# SUPPLEMENTARY INFORMATION

# Discovery of artemargyins A-E: rare 9'-*nor*-dibenzylbutane lignans and a lignan-coumarin hybrid with antihepatic fibrosis activities from *Artemisia argyi* var. *gracilis*

Ying Wu[a,b], Ze Ma[a,b], Yong-Xiang Huang[a,b], Tian-Ze Li[a], Yong-Cui Wang[a], Ji-Jun Chen[a,b*]

[a] *Kunming Institute of Botany, Chinese Academy of Sciences, State Key Laboratory of Phytochemistry and Natural Medicines, Kunming 650201, People's Republic of China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

* Corresponding author. Prof. Dr. Ji-Jun Chen, Kunming Institute of Botany, Chinese Academy of Sciences, No. 132 Lanhei Road, Kunming 650201, Yunnan, People's Republic of China

ORCID number: 0000-0002-1942-5725

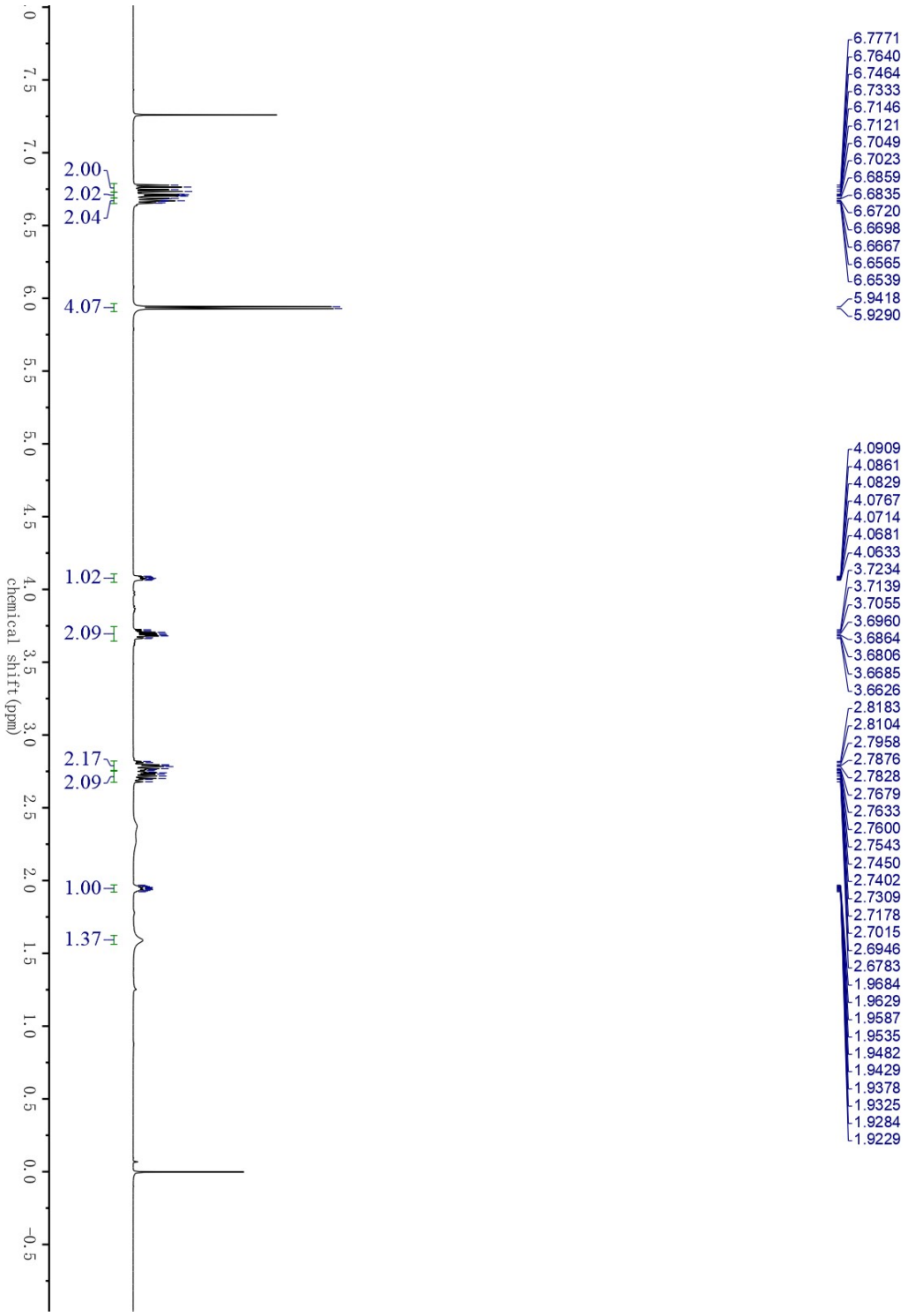
Phone: + 86-871-65223265, Fax: + 86-871-65227197, E-mail address: chenjj@mail.kib.ac.cn

## List of Supplementary materials

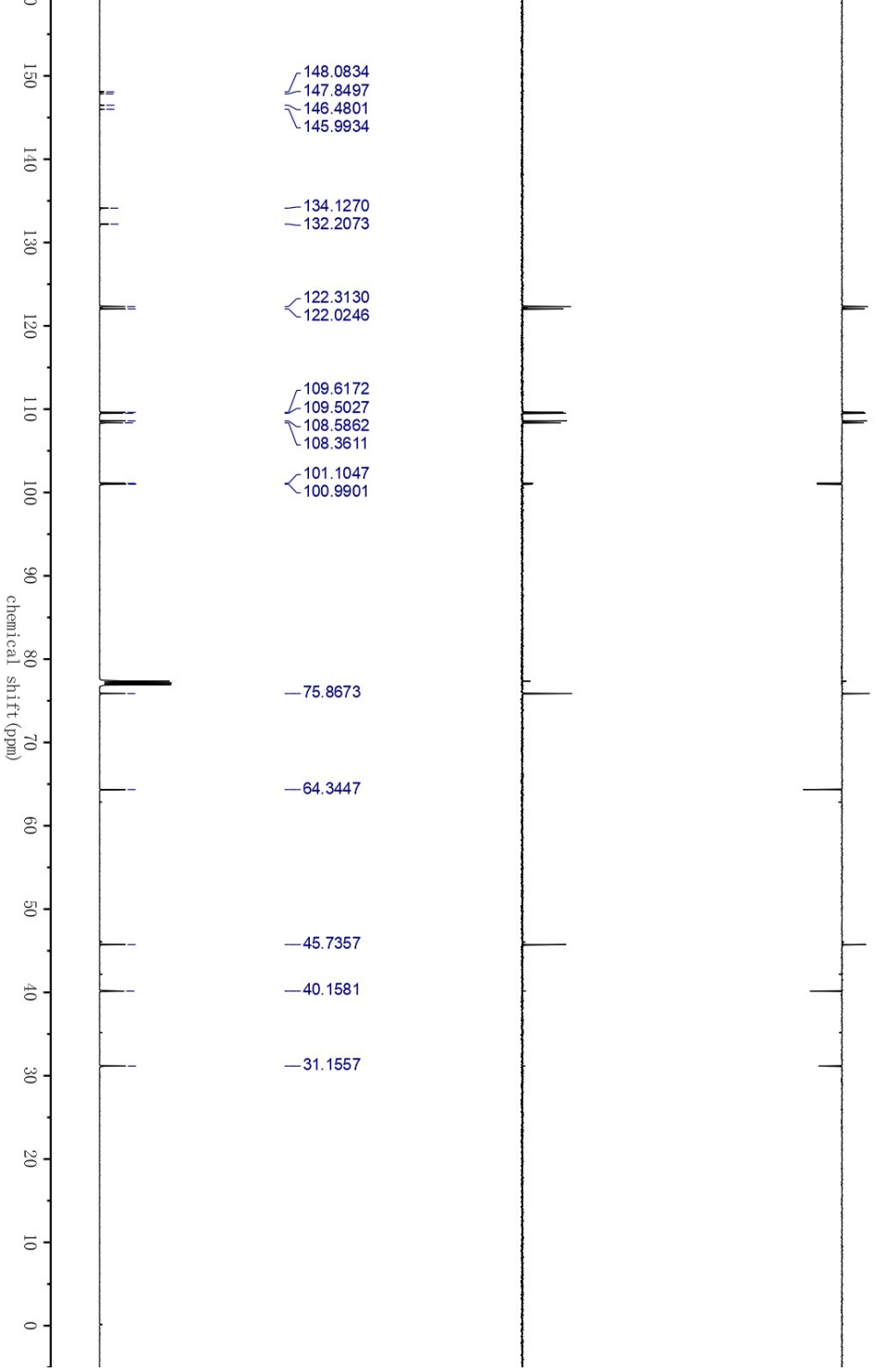
## General Experimental Instruments

High-resolution mass spectra were acquired using a Shimadzu LC/MS-IT-TOF system (Kyoto, Japan). UV absorption profiles were recorded on a Shimadzu UV2401PC spectrophotometer (Kyoto, Japan), while IR spectra (KBr pellets) were collected via a Bio-Rad FTS-135 spectrometer (CA, USA). Nuclear magnetic resonance (NMR) data were analyzed with a Bruker Advance III-600 spectrometer (Germany, 600 MHz) using TMS as the internal standard. Melting points were obtained on an SGW® X-4B microscopic melting point apparatus (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). Optical rotations were quantified with a JASCO P-1020 polarimeter (Tokyo, Japan). Electronic circular dichroism (ECD) spectra were captured on an Applied Photophysics dichromatograph (UK). Thin-layer chromatography (TLC) was conducted using silica gel GF254 plates sourced from Yantai Jiangyou Silicon Development Company (Yantai, China). The spots were visualized under UV light or by heating after being sprayed with a 10% $H_2SO_4$ solution in ethanol (*v/v*). For column chromatography, 200–300 mesh silica gel (Linyi Haixiang, Linyi, China), and Sephadex LH-20 (GE Healthcare Bio-Sciences AB, Uppsala, Sweden) were employed. High-performance liquid chromatography (HPLC) was performed on a CXTH-LC-3000 system fitted with Agilent XDB-C18 (5 μm, 9.4 × 250 mm) columns.

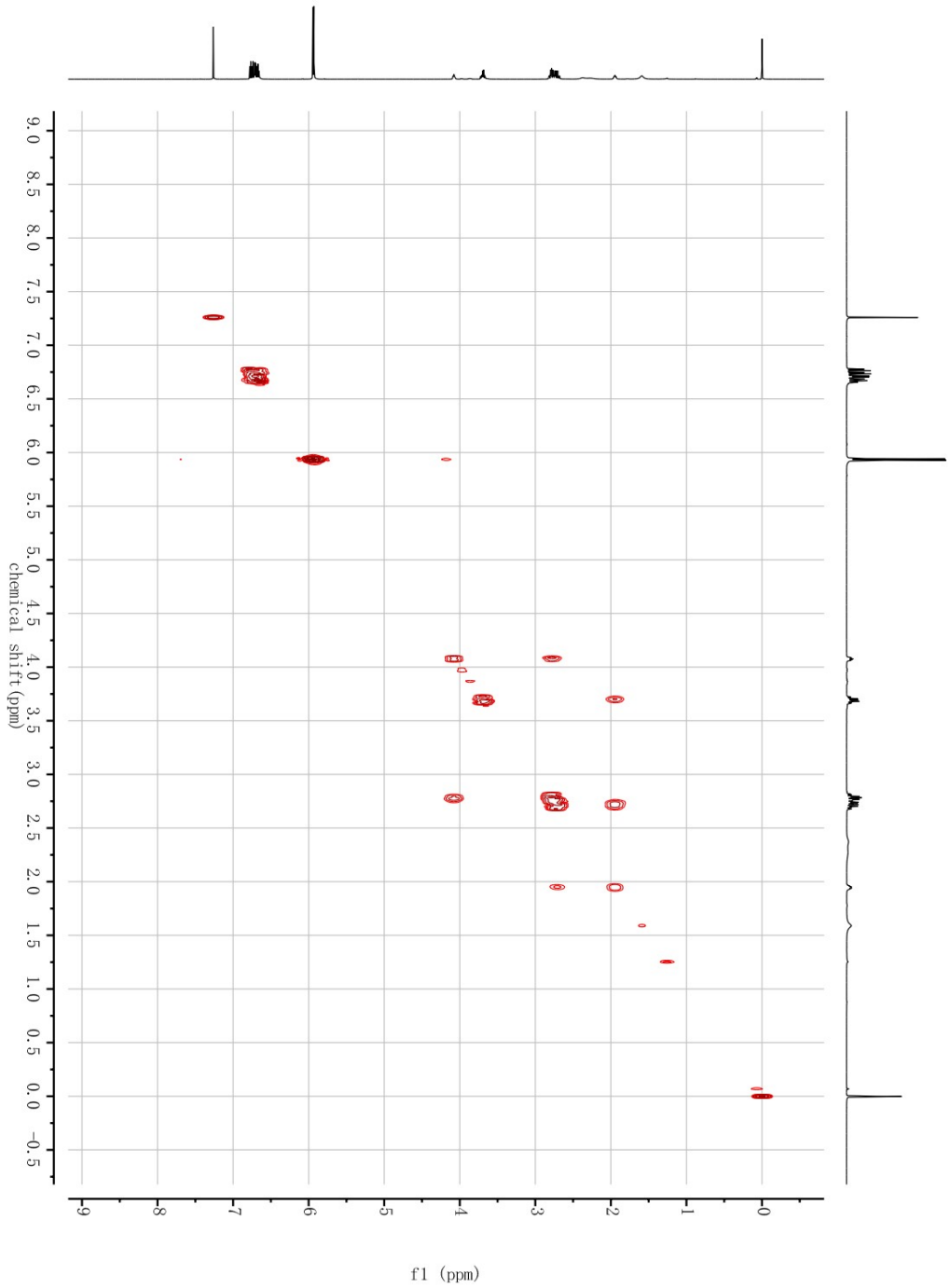
**S1.** **$^{1}$H NMR (600**



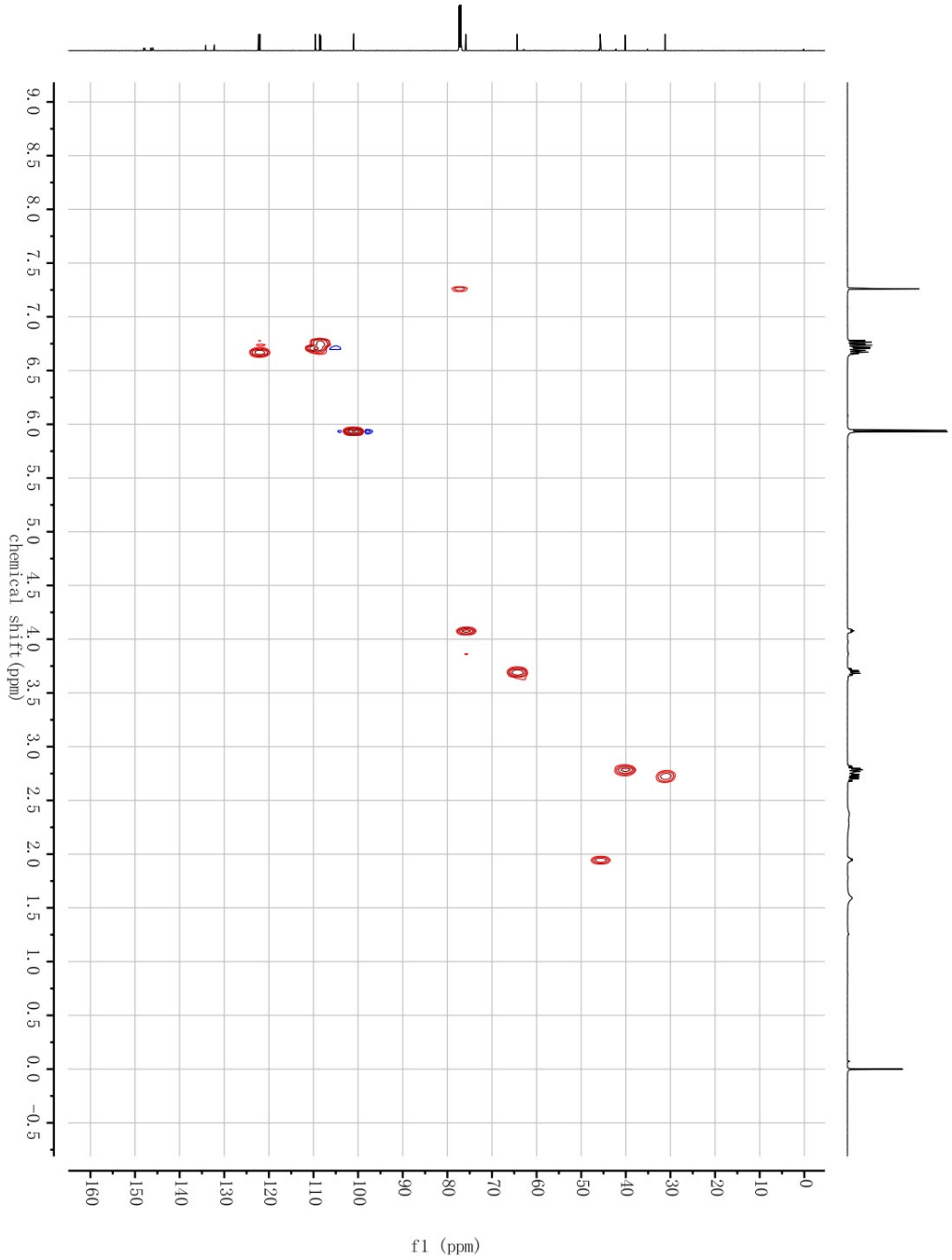

**S2**. **$^{13}$C NMR (DEPT) (150 MHz, $CDCl_3$) spectrum of compound 1**



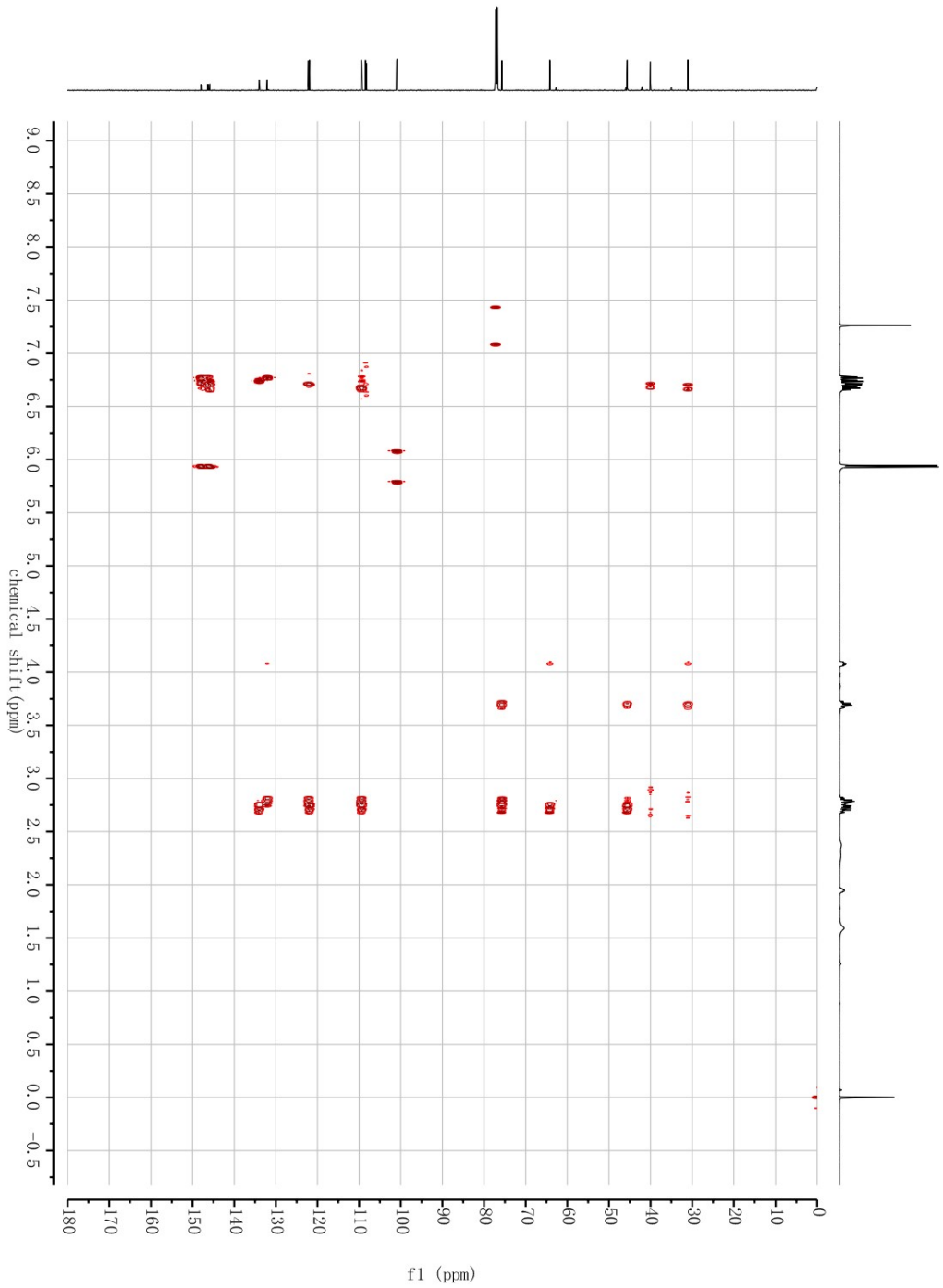

**S3. $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) spectrum of compound 1**



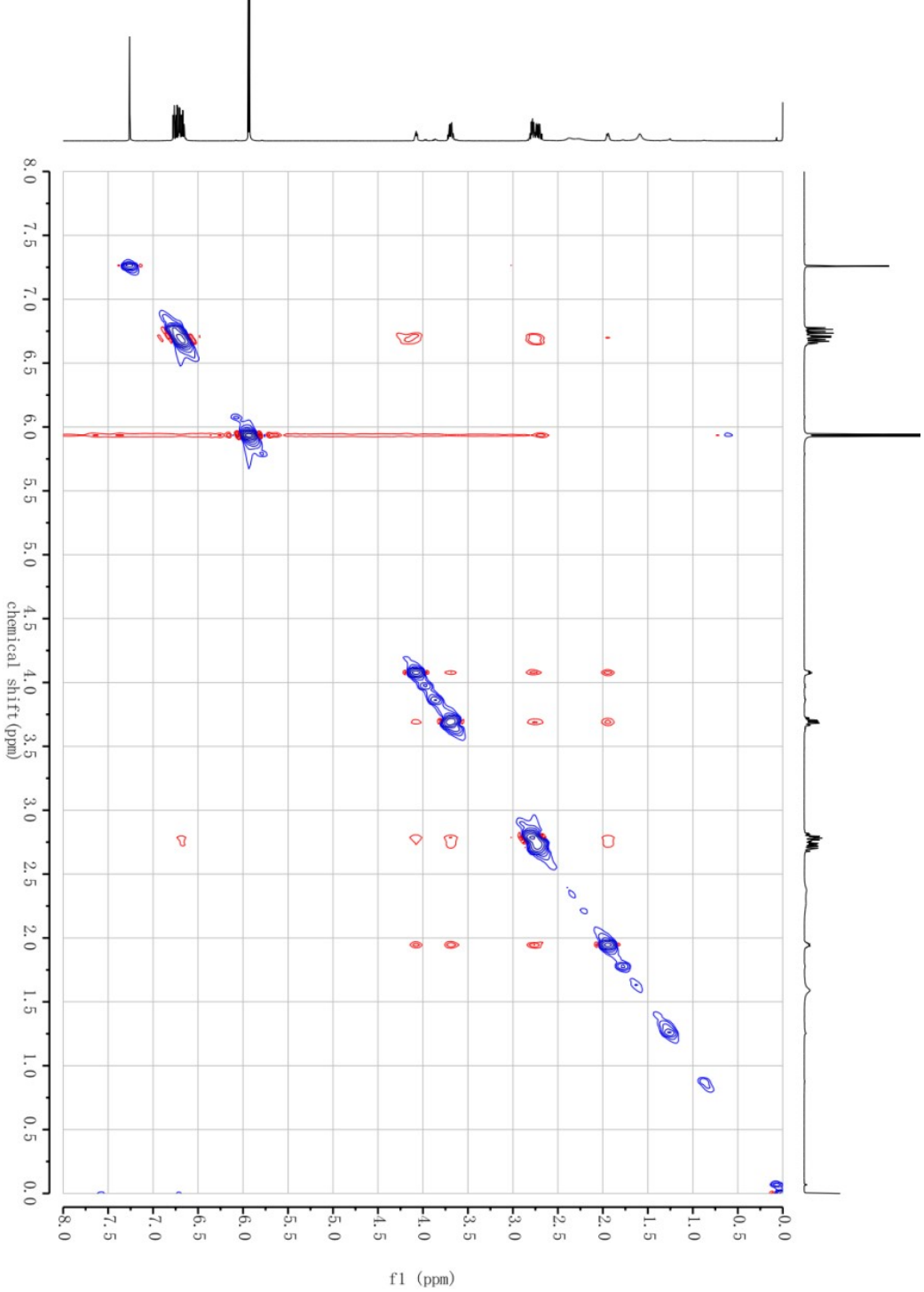

**S4. HSQC spectrum of compound 1**




**S5. HMBC spectrum of compound 1**




**S6. ROESY spectrum of compound 1**




## S7. $[\alpha]_D$ spectrum of compound 1 in MeOH

**Rudolph Research Analytical**

This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Friday, 12-DEC-2025

Set Temperature : 20.0

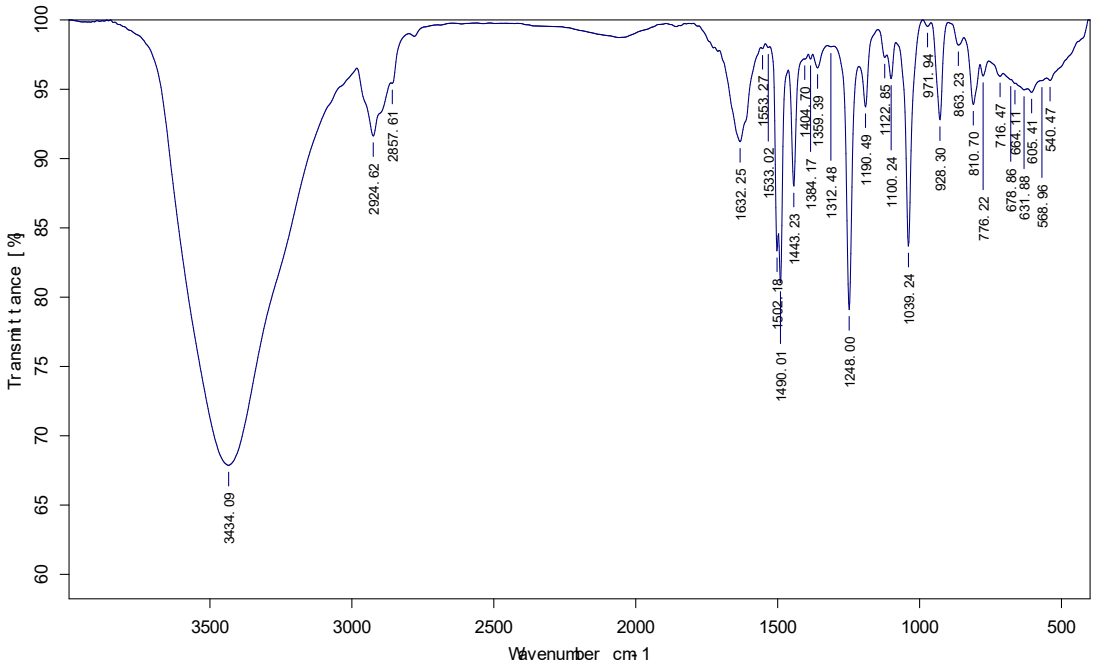
Time Delay : Disabled

Delay between Measurement : Disabled

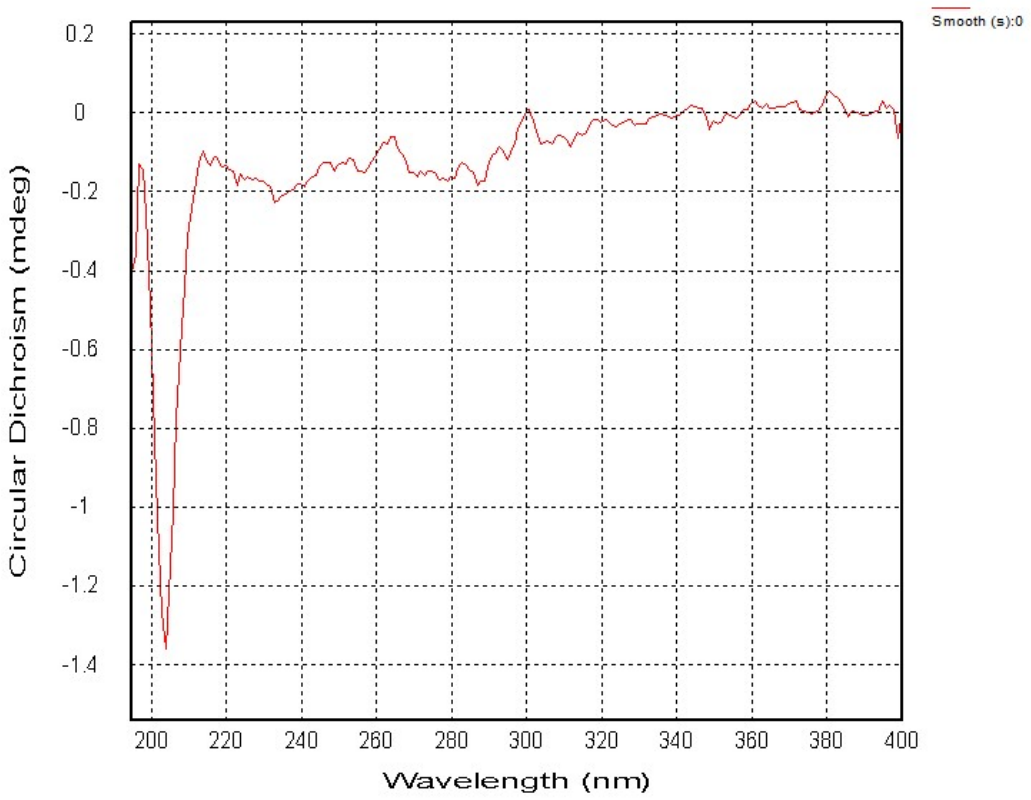
| n | Average | Std.Dev. | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|
| 5 | -5.94 | 0.70 | -11.78 | -4.95 | -6.93 |

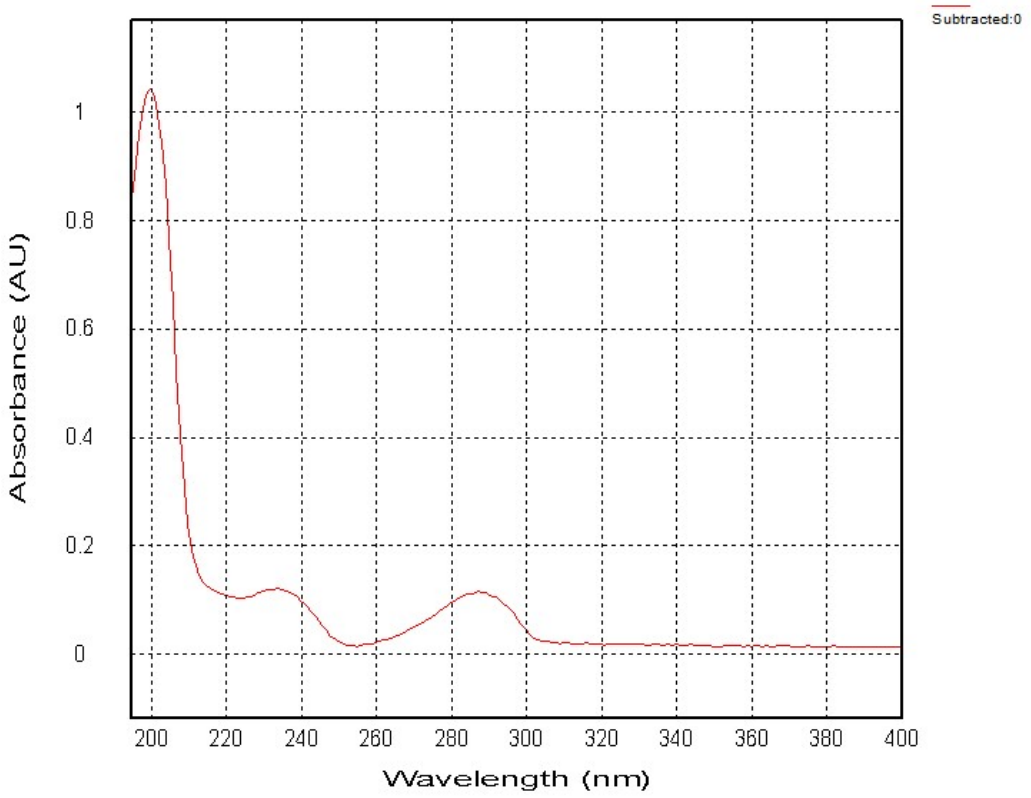
| S.No | Sample ID | Time | Result | Scale | OR °Arc | WLG.nm | Lg.mm | Conc.g/100ml | Temp. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | JK63392 | 04:17:18 PM | -4.95 | SR | -0.005 | 589 | 100.00 | 0.101 | 20.0 |
| 2 | JK63392 | 04:17:25 PM | -6.93 | SR | -0.007 | 589 | 100.00 | 0.101 | 20.0 |
| 3 | JK63392 | 04:17:31 PM | -5.94 | SR | -0.006 | 589 | 100.00 | 0.101 | 20.0 |
| 4 | JK63392 | 04:17:37 PM | -5.94 | SR | -0.006 | 589 | 100.00 | 0.101 | 20.0 |
| 5 | JK63392 | 04:17:44 PM | -5.94 | SR | -0.006 | 589 | 100.00 | 0.101 | 20.0 |

## S8. IR spectrum of compound 1




## S9. ECD and UV spectra of compound 1




**S10. HRESIMS of compound 1**

| Elmt | Val. | Min | Max |
|---|---|---|---|
| H | 1 | 0 | 300 |
| C | 4 | 0 | 19 |
| N | 3 | 0 | 0 |

| Elmt | Val. | Min | Max |
|---|---|---|---|
| O | 2 | 5 | 10 |

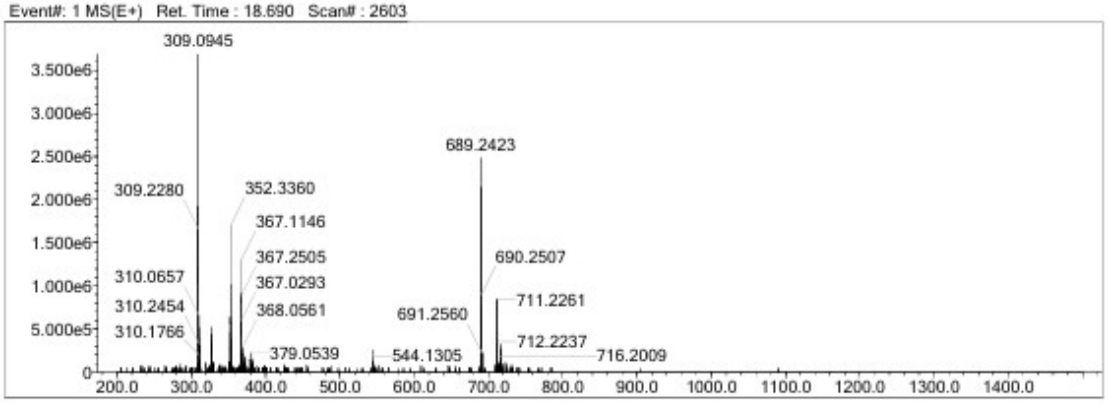
| Use Adduct |
|---|
| H |
| Na |
| H2O |

Error Margin (ppm): 1000
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

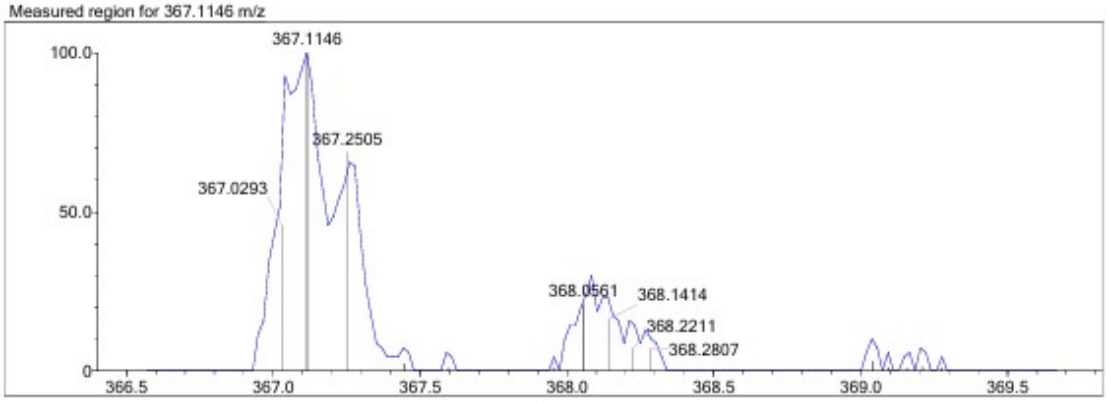
DBE Range: 0.0 - 20.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: odd
Use MSn Info: no
Isotope Res: 10000
Max Results: 1000

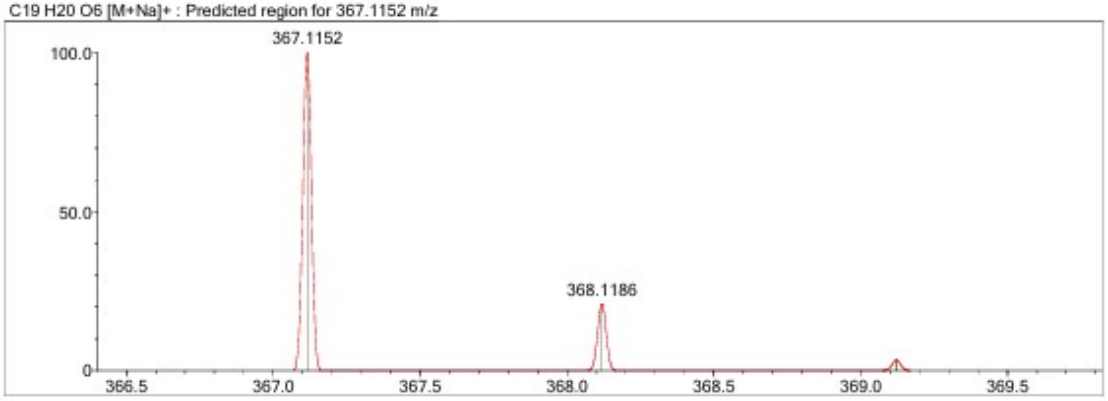
Event#: 1 MS(E+) Ret. Time : 18.690 Scan# : 2603




Measured region for 367.1146 m/z

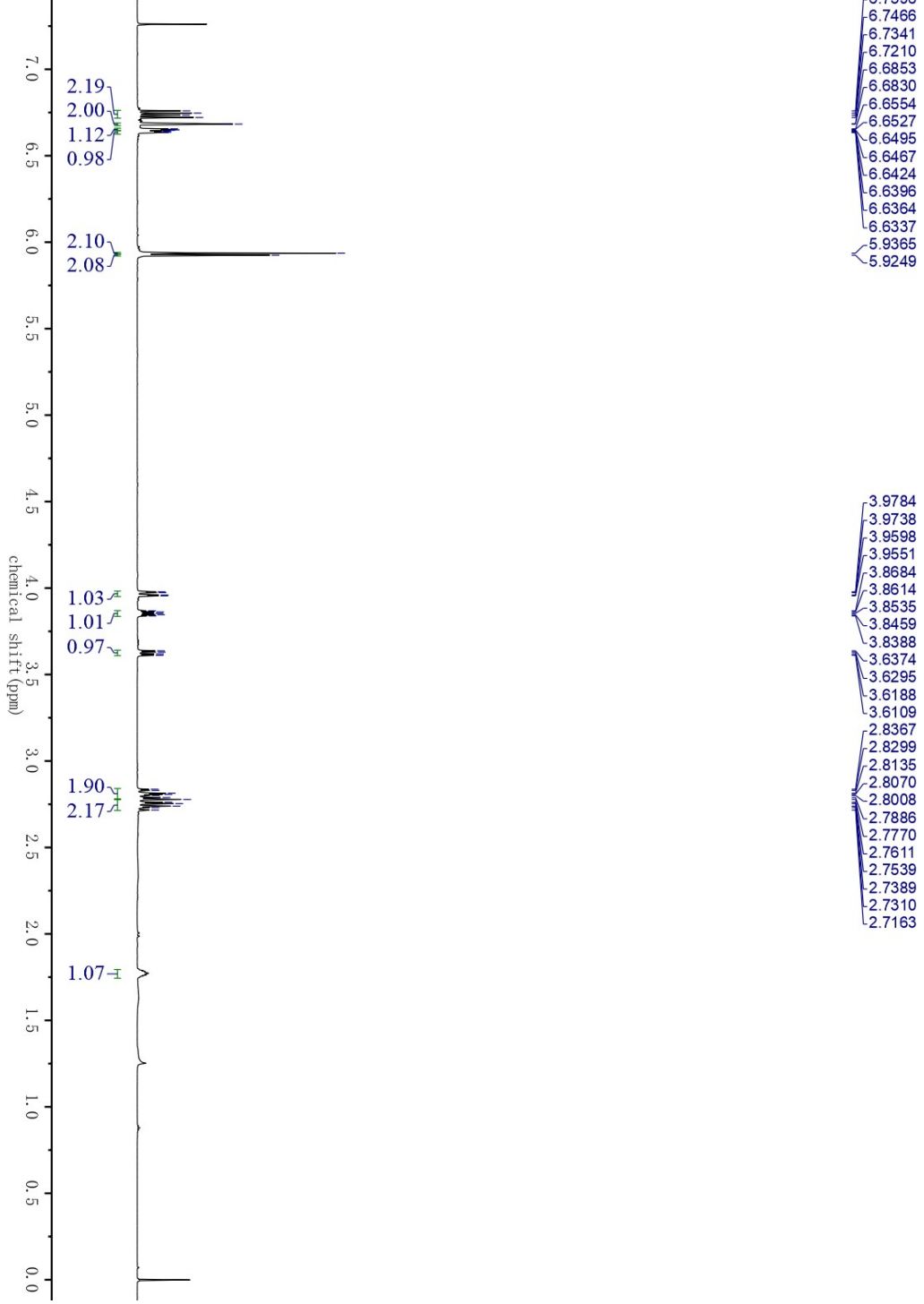



C19 H20 O6 [M+Na]+ : Predicted region for 367.1152 m/z

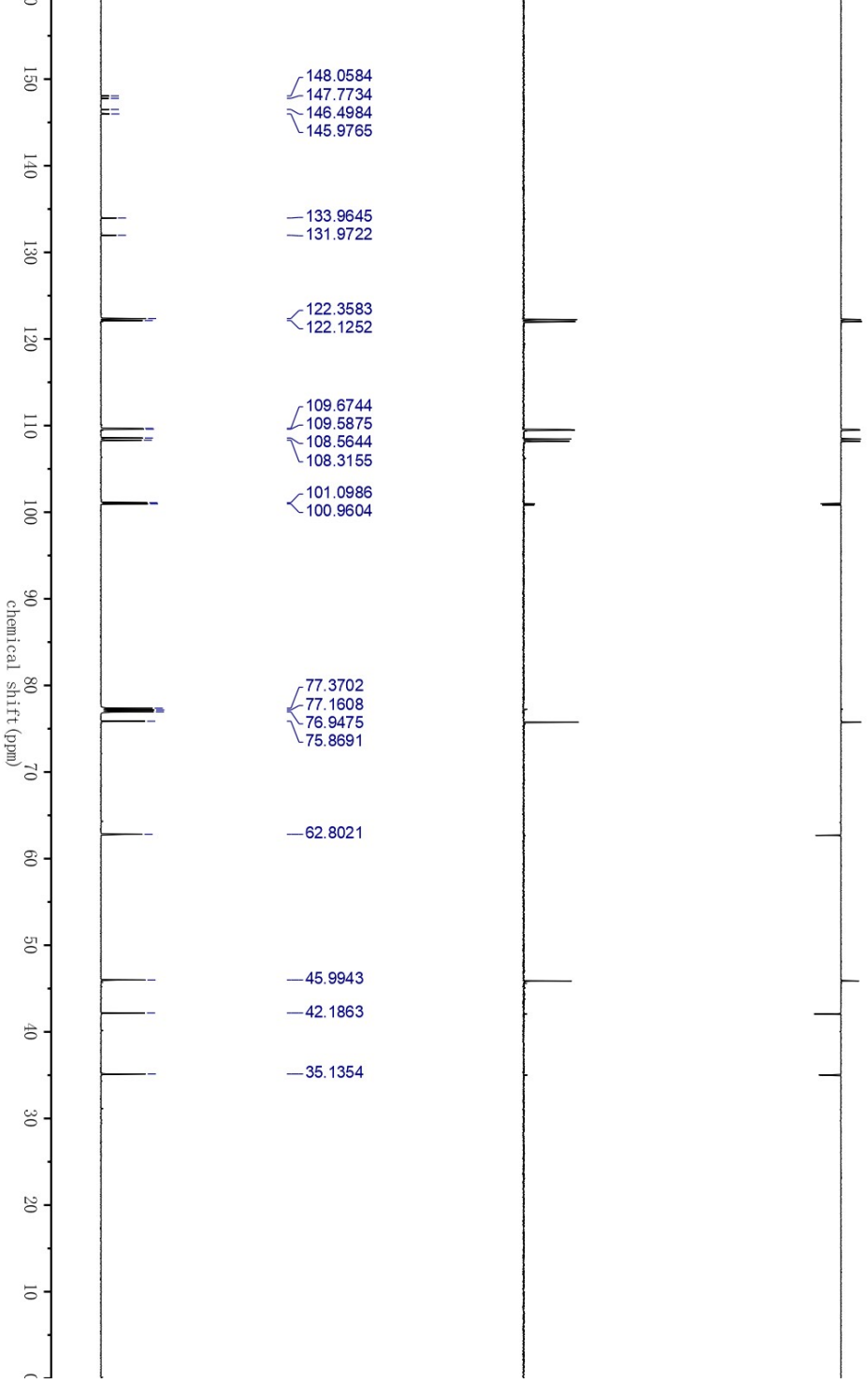



| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 63.62 | C19 H20 O6 | [M+Na]+ | 367.1146 | 367.1152 | -0.6 | -1.63 | 64.64 | 10.0 |

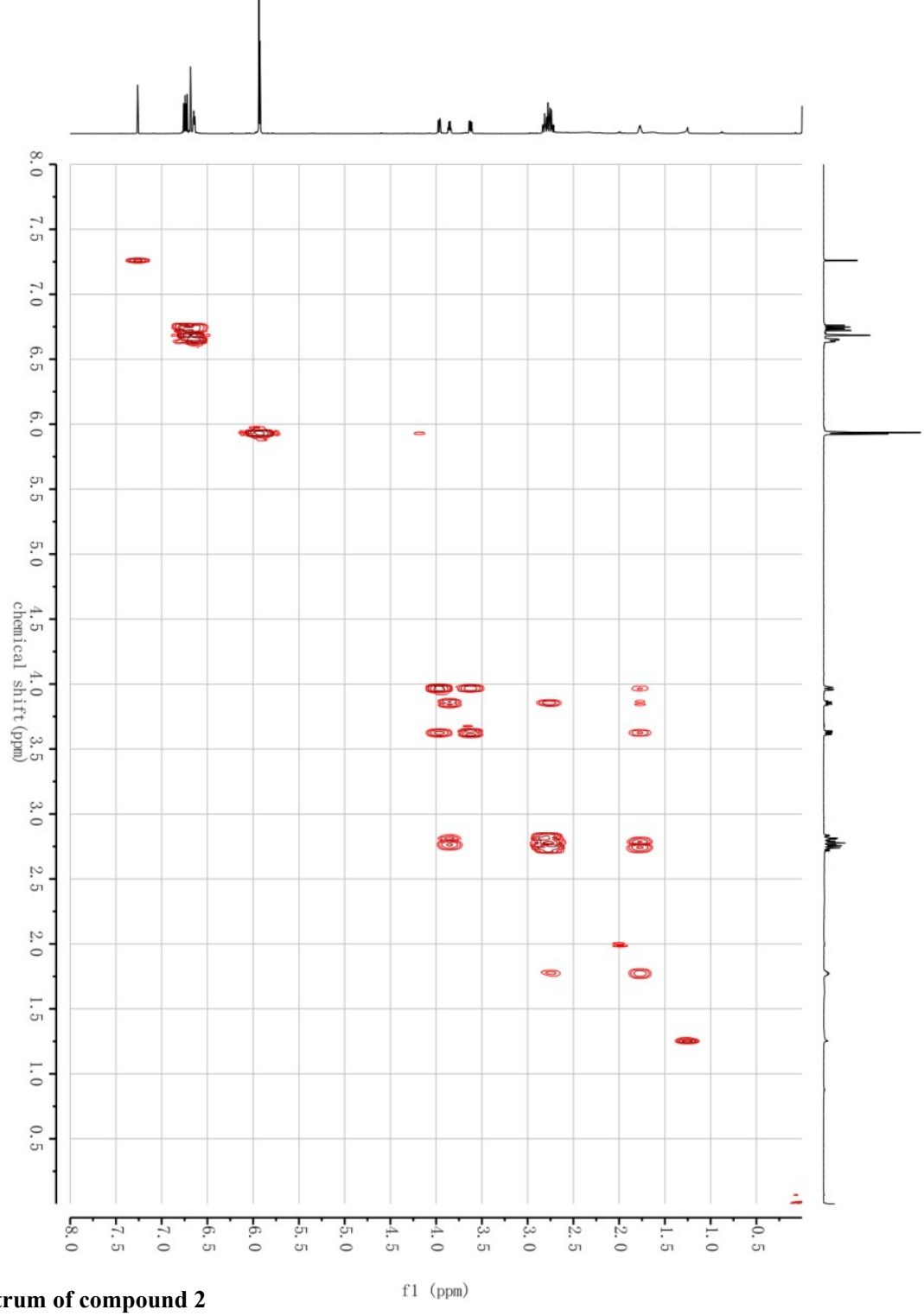
## S11. $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of compound 2



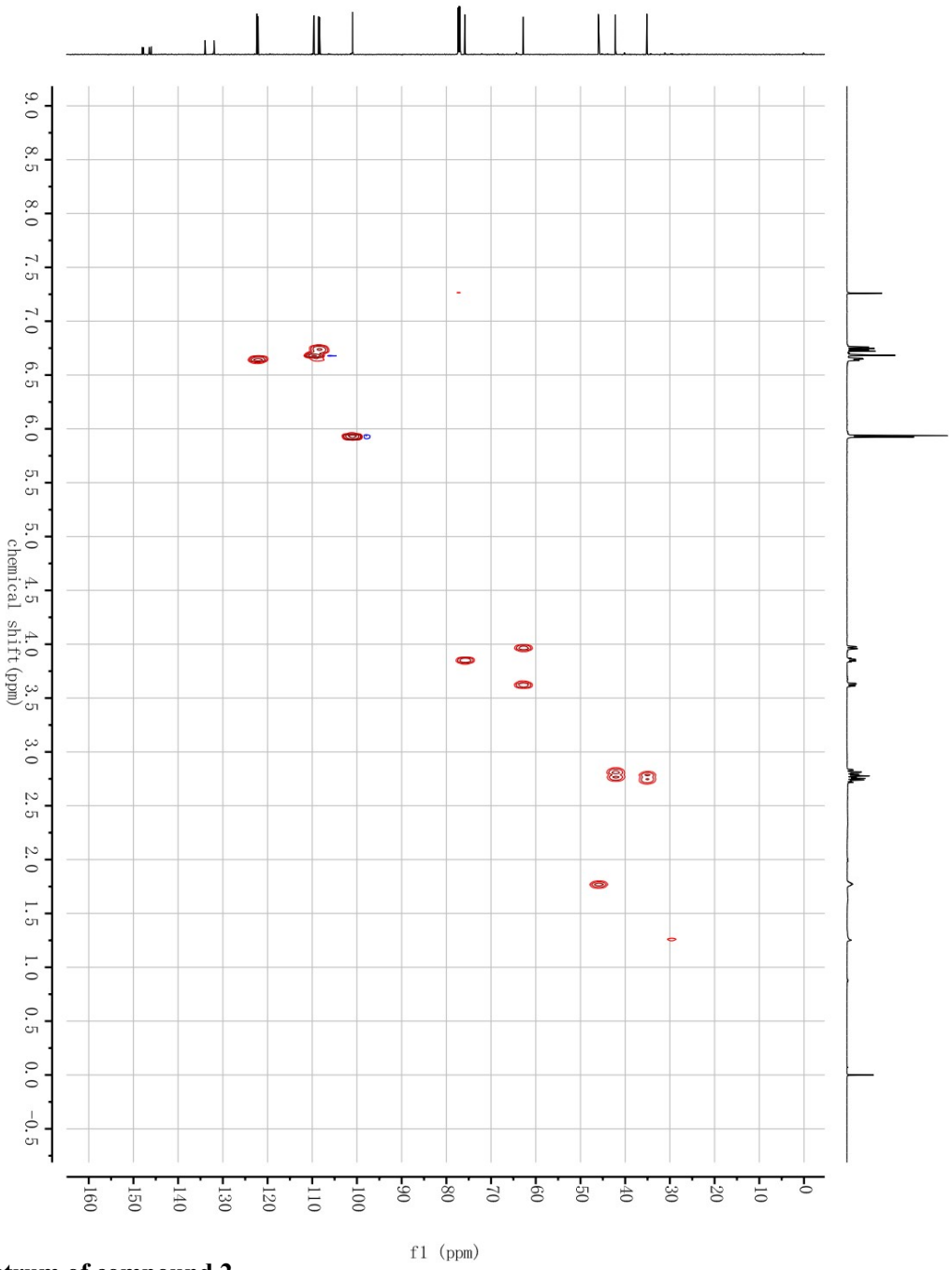

**S12.** **$^{13}$C NMR (DEPT) (150 MHz, $CDCl_3$) spectrum of compound 2**



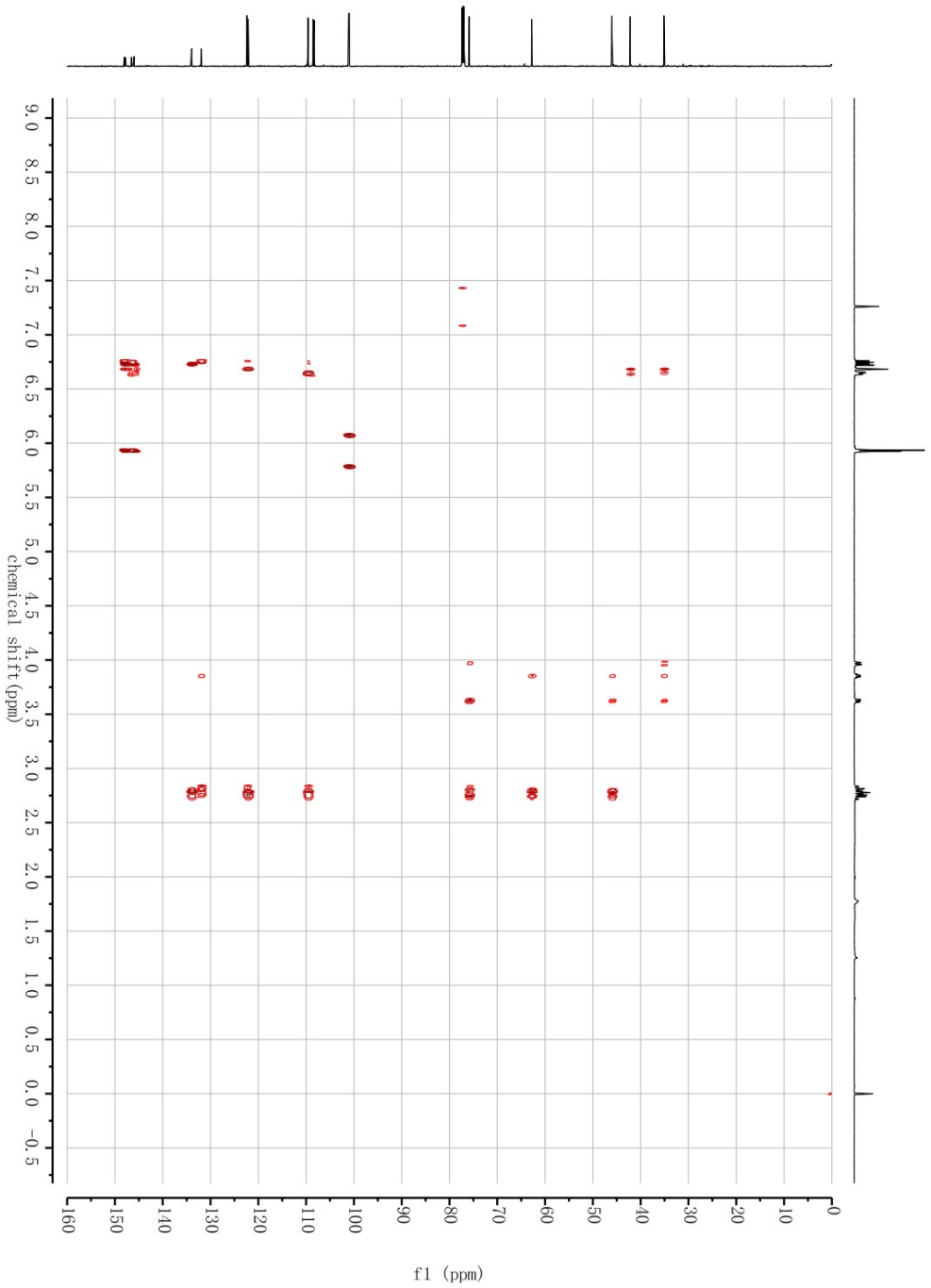

**S13. $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) spectrum of compound 2**



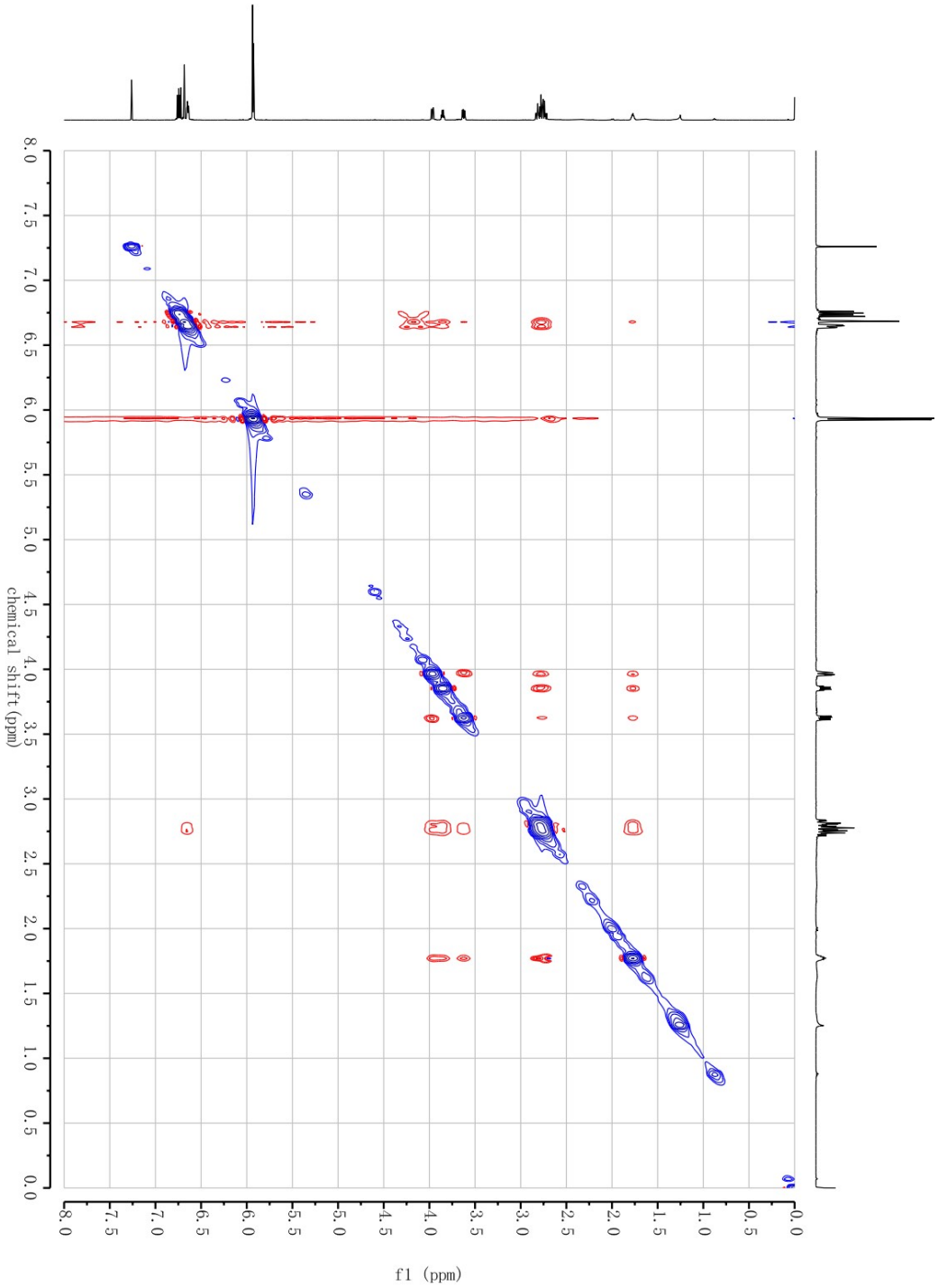

**S14. HSQC spectrum of compound 2**




**S15. HMBC spectrum of compound 2**




**S16. ROESY spectrum of compound 2**




## S17. $[\alpha]_D$ spectrum of compound 2 in MeOH

**Rudolph Research Analytical**

This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Monday, 05-JAN-2026

Set Temperature : 20.0

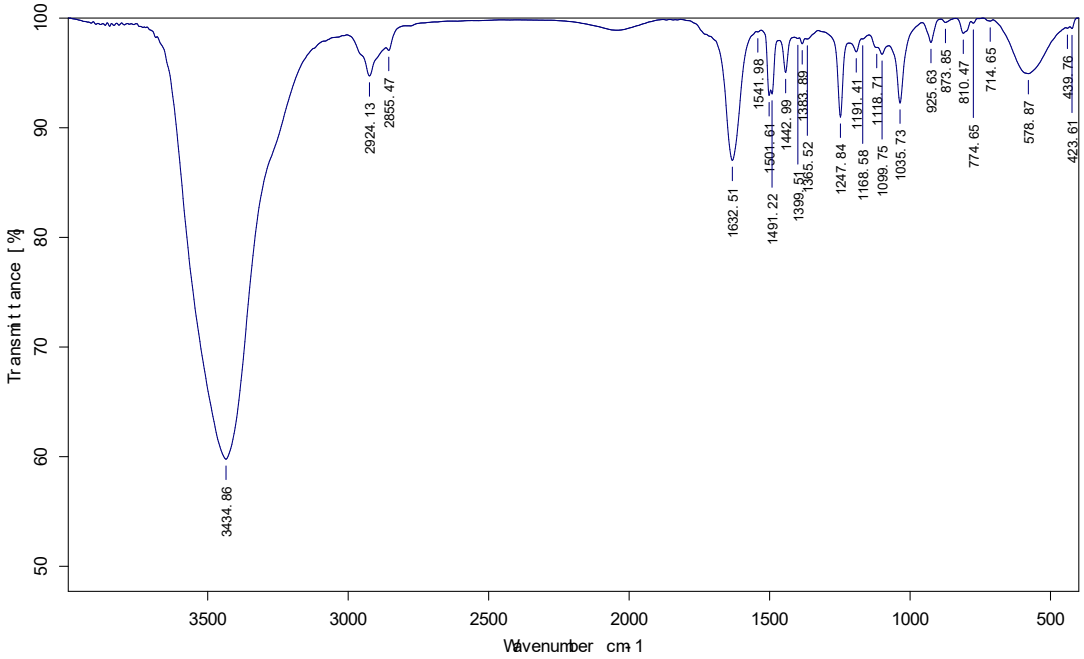
Time Delay : Disabled

Delay between Measurement : Disabled

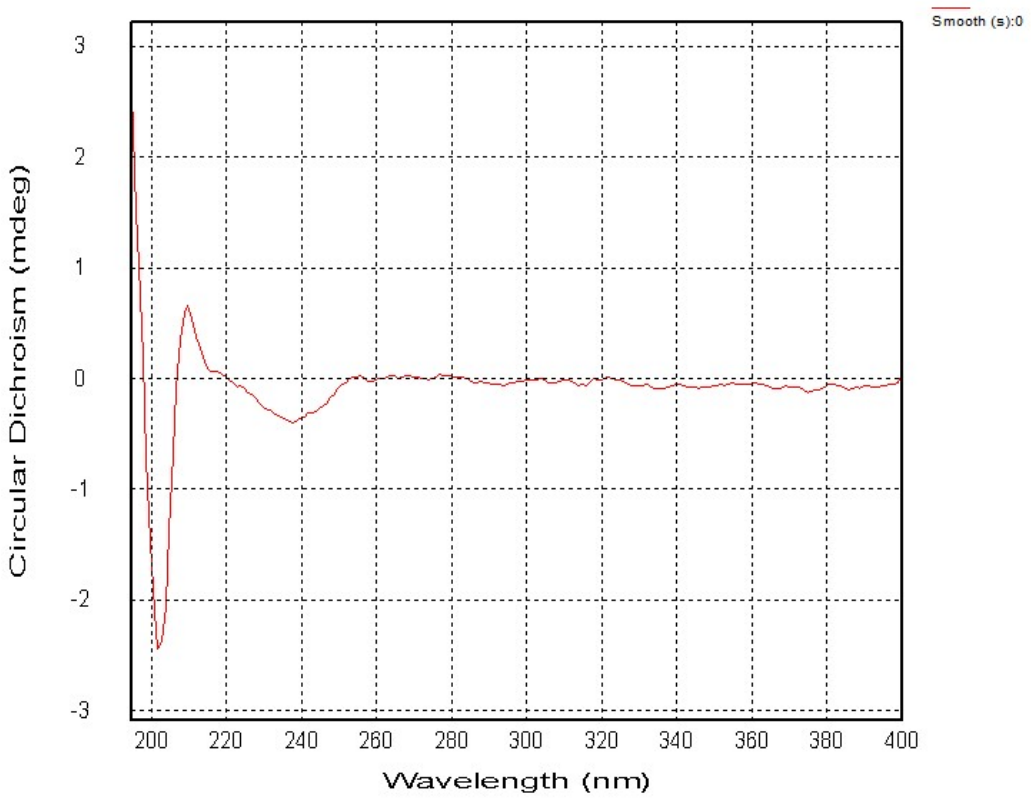
| n | Average | Std.Dev. | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|
| 5 | -10.49 | 0.00 | 0.00 | -10.49 | -10.49 |

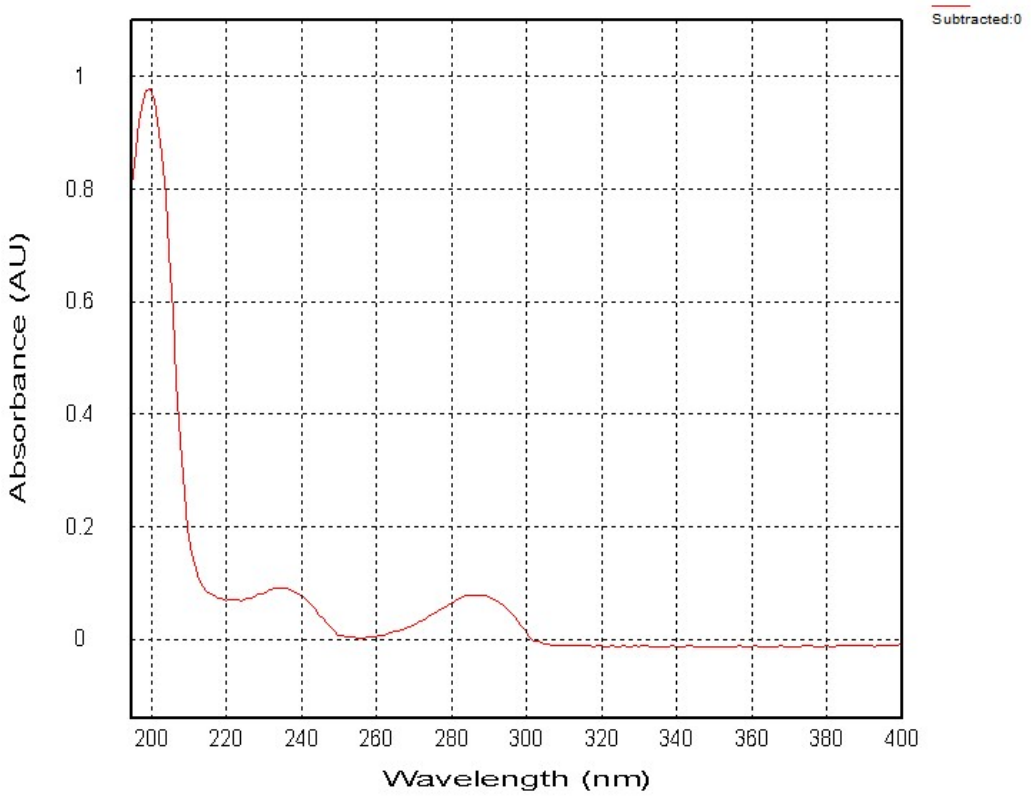
| S.No | Sample ID | Time | Result | Scale | OR °Arc | WLG.nm | Lg.mm | Conc.g/100ml | Temp. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | JK6542 | 11:06:30 AM | -10.49 | SR | -0.015 | 589 | 100.00 | 0.143 | 20.0 |
| 2 | JK6542 | 11:06:36 AM | -10.49 | SR | -0.015 | 589 | 100.00 | 0.143 | 20.0 |
| 3 | JK6542 | 11:06:43 AM | -10.49 | SR | -0.015 | 589 | 100.00 | 0.143 | 20.0 |
| 4 | JK6542 | 11:06:49 AM | -10.49 | SR | -0.015 | 589 | 100.00 | 0.143 | 20.0 |
| 5 | JK6542 | 11:06:56 AM | -10.49 | SR | -0.015 | 589 | 100.00 | 0.143 | 20.0 |

## S18. IR spectrum of compound 2




## S19. ECD and UV spectra of compound 2




**S20. HRESIMS of compound 2**

| Elmt | Val. | Min | Max |
|---|---|---|---|
| H | 1 | 0 | 300 |
| C | 4 | 0 | 100 |
| N | 3 | 0 | 0 |

| Elmt | Val. | Min | Max |
|---|---|---|---|
| O | 2 | 0 | 10 |

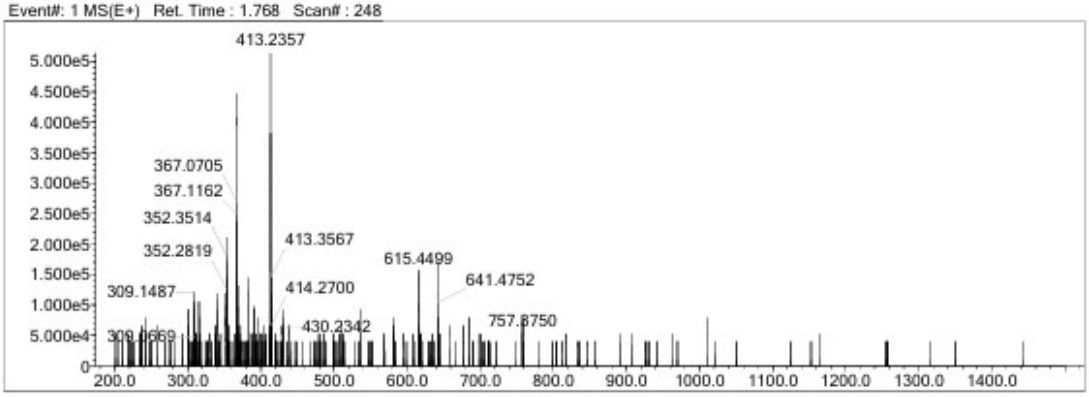
| Use Adduct |
|---|
| H |
| Na |
| H2O |

Error Margin (ppm): 1000
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

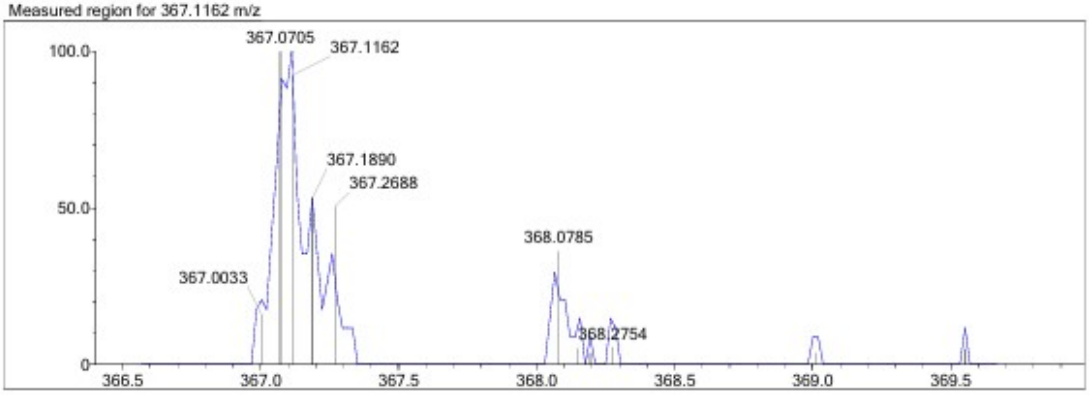
DBE Range: 0.0 - 20.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: odd
Use MSn Info: no
Isotope Res: 10000
Max Results: 1000

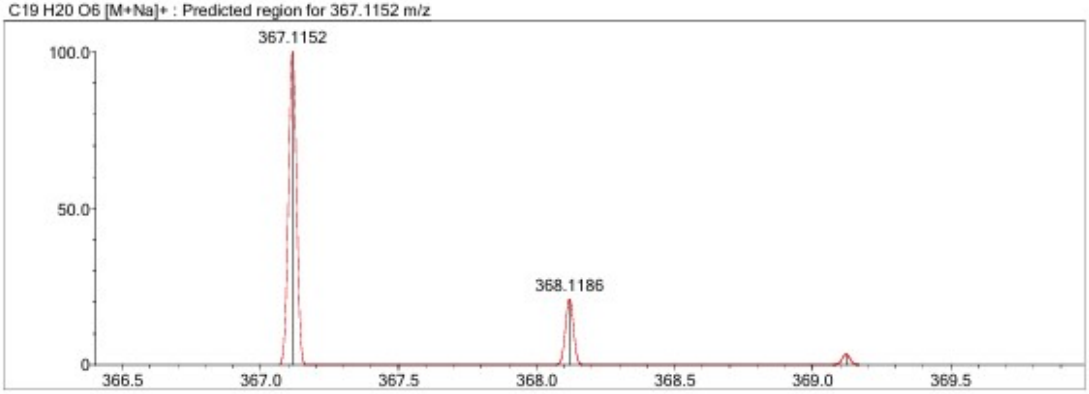
Event#: 1 MS(E+) Ret. Time : 1.768 Scan# : 248




Measured region for 367.1162 m/z

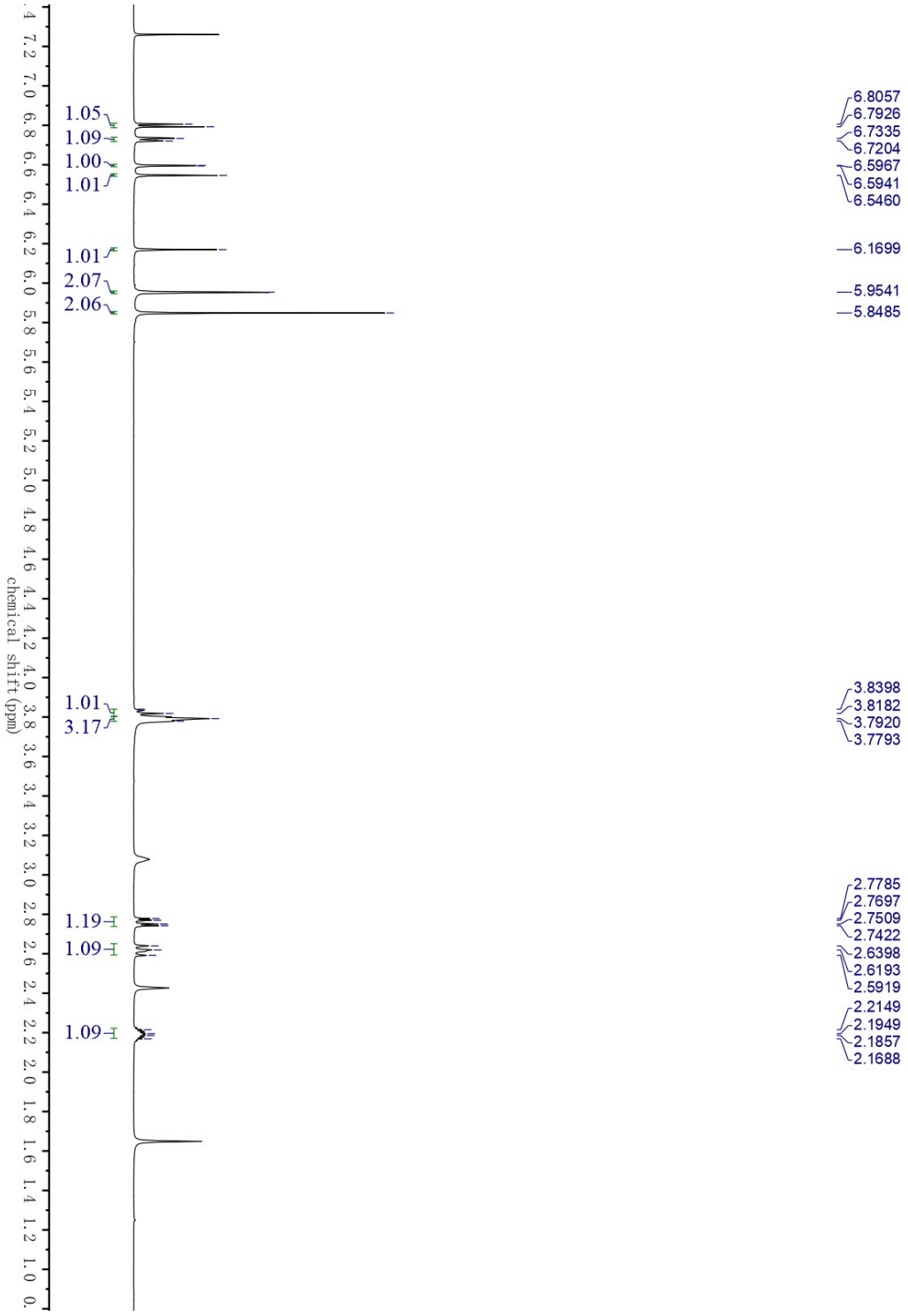



C19 H20 O6 [M+Na]+ : Predicted region for 367.1152 m/z

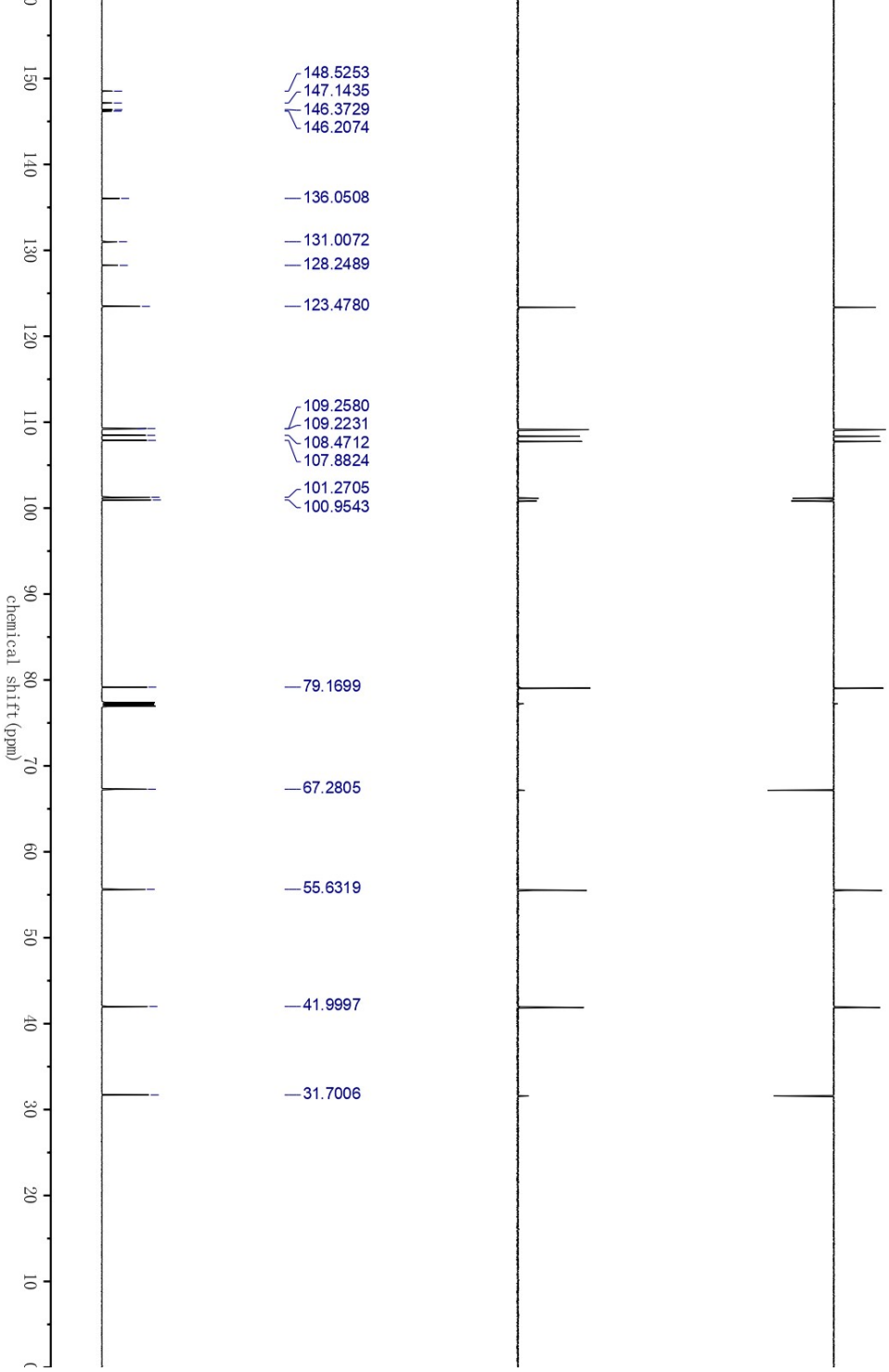



| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 13.04 | C19 H20 O6 | [M+Na]+ | 367.1162 | 367.1152 | 1.0 | 2.72 | 13.63 | 10.0 |

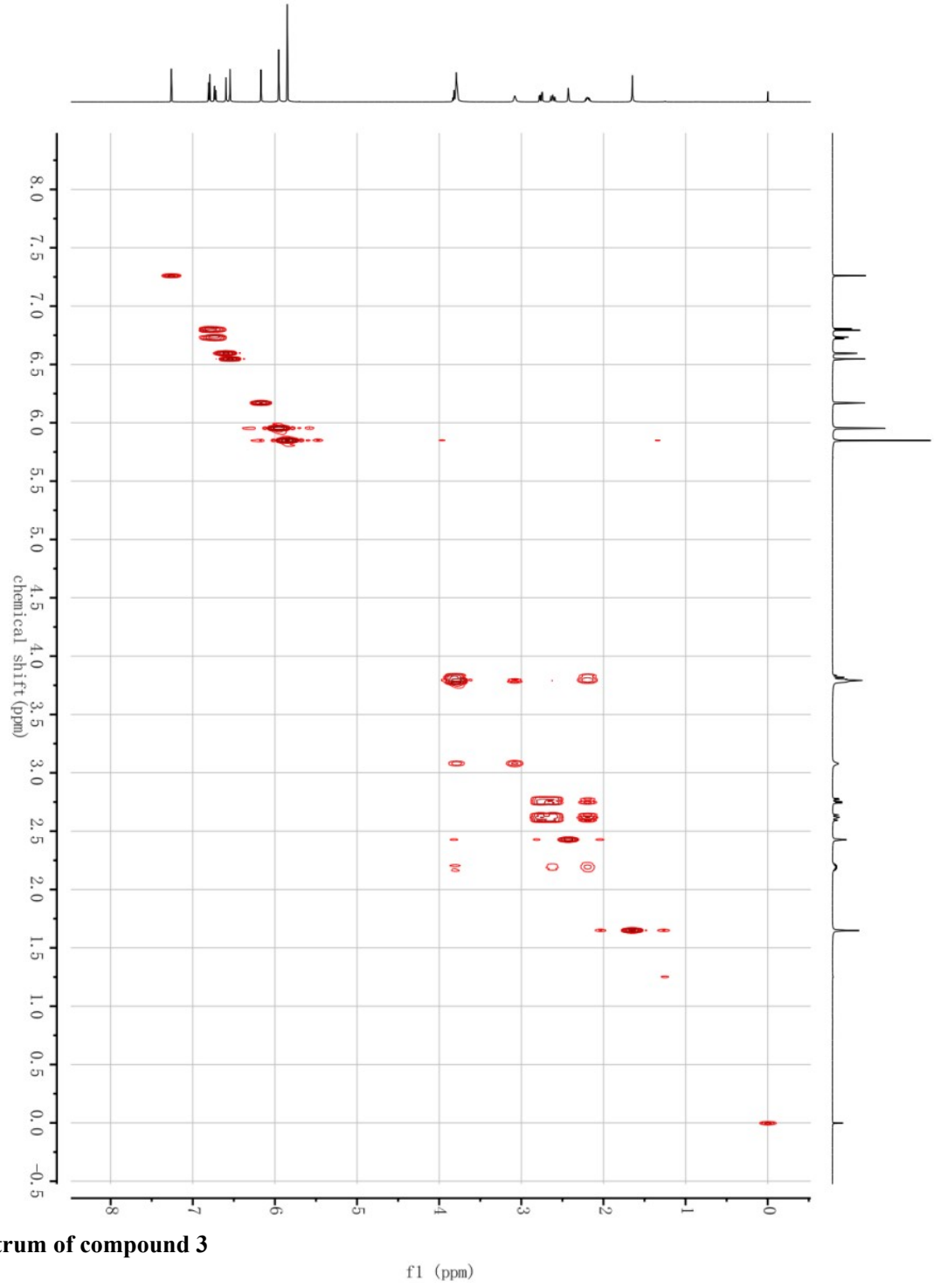
## S21. $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of compound 3



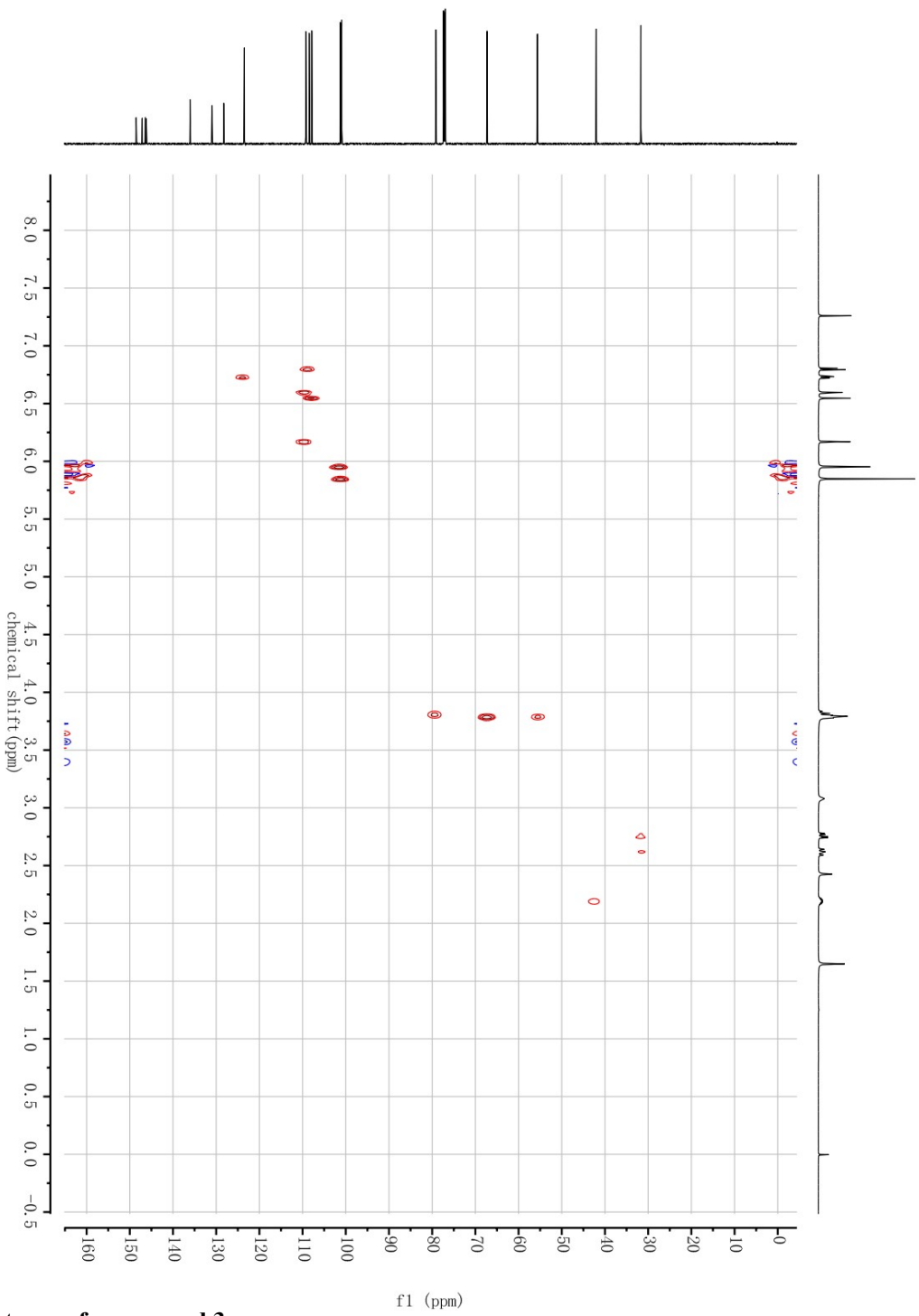

**S22. $^{13}C$ NMR (DEPT) (150 MHz, $CDCl_3$) spectrum of compound 3**



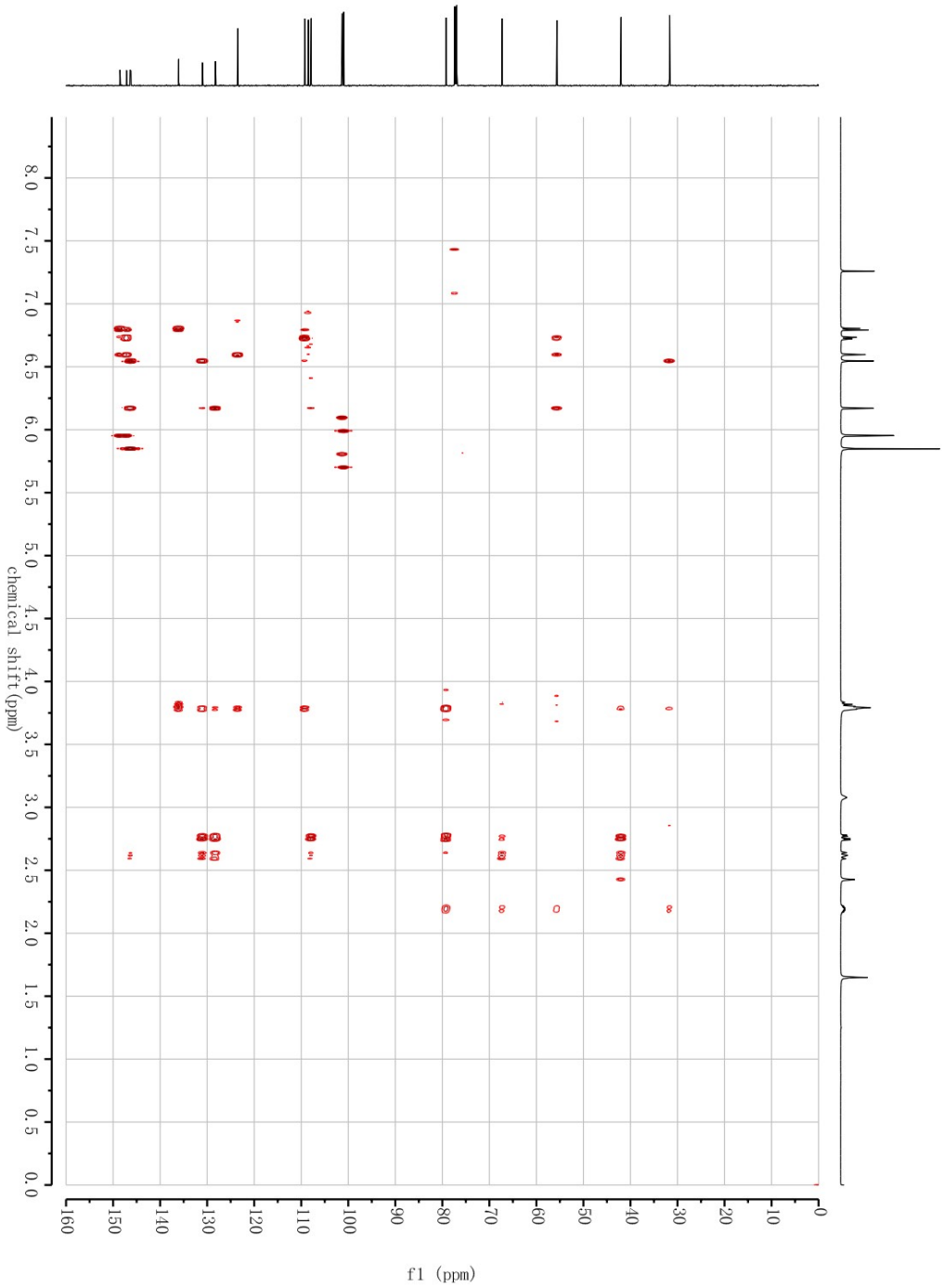

**S23. $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) spectrum of compound 3**



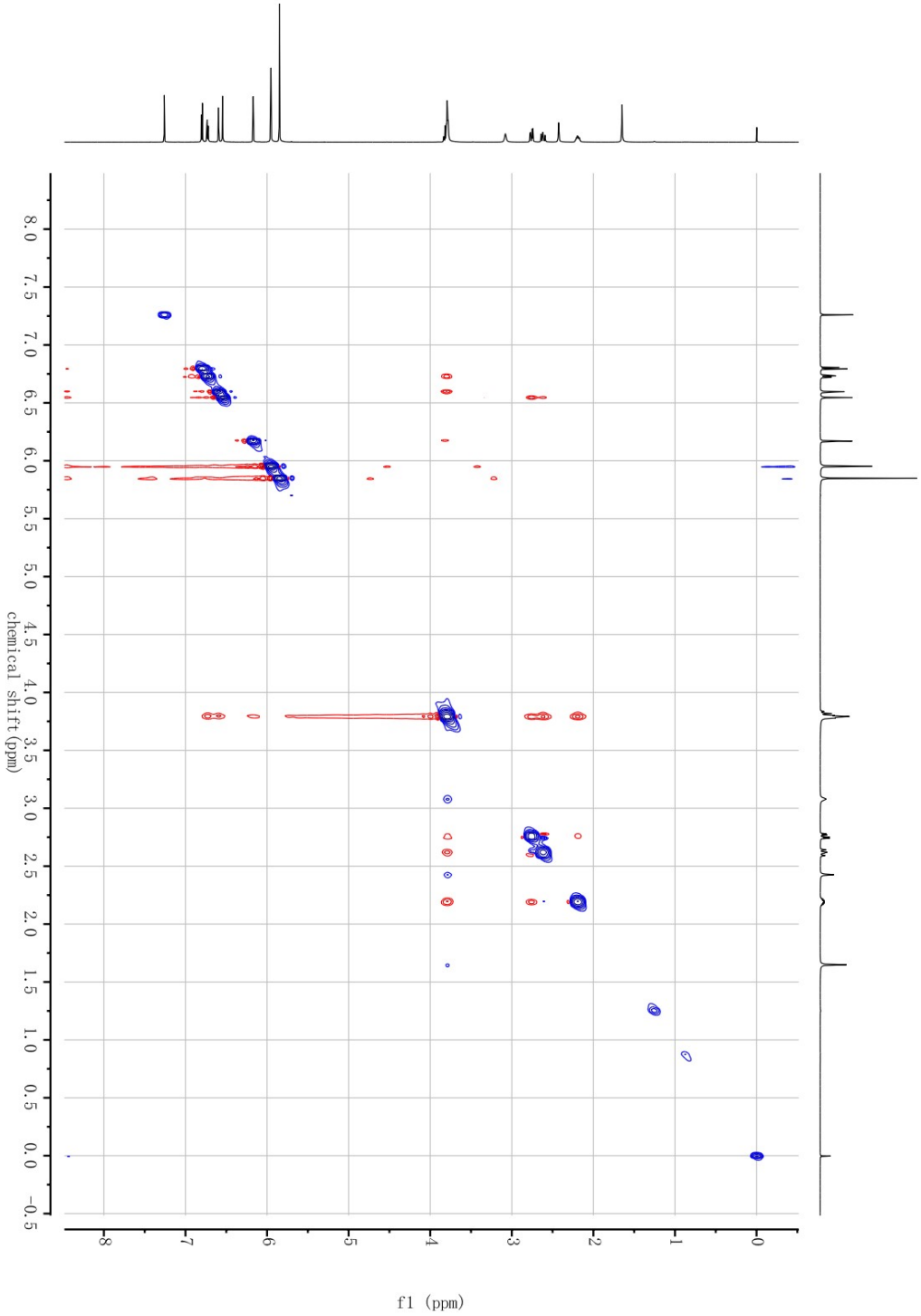

**S24. HSQC spectrum of compound 3**




**S25. HMBC spectrum of compound 3**




**S26. ROESY spectrum of compound 3**




## S27. $[\alpha]_D$ spectrum of compound 3 in MeOH

**Rudolph Research Analytical**

This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Friday, 12-DEC-2025

Set Temperature : 20.0

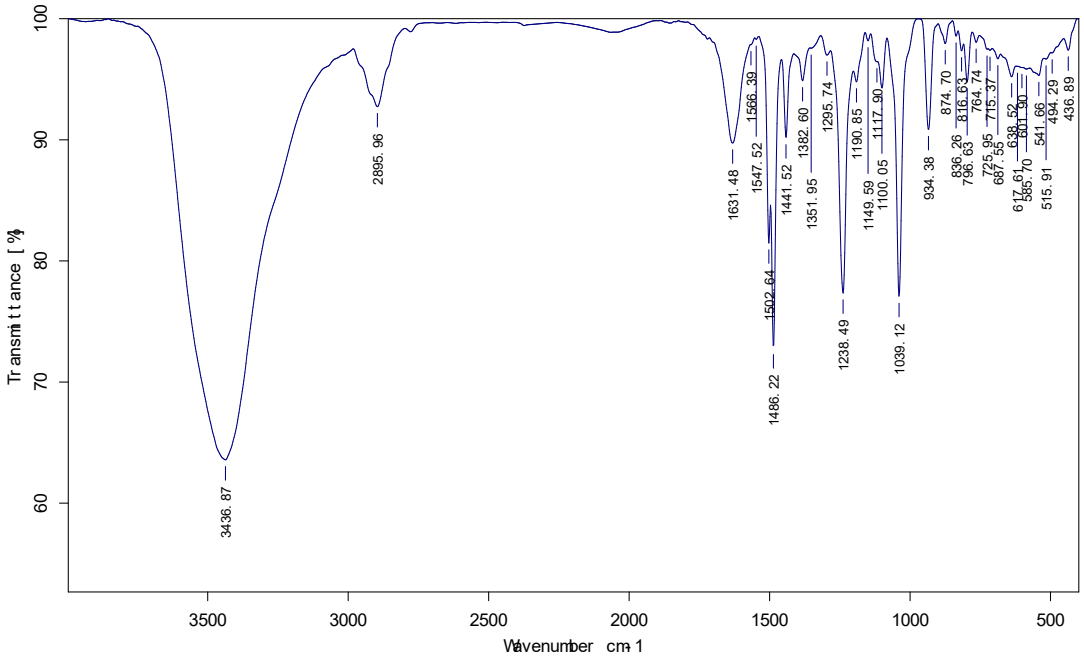
Time Delay : Disabled

Delay between Measurement : Disabled

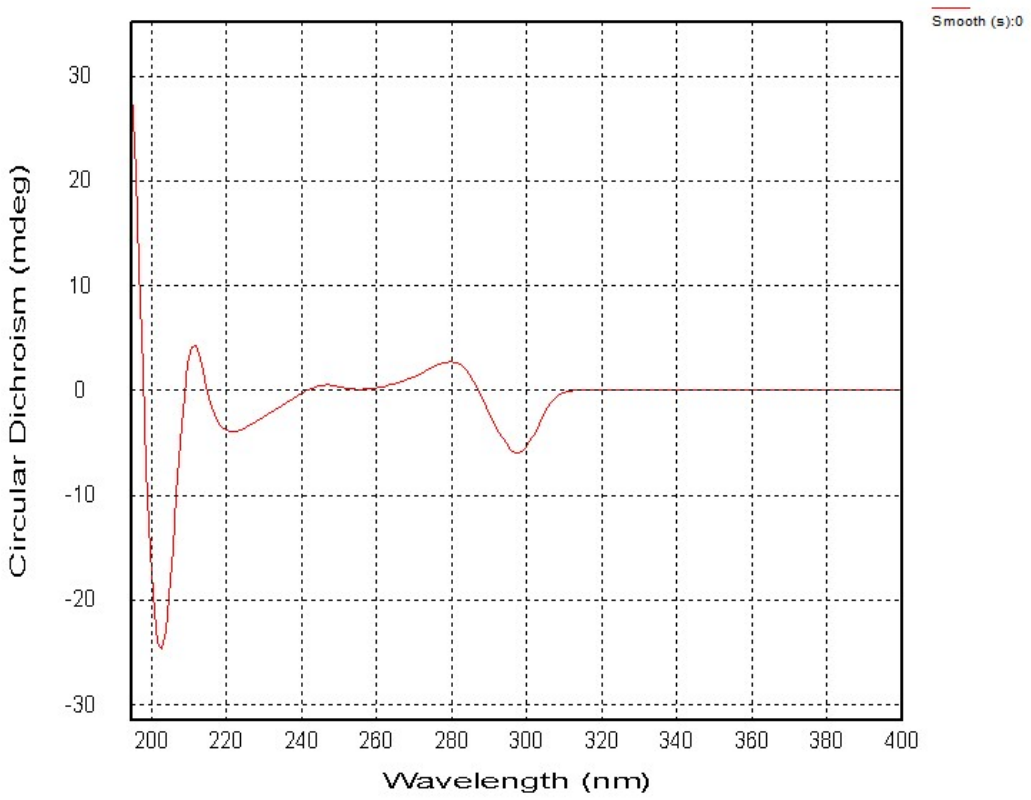
| n | Average | Std.Dev. | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|
| 5 | -17.08 | 0.40 | -2.34 | -16.79 | -17.52 |

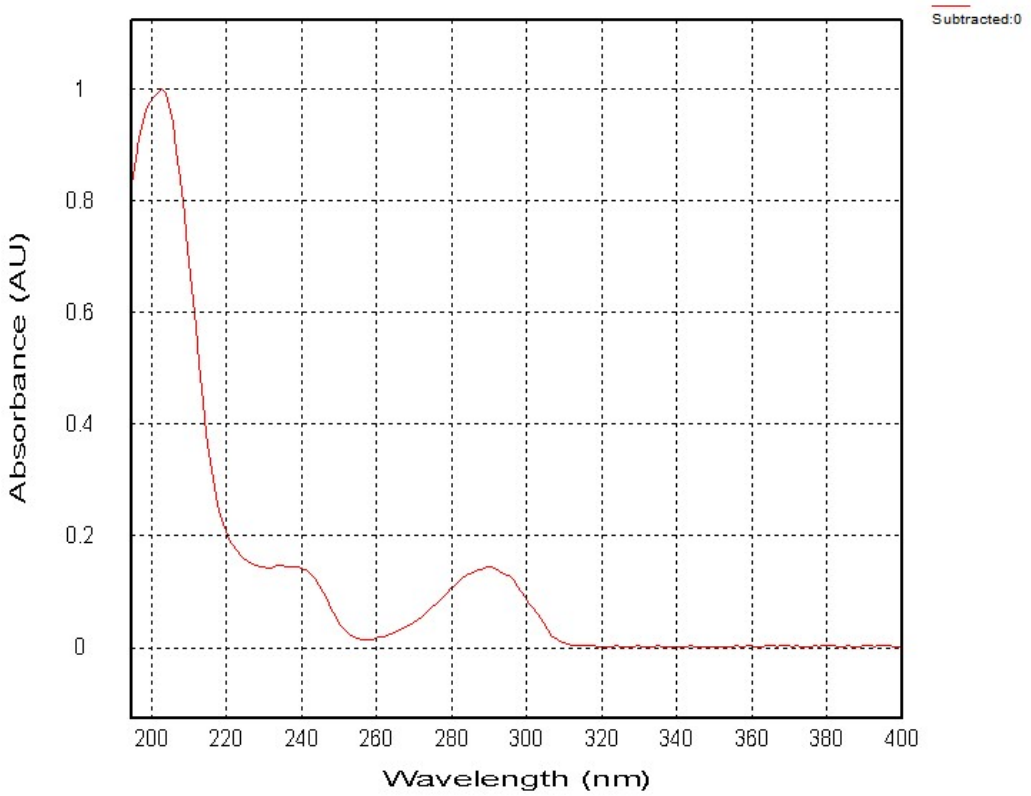
| S.No | Sample ID | Time | Result | Scale | OR °Arc | WLG.nm | Lg.mm | Conc.g/100ml | Temp. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | JK662 | 04:09:05 PM | -17.52 | SR | -0.024 | 589 | 100.00 | 0.137 | 20.0 |
| 2 | JK662 | 04:09:11 PM | -16.79 | SR | -0.023 | 589 | 100.00 | 0.137 | 20.0 |
| 3 | JK662 | 04:09:18 PM | -16.79 | SR | -0.023 | 589 | 100.00 | 0.137 | 20.0 |
| 4 | JK662 | 04:09:24 PM | -17.52 | SR | -0.024 | 589 | 100.00 | 0.137 | 20.0 |
| 5 | JK662 | 04:09:31 PM | -16.79 | SR | -0.023 | 589 | 100.00 | 0.137 | 20.0 |

## S28. IR spectrum of compound 3




## S29. ECD and UV spectra of compound 3




## S30. HRESIMS of compound 3

| Elmt | Val. | Min | Max |
|---|---|---|---|
| H | 1 | 0 | 300 |
| C | 4 | 0 | 19 |
| N | 3 | 0 | 0 |

| Elmt | Val. | Min | Max |
|---|---|---|---|
| O | 2 | 5 | 10 |

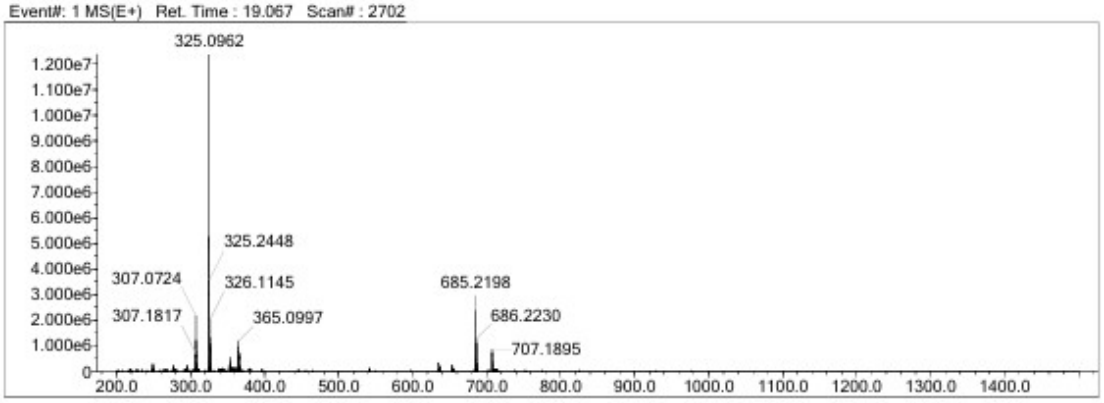
| Use Adduct |
|---|
| H |
| Na |
| H2O |

Error Margin (ppm): 1000
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

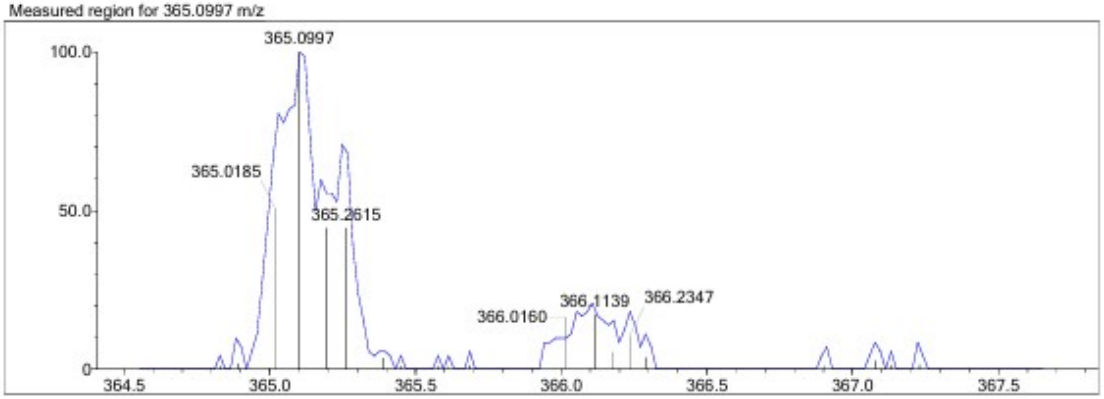
DBE Range: 0.0 - 20.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: odd
Use MSn Info: no
Isotope Res: 10000
Max Results: 1000

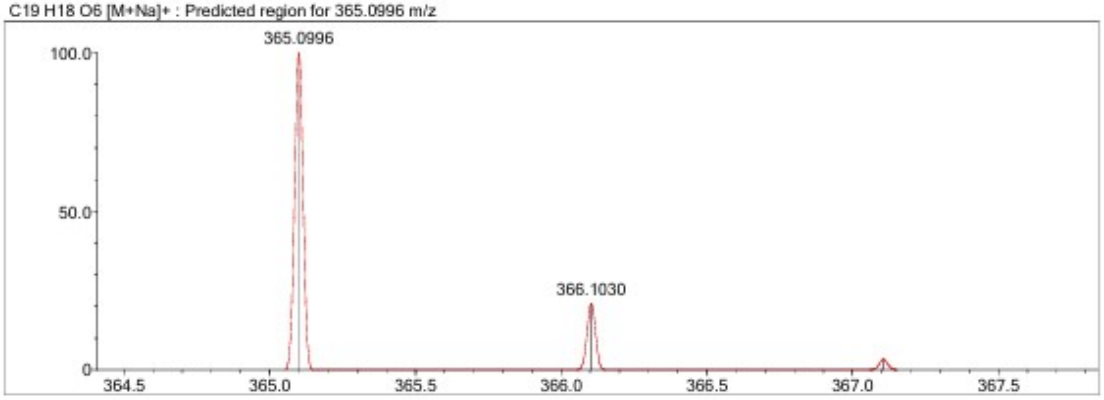
Event#: 1 MS(E+) Ret. Time : 19.067 Scan# : 2702




Measured region for 365.0997 m/z

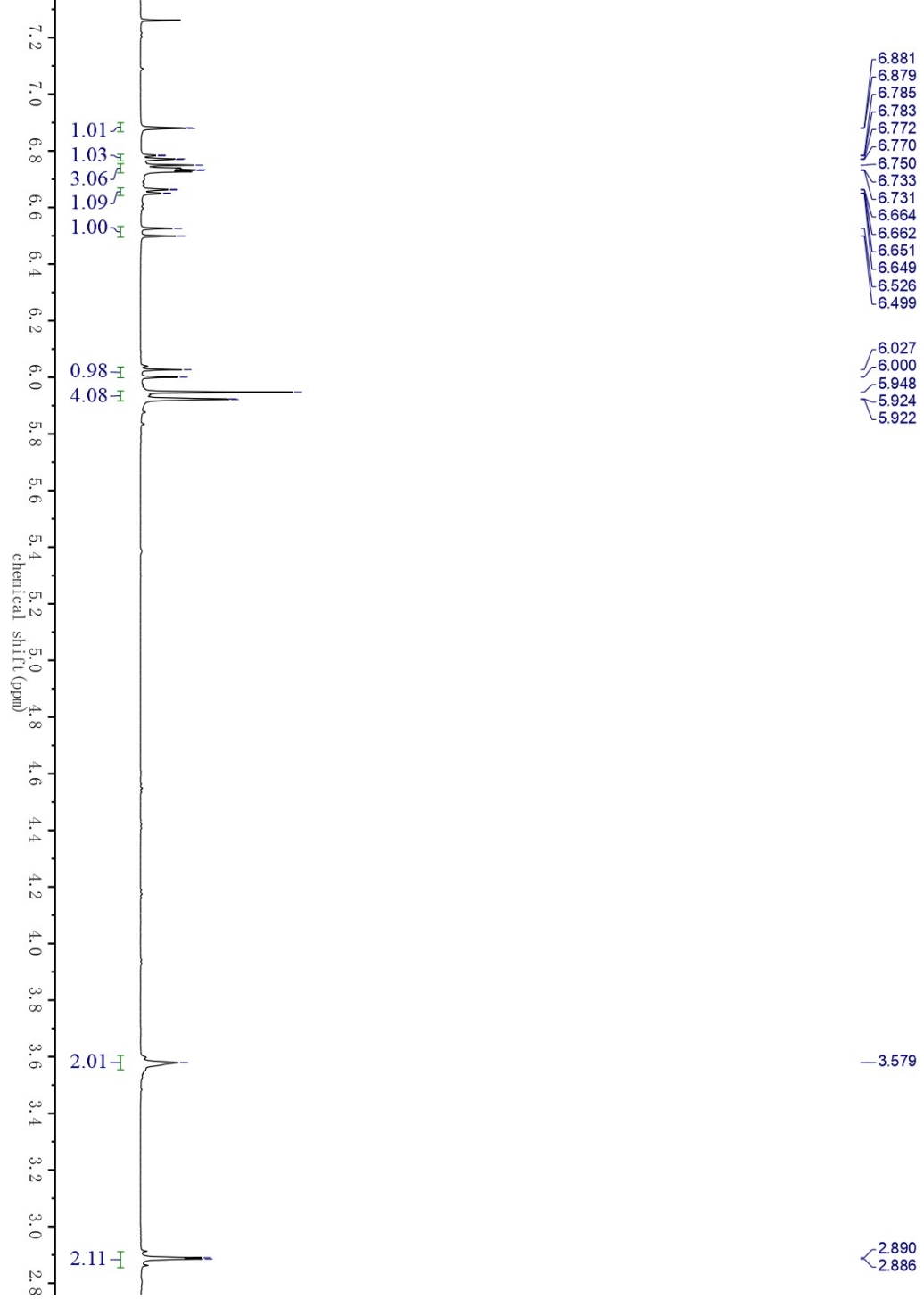



C19 H18 O6 [M+Na]+ : Predicted region for 365.0996 m/z

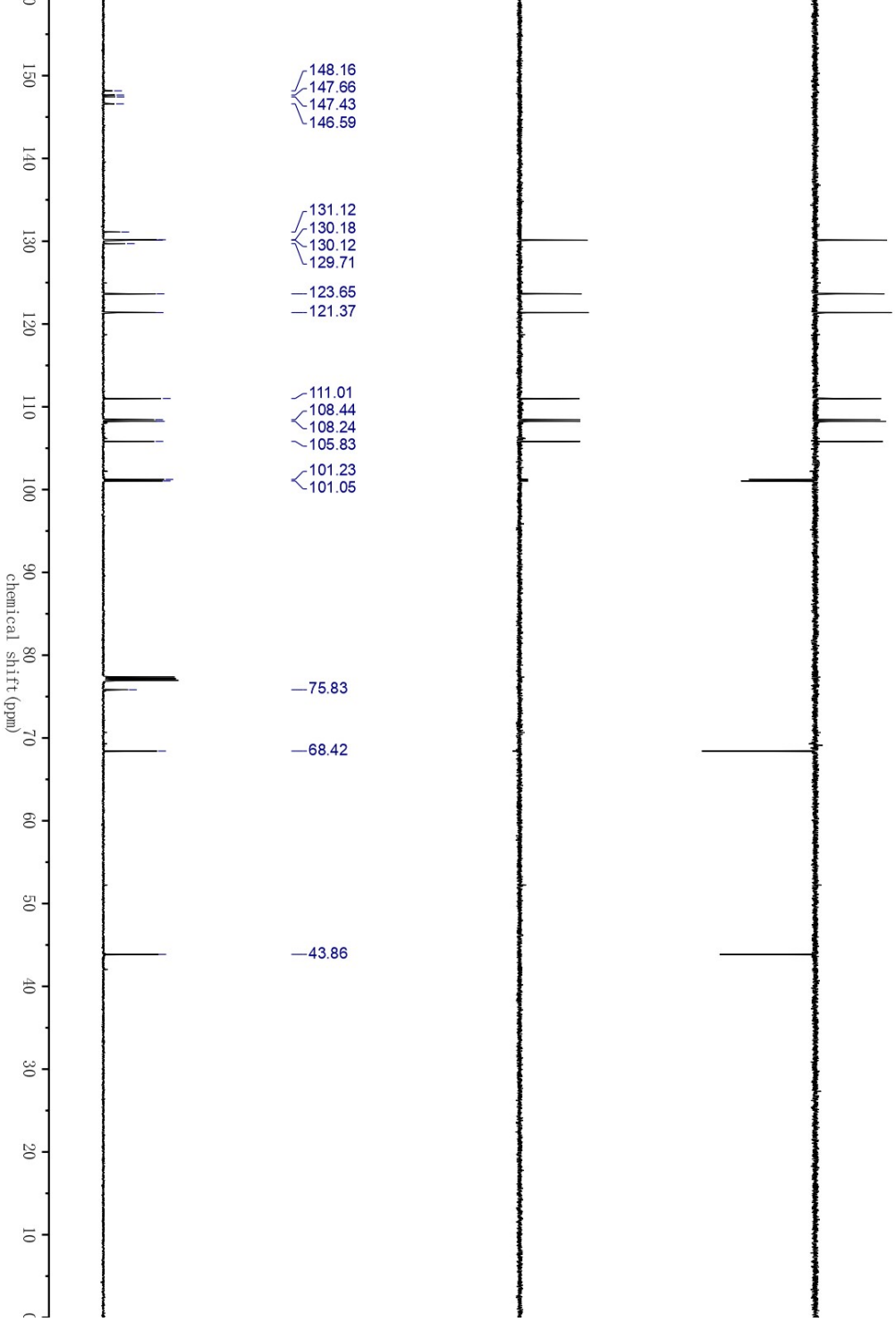



| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 51.66 | C19 H18 O6 | [M+Na]+ | 365.0997 | 365.0996 | 0.1 | 0.27 | 51.66 | 11.0 |

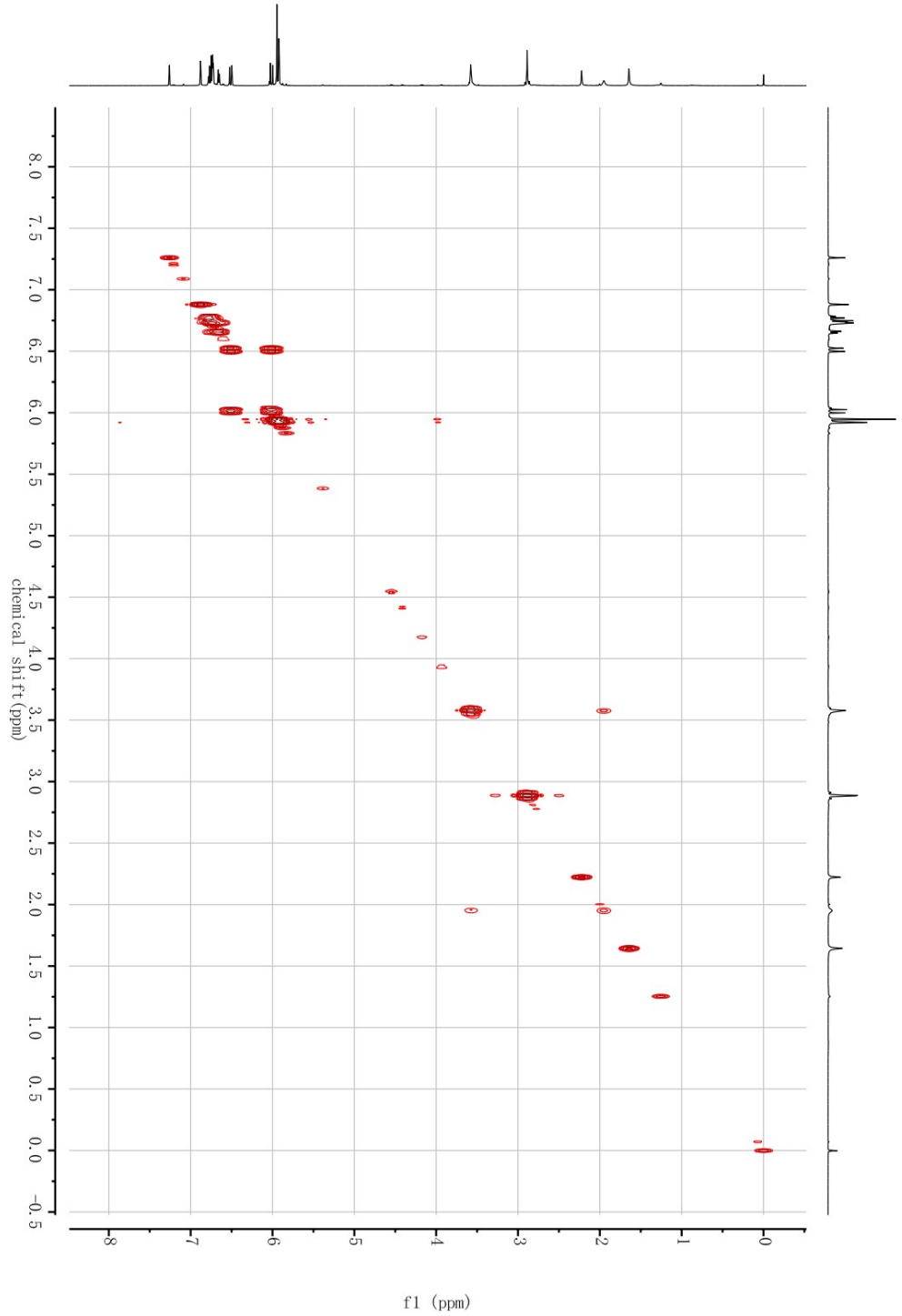
**S31. $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of compound 4**



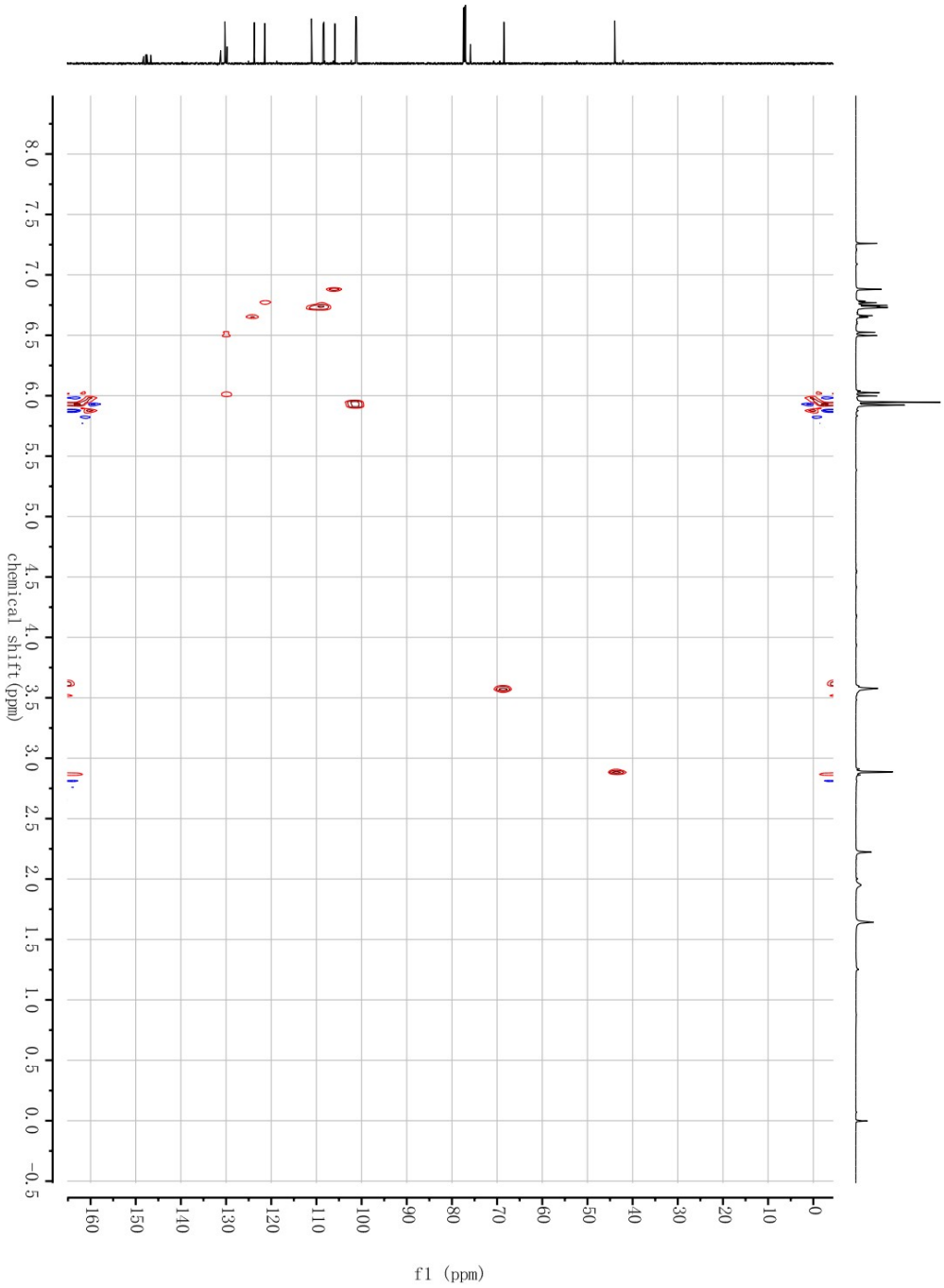

**S32. $^{13}C$ NMR (DEPT) (150 MHz, $CDCl_3$) spectrum of compound 4**



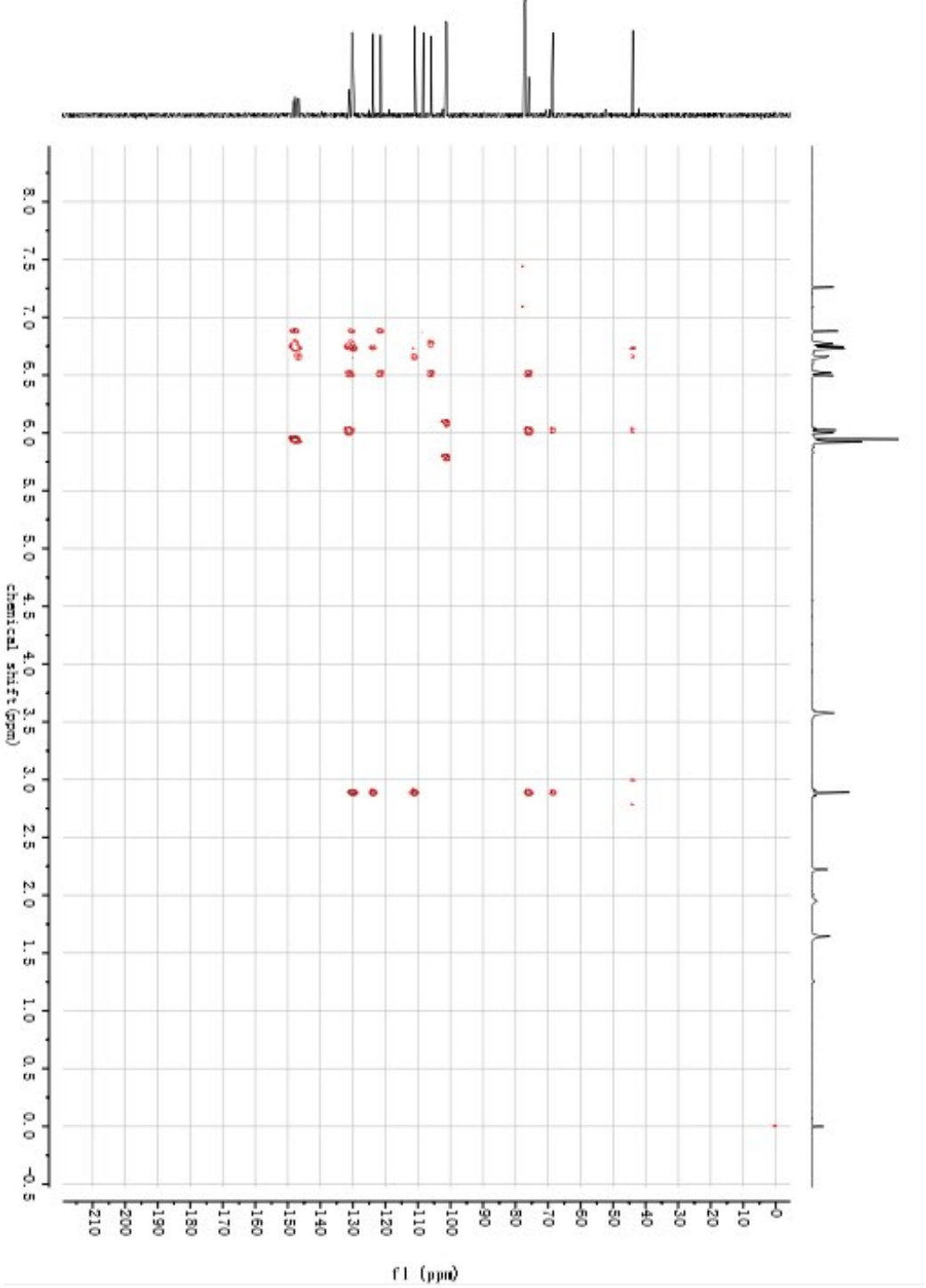

**S33. $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) spectrum of compound 4**



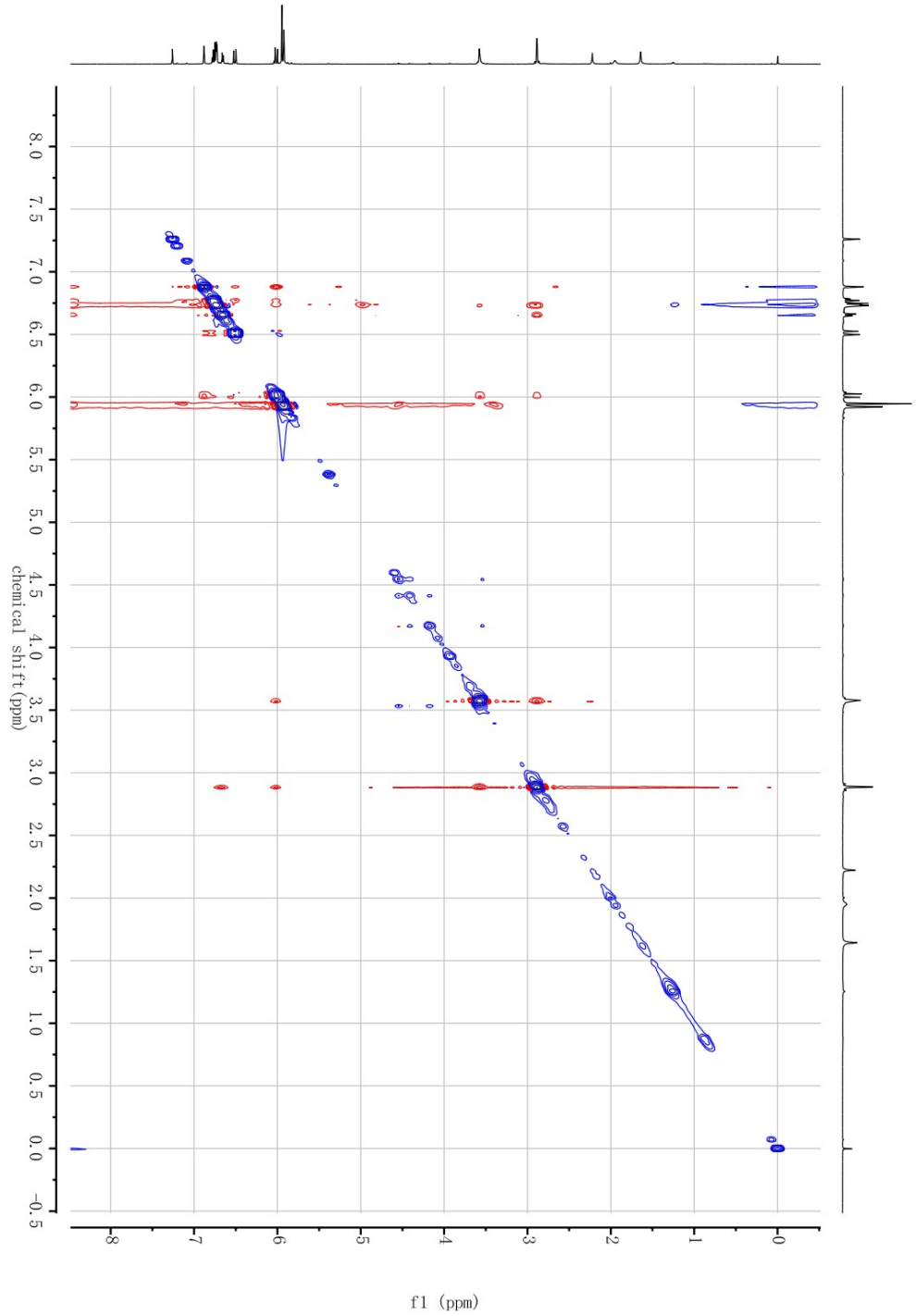

**S34. HSQC spectrum of compound 4**




**S35. HMBC spectrum of compound 4**




**S36. ROESY spectrum of compound 4**




## S37. $[\alpha]_D$ spectrum of compound 4 in MeOH

**Rudolph Research Analytical**

This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Friday, 12-DEC-2025

Set Temperature : 20.0

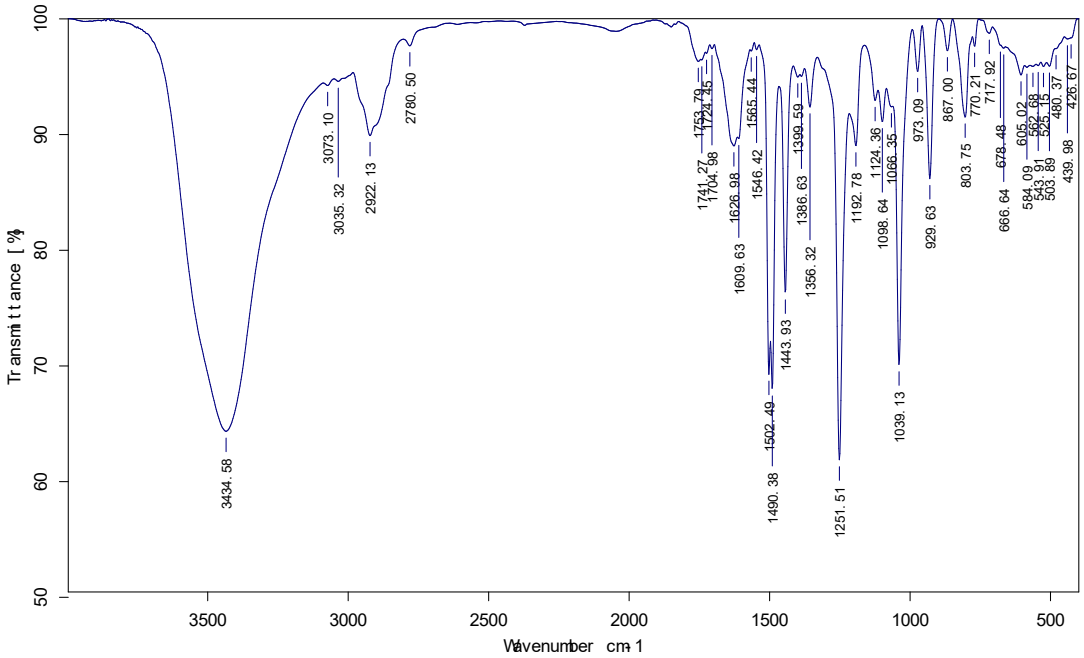
Time Delay : Disabled

Delay between Measurement : Disabled

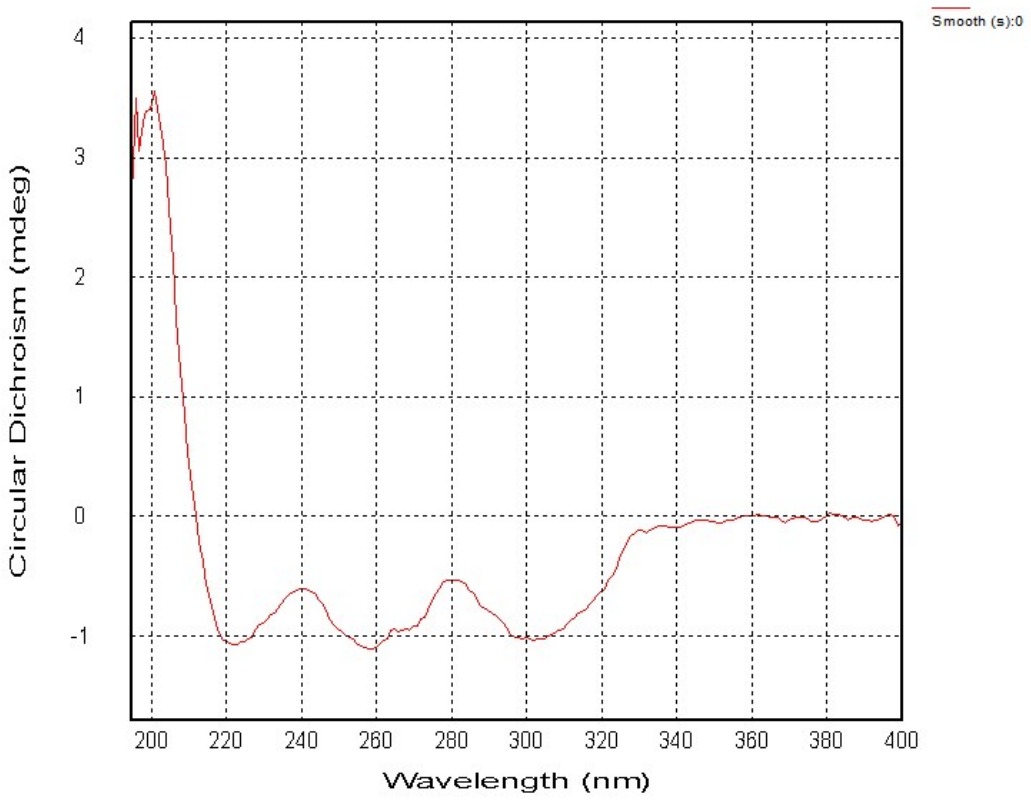
| n | Average | Std.Dev. | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|
| 5 | -51.47 | 0.39 | -0.75 | -51.30 | -52.17 |

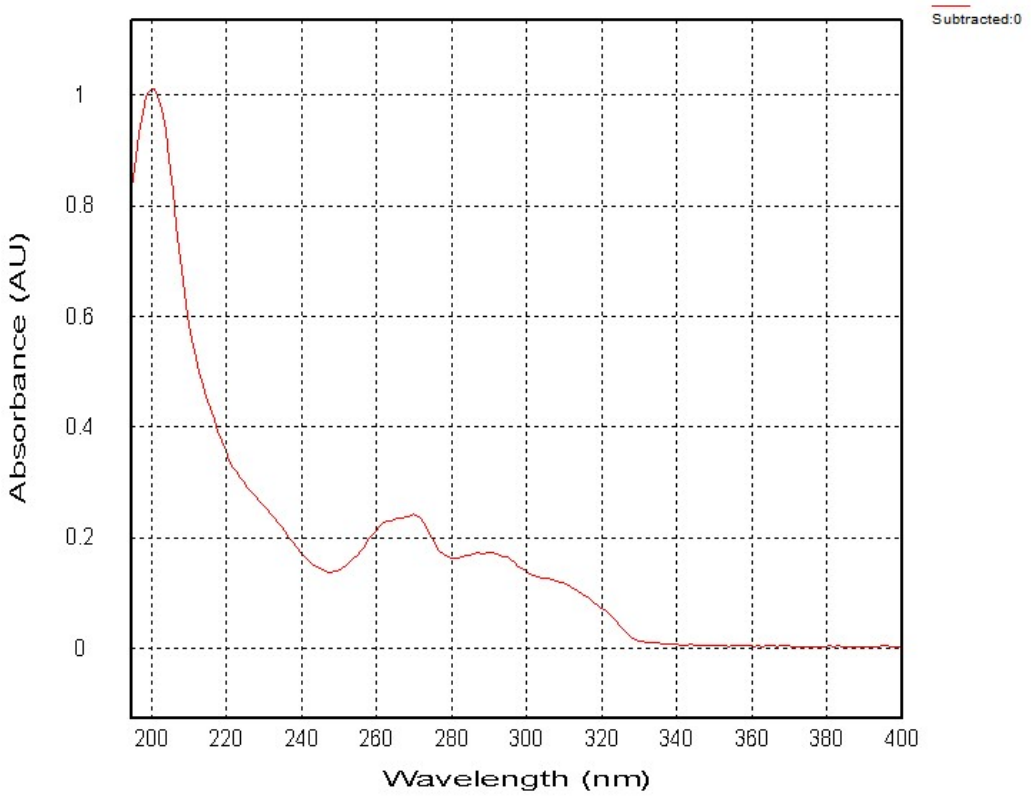
| S.No | Sample ID | Time | Result | Scale | OR °Arc | WLG.nm | Lg.mm | Conc.g/100ml | Temp. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | JK661 | 03:59:27 PM | -51.30 | SR | -0.059 | 589 | 100.00 | 0.115 | 20.0 |
| 2 | JK661 | 03:59:33 PM | -51.30 | SR | -0.059 | 589 | 100.00 | 0.115 | 20.0 |
| 3 | JK661 | 03:59:40 PM | -51.30 | SR | -0.059 | 589 | 100.00 | 0.115 | 20.0 |
| 4 | JK661 | 03:59:46 PM | -51.30 | SR | -0.059 | 589 | 100.00 | 0.115 | 20.0 |
| 5 | JK661 | 03:59:52 PM | -52.17 | SR | -0.060 | 589 | 100.00 | 0.115 | 20.0 |

## S38. IR spectrum of compound 4




## S39. ECD and UV spectra of compound 4




**S40. HRESIMS of compound 4**

| Elmt | Val. | Min | Max |
|---|---|---|---|
| H | 1 | 0 | 300 |
| C | 4 | 0 | 19 |
| N | 3 | 0 | 0 |

| Elmt | Val. | Min | Max |
|---|---|---|---|
| O | 2 | 5 | 10 |

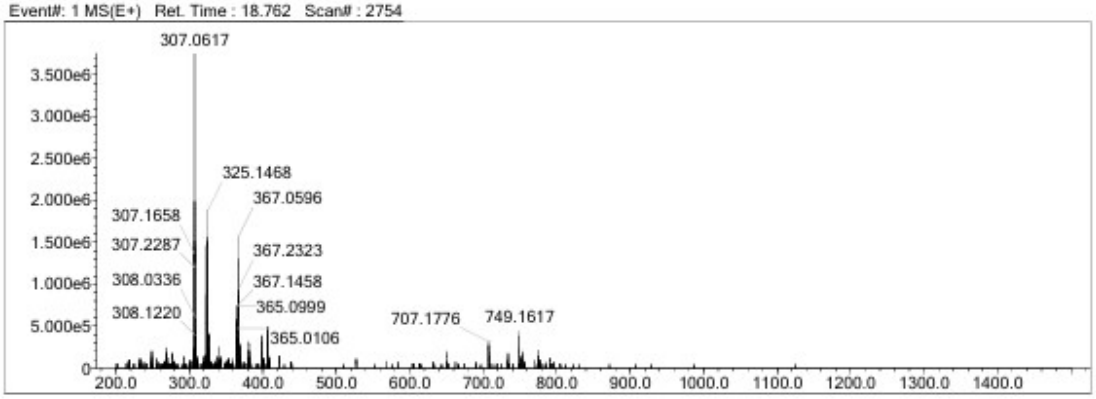
| Use Adduct |
|---|
| H |
| Na |
| H2O |

Error Margin (ppm): 1000
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

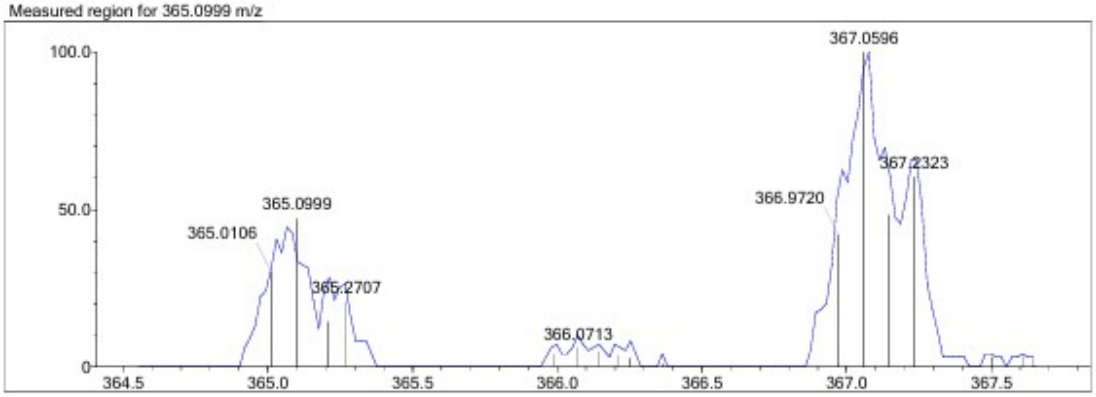
DBE Range: 0.0 - 20.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: odd
Use MSn Info: no
Isotope Res: 10000
Max Results: 1000

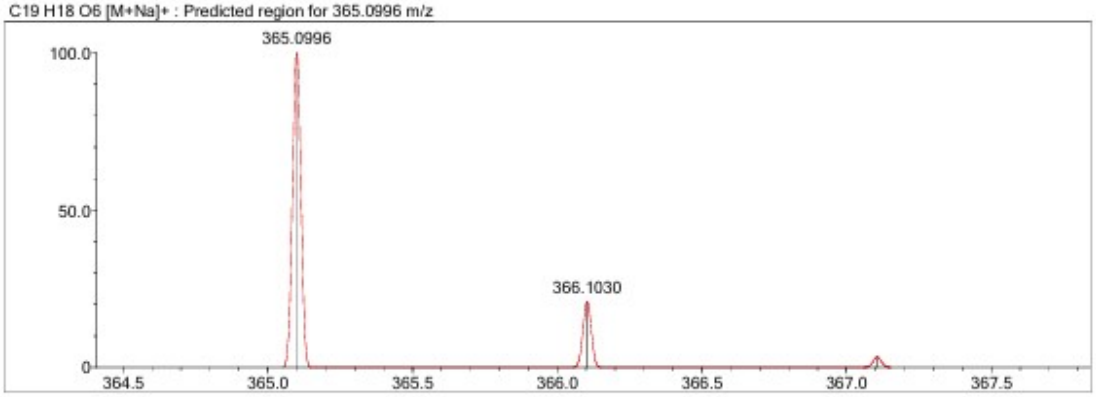
Event#: 1 MS(E+) Ret. Time : 18.762 Scan# : 2754




Measured region for 365.0999 m/z

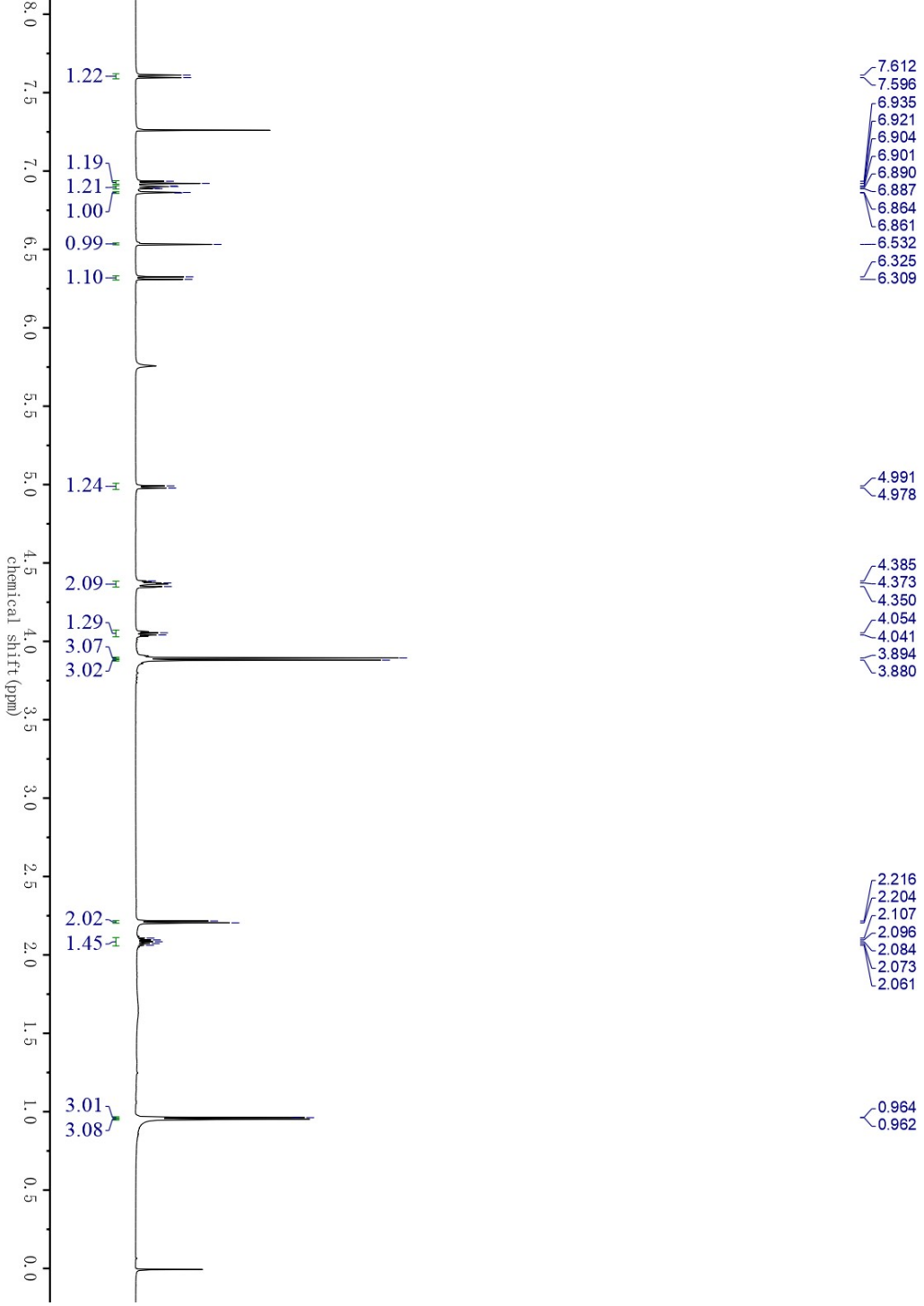



C19 H18 O6 [M+Na]+ : Predicted region for 365.0996 m/z

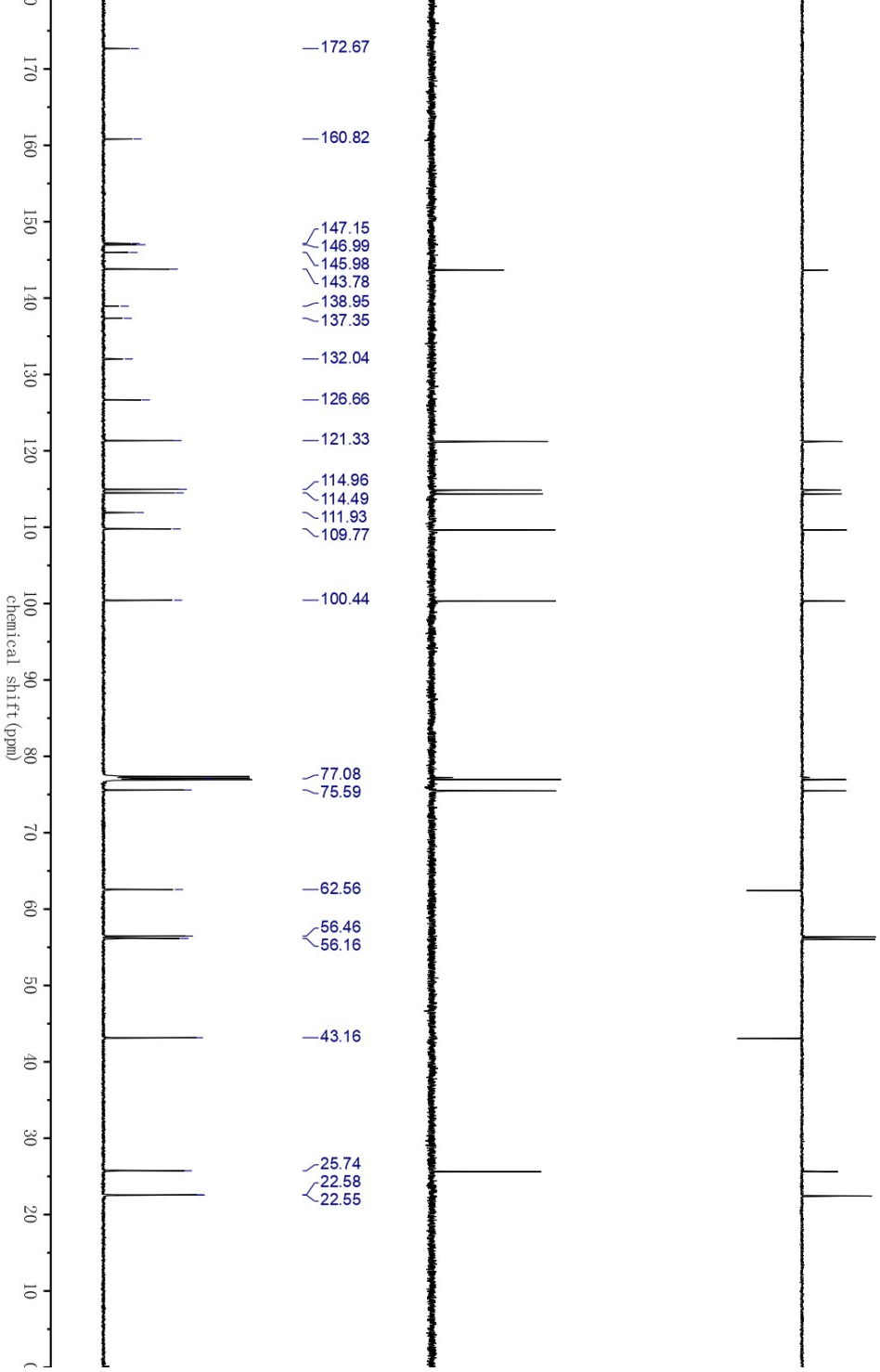



| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 0.00 | C19 H18 O6 | [M+Na]+ | 365.0999 | 365.0996 | 0.3 | 0.82 | 0.00 | 11.0 |

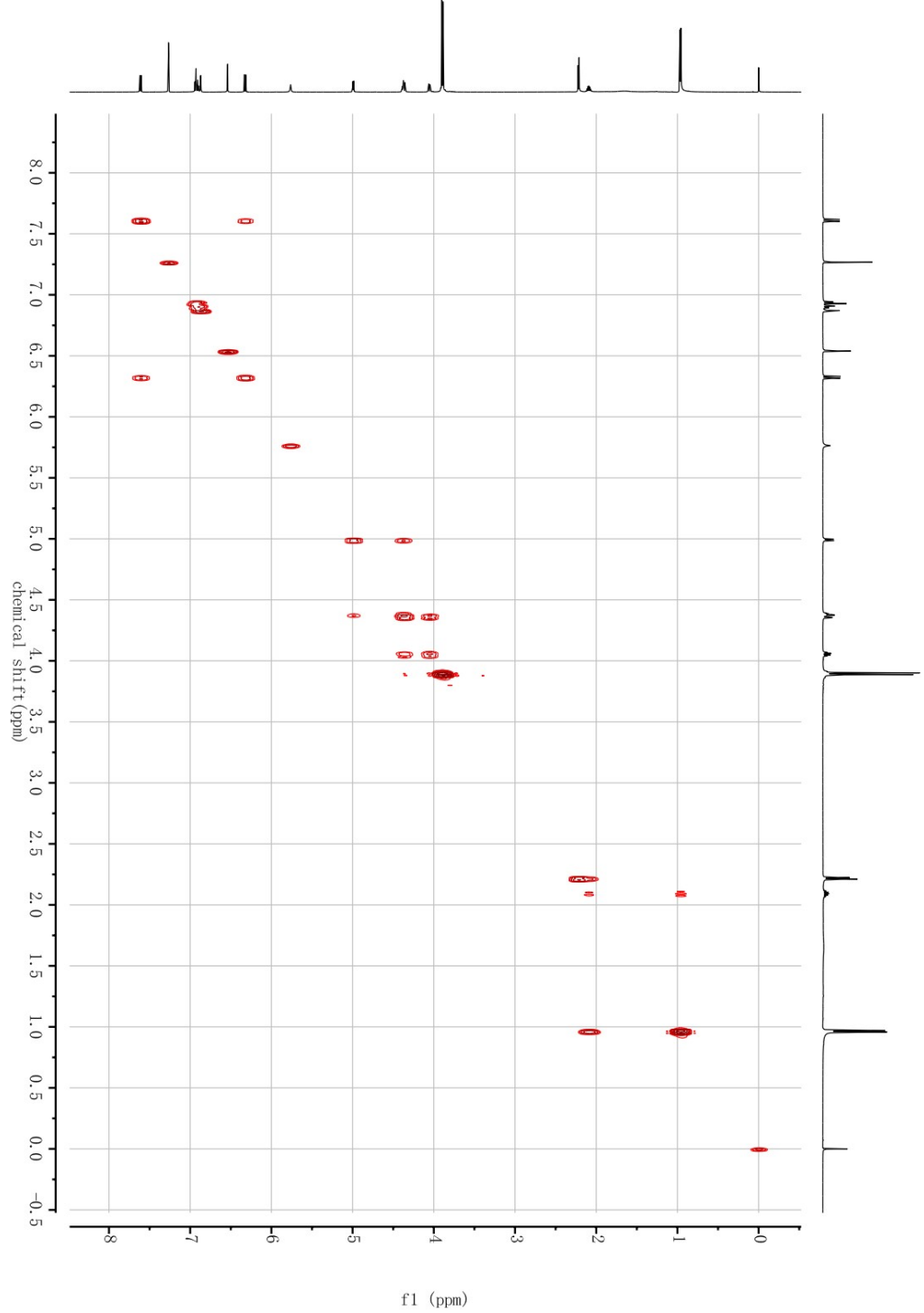
**S41. $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of compound 5**



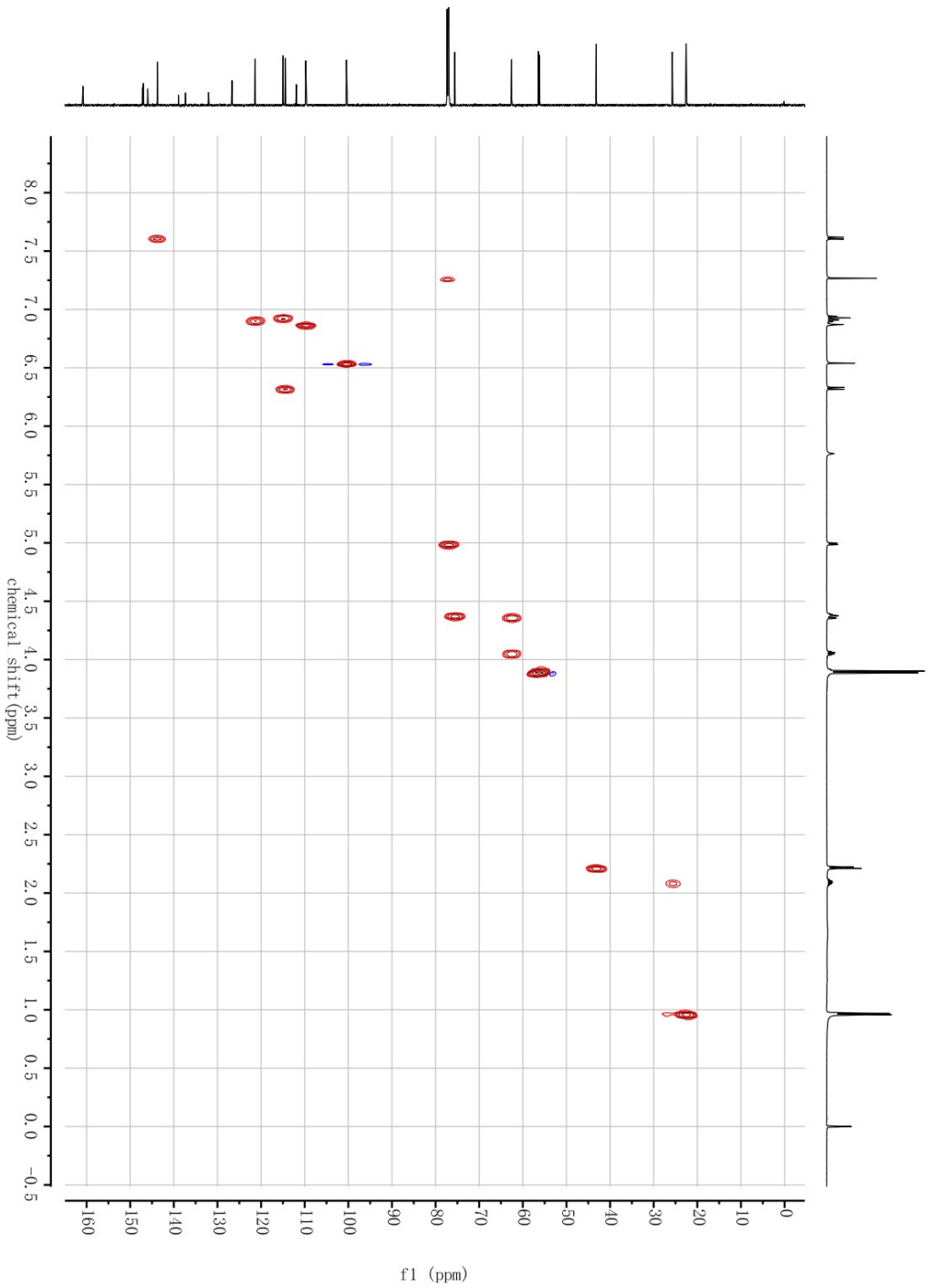

**S42. $^{13}C$ NMR (DEPT) (150 MHz, $CDCl_3$) spectrum of compound 5**



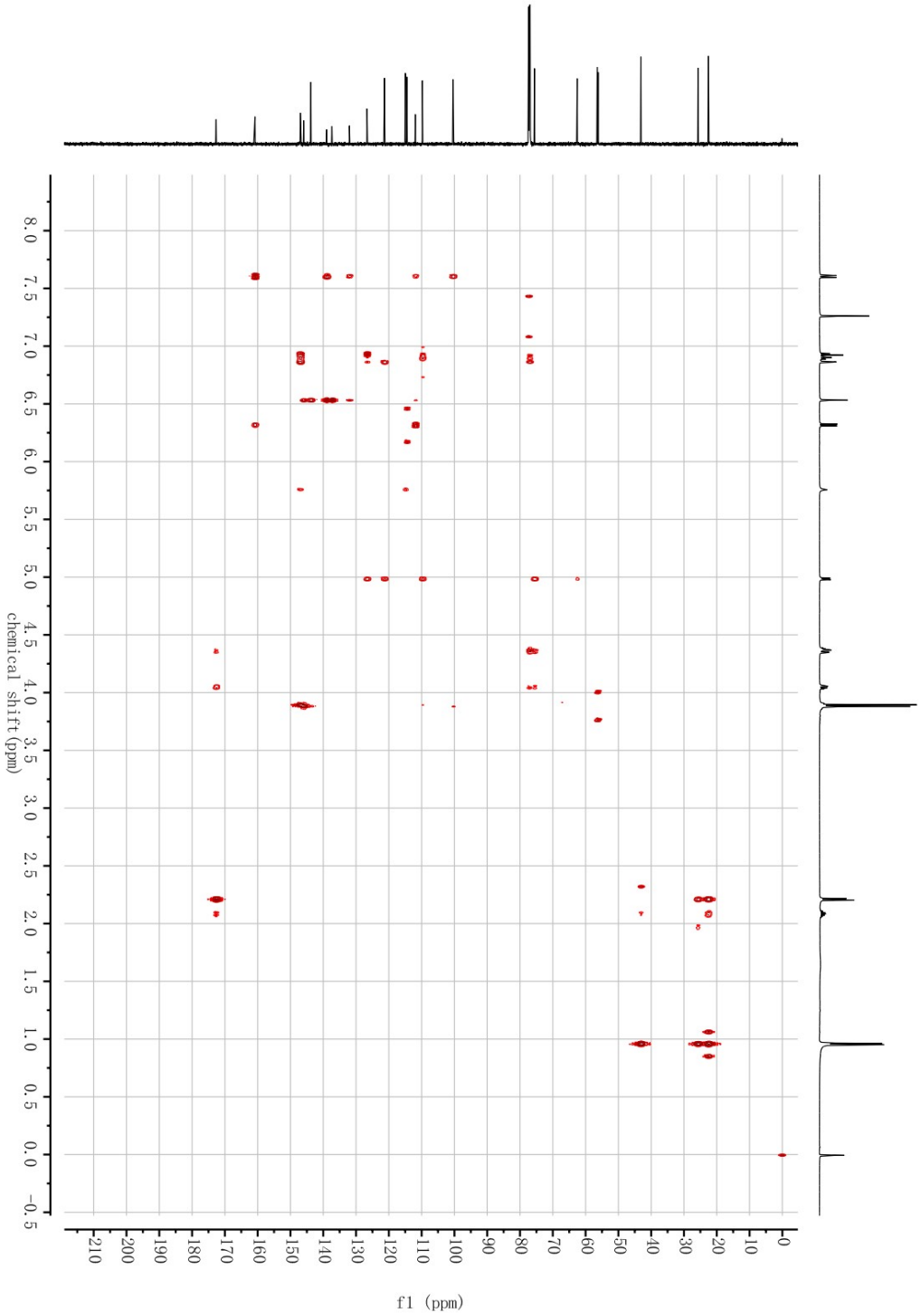

**S43. $^{1}$H-$^{1}$H COSY (600 MHz, $CDCl_3$) spectrum of compound 5**



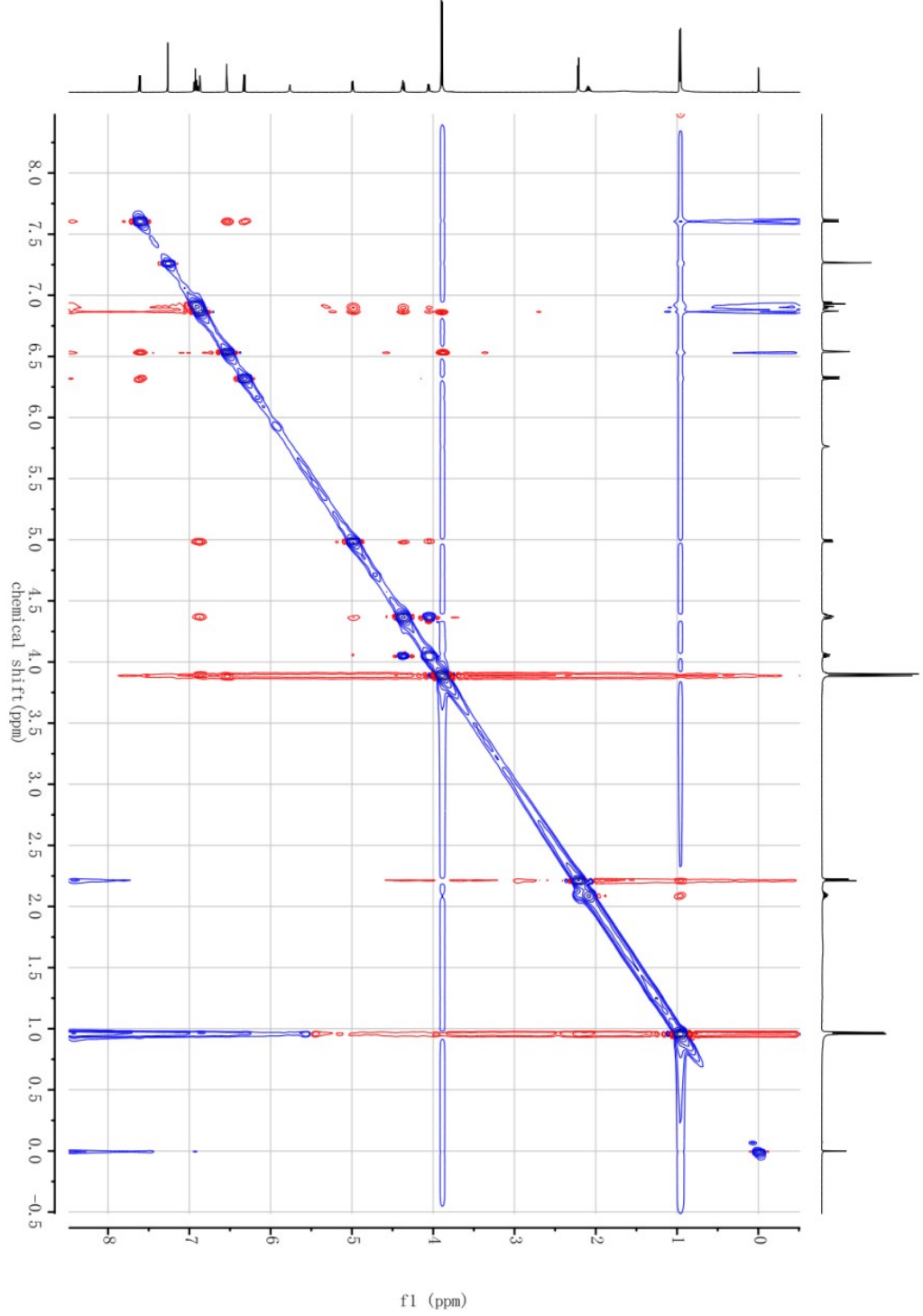

**S44. HSQC spectrum of compound 5**




**S45. HMBC spectrum of compound 5**




**S46. ROESY spectrum of compound 5**




## S47. $[\alpha]_D$ spectrum of compound 5 in MeOH

**Rudolph Research Analytical**

This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Monday, 05-JAN-2026

Set Temperature : 20.0

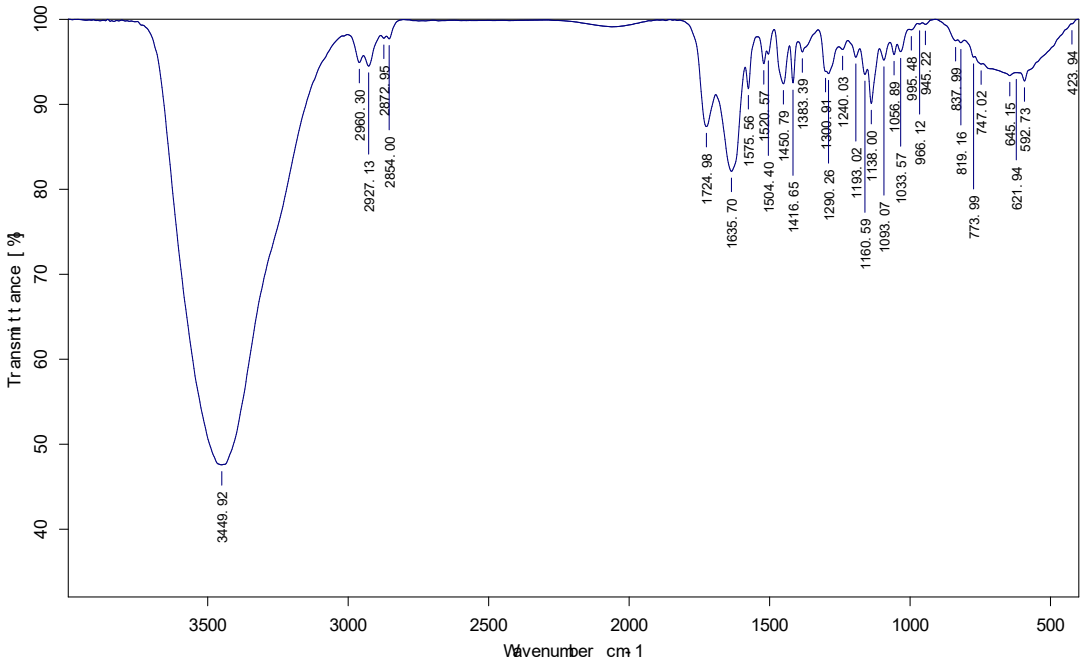
Time Delay : Disabled

Delay between Measurement : Disabled

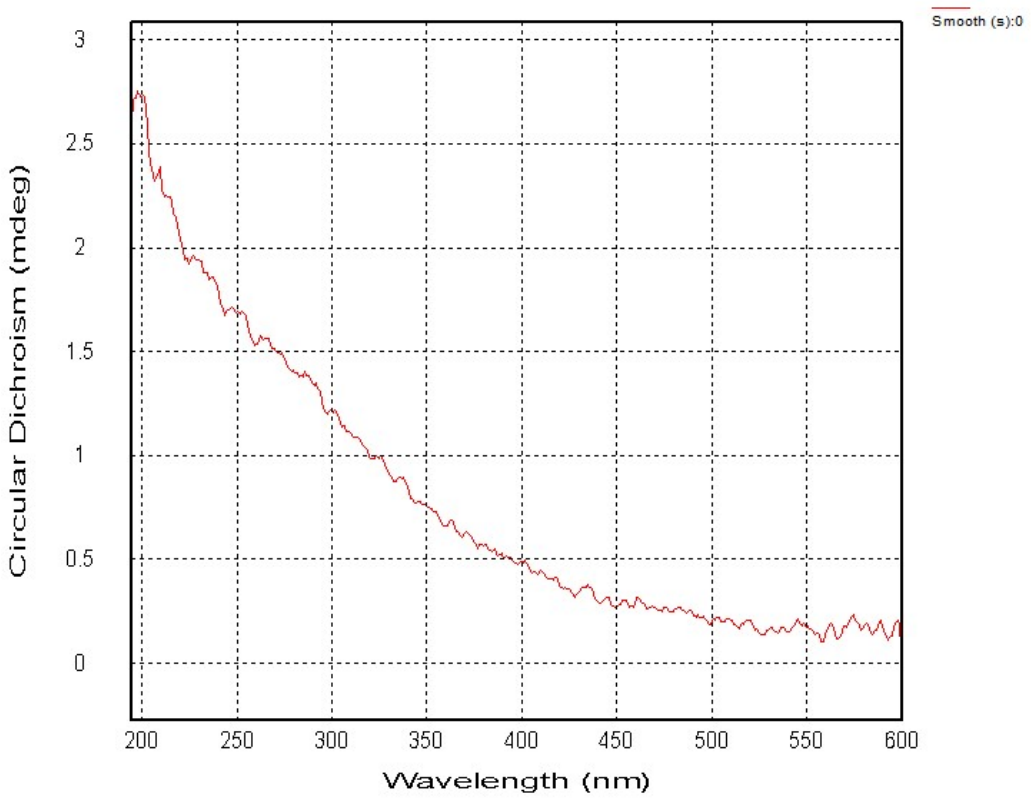
| n | Average | Std.Dev. | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|
| 5 | -18.34 | 0.65 | -3.54 | -17.86 | -19.05 |

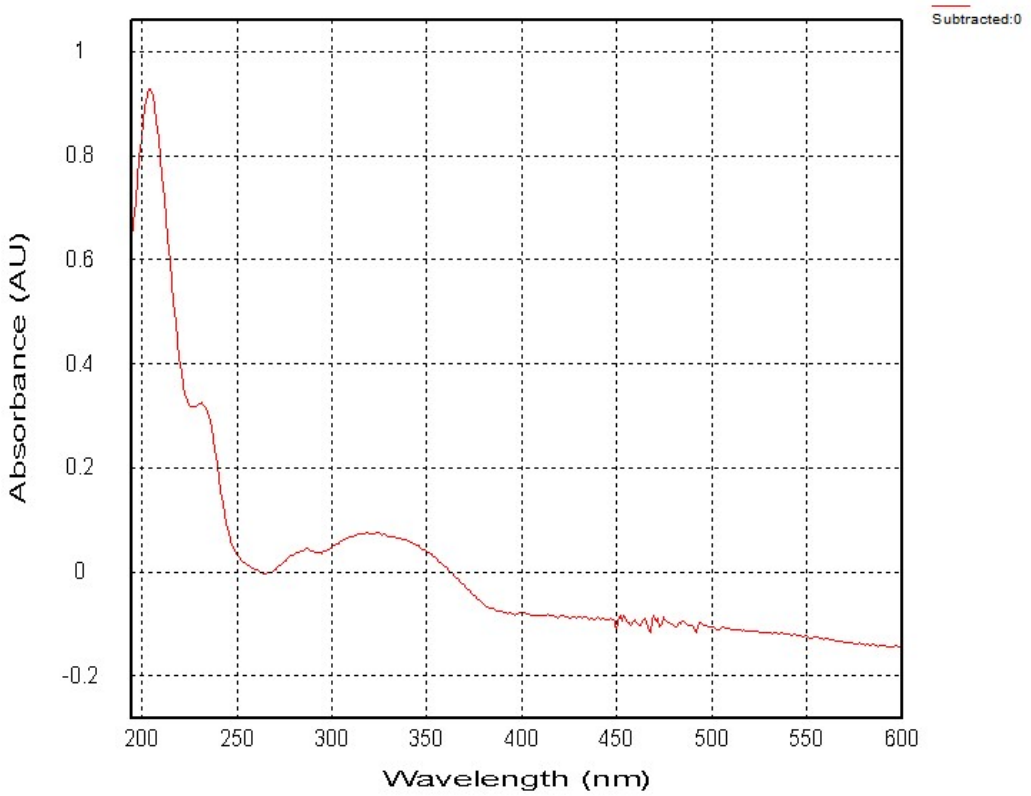
| S.No | Sample ID | Time | Result | Scale | OR °Arc | WLG.nm | Lg.mm | Conc.g/100ml | Temp. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | JK73823 | 11:16:48 AM | -19.05 | SR | -0.016 | 589 | 100.00 | 0.084 | 20.0 |
| 2 | JK73823 | 11:16:54 AM | -17.86 | SR | -0.015 | 589 | 100.00 | 0.084 | 20.0 |
| 3 | JK73823 | 11:17:00 AM | -17.86 | SR | -0.015 | 589 | 100.00 | 0.084 | 20.0 |
| 4 | JK73823 | 11:17:07 AM | -19.05 | SR | -0.016 | 589 | 100.00 | 0.084 | 20.0 |
| 5 | JK73823 | 11:17:13 AM | -17.86 | SR | -0.015 | 589 | 100.00 | 0.084 | 20.0 |

## S48. IR spectrum of compound 5




## S49. ECD and UV spectra of compound 5




**S50. HRESIMS of compound 5**

| Elmt | Val. | Min | Max |
|---|---|---|---|
| H | 1 | 0 | 300 |
| C | 4 | 0 | 100 |
| N | 3 | 0 | 0 |

| Elmt | Val. | Min | Max |
|---|---|---|---|
| O | 2 | 0 | 10 |

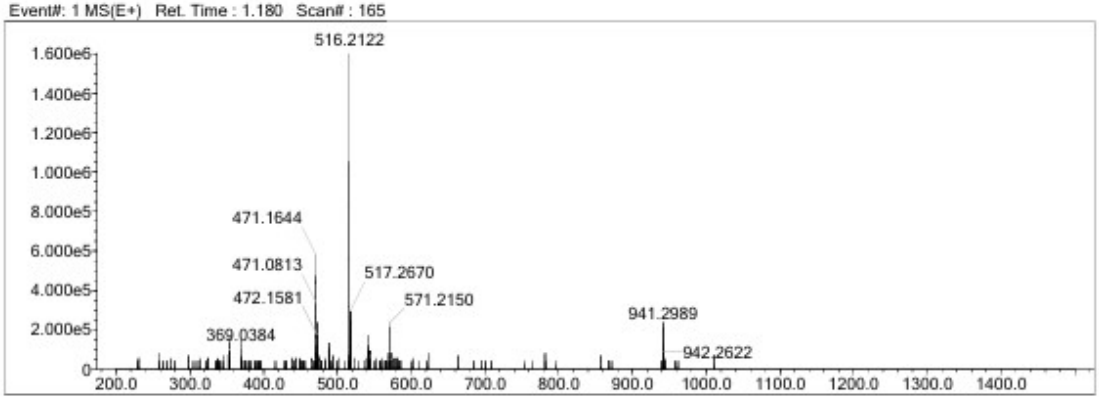
| Use Adduct |
|---|
| H |
| Na |
| H2O |

Error Margin (ppm): 1000
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

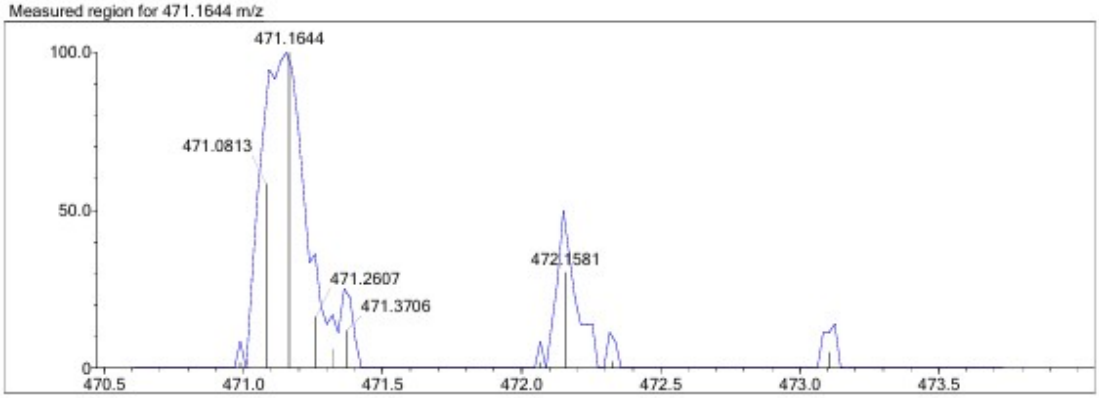
DBE Range: 0.0 - 20.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: odd
Use MSn Info: no
Isotope Res: 10000
Max Results: 1000

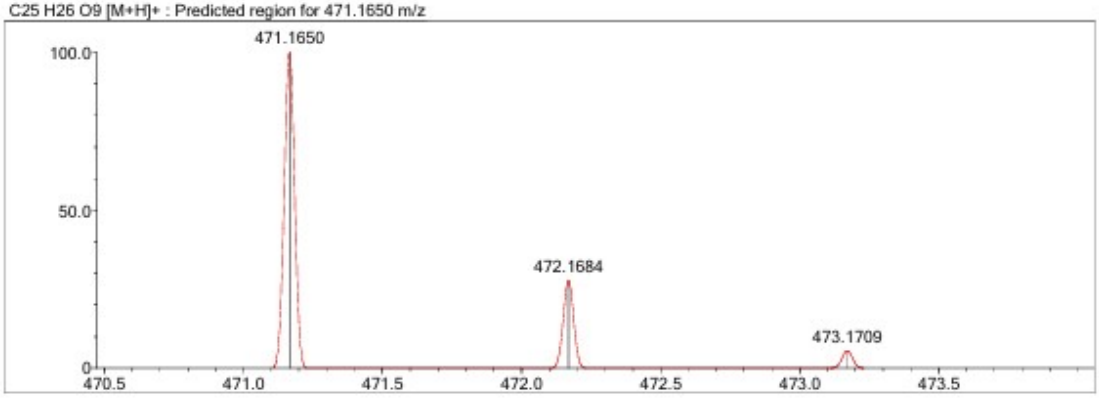
Event#: 1 MS(E+) Ret. Time : 1.180 Scan# : 165




Measured region for 471.1644 m/z



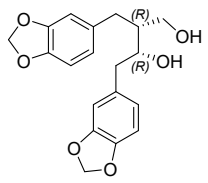

C25 H26 O9 [M+H]+ : Predicted region for 471.1650 m/z



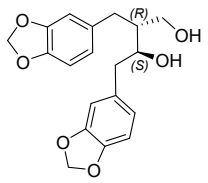

| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 33.10 | C25 H26 O9 | [M+H]+ | 471.1644 | 471.1650 | -0.6 | -1.27 | 33.32 | 13.0 |

**General results for NMR calculation**

**S51. Structures of two possible diastereoisomers of 2 (2a-2b).**



(8*R*, 8′*R*)-**2a**



(8*R*, 8′*S*)-**2b**

**S52. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 2a inthe gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **2a-1** | −1187. 262219 | −745018. 3214 | 0. 2064 | 41. 208% |
| **2a-2** | −1187. 257848 | −745015. 5783 | 2. 9495 | 0. 402% |
| **2a-3** | −1187. 253391 | −745012. 7819 | 5. 7458 | 0. 004% |
| **2a-4** | −1187. 262548 | −745018. 5278 | 0 | 58. 387% |

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory;

[b]Gibbs free energ (E*627.51);

[c]The relative Gibbs free energy;

[d]The Boltzmann distribution of eac conformer.

**S53. Cartesian coordinates for the low-energy Conf. of Compound 2a at B3LYP/6311+G(d,p) level of theory in methanol.**

Conformer 2a-1

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.842379 | 1.421824 | -0.661095 |
| 2 | 6 | 0 | -1.799412 | 2.563013 | 0.134302 |
| 3 | 6 | 0 | -0.607590 | 3.196350 | 0.420149 |
| 4 | 6 | 0 | 0.560781 | 2.620830 | -0.110034 |
| 5 | 6 | 0 | 0.531984 | 1.457445 | -0.886171 |
| 6 | 6 | 0 | -0.704490 | 0.849981 | -1.185476 |
| 7 | 8 | 0 | -3.153560 | 1.013450 | -0.804064 |
| 8 | 6 | 0 | -3.874892 | 1.770259 | 0.176595 |
| 9 | 8 | 0 | -3.077170 | 2.905231 | 0.522282 |
| 10 | 6 | 0 | 2.324104 | -1.324415 | 1.077038 |
| 11 | 6 | 0 | 2.655529 | 0.183981 | 0.992638 |
| 12 | 6 | 0 | 2.981170 | 0.749651 | -0.413714 |
| 13 | 6 | 0 | 1.801114 | 0.815522 | -1.407511 |
| 14 | 6 | 0 | 0.963445 | -1.733519 | 0.561495 |
| 15 | 6 | 0 | -0.193999 | -1.299303 | 1.246446 |
| 16 | 6 | 0 | -1.417590 | -1.688995 | 0.749476 |
| 17 | 6 | 0 | -1.535010 | -2.492159 | -0.382634 |
| 18 | 6 | 0 | -0.424829 | -2.936348 | -1.069671 |
| 19 | 6 | 0 | 0.831309 | -2.539643 | -0.571558 |
| 20 | 8 | 0 | 3.731201 | 0.482069 | 1.881800 |
| 21 | 6 | 0 | 4.144347 | 0.019708 | -1.097553 |
| 22 | 8 | 0 | -2.669735 | -1.379442 | 1.227973 |

| | | | | | |
|---|---|---|---|---|---|
| 23 | 6 | 0 | -3.602506 | -1.984607 | 0.319836 |
| 24 | 8 | 0 | -2.860585 | -2.732941 | -0.650315 |
| 25 | 8 | 0 | 5.343757 | -0.028799 | -0.310379 |
| 26 | 1 | 0 | -0.574790 | 4.088770 | 1.035047 |
| 27 | 1 | 0 | 1.514104 | 3.087243 | 0.118609 |
| 28 | 1 | 0 | -0.752721 | -0.061718 | -1.769355 |
| 29 | 1 | 0 | -4.820960 | 2.107612 | -0.250921 |
| 30 | 1 | 0 | -4.029043 | 1.145478 | 1.068249 |
| 31 | 1 | 0 | 3.104844 | -1.909364 | 0.576953 |
| 32 | 1 | 0 | 2.396549 | -1.568409 | 2.143273 |
| 33 | 1 | 0 | 1.798169 | 0.739768 | 1.383111 |
| 34 | 1 | 0 | 3.317791 | 1.778994 | -0.219436 |
| 35 | 1 | 0 | 1.559844 | -0.194936 | -1.751431 |
| 36 | 1 | 0 | 2.150043 | 1.363641 | -2.295621 |
| 37 | 1 | 0 | -0.124167 | -0.665529 | 2.124031 |
| 38 | 1 | 0 | -0.518872 | -3.565663 | -1.947663 |
| 39 | 1 | 0 | 1.727286 | -2.878935 | -1.084186 |
| 40 | 1 | 0 | 4.519813 | 0.081863 | 1.470716 |
| 41 | 1 | 0 | 3.886210 | -1.026333 | -1.286013 |
| 42 | 1 | 0 | 4.351206 | 0.481508 | -2.074239 |
| 43 | 1 | 0 | -4.259223 | -2.662271 | 0.875776 |
| 44 | 1 | 0 | -4.168685 | -1.198929 | -0.189056 |
| 45 | 1 | 0 | 5.664810 | 0.883222 | -0.221573 |

Conformer 2a-2

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 4.975789 | 0.830721 | -0.017278 |
| 2 | 6 | 0 | 5.786503 | -0.257767 | -0.335263 |
| 3 | 6 | 0 | 5.271269 | -1.393538 | -0.921690 |
| 4 | 6 | 0 | 3.887654 | -1.401165 | -1.183275 |
| 5 | 6 | 0 | 3.062655 | -0.317938 | -0.869467 |
| 6 | 6 | 0 | 3.621082 | 0.833392 | -0.268299 |
| 7 | 8 | 0 | 5.736165 | 1.814263 | 0.573082 |
| 8 | 6 | 0 | 7.094206 | 1.380875 | 0.436863 |
| 9 | 8 | 0 | 7.083397 | 0.003861 | 0.046993 |
| 10 | 6 | 0 | -1.667303 | -0.126661 | 1.077117 |
| 11 | 6 | 0 | -0.747990 | -0.130297 | -0.162693 |
| 12 | 6 | 0 | 0.718399 | -0.468225 | 0.143567 |
| 13 | 6 | 0 | 1.576781 | -0.354404 | -1.142153 |
| 14 | 6 | 0 | -3.089878 | 0.219961 | 0.706294 |
| 15 | 6 | 0 | -3.973415 | -0.806236 | 0.301869 |
| 16 | 6 | 0 | -5.244817 | -0.440597 | -0.084252 |
| 17 | 6 | 0 | -5.664143 | 0.889277 | -0.090862 |
| 18 | 6 | 0 | -4.824791 | 1.913018 | 0.292332 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 6 | 0 | -3.523199 | 1.551504 | 0.692050 |
| 20 | 8 | 0 | -0.753606 | 1.156610 | -0.778792 |
| 21 | 6 | 0 | 0.902892 | -1.862549 | 0.758734 |
| 22 | 8 | 0 | -6.265505 | -1.247697 | -0.526786 |
| 23 | 6 | 0 | -7.409152 | -0.393391 | -0.647086 |
| 24 | 8 | 0 | -6.962959 | 0.962751 | -0.538255 |
| 25 | 8 | 0 | 0.452908 | -1.994342 | 2.105265 |
| 26 | 1 | 0 | 5.903611 | -2.239135 | -1.168311 |
| 27 | 1 | 0 | 3.448823 | -2.277777 | -1.651352 |
| 28 | 1 | 0 | 3.005282 | 1.692184 | -0.021281 |
| 29 | 1 | 0 | 7.592103 | 1.978274 | -0.340251 |
| 30 | 1 | 0 | 7.605618 | 1.482533 | 1.397663 |
| 31 | 1 | 0 | -1.617168 | -1.100859 | 1.567987 |
| 32 | 1 | 0 | -1.271110 | 0.610777 | 1.785557 |
| 33 | 1 | 0 | -1.130952 | -0.884992 | -0.873336 |
| 34 | 1 | 0 | 1.085807 | 0.281354 | 0.861143 |
| 35 | 1 | 0 | 1.270078 | 0.552173 | -1.669510 |
| 36 | 1 | 0 | 1.341766 | -1.200033 | -1.802197 |
| 37 | 1 | 0 | -3.663263 | -1.845962 | 0.301275 |
| 38 | 1 | 0 | -5.155073 | 2.945759 | 0.289774 |
| 39 | 1 | 0 | -2.839375 | 2.329076 | 1.020353 |
| 40 | 1 | 0 | -1.684519 | 1.397498 | -0.920022 |
| 41 | 1 | 0 | 0.327091 | -2.598955 | 0.185551 |
| 42 | 1 | 0 | 1.961226 | -2.146750 | 0.682915 |
| 43 | 1 | 0 | -7.874420 | -0.545734 | -1.624637 |
| 44 | 1 | 0 | -8.116021 | -0.612934 | 0.165116 |
| 45 | 1 | 0 | 0.972041 | -1.375933 | 2.642468 |

Conformer 2a-3

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 2.966390 | 1.576253 | 0.578060 |
| 2 | 6 | 0 | 3.993678 | 1.624110 | -0.362283 |
| 3 | 6 | 0 | 4.550216 | 0.474344 | -0.881171 |
| 4 | 6 | 0 | 4.025114 | -0.747224 | -0.420552 |
| 5 | 6 | 0 | 2.989137 | -0.809005 | 0.516531 |
| 6 | 6 | 0 | 2.445435 | 0.386921 | 1.040303 |
| 7 | 8 | 0 | 2.626054 | 2.856778 | 0.951729 |
| 8 | 6 | 0 | 3.344524 | 3.718551 | 0.064027 |
| 9 | 8 | 0 | 4.333453 | 2.934150 | -0.612709 |
| 10 | 6 | 0 | -1.390708 | -2.172307 | -0.023450 |
| 11 | 6 | 0 | -0.036747 | -1.642777 | 0.482558 |
| 12 | 6 | 0 | 1.149093 | -2.593915 | 0.207993 |
| 13 | 6 | 0 | 2.430994 | -2.145198 | 0.960139 |
| 14 | 6 | 0 | -2.497504 | -1.155085 | 0.109638 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 6 | 0 | -2.688786 | -0.213043 | -0.924432 |
| 16 | 6 | 0 | -3.670137 | 0.738889 | -0.748300 |
| 17 | 6 | 0 | -4.461190 | 0.781575 | 0.397231 |
| 18 | 6 | 0 | -4.301891 | -0.130137 | 1.419637 |
| 19 | 6 | 0 | -3.297079 | -1.099843 | 1.253358 |
| 20 | 8 | 0 | -0.122617 | -1.309273 | 1.872266 |
| 21 | 6 | 0 | 1.457898 | -2.759694 | -1.290516 |
| 22 | 8 | 0 | -4.062849 | 1.732438 | -1.617137 |
| 23 | 6 | 0 | -4.993654 | 2.532984 | -0.880884 |
| 24 | 8 | 0 | -5.379790 | 1.802518 | 0.287513 |
| 25 | 8 | 0 | 0.481066 | -3.482120 | -2.035774 |
| 26 | 1 | 0 | 5.357837 | 0.513053 | -1.603654 |
| 27 | 1 | 0 | 4.443390 | -1.672414 | -0.806876 |
| 28 | 1 | 0 | 1.645721 | 0.359963 | 1.771627 |
| 29 | 1 | 0 | 2.650150 | 4.146622 | -0.673201 |
| 30 | 1 | 0 | 3.837946 | 4.505306 | 0.640833 |
| 31 | 1 | 0 | -1.274311 | -2.485386 | -1.064013 |
| 32 | 1 | 0 | -1.638458 | -3.079622 | 0.548896 |
| 33 | 1 | 0 | 0.171523 | -0.686014 | -0.007636 |
| 34 | 1 | 0 | 0.885017 | -3.590100 | 0.606162 |
| 35 | 1 | 0 | 3.194416 | -2.919730 | 0.818416 |
| 36 | 1 | 0 | 2.202981 | -2.108962 | 2.028257 |
| 37 | 1 | 0 | -2.086229 | -0.238489 | -1.826682 |
| 38 | 1 | 0 | -4.923833 | -0.097500 | 2.307252 |
| 39 | 1 | 0 | -3.137711 | -1.827041 | 2.044051 |
| 40 | 1 | 0 | -0.407313 | -2.107072 | 2.346619 |
| 41 | 1 | 0 | 1.526503 | -1.778960 | -1.769773 |
| 42 | 1 | 0 | 2.444037 | -3.237350 | -1.398582 |
| 43 | 1 | 0 | -4.509599 | 3.473991 | -0.581512 |
| 44 | 1 | 0 | -5.875527 | 2.724122 | -1.497774 |
| 45 | 1 | 0 | 0.402229 | -4.362747 | -1.636828 |

Conformer 2a-4

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -1.749367 | 1.461668 | -0.629988 |
| 2 | 6 | 0 | -1.689037 | 2.631068 | 0.121648 |
| 3 | 6 | 0 | -0.490558 | 3.273533 | 0.357561 |
| 4 | 6 | 0 | 0.665610 | 2.675354 | -0.173928 |
| 5 | 6 | 0 | 0.619823 | 1.481678 | -0.903178 |
| 6 | 6 | 0 | -0.623079 | 0.867216 | -1.154827 |
| 7 | 8 | 0 | -3.063198 | 1.051508 | -0.733107 |
| 8 | 6 | 0 | -3.766192 | 1.847142 | 0.229749 |
| 9 | 8 | 0 | -2.957966 | 2.990186 | 0.522334 |
| 10 | 6 | 0 | 2.261232 | -1.427778 | 0.988812 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 6 | 0 | 2.613450 | 0.068589 | 0.968325 |
| 12 | 6 | 0 | 3.028965 | 0.684017 | -0.389130 |
| 13 | 6 | 0 | 1.881889 | 0.817253 | -1.413476 |
| 14 | 6 | 0 | 0.877967 | -1.773425 | 0.486600 |
| 15 | 6 | 0 | -0.252285 | -1.348044 | 1.220500 |
| 16 | 6 | 0 | -1.495590 | -1.689078 | 0.737061 |
| 17 | 6 | 0 | -1.656690 | -2.439992 | -0.425634 |
| 18 | 6 | 0 | -0.572969 | -2.876027 | -1.158628 |
| 19 | 6 | 0 | 0.703228 | -2.525288 | -0.676768 |
| 20 | 8 | 0 | 3.706555 | 0.192440 | 1.909859 |
| 21 | 6 | 0 | 4.217608 | -0.041649 | -1.040337 |
| 22 | 8 | 0 | -2.728139 | -1.379340 | 1.261767 |
| 23 | 6 | 0 | -3.694994 | -1.922718 | 0.349929 |
| 24 | 8 | 0 | -2.992182 | -2.645624 | -0.667286 |
| 25 | 8 | 0 | 5.394447 | -0.031477 | -0.253934 |
| 26 | 1 | 0 | -0.445523 | 4.191890 | 0.932328 |
| 27 | 1 | 0 | 1.624235 | 3.152924 | 0.007113 |
| 28 | 1 | 0 | -0.684882 | -0.063677 | -1.705594 |
| 29 | 1 | 0 | -4.716914 | 2.174077 | -0.195578 |
| 30 | 1 | 0 | -3.910476 | 1.255148 | 1.145202 |
| 31 | 1 | 0 | 3.015475 | -1.998641 | 0.438312 |
| 32 | 1 | 0 | 2.351367 | -1.732880 | 2.038124 |
| 33 | 1 | 0 | 1.753599 | 0.631087 | 1.353582 |
| 34 | 1 | 0 | 3.382445 | 1.700605 | -0.153606 |
| 35 | 1 | 0 | 1.623822 | -0.174310 | -1.797756 |
| 36 | 1 | 0 | 2.277134 | 1.383433 | -2.268737 |
| 37 | 1 | 0 | -0.148478 | -0.759417 | 2.125826 |
| 38 | 1 | 0 | -0.701137 | -3.464018 | -2.060492 |
| 39 | 1 | 0 | 1.579472 | -2.855166 | -1.227577 |
| 40 | 1 | 0 | 3.961291 | 1.129176 | 1.938745 |
| 41 | 1 | 0 | 3.916824 | -1.071088 | -1.302427 |
| 42 | 1 | 0 | 4.466732 | 0.458641 | -1.983392 |
| 43 | 1 | 0 | -4.355662 | -2.607963 | 0.891242 |
| 44 | 1 | 0 | -4.253400 | -1.103451 | -0.112534 |
| 45 | 1 | 0 | 5.113880 | -0.249035 | 0.654414 |

**S54. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 2b in the gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **2b-1** | −1187. 261232 | −745017. 7023 | 0 | 53. 685% |
| **2b-2** | −1187. 257971 | −745015. 6557 | 2. 0466 | 1. 696% |
| **2b-3** | −1187. 256368 | −745014. 65 | 3. 0523 | 0. 311% |
| **2b-4** | −1187. 259401 | −745016. 5534 | 1. 1489 | 7. 719% |
| **2b-5** | −1187. 260358 | −745017. 1534 | 0. 5489 | 21. 254% |
| **2b-6** | −1187. 25862 | −745016. 0631 | 1. 6392 | 3. 373% |
| **2b-7** | −1187. 259225 | −745016. 4423 | 1. 2599 | 6. 400% |
| **2b-8** | −1187. 259092 | −745016. 3593 | 1. 343 | 5. 563% |

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory;

[b]Gibbs free energ (E*627.51);

[c]The relative Gibbs free energy;

[d]The Boltzmann distribution of eac conformer.

**S55. Cartesian coordinates for the low-energy Conf. of Compound 2b at B3LYP/6311+G(d,p) level of theory in methanol.**

Conformer 2b-1

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.470469 | -1.869873 | -0.214868 |
| 2 | 6 | 0 | 2.262950 | -2.109595 | -0.838630 |
| 3 | 6 | 0 | 1.562298 | -0.989981 | -1.318847 |
| 4 | 6 | 0 | 2.050076 | 0.314498 | -1.174804 |
| 5 | 6 | 0 | 3.288179 | 0.527066 | -0.531931 |
| 6 | 6 | 0 | 3.970391 | -0.579550 | -0.068617 |
| 7 | 8 | 0 | 5.170898 | -0.621968 | 0.602930 |
| 8 | 6 | 0 | 5.503457 | -2.012185 | 0.699258 |
| 9 | 8 | 0 | 4.337916 | -2.771197 | 0.361794 |
| 10 | 6 | 0 | -3.820774 | -0.517503 | -0.208862 |
| 11 | 6 | 0 | -3.704453 | -1.622820 | 0.631129 |
| 12 | 6 | 0 | -2.845075 | -1.623872 | 1.710082 |
| 13 | 6 | 0 | -2.091092 | -0.455245 | 1.920248 |
| 14 | 6 | 0 | -2.199975 | 0.659790 | 1.084950 |
| 15 | 6 | 0 | -3.089140 | 0.634532 | -0.012439 |
| 16 | 8 | 0 | -4.761313 | -0.774827 | -1.180596 |
| 17 | 6 | 0 | -5.094266 | -2.158859 | -1.033977 |
| 18 | 8 | 0 | -4.569044 | -2.611871 | 0.218748 |
| 19 | 6 | 0 | 1.232460 | 1.488638 | -1.662522 |
| 20 | 6 | 0 | -0.105054 | 1.650961 | -0.908373 |
| 21 | 6 | 0 | 0.046583 | 1.796518 | 0.621393 |
| 22 | 6 | 0 | -1.332313 | 1.874161 | 1.318324 |
| 23 | 8 | 0 | -0.865051 | 2.719969 | -1.465585 |
| 24 | 6 | 0 | 0.917376 | 2.994841 | 1.015160 |
| 25 | 8 | 0 | 0.433184 | 4.245568 | 0.491650 |
| 26 | 1 | 0 | 1.876461 | -3.116266 | -0.952480 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1 | 0 | 0.611867 | -1.146287 | -1.820820 |
| 28 | 1 | 0 | 3.697613 | 1.524738 | -0.412560 |
| 29 | 1 | 0 | 6.310647 | -2.244296 | -0.010175 |
| 30 | 1 | 0 | 5.803464 | -2.243010 | 1.724712 |
| 31 | 1 | 0 | -2.761710 | -2.483914 | 2.365148 |
| 32 | 1 | 0 | -1.401027 | -0.420764 | 2.759037 |
| 33 | 1 | 0 | -3.167963 | 1.483035 | -0.683430 |
| 34 | 1 | 0 | -6.181481 | -2.273438 | -1.034596 |
| 35 | 1 | 0 | -4.637017 | -2.734054 | -1.851976 |
| 36 | 1 | 0 | 1.814737 | 2.414148 | -1.585248 |
| 37 | 1 | 0 | 0.979691 | 1.372115 | -2.722758 |
| 38 | 1 | 0 | -0.697276 | 0.749931 | -1.093113 |
| 39 | 1 | 0 | 0.560667 | 0.898253 | 0.987784 |
| 40 | 1 | 0 | -1.167292 | 2.002920 | 2.396158 |
| 41 | 1 | 0 | -1.860934 | 2.764688 | 0.959948 |
| 42 | 1 | 0 | -0.451683 | 3.535617 | -1.123831 |
| 43 | 1 | 0 | 1.007960 | 3.053950 | 2.109413 |
| 44 | 1 | 0 | 1.926323 | 2.890285 | 0.611253 |
| 45 | 1 | 0 | -0.368338 | 4.477815 | 0.985953 |

Conformer 2b-2

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -5.863568 | -0.461178 | -0.335785 |
| 2 | 6 | 0 | -5.060514 | -1.583735 | -0.326844 |
| 3 | 6 | 0 | -3.745529 | -1.424615 | 0.142216 |
| 4 | 6 | 0 | -3.259824 | -0.186990 | 0.579536 |
| 5 | 6 | 0 | -4.101905 | 0.944967 | 0.553352 |
| 6 | 6 | 0 | -5.391871 | 0.774459 | 0.094302 |
| 7 | 8 | 0 | -6.382750 | 1.722335 | -0.043845 |
| 8 | 6 | 0 | -7.562433 | 0.987526 | -0.388004 |
| 9 | 8 | 0 | -7.169113 | -0.336352 | -0.761061 |
| 10 | 6 | 0 | 5.201580 | -0.335874 | -0.459302 |
| 11 | 6 | 0 | 5.660061 | 0.893104 | 0.005515 |
| 12 | 6 | 0 | 4.812585 | 1.973331 | 0.148469 |
| 13 | 6 | 0 | 3.462893 | 1.774058 | -0.190552 |
| 14 | 6 | 0 | 2.984511 | 0.543823 | -0.654192 |
| 15 | 6 | 0 | 3.877583 | -0.542079 | -0.794879 |
| 16 | 8 | 0 | 6.239429 | -1.233816 | -0.498490 |
| 17 | 6 | 0 | 7.417560 | -0.476592 | -0.188367 |
| 18 | 8 | 0 | 7.005317 | 0.811775 | 0.281219 |
| 19 | 6 | 0 | -1.831349 | -0.041853 | 1.052748 |
| 20 | 6 | 0 | -0.799728 | -0.162997 | -0.090867 |
| 21 | 6 | 0 | 0.599657 | 0.370038 | 0.298764 |
| 22 | 6 | 0 | 1.516995 | 0.342279 | -0.950863 |

| | | | | | |
|---|---|---|---|---|---|
| 23 | 8 | 0 | -0.722732 | -1.502382 | -0.573326 |
| 24 | 6 | 0 | 1.201459 | -0.387282 | 1.489891 |
| 25 | 8 | 0 | 1.410478 | -1.782406 | 1.213175 |
| 26 | 1 | 0 | -5.430544 | -2.544141 | -0.668402 |
| 27 | 1 | 0 | -3.076893 | -2.277237 | 0.146822 |
| 28 | 1 | 0 | -3.751687 | 1.916999 | 0.885470 |
| 29 | 1 | 0 | -8.230487 | 0.939482 | 0.484529 |
| 30 | 1 | 0 | -8.057605 | 1.471765 | -1.233893 |
| 31 | 1 | 0 | 5.176189 | 2.930463 | 0.505480 |
| 32 | 1 | 0 | 2.770218 | 2.605067 | -0.090576 |
| 33 | 1 | 0 | 3.545247 | -1.497210 | -1.191863 |
| 34 | 1 | 0 | 7.980013 | -0.987807 | 0.597519 |
| 35 | 1 | 0 | 8.024216 | -0.359762 | -1.096658 |
| 36 | 1 | 0 | -1.708815 | 0.931527 | 1.545131 |
| 37 | 1 | 0 | -1.605386 | -0.808118 | 1.804578 |
| 38 | 1 | 0 | -1.165983 | 0.431946 | -0.937031 |
| 39 | 1 | 0 | 0.484062 | 1.413382 | 0.626809 |
| 40 | 1 | 0 | 1.369907 | -0.618122 | -1.453504 |
| 41 | 1 | 0 | 1.160822 | 1.109781 | -1.649086 |
| 42 | 1 | 0 | -0.126508 | -1.971707 | 0.043467 |
| 43 | 1 | 0 | 2.143564 | 0.080220 | 1.797991 |
| 44 | 1 | 0 | 0.522616 | -0.356620 | 2.345806 |
| 45 | 1 | 0 | 2.223041 | -1.845473 | 0.685200 |

Conformer 2b-3

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 5.217082 | -0.157826 | -0.640866 |
| 2 | 6 | 0 | 4.766232 | 1.027292 | -1.213590 |
| 3 | 6 | 0 | 3.630679 | 1.632340 | -0.624289 |
| 4 | 6 | 0 | 2.977508 | 1.076955 | 0.489303 |
| 5 | 6 | 0 | 3.466770 | -0.129281 | 1.056817 |
| 6 | 6 | 0 | 4.581994 | -0.718606 | 0.468933 |
| 7 | 8 | 0 | 5.250758 | -1.862620 | 0.853588 |
| 8 | 6 | 0 | 6.219759 | -2.106237 | -0.175219 |
| 9 | 8 | 0 | 6.307152 | -0.930598 | -0.989642 |
| 10 | 6 | 0 | -4.468300 | -1.049043 | -0.374663 |
| 11 | 6 | 0 | -5.129699 | 0.162409 | -0.157575 |
| 12 | 6 | 0 | -4.479998 | 1.384627 | -0.324150 |
| 13 | 6 | 0 | -3.120393 | 1.348189 | -0.724401 |
| 14 | 6 | 0 | -2.437325 | 0.136139 | -0.942989 |
| 15 | 6 | 0 | -3.129990 | -1.098142 | -0.768997 |
| 16 | 8 | 0 | -5.329790 | -2.097538 | -0.129674 |
| 17 | 6 | 0 | -6.611411 | -1.501672 | 0.123603 |
| 18 | 8 | 0 | -6.429128 | -0.083558 | 0.235543 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 6 | 0 | 1.735419 | 1.735594 | 1.044723 |
| 20 | 6 | 0 | 0.506003 | 1.636166 | 0.111075 |
| 21 | 6 | 0 | 0.104036 | 0.184538 | -0.231825 |
| 22 | 6 | 0 | -0.974771 | 0.109297 | -1.356742 |
| 23 | 8 | 0 | -0.568363 | 2.395348 | 0.648547 |
| 24 | 6 | 0 | -0.264565 | -0.635560 | 1.014315 |
| 25 | 8 | 0 | -1.253465 | -0.015764 | 1.850098 |
| 26 | 1 | 0 | 5.269226 | 1.467861 | -2.068025 |
| 27 | 1 | 0 | 3.254860 | 2.560977 | -1.046171 |
| 28 | 1 | 0 | 2.995387 | -0.574146 | 1.927542 |
| 29 | 1 | 0 | 7.192718 | -2.305605 | 0.281936 |
| 30 | 1 | 0 | 5.892066 | -2.956105 | -0.791509 |
| 31 | 1 | 0 | -4.995382 | 2.323903 | -0.152721 |
| 32 | 1 | 0 | -2.573199 | 2.277548 | -0.826205 |
| 33 | 1 | 0 | -2.637840 | -2.049351 | -0.947113 |
| 34 | 1 | 0 | -7.287059 | -1.719516 | -0.714839 |
| 35 | 1 | 0 | -7.013918 | -1.892300 | 1.063015 |
| 36 | 1 | 0 | 1.481941 | 1.309510 | 2.022222 |
| 37 | 1 | 0 | 1.907889 | 2.805228 | 1.209427 |
| 38 | 1 | 0 | 0.770236 | 2.129085 | -0.833567 |
| 39 | 1 | 0 | 1.007165 | -0.285288 | -0.644830 |
| 40 | 1 | 0 | -0.785762 | 0.925855 | -2.063263 |
| 41 | 1 | 0 | -0.805744 | -0.822532 | -1.909687 |
| 42 | 1 | 0 | -0.955040 | 1.829306 | 1.346210 |
| 43 | 1 | 0 | -0.595459 | -1.641559 | 0.720230 |
| 44 | 1 | 0 | 0.611972 | -0.760707 | 1.654491 |
| 45 | 1 | 0 | -2.085552 | -0.087396 | 1.384390 |

Conformer 2b-4

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -5.846560 | 0.807589 | -0.210918 |
| 2 | 6 | 0 | -5.172333 | 1.991578 | -0.002754 |
| 3 | 6 | 0 | -3.828080 | 1.891176 | 0.402363 |
| 4 | 6 | 0 | -3.195644 | 0.659475 | 0.592174 |
| 5 | 6 | 0 | -3.912348 | -0.539255 | 0.373249 |
| 6 | 6 | 0 | -5.225615 | -0.426374 | -0.027030 |
| 7 | 8 | 0 | -6.130123 | -1.436131 | -0.274583 |
| 8 | 6 | 0 | -7.283584 | -0.789609 | -0.818963 |
| 9 | 8 | 0 | -7.160360 | 0.616376 | -0.578207 |
| 10 | 6 | 0 | 5.076681 | 0.794033 | -0.353872 |
| 11 | 6 | 0 | 5.710865 | -0.441401 | -0.216172 |
| 12 | 6 | 0 | 5.020685 | -1.625455 | -0.353361 |
| 13 | 6 | 0 | 3.643112 | -1.526884 | -0.634954 |
| 14 | 6 | 0 | 2.992876 | -0.295908 | -0.770188 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 6 | 0 | 3.730103 | 0.901465 | -0.626022 |
| 16 | 8 | 0 | 5.985954 | 1.803085 | -0.156001 |
| 17 | 6 | 0 | 7.262649 | 1.160921 | -0.041674 |
| 18 | 8 | 0 | 7.040448 | -0.248698 | 0.075092 |
| 19 | 6 | 0 | -1.743960 | 0.607187 | 1.010905 |
| 20 | 6 | 0 | -0.818286 | -0.021490 | -0.053519 |
| 21 | 6 | 0 | 0.676660 | 0.302163 | 0.179992 |
| 22 | 6 | 0 | 1.503524 | -0.244628 | -1.012393 |
| 23 | 8 | 0 | -1.027203 | -1.429638 | -0.152290 |
| 24 | 6 | 0 | 1.180654 | -0.220123 | 1.532427 |
| 25 | 8 | 0 | 1.112503 | -1.651953 | 1.632443 |
| 26 | 1 | 0 | -5.657347 | 2.951341 | -0.142384 |
| 27 | 1 | 0 | -3.265604 | 2.805031 | 0.573215 |
| 28 | 1 | 0 | -3.431455 | -1.501909 | 0.489885 |
| 29 | 1 | 0 | -7.329534 | -0.972330 | -1.902564 |
| 30 | 1 | 0 | -8.180854 | -1.165584 | -0.320185 |
| 31 | 1 | 0 | 5.516803 | -2.584428 | -0.254983 |
| 32 | 1 | 0 | 3.075389 | -2.441625 | -0.790341 |
| 33 | 1 | 0 | 3.255191 | 1.871981 | -0.725533 |
| 34 | 1 | 0 | 7.855421 | 1.365603 | -0.943412 |
| 35 | 1 | 0 | 7.772080 | 1.524552 | 0.854836 |
| 36 | 1 | 0 | -1.398483 | 1.625181 | 1.231830 |
| 37 | 1 | 0 | -1.641776 | 0.029918 | 1.939073 |
| 38 | 1 | 0 | -1.105412 | 0.385771 | -1.031095 |
| 39 | 1 | 0 | 0.783031 | 1.396286 | 0.213489 |
| 40 | 1 | 0 | 1.135243 | -1.248185 | -1.243696 |
| 41 | 1 | 0 | 1.281054 | 0.373641 | -1.891277 |
| 42 | 1 | 0 | -0.497218 | -1.827588 | 0.567040 |
| 43 | 1 | 0 | 2.207073 | 0.120190 | 1.711125 |
| 44 | 1 | 0 | 0.560326 | 0.162008 | 2.346994 |
| 45 | 1 | 0 | 1.867936 | -2.000933 | 1.130613 |

Conformer 2b-5

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 5.118814 | -0.872258 | 0.214155 |
| 2 | 6 | 0 | 4.395855 | -1.235818 | 1.329849 |
| 3 | 6 | 0 | 3.280016 | -0.439600 | 1.650473 |
| 4 | 6 | 0 | 2.908635 | 0.669878 | 0.885791 |
| 5 | 6 | 0 | 3.672851 | 1.019140 | -0.251632 |
| 6 | 6 | 0 | 4.762812 | 0.233156 | -0.556626 |
| 7 | 8 | 0 | 5.635207 | 0.358769 | -1.612666 |
| 8 | 6 | 0 | 6.670001 | -0.601769 | -1.371619 |
| 9 | 8 | 0 | 6.225923 | -1.480848 | -0.332873 |
| 10 | 6 | 0 | -4.521063 | -0.939105 | -0.433045 |

| | | | | | |
|---|---|---|---|---|---|
| 11 | 6 | 0 | -5.093160 | 0.329031 | -0.388374 |
| 12 | 6 | 0 | -4.349338 | 1.464684 | -0.640094 |
| 13 | 6 | 0 | -2.986959 | 1.287004 | -0.937004 |
| 14 | 6 | 0 | -2.394105 | 0.019144 | -0.980279 |
| 15 | 6 | 0 | -3.185567 | -1.127694 | -0.730579 |
| 16 | 8 | 0 | -5.481832 | -1.890236 | -0.183412 |
| 17 | 6 | 0 | -6.649887 | -1.158329 | 0.210210 |
| 18 | 8 | 0 | -6.435220 | 0.221514 | -0.106081 |
| 19 | 6 | 0 | 1.683275 | 1.480634 | 1.233492 |
| 20 | 6 | 0 | 0.546729 | 1.383761 | 0.188702 |
| 21 | 6 | 0 | 0.069623 | -0.061203 | -0.075319 |
| 22 | 6 | 0 | -0.916449 | -0.156734 | -1.276568 |
| 23 | 8 | 0 | -0.513553 | 2.257635 | 0.552961 |
| 24 | 6 | 0 | -0.459113 | -0.748612 | 1.190760 |
| 25 | 8 | 0 | -1.465042 | 0.008132 | 1.881772 |
| 26 | 1 | 0 | 4.677008 | -2.093277 | 1.931059 |
| 27 | 1 | 0 | 2.696372 | -0.690560 | 2.531531 |
| 28 | 1 | 0 | 3.416859 | 1.879065 | -0.861752 |
| 29 | 1 | 0 | 6.849727 | -1.177801 | -2.283183 |
| 30 | 1 | 0 | 7.582400 | -0.081833 | -1.046887 |
| 31 | 1 | 0 | -4.799025 | 2.450839 | -0.609264 |
| 32 | 1 | 0 | -2.361941 | 2.157902 | -1.092361 |
| 33 | 1 | 0 | -2.762724 | -2.125762 | -0.781275 |
| 34 | 1 | 0 | -7.514469 | -1.528956 | -0.346345 |
| 35 | 1 | 0 | -6.800323 | -1.266969 | 1.293507 |
| 36 | 1 | 0 | 1.296576 | 1.178117 | 2.213084 |
| 37 | 1 | 0 | 1.933874 | 2.544846 | 1.315874 |
| 38 | 1 | 0 | 0.933251 | 1.774044 | -0.761927 |
| 39 | 1 | 0 | 0.966746 | -0.622156 | -0.369599 |
| 40 | 1 | 0 | -0.608435 | 0.575842 | -2.031522 |
| 41 | 1 | 0 | -0.783593 | -1.144516 | -1.734074 |
| 42 | 1 | 0 | -1.000615 | 1.784924 | 1.256153 |
| 43 | 1 | 0 | -0.840037 | -1.750466 | 0.947460 |
| 44 | 1 | 0 | 0.351034 | -0.880067 | 1.911385 |
| 45 | 1 | 0 | -2.274386 | -0.054792 | 1.346770 |

Conformer 2b-6

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -5.920447 | 0.510047 | -0.220860 |
| 2 | 6 | 0 | -5.371396 | 1.760178 | -0.032593 |
| 3 | 6 | 0 | -4.024355 | 1.804764 | 0.373275 |
| 4 | 6 | 0 | -3.269190 | 0.647691 | 0.582984 |
| 5 | 6 | 0 | -3.859045 | -0.621640 | 0.384479 |
| 6 | 6 | 0 | -5.176501 | -0.650607 | -0.016888 |

| | | | | | |
|---|---|---|---|---|---|
| 7 | 8 | 0 | -5.972535 | -1.751643 | -0.247379 |
| 8 | 6 | 0 | -7.184163 | -1.235509 | -0.804402 |
| 9 | 8 | 0 | -7.207259 | 0.179017 | -0.584336 |
| 10 | 6 | 0 | 5.110506 | -0.665152 | -0.329753 |
| 11 | 6 | 0 | 5.697293 | 0.593249 | -0.236042 |
| 12 | 6 | 0 | 4.962482 | 1.748151 | -0.414376 |
| 13 | 6 | 0 | 3.592101 | 1.595953 | -0.688682 |
| 14 | 6 | 0 | 2.985489 | 0.338686 | -0.781160 |
| 15 | 6 | 0 | 3.765109 | -0.825528 | -0.598600 |
| 16 | 8 | 0 | 6.054840 | -1.635660 | -0.103571 |
| 17 | 6 | 0 | 7.308074 | -0.943134 | -0.017519 |
| 18 | 8 | 0 | 7.034459 | 0.460374 | 0.058159 |
| 19 | 6 | 0 | -1.819976 | 0.751328 | 1.000560 |
| 20 | 6 | 0 | -0.834622 | 0.204561 | -0.055561 |
| 21 | 6 | 0 | 0.618782 | 0.684753 | 0.169570 |
| 22 | 6 | 0 | 1.498659 | 0.208280 | -1.014741 |
| 23 | 8 | 0 | -0.897018 | -1.219000 | -0.131715 |
| 24 | 6 | 0 | 1.172927 | 0.245406 | 1.531405 |
| 25 | 8 | 0 | 1.238815 | -1.184065 | 1.669228 |
| 26 | 1 | 0 | -5.952062 | 2.662742 | -0.187784 |
| 27 | 1 | 0 | -3.558626 | 2.774150 | 0.528515 |
| 28 | 1 | 0 | -3.282136 | -1.527896 | 0.516522 |
| 29 | 1 | 0 | -7.206411 | -1.437722 | -1.885312 |
| 30 | 1 | 0 | -8.039972 | -1.694566 | -0.302426 |
| 31 | 1 | 0 | 5.425806 | 2.726121 | -0.345994 |
| 32 | 1 | 0 | 2.986071 | 2.485629 | -0.835632 |
| 33 | 1 | 0 | 3.332114 | -1.816187 | -0.705444 |
| 34 | 1 | 0 | 7.835766 | -1.260531 | 0.885882 |
| 35 | 1 | 0 | 7.902272 | -1.153603 | -0.917109 |
| 36 | 1 | 0 | -1.580880 | 1.802732 | 1.205170 |
| 37 | 1 | 0 | -1.658935 | 0.202116 | 1.937397 |
| 38 | 1 | 0 | -1.162639 | 0.564012 | -1.038957 |
| 39 | 1 | 0 | 0.612351 | 1.784403 | 0.182372 |
| 40 | 1 | 0 | 1.247116 | -0.836177 | -1.220931 |
| 41 | 1 | 0 | 1.202163 | 0.775198 | -1.905893 |
| 42 | 1 | 0 | -0.335468 | -1.547705 | 0.598439 |
| 43 | 1 | 0 | 2.163067 | 0.685177 | 1.696415 |
| 44 | 1 | 0 | 0.520827 | 0.588050 | 2.338699 |
| 45 | 1 | 0 | 2.028807 | -1.476999 | 1.186419 |

Conformer 2b-7

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 4.219419 | -1.488073 | 0.634611 |
| 2 | 6 | 0 | 3.523127 | -1.396708 | 1.820602 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 6 | 0 | 2.597241 | -0.342412 | 1.930929 |
| 4 | 6 | 0 | 2.386055 | 0.576534 | 0.899538 |
| 5 | 6 | 0 | 3.115999 | 0.459772 | -0.305283 |
| 6 | 6 | 0 | 4.015674 | -0.578949 | -0.401672 |
| 7 | 8 | 0 | 4.855344 | -0.883781 | -1.450957 |
| 8 | 6 | 0 | 5.445421 | -2.141947 | -1.113061 |
| 9 | 8 | 0 | 5.193572 | -2.392724 | 0.273736 |
| 10 | 6 | 0 | -4.081805 | -1.036275 | 0.322091 |
| 11 | 6 | 0 | -3.555928 | -1.895391 | -0.639844 |
| 12 | 6 | 0 | -2.619937 | -1.467150 | -1.558197 |
| 13 | 6 | 0 | -2.219579 | -0.121329 | -1.478832 |
| 14 | 6 | 0 | -2.742184 | 0.750929 | -0.518482 |
| 15 | 6 | 0 | -3.699753 | 0.285821 | 0.408559 |
| 16 | 8 | 0 | -5.012134 | -1.707691 | 1.082529 |
| 17 | 6 | 0 | -4.904518 | -3.080864 | 0.689036 |
| 18 | 8 | 0 | -4.138683 | -3.137204 | -0.518269 |
| 19 | 6 | 0 | 1.361808 | 1.676575 | 1.059989 |
| 20 | 6 | 0 | 0.163919 | 1.539445 | 0.096448 |
| 21 | 6 | 0 | -1.062178 | 2.371650 | 0.536412 |
| 22 | 6 | 0 | -2.253034 | 2.177372 | -0.432020 |
| 23 | 8 | 0 | 0.538846 | 1.851700 | -1.246563 |
| 24 | 6 | 0 | -0.730951 | 3.861507 | 0.691717 |
| 25 | 8 | 0 | -0.213866 | 4.451048 | -0.515092 |
| 26 | 1 | 0 | 3.684740 | -2.102524 | 2.627783 |
| 27 | 1 | 0 | 2.027693 | -0.242935 | 2.850876 |
| 28 | 1 | 0 | 2.947849 | 1.145495 | -1.125674 |
| 29 | 1 | 0 | 4.985464 | -2.937089 | -1.717956 |
| 30 | 1 | 0 | 6.524334 | -2.095092 | -1.283005 |
| 31 | 1 | 0 | -2.213835 | -2.138990 | -2.306062 |
| 32 | 1 | 0 | -1.464690 | 0.250755 | -2.164487 |
| 33 | 1 | 0 | -4.125838 | 0.943971 | 1.159213 |
| 34 | 1 | 0 | -4.388517 | -3.647167 | 1.477697 |
| 35 | 1 | 0 | -5.903433 | -3.484862 | 0.505230 |
| 36 | 1 | 0 | 0.991998 | 1.672425 | 2.093258 |
| 37 | 1 | 0 | 1.830408 | 2.656223 | 0.896355 |
| 38 | 1 | 0 | -0.132727 | 0.487213 | 0.074546 |
| 39 | 1 | 0 | -1.369151 | 2.009603 | 1.528644 |
| 40 | 1 | 0 | -3.075195 | 2.828460 | -0.105290 |
| 41 | 1 | 0 | -1.949158 | 2.509549 | -1.430288 |
| 42 | 1 | 0 | 0.609914 | 2.825557 | -1.271346 |
| 43 | 1 | 0 | -1.618214 | 4.414973 | 1.031647 |
| 44 | 1 | 0 | 0.053739 | 4.009674 | 1.437393 |
| 45 | 1 | 0 | -0.952790 | 4.540934 | -1.136855 |

Conformer 2b-8

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.249178 | -0.641020 | 0.473089 |
| 2 | 6 | 0 | -3.887347 | 0.335377 | 1.378607 |
| 3 | 6 | 0 | -2.883649 | 1.234196 | 0.978920 |
| 4 | 6 | 0 | -2.276324 | 1.156096 | -0.278399 |
| 5 | 6 | 0 | -2.667899 | 0.148202 | -1.185131 |
| 6 | 6 | 0 | -3.650485 | -0.730954 | -0.779750 |
| 7 | 8 | 0 | -4.219083 | -1.765428 | -1.490852 |
| 8 | 6 | 0 | -5.050211 | -2.455281 | -0.551193 |
| 9 | 8 | 0 | -5.217568 | -1.614809 | 0.594176 |
| 10 | 6 | 0 | 2.759379 | -1.728376 | 0.695909 |
| 11 | 6 | 0 | 3.451679 | -2.226839 | -0.406021 |
| 12 | 6 | 0 | 3.937683 | -1.393758 | -1.391894 |
| 13 | 6 | 0 | 3.697749 | -0.016744 | -1.232278 |
| 14 | 6 | 0 | 3.003976 | 0.494123 | -0.132091 |
| 15 | 6 | 0 | 2.520046 | -0.381524 | 0.865784 |
| 16 | 8 | 0 | 2.417322 | -2.766660 | 1.531855 |
| 17 | 6 | 0 | 2.745958 | -3.959667 | 0.813603 |
| 18 | 8 | 0 | 3.569168 | -3.594096 | -0.300055 |
| 19 | 6 | 0 | -1.163128 | 2.104857 | -0.654850 |
| 20 | 6 | 0 | 0.186888 | 1.708658 | -0.018950 |
| 21 | 6 | 0 | 1.395714 | 2.420691 | -0.667168 |
| 22 | 6 | 0 | 2.731173 | 1.976131 | -0.024217 |
| 23 | 8 | 0 | 0.168162 | 1.907303 | 1.393726 |
| 24 | 6 | 0 | 1.263597 | 3.948634 | -0.626142 |
| 25 | 8 | 0 | 1.109816 | 4.463131 | 0.709242 |
| 26 | 1 | 0 | -4.357976 | 0.403075 | 2.353164 |
| 27 | 1 | 0 | -2.552260 | 1.998296 | 1.672885 |
| 28 | 1 | 0 | -2.215429 | 0.066518 | -2.168220 |
| 29 | 1 | 0 | -6.025531 | -2.650721 | -1.004359 |
| 30 | 1 | 0 | -4.560284 | -3.392892 | -0.249673 |
| 31 | 1 | 0 | 4.483063 | -1.784586 | -2.243692 |
| 32 | 1 | 0 | 4.066349 | 0.670235 | -1.989523 |
| 33 | 1 | 0 | 1.962470 | -0.002241 | 1.715165 |
| 34 | 1 | 0 | 3.300883 | -4.636949 | 1.467977 |
| 35 | 1 | 0 | 1.823509 | -4.432344 | 0.446856 |
| 36 | 1 | 0 | -1.050943 | 2.125645 | -1.746777 |
| 37 | 1 | 0 | -1.416113 | 3.124919 | -0.340630 |
| 38 | 1 | 0 | 0.316272 | 0.631415 | -0.156913 |
| 39 | 1 | 0 | 1.419929 | 2.131639 | -1.728121 |
| 40 | 1 | 0 | 3.546411 | 2.532392 | -0.505363 |
| 41 | 1 | 0 | 2.722057 | 2.260577 | 1.033863 |
| 42 | 1 | 0 | 0.251901 | 2.872346 | 1.516524 |

| | | | | | |
|---|---|---|---|---|---|
| 43 | 1 | 0 | 2.129578 | 4.418782 | -1.114100 |
| 44 | 1 | 0 | 0.368673 | 4.276163 | -1.160459 |
| 45 | 1 | 0 | 1.971191 | 4.395388 | 1.149700 |

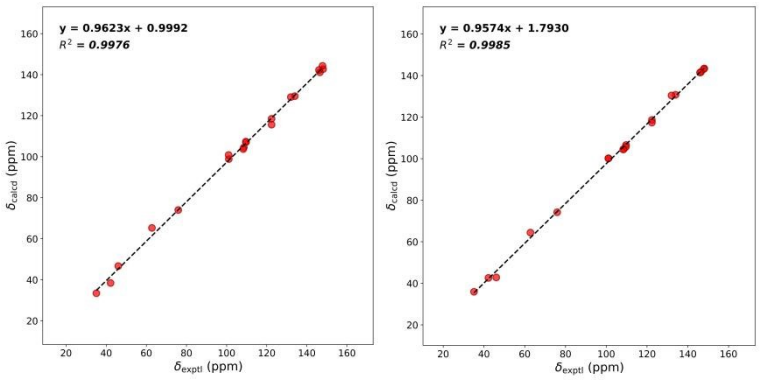
**S56. Experimental and calculated $^{13}$C NMR chemical shifts of 2a and 2b**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **2a** | **2b** | | | **2a** | **2b** |
| 7' | 42.2 | 38.4 | 42.6 | 10 | 101.1 | 98.8 | 100.2 |
| 8' | 75.9 | 74.0 | 74.2 | 9 | 62.8 | 65.3 | 64.4 |
| 8 | 46.0 | 46.7 | 42.9 | 1' | 132.0 | 129.1 | 130.4 |
| 7 | 35.1 | 33.40 | 35.9 | 2' | 109.6 | 107.4 | 105.6 |
| 1 | 134.0 | 129.5 | 130.7 | 3' | 147.8 | 144.3 | 143.1 |
| 2 | 109.7 | 107.1 | 106.6 | 4' | 146.0 | 142.3 | 141.4 |
| 3 | 148.1 | 142.7 | 143.4 | 5' | 108.3 | 103.7 | 104.4 |
| 4 | 146.5 | 141.1 | 141.7 | 6' | 122.4 | 118.5 | 117.4 |
| 5 | 108.6 | 104.5 | 104.7 | 10' | 101.0 | 100.8 | 100.2 |
| 6 | 122.4 | 115.6 | 118.6 | | | | |
| | | | | $R^2$ | | 0.9976 | 0.9985 |
| | | | | MAE | | 2.85 | 2.60 |
| | | | | CMAE | | 2.59 | 1.00 |

**S57. Experimental and calculated $^{1}$H NMR chemical shifts of 2a and 2b**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **2a** | **2b** | | | **2a** | **2b** |
| 7a | 2.78 | 2.45 | 1.95 | 10a | 5.93 | 5.61 | 5.59 |
| 7b | 2.78 | 2.23 | 2.58 | 10b | 5.93 | 5.33 | 6.68 |
| 8' | 3.85 | 3.42 | 3.21 | 9a | 3.62 | 3.75 | 3.19 |
| 8 | 1.77 | 1.97 | 0.43 | 9b | 3.96 | 3.20 | 3.75 |
| 7'a | 2.78 | 1.21 | 1.98 | 2' | 6.68 | 5.83 | 6.51 |
| 7'b | 2.78 | 1.88 | 2.41 | 5' | 6.74 | 6.43 | 6.32 |
| 2 | 6.68 | 4.61 | 6.42 | 6' | 6.64 | 6.39 | 6.12 |
| 5 | 6.74 | 6.50 | 6.49 | 10'a | 5.93 | 5.76 | 5.55 |
| 6 | 6.64 | 6.55 | 5.75 | 10'b | 5.93 | 5.80 | 5.66 |

**S58. Linear regression analysis between the experimental and calculated $^{13}$C NMR chemical shifts of 2a/2b**

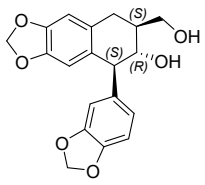


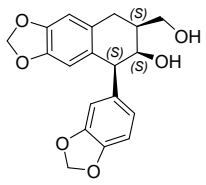

**S59. DP4+ probability analysis of 2a/2b**

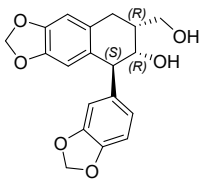
| Functional | Solvent? | Basis Set | Type of Data |
|---|---|---|---|
| mPW1PW91 | PCM | 6-31+G(d,p) | Unscaled Shifts |

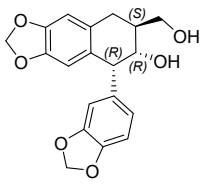
| | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
|---|---|---|---|---|---|---|
| sDP4+ (H data) | 0.00% | 100.00% | | | | |
| sDP4+ (C data) | 82.35% | 17.65% | | | | |
| sDP4+ (all data) | 0.00% | 100.00% | | | | |
| uDP4+ (H data) | 22.77% | 77.23% | | | | |
| uDP4+ (C data) | 5.94% | 94.06% | | | | |
| uDP4+ (all data) | 1.83% | 98.17% | | | | |
| DP4+ (H data) | 0.00% | 100.00% | | | | |
| DP4+ (C data) | 22.76% | 77.24% | | | | |
| DP4+ (all data) | 0.00% | 100.00% | | | | |

**S60. Structures of two possible diastereoisomers of 3 (3a-3d).**


(8*S*, 7'*S*, 8'*R*)-3a


(8*S*, 7'*S*, 8'*S*)-3b


(8*R*, 7'*S*, 8'*R*)-3c


(8*S*, 7'*R*, 8'*R*)-3d

**S61. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 3a inthe gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **3a-1** | -1186.067787 | -744268.8037 | 3.2368 | 0.310% |
| **3a-2** | -1186.066911 | -744268.2545 | 3.7861 | 0.123% |
| **3a-3** | -1186.071966 | -744271.4262 | 0.6143 | 25.908% |
| **3a-4** | -1186.072945 | -744272.0405 | 0 | 73.082% |
| **3a-5** | -1186.067827 | -744268.8289 | 3.2117 | 0.323% |
| **3a-6** | -1186.067603 | -744268.6885 | 3.352 | 0.255% |

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory;

[b]Gibbs free energ (E*627.51);

[c]The relative Gibbs free energy;

[d]The Boltzmann distribution of eac conformer.

**S62. Cartesian coordinates for the low-energy Conf. of Compound 3a at B3LYP/6311+G(d,p)**

**level of theory in methanol.**

Conformer 3a-1

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.839686 | -0.882780 | 0.401847 |
| 2 | 6 | 0 | -3.486179 | -0.336107 | 1.616068 |
| 3 | 6 | 0 | -2.200935 | 0.232941 | 1.704249 |
| 4 | 6 | 0 | -1.319202 | 0.244351 | 0.624306 |
| 5 | 6 | 0 | -1.702476 | -0.334294 | -0.605999 |
| 6 | 6 | 0 | -2.963370 | -0.880788 | -0.683894 |
| 7 | 8 | 0 | -3.551456 | -1.517905 | -1.750910 |
| 8 | 6 | 0 | -4.907376 | -1.756562 | -1.356465 |
| 9 | 8 | 0 | -5.006426 | -1.521454 | 0.052593 |
| 10 | 6 | 0 | 3.288656 | -1.729335 | -0.240217 |
| 11 | 6 | 0 | 2.180084 | -2.193705 | 0.464882 |
| 12 | 6 | 0 | 1.126639 | -1.368546 | 0.778109 |
| 13 | 6 | 0 | 1.194899 | -0.018651 | 0.360693 |
| 14 | 6 | 0 | 2.313228 | 0.451924 | -0.340092 |
| 15 | 6 | 0 | 3.382697 | -0.419549 | -0.648926 |
| 16 | 8 | 0 | 4.197535 | -2.748066 | -0.398718 |
| 17 | 6 | 0 | 3.543143 | -3.926226 | 0.089255 |
| 18 | 8 | 0 | 2.355154 | -3.522245 | 0.778077 |
| 19 | 6 | 0 | 0.041468 | 0.906426 | 0.743084 |
| 20 | 6 | 0 | 0.070831 | 2.235105 | -0.036140 |
| 21 | 6 | 0 | 1.474771 | 2.846568 | -0.055923 |
| 22 | 6 | 0 | 2.409357 | 1.889782 | -0.804013 |
| 23 | 8 | 0 | -0.922303 | 3.134805 | 0.483338 |
| 24 | 6 | 0 | 1.497769 | 4.237368 | -0.707246 |
| 25 | 8 | 0 | 0.813447 | 5.224414 | 0.039055 |
| 26 | 1 | 0 | -4.165399 | -0.347326 | 2.460990 |
| 27 | 1 | 0 | -1.889490 | 0.676398 | 2.646006 |
| 28 | 1 | 0 | -1.023696 | -0.360687 | -1.451362 |
| 29 | 1 | 0 | -5.571143 | -1.062736 | -1.891043 |
| 30 | 1 | 0 | -5.170063 | -2.795840 | -1.570421 |
| 31 | 1 | 0 | 0.264251 | -1.738955 | 1.319832 |
| 32 | 1 | 0 | 4.252642 | -0.062176 | -1.190297 |
| 33 | 1 | 0 | 3.274241 | -4.571257 | -0.758731 |
| 34 | 1 | 0 | 4.206758 | -4.447873 | 0.784222 |
| 35 | 1 | 0 | 0.180395 | 1.177402 | 1.803729 |
| 36 | 1 | 0 | -0.247694 | 2.055226 | -1.070143 |
| 37 | 1 | 0 | 1.822035 | 2.956456 | 0.982470 |
| 38 | 1 | 0 | 2.177585 | 1.941799 | -1.879780 |
| 39 | 1 | 0 | 3.444558 | 2.238964 | -0.706512 |
| 40 | 1 | 0 | -0.813834 | 3.158785 | 1.448708 |

| | | | | | |
|---|---|---|---|---|---|
| 41 | 1 | 0 | 1.095245 | 4.153875 | -1.733495 |
| 42 | 1 | 0 | 2.535986 | 4.577220 | -0.797877 |
| 43 | 1 | 0 | -0.085895 | 4.866808 | 0.154753 |

Conformer 3a-2

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.606190 | -1.251407 | 0.769305 |
| 2 | 6 | 0 | 2.551205 | -1.169344 | 1.656192 |
| 3 | 6 | 0 | 1.388947 | -0.525048 | 1.202000 |
| 4 | 6 | 0 | 1.293185 | 0.010208 | -0.086316 |
| 5 | 6 | 0 | 2.381989 | -0.093989 | -0.973378 |
| 6 | 6 | 0 | 3.520392 | -0.726068 | -0.516384 |
| 7 | 8 | 0 | 4.689575 | -0.974944 | -1.197119 |
| 8 | 6 | 0 | 5.592644 | -1.505701 | -0.219606 |
| 9 | 8 | 0 | 4.832456 | -1.851302 | 0.943481 |
| 10 | 6 | 0 | -3.569007 | -1.492560 | 0.125066 |
| 11 | 6 | 0 | -2.416165 | -2.112321 | -0.353534 |
| 12 | 6 | 0 | -1.248818 | -1.413725 | -0.547235 |
| 13 | 6 | 0 | -1.245972 | -0.030511 | -0.249495 |
| 14 | 6 | 0 | -2.407193 | 0.595421 | 0.221849 |
| 15 | 6 | 0 | -3.593014 | -0.149197 | 0.418070 |
| 16 | 8 | 0 | -4.575730 | -2.419791 | 0.250837 |
| 17 | 6 | 0 | -4.064060 | -3.623928 | -0.334340 |
| 18 | 8 | 0 | -2.658675 | -3.453186 | -0.546098 |
| 19 | 6 | 0 | 0.037695 | 0.752287 | -0.514460 |
| 20 | 6 | 0 | 0.013209 | 2.164377 | 0.104332 |
| 21 | 6 | 0 | -1.320834 | 2.874649 | -0.141468 |
| 22 | 6 | 0 | -2.431569 | 2.073632 | 0.546086 |
| 23 | 8 | 0 | 1.141310 | 2.923562 | -0.362506 |
| 24 | 6 | 0 | -1.313467 | 4.324383 | 0.366282 |
| 25 | 8 | 0 | -0.439262 | 5.174371 | -0.350620 |
| 26 | 1 | 0 | 2.618654 | -1.588569 | 2.653824 |
| 27 | 1 | 0 | 0.534197 | -0.450300 | 1.867246 |
| 28 | 1 | 0 | 2.331419 | 0.306602 | -1.980405 |
| 29 | 1 | 0 | 6.073527 | -2.402304 | -0.618943 |
| 30 | 1 | 0 | 6.337134 | -0.740803 | 0.043041 |
| 31 | 1 | 0 | -0.352085 | -1.906637 | -0.903973 |
| 32 | 1 | 0 | -4.494820 | 0.328238 | 0.787293 |
| 33 | 1 | 0 | -4.229738 | -4.458858 | 0.351836 |
| 34 | 1 | 0 | -4.561371 | -3.800874 | -1.298149 |
| 35 | 1 | 0 | 0.102979 | 0.905105 | -1.605285 |
| 36 | 1 | 0 | 0.176026 | 2.084320 | 1.185669 |
| 37 | 1 | 0 | -1.509179 | 2.898311 | -1.225631 |
| 38 | 1 | 0 | -2.341245 | 2.210568 | 1.635475 |

| | | | | | |
|---|---|---|---|---|---|
| 39 | 1 | 0 | -3.407381 | 2.493835 | 0.273905 |
| 40 | 1 | 0 | 1.113732 | 2.908193 | -1.334043 |
| 41 | 1 | 0 | -1.077201 | 4.319382 | 1.446050 |
| 42 | 1 | 0 | -2.318334 | 4.749259 | 0.260673 |
| 43 | 1 | 0 | 0.434142 | 4.747906 | -0.280183 |

Conformer 3a-3

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.602762 | -1.322355 | 0.746365 |
| 2 | 6 | 0 | 2.521983 | -1.314836 | 1.606252 |
| 3 | 6 | 0 | 1.359408 | -0.663907 | 1.162327 |
| 4 | 6 | 0 | 1.284834 | -0.051213 | -0.094143 |
| 5 | 6 | 0 | 2.407552 | -0.068222 | -0.950928 |
| 6 | 6 | 0 | 3.544586 | -0.712763 | -0.503339 |
| 7 | 8 | 0 | 4.752698 | -0.849795 | -1.142707 |
| 8 | 6 | 0 | 5.532148 | -1.720468 | -0.312126 |
| 9 | 8 | 0 | 4.850312 | -1.866213 | 0.939446 |
| 10 | 6 | 0 | -3.647698 | -1.388381 | 0.109158 |
| 11 | 6 | 0 | -2.512092 | -2.059556 | -0.339539 |
| 12 | 6 | 0 | -1.316058 | -1.408454 | -0.525637 |
| 13 | 6 | 0 | -1.265032 | -0.021630 | -0.250821 |
| 14 | 6 | 0 | -2.409988 | 0.656997 | 0.189949 |
| 15 | 6 | 0 | -3.625472 | -0.039940 | 0.378505 |
| 16 | 8 | 0 | -4.690576 | -2.275573 | 0.235252 |
| 17 | 6 | 0 | -4.218289 | -3.503396 | -0.332635 |
| 18 | 8 | 0 | -2.802199 | -3.394138 | -0.512074 |
| 19 | 6 | 0 | 0.041456 | 0.719033 | -0.509408 |
| 20 | 6 | 0 | 0.059759 | 2.108826 | 0.158783 |
| 21 | 6 | 0 | -1.213043 | 2.892044 | -0.144899 |
| 22 | 6 | 0 | -2.391567 | 2.143253 | 0.486219 |
| 23 | 8 | 0 | 1.186682 | 2.860275 | -0.301232 |
| 24 | 6 | 0 | -1.146496 | 4.337489 | 0.371214 |
| 25 | 8 | 0 | -0.282253 | 5.166875 | -0.377351 |
| 26 | 1 | 0 | 2.572346 | -1.791768 | 2.578664 |
| 27 | 1 | 0 | 0.484403 | -0.651061 | 1.804247 |
| 28 | 1 | 0 | 2.373976 | 0.397637 | -1.930215 |
| 29 | 1 | 0 | 5.622446 | -2.702294 | -0.796492 |
| 30 | 1 | 0 | 6.515329 | -1.274134 | -0.140856 |
| 31 | 1 | 0 | -0.434695 | -1.940946 | -0.863411 |
| 32 | 1 | 0 | -4.514962 | 0.477312 | 0.723335 |
| 33 | 1 | 0 | -4.435407 | -4.326736 | 0.352935 |
| 34 | 1 | 0 | -4.700029 | -3.663725 | -1.307404 |
| 35 | 1 | 0 | 0.117337 | 0.913568 | -1.588778 |
| 36 | 1 | 0 | 0.131912 | 1.973355 | 1.250916 |

| | | | | | |
|---|---|---|---|---|---|
| 37 | 1 | 0 | -1.342730 | 2.933608 | -1.234890 |
| 38 | 1 | 0 | -2.364251 | 2.295298 | 1.576973 |
| 39 | 1 | 0 | -3.331411 | 2.594963 | 0.146708 |
| 40 | 1 | 0 | 1.985501 | 2.343916 | -0.103237 |
| 41 | 1 | 0 | -0.869908 | 4.318174 | 1.441985 |
| 42 | 1 | 0 | -2.143298 | 4.789823 | 0.307555 |
| 43 | 1 | 0 | 0.563599 | 4.686453 | -0.420492 |

Conformer 3a-4

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -3.878539 | -0.844250 | 0.362807 |
| 2 | 6 | 0 | -3.584988 | -0.152990 | 1.517644 |
| 3 | 6 | 0 | -2.285023 | 0.382162 | 1.623951 |
| 4 | 6 | 0 | -1.331627 | 0.225155 | 0.613840 |
| 5 | 6 | 0 | -1.664493 | -0.483009 | -0.564533 |
| 6 | 6 | 0 | -2.935412 | -1.004144 | -0.654175 |
| 7 | 8 | 0 | -3.492465 | -1.711749 | -1.690826 |
| 8 | 6 | 0 | -4.782294 | -2.131289 | -1.229462 |
| 9 | 8 | 0 | -5.057641 | -1.447282 | -0.000818 |
| 10 | 6 | 0 | 3.335038 | -1.661320 | -0.249630 |
| 11 | 6 | 0 | 2.241575 | -2.155068 | 0.458841 |
| 12 | 6 | 0 | 1.164745 | -1.359192 | 0.769010 |
| 13 | 6 | 0 | 1.194771 | -0.008496 | 0.349488 |
| 14 | 6 | 0 | 2.299116 | 0.492239 | -0.354200 |
| 15 | 6 | 0 | 3.390497 | -0.351137 | -0.664234 |
| 16 | 8 | 0 | 4.251196 | -2.667196 | -0.447636 |
| 17 | 6 | 0 | 3.775311 | -3.775930 | 0.325210 |
| 18 | 8 | 0 | 2.432642 | -3.490525 | 0.732032 |
| 19 | 6 | 0 | 0.027953 | 0.892247 | 0.734990 |
| 20 | 6 | 0 | 0.020440 | 2.207526 | -0.070203 |
| 21 | 6 | 0 | 1.395385 | 2.867320 | -0.075785 |
| 22 | 6 | 0 | 2.364697 | 1.935862 | -0.811045 |
| 23 | 8 | 0 | -0.929011 | 3.118269 | 0.489097 |
| 24 | 6 | 0 | 1.372728 | 4.257605 | -0.728906 |
| 25 | 8 | 0 | 0.738400 | 5.243108 | 0.059532 |
| 26 | 1 | 0 | -4.318015 | -0.032446 | 2.307233 |
| 27 | 1 | 0 | -2.010761 | 0.920880 | 2.526413 |
| 28 | 1 | 0 | -0.938545 | -0.624759 | -1.357102 |
| 29 | 1 | 0 | -5.538568 | -1.862690 | -1.972122 |
| 30 | 1 | 0 | -4.771869 | -3.214754 | -1.050263 |
| 31 | 1 | 0 | 0.313349 | -1.753592 | 1.311534 |
| 32 | 1 | 0 | 4.247655 | 0.027497 | -1.211547 |
| 33 | 1 | 0 | 3.784053 | -4.678152 | -0.292132 |
| 34 | 1 | 0 | 4.409219 | -3.899937 | 1.214370 |

| | | | | | |
|---|---|---|---|---|---|
| 35 | 1 | 0 | 0.156193 | 1.193137 | 1.784460 |
| 36 | 1 | 0 | -0.259585 | 1.981953 | -1.113170 |
| 37 | 1 | 0 | 1.722933 | 2.993939 | 0.965039 |
| 38 | 1 | 0 | 2.152931 | 1.984846 | -1.890997 |
| 39 | 1 | 0 | 3.388388 | 2.310534 | -0.691541 |
| 40 | 1 | 0 | -1.785089 | 2.659523 | 0.531956 |
| 41 | 1 | 0 | 0.907710 | 4.171157 | -1.728738 |
| 42 | 1 | 0 | 2.402591 | 4.600226 | -0.884818 |
| 43 | 1 | 0 | -0.126828 | 4.865886 | 0.298726 |

Conformer 3a-5

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.860873 | -0.835909 | -0.360736 |
| 2 | 6 | 0 | 3.563996 | -0.184300 | -1.538756 |
| 3 | 6 | 0 | 2.273707 | 0.365919 | -1.652184 |
| 4 | 6 | 0 | 1.330029 | 0.257287 | -0.630724 |
| 5 | 6 | 0 | 1.658437 | -0.420365 | 0.564290 |
| 6 | 6 | 0 | 2.926263 | -0.948157 | 0.667026 |
| 7 | 8 | 0 | 3.468710 | -1.672719 | 1.705769 |
| 8 | 6 | 0 | 4.852330 | -1.830404 | 1.375375 |
| 9 | 8 | 0 | 5.021195 | -1.486988 | -0.003470 |
| 10 | 6 | 0 | -3.255784 | -1.744901 | 0.251342 |
| 11 | 6 | 0 | -2.186709 | -2.179841 | -0.529590 |
| 12 | 6 | 0 | -1.143916 | -1.346102 | -0.855353 |
| 13 | 6 | 0 | -1.178341 | -0.016948 | -0.371590 |
| 14 | 6 | 0 | -2.258113 | 0.421703 | 0.404894 |
| 15 | 6 | 0 | -3.319455 | -0.455632 | 0.725397 |
| 16 | 8 | 0 | -4.165099 | -2.765711 | 0.403189 |
| 17 | 6 | 0 | -3.536281 | -3.923165 | -0.161371 |
| 18 | 8 | 0 | -2.389090 | -3.490614 | -0.899027 |
| 19 | 6 | 0 | -0.035494 | 0.910450 | -0.771085 |
| 20 | 6 | 0 | -0.048598 | 2.263878 | -0.035470 |
| 21 | 6 | 0 | -1.471789 | 2.818572 | 0.113079 |
| 22 | 6 | 0 | -2.314256 | 1.837215 | 0.934861 |
| 23 | 8 | 0 | 0.797595 | 3.121946 | -0.783400 |
| 24 | 6 | 0 | -1.497301 | 4.194625 | 0.787316 |
| 25 | 8 | 0 | -0.750214 | 5.203801 | 0.093749 |
| 26 | 1 | 0 | 4.292225 | -0.100956 | -2.337754 |
| 27 | 1 | 0 | 2.009541 | 0.909373 | -2.553472 |
| 28 | 1 | 0 | 0.934105 | -0.534260 | 1.363308 |
| 29 | 1 | 0 | 5.456510 | -1.154373 | 1.997883 |
| 30 | 1 | 0 | 5.145905 | -2.872119 | 1.528745 |
| 31 | 1 | 0 | -0.311076 | -1.694432 | -1.455256 |
| 32 | 1 | 0 | -4.159253 | -0.119051 | 1.324754 |

| | | | | | |
|---|---|---|---|---|---|
| 33 | 1 | 0 | -3.220043 | -4.597045 | 0.647367 |
| 34 | 1 | 0 | -4.235993 | -4.422306 | -0.837011 |
| 35 | 1 | 0 | -0.168191 | 1.167149 | -1.831159 |
| 36 | 1 | 0 | 0.356065 | 2.113688 | 0.982554 |
| 37 | 1 | 0 | -1.907364 | 2.908700 | -0.894645 |
| 38 | 1 | 0 | -1.958666 | 1.855135 | 1.977318 |
| 39 | 1 | 0 | -3.356904 | 2.177239 | 0.969293 |
| 40 | 1 | 0 | 0.655215 | 4.022724 | -0.436776 |
| 41 | 1 | 0 | -1.033612 | 4.132321 | 1.777856 |
| 42 | 1 | 0 | -2.537254 | 4.524054 | 0.930634 |
| 43 | 1 | 0 | -1.143575 | 5.302892 | -0.788449 |

Conformer 3a-6

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.564943 | -1.343342 | 0.760364 |
| 2 | 6 | 0 | 2.467928 | -1.359529 | 1.585696 |
| 3 | 6 | 0 | 1.325502 | -0.693352 | 1.129234 |
| 4 | 6 | 0 | 1.292201 | -0.041682 | -0.102848 |
| 5 | 6 | 0 | 2.429622 | -0.037691 | -0.924645 |
| 6 | 6 | 0 | 3.542666 | -0.695016 | -0.466471 |
| 7 | 8 | 0 | 4.760541 | -0.832189 | -1.087484 |
| 8 | 6 | 0 | 5.570936 | -1.606266 | -0.198399 |
| 9 | 8 | 0 | 4.795738 | -1.918355 | 0.963884 |
| 10 | 6 | 0 | -3.593066 | -1.422475 | 0.126962 |
| 11 | 6 | 0 | -2.480809 | -2.049738 | -0.422388 |
| 12 | 6 | 0 | -1.306341 | -1.381989 | -0.627257 |
| 13 | 6 | 0 | -1.245185 | -0.021316 | -0.263431 |
| 14 | 6 | 0 | -2.367591 | 0.610745 | 0.278527 |
| 15 | 6 | 0 | -3.565606 | -0.101630 | 0.480815 |
| 16 | 8 | 0 | -4.631503 | -2.313443 | 0.224781 |
| 17 | 6 | 0 | -4.134915 | -3.553635 | -0.292687 |
| 18 | 8 | 0 | -2.775405 | -3.362918 | -0.694894 |
| 19 | 6 | 0 | 0.053771 | 0.725789 | -0.540699 |
| 20 | 6 | 0 | 0.091130 | 2.149650 | 0.047516 |
| 21 | 6 | 0 | -1.260395 | 2.862935 | -0.089853 |
| 22 | 6 | 0 | -2.328124 | 2.070294 | 0.671144 |
| 23 | 8 | 0 | 1.136501 | 2.824611 | -0.633990 |
| 24 | 6 | 0 | -1.220642 | 4.299913 | 0.441592 |
| 25 | 8 | 0 | -0.259385 | 5.142249 | -0.209662 |
| 26 | 1 | 0 | 2.488389 | -1.868906 | 2.542240 |
| 27 | 1 | 0 | 0.434043 | -0.695627 | 1.747855 |
| 28 | 1 | 0 | 2.432210 | 0.484673 | -1.873585 |
| 29 | 1 | 0 | 5.871898 | -2.536333 | -0.695470 |
| 30 | 1 | 0 | 6.450173 | -1.021185 | 0.096419 |

| | | | | | |
|---|---|---|---|---|---|
| 31 | 1 | 0 | -0.440551 | -1.882952 | -1.043359 |
| 32 | 1 | 0 | -4.439278 | 0.384642 | 0.901521 |
| 33 | 1 | 0 | -4.179837 | -4.318170 | 0.491661 |
| 34 | 1 | 0 | -4.734164 | -3.850743 | -1.161289 |
| 35 | 1 | 0 | 0.125373 | 0.872288 | -1.627489 |
| 36 | 1 | 0 | 0.319065 | 2.074563 | 1.126464 |
| 37 | 1 | 0 | -1.525057 | 2.886377 | -1.158810 |
| 38 | 1 | 0 | -2.129181 | 2.157811 | 1.751025 |
| 39 | 1 | 0 | -3.314905 | 2.522495 | 0.511397 |
| 40 | 1 | 0 | 1.059024 | 3.767701 | -0.396274 |
| 41 | 1 | 0 | -0.924384 | 4.298366 | 1.496209 |
| 42 | 1 | 0 | -2.222315 | 4.751094 | 0.381430 |
| 43 | 1 | 0 | -0.498559 | 5.184281 | -1.150054 |

**S63. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 3b inthe gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **3b-1** | -1186.067554 | -744268.6575 | 0.6302 | 25.267% |
| **3b-2** | -1186.064221 | -744266.5665 | 2.7213 | 0.741% |
| **3b-3** | -1186.064276 | -744266.6006 | 2.6871 | 0.784% |
| **3b-4** | -1186.068558 | -744269.2877 | 0 | 73.208% |

**S64. Cartesian coordinates for the low-energy Conf. of Compound 3b at B3LYP/6311+G(d,p) level of theory in methanol.**

Conformer 3b-1

| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -4.036144 | -0.409703 | 0.507532 |
| 2 | 6 | 0 | -3.606270 | -0.003245 | 1.752295 |
| 3 | 6 | 0 | -2.261386 | 0.398363 | 1.856353 |
| 4 | 6 | 0 | -1.391738 | 0.392652 | 0.763028 |
| 5 | 6 | 0 | -1.858897 | -0.038506 | -0.499564 |
| 6 | 6 | 0 | -3.176868 | -0.426114 | -0.590230 |
| 7 | 8 | 0 | -3.847961 | -0.904615 | -1.692023 |
| 8 | 6 | 0 | -5.218384 | -1.006160 | -1.292010 |
| 9 | 8 | 0 | -5.274350 | -0.876249 | 0.133699 |
| 10 | 6 | 0 | 3.102909 | -1.912731 | -0.180170 |
| 11 | 6 | 0 | 1.841280 | -2.365464 | 0.200529 |
| 12 | 6 | 0 | 0.834921 | -1.495215 | 0.545938 |
| 13 | 6 | 0 | 1.115050 | -0.108946 | 0.511840 |
| 14 | 6 | 0 | 2.391107 | 0.349704 | 0.141064 |
| 15 | 6 | 0 | 3.401989 | -0.571279 | -0.220623 |
| 16 | 8 | 0 | 3.902446 | -2.982940 | -0.501303 |
| 17 | 6 | 0 | 3.147354 | -4.148033 | -0.144502 |
| 18 | 8 | 0 | 1.803903 | -3.739018 | 0.133653 |
| 19 | 6 | 0 | 0.032722 | 0.882025 | 0.943880 |
| 20 | 6 | 0 | 0.271290 | 2.247823 | 0.267758 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 6 | 0 | 1.666417 | 2.777309 | 0.626182 |
| 22 | 6 | 0 | 2.748615 | 1.825617 | 0.093560 |
| 23 | 8 | 0 | 0.094107 | 2.182995 | -1.159475 |
| 24 | 6 | 0 | 1.880734 | 4.209535 | 0.109314 |
| 25 | 8 | 0 | 1.910388 | 4.296842 | -1.304920 |
| 26 | 1 | 0 | -4.271350 | 0.000046 | 2.608486 |
| 27 | 1 | 0 | -1.889470 | 0.726538 | 2.822965 |
| 28 | 1 | 0 | -1.211090 | -0.064221 | -1.365155 |
| 29 | 1 | 0 | -5.796854 | -0.194769 | -1.755813 |
| 30 | 1 | 0 | -5.610402 | -1.984312 | -1.582498 |
| 31 | 1 | 0 | -0.145484 | -1.856497 | 0.830394 |
| 32 | 1 | 0 | 4.386623 | -0.224929 | -0.517986 |
| 33 | 1 | 0 | 3.147688 | -4.850444 | -0.982406 |
| 34 | 1 | 0 | 3.584990 | -4.605134 | 0.753683 |
| 35 | 1 | 0 | 0.163886 | 1.065852 | 2.019762 |
| 36 | 1 | 0 | -0.497778 | 2.949600 | 0.604852 |
| 37 | 1 | 0 | 1.719299 | 2.812496 | 1.723638 |
| 38 | 1 | 0 | 2.974895 | 2.114167 | -0.941151 |
| 39 | 1 | 0 | 3.678914 | 1.991856 | 0.651067 |
| 40 | 1 | 0 | 0.675231 | 1.471919 | -1.481251 |
| 41 | 1 | 0 | 2.845420 | 4.591346 | 0.463397 |
| 42 | 1 | 0 | 1.095828 | 4.859660 | 0.533435 |
| 43 | 1 | 0 | 1.133196 | 3.794917 | -1.615512 |

Conformer 3b-2

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -3.370943 | -1.487456 | 0.378321 |
| 2 | 6 | 0 | -3.448379 | -0.613663 | 1.442468 |
| 3 | 6 | 0 | -2.320658 | 0.188289 | 1.690661 |
| 4 | 6 | 0 | -1.165581 | 0.120306 | 0.901690 |
| 5 | 6 | 0 | -1.107344 | -0.803819 | -0.164351 |
| 6 | 6 | 0 | -2.221980 | -1.578647 | -0.401749 |
| 7 | 8 | 0 | -2.390532 | -2.555811 | -1.358185 |
| 8 | 6 | 0 | -3.771882 | -2.923244 | -1.282608 |
| 9 | 8 | 0 | -4.302849 | -2.401167 | -0.059794 |
| 10 | 6 | 0 | 3.663725 | -0.484560 | -0.416712 |
| 11 | 6 | 0 | 3.009489 | -1.146202 | 0.621251 |
| 12 | 6 | 0 | 1.847594 | -0.655516 | 1.165245 |
| 13 | 6 | 0 | 1.324198 | 0.553422 | 0.646156 |
| 14 | 6 | 0 | 1.986866 | 1.223543 | -0.390056 |
| 15 | 6 | 0 | 3.179632 | 0.692010 | -0.936817 |
| 16 | 8 | 0 | 4.788645 | -1.185258 | -0.779071 |
| 17 | 6 | 0 | 4.827803 | -2.339238 | 0.070621 |
| 18 | 8 | 0 | 3.699596 | -2.288726 | 0.951209 |

| | | | | | |
|---|---|---|---|---|---|
| 19 | 6 | 0 | 0.008460 | 1.047596 | 1.226063 |
| 20 | 6 | 0 | -0.239861 | 2.545735 | 0.874199 |
| 21 | 6 | 0 | 0.049783 | 2.895240 | -0.596556 |
| 22 | 6 | 0 | 1.515920 | 2.567677 | -0.912972 |
| 23 | 8 | 0 | -1.513822 | 3.000509 | 1.293138 |
| 24 | 6 | 0 | -0.897745 | 2.248259 | -1.613839 |
| 25 | 8 | 0 | -2.282845 | 2.479566 | -1.324825 |
| 26 | 1 | 0 | -4.336074 | -0.554549 | 2.062380 |
| 27 | 1 | 0 | -2.348783 | 0.893868 | 2.513269 |
| 28 | 1 | 0 | -0.215254 | -0.914105 | -0.768791 |
| 29 | 1 | 0 | -4.314109 | -2.485453 | -2.133210 |
| 30 | 1 | 0 | -3.858401 | -4.012792 | -1.279808 |
| 31 | 1 | 0 | 1.328945 | -1.185295 | 1.957054 |
| 32 | 1 | 0 | 3.699384 | 1.204000 | -1.740254 |
| 33 | 1 | 0 | 4.770666 | -3.245500 | -0.543829 |
| 34 | 1 | 0 | 5.751897 | -2.325041 | 0.660048 |
| 35 | 1 | 0 | 0.102707 | 1.033629 | 2.319631 |
| 36 | 1 | 0 | 0.480060 | 3.115905 | 1.474775 |
| 37 | 1 | 0 | -0.083083 | 3.983976 | -0.680454 |
| 38 | 1 | 0 | 1.691263 | 2.623836 | -1.995640 |
| 39 | 1 | 0 | 2.148132 | 3.350852 | -0.471012 |
| 40 | 1 | 0 | -2.148586 | 2.603363 | 0.666853 |
| 41 | 1 | 0 | -0.786518 | 1.165035 | -1.628108 |
| 42 | 1 | 0 | -0.652510 | 2.619054 | -2.620952 |
| 43 | 1 | 0 | -2.429873 | 3.437914 | -1.377820 |

Conformer 3b-3

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.114340 | -1.630629 | 0.699364 |
| 2 | 6 | 0 | 1.892246 | -1.597960 | 1.335978 |
| 3 | 6 | 0 | 0.871148 | -0.854226 | 0.717643 |
| 4 | 6 | 0 | 1.068610 | -0.169933 | -0.485738 |
| 5 | 6 | 0 | 2.326395 | -0.243299 | -1.128387 |
| 6 | 6 | 0 | 3.320411 | -0.968157 | -0.508137 |
| 7 | 8 | 0 | 4.605117 | -1.200721 | -0.946729 |
| 8 | 6 | 0 | 5.262396 | -1.863166 | 0.138143 |
| 9 | 8 | 0 | 4.260255 | -2.300802 | 1.062767 |
| 10 | 6 | 0 | -3.904269 | -0.465546 | 0.330818 |
| 11 | 6 | 0 | -3.152616 | -1.343729 | -0.449340 |
| 12 | 6 | 0 | -1.919193 | -0.991415 | -0.940218 |
| 13 | 6 | 0 | -1.423823 | 0.300466 | -0.639488 |
| 14 | 6 | 0 | -2.183250 | 1.186312 | 0.135394 |
| 15 | 6 | 0 | -3.447849 | 0.794170 | 0.636779 |
| 16 | 8 | 0 | -5.074248 | -1.075762 | 0.717458 |

| | | | | | |
|---|---|---|---|---|---|
| 17 | 6 | 0 | -5.115843 | -2.314837 | -0.001092 |
| 18 | 8 | 0 | -3.825253 | -2.537291 | -0.578531 |
| 19 | 6 | 0 | -0.036749 | 0.651698 | -1.153885 |
| 20 | 6 | 0 | 0.200217 | 2.191725 | -1.130745 |
| 21 | 6 | 0 | -0.240832 | 2.866574 | 0.180377 |
| 22 | 6 | 0 | -1.738868 | 2.612576 | 0.400477 |
| 23 | 8 | 0 | 1.521205 | 2.547436 | -1.498272 |
| 24 | 6 | 0 | 0.581569 | 2.474701 | 1.414011 |
| 25 | 8 | 0 | 1.992089 | 2.666699 | 1.233717 |
| 26 | 1 | 0 | 1.725017 | -2.127341 | 2.267369 |
| 27 | 1 | 0 | -0.103240 | -0.820181 | 1.191656 |
| 28 | 1 | 0 | 2.502109 | 0.264929 | -2.068350 |
| 29 | 1 | 0 | 5.808142 | -2.730335 | -0.242537 |
| 30 | 1 | 0 | 5.940816 | -1.158761 | 0.640672 |
| 31 | 1 | 0 | -1.325510 | -1.686629 | -1.523944 |
| 32 | 1 | 0 | -4.041208 | 1.473018 | 1.240900 |
| 33 | 1 | 0 | -5.349109 | -3.127989 | 0.691468 |
| 34 | 1 | 0 | -5.868520 | -2.248416 | -0.799139 |
| 35 | 1 | 0 | -0.001903 | 0.383813 | -2.218389 |
| 36 | 1 | 0 | -0.439542 | 2.603035 | -1.921813 |
| 37 | 1 | 0 | -0.096813 | 3.946627 | 0.028793 |
| 38 | 1 | 0 | -2.026599 | 2.904664 | 1.419371 |
| 39 | 1 | 0 | -2.303501 | 3.278736 | -0.267118 |
| 40 | 1 | 0 | 2.070243 | 2.347908 | -0.715797 |
| 41 | 1 | 0 | 0.466043 | 1.418201 | 1.650801 |
| 42 | 1 | 0 | 0.228427 | 3.051659 | 2.282297 |
| 43 | 1 | 0 | 2.137585 | 3.618640 | 1.108763 |

Conformer 3b-4

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.421847 | -1.367410 | -0.387093 |
| 2 | 6 | 0 | 3.486231 | -0.444744 | -1.412107 |
| 3 | 6 | 0 | 2.333129 | 0.322572 | -1.654877 |
| 4 | 6 | 0 | 1.163544 | 0.177912 | -0.895297 |
| 5 | 6 | 0 | 1.121342 | -0.790359 | 0.134540 |
| 6 | 6 | 0 | 2.261166 | -1.534763 | 0.364084 |
| 7 | 8 | 0 | 2.447036 | -2.541714 | 1.282403 |
| 8 | 6 | 0 | 3.840073 | -2.869343 | 1.212482 |
| 9 | 8 | 0 | 4.379103 | -2.259945 | 0.033218 |
| 10 | 6 | 0 | -3.664551 | -0.520532 | 0.425484 |
| 11 | 6 | 0 | -3.012928 | -1.146502 | -0.636547 |
| 12 | 6 | 0 | -1.855591 | -0.633452 | -1.170072 |
| 13 | 6 | 0 | -1.335229 | 0.561194 | -0.616246 |
| 14 | 6 | 0 | -1.995251 | 1.196104 | 0.445830 |

| | | | | | |
|---|---|---|---|---|---|
| 15 | 6 | 0 | -3.181672 | 0.640085 | 0.981552 |
| 16 | 8 | 0 | -4.771003 | -1.252654 | 0.785399 |
| 17 | 6 | 0 | -4.892776 | -2.278886 | -0.207320 |
| 18 | 8 | 0 | -3.687820 | -2.294736 | -0.980577 |
| 19 | 6 | 0 | -0.029642 | 1.086408 | -1.194180 |
| 20 | 6 | 0 | 0.184507 | 2.580264 | -0.802281 |
| 21 | 6 | 0 | -0.064690 | 2.858740 | 0.688050 |
| 22 | 6 | 0 | -1.525208 | 2.523296 | 1.015780 |
| 23 | 8 | 0 | 1.424307 | 3.100840 | -1.242803 |
| 24 | 6 | 0 | 0.879263 | 2.128332 | 1.657898 |
| 25 | 8 | 0 | 2.249674 | 2.133625 | 1.230896 |
| 26 | 1 | 0 | 4.385118 | -0.322471 | -2.005941 |
| 27 | 1 | 0 | 2.354353 | 1.073714 | -2.435173 |
| 28 | 1 | 0 | 0.222919 | -0.955940 | 0.715978 |
| 29 | 1 | 0 | 4.354247 | -2.469809 | 2.097946 |
| 30 | 1 | 0 | 3.955096 | -3.954032 | 1.145732 |
| 31 | 1 | 0 | -1.339762 | -1.134934 | -1.982088 |
| 32 | 1 | 0 | -3.697324 | 1.121873 | 1.806032 |
| 33 | 1 | 0 | -5.020857 | -3.246519 | 0.285256 |
| 34 | 1 | 0 | -5.745779 | -2.053501 | -0.862272 |
| 35 | 1 | 0 | -0.128607 | 1.094476 | -2.287384 |
| 36 | 1 | 0 | -0.583511 | 3.136371 | -1.356007 |
| 37 | 1 | 0 | 0.091205 | 3.936356 | 0.820734 |
| 38 | 1 | 0 | -1.683336 | 2.532473 | 2.102714 |
| 39 | 1 | 0 | -2.167109 | 3.321192 | 0.616799 |
| 40 | 1 | 0 | 2.056378 | 2.912625 | -0.521949 |
| 41 | 1 | 0 | 0.541182 | 1.099436 | 1.814387 |
| 42 | 1 | 0 | 0.845108 | 2.632667 | 2.630448 |
| 43 | 1 | 0 | 2.428927 | 1.259200 | 0.848415 |

**S65. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 3c inthe gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **3c-1** | -1186.070844 | -744270.7222 | 0 | 50.974% |
| **3c-2** | -1186.070807 | -744270.6991 | 0.0231 | 49.025% |

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory;

[b]Gibbs free energ (E*627.51);

[c]The relative Gibbs free energy;

**S66. Cartesian coordinates for the low-energy Conf. of Compound 3c at B3LYP/6311+G(d,p) level of theory in methanol.**

Conformer 3c-1

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.554787 | -1.388013 | -0.749670 |
| 2 | 6 | 0 | -2.369938 | -1.441346 | -1.452334 |
| 3 | 6 | 0 | -1.247048 | -0.835589 | -0.858315 |
| 4 | 6 | 0 | -1.317340 | -0.208589 | 0.387494 |
| 5 | 6 | 0 | -2.543291 | -0.175037 | 1.089243 |
| 6 | 6 | 0 | -3.636374 | -0.767714 | 0.495864 |
| 7 | 8 | 0 | -4.913885 | -0.888671 | 0.989288 |
| 8 | 6 | 0 | -5.685471 | -1.457164 | -0.075628 |
| 9 | 8 | 0 | -4.778384 | -1.920848 | -1.082006 |
| 10 | 6 | 0 | 3.600973 | -1.068673 | -0.435589 |
| 11 | 6 | 0 | 2.878063 | -1.743404 | 0.549313 |
| 12 | 6 | 0 | 1.693553 | -1.246747 | 1.036140 |
| 13 | 6 | 0 | 1.218304 | -0.024693 | 0.504063 |
| 14 | 6 | 0 | 1.940946 | 0.654906 | -0.487217 |
| 15 | 6 | 0 | 3.163444 | 0.122417 | -0.963909 |
| 16 | 8 | 0 | 4.750969 | -1.763638 | -0.721415 |
| 17 | 6 | 0 | 4.651767 | -2.994045 | 0.006501 |
| 18 | 8 | 0 | 3.550706 | -2.885000 | 0.915720 |
| 19 | 6 | 0 | -0.116571 | 0.496574 | 1.008623 |
| 20 | 6 | 0 | -0.206672 | 2.022624 | 0.817211 |
| 21 | 6 | 0 | 0.066739 | 2.416980 | -0.639061 |
| 22 | 6 | 0 | 1.478878 | 1.983012 | -1.057975 |
| 23 | 8 | 0 | 0.686235 | 2.692843 | 1.729018 |
| 24 | 6 | 0 | -0.140436 | 3.923012 | -0.863365 |
| 25 | 8 | 0 | 0.806367 | 4.727163 | -0.179795 |
| 26 | 1 | 0 | -2.307076 | -1.933336 | -2.416514 |
| 27 | 1 | 0 | -0.297525 | -0.864578 | -1.381113 |
| 28 | 1 | 0 | -2.621981 | 0.296667 | 2.063661 |
| 29 | 1 | 0 | -6.265800 | -2.300932 | 0.307059 |
| 30 | 1 | 0 | -6.342932 | -0.686667 | -0.501876 |
| 31 | 1 | 0 | 1.129334 | -1.775595 | 1.797021 |
| 32 | 1 | 0 | 3.736130 | 0.642412 | -1.725056 |
| 33 | 1 | 0 | 4.467230 | -3.819220 | -0.694770 |
| 34 | 1 | 0 | 5.574189 | -3.156797 | 0.570573 |
| 35 | 1 | 0 | -0.161530 | 0.327778 | 2.092417 |
| 36 | 1 | 0 | -1.203556 | 2.364805 | 1.111653 |
| 37 | 1 | 0 | -0.674023 | 1.884753 | -1.249468 |
| 38 | 1 | 0 | 2.180237 | 2.771324 | -0.754863 |
| 39 | 1 | 0 | 1.534837 | 1.948886 | -2.153240 |
| 40 | 1 | 0 | 1.558304 | 2.273733 | 1.628729 |
| 41 | 1 | 0 | -1.172281 | 4.184999 | -0.571143 |
| 42 | 1 | 0 | -0.035351 | 4.158695 | -1.928846 |
| 43 | 1 | 0 | 0.837271 | 4.377224 | 0.730943 |

Conformer 3c-2

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.848551 | -1.029324 | 0.359419 |
| 2 | 6 | 0 | -3.710240 | -0.306402 | 1.526593 |
| 3 | 6 | 0 | -2.445147 | 0.252011 | 1.778807 |
| 4 | 6 | 0 | -1.369729 | 0.089497 | 0.899812 |
| 5 | 6 | 0 | -1.536718 | -0.662299 | -0.282276 |
| 6 | 6 | 0 | -2.783404 | -1.201169 | -0.520920 |
| 7 | 8 | 0 | -3.180902 | -1.986872 | -1.577950 |
| 8 | 6 | 0 | -4.594989 | -2.152193 | -1.422558 |
| 9 | 8 | 0 | -4.952620 | -1.701217 | -0.110908 |
| 10 | 6 | 0 | 3.275058 | -1.273245 | -0.549241 |
| 11 | 6 | 0 | 2.689669 | -1.745900 | 0.626340 |
| 12 | 6 | 0 | 1.637104 | -1.090226 | 1.217097 |
| 13 | 6 | 0 | 1.154223 | 0.084762 | 0.593875 |
| 14 | 6 | 0 | 1.738271 | 0.561352 | -0.588879 |
| 15 | 6 | 0 | 2.827789 | -0.131575 | -1.170368 |
| 16 | 8 | 0 | 4.315614 | -2.094820 | -0.908910 |
| 17 | 6 | 0 | 4.262236 | -3.205626 | -0.005176 |
| 18 | 8 | 0 | 3.343933 | -2.880209 | 1.044528 |
| 19 | 6 | 0 | -0.045975 | 0.776549 | 1.218022 |
| 20 | 6 | 0 | -0.077477 | 2.264657 | 0.821491 |
| 21 | 6 | 0 | -0.025870 | 2.438094 | -0.700990 |
| 22 | 6 | 0 | 1.267437 | 1.834512 | -1.268210 |
| 23 | 8 | 0 | 0.992379 | 2.976136 | 1.475658 |
| 24 | 6 | 0 | -0.173493 | 3.913326 | -1.105887 |
| 25 | 8 | 0 | 0.922057 | 4.717992 | -0.702999 |
| 26 | 1 | 0 | -4.537140 | -0.183660 | 2.217058 |
| 27 | 1 | 0 | -2.299337 | 0.829226 | 2.687996 |
| 28 | 1 | 0 | -0.714122 | -0.821797 | -0.969133 |
| 29 | 1 | 0 | -5.119035 | -1.544755 | -2.173861 |
| 30 | 1 | 0 | -4.850608 | -3.210105 | -1.524941 |
| 31 | 1 | 0 | 1.178277 | -1.462526 | 2.126980 |
| 32 | 1 | 0 | 3.293621 | 0.230678 | -2.081114 |
| 33 | 1 | 0 | 3.905130 | -4.095553 | -0.541185 |
| 34 | 1 | 0 | 5.255116 | -3.374846 | 0.420109 |
| 35 | 1 | 0 | 0.077061 | 0.760314 | 2.308222 |
| 36 | 1 | 0 | -0.990324 | 2.721337 | 1.215739 |
| 37 | 1 | 0 | -0.890024 | 1.896112 | -1.106100 |
| 38 | 1 | 0 | 2.055884 | 2.595151 | -1.197785 |
| 39 | 1 | 0 | 1.137292 | 1.648556 | -2.341685 |
| 40 | 1 | 0 | 1.809405 | 2.477042 | 1.303647 |
| 41 | 1 | 0 | -1.123864 | 4.298253 | -0.696872 |
| 42 | 1 | 0 | -0.233204 | 3.995252 | -2.197465 |

| | | | | | |
|---|---|---|---|---|---|
| 43 | 1 | 0 | 1.081020 | 4.492440 | 0.233345 |

**S67. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimizes conformers of 3d inthe gas phase (T = 298.15 K)**

| Conformer | E (Hartree)[a] | G (kcal/mol)[b] | ΔG (kcal/mol)[c] | population[d] |
|---|---|---|---|---|
| **3d-1** | -1186.070618 | -744270.5807 | 0.4561 | 17.967821 |
| **3d-2** | -1186.071345 | -744271.0368 | 0 | 38.806166 |
| **3d-3** | -1186.070517 | -744270.517 | 0.5198 | 16.137217 |
| **3d-4** | -1186.071006 | -744270.8239 | 0.2129 | 27.088796 |

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory;

[b]Gibbs free energ (E*627.51);

[c]The relative Gibbs free energy;

**S68. Cartesian coordinates for the low-energy Conf. of Compound 3d at B3LYP/6311+G(d,p) level of theory in methanol.**

Conformer 3d-1

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -3.145089 | -1.671552 | 0.883250 |
| 2 | 6 | 0 | -2.006106 | -1.388568 | 1.608823 |
| 3 | 6 | 0 | -0.981399 | -0.692208 | 0.944924 |
| 4 | 6 | 0 | -1.094989 | -0.300584 | -0.393103 |
| 5 | 6 | 0 | -2.271428 | -0.612569 | -1.115892 |
| 6 | 6 | 0 | -3.271281 | -1.293250 | -0.451029 |
| 7 | 8 | 0 | -4.477004 | -1.729048 | -0.943781 |
| 8 | 6 | 0 | -5.187688 | -2.254674 | 0.184921 |
| 9 | 8 | 0 | -4.267350 | -2.359366 | 1.277667 |
| 10 | 6 | 0 | 3.871215 | -0.591994 | 0.373782 |
| 11 | 6 | 0 | 3.166275 | -1.435197 | -0.485178 |
| 12 | 6 | 0 | 1.928177 | -1.091822 | -0.971705 |
| 13 | 6 | 0 | 1.385550 | 0.154994 | -0.582153 |
| 14 | 6 | 0 | 2.090645 | 1.003069 | 0.280065 |
| 15 | 6 | 0 | 3.361707 | 0.621298 | 0.771582 |
| 16 | 8 | 0 | 5.058507 | -1.185095 | 0.731780 |
| 17 | 6 | 0 | 5.156602 | -2.367414 | -0.071621 |
| 18 | 8 | 0 | 3.886712 | -2.587918 | -0.695286 |
| 19 | 6 | 0 | -0.001600 | 0.505850 | -1.089284 |
| 20 | 6 | 0 | -0.267999 | 2.029269 | -0.989388 |
| 21 | 6 | 0 | 0.057979 | 2.571916 | 0.405031 |
| 22 | 6 | 0 | 1.553139 | 2.362494 | 0.678885 |
| 23 | 8 | 0 | -1.600919 | 2.345526 | -1.415495 |
| 24 | 6 | 0 | -0.300105 | 4.058911 | 0.549320 |
| 25 | 8 | 0 | -1.690262 | 4.313453 | 0.510911 |
| 26 | 1 | 0 | -1.906243 | -1.695818 | 2.643771 |

| | | | | | |
|---|---|---|---|---|---|
| 27 | 1 | 0 | -0.067140 | -0.466989 | 1.482317 |
| 28 | 1 | 0 | -2.377652 | -0.339252 | -2.160396 |
| 29 | 1 | 0 | -6.001467 | -1.568224 | 0.455750 |
| 30 | 1 | 0 | -5.574892 | -3.247069 | -0.060570 |
| 31 | 1 | 0 | 1.373178 | -1.758496 | -1.623224 |
| 32 | 1 | 0 | 3.916437 | 1.269206 | 1.442544 |
| 33 | 1 | 0 | 5.923985 | -2.220893 | -0.844267 |
| 34 | 1 | 0 | 5.400470 | -3.220685 | 0.567046 |
| 35 | 1 | 0 | -0.052160 | 0.256707 | -2.156535 |
| 36 | 1 | 0 | 0.377519 | 2.534246 | -1.718438 |
| 37 | 1 | 0 | -0.535112 | 2.014924 | 1.142177 |
| 38 | 1 | 0 | 2.117333 | 3.135418 | 0.133027 |
| 39 | 1 | 0 | 1.759034 | 2.542972 | 1.741337 |
| 40 | 1 | 0 | -2.199557 | 1.760260 | -0.917426 |
| 41 | 1 | 0 | 0.237520 | 4.630250 | -0.229893 |
| 42 | 1 | 0 | 0.058775 | 4.425274 | 1.518350 |
| 43 | 1 | 0 | -1.989124 | 3.919932 | -0.329323 |

Conformer 3d-2

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.243454 | -1.903121 | 0.301723 |
| 2 | 6 | 0 | 3.249187 | -1.294886 | 1.538511 |
| 3 | 6 | 0 | 2.173288 | -0.432665 | 1.826273 |
| 4 | 6 | 0 | 1.139598 | -0.196246 | 0.910766 |
| 5 | 6 | 0 | 1.156708 | -0.842984 | -0.345612 |
| 6 | 6 | 0 | 2.216470 | -1.680576 | -0.615363 |
| 7 | 8 | 0 | 2.436812 | -2.432006 | -1.743797 |
| 8 | 6 | 0 | 3.734979 | -3.014016 | -1.575735 |
| 9 | 8 | 0 | 4.142621 | -2.801296 | -0.218343 |
| 10 | 6 | 0 | -3.681881 | -0.396359 | -0.490706 |
| 11 | 6 | 0 | -3.169141 | -1.065547 | 0.620512 |
| 12 | 6 | 0 | -1.986425 | -0.683115 | 1.205850 |
| 13 | 6 | 0 | -1.297768 | 0.419496 | 0.648676 |
| 14 | 6 | 0 | -1.809589 | 1.092873 | -0.467157 |
| 15 | 6 | 0 | -3.029992 | 0.676984 | -1.050432 |
| 16 | 8 | 0 | -4.876522 | -0.965721 | -0.862219 |
| 17 | 6 | 0 | -5.018972 | -2.132873 | -0.043499 |
| 18 | 8 | 0 | -4.024960 | -2.078324 | 0.985854 |
| 19 | 6 | 0 | 0.036796 | 0.797830 | 1.264678 |
| 20 | 6 | 0 | 0.437053 | 2.247290 | 0.890321 |
| 21 | 6 | 0 | 0.344488 | 2.489854 | -0.619048 |
| 22 | 6 | 0 | -1.113060 | 2.301320 | -1.060366 |
| 23 | 8 | 0 | 1.721889 | 2.579729 | 1.433279 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 6 | 0 | 0.839060 | 3.889829 | -1.013243 |
| 25 | 8 | 0 | 2.229132 | 4.069322 | -0.830358 |
| 26 | 1 | 0 | 4.039382 | -1.480406 | 2.257207 |
| 27 | 1 | 0 | 2.137786 | 0.055317 | 2.795979 |
| 28 | 1 | 0 | 0.355592 | -0.701329 | -1.060770 |
| 29 | 1 | 0 | 3.680351 | -4.087724 | -1.774043 |
| 30 | 1 | 0 | 4.446680 | -2.522408 | -2.252702 |
| 31 | 1 | 0 | -1.582475 | -1.213801 | 2.061552 |
| 32 | 1 | 0 | -3.438810 | 1.192805 | -1.913253 |
| 33 | 1 | 0 | -6.013238 | -2.137372 | 0.411331 |
| 34 | 1 | 0 | -4.861487 | -3.030635 | -0.657020 |
| 35 | 1 | 0 | -0.067796 | 0.781980 | 2.356345 |
| 36 | 1 | 0 | -0.258492 | 2.929866 | 1.394035 |
| 37 | 1 | 0 | 0.984651 | 1.759112 | -1.130272 |
| 38 | 1 | 0 | -1.679983 | 3.203166 | -0.779362 |
| 39 | 1 | 0 | -1.159987 | 2.253354 | -2.155393 |
| 40 | 1 | 0 | 2.320962 | 1.846931 | 1.200145 |
| 41 | 1 | 0 | 0.255624 | 4.642994 | -0.451797 |
| 42 | 1 | 0 | 0.637915 | 4.058989 | -2.077711 |
| 43 | 1 | 0 | 2.386026 | 3.837000 | 0.103506 |

Conformer 3d-3

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | -3.332900 | -1.543338 | 0.842573 |
| 2 | 6 | 0 | -2.155202 | -1.446731 | 1.554394 |
| 3 | 6 | 0 | -1.083012 | -0.785079 | 0.929717 |
| 4 | 6 | 0 | -1.190870 | -0.243476 | -0.355254 |
| 5 | 6 | 0 | -2.411083 | -0.359727 | -1.063236 |
| 6 | 6 | 0 | -3.454315 | -1.012550 | -0.439276 |
| 7 | 8 | 0 | -4.725001 | -1.235114 | -0.913581 |
| 8 | 6 | 0 | -5.356047 | -2.080973 | 0.056076 |
| 9 | 8 | 0 | -4.523155 | -2.118327 | 1.220807 |
| 10 | 6 | 0 | 3.788231 | -0.846563 | 0.342293 |
| 11 | 6 | 0 | 3.018551 | -1.618080 | -0.527749 |
| 12 | 6 | 0 | 1.790584 | -1.189771 | -0.971157 |
| 13 | 6 | 0 | 1.325428 | 0.068875 | -0.524123 |
| 14 | 6 | 0 | 2.096082 | 0.845943 | 0.352686 |
| 15 | 6 | 0 | 3.354825 | 0.376468 | 0.797025 |
| 16 | 8 | 0 | 4.948792 | -1.517155 | 0.650255 |
| 17 | 6 | 0 | 4.967218 | -2.664863 | -0.206729 |
| 18 | 8 | 0 | 3.669282 | -2.800828 | -0.795400 |
| 19 | 6 | 0 | -0.043336 | 0.522155 | -1.005911 |
| 20 | 6 | 0 | -0.200347 | 2.048542 | -0.816952 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | 6 | 0 | 0.138918 | 2.461156 | 0.618130 |
| 22 | 6 | 0 | 1.634841 | 2.209804 | 0.830208 |
| 23 | 8 | 0 | -1.473204 | 2.529176 | -1.249528 |
| 24 | 6 | 0 | -0.252091 | 3.923686 | 0.882383 |
| 25 | 8 | 0 | 0.139347 | 4.797497 | -0.167883 |
| 26 | 1 | 0 | -2.061502 | -1.867261 | 2.549404 |
| 27 | 1 | 0 | -0.136273 | -0.710001 | 1.452767 |
| 28 | 1 | 0 | -2.517345 | 0.039878 | -2.065938 |
| 29 | 1 | 0 | -6.331983 | -1.664900 | 0.320138 |
| 30 | 1 | 0 | -5.456926 | -3.094980 | -0.354621 |
| 31 | 1 | 0 | 1.186383 | -1.799448 | -1.634699 |
| 32 | 1 | 0 | 3.958999 | 0.967202 | 1.477953 |
| 33 | 1 | 0 | 5.715255 | -2.517411 | -0.998309 |
| 34 | 1 | 0 | 5.192503 | -3.555921 | 0.385231 |
| 35 | 1 | 0 | -0.105636 | 0.337283 | -2.085791 |
| 36 | 1 | 0 | 0.512831 | 2.539088 | -1.487102 |
| 37 | 1 | 0 | -0.434953 | 1.830589 | 1.312335 |
| 38 | 1 | 0 | 2.187975 | 2.995363 | 0.294949 |
| 39 | 1 | 0 | 1.886867 | 2.330562 | 1.891485 |
| 40 | 1 | 0 | -2.150820 | 2.069466 | -0.725010 |
| 41 | 1 | 0 | 0.247903 | 4.284707 | 1.788026 |
| 42 | 1 | 0 | -1.335217 | 3.988445 | 1.056825 |
| 43 | 1 | 0 | -0.459395 | 4.592482 | -0.905584 |

Conformer 3d-4

| Center | Atomic | Atomic | Coordinates (Angstroms) | | |
|---|---|---|---|---|---|
| Number | Number | Type | X | Y | Z |
| 1 | 6 | 0 | 3.562993 | -1.507066 | 0.272417 |
| 2 | 6 | 0 | 3.534723 | -0.792847 | 1.451409 |
| 3 | 6 | 0 | 2.359117 | -0.068483 | 1.726456 |
| 4 | 6 | 0 | 1.263966 | -0.061419 | 0.852547 |
| 5 | 6 | 0 | 1.322336 | -0.805462 | -0.346990 |
| 6 | 6 | 0 | 2.477966 | -1.511534 | -0.602500 |
| 7 | 8 | 0 | 2.773602 | -2.286547 | -1.698530 |
| 8 | 6 | 0 | 4.028469 | -2.911367 | -1.404681 |
| 9 | 8 | 0 | 4.577055 | -2.279049 | -0.241649 |
| 10 | 6 | 0 | -3.561966 | -0.826737 | -0.457927 |
| 11 | 6 | 0 | -2.943848 | -1.426702 | 0.638619 |
| 12 | 6 | 0 | -1.789536 | -0.914561 | 1.180372 |
| 13 | 6 | 0 | -1.243207 | 0.252053 | 0.596609 |
| 14 | 6 | 0 | -1.861015 | 0.856380 | -0.507945 |
| 15 | 6 | 0 | -3.046067 | 0.303023 | -1.047929 |
| 16 | 8 | 0 | -4.673847 | -1.552685 | -0.815521 |
| 17 | 6 | 0 | -4.837430 | -2.536009 | 0.213193 |

| | | | | | |
|---|---|---|---|---|---|
| 18 | 8 | 0 | -3.646012 | -2.551301 | 1.007092 |
| 19 | 6 | 0 | 0.047239 | 0.794785 | 1.188684 |
| 20 | 6 | 0 | 0.255562 | 2.266814 | 0.764612 |
| 21 | 6 | 0 | 0.139214 | 2.422635 | -0.754738 |
| 22 | 6 | 0 | -1.312494 | 2.121722 | -1.140126 |
| 23 | 8 | 0 | 1.457130 | 2.825723 | 1.292937 |
| 24 | 6 | 0 | 0.586672 | 3.822568 | -1.203839 |
| 25 | 8 | 0 | 0.057090 | 4.858813 | -0.387871 |
| 26 | 1 | 0 | 4.375276 | -0.797475 | 2.136252 |
| 27 | 1 | 0 | 2.292483 | 0.490957 | 2.654746 |
| 28 | 1 | 0 | 0.482150 | -0.834561 | -1.030154 |
| 29 | 1 | 0 | 3.866706 | -3.978270 | -1.198548 |
| 30 | 1 | 0 | 4.709649 | -2.773012 | -2.248642 |
| 31 | 1 | 0 | -1.301317 | -1.392613 | 2.023134 |
| 32 | 1 | 0 | -3.532009 | 0.759368 | -1.904218 |
| 33 | 1 | 0 | -5.695106 | -2.264677 | 0.844518 |
| 34 | 1 | 0 | -4.981710 | -3.518612 | -0.243878 |
| 35 | 1 | 0 | -0.049164 | 0.799614 | 2.281451 |
| 36 | 1 | 0 | -0.542176 | 2.858153 | 1.225543 |
| 37 | 1 | 0 | 0.801042 | 1.690697 | -1.239371 |
| 38 | 1 | 0 | -1.926817 | 2.981971 | -0.836539 |
| 39 | 1 | 0 | -1.402927 | 2.054222 | -2.231723 |
| 40 | 1 | 0 | 2.192320 | 2.260783 | 0.997868 |
| 41 | 1 | 0 | 0.231815 | 4.018257 | -2.221857 |
| 42 | 1 | 0 | 1.684393 | 3.867495 | -1.223117 |
| 43 | 1 | 0 | 0.539101 | 4.791316 | 0.453404 |

**S69. Experimental and calculated $^{13}$C NMR chemical shifts of 3a and 3b**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **3a** | **3b** | | | **3a** | **3b** |
| 7' | 55.6 | 56.7 | 50.3 | 10 | 100.9 | 100.1 | 101.0 |
| 8' | 79.2 | 80.7 | 74.0 | 1' | 136.1 | 133.3 | 133.8 |
| 8 | 42.0 | 41.8 | 39.0 | 9 | 67.3 | 67.7 | 64.5 |
| 7 | 31.7 | 32.0 | 31.2 | 2' | 109.2 | 105.5 | 105.9 |
| 1 | 128.3 | 126.6 | 126.5 | 3' | 147.1 | 144.4 | 143.0 |
| 2 | 107.9 | 104.1 | 104.7 | 4' | 148.5 | 143.2 | 142.0 |
| 3 | 146.2 | 142.0 | 142.9 | 5' | 108.5 | 104.6 | 103.6 |
| 4 | 146.4 | 141.6 | 141.8 | 6' | 123.5 | 119.6 | 121.9 |
| 5 | 109.3 | 105.7 | 107.3 | 10' | 101.3 | 100.9 | 100.4 |
| 6 | 131.0 | 127.9 | 126.6 | | | | |
| | | | | $R^2$ | | 0.9986 | 0.9977 |
| | | | | MAE | | 2.32 | 3.10 |
| | | | | CMAE | | 1.13 | 1.38 |

**S70. Experimental and calculated $^{1}$H NMR chemical shifts of 3a and 3b**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **3a** | **3b** | | | **3a** | **3b** |
| 7' | 3.79 | 3.21 | 3.71 | 10b | 5.85 | 5.49 | 5.55 |
| 8' | 3.80 | 3.07 | 3.68 | 9a | 3.78 | 3.22 | 3.17 |
| 8 | 2.19 | 1.52 | 1.72 | 9b | 3.78 | 3.08 | 3.24 |
| 7a | 2.62 | 2.01 | 2.15 | 2' | 6.60 | 6.30 | 5.97 |
| 7b | 2.76 | 2.03 | 2.38 | 5' | 6.80 | 6.53 | 6.59 |
| 2 | 6.55 | 6.27 | 6.39 | 6' | 6.73 | 6.49 | 7.00 |
| 5 | 6.17 | 5.91 | 6.12 | 10'a | 5.95 | 5.76 | 5.50 |
| 10a | 5.85 | 5.70 | 5.74 | 10'b | 5.95 | 5.68 | 5.74 |

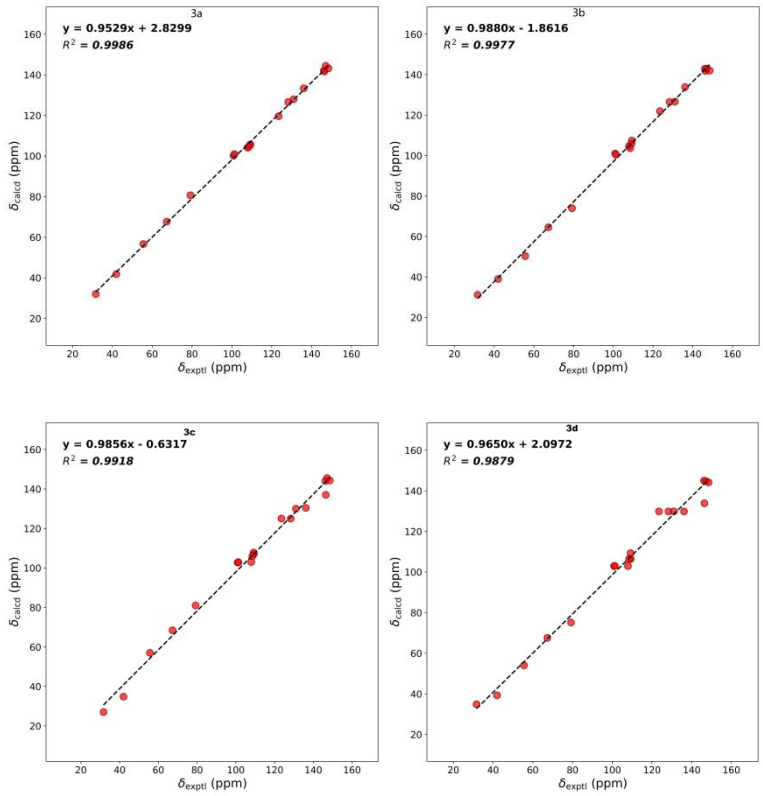
**S71. Experimental and calculated $^{13}$C NMR chemical shifts of 3c and 3d**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **3c** | **3d** | | | **3c** | **3d** |
| 7' | 55.6 | 57.0 | 54.0 | 10 | 100.9 | 102.7 | 102.9 |
| 8' | 79.2 | 81.1 | 75.2 | 1' | 136.1 | 130.4 | 129.8 |
| 8 | 42.0 | 34.8 | 39.3 | 9 | 67.3 | 68.4 | 67.6 |
| 7 | 31.7 | 27.0 | 34.9 | 2' | 109.2 | 107.8 | 109.3 |
| 1 | 128.3 | 125.0 | 129.9 | 3' | 147.1 | 145.5 | 144.7 |
| 2 | 107.9 | 103.0 | 102.9 | 4' | 148.5 | 144.3 | 144.1 |
| 3 | 146.2 | 144.0 | 145.0 | 5' | 108.5 | 106.0 | 106.5 |
| 4 | 146.4 | 137.6 | 133.9 | 6' | 123.5 | 125.0 | 129.9 |
| 5 | 109.3 | 107.7 | 106.4 | 10' | 101.3 | 102.9 | 103.0 |
| 6 | 131.0 | 130.0 | 129.8 | | | | |
| | | | | $R^2$ | | 0.9918 | 0.9879 |
| | | | | MAE | | 2.59 | 2.90 |
| | | | | CMAE | | 2.14 | 1.75 |

**S72. Experimental and calculated $^{1}$H NMR chemical shifts of 3c and 3d**

| NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | | NO. | $\delta_{exptl.}$ | $\delta_{calcd.}$(ppm) | |
|---|---|---|---|---|---|---|---|
| | | **3c** | **3d** | | | **3c** | **3d** |
| 7' | 3.79 | 3.85 | 3.51 | 10b | 5.85 | 6.16 | 6.19 |
| 8' | 3.80 | 3.52 | 3.68 | 9a | 3.78 | 3.45 | 2.66 |
| 8 | 2.19 | 1.64 | 1.71 | 9b | 3.78 | 3.50 | 2.80 |
| 7a | 2.62 | 2.67 | 2.63 | 2' | 6.60 | 6.68 | 6.55 |
| 7b | 2.76 | 1.71 | 1.07 | 5' | 6.80 | 7.04 | 6.87 |
| 2 | 6.55 | 6.61 | 6.79 | 6' | 6.73 | 6.92 | 7.02 |
| 5 | 6.17 | 6.20 | 6.20 | 10'a | 5.95 | 4.10 | 4.13 |
| 10a | 5.85 | 6.10 | 6.13 | 10'b | 5.95 | 4.07 | 4.01 |

**S73. Linear regression analysis between the experimental and calculated $^{13}$C NMR chemical shifts of 3a/3b/3c/3d**



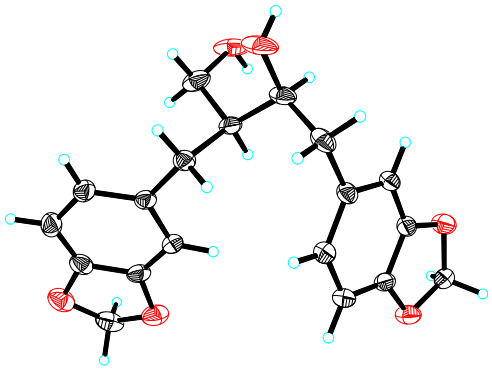

**S74. DP4+ probability analysis of 3a/3b/3c/3d**

| Functional | Solvent? | Basis Set | Type of Data |
|---|---|---|---|
| mPW1PW91 | PCM | 6-31+G(d,p) | Unscaled Shifts |

| | Isomer 1 | Isomer 2 | Isomer 3 | Isomer 4 | Isomer 5 | Isomer 6 |
|---|---|---|---|---|---|---|
| sDP4+ (H data) | 100.00% | 0.00% | 0.00% | 0.00% | | |
| sDP4+ (C data) | 98.06% | 1.94% | 0.00% | 0.00% | | |
| sDP4+ (all data) | 100.00% | 0.00% | 0.00% | 0.00% | | |
| uDP4+ (H data) | 0.00% | 99.77% | 0.23% | 0.00% | | |
| uDP4+ (C data) | 0.66% | 0.00% | 6.65% | 92.69% | | |
| uDP4+ (all data) | 0.03% | 0.00% | 99.97% | 0.00% | | |
| DP4+ (H data) | 72.88% | 27.12% | 0.00% | 0.00% | | |
| DP4+ (C data) | 100.00% | 0.00% | 0.00% | 0.00% | | |
| DP4+ (all data) | 100.00% | 0.00% | 0.00% | 0.00% | | |

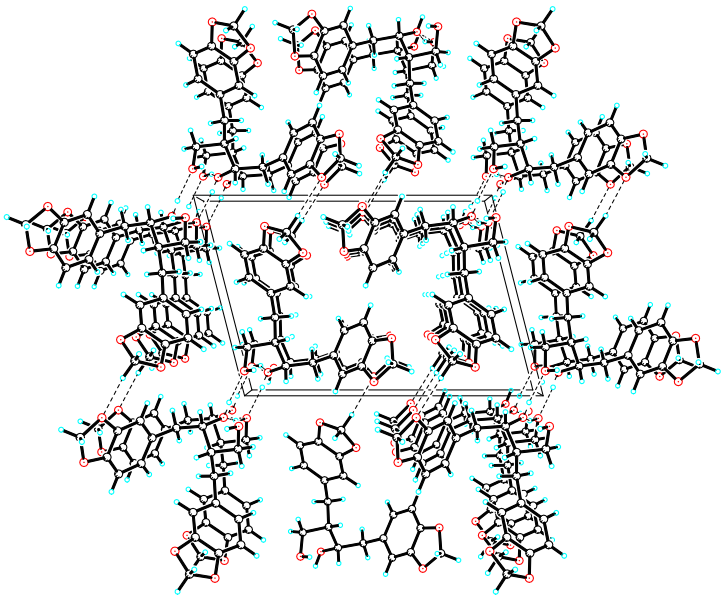
**S75. Crystal data for compound 1**

Crystal data for compound **1**: $C_{19}H_{20}O_6$, $M$ = 344.35, $a$ = 10.4759(2) Å, $b$ = 5.47890(10) Å, $c$ = 15.0364(3) Å, $\alpha$ = 90°, $\beta$ = 104.2890(10)°, $\gamma$ = 90°, $V$ = 836.34(3) Å$^3$, $T$ = 150.(2) K, space group $P1211$, $Z$ = 2, $\mu$(Cu Kα) = 0.848 mm$^{-1}$, 14587 reflections measured, 3103 independent reflections ($R_{int}$ = 0.0554). The final $R_1$ values were 0.0364 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0938 ($I > 2\sigma(I)$). The final $R_1$ values were 0.0388 (all data). The final $wR(F^2)$ values were 0.0964 (all data). The goodness of fit on $F^2$ was 1.032. Flack parameter = 0.23(10).



View of a molecule of **1** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **1**.

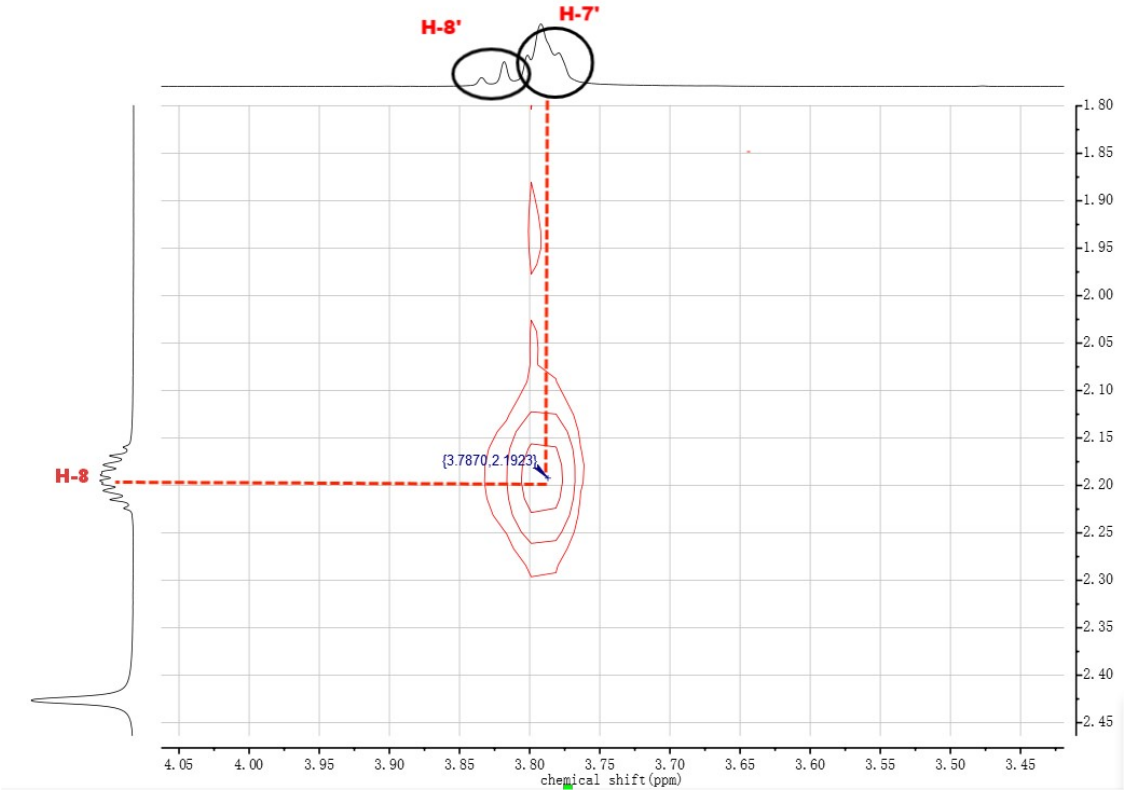
Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for compound **1.**

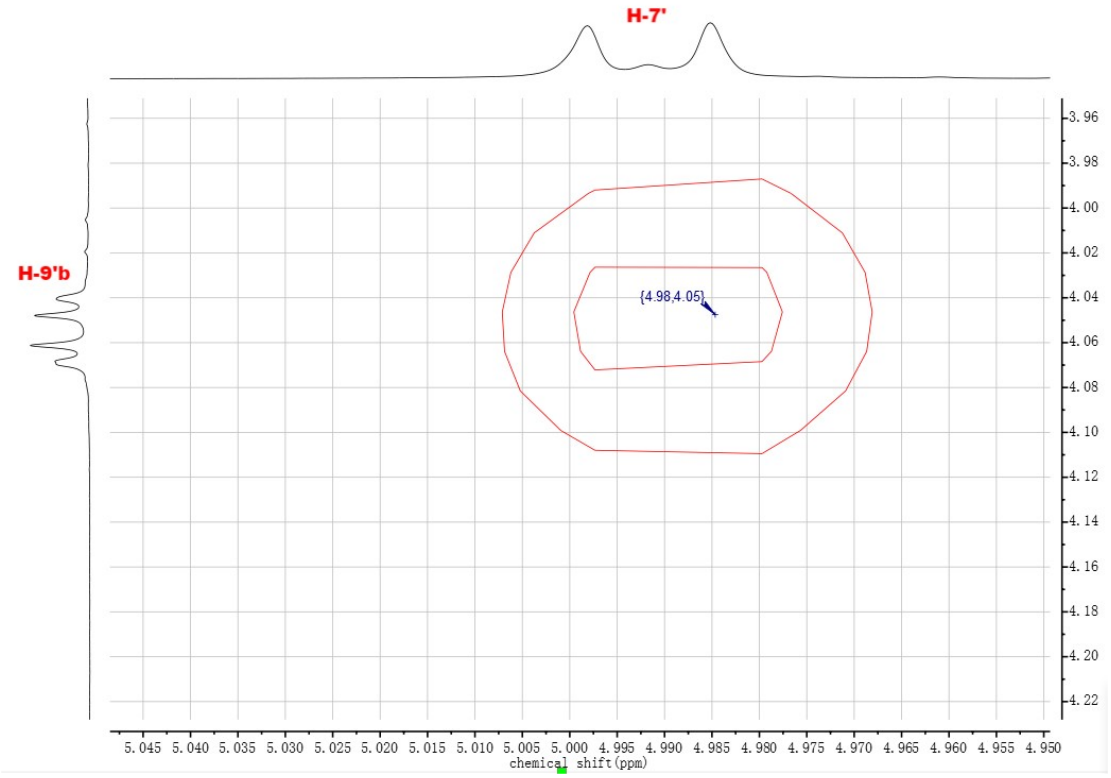
| | |
|---|---|
| Identification code | global |
| Empirical formula | C19 H20 O6 |
| Formula weight | 344.35 |
| Temperature | 150(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | P 1 21 1 |

| | | |
|---|---|---|
| Unit cell dimensions | a = 10.4759(2) Å | α= 90°. |
| | b = 5.47890(10) Å | β= 104.2890(10)°. |
| | c = 15.0364(3) Å | γ = 90°. |
| Volume | 836.34(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.367 $Mg/m^3$ | |
| Absorption coefficient | 0.848 $mm^{-1}$ | |
| F(000) | 364 | |
| Crystal size | 0.330 x 0.210 x 0.130 $mm^3$ | |
| Theta range for data collection | 3.03 to 69.93°. | |
| Index ranges | -12<=h<=12, -5<=k<=6, -18<=l<=18 | |
| Reflections collected | 14587 | |
| Independent reflections | 3103 [R(int) = 0.0554] | |
| Completeness to theta = 69.93° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.90 and 0.76 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3103 / 1 / 228 | |
| Goodness-of-fit on $F^2$ | 1.032 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0364, wR2 = 0.0938 | |
| R indices (all data) | R1 = 0.0388, wR2 = 0.0964 | |
| Absolute structure parameter | 0.23(10) | |
| Largest diff. peak and hole | 0.235 and -0.247 $e.Å^{-3}$ | |

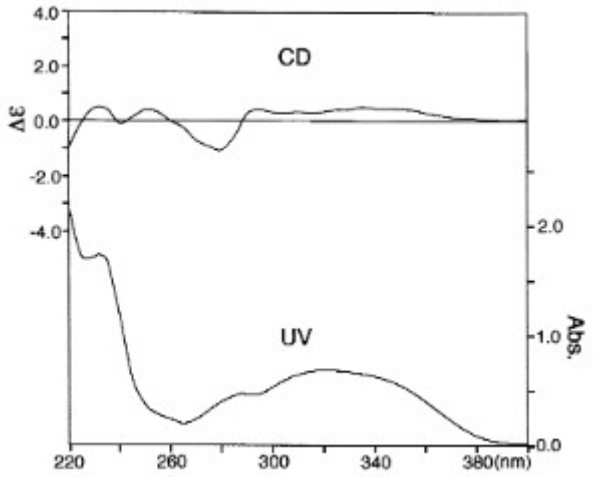
## S76. The ROESY correlation of compound 3 between H-7' and H-8




**S77. The ROESY correlation of compound 5 between H-7' and H-9'b**




**S78. The CD and UV spectura of Venkatasin [1]**




[1] B. Sajeli, M. Sahai, R. Suessmuth, T. Asai, N. Hara, Y. Fujimoto, *Chem. Pharm. Bull.*, 2006, **54**, 538–541.