Supporting Information

for

First total synthesis of hoshinoamide A

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NMR (\(^1\)H NMR and \(^{13}\)C NMR) spectra of compounds 2–8, and comparison of the spectral data of natural and synthetic hoshinoamide A
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1. Experimental and analytical data

1.1 Synthesis of Fmoc-\textit{N}-Me-\textit{d}-Phe/Val-OH and Fmoc-Aha-OH

Fmoc-\textit{N}-Me-\textit{d}-Phe-OH and Fmoc-\textit{N}-Me-\textit{d}-Val-OH were synthesized using a modified procedure\textsuperscript{[1]} reported by Boc-\textit{d}-Phe-OH \textsuperscript{[2]} and Boc-\textit{d}-Val-OH \textsuperscript{[2]}. Fmoc-Aha-OH was synthesized using a modified procedure reported by aminocaproic acid \textsuperscript{[3]}. All data for known compounds are consistent with those reported in literature.

**Scheme S1: Synthesis of Fmoc-\textit{N}-Me-\textit{d}-Phe.**

Boc-\textit{d}-Phe-OH (5.00 g, 18.9 mmol) and MeI (1.8 mL, 28.4 mmol) were dissolved in DMF (50 mL). The reaction mixture was stirred at 0 °C for 45 min, then NaH (2.27 g, 56.7 mmol, 60%) was slowly added to the reaction mixture. The reaction mixture was stirred at room temperature for an additional 3 h, then quenched with water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL). The organic phase was dried over \( \text{Na}_2\text{SO}_4 \), filtered and concentrated to afford Boc-\textit{N}-Me-\textit{d}-Phe-OH which was used without purification.

Boc-\textit{N}-Me-\textit{d}-Phe-OH was dissolved in 10% HCl-dioxane (50 mL). The mixture was stirred at room temperature for 4 h, then concentrated to give a brown oil. The resulting crude oil was azeotroped with toluene (3 × 10 mL) and concentrated in vacuo to remove any residual HCl. The concentrated crude material was then dissolved in a mixture of THF (25 mL), \( \text{H}_2\text{O} \) (25 mL) and \( \text{NaHCO}_3 \) (3.2 g, 37.8 mmol), Fmoc-OSu (9.5 g, 28.4 mmol) was added to this mixture and the reaction mixture was stirred at room temperature for 8 h. Then added with water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL). The mixture was concentrated to give a
crude white foam which was purified by flash chromatography (n-hexanes/EA = 2:1) to afford Fmoc-N-Me-d-Phe-OH (5.6 g, 14.0 mmol, 74%) as a white foam. **^1H NMR** (400 MHz, DMSO-**d**6) δ 12.97 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.52 (m, 2H), 7.40 (q, *J* = 7.3 Hz, 2H), 7.33-7.05 (m, 7H), 4.79 (m, 4.7 Hz, 1H), 4.24 (m, 3H), 3.33-2.82 (m, 2H), 2.72 (d, *J* = 6.5 Hz, 3H). **^13C NMR** (101 MHz, DMSO-**d**6) δ 172.56, 172.41, 156.23, 156.03, 144.35, 144.25, 144.13, 141.23, 141.20, 138.38, 138.21, 129.24, 129.21, 128.74, 128.10, 127.57, 126.82, 125.52, 125.42, 125.36, 120.54, 67.31, 60.70, 60.16, 47.18, 47.03, 34.85, 34.56, 32.19, 31.79. **HRMS**: (+ESI) Calc. for C_{25}H_{23}NO_{4}: 402.1700 [M+H]^+, Found: 402.1698 [M+H]^+.

**Scheme S2: Synthesis of Fmoc-N-Me-d-Val-OH.**

Boc-d-Val-OH (5.0 g, 23.0 mmol) and MeI (2.2 mL, 28.4 mmol) were dissolved in DMF (50 mL). The reaction mixture was stirred at 0 °C for 45 min, then NaH (2.7 g, 68.0 mmol, 60%) was slowly added to the reaction mixture. The reaction mixture was stirred at room temperature for an additional 5 h, then quenched with water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL). The organic phase was dried over Na_{2}SO_{4}, filtered and concentrated to afford Boc-N-Me-d-Val-OH which was used without purification.

Boc-N-Me-d-Val-OH was dissolved in 10% HCl-dioxanone (50 mL). The mixture was stirred at room temperature for 3 h, then concentrated to give a brown oil. The resulting crude oil was azeotroped with toluene (3 × 10 mL) and concentrated in vacuo to remove any residual HCl. The concentrated crude material was then dissolved in a mixture of THF (25 mL), H_{2}O (25 mL) and NaHCO_{3} (3.8 g, 45.4 mmol), Fmoc-OSu (11.4 g, 34.1 mmol) was added to this mixture and the reaction mixture was stirred at room temperature for 8 h. Then added with water (150 mL) and
extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL). The mixture was concentrated to give a crude white foam which was purified by flash chromatography (DCM/MeOH = 100:1) to afford Fmoc-N-Me-Val-OH (6.6 g, 18.6 mmol, 81%) as a white foam.\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 12.78 (s, 1H), 7.85 (d, \(J = 7.1\) Hz, 2H), 7.71-7.58 (m, 2H), 7.38 (t, \(J = 7.1\) Hz, 2H), 7.31 (t, \(J = 7.1\) Hz, 2H), 4.39 (m, 2H), 4.25 (m, 2H), 2.76 (s, 3H), 2.05 (m, 1H), 0.99-0.56 (m, 6H). \(^1\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 172.50, 172.33, 156.61, 156.00, 144.39, 144.25, 141.37, 128.13, 127.58, 125.49, 125.44, 120.56, 67.34, 64.33, 47.33, 47.26, 30.66, 27.49, 27.37, 20.22, 20.15, 19.32, 19.02. HRMS: (+ESI) Calc. for C\(_{21}\)H\(_{23}\)NO\(_4\): 354.1700 [M+H]\(^+\), Found: 354.1696 [M+H]\(^+\).

Scheme S3: Synthesis of Fmoc-Aha-OH

Aminocaproic acid (2.0 g, 15.2 mmol) dissolved in a mixture of THF (25 mL), H\(_2\)O (25 mL) and NaHCO\(_3\) (2.5 g, 30.4 mmol), Fmoc-OSu (10.2 g, 30.4 mmol) was added to this mixture and the reaction mixture was stirred at room temperature for 7 h. Then added with water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL). The mixture was concentrated to give a crude white foam which was purified by flash chromatography (DCM:MeOH = 50:1) to afford Fmoc-Aha-OH (4.8 g, 13.7 mmol, 90%) as a white foam. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.70 (s, 1H), 7.71 (d, \(J = 7.5\) Hz, 2H), 7.55 (d, \(J = 6.9\) Hz, 2H), 7.31 (m, 4H), 4.97 (s, 1H), 4.53-4.30 (m, 2H), 4.24-4.09 (m, 1H), 3.13 (d, \(J = 6.0\) Hz, 1H), 3.00 (s, 1H), 2.29 (t, \(J = 7.2\) Hz, 2H), 1.67-1.51 (m, 2H), 1.50-1.40 (m, 1H), 1.39-1.15 (m, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 179.02, 157.88, 156.62, 143.98, 141.31, 127.68, 127.05, 125.05, 124.87, 119.97, 67.18, 66.57, 47.27, 41.35, 40.80, 34.06, 29.53, 26.13, 24.34. HRMS: (+ESI) Calc. for C\(_{21}\)H\(_{23}\)NO\(_4\): 354.1700 [M+H]\(^+\), Found: 354.1696 [M+H]\(^+\).
1.2 Solid phase synthesis of tripeptide 3

Fmoc-Pro-OH (674 mg, 2 mmol) was then dissolved in a mixture of DCM (10 mL) and DMF (10 mL). DIPEA (1.7 mL, 10 mmol), 2-CTC resin (1 g) were added to this mixture and the reaction was stirred at room temperature for 2h. The resin was filtered and washed with MeOH (3 × 20 mL), DCM (3 × 20 mL). The unreacted resin was capped with MeOH in a mixture of MeOH:DIPEA:DCM (1:2:7, 10 mL) for 3h. The resin-bound peptide was added to a mixture of 20% piperidine in DMF (20 mL), and the mixture was shaken to for 30 minutes. Then the mixture was filtered, the resin was washed with MeOH (3 × 20 mL) and DCM (3 × 20 mL). Fmoc-N-Me-D-Phe-OH (1000 mg, 2.5 mmol), HATU (950 mg, 2.5 mmol) and DIPEA (871 µL, 5.0 mmol) in DMF were added on the resin and the reactor was shaken for 1h at room temperature. Then the mixture was filtered, the resin was washed with MeOH (3 × 20 mL) and DCM (3 × 20 mL) to afford the resin-bound dipeptide. The resin-bound dipeptide was added to a mixture of 20% piperidine in DMF (20 mL), and the mixture was shaken to for 30 minutes. Then the mixture was filtered, the resin was washed with MeOH (3 × 20 mL) and DCM (3 × 20 mL). Fmoc-Val-OH (848 mg, 2.5 mmol), HATU (950 mg, 2.5 mmol) and DIPEA (871 µL, 5.0 mmol) in DMF were added on the resin and the reactor was shaken for 1h at room temperature. The resulting tripeptide 3 was analysed on a Thermo Scientific MSQ instrument, and few product was observed.
1.3 Synthesis of tripeptide 7

Scheme S5: synthesis of tripeptide 7.

Pro-OBn.HCl (2.41 g, 10 mmol), Fmoc-\text{-}N\text{-}Me\text{-}D\text{-}Phe\text{-}OH (4.01 g, 10 mmol) and DIPEA (5.2 mL, 30 mmol) was dissolved in 50 mL anhydrous DCM. HATU (5.7 g, 15 mmol) was added to the solution and the mixture was stirred at room temperature for 6 h. The reaction mixture was then washed by 1.0 M HCl (20 mL), aqueous NaHCO$_3$ (20 mL) and brine (20 mL). The organic phase was dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude residue was purified by flash column chromatography (\textit{n}-hexanes/EA = 2:1) to afford dipeptide 6 (4.9 g, 83%). $^1$H NMR (400 MHz, Methanol-$d_4$) δ 7.39-7.27 (m, 19H), 5.20-5.12 (m, 4H), 4.85 (s, 6H), 4.44 (m, 4H), 3.50 (m, 2H), 3.31-3.23 (m, 4H), 3.07 (dd, $J =$ 12.8, 10.3 Hz, 2H), 2.57 (s, 6H), 2.46 (dt, $J =$ 9.9, 7.0 Hz, 2H), 2.03-1.94 (m, 2H), 1.89-1.71 (m, 4H), 1.48 (m, 2H). $^{13}$C NMR (101 MHz, Methanol-$d_4$) δ 171.21, 165.90, 135.71, 133.51, 129.37, 128.70, 128.24, 128.07, 127.93, 127.74, 66.74, 60.75, 59.32, 36.55, 30.88, 28.45, 23.94. HRMS: (+ESI) Calc. for C$_{22}$H$_{26}$N$_2$O$_3$: 588.2671[M+H]$^+$, Found:588.2673[M+H]$^+$. 

To a stirred solution of dipeptide 6 (118 mg, 0.20 mmol) was added 20% Et$_2$NH in CH$_3$CN (5 mL) at rt for 0.5 h. The Et$_2$NH and CH$_3$CN are evaporated in vacuo and the residue is triturated with ether (10 mL), the crude amine washed with ether (quintic, 10 mL each time) and dried in vacuo. To a stirred solution of crude amine and Fmoc-Val-OH (71 mg, 0.20 mmol) was dissolved in 10 mL anhydrous DMF. Coupling reagents was added to the solution and the mixture was stirred at room temperature for 3 h. This mixture poured onto water (10 mL) and extracted with CH$_2$Cl$_2$ (3 × 10 mL). Then washed by 1.0 M HCl (10 mL), aqueous NaHCO$_3$ (10 mL) and brine (10 mL). The organic phase was dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude residue was purified by flash column
chromatography (n-hexanes/EA = 2:1) to afford tripeptide 7. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.75 \,(d, \, J = 7.7 \, Hz, \, 2H)\), 7.57 (t, \, J = 7.2 \, Hz, \, 2H), 7.40-7.17 (m, \, 14H), 5.72 (dd, \, J = 8.9, \, 6.5 \, Hz, \, 1H), 5.46 (d, \, J = 9.5 \, Hz, \, 1H), 5.23-5.20 (m, \, 1H), 5.06 (d, \, J = 12.2 \, Hz, \, 1H), 4.50-4.18 (m, \, 5H), 3.48-3.43 (m, \, 1H), 3.28 (dt, \, J = 11.3, \, 5.8 \, Hz, \, 2H), 3.10 (s, \, 1H), 2.95-2.86 (m, \, 3H), 2.21-2.14 (m, \, 2H), 1.78-1.62 (m, \, 5H), 1.28 (s, \, 2H), 0.76 (m, \, 3H), 0.47 (m, \, 6.7 \, Hz, \, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 171.70, \, 171.60, \, 168.26, \, 156.39, \, 143.88, \, 141.30, \, 137.01, \, 129.54, \, 128.88, \, 128.69, \, 128.60, \, 128.50, \, 128.39, \, 128.31, \, 128.20, \, 127.72, \, 127.08, \, 126.65, \, 125.17, \, 125.08, \, 119.99, \, 67.04, \, 66.84, \, 59.43, \, 55.87, \, 55.59, \, 47.17, \, 46.92, \, 35.00, \, 30.72, \, 30.47, \, 28.78, \, 25.25, \, 19.82, \, 16.33.\) HRMS: (+ESI) Calc. for C\(_{42}\)H\(_{45}\)N\(_3\)O\(_6\): 688.3381 [M+H]\(^+\), Found:688.3384 [M+H]\(^+\).

Comparison of the effects of different coupling reagents on the reaction yield (Table S1).

1.4 Synthesis of hoshinoamide A

![Scheme S6: synthesis of hoshinoamide A.](image)

Tripeptide 7 (2.3 g, 3.3 mmol) was was dissolved in 30 mL of MeOH/HCOOH(v/v = 9:1) and hydrogenized with Pd(OH)\(_2\) (500 mg) under H\(_2\) for 10 hours to remove the Bn groups. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo to a give brown oil which was
purified by flash chromatography (n-hexanes:EA = 2:1), affording tripeptide 8 (1.87 g, 95%) as a white foam. $^1$H NMR (400 MHz, Methanol-$d_4$) δ 7.59 (d, J = 8 Hz, 2H), 7.45 (d, J = 8 Hz, 2H), 7.21-6.96 (m, 10H), 5.52 (m, 1H), 4.81 (s, 2H), 4.20-3.98 (m, 4H), 3.29-3.10 (m, 2H), 3.04–2.91 (m, 4H), 2.80-2.67 (m, 2H), 2.62 (s, 3H), 2.01-1.83 (m, 2H), 1.53 (m, 4H), 1.13-1.09 (m, 2H), 0.52-0.45 (m, 4H). $^{13}$C NMR (101 MHz, Methanol-$d_4$) δ 175.49, 175.06, 174.95, 173.81, 173.14, 171.16, 170.16, 167.42, 164.85, 158.64, 158.58, 158.53, 145.38, 145.35, 145.20, 145.13, 145.09, 142.88, 142.55, 138.50, 138.42, 131.03, 130.75, 130.66, 130.27, 129.77, 129.64, 129.57, 129.42, 128.86, 128.83, 128.55, 128.28, 128.21, 127.77, 127.66, 126.35, 126.29, 126.21, 125.76, 121.02, 70.63, 68.11, 68.04, 66.85, 60.78, 60.68, 59.15, 58.19, 57.76, 57.67, 57.41, 57.06, 56.41, 56.08, 38.96, 37.58, 37.01, 36.60, 35.79, 35.61, 33.11, 32.20, 31.89, 31.73, 31.53, 31.40, 30.88, 30.83, 30.66, 30.53, 30.39, 29.98, 29.64, 28.18, 26.97, 26.10, 23.80, 23.34, 19.88, 19.48, 18.17, 18.07, 17.64, 14.58. HRMS: (+ESI) Calc. for C$_{35}$H$_{39}$N$_3$O$_6$: 598.2912 [M+H]$^+$, Found: 598.2915 [M+H]$^+$. 

Tripeptide 8 (1.20 g, 2 mmol) was then dissolved in a mixture of DCM (10 mL) and DMF (10 mL). DIPEA (1.7 mL, 10 mmol), 2-CTC resin (1 g) were added to this mixture and the reaction was stirred at room temperature was for 3h. The resin was filtered and washed with MeOH (3 × 20 mL), DCM (3 × 20 mL). The unreacted resin was capped with MeOH in a mixture of MeOH:DIPEA:DCM (1:2:7, 10 mL) for 5 h. Fmoc protecting group was removed following the general procedure and the remain amino acids were successively coupled using the standard SPPS method. (Ile$_6$ and Ahas$_8$ are coupled with coupling reagent. Gln$^4$, N-Me-D-Val$^5$, N-Me-L-Leu$^7$ and Hba$^9$ are coupled with HATU and DIPEA.) 0.5% TFA in DCM (20 mL) were added on the resin and the mixture was shaken for 2h to cleavage the peptide from the resin. The mixture was filtered and the filtrate was concentrated in vacuo to give a white foam. The peptide was re-dissolved in a mixture of TFA:Et$_3$SiH:H$_2$O (10 mL, 50/50/50 v/v/v). The reaction mixture was stirred for 3 h, and then concentrated in vacuo. The crude peptide was precipitated using cold Et$_2$O and centrifuged at 7000 rpm to give a white solid. This solid was further purified by RP-HPLC using protocols described in the general method. Fractions were collected, concentrated and
lyophilized to give nanopeptide 10 as a white solid. Nanopeptide 10 was dissolved in dry DMF (5 mL). K$_2$CO$_3$ (3.1 mg, 0.022 mmol) and MeI (3.13 mg, 0.022 mmol) was added to this solution. The reaction mixture was stirred for 3 h. This mixture poured onto water (5 mL) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). Then washed by 1.0 M HCl (10 mL), aqueous NaHCO$_3$ (10 mL) and brine (10 mL). The organic phase was dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo to give brown oil. This oil was further purified by RP-HPLC using protocols described in the general method. Fractions were collected, concentrated and lyophilized to give Hoshinoamide A as a white solid (10 mg, 2% yield). HRMS: (+ESI) Calc. for C$_{56}$H$_{56}$N$_{9}$O$_{12}$: 1146.7173 [M+H]$^+$, Found: 1146.7173 [M+H]$^+$; The $^1$H NMR and $^{13}$C NMR spectra of synthetic product were fully consistent with the data of isolated samples reported in the literature.$^4$ See table S2 and table S3 for details. $^1$H NMR (400 MHz, Methanol-$d_4$) $\delta$ 7.30 - 7.11 (m, 6H), 7.02 - 6.94 (m, 2H), 6.72 - 6.65 (m, 2H), 5.73 (dd, $J$ = 9.2, 6.4 Hz, 1H), 4.82 - 4.73 (m, 1H), 4.64 - 4.53 (m, 2H), 4.43 - 4.25 (m, 2H), 3.69 (s, 2H), 3.50 (dt, $J$ = 11.2, 6.0 Hz, 1H), 3.41 - 3.31 (m, 1H), 3.20 - 3.06 (m, 9H), 2.99 - 2.92 (m, 3H), 2.91 - 2.86 (m, 1H), 2.52 (t, $J$ = 7.6 Hz, 2H), 2.47 - 2.38 (m, 2H), 2.29 - 2.22 (m, 3H), 2.18 (q, $J$ = 7.7 Hz, 3H), 2.05 - 1.99 (m, 1H), 1.99 - 1.71 (m, 9H), 1.68 - 1.46 (m, 6H), 1.46 - 1.34 (m, 4H), 1.11 - 0.97 (m, 3H), 0.97 - 0.81 (m, 16H), 0.68 - 0.55 (m, 6H). $^{13}$C NMR (101 MHz, Methanol-$d_4$) $\delta$ 177.43, 176.52, 176.00, 174.55, 173.86, 173.15, 173.09, 172.87, 171.89, 170.47, 156.60, 138.40, 133.75, 130.69, 130.40, 129.45, 127.70, 116.18, 64.21, 60.84, 57.23, 55.69, 55.64, 55.52, 54.32, 52.69, 40.23, 38.43, 37.82, 36.62, 35.76, 35.51, 34.59, 32.62, 31.80, 31.59, 31.56, 30.22, 29.98, 29.20, 27.72, 26.21, 26.17, 26.06, 25.95, 25.90, 25.11, 23.80, 22.17, 20.39, 19.90, 19.49, 18.13, 16.50, 11.60. HRMS: (+ESI) Calc. for C$_{56}$H$_{56}$N$_{9}$O$_{12}$: 1146.7173 [M+H]$^+$, Found: 1146.7173 [M+H]$^+$;
Table S1. $^1$H and $^{13}$C NMR Spectroscopic Data of Naturally Occurring and Synthetic Hoshinoamide A

| Position | Natural Product $^\delta$H (CD$_3$OD, 400 MHz) | Natural Product $^\delta$C (CD$_3$OD, 100 MHz) | Synthetic Product $^\delta$H (CD$_3$OD, 400 MHz) | Synthetic Product $^\delta$C (CD$_3$OD, 100 MHz) |
|----------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| 1        | 3.7                                         | 52.7                                        | 3.69                                         | 52.7                                        |
| 2        |                                              | 173.8                                       |                                              | 173.9                                       |
| 3        | 4.38                                         | 60.8                                        | 4.38                                         | 60.8                                        |
| 4a       | 2.23                                         | 29.7                                        | 2.24                                         |                                              |
| 4b       | 1.86                                         |                                              | 1.85                                         |                                              |
| 5a       | 1.97                                         | 26.2                                        | 1.96                                         | 26.2                                        |
| 5b       | 1.87                                         |                                              | 1.87                                         |                                              |
| 6a       | 3.5                                          | 48.2                                        | 3.50                                         |                                              |
| 6b       | 3.34                                         |                                              | 3.35                                         |                                              |
| 7        |                                              | 170.5                                       |                                              | 170.5                                       |
| 8        | 5.74                                         | 57.2                                        | 5.74                                         | 57.2                                        |
| 9a       | 3.17                                         | 35.7                                        | 3.16                                         | 35.7                                        |
| 9b       | 2.9                                          |                                              | 2.89                                         |                                              |
| 10       |                                              | 138.4                                       |                                              | 138.4                                       |
| 11       | 7.24                                         | 130.7                                       | 7.24                                         | 130.7                                       |
| 12       | 7.25                                         | 129.4                                       | 7.25                                         | 129.5                                       |
| 13       | 7.16                                         | 127.7                                       | 7.16                                         | 127.7                                       |
| 16       | 3.09                                         | 31.5                                        | 3.08                                         | 31.6                                        |
| 17       |                                              | 173.14                                      |                                              | 173.15                                      |
| 18       | 4.57                                         | 55.6                                        | 4.57                                         | 55.6                                        |
| 19       | 1.76                                         | 31.5                                        | 1.77                                         | 31.6                                        |
| 20       | 0.65                                         | 18.1                                        | 0.64                                         | 18.1                                        |
| 21       | 0.6                                          | 19.9                                        | 0.59                                         | 19.9                                        |
| 22       |                                              | 173.06                                      |                                              | 173.09                                      |
| 23       | 4.3                                          | 54.3                                        | 4.30                                         | 54.3                                        |
| 24a      | 2.02                                         | 26                                           | 2.01                                         | 26                                           |
| 24b      | 1.93                                         |                                              | 1.93                                         |                                              |
| 25a      | 2.25                                         | 29.9                                        | 2.25                                         | 30.0                                        |
| 25b      | 1.87                                         |                                              | 1.87                                         |                                              |
| 26       |                                              | 177.4                                       |                                              | 177.4                                       |

S10
|     |        |        |        |        |
|-----|--------|--------|--------|--------|
| 27  | 171.9  | 171.9  |        |        |
| 28  | 4.61   | 64.1   | 4.61   | 64.2   |
| 29  | 2.28   | 27.7   | 2.27   | 27.7   |
| 30  | 0.98   | 20.3   | 0.98   | 20.4   |
| 31  | 0.85   | 19.5   | 0.85   | 19.5   |
| 32  | 3.09   | 32.6   | 3.08   | 32.6   |
| 33  | 174.5  |        | 174.6  |        |
| 34  | 4.78   | 55.5   | 4.78   | 55.5   |
| 35  | 1.84   | 38.4   | 1.83   | 38.4   |
| 36a | 1.46   | 25.1   | 1.46   | 25.1   |
| 36b | 1.07   |        | 1.07   |        |
| 37  | 0.86   | 11.6   | 0.85   | 11.6   |
| 38  | 0.93   | 16.5   | 0.93   | 16.5   |
| 39  | 172.9  |        | 172.9  |        |
| 40  | 5.52   | 55.6   | 5.52   | 55.7   |
| 41a | 1.75   | 37.8   | 1.75   | 37.8   |
| 41b | 1.59   |        | 1.59   |        |
| 42  | 1.4    | 26.7   | 1.40   |        |
| 43  | 0.94   | 23.8   | 0.94   | 23.8   |
| 44  | 0.89   | 22.1   | 0.89   | 22.2   |
| 45  | 2.97   | 31.8   | 2.96   | 31.8   |
| 46  | 176.5  |        | 176.5  |        |
| 47  | 2.43   | 34.6   | 2.42   | 34.6   |
| 48  | 1.64   | 25.9   | 1.63   | 25.9   |
| 49  | 1.39   | 27.7   | 1.39   |        |
| 50  | 1.53   | 30.2   | 1.52   | 30.2   |
| 51  | 3.17   | 40.2   | 3.16   | 40.2   |
| 52  | 176    |        | 176    |        |
| 53  | 2.16   | 36.6   | 2.17   | 36.6   |
| 54  | 1.86   | 29.2   | 1.86   | 29.2   |
| 55  | 2.52   | 35.5   | 2.52   | 35.5   |
| 56  | 133.7  |        | 133.8  |        |
| 57/61 | 6.99 | 130.4  | 6.99   | 130.4  |
| 58/60 | 6.7  | 116.1  | 6.69   | 116.2  |
| 59  | 156.6  |        | 156.6  |        |

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2. References

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3. $^1$H-NMR and $^{13}$C-NMR Spectra
4. $^1$H NMR spectra, high resolution mass spectra, and analytical HPLC spectra of hoshinoamide A
Figure S1. High resolution mass spectra of hoshinoamide A.