Synthesis of (-)-Gloeosporone, a fungal autoinhibitor of spore germination using a π-allyltricarbonyliron lactone complex as a templating architecture for 1,7-diol construction.

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Preparation of lithium naphthalenide solution

A suspension of naphthalene (6.5g, 50.7 mmol) and lithium (1.15g, 50.0 mmol, 30 wt.% dispersion in mineral oil) in THF (50 cm3) was sonicated for 30 min to yield a dark green solution (1 mol dm–3).

(7*E*,9*E*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyldimethyl-silanyl-oxy)-6-hydroxy-tetradeca-7,9-diene **7-*E,E***, (7*E*,9*Z*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyldimethylsilanyloxy)-6-hydroxy-tetradeca-7,9-diene**7-*E,Z*** and (7*Z*,9*E*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyldimethylsilanyloxy)-6-hydroxy-tetradeca-7,9-diene **7-*Z,E***

Acetate **6** (55 mg, 0.08 mmol, MW=672.66) in THF (1 ml) was cooled to -78°C and lithium naphthalenide (5 eq., 0.41 mmol, 0.41 ml, 1M solution in THF, freshly prepared according to the above method was added. The solution was stirred at this temperature overnight. The solution was warmed to room temperature and filtered through a pad of silica, washing with Et_2O, the solvent was then removed and the residue purified by flash column chromatography (eluent PE:Et_2O 5:1 to 1:1, gradient) to afford an inseparable mixture of dienes 7-*E,E*, 7-*E,Z* and 14-*Z,E* (0.5 : 0.2 : 0.3) as an oil (36 mg, 0.08 mmol, 98%); ν_{max} (neat)/cm^{-1}: 3358 (OH), 2927, 2855, 2079, 1973, 1455, 1361, 1252, 1092, 1043, 989, 835, 774, 734, 697; δ_H (400 MHz, $CDCl_3$): 0.05 (3H, s, $Si(CH_3)$), 0.08 (3H, s, $Si(CH_3)$), 0.84 (9H, s, $SiC(CH_3)_3$), 0.89 (3H, t, *J* 7.1, 1-H x 3), 1.21-1.63 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.75 (2H, m, 11-H x 2), 2.26 (2H, m, 13-H x 2), 3.54 (1H, s, OH), 3.58 (1H, m, 12-H), 3.91 (0.5H, m, 6-H x 0.5), 4.12 (0.5H, m, 6-H x 0.5), 4.49 (2H, app. q, *J* 11.7, $CH_2C_6H_5$), 5.29 (0.3H, m, 7-H x 0.3), 5.49 (0.2H, m, 10-H x 0.2), 5.58 (0.5H, dd, *J* 15.0, 6.9, 7-H x 0.5), 5.69 (1H, m, 7-H x 0.2, 10-H x 0.8), 6.04 (1H, m, 8-H x 0.3, 9-H x 0.7), 6.17 (0.5H, dd, *J* 15.3 10.2, 8-H x 0.5), 6.32 (0.3H, dd, *J* 15.0 10.9, 9-H x 0.3),

6.44 (0.2H, dd, *J* 15.0 10.9, 8-H x 0.2), 7.24-7.38 (5H, m, $CH_2C_6H_5$); δ_C (100 MHz, $CDCl_3$): 138.5, 134.3, 131.9, 130.6, 128,3, 127.7, 127.4, 125.8, 72.9, 72.7, 69.2, 67.0, 41.2, 41.0, 37.4, 37.3, 36.9, 31.8, 25.8 ($SiC(CH_3)_3$), 25.1, 24.9, 22.6, 18.1 ($SiC(CH_3)_3$), 14.0, -4.3 ($Si(CH_3)$), -4.7 ($Si(CH_3)$); *m/z* (ES) Found: $[MH]^+$ 447.3267. $C_{27}H_{47}O_3Si$ requires *M*H, 447.3294.