Supporting Information

Figure S1. Selected 2D NMR correlations of daphnicyclidin N (2).



Figure S2. Selected 2D NMR correlations of calyciphylline R (4).



Figure S3. Selected 2D NMR correlations of calyciphylline S (5).





Figure S4. ¹H-NMR (500 MHz, CD₃OD) spectrum of daphnicyclidin M (1).



Figure S5. ¹³C-NMR (125 MHz, CD₃OD) spectrum of daphnicyclidin M (1).



Figure S6. HSQC spectrum of daphnicyclidin M (1) in CD₃OD.



Figure S7. ¹H-¹H COSY spectrum of daphnicyclidin M (1) in CD₃OD.



Figure S8. HMBC spectrum of daphnicyclidin M (1) in CD₃OD.



Figure S9. NOESY spectrum of daphnicyclidin M (1) in CD₃OD.



Figure S10. ESIMS spectrum of daphnicyclidin M (1).



| Elementa | I Composi | tion Report | | | | | | | Page 1 |
|--|--|---|----------------------|-----------------------|--------------------|------------|-------------|---------------|---------------------------------------|
| Tolerance Selected f | = 10.0 PP ilters: None | M / DBE:n | nin = -1.5 | , max = 5 | 0.0 | | | | |
| Monoisotopi 45 formula(e Elements Us C: 5-30 H: | c Mass, Ever e) evaluated v sed: 5-40 N: 1- | n Electron lons with 1 results wit 3 O: 1-5 Na: | hin limits (u 1-1 | ip to 50 clo | sest result | s for each | mass) | | |
| SIPI | 95 | | | Q-Tof m | icro | | | 29-1 | lov-2013,16:57:53 |
| WQ13-199H1 | 50 (2.071) AM (0 | Cen,4, 80.00, Ar,500 | 0.0,406.06,0. | 70); Sm (Mn, 418.1 | 2x3.00); Cm 532 | (50:65) | | | TOF MS ES+ 8.70e4 |
| % 410. | 0785 413 | .2765 414.1357 | 416.1579 | 9 | 419.1763 | 420.1065 | 21.1065 423 | .1187 424.210 | ⁶⁷ 426.2259 _{m/7} |
| 410.0 | 412.0 | 414.0 | 416.0 | 418.0 | 4 | 20.0 | 422.0 | 424.0 | 426.0 |
| Minimum: Maximum: | 50.00 100.00 | | 5.0 | 10.0 | -1.5 50.0 | | | | |
| Mass | RA (| Calc. Mass | mDa | PPM | DBE | i-FIT | Form | ula | |
| 418, 1632 | 100 00 | 110 1620 | 0.2 | 0 5 | 11 5 | 1700 0 | | | |



Figure S12. ¹H-NMR (500 MHz, CD₃OD) spectrum of daphnicyclidin N (2).



Figure S13. ¹³C-NMR (125 MHz, CD₃OD) spectrum of daphnicyclidin N (2).



Figure S14. HSQC spectrum of daphnicyclidin N (2) in CD₃OD.



Figure S15. ¹H-¹H COSY spectrum of daphnicyclidin N (2) in CD₃OD.



Figure S16. HMBC spectrum of daphnicyclidin N (2) in CD₃OD.



Figure S17. NOESY spectrum of daphnicyclidin N (2) in CD₃OD.



Figure S18. ESIMS spectrum of daphnicyclidin N (2).



| Elementa | I Compo | sition | Repo | rt | | | | | | | | | Pa | ge 1 |
|---|---|--------------------------------|------------------------------|-----------------------------|------------|------------------|-----------------------|-------------|---------|------|------|---------|------------|-----------------|
| Tolerance Selected f | = 10.0 P ilters: No | PM / ne | DBE | : min = | -1.5, | max | = 50.0 | | | | | | | |
| Monoisotopia 50 formula(e Elements Us C: 5-30 H: | c Mass, Ev e) evaluated sed: 5-40 N: 1 | en Elect I with 1 I-3 O: | tron Ion results 1-6 N | is within lin Na: 1-1 | nits (u | p to 50 | closest res | sults for e | ach mas | ss) | | | | |
| SIPI Aa533 MW=4 | 125 | | | | | Q-1 | Tof micro | | | | | 29- | Nov-2013,1 | 7:15:38 |
| WQ13-200H1 3 | 33 (1.140) AM | (Cen,4, 8 | 30.00, Ar, | ,5000.0,44(| 0.16,0.7 | 70); Sm (448 | (Mn, 2x3.00); 1738 | Cm (17:33) | | | | | TOF M | S ES+ 2.19e4 |
| 406.0 | 976 41 | 8.1897 | 427.220 | 09 434.180 | 441.1 B | 759 | 449.1869 | 56.1629 | 472.2 | 2842 | 4 | 86,1807 | 494 2831 | |
| 400 405 | 410 415 | 420 | 425 4 | 430 435 | 440 | 445 | 450 455 | 460 46 | 5 470 | 475 | 480 | 485 49 | 0 495 | m/z |
| Minimum: Maximum: | 50.00 100.00 | | | 5.0 | | 10.0 | -1.5 50.0 | | | | | | | |
| Mass | RA | Calc. | Mass | mDa | | PPM | DBE | i-F | IT | Form | nula | | | |
| 448.1738 | 100.00 | 448.17 | 736 | 0.2 | | 0.4 | 11.5 | 289 | 6.1 | C24 | H27 | N 06 | Na | |



Figure S20. ¹H-NMR (500 MHz, CD₃OD) spectrum of calyciphylline Q (3).



Figure S21. ¹³C-NMR (125 MHz, CD₃OD) spectrum of calyciphylline Q (**3**).



Figure S22. HSQC spectrum of calyciphylline Q (3) in CD₃OD.



Figure S23. ¹H-¹H COSY spectrum of calyciphylline Q (**3**) in CD₃OD.



Figure S24. HMBC spectrum of calyciphylline Q (3) in CD₃OD.



Figure S25. NOESY spectrum of calyciphylline Q (3) in CD₃OD.



Figure S26. ESIMS spectrum of calyciphylline Q (3).

Figure S27. HRESIMS spectrum of calyciphylline Q (3).

| Elementa | nental Composition Report | | | | | | | | | |
|---|--|-----------------------------------|------------------------------------|-----------------------|----------------|---------------|----------------|----------------------|---------------------|--|
| Tolerance Selected f | = 10.0 Pl ilters: Nor | PM / DBE | :: min = -1.5, | max = | 50.0 | | | | | |
| Monoisotopi 45 formula(Elements U C: 5-30 H | c Mass, Eve e) evaluated sed: 5-40 N: 1 | en Electron lor with 2 results | ns within limits (up Na: 1-1 | o to 50 c | losest res | ults for each | mass) | | | |
| SIPI | | | | Q-Tot | fmicro | | | 29-Nov-2013,16:38:16 | | |
| Ma723 M.W=, WQ13-198H2 | юэ 35 (1.209) АМ | (Cen,4, 80.00, Ar | ,5000.0,377.99,0.7 | 0); Sm (M 388.1886 | in, 2x3.00); (| Cm (25:35) | | т | DF MS ES+ 1.87e4 | |
| - | 384.3 | 022 38 | 86.2349 | | 389.2328 | | | | | |
| 38 | 3.2163 | 385.3023 | 387.2375 | | | 390.2465 391 | .2532 392.2521 | 393.9667 | 394.7795 | |
| 383 | .0 384.0 | 385.0 38 | 6.0 387.0 | 388.0 | 389.0 | 390.0 391 | 0 392.0 393.0 | 394.0 | 395.0 | |
| Minimum: Maximum: | 50.00 100.00 | | 5.0 | 10.0 | -1.5 50.0 | | | | | |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula | | | |
| 388.1886 | 100.00 | 388.1889 | -0.1 | -0.3 | 9.5 | 281.4 | C23 H27 | N O3 Na | | |



Figure S28. ¹H-NMR (500 MHz, CD₃OD) spectrum of calyciphylline R (4).



Figure S29. ¹³C-NMR (125 MHz, CD₃OD) spectrum of calyciphylline R (4).



Figure S30. HSQC spectrum of calyciphylline R (4) in CD₃OD.



Figure S31. ¹H-¹H COSY spectrum of calyciphylline R (4) in CD₃OD.



Figure S32. HMBC spectrum of calyciphylline R (4) in CD₃OD.



Figure S33. NOESY spectrum of calyciphylline R (4) in CD₃OD.



Figure S34. ESIMS spectrum of calyciphylline R (4).



| 01/09/201 | 4 15:14 | 5 | | | | | | | PAGE | 01 |
|-------------------------------------|--------------------------|---|---------------|----------------------------------|-------------------------|----------|--------------|------------|-----------|--------------------|
| Elemental | Compos | ition Report | | | | | :J. 7. [10] | 12 | 1 | Page 1 |
| Tolerance Selected fi | = 20.0 PF | PM / DBE: m | in = -1.5, | max = 50 | 0.0 | | | | | |
| Monoisotopio 16 formula(e | Mass, Eve) evaluated | en Electron lons with 1 results with | nin limits (u | p to 50 clos | est results | for each | mass) | | | |
| C: 10-25 H | : 10-30 N | : 1-3 0: 1-3 | | 0 7.4 | | | | | 09-Jan-20 | 14,14:53:02 |
| SIPI Aa51 M.W=34 WQ14-012H2 3 | 1 34 (1,175) AM | (Cen,4, 80.00, Ar,500 | 0.0,337.18.0. | YA01 70); Sm (Mn. 3 342.20 | 9 2x3.00); Cm 068 | (34:47) | | | тс | F MS ES+ 3.89e3 |
| %- | 340. | 2764 | | | | 343.2 | 105 | | | |
| | | 340 9325 3 | 41.2811 | 341,8820 | 34 | 3.0405 | 344.0 | 549 344.21 | 94 344.66 | 378 m/z |
| 339.50 | 339.9988 | 340.50 341.00 | 341.50 | 342.00 | 342.50 | 343.00 | 343.50 | 344.00 | 344.50 | 345.00 |
| Minimum: Maximum: | 85.00 100.00 | | 5.0 | 20.0 | -1.5 50.0 | | | | | |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Form | la | | |
| 342.2068 | 100.00 | 342.2069 | -0.1 | -0.3 | 8.5 | 10.8 | C21 | H28 N | 03 | |



Figure S36. ¹H-NMR (500 MHz, DMSO-*d*₆) spectrum of calyciphylline S (5).



Figure S37. ¹³C-NMR (125 MHz, DMSO-*d*₆) spectrum of calyciphylline S (5).



Figure S38. HSQC spectrum of calyciphylline S (5) in DMSO-*d*₆.



Figure S39. ¹H-¹H COSY spectrum of calyciphylline S (**5**) in DMSO-*d*₆.



Figure S40. HMBC spectrum of calyciphylline S (5) in DMSO-*d*₆.



Figure S41. ESIMS spectrum of calyciphylline S (5).

Figure S42. HRESIMS spectrum of calyciphylline S (5).

| Elementa | | Page 1 | | | | | | | |
|--|------------------------------------|-------------------------------------|-----------------------|------------------------------|-------------------------|-------------------------|---------------|-----------------|--------------------|
| Tolerance Selected f | = 10.0 P ilters: No | PM / DBE ne | : min = -1.5, | max = : | 50.0 | | | | |
| Monoisotopi 36 formula(e Elements Us | c Mass, Ev e) evaluated sed: | en Electron Ion d with 1 results | s within limits (u | p to 50 clo | osest resul | ts for each mas | s) | | |
| C: 5-23 H: SIPI | 5-35 N: | 1-3 0: 1-6 | | Q-Tof | micro | | | 16-Oct-201 | 3,15:25:10 |
| A10 M.W=359 WQ13-240H 2 100 |) 4 (0.829) AM (| (Cen,4, 80.00, Ar,5 | 000.0,343.12,0.70 | YAC); Sm (Mn, 360.217 | 119 2x3.00); Cm 2 | (22:32) | | то | F MS ES+ 1.68e4 |
| % | 827 350.0786 | 354.0963 355.0 | 357.0507 | 9.0911 | 1.2274 362.3 | 203 3318_364.2054_36 | 370 6.2039 | 0.0578 371.0651 | 373.0686 |
| 348.0 | 350.0 35 | 52.0 354.0 | 356.0 358.0 | 360.0 | 362.0 | 364.0 366.0 | 368.0 37 | 70.0 372.0 | 374.0 |
| Minimum: Maximum: | 75.00 100.00 | | 5.0 | 10.0 | -1.5 50.0 | | | | |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula | | |
| 360.2172 | 100.00 | 360.2175 | -0.3 | -0.8 | 7.5 | 2782460.8 | C21 H30 | N 04 | |



Figure S43. ¹H-NMR (500 MHz, CD₃OD) spectrum of paxiphylline C (6).



Figure S44. ¹³C-NMR (125 MHz, CD₃OD) spectrum of paxiphylline C (6).



Figure S45. ¹H-NMR (500 MHz, DMSO-*d*₆) spectrum of macropodumine B (7).



Figure S46. ¹³C-NMR (125 MHz, DMSO-*d*₆) spectrum of macropodumine B (**7**).



Figure S47. ¹H-NMR (500 MHz, CD₃OD) spectrum of macropodumine C (8).



Figure S48. ¹³C-NMR (125 MHz, CD₃OD) spectrum of macropodumine C (8).



Figure S49. ¹H-NMR (500 MHz, DMSO-*d*₆) spectrum of daphnicyclidin A (9).



Figure S50. ¹³C-NMR (125 MHz, DMSO- d_6) spectrum of daphnicyclidin A (9).