Supporting Information

Pd(II)-Catalyzed Asymmetric 1,6-Conjugate Addition of Arylboronic Acids to Meldrum’s Acid-Derived Dienes

Song Chen, Liang Wu, Qihang Shao, Guoqiang Yang,* and Wanbin Zhang*

* Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China. Fax: +86-21-5474-3265; Tel:+86-21-5474-3265; E-mail: gqyang@sjtu.edu.cn; wanbin@sjtu.edu.cn.

CONTENTS

1. General Details S2
2. Preparation of Ligands S2
3. Preparation of Substrates S7
4. Condition Optimization S12
5. General Procedure for Pd-Catalyzed 1,6-Conjugate Addition S14
   5.1 Scope of Substrates S15
   5.2 Scope of Arylboronic Acids S21
6. Transformations S26
7. Single Crystal of Enantioenriched 3qq S29
8. References S31
9. NMR and HPLC Spectra Charts S32
1. General Details

$^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed at the Analysis Center of Shanghai Jiao Tong University. Optical rotations were measured with a SPSI SGW-1 polarimeter. Enantioselectivity was performed on a Shimadzu LC-2010 HPLC system and using Daicel Chiralcel columns with n-hexane/i-propyl alcohol as an eluent. Chiralpak AD-H, Chiralpak OJ-H were purchased from Daicel Chiral Technologies (China) Co., Ltd., and Enantiopak AD was purchased from Guangzhou Research & Creativity Biotechnology Co. Ltd. Column chromatography was performed using 200 – 300 mesh silica gel. Melting points were measured with SGW X-4 micro melting point apparatus. Nitromethane (CH$_3$NO$_2$) was obtained from Sinopham Chemical Reagent Co. Ltd. The other reagents were purchased from Bide Pharmatech Ltd., Adamas-Beta Ltd., Energy Chemical Inc. or J&K Scientific Inc. and used without further purification unless otherwise specified.

2. Preparation of Ligands

**General Procedure for the Synthesis of Ligands In-Pyrox-2~10**

A reported procedure was followed with some modifications to synthesize compound A.$^1$

**Step (a):**

A reported procedure was followed with some modifications.$^1$ To a nitrogen-filled round-bottom flask, A (1 g, 4 mmol, 1.0 equiv.), Pd(PPh)$_3$ (0.230 g, 1.1 mmol, 0.05 equiv.), Cs$_2$CO$_3$ (2.58 g, 8 mmol, 2.0 equiv.) and aryl bromide acid (4.4 mmol, 1.1 equiv.) was added, followed by THF (20 mL) and H$_2$O (5 mL). The round-bottom flask was heated to 90 °C and stirred for 24 h before it was cooled to r.t. The reaction mixture was quenched with water (200 mL), and extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (PE/EA = 1/2) to afford crude compound B, which was used for the next step directly without any further purification.

**Step (b):**

The B and KOH (0.8 g, 14.4 mmol, 3.6 equiv.) were dissolved in EtOH (10 mL), H$_2$O (10 mL) and then heated to 100 °C with stirring for 6 h before it was cooled to r.t.
The mixture was concentrated under vacuum to remove EtOH. The residue was extracted with EtOAc (20 mL × 3). After simple flash silica gel chromatography (PE/EA = 1/2) target crude compound C was obtained, which was used for the next step directly without any further purification.

Step (c):

Compound D (1.1 equiv.) was placed in a 25 mL sealed tube. Compound C (1.0 equiv.) and 2.5 mL DCM (dried before used) was added. The mixture was stirred at 65 °C for 16 h before it was cooled to rt. The product was purified by flash silica gel column chromatography (PE/EA = 1/1, with 1% Et3N) to afford target ligands.

(3aS,8aR)-5-Phenyl-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyrox-2)

Colorless solid, 0.54 g, total yield 21%. M.p. 111-113 °C. 1H NMR (400 MHz, CDCl3) δ 8.71 – 8.65 (s, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.82 (s, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.82 (d, J = 7.6 Hz, 1H), 5.65 – 5.55 (m, 1H), 3.61 – 3.39 (m, 2H).

13C NMR (100 MHz, CDCl3) δ 163.3, 149.7, 146.8, 142.3, 140.9, 138.9, 136.6, 128.7, 127.8, 127.2, 127.1, 125.6, 125.5, 124.3, 124.1, 84.2, 77.1, 39.5. HRMS (ESI) calcd for C21H17N2O ([M+H]+): 313.1341. Found: 313.1342.

(3aS,8aR)-5-(4-Methoxyphenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyrox-3)

Colorless solid, 0.23 g, total yield 27%. M.p. 138-140 °C. 1H NMR (400 MHz, CDCl3) δ 8.68 (d, J = 4.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.73 (t, J = 7.8 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 (dd, J = 8.0, 1.6 Hz, 1H), 7.38 – 7.28 (m, 2H), 6.99 – 6.93 (m, 3H), 5.84 (d, J = 8.0 Hz, 1H), 5.64 – 5.57 (m, 1H), 3.84 (s, 3H), 3.54 (dd, J = 14.0, 6.4 Hz, 1H), 3.47 (dd, J = 14.0, 1.2 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 163.2, 159.1, 149.7, 146.8, 142.2, 140.4, 138.2, 136.6, 133.5, 128.1, 127.4, 125.6, 125.5, 124.1, 123.8, 114.2, 84.3, 77.1, 55.3, 39.4. HRMS (ESI) calced for C22H17N2O2 ([M+H]+): 343.1482, Found: 343.1445.

(3aS,8aR)-2-(Pyridin-2-yl)-5-(4-(trifluoromethyl)phenyl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyrox-4)

Colorless solid, 0.17 g, total yield 25%. M.p. 153-155 °C. 1H NMR (400 MHz, CDCl3) δ 8.74 – 8.70 (m, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.85 (s, 1H), 7.80 – 7.68 (m, 5H), 7.54
(3aS,8aR)-5-[(1,1'-Biphenyl)-4-yl]-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyroxo-5)

Colorless solid, 0.65 g, total yield 27%. M.p. 153-155 °C. 1H NMR (400 MHz, CDCl3) δ 8.72 – 8.69 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.78 – 7.62 (m, 7H), 7.57 (dd, J = 8.0, 1.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.37-7.34 (m, 3H), 5.87 (d, J = 8.0 Hz, 1H), 5.64 (ddd, J = 8.0, 6.4, 2.0 Hz, 1H), 3.59 (dd, J = 18.0, 6.4 Hz, 1H), 3.52 (dd, J = 18.0, 1.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 163.3, 149.7, 146.8, 142.4, 140.7, 140.3, 140.0, 139.8, 139.1, 136.6, 128.8, 127.6, 127.5, 127.3, 127.0, 125.7, 125.6, 124.2, 124.1, 84.3, 77.1, 39.5. HRMS (ESI) calcd for C27H21N2O ([M+H]+): 389.1654, Found: 389.1649.

(3aS,8aR)-5-{4-(tert-Butyl)phenyl}-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyroxo-6)

Colorless solid, 0.47 g, total yield 29%. M.p. 126-128 °C. 1H NMR (400 MHz, CDCl3) δ 8.74 – 8.69 (m, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.84 (s, 1H), 7.77 (td, J = 7.8, 1.8 Hz, 1H), 7.60 – 7.45 (m, 5H), 7.41 – 7.32 (m, 2H), 5.88 (d, J = 8.0 Hz, 1H), 5.64 (ddd, J = 8.0, 6.4, 2.0 Hz, 1H), 3.58 (dd, J = 18.0, 6.4 Hz, 1H), 3.51 (dd, J = 18.0, 1.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 163.2, 150.2, 149.8, 146.0, 142.2, 140.6, 138.6, 138.0, 136.6, 127.6, 126.8, 125.7, 125.6, 124.2, 124.1, 84.2, 77.1, 39.5, 34.5, 31.4. HRMS (ESI) calcd for C27H21N2O ([M+H]+): 369.1961. Found: 369.1962.

(3aS,8aR)-5-{3,5-Dimethylphenyl}-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyroxo-7)

Colorless solid, 0.25 g, total yield 23%. M.p. 116-118 °C. 1H NMR (400 MHz, CDCl3) δ 8.71-8.67 (m, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.74 (td, J = 7.8, 1.6 Hz, 1H), 7.50 (dd, J = 7.8, 1.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.24 (s, 2H), 6.98 (s, 1H), 5.85 (d, J = 8.0 Hz, 1H), 5.62 (ddd, J = 8.2, 6.4, 2.0 Hz, 1H), 3.56 (dd, J = 18.0, 6.4 Hz, 1H), 3.49 (dd, J = 18.0, 2.0 Hz, 1H), 2.37 (s, 6H). 13C NMR (100
Methyl 2-(adamantan-1-yl)phenyl)pentanoate \( \text{(6aR,8aS)} \)-1-(adamantan-1-yl)-2,3-dihydro-1H-indeno[1,2-d]oxazole \( \text{(In-Pyrox-8)} \)

Colorless solid, 0.29 g, total yield 18%. M.p. 166-168 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 8.73 – 8.65 (m, 1H), 8.05 (d, \( J = 8.0 \) Hz, 1H), 7.82 (s, 1H), 7.74 (td, \( J = 7.8, 1.6 \) Hz, 1H), 7.57 (d, \( J = 8.4 \) Hz, 2H), 7.51 (dd, \( J = 8.0, 1.6 \) Hz, 1H), 7.43 (d, \( J = 8.4 \) Hz, 2H), 7.38 – 7.31 (m, 2H), 5.85 (d, \( J = 8.0 \) Hz, 1H), 5.62 (ddd, \( J = 8.0, 6.4, 2.0 \) Hz, 1H), 3.60 – 3.45 (m, 2H), 2.12 (s, 3H), 1.96 (d, \( J = 2.4 \) Hz, 6H), 1.77 (s, 6H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\) \( \delta \) 163.2, 150.5, 149.7, 146.9, 142.2, 140.7, 138.6, 138.0, 136.6, 127.6, 125.6, 125.5, 125.3, 124.2, 124.1, 121.7, 84.3, 77.1, 39.5, 36.8, 36.1, 29.0, 24.9. HRMS (ESI) calcd for C\(_{31}\)H\(_{31}\)N\(_2\)O ([M+H]\(^+\)) : 447.2431, Found: 447.2433.

\( \text{(3aS,8aR)} \)-5-(3,5-Di-tert-butylphenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole \( \text{(In-Pyrox-9)} \)

2-(4-(Adamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane\(^2\) was used instead of the corresponding arylboronic acid. Colorless solid, 0.29 g, total yield 18%. M.p. 166-168 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\) \( \delta \) 8.73 – 8.65 (m, 1H), 8.05 (d, \( J = 8.0 \) Hz, 1H), 7.82 (s, 1H), 7.74 (td, \( J = 7.8, 1.6 \) Hz, 1H), 7.57 (d, \( J = 8.4 \) Hz, 2H), 7.51 (dd, \( J = 8.0, 1.6 \) Hz, 1H), 7.43 (d, \( J = 8.4 \) Hz, 2H), 7.38 – 7.31 (m, 2H), 5.85 (d, \( J = 8.0 \) Hz, 1H), 5.62 (ddd, \( J = 8.0, 6.4, 2.0 \) Hz, 1H), 3.60 – 3.45 (m, 2H), 2.12 (s, 3H), 1.96 (d, \( J = 2.4 \) Hz, 6H), 1.77 (s, 6H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\) \( \delta \) 163.2, 150.5, 149.7, 146.9, 142.2, 140.7, 138.6, 138.0, 136.6, 127.6, 125.6, 125.5, 125.3, 124.2, 124.1, 121.7, 84.3, 77.1, 43.2, 39.5, 36.8, 36.1, 29.0, 24.9. HRMS (ESI) calcd for C\(_{31}\)H\(_{31}\)N\(_2\)O ([M+H]\(^+\)) : 447.2431, Found: 447.2433.
(d, J = 8.0 Hz, 1H), 5.61 (t, J = 6.0 Hz, 1H), 3.54 (dd, J = 18.0, 6.0 Hz, 1H), 3.48 (d, J = 18.0 Hz, 1H), 3.09 (s, 3H), 1.94 – 1.82 (m, 4H), 0.74 (t, J = 7.2 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.2, 149.7, 146.8, 143.3, 142.2, 140.5, 138.9, 138.8, 136.6, 127.6, 127.0, 126.5, 125.6, 125.5, 124.2, 124.1, 84.3, 81.4, 77.1, 49.4, 39.5, 28.2, 7.5. HRMS (ESI) calcd for C$_{27}$H$_{29}$N$_2$O$_2$ ([M+H]$^+$): 413.2229, Found: 413.2234.

Procedure for the Synthesis of Ligand In-Pyrox-1

The procedure for the synthesis of ligand In-Pyrox-1 is almost the same as the general procedure, except the hydrogenation of In-Pyrox-1-E to give In-Pyrox-1-B. To a solution of In-Pyrox-1-E (0.5g, 2.0 mmol, 1.0 equiv.) in ethanol (5 mL), Pd/C (10%, 0.21 g, 0.2 mmol, 0.1 equiv.) was added and the reaction was kept under H$_2$ atmosphere (5 atm) for 10 h at r.t. Then the reaction mixture was filtered through a Celite pad and washed with EtOH (2 × 5 mL). The combined organic layers were added H$_2$O (5 mL) and KOH (0.4 g, 7.2 mmol, 3.6 equiv), heated to 100 °C with stirring for 6 h before it was cooled to rt. The mixture was concentrated under vacuum to remove EtOH. The residue was extracted with EtOAc (20 mL × 3) to give target crude compound C, which was used for the next step directly without any further purification.

(3aS,8aR)-5-Cyclohexyl-2-(pyridin-2-yl)-8,8a-dihydro-3aH-indeno[1,2-d]oxazole (In-Pyrox-1)

Prepared according to the general procedure. Colorless oil, 0.51 g, total yield 28%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (s, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.34 – 7.28 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 5.76 (d, J = 7.6 Hz, 1H), 5.54 (t, J = 7.0 Hz, 1H), 3.47 (dd, J = 18.0, 6.4 Hz, 1H), 3.39 (d, J = 18.0 Hz, 1H), 2.56 (pseudo t, J = 10.0 Hz, 1H), 1.94 – 1.68 (m, 5H), 1.47 – 1.19 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.0, 149.6, 147.4, 146.9, 141.6, 137.2, 136.4, 127.5, 125.4, 125.0, 124.0, 123.8, 84.2, 77.1, 44.4, 39.4, 34.7, 34.4, 26.9, 26.1.
3. Preparation of Substrates

A procedure similar with reported method was used for preparation of substrate 1. In a typical reaction, a solution of TiCl$_4$ (2.1 equiv.) was added dropwise under nitrogen to dry THF at 0 °C, which resulted in a yellow suspension. A solution containing the ketone (1.0 equiv.) and Meldrum’s acid (1.1 equiv.) in dry THF was added dropwise via a syringe to the TiCl$_4$•THF complex. The flask containing the solution of ketone and Meldrum’s acid was rinsed with THF and added to the reaction mixture. Subsequently, pyridine (5.0 equiv.) was added to the reaction mixture dropwise at 0 °C. The reaction was allowed to warm up slowly to room temperature and stirred for 18 hours. The reaction was quenched by the addition of water and diluted with ethyl acetate. After the solid was dissolved, the layers were partitioned. The aqueous layer was extracted with ethyl acetate (2X), and the combined organic layers were washed with NaHCO$_3$ (2X), brine (1X), dried over MgSO$_4$, filtered and concentrated. Purification by either crystallization or flash chromatography (PE/EA = 5/1) provided the alkylidene Meldrum’s acids.

**(E)-2,2-Dimethyl-5-(4-(p-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1a)**
Yellow solid, 1.3 g, total yield 63%. M.p. 143-145 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.32 (d, $J$ = 16.0 Hz, 1H), 7.50 (d, $J$ = 8.0 Hz, 2H), 7.45 (d, $J$ = 16.0 Hz, 1H), 7.20 (d, $J$ = 8.0 Hz, 2H), 2.66 (s, 3H), 2.37 (s, 3H), 1.76 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.4, 162.3, 161.8, 144.4, 141.5, 133.0, 130.0, 128.8, 126.7, 114.0, 103.7, 27.3, 21.8, 18.5. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_4$Na ([M+Na]$^+$): 309.1103, Found: 309.1106.

**(E)-2,2-Dimethyl-5-(4-(o-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1b)**
Yellow solid, 0.9 g, total yield 63%. M.p. 121-123 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.26 (d, $J$ = 16.0 Hz, 1H), 7.77 (d, $J$ = 16.0 Hz, 1H), 7.73 (d, $J$ = 7.2 Hz, 1H), 7.34 – 7.21 (m, 3H), 2.72 (s, 3H), 2.48 (s, 3H), 1.78 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.0, 162.0, 161.4, 141.2, 137.7, 134.4, 130.9, 130.3, 128.6, 126.9, 126.7, 114.4, 103.6, 27.2, 19.8, 18.5. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_4$Na ([M+Na]$^+$): 309.1103, Found: 309.1106.
(E)-2,2-Dimethyl-5-(4-(m-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1c)  
Yellow solid, 1.9 g, total yield 61%. M.p. 143-145 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 16.0$ Hz, 1H), 7.44 (s, 1H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 2.67 (s, 3H), 2.39 (s, 3H), 1.76 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.9, 162.0, 161.6, 144.2, 138.8, 135.4, 131.6, 129.0, 128.9, 127.2, 126.0, 114.2, 103.6, 27.1, 21.4, 18.3. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_4$Na ([M+Na]$^+$): 309.1103, Found: 309.1106.

(1c)

(E)-5-(4-(2-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1d)  
Yellow solid, 2.0 g, total yield 57%. M.p. 151-153 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.39 (d, $J = 16.2$ Hz, 1H), 7.92 (d, $J = 16.2$ Hz, 1H), 7.69 (dd, $J = 7.6$, 1.2 Hz, 1H), 7.42 – 7.31 (m, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 3.91 (s, 3H), 2.69 (s, 3H), 1.75 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 162.2, 161.6, 158.3, 139.0, 132.0, 128.3, 127.5, 124.5, 121.0, 113.7, 111.1, 103.4, 55.6, 27.1, 18.4. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_4$Na ([M+Na]$^+$): 309.1103, Found: 309.1106.

(1d)

(E)-5-(4-(3-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1e)  
Yellow solid, 0.8 g, total yield 57%. M.p. 141-143 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 16.0$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.14 (s, 1H), 6.97 (dd, $J = 8.0$, 2.2 Hz, 1H), 3.87 (s, 3H), 2.69 (s, 3H), 1.78 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.7, 162.0, 161.5, 160.0, 143.7, 136.9, 130.0, 127.7, 121.3, 116.7, 114.5, 113.1, 103.6, 55.4, 27.2, 18.4. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_3$Na ([M+Na]$^+$): 325.1052, Found: 325.1055.

(1e)

(E)-5-(4-(4-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1f)  
Yellow solid, 1.3 g, total yield 67%. M.p. 151-153 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.61 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 16.0$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H), 2.69 (s, 3H), 1.77 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$)
δ 166.4, 161.9, 144.1, 130.4, 128.4, 127.9, 125.3, 114.6, 114.0, 113.0, 103.4, 55.5, 27.1, 18.3. HRMS (ESI) calcd for C₁₇H₁₈O₅Na ([M+Na]+): 325.1052, Found: 325.1055.

(E)-5-(4-(2-Fluorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1g)

Yellow solid, 1.3 g, total yield 67%. M.p. 98-100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, J = 16.2 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 16.2 Hz, 1H), 7.40 (dd, J = 13.4, 6.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.15 – 7.11 (m, 1H), 2.71 (s, 3H), 1.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 161.8, 161.4, 161.2 (d, J = 251.8 Hz), 135.1 (d, J = 4.8 Hz), 132.0 (d, J = 8.8 Hz), 128.9 (d, J = 3.7 Hz), 127.9 (d, J = 2.4 Hz), 124.7 (d, J = 3.6 Hz), 123.6 (d, J = 11.3 Hz), 116.1 (d, J = 21.8 Hz), 115.1, 103.7, 27.2, 18.4. HRMS (ESI) calcd for C₁₇H₁₈O₅FNa ([M+Na]+): 314.0930, Found: 314.0931.

(E)-5-(4-(4-Fluorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1h)

Yellow solid, 1.5 g, total yield 55%. M.p. 159-160 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 16.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.45 (d, J = 16.0 Hz, 1H), 7.16 – 7.09 (m, 2H), 2.69 (s, 3H), 1.78 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 164.1 (d, J = 250.0 Hz), 162.0, 161.5, 142.4, 131.8 (d, J = 3.3 Hz), 130.4 (d, J = 8.5 Hz), 127.2 (d, J = 2.4 Hz), 116.3 (d, J = 21.8 Hz), 114.4, 103.6, 27.2, 18.3. HRMS (ESI) calcd for C₁₇H₁₅O₄FNa ([M+Na]+): 314.0930, Found: 314.0931.

(E)-5-(4-(3-Chlorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1i)

Yellow solid, 1.7 g, total yield 54%. M.p. 131-133 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, J = 16.0 Hz, 1H), 7.60 (s, 1H), 7.53 – 7.49 (m, 1H), 7.39 (d, J = 16.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 2.69 (s, 3H), 1.79 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 161.8, 161.4, 141.8, 137.3, 135.1, 130.3, 130.2, 128.7, 128.2, 126.5, 115.3, 103.8, 27.2, 18.4. HRMS (ESI) calcd for C₁₇H₁₅O₄ClNa ([M+Na]+): 329.0557, Found: 329.0557.

(E)-5-(4-(3-Bromophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1j)

59
Yellow solid, 1.7 g, total yield 56%. M.p. 122-123 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.31 (d, $J = 16.0$ Hz, 1H), 7.75 (t, $J = 1.6$ Hz, 1H), 7.58 – 7.51 (m, 2H), 7.38 (d, $J = 16.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 2.69 (s, 3H), 1.79 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.0, 161.8, 161.3, 141.7, 137.6, 133.2, 131.2, 130.5, 128.7, 126.9, 123.2, 115.3, 103.7, 27.2, 18.4. HRMS (ESI) calcd for C$_{16}$H$_{15}$O$_4$BrNa ([M+Na$^+$]): 373.0051, Found: 373.0055.

$^{(E)}$-5-(4-(3,4-Dichlorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1k)

Yellow solid, 2.1 g, total yield 58%. M.p. 164-165 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, $J = 16.0$ Hz, 1H), 7.69 (d, $J = 1.6$ Hz, 1H), 7.52 – 7.44 (m, 2H), 7.34 (d, $J = 16.0$ Hz, 1H), 2.68 (s, 3H), 1.78 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.6, 161.7, 161.3, 140.5, 135.6, 134.4, 133.4, 131.0, 130.0, 129.1, 127.2, 115.5, 103.8, 27.2, 18.4. HRMS (ESI) calcd for C$_{16}$H$_{14}$O$_4$Cl$_2$Na ([M+Na$^+$]): 363.0167, Found: 363.0175.

$^{(E)}$-2,2-Methyl-5-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1l)

Yellow solid, 1.1 g, total yield 48%. M.p. 123-125 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.38 (d, $J = 16.0$ Hz, 1H), 7.71 (d, $J = 8.6$ Hz, 2H), 7.71 (d, $J = 8.6$ Hz, 2H), 7.44 (d, $J = 16.0$ Hz, 1H), 2.69 (s, 3H), 1.77 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.7, 161.7, 161.3, 140.5, 135.6, 134.4, 133.4, 131.0, 130.0, 129.1, 127.2, 115.8, 103.8, 27.2, 18.4. HRMS (ESI) calcd for C$_{16}$H$_{12}$O$_4$F$_3$Na ([M+Na$^+$]): 363.0820, Found: 363.0822.

$^{(E)}$-5-(4-Cyclohexylbut-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1n)

White solid, 1.7 g, total yield 58%. M.p. 87-89 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, $J = 15.8$, 1.0 Hz, 1H), 6.69 (dd, $J = 15.8$, 7.2 Hz, 1H), 2.54 (s, 3H), 1.85 – 1.73 (m, 5H), 1.75 (s, 6H), 1.36 – 1.14 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.0, 162.1, 161.3, 154.3, 127.8, 113.6, 103.4, 42.3, 32.1, 27.1, 25.9, 25.7, 18.6. HRMS (ESI) calcd for C$_{16}$H$_{20}$O$_4$Na ([M+Na$^+$]): 301.1416, Found: 301.1422.

$^{(E)}$-2,2-Dimethyl-5-(pent-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1n)
White solid, 1.1 g, total yield 45%. M.p. 76-77 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (dq, $J = 15.6, 1.6$ Hz, 1H), 6.82 (dq, $J = 15.6, 6.8$ Hz, 1H), 2.54 (s, 3H), 2.04 (dd, $J = 6.8, 1.6$ Hz, 3H), 1.74 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.2, 162.0, 161.3, 144.2, 131.4, 113.5, 103.5, 27.1, 19.9, 18.5. HRMS (ESI) calcd for C$_{11}$H$_{14}$O$_4$Na ([M+Na]$^+$): 233.0790, Found: 233.0793.

(E)-2,2-Dimethyl-5-(1-phenylpent-1-en-3-ylidene)-1,3-dioxane-4,6-dione (1o)
Prepared according to the general procedure. Yellow solid, 1.7 g, total yield 57%. M.p. 90-92 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 (d, $J = 16.0$ Hz, 1H), 7.69 – 7.59 (m, 2H), 7.49 (d, $J = 16.0$ Hz, 1H), 3.14 (q, $J = 7.6$ Hz, 2H), 1.77 (s, 6H), 1.35 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.1, 161.8, 161.5, 143.4, 135.6, 130.6, 129.0, 128.5, 125.9, 113.8, 103.5, 27.1, 24.4, 15.3. HRMS (ESI) calcd for C$_{17}$H$_{18}$O$_4$Na ([M+Na]$^+$): 309.1103, Found: 309.1098.

(E)-2,2-Dimethyl-5-(4-phenylbut-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1q)
Prepared according to the general procedure. Yellow solid, 5.4 g, yield 74%. M.p. 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, $J = 16.0$ Hz, 1H), 7.62 (dd, $J = 6.5, 2.8$ Hz, 2H), 7.47 (d, $J = 16.0$ Hz, 1H), 7.43 – 7.40 (m, 3H), 2.68 (s, 3H), 1.76 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.8, 162.0, 161.5, 143.8, 135.5, 130.6, 129.0, 128.5, 127.4, 114.4, 103.6, 27.2, 18.4. HRMS (ESI) calcd for C$_{16}$H$_{16}$O$_4$Na ([M+Na]$^+$): 295.0946, Found: 295.0946.

(E)-2,2-Diethyl-5-(4-phenylbut-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1p)
Yellow solid, 1.3 g, total yield 51%. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.40 (d, $J = 16.0$ Hz, 1H), 7.65 – 7.63 (m, 2H), 7.48 (d, $J = 16.0$ Hz, 1H), 7.45 – 7.41 (m, 3H), 2.07 (s, 3H), 2.01 (q, $J = 7.6$ Hz, 4H), 1.07 (t, $J = 7.6$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.5, 162.1, 161.6, 143.6, 135.6, 130.5, 129.0, 128.5, 127.7, 114.6, 107.5, 30.3, 18.5, 7.6. HRMS (ESI) calcd for C$_{18}$H$_{20}$O$_4$Na ([M+Na]$^+$): 323.1259, Found: 323.1265.
4. Condition Optimization

**Table S1. Effects of Solvents**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCE</td>
<td>62</td>
<td>54</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>toluene</td>
<td>trace</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>TFE</td>
<td>85</td>
<td>46</td>
</tr>
<tr>
<td>7</td>
<td>CH$_3$NO$_2$</td>
<td>91</td>
<td>59</td>
</tr>
</tbody>
</table>

$^a$) Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol% ligand and PhB(OH)$_2$ (0.30 mmol) in CH$_3$NO$_2$ (1 mL) at 60 °C for 24 h under an air atmosphere. $^b$) Yield of isolated product. $^c$) The ee values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_{R1}$ = 22.0 min (major), $t_{R2}$ = 23.8 min (minor)].

**Table S2. Effects of Ligands**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph-Nicox</td>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>tBu-Nicox</td>
<td>37</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>iPr-Pyrox</td>
<td>89</td>
<td>26</td>
</tr>
<tr>
<td>4</td>
<td>tBu-Pyrox</td>
<td>40</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>In-Pyrox</td>
<td>91</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>diPh-Pyrox</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>OH-Pyrox</td>
<td>51</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>In-Quinox</td>
<td>47</td>
<td>&lt;5</td>
</tr>
<tr>
<td>9</td>
<td>Binap</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>iPr-Phox</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>11</td>
<td>Ph-Box</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>12</td>
<td>Binnol</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>13</td>
<td>tBu-RuPhox</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>14</td>
<td>tBu-IkedaPhox</td>
<td>NR</td>
<td>--</td>
</tr>
</tbody>
</table>
Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and PhB(OH)$_2$ (0.30 mmol) in CH$_3$NO$_2$ (1 mL) at 60 ºC for 24 h under an air atmosphere. Yield of isolated product. The ee values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_{R1}$ = 22.0 min (major), $t_{R2}$ = 23.8 min (minor)]

Table S3. Effects of Pd Source$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd</th>
<th>Yield (%)$^b$</th>
<th>ee (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(TFA)$_2$</td>
<td>91</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)$_2$</td>
<td>47</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OH)$_2$</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>PdCl$_2$</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>PdBr$_2$</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>PdCl$_2$(CH$_3$CN)$_2$</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>NR</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>Pd$_2$(dba)$_3$</td>
<td>NR</td>
<td>---</td>
</tr>
</tbody>
</table>

Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and PhB(OH)$_2$ (0.30 mmol) in CH$_3$NO$_2$ (1 mL) at 60 ºC for 24 h under an air atmosphere. Yield of isolated product. The ee values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_{R1}$ = 22.0 min (major), $t_{R2}$ = 23.8 min (minor)]

Table S4. Effects of Temperature and Time$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (ºC)</th>
<th>Time (h)</th>
<th>Yield (%)$^b$</th>
<th>ee (%)$^c$</th>
</tr>
</thead>
</table>

S13
Table S5. Second Ligand Optimization

<table>
<thead>
<tr>
<th></th>
<th>R.T.</th>
<th>48</th>
<th>24</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>24</td>
<td>52</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>48</td>
<td>89</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>24</td>
<td>91</td>
<td>59</td>
</tr>
</tbody>
</table>

Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol% ligand and PhB(OH)$_2$ (0.30 mmol) in CH$_3$NO$_2$ (1 mL) at 40 °C for 48 h under an air atmosphere. $^b$ Yield of isolated product. $^c$ The ee values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_R^1 = 50.5$ min (major), $t_R^2 = 56.2$ min (minor)]

5. General Procedure for Pd-Catalyzed 1,6-Conjugate Addition

General procedure: A common test tube (20 cm x 18 mm) was charged with Pd(TFA)$_2$ (6.65 mg, 0.20 mmol, 0.1 equiv) and In-Pyrox-6 (8.8 mg, 0.12 equiv). Unpurified CH$_3$NO$_2$ (2.0 mL) was added. The resulting mixture was stirred at room temperature for 30 min. The substrate (0.2 mmol, 1.0 equiv) and arylboronic acid (0.60
mmol, 3.0 equiv) were then added. The temperature was increased to 40 °C. After stirring for 48 h under an air atmosphere, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on 200-300 mesh silica gel (dried before used) to give the corresponding products.

5.1 Scope of Substrates

(S)-2,2-Dimethyl-5-(4-phenyl-4-(p-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3aa)
Colorless oil, 66 mg, yield 91%, ee = 90%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.28 (m, 4H), 7.22 – 7.08 (m, 5H), 4.38 (t, $J = 8.0$ Hz, 1H), 3.83 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.7, 161.1, 161.0, 143.4, 143.2, 138.6, 129.0, 128.9, 128.7, 128.0, 127.9, 127.1, 125.0, 117.9, 103.7, 50.2, 43.2, 27.0, 26.9, 24.5, 21.7. HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_4$Na ([M+Na$^+$]): 387.1572. Found: 387.1571. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_R1 = 50.5$ min (major), $t_R2 = 56.2$ min (minor)]; [$\alpha$]$^D_{20} = 1.16$ (c = 1.07, CHCl$_3$).

(S)-2,2-Dimethyl-5-(4-phenyl-4-(o-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3ba)
Colorless oil, 65 mg, yield 89%, ee = 90%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.29 (m, 4H), 7.23 – 7.17 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 2H), 4.64 (t, $J = 8.0$ Hz, 1H), 3.84 (dd, $J = 12.8$, 8.0 Hz, 1H), 3.80 (dd, $J = 12.8$, 8.0 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.7, 161.4, 161.3, 143.4, 143.2, 138.6, 129.0, 128.9, 128.7, 128.0, 127.9, 127.1, 125.0, 117.9, 103.7, 50.2, 43.2, 27.0, 26.9, 24.5, 21.7. HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_4$Na ([M+Na$^+$]): 387.1572. Found: 387.1571. HPLC [Daicel Chiralcel AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min. $t_R1 = 16.0$ min (minor), $t_R2 = 19.1$ min (major)]; [$\alpha$]$^D_{20} = 4.25$ (c = 1.02, CHCl$_3$).
(S)-2,2-Dimethyl-5-(4-phenyl-4-(m-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3ca)
Colorless oil, 64 mg, yield 88%, ee = 90%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.28 (m, 4H), 7.23 – 7.16 (m, 2H), 7.10 (s, 1H), 7.09 (d, $J$ = 6.4 Hz, 1H), 7.02 (d, $J$ = 7.6 Hz, 1H), 4.37 (t, $J$ = 8.0 Hz, 1H), 3.85 (dd, $J$ = 12.4, 8.0 Hz, 1H), 3.80 (dd, $J$ = 12.4, 8.0 Hz, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 1.41 (s, 3H), 1.407 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.5, 161.12, 161.07, 143.2, 143.0, 138.4, 128.8, 128.7, 128.5, 127.7, 127.6, 126.8, 124.7, 117.7, 103.5, 50.0, 43.0, 26.8, 26.7, 24.2, 21.5. HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_4$Na ([M+Na]$^+$): 387.1572, Found: 387.1575. HPLC [Enantiopak AD, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min. $t_R$1 = 34.7 min (major), $t_R$2 = 36.9 min (minor)]; [α]$^D_{20}$ = 2.30 (c = 1.04, CHCl$_3$).

(S)-5-(4-(2-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3da)
Colorless oil, 68 mg, yield 89%, ee = 96%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.23 (m, 5H), 7.18 (m, 2H), 6.92 (td, $J$ = 7.6, 0.8 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 4.93 (t, $J$ = 8.0 Hz, 1H), 3.97 (dd, $J$ = 13.2, 8.4 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, $J$ = 13.2, 7.6 Hz, 1H), 2.49 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 178.1, 161.2, 161.1, 156.5, 142.7, 131.6, 128.6, 128.2, 128.1, 127.8, 126.6, 125.5, 117.5, 110.7, 103.4, 55.4, 42.0, 41.9, 26.9, 26.6, 23.6. HRMS (ESI) calcd for C$_{23}$H$_{24}$O$_5$Na ([M+Na]$^+$): 403.1521, Found: 403.1522. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; $t_R$1 = 20.3 min (major), $t_R$2 = 24.4 min (minor)]; [α]$^D_{20}$ = -7.82 (c = 1.15, CHCl$_3$).

(S)-5-(4-(3-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ea)
Colorless oil, 68 mg, yield 89%, ee = 89%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J$ = 4.4 Hz, 4H), 7.24 – 7.11 (m, 2H), 6.87 (d, $J$ = 7.6 Hz, 1H), 6.82 (t, $J$ = 2.4 Hz, 1H), 6.77 (dd, $J$ = 8.0, 2.4 Hz, 1H), 4.38 (t, $J$ = 8.0 Hz, 1H), 3.88 ($J$ = 12.8, 8.4 Hz, 1H), 3.77 (s,
3H), 3.74 (J = 12.8, 8.4 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)) \(\delta 177.3, 161.12, 161.07, 159.8, 144.6, 143.0, 129.8, 128.8, 127.7, 126.9, 120.1, 117.8, 113.5, 112.2, 103.5, 55.2, 49.9, 42.9, 27.1, 26.8, 26.7, 24.2. HRMS (ESI) calcd for C\(_{23}\)H\(_{24}\)O\(_5\)Na ([M+Na]+): 403.1521, Found: 403.1522. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t\_R1 = 23.8 \text{ min} \) (minor), \(t\_R2 = 26.2 \text{ min} \) (major)]; [\(\alpha\)]\(_D\)\(_{20}\) = -7.82 (c = 1.15, CHCl\(_3\)).

**Colorless oil, 69 mg, yield 91%, ee = 92%.** \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)) \(\delta 7.32 – 7.26 \) (m, 4H), 7.21 – 7.18 (m, 3H), 6.83 (d, \(J = 8.4 \text{ Hz} \), 2H), 4.36 (t, \(J = 8.0 \text{ Hz} \), 1H), 3.82 (J = 12.4, 8.0 Hz, 1H), 3.78 (J = 12.4, 8.4 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)) \(\delta 177.7, 161.10, 161.07, 158.4, 143.4, 135.1, 128.8, 128.7, 127.6, 126.8, 117.6, 114.1, 103.5, 55.2, 49.2, 43.3, 26.8, 26.7, 24.2.

HRMS (ESI) calcd for C\(_{23}\)H\(_{24}\)O\(_5\)Na ([M+Na]+): 403.1521, Found: 403.1523. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t\_R1 = 24.5 \text{ min} \) (minor), \(t\_R2 = 35.9 \text{ min} \) (major)]; [\(\alpha\)]\(_D\)\(_{20}\) = -1.99 (c = 1.10, CHCl\(_3\)).

\((S)-5-(4-(2-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ga)\)

Colorless oil, 61 mg, yield 83%, ee = 93%. \(^1\text{H} \text{NMR} \) (400 MHz, CDCl\(_3\)) \(\delta 7.38 – 7.30 \) (m, 5H), 7.24 – 7.16 (m, 2H), 7.11 (td, \(J = 7.6, 1.2 \text{ Hz} \), 1H), 7.05 – 6.97 (m, 1H), 4.80 (t, \(J = 8.0 \text{ Hz} \), 1H), 3.99 (dd, \(J = 12.8, 8.4 \text{ Hz} \), 1H), 3.68 (dd, \(J = 12.8, 7.6 \text{ Hz} \), 1H), 2.46 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H). \(^{13}\text{C} \text{NMR} \) (100 MHz, CDCl\(_3\)) \(\delta 176.9, 161.2\) (d, \(J = 244.0 \text{ Hz} \)), 176.9, 161.02, 160.99, 160.2 (d, \(J = 243.7 \text{ Hz} \)), 141.8, 130.2 (d, \(J = 14.0 \text{ Hz} \)), 128.83 (d, \(J = 9.3 \text{ Hz} \)), 128.82, 128.4 (d, \(J = 8.4 \text{ Hz} \)), 127.9, 127.1, 124.5 (d, \(J = 3.5 \text{ Hz} \)), 117.8, 115.6 (d, \(J = 22.7 \text{ Hz} \)), 103.5, 42.0 (d, \(J = 2.5 \text{ Hz} \)), 41.9, 26.9, 26.7, 24.0. HRMS (ESI) calcd for C\(_{22}\)H\(_{22}\)FO\(_4\) ([M+H]+): 369.1502, Found: 369.1505. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t\_R1 = 17.9 \text{ min} \) (minor), \(t\_R2 = 20.8 \text{ min} \) (major)]; [\(\alpha\)]\(_D\)\(_{20}\) = 2.37 (c = 1.08, CHCl\(_3\)).
(S)-5-(4-(4-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ha)
Colorless oil, 65 mg, yield 88%, ee = 93%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.19 (m, 8H), 6.99 (t, $J$ = 8.6 Hz, 2H), 4.40 (t, $J$ = 8.0 Hz, 1H), 3.79 (d, $J$ = 8.0 Hz, 2H), 2.40 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.2, 161.7 (d, $J$ = 245.6 Hz), 161.02, 160.99, 142.8, 138.9 (d, $J$ = 3.3 Hz), 129.2 (d, $J$ = 21.3 Hz), 103.5, 49.3, 43.2, 26.8, 26.8, 24.4. HRMS (ESI) calcd for C$_{22}$H$_{22}$FO$_4$ ([M+H]$^+$): 369.1502, Found: 369.1504. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; $t_{R1}$ = 51.4 min (major), $t_{R2}$ = 54.2 min (minor)]; [α]$^D_{20}$ = 6.62 (c = 1.04, CHCl$_3$).

(3ia)

(S)-5-(4-(3-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ia)
Colorless oil, 69 mg, yield 90%, ee = 92%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.24 (m, 6H), 7.22 – 7.17 (m, 3H), 4.39 (t, $J$ = 8.0 Hz, 1H), 3.83 (dd, $J$ = 12.8, 8.4 Hz, 1H), 3.75 (dd, $J$ = 12.8, 7.6 Hz, 1H), 2.39 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.8, 161.01, 160.99, 145.2, 142.2, 134.6, 130.1, 129.0, 127.9, 127.8, 127.2, 127.1, 126.0, 117.8, 103.6, 49.7, 42.9, 26.9, 26.8, 24.4. HRMS (ESI) calcd for C$_{22}$H$_{21}$ClO$_4$Na ([M+Na]$^+$): 407.1026, Found: 407.1023. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; $t_{R1}$ = 17.1 min (major), $t_{R2}$ = 20.8 min (minor)]; [α]$^D_{20}$ = 10.96 (c = 1.13, CHCl$_3$).

(3ja)

(S)-5-(4-(3-Bromophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ja)
Colorless oil, 78 mg, yield 91%, ee = 89%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.21 (m, 6H), 7.20 – 7.15 (m, 3H), 4.39 (t, $J$ = 8.0 Hz, 1H), 3.80 (dd, $J$ = 12.8, 8.4 Hz, 1H), 3.72 (dd, $J$ = 12.8, 7.6 Hz, 1H), 2.40 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.8, 160.97, 160.94, 145.5, 142.2, 130.8, 130.3, 130.0, 129.0, 127.8,
127.2, 126.4, 122.8, 117.9, 103.6, 49.7, 42.9, 26.9, 26.8, 24.4. HRMS (ESI) calcd for C$_{22}$H$_{21}$BrO$_4$Na ($[\text{M+Na}]^+$): 451.0521, Found: 451.0528. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; $t_{R1} = 18.2$ min (major), $t_{R2} = 22.3$ min (minor)]; $[\alpha]_{D}^{20} = 8.03$ (c = 1.10, CHCl$_3$).

**$\text{(S)}$-5-(4-(3,4-Dichlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ka)**

Colorless oil, 73 mg, yield 87%, ee = 93%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.29 (m, 4H), 7.26 – 7.21 (m, 3H), 7.15 (dd, $J = 8.2$, 2.2 Hz, 1H), 4.37 (t, $J = 8.0$ Hz, 1H), 3.78 (dd, $J = 12.4$, 8.4 Hz, 1H), 3.73 (dd, $J = 12.4$, 7.6 Hz, 1H), 2.37 (s, 3H), 1.51 (s, 3H), 1.43 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.5, 161.0, 160.9, 143.5, 141.7, 132.7, 130.9, 130.6, 129.6, 129.1, 127.7, 127.4, 127.2, 117.9, 103.6, 49.2, 42.9, 26.9, 26.8, 24.6. HRMS (ESI) calcd for C$_{22}$H$_{20}$ClO$_4$Na ($[\text{M+Na}]^+$): 441.0636, Found: 441.0634. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.5 mL/min; $t_{R1} = 26.3$ min (major), $t_{R2} = 32.2$ min (minor)]; $[\alpha]_{D}^{20} = 8.35$ (c = 1.10, CHCl$_3$).

**$\text{(S)}$-2,2-Dimethyl-5-(4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3la)**

Colorless oil, 76 mg, yield 91%, ee = 90%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.35 – 7.21 (m, 5H), 4.48 (t, $J = 8.0$ Hz, 1H), 3.88 (dd, $J = 12.6$, 7.6 Hz, 1H), 3.79 (dd, $J = 12.6$, 8.4 Hz, 1H), 2.41 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.7, 161.0, 160.9, 147.2, 142.0, 129.2 (q, $J = 32.3$ Hz), 129.0, 128.1, 127.8, 127.3, 125.7 (q, $J = 3.0$ Hz), 124.0 (q, $J = 270.2$ Hz), 117.9, 103.6, 49.8, 42.8, 26.8, 24.4. HRMS (ESI) calcd for C$_{23}$H$_{21}$F$_3$O$_4$Na ($[\text{M+Na}]^+$): 441.1290, Found: 441.1293. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.5 mL/min; $t_{R1} = 46.2$ min (major), $t_{R2} = 56.6$ min (minor)]; $[\alpha]_{D}^{20} = 5.39$ (c = 1.37, CHCl$_3$).

**($R$)-5-(4-Cyclohexyl-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ma)**
Colorless oil, 65 mg, yield 91%, ee = 63%. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.22 (t, \(J = 7.4\) Hz, 2H), 7.16 – 7.09 (m, 1H), 7.07 – 7.02 (m, 2H), 3.88 (t, \(J = 12.2\) Hz, 1H), 3.00 (dd, \(J = 12.8, 4.0\) Hz, 1H), 2.70 (ddd, \(J = 12.0, 8.4, 4.0\) Hz, 1H), 2.30 (s, 3H), 2.04 (d, \(J = 12.8\) Hz, 1H), 1.84 – 1.77 (m, 1H), 1.69 – 1.57 (m, 3H), 1.59 (s, 3H), 1.35 – 1.23 (m, 3H), 1.15 – 0.98 (m, 2H), 1.04 (s, 3H), 0.83 – 0.73 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 179.8, 161.18, 161.16, 142.3, 128.6, 128.2, 126.7, 117.2, 103.3, 51.5, 43.5, 41.0, 31.4, 31.2, 27.4, 26.4, 26.3, 26.0, 24.1. HRMS (ESI) calcd for C\(_{22}\)H\(_{28}\)O\(_4\)Na ([M+Na]+): 380.1964, Found: 380.1968. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t_R1 = 14.9\) min (major), \(t_R2 = 22.2\) min (minor)]; \([\alpha]_{D}^{20} = 7.03\) (c = 1.08, CHCl\(_3\)).

\(\text{(S)}-2,2\)-Dimethyl-5-(5-phenylhexan-3-ylidene)-1,3-dioxane-4,6-dione (3na)

Colorless oil, 53 mg, yield 92%, ee = 74%. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 3.49 (dd, \(J = 12.0, 9.2\) Hz, 1H), 3.25 – 3.16 (m, 1H), 2.35 (s, 3H), 1.67 (s, 3H), 1.38 (d, \(J = 6.8\) Hz, 3H), 1.32 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 178.6, 161.2, 161.0, 145.1, 128.8, 126.9, 126.8, 117.1, 103.4, 46.2, 40.0, 27.4, 26.3, 24.8, 22.7. HRMS (ESI) calcd for C\(_{17}\)H\(_{20}\)O\(_4\)Na ([M+Na]+): 311.1259, Found: 311.1261. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t_R1 = 10.4\) min (major), \(t_R2 = 15.0\) min (minor)]; \([\alpha]_{D}^{20} = 12.64\) (c = 1.09, CHCl\(_3\)).

\(\text{(R)}-2,2\)-Dimethyl-5-(1-phenyl-1-(p-tolyl)pentan-3-ylidene)-1,3-dioxane-4,6-dione (3ob)

Colorless oil, 46 mg, yield 61%, ee = 90%. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.26 (m, 4H), 7.23 – 7.14 (m, 3H), 7.10 (d, \(J = 8.0\) Hz, 1H), 4.33 (t, \(J = 8.0\) Hz, 1H), 3.83 (d, \(J = 8.0\) Hz, 2H), 2.73 (q, \(J = 7.4\) Hz, 2H), 2.30 (s, 3H), 1.394 (s, 3H), 1.386 (s, 3H), 1.24 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 182.1, 161.5, 160.6, 143.4, 140.2, 136.4, 129.5, 128.8, 127.7, 127.6, 117.4, 103.5, 50.0, 39.8, 29.2, 26.7, 26.6, 21.0, 13.3. HRMS (ESI) calcd for C\(_{24}\)H\(_{26}\)O\(_4\)Na ([M+Na]+): 379.1909, Found: 379.1915. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t_R1 = 47.4\) min (minor), \(t_R2 = 53.4\) min (major)]; \([\alpha]_{D}^{20} = 12.64\) (c = 1.09, CHCl\(_3\)).
(R)-2,2-Diethyl-5-(4-phenyl-4-(p-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3pb)

Colorless oil, 48 mg, yield 61%, ee = 91%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.27 (m, 4H), 7.25 – 7.17 (m, 3H), 7.13 – 7.10 (m, 2H) 4.39 (t, $J = 8.0$ Hz, 1H), 3.83 (dd, $J$ = 12.8, 8.0 Hz, 1H), 3.79 (dd, $J = 12.8$, 8.0 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.74 – 1.54 (m, 4H), 0.94 (t, $J = 7.6$ Hz, 6H), 0.93 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.9, 161.2, 161.1, 143.4, 140.1, 136.4, 129.4, 128.7, 127.7, 127.6, 126.7, 117.5, 107.4, 49.6, 43.5, 30.0, 24.7, 21.0, 7.5. HRMS (ESI) calcd for C$_{25}$H$_{28}$O$_4$Na ([M+Na]$^+$): 415.1885, Found: 415.1885. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t$_{R1}$ = 28.7 min (minor), t$_{R2}$ = 31.4 min (major)]; $[\alpha]_{D}^{20}$ = 4.86 (c = 1.11, CHCl$_3$).

5.2 Scope of Arylboronic Acids

(R)-2,2-Dimethyl-5-(4-phenyl-4-(p-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qb)

Colorless oil, 65 mg, yield 91%, ee = 90%. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; t$_{R1}$ = 46.9 min (minor), t$_{R2}$ = 52.3 min (major)].

(R)-5-(4-(4-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qc)

Colorless oil, 69 mg, yield 91%, ee = 89%. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 90/10, 254 nm, 1.0 mL/min; t$_{R1}$ = 25.1 min (major), t$_{R2}$ = 36.8 min (minor)].

(R)-5-(4-(4-(tert-Butyl)phenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qd)

Colorless oil, 71 mg, yield 88%, ee = 93%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.28 (m, 6H), 7.20 – 7.17 (m, 3H), 4.38 (t, $J = 8.0$ Hz, 1H), 3.83 (d, $J = 8.0$ Hz, 2H), 2.43 (s,
(R)-5-(4-((1,1'-Biphenyl)-4-yl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qe)

Colorless oil, 42 mg, yield 50%, ee = 89%. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 – 7.46 (m, 4H), 7.42 (t, \(J = 7.6\) Hz, 2H), 7.34 – 7.29 (m, 7H), 7.23 – 7.18 (m, 1H), 4.43 (t, \(J = 8.0\) Hz, 1H), 3.92 (dd, \(J = 12.6, 8.4\) Hz, 1H), 3.78 (dd, \(J = 12.6, 8.0\) Hz, 1H), 2.43 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 177.3, 161.08, 161.08, 143.0, 142.1, 140.6, 139.8, 128.9, 128.8, 128.2, 127.8, 127.5, 127.3, 127.0, 126.9, 117.8, 103.5, 49.7, 43.0, 26.8, 26.7, 24.3. HRMS (ESI) calcd for C\(_{26}\)H\(_{26}\)O\(_4\)Na ([M+Na]^+): 449.1729, Found: 449.172.

HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; \(t_{R1}\) = 23.8 min (minor), \(t_{R2}\) = 26.2 min (major)]; \([\alpha]^{D}_{20} = -2.75\) (c = 1.09, CHCl\(_3\)).

(R)-5-(4-((4-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qf)

Colorless oil, 55 mg, yield 75%, ee = 87%. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min; \(t_{R1}\) = 51.5 min (minor), \(t_{R2}\) = 54.0 min (major)].

(R)-2,2-Dimethyl-5-(4-phenyl-4-(trifluoromethyl)phenyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qg)

Colorless oil, 43 mg, yield 51%, ee = 90%. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.5 mL/min; \(t_{R1}\) = 52.5 min (minor), \(t_{R2}\) = 64.3 min (major)].
(R)-Methyl 4-(3-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-1-phenylbutyl)-benzoate (3qh)

Colorless oil, 35 mg, yield 43%, ee = 93%. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.4 Hz, 2H), 7.40 – 7.19 (m, 7H), 4.46 (t, J = 7.8 Hz, 1H), 3.94 – 3.71 (m, 2H), 3.90 (s, 3H), 2.38 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 166.7, 161.0, 160.9, 148.4, 142.1, 130.1, 129.0, 128.8, 127.8, 127.2, 117.8, 103.5, 52.1, 50.0, 42.9, 26.9, 26.8, 24.5. HRMS (ESI) calcd for C₂₄H₂₅O₆ ([M+H]+): 409.1651, Found: 409.1655.

HPLC [Daicel CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.5 mL/min; t₁ = 47.5 min (major), t₂ = 53.2 min (minor)]; [α]D₂₀ = -11.95 (c = 1.07, CHCl₃).

(R)-2,2-Dimethyl-5-(4-phenyl-4-(m-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qi)

Colorless oil, 67 mg, yield 92%, ee = 91%. HPLC [Daicel Chiralcel AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.50 mL/min. t₁ = 34.6 min (minor), t₂ = 36.8 min (major)].

(R)-5-(4-(3-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qj)

Colorless oil, 55 mg, yield 75%, ee = 94%. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (m, 6H), 7.09 (d, J = 8.0 Hz, 1H), 7.04 – 6.97 (m, 1H), 6.94 – 6.87 (m, 1H), 4.41 (t, J = 8.0 Hz, 1H), 3.84 (dd, J = 12.8, 8.4 Hz, 1H), 3.74 (dd, J = 12.8, 7.6 Hz, 1H), 2.39 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 162.9 (d, J = 246.5 Hz), 160.99, 160.98, 145.7 (d, J = 6.8 Hz), 142.3, 140.2 (d, J = 8.3 Hz), 128.9, 127.8, 127.2, 123.4 (d, J = 2.8 Hz), 117.8, 114.7 (d, J = 21.7 Hz), 113.8 (d, J = 21.0 Hz), 103.6, 49.7, 43.0, 26.9, 26.8, 24.4. HRMS (ESI) calcd for C₂₂H₂₂FO₄ ([M+H]+): 369.1502, Found: 369.1508. HPLC [Daicel Chiralcel AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min. t₁ = 18.4 min (minor), t₂ = 20.8 min (major)]; [α]D₂₀ = -6.73 (c = 1.15, CHCl₃).
(S)-5-(4-(3-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qk)
Colorless oil, 39 mg, yield 51%, ee = 92%. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_R1 = 26.5 min (minor), t_R2 = 31.3 min (major)].

(R)-5-(4-(3-Bromophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ql)
Colorless oil, 48 mg, yield 56%, ee = 91%. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_R1 = 28.6 min (minor), t_R2 = 34.7 min (major)].

(R)-5-(4-(2-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qm)
Colorless oil, 20 mg, yield 28%, ee = 95%. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_R1 = 20.3 min (major), t_R2 = 23.7 min (minor)].

(R)-5-(4-(2-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qn)
Colorless oil, 23 mg, yield 30%, ee = 92%. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (dd, J = 7.8, 1.6 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.26 – 7.19 (m, 2H), 7.15 (td, J = 7.6, 1.6 Hz, 1H), 5.04 (t, J = 8.0 Hz, 1H), 3.94 (dd, J = 13.2, 8.4 Hz, 1H), 3.73 (dd, J = 13.2, 7.6 Hz, 1H), 2.49 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H). ^13C NMR (100 MHz, CDCl_3) δ 176.8, 161.1, 161.0, 141.6, 140.5, 133.6, 129.9, 129.0, 128.8, 128.06, 128.05, 127.4, 127.1,
117.8, 103.5, 45.1, 42.0, 26.9, 26.8, 23.8. HRMS (ESI) calcd for C_{22}H_{21}ClO_4Na ([M+Na]^+): 407.1026, Found: 407.1023. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 15.2 min (major), t_{R2} = 22.2 min (minor)]; [α]_D^{20} = 12.3 (c = 1.07, CHCl_3).

(R)-5-(4-(3,4-Dimethylphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qo)

Colorless oil, 55 mg, yield 73%, ee = 94%. ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.24 – 7.13 (m, 2H), 6.87 (s, 2H), 6.82 (d, J = 9.2 Hz, 2H), 4.29 (t, J = 8.0 Hz, 1H), 3.82 (dd, J = 12.8, 8.0 Hz, 1H), 3.73 (dd, J = 12.8, 8.0 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 6H), 1.39 (s, 3H), 1.36 (s, 3H). ^13C NMR (100 MHz, CDCl_3) δ 177.5, 161.1, 161.0, 143.3, 142.9, 138.2, 128.8, 128.7, 127.7, 126.8, 117.7, 125.5, 103.5, 49.9, 43.0, 26.6, 24.2, 21.3. HRMS (ESI) calcd for C_{24}H_{26}O_4Na ([M+Na]^+): 401.1729, Found: 401.1730. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 12.8 min (minor), t_{R2} = 15.1 min (major)]; [α]_D^{20} = -0.77 (c = 0.78, CHCl_3).

(R)-5-(4-(Benz[d][1,3]dioxol-5-yl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qp)

Colorless oil, 66 mg, yield 84%, ee = 86%. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.17 (m, 5H), 6.79 – 6.70 (m, 3H), 5.91 (d, J = 5.4 Hz, 2H), 4.34 (t, J = 8.0 Hz, 1H), 3.78 (dd, J = 12.8, 8.0 Hz, 1H), 3.74 (dd, J = 12.8, 8.0 Hz, 1H), 2.40 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H). ^13C NMR (100 MHz, CDCl_3) δ 177.5, 161.1, 161.0, 149.7, 146.4, 143.1, 137.0, 128.8, 127.6, 126.9, 120.7, 117.7, 108.3, 108.26, 103.5, 101.0, 49.6, 43.2, 26.8, 24.4. HRMS (ESI) calcd for C_{23}H_{26}O_6Na ([M+Na]^+): 417.1314, Found: 417.1318. HPLC [DAICEL CHIRALPAK AS-H, hexane/i-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 30.7 min (major), t_{R2} = 40.3 min (minor)]; [α]_D^{20} = -0.77 (c = 0.78, CHCl_3).

(R)-2,2-Dimethyl-5-(4-(naphthalen-2-yl)-4-phenylbutan-2-ylidene)-1,3-dioxane-
4,6-dione (3qq)
Colorless solid, 64 mg, yield 80%, ee = 93%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.72 (m, 4H), 7.58 – 7.42 (m, 2H), 7.39 – 7.24 (m, 5H), 7.22 (m, 1H), 4.58 (t, $J$ = 8.0 Hz, 1H), 4.05 (dd, $J$ = 12.8, 8.4 Hz, 1H), 3.86 (dd, $J$ = 12.8, 7.8 Hz, 1H), 2.47 (s, 3H), 1.37 (s, 3H), 1.15 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.3, 161.07, 161.05, 142.9, 140.4, 133.5, 132.4, 128.8, 128.6, 127.8, 127.8, 127.5, 127.0, 126.4, 126.3, 125.9, 125.8, 117.8, 103.5, 50.0, 42.8, 26.8, 26.4, 24.4. HRMS (ESI) calcd for C$_{26}$H$_{24}$O$_4$Na ([M+Na]$^+$): 423.1572, Found: 423.1573. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-PrOH = 95/5, 254 nm, 0.5 mL/min; $t_R1$ = 35.4 min (major), $t_R2$ = 45.3 min (minor)]; $[\alpha]_D^{20}$ = -12.26 (c = 1.14, CHCl$_3$).

6. Transformations

According to a reported procedure. $^6$ Under nitrogen atmosphere, Me-MgBr (3.0 M in Et$_2$O, 0.08 mL, 0.24 mmol, 1.2 equiv.) was added dropwise to a solution of 3ea (76 mg, 0.2 mmol) in anhydrous THF (2.0 mL) was cooled to 0 °C. The resulting solution was allowed to warm to rt and stirred for 12 hours. Then 5% aq. HCl and EtOAc were added to the reaction mixture. The layers were partitioned and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over anhydrous MgSO$_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to yield the desired product 4.

To a mixture of 4 (63 mg, 0.16 mmol) and copper powder (2.0 mg, 0.032 mmol, 0.2 equiv.), a mix solvent of pyridine/methanol (10:1, 0.1 M) was added. The resulting mixture was heated to 100 °C and stirred for 3 hours. After cooled to rt, the solvent was removed by vacuum evaporation. Purification via flash column chromatography using silica gel while eluting with hexanes : EtOAc (10:1) afforded 5 as a colorless oil in 75% yield.
(S)-5-(4-(3-Methoxyphenyl)-2-methyl-4-phenylbutan-2-yl)-2,2-dimethyl-1,3-dioxane-4,6-dion (4)

Colorless oil, 63 mg, yield 78%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.22 (m, 4H), 7.23 – 7.10 (m, 2H), 6.91 (d, $J$ = 7.6 Hz, 1H), 6.86 (s, 1H), 6.68 (dd, $J$ = 8.2, 1.8 Hz, 1H), 4.12 (t, $J$ = 7.2 Hz, 1H), 3.77 (s, 3H), 3.19 (s, 1H), 2.71 (dd, $J$ = 14.6, 7.6 Hz, 1H), 2.56 (dd, $J$ = 14.6, 6.8 Hz, 1H), 1.59 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.21 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.0, 163.9, 160.1, 147.2, 145.6, 130.0, 129.0, 127.9, 126.7, 120.4, 113.6, 112.1, 104.2, 55.4, 54.4, 48.2, 45.4, 37.2, 28.8, 26.6, 26.5, 26.4. The ee of compound 4 could not be detected by HPLC using any of our chiral columns.

(S)-Methyl 5-(3-methoxyphenyl)-3,3-dimethyl-5-phenylpentanoate (5)

Colorless oil, 49 mg, yield 75%, ee = 83%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.26 (m, 4H), 7.24 – 7.12 (m, 2H), 6.92 (d, $J$ = 7.6 Hz, 1H), 6.87 (d, $J$ = 2.0 Hz, 1H), 6.71 (dd, $J$ = 7.8, 2.2 Hz, 1H), 4.07 (t, $J$ = 6.8 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 2.28 (dd, $J$ = 14.4, 6.8 Hz, 1H), 2.24 (dd, $J$ = 14.4, 6.8 Hz, 1H), 2.17 (s, 2H), 0.97 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.6, 159.6, 147.8, 146.8, 146.0, 129.4, 128.5, 127.7, 126.1, 120.2, 114.0, 110.8, 55.1, 51.1, 48.0, 47.2, 46.1, 34.1, 28.1. HRMS (ESI) calcd for C$_{21}$H$_{27}$O$_3$Na ([M+Na]$^+$): 349.1780, Found: 349.1783. HPLC [ENANTIOPAK SCDP, Hexane/i-PrOH = 90/10, 254 nm, 1.0 mL/min; $t_{R1}$ =14.4 min (minor), $t_{R2}$ = 17.4 min (major)]; [$\alpha$]$^D_{20}$ = 8.06 (c = 1.10, CHCl$_3$).

According to a reported procedure, the reaction was carried out as follows. $^7$ Sc(OTf)$_3$ (20 mg, 0.040 mmol, 20 mol%) and 3qp (79 mg, 0.20 mmol) were added to a Schlenk tube. The Schlenk tube was charged...
with 2 mL CH$_3$NO$_2$ (dried before used). The reaction mixture was then placed in a pre-
heated bath at 70 °C. After 2 hours, the crude mixture was concentrated and purified by 
flash column chromatography on silica gel using petroleum ether : EtOAc (5:1) to 
afford a light yellow oil in 35% yield.

\[
\text{(R)-7-Methyl-9-phenyl-8,9-dihydro-5H-cyclohepta[4,5]benzo[1,2-\text{d}]1,3]dioxol-5-one (6)}
\]

Light yellow oil, 21 mg, yield 35%, ee = 81%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 
7.26 (m, 3H), 7.25 – 7.18 (m, 3H), 6.75 – 6.69 (m, 2H), 5.94 – 5.87 (m, 2H), 4.53 (t, $J$
 = 7.6 Hz, 1H), 3.15 (d, $J$ = 7.6 Hz, 2H), 2.11 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
206.8, 147.8, 146.1, 143.9, 137.8, 128.6, 127.5, 126.5, 120.6, 108.3, 108.2, 100.9, 49.8, 
45.7, 30.7. HPLC [DAICEL CHIRALPAK AD-H, hexane/i-ProOH = 95/5, 254 nm, 0.5
mL/min; $t_{R1} = 21.1$ min (major), $t_{R2} = 24.9$ min (minor)]; [$\alpha$]$^D_{20} = 3.26$ (c = 1.11, CHCl$_3$).

The number of observed carbons is lower due to an expected overlap of some of the
carbon peaks.
7. Single Crystal of Enantioenriched 3qq

Colorless crystals of 3qq suitable for X-ray crystallographic analysis were obtained by recrystallization from i-PrOH in fridge. The ORTEP drawing of (R)-3qq is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 1813609).

(R)-2,2-Dimethyl-5-(4-(naphthalen-2-yl)-4-phenylbutan-2-ylidene)-1,3-dioxane-4,6-dione (3qq)

Figure S1
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) P

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: P

Bond precision: C-C = 0.0825 A

Wavelength=1.54178

Cell:
\[ a=7.4682(3) \quad b=13.9250(6) \quad c=21.7018(10) \]
\[ \alpha=90 \quad \beta=90 \quad \gamma=90 \]

Temperature: 293 K

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>2115.12(16)</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21 21 21</td>
</tr>
<tr>
<td>Hall group</td>
<td>P 2ac 2ab</td>
</tr>
<tr>
<td>MoIety formula</td>
<td>C26 H24 O4</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C26 H24 O4</td>
</tr>
<tr>
<td>Mr</td>
<td>400.45</td>
</tr>
<tr>
<td>Dx,g cm^-3</td>
<td>1.258</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Mu (mm-3)</td>
<td>0.675</td>
</tr>
<tr>
<td>F000</td>
<td>940.0</td>
</tr>
<tr>
<td>F000'</td>
<td>850.57</td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>8,15,25</td>
</tr>
<tr>
<td>Nref</td>
<td>3731 (2154)</td>
</tr>
<tr>
<td>Tmin,Tmax</td>
<td>0.960,0.990</td>
</tr>
<tr>
<td>Tmin'</td>
<td>0.967</td>
</tr>
</tbody>
</table>

Correction method: Not given

Data completeness= 1.73/1.80
Theta(max)= 66.619

\[ R(reflections) = 0.0262 (3586) \quad wR2(reflections) = 0.0717 (3719) \]

\[ S = 1.090 \quad Npar = 275 \]

The following ALERTS were generated. Each ALERT has the format test-name ALERT alert_type alert-level.
Click on the hyperlinks for more details of the test.
8. References

9. NMR and HPLC Spectra Charts