Electronic Supplementary Material (ESI) for RSC Advances.


*Supporting information for*

# Melodinines $Y_1$–$Y_4$, four monoterpene indole alkaloids from *Melodinus henryi*

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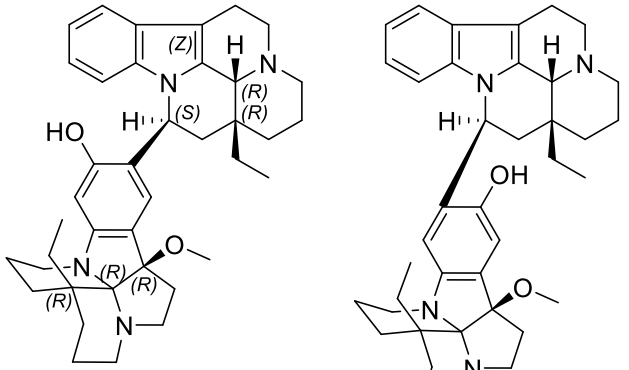
## Contents

## Section S1. Calculational details for 1

### *S1.1. Computational details for compound 1 (NMR)*



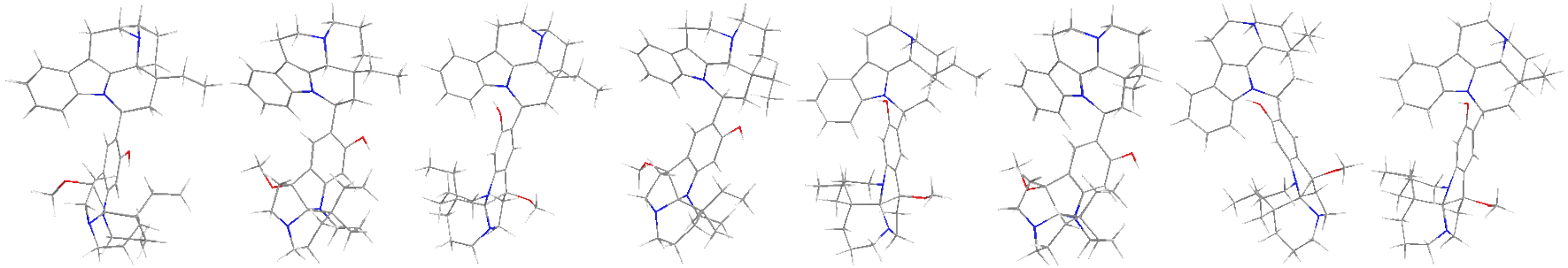

Conformation search based on molecular mechanics with MMFF force fields were performed for **1A** and **1B** gave 8 and 2 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. Gauge Independent Atomic Orbital (GIAO) calculations of their $^{1}$H and $^{13}$C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The $^{1}$H and $^{13}$C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by linear correlation coefficients ($R^2$) and the improved probability DP4+ method.

**Table S1.** Energy analysis for optimized geometries of dominant conformers **1Aa**–**1Ah** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′*=*E*+*ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **1Aa** | -1884.808178 | -1884.770215 | -1884.769271 | -1884.875361 | 0.002622 | 1.645330 | 3.68% |
| **1Ab** | -1884.809349 | -1884.771231 | -1884.770287 | -1884.876480 | 0.001503 | 0.943147 | 12.06% |
| **1Ac** | -1884.812073 | -1884.774476 | -1884.773532 | -1884.877983 | 0 | 0 | 59.29% |
| **1Ad** | -1884.806825 | -1884.768842 | -1884.767897 | -1884.873824 | 0.004159 | 2.609812 | 0.72% |
| **1Ae** | -1884.806714 | -1884.768818 | -1884.767874 | -1884.873593 | 0.004390 | 2.754767 | 0.57% |
| **1Af** | -1884.808107 | -1884.769971 | -1884.769027 | -1884.875017 | 0.002966 | 1.861193 | 2.56% |
| **1Ag** | -1884.810750 | -1884.773088 | -1884.772144 | -1884.877005 | 0.000978 | 0.613704 | 21.03% |
| **1Ah** | -1884.805382 | -1884.767470 | -1884.766526 | -1884.871942 | 0.006041 | 3.790785 | 0.10% |

*E*, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

**Figure S1.** Main conformers of **1A** in NMR and ECD calculations.

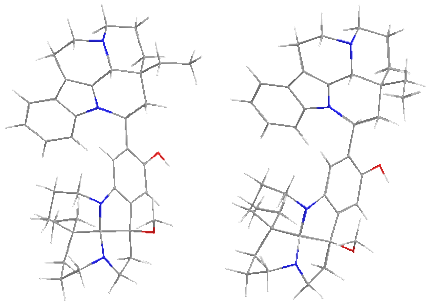


**1Aa** **1Ab** **1Ac** **1Ad** **1Ae** **1Af** **1Ag** **1Ah**

**Table S2.** Energy analysis for optimized geometries of dominant conformers **1Ba**–**1Bb** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **1Ba** | -1884.807065 | -1884.769150 | -1884.768206 | -1884.873448 | 0 | 0 | 79.01% |
| **1Bb** | -1884.805710 | -1884.767744 | -1884.766799 | -1884.872197 | 0.001251 | 0.785014 | 20.99% |

**Figure S2.** Main conformers of **1B** in NMR calculation.



**1Ba** **1Bb**

**Table S3.** Calculated $^{13}$C NMR results for **1A**

| No. | **1Aa** | **1Ab** | **1Ac** | **1Ad** | **1Ae** | **1Af** | **1Ag** | **1Ah** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 43.8155 | 43.6622 | 42.6273 | 43.3929 | 44.3148 | 43.1404 | 42.1378 | 43.8331 | 145.5 | 131.9 | 138.1 | -6.2 |
| 3 | 141.1333 | 140.5529 | 138.7807 | 142.1730 | 139.9825 | 141.7676 | 139.1767 | 140.0338 | 48.9 | 45.5 | 47.7 | -2.2 |
| 5 | 132.8267 | 133.1572 | 133.7171 | 133.1148 | 132.3610 | 133.3152 | 133.2178 | 132.4859 | 54.7 | 52.0 | 53.1 | -1.1 |
| 6 | 167.4083 | 167.1311 | 167.1578 | 167.3096 | 167.0873 | 167.1782 | 167.1042 | 167.3670 | 21.0 | 17.6 | 21.6 | -4.0 |
| 7 | 76.5263 | 76.8001 | 72.0424 | 76.4946 | 78.2087 | 76.7019 | 72.7938 | 78.0917 | 115.0 | 105.2 | 109.6 | -4.4 |
| 8 | 53.0169 | 52.8209 | 51.6815 | 53.0291 | 53.6364 | 52.8697 | 51.8084 | 53.7005 | 136.2 | 129.3 | 129.5 | -0.2 |
| 9 | 65.8718 | 65.8850 | 65.0040 | 65.8500 | 65.6984 | 65.9235 | 65.1764 | 65.6922 | 123.0 | 119.2 | 117.1 | 2.1 |
| 10 | 64.1157 | 63.9992 | 61.8716 | 63.9088 | 64.2758 | 63.8765 | 62.1227 | 64.5344 | 125.8 | 120.7 | 119.7 | 1.0 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 63.3999 | 63.1303 | 62.0009 | 63.4842 | 63.5846 | 63.1126 | 62.0563 | 63.7978 | 125.9 | 121.9 | 119.8 | 2.1 |
| 12 | 70.1313 | 70.0448 | 69.8822 | 69.5427 | 71.1770 | 69.5109 | 69.7349 | 71.2682 | 118.3 | 113.1 | 112.7 | 0.4 |
| 13 | 44.7158 | 44.6233 | 42.1339 | 45.6239 | 45.3714 | 45.3320 | 42.1187 | 45.2570 | 145.5 | 137.7 | 138.2 | -0.5 |
| 14 | 163.3000 | 163.2943 | 162.8873 | 163.5044 | 162.8680 | 163.5494 | 163.3785 | 163.0179 | 25.1 | 20.6 | 25.4 | -4.8 |
| 15 | 163.2791 | 162.9269 | 163.4354 | 156.0707 | 162.7263 | 156.2997 | 156.2767 | 155.9682 | 26.6 | 24.4 | 26.7 | -2.3 |
| 16 | 134.5396 | 134.9375 | 126.2983 | 134.6211 | 128.0156 | 135.4756 | 126.3932 | 127.8352 | 60.2 | 49.9 | 58.3 | -8.4 |
| 17 | 142.2479 | 142.5618 | 144.3825 | 143.3194 | 145.5394 | 143.6704 | 145.5056 | 146.7193 | 43.9 | 42.7 | 43.0 | -0.3 |
| 18 | 178.5711 | 178.6659 | 178.6669 | 177.6490 | 178.9128 | 177.4698 | 177.2888 | 177.4463 | 9.8 | 7.7 | 11.1 | -3.4 |
| 19 | 155.6013 | 155.1907 | 154.9892 | 156.9633 | 155.2830 | 157.0073 | 156.1506 | 156.1262 | 32.8 | 29.3 | 32.6 | -3.3 |
| 20 | 148.5956 | 148.7386 | 148.0116 | 148.4842 | 147.7107 | 148.6739 | 148.5075 | 148.7831 | 39.9 | 36.4 | 39.3 | -2.9 |
| 21 | 123.8228 | 123.5435 | 125.5633 | 130.0157 | 123.9896 | 130.0591 | 132.1584 | 130.8793 | 61.4 | 61.2 | 59.4 | 1.8 |
| 2' | 143.4163 | 142.8184 | 143.6746 | 143.3703 | 143.6014 | 142.9225 | 143.6440 | 143.7273 | 44.6 | 58.2 | 43.7 | 14.5 |
| 3' | 143.3455 | 143.7753 | 143.6143 | 142.6189 | 143.0523 | 143.6835 | 143.1440 | 142.6486 | 44.7 | 63.6 | 43.7 | 19.9 |
| 5' | 124.2437 | 125.7541 | 124.4432 | 124.2493 | 124.3441 | 125.5940 | 124.2478 | 124.4377 | 63.6 | 64.5 | 61.4 | 3.1 |
| 6' | 155.6124 | 162.6077 | 155.3228 | 155.5498 | 155.4600 | 162.7071 | 155.4009 | 155.6412 | 31.8 | 34.0 | 31.6 | 2.4 |
| 7' | 83.6939 | 84.5654 | 83.9632 | 83.5959 | 83.9250 | 84.2065 | 83.8489 | 84.0144 | 104.2 | 94.3 | 99.5 | -5.2 |
| 8' | 62.9919 | 60.9399 | 62.8438 | 62.5864 | 63.3388 | 60.9208 | 62.8868 | 63.4819 | 125.6 | 117.4 | 119.5 | -2.1 |
| 9' | 60.0853 | 59.4859 | 58.8750 | 60.2396 | 56.6900 | 59.6629 | 59.0665 | 56.9409 | 129.1 | 124.9 | 122.8 | 2.1 |
| 10' | 65.1296 | 67.7496 | 67.4285 | 64.9315 | 66.6981 | 67.5545 | 67.3657 | 66.7402 | 120.8 | 122.7 | 115.1 | 7.6 |
| 11' | 26.6068 | 26.9020 | 23.0602 | 26.8190 | 24.5974 | 27.1919 | 22.7305 | 24.2852 | 164.5 | 158.5 | 155.9 | 2.6 |
| 12' | 90.0227 | 89.7506 | 87.0925 | 89.8724 | 88.9909 | 89.5192 | 87.0933 | 88.9897 | 100.6 | 98.3 | 96.1 | 2.2 |
| 13' | 24.9391 | 23.3038 | 23.5993 | 24.7622 | 23.9617 | 23.5321 | 23.4971 | 24.1932 | 164.6 | 150.8 | 156.0 | -5.2 |
| 14' | 167.3224 | 167.4382 | 167.3659 | 167.1072 | 166.6544 | 167.1307 | 166.3516 | 166.0066 | 21.0 | 26.3 | 21.6 | 4.7 |
| 15' | 158.5885 | 158.0603 | 160.0394 | 159.1285 | 159.9295 | 159.2984 | 160.2610 | 160.2505 | 28.4 | 26.9 | 28.5 | -1.6 |
| 16' | 167.1504 | 167.3068 | 167.1129 | 167.0357 | 167.1533 | 166.9743 | 167.4742 | 167.0906 | 21.0 | 20.0 | 21.5 | -1.5 |
| 17' | 156.4030 | 156.6812 | 156.8002 | 156.1472 | 156.6707 | 156.6551 | 156.9604 | 156.5429 | 31.4 | 33.2 | 31.3 | 1.9 |
| 18' | 179.0541 | 178.7881 | 178.5631 | 178.4839 | 178.1884 | 178.2497 | 178.5247 | 178.2841 | 9.6 | 7.1 | 10.8 | -3.7 |
| 19' | 158.3389 | 158.2044 | 158.1868 | 158.1922 | 158.6673 | 157.8750 | 158.2018 | 158.4950 | 30.0 | 34.5 | 30.0 | 4.5 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 20' | 140.8938 | 140.7694 | 139.3168 | 140.8448 | 139.3834 | 140.3925 | 139.3655 | 139.3930 | 48.6 | 32.8 | 47.4 | -14.6 |
| 21' | 83.7195 | 79.0207 | 84.6484 | 83.8676 | 84.5397 | 79.8504 | 84.2893 | 84.4205 | 104.5 | 103.7 | 99.7 | 4.0 |
| -$OCH_3$ | 134.5929 | 138.8864 | 133.8743 | 134.1624 | 133.9411 | 138.7728 | 134.0304 | 134.0527 | 53.5 | 53.0 | 52.0 | 1.0 |
| Population | 3.68% | 12.06% | 59.29% | 0.72% | 0.57% | 2.56% | 21.03% | 0.10% | | | RMSD | 5.71 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Table S4.** Calculated $^{13}$C NMR results for **1B**

| No. | **1Ba** | **1Bb** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|
| 2 | 43.1312 | 43.1532 | 145.0 | 131.9 | 138.6 | -6.7 |
| 3 | 142.5085 | 141.2367 | 45.9 | 45.5 | 45.2 | 0.3 |
| 5 | 132.9010 | 133.5056 | 55.2 | 52.0 | 53.9 | -1.9 |
| 6 | 167.0130 | 166.3282 | 21.3 | 17.6 | 22.0 | -4.4 |
| 7 | 76.8020 | 76.6709 | 111.4 | 105.2 | 106.9 | -1.7 |
| 8 | 53.1251 | 52.8565 | 135.1 | 129.3 | 129.2 | 0.1 |
| 9 | 65.3881 | 65.2540 | 122.8 | 119.2 | 117.6 | 1.6 |
| 10 | 63.5722 | 63.6879 | 124.6 | 120.7 | 119.3 | 1.4 |
| 11 | 63.2386 | 63.1275 | 125.0 | 121.9 | 119.7 | 2.2 |
| 12 | 69.8157 | 69.5210 | 118.4 | 113.1 | 113.5 | -0.4 |
| 13 | 45.5483 | 45.6453 | 142.6 | 137.7 | 136.3 | 1.4 |
| 14 | 163.0851 | 163.2316 | 25.1 | 20.6 | 25.5 | -4.9 |
| 15 | 161.4662 | 155.1986 | 28.0 | 24.4 | 28.3 | -3.9 |
| 16 | 133.0036 | 133.6690 | 55.0 | 49.9 | 53.7 | -3.8 |
| 17 | 143.2273 | 145.6493 | 44.4 | 42.7 | 43.8 | -1.1 |
| 18 | 178.7125 | 177.5026 | 9.7 | 7.7 | 11.0 | -3.3 |
| 19 | 154.7919 | 155.7944 | 33.2 | 29.3 | 33.1 | -3.8 |
| 20 | 147.9192 | 148.7242 | 40.1 | 36.4 | 39.7 | -3.3 |
| 21 | 124.5112 | 129.7295 | 62.6 | 61.2 | 60.9 | 0.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2' | 144.3497 | 144.3015 | 43.8 | 58.2 | 43.2 | 15.0 |
| 3' | 143.2106 | 143.2866 | 45.0 | 63.6 | 44.2 | 19.4 |
| 5' | 125.1541 | 125.2281 | 63.0 | 64.5 | 61.3 | 3.2 |
| 6' | 155.1687 | 155.4165 | 33.0 | 34.0 | 32.9 | 1.1 |
| 7' | 85.0082 | 83.8912 | 103.4 | 94.3 | 99.3 | -5.0 |
| 8' | 55.1539 | 55.7621 | 132.9 | 117.4 | 127.1 | -9.7 |
| 9' | 76.2547 | 76.0097 | 112.0 | 98.3 | 107.4 | -9.1 |
| 10' | 52.2437 | 52.5207 | 135.9 | 158.5 | 129.9 | 28.6 |
| 11' | 36.3433 | 36.1454 | 151.9 | 122.7 | 145.0 | -22.3 |
| 12' | 73.7739 | 73.9181 | 114.4 | 124.9 | 109.7 | 15.2 |
| 13' | 30.9768 | 31.3281 | 157.1 | 150.8 | 150.0 | 0.8 |
| 14' | 167.4953 | 167.3047 | 20.7 | 26.3 | 21.4 | 4.9 |
| 15' | 158.8980 | 158.9796 | 29.3 | 26.9 | 29.5 | -2.6 |
| 16' | 168.5091 | 168.4037 | 19.7 | 20.0 | 20.4 | -0.4 |
| 17' | 156.6775 | 156.9392 | 31.4 | 33.2 | 31.5 | 1.7 |
| 18' | 177.8028 | 177.8630 | 10.4 | 7.1 | 11.6 | -4.5 |
| 19' | 158.4859 | 158.4520 | 29.7 | 34.5 | 29.9 | 4.6 |
| 20' | 141.5538 | 141.6426 | 46.6 | 32.8 | 45.8 | -13.0 |
| 21' | 85.0326 | 84.3559 | 103.3 | 103.7 | 99.2 | 4.5 |
| -$OCH_3$ | 133.5116 | 133.6287 | 54.6 | 53.0 | 53.4 | -0.4 |
| Population | 79.01% | 20.99% | | | RMSD | 8.47 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Figure S3.** $^{13}$C NMR calculation results of two possible isomers of **1**. (a) Linear correlation plots of predicted versus experimental $^{13}$C NMR chemical shifts. (b) Relative errors between the predicted $^{13}$C NMR chemical shifts of two potential structures and recorded $^{13}$C NMR data.

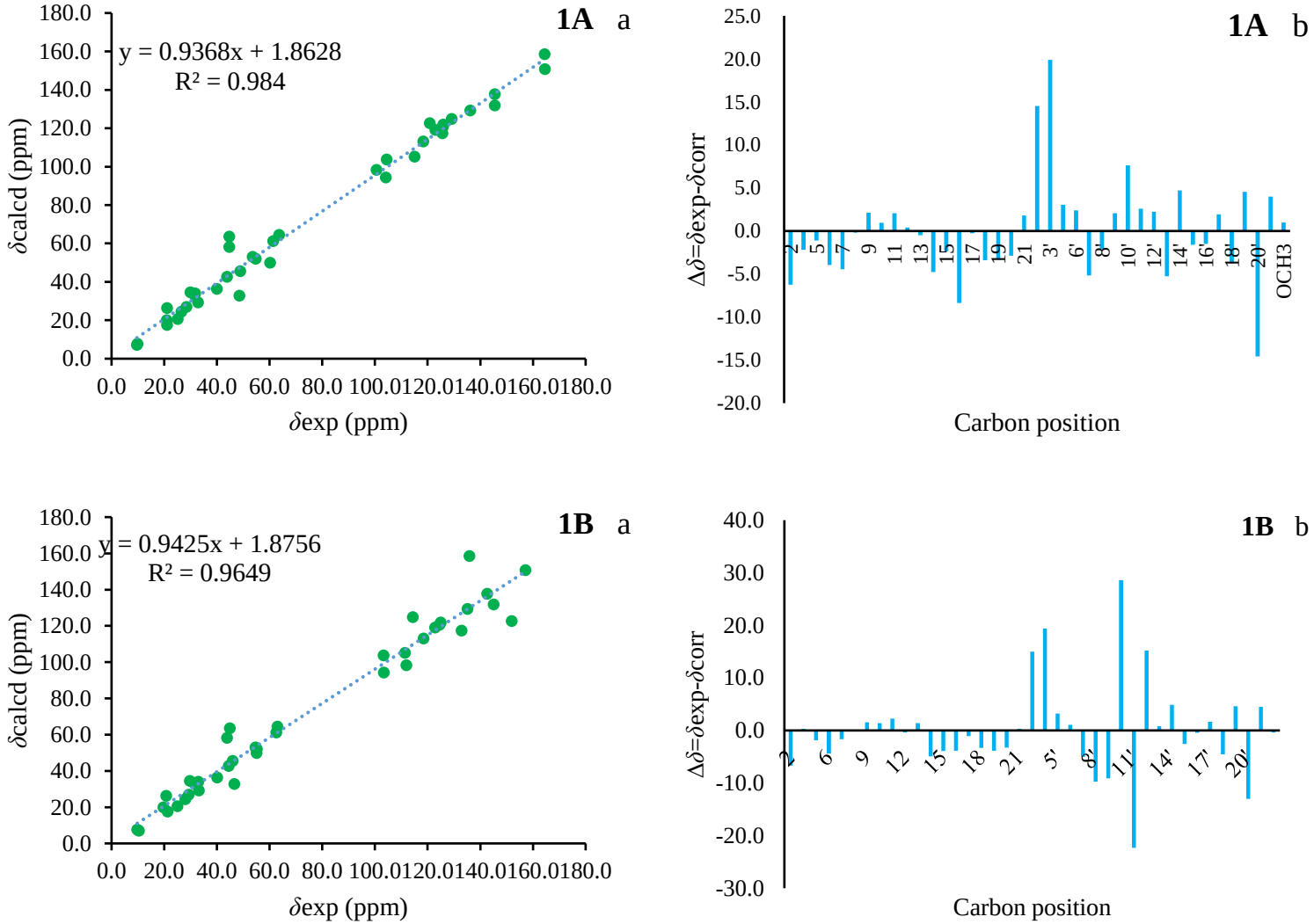


**Table S5.** DP4+ analysis results of **1A** (Isomer 1) and **1B** (Isomer 2)

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 12 | | | DP4+ | 100.00% | 0.00% | - | - | - |
| 14 | Nuclei | sp2? | xperimenta | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 |
| 15 | C | x | 131.9 | 42.72 | 43.14 | | | |
| 16 | C | | 45.5 | 139.27 | 142.24 | | | |
| 17 | C | | 52 | 133.49 | 133.03 | | | |
| 18 | C | | 17.6 | 167.15 | 166.87 | | | |
| 19 | C | x | 105.2 | 73.13 | 76.77 | | | |
| 20 | C | x | 129.3 | 51.95 | 53.07 | | | |
| 21 | C | x | 119.2 | 65.21 | 65.36 | | | |
| 22 | C | x | 120.7 | 62.35 | 63.60 | | | |
| 23 | C | x | 121.9 | 62.25 | 63.22 | | | |
| 24 | C | x | 113.1 | 69.88 | 69.75 | | | |
| 25 | C | x | 137.7 | 42.65 | 45.57 | | | |
| 26 | C | | 20.6 | 163.08 | 163.12 | | | |
| 27 | C | | 24.4 | 161.62 | 160.15 | | | |
| 28 | C | | 49.9 | 127.97 | 133.14 | | | |
| 29 | C | | 42.7 | 144.30 | 143.74 | | | |
| 30 | C | | 7.7 | 178.34 | 178.46 | | | |
| 31 | C | | 29.3 | 155.35 | 155.00 | | | |
| 32 | C | | 36.4 | 148.24 | 148.09 | | | |
| 33 | C | | 61.2 | 126.79 | 125.61 | | | |
| 34 | C | | 58.2 | 143.53 | 144.34 | | | |
| 35 | C | | 63.6 | 143.52 | 143.23 | | | |
| 36 | C | | 64.5 | 124.58 | 125.17 | | | |
| 37 | C | | 34 | 156.42 | 155.22 | | | |
| 38 | C | | 94.3 | 84.01 | 84.77 | | | |
| 39 | C | x | 117.4 | 62.58 | 55.28 | | | |
| 40 | C | x | 124.9 | 59.05 | 76.20 | | | |
| 41 | C | x | 122.7 | 67.35 | 52.30 | | | |
| 42 | C | x | 158.5 | 23.73 | 36.30 | | | |
| 43 | C | x | 98.3 | 87.62 | 73.80 | | | |
| 44 | C | x | 150.8 | 23.60 | 31.05 | | | |
| 45 | C | | 26.3 | 167.15 | 167.46 | | | |
| 46 | C | | 26.9 | 159.77 | 158.92 | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 47 | C | | 20 | 167.21 | 168.49 | | | |
| 48 | C | | 33.2 | 156.80 | 156.73 | | | |
| 49 | C | | 7.1 | 178.59 | 177.82 | | | |
| 50 | C | | 34.5 | 158.19 | 158.48 | | | |
| 51 | C | | 32.8 | 139.60 | 141.57 | | | |
| 52 | C | | 103.7 | 83.73 | 84.89 | | | |
| 53 | C | | 53 | 134.67 | 133.54 | | | |
| 54 | | | | | | | | |
| 55 | H | | 2.58 | 29.09 | 29.28 | | | |
| 56 | H | | 2.8 | 29.07 | 29.20 | | | |
| 57 | H | | 3.46 | 28.51 | 28.57 | | | |
| 58 | H | | 3.46 | 28.32 | 28.41 | | | |
| 59 | H | | 2.82 | 29.30 | 29.12 | | | |
| 60 | H | | 3.03 | 28.59 | 28.61 | | | |
| 61 | H | x | 7.41 | 24.04 | 23.87 | | | |
| 62 | H | x | 6.94 | 24.31 | 24.37 | | | |
| 63 | H | x | 6.81 | 24.48 | 24.52 | | | |
| 64 | H | x | 6.63 | 24.36 | 24.69 | | | |
| 65 | H | | 1.46 | 30.27 | 30.33 | | | |
| 66 | H | | 1.82 | 30.05 | 29.90 | | | |
| 67 | H | | 1.15 | 30.60 | 30.55 | | | |
| 68 | H | | 1.54 | 30.45 | 30.40 | | | |
| 69 | H | | 5.55 | 26.77 | 26.15 | | | |
| 70 | H | | 1.67 | 29.84 | 30.24 | | | |
| 71 | H | | 2.37 | 29.74 | 29.42 | | | |
| 72 | H | | 0.93 | 30.87 | 31.00 | | | |
| 73 | H | | 0.93 | 30.88 | 30.87 | | | |
| 74 | H | | 0.93 | 30.99 | 30.88 | | | |
| 75 | H | | 1.54 | 30.30 | 30.41 | | | |
| 76 | H | | 2.09 | 29.60 | 29.63 | | | |
| 77 | H | | 4.38 | 27.65 | 27.47 | | | |
| 78 | H | | 2.97 | 28.50 | 28.84 | | | |
| 79 | H | | 3.26 | 28.33 | 28.82 | | | |
| 80 | H | | 2.75 | 28.75 | 28.64 | | | |
| 81 | H | | 3.45 | 28.42 | 28.60 | | | |
| 82 | H | | 2.91 | 28.42 | 28.44 | | | |
| 83 | H | | 3.33 | 27.75 | 27.84 | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 84 | H | | 2.39 | 29.73 | 29.72 | | | |
| 85 | H | | 2.48 | 29.63 | 29.55 | | | |
| 86 | H | x | 6.78 | 24.67 | 25.55 | | | |
| 87 | H | x | 6.48 | 25.71 | 25.03 | | | |
| 88 | H | | 1.7 | 30.14 | 30.27 | | | |
| 89 | H | | 1.7 | 29.73 | 29.68 | | | |
| 90 | H | | 1.91 | 30.54 | 30.70 | | | |
| 91 | H | | 2.41 | 30.28 | 30.21 | | | |
| 92 | H | | 1.82 | 30.56 | 31.11 | | | |
| 93 | H | | 2.3 | 29.80 | 30.61 | | | |
| 94 | H | | 1.4 | 30.04 | 30.21 | | | |
| 95 | H | | 1.61 | 29.85 | 30.03 | | | |
| 96 | H | | 0.89 | 31.03 | 30.96 | | | |
| 97 | H | | 0.89 | 31.07 | 31.10 | | | |
| 98 | H | | 0.89 | 30.98 | 31.12 | | | |
| 99 | H | | 1.34 | 30.82 | 30.94 | | | |
| 100 | H | | 1.34 | 30.50 | 30.66 | | | |
| 101 | H | | 2.68 | 28.82 | 29.20 | | | |
| 102 | H | | 2.68 | 28.37 | 28.21 | | | |
| 103 | H | | 2.68 | 29.15 | 28.81 | | | |

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 2.27% | 97.73% | – | – | – | – |
| 6 | sDP4+ (C data) | | 100.00% | 0.00% | – | – | – | – |
| 7 | sDP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |
| 8 | uDP4+ (H data) | | 6.07% | 93.93% | – | – | – | – |
| 9 | uDP4+ (C data) | | 100.00% | 0.00% | – | – | – | – |
| 10 | uDP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |
| 11 | DP4+ (H data) | | 0.15% | 99.85% | – | – | – | – |
| 12 | DP4+ (C data) | | 100.00% | 0.00% | – | – | – | – |
| 13 | DP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |

### *S1.2. Computational details for compound 1 (ECD)*

Conformation search based on molecular mechanics with MMFF force fields were performed for **1A** gave 8 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-311G(2d,p) level by Gaussian 16 program package. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-311G(d) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 program package ($\sigma$ = 0.15 eV, and UV shift -31 nm) and the calculated ECD data of all conformers were Boltzmann averaged by Gibbs free energy.

**Figure S4.** Comparison of the calculated ECD spectra for with the experimental spectrum of **1** in methanol with PCM model.

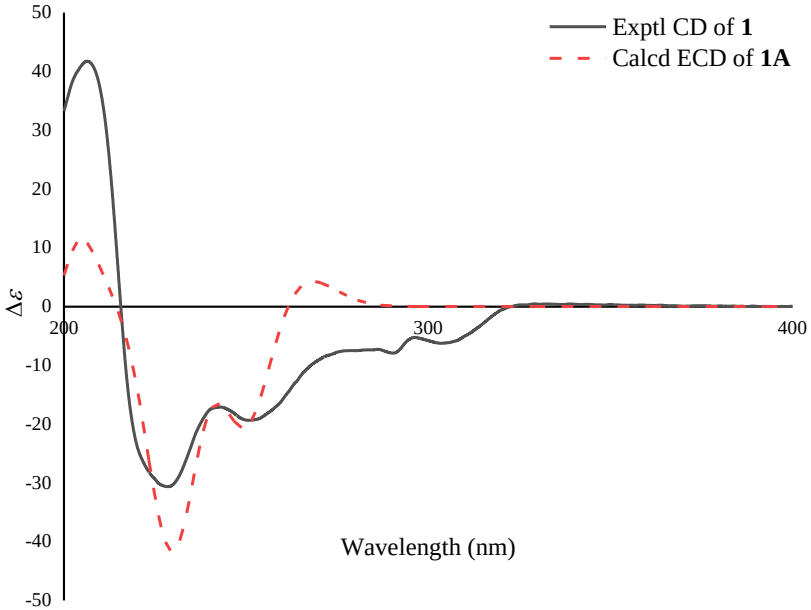


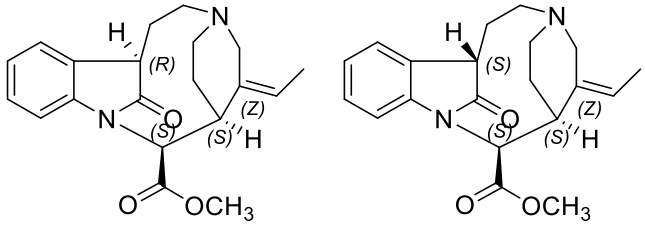
**Table S6.** Energy analysis for optimized geometries of dominant conformers **1Aa**–**1Ah** at B3LYP/6-311G(2d,p) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **1Aa** | -1885.319891 | -1885.281611 | -1885.280667 | -1885.387417 | 0.002103 | 1.319652 | 4.78% |
| **1Ab** | -1885.321033 | -1885.282544 | -1885.2816 | -1885.388853 | 0.000667 | 0.418549 | 21.87% |
| **1Ac** | -1885.323068 | -1885.285164 | -1885.28422 | -1885.38952 | 0 | 0 | 44.35% |
| **1Ad** | -1885.318496 | -1885.280166 | -1885.279222 | -1885.386149 | 0.003371 | 2.115335 | 1.25% |
| **1Ae** | -1885.318432 | -1885.280223 | -1885.279279 | -1885.385334 | 0.004186 | 2.626755 | 0.53% |
| **1Af** | -1885.319663 | -1885.281107 | -1885.280162 | -1885.387746 | 0.001774 | 1.113202 | 6.77% |
| **1Ag** | -1885.321953 | -1885.283946 | -1885.283002 | -1885.388782 | 0.000738 | 0.463102 | 20.29% |
| **1Ah** | -1885.317177 | -1885.278892 | -1885.277948 | -1885.384282 | 0.005238 | 3.286895 | 0.17% |

*E*, *E′*, *H*, *G*: total energy, total energy with zero point energy (*ZPE*), enthalpy, and Gibbs free energy

## Section S2. Calculational details for 3

### *S2.1. Computational details for compound 3 (NMR)*



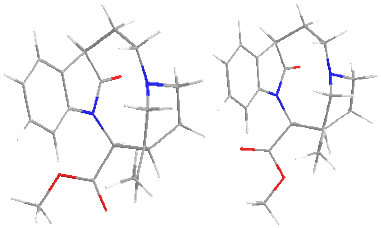

**3a** **3b**

Conformation search based on molecular mechanics with MMFF force fields were performed for **3a**, and **3b** gave 2, and 1 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. Gauge Independent Atomic Orbital (GIAO) calculations of their $^{1}$H and $^{13}$C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The $^{1}$H and $^{13}$C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by linear correlation coefficients ($R^2$) and the improved probability DP4+ method.

**Table S7.** Energy analysis for optimized geometries of dominant conformers **3aA**–**3aB** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **3aA** | -1111.332647 | -1111.310645 | -1111.309701 | -1111.382716 | 0 | 0 | 91.65% |
| **3aB** | -1111.330373 | -1111.308376 | -1111.307431 | -1111.380455 | 0.002261 | 1.418799 | 8.35% |

**Figure S5.** Main conformers of **3a** in NMR and ECD calculations.

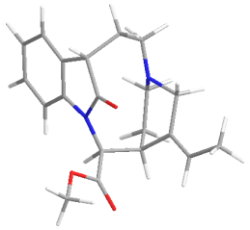


**3aA** **3aB**

**Table S8.** Energy analysis for optimized geometries of dominant conformers **3bA** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **3bA** | -1111.331138 | -1111.309237 | -1111.308293 | -1111.380773 | 0 | 0 | 100.00% |

**Figure S6.** Main conformers of **3b** in NMR calculation.



**3bA**

**Table S9.** Calculated $^{13}C$ NMR results for **3a**

| No. | **3aA** | **3aB** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|
| 2 | -1.4116 | -2.2914 | 189.67 | 184.1 | 181.4 | 2.7 |
| 3 | 141.9232 | 142.2114 | 46.23 | 46.1 | 43.0 | 3.1 |
| 5 | 134.2861 | 134.4603 | 53.88 | 51.7 | 50.4 | 1.3 |
| 6 | 151.2742 | 151.6327 | 36.88 | 31.9 | 34.0 | -2.1 |
| 7 | 138.1072 | 137.8675 | 50.09 | 45.2 | 46.7 | -1.5 |
| 8 | 51.3223 | 51.1203 | 136.88 | 130.1 | 130.4 | -0.3 |
| 9 | 56.7021 | 57.4232 | 131.42 | 125.0 | 125.2 | -0.2 |
| 10 | 60.9598 | 61.0471 | 127.21 | 123.2 | 121.1 | 2.1 |
| 11 | 55.4534 | 55.5887 | 132.72 | 127.3 | 126.4 | 0.9 |
| 12 | 70.1696 | 67.2080 | 118.26 | 114.3 | 112.5 | 1.8 |
| 13 | 35.6491 | 35.4396 | 152.55 | 145.8 | 145.6 | 0.2 |
| 14 | 154.5225 | 153.8186 | 33.72 | 31.0 | 30.9 | 0.1 |
| 15 | 143.5664 | 140.4704 | 44.87 | 35.2 | 41.7 | -6.5 |
| 16 | 121.2378 | 118.1563 | 67.20 | 63.2 | 63.2 | 0.0 |
| 17 | 5.2266 | 6.4705 | 182.85 | 172.7 | 174.8 | -2.1 |
| 18 | 172.2769 | 172.6176 | 15.88 | 13.9 | 13.7 | 0.2 |
| 19 | 56.2750 | 57.7685 | 131.78 | 121.7 | 125.5 | -3.8 |
| 20 | 42.6596 | 41.4894 | 145.62 | 136.5 | 138.9 | -2.4 |
| 21 | 129.8492 | 130.3397 | 58.29 | 59.6 | 54.6 | 5.0 |
| -$OCH_3$ | 132.9766 | 132.7825 | 55.22 | 53.0 | 51.7 | 1.3 |
| Population | 91.65% | 8.35% | | | RMSD | 2.5 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Table S10.** Calculated $^{13}C$ NMR results for **3b**

| No. | **3bA** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|
| 2 | -0.2863 | 188.47 | 184.1 | 180.7 | 3.4 |
| 3 | 136.1902 | 51.99 | 46.1 | 48.7 | -2.6 |
| 5 | 134.6476 | 53.53 | 51.7 | 50.2 | 1.5 |
| 6 | 152.0603 | 36.12 | 31.9 | 33.4 | -1.5 |
| 7 | 138.2472 | 49.93 | 45.2 | 46.8 | -1.6 |
| 8 | 50.9131 | 137.27 | 130.1 | 131.2 | -1.1 |
| 9 | 56.2807 | 131.90 | 125.0 | 126.0 | -1.0 |
| 10 | 61.0550 | 127.13 | 123.2 | 121.4 | 1.8 |
| 11 | 54.0685 | 134.11 | 127.3 | 128.1 | -0.8 |
| 12 | 74.0292 | 114.15 | 114.3 | 108.8 | 5.5 |
| 13 | 34.7420 | 153.44 | 145.8 | 146.8 | -1.0 |
| 14 | 156.3956 | 31.79 | 31.0 | 29.2 | 1.8 |
| 15 | 141.5133 | 46.67 | 35.2 | 43.6 | -8.4 |
| 16 | 121.4071 | 66.77 | 63.2 | 63.0 | 0.2 |
| 17 | 7.8113 | 180.37 | 172.7 | 172.9 | -0.2 |
| 18 | 172.1963 | 15.98 | 13.9 | 13.9 | 0.0 |
| 19 | 56.3919 | 131.79 | 121.7 | 125.9 | -4.2 |
| 20 | 42.1198 | 146.06 | 136.5 | 139.7 | -3.2 |
| 21 | 135.0487 | 53.13 | 59.6 | 49.9 | 9.7 |
| -$OCH_3$ | 133.6053 | 54.58 | 53.0 | 51.2 | 1.8 |
| Population | 100% | | | RMSD | 3.6 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Figure S7.** $^{13}$C NMR calculation results of two possible isomers of **3**. (a) Linear correlation plots of predicted versus experimental $^{13}$C NMR chemical shifts. (b) Relative errors between the predicted $^{13}$C NMR chemical shifts of two potential structures and recorded $^{13}$C NMR data.

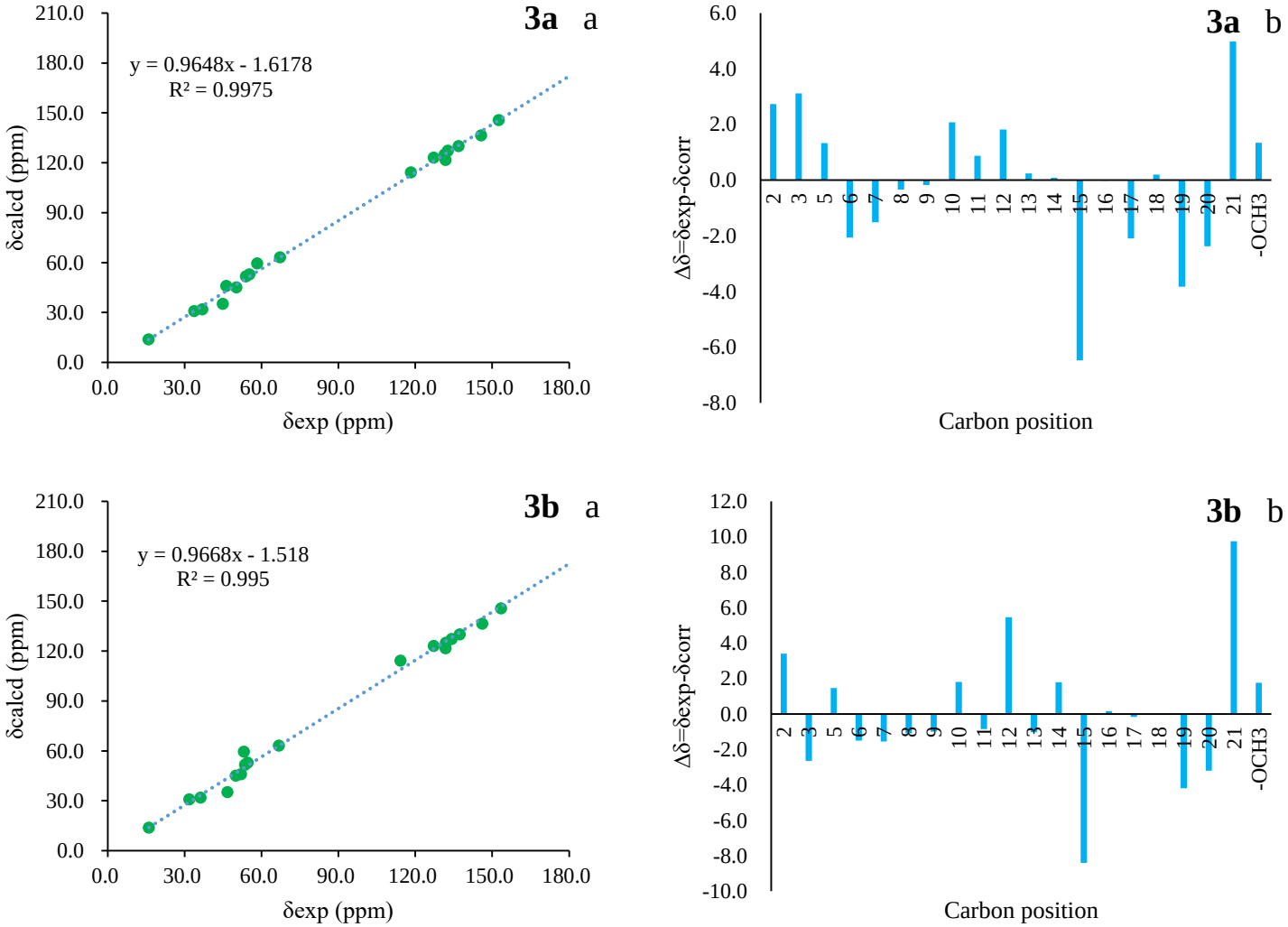


**Table S11.** DP4+ analysis results of **3a** (Isomer 1) and **3b** (Isomer 2)

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 12 | | | DP4+ | 100.00% | 0.00% | - | - | - |
| 14 | Nuclei | sp2? | xperimenta | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 |
| 15 | C | x | 184.1 | -1.49 | -0.29 | | | |
| 16 | C | | 46.1 | 141.95 | 136.19 | | | |
| 17 | C | | 51.7 | 134.30 | 134.65 | | | |
| 18 | C | | 31.9 | 151.30 | 152.06 | | | |
| 19 | C | | 45.2 | 138.09 | 138.25 | | | |
| 20 | C | x | 130.1 | 51.31 | 50.91 | | | |
| 21 | C | x | 125 | 56.76 | 56.28 | | | |
| 22 | C | x | 123.2 | 60.97 | 61.06 | | | |
| 23 | C | x | 127.3 | 55.46 | 54.07 | | | |
| 24 | C | x | 114.3 | 69.92 | 74.03 | | | |
| 25 | C | x | 145.8 | 35.63 | 34.74 | | | |
| 26 | C | | 31 | 154.46 | 156.40 | | | |
| 27 | C | | 35.2 | 143.31 | 141.51 | | | |
| 28 | C | | 63.2 | 120.98 | 121.41 | | | |
| 29 | C | x | 172.7 | 5.33 | 7.81 | | | |
| 30 | C | | 13.9 | 172.31 | 172.20 | | | |
| 31 | C | x | 121.7 | 56.40 | 56.39 | | | |
| 32 | C | x | 136.5 | 42.56 | 42.12 | | | |
| 33 | C | | 59.6 | 129.89 | 135.05 | | | |
| 34 | C | | 53 | 132.96 | 133.61 | | | |
| 35 | | | | | | | | |
| 36 | H | | 1.96 | 29.77 | 29.54 | | | |
| 37 | H | | 2.72 | 29.12 | 30.39 | | | |
| 38 | H | | 1.94 | 29.74 | 29.76 | | | |
| 39 | H | | 2.21 | 29.35 | 29.44 | | | |
| 40 | H | | 2.19 | 29.52 | 29.56 | | | |
| 41 | H | | 2.55 | 29.12 | 29.15 | | | |
| 42 | H | | 3.39 | 28.31 | 28.51 | | | |
| 43 | H | x | 7.27 | 24.11 | 24.09 | | | |
| 44 | H | x | 7.03 | 24.37 | 24.31 | | | |
| 45 | H | x | 7.05 | 24.32 | 24.09 | | | |
| 46 | H | x | 6.68 | 25.03 | 24.47 | | | |

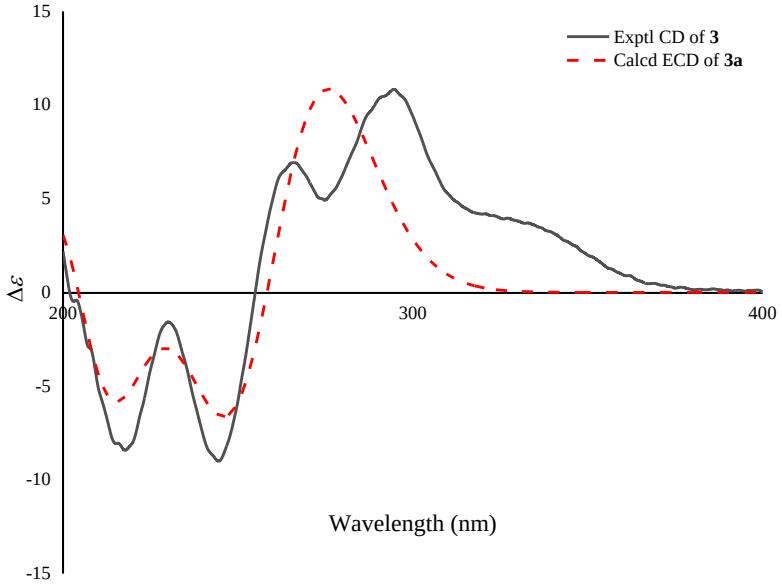
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 47 | H | | 1.67 | 30.07 | 29.84 | | | |
| 48 | H | | 2.25 | 29.68 | 30.11 | | | |
| 49 | H | | 3.78 | 28.24 | 28.61 | | | |
| 50 | H | | 5.43 | 26.37 | 27.17 | | | |
| 51 | H | | 1.73 | 30.35 | 30.03 | | | |
| 52 | H | | 1.73 | 30.47 | 30.13 | | | |
| 53 | H | | 1.73 | 30.44 | 30.18 | | | |
| 54 | H | x | 4.86 | 25.95 | 25.80 | | | |
| 55 | H | | 1.6 | 29.93 | 28.46 | | | |
| 56 | H | | 2.68 | 28.85 | 28.96 | | | |
| 57 | H | | 3.84 | 28.08 | 28.20 | | | |
| 58 | H | | 3.84 | 27.89 | 27.88 | | | |
| 59 | H | | 3.84 | 27.91 | 28.19 | | | |

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 100.00% | 0.00% | – | – | – | – |
| 6 | sDP4+ (C data) | | 100.00% | 0.00% | – | – | – | – |
| 7 | sDP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |
| 8 | uDP4+ (H data) | | 100.00% | 0.00% | – | – | – | – |
| 9 | uDP4+ (C data) | | 99.98% | 0.02% | – | – | – | – |
| 10 | uDP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |
| 11 | DP4+ (H data) | | 100.00% | 0.00% | – | – | – | – |
| 12 | DP4+ (C data) | | 100.00% | 0.00% | – | – | – | – |
| 13 | DP4+ (all data) | | 100.00% | 0.00% | – | – | – | – |

## *S2.2. Computational details for compound 3 (ECD)*

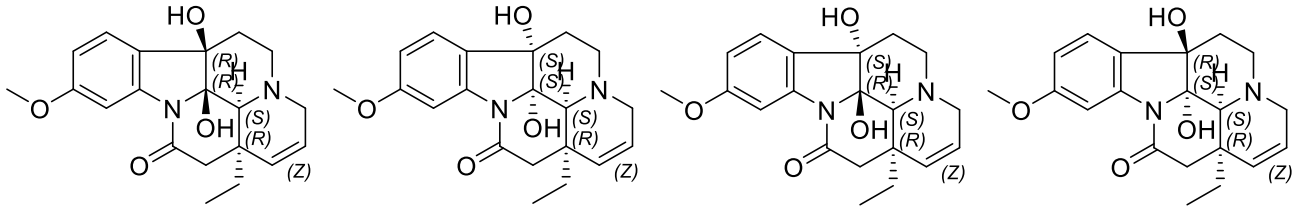
Conformation search based on molecular mechanics with MMFF force fields were performed for **3a** gave 2 stable conformers with populations higher than 1%. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d,p) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 program package ($\sigma$ = 0.30 eV, and UV shift -22 nm) and the calculated ECD data of all conformers were Boltzmann averaged by Gibbs free energy.

**Figure S8.** Comparison of the calculated ECD spectra with the experimental spectrum of **3** in methanol with PCM model.



## Section S3. Calculational details for 4

### *S3.1. Computational details for compound 4 (NMR)*

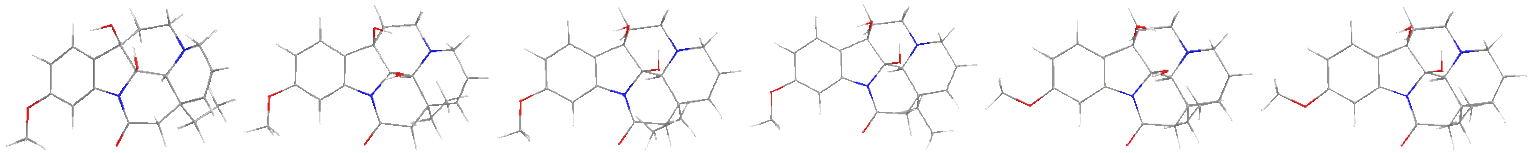



Conformation search based on molecular mechanics with MMFF force fields were performed for **4a**, **4b**, **4c**, **4d** gave 6, 4, 5, and 4 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. Gauge Independent Atomic Orbital (GIAO) calculations of their $^{1}$H and $^{13}$C NMR chemical shifts using density functional theory (DFT) at the mPW1PW91/6-311+G(d,p) level with the PCM model in methanol. The calculated NMR data of these conformers were averaged according to the Boltzmann distribution theory and their relative Gibbs free energy. The $^{1}$H and $^{13}$C NMR chemical shifts for TMS were also calculated by the same procedures and used as the reference. After calculation, the experimental and calculated data were evaluated by linear correlation coefficients ($R^2$) and the improved probability DP4+ method.

**Table S12.** Energy analysis for optimized geometries of dominant conformers **4aA**–**4aF** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **4aA** | -1186.528244 | -1186.506097 | -1186.505153 | -1186.577142 | 0 | 0 | 59.12% |
| **4aB** | -1186.525993 | -1186.503870 | -1186.502926 | -1186.574886 | 0.002256 | 1.415661 | 5.41% |
| **4aC** | -1186.526787 | -1186.504603 | -1186.503659 | -1186.575685 | 0.001457 | 0.914281 | 12.62% |
| **4aD** | -1186.526534 | -1186.504343 | -1186.503399 | -1186.575567 | 0.001575 | 0.988327 | 11.14% |
| **4aE** | -1186.524416 | -1186.502260 | -1186.501316 | -1186.573463 | 0.003679 | 2.308607 | 1.20% |
| **4aF** | -1186.526495 | -1186.504312 | -1186.503368 | -1186.575513 | 0.001629 | 1.022213 | 10.52% |

**Figure S9.** Main conformers of **4a** in NMR and ECD calculations.

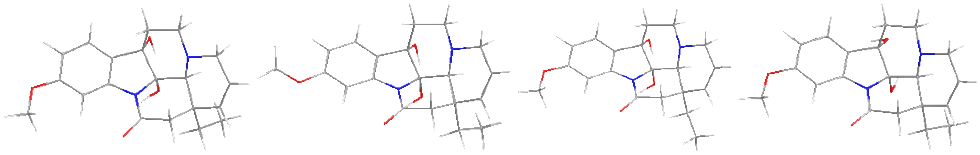


**4aA** **4aB** **4aC** **4aD** **4aE** **4aF**

**Table S13.** Energy analysis for optimized geometries of dominant conformers **4bA**–**4bD** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **4bA** | -1186.534528 | -1186.512406 | -1186.511462 | -1186.583146 | 0 | 0 | 66.88% |
| **4bB** | -1186.533465 | -1186.511333 | -1186.510389 | -1186.582148 | 0.000998 | 0.626254 | 23.23% |
| **4bC** | -1186.531817 | -1186.509571 | -1186.508627 | -1186.581101 | 0.002045 | 1.283257 | 7.66% |
| **4bD** | -1186.531036 | -1186.508745 | -1186.507801 | -1186.579939 | 0.003207 | 2.012423 | 2.23% |

**Figure S10.** Main conformers of **4b** in NMR and ECD calculations.

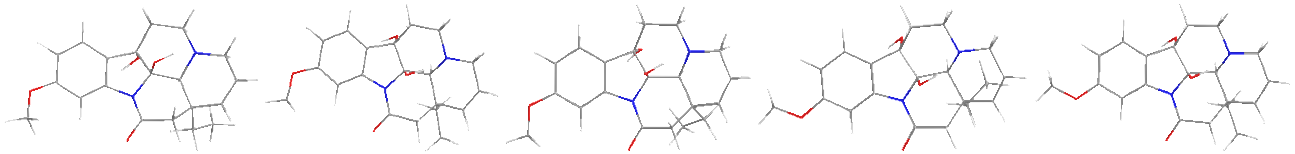


**4bA** **4bB** **4bC** **4bD**

**Table S14.** Energy analysis for optimized geometries of dominant conformers **4cA**–**4cE** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **4cA** | -1186.519276 | -1186.497403 | -1186.496459 | -1186.567421 | 0 | 0 | 35.86% |
| **4cB** | -1186.518530 | -1186.496628 | -1186.495684 | -1186.566970 | 0.000451 | 0.283007 | 22.23% |
| **4cC** | -1186.518832 | -1186.496958 | -1186.496013 | -1186.566969 | 0.000452 | 0.283634 | 22.21% |
| **4cD** | -1186.518146 | -1186.496216 | -1186.495271 | -1186.566439 | 0.000982 | 0.616214 | 12.66% |
| **4cE** | -1186.517382 | -1186.495455 | -1186.494511 | -1186.565884 | 0.001537 | 0.964482 | 7.03% |

**Figure S11.** Main conformers of **4c** in NMR and ECD calculations.

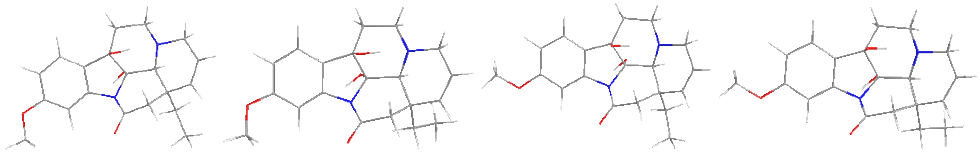


**4cA** **4cB** **4cC** **4cD** **4cE**

**Table S15.** Energy analysis for optimized geometries of dominant conformers **4dA**–**4dD** at B3LYP/6-31G(d) level in the gas phase

| Species | *E′=E+ZPE* | *E* | *H* | *G* | *ΔG* | *ΔE*(kcal/mol) | *PE*% |
|---|---|---|---|---|---|---|---|
| **4dA** | -1186.510799 | -1186.488883 | -1186.487939 | -1186.559356 | 0.000782 | 0.490712 | 22.61% |
| **4dB** | -1186.511231 | -1186.489191 | -1186.488247 | -1186.560138 | 0 | 0 | 51.78% |
| **4dC** | -1186.509823 | -1186.487913 | -1186.486969 | -1186.558397 | 0.001741 | 1.092494 | 8.18% |
| **4dD** | -1186.510254 | -1186.488225 | -1186.487281 | -1186.559111 | 0.001027 | 0.644452 | 17.44% |

**Figure S12.** Main conformers of **4d** in NMR and ECD calculations.



**4dA** **4dB** **4dC** **4dD**

**Table S16.** Calculated $^{13}C$ NMR results for **4a**

| No. | **4aA** | **4aB** | **4aC** | **4aD** | **4aE** | **4aF** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 89.0177 | 89.5332 | 89.9805 | 89.3992 | 89.5428 | 88.7698 | 98.99 | 93.1 | 95.1 | -2.0 |
| 3 | 133.6251 | 133.5503 | 133.4514 | 132.9541 | 133.5633 | 133.6545 | 54.65 | 55.7 | 52.7 | 3.0 |
| 5 | 137.6755 | 138.2344 | 137.2596 | 137.4291 | 137.9413 | 137.3635 | 50.58 | 50.3 | 48.8 | 1.5 |
| 6 | 152.1772 | 152.2745 | 152.2488 | 152.0981 | 152.5340 | 152.2037 | 35.99 | 37.5 | 34.9 | 2.6 |
| 7 | 104.3283 | 104.3076 | 104.3050 | 103.9541 | 104.5018 | 104.0856 | 83.92 | 79.3 | 80.7 | -1.4 |
| 8 | 58.4256 | 59.4498 | 57.8696 | 58.0508 | 57.8628 | 56.1965 | 130.05 | 130.9 | 124.8 | 6.1 |
| 9 | 56.9562 | 55.9223 | 57.2173 | 57.4222 | 55.8074 | 56.6506 | 131.24 | 124.0 | 126.0 | -2.0 |
| 10 | 69.2695 | 69.7522 | 69.3952 | 68.8567 | 78.2474 | 78.1369 | 117.88 | 111.3 | 113.2 | -1.9 |
| 11 | 18.0590 | 18.7775 | 18.2972 | 18.1358 | 18.3554 | 17.5278 | 170.10 | 161.6 | 163.2 | -1.6 |
| 12 | 86.1268 | 86.2579 | 85.6547 | 85.8326 | 79.0918 | 78.6414 | 103.01 | 106.1 | 99.0 | 7.1 |
| 13 | 37.2620 | 37.8712 | 37.8784 | 37.6444 | 38.9139 | 38.2124 | 150.65 | 141.2 | 144.5 | -3.3 |
| 14 | 55.2473 | 55.5883 | 58.6018 | 56.9179 | 55.6711 | 55.3142 | 132.29 | 125.2 | 127.0 | -1.8 |
| 15 | 49.9002 | 50.3988 | 47.2530 | 50.8275 | 50.6877 | 50.2417 | 138.44 | 135.4 | 132.9 | 2.5 |
| 16 | 9.5194 | 10.1536 | 9.3113 | 9.8039 | 10.3477 | 9.8263 | 178.58 | 170.2 | 171.3 | -1.1 |
| 17 | 136.6527 | 136.7124 | 140.2162 | 143.0717 | 136.6333 | 136.5770 | 50.37 | 45.1 | 48.6 | -3.5 |
| 18 | 176.0864 | 176.1143 | 177.0339 | 177.4802 | 176.4510 | 176.3818 | 11.78 | 9.5 | 11.7 | -2.2 |
| 19 | 147.6877 | 147.4271 | 148.4931 | 148.0706 | 147.0265 | 147.3145 | 40.41 | 34.0 | 39.1 | -5.1 |
| 20 | 144.9104 | 145.3587 | 145.8976 | 145.9838 | 145.3559 | 144.9426 | 42.99 | 40.4 | 41.6 | -1.2 |
| 21 | 126.3261 | 126.5133 | 129.8561 | 122.4294 | 126.1545 | 125.8239 | 61.89 | 61.8 | 59.6 | 2.2 |
| -$OCH_3$ | 132.3480 | 132.3539 | 132.1058 | 132.5203 | 131.7331 | 131.7411 | 55.92 | 56.0 | 53.9 | 2.1 |
| Population | 59.12% | 5.41% | 12.62% | 11.14% | 1.20% | 10.52% | | | RMSD | 3.1 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Table S17.** Calculated $^{13}C$ NMR results for **4b**

| No. | **4bA** | **4bB** | **4bC** | **4bD** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|---|---|
| 2 | 89.2092 | 89.1430 | 89.3242 | 90.9718 | 98.94 | 93.1 | 94.8 | -1.7 |
| 3 | 130.8292 | 130.8784 | 130.6541 | 130.9717 | 57.35 | 55.7 | 54.8 | 0.9 |
| 5 | 137.2352 | 136.7294 | 136.9658 | 136.7054 | 51.10 | 50.3 | 48.8 | 1.5 |
| 6 | 149.5743 | 149.6063 | 149.8007 | 148.1514 | 38.61 | 37.5 | 36.9 | 0.6 |
| 7 | 104.6621 | 104.7230 | 104.3950 | 102.3634 | 83.58 | 79.3 | 80.0 | -0.7 |
| 8 | 55.1282 | 53.4416 | 54.9969 | 54.8533 | 133.46 | 130.9 | 127.9 | 3.0 |
| 9 | 57.1346 | 56.9793 | 57.0098 | 59.8330 | 131.03 | 124.0 | 125.6 | -1.6 |
| 10 | 68.4434 | 77.4543 | 68.4361 | 69.3366 | 117.63 | 111.3 | 112.7 | -1.4 |
| 11 | 19.8935 | 20.1358 | 19.8556 | 19.5813 | 168.24 | 161.6 | 161.3 | 0.3 |
| 12 | 82.5999 | 75.9516 | 82.4166 | 82.7730 | 107.14 | 106.1 | 102.6 | 3.5 |
| 13 | 41.8657 | 42.3290 | 42.0452 | 38.6640 | 146.27 | 141.2 | 140.2 | 1.0 |
| 14 | 52.8505 | 52.7511 | 53.7829 | 53.2440 | 135.27 | 125.2 | 129.7 | -4.5 |
| 15 | 45.3875 | 45.3915 | 49.2412 | 45.3368 | 142.50 | 135.4 | 136.6 | -1.2 |
| 16 | 11.7760 | 11.7412 | 11.6758 | 11.8231 | 176.42 | 170.2 | 169.2 | 1.0 |
| 17 | 139.0748 | 139.2158 | 144.5157 | 139.2289 | 48.65 | 45.1 | 46.5 | -1.4 |
| 18 | 176.5640 | 176.3911 | 179.3350 | 176.5019 | 11.45 | 9.5 | 10.8 | -1.3 |
| 19 | 151.7688 | 151.6772 | 155.5089 | 152.2258 | 36.14 | 34.0 | 34.5 | -0.5 |
| 20 | 142.6134 | 142.9094 | 143.2746 | 143.0104 | 45.44 | 40.4 | 43.4 | -3.0 |
| 21 | 127.9784 | 128.2626 | 122.0192 | 123.4066 | 60.70 | 61.8 | 58.1 | 3.7 |
| -$OCH_3$ | 131.5552 | 131.6037 | 131.2107 | 131.6207 | 56.64 | 56.0 | 54.2 | 1.8 |
| Population | 66.88% | 23.23% | 7.66% | 2.23% | | | RMSD | 2.1 |

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Table S18.** Calculated $^{13}C$ NMR results for **4c**

| No. | **4cA** | **4cB** | **4cC** | **4cD** | **4cE** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 92.4096 | 92.5280 | 91.8986 | 92.0786 | 92.4535 | 95.90 | 93.1 | 91.9 | 1.2 |
| 3 | 136.6348 | 136.4538 | 137.3523 | 136.4798 | 136.5256 | 51.45 | 55.7 | 50.1 | 5.6 |
| 5 | 135.1209 | 134.6970 | 134.9328 | 135.1732 | 134.7981 | 53.21 | 50.3 | 51.8 | -1.5 |
| 6 | 154.1896 | 154.3355 | 154.5519 | 154.1612 | 154.3024 | 33.87 | 37.5 | 33.6 | 3.9 |
| 7 | 105.0537 | 105.3532 | 104.8041 | 105.0590 | 105.1196 | 83.11 | 79.3 | 79.9 | -0.6 |
| 8 | 55.5867 | 55.6083 | 55.7197 | 54.0527 | 54.1316 | 132.86 | 130.9 | 126.6 | 4.3 |
| 9 | 55.9566 | 55.9357 | 56.1577 | 55.6819 | 55.6334 | 132.24 | 124.0 | 126.1 | -2.1 |
| 10 | 69.9172 | 69.8629 | 69.9018 | 78.6156 | 78.5655 | 116.57 | 111.3 | 111.3 | 0.0 |
| 11 | 18.6166 | 18.7137 | 18.6904 | 18.6499 | 18.9610 | 169.50 | 161.6 | 161.1 | 0.5 |
| 12 | 84.9383 | 85.0306 | 84.7737 | 77.2812 | 77.8188 | 104.73 | 106.1 | 100.2 | 5.9 |
| 13 | 35.0535 | 35.1127 | 35.3381 | 35.7557 | 35.8236 | 152.91 | 141.2 | 145.5 | -4.3 |
| 14 | 52.0986 | 53.9120 | 55.0934 | 52.2241 | 53.9534 | 134.87 | 125.2 | 128.5 | -3.3 |
| 15 | 48.3921 | 47.8674 | 44.3066 | 48.7933 | 47.8510 | 140.80 | 135.4 | 134.1 | 1.3 |
| 16 | 7.8659 | 8.4225 | 7.5004 | 8.1377 | 8.6616 | 180.18 | 170.2 | 171.1 | -0.9 |
| 17 | 136.5053 | 142.8966 | 139.7183 | 136.1307 | 142.6987 | 49.15 | 45.1 | 48.0 | -2.9 |
| 18 | 178.0841 | 177.9557 | 177.2136 | 178.0253 | 177.7266 | 10.35 | 9.5 | 11.5 | -2.0 |
| 19 | 149.3819 | 147.5538 | 145.2269 | 149.1272 | 147.0171 | 40.33 | 34.0 | 39.7 | -5.7 |
| 20 | 143.9726 | 145.0842 | 144.4794 | 143.9453 | 144.5618 | 43.81 | 40.4 | 43.0 | -2.6 |
| 21 | 129.0168 | 122.6914 | 127.0535 | 128.8618 | 122.2869 | 61.50 | 61.8 | 59.6 | 2.2 |
| -$OCH_3$ | 131.5043 | 131.8302 | 131.5289 | 131.6014 | 131.7760 | 56.57 | 56.0 | 54.9 | 1.1 |
| Population | 35.86% | 22.23% | 22.21% | 12.66% | 7.03% | | | RMSD | 3.1 |

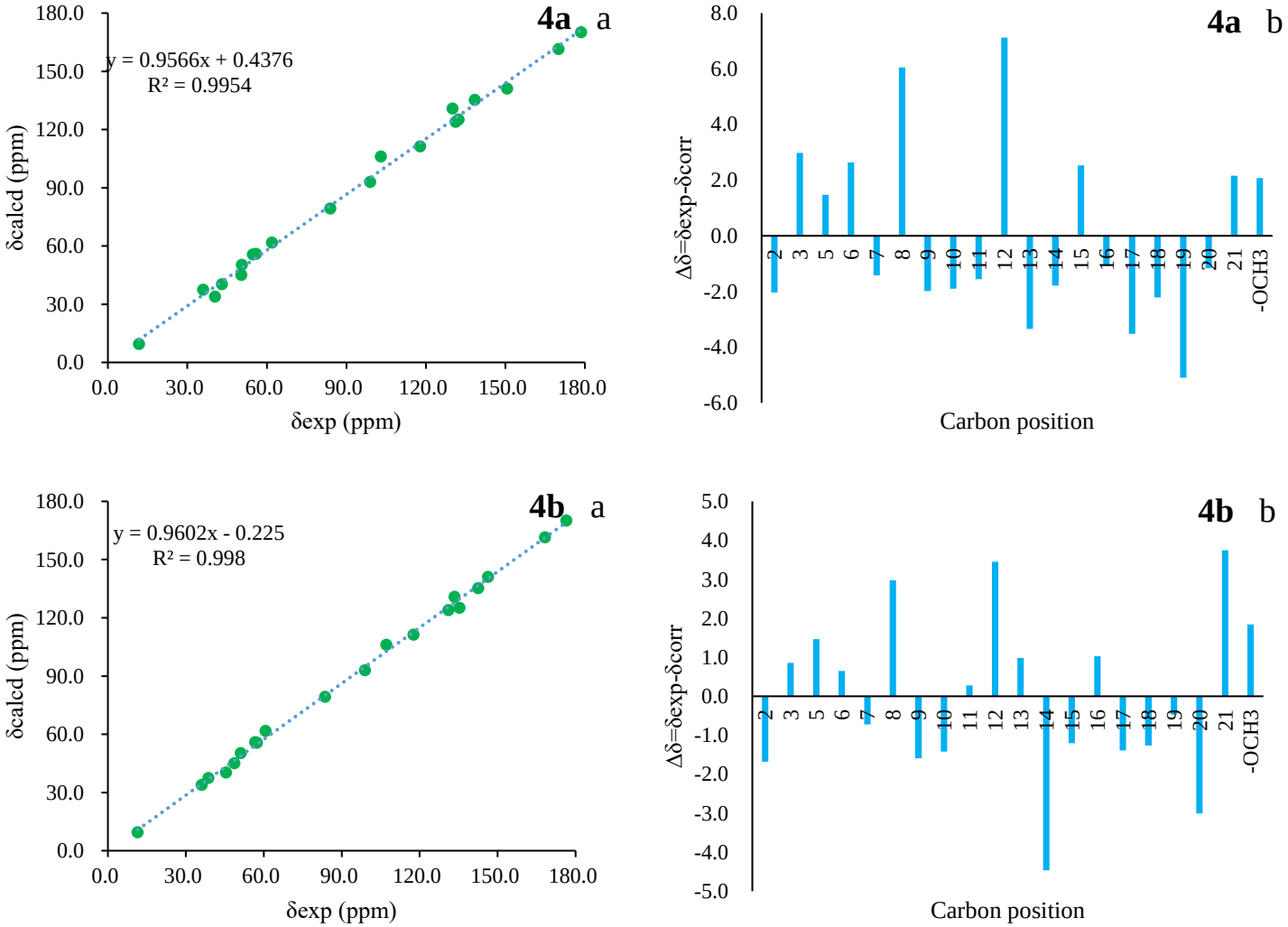
[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

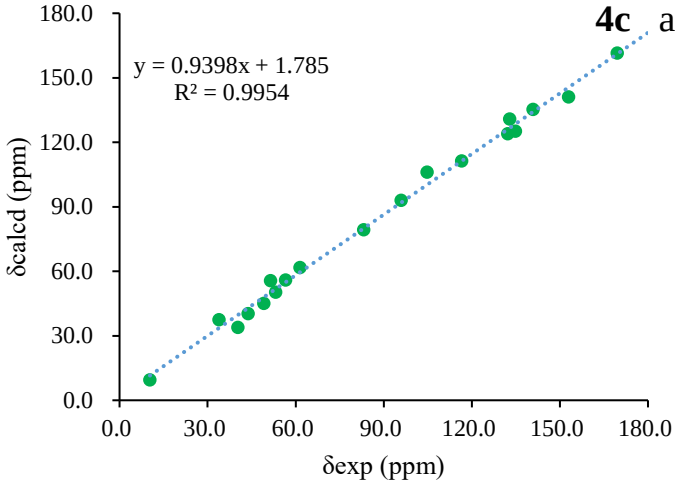
**Table S19.** Calculated $^{13}C$ NMR results for **4d**

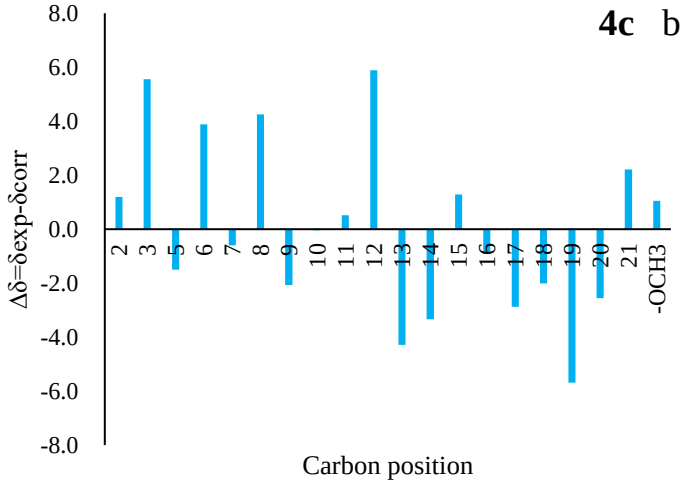
| No. | **4dA** | **4dB** | **4dC** | **4dD** | $\delta_{Calcd}$[a] | $\delta_{Exp}$ | $\delta_{Corr}$[b] | Relative errors[c] |
|---|---|---|---|---|---|---|---|---|
| 2 | 89.6777 | 89.0505 | 89.7498 | 89.0167 | 98.94 | 93.1 | 94.3 | -1.2 |
| 3 | 134.1612 | 134.3055 | 133.9316 | 134.2523 | 53.95 | 55.7 | 52.3 | 3.4 |
| 5 | 134.9985 | 135.1200 | 135.1446 | 135.2425 | 53.07 | 50.3 | 51.5 | -1.2 |
| 6 | 158.9561 | 158.9986 | 158.6318 | 158.6779 | 29.28 | 37.5 | 29.3 | 8.2 |
| 7 | 101.8580 | 101.9320 | 101.8417 | 101.8671 | 86.28 | 79.3 | 82.5 | -3.2 |
| 8 | 55.6014 | 55.4457 | 54.4665 | 54.2527 | 132.99 | 130.9 | 126.1 | 4.8 |
| 9 | 55.9095 | 55.9498 | 56.0335 | 56.0471 | 132.22 | 124.0 | 125.4 | -1.4 |
| 10 | 68.4665 | 68.4436 | 77.1029 | 77.2751 | 117.48 | 111.3 | 111.6 | -0.3 |
| 11 | 19.3492 | 19.4181 | 19.2517 | 19.1955 | 168.83 | 161.6 | 159.5 | 2.1 |
| 12 | 79.0999 | 78.7711 | 71.0959 | 70.6026 | 111.39 | 106.1 | 105.9 | 0.2 |
| 13 | 33.6100 | 33.7169 | 34.3396 | 34.2427 | 154.35 | 141.2 | 146.0 | -4.8 |
| 14 | 55.5220 | 53.6686 | 55.6507 | 53.7456 | 133.92 | 125.2 | 126.9 | -1.7 |
| 15 | 50.9389 | 49.2935 | 50.7199 | 49.0984 | 138.43 | 135.4 | 131.2 | 4.2 |
| 16 | 8.0095 | 8.4351 | 8.3766 | 8.7156 | 179.80 | 170.2 | 169.7 | 0.5 |
| 17 | 145.3910 | 139.9229 | 145.3395 | 140.0015 | 46.57 | 45.1 | 45.5 | -0.4 |
| 18 | 178.5562 | 177.3207 | 178.1597 | 177.3726 | 10.50 | 9.5 | 11.8 | -2.3 |
| 19 | 152.0918 | 152.8630 | 151.3424 | 152.8356 | 35.62 | 34.0 | 35.3 | -1.3 |
| 20 | 146.1676 | 145.5353 | 145.8422 | 145.4948 | 42.48 | 40.4 | 41.7 | -1.3 |
| 21 | 113.8386 | 120.2023 | 114.0531 | 120.5280 | 69.86 | 61.8 | 67.2 | -5.4 |
| -$OCH_3$ | 131.6204 | 131.4389 | 131.6028 | 131.5975 | 56.66 | 56.0 | 54.9 | 1.1 |
| Population | 22.61% | 51.78% | 8.18% | 17.44% | | | RMSD | 3.2 |

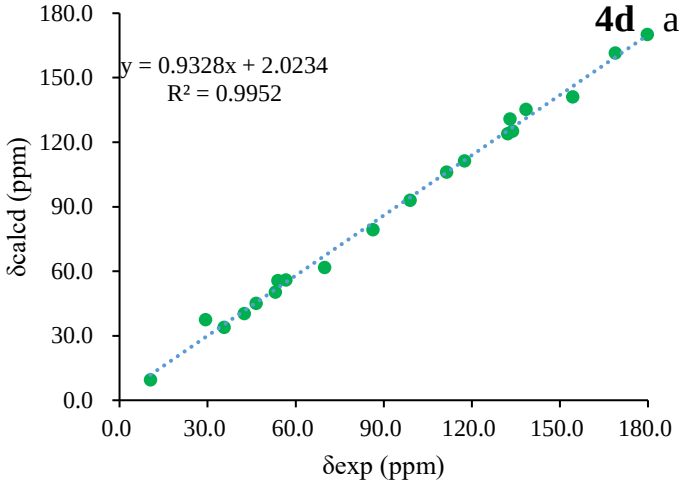
[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta_{exp} - \delta_{corr}$.

**Figure S13.** $^{13}$C NMR calculation results of four possible isomers of **4**. (a) Linear correlation plots of predicted versus experimental $^{13}$C NMR chemical shifts. (b) Relative errors between the predicted $^{13}$C NMR chemical shifts of two potential structures and recorded $^{13}$C NMR data.




4c a
y = 0.9398x + 1.785
R² = 0.9954
δcalcd (ppm)
δexp (ppm)
0.0
30.0
60.0
90.0
120.0
150.0
180.0


4c b
Δδ=δexp-δcorr
Carbon position
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
2
3
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
-OCH3


4d a
y = 0.9328x + 2.0234
R² = 0.9952
δcalcd (ppm)
δexp (ppm)
0.0
30.0
60.0
90.0
120.0
150.0
180.0

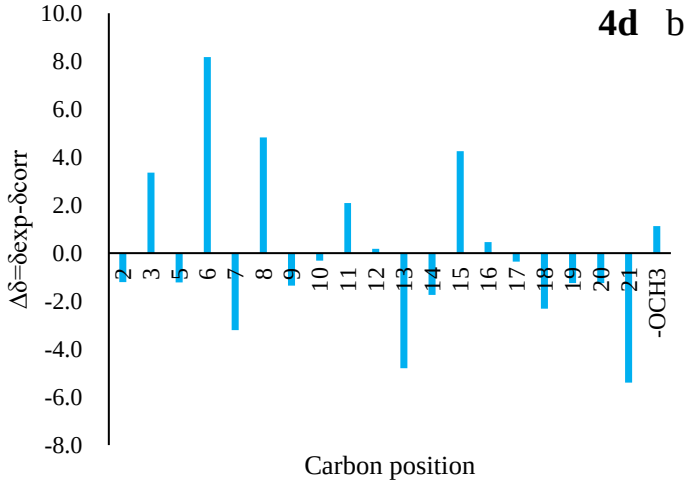

4d b
Δδ=δexp-δcorr
Carbon position
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
2
3
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
-OCH3

**Table S20.** DP4+ analysis results of **4a** (Isomer 1), **4b** (Isomer 2), **4c** (Isomer 3), and **4d** (Isomer 4)

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 12 | | | DP4+ | 0.00% | 100.00% | 0.00% | 0.00% | - |
| 14 | Nuclei | sp2? | xperimenta | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 |
| 15 | C | | 93.1 | 89.19 | 89.24 | 92.28 | 89.24 | |
| 16 | C | | 55.7 | 133.53 | 130.83 | 136.73 | 134.23 | |
| 17 | C | | 50.3 | 137.60 | 137.09 | 134.97 | 135.12 | |
| 18 | C | | 37.5 | 152.19 | 149.57 | 154.31 | 158.90 | |
| 19 | C | | 79.3 | 104.26 | 104.60 | 105.07 | 101.90 | |
| 20 | C | x | 130.9 | 58.13 | 54.72 | 55.32 | 55.19 | |
| 21 | C | x | 124 | 56.94 | 57.15 | 55.94 | 55.96 | |
| 22 | C | x | 111.3 | 70.31 | 70.56 | 71.61 | 70.70 | |
| 23 | C | x | 161.6 | 18.08 | 19.94 | 18.68 | 19.35 | |
| 24 | C | x | 106.1 | 85.17 | 81.05 | 83.45 | 76.79 | |
| 25 | C | x | 141.2 | 37.54 | 41.92 | 35.27 | 33.84 | |
| 26 | C | x | 125.2 | 55.89 | 52.91 | 53.31 | 54.26 | |
| 27 | C | x | 135.4 | 49.74 | 45.68 | 47.38 | 49.75 | |
| 28 | C | x | 170.2 | 9.60 | 11.76 | 8.00 | 8.38 | |
| 29 | C | | 45.1 | 137.81 | 139.53 | 139.03 | 141.62 | |
| 30 | C | | 9.5 | 176.40 | 176.73 | 177.83 | 177.68 | |
| 31 | C | | 34 | 147.77 | 152.04 | 147.85 | 152.56 | |
| 32 | C | | 40.4 | 145.19 | 142.74 | 144.37 | 145.70 | |
| 33 | C | | 61.8 | 126.29 | 127.49 | 126.68 | 118.32 | |
| 34 | C | | 56 | 132.27 | 131.54 | 131.61 | 131.52 | |
| 35 | | | | | | | | |
| 36 | H | | 2.88 | 28.42 | 28.60 | 28.58 | 28.73 | |
| 37 | H | | 3.29 | 28.41 | 28.40 | 28.57 | 28.37 | |
| 38 | H | | 2.59 | 28.87 | 29.12 | 28.95 | 28.66 | |
| 39 | H | | 2.7 | 28.22 | 28.96 | 28.78 | 29.03 | |
| 40 | H | | 1.6 | 29.39 | 30.29 | 29.39 | 29.49 | |
| 41 | H | | 2.01 | 29.39 | 29.74 | 29.61 | 29.36 | |
| 42 | H | x | 7.26 | 24.10 | 24.11 | 24.06 | 24.04 | |
| 43 | H | x | 6.71 | 24.74 | 24.80 | 24.77 | 24.68 | |
| 44 | H | x | 7.65 | 23.80 | 23.68 | 23.86 | 24.26 | |
| 45 | H | x | 5.77 | 25.52 | 25.57 | 25.32 | 25.49 | |
| 46 | H | x | 5.47 | 25.96 | 25.92 | 25.85 | 25.87 | |

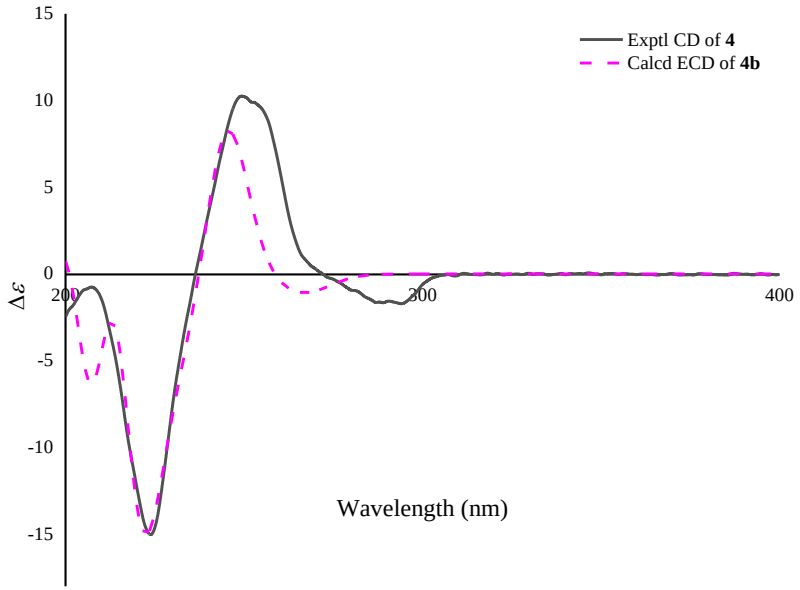
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 47 | H | | 2.35 | 29.49 | 29.51 | 29.45 | 29.49 |
| 48 | H | | 2.91 | 28.64 | 28.73 | 28.65 | 29.07 |
| 49 | H | | 0.96 | 30.94 | 30.90 | 30.85 | 30.84 |
| 50 | H | | 0.96 | 30.86 | 30.84 | 30.81 | 30.81 |
| 51 | H | | 0.96 | 30.89 | 30.55 | 30.83 | 30.71 |
| 52 | H | | 1.42 | 30.34 | 30.26 | 30.31 | 30.11 |
| 53 | H | | 2.28 | 30.32 | 29.62 | 30.20 | 30.08 |
| 54 | H | | 2.79 | 28.71 | 28.94 | 28.17 | 28.81 |
| 55 | H | | 3.79 | 27.67 | 27.68 | 27.66 | 27.67 |
| 56 | H | | 3.79 | 28.05 | 28.02 | 28.01 | 27.99 |
| 57 | H | | 3.79 | 28.03 | 28.03 | 28.03 | 27.99 |

| | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| 1 | Functional | | Solvent? | | Basis Set | | Type of Data | |
| 2 | mPW1PW91 | | PCM | | 6-311+G(d,p) | | Shielding Tensors | |
| 3 | | | | | | | | |
| 4 | | | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
| 5 | sDP4+ (H data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 6 | sDP4+ (C data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 7 | sDP4+ (all data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 8 | uDP4+ (H data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 9 | uDP4+ (C data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 10 | uDP4+ (all data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 11 | DP4+ (H data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 12 | DP4+ (C data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |
| 13 | DP4+ (all data) | | 0.00% | 100.00% | 0.00% | 0.00% | – | – |

### *S3.2. Computational details for compound 4 (ECD)*

Conformation search based on molecular mechanics with MMFF force fields were performed for **4a**, **4b**, **4c**, **4d** gave 6, 4, 5, and 4 stable conformers with populations higher than 1%, respectively. All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level by Gaussian 16 program package with g09 default keyword. The ECD were calculated using density functional theory (TDDFT) at B3LYP/6-31+G(d,p) level in methanol with IEFPCM model. The calculated ECD curves were all generated using SpecDis 1.71 program package and the calculated ECD data of all conformers were Boltzmann averaged by Gibbs free energy.

**Figure S14.** Comparison of the calculated ECD spectra with the experimental spectrum of **4** in methanol with PCM model.



## Section S4. NMR, MS, IR, and CD spectra for 1

**Figure S15.** $^{1}H$ NMR of compound **1** in $CD_3OD$

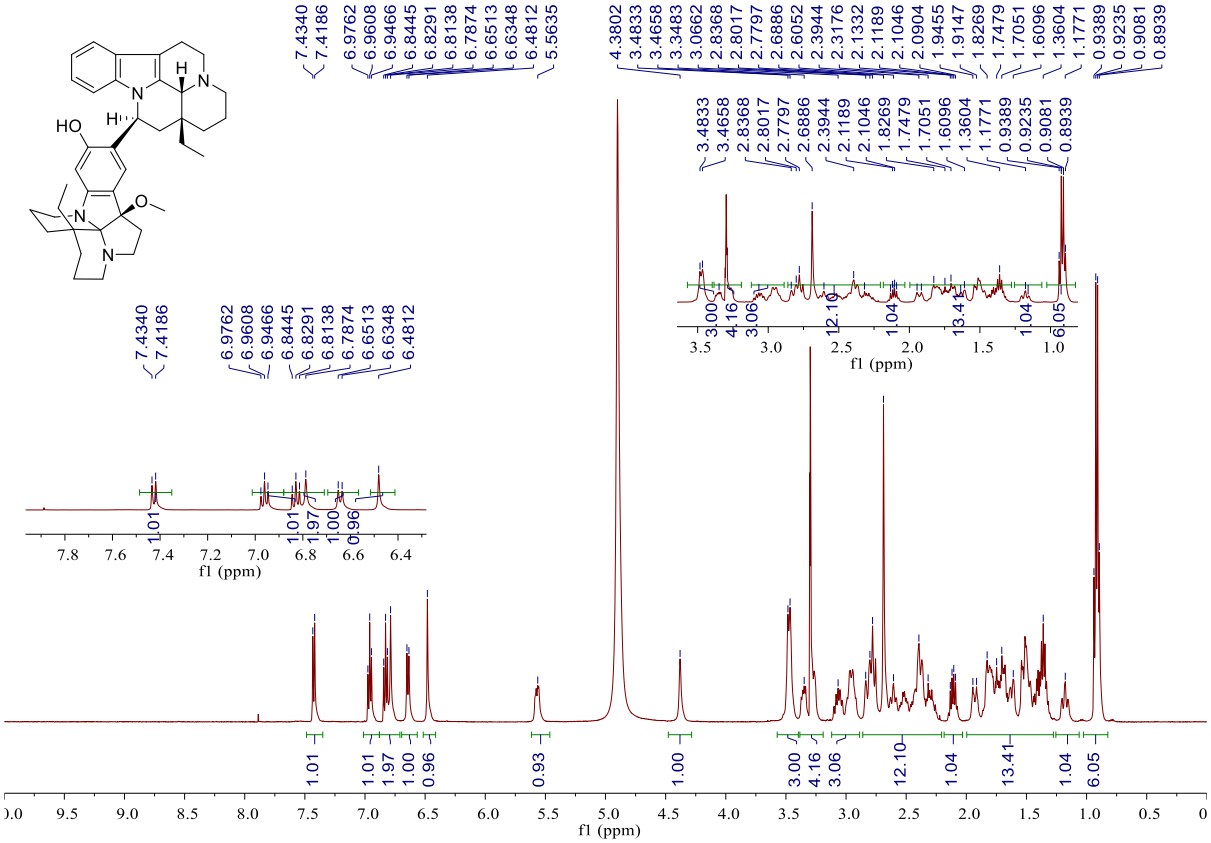



**Figure S16.** $^{13}C$ NMR and DEPT of compound **1** in $CD_3OD$

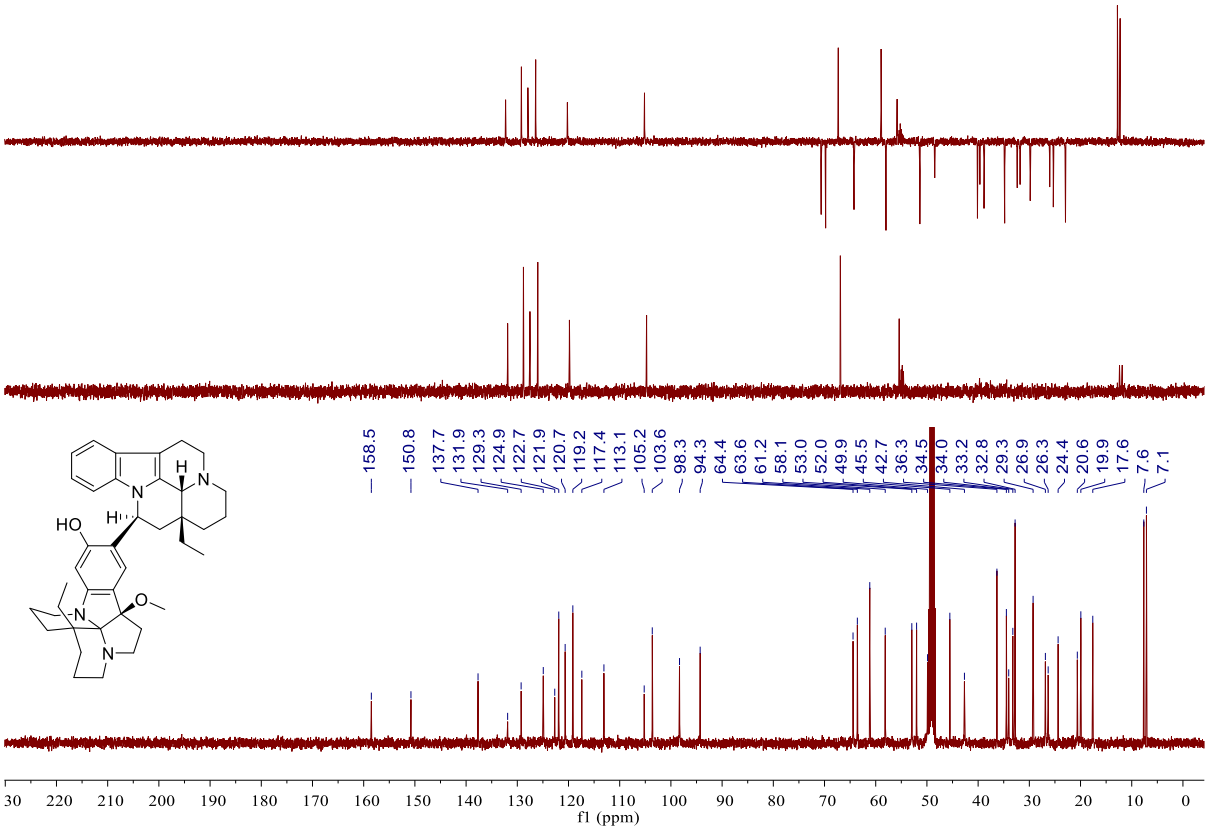


**Figure S17.** HSQC of compound **1** in $CD_3OD$

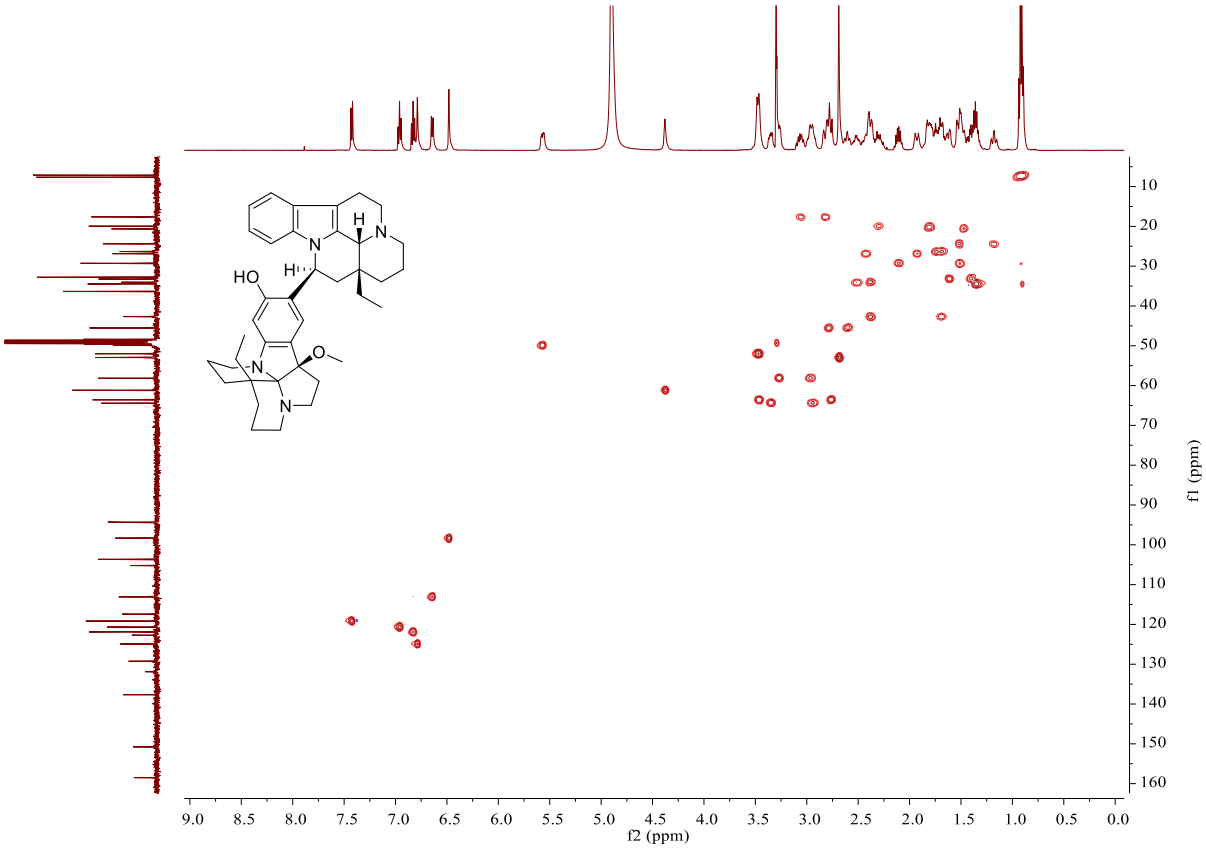



**Figure S18.** HMBC of compound **1** in $CD_3OD$

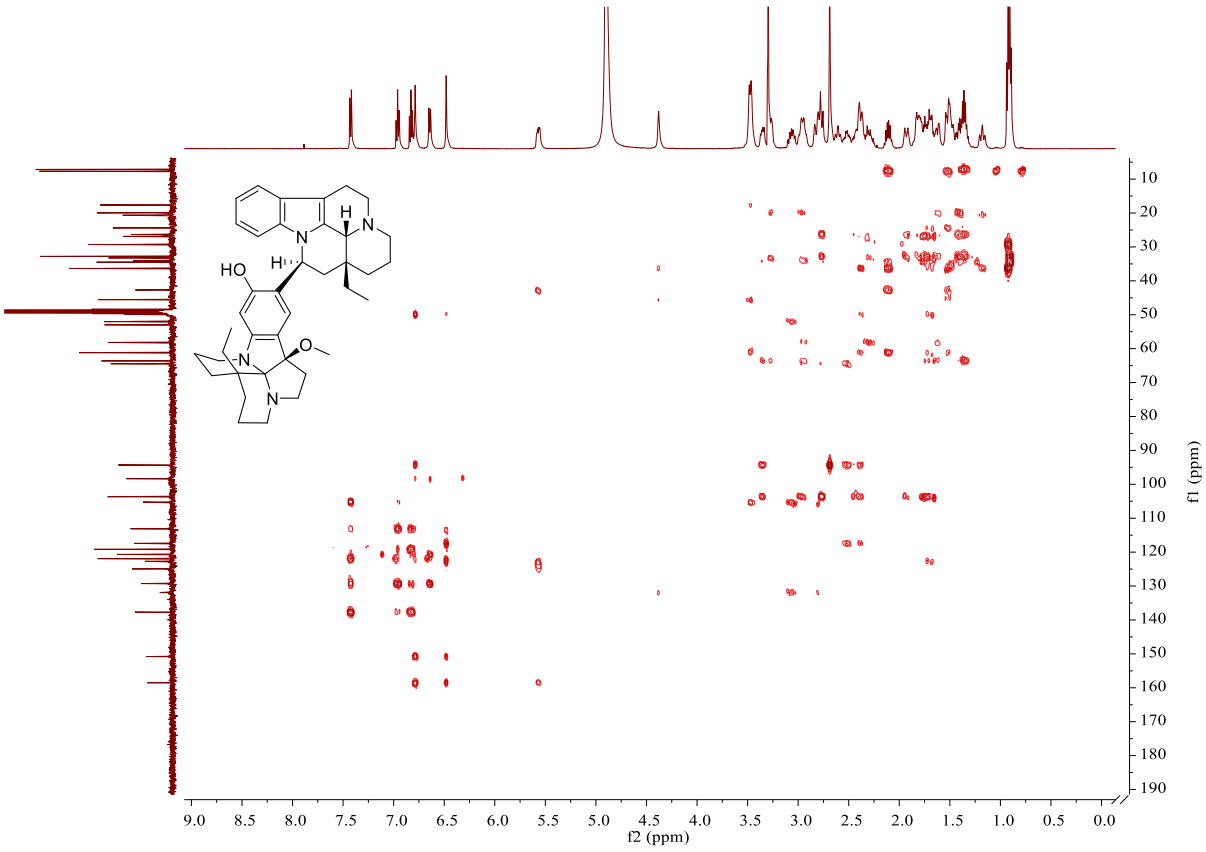


**Figure S19.** $^{1}H$-$^{1}H$ COSY of compound **1** in $CD_3OD$

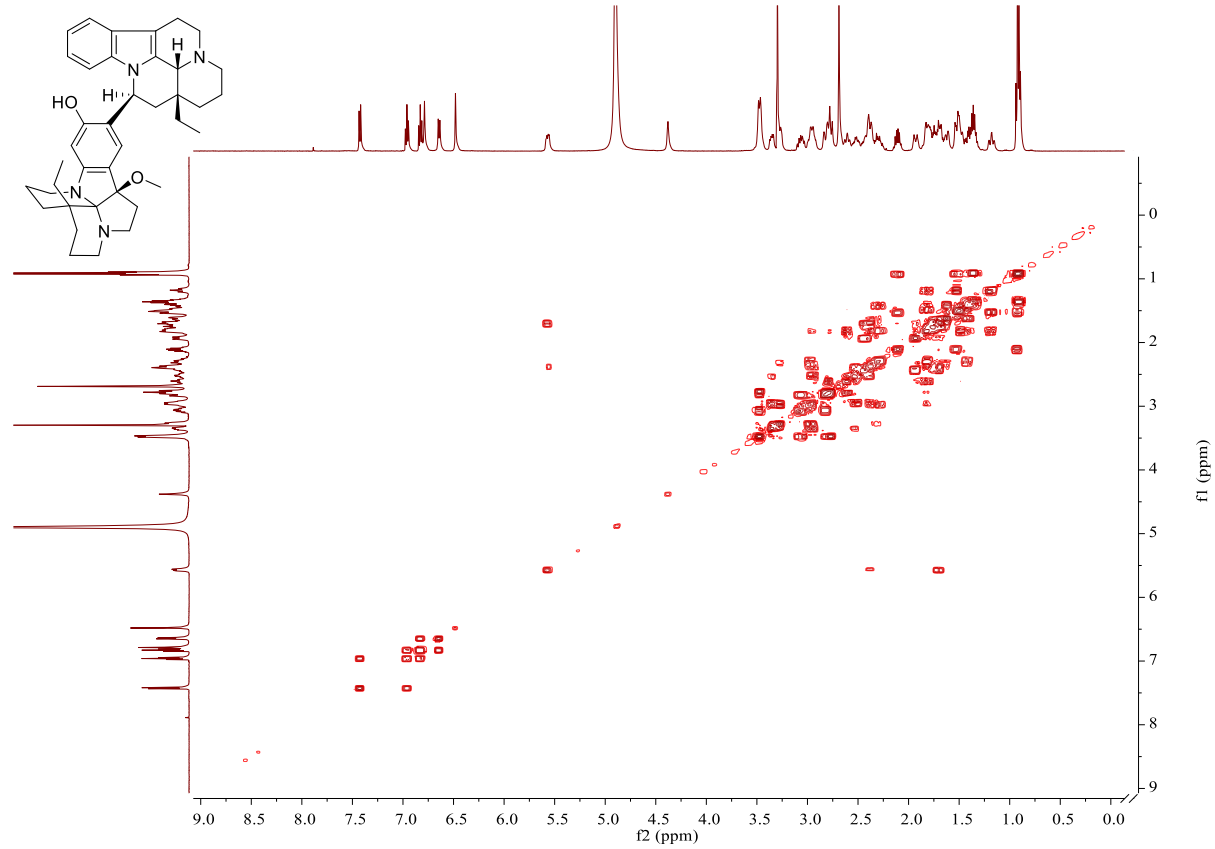



**Figure S20.** ROESY of compound **1** in $CD_3OD$

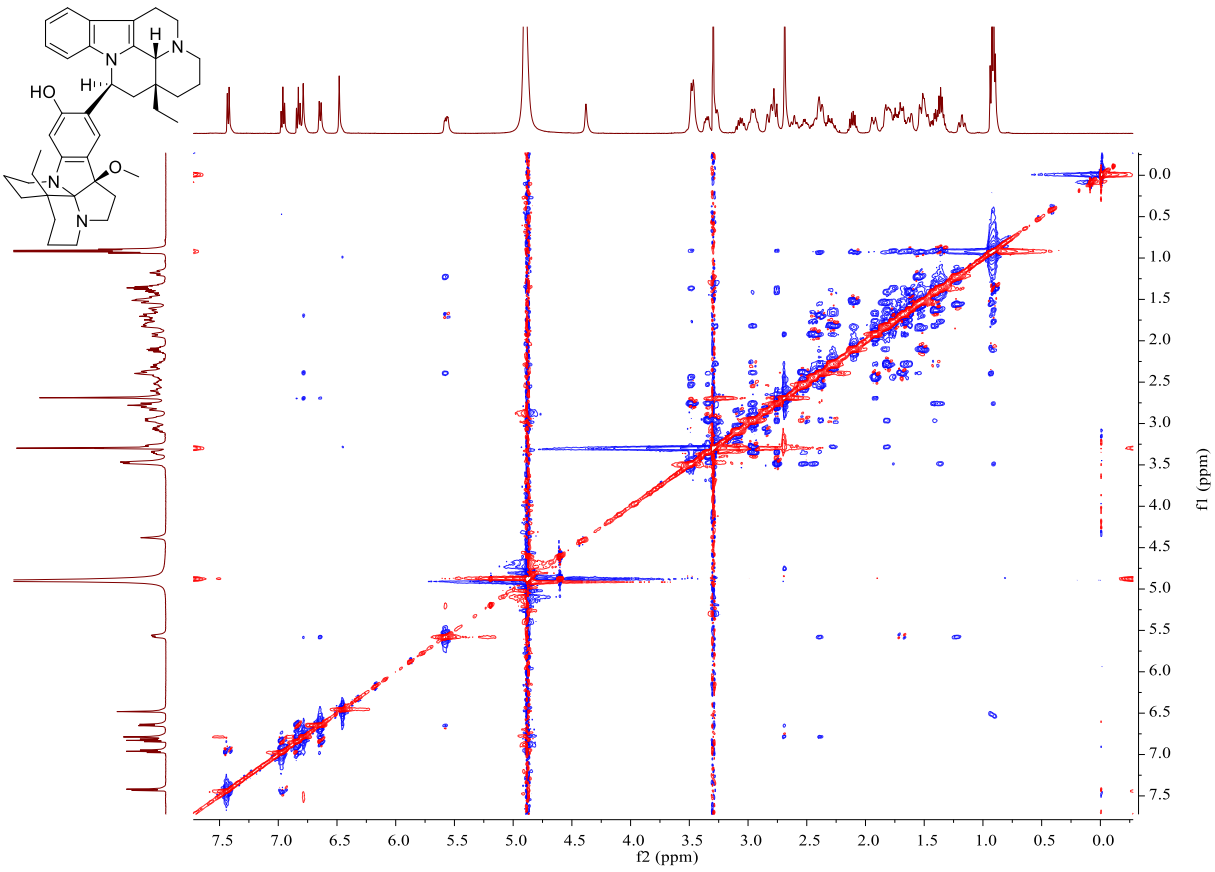


**Figure S21.** HR-ESIMS of compound **1**

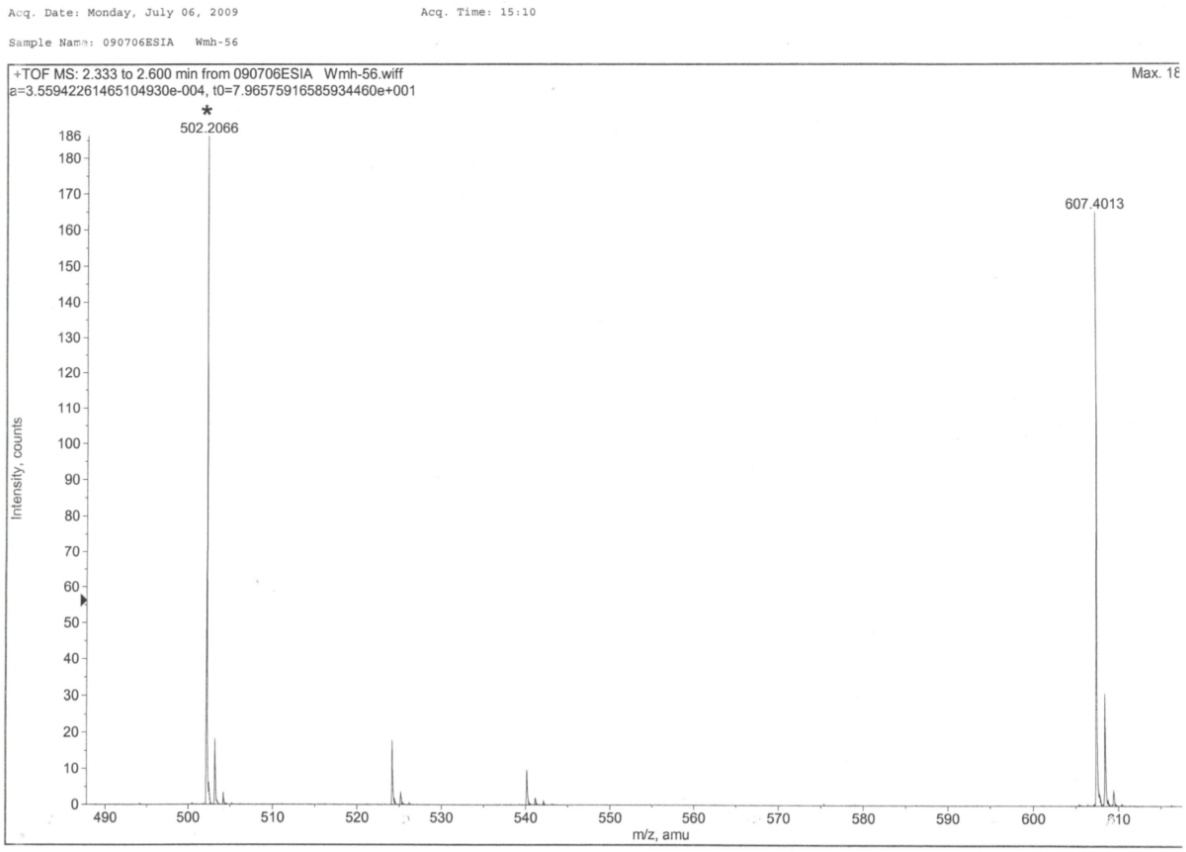



**Figure S22.** IR spectra of compound **1**

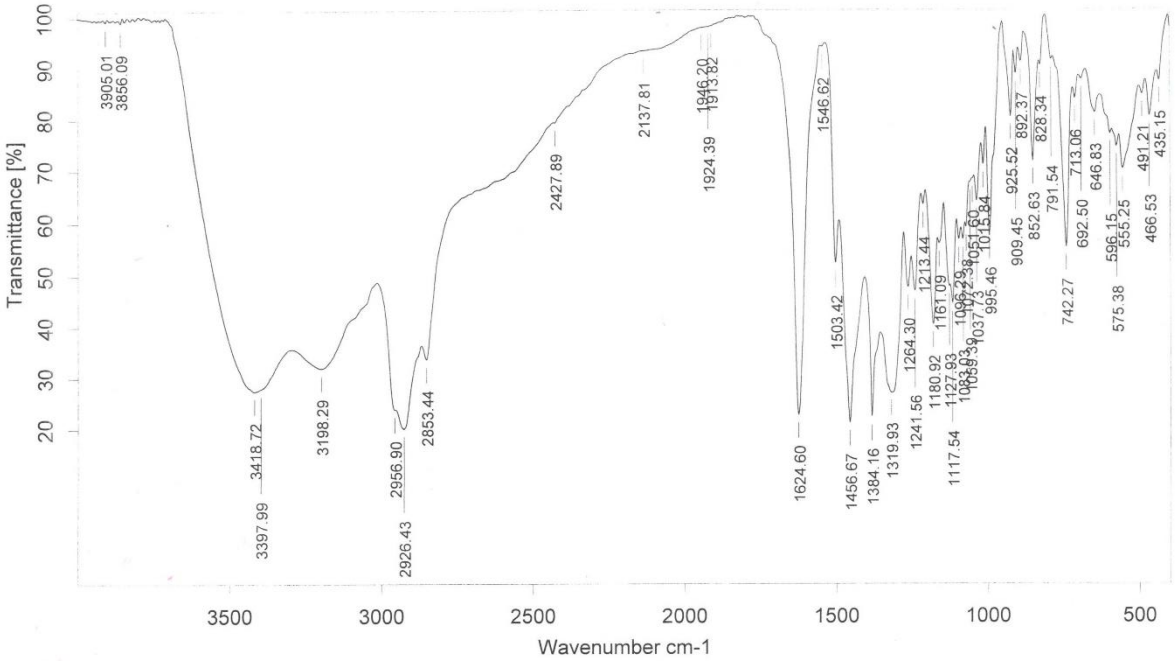
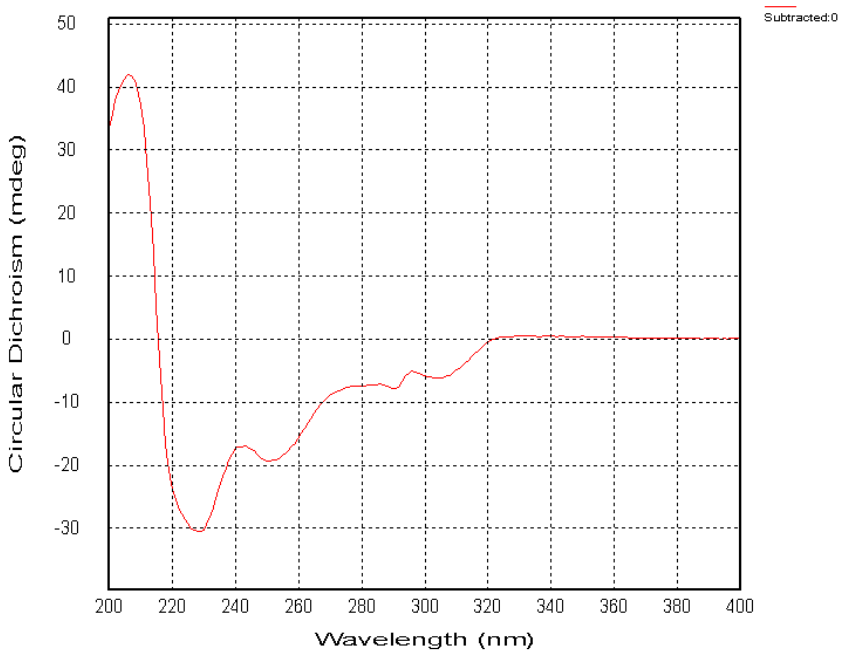


**Figure S23.** CD spectra of compound **1** in $CH_3OH$



## Section S5. NMR, MS, IR, and CD spectra for 2

**Figure S24.** $^{1}H$ NMR of compound **2** in $CD_3OD$

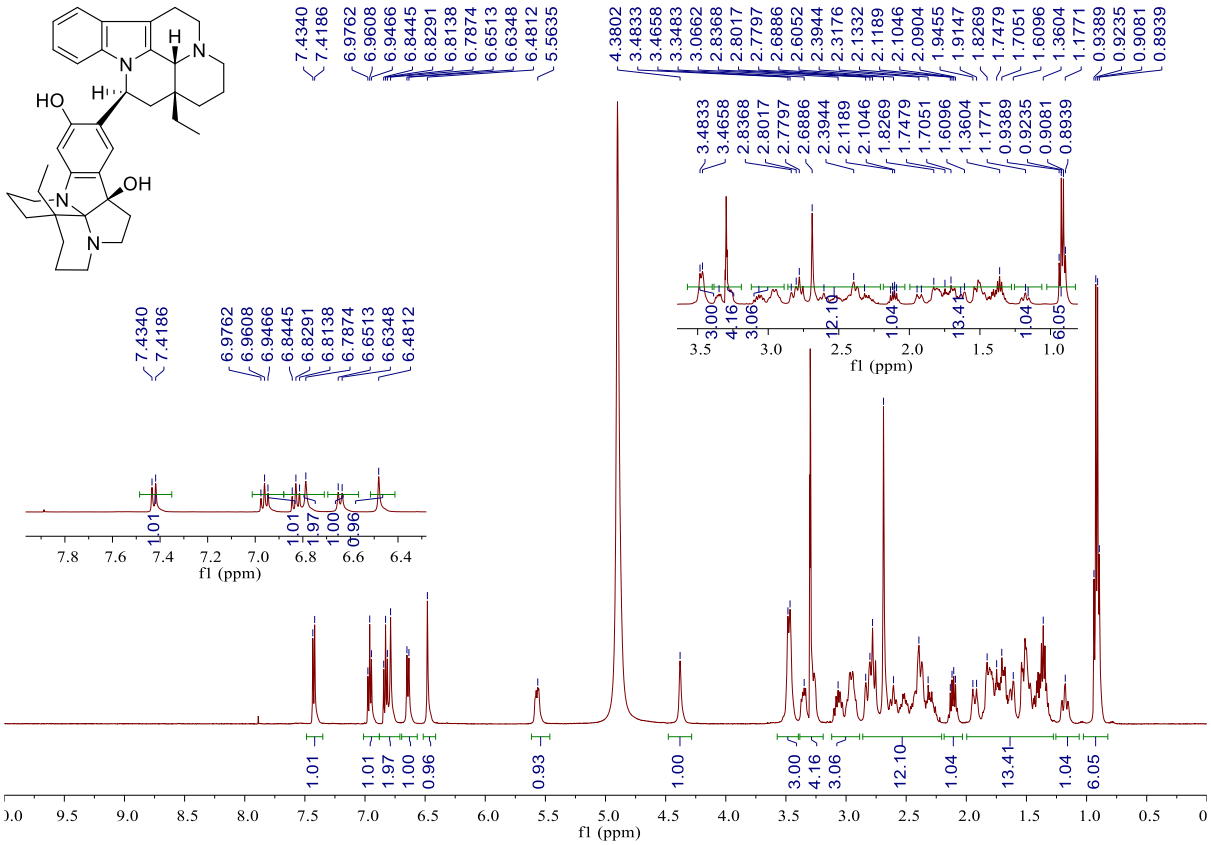



**Figure S25.** $^{13}C$ NMR and DEPT of compound **2** in $CD_3OD$

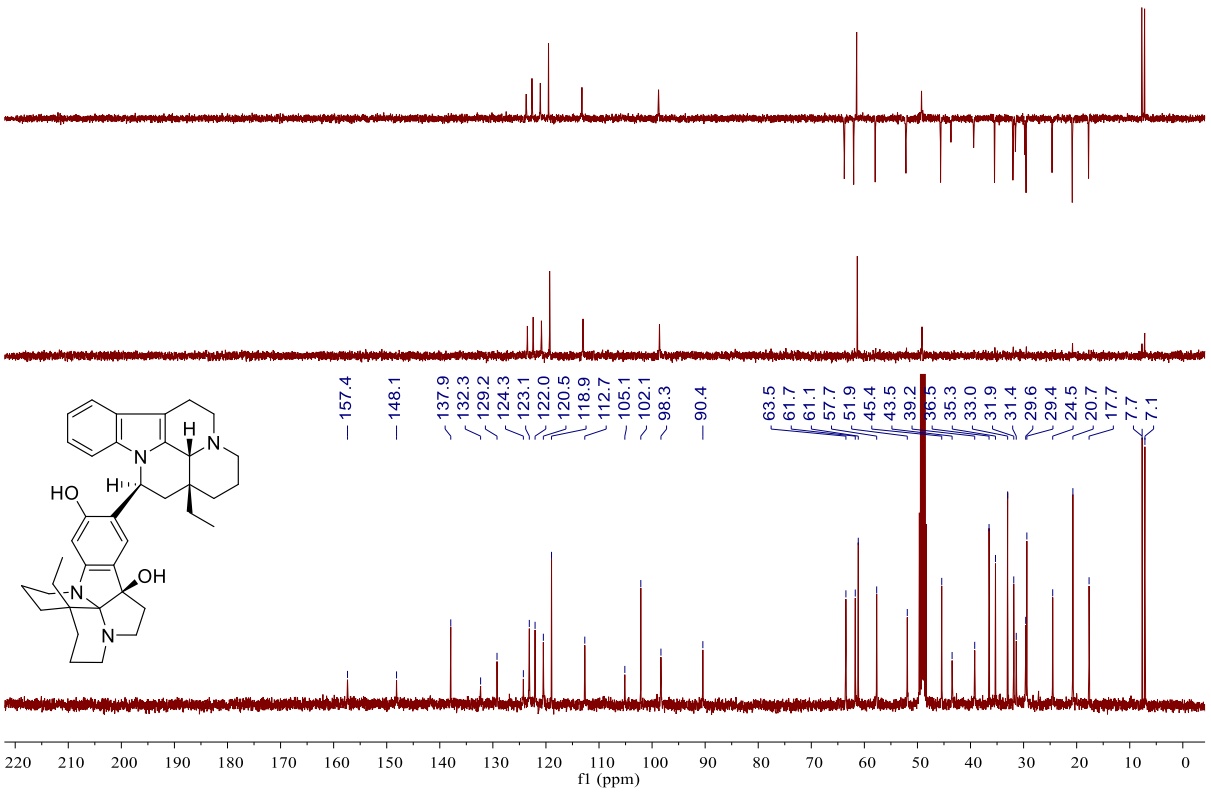


**Figure S26.** HSQC of compound **2** in $CD_3OD$

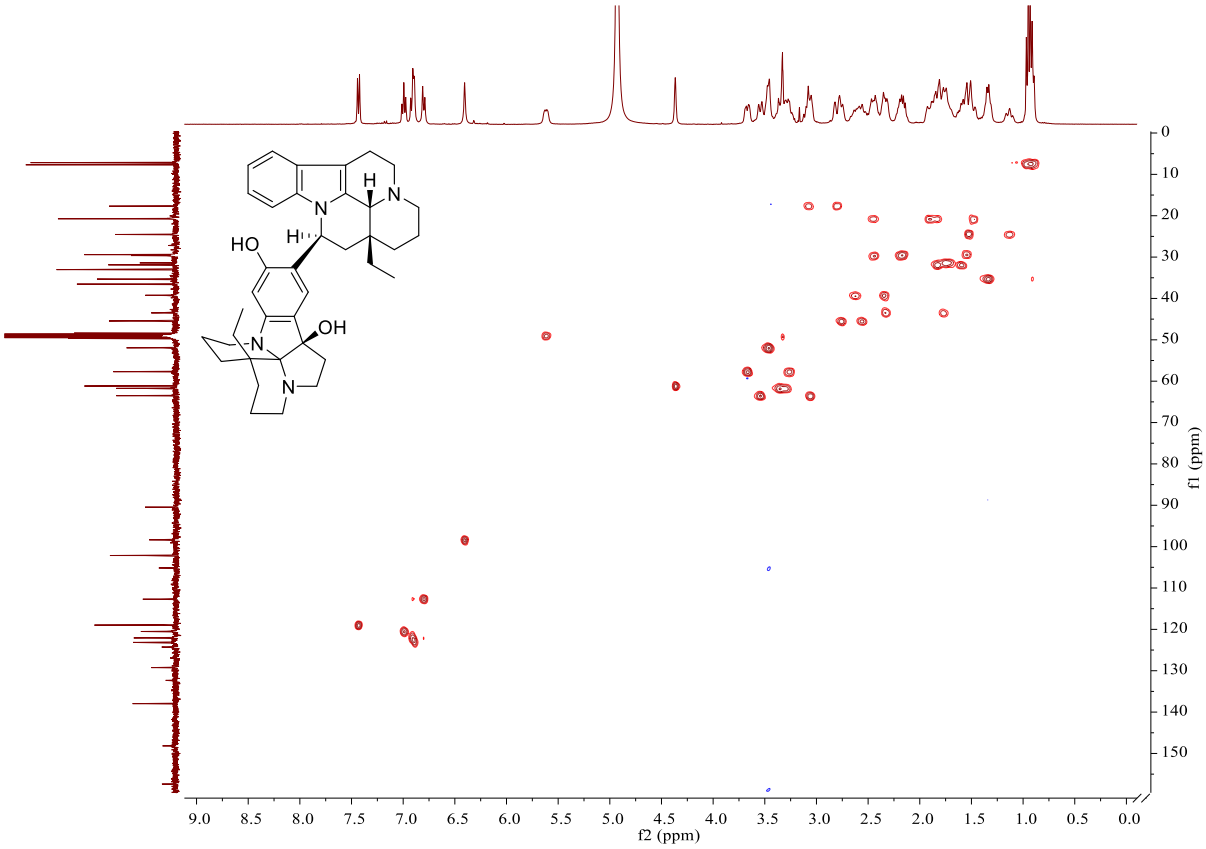



**Figure S27.** HMBC of compound **2** in $CD_3OD$

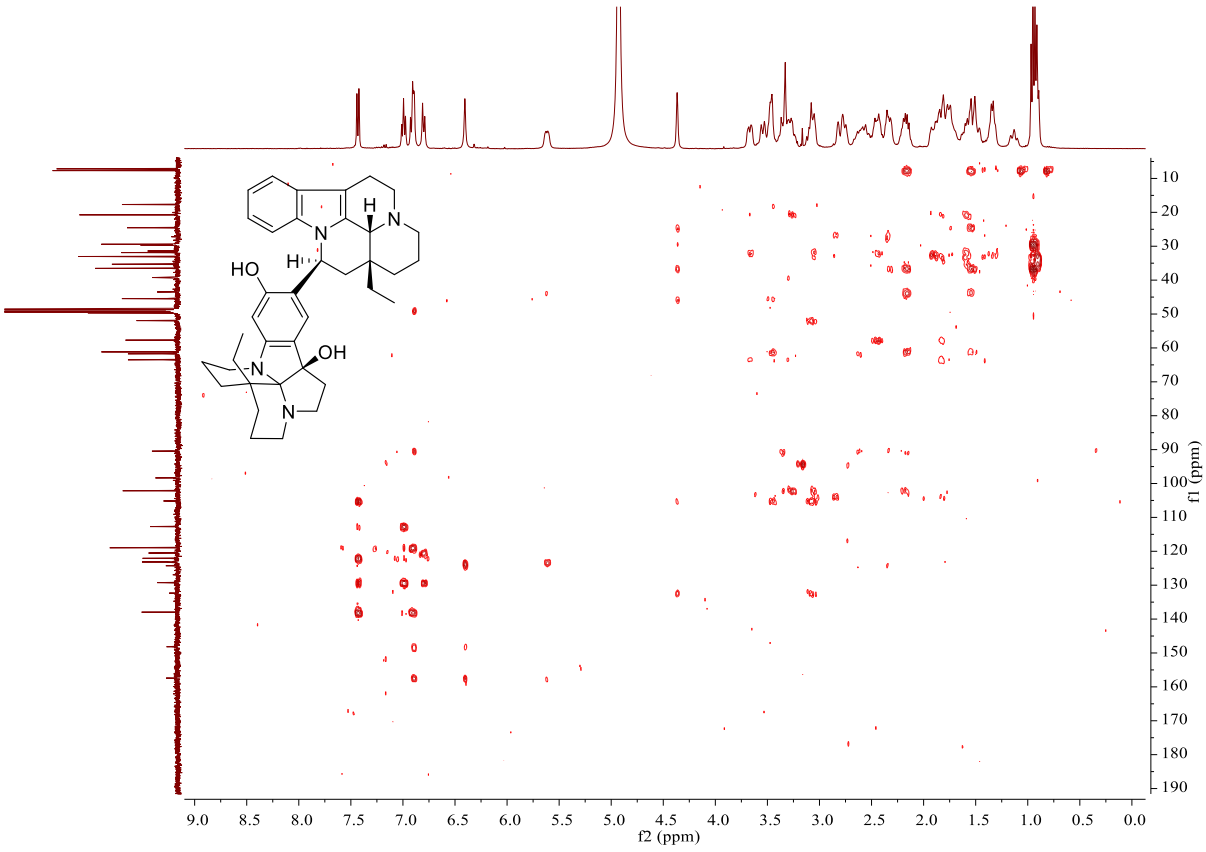


**Figure S28.** $^{1}H$-$^{1}H$ COSY of compound **2** in $CD_3OD$

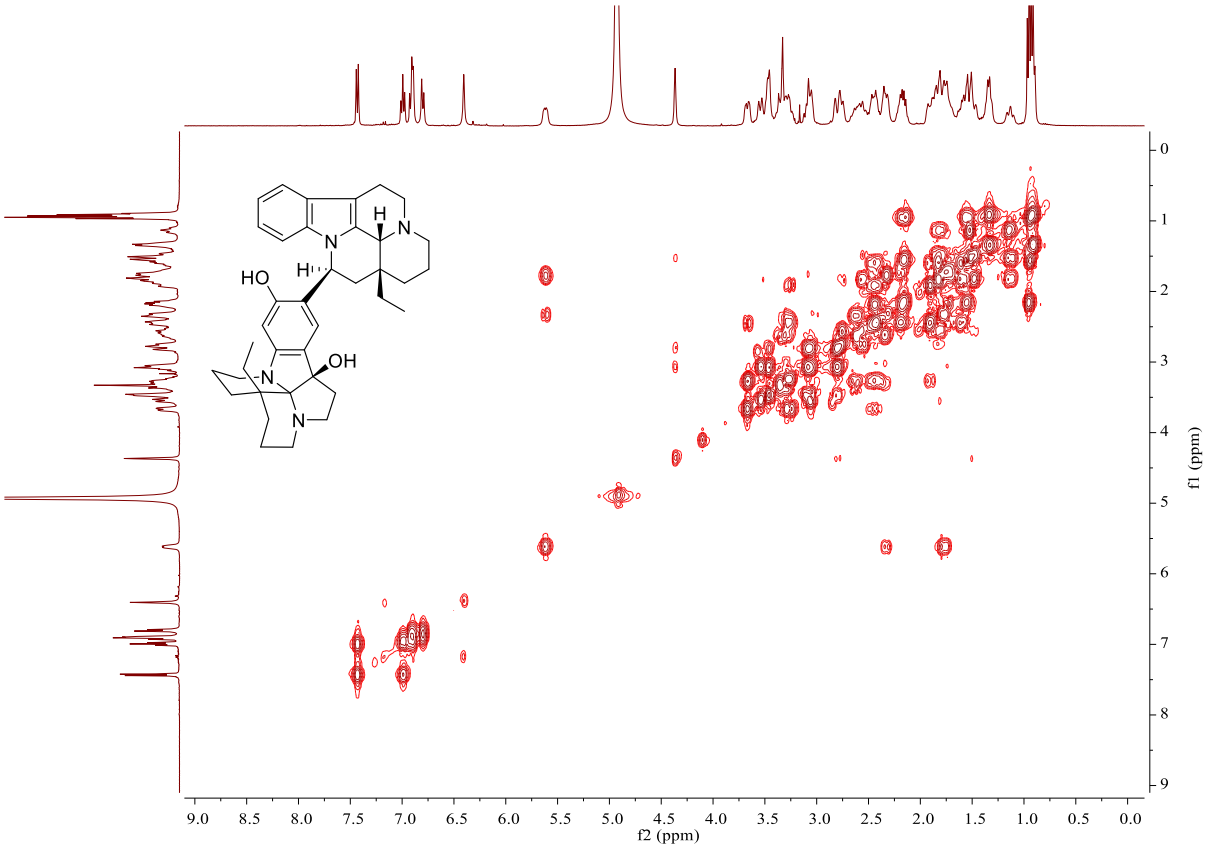



**Figure S29.** ROESY of compound **2** in $CD_3OD$

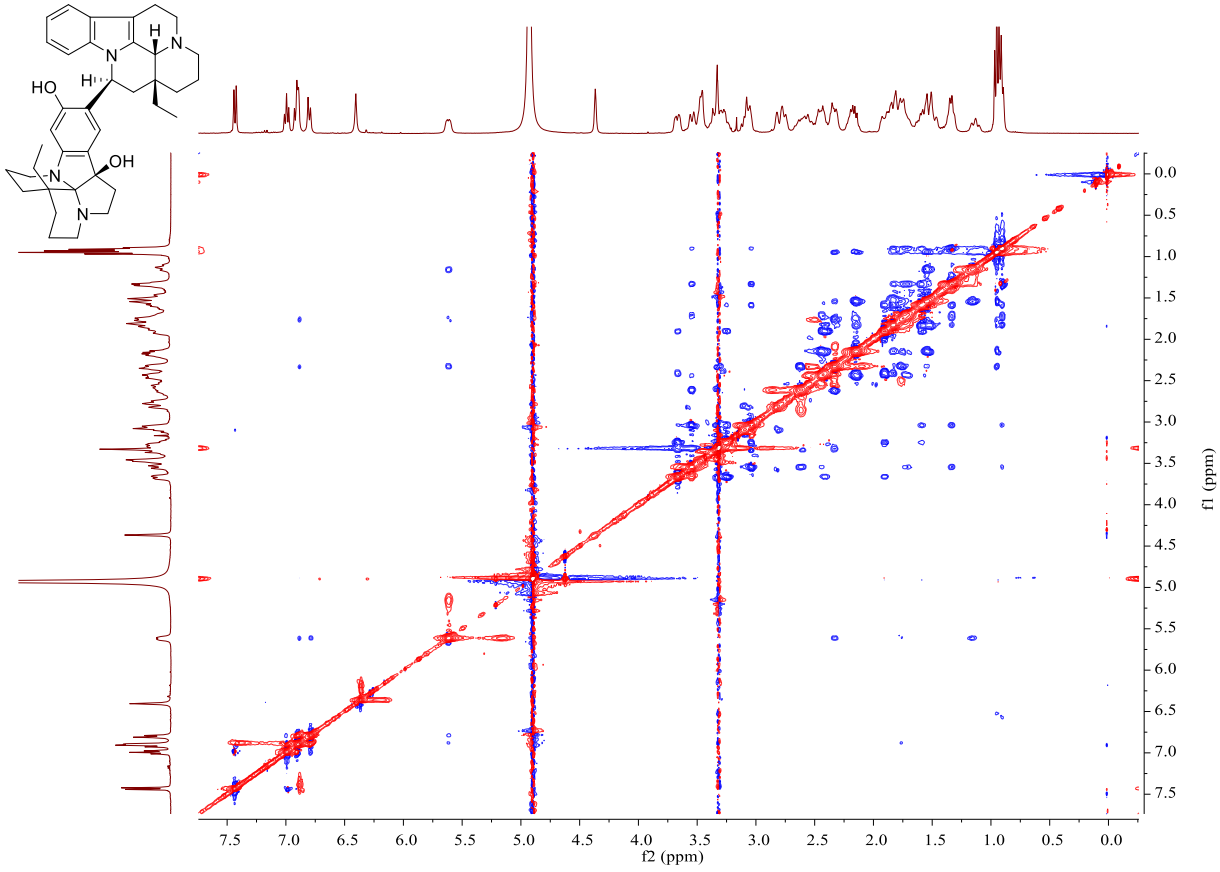


**Figure S30.** HR-ESIMS of compound **2**

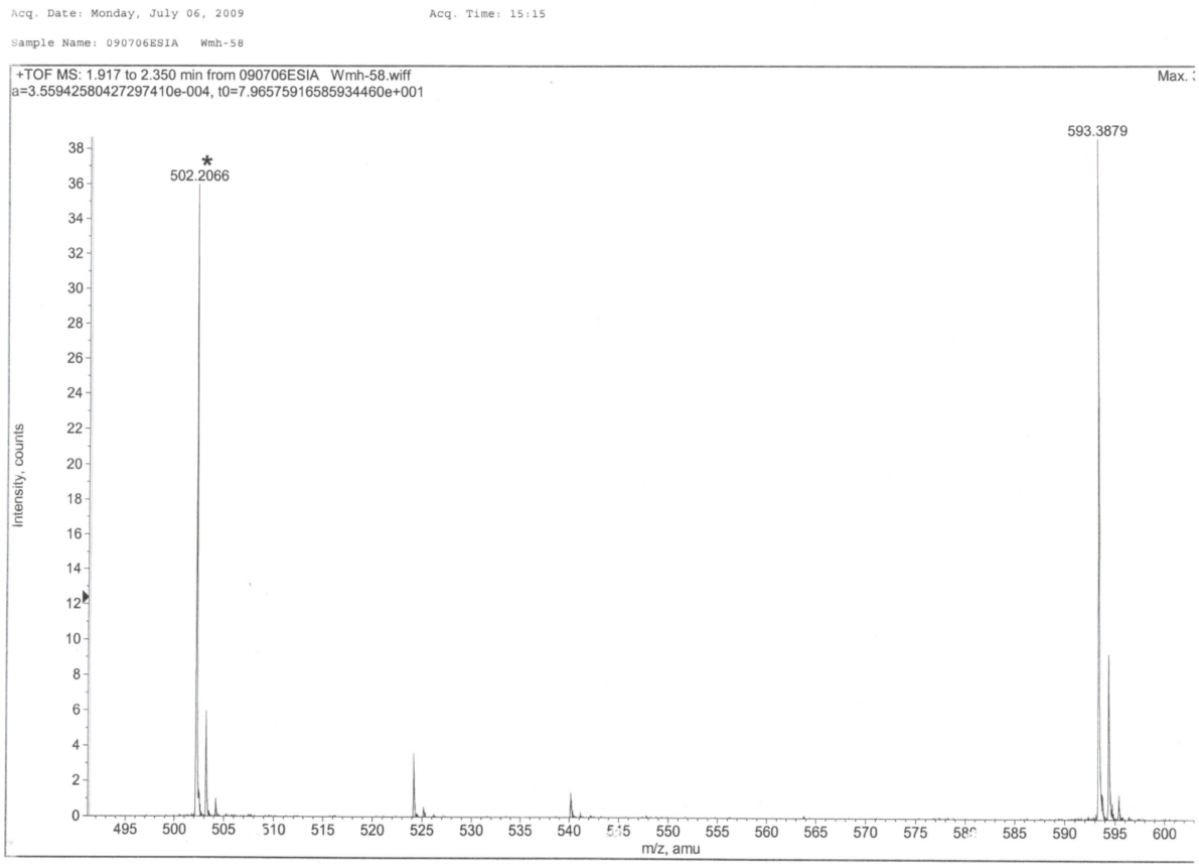



**Figure S31.** IR spectra of compound **2**

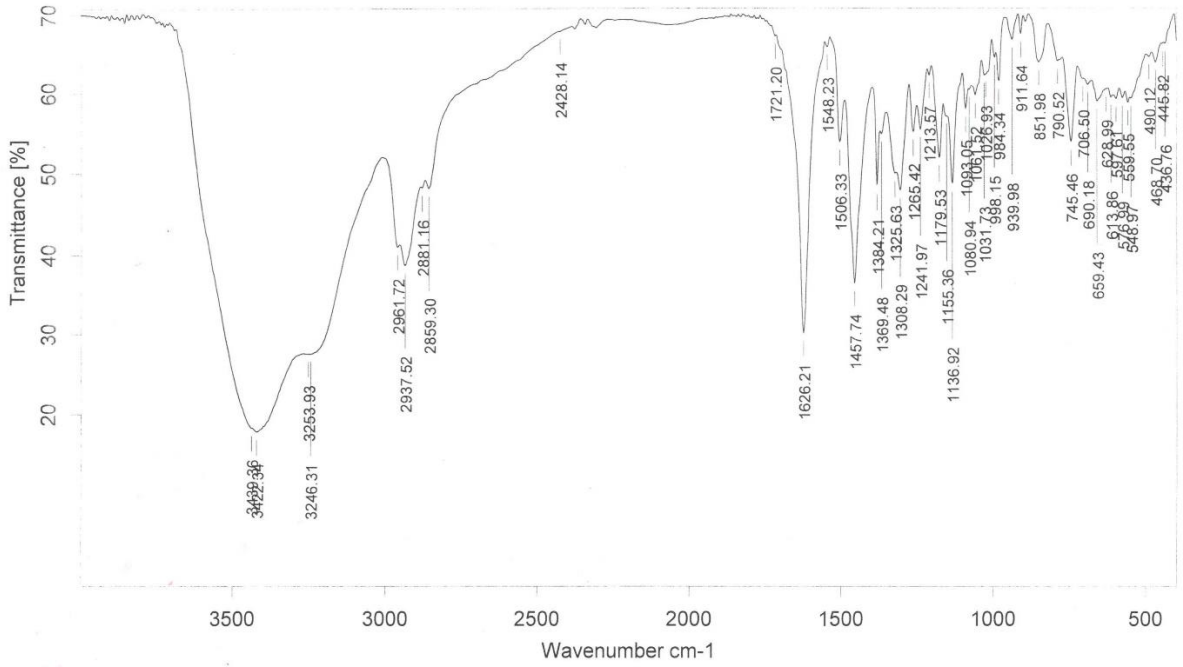
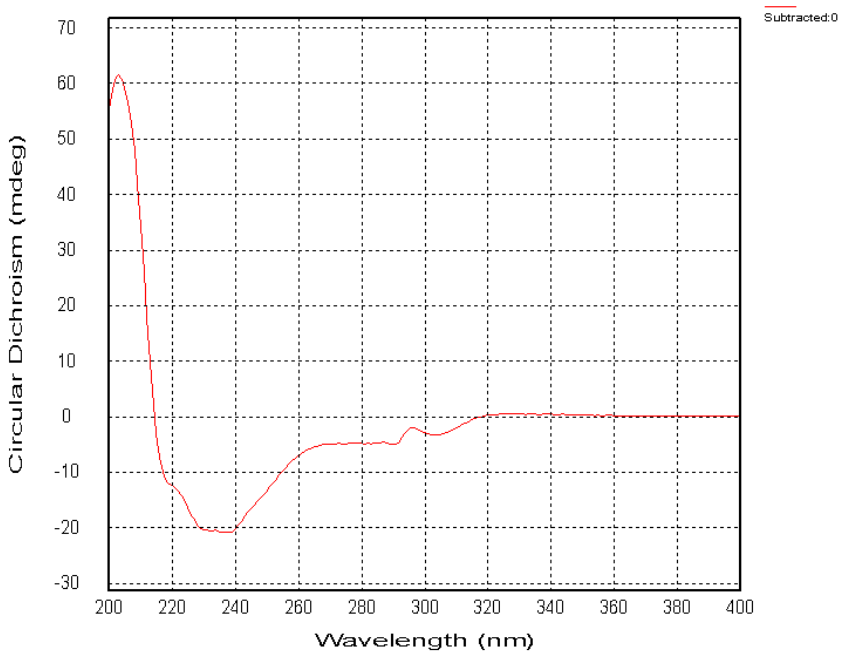


**Figure S32.** CD spectra of compound **2** in $CH_3OH$



## Section S6. NMR, MS, IR, and CD spectra for 3

**Figure S33.** $^{1}$H NMR of compound **3** in $CD_3OD$

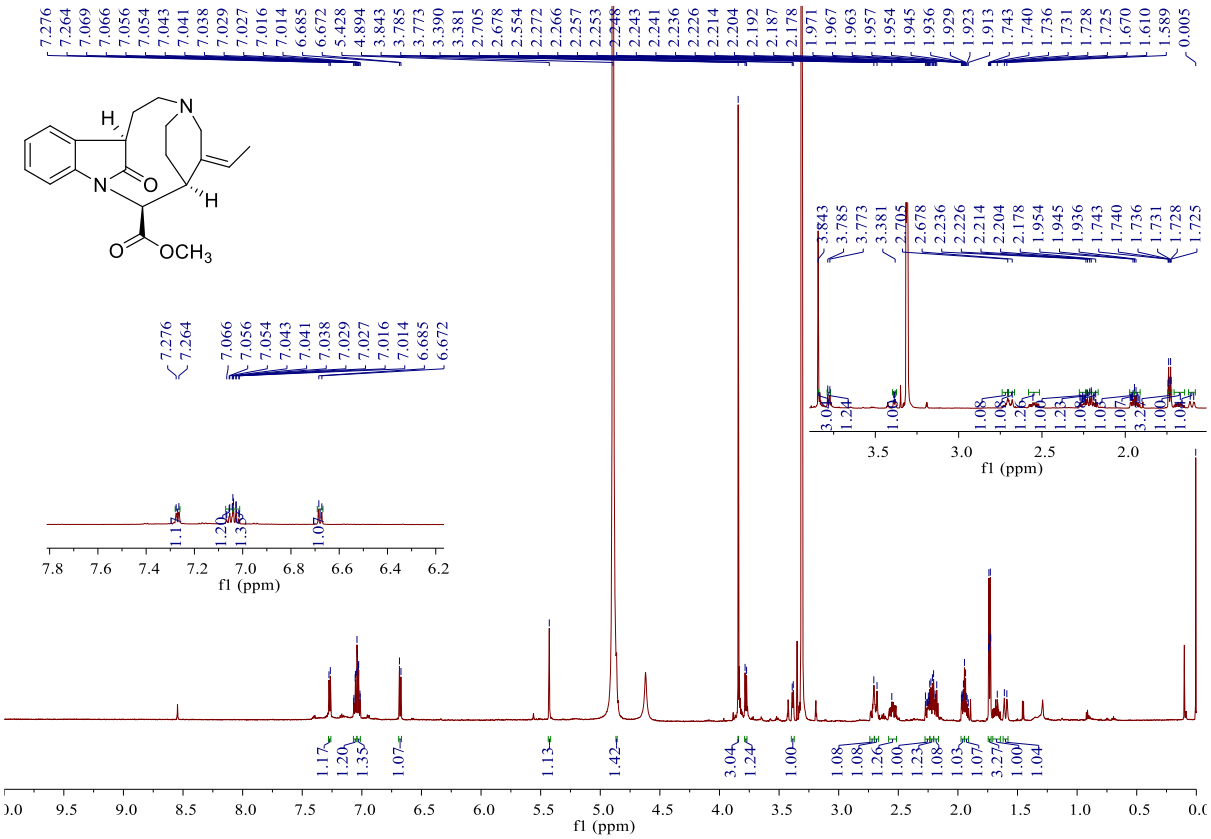



**Figure S34.** $^{13}$C NMR and DEPT of compound **3** in $CD_3OD$

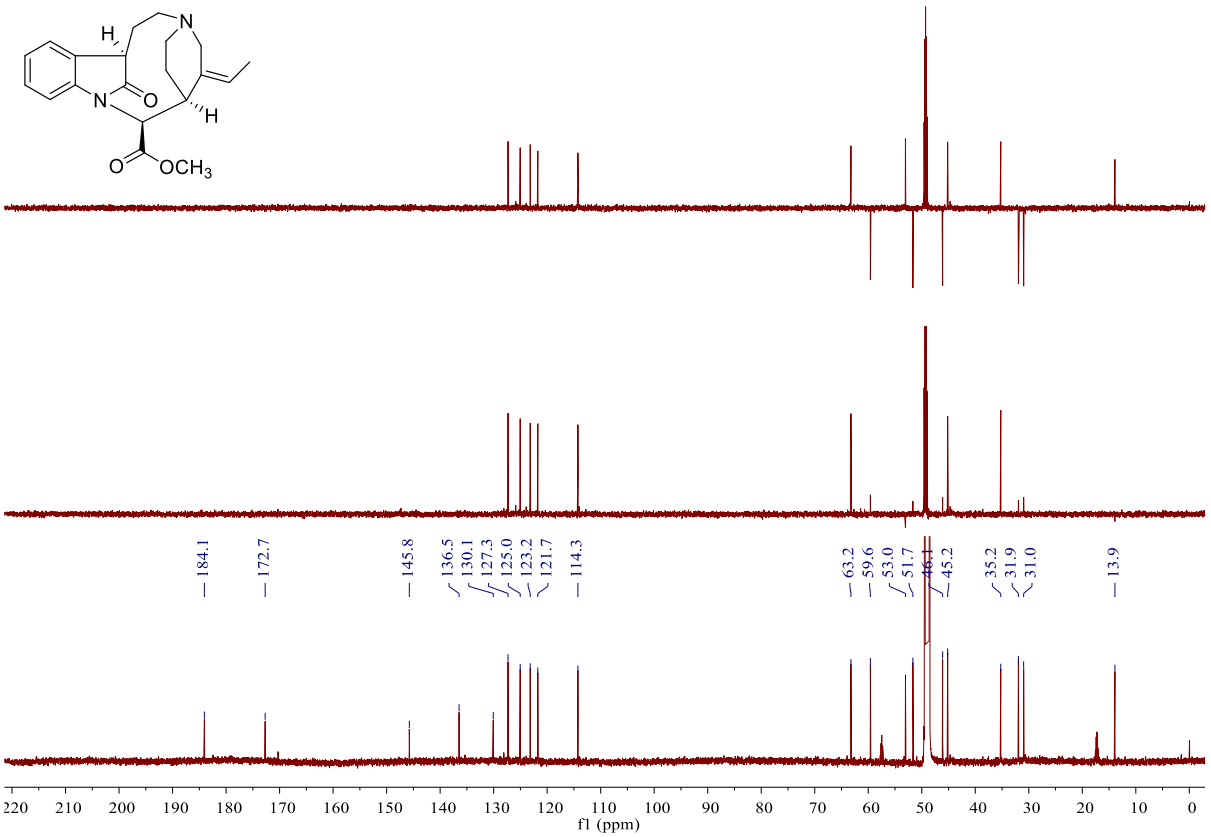


**Figure S35.** HSQC of compound **3** in $CD_3OD$

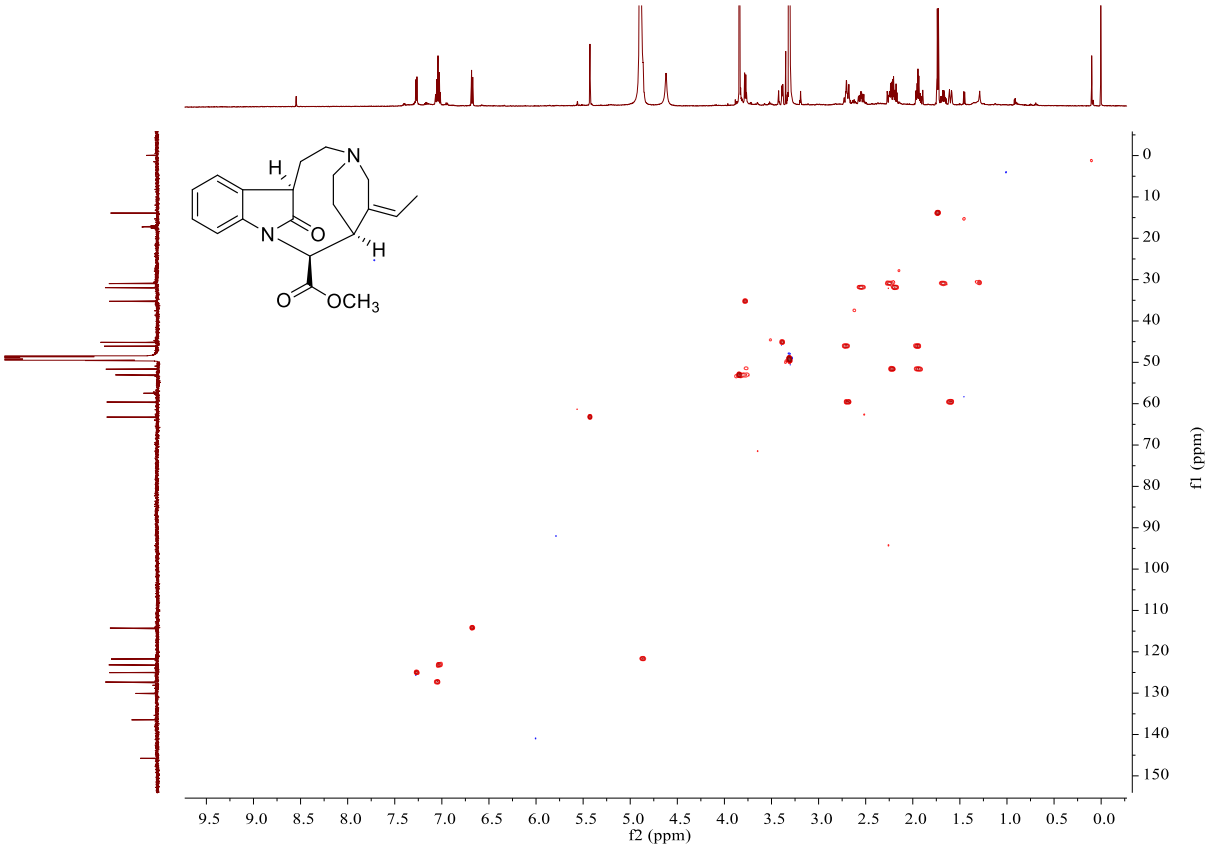



**Figure S36.** HMBC of compound **3** in $CD_3OD$

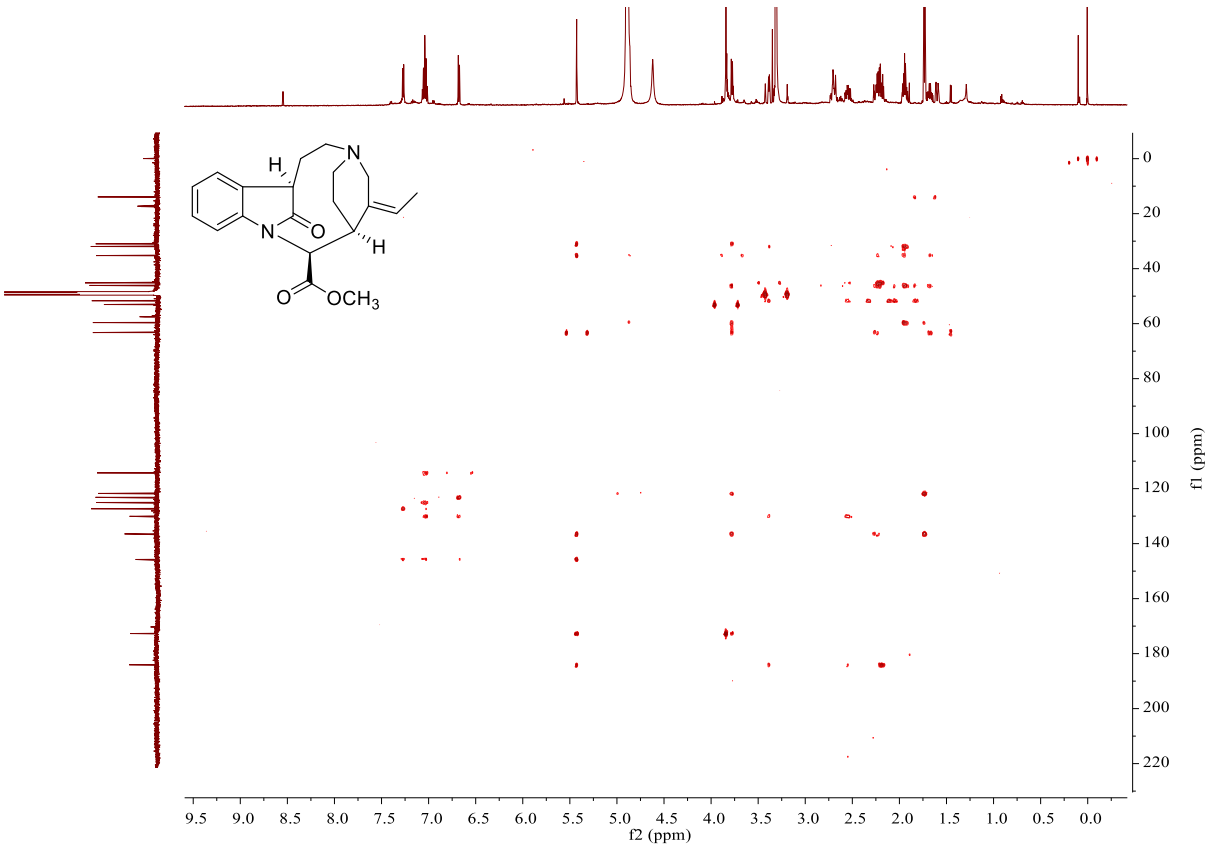


**Figure S37.** $^{1}H$-$^{1}H$ COSY of compound **3** in $CD_3OD$

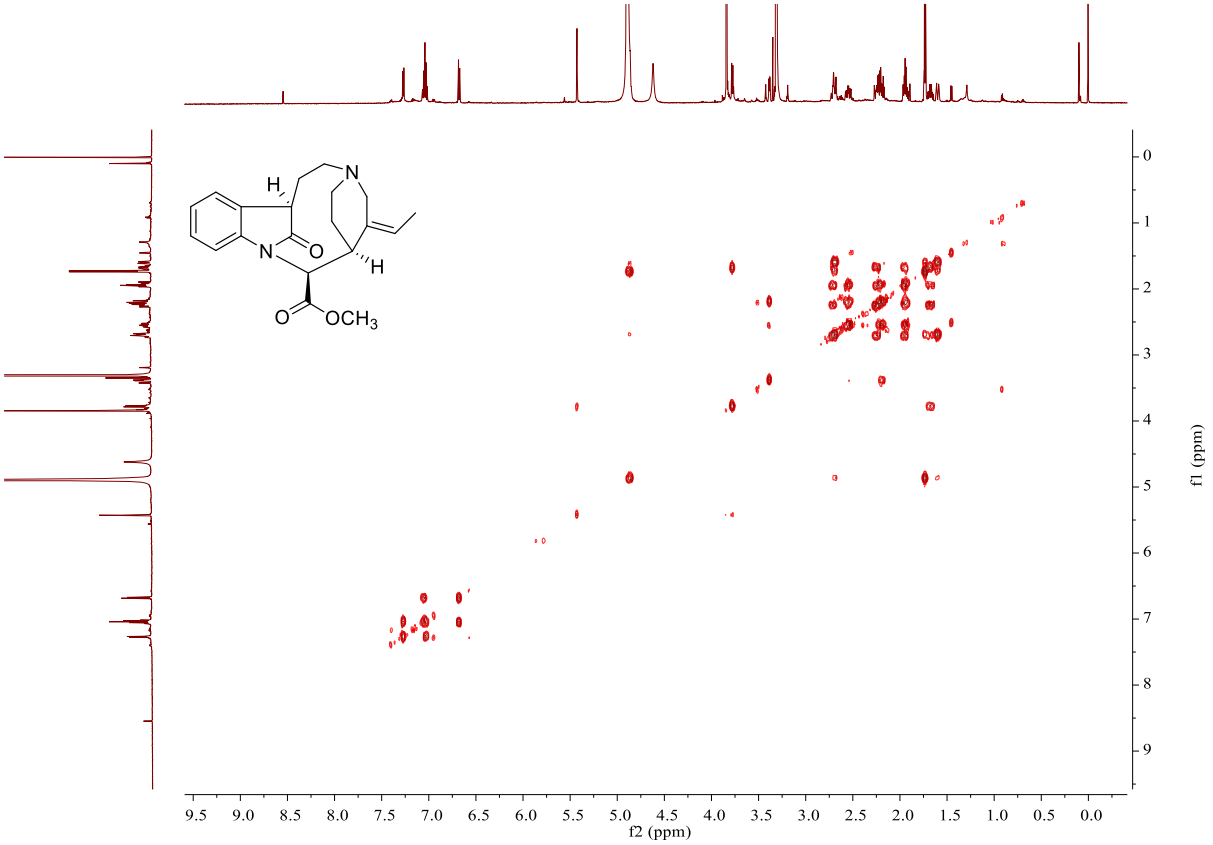



**Figure S38.** ROESY of compound **3** in $CD_3OD$

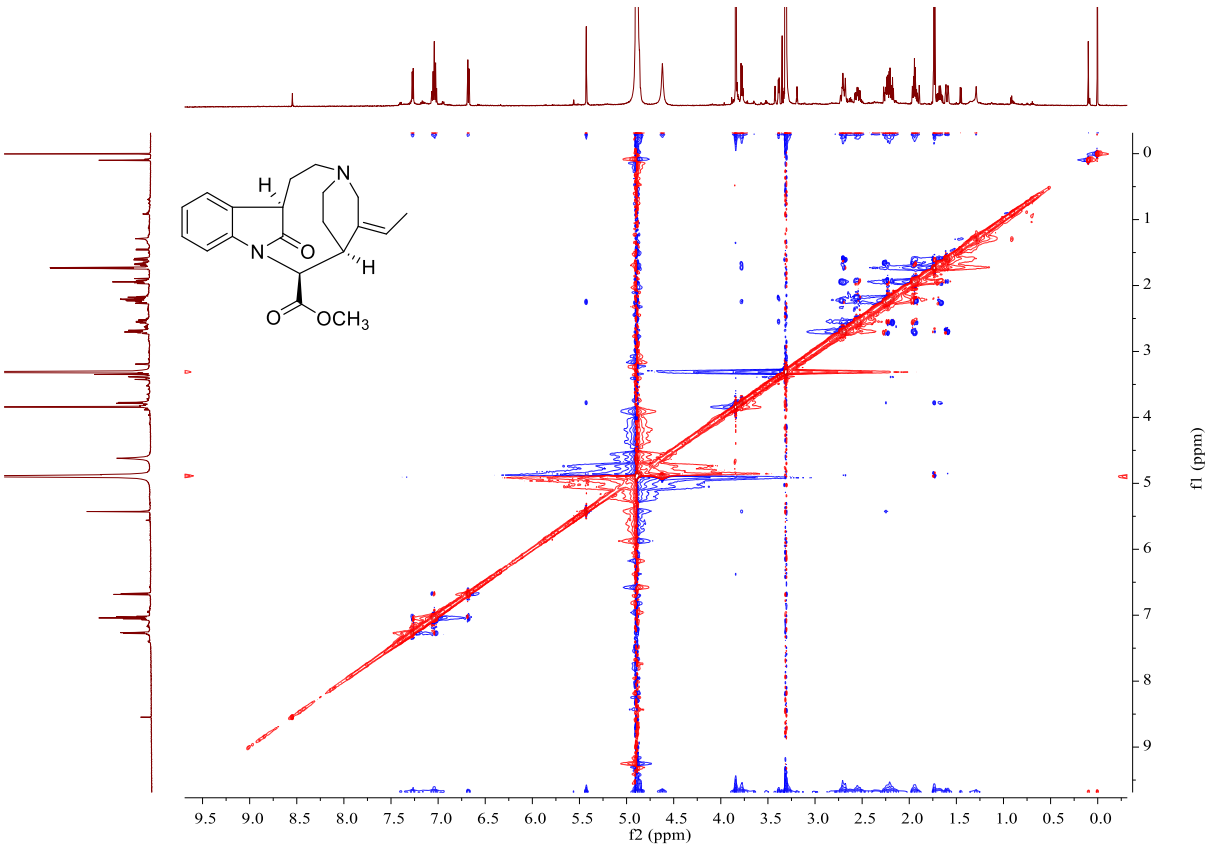


**Figure S39.** HR-ESIMS of compound **3**

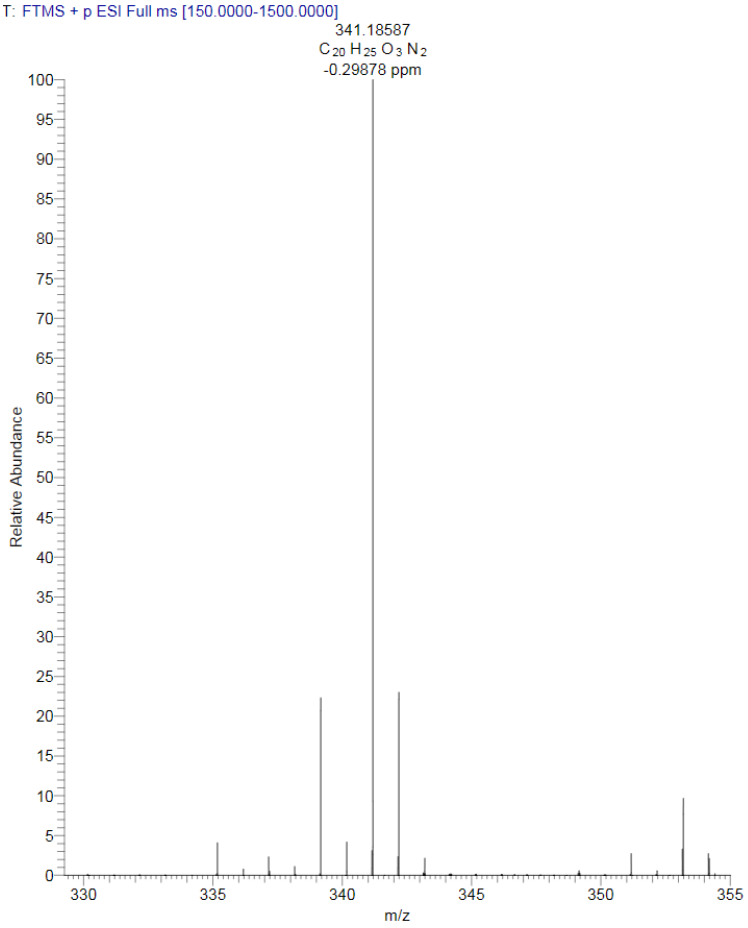



**Figure S40.** IR spectra of compound **3**

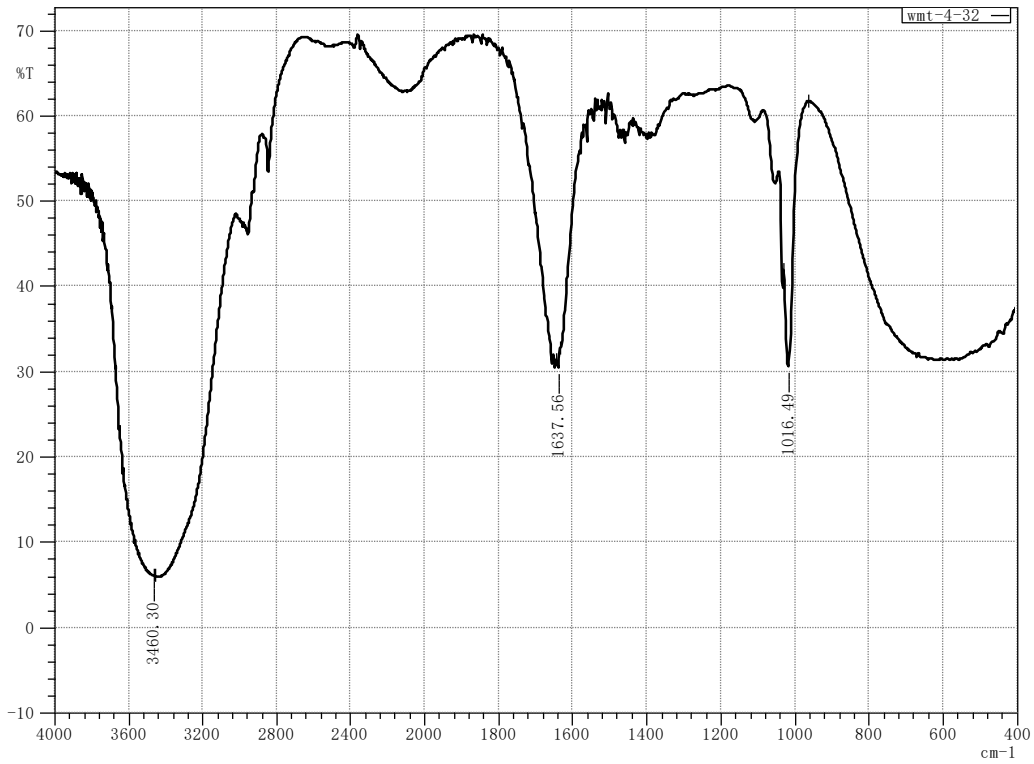
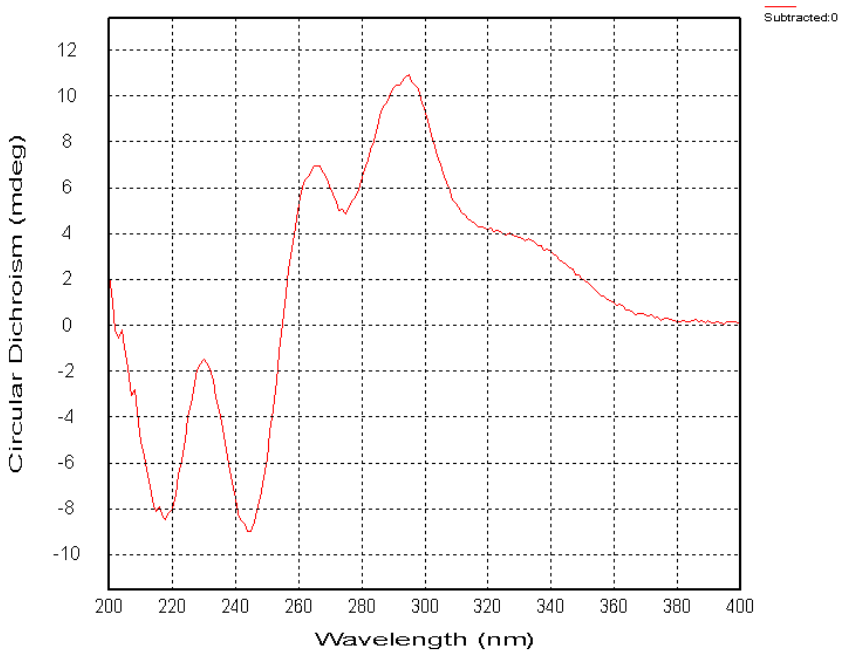


**Figure S41.** CD spectra of compound **3** in $CH_3OH$



## Section S7. NMR, MS, IR, and CD spectra for 4

**Figure S42.** $^{1}$H NMR of compound **4** in $CD_3OD$

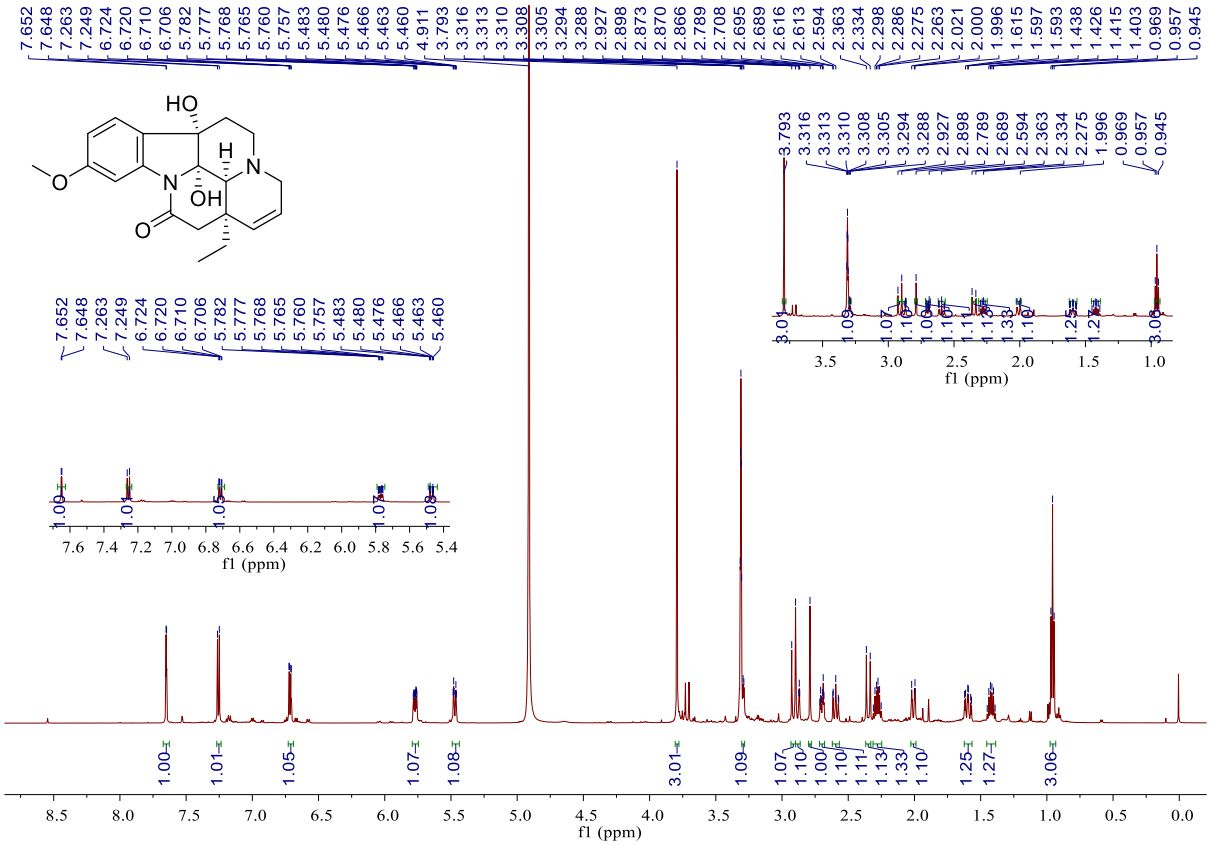



**Figure S43.** $^{13}$C NMR and DEPT of compound **4** in $CD_3OD$

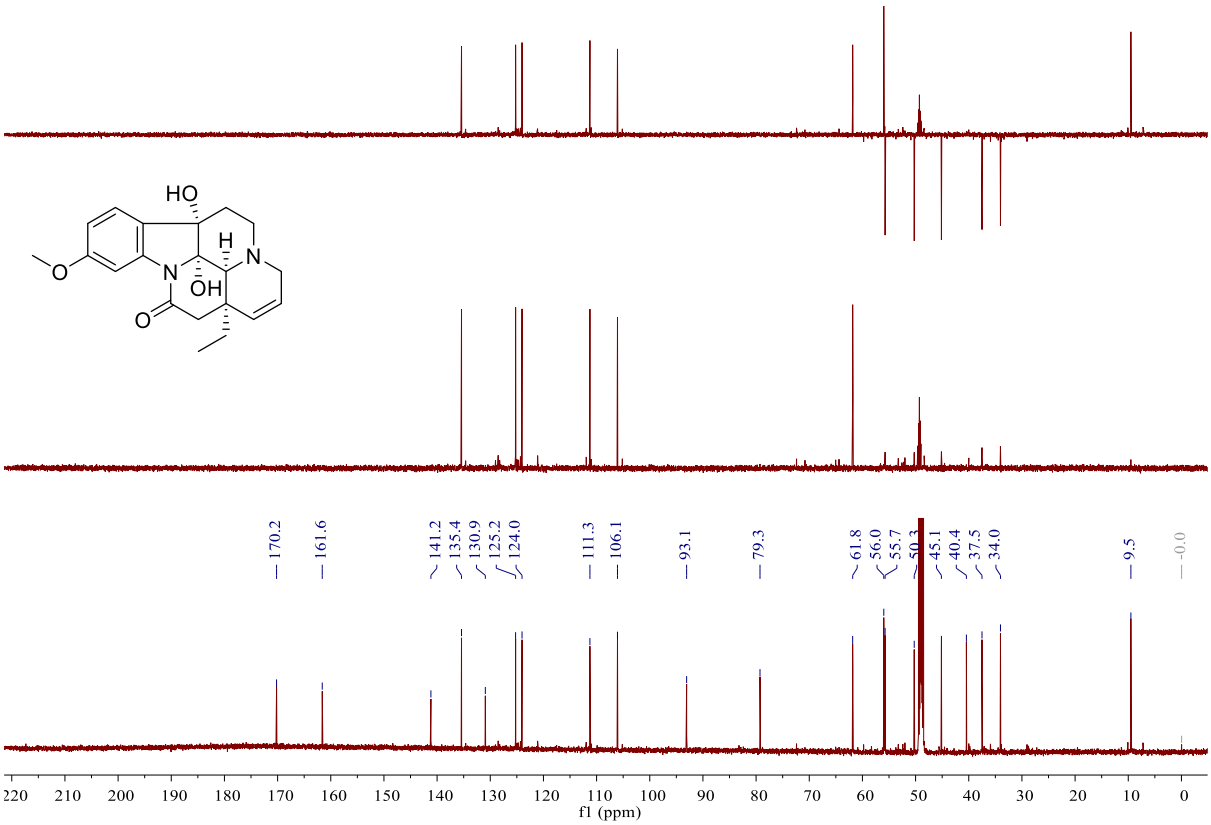


**Figure S44.** HSQC of compound **4** in $CD_3OD$

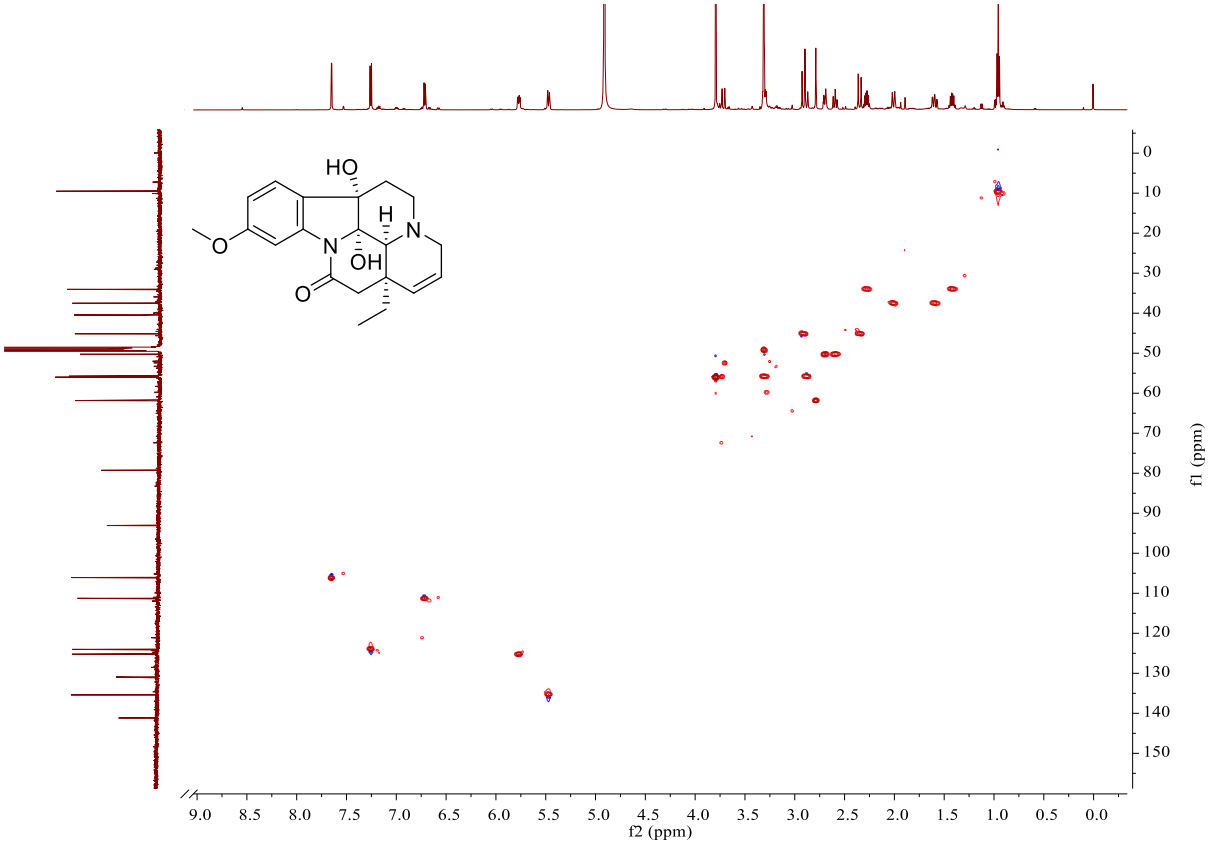



**Figure S45.** HMBC of compound **4** in $CD_3OD$

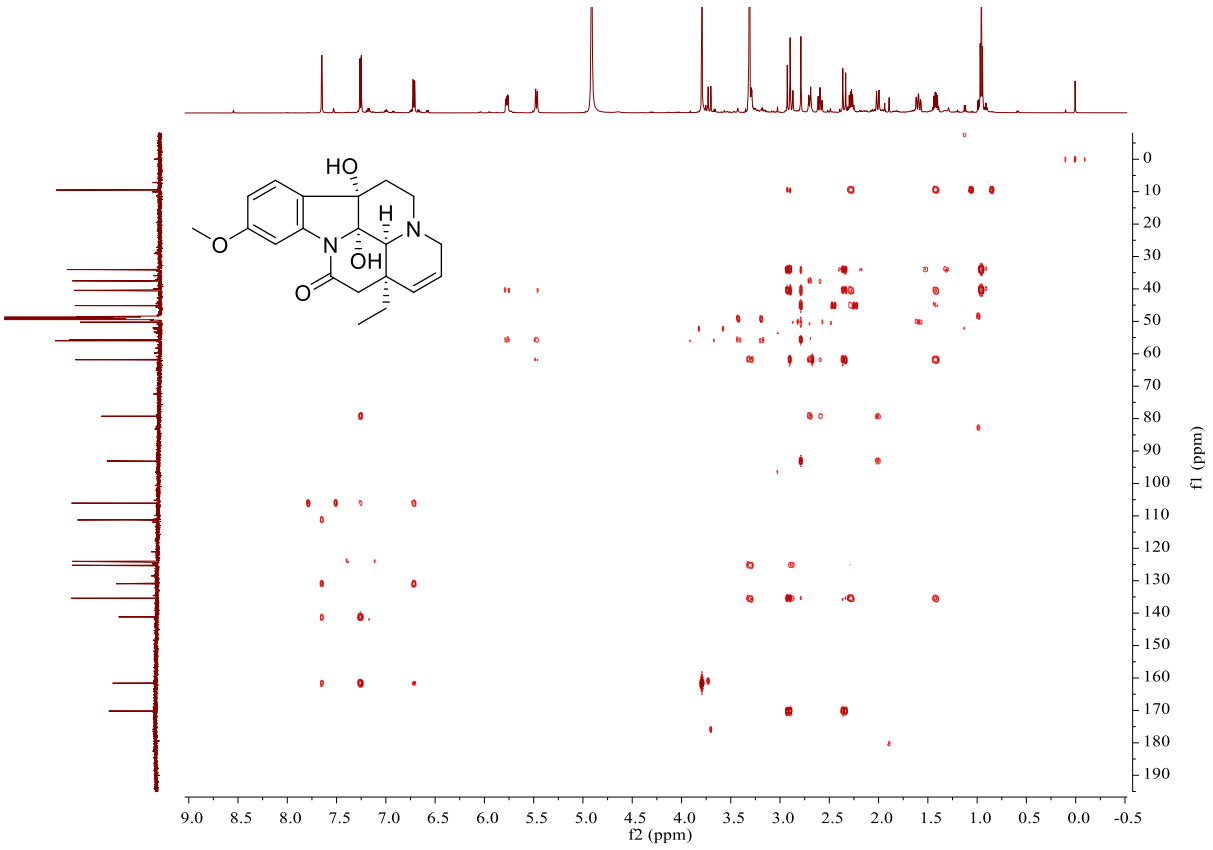


**Figure S46.** $^{1}H$-$^{1}H$ COSY of compound **4** in $CD_3OD$

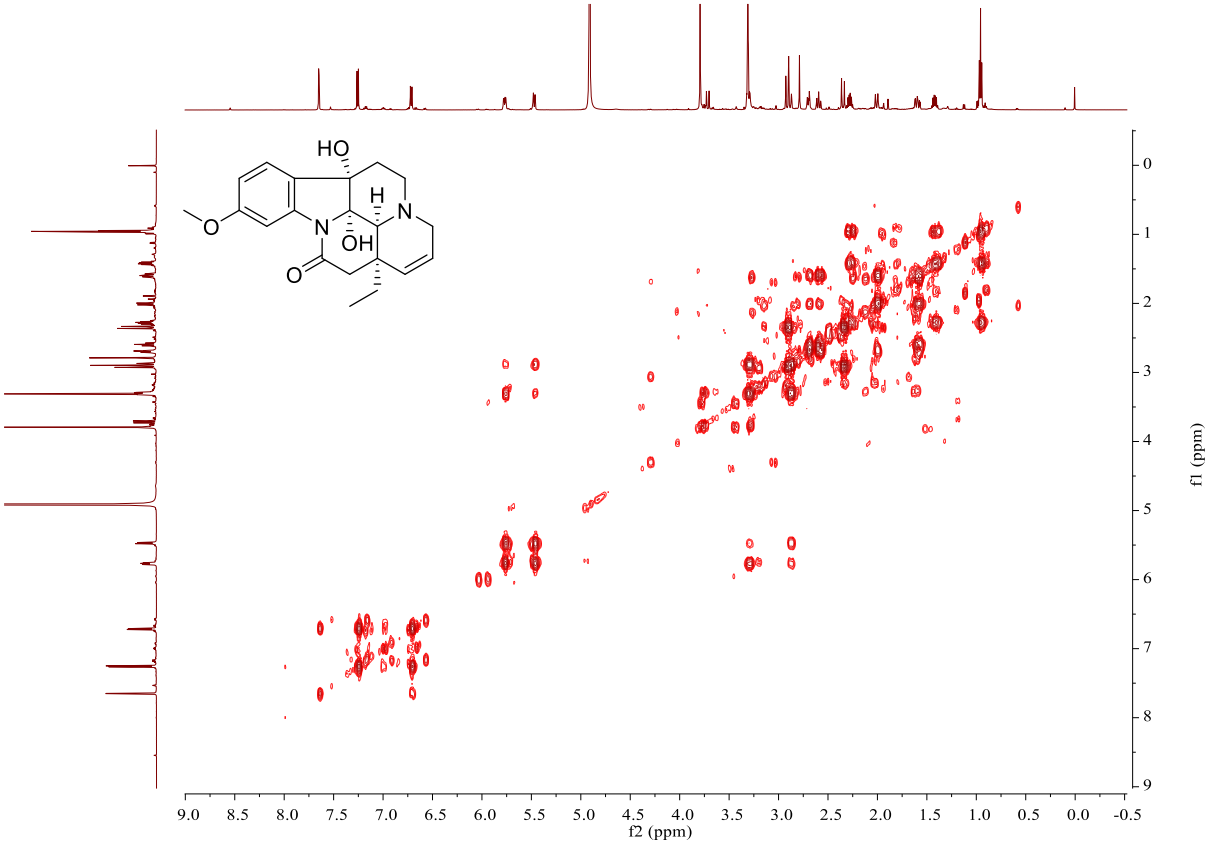



**Figure S47.** ROESY of compound **4** in $CD_3OD$

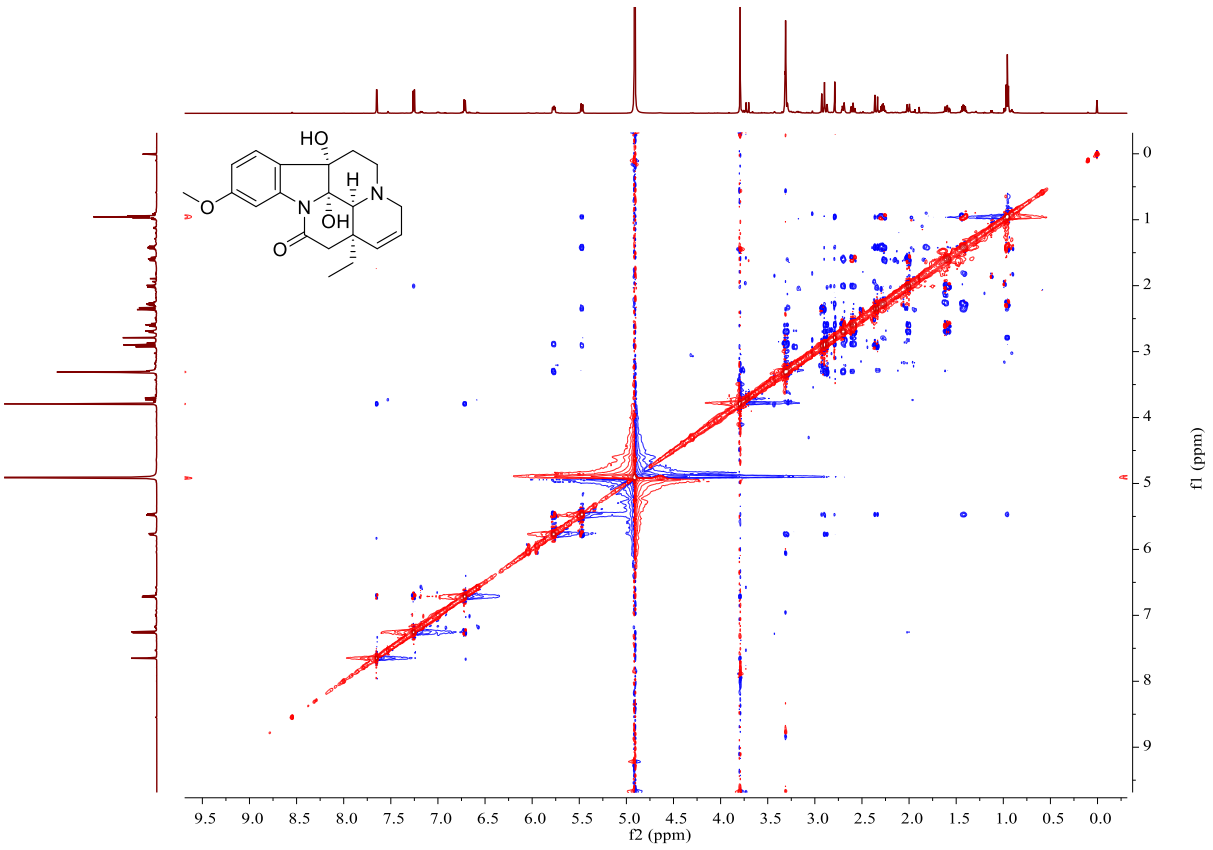


**Figure S48.** HR-ESIMS of compound **4**

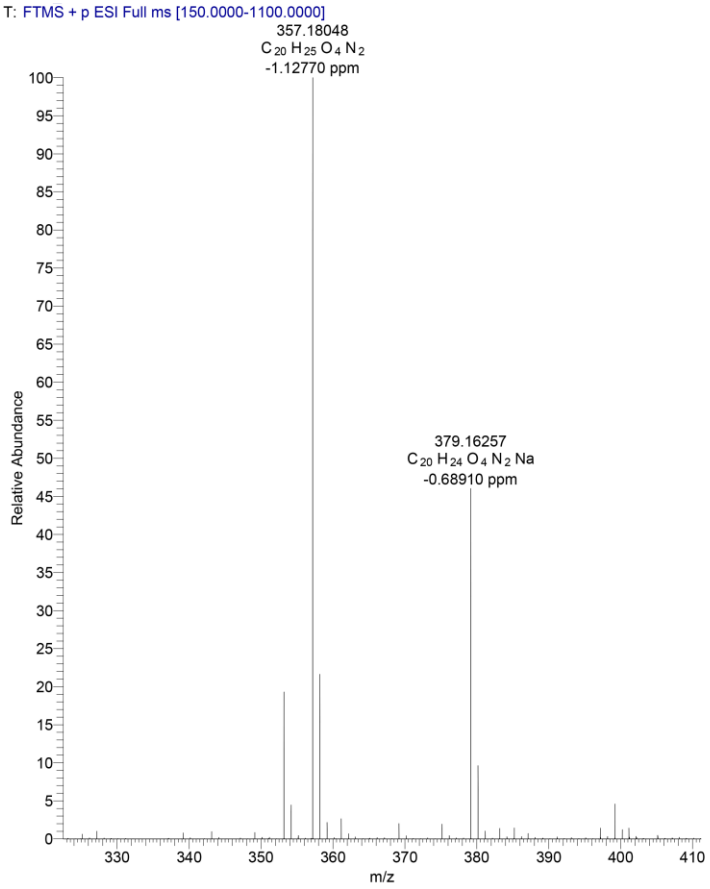



**Figure S49.** IR spectra of compound **4**

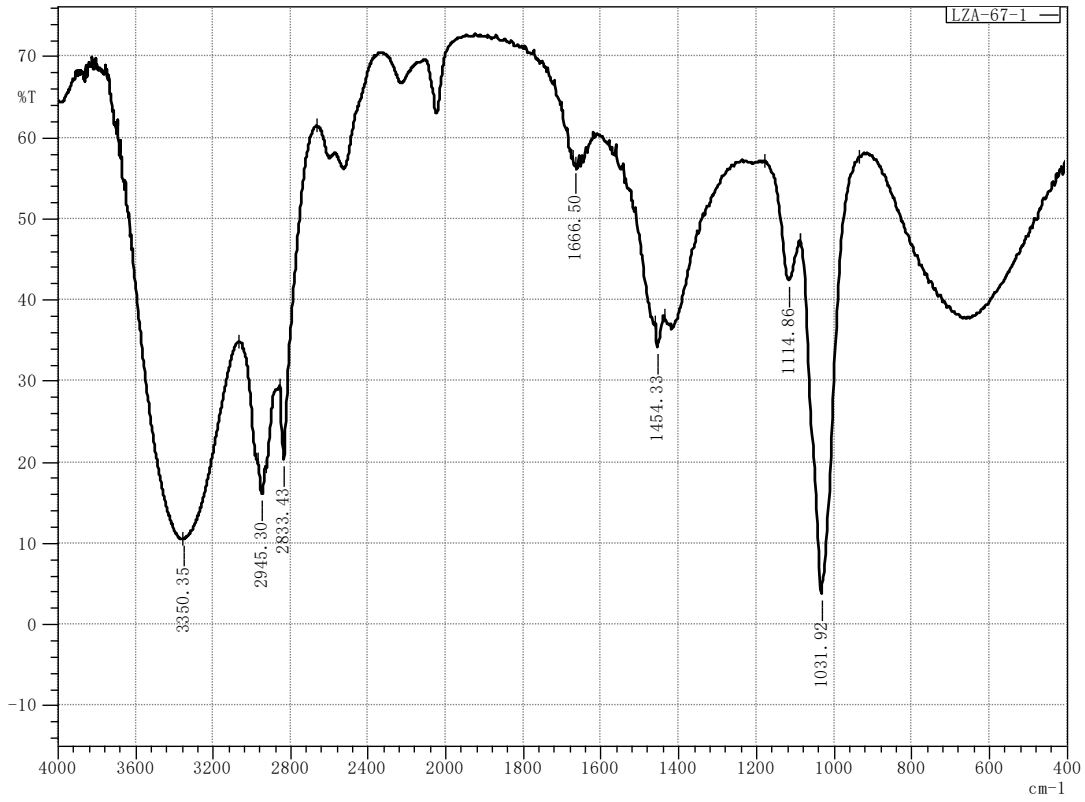


**Figure S50.** CD spectra of compound **4** in $CH_3OH$