Copper(I)-Catalyzed Enantioselective Boryl Substitution of Allyl Acylals: An Efficient Approach for Enantioenriched \( \alpha \)-Chiral \( \gamma \)-Acetoxyallylboronates

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1. General and Materials

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Solvents were also purchased from commercial suppliers, distilled, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieve (MS 4Å). NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 spectrometer \(^1\)H: 400 MHz and \(^{13}\)C: 99 MHz). Tetramethylsilane \(^1\)H) and CDCl\(_3\) \(^{13}\)C) were employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t= triplet, q= quartet, quint = quintet, sept = septet, o = octet, m = multiplet. CuCl (ReagentPlus® grade, 224332-25G, ≥99%) and ZnBr\(_2\) (230022-10G, 99.999% trace metal basis) were purchased from Sigma-Aldrich Co. K(O-t-Bu) was purchased from TCI, and used as received. ZnBr\(_2\) was handled in glovebox. Mesitylene and 1,3,5-triisopropylbenzene were used as internal standards to determine
NMR yield. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. HPLC analyses with chiral stationary phase were carried out using a Hitachi LaChrome Elite HPLC system with a L-2400 UV detector. Specific optical rotation was measured with HORIBA SEPA-300. Recycle preparative gel permeation chromatography was conducted with a JAI LC-9101 using CHCl₃ as the eluent. High-resolution mass spectra were recorded at the Instrumental Analysis Division Global Facility Center, Hokkaido University.

2. General Experimental Procedures

A representative procedure for the copper(I)-catalyzed enantioselective boryl substitution of (Z)-1a (Table 1).

CuCl (2.6 mg, 0.026 mmol), (R,R)-BenzP* (7.2 mg, 0.026 mol), bis(pinacolato)diboron (254.8 mg, 1.00 mmol) and K(O-t-Bu) (84.3 mg, 0.75 mmol) were placed in a screw-capped test tube. K(O-t-Bu) was used in a glove box under argon atmosphere. After the vial was sealed with a screw cap containing a teflon-coated rubber septum, the test tube was removed from the glove box and connected to a vacuum/nitrogen manifold through a needle. Then, dry DMI (1.0 ml) was added to the mixture via a syringe with stirring at room temperature. After 15–30 min, acylal (Z)-1a (129.5 mg, 0.5 mmol) was added to the reaction mixture with vigorous stirring at 0 °C. After the completion of the reaction was checked by GLC analysis, the mixture was directly filtered through a short silica-gel column with hexane/EtOAc (90:10) as the eluent. After removal of the solvents under reduced pressure, NMR yield was determined by ¹H NMR analysis of the crude reaction mixture [(S,E)-2a; 79%] by using mesitylene (26.7 mg, 0.22 mmol) as an internal standard. The crude product was purified with flash chromatography (SiO₂, hexane/Et₂O = 100:0 to 90:10) to give the corresponding γ-acetoxyallylboronate (S,E)-2a (84.8 mg, 0.257 mmol, 52% isolated yield).
3. **Preparation of Allyl Acylal Substrates**

The allyl acylal 1k and allyl acetal 3 were synthesized according to the literature procedure.\(^2,3\)

**Preparation of (Z)-5-phenylpent-2-ene-1,1-diyl diacetate [(Z)-1a].\(^1\)**

![Chemical structure of (Z)-1a](image)

Propargyl diacetate was synthesized through the reaction of propargyl aldehyde and acetic anhydride according to the literature procedure.\(^4\) To an oven-dried 50 mL two-neck round bottomed flask, 5-phenylpent-2-yne-1,1-diyl diacetate (1.4353 g, 5.51 mmol) and dry EtOH (13 mL) were charged under nitrogen atmosphere at room temperature. After addition of Me₂NHBH₃ (603.1 mg, 10.2 mmol), Au/TiO₂ (653.5 mg) were added immediately to the solution. After the completion of the reaction was checked by GLC, the mixture was directly filtered through a short silica-gel column with ethyl acetate/hexane (10:90) as the eluent. After removal of the solvents under reduced pressure, the crude product was purified with flash column chromatography (SiO₂, ethyl acetate/hexane, 1:99–6:94) to give the corresponding (Z)-allyl acylal 1a as a colorless liquid (514.9 mg, 1.96 mmol, 36% isolated yield).

\(^1\)H NMR (392 MHz, CDCl₃, δ): 2.05 (s, 6H), 2.55–2.64 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 5.49 (ddt, J = 1.4, 8.3, 11.0 Hz, 1H), 5.76 (dt, J = 7.6, 10.8 Hz, 1H), 7.14–7.30 (m, 5H), 7.38 (d, J = 9.0 Hz, 1H). \(^13\)C NMR (99 MHz, CDCl₃, δ): 20.8 (CH₃), 29.7 (CH₂), 35.3 (CH₂), 86.0 (CH), 123.3 (CH), 125.9 (CH), 128.3 (CH), 128.5 (CH), 136.6 (CH), 141.0 (C), 168.6 (C). HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₅H₁₈O₄Na, 285.10973; found, 285.10964.

**(Z)-But-2-ene-1,1-diyl diacetate [(Z)-1b].**

![Chemical structure of (Z)-1b](image)

\(^1\)H NMR (392 MHz, CDCl₃, δ): 1.84 (dd, J = 1.8, 7.3 Hz, 3H), 2.09 (s, 6H), 5.51 (ddq, J = 1.8, 8.7, 10.6 Hz, 1H), 5.84 (ddq, J = 0.8, 7.1, 10.9 Hz, 1H), 7.48 (dd, J = 0.8, 8.6 Hz, 1H). \(^13\)C NMR (99 MHz, CDCl₃, δ): 13.7 (CH₃), 20.9 (CH₂), 86.0 (CH), 123.8 (CH), 132.5 (CH), 168.7 (C). HRMS-EI (m/z): [M–CH₃]⁺ calcd for C₇H₉O₄, 157.05008; found, 157.05005.
(Z)-Non-2-ene-1,1-diyl diacetate [(Z)-1c].

\[ \text{AcO} - \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{C} - \text{AcO} \]

\((Z)-1c\)

\[ ^1H \text{ NMR (392 MHz, CDCl}_3, \delta): 0.88 (t, J = 6.9 Hz, 3H), 1.21–1.43 (m, 8H), 2.08 (s, 6H), 2.24 (dq, J = 1.4, 7.7 Hz, 2H), 5.48 (ddt, J = 1.5, 8.3, 11.2 Hz, 1H), 5.74 (dt, J = 7.6, 11.8 Hz, 1H), 7.46 (dd, J = 1.0, 8.0 Hz, 1H). \]

\[ ^13C \text{ NMR (99 MHz, CDCl}_3, \delta): 14.0 (CH), 20.8 (CH), 22.5 (CH), 28.0 (CH), 28.8 (CH), 29.2 (CH), 31.6 (CH), 86.1 (CH), 122.7 (CH), 138.2 (CH), 168.6 (C). \]

HRMS-ESI (m/z): [M+Na]^+ calcd for C_{13}H_{22}O_4Na, 265.14103; found, 265.14106.

(Z)-4-Cyclopentylbut-2-ene-1,1-diyl diacetate [(Z)-1d].

\[ \text{AcO} - \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{AcO} \]

\((Z)-1d\)

\[ ^1H \text{ NMR (392 MHz, CDCl}_3, \delta): 1.08–1.19 (m, 2H), 1.45–1.67 (m, 4H), 1.69–1.79 (m, 2H), 1.83 \text{(sex, J = 7.4 Hz, 1H), 2.08 (s, 6H), 2.26 dt, J = 1.7, 7.4 Hz, 2H), 5.50 (ddt, J = 1.5, 8.2, 11.0 Hz, 1H), 5.77 (dt, J = 7.4, 11.5 Hz, 1H), 7.46 (dd, J = 0.8, 8.2 Hz, 1H). \]

\[ ^13C \text{ NMR (99 MHz, CDCl}_3, \delta): 20.8 (CH), 24.9 (CH), 32.1 (CH), 33.9 (CH), 39.7 (CH), 86.1 (CH), 122.8 (CH), 137.4 (CH), 168.6 (C). \]

HRMS-ESI (m/z): [M+Na]^+ calcd for C_{13}H_{20}O_4Na, 263.12538; found, 263.12506.

(Z)-5-[(tert-Butyldimethylsilyl)oxy]pent-2-ene-1,1-diyl diacetate [(Z)-1e].

\[ \text{TBSO} - \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{C} - \text{AcO} \]

\((Z)-1e\)

\[ ^1H \text{ NMR (392 MHz, CDCl}_3, \delta): 0.04 (s, 6H), 0.88 (s, 9H), 2.08 (s, 6H), 2.48 (dq, J = 1.7, 6.6 Hz, 2H), 3.66 (t, J = 6.3 Hz, 2H), 5.57 (ddt, J = 1.5, 8.4, 11.2 Hz, 1H), 5.84 (dt, J = 7.4, 10.8 Hz, 1H), 7.43 (dd, J = 0.6, 8.4 Hz, 1H). \]

\[ ^13C \text{ NMR (99 MHz, CDCl}_3, \delta): -5.4 (CH), 18.2 (C), 20.8 (CH), 25.8 (CH), 31.4 (CH), 62.1 (CH), 86.1 (CH), 124.0 (CH), 134.5 (CH), 168.6 (C). \]

HRMS-ESI (m/z): [M+Na]^+ calcd for C_{15}H_{36}O_5Si, 339.15982; found, 339.16010.

(Z)-5-[(tert-Butyldiphenylsilyl)oxy]pent-2-ene-1,1-diyl diacetate [(Z)-1f].
$^1$H NMR (392 MHz, CDCl$_3$, δ): 1.03 (s, 9H), 2.05 (s, 6H), 2.54 (dq, $J = 1.6$, 13.7 Hz, 2H), 3.71 (t, $J = 6.3$ Hz, 2H), 5.58 (ddt, $J = 1.5$, 8.2, 11.1 Hz, 1H), 5.87 (dt, $J = 7.4$, 11.2 Hz, 1H), 7.34–7.47 (m, 7H), 7.62–7.69 (m, 4H). $^{13}$C NMR (99 MHz, CDCl$_3$, δ): 19.2 (C), 20.9 (CH$_3$), 26.7 (CH$_3$), 31.3 (CH$_2$), 62.9 (CH$_2$), 86.2 (CH), 124.1 (CH), 127.6 (CH), 129.6 (CH), 133.6 (C), 134.7 (CH), 135.5 (CH), 168.6 (C). HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{25}$H$_{32}$O$_5$NaSi, 463.19112; found, 463.19195.

(Z)-Pent-2-ene-1,1,5-triyl triacetate [(Z)-1g].

$^1$H NMR (392 MHz, CDCl$_3$, δ): 2.04 (s, 3H), 2.09 (s, 6H), 2.62 (dq, $J = 1.5$, 6.9 Hz, 2H), 4.11 (t, $J = 6.7$ Hz, 2H), 5.62 (ddt, $J = 1.5$, 8.2, 11.0 Hz, 1H), 5.75 (dt, $J = 7.5$, 11.1 Hz, 1H), 7.43 (dd, $J = 1.2$, 7.8 Hz, 1H). $^{13}$C NMR (99 MHz, CDCl$_3$, δ): 20.8 (CH$_3$), 27.4 (CH$_2$), 63.0 (CH$_2$), 85.9 (CH), 125.3 (CH), 132.7 (CH), 168.6 (C), 170.9 (C). HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{11}$H$_{16}$O$_6$Na, 267.08391; found, 267.08394.

(Z)-4-Methylpent-2-ene-1,1-diyl diacetate [(Z)-1h].

$^1$H NMR (392 MHz, CDCl$_3$, δ): 0.98 (d, $J = 6.7$ Hz, 6H), 2.08 (s, 6H), 2.78–2.93 (m, 1H), 5.37 (dd, $J = 8.2$, 11.0 Hz, 1H), 5.55 (t, $J = 10.6$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H). $^{13}$C NMR (99 MHz, CDCl$_3$, δ): 20.9 (CH$_3$), 22.8 (CH$_3$), 27.5 (CH), 86.2 (CH), 120.3 (CH), 144.9 (CH), 168.6 (C). HRMS-ESI ($m/z$): [M+Na]$^+$ calcd for C$_{10}$H$_{16}$O$_4$Na, 223.09408; found, 223.09427.

(Z)-4,4-Dimethylpent-2-ene-1,1-diyl diacetate [(Z)-1i].

$^1$H NMR (392 MHz, CDCl$_3$, δ): 1.17 (s, 9H), 2.08 (s, 6H), 5.29 (dd, $J = 9.0$, 12.2 Hz, 1H), 5.67 (dd,
\[ J = 1.2, 12.7 \text{ Hz, 1H}, 7.71 (\text{dd, } J = 0.8, 9.0 \text{ Hz, 1H}) \]. \(^{13}\text{C NMR (99 MHz, CDCl}_3, \delta): 20.9 (\text{CH}_3), 30.7 (\text{CH}_3), 34.2 (\text{C}), 85.8 (\text{CH}), 120.6 (\text{CH}), 147.0 (\text{CH}), 168.6 (\text{C}). \] HRMS-ESI (\text{m/z}): [M+Na]^+ calcd for C\(_{11}\)H\(_{18}\)O\(_4\)Na, 237.10973; found, 237.10982.

\((E)\)-Oct-2-ene-1,1-diyi diacetate \([(E)-1j]\).

\((E)\)-Allyl acylal was synthesized from the corresponding \(\alpha,\beta\)-unsaturated aldehyde.\(^2\)

\(^1\text{H NMR (392 MHz, CDCl}_3, *\) indicates signals of the minor isomer, \(\delta): 0.73^* (t, J = 7.1 \text{ Hz, 3H}), 0.89 (t, J = 6.7 \text{ Hz, 3H}), 1.21–1.36 (m, 6H), 1.40 (quint, J = 7.4 \text{ Hz, 2H}), 2.09 (s, 6H), 5.22–5.29^* (m, 1H), 5.35–5.42^* (m, 1H), 5.53 (dd, \(J = 6.5, 15.5 \text{ Hz, 1H}), 6.03 (dt, J = 6.7, 15.3 \text{ Hz, 1H}), 7.10 (d, J = 6.7 \text{ Hz, 1H}), 7.37^* (d, J = 12.5 \text{ Hz, 1H}). \(^{13}\text{C NMR (99 MHz, CDCl}_3, \delta): 13.9 (\text{CH}_3), 20.8 (\text{CH}_3), 21.1^* (\text{CH}_3), 22.3 (\text{CH}_2), 24.6^* (\text{CH}_2), 28.0 (\text{CH}_2), 31.2 (\text{CH}_2), 31.3^* (\text{CH}_2), 31.8 (\text{CH}_2), 34.5^* (\text{CH}_2), 71.2^* (\text{CH}), 89.7 (\text{CH}), 112.8^* (\text{CH}), 123.0 (\text{CH}), 138.2 (\text{CH}), 138.7^* (\text{CH}), 168.6 (\text{C}). \] HRMS-ESI (\text{m/z}): [M+Na]^+ calcd for C\(_{12}\)H\(_{20}\)O\(_4\)Na, 251.12538; found, 251.12566.

4. Characterization of Boryl Substitution Products

\((S,E)\)-5-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl acetate \([(S,E)-2a]\).

The reaction was performed according to the representative procedure with \((Z)-1a\) (129.5 mg, 0.494 mmol) and \(^1\text{H NMR yield of } \((S,E)-2a\) was 79%. The title compound was purified by silica-gel chromatography (Et\(_2\)O:hexane = 0/100 to 10/90). 52% isolated yield (84.8 mg, 0.257 mmol), 95% ee.

\(^1\text{H NMR (392 MHz, CDCl}_3, \delta): 1.25 (s, 12H), 1.63–1.93 (m, 3H), 2.11 (s, 3H), 2.52–2.71 (m, 2H), 5.45 (dd, \(J = 9.4, 12.5 \text{ Hz, 1H}), 7.09 (d, J = 12.2 \text{ Hz, 1H}), 7.13–7.31 (m, 5H). \(^{13}\text{C NMR (99 MHz,} \]
CDCl₃, δ): 20.7 (CH₃), 22.9 (br, B–CH), 24.6 (CH₃), 24.7 (CH₃), 32.8 (CH₂), 35.0 (CH₂), 83.4 (C), 115.4 (CH), 125.6 (CH), 128.2 (CH), 128.4 (CH), 135.2 (CH), 142.3 (C), 168.1 (C). HRMS-EI (m/z): [M⁺] calcd for C₁₀H₁₇BO₄, 329.20387; found, 329.20481. [α]D²² = +5.4 (c 1.0, CHCl₃, 95% ee). The ee value was determined by HPLC analysis [Daicel CHIRALPAK® OD-3, 2-PrOH:hexane = 0.25:99.75, 0.5 mL/min, 40 °C, retention time: 25.44 min (major enantiomer) and 24.83 min (minor enantiomer)].

(S,E)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl acetate [(S,E)-2b].

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{B} & \quad \text{OAc}
\end{align*}
\]

(S,E)-2b

The reaction was performed according to the representative procedure for (Z)-1b (86.4 mg, 0.502 mmol). The title compound was purified by silica-gel chromatography (Et₂O:hexane = 4/96 to 7/93). 80% isolated yield (96.7 mg, 0.403 mmol), 99% ee.

¹H NMR (392 MHz, CDCl₃, δ): 1.11 (d, J = 7.1 Hz, 3H), 1.24 (s, 12H), 1.84 (quint, J = 7.4 Hz, 1H), 2.10 (s, 3H), 5.54 (dd, J = 8.6, 12.5 Hz, 1H), 7.06 (dd, J = 1.4, 12.7 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 15.2 (CH₃), 16.7 (br, B–CH), 20.7 (CH₃), 24.6 (CH₃), 83.4 (C), 117.4 (CH), 134.3 (CH), 168.2 (C). HRMS-EI (m/z): [M⁺] calcd for C₁₂H₂₁BO₄, 239.15692; found, 239.15697. [α]D²⁴ = –19.8 (c 1.0, CHCl₃, 99% ee). To determine the ee value, the C=C bond of the product was hydrogenated with Pd/C, then the boryl group was oxidized with NaBO₃・4H₂O followed by esterification with p-nitro benzoyl chloride. The ee value of the product was determined by HPLC analysis of the corresponding p-nitro benzoyl ester [Daicel CHIRALPAK® OD-3, 2-PrOH:hexane = 1:99, 0.5 mL/min, 40 °C, retention time: 60.99 min (major enantiomer) and 8.22 min (minor enantiomer)].

(S,E)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)non-1-en-1-yl acetate [(S,E)-2c].

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{B} & \quad \text{OAc}
\end{align*}
\]

(S,E)-2c
The reaction was performed according to the representative procedure with (Z)-1c (123.0 mg, 0.508 mmol). The title compound was purified by silica-gel column chromatography (EtOAc:hexane = 1/99 to 5/95). 80% isolated yield (126.0 mg, 0.406 mmol), 98% ee.

1H NMR (392 MHz, CDCl₃, δ): 0.87 (t, J = 6.9 Hz, 3H), 1.18–1.44 (m, 9H), 1.24 (s, 12H), 1.48–1.62 (m, 1H), 1.73 (q, J = 8.2 Hz, 1H), 2.10 (s, 3H), 5.41 (dd, J = 9.8, 12.5 Hz, 1H), 7.06 (dd, J = 1.0, 12.7 Hz, 1H). 13C NMR (99 MHz, CDCl₃, δ): 14.0 (CH₃), 20.7 (CH₃), 22.6 (CH₂), 23.2 (br, B–CH), 24.6 (CH₃), 24.7 (CH₃), 28.8 (CH₂), 29.2 (CH₂), 30.9 (CH₂), 31.7 (CH₂), 83.2 (C), 115.8 (CH), 134.7 (CH), 168.1 (C). HRMS-ESI (m/z): [M]+ calcd for C₁₇H₃₁BO₄, 309.23517; found, 309.23560. [α]D²⁵ = –7.4 (c 1.0, CHCl₃, 98% ee).

The ee value was determined by HPLC analysis [Daicel CHIRALPAK® OZ-3, 2-PrOH:hexane = 0.1:99.9, 0.5 mL/min, 40 °C, retention time: 29.60 min (major enantiomer) and 28.15 min (minor enantiomer). The UV light having wavelength in 220 nm was used to detect the product.]

(S,E)-4-Cyclopentyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl acetate [(S,E)-2d].

The reaction was performed according to the representative procedure with (Z)-1d (121.9 mg, 0.507 mmol). The title compound was purified by silica-gel column chromatography (EtOAc:hexane = 0/100 to 4/96). 76% isolated yield (119.1 mg, 0.386 mmol), 94% ee.

1H NMR (396 MHz, CDCl₃, δ): 0.99–1.13 (m, 2H), 1.24 (s, 12H), 1.38–1.64 (m, 6H), 1.67–1.85 (m, 4H), 2.09 (s, 3H), 5.39 (dd, J = 9.9, 12.3 Hz, 1H), 7.06 (dd, J = 0.8, 12.3 Hz, 1H). 13C NMR (100 MHz, CDCl₃, δ): 20.7 (CH₃), 22.4 (br, B–CH), 24.6 (CH₃), 25.0 (CH₂), 25.2 (CH₂), 32.1 (CH₂), 32.8 (CH₂), 37.1 (CH₂), 39.0 (CH), 83.2 (C), 115.9 (CH), 134.6 (CH), 168.1 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C₁₇H₂₉BO₄Na, 330.20874; found, 330.20889. [α]D²⁷ = +11.4 (c 0.7, CHCl₃, 94% ee). To determine the ee value, the C=C bond of the product was hydrogenated with Pd/C, then the boryl group was oxidized with NaBO₃·4H₂O followed by esterification with p-nitro benzoic chloride. The ee value of the product was determined by HPLC analysis of the corresponding p-nitro benzoyl ester [Daicel CHIRALPAK® OZ-3, 2-PrOH:hexane = 0:99, 0.5 mL/min. 40 °C, retention
time: 69.55 min (major enantiomer) and 135.57 min (minor enantiomer)].

(S,E)-5-[((tert-Butyldimethylsilyl)oxy]-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl acetate [(S,E)-2e].

The reaction was performed according to the representative procedure with (Z)-1e (158.4 mg, 0.501 mmol). The title compound was purified by silica-gel column chromatography (EtOAc:hexane = 2/98 to 4.5/95.5). 77% isolated yield (147.3 mg, 0.383 mmol), 93% ee.

$^1$H NMR (392 MHz, CDCl$_3$, $\delta$): 0.04 (s, 6H), 0.88 (s, 9H), 1.24 (s, 12H), 1.53–1.65 (m, 1H), 1.79 (sex, $J = 6.7$ Hz, 1H), 1.84–1.94 (m, 1H), 2.10 (s, 3H), 3.60 (t, $J = 6.7$ Hz, 2H), 5.40 (dd, $J = 9.8$, 12.5 Hz, 1H), 7.07 (dd, $J = 0.8$, 12.5 Hz, 1H). $^{13}$C NMR (99 MHz, CDCl$_3$, $\delta$): −5.4 (CH$_3$), −5.3 (CH$_3$), 18.3 (C), 19.1 (br, B–CH), 20.7 (CH$_3$), 24.6 (CH$_3$), 24.7 (CH$_3$), 25.9 (CH$_3$), 33.5 (CH$_2$), 61.9 (CH$_2$), 83.3 (C), 115.1 (CH), 135.1 (CH), 168.0 (C). HRMS-EI (m/z): [M–CH$_3$]$^+$ calcd for C$_{18}$H$_{34}$BO$_5$Si, 368.23049; found, 368.23094. $[\alpha]_{D}^{24.4}$ = +5.5 (c 1.0, CHCl$_3$, 93% ee). To determine the ee value, the C=C bond of the product was hydrogenated with Pd/C, then the boryl group was oxidized with NaBO$_2$·4H$_2$O followed by esterification with p-nitro benzoyl chloride. The ee value of the product was determined by HPLC analysis of the corresponding p-nitro benzoyl ester [Daicel CHIRALPAK® OD-3, 2-ProH:hexane = 3:97, 0.5 mL/min. 40 °C, retention time: 17.16 min (major enantiomer) and 19.12 min (minor enantiomer)].

(S,E)-5-[((tert-Butyldiphenylsilyl)oxy]-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl acetate [(S,E)-2f].

The reaction was performed according to the representative procedure with (Z)-1f (221.3 mg, 0.502 mmol) and $^1$H NMR yield of (S,E)-2f was 60%. The title compound was purified by silica-gel
column chromatography (Et₂O:hexane = 5/95 to 7.5/92.5). 11% isolated yield (28.8 mg, 0.0566 mmol), 93% ee.

¹H NMR (392 MHz, CDCl₃, δ): 1.04 (s, 9H), 1.19 (s, 6H), 1.20 (s, 6H), 1.59–1.70 (m, 1H), 1.86 (sex, J = 6.7 Hz, 1H), 1.93–2.02 (m, 1H), 2.09 (s, 3H), 3.65 (t, J = 6.7 Hz, 2H), 5.38 (dd, J = 9.8, 12.5 Hz, 1H), 7.07 (d, J = 12.5 Hz, 1H), 7.32–7.44 (m, 6H), 7.63–7.69 (m, 4H). ¹³C NMR (99 MHz, CDCl₃, δ): 19.2 (CH), 20.7 (CH₃), 24.6 (CH₃), 24.7 (CH₃), 26.8 (CH₃), 33.4 (CH₂), 62.6 (CH₂), 83.4 (C), 115.2 (CH), 127.5 (CH), 129.4 (CH), 133.9 (C), 134.0 (C), 135.1 (CH), 135.5 (CH), 168.0 (C).

The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₂₉H₄₁O₅BNaSi, 530.27448; found, 530.27582. [α]D²⁶.⁴ = +5.7 (c 0.6, CHCl₃, 93% ee). To determine the ee value, the C=C bond of the product was hydrogenated with Pd/C. The ee value of the product was determined by HPLC analysis of the corresponding alkyl boronate. [Daicel CHIRALPAK® OD-3, 2-PrOH:hexane = 0.25:99.75, 0.5 mL/min, 40 °C, retention time: 16.48 min (major enantiomer) and 15.60 min (minor enantiomer)].

(S,E)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1,5-diyldiacetate [(S,E)-2g].

The reaction was performed according to the representative procedure with (Z)-1g (122.9 mg, 0.503 mmol). The title compound was purified by silica-gel column chromatography (EtOAc:hexane = 9/91 to 14/86). 62% isolated yield (96.7 mg, 0.310 mmol), 95% ee.

¹H NMR (392 MHz, CDCl₃, δ): 1.24 (s, 12H), 1.64–1.77 (m, 1H), 1.82–1.96 (m, 2H), 2.04 (s, 3H), 2.10 (s, 3H), 3.98–4.16 (m, 2H), 5.39 (dd, J = 9.6, 12.3 Hz, 1H), 7.09 (d, J = 12.2 Hz, 1H). ¹³C NMR (99 MHz, CDCl₃, δ): 19.6 (br, B–CH), 20.6 (CH₂), 20.9 (CH₃), 24.55 (CH₃), 24.63 (CH₂), 29.4 (CH₂), 63.3 (CH₂), 83.5 (C), 114.3 (CH), 135.4 (CH), 167.9 (C), 171.0 (C). HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₅H₂₅O₆BNa, 334.16727; found, 334.16773. [α]D²⁷.⁶ = +28.6 (c 1.0, CHCl₃, 95% ee). The ee value was determined by HPLC analysis [Daicel CHIRALPAK® AY-3, 2-PrOH:hexane = 5:95, 0.5 mL/min, 40 °C, retention time: 12.12 min (major enantiomer) and 11.05 min (minor enantiomer)].

(S,E)-4-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl acetate

S10
The reaction was performed according to the representative procedure with (Z)-1h (38.6 mg, 0.193 mmol). The title compound was purified by silica-gel column chromatography. 58% isolated yield (29.8 mg, 0.111 mmol), 59% ee.

1H NMR (392 MHz, CDCl3, δ): 0.89 (d, J = 7.1 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 1.24 (s, 12H), 1.52 (dd, J = 7.6, 10.8 Hz, 1H), 1.82 (sept, J = 6.9 Hz, 1H), 2.10 (s, 3H), 5.40 (dd, J = 11.0, 12.1 Hz, 1H), 7.05 (d, J = 12.5 Hz, 1H). 13C NMR (99 MHz, CDCl3, δ): 20.8 (CH3), 21.5 (CH3), 22.3 (CH3), 24.7 (CH3), 29.6 (CH3), 31.5 (br, B–CH), 83.2 (C), 114.3 (CH), 135.3 (CH), 168.1 (C). HRMS-EI (m/z): [M]⁺ calcld for C14H25BO4, 268.18485; found, 268.18509. [α]D²².5 = +20.7 (c 1.0, CHCl3, 59% ee). The ee value was determined by HPLC analysis [Daicel CHIRALPAK® OZ-3, 2-PrOH:hexane = 0.5:99.5, 0.5 mL/min, 40 °C, retention time: 9.87 min (major enantiomer) and 8.97 min (minor enantiomer). The UV light having wavelength in 220 nm was used to detect the product.]

(R,E)-4,4-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl acetate
[(R,E)-2i].

The reaction was performed according to the representative procedure with (Z)-1i (108.1 mg, 0.505 mmol) and 1H NMR yield of (R,E)-2i was 42%. The title compound was purified by silica-gel column chromatography (Et2O:hexane = 2/98 to 10/90). 20% isolated yield (28.6 mg, 0.101 mmol), 55% ee.

1H NMR (392 MHz, CDCl3, δ): 0.94 (s, 9H), 1.24 (s, 12H), 1.54–1.65 (m, 1H), 2.11 (s, 3H), 5.49 (dd, J = 11.4, 12.2 Hz, 1H), 7.02 (d, J = 12.5 Hz, 1H). 13C NMR (99 MHz, CDCl3, δ): 20.8 (CH3), 20.9 (br, B–CH), 24.7 (CH3), 24.8 (CH3), 29.2 (CH3), 32.4 (C), 83.1 (C), 113.6 (CH), 135.4 (CH), 168.1 (C). HRMS-ESI (m/z): [M+Na]⁺ calcld for C15H27O4BNa, 304.19309; found, 304.19284.
$[\alpha]_D^{26.5} = +13.8 \ (c \ 1.0, \ \text{CHCl}_3, \ 55\% \ ee). \ The \ ee \ value \ was \ determined \ by \ HPLC \ analysis \ [\text{Daicel CHIRALPAK® OZ-3, 2-PrOH:hexane = 0.5:99.5, 0.5 mL/min, 40 °C, retention time: 9.22 min (major enantiomer) and 8.63 min (minor enantiomer). The UV light having wavelength in 220 nm was used to detect the product.}].$

$\text{(R,E)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl acetate [(R,E)-2j].}$

The reaction was performed according to the representative procedure with (E)-1j (E/Z 95:5, 111.6 mg, 0.489 mmol). The title compound was purified by silica-gel column chromatography (Et₂O:hexane = 1:99 to 6:94). 81% isolated yield (118.0 mg, 0.398 mmol), 74% ee, E/Z 91:9.

$^1\text{H NMR (392 MHz, CDCl}_3, \ * \ \text{indicates signals of the minor isomer, } \delta): 0.87 (t, J = 6.7 Hz, 3H), 1.14–1.30 (m, 7H), 1.24 (s, 12H), 1.46–1.59 (m, 1H), 1.64–1.77 (m, 1H), 2.10 (s, 2.73H), 2.13* (s, 0.27H), 4.85* (dd, J = 6.3, 9.8 Hz, 0.09H), 5.41 (dd, J = 9.6, 12.3 Hz, 0.91H), 7.01* (d, J = 6.3 Hz, 0.09H), 7.06 (d, J = 12.5 Hz, 0.91H). ^{13}\text{C NMR (99 MHz, CDCl}_3, \ \delta): 14.0 (\text{CH}_3), 20.7 (\text{CH}_3), 22.4 (\text{CH}_2), 23.2 (\text{br, B–CH}), 24.57 (\text{CH}_3), 24.63 (\text{CH}_3), 28.4 (\text{CH}_2), 28.6* (\text{CH}_2), 30.7* (\text{CH}_2), 30.8 (\text{CH}_2), 31.7 (\text{CH}_2), 83.2 (\text{C}), 115.3* (\text{CH}), 115.8 (\text{CH}), 133.4* (\text{CH}), 134.7 (\text{CH}), 168.0 (\text{C}). \ \text{HRMS-EI (m/z): [M]+ calcd for C}_{16}\text{H}_{29}\text{BO}_4, 295.21952; \ \text{found}, 295.22001. \ [\alpha]_D^{27.0} = -14.2 \ (c \ 1.0, \ \text{CHCl}_3, 74\% \ ee). \ To \ determine \ the \ ee \ value, \ the \ C=C \ bond \ of \ the \ product \ was \ hydrogenated \ with \ Pd/C, \ then \ the \ boryl \ group \ was \ oxidized \ with \ NaBO}_3・4\text{H}_2\text{O} \ followed \ by \ esterification \ with \ p$-\text{nitro benzoic chloride. The ee value of the product was determined by HPLC analysis of the corresponding p-nitro benzoate ester [Daicel CHIRALPAK® OD-3, 2-PrOH:hexane = 1.5:98.5, 0.5 mL/min. 40 °C, retention time: 44.13 min (major enantiomer) and 28.69 min (minor enantiomer)].}$

$\text{(E)-3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl acetate [(E)-2k].}$

\[ \text{S12} \]
The reaction was performed according to the representative procedure with 1k (93.2 mg, 0.501 mmol) using Xantphos as a ligand instead of \((R,R)\)-BenzP* and \(^1\)H NMR yield of \((E)\)-2k in 4 h and 24 h were 39% and 49%, respectively. The title compound was purified by silica-gel column chromatography (EtOAc:hexane = 1:99 to 5:95). 3% isolated yield (3.5 mg, 0.0138 mmol).

\(^1\)H NMR (392 MHz, CDCl\(_3\), \(\delta\)): 1.09 (s, 6H), 1.23 (s, 12H), 2.10 (s, 3H), 5.57 (d, \(J = 12.5\) Hz, 1H), 7.03 (d, \(J = 12.5\) Hz, 1H). \(^{13}\)C NMR (99 MHz, CDCl\(_3\), \(\delta\)): 20.8 (CH\(_3\)), 24.1 (CH\(_3\)), 24.6 (CH\(_3\)), 83.4 (C), 123.2 (CH), 133.5 (CH), 168.3 (C). The carbon directly attached to the boron atom was not detected, likely due to quadrupolar relaxation. HRMS-ESI (m/z): \([M+Na]^+\) calcld for C\(_{13}\)H\(_{23}\)O\(_4\)BNa, 276.16179; found, 276.16163.

5. Procedures of Aldehyde Allylations and Characterization of Products

ZnBr\(_2\)-catalyzed allylation of 2-octynal with allylboronate \((S,E)\)-2f in CH\(_2\)Cl\(_2\).

\[
\begin{align*}
\text{TBDPSO} & \quad \text{B(pin)} \quad \text{OAc} \\
(S,E)\text{-2f, 95% ee} & + \quad \text{O} \quad \text{O} \quad \text{OAc} \quad \text{C}_2\text{H}_{11} \\
\text{CH}_2\text{Cl}_2, 0^\circ\text{C}, 8\text{ h} & \quad \text{ZnBr}_2 (15\text{ mol %}) (2\text{ equiv})
\end{align*}
\]

\[
\begin{align*}
\text{TBDPSO} & \quad \text{OAc} \quad \text{O} \quad \text{OAc} \quad \text{C}_2\text{H}_{11} \\
\text{(S)\text{-anti-5} & + \quad \text{OTBDPS} \quad \text{OAc} \quad \text{C}_2\text{H}_{11} \\
\text{(Z)\text{-anti-5}} & \quad (2\text{ equiv})
\end{align*}
\]

68% yield, E/Z 94:6, anti/syn = >95:5, 100% ee

Dry ZnBr\(_2\) (7.0 mg, 15 mol %) was added to a reaction vial sealed with a screw cap containing a silicon-coated rubber septum in the glove box under argon atmosphere. After the reaction vial was removed from the glove box, it was connected to a vacuum/nitrogen manifold through a needle. Dry CH\(_2\)Cl\(_2\) (0.4 mL), \((S,E)\)-2f (97.5 mg, 0.192 mmol) and 2-octynal (50.8 mg, 0.409 mmol) was successively added to the vial using a syringe, and stirred for 10 h at 0 °C. The use of dry ZnBr\(_2\) is necessary for the high stereoselectivity of this aldehyde allylation. The reaction mixture was quenched by a CH\(_2\)Cl\(_2\) solution of triethanolamine (10% v/v, 2.5 mL). The mixture was separated with water and EtOAc, and then extracted three times with EtOAc. The combined organic layer was dried over Na\(_2\)SO\(_4\), filtered and evaporated. The crude product was purified by silica-gel
chromatography (EtOAc:hexane = 11/89 to 14/86) to give the corresponding anti-1,2-diol derivatives as a colorless oil. 68% isolated yield (66.3 mg, 0.131 mmol), 96% ee (100% es) and E/Z = 94:6.

1H NMR (392 MHz, CDCl3, * indicates signals of the minor isomer, δ): 0.89 (t, J = 7.3 Hz, 3H), 1.04 (s, 9H), 1.18–1.40 (m, 4H), 1.42–1.54 (m, 2H), 2.06–2.15 (m, 1H), 2.09 (s, 3H), 2.18 (dt, J = 2.0, 7.1 Hz, 2H), 2.27–2.43 (m, 1.88H), 2.44–2.54* (m, 0.12H), 3.71 (t, J = 6.5 Hz, 2H), 4.17–4.24* (m, 0.06H), 4.38–4.48 (m, 0.94H), 5.31 (q, J = 3.4 Hz, 0.94H), 5.34–5.38* (m, 0.06H), 5.62 (dd, J = 6.9, 15.5 Hz, 1H, Signals of minor isomer are hidden in those of major isomer.), 5.88 (ddt, J = 0.8, 7.1, 14.6 Hz, 1H, Signals of minor isomer are hidden in those of major isomer.), 7.34–7.47 (m, 6H), 7.62–7.70 (m, 4H). 13C NMR (99 MHz, CDCl3, δ): 14.0 (C3H3), 18.6 (C3H2), 19.2 (C), 21.0* (CH3), 21.2 (CH3), 22.1 (CH2), 26.8 (CH3), 28.1 (CH2), 29.7* (CH2), 30.9 (CH2), 31.6* (CH2), 35.8 (CH2), 63.1 (CH2), 63.2* (CH2), 64.6 (CH), 64.8* (CH), 76.8 (CH), 77.2 (C), 87.8 (C), 124.7* (CH), 125.1 (CH), 125.8* (CH), 127.6 (CH), 129.0* (CH), 129.6 (CH), 131.7* (CH), 133.5* (CH), 133.6 (CH), 133.7 (C), 135.5 (CH), 170.2 (C). HRMS-ESI (m/z): [M+Na]+ calcd for C31H42O4NaSi, 529.27446; found, 529.27532. [α]D25 = –3.4 (c 1.0, CHCl3, 96% ee). The ee value and E/Z ratio was determined by HPLC analysis after derivatization to the p-nitrobenzoic acid ester {Daicel CHIRALPAK® OD-3, 2-PrOH:hexane = 0.75:99.25, 0.5 mL/min. 40 °C, retention time: 36.21 min [(E)-anti-5 major enantiomer], 33.68 min [(E)-anti-5 minor enantiomer], and 25.5 min [(Z)-anti-5 major enantiomer]}. Minor enantiomer of (Z)-anti-5 was not detected by HPLC analysis.

6. Deprotection of Acetyl Group in Allylation Product

Deprotection of the acetyl group in the allylation products under acidic condition (Condition A).

(E)-anti-5 (10.9 mg, 0.0215 mmol) was dissolved in MeOH/H2O (4:1) solvent. Sc(OTf)3 (19.7 mg, 0.0400 mmol) was added to the solution and stirred for 24 h at room temperature. Then, the mixture was separated with water and EtOAc, and then extracted with EtOAc for two times. The combined organic layer was dried over MgSO4, filtered and evaporated. The crude mixture was
purified by silica-gel column chromatography (EtOAc: hexane = 10/90 to 25/75) to give the corresponding anti-1,2-diol (E)-anti-6 (7.3 mg, 0.0157 mmol, 73% isolated yield).

**Deprotection of the acetyl group in the allylation products under basic condition**

(Condition B).

(E)-anti-5 (10.7 mg, 0.0211 mmol) was dissolved in MeOH/H2O (9:1) solvent. K2CO3 (6.2 mg, 0.0449 mmol) was added to the solution and stirred for 30 min at rt. Then, the mixture was separated with water and EtOAc, and then extracted with EtOAc for two times. The combined organic layer was dried over MgSO4, filtered and evaporated. The crude mixture was purified by silica-gel column chromatography (EtOAc: hexane = 10/90 to 25/75) and gel-permeation chromatography to give the corresponding anti-1,2-diol (E)-anti-6 (6.0 mg, 0.0129 mmol, 61% isolated yield).

1H NMR (392 MHz, CDCl3, * indicates signals of the minor isomer, δ): 0.89 (t, J = 6.9 Hz, 3H), 1.05 (s, 9H), 1.17–1.40 (m, 5H), 1.44–1.55 (m, 2H), 1.90–2.08 (m, 0.89H), 2.20 (dt, J = 2.0, 7.2 Hz, 2H), 2.34 (q, J = 6.7 Hz, 2H), 3.72 (t, J = 6.7 Hz, 2H), 3.83–3.88* (m, 0.11H), 4.08–4.19 (m, 0.89H), 4.25–4.36 (m, 1.11H), 4.81* (dt, J = 5.1, 9.5 Hz, 0.11H), 5.61 (dd, J = 6.5, 15.5 Hz, 0.89H), 5.65–5.76* (m, 0.11H), 5.82 (dt, J = 7.3, 14.9 Hz, 0.89H), 7.33–7.46 (m, 6H), 7.62–7.69 (m, 4H).

13C NMR (99 MHz, CDCl3, δ): 14.0 (CH3), 18.7 (CH2), 19.2 (C), 22.1 (CH2), 26.8 (CH3), 28.2 (CH2), 31.0 (CH2), 35.8 (CH2), 63.3 (CH2), 66.4 (CH2), 75.2 (CH), 77.2 (C), 88.1 (C), 127.6 (CH), 129.5 (CH), 131.6 (CH), 133.8 (C), 135.6 (CH). HRMS-ESI (m/z): [M+Na]+ calc'd for C29H40O3NaSi, 487.26389; found, 487.26495. [α]D24 = +24.2 (c 0.6, CHCl3, 96% ee). The ee value and the E/Z ratio was determined by HPLC analysis (Daicel CHIRALPAK® OZ-3, 2-ProOH:hexane = 7:93, 0.5 mL/min. 40 °C, retention time: 15.51 min [(E)-anti-6 major enantiomer], 20.71 min [(E)-anti-6 minor enantiomer], and 18.92 min [(Z)-anti-6 major enantiomer]). Minor enantiomer of (Z)-anti-6 was not detected by HPLC analysis.

7. **Proposed Mechanism**
The enantiofacial selective addition of the Cu–B bond of the borylcopper(I) intermediate to the C–C double bond of the allyl acylal A would proceed via the transition state B to give the alkylcopper intermediate C. Subsequent β-acetoxy elimination would afford the optically active γ-acetoxyallylboronate (S,E)-2. The conformation of the allyl acylal A would be fixed due to 1,3-allylic strain. Thus, the substitution reaction via the anti-S_N2’ passway provided the (E)-isomer.

8. References

D-2000 Elite HPLC System Manager Report

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Sample Name: RYO-980_PheEt_OA_O23_0.25% Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.25/99.75 iPrOH/Hexane
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S17
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D-2000 Elite HPLC System Manager Report

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Application(data): Isocratic HPLC Vial Number: 191
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Injection from this vial: 1 of 1 Volume: 10.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Retention Time (min)

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Chrom Type: HPLC Channel : 1

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D-2000 Elite HPLC System Manager Report

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Processed Date and Time: 2016/08/06 23:25
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Sample Description:

Chrom Type: HPLC Channel : 1

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Method Developer: Administrator
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D-2000 Elite HPLC System Manager Report

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D-2000: Isocratic Series: 0342

Processed Date and Time: 2016/08/01 09:32

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Injection from this vial: 1 of 1 Volume: 10.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

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Pump A Solvent C: iPrOH
Pump A Solvent D: EtOH
Method Developer: Administrator

Retention Time (min)

Processing Method: 01/99 iPrOH/Hexane
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Chrom Type: HPLC Channel : 1
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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

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Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.25/99.75 iPrOH/Hexane
Column Type: OD-H 2.0 x 250 mm 5.0 Method Developer: Administrator
Pump A: L-2130 Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0

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S21
Page Indicator: 1 / 4
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/02/01 13:31
Processed Date and Time: 2016/07/30 19:42

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0353\
Processing Method: 99.75 iPrOH/Hexane
System (acquisition): Sys 1 Series: 0353
Application(data): Isocratic HPLC Vial Number: 151
Sample Name: RYO-844_Hex_rac_OZ-3_0.1% Vial Type: UNK
          -220n Volume: 0.5 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

[Graph showing chromatogram]

Processing Method: 99.75 iPrOH/Hexane
Column Type: OD-H 2
Pump A: 1-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Method Developer: Administrator
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0


Page Indicator: 1 / 4
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/01/28 14:40
Processed Date and Time: 2016/08/01 23:07
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0344\n
System (acquisition): Sys 1
Application (data): Isocratic HPLC
Sample Name: RYO-834_Cy_OA_OZ-3_1%
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 01/99 iPrOH/Hexane
Column Type: OD-H 2
Pump A: L-2130
  Pump A Solvent A: Hexane
  Pump A Solvent C: iPrOH
Method Developer: Administrator

Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000: Isocratic Series: 0343  
System: Sys 1
HPLC

Report Name: modified  
System: Sys 1

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/01/28  
11:37
Processed Date and Time: 2016/08/01  
23:09
Reported Date and Time: 2016/08/01  
23:09

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0343\  
Processing Method: 01/99 iPrOH/Hexane

System (acquisition): Sys 1
Series: 0343
Application(data): Isocratic HPLC
Vial Number: 151
Sample Name: RIKO-310_Oy_rac_OZ-3 1%
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 1.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 01/99 iPrOH/Hexane
Column Type: OD-H 2
Method Developer: Administrator
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
**D-2000 Elite HPLC System Manager Report**

**Analyzed Date and Time:** 2016/01/21 17:26  
**Processed Date and Time:** 2016/07/30 19:59  
**Data Path:** C:\WIN32APP\D2000HSM\Isocratic\DATA\0327\  
**Processing Method:** 0.25/99.75 iPrOH/Hexane  
**System (acquisition):** Sys 1  
**Application(data):** Isocratic HPLC  
**Sample Name:** RYO-841_OTBS_OA_OD-3_3%  
**Injection from this vial:** 1 of 1  
**Volume:** 1.0 ul  
**Sample Description:**

Chrom Type: HPLC Channel : 1

![Graph with retention time and intensity](image)

**Processing Method:** 0.25/99.75 iPrOH/Hexane  
**Column Type:** OD-H 2  
**Method Developer:** Administrator  
**Pump A:** L-2130  
  **Pump A Solvent A:** Hexane  
  **Pump A Solvent C:** iPrOH  
**Pump A Solvent B:** 10/90 iPrOH/Hexane  
**Pump A Solvent D:** iPrOH

**Method Description:**

Chrom Type: HPLC Channel : 1  
**Peak Quantitation:** AREA  
**Calculation Method:** AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/01/21 16:44
Processed Date and Time: 2016/07/30 20:00
Reported Date and Time: 2016/07/30 20:00

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0326\DATA\0326
Processing Method: 0.28/99.75 iPrOH/Hexane

System (acquisition): Sys 1, Series: 0326
Application (data): Isocratic HPLC, Vial Number: 175
Sample Name: RYO-839_OTBS_rac_OD-3_3%
Injection from this vial: 1 of 1, Volume: 1.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.28/99.75 iPrOH/Hexane
Column Type: OD-H 2 4
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: iPrOH
Method Developer: Administrator

Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/07 19:04  Reported Date and Time: 2016/08/07 19:46

Processed Date and Time: 2016/08/07 19:46

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0799\DATA\1014_OS1_Pd\C_OA_OD3_0.25% Volume: 40.0 ul

Injection from this vial: 1 of 1

Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.25/99.75 iPrOH/Hexane

Column Type: OD-H 2

Method Developer: Administrator

Pump A: L-2130

Pump A Solvent A: Hexane

Pump A Solvent C: iPrOH

Pump A Solvent B: 10/90 iPrOH/Hexane

Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA

Calculation Method: AREA%

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805535 100.000

Peak rejection level: 0

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/07/05 17:14
Processed Date and Time: 2016/08/07 19:47
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0691 RYO-873 OD3 025\
Processing Method: 0.25/99.75 iPrOH/Hexane

System (acquisition): Sys 1
Application(data): Isocratic HPLC
Sample Name: RYO-873_OSi-Hyd_rac_OD-3_0.25%
Injection from this vial: 1 of 1

Sample Description:

Chrom Type: HPLC Channel : 1

Retention Time (min)

Processing Method: 0.25/99.75 iPrOH/Hexane
Column Type: OD-H 2
Pump A: L-2130
  Pump A Solvent A: Hexane
  Pump A Solvent C: iPrOH
Method Developer: Administrator
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000: Isocratic Series: 0834 RYO-981 Report Name: modified System: Sys 1 c HPLC AY3 5%

D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/13 22:30
Reported Date and Time: 2016/08/13 23:32
Processed Date and Time: 2016/08/13 23:32
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0834 RYO-981 AY3 5%\
Processing Method: 05/95 iPrOH/Hexane - 220nm
System (acquisition): Sys 1 Series: 0834 RYO-981 AY3 5%
Application(data): Isocratic HPLC Vial Number: 111
Sample Name: RYO-981_OAc_OA_AY3-5%220nm Vial Type: UNK
Injection from this vial: 1 of 1 Volume: 10.0 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 05/95 iPrOH/Hexane - 220nm
Column Type: OD-H 2 Method Developer: Administrator
Pump A: L-2130 Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane Pump A Solvent D: iPrOH
Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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3454573 | 100.000 |

Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/13 22:04
Processed Date and Time: 2016/08/13 23:31
Reported Date and Time: 2016/08/13 23:31

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0833 RYO-1000 AY3 5%\n
System (acquisition): Sys 1
Application (data): Isocratic HPLC
Series: 0833 RYO-1000 AY3 5%
Sample Name: RYO-1000_OAc_rac_AY3_5%
Vial Number: 102
220nm
Vial Type: UNK
Injection from this vial: 1 of 1
Volume: 3.0 ul

Sample Description:

Chrom Type: HPLC Channel : 1

Retention Time (min)

Processing Method: 05/95 iPrOH/Hexane - 220nm
Column Type: OD-H 2
Method Developer: Administrator
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: iPrOH

Method Description:

Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/13 14:57
Processed Date and Time: 2016/08/13 15:15
Reported Date and Time: 2016/08/13 15:16

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0827\DATA.4
Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm

System (acquisition): Sys 1 Series: 0827
Application (data): Isocratic HPLC Vial Type: UNK
Sample Name: TAK-1339 1Pr_OA_OZ3 0.5% Volume: 0.5 μl

Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Retention Time (min) vs. Intensity (mV)

Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
Column Type: OD-H 2
Method Developer: Administrator

Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH

Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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822896 100.000

Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/13 14:18
Reported Date and Time: 2016/08/13 15:17
Processed Date and Time: 2016/08/13 15:16
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0826 iPr rac OZ3\nProcessing Method: 0.5/99.5 iPrOH/Hexane - 220nm
System (acquisition): Sys 1 Series: 0826 iPr rac OZ3
Application(data): Isocratic HPLC Vial Number: 102
Sample Name: iPr_borylation_rac_OZ3_0.5 Vial Type: UNK
%220 Volume: 0.5 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
Column Type: OD-H 2 Method Developer: Administrator
Pump A: L-2130 Pump A Solvent A: Hexane Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent C: iPrOH Pump A Solvent D: EtOH
Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA Calculation Method: AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/07/30 02:28
Processed Date and Time: 2016/07/30 08:55
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0770\DATA
Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
System (acquisition): Sys 1 Series: 0770
Application (data): Isocratic HPLC Vial Number: 109
Sample Name: RYO-1005_tBu_OA_OZ-3_0.5% Vial Type: UNK
-220n Volume: 0.5 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel: 1

Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
Column Type: OD-H 2
Pump A: L-2130
   Pump A Solvent A: Hexane
   Pump A Solvent C: iPrOH
   Pump A Solvent D: EtOH
Method Developer: Administrator

Method Description:
Chrom Type: HPLC Channel: 1
Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/06/07   Reported Date and Time: 2016/07/30 13:15
Processed Date and Time: 2016/07/30 08:57
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0606\DATA
Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
System (acquisition): Sys 1   Series: 0606
Application(data): Isocratic HPLC   Vial Number: 191
Sample Name: TAK-tBu-rac-OZ3-0.5%-220   Vial Type: UNK
Injection from this vial: 1 of 1   Volume: 0.5 ul
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.5/99.5 iPrOH/Hexane - 220nm
Column Type: OD-H 2   Method Developer: Administrator
Pump A: L-2130
  Pump A Solvent A: Hexane
  Pump A Solvent C: iPrOH
  Pump A Solvent B: 10/90 iPrOH/Hexane
  Pump A Solvent D: EtOH
Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

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4269375  100.000

Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/03/18 18:47
Processed Date and Time: 2016/08/06 22:13
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0450\ 
Processing Method: 0.75/99.25 iPrOH/Hexane

System (acquisition): Sys 1  
Series: 0450
Application(data): Isocratic HPLC  
Vial Number: 162
Sample Name: RYO-862_crude_Pent_OA_OD-3_1.5  
Vial Type: UNK  
Volume: 0.5 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.75/99.25 iPrOH/Hexane
Column Type: OD-H 2  
Method Developer: Administrator

Pump A: 1.2130
Pump A Solvent A: Hexane
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent C: iPrOH
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/03/18 17:34
Processed Date and Time: 2016/08/06 22:12
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0449\ 
Processing Method: 0.75/99.25 iPrOH/Hexane
System (acquisition): Sys 1 Series: 0449
Application(data): Isocratic HPLC Vial Number: 161
Sample Name: RIKO-100_Pent_rac_OD- Vial Type: UNK
3 1.5% Volume: 0.5 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.75/99.25 iPrOH/Hexane
Column Type: OD-H 2
Pump A: L-2130
   Pump A Solvent A: Hexane
   Pump A Solvent C: iPrOH
Method Developer: Administrator
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH
Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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<tr>
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8578370 100.000

Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/12 15:10
Reported Date and Time: 2016/08/17 17:17

Processed Date and Time: 2016/08/17 17:17

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0824 RYO-1012 OA\nProcessing Method: 0.75/99.25 iPrOH/Hexane

System (acquisition): Sys 1  
Series: 0824 RYO-1012 OA
Application (data): Isocratic HPLC  
Sample Name: RYO-1007_OSiOC_acyl_rac_OD3_75
Vial Number: 101  
Vial Type: UNK
Volume: 1.0 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.75/99.25 iPrOH/Hexane

Column Type: OD-H 2
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Method Developer: Administrator

Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtOH

Method Description:

Chrom Type: HPLC Channel : 1

Peak Quantitation: AREA
Calculation Method: AREA%

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1384253 100.000

Peak rejection level: 0
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/17 16:40  Reported Date and Time: 2016/08/17 17:51
Processed Date and Time: 2016/08/17 17:51
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0852 RYO-1007' rac\ Processing Method: 0.75/99.25 iPrOH/Hexane
System (acquisition): Sys 1 Series: 0852 RYO-1007' rac
Application(data): Isocratic HPLC Vial Number: 123
Sample Name: RYO- Vial Type: UNK
1007.OSiOc_acyl_rac_OD3_75 Volume: 10.0 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 0.75/99.25 iPrOH/Hexane
Column Type: OD-H 2
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Method Developer: Administrator
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: EtoH
Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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5668697  100.000

Peak rejection level: 0

Page Indicator: 1 / 4
D-2000 Elite HPLC System Manager Report

Analyzed Date and Time: 2016/08/15 19:34
Processed Date and Time: 2016/08/16 10:19
Reported Date and Time: 2016/08/16 10:19

Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0846 RYO-997 diol OA\n
System (acquisition): Sys 1
Series: 0846 RYO-997 diol OA
Application (data): Isocratic HPLC
Sample Name: RYO-997 diol K2CO3 OA_OZ3_7%
Vial Number: 97
Vial Type: UNK
Volume: 10.0 ul

Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

Processing Method: 07/93 iPrOH/Hexane
Method Developer: Administrator

Column Type: OD-H 2
Pump A: L-2130
Pump A Solvent A: Hexane
Pump A Solvent C: iPrOH
Pump A Solvent B: 10/90 iPrOH/Hexane
Pump A Solvent D: iPrOH

Method Description:

Chrom Type: HPLC Channel : 1
Peak Quantitation: AREA
Calculation Method: AREA%

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Peak rejection level: 0
**D-2000 Elite HPLC System Manager Report**

Analyzed Date and Time: 2016/08/15 19:02
Reported Date and Time: 2016/08/16 10:15
Processed Date and Time: 2016/08/16 10:14
Data Path: C:\WIN32APP\D2000HSM\Isocratic\DATA\0845 RYO-968 diol OZ\ Processing Method: 07/93 iPrOH/Hexane

System (acquisition): Sys 1 Series: 0845 RYO-968 diol OZ
Application (data): Isocratic HPLC Vial Number: 110
Sample Name: RYO- Vial Type: UNK
968_diol_column_rac_OZ3_7% Volume: 90.0 ul
Injection from this vial: 1 of 1
Sample Description:

Chrom Type: HPLC Channel : 1

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<tr>
<th>No.</th>
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<tbody>
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Total Area: 972821
Peak rejection level: 0
Aco OAc
(21-1b)

X : parts per Million : 13C

S44
TBDPSO

\(\text{A}^\text{OAc}\)

\((\text{E}) - 14\)

\(X\) : parts per Million : 1H

Filename = /Volumes/element_data/RYO/
Author = element
Experiment = single_pulse.ex2
Sample_Id = 969
Solvent = CHLOROFORM-D
Creation_Time = 26-JUL-2016 21:42:34
Revision_Time = 27-JUL-2016 19:03:51
Current_Time = 27-JUL-2016 19:04:11
Comment = single_pulse
Data_Format = ID COMPLEX
Dim_Title = 1H
Dim_Unit = [ppm]
Dimensions = X
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Spectrometer = JNM-ECS400
Field_Strength = 9.20197068[T] (390[MHz])
X_Acq_Duration = 2.288224[s]
X_Domain = 1H
X_Freq = 351.78655441[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Freqscan = 1
X Resolution = 0.44678791[HHz]
X_Sweep = 7.35294118[KHz]
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Xtr_Freq = 351.78655441[MHz]
Xtr_Offset = 5[ppm]
Xtr_Domain = 1H
Xtr_Freq = 351.78655441[MHz]
Xtr_Offset = 5[ppm]
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Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr Gain = 34
Temp_Cal = 20.5[°C]
X 90°_Width = 10.7[us]
X_Acq_Time = 2.288224[s]
X_Angle = 45[deg]
X_Amp = 1.8[db]
X_Pulse = 5.38[us]
Xtr_Mode = Off
Xtr_Mode = Off
Data_Preset = FALSE
Initial_Wait = 1[s]
Repetition_Time = 7.228224[s]

S51
X : parts per Million : 13C
S71
Filename = /Volumes/element_data/RYO/
Author = element
Experiment = single_pulse.ex2
Sample_Id = 54855090
Solvent = CHLOROFORM-D
Creation_Time = 29-JUL-2016 22:44:17
Revision_Time = 2-AUG-2016 14:06:12
Current_Time = 2-AUG-2016 14:06:12
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
Dim_Title = 1H
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Dimensions = X
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Spectrometer = JNM-ECS400
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X_Domain = 1H
X_Offset = 391.76655441[MHz]
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X_Accept = 7.5294118[MHz]
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Irr_Freq = 391.76655441[MHz]
Irr_Offset = 391.76655441[MHz]
Tri_Domain = 1H
Tri_Freq = 391.76655441[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 8
Total_Scans = 8
Relaxation_Delay = 5[s]
Recvr_Gain = 44
Temp_Gat = 20.0[dc]
X_90_Width = 10.7[us]
X_Acq_Time = 2.228224[s]
X_Angle = 45[deg]
X_Atm = 1.9[db]
X_Pulse = 5.35[us]
Irr_Mode = Off
Tri_Mode = Off
Data_Presat = FALSE
InitiEl_Wait = 1[s]
Repetition_Time = 7.228224[s]
X : parts per Million : 1H

S81