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 (6.5 g, 50.7 mmol) and lithium (1.15 g, 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).


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 Et₂O, the solvent was then removed and the residue purified by flash column chromatography (eluent PE:Et₂O 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%); νmax (neat)/cm⁻¹: 3358 (OH), 2927, 2855, 2079, 1973, 1455, 1361, 1252, 1092, 1043, 989, 835, 774, 734, 697; δH (400 MHz, CDCl₃): 0.05 (3H, s, Si(CH₃)), 0.08 (3H, s, Si(CH₃)), 0.84 (9H, s, Si(C(H₃)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, CH₂C₆H₅), 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, CH₂C₆H₅); δC (100 MHz, CDCl₃): 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(CH₃)₃), 25.1, 24.9, 22.6, 18.1 (SiC(CH₃)₃), 14.0, -4.3 (Si(CH₃)), -4.7 (Si(CH₃)); m/z (ES) Found: [MH]⁺ 447.3267. C₂₇H₄₇O₃Si requires MH, 447.3294.