6-Azido hyacinthacine A₂ gives a straightforward access to the first multivalent pyrrolizidine architectures

Giampiero D'Adamio,^{*a,b*} Camilla Parmeggiani,^{*a,b,c*} Andrea Goti,^{*a**} Antonio J. Moreno-Vargas,^{*d*} Elena Moreno-Clavijo,^{*d*} Inmaculada Robina^{*d*} and Francesca Cardona^{*a**}

^aDipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy ^bEuropean Laboratory for Non Linear Spectroscopy (LENS), via Nello Carrara 1, 50019 Sesto Fiorentino (FI), Italy ^cCNR-INO, U.O.S. Sesto Fiorentino and LENS, via Nello Carrara 1, 50019 Sesto Fiorentino (FI), Italy. ^dDepartamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, c/ Prof. García González 1, E-41012, Sevilla, Spain.

E-mail: francesca.cardona@unifi.it, andrea.goti@unifi.it

Supporting Information

Figure S1. ¹ H-NMR Spectrum of compound 4 .	S7
Figure S2. ¹³ C-NMR Spectrum of compound 4 .	S7
Figure S3. ¹ H-NMR Spectrum of compound 5 .	S8
Figure S4. ¹³ C-NMR Spectrum of compound 5 .	S 8
Figure S5. ¹ H-NMR Spectrum of compound 7a .	S9
Figure S6. ¹³ C-NMR Spectrum of compound 7a .	S9
Figure S7. ¹ H-NMR Spectrum of compound 7b .	S10
Figure S8. ¹³ C-NMR Spectrum of compound 7b .	S10
Figure S9. ¹ H-NMR Spectrum of compound 7c .	S11
Figure S10. ¹³ C-NMR Spectrum of compound 7c .	S11
Figure S11. ¹ H-NMR Spectrum of compound 7d.	S12
Figure S12. ¹³ C-NMR Spectrum of compound 7d .	S12
Figure S13. ¹ H-NMR Spectrum of compound 7e.	S13
Figure S14. ¹³ C-NMR Spectrum of compound 7e.	S13
Figure S15. ¹ H-NMR Spectrum of compound 7f .	S14
Figure S16. ¹³ C-NMR Spectrum of compound 7f .	S14
Figure S17. ¹ H-NMR Spectrum of compound 8a .	S15

Figure S18. ¹³ C-NMR Spectrum of compound 8a .	S15
Figure S19. ¹ H-NMR Spectrum of compound 8b .	S16
Figure S20. ¹³ C-NMR Spectrum of compound 8b .	S16
Figure S21. ¹ H-NMR Spectrum of compound 8c.	S17
Figure S22 ¹³ C-NMR Spectrum of compound 8c .	S17
Figure S23. ¹ H-NMR Spectrum of compound 8d .	S18
Figure S24. ¹³ C-NMR Spectrum of compound 8d.	S18
Figure S25. ¹ H-NMR Spectrum of compound 8e' .	S19
Figure S26. ¹³ C-NMR Spectrum of compound 8e' .	S19
Figure S27. ¹ H-NMR Spectrum of compound 8e''.	S20
Figure S28 ¹³ C-NMR Spectrum of compound 8e'' .	S20
Figure S29. ¹ H-NMR Spectrum of compound 8f .	S21
Figure S30 ¹³ C-NMR Spectrum of compound 8f .	S21
Figure S31. ¹ H-NMR Spectrum of compound 10 .	S22
Figure S32. ¹³ C-NMR Spectrum of compound 10 .	S22
Figure S33. ¹ H-NMR Spectrum of compound 12 .	S23
Figure S34. ¹³ C-NMR Spectrum of compound 12 .	S23
Figure S35. ¹ H-NMR Spectrum of compound 13 .	S24
Figure S36. ¹³ C-NMR Spectrum of compound 13 .	S24

Figure S37. ¹ H-NMR Spectrum of compound 16 .	S25
Figure S38. ¹³ C-NMR Spectrum of compound 16 .	S25
Figure S39. ¹ H-NMR Spectrum of compound 17 .	S26
Figure S40. ¹³ C-NMR Spectrum of compound 17 .	S26
Figure S41. ¹ H-NMR Spectrum of compound 18 .	S27
Figure S42 ¹³ C-NMR Spectrum of compound 18 .	S27
Figure S43. ¹ H-NMR Spectrum of compound 19 .	S28
Figure S44. ¹³ C-NMR Spectrum of compound 19 .	S28
Figure S45. ¹ H-NMR Spectrum of compound 20 .	S29
Figure S46. ¹³ C-NMR Spectrum of compound 20 .	S29
Figure S47. ¹ H-NMR Spectrum of compound 22 .	S30
Figure S48 ¹³ C-NMR Spectrum of compound 22 .	S30
Figure S49. ¹ H-NMR Spectrum of compound 23 .	S31
Figure S50 ¹³ C-NMR Spectrum of compound 23 .	S31
Figure S51. ¹ H-NMR Spectrum of compound 24 .	S32
Figure S52 ¹³ C-NMR Spectrum of compound 24 .	S32
Figure S53. ¹ H-NMR Spectrum of compound 28 .	S33
Figure S54. ¹³ C-NMR Spectrum of compound 28 .	S33
Figure S55. ¹ H-NMR Spectrum of compound 29 .	S34

Figure S56. ¹³ C-NMR Spectrum of compound 29 .	S34
Figure S57. ¹ H-NMR Spectrum of compound 30 .	S35
Figure S58 ¹³ C-NMR Spectrum of compound 30 .	S35
Figure S59. ¹ H-NMR Spectrum of compound 31 .	S36
Figure S60 ¹³ C-NMR Spectrum of compound 31 .	S36
Figure S61. ¹ H-NMR Spectrum of compound 32 .	S37
Figure S62 ¹³ C-NMR Spectrum of compound 32 .	S37
Figure S63. IC ₅₀ of 6- <i>epi</i> - 7-deoxycasuarine towards Amyloglucosidase.	S38
Figure S64. Lineweaver-Burk Plot of 6-epi-7-deoxycasuarine towards Amyloglucosidas	se. S38
Figure S65. IC ₅₀ of compound 5 towards Amyloglucosidase.	S39
Figure S66. Lineweaver-Burk Plot of compound 5 towards Amyloglucosidase.	S39
Figure S67. IC ₅₀ of compound 8a towards Amyloglucosidase.	S40
Figure S68. Lineweaver-Burk Plot of compound 8a towards Amyloglucosidase.	S40
Figure S69. IC ₅₀ of compound 8b towards Amyloglucosidase.	S41
Figure S70. Lineweaver-Burk Plot of compound 8b towards Amyloglucosidase.	S41
Figure S71. IC ₅₀ of compound 8c towards Amyloglucosidase.	S42
Figure S72. IC ₅₀ of compound 8d towards Amyloglucosidase.	S43
Figure S73. Lineweaver-Burk Plot of compound 8d towards Amyloglucosidase.	S43
Figure S74. IC ₅₀ of compound 8e' towards Amyloglucosidase.	S44

Figure S75.	Lineweaver-Burk Plot of compound 8e' towards Amyloglucosidase.	S44
Figure S76.	IC ₅₀ of compound 8e'' towards Amyloglucosidase.	S45
Figure S77.	Lineweaver-Burk Plot of compound 8e'' towards Amyloglucosidase.	S45
Figure S78.	IC ₅₀ of compound 8f towards Amyloglucosidase.	S46
Figure S79.	IC ₅₀ of compound 13 towards Amyloglucosidase.	S47
Figure S80.	Lineweaver-Burk Plot of compound 13 towards Amyloglucosidase.	S47
Figure S81.	IC ₅₀ of compound 24 towards Amyloglucosidase.	S48
Figure S82.	Lineweaver-Burk Plot of compound 24 towards Amyloglucosidase.	S48
Figure S83.	IC ₅₀ of compound 31 towards Amyloglucosidase.	S49
Figure S84.	Lineweaver-Burk Plot of compound 31 towards Amyloglucosidase.	S49
Figure S85.	IC ₅₀ of compound 32 towards Amyloglucosidase.	S50
Figure S86.	Lineweaver-Burk Plot of compound 32 towards Amyloglucosidase.	S50



S1. ¹H-NMR spectrum of compound 4 (400 MHz, CDCl₃).



S2. ¹³C-NMR spectrum of compound 4 (50 MHz, CDCl₃).



S3. ¹H-NMR spectrum of compound 5 (400 MHz, D₂O).



S4. ¹³C-NMR spectrum of compound 5 (50 MHz, D₂O).



S5. ¹H-NMR spectrum of compound 7a (400 MHz, CDCl₃).



S6. ¹³C-NMR spectrum of compound 7a (50 MHz, CDCl₃).



S7. ¹H-NMR spectrum of compound 7b (400 MHz, CDCl₃).



S8. ¹³C-NMR spectrum of compound 7b (50 MHz, CDCl₃).



S9. ¹H-NMR spectrum of compound 7c (400 MHz, CDCl₃).



S10. ¹³C-NMR spectrum of compound 7c (50 MHz, CDCl₃).



S11. ¹H-NMR spectrum of compound 7d (400 MHz, CDCl₃).



S12. ¹³C-NMR spectrum of compound 7d (50 MHz, CDCl₃).



S13. ¹H-NMR spectrum of compound 7e (400 MHz, CDCl₃).



S14. ¹³C-NMR spectrum of compound 7e (50 MHz, CDCl₃).



S15. ¹H-NMR spectrum of compound 7f (400 MHz, CDCl₃).



S16. ¹³C-NMR spectrum of compound 7f (50 MHz, CDCl₃).



S18. ¹³C-NMR spectrum of compound 8a (50 MHz, CD₃OD).



S20. ¹³C-NMR spectrum of compound 8b (50 MHz, CD₃OD).



S21. ¹H-NMR spectrum of compound 8c (400 MHz, CD₃OD).



S22. ¹³C-NMR spectrum of compound 8c (50 MHz, CD₃OD).



S24. ¹³C-NMR spectrum of compound 8d (50 MHz, CD₃OD).





S26. ¹³C-NMR spectrum of compound 8e' (50 MHz, CD₃OD).



S28. ¹³C-NMR spectrum of compound 8e'' (50 MHz, CD₃OD).



S29. ¹H-NMR spectrum of compound 8f (400 MHz, CD₃OD).



S30. ¹³C-NMR spectrum of compound 8f (50 MHz, CD₃OD).



S32. ¹³C-NMR spectrum of compound 10 (50 MHz, CDCl₃).



S34. ¹³C-NMR spectrum of compound 12 (50 MHz, CDCl₃).



S36. ¹³C-NMR spectrum of compound 13 (50 MHz, CD₃OD).



S37. ¹H-NMR spectrum of compound 16 (400 MHz, CDCl₃).



S38. ¹³C-NMR spectrum of compound 16 (50 MHz, CDCl₃).



S39. ¹H-NMR spectrum of compound 17 (400 MHz, CDCl₃).



S40. ¹³C-NMR spectrum of compound 17 (50 MHz, CDCl₃).





S42. ¹³C-NMR spectrum of compound 18 (50 MHz, CDCl₃).



S44. ¹³C-NMR spectrum of compound 19 (50 MHz, CD₃OD).



S46. ¹³C-NMR spectrum of compound 20 (50 MHz, CD₃OD).



S48. ¹³C-NMR spectrum of compound 22 (50 MHz, CDCl₃).





S50. ¹³C-NMR spectrum of compound 23 (50 MHz, CDCl₃).



S52. ¹³C-NMR spectrum of compound 24 (50 MHz, CD₃OD).



S54. ¹³C-NMR spectrum of compound 28 (50 MHz, CDCl₃).



S56. ¹³C-NMR spectrum of compound 29 (50 MHz, CDCl₃).



S57. ¹H-NMR spectrum of compound 30 (400 MHz, CD₃OD).



S58. ¹³C-NMR spectrum of compound 30 (50 MHz, CD₃OD).



S59. ¹H-NMR spectrum of compound 31 (400 MHz, D₂O).



S60. $^{13}\text{C-NMR}$ spectrum of compound 31 (50 MHz, $D_2\text{O}).$



S61. ¹H-NMR spectrum of compound 32 (400 MHz, D₂O).



S62. ¹³C-NMR spectrum of compound 32 (50 MHz, D₂O).



S63. IC $_{50}$ of 6-epi-7-deoxy casuarine towards Amyloglucosidase



S64. Lineweaver-Burk Plot of 6-epi-7-deoxycasuarine towards Amyloglucosidase



S65. IC $_{50}$ of compound 5 towards Amyloglucosidase



S66. Lineweaver-Burk Plot of compound 5 towards Amyloglucosidase



S67. IC $_{\rm 50}$ of compound 8a towards Amyloglucosidase



S68. Lineweaver-Burk Plot of compound 8a towards Amyloglucosidase



S69. IC $_{\rm 50}$ of compound 8b towards Amyloglucosidase



S70. Lineweaver-Burk Plot of compound 8b towards Amyloglucosidase



S71. IC $_{50}$ of compound 8c towards Amyloglucosidase



S72. IC_{50} of compound 8d towards Amyloglucosidase



S73. Lineweaver-Burk Plot of compound 8d towards Amyloglucosidase



S74. IC₅₀ of compound 8e' towards Amyloglucosidase



S75. Lineweaver-Burk Plot of compound 8e' towards Amyloglucosidase



S76. IC₅₀ of compound 8e'' towards Amyloglucosidase



S77. Lineweaver-Burk Plot of compound 8e'' towards Amyloglucosidase



S78. IC $_{50}$ of compound 8f towards Amyloglucosidase



S79. IC $_{50}$ of compound 13 towards Amyloglucosidase



S80. Lineweaver-Burk Plot of compound 13 towards Amyloglucosidase



S81. IC $_{50}$ of compound 24 towards Amyloglucosidase



S82. Lineweaver-Burk Plot of compound 24 towards Amyloglucosidase



S83. IC_{50} of compound 31 towards Amyloglucosidase



S84. Lineweaver-Burk Plot of compound 31 towards Amyloglucosidase



S85. IC_{50} of compound 32 towards Amyloglucosidase



S86. Lineweaver-Burk Plot of compound 32 towards Amyloglucosidase