Supplementary Material (ESI) for Chemical Communications

Asymmetric Synthesis of (+)-*cis*-Nemorensic acid from chiral Diels-Alder Adduct of 2,5-dimethyl Furan

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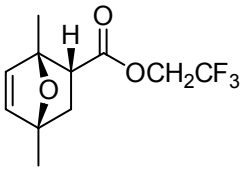
Supporting Information

General: All reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Tetrahydrofuran(THF) was dried by refluxing over sodium/benzophenone ketyl until a permanent purple coloration was presented and other solvents(dichloromethane, toluene) also were distilled prior to use. All liquid reagents purchased from the Aldrich, T.C.I. and Acros companies were distilled properly prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230-400 mesh), eluting with a mixture of hexane and ethyl acetate unless otherwise stated. All reactions were monitored by thin layer chromatography carried out on Merck glass silica gel plate using UV light as visualizing agent and ethanolic anisaldehyde, $KMnO_4$, PMA solution and heat developing agent. FT-IR spectra were recorded on Nicolet 205. ^1H NMR spectra were recorded on a Varian Unity Inova at 300 and 500 MHz in $CDCl_3$ as a solvent with TMS or residual chloroform as the internal standard. ^{13}C NMR spectra were measured on a Varian Unity Inova at 75 and 125 MHz in $CDCl_3$ as a solvent. Gas chromatography (G.C) analysis were performed on Younglin Acme 6000 Series GC system equipped with flame ionization detector using J & W Scientific Cyclosil-B column (30 x 0.25 mm) or γ-TA column(30 x 0.25 mm).

Experimental Section

(1R, 2R, 4R)-2,2,2-trifluoroethyl-1, 4-dimethyl-7-oxa-bicyclo[2. 2. 1]hept-5-ene-2-carboxylate (4).



A 100-ml, two-necked, round bottomed flask equipped with a stir, a glass stopper and a 50-ml pressure-equalizing addition funnel (containing a cotton plug and ca. 10 g of 4Å molecular seives and functioning as a Soxhlet extractor) fitted on top with a reflux condenser and a nitrogen inlet adaptor was charged with (S)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (82.0 mg, 0.324 mmol, from Acros), tri -o-tolylboroxine (38.0 mg, 0.107 mmol) and 25 ml of toluene.

The resulting solution was heated to reflux (bath temperature ~ 145 °C). After 3 h, the reaction mixture was cooled to ca. 60 °C and addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of ca. 5 ml. The distillation protocol was repeated three times by re-charging with 3 x 5 ml of toluene. The solution was then allowed to cool to room temperature and the distillation head was quickly replaced with a nitrogen inlet adaptor. Concentration in vacuo (ca. 0.1 mmHg, 1 h) afforded the corresponding oxazaborolidine as a clear oil, which can then be dissolved in CH_2Cl_2 and used in Diels-Alder experiment.

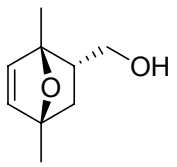
To an aliquot of oxazaborolidine precursor (0.160 mmol, theoretical) in 2.0 mL of CH_2Cl_2 at -45 °C was added trifluoromethanesulfonic acid (667 µl, 0.133 mmol)

dropwise. After 10 min at -45 °C, a colorless homogeneous catalyst solution was ready for use in Diels-Alder reaction. Trifluoroethyl acrylate(340 μl, 2.68 mmol) and 2, 5-dimethylfuran(714 μl, 6.70 mmol) were added successively at -95 °C. The reaction mixture was stirred for 2 h at same temperature and then quenched by addition of 20 μl Et_3N. After the mixture was warmed to room temperature, the solvent was removed by rotary evaporation and residue was purified by silica gel chromatography (ethyl acetate–hexane, 1 : 5) to afford 640 mg (95%, *endo*) of **4**, Diels-Alder adduct: TLC : *Rf*= 0.54(ethyl acetate-hexane , 1 : 3); FT-IR 3076, 2977, 1754, 1634, 1284, 1171 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.27(d, J= 5.7 Hz, 1 H), 6.04(d, J= 5.7 Hz, 1 H), 4.56(dq, J= 3.9, 17.1 Hz, 1 H), 4.31(dq, J= 4.2, 17.1 Hz, 1 H), 2.99(dd, J= 3.9, 9 Hz, 1 H), 2.01(dd, J= 9.0, 11.7 Hz, 1 H), 1.86(dd, J= 3.9, 11.7 Hz, 1 H), 1.74(s, 3 H), 1.60(s, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 170.7, 140.5, 135.8, 122.8(q, 1C, J= 277 Hz), 87.3, 86.2, 60.1(q, 1C, J= 37 Hz), 50.8, 38.1, 81.6, 81.4; LRMS calcd for $C_{11}H_{13}F_3O_3$: 250.08 ; found 250.1; $[\alpha]^{21}_D$ +29 (c 1.0, $CHCl_3$, >99% ee). Diastereoselectivity (*endo-exo* ratio) was determined by ^1H NMR analysis of the crude mixture ^1H NMR δ 6.17 (d, 1H, J= 5.6 Hz, *exo* minor), 6.04 (d, 1H, J=5.2 Hz, *endo* major). Enantioselectivity was determined by double bond reduction with H_2 in the presence of 10% Pd/C and GC analysis (γ-TA, 110℃, 10psi) retention times: 3.72 min(endo, major), 3.99min (endo, minor).

Ref: 1) D. H. Ryu, K. H. Kim, J. Y. Sim, E. J. Corey, *Tetrahedron Lett.* 2007, **48**, 5735.

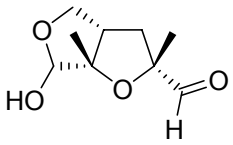
2) D. Liu, E. Canales, E. J. Corey, *J. Am. Chem. Soc.* 2007, **129**, 1498

((1R, 2S, 4R)-1,4-dimethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)methanol (6).



To a cold(-30 ~ -40 °C) slurry of $LiAlH_4$ (120 mg, 3.16 mmol) in dry THF (5 ml) was added a solution of **4** (660 mg, 2.64 mmol) in the same solvent (5 ml) under N_2. The reaction mixture was stirred at same temperature for 1 h and quenched with NH_4OH(28%). The resulting mixture was extracted with ethyl acetate (4 x 5 ml). Ethyl acetate extracts were washed with brine, dried, and concentrated. Chromatography of the residue on silica gel (elution with ethyl acetate-hexane, 1 : 1) furnished 406 mg (95%) of **6** as a white solid: TLC : *Rf* = 0.53(ethyl acetate); FT-IR 3431, 2930, 2868, 1379 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.22(d, J= 3.3 Hz, 1 H), 6.11(d, J= 3.3 Hz, 1 H), 3.46(dd, J= 3.9, 6.6 Hz, 1 H), 3.38(dd, J= 4.8, 6.6 Hz, 1 H), 2.22-2.28(m, 1 Hz), 1.92(dd, J= 5.4, 7.2 Hz, 1 H), 1.65(s, 3 H), 1.60(d, J= 1.5 Hz, 1 H), 1.57(s, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 140.2, 136.4, 87.4, 85.5, 65.3, 49.5, 38.2,19.3, 19.29; HRMS (FAB) calcd for $[C_9H_{14}O_2]$ ($[M]^+$): 154.2063; found 154.2061 ; $[\alpha]^{21}_D$ +16.4 (c 1.00, $CHCl_3$).

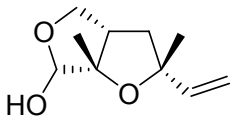
(2R, 3aS, 6aS)-6-hydroxy-2,6a-dimethyl-hexahydrofuro[3,4-b]furan-2-carbaldehyde (7).



Osmium tetroxide in tert-butyl alcohol (0.04 M solution, 25 ml, 1.0 mmol) and N-methylmorpholine oxide (323 mg, 2.75 mmol), sodium metaperiodate(5.36 g, 25.0 mmol) were added successively to a solution of ((1R, 2S, 4R)-1,4-dimethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)methanol (**6**) in tert-butyl alcohol-THF-H_2O (25 ml, 8:6:3) at 0 °C and the mixture was allowed to warm up room temperature. After 2 days, the reaction was quenched with 10% aqueous sodium thiosulfate (10 ml), and the resulting

mixture was extracted with ethyl acetate (4 x 25 ml). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate (2 x 20ml) and brine (3 x 30 ml), then dried over Na_2SO_4. Concentration of solvent in vacuo afforded a residue, which was purified by column chromatography (elution with ethyl acetate-hexane, 1 : 3) to give **7** (312 mg, 67%): TLC : *Rf* = 0.65(ethyl acetate); FT-IR 3418, 2973, 1726, 1641, 1454 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$, dr 1 :1 mixture) δ 9.62(s, 1 H), 9.59(s, 1 H), 4.94(d, J= 9.0 Hz, 1 H), 4.71(d, J= 5.7 Hz, 1 H), 4.17(dd, J= 4.2, 5.7 Hz, 1 H), 4.06(dd, J= 1.5, 7.8 Hz, 1 H), 3.36(d, J= 6 Hz, 1 H), 3.34(d, J= 2.4 Hz, 1 H), 2.32-2.42(m, 2 H), 2.28(dd, J= 1.5, 8.1 Hz, 1 H), 2.09(dd, J= 6.3, 8.1 Hz, 1 H), 1.96(dd, J= 2.1, 8.1 Hz, 1 H), 1.76(dd, J= 6.3, 8.1 Hz, 1 H), 1.46(s, 3 H), 1.43(s, 3 H), 1.37(s, 3 H), 1.33(s, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 204.4, 202.1, 102.3, 96.1, 89.7, 87.4, 82.4, 81.9, 45.3, 44.3, 43.4, 37.7, 23.2, 21.1, 20.8, 20.3; LRMS (EI) calcd for $[C_9H_{14}O_4]$ ($[M]^+$): 186.21; found ;186.2; $[\alpha]^{22}_D$ -16.1 (c 0.50, $CHCl_3$).

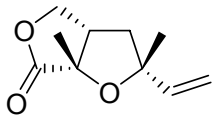
(2R, 3aS, 6aS)-2,6a-dimethyl-2-vinyl-hexahydrofuro[3,4-b]furan-6-ol (8).



To a suspension of $CH_3P^+Ph_3Br^-$(2.39 g, 6.70 mmol) in THF(10 ml) at 0 °C, NaHMDS(2.0 M in THF, 3.35 ml, 6.70 mmol) was added dropwise and the reaction mixture was stirred for 1 h. The diastereomeric mixture of lactols **7** (310 mg, 1.66 mmol) in THF(3 ml) was then added to the so generated yellow ylide and the resulting mixture was stirred for 1 h at 0 °C. After quenching the reaction with saturated aqueous NH_4Cl (10 ml), EtOAc(50 ml), brine(25 ml) and water(25 ml) were added and the two

phases were separated. The aqueous phase was extracted with EtOAc(3 x 30ml) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography (elution with ethyl acetate-hexane, 1 : 3) to furnish **8** (213 mg, 70%) as a colorless oil: TLC : *Rf* = 0.53(ethyl acetate-hexane , 1 : 1); FT-IR 1642, 1550 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 6.04(dd, J= 10.8, 17.4 Hz, 1 H), 5.22(dd, J= 0.9, 17.4 Hz, 1 H), 5.07(dd, J= 0.9, 10.8 Hz, 1 H), 4.69(d, J= 9.0 Hz, 1 H), 3.73(d, J= 4.5 Hz, 2 H), 2.67(m, 1 H), 2.16(dd, J= 8.4, 12.6 Hz, 1 H), 1.92(dd, J= 7.8, 12.6 Hz, 1 H), 1.42(s, 3 H), 1.38(s, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 143.1, 112.9, 102.4, 89.3, 86.7, 67.8, 49.4, 44.3, 27.0, 24.6; HRMS (FAB) calcd for [$C_{10}H_{16}O_3$] ([M]$^+$): 184.2322; found ; 184.2319; $[\alpha]^{22}_D$ +44.6 (c 0.50, $CHCl_3$).

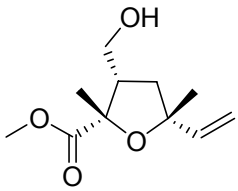
(2R, 3aS, 6aS)-2,6a-dimethyl-2-vinyl-tetrahydrofuro[3,4-b]furan-6(6aH)-one (3).



The starting material **8** (213 mg, 1.16 mmol) was dissolved in CH_2Cl_2(5 ml) and PCC(748 mg, 3.47 mmol) with celite(748 mg) was added to a reaction mixture and stirred for 3 h at room temperature. The reaction mixture was then filtered through silica gel and celite. The residue was purified by flash column chromatography (elution with ethyl acetate-hexane, 1 : 3) to furnish **3** (203 mg, 97%) as a colorless oil: TLC : *Rf* = 0.45(ethyl acetate-hexane , 1 : 1); FT-IR 3085, 2974, 2869, 1775, 1235 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 5.91(dd, J= 6.3, 10.2 Hz, 1 H), 5.29(dd, J= 0.6, 10.2 Hz, 1 H), 5.05(dd, J= 0.6, 6.3 Hz), 4.36(dd, J= 4.5, 6.0 Hz, 1H), 4.13(dd, J= 2.1, 6.0 Hz, 1 H), 2.91(m, 1H), 2.24(dd, J= 2.4, 7.8 Hz, 1 H), 2.06(dd, J= 3.3, 7.8 Hz, 1 H), 1.53(s, 3 H),

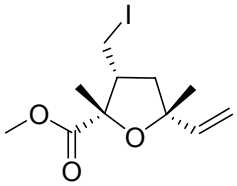
1.36(s, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 177.9, 142.6, 113.6, 86.3, 83.8, 69.5, 45.5, 43.6, 28.1, 22.6; LRMS(EI) calcd for $C_{10}H_{14}O_3$: 182.09; found 182.1; $[\alpha]^{21}_D$ +66.1 (c 1.00, $CHCl_3$).

(2R, 3S, 5R)-methyl-3-(hydroxymethyl)-2,5-dimethyl-5-vinyl-tetrahydrofuran-2-carboxylate (9).



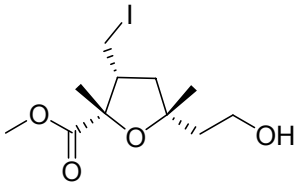
Hydrolysis of **3** (203 mg, 1.11 mmol) was performed with aq. 1N CsOH (3.34 ml, 3.34 mmol) in tert-butyl alcohol for 1 day at room temperature. After quenching the reaction with saturated aqueous 10% citric acid (pH : 6~7), the aqueous phase was extracted with EtOAc(3 x 10ml). The extracts were dried over Na_2SO_4 and then concentration of solvent in vacuo afforded a residue. To a solution of crude residue in anhydrous MeOH(2.0 ml), excess $TMSCHN_2$ (1.0 ml, 2.0 M in diethyl ether) was added and stirred at 0 °C for 10 min. After quenching the reaction with aqueous saturated NH_4Cl(10 ml), EtOAc(30 ml) and brine(20 ml) were added and the two phases were separated. The aqueous phase was extracted with EtOAc(3 x 20ml) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography (elution with ethyl acetate-hexane, 1 : 3) to furnish **9** (191 mg, 80%): TLC : *Rf* = 0.42(ethyl acetate-hexane, 1 : 1); ^1H NMR(300 MHz, $CDCl_3$) δ 6.15(dd, J= 10.5, 17.7 Hz, 1 H), 5.23(dd, J= 1.2, 17.7 Hz, 1 H), 5.05(dd, J= 1.2, 10.8 Hz, 1 H), 3.74(s, 3 H), 3.61(d, J= 8.1 Hz, 2 H), 2.59(m, 1 H), 1.89(dd, J= 7.2, 9.9 Hz, 2 H), 1.60(s, 3 H), 1.37(s, 3 H).

(2S, 3R, 5R)-methyl-3-(iodomethyl)-2,5-dimethyl-5-vinyl-tetrahydrofuran-2-carboxylate (10).



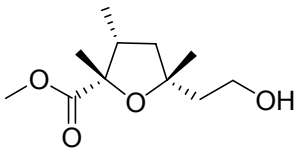
Iodine(396 mg, 3.12 mmol), triphenylphosphine(350 mg, 1.34 mmol) and imidazole(113 mg, 1.78 mmol) were added to a stirred solution of alcohol **9** (191 mg, 0.89 mmol) at room temperature under a nitrogen atmosphere. After 1 h 30 min the mixture was diluted with saturated aqueous 10% sodium thiosulfate solution(2 ml) and twice extracted with ethyl acetate (30 ml). The combined organic layer was washed with brine (30 ml), dried (Na_2SO_4) and the solvent was removed in vacuo. The residue was purified by flash column chromatography (elution with ethyl acetate-hexane, 1 : 5) to furnish **10** (242 mg, 84%): TLC : *Rf* = 0.59(ethyl acetate-hexane , 1 : 3); FT-IR 3083, 2974, 2859, 1731, 1642, 1244 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 6.16(dd, J= 10.5, 17.7 Hz, 1 H), 5.23(dd, J= 1.2, 17.7 Hz, 1 H), 5.06(dd, J= 1.2, 10.8 Hz, 1 H), 3.71(s, 3H), 3.30(dd, J= 4.2, 9.9 Hz, 1 H), 2.92(dd, J= 9.9, 11.1 Hz, 1 H), 2.69(m, 1 H), 2.28(dd, J= 6.6, 12.6 Hz, 1 H), 2.00(t, J= 12.6 Hz, 1 H), 1.54(s, 3 H), 1.36(s, 3 H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 173.4, 143.6, 112.4, 85.3, 82.5, 53.1, 52.0, 44.8, 26.9, 25.2, 2.8; HRMS (FAB) calcd for [$C_{11}H_{17}IO_3$] ([M]$^+$): 325.0301; found 325.0314; $[\alpha]^{21}_D$ -42.2 (c 0.50, $CHCl_3$).

(2S, 3R, 5R)-methyl-5-(2-hydroxyethyl)-3-(iodomethyl)-2,5-dimethyl-tetrahydrofuran-2-carboxylate (11).



A solution of **10** (43 mg, 0.13 mmol) in THF(0.5 ml) was added to BH_3·THF(1.0 M solution, 663 μl, 0.66 mmol) at -40 °C and stirred for 5 h at 0 °C before being treated with 15% NaOH solution (0.2 ml) and 30% hydrogen peroxide (0.2 ml) at 0 °C. The ice bath was removed, and the mixture was stirred at room temperature for 1 h and diluted with water and ethyl acetate. The aqueous phase was extracted with ethyl acetate. The combined organic layer was washed with brine, dried, and concentrated. The residue was chromatography on silica gel (elution with ethyl acetate-hexane, 1 : 1) to give **11** (34 mg, 77%): TLC : *Rf* = 0.29(ethyl acetate-hexane, 1 : 1); FT-IR 3537, 2964, 2876, 1731, 1452 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 3.83(m, 2 H), 3.73(s, 3 H), 3.33(dd, J= 3.9, 9.6 Hz, 1 H), 2.87(dd, J= 9.9, 11.4 Hz, 1 H), 2.71(m, 1 H), 2.26(dd, J= 6.3, 12.3 Hz, 1 H), 2.00(dd, J= 3.9, 8.1 Hz, 1 H), 1.90(m, 2 H), 1.53(s, 3 H), 1.30(s, 3 H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 173.7, 85.3, 83.8, 59.2, 52.5, 52.3, 45.3, 42.5, 27.5, 25.7, 2.7; LRMS(EI) calcd for $C_{11}H_{18}IO_4$: 342.03; found 342.0; $[\alpha]^{21}_D$ -25.1 (c 0.50, $CHCl_3$).

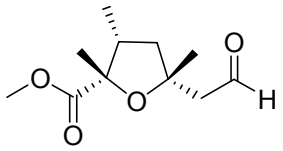
(2S, 3R, 5R)-methyl-5-(2-hydroxyethyl)-2,3,5-trimethyl-tetrahydrofuran-2-carboxylate (12).



To a solution of **11** (34 mg, 0.1 mmol) in a mixture of acetic acid (0.3 ml) and

ethanol(1.8 ml) was added zinc dust(1mmol) and the reaction mixture was stirred at room temperature for 6 h. After addition of water and ethyl acetate, the aqueous layer was extracted with ethyl acetate (3 x 15 ml). The combined organic layer was washed (10% aq. $NaHCO_3$ and brine, successively), then dried over Na_2SO_4. The solvent was removed, and the residue was purified by chromatography on silica gel (elution with ethyl acetate-hexane, 1 : 1) to furnish **12** (20 mg, 97%): TLC : *Rf* = 0.25(ethyl acetate-hexane, 1 : 1); FT-IR 3434, 2958, 2851, 1734, 1454 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 3.82(m, 2 H), 3.71(s, 3 H), 2.39(m, 1 H), 2.07(dd, J= 4.5, 7.8 Hz, 1 H), 2.02(dd, J= 4.5, 7.8 Hz, 1 H), 1.85(dd, J= 11.4 Hz, 1 H), 1.62(dd, J= 7.5, 11.4 Hz, 1 H), 1.47(s, 3 H),1.27(s, 3 H), 0.98(d, J= 6.9 Hz, 3 H); ^{13}C NMR(75 MHz, $CDCl_3$) δ 174.6, 87.0, 84.5, 59.3, 51.7, 45.3, 43.7, 42.4, 27.8, 27.6, 14.6; HRMS (FAB) calcd for $[C_{11}H_{20}O_4]$ ($[M]^+$): 217.1440; found 217.1432; $[\alpha]^{21}_D$ +31.9 (c 0.50, $CHCl_3$).

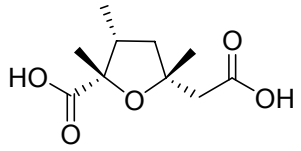
(2S, 3R, 5R)-methyl-2,3,5-trimethyl-5-(2-oxoethyl)-tetrahydrofuran-2-carboxylate (13).



The starting material **12** (20 mg, 0.09 mmol) was dissolved in CH_2Cl_2(2 ml) and PCC(60 mg, 0.27 mmol) with celite(60 mg) was added to a reaction mixture and stirred for 3 h at room temperature. The reaction mixture was then filtered through silica gel and celite to afford crude product **13** (17 mg, 86%): TLC : *Rf* = 0.74 (ethyl acetate-hexane, 1 : 1); FT-IR 3427, 2958, 2855, 1731, 1453 cm^{-1}; ^1H NMR(300 MHz, $CDCl_3$) δ 9.84(s, 1H), 3.69(s, 3H), 2.91(d, J= 6.3Hz, 2H), 2.35(m, 1H), 2.04(dd, J= 6.6, 12.3Hz,

1H), 1.82(t, J= 12.3Hz, 1H), 1.48(s, 3H), 1.31(s, 3H), 0.96(d, J= 6.9Hz, 3H); ^{13}C NMR(75MHz, $CDCl_3$) δ 202.3, 174.3, 87.1, 81.3, 55.4, 51.6, 45.1, 43.9, 28.4, 27.8, 14.1; LRMS (EI) calcd for $C_{11}H_{18}O_4$: 214.12; found 214.1.

(2S, 3R, 5R)-5-(carboxymethyl)-2,3,5-trimethyl-tetrahydrofuran-2-carboxylic acid (1).



This crude aldehyde **13** (17 mg, 0.079 mmol) was dissolved in THF-H_2O- tert-butyl alcohol (0.5 ml, 4:4:1) and 2-methyl-2-butene(0.2 ml, excess). A solution of 1 N $NaClO_2$ (180 µl, 0.18 mmol) and 1 N NaH_2PO_4 (365 µl, 0.365 mmol) in water was added dropwise. The pale yellow reaction mixture was stirred at room temperature for 3 h. The mixture was then diluted with saturated aqueous NH_4Cl(2 ml) and extracted with ethyl acetate(5 x 10 ml). The combined organic extracts were washed with brine (5 ml), dried over Na_2SO_4, filtered, and concentrated to give crude monoester adduct. This crude monoester was dissolved in aqueous NaOH (0.3 ml, 2.0 N) and the solution was stirred for 6 h. Hydrochloric acid (1.0 M) was added to adjust the solution to pH=1. The aqueous phase was then extracted five times with ethyl acetate. The combined organic phase was dried over Na_2SO_4. The solvent was removed, and the residue was purified by chromatography on silica gel (elution with $CHCl_3$-MeOH, 9 : 1) to furnish 15 mg, 90% of (+)-cis-nemorensic acid (**1**): FT-IR 3129, 2921, 1716, 1650, 1457, 1115 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 2.84(d, J= 15.0 Hz, 1 H), 2.80(d, J= 15.0 Hz, 1 H), 2.46(dq, 1 H), 2.09(dd, J= 6.5, 12.5 Hz, 1 H), 1.87(t, J= 12.5 Hz, 1 H), 1.53(s, 3 H), 1.37(s, 3 H),

1.10(d, J= 7.0 Hz, 3 H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 177.2, 175.2, 87.1, 81.6, 45.2, 44.5, 43.9, 27.9, 25.1, 14.8; $[\alpha]^{21}_D$ +47 (c 0.18,EtOH).