**Sequential Mukaiyama–Michael reaction induced by carbon acids**

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**Electronic Supplementary Information**

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### 1. General and materials

All reactions were carried out under Ar atmosphere. Melting points were uncorrected. **1**H NMR spectra were recorded on a Bruker DPX400 (400 MHz) spectrometer or a Bruker Avance III 400 Nanobay spectrometer. Chemical shifts are reported in parts per million (ppm) using residual CHCl₃ (7.26 ppm) as an internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sex = sextet, m = multiplet), integration and coupling constants. **13**C NMR spectra were recorded on a Bruker DPX400 (100 MHz) spectrometer or a Bruker Avance III 400 Nanobay spectrometer (100 MHz), using broadband proton decoupling. Chemical shifts are reported in ppm using the middle resonance of CDCl₃ (77.01 ppm) as an internal standard. **19**F NMR spectra were taken on a Bruker Avance III 400 Nanobay spectrometer (376 MHz), and chemical shifts were reported in ppm using trifluoromethylbenzene (0 ppm) as a standard. Mass spectra were recorded by a Micromass LCT spectrometer (ESI-TOF). Column chromatography was performed on neutral silica gel (Kanto Chemical, 75-150 μm). MPLC was performed using 40 × 300 mm i. d. pre-packed column (silica gel, 50 μm) with UV and RI detectors. Size exclusion chromatography (SEC) measurements for polymers were performed at 40 °C using a Jasco GPC-900 system equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min⁻¹. The number average molecular weight (**Mn**SEC) and dispersity (**Mw**/**Mn**) were determined using poly(methyl methacrylate) standards with the **Mw** (**Mw**/**Mn**)s of 1.25 × 10⁶ g mol⁻¹ (1.07), 6.59 × 10⁵ g mol⁻¹ (1.02), 3.003 × 10⁵ g mol⁻¹ (1.02), 1.385 × 10⁵ g mol⁻¹ (1.05), 6.015 × 10⁴ g mol⁻¹ (1.03), 3.053 × 10⁴ g mol⁻¹ (1.02), and 1.155 × 10⁴ g mol⁻¹ (1.04), 4.90 × 10³ g mol⁻¹ (1.10), 2.87 × 10³ g mol⁻¹ (1.06), and 1.43 × 10³ g mol⁻¹ (1.15). Tf₂CH₂ was provided from Central Glass Co., Ltd. and it can be also prepared by the Waller’s procedure in the laboratory.¹
2. Mukaiyama–Michael reaction of α,β-unsaturated lactones

Ethyl 2-(2-oxo-oxochroman-4-yl)acetate (6a)

![Chemical structure of 6a](image)

To a solution of 2H-chromen-2-one 3a (72.7 mg, 0.497 mmol) and triple carbon acid 1a (5.3 mg, 5.3 μmol) in CH₂Cl₂ (1.5 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol) in CH₂Cl₂ (0.5 mL) was slowly added at −78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched with saturated NaHCO₃ aqueous solution (15 mL), then it was extracted with Et₂O (15 mL x 3) and washed with brine (15 mL). The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the adduct² in 91% yield (106 mg, 0.453 mmol). Colorless crystals (from EtOAc/hexane); Mp. 50.0-52.5 °C; IR (neat) ν 1762, 1715, 1145, 766 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (3H, t, J = 7.1 Hz), 2.56 (1H, dd, J = 16.1, 7.9 Hz), 2.65 (1H, dd, J = 16.1, 6.8 Hz), 2.82 (1H, dd, J = 16.1, 4.6 Hz), 2.90 (1H, dd, J = 16.1, 5.8 Hz), 3.53-3.62 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 7.06 (1H, d, J = 8.1 Hz), 7.11 (1H, td, J = 7.5, 1.0 Hz), 7.22-7.32 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 31.5, 34.5, 39.0, 50.0, 117.2, 124.7, 125.0, 127.4, 128.9, 151.3, 167.5, 170.8; MS (ESI-TOF) m/z 257 [M+Na]⁺; HRMS calcd for C₁₃H₁₄NaO₃ [M+Na]⁺, 257.0790; found, 257.0788. Anal. Calcd for C₁₃H₁₄O₃: C, 66.66; H, 6.02. Found: C, 66.81; H, 5.99.

Ethyl 2-(5-iodo-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-yl)acetate

![Chemical structure of 6a](image)

According to the synthetic procedure for 6a, this compound was obtained in 96% yield (187 mg, 0.484 mmol) by the reaction of 5-iodo-6-phenyl-2H-pyran-2-one ³ 3f (150 mg, 0.503 mmol) with tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (127 mg, 0.628 mmol) in the presence of triple carbon acid 1a (5.1 mg, 5.1 μmol) in CH₂Cl₂ (2.0 mL) for 30 min at −78 °C and the following column chromatography on silica gel (hexane/EtOAc = 5 : 1). Pale yellow oil; IR (neat) ν 2980, 1775, 1729, 1152, 1113, 1042, 1022, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (3H, t, J = 7.2 Hz), 2.53 (1H, dd, J = 16.6, 9.8 Hz), 2.78 (1H, dd, J = 16.6, 3.6 Hz), 2.87 (1H, dd, J = 16.4, 7.2 Hz), 3.08 (1H, dd, J = 16.4, 2.6 Hz), 3.24-3.32 (1H, m), 4.19 (2H, q, J = 7.2 Hz), 7.35-7.42 (3H, m), 7.52-7.57 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 34.0, 36.5, 40.9, 61.2, 75.3, 128.1, 129.3, 129.8, 134.4, 150.9, 166.3, 170.4; MS (ESI-TOF) m/z 387 [M+H]⁺; HRMS calcd for C₁₅H₁₃IO₄ [M+H]⁺, 387.0093; found, 387.0090. Anal. Calcd for C₁₅H₁₃IO₄: C, 46.65; H, 3.92. Found: C, 46.90; H, 4.04.
3. Mukaiyama–Michael/Mukaiyama aldol reaction

**Ethyl 2-((3R*,4S*)-3-(1-((tert-butyldimethylsilyl)oxy)cyclohexyl)-2-oxochroman-4-yl)acetate (7a)**

![Chemical Structure](image)

To a solution of 2H-chromen-2-one 3a (146 mg, 0.999 mmol) and triple carbon acid 1a (10 mg, 10 μmol) in CH₂Cl₂ (3.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (243 mg, 1.20 mmol) in CH₂Cl₂ (0.5 mL) was added at −78 °C. After being stirred for 30 min, a solution of cyclohexanone (199 mg, 2.03 mmol) in CH₂Cl₂ (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the resulting mixture was quenched with saturated NaHCO₃ aqueous solution (15 mL), extracted with Et₂O (15 mL x 3), and washed with brine (15 mL). The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. Thus obtained residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20 : 1) to give the adduct in 99% yield (443 mg, 0.993 mmol). Its structure was also confirmed by an X-ray crystallographic analysis. Colorless crystals (from EtOAc); Mp. 90.0-91.5 °C; IR (ATR) ν 2928, 1750, 1732, 1151, 773 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ –0.44 (3H, s), 0.05 (3H, s), 0.70 (9H, s), 1.20 (3H, t, J = 7.1 Hz), 1.28-1.38 (1H, m), 1.38-1.49 (2H, m), 1.49-1.62 (3H, m), 1.65-1.75 (2H, m), 1.93-2.06 (2H, m), 2.48 (1H, dd, J = 15.9, 7.4 Hz), 2.54 (1H, dd, J = 15.9, 7.4 Hz), 3.10 (1H, s), 3.64 (1H, t, J = 7.4 Hz), 4.10 (2H, q, J = 7.1 Hz), 6.94 (1H, d, J = 8.0 Hz), 7.04 (1H, t, J = 7.4 Hz), 7.16-7.23 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ –1.6, −0.7, 15.1, 19.2, 24.1, 24.6, 26.3, 26.9, 33.9, 37.7, 38.9, 42.8, 52.0, 61.8, 78.5, 118.0, 125.4, 125.7, 128.6, 129.2, 152.3, 169.1, 171.9; MS (ESI-TOF) m/z 469 [M+Na]⁺; HRMS calcd for C₂₅H₃₆NaO₃Si [M+Na]⁺, 469.2386; found, 469.2383. Anal. Calcd for C₂₅H₃₆O₃Si: C, 67.23; H, 8.58. Found: C, 66.98; H, 8.62.

**Ethyl 2-((3R*,4S*)-3-(1-((tert-butyldimethylsilyl)oxy)cyclopentyl)-2-oxochroman-4-yl)acetate (8a)**

![Chemical Structure](image)

According to the synthetic procedure for 7a, this compound was obtained in 87% yield (375 mg, 0.867 mmol) by the reaction of 2H-chromen-2-one 3a (146 mg, 0.999 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (243 mg, 1.20 mmol), and cyclopentanone (171 mg, 2.03 mmol) in the presence of triple carbon acid 1a (10 mg, 10 μmol) in CH₂Cl₂ (4.0 mL) at −78 °C for 30 min and the following flash column chromatography on silica gel (hexane/EtOAc = 20 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2951, 2851, 1760, 1737, 1220, 1168, 1062, 837, 777 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ −0.02 (3H, s), 0.07 (3H, s), 0.80 (9H, s), 1.11-1.19 (1H, m), 1.19 (3H, t, J = 7.2 Hz), 1.34-1.44 (1H, m), 1.45-1.81 (5H, m), 2.03-2.15 (1H, m), 2.48 (1H, dd, J = 15.6, 8.0 Hz), 2.55 (1H, dd, J = 15.6, 6.9 Hz), 2.99
(1H, d, J = 0.9 Hz), 3.90 (1H, m), 4.08 (2H, q, J = 7.2 Hz), 6.96 (1H, d, J = 8.0 Hz), 7.07 (1H, t, J = 7.5 Hz), 7.17-7.25 (2H, m); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) –2.78. –2.73, 14.1, 18.3, 22.1, 23.5, 25.9, 33.6, 37.78, 37.82, 42.0, 54.3, 60.8, 85.7, 116.7, 124.5, 124.7, 128.4, 128.5, 151.1, 168.1, 170.7; MS (ESI-TOF) \(m/z\) 433 [M+H]; HRMS calcd for C\(_{23}\)H\(_{37}\)O\(_5\)Si [M+H]\(^+\), 433.2410; found, 433.2417. Anal. Calcd for C\(_{23}\)H\(_{36}\)O\(_5\)Si: C, 66.63; H, 8.39. Found: C, 66.42; H, 8.45.

Ethyl 2-((3R*,4S*)-3-(2-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-y1)acetate (9a)

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{H} & \quad \text{O} & \quad \text{O} \\
\text{TBSO} & \quad \text{C} & \quad \text{EtO}_2 & \quad \\
\text{9a} & & & \\
\end{align*}
\]

According to the synthetic procedure for 7a, this compound was obtained in 97% yield (396 mg, 0.974 mmol) by the reaction of 2\(H\)-chromen-2-one 3a (146 mg, 0.999 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (247 mg, 1.22 mmol), and acetone (118 mg, 2.03 mmol) in the presence of triple carbon acid 1a (10 mg, 10 \(\mu\)mol) in CH\(_2\)Cl\(_2\) (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 15 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) \(\nu\) 2936, 2853, 1764, 1673, 1253, 1221, 1162, 1038, 838, 779 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) –0.14 (3H, s), 0.02 (3H, s), 0.77 (9H, s), 1.11 (3H, s), 1.20 (3H, t, J = 7.2 Hz), 1.40 (3H, s), 2.48 (1H, dd, \(J = 15.9, 7.2\) Hz), 2.56 (1H, dd, \(J = 15.9, 7.2\) Hz), 2.80 (1H, d, \(J = 0.9\) Hz), 3.85 (1H, brt, \(J = 7.2\) Hz), 4.08 (2H, q, \(J = 7.2\) Hz), 7.07-7.09 (1H, m), 7.12-7.15 (1H, m), 7.18-7.22 (2H, m); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) –2.5, –2.2, 14.1, 18.0, 25.7, 28.4, 29.8, 33.4, 42.0, 57.1, 60.8, 74.9, 116.8, 124.4, 124.6, 128.0, 128.4, 151.2, 167.7, 170.8; MS (ESI-TOF) \(m/z\) 407 [M+H]; HRMS calcd for C\(_{25}\)H\(_{38}\)O\(_5\)Si [M+H]\(^+\), 407.2254; found, 407.2258. Anal. Calcd for C\(_{23}\)H\(_{36}\)O\(_5\)Si: C, 64.99; H, 8.43. Found: C, 64.94; H, 8.48.

Ethyl 2-((3R*,4S*)-3-((1R*,2S*)-1-((tert-butyldimethylsilyl)oxy)-2-methylcyclohexyl)-2-oxochroman-4-y1)acetate (3,1’-anti-10a) and ethyl 2-((3R*,4S*)-3-((1S*,2S*)-1-((tert-butyldimethylsilyl)oxy)-2-methylcyclohexyl)-2-oxochroman-4-y1)acetate (3,1’-syn-10a)

\[
\begin{align*}
\text{TBSO} & \quad \text{Me} & \quad \text{O} & \quad \text{O} \\
\text{EtO}_2 & \quad \\
\text{3,1’-anti-10a} & & & \\
\text{3,1’-syn-10a} & & & \\
\end{align*}
\]

According to the synthetic procedure for 7a, these compounds were obtained in 82% yield (380 mg, 0.794 mmol, 3’1-antilsyn = 8.1 : 1) by the reaction of 2\(H\)-chromen-2-one 3a (146 mg, 0.999 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (242 mg, 1.20 mmol), and 2-methylcyclohexanone (170 mg, 1.52 mmol) in the presence of triple carbon acid 1a (10 mg, 10 \(\mu\)mol) in CH\(_2\)Cl\(_2\) (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 15 : 1). Additional recycling HPLC (hexane/EtOAc = 15 : 1) was effective for separation the diastereomers to give less polar isomer 3,1’-syn-10a.
(41.7 mg, 90.5 μmol, 9.1% yield) and more polar one 3,1'-anti-10a (338 mg, 0.734 mmol, 73% yield). The configurations of both diastereomers were assigned by their NOESY spectra.

For 3,1'-syn-10a Colorless oil; IR (neat) ν 2935, 2852, 1763, 1738, 1459, 1222, 1167, 1063, 837, 774 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.22 (3H, s), 0.24 (3H, s), 0.75-0.85 (1H, m), 0.96 (9H, s), 1.04-1.13 (1H, m), 1.11 (3H, d, J = 6.5 Hz), 1.16 (3H, t, J = 7.1 Hz), 1.19-1.28 (2H, m), 1.30-1.44 (3H, m), 1.52 (1H, brd, J = 12.8 Hz), 1.62-1.72 (1H, m), 2.49 (1H, dd, J = 15.2, 10.1 Hz), 2.56 (1H, dd, J = 15.2, 4.6 Hz), 3.17 (1H, s), 3.82 (1H, dd, J = 10.1, 4.6 Hz), 4.05 (2H, q, J = 7.1 Hz), 6.97 (1H, d, J = 7.9 Hz), 7.03-7.09 (1H, m), 7.22 (1H, d, J = 7.5 Hz), 7.22-7.26 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ −1.5, 14.0, 16.2, 19.7, 21.6, 25.0, 26.5, 30.5, 32.4, 34.2, 396.1, 42.7, 53.3, 60.7, 81.0, 116.5, 124.67, 124.70, 128.1, 128.7, 150.08, 167.4, 170.5; MS (ESI-TOF) m/z 406 [M+Na]⁺; HRMS calcd for C₂₆H₄₀NaO₅Si [M+Na]⁺, 483.2543; found, 483.2548. Anal. Calcd for C₂₆H₄₀O₅Si: C, 67.79; H, 8.75. Found: C, 68.00; H, 8.85.

For 3,1'-anti-10a Colorless oil; IR (neat) ν 2978, 2851, 1769, 1732, 1460, 1142, 1087, 839, 778, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.09 (3H, s), 0.16 (3H, s), 0.67-0.78 (1H, m), 0.87-0.96 (1H, m), 0.90 (9H, s), 0.99 (3H, d, J = 6.6 Hz), 1.15-1.24 (1H, m), 1.20 (3H, t, J = 7.2 Hz), 1.33-1.69 (6H, m), 2.50 (2H, d, J = 7.6 Hz), 3.19 (1H, d, J = 0.8 Hz), 3.52-3.61 (1H, m), 4.03-4.17 (2H, m), 6.98 (1H, d, J = 7.5 Hz), 7.08 (1H, td, J = 7.5, 0.9 Hz), 7.21 (1H, d, J = 7.5 Hz), 7.23-7.29 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ −2.0, −1.7, 14.1, 15.5, 19.7, 21.4, 24.5, 26.7, 30.5, 34.2, 34.7, 38.0, 41.8, 54.3, 60.9, 80.2, 116.7, 124.1, 124.6, 128.0, 128.9, 151.4, 167.7, 170.7; MS (ESI-TOF) m/z 406 [M+Na]⁺; HRMS calcd for C₂₆H₄₀NaO₅Si [M+Na]⁺, 483.2543; found, 483.2549. Anal. Calcd for C₂₆H₄₀O₅Si: C, 67.79; H, 8.75. Found: C, 67.59; H, 8.80.

Ethyl 2-((3R*,4S*)-6-bromo-3-(2-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-yl)acetate (9b)

Due to low solubility of the starting lactone 3b, this reaction was conducted under highly diluted conditions. To a solution of 6-bromo-2H-chromen-2-one⁴ 3b (112 mg, 0.498 mmol) and triple carbon acid 1a (4.9 mg, 4.9 μmol) in CH₂Cl₂ (9.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol) in CH₂Cl₂ (0.5 mL) was added at −78 °C. After being stirred for 30 min, a solution of acetone (55 μL, 0.75 mmol) in CH₂Cl₂ (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. After usual extractive workup, the obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give the adduct in 89% yield (214 mg, 0.441 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2939, 2854, 1766, 1734, 1479, 1163, 1034, 838, 778 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ −0.13 (3H, s), 0.03 (3H, s), 0.75 (9H, s), 1.17 (3H, s), 1.21 (3H, t, J = 7.1 Hz), 1.41 (3H, s), 2.49 (1H, dd, J = 16.1, 7.0 Hz), 2.56 (1H, dd, J = 16.1, 7.3 Hz), 2.77 (1H, d, J = 0.8 Hz), 3.76-3.83 (1H, m), 4.07-4.15 (2H, m), 6.86 (1H, brd, J = 7.8 Hz), 7.31-7.35 (1H, m), 7.34 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ −0.3, −0.0, 16.3, 20.2, 27.9, 30.9, 31.6, 35.5,
Ethyl 2-((3R*,4S*)-7-bromo-3-(2-((tert-butyldimethylsilyl)oxy)propan-2-yl)-2-oxochroman-4-yl)acetate (9c)

According to the synthetic procedure for 9b, this compound was obtained in 89% yield (214 mg, 0.441 mmol) by the reaction of 7-bromo-2H-chromen-2-one 3c (112 mg, 0.498 mmol), tert-butyl ((1-ethoxyvinyl)oxy)dimethylsilane 4 (122 mg, 0.603 mmol), and acetone (55 µL, 0.75 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 µmol) in CH₂Cl₂ (10 mL) at −78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10:1). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 2950, 2930, 2850, 1750, 1730, 1600, 1580, 1480, 1405, 1160, 940, 835, 775 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ−0.14 (3H, s), 0.03 (3H, s), 0.75 (9H, s), 1.15 (3H, s), 1.20 (3H, t, J = 7.1 Hz), 1.40 (3H, s), 2.47 (1H, dd, J = 16.1, 7.2 Hz), 2.53 (1H, dd, J = 16.1, 7.2 Hz), 2.77 (1H, d, J = 0.8 Hz), 3.81 (1H, brt, J = 7.2 Hz), 4.09 (2H, q, J = 7.1 Hz), 7.08 (1H, d, J = 8.1 Hz), 7.13 (1H, d, J = 1.9 Hz), 7.20 (1H, dd, J = 8.1, 1.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ−2.5, −2.2, 14.1, 18.0, 25.6, 28.6, 29.6, 33.0, 41.7, 56.8, 60.9, 75.0, 120.1, 121.2, 123.6, 127.6, 129.3, 151.8, 166.9, 170.6; MS (ESI-TOF) m/z 507 [M+Na]⁺, 509 [M+2+Na]⁺; HRMS calcd for C₂₂H₂₅BrNaO₅Si [M+Na]⁺, 507.1178; found, 507.1183. Anal. Calcd for C₂₂H₂₅BrO₅Si: C, 54.43; H, 6.85. Found: C, 54.20; H, 6.84.

Ethyl 2-((3R*,4S*)-3-(2-((tert-butyldimethylsilyl)oxy)propan-2-yl)-6-methyl-2-oxochroman-4-yl)acetate (9d)

According to the synthetic procedure for 7a, this compound was obtained in 90% yield (190 mg, 0.452 mmol) by the reaction of 6-methyl-2H-chromen-2-one 3d (80.1 mg, 0.500 mmol), tert-butyl ((1-ethoxyvinyl)oxy)dimethylsilane 4 (122 mg, 0.603 mmol), and acetone (55 µL, 0.75 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 µmol) in CH₂Cl₂ (4.0 mL) at −78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10: 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2932, 2852, 1759, 1736, 1498, 1214, 1162, 1036, 837, 778 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ−0.01 (3H, s), 0.03 (3H, s), 0.78 (9H, s), 1.10 (3H, s), 1.13 (3H, s), 2.00 (3H, s), 2.20 (3H, s), 2.47 (1H, dd, J = 16.1, 7.2 Hz), 2.53 (1H, dd, J = 16.1, 7.2 Hz), 2.77 (1H, d, J = 0.8 Hz), 3.81 (1H, brt, J = 7.2 Hz), 4.09 (2H, q, J = 7.1 Hz), 7.08 (1H, d, J = 8.1 Hz), 7.13 (1H, d, J = 1.9 Hz), 7.20 (1H, dd, J = 8.1, 1.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ−2.5, −2.2, 14.1, 18.0, 25.6, 28.6, 29.6, 33.0, 41.7, 56.8, 60.9, 75.0, 120.1, 121.2, 123.6, 127.6, 129.3, 151.8, 166.9, 170.6; MS (ESI-TOF) m/z 507 [M+Na]⁺, 509 [M+2+Na]⁺; HRMS calcd for C₂₂H₂₅BrNaO₅Si [M+Na]⁺, 507.1178; found, 507.1183. Anal. Calcd for C₂₂H₂₅BrO₅Si: C, 54.43; H, 6.85. Found: C, 54.22; H, 6.90.
1.20 (3H, s), 1.40 (3H, s), 2.30 (3H, s), 2.48 (1H, dd, J = 15.8, 7.2 Hz), 2.54 (1H, dd, J = 15.8, 7.2 Hz), 2.78 (1H, brs), 3.80 (1H, t, J = 7.2 Hz), 4.10 (2H, q, J = 7.2 Hz), 6.85 (1H, d, J = 8.1 Hz), 6.97-7.03 (1H, m), 6.99 (1H, s); 13C NMR (100 MHz, CDCl3) δ -1.5, -1.2, 15.1, 19.0, 21.7, 26.7, 29.3, 30.9, 34.4, 43.0, 58.1, 61.7, 75.9, 117.4, 125.0, 129.3, 130.0, 135.2, 150.1, 169.0, 171.9; MS (ESI-TOF) m/z 443 [M+Na]+; HRMS calcd for C22H36NaO5Si [M+Na]+, 443.2230; found, 443.2246. Anal. Calcd for C22H36OsSi: C, 65.68; H, 8.63. Found: C, 65.38; H, 8.63.

Ethyl 2-((3R*,4S*)-3-(2-(tert-butyldimethylsilyl)oxy)propan-2-yl)-6-nitro-2-oxochroman-4-yl)acetate (9e)

![Chemical structure of 9e]

To a solution of 6-nitro-2H-chromen-2-one5 3e (95.6 mg, 0.500 mmol) and triple carbon acid 1a (15 mg, 15 μmol) in CH2Cl2 (9.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (155 mg, 0.766 mmol) in CH2Cl2 (0.5 mL) was added at -78 °C. After being stirred for 30 min, the reaction mixture was treated with a solution of acetone (74 μL, 1.0 mmol) in CH2Cl2 (0.5 mL) for 30 min at the same temperature. Since a small amount of in situ-generated KSA was observed by TLC analysis at this stage, further acetone (74 μL, 1.0 mmol) was added to the reaction mixture and the resulting mixture was stirred for 30 min at -78 °C. After usual extractive workup, the obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 6 : 1) to give the adduct in 90% yield (183 mg, 0.451 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 2960, 2930, 2850, 1770, 1730, 1530, 1340, 1250, 1160, 1030, 838, 780 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ -0.21 (3H, s), 0.02 (3H, s), 0.71 (9H, s), 1.22 (3H, t, J = 7.1 Hz), 1.24 (3H, s), 1.44 (3H, s), 2.54 (1H, dd, J = 16.5, 6.6 Hz), 2.64 (1H, dd, J = 16.5, 7.2 Hz), 2.82 (1H, d, J = 0.4 Hz), 3.89-3.95 (1H, m), 4.11 (2H, q, J = 7.1 Hz), 7.09 (1H, d, J = 7.1 Hz), 8.11-8.17 (2H, m); 13C NMR (100 MHz, CDCl3) δ -2.5, -2.3, 14.1, 18.0, 25.7, 29.0, 29.4, 33.8, 41.7, 56.4, 61.2, 75.2, 117.7, 123.9, 124.3, 125.7, 144.2, 155.9, 165.9, 170.2; MS (ESI-TOF) m/z 474 [M+Na]+; HRMS calcd for C22H33NNaO5Si [M+Na]+, 474.1924; found, 474.1933. Anal. Calcd for C22H33NaO5Si: C, 58.51; H, 7.37; N, 3.10. Found: C, 58.75; H, 7.58; N, 3.12.

Ethyl 2-((3R*,4S*)-3-(2-(tert-butyldimethylsilyl)oxy)propan-2-yl)-5-iodo-2-oxo-6-phenyl-3,4-dihydro-2H-pyran-4-yl)acetate (9f)

![Chemical structure of 9f]

According to the synthetic procedure for 7a, this compound was obtained in 90% yield (251 mg, 0.449 mmol) by the reaction of 5-iodo-6-phenyl-2H-pyran-2-one3 3f (149 mg, 0.500 mmol),...
**Ethyl 2-((3R',4S')-3-((tert-butyl(dimethyl)silyl)oxy)propan-2-yl)-2-oxo-6-phenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-4-yl)acetate (9g)**

![Diagram of compound 9g](image)

According to the synthetic procedure for 7a, this compound was obtained in 86% yield (231 mg, 0.434 mmol) by the reaction of 6-phenyl-5-(phenylethynyl)-2H-pyran-2-one \(^6\) 3g (137 mg, 0.503 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethyldimethylsilane 4 (185 mg, 0.916 mmol), and acetone (74 µL, 1.0 mmol) in the presence of triple carbon acid 1a (9.9 mg, 9.9 µmol) in CH\(_2\)Cl\(_2\) (4.0 mL) at –78 °C for 30 min and the following column chromatography on silica gel (hexane/EtOAc = 10 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Yellow oil; IR (neat) \(\nu\) 2961, 2926, 2852, 1764, 1729, 1159, 1035, 837, 778, 696 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.12 (3H, s), 0.13 (3H, s), 0.86 (9H, s), 1.24 (3H, t, \(J = 7.2\) Hz), 1.37 (3H, s), 1.50 (3H, s), 2.66 (1H, dd, \(J = 16.0, 5.5\) Hz), 2.72 (1H, dd, \(J = 16.0, 7.6\) Hz), 2.82 (1H, d, \(J = 0.7\) Hz), 3.50-3.56 (1H, m), 4.14 (2H, q, \(J = 7.2\) Hz), 7.31-7.36 (3H, m), 7.38-7.44 (5H, m), 8.01-8.05 (2H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) –2.14, –2.12, 14.1, 18.1, 25.8, 27.4, 30.1, 35.8, 39.1, 55.9, 60.9, 75.0, 86.7, 95.5, 99.8, 123.2, 127.5, 127.9, 128.3, 128.4, 129.6, 131.2, 132.2, 152.8, 166.6, 171.0; MS (ESI-TOF) \(m/z\) 555 [M+Na]*; HRMS calc for C\(_{35}\)H\(_{40}\)NaO\(_2\)Si [M+Na]*, 555.2543; found, 555.2543. Anal. Calcld for C\(_{32}\)H\(_{35}\)O\(_2\)Si: C, 72.14; H, 7.57. Found: C, 71.99; H, 7.60.
4. Sequential Mukaiyama–Michael reaction

Ethyl 2-((3S*,4S*)-2-oxo-3-(3-oxobutyl)chroman-4-yl)acetate (11a)

![11a](image)

To a solution of 2H-chromen-2-one 3a (73.0 mg, 0.499 mmol) and triple carbon acid 1a (5.1 mg, 5.1 μmol) in CH2Cl2 (1.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (123 mg, 0.608 mmol) in CH2Cl2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of freshly distilled methyl vinyl ketone (63 μL, 0.76 mmol) in CH2Cl2 (0.5 mL) was added to the reaction mixture over 1 h using a syringe pump. This mixture was additionally stirred for 30 min at –78 °C, then the resultant was treated with a 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. After extractive workup and evaporation, thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give this product in 59% yield (90.1 mg, 0.296 mmol) along with isolation of simple Michael adduct 6a (24.1 mg, 0.103 mmol, 21% yield). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless crystals (from CH2Cl2); Mp. 34.0-35.0 °C; IR (ATR) ν 1767, 1709, 1219, 1174, 1137, 757 cm⁻¹; ¹H NMR (400 MHz, CDCl3) δ 1.21 (3H, t, J = 7.1 Hz), 1.62-1.74 (1H, m), 1.77-1.88 (1H, m), 2.13 (3H, s), 2.47-2.67 (4H, m), 2.82 (1H, ddd, J = 10.3, 5.6, 1.7 Hz), 3.34 (1H, td, J = 7.4, 1.7 Hz), 4.11 (2H, q, J = 7.1 Hz), 7.03 (1H, d, J = 8.1 Hz), 7.11 (1H, td, J = 7.4, 1.0 Hz), 7.22-7.31 (2H, m); ¹³C NMR (100 MHz, CDCl3) δ 14.1, 24.1, 300.1, 37.9, 40.0, 40.3, 44.4, 60.9, 116.8, 123.1, 124.9, 129.0, 129.1, 150.3, 169.3, 170.7, 207.0; MS (ESI-TOF) m/z 327 [M+Na]⁺; HRMS calcd for C17H30NaO5 [M+Na]⁺, 327.1208; found, 327.1203. Anal. Calcd for C17H30O5: C, 67.09; H, 6.62. Found: C, 66.86; H, 6.68.

Ethyl 2-((3S*,4S*)-2-oxo-3-(3-oxobutyl)chroman-4-yl)acetate (12a)

![12a](image)

To a solution of 2H-chromen-2-one 3a (72.9 mg, 0.499 mmol) and triple carbon acid 1a (5.0 mg, 5.0 μmol) in CH2Cl2 (1.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol) in CH2Cl2 (0.5 mL) was added at –78 °C. After being stirred for 30 min, a solution of phenyl vinyl ketone⁷ (101 mg, 0.764 mmol) in CH2Cl2 (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the reaction mixture was treated with TfOH (0.1 mL) for 30 min at –78 °C. The resulting mixture was quenched with a saturated NaHCO₃ aqueous solution (15 mL), extracted with EtO (20 mL x 3), and washing with brine (20 mL). The combined organic layer was dried over anhydrous MgSO₄.
and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/EtOAc = 3:1) to give the adduct in 83% yield (152 mg, 0.415 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless crystals (from CH₂Cl₂); Mp. 62.0-63.0 °C; IR (ATR) ν 2947, 1767, 1734, 1719, 1682, 1221, 1209, 1173, 1133, 764, 687 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.22 (3H, t, J = 7.2 Hz), 1.92-1.97 (1H, m), 1.98-2.04 (1H, m), 2.54 (1H, dd, J = 16.2, 7.5 Hz), 2.61 (1H, dd, J = 16.2, 7.7 Hz), 2.95 (1H, ddd, J = 10.2, 5.5, 1.7 Hz), 3.06 (1H, ddd, J = 18.1, 8.6, 5.6 Hz), 3.19 (1H, ddd, J = 18.1, 8.3, 6.8 Hz), 3.43 (1H, td, J = 7.4, 1.7 Hz), 4.13 (2H, q, J = 7.2 Hz), 7.06 (1H, d, J = 7.2 Hz), 7.09-7.15 (1H, m), 7.24-7.32 (2H, m), 7.41-7.48 (2H, m), 7.52-7.59 (1H, m), 7.89-7.96 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 25.6, 26.3, 31.0, 62.0 °C; MS (ESI-TOF) m/z 389 [M+Na]+; HRMS calcd for C₂₂H₂₄NaO₅ [M+Na]⁺, 389.1365; found, 389.1360. Anal. Calcd for C₂₂H₂₄O₅: C, 72.12; H, 6.05. Found: C, 72.22; H, 6.23.

**Ethyl 2-((3R*,4S*)-3-(2-methyl-4-oxopentan-2-yl)-2-oxochroman-4-yl)acetate (13a)**

![Chemical Structure of 13a](image)

According to the synthetic procedure for 11a, the reaction of 2H-chromen-2-one 3a (73.4 mg, 0.502 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (121 mg, 0.598 mmol), and mesityl oxide (73.7 mg, 0.751 mmol) in the presence of triple carbon acid 1a (5.0 mg, 0.50 µmol) in CH₂Cl₂ (2.0 mL) was carried out at −78 °C for 30 min. Then, the mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature and quenched with a saturated NaHCO₃ aqueous solution (15 mL). After usual extractive workup, column chromatography of the resulting mixture on silica gel (hexane/EtOAc = 4:1) gave this product (102 mg, 0.305 mmol, 61% yield) and 1,2-adduct (21.2 mg, 63.3 µmol, 13% yield). Relative configuration of 13a was assigned by its NOESY spectrum. Yellow crystals (from CH₂Cl₂); Mp. 52.0-53.0 °C; IR (ATR) ν 2973, 2930, 1756, 1729, 1718, 1145, 1028, 733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.76 (3H, s), 1.09 (3H, s), 1.21 (3H, t, J = 7.2 Hz), 2.10 (3H, s), 2.31 (1H, d, J = 17.5 Hz), 2.50 (1H, dd, J = 15.9, 7.4 Hz), 2.57 (1H, dd, J = 15.9, 7.4 Hz), 2.61 (1H, d, J = 17.5 Hz), 3.22 (1H, brs), 3.57 (1H, t, J = 7.4 Hz), 4.05-4.18 (2H, m), 6.98 (1H, dd, J = 7.2, 0.9 Hz), 7.09 (1H, td, J = 7.4, 0.9 Hz), 7.20-7.28 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 25.6, 26.3, 31.7, 33.7, 36.5, 42.0, 51.0, 52.7, 60.9, 116.6, 124.5, 124.9, 128.1, 128.8, 151.0, 168.5, 170.7, 207.2; MS (ESI-TOF) m/z 335 [M+Na]+; HRMS calcd for C₁₉H₂₃NaO₅ [M+Na]⁺, 335.1521; found, 335.1520. Anal. Calcd for C₁₉H₂₃O₅: C, 68.66; H, 7.28. Found: C, 68.41; H, 7.30.
Ethyl 2-((3S*,4S*)-6-bromo-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12b)

To a solution of 6-bromo-2H-chromen-2-one$^4$ 3b (113 mg, 0.502 mmol) and triple carbon acid 1a (5.2 mg, 5.2 μmol) in CH$_2$Cl$_2$ (9.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (122 mg, 0.603 mmol) in CH$_2$Cl$_2$ (0.5 mL) was added at −78 °C. After being stirred for 30 min, a solution of phenyl vinyl ketone$^7$ (102 mg, 0.772 mmol) in CH$_2$Cl$_2$ (0.5 mL) was added to the reaction mixture and it was additionally stirred for 30 min at the same temperature. Then, the reaction mixture was treated with TfOH (0.1 mL) for 1 h at −78 °C. The resulting mixture was quenched with a saturated NaHCO$_3$ aqueous solution (15 mL), extracted with Et$_2$O (20 mL x 3), and washing with brine (20 mL). The combined organic layer was dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. Thus obtained resid was purified by column chromatography on silica gel (hexane/EtOAc = 5 : 1) to give the adduct in 83% yield (186 mg, 0.418 mmol). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2980, 2930, 1765, 1730, 1690, 1480, 1220, 1180, 820, 750, 735, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.23 (3H, t, J = 7.1 Hz), 1.81-1.93 (1H, m), 1.96-2.07 (1H, m), 2.53 (1H, dd, J = 16.3, 7.6 Hz), 2.61 (1H, dd, J = 16.3, 7.2 Hz), 2.94 (1H, ddd, J = 10.2, 5.5, 1.7 Hz), 3.06 (1H, ddd, J = 18.2, 7.7, 6.6 Hz), 3.17 (1H, dt, J = 18.2, 7.2 Hz), 3.36-3.43 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 6.94 (1H, d, J = 8.4 Hz), 7.38-7.48 (4H, m), 7.56 (1H, t, J = 7.7 Hz), 7.92 (2H, d, J = 8.4 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.1, 24.6, 35.4, 37.9, 39.8, 44.3, 61.1, 117.4, 118.6, 125.4, 128.0, 128.6, 131.9, 132.0, 133.3, 136.5, 149.5, 168.6, 170.4, 198.2; MS (ESI-TOF) m/z 467 [M+H]$^+$, 469 [M+2H]$^+$; HRMS calcd for C$_{22}$H$_{21}$BrNaO$_5$ [M+Na]$^+$, 467.0470; found, 467.0469. Anal. Calcd for C$_{22}$H$_{21}$BrO$_5$: C, 59.34; H, 4.75. Found: C, 59.53; H, 4.86.

Ethyl 2-((3S*,4S*)-7-bromo-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12c)

According to the synthetic procedure for 12b, this compound was obtained in 73% yield (162 mg, 0.365 mmol) by the reaction of 7-bromo-2H-chromen-2-one$^4$ 3c (113 mg, 0.502 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (124 mg, 0.613 mmol), and phenyl vinyl ketone$^7$ (102 mg, 0.772 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 μmol) in CH$_2$Cl$_2$ (10 mL) for 30 min at −78 °C and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 3 : 1). Relative configuration of this compound was assigned by
its NOESY spectrum. Pale yellow oil; IR (neat) ν 2980, 2930, 1771, 1730, 1680, 1600, 1481, 1408, 1212, 1179, 1075, 690 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 1.22 (3H, t, J = 7.1 Hz), 1.81-1.92 (1H, m), 1.97-2.08 (1H, m), 2.52 (1H, dd, J = 16.3, 7.7 Hz), 2.60 (1H, dd, J = 16.3, 7.1 Hz), 2.94 (1H, ddd, J = 10.2, 5.4, 1.4 Hz), 3.05 (1H, ddd, J = 18.2, 8.0, 5.9 Hz), 3.17 (1H, dt, J = 18.2, 7.5 Hz), 3.37-3.43 (1H, m), 4.08-4.17 (2H, m), 7.16 (1H, d, J = 8.0 Hz), 7.22-7.28 (2H, m), 7.45 (2H, t, J = 7.5 Hz), 7.56 (1H, t, J = 7.0 Hz), 7.92 (2H, d, J = 7.7 Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 14.1, 24.6, 35.4, 37.7, 39.8, 44.4, 61.0, 120.2, 121.9, 122.3, 128.0, 128.6, 130.4, 133.3, 136.5, 151.0, 168.5, 170.5, 198.2; MS (ESI-TOF) m/z 467 [M+Na]\(^+\), 469 [M+2Na]\(^+\); HRMS calcd for C\(_{22}\)H\(_{21}\)BrNaO\(_3\) [M+Na]\(^+\), 467.0470; found, 467.0471. Anal. Calcd for C\(_{22}\)H\(_{21}\)BrO\(_3\): C, 59.34; H, 4.75. Found: C, 59.24; H, 4.77.

**Ethyl 2-((3S*,4S*)-6-methyl-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12d)**

![Structure of 12d](image)

According to the synthetic procedure for 12a, this compound was obtained in 79% yield (151 mg, 0.397 mmol) by the reaction of 6-methyl-2H-chromen-2-one 3d (80.1 mg, 0.500 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (124 mg, 0.613 mmol), and phenyl vinyl ketone⁷ (101 mg, 0.764 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 μmol) in CH\(_2\)Cl\(_2\) (4.0 mL) at −78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2980, 2920, 1760, 1730, 1680, 1494, 1203, 686 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 1.22 (3H, t, J = 7.1 Hz), 1.82-1.93 (1H, m), 1.95-2.06 (1H, m), 2.31 (3H, s), 2.53 (1H, dd, J = 16.2, 7.3 Hz), 2.58 (1H, dd, J = 16.2, 7.6 Hz), 2.92 (1H, ddd, J = 10.0, 5.5, 1.5 Hz), 3.05 (1H, ddd, J = 18.0, 8.6, 5.6 Hz), 3.17 (1H, ddd, J = 18.0, 8.6, 6.8 Hz), 3.33-3.40 (1H, m), 4.13 (2H, q, J = 7.1 Hz), 6.93 (1H, d, J = 8.0 Hz), 7.05 (1H, s), 7.07 (1H, d, J = 8.0 Hz), 7.40-7.48 (2H, m), 7.55 (1H, tt, J = 7.3, 1.2 Hz), 7.90-7.94 (2H, m); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 14.1, 20.7, 24.6, 35.6, 38.0, 40.0, 44.6, 60.5, 116.5, 122.8, 128.0, 128.6, 129.42, 129.44, 133.2, 134.5, 136.5, 148.3, 169.6, 170.8, 198.4; MS (ESI-TOF) m/z 403 [M+Na]\(^+\); HRMS calcd for C\(_{23}\)H\(_{23}\)NO\(_5\) [M+Na]\(^+\), 403.1521; found, 403.1520.

**Ethyl 2-((3S*,4S*)-6-nitro-2-oxo-3-(3-oxo-3-phenylpropyl)chroman-4-yl)acetate (12e)**

![Structure of 12e](image)

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-S12-
According to the synthetic procedure for 12b, this compound was obtained in 77% yield (157 mg, 0.382 mmol) by the reaction of 6-nitro-2H-chromen-2-one5 3e (95.3 mg, 0.499 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (153 mg, 0.756 mmol), and phenyl vinyl ketone7 (106 mg, 0.802 mmol) in the presence of triple carbon acid 1a (15 mg, 15 µmol) in CH2Cl2 (10 mL) at −78 °C for 30 min and the following desilylation with TIOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 2975, 2925, 1779, 1748, 1715, 1597, 1505, 1469, 1450, 1341, 1230, 1091, 751, 693 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.24 (3H, t, J = 7.1 Hz), 1.83-1.96 (1H, m), 2.00-2.12 (1H, m), 2.59 (1H, dd, J = 16.6, 7.5 Hz), 2.69 (1H, dd, J = 16.6, 6.9 Hz), 3.03 (1H, ddd, J = 10.2, 5.4, 2.0 Hz), 3.09 (1H, ddd, J = 18.2, 7.5, 6.0 Hz), 3.19 (1H, dt, J = 18.2, 7.3 Hz), 3.52-3.58 (1H, m), 4.15 (2H, q, J = 7.1 Hz), 7.20 (1H, d, J = 8.0 Hz), 7.43-7.49 (2H, m), 7.57 (1H, t, J = 7.3 Hz), 7.90-7.94 (2H, m), 8.21 (1H, dd, J = 8.0, 2.6 Hz), 8.25 (1H, d, J = 2.6 Hz); 13C NMR (100 MHz, CDCl3) δ 14.1, 24.6, 35.2, 37.9, 43.9, 61.3, 117.8, 124.5, 125.0, 125.2, 128.0, 128.7, 133.4, 136.4, 144.4, 155.0, 167.5, 170.0, 198.0. MS (ESI-TOF) m/z 434 [M+Na]+; HRMS calcld for C22H21NaNO5 [M+Na]+, 434.1216; found, 434.1213. Anal. Calcld for C22H21NO6: C, 64.23; H, 5.15; N, 3.40. Found: C, 64.22; H, 5.16; N, 3.36.

Ethyl 2-((3S*,4S*)-5-iodo-2-oxo-3-(3-oxo-3-phenylpropyl)-6-phenyl-3,4-dihydro-2H-pyran-4-yl)acetate (12f)

According to the synthetic procedure for 12a, this compound was obtained in 84% yield (218 mg, 0.421 mmol) by the reaction of 5-iodo-6-phenyl-2H-pyran-2-one4 3f (149 mg, 0.500 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol), and phenyl vinyl ketone7 (102 mg, 0.772 mmol) in the presence of triple carbon acid 1a (5.1 mg, 5.1 µmol) in CH2Cl2 (3.0 mL) at −78 °C for 30 min and the following desilylation with TIOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 4 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Colorless oil; IR (neat) ν 3050, 2970, 2920, 1760, 1730, 1680, 1600, 1580, 1495, 1450, 1370, 1230, 1180, 1105, 1000, 960, 760, 695 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.29 (3H, t, J = 7.2 Hz), 2.21-2.32 (1H, m), 2.32-2.41 (1H, m), 2.56 (1H, dd, J = 16.7, 9.8 Hz), 2.79 (1H, dd, J = 16.7, 3.7 Hz), 2.92 (1H, ddd, J = 9.8, 6.0, 1.2 Hz), 3.09-3.27 (3H, m), 4.19 (2H, q, J = 7.2 Hz), 7.38-7.42 (3H, m), 7.46 (2H, t, J = 7.4 Hz), 7.54-7.61 (3H, m), 7.97 (2H, brd, J = 7.1 Hz); 13C NMR (100 MHz, CDCl3) δ 15.2, 26.3, 36.6, 37.4, 45.7, 48.6, 62.2, 74.5, 129.0, 129.1, 129.6, 130.3, 134.2, 129.44, 133.2, 134.3, 135.1, 150.9, 169.5, 171.4, 199.3; MS (ESI-TOF) m/z 541 [M+Na]+; HRMS calcld for C24H23INaO5 [M+Na]+, 541.0488; found, 541.0485. Anal. Calcld for C24H23NO5: C, 55.61; H, 4.47. Found: C, 55.45; H, 4.65.
Ethyl 2-((3S*,4S*)-2-oxo-3-(3-oxo-3-phenylpropyl)-6-phenyl-5-(phenylethynyl)-3,4-dihydro-2H-pyran-4-yl)acetate (12g)

According to the synthetic procedure for 12a, this compound was obtained in 72% yield (177 mg, 0.359 mmol) by the reaction of 6-phenyl-5-(phenylethynyl)-2H-pyran-2-one6 3g (136 mg, 0.499 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (155 mg, 0.766 mmol), and phenyl vinyl ketone7 (119 mg, 0.902 mmol) in the presence of triple carbon acid 1a (10 mg, 10 μmol) in CH₂Cl₂ (5.0 mL) at –78 °C for 30 min and the following desilylation with TfOH (0.1 mL). Its isolation was achieved by column chromatography on silica gel (hexane/EtOAc = 5 : 1). Relative configuration of this compound was assigned by its NOESY spectrum. Pale yellow oil; IR (neat) ν 3153, 2991, 2938, 1964, 1892, 1769, 1730, 1681, 1597, 1487, 1443, 1374, 1260, 1229, 1180, 1099, 1000, 759, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.26 (3H, t, J = 7.1 Hz), 2.25 (2H, q, J = 7.5 Hz), 2.63 (1H, dd, J = 16.6, 9.0 Hz), 2.83 (1H, dd, J = 16.6, 4.8 Hz), 2.95 (1H, td, J = 7.5, 2.6 Hz), 3.10-3.20 (2H, m), 3.25 (1H, dt, J = 18.0, 7.5 Hz), 4.17 (2H, q, J = 7.1 Hz), 7.31-7.36 (3H, m), 7.38-7.48 (7H, m), 7.53-7.59 (1H, m), 7.94-7.99 (2H, m), 8.02-8.07 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 24.8, 35.6, 37.2, 40.0, 42.9, 61.1, 86.3, 95.8, 99.2, 122.9, 127.7, 128.0, 128.4, 128.5, 128.6, 129.9, 131.1, 131.9, 133.2, 136.6, 153.0, 168.6, 171.0, 198.4; MS (ESI-TOF) m/z 493 [M+H]⁺; HRMS calcd for C₂₂H₂₉O₈ [M+H]⁺, 493.2015; found, 493.2018.

Ethyl 2-((3S*,4S*)-2-oxo-3-((R*)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3’-syn-14a) and ethyl 2-((3S*,4S*)-2-oxo-3-((S*)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3’-anti-14a)

According to the synthetic procedure for 12a, the reaction of 2H-chromen-2-one 3a (146 mg, 0.999 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (251 mg, 1.24 mmol), and cyclopent-2-en-1-one (124 mg, 1.51 mmol) in the presence of triple carbon acid 1a (10 mg, 10 μmol) in CH₂Cl₂ (4.0 mL) was conducted. After being stirred for 30 min at –78 °C, this mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was quenched with a saturated NaHCO₃ aqueous solution (10 mL) and extracted with Et₂O (15 mL x 3). The combined organic layer was washed with a saturated NaHCO₃ aqueous solution (10 mL) and brine (10 mL), dried over anhydrous MgSO₄, and evaporated. Column chromatography on
silica gel (hexane/EtOAc = 2 : 1) of the resulting residue gave a mixture of two diastereomers in 84% yield (267 mg, 0.844 mmol, 3,3'-syn/anti = 1 : 2.9) by. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2 : 1) to give less polar isomer 3,3'-syn-14a and more polar one 3,3'-anti-14a in 21% (67 mg, 0.212 mmol) and 59% (188 mg, 0.595 mmol) yields, respectively. Structure of 3,3'-syn-14a was confirmed by an X-ray crystallographic analysis. 3,4-Anti configuration of 3,3'-anti-14a was assigned by its NOESY spectrum.

For 3,3'-syn-14a Colorless crystals (from EtOAc/hexane); Mp. 89.0-90.5 °C; IR (ATR) ν 2964, 1753, 1735, 1458, 1134, 910, 850, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (3H, t, J = 7.2 Hz), 1.75-1.89 (1H, m), 1.97-2.21 (4H, m), 2.29-2.46 (2H, m), 2.56 (2H, d, J = 7.3 Hz), 2.79 (1H, dd, J = 10.1, 1.4 Hz), 3.35-3.42 (1H, m), 4.13 (2H, q, J = 7.2 Hz), 7.07 (1H, dd, J = 8.1, 1.0 Hz), 7.14 (1H, td, J = 7.6, 1.0 Hz), 7.24 (1H, dd, J = 7.6, 1.7 Hz), 7.29-7.35 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 27.9, 36.4, 36.8, 37.4, 39.8, 43.0, 50.6, 61.1, 116.9, 122.9, 125.2, 128.9, 129.2, 150.6, 167.8, 170.6, 216.0; MS (ESI-TOF) m/z 339 [M+Na]+; HRMS calc'd for C₁₈H₂₇NaO₅ [M+Na]+; found, 339.1211. Analog. Calcd for C₁₈H₂₇O₅: C, 68.34; H, 6.37. Found: C, 68.13; H, 6.34.

For 3,3'-anti-14a Colorless crystals (from EtOAc/hexane); Mp. 40.0-42.5 °C; IR (ATR) ν 2957, 1765, 1738, 1725, 1457, 1215, 1160, 855, 759 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.21 (3H, t, J = 7.1 Hz), 1.63-1.76 (1H, m), 1.98-2.38 (6H, m), 2.56 (2H, d, J = 7.5 Hz), 2.79 (1H, d, J = 9.0 Hz), 3.55 (1H, t, J = 7.5 Hz), 4.12 (2H, q, J = 7.1 Hz), 7.03 (1H, d, J = 8.1 Hz), 7.13 (1H, t, J = 7.3 Hz), 7.24-7.33 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 27.6, 35.4, 36.2, 38.1, 39.8, 43.1, 50.4, 61.0, 116.9, 122.9, 125.1, 128.9, 129.2, 150.5, 168.2, 170.7, 216.2; MS (ESI-TOF) m/z 339 [M+Na]+; HRMS calc'd for C₁₈H₂₇NaO₅ [M+Na]+; found, 339.1208; found, 339.1219. Analog. Calcd for C₁₈H₂₇O₅: C, 68.34; H, 6.37. Found: C, 68.16; H, 6.37.

Ethyl 2-((3S*,4S*)-6-bromo-2-oxo-3-(R*)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-syn-14b) and Ethyl 2-((3S*,4S*)-6-bromo-2-oxo-3-((S*)-3-oxocyclopentyl)chroman-4-yl)acetate (3,3'-anti-14b)

According to the synthetic procedure for 12b, the reaction of 6-bromo-2H-chromen-2-one[4] 3b (113 mg, 0.502 mmol), tert-butyl(1-ethoxyvinyl)oxydimethylsilane 4 (123 mg, 0.608 mmol), and cyclopent-2-en-1-one (62 mg, 0.755 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 μmol) in CH₂Cl₂ (10 mL) was conducted. After being stirred for 30 min at −78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H₂O (10 mL) and extracted with Et₂O (20 mL x 3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO₄, and evaporated. A mixture of two diastereomers was obtained in 72% yield (143 mg, 0.362 mmol, 3,3'-syn/anti = 1 : 2.4) by column chromatography on silica gel (hexane/EtOAc =
3 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1.5 : 1) to give less polar isomer 3,3'-syn-14b and more polar one 3,3'-anti-14b in 18% (35.9 mg, 90.8 μmol) and 42% (83.8 mg, 0.212 mmol) yields, respectively. Structure of 3,3'-syn-14b was confirmed by an X-ray crystallographic analysis. 3,4-Anti configuration of 3,3'-anti-14b was assigned by its NOESY spectrum.

For 3,3'-syn-14b Colorless crystals (from EtOAc/hexane); Mp. 94.0-95.5 °C. IR (ATR) ν 2948, 1765, 1735, 1720, 1478, 1160, 1138, 824, 486 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (3H, t, J = 7.1 Hz), 1.73-1.87 (1H, m), 1.96-2.20 (4H, m), 2.29-2.48 (2H, m), 2.55 (2H, d, J = 7.5 Hz), 2.77 (1H, d, J = 10.2 Hz), 3.35 (1H, t, J = 7.5 Hz), 4.14 (2H, q, J = 7.1 Hz), 6.95 (1H, d, J = 8.5 Hz), 7.37-7.45 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 27.9, 36.4, 36.6, 38.4, 39.6, 42.9, 50.2, 61.2, 117.6, 118.7, 125.0, 131.6, 132.2, 149.6, 167.0, 170.2, 215.6; MS (ESI-TOF) m/z 417 [M+Na]+, 419 [M+2+Na]+; HRMS calcd for C₁₈H₁₉BrNaO₅ [M+Na]+, 417.0314; found, 417.0310. Anal. Calcd for C₁₈H₁₉BrNaO₅: C, 54.70; H, 4.85. Found: C, 54.75; H, 4.86.

For 3,3'-anti-14b Colorless oil; IR (neat) ν 2991, 1778, 1741, 1731, 1480, 1220, 1169, 821, 757 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (3H, t, J = 7.1 Hz), 1.60-1.76 (1H, m), 2.05-2.19 (3H, m), 2.19-2.31 (2H, m), 2.36 (1H, dd, J = 18.1, 7.1 Hz), 2.56 (2H, d, J = 7.5 Hz), 2.76 (1H, d, J = 10.2 Hz), 3.53 (1H, t, J = 7.5 Hz), 4.07-4.20 (2H, m), 6.92-6.97 (1H, m), 7.39-7.45 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 27.7, 35.3, 36.1, 38.0, 39.5, 43.0, 50.0, 61.2, 117.5, 118.2, 125.0, 131.6, 132.3, 149.6, 167.4, 170.3, 215.8; MS (ESI-TOF) m/z 417 [M+Na]+, 419 [M+2+Na]+; HRMS calcd for C₁₈H₁₉BrNaO₅ [M+Na]+, 417.0314; found, 417.0318. Anal. Calcd for C₁₈H₁₉BrNaO₅: C, 54.70; H, 4.85. Found: C, 54.46; H, 4.80.

Ethyl 2-((3S*,4S*)-2-oxo-3-((R*)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-syn-15a) and ethyl 2-((3S*,4S*)-2-oxo-3-((S*)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-anti-15a)

![Diagram](https://via.placeholder.com/150)

According to the synthetic procedure for 12a, the reaction of 2H-chromen-2-one 3a (147 mg, 1.01 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (243 mg, 1.20 mmol), and cyclohex-2-en-1-one (146 mg, 1.52 mmol) in the presence of triple carbon acid 1a (10 mg, 10 μmol) in CH₂Cl₂ (4.0 mL) was conducted. After being stirred for 30 min at ~78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H₂O (10 mL) and extracted with Et₂O (20 mL x 3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO₄, and evaporated. A mixture of two diastereomers was obtained in 93% yield (308 mg, 0.929 mmol, 3,3'-syn/anti = 1.1 : 1) by column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1.5 : 1) to give less polar isomer 3,3'-syn-15a and more polar one 3,3'-anti-15a in 46% (154 mg, 0.466 mmol)
and 42% (140 mg, 0.424 mmol) yields, respectively. Structure of 3,3'-syn-15a was confirmed by an X-ray crystallographic analysis. 3,4-anti configuration of 3,3'-anti-15a was assigned by its NOESY spectrum.

For 3,3'-syn-15a Colorless crystals (from hexane); Mp. 97.5-99.0 °C; IR (ATR) ν 2961, 1758, 1732, 1707, 1487, 1223, 1148, 764, 504 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.22 (3H, t, J = 7.2 Hz), 1.42-1.62 (2H, m), 1.71-1.89 (2H, m), 2.00-2.16 (2H, m), 2.18-2.29 (1H, m), 2.29-2.38 (1H, m), 2.50-2.58 (1H, m), 2.53 (2H, d, J = 7.5 Hz), 2.73 (1H, dd J = 9.3, 1.5 Hz), 3.47 (1H, td, J = 7.5, 1.5 Hz), 4.13 (2H, q, J = 7.2 Hz), 7.03 (1H, dd, J = 8.1, 1.0 Hz), 7.12 (1H, td, J = 7.6, 1.0 Hz), 7.23 (1H, dd, J = 7.6, 1.6 Hz), 7.26-7.32 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 24.4, 29.5, 34.8, 37.6, 39.8, 41.0, 45.3, 50.9, 61.0, 116.8, 122.9, 125.1, 128.9, 129.2, 150.6, 167.9, 170.5, 209.2; MS (ESI-TOF) m/z 353 [M+Na]+; HRMS calcd for C₁₉H₂₂NaO₅ [M+Na]+, 353.1365; found, 353.1354. Anal. Calcd for C₁₉H₂₂O₅: C, 69.07; H, 6.71. Found: C, 69.05; H, 6.70.

For 3,3'-anti-15a Pale yellow oil; IR (neat) ν 2945, 1766, 1729, 1711, 1484, 1458, 1223, 1180, 1146, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.22 (3H, t, J = 7.1 Hz), 1.47-1.54 (2H, m), 1.72-1.85 (1H, m), 2.01-2.11 (2H, m), 2.17-2.36 (4H, m), 2.55 (2H, d, J = 7.5 Hz), 2.73 (1H, d, J = 9.0 Hz), 3.56 (1H, t, J = 7.5 Hz), 4.12 (2H, q, J = 7.1 Hz), 7.05 (1H, brd, J = 8.1 Hz), 7.11 (1H, td, J = 7.5, 1.0 Hz), 7.22 (1H, dd, J = 7.5, 1.4 Hz), 7.25-7.32 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 24.5, 29.2, 35.4, 37.9, 39.9, 40.9, 45.8, 50.9, 61.0, 117.0, 123.0, 125.0, 128.7, 129.2, 150.5, 167.7, 170.7, 209.2; MS (ESI-TOF) m/z 353 [M+Na]+; HRMS calcd for C₁₉H₂₂NaO₅ [M+Na]+, 353.1365; found, 353.1362. Anal. Calcd for C₁₉H₂₂O₅: C, 69.07; H, 6.71. Found: C, 69.13; H, 6.81.

**Ethyl 2-((3S*,4S*)-6-bromo-2-oxo-3-((R*)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-syn-15b) and ethyl 2-((3S*,4S*)-6-bromo-2-oxo-3-((S*)-3-oxocyclohexyl)chroman-4-yl)acetate (3,3'-anti-15b)**

According to the synthetic procedure for 12b, the reaction of 6-bromo-2H-chromen-2-one₄ 3b (113 mg, 0.502 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol), and cyclohex-2-en-1-one (73 mg, 0.76 mmol) in the presence of triple carbon acid 1a (5.1 mg, 5.1 µmol) in CH₂Cl₂ (10 mL) was conducted. After being stirred for 30 min at ~78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H₂O (10 mL) and extracted with Et₂O (20 mL x 3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO₄, and evaporated. A mixture of two diastereomers was obtained in 87% yield (177 mg, 0.432 mmol, 3,3'-syn/anti = 1.1 : 1) by column chromatography on silica gel (hexane/EtOAc = 4 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2 : 1) to give less polar isomer 3,3'-syn-15b and more polar one 3,3'-anti-15b in 43% (88.4 mg, 0.216 mmol) and 40% (82.3 mg, 0.201 mmol) yields, respectively. Structure of 3,3'-syn-15b was confirmed...
by an X-ray crystallographic analysis. 3,4- Anti configuration of 3,3’-anti-15b was assigned by its NOESY spectrum.

For 3,3’-syn-15b  Colorless crystals (from Et2O); Mp. 97.0-98.5 °C; IR (ATR) ν 2950, 1757, 1732, 1702, 1474, 1218, 1151, 819, 503 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (3H, t, J = 7.1 Hz), 1.47-1.61 (2H, m), 1.72-1.87 (2H, m), 2.02-2.17 (2H, m), 2.20-2.30 (1H, m), 2.31-2.40 (1H, m), 2.50-2.57 (1H, m), 2.53 (2H, d, J = 7.5 Hz), 2.72 (1H, dd J = 9.2, 1.3 Hz), 3.41-3.47(1H, m), 4.15 (2H, q, J = 7.1 Hz), 6.93 (1H, d, J = 8.5 Hz), 7.37-7.44 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 24.3, 29.4, 34.7, 37.6, 39.6, 40.9, 45.2, 50.4, 61.2, 117.5, 118.5, 125.0, 131.6, 132.2, 149.6, 167.1, 170.1, 208.9; MS (ESI-TOF) m/z 431 [M+Na]⁺, 433 [M+2+Na]⁺; HRMS calcd for C₁₉H₂₃BrNaO₅ [M+Na]⁺, 431.0470; found, 431.0475. Anal. Calcd for C₁₀H₅BrO₅: C, 55.76; H, 5.17. Found: C, 55.73; H, 5.04.

For 3,3’-anti-15b  Colorless oil; IR (neat) ν 2949, 1769, 1734, 1717, 1480, 1221, 1182, 1144, 822 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (3H, t, J = 7.2 Hz), 1.36-1.58 (2H, m), 1.71-1.83 (1H, m), 2.01-2.13 (2H, m), 2.17-2.37 (4H, m), 2.54 (2H, d, 7.4 Hz), 2.72 (1H, dd, J = 9.2, 1.4 Hz), 3.53 (1H, td, J = 7.4, 1.4 Hz), 4.14 (2H, q, J = 7.2 Hz), 6.93 (1H, d, J = 8.5 Hz), 7.36-7.42 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 24.4, 29.1, 35.1, 37.8, 39.7, 40.8, 45.8, 50.5, 61.2, 117.4, 118.7, 125.1, 131.5, 132.2, 149.6, 166.9, 170.3, 209.0; MS (ESI-TOF) m/z 431 [M+Na]⁺, 433 [M+2+Na]⁺; HRMS calcd for C₁₀H₅BrNaO₅ [M+Na]⁺, 431.0470; found, 431.0465. Anal. Calcd for C₁₀H₅BrO₅: C, 55.76; H, 5.17. Found: C, 55.55.; H, 5.27.

**Ethyl 2-((3S*,4S*)-2-oxo-3-((R*)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3’-syn-16a) and ethyl 2-((3S*,4S*)-2-oxo-3-((S*)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3’-anti-16a)**

According to the synthetic procedure for 12a, the reaction of 2H-chromen-2-one 3a (146 mg, 0.999 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (243 mg, 1.20 mmol), and cyclohept-2-en-1-one (167 mg, 1.52 mmol) in the presence of triple carbon acid 1a (9.9 mg, 9.9 μmol) in CH₂Cl₂ (4.0 mL) was conducted. After being stirred for 30 min at −78 °C, this reaction mixture was treated with 2% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H₂O (10 mL) and extracted with Et₂O (20 mL x 3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO₄, and evaporated. A mixture of two diastereomers was obtained in 88% yield (304 mg, 0.883 mmol, 3,3’-syn/anti = 3:9) by column chromatography on silica gel (hexane/EtOAc = 2:1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 2:1) to give less polar isomer 3,3’-syn-16a and more polar one 3,3’-anti-16a in 65% (224 mg, 0.650 mmol) and 18% (62.0 mg, 0.180 mmol) yields, respectively. 3,4-Anti configurations of both isomers were assigned by their NOESY spectra.

For 3,3’-syn-16a  Colorless oil; IR (neat) ν 2931, 1762, 1731, 1700, 1457, 1220, 1158, 762 cm⁻¹; ¹H NMR
(400 MHz, CDCl₃) δ 1.21 (3H, t, J = 7.1 Hz), 1.29-1.41 (1H, m), 1.46-1.57 (1H, m), 1.58-1.94 (5H, m), 2.30-2.47 (2H, m), 2.48-2.59 (2H, m), 2.52 (2H, d, J = 7.5 Hz), 2.72 (1H, dd, J = 9.7, 1.0 Hz), 3.54 (1H, td, J = 7.5, 1.0 Hz), 4.11 (2H, q, J = 7.1 Hz), 7.02 (1H, d, J = 8.2 Hz), 7.11 (1H, t, J = 7.5 Hz), 7.23-7.31 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 23.7, 27.1, 34.2, 35.1, 35.2, 39.9, 43.6, 46.7, 49.9, 60.9, 116.7, 123.1, 125.0, 128.9, 129.1, 150.6, 168.2, 170.4, 212.1; MS (ESI-TOF) m/z 345 [M+H]⁺; HRMS calcd for C₂₀H₂₅O₅ [M+H]⁺, 345.1702; found, 345.1702; Anal. Calcd for C₂₀H₂₅O₅: C, 69.75; H, 7.02. Found: C, 69.58; H, 6.97.

Ethyl 2-((35S,45S)-6-bromo-2-oxo-3-((R*)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-syn-16b) and ethyl 2-((35S,45S)-6-bromo-2-oxo-3-((S*)-3-oxocycloheptyl)chroman-4-yl)acetate (3,3'-anti-16b)

According to the synthetic procedure for 12b, the reaction of 6-bromo-2H-chromen-2-one⁴ 3b (112 mg, 0.498 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (122 mg, 0.604 mmol), and cyclohept-2-en-1-one (166 mg, 1.51 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 µmol) in CH₂Cl₂ (10 mL) was conducted. After being stirred for 30 min at −78 °C, this reaction mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H₂O (10 mL) and extracted with Et₂O (20 mL x 3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO₄, and evaporated. A mixture of two diastereomers was obtained in 82% yield (173 mg, 0.409 mmol, 3,3'-syn/anti = 5.8 : 1) by column chromatography on silica gel (hexane/EtOAc = 4 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 3 : 1) to give less polar isomer 3,3'-syn-16b and more polar one 3,3'-anti-16b in 64% (135 mg, 0.319 mmol) and 13% (27.4 mg, 64.7 µmol) yields, respectively. Structures of both isomers were confirmed by X-ray crystallographic analyses.

For 3,3'-syn-16b Colorless solid (from hexane); Mp. 84.0-85.0 °C; IR (neat) ν 2930, 1754, 1732, 1704, 1475, 1216, 1153, 1119, 819 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24 (3H, t, J = 7.2 Hz), 1.33-1.44 (1H, m), 1.48-1.59 (1H, m), 1.61-1.94 (5H, m), 2.35-2.43 (2H, m), 2.43-2.61 (2H, m), 2.52 (2H, d, J = 7.4 Hz), 2.72 (1H,
dd, J = 9.6, 1.5 Hz), 3.53 (1H, td, J = 7.4, 1.5 Hz), 4.14 (2H, q, J = 7.2 Hz), 6.93 (1H, d, J = 8.4 Hz), 7.38-7.43 (2H, m); 13C NMR (100 MHz, CDCl3) δ 14.1, 23.6, 27.0, 34.2, 35.0, 35.2, 39.7, 43.6, 46.6, 49.4, 61.1, 117.4, 118.4, 125.3, 131.7, 132.1, 149.6, 167.4, 170.1, 211.9; MS (ESI-TOF) m/z 445 [M+Na]+, 447 [M+2+Na]+; HRMS calcd for C20H2BrNaO3 [M+Na]+, 445.0627; found, 445.0634. Anal. Calcd for C20H2BrO3: C, 56.75; H, 5.48. Found: C, 56.52; H, 5.50.

For 3,3’-anti-16b Colorless solid (from hexane); Mp. 127-130 °C; IR (neat) ν 2932, 1755, 1732, 1694, 1474, 1218, 1162, 1113, 824 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.23 (3H, t, J = 7.1 Hz), 1.27-1.39 (2H, m), 1.53-1.66 (1H, m), 1.70-1.88 (2H, m), 1.88-1.98 (2H, m), 2.32-2.42 (2H, m), 2.46 (1H, dt, J = 15.2, 4.9 Hz), 2.54 (2H, d, J = 7.4 Hz), 2.60 (1H, dd, J = 15.2, 11.2 Hz), 2.70 (1H, dd, J = 9.0, 1.6 Hz), 3.47-3.54 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 6.94 (1H, d, J = 8.5 Hz), 7.38 (1H, d, J = 2.1 Hz), 7.40 (1H, dd, J = 8.5, 2.1 Hz); 13C NMR (100 MHz, CDCl3) δ 14.1, 23.9, 27.5, 33.8, 35.0, 35.7, 39.8, 43.5, 47.0, 50.3, 61.2, 117.4, 118.7, 125.3, 131.3, 132.2 149.7, 167.5, 170.4, 211.6; MS (ESI-TOF) m/z 445 [M+Na]+, 447 [M+2+Na]+; HRMS calcd for C20H2BrNaO3 [M+Na]+, 445.0627; found, 445.0631. Anal. Calcd for C20H2BrO3: C, 56.75; H, 5.48. Found: C, 57.02; H, 5.63.

Ethyl 2-((2R*,3'R*,4'S*)-2',4-dioxo-[2,3'-bichromen]-4'-yl)acetate (3,2’-syn-17) and ethyl 2-((2S*,3'R*,4'S*)-2',4-dioxo-[2,3'-bichromen]-4'-yl)acetate (3,2’-anti-17)

According to the synthetic procedure for 12a, the reaction of 2H-chromen-2-one 3a (73.1 mg, 0.500 mmol), tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (125 mg, 0.618 mmol), and 4H-chromen-4-one (109 mg, 0.746 mmol) in the presence of triple carbon acid 1a (5.0 mg, 5.0 μmol) in CH2Cl2 (2.5 mL) was conducted. After being stirred for 30 min at –78 °C, this reaction mixture was treated with 10% hydrochloric acid (5.0 mL) for 30 min at room temperature. Then, the mixture was diluted with H2O (20 mL) and extracted with Et2O (20 mL x 3). The combined organic layer was washed with saturated NaHCO3 aqueous solution (15 mL) and brine (15 mL), dried over anhydrous MgSO4, and evaporated. A mixture of two diastereomers was obtained in 99% yield (189 mg, 0.497 mmol, 3,2’-syn/anti = 8.5 : 1) by column chromatography on silica gel (hexane/EtOAc = 2 : 1) of the resulting residue. Separation of the diastereomers was achieved by recycling HPLC technique (hexane/EtOAc = 1 : 1) to give less polar isomer 3,2’-anti-17 and more polar one 3,2’-syn-17 in 81% (154 mg, 0.405 mmol) and 9.2% (17.5 mg, 46.0 μmol) yields, respectively. Structure of 3,2’-anti-17 was confirmed by an X-ray crystallographic analysis. 3,4-Anti configuration of 3,2’-syn-17 was assigned by its NOESY spectrum. For 3,2’-syn-17 Pale yellow oil; IR (neat) ν 2978, 2922, 1757, 1730, 1688, 1603, 1460, 1221, 759 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 1.23 (3H, t, J = 7.1 Hz), 2.63 (1H, dd, J = 16.7, 6.8 Hz), 2.68 (1H, dd, J = 16.7, 7.8 Hz), 2.78 (1H, dd, J = 16.8, 3.2 Hz), 2.89 (1H, dd, J = 16.8, 12.7 Hz), 3.31 (1H, dd, J = 6.6, 1.6 Hz), 3.53-3.59 (1H, m), 4.14 (2H, q, J = 7.1 Hz), 4.52 (1H, dd, J = 12.7, 6.6, 3.2 Hz), 6.67 (1H, brd, J = 8.4 Hz), 6.99 (1H, td,
\( J = 7.5, 1.0 \) Hz, 7.08 (1H, dd, \( J = 8.2, 1.0 \) Hz), 7.14 (1H, td, \( J = 7.5, 1.0 \) Hz), 7.24 (1H, dd, \( J = 7.5, 1.7 \) Hz), 7.28-7.35 (1H, m), 7.37-7.44 (1H, m), 7.81 (1H, dd, \( J = 7.2, 1.7 \) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 14.2, 35.3, 40.0, 40.9, 49.4, 61.2, 76.9, 117.0, 118.0, 120.7, 122.1, 122.8, 125.1, 126.9, 128.3, 129.3, 136.3, 150.9, 160.4, 165.7, 170.4, 190.5; MS (ESI-TOF) \( m/z \) 403 [M+Na]\(^{+}\); HRMS calcd for C\(_{22}\)H\(_{20}\)NaO\(_6\) [M+Na]\(^{+}\), 403.1158; found, 403.1167.

For 3,2'-anti-17 Colorless crystals (from Et\(_2\)O); Mp. 86.0-87.5 °C; IR (ATR) \( \nu \) 2983, 2926, 1761, 1728, 1682, 1605, 1216, 1149, 1029, 767 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.22 (3H, \( t, J = 7.1 \) Hz), 2.61 (1H, dd, \( J = 16.2, 7.5 \) Hz), 2.66 (1H, dd, \( J = 16.2, 7.5 \) Hz), 2.70 (1H, dd, \( J = 16.9, 2.9 \) Hz), 2.92 (1H, dd, \( J = 16.9, 12.8 \) Hz), 3.33 (1H, dd, \( J = 8.9, 1.4 \) Hz), 4.00 (1H, td, \( J = 7.5, 1.4 \) Hz), 4.13 (2H, q, \( J = 7.1 \) Hz), 4.34 (1H, ddd \( J = 12.8, 8.9, 2.9 \) Hz), 6.94 (1H, brd, \( J = 8.4 \) Hz), 6.99-7.04 (1H, m), 7.06 (1H, d, \( J = 8.0 \) Hz), 7.12 (1H, td, \( J = 7.5, 1.1 \) Hz), 7.26-7.30 (1H, m), 7.30 (1H, d, \( J = 7.5 \) Hz), 7.44-7.50 (1H, m), 7.83 (1H, dd, \( J = 7.8, 1.7 \) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 14.1, 33.6, 39.8, 41.3, 50.6, 61.1, 74.1, 117.0, 117.8, 120.9, 122.1, 122.7, 125.3, 127.0, 129.1, 129.3, 136.2, 150.5, 160.3, 165.8, 170.5, 190.3; MS (ESI-TOF) \( m/z \) 403 [M+Na]\(^{+}\); HRMS calcd for C\(_{22}\)H\(_{20}\)NaO\(_6\) [M+Na]\(^{+}\), 403.1158; found, 403.1148. Anal. Calcd for C\(_{22}\)H\(_{20}\)O\(_6\): C, 69.46; H, 5.30. Found: C, 69.48; H, 5.31.

**Ethyl-2-((2S',3S',3'R',4'S')-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-syn-18) and ethyl 2-((2'R',3'R',3'R',4'S')-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-anti-18)**

![ Diagram of ethyl-2-((2S',3S',3'R',4'S')-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-syn-18) and ethyl 2-((2'R',3'R',3'R',4'S')-3-bromo-3-methyl-2',4-dioxo-[2,3'-bichroman]-4'-yl)acetate (3,2'-anti-18) ](image)

To a solution of 2H-chromen-2-one 3a (73.2 mg, 0.501 mmol) and triple carbon acid 1a (5.0 mg, 5.0 \( \mu \)mol) in CH\(_2\)Cl\(_2\) (1.0 mL), a solution of tert-butyl((1-ethoxyvinyl)oxy)dimethylsilane 4 (124 mg, 0.613 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL) was added at \( -78 \) °C. After being stirred for 30 min, a solution of 3-methylchromone\(^{8}\) (120 mg, 0.749 mmol) in CH\(_2\)Cl\(_2\) (1.0 mL) was added to the reaction mixture and it was additionally stirred for 1.5 h at the same temperature. After that, the reaction mixture was treated with a solution of bromine (170 mg, 1.06 mmol) for 30 min at \( -78 \) °C. The resulting mixture was quenched with a saturated aqueous Na\(_2\)S\(_2\)O\(_3\) solution (15 mL) and extracted with Et\(_2\)O (20 mL x 3). The combined organic layer was washed with brine (20 mL), dried over anhydrous MgSO\(_4\) and concentrated under reduced pressure. Thus obtained residue was purified by column chromatography on silica gel (hexane/ EtOAc = 6 : 1) to give an inseparable mixture of the desired adduct and a small amount of 6a. Isolation of the products was achieved by recycling HPLC technique (hexane/EtOAc = 4 : 1) to give less polar isomer 3,2'-anti-18 and more polar isomer 3,2'-syn-18 in 42% (100 mg, 0.212 mmol) and 30% (70.3 mg, 0.149 mmol) yields, respectively. Structure of 3,2'-anti-18 was determined by an X-ray crystallographic analysis. 3,4-Anti and 2',3'-anti configurations of 3,2'-syn-18 were assigned by its NOESY spectrum.

For 3,2'-syn-18 Colorless crystals (from EtOAc); Mp. 117-118 °C; IR (ATR) \( \nu \) 2980, 1748, 1727, 1693,
1606, 1459, 1166, 1145, 1040, 751, 478 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.23 (3H, t, \(J = 7.2\) Hz), 2.07(3H, s), 2.59 (1H, dd, \(J = 16.4, 7.2\) Hz), 2.64 (1H, dd, \(J = 16.4, 8.0\) Hz), 3.58-3.63 (1H, m), 3.65 (1H, dd, \(J = 3.7, 1.6\) Hz), 4.09-4.19 (2H, m), 4.53 (1H, d, \(J = 3.7\) Hz), 6.38 (1H, brd, \(J = 8.3\) Hz), 6.99-7.07 (2H, m), 7.13 (1H, td, \(J = 7.5, 1.1\) Hz), 7.28-7.32 (2H, m), 7.32-7.38 (1H, m), 7.87 (1H, dd, \(J = 7.9, 1.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 21.6, 38.9, 39.5, 46.3, 61.2, 64.5, 85.0, 116.9, 117.4, 117.7, 122.6, 123.0, 125.1, 128.3, 129.0, 129.3, 136.5, 151.1, 158.1, 165.6, 170.3, 186.6; MS (ESI-TOF) \(m/z\) 495 [M+Na]\(^+\), 497 [M+2+Na]\(^+\); HRMS calcd for C\(_{23}\)H\(_{21}\)BrNaO\(_6\) [M+Na]\(^+\), 495.0419; found, 495.0418.

For 3,2’-anti-18 Colorless crystals (from EtOAc); Mp. 149-150 °C; IR (ATR) \(\nu\) 2932, 1751, 1725, 1685, 1608, 1459, 1202, 1179, 1028, 749, 479 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.18 (3H, t, \(J = 7.2\) Hz), 2.12 (3H, s), 2.47 (2H, d, \(J = 7.5\) Hz), 3.42 (1H, dd, \(J = 6.2, 1.2\) Hz), 3.49 (1H, brt, \(J = 7.4\) Hz), 4.03-4.13 (2H, m), 4.83 (1H, d, \(J = 6.2\) Hz), 6.52 (1H, d, \(J = 8.3\) Hz), 6.79 (1H, d, \(J = 7.2\) Hz), 6.85-6.92 (1H, m), 7.00 (1H, t, \(J = 8.1\) Hz), 7.05 (1H, d, \(J = 8.1\) Hz), 7.18-7.24 (1H, m), 7.28-7.34 (1H, m), 7.86 (1H, dd, \(J = 7.8, 1.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.1, 21.8, 34.1, 39.9, 46.6, 61.1, 61.3, 84.0, 116.8, 117.3, 117.5, 112.3, 112.8, 125.1, 127.7, 128.3, 129.1, 136.8, 150.3, 158.3, 166.7, 170.1, 186.3; MS (ESI-TOF) \(m/z\) 495 [M+Na]\(^+\), 497 [M+2+Na]\(^+\); HRMS calcd for C\(_{23}\)H\(_{21}\)BrNaO\(_6\) [M+Na]\(^+\), 495.0419; found, 495.0417. Anal. Calcd for C\(_{23}\)H\(_{21}\)BrO\(_6\): C, 58.37; H, 4.47. Found: C, 58.40; H, 4.94.
5. GTP studies by using carbon acids

*Typical procedure:* Tf₂CHCH₂CHTF₂ 1b (1.43 mg, 2.50 μmol) was added to a solution of methyl methacrylate 19a (500 mg, 5.00 mmol) and KSA 20 (8.7 mg, 50 μmol) in CH₂Cl₂ (4.50 mL) under an argon atmosphere at room temperature. After stirring for 3 h, the polymerization was quenched by adding a small amount of methanol. Aliquots were removed from the reaction mixture to determine the conversion of 19a based on its ¹H NMR spectrum. The reaction mixture was purified by reprecipitated to large amount of n-hexane, followed by drying the product to give the 21a as a white solid. Yield, 495 mg (99 %). SEC (RI): \(M_m/\text{SEC}\), 11,300 g mol⁻¹; \(M_n/M_m\), 1.04.

The GTPs of methyl methacrylate 19a and butyl acrylate 19b in the presence of carbon acid 1a (3.56 mg, 5.0 μmol) or zwitterion 2 (2.63 mg, 5.0 μmol) as an acid catalyst were carried out with KSA 20 or 22 by a similar procedure. These results are summarized in Table S1. Tf₂CHCH₂CHTF₂ 1b nicely promoted desired polymerization in both cases of 19a and 19b (entries 1, 4 and 5), while triple carbon acid 1a did not show a considerable level of catalysis in the GTP of 19a with KSA 20 (entry 2). On the other hand, monomer 19b was polymerized with KSA 22 to give the corresponding polymer 21b in the presence of a catalytic amount of 1a (entry 6). Compared to methacrylate 19a, acrylate 19b has relatively higher reactivity. For this, less effective carbon acid 1a worked as a suitable polymerization catalyst for 19b.

### Table S1. GTP of methyl methacrylate 19a and butyl acrylate 19b

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid (equiv)</th>
<th>KSA</th>
<th>Solvent</th>
<th>Conversion of 19b (%)</th>
<th>(M_m/\text{SEC}) ((\text{g mol}^{-1}))</th>
<th>(M_n/M_m) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 19a</td>
<td>Tf₂CHCH₂CHTF₂ 1b (0.02 equiv)</td>
<td>20</td>
<td>CH₂Cl₂</td>
<td>&gt;99</td>
<td>11,300</td>
<td>1.04</td>
</tr>
<tr>
<td>2 19a</td>
<td>Carbon acid 1a (0.05 equiv)</td>
<td>20</td>
<td>CH₂Cl₂</td>
<td>&lt;1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3 19a</td>
<td>Zwitterion 2 (0.05 equiv)</td>
<td>20</td>
<td>CH₂Cl₂</td>
<td>&lt;1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>4 19b</td>
<td>Tf₂CHCH₂CHTF₂ 1b (0.02 equiv)</td>
<td>20</td>
<td>CH₂Cl₂</td>
<td>77.0</td>
<td>11,400</td>
<td>1.47</td>
</tr>
<tr>
<td>5 19b</td>
<td>Tf₂CHCH₂CHTF₂ 1b (0.02 equiv)</td>
<td>22</td>
<td>toluene</td>
<td>&gt;99</td>
<td>14,400</td>
<td>1.02</td>
</tr>
<tr>
<td>6 19b</td>
<td>Carbon acid 1a (0.02 equiv)</td>
<td>22</td>
<td>toluene</td>
<td>&gt;99</td>
<td>14,500</td>
<td>1.02</td>
</tr>
<tr>
<td>7 19b</td>
<td>Zwitterion 2 (0.05 equiv)</td>
<td>22</td>
<td>toluene</td>
<td>&lt;1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

a Ar atmosphere; 19/KSA/Acid = 100 : 1 : 0.02-0.05, [19]₀ = 1.0 mol L⁻¹.  
Reactivity time; 3 h for GTP of 19a, 5 min for GTP of 19b.  
b Determined by \(^1\)H NMR in CDCl₃.  
c Determined by size exclusion chromatography (SEC) in THF using poly(methyl methacrylate) standards.
6. X-ray crystallographic data

Crystallographic data for the X-ray crystal structure analysis of 7a, 3,3’-syn-14a, 3,3’-syn-14b, 3,3’-syn-15a, 3,3’-syn-15b, 3,3’-syn-16b, 3,3’-anti-16b, 3,2’-anti-17, and 3,2’-anti-18 have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication Nos. CCDC 1440383 (7a), 1440387 (3,3’-syn-14a), 1440388 (3,3’-syn-14b), 1440389 (3,3’-syn-15a), 1440390 (3,3’-syn-15b), 1440391 (3,3’-syn-16b), 1440384 (3,3’-anti-16b), 1440385 (3,2’-anti-17), and 1440386 (3,2’-anti-18). These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement for 7a.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C$<em>{25}$H$</em>{38}$O$_5$Si</strong></td>
<td>$F(000) = 968$</td>
</tr>
<tr>
<td>$M_r = 446.64$</td>
<td>$D_x = 1.178$ Mg m$^{-3}$</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/n$</td>
<td>Mo Kα radiation, $\lambda = 0.71073$ Å</td>
</tr>
<tr>
<td>Hall symbol: $\ -P$ 2yn</td>
<td>Cell parameters from 5017 reflections</td>
</tr>
<tr>
<td>$a = 10.5246$ (7) Å</td>
<td>$\theta = 2.5$–27.5°</td>
</tr>
<tr>
<td>$b = 7.1824$ (5) Å</td>
<td>$\mu = 0.12$ mm$^{-1}$</td>
</tr>
<tr>
<td>$c = 33.424$ (2) Å</td>
<td>$T = 90$ K</td>
</tr>
<tr>
<td>$\beta = 94.7154$ (10°)</td>
<td>Block, colorless</td>
</tr>
<tr>
<td>$V = 2518.0$ (3) Å$^3$</td>
<td>$0.29 \times 0.17 \times 0.06$ mm</td>
</tr>
<tr>
<td>$Z = 4$</td>
<td></td>
</tr>
</tbody>
</table>

Bruker APEXII CCD area detector diffractometer 4464 independent reflections
Radiation source: Bruker TXS fine-focus rotating anode 3789 reflections with $I \geq 2\sigma(I)$
Bruker Helios multilayer confocal mirror $R_{int} = 0.021$
Detector resolution: 8.333 pixels mm$^{-1}$ $\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
phi and o scans $h = -9 \rightarrow 12$
Absorption correction: analytical $k = -8 \rightarrow 7$
Crystal Faces plugin in Bruker APEX2 software $l = -39 \rightarrow 37$

11783 measured reflections

Refinement on $F^2$ Primary atom site location: structure-invariant direct methods

-S24-
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.099$

$S = 1.03$

$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 1.2637P]$

where $P = (F_o^2 + 2F_c^2)/3$

4464 reflections

355 parameters

48 restraints

$\langle \Delta/\sigma \rangle_{\text{max}} < 0.001$

$\Delta_{\text{max}} = 0.26$ e $\text{Å}^{-3}$

$\Delta_{\text{min}} = -0.23$ e $\text{Å}^{-3}$

**Table S3.** Crystal data and structure refinement for 3,3'-syn-14a.

![Crystal structure diagram](image)

C$_{18}$H$_{20}$O$_5$  
$F(000) = 1344$

$M_r = 316.34$

Orthorhombic, $Pca2_1$

Hall symbol:  P 2c -2ac

$a = 25.583$ (3) Å  
$	heta = 2.3$–27.5°

$b = 6.8787$ (8) Å  
$\mu = 0.10$ mm$^{-1}$

$c = 17.4038$ (19) Å  
$T = 90$ K

$V = 3062.7$ (6) Å$^3$

$Z = 8$

$0.20 \times 0.18 \times 0.08$ mm

Bruker APEXII CCD area detector diffractometer  
4775 independent reflections

Radiation source: Bruker TXS fine-focus rotating anode  
4424 reflections with $I > 2\sigma(I)$

Bruker Helios multilayer confocal mirror  
$R_{int} = 0.029$

Detector resolution: 8.333 pixels mm$^{-1}$

$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 1.6^\circ$

phi and o scans  
$h = -30 \rightarrow 27$

Absorption correction: analytical  
$k = -8 \rightarrow 8$

Crystal Faces plugin in Bruker APEX2 software

$T_{\text{min}} = 0.980$, $T_{\text{max}} = 0.992$

14062 measured reflections

Refinement on $F^2$  
Secondary atom site location: difference Fourier map
Least-squares matrix: full

R[F^2 > 2σ(F^2)] = 0.033

H-atom parameters constrained

wR(F^2) = 0.080

w = 1/[σ^2(F_o^2) + (0.0397P)^2 + 0.7653P]

where P = (F_o^2 + 2F_c^2)/3

S = 1.04

(Δ/σ)_{max} = 0.001

4775 reflections

Δ_{max} = 0.16 e Å^-3

417 parameters

Δ_{min} = -0.19 e Å^-3

1 restraint


Primary atom site location: structure-invariant direct Flack parameter: 1.0 (7)

methods

Table S4. Crystal data and structure refinement for 3,3'-syn-14b.

<table>
<thead>
<tr>
<th>C_{18}H_{19}BrO_5</th>
<th>F(000) = 1212</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_r = 395.24</td>
<td>D_x = 1.531 Mg m^-3</td>
</tr>
<tr>
<td>Monoclinic, Pc</td>
<td>Mo Kα radiation, λ = 0.71073 Å</td>
</tr>
<tr>
<td>Hall symbol: P -2yc</td>
<td>Cell parameters from 3963 reflections</td>
</tr>
<tr>
<td>a = 11.3068 (19) Å</td>
<td>( \theta = 3.1-27.1^\circ )</td>
</tr>
<tr>
<td>b = 9.6829 (16) Å</td>
<td>( \mu = 2.42 \text{ mm}^{-1} )</td>
</tr>
<tr>
<td>c = 24.116 (4) Å</td>
<td>( T = 90 \text{ K} )</td>
</tr>
<tr>
<td>( \beta = 103.091 (2)^\circ )</td>
<td>Block, colourless</td>
</tr>
<tr>
<td>( V = 2571.7 (7) \text{ Å}^3 )</td>
<td>( 0.15 \times 0.13 \times 0.06 \text{ mm} )</td>
</tr>
<tr>
<td>( Z = 6 )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bruker APEXII CCD area detector</th>
<th>6361 independent reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation source: Bruker TXS fine-focus rotating anode</td>
<td>5637 reflections with ( I &gt; 2\sigma(I) )</td>
</tr>
<tr>
<td>Bruker Helios multilayer confocal mirror</td>
<td>( R_{int} = 0.031 )</td>
</tr>
<tr>
<td>Detector resolution: 8.333 pixels mm^-1</td>
<td>( \theta_{max} = 25.0^\circ, \theta_{min} = 1.7^\circ )</td>
</tr>
<tr>
<td>phi and ω scans</td>
<td>( h = -12 \rightarrow 13 )</td>
</tr>
</tbody>
</table>
Absorption correction: analytical  
Crystal Faces plugin in Bruker APEX2 software  
k = -9→11  

$T_{\text{min}} = 0.713, \ T_{\text{max}} = 0.868$  
l = -28→15

12184 measured reflections

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.029$  
$wR(F^2) = 0.059$

H-atom parameters constrained  
$w = 1/\left[\sigma^2(F_o^2) + (0.00P)^2\right]$  
where $P = (F_o^2 + 2F_c^2)/3$

$\delta = 0.96$  
$(\Delta \sigma)_{\text{max}} = 0.001$

6361 reflections  
$\Delta \rho_{\text{max}} = 0.49$ e Å$^{-3}$

652 parameters  
$\Delta \rho_{\text{min}} = -0.47$ e Å$^{-3}$

452 restraints


Primary atom site location: structure-invariant direct Flack parameter: -0.001 (6) methods

---

**Table S5.** Crystal data and structure refinement for 3,3'-syn-15a.

<table>
<thead>
<tr>
<th>Formula</th>
<th>$F(000) = 704$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r = 330.37$</td>
<td>$D_x = 1.362 \text{ Mg m}^{-3}$</td>
</tr>
<tr>
<td>Monoclinic, $P2_1/c$</td>
<td>Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å</td>
</tr>
<tr>
<td>Hall symbol: -P 2ywbc</td>
<td>Cell parameters from 3451 reflections</td>
</tr>
<tr>
<td>$a = 15.1059$ (12) Å</td>
<td>$\theta = 2.5–27.6^\circ$</td>
</tr>
<tr>
<td>$b = 7.0831$ (6) Å</td>
<td>$\mu = 0.10$ mm$^{-1}$</td>
</tr>
<tr>
<td>$c = 16.4912$ (13) Å</td>
<td>$T = 90$ K</td>
</tr>
<tr>
<td>$\beta = 114.080$ (1)$^\circ$</td>
<td>Block, colourless</td>
</tr>
<tr>
<td>$V = 1610.9$ (2) Å$^3$</td>
<td>$0.22 \times 0.14 \times 0.07$ mm</td>
</tr>
<tr>
<td>$Z = 4$</td>
<td></td>
</tr>
</tbody>
</table>

Bruker APEXII CCD area detector diffractometer  
2841 independent reflections

-S27-
Radiation source: Bruker TXS fine-focus rotating anode

Bruker Helios multilayer confocal mirror

Detector resolution: 8.333 pixels mm\(^{-1}\)

phi and \(\phi\) scans

Absorption correction: analytical

Crystal Faces plugin in Bruker APEX2 software

\(T_{\text{min}} = 0.979, T_{\text{max}} = 0.993\)

7482 measured reflections

Refinement on \(F^2\)

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

\(R[F^2 > 2\sigma(F^2)] = 0.033\)

Hydrogen site location: inferred from neighbouring sites

\(wR(F^2) = 0.087\)

H-atom parameters constrained

\(S = 1.02\)

\(w = 1/\sigma^2(F_o^2) + (0.0426P)^2 + 0.6685P\]

where \(P = (F_o^2 + 2F_c^2)/3\)

2841 reflections

218 parameters

156 restraints

\(\Delta_f^2\) max = 0.001

\(\Delta_f^2\) min = -0.02 e \(\text{Å}^{-3}\)

Table S6. Crystal data and structure refinement for 3,3'-syn-15b.

![Crystal structure diagram](image)

C\(_{19}\)H\(_{21}\)BrO\(_5\)

\(Z = 4\)

\(M_r = 409.27\)

Triclinic, \(P\overline{1}\)

\(D_x = 1.546 \text{ Mg m}^{-3}\)

Hall symbol: -P 1

Mo K\(\alpha\) radiation, \(\lambda = 0.71073 \text{ Å}\)

\(a = 8.854 (3) \text{ Å}\)

Cell parameters from 4477 reflections

\(b = 14.268 (4) \text{ Å}\)

\(\theta = 2.4–27.4^\circ\)

\(c = 14.396 (4) \text{ Å}\)

\(\mu = 2.37 \text{ mm}^{-1}\)

\(\alpha = 94.289 (4)^\circ\)

\(T = 90 \text{ K}\)

\(\beta = 102.730 (4)^\circ\)

Block, colourless

\(\gamma = 95.207 (4)^\circ\)

0.31 \(\times\) 0.11 \(\times\) 0.05 mm

-S28-
**Table S7.** Crystal data and structure refinement for 3,3’-syn-16b.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C_{20}H_{23}BrO_{5.5}</td>
</tr>
<tr>
<td><strong>Mr</strong></td>
<td>423.29</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2_{1}/n</td>
</tr>
<tr>
<td><strong>Cell dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>12.0177 (12) Å</td>
</tr>
<tr>
<td>b</td>
<td>6.6196 (6) Å</td>
</tr>
<tr>
<td>c</td>
<td>23.898 (2) Å</td>
</tr>
<tr>
<td>α</td>
<td>93.302 (1)°</td>
</tr>
<tr>
<td>V</td>
<td>1758.1 (9) Å³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Radiation</strong></th>
<th><strong>Refinement</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Source: Bruker TXS fine-focus rotating anode</td>
<td></td>
</tr>
<tr>
<td>Detector resolution: 8.333 pixels mm⁻¹</td>
<td></td>
</tr>
<tr>
<td>phi and θ scans</td>
<td>h = -10→10 k = -16→16</td>
</tr>
<tr>
<td>Absorption correction: analytical</td>
<td></td>
</tr>
<tr>
<td>Crystal Faces plugin in Bruker APEX2 software</td>
<td></td>
</tr>
<tr>
<td>T_{min} = 0.528, T_{max} = 0.891</td>
<td>l = -17→17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement on F²</th>
<th>Primary atom site location: structure-invariant direct methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least-squares matrix: full</td>
<td>Secondary atom site location: difference Fourier map</td>
</tr>
<tr>
<td>( R[F² &gt; 2\sigma(F²)] = 0.074 )</td>
<td>Hydrogen site location: inferred from neighbouring sites</td>
</tr>
<tr>
<td>( wR(F²) = 0.199 )</td>
<td>H-atom parameters constrained</td>
</tr>
<tr>
<td>( S = 1.18 )</td>
<td>( w = 1/[(σ²(F_o²) + (0.0009P)² + 30.7076P]/3 )</td>
</tr>
</tbody>
</table>

6156 reflections (\(Δ/σ\))_{max} = 0.001
453 parameters
312 restraints

\(Δ\)_max = 2.06 e Å⁻³
\(Δ\)_min = -0.94 e Å⁻³

**Bruker APEXII CCD area detector diffractometer**

6156 independent reflections

4996 reflections with \( I > 2\sigma(I) \)

**Crystal Faces plugin in Bruker APEX2 software**

- S29 -
V = 1898.0 (3) Å³
Z = 4

Bruker APEXII CCD area detector
diffractometer

Radiation source: Bruker TXS fine-focus rotating anode
Bruker Helios multilayer confocal mirror
Detector resolution: 8.333 pixels mm⁻¹
phi and ω scans
Absorption correction: analytical
Crystal Faces plugin in Bruker APEX2 software

T_min = 0.644, T_max = 0.880

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.023
wR(F²) = 0.056
S = 1.06

3352 reflections
236 parameters
162 restraints

Table S8. Crystal data and structure refinement for 3,3'-anti-16b.

C_{20}H_{23}BrO_{5} F(000) = 872
M_r = 423.29 D_x = 1.559 Mg m⁻³
Monoclinic, P2_1/c Mo Kα radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc Cell parameters from 3254 reflections
a = 7.1552 (8) Å θ = 2.4–27.4°
b = 17.356 (2) Å
\mu = 2.31 mm⁻¹
\[ c = 14.5825 \text{ (17)} \, \text{Å} \quad T = 90 \, \text{K} \]

\[ \beta = 95.177 \text{ (2)}^\circ \quad \text{Block, colourless} \]

\[ V = 1803.5 \text{ (4)} \, \text{Å}^3 \quad 0.13 \times 0.11 \times 0.11 \, \text{mm} \]

\[ Z = 4 \]

**Bruker APEXII CCD area detector diffractometer**

3188 independent reflections

**Radiation source:** Bruker TXS fine-focus rotating anode

2741 reflections with \( I > 2\sigma(I) \)

**Bruker Helios multilayer confocal mirror**

\( R_{int} = 0.027 \)

**Detector resolution:** 8.333 pixels mm\(^{-1} \)

\( \theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 1.8^\circ \)

**phi and o scans**

\( h = -8 \rightarrow 4 \)

**Absorption correction:** analytical

\( k = -20 \rightarrow 20 \)

**Crystal Faces plugin in Bruker APEX2 software**

**Refinement on \( F^2 \)**

Primary atom site location: structure-invariant direct methods

**Least-squares matrix: full**

Secondary atom site location: difference Fourier map

**\( R[F^2 > 2\sigma(F^2)] = 0.029 \)**

Hydrogen site location: inferred from neighbouring sites

**\( wR(F^2) = 0.074 \)**

H-atom parameters constrained

\( S = 1.04 \)

\[ w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.4382P] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

3188 reflections

\( (\Delta/\sigma)_{\text{max}} = 0.001 \)

236 parameters

\( \Delta \rho_{\text{max}} = 0.50 \, \text{e Å}^{-3} \)

162 restraints

\( \Delta \rho_{\text{min}} = -0.37 \, \text{e Å}^{-3} \)

**Table S9.** Crystal data and structure refinement for 3,2’-anti-17.
Orthorhombic, Pca2₁

Hall symbol:  P 2c -2ac

Cell parameters from 5244 reflections

\( a = 34.732 (4) \) Å
\( b = 13.1317 (14) \) Å
\( c = 8.2791 (9) \) Å

\( V = 3776.0 (7) \) Å³

Z = 8

Block, colourless

0.18 × 0.07 × 0.05 mm

Bruker APEXII CCD area detector diffractometer

Radiation source: Bruker TXS fine-focus rotating anode

Bruker Helios multilayer confocal mirror

Detector resolution: 8.333 pixels mm⁻¹

\( \theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 1.2^\circ \)

phi and ω scans

Absorption correction: analytical

Crystal Faces plugin in Bruker APEX2 software

Min. and Max. transmission: 0.983, 0.995

17978 measured reflections

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.033 \)

\( wR(F^2) = 0.075 \)

\( w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.5188P] \)

where \( P = (F_o^2 + 2F_c^2)/3 \)

\( S = 1.00 \)

\( \Delta \sigma \)max = 0.001

6383 reflections

507 parameters

\( \Delta \rho \)max = 0.15 e Å⁻³

\( \Delta \rho \)min = -0.16 e Å⁻³

Table S10. Crystal data and structure refinement for 3,2'-anti-18.

C₁₁H₁₈BrO₆

\( F(000) = 968 \)

\( M_r = 473.31 \)

Monoclinic, P2₁/n

Hall symbol:  -P 2yn

Mo Kα radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 2685 reflections

-C32-
\[ a = 12.6704 (12) \text{ Å} \]
\[ b = 9.7676 (9) \text{ Å} \]
\[ c = 16.2166 (16) \text{ Å} \]
\[ \beta = 97.059 (1)° \]
\[ V = 1991.7 (3) \text{ Å}^3 \]
\[ Z = 4 \]

**Crystallographic Data**

- **Space Group:** Block, colourless
- **Unit Cell Parameters:**
  - \( a = 12.6704 (12) \text{ Å} \)
  - \( b = 9.7676 (9) \text{ Å} \)
  - \( c = 16.2166 (16) \text{ Å} \)
  - \( \beta = 97.059 (1)° \)
- **Cell Volume:** \( V = 1991.7 (3) \text{ Å}^3 \)
- **Temperature:** \( T = 90 \text{ K} \)
- **Absorption Correction:** Analytical

**Instrument Parameters**

- **Diffractometer:** Bruker APEXII CCD area detector
- **Radiation Source:** Bruker TXS fine-focus rotating anode
- **Confocal Mirror:** Bruker Helios multilayer
- **Detector Resolution:** 8.333 pixels mm\(^{-1}\)
- **Max. and Min. Angles:** \( \theta_{\text{max}} = 25.0°, \theta_{\text{min}} = 1.9° \)
- **Scan Mode:** Phi andomega scans
- **Detector:** 3501 independent reflections
- **Reflections:** 3501 independent reflections
- **Data Range:** \( h = -15 \rightarrow 14 \)
- **Crystal Faces:** Software plugin in Bruker APEX2
- **Resolution:** 9184 measured reflections
- **Min. and Max. Values:**
  - \( T_{\text{min}} = 0.802, T_{\text{max}} = 0.921 \)

**Refinement**

- Primary atom site location: structure-invariant direct methods
- Secondary atom site location: difference Fourier map
- Hydrogen site location: inferred from neighbouring sites
- H-atom parameters constrained
- \( R[F^2 > 2\sigma(F^2)] = 0.029 \)
- \( wR(F^2) = 0.063 \)
- \( S = 1.01 \)
- \( w = 1/\sigma^2(F_o^2) + (0.0271P)^2 + 0.658P \)
  - where \( P = (F_o^2 + 2F_c^2)/3 \)
- \( \Delta/\sigma_{\text{max}} = 0.001 \)
- \( \Delta_\text{max} = 0.39 \text{ e Å}^{-3} \)
- \( \Delta_\text{min} = -0.32 \text{ e Å}^{-3} \)
7. $^1$H and $^{13}$C NMR spectra
3,3'-syn-15b

Current Data Parameters
NAME NO-163B-1
EXPED 6
PROCNO 1

F2 - Acquisition Parameters
T1ms 10041279
Tmea 23.90
CHEMST 9.904
PROBND 5.000000 BR
DILANG 600.50
TD 65536
SOLVENT CCl4
RD 20
DF 24378.44 Hz
FDBS 0.962396 Hz
RF 1.522750 Hz
RG 204.49
DW 20.999 ussec
DS 78.7 Hz
DI 0.000000 sec
TO 1

--- CHANNEL F1 ---
POC 130
F1 10.00 ussec
FWM 78.0000000 W
SPL 150.624929 MHz

--- CHANNEL F2 ---
CPOER2 water
POC 18
FWM 90.00 ussec
PLM 16.0000000 W
PLM2 0.0955060 W
PLM3 0.1900000 W
SPL 400.131400 MHz
F2 - Processing parameters
F1 100.627735 MHz
KIN 0
EB 1.00 Hz
GB 0
PC 1.40
8. References


