

## SUPPORTING INFORMATION

### Total synthesis of Noricumazole B establishes D-arabinose as glycon unit

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### Experimental

#### General Remarks

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker DPX-400, AVANCE-400 and DRX-500. The numbering of the protons relate to the numbering chosen in Fig. 1. High resolution mass spectra were obtained with a Micromass LCT via loop-mode injection from a Waters (Alliance 2695) HPLC system. Alternatively a Micromass Q-TOF in combination with a Waters Aquity Ultrapformance LC system was employed. Ionization was achieved by ESI or APCI. Modes of ionization, calculated and found mass are given. RP-HPLC was performed on RP-CN with CH<sub>3</sub>CN/H<sub>2</sub>O gradient elution. CD spectra were obtained using a Jasco J-810 circular dichroism spectropolarimeter. Analytical thin-layer chromatography was performed using precoated silica gel 60 F<sub>254</sub> plates (Merck, Darmstadt). Flash column chromatography was performed on Merck silica gel (230-400 mesh). Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in dry glassware. Commercially available reagents and dry solvents were used as received.

#### Masamune ester 6:

To a solution of alcohol **5**<sup>5</sup> (11.3 g, 21.0 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) were sequentially added 4-methoxybenzyl 2,2,2-trichloroacetimidate (13.1 g, 46.5 mmol, 2.2 eq) and Campher-10-sulfonic acid (0.9 g, 3.7 mmol, 0.2 eq) at room temperature. The reaction was stirred 16 h at room temperature and terminated by addition of sat. aq. NaHCO<sub>3</sub> solution. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic extracts were dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether : ethyl acetate = 10:1 → 3:1) to furnish the PMB-ether **6** as light yellow oil (19.4 g, 29.6 mmol, quant).

[α]<sub>D</sub><sup>25</sup> = +35.0 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 7.35–7.08 (m, 12H, Bn, Mes, Ph), 6.79 (d, *J* = 7.9 Hz, 2H, PMB), 6.74 (d, *J* = 7.9 Hz, 2H, PMB), 5.72 (d, *J* = 4.4 Hz, 1H, OCHPh), 4.69 (d, *J* = 16.0 Hz, 1H, Bn), 4.42 (d, *J* = 11.0 Hz, 1H, PMB), 4.41 (d, *J* = 16.0 Hz, 1H, Bn), 4.38 (d, *J* = 11.0 Hz, 1H, PMB), 3.97 (dddd, *J* = 7.1, 7.1, 7.1, 4.4 Hz, 1H, H-9), .77 (s, 3H, PMB), 3.64 (ddd, *J* = 7.5, 6.4, 3.7 Hz, 1H, H-8), 2.75 (quin, *J* = 7.5 Hz, 1H, H-19), 2.46 (s, 6H, Mes), 2.30 (s, 3H, Mes), 1.60 (dddd, *J* = 14.0, 7.3, 7.3, 3.7 Hz, 1H, H-21), 1.48 (dddd, *J* = 14.0, 7.3, 7.3, 6.4 Hz, 1H, H-21'), 1.07 (d, *J* = 7.5 Hz, 3H, H-23), 1.03 (d, *J* = 7.1 Hz, 3H, NCHCH<sub>3</sub>), 0.91 (t, *J* = 7.3 Hz, 3H, H-22) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 173.7 (q, C-18), 159.1 (q, PMB), 142.4 (q, Mes), 140.3 (q, Ph), 138.9 (q, Mes), 138.5 (q, Mes), 133.5 (q, Mes), 132.1 (2x t, ), 130.5 (q, Bn), 129.4 (2x t, PMB), 129.3 (2x t, Bn), 129.26 (2x t, Mes), 128.3 (t, Ph), 128.2 (t, Ph), 127.9 (2x t, Bn), 127.7 (t, Ph), 127.0 (t, Bn), 125.9 (2x t, Ph), 113.7 (2x t, PMB), 80.6 (t, C-20), 77.9 (t, OCHPh), 71.4 (s, PMB), 56.8 (t, NCCH<sub>3</sub>), 55.3 (p, PMB), 48.1 (s, Bn), 42.8 (t, C-19), 29.7 (s, C-21), 22.3 (2x p, Mes), 20.9 (p, Mes), 13.6 (p, C-23), 12.6 (p, NCCH<sub>3</sub>), 8.3 (p, C-22) ppm; HRMS (ESI): *m/z*: calculated for C<sub>39</sub>H<sub>47</sub>NO<sub>6</sub>Na: 680.3022 [M+Na]<sup>+</sup>, found: 680.3016 [M+Na]<sup>+</sup>.

#### (2S,3R)-3-(4-methoxybenzyloxy)-2-methylpentan-1-ole (S1):

To a solution of PMB-ether **6** (9.7 g, 14.7 mmol, 1.0 eq) in THF (100 mL) was added DIBAL-H (1.0 mol/L in hexane, 44 mL, 44.0 mmol, 3.0 eq) at -78 °C. After 1 h, the reaction was warmed up to -20 °C. After 2 h a sat. aq. solution of Rochelle's salt was added and the mixture was stirred 30 min at room temperature. After extraction with CH<sub>2</sub>Cl<sub>2</sub> the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 5:1) furnished alcohol **S1** as colorless oil (3.2 g, 13.4 mmol, 91%).

[α]<sub>D</sub><sup>20</sup> = -39.8 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 7.26 (d, *J* = 8.5 Hz, 2H, PMB), 6.88 (d, *J* = 8.5 Hz, 2H, PMB), 4.56 (d, *J* = 10.9 Hz, 1H, PMB), 4.37 (d, *J* = 10.9 Hz, 1H, PMB), 3.80 (s, 3H, PMB), 3.64 (dd, *J* = 10.9, 3.8 Hz, 1H, H-18), 3.55 (dd, *J* = 10.9, 6.9 Hz, 1H, H-18'), 3.35 (ddd, *J* = 6.9, 4.8, 4.8 Hz, 1H, H-20), 2.69 (bs, 1H, OH), 1.90 (dsxt, *J* = 6.9, 3.8 Hz, 1H, H-19), 1.74 (dddd, *J* = 14.7, 7.5, 7.5, 7.5, 4.8 Hz, 1H, H-21), 1.60 (dddd, *J* = 14.7, 7.5, 7.5, 7.5, 4.8 Hz, 1H, H-21'), 0.93 (t, *J* = 7.5 Hz, 3H, H-22), 0.89 (d, *J* = 6.9 Hz, 3H, H-23) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub>

= 77.0 ppm)  $\delta$  159.2 (q, PMB), 130.3 (q, PMB), 129.4 (2x t, PMB), 113.9 (2x t, PMB), 84.7 (t, C-20), 71.2 (s, PMB), 67.0 (s, C-18), 55.2 (p, PMB), 37.1 (t, C-19), 23.0 (s, C-21), 14.1 (t, C-23), 8.3 (p, C-22); HRMS (ESI):  $m/z$ : calculated for  $C_{14}H_{22}O_3Na$ : 261.1467  $[M+Na]^+$ , found: 261.1471  $[M+Na]^+$ .

#### (2S,3R)-3-(4-methoxybenzyloxy)-2-methylpentanal (S2):

To a solution of carbinol **S1** (1.6 g, 6.5 mmol, 1.0 eq) in  $CH_2Cl_2$  (120 mL) were sequentially added  $NaHCO_3$  (2.7 g, 32.5 mmol, 5.0 eq) and DESS-MARTIN periodinane (4.1 g, 9.8 mmol, 1.5 eq) at room temperature. After 30 min, the reaction was terminated by addition of a sat. aq.  $Na_2S_2O_3$  solution and the aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic extracts were dried over  $MgSO_4$  and concentrated under reduced pressure. The crude aldehyde **S2** was used in the next step without further purification.

#### (3S,4R,5R)-3-(tert-butyldimethylsilyloxy)-1-[(R)-4-isopropyl-2-thioxothiazolidin-3-yl]-5-(4-methoxybenzyloxy)-4-methylheptan-1-one (S3):

$TiCl_4$  (1.3 mL, 11.7 mmol, 1.8 eq) was added to a solution of 1-[(R)-4-isopropyl-2-thioxothiazolidin-3-yl]ethanone (**11**)<sup>6</sup> (2.3 g, 11.1 mmol, 1.7 eq) in  $CH_2Cl_2$  (250 mL) at  $-50^\circ C$ . After stirring for 20 min DIPEA (1.9 mL, 11.7 mmol, 1.8 eq) was added to the reaction mixture. After stirring for 2 h at  $-40^\circ C$  the reaction mixture was cooled to  $-78^\circ C$  and aldehyde **S2** (1.5 g, 6.5 mmol, 1.0 eq) in  $CH_2Cl_2$  (80 mL) was added. After 2 h the reaction mixture was terminated by addition of a sat. aq.  $NH_4Cl$  solution and was warmed up to room temperature. The aqueous layer was extracted with  $CH_2Cl_2$  and the combined organic extracts were dried over  $MgSO_4$  and concentrated under reduced pressure to furnish the crude product as an orange oil.

This material was dissolved in  $CH_2Cl_2$  (250 mL) and 2,6-lutidine (1.3 mL, 11.4 mmol, 1.8 eq) as well as TBSOTf (2.1 mL, 9.1 mmol, 1.4 eq) were sequentially added at  $-78^\circ C$ . The mixture was warmed to room temperature and stirred for 3 h. The reaction was terminated by addition of a sat. aq.  $NH_4Cl$  solution and extracted with  $CH_2Cl_2$ . The combined organic extracts were dried over  $MgSO_4$  and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 15:1) yields the TBS-PMB-ether **S3** as a yellow oil (3.5 g, 6.3 mmol, 97%).

$[\alpha]_D^{30} = -200.5$  ( $c$  2.0,  $CDCl_3$ );  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $CHCl_3 = 7.26$  ppm)  $\delta$  7.28 (d,  $J = 8.7$  Hz, 2H, PMB), 6.85 (d,  $J = 8.7$  Hz, 2H, PMB), 5.04 [pt,  $J = 6.6$  Hz, 1H,  $CH(CH_3)_2$ ], 4.69 (ddd,  $J = 9.2, 3.8, 2.2$  Hz, 1H, H-18), 4.46 (d,  $J = 10.9$  Hz, 1H, PMB), 4.35 (d,  $J = 10.9$  Hz, 1H, PMB), 3.79 (s, 3H, PMB), 3.57 (dd,  $J = 17.1, 9.2$  Hz, 1H, H-17), 3.46 (dd,  $J = 11.4, 6.6$  Hz, 1H,  $SCH_2$ ), 3.20 (ddd,  $J = 7.7, 6.6, 3.9$  Hz, 1H, H-20), 3.01 (dd,  $J = 11.4, 0.7$  Hz, 1H,  $SCH_2$ ), 2.97 (dd,  $J = 17.1, 2.2$  Hz, 1H, H-17'), 2.40 [psext,  $J = 6.6$  Hz, 1H,  $CH(CH_3)_2$ ], 1.95 (ddq,  $J = 14.6, 6.6, 3.8$  Hz, 1H, H-19), 1.70 (ddq,  $J = 14.6, 14.2, 3.9$  Hz, 1H, H-21), 1.49 (ddq,  $J = 14.2, 7.7, 7.1$  Hz, 1H, H-21'), 1.06 [d,  $J = 6.6$  Hz, 3H,  $CH(CH_3)_2$ ], 0.97 [d,  $J = 6.6$  Hz, 3H,  $CH(CH_3)_2$ ], 0.93 (t,  $J = 7.1$  Hz, 3H, H-22), 0.84 (s, 9H, TBS), 0.82 (d,  $J = 7.2$  Hz, 3H, H-23), 0.08 (s, 3H, TBS), 0.02 (s, 3H, TBS) ppm;  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ ,  $CDCl_3 = 77.0$  ppm)  $\delta$  202.8 (q,  $CS_2$ ), 172.5 (q, NCO), 159.0 (q, PMB), 30.9 (q, PMB), 129.4 (2x t, PMB), 113.7 (2x t, PMB), 80.7 (t, C-20), 71.7 (t, NCCH), 70.9 (s, PMB), 69.3 (t, C-18), 55.2 (p, PMB), 41.8 (t, C-19), 41.5 (s, C-17), 30.9 [t,  $CH(CH_3)_2$ ], 30.8 (s,  $SCH_2$ ), 25.8 (3x p, TBS), 23.1 (s, C-21), 19.2 [p,  $CH(CH_3)_2$ ], 18.0 (q, TBS), 17.9 [p,  $CH(CH_3)_2$ ], 10.7 (p, C-23), 8.7 (p, C-22), -4.66 (p, TBS), -4.7 (p, TBS) ppm; HRMS (ESI):  $m/z$ : calculated for  $C_{28}H_{47}NO_4S_2SiNa$ : 576.2614  $[M+Na]^+$ , found: 576.2604  $[M+Na]^+$ .

#### (3S,4R,5R)-3-(tert-butyldimethylsilyloxy)-5-(4-methoxybenzyloxy)-4-methylheptanoic acid (7):

To a solution of **S3** (198 mg, 0.4 mmol, 1.0 eq) in THF/ $H_2O$  (4:1, 8.3 mL) were sequentially added  $H_2O_2$  (30%, 88  $\mu L$ , 2.9 mmol, 8.0 eq) and 1 N aqueous LiOH (1.4 mL,  $c = 1$  mol/L, 1.4 mmol, 4.0 eq) at  $0^\circ C$  and the reaction mixture was allowed to warm to room temperature. After 3 h, the reaction was terminated by addition of a sat. aq.  $Na_2S_2O_3$  solution and  $H_2O$  and the aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic extracts were dried over  $MgSO_4$  and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 5:1) furnished carboxylic acid **7** as a colorless oil (132 mg, 0.5 mmol, 90%).

$[\alpha]_D^{23} = -22.3$  ( $c$  1.0,  $CDCl_3$ );  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $CHCl_3 = 7.26$  ppm)  $\delta$  7.27 (d,  $J = 8.7$  Hz, 2H, PMB), 6.86 (d,  $J = 8.7$  Hz, 2H, PMB), 4.48 (d,  $J = 11.1$  Hz, 1H, PMB), 4.45 (dt,  $J = 7.9, 4.2$  Hz, 1H, H-18), 4.35 (d,  $J = 11.1$  Hz, 1H, PMB), 3.79 (s, 3H, PMB), 3.23 (ddd,  $J = 7.5, 4.6, 4.2$  Hz, 1H, H-20), 2.46 (dd,  $J = 15.0, 4.2$  Hz, 1H, H-17), 2.39 (dd,  $J = 15.0, 7.9$  Hz, 1H, H-17'), 1.98 (ddq,  $J = 7.9, 7.3, 4.2$  Hz, 1H, H-19), 1.69 (pdddd,  $J = 14.7, 14.5, 7.3, 4.6$  Hz, 1H, H-21), 1.49 (pdddd,  $J = 14.5, 13.2, 7.5, 7.3$  Hz, 1H, H-21'), 0.93 (t,  $J = 7.3$  Hz, 3H, H-22), 0.87 (s, 9H, TBS), 0.86 (d,  $J = 7.3$  Hz, 3H, H-23), 0.06 (s, 3H, TBS), 0.058 (s, 3H, TBS) ppm;  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ ,  $CDCl_3 = 77.0$  ppm)  $\delta$  177.9 (q, C-16), 159.1 (q, PMB), 130.7 (q, PMB), 129.4 (2x t, PMB), 113.7 (2x t, PMB), 80.2 (t, C-20), 70.7 (s, PMB), 69.8 (t, C-18), 55.2 (p, PMB), 41.3 (t, C-19), 38.4 (s, C-17), 25.8 (3x p, TBS), 22.7 (s, C-21), 18.0 (q, TBS), 10.5 (p, C-23), 8.5 (p, C-22), -4.7 (p, TBS), -4.8 (p, TBS) ppm; HRMS (ESI):  $m/z$ : calculated for  $C_{22}H_{37}O_5Si$ : 409.2410  $[M-H]^-$ , found: 409.2417  $[M-H]^-$ .

#### (R)-Methyl-2-[(3S,4R,5R)-3-(tert-butyldimethylsilyloxy)-5-(4-methoxybenzyloxy)-4-methylheptanamido]-3-hydroxypropanoate (S4):

To a solution of TBTU (103 mg, 0.3 mmol, 1.0 eq) and HOBt (49 mg, 0.3 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) were sequentially added acid **7** (132 mg, 0.3 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and DIPEA (0.2 mL, 1.0 mmol, 3.0 eq). After stirring for 2 h at room temperature *L*-serine methyl ester (**12**) (60 mg, 0.4 mmol, 1.2 eq) was added to the reaction mixture and stirring was continued for 3 d at room temperature. The reaction was terminated by addition of a sat. aq. NH<sub>4</sub>Cl solution and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 3:1 → 1:1) furnished amide **S4** as a colorless solid (136 mg, 0.3 mmol, 83%).

m.p. = 83-84 °C; [α]<sub>D</sub><sup>20</sup> = +7.0 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 7.29 (d, *J* = 8.5 Hz, 2H, PMB), 7.11 (d, *J* = 7.3 Hz, 1H, NH), 6.86 (d, *J* = 8.5 Hz, 2H, PMB), 4.63 (ddd, *J* = 7.3, 3.9, 3.8 Hz, 1H, H-14), 4.43 (d, *J* = 10.9 Hz, 1H, PMB), 4.41 (d, *J* = 10.9 Hz, 1H, PMB), 4.20 (q, *J* = 5.9 Hz, 1H, H-18), 3.89 (dd, *J* = 11.0, 3.9 Hz, 1H, H-15), 3.81 (dd, *J* = 11.0, 3.8 Hz, 1H, H-15'), 3.79 (s, 3H, PMB), 3.74 (s, 3H, CH<sub>3</sub>O), 3.42 (ddd, *J* = 6.9, 6.7, 3.6 Hz, 1H, H-20), 2.55 (dd, *J* = 14.3, 5.9 Hz, 1H, H-17), 2.47 (bs, 1H, OH), 2.34 (dd, *J* = 14.3, 5.9 Hz, 1H, H-17'), 2.13 (pdddd, *J* = 12.4, 6.7, 6.7, 5.9 Hz, 1H, H-19), 1.62 (dddd, *J* = 14.4, 7.7, 7.3, 6.9, 3.6 Hz, 1H, H-21), 1.45 (dq, *J* = 14.4, 6.8 Hz, 1H, H-21'), 0.92 (t, *J* = 7.7 Hz, 3H, H-22), 0.90 (s, 9H, TBS), 0.85 (d, *J* = 6.8 Hz, 3H, H-23), 0.08 (s, 3H, TBS), 0.07 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 172.0 (q, C-16), 170.8 (q, C-13), 159.1 (q, PMB), 130.9 (q, PMB), 129.6 (2x t, PMB), 113.7 (2x t, PMB), 80.0 (t, C-20), 71.2 (t, C-18), 70.7 (s, PMB), 63.5 (s, C-15), 55.2 (p, PMB), 54.6 (t, C-14), 52.5 (p, CH<sub>3</sub>O), 41.4 (s, C-17), 39.9 (t, C-19), 25.8 (3x p, TBS), 22.4 (s, C-21), 18.0 (q, TBS), 11.7 (p, C-23), 8.7 (p, C-22), -4.5 (p, TBS), -4.8 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>26</sub>H<sub>46</sub>NO<sub>7</sub>Si: 512.3044 [M+H]<sup>+</sup>, found: 512.3034 [M+H]<sup>+</sup>.

#### **(R)-Methyl-2-[(2S,3R,4R)-2-(tert-butylidimethylsilyloxy)-4-(4-methoxybenzyloxy)-3-methylhexyl]-4,5-dihydrooxazol-4-carboxylate (S5):**

To a solution of **S4** (1.7 g, 3.2 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added DAST (0.5 mL, 3.9 mmol, 1.2 eq) at -78 °C. After stirring for 2 h at -78 °C K<sub>2</sub>CO<sub>3</sub> (807 mg, 5.8 mmol, 1.8 eq) and a sat. aq. K<sub>2</sub>CO<sub>3</sub> solution were added and the reaction mixture was allowed to warm up to room temperature. After extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl amine = 4:1) furnished oxazolidine **S5** as a colorless oil (1.3 g, 2.7 mmol, 82%).

[α]<sub>D</sub><sup>20</sup> = +32.1 (c 2.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 7.28 (d, *J* = 8.6 Hz, 2H, PMB), 6.85 (d, *J* = 8.6 Hz, 2H, PMB), 4.70 (dd, *J* = 11.0, 8.3 Hz, 1H, H-15), 4.49 (dd, *J* = 8.3, 6.0 Hz, 1H, H-15'), 4.44 (d, *J* = 10.7 Hz, 1H, PMB), 4.41 (ddd, *J* = 6.9, 4.4, 2.9 Hz, 1H, H-18), 4.36 (d, *J* = 10.7 Hz, 1H, PMB), 4.34 (dd, *J* = 11.0, 6.0 Hz, 1H, H-14), 3.79 (s, 3H, PMB), 3.75 (s, 3H, CH<sub>3</sub>O), 3.23 (ddd, *J* = 7.1, 7.0, 4.9 Hz, 1H, H-20), 2.46 (dd, *J* = 14.5, 6.9 Hz, 1H, H-17), 2.44 (dd, *J* = 14.5, 2.9 Hz, 1H, H-17'), 1.99 (dddd, *J* = 14.3, 7.1, 7.0, 4.4 Hz, 1H, H-19), 1.67 (dddd, *J* = 14.6, 14.6, 7.1, 4.1 Hz, 1H, H-21), 1.51-1.41 (m, 1H, H-21'), 0.91 (t, *J* = 7.5 Hz, 3H, H-22), 0.87 (d, *J* = 7.2 Hz, 3H, H-23), 0.84 (s, 9H, TBS), 0.02 (s, 3H, TBS), -0.00 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 171.6 (q, C-16), 169.2 (q, C-2), 159.0 (q, PMB), 131.1 (q, PMB), 129.2 (2x t, PMB), 113.7 (2x t, PMB), 80.5 (t, C-20), 70.7 (s, PMB), 69.9 (t, C-18), 68.9 (t, C-14), 68.2 (s, C-15), 55.2 (p, PMB), 52.5 (p, CH<sub>3</sub>O), 41.4 (t, C-19), 32.2 (s, C-17), 25.7 (3x p, TBS), 22.9 (s, C-21), 17.9 (q, TBS), 10.1 (p, C-22), 8.7 (p, C-22), -4.6 (p, TBS), -4.9 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>26</sub>H<sub>44</sub>NO<sub>6</sub>Si: 494.2938 [M+H]<sup>+</sup>, found: 494.2932 [M+H]<sup>+</sup>.

#### **Methyl-2-[(2S,3R,4R)-2-(tert-butylidimethylsilyloxy)-4-(methoxybenzyloxy)-3-methylhexyl]oxazol-4-carboxylate (8):**

To a suspension of anhydrous CuBr<sub>2</sub> (0.9 g, 4.1 mmol, 4.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were added HMTA (0.6 g, 4.1 mmol, 4.0 eq) and DBU (0.6 mL, 4.1 mmol, 4.0 eq). A solution of **S5** (0.5 g, 1.0 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added to the suspension and the reaction mixture was stirred for 2 h at room temperature. The organic solvent was removed under reduced pressure and ethyl acetate and a solution of sat. aq. NH<sub>4</sub>Cl/30%-NH<sub>3</sub> (1:1, 100 mL) were sequentially added to the oily residue. The aqueous layer was extracted with ethyl acetate and the combined organic extracts were sequentially washed with a solution of sat. aq. NH<sub>4</sub>Cl/30%-NH<sub>3</sub> (1:1; 3x), 10%-citric acid, sat. aq. NaHCO<sub>3</sub> and NaCl. The organic extract were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 5:1) furnished oxazole **8** as a colorless oil (0.5 g, 1.0 mmol, quant).

[α]<sub>D</sub><sup>24</sup> = -18.1 (c 0.4, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 8.14 (s, 1H, H-15), 7.28 (d, *J* = 8.5 Hz, 2H, PMB), 6.85 (d, *J* = 8.5 Hz, 2H, PMB), 4.48 (d, *J* = 11.3 Hz, 1H, PMB), 4.47 (ddd, *J* = 8.4, 4.7, 3.8 Hz, 1H, H-18), 4.34 (d, *J* = 11.3 Hz, 1H, PMB), 3.90 (s, 3H, CH<sub>3</sub>O), 3.79 (s, 3H, PMB), 3.27 (ddd, *J* = 7.3, 5.8, 4.2 Hz, 1H, H-20), 2.91 (dd, *J* = 14.7, 8.4 Hz, 1H, H-17), 2.87 (dd, *J* = 14.7, 4.7 Hz, 1H, H-17'), 1.98 (pdddd, *J* = 14.3, 7.3, 7.0, 3.8 Hz, 1H, H-19), 1.71 (pdddd, *J* = 14.7, 14.7, 7.3, 4.2 Hz, 1H, H-21), 1.44-1.55 (m, 1H, H-21'), 0.92 (t, *J* = 7.3 Hz, 3H, H-22), 0.91 (d, *J* = 7.0 Hz, 3H, H-23), 0.78 (s, 9H, TBS), -0.02 (s, 3H, TBS), -0.23 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 164.6 (q, C-13), 161.8 (q, PMB), 159.0 (q, C-16), 143.6 (t, C-15), 133.2 (q, C-14), 131.0 (q, PMB), 129.2 (2x t, PMB), 113.7 (2x t, PMB), 80.5 (t, C-20), 70.8 (s, PMB), 70.7 (t, C-18), 55.2 (p, CH<sub>3</sub>O), 52.0 (p, PMB), 41.5 (t, C-19), 32.1 (s, C-17), 25.6 (3x p, TBS), 22.8 (s, C-21), 17.8 (q, TBS), 10.2 (p, C-23), 8.6 (p, C-22), -4.7 (p, TBS), -5.2 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>26</sub>H<sub>42</sub>NO<sub>6</sub>Si: 492.2781 [M+H]<sup>+</sup>, found: 492.2780 [M+H]<sup>+</sup>.

### 2-[(2S,3R,4R)-2-(tert-butyldimethylsilyloxy)-4-(methoxybenzyloxy)-3-methylhexyl]oxazol-4-carbaldehyde (S6):

To a solution of **8** (250 mg, 1.0 mmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added Dibal-H (1.2 mol/L in toluene, 3.0 mL, 3.6 mmol, 6.0 eq) at -78 °C within 45 min. After 30 min the reaction was terminated by addition of methanol. A saturated aqueous solution of Rochelle's salt was added and the mixture was stirred at room temperature over night. After extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 6:1 → 1:1) furnished aldehyde **S6** as a colorless oil (438 mg, 0.9 mmol, 94%).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = -18.1 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm)  $\delta$  9.91 (s, 1H, H-13) 8.15 (s, 1H, H-15), 7.29 (d, *J* = 8.9 Hz, 2H, PMB), 6.85 (d, *J* = 8.9 Hz, 2H, PMB), 4.54-4.48 (m, 1H, H-18), 4.51 (d, *J* = 11.1 Hz, 1H, PMB), 4.35 (d, *J* = 11.1 Hz, 1H, PMB), 3.79 (s, 3H, PMB), 3.26 (ddd, *J* = 7.2, 5.5, 4.7 Hz, 1H, H-20), 2.90-2.85 (m, 2H, H-17), 1.99 (pdddd, *J* = 14.3, 7.2, 7.2, 4.1 Hz, 1H, H-19), 1.78-1.66 (m, 1H, H-21), 1.57-1.48 (m, 1H, H-21'), 0.94 (t, *J* = 7.3 Hz, 3H, H-22), 0.92 (d, *J* = 7.2 Hz, 3H, H-23), 0.78 (s, 9H, TBS), -0.01 (s, 3H, TBS), -0.23 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm)  $\delta$  184.2 (t, C-13), 165.3 (q, PMB), 159.0 (q, C-16), 143.8 (t, C-15), 140.9 (q, C-14), 130.9 (q, PMB), 129.2 (2x t, PMB), 113.7 (2x t, PMB), 80.4 (t, C-20), 70.8 (s, C-18), 70.7 (s, PMB), 55.2 (p, PMB), 41.4 (t, C-19), 31.9 (s, C-17), 25.6 (3x p, TBS), 22.8 (s, C-21), 17.8 (q, TBS), 10.2 (p, C-23), 8.5 (p, C-22), -4.7 (p, TBS), -5.2 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>25</sub>H<sub>40</sub>NO<sub>5</sub>Si: 462.2676 [M+H]<sup>+</sup>, found: 462.2676 [M+H]<sup>+</sup>.

### 2-[(2S,3R,4R)-2-(tert-butyldimethylsilyloxy)-4-(4-methoxybenzyloxy)-3-methylhexyl]-4-ethynylloxazole (S7):

To a solution of **S6** (438 mg, 0.9 mmol, 1.0 eq) in MeOH (10 mL) were sequentially added K<sub>2</sub>CO<sub>3</sub> (328 mg, 2.4 mmol, 2.5 eq) and the OHIRA-BESTMANN reagent **13**<sup>8</sup> (456 mg, 2.4 mmol, 1.5 eq) at 0 °C. The reaction mixture was allowed to warm to room temperature over night and was terminated by addition of Et<sub>2</sub>O and H<sub>2</sub>O. After extraction with Et<sub>2</sub>O, the combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 6:1) furnished alkyne **S7** as a colorless oil (376 mg, 0.8 mmol, 84%).

[ $\alpha$ ]<sub>D</sub><sup>23</sup> = -11.2 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm)  $\delta$  7.71 (s, 1H, Ar-OH), 7.28 (d, *J* = 8.9 Hz, 2H, PMB), 6.86 (d, *J* = 8.9 Hz, 2H, PMB), 4.47 (d, *J* = 11.3 Hz, 1H, PMB), 4.44 (ddd, *J* = 5.9, 5.9, 4.5 Hz, 1H, H-18), 4.35 (d, *J* = 11.3 Hz, 1H, PMB), 3.79 (s, 3H, PMB), 3.26 (ddd, *J* = 7.3, 6.0, 4.3 Hz, 1H, H-20), 3.16 (s, 1H, H-12), 2.84-2.82 (m, 2H, H-17), 1.98 (ddd, *J* = 7.3, 7.1, 4.5 Hz, 1H, H-19), 1.76-1.66 (m, 1H, H-21), 1.54-1.46 (m, 1H, H-21'), 0.93 (t, *J* = 8.0 Hz, 3H, H-22), 0.91 (d, *J* = 7.1 Hz, 3H, H-23), 0.80 (s, 9H), -0.02 (s, 3H), -0.19 (s, 3H) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm)  $\delta$  163.7 (q, C-16), 159.0 (q, PMB), 141.6 (t, C-15), 131.0 (q, PMB), 129.3 (2x t, PMB), 122.8 (q, C-14), 113.7 (2x t, PMB), 80.5 (q, C-13), 80.4 (t, C-20), 74.0 (t, C-12), 70.9 (s, C-18), 70.8 (t, PMB), 55.2 (p, PMB), 41.4 (t, C-19), 32.1 (s, C-17), 25.7 (3x p, TBS), 22.8 (s, C-21), 17.8 (q, TBS), 10.2 (p, C-23), 8.7 (p, C-22), -4.8 (p, TBS), -5.2 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for: 458.2727 [M+H]<sup>+</sup>, found: 458.2724 [M+H]<sup>+</sup>.

### 2-[(2S,3R,4R)-2-(tert-butyldimethylsilyloxy)-4-[(4-methoxybenzyl)oxy]-3-methylhexyl]-4-[(E)-2-iodovinyl]oxazole (9):

To a suspension of SCHWARTZ reagent **14** (433 mg, 1.7 mmol, 2.5 eq) in THF (7 mL) was added **S7** (308 mg, 0.7 mmol, 1.0 eq) in THF (7 mL) at 0 °C. After 1 h NIS (378 mg, 1.7 mmol, 2.5 eq) in THF (8 mL) was added at -78 °C and the reaction mixture was stirred in the dark for 40 min. The reaction mixture was terminated by addition of a sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and the aqueous layer was extracted with Et<sub>2</sub>O. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 12:1) furnished vinyl iodide **9** as a colorless oil (348 mg, 0.6 mmol, 88%).

[ $\alpha$ ]<sub>D</sub><sup>23</sup> = -12.5 (c 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>H<sub>6</sub> = 7.16 ppm)  $\delta$  7.35 (d, *J* = 8.8 Hz, 2H, PMB), 7.27 (dd, *J* = 14.4, 0.6 Hz, 1H, H-13), 6.93 (dd, *J* = 14.4, 0.4 Hz, 1H, H-12), 6.87 (d, *J* = 8.8 Hz, 2H, PMB), 6.74 (s, 1H, H-15), 4.73 (ddd, *J* = 8.7, 3.8, 3.6 Hz, 1H, H-18), 4.41 (d, *J* = 11.1 Hz, 1H, PMB), 4.22 (d, *J* = 11.1 Hz, 1H, PMB), 3.34 (s, 3H, PMB), 3.04 (ddd, *J* = 7.9, 4.8, 4.3 Hz, 1H, H-20), 2.74 (dd, *J* = 14.6, 8.7 Hz, 1H, H-17), 2.68 (dd, *J* = 14.6, 3.6 Hz, 1H, H-17'), 2.12-2.01 (m, 1H, H-19), 1.59 (pdddd, *J* = 21.9, 7.4, 7.4, 4.3 Hz, 1H, H-21), 1.36 (pdddd, *J* = 21.9, 7.4, 7.4, 4.8 Hz, 1H, H-21'), 0.94 (t, *J* = 7.4 Hz, 3H, H-22), 0.93 (s, 9H, TBS), 0.84 (d, *J* = 7.0 Hz, 3H, H-23), 0.04 (s, 3H, TBS), -0.13 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>H<sub>6</sub> = 128.0 ppm)  $\delta$  164.3 (q, PMB), 159.8 (q, C-16), 140.2 (t, C-13), 134.3 (q, C-14), 133.9 (t, C-15), 131.4 (q, PMB), 129.7 (2x t, PMB), 114.1 (2x t, PMB), 80.4 (t, C-20), 78.3 (t, C-18), 71.4 (t, C-12), 71.1 (s, PMB), 54.8 (p, PMB), 42.0 (t, C-19), 32.0 (s, C-17), 26.0 (3x p, TBS), 22.9 (s, C-21), 18.2 (q, TBS), 10.1 (p, C-23), 8.3 (p, C-22), -4.6 (p, TBS), -5.0 (q, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>26</sub>H<sub>40</sub>NO<sub>4</sub>ISiNa: 608.1669 [M+Na]<sup>+</sup>, found: 608.1674 [M+Na]<sup>+</sup>.

### 18-TBS-20-PMB-protected noricumazole A 15a and 11-epi-18-TBS-20-PMB-protected noricumazole A 15b:

**Method A:** To a solution of *t*-BuLi (1.7 mol/L in pentane, 0.8 mL, 1.4 mmol, 4.1 eq) in degassed Et<sub>2</sub>O (10 mL) was added vinyl iodide **9** (388 mg, 0.7 mmol, 2.0 eq) in Et<sub>2</sub>O (8 mL) at -78 °C under an argon atmosphere. After 1 h, dimethylzinc (1.2 mol/L in toluene, 0.6 mL, 0.7 mmol, 2.0 eq) was added at -78 °C and the reaction mixture was stirred for 15 min. Aldehyde **4** (92 mg, 0.3 mmol, 1.0 eq) in Et<sub>2</sub>O (8 mL) was added and stirring was continued at -78 °C for 3 h. H<sub>2</sub>O and Et<sub>2</sub>O were added

and the aqueous layer was extracted with Et<sub>2</sub>O. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate= 15:1 → 4:1) furnished allylic alcohols **15a** (82 mg, 0.1 mmol, 34%) and 11-*epi*-**15b** (82 mg, 0.1 mmol, 34%) as light yellow oils.

**Method B:** To a solution of nitrobenzoate **S8** (2 mg, 2.3 μmol, 1.0 eq) in THF/MeOH (2:1, 0.15 mL) were added NaOH (0.5 mg, 13.6 μmol, 6.0 eq) and H<sub>2</sub>O (0.1 mL) at 0 °C. The reaction mixture was stirred for 16 h. H<sub>2</sub>O was added and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. Purification by flash chromatography (PE:EA = 6:1) furnished allylic alcohol **15a** as a colorless oil (2 mg, 2.0 μmol, 90%).

**15a:**  $[\alpha]_D^{26} = -15.4$  (*c* 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 11.20 (s, 1H, Ar-OH), 7.45 (s, 1H, H-15), 7.30 (d, *J* = 8.9 Hz, 2H, PMB), 7.22 (d, *J* = 7.5 Hz, 1H, H-5), 6.85 (d, *J* = 8.9 Hz, 2H, PMB), 6.60 (d, *J* = 7.5 Hz, 1H, H-6), 6.48 (pd, *J* = 2.0 Hz, 2H, H-12, H-13), 4.92 (dddd, *J* = 11.1, 10.0, 3.4, 3.0 Hz, 1H, H-9), 4.70 (dq, *J* = 9.6, 2.8 Hz, 1H, H-11), 4.50 (ddd, *J* = 7.0, 4.6, 4.4 Hz, 1H, H-18), 4.48 (d, *J* = 11.0 Hz, 1H, PMB), 4.36 (d, *J* = 11.0 Hz, 1H, PMB), 3.79 (s, 3H, PMB), 3.25 (ddd, *J* = 7.4, 5.9, 4.0 Hz, 1H, H-20), 2.98 (dd, *J* = 16.4, 11.1 Hz, 1H, H-8), 2.88 (dd, *J* = 16.4, 3.4 Hz, 1H, H-8'), 2.85 (dd, *J* = 7.0, 2.4 Hz, 1H, H-17), 2.82 (dd, *J* = 7.0, 4.6 Hz, 1H, H-17'), 2.64 (dd, *J* = 13.3, 6.1 Hz, 1H, H-24), 2.39 (dd, *J* = 13.3, 8.2 Hz, 1H, H-24'), 2.11 (ddd, *J* = 14.7, 9.6, 3.0 Hz, 1H, H-10), 1.99 (dddd, *J* = 14.5, 7.4, 7.1, 4.4 Hz, 1H, H-19), 1.87 (ddd, *J* = 14.7, 10.9, 2.8 Hz, 1H, H-10'), 1.79-1.68 (m, 1H, H-21, H-25), 1.57-1.45 (m, 1H, H-21), 1.44-1.35 (m, 1H, H-26), 1.20-1.13 (m, 1H, H-26'), 0.94 (t, *J* = 7.5 Hz, 3H, H-22), 0.91 (s, 9H, TBS), 0.89 (t, *J* = 7.5 Hz, 3H, H-27), 0.85 (d, *J* = 7.1 Hz, 3H, H-23), 0.84 (d, *J* = 6.5 Hz, 3H, H-28), -0.03 (s, 3H, TBS), -0.23 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 170.2 (q, C-1), 164.0 (q, C-3), 160.5 (q, PMB), 159.0 (q, C-16), 137.8 (q, C-7), 137.2 (t, C-15), 136.7 (q, C-14), 134.9 (t, C-5), 133.4 (t, C-12), 131.0 (q, PMB), 129.3 (t, PMB), 128.8 (q, C-4), 118.4 (t, C-13), 117.0 (t, C-6), 113.6 (t, PMB), 107.7 (s, C-2), 80.5 (t, C-20), 76.5 (t, C-9), 70.8 (t, C-18), 70.79 (s, PMB), 69.9 (t, C-11), 55.2 (p, PMB), 42.0 (t, C-19), 41.6 (s, C-10), 36.8 (s, C-24), 34.7 (t, C-25), 33.3 (s, C-8), 32.0 (s, C-17), 29.4 (s, C-26), 25.7 (3x p, TBS), 22.9 (s, C-21), 19.0 (t, C-28), 17.9 (q, TBS), 11.5 (p, C-27), 10.1 (p, C-22), 8.6 (p, C-23), -4.8 (p, TBS), -5.3 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>42</sub>H<sub>62</sub>NO<sub>8</sub>Si: 736.4245 [M+H]<sup>+</sup>, found: 736.4271 [M+H]<sup>+</sup>.

11-*epi*-**15b:**  $[\alpha]_D^{26} = +6.2$  (*c* 1.0, CDCl<sub>3</sub>); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub> = 7.26 ppm) δ 11.17 (s, 1H, Ar-OH), 7.46 (s, 1H, H-15), 7.29 (d, *J* = 8.5 Hz, 2H, PMB), 7.21 (d, *J* = 7.5 Hz, 1H, H-5), 6.84 (d, *J* = 8.5 Hz, 2H, PMB), 6.59 (d, *J* = 7.5 Hz, 1H, H-6), 6.49 (d, *J* = 15.7 Hz, 1H, H-13), 6.44 (dd, *J* = 15.7, 5.7 Hz, 1H, H-12), 4.69 (dddd, *J* = 8.6, 7.5, 7.2, 3.6 Hz, 1H, H-9), 4.63 (q, *J* = 5.7 Hz, 1H, H-11), 4.50 (ddd, *J* = 7.8, 4.6, 2.9 Hz, 1H, H-18), 4.47 (d, *J* = 10.9 Hz, 1H, PMB), 4.35 (d, *J* = 10.9 Hz, 1H, PMB), 3.78 (s, 3H, PMB), 3.25 (ddd, *J* = 7.9, 5.8, 4.1 Hz, 1H, H-20), 3.00 (dd, *J* = 16.3, 8.6 Hz, 1H, H-8), 2.91 (dd, *J* = 16.3, 3.6 Hz, 1H, H-8'), 2.88-2.82 (m, 2H, H-17), 2.64 (dd, *J* = 13.3, 6.5 Hz, 1H, H-24), 2.38 (dd, *J* = 13.3, 7.9 Hz, 1H, H-24'), 2.24 (ddd, *J* = 14.2, 7.5, 7.2 Hz, 1H, H-10), 1.97 (ddd, *J* = 14.2, 7.2, 4.5 Hz, 1H, H-10'), 2.04-1.93 (m, 1H, H-19), 1.79-1.66 (m, 1H, H-25), 1.58-1.45 (m, 1H, H-21), 1.44-1.34 (m, 1H, H-21'), 1.24-1.14 (m, 2H, H-26), 0.93 (t, *J* = 7.5 Hz, 3H, H-22), 0.90 (s, 9H, TBS), 0.89 (t, *J* = 7.5 Hz, 3H, H-27), 0.84 (d, *J* = 7.2 Hz, 3H, H-23), 0.83 (d, *J* = 6.5 Hz, 3H, H-28), -0.04 (s, 3H, TBS), -0.24 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, CDCl<sub>3</sub> = 77.0 ppm) δ 170.1 (q, C-1), 164.1 (q, C-3), 160.5 (q, PMB), 159.0 (q, C-16), 137.6 (q, C-7), 137.2 (t, C-15), 136.5 (q, C-14), 135.1 (t, C-5), 132.6 (t, C-12), 131.0 (q, PMB), 129.3 (2x t, PMB), 128.9 (q, C-4), 119.5 (t, C-13), 117.1 (t, C-6), 113.6 (3x t, PMB), 107.7 (s, C-2), 80.5 (t, C-20), 77.7 (t, C-9), 70.8 (t, C-18), 70.7 (s, PMB), 69.4 (t, C-11), 55.2 (p, PMB), 41.9 (t, C-19), 41.5 (s, C-10), 36.8 (s, C-24), 34.7 (t, C-25), 33.0 (s, C-8), 32.0 (s, C-17), 29.7 (s, C-26), 25.7 (3x p, TBS), 22.9 (s, C-21), 19.0 (t, C-28), 17.8 (q, TBS), 11.5 (p, C-27), 10.1 (p, C-22), 8.6 (p, C-23), -4.8 (p, TBS), -5.3 (p, TBS) ppm; HRMS (ESI): *m/z*: calculated for C<sub>42</sub>H<sub>62</sub>NO<sub>8</sub>Si: 736.4245 [M+H]<sup>+</sup>, found: 736.4271 [M+H]<sup>+</sup>.

#### 4-Nitrobenzoate **S8**:

To a solution of 11-*epi*-**15a** (5 mg, 6.8 μmol, 1.0 eq) in THF (2 mL) were sequentially added triphenylphosphine (18 mg, 0.1 mmol, 10.0 eq), 4-nitrobenzoic acid (11 mg, 0.1 mmol, 10.0 eq) and diethyl azodicarboxylate (40% in toluene, 32 μL, 0.1 mmol, 10.0 eq) at 0 °C. The reaction temperature was raised to room temperature and the reaction stirred for 30 min. H<sub>2</sub>O was added and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 6:1 → 4:1) furnished nitrobenzoate **S8** as a colorless oil (5 mg, 5.9 μmol, 86%).

$[\alpha]_D^{21} = +12.7$  (*c* 0.5, MeOH); <sup>1</sup>H-NMR (500 MHz, Me<sub>2</sub>CO d<sub>6</sub>, Me<sub>2</sub>CO = 2.05 ppm) δ 11.41 (s, 1H, Ar-OH), 8.39 (d, *J* = 8.9 Hz, 2H, CO<sub>2</sub>CCH), 8.28 (d, *J* = 8.9 Hz, 2H, NO<sub>2</sub>CCH), 7.34 (d, *J* = 7.6 Hz, 1H, H-5), 7.31 (d, *J* = 8.6 Hz, 2H, PMB), 7.24 (s, 1H, H-15), 6.96 (dd, *J* = 15.4, 10.8 Hz, 1H, H-12), 6.84 (d, *J* = 8.6 Hz, 2H, PMB), 6.75 (d, *J* = 7.6 Hz, 1H, H-6), 6.22 (d, *J* = 10.8 Hz, 1H, H-13), 5.97 (ddd, *J* = 15.4, 11.7, 7.4 Hz, 1H, H-11), 4.78 (dddd, *J* = 9.9, 5.7, 5.7, 5.6 Hz, 1H, H-9), 4.71 (ddd, *J* = 9.2, 6.1, 2.8 Hz, 1H, H-18), 4.47 (d, *J* = 11.2 Hz, 1H, PMB), 4.35 (d, *J* = 11.2, 1H, PMB), 3.72 (s, 3H, PMB), 3.33 (ddd, *J* = 11.8, 8.5, 4.5 Hz, 1H, H-20), 3.06-3.01 (m, 2H, H-8), 2.76-2.68 (m, 2H, H-10), 2.75 (dd, *J* = 14.6, 6.1 Hz, 1H, H-17), 2.64 (dd, *J* = 13.2, 6.2 Hz, 1H, H-24), 2.54 (dd, *J* = 14.6, 9.2 Hz, 1H, H-17'), 2.39 (dd, *J* = 13.2, 8.1 Hz, 1H, H-24'), 2.09-2.01 (m, 1H, H-19), 1.86-1.77 (m, 1H, H-21), 1.77-1.69 (m, 1H, H-25), 1.54-1.44 (m, 1H, H-21'), 1.43-1.35 (m, 1H, H-26), 1.22-1.25 (m, 1H, H-26'), 0.92 (s, 9H, TBS), 0.91 (d, *J* = 7.6 Hz, 3H, H-23), 0.89 (t, *J* = 7.1 Hz, 3H, H-27), 0.88 (t, *J* = 8.0 Hz, 3H, H-28), 0.85 (s, 3H, H-22), 0.07 (s, 3H, TBS), 0.05 (s, 3H, TBS) ppm; <sup>13</sup>C-NMR (125 MHz, Me<sub>2</sub>CO d<sub>6</sub>, Me<sub>2</sub>CO = 29.84 ppm) δ 171.3 (q, C-1), 164.4 (q, C-16), 161.1 (q, CO<sub>2</sub>CCH), 160.0 (q, C-3), 152.0 (q, NO<sub>2</sub>C), 147.5 (q, PMB), 138.4 (q, C-7), 138.1

(t, C-5), 135.3 (q, CO<sub>2</sub>CCH), 132.0 (2x t, CO<sub>2</sub>CCH), 130.4 (t, C-11), 130.2 (2x t, PMB), 130.2 (t, C-12), 130.0 (q, C-14), 128.8 (q, C-4), 124.7 (2x t, NO<sub>2</sub>CCH), 119.3 (t, C-13), 118.3 (t, C-6), 114.3 (2x t, PMB), 108.8 (q, C-2), 96.2 (t, C-15), 80.6 (t, C-20), 80.0 (t, C-9), 71.3 (s, PMB), 70.6 (t, C-18), 55.4 (p, PMB), 42.3 (t, C-19), 38.8 (s, C-10), 37.2 (s, C-24), 35.6 (t, C-25), 32.9 (s, C-8), 32.7 (s, C-17), 29.2 (s, C-26), 26.2 (3x p, TBS), 23.1 (s, C-21), 19.2 (q, TBS), 18.6 (p, C-27), 11.7 (p, C-22), 10.1 (p, C-28), 8.3 (p, C-23), -4.37 (p, TBS), -4.4 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for C<sub>49</sub>H<sub>65</sub>N<sub>2</sub>O<sub>11</sub>Si: 885.4358 [M+H]<sup>+</sup>, found: 885.4360 [M+H]<sup>+</sup>.

### 3,11-Acetate-18-TBS-20-PMB protected 11-*epi*-noricumazole A **S9a** und 11-*epi*-**S9b**:

To a solution of alcohol **15a** (27 mg, 36.0 μmol, 1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) was added DMAP (0.9 mg, 7.2 μmol, 0.2 eq), pyridine (13 μL, 158.4 μmol, 4.4 eq) and acidic anhydride (8 μL, 79.2 μmol, 2.2 eq) at room temperature. The reaction was terminated after 16 h by addition of H<sub>2</sub>O and Et<sub>2</sub>O. The aqueous layer was extracted with Et<sub>2</sub>O. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Purification by flash chromatography (petroleum ether : ethyl acetate = 4:1 → 2:1) furnished **16a** (25 mg, 29.9 μmol, quant) as colorless oil.

**S9a**: [α]<sub>D</sub><sup>24</sup> = -22.4 (c 1.0, MeOH); **<sup>1</sup>H-NMR** (400 MHz, Me<sub>2</sub>CO d<sub>6</sub>, Me<sub>2</sub>CO = 2.05 ppm) δ 7.80 (s, 1H, H-15), 7.49 (d, *J* = 7.8 Hz, 1H, H-5), 7.37 (d, *J* = 8.8 Hz, 2H, PMB), 7.19 (d, *J* = 7.8 Hz, 1H, H-6), 6.88 (d, *J* = 8.8 Hz, 2H, PMB), 6.59 (dd, *J* = 15.5, 0.8 Hz, 1H, H-13), 6.40 (ddd, *J* = 15.5, 7.2, 0.5 Hz, 1H, H-12), 5.67 (dq, *J* = 7.2, 0.8 Hz, 1H, H-11), 4.68 (ddd, *J* = 9.2, 4.5, 3.0 Hz, 1H, H-9), 4.57-4.53 (m, 1H, H-18), 4.51 (d, *J* = 11.0 Hz, 1H, PMB), 4.39 (d, *J* = 11.0 Hz, 1H, PMB), 3.78 (s, 3H, PMB), 3.34 (ddd, *J* = 8.2, 5.2, 4.0 Hz, 1H, H-20), 3.12 (dd, *J* = 16.1, 3.0 Hz, 1H, H-17), 3.04 (dd, *J* = 16.1, 10.1 Hz, 1H, H-17'), 2.87 (dd, *J* = 15.0, 3.0 Hz, 1H, H-8), 2.73 (dd, *J* = 15.0, 9.2 Hz, 1H, H-8'), 2.58 (dd, *J* = 13.3, 5.9 Hz, 1H, H-24), 2.33 (dd, *J* = 13.3, 8.7 Hz, 1H, H-24'), 2.32-2.27 (m, 1H, H-10), 2.29 (s, 3H, Ac), 2.10 (ddd, *J* = 13.9, 7.2, 4.5 Hz, 1H, H-10'), 2.06 (s, 3H, Ac), 1.98 (ddd, *J* = 6.6, 4.0, 1.9 Hz, 1H, H-19), 1.82 (pdddd, *J* = 14.6, 7.3, 7.3, 4.3 Hz, 1H, H-21), 1.69-1.59 (m, 1H, H-25), 1.50 (pdddd, *J* = 14.6, 7.3, 7.3, 5.2 Hz, 1H, H-21'), 1.41-1.32 (m, 1H, H-26), 1.26-1.14 (m, 1H, H-26'), 0.93 (d, *J* = 6.6 Hz, 3H, H-23), 0.91 (t, *J* = 7.3 Hz, 3H, H-22), 0.90 (t, *J* = 7.4 Hz, 3H, H-27), 0.83 (d, *J* = 6.7 Hz, 3H, H-28), 0.75 (s, 9H, TBS), -0.03 (s, 3H, TBS), -0.25 (s, 3H, TBS) ppm; **<sup>13</sup>C-NMR** (100 MHz, Me<sub>2</sub>CO d<sub>6</sub>, Me<sub>2</sub>CO = 29.84 ppm) δ 170.3 (2x q, Ac), 169.5 (q, C-1), 164.5 (q, C-16), 160.1 (q, PMB), 150.9 (q, C-3), 140.1 (q, C-7), 139.1 (q, C-14), 136.8 (t, C-15), 136.7 (t, C-5), 135.3 (q, C-4), 132.1 (q, PMB), 130.2 (2x t, PMB), 129.5 (t, C-12), 125.6 (t, C-6), 121.8 (t, C-13), 118.6 (q, C-2), 114.4 (2x t, PMB), 81.1 (t, C-20), 75.3 (t, C-18), 71.9 (t, C-9), 71.5 (s, PMB), 70.7 (t, C-11), 55.5 (p, PMB), 42.5 (t, C-19), 40.4 (s, C-10), 37.7 (s, C-24), 36.3 (t, C-25), 34.1 (s, C-17), 32.2 (s, C-8), unter Me<sub>2</sub>CO-Signal (s, C-26), 26.2 (3x p, TBS), 23.4 (s, C-21), 21.1 (p, Ac), 21.07 (p, Ac), 19.3 (t, C-28), 18.5 (q, TBS), 11.8 (p, C-27), 10.2 (p, C-23), 8.5 (p, C-22), -4.5 (p, TBS), -4.9 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for C<sub>46</sub>H<sub>66</sub>NO<sub>10</sub>Si: 820.4456 [M+H]<sup>+</sup>, found: 820.4437 [M+H]<sup>+</sup>.

11-*epi*-**S9b**: yield: quant., 0.1 mmol; [α]<sub>D</sub><sup>25</sup> = -12.6 (c 0.9, MeOH); **<sup>1</sup>H-NMR** (400 MHz, Me<sub>2</sub>CO d<sub>6</sub>, Me<sub>2</sub>CO = 2.05 ppm) δ 7.80 (s, 1H, H-15), 7.49 (d, *J* = 7.8 Hz, 1H, H-5), 7.37 (d, *J* = 8.8 Hz, 2H, PMB), 7.19 (d, *J* = 7.8 Hz, 1H, H-6), 6.88 (d, *J* = 8.8 Hz, 2H, PMB), 6.59 (dd, *J* = 15.5, 0.8 Hz, 1H, H-13), 6.40 (ddd, *J* = 15.5, 7.2, 0.5 Hz, 1H, H-12), 5.67 (dq, *J* = 7.2, 0.8 Hz, 1H, H-11), 4.68 (ddd, *J* = 9.2, 4.5, 3.0 Hz, 1H, H-9), 4.57-4.53 (m, 1H, H-18), 4.51 (d, *J* = 11.0 Hz, 1H, PMB), 4.39 (d, *J* = 11.0 Hz, 1H, PMB), 3.78 (s, 3H, PMB), 3.34 (ddd, *J* = 8.2, 5.2, 4.0 Hz, 1H, H-20), 3.12 (dd, *J* = 16.1, 3.0 Hz, 1H, H-17), 3.04 (dd, *J* = 16.1, 10.1 Hz, 1H, H-17'), 2.87 (dd, *J* = 15.0, 3.0 Hz, 1H, H-8), 2.73 (dd, *J* = 15.0, 9.2 Hz, 1H, H-8'), 2.58 (dd, *J* = 13.3, 5.9 Hz, 1H, H-24), 2.33 (dd, *J* = 13.3, 8.7 Hz, 1H, H-24'), 2.32-2.27 (m, 1H, H-10), 2.29 (s, 3H, Ac), 2.10 (ddd, *J* = 13.9, 7.2, 4.5 Hz, 1H, H-10'), 2.06 (s, 3H, Ac), 1.98 (ddd, *J* = 6.6, 4.0, 1.9 Hz, 1H, H-19), 1.82 (pdddd, *J* = 14.6, 7.3, 7.3, 4.3 Hz, 1H, H-21), 1.69-1.59 (m, 1H, H-25), 1.50 (pdddd, *J* = 14.6, 7.3, 7.3, 5.2 Hz, 1H, H-21'), 1.41-1.32 (m, 1H, H-26), 1.26-1.14 (m, 1H, H-26'), 0.93 (d, *J* = 6.6 Hz, 3H, H-23), 0.91 (t, *J* = 7.3 Hz, 3H, H-22), 0.90 (t, *J* = 7.4 Hz, 3H, H-27), 0.83 (d, *J* = 6.7 Hz, 3H, H-28), 0.75 (s, 9H, TBS), -0.03 (s, 3H, TBS), -0.25 (s, 3H, TBS) ppm; **<sup>13</sup>C-NMR** (125 MHz, MeOH d<sub>4</sub>, MeOH d<sub>3</sub> = 49.0 ppm) δ 171.9 (2x q, Ac), 165.8 (2x q, C-1, C-3), 160.7 (2x q, C-16, PMB), 140.7 (q, C-14), 139.0 (q, C-7), 137.73 (t, C-12), 137.7 (2x t, C-5, C-15), 132.1 (2x t, PMB), 130.8 (1x q, 1x s, PMB, C-4), 129.1 (t, C-15), 126.1 (q, C-2), 123.0 (2x t, C-6, C-13), 114.7 (2x t, PMB), 81.6 (t, C-20), 77.1 (t, C-18), 72.6 (t, C-9), 72.1 (t, C-11), 71.9 (s, PMB), 55.7 (p, PMB), 42.8 (t, C-19), 40.2 (s, C-10), 38.1 (s, C-24), 36.8 (t, C-25), 34.3 (s, C-8), 32.2 (s, C-17), 30.5 (s, C-26), 26.2 (3x p, TBS), 23.6 (s, C-21), 21.14 (p, Ac), 21.1 (p, Ac), 19.4 (t, C-28), 18.7 (q, TBS), 11.9 (p, C-27), 10.1 (p, C-22), 8.4 (p, C-23), -4.4 (p, TBS), -5.0 (p, TBS) ppm; **HRMS** (ESI): *m/z*: calculated for C<sub>46</sub>H<sub>66</sub>NO<sub>10</sub>Si: 820.4456 [M+H]<sup>+</sup>, found: 820.4437 [M+H]<sup>+</sup>.

### 3,11-Acetate-PMB protected noricumazole A **16a** and 11-*epi*-**16b**:

To a solution of protected noricumazole A **S9a** (14 mg, 17.3 μmol, 1.0 eq) in THF (7 mL) was added hydrofluoric acid in pyridine (70%, as HF 30%, 0.7 mL) via a syringe pump over 14 h at room temperature. The reaction was terminated by addition of sat. aq. NaHCO<sub>3</sub> solution and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was taken up in MeOH and H<sub>2</sub>O (1:1) and purified by RP-HPLC (MeOH:H<sub>2</sub>O, gradient elution). Compound **16a** (8 mg, 11.9 μmol, 69%, 89% b.r.s.m.) was obtained as a colorless oil. As a side product acetate-protected **17a** was obtained.

**16a**: [α]<sub>D</sub><sup>20</sup> = -27.1 (c 0.8, MeOH); **<sup>1</sup>H-NMR** (500 MHz, MeOH d<sub>4</sub>, MeOH d<sub>3</sub> = 3.31 ppm) δ 7.78 (s, 1H, H-15), 7.49 (d, *J* = 7.9 Hz, 1H, H-5), 7.28 (d, *J* = 8.9 Hz, 2H, PMB), 7.19 (d, *J* = 7.9 Hz, 1H, H-6), 6.86 (d, *J* = 8.9 Hz, 2H, PMB), 6.54 (dd, *J* = 15.6, 0.3 Hz, 1H, H-13), 6.33 (dd, *J* = 15.6, 6.7 Hz, 1H, H-12), 5.65 (dq, *J* = 6.7, 0.5 Hz, 1H, H-11), 4.64 (dddd, *J* = 10.4, 5.8,

5.8, 4.2 Hz, 1H, H-9), 4.43 (d,  $J = 11.3$  Hz, 1H, PMB), 4.40 (d,  $J = 11.3$  Hz, 1H, PMB), 4.17 (ddd,  $J = 9.4, 6.6, 3.2$  Hz, 1H, H-18), 3.77 (s, 3H, PMB), 3.49 (ddd,  $J = 7.2, 6.6, 3.6$  Hz, 1H, H-20), 3.05 (dd,  $J = 14.6, 4.2$  Hz, 1H, H-8), 3.01 (dd,  $J = 16.6, 10.4$  Hz, 1H, H-8'), 2.94 (dd,  $J = 15.2, 3.2$  Hz, 1H, H-17), 2.77 (dd,  $J = 15.2, 9.4$  Hz, 1H, H-17'), 2.59 (dd,  $J = 13.3, 6.1$  Hz, 1H, H-24), 2.38-2.31 (m, 1H, H-24'), 2.31 (s, 3H, Ac), 2.14 (dd,  $J = 6.7, 5.8$  Hz, 2H, H-10), 2.06 (s, 3H, Ac), 2.02 (sext,  $J = 6.6$  Hz, 1H, H-19), 1.70 (pdddd,  $J = 7.2, 7.2, 6.6, 3.6$  Hz, 1H, H-21), 1.64-1.58 (m, 1H, H-25), 1.47 (sext,  $J = 7.2$  Hz, 1H, H-21'), 1.41-1.30 (m, 1H, H-26), 1.30-1.17 (m, 1H, H-26'), 0.94 (t,  $J = 7.2$  Hz, 3H, H-27), 0.91 (t,  $J = 8.7$  Hz, 3H, H-22), 0.90 (d,  $J = 7.9$  Hz, 3H, H-23), 0.85 (d,  $J = 6.6$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.1 (2x q, Ac), 171.2 (q, C-1), 165.7 (q, C-16), 160.8 (q, PMB), 149.7 (q, C-3), 140.6 (q, C-7), 139.0 (q, C-14), 137.8 (t, C-15), 137.7 (t, C-5), 135.5 (q, C-4), 132.1 (q, PMB), 130.8 (2x t, PMB), 129.8 (t, C-12), 126.1 (t, C-6), 122.0 (t, C-13), 118.6 (q, C-2), 114.7 (2x t, PMB), 82.1 (t, C-20), 76.3 (t, C-9), 72.0 (s, PMB), 71.7 (t, C-11), 71.6 (t, C-18), 55.7 (p, PMB), 42.1 (t, C-19), 40.5 (s, C-10), 38.1 (s, C-24), 36.9 (t, C-25), 34.3 (s, C-8), 33.8 (s, C-17), 30.5 (s, C-26), 23.1 (s, C-21), 21.1 (p, Ac), 21.0 (p, Ac), 19.4 (t, C-28), 11.9 (p, C-27), 10.8 (p, C-23), 9.6 (p, C-22) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{40}\text{H}_{52}\text{NO}_{10}$ : 706.3591  $[\text{M}+\text{H}]^+$ , found: 706.3591  $[\text{M}+\text{H}]^+$ .

**11-*epi*-16b**: yield: 61%, 16.7  $\mu\text{mol}$ ;  $[\alpha]_{\text{D}}^{25} = -12.6$  ( $c$  0.9, MeOH);  $^1\text{H-NMR}$  (500 MHz, MeOH  $d_4$ , MeOH  $d_3 = 3.31$  ppm)  $\delta$  7.79 (s, 1H, H-15), 7.48 (d,  $J = 7.8$  Hz, 1H, H-5), 7.27 (d,  $J = 8.7$  Hz, 2H, PMB), 7.19 (d,  $J = 7.8$  Hz, 1H, H-6), 6.85 (d,  $J = 8.7$  Hz, 2H, PMB), 6.56 (d,  $J = 15.7$  Hz, 1H, H-13), 6.32 (dd,  $J = 15.7, 7.2$  Hz, 1H, H-12), 5.66 (ddd,  $J = 7.2, 7.0, 6.7$  Hz, 1H, H-11), 4.57 (ddd,  $J = 14.9, 8.1, 3.9$  Hz, 1H, H-9), 4.42 (d,  $J = 11.0$  Hz, 1H, PMB), 4.39 (d,  $J = 11.0$  Hz, 1H, PMB), 4.15 (ddd,  $J = 9.5, 6.6, 3.2$  Hz, 1H, H-18), 3.76 (s, 3H, PMB), 3.48 (ddd,  $J = 6.6, 6.1, 3.4$  Hz, 1H, H-20), 3.08 (dd,  $J = 16.1, 3.9$  Hz, 1H, H-8), 3.00 (dd,  $J = 16.1, 8.1$  Hz, 1H, H-8'), 2.92 (dd,  $J = 15.1, 3.2$  Hz, 1H, H-17), 2.76 (dd,  $J = 15.1, 9.5$  Hz, 1H, H-17'), 2.58 (dd,  $J = 13.4, 6.4$  Hz, 1H, H-24), 2.37-2.30 (m, 1H, H-24'), 2.31 (s, 3H, Ac), 2.28 (ddd,  $J = 14.3, 8.1, 6.7$  Hz, 1H, H-10), 2.07 (s, 3H, Ac), 2.02 (ddd,  $J = 14.3, 7.0, 3.9$  Hz, 1H, H-10'), 2.01 (sext,  $J = 6.6$  Hz, 1H, H-19), 1.68 (pdddd,  $J = 14.0, 7.5, 7.5, 3.4$  Hz, 1H, H-21), 1.61 (oct,  $J = 6.4$  Hz, 1H, H-25), 1.45 (sext,  $J = 7.3$  Hz, 1H, H-26), 1.36 (pddd,  $J = 14.0, 7.5, 6.1$  Hz, 1H, H-21'), 1.24-1.14 (m, 1H, H-26'), 0.93 (t,  $J = 7.3$  Hz, 3H, H-27), 0.91 (t,  $J = 7.5$  Hz, 3H, H-22), 0.90 (d,  $J = 6.6$  Hz, 3H, H-23), 0.84 (d,  $J = 6.4$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.0 (2x q, Ac), 171.1 (q, C-1), 165.7 (q, C-16), 160.8 (q, PMB), 150.0 (q, C-3), 140.1 (q, C-14), 138.9 (t, C-15), 137.9 (t, C-15), 137.8 (q, C-7), 136.0 (q, C-4), 132.0 (q, PMB), 130.8 (2x t, PMB), 129.2 (t, C-12), 126.1 (t, C-6), 122.8 (t, C-13), 118.4 (q, C-2), 114.6 (2x t, PMB), 82.0 (t, C-20), 77.2 (t, C-9), 72.5 (t, C-11), 71.9 (s, PMB), 71.5 (t, C-18), 55.6 (p, PMB), 42.1 (t, C-19), 40.2 (s, C-10), 38.1 (s, C-24), 36.9 (t, C-25), 34.2 (s, C-8), 33.7 (s, C-17), 30.5 (s, C-26), 23.1 (s, C-21), 21.14 (p, Ac), 21.1 (p, Ac), 19.4 (t, C-28), 11.9 (p, C-27), 10.7 (p, C-22), 9.6 (p, C-23) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{40}\text{H}_{52}\text{NO}_{10}$ : 706.3591  $[\text{M}+\text{H}]^+$ , found: 706.3591  $[\text{M}+\text{H}]^+$ .

### 3,11-Diacetyl protected noricumazole A 17a and 11-*epi*-17b:

**17a**: yield: 6%, 1.0  $\mu\text{mol}$ ;  $[\alpha]_{\text{D}}^{24} = -12.5$  ( $c$  0.9, MeOH);  $^1\text{H-NMR}$  (500 MHz, MeOH  $d_4$ , MeOH  $d_3 = 3.31$  ppm)  $\delta$  7.79 (s, 1H, H-15), 7.49 (d,  $J = 7.8$  Hz, 1H, H-5), 7.21 (d,  $J = 7.8$  Hz, 1H, H-6), 6.54 (dd,  $J = 15.8, 0.6$  Hz, 1H, H-13), 6.32 (dd,  $J = 15.8, 6.5$  Hz, 1H, H-12), 5.65 (q,  $J = 6.5$  Hz, 1H, H-11), 4.69-4.63 (m, 1H, H-9), 4.18 (ddd,  $J = 9.5, 6.7, 3.3$  Hz, 1H, H-18), 3.54 (ddd,  $J = 9.0, 6.7, 2.6$  Hz, 1H, H-20), 3.09-3.05 (m, 1H, H-8), 3.00 (dd,  $J = 16.4, 3.9$  Hz, 1H, H-8'), 3.00 (dd,  $J = 15.1, 3.3$  Hz, 1H, H-17), 2.81 (dd,  $J = 15.1, 9.5$  Hz, 1H, H-17'), 2.59 (dd,  $J = 13.4, 6.1$  Hz, 1H, H-24), 2.41-2.32 (m, 1H, H-24'), 2.32 (s, 3H, Ac), 2.15 (pt,  $J = 6.5$  Hz, 2H, H-10), 2.07 (s, 3H, Ac), 1.77 (sext,  $J = 6.7$  Hz, 1H, H-19), 1.69-1.58 (m, 2H, H-21, H-25), 1.45-1.33 (m, 2H, H-21', H-26), 1.25-1.17 (sext,  $J = 7.2$  Hz, 1H, H-26'), 0.98 (t,  $J = 7.4$  Hz, 3H, H-27), 0.92 (t,  $J = 7.5$  Hz, 3H, H-22), 0.91 (d,  $J = 7.0$  Hz, 3H, H-23), 0.85 (d,  $J = 6.6$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.1 (2x q, Ac), 171.2 (q, C-1), 165.9 (q, C-16), 149.6 (q, C-3), 140.7 (q, C-7), 138.9 (t, C-5), 137.8 (t, C-15), 130.7 (q, C-14), 129.8 (t, C-12), 126.1 (t, C-6), 122.0 (t, C-13), 118.5 (q, C-4), 114.8 (q, C-2), 76.3 (t, C-9), 75.4 (t, C-20), 72.3 (t, C-18), 71.6 (t, C-11), 45.6 (t, C-19), 40.5 (s, C-10), 38.1 (s, C-24), 36.9 (t, C-25), 34.3 (s, C-8), 33.7 (s, C-17), 30.5 (s, C-26), 27.2 (s, C-21), 21.1 (p, Ac), 21.0 (p, Ac), 19.4 (t, C-28), 11.9 (p, C-23), 11.3 (p, C-22), 10.4 (p, C-27) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{32}\text{H}_{44}\text{NO}_9$ : 586.3016  $[\text{M}+\text{H}]^+$ , found: 586.3002  $[\text{M}+\text{H}]^+$ .

**11-*epi*-17b**: yield: 13%, 3.6  $\mu\text{mol}$ ;  $[\alpha]_{\text{D}}^{25} = -12.6$  ( $c$  0.9, MeOH);  $^1\text{H-NMR}$  (500 MHz, MeOH  $d_4$ , MeOH  $d_3 = 3.31$  ppm)  $\delta$  7.78 (s, 1H, H-15), 7.49 (d,  $J = 7.8$  Hz, 1H, H-5), 7.19 (d,  $J = 7.8$  Hz, 1H, H-6), 6.55 (dd,  $J = 15.6, 0.2$  Hz, 1H, H-13), 6.31 (dd,  $J = 15.6, 7.1$  Hz, 1H, H-12), 5.66 (ddd,  $J = 7.1, 6.9, 6.9$  Hz, 1H, H-11), 4.58 (ddd,  $J = 7.1, 6.9, 6.9$  Hz, 1H, H-9), 4.17 (dddd,  $J = 10.5, 8.1, 3.9, 3.6$  Hz, 1H, H-18), 3.53 (ddd,  $J = 8.9, 6.6, 2.7$  Hz, 1H, H-20), 3.06 (dd,  $J = 16.0, 3.6$  Hz, 1H, H-8), 3.04 (dd,  $J = 16.0, 3.9$  Hz, 1H, H-8'), 3.00 (dd,  $J = 15.0, 3.2$  Hz, 1H, H-17), 2.80 (dd,  $J = 15.0, 9.6$  Hz, 1H, H-17'), 2.58 (dd,  $J = 13.4, 6.1$  Hz, 1H, H-24), 2.34-2.31 (m, 1H, H-24'), 2.31 (s, 3H, Ac), 2.28 (ddd,  $J = 14.4, 8.1, 6.9$  Hz, 1H, H-10), 2.11-2.06 (m, 1H, H-10'), 2.08 (s, 3H, Ac), 1.76 (sext,  $J = 6.6$  Hz, 1H, H-19), 1.67-1.57 (m, 2H, H-21, H-25), 1.43-1.33 (m, 2H, H-21', H-26), 1.27-1.15 (m, 1H, H-26'), 0.97 (t,  $J = 7.4$  Hz, 3H, H-27), 0.91 (t,  $J = 7.5$  Hz, 3H, H-22), 0.89 (d,  $J = 6.6$  Hz, 3H, H-23), 0.84 (d,  $J = 6.6$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.0 (2x q, Ac), 171.1 (q, C-1), 165.9 (q, C-16), 151.9 (q, C-3), 138.8 (t, C-15), 137.9 (t, C-5), 137.8 (q, C-7), 130.7 (q, C-14), 129.2 (2x t, C-6, C-12), 126.1 (t, C-4), 122.7 (t, C-13), 114.8 (q, C-2), 77.2 (t, C-9), 75.4 (t, C-20), 72.5 (t, C-11), 72.3 (t, C-18), 45.6 (t, C-19), 40.2 (s, C-10), 38.1 (s, C-24), 36.9 (t, C-25), 34.7 (t, C-25), 34.2 (s, C-8), 33.7 (s, C-17), 30.5 (s, C-26), 27.2 (s, C-21), 21.1 (p, Ac), 21.08 (p, Ac), 19.4 (t, C-28), 11.9 (p, C-23), 11.3 (p, C-22), 10.4 (p, C-27) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{32}\text{H}_{44}\text{NO}_9$ : 586.3016  $[\text{M}+\text{H}]^+$ , found: 586.3002  $[\text{M}+\text{H}]^+$ .

### Aglycon **S10**:

A solution of acceptor **16a** (8 mg, 11.9  $\mu\text{mol}$ , 1.0 eq) in  $\text{CH}_2\text{Cl}_2$  (2.3 mL) was added to activated molecular sieves (powder, 4 $\text{\AA}$ ) under an atmosphere of argon.  $\text{Hg}(\text{CN})_2$  (7 mg, 26.1  $\mu\text{mol}$ , 2.2 eq) was added to the suspension at room temperature. After stirring for 45 min glycosyl donor **18** (45 mg, 85.6  $\mu\text{mol}$ , 7.2 eq) in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) which was codistilled before with benzene was added. After 2.25 h the reaction was quenched by addition of MeOH. The reaction mixture was filtered over Celite<sup>®</sup> and the organic layer washed with a sat. aq. KBr solution and water. The organic extract was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was taken up in MeOH and  $\text{H}_2\text{O}$  (1:1) and purified by RP-HPLC (MeOH: $\text{H}_2\text{O}$ , gradient elution). Aglycon **S10** (6 mg, 5.2  $\mu\text{mol}$ , 47%) was obtained as a colorless oil.

$[\alpha]_{\text{D}}^{22} = -10.3$  (c 0.5, MeOH);  $^1\text{H-NMR}$  (500 MHz, MeOH  $d_4$ , MeOH  $d_3 = 3.31$  ppm)  $\delta$  8.08-8.02 (m, 2 H, Bz), 7.98-7.91 (m, 4 H, Bz), 7.69 (s, 1H, H-15), 7.67-7.59 (m, 2H, Bz), 7.46-7.45 (m, 5H, Bz), 7.44 (d,  $J = 7.8$  Hz, 1H, H-5), 7.28-7.20 (m, 2H, Bz), 7.19 (d,  $J = 8.7$  Hz, 2H, PMB), 7.15 (d,  $J = 7.8$  Hz, 1H, H-6), 6.78 (d,  $J = 8.7$  Hz, 2H, PMB), 6.32 (d,  $J = 15.8$  Hz, 1H, H-13), 6.26 (dd,  $J = 15.8, 6.4$  Hz, 1H, H-12), 5.60-5.50 (m, 1H, H-11), 5.41 (pd,  $J = 4.7$  Hz, 1H, H-4'), 5.39 (ps, 1H, H-2'), 5.17 (ps, 1H, H-1'), 4.69 (dd,  $J = 11.9, 3.4$  Hz, 1H, H-5'), 4.61 (d,  $J = 11.1$  Hz, 1H, PMB), 4.59 (dd,  $J = 11.9, 5.1$  Hz, 1H, H-5''), 4.58-4.56 (m, 1H, H-9), 4.47 (d,  $J = 11.1$  Hz, 1H, PMB), 4.48 (dd,  $J = 8.3, 4.7$  Hz, 1H, H-3'), 4.41-4.36 (m, 1H, H-18), 3.71 (s, 3H, PMB), 3.47-3.42 (m, 1H, H-20), 3.00 (dd,  $J = 15.8, 4.0$  Hz, 1H, H-17), 2.98-2.93 (m, 2H, H-8), 2.89 (dd,  $J = 15.8, 10.8$  Hz, 1H, H-17'), 2.56 (dd,  $J = 13.5, 6.1$  Hz, 1H, H-24), 2.29 (dd,  $J = 13.5, 8.4$  Hz, 1H, H-24'), 2.28-2.24 (m, 1H, H-19), 2.03 (ddd,  $J = 14.7, 9.0, 4.1$  Hz, 1H, H-10), 1.91 (ddd,  $J = 14.7, 6.8, 3.5$  Hz, 1H, H-10'), 1.73 (ddd,  $J = 14.5, 7.1, 3.7$  Hz, 1H, H-21), 1.63-1.55 (m, 1H, H-25), 1.46-1.37 (m, 1H, H-21'), 1.45 (sext,  $J = 7.0$  Hz, 1H, H-26), 1.18 (sext,  $J = 7.0$  Hz, 1H, H-26'), 0.98 (t,  $J = 7.0$  Hz, 3H, H-22), 0.91 (t,  $J = 7.1$  Hz, 3H, H-27), 0.90 (d,  $J = 7.0$  Hz, 3H, H-23), 0.82 (d,  $J = 6.6$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.0 (2x q, Ac), 171.2 (q, C-1), 167.6 (q, Bz), 167.1 (q, Bz), 166.5 (q, Bz), 164.7 (q, C-16), 160.7 (q, PMB), 149.0 (q, C-3), 140.6 (t, C-7), 139.1 (t, C-15), 137.8 (q, C-5), 134.9 (q, C-14), 130.91 (q, PMB), 130.9 (3x t, Bz), 130.89 (2x t, PMB), 130.8 (2x t, Bz), 129.9 (2x t, Bz), 129.86 (t, C-12), 129.8 (q, C-4), 129.77 (3x t, Bz), 128.9 (t, C-5), 127.0 (t, C-6), 121.8 (t, C-13), 118.5 (q, C-2), 114.7 (2x t, PMB), 107.4 (t, C-1'), 83.3 (t, C-4'), 83.1 (t, C-2'), 81.2 (t, C-20), 79.2 (t, C-3'), 79.1 (t, C-18), 76.1 (t, C-9), 71.6 (s, PMB), 71.4 (t, C-11), 65.0 (s, C-5'), 55.6 (p, PMB), 40.5 (t, C-19), 40.2 (s, C-10), 38.1 (s, C-24), 36.8 (t, C-25), 34.3 (s, C-8), 31.1 (s, C-17), 30.5 (s, C-26), 23.2 (s, C-21), 21.1 (p, Ac), 21.0 (p, Ac), 19.4 (t, C-28), 11.9 (p, C-22), 10.9 (p, C-23), 19.7 (p, C-27) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{66}\text{H}_{72}\text{NO}_{17}$ : 1150.4800  $[\text{M}+\text{H}]^+$ , found: 1150.4789  $[\text{M}+\text{H}]^+$ .

### Aglycon (-PMB) **S11**:

To a solution of aglycon **S10** (3 mg, 2.9  $\mu\text{mol}$ , 1.0 eq) in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) were added phosphate buffer (0.3 mL) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1 mg, 5.7  $\mu\text{mol}$ , 2.0 eq) in  $\text{CH}_2\text{Cl}_2$  (0.7 mL) at room temperature. After stirring for 1.5 h the reaction was quenched by addition of a sat. aq.  $\text{NaHCO}_3$  solution and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic extracts were dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was taken up in MeOH and  $\text{H}_2\text{O}$  (1:1) and purified by RP-HPLC (MeOH: $\text{H}_2\text{O}$ , gradient elution). Compound **S11** (3 mg, 2.8  $\mu\text{mol}$ , 98%) was obtained as a colorless oil.

$[\alpha]_{\text{D}}^{22} = -21.8$  (c 0.3, MeOH);  $^1\text{H-NMR}$  (500 MHz, MeOH  $d_4$ , MeOH  $d_3 = 3.31$  ppm)  $\delta$  8.08-8.03 (m, 2H, Bz), 7.98-7.92 (m, 4H, Bz), 7.70 (s, 1H, H-15), 7.68-7.63 (m, 2H, Bz), 7.54-7.49 (m, 2H, Bz), 7.98-7.95 (m, 1H, Bz), 7.44 (d,  $J = 7.9$  Hz, 1H, H-5), 7.30-7.25 (m, 2H, Bz), 7.16 (d,  $J = 7.9$  Hz, 1H, H-6), 6.33 (d,  $J = 15.6$  Hz, 1H, H-13), 6.24 (dd,  $J = 15.6, 6.3$  Hz, 1H, H-12), 5.55-5.48 (m, 1H, H-11), 5.45 (pdd,  $J = 4.6, 1.2$  Hz, 1H, H-4'), 5.35 (ps, 1H, H-2'), 5.15 (ps, 1H, H-1'), 4.74 (dd,  $J = 11.7, 4.6$  Hz, 1H, H-5'), 4.63 (dd,  $J = 11.7, 4.6$  Hz, 1H, H-5''), 4.57 (dd,  $J = 9.2, 4.6$  Hz, 1H, H-3'), 4.55-4.59 (m, 2H, H-9, H-18), 3.50-3.47 (m, 1H, H-20), 3.09-2.99 (m, 2H, H-8), 2.97 (dd,  $J = 16.6, 3.9$  Hz, 1H, H-17), 2.92 (dd,  $J = 16.6, 10.6$  Hz, 1H, H-17'), 2.57 (dd,  $J = 13.5, 6.3$  Hz, 1H, H-24), 2.36-2.31 (m, 1H, H-24'), 2.31 (s, 3H, Ac), 2.14-2.09 (m, 1H, H-19), 2.03-1.94 (m, 2H, H-10), 2.00 (s, 3H, Ac), 1.69-1.63 (m, 1H, H-21), 1.62-1.54 (m, 1H, H-25), 1.46-1.39 (m, 1H, H-21'), 1.31-1.25 (m, 1H, H-26), 1.19-1.13 (m, 1H, H-26'), 1.03 (d,  $J = 6.8$  Hz, 3H, H-23), 1.00 (t,  $J = 7.3$  Hz, 3H, H-22), 0.92 (t,  $J = 7.3$  Hz, 3H, H-27), 0.83 (d,  $J = 6.5$  Hz, 3H, H-28) ppm;  $^{13}\text{C-NMR}$  (125 MHz, MeOH  $d_4$ , MeOH  $d_3 = 49.0$  ppm)  $\delta$  172.0 (2x q, Ac), 171.2 (q, C-1), 167.6 (q, Bz), 167.1 (q, Bz), 166.5 (q, Bz), 165.1 (q, C-16), 150.0 (q, C-3), 140.6 (q, C-14), 139.0 (q, C-7), 137.8 (t, C-5), 134.8 (t, C-12), 134.4 (t, C-15), 130.9 (6x t, Bz), 130.6 (4x t, Bz), 129.9 (2x t, Bz), 129.8 (2x t, Bz), 129.6 (4x t, Bz), 127.1 (q, C-2), 126.1 (t, C-6), 121.8 (t, C-13), 118.6 (q, C-4), 107.7 (t, C-1'), 83.4 (t, C-2'), 82.9 (t, C-3'), 79.2 (t, C-4'), 79.1 (t, C-18), 76.2 (t, C-9), 74.9 (t, C-20), 71.4 (t, C-11), 64.9 (s, C-5'), 44.4 (t, C-19), 40.2 (s, C-10), 38.1 (s, C-24), 36.8 (t, C-25), 34.2 (s, C-17), 30.5 (s, C-26), 30.4 (s, C-8), 27.8 (s, C-21), 21.0 (2x p, Ac), 19.4 (t, C-28), 11.9 (p, C-23), 11.0 (p, C-22), 10.5 (p, C-27) ppm; HRMS (ESI):  $m/z$ : calculated for  $\text{C}_{58}\text{H}_{64}\text{NO}_{16}$ : 1030.4225  $[\text{M}+\text{H}]^+$ , found: 1030.4240  $[\text{M}+\text{H}]^+$ .

### Noricumazole **B (1b)**:

A solution of aglycon **S11** (2 mg, 1.5  $\mu\text{mol}$ , 1.0 eq) in MeOH/THF/ $\text{H}_2\text{O}$ / $\text{Et}_3\text{N}$  (1.4 mL, 6:5:1:2) was stirred at 55  $^\circ\text{C}$ . After stirring for 2 d the solvent of the reaction mixture was removed and the residue directly taken up in MeOH and  $\text{H}_2\text{O}$  (1:1) and purified by RP-HPLC (MeOH: $\text{H}_2\text{O}$ , gradient elution). Noricumazole **B (1b)** (1 mg, 1.4  $\mu\text{mol}$ , 98%) was obtained as a colorless oil.



Synthetic noricumazole B:  $[\alpha]_{D=20}^{22} = +14.8$  (c 0.1, MeOH); authentic noricumazole B<sup>1</sup>:  $[\alpha]_{D=20}^{20} = +13.3$  (c 0.86 in MeOH);  
HRMS (ESI): *m/z*: calculated for C<sub>33</sub>H<sub>48</sub>NO<sub>11</sub>: 634.3227 [M+H]<sup>+</sup>, found: 634.3228 [M+H]<sup>+</sup>. For NMR-spectra and data see figure 2 and refer to ref. 1.