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Supporting Information for

Enantioselective Diels–Alder Reaction Induced by Chiral Supramolecular Lewis Acid Catalysts Based on CN···B and PO···B Coordination Bonds

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1. General methods.

$^1$H NMR spectra were measured on a JEOL ECS400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. $^{13}$C NMR spectra were measured on a JEOL ECS400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.10 ppm). $^{19}$F NMR spectra were measured on a JEOL ECS-400 (376 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard (CFCl$_3$ at 0 ppm). $^{31}$P NMR spectra were measured on a JEOL ECS-400 (161 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard (H$_3$PO$_4$ at 0 ppm). Gas-liquid-phase chromatography (GC) was performed with Shimadzu GC-2010 instrument with a flame-ionization detector and a capillary column of ULBON HR-20M (PEG-20M) (i.d., 0.25 mm × 25 m; GL Science Inc.), or CHIRALDEX B-DM, G-TA (i.d., 0.25 mm × 20 m; Tokyo Kasei Kogyo Co., LTD). High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-M20A and chiral column of Daicel CHIRALPAK AD-H. Optical rotations were measured on Rudolph Autopol IV digital polarimeter. The products were purified by column chromatography on silica gel (Kanto Chemical Co., Inc. 37560; Merck silica gel 60, Prod. No. 1.09385.9929). Mass spectral analyses were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700 (FAB), JEOL JMS-T100GCV (EI), Bruker Daltonics micrOTOF-QII (ESI)). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO$_4$, and phosphomolybdic acid. Dichloromethane (with P$_4$O$_{10}$) was freshly distilled in prior to use. Cyclopentadiene (3) was freshly distilled from dicyclopentadiene in prior to use. Methacrolein (4a), α-ethylacrolein (4b), tiglic aldehyde (4d), acrolein (4e), ethyl trans-4-oxo-2-butenoate (4f), and cyclohexadiene (12) are commercially available, and were used without any purification. α-Bromoacrolein (4e)$^1$ and 6-methoxy-3,4-dihydro-2-vinylchromephene (8)$^2$ were synthesized as reported procedures.
2. Preparation of chiral BINOLs.

(R)-3,3'-Bis(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphorinan-2-yl)-BINOL (Compound for catalyst 6): The titled compound was known and prepared based on the reported procedure.\(^1\)

31P NMR (161 MHz, CDCl\(_3\)) \(\delta 18.66\) (s).

IR (KBr) 3188, 2967, 1623, 1596, 1499, 1467, 1427, 1377, 1340, 1280, 1146, 1071, 1001 cm\(^{-1}\). \([\alpha]_D^{23} = +25.2\) (c 1.00, CHCl\(_3\)).

HRMS (FAB+) calcd for C\(_{25}\)H\(_{24}\)O\(_8\)P [M+H]\(^+\) 435.1361, found 435.1356.

(R)-3-(5,5-Dimethyl-2-oxido-1,3,2-dioxaphosphorinan-2-yl)-BINOL (Compound for catalyst 2a): The titled compound was prepared based on the reported procedure.\(^3\) 1H NMR (400 MHz, CDCl\(_3\)) \(\delta 1.03\) (s, 3H), 1.40 (s, 3H), 4.01 (m, 2H), 4.46 (m, 2H), 5.45 (bs, 1H), 7.07 (d, \(J = 8.1\) Hz, 1H), 7.17 (m, 1H), 7.24 (t, \(J = 6.9\) Hz, 1H), 7.31 (t, \(J = 6.9\) Hz, 1H), 7.33-7.40 (m, 3H), 7.85 (d, \(J = 7.8\) Hz, 1H), 7.90 (d, \(J = 9.0\) Hz, 2H), 8.37 (d, \(J_{\text{H-P}} = 17.4\) Hz, 1H), 9.31 (bs, 1H).

13C NMR (100 MHz, CDCl\(_3\)) \(\delta 21.5, 22.3, 32.9\) (d, \(J_{\text{C-P}} = 5.7\) Hz), 75.8 (d, \(J_{\text{C-P}} = 5.7\) Hz, 2C), 111.8 (d, \(J_{\text{C-P}} = 191.6\) Hz), 113.3, 114.8 (d, \(J_{\text{C-P}} = 11.4\) Hz), 117.7, 123.5, 124.6 (2C), 124.9, 126.8, 127.7 (d, \(J_{\text{C-P}} = 16.2\) Hz), 128.3, 129.3, 129.4, 130.0, 130.5, 133.4, 136.6 (d, \(J_{\text{C-P}} = 5.7\) Hz), 137.3, 151.8, 154.6 (d, \(J_{\text{C-P}} = 6.7\) Hz). 31P NMR (161 MHz, CDCl\(_3\)) \(\delta 18.66\) (s).

IR (KBr) 3188, 2967, 1623, 1596, 1499, 1467, 1427, 1377, 1340, 1280, 1146, 1071, 1001 cm\(^{-1}\). \([\alpha]_D^{23} = +25.2\) (c 1.00, CHCl\(_3\)).

HRMS (FAB+) calcd for C\(_{25}\)H\(_{24}\)O\(_8\)P [M+H]\(^+\) 435.1361, found 435.1356.
11.1 Hz, 1H), 4.48 (d, J = 11.4 Hz, 1H), 4.50 (d, J = 11.4 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 7.30 (d, J_{C-P} = 15.1 Hz, 1H), 9.82 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 22.4, 22.6, 22.7, 23.0, 23.1, 27.1, 27.7, 29.2, 29.3, 32.7 (d, J_{C-P} = 5.7 Hz, 2C), 75.2 (d, J_{C-P} = 5.7 Hz), 104.9 (d, J_{C-P} = 193.5 Hz), 129.5 (d, J_{C-P} = 7.6 Hz), 129.6 (d, J_{C-P} = 17.1 Hz), 130.1, 132.3 (d, J_{C-P} = 5.7 Hz), 136.1, 146.4, 150.1, 157.7 (d, J_{C-P} = 7.6 Hz). ^{31}P NMR (161 MHz, CDCl_3) δ 21.68 (s).

IR (KBr) 3246, 2930, 1593, 1444, 1258, 1216, 1053, 1001 cm^{-1}. [α]_D^{24} = +56.4 (c 1.0, CHCl₃).

HRMS (FAB+) calcd for C_{25}H_{32}O_5P [M+H]^+ 443.1987, found 443.2003.

(R)-3-(3,3′,5,5′′-Tetrakis(trifluoromethyl)-[1,1′:3′,1′′-terphenyl]-5′-yl)-5,5′,6,6′,7,7′,8,8′-H$_8$-BINOL (Compound for catalyst 7a): The titled compound was prepared based on the reported procedure. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.65-1.85 (m, 8H), 2.23 (m, 2H), 2.35 (m, 2H), 2.76 (t, J = 5.8 Hz, 2H), 2.84 (t, J = 5.9 Hz, 2H), 4.73 (s, 1H), 4.93 (s, 1H), 6.83 (d, J = 8.3 Hz, 1H), 7.11 (d, J = 8.7 Hz, 1H), 7.28 (s, 1H), 7.78 (t, J = 1.8 Hz, 1H), 7.95 (s, 4H), 8.15 (s, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 23.0 (4C), 27.3 (2C), 29.3 (2C), 113.4, 118.4, 120.2, 121.5 (2C), 123.4 (q, J_{C-F} = 272 Hz, 4C), 124.5, 124.8, 127.7 (4C), 128.9 (2C), 130.6, 130.9, 131.6, 131.8, 132.4 (q, J_{C-F} = 33.4 Hz, 4C), 137.2, 137.9, 139.6 (2C), 140.5, 143.0 (2C), 148.3, 151.5. ^{19}F NMR (376 MHz, CDCl$_3$) δ –62.5 (s). IR (KBr) 3516, 2935, 2860, 1733, 1595, 1476, 1366, 1279, 1133 cm^{-1}. M.p. 116-122 °C (decomposition). [α]_D^{24} = +47.8 (c 1.03, CHCl₃). HRMS (ESI–) calcd for C_{42}H_{29}F_{12}O_2 [M–H]^- 793.1981,

(R)-3-(3,5-Bis(trifluoromethyl)phenyl)-5,5′,6,6′,7,7′,8,8′-H$_8$-BINOL (Compound for catalyst
7b): The titled compound was prepared based on the reported procedure.\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.67-1.82 (m, 8H), 2.17-2.26 (m, 2H), 2.27-2.40 (m, 2H), 2.76 (t, \(J = 6.0\) Hz, 2H), 2.83 (t, \(J = 6.0\) Hz, 2H), 4.56 (s, 1H), 4.89 (s, 1H), 6.86 (d, \(J = 8.2\) Hz, 1H), 7.10 (d, \(J = 8.2\) Hz, 1H), 7.19 (s, 1H), 7.80 (s, 1H), 8.09 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 23.0 (4C), 27.2, 27.3, 29.3 (2C), 113.3, 118.2, 120.5 (2C), 122.9, 123.6 (q, \(J_{C-F} = 272\) Hz, 2C), 129.5 (2C), 130.6, 130.9, 131.3 (q, \(J_{C-F} = 32\) Hz, 2C), 131.5 (2C), 137.3, 138.6, 140.3, 148.4, 151.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –62.7 (s). IR (KBr) 3511, 2934, 2859, 1591, 1477, 1384, 1278, 1181, 1133 cm\(^{-1}\). M.p. 102-104 °C (decomposition). \([\alpha]_D^{27} = +71.1\) (c 1.04, CHCl\(_3\)). HRMS (ESI–) calcd for C\(_{28}\)H\(_{23}\)F\(_6\)O\(_2\) [M–H]– 505.1608, found 505.1602.


**2-Cyano-5-fluorophenylboronic acid (Compound for catalyst 2a and 2b):** The titled compound was prepared from 2-bromo-4-fluorobenzonitrile according to the reported procedure.\(^5\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.29 (td, \(J_{H-H, H-F} = 8.7, 2.8\) Hz, 1H), 7.41 (dd, \(J_{H-H, H-F} = 8.7, 5.0\) Hz, 1H), 7.80 (dd, \(J_{H-H, H-F} = 8.7, 2.8\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 112.7, 118.2 (d, \(J_{C-F} = 22.9\) Hz), 119.8, 121.7 (d, \(J_{C-F} = 21.0\) Hz), 137.0 (d, \(J_{C-F} = 8.6\) Hz), 165.8 (d, \(J_{C-F} = 253.6\) Hz). \(^{19}\)F (376 MHz, CD\(_3\)OD) \(\delta\) –106.3. IR (KBr) 3313, 2241, 1598, 1434, 1330, 1219, 1150, 1072 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_7\)H\(_4\)BFNO \([M–H]^{-}\) 164.0324, found 164.0320.

**2-Cyano-5-(trifluoromethyl)phenylboronic acid (Compound for catalyst 2c, 7a, and 7b):** The titled compound was prepared from 4-(trifluoromethyl)benzonitrile according to the reported procedure.\(^6\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.84 (d, \(J = 8.0\) Hz, 1H), 7.93 (d, \(J = 7.8\) Hz, 1H), 8.00 (s, 1H). \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 119.3, 120.5, 125.0 (q, \(J_{C-F} = 270\) Hz), 125.3, 127.6 (q, \(J_{C-F} = 2.9\) Hz), 131.4, 134.2 (q, \(J_{C-F} = 32.4\) Hz), 134.7. \(^{19}\)F (376 MHz, CD\(_3\)OD) \(\delta\) –64.9. IR (KBr) 3389, 1446, 1398, 1334, 1289, 1185, 1127 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_8\)H\(_4\)BF\(_3\)NO \([M–H]^{-}\) 214.0292, found 214.0293.
2-Cyano-4-(trifluoromethyl)phenylboronic acid (Compound for catalyst 2d): The titled compound was prepared from 4-(trifluoromethyl)benzonitrile according to the reported procedure.\(^6\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.87 (d, \(J = 7.8\) Hz, 1H), 7.94 (d, \(J = 7.8\) Hz, 1H), 8.08 (s, 1H). \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 117.7, 119.1, 124.6 (q, \(J_{C-F} = 270\) Hz), 129.2 (d, \(J_{C-F} = 3.8\) Hz), 130.5 (d, \(J_{C-F} = 2.8\) Hz), 132.9 (q, \(J_{C-F} = 33.4\) Hz), 135.8. \(^{19}\)F (376 MHz, CD\(_3\)OD) \(\delta\) –64.7. IR (KBr) 3419, 2985, 2232, 1433, 1330, 1178, 1132 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_8\)H\(_5\)BF\(_3\)NO\(_2\) [M–H] \(^{-}\) 214.0292, found 214.0289.

2-Cyanophenylboronic acid (Compound for catalyst 2e): Commercially available.

2-Cyano-5-methylphenylboronic acid (Compound for catalyst 2f): The titled compound was prepared from 4-methylbenzonitrile according to the reported procedure.\(^6\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 2.42 (s, 3H), 7.36 (d, \(J = 7.8\) Hz, 1H), 7.44 (brs, 1H), 7.61 (d, \(J = 7.8\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 21.6, 113.5, 120.8, 131.6, 133.9, 135.6, 143.9. IR (KBr) 3389, 2232, 1606, 1561, 1426, 1323, 1218, 1156, 1105, 1047 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_8\)H\(_7\)BNO\(_2\) [M–H] \(^{-}\) 160.0575, found 160.0578.

2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (Compound for catalyst 14a): Commercially available.

2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-4-methylbenzonitrile (Compound for catalyst 14b): The titled compound was prepared from 4-methylbenzonitrile according to the reported procedure.\(^7,8\) \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 1.04 (s, 6H), 2.39 (s, 3H), 3.81 (s, 4H), 7.31 (d, \(J =

S6
7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.70 (s, 1H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 21.8, 21.9 (2C), 32.1, 72.8 (2C), 113.8, 120.1, 131.6, 134.0, 136.2, 142.6. IR (KBr) 3433, 2963, 2220, 1601, 1563, 1486, 1433, 1308, 1264, 1221, 1146, 1103 cm$^{-1}$. HRMS (ESI+) calcd for C$_{13}$H$_{17}$BNO$_2$ [M+H]$^+$ 230.1346, found 230.1344.

2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-4-(trifluoromethyl)benzonitrile (Compound for catalyst 14c): The titled compound was prepared according to the reported procedure.$^9$ $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.05 (s, 6H), 3.85 (s, 4H), 7.76 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 8.17 (s, 1H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 21.9 (2C), 32.2, 73.0 (2C), 118.6, 120.5, 123.9 (q, $J_{C-F} = 272$ Hz), 127.6 (d, $J_{C-F} = 3.8$ Hz), 132.3 (d, $J_{C-F} = 3.8$ Hz), 133.2 (q, $J_{C-F} = 31.5$ Hz), 134.5. $^{19}$F (376 MHz, CD$_2$Cl$_2$) δ −63.7. IR (KBr) 3418, 2965, 2231, 1608, 1486, 1340, 1276, 1174, 1129, 1104 cm$^{-1}$. HRMS (ESI+) calcd for C$_{13}$H$_{14}$BF$_3$NO$_2$ [M+H]$^+$ 284.1064, found 284.1058.

2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-5-(trifluoromethyl)benzonitrile (Compound for catalyst 14d): The titled compound was prepared according to the reported procedure.$^9$ $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.05 (s, 6H), 3.85 (s, 4H), 7.81 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 21.9 (2C), 32.2, 73.0 (2C), 117.8, 118.6, 123.6 (q, $J_{C-F} = 271$ Hz), 128.3 (d, $J_{C-F} = 3.8$ Hz), 130.6 (d, $J_{C-F} = 3.8$ Hz), 132.8 (q, $J_{C-F} = 33.4$ Hz), 136.2. $^{19}$F (376 MHz, CD$_2$Cl$_2$) δ −63.6. IR (KBr) 3420, 2238, 1500, 1434, 1330, 1179, 1134, 1096, 1079 cm$^{-1}$. HRMS (ESI+) calcd for C$_{13}$H$_{14}$BF$_3$NO$_2$ [M+H]$^+$ 284.1064, found 284.1065.

A solution of \((R)-3-(5,5\text{-dimethyl}-2\text{-oxido-1,3,2-dioxaphosphorinan-2-yl})-5,5',6,6',7,7',8,8'\text{-H}_8\text{BINOL}\) (22.1 mg, 0.050 mmol) and 2-cyano-5-(trifluoromethyl)phenylboronic acid (10.7 mg, 0.050 mmol) in dichloromethane (1 mL), THF (0.3 mL), and water (9 µL, 0.5 mmol) was stirred at room temperature for 12 h in a Pyrex Schlenk tube under a nitrogen atmosphere. Volatile compounds were removed under reduced pressure, and powdered MS 4Å (250 mg, used as received from a commercial source) was added. The resulting white solid was heated to 100 °C (bath temperature) under <5 Torr for 2 h. After the resulting substance was cooled to room temperature under a nitrogen atmosphere, tris(pentafluorophenyl)borane (51.2 mg, 0.10 mmol) and freshly-distilled dichloromethane (2 mL) were added under an argon atmosphere in a glove box. The pale brown mixture was stirred at room temperature for 1 h and then cooled to −78 °C, and methacrolein 4a (95% purity, 43.4 µL, 0.50 mmol) was added. Subsequently, freshly-distilled cyclopentadiene 3 (210 µL, 2.5 mmol) was added at −78 °C over 15 min. The resultant mixture was then stirred at −78 °C for 3 h. To quench the reaction, triethylamine (0.5 mL) was poured into the reaction mixture at −78 °C. The product mixture was directly purified by silica gel column chromatography (eluent: \(n\)-pentane:diethyl ether = 100:1–8:1). Solvents were removed under 200 Torr at 15 °C by a rotary evaporator, and the product mixture (5a) was obtained. \(^1\)H NMR, \(^{13}\)C NMR, IR, HRMS, etc. were consistent with previously reported values.\(^1\)
A solution of chiral \((R)-3-(3,3''',5,5'''\text{-tetrakis(trifluoromethyl)}-1,1''\text{-terphenyl})-5\text{-yl})\)
-5,5',6,6',7,7',8,8''-H8-BINOL (39.7 mg, 0.050 mmol) and 2-cyano-5-(trifluoromethyl)
phenylboronic acid (10.7 mg, 0.050 mmol) in dichloromethane (1 mL), THF (0.3 mL), and water
(9 µL, 0.5 mmol) was stirred at room temperature for 12 h in a Pyrex Schlenk tube under a
nitrogen atmosphere. Volatile compounds were removed under reduced pressure, and powdered
MS 4Å (250 mg, used as received from a commercial source) was added. The resulting white
solid was heated to 100 °C (bath temperature) under <5 Torr for 2 h. After the resulting
substance was cooled to room temperature under a nitrogen atmosphere, tris(pentafluorophenyl)borane
(25.6 mg, 0.05 mmol) and freshly-distilled dichloromethane (2 mL)
were added under an argon atmosphere in a glove box. The pale brown mixture was stirred at
room temperature for 1 h and then cooled to -78 °C, and methacrolein 4a (95% purity, 43.4 µL,
0.50 mmol) was added. Subsequently, freshly-distilled cyclopentadiene 3 (210 µL, 2.5 mmol)
was added at -78 °C over 15 min. The resultant mixture was then stirred at -78 °C for 3 h. To
quench the reaction, triethylamine (0.5 mL) was poured into the reaction mixture at -78 °C. The
product mixture was directly purified by silica gel column chromatography (eluent: n-pentane:diethyl ether = 100:1–20:1). Solvents were removed under 200 Torr at 15 °C by a
rotary evaporator, and the product mixture (5a) was obtained. 1H NMR, 13C NMR, IR, HRMS,
etc. were consistent with previously reported values.1
The endo/exo ratio was determined by $^1$H NMR analysis; δ 9.40 (s, 1H, CHO (endo-5a)), 9.69 (s, 1H, CHO (exo-5a)). The enantioselectivity was determined by GC analysis after conversion to chiral acetals by (−)-(2R,4R)-2,4-pentanediol [General procedure for acetalization: A mixture of the Diels–Alder adduct, (−)-(2R,4R)-2,4-pentanediol (2 equiv), triethyl orthoformate (2 equiv), and p-toluenesulfonic acid monohydrate (0.4 equiv) in chloroform was stirred at room temperature for 2 h. After the full conversion (TLC check), neutral silica gel column chromatography (elucent: pentane:diethyl ether = 100:1 to 8:1) afforded the purified chiral acetals.]; GC analysis (ULBON HR-20M (PEG-20M), 80 °C), $t_R$ = 19.5 min. (endo-(1S,2S,4S)-isomer), 25.2 min. (endo-(1R,2R,4R)-isomer), 27.3 min. (exo-(1S,2R,4S)-isomer), and 28.7 min (exo-(1R,2S,4R)-isomer).

(1R,2S,4R)-2-Methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (exo-(2S)-5a): $^1$H NMR (400 MHz, CDCl$_3$) δ 0.76 (d, $J = 12.0$ Hz, 1H), 1.01 (s, 3H), 1.39 (m, 2H), 2.25 (dd, $J = 12.0, 3.9$ Hz, 1H), 2.82 (brs, 1H), 2.90 (brs, 1H), 6.11 (dd, $J = 6.0, 3.0$ Hz, 1H), 6.30 (dd, $J = 6.0, 3.0$ Hz, 1H), 9.69 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.1, 34.6, 43.2, 47.6, 48.5, 53.9, 133.1, 139.6, 205.9. HRMS (EI) calcd for C$_9$H$_{12}$O $[M]^+$ 136.0883, found 136.0893.

(4R,6R)-4,6-Dimethyl-2-((1R,2S,4R)-2-methylbicyclo[2.2.1]hept-5-en-2-yl)-1,3-dioxane (exo-(2S)-5a): $^1$H NMR (400 MHz, CDCl$_3$) δ 0.74 (dd, $J = 12.0, 2.7$ Hz, 1H), 0.87 (s, 3H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.35 (d, $J = 6.9$ Hz, 3H), 1.25-1.84 (m, 5H), 2.74 (brs, 2H), 3.94 (m, 1H), 4.32 (m, 1H), 4.70 (s, 1H), 6.10 (dd, $J = 5.4, 2.7$ Hz, 1H), 6.14 (dd, $J = 5.4, 2.7$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 17.4, 18.6, 22.0, 36.9, 37.4, 43.3, 45.5, 47.6, 48.0, 67.5, 68.0, 99.5, 135.8, 137.2. IR (neat) 2970, 2876, 1450, 1375, 1334, 1240, 1158, 1137, 1057, 1023 cm$^{-1}$. HRMS (EI) calcd for C$_{14}$H$_{22}$O$_2$ [M]$^+$ 222.1620, found 222.1623.

$^1$H NMR, $^{13}$C NMR, and HRMS data were consistent with previously reported values.$^{10}$ The endo/exo ratio of 5b was determined by $^1$H NMR (CDCl$_3$) analysis; δ 9.42 (s, 1H, CHO (endo-5b)),
9.69 (s, 1H, CHO (exo-5b)). The enantioselectivity and absolute stereochemistry of 5b was determined by GC analysis according to the literature.\(^\text{10}\)

\[
\begin{align*}
&\text{endo-(2R)-5c} \\
&\text{exo-(2R)-5c}
\end{align*}
\]

\(^\text{1}\)H NMR, \(^\text{13}\)C NMR, IR, and HRMS data were consistent with previously reported values.\(^\text{1}\) The endo/exo ratio of 5c was determined by \(^\text{1}\)H NMR (CDCl\(_3\)) analysis; \(\delta 9.32\) (s, 1H, CHO (endo-5c)), 9.54 (s, 1H, CHO (exo-5c)). The enantioselectivity and absolute stereochemistry of 5c was determined by GC analysis according to the literature.\(^\text{1}\)

The reaction was conducted in 1.25 mL of dichlormethane (0.4 M for 4d). \(^\text{1}\)H NMR, \(^\text{13}\)C NMR, and HRMS data were consistent with previously reported values.\(^\text{10}\) The endo/exo ratio of 8 was determined by \(^\text{1}\)H NMR (CDCl\(_3\)) analysis; 9.34 (s, 1H, CHO (endo-5d)) and 9.62 (s, 1H, CHO (exo-5d)). The enantioselectivity and absolute stereochemistry of 5d was determined by GC analysis according to the literature.\(^\text{10}\)

\[
\begin{align*}
&\text{endo-(2S)-5d} \\
&\text{exo-(2S)-5d}
\end{align*}
\]

\(^\text{1}\)H NMR, \(^\text{13}\)C NMR, IR, and HRMS data were consistent with previously reported values.\(^\text{1}\) The endo/exo ratio was determined by \(^\text{1}\)H NMR (CDCl\(_3\)) analysis; \(\delta 9.42\) (d, \(J = 2.7\) Hz, 1H, CHO (endo-5e)), 9.79 (d, \(J = 2.7\) Hz, 1H, CHO (exo-5e)). The enantioselectivity and absolute stereochemistry of 5e was determined by GC analysis according to the literature.\(^\text{1}\)

\[
\begin{align*}
&\text{endo-(3R)-5f} \\
&\text{exo-(3R)-5f}
\end{align*}
\]

\(^\text{1}\)H NMR and IR data were consistent with previously reported values.\(^\text{11}\) The endo/exo ratio was
determined by $^1$H NMR analysis; δ 9.54 (d, J = 0.9 Hz, 1H, CHO (endo-$^{5f}$)), 9.83 (d, J = 0.9 Hz, 1H, CHO (s, CHO (exo-$^{5f}$)). The enantioselectivity was determined by GC analysis. GC (CHIRALDEX G-TA, 90 °C, 40 kPa) $t_R$ = 53.8 min. (exo-(1S, 2R, 3R, 4R)-isomer, minor), 55.5 min. (endo-(1R, 2R, 3R, 4S)-isomer, minor), 56.8 min. (exo-(1R 2S, 3S, 4S)-isomer, major), and 60.7 min. (endo-(1S, 2S, 3S, 4R)-isomer, major). The absolute configuration of the adduct was determined by conversion of the known diol$^{12}$ by reduction with LiAlH$_4$.

Ethyl (1R,2R,3R,4S)-3-formylbicyclo[2.2.1]hept-5-ene-2-carboxylate (endo-$^{5f}$):$^{11} \quad ^1$H NMR (400 MHz, CDCl$_3$) δ 1.26 (t, J = 7.3 Hz, 2H), 1.49 (dd, J = 8.7, 1.4 Hz, 1H), 1.66 (d, J = 8.7 Hz, 1H), 2.68 (dd, J = 4.6, 1.8 Hz, 1H), 3.17 (s, 1H), 3.34 (s, 1H), 3.37 (m, 1H), 6.07 (m, 1H), 6.24 (m, 1H), 9.54 (d, J = 0.9 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.3, 44.3, 44.9, 47.4, 47.8, 56.8, 61.1, 134.5, 137.8, 174.2, 201.6.

Ethyl (1S,2R,3R,4R)-3-formylbicyclo[2.2.1]hept-5-ene-2-carboxylate (exo-$^{5f}$):$^{11} \quad ^1$H NMR (400 MHz, CDCl$_3$) δ 1.22 (t, J = 6.9 Hz, 3H), 1.32 (d, J = 8.7 Hz, 1H), 1.43 (dd, J = 9.2, 1.4 Hz, 2H), 2.81 (d, J = 4.2 Hz, 1H), 3.19 (s, 1H), 3.27 (s, 1H), 3.40 (t, J = 4.1 Hz, 1H), 6.11 (m, 1H), 6.28 (m, 1H), 9.83 (d, J = 0.9 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.3, 44.5, 44.6, 45.5, 46.8, 56.0, 60.8, 135.9, 137.1, 173.2, 201.2. IR (neat, endo/exo = 20/80 mixture) 2980, 2821, 2721, 1727, 1457, 1373, 1261, 1187, 1114, 1034 cm$^{-1}$. HRMS (ESI+) calcd for C$_{11}$H$_{14}$O$_3$Na [M+Na]$^+$ 217.0847, found 217.0835.

(2R,10aR)-7-Methoxy-2-methyl-1,2,3,9,10,10a-hexahydrophenanthrene-2-carbaldehyde (endo-$^9$): $^1$H NMR, $^{13}$C NMR, and HRMS data were consistent with previously reported values.$^{12}$ The enantioselectivity and absolute stereochemistry of $^9$ was determined by HPLC analysis. HPLC analysis; AD-H, hexane:i-PrOH = 99:1, 1.0 mL/min, $t_R$ = 11.7 min (major, 2R), 14.8 min (minor, 2S).
5. ESI-MS analysis of catalysts 2c.

We observed complex 2c in ESI-MS analysis (positive mode). Freshly-distilled dichloromethane (2 mL) was added to 2c in a well-dried Schlenk tube at room temperature (concentration: 25 mM). Then, 100 µL of the solution passed through a membrane filter (200 mm mesh) and was diluted with freshly-distilled dichloromethane (5 mL) in a well-dried test tube (final concentration: 0.5 mM), and injection to ESI-MS (positive mode). The spectrum with ion distribution for the peak (m/z = 1664.1718) is shown in Figure S1. C_{69}H_{38}B_{3}F_{33}NO_{6}P is identified to [2c + H_2O + H]^+.

![ESI-MS spectrum of complex 2c with a theoretical ion distribution.](image)

**Figure S1.** ESI-MS spectrum of complex 2c with a theoretical ion distribution.
6. Investigation of other catalysts in the probe reaction of 4a with 3.

Other catalysts were investigated in the probe reaction of 4a with 3 (Schemes S1 and S2). Catalysts S1–S4 were derived from (R)-3,3’-(4-F-C₆F₄)₂BINOL, and the substitution effect of F in arylboronic acid was investigated (Scheme S1). As a result, S4 with a F-substituent at the 5-position gave the best results.

Catalyst, yield, enantioselectivity, endo/exo selectivity:

- **S1**
  - Yield: 73%, 15% ee (exo)
  - Enantiomeric excess: 73%, 19% ee
  - Endo:exo = 8:92

- **S2**
  - Yield: 73%, 19% ee (exo)
  - Enantiomeric excess: 73%, 19% ee
  - Endo:exo = 7:93

- **S3**
  - Yield: 78%, 6% ee (exo)
  - Enantiomeric excess: 78%, 6% ee
  - Endo:exo = 7:93

- **S4**
  - Yield: 79%, 58% ee (exo)
  - Enantiomeric excess: 79%, 58% ee
  - Endo:exo = 12:88

Moreover, the substitution (R) effect of (R)-3-R-BINOL with the use of 2-cyano-5-fluorophenylboronic acid was investigated (Scheme S2). As a result, a bulky aryl moiety was generally effective, while too bulky catalysts S8 and S9 were less effective. Interestingly, when catalyst S7 was used, exo-5a was obtained with −81% ee and an opposite absolute stereochemistry (i.e., exo-(2R)-5a was obtained as a major product.).
Scheme S2  Investigation of other catalysts in the probe reaction of 4a with 3.
Diels–Alder reactions of various acroleins (0.25 M for 4a, 4b, 4c, 4e, and 0.4 M for 4d) were performed with the use of catalyst S7 (Scheme S3). As a result, the opposite stereochemistry was generally observed among the corresponding products 5a–f. However, the enantioselectivities of 5b–f were not high (Schemes S3b–S3f). Therefore, the high enantioselectivity (–81% ee) of 5a might be a limited case (Scheme S3a).

Scheme S3  Diels–Alder reactions of various acroleins with the use of catalyst S7.
Compounds for Schemes S1–S3:

(R)-3-(4-(Trifluoromethyl)phenyl)-BINOL: The titled compound was prepared based on the reported procedure.\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 5.11 (s, 1H), 5.28 (s, 1H), 7.15 (d, \(J = 8.3\) Hz, 1H), 7.21 (d, \(J = 8.3\) Hz, 1H), 7.28-7.46 (m, 5H), 7.73 (d, \(J = 8.3\) Hz, 2H), 7.86 (d, \(J = 7.8\) Hz, 2H), 7.89-8.07 (m, 4H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ 110.5, 112.0, 117.7, 124.0, 124.2 (q, \(J_{C-F} = 279\) Hz), 124.1 (2C), 124.6, 125.1 (q, \(J_{C-F} = 2.9\) Hz), 127.6, 127.8, 128.4, 128.5, 129.2, 129.3, 129.4, 129.5 (q, \(J_{C-F} = 32.4\) Hz), 129.9 (2C), 131.6, 131.8, 133.1, 133.2, 141.2, 149.9, 152.8. \(^1\)F NMR (376 MHz, CDCl\(_3\)) δ –62.4. IR (KBr) 3498, 3059, 1618, 1596, 1324, 1169, 1126, 1071 cm\(^{-1}\). M.p. 98-102 °C (decomposition). \([\alpha]_D^{25} = +132.4\ (c\ 1.00,\ CHCl_3).\) HRMS (ESI–) calcd for C\(_{27}\)H\(_{16}\)F\(_3\)O\(_2\) [M–H]– 429.1108, found 429.1108.

(R)-3-(3,3'',5,5''-Tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)-BINOL: The titled compound was prepared based on the reported procedure.\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 5.14 (s, 1H), 5.38 (s, 1H), 7.19 (d, \(J = 8.2\) Hz, 1H), 7.25 (d, \(J = 8.2\) Hz, 1H), 7.32-7.46 (m, 5H), 7.79 (m, 1H), 7.93 (s, 2H), 7.99 (d, \(J = 8.2\) Hz, 1H), 8.00 (d, \(J = 8.7\) Hz, 1H), 8.04-8.06 (m, 2H), 8.12 (s, 4H), 8.16 (s, 1H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ 110.5, 112.3, 117.8, 121.5 (septet, \(J_{C-F} = 3.8\) Hz, 2C), 123.3 (q, \(J_{C-F} = 272\) Hz, 4C), 124.1, 124.2 (2C), 124.8, 125.4, 127.6, 127.7, 128.0, 128.5, 129.1, 129.2 (4C), 129.4, 129.5, 131.7, 131.8, 132.4 (q, \(J_{C-F} = 33.4\) Hz, 4C), 133.2, 133.3, 133.4 (2C), 140.0, 142.7 (2C), 150.0, 152.9. \(^1\)F NMR (376 MHz, CDCl\(_3\)) δ –62.4. IR (KBr) 3528, 3059, 1621, 1367, 1280, 1178, 1135 cm\(^{-1}\). M.p. 124-130 °C (decomposition). \([\alpha]_D^{26} = +96.0\ (c\ 1.00,\ CHCl_3).\) HRMS (ESI–) calcd for C\(_{42}\)H\(_{21}\)F\(_{12}\)O\(_2\) [M–H]– 785.1355, found 785.1341.
(R)-3-(3,3′′,5,5′′-Tetrakis(pentafluoro-6-sulfanyl)-[1,1′:3′,1″-terphenyl]-5′-yl)-BINOL: The titled compound was prepared based on the reported procedure.\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 5.13 (s, 1H), 5.37 (s, 1H), 7.20 (d, \(J = 8.7\) Hz, 1H), 7.25 (d, \(J = 8.7\) Hz, 1H), 7.29-7.50 (m, 5H), 7.67 (t, \(J = 1.4\) Hz, 1H), 7.91 (d, \(J = 7.8\) Hz, 1H), 7.95-8.26 (m, 11H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 110.4, 112.5, 117.9, 123.3 (2C), 124.0, 124.3 (2C), 124.9, 125.7, 127.7, 128.2 (5C), 128.5, 128.6 (2C), 129.4, 129.6, 129.7 (2C), 131.8, 131.9, 133.2, 133.3, 139.4 (2C), 140.4, 142.9 (2C), 149.9, 152.9, 154.2 (quintet, \(J_{C-F} = 19.1\) Hz, 4C). \(^19\)F NMR (376 MHz, CDCl\(_3\)) δ 63.3 (d, \(J = 150\) Hz, 8F), 81.6 (quintet, \(J = 150\) Hz, 2F). IR (KBr) 3529, 1598, 1467, 1399, 1258, 1233, 1181, 1140 cm\(^{-1}\). M.p. 158-165 °C. \([\alpha]_D^{25} = +69.6\) (c 1.00, CHCl\(_3\)). HRMS (ESI–) calcd for C\(_{38}\)H\(_{21}\)F\(_{20}\)O\(_2\)S\(_4\) [M−H]\(^−\) 1017.0111, found 1017.0108.

(R)-3-Triphenylsilyl-BINOL: The titled compound was prepared based on the reported procedure.\(^13\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 5.08 (s, 1H), 5.21 (s, 1H), 7.16-7.25 (m, 2H), 7.29-7.45 (m, 8H), 7.38 (d, \(J = 7.8\) Hz, 6H), 7.66 (d, \(J = 7.8\) Hz, 6H), 7.73 (m, 1H), 7.84 (m, 1H), 7.90 (d, \(J = 8.7\) Hz, 1H), 7.97 (s, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) Many peaks overlapped. δ 110.3, 110.9, 117.6, 123.6, 123.8, 123.9, 124.0, 124.1, 127.3, 127.8, 128.3, 128.4, 129.0, 129.1, 129.4, 129.5, 131.3, 133.1, 134.2, 134.7, 136.2, 142.2, 152.6, 156.5. IR (KBr) 3477, 3418, 3064, 1617, 1579, 1427, 1359, 1208, 1171, 1144, 1105 cm\(^{-1}\). M.p. 235-239 °C (decomposition). \([\alpha]_D^{26} = +107.2\) (c 1.00, CHCl\(_3\)). HRMS (ESI–) calcd for C\(_{38}\)H\(_{27}\)O\(_2\)Si [M−H]\(^−\) 543.1786, found 543.1789.
**2-Cyano-3-fluorophenylboronic acid:** The titled compound was prepared from 2-bromo-6-fluorobenzonitrile according to the reported procedure.\(^5\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.35 (t, \(J_{H,H,F} = 8.5\) Hz, 1H), 7.49 (m, 1H), 7.35 (td, \(J_{H,H,F} = 8.5, 5.5\) Hz, 1H). \(^19\)F (376 MHz, CD\(_3\)OD) \(\delta\) –109.5. IR (KBr) 3355, 1672, 1447, 1417, 1274, 1238, 1161, 1080 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_7\)H\(_4\)BFNO\(_2\) [M–H] 164.0324, found 164.0321.

**2-Cyano-4-fluorophenylboronic acid:** The titled compound was prepared from 2-bromo-5-fluorobenzonitrile according to the reported procedure.\(^5\) \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.40 (t, \(J_{H,H,F} = 8.7\) Hz, 1H), 7.40 (d, \(J = 8.7\) Hz, 1H), 7.74 (br, 1H). \(^19\)F (376 MHz, CD\(_3\)OD) \(\delta\) –111.4. IR (KBr) 3361, 1595, 1575, 1491, 1266, 1232 cm\(^{-1}\). HRMS (ESI–) calcd for C\(_7\)H\(_4\)BFNO\(_2\) [M–H] 164.0324, found 164.0324.

### 7. Possible transition states.

Possible transition states with catalyst 2c are shown in Figure S2, where each 3-phosphoryl moiety is located far from the Ar moiety of arylboronic acid due to steric reasons (also see Figure 6a in the main text.). Catalyst 2c has successive rotamers due to the flexible conformations. TS-15 with a syn-conformation might be most favored without significant steric repulsion. In contrast, TS-S10 with an anti-conformation would be disfavored due to steric repulsion between tris(pentafluorophenyl)borane and the aryl moiety.

Next, a possible transition state with catalyst 7a is shown in Figure S3a. TS-16 might be the most favored without significant steric repulsion, where 3,5-(3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\))\(_2\)C\(_6\)H\(_3\) is located far from the Ar moiety of arylboronic acid due to steric reasons (also see Figure 6a in the main text.). A possible transition state with catalyst S7 is shown in Figure S3b. S7 has a binaphthyl skeleton, unlike the H\(_8\)-binaphthyl skeleton of 7a, and the dihedral angle of the binaphthyl skeleton might be smaller than that of the H\(_8\)-binaphthyl skeleton. Moreover, a 5-F substituent in place of a 5-CF\(_3\) substituent in the aryl moiety would relieve the steric repulsion. As a result, TS-S11 might be favored without significant steric repulsion, where 3,5-(3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\))\(_2\)C\(_6\)H\(_3\) is located close to the Ar moiety of arylboronic acid due to the relief of steric repulsion by F in place of CF\(_3\).

Overall, for the absolute stereochemistry of 5a, exo-(2S)-5a (98% ee) can be rationalized via TS-16, and exo-(2R)-5a (81% ee) can be rationalized via TS-S11.
Figure S2. Possible transition states with catalyst 2c.

Figure S3. Possible transition states with catalyst 7a and S7.
8. References.
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