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Supporting Information

J3050-1

A New Powerful and Practical BLA Catalyst for Highly Enantioselective Diels-Alder Reaction: An Extreme Acceleration Effect of Diels-Alder Reaction by Brønsted Acid

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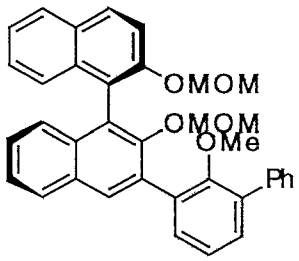
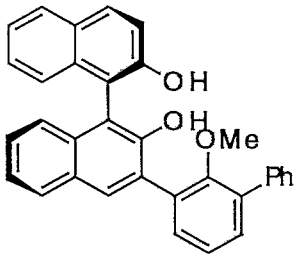


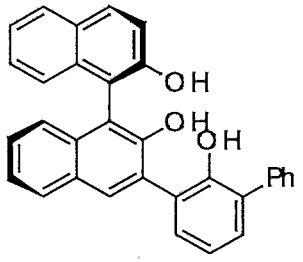
(*R*)-3-(2-Methoxy-3-phenylphenyl)-2,2'-di(methoxymethoxy)-1,1'-binaphthyl. To a mixture of (*R*)-3-bromo-2,2'-di(methoxymethoxy)-1,1-binaphthyl (2.90 g, 6.4 mmol), 2-methoxy-3-phenylphenylboronic acid (2.92 g, 12.8 mmol), and barium hydroxide octahydrate (4.04 g, 12.8 mmol) in DME-H_2O (6:1, 56 mL) under argon was added $Pd(PPh_3)_4$ (148 mg, 0.13 mmol), and then the mixture was degassed three times, and charged with argon. The mixture was warmed to 80 °C and stirred for 12 h. The resulting mixture was cooled to ambient temperature, filtered through a Celite pad, and the filtrate was diluted with saturated NH_4Cl aq., extracted with ether twice, and the combined extracts were dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate-dichloromethane (10:1:1) as eluent to give 3.49 g (98%) of (*R*)-3-(2-methoxy-3-phenylphenyl)-2,2'-di(methoxymethoxy)-1,1-binaphthyl as a white solid. TLC (hexane-EtOAc, 4 : 1), R_f=0.37; IR ($CHCl_3$) 3011, 1593, 1472, 1460, 1240, 1200, 1150, 1073, 1036, 972, 924, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H, CH_3O), 3.22

(s, 3H, CH_3O), 3.31 (s, 3H, CH_3O), 4.38 (d, *J*=5.9 Hz, 1H, C*H*H), 4.49 (d, *J*=5.9 Hz, 1H, CH*H*), 5.06 (d, *J*=6.9 Hz, 1H, C*H*H), 5.18 (d, *J*=6.9 Hz, 1H CH*H*), 7.22-7.65 (m, 15H, ArH), 7.86 (d, *J*=8.3 Hz, 1H, ArH), 7.91 (d, *J*=8.2 Hz, 1H, ArH), 7.95 (d, *J*=9.3 Hz, 1H, ArH), 8.01 (s, 1H, ArH); $[\alpha]^{25}_D$=+115.5° (*c*=1.0, $CHCl_3$); Anal. Calcd for $C_{37}H_{32}O_5$: C, 79.84; H, 5.79. Found. C, 79.80; H, 5.88.



(*R*)-3-(2-Methoxy-3-phenylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl: A solution of (*R*)-3-(2-methoxy-3-phenylphenyl)-2,2'-di(methoxymethoxy)-1,1-binaphthyl (3.28 g, 5.9 mmol) in 4 *M* HCl-THF (1:1, 40 mL) was refluxed for 5 h, and cooled to ambient temperature. After being diluted with H_2O, the mixture was extracted with ether twice. The combined extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel using hexane-ethyl acetate-dichloromethane (10:1:1 ~ 7:1:1) as eluent to give 2.63 g (95%) of (*R*)-3-(2-methoxy-3-phenylphenyl)-2,2'-dihydroxy-1,1-binaphthyl as a white solid. TLC (hexane-EtOAc, 4 : 1) R_f=0.25; IR ($CHCl_3$) 3260, 1622, 1597, 1460, 1412, 1177, 1146, 1132, 1003 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.31 (s, 3H, CH_3O), 7.18-7.60 (m, 15H, ArH), 7.89 (d, *J*=8.8 Hz, 1H, ArH), 7.95 (d, *J*=8.5 Hz, 1H, ArH), 7.96 (d, *J*=9.1 Hz, 1H, ArH), 8.09 (s, 1H, ArH); Anal. Calcd for $C_{13}H_{14}O_3$: C, 84.59; H, 5.16. Found. C, 84.62; H, 5.34; $[\alpha]^{25}_D$=+132.4° (*c*=0.82, $CHCl_3$).

J3050-3

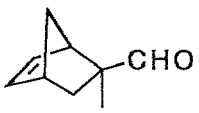


(*R*)-3-(2-Hydroxy-3-phenylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl: To a solution of (*R*)-3-(2-methoxy-3-phenylphenyl)-2,2'-dihydroxy-1,1-binaphthyl (2.57 g, 5.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C under argon was added BBr_3 (1.56 mL, 16.5 mmol) slowly, the mixture was stirred at same temperature for 1 h. After ice-cold H_2O was added to the reaction mixture to quench an excess of BBr_3, the mixture was extracted with CH_2Cl_2 twice. The combined extracts was washed with saturated $NaHCO_3$ aq., dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash column chromatograohy on silica gel using hexane-ethyl acetate-dichloromethane (7:1:1) as eluent to give 2.30 g (93%) of (*R*)-3-(2-hydroxy-3-phenylphenyl)-2,2'-dihydroxy-1,1-binaphthyl as a white solid. Mp. 96-97 °C; TLC (hexane-EtOAc, 4 : 1), R_f=0.29; IR ($CHCl_3$) 3400, 1622, 1599, 1501, 1431, 1383, 1202, 1181, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15-7.24 (m, 3H, ArH), 7.27-7.57 (m, 12 H, ArH), 7.89 (d, *J*=7.5 Hz, 1H, ArH), 7.93-7.96 (m, 1H, ArH), 7.98 (d, *J*=8.8 Hz, 1H, ArH), 8.09 (s, 1H, ArH); $[\alpha]^{23.5}_D$=+121.6 ° (*c*=1.25, $CHCl_3$); HRMS (EI) *m/z* cald for $[C_{32}H_{22}O_3]$ 454.1569, found 454.1561.

Preparation of BLA (method A) and the Representative Procedure of Diels-Alder Reaction. A mixture of the chiral ligand **3a** (27.3 mg, 0.06 mmol) and a solution of monomeric 3,5-bis(trifluoromethyl)benzeneboronic acid **4** (1.16 mL, 0.05 mmol, 0.043 *M*) in CH_2Cl_2-THF-H_2O (20:3:0.054) was stirred at ambient temperature for 2 h. The resulting colorless solution was transferred into a Schlenk tube comntaining anhydrous dichloromethane and powdered MS 4A [250 mg, activated by heating at 200 °C under vacuum (ca. 3 torr) for 12 h], and the mixture was stirred at ambient temperature for another 12 h. Then the solvents were evaporated and the resulting solid was heated to 100 °C (oil bath) for 2 h under vacuum (ca. 3

torr) to dry catalyst. After cooling to ambient temperature, the flask was purged with argon and then charged with dichloromethane (2 mL, distilled from CaH_2). The mixture was cooled to -78 °C, dienophile (1 mmol) was added dropwise and 1 min later freshly distilled diene (4 mmol) was slowly added along the wall of the flask. After the recation mixture was stirred under the conditions indicated in Table 2, the reaction was quenched with pyridine (20 μL, 0.25 mmol), warmed to ambient temperature, and filtered to remove molecular sieves. The filtrate was washed with ether, dried ($MgSO_4$), and concentrated to afford the crude products. Purification by silica gel chromatography eluting with pentane-ether provided the pure Diels-Alder adduct.

The exo/endo ratios, % ee's, and absolute configurations of the Diels-Alder adducts were determined as follows.



(1*R*,2*S*,4*R*)-2-Methylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde[1] (Table 1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76 (d, *J*=12.0 Hz, 1H, C*H*H), 1.01 (s, 3H, CH_3), 1.38-1.40 (m, 2H, CH_2), 2.25 (dd, *J*=3.8, 12.0 Hz, 1H, C*H*H), 2.82 (br, 1H, C*H*CH=C), 2.90 (br, 1H, C*H*-CH=C), 6.11 (dd, *J*=3.0, 5.7 Hz, 1H, C*H*=CH), 6.30 (dd, *J*=3.0, 5.7 Hz, 1H, CH=C*H*), 9.69 (s, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis of Diels-Alder adducts and GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 1H, CHO (endo)), 9.69 (s, 1H, CHO (exo)). The ee was determined by GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[1] GC (80 °C, PEG-HT Bonded (25 m x 0.25 mm)) t_R=37.7 min (major endo-isomer), 47.6 min (minor endo-isomer), 51.5 min ((1*S*,2*R*,4*S*)-isomer), 54.7 min ((1*R*,2*S*,4*R*)-isomer). The absolute configuration was established by comparison of optical rotation values with data in the literature.[2]

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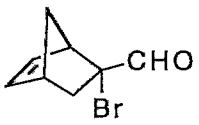
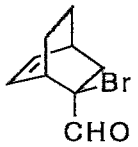
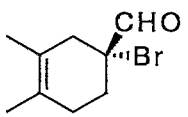


(1*R*,2*R*,4*S*)-2-Bromobicyclo[2.2.1]hept-5-ene-2-carboxaldehyde[3] (Table 2): The exo/endo ratio was determined by ^{1}H NMR and GC analyses.[3] The ee was determined by reduction with $NaBH_4$, conversion to the Mosher ester, and ^{1}H NMR and HPLC analyses (Daicel AD).[3] The absolute configuration was determined by conversion to the known norbornen-2-one by a literature procedure.[4]

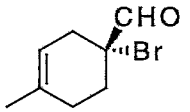


Endo-2-bromobicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (Table 2):[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30-1.52 (m, 2H), 1.74-1.83 (m, 1H), 1.91 (dd, *J*=2.2, 14.5 Hz, 1H), 2.30-2.40 (m, 1H), 2.59 (dt, *J*=3.0, 14.5 Hz, 1H), 2.65-2.73 (m, 1H, C*H*CH=CHCH), 2.96-3.02 (m, 1H, CHCH=CHC*H*), 6.07-6.11 (m, 1H, C*H*=CH), 6.29-6.33 (m, 1H, CH=C*H*), 8.91 (s, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis:[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H, CHO (endo), 9.40 (s, 1H, CHO (exo)). The ee was determined from ^{1}H NMR spectrum of Diels-Alder adducts (5 mg) in the presence of the chiral shift reagent Eu(hfc)$_3$ (ca. 30 mg)[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H, CHO (minor endo-isomer)), 9.73 (s, 1H, CHO (major endo-isomer)), 9.84 (s, 1H, CHO (one exo-iomer)), 9.88 (s, 1H, CHO (another exo-isomer)). The absolute configuration was not determined.

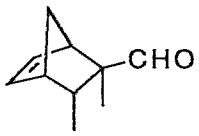


1-Bromo-3,4-dimethyl-3-cyclohexene-1-carboxaldehyde (Table 2):[3] The ee was determined by reduction with $NaBH_4$, conversion to benzoyl ester, and HPLC analysis

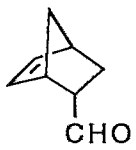
(Daicel OD-H, hexane-*i*-PrOH=1000:1, flow rate=0.5 mL/min): t_R=20.3 min (major isomer) and 22.7 min (minor isomer). The absolute configuration was not determined.



(*R*)-1-Bromo-4-methyl-3-cyclohexene-1-carboxaldehyde (Table 2):[3] The ee was determined by reduction with $NaBH_4$, conversion to benzoyl ester, and HPLC analysis (Daicel AD).[3] Absolute stereochemistry was assigned by analogy with cyclopentadiene.[4]

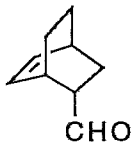


Exo-2,3-Dimethylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (Table 2):[3] The exo/endo ratio was determined by ^{1}H NMR and GC analyses.[3] The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis.[3]

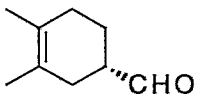


(1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (Table 2):[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (d, *J*=8.2 Hz, 1H, C(7)*H*H), 1.40-1.52 (m, 2H, C(6)*H*H, C(7)H*H*), 1.91 (ddd, *J*=3.6, 9.1, 12.0 Hz, 1H, C(6)H*H*), 2.90 (m, 1H, C*H*CHO), 2.99 (br, 1H, C*H*CH=CHCH), 3.25 (br, 1H, CHCH=CHC*H*), 6.00 (dd, *J*=2.8, 5.9 Hz, 1H, C*H*=CH), 6.22 (dd, *J*=3.2, 5.9 Hz, 1H, CH=C*H*), 9.42 (d, *J*=3.0 Hz, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis of Diels-Alder adducts and GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.42 (d, *J*=3.0 Hz, 1H, CHO (endo)), 9.79 (d, *J*=3.0 Hz, 1H, CHO (exo)). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis:[1] GC (90 °C,

PEG-HT Bonded (25 m x 0.25 mm)) t_R=35.4 min ((1*S*,2*S*,4*S*)-isomer), 41.1 min ((1*R*,2*R*,4*R*)-isomer), 42.6 min (minor exo-isomer) and 44.6 min (major exo-isomer). The absolute configuration was established by comparison of optical rotation values with data in the literature.[2]

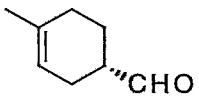


(1*S*,2*S*,4*S*)-Bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (Table 2):[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.41 (m, 2H, CH_2), 1.50-1.78 (m, 4H, $2CH_2$), 2.56 (m, 2H, CH_2), 2.65 (m, 1H, C*H*CH=CHCH), 2.96 (m, 1H, CHCH=CHC*H*), 6.12 (t, *J*=6.9 Hz, 1H, C*H*=CH), 6.34 (t, *J*=6.9 Hz, 1H, CH=C*H*), 9.46 (d, *J*=1.4 Hz, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis of Diels-Alder adducts and GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (d, *J*=1.4 Hz, 1H, CHO). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis:[1] GC (80 °C, PEG-HT Bonded (25 m x 0.25 mm)) t_R=72.9 ((1*S*,2*S*,4*S*)-isomer) and 75.5 ((1*R*,2*R*,4*R*)-isomer) min. The absolute configuration was established by comparison with authentic material prepared independently.[6]

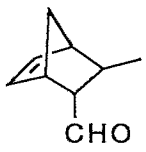


3,4-Dimethyl-3-cyclohexene-1-carboxaldehyde (Table 2):[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H, Me), 1.65 (s, 3H, Me), 1.90-2.06 (m, 4H, CH_2CHHC=CCHH), 2.09-2.19 (m, 2H, CHHC=CCHH), 2.42-2.58 (m, 1H, CHCHO), 9.69 (s, 1H, CHO). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and ^{1}H NMR analysis:[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, *J*=6.0 Hz, 1 H, CHO_2 (major isomer)), 4.61 (d, *J*=6.0 Hz, CHO_2 (minor isomer)). The absolute configuration was not determined.

J3050-8

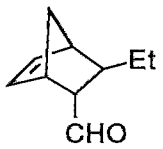


4-Methyl-3-cyclohexene-1-carboxaldehyde (Table 2):[7] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (s, 3H, Me), 1.67-1.78 (m, 1H, CH_2), 1.93-2.05 (m, 4H, $2CH_2$), 2.17-2.24 (m, 2H, CH_2), 2.40-2.50 (m, 1H, CH_2), 5.40 (br, 1H, CH=C), 9.70 (s, 1H, CHO). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and ^{1}H NMR and GC analyses: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.59 (d, *J*=6.0 Hz, CHO_2 (minor isomer)), 4.62 (d, *J*=6.0 Hz, CHO_2 (major isomer)); GC (80 °C, PEG-HT Bonded (25 m x 0.25 mm)) t_R=91.9 min (minor isomer), 93.9 min (major isomer). The absolute configuration was not established.

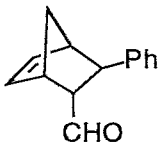


(1*S*,2*S*,3*S*,4*R*)-3-Methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2):[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (d, *J*=6.9 Hz, 3H, Me), 1.44-1.51 (m, 1H, C*H*H), 1.55-1.60 (m, 1H, CH*H*), 1.77-1.87 (m, 1H, C*H*CH_3), 2.34 (dd, *J*=3.2, 4.3 Hz, 1H, C*H*CHO), 2.56 (br, 1H, C*H*CH=CHCH), 3.13 (br, 1H, CHCH=CHC*H*), 6.05 (dd, *J*=2.8, 5.6 Hz, 1H, C*H*=CH), 6.29 (dd, *J*=3.0, 5.8 Hz, 1H, CH=C*H*), 9.37 (d, *J*=3.2 Hz, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis of Diels-Alder adducts and GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[1] ^{1}H NMR ($CDCl_3$) δ 9.37 (d, *J*=3.2 Hz, 1H, CHO (endo)), 9.78 (d, *J*=3.2 Hz, 1H, CHO (exo)). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis:[1] GC (90 °C, PEG-HT Bonded (25 m x 0.25 mm)) t_R=22.9 min ((1*S*,2*S*,3*S*,4*R*)-isomer), 25.5 min ((1*R*,2*R*,3*R*,4*S*)-isomer), 27.1 min (minor exo-isomer), 28.7 min (major exo-isomer). The absolute configuration was established by comparison with authentic material prepared independently.[8]

J3050-9

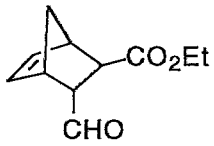


Endo-3-ethylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2):[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, *J*=7.4 Hz, 3H, Me), 1.41-1.63 (m, 5H, C*H*$_2$, C*H*C*H*$_2$CH$_3$), 2.67-2.71 (br, 1H, C*H*CH=CHCH), 3.10-3.14 (br, 1H, CHCH=CHC*H*), 6.28 (dd, *J*=3.1, 5.7 Hz, 1H, C*H*=CH), 9.38 (d, *J*=3.3 Hz, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis (500 MHz): δ 9.38 (d, *J*=3.3 Hz, 1H, CHO (endo)), 9.79 (d, *J*=2.9 Hz, 1H, CHO (exo)). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis (90 °C, PEG-HT Bonded (25 m x 0.25 mm)): t_R=29.0 min (major endo-isomer), 36.0 min (minor endo-isomer), 37.8 min (minor exo-isomer), 38.5 min (major exo-isomer). The absolute configuration was not established.

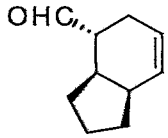


Endo-3-phenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2):[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59-1.65 (m, 1H, C*H*H), 1.79-1.84 (m, 1H, CH*H*), 2.98 (ddd, *J*=2.3, 3.5, 4.9 Hz, 1H, C*H*CHO), 3.09 (dd, *J*=1.6, 4.9 Hz, 1H, C*H*Ph), 3.14 (br, 1H, C*H*CH=CHCH), 6.17 (dd, *J*=2.8, 5.8 Hz, 1H, C*H*=CH), 3.34 (br, 1H, CHCH=CHC*H*), 6.17 (dd, *J*=2.8, 5.8 Hz, 1H, C*H*=CH), 6.42 (dd, *J*=3.3, 5.8 Hz, 1H, CH=C*H*), 7.13-7.34 (m, 5H, Ph), 9.60 (d, *J*=2.3 Hz, 1H, CHO). The exo/endo ratio was determined by ^{1}H NMR analysis (500 MHz): δ 9.60 (d, *J*=2.3 Hz, 1H, CHO (endo)), 9.93 (d, *J*=2.3 Hz, 1H, CHO (exo)). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis (180 °C, PEG-HT Bonded (25 m x 0.25 mm)): t_R=13.2 min (major endo-isomer),

13.9 min (exo-isomers), 14.4 min (minor endo-isomer). The absolute configuration was not established, $[\alpha]^{23}_{D}$=-107.6° (*c*=1.2, $CHCl_3$).



Ethyl Endo-(1*R*,2*R*,3*R*,4*S*)-3-formylbicyclo[2.2.1]hept-5-ene-2-carboxylate: TLC (hexane-EtOAc, 4 : 1), R_f=0.33; IR (film) 2982, 1717, 1453, 1393, 1352, 1333, 1262, 1036, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49-1.54 (m, 1H, C(7)*H*H), 1.65-1.70 (m, 1H, C(7)H*H*), 2.70 (dd, *J*=1.4, 3.9 Hz, 1H, C(2)*H*CO_2Et), 3.19 (brs, 1H, CH), 3.33-3.39 (m, 2H, CH and C(3)*H*CHO), 4.17 (q, *J*=7.1 Hz, 2H, OCH_2CH_3), 6.09 (dd, *J*=2.5, 5.6 Hz, 1H, C*H*=CH), 6.27 (dd, *J*=3.2, 5.6 Hz, 1H, CH=C*H*), 9.55 [d, *J*=1.1 Hz, 1H, CHO (endo), cf. 9.85 (s, 1H, CHO (exo))]; $[\alpha]^{23}_{D}$=-77.6° (*c*=1.2, $CHCl_3$); Anal. Calcd for $C_{13}H_{14}O_3$: C, 68.02; H, 7.26. Found. C, 68.08; H, 7.30. The absolute configuration of the adduct was determined by conversion of the known diol[11] by reduction with $LiAlH_4$. The ee was determined by analytical gas-liquid phase chromatography [GC, Shimadzu Model 8A instrument with a flame-ionization detector and a capillary column of PEG-HT Bonded (25 m x 0.25 mm) using nitrogen as carrier gas] of the chiral acetal derived from the Diels-Alder adduct and (2*R*,4*R*)-2,4-pentanediol: t_R=15.2 min (endo-3*R*-isomer), 17.0 min (endo-3*S*-isomer), 18.6 min (exo-isomers).



(1*R*,2*R*,6*R*)-Bicyclo[4.3.0]non-4-ene-2-carboxaldehyde:[12] TLC (hexane-EtOAc, 4 : 1) R_f=0.46; IR (film) 2957, 2870, 1725, 1455, 1435, 1111, 1067, 681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.10-1.51 (m, 3H), 1.71-2.02 (m, 5H), 2.19-2.40 (m, 2H), 2.45-2.56 (m, 1H), 5.63 (dq, J=3.6, 9.9 Hz, 1H, C*H*=CH), 5.88 (m, 1H, CH=C*H*), 9.69 (d,

J=3.0 Hz, 1H, CHO (endo)); $[\alpha]^{25.2}_{D}$=-92.3 ° (c=1.05, $CHCl_3$). The exo/endo ratio was determined by ^{1}H NMR analysis of Diels-Alder adducts and GC analysis after conversion to chiral acetals by (2*R*,4*R*)-2,4-pentanediol:[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (d, J=2.4 Hz, 1H, CHO (exo)), 9.69 (d, J=3.0 Hz, 1H, CHO (endo)). The ee was determined by acetalization with (-)-(2*R*,4*R*)-2,4-pentanediol and GC analysis:[12] GC (110 °C, PEG-HT Bonded(25 m x 0.25 mm) t_R=44.4 min (1*R*,2*R*,6*R*)-isomer), 45.4 min (one exo-isomer), 46.4 min (another exo-isomer), 49.9 min ((1*S*,2*S*,4*S*)-isomer). The absolute configuration was determined by conversion to the known alcohol by a literature procedure.[13]

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