

Supporting Information

First total Synthesis of Cyclodepsipeptides Clavatustide A and B and their enantiomers

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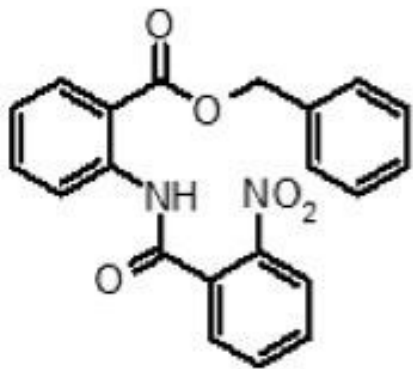
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Correspondence to Dr. Syed Shafi, Jamia Hamdard (Hamdard University) Hamdard Nagar, New Delhi 110 062, Email ID. Syedshafi@jamiahamdard.ac.in. Phone: +91 9990806873.

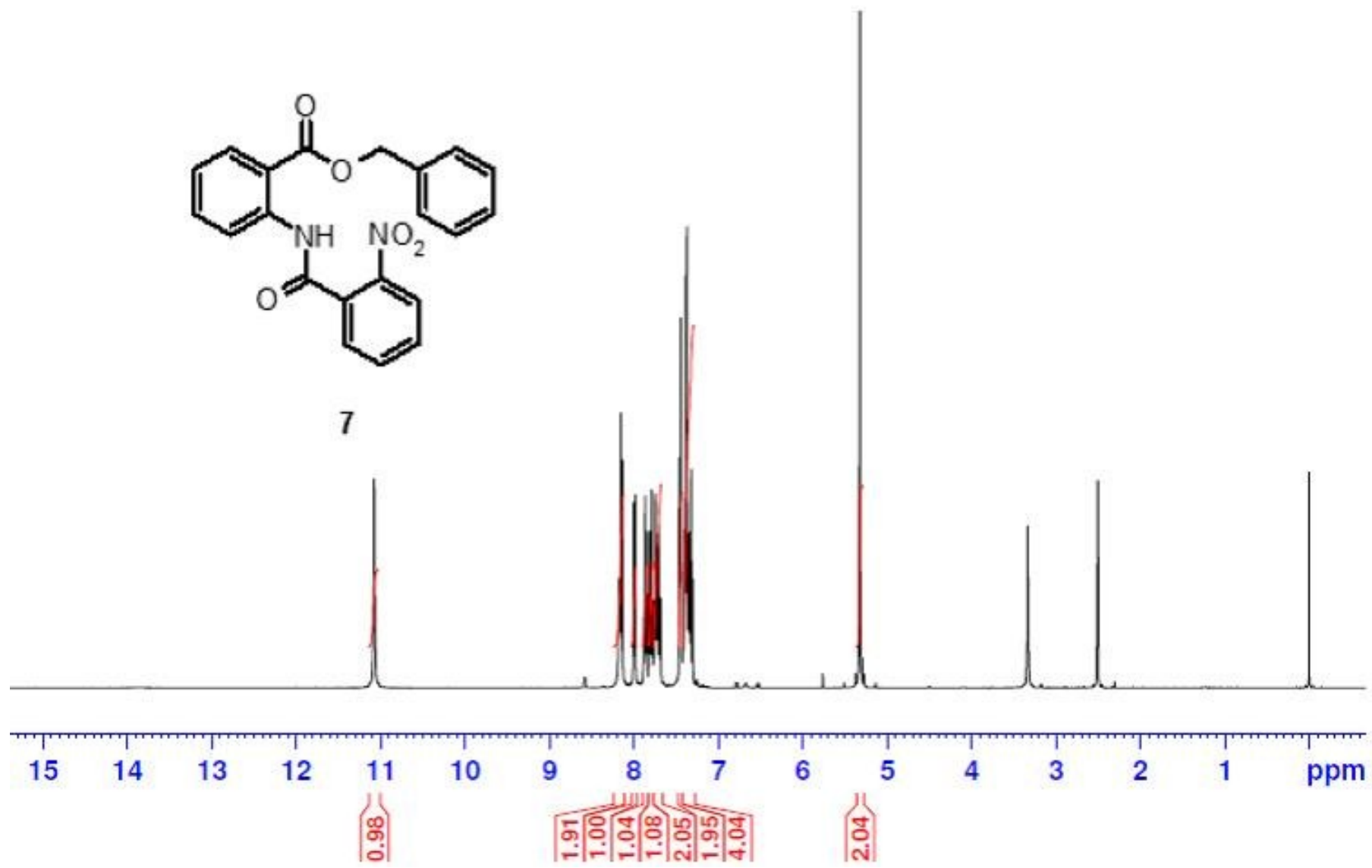
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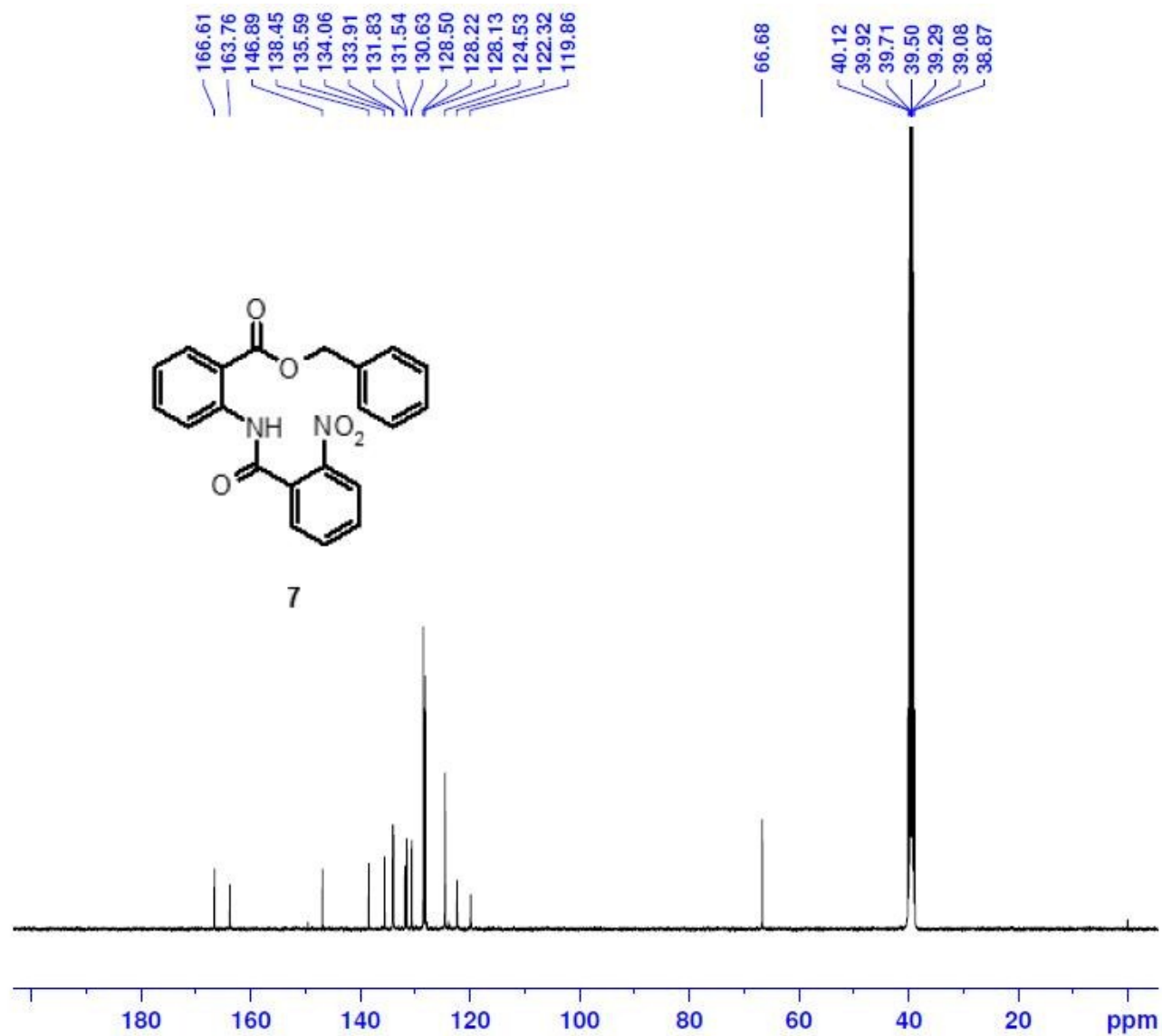
¹H NMR of Compound 7 in DMSO-d₆



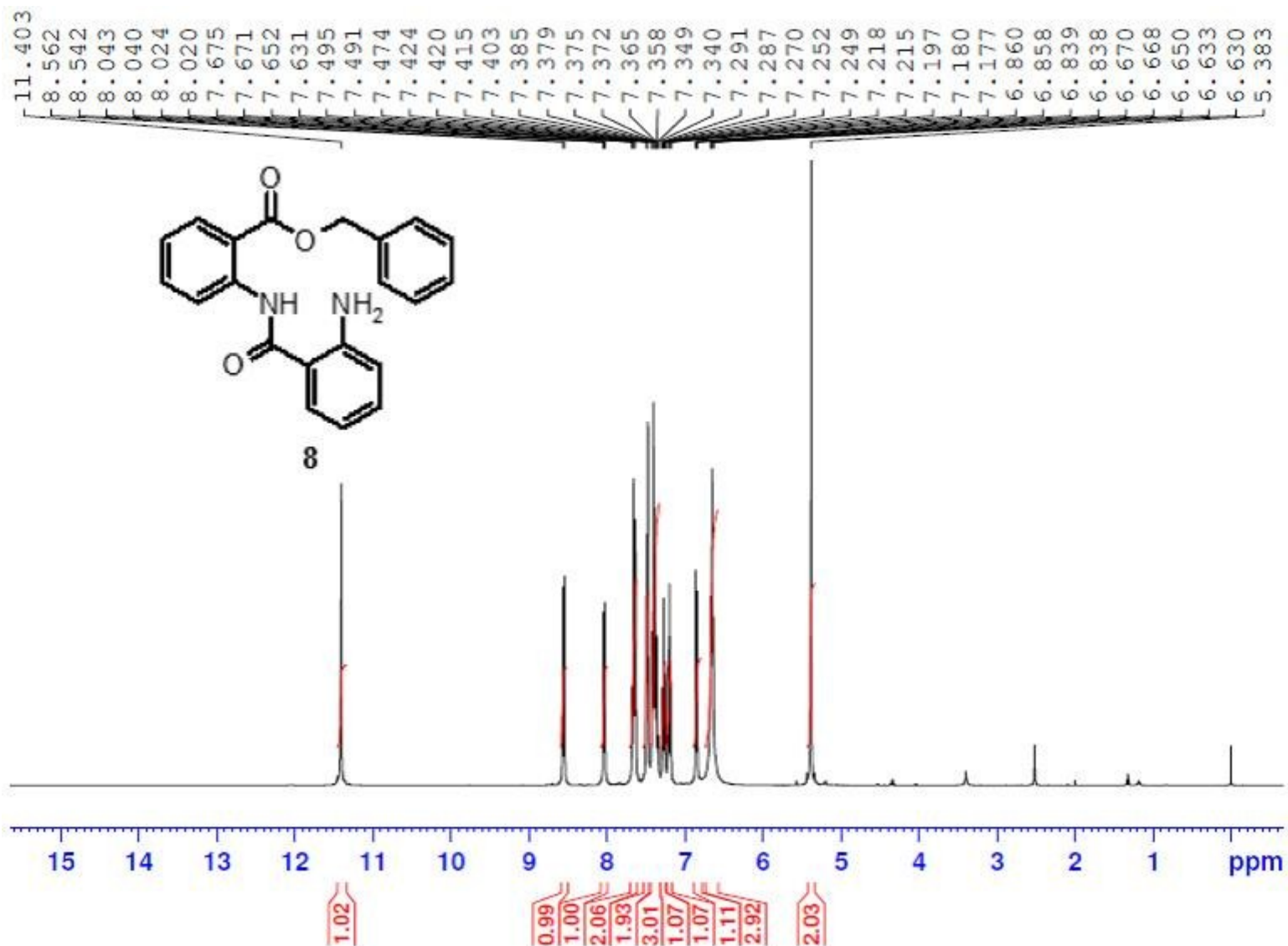
7



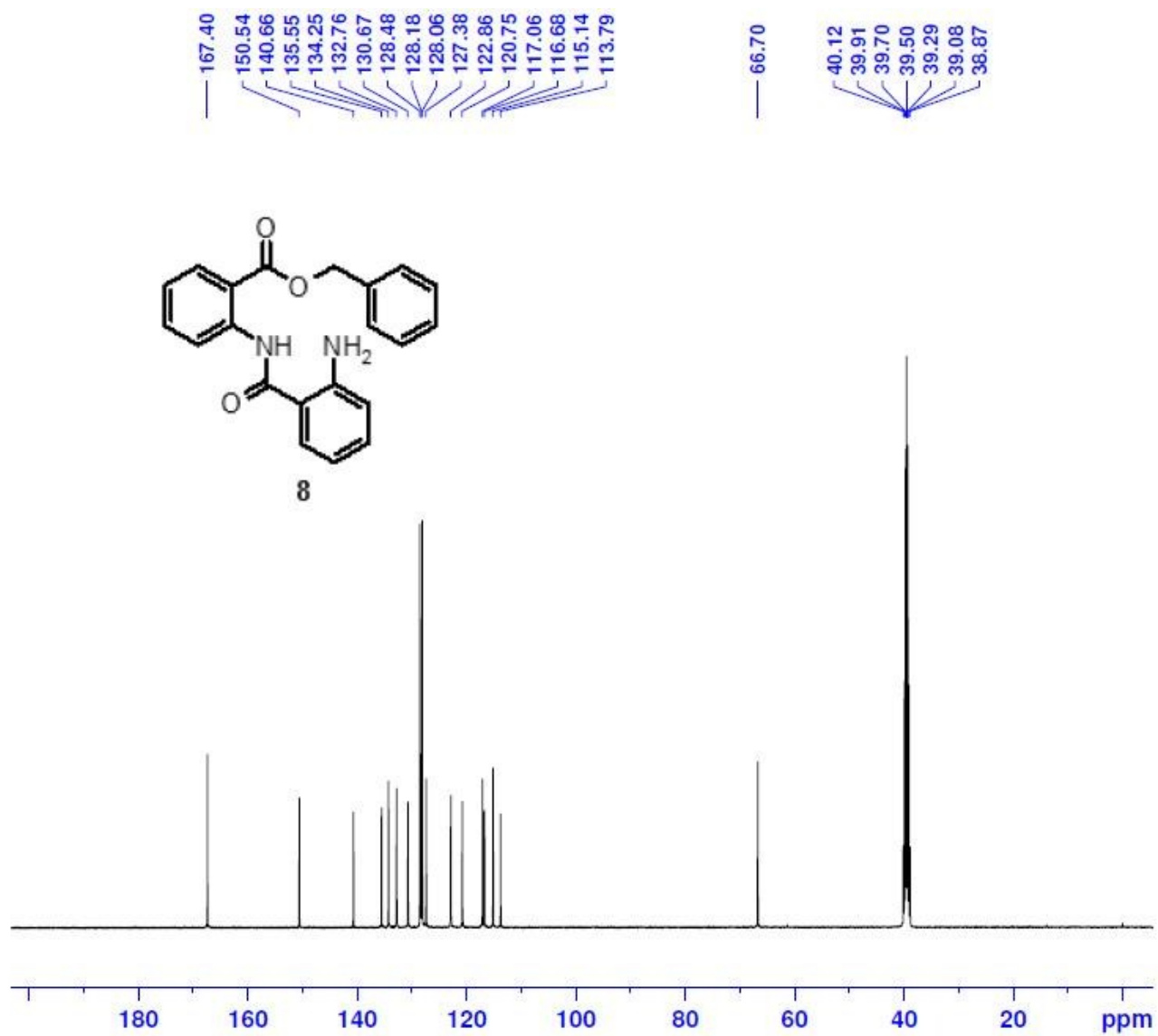
¹³C NMR of Compound 7 in DMSO-d₆



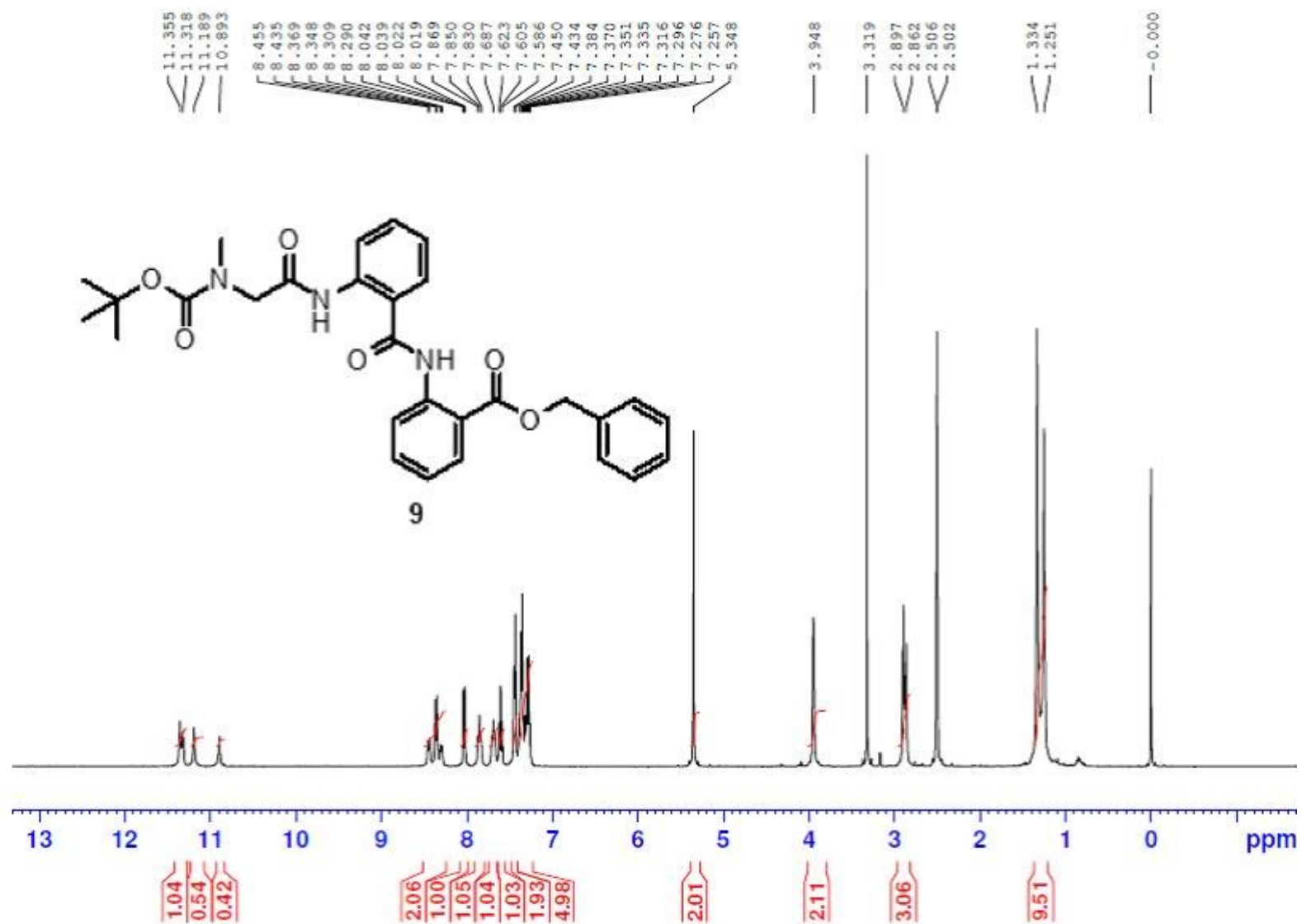
¹H NMR of Compound 8 in DMSO-d₆



¹³C NMR of Compound 8 in DMSO-d₆

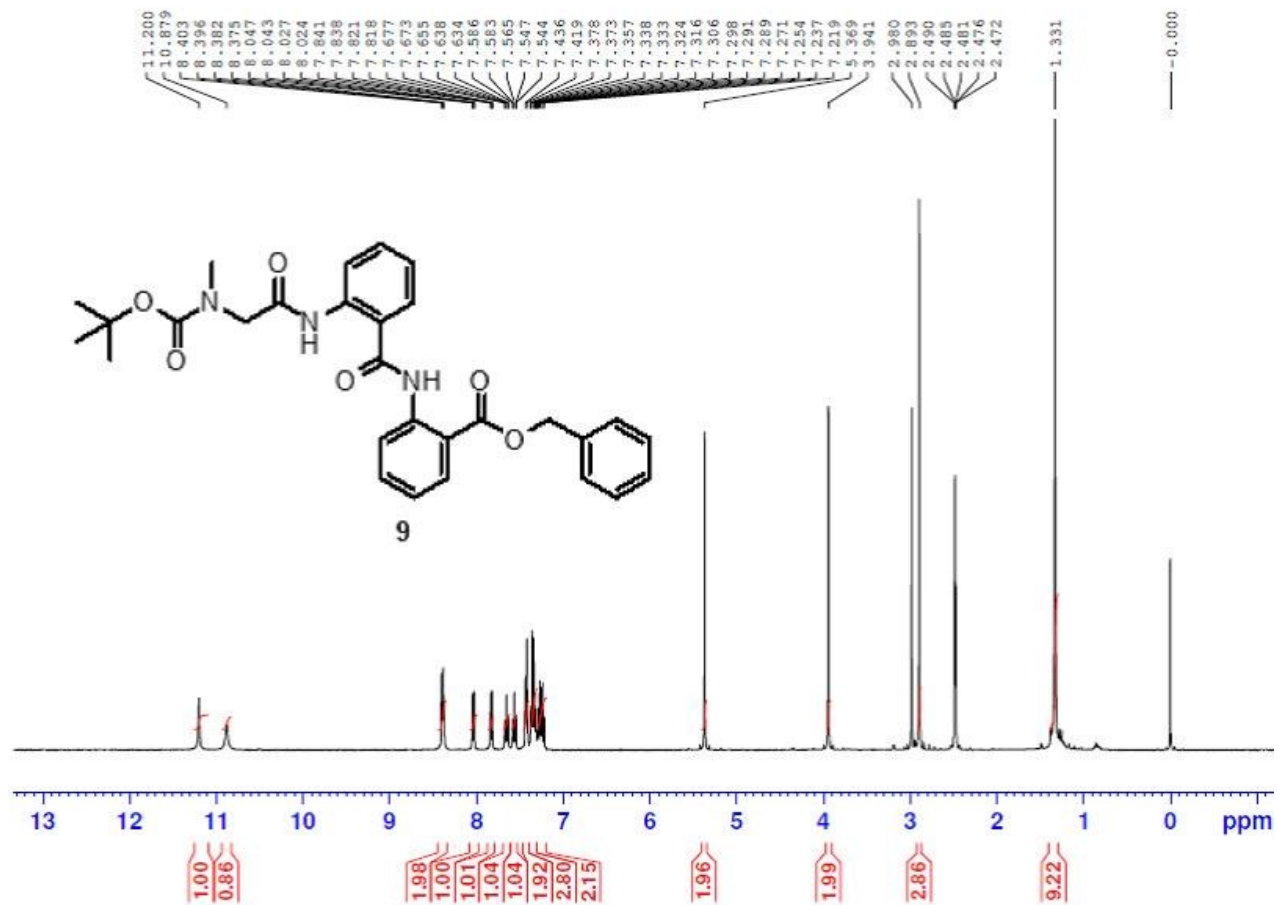


¹H NMR of Compound 9 in DMSO-d₆

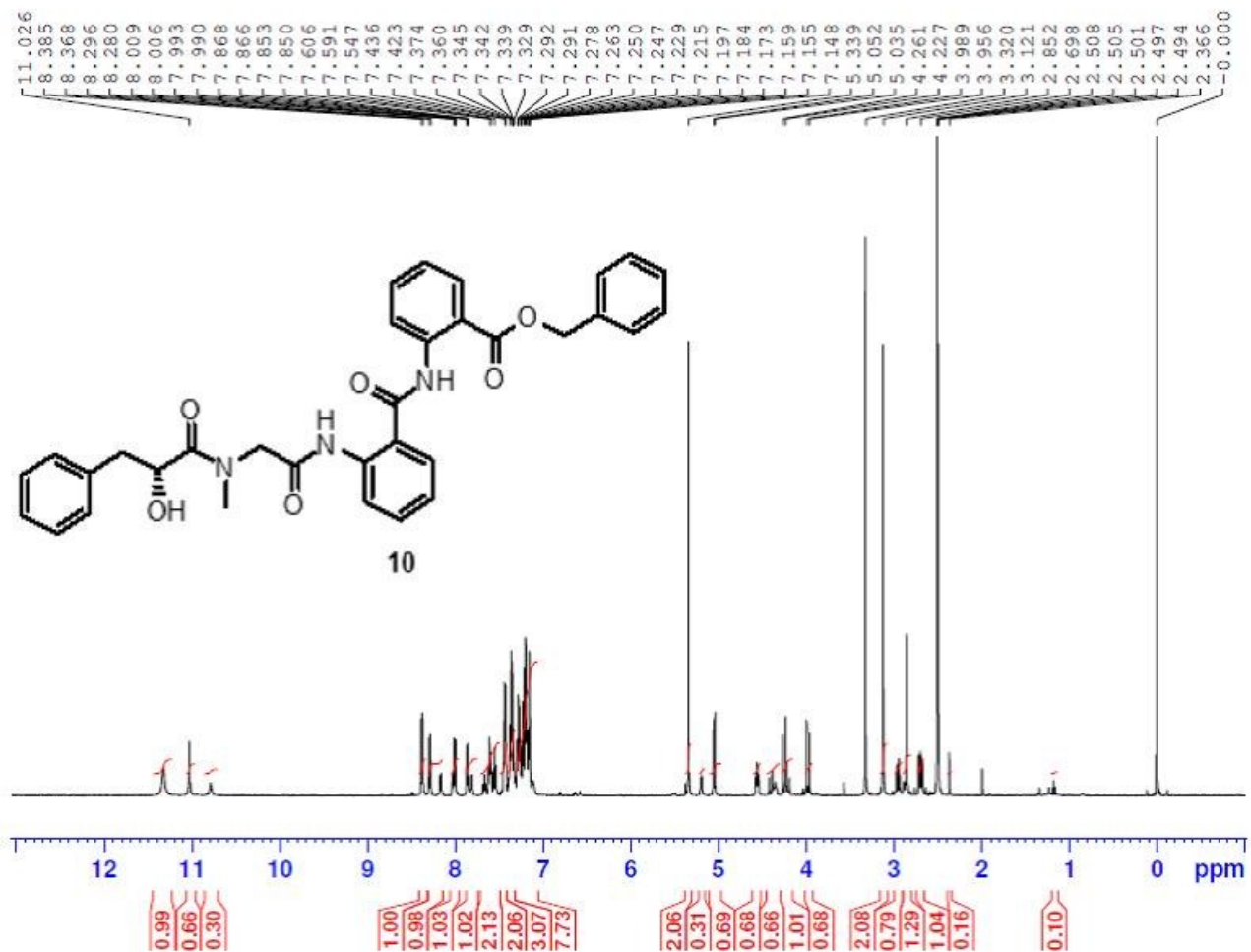


VT ¹H NMR of Compound 9 in DMSO-d₆

temp at 90 degrees

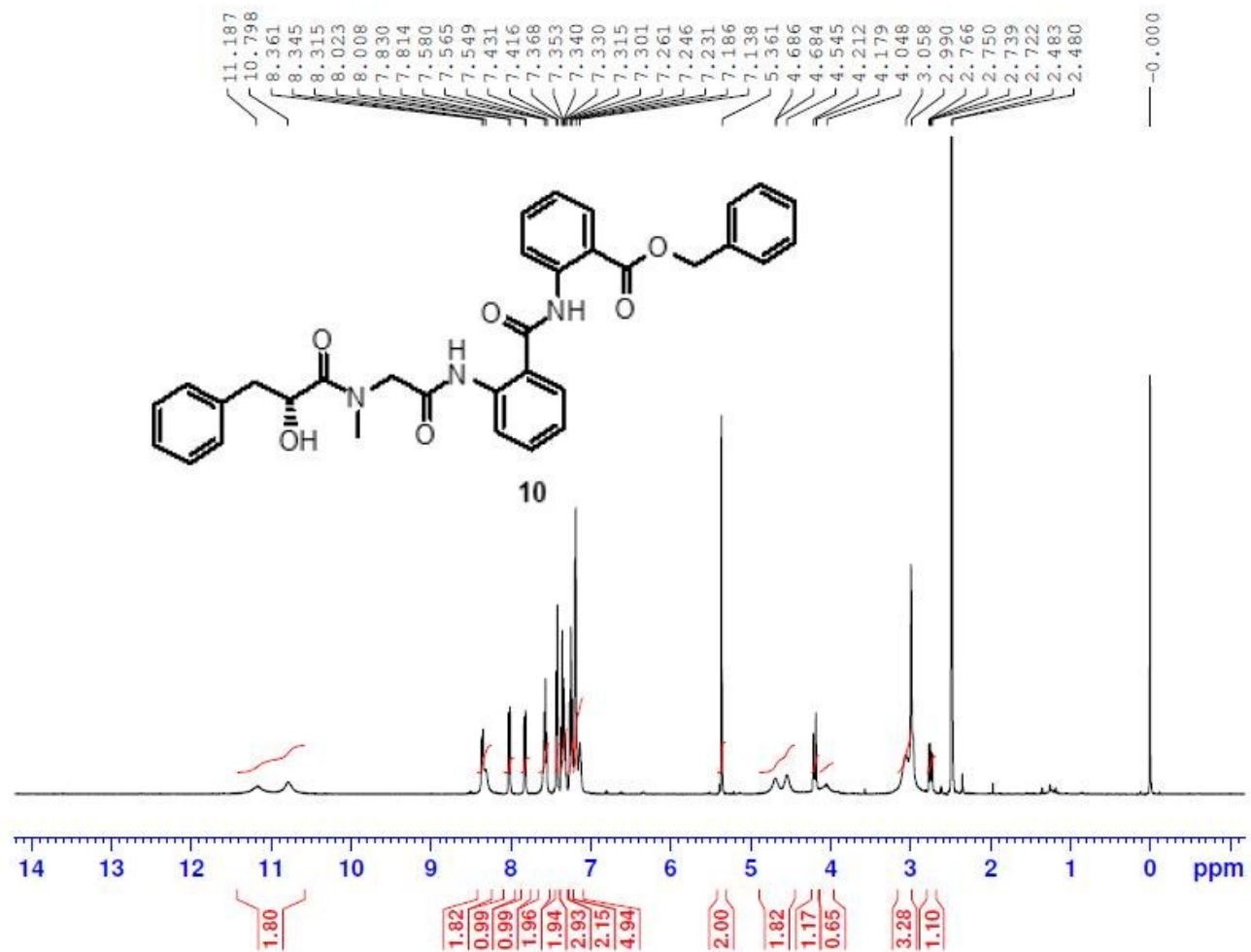


¹H NMR of Compound 10 in DMSO-d₆

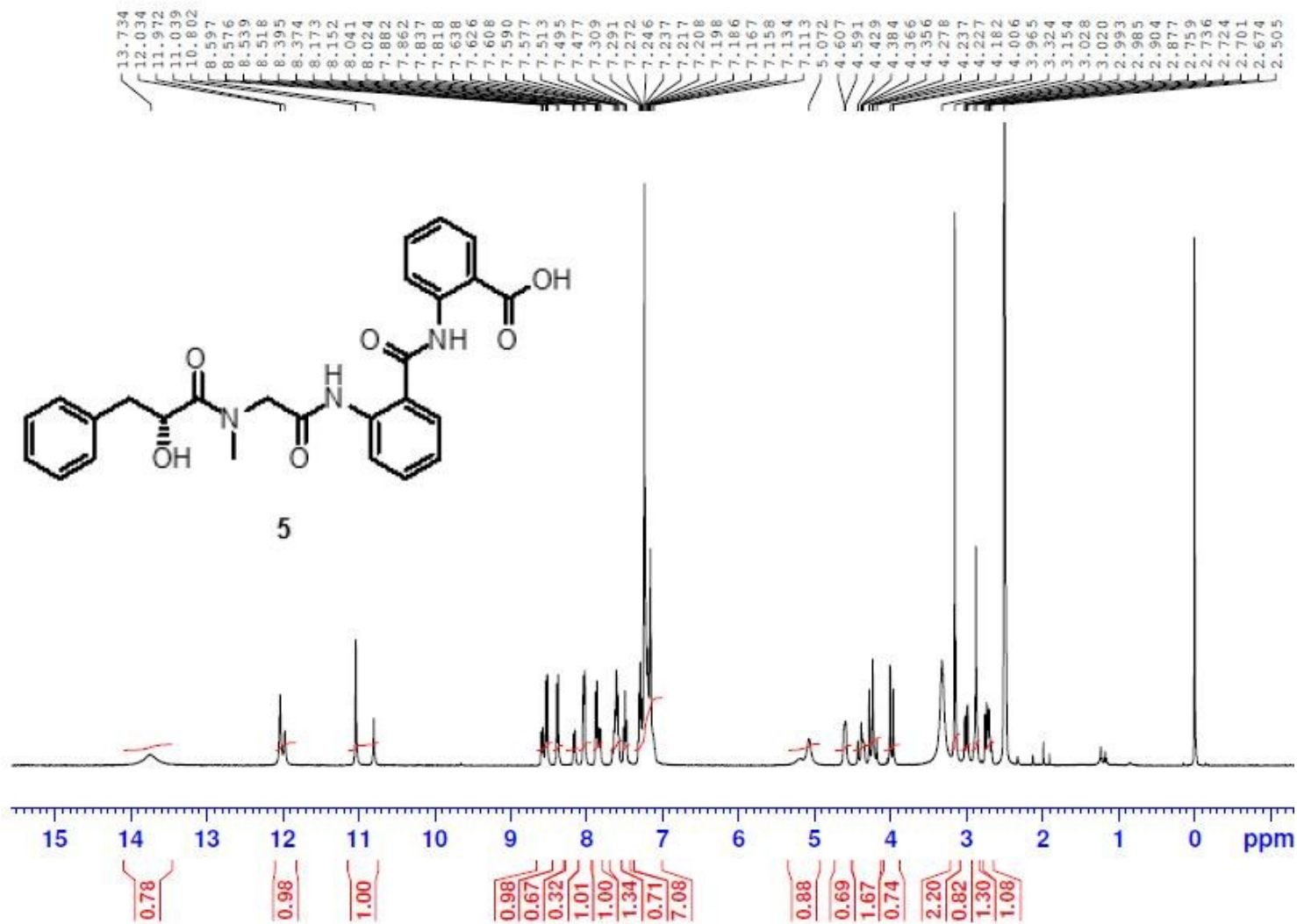


VT ¹H NMR of Compound 10 in DMSO-d₆

AT 90°C

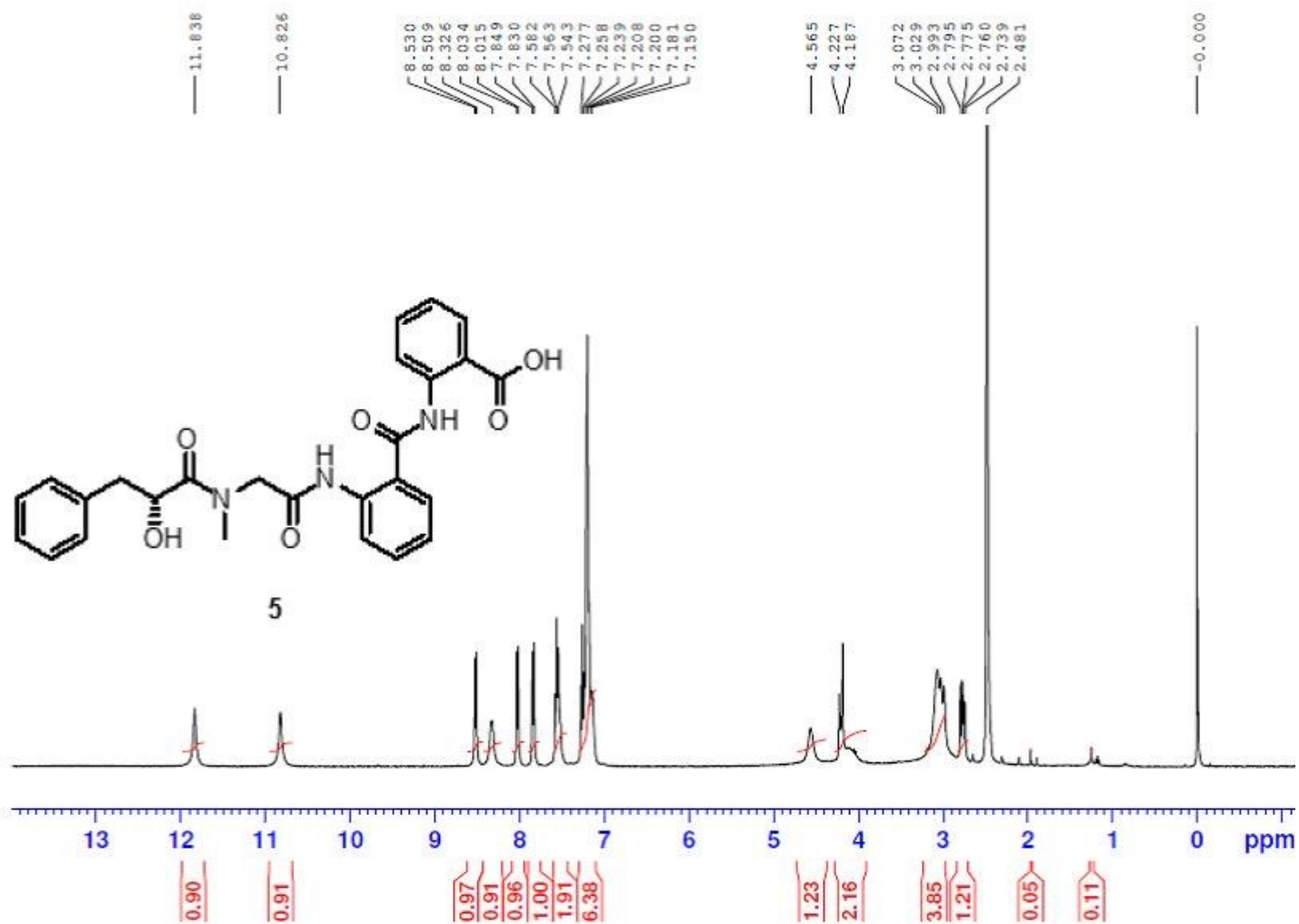


¹H NMR of Compound 5 in DMSO-d₆

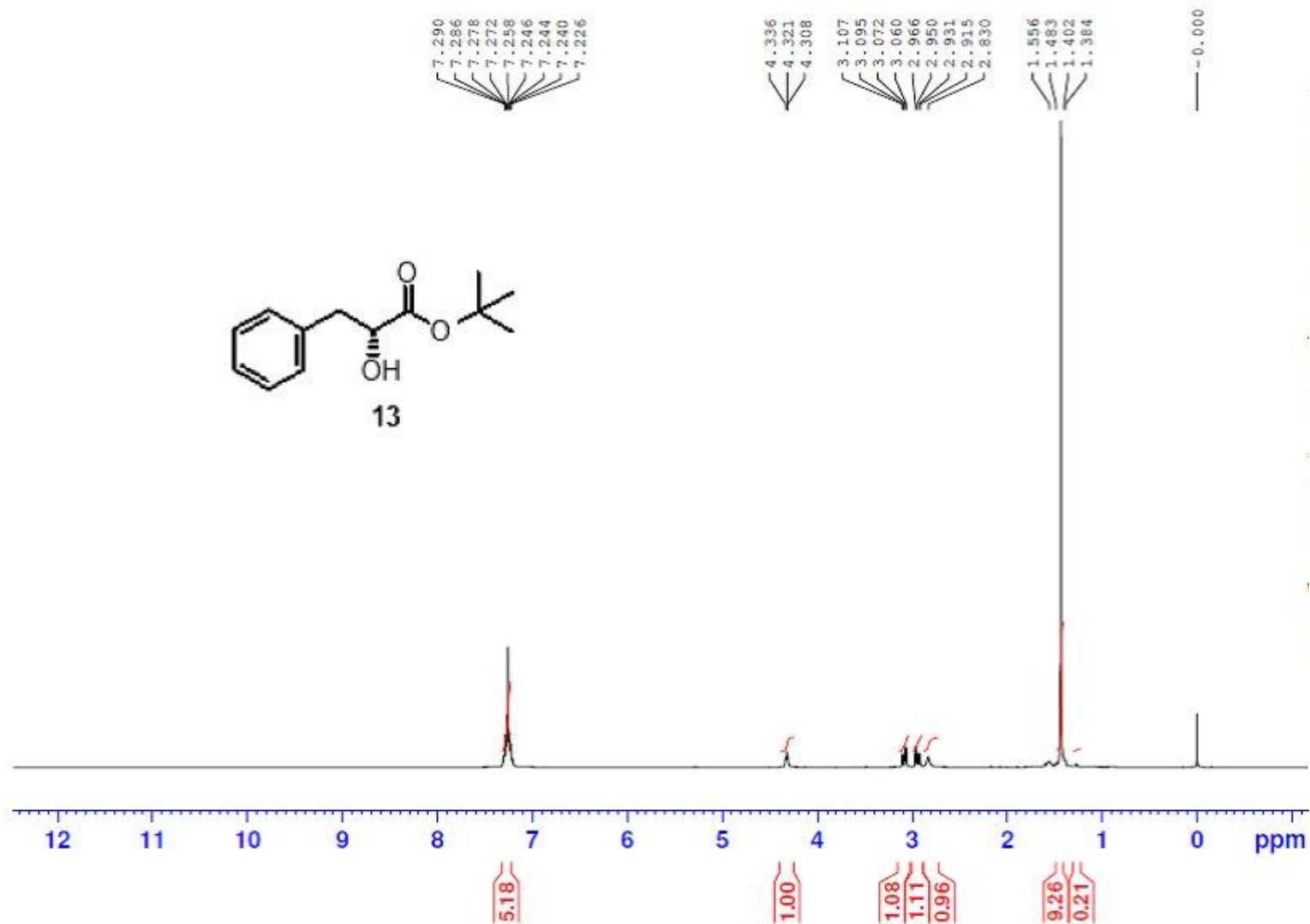


VT ¹H NMR of Compound 5 in DMSO-d₆

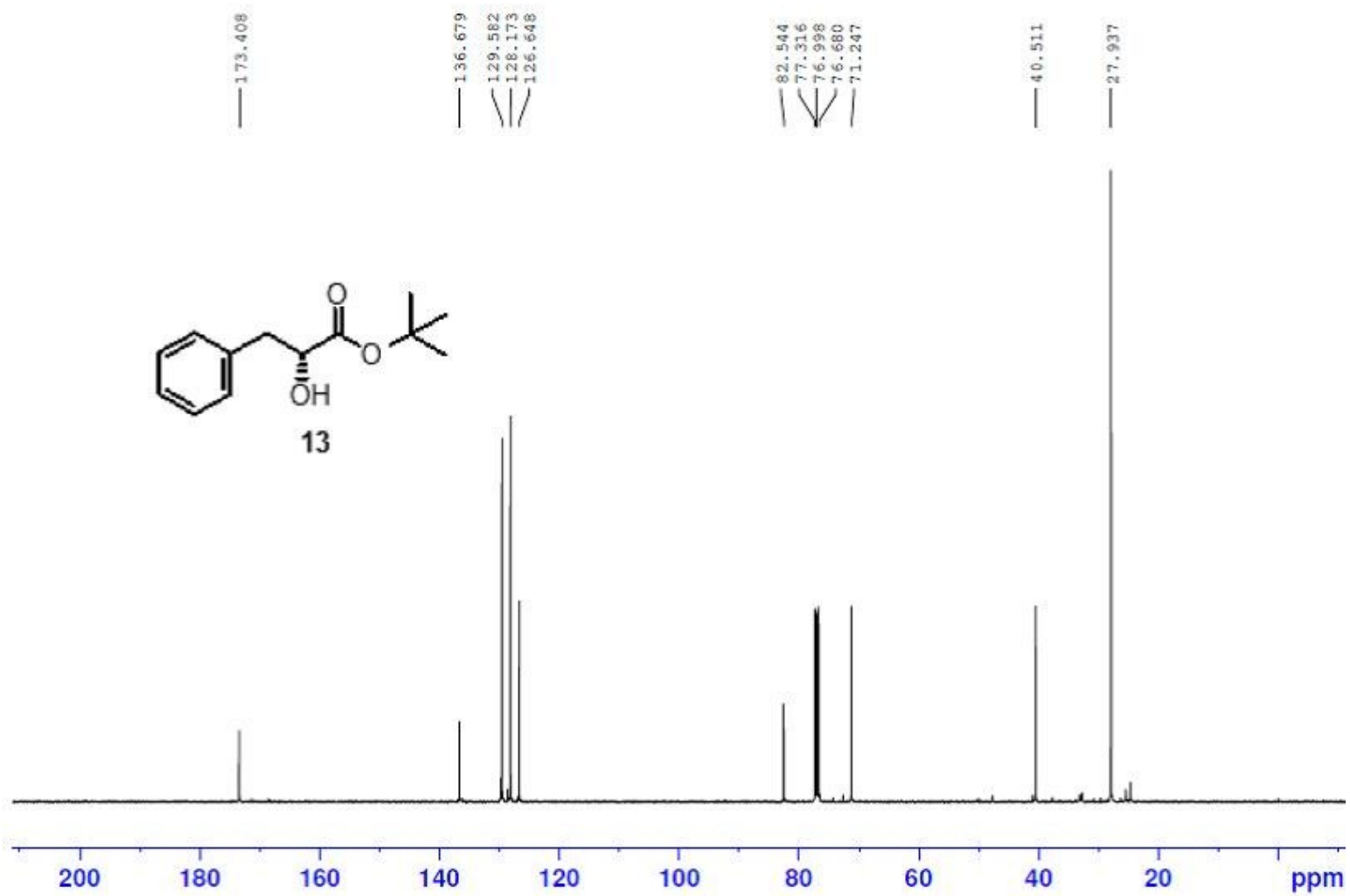
AT 90°C



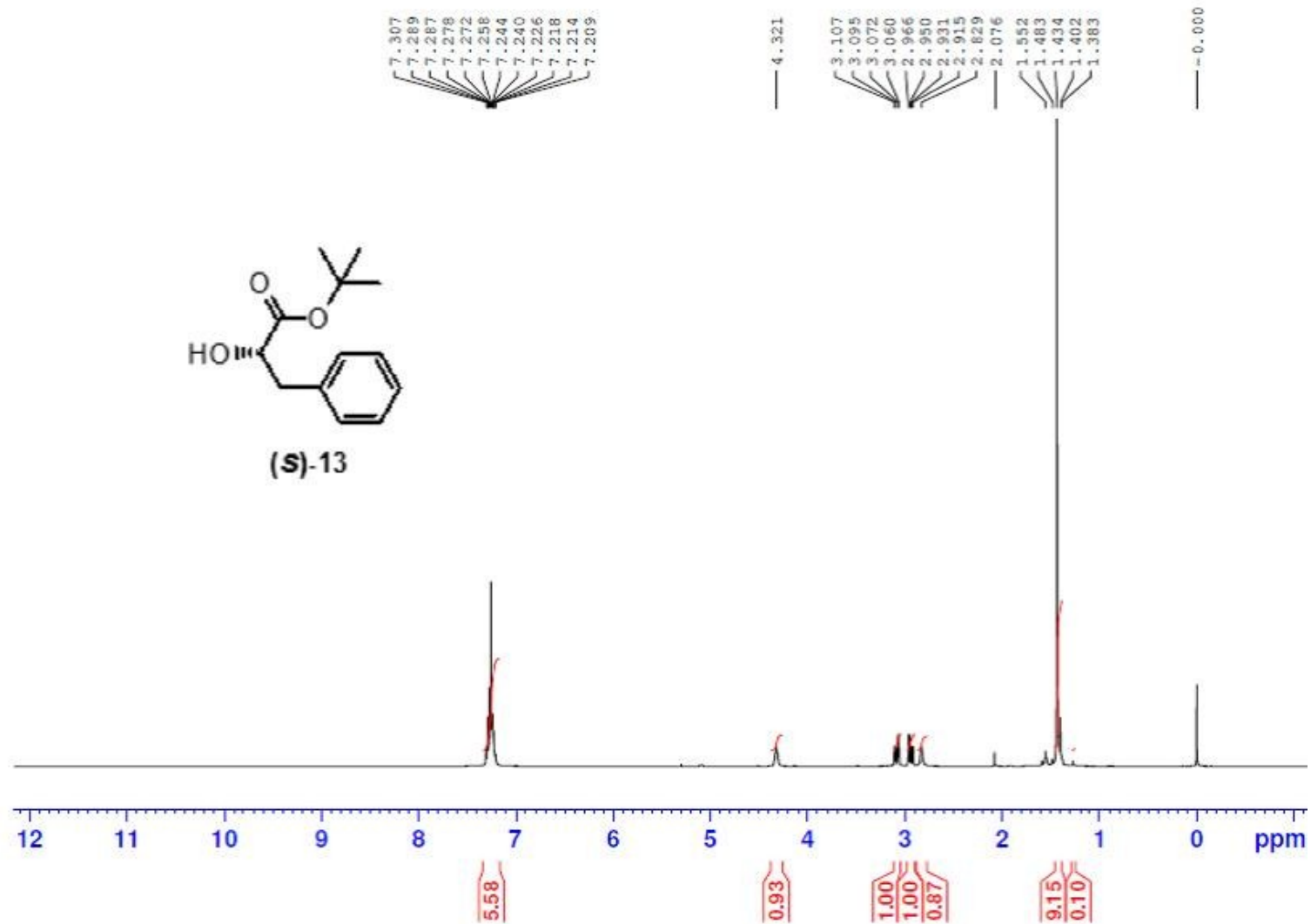
¹H NMR of Compound 13 in CDCl₃



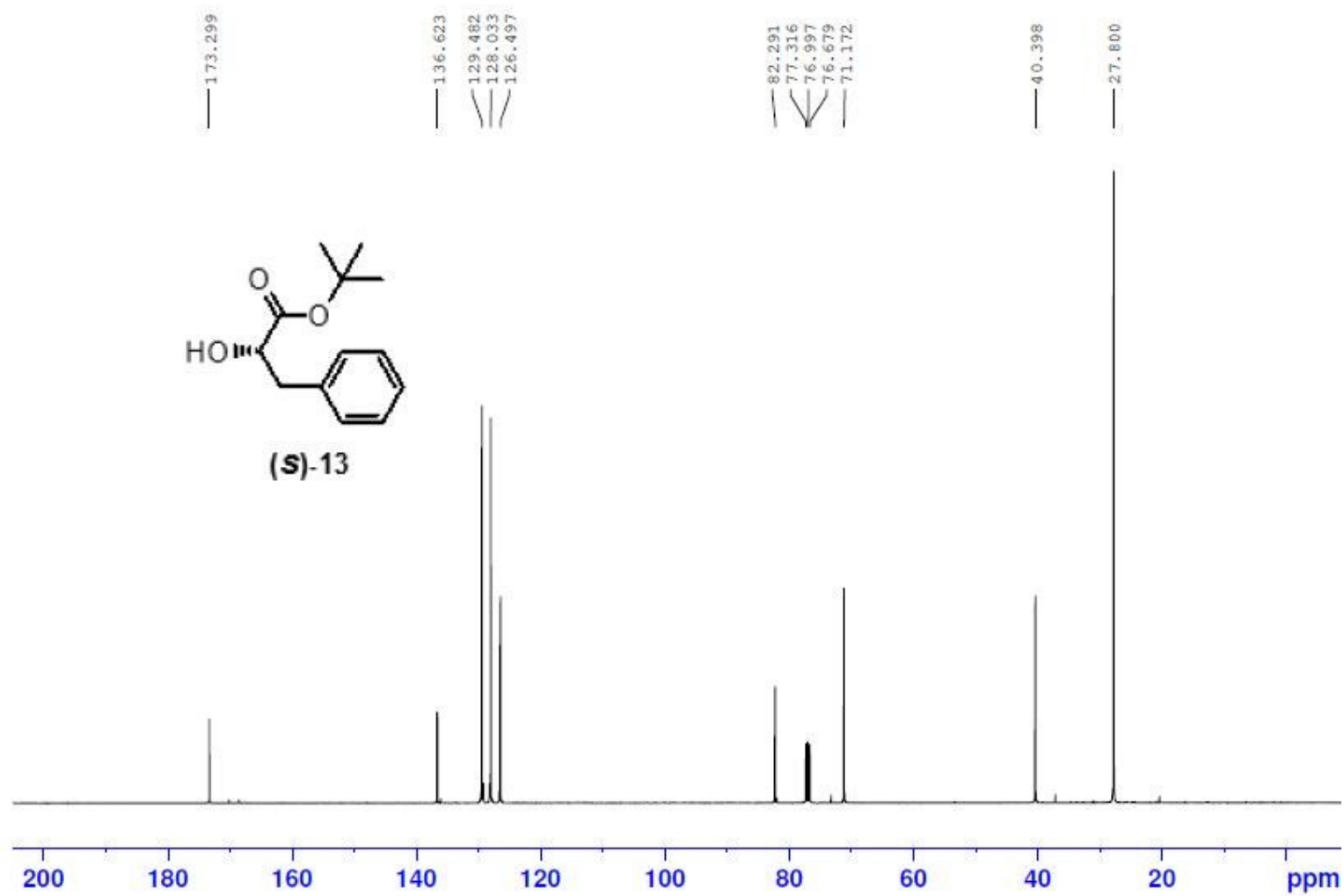
^{13}C NMR of Compound 13 in CDCl_3



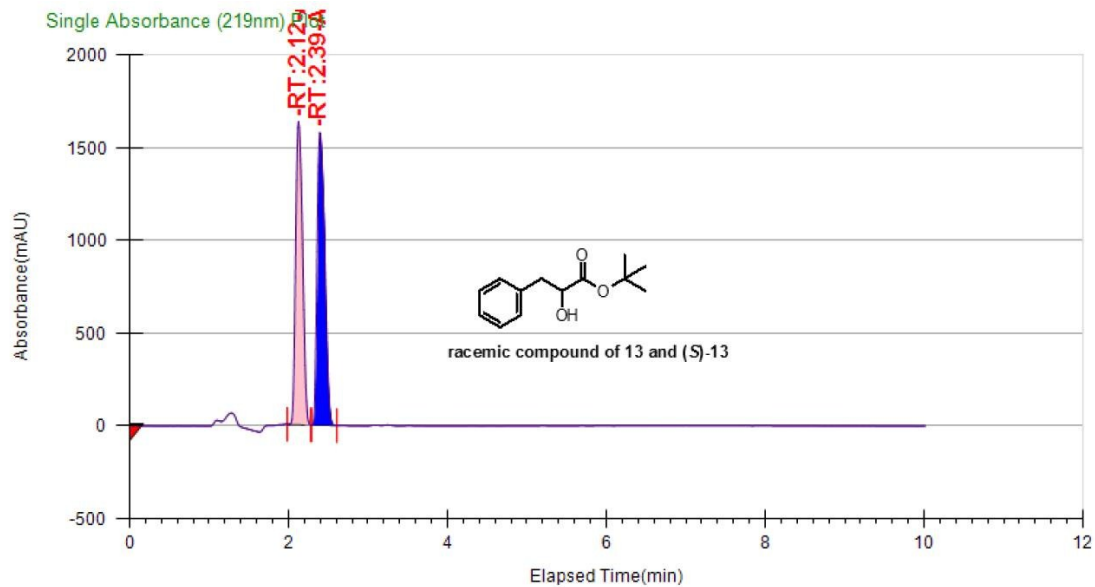
¹H NMR of Compound (S)-13 in CDCl₃



¹³C NMR of Compound (*S*)-13 in CDCl₃



Racemic of compound 13 and (S)-13



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
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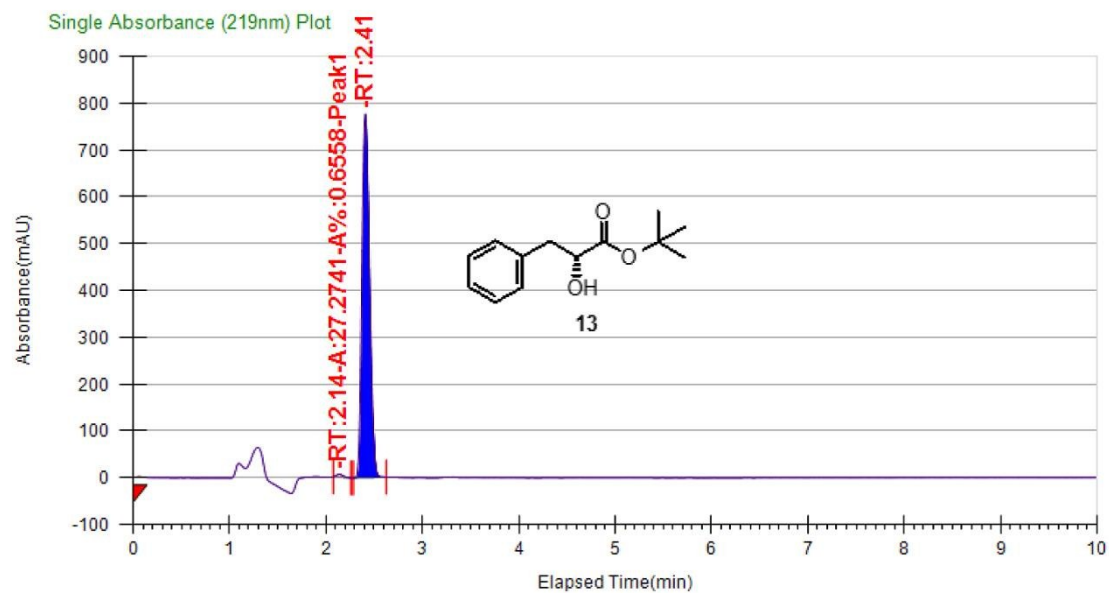
Run Information

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|-------------------|-----------|-------------------------|--------------------------------------|-------------------------------|---------------|-------|------|------------|----------|
| 3g-10%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak AD- H(4.6*250)- mm5u | GVKP-SK- B1329-110- Rac | 21B | 29.9 | 3 | 10 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 48.4422 | 9572.8763 | 2.12 min | 1632.6803 | 2124 |
| 2 | 51.5578 | 10188.5709 | 2.39 min | 1575.5709 | 2390.6667 |

Chiral HPLC of Compound 13



General Information

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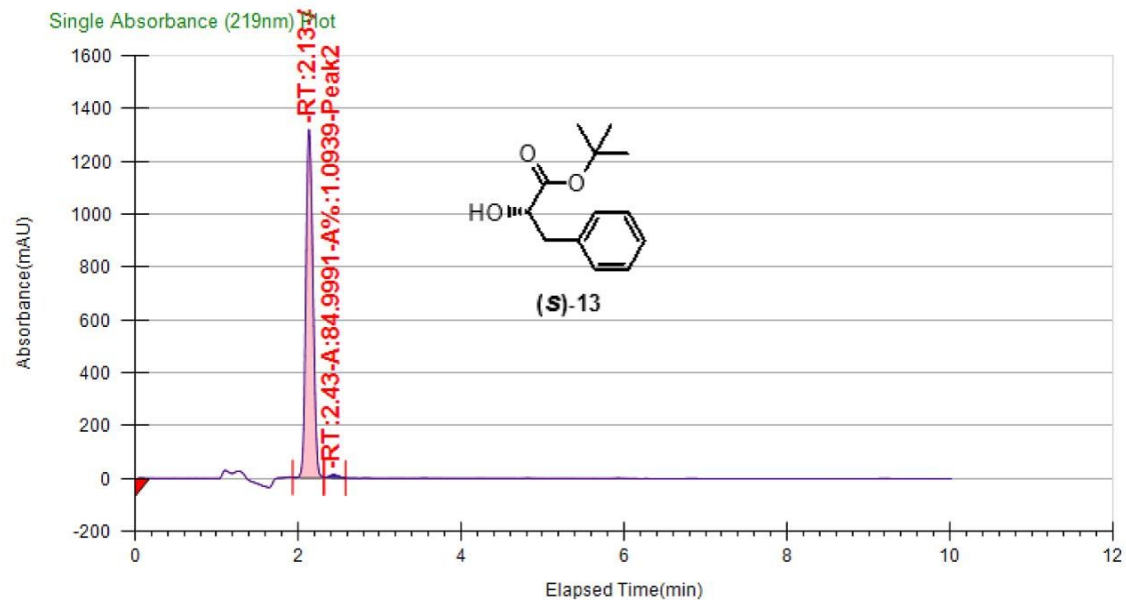
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|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|------|------------|----------|
| 3g-10%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak AD- H(4.6*250) mm5u | GVKP-SK- B1329-87 | 22B | 30.2 | 3 | 10 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 0.6558 | 27.2741 | 2.14 min | 6.0413 | 2140.6667 |
| 2 | 99.3442 | 4131.4994 | 2.41 min | 776.0687 | 2407.3333 |

Chiral HPLC of Compound (S)-13



General Information

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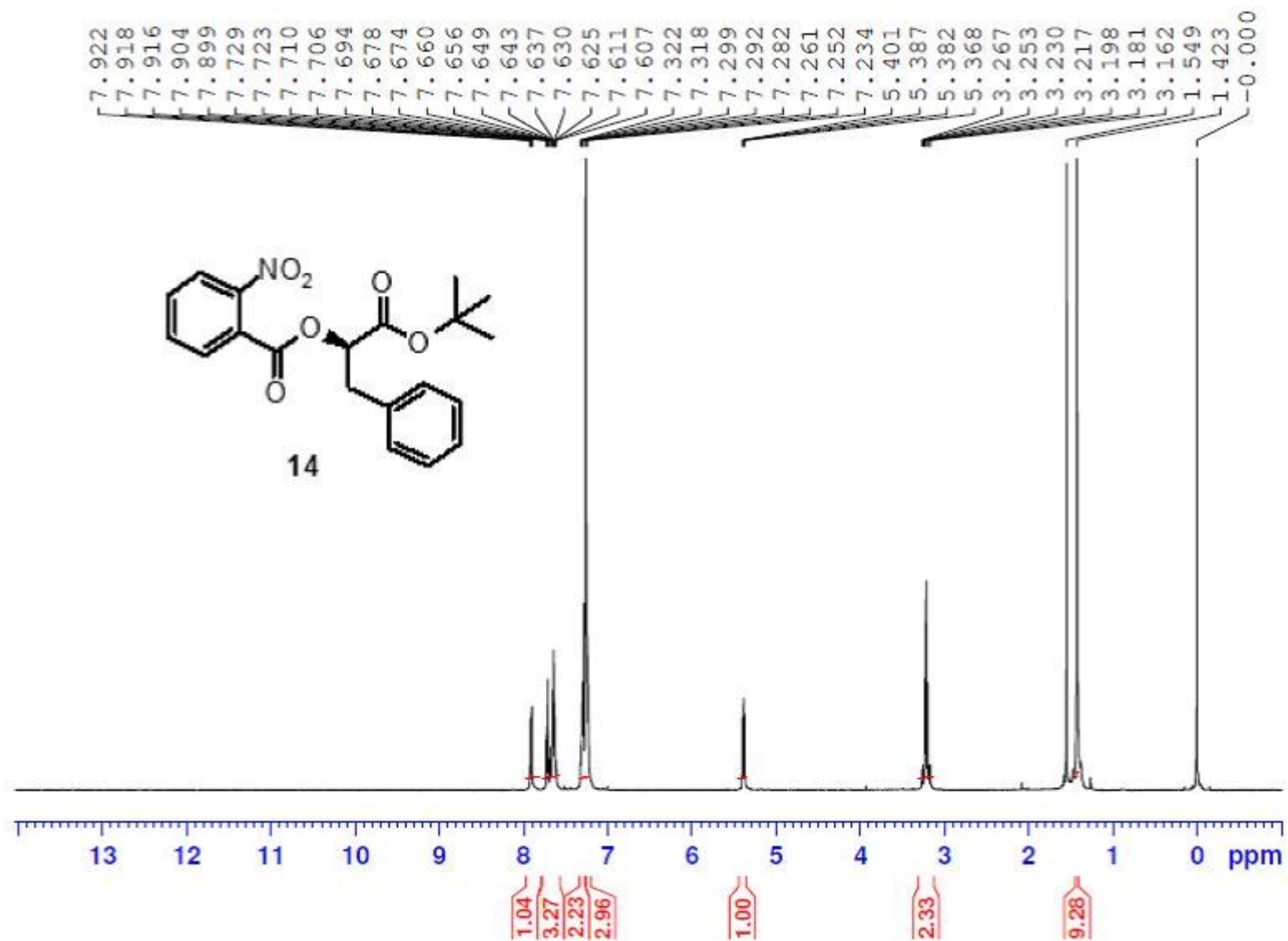
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|------|------------|----------|
| 3g-10%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak AD- H(4.6*250) mm5u | GVKP-SK- B1329-62 | 23B | 29.9 | 3 | 10 | 100 |

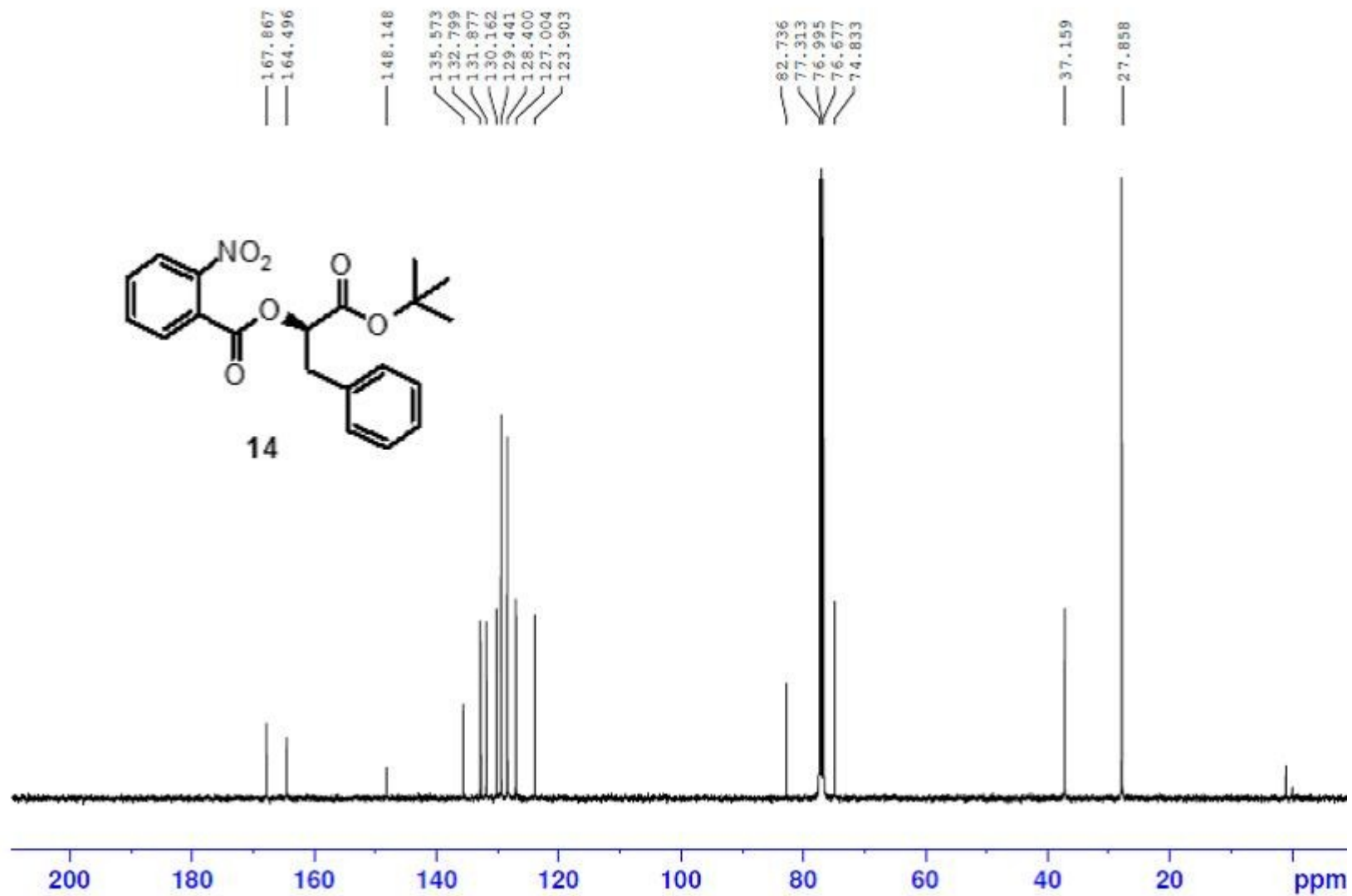
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
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| 1 | 98.9061 | 7685.035 | 2.13 min | 1317.2318 | 2132.3333 |
| 2 | 1.0939 | 84.9991 | 2.43 min | 10.7331 | 2424 |

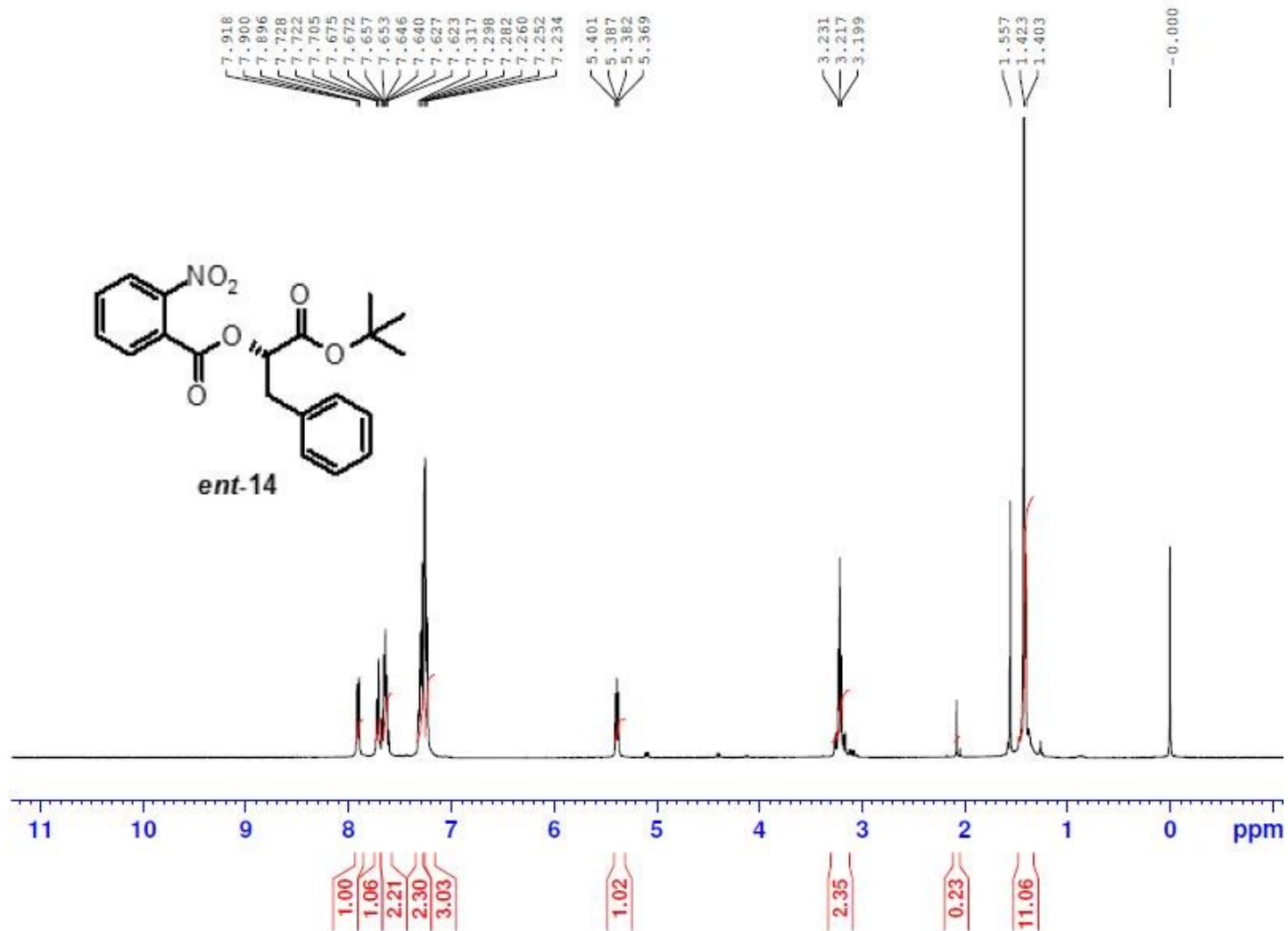
¹H NMR of Compound 14 in CDCl₃



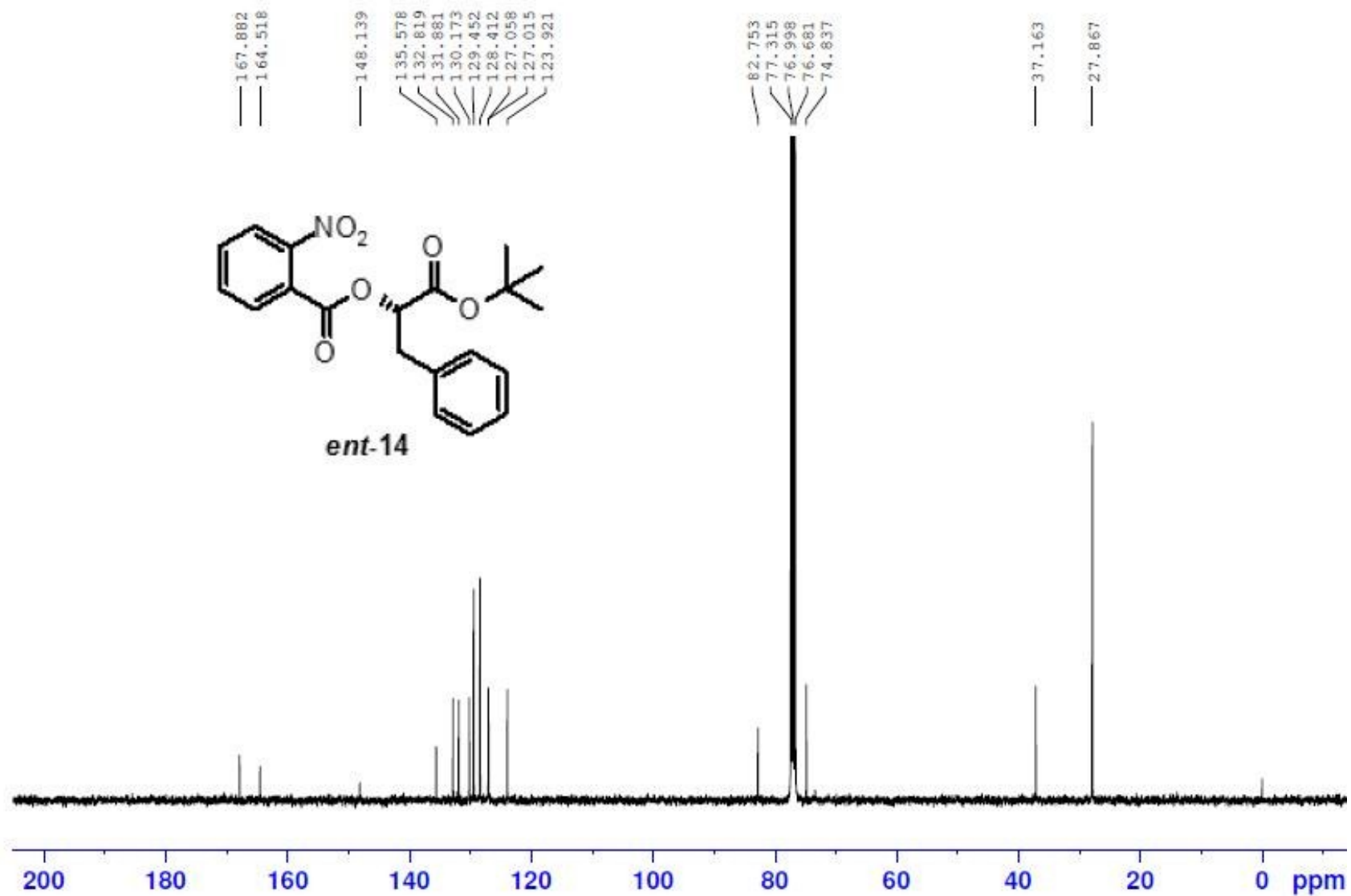
¹³C NMR of Compound 14 in CDCl₃



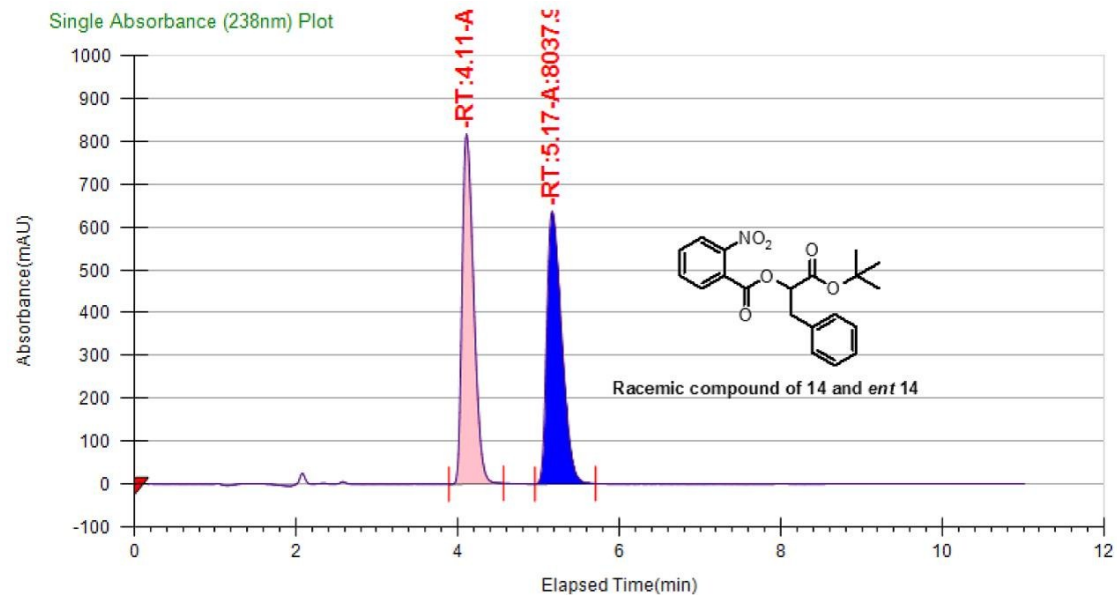
¹H NMR of Compound *ent-14* in CDCl₃



¹³C NMR of Compound-14 in CDCl₃



Racemic of compound 14 and *ent*-14



General Information

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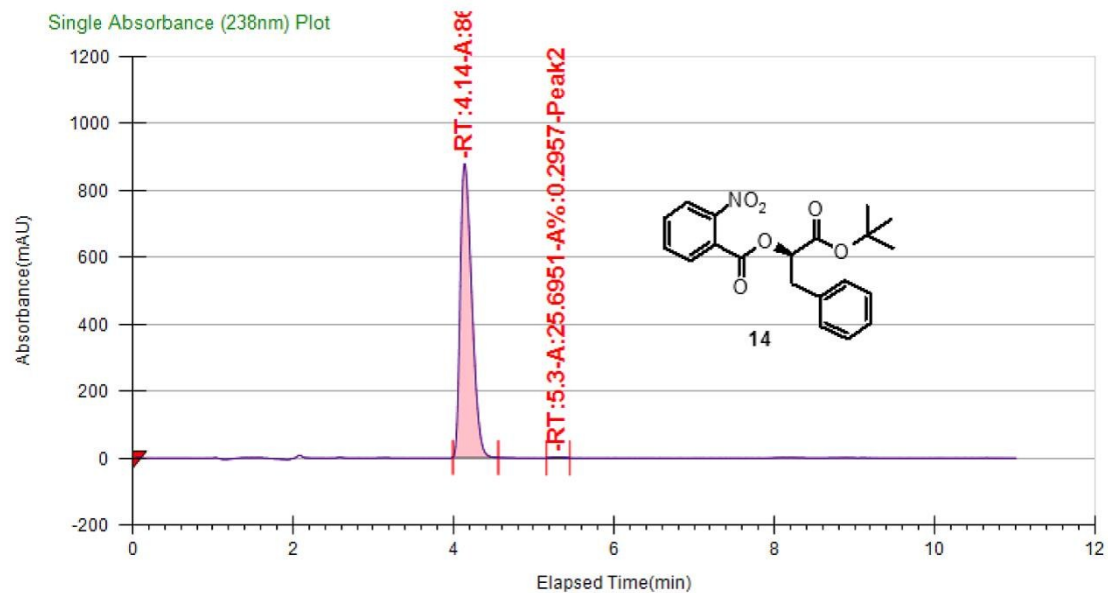
Run Information

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|-------------------|-----------|---------------------------------|------------------------------------|-------------------------------|---------------|-------|-------|------------|----------|
| 3g-15%-100bar | 10 | 0.5% Iso propyl amine in IPA | Lux amylose-2 (4,6*250) mm5u | GVKP-SK- B1329-111- Rac | 11B | 30.1 | 2.999 | 14.9717 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 49.9013 | 8006.3336 | 4.11 min | 816.5615 | 0 |
| 2 | 50.0987 | 8037.9928 | 5.17 min | 635.4853 | 0 |

Chiral HPLC of Compound 14



General Information

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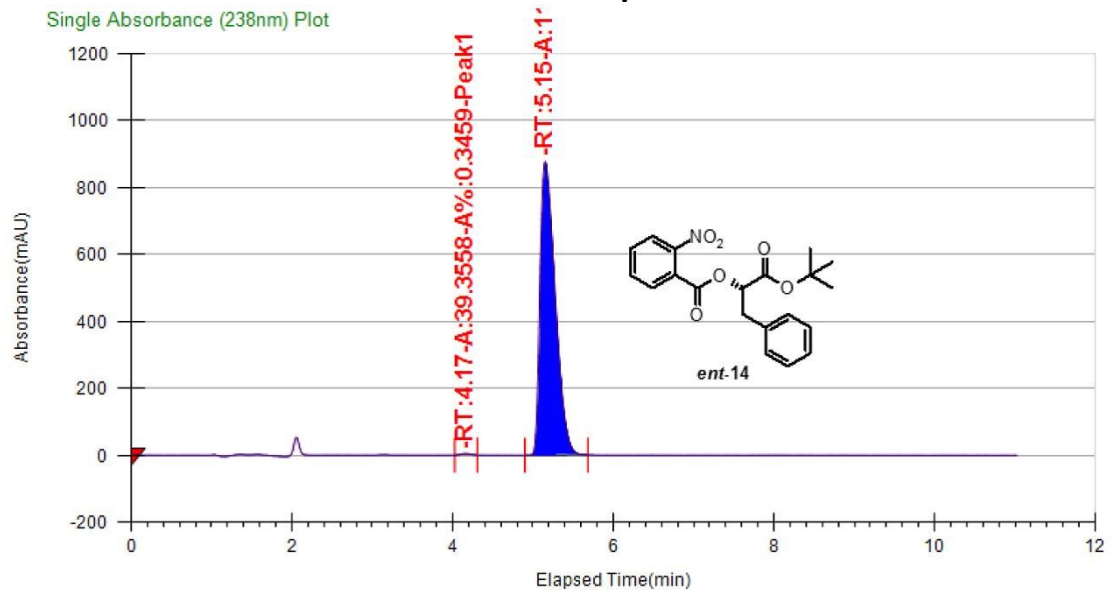
Run Information

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|-------------------|-----------|---------------------------------|------------------------------------|------------------------|---------------|-------|-------|------------|----------|
| 3g-15%-100bar | 10 | 0.5% Iso propyl amine in IPA | Lux amylose-2 (4,6*250) mm5u | GVKP-SK- B1329-80-R | 12B | 30 | 2.999 | 14.9717 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 99.7043 | 8663.6863 | 4.14 min | 877.7471 | 0 |
| 2 | 0.2957 | 25.6951 | 5.3 min | 2.7786 | 0 |

Chiral HPLC of Compound *ent*-14



General Information

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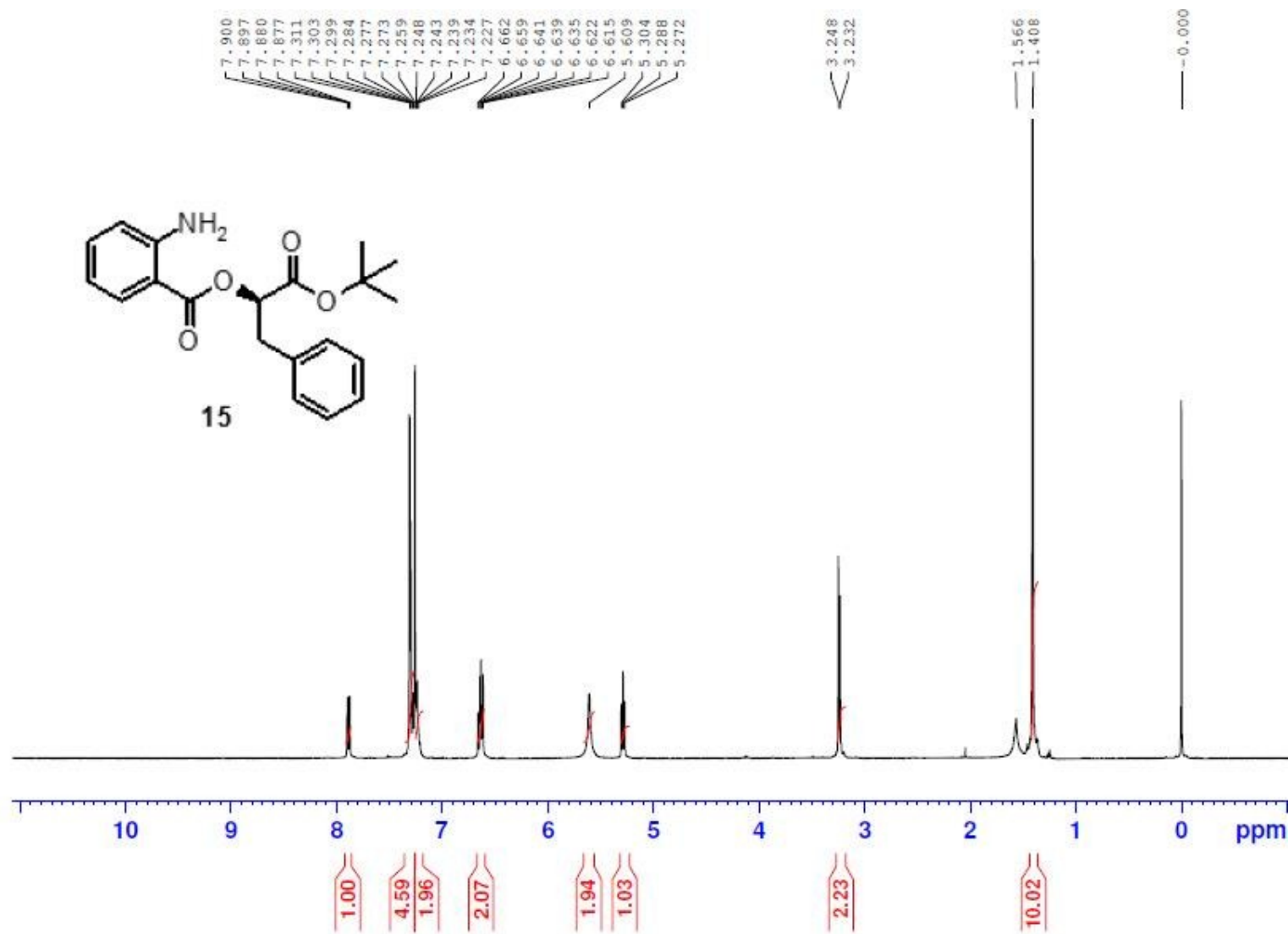
Run Information

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|-------------------|-----------|------------------------------|------------------------------|--------------------|---------------|-------|-------|------------|----------|
| 3g-15%-100bar | 10 | 0.5% Iso propyl amine in IPA | Lux amylose-2 (4.6*250) mm5u | GVKP-SK-B1329-63-S | 13B | 30 | 2.999 | 14.9717 | 100 |

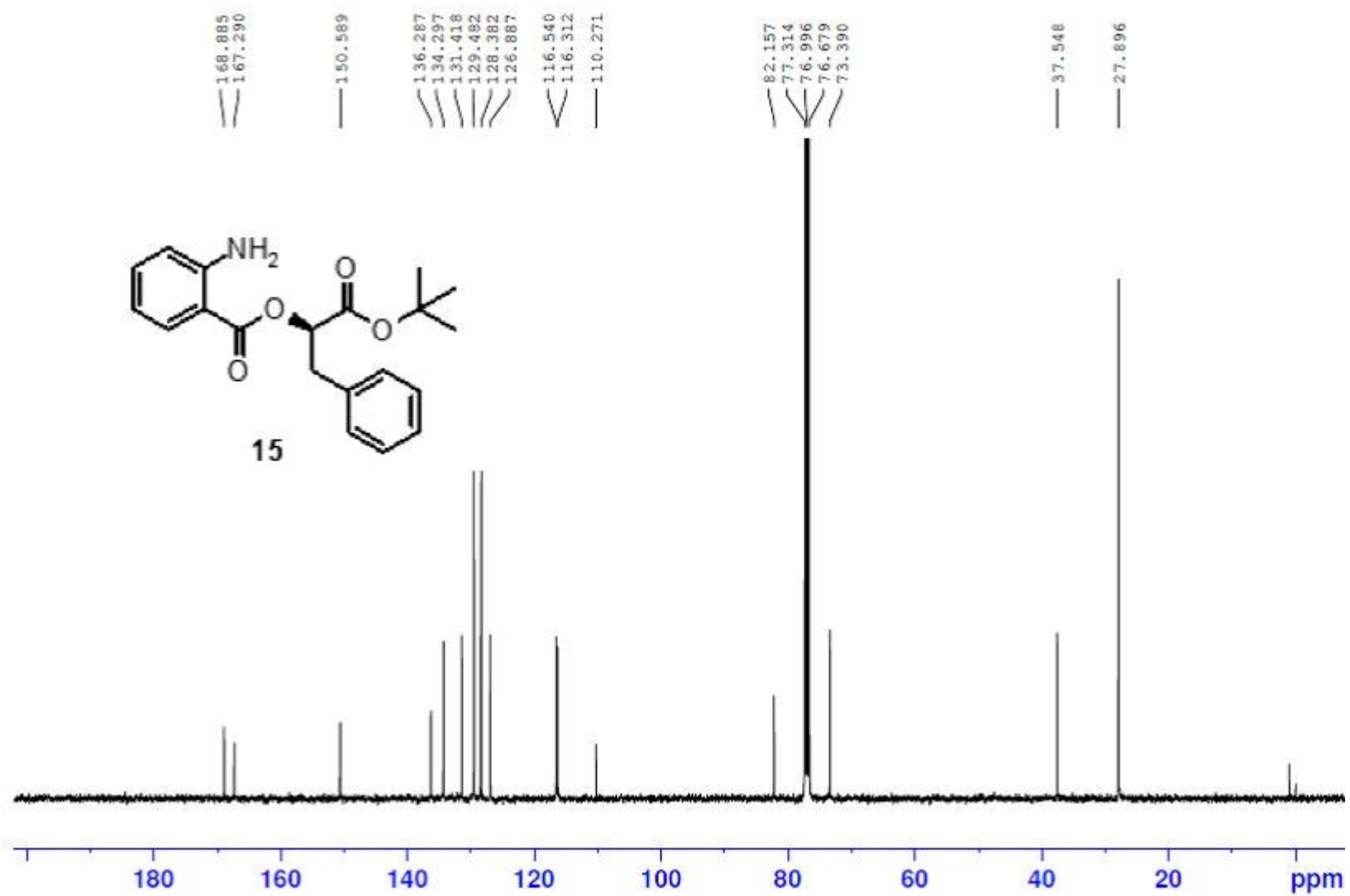
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|----------|-------------|
| 1 | 0.3459 | 39.3558 | 4.17 min | 4.5538 | 4165.6167 |
| 2 | 99.6541 | 11339.7098 | 5.15 min | 877.4906 | 5148.9333 |

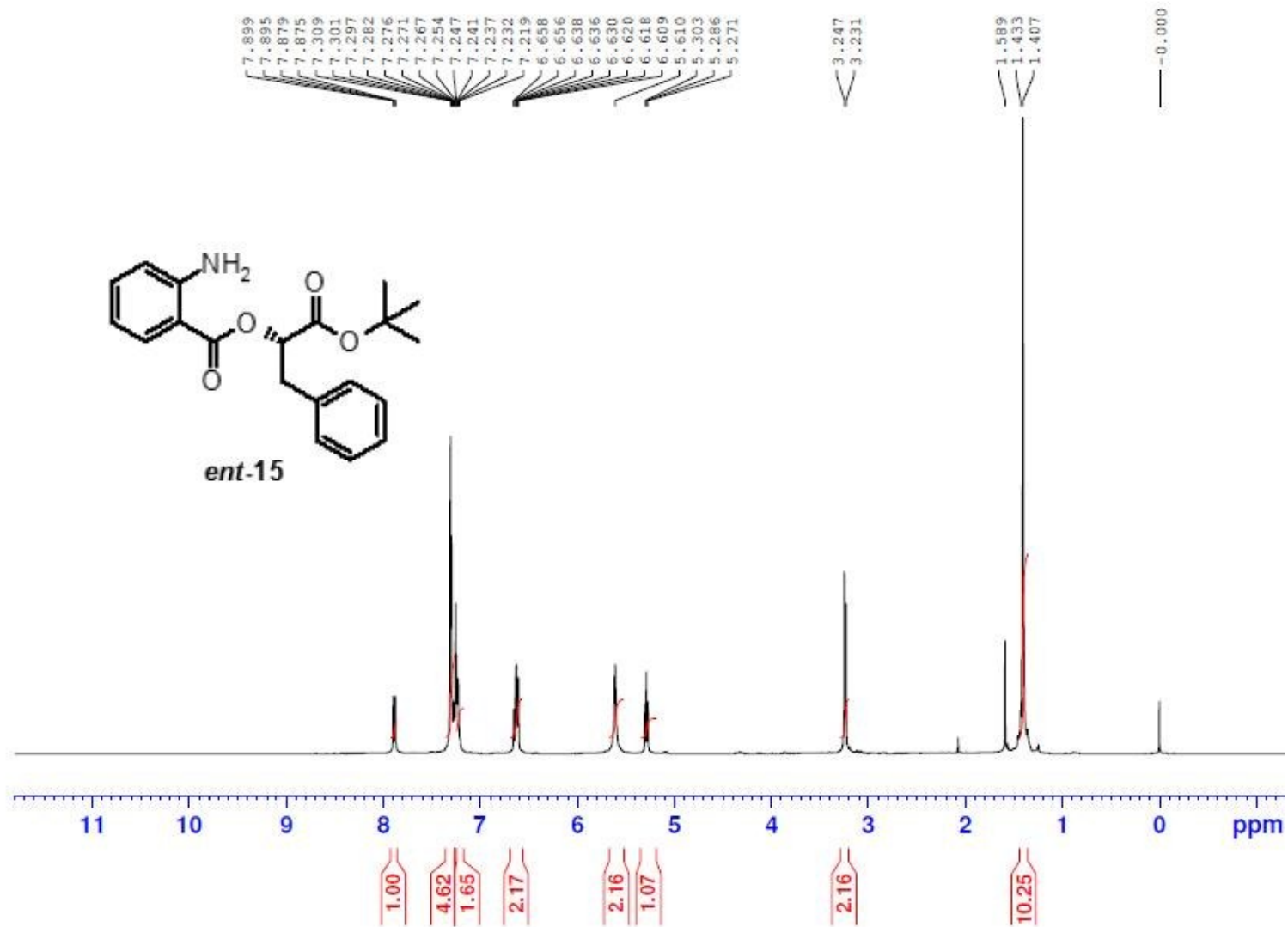
¹H NMR of Compound 15 in CDCl₃



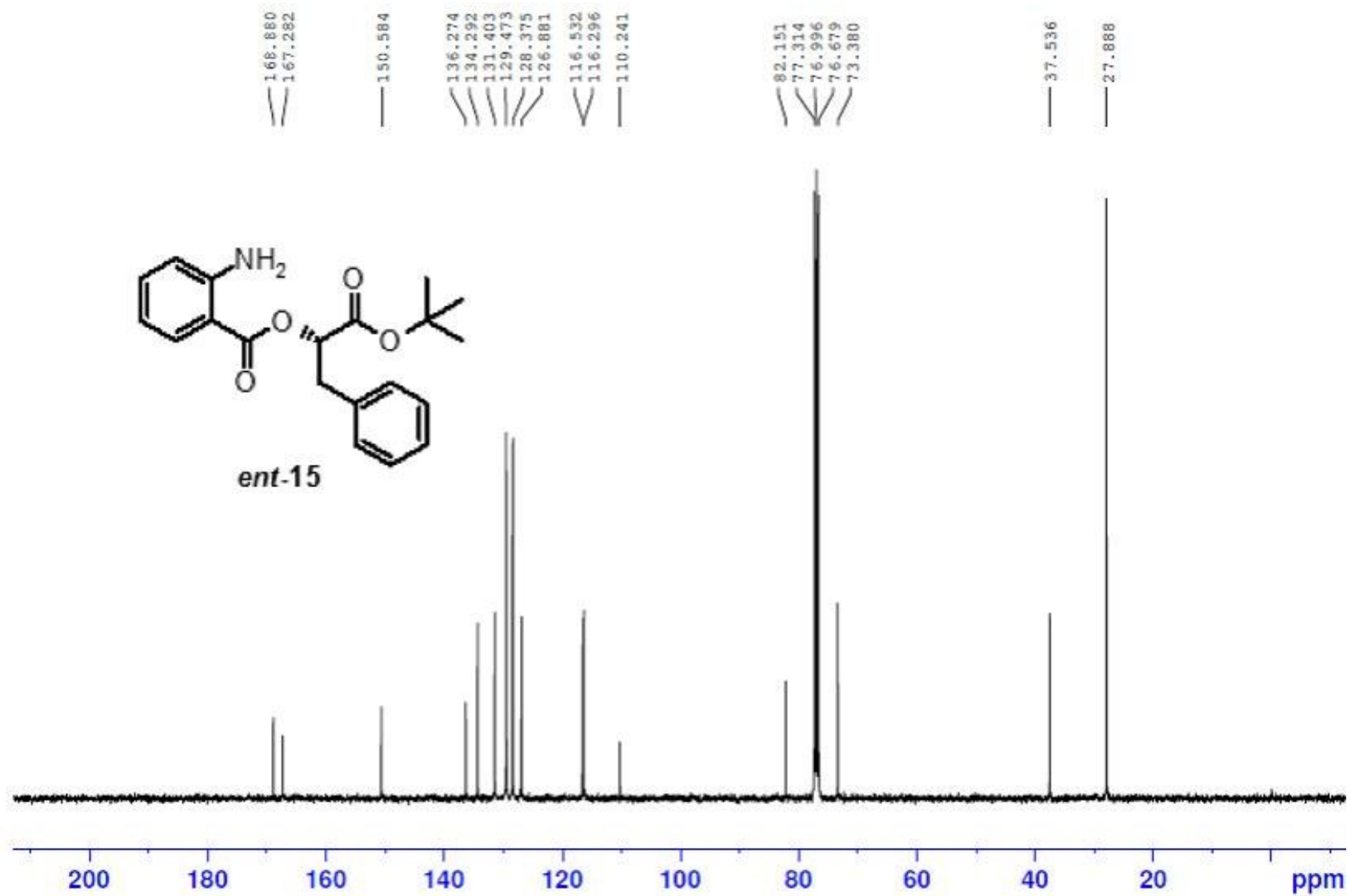
¹³C NMR of Compound 15 in CDCl₃



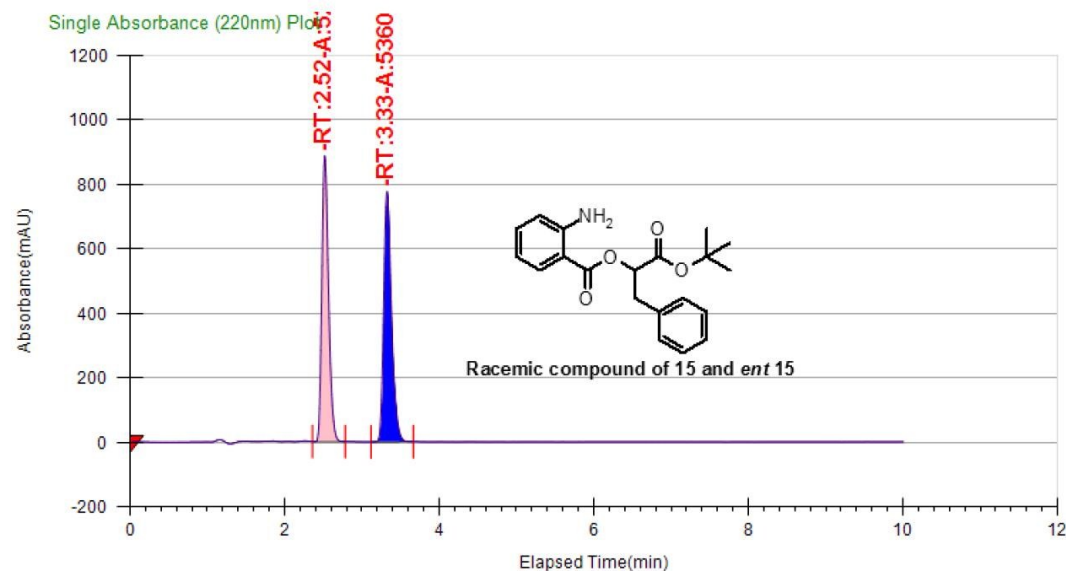
¹H NMR of Compound *ent*-15 in CDCl₃



^{13}C NMR of Compound *ent*-15 in CDCl_3



Racemic of compound 15 and *ent*-15



General Information

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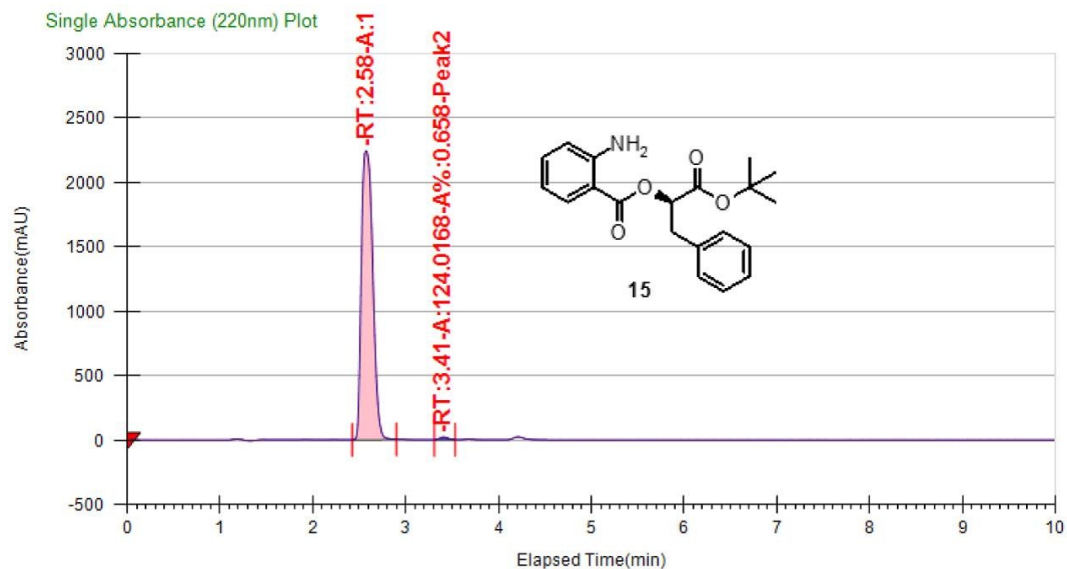
Run Information

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|-------------------|-----------|-------------------------|-------------------------------------|-------------------------------|---------------|-------|------|------------|----------|
| 3g-20%-100bar | 7 | 0.5% DEA in METHANOL | Chiralcel OJ- H(4.6*250) mm5u | GVKP-SK- B1329-112- RAC | 26C | 30.3 | 3 | 20 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 49.3211 | 5216.6826 | 2.52 min | 886.8991 | 0 |
| 2 | 50.6789 | 5360.3012 | 3.33 min | 776.8026 | 0 |

Chiral HPLC of Compound 15



General Information

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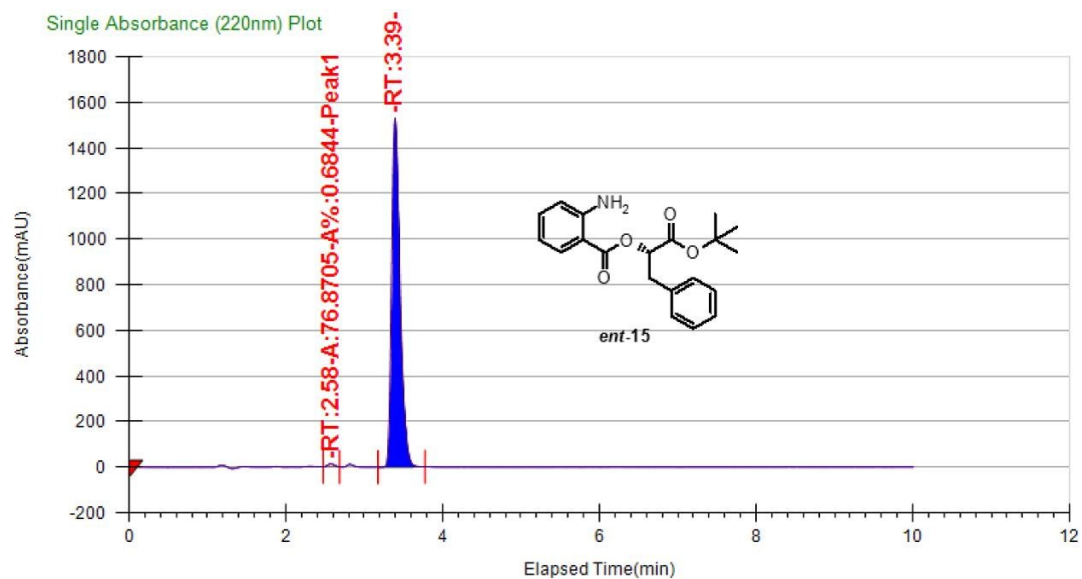
Run Information

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|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|------|------------|----------|
| 3g-20%-100bar | 7 | 0.5% DEA in METHANOL | Chiralcel OJ- H(4.6*250) mm5u | GVKP-SK- B1329-82 | 28C | 30 | 3 | 20 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|--------|------------|-----------|-----------|-------------|
| 1 | 99.342 | 18723.7264 | 2.58 min | 2242.0352 | 2574 |
| 2 | 0.658 | 124.0168 | 3.41 min | 20.5891 | 3407.35 |

Chiral HPLC of Compound *ent*-15



General Information

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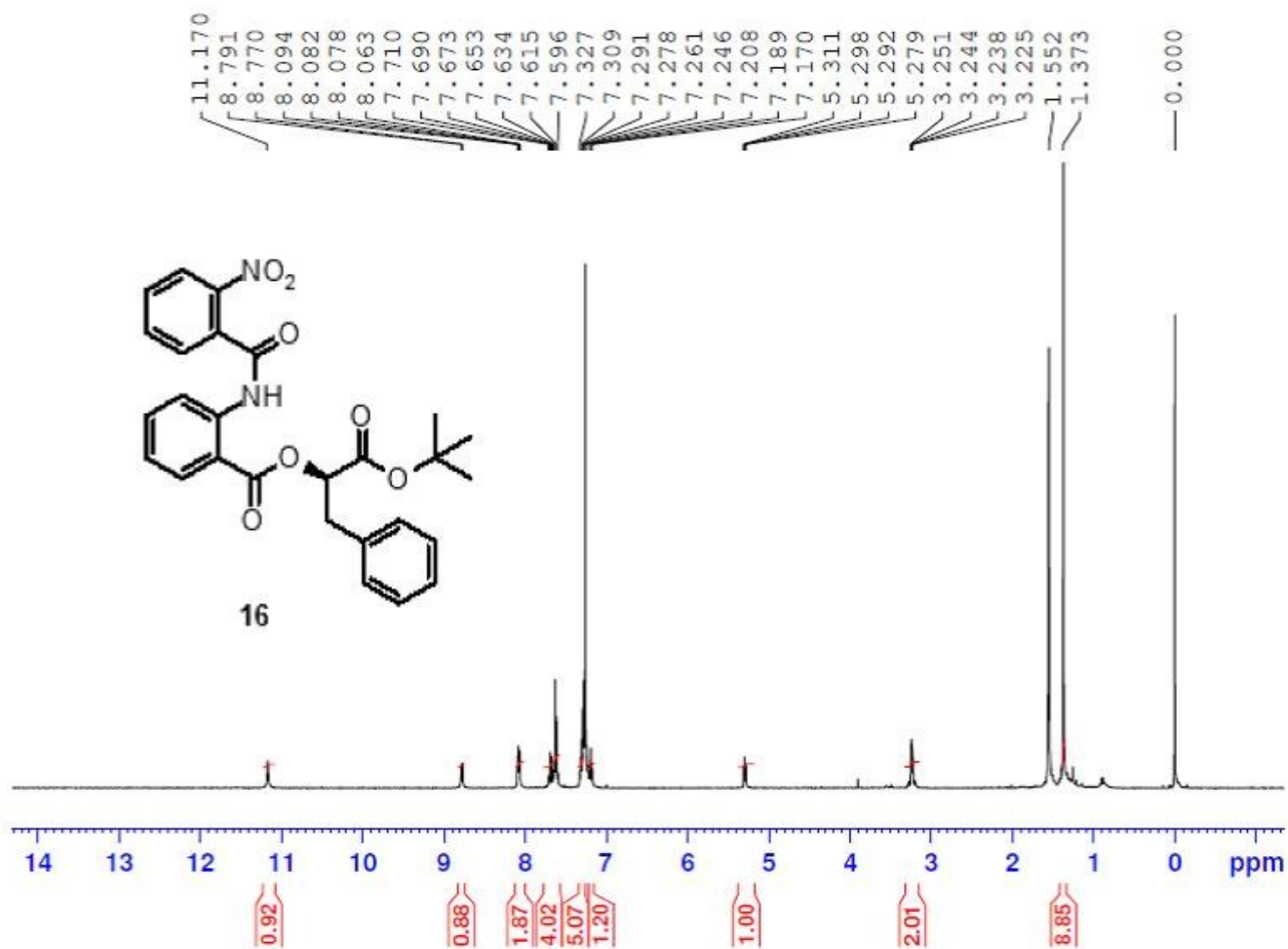
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|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|------|------------|----------|
| 3g-20%-100bar | 7 | 0.5% DEA in METHANOL | Chiralcel OJ- H(4.6*250) mm5u | GVKP-SK- B1329-64 | 27C | 30 | 3 | 20 | 100 |

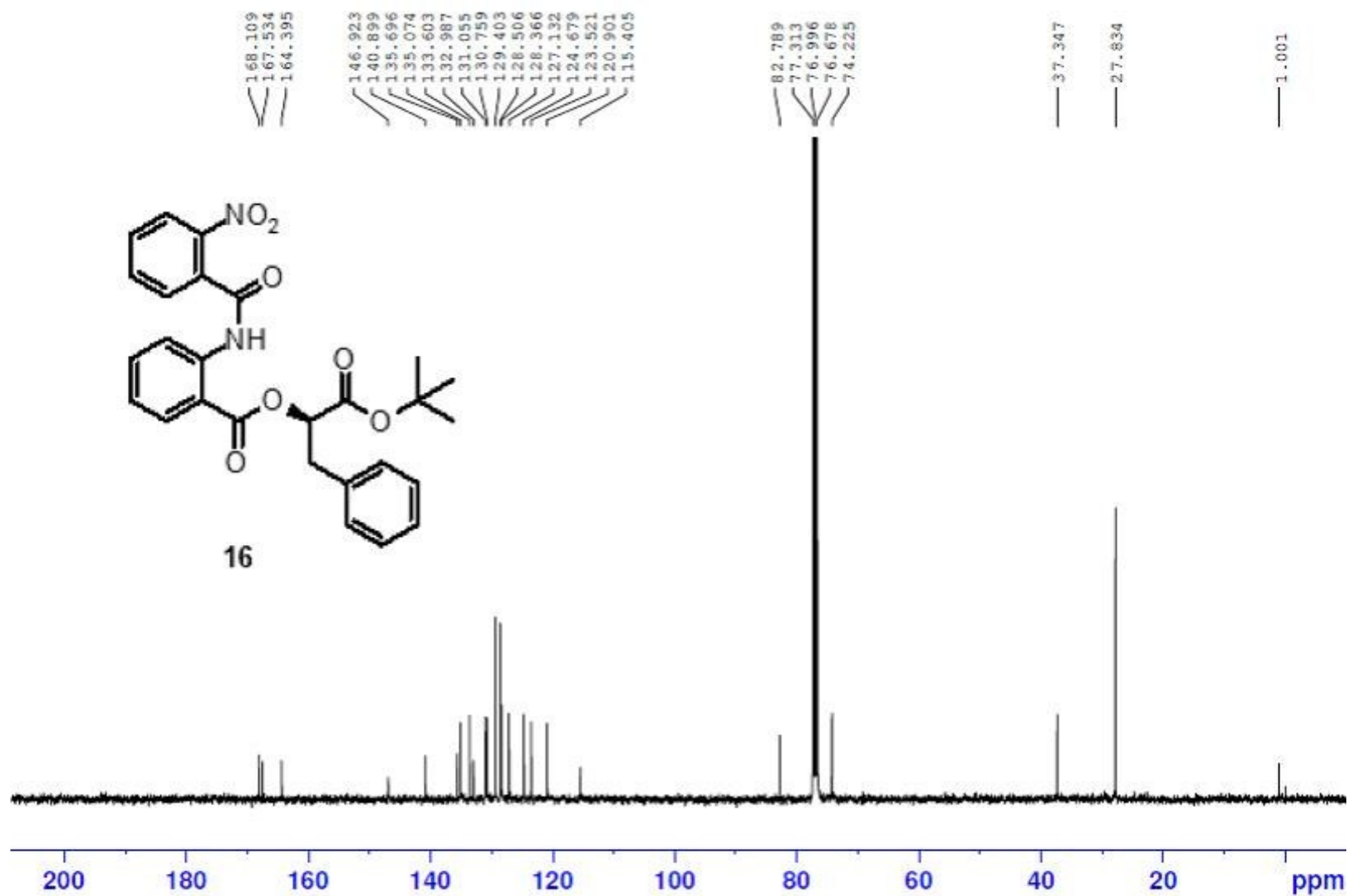
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 0.6844 | 76.8705 | 2.58 min | 13.8241 | 2574 |
| 2 | 99.3156 | 11154.6875 | 3.39 min | 1528.4667 | 3390.6833 |

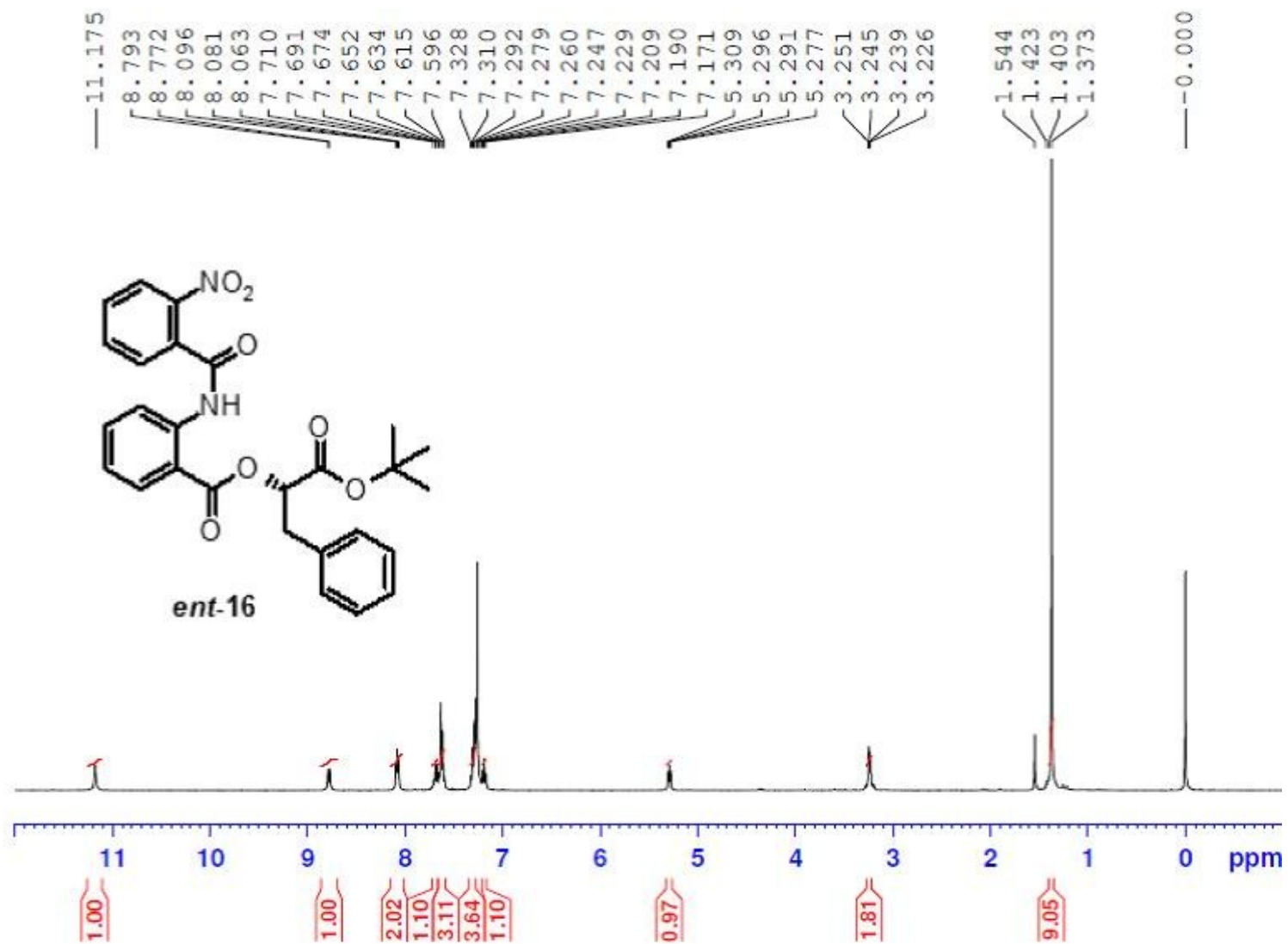
¹H NMR of Compound 16 in CDCl₃



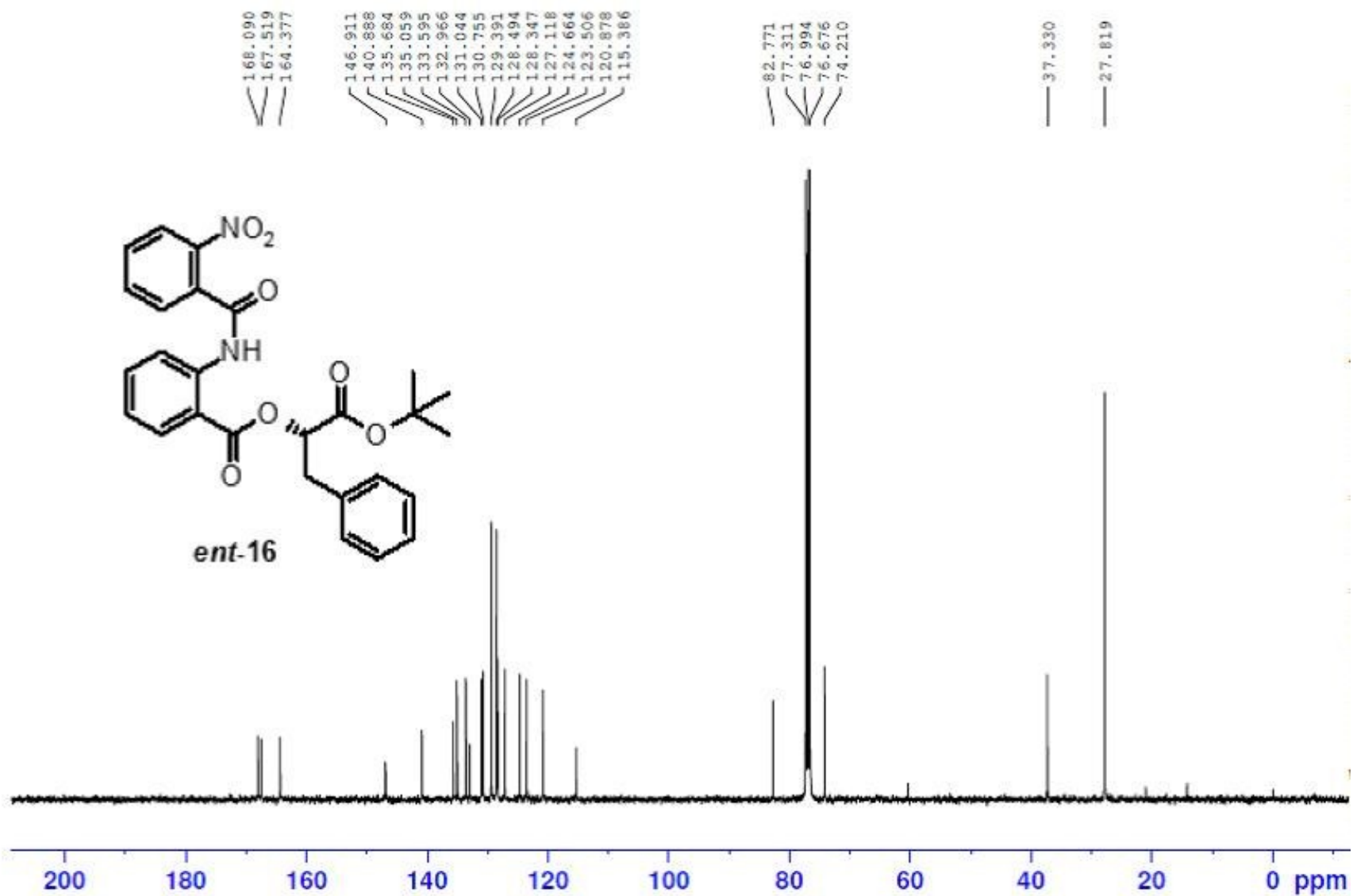
^{13}C NMR of Compound 16 in CDCl_3



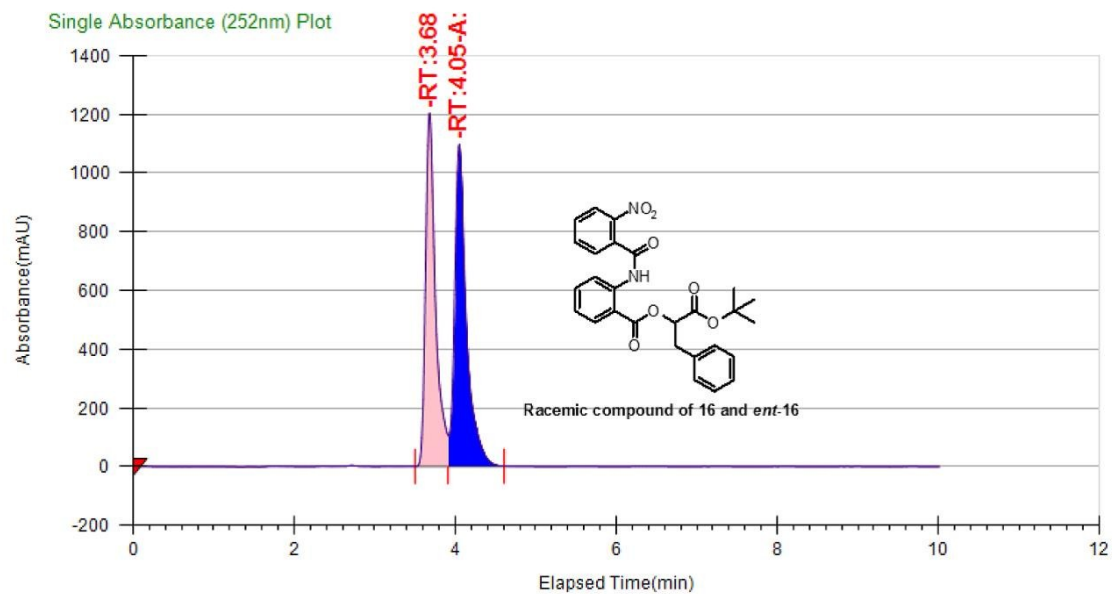
¹H NMR of Compound *ent*-16 in CDCl₃



¹³C NMR of Compound *ent*-16 in CDCl₃



Racemic of compound 16 and *ent*-16



General Information

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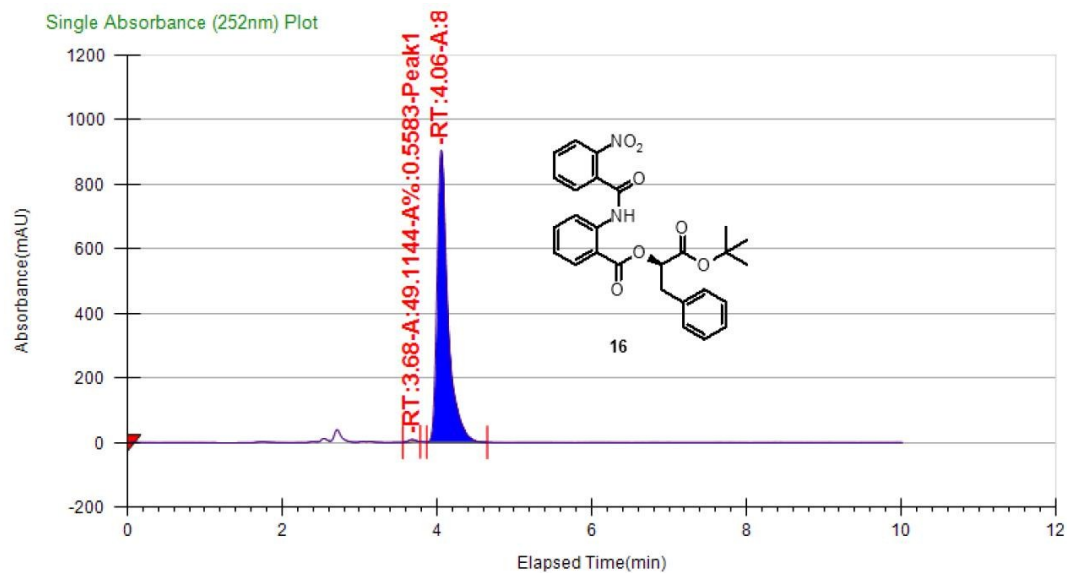
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|-------------------|-----------|-------------------------|-------------------------------------|-------------------------------|---------------|-------|-------|------------|----------|
| 3g-30%-100bar | 5 | 0.5% DEA in METHANOL | Chiralcel OD- H(4.6*250) mm5u | GVKP-SK- B1329-113- Rac | 14B | 30.1 | 2.999 | 29.9767 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 48.1041 | 10218.8976 | 3.68 min | 1202.6786 | 0 |
| 2 | 51.8959 | 11024.4167 | 4.05 min | 1097.5249 | 0 |

Chiral HPLC of Compound 16



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
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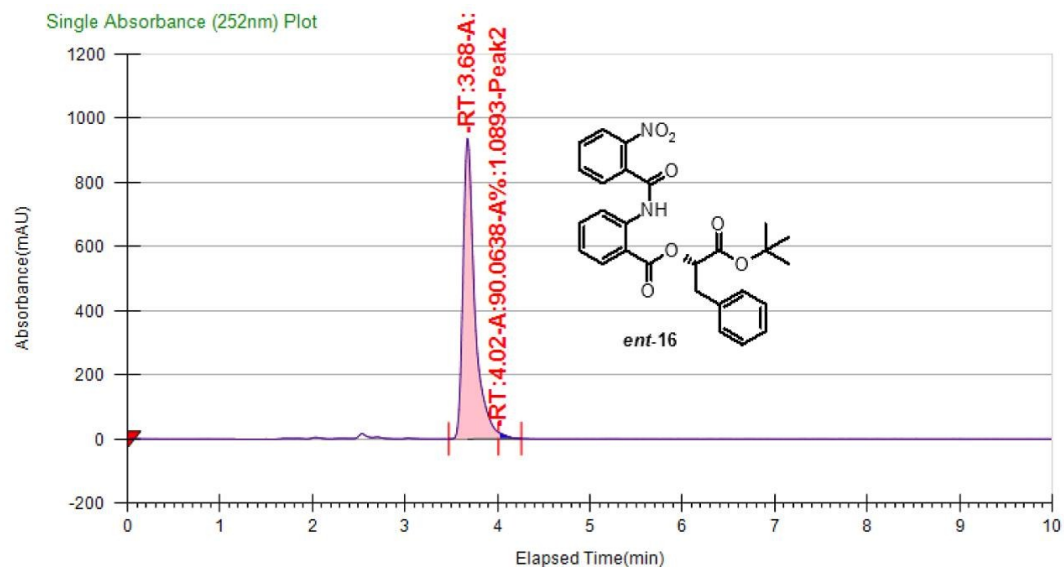
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|-------|------------|----------|
| 3g-30%-100bar | 5 | 0.5% DEA in METHANOL | Chiralcel OD- H(4,6*250) mm5u | GVKP-SK- B1329-83 | 16B | 30 | 2.999 | 29.9767 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 0.5583 | 49.1144 | 3.68 min | 7.7594 | 0 |
| 2 | 99.4417 | 8748.0234 | 4.06 min | 904.2011 | 0 |

Chiral HPLC of Compound *ent*-16



General Information

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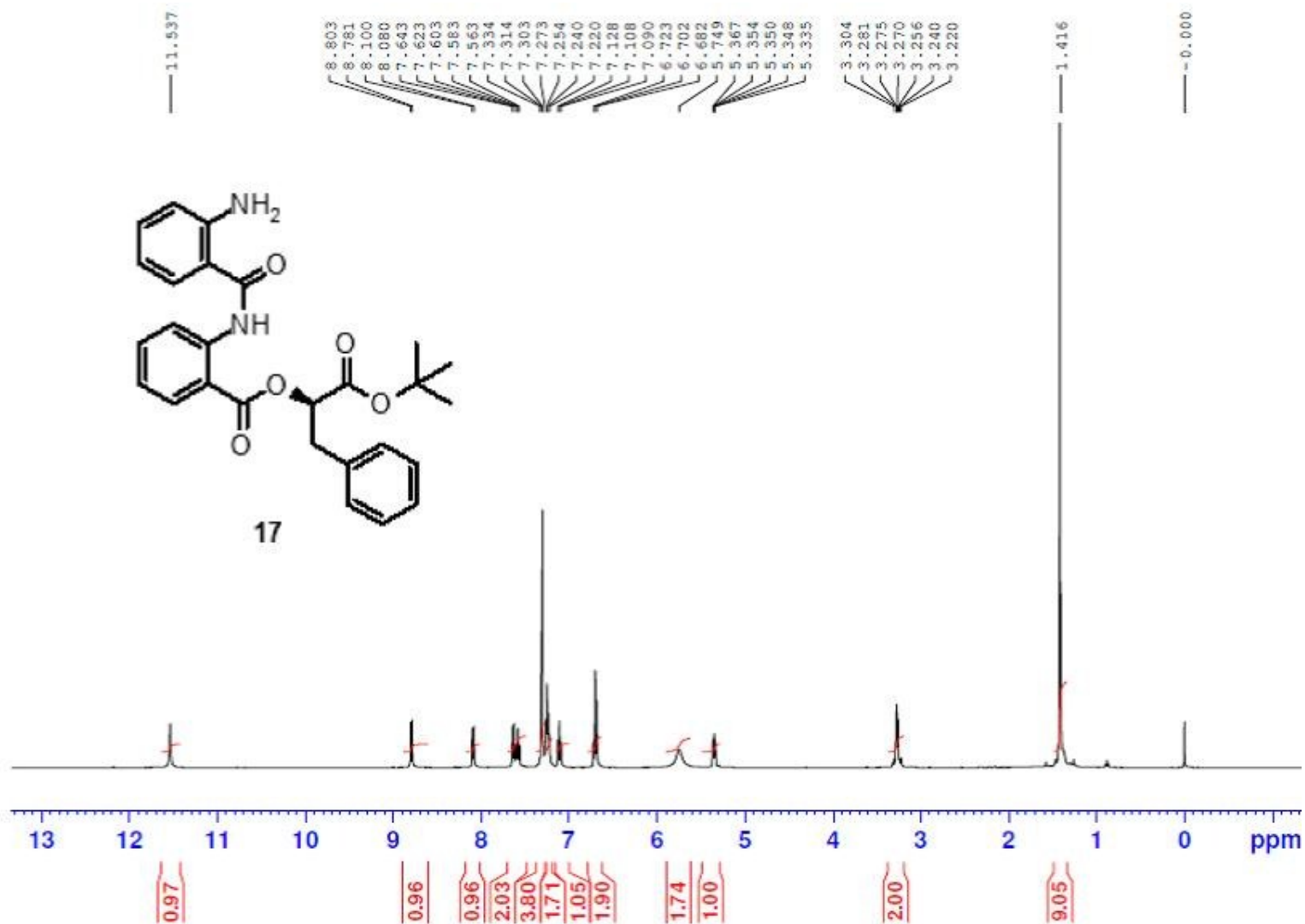
Run Information

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|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|-------|------------|----------|
| 3g-30%-100bar | 5 | 0.5% DEA in METHANOL | Chiralcel OD- H(4.6*250) mm5u | GVKP-SK- B1329-65 | 15B | 30.1 | 2.999 | 29.9767 | 100 |

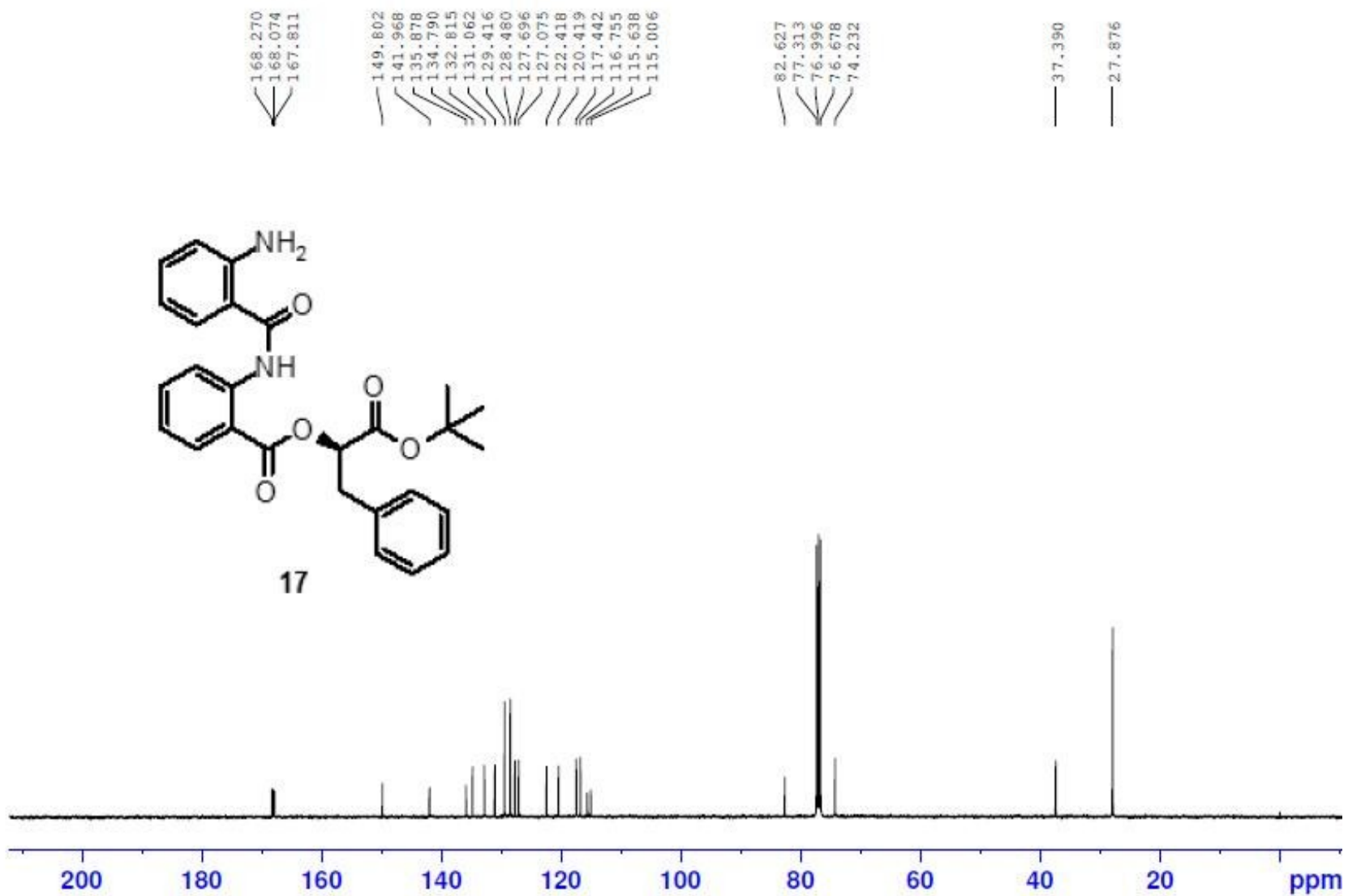
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 98.9107 | 8178.0594 | 3.68 min | 937.3977 | 0 |
| 2 | 1.0893 | 90.0638 | 4.02 min | 19.1097 | 0 |

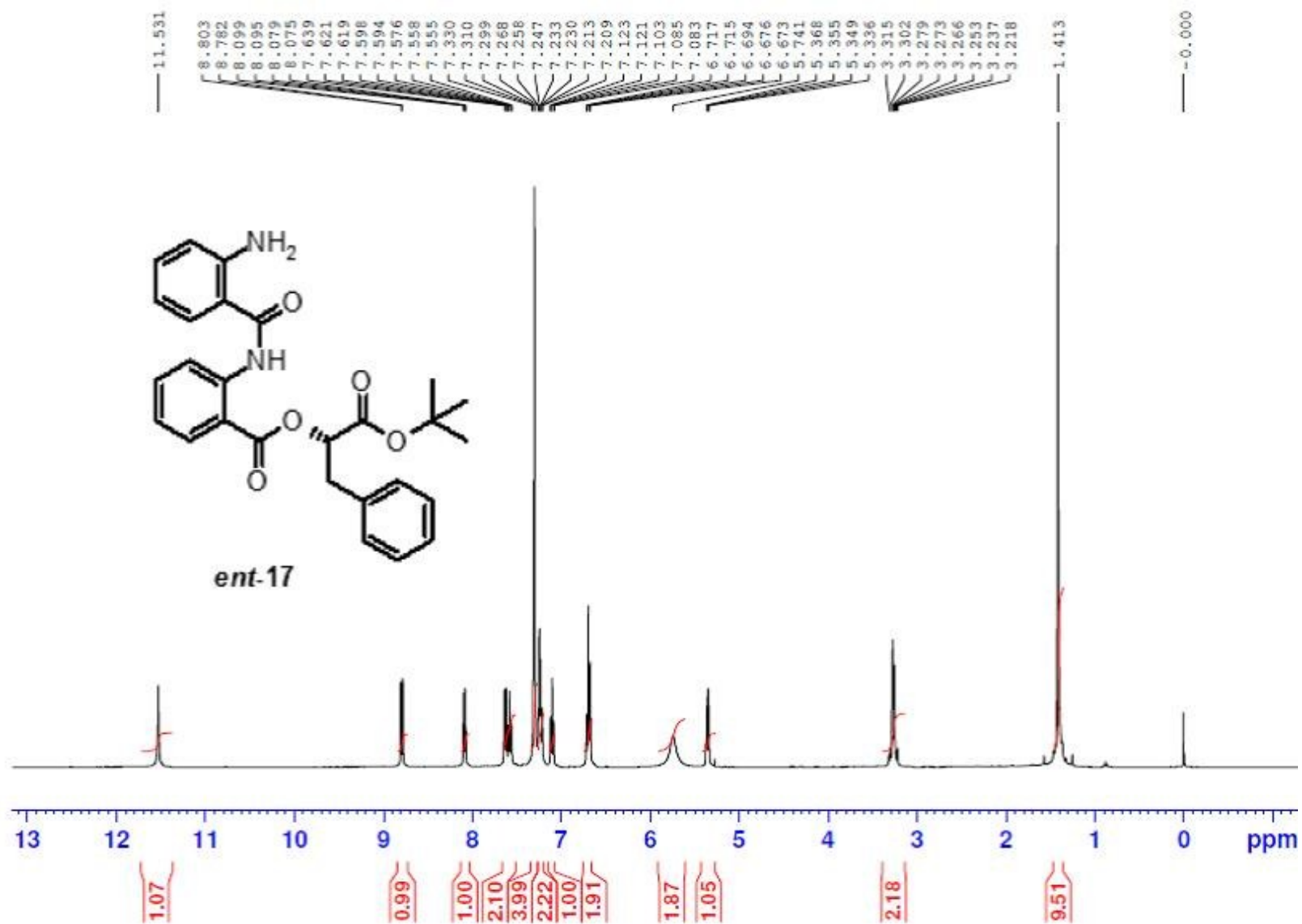
¹H NMR of Compound 17 in CDCl₃



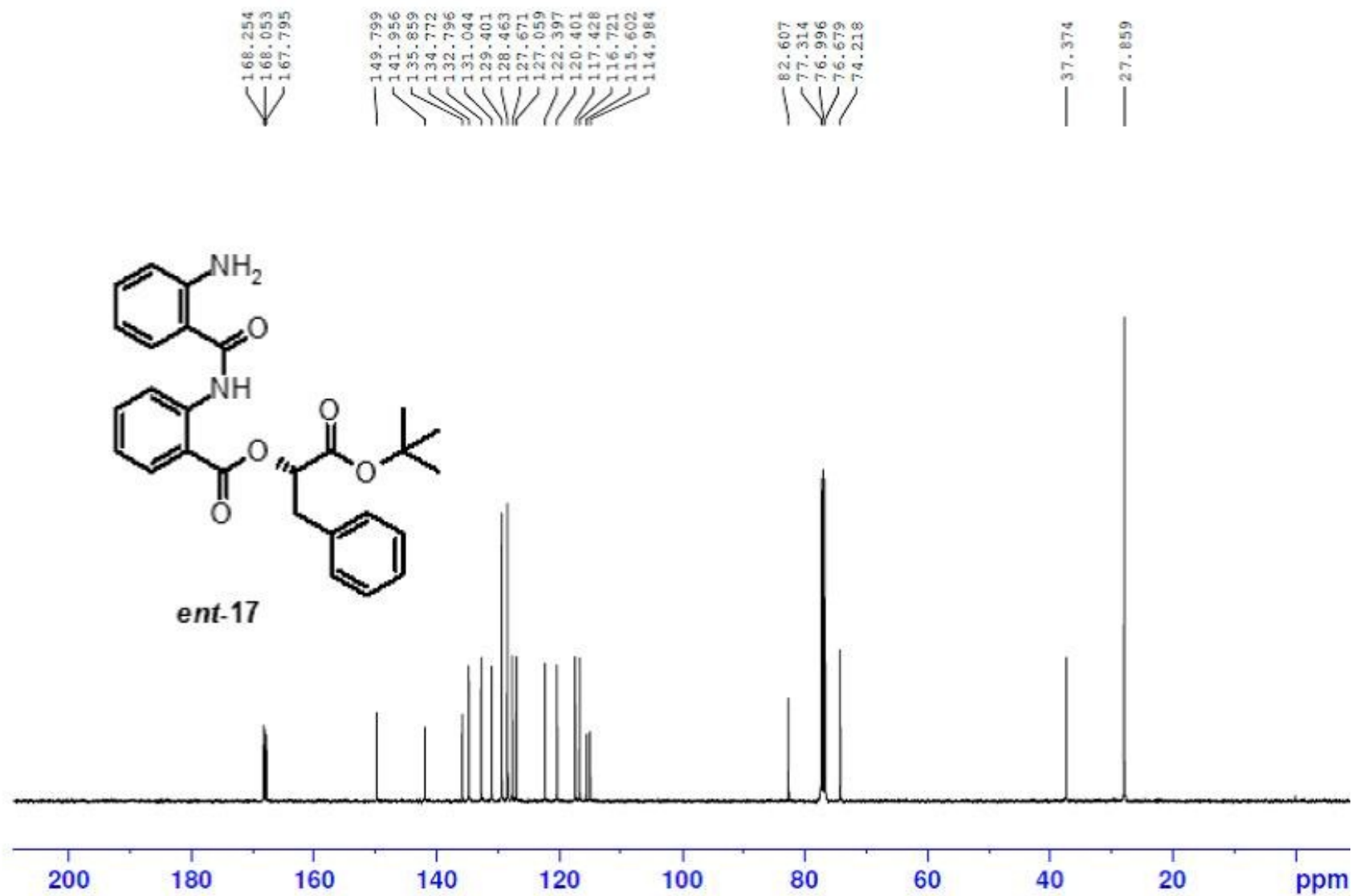
^{13}C NMR of Compound 17 in CDCl_3



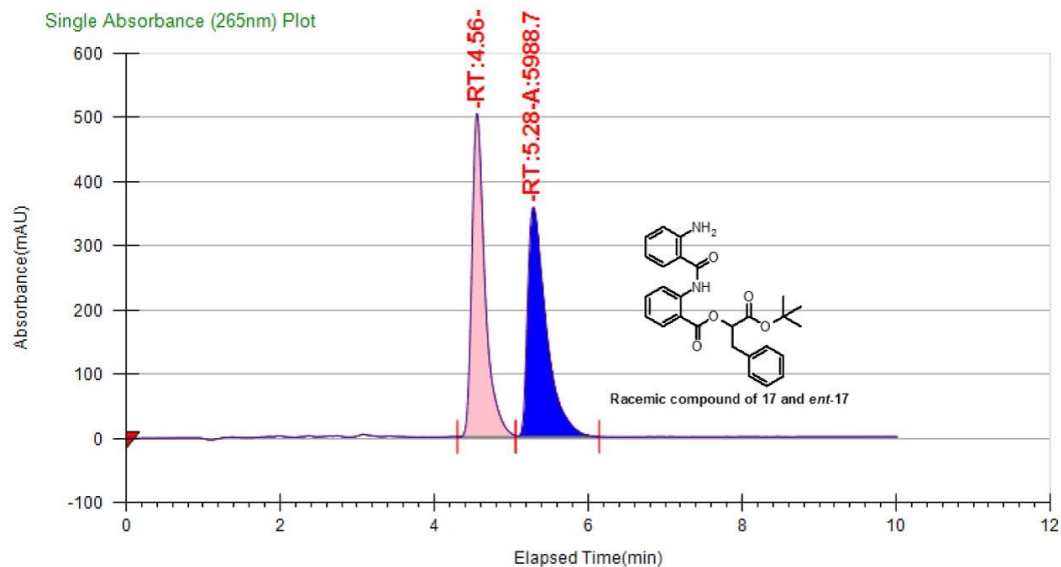
¹H NMR of Compound *ent-17* in CDCl₃



¹³C NMR of Compound *ent*-17 in CDCl₃



Racemic of compound 17 and *ent*-17



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/13/2015 1:45:16 PM | Administrator | 5/13/2015 | |

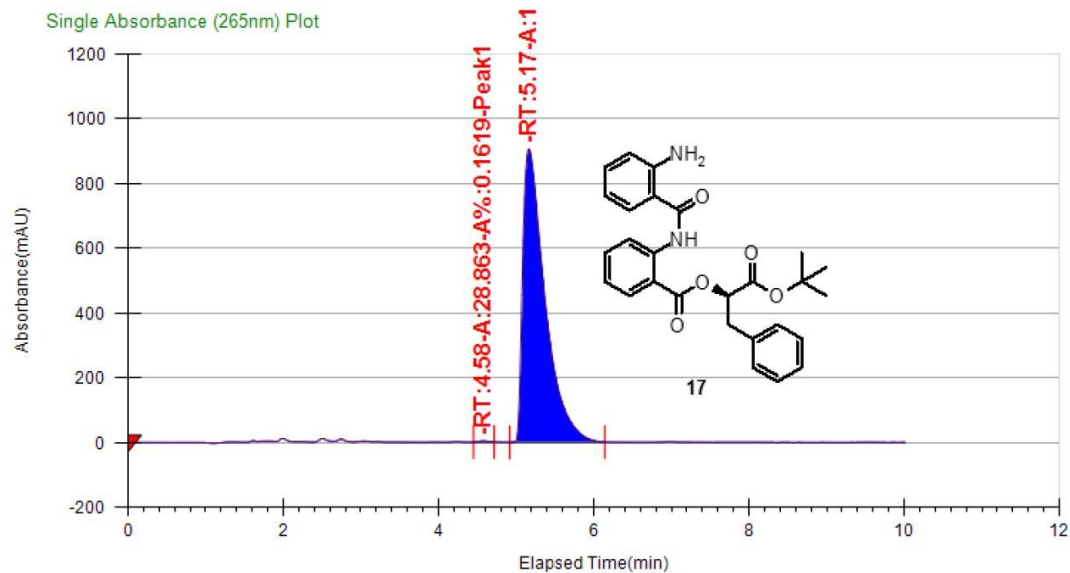
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-------------------------------------|-------------------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralcel OD- H(4.6*250) mm5u | GVKP-SK- B1329-114- Rac | 25A | 29.7 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 49.6581 | 5907.3868 | 4.56 min | 503.8947 | 4557.35 |
| 2 | 50.3419 | 5988.7235 | 5.28 min | 357.6203 | 5282.3333 |

Chiral HPLC of Compound 17



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/13/2015 2:07:51 PM | Administrator | 5/13/2015 | |

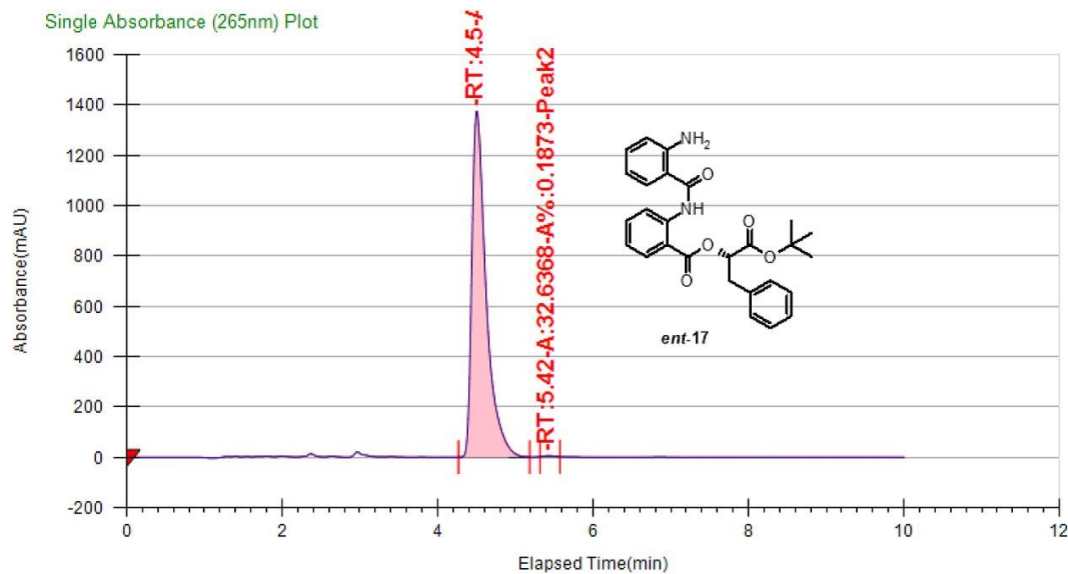
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-------------------------------------|-----------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralcel OD- H(4.6*250) mm5u | GVKP-SK- B1329-83C | 27A | 29.9 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|----------|-------------|
| 1 | 0.1619 | 28.863 | 4.58 min | 3.4472 | 0 |
| 2 | 99.8381 | 17794.6742 | 5.17 min | 906.5874 | 0 |

Chiral HPLC of Compound *ent-17*



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/13/2015 1:56:33 PM | Administrator | 5/13/2015 | |

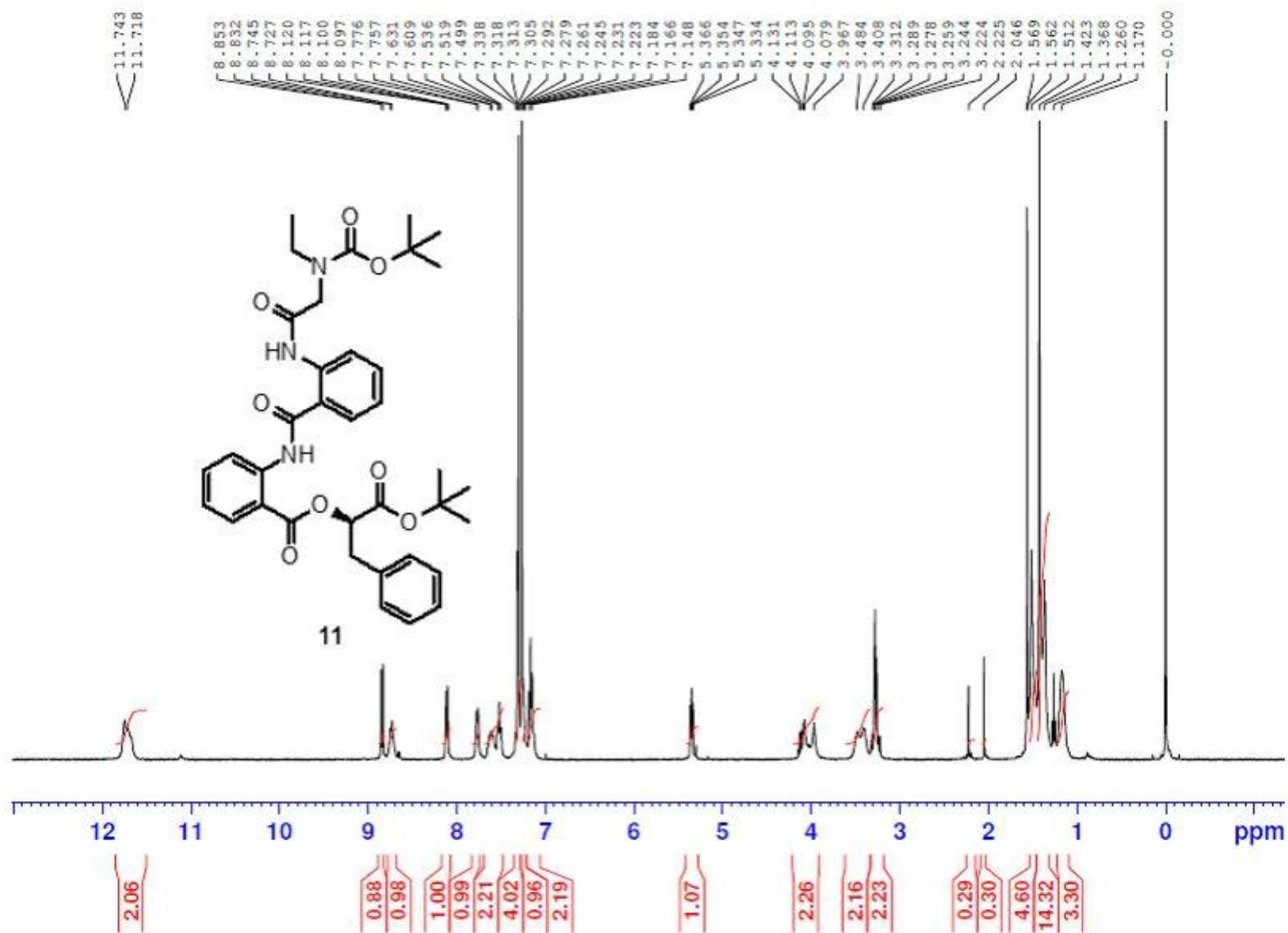
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-------------------------------------|----------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralcel OD- H(4.6*250) mm5u | GVKP-SK- B1329-66 | 26A | 30 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 99.8127 | 17389.4614 | 4.5 min | 1374.4524 | 4499.0167 |
| 2 | 0.1873 | 32.6368 | 5.42 min | 3.7678 | 5424 |

¹H NMR of Compound 11 in CDCl₃



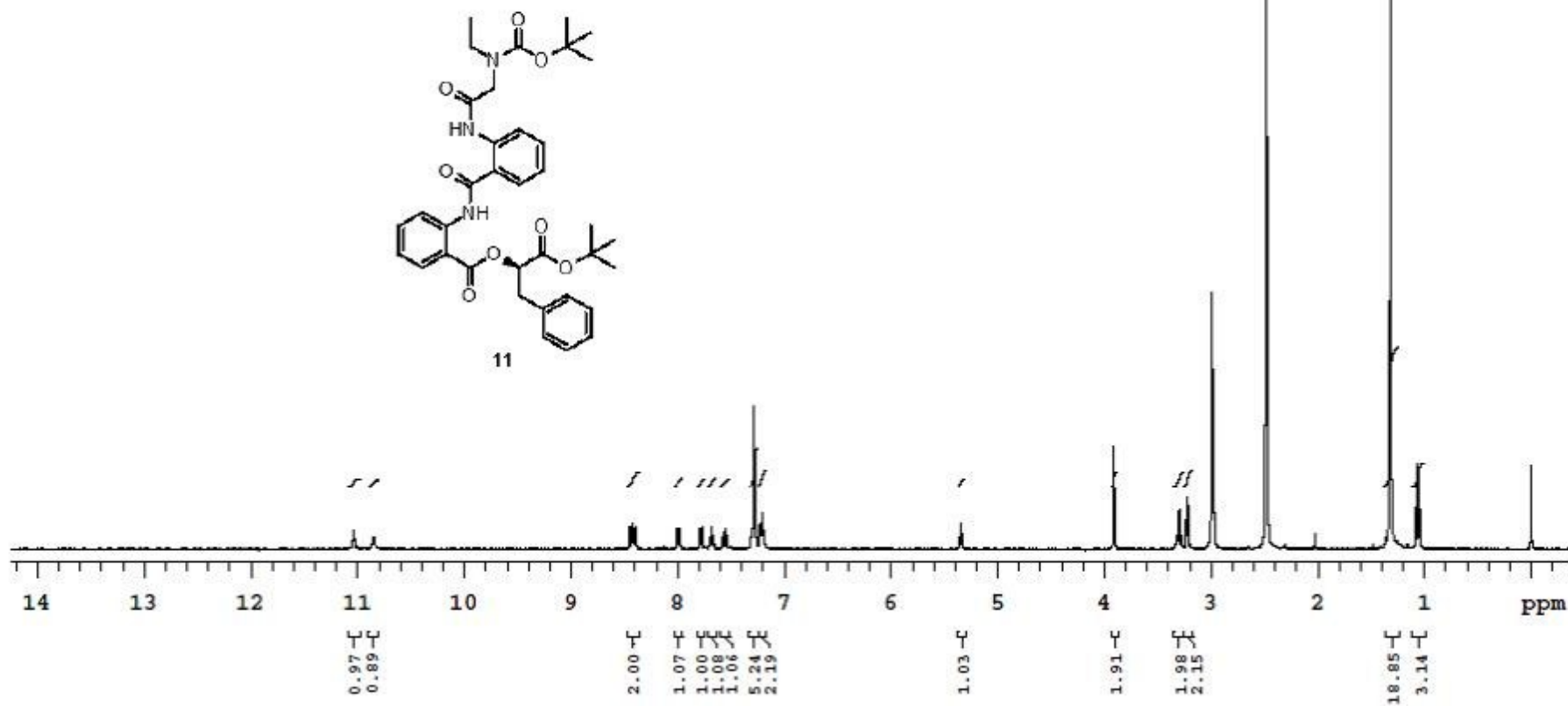
VT ¹H NMR of Compound 11 in DMSO-d₆

GVKP-SK-B1329-90-R-VT AT 90C

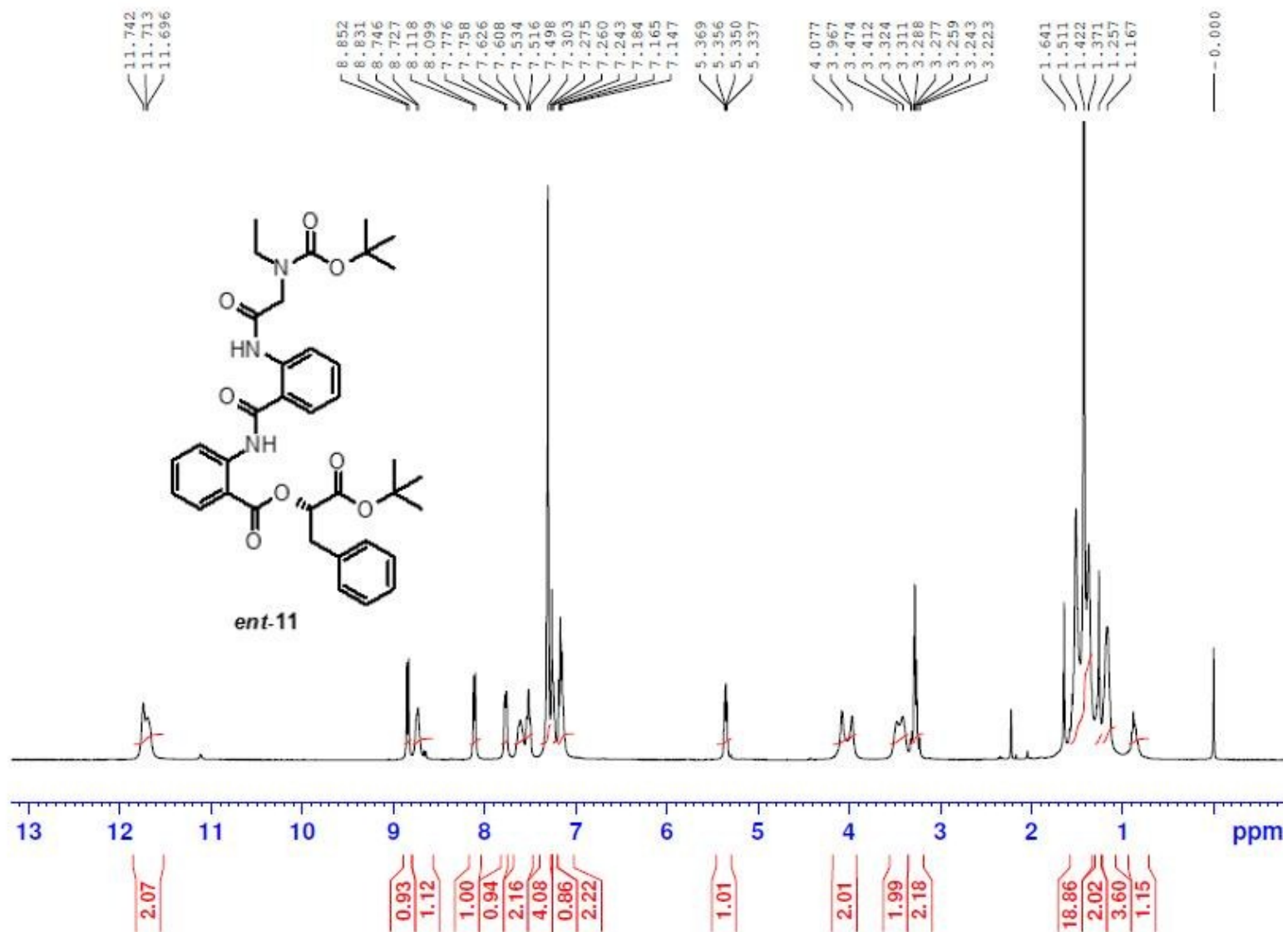
Solvent: dmsO

400-MR/NRM-1/NMR-001

Date: Jun 13 2015



¹H NMR of Compound-11 in CDCl₃



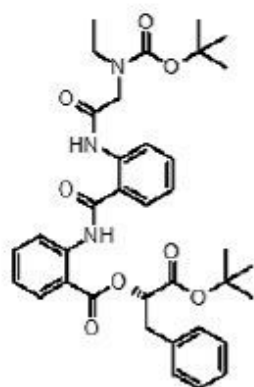
VT ¹H NMR of Compound *ent-11* in DMSO-d₆

GVKP-SK-B1329-70-S-VT AT 90C

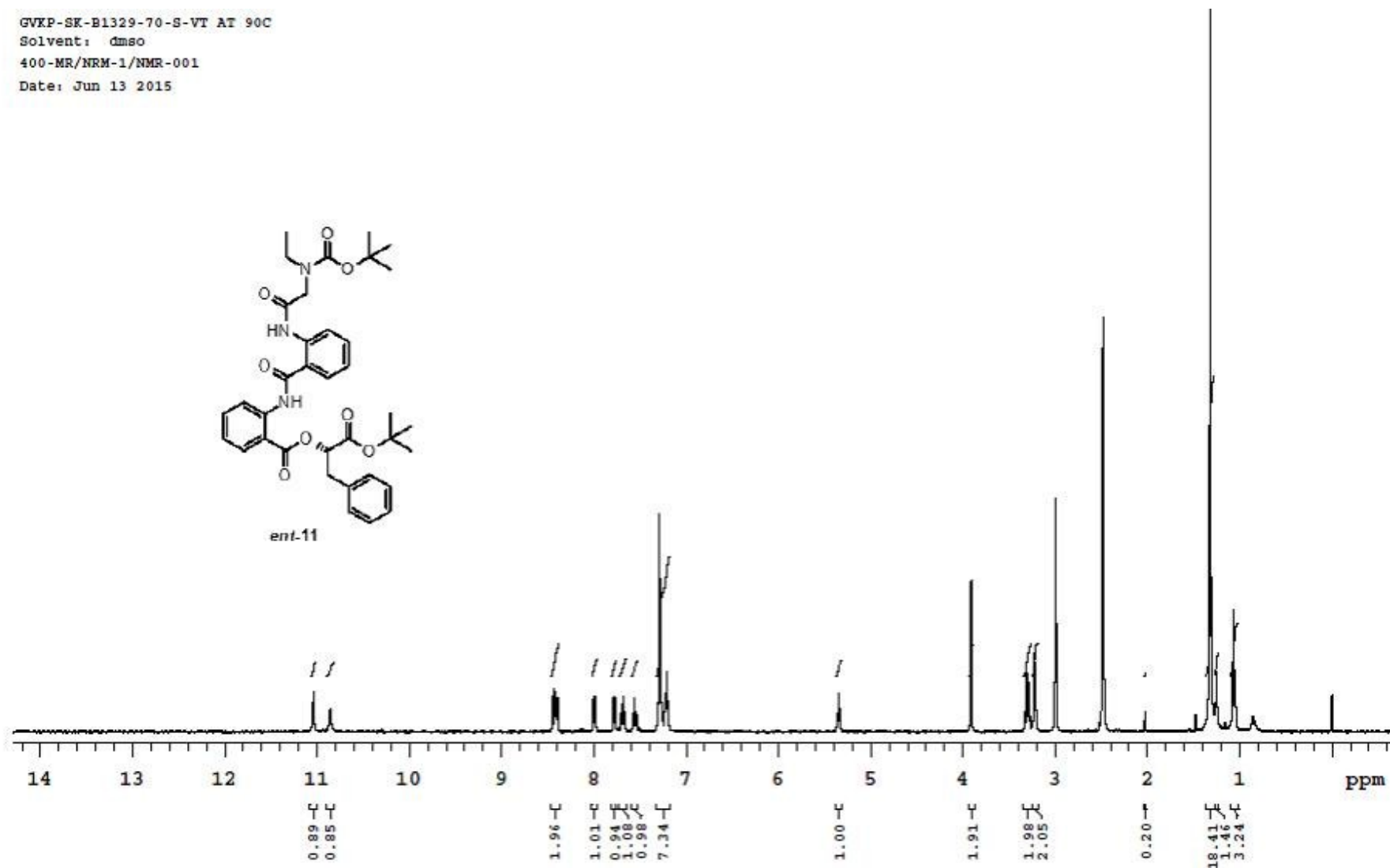
Solvent: dmsO

400-MR/NRM-1/NMR-001

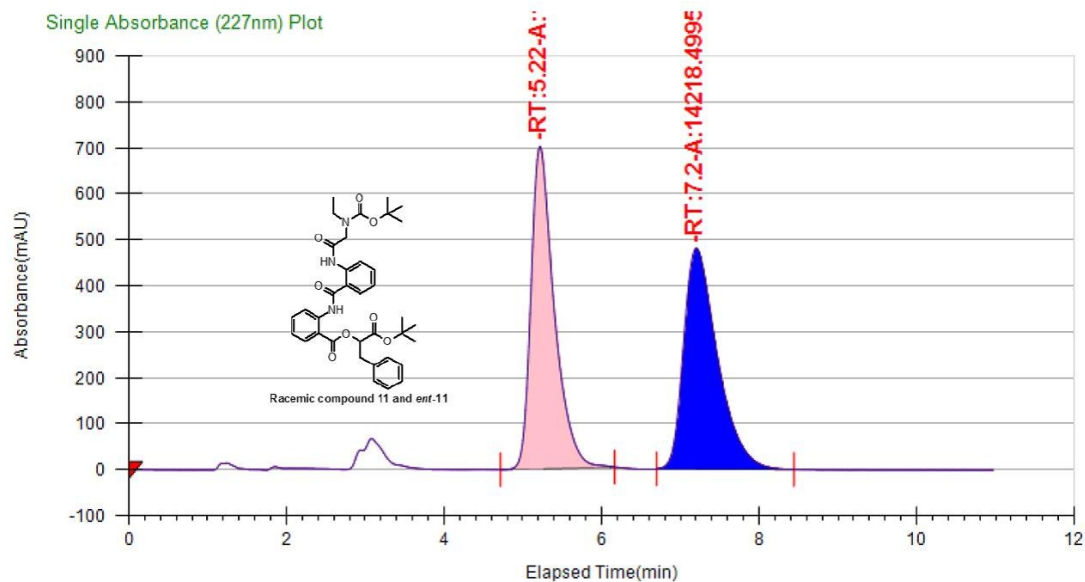
Date: Jun 13 2015



ent-11



Racemic of compound 11 and *ent*-11



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|---------------------|---------------|-------------|-------|
| Administrator | 6/4/2015 7:10:20 PM | Administrator | 6/4/2015 | |

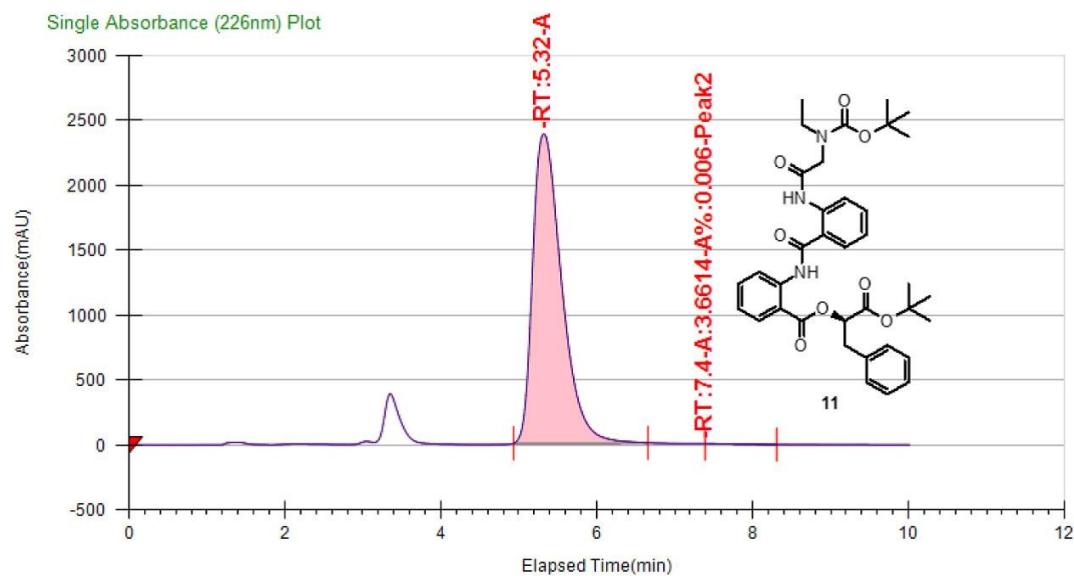
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|----------------------|-----------------------------|-----------------------|---------------|-------|-------|------------|----------|
| 3g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak-IC (4.6*250) mm5u | GVKP-SK-B1329-118-Rac | 24B | 29.2 | 2.999 | 40.0133 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|----------|-------------|
| 1 | 50.1134 | 14283.1321 | 5.22 min | 701.4833 | 0 |
| 2 | 49.8866 | 14218.4995 | 7.2 min | 480.3908 | 0 |

Chiral HPLC of Compound 11



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/16/2015 2:30:22 AM | Administrator | 5/16/2015 | |

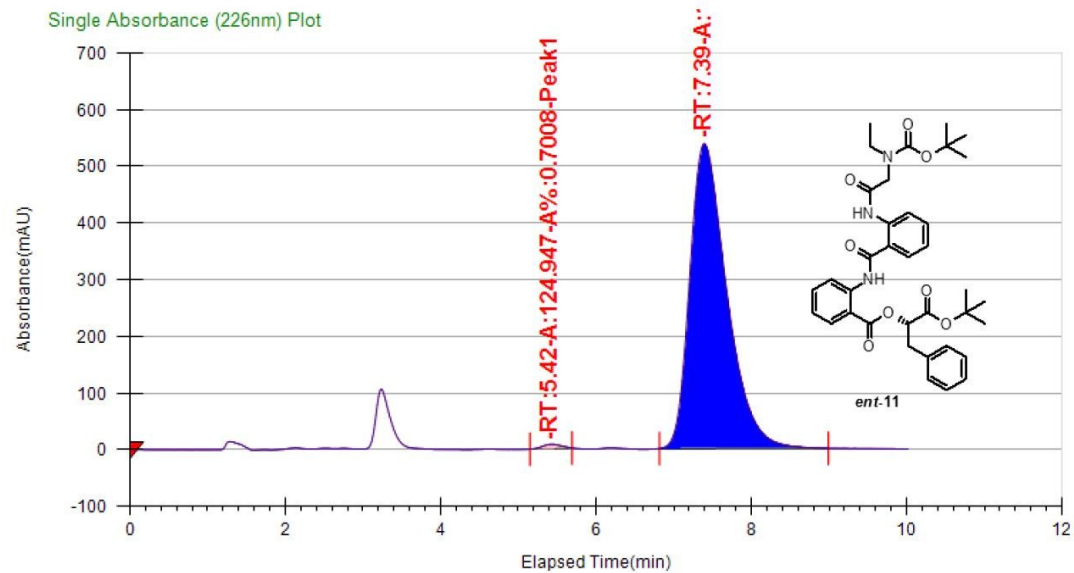
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-----------------------------------|----------------------|---------------|-------|-------|------------|----------|
| 3g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak-IC (4.6*250) mm5u | GVKP-SK- B1329-90 | 16B | 30 | 2.999 | 40.0133 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|--------|------------|-----------|-----------|-------------|
| 1 | 99.994 | 61321.8709 | 5.32 min | 2383.3163 | 5324 |
| 2 | 0.006 | 3.6614 | 7.4 min | 0.0662 | 7398.9667 |

Chiral HPLC of Compound *ent-11*



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/16/2015 2:07:36 AM | Administrator | 5/16/2015 | |

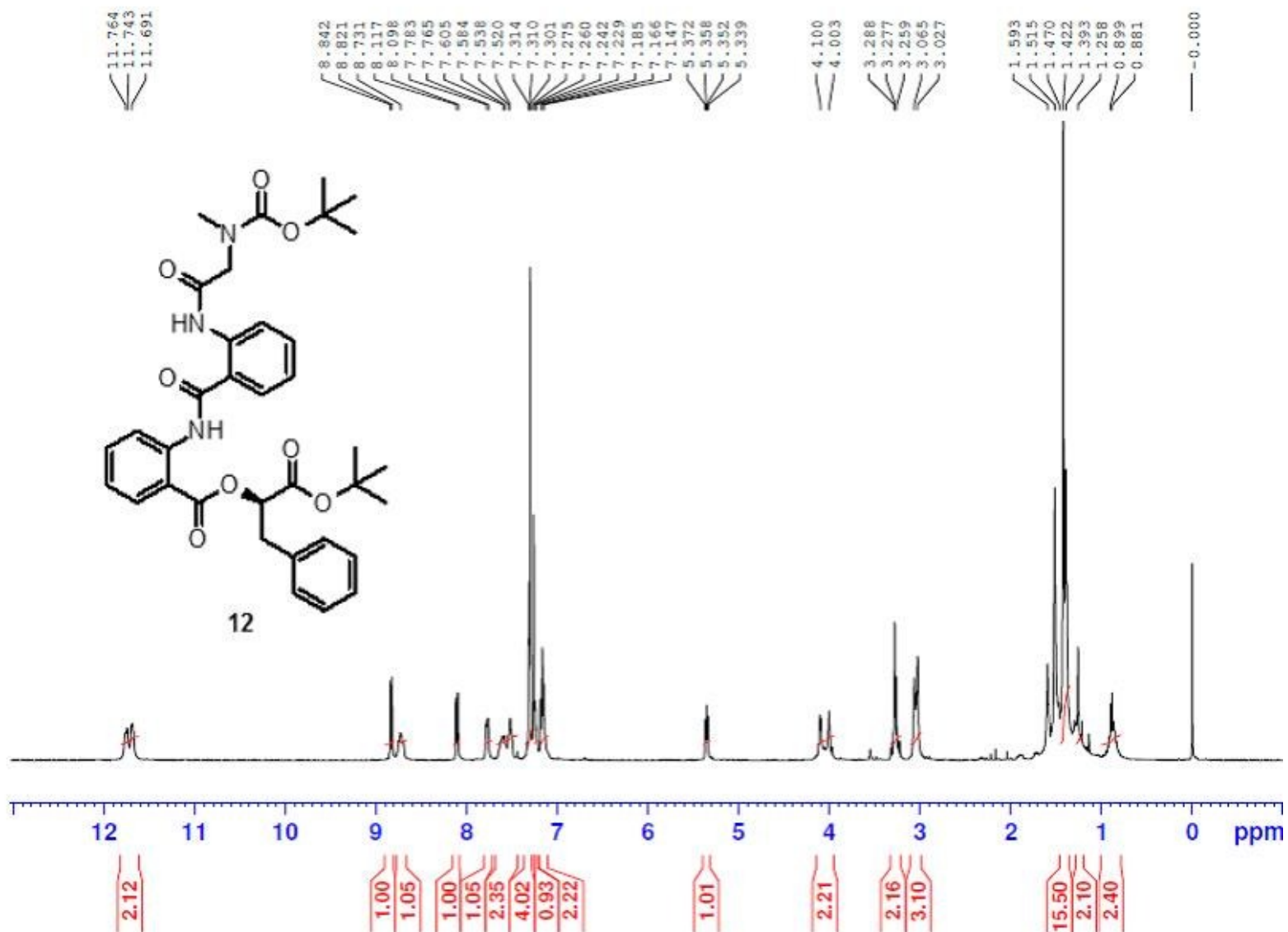
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-----------------------------------|----------------------|---------------|-------|-------|------------|----------|
| 3g-40%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak-IC (4.6*250) mm5u | GVKP-SK- B1329-70 | 15B | 29.9 | 2.999 | 40.0133 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|---------|-------------|
| 1 | 0.7008 | 124.947 | 5.42 min | 7.655 | 0 |
| 2 | 99.2992 | 17705.3701 | 7.39 min | 538.372 | 0 |

¹H NMR of Compound 12 in CDCl₃



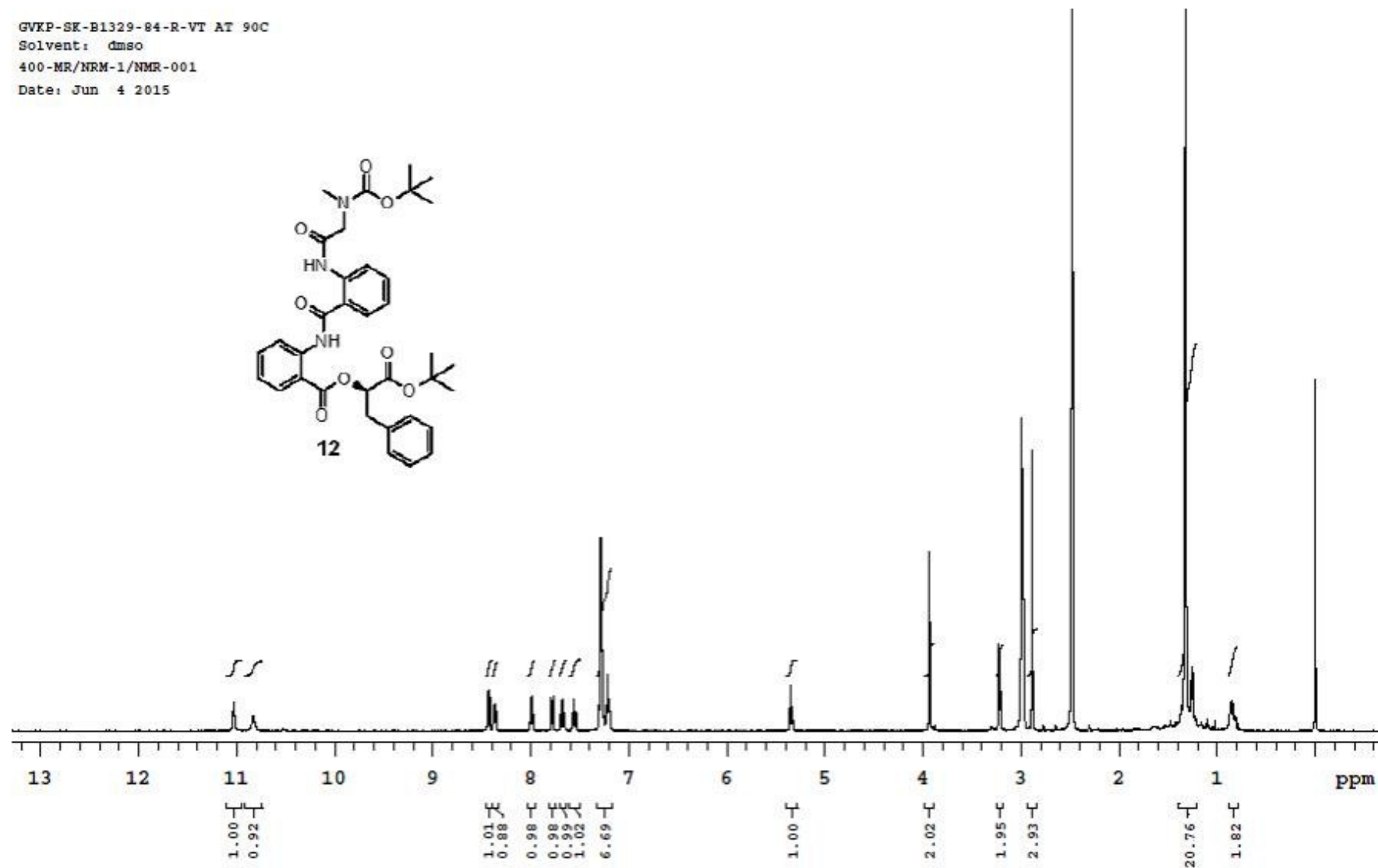
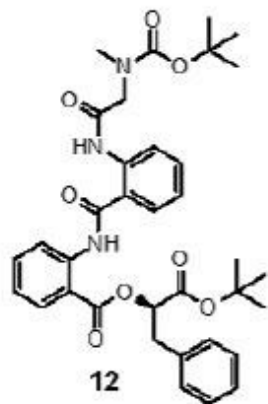
VT ^1H NMR of Compound 12 in DMSO-d_6

GVKP-SK-B1329-84-R-VT AT 90C

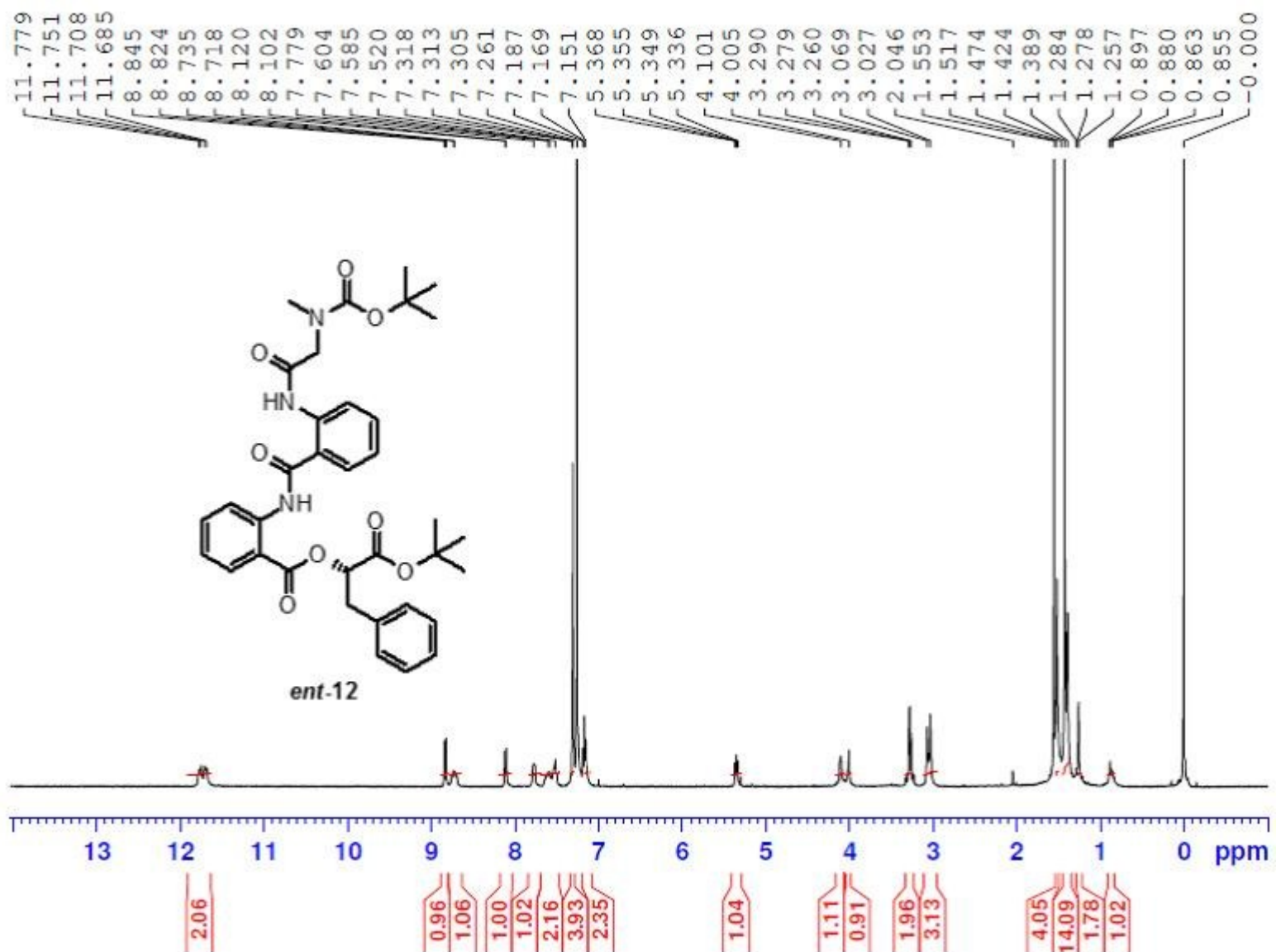
Solvent: dms

400-MR/NRM-1/NMR-001

Date: Jun 4 2015



¹H NMR of Compound *ent*-12 in CDCl₃



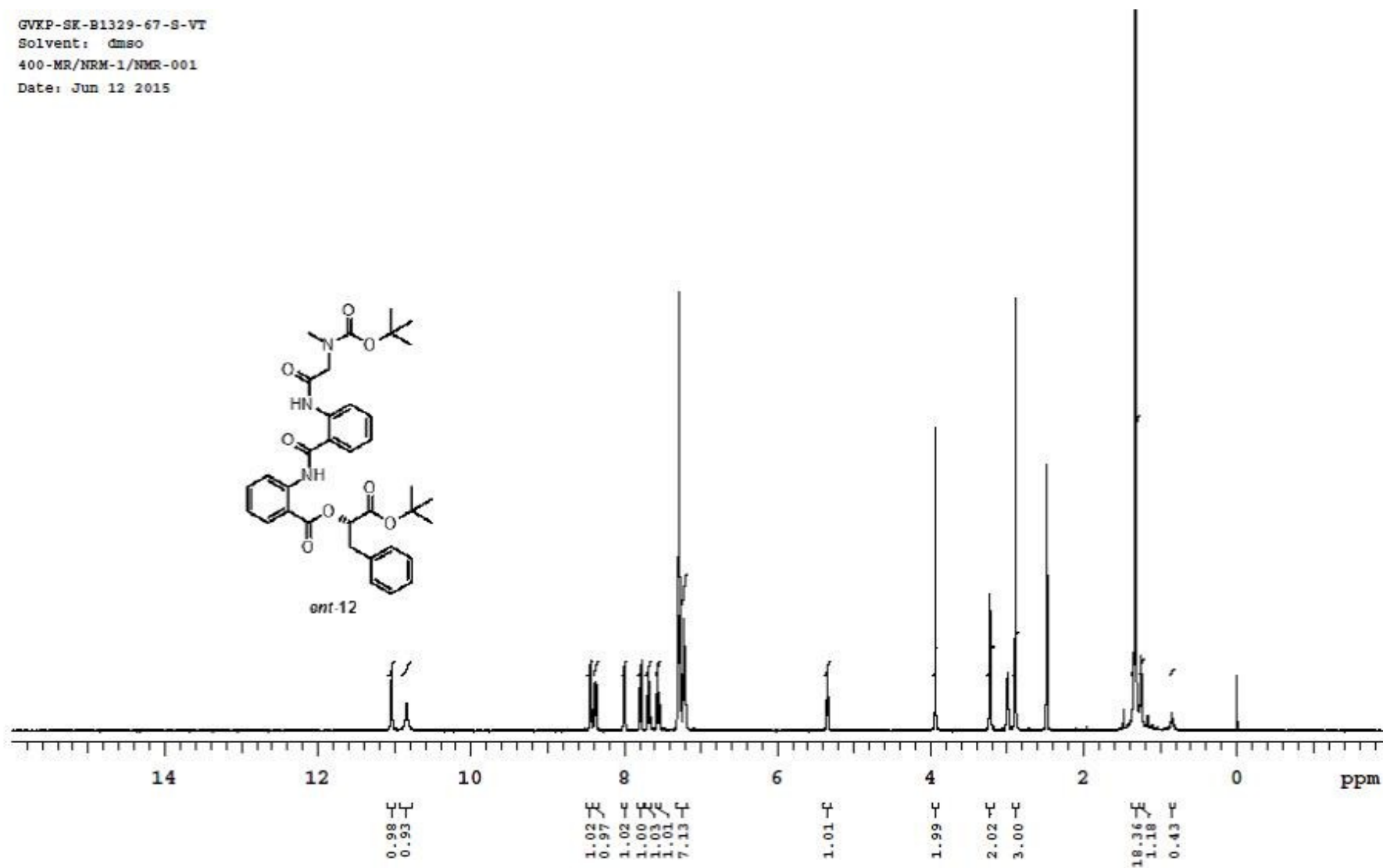
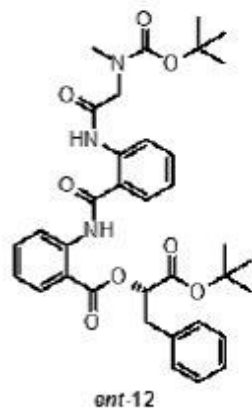
VT ^1H NMR of Compound *ent*-12 in DMSO-d_6

GVKP-SK-B1329-67-S-VT

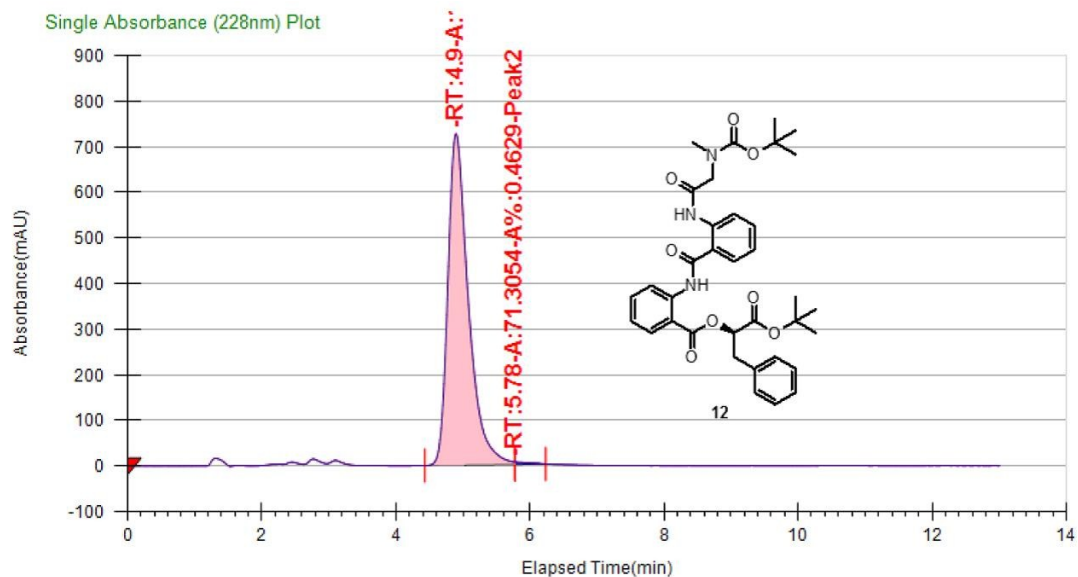
Solvent: dmsc

400-MR/NRM-1/NMR-001

Date: Jun 12 2015



Chiral HPLC of Compound 12



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/16/2015 7:55:50 PM | Administrator | 5/18/2015 | |

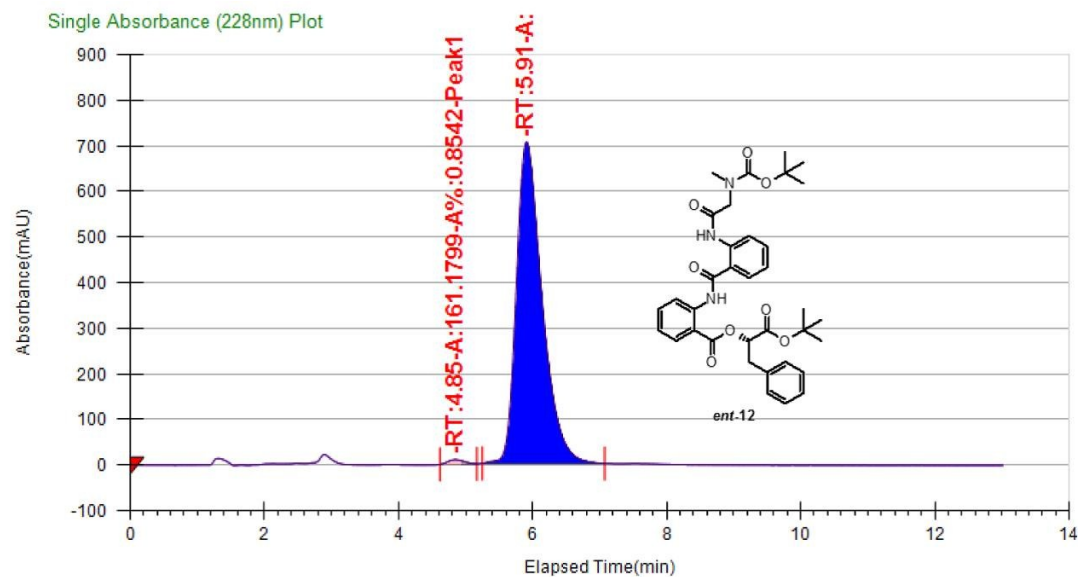
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-----------------------------------|-----------------------|---------------|-------|------|------------|----------|
| 3g-45%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak-IC (4.6*250) mm5u | GVKP-SK- B1329-84C | 21B | 29.9 | 3 | 45 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 99.5371 | 15333.051 | 4.9 min | 726.7838 | 4899.0167 |
| 2 | 0.4629 | 71.3054 | 5.78 min | 5.1824 | 5782.3333 |

Chiral HPLC of Compound *ent*-12



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 5/16/2015 8:24:24 PM | Administrator | 5/18/2015 | |

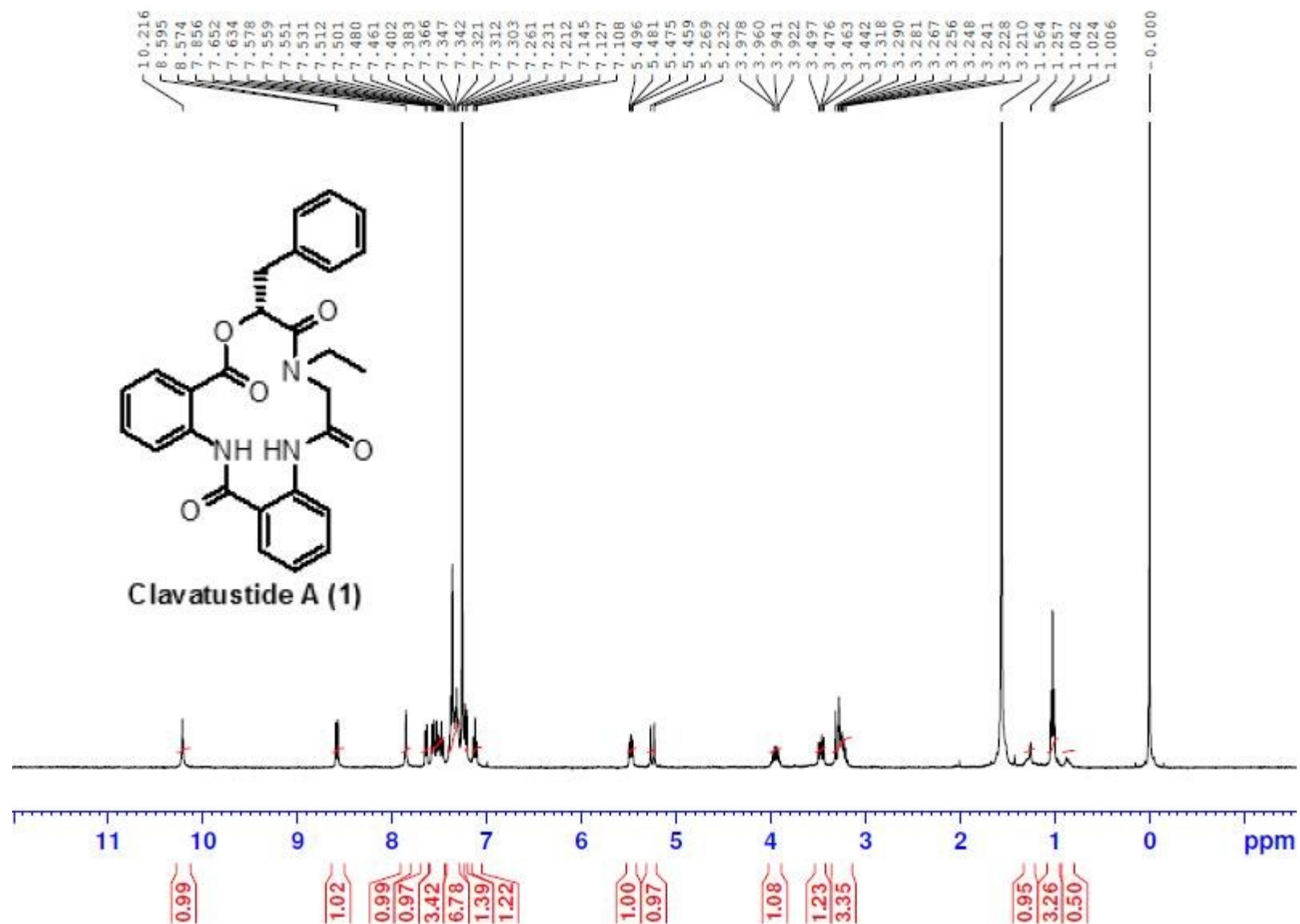
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|-----------------------------------|----------------------|---------------|-------|------|------------|----------|
| 3g-45%-100bar | 10 | 0.5% DEA in METHANOL | Chiralpak-IC (4.6*250) mm5u | GVKP-SK- B1329-66 | 22B | 30.1 | 3 | 45 | 100 |

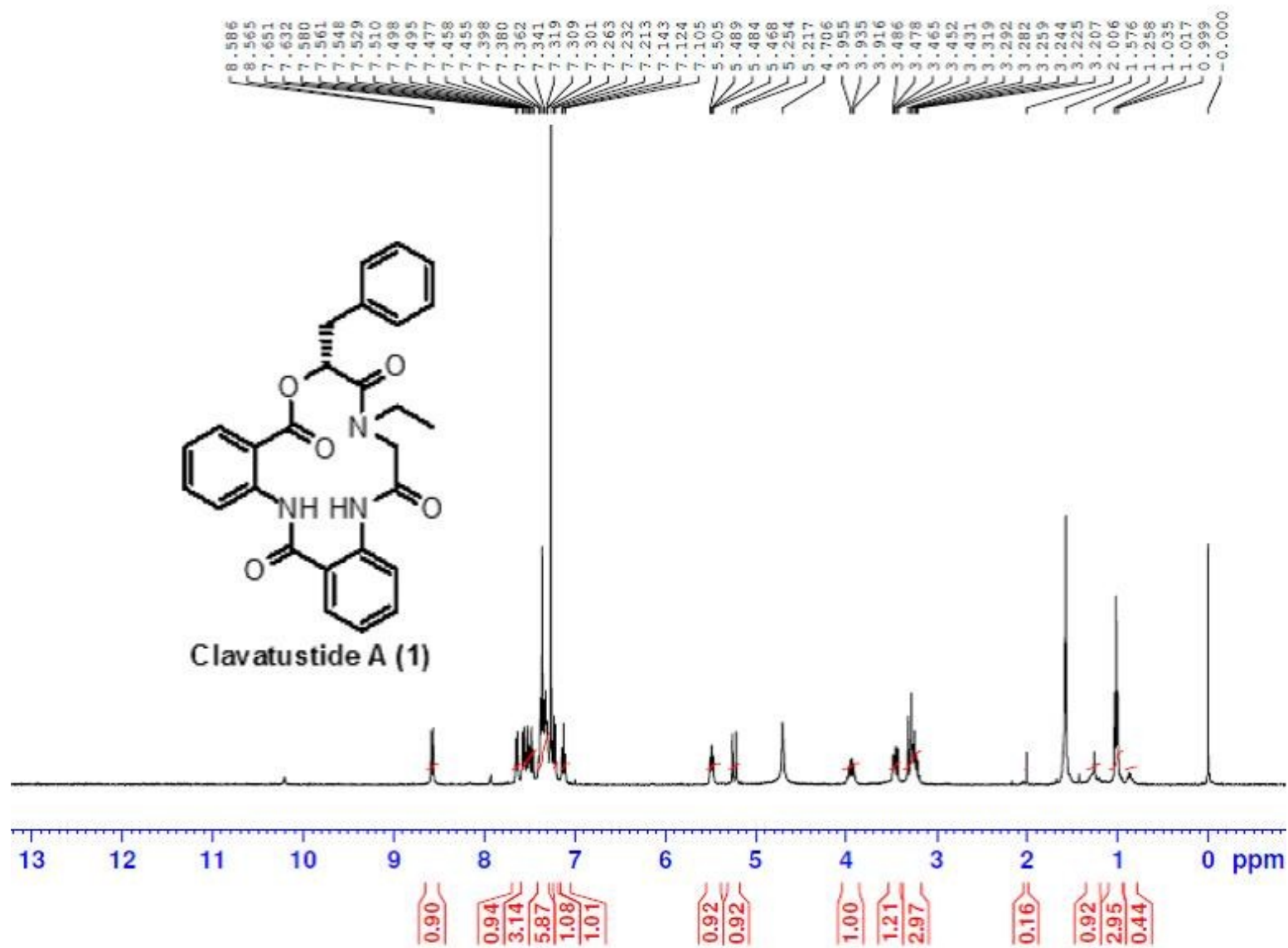
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|----------|-------------|
| 1 | 0.8542 | 161.1799 | 4.85 min | 9.795 | 4849.0167 |
| 2 | 99.1458 | 18707.4694 | 5.91 min | 705.2798 | 5907.3333 |

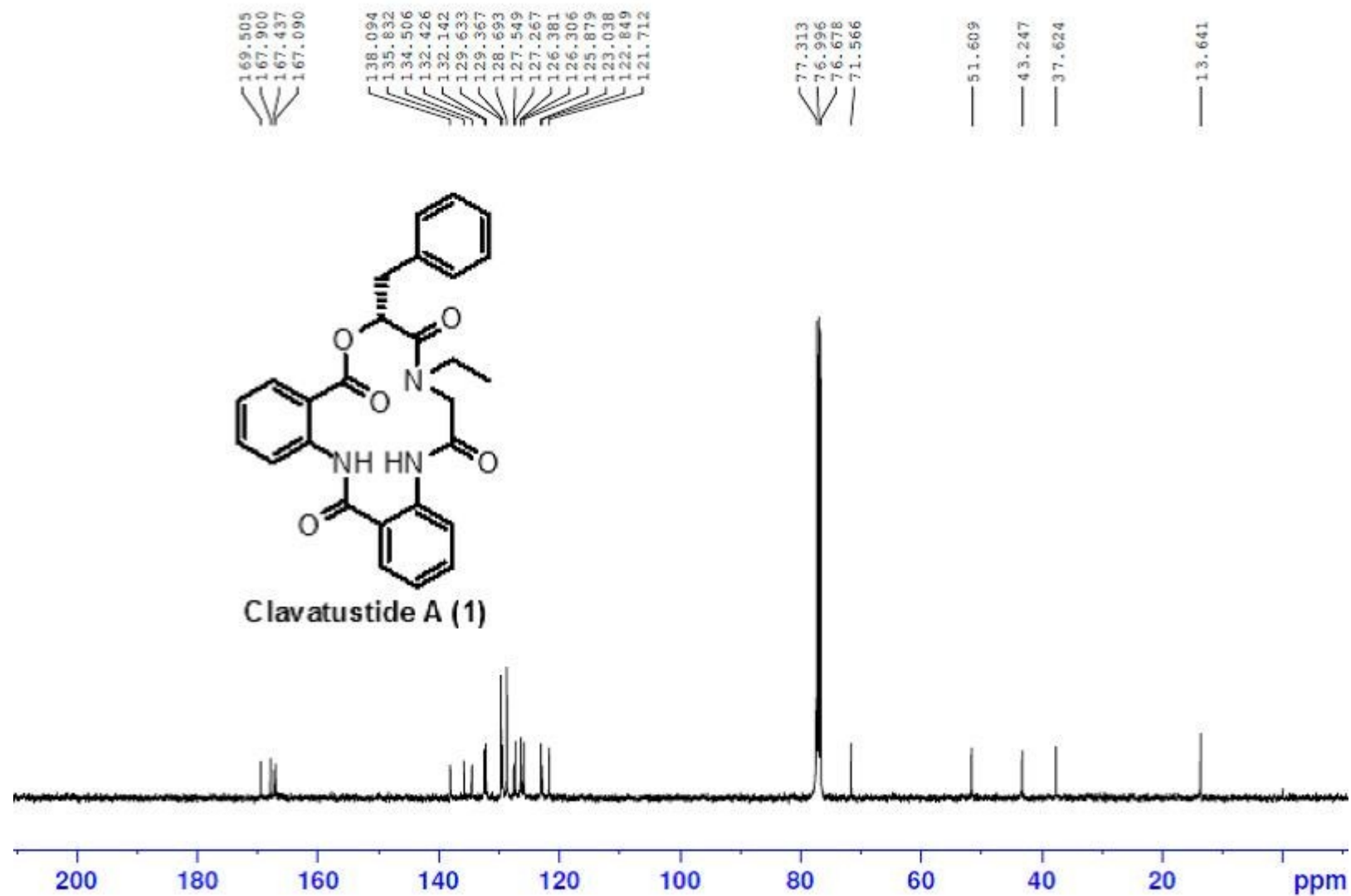
¹H NMR of Clavatustide A (1) in CDCl₃



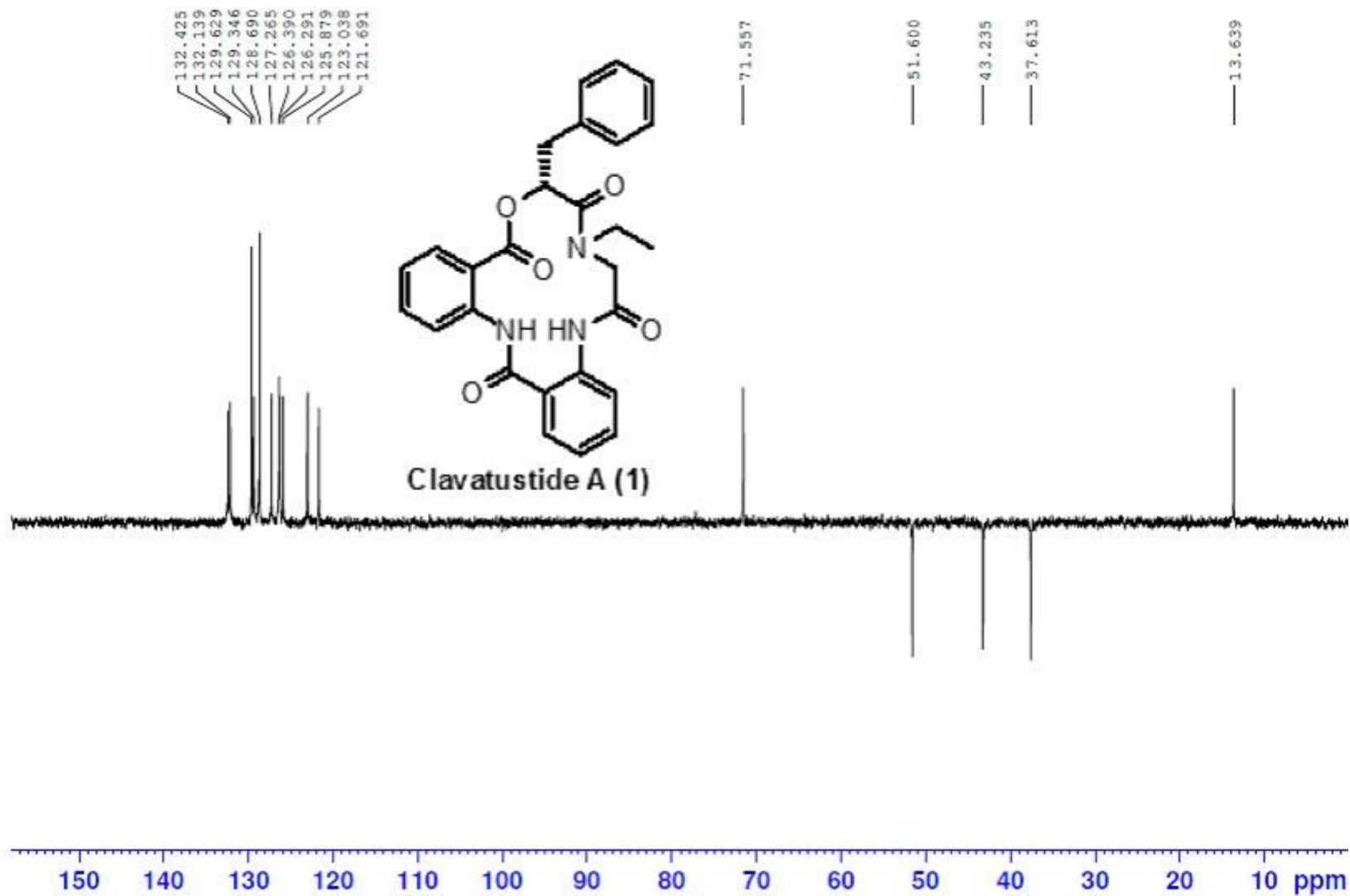
D₂O exchange ¹H NMR of Clavatustide A (1) in CDCl₃



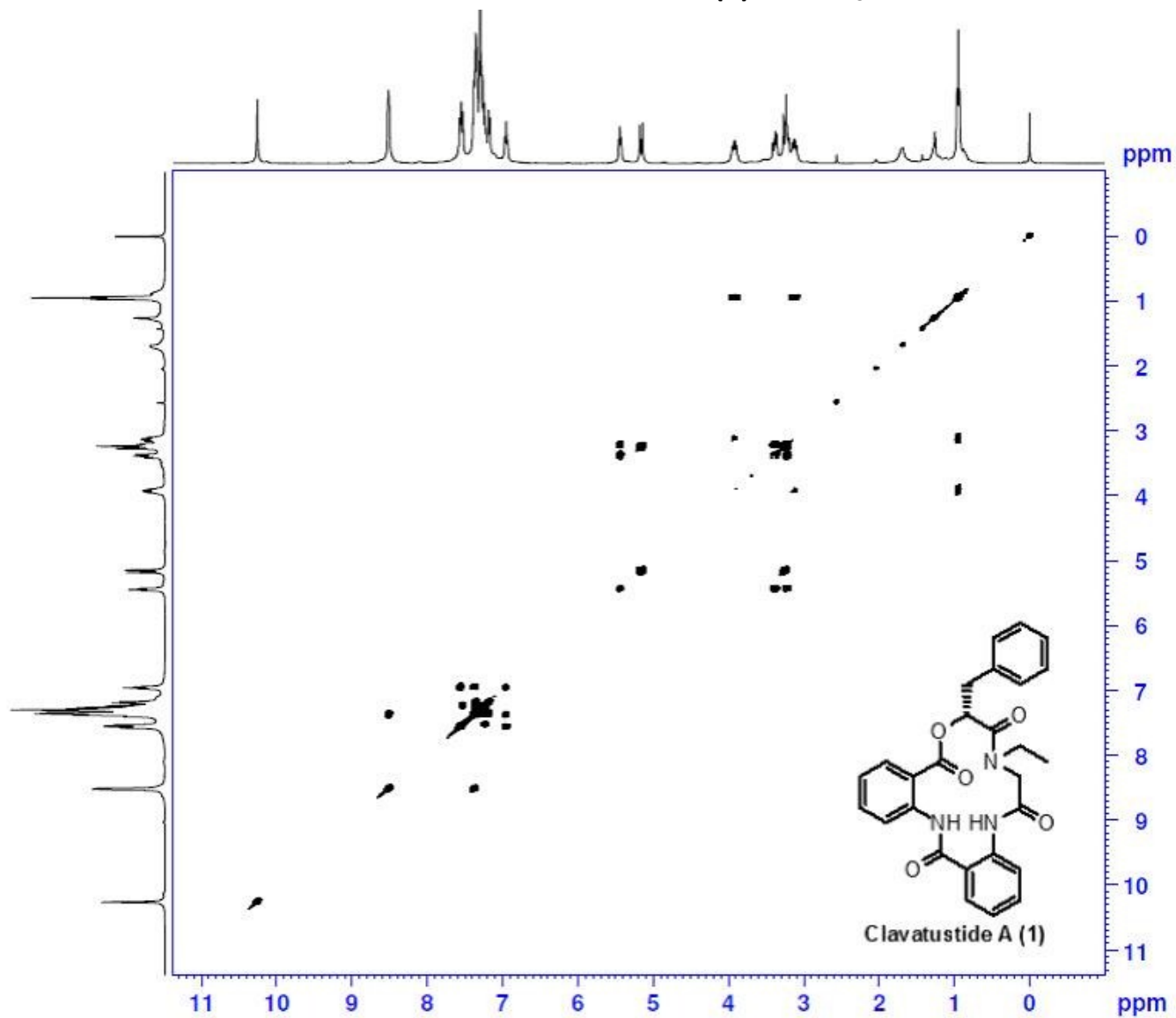
¹³C NMR of Clavatustide A (1) in CDCl₃



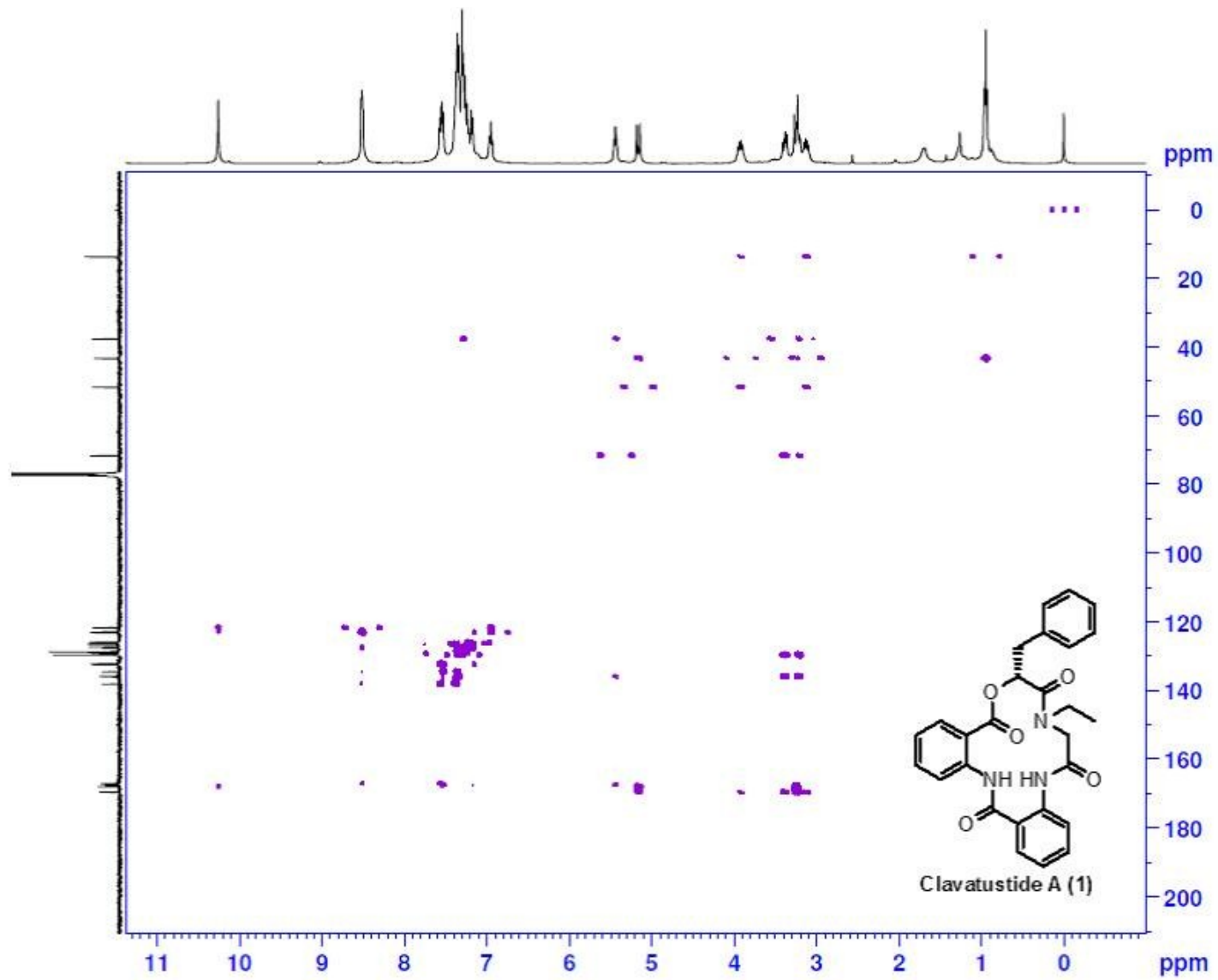
DEPT NMR of Clavatustide A (1) in CDCl₃



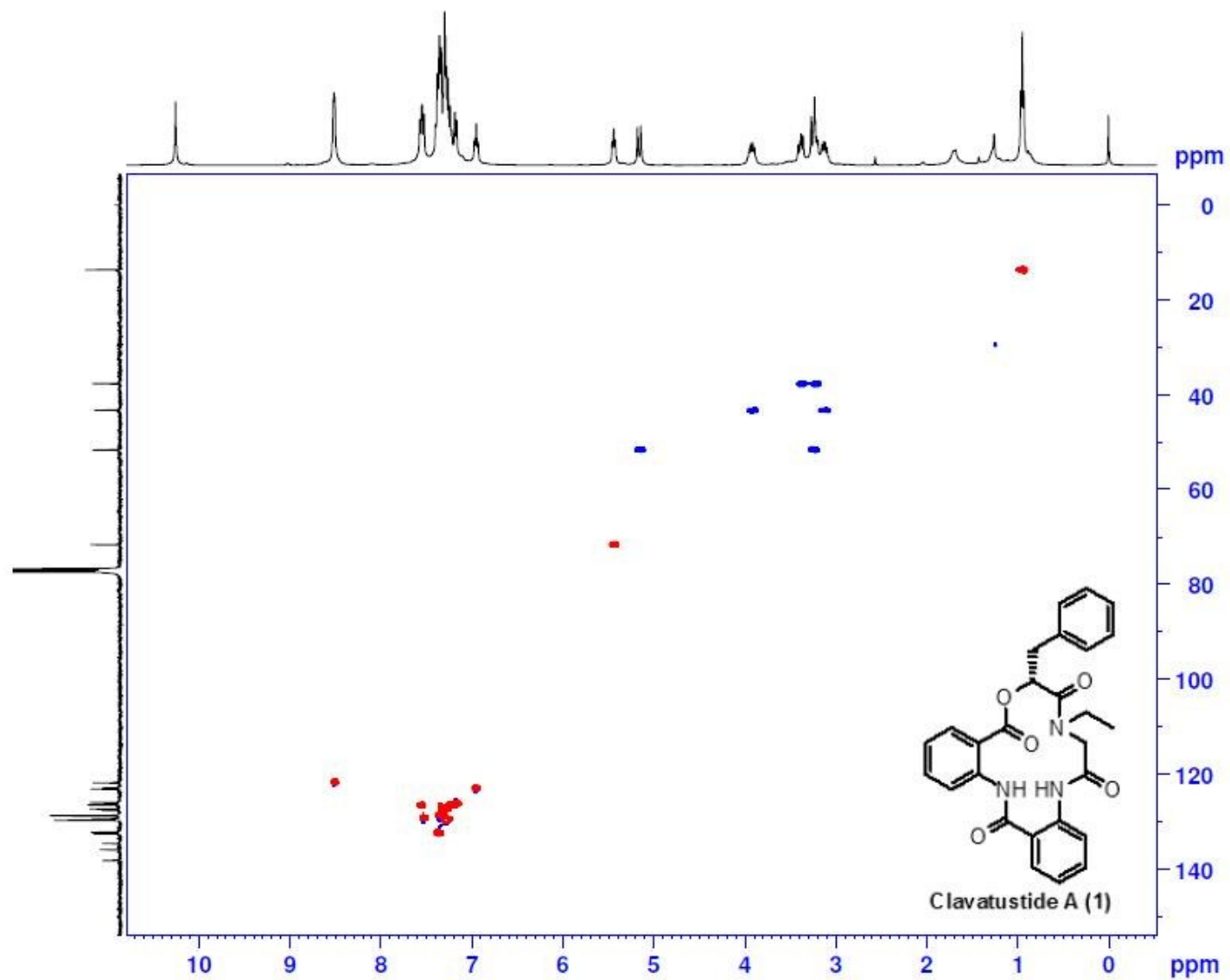
COSY NMR of Clavatustide A (1) in CDCl₃



HMBC NMR of Clavatustide A (1) in CDCl₃



HSQC of Clavatustide A (1) in CDCl₃



HRMS of Clavatuside A (1)

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

19 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

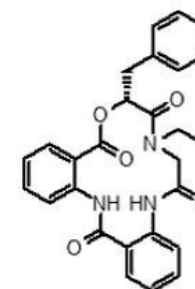
Elements Used:

C: 0-27 H: 0-26 N: 0-3 O: 0-5

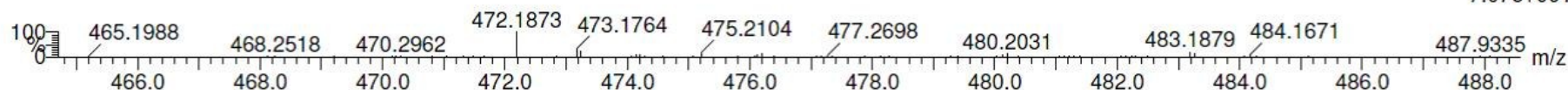
GVKP-SK-B1329-92-R-1

13082015-017-GVKP-SK-B1329-92-R-1 9 (0.275) AM (Top,4, Ht,5000.0,195.05,1.00,LS 10); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (6:10)

2: TOF MS ES+
7.07e+001



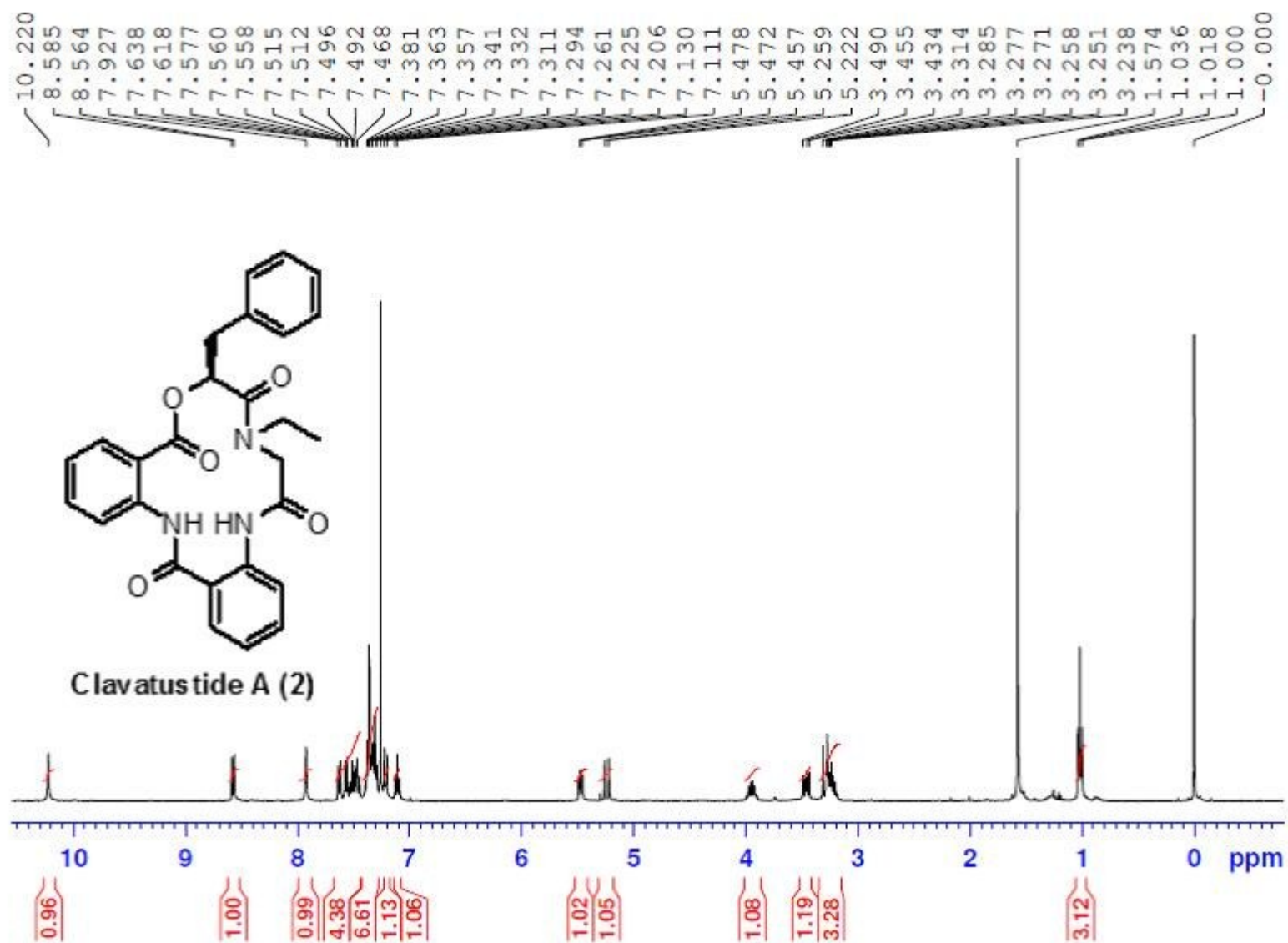
Clavatuside A (1)



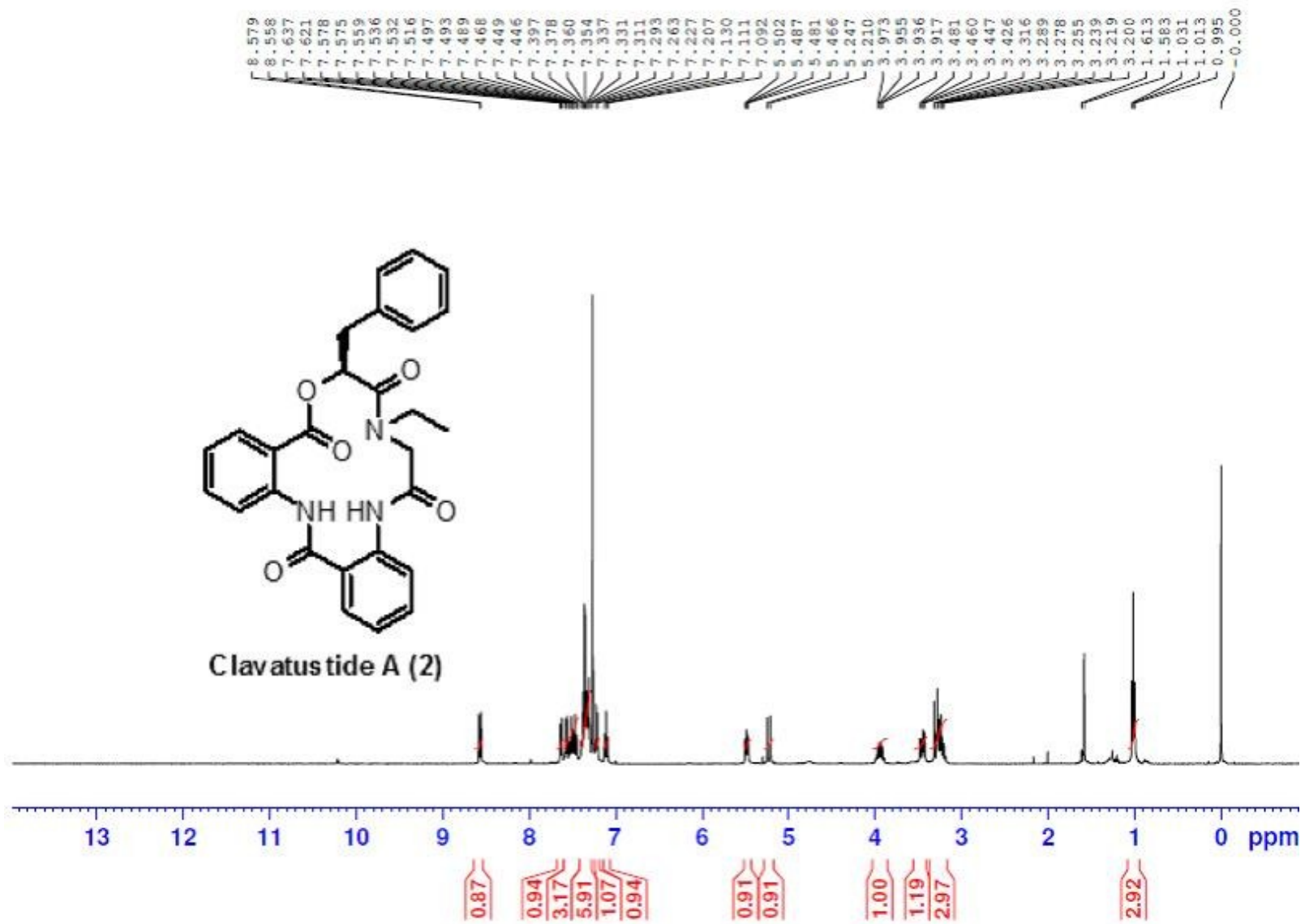
Minimum: -1.5
Maximum: 5.0 1000.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf (%) | Formula |
|----------|------------|-----|-----|------|-------|------|----------|---------------|
| 472.1873 | 472.1872 | 0.1 | 0.2 | 16.5 | 21.3 | n/a | n/a | C27 H26 N3 O5 |

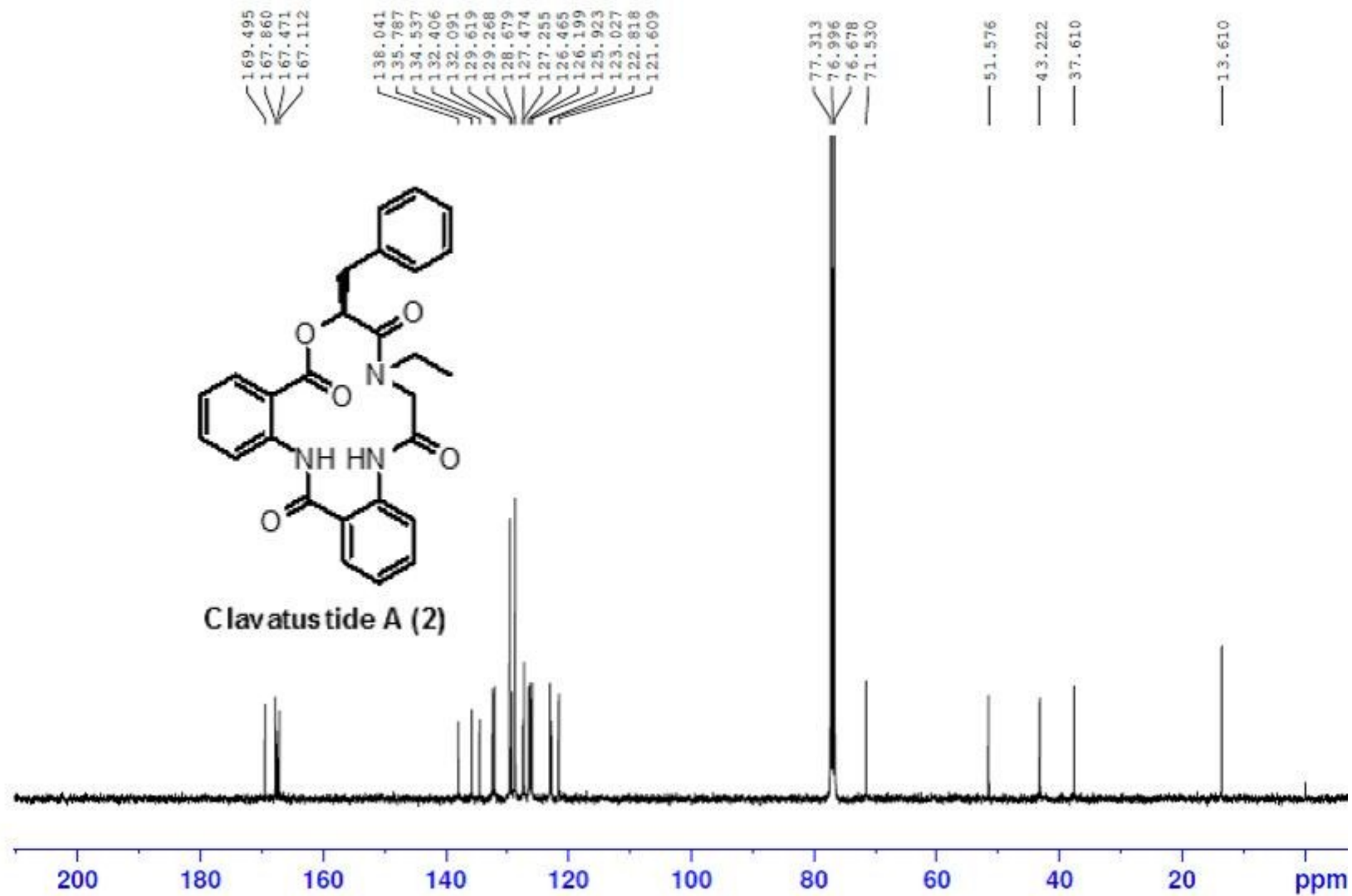
¹H NMR of Clavatuside A enantiomer (2) in CDCl₃



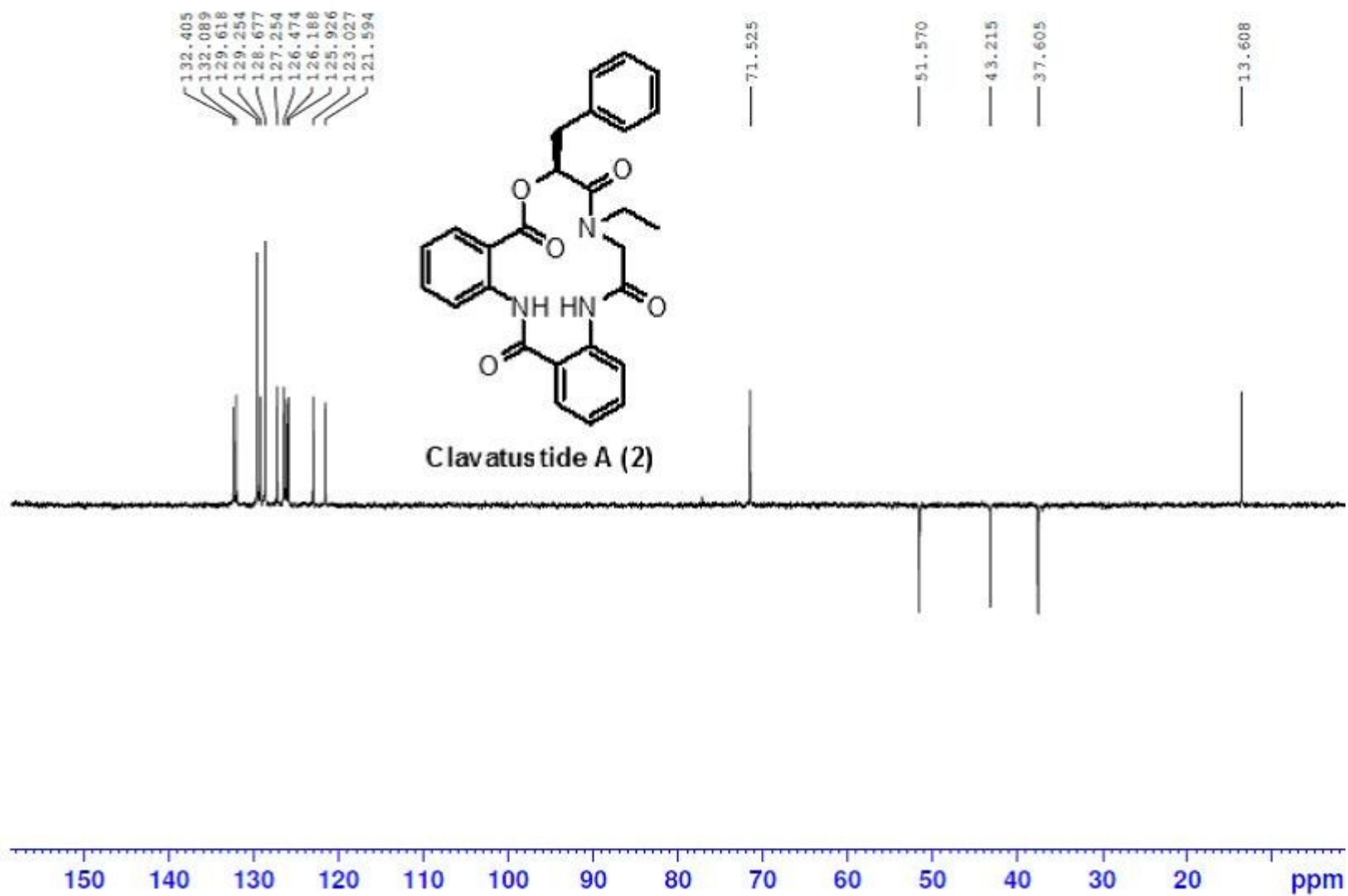
D₂O exchange ¹H NMR of Clavatustide A enantiomer (2) in CDCl₃



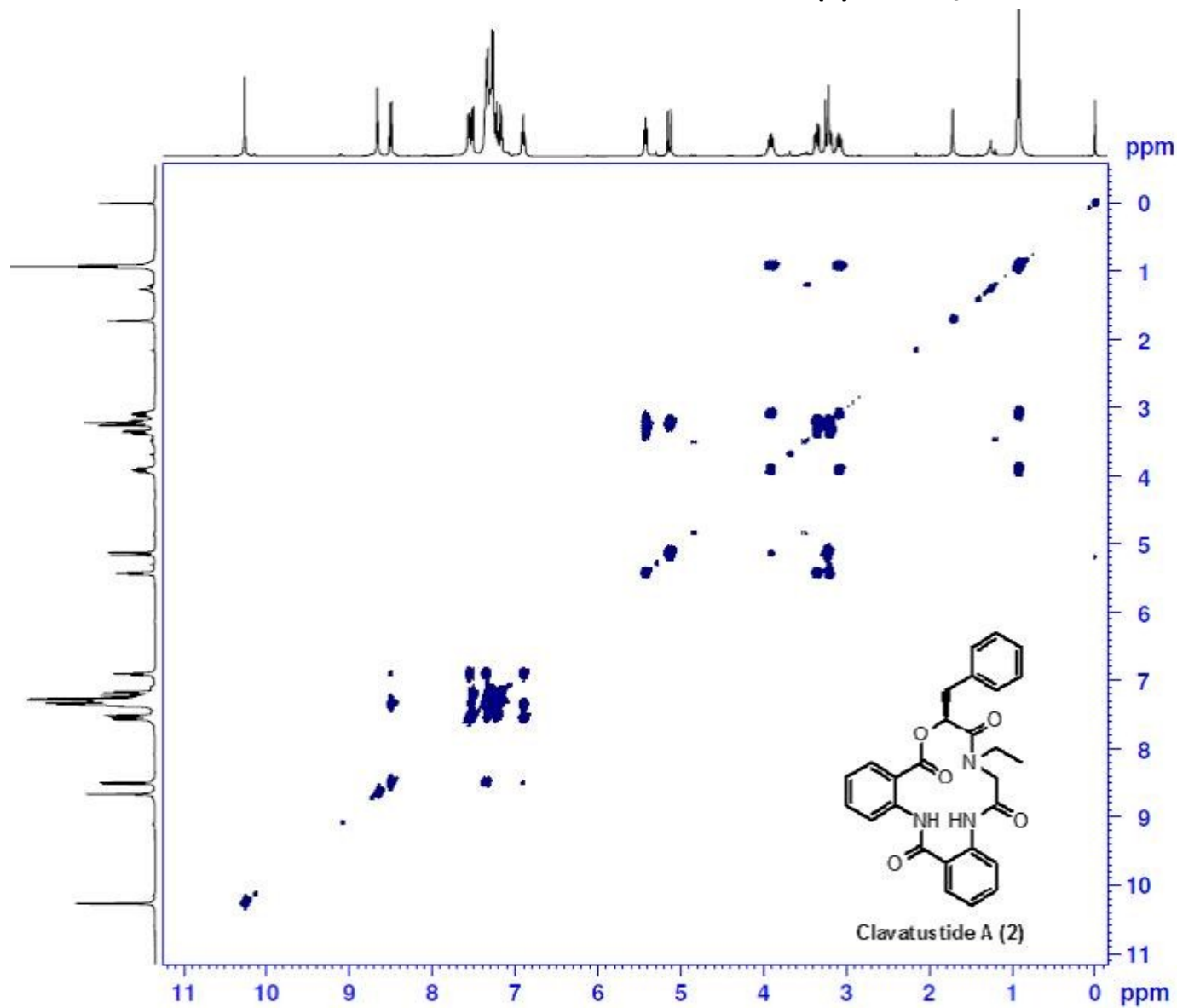
¹³C NMR of Clavatuside A enantiomer (2) in CDCl₃



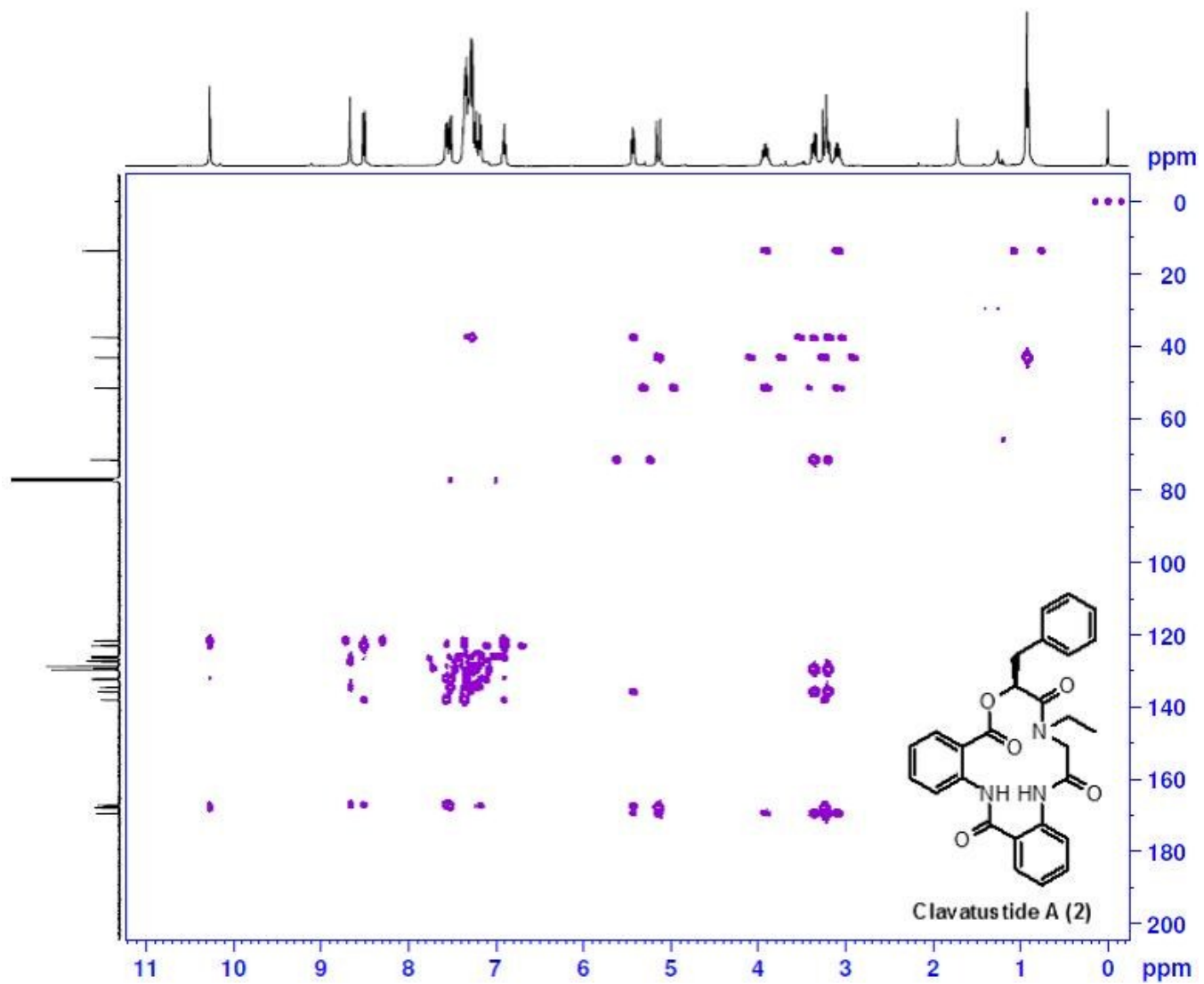
DEPT NMR of Clavatuside A enantiomer (2) in



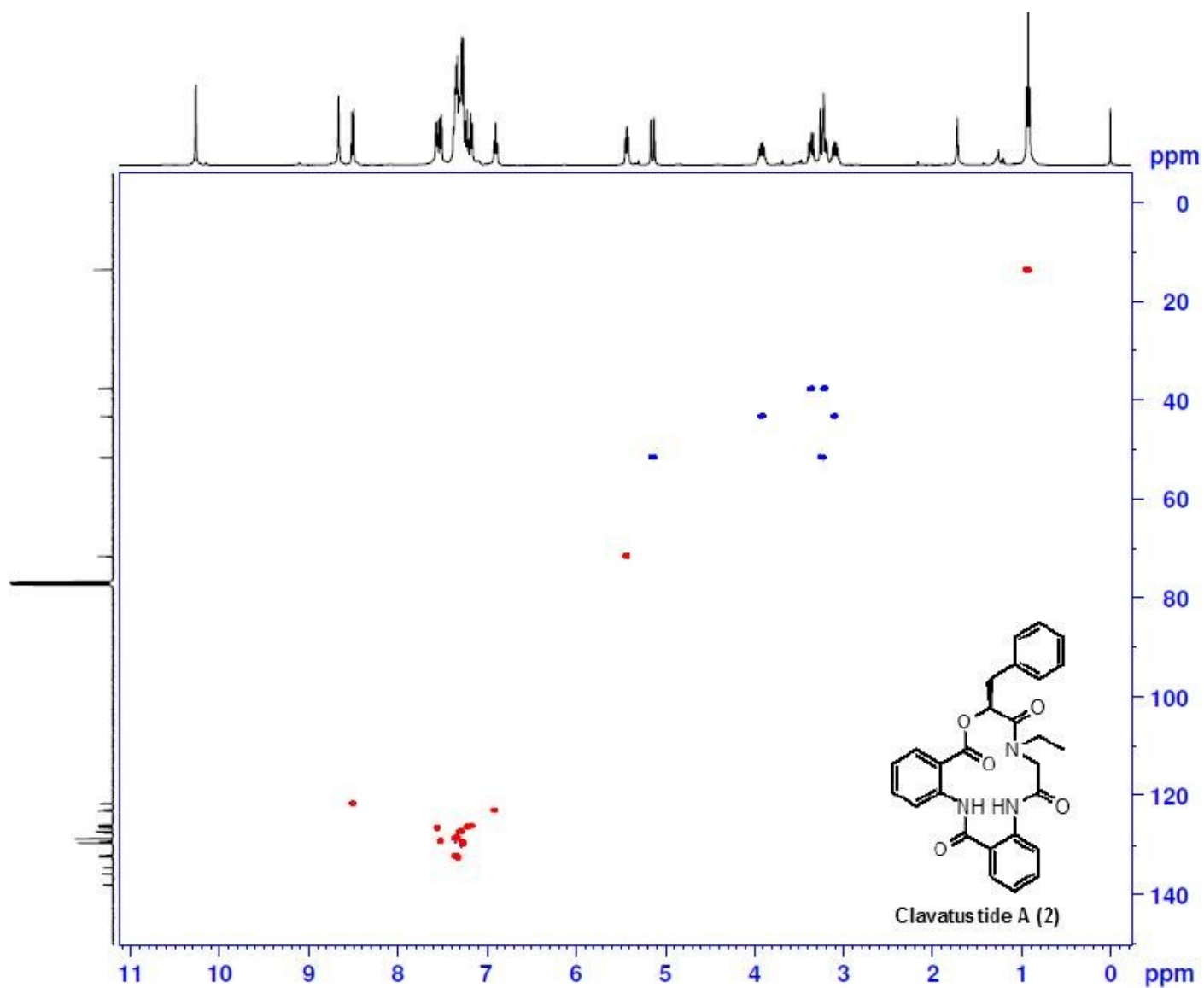
COSY NMR of enantiomer of Clavatuside A (2) in CDCl₃



HMBC NMR of Clavatuside A enantiomer (2) in CDCl₃



HSQC of Clavatuside A enantiomer (2) in CDCl₃



HRMS of enantiomer of Clavatustide A (2)

Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

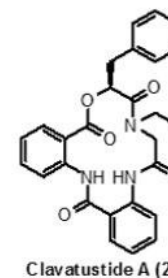
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

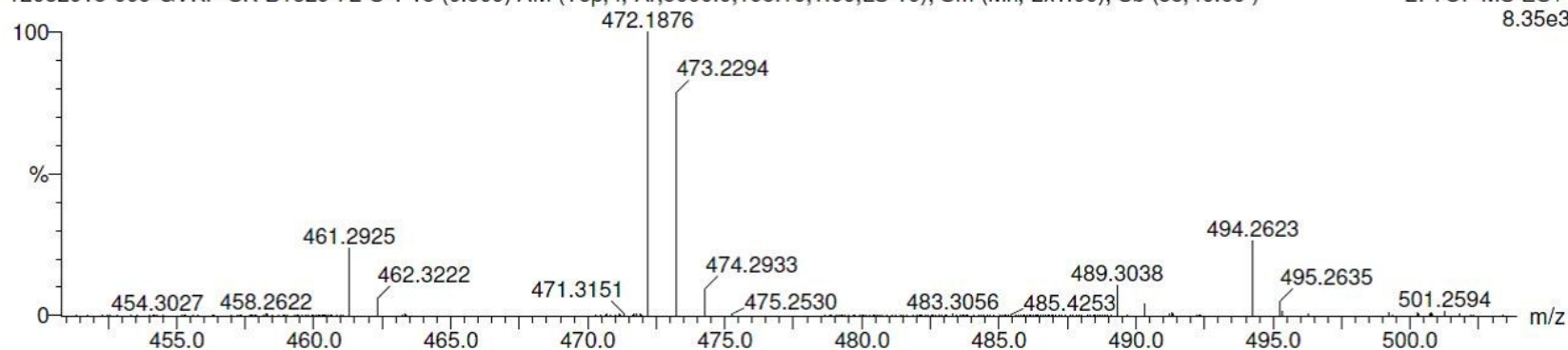
C: 0-27 H: 0-26 N: 0-3 O: 0-5

SAMPLE CODE: GVKP-SK-B1329-72-S-1

12082015-009-GVKP-SK-B1329-72-S-1 15 (0.509) AM (Top,4, Ar,5000.0,195.10,1.00,LS 10); Sm (Mn, 2x1.00); Sb (35,40.00)



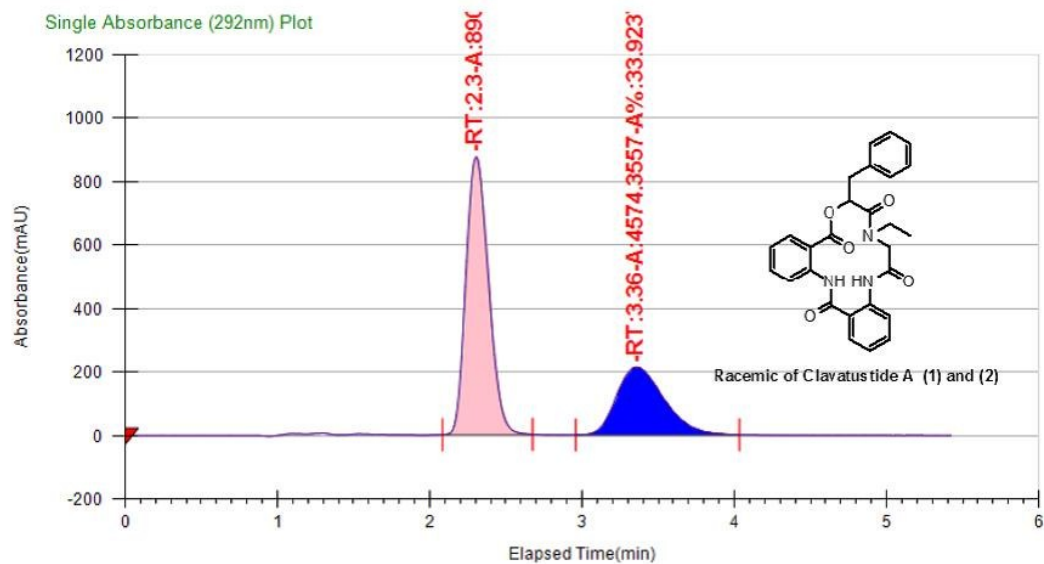
2: TOF MS ES+
8.35e3



Minimum: -1.5
Maximum: 5.0 1000.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|----------|------------|-----|-----|------|--------|---------------|
| 472.1876 | 472.1872 | 0.4 | 0.8 | 16.5 | 1276.5 | C27 H26 N3 O5 |

Racemic of Clavatuside A (1) and A (2)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|--------------------------|---------------|-------------|-------|
| Administrator | 5/12/2015 10:42:31 AM | Administrator | 5/12/2015 | |

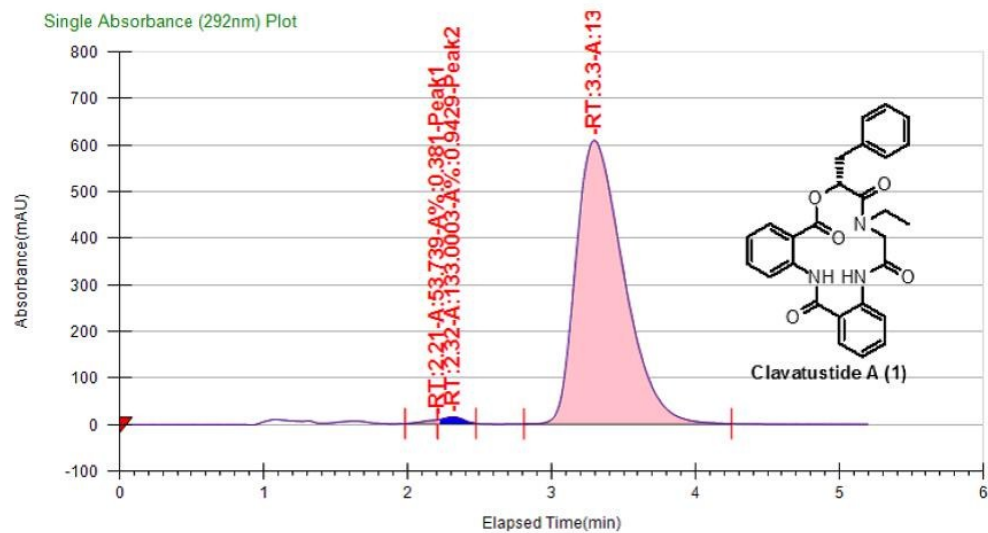
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|---|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 15 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329- 92+GVKP-SK- B1329-72 | 11D | 30 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 66.0763 | 8909.8929 | 2.3 min | 874.4468 | 0 |
| 2 | 33.9237 | 4574.3557 | 3.36 min | 213.3956 | 0 |

Chiral HPLC of Clavatustide A (1)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|--------------------------|---------------|-------------|-------|
| Administrator | 5/12/2015 10:58:46 AM | Administrator | 5/12/2015 | |

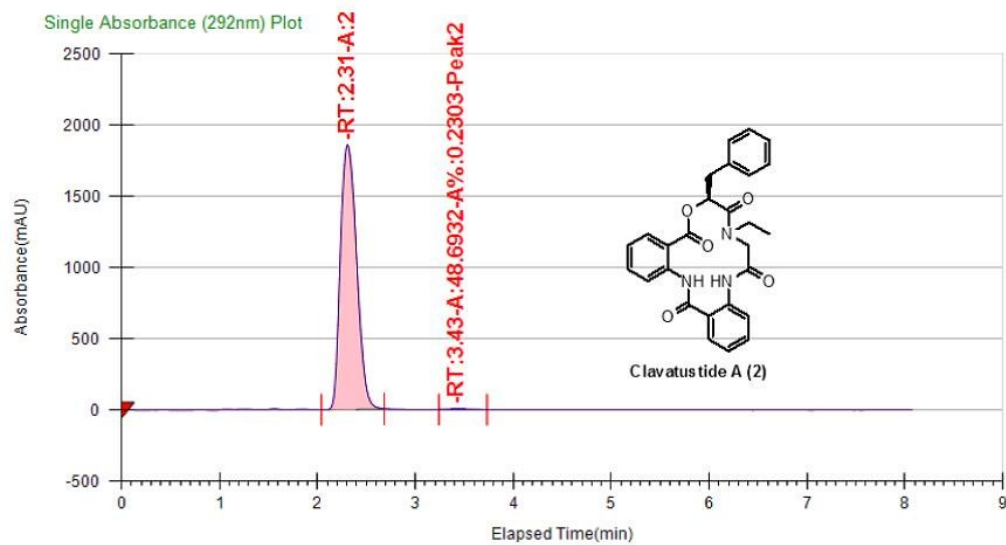
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|----------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 15 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329-92 | 13D | 30 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|----------|-------------|
| 1 | 0.381 | 53.739 | 2.21 min | 8.1378 | 0 |
| 2 | 0.9429 | 133.0003 | 2.32 min | 14.1061 | 0 |
| 3 | 98.6761 | 13918.4041 | 3.3 min | 608.2497 | 0 |

Chiral HPLC of Clavatuside A enantiomer (2)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|--------------------------|---------------|-------------|-------|
| Administrator | 5/12/2015 10:49:19 AM | Administrator | 5/12/2015 | |

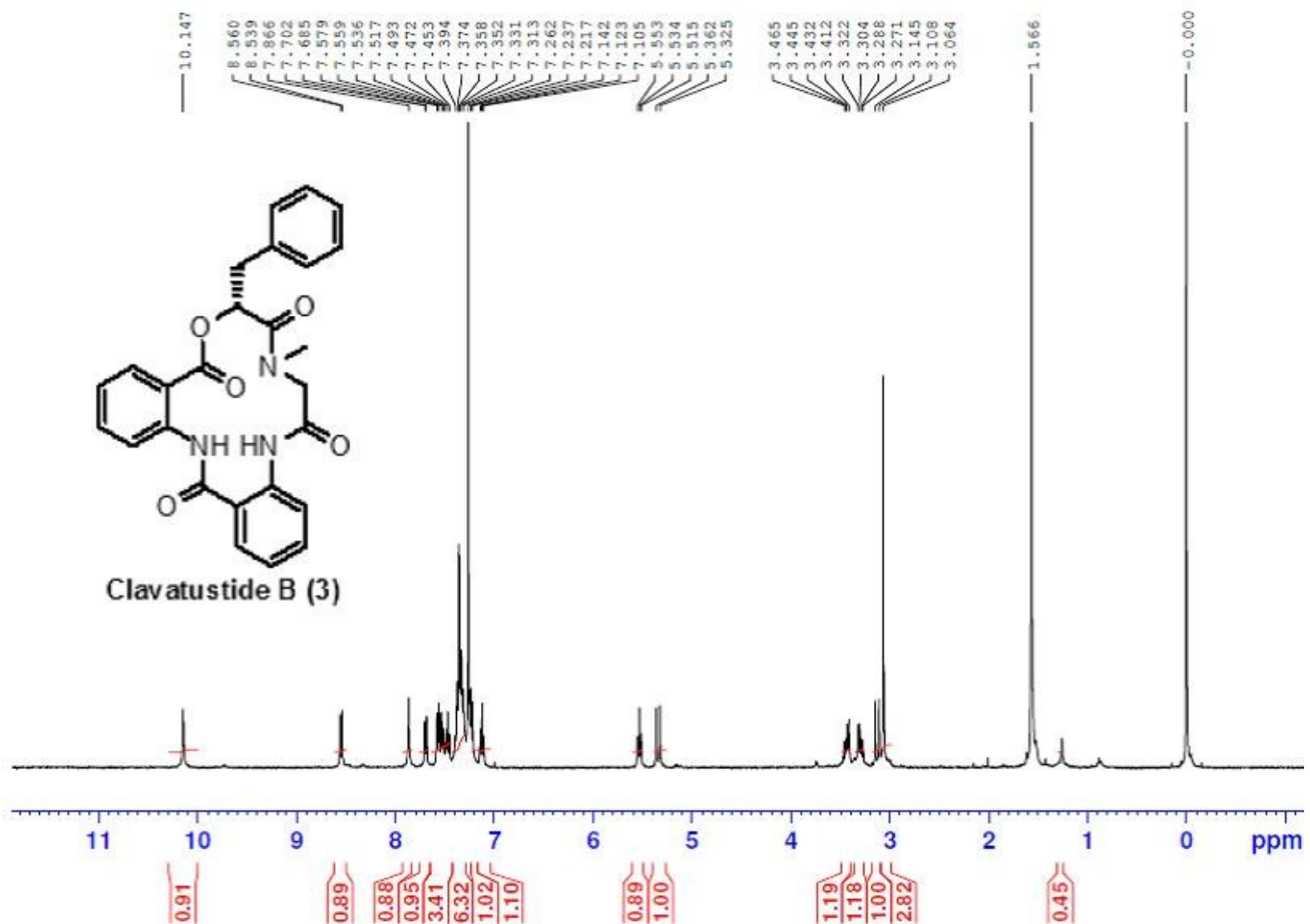
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|----------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 15 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329-72 | 12D | 30 | 4 | 40 | 100 |

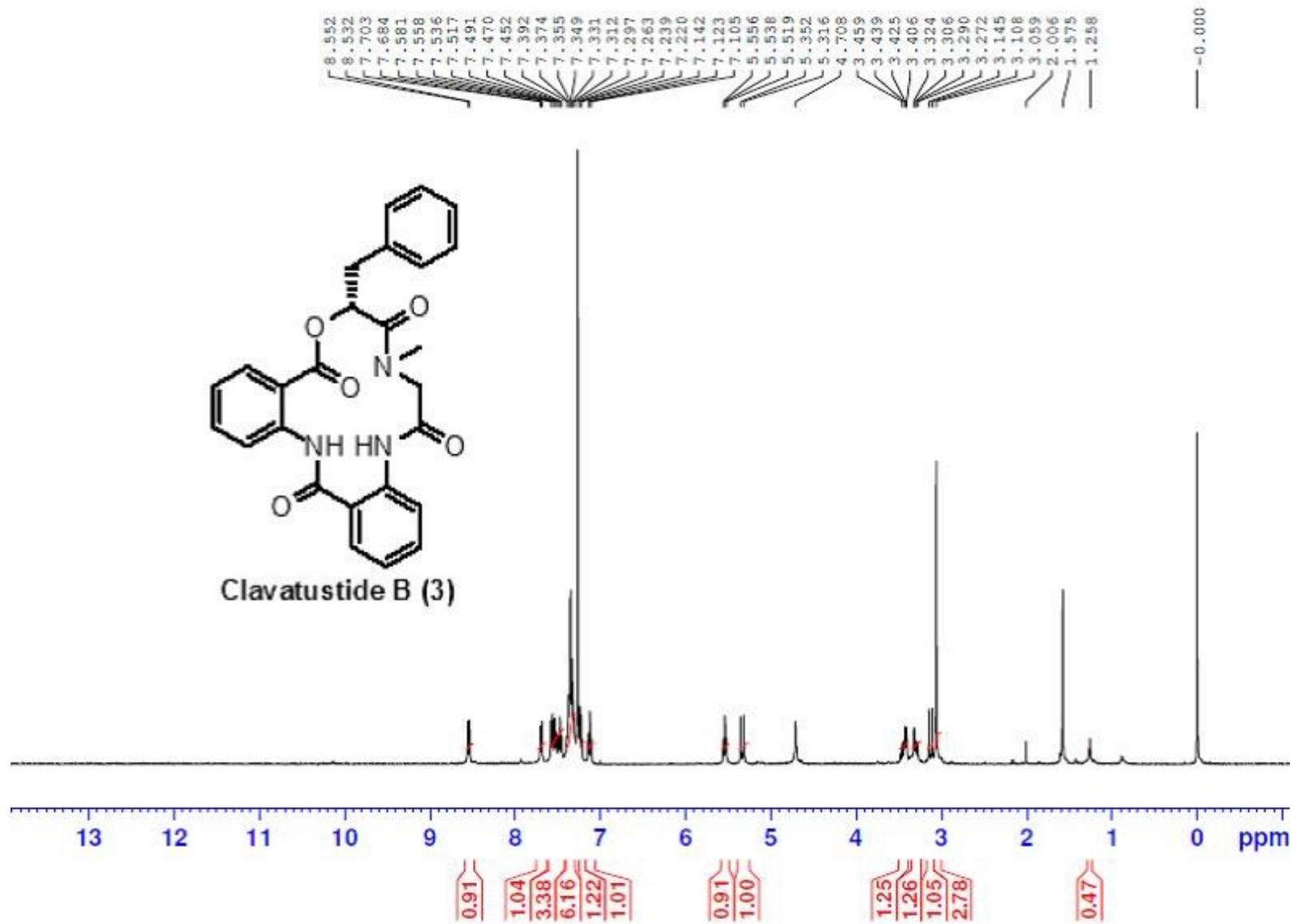
Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 99.7697 | 21097.0338 | 2.31 min | 1858.3254 | 0 |
| 2 | 0.2303 | 48.6932 | 3.43 min | 3.0338 | 0 |

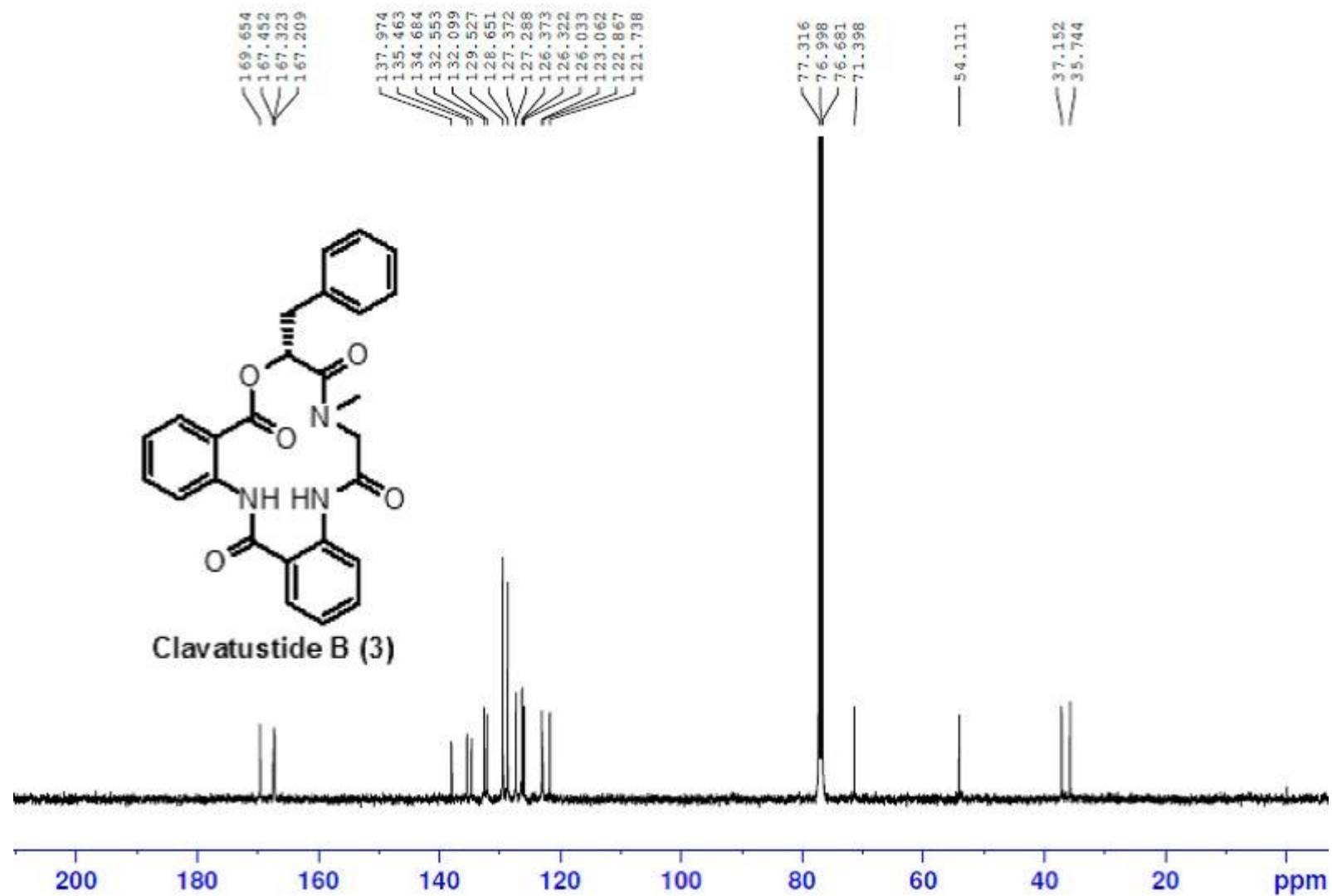
¹H NMR of Clavatustide B (3) in CDCl₃



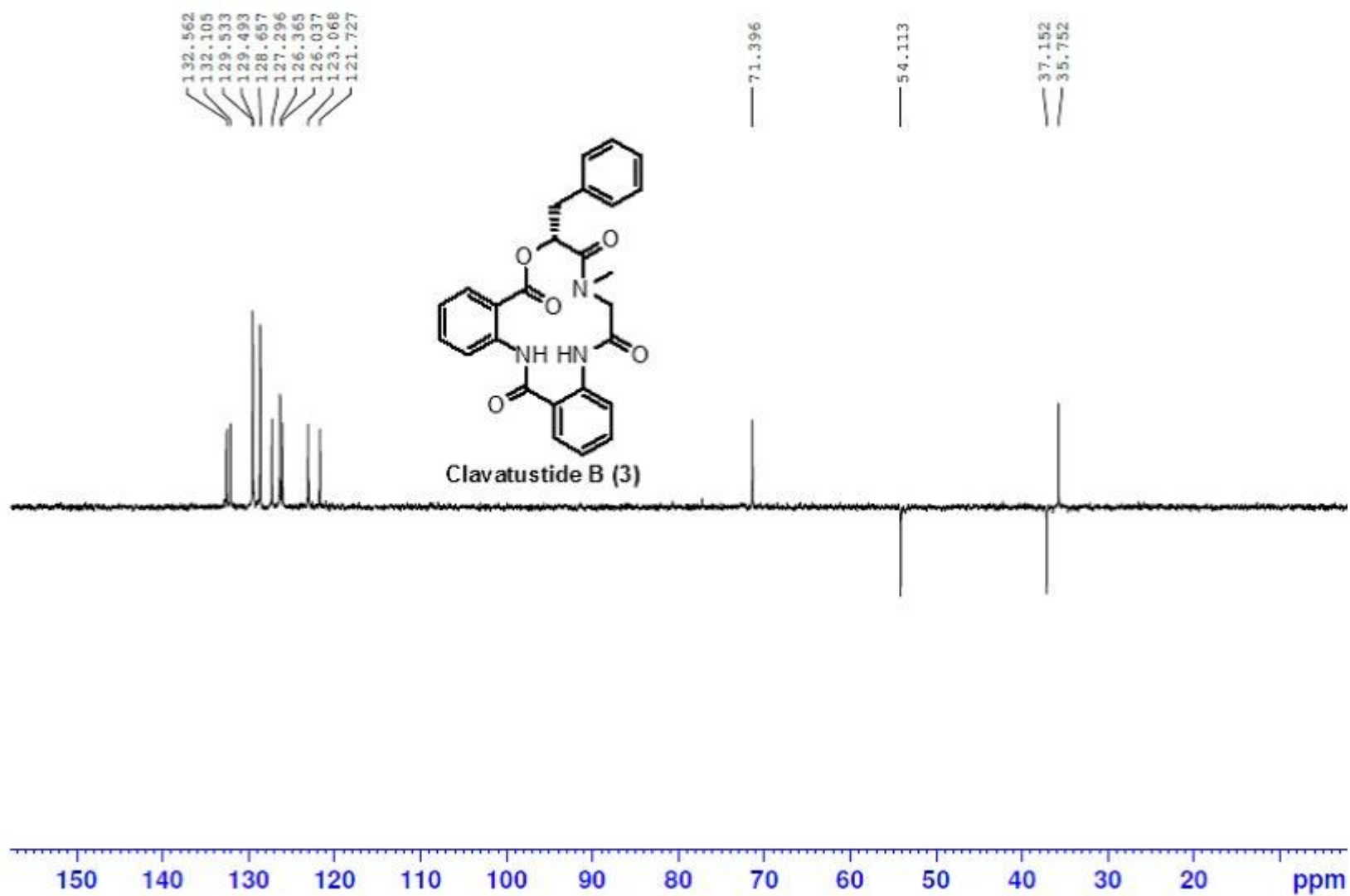
D₂O exchange ¹H NMR of Clavatustide B (3) in CDCl₃



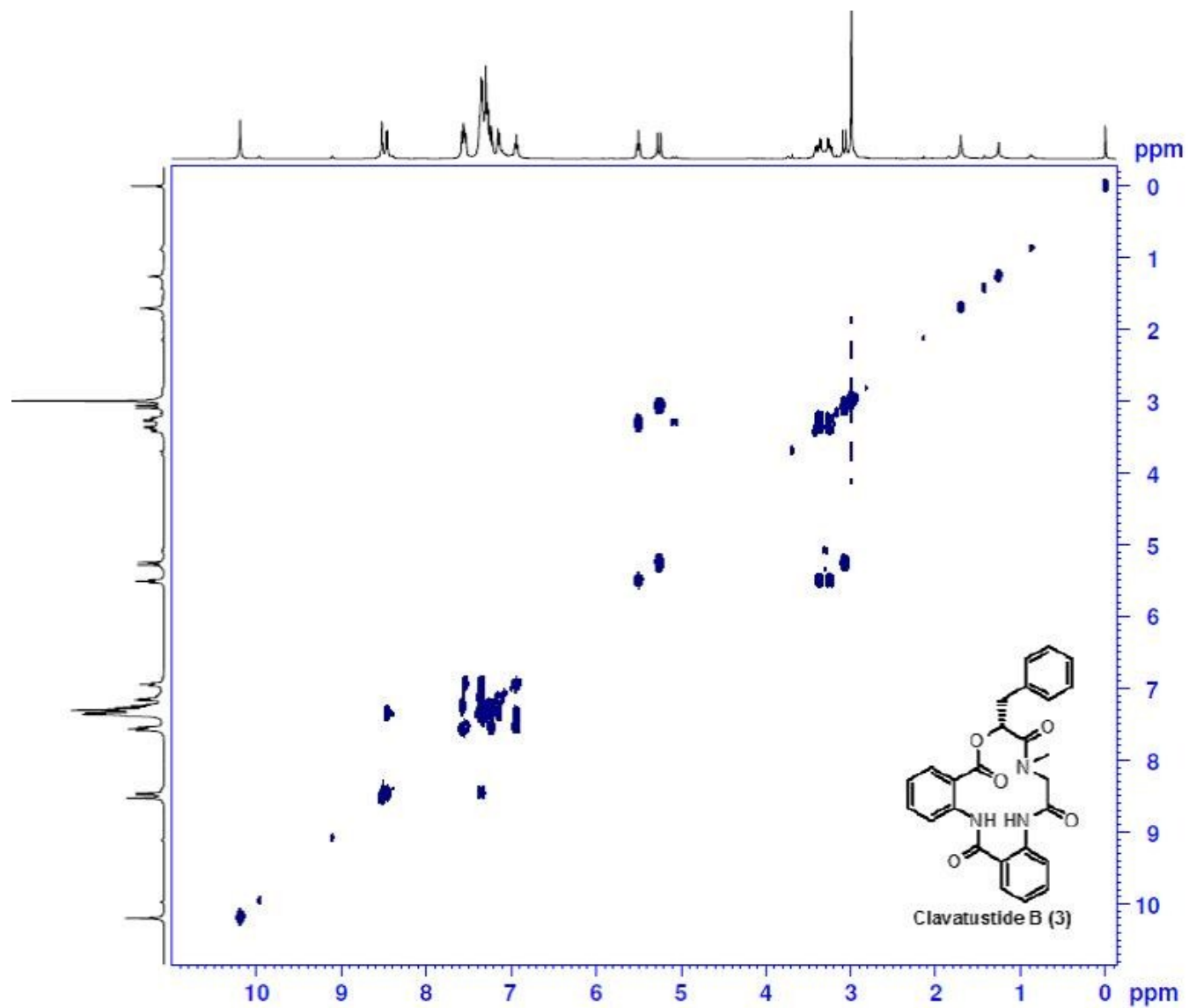
¹³C NMR of Clavatustide B (3) in CDCl₃



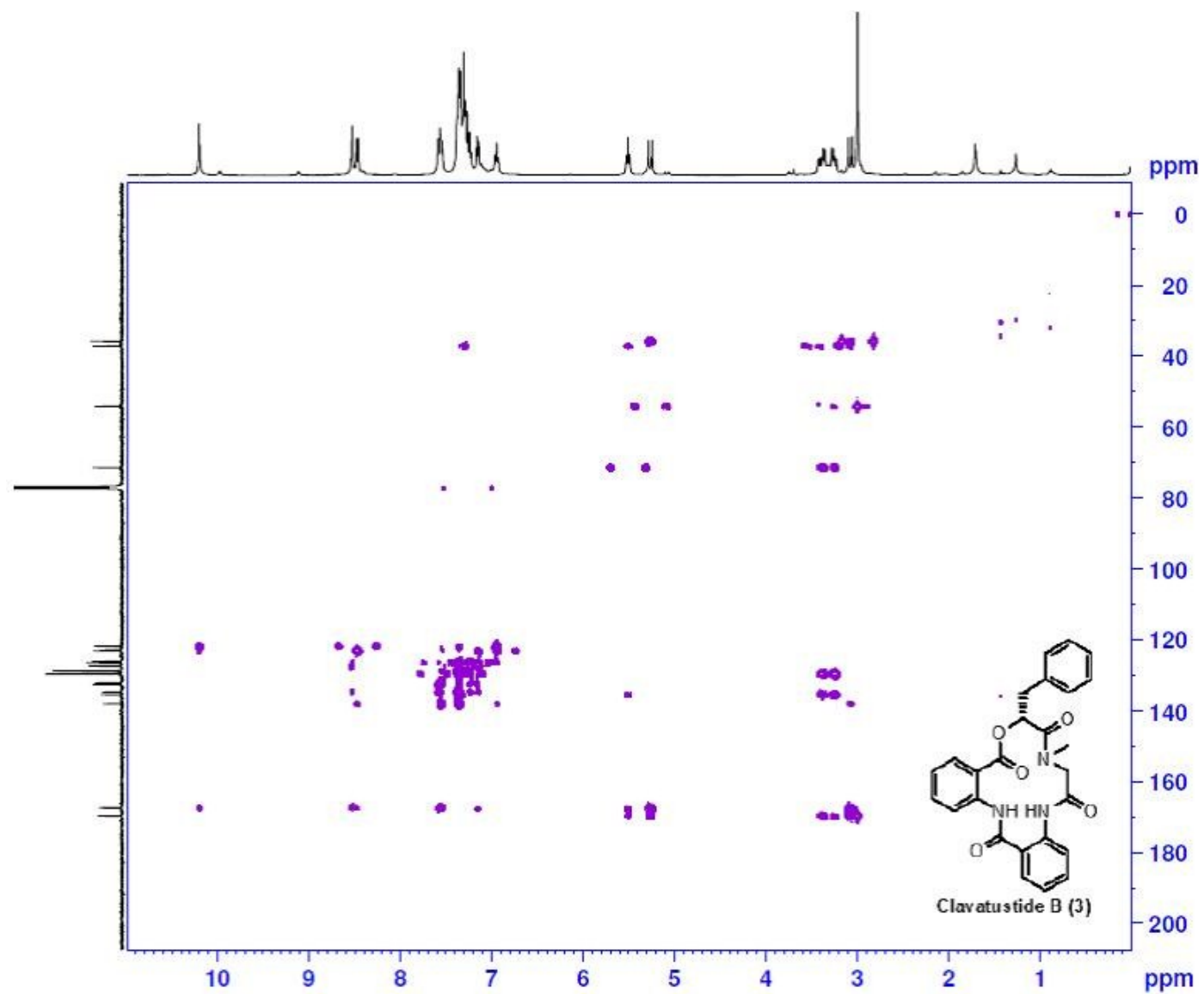
DEPT NMR of Clavatustide B (3) in CDCl₃



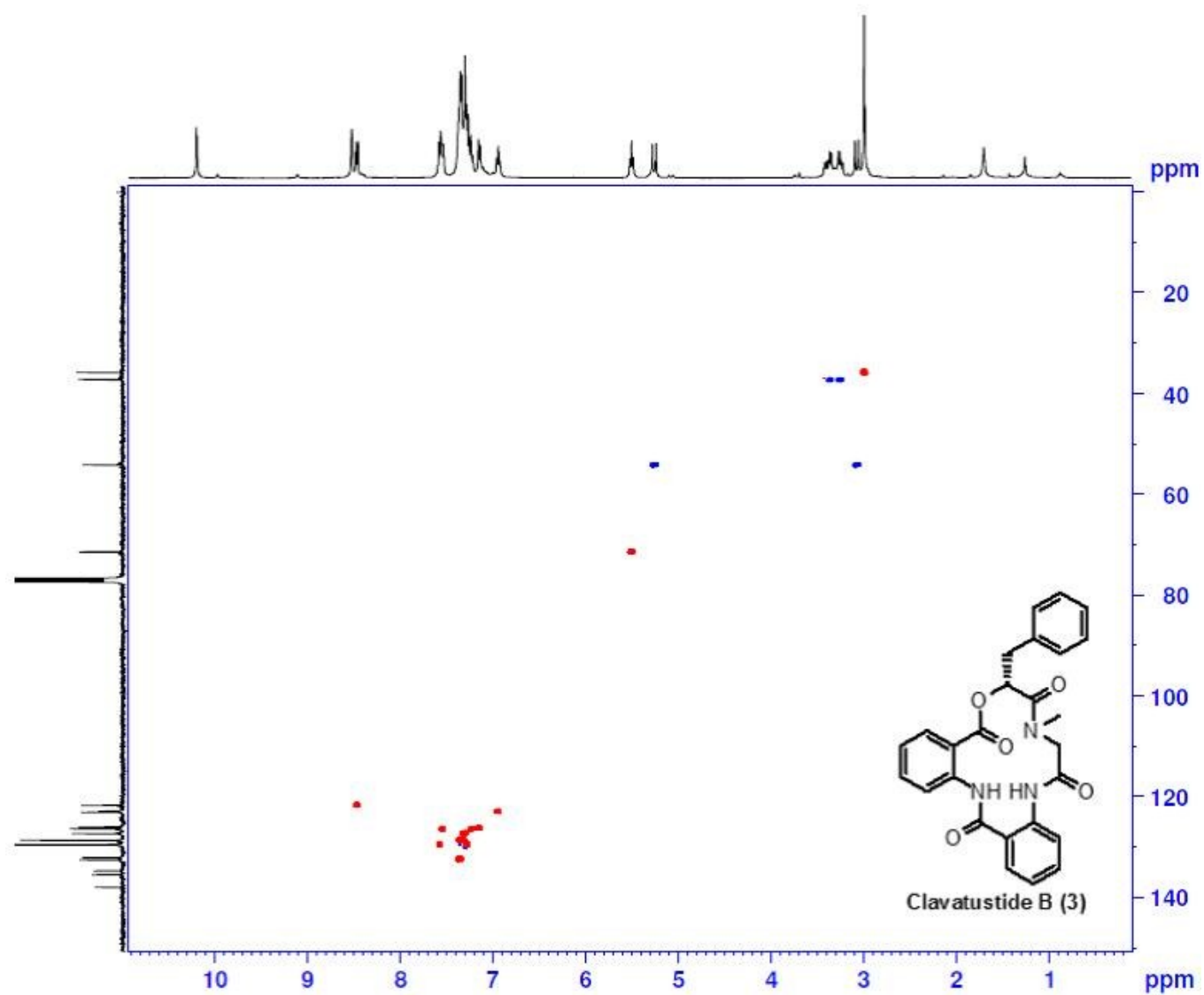
COSY NMR of Clavatustide B (3) in CDCl₃



HMBC NMR of Clavatustide B (3) in CDCl₃



HSQC NMR of Clavatustide B (3) in CDCl₃



HRMS of Clavatustide B (3)

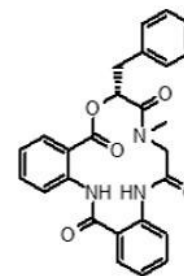
Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None



Clavatustide B (3)

Monoisotopic Mass, Even Electron Ions

19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

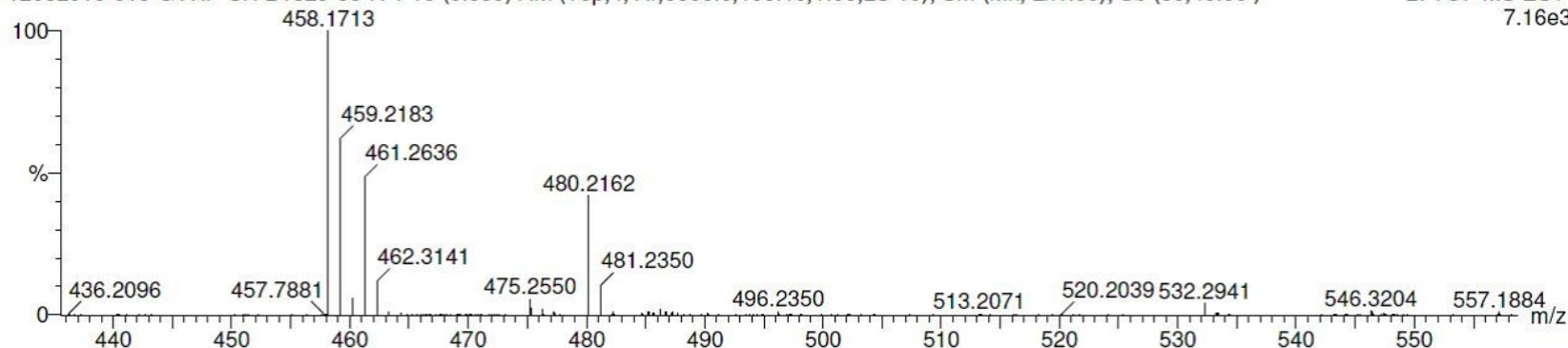
Elements Used:

C: 0-26 H: 0-24 N: 0-3 O: 0-5

SAMPLE CODE: GVKP-SK-B1329-86-R-1

12082015-015-GVKP-SK-B1329-86-R-1 16 (0.539) AM (Top,4, Ar,5000.0,195.10,1.00,LS 10); Sm (Mn, 2x1.00); Sb (35,40.00)

2: TOF MS ES+
7.16e3

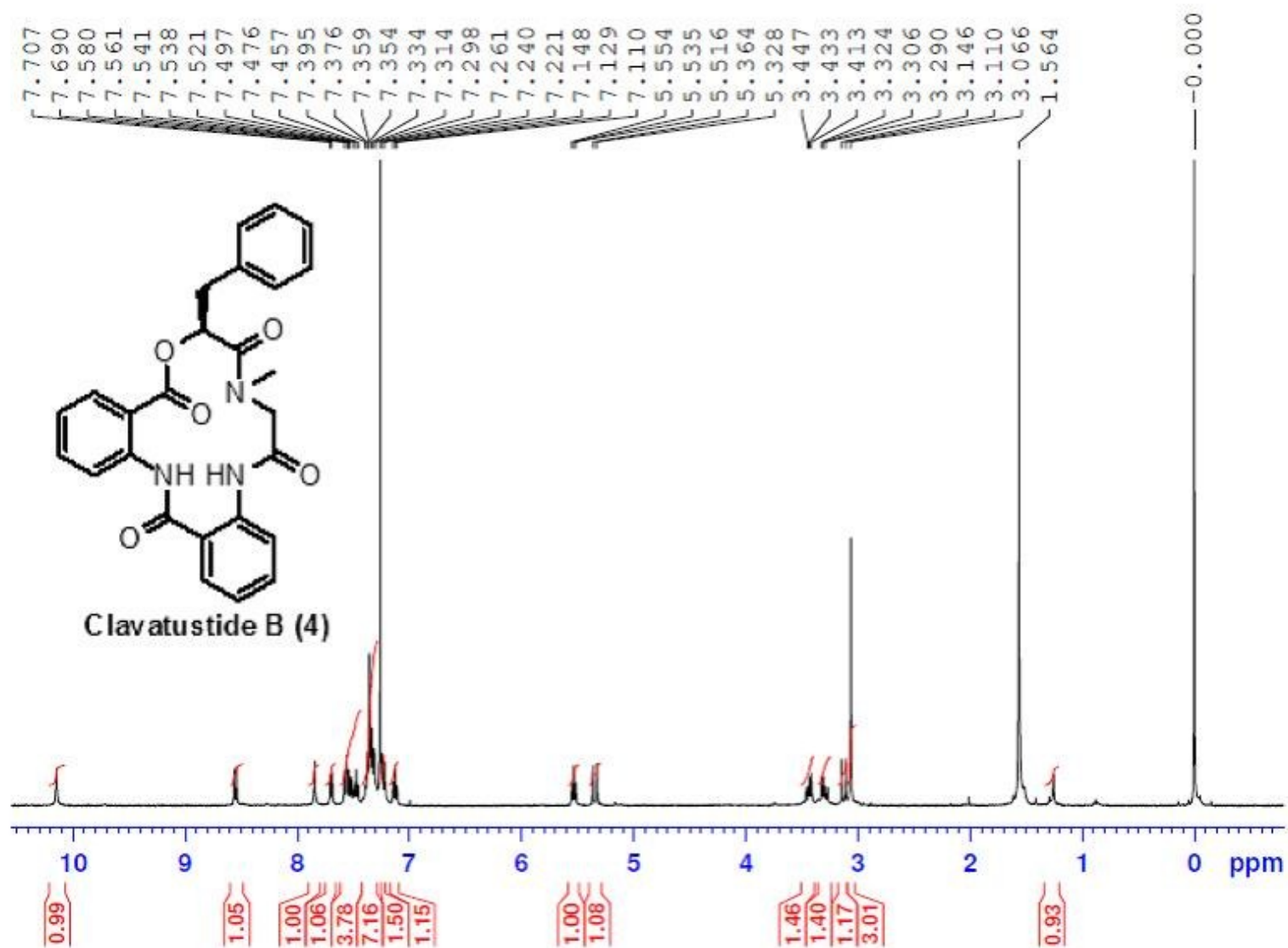


Minimum: -1.5

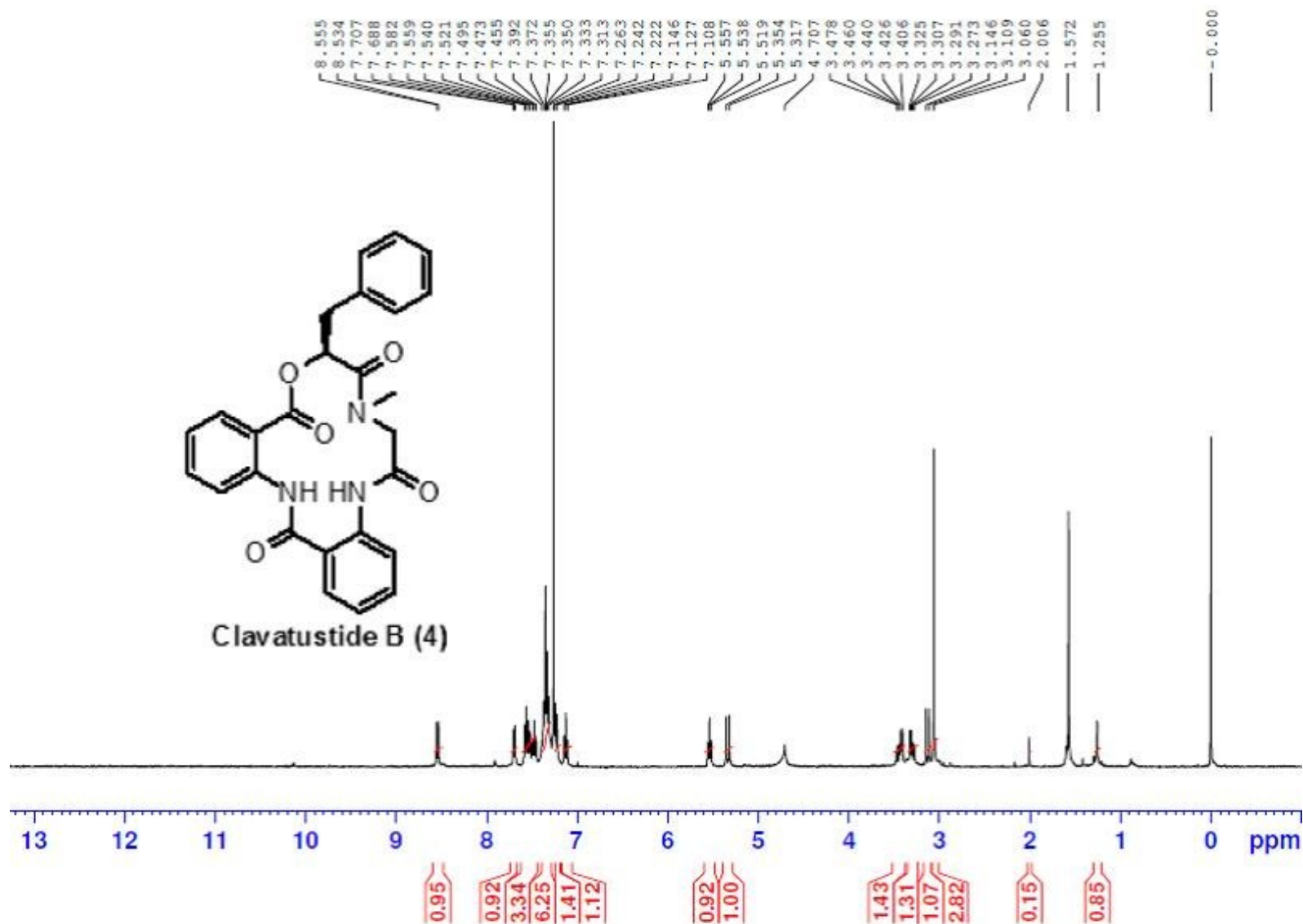
Maximum: 5.0 1000.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|----------|------------|------|------|------|-------|---------------|
| 458.1713 | 458.1716 | -0.3 | -0.7 | 16.5 | 653.4 | C26 H24 N3 O5 |

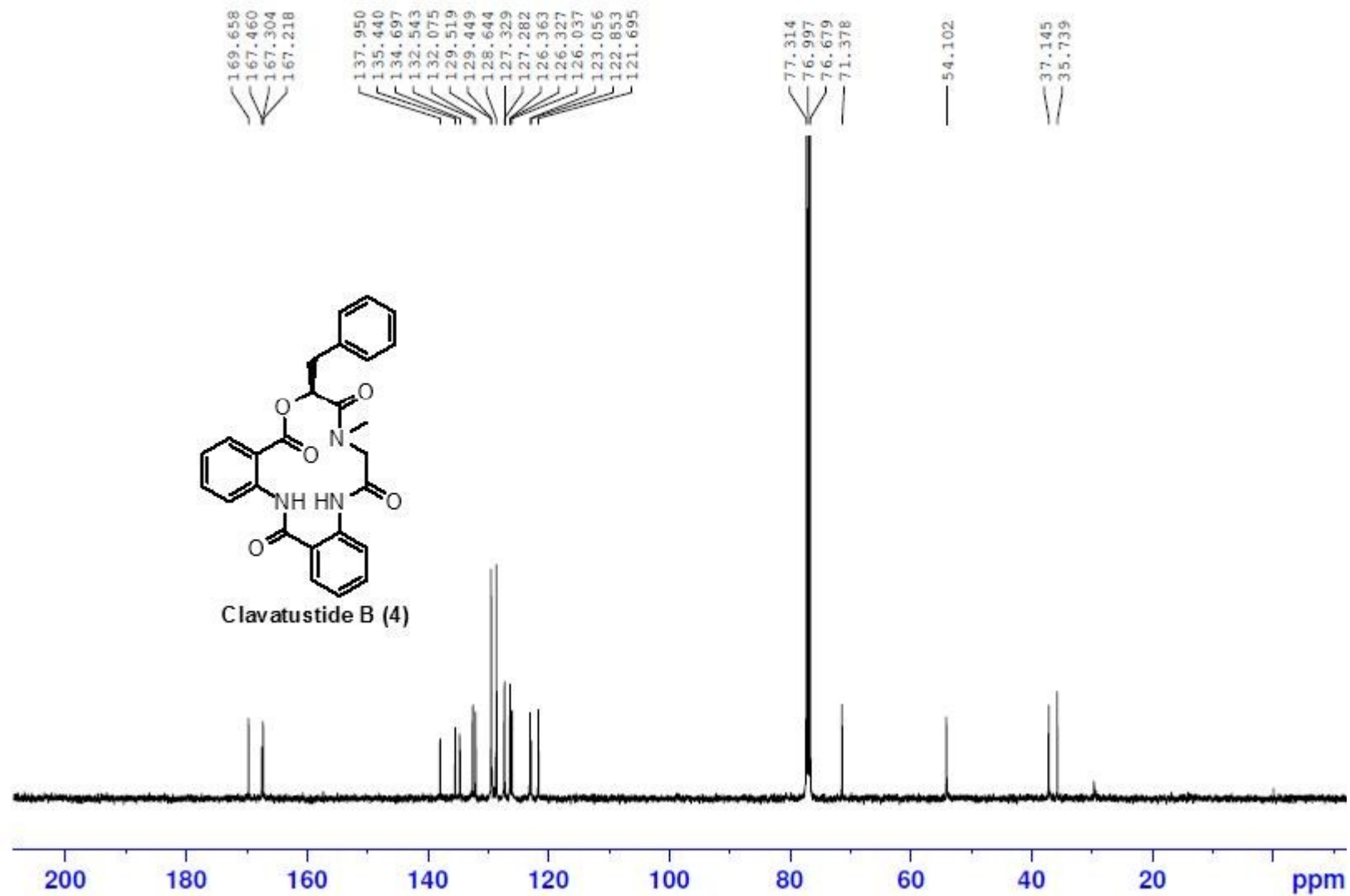
¹H NMR of Clavatustide B enantiomer (4) in CDCl₃



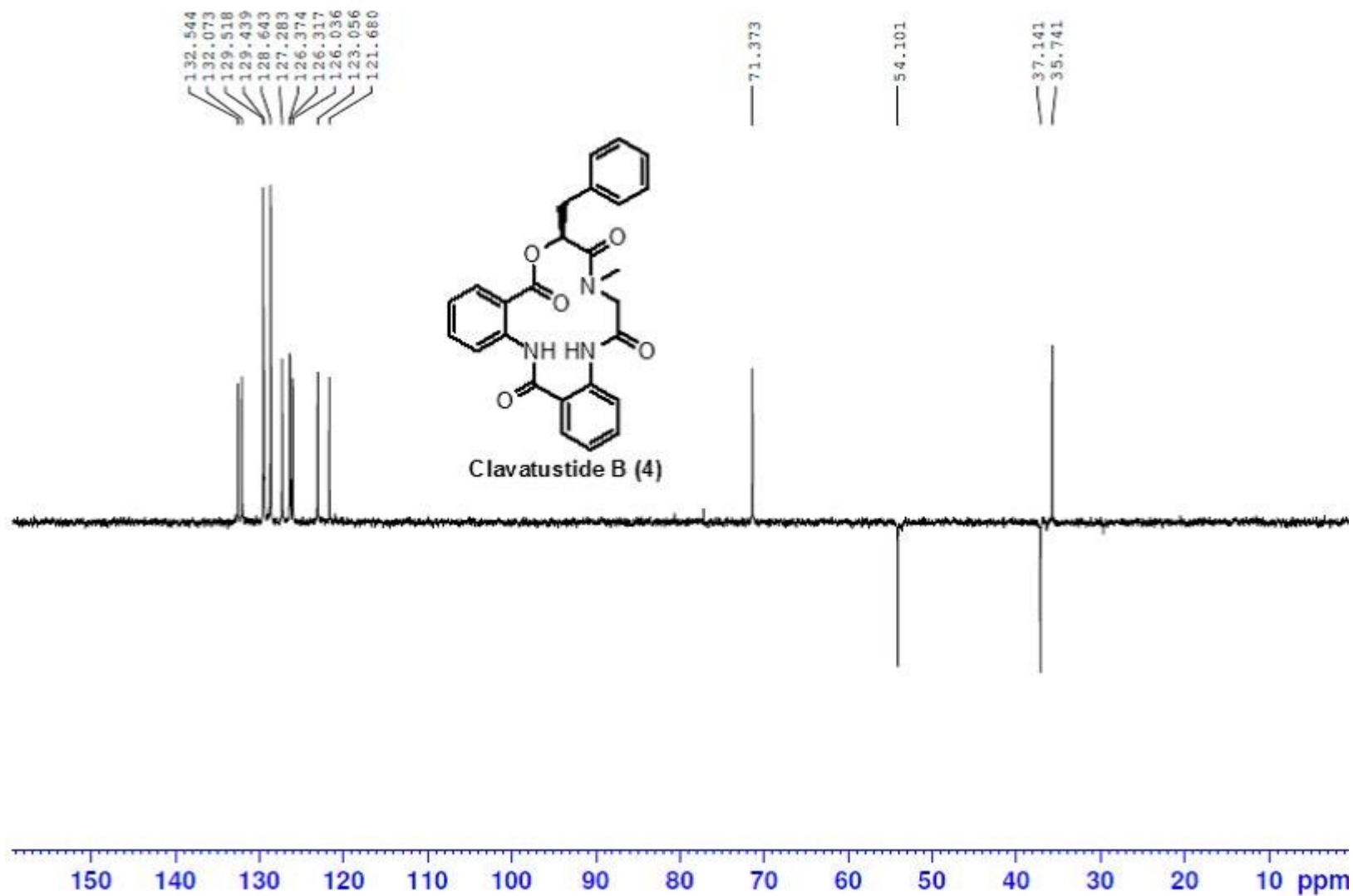
D₂O exchange ¹H NMR of Clavatustide B enantiomer (4) in CDCl₃



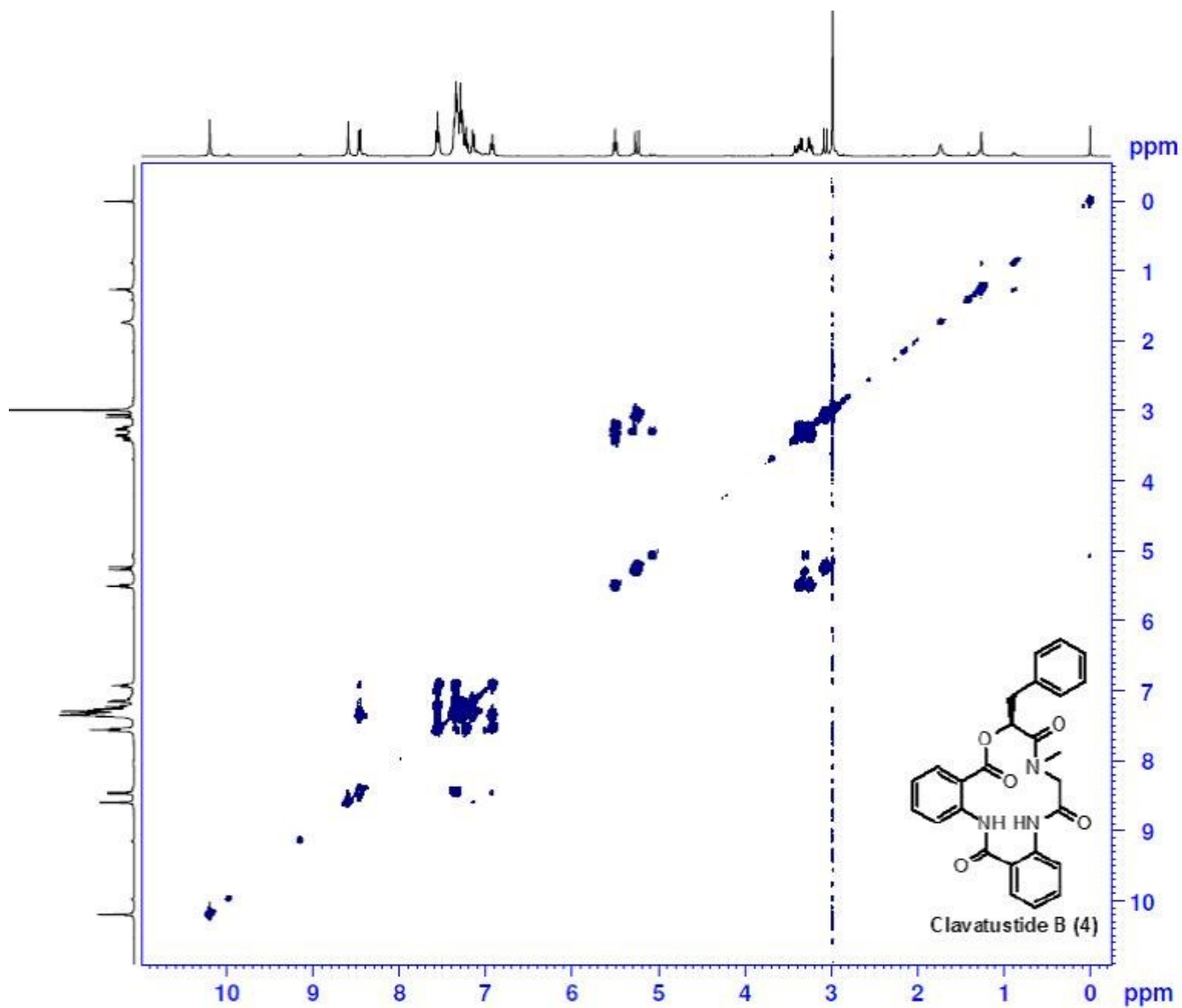
^{13}C NMR of Clavatustide B enantiomer (4) in CDCl_3



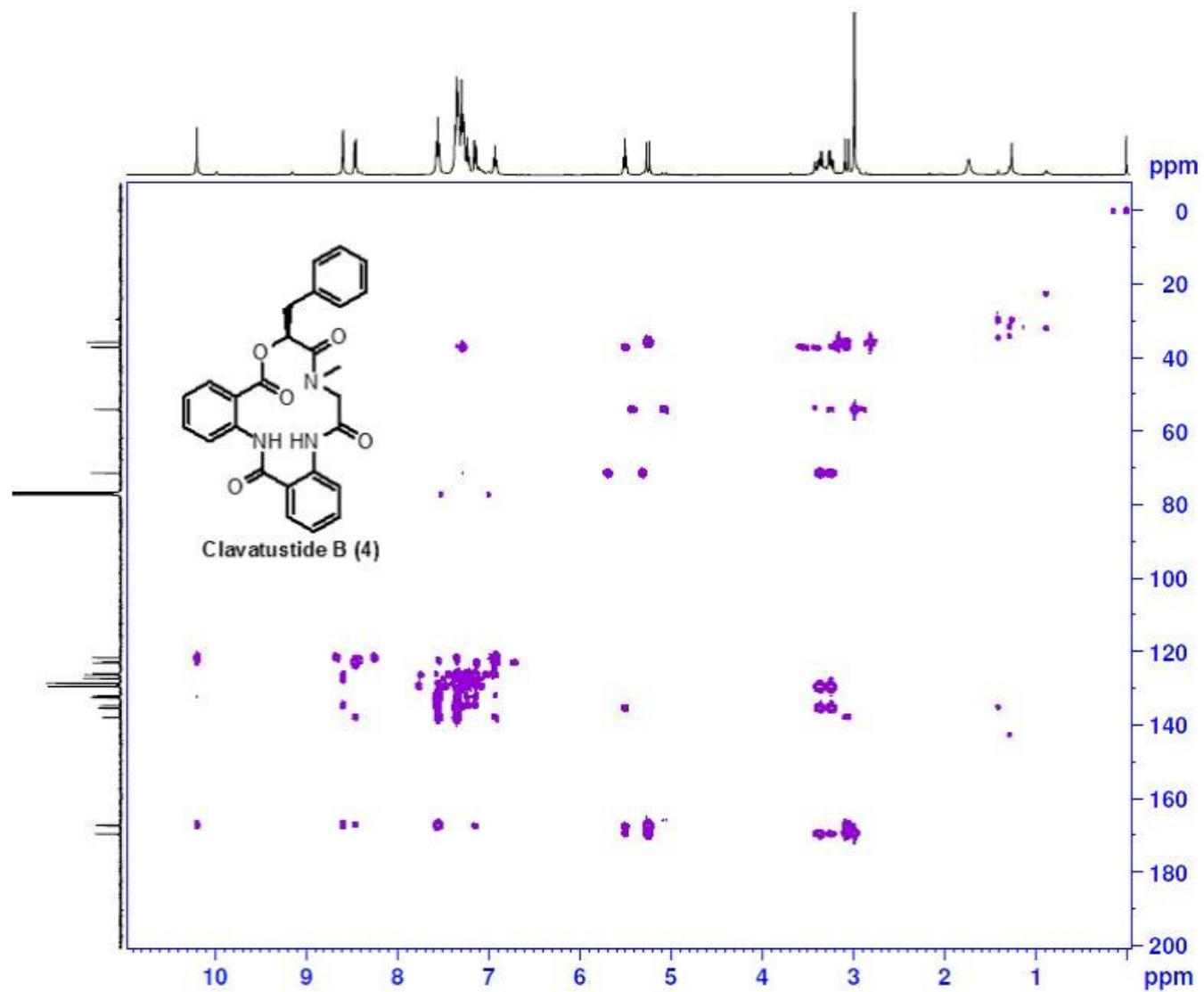
DEPT NMR of Clavatustide B enantiomer (4) in CDCl₃



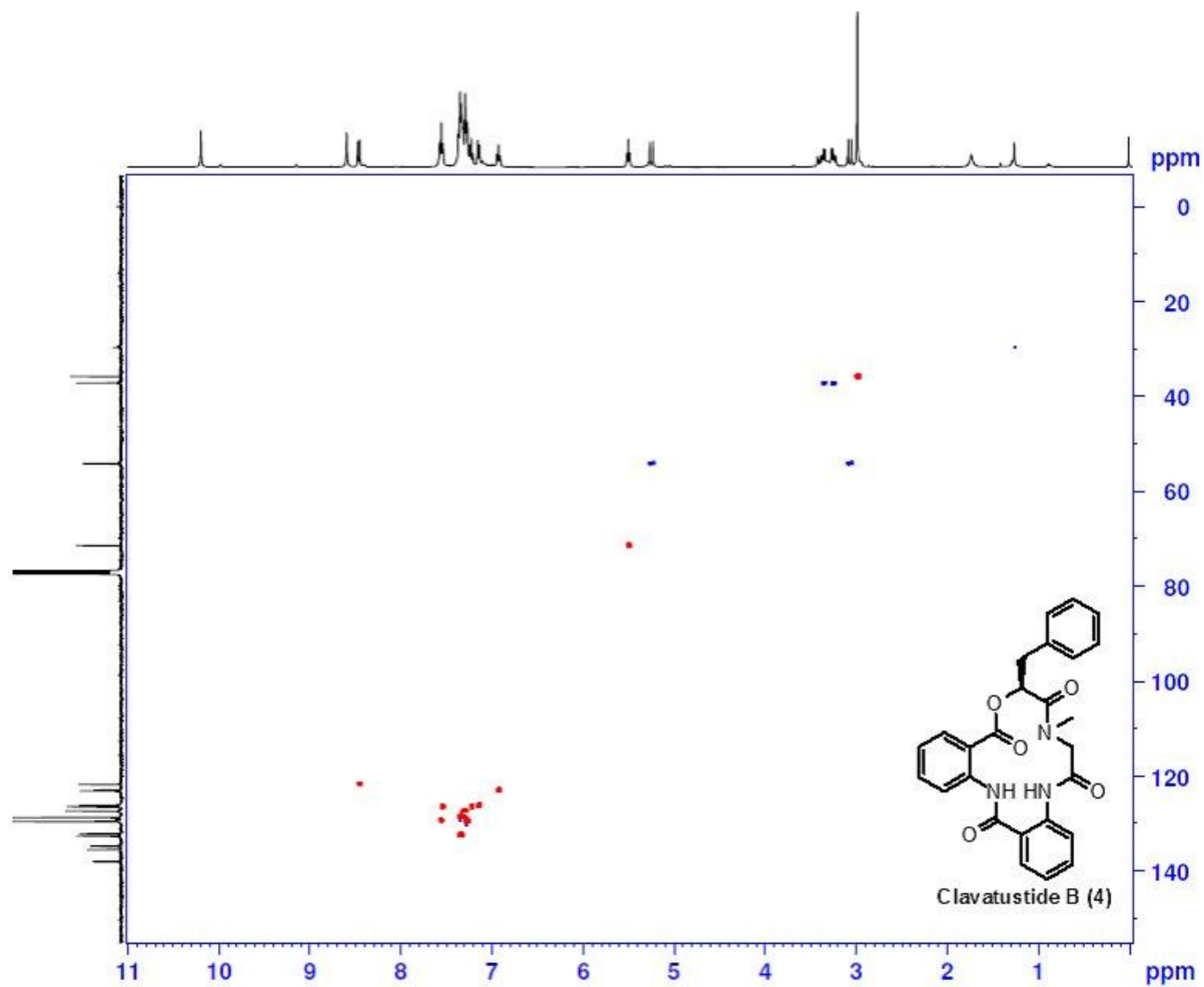
COSY NMR of Clavatustide B enantiomer (4) in CDCl₃



HMBC NMR of Clavatustide B enantiomer (4) in CDCl₃



HSQC NMR of Clavatuside B enantiomer (4) in CDCl₃



HRMS of ClavatustideB enantiomer (4)

Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 1000.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

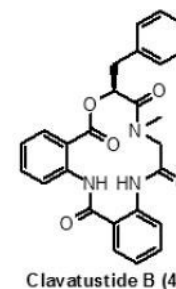
19 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

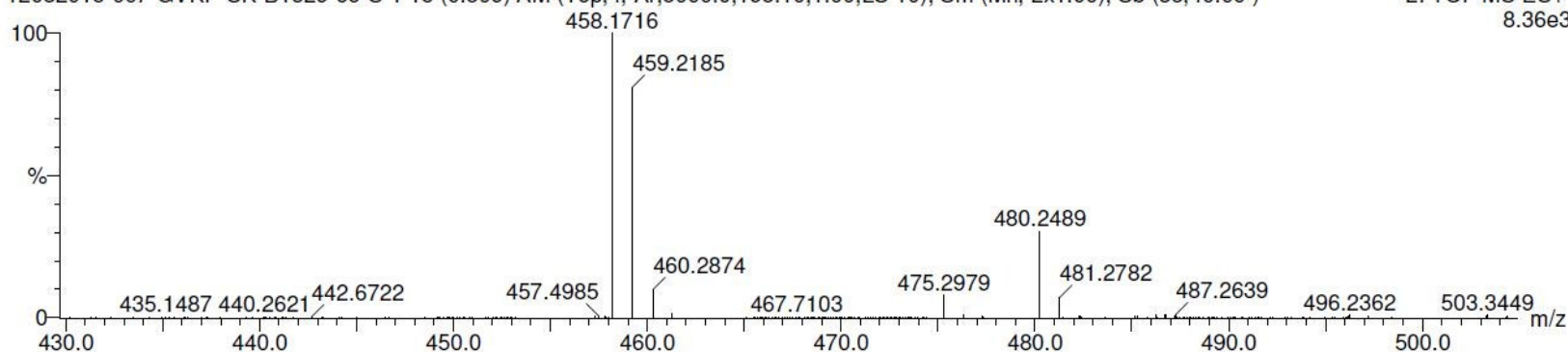
C: 0-26 H: 0-24 N: 0-3 O: 0-5

SAMPLE CODE: GVKP-SK-B1329-69-S-1

12082015-007-GVKP-SK-B1329-69-S-1 15 (0.509) AM (Top,4, Ar,5000.0,195.10,1.00,LS 10); Sm (Mn, 2x1.00); Sb (35,40.00)



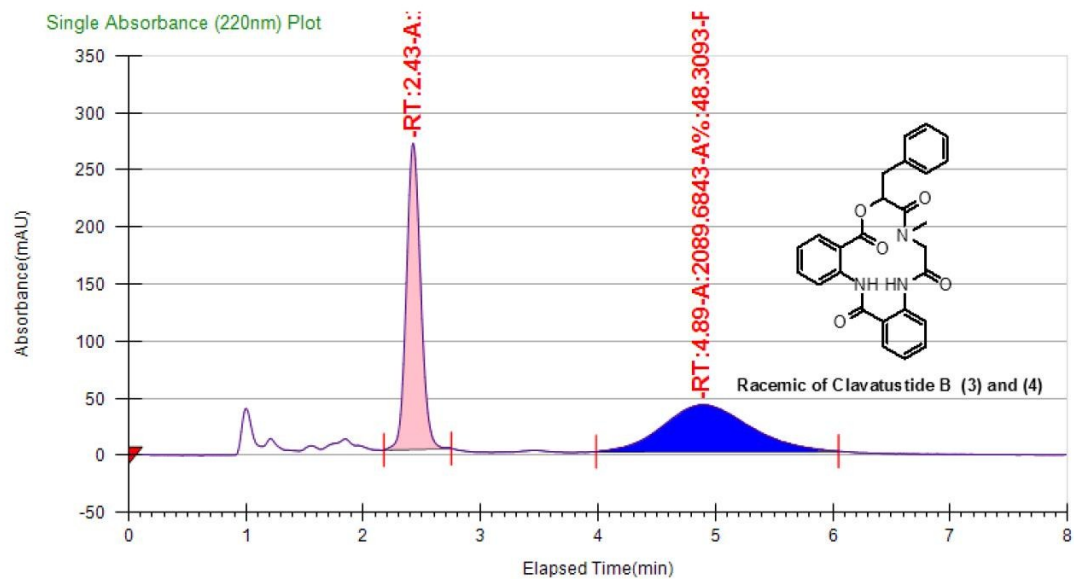
2: TOF MS ES+
8.36e3



Minimum: -1.5
Maximum: 5.0 1000.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|----------|------------|-----|-----|------|--------|---|
| 458.1716 | 458.1716 | 0.0 | 0.0 | 16.5 | 1508.8 | C ₂₆ H ₂₄ N ₃ O ₅ |

Racemic of Clavatuside B (3) and B (4)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|--------------------------|---------------|-------------|-------|
| Administrator | 5/11/2015 10:30:56 PM | Administrator | 5/12/2015 | |

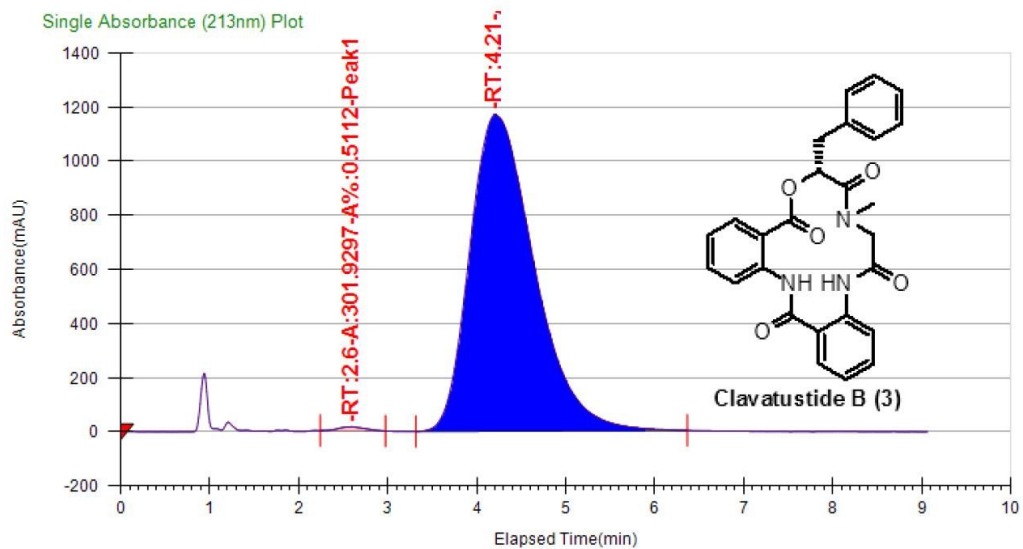
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|-------------------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329-117- Rac | 11A | 30.1 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|-----------|-----------|----------|-------------|
| 1 | 51.6907 | 2235.9534 | 2.43 min | 268.3872 | 0 |
| 2 | 48.3093 | 2089.6843 | 4.89 min | 40.9265 | 0 |

Chiral HPLC of Clavatustide B (3)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|-------------------------|---------------|-------------|-------|
| Administrator | 6/11/2015 4:45:53 PM | Administrator | 6/11/2015 | |

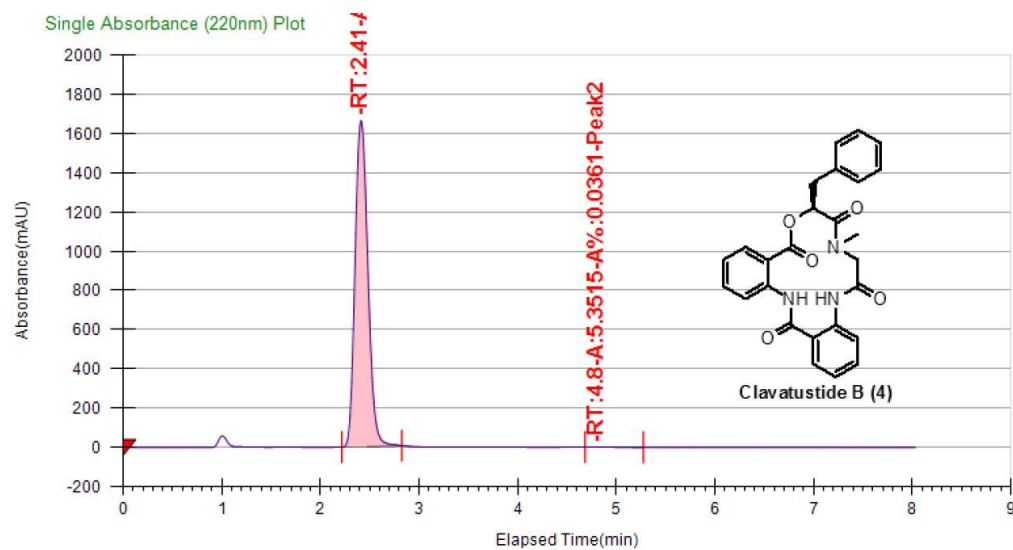
Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|------------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329-86-R | 23A | 29.8 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 0.5112 | 301.9297 | 2.6 min | 14.7343 | 0 |
| 2 | 99.4888 | 58759.5428 | 4.21 min | 1173.3261 | 0 |

Chiral HPLC of Clavatustide B (4)



General Information

| Log Author | Log Date | Report By | Report Date | Notes |
|---------------|--------------------------|---------------|-------------|-------|
| Administrator | 5/11/2015 10:40:14 PM | Administrator | 5/12/2015 | |

Run Information

| Instrument Method | Inj. Vol. | Solvent | Column | Sample | Well Location | Temp. | Flow | % Modifier | Pressure |
|-------------------|-----------|-------------------------|--|----------------------|---------------|-------|------|------------|----------|
| 4g-40%-100bar | 10 | 0.5% DEA in METHANOL | CHIRALPAK AS-H (4.6*250) mm5u | GVKP-SK- B1329-69 | 12A | 29.9 | 4 | 40 | 100 |

Peak Information

| Peak No | % Area | Area | Ret. Time | Height | Cap. Factor |
|---------|---------|------------|-----------|-----------|-------------|
| 1 | 99.9639 | 14813.0936 | 2.41 min | 1662.1207 | 0 |
| 2 | 0.0361 | 0.1922 | 4.8 min | 0.1922 | 0 |