SUPPLEMENTARY MATERIAL

(±) Benzomalvins E isolated from Penicillium sp. SYPF 8411 in the rhizosphere soil of Codonopsis clematidea

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Abstract

(+) Benzomalvins E (1) and (-) Benzomalvins E (2), a pair of epimeric derivatives, together with three known benzomalvins (3-5), were isolated from solid cultures of an interrhizospheric fungus Penicillium sp. SYPF 8411. The planar structure of (+) Benzomalvins E (1) has been previously reported. While, the absolute configuration of compound 1 was established by X-ray crystallographic analysis for the first time. The planar structure of the new compound 2 were elucidated by detailed interpretation of their HR ESI-TOF MS and NMR spectroscopic data. The absolute configuration of compound 2 was established by Rh2(OOCF3)4-induced CD spectral data and the electronic circular dichroic (ECD) method. Furthermore, the epimerization induced by pH, temperature and H2O was revealed. Benzomalvins (1-5), a type of indoximod, enhanced the cytotoxic capability of 5-fluorouracil against A549.

Keywords: benzodiazepine alkaloid; benzomalvin; Penicillium sp.; X-ray crystallography; cytotoxic capability.
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1 pH-, H2O- and temperature-dependent epimerization effect

Two single epimers, (+) Benzomalvins (1) and (-) Benzomalvins (2), were successfully separated by HPLC employing a YMC C18 HPLC column (250×4.6mm, 5μm) with 58% MeOH-H2O at a flow rate of 0.4 mL·min⁻¹.

![Figure S1. HPLC spectra of 1 and 2 on YMC C18 HPLC column (250×4.6mm, 5μm) with 58% MeOH-H2O at a flow rate of 0.4 mL·min⁻¹.](image)

1.1 pH-dependent epimerization effect:

![Figure S2. HPLC spectra of compound 1 dissolved in anhydrous methanol at pH = 8.0, 7.0, 6.0.](image)
Figure S3. HPLC spectra of compound 2 dissolved in anhydrous methanol at pH = 8.0, 7.0, 6.0.

1.2 Temperature-dependent epimerization effect:
b) control

-20°C 5h
-20°C 15h
-20°C 36h
4°C 5h
4°C 15h
4°C 36h

(c) 20°C 72h
20°C 60h
20°C 48h
20°C 36h
20°C 24h
20°C 10h
20°C 5h
20°C 3h

(d) control

-20°C 2h
4°C 2h
20°C 2h
30°C 2h
Figure S4. HPLC spectra: a) 2 dissolved in anhydrous methanol heating at -20, 4, 20, 30 °C; b) 2 dissolved in anhydrous methanol heating at -20, 4 °C; c) 2 dissolved in anhydrous ethanol heating at 20 °C; d) 1 dissolved in anhydrous methanol heating at -20, 4, 20, 30 °C; e) 1 and 2 dissolved in anhydrous methanol heating at 20 °C.

1.3 H2O-dependent epimerization effect:

Figure S5. HPLC spectra of 1 dissolved in H2O heating at 28 °C
**Figure S6.** HPLC chromatogram of 1 dissolved in the mixed solution of methanol and H₂O heating at 20 °C for 6h

**Figure S7.** HPLC chromatogram of 2 dissolved in the mixed solution of methanol and H₂O heating at 20 °C for 6h

**2 The spectra of (+) Benzomalvin E (1)**

A white crystal; \([\alpha]_D^{20} +107.7\) (c 0.0018, CH₃OH); IR (KBr) \(v_{\text{max}}\): 3449, 1697, 1632, 1596 cm⁻¹; HR ESI-TOF MS \(m/z 398.1499\) [M+H]⁺ (calcd for C₂₄H₂₀N₃O₃ 398.1497).

**Table S1:** \(^1\)H and \(^{13}\)C NMR data for compound 1 and 2 (CDCl₃).
| Position | $\delta C_1$ | $\delta H_1$ ($J$ in Hz) | $\delta C_2$ | $\delta H_2$ ($J$ in Hz) |
|----------|-------------|------------------------|-------------|------------------------|
| 1        |             |                        |             |                        |
| 2        | 165.5       |                        | 167.3       |                        |
| 3        | 132.0       |                        | 131.4       |                        |
| 4        | 131.0       | 8.03 brd (7.70)        | 130.1       | 7.90 brd (7.50)        |
| 5        | 129.4       | 7.62 t (7.56)          | 129.1       | 7.55 t (7.67)          |
| 6        | 131.2       | 7.72 t (7.60)          | 130.9       | 7.59 t                 |
| 7        | 128.7       | 7.60 d (8.02)          | 127.9       | 7.53 t (7.88)          |
| 8        | 133.0       |                        | 132.6       |                        |
| 9        |             |                        |             |                        |
| 10       | 161.4       |                        | 160.7       |                        |
| 11       | 121.1       |                        | 121.5       |                        |
| 12       | 127.4       | 8.22 brd (7.91)        | 127.6       | 8.29 brd (7.85)        |
| 13       | 127.8       | 7.50 t (7.72)          | 127.2       | 7.74 brd (7.85)        |
| 14       | 135.0       | 7.69 t (7.72)          | 135.0       | 7.82 t (7.16)          |
| 15       | 127.6       | 7.47 d (8.17)          | 127.3       | 7.59 d                 |
| 16       | 146.4       |                        | 145.0       |                        |
| 17       |             |                        |             |                        |
| 18       | 152.1       |                        | 152.4       |                        |
| 19       | 75.6        | 4.82 d (9.96)          | 60.3        | 4.84 d (6.17)          |
| 20       | 73.2        | 4.12 d (9.96)          | 71.0        | 5.70 d (6.17)          |
| 21       | 138.9       |                        | 139.5       |                        |
| 22       | 126.5       | 7.05 d (6.91)          | 126.6       | 7.41 d (7.50)          |
| 23       | 128.8       | 7.20 brt (7.38)        | 128.6       | 7.28 brt (7.18)        |
| 24       | 129.2       | 7.18 t (6.89)          | 128.1       | 7.24 t (7.25)          |
| 25       | 128.8       | 7.20 brt (7.38)        | 128.6       | 7.28 brt (7.18)        |
| 26       | 126.5       | 7.05 d (6.91)          | 126.6       | 7.41 d (7.50)          |
| 27       | 39.1        | 3.43 s                 | 29.3        | 3.25 s                 |
2.1 X-ray crystallographic analysis for compound 1

**Figure S8.** Diamond plot of X-ray crystal structure for 1.

**Table S2:** Crystal data and structure refinement for exp_5540

| Property                                | Value                                                                 |
|------------------------------------------|-----------------------------------------------------------------------|
| Identification code                      | exp_5540                                                              |
| Empirical formula                        | C_{24}H_{19}N_{3}O_{3}                                                  |
| Formula weight                           | 397.42                                                               |
| Temperature / K                          | 108.00(14)                                                           |
| Crystal system                           | monoclinic                                                            |
| Space group                              | P2₁                                                                  |
| a / Å, b / Å, c / Å                      | 6.27136(18), 12.6695(4), 12.2696(4)                                  |
| α°, β°, γ°                               | 90, 97.911(3), 90                                                   |
| Volume / Å³                              | 965.61(6)                                                            |
| Z                                        | 2                                                                    |
| ρ_{calc} / mg mm⁻³                       | 1.367                                                                |
| μ / mm⁻¹                                 | 0.746                                                                |
| F(000)                                   | 416                                                                  |
| Crystal size / mm³                       | 0.450 × 0.250 × 0.240                                                 |
2Θ range for data collection  13.98 to 142.198°

Index ranges  
-7 ≤ h ≤ 3, -15 ≤ k ≤ 15, -14 ≤ l ≤ 15

Reflections collected  5927

Independent reflections  3621 [R(int) = 0.0239 (inf-0.9Å)]

Data/restraints/parameters  3621/1/273

Goodness-of-fit on F^2  1.047

Final R indexes [I＞2σ (I) i.e. F_o＞4σ (F_o)]  
R_1 = 0.0334, wR_2 = 0.0863

Final R indexes [all data]  
R_1 = 0.0341, wR_2 = 0.0870

Largest diff. peak/hole / e Å^3  0.186/-0.213

Flack Parameters  0.07(10)

Completeness  0.9972

**Table S3:** Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_5540. U(eq) is defined as 1/3 of of the trace of the orthogonalised U_ij tensor.

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| O3   | -3268(3) | -3198.2(14) | -227.0(13) | 21.5(4) |
| O1   | -4148(3) | -6605.3(13) | 1256.2(14) | 21.1(4) |
| N1   | -4953(3) | -3051.2(15) | 2918.9(16) | 16.5(4) |
| O2   | -1849(3) | -4917.5(13) | 5349.4(13) | 21.3(4) |
| C11  | -4563(3) | -3642.2(18) | 4828.5(19) | 16.2(4) |
| N3   | -4085(3) | -4809.2(15) | 1216.9(15) | 16.0(4) |
| C10  | -2793(4) | -4348.5(17) | 4648.4(18) | 15.0(4) |
| C1   | -3421(3) | -3676.4(18) | 2758.1(18) | 14.0(4) |
| N2   | -2307(3) | -4342.8(15) | 3549.4(15) | 13.6(4) |
| C2   | -2902(3) | -3839.5(17) | 1602.7(18) | 14.9(4) |
| C12  | -5593(4) | -3030.4(18) | 3961.7(19) | 16.3(4) |
| C16  | -5299(4) | -3639.1(19) | 5854(2)    | 18.9(5) |
| C15  | -7049(4) | -3020(2)   | 6012(2)    | 22.2(5) |
| C13  | -7358(4) | -2401.0(19) | 4127(2)    | 20.7(5) |
| C23  | 17(4)   | -1893(2)   | 823.2(19)  | 20.5(5) |
| C3   | -3289(4) | -5757.8(19) | 1565.8(18) | 16.1(4) |
| C14  | -8074(4) | -2405.4(19) | 5148(2)    | 23.0(5) |
| C9   | 275(4)   | -6542.7(19) | 2165.9(19) | 18.6(5) |
| C6   | 1219(3)  | -5178.3(18) | 3934.8(19) | 16.6(5) |
| C19  | -2502(4) | -1175.3(19) | 1938(2)    | 20.8(5) |
| C5   | -747(3)  | -5095.2(17) | 3257.9(17) | 13.7(4) |
| C24  | -6308(4) | -4715(2)   | 667(2)     | 22.0(5) |
|   |   |   |   |   |
|---|---|---|---|---|
| C21 | 792(4) | -243(2) | 1774(2) | 26.8(6) |
| C8  | 2220(4) | -6628.5(19) | 2846(2) | 21.2(5) |
| C7  | 2698(3) | -5942.5(19) | 3730(2) | 19.6(5) |
| C22 | 1368(4) | -1029(2) | 1081(2) | 25.7(6) |
| C20 | -1115(4) | -331(2) | 2215(2) | 25.7(5) |
| C4  | -1228(3) | -5770.1(18) | 2350.7(18) | 14.7(4) |
| C18 | -1945(4) | -1962.7(18) | 1229.9(18) | 16.6(5) |
| C17 | -3470(4) | -2872.8(17) | 866.2(18) | 16.2(5) |

**Figure S9.** The IR spectrum of compound 1
Figure S10. The HR ESI-TOF MS spectrum of compound 1
Figure S11. The $^1$H-NMR spectrum (CDCl$_3$, 600MHz) of compound 1

Figure S12. The $^{13}$C-NMR spectrum (CDCl$_3$, 150MHz) of compound 1
Figure S13. The HSQC spectrum (CDCl$_3$, 600MHz) of compound 1
The energy-minimized conformers of compound 1 were generated via the Dreiding force field in MarvinSketch, and the geometries were further optimized at the B3LYP/6-31G (d) level in methanol with the integral equation formalism variant polarizable continuum model (IEF-PCM) without vibrational imaginary frequencies. The predominant conformer of Compound 1 were subjected to the theoretical calculation of ECD spectra at the RB3LYP/6-31G (d, p) level using the time dependent density functional theory (TDDFT) method. Compound 1 was drawn via SpecDic software with sigma = 0.3 and UV shift = 10 nm.

**Table S4:** Experimental CD spectra data for compound 1 (CH$_3$OH).

| Lambda | Delta | Lambda | Delta | Lambda | Delta | Lambda | Delta |
|--------|-------|--------|-------|--------|-------|--------|-------|
| 190    | -11.8197 | 243    | 25.5314 | 296    | 10.4567 | 349    | -0.36555 |
| 191    | -12.754  | 244    | 22.1014 | 297    | 10.9614 | 350    | -0.35858 |
| 192    | -12.3184 | 245    | 18.1821 | 298    | 11.5189 | 351    | -0.34919 |
|   |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|
| 193 | -10.7611 | 246 | 13.9821 | 299 | 12.1272 |
| 194 | -8.32984 | 247 | 9.58089 | 300 | 12.7843 |
| 195 | -5.27272 | 248 | 5.15408 | 301 | 13.4922 |
| 196 | -1.83768 | 249 | 0.753744 | 302 | 14.2511 |
| 197 | 1.72732 | 250 | -3.60741 | 303 | 15.0577 |
| 198 | 5.1118 | 251 | -7.92186 | 304 | 15.9043 |
| 199 | 7.92176 | 252 | -12.1146 | 305 | 16.7839 |
| 200 | 9.9472 | 253 | -16.0782 | 306 | 17.6803 |
| 201 | 11.0069 | 254 | -19.7409 | 307 | 18.5688 |
| 202 | 11.1728 | 255 | -23.0581 | 308 | 19.4195 |
| 203 | 10.5588 | 256 | -25.9223 | 309 | 20.2016 |
| 204 | 9.26026 | 257 | -28.2154 | 310 | 20.8821 |
| 205 | 7.55332 | 258 | -29.8346 | 311 | 21.4323 |
| 206 | 5.48178 | 259 | -30.7146 | 312 | 21.8316 |
| 207 | 3.25475 | 260 | -30.8073 | 313 | 22.0731 |
| 208 | 1.27246 | 261 | -30.128 | 314 | 22.1629 |
| 209 | -0.29486 | 262 | -28.7015 | 315 | 22.1222 |
| 210 | -1.32232 | 263 | -26.6413 | 316 | 21.9779 |
| 211 | -1.76364 | 264 | -24.0724 | 317 | 21.7649 |
| 212 | -1.68789 | 265 | -21.1423 | 318 | 21.518 |
| 213 | -1.26423 | 266 | -18.0028 | 319 | 21.2659 |
| 214 | -0.54345 | 267 | -14.8007 | 320 | 21.0219 |
| 215 | 0.280961 | 268 | -11.6722 | 321 | 20.7823 |
| 216 | 1.26025 | 269 | -8.72555 | 322 | 20.5267 |
| 217 | 2.2128 | 270 | -6.02897 | 323 | 20.2205 |
| 218 | 3.02738 | 271 | -3.63169 | 324 | 19.8179 |
| 219 | 3.77632 | 272 | -1.55898 | 325 | 19.2691 |
| 220 | 4.41992 | 273 | 0.198827 | 326 | 18.5338 |
| 221 | 5.12655 | 274 | 1.66679 | 327 | 17.5852 |
| 222 | 6.10023 | 275 | 2.88754 | 328 | 16.4158 |
| 223 | 7.21743 | 276 | 3.9014 | 329 | 15.0396 |
| 224 | 8.4299 | 277 | 4.75017 | 330 | 13.4909 |
| 225 | 9.75123 | 278 | 5.47576 | 331 | 11.8264 |
| 226 | 11.265 | 279 | 6.10537 | 332 | 10.1116 |
| 227 | 12.9798 | 280 | 6.65075 | 333 | 8.41636 |
| 228 | 14.8936 | 281 | 7.12204 | 334 | 6.80638 |
| 229 | 16.854 | 282 | 7.52124 | 335 | 5.33604 |
| 230 | 18.8903 | 283 | 7.84788 | 336 | 4.04292 |
| 231 | 20.8715 | 284 | 8.10343 | 337 | 2.94747 |
| 232 | 22.873 | 285 | 8.28972 | 338 | 2.05171 |
| 233 | 24.8758 | 286 | 8.41795 | 339 | 1.34523 |
| 234 | 26.8737 | 287 | 8.50654 | 340 | 0.810171 |
| 235 | 28.8323 | 288 | 8.57546 | 341 | 0.417479 |
| 236 | 30.5956 | 289 | 8.64796 | 342 | 0.137819 |
The spectra of (-) Benzomalvin E (2)

\[(R^*, R^*), J = 9.96\text{Hz}\]

\[(S^*, R^*), J = 6.17\text{Hz}\]

Figure S16. Threo- and erythro-configurations of compound 1 and 2, respectively.

Figure S17. The IR spectrum of compound 2
Figure S18. The HR ESI-TOF MS spectrum of compound 2
Figure S19. The $^1$H-NMR spectrum (CDCl$_3$, 400MHz) of compound 2

Figure S20. The $^{13}$C-NMR spectrum (CDCl$_3$, 100MHz) of compound 2
Figure S21. The HSQC spectrum (CDCl₃, 600MHz) of compound 2
**Figure S22.** The HMBC spectrum (CDCl₃, 600MHz) of compound 2

**Figure S23.** Calculated and experimental ECD spectra of 2(CH₃OH).

In order to further verified the absolute configuration of compound 2, the ECD spectra of (19S,20S)-2 and it’s enantiomer were calculated at B3LYP/6-31G (d) level in methanol on the base of TDDFT method. Compound 2 was drawn via SpecDic software with sigma = 0.2 and UV shift = -8 nm. The ECD spectrum of 2 showed a positive Cotton effect at 260 nm, and a negative Cotton effect at 230 nm and 278 nm (Fig.4a).

**Table S5:** Experimental CD spectra data for compound 2 (CH₃OH).

| Number | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|--------|---------|---------|---------|---------|---------|---------|
| 190    | 25.4324 | 243     | -13.0404| 296     | -10.8861| 349     | -2.432 |
| 191    | 12.2308 | 244     | -9.40697| 297     | -10.6224| 350     | -2.46023|
| 192    | 2.69062 | 245     | -5.96551| 298     | -10.4515| 351     | -2.4873 |
| 193    | -3.66803| 246     | -2.74772| 299     | -10.3708| 352     | -2.51058|
| 194    | -7.32484| 247     | 0.237654| 300     | -10.3765| 353     | -2.52789|
| 195    | -8.75955| 248     | 2.9926  | 301     | -10.462 | 354     | -2.53798|
| 196    | -8.45191| 249     | 5.52357 | 302     | -10.6181| 355     | -2.54065|
| 197    | -6.88167| 250     | 7.8395  | 303     | -10.8317| 356     | -2.53649|
| 198    | -4.82267| 251     | 9.95167 | 304     | -11.0868| 357     | -2.52684|
|   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|
| 199 | -2.7171 | 252 | 11.8642 | 305 | -11.3647 | 358 | -2.51379 |
| 200 | -0.93452 | 253 | 13.5689 | 306 | -11.6446 | 359 | -2.49995 |
| 201 | 0.286825 | 254 | 15.0449 | 307 | -11.9064 | 360 | -2.48809 |
| 202 | 0.848687 | 255 | 16.2582 | 308 | -12.1316 | 361 | -2.48011 |
| 203 | 0.776782 | 256 | 17.1709 | 309 | -12.3059 | 362 | -2.47668 |
| 204 | 0.202814 | 257 | 17.7446 | 310 | -12.42 | 363 | -2.47772 |
| 205 | -0.65505 | 258 | 17.9446 | 311 | -12.4712 | 364 | -2.48202 |
| 206 | -1.59408 | 259 | 17.7451 | 312 | -12.4626 | 365 | -2.48745 |
| 207 | -2.38485 | 260 | 17.1325 | 313 | -12.4019 | 366 | -2.49142 |
| 208 | -2.84173 | 261 | 16.1041 | 314 | -12.3003 | 367 | -2.49116 |
| 209 | -2.85475 | 262 | 14.6708 | 315 | -12.1697 | 368 | -2.48435 |
| 210 | -2.36055 | 263 | 12.86 | 316 | -12.0201 | 369 | -2.46983 |
| 211 | -1.34729 | 264 | 10.7155 | 317 | -11.8574 | 370 | -2.44756 |
| 212 | 0.124934 | 265 | 8.29527 | 318 | -11.6824 | 371 | -2.41885 |
| 213 | 1.96089 | 266 | 5.66681 | 319 | -11.4906 | 372 | -2.38632 |
| 214 | 4.05087 | 267 | 2.90557 | 320 | -11.2727 | 373 | -2.35371 |
| 215 | 6.28127 | 268 | 0.090009 | 321 | -11.0134 | 374 | -2.32536 |
| 216 | 8.53046 | 269 | -2.70296 | 322 | -10.7006 | 375 | -2.30504 |
| 217 | 10.6499 | 270 | -5.40109 | 323 | -10.321 | 376 | -2.29555 |
| 218 | 12.4802 | 271 | -7.94075 | 324 | -9.86647 | 377 | -2.2987 |
| 219 | 13.8652 | 272 | -10.2694 | 325 | -9.33479 | 378 | -2.31476 |
| 220 | 14.6541 | 273 | -12.3471 | 326 | -8.73104 | 379 | -2.34261 |
| 221 | 14.7269 | 274 | -14.1478 | 327 | -8.06799 | 380 | -2.37978 |
| 222 | 13.9574 | 275 | -15.6599 | 328 | -7.36528 | 381 | -2.42291 |
| 223 | 12.2538 | 276 | -16.8838 | 329 | -6.64705 | 382 | -2.46852 |
| 224 | 9.60286 | 277 | -17.8299 | 330 | -5.93883 | 383 | -2.51332 |
| 225 | 6.0521 | 278 | -18.5152 | 331 | -5.26525 | 384 | -2.55414 |
| 226 | 1.70741 | 279 | -18.9609 | 332 | -4.6482 | 385 | -2.58855 |
| 227 | -3.25075 | 280 | -19.1899 | 333 | -4.1043 | 386 | -2.61482 |
| 228 | -8.58228 | 281 | -19.224 | 334 | -3.64305 | 387 | -2.6322 |
| 229 | -14.0062 | 282 | -19.0843 | 335 | -3.26739 | 388 | -2.64035 |
| 230 | -19.228 | 283 | -18.7917 | 336 | -2.97421 | 389 | -2.6393 |
| 231 | -23.9718 | 284 | -18.3665 | 337 | -2.7553 | 390 | -2.6295 |
| 232 | -27.9817 | 285 | -17.8283 | 338 | -2.59913 | 391 | -2.61179 |
| 233 | -31.049 | 286 | -17.1984 | 339 | -2.49263 | 392 | -2.58719 |
| 234 | -33.0362 | 287 | -16.4995 | 340 | -2.4234 | 393 | -2.55694 |
| 235 | -33.8893 | 288 | -15.7564 | 341 | -2.38112 | 394 | -2.52237 |
| 236 | -33.6467 | 289 | -14.9945 | 342 | -2.35771 | 395 | -2.48573 |
| 237 | -32.4022 | 290 | -14.2388 | 343 | -2.34726 | 396 | -2.44852 |
| 238 | -30.2906 | 291 | -13.5124 | 344 | -2.34583 | 397 | -2.41225 |
| 239 | -27.4856 | 292 | -12.8354 | 345 | -2.35145 | 398 | -2.3784 |
| 240 | -24.1762 | 293 | -12.2241 | 346 | -2.36364 | 399 | -2.34849 |
| 241 | -20.5535 | 294 | -11.6905 | 347 | -2.38197 | 400 | -2.32399 |
| 242 | -16.7927 | 295 | -11.2428 | 348 | -2.40526 | | |
Figure S24. The CD spectrum of compound 2 in a CH₂Cl₂ of [Rh₂(OCOCF₃)₄].

Table S6: Experimental CD spectra data (A) and the [Rh2(OCOCF3)4]-induced CD spectra data (B) for compound 2 (CH₂Cl₂).

|   | CD(A) | induced CD(B) | D-value(B-A) |
|---|-------|---------------|--------------|
| 190 | 27.4324 | 14.3371       | -13.0953     |
| 191 | 14.2308 | 2.7011        | -11.5297     |
| 192 | 4.69062 | -5.5978       | -10.2884     |
| 193 | -1.66803 | -10.9981     | -9.33007     |
| 194 | -5.32484 | -13.9385     | -8.61366     |
| 195 | -6.75955 | -14.8573     | -8.09775     |
| 196 | -6.45191 | -14.1932     | -7.74129     |
| 197 | -4.88167 | -12.3847     | -7.50303     |
| 198 | -2.82267 | -10.1288     | -7.30613     |
| 199 | -0.7171 | -7.80395     | -7.08685     |
| 200 | 1.06548 | -5.76494     | -6.83042     |
| 201 | 2.28682 | -4.35633     | -6.64316     |
| 202 | 2.84869 | -3.64718     | -6.49587     |
| 203 | 2.77678 | -3.62654     | -6.40332     |
| 204 | 2.20281 | -4.23884     | -6.44165     |
| 205 | 1.34495 | -5.25286     | -6.59781     |
| 206 | 0.40592 | -6.28657     | -6.69249     |
| 207 | -0.38485 | -7.1937     | -6.80885     |
| 208 | -0.84173 | -7.75608     | -6.91435     |
| 209 | -0.85475 | -7.91445     | -7.0597      |
| 210 | -0.36055 | -7.58926     | -7.22871     |
| 211 | 0.65271 | -6.88479     | -7.5375      |
| 212 | 2.12493 | -6.05936     | -8.18429     |
| 213 | 3.96089 | -5.12041     | -9.0813      |
| 214 | 6.05087 | -4.21238     | -10.2633     |
|   |      |      |      |      |
|---|------|------|------|------|
| 215 | 8.28127 | -3.43844 | -11.7197 |
| 216 | 10.53046 | -2.65062 | -13.1811 |
| 217 | 12.6499 | -1.85314 | -14.5030 |
| 218 | 14.4802 | -1.07066 | -15.5509 |
| 219 | 15.8652 | 0.16085  | -16.0261 |
| 220 | 16.6541 | 0.92575  | -15.7284 |
| 221 | 16.7269 | 1.97659  | -14.7503 |
| 222 | 15.9574 | 2.97235  | -12.9851 |
| 223 | 14.2538 | 3.7179   | -10.5359 |
| 224 | 11.60286| 4.0758   | -7.52706 |
| 225 | 8.0521 | 3.83083  | -4.22127 |
| 226 | 3.70741 | 2.94553  | -0.76188 |
| 227 | -1.25075| 1.49019  | 2.74094 |
| 228 | -6.58228| -0.47781 | 6.10447 |
| 229 | -12.0062| -2.7668  | 9.2394 |
| 230 | -17.2282| -5.17861 | 12.04959|
| 231 | -21.9718| -7.61883 | 14.35297|
| 232 | -25.9817| -9.99806 | 15.98364|
| 233 | -29.049 | -12.1837 | 16.8653 |
| 234 | -31.0362| -14.1661 | 16.8701 |
| 235 | -31.8893| -16.0081 | 15.8812 |
| 236 | -31.6467| -17.689  | 13.9577 |
| 237 | -30.4022| -19.3274 | 11.0748 |
| 238 | -28.2906| -20.97   | 7.3206  |
| 239 | -25.4856| -22.5882 | 2.8974  |
| 240 | -22.1762| -24.0371 | -1.8609 |
| 241 | -18.5535| -25.2054 | -6.6519 |
| 242 | -14.7927| -25.8618 | -11.0691|
| 243 | -11.0404| -25.8352 | -14.7948|
| 244 | -7.40697 | -25.0151 | -17.6081|
| 245 | -3.96551 | -23.313 | -19.3658|
| 246 | 0.74772  | -20.761  | -20.0133|
| 247 | 2.23765  | -17.3276 | -19.5653|
| 248 | 4.9926   | -13.1633 | -18.1559|
| 249 | 7.52357  | -8.47342 | -15.997 |
| 250 | 9.8395   | -3.49683 | -13.3363|
| 251 | 11.95167 | 1.42762  | -10.4791|
| 252 | 13.8642  | 6.16967  | -7.69453|
| 253 | 15.5689  | 10.4042  | -5.1647 |
| 254 | 17.0449  | 14.0361  | -3.0088 |
| 255 | 18.2582  | 16.977   | -1.2812 |
| 256 | 19.1709  | 19.2147  | 0.0438  |
| 257 | 19.7446  | 20.7244  | 0.9798  |
| 258 | 19.9446  | 21.5459  | 1.6013  |
|   |       |       |       |
|---|-------|-------|-------|
| 259 | 19.7451 | 21.7324 | 1.9873 |
| 260 | 19.1325 | 21.366  | 2.2335 |
| 261 | 18.1041 | 20.5224 | 2.4183 |
| 262 | 16.6708 | 19.2439 | 2.5731 |
| 263 | 14.86   | 17.587  | 2.727  |
| 264 | 12.7155 | 15.6023 | 2.8868 |
| 265 | 10.2952 | 13.3191 | 3.02383|
| 266 | 7.66681 | 10.7736 | 3.10679|
| 267 | 4.90557 | 8.03131 | 3.12574|
| 268 | -0.70296| 2.27157 | 2.97453|
| 269 | -3.40109| -0.59078| 2.81031|
| 270 | -5.94075| -3.34276| 2.59799|
| 271 | -8.2694 | -5.91135| 2.35805|
| 272 | -10.3471| -8.24904| 2.09806|
| 273 | -12.1478| -10.3056| 1.8422 |
| 274 | -13.6599| -12.0723| 1.5876 |
| 275 | -14.8838| -13.5621| 1.3217 |
| 276 | -15.8299| -14.7818| 1.0481 |
| 277 | -16.5152| -15.7634| 0.7518 |
| 278 | -16.9609| -16.5412| 0.4197 |
| 279 | -17.1899| -17.1466| 0.0433 |
| 280 | -17.224 | -17.6028| -0.3788|
| 281 | -17.0843| -17.9172| -0.8329|
| 282 | -16.7917| -18.0932| -1.3015|
| 283 | -16.3665| -18.1314| -1.7649|
| 284 | -15.8283| -18.0282| -2.1999|
| 285 | -15.1984| -17.7831| -2.5847|
| 286 | -14.4995| -17.3986| -2.8991|
| 287 | -13.7564| -16.8812| -3.1248|
| 288 | -12.9945| -16.2549| -3.2604|
| 289 | -12.2388| -15.5477| -3.3089|
| 290 | -11.5124| -14.7837| -3.2713|
| 291 | -10.8354| -13.9916| -3.1562|
| 292 | -10.2241| -13.1922| -2.9681|
| 293 | -9.6905 | -12.4093| -2.7188|
| 294 | -9.2428 | -11.6594| -2.4166|
| 295 | -8.8861 | -10.9491| -2.063 |
| 296 | -8.6224 | -10.2877| -1.6653|
| 297 | -8.4515 | -9.68015| -1.22865|
| 298 | -8.3708 | -9.13471| -0.76391|
| 299 | -8.3765 | -8.65263| -0.27613|
| 300 | -8.462  | -8.23424| 0.2276 |
| 301 | -8.6181 | -7.88003| 0.73807|
|   |   |   |   |
|---|---|---|---|
|303| -8.8317| -7.5905| 1.2412 |
|304| -9.0868| -7.36188| 1.72492 |
|305| -9.3647| -7.18116| 2.18354 |
|306| -9.6446| -7.03384| 2.61076 |
|307| -9.9064| -6.90219| 3.00421 |
|308| -10.1316| -6.77395| 3.35765 |
|309| -10.3059| -6.63606| 3.66984 |
|310| -10.42| -6.48289| 3.93711 |
|311| -10.4712| -6.31875| 4.15245 |
|312| -10.4626| -6.14747| 4.31513 |
|313| -10.4019| -5.98367| 4.41823 |
|314| -10.3003| -5.83638| 4.46392 |
|315| -10.1697| -5.71529| 4.45441 |
|316| -10.0201| -5.62986| 4.39024 |
|317| -9.8574| -5.58155| 4.27585 |
|318| -9.6824| -5.56104| 4.12136 |
|319| -9.4906| -5.5362| 3.93698 |
|320| -9.272| -5.54019| 3.73181 |
|321| -9.0134| -5.49476| 3.51864 |
|322| -8.7006| -5.39657| 3.30403 |
|323| -8.321| -5.22643| 3.09457 |
|324| -7.86647| -4.97755| 2.88892 |
|325| -7.33479| -4.65112| 2.68367 |
|326| -6.73104| -4.25383| 2.47721 |
|327| -6.06799| -3.8049| 2.26309 |
|328| -5.36528| -3.32395| 2.04133 |
|329| -4.64705| -2.83682| 1.81023 |
|330| -3.93883| -2.37178| 1.56705 |
|331| -3.26525| -1.95038| 1.31487 |
|332| -2.6482| -1.59042| 1.05778 |
|333| -2.1043| -1.30422| 0.80008 |
|334| -1.64305| -1.09329| 0.54976 |
|335| -1.26739| -0.94853| 0.31886 |
|336| -0.97421| -0.86286| 0.11136 |
|337| -0.7553| -0.82373| -0.06843 |
|338| -0.59913| -0.81957| -0.22044 |
|339| -0.49263| -0.83775| -0.34512 |
|340| -0.4234| -0.8653| -0.4419 |
|341| -0.38112| -0.8939| -0.51278 |
|342| -0.35771| -0.91798| -0.56027 |
|343| -0.34726| -0.93466| -0.5874 |
|344| -0.34583| -0.94434| -0.59851 |
|345| -0.35145| -0.94775| -0.5963 |
|346| -0.36364| -0.94871| -0.58507 |
| 391 | -0.61179 | -0.05681 | 0.55498 |
| 392 | -0.58719 | -0.03393 | 0.55326 |
| 393 | -0.55694 | -0.00502 | 0.55192 |
| 394 | -0.52237 | 0.02823  | 0.5506  |
| 395 | -0.48573 | 0.06129  | 0.54702 |
| 396 | -0.44852 | 0.09182  | 0.54034 |
| 397 | -0.41225 | 0.11749  | 0.52974 |
| 398 | -0.3784  | 0.13596  | 0.51436 |
| 399 | -0.34849 | 0.1449   | 0.49339 |
| 400 | -0.32399 | 0.14197  | 0.46596 |

4 The spectra of Benzomalvin C (3)
Figure S25. The $^1$H-NMR spectrum (CDCl$_3$, 400MHz) of compound 3

Figure S26. The $^{13}$C-NMR spectrum (CDCl$_3$, 100MHz) of compound 3
5 The spectra of N-Methylnovobenzomalvin A (4)

Figure S27. The $^1$H-NMR spectrum (CDCl$_3$, 400MHz) of compound 4

Figure S28. The $^{13}$C-NMR spectrum (CDCl$_3$, 100MHz) of compound 4
6 The spectra of (-) benzomalvin A (5)

Figure S29. The $^1$H-NMR spectrum (CDCl$_3$, 400MHz) of compound 5

Figure S30. The $^{13}$C-NMR spectrum (CDCl$_3$, 100MHz) of compound 5