Electronic Supplementary Material (ESI) for RSC Advances.


# Fused Multicyclic Polyketides with a Two-Spiro-Carbon Skeleton from Mangrove-Derived Endophytic Fungus *Epicoccum nigrum* SCNU-F0002

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# Contents

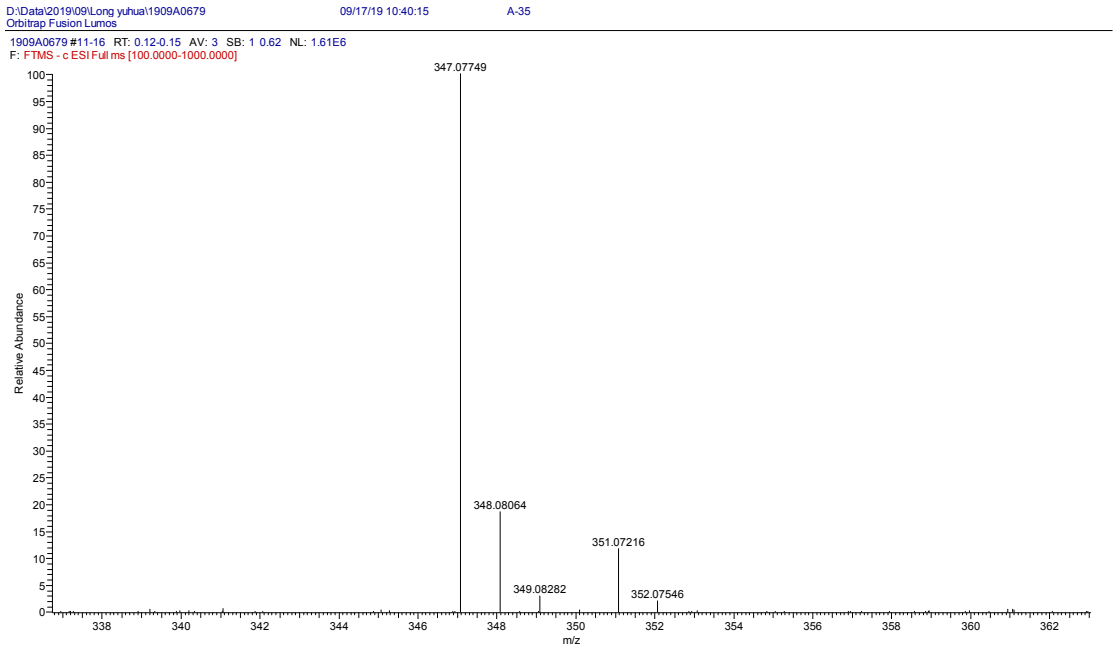


**Fig.S1.** HR-ESI-MS spectrum of (±**1**)

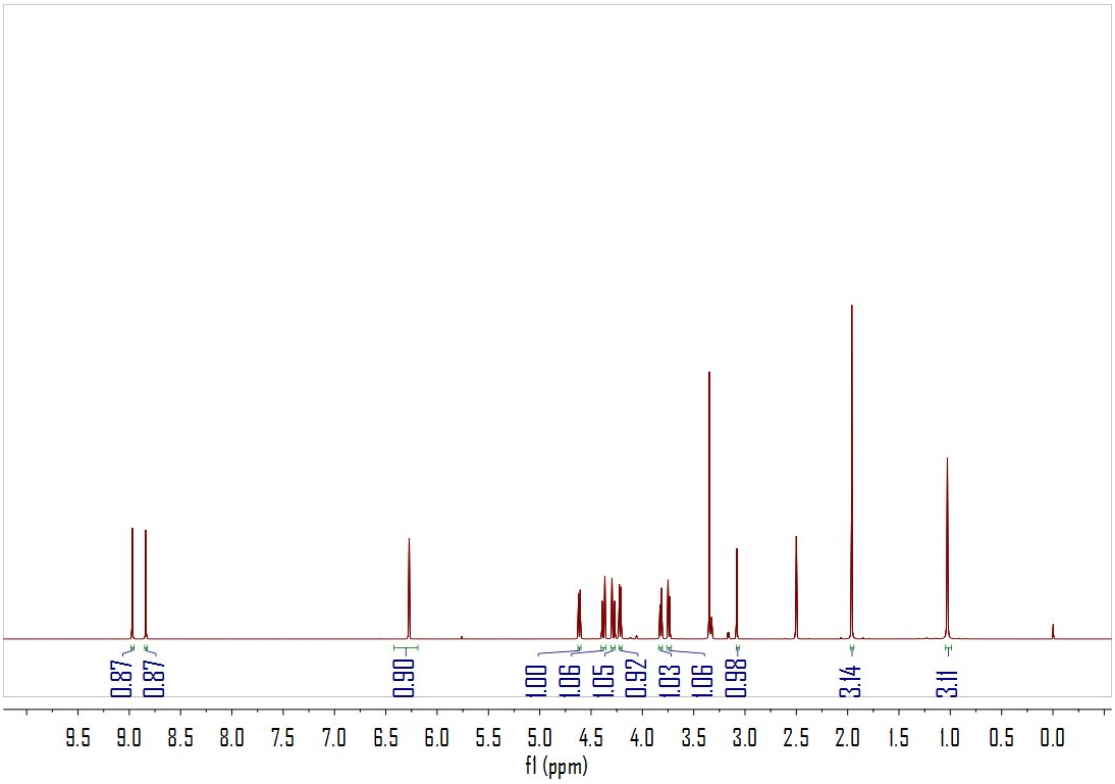


**Fig.S2.** $^{1}$H- NMR spectrum (DMSO, 600MHz) of (±**1**)

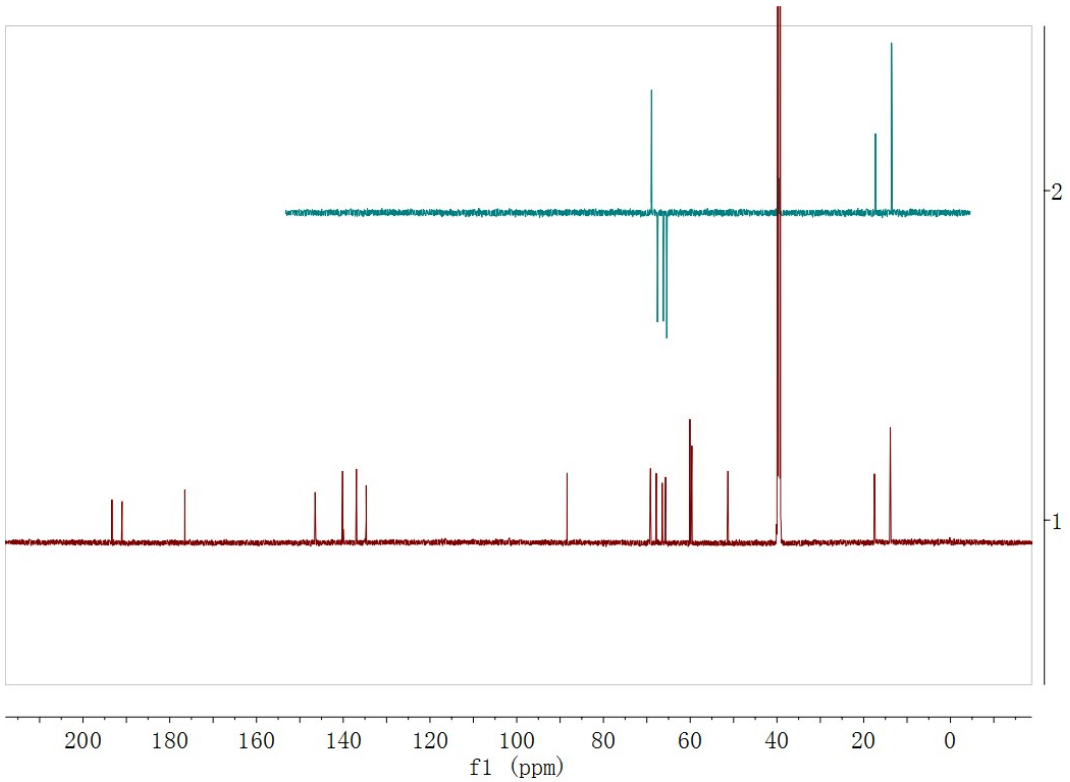


**Fig.S3.** DEPT 135 and $^{13}$C-NMR spectrum (DMSO, 600MHz) of compound (**±1**)

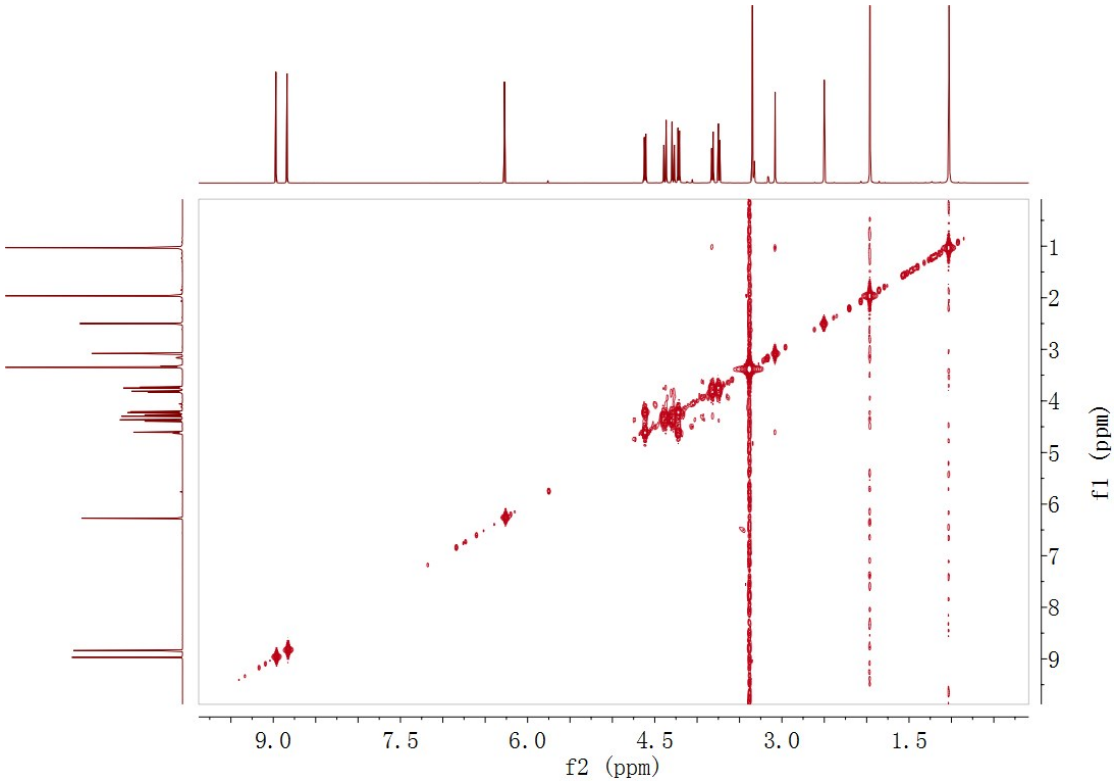


**Fig.S4.** $^{1}$H-$^{1}$H COSY spectrum (DMSO, 600MHz) of compound (**±1**)

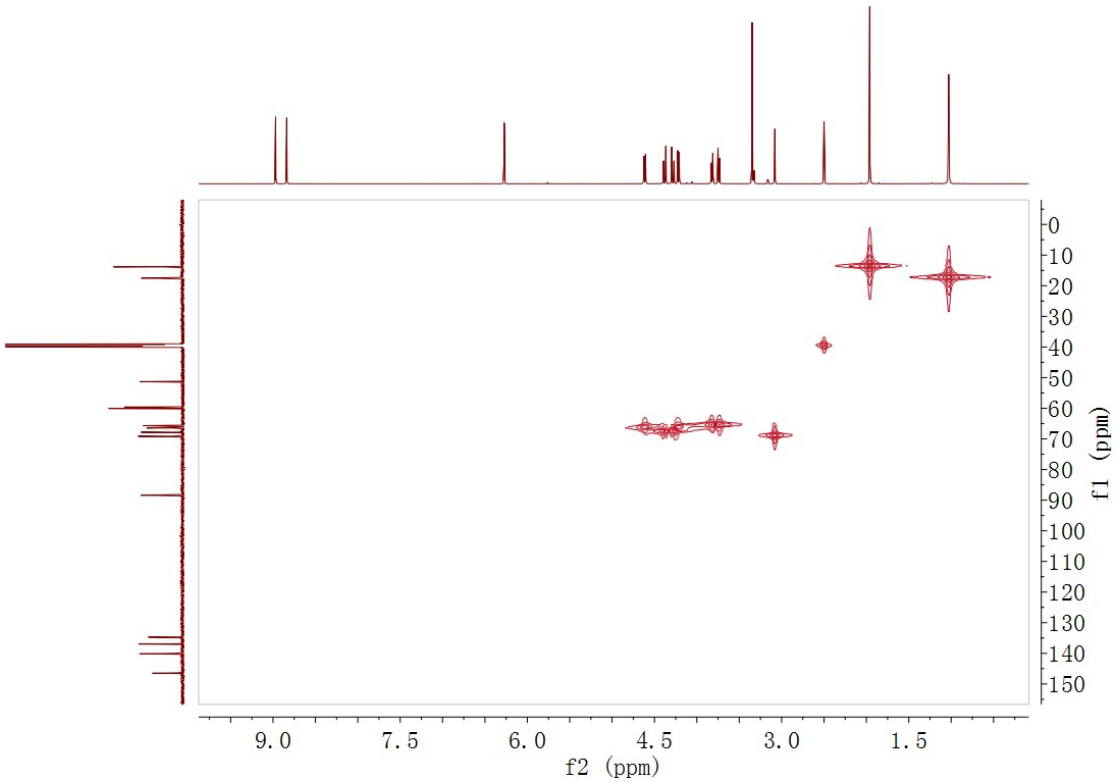


**Fig.S5.** HSQC spectrum (DMSO, 600MHz) of compound (±**1**)

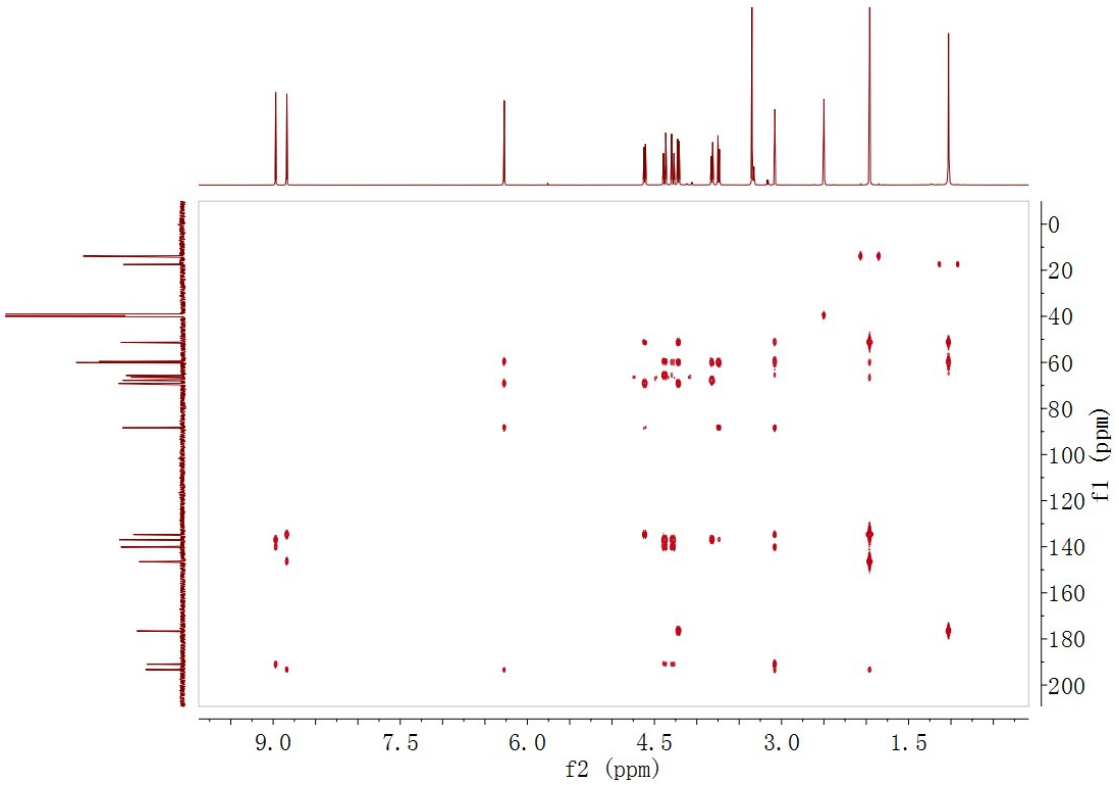


**Fig.S6.** HMBC spectrum (DMSO, 600MHz) of compound (±**1**)

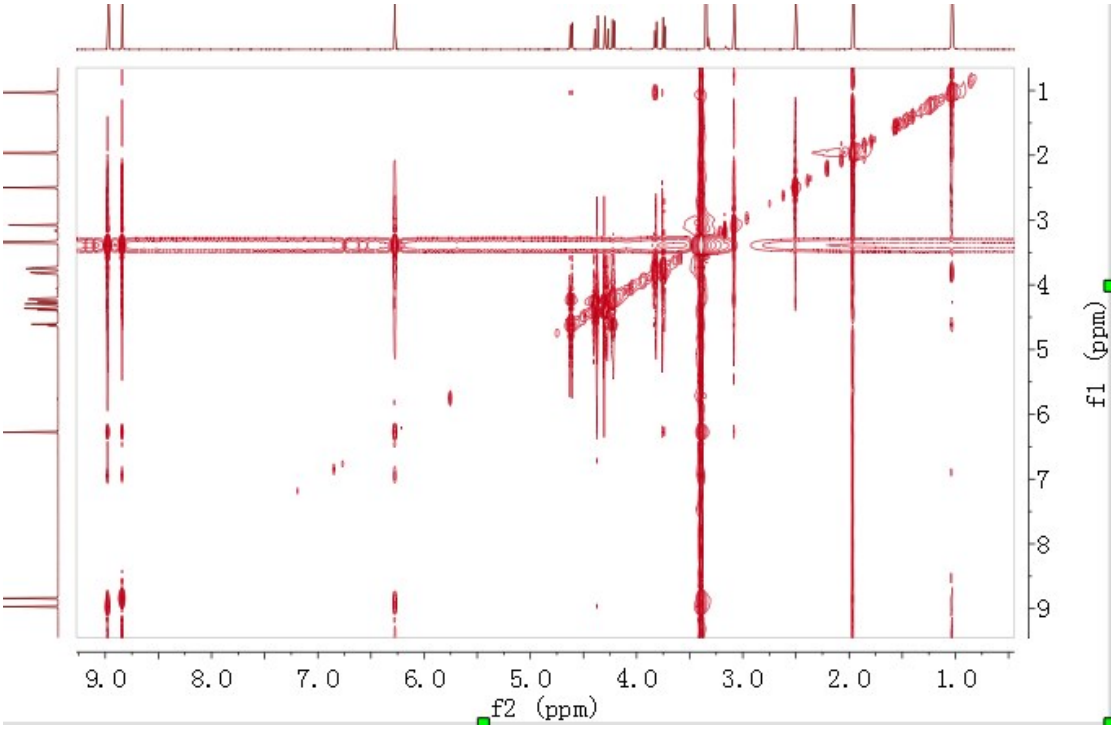


**Fig.S7.** NOESY spectrum of (DMSO, 600MHz) compound (±**1**)

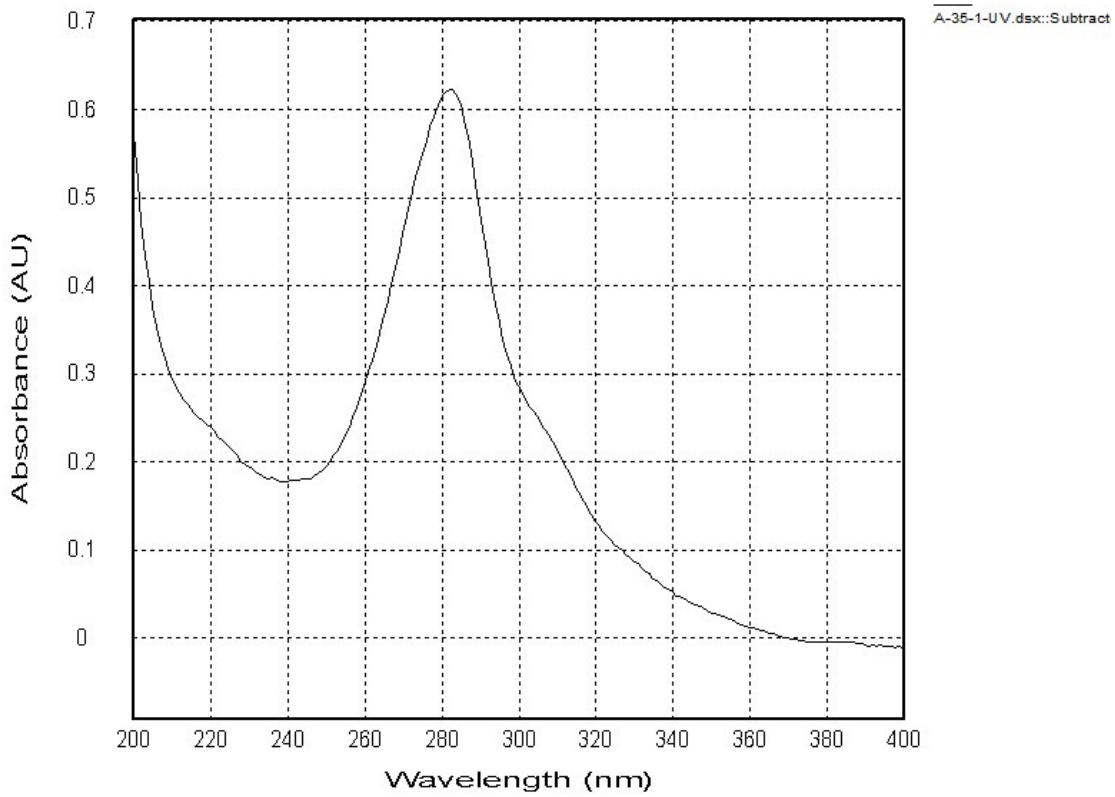


**Fig.S8.** UV spectrum of **(+)-1** in MeOH

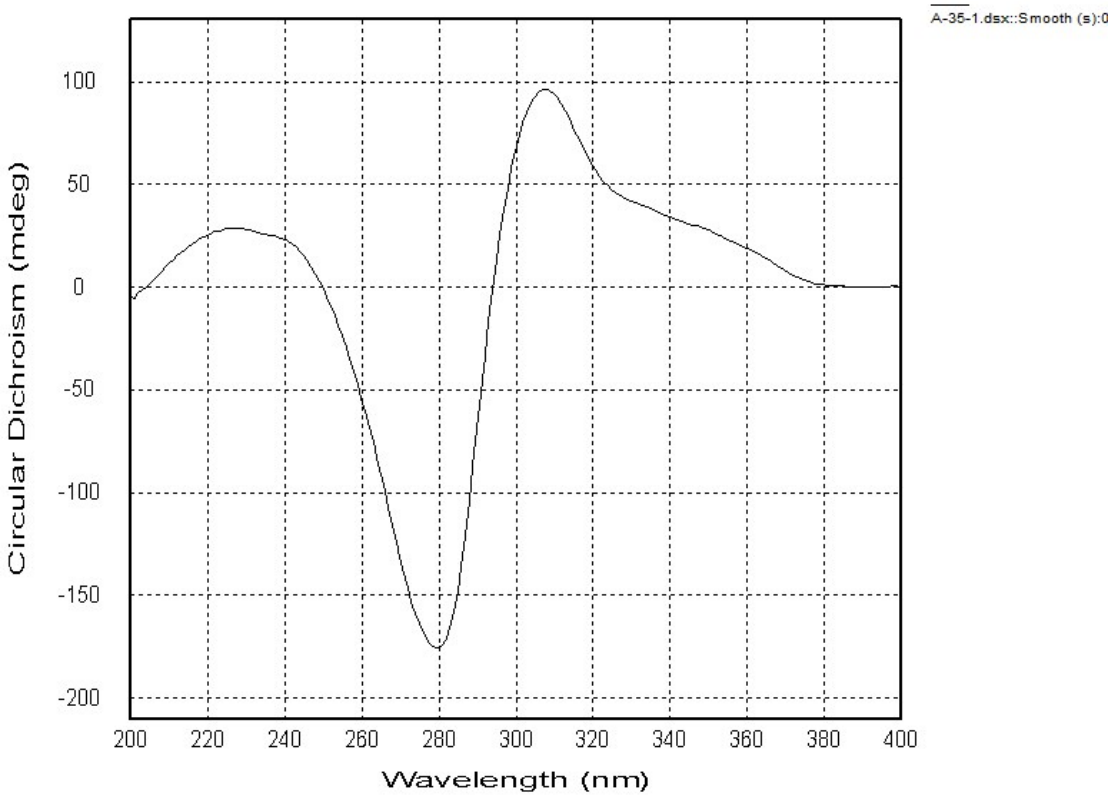


**Fig.S9.** Experimental ECD spectrum of **(+)-1**

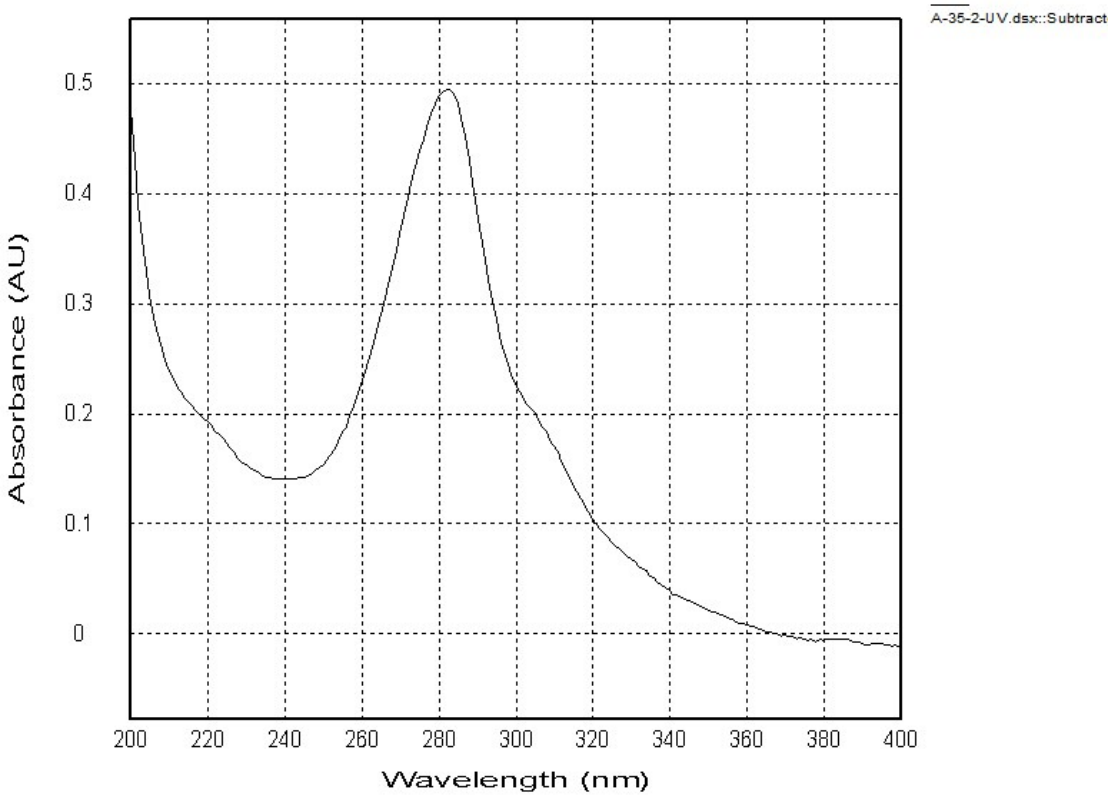


**Fig.S10.** UV spectrum of **(-)-1** in MeOH

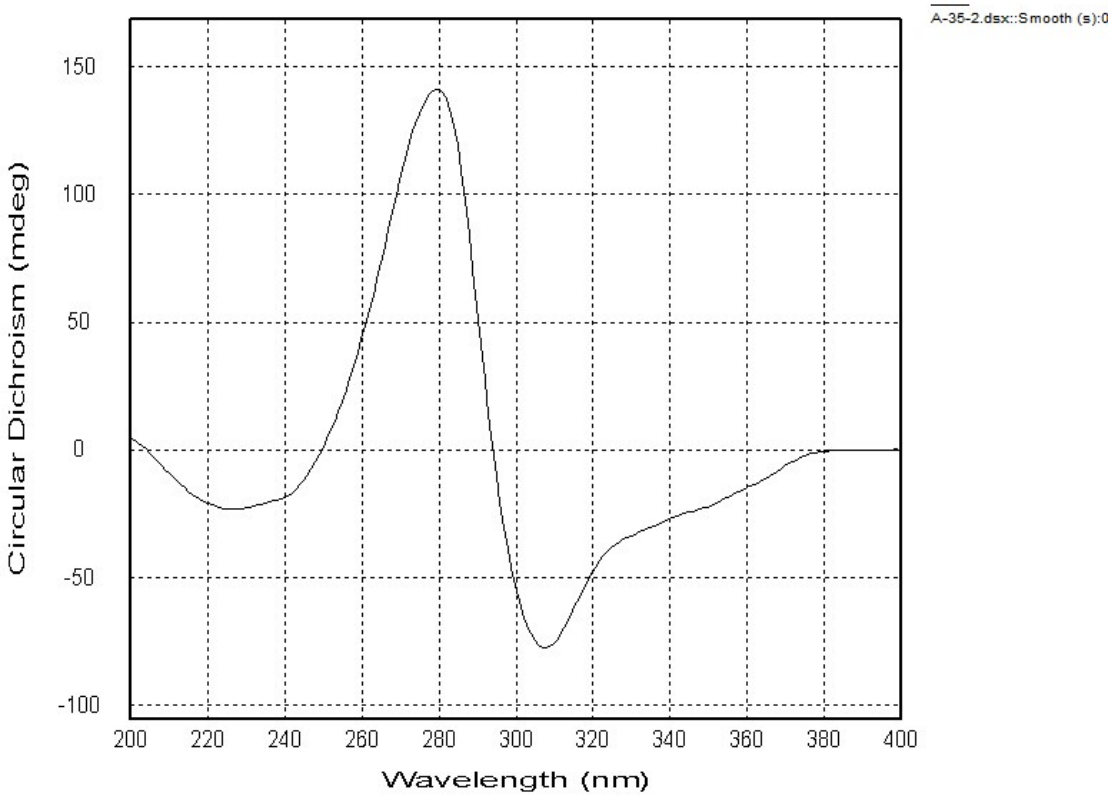


**Fig.S11.** Experimental ECD spectrum of **(-)-1**

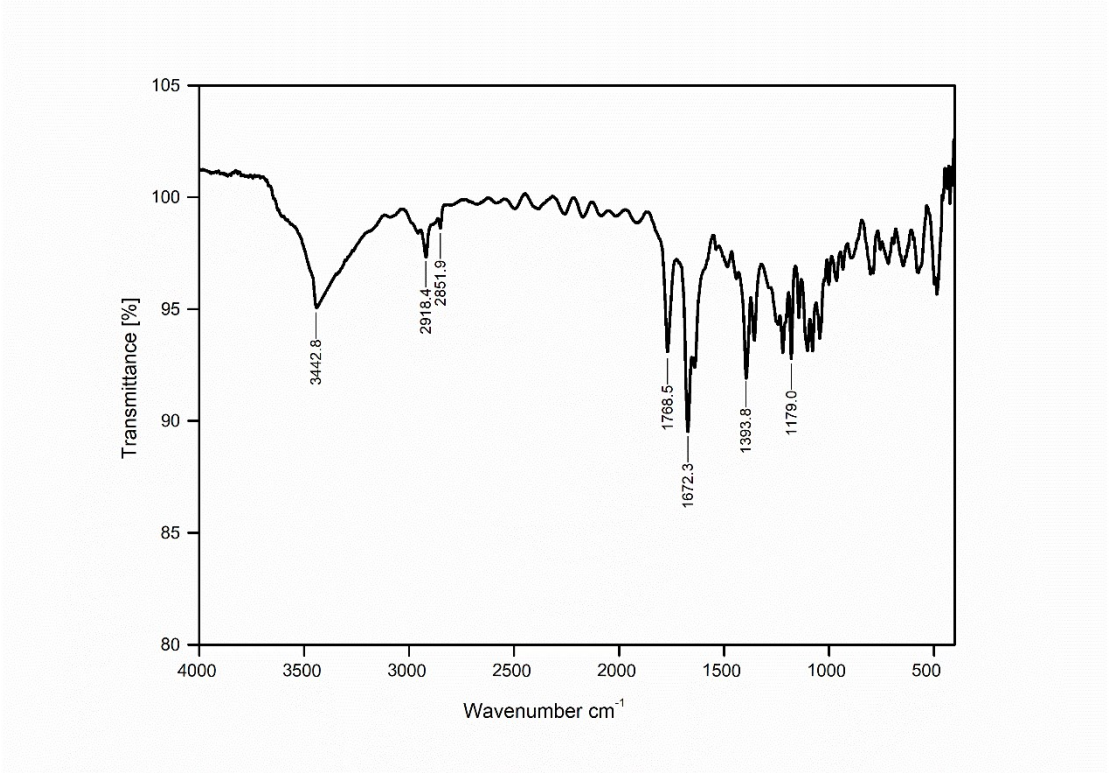


**Fig.S12.** IR spectrum of compound (±**1**)

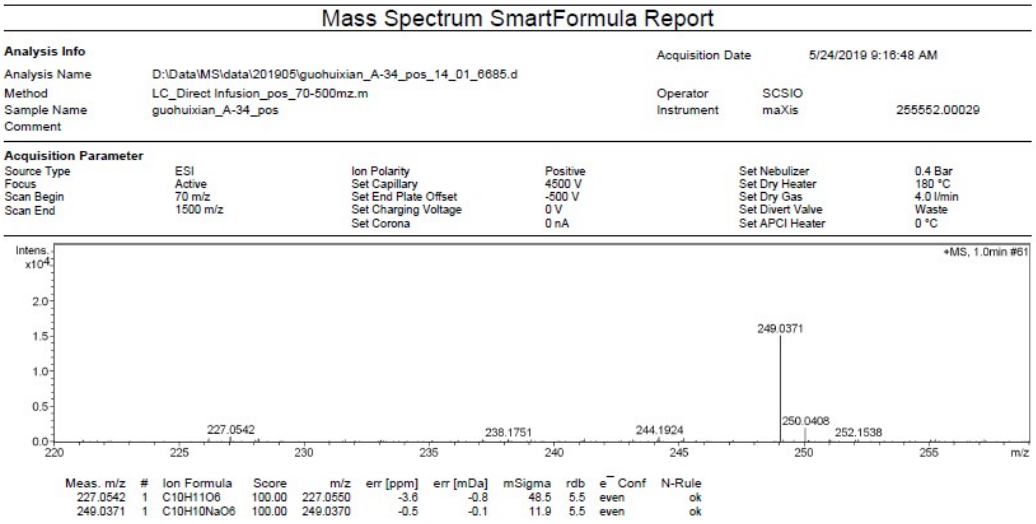


**Fig.S13.** HR-ESI-MS spectrum of compound **(2)**

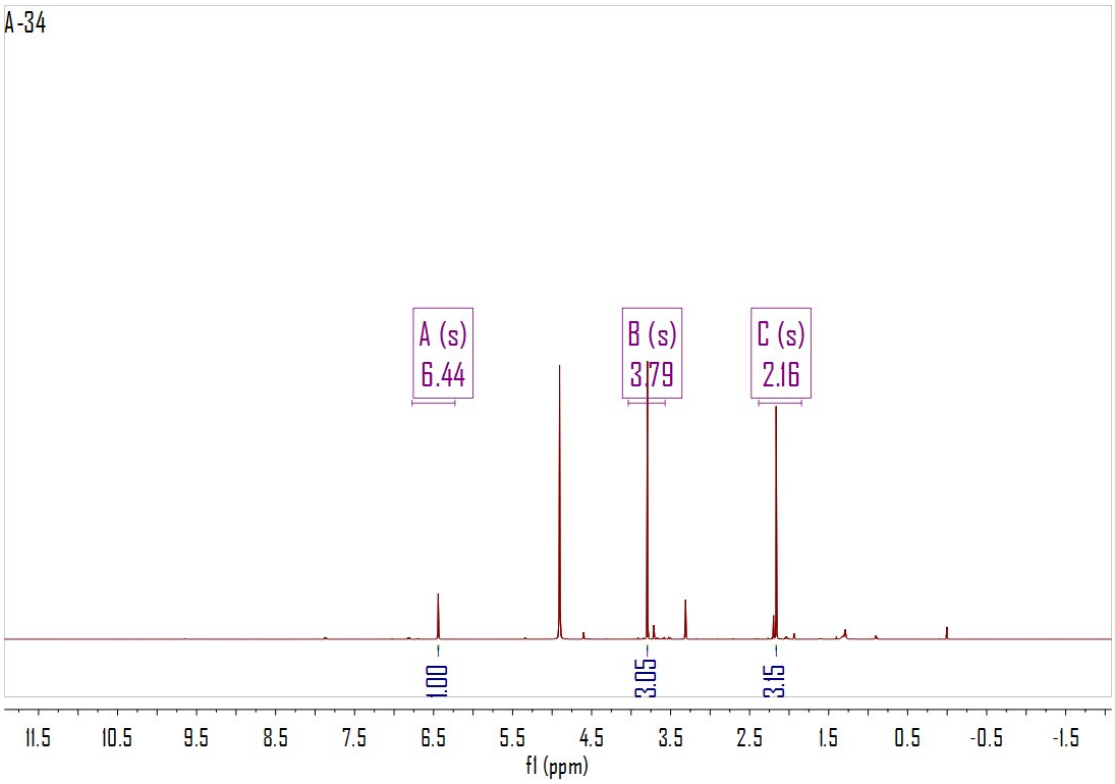


**Fig.S14.** $^{1}$H- NMR spectrum ($CD_3OD$, 600MHz) of compound **(4)**

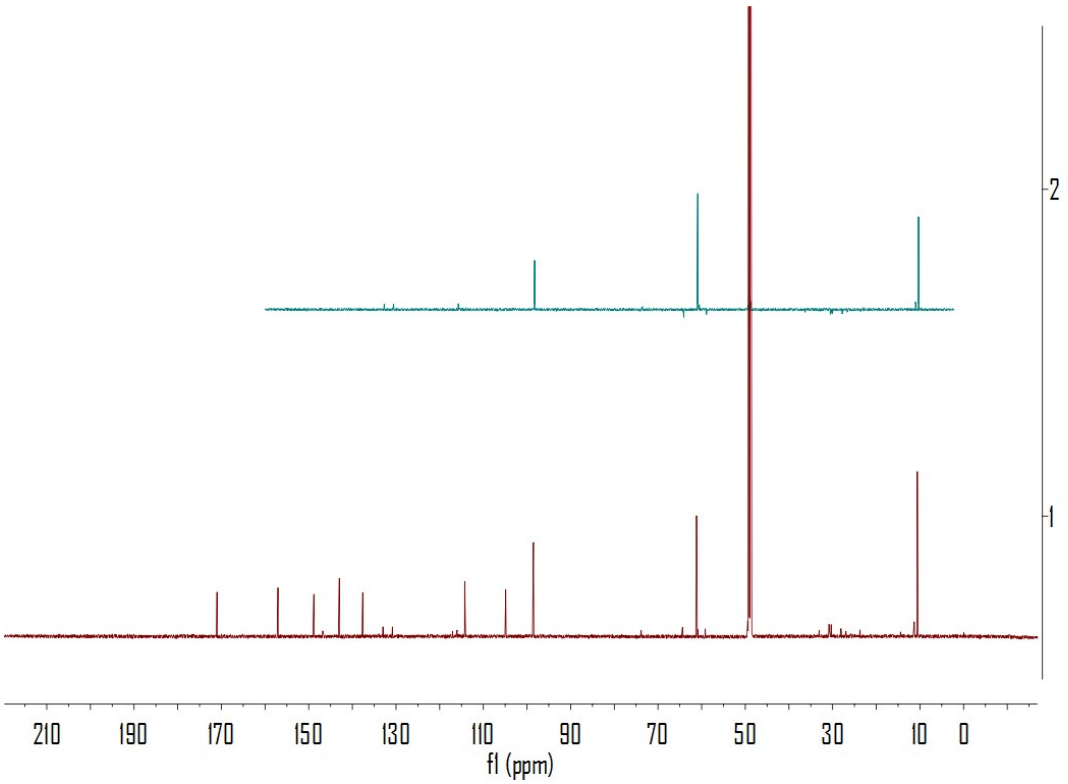


**Fig.S15.** DEPT 135 and $^{13}$C-NMR spectrum ($CD_3OD$, 150MHz) of compound **(4)**

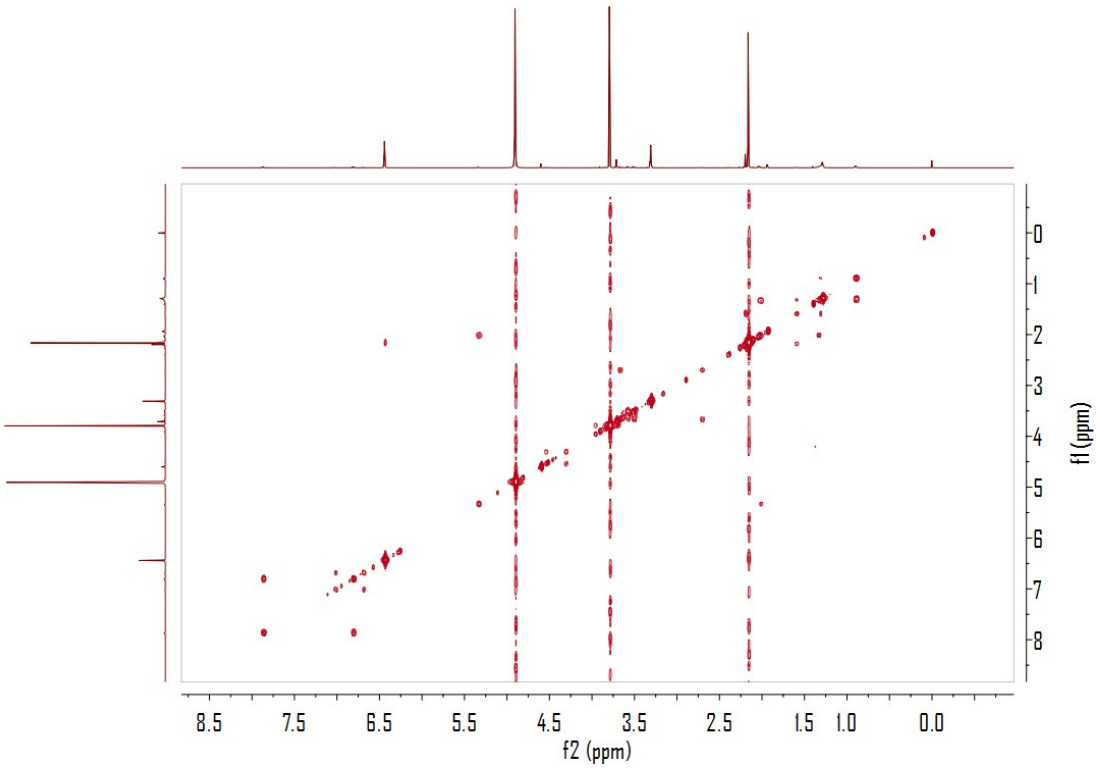


**Fig.S16.** $^{1}$H-$^{1}$H COSY spectrum ($CD_3OD$, 600MHz) of compound **(4)**

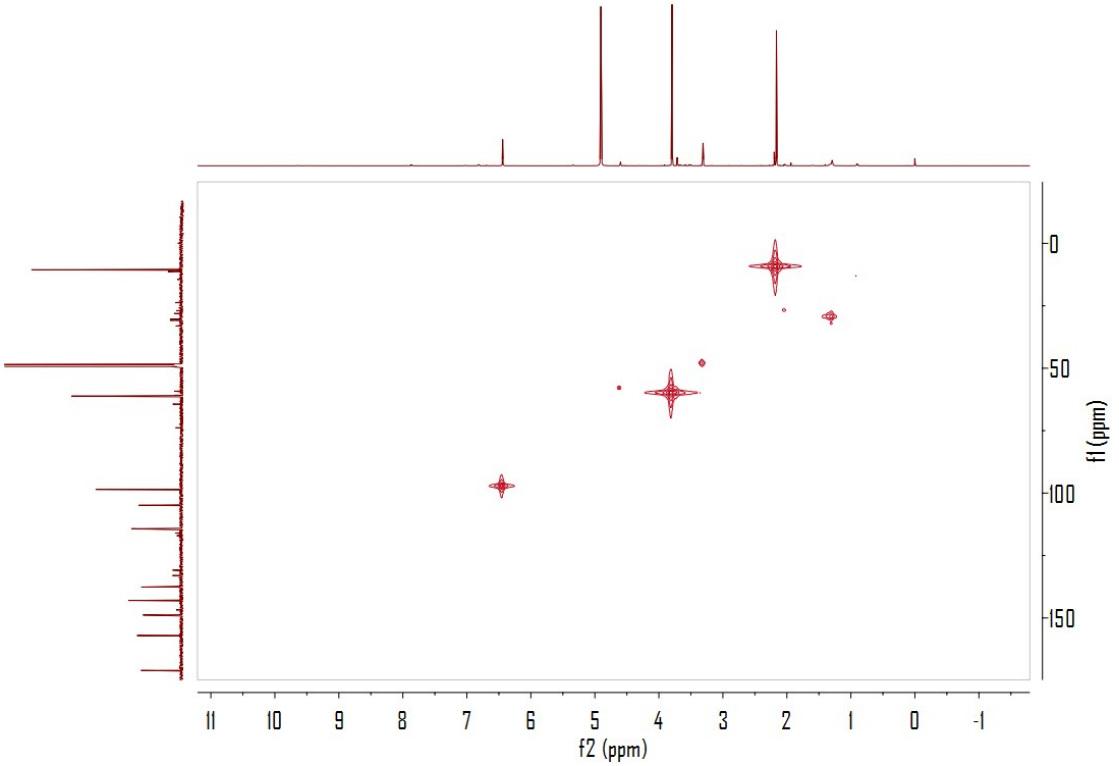


**Fig.S17.** HSQC spectrum ($CD_3OD$, 600MHz) of compound **(4)**

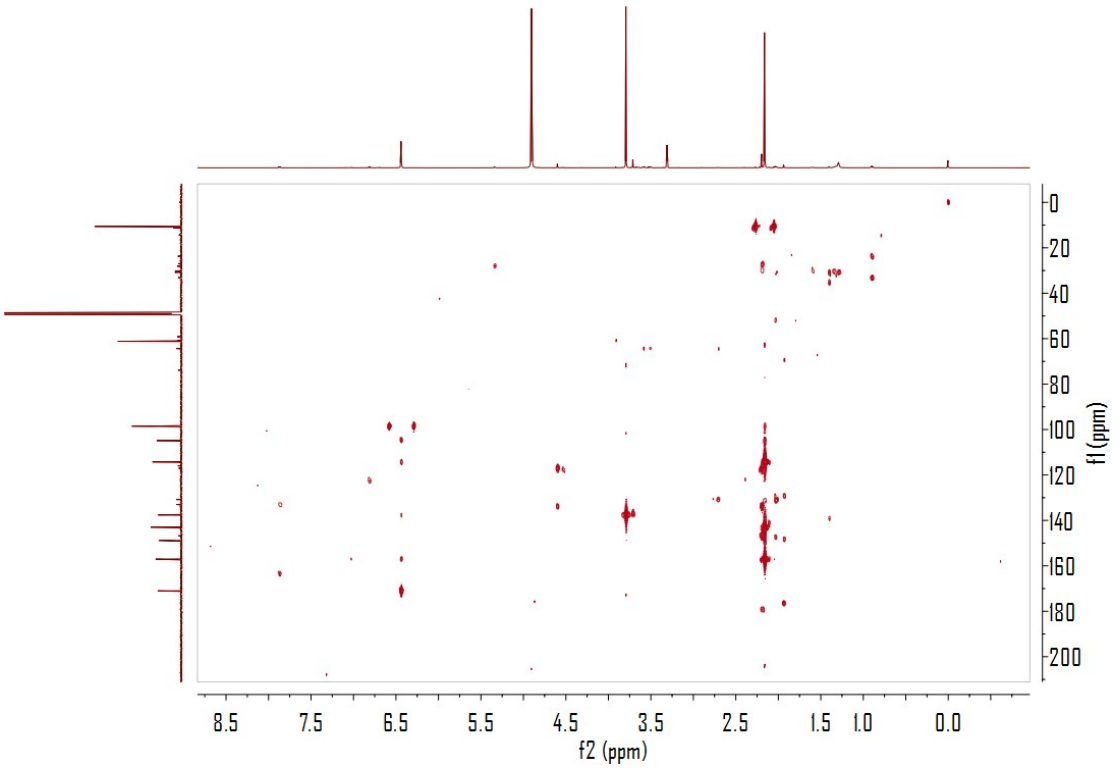


**Fig.S18.** HMBC spectrum ($CD_3OD$, 600MHz) of compound **(2)**

**Table S1**.deviations in NMR data between natural and synthetic[1] samples of **1**

| No. | $\delta_C$, type (N.S) | $\delta_C$, type (S.S) | Δδ/ppm | $\delta_C$, type (N.S) | $\delta_C$, type (S.S) | Δδ/ppm |
|---|---|---|---|---|---|---|
| 1 | 51.3, C | 51.3, C | 0.0 | | | |
| 2 | 66.4, $CH_2$ | 66.4, $CH_2$ | 0.0 | 4.21, d, ($J$ = 10.1); 4.61, d, ($J$ = 10.1) | 4.22, d, ($J$ = 10.1); 4.61, d, ($J$ = 10.1) | +0.01 |
| 4 | 176.5, C | 176.4, C | -0.1 | | | |
| 5 | 60.1, C | 60.0, C | -0.1 | | | |
| 6 | 59.6, C | 59.6, C | 0.0 | | | |
| 7 | 65.6, $CH_2$ | 65.6, $CH_2$ | 0.0 | 3.74, d, ($J$ = 10.0); 3.82, d, ($J$ = 10.0) | 3.75, d, ($J$ = 10.0); 3.82, d, ($J$ = 10.0) | +0.01 |
| 9 | 67.8, $CH_2$ | 67.8, $CH_2$ | 0.0 | 4.28, d, ($J$ = 16.1); 4.38, d, ($J$ = 16.1) | 4.29, d, ($J$ = 16.1); 4.38, d, ($J$ = 16.1) | +0.01 |
| 10 | 136.9, C | 136.9, C | 0.0 | | | |
| 11 | 140.1, C | 140.1, C | 0.0 | | | |
| 12 | 190.1, C | 190.9, C | +0.8 | | | |
| 13 | 69.1, CH | 69.1, CH | 0.0 | 3.08, s | 3.08, s | 0.0 |
| 14 | 88.4, C | 88.4, C | 0.0 | | | |
| 15 | 193.3, C | 193.2, C | -0.1 | | | |
| 16 | 146.5, C | 146.4, C | -0.1 | | | |
| 17 | 134.7, C | 134.6, C | -0.1 | | | |
| 18 | 13.8, $CH_3$ | 13.8, $CH_3$ | 0.0 | 1.96, s | 1.96, s | 0.0 |
| 19 | 17.5, $CH_3$ | 17.5, $CH_3$ | 0.0 | 1.03, s | 1.03, s | 0.0 |
| 11-OH | | | | 8.97, s | 8.93, s | -0.04 |
| 14-OH | | | | 6.27, s | 6.24, s | +0.03 |
| 16-OH | | | | 8.84, s | 8.93, s | +0.09 |

N.S: natural sample; S.S: synthetic sample.

**Table S2**. ECD Computational Result.

**S2.1** Gibbs free energies and Boltzmann-population of low-energy comformers of 1*R*,5*R*,6*S*,13*R*,14*R*-**1**

| Conformers of 1*R*,5*R*,6*S*,13*R*,14*R*-**1** | In MeOH | |
|---|---|---|
| | $\Delta G^a$ | P (%)[b] |
| **1a** | 0.0 | 83.3 |
| **1b** | 2.12 | 3.6 |
| **1c** | 2.62 | 5.7 |
| **1d** | 3.12 | 7.4 |

$\Delta G^a$, B3LYP/ 6-31+G (d, p), in kcal/mol. [b]Boltzmann-population.

**S2.2** Cartesian coordinates for the low-energy optimized conformers of 3*R*-**1** at B3LYP/6-31+G (d, p) level of theory in MeOH.

| Conformer **1a** | | Standard Orientation(Ångstroms) | | | |
|---|---|---|---|---|---|
| Center Number | Atom | Type | X | Y | Z |
| 1 | 6 | 0 | -2.241719 | -0.288180 | -1.025922 |
| 2 | 6 | 0 | -1.814560 | 0.896912 | -0.207483 |
| 3 | 6 | 0 | -0.476924 | 0.740643 | 0.633543 |
| 4 | 6 | 0 | 0.191382 | 1.062678 | -0.746580 |
| 5 | 6 | 0 | 0.336929 | -0.354079 | -1.347946 |
| 6 | 6 | 0 | -1.031004 | -0.932142 | -1.727269 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 6 | 0 | 1.506639 | 1.777816 | -0.753392 |
| 8 | 6 | 0 | 2.681302 | 0.868296 | -0.366537 |
| 9 | 6 | 0 | 2.448892 | -0.524237 | -0.081031 |
| 10 | 6 | 0 | 1.038103 | -1.073752 | -0.137304 |
| 11 | 8 | 0 | 1.657428 | 2.975606 | -1.001391 |
| 12 | 8 | 0 | -3.399717 | -0.665895 | -1.196925 |
| 13 | 8 | 0 | -1.150418 | -1.857996 | -2.531923 |
| 14 | 6 | 0 | 0.882776 | -2.607136 | -0.138346 |
| 15 | 8 | 0 | -0.419380 | -2.868273 | 0.517749 |
| 16 | 6 | 0 | -0.877232 | -1.759916 | 1.209259 |
| 17 | 6 | 0 | 0.131598 | -0.612934 | 1.098058 |
| 18 | 6 | 0 | -2.762389 | 1.732246 | 0.598435 |
| 19 | 8 | 0 | -1.879635 | 2.596303 | 1.379470 |
| 20 | 8 | 0 | -1.031106 | 1.722086 | -1.243217 |
| 21 | 8 | 0 | 3.847180 | 1.376609 | -0.296367 |
| 22 | 6 | 0 | 3.619912 | -1.386728 | 0.266283 |
| 23 | 8 | 0 | -1.933560 | -1.748996 | 1.828067 |
| 24 | 6 | 0 | 0.892304 | -0.545569 | 2.443353 |
| 25 | 6 | 0 | -0.637269 | 1.878822 | 1.671805 |
| 26 | 1 | 0 | 0.966148 | -0.389753 | -2.241604 |
| 27 | 1 | 0 | 0.815450 | -3.037213 | -1.138068 |
| 28 | 1 | 0 | 1.651279 | -3.119785 | 0.441758 |
| 29 | 1 | 0 | -3.376921 | 1.088117 | 1.241320 |
| 30 | 1 | 0 | -3.399198 | 2.375262 | -0.008858 |
| 31 | 1 | 0 | 3.743664 | -2.203417 | -0.459599 |
| 32 | 1 | 0 | 4.531413 | -0.787445 | 0.273076 |
| 33 | 1 | 0 | 3.500204 | -1.859907 | 1.250797 |
| 34 | 1 | 0 | 1.439420 | -1.477079 | 2.621811 |
| 35 | 1 | 0 | 1.609312 | 0.280515 | 2.459315 |
| 36 | 1 | 0 | 0.188620 | -0.418523 | 3.269954 |
| 37 | 1 | 0 | -0.693546 | 1.458534 | 2.680429 |
| 38 | 1 | 0 | 0.165374 | 2.618702 | 1.632425 |

| Conformer **1b** | | Standard Orientation(Ångstroms) | | | |
|---|---|---|---|---|---|
| Center Number | Atom | Type | X | Y | Z |
| 1 | 6 | 0 | -2.241719 | -0.288180 | -1.025922 |
| 2 | 6 | 0 | -1.814560 | 0.896912 | -0.207483 |
| 3 | 6 | 0 | -0.476924 | 0.740643 | 0.633543 |
| 4 | 6 | 0 | 0.191382 | 1.062678 | -0.746580 |
| 5 | 6 | 0 | 0.336929 | -0.354079 | -1.347946 |
| 6 | 6 | 0 | -1.031004 | -0.932142 | -1.727269 |
| 7 | 6 | 0 | 1.506639 | 1.777816 | -0.753392 |
| 8 | 6 | 0 | 2.681302 | 0.868296 | -0.366537 |
| 9 | 6 | 0 | 2.448892 | -0.524237 | -0.081031 |
| 10 | 6 | 0 | 1.038103 | -1.073752 | -0.137304 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 8 | 0 | 1.657428 | 2.975606 | -1.001391 |
| 12 | 8 | 0 | -3.399717 | -0.665895 | -1.196925 |
| 13 | 8 | 0 | -1.150418 | -1.857996 | -2.531923 |
| 14 | 6 | 0 | 0.882776 | -2.607136 | -0.138346 |
| 15 | 8 | 0 | -0.419380 | -2.868273 | 0.517749 |
| 16 | 6 | 0 | -0.877232 | -1.759916 | 1.209259 |
| 17 | 6 | 0 | 0.131598 | -0.612934 | 1.098058 |
| 18 | 6 | 0 | -2.762389 | 1.732246 | 0.598435 |
| 19 | 8 | 0 | -1.879635 | 2.596303 | 1.379470 |
| 20 | 8 | 0 | -1.031106 | 1.722086 | -1.243217 |
| 21 | 8 | 0 | 3.847180 | 1.376609 | -0.296367 |
| 22 | 6 | 0 | 3.619912 | -1.386728 | 0.266283 |
| 23 | 8 | 0 | -1.933560 | -1.748996 | 1.828067 |
| 24 | 6 | 0 | 0.892304 | -0.545569 | 2.443353 |
| 25 | 6 | 0 | -0.637269 | 1.878822 | 1.671805 |
| 26 | 1 | 0 | 0.966148 | -0.389753 | -2.241604 |
| 27 | 1 | 0 | 0.815450 | -3.037213 | -1.138068 |
| 28 | 1 | 0 | 1.651279 | -3.119785 | 0.441758 |
| 29 | 1 | 0 | -3.376921 | 1.088117 | 1.241320 |
| 30 | 1 | 0 | -3.399198 | 2.375262 | -0.008858 |
| 31 | 1 | 0 | 3.743664 | -2.203417 | -0.459599 |
| 32 | 1 | 0 | 4.531413 | -0.787445 | 0.273076 |
| 33 | 1 | 0 | 3.500204 | -1.859907 | 1.250797 |
| 34 | 1 | 0 | 1.439420 | -1.477079 | 2.621811 |
| 35 | 1 | 0 | 1.609312 | 0.280515 | 2.459315 |
| 36 | 1 | 0 | 0.188620 | -0.418523 | 3.269954 |
| 37 | 1 | 0 | -0.693546 | 1.458534 | 2.680429 |
| 38 | 1 | 0 | 0.165374 | 2.618702 | 1.632425 |

| Conformer **1c** | | Standard Orientation(Ångstroms) | | | |
|---|---|---|---|---|---|
| Center Number | Atom | Type | X | Y | Z |
| 1 | 6 | 0 | -2.241719 | -0.288180 | -1.025922 |
| 2 | 6 | 0 | -1.814560 | 0.896912 | -0.207483 |
| 3 | 6 | 0 | -0.476924 | 0.740643 | 0.633543 |
| 4 | 6 | 0 | 0.191382 | 1.062678 | -0.746580 |
| 5 | 6 | 0 | 0.336929 | -0.354079 | -1.347946 |
| 6 | 6 | 0 | -1.031004 | -0.932142 | -1.727269 |
| 7 | 6 | 0 | 1.506639 | 1.777816 | -0.753392 |
| 8 | 6 | 0 | 2.681302 | 0.868296 | -0.366537 |
| 9 | 6 | 0 | 2.448892 | -0.524237 | -0.081031 |
| 10 | 6 | 0 | 1.038103 | -1.073752 | -0.137304 |
| 11 | 8 | 0 | 1.657428 | 2.975606 | -1.001391 |
| 12 | 8 | 0 | -3.399717 | -0.665895 | -1.196925 |
| 13 | 8 | 0 | -1.150418 | -1.857996 | -2.531923 |
| 14 | 6 | 0 | 0.882776 | -2.607136 | -0.138346 |
| 15 | 8 | 0 | -0.419380 | -2.868273 | 0.517749 |

| | | | | | |
|---|---|---|---|---|---|
| 16 | 6 | 0 | -0.877232 | -1.759916 | 1.209259 |
| 17 | 6 | 0 | 0.131598 | -0.612934 | 1.098058 |
| 18 | 6 | 0 | -2.762389 | 1.732246 | 0.598435 |
| 19 | 8 | 0 | -1.879635 | 2.596303 | 1.379470 |
| 20 | 8 | 0 | -1.031106 | 1.722086 | -1.243217 |
| 21 | 8 | 0 | 3.847180 | 1.376609 | -0.296367 |
| 22 | 6 | 0 | 3.619912 | -1.386728 | 0.266283 |
| 23 | 8 | 0 | -1.933560 | -1.748996 | 1.828067 |
| 24 | 6 | 0 | 0.892304 | -0.545569 | 2.443353 |
| 25 | 6 | 0 | -0.637269 | 1.878822 | 1.671805 |
| 26 | 1 | 0 | 0.966148 | -0.389753 | -2.241604 |
| 27 | 1 | 0 | 0.815450 | -3.037213 | -1.138068 |
| 28 | 1 | 0 | 1.651279 | -3.119785 | 0.441758 |
| 29 | 1 | 0 | -3.376921 | 1.088117 | 1.241320 |
| 30 | 1 | 0 | -3.399198 | 2.375262 | -0.008858 |
| 31 | 1 | 0 | 3.743664 | -2.203417 | -0.459599 |
| 32 | 1 | 0 | 4.531413 | -0.787445 | 0.273076 |
| 33 | 1 | 0 | 3.500204 | -1.859907 | 1.250797 |
| 34 | 1 | 0 | 1.439420 | -1.477079 | 2.621811 |
| 35 | 1 | 0 | 1.609312 | 0.280515 | 2.459315 |
| 36 | 1 | 0 | 0.188620 | -0.418523 | 3.269954 |
| 37 | 1 | 0 | -0.693546 | 1.458534 | 2.680429 |
| 38 | 1 | 0 | 0.165374 | 2.618702 | 1.632425 |

| Conformer **1d** | | Standard Orientation(Ångstroms) | | | |
|---|---|---|---|---|---|
| Center Number | Atom | Type | X | Y | Z |
| 1 | 6 | 0 | -2.241719 | -0.288180 | -1.025922 |
| 2 | 6 | 0 | -1.814560 | 0.896912 | -0.207483 |
| 3 | 6 | 0 | -0.476924 | 0.740643 | 0.633543 |
| 4 | 6 | 0 | 0.191382 | 1.062678 | -0.746580 |
| 5 | 6 | 0 | 0.336929 | -0.354079 | -1.347946 |
| 6 | 6 | 0 | -1.031004 | -0.932142 | -1.727269 |
| 7 | 6 | 0 | 1.506639 | 1.777816 | -0.753392 |
| 8 | 6 | 0 | 2.681302 | 0.868296 | -0.366537 |
| 9 | 6 | 0 | 2.448892 | -0.524237 | -0.081031 |
| 10 | 6 | 0 | 1.038103 | -1.073752 | -0.137304 |
| 11 | 8 | 0 | 1.657428 | 2.975606 | -1.001391 |
| 12 | 8 | 0 | -3.399717 | -0.665895 | -1.196925 |
| 13 | 8 | 0 | -1.150418 | -1.857996 | -2.531923 |
| 14 | 6 | 0 | 0.882776 | -2.607136 | -0.138346 |
| 15 | 8 | 0 | -0.419380 | -2.868273 | 0.517749 |
| 16 | 6 | 0 | -0.877232 | -1.759916 | 1.209259 |
| 17 | 6 | 0 | 0.131598 | -0.612934 | 1.098058 |
| 18 | 6 | 0 | -2.762389 | 1.732246 | 0.598435 |
| 19 | 8 | 0 | -1.879635 | 2.596303 | 1.379470 |

| | | | | | |
|---|---|---|---|---|---|
| 20 | 8 | 0 | -1.031106 | 1.722086 | -1.243217 |
| 21 | 8 | 0 | 3.847180 | 1.376609 | -0.296367 |
| 22 | 6 | 0 | 3.619912 | -1.386728 | 0.266283 |
| 23 | 8 | 0 | -1.933560 | -1.748996 | 1.828067 |
| 24 | 6 | 0 | 0.892304 | -0.545569 | 2.443353 |
| 25 | 6 | 0 | -0.637269 | 1.878822 | 1.671805 |
| 26 | 1 | 0 | 0.966148 | -0.389753 | -2.241604 |
| 27 | 1 | 0 | 0.815450 | -3.037213 | -1.138068 |
| 28 | 1 | 0 | 1.651279 | -3.119785 | 0.441758 |
| 29 | 1 | 0 | -3.376921 | 1.088117 | 1.241320 |
| 30 | 1 | 0 | -3.399198 | 2.375262 | -0.008858 |
| 31 | 1 | 0 | 3.743664 | -2.203417 | -0.459599 |
| 32 | 1 | 0 | 4.531413 | -0.787445 | 0.273076 |
| 33 | 1 | 0 | 3.500204 | -1.859907 | 1.250797 |
| 34 | 1 | 0 | 1.439420 | -1.477079 | 2.621811 |
| 35 | 1 | 0 | 1.609312 | 0.280515 | 2.459315 |
| 36 | 1 | 0 | 0.188620 | -0.418523 | 3.269954 |
| 37 | 1 | 0 | -0.693546 | 1.458534 | 2.680429 |
| 38 | 1 | 0 | 0.165374 | 2.618702 | 1.632425 |

**References**

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