Supporting Information

Copper(I)-catalyzed enantioselective hydroboration of cyclopropenes: facile synthesis of optically active cyclopropylboronates

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1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in $\delta$ (ppm) referenced to an internal TMS standard for $^1$H NMR and CDCl$_3$ ($\delta = 7.26$ ppm) for $^{13}$C NMR. Coupling constants ($J$) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A. HRMS of boron-containing compounds is based on $^{10}$B.

2. SUBSTRATE PREPARATION

Cyclopropene 1o was prepared according to the literature procedure.$^{[1]}$

General procedures for the preparation of other cyclopropenes substrates$^{[2-3]}$

\[
\begin{align*}
\text{Ar} & \quad \text{CO}_2\text{Me} \\
\text{TMS} & \quad \text{Rh}_2(\text{OAc})_4 \\
\text{K}_2\text{CO}_3 & \quad \text{THF/H}_2\text{O} \\
0^\circ & \quad \text{C–RT}
\end{align*}
\]

Starting material, methyl diazoarylacetate 11 was prepared according to the literature procedure.$^{[3]}$

A solution of methyl diazoarylacetate (11, 7 mmol, 1.0 equiv) in trimethylsilylacetylene (10 mL) was added via syringe pump over 16 h to a stirred mixture of Rh$_2$(OAc)$_4$ (1 mol%) in trimethylsilylacetylene (5 mL). After the addition was complete, the reaction mixture was stirred at room temperature for additional 12 h. Then the trimethylsilylacetylene was removed under reduced pressure to give the crude product 12.

Crude material 12 was dissolved in THF (15 mL) and stirred at 0°C. 10% aqueous K$_2$CO$_3$ (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 5 h, when the reaction completed. Ethyl acetate (20 mL) and water (20 mL) were added to the mixture, aqueous phase was separated, and the water layer was extracted with ethyl acetate (50 mL $\times$ 3), the combined organic phase was washed by brine (100 mL), dried (MgSO$_4$), filtered, and evaporated. The residue was purified by silica gel column chromatography (eluent: n-hexane / EtOAc = 15:1) to give pure cyclopropene products 1.

Methyl 1-phenylcycloprop-2-enecarboxylate (1a)$^{[3]}$

Light yellow oil, 640 mg, 52% yield for two steps. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.33–7.24 (m, 5H), 7.22 (s, 2H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 175.52, 141.44, 128.16, 128.13, 126.59, 107.68 (2C), 52.25, 30.58 ESI-MS: [M+Na]$^+$ 197.1; HRMS (FTMS-ESI): [M+Na]$^+$ calcld for C$_{11}$H$_{10}$O$_2$Na$^+$ 197.0573, found 197.0565; IR (KBr) $\nu$ (cm$^{-1}$) 3155, 3113, 3058, 3025, 2951, 1724, 1662, 1601, 1495, 1435, 1228, 1113, 1021, 1009, 998, 892, 791, 762, 738, 699.

Methyl 1-p-tolylcycloprop-2-ene carboxylate (1b)

Light yellow oil, 315 mg, 24% yield for two steps. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.20 (s, 2H), 7.17–7.10 (m, 4H), 3.69 (s, 3H), 2.32 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 175.71, 138.50, 136.22, 128.86, 128.03, 107.84 (2C), 52.24, 30.28, 21.05; ESI-MS: [M+Na]\(^+\) 211.1; HRMS (FTMS-ESI): [M+Na]\(^+\) calcd for C\(_{12}\)H\(_{12}\)O\(_2\)Na\(^+\) 211.0730, found 211.0734; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3128, 3088, 3053, 3001, 2948, 2925, 2840, 1710, 1651, 1515, 1434, 1292, 1219, 1033, 1019, 1003, 899, 863, 812, 741, 638, 547.

Methyl 1-(4-methoxyphenyl)cycloprop-2-ene carboxylate (1c)

Yellow oil, 250 mg, 18% yield for two steps. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.21 (s, 2H), 7.18 (d, \(J = 8.8\) Hz, 2H), 6.84 (d, \(J = 8.8\) Hz, 2H), 3.78 (s, 3H), 3.69 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 175.81, 158.25, 133.66, 129.23, 113.57, 107.92 (2C), 55.23, 52.25, 29.92; ESI-MS: [M+Na]\(^+\) 227.1; HRMS (FTMS-ESI): [M+Na]\(^+\) calcd for C\(_{12}\)H\(_{12}\)O\(_2\)Na\(^+\) 227.0679, found 227.0677; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3151, 3109, 3005, 2958, 2840, 1713, 1663, 1611, 1516, 1442, 1436, 1250, 1223, 1119, 926, 829, 806, 771, 626, 550.

Methyl 1-(4-(trifluoromethyl)phenyl)cycloprop-2-ene carboxylate (1d)

Yellow oil, 863 mg, 51% yield for two steps. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.56 (d, \(J = 8.0\) Hz, 2H), 7.39 (d, \(J = 8.0\) Hz, 2H), 7.21 (s, 2H), 3.71 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 174.79, 145.41, 129.02, 128.90, 125.15 (q, \(J_{CF} = 3.8\) Hz), 122.95, 107.24 (2C), 52.47, 30.42; ESI-MS: [M+H]\(^+\) 243.0; HRMS (FTMS-ESI): [M+Na]\(^+\) calcd for C\(_{12}\)F\(_3\)H\(_3\)O\(_2\)Na\(^+\) 265.0447, found 265.0447; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3120, 2955, 1727, 1666, 1618, 1436, 1409, 1327, 1292, 1225, 1165, 1120, 1069, 1014, 872, 833, 796, 767, 606.

Methyl 1-(4-fluorophenyl)cycloprop-2-ene carboxylate (1e)

Yellow oil, 445 mg, 34% yield for two steps. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.26–7.20 (m, 2H), 7.20 (s, 2H), 7.00–6.95 (m, 2H), 3.69 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 175.32, 161.55 (d, \(J_{CF} = 243.7\) Hz), 137.23 (d, \(J_{CF} = 3.8\) Hz), 129.80 (d, \(J_{CF} = 8.3\) Hz, 2C), 114.92 (d, \(J_{CF} = 20.5\) Hz, 2C), 107.67 (2C), 52.30, 29.89; ESI-MS: [M+ Na]\(^+\) 215.1; HRMS (FTMS-ESI): [M+Na]\(^+\) calcd for C\(_{12}\)H\(_9\)F\(_2\)O\(_2\)Na\(^+\) 215.0479, found 215.0488; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3433, 3158, 3117, 2999, 2953, 2844, 1724, 1660, 1604, 1510, 1435, 1293, 1224, 1030, 1006, 870, 832, 625, 544.

Methyl 1-(4-chlorophenyl)cycloprop-2-ene carboxylate (1f)

Light yellow oil, 728 mg, 50% yield for two steps. \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.27 (d, \(J = 8.0\) Hz, 2H), 7.22–7.19 (m, 4H), 3.70 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 175.05, 139.96, 132.37, 129.61, 128.22, 107.42 (2C), 52.32, 29.98; ESI-MS: [M+H]\(^+\) 209.1; HRMS (FTMS-ESI): [M+Na]\(^+\) calcd for C\(_{12}\)H\(_9\)Cl\(_2\)O\(_2\)Na\(^+\) 231.0183, found 231.0186; IR (KBr) \(\nu\) (cm\(^{-1}\)) 3432, 3153, 3114, 2959, 2849, 1725, 1686, 1657, 1488, 1436, 1280, 1236, 1086, 1005, 996, 875, 789, 748, 614, 548, 464.
Methyl 1-(4-bromophenyl)cycloprop-2-ene-carboxylate (1g)

Light yellow oil, 243 mg, 35% yield for two steps. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.42 (d, J = 8.4 Hz, 2H), 7.19 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 174.98, 140.49, 131.16, 129.99, 120.50, 107.36 (2C), 52.33, 30.05; ESI-MS: [M+Na]$^+$ 274.9; HRMS (FTMS-ESI): [M+Na]^+ calcld for C$_{11}$H$_8$BrO$_2$Na$^+$ 274.9678, found 274.9687; IR (KBr) ν (cm$^{-1}$) 3152, 3114, 3043, 3025, 2956, 1725, 1656, 1483, 1436, 1412, 1280, 1237, 1069, 1030, 1005, 897, 876, 788, 746, 718, 612.

Methyl 1-(3-bromophenyl)cycloprop-2-ene-carboxylate (1h)

Light yellow oil, 413 mg, 24% yield for two steps. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.40 (s, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.23–7.14 (m, 4H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 174.80, 143.80, 131.33, 129.68, 129.65, 126.95, 122.16, 107.32 (2C), 52.36, 30.17; ESI-MS: [M+H]^+ 253.0; HRMS (FTMS-ESI): [M+Na]^+ calcld for C$_{11}$H$_8$BrO$_2$Na$^+$ 274.9678, found 274.9671; IR (KBr) ν (cm$^{-1}$) 3157, 3116, 2997, 2950, 2848, 1940, 1724, 1661, 1593, 1564, 1476, 1434, 1223, 1033, 1011, 738, 711, 604.

Methyl 1-(2-bromophenyl)cycloprop-2-ene-carboxylate (1i)

Light yellow oil, 552 mg, 32% yield for two steps. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.54–7.51 (m, 1H), 7.33 (s, 2H), 7.29–7.09 (m, 3H), 3.67 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 175.07, 141.71, 132.60, 130.23, 128.65, 127.63, 125.18, 108.78 (2C), 52.55, 32.31; ESI-MS: [M+Na]^+ 275.0; HRMS (FTMS-ESI): [M+Na]^+ calcld for C$_{11}$H$_8$BrO$_2$Na$^+$ 274.9678, found 274.9683; IR (KBr) ν (cm$^{-1}$) 3430, 3139, 3097, 3065, 2950, 2838, 1731, 1651, 1589, 1466, 1432, 1285, 1225, 1051, 1023, 877, 745, 650, 562.

Methyl 1-(naphthalen-2-yl)cycloprop-2-ene-carboxylate (1j)

Light yellow oil, 564 mg, 36% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.81–7.60 (m, 3H), 7.66 (s, 1H), 7.45–7.41 (m, 3H), 7.29 (s, 2H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 175.60, 139.08, 133.31, 132.28, 127.72, 127.65, 127.59, 126.73, 126.61, 125.99, 125.67, 107.89 (2C), 52.33, 30.77; ESI-MS: [M+H]^+ 225.1; HRMS (FTMS-ESI): [M+H]^+ calcld for C$_{15}$H$_9$O$_2$ 225.0910, found 225.0905; IR (KBr) ν (cm$^{-1}$) 3155, 3114, 3055, 3019, 1950, 1724, 1661, 1631, 1434, 1243, 1214, 1186, 1035, 1013, 818, 749, 635, 613.

Methyl 1-(3,4-dichlorophenyl)cycloprop-2-ene-carboxylate (1k)

Light yellow oil, 300 mg, 20% yield for two steps. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.37–7.35 (m, 2H), 7.18 (s, 2H), 7.14–7.12 (m, 1H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 174.57, 141.88, 130.43, 130.09, 127.84, 107.19 (2C), 52.52, 29.82; ESI-MS: [M+Na]^+ 265.0; HRMS (FTMS-ESI): [M+ Na]^+ calcld for C$_{11}$H$_3$Cl$_2$O$_2$ Na$^+$ 264.9794, found 264.9788; IR (KBr) ν (cm$^{-1}$) 3429, 3160, 3119, 2951, 2848, 1726, 1663, 1471, 1435, 1292, 1252, 1223, 1135, 1031, 887, 813, 741, 616, 598, 440.
Methyl 1-(3,5-difluorophenyl)cycloprop-2-enecarboxylate (1m)

Yellow oil, 350 mg, 23% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.15 (s, 2H), 6.81 (d, $J = 7.2$ Hz, 2H), 6.60 (t, $J = 9.2$ Hz, 1H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 174.30, 164.14, 145.63, 111.36, 106.82 (2C), 102.44, 52.49, 30.19; ESI-MS: [M+H]$^+$ 211.2; HRMS (FTMS-ESI) [M+Na]$^+$ calcd for C$_{11}$H$_8$F$_2$O$_2$Na$^+$ 233.0385, found 233.0377.

Ethyl 1-methylcycloprop-2-enecarboxylate (1n).

Preparation of this cyclopropene used the same procedure with literature.[1]

Dimethyl cycloprop-2-ene-1,1-dicarboxylate (1p).[2]

Light yellow oil, 568 mg, 52% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 6.91 (s, 2H), 3.74 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 171.33, 102.41 (2C), 52.45, 29.83; ESI-MS: [M+Na]$^+$ 179.1; HRMS (FTMS-ESI) [M+Na]$^+$ calcd for C$_7$H$_8$O$_4$Na$^+$ 179.0315, found 179.0312; IR (KBr) $\nu$ (cm$^{-1}$) 3617, 3167, 3122, 3004, 2956, 2847, 1728, 1671, 1436, 1293, 1192, 1143, 1069, 987, 950, 883, 817, 766, 720, 635, 519.

3. X-RAY CRYSTAL STRUCTURE OF 6

Preparation of the crystal: To a one-neck round-bottomed flask was added 30 mg of product 3g, dissolved with 0.5 mL dichloromethane, added 5.0 mL n-hexane. Then the flask was sealed with rubber plug for two weeks to gives the crystal 6. CCDC 1004894 (6) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Colorless crystal, 5 mg. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 7.50–7.28 (m, 6H), 7.21–7.15 (m, 2H), 3.72 (s, 6H), 2.36 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 169.85, 132.20, 131.33, 130.18, 127.85, 122.59, 54.15, 52.55, 30.09.


S6
4. DEUTERATED EXPERIMENT

To probe the 'hydrogen' source of this hydroboration reaction, [D4]-methanol experiment was investigated.

**Procedure:** A dried Schlenk flask was charged with CuCl (1.5 mg, 0.015 mmol, 10 mol%), (R)-(+-)BINAP (14 mg, 0.0225 mmol, 15 mol%), B2Pin2 (2, 76.2 mg, 0.3 mmol, 2.0 equiv), NaOttBu (1.6 mg, 0.0165 mmol, 11 mol%) and anhydrous toluene (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 40 min, a solution of cyclopropene 1f (0.15 mmol) in anhydrous toluene (0.5 mL) was added, followed by anhydrous [D4]-MeOH (12.2 μL, 0.30 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 6h, then filtered through Celite®, and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product 3f. Deuterated product 3f (50%) was observed, which was proved that the proton partially came from methanol.
5. $^1$H nmr, $^{13}$C nmr, Nosey & HPLC
$^{1}$H NMR

Solute: CDCl$_3$
1a (13C NMR)
Solvent: CDCl₃
1b ($^1$H NMR)
Solvent: CDCl$_3$
$1c$ (\textsuperscript{1}H NMR) 
Solvent: CDCl$_3$
$^{13}$C NMR
Solvent: CDCl$_3$
1H NMR
Solvent: CDCl₃

F₃C

CO₂Me

2.02
1.95
2.01

7.565
7.545
7.399
7.379
7.213

3.711

-0.000

2.02
1.95
2.01

8 7 6 5 4 3 2 1 0 PPM
$^{13}$C NMR
Solvent: CDCl$_3$
1e (1H NMR)
Solvent: CDCl₃
S19

1e ($^{13}$C NMR)
Solvent: CDCl$_3$
1f (1H NMR)
Solvent: CDCl₃
1f ($^{13}$C NMR)
Solvent: CDCl$_3$
$^{1}H$ NMR
Solvent: CDCl$_3$
$^{13}$C NMR

Solvent: CDCl$_3$
$1^h$ ($^1$H NMR) Solvent: CDCl$_3$
$1^\text{H} \text{NMR}$
Solvent: CDCl$_3$
S27

$1^1$ ($^{13}$C NMR)

Solvent: CDCl$_3$
$1^J (^{1}H \text{ NMR})$  
Solvent: CDCl$_3$
1k (°H NMR)
Solvent: CDCl₃
$^{13}$C NMR

Solvent: CDCl$_3$
1m $^1$H NMR
Solvent: CDCl$_3$
1H (1H NMR)
Solvent: CDCl₃
$\text{MeO}_2\text{C} = \text{CO}_2\text{Me}$

$1^p\{^1\text{H NMR}\}$

Solvent: CDCl$_3$

S34
MeO₂C—CO₂Me

1p (¹³C NMR)
Solvent: CDCl₃

S35
3a (1H NMR)
Solvent: CDCl₃

5.60

8 7 6 5 4 3 2 1 0 PPM

3.601

1.720 1.712 1.695 1.686 1.674 1.612 1.604 1.289 1.052 0.825

0.000
3b (1H NMR)
Solvent: CDCl₃
3c (1H NMR)
Solvent: CDCl₃
$3c$ ($^{13}$C NMR)

Solvent: CDCl$_3$
$^1$H NMR
Solvent: CDCl$_3$
\[ \text{F}_3\text{C} - \text{CO}_2\text{Me} \]

3d (\(^{13}\text{C}-\text{NMR})

Solvent: CDCl\(_3\)
$3e$ ($^1$H NMR)

Solvent: CDCl$_3$
3e $^{13}$C NMR
Solvent: CDCl$_3$
3f (¹H NMR)
Solvent: CDCl₃
3f (\textsuperscript{13}C NMR)

Solvent: CDCl$_3$
3g (1H NMR)
Solvent: CDCl₃
Sample Name: 20135601qtb-br
Data Collected on: 20135601qtb-br
Archive directory: /home/sloc/date
Sample directory: 20135601qtb-br_20140908_01
Fidfile: NOESY_01

Pulse Sequence: NOESY
Solvent: CDCl3
Date collected on: Sep 3 2014

Temp. 25.0 C / 298.1 K
Operator: sloc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 2856.0 Hz
IR Width 2856.0 Hz
B repetitions
2 x 280 increments

OBSERVE H1, 399.6538482 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.048 sec
FT size 2048 x 2040
Total time 1 hr, 41 min

3g (NOESY)
Solvent: CDCl3
3h (1H NMR)
Solvent: CDCl₃
$\text{Br}$

3h ($^{13}$C NMR)

Solvent: CDCl$_3$
$\text{S55}$

\[ \text{CO}_2\text{Me} \]

$3\_\text{H NMR}$

Solvent: CDCl$_3$
$^{13}$C NMR

Solvent: CDCl$_3$
Sample Name: 20135681gtb-cf3
Data Collected on: Agilent-NMR-vwrsv400
Archive directory: /home/sloc/data
Sample directory: 20135681gtb-cf3_20140664_01
FidFile: NOESY_01
Pulse Sequence: NOESY
Solvent: CDC13
Data collected on: Sep 4 2014

Temp. 25.0 C / 298.1 K
Operator: sloc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4.921.3 Hz
2D Width 4.921.3 Hz
8 repetitions
2 x 256 increments
OBSEVE H1, 399.6538482 MHz
DATA PROCESSING
Gauss apodization 0.869 sec
F1 DATA PROCESSING
Gauss apodization 0.837 sec
FT size 2048 x 2048
Total time 2 hr, 9 min
3k (¹H NMR)
Solvent: CDCl₃
$3k$ (13C NMR)
Solvent: CDCl$_3$
$3^\text{m} \left( ^1H \text{ NMR} \right)$
Solvent: CDCl$_3$
$^{13}$C NMR

Solvent: CDCl$_3$
3\(p\) \(\left( ^1H\text{ NMR}\right) \)

Solvent: CDCl\(_3\)
MeO₂C₃ uphold CO₂Me

3p (¹³C NMR)

Solvent: CDCl₃
$\text{CO}_2\text{Me}$

$\text{Ph}$

$5 \left( ^1H \text{NMR} \right)$

Solvent: CDCl$_3$
5 ($^{13}$C NMR)
Solvent: CDCl$_3$
$6 \left( ^1H \text{ NMR} \right)$

Solvent: CDCl$_3$
$6 \left( ^{13}C \text{NMR} \right)$

Solvent: CDCl$_3$
(1R,2R)-Methyl 1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (3a)
(1R,2R)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-p-tolylcyclopropanecarboxylate (3b)

Results

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(1R,2R)-Methyl 1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3c)

![Chromatogram](04-10.org)

### Results

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![Chromatogram](04-9.org)

### Results

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![Chromatogram](04-54AA.org)

**Results**

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![Chromatogram](04-68AAAA.org)

**Results**

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Results

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Results

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**Chromatogram (01-62.org)**

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**Chromatogram (01-3.org)**

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S74
(1R,2R)-Methyl 1-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3g)

Results

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Results

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(1R,2R)-Methyl 1-(3-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (3h)

Results

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Results

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S76
(1R,2R)-Methyl 1-(2-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (3i)

Results

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Results

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Results

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(1R,2R)-Methyl 1-(3,5-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3m)

**Results**

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**Results**

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<td>3854167.547</td>
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</table>
(R)-Dimethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1,1-dicarboxylate (3p)

Results

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>11.392</td>
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<td></td>
<td>63741.855</td>
<td>2165330.375</td>
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</tbody>
</table>

Results

<table>
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<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
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<td>40943.512</td>
<td>1422573.125</td>
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</tr>
</tbody>
</table>
(1R,2S)-Methyl 1,2-diphenylcyclopropanecarboxylate (5)

![Chromatogram](5-87.org)

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
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</thead>
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![Chromatogram](5-86.org)

<table>
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