

An efficient synthesis of Nepetoidin B

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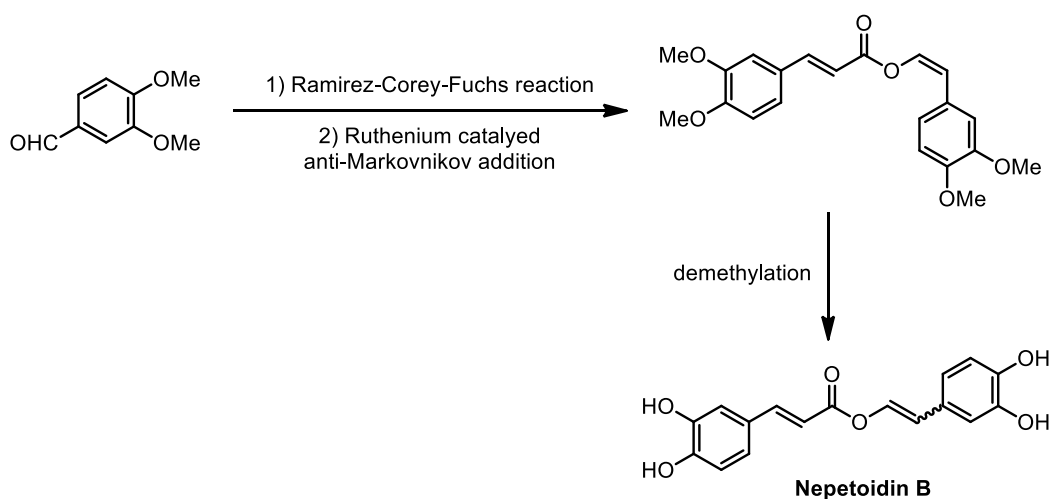
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Abstract

The synthesis of nepetoidin B from readily and commercially available 3,4-dimethoxybenzaldehyde in an overall yield of 52% is achieved. The present three-step protocol involves Ramirez–Corey–Fuchs reaction, ruthenium-catalyzed *anti*-Markovnikov addition of a carboxylic acid to a terminal alkyne and demethylation using iodotrimethylsilane (Me₃SiI) and quinoline. In this work, the two isomers of (*Z*, *E*)- nepetoidin B / (*E*, *E*)-nepetoidin B and the single isomer of (*E*, *E*)- nepetoidin B can be obtained through the demethylation of (*Z*, *E*)-**5** and (*E*, *E*)-**5**, respectively.



Keywords: Nepetoidin B, 3,4-dimethoxybenzaldehyde, terminal alkyne, *anti*-Markovnikov addition, demethylation, synthesis

Introduction

Nepetoidin B (**1**) is a phenolic compound with (*Z*, *E*)-**1** and (*E*, *E*)-**1** isomers (Figure 1). It could be isolated from *Perilla frutescens*,¹ *Plectranthus forsteri*,²⁻³ *Salvia miltiorrhiza* Bunge⁴ and other plants.⁵⁻¹⁴ The amounts of (*Z*, *E*)-**1** and (*E*, *E*)-**1** vary from 9:1 to 1:1 in different plants. Nepetoidin B possesses remarkable biological activities, such as *anti*-oxidant, *anti*-viral and *anti*-fungal activities, and it could also be used to inhibit xanthine oxidase and the production of nitric oxide.^{4,8,11}

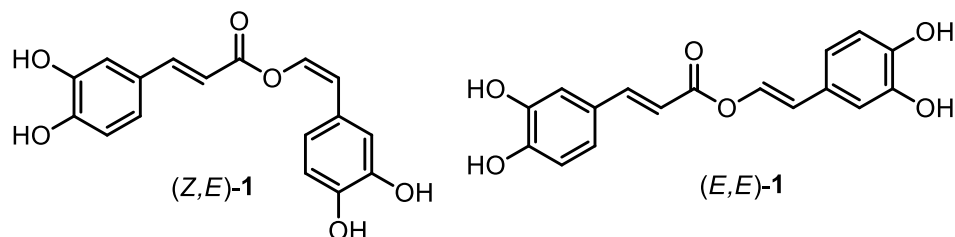


Figure 1. The two isomers of nepetoidin B.

The level of nepetoidin B in plants is rather low. 100 kg of *Salvia miltiorrhiza* Bunge (Danshen) could only provide 37 mg nepetoidin B.⁴ It would hardly be possible to provide large quantities of nepetoidin B by extraction to conduct further biological research. Therefore, efficient synthetic approaches for large-scale preparation of nepetoidin B are highly desired. The first synthesis of nepetoidin B was developed by Timokhin *et al.* through Baeyer-Villiger oxidation of 1,5-bis(3,4-dimethoxyphenyl)-1,4-pentadien-3-one with oxone and demethylation with boron tribromide. The overall yield of this approach was 17%.¹⁵ The first step of this approach required a tedious workup and purification to afford tetramethylated nepetoidin B in 40% yield and to recover the starting material.¹⁵

Due to our interest in the synthesis of biological active phenolic compounds,¹⁶⁻²⁰ we developed an efficient route for the synthesis of nepetoidin B in three steps from the commercially available and inexpensive 3,4-dimethoxybenzaldehyde.

Results and Discussion

As illustrated in Figure 2, we undertook a retrosynthetic analysis of nepetoidin B. First, demethylation of the tetramethylated nepetoidin B could afford nepetoidin B. Further disconnection at the O10-C11 bond of tetramethylated nepetoidin B provided two fragments **3** and **4**, which could be forged together by a Ru-catalyzed *anti*-Markovnikov addition of the carboxylic acid to the terminal alkyne. The carboxylic acid **4** and alkyne **3** could be prepared from 3,4-dimethoxybenzaldehyde.

As shown in figure 3, the synthesis commenced by preparing the 3,4-dimethoxyphenylacetylene **3**. Ramirez–Corey–Fuchs reaction of 3,4-dimethoxybenzaldehyde afforded the corresponding terminal alkyne **3** in 95% yield.²¹⁻²² The 3,4-dimethoxycinnamic acid is a very cheap raw material, although it can be prepared via a Knoevenagel–Doebner condensation in high yield.²³ Subsequently, we employed the Ru-catalyzed *anti*-Markovnikov addition reaction developed by Dixneuf *et al.*²⁴ to prepare the tetramethylated nepetoidin B **5** from 3,4-dimethoxyphenylacetylene **3** and 3,4-dimethoxycinnamic acid **4**. In the presence of [Ru]cat., the addition occurred smoothly to afford compound **5** in 90% yield at 45 °C, with toluene as solvent. Delightfully, we obtained the single isomer as (*E*, *Z*)-**5** and did not observe the isomer of (*E*, *Z*)-**5** (as determined by ¹H-NMR

and ^{13}C -NMR analysis). Replacement of the toluene with THF or hexane resulted in a poor yield of the desired product. Efforts to increase the reaction temperature to 60 °C or decrease the temperature to 20 °C only led to low yields.

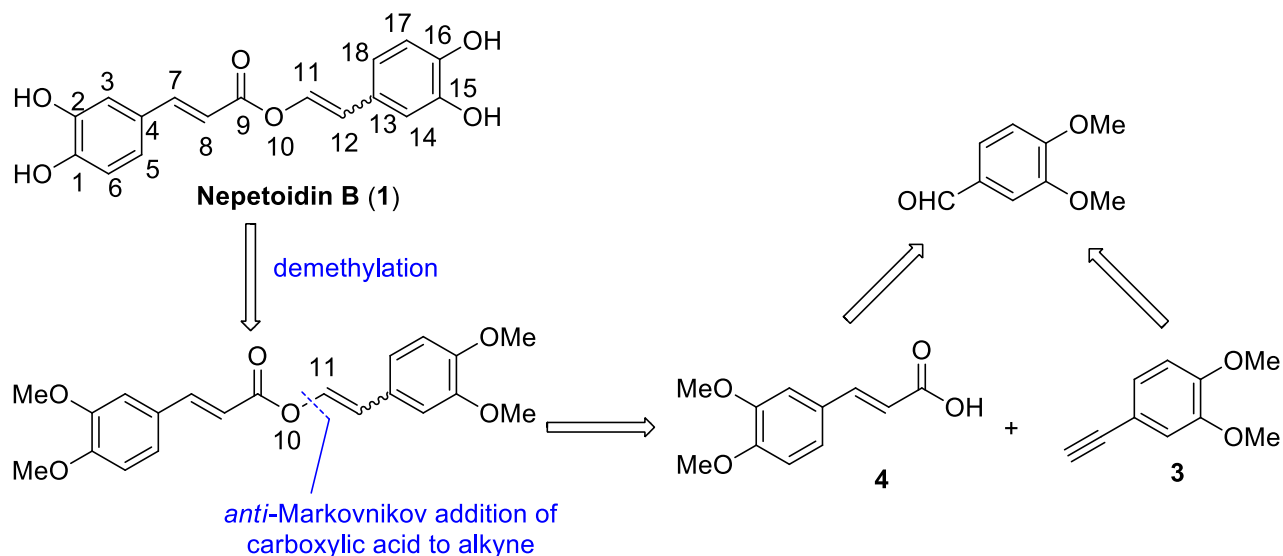


Figure 2. Retrosynthetic analysis of nepetoidin B.

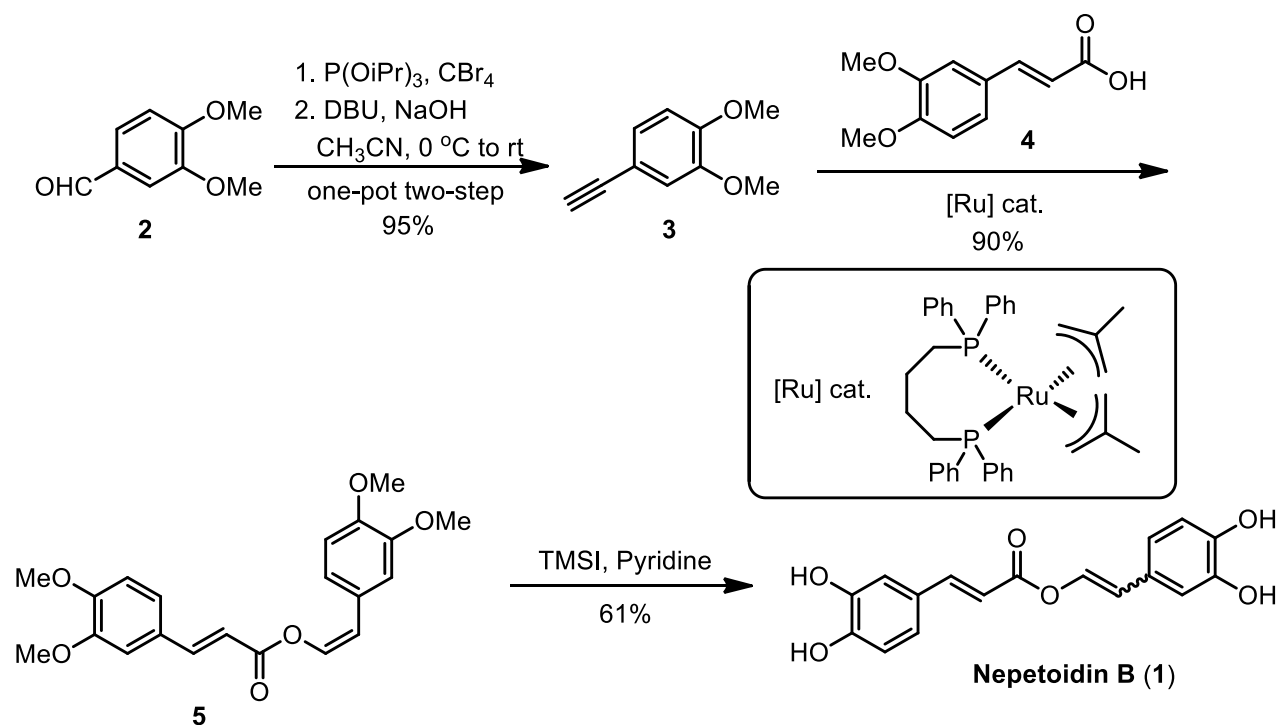


Figure 3. Synthesis of nepetoidin B

The final step in the synthesis required the demethylation of compound **5**. Though Timokhin et al.¹⁵ used boron tribromide to conduct the demethylation of compound **5**, the isolated yield of this method was 43% and the obtained compound **1** was a mixture of the two isomers in a ratio of 94:6 (*E, E*)-**1**/(*Z, E*)-**1**. Therefore, we further examined various demethylation methods as shown in Table 1.²⁵⁻²⁶ Treatment of compound (*Z, E*)-**5**

with Me₃SiI and quinoline at 175 °C for 4h afforded the desired product in 61% yield as a mixture of the two isomers in a ratio of 2.8:1 (*Z*, *E*)-**1**/(*E*, *E*)-**1** (as estimated by ¹H-NMR analysis)(entry 7). However, treatment of the compound (*E*, *E*)-**5** under the same conditions could provide a single isomer of (*E*, *E*)-**1** in 59% yield (entry 7). The clear reason for the formation of (*E*, *E*)-**1** is unclear. The reaction temperature (175 °C) is perhaps the reason for the partial isomerisation of the double bond. In addition, we also probed other demethylation methods, but low yields of compound **1** (entry 6), complex products (entry 3-5) or ester bond (C9-O10) cleavage products (entry 1-2) were obtained.

Table 1. Demethylation of compound **5**^a

Entry	Reagents and Conditions	Yield/%
1	46% HBr, TBAB or nBu ₄ PBr, reflux	— ^b
2	All ₃ , CH ₃ CN, rt or 75 °C	— ^b
3	Me ₃ SiI, CHCl ₃ , rt	— ^c
4	NaI, Me ₃ SiCl, CH ₃ CN	— ^c
5	BF ₃ •Et ₂ O, SHCH ₂ CH ₂ SH, CH ₂ Cl ₂ , rt	— ^c
6	All ₃ , DIC, CH ₃ CN, rt or 75 °C	< 5
7	MeSiI, quinoline, 4h, 175°C	61 ^d (59) ^e

^a Unless noted otherwise, all the reaction were conducted with compound (*Z*, *E*)-**5** (0.4 mmol) in the presence of the specified demethylation methods; ^b The major products were the ester bond (C9-O10) cleavage products; ^c complex products; ^d The obtained product was as a mixture of the two isomers in a ratio of 2.8:1 (*Z*, *E*)-**1**/(*E*, *E*)-**1**; ^e The (*E*, *E*)-**5** was used as the starting material. Value in parentheses was the isolated yield of (*E*, *E*)-**1**. TBAB = Tetrabutylammonium bromide; DIC = 1,3-diisopropylcarbodiimide.

Conclusions

In conclusion, we have developed a concise approach to the synthesis of nepetoidin B in three steps and 52% overall yield from commercially available 3,4-dimethoxybenzaldehyde. In the presence of Me₃SiI and quinoline at 175 °C, the (*Z*, *E*)-**5** could afford two isomers of (*Z*, *E*)-**1**/(*E*, *E*)-**1** (the ratio of (*Z*, *E*)-**1**/(*E*, *E*)-**1** was 2.8:1) in 61% yield and the (*E*, *E*)-**5** could afford the single isomer of (*E*, *E*)-**1** in 59% yield. This protocol offered a straightforward and sustainable access to nepetoidin B from readily and commercially available starting materials with high efficiency.

Experimental Section

General. Commercial reagents and solvents were used as received without further purification. CH₃CN was of HPLC grade with less than 500 ppm of H₂O. All₃ was prepared *in situ* by mixing Al powder and I₂.²⁷ [Ru]cat. was

prepared by displacement of cyclooctadiene from bis(2-methylpropenyl)(cycloocta-1,5-diene)ruthenium by 1 equiv of the 1,4-bis(diphenylphosphino)butane according to Genet's method.²⁸ The (*E*, *E*)-**5** was synthesized according to the procedure developed by Timokhin et al.¹⁵ TLC analyses were performed on precoated GF254 silica gel plates and were visualized under UV254 nm light or by I2 staining. NMR spectra were detected using a Bruker Avance 400 FTNMR spectrometer. Column chromatography was carried out using 200-300 mesh silica gel.

One-pot two-step procedure for the preparation of 3,4-Dimethoxyphenylacetylene (3). To a stirred solution of 3,4-dimethoxybenzaldehyde **2** (831 mg, 5.0 mmol) and tetrabromomethane (2.49 g, 7.5 mmol) in CH₃CN (10 mL), triisopropyl phosphate (2.5 mL, 10.0 mmol) was added drop wise over a period of 20 min at 0 °C. After 15 min, DBU (3.0 mL, 20.0 mmol) was added to the reaction mixture drop wise over 20 min while maintaining the temperature of the reaction at 0 °C. The reaction mixture was then warmed to 25 °C over 30 min. Powdered NaOH (50 mmol) was added to the reaction mixture in portion. After completion of the reaction (usually 5h), 50 mL water was added to the reaction mixture. The reaction mixture was extracted with EtOAc (50 mL) for three times and the organic layers were washed with saturated NaCl aq. (60 mL). The organic layers were dried with Na₂SO₄ and evaporated under reduced pressure to provide a crude residue, which was purified via using petroleum/EtOAc (20:1) as eluent to afford the terminal alkyne **3** as a white solid (770 mg, 95% yield). ¹H-NMR(CDCl₃, 400Hz): δ 7.10 (dd, *J* 8.0, 2.0 Hz, 1H), 6.99 (d, *J* 2.0 Hz, 1H), 6.80 (d, *J* 8.0 Hz, 1H), 3.89 (s, 3H), 3.88(s, 3H), 3.00 (s, 1H).²⁹

(*Z*,*E*)-Tetramethylated nepetoidin B (5). 3,4-Dimethoxycinnamic acid **4** (416 mg, 2.0 mmol), 3,4-Dimethoxyphenylacetylene **3** (324 mg, 2.0 mmol) and [Ru]cat. (12.8 mg, 0.02 mmol) in 10 mL of toluene were stirred at 45 °C for 12 h under an inert atmosphere of nitrogen. The reaction mixture was quenched with NaHCO₃ aq. (10 mL) and extracted with EtOAc (20 mL) for three times. The organic layers were washed with NaCl aq. (30 mL). The organic layers were dried with Na₂SO₄ and evaporated under reduced pressure to provide a crude residue, which was purified via using petroleum/EtOAc (3:1) as eluent to afford the tetramethylated nepetoidin B **5** as a yellow solid (667 mg, 90% yield). (*Z*, *E*)-**5**: mp 109-110 °C, ¹H-NMR(acetone *d*₆, 400Hz): δ 7.82 (d, *J* 16 Hz, 1H), 7.38 (d, *J* 7.2 Hz, 1H), 7.28 (d, *J* 2.0 Hz, 1H), 7.21 (dd, *J* 8.4, 2.0 Hz, 1H), 7.15 (dd, *J* 8.4, 2.0 Hz, 1H), 7.08 (d, *J* 2.0 Hz, 1H), 6.91 (d, *J* 2.8 Hz, 1H), 6.89 (d, *J* 2.8 Hz, 1H), 6.42 (d, *J* 16 Hz, 1H), 5.72 (d, *J* 7.2 Hz, 1H), 3.94 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H);¹² ¹³C-NMR(acetone *d*₆, 100Hz): δ 164.2, 153.1, 150.6, 145.0, 149.7, 147.6, 133.5, 128.2, 127.9, 124.1, 123.1, 114.8, 113.7, 112.5, 112.5, 112.3, 111.3, 56.1, 56.1, 56.0, 56.0.

Nepetoidin B (*Z*, *E*)-1/(*E*, *E*)-1. To a stirred solution of quinoline (5.0 mL) in a 10 mL round bottom flask, Me₃SiI (1.0 mL) was added drop wise at 0 °C under an inert atmosphere of nitrogen. After 15 min, tetramethylated nepetoidin B (*Z*, *E*)-**5** (148 mg, 0.4 mmol) was added quickly. The reaction mixture was then warmed to 175 °C and stirred for 4 h at this temperature. After the reaction mixture was cooled to rt, it was quenched with HCl (30 mL, 1.0 mol/L) and stirred for 1h. The reaction mixture was extracted with EtOAc (30 mL) for three times. The organic layers were washed with NaCl aq. (30 mL). The organic layers were dried with MgSO₄ and evaporated under reduced pressure to provide a crude residue, which was purified via using CH₂Cl₂/MeOH (15:1) as eluent to afford the nepetoidin B (*Z*, *E*)-1/(*E*, *E*)-**1** as a yellow solid (77 mg, 61% yield). The ratio of isomers (*Z*, *E*)-1/(*E*, *E*)-**1** is 2.8:1, as determined by ¹H-NMR spectroscopic analysis (signals at 7.75 (d, *J* 16 Hz, 1H, H-7) and 7.82 (d, *J* 12.8 Hz, 1H, H-11) for the (*Z*, *E*)-1 and (*E*, *E*)-1 isomers, respectively).

(*Z*, *E*)-**1** : ¹H-NMR(acetone *d*₆, 400Hz): δ 7.75 (d, *J* 16 Hz, 1H), 7.38 (d, *J* 2.0 Hz, 1H), 7.27 (d, *J* 7.2 Hz, 1H), 7.26 (d, *J* 2.0 Hz, 1H), 7.14 (dd, *J* 8.2, 2.0 Hz, 1H), 7.02 (dd, *J* 8.0, 2.0 Hz, 1H), 6.91 (d, *J* 8.4 Hz, 1H), 6.83 (d, *J* 8.4 Hz, 1H), 6.51 (d, *J* 16 Hz, 1H), 5.68 (d, *J* 7.2 Hz, 1H); ¹³C-NMR(acetone *d*₆, 100Hz): δ 164.4, 149.2, 148.0, 146.3, 145.5,

145.5, 132.9, 127.5, 127.4, 123.2, 122.6, 117.0, 116.4, 116.0, 115.4, 114.0, 112.5. (*E, E*)-**1** : $^1\text{H-NMR}$ (acetone d_6 , 400Hz): δ 7.82 (d, J 12.8 Hz, 1H), 7.70 (d, J 16 Hz, 1H), 7.23 (d, J 2.0 Hz, 1H), 7.12 (dd, J 8.0, 2.0 Hz, 1H), 6.94 (m, 1H), 6.90 (d, J 8.4 Hz, 1H), 6.79 (m, 2H), 6.38 (d, J 12.8 Hz, 1H), 6.37 (d, J 16 Hz, 1H); $^{13}\text{C-NMR}$ (acetone d_6 , 100Hz): δ 164.8, 149.2, 147.7, 146.3, 146.1, 145.7, 135.4, 127.4, 127.3, 123.1, 119.3, 116.4, 116.4, 115.9, 115.4, 113.9, 113.6.^{5,15}

(*Z, E*)-**1** : $^1\text{H-NMR}$ (CD_3OD , 400Hz): δ 7.72 (d, J 16 Hz, 1H), 7.30 (d, J 2.0 Hz, 1H), 7.23 (d, J 7.2 Hz, 1H), 7.13 (d, J 2.0 Hz, 1H), 7.03 (dd, J 8.0, 2.0 Hz, 1H), 6.91 (dd, J 8.4, 2.0 Hz, 1H), 6.82 (d, J 8.0 Hz, 1H), 6.76 (d, J 8.4 Hz, 1H), 6.45 (d, J 16 Hz, 1H), 5.62 (d, J 7.2 Hz, 1H); $^{13}\text{C-NMR}$ (CD_3OD , 100Hz): δ 165.7, 149.8, 148.8, 148.8, 146.6, 145.8, 132.9, 127.8, 127.5, 123.4, 122.8, 117.2, 116.5, 116.1, 115.5, 113.6, 113.1. (*E, E*)-**1** : $^1\text{H-NMR}$ (CD_3OD , 400Hz): δ = 7.79 (d, J = 12.8 Hz, 1H), 7.66 (d, J = 15.6 Hz, 1H), 7.09 (d, J = 2.4 Hz, 1H), 6.99 (dd, J 8.2, 2.0 Hz, 1H), 6.84 (d, J 1.6 Hz, 1H), 6.80 (d, J 8.0 Hz, 1H), 6.73-6.70 (m, 2H), 6.35 (d, J 12.8 Hz, 1H), 6.32 (d, J 15.6 Hz, 1H); $^{13}\text{C-NMR}$ (CD_3OD , 100Hz): δ 166.3, 149.7, 148.4, 146.6, 146.3, 146.0, 145.8, 135.5, 119.7, 116.6, 116.5, 115.3, 113.6.⁸

Nepetoidin B (*E, E*)-**1**

To a stirred solution of quinoline (5.0 mL) in a 10 mL round bottom flask, Me_3SiI (1.0 mL) was added drop wise at 0 °C under an inert atmosphere of nitrogen. After 15 min, tetramethylated nepetoidin B (*E, E*)-**5** (148 mg, 0.4 mmol) was added quickly. The reaction mixture was then warmed to 175 °C and stirred for 4 h at this temperature. After the reaction mixture was cooled to rt, it was quenched with HCl (30 mL, 1.0 mol/L) and stirred for 1h. The reaction mixture was extracted with EtOAc (30 mL) for three times. The organic layers were washed with NaCl aq. (30 mL). The organic layers were dried with MgSO_4 and evaporated under reduced pressure to provide a crude residue, which was purified via using $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (15:1) as eluent to afford the nepetoidin B (*E, E*)-**1** as a yellow solid (74 mg, 59% yield). $^1\text{H-NMR}$ (acetone d_6 , 400Hz): δ 8.61 (s, 1H), 8.29 (s, 1H), 8.01 (s, 1H), 7.95 (s, 1H), 7.83 (d, J 12.8 Hz, 1H), 7.70 (d, J 16 Hz, 1H), 7.23 (d, J 2.0 Hz, 1H), 7.12 (dd, J 8.2, 2.0 Hz, 1H), 6.91 (m, 2H), 6.79 (m, 2H), 6.38 (d, J 12 Hz, 1H), 6.37 (d, J 16.4 Hz, 1H); $^{13}\text{C-NMR}$ (acetone d_6 , 100Hz): δ 164.8, 149.3, 147.7, 146.4, 146.2, 145.8, 135.4, 127.4, 127.3, 123.1, 119.3, 116.4, 116.4, 115.9, 115.4, 113.9, 113.6.^{5,15} $^1\text{H-NMR}$ (DMSO d_6 , 400Hz): δ 9.17 (br. s, 4H), 7.71 (d, J 12.8 Hz, 1H), 7.64 (d, J 15.8 Hz, 1H), 7.12 (d, J 2.0 Hz, 1H), 7.07 (dd, J 8.2, 2.0 Hz, 1H), 6.82 (s, 1H), 6.79 (d, J 8.1 Hz, 1H), 6.69 (m, 2H), 6.37 (d, J 12.8 Hz, 1H), 6.36 (d, J 16 Hz, 1H); $^{13}\text{C-NMR}$ (DMSO d_6 , 100Hz): δ 164.1, 149.0, 147.2, 145.69, 145.5, 145.2, 134.2, 125.4, 125.1, 12.0, 118.0, 159.9, 115.8, 115.4, 115.1, 113.1, 112.3.

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Supplementary Material

Characterization data, copies of ^1H and ^{13}C NMR spectra associated with article can be found in the online version.

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