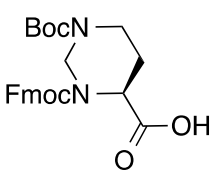
Supplementary Information

General.

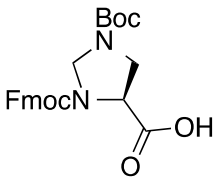
Protected amino acids Fmoc-L-Dap(Boc)-OH and Fmoc-L-Orn(Boc)-OH were purchased from Chemimpex, and, Fmoc-L-Dab(Boc)-OH from GL Biochem. Solvents and other reagents were purchased from Sigma Aldrich and used without further purification. Biotage Initiator Eight microwave reactor system was used for all reactions. Jasco P1010 Polarimeter was used to measure optical rotation. Analytical LC/MS was performed on an Agilent 1200 Series system with a single quadrupole mass spectrometer (6110), a UV detector operating at 210 nm and an ELSD detector, and using an analytical reverse phase column (Eclipse XDB-Phenyl, 5 μm, 4.6x150 mm), flow rate 1 mL/min. Alternatively LCMS analysis was performed using a Shimadzu Prominence system using an Agilent Zorbax Eclipse XDB-Phenyl column maintained at 40ºC with SPD-M20A diode array UV-Vis detector, ELSD –LT II evaporative light scattering detector and LCMS-2020 mass spectrometer. Reverse phase eluent for analytical purposes was effected using an appropriate gradient from water (0.05% formic acid) and acetonitrile (0.05% formic acid), flow rate of 1 ml/min. High resolution mass spectra were obtained on a Bruker micrOTOF 232. NMR spectra were obtained on a Bruker 600 MHz.

Experimental Procedures.

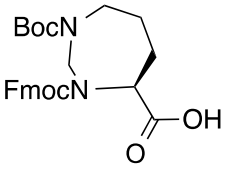
Synthesis of **4**, **7** and **8**:



4
pyrimidine



7
imidazolidine



8
diazepane

Example of **4**:

To Fmoc-L-Dab(Boc)-OH (2 mmol, 881 mg) in a microwave reactor tube with a magnetic stirrer, was added solid paraformaldehyde (4 mmol, 133 mg), camphorsulfonic acid (0.17 mmol, 40 mg, 8.6mol%) and acetonitrile (10 mL). The tube was then sealed and subjected to a 2 min run at 120 °C (microwave settings at 400 Watts). Resulting cooled mixture was concentrated under vacuo and put through a short silica pad using ethyl acetate and petroleum spirits (3:7) as eluent, dried with $MgSO_4$ and finally concentrated under vacuo to give a colourless oily residue. Lyophilisation from water/acetonitrile (1:1) yields a white powder of respective compound **4**, **7** and **8**. The powders of compounds **4**, **7** and **8** are air sensitive and become oils within minutes and thus requires N_2 atmosphere or cooled conditions for storage.

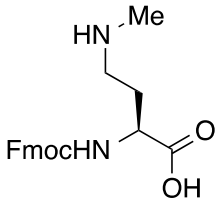
4: FL_7023_74_1 (Trans/Cis isomers) ^{1}H NMR (600 MHz, $CDCl_3$): 1.48 (br, s, 9H); 2.00-2.22 (br, m, 2H); 2.96, 3.09, 3.95 (br, 2H); 4.22-4.38 (br, m, 1H); 4.40-4.50 (br, 2H); 4.64 (br, 1H); 5.00 (br, 1H); 7.34 (m, 2H); 7.39 (br, 2H); 7.51 (br, m, 1H); 7.62 (br, 1H); 7.76 (br, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 25.6 (s), 28.3 (s), 39.6 (br), 47.0 (s), 53.0 (s), 67.5 (s), 68.5 (br), 80.9 (s), 119.9 (s), 124.9 (s), 127.2 (s), 128.1 (s), 141.4 (s), 143.7 (s), 154.0 (br), 155.2 (s), 175.4 (br, s). MS: *m/z* 453 $[M+H]^+$, 353 $[M-Boc]^+$. HRMS calculated for $C_{25}H_{28}N_2O_6Na$: 475.1840. Found 475.1860.

7: FL_7292_36_1 (Trans/Cis at Fmoc amide bond) ^{1}H NMR (600 MHz, $CDCl_3$): 1.49 (s, 9H); 3.78, 3.98 (m, 2H); 4.20, 4.30 (m, 1H); 4.38, 4.67 (m, 1H); 4.44, 4.54 (m, 2H); 4.78, 4.84 (m, 2H); 7.33 (m, 2H); 7.41 (t, 2H); 7.54 (m, 2H); 7.56 (m, 2H); 7.74 (m, 2H); 7.78 (m, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 28.2 (s), 47.0 (br), 47.1 (s), 48.0 (br), 56.3 (br), 60.2 (s), 67.8 (s), 120.1 (s), 124.8 (d), 125.0 (d), 127.1 (s), 127.8 (s), 127.9 (s), 141.3 (s), 143.5 (m), 152.8 (s), 173.4 (s). MS: *m/z* 439 $[M+H]^+$, 339 $[M-Boc]^+$. HRMS calculated for $C_{24}H_{26}N_2O_6Na$: 461.1683. Found 461.1699.

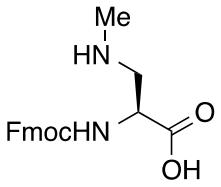
8: FL-7292-35-1 ^{1}H NMR (600 MHz, $CDCl_3$): 1.46 (br, s, 9H); 1.76, 1.86 (br, m, 2H); 2.09, 2.24 (br, m, 2H); 3.29, 3.51 (br, m, 2H); 4.2-4.35 (br, 1H); 4.47, 4.77 (br, 1H); 4.51 (m, 2H); 4.97-5.19 (m, 2H); 7.35 (br, 2H); 7.43 (br, 2H); 7.58 (br, 2H); 7.79

(br, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 25.7 (s), 27.5 (s), 28.2 (br), 46.4 (s), 47.1 (s), 57.6 (s), 58.1 (s), 67.7 (s), 120.0 (s), 125.1 (s), 127.0 (s), 127.8 (s). MS: *m/z* 467 $[M+H]^+$, 367 $[M\text{-}Boc]^+$. HRMS calculated for $C_{26}H_{31}N_2O_6$: 467.2177. Found 467.2165.

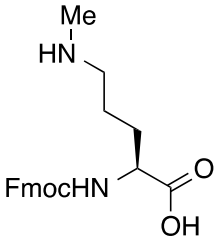
Synthesis of **9** – **11**:



9



10



11

Example of **10**:

To crude **4** (2.2 mmol, 100 mg) in a 1 mL vial with a stirrer bar was added triethylsilane (12 mmol, 0.2 mL), trifluoroacetic acid (0.2 mL) and chloroform (0.2 mL). The mixture was sealed and stirred for 8 h at ambient temperature. LCMS analysis revealed full conversion of starting material and addition of a new single peak corresponding to the desired product. The crude mixture was then concentrated under vacuo followed by drying on a high vacuum set up (~2 h) to yield 75 mg (96 %) of a bright yellow oil. Compounds **9** and **11** required 8 h at 60 °C for complete conversion. Lyophilisation from water/acetonitrile (1:1) yields a white powder of respective compound **9** - **11**. The powders of compounds **9** – **11** are air sensitive and become oils within minutes and thus requires N_2 atmosphere or cooled conditions for storage.

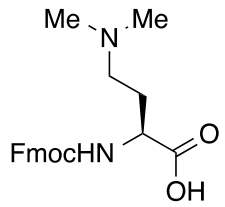
9: FL_7292_51_8_14 ^{1}H NMR (600 MHz, $CDCl_3$): 2.16-2.21 (br, m, 2H); 2.67 (s, 3H); 3.04, 3.17 (br, m, 2H); 4.15 (br, 1H); 4.33 (br, m, 1H); 4.20 (t, J = 6.92 Hz, 2H); 4.35 (d, J = 6.92 Hz, 2H); 6.33 (d, 3J = 4.67 Hz, 1H); 7.30 (t, J = 7.52 Hz, 2H); 7.40 (t, J = 7.52 Hz, 2H); 7.60 (t, J = 8.20 Hz, 2H); 7.80 (d, J = 7.50 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 30.2 (s), 33.3 (s), 47.1 (s), 47.7 (s), 54.2 (s), 67.2 (s), 120.3 (s), 125.2 (s), 127.1 (s), 127.8 (s), 141.3 (s), 143.8 (s), 144.0 (s), 156.6 (s), 176.0 (s). MS:

m/z 355 [M+H]+. HRMS calculated for $C_{20}H_{23}N_2O_4$: 355.1652. Found 355.1643. $[\alpha]_D^{20}$ +20±0.74 (*c* 0.033, $CHCl_3$)

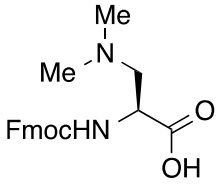
10: FL_7292_52_10_14 ^{1}H NMR (600 MHz, DMSO-d_6): 2.54 (s, 6H); 2.86, 3.04 (m, 2H); 3.79 (m, 1H); 4.24 (m, 1H); 4.25, 4.30 (m, 2H); 6.87 (d, 3J = 6.63 Hz, 1H); 7.34 (m, 2H); 7.42 (t, 2H); 7.71 (m, 2H); 7.89 (d, J = 7.9 Hz, 2H). ^{13}C NMR (150.9 MHz, DMSO-d_6): 33.4 (s), 47.1 (s), 50.5 (s), 50.8 (s), 66.2 (s), 120.6 (s), 125.7 (d), 127.6 (s), 128.1 (s), 141.2 (s), 144.3 (s), 144.4 (s), 156.2 (s), 171.6 (s). MS: *m/z* 341 $[M+H]^+$. HRMS calculated for $C_{19}H_{21}N_2O_4$: 341.1496. Found 341.1510. $[\alpha]_D^{20}$ +87±0.95 (*c* 0.112, MeOH)

11: FL-7292-43-1 ^{1}H NMR (600 MHz, $CDCl_3$): 1.77 (br, 2H); 1.77-1.91 (br, 2H); 2.62 (br, s, 3H); 2.94 (br, m, 2H); 4.14-4.24 (br, 1H); 4.01, 4.29 (br, 1H); 4.30-4.46 (m, 2H); 7.26 (br, 2H); 7.35 (t, J = 7.92 Hz, 2H); 7.51 (br, 2H); 7.71 (d, J = 7.3 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 21.9 (br), 28.0 (br), 33.3 (s), 47.1 (s), 49.2 (br), 53.2 (s), 67.4 (s), 120.1 (s), 125.2 (br), 127.3 (s), 127.8 (s), 141.3 (s), 143.5 (s), 143.6 (s), 156.8 (s), 175.0 (s).MS: *m/z* 369 $[M+H]^+$. HRMS calculated for $C_{21}H_{25}N_2O_4$: 369.1809. Found 369.1807. +33±1.17 (*c* 0.1264, MeOH)

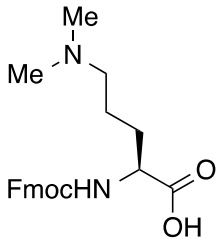
Synthesis of **12** – **14**:



12



13



14

Example of **12**:

Crude **4** (0.146 mmol, 66 mg) was stirred in neat formic acid (0.5 mL) for 2 h followed by concentration under vacuo to form an oil. To this residue was added MeOH (2 mL) and 1,4-dioxane (6 drops) and aqueous formaldehyde (0.876 mmol, 0.064 mL). The mixture turned milky. Sodium cyanoborohydride (0.31 mmol, 19.3

mg, 2.1 eq) was then added in portions during 2 min. The mixture turned transparent and then back to milky. LCMS analysis of the reaction mixture revealed full conversion after 15 min and the mixture was concentrated under vacuo. To this residue was added triethylsilane (0.876 mmol, 0.14 mL), trifluoroacetic acid (0.14 mL) and chloroform (0.14 mL) followed by heating for 8 h at 60 °C. LCMS analysis revealed full conversion of starting material and addition of a new single peak corresponding to the desired product **12**. Yield 52 mg (97 %) with a purity >95 % (LCMS). Compounds **13** and **14** required 3 h at 100 °C for full conversion giving similar yields and purity in both cases. Lyophilisation from water/acetonitrile (1:1) yields a white powder of respective compound **12** - **14**. The powders of compounds **12** – **14** are air sensitive and become oils within minutes and thus requires N_2 atmosphere or cooled conditions for storage.

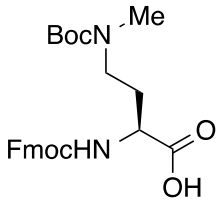
12: FL_7292-50-1 ^{1}H NMR (600 MHz, $CDCl_3$): 2.12, 2.33 (br, m, 2H); 2.74 (s, 3H); 3.00, 3.19 (br, m, 2H); 4.07 (br, 1H); 4.25 (t, J = 6.88 Hz, 1H); 4.38 (m, 2H); 6.31 (br, 1H); 7.35 (t, J = 7.60 Hz, 2H); 7.44 (t, J = 7.60 Hz, 2H); 7.65 (t, J = 6.66 Hz, 2H); 7.80 (d, J = 7.29 Hz, 2H). ^{13}C NMR (150.9 MHz, DMSO-d_6): 29.3 (br), 44.2 (s), 47.1 (s), 54.5 (s), 56.3 (s), 66.1 (s), 120.7 (s), 125.8 (s), 127.6 (s), 128.0 (s), 140.6 (s), 141.4 (s), 144.3 (s), 150.0 (br), 173.7 (br). MS: *m/z* 369 $[M+H]^+$. HRMS calculated for $C_{21}H_{25}N_2O_4$: 369.1809. Found 369.1796. $[\alpha]_D^{20}$ +60±0.66 (*c* 0.15, $CHCl_3$)

13: FL-7292-64-1 ^{1}H NMR (600 MHz, $CDCl_3$): 2.88 (s, 6H); 3.19, 3.38 (br, m, 2H); 4.22 (m, 1H); 4.23 (m, 1H); 4.39 (m, 2H); 6.15 (br, s, 1H); 7.33 (t, J = 7.10 Hz, 2H); 7.41 (t, J = 6.77 Hz, 2H); 7.61 (t, J = 6.09 Hz, 2H); 7.78 (d, J = 4.0 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 44 (br), 28.0 (br), 47.0 (s), 50.4 (s), 58.6 (s), 67.0 (s), 120.1 (s), 125.0 (br), 127.3 (s), 127.8 (s), 141.2 (s), 141.3 (s), 143.6 (s), 143.9 (s), 156.0 (s), 172.2 (s).MS: *m/z* 355 $[M+H]^+$. HRMS calculated for $C_{20}H_{23}N_2O_4$: 355.1652. Found 355.1641. $[\alpha]_D^{20}$ +76±3.93 (*c* 0.118, $CHCl_3$)

14: FL-7292-65-1 ^{1}H NMR (600 MHz, $CDCl_3$): 1.67, 187 (m, 2H); 1.90 (m, 2H); 2.71 (s, 6H); 2.81, 2.99 (m, 2H); 4.18 (m, 1H); 4.23 (t, J = 6.87 Hz, 1H); 4.32-4.38 (m, 2H); 7.33 (m, 2H); 7.41 (m, 2H); 7.65 (m, 2H); 7.78 (d, J = 7.3 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 20.7 (s), 29.7 (s), 42.9 (s), 47.4 (s), 54.7 (s), 57.8 (s), 66.7 (s), 120.0 (s), 125.2 (s), 125.3 (s), 127.0 (s), 127.6 (s), 141.3 (s), 144.0 (s), 144.2 (s),

155.8 (s), 176.1 (s).MS: *m/z* 383 $[M+H]^+$. HRMS calculated for $C_{22}H_{27}N_2O_4$: 383.1965. Found 383.1977. $[\alpha]_D^{20}$ +116±1 (*c* 0.10, MeOH)

Synthesis of the Boc derivative of compound **9**:



See literature procedure from Sakura *et al.*[1] using compound **9** as starting material. Yield ~100%.

^{1}H NMR (600 MHz, $CDCl_3$): 1.48 (br, s, 9H); 1.87, 2.25 (br, m, 2H); 2.66 (s, 3H); 3.03, 3.83 (br, m, 2H); 4.23 (t, J = 7.23 Hz, 1H); 4.33 (br, m, 1H); 4.39 (br, m, 2H); 6.19 (br, s, 1H); 7.31 (t, J = 7.59 Hz) 2H); 7.40 (t, J = 7.59 Hz, 2H); 7.61 (br, m, 2H); 7.76 (d, J = 7.3 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$): 28.3 (s), 30.6 (s), 40.3 (s), 44.9 (s), 47.0 (s), 51.3 (s), 66.9 (s), 81.6 (s), 119.9 (s), 125.3 (s), 127.1 (s), 127.7 (s), 141.3 (s), 141.4 (s), 143.8 (s), 143.9 (s), 155.9 (s), 173.8 (br, s).

1. N. Sakura, T. Itoh, Y. Uchida, K. Ohki, K. Okimura, K. Chiba, Y. Sato and H. Sawanishi, *Bulletin of the Chemical Society of Japan*, 2004, **77**, 1915-1924.

Sample Name : FL_7292_57_1
Data File : D:\SHARE\DATA\RES_2014_11_26\A_FL_7292_57_1.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C1T13_G0008_U210P_1MLMIN.M
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Sample Location : P2-D-05 Injection Number : 1
Sample Name : FL_7292_57_1 Injection Volume : 20.0
Sample Info :

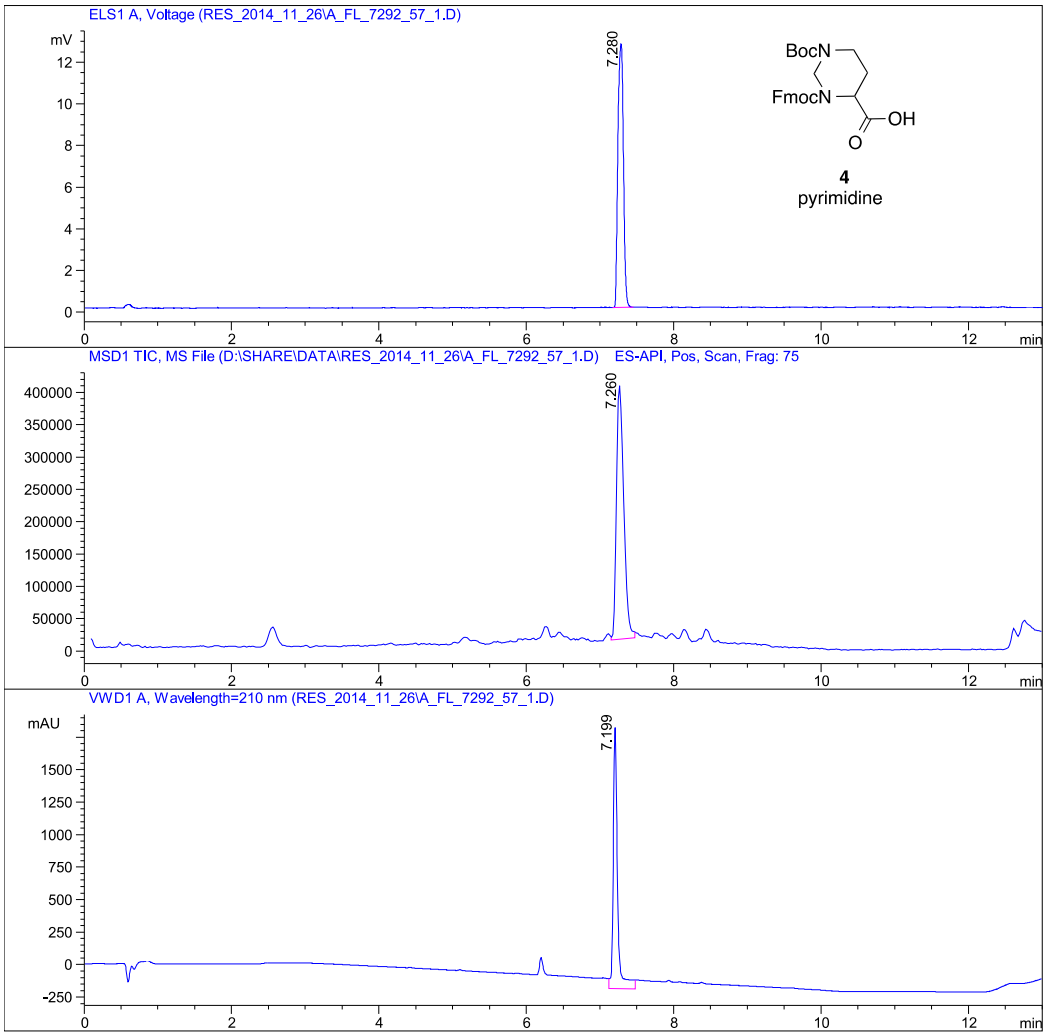

Figure S1. Analytical LCMS of compound **4**

Sample Name : FL_7292_36_1
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Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C1T13_G0008_U210P_1MLMIN.M
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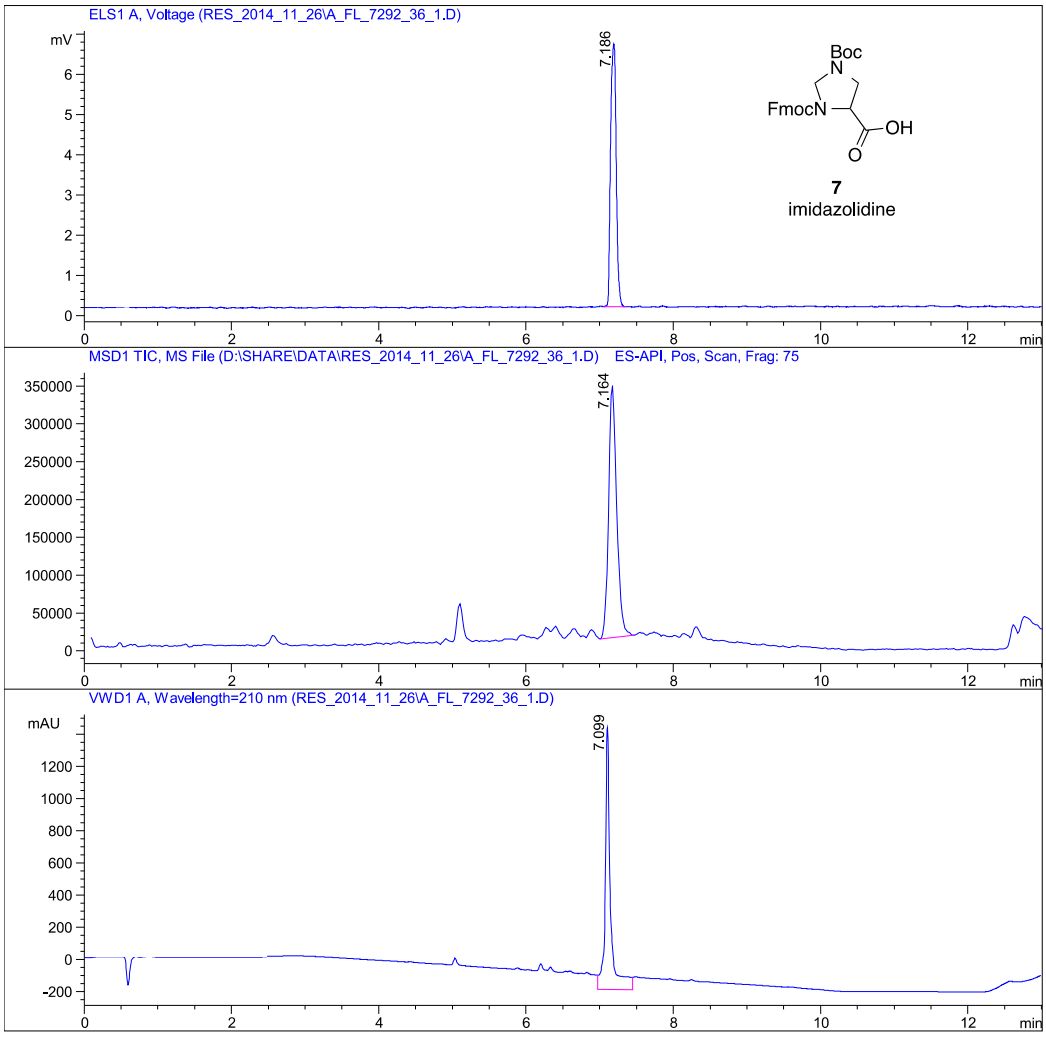

Figure S2. Analytical LCMS of compound **7**

Sample Name : FL_7292_35_1
Data File : D:\SHARE\DATA\RES_2014_11_26\A_FL_7292_35_1.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

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Method Info : <None specified>
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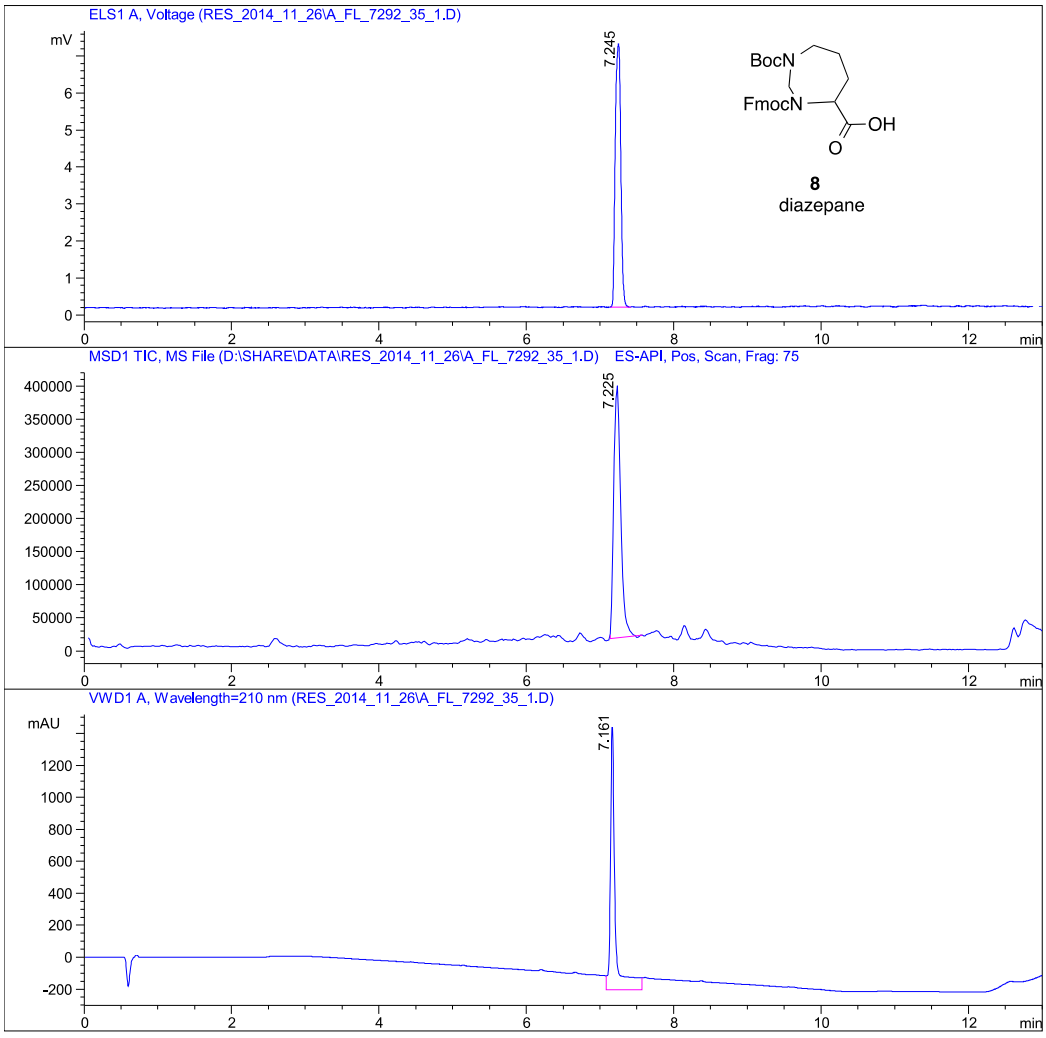
Sample Location : P2-D-03 Injection Number : 1
Sample Name : FL_7292_35_1 Injection Volume : 20.0
Sample Info :



Injection date:Wed, 26 Nov. 2014 Page 1 of 2 Report Date:Fri, 28 Nov. 2014

Figure S3. Analytical LCMS of compound **8**

Sample Name : FL_7292_51_1
Data File : D:\SHARE\DATA\RES_2014_11_26\A_FL_7292_51_1.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C1T13_G0008_U210P_1MLMIN.M
Method Info : <None specified>
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Sample Name : FL_7292_51_1 Injection Volume : 20.0
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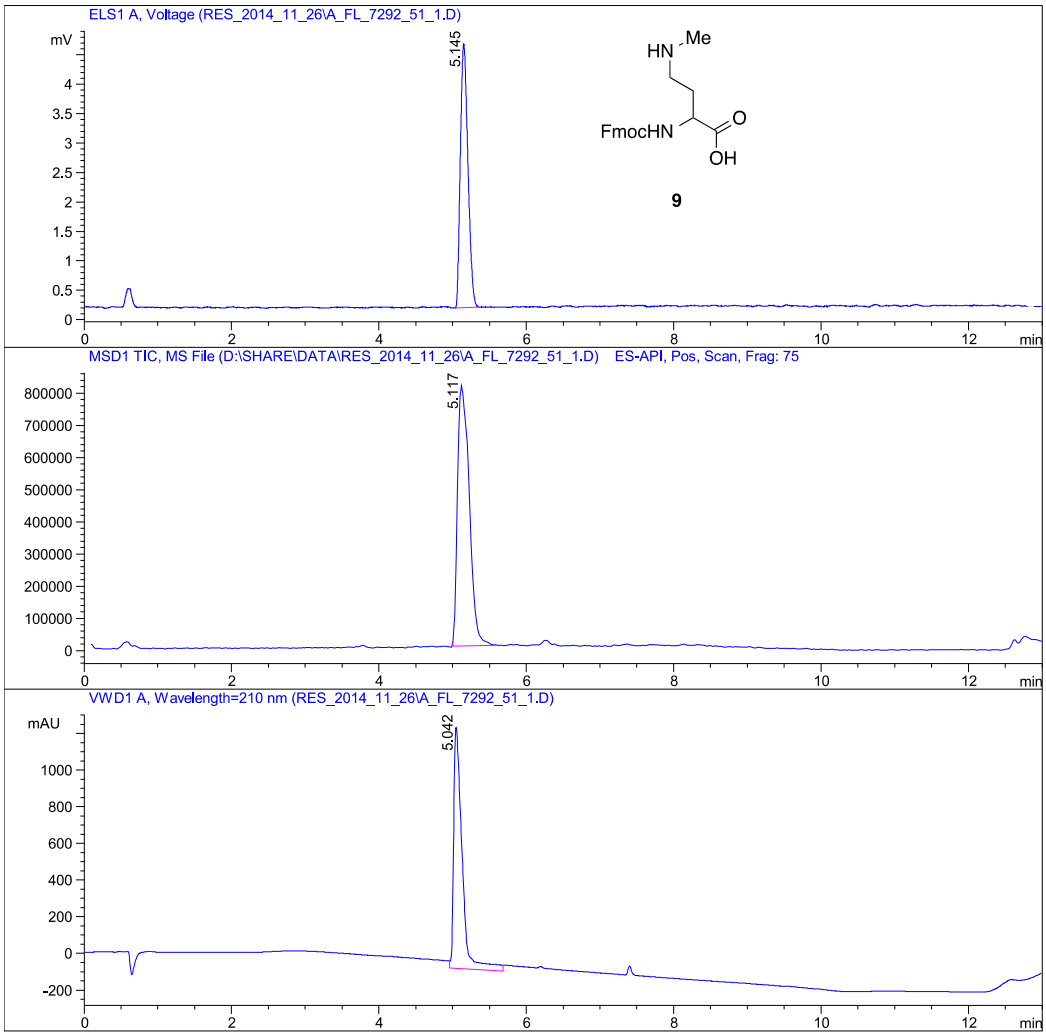

Figure S4. Analytical LCMS of compound **9**

Sample Name : FL_7292_52_1
Data File : D:\SHARE\DATA\RES_2014_11_26\A_FL_7292_52_1.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C1T13_G0008_U210P_1MLMIN.M
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Sample Name : FL_7292_52_1 Injection Volume : 20.0
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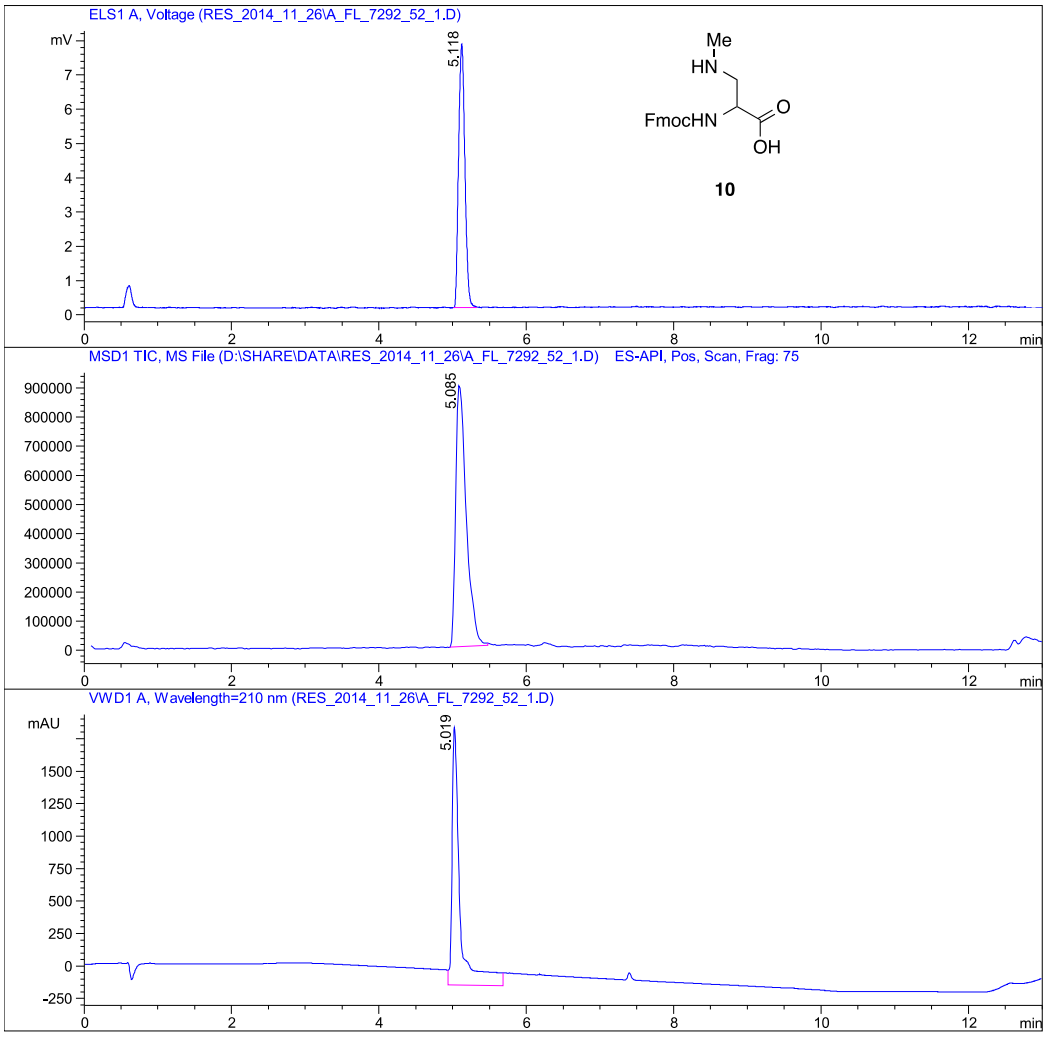


Figure S5. Analytical LCMS of compound **10**

Sample Name : FL_7292_43_1
Data File : D:\SHARE\DATA\RES_2014_11_27\A_FL_7292_43_1C.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C1T13_G0008_U210P_1MLMIN.M
Method Info : <None specified>
Injection Date : Fri, 28. Nov. 2014 Injection Time : 17:51:43
Sample Location : P2-A-01 Injection Number : 1
Sample Name : FL_7292_43_1 Injection Volume : 1.0
Sample Info :

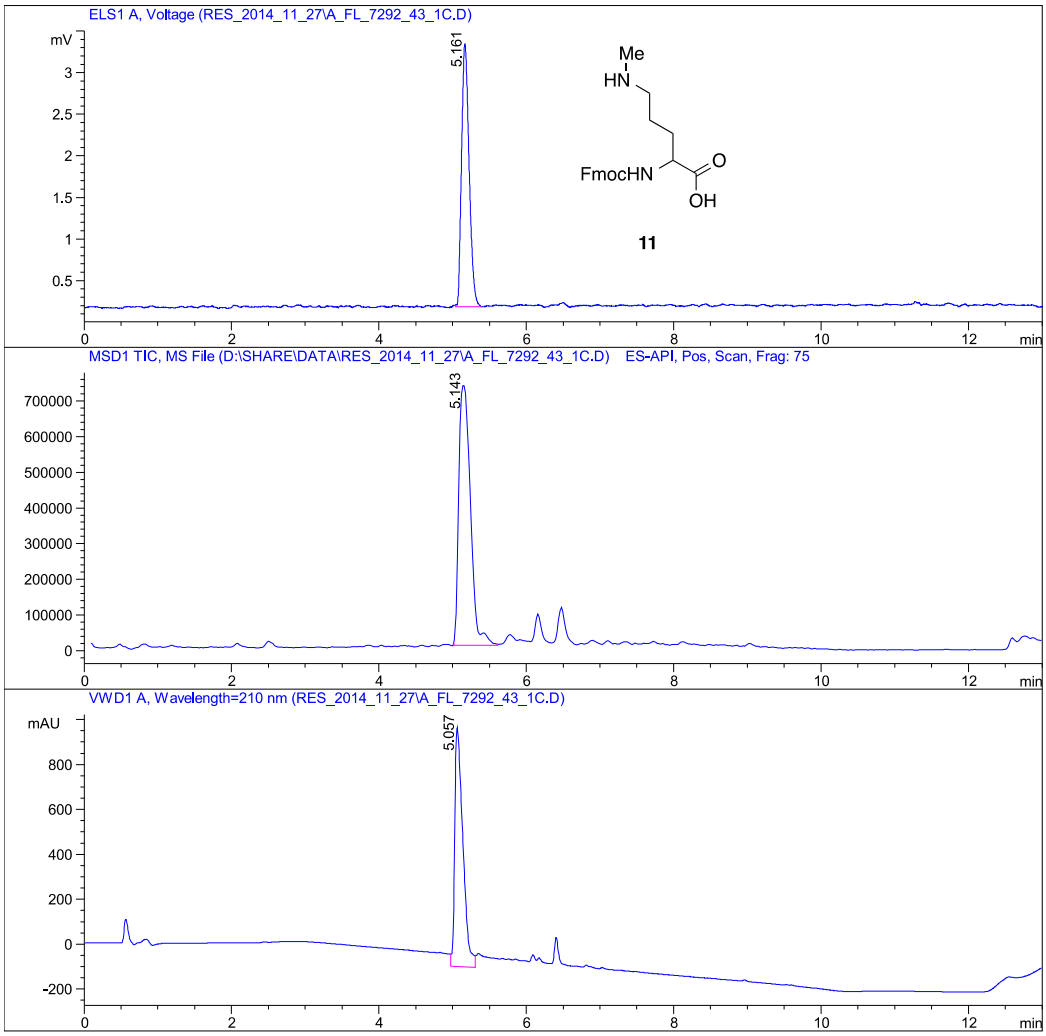


Figure S6. Analytical LCMS of compound **11**

Sample Name : FL_7292_67_1_frzON
Data File : D:\SHARE\DATA\RES_2014_12_03\A_FL_7292_67_1_FRZON.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C4T13_G0008_U210P.M
Method Info : <None specified>
Injection Date : Wed, 3. Dec. 2014 Injection Time : 12:41:59
Sample Location : P1-F-07 Injection Number : 1
Sample Name : FL_7292_67_1_frzON Injection Volume : 5.0
Sample Info : Fmoc-Dab(Me2)-OH, 1.34mg/1mL

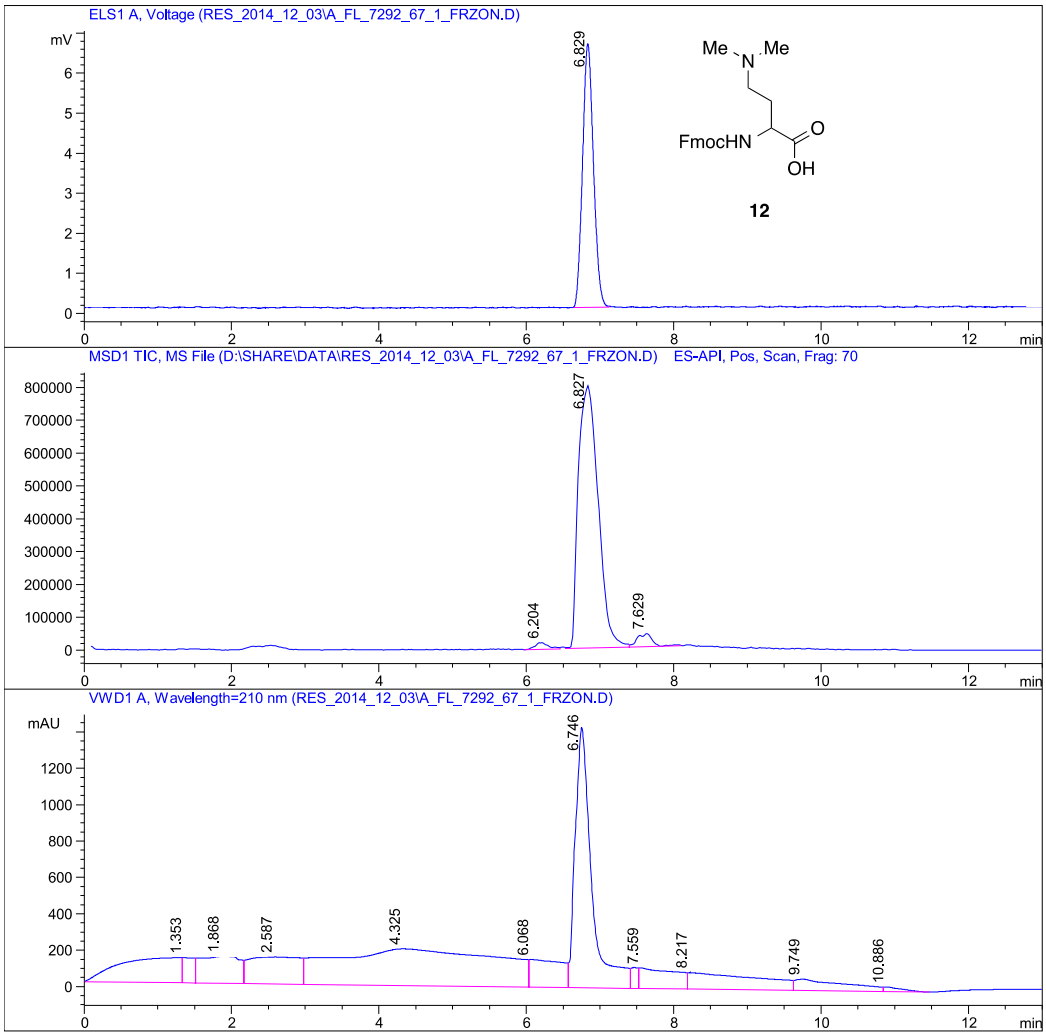


Figure S7. Analytical LCMS of compound **12**

Sample Name : FL_7292_64_fra18
Data File : D:\SHARE\DATA\RES_2014_11_24\A_FL_7292_64_FRA18.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C4T13_G0008_U210P.M
Method Info : <None specified>
Injection Date : Tue, 25. Nov. 2014 Injection Time : 00:03:49
Sample Location : P1-F-01 Injection Number : 1
Sample Name : FL_7292_64_fra18 Injection Volume : 30.0
Sample Info :

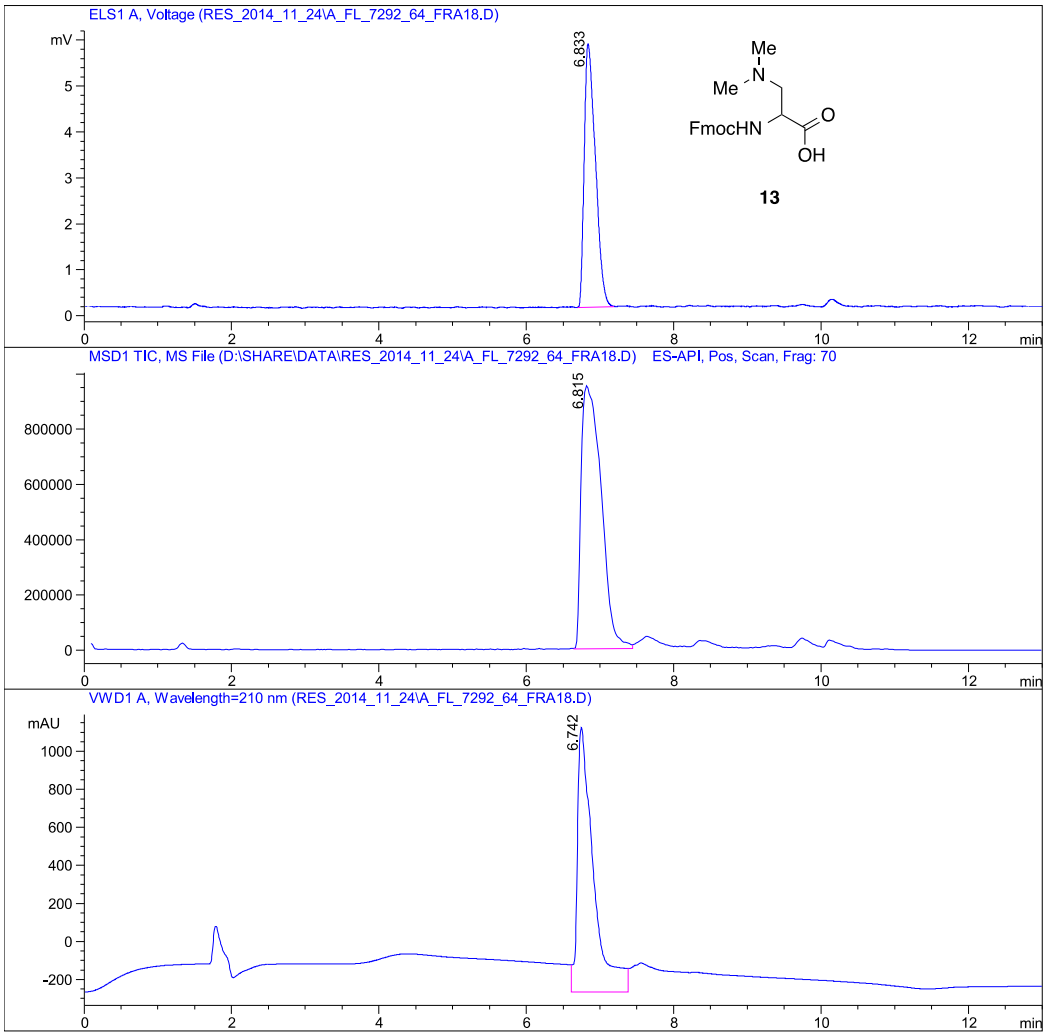


Figure S8. Analytical LCMS of compound **13**

Sample Name : FL_7292_65_fra30
Data File : D:\SHARE\DATA\RES_2014_11_24\A_FL_7292_65_FRA30.D

Cooper Group: Institute for Molecular Biosciences, The University of Queensland

Acquisition Method : D:\SHARE\METHODS\C4T13_G0008_U210P.M
Method Info : <None specified>
Injection Date : Tue, 25. Nov. 2014 Injection Time : 11:40:09
Sample Location : P1-F-06 Injection Number : 1
Sample Name : FL_7292_65_fra30 Injection Volume : 30.0
Sample Info :

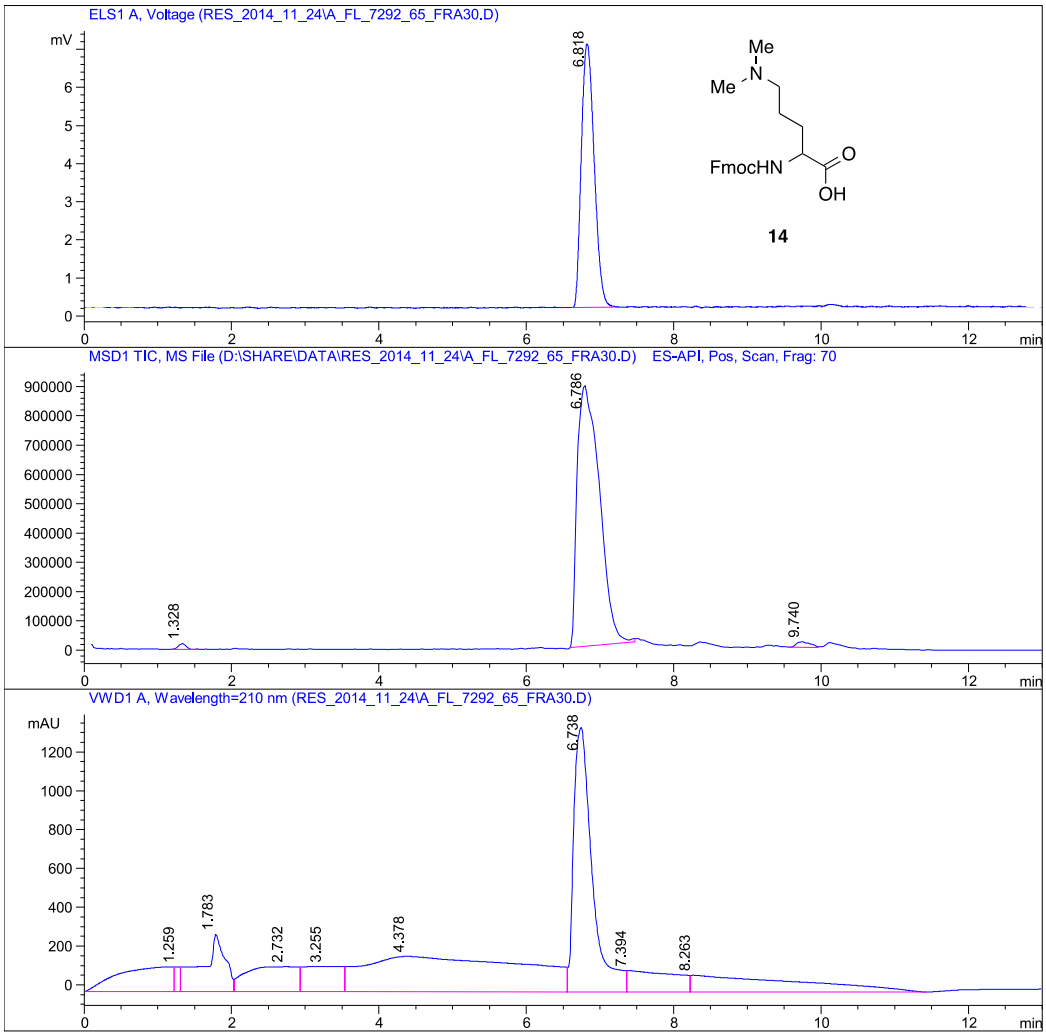


Figure S9. Analytical LCMS of compound **14**

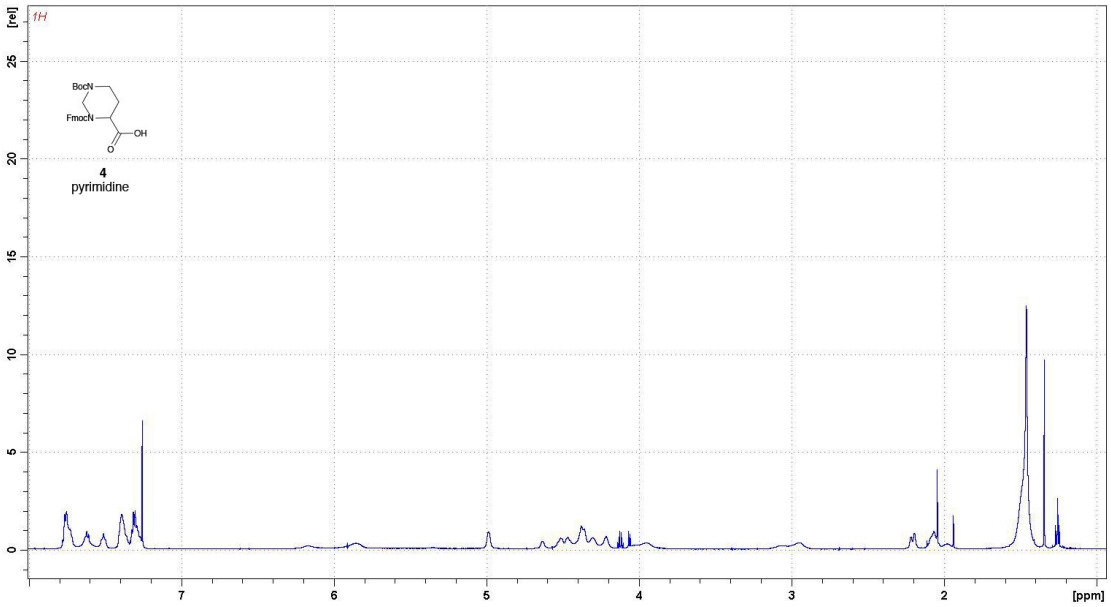


Figure S10. 600 MHz ^{1}H NMR spectrum for **4** in $CDCl_3$ at 298K.

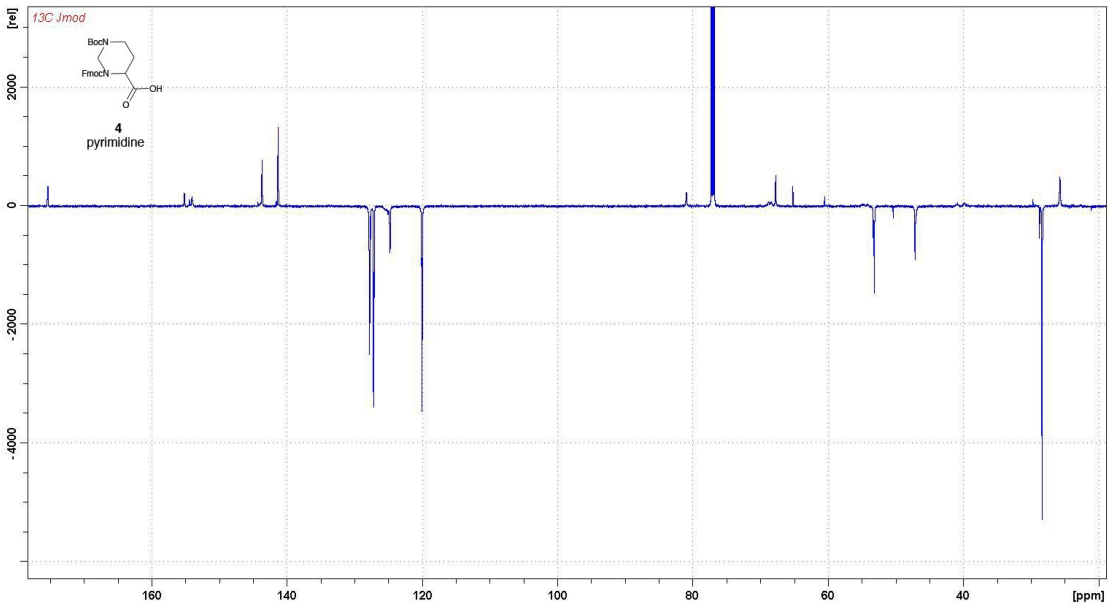


Figure S11. 150.9 MHz ^{13}C j-mod NMR spectrum for **4** in $CDCl_3$ at 298K.

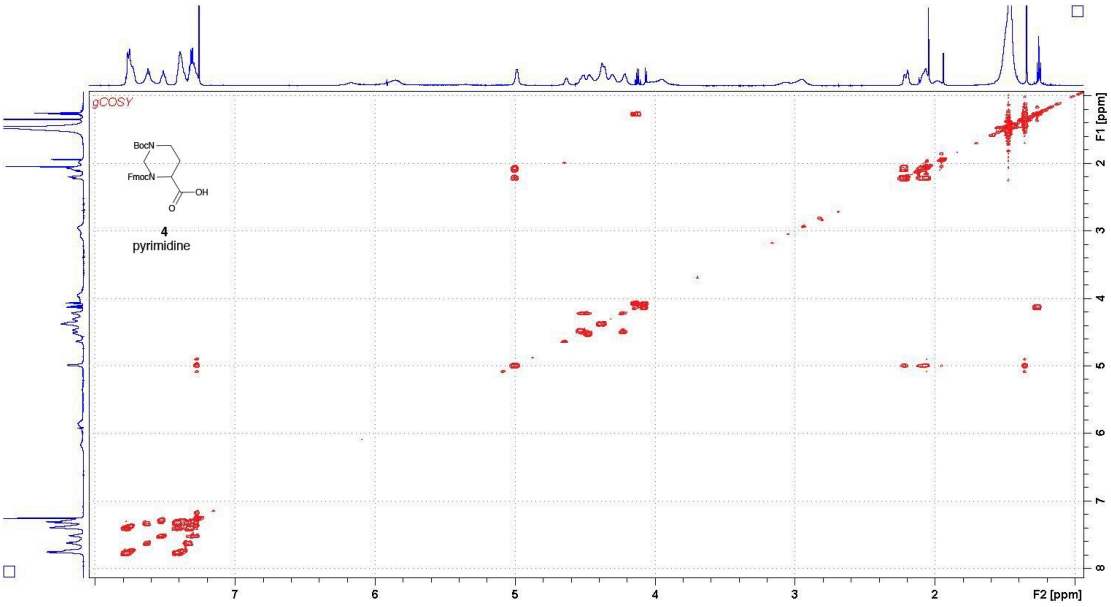


Figure S12. ^{1}H-^{1}H COSY NMR spectrum for **4** in $CDCl_3$ at 298K

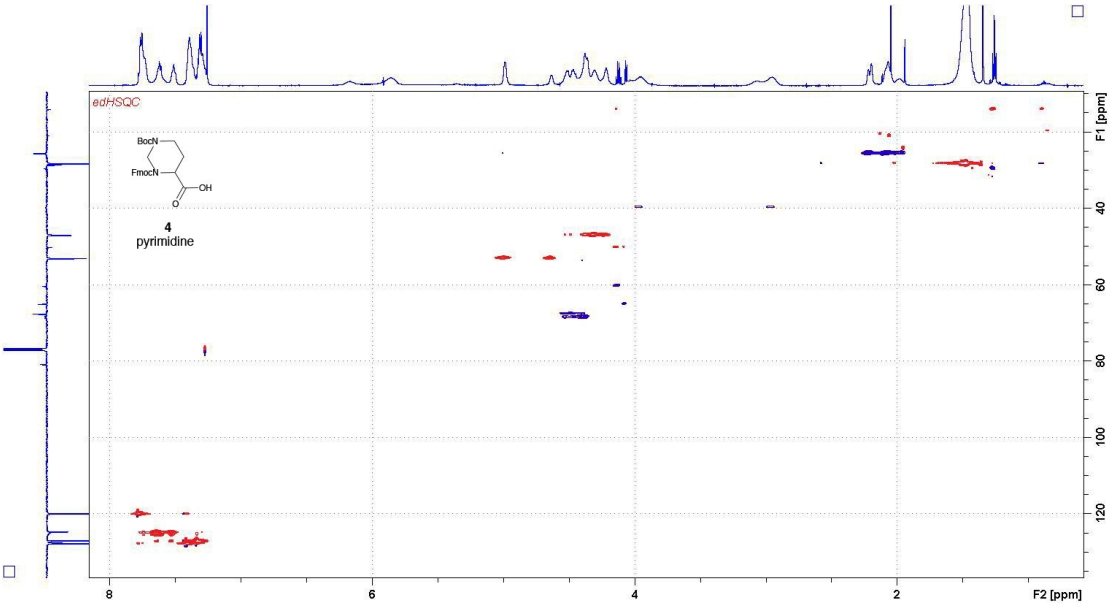


Figure S13. ^{1}H-^{13}C HSQC NMR spectrum for **4** in $CDCl_3$ at 298K.

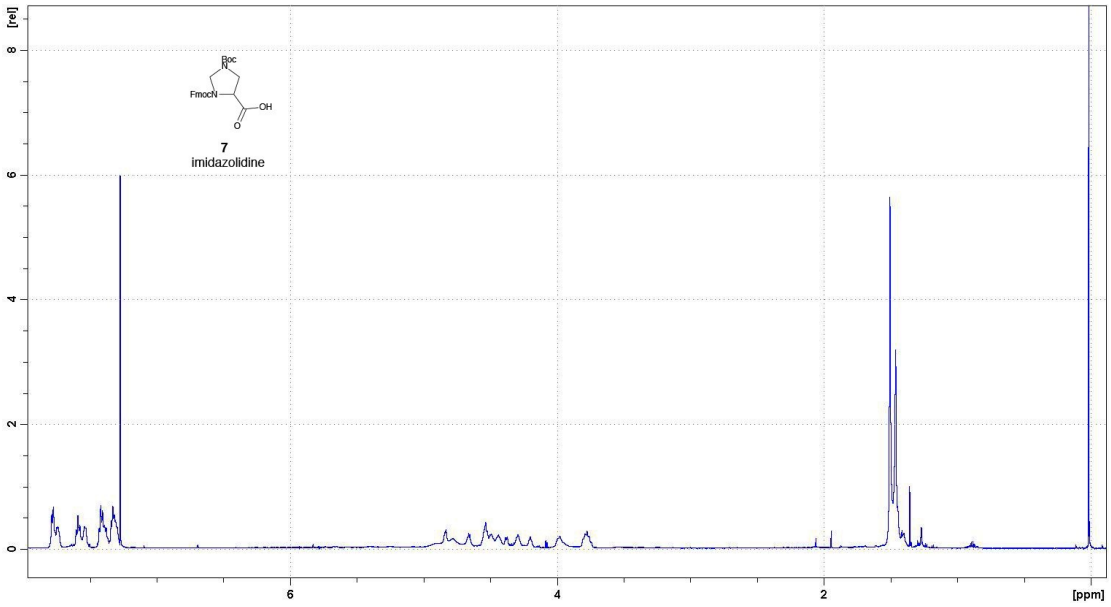


Figure S14. 600 MHz ^{1}H NMR spectrum for **7** in $CDCl_3$ at 298K.

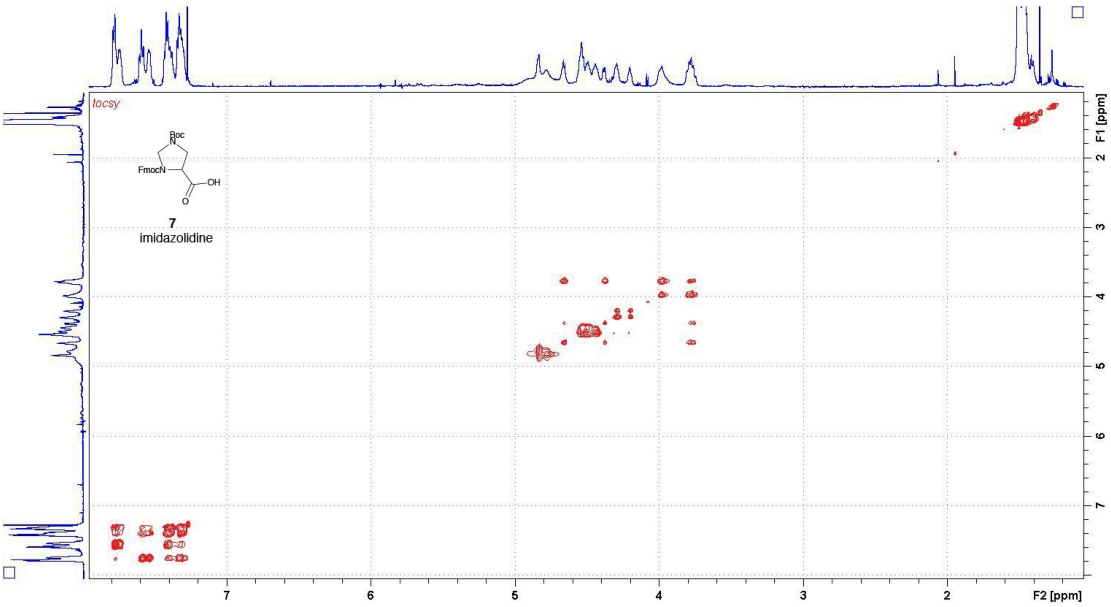


Figure S15. ^{1}H-^{1}H COSY NMR spectrum for **7** in $CDCl_3$ at 298K

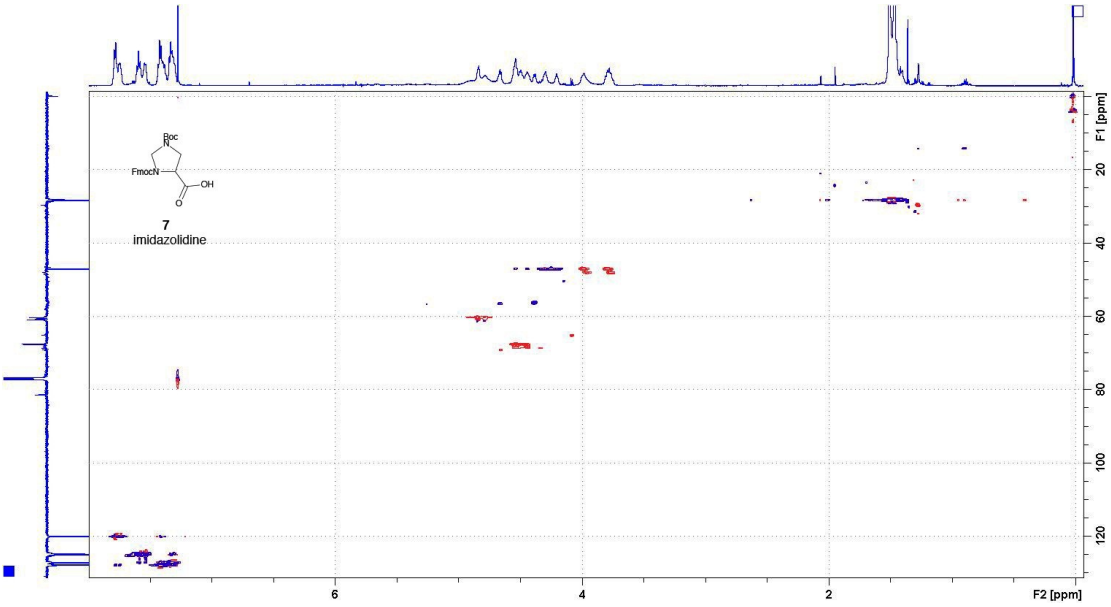


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum for **7** in $CDCl_3$ at 298K.

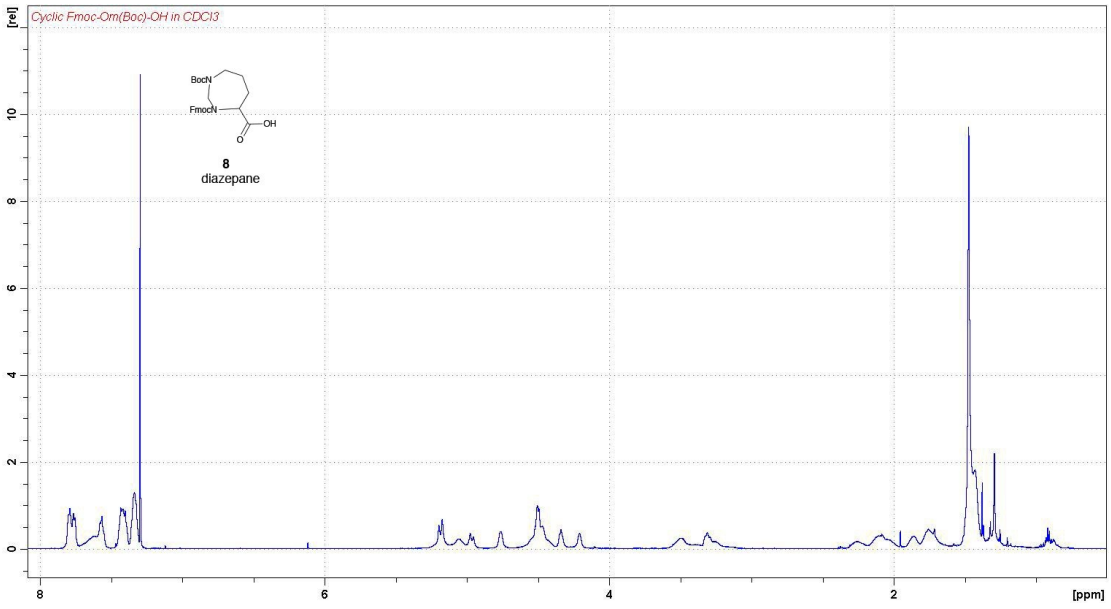


Figure S17. 600 MHz ^{1}H NMR spectrum for **8** in $CDCl_3$ at 298K.

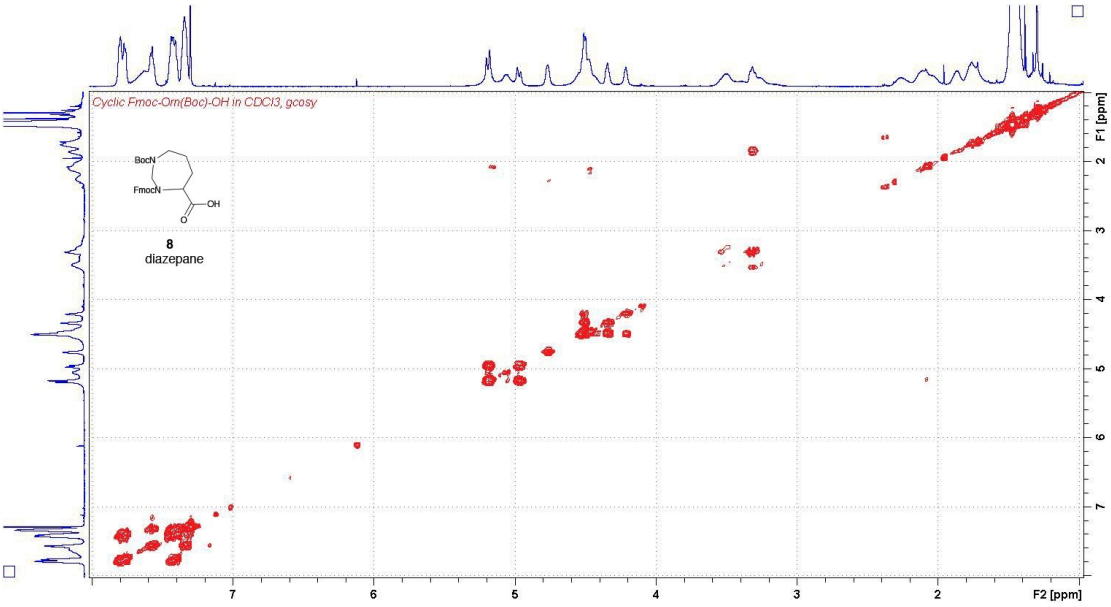


Figure S18. ^{1}H-^{1}H COSY NMR spectrum for **8** in $CDCl_3$ at 298K

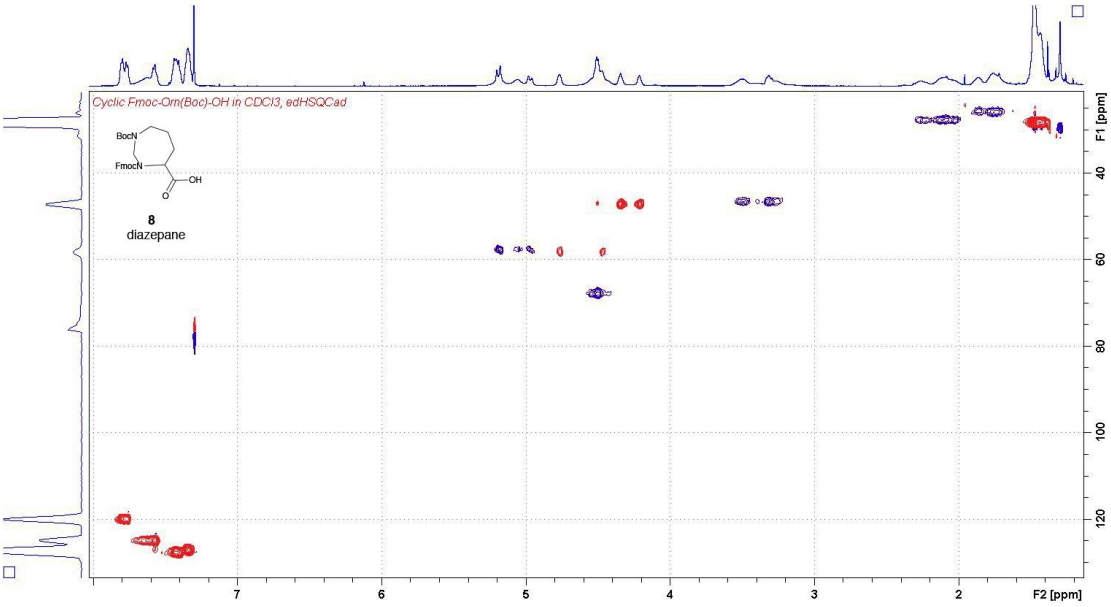


Figure S19. ^{1}H-^{13}C HSQC NMR spectrum for **8** in $CDCl_3$ at 298K.

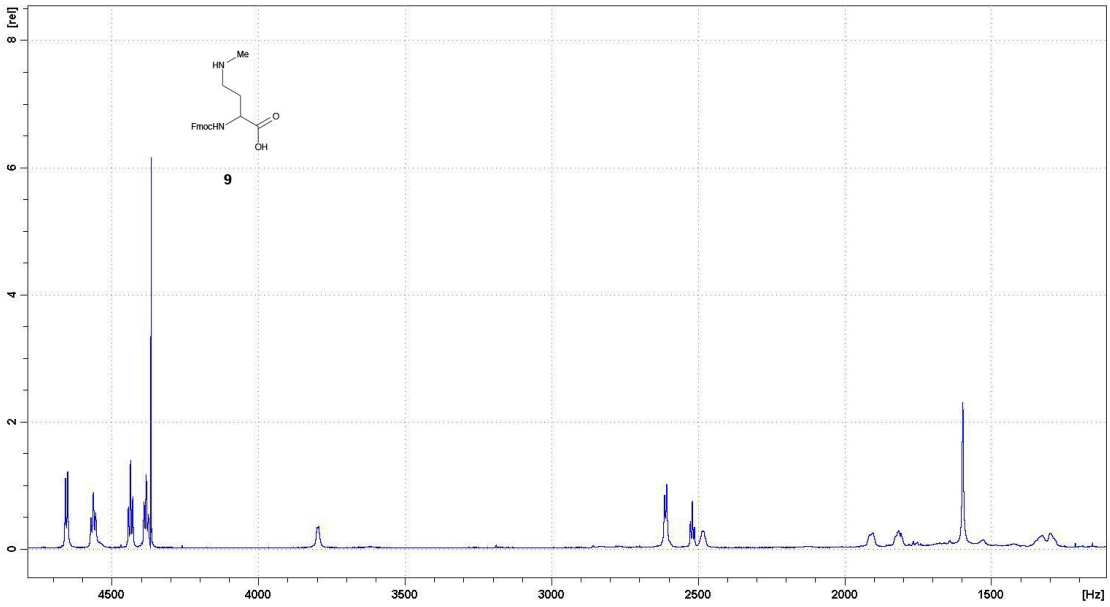


Figure S20. 600 MHz ^{1}H NMR spectrum for **9** in $CDCl_3$ at 298K.

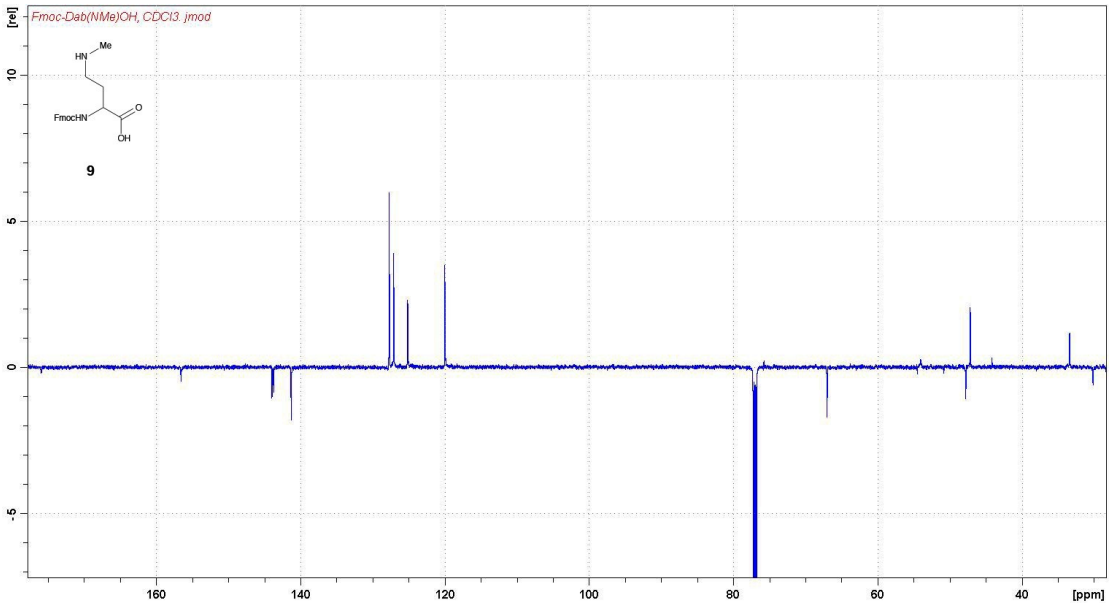


Figure S21. 150.9 MHz ^{13}C j-mod NMR spectrum for **9** in $CDCl_3$ at 298K.

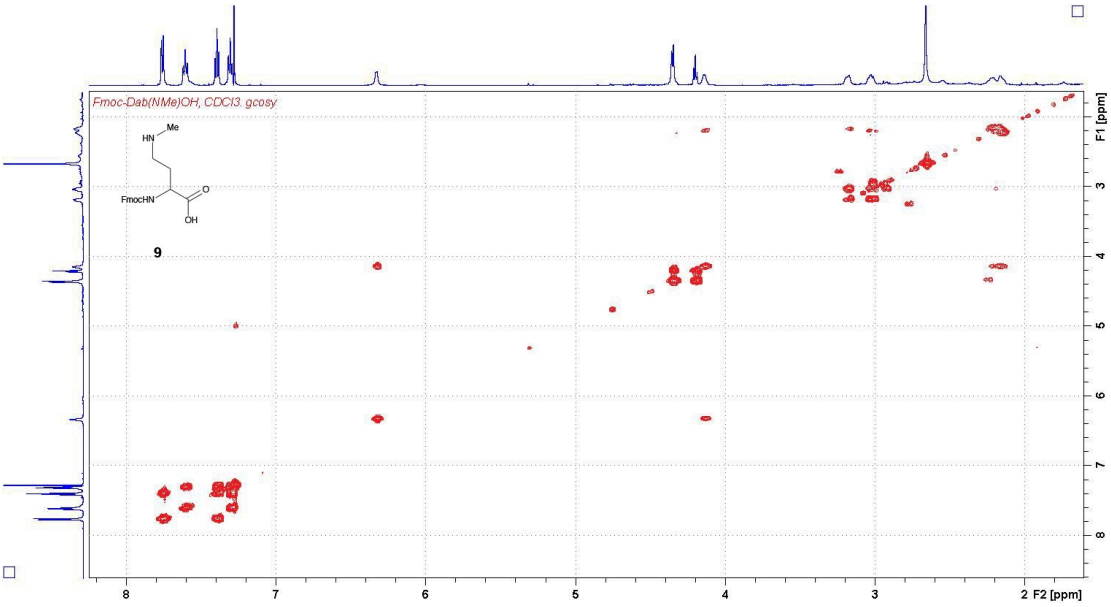


Figure S22. ^{1}H-^{1}H COSY NMR spectrum for **9** in $CDCl_3$ at 298K

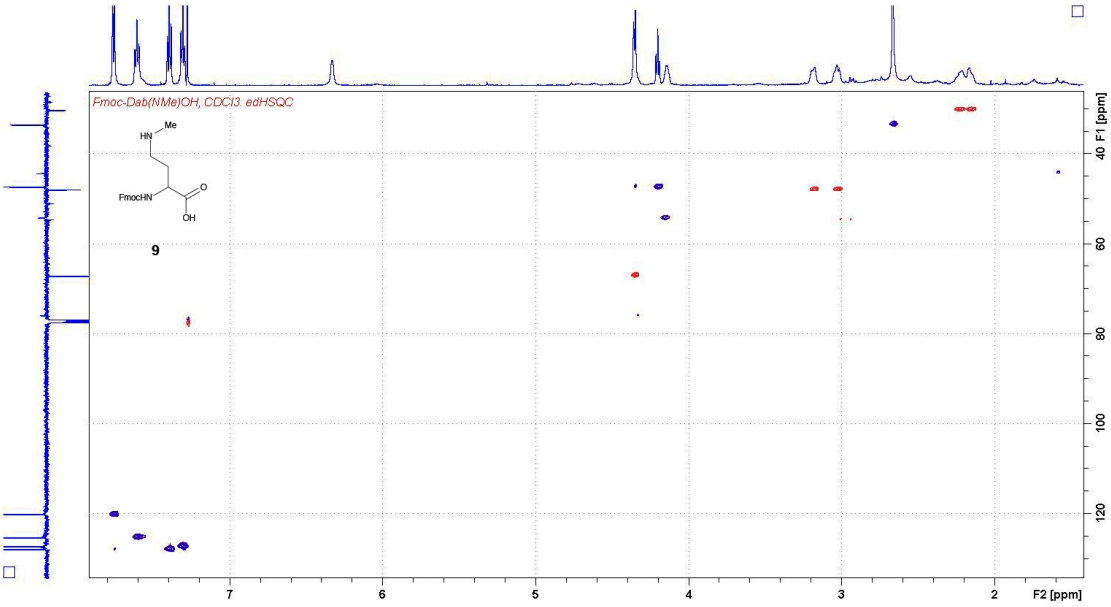


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum for **9** in $CDCl_3$ at 298K.

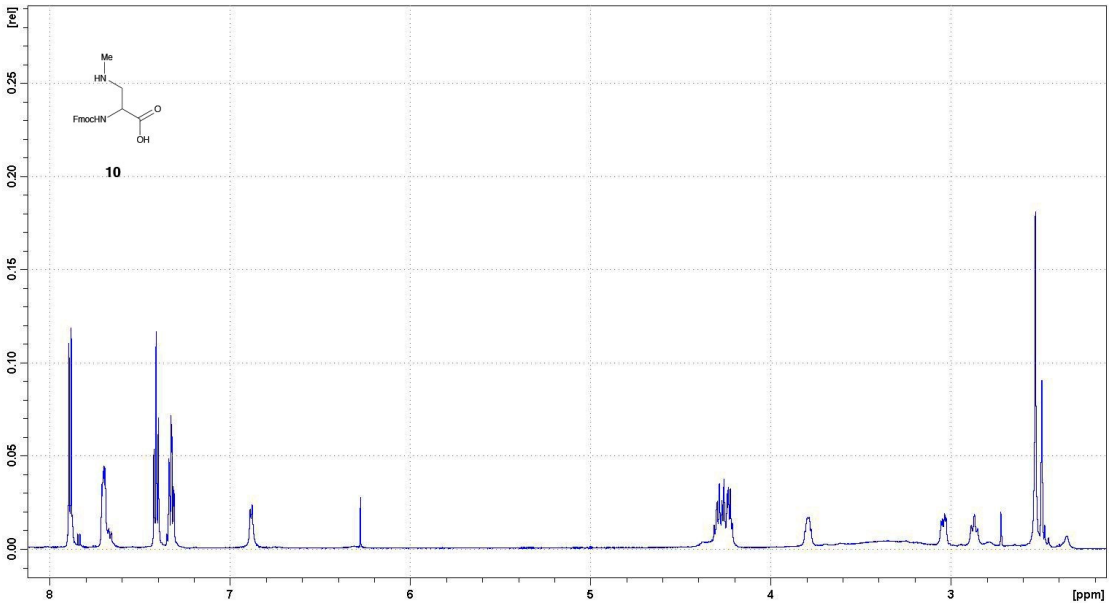


Figure S24. 600 MHz ^{1}H NMR spectrum for **10** in $CDCl_3$ at 298K.

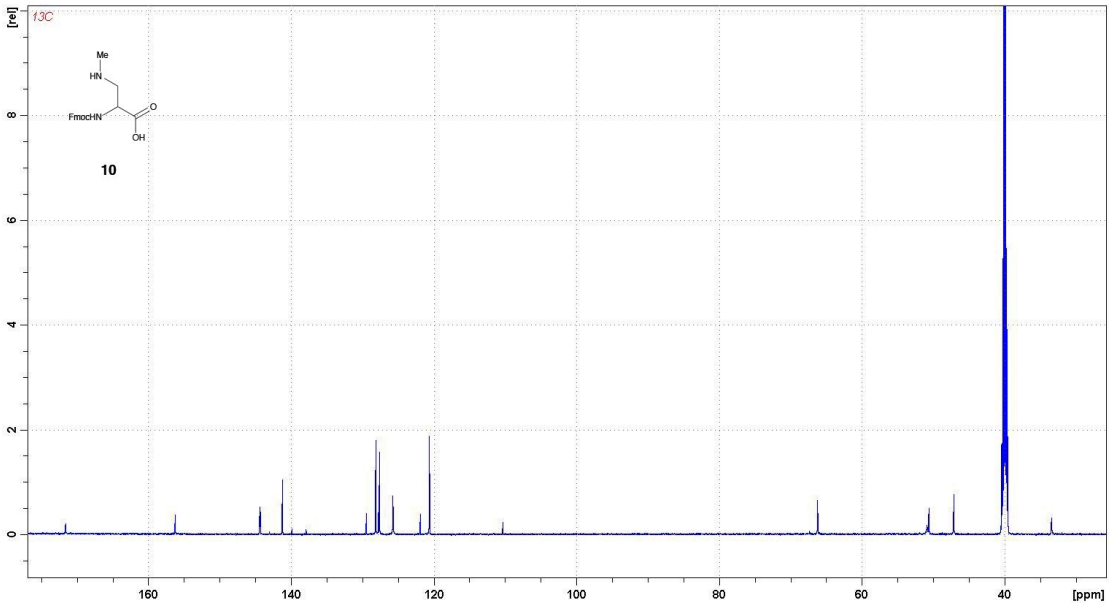


Figure S25. 150.9 MHz ^{13}C NMR spectrum for **10** in $CDCl_3$ at 298K.

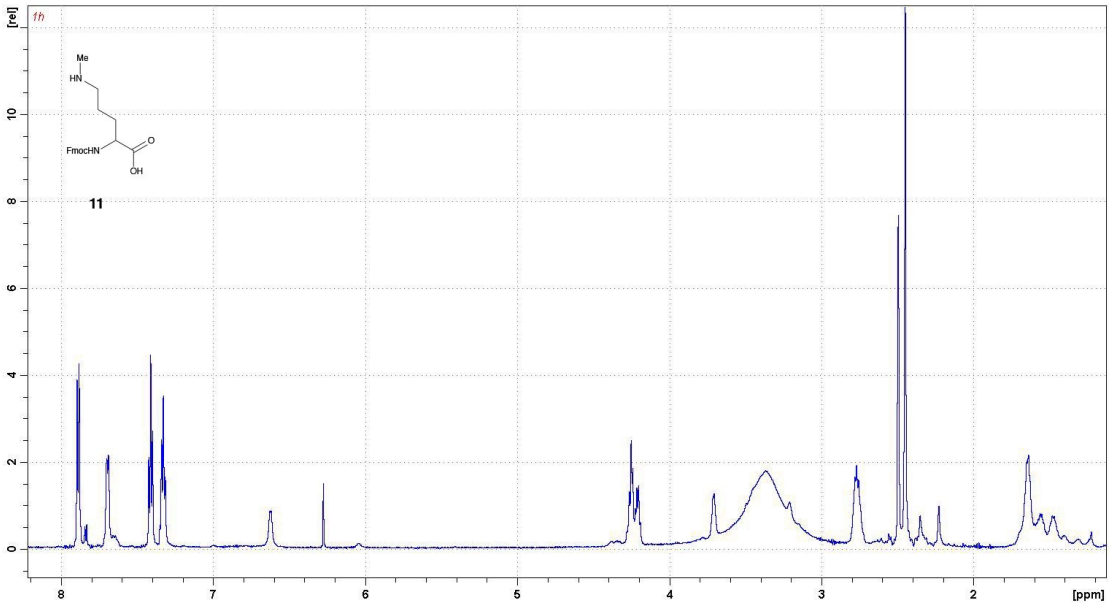


Figure S26. 600 MHz ^{1}H NMR spectrum for **11** in $CDCl_3$ at 298K.

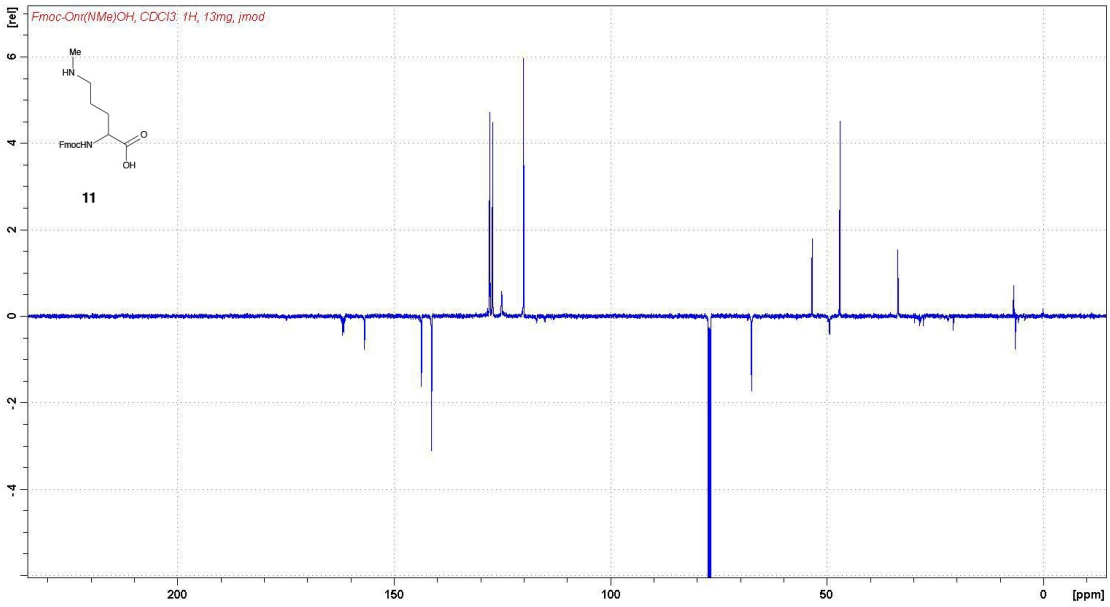


Figure S27. 150.9 MHz ^{13}C j-mod NMR spectrum for **11** in $CDCl_3$ at 298K.

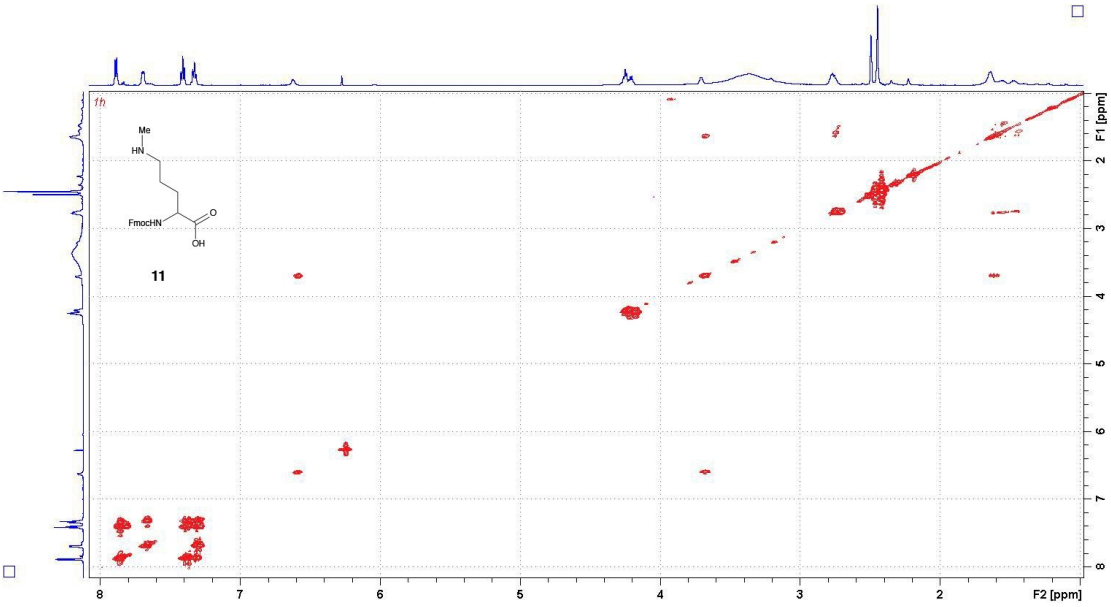


Figure S28. ^{1}H-^{1}H COSY NMR spectrum for **11** in $CDCl_3$ at 298K

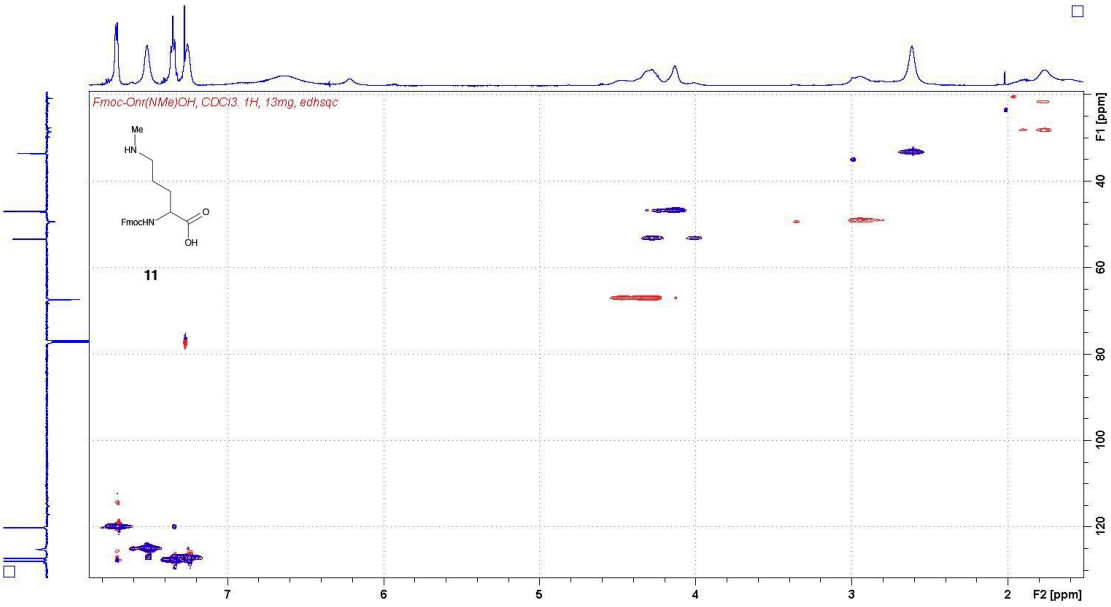


Figure S29. ^{1}H-^{13}C HSQC NMR spectrum for **11** in $CDCl_3$ at 298K.

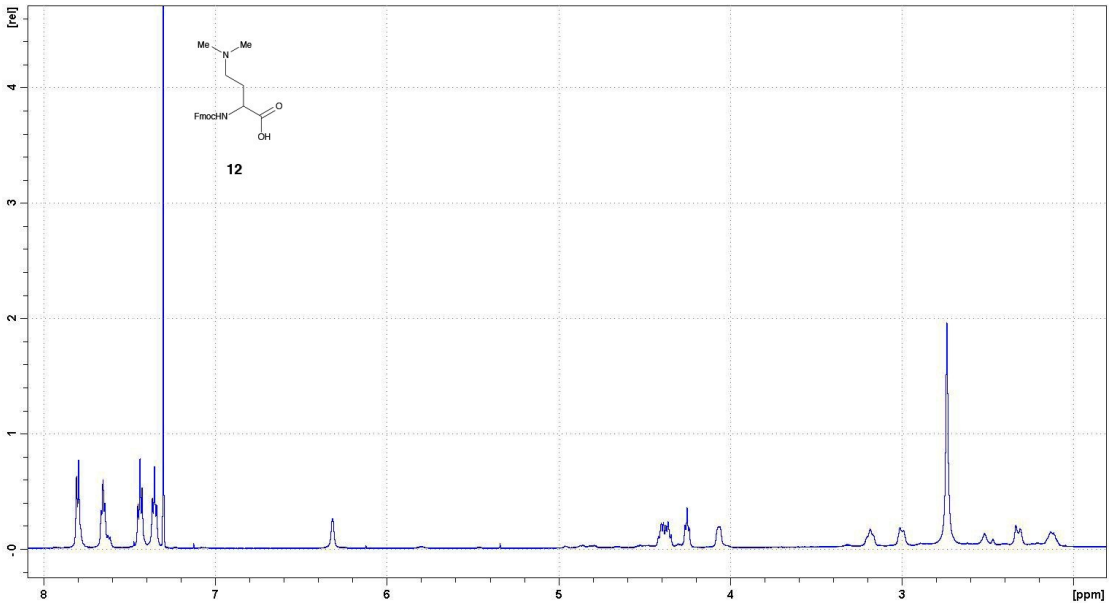


Figure S30. 600 MHz ^{1}H NMR spectrum for **12** in $CDCl_3$ at 298K.

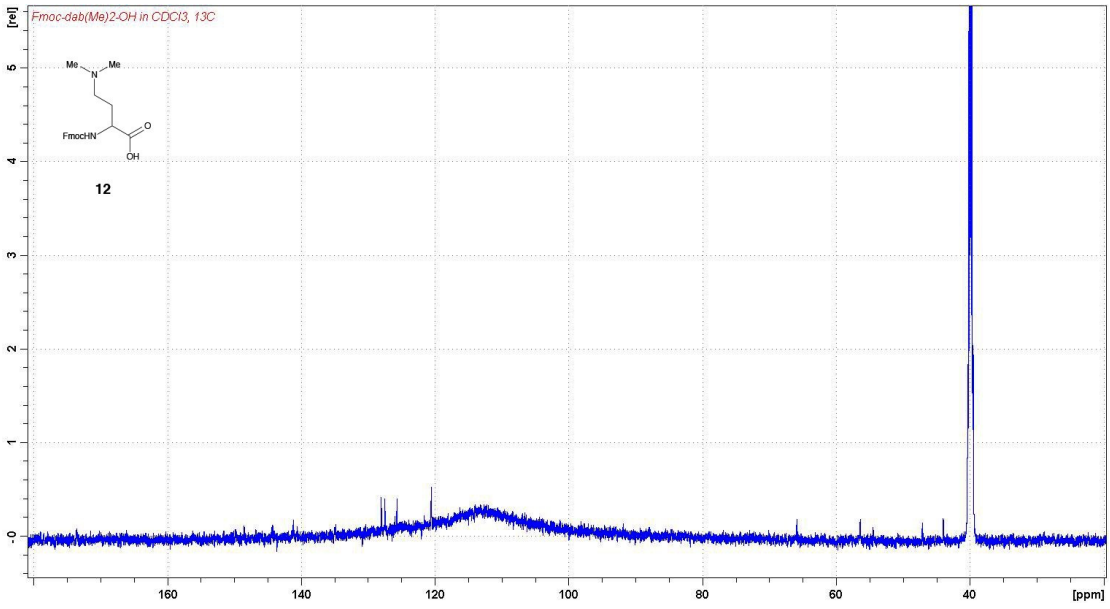


Figure S31. 150.9 MHz ^{13}C NMR spectrum for **12** in $CDCl_3$ at 298K.

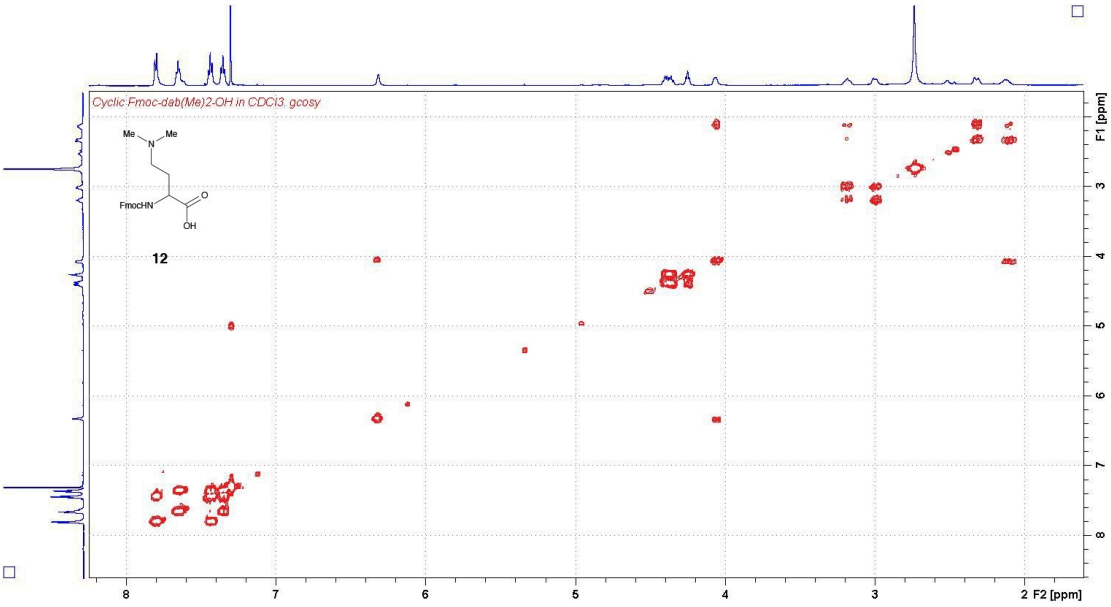


Figure S32. ^{1}H-^{1}H COSY NMR spectrum for **12** in $CDCl_3$ at 298K.

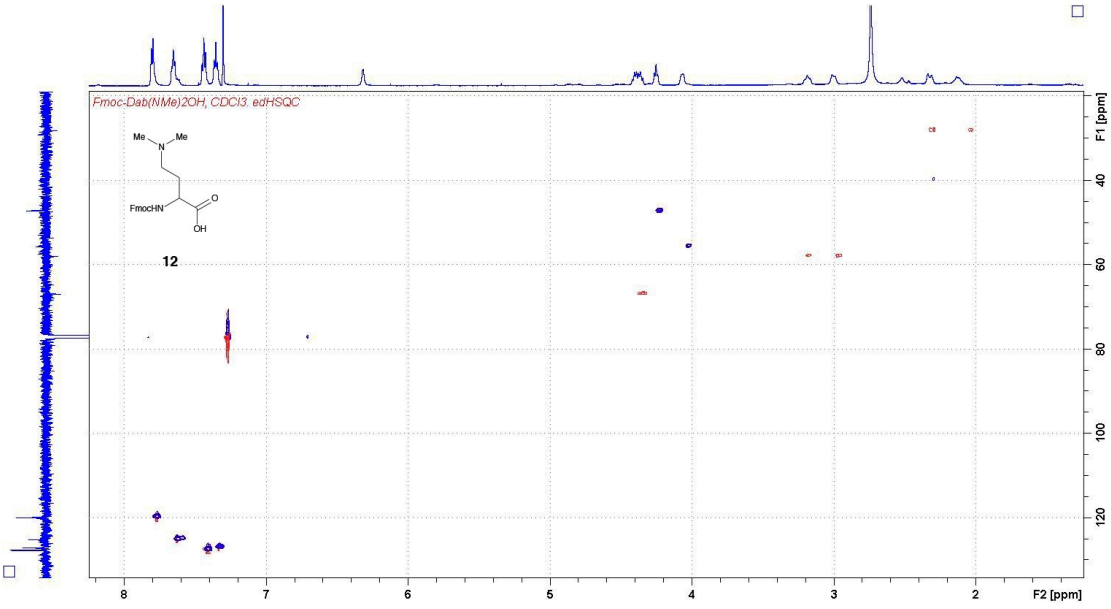


Figure S33. ^{1}H-^{13}C HSQC NMR spectrum for **12** in $CDCl_3$ at 298K.

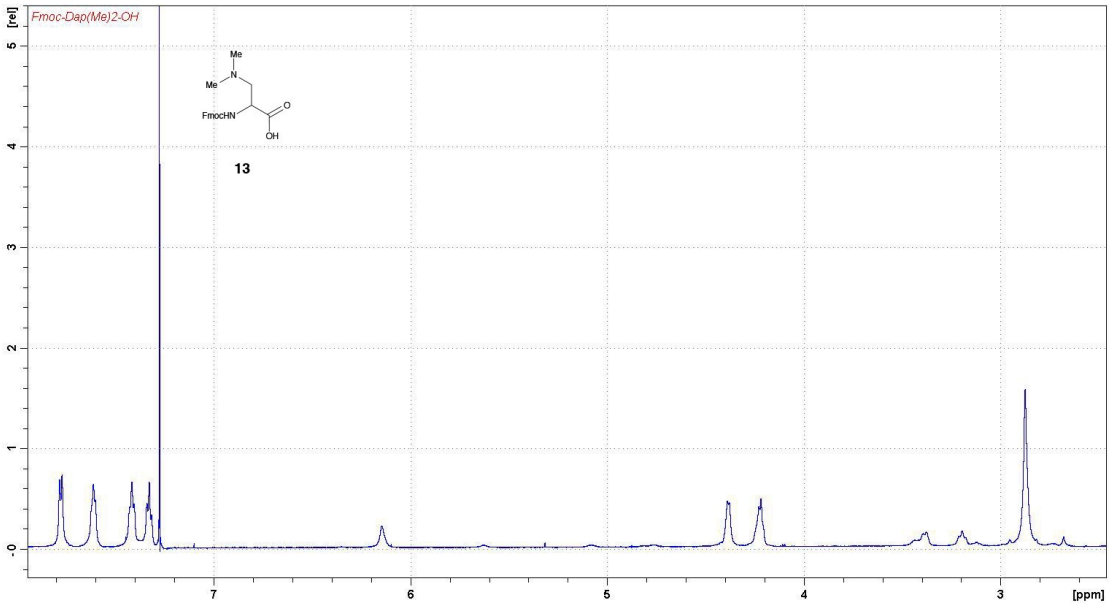


Figure S34. 600 MHz ^{1}H NMR spectrum for **13** in $CDCl_3$ at 298K.

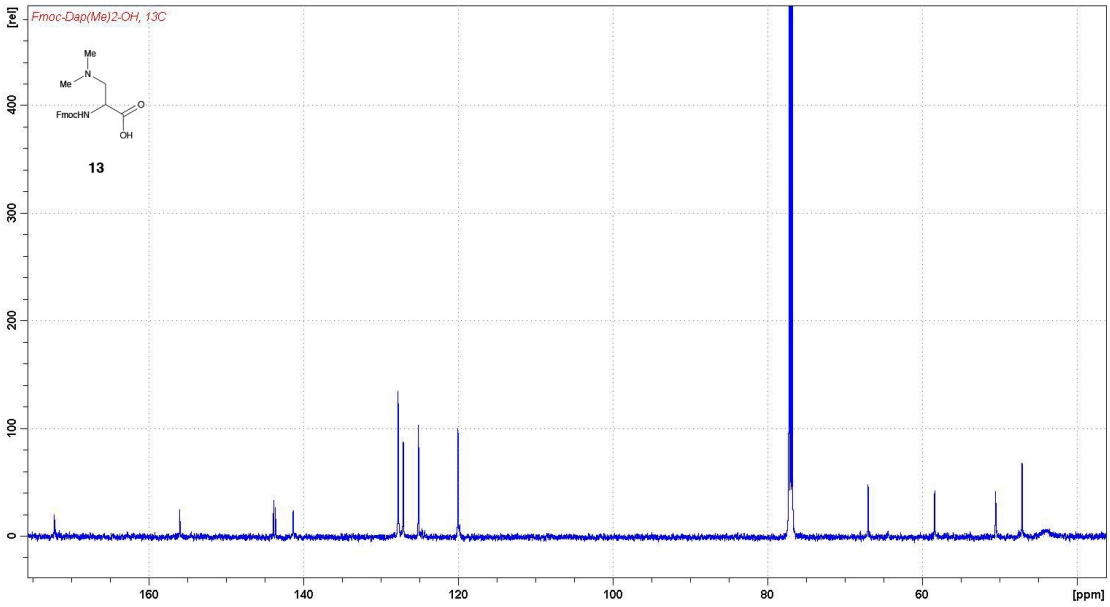


Figure S35. 150.9 MHz ^{13}C NMR spectrum for **13** in $CDCl_3$ at 298K.

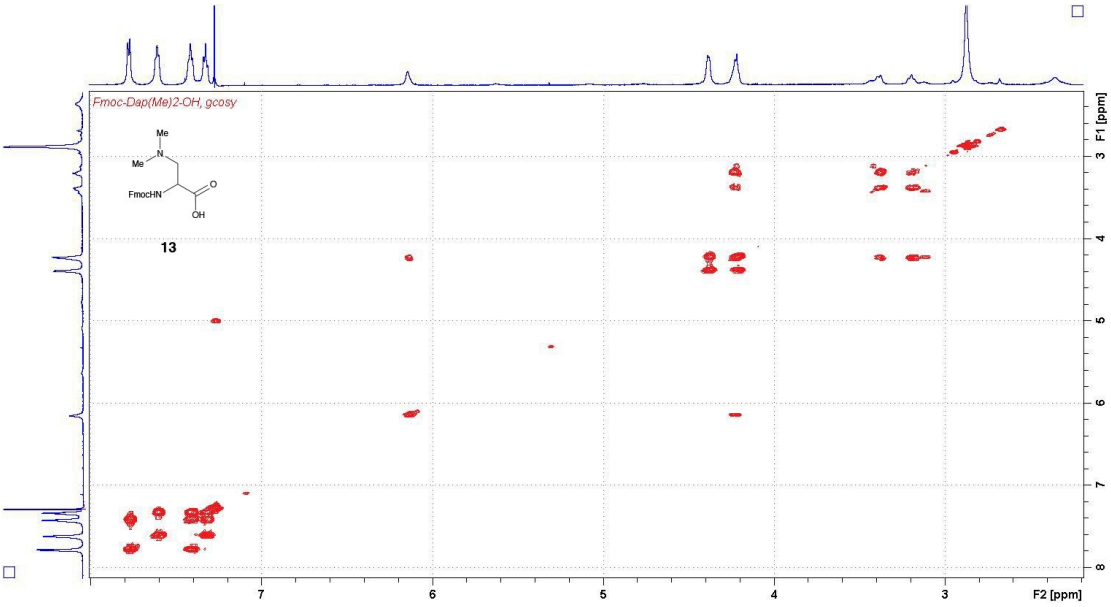


Figure S36. ^{1}H-^{1}H COSY NMR spectrum for **13** in $CDCl_3$ at 298K.

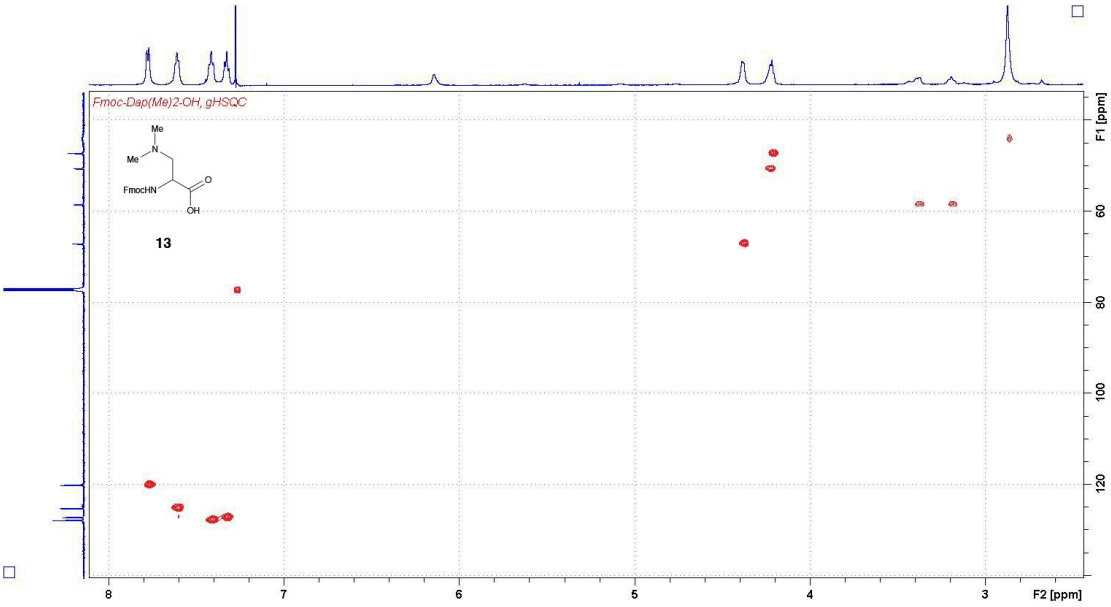


Figure S37. ^{1}H-^{13}C HSQC NMR spectrum for **13** in $CDCl_3$ at 298K.

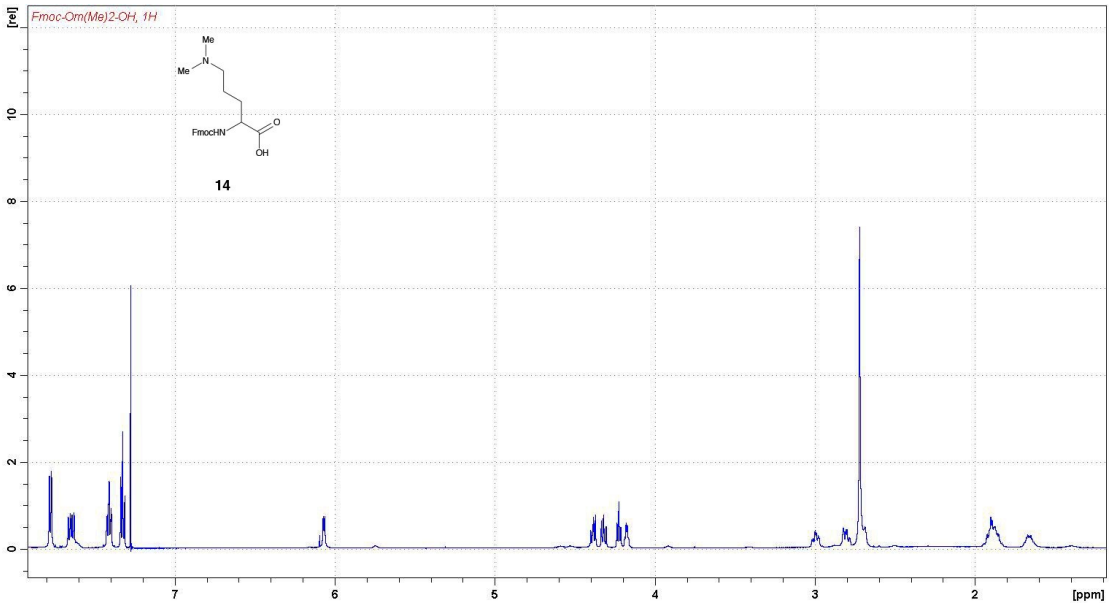


Figure S38. 600 MHz ^{1}H NMR spectrum for **14** in $CDCl_3$ at 298K.

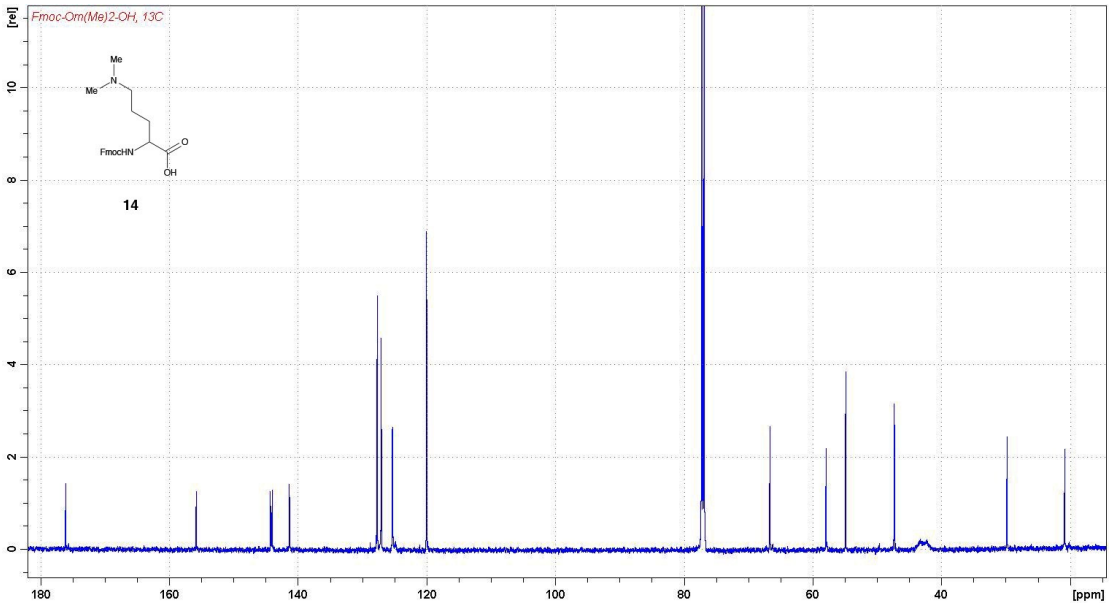


Figure S39. 150.9 MHz ^{13}C NMR spectrum for **14** in $CDCl_3$ at 298K.

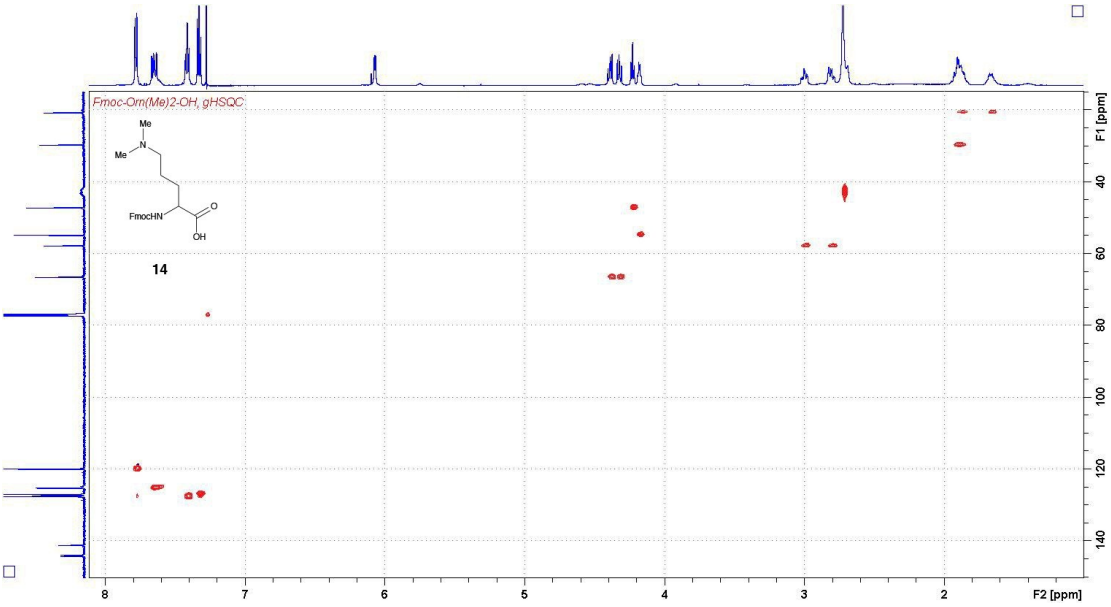


Figure S40. ^{1}H-^{13}C HSQC NMR spectrum for **14** in $CDCl_3$ at 298K.

Mass Spectrum Molecular Formula Report

Analysis Info

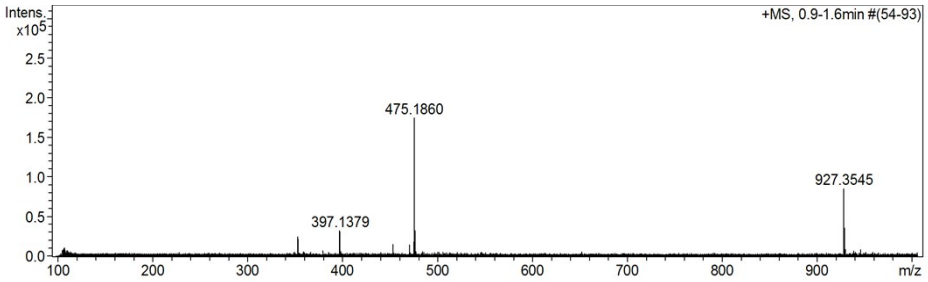
Analysis Name	D:\Data\cooper\FL_7292_57_1_RB4_01_8873.d	Acquisition Date	11/25/2014 7:15:21 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_57_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

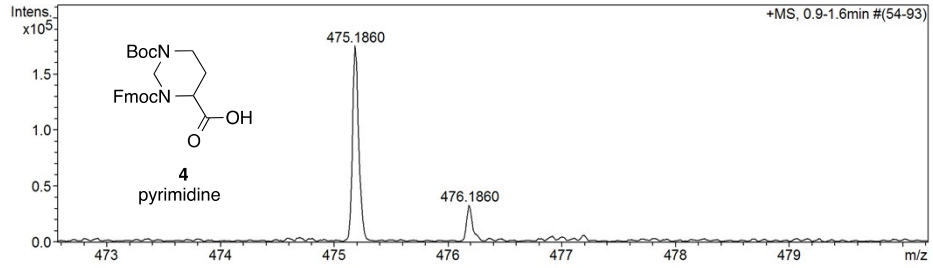
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C25H28N2O6Na						
Formula, max.	C25H28N2O6Na						
Measured m/z	475.186	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 25 H 28 N 2 Na 1 O 6	0.062	475.1840	-4.24	-2.88	-2.01	12.50	ok	even

Figure S41. HRMS of compound **4**

Mass Spectrum Molecular Formula Report

Analysis Info

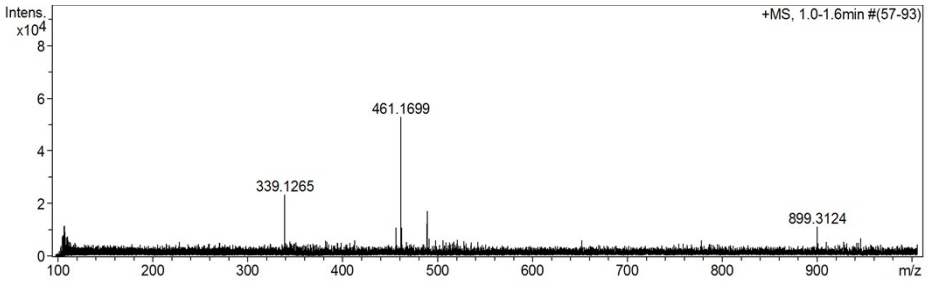
Analysis Name	D:\Data\cooper\FL_7292_36_1_RB3_01_8872.d	Acquisition Date	11/25/2014 7:09:51 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_36_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

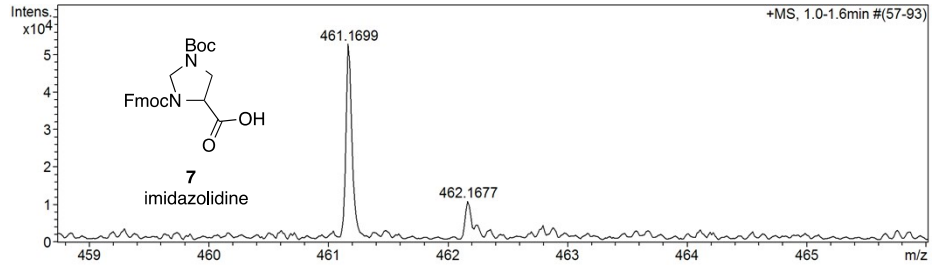
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C24H26N2O6Na						
Formula, max.	C24H26N2O6Na						
Measured m/z	461.17	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 24 H 26 N 2 Na 1 O 6	0.047	461.1683	-3.46	-1.22	-1.60	12.50	ok	even

Figure S42. HRMS of compound **7**

Mass Spectrum Molecular Formula Report

Analysis Info

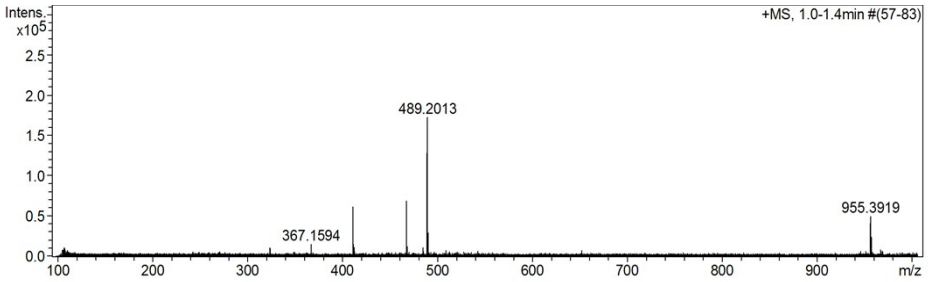
Analysis Name	D:\Data\cooper\FL_7292_35_1_RB2_01_8871.d	Acquisition Date	11/25/2014 7:04:21 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_35_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

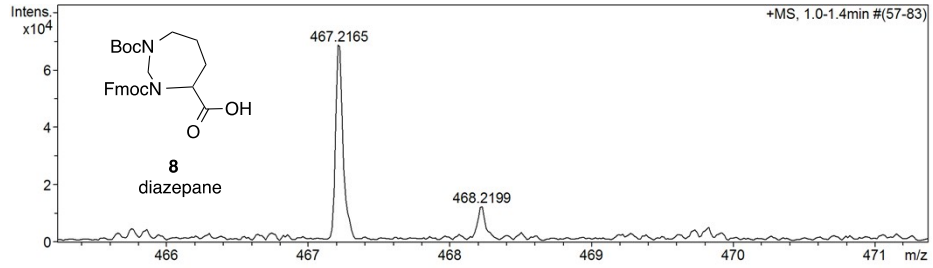
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C26H31N2O6						
Formula, max.	C26H31N2O6						
Measured m/z	467.217	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 26 H 31 N 2 O 6	0.073	467.2177	2.53	2.35	1.18	12.50	ok	even

Figure S43. HRMS of compound **8**

Mass Spectrum Molecular Formula Report

Analysis Info

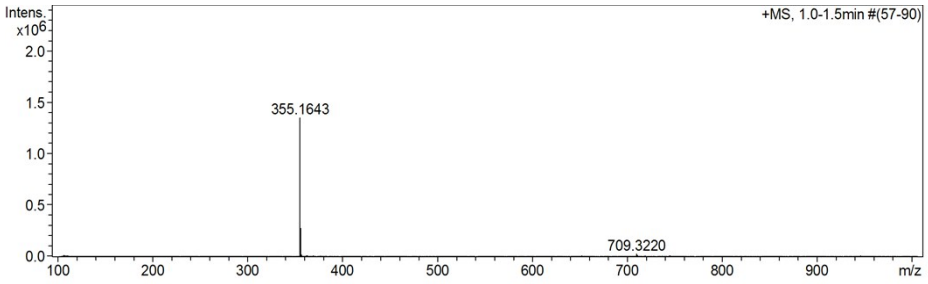
Analysis Name	D:\Data\cooper\FL_7292_51_1_RB5_01_8874.d	Acquisition Date	11/25/2014 7:20:52 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_51_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

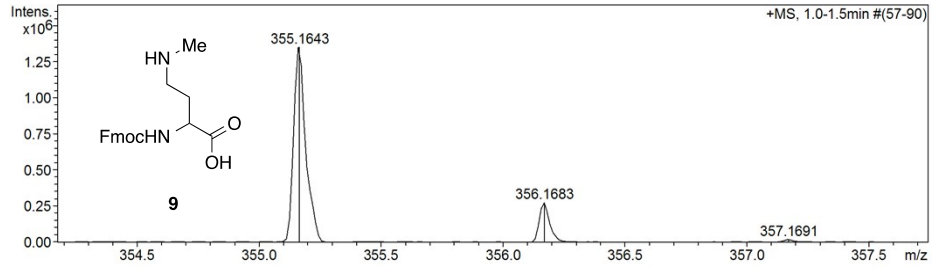
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C20H23N2O4						
Formula, max.	C20H23N2O4						
Measured m/z	355.164	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 20 H 23 N 2 O 4	0.018	355.1652	2.49	2.20	0.89	10.50	ok	even

Figure S44. HRMS of compound **9**

Mass Spectrum Molecular Formula Report

Analysis Info

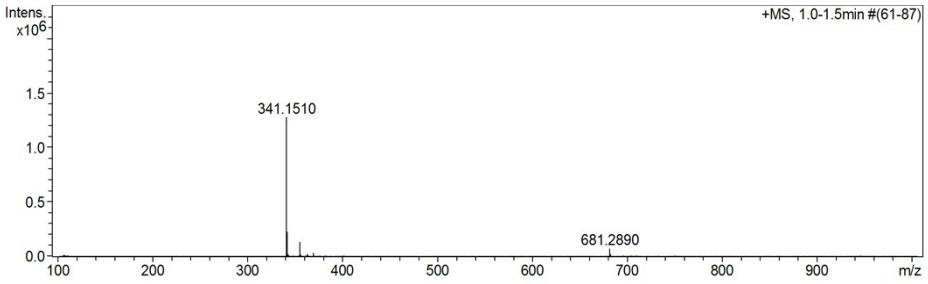
Analysis Name	D:\Data\cooper\FL_7292_52_1_RB6_01_8875.d	Acquisition Date	11/25/2014 7:26:24 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_52_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

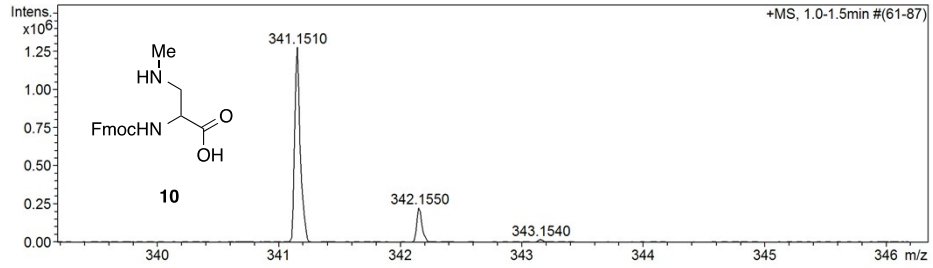
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C19H21N2O4						
Formula, max.	C19H21N2O4						
Measured m/z	341.151	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 19 H 21 N 2 O 4	0.025	341.1496	-4.13	-4.25	-1.41	10.50	ok	even

Figure S45. HRMS of compound **10**

Mass Spectrum Molecular Formula Report

Analysis Info

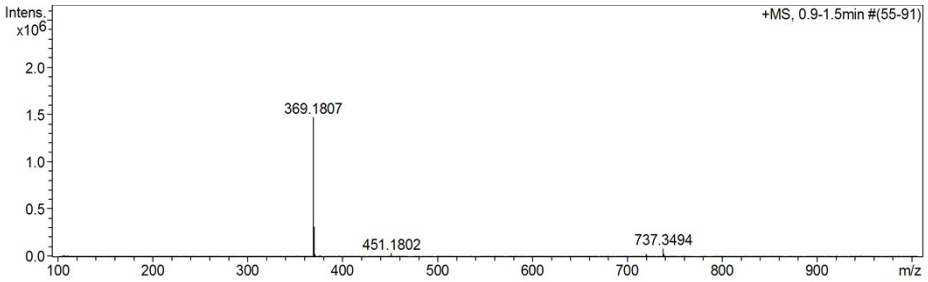
Analysis Name	D:\Data\cooper\FL_7292_13_1_RB7_01_8876.d	Acquisition Date	11/25/2014 7:31:54 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_13_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

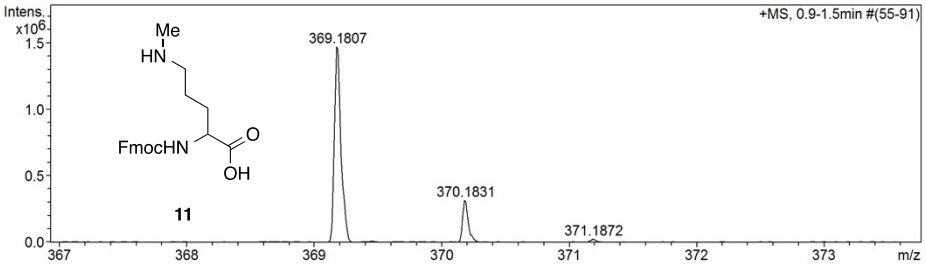
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C21H25N2O4						
Formula, max.	C21H25N2O4						
Measured m/z	369.181	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 21 H 25 N 2 O 4	0.019	369.1809	0.52	0.84	0.19	10.50	ok	even

Figure S46. HRMS of compound **11**

Mass Spectrum Molecular Formula Report

Analysis Info

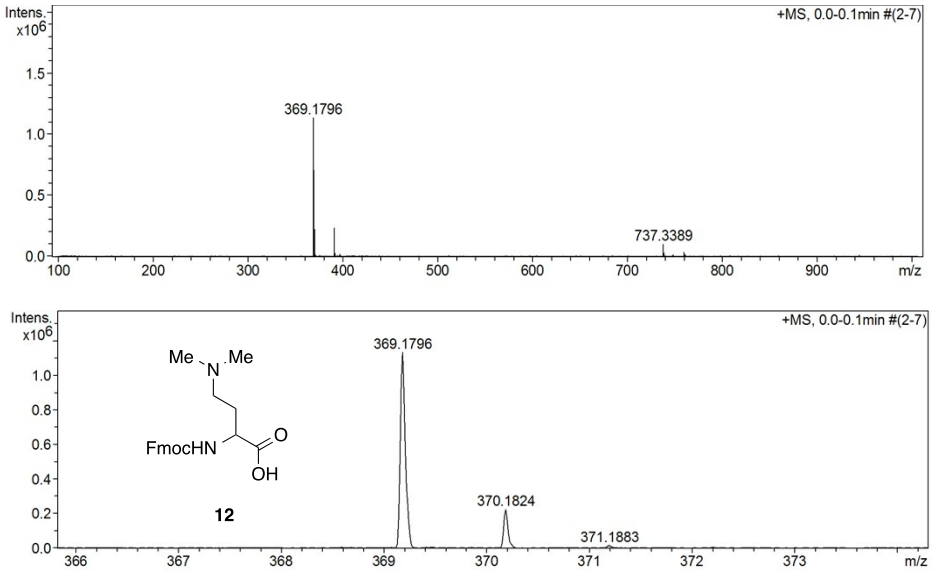
Analysis Name	D:\Data\cooper\FL_7292_67_1_2.d	Acquisition Date	12/3/2014 2:02:14 PM
Method	tune-med_AP.m	Operator	a.piggott
Sample Name		Instrument / Ser#	micrOTOF 232
Comment	Comments		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C21H25N2O4						
Formula, max.	C21H25N2O4						
Measured m/z	369.18	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	even				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						



Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 21 H 25 N 2 O 4	0.027	369.1809	3.56	3.44	1.31	10.50	ok	even

Figure S47. HRMS of compound **12**

Mass Spectrum Molecular Formula Report

Analysis Info

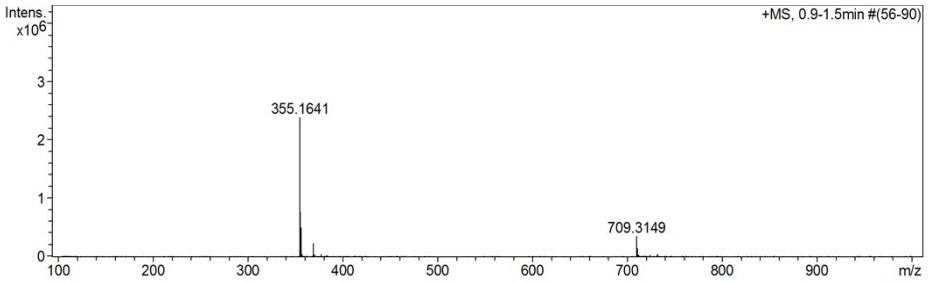
Analysis Name	D:\Data\cooper\FL_7292_64_1_RC1_01_8886.d	Acquisition Date	11/28/2014 6:14:26 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_64_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

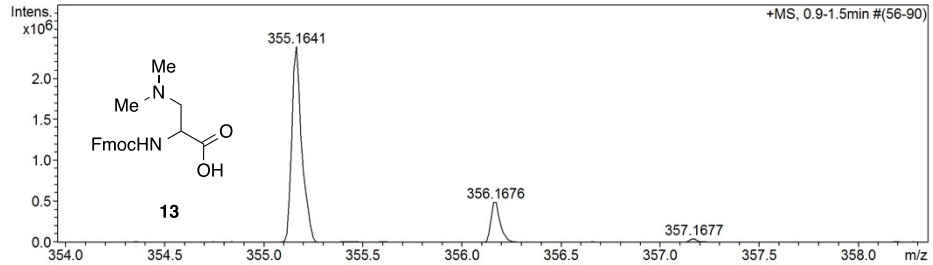
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C20H23N2O4						
Formula, max.	C20H23N2O4						
Measured m/z	355.164	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 20 H 23 N 2 O 4	0.016	355.1652	3.18	3.20	1.13	10.50	ok	even

Figure S48. HRMS of compound **13**

Mass Spectrum Molecular Formula Report

Analysis Info

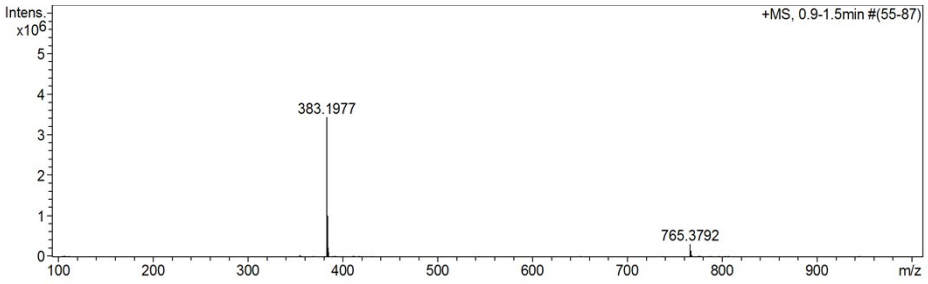
Analysis Name	D:\Data\cooper\FL_7292_65_1_RC2_01_8887.d	Acquisition Date	11/28/2014 6:19:56 PM
Method	tune-wide_50ul_hystar_withcal_direct_medhighmass_2.m	Operator	a.piggott
Sample Name	FL_7292_65_1	Instrument / Ser#	micrOTOF 232
Comment	Comments		

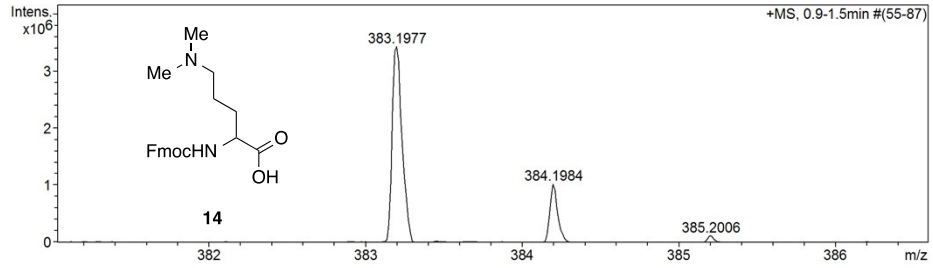
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	100 m/z	Set Capillary	4500 V	Set Dry Gas	5.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Generate Molecular Formula Parameter

Formula, min.	C22H27N2O4						
Formula, max.	C22H27N2O4						
Measured m/z	383.198	Tolerance	5	mDa	Charge	1	
Check Valence	no	Minimum	0		Maximum	0	
Nirogen Rule	yes	Electron Configuration	both				
Filter H/C Ratio	yes	Minimum	0		Maximum	3	
Estimate Carbon	yes						





Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 22 H 27 N 2 O 4	0.027	383.1965	-3.06	-1.55	-1.17	10.50	ok	even

Figure S49. HRMS of compound **14**