As it has shown in the manuscript treatment of 26 with (S)-2-methyl-CBS-oxazaborolidine using borane dimethysulfide as reducting agent under inert atmosphere and low temperature, produced diastereoselectively 27 and 28.

The generated stereogenic center at C-16 has R configuration as expected. Confirmation of the diastereoselectivity of the reduction was done applying Mosher methodology (Scheme S1). The mixture of diastereoisomers 29/29b, obtained after deprotection of mixture 20a/20b, was esterified with (+)-MTPA leading to the diester mixture 31a/31b (Scheme S1).

Comparison between the $^1$H NMR spectra of the mixture (29/29b) and compound 29 obtained from Corey-Bakshi-Shibata reduction indicated that this reaction afforded only one of the diastereoisomers.

Isobe et al. [1] have established that for secondary alcohols with an $\alpha$-furyl substituent, the ring protons (H-18 in this case) can be used for the analysis that allow determination of the absolute configuration of the centre observed.

Tables S1 and S2 show the chemical shifts for H-18 for 29 and 31a as well as for 29b and 31b.
Tables S1. Comparative studies for the signals of H-18 in $^1$H-NMR for compounds 29 and 31a.

|          | 29  | 31a |
|----------|-----|-----|
| $\delta$ H-18 (ppm) | 6.41 | 6.40 |

Table S2. Comparative studies for the signals of H-18 in $^1$H-NMR for compounds 29b and 31b.

|          | 29b | 31b |
|----------|-----|-----|
| $\delta$ H-18 (ppm) | 6.41 | 6.28 |

The comparison between the chemical shifts of H-18 in 31a ($\delta$ 6.40) and 31b ($\delta$ 6.26) permit us to conclude that the isomer with the signal in the $^1$H NMR spectrum of H-18, at lower field (31a) is 16$R$ and the one at higher field (31b) is 16$S$, due to the shielding effect of the aromatic ring. This analysis confirmed the diastereoselectivity of the reduction of 26 that lead to compounds 27 and 28 [1].

19,20-Epoxy-luffara-8,13Z,17(20),18-tetraen-16($R$,S),21-diol (29/29b): To a solution of 20a/20b (14 mg, 0.03 mmol) in MeOH (3.5 mL) was added p-toluenesulfonic acid (1 mg, 0.005 mmol). The reaction mixture was stirred for 48 h. Then, water was added and it was extracted with AcOEt. The combined organic layers were washed with water and brine, dried (Na$_2$SO$_4$), filtered, and concentrated in vacuo to obtain 29/29b (7 mg, 66%). IR $\nu$ 3345 (OH), 2928, 2866, 1456, 1161, 1024; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (2H, s, H-19, H-20), 6.41 (1H, s, H-18), 5.41 (1H, t, $J$ = 7.9 Hz, H-14), 4.73 (1H, dd, $J$ = 4.4 and 8.0 Hz, H-16), 4.20 (1H, d, $J$ = 11.6 Hz, H$_A$-21), 4.05 (1H, d, $J$ = 11.6 Hz, H$_B$-21), 2.60–2.50 (2H, m, H-15), 2.20–2.10 (4H, m, H-11, H-12), 2.00–1.00 (11H, m), 1.58 (3H, s, Me-22), 0.95 (3H, s, Me-23), 0.88 (3H, s, Me-25), 0.83 (3H, s, Me-24); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 144.0 (C), 143.3 (CH), 140.1 (C), 138.9 (CH), 128.7 (C), 126.1 (C), 123.0 (CH), 108.5 (CH), 66.0 (CH), 60.2 (CH$_2$), 51.9 (CH), 41.8 (CH$_2$), 39.0 (C), 37.1 (CH$_2$), 37.0 (CH$_2$), 36.3 (CH$_2$), 33.6 (CH$_2$), 33.3 (C, CH$_3$), 27.4 (CH$_2$), 21.7 (CH$_3$), 20.1 (CH$_3$), 19.5 (CH$_3$), 19.0 (CH$_2$ $\times$ 2); HRMS (ESI) $m/z$ calcd for C$_{25}$H$_{38}$O$_3$Na (M + Na)$^+$ 409.2713, found 409.2695.

Di-(R-\alpha-methoxy-\alpha-trifluoromethyl-phenyl)-acetate of 19,20-epoxy-luffara-8,13Z,17(20),18-tetraen-16($R$,S),21-diol (31a/31b): To a solution of 29/29b (7 mg, 0.017 mmol) in DCM (0.6 mL), R-\alpha-methoxy-\alpha-trifluoromethylphenylacetic acid (9 mg, 0.04 mmol) and DMAP (1 mg, 0.006 mmol)
were added. It was cooled to 0 °C and under argon atmosphere, N,N'-dicyclohexylcarbodiimide (DCC) (38 μL, 0.38 mmol) was added. The mixture was reacted at 0 °C for 90 min, and then, it was allowed to warm to room temperature. The reaction mixture was stirred for 24 h. The resulting crude was filtered and water was added. Then it was extracted with AcOEt and the combined organic layers were washed with 2 M aqueous solution of HCl, 10% aqueous solution of NaHCO₃ and water until neutral pH was reached, dried (Na₂SO₄), and concentrated in vacuo to obtain 31a/31b (6 mg, 45%). [α]D⁰⁺⁰ = +28.7 (c 0.39, CHCl₃); IR ν 2932, 2859, 1748 (C=O), 1668 (C=C), 1456, 1271, 1169, 1022; ¹H-NMR (400 MHz, CDCl₃) δ 7.45–7.30 (12H, m, H-19, H-20, Ph-), 6.39 (1H, s, H-18, 16R, minor.), 6.27 (1H, s, H-18, 16S, major.), 5.98 (1H, t, J = 5.8 Hz, H-16 major.), 5.97 (1H, t, J = 5.8 Hz, H-16 minor.), 5.46 (1H, t, J = 7.2 Hz, H-14, major.), 5.37 (1H, t, J = 7.8 Hz, H-14, minor.), 4.83 (1H, d, J = 12.0 Hz, HA-21, major.), 4.78 (1H, d, J = 12.0 Hz, HA-21, minor.), 4.70 (1H, d, J = 12.0 Hz, HB-21, major.), 4.63 (1H, d, J = 12.0 Hz, HB-21, minor.), 3.51 (3H, s, MeO), 3.50 (3H, s, MeO), 3.45 (3H, s, MeO), 2.85–2.60 (2H, m, H-15), 2.20–2.00 (4H, m, H-11, H-12), 2.00–1.00 (11H, m), 1.54 (3H, s, Me-22), 0.94 (3H, s, Me-23), 0.88 (3H, s, Me-25), 0.82 (3H, s, Me-24); HRMS (ESI) m/z calcd for C₄₅H₆₅NO₇F₆ (M + NH₄) 836.3956, found 836.3985.

Di-(R-α-methoxy-α-trifluoromethyl-phenyl)-acetate of 19,20-epoxy-luffara-8,13Z,17(20), 18-tetraen-16R,21-diol (31a): To a solution of 29 (5 mg, 0.013 mmol) in DCM (0.45 mL), R-α-methoxy-α-trifluoromethylphenylacetic acid (7 mg, 0.03 mmol) and DMAP (1 mg, 0.005 mmol) were added. It was cooled to 0 °C and under argon atmosphere, DCC (28 μL, 0.28 mmol) was added. The mixture was reacted at 0 °C for 90 min, and then, it was allowed to warm to room temperature. The reaction mixture was stirred for 24 h. The resulting crude was filtered and water was added. Then it was extracted with AcOEt and the combined organic layers were washed with 2 M aqueous solution of HCl, 10% aqueous solution of NaHCO₃ and water until neutral pH was reached, dried (Na₂SO₄), and concentrated in vacuo to obtain 31a (9 mg, 80%). [α]D⁰⁺⁰ = +12.3 (c 0.36, CHCl₃); IR ν 3065, 2926, 2855, 1748 (C=O), 1670 (C=C), 1464, 1271, 1169, 1022; ¹H-NMR (400 MHz, CDCl₃) δ 7.45–7.30 (12H, m, H-19, H-20, Ph-), 5.39 (1H, s, H-18), 5.97 (1H, t, J = 5.8 Hz, H-16), 5.37 (1H, t, J = 7.8 Hz, H-14), 4.78 (1H, d, J = 12.0 Hz, HA-21), 4.63 (1H, d, J = 12.0 Hz, HB-21), 3.50 (3H, s, MeO), 3.45 (3H, s, MeO), 2.85–2.60 (2H, m, H-15), 2.20–2.00 (4H, m, H-11, H-12), 2.00–1.00 (11H, m), 1.54 (3H, s, Me-22), 0.94 (3H, s, Me-23), 0.88 (3H, s, Me-25), 0.82 (3H, s, Me-24); HRMS (ESI) m/z calcd for C₄₅H₆₅NO₇F₆ (M + NH₄) 836.3956, found 836.3985.
Figure S1. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S2. IR of 16.
Figure S3. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S4. IR and HRMS of 17.
Figure S5. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S6. IR and HRMS of 18.
Figure S7. ROESY of 18.
Figure S8. $^1$H-NMR CDCl$_3$ and IR.
Figure S9. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S10. IR and HRMS of 20a/20b.
Figure S11. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S12. IR and HRMS of 21a/21b.
Figure S13. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S14. IR and HRMS of 22a/22b.
Figure S15. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S16. IR and HRMS of 23a/23b.
Figure S17. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S18. IR and HRMS of 24a/24b.
Figure S19. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S20. IR and HRMS of 27.
Figure S21. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S22. IR and HRMS of 28.
Figure S23. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S24. IR and HRMS of 29/29b.
Figure S25. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S26. IR and HRMS of 29.
Figure S27. $^1$H-NMR CDCl$_3$ and expansion of $^1$H-NMR CDCl$_3$. 
Figure S28. IR and HRMS of 31a/31b.
Figure S29. $^1$H-NMR CDCl$_3$ and expansion of $^1$H-NMR CDCl$_3$. 
Figure S30. IR and HRMS of 31a.
Figure S31. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S32. IR of 30.
Figure S33. $^1$H-NMR CDCl$_3$ and $^{13}$C-NMR CDCl$_3$. 
Figure S34. IR and HRMS of 9.

Reference

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