# Supporting Information

# OSMAC-Based Discovery and Biosynthetic Gene Clusters Analysis of Secondary Metabolites from Marine-Derived *Streptomyces globisporus* SCSIO LCY30

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**Table S1.** The antiSMASH-predicted BGCs for *Streptomyces* sp. SCSIO LCY30

| BGC | From | To | Type | Most similar known cluster | Similarity |
|---|---|---|---|---|---|
| Cluster1 | 111,597 | 131,563 | terpene | 2-methylisoborneol | 100% |
| Cluster2 | 175,613 | 185,779 | butyrolactone | coelimycin P1 | 16% |
| Cluster3 | 213,615 | 280,831 | NRPS, terpene, NAPAA | stenothricin | 13% |
| Cluster4 | 307,996 | 353,352 | NRPS | streptobactin | 100% |
| Cluster5 | 360,960 | 410,654 | NRPS | coelichelin | 81% |
| Cluster6 | 411,713 | 485,146 | terpene, NRPS | isorenieratene | 100% |
| Cluster7 | 496,705 | 535,481 | T3PKS | herboxidiene | 7% |
| Cluster8 | 1,133,865 | 1,152,667 | terpene | steffimycin D | 19% |
| Cluster9 | 1,585,298 | 1,595,726 | ecotine | ectoine | 100% |
| Cluster10 | 2,213,771 | 2,286,646 | NRPS, NRPS-like, T3PKS | viguiepinol | 73% |
| Cluster11 | 2,608,509 | 2,638,799 | lanthipeptide-class-ii, lanthipeptide-class-iii | | |
| Cluster12 | 2,693,162 | 2,703,155 | siderophore | desferrioxamin B | 100% |
| Cluster13 | 3,096,186 | 3,128,710 | thiopeptide, LAP | | |
| Cluster14 | 3,806,311 | 3,829,364 | lanthipeptide-class-i | | |
| Cluster15 | 4,456,955 | 4,479,652 | lassopeptide | keywimysin | 100% |
| Cluster16 | 4,612,207 | 4,621,963 | butyrolactone | kedarcidin | 1% |
| Cluster17 | 5,195,441 | 5,236,957 | T1PKS | | |
| Cluster18 | 5,332,444 | 5,355,164 | lanthipeptide-class-iii | AmfS | 100% |
| Cluster19 | 5,684,214 | 5,703,231 | terpene | | |
| Cluster20 | 5,724,303 | 5,815,609 | T2PKS, T1PKS, PKS-like, phenazine | streptophenazines | 100% |
| Cluster21 | 6,163,107 | 6,177,812 | siderophore | ficellomycin | 3% |
| Cluster22 | 6,251,244 | 6,323,647 | NRPS, NRPS-like | daptomycin | 14% |
| Cluster23 | 6,504,656 | 6,513,179 | RiPP-like | | |
| Cluster24 | 7,096,294 | 7,122,422 | terpene | hopene | 69% |
| Cluster25 | 7,176,618 | 7,225,311 | NRPS, T1PKS | SGR PTMs | 100% |
| Cluster26 | 7,316,149 | 7,357,492 | butyrolactone, terpene, lanthipeptide-class-i | isorenieratene | 87% |
| Cluster27 | 7,392,554 | 7,403,351 | RiPP-like | tetronasin | 3% |
| Cluster28 | 7,608,211 | 7,618,690 | melanin | melanin | 100% |
| Cluster29 | 7,657,838 | 7,821,877 | T3PKS, NRPS, NRPS-like | herboxidiene | 11% |
| Cluster30 | 7,872,061 | 7,924,327 | T1PKS, NRPS | kanamycin | 2% |

**Table S2.** Deduced functions of *orfs* in the *mry* BGC

| *orfs* | Size (aa) | Proposed function | ID/SI | Protein homologue | origion |
|---|---|---|---|---|---|
| *mry1* | 543 | MFS transporter | 99/100 | WP_260821961.1 | *Streptomyces* sp. CS-7 |
| *mry2* | 158 | nuclear transport factor 2 family protein | 100/100 | WP_260821960.1 | *Streptomyces* sp. CS-7 |
| *mry3* | 266 | 4'-phosphopantetheinyl transferase superfamily protein | 99/100 | WP_260821958.1 | *Streptomyces* sp. CS-7 |
| *mry4* | 295 | alpha/beta hydrolase | 99/100 | WP_260821956.1 | *Streptomyces* sp. CS-7 |
| *mry5* | 470 | NDP-hexose 2,3-dehydratase family protein | 100/100 | WP_260821954.1 | *Streptomyces* sp. CS-7 |
| *mry6* | 253 | class I SAM-dependent methyltransferase | 100/100 | WP_260821952.1 | *Streptomyces* sp. CS-7 |
| *mry7* | 373 | aminotransferase | 99/99 | WP_086672685.1 | *Streptomyces* sp. TSRI0445 |
| *mry8* | 504 | FAD-dependent monooxygenase | 99/99 | WP_260821949.1 | *Streptomyces* sp. CS-7 |
| *mry9* | 331 | dTDP-glucose 4,6-dehydratase | 98/99 | NED04942.1 | *Streptomyces* sp. SID6648 |
| *mry10* | 288 | glucose-1-phosphate thymidylyltransferase RfbA | 98/99 | NED04943.1 | *Streptomyces* sp. SID6648 |
| *mry11* | 536 | FAD-dependent monooxygenase | 99/100 | WP_260821947.1 | *Streptomyces* sp. CS-7 |
| *mry12* | 313 | aromatase/cyclase | 99/100 | WP_260821945.1 | *Streptomyces* sp. CS-7 |
| *mry13* | 262 | 3-oxoacyl-ACP reductase | 98/100 | AVO00812.1 | *Streptomyces* sp. |
| *mry14* | 117 | acyl carrier protein | 98/98 | AVO00813.1 | *Streptomyces* sp. |
| *mry15* | 404 | ketosynthase chain-length factor | 99/99 | WP_260821940.1 | *Streptomyces* sp. CS-7 |
| *mry16* | 423 | beta-ketoacyl-[acyl-carrier-protein] synthase | 99/99 | WP_073774800.1 | *Streptomyces* sp. CS-7 |
| *mry17* | 109 | TcmI family type II polyketide cyclase | 99/100 | WP_073774798.1 | *Streptomyces* sp. CS-7 |
| *mry18* | 224 | response regulator transcription factor | 97/98 | AVO00817.1 | *Streptomyces* sp. |
| *mry19* | 235 | monooxygenase | 45/60 | MBT2507467.1 | *Streptomyces sp.* ISL-98 |
| *mry20* | 159 | hypothetical protein | 97/98 | WP_086670719.1 | *Streptomyces* sp. |
| *mry21* | 379 | glycosyltransferase | 100/100 | WP_260821935.1 | *Streptomyces* sp. CS-7 |
| *mry22* | 308 | NAD-dependent epimerase/dehydratase | 100/100 | WP_260821933.1 | *Streptomyces* sp. CS-7 |

**Table S3.** Deduced functions of *orfs* in the *spn* BGC

| *orfs* | Size | Proposed function | ID/SI | Protein homologue | origion |
|---|---|---|---|---|---|
| *spn1* | 329 | cytochrome d ubiquinol oxidase subunit II | 99/100 | WP_073774786.1 | *Streptomyces* |
| *spn2* | 439 | cytochrome ubiquinol oxidase subunit I | 99/99 | WP_260821929.1 | *Streptomyces* sp. CS-7 |
| *spn3* | 293 | LysR substrate-binding domain-containing protein | 100/100 | WP_073774781.1 | *Streptomyces* |
| *spn4* | 598 | fatty acyl-AMP ligase | 100/100 | WP_260821926.1 | *Streptomyces* sp. CS-7 |
| *spn5* | 416 | crotonyl-CoA carboxylase/reductase | 100/100 | WP_260821924.1 | *Streptomyces* sp. CS-7 |
| *spn6* | 800 | type I PKs | 100/100 | WP_260821922.1 | *Streptomyces* sp. CS-7 |
| *spn7* | 351 | aldo/keto reductase | 100/100 | WP_260821920.1 | *Streptomyces* sp. CS-7 |
| *spn8* | 264 | alpha/beta fold hydrolase | 97/97 | WP_086670711.1 | *Streptomyces* |
| *spn9* | 913 | type I PKs | 99/100 | WP_260821917.1 | *Streptomyces* sp. CS-7 |
| *spn10* | 109 | phosphopantetheine-binding protein | 100/100 | WP_073774770.1 | *Streptomyces* |
| *spn11* | 477 | aldehyde dehydrogenase family protein | 100/100 | WP_260821914.1 | *Streptomyces* sp. CS-7 |
| *spn12* | 365 | phenazine antibiotic biosynthesis protein | 98/99 | WP_079198636.1 | *Streptomyces* |
| *spn13* | 110 | hypothetical protein | 96/99 | WP_181852409.1 | *Streptomyces* |
| *spn14* | 455 | FAD-binding protein | 99/99 | WP_260821909.1 | *Streptomyces* sp. CS-7 |
| *spn15* | 545 | amino acid adenylation domain-containing protein | 99/99 | WP_260821907.1 | *Streptomyces* sp. CS-7 |
| *spn16* | 220 | phenazine biosynthesis FMN-dependent oxidase (PhzG) | 99/100 | WP_260821905.1 | *Streptomyces* sp. CS-7 |
| *spn17* | 283 | phenazine biosynthesis isomerase (PhzF) | 99/99 | WP_086670700.1 | *Streptomyces albovinaceus* |
| *spn18* | 627 | anthranilate synthase family protein (PhzE) | 99/100 | WP_260821902.1 | *Streptomyces* sp. CS-7 |
| *spn19* | 207 | isochorismatase family protein (PhzD) | 99/99 | WP_073774760.1 | *Streptomyces* |
| *spn20* | 391 | Phospho-2-dehydro-3-deoxyheptonate aldolase (DAHP synthetase) (PhzC) | 99/99 | WP_260821899.1 | *Streptomyces* sp. CS-7 |
| *spn21* | 166 | PhzA/PhzB family protein | 98/98 | WP_073774756.1 | *Streptomyces* |
| *spn22* | 344 | ketoacyl-ACP synthase III family protein (FabH) | 99/99 | WP_073774754.1 | *Streptomyces* |
| *spn23* | 97 | phosphopantetheine-binding protein | 100/100 | WP_260821896.1 | *Streptomyces* sp. CS-7 |
| *spn24* | 846 | LuxR family transcriptional regulator | 99/99 | WP_260821894.1 | *Streptomyces* sp. CNB091 |
| *spn25* | 289 | methyltransferase | 99/97 | WP_018960036.1 | *Streptomyces* sp. CNB091 |
| *spn26* | 516 | MFS_transporter | 99/100 | WP_018960037.1 | *Streptomyces* sp. CNB091 |
| *spn27* | 781 | FAD-dependent_oxidoreductase | 97/100 | WP_018960038.1 | *Streptomyces* sp. CNB091 |
| *spn28* | 209 | TetR/AcrR_family_transcriptional_regulator | 97/99 | WP_018960039.1 | *Streptomyces* sp. CNB091 |

**Table S4.** Deduced functions of *orfs* in the *din* BGC

| *orfs* | Size | Proposed function | ID/SI | Protein homologue | origion |
|---|---|---|---|---|---|
| *dyn1* | 349 | nonC | 89/93 | AAD37456.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn2* | 175 | nonB | 89/92 | AAD37455.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn3* | 279 | tetranactin resistance protein (nonR) | 89/93 | AAD37454.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn4* | 297 | enoyl-CoA hydratase homolog (nonS) | 93/94 | AAC26135.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn5* | 555 | putative nonactic acid:CoASH ligase (nonL) | 89/92 | AAC26134.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn6* | 569 | putative diester hydrolase (nonD) | 89/93 | AAC26133.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn7* | 271 | putative ketoacyl reductase (nonE) | 93/94 | AAD37453.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn8* | 520 | putative ketoacyl reductase (nonM) | 83/88 | AAD37452.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn9* | 427 | ketoacyl synthase II homolog (nonJ) | 93/95 | AAD37451.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |
| *dyn10* | 462 | ketoacyl synthase I homolog (nonK) | 92/95 | AAD37450.1 | *Streptomyces griseus* subsp. *griseus* DSM 40695 |

**Table S5.** Summary of $^{1}H$ and $^{13}C$ NMR data for compounds **1-2** ($\delta$ in ppm)

| | Compound **1** | | Compound **2** | |
|---|---|---|---|---|
| position | $\delta_C$ mult | $\delta_H$ ($J$ in Hz) | $\delta_C$ mult | $\delta_H$ ($J$ in Hz) |
| | $CDCl_3$, 126 MHz | $CDCl_3$, 500 MHz | MeOD, 176 MHz, | MeOD, 700 MHz |
| 1 | 154.0, C | | 156.5, C | |
| 2 | 118.6, CH | 6.97, s | 114.9, CH | 6.67, s |
| 3 | 142.5, C | | 143.5, C | |
| 3-$CH_3$ | 22.3, $CH_3$ | 2.49, s | 22.7, $CH_3$ | 2.42, s |
| 4 | 118.1, CH | 8.16, s | 117.5, CH | 7.97, s |
| 4a | 138.9, C | | 139.9, C | |
| 5 | 130.0, C | | 126.7, C | |
| 6 | 153.7, C | | 154.5, C | |
| 6a | 133.3, C | | 138.9, C | |
| 7 | 193.3, C | | 194.3, C | |
| 7a | 114.7, C | | 116.3, C | |
| 8 | 161.9, C | | 162.8, C | |
| 9 | 125.2, CH | 7.34, d, $J$ = 8.3 Hz | 124.8, CH | 7.21, d, $J$ =8.1 Hz |
| 10 | 137.9, CH | 7.73, t, $J$ = 8.0 Hz | 138.4, CH | 7.51, t, $J$ = 7.1 Hz |
| 11 | 121.4, CH | 7.86, t, $J$ = 7.3 Hz | 120.4, CH | 7.66, t, $J$ = 7.8 Hz |
| 11a | 135.1, C | | 137.7, C | |
| 12 | 189.2, C | | 188.0, C | |
| 12a | 118.7, C | | 119.4, C | |
| 12b | 118.5, C | | 117.8, C | |
| 1′ | 71.7, CH | 5.73, d, $J$ = 10.0 Hz | 72.2, CH | 5.67, d, $J$ = 11.6 Hz |
| 2′a | 31.7, $CH_2$ | 2.31, d, $J$ = 13.7 Hz | 34.9, $CH_2$ | 2.22, d, $J$ = 12.8 Hz |
| 2′b | 31.7, $CH_2$ | 2.55, d, $J$ = 12.3 Hz | 34.9, $CH_2$ | 2.50, q, $J$ = 11.8 Hz |
| 3′ | 62.2, CH | 3.35, t, $J$ = 13.1 Hz | 55.6, CH | 3.44, d, $J$ = 11.2 Hz |
| 3′-N-$CH_3$ | 30.5, $CH_3$ | 2.71, s | | |
| 4′ | 72.9, CH | 3.75, d, $J$ = 9.3 Hz | 74.7, CH | 3.56, m |
| 5′ | 77.9, CH | 3.67, p, $J$ = 6.0 Hz | 79.3, CH | 3.46, d, $J$ = 9.7 Hz |
| 5′-$CH_3$ | 18.4, $CH_3$ | 1.52, s | 18.6, $CH_3$ | 1.44, d, $J$ = 6.0 Hz |

# Summary of NMR data and HRESI-MS data for compounds **3-6**

The HRESI-MS data of compound **3** showed $[M+H]^+$=339.0858，$[M+Na]^+$=361.0690, the molecular formula of **3** was established as $C_{19}H_{14}O_6$, $^1H$ NMR ($CDCl_3$, 700 MHz,) $\delta$ 12.28 (s, 1H), 11.64 (s, 1H), 7.68-7.62 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 3.44 (s, 1H), 3.08 (s, 2H), 3.01 (d, *J* = 15.0 Hz, 1H), 2.97 (d, *J* = 15.0 Hz, 1H), 1.49 (s, 3H); $^{13}C$ NMR (176 MHz, $CDCl_3$) δ 196.9, 193.0, 183.2, 163.7, 162.0, 150.7, 138.0, 137.8, 135.4, 128.9, 124.0, 122.0, 119.5, 117.5, 115.0, 72.8, 53.8, 45.7, 30.0. The structure of compound **3** was elucidated by comparing the data with previous literature, they were identified as rebelomycin (**3**).

The HRESI-MS data of compound **4** showed $[M+H]^+$=425.2066，$[M+Na]^+$=447.1883, the molecular formula of **4** was established as $C_{24}H_{28}N_2O_5$，$^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.35 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.87 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.80 (dd, *J* = 8.6, 7.0 Hz, 1H), 7.74 (d, *J* = 6.6 Hz, 1H), 5.45 (t, *J* = 7.8 Hz, 1H), 5.38 (d, *J* = 8.4 Hz, 1H).$^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 175.3, 166.9, 144.2, 141.5, 140.8, 140.6, 138.4, 133.2, 132.3, 131.5, 130.5, 130.1, 129.7, 129.5, 75.6, 53.5, 52.8, 51.4, 31.6, 29.2, 28.6, 27.6, 22.6, 14.0. The structure of compound **3** was elucidated by comparing the data with previous literature, they were identified as streptophenazine O (**4**).

The HRESI-MS data of compound **5** showed $[M+H]^+$=439.2226，$[M+Na]^+$=461.2038, the molecular formula of **5** was established as $C_{25}H_{30}N_2O_5$, $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ $\delta$ 8.39 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.29 (m, 1H), 8.27 (d, *J* = 1.5 Hz, 1H), 7.91 (dd, *J* = 8.7, 6.9 Hz, 1H), 7.83 (dd, *J* = 8.7, 6.8 Hz, 1H), 7.78 (d, *J* = 5.5 Hz, 1H), 5.48 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 1H), 4.14 (s, 3H), 4.01 (s, 1H), 3.89 (s, 3H), 1.58 (s, 2H), 1.57 (s, 2H), 1.55 (s, 1H), 1.28 (s, 4H), 0.85 (d, *J* = 2.6 Hz, 3H), 0.84 (d, *J* = 2.6 Hz, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 175.3, 166.9, 144.2, 141.5, 140.8, 138.4, 133.1, 132.3, 131.5, 130.5, 130.1, 129.7, 129.5, 128.1, 75.6, 53.5, 52.8, 51.4, 38.7, 28.6, 27.9, 27.9, 27.3, 22.6, 22.5. The structure of compound **5** was elucidated by comparing the data with previous literature, they were identified as streptophenazine M (**5**).

The HRESI-MS data of compound **6** showed $[M+H]^+$=383.2424, the molecular formula of **6** was established as $C_{21}H_{24}O_6$, $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.02 (m, 1H), 4.05 (q, *J* = 7.5 Hz, 2H), 3.87 (d, *J* = 7.2 Hz, 2H), 2.54 (d, *J* = 3.8 Hz, 1H), 2.07-1.89 (m, 1H), 1.85-1.72 (m, 3H), 1.64 (q, *J* = 5.0 Hz, 1H), 1.61-1.46 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 7H), 0.90 (t, *J* = 7.4 Hz, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 174.5, 174.2, 80.0, 79.9, 76.4, 76.3, 73.3, 69.1, 45.3, 45.1, 42.3, 39.9, 31.5, 31.4, 28.2, 28.0, 27.4, 20.5, 13.2, 12.6, 9.3. The structure of compound **6** was elucidated by comparing the data with previous literature, they were identified as dimeric dynactin (**6**).

**Table S6.** High resolution MS (HRMS), retention time, and predicted chemical formula for nodes in streptophenazine cluster from GNPS molecular network. (Related to **Figure 3** and **Figure 5**)

| Precursor ion mass from molecular network | Determined m/z | Retention time (min) | Predicted formula | Predicted Structure |
|---|---|---|---|---|
| 383.2 | 383.161 | 18.6 | $C_{21}H_{23}N_2O_5^+$ | lacked methylene unit from 397.2 |
| 397.2 | 397.176 | 20.0 | $C_{22}H_{25}N_2O_5^+$ | streptophenazine E (**42**) |
| 411.2 | 411.191 | 21.7 | $C_{23}H_{27}N_2O_5^+$ | streptophenazine C (**41**) |
| | | | | streptophenazine D (**31**) |
| | | | | streptophenazine P (**40**) |
| 423.2 | 423.191 | 24.1 | $C_{24}H_{27}N_2O_5^+$ | oxo-streptophenazine A (**45**) |
| | | | | oxo-streptophenazine B (**46**) |
| 425.2 | 425.172 | 13.9 | $C_{24}H_{29}N_2O_5^+$ | streptophenazine A (**29**) |
| | | | | streptophenazine B (**30**) |
| | 425.210 | 6.6 | $C_{24}H_{29}N_2O_5^+$ | streptophenazine O (**4**) |
| 437.2 | 437.209 | 26.3 | $C_{25}H_{29}N_2O_5^+$ | oxo-streptophenazine G (**24**) |
| | | | | oxo-streptophenazine F (**25**) |
| 439.2 | 439.226 | 8.6 | $C_{25}H_{31}N_2O_5^+$ | streptophenazine M (**5**) |
| | 439.187 | 15.9 | $C_{25}H_{31}N_2O_5^+$ | diastereomer at C-2' of streptophenazine G (**49**) |
| | | | | diastereomer at C-2' of streptophenazine F (**50**) |
| | 439.231 | 0.7 | $C_{25}H_{31}N_2O_5^+$ | streptophenazine G (**34**) |
| | | | | streptophenazine F (**35**) |
| 443.2 | 443.164 | 19.5 | | |
| 453.2 | 453.203 | 11.6 | $C_{29}H_{33}N_2O_5^+$ | streptophenazine L (**39**) |
| | 453.237 | 26.4 | $C_{29}H_{33}N_2O_5^+$ | diastereomer of streptophenazine L |
| 467.2 | 467.181 | 14.4 | $C_{26}H_{31}N_2O_6^+$ | streptophenazine K (**38**) |
| | 467.217 | 21.9 | $C_{26}H_{31}N_2O_6^+$ | streptophenazine J (**37**) |
| 467.3 | 467.254 | 28.0 | $C_{26}H_{31}N_2O_6^+$ | diastereomer of streptophenazine K or J |
| 481.2 | 481.197 | 17.8 | $C_{27}H_{33}N_2O_6^+$ | additional methylene unit from 467.2 |

**Figure S1**. The whole genome phylogenetic tree of marine-derived SCSIO LCY30

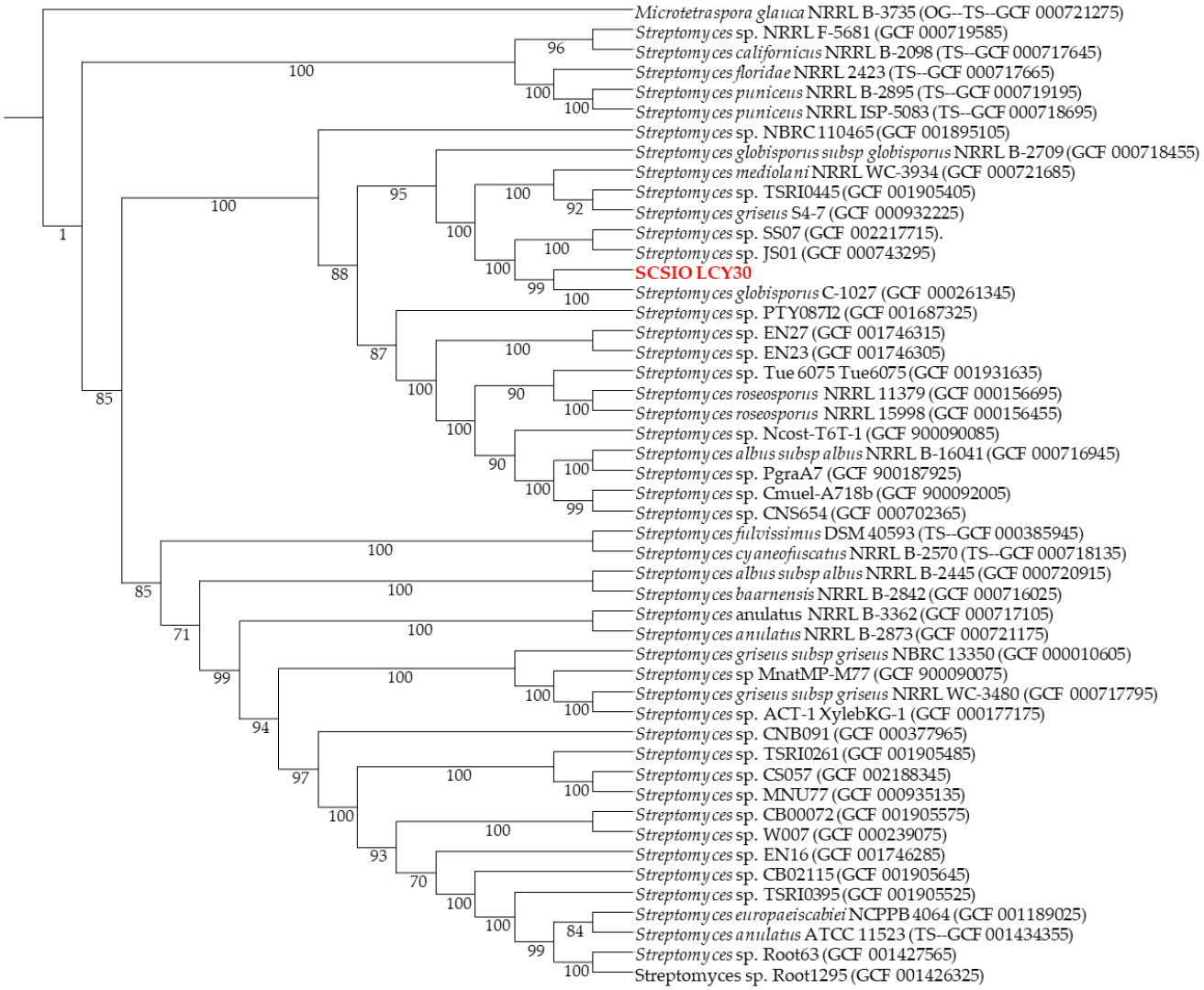


**Figure S2**. Molecular network showing production of streptophenazines, related to **Figure 7**.

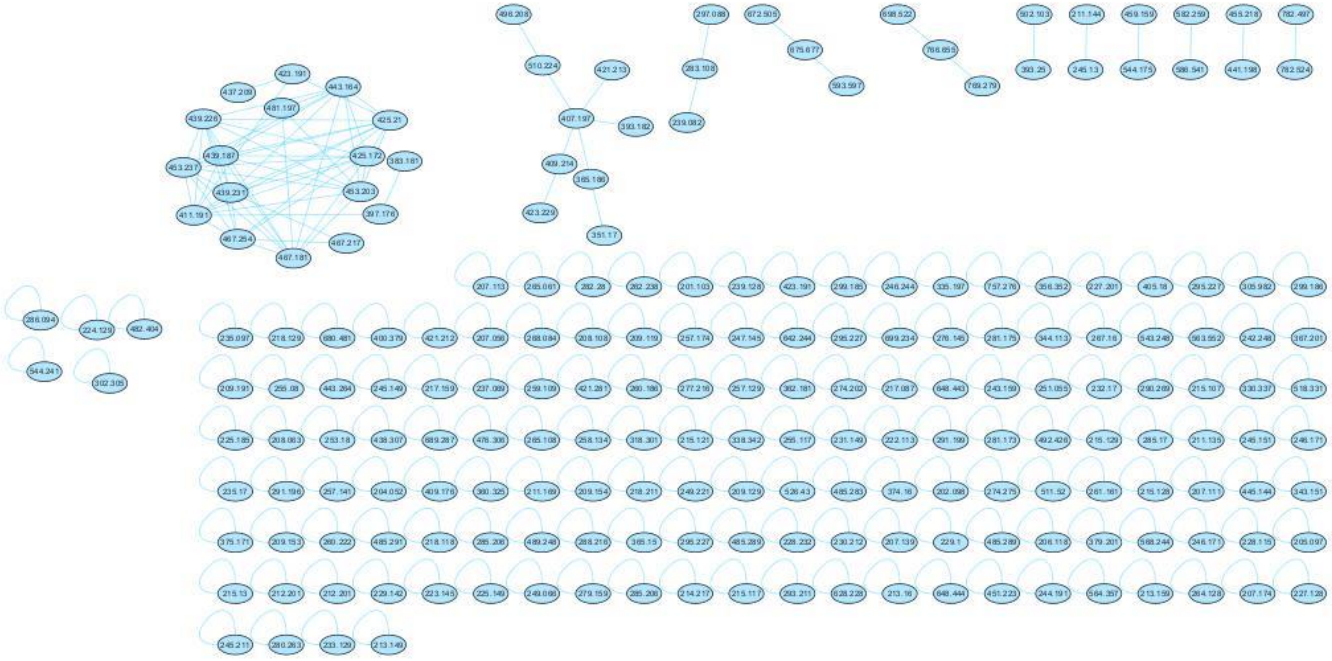
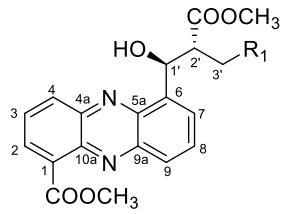


**Figure S3**. Structures of streptophenazines.




streptophenazine A (**29**), $R_1$=

streptophenazine B (**30**), $R_1$=

streptophenazine D (**31**), $R_1$=

streptophenazine E (**32**), $R_1$=

streptophenazine F (**33**), $R_1$=

streptophenazine G (**34**), $R_1$=

streptophenazine H (**35**), $R_1$= OH

streptophenazine I (**36**), $R_1$= OH

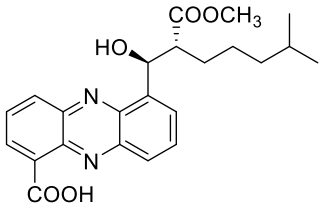
streptophenazine J (**37**), $R_1$=

streptophenazine K (**38**), $R_1$=

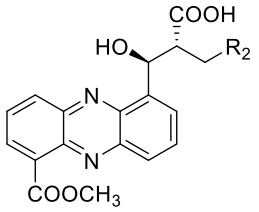
streptophenazine L (**39**), $R_1$=

streptophenazine M (**5**), $R_1$=

streptophenazine P (**40**), $R_1$=

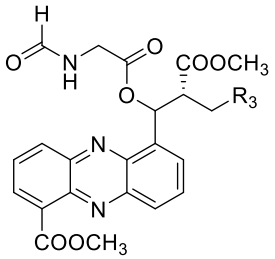



streptophenazine C (**41**)



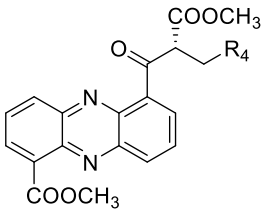

streptophenazine N (**42**), $R_2$=

streptophenazine O (**4**), $R_2$=




streptophenzene Q (**43**), $R_3$=

streptophenzene R (**44**), $R_3$=

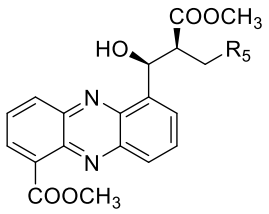



oxo-streptophenazine A (**45**), $R_4$=

oxo-streptophenazine B (**46**), $R_4$=

oxo-streptophenazine F (**47**), $R_4$=

oxo-streptophenazine G (**48**), $R_4$=




diastereomer at C-2' of streptophenazine F (**49**), $R_5$=

diastereomer at C-2' of streptophenazine G (**50**), $R_5$=

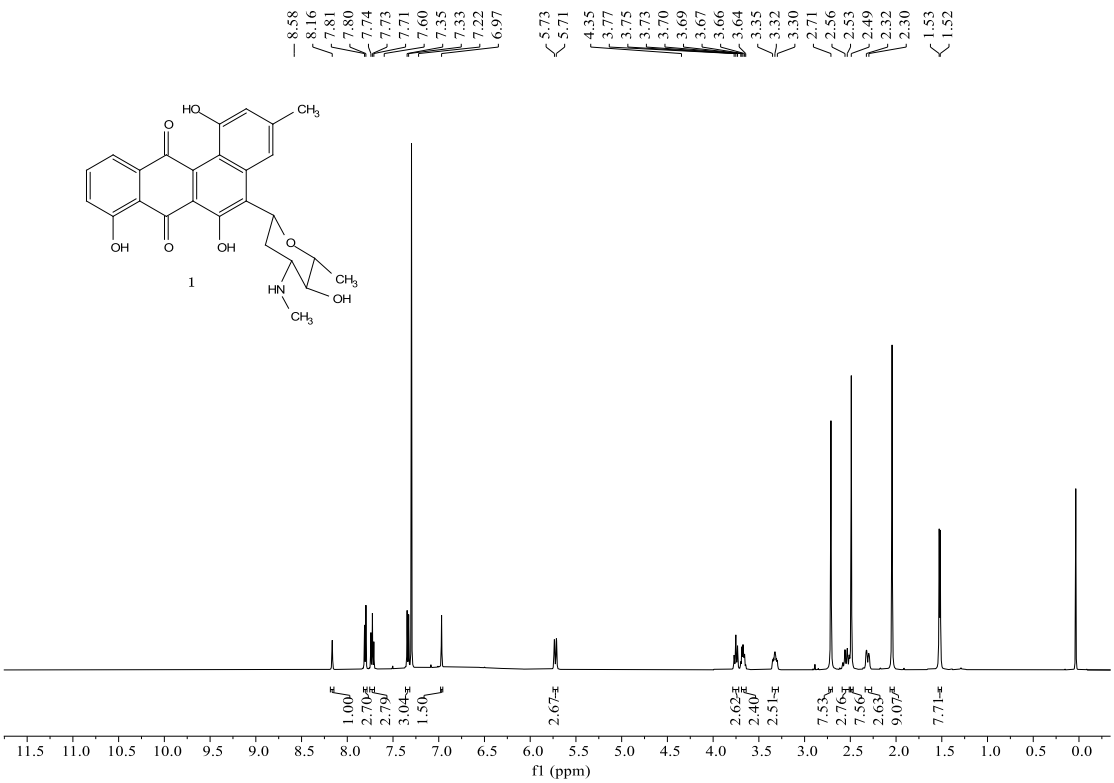



**Figure S4.** $^{1}$H NMR (500 MHz, Chloroform-*d*) spectrum of **1**

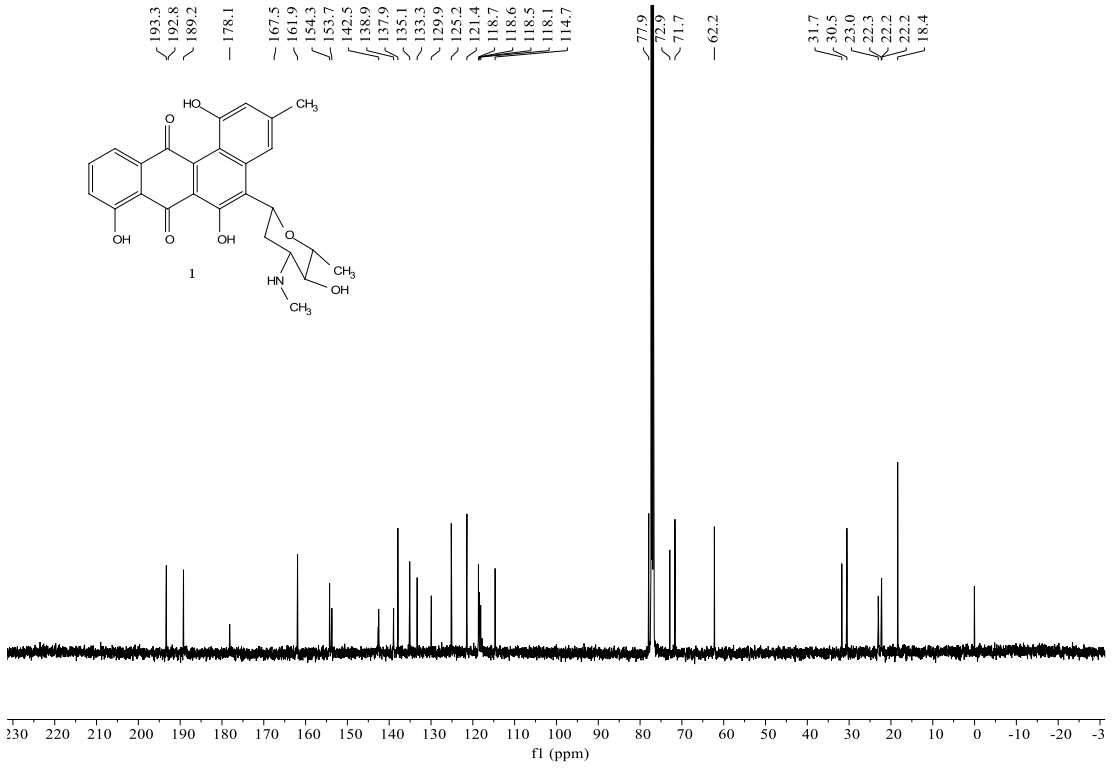



**Figure S5.** $^{13}$C NMR (176MHz, Chloroform-*d*) spectrum of **1**

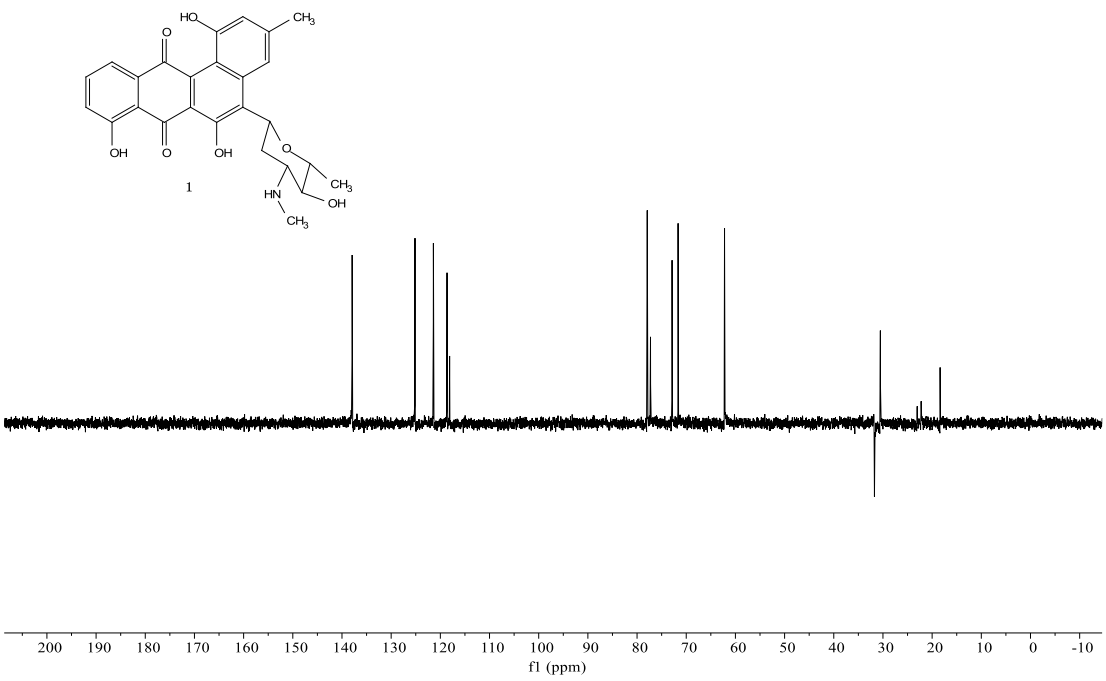



**Figure S6.** DEPT135 spectrum of **1**

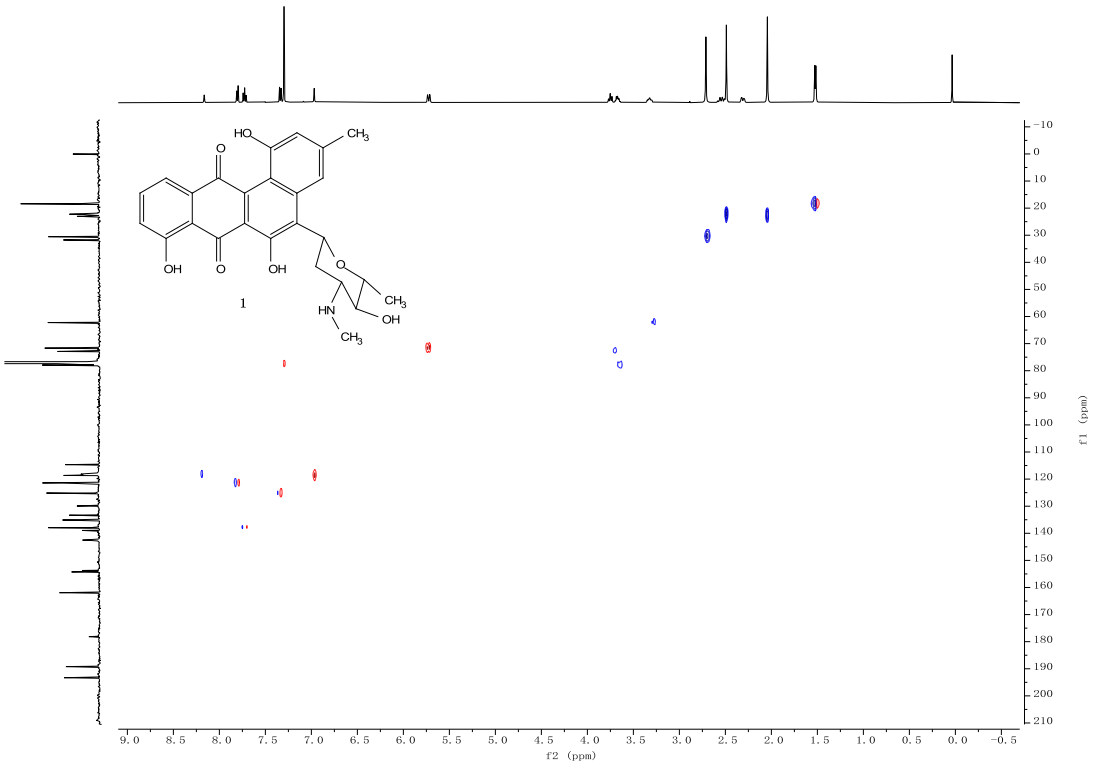



**Figure S7.** HSQC spectrum of **1**

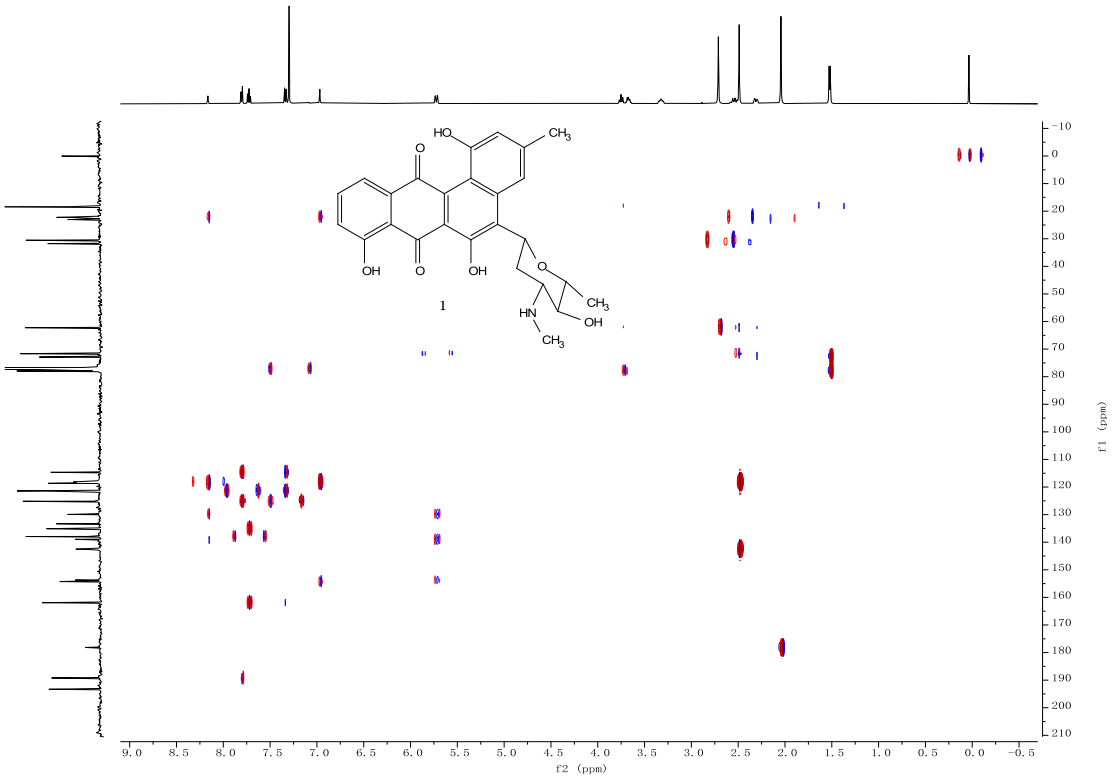



**Figure S8.** HMBC spectrum of **1**

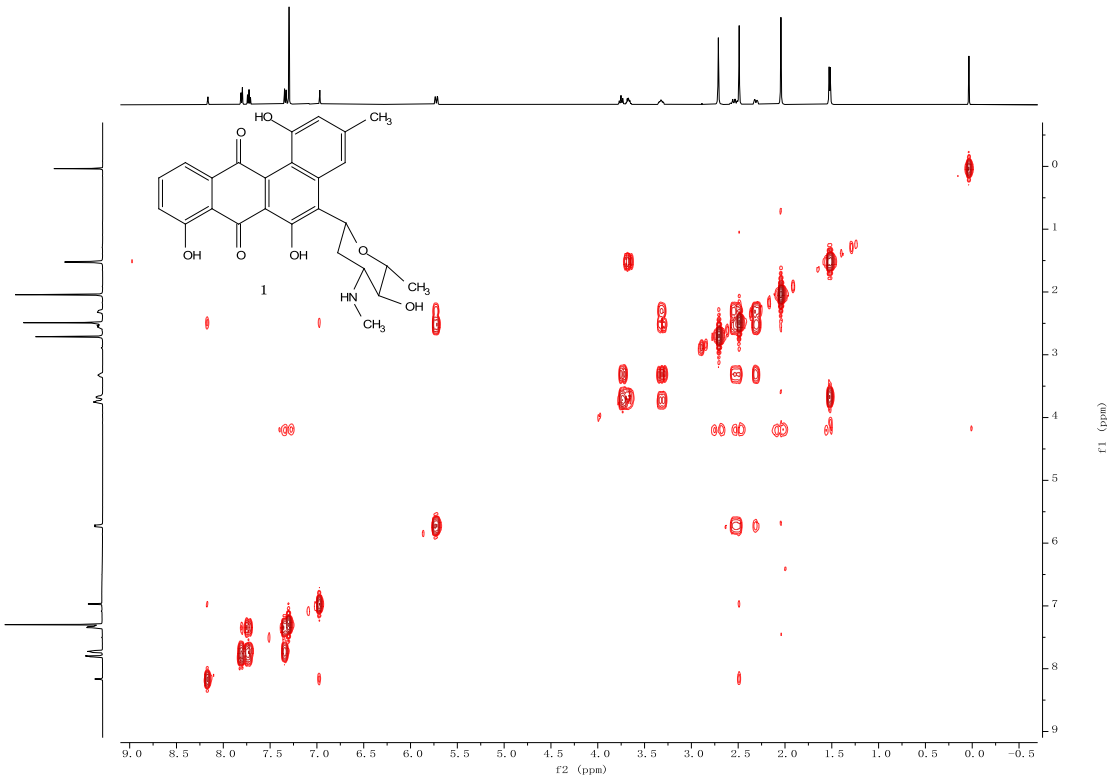



**Figure S9.** $^{1}$H-$^{1}$H COSY spectrum of **1**

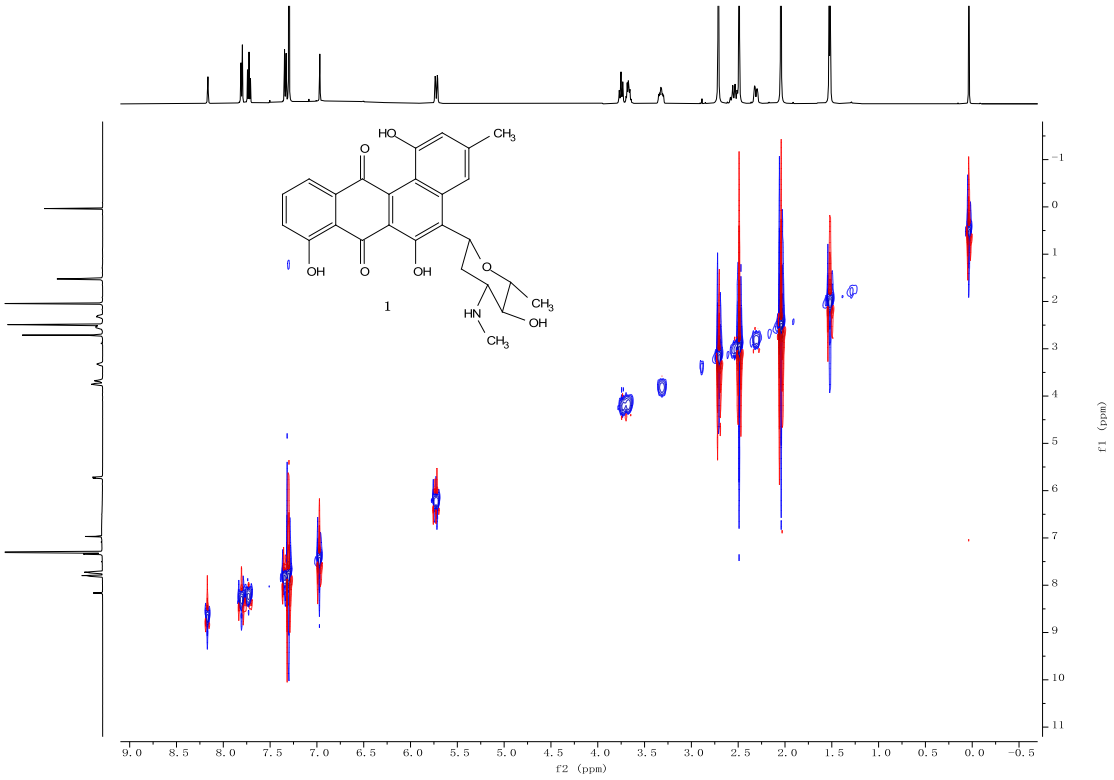
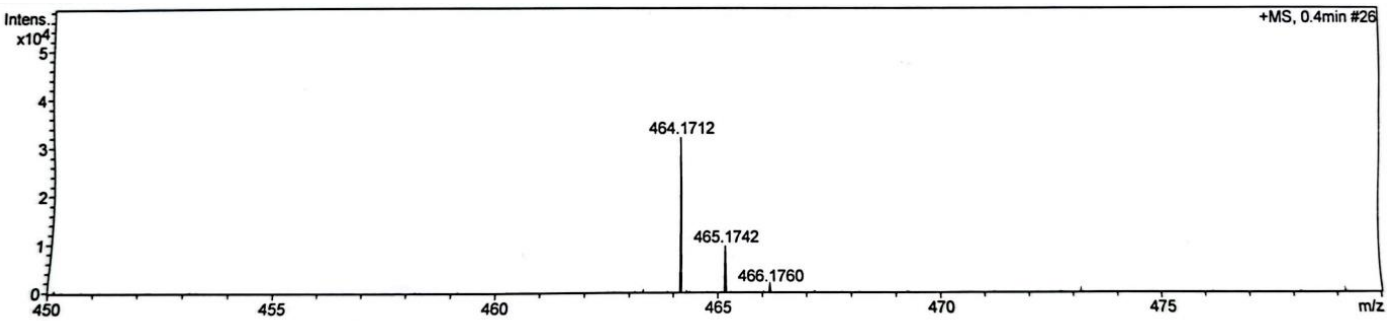



**Figure S10.** NOESY spectrum of **1**




| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | err [mDa] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 464.1712 | 1 | C26H26NO7 | 100.00 | 464.1704 | -1.8 | -0.8 | 6.7 | 14.5 | even | ok |
| 927.3353 | 1 | C52H51N2O14 | 100.00 | 927.3335 | -1.9 | -1.8 | 15.4 | 28.5 | even | ok |

**Figure S11.** HRESI-MS spectrum of **1**

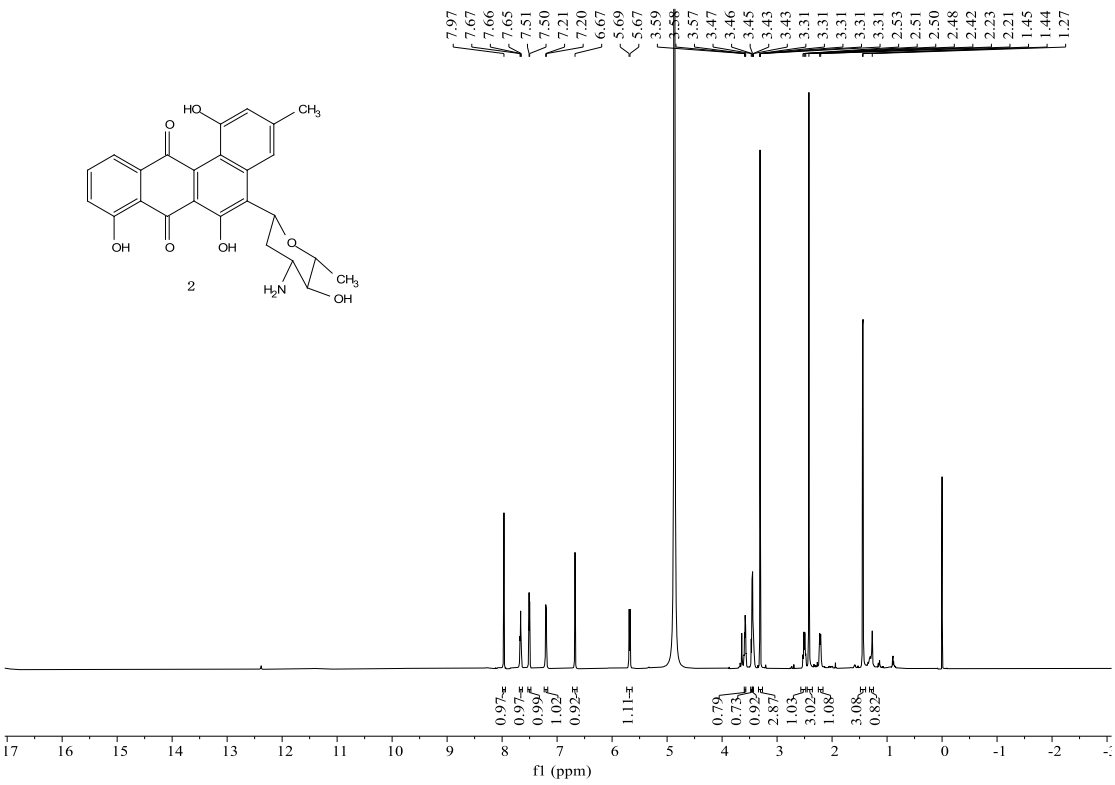



**Figure S12.** $^{1}$H NMR (500 MHz, MeOD) spectrum of **2**

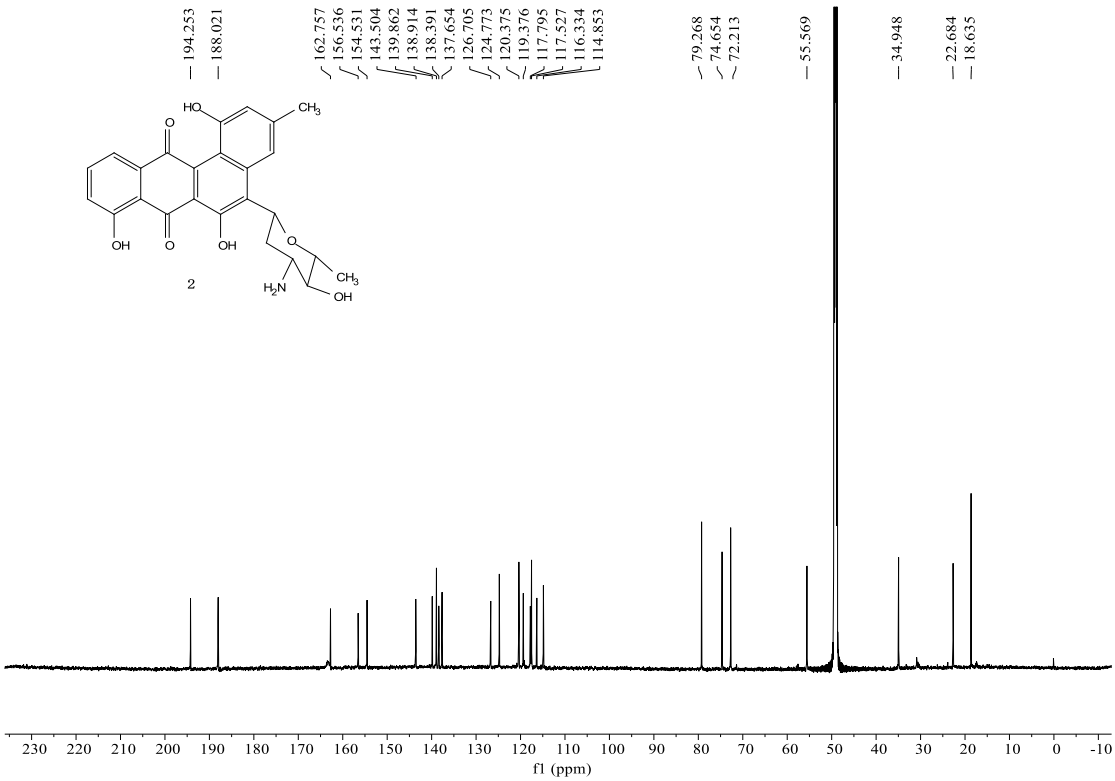
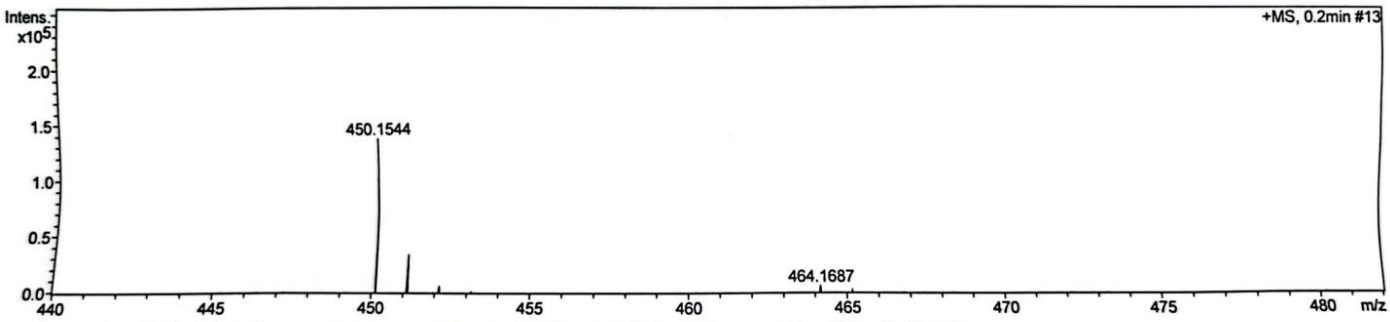



**Figure S13.** $^{13}$C NMR (176MHz, MeOD) spectrum of **2**




| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | err [mDa] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 450.1544 | 1 | C25H24NO7 | 100.00 | 450.1547 | 0.7 | 0.3 | 14.7 | 14.5 | even | ok |
| 472.1347 | 1 | C25H23NNaO7 | 100.00 | 472.1367 | 4.2 | 2.0 | 21.5 | 14.5 | even | ok |
| 899.3019 | 1 | C50H47N2O14 | 100.00 | 899.3022 | -0.3 | -0.3 | 17.4 | 28.5 | even | ok |
| 921.2818 | 1 | C50H46N2NaO14 | 100.00 | 921.2841 | -2.5 | -2.3 | 40.6 | 28.5 | even | ok |

**Figure S14.** HRESI-MS spectrum of **2**

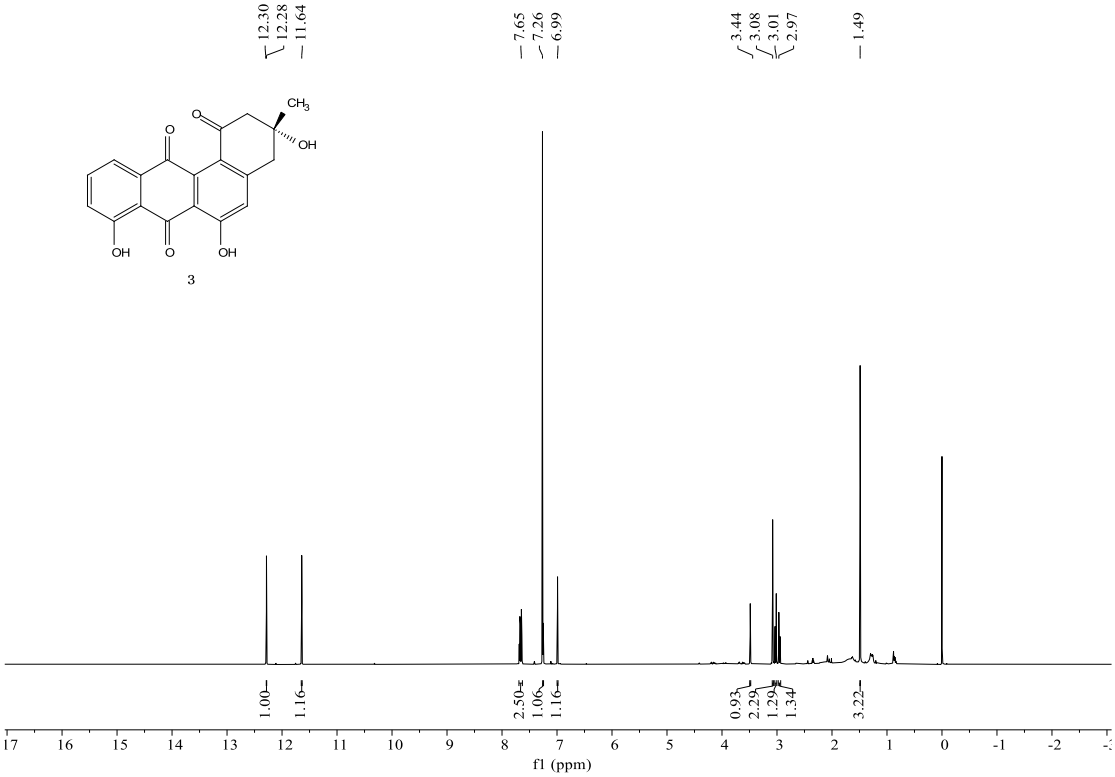



**Figure S15.** $^{1}$H NMR (700 MHz, Chloroform-*d*) spectrum of **3**

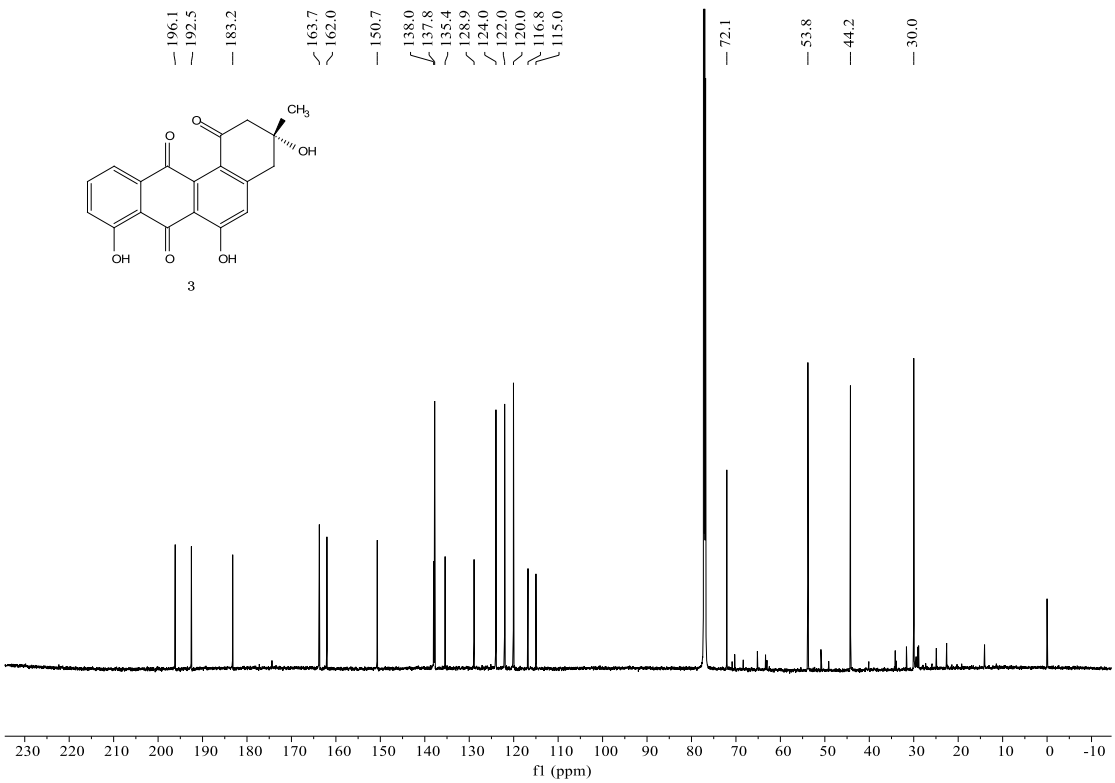
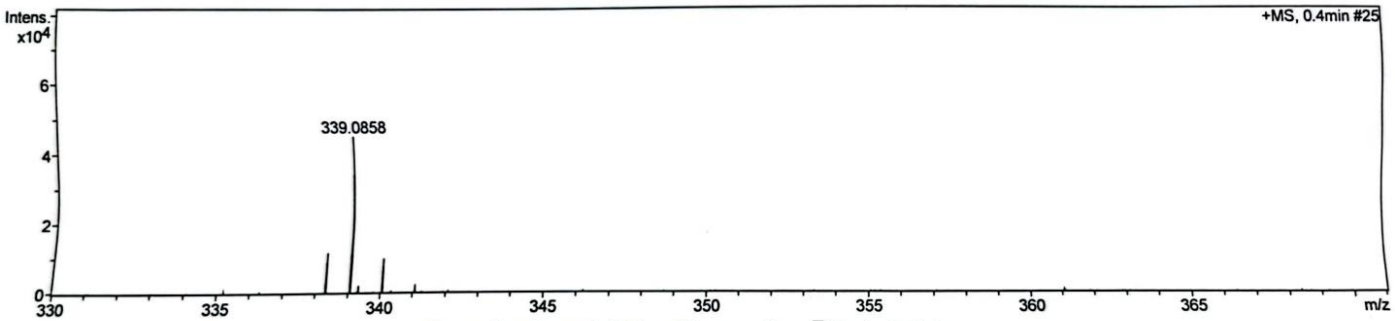



**Figure S16.** $^{13}$C NMR (176MHz, Chloroform-*d*) spectrum of **3**




| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | err [mDa] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 339.0858 | 1 | C19H15O6 | 100.00 | 339.0863 | -1.4 | -0.5 | 5.2 | 12.5 | even | ok |
| 361.0690 | 1 | C19H14NaO6 | 99.47 | 361.0683 | 1.9 | 0.7 | 18.0 | 12.5 | even | ok |
| 699.1461 | 1 | C38H28NaO12 | 100.00 | 699.1473 | -1.7 | -1.2 | 51.1 | 24.5 | even | ok |

**Figure S17.** HRESI-MS spectrum of **3**

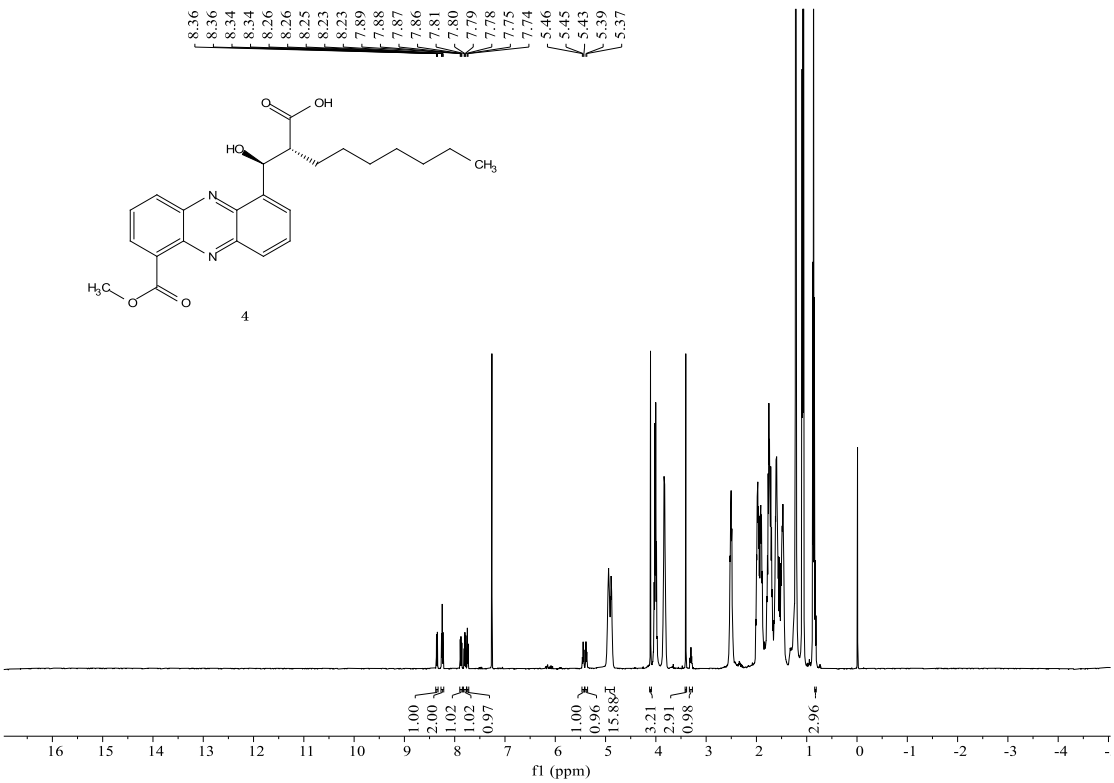



**Figure S18.** $^{1}$H NMR (700 MHz, Chloroform-*d*) spectrum of **4**

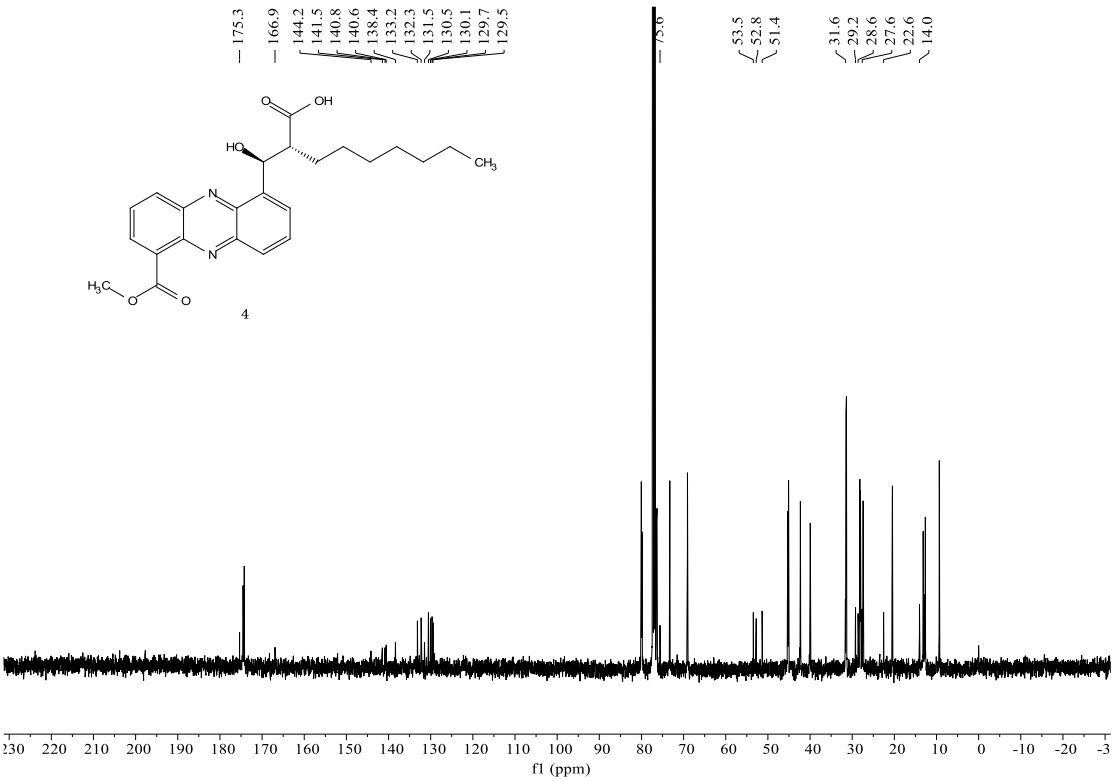
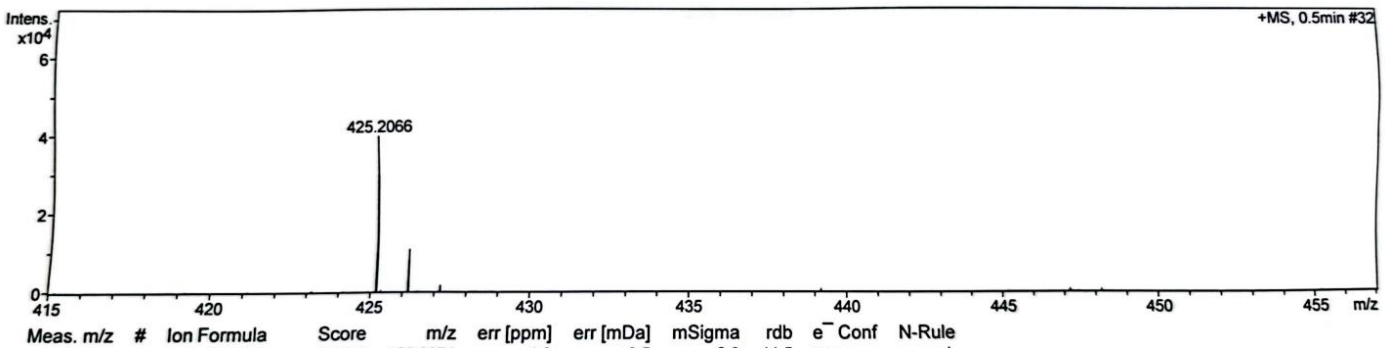



**Figure S19.** $^{13}$C NMR (176MHz, Chloroform-*d*) spectrum of **4**




| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | err [mDa] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 425.2066 | 1 | C24H29N2O5 | 100.00 | 425.2071 | -1.2 | -0.5 | 2.0 | 11.5 | even | ok |
| 447.1883 | 1 | C24H28N2NaO5 | 100.00 | 447.1890 | 1.6 | 0.7 | 151.9 | 11.5 | even | ok |

**Figure S20.** HRESI-MS spectrum of **4**

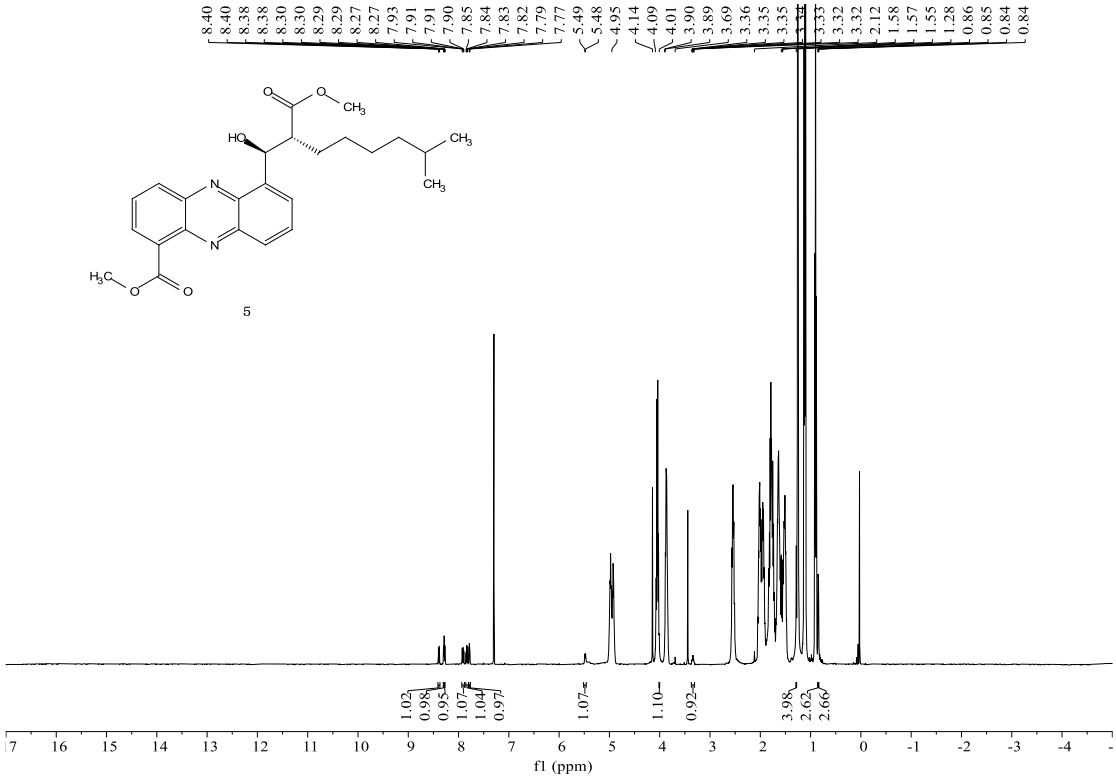



**Figure S21.** $^{1}$H NMR (700 MHz, Chloroform-*d*) spectrum of **5**

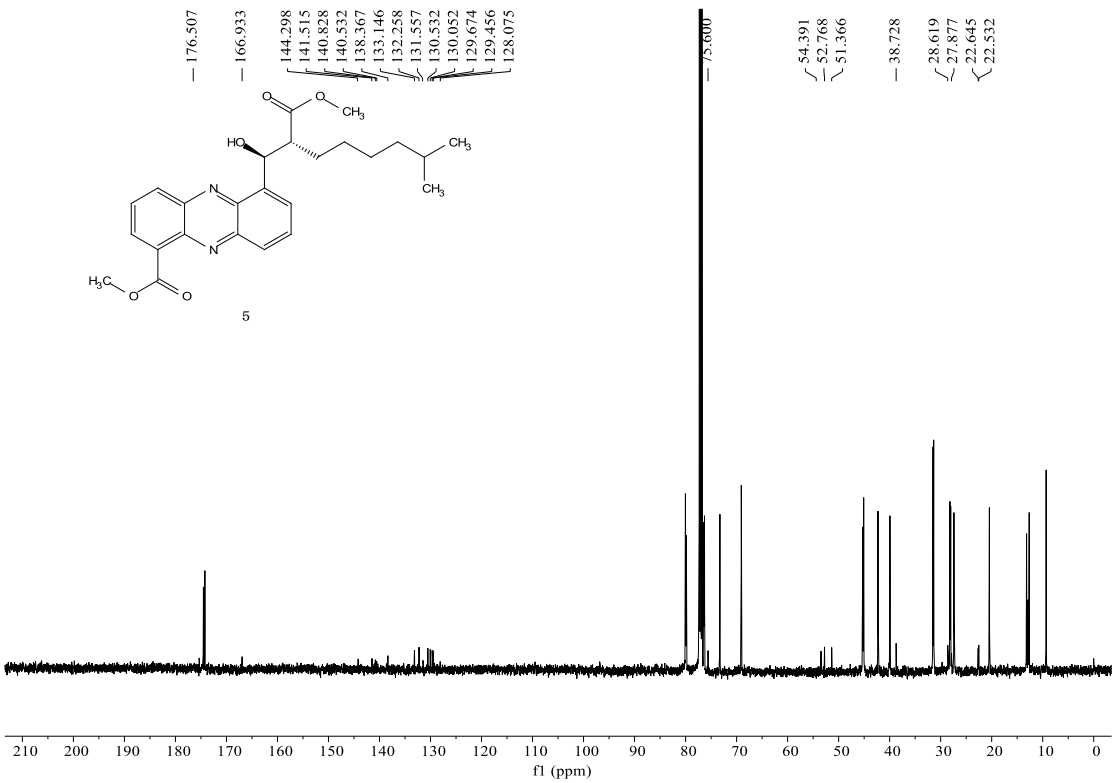
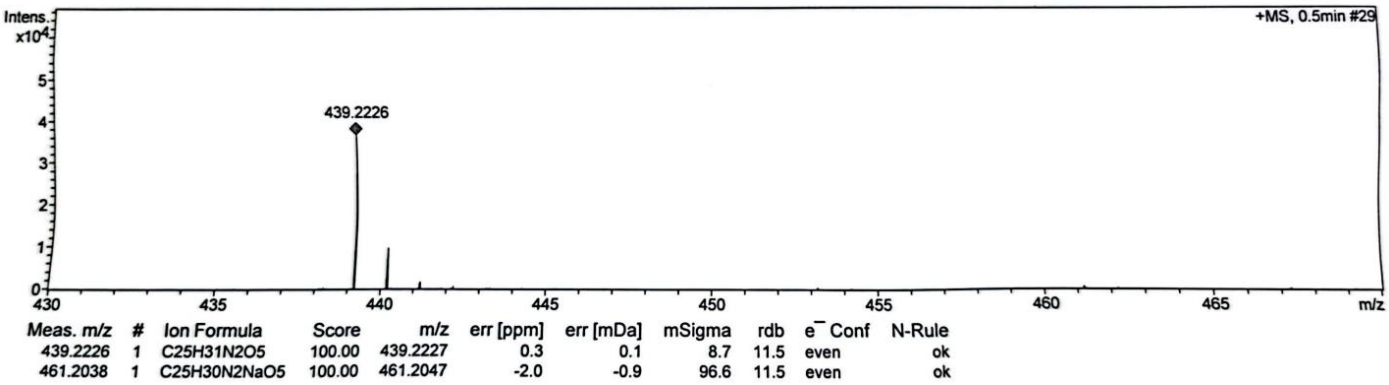
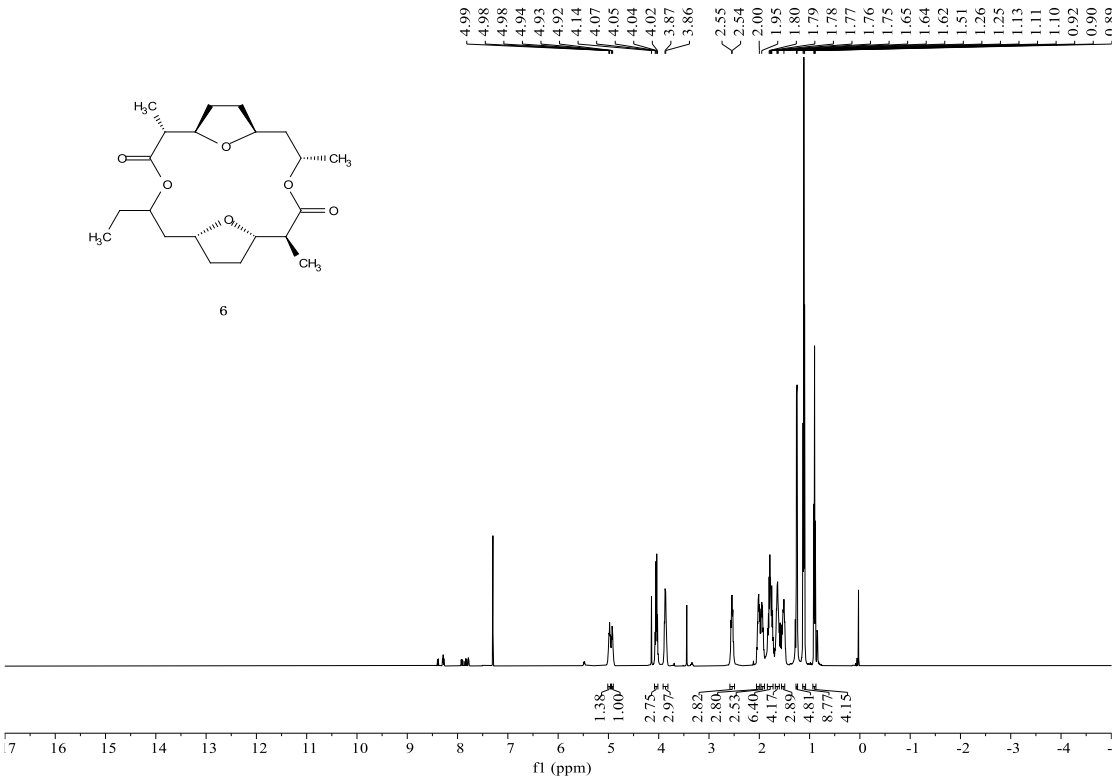



**Figure S22.** $^{13}$C NMR (176MHz, Chloroform-*d*) spectrum of **5**



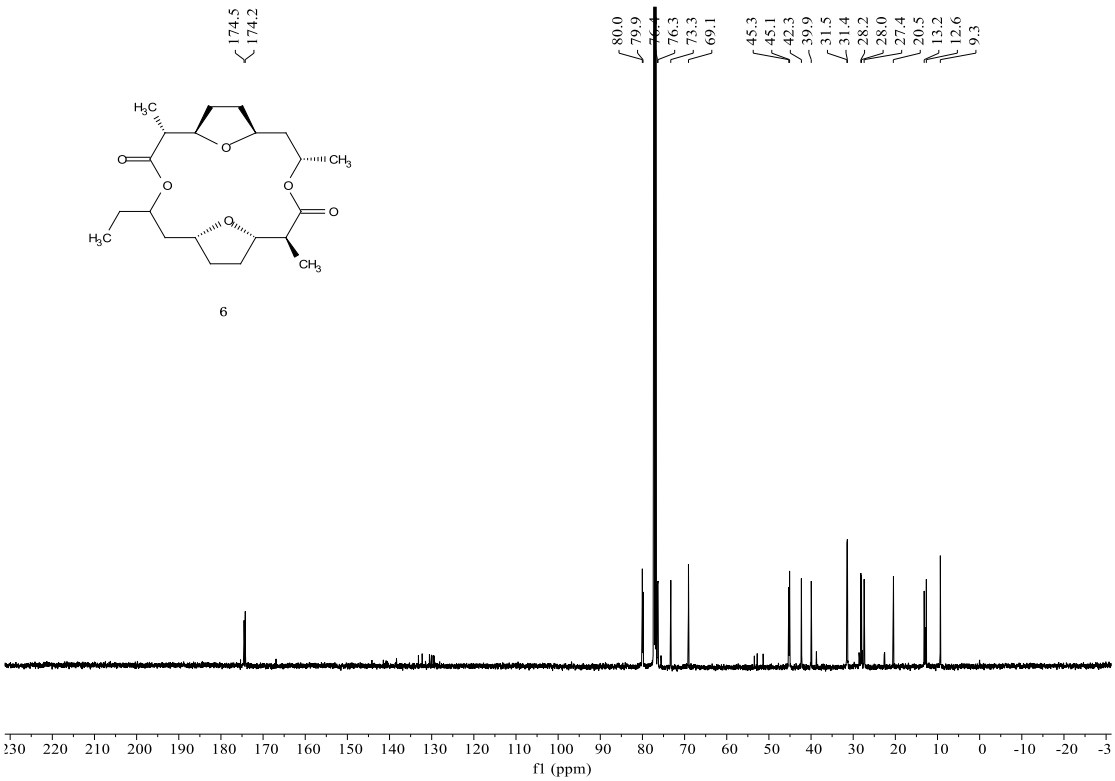

| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | err [mDa] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 439.2226 | 1 | C25H31N2O5 | 100.00 | 439.2227 | 0.3 | 0.1 | 8.7 | 11.5 | even | ok |
| 461.2038 | 1 | C25H30N2NaO5 | 100.00 | 461.2047 | -2.0 | -0.9 | 96.6 | 11.5 | even | ok |

**Figure S23.** HRESI-MS spectrum of **5**




6

**Figure S24.** $^{1}$H NMR (700 MHz, Chloroform-*d*) spectrum of **6**




6

**Figure S25.** $^{13}$C NMR (176MHz, Chloroform-*d*) spectrum of **6**