (M^+, 0.5%), 333 (M^+–C_5H_{11}, 12%), 299 (M^+–$C_{13}H_{17}O$, 3%), 105 (M^+–$C_{21}H_{31}O$, 100%). HRMS Calcd for $C_{28}H_{36}O_2$: 404.2715. Found: 404.2705.

Deuteration experiment. Under an argon atmosphere, a solution of 1.0 M $GaCl_3$ (2 mmol) in methylcyclohexane (2 mL) was added to a mixture of (*Z*)-1-phenyl-1-trimethylsilyloxy-1-heptene (131 mg, 0.5 mmol) and chlorotrimethylsilylethyne (132 mg, 1.0 mmol) in a mixed solvent of methylcyclohexane (18 mL) and chlorobenzene (2 mL) at –40 °C. The mixture was stirred for 30 sec, when MeOD (2 mL) was added. After being stirred 5 min at –40 °C, 6 M D_2SO_4 in D_2O (7 mL) was added, and the solution was warmed to room temperature. Stirring was continued for 1 h, and the organic materials were extracted twice with diethyl ether. The combined organic layers were washed with brine, and dried over $MgSO_4$. The extract was passed through short silica gel column (hexane/diethyl ether = 10), and concentrated. The residue was purified by flash column chromatography (Kanto Chemical, silica gel 60 N (spherical, neutral), 40-100 μm, hexane/ethyl acetate = 400) at -78 °C to give 4-deutero-2-pentyl-1-phenyl-3-butyn-1-one **7**-*d* (99 mg, 92%). The deuteration ratio (98%-*d*) was determind by ^{1}H-NMR.

Reference

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