(3) Supporting information

Experimental

General Experimental Procedures

All compounds were purchased from Aldrich except α-ganefromycin, which was obtained by the procedures described in ref. 2. Methylene chloride was distilled from calcium hydride under nitrogen. Analytical and preparative HPLC was performed on Waters (Rochester, MN) or Rainin (Woburn, MA) HPLC. ^{1}H, ^{1}H -^{1}H COSY and ^{1}H -^{1}H ROESY spectra were recorded on a Bruker DMX 500-MHz spectrometer. ^{1}H -^{1}H ROESY was performed with continuous spin lock during mixing (RF power 2.5kHz, mixing time 300 ms), relaxation delay of 2s, and acquisition time 0.255 s. UV spectra were taken on a Perkin-Lambda 6 model. CD spectra were measured on a JASCO J-720 spectropolarimeter. Compound **(4)** and **(5)** were purified, using reversed phase HPLC (column Hypersil ODS 5um) prior to UV and CD measurement. ESI mass spectra were measured on a JEOL JMS-mate LSMS-system. Preparative TLC-plates used were Uniplate Silicagel GF 20x20cm 500 or 1000 microns, and was bought from Analtech Inc. All calculations were carried out with Indigo Silicon Graphics 3D workstation at the Department of Chemistry, Columbia University.

Compound (4)

3mg of **2** was dissolved in dry CH_2Cl_2 along with excess of both 4-dimethylaminobenzoic acid and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide) hydrochloride (EDC). This solution was allowed to stir for 10min then catalytic amount of dimethylaminopyridine (DMAP) was added. After stirring at room temperature for 4 h, the solution was applied to preparative TLC plate without further workup and gave **4** in ca 50% yield. ^{1}H-NMR (MeOD, 500 MHz) δ_H 0.79 (3H, 12-Me), 0.9 (3H, s, 25-Me), 0.91 (3H, s, 25-Me), 1.66 (3H, s, 14-Me), 1.75 (3H, 30-Me), 1.78 (1H, H-12), 2.17 (1H, H-10eq), 2.25 (1H, H-10ax), 3.03 (6H, N-Me), 3.13 (H, H-21), 3.17 (3H, 13-OMe), 3.42 (1H, H-13), 3.44 (H, 21-CH2), 3.50 (2H, CH2-Ph), 3.59 (1H, H-24), 3.62 (1H, 21-CH2), 3.69 (1H, H-23), 3.72 (3H, -COOMe), 3.75 (1H, H-18), 3.90 1(H, H-18b), 4.21 (1H, H-26), 4.68 (1H, broad, H-8) 4.68 (1H, H-11), 5.50 (1H, H-30), 5.53 (1H, H-9), 5.61 (1H, H-17), 5.63 (1H, H-27), 5.88 (1H, H-2), 5.98 (H, H-7), 5.98 (1H, H-15), 5.98 (1H, H-29), 6.35 (H, H-4), 6.50 (4H, H-6,H-16,H-28,H-5), 6.70 (2H, dmabz), 7.26 (6H, m, -Ph,H-3), 7.81 (2H, dmabz). MS (ESI-pos.) m/z 954.6 ($M+H^+$).

(3) Supporting information

Compound (5)

5mg of **2** was dissolved in dry CH_2Cl_2 along with excess of both 2-naphtoic acid and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide) hydrochloride (EDC). This solution was allowed to stir for 10min then catalytic amount of dimethylaminopyridine (DMAP) was added. After refluxing for 8 h, the solution was applied to preparative TLC plate without further workup and gave **5** in less then 10% yield.

^{1}H-NMR (C_6D_6, 500 MHz) δ_H 0.84 (3H, 12-Me), 0.92 (3H, 25-Me), 1.62 (3H, 25-Me), 1.62 (3H, 14-Me), 1.65 (3H, 30-Me), 1.78 (1H, H-12), 1.98 (1H, H-10), 2.17 (1H, H-10), 2.71 (1H, CH2-Ph), 2.79 (1H, CH2-Ph), 3.07 (3H, 13-OMe), 3.12 (H, 21-CH2), 3.39 (3H, s,-COOMe), 3.43 (H, 21-CH2), 3.56 (1H, H-13), 3.66 (H, H-18), 3.72 (H, H-18), 4.44 (1H, H-8), 4.94 (1H, H-26), 5.02 (1H, H-11), 5.06 (1H, H-21), 5.39 (1H, H-17), 5.52 (1H, H-30), 5.64 (1H, H-9), 5.76 (1H, H-2), 5.91 (3H, H-27, H-4, H-7), 6.06 (2H, H-5, H-15), 6.16 (1H, H-23 or H-24), 6.18 (1H, H-29), 6.20 (1H, H-23 or H-24), 6.30 (1H, H-16), 6.44 (H, H-6), 6.75-7.55 (13H,H-3,H-28,-Naph.,-Ph), 8.21 (1H,-Naph.) 8.25 (1H,-Naph.), 8.32 (1H,-Naph.), 8.68 (1H, -Naph.), 8.77 (1H,-Naph.), 8.91 (1H,-Naph.). MS (ESI-pos.) m/z 1267.6 ($M+H^+$).