General Methods.
The IR spectra were recorded on a JASCO FTIR-4100 Type A spectrometer using a NaCl cell. The $^1$H NMR and $^{13}$C NMR spectra were recorded using a JNM-EX 400 (400 MHz and 100 MHz) spectrometer. Chemical shifts were reported in ppm relative to CHCl$_3$ in CDCl$_3$ for $^1$H NMR ($\delta = 7.26$) and $^{13}$C NMR ($\delta = 77.0$) and CHD$_2$OH in CD$_3$OD for $^1$H NMR ($\delta = 3.35$) and $^{13}$C NMR ($\delta = 49.3$). Splitting patterns for $^1$H NMR were designated as “s, d, t, q, m, dt, dd, and td”. These symbols indicate “singlet, doublet, triplet, quartet, multiplet, doubletriplet, doubletdoublet, and tripletdoublet” respectively. All commercially obtained reagents were employed as received.

Analytical TLC was carried out using pre-coated silica gel plates (Wako TLC Silicagel 70F 254). Wakogel 60N 63-212 μm was used for column chromatography. Reversed-phase high performance liquid chromatography (HPLC) was carried out using HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm).

Ketone 3a and 4a
To a solution of 1-hexyne (0.109 mL, 0.957 mmol) in THF (5.0 mL) was added nBuLi (0.601 mL, 0.957 mmol, 1.59 M) at 0 °C to give 1a. After 30 minutes, a solution of 2 (111 mg, 0.319 mmol) in THF (3.0 mL) was added. The mixture was stirred for 10 minutes at 0 °C, quenched with 0.390 mL of 4.00 M HCl in 1,4-dioxane then excess of H$_2$O, extracted with EtOAc, washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (116 mg, 98%) of dichloro ketone 3a and unsaturated ketone 4a with ratio 85:15. For further purification, the partial (ca. 10.0 mg) of mixture products were separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H$_2$O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3a as a colorless oil and 4a as a colorless oil.

3a: IR (neat) 3019, 2960, 2936, 2214, 1726, 1683, 1647, 756, 699, 669 cm$^{-1}$; $^1$H NMR (CD$_3$OD, 400 MHz) δ 0.94 (3H, t, $J = 7.3$ Hz), 1.46-1.81 (9H, m), 2.06-2.18 (1H, m), 2.48 (2H, t, $J = 6.8$ Hz), 3.51 (2H, t, $J = 5.8$ Hz), 4.35 (1H, td, $J = 9.2$, 2.4 Hz), 4.46 (1H, d, $J = 8.8$ Hz), 4.49 (2H, s), 7.24-7.33 (5H, m); $^{13}$C NMR (CD$_3$OD, 100 MHz) δ 13.7, 19.2, 22.9, 23.4, 29.9, 30.7, 34.4, 61.6, 66.9, 70.8, 73.9, 78.8, 100.2, 128.6, 128.8, 129.3, 139.8, 179.8; HRMS (ESI) m/z: [M + Na]$^+$; Calcd for C$_{20}$H$_{26}$O$_2$Cl$_2$Na 391.1202; Found 391.1201.

4a: IR (neat) 3065, 3019, 2959, 2936, 2865, 2214, 1716, 1649, 1617, 1216, 759, 698, 667 cm$^{-1}$; $^1$H NMR (CD$_3$OD, 400 MHz) δ 0.94 (3H, t, $J = 7.3$ Hz), 1.43-1.50 (2H, m), 1.46-1.66 (6H, m), 2.45-2.52 (4H, m), 3.51 (2H, t, $J = 6.3$ Hz), 4.49 (2H, s), 7.25-7.32 (5H, m), 7.46 (1H, t, $J = 7.3$ Hz); $^{13}$C NMR (CD$_3$OD, 100 MHz) δ 13.8, 19.2, 23.0, 25.5, 30.3, 30.6, 30.8, 70.7, 73.9, 78.5, 98.6, 128.6, 128.8, 129.3, 136.1, 139.7, 149.3, 173.0; HRMS (ESI) m/z: [M + Na]$^+$; Calcd for
Ketone 3b
To a solution of 2 (157 mg, 0.451 mmol) in THF (5.0 mL) was added nBuLi (1b) (0.427 mL, 0.680 mmol, 1.59 M) at −20 °C. The mixture was stirred for 30 minutes, quenched with 0.560 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (155 mg, 98%) of dichloro ketone 3b and unsaturated ketone 4b. For further purification to obtain pure 3b, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 µm, φ8.0×250 mm, elution with H2O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3b as a colorless oil: IR (neat) 3063, 3029, 2957, 2933, 2868, 1729, 1495, 1454, 1103, 735, 698, 664 cm−1; 1H NMR (CD3OD, 400 MHz) δ 0.91 (3H, t, J = 7.3 Hz), 1.31-1.38 (2H, m), 1.53-1.79 (7H, m), 2.08-2.10 (1H, m), 2.64-2.75 (2H, m), 3.50 (2H, t, J = 5.8 Hz), 4.32 (1H, td, J = 9.2, 2.4 Hz), 4.49 (2H, s), 4.51 (1H, d, J = 8.7 Hz), 7.24-7.33 (5H, m); 13C NMR (CD3OD, 100 MHz) δ 14.1, 23.1, 23.3, 26.4, 29.9, 34.6, 40.7, 61.5, 64.3, 70.9, 73.9, 128.6, 128.8, 129.3, 139.7, 203.7; HRMS (ESI) m/z: [M + Na]+; Calcd for C18H26O2Cl2Na 367.1202; Found 367.1202.

Ketone 3c
To a solution of 2 (50.0 mg, 0.144 mmol) in THF (2.0 mL) was added PhLi (1c) (0.120 mL, 0.216 mmol, 1.80 M) at −20 °C. The mixture was stirred for 30 minutes, quenched with 0.200 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (49.0 mg, 94%) of dichloro ketone 3c and unsaturated ketone 4c. For further purification to obtain pure 3c, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 µm, φ8.0×250 mm, elution with H2O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3c as a colorless oil: IR (neat) 3062, 3030, 2941, 2864, 1695, 1596, 1580, 1449, 1100, 738, 688, 663 cm−1; 1H NMR (CD3OD, 400 MHz) δ 1.27-1.93 (5H, m), 2.24-2.30 (1H, m), 3.53 (2H, t, J = 5.8 Hz), 4.50 (2H, s), 4.51 (1H, td, J = 9.2, 2.4 Hz), 5.53 (1H, d, J = 9.7 Hz), 7.24-7.33 (5H, m), 7.54 (2H, dd, J = 8.7, 7.8 Hz), 7.64-7.68 (1H, m), 8.05 (2H, dd, J = 7.3, 1.4 Hz); 13C NMR (CD3OD, 100 MHz) δ 23.3, 30.0, 34.5, 58.5, 61.4, 70.9, 73.9, 127.7, 128.6, 128.8, 129.3, 130.0, 135.3, 136.0, 139.7, 193.2; HRMS (ESI) m/z: [M + Na]+; Calcd for C18H20O2Cl2Na 378.0889; Found 378.0888.
Ketone 3d
To a solution of 2 (114 mg, 0.327 mmol) in THF (4.0 mL) was added CH₃MgBr (1d) (0.163 mL, 0.491 mmol, 3.00 M) at 0 °C. The mixture was stirred for 2 hours, quenched with 0.460 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (97.0 mg, 98%) of dichloro ketone 3d and unsaturated ketone 4d. For further purification to obtain pure 3d, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H₂O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3d as a colorless oil: IR (neat) 3031, 2940, 2866, 1721, 1495, 1454, 1100, 714, 698 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 1.53-1.80 (5H, m), 2.07-2.17 (1H, m), 2.31 (3H, s), 3.50 (2H, t, J = 5.8 Hz), 4.33 (1H, td, J = 9.2, 2.4 Hz), 4.49 (2H, s), 4.50 (1H, d, J = 7.3 Hz), 7.26-7.34 (5H, m); ¹³C NMR (CD₃OD, 100 MHz) δ 23.4, 26.9, 29.9, 34.6, 61.6, 65.4, 70.9, 73.9, 128.6, 128.8, 129.3, 139.7, 201.4; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₁₅H₂₀O₂Cl₂Na 325.0732; Found 325.0728.

Ketone 3e
To a solution of 2 (131 mg, 0.376 mmol) in THF (4.0 mL) was added VinylMgCl (1e) (0.427 mL, 0.680 mmol, 1.35 M) at 0 °C. The mixture was stirred for 2 hours, quenched with 0.460 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (115 mg, 97%) of dichloro ketone 3e and unsaturated ketone 4e. For further purification to obtain pure 3e, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H₂O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3e as a colorless oil: IR (neat) 3063, 3029, 2930, 2866, 1725, 1558, 1455, 1275, 1101, 714, 700, 667 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.61-1.81 (5H, m), 2.13-2.17 (1H, m), 3.50 (2H, t, J = 5.8 Hz), 4.31 (1H, td, J = 9.2, 2.4 Hz), 4.49 (2H, s), 4.51 (1H, d, J = 8.8 Hz), 5.96 (1H, dd, J = 10.4, 0.9 Hz), 6.45 (1H, dd, J = 17.5, 0.9 Hz), 6.62 (1H, dd, J = 17.5, 10.2 Hz), 7.26-7.35 (5H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 22.2, 29.1, 33.6, 59.7, 61.5, 69.8, 72.9, 127.5, 127.6, 128.3, 131.5, 132.1, 138.4, 190.7; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₁₆H₂ₐO₂Cl₂Na 337.0732; Found 337.0728.
Ketone **3f**

To a solution of 2 (110 mg, 0.315 mmol) in THF (5.0 mL) was added nC₅H₁₁MgBr (1f) (0.236 mL, 0.473 mmol, 2.00 M) at 0 °C. The mixture was stirred for 2 hours, quenched with 0.390 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (109 mg, 96%) of dichloro ketone **3f** and unsaturated ketone **4f**. For further purification to obtain pure **3f**, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H₂O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford **3f** as a colorless oil: IR (neat) 3064, 3031, 2931, 2862, 1730, 1558, 1455, 1274, 1101, 739, 698, 663 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 0.90 (3H, t, J = 6.8 Hz), 1.27-1.36 (4H, m), 1.53-1.79 (7H, m), 2.07-2.16 (1H, m), 2.63-2.74 (2H, m), 3.51 (2H, t, J = 5.8 Hz), 4.32 (1H, td, J = 9.2, 2.4 Hz), 4.49 (2H, s), 4.51 (1H, d, J = 9.3 Hz), 7.23-7.33 (5H, m); ¹³C NMR (CD₃OD, 100 MHz) δ 14.3, 23.3, 23.5, 24.1, 29.9, 32.2, 34.6, 40.9, 61.5, 64.3, 70.9, 73.9, 128.6, 128.8, 129.3, 139.7, 203.7; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₁₉H₂₈O₂Cl₂Na 381.1358; Found 381.1353.

Ketone **3g**

To a solution of 2 (111 mg, 0.319 mmol) in THF (4.0 mL) was added PhMgBr (1g) (0.159 mL, 0.478 mmol, 3.00 M) at 0 °C. The mixture was stirred for 4 hours, quenched with 0.390 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (111 mg, 96%) of dichloro ketone **3g** and unsaturated ketone **4g**. For further purification to obtain pure **3g**, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H₂O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford **3g** as a colorless oil: IR (neat) 3063, 3030, 2939, 2865, 1695, 1596, 1580, 1449, 1273, 1100, 746, 688, 663 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 1.27-1.93 (5H, m), 2.24-2.30 (1H, m), 3.53 (2H, t, J = 5.8 Hz), 4.50 (2H, s), 4.51 (1H, td, J = 9.2, 2.4 Hz), 5.53 (1H, d, J = 9.7 Hz), 7.24-7.33 (5H, m), 7.54 (2H, dd, J = 8.7, 7.8 Hz), 7.64-7.68 (1H, m), 8.05 (2H, dd, J = 7.3, 1.4 Hz); ¹³C NMR (CD₃OD, 100 MHz) δ 23.3, 30.0, 34.5, 58.5, 61.4, 70.9, 73.9, 127.7, 128.6, 128.8, 129.3, 130.0, 135.3, 136.0, 139.7, 193.2; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₂₀H₂₉O₂Cl₂Na 387.0889; Found 387.0888.

Ketone **3h** and **4h**
To a solution of 2 (64.2 mg, 0.184 mmol) in THF (2.0 mL) was added HC≡CMgCl (1h) (0.553 mL, 0.277 mmol, 0.500 M) at 0 °C. The mixture was stirred for 4 hours, quenched with 0.230 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (52.0 mg, 90%) of dichloro ketone 3h and unsaturated ketone 4h with ratio 35:65. For further purification, the partial (ca. 10.0 mg) of mixture products were separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H2O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 3h as a colorless oil and 4h as a colorless oil.

3h: IR (neat) 3273, 3066, 2921, 2851, 2098, 1697, 1660, 1587, 1259, 1101, 909, 735, 698 cm⁻¹; ¹H NMR (CDCl3, 400 MHz) δ 1.55-1.80 (5H, m), 2.10-2.16 (1H, m), 3.41 (1H, s), 3.50 (2H, t, J = 5.8 Hz), 4.31-4.32 (2H, m), 4.51 (2H, s), 7.25-7.35 (5H, m); ¹³C NMR (CDCl3, 100 MHz) δ 22.1, 28.9, 33.3, 59.5, 64.8, 69.8, 72.9, 78.1, 82.5, 127.5, 127.6, 128.3, 138.4, 177.7; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C16H18O2Cl2Na 335.0576; Found 335.0581.

4h: IR (neat) 3251, 3064, 2925, 2855, 2096, 1717, 1659, 1614, 1455, 1233, 1101, 883, 733, 698 cm⁻¹; ¹H NMR (CDCl3, 400 MHz) δ 1.67-1.70 (4H, m), 2.53 (2H, q, J = 7.3 Hz), 3.34 (1H, s), 3.51 (2H, t, J = 5.8 Hz), 4.51 (2H, s), 7.26-7.35 (5H, m), 7.46 (1H, t, J = 7.3 Hz); ¹³C NMR (CDCl3, 100 MHz) δ 24.3, 29.3, 29.8, 69.6, 72.9, 78.5, 81.3, 127.5, 127.5, 128.3, 134.9, 138.3, 149.3, 171.1; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C16H17O2ClNa 299.0809; Found 299.0801.

Amide 6

To a solution of 2 (182 mg, 0.524 mmol) in THF (6.0 mL) was added iPrMgBr (1i) (1.07 mL, 0.786 mmol, 0.730 M) at 0 °C. The mixture was stirred for 4 hours, quenched with 0.650 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give unsaturated amide 6 (135 mg, 0.487 mmol, 93%) as a colorless oil: IR (neat) 3063, 3029, 2936, 2857, 1664, 1633, 1495, 1455, 1412, 1379, 1273, 1104, 997, 746, 737, 698 cm⁻¹; ¹H NMR (CDCl3, 400 MHz) δ 1.54-1.60 (2H, m), 1.61-1.67 (2H, m), 2.25 (2H, q, J = 7.3 Hz), 3.23 (3H, s), 3.48 (2H, t, J = 6.3 Hz), 3.68 (3H, s), 4.49 (2H, s), 6.39 (1H, d, J = 15.6 Hz), 6.97 (1H, dt, J = 15.7, 6.8 Hz), 7.26-7.34 (5H, m); ¹³C NMR (CDCl3, 100 MHz) δ 24.8, 29.1, 32.1, 32.7, 61.5, 69.8, 72.7, 71.8, 127.4, 127.5, 128.2, 138.3, 147.4, 166.8; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C16H23NO3Na 300.1567; Found 300.1567.

Ketone 8a

To a solution of 1-hexyne (0.083 mL, 0.722 mmol) in THF (4.0 mL) was added nBuLi (0.453 mL,
0.722 mmol, 1.59 M) at 0 °C to give 1a. The mixture was cooled at −40 °C and added cold solution of 7 (84.0 mg, 0.241 mmol) in THF (3.0 mL), stirred for 10 minutes at −40 °C, quenched with 0.310 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (84.0 mg, 95%) of dichloro ketone 8a and unsaturated ketone 4a. For further purification to obtain pure 8a, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 µm, φ8.0×250 mm, elution with H2O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 8a as a colorless oil: IR (neat) 3030, 2956, 2933, 2863, 2211, 1697, 1671, 1653, 1102, 771, 736, 698 cm⁻¹; ¹H NMR (CD3OD, 400 MHz) δ 0.75 (3H, t, J = 7.3 Hz), 1.25-1.46 (8H, m), 1.71 (2H, q, J = 7.3 Hz), 2.29 (2H, t, J = 6.8 Hz), 3.32 (2H, t, J = 5.8 Hz), 4.30 (2H, s), 4.49 (1H, td, J = 7.1, 3.4 Hz), 4.70 (1H, d, J = 3.4 Hz), 7.26-7.33 (5H, m); ¹³C NMR (CD3OD, 100 MHz) δ 13.7, 19.3, 22.9, 24.2, 29.9, 30.6, 36.6, 62.6, 70.8, 70.9, 73.9, 79.3, 101.1, 128.6, 128.8, 129.3, 139.7, 180.4; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C20H26O2Cl2Na 391.1202; Found 391.1203.

Ketone 8b

To a solution of 7 (54.0 mg, 0.155 mmol) in THF (2.0 mL) was added nBuLi (1b) (0.145 mL, 0.232 mmol, 1.59 M) at −40 °C. The mixture was stirred for 30 minutes, quenched with 0.200 mL 4.00 M HCl in 1,4-dioxane then excess of H2O, extracted with EtOAc, washed with brine, dried over Na2SO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (51.0 mg, 95%) of dichloro ketone 8b and unsaturated ketone 4b. For further purification to obtain pure 8b, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 µm, φ8.0×250 mm, elution with H2O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 8b as a colorless oil: IR (neat) 3063, 3030, 2956, 2933, 2865, 1717, 1540, 1455, 1397, 1100, 772, 737, 698 cm⁻¹; ¹H NMR (CD3OD, 400 MHz) δ 0.91 (3H, t, J = 7.3 Hz), 1.28-1.37 (2H, m), 1.49-1.66 (6H, m), 1.86 (2H, q, J = 6.8 Hz), 2.71 (2H, t, J = 7.3 Hz), 3.50 (2H, t, J = 5.8 Hz), 4.48 (2H, s), 4.54 (1H, td, J = 7.1, 3.4 Hz), 4.77 (1H, d, J = 3.4 Hz), 7.24-7.33 (5H, m); ¹³C NMR (CD3OD, 100 MHz) δ 13.7, 19.3, 22.9, 24.2, 29.9, 30.6, 36.6, 62.6, 70.8, 70.9, 73.9, 79.3, 101.1, 128.6, 128.8, 129.3, 139.7, 205.1; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C18H26O2Cl2Na 367.1202; Found 367.1203.

Ketone 4c
To a solution of 7 (87.0 mg, 0.249 mmol) in THF (3.0 mL) was added PhLi (1c) (0.207 mL, 0.373 mmol, 1.80 M) at −20 °C. The mixture was stirred for 30 minutes, quenched with 0.310 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give unsaturated ketone 4c (65.0 mg, 0.197 mmol, 78%) as a colorless oil: IR (neat) 3063, 3031, 2941, 2861, 1718, 1688, 1670, 1449, 1273, 1177, 713, 696, 666 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 1.34-1.66 (4H, m), 2.49 (2H, td, J = 7.3, 6.8 Hz), 3.50 (2H, t, J = 5.8 Hz), 4.47 (2H, s), 6.70 (1H, t, J = 7.3 Hz), 7.24-7.30 (5H, m), 7.47 (2H, dd, J = 8.7, 7.8 Hz), 7.57-7.61 (1H, m), 7.65 (2H, dd, J = 7.3, 1.4 Hz); ¹³C NMR (CD₃OD, 100 MHz) δ 25.5, 30.3, 30.5, 70.8, 73.9, 128.6, 128.8, 129.3, 129.6, 130.3, 133.7, 134.1, 138.2, 139.7, 147.1, 191.9; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₂₀H₂₁O₂ClNa 351.1122; Found 351.1123.

Ketone 8d
To a solution of 7 (88.0 mg, 0.253 mmol) in THF (3.0 mL) was added CH₃MgBr (1d) (0.126 mL, 0.378 mmol, 3.00 M) at −20 °C. The mixture was stirred for 2 hours, quenched with 0.310 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (73.0 mg, 95%) of dichloro ketone 8d and unsaturated ketone 4d. For further purification to obtain pure 8d, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 μm, φ8.0×250 mm, elution with H₂O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 8d as a colorless oil: IR (neat) 3032, 2937, 2862, 1717, 1652, 1616, 1455, 1274, 1101, 714, 699 cm⁻¹; ¹H NMR (CD₃OD, 400 MHz) δ 1.40-1.55 (4H, m), 1.77-1.88 (2H, m), 2.24 (3H, s), 3.41 (2H, t, J = 5.8 Hz), 4.39 (2H, s), 4.46 (1H, td, J = 9.2, 2.4 Hz), 4.69 (1H, d, J = 2.9 Hz), 7.16-7.23 (5H, m); ¹³C NMR (CD₃OD, 100 MHz) δ 24.2, 27.9, 29.9, 36.7, 62.8, 69.9, 70.9, 73.9, 128.6, 128.8, 129.3, 139.7, 202.9; HRMS (ESI) m/z: [M + Na]⁺; Calcd for C₁₅H₂₀O₂Cl₂Na 325.0733; Found 325.0732.

Ketone 4e
To a solution of 7 (88.0 mg, 0.253 mmol) in THF (3.0 mL) was added VinylMgCl (1e) (0.146 mL, 0.308 mmol, 2.10 M) at 0 °C. The mixture was stirred for 2 hours, quenched with 0.250 mL 4.00 M HCl in 1,4-dioxane then excess of H₂O, extracted with EtOAc, washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give unsaturated ketone 4e (52.0 mg, 0.187 mmol, 90%) as a colorless oil: IR (neat) 3029, 2932, 2862, 1717, 1652, 1616, 1455, 1274, 1101, 714,
700 cm\(^{-1}\); \(^1\)H NMR (CD\(_3\)OD, 400 MHz) \(\delta\) 1.60-1.70 (4H, m), 2.42-2.52 (2H, m), 3.51 (2H, t, \(J = 5.8\) Hz), 4.48 (2H, s), 5.84 (1H, dd, \(J = 10.4, 1.9\) Hz), 6.31 (1H, dd, \(J = 16.8, 1.9\) Hz), 7.11 (1H, dd, \(J = 17.5, 10.2\) Hz), 7.18 (1H, t, \(J = 6.8\) Hz), 7.25-7.32 (5H, m); \(^{13}\)C NMR (CD\(_3\)OD, 100 MHz) \(\delta\) 25.4, 30.3, 30.6, 70.8, 73.9, 128.6, 128.8, 129.3, 130.7, 131.9, 135.2, 139.7, 145.1, 185.7; HRMS (ESI) m/z: [M + Na]\(^+\); Calcd for C\(_{16}\)H\(_{19}\)O\(_2\)ClNa 301.0965; Found 301.0959.

**Ketone 8f**

To a solution of 7 (83.0 mg, 0.238 mmol) in THF (3.0 mL) was added \(n\)C\(_5\)H\(_{11}\)MgBr (1f) (0.178 mL, 0.358 mmol, 2.00 M) at –20 °C. The mixture was stirred for 2 hours, quenched with 0.290 mL 4.00 M HCl in 1,4-dioxane then excess of H\(_2\)O, extracted with EtOAc, washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated \(in\ vacuo\). The residue was purified by silica gel column chromatography (EtOAc:Hexane = 2:98) to give a mixture (77.0 mg, 90%) of dichloro ketone 8f and unsaturated ketone 4f. For further purification to obtain pure 8f, a partial (ca. 10.0 mg) of the mixture was separated by HPLC (NOMURA CHEMICAL, DEVELOSIL C30-UG 5 \(\mu\)m, φ8.0×250 mm, elution with H\(_2\)O:Acetonitrile = 80:20 to 0:100 gradiently for 90 min, 2 mL/min) to afford 8f as a colorless oil: IR (neat) 3068, 3030, 2931, 2859, 1717, 1558, 1455, 1362, 1100, 772, 735, 697 cm\(^{-1}\); \(^1\)H NMR (CD\(_3\)OD, 400 MHz) \(\delta\) 0.90 (3H, t, \(J = 6.8\) Hz), 1.27-1.34 (4H, m), 1.48-1.66 (6H, m), 1.87 (2H, q, \(J = 6.8\) Hz), 2.70 (2H, t, \(J = 6.8\) Hz), 3.50 (2H, t, \(J = 5.8\) Hz), 4.48 (2H, s), 4.53 (1H, td, \(J = 6.8, 3.4\) Hz), 4.76 (1H, d, \(J = 2.9\) Hz), 7.24-7.33 (5H, m); \(^{13}\)C NMR (CD\(_3\)OD, 100 MHz) \(\delta\) 14.2, 23.5, 24.1, 24.2, 29.9, 32.2, 36.6, 40.9, 63.0, 69.6, 70.9, 73.9, 128.6, 128.8, 129.3, 139.8, 205.0; HRMS (ESI) m/z: [M + Na]\(^+\); Calcd for C\(_{19}\)H\(_{28}\)O\(_2\)Cl\(_2\)Na 381.1358; Found 381.1358.

**Ketone 4g**

To a solution of 7 (103 mg, 0.295 mmol) in THF (3.0 mL) was added PhMgBr (1g) (0.147 mL, 0.442 mmol, 3.00 M) at –20 °C. The mixture was stirred for 2 hours, quenched with 0.360 mL 4.00 M HCl in 1,4-dioxane then excess of H\(_2\)O, extracted with EtOAc, washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated \(in\ vacuo\). The residue was purified by silica gel chromatography (EtOAc:Hexane = 2:98) to give unsaturated ketone 4f (62.0 mg, 0.189 mmol, 74%) as a colorless oil: IR (neat) 3063, 3030, 2931, 2859, 1717, 1558, 1455, 1362, 1100, 772, 735, 697 cm\(^{-1}\); \(^1\)H NMR (CD\(_3\)OD, 400 MHz) \(\delta\) 1.34-1.66 (4H, m), 2.49 (2H, q, \(J = 6.8\) Hz), 3.50 (2H, t, \(J = 5.8\) Hz), 4.47 (2H, s), 6.70 (1H, t, \(J = 7.3\) Hz), 7.24-7.30 (5H, m), 7.47 (2H, dd, \(J = 8.7, 7.8\) Hz), 7.57-7.61 (1H, m), 7.65 (2H, dd, \(J = 7.3, 1.4\) Hz); \(^{13}\)C NMR (CD\(_3\)OD, 100 MHz) \(\delta\) 25.5, 30.3, 30.5, 70.8, 73.9, 128.6, 128.8, 129.3, 129.6, 130.3, 133.7, 134.1, 138.2, 139.7, 147.1,
191.9; HRMS (ESI) m/z: [M + Na]$^+$; Calcd for C$_{20}$H$_{21}$O$_2$ClNa 351.1122; Found 351.1123.