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Supporting Information

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exo-Selective Asymmetric Diels-Alder Reaction Catalyzed by Diamine Salts as Organocatalysts

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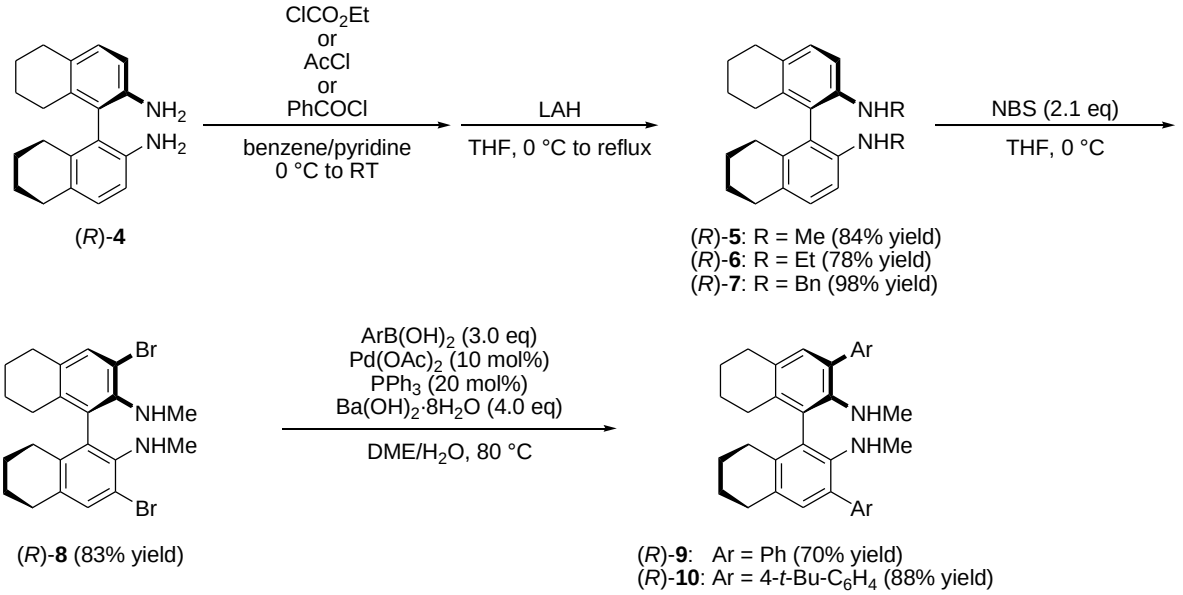
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Analytical gas-liquid phase chromatography (GLC) was performed on Shimadzu GC-14B instruments equipped with a flame ionization detector using an Astec Chiraldex G-TA (30 m x 0.25 mm) column, Astec Chiraldex B-DM (30 m x 0.25 mm) column or a Gasukuro Kogyo Inc. PEG-HT Bonded (25 m x 0.25 mm) column. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK AD-H (4.6 mm × 25 cm) column or AS-H (4.6 mm × 25 cm) column. The high-resolution mass spectra (HRMS) were performed on an Applied Biosystems Mariner 8295 API-TOF workstation and BRUKER microTOF. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh).

In experiments requiring dry solvents, tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Inc. as "Dehydrated". Dichloromethane (CH_2Cl_2) and α,α,α-trifluorotoluene were stored over 4Å molecular sieves. Toluene was dried over sodium metal. α,β-Unsaturated aldehydes were distilled and stored under argon atmosphere at –17 °C. The following aniline derivatives are all known: 2-*tert*-Butyl-*N*-methylaniline;[1] *N*,2,6-Trimethylaniline;[2] *N*,*N*'-Dimethyl-biphenyl-2,2'-diamine **1**;[3] *N*,*N*',6,6'-Tetramethyl-biphenyl-2,2'-diamine **2**;[4] *N*,*N*'-Dimethyl-1,1'-binaphthyl-2,2'-diamine **3**.[5] 5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diamine (*R*)-**4** was prepared according to the literature procedure.[6] The following products are all known: *exo*-3-Propyl-bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde;[7] *exo*-3-Isopropyl-bicyclo[2.2.1]hex-5-ene-

2-carboxaldehyde;[7] *exo*-3-Furan-2-yl-bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde.[7] Other simple chemicals were purchased and used as such.

Representative Procedure for the Synthesis of Chiral Diamines (*R*)-9 and (*R*)-10



Diamine (*R*)-5: To a stirred solution of (*R*)-**4** (292 mg, 1.0 mmol) in benzene (10 mL) and pyridine (1 mL) was added dropwise ethyl chloroformate (478 μL, 5.0 mmol) at 0 °C. After 3 h of stirring at room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic extracts were dried over Na_2SO_4. Evaporation of solvents gave the crude biscarbamate which was directly used for the following reaction without any purification. To a stirred solution of the biscarbamate in anhydrous THF (10 mL) was added $LiAlH_4$ (379 mg, 10 mmol) portionwise at 0 °C. The reaction mixture was heated under reflux overnight. The reaction mixture was then quenched with 1N NaOH at 0 °C and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 20:1 as eluent) to afford (*R*)-**5** (269 mg, 0.84 mmol, 84% yield): $[\alpha]_D^{21}$ 73.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (2H, d, *J* = 8.0 Hz, Ar-H), 6.54 (2H, d, *J* = 8.0 Hz, Ar-H), 3.26 (2H, br s, NH), 2.72 (4H, t, *J* = 6.4 Hz, $ArCH_2$), 2.71 (6H, s, $NHCH_3$), 2.06-2.21 (4H, m, $ArCH_2$), 1.58-1.76 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 135.9, 129.1, 126.0, 121.1, 107.9, 31.2, 29.4, 27.0, 23.6, 23.4; IR (neat) 3414, 2924, 2831, 1595, 1497, 1456, 1301, 1273, 1155, 800, 756 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{22}H_{29}N_2$: 321.2325 ($[M + H]^+$), Found: 321.2325 ($[M + H]^+$).

Diamine (*R*)-6: Diamine (*R*)-**6** was prepared in a similar manner as described above using acetyl chloride instead of ethyl chloroformate (78% yield): $[\alpha]_D^{25}$ 64.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.99 (2H, d, J = 8.4 Hz, Ar-H), 6.56 (2H, d, J = 8.4 Hz, Ar-H), 3.19 (2H, br s, NH), 3.09 (4H, q, J = 7.2 Hz, NHCH_2), 2.72 (4H, t, J = 6.2 Hz, ArCH_2), 2.07-2.22 (4H, m, ArCH_2), 1.56-1.74 (8H, m, $CH_2CH_2CH_2CH_2$), 1.04 (6H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.1, 129.1, 126.0, 121.3, 108.6, 38.7, 29.4, 27.1, 23.6, 23.5, 15.1; IR (neat) 3395, 2924, 2853, 2361, 1595, 1494, 1456, 1301, 1281, 1263, 1150, 798 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{24}H_{33}N_2$: 349.2638 ([M + H]$^+$), Found: 349.2641 ([M + H]$^+$).

Diamine (*R*)-7: Diamine (*R*)-**7** was prepared in a similar manner as described above using benzoyl chloride instead of ethyl chloroformate (98% yield): $[\alpha]_D^{25}$ 37.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (8H, app d, Ar-H), 7.16 (2H, m, Ar-H), 6.91 (2H, d, J = 8.2 Hz, Ar-H), 6.47 (2H, d, J = 8.2 Hz, Ar-H), 4.26 (4H, s, NHCH_2), 3.90 (2H, br s, NH), 2.69 (4H, t, J = 5.6 Hz, ArCH_2), 2.24-2.32 (2H, m, ArC*H*H), 2.12-2.22 (2H, m, ArCH*H*), 1.58-1.74 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.2, 136.2, 129.1, 128.2, 126.7, 126.6, 126.2, 121.0, 108.6, 47.8, 29.4, 27.2, 23.6, 23.5; IR (neat) 3420, 3026, 2926, 2853, 1595, 1494, 1450, 1296, 826, 800, 737, 696 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{34}H_{37}N_2$: 473.2951 ([M + H]$^+$), Found: 473.2950 ([M + H]$^+$).

Dibromide (*R*)-8: To a stirred solution of (*R*)-**5** (269 mg, 0.84 mmol) in anhydrous THF (5 mL) was added NBS (314 mg, 1.76 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 10 seconds. The reaction mixture was then quenched with saturated $NaHCO_3$ and saturated Na_2SO_3 at 0 °C, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 20:1 as eluent) to afford (*R*)-**8** (332 mg, 0.69 mmol, 83% yield): $[\alpha]_D^{21}$ –22.2 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, s, Ar-H), 3.35 (2H, br s, NH), 2.72 (4H, m, ArCH_2), 2.62 (6H, s, NHCH_3), 2.16-2.23 (2H, m, ArC*H*H), 1.95-2.04 (2H, m, ArCH*H*), 1.61-1.71 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 135.8, 133.5, 131.4, 128.3, 111.9, 34.8, 29.2, 27.5, 23.1, 22.9; IR (neat) 3370, 2930, 2855, 2357, 2328, 1496, 1456, 1409, 771, 552 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{22}H_{27}Br_2N_2$: 477.0535 ([M + H]$^+$), Found: 477.0538 ([M + H]$^+$).

Diamine (*R*)-9: A mixture of (*R*)-**8** (332 mg, 0.69 mmol), $Pd(OAc)_2$ (15.4 mg, 0.069 mmol), PPh_3 (36.2 mg, 0.138 mmol), $Ba(OH)_2{\cdot}8H_2O$ (871 mg, 2.76 mmol), and phenylboronic acid (252 mg, 2.07 mmol) in degassed DME (3 mL) and H_2O (300 μL) was refluxed overnight. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 50:1 as eluent) to afford (*R*)-**9** (227 mg, 0.48 mmol, 70% yield): $[\alpha]_D^{20}$ –57.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (4H, d, J = 8.0 Hz, Ar-H), 7.37 (4H, dd, J = 8.0, 8.0 Hz, Ar-H), 7.24 (2H, t, J = 8.0 Hz, Ar-H), 6.98 (2H, s, Ar-H), 3.12 (2H, br s, NH), 2.77 (4H, t, J = 6.0 Hz, ArCH_2), 2.30-2.38 (2H, m, ArC*H*H), 2.20 (6H, s, NHCH_3), 2.15-2.22 (2H, m, ArCH*H*), 1.67-1.78 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100

MHz, $CDCl_3$) δ 144.1, 141.9, 135.2, 132.0, 129.3, 128.7, 128.6, 128.1, 126.5, 126.2, 35.3, 29.5, 27.6, 23.6, 23.3; IR (neat) 3371, 2927, 2359, 1458, 1134, 771, 700 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{34}H_{37}N_2$: 473.2951 ($[M + H]^+$), Found: 473.2954 ($[M + H]^+$).

Diamine (*R*)-10: Diamine (*R*)-**10** was prepared in a similar manner as described above using 4-*tert*-butylphenylboronic acid instead of phenylboronic acid (88% yield): $[\alpha]_D^{23}$ –85.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (4H, d, *J* = 8.8 Hz, Ar-H), 7.39 (4H, d, *J* = 8.8 Hz, Ar-H), 7.00 (2H, s, Ar-H), 3.13 (2H, br s, NH), 2.76 (4H, t, *J* = 6.0 Hz, $ArCH_2$), 2.30-2.38 (2H, m, ArC*H*H), 2.20 (6H, s, NHCH_3), 2.12-2.21 (2H, m, ArCH*H*), 1.66-1.78 (8H, m, $CH_2CH_2CH_2CH_2$), 1.35 (18H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 144.2, 138.8, 135.0, 131.9, 129.2, 128.7, 128.2, 126.5, 125.0, 35.3, 34.6, 31.5, 29.5, 27.6, 23.6, 23.4; IR (neat) 3371, 2959, 2931, 2864, 2310, 1458, 1265, 1134, 837, 756 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{42}H_{53}N_2$: 585.4203 ($[M + H]^+$), Found: 585.4203 ($[M + H]^+$).

Amine (*R*)-11: Amine (*R*)-**11** was prepared by methylation of 2-methoxy-1,1'-binaphthyl-2'-amine[8] in a similar manner as described above: $[\alpha]_D^{26}$ 119.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (1H, d, *J* = 9.2 Hz, Ar-H), 7.87 (2H, app t, Ar-H), 7.76 (1H, d, *J* = 8.4 Hz, Ar-H), 7.45 (1H, d, *J* = 9.2 Hz, Ar-H), 7.32 (1H, app t, Ar-H), 7.08-7.26 (5H, m, Ar-H), 6.89 (1H, d, *J* = 8.4 Hz, Ar-H), 3.73 (3H, s, OCH_3), 3.48 (1H, br s, NH), 2.81 (3H, s, NHCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.7, 133.7, 129.8, 129.5, 129.0, 127.8, 127.2, 126.7, 126.0, 124.9, 123.9, 123.8, 121.4, 118.8, 114.4, 113.3, 113.2, 56.9, 31.4 (The signals for two aromatic carbons were not identified due to the overlap of peaks); IR (neat) 3424, 3053, 2933, 2835, 2364, 1616, 1597, 1341, 1267, 1246, 810, 746 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{22}H_{20}NO$: 314.1539 ($[M + H]^+$), Found: 314.1538 ($[M + H]^+$).

Amine (*R*)-12: Amine (*R*)-**12** was prepared by conversion of (*R*)-2-hydroxy-2'-ethylbinaphthyl[9] to (*R*)-2-methoxycarbonyl-2'-ethylbinaphthyl according to the literature procedure,[10] hydrolysis of the methyl ester under standard conditions [20% NaOH aq, MeOH, THF, 70 °C], Curtius rearrangement of the resulting carboxylic acid to the methylcarbamate,[11] and subsequent reduction of the methylcarbamate in a similar procedure for synthesis of (*R*)-**5**: $[\alpha]_D^{24}$ 39.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.94 (3H, m, Ar-H), 7.78 (1H, d, *J* = 7.6 Hz, Ar-H), 7.59 (1H, d, *J* = 8.4 Hz, Ar-H), 7.40 (1H, app t, Ar-H), 7.08-7.26 (5H, m, Ar-H), 6.83 (1H, d, *J* = 8.4 Hz, Ar-H), 3.36 (1H, br s, NH), 2.80 (3H, s, NHCH_3), 2.41 (2H, q, *J* = 7.6 Hz, CH_2CH_3), 1.02 (3H, t, *J* = 7.6 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.2, 133.9, 133.0, 132.7, 131.4, 129.0, 128.3, 127.9, 127.5, 127.2, 126.3, 126.2, 125.8, 125.3, 124.0, 121.6, 115.5, 113.2, 31.1, 26.8. 15.0 (The signal for an aromatic carbon was not identified due to the overlap of peaks); IR (neat) 3422, 3051, 2965, 2820, 1616, 1597, 1512, 1495, 1341, 810, 746 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{23}H_{22}N$: 312.1747 ($[M + H]^+$), Found: 312.1738 ($[M + H]^+$).

General Procedure for the Diamine Salt Catalyzed Asymmetric Diels-Alder Reaction: To a

solution of diamine (*R*)-**10** (17.4 mg, 0.03 mmol) and *p*-TsOH·H_2O (4.8 mg, 0.025 mmol) in α,α,α-trifluorotoluene (1 mL) was added (*E*)-cinnamaldehyde (32 μL, 0.25 mmol) at –20 °C. After stirring for 1-2 minutes, cyclopentadiene (62 μL, 0.75 mmol followed by 2 x 41 μL, 2 x 0.5 mmol, after 48 and 96 h) was added to the reaction mixture. Upon consumption of the starting material, the reaction mixture was directly purified by flash column chromatography on silica gel (hexane/ethyl acetate = 10:1 as eluent) to afford the desired Diels-Alder adduct [80% yield, *exo*/*endo* = 13:1, 92% ee (*exo* isomer), 91% ee (*endo* isomer)].

***exo*-Bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 1 in Table 6)**: $[\alpha]_D^{25}$ –7.4 [*c* 0.2, $CHCl_3$ (86% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (1H, d, *J* = 2.4 Hz, CHO), 6.19 (1H, dd, *J* = 2.8, 5.6 Hz, C*H*=CH), 6.13 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 3.12 (1H, br s, C*H*CH=CH), 2.98 (1H, br s, C*H*CH=CH), 2.29 (1H, m, C*H*CHO), 1.96 (1H, ddd, *J* = 4.0, 4.0, 12.0 Hz, C*H*HCHCHO), 1.37 (1H, m), 1.28 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 138.5, 135.2, 51.8, 45.9, 44.3, 41.9, 27.2; IR (neat) 2936, 2870, 1719, 1332, 912, 742, 717 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_8H_{11}O$: 123.0804 ($[M + H]^+$), Found: 123.0809 ($[M + H]^+$).

The enantiomeric excess was determined by acetalization with (–)-(2*R*,4*R*)-2,4-pentanediol and GLC analysis according to the literature procedure:[12] PEG-HT Bonded (25 m x 0.25 mm) column (90 °C isotherm, N_2: 80 kPa, He: 85 kPa), retention time; *exo* isomer: 27.5 min and 29.0 min (major), *endo* isomer: 22.5 min and 26.5 min.

(1*R*,2*S*,3*R*,4*S*)-3-Methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 2 in Table 6): ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[7] GLC analysis: Astec Chiraldex G-TA (30 m x 0.25 mm) column (60 °C isotherm, N_2: 80 kPa, He: 85 kPa), retention time; *exo* isomer: 17.1 min (2*S*) and 19.4 min (2*R*), *endo* isomer: 24.6 min (2*S*) and 27.2 min (2*R*).

(–)-Ethyl *exo*-3-formylbicyclo[2.2.1]hept-5-ene-2-carboxylate (Entry 3 in Table 6): $[\alpha]_D^{27}$ –68.3 [*c* 2.0, $CHCl_3$ (83% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (1H, d, *J* = 0.8 Hz, CHO), 6.30 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.13 (1H, dd, *J* = 2.8, 5.6 Hz, CH=C*H*), 4.11 (2H, q, *J* = 6.8 Hz, C$H_2$$CH_3$), 3.41 (1H, app t, C*H*CHO), 3.29 (1H, br s, C*H*CH=CH), 3.20 (1H, br s, C*H*CH=CH), 2.81 (1H, app d, C*H*CO_2Et), 1.29-1.46 (2H, m, CH_2), 1.23 (3H, t, *J* = 6.8 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 172.8, 136.9, 135.7, 60.7, 55.9, 46.7, 45.5, 44.6, 44.5, 14.3; IR (neat) 2980, 2719, 1718, 1301, 1261, 1188, 1033, 862, 732, 659 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{14}O_3Na$: 217.0835 ($[M + Na]^+$), Found: 217.0834 ($[M + Na]^+$).

The enantiomeric excess was determined by reduction of the formyl group [2.0 eq $NaBH_4$, MeOH (0.2 M)] followed by conversion of the resulting alcohol to the benzoyl ester [3.0 eq Et_3N and 1.0 eq BzCl, CH_2Cl_2 (0.2 M)]. Ethyl *exo*-3-benzoyloxymethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate: $[\alpha]_D^{25}$ –9.9 [*c* 1.0, $CHCl_3$ (83% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (2H, d, *J* = 7.2 Hz, Ar-H), 7.56 (1H, t, *J* = 7.2 Hz, Ar-H), 7.44 (2H, t, *J* = 7.2 Hz, Ar-H), 6.31 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.10 (1H,

dd, *J* = 2.8, 5.6 Hz, CH=C*H*), 4.40 (2H, m, CH_2OBz), 4.05 (2H, q, *J* = 7.2 Hz, $CO_2CH_2CH_3$), 3.22 (1H, br s, C*H*CH=CH), 2.83 (1H, br s, C*H*CH=CH), 2.66 (1H, dd, *J* = 3.6, 4.4 Hz, C*H*CO_2Et), 2.28 (1H, m, C*H*CH_2OBz), 1.50-1.63 (2H, m, CH_2), 1.19 (1H, t, *J* = 7.2 Hz, $CO_2CH_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 166.3, 137.8, 134.3, 132.8, 130.1, 129.5, 128.2, 67.9, 60.4, 48.2, 46.5, 45.6, 44.7, 42.9, 14.3; IR (neat) 3063, 2978, 2358, 2330, 1718, 1271, 1178, 1113, 1026, 850, 806, 711 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{18}H_{21}O_4$: 301.1434 ([M + H]$^+$), Found: 301.1439 ([M + H]$^+$); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 30:1, flow rate = 0.5 mL/min, retention time; *exo* isomer: 18.3 min and 19.6 min (major), *endo* isomer: 15.2 min and 17.4 min.

(1*R*,2*R*,3*R*,4*S*)-3-Phenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 4 in Table 6): $[\alpha]_D^{21}$ –87.7 [*c* 0.23, $CHCl_3$ (92% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (1H, d, *J* = 2.0 Hz, CHO), 7.13-7.32 (5H, m, Ar-H), 6.33 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.07 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 3.72 (1H, dd, *J* = 3.6, 5.2 Hz, C*H*Ph), 3.23 (1H, br s, C*H*CH=CH), 3.22 (1H, br s, C*H*CH=CH), 2.60 (1H, m, C*H*CHO), 1.56-1.63 (2H, m, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 142.3, 136.3, 136.0, 127.9, 127.7, 126.1, 59.3, 48.4, 47.5, 45.42, 45.39; IR (neat) 2358, 1716, 1219, 771 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{14}H_{14}ONa$: 221.0937 ([M + Na]$^+$), Found: 221.0937 ([M + Na]$^+$); GLC analysis: Astec Chiraldex B-DM (30 m x 0.25 mm) column (140 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; *exo* isomer: 43.0 min (2*R*) and 49.1 min (2*S*), *endo* isomer: 45.7 min (2*R*) and 50.4 min (2*S*).

***exo*-3-(4-Chlorophenyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 5 in Table 6)**: ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[13] GLC analysis: Astec Chiraldex B-DM (30 m x 0.25 mm) column (160 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; *exo* isomer: 54.6 min (major) and 60.7 min, *endo* isomer: 57.9 min and 62.3 min.

***exo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 6 in Table 6)**: ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[13] HPLC analysis: Daicel Chiralpak AS-H, hexane/*i*-PrOH = 9:1, flow rate = 0.5 mL/min, retention time; *exo* isomer: 41.6 min and 57.2 min (major), *endo* isomer: 40.0 min and 43.4 min.

***exo*-3-(2-Nitrophenyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 7 in Table 6)**: ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values. [13] HPLC analysis: *exo* isomer; Daicel Chiralpak AS-H, hexane/*i*-PrOH = 9:1, flow rate = 0.5 mL/min, retention time; 21.3 min and 24.4 min (major), *endo* isomer; Daicel Chiralpak AD-H, hexane/*i*-PrOH = 19:1, flow rate = 0.5 mL/min, retention time; 31.2 min and 41.4 min.

***exo*-3-(4-Isopropylphenyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 8 in Table 6)**: ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[13] GLC

analysis: Astec Chiraldex B-DM (30 m x 0.25 mm) column (160 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; *exo* isomer: 55.4 min (major) and 59.9 min, *endo* isomer: 61.6 min and 65.5 min.

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