

Supporting Information

Catalytic Asymmetric Total Synthesis of (+)-Artalbic Acid

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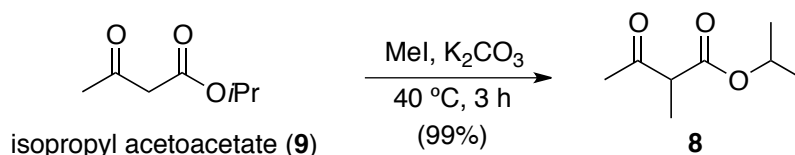
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General

All reactions involving air- and moisture-sensitive reagents were carried out using standard syringe-septum cap techniques. Unless otherwise noted, all solvents and reagents were obtained from commercial suppliers and used without further purification. Routine monitoring of reactions were carried out Merck silica gel 60 F254 TLC plates. Column chromatography was performed on Kanto Chemical Silica gel 60N (spherical, neutral 60-230 μm) with the solvents indicated. ^1H and ^{13}C NMR spectra were measured with a Jeol ECZ-400s (400 MHz) or a Burker AV-600 (600 MHz) spectrometer. Chemical shifts were expressed in ppm using CHCl_3 (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR) in CDCl_3 as internal standard. Infrared spectral measurements were carried out with a JASCO FT/IR-4700 FT-IR and only noteworthy absorptions were listed. HRMS spectra measured on a Micromass LCT spectrometer.

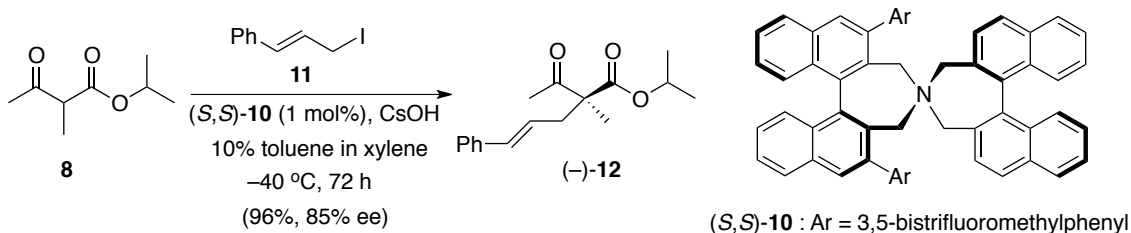
Isopropyl 2-methyl-3-oxobutanoate (**8**).



To a mixture of isopropyl acetoacetate (**9**) (5.0 g, 34.7 mmol) and methyl iodide (4.9 g, 2.1 mL, 34.7 mmol) was added K_2CO_3 (9.5 g, 69.4 mmol) at $0\text{ }^\circ\text{C}$, and the mixture was stirred for 3 h at $40\text{ }^\circ\text{C}$. The reaction mixture was filtered under vacuo and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 20:1) to afford **8** (5.5 g, 99%) as colorless oil. The spectral data of **8** was identified with those of the previous report.¹

1. C. Palomo, M. Oiarbide, J. M. Garcia, P. Banuelos, J. M. Odriozola, J. Razkin and A. Linden, *Org. Lett.*, 2008, **10**, 2637.

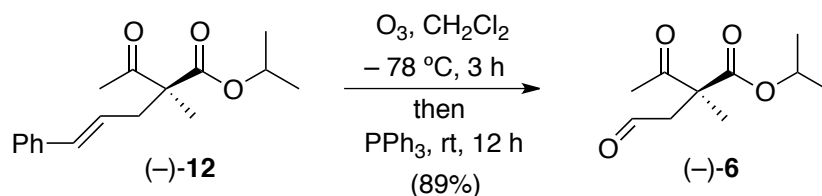
(*S,E*)-Isopropyl 2-acetyl-2-methyl-5-phenylpent-4-enoate (–)-(**12**).



To a stirred solution of **8** (20.0 mg, 0.126 mmol), (*S,S*)-**10** (1.4 mg, 1.26 μ mol) and **11** (40.0 mg, 0.16 mmol) in 10% toluene in xylene (3 mL) was added CsOH (75.5 mg, 0.50 mmol) at -40 $^{\circ}$ C, and the mixture was stirred for 72 h at same temperature. The reaction was quenched with 1 M HCl aqueous solution, and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 30:1) to afford (–)-**12** (33.3 mg, 96%, 85% ee) as yellow oil.

$[\alpha]_{\text{D}}^{25} = -31.3$ (c 1.26, CHCl₃); IR (neat) 2981, 1712, 1450, 1375, 1238, 1101 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (3H, d, $J = 6.4$ Hz), 1.24 (3H, d, $J = 6.4$ Hz), 1.37 (3H, s), 2.18 (3H, s), 2.64 (1H, ddd, $J = 14.5, 7.8, 1.4$ Hz), 2.78 (1H, dd, $J = 14.2, 7.3$ Hz), 5.07 (1H, qq, $J = 6.4, 6.4$ Hz), 6.05 (1H, ddd, $J = 15.6, 7.3, 7.3$ Hz), 6.43 (1H, d, $J = 16.0$ Hz), 7.18–7.23 (1H, m), 7.28–7.33 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.1, 21.5, 21.6, 26.2, 38.5, 59.7, 68.9, 124.3, 126.1, 127.3, 128.5, 133.8, 137.0, 171.9, 205.2; HRESIMS calcd for C₁₇H₂₂O₃Na [M+Na]⁺ 297.1467, found 297.1470.

(*S*)-Isoprppyl 2-acetyl-2-methyl-4-oxobutanoate (–)-(**6**).

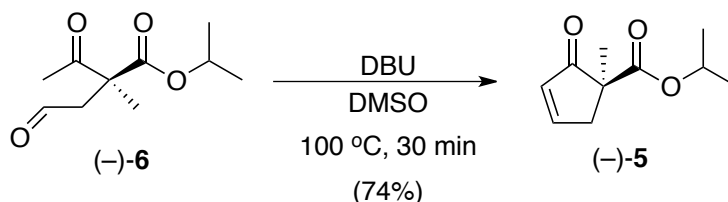


The compound (–)-**12** (1.65 g, 6.02 mmol) was dissolved in CH₂Cl₂ (60 mL) and cooled to -78 $^{\circ}$ C. Ozone gas was bubbled for 3 h at -78 $^{\circ}$ C. Triphenylphosphine (4.0 g, 15.05 mmol) was added and the reaction mixture warmed to room temperature. After the reaction mixture was stirred for 12 h, the solvent was removed in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 5:1) to afford (–)-**6** (1.07 g, 89%) as colorless oil.

$[\alpha]_{\text{D}}^{25} = -41.4$ (c 1.22, CHCl₃); IR (neat) 2983, 1713, 1456, 1377, 1281, 1240, 1200, 1101 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ 1.22 (3H, d, $J = 6.4$ Hz), 1.24 (3H, d, $J = 6.4$ Hz), 1.48 (3H, s), 2.24 (3H, s), 2.86 (1H, dd, $J = 17.4, 1.9$ Hz), 2.97 (1H, dd, $J = 17.3, 1.9$ Hz), 5.06 (1H, qq, $J = 6.4, 6.4$ Hz), 9.70 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.4, 21.41, 21.44, 26.0, 48.5, 57.1, 69.6, 171.1, 199.0, 204.6; HRESIMS calcd for C₁₀H₁₆O₄Na [M+Na]⁺ 223.0946, found

223.0940.

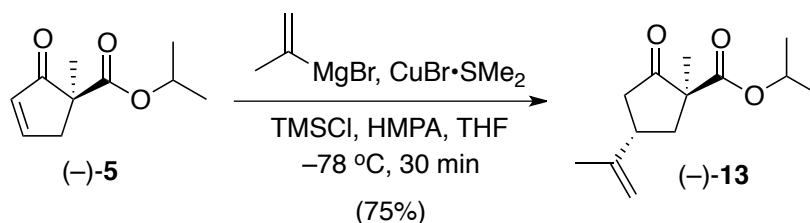
(*S*)-Isopropyl 1-methyl-2-oxocyclopent-3-enecarboxylate (–)-(5).



To a stirred solution of (–)-6 (400 mg, 2.00 mmol) in DMSO (75 mL) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (0.30 mL, 305 mg, 2.00 mmol) at room temperature. After the reaction mixture was stirred for 30 min at 100 °C, the reaction was quenched by adding with 1 M HCl aqueous solution, and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄. After the solvent was removed in vacuo, the resulting residue was purified by column chromatography (hexane-AcOEt, 10:1) to afford (–)-5 (268 mg, 74%) as colorless oil.

$[\alpha]_D^{25} = -19.9$ (c 0.98, CHCl₃); IR (neat) 2981, 1738, 1709, 1375, 1272, 1190, 1104 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.17 (3H, d, *J* = 6.0 Hz), 1.19 (3H, d, *J* = 5.9 Hz), 1.37 (3H, s), 2.52 (1H, dt, *J* = 19.2, 2.3 Hz), 3.21 (1H, dd, *J* = 19.2, 2.3 Hz), 4.90 (1H, qq, *J* = 6.0, 6.0 Hz), 6.16 (1H, dt, *J* = 5.9, 2.7 Hz), 7.73 (1H, dt, *J* = 5.9, 2.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.4, 21.43, 21.51, 42.7, 53.4, 68.8, 131.7, 163.0, 171.0, 206.8; HRESIMS calcd for C₁₀H₁₄O₃Na [M+Na]⁺ 205.0841, found 205.0843.

(1*S*,4*S*)-Isopropyl 1-methyl-2-oxo-4-(prop-1-en-2-yl)cyclopentanecarboxylate (–)-(13).

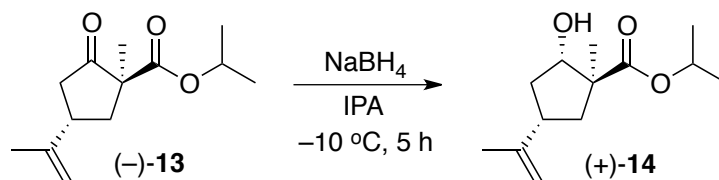


To a stirred mixture of (–)-5 (600 mg, 3.29 mmol), CuBr·SMe₂ (67 mg, 0.33 mmol), HMPA (1.14 mL, 1.18 g, 6.59 mmol) and chlorotrimethylsilane (1.25 mL, 1.07 g, 9.88 mmol) in THF

(65 mL) was added isopropenylmagnesium bromide (0.5 M in THF, 16.4 mL, 8.22 mmol) at $-78\text{ }^{\circ}\text{C}$ under Ar. After the reaction mixture was stirred for 30 min at same temperature, the reaction was quenched by adding with sat. NH_4Cl aqueous solution, and extracted with AcOEt. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting residue was dissolved in MeOH and KF was added. After the mixture was stirred for 15 min at same temperature, H_2O was added and extracted with AcOEt. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 30:1) to afford (-)-**13** (580 mg, 75%) as colorless oil.

$[\alpha]_{\text{D}}^{25} = -16.6$ (c 1.03, CHCl_3); IR (neat) 2980, 1752, 1729, 1455, 1376, 1204, 1155, 1106 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.22 (3H, d, $J = 6.0$ Hz), 1.23 (3H, d, $J = 5.5$ Hz) 1.33 (3H, s), 1.63 (1H, t, $J = 12.6$ Hz), 1.76 (3H, s), 2.20 (1H, dd, $J = 19.2, 11.9$ Hz), 2.58-2.64 (2H, m), 2.91-3.00 (1H, m), 4.75 (1H, s), 4.81 (1H, s), 5.00 (1H, qq, $J = 6.0, 6.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.3, 21.0, 21.5, 21.6, 40.0, 41.4, 42.4, 57.4, 69.0, 109.9, 145.8, 171.5, 214.1; HRESIMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 247.1310, found 247.1301.

(1*S*, 2*S*, 4*S*)-Isopropyl 2-hydroxy-1-methyl-4-(prop-1-en-2-yl)cyclopentanecarboxylate (+)-(**14**).

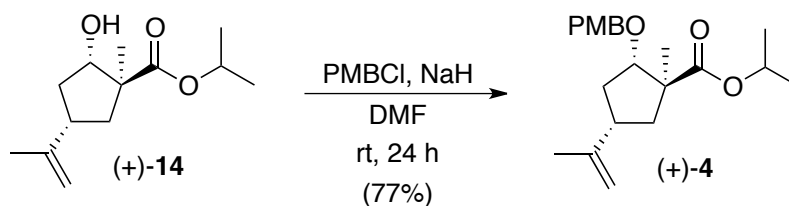


To a stirred solution of (-)-**13** (363 mg, 1.46 mmol) in isopropyl alcohol (15 mL) was added sodium borohydride (66 mg, 1.75 mmol) at $-10\text{ }^{\circ}\text{C}$ under Ar, and the mixture was stirred for 5 h at same temperature. The reaction was quenched by adding with sat. NH_4Cl aqueous solution, and extracted with AcOEt. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 15:1) to afford (+)-**14** (265 mg, 85%) as colorless oil and its C2-epimer (32 mg, 10%) as colorless oil.

$[\alpha]_{\text{D}}^{25} = +14.4$ (c 1.10, CHCl_3); IR (neat) 3465, 2979, 1720, 1456, 1375, 1270, 1108 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.21 (3H, s), 1.23 (6H, d, $J = 6.4$ Hz), 1.51 (1H, dd, $J = 13.3, 9.6$ Hz), 1.62 (1H, ddd, $J = 12.3, 11.0, 9.1$ Hz), 1.71 (3H, s), 2.10-2.16 (2H, m), 2.33 (1H, dd, $J =$

13.3, 8.7 Hz), 2.44-2.53 (1H, m), 4.39 (1H, dd, $J = 9.2, 6.4$ Hz), 4.69 (1H, s), 4.71 (1H, s), 5.00 (1H, qq, $J = 6.4, 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 19.6, 21.0, 21.7, 37.3, 39.8, 40.4, 51.6, 67.8, 76.3, 108.7, 147.4, 177.3; HRESIMS calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 249.1467, found 249.1459.

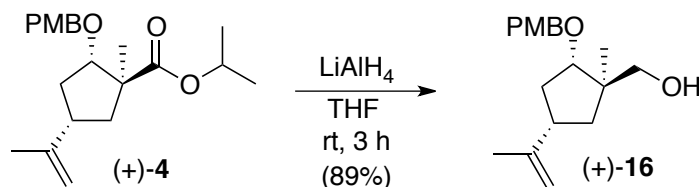
(1*S*, 2*S*, 4*S*)-Isopropyl 2-{(4-methoxybenzyl)oxy}-1-methyl-4-(prop-1-en-2-yl)cyclopentane-carboxylate (+)-**4**.



To a stirred solution of (+)-**14** (50 mg, 0.22 mmol) in DMF (2.2 mL) was added NaH (6.4 mg, 0.27 mmol) at 0 °C under Ar, and the mixture was stirred for 30 min at same temperature. To a mixture was added 4-methoxybenzylchloride (0.41 mL, 48 mg, 0.31 mmol) and tetrabutylammonium iodide (114 mg, 0.31 mmol) at 0 °C, the reaction mixture was stirred for 24 h at room temperature. The reaction was quenched by adding with sat. NaHCO_3 aqueous solution and extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 30:1) to afford (+)-**4** (59 mg, 77%) as colorless oil.

$[\alpha]_{\text{D}}^{25} = +14.1$ (c 1.18, CHCl_3); IR (neat) 2976, 1721, 1514, 1457, 1374, 1247, 1109 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.23 (3H, d, $J = 6.4$ Hz), 1.24 (3H, d, $J = 6.4$ Hz), 1.28 (3H, s), 1.50 (1H, dd, $J = 12.8, 11.0$ Hz), 1.61-1.69 (1H, m), 1.70 (3H, s), 2.09-2.17 (1H, m), 2.26-2.31 (1H, m), 2.44-2.53 (1H, m), 3.80 (3H, s), 4.25 (1H, dd, $J = 8.7, 5.9$ Hz), 4.42 and 4.47 (2H, ABq, $J = 11.4$ Hz), 4.69 (1H, br s), 4.70 (1H, br s), 5.02 (1H, qq, $J = 6.4, 6.4$ Hz), 6.87 (2H, d, $J = 8.6$ Hz), 7.26 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 19.8, 20.8, 21.8, 36.7, 41.5, 42.5, 51.4, 55.2, 67.7, 71.5, 83.3, 108.9, 113.7, 129.0, 130.8, 147.2, 159.0, 177.4; HRESIMS calcd for $\text{C}_{21}\text{H}_{30}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 369.2042, found 369.2044.

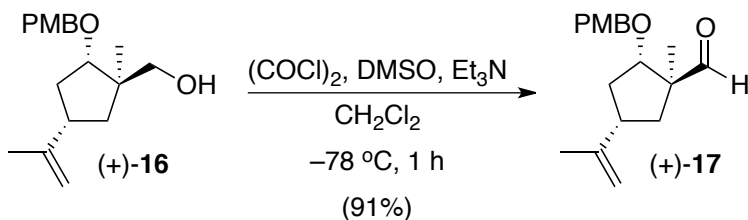
[(1*R*, 2*S*, 4*S*)-2-{{(4-methoxybenzyl)oxy}}-1-methyl-4-(prop-1-en-2-yl)cyclopentyl]methanol
(+)-**16**.



To a stirred solution of (+)-**4** (130 mg, 0.37 mmol) in THF (4 mL) was added lithium aluminium hydride (14 mg, 0.37 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched by adding with sat. potassium sodium tartrate aqueous solution and extracted with AcOEt. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 5:1) to afford (+)-**16** (97 mg, 89%) as colorless oil.

$[\alpha]_D^{25} = +53.1$ (c 1.03, CHCl₃); IR (neat) 3425, 2935, 1613, 1514, 1248, 1098 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.05 (3H, s), 1.35 (1H, dd, $J = 13.3, 9.6$ Hz), 1.60-1.68 (2H, m), 1.72 (3H, s), 1.76 (1H, dd, $J = 13.3, 8.7$ Hz), 2.16 (1H, ddd, $J = 11.9, 5.9, 5.9$ Hz), 2.35-2.44 (1H, m), 3.42 (2H, s), 3.70 (1H, dd, $J = 9.6, 5.9$ Hz), 3.80 (3H, s), 4.42 and 4.55 (2H, ABq, $J = 11.4$ Hz), 4.69 (1H, br s), 4.71 (1H, br s), 6.88 (2H, d, $J = 8.7$ Hz), 7.26 (2H, d, $J = 8.7$ Hz); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 20.8, 35.5, 39.6, 40.7, 45.5, 55.2, 71.0, 71.4, 83.0, 108.5, 113.7, 128.9, 130.9, 147.8, 159.0; HRESIMS calcd for C₁₈H₂₆O₃Na [M+Na]⁺ 313.1780, found 313.1777.

(1*S*, 2*S*, 4*S*)-2-{{(4-methoxybenzyl)oxy}}-1-methyl-4-(prop-1-en-2-yl)cyclopentanecarbaldehyde
(+)-**17**.

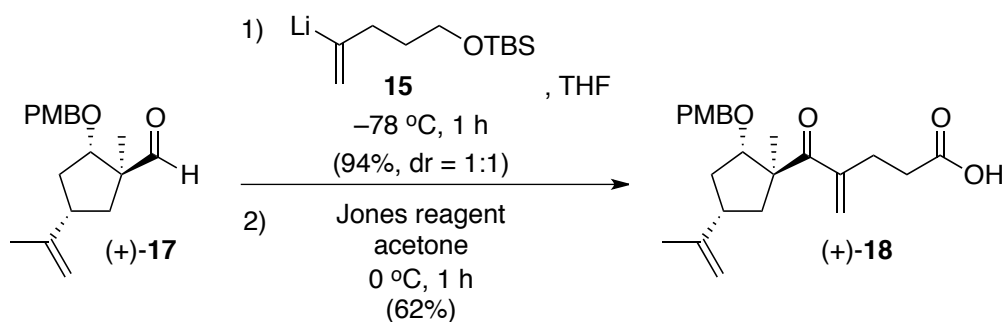


To a stirred solution of oxalyl chloride (0.06 mL, 87.3 mg, 0.688 mmol) in CH₂Cl₂ (0.6 mL) was added dropwise a solution of dimethylsulfoxide (0.1 mL, 108 mg, 1.38 mmol) in CH₂Cl₂ (0.6 mL) at -78 °C under Ar. After stirred for 20 min at -78 °C, a solution of (+)-**16** (100 mg, 0.344 mmol) in CH₂Cl₂ (0.5 mL) was added dropwise to this reaction

mixture at $-78\text{ }^{\circ}\text{C}$, and the mixture was continuously stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. To this mixture was added dropwise triethylamine (0.3 mL, 209 mg, 2.06 mmol) at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred for 30 min at room temperature. The reaction was quenched by adding with H_2O , and extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 20:1) to afford (+)-**17** (90.0 mg, 91%) as colorless oil.

$[\alpha]_{\text{D}}^{25} = +34.4$ (c 1.06, CHCl_3); IR (neat) 2935, 1722, 1613, 1513, 1248, 1104 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.22 (3H, s), 1.46 (1H, dd, $J = 13.3, 10.5$ Hz), 1.68-1.76 (1H, m), 1.71 (3H, s), 2.15-2.21 (2H, m), 2.32-2.41 (1H, m), 3.80 (3H, s), 4.11 (1H, dd, $J = 8.7, 6.4$ Hz), 4.38 and 4.42 (2H, ABq, $J = 11.4$ Hz), 4.72 (2H, br s), 5.02 (1H, qq, $J = 6.4, 6.4$ Hz), 6.87 (2H, d, $J = 8.7$ Hz), 7.24 (2H, d, $J = 6.4$ Hz), 9.53 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 16.5, 20.7, 36.4, 38.7, 41.2, 55.2, 56.2, 71.5, 80.1, 109.3, 113.8, 129.0, 130.3, 146.6, 159.2, 204.4; HRESIMS calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 311.1623, found 311.1628.

PMB protected artalbic acid (+)-(**18**).



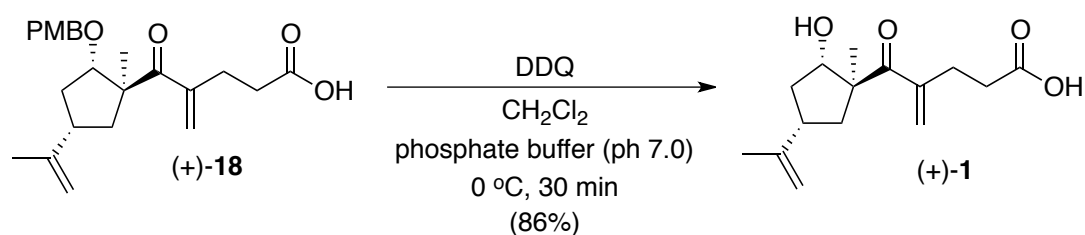
To a stirred solution of {(4-bromopent-4-en-1-yl)oxy}(tert-butyl)dimethylsilane (410 mg, 1.47 mmol) in THF (3 mL) was added dropwise 1.65 M solution of *tert*-butyllithium in pentane (1.78 mL, 2.94 mmol) at $-78\text{ }^{\circ}\text{C}$ under Ar, and the mixture was stirred for 30 min at same temperature. Then to this mixture a solution of (+)-**17** (170 mg, 0.589 mmol) in THF (3 mL) was added dropwise at $-78\text{ }^{\circ}\text{C}$, and the reaction mixture was stirred for 1 h at same temperature. The reaction was quenched by adding with 1 M HCl aqueous solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO_4 , and concentrated in vacuo. The resulting

residue was purified by column chromatography (hexane-AcOEt, 30:1) to afford the desired adduct (270 mg, 94%) as a 1:1 diastereomeric mixture. The mixture was used for next step without further separation.

To a stirred solution of the diastereomeric mixture obtained above (12.9 mg, 0.026 mmol) in acetone (1 mL) was added dropwise 2.67 N Jones reagent at 0 °C. After the reaction mixture was stirred for 1 h at room temperature, brine was added, and the resulting mixture was extracted with AcOEt. The organic layers were combined, washed with 10% NaHSO₃ solution and brine, dried over MgSO₄, and concentrated in vacuo. The resulting residue was purified by column chromatography (hexane-AcOEt, 3:1) to afford (+)-**18** (6.3 mg, 62%) as colorless oil.

$[\alpha]_D^{25} = +32.2$ (c 0.34, CHCl₃); IR (neat) 3647, 2925, 1714, 1663, 1613, 1513, 1248, 1034 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.36 (3H, s), 1.50 (1H, dd, *J* = 12.8, 11.4 Hz), 1.56-1.66 (1H, m), 1.71 (3H, s), 2.12-2.18 (1H, m), 2.25-2.34 (1H, m), 2.47-2.62 (5H, m), 3.80 (3H, s), 4.32 (1H, dd, *J* = 15.1, 9.1 Hz), 4.38 and 4.51 (2H, ABq, *J* = 11.0 Hz), 4.71 (2H, br s), 5.73 (1H, s), 5.95 (1H, s), 6.87 (2H, d, *J* = 8.7 Hz), 7.26 (2H, d, *J* = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.8, 22.4, 28.5, 32.7, 36.1, 41.3, 42.8, 55.3, 56.5, 71.4, 82.0, 109.0, 113.7, 123.7, 129.1, 130.7, 143.9, 147.0, 159.1, 177.3, 206.7; HRESIMS calcd for C₂₃H₃₀O₅Na [M+Na]⁺ 409.1991, found 409.1995.

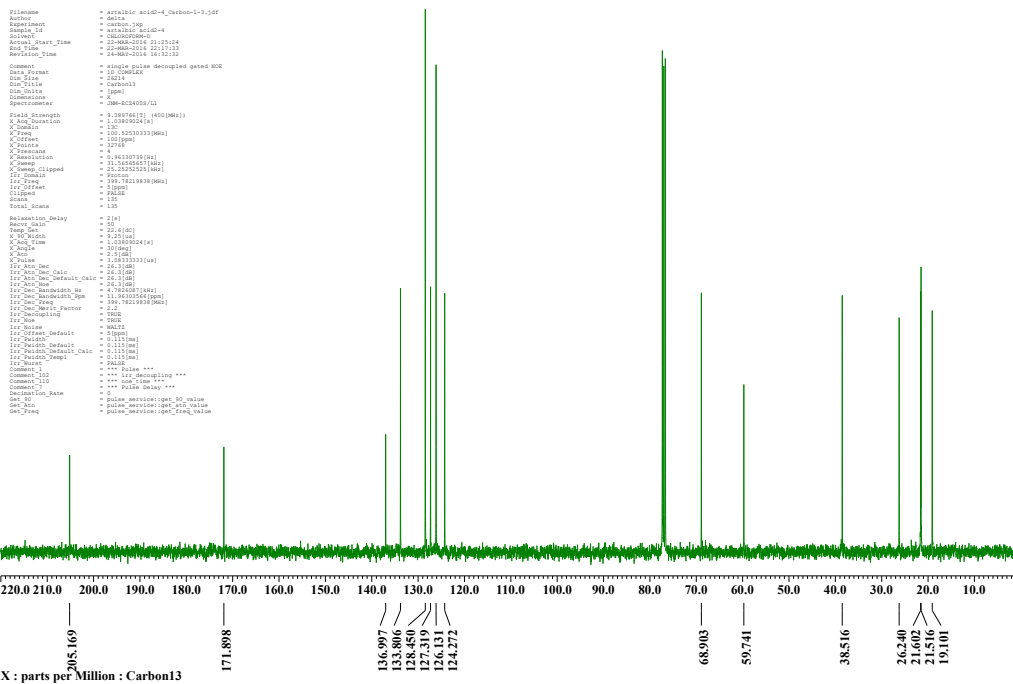
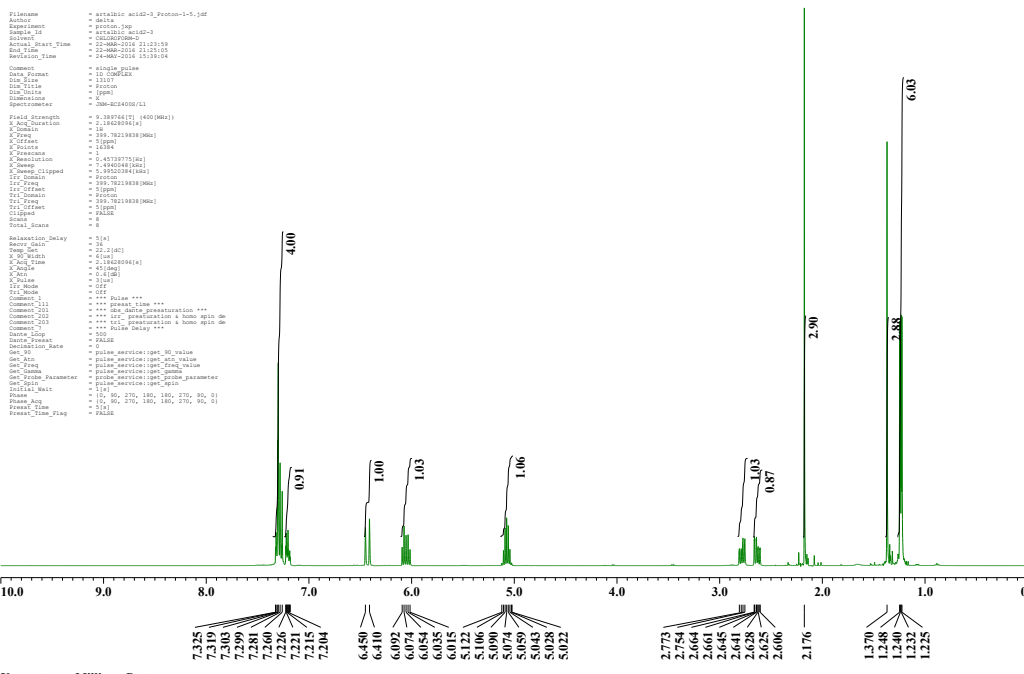
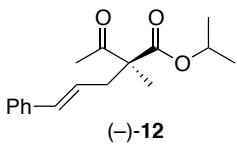
Artalbic acid (+)-**(1)**.

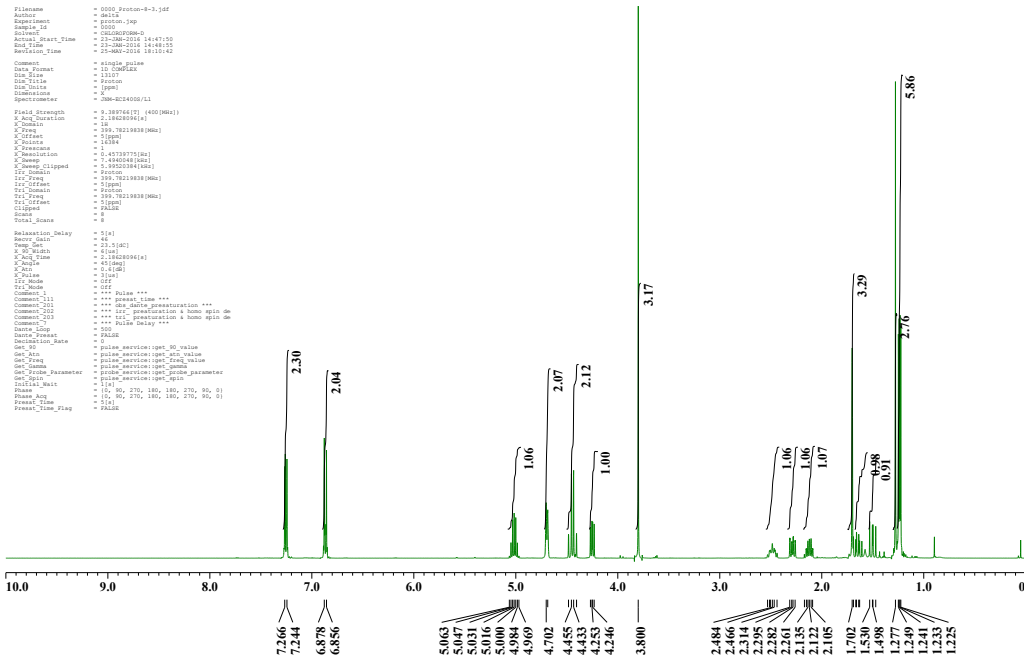
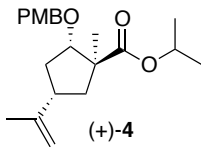


To a stirred solution of (+)-**18** (10 mg, 0.026 mmol) in CH₂Cl₂ (0.1 mL) and phosphate buffer (pH 7.0) (10 μL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (5.8 mg, 0.026 mmol) at 0 °C, and the mixture was stirred for 30 min at same temperature. The reaction was quenched by adding with sat. NaHCO₃ aqueous solution and then 1 M HCl was added until pH 3. The mixture was extracted with CH₂Cl₂ and the combined organic layers were dried over Na₂SO₄, and concentrated in vacuo. The resulting residue was purified by column

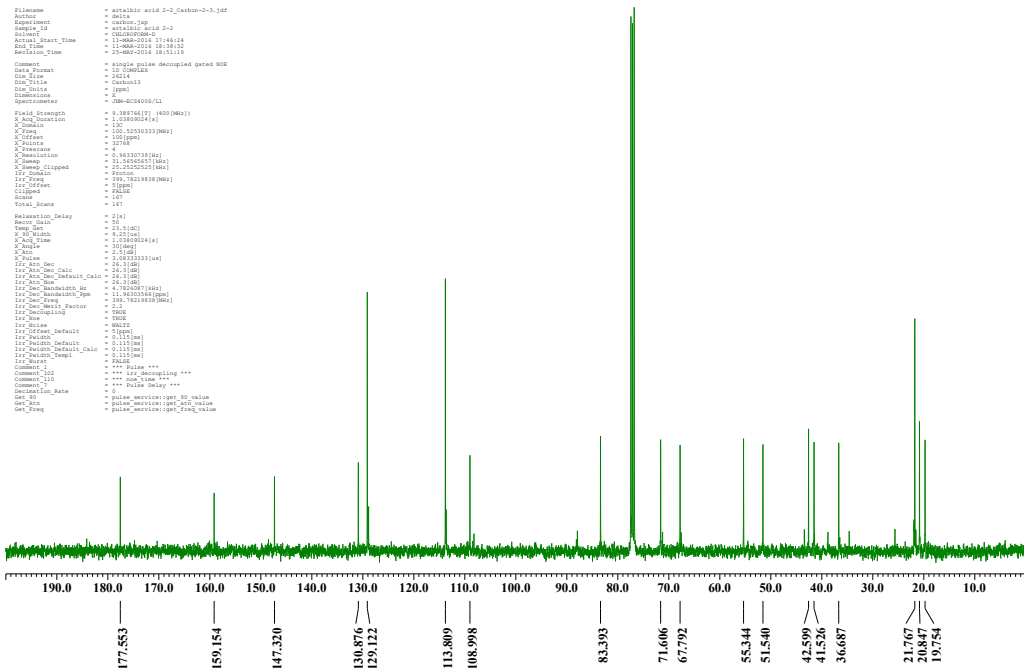
chromatography (hexane-AcOEt, 2:1) to afford (+)-**1** (6 mg, 86%) as colorless oil.

$[\alpha]_D^{25} = +11.2$ (c 0.10, CHCl_3); IR (neat) 3269, 2923, 1712, 1644, 1596, 1414, 1261, 1119 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.32 (3H, s), 1.66-1.75 (2H, m), 1.74 (3H, s), 2.01-2.07 (1H, m), 2.37-2.52 (4H, m), 2.58-2.62 (2H, m), 4.44 (1H, dd, $J = 10.9, 5.9$ Hz), 4.73 (1H, br s), 4.75 (1H, br s), 5.88 (1H, br s), 5.97 (1H, br s); ^{13}C NMR (100 MHz, benzene- d_6) δ 20.8, 21.9, 28.4, 33.2, 36.5, 40.4, 41.4, 55.8, 76.3, 109.2, 124.5, 144.4, 147.4, 178.3, 207.7; HRESIMS calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 289.1416, found 289.1416.

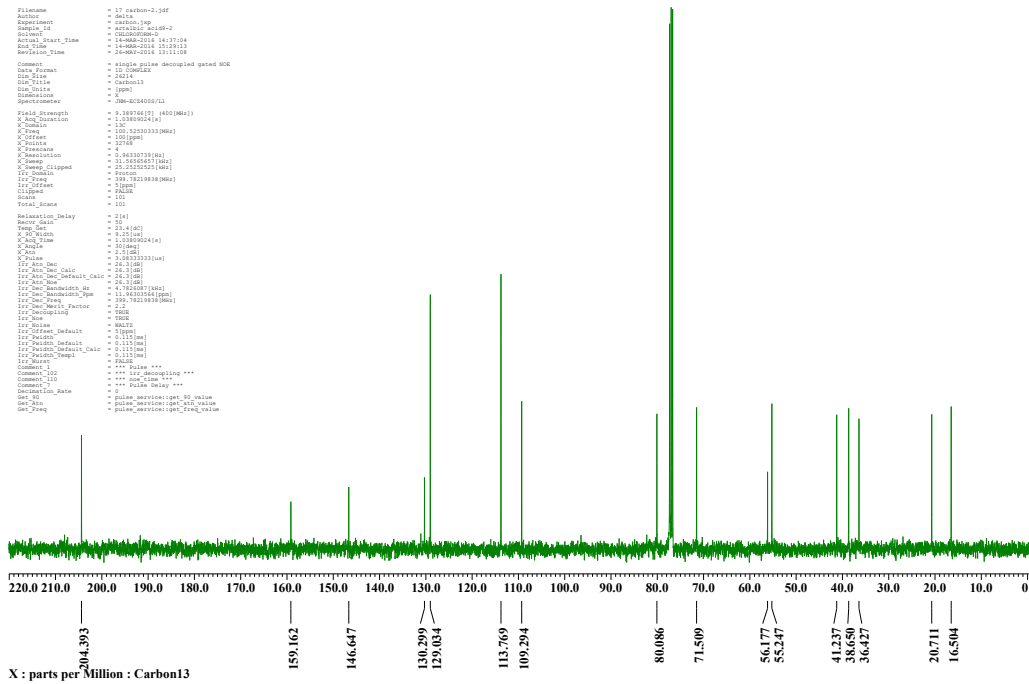
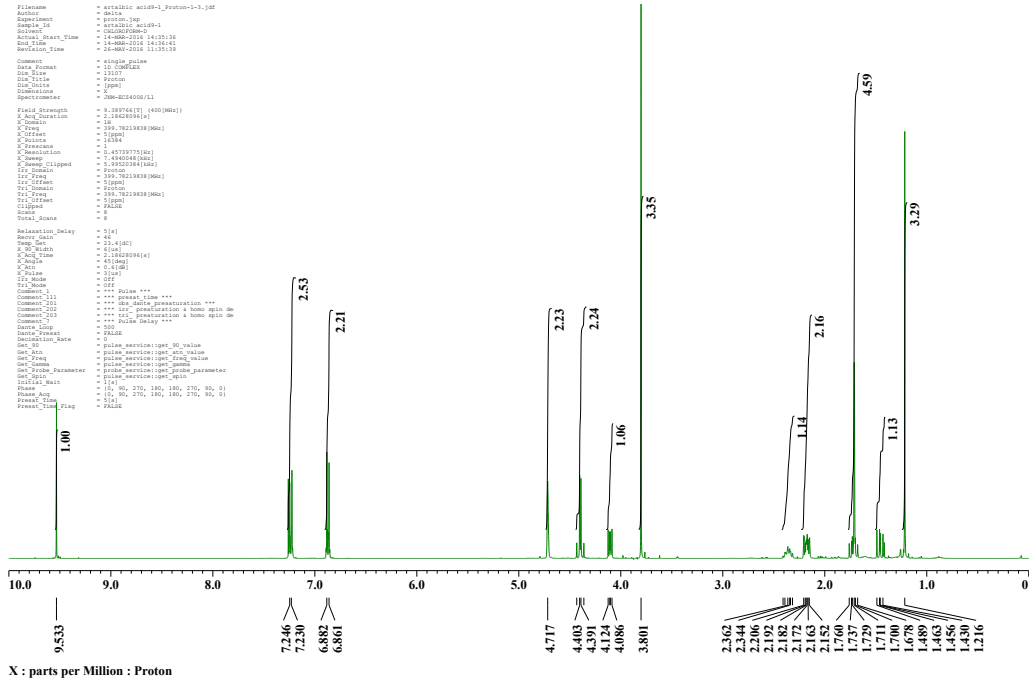
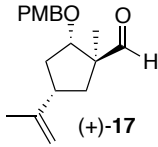


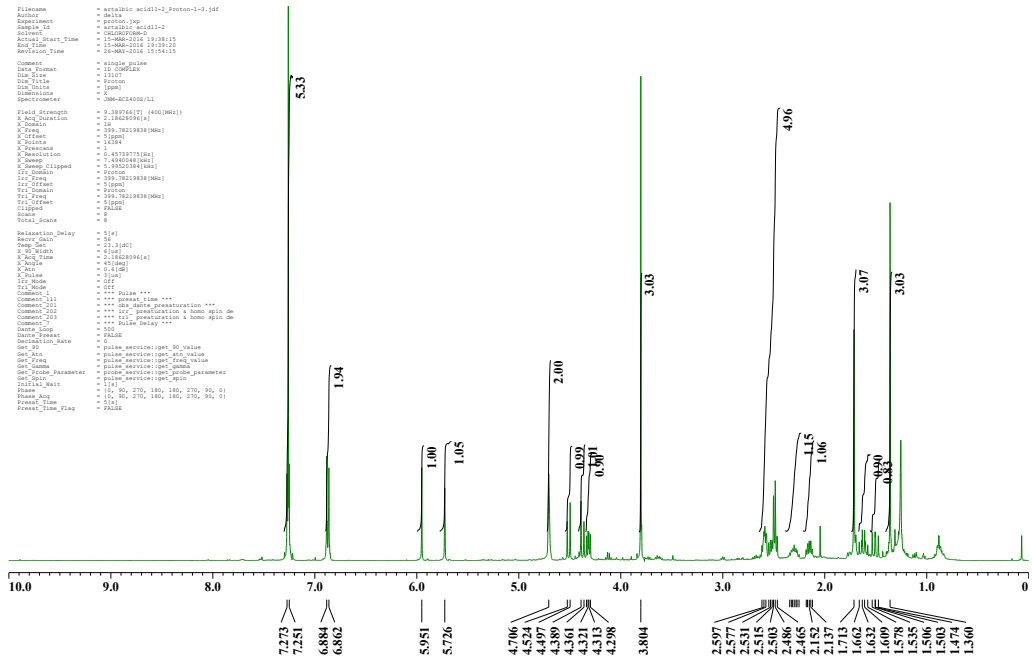
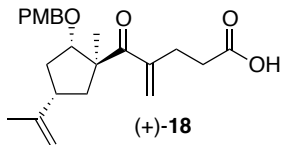


X : parts per Million : Proton

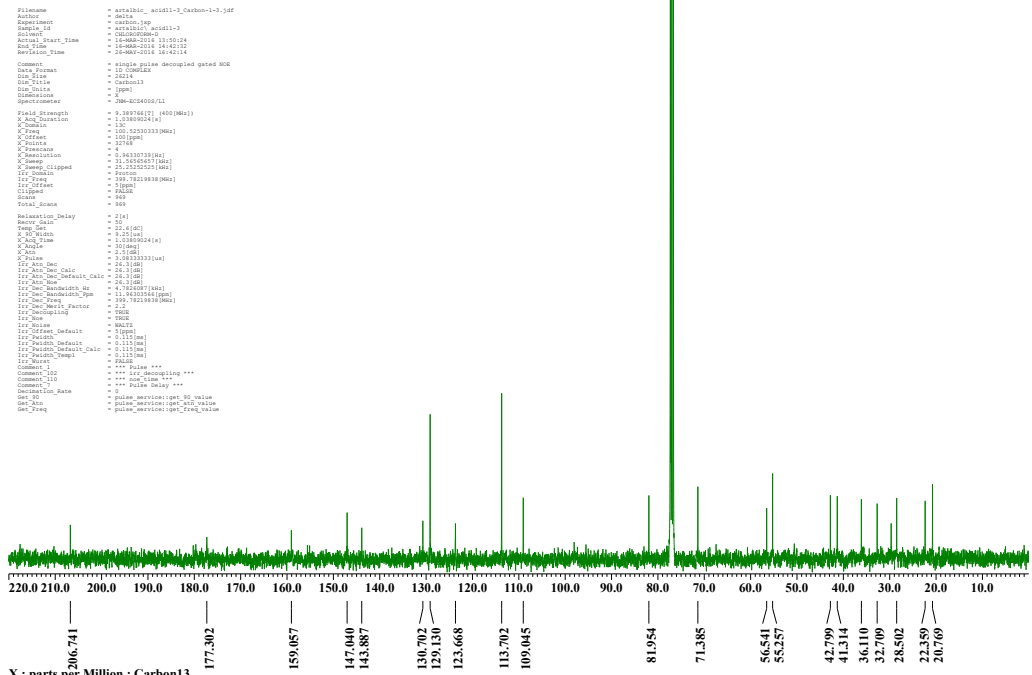


X : parts per Million : Carbon13





X : parts per Million : Proton



X : parts per Million : Carbon13

Chiralcel AD-H column, hexane : *i*PrOH = 300 : 1, 1.0 mL/min;

(+)-**12** (minor) ; $t_R = 13.3$ min, (-)-**12** (major) ; $t_R = 16.9$ min

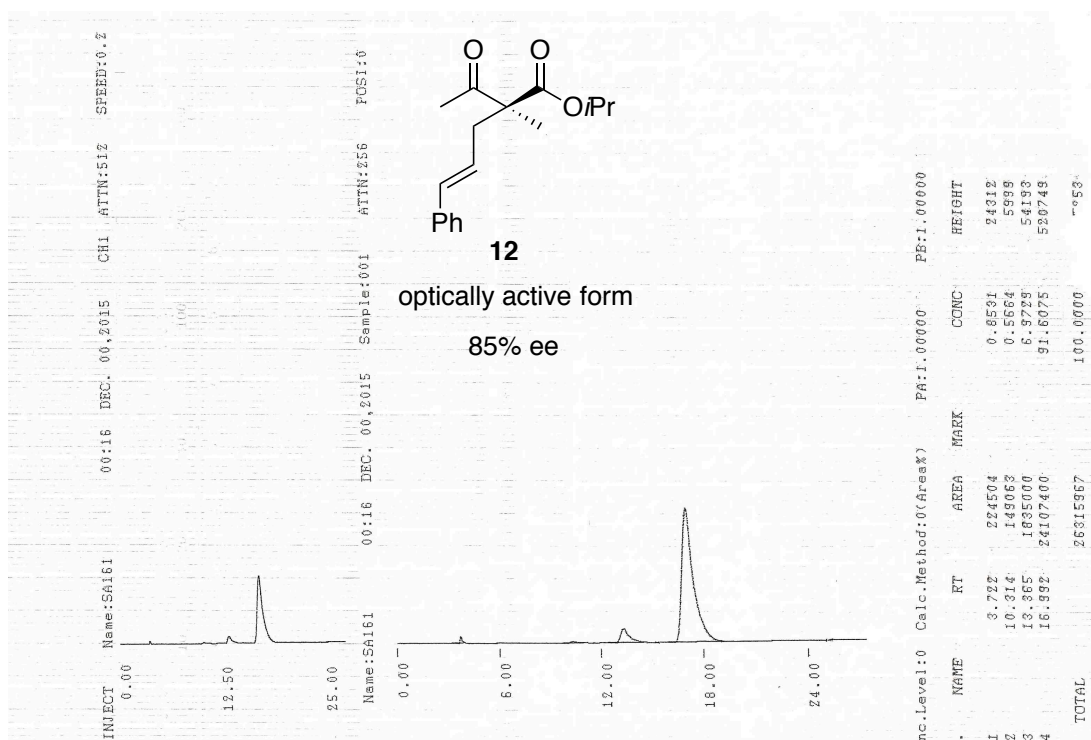
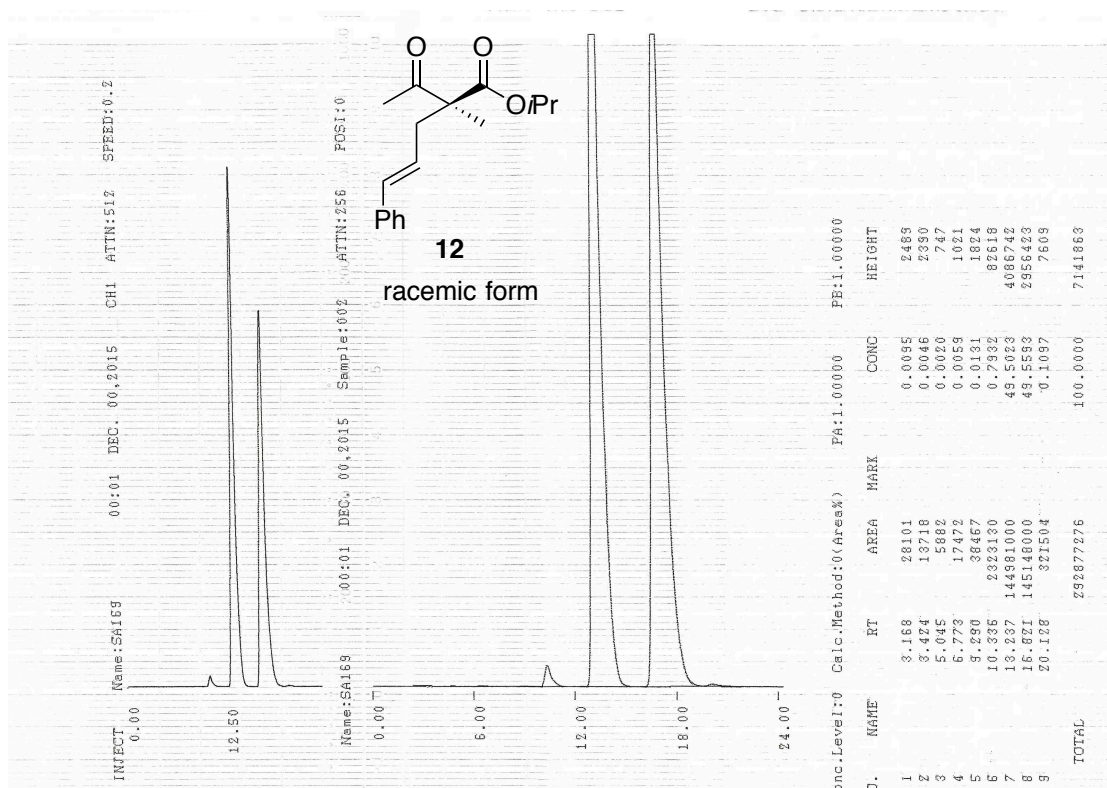
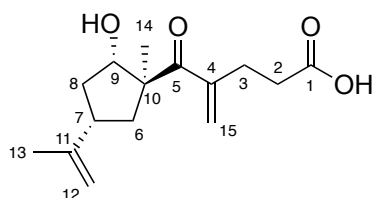


Table S1. Comparison of the chemical shift of ^1H and ^{13}C NMR spectra of natural product with those of synthetic sample **1**.



reported artalbic acid (1)			synthetic artalbic acid (1)		
C/H no.	δ_{H} (J in Hz) ^a	δ_{C} ^b	C/H no.	δ_{H} (J in Hz) ^a	δ_{C} ^{b, d}
1	–	178.9	1	–	178.3
2	2.48, br t (7.2)	33.9	2	2.37-2.52, m ^c	33.2
3	2.61, br t (7.2)	29.2	3	2.58-2.62, m	28.4
4	–	145.2	4	–	144.4
5	–	208.5	5	–	207.7
6	2.36 ^c 1.69 ^c	42.2	6	2.37-2.52, m ^c 1.66-1.75, m ^c	41.4
7	2.39 ^c	41.2	7	2.37-2.52, m ^c	40.4
8	2.05 1.69 ^c	37.3	8	2.01-2.07, m 1.66-1.75, m ^c	36.5
9	4.45, dd (10.8, 6.0)	77.0	9	4.44, dd (10.9, 5.9)	76.3
10	–	56.6	10	–	55.8
11	–	148.1	11	–	147.4
12	4.75, br s 4.73, br s	109.9	12	4.75, br s 4.73, br s	109.2
13	1.72, br s	21.5	13	1.74, s	20.8
14	1.32, s	22.6	14	1.32, s	21.9
15	5.96, br s 5.87, br s	125.2	15	5.97, br s 5.88, br s	124.5

^a CDCl_3 , ^b Benzene- d_6 , ^c Overlapped signal, ^d Chemical shifts were expressed using benzene- d_6 (128.0 ppm) as internal standard.