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Semisynthetic routes to PF1022H—A precursor for new derivatives of the anthelmintic cyclooctadepsipeptide PF1022A

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ABSTRACT

The cyclooctadepsipeptide PF1022A and its semisynthetic, commercial analogue emodepside show excellent anthelmintic properties. Bis-hydroxy PF1022 (PF1022H), a minor fermentative side-product represents an interesting precursor for new PF1022 related anthelmintics. We report herein two complementary routes which allow a highly efficient conversion of PF1022A to a regioisomeric mixture consisting mainly of the bis-*para* isomer PF1022H and the *meta*–*para* analogue.

1. Introduction

According to the World Health Organization (WHO) parasitic worm infections constitute the most important class of neglected tropical diseases.[1] Those worm infections are a major cause of morbidity and loss of disability-adjusted life years in several underdeveloped African and Asian countries.[2,3] In addition, worm infections cause tremendous health problems and economic losses in livestock and domestic animals. In particular, in the livestock industry, treatment with standard anthelmintics such as the macrolides avermectin and milbemycin or derivatives of these natural products has become problematic due to rapidly developing resistances.[4–6]

The 24-membered cyclooctadepsipeptide PF1022A (**1**, Fig. 1), a metabolite of *Mycelia sterilia* (*Rosselinia* sp.) has been established as the only novel, resistance-breaking anthelmintic during the past two decades. A semi-synthetic analogue of PF1022A, emodepside (**3**), has been introduced recently into the market for the treatment of parasitic helminth infections in companion animals.[4,7]

Structure–activity studies have demonstrated that the two phenyllactic acids are the positions of choice for modifications of PF1022A (**1**).[4,8–13] However, the introduction of functionality into the phenyl rings is far from being trivial. The drastic reaction conditions required to introduce for instance nitro- or sulfonic acid-groups, cause side-reactions and partial decomposition of the macrocycle. Bromine or iodine substituents can be introduced under milder conditions but subsequent Pd-catalyzed cross-coupling reactions to obtain aryl or aryl-substituted derivatives fail completely. The additional synthetic steps needed for the preparation of advanced PF1022A analogs turn out cumbersome and costly.

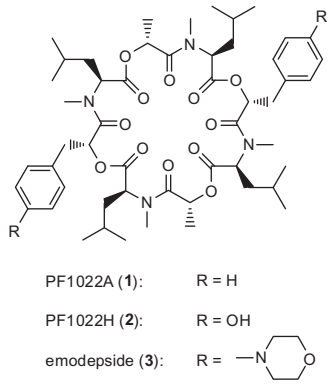

Figure 1. Structures of cyclooctadepsipeptides PF1022A, PF1022H and emodepside.

The bis-hydroxy derivative PF1022H (**2**), a minor side-product in the fermentation process of PF1022A (**1**), might be an interesting alternative. Some lipophilic derivatives of PF1022H (**2**), accessible in only one step, show excellent anthelmintic activities.[8] Unfortunately, PF1022H (**2**) is currently available only in limited amounts from the fermentation broth. Thus, an efficient access to PF1022H (**2**) appears mandatory for the preparation of a larger number of

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screening-compounds needed for the identification of a 'second-generation' PF1022 derived anthelmintic with improved spectrum of activity, drug metabolism and pharmacokinetics.

The most straightforward route to PF1022H (**2**) would be of course a direct hydroxylation of PF1022A (**1**). Unfortunately, standard procedures for the direct hydroxylation of benzene rings such as the $Cu(NO_3)_2$ catalyzed oxidation with H_2O_2 failed completely in our hands.[14] Instead of a one-step hydroxylation of PF1022A (**1**), we established two short sequences which provide PF1022H (**2**) in good to excellent yields.

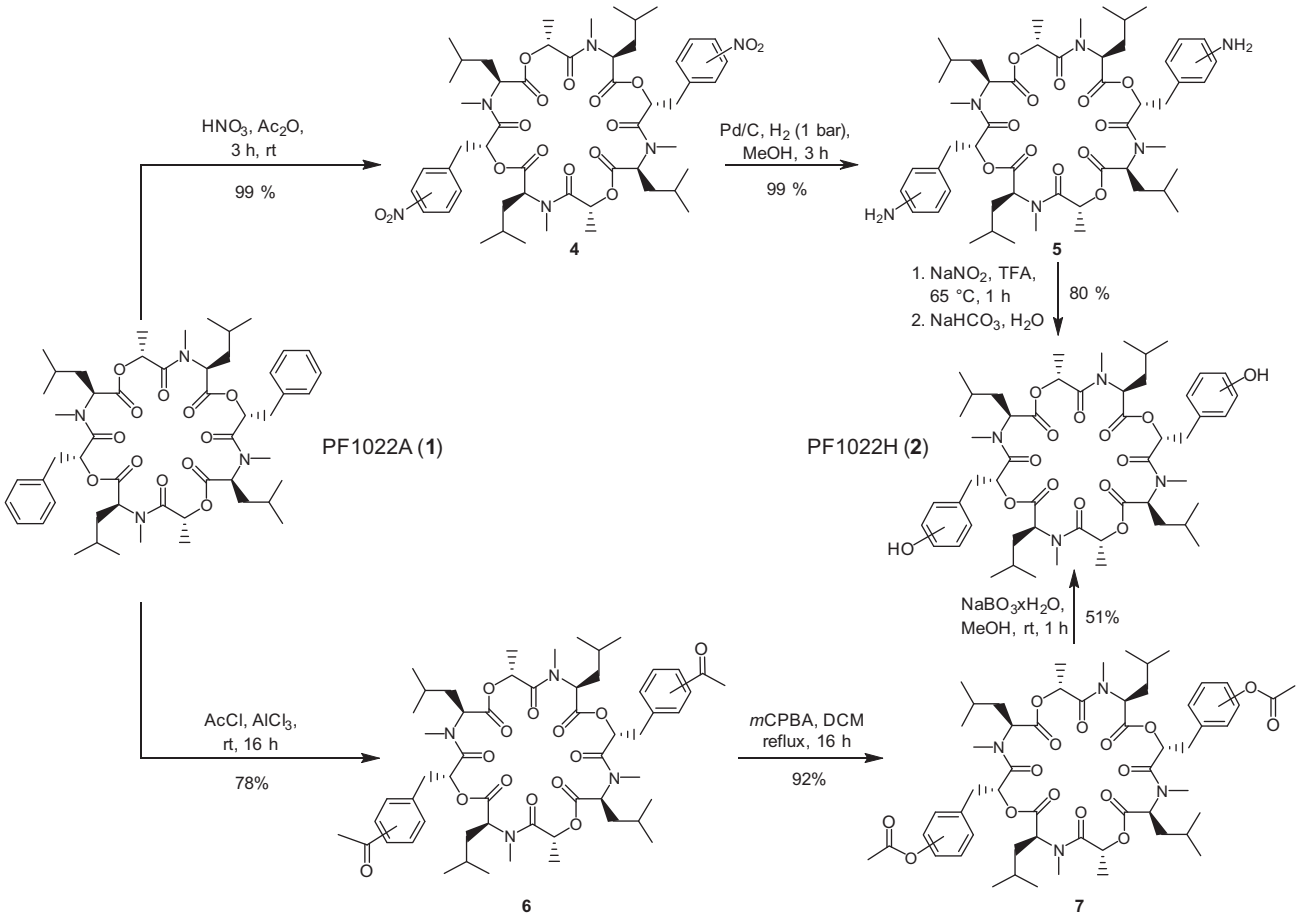
2. Results and discussion

2.1. Route 1: PF1022H by diazotization of bis-amino PF1022 and subsequent hydrolysis

The basic route to bis-amino PF1022 (**5**) and subsequent diazotation has already been described in a previous patent by Nishiyama et al., albeit with remarkably low yields in each step.[15] Based on this basic procedure we developed a process which allows the preparation of PF1022H (**2**) in an excellent yield and gram-amounts. First, PF1022A was nitrated in almost quantitative yield with fumic nitric acid in acetic anhydride (Scheme 1). The regioisomers formed, correspond to bis-*para* nitro-PF1022 (**4**) (45%), followed by the *para–meta* (42%) and *meta–meta* (13%) isomers. Those were not separated since it is known, that the anthelmintic activities of the different regioisomers are similar. The remarkable stability of PF1022A (**1**) against concentrated nitric and also sulfuric acid can be attributed to the *N*-methyl groups which hamper both, oxidation and hydrolysis reactions of the amide functions. Subsequent hydrogenation under standard conditions afforded the bis-amino PF1022 (**5**) again in almost quantitative yield (Scheme 1). Diazotization with $NaNO_2$ in TFA (1 h, 65 °C) followed by a weakly basic hydrolysis with an aqueous $NaHCO_3$ solution afforded in a one-pot reaction the bis-hydroxy PF1022 isomers in 80% yield after chromatographic purification (Scheme 1).

2.2. Route 2: PF1022H by Baeyer–Villiger oxidation of PF1022A and subsequent ester cleavage

One of the few methods which allow the direct introduction of a hydroxy-group in a phenyl-ring under mild conditions is the Baeyer–Villiger oxidation of the corresponding acetophenone which can be obtained easily by a Friedel–Crafts acylation. However, for PF1022A (**1**), the acylation turned out to be troublesome. With the standard Lewis acid $AlCl_3$ and a mixture of acetic anhydride and acetyl chloride in nitromethane or dichloromethane no reaction was observed even with an excess (2–5 equiv) of $AlCl_3$. Other Lewis acids employed for Friedel–Crafts acylations such as $Sc(OTf)_3$,[16] $Bi(OTf)_3$,[17] $Ga(OTf)_3$,[18] $Hf(OTf)_4$,[19] $TiCl_4$, ZnO,[20] $BF_3 \times OEt_2$ or $AlBr_3$ in nitromethane resulted in either no reaction or decomposition of PF1022A (**1**). Even the addition of $LiClO_4$ which is a known Lewis acid activator did not improve the acetylation reaction at all.[19] Remarkably, the 1-methyl-3-ethylimidazolium chloride–aluminum(III) chloride ([EMIM]–$AlCl_3$) ionic liquid which has been described as an exceptionally mild and selective acylation system caused a complete decomposition of the cyclodepsipeptide.[21] As an alternative to the direct acetylation



Scheme 1. Semisynthetis routes to PF1022H.

Table 1
Conditions tested for the selective ester cleavage of PF1022 bis-acetate X

Entry	Reagent	Reaction condition	Result
1	K_2CO_3	THF/H_2O, 0 °C	Decomposition
2	K_2CO_3	MeOH, 0 °C	Decomposition
3	K_2CO_3	EtOH, 0 °C	Decomposition
4	K_2CO_3	*i*PrOH, 0 °C	Decomposition
5	LiOH	THF/H_2O, 0 °C	Decomposition
6	LiOH	MeOH, 0 °C	Decomposition
7	$NaHCO_3$	THF/H_2O, rt	No conversion
8	*p*-TsOH on silica gel	H_2O/toluene, 80 °C	Decomposition
9	CH_3COONH_4	MeOH/H_2O, rt	Traces PF1022H (**2**)
10	$Yb(TOf)_3$	*i*PrOH, reflux	Decomposition
11	Esterase	pH ~8, H_2O/Et_2O, rt	No conversion
12	**$NaBO_3{}^*H_2O$**	**MeOH, rt**	**51 % PF1022H (2)**

a Ni-catalyzed Negishi coupling of bis-bromo PF1022, prepared according to a literature procedure and acetyl chloride, was tested unsuccessfully, too.[22] No turn-over could be observed using the reaction conditions described.

With those disappointing results in our hands we drew back our attention to the standard Lewis acid $AlCl_3$. In fact, we were able to obtain a low yield of the monoacetylation product when we used the acetylation reagent AcCl as solvent together with an excess of 10 equiv of $AlCl_3$. Increasing the excess to 500 equiv of freshly sublimated $AlCl_3$ finally afforded a 78% yield of the bis-acetylation product **6**, obtained as 10:5:1 mixture of the *bis-para*, *meta–para* and *meta–meta* isomers. The subsequent Baeyer–Villiger oxidation with *m*CPBA gave regioselectively the phenol acetate **7** in an excellent yield of 92%. However, the selective ester hydrolysis of the acetates in the presence of the lactic and phenyllactic ester bonds, not completely unexpected, turned out difficult again. Several reaction conditions tested (Table 1) either led to decomposition of the depsipeptide ring or for very weak bases such as $NaHCO_3$ no reaction was observed. Though it was not a problem at all, to hydrolyze *p*-cresol acetate as a test substrate with pig-liver esterase, the same enzyme failed in the cleavage reaction of PF1022H acetate **7**, probably due to the steric hindrance of the large macrocycle. Finally, the reagent of choice proved to be $NaBO_3 \times H_2O$ which yielded 51% of PF1022H after a reaction time of 1 h.

3. Conclusions

To summarize, PF1022H (**2**) represents an important precursor for new, anthelmintically highly active PF1022 derivatives. Due to its limited availability as a minor side-product in the production process of PF1022A (**1**), we developed two complementary methods which allow the preparation of PF1022H (**2**) in gram-amounts from PF1022A (**1**) with good to excellent yields as a mixture of mainly the bis-*para* and the *meta–para* isomer.

4. Experimental

4.1. General chemical methods

PF1022A (**1**) was provided by Bayer Health Care. The reagents $AlCl_3$, $NaBO_3 \times H_2O$, *m*CPBA, HNO_3 (70%, aqueous solution), Pd/C and $NaNO_2$ were purchased. All reactions were performed in dried solvents. Methanol was refluxed over magnesium and distilled. Acetyl chloride and acetic anhydride were distilled. ^1H and ^{13}C NMR spectra were measured on a 400 or 600 MHz (101 or 151 MHz) NMR spectrometer. IR-spectra were recorded on a FT-IR instrument. Mass spectra were recorded using ESI and APCI ionization methods. For the preparative low pressure chromatography (LPLC) silica gel (60 μm) was used. TLC was performed on Silica gel 60 F_{254}.

4.2. Experimental procedures

4.2.1. Cyclo-[(L)-MeLeu-(D)-Lac-(L)-MeLeu-(D)-(NO_2)PhLac]$_2$ (4)

To a solution of PF1022A (**1**, 200.00 mg, 0.21 mmol) in acetic anhydride nitric acid (10 mL, 111.09 mmol, 70%) was added dropwise at 0 °C. After stirring for 3 h at room temperature ethyl acetate (40 mL) was added and the mixture was extracted with water (3 × 30 mL). The combined organic phases were dried over sodium sulfate. Concentration under reduced pressure and chromatographic purification (solvent: cyclohexane/ethyl acetate, 1:1) of the residue gave product **4** (229.00 mg, 0.22 mmol) as a yellow solid in quantitative yield. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.66–1.47 (m, 34H, CH_3-Leu, CH_3-Lac, $C_\gamma H$-Leu), 1.49–1.81 (m, 8H, $C_\beta H$-Leu), 2.62–3.04 (m, 12H, NCH_3), 3.05–3.41 (m, 4H, $C_\beta H$-Phe-Lac), 4.50 (m, 1H, $C_\alpha H$-Leu), 5.03–5.90 (m, 7H, $C_\alpha H$-Leu, $C_\alpha H$-Phe-Lac, $C_\alpha H$-Lac), 7.06–8.23 (m, 8H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 14.1, 15.8, 17.0, 20.6, 20.7, 20.9, 21.1, 21.4, 23.4, 23.5, 24.6, 24.7, 24.9, 25.0, 25.1, 29.3, 29.6, 30.1, 30.5, 30.6, 31.3, 36.8, 37.5, 53.9, 54.3, 57.1, 60.3, 66.9, 67.3, 68.5, 68.6, 69.8, 70.3, 123.5, 123.6, 123.7, 125.2, 128.1, 128.9, 130.4, 130.5, 133.2, 134.6, 137.8, 147.1, 148.3, 148.9, 149.2, 169.5, 170.4, 171.1, 171.6, 174.3 ppm. IR (ATR): 1742 (C=O), 1656 (C=O) cm^{-1}. MS (ESI): *m*/*z* (%) = 1056 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $C_{52}H_{74}N_6NaO_{16}^+$ $[M+Na]^+$: 1061.5054; found: 1061.5057.

4.2.2. Cyclo-[(L)-MeLeu-(D)-Lac-(L)-MeLeu-(D)-(NH_2)PhLac]$_2$ (5)

Derivative **4** (154.00 mg, 0.15 mmol) was dissolved in methanol (20 mL). Palladium (15.77 mg, 14.82 mmol, 10% Pd/C) was added and the mixture was stirred for 3 h at a pressure of 1 bar H_2. The catalyst was removed by filtration and washed with ethyl acetate. The solvent was removed under reduced pressure. Product **5** was obtained as a colorless solid (144.00 mg, 0.15 mmol) in quantitative yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.66–1.48 (m, 34H, CH_3-Leu, CH_3-Lac, $C_\gamma H$-Leu), 1.50–1.92 (m, 8H, $C_\beta H$-Leu), 2.68–2.98 (m, 12H, NCH_3), 2.99–3.11 (m, 4H, $C_\beta H$-PheLac), 4.48 (m, 1H, $C_\alpha H$-Leu), 5.03–5.90 (m, 7H, $C_\alpha H$-Leu, $C_\alpha H$-PheLac, $C_\alpha H$-Lac), 6.50–6.77, 6.95–7.14 (2 m, 8H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 15.8, 17.1, 20.9, 21.1, 21.2, 21.4, 21.6, 21.7, 23.2, 23.4, 23.6, 24.4, 24.7, 25.1, 29.4, 29.7, 30.2, 30.5, 31.2, 31.4, 36.3, 36.5, 36.8, 37.0, 37.2, 38.0, 54.0, 57.2, 58.6, 66.8, 68.6, 69.1, 71.1, 105.9, 113.7, 115.1, 116.1, 116.4, 116.5, 117.7, 118.9, 119.4, 124.6, 125.3, 128.4, 129.4, 130.4, 131.1, 141.5, 145.4, 145.6, 146.6, 169.8, 169.9, 170.4, 170.6, 171.0, 171.1, 171.3, 171.7 ppm. IR (ATR): 1741 (C=O), 1652 (C=O) cm^1. MS (ESI): *m*/*z* (%) = 996 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $C_{52}H_{78}N_6NaO_{12}^+$ $[M+Na]^+$: 1001.5570; found: 1001.5570.

4.2.3. Cyclo-[(L)-MeLeu-(D)-Lac-(L)-MeLeu-(D)-($COCH_3$)PhLac]$_2$ (6)

Freshly sublimated $AlCl_3$ (11.23 g, 84.28 mmol) was dissolved in acetyl chloride (40 mL). To the yellow solution PF1022A (**1**, 160.00 mg, 0.17 mmol) was added dropwise at room temperature. After stirring for 16 h the mixture was poured in an ice bath. The aqueous phase was washed with ethyl acetate (4 × 50 mL). The combined organic phases were extracted with a saturated $NaHCO_3$ solution (3 × 50 mL), dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification (solvent: cyclohexane/ethyl acetate, 1:1) of the residue gave the acetylation product **6** (135.26 mg, 0.13 mmol) in a yield of 78%. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.71–1.45 (m, 34H, CH_3-Leu, CH_3-Lac, $C_\gamma H$-Leu), 1.46–1.79 (m, 8H, $C_\beta H$-Leu), 2.61 (s, 6H, CH_3-acetyl), 2.72–3.12 (m, 12H, NCH_3), 3.12–3.29 (m, 4H, $C_\beta H$-PheLac), 4.49 (m, 1H, $C_\alpha H$-Leu), 5.05–5.77 (m, 7H, $C_\alpha H$-Leu, $C_\alpha H$-PheLac, $C_\alpha H$-Lac), 7.37 (m, 4H, Ar-H), 7.92 (m, 4H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ = 15.9, 16.5, 17.1, 20.8, 21.1, 21.2, 21.6, 23.1, 23.2, 23.3, 23.5, 24.5, 24.7, 24.8, 24.9, 25.1, 26.5, 29.3, 30.6, 31.3, 36.1, 36.7, 36.9, 37.5, 37.6, 37.9, 38.1, 54.0, 54.1, 54.2, 54.8, 57.1, 67.0, 67.5,

68.6, 70.2, 70.6, 128.5, 128.6, 128.7, 129.8, 129.9, 126.0, 136.1, 136.2, 140.6, 141.2, 169.6, 169.7, 169.9, 170.4, 170.8, 171.1, 171.6, 197.3, 197.4, 197.5 ppm. IR (ATR): 1741 (C=O), 1659 (C=O) cm^{-1}. MS (ESI): *m/z* (%) = 1050 (100) $[M+NH_4]^+$, 1055 (1) $[M+Na]^+$. HRMS (ESI): calcd for $C_{56}H_{80}N_4NaO_{14}^+$ $[M+Na]^+$: 1056.5596; found: 1056.5597.

4.2.4. Cyclo-[(L)-MeLeu-(D)-Lac-(L)-MeLeu-(D)-($COCH_3O$)PhLac]$_2$ (7)

Acetyl derivative **6** (16.70 mg, 16.16 μmol) was dissolved in DCM (20 mL). *m*CPBA (199.22 mg, 808.13 μmol) was added at 0 °C. The mixture was stirred for 6 h under reflux. After adding an aqueous saturated solution of Na_2SO_3 and stirring for additional 30 min at room temperature, the two phases were separated. The aqueous phase was washed with ethyl acetate (3 × 20 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. Chromatographic purification (solvent: cyclohexane/ethyl acetate 1:1) of the residue furnished ester **7** (15.90 mg, 14.93 μmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67–1.45 (m, 34H, CH_3-Leu, CH_3-Lac, C_γH-Leu), 1.46–1.81 (m, 8H, C_βH-Leu), 1.92, 2.01, 2.14, 2.29 (4s, 6H, CH_3-*O*-acetyl), 2.78–3.21 (m, 16H, NCH_3, C_βH-PheLac), 4.43–6.18 (m, 8H, C_αH-Leu, C_αH-PheLac, C_αH-Lac), 6.90–7.41 (m, 8H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.7, 22.4, 23.1, 23.2, 24.7, 29.7, 31.8, 37.1, 37.3, 52.1, 54.1, 67.9, 71.6, 120.3, 121.7, 122.5, 126.2, 126.9, 128.5, 129.6, 130.3, 149.8, 150.8, 169.3, 169.8, 170.1, 170.5, 171.6, 173.2 ppm. IR (ATR): 1747 (C=O), 1664 (C=O) cm^{-1}. MS (ESI): *m/z* (%) = 1082 (100) $[M+NH_4]^+$. HRMS (ESI): calcd for $C_{56}H_{80}N_4NaO_{16}^+$ $[M+Na]^+$: 1087.5462; found: 1087.5464.

4.2.5. Cyclo-[(L)-MeLeu-(D)-Lac-(L)-MeLeu-(D)-(OH)PhLac]$_2$ (PF1022H, 2)

A solution of derivative **7** (17.00 mg, 15.96 μmol) in methanol (2 mL) was treated with sodium perborate (12.27 mg, 79.79 μmol). The mixture was stirred for 1 h at room temperature. After that time the solvent was removed under reduced pressure. Chromatographic purification (solvent: toluene/IPA, 15:1) yielded a yellow solid (8.00 mg, 8.15 μmol, 51%). ^{1}H NMR (400 MHz, Methanol-d_4): δ = 0.76–1.46 (m, 34H, CH_3-Leu, CH_3-Lac, C_γH-Leu), 1.47–1.93 (m, 8H, C_βH-Leu), 2.79–3.20 (m, 16H, NCH_3, C_βH-PheLac), 4.72–5.90 (m, 8H, C_αH-Leu, C_αH-PheLac, C_αH-Lac), 6.66–6.86, 7.03–7.19 (2 m, 8H, Ar-H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, Methanol-d_4): δ = 17.2, 17.5, 21.1, 21.3, 21.6, 21.7, 23.6, 23.7, 23.8, 23.9, 25.2, 25.5, 25.9, 26.1, 26.2, 30.0, 31.2, 31.4, 32.1, 37.5, 38.0, 38.6, 39.0, 55.5, 55.7, 58.6, 68.5, 69.5, 69.9, 72.2, 72.4, 72.6, 115.1, 116.5, 117.7, 121.5, 126.4, 126.8, 130.8, 131,8, 137.3, 137.7, 157.9, 158.9, 170.8, 171.2, 172.2, 172.3, 173.1, 173.6, 174.5 ppm. IR (ATR): 3270 (O–H), 1743 (C=O), 1647 (C=O) cm^{-1}. MS (ESI): *m/z* (%) = 998 (100) $[M+NH_4]^+$, 1003 (3) $[M+Na]^+$. HRMS (ESI): calcd for $C_{52}H_{76}N_4NaO_{14}^+$ $[M+Na]^+$: 1003.5250, found: 1003.5252.

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