

Supplementary Material



Supplementary Figure 1. (A) Scaled up biotransformation reaction of ferulic acid with the enzymatic secretome of *Botrytis cinerea* and 10% of acetone. (B) UHPLC-PDA analysis with optimized chromatographic conditions. (C) HPLC-PDA analysis using the transferred optimized chromatographic conditions. (D) Semi-preparative HPLC-UV analysis using the transferred optimized chromatographic conditions and isolation of the generated compounds.



Supplementary Figure 2. (A) Scaled up biotransformation reaction of caffeic acid with the enzymatic secretome of *Botrytis cinerea* and 10% of acetone. (B) UHPLC-PDA analysis with optimized chromatographic conditions. (C) HPLC-PDA analysis using the transferred optimized chromatographic conditions. (D) Semi-preparative HPLC-UV analysis using the transferred optimized chromatographic conditions and isolation of the generated compounds.



Supplementary Figure 3. Proposed chemo-enzymatic pathway for the formation of compounds 6 and **11** through 8-O-4' phenoxy radical coupling.



Supplementary Figure 4. (A) UHPLC-PDA-ELSD-MS and (B) NMR analysis showing the degradation of the compound 5 into 23.



Supplementary Figure 5. Structure of compound 16 and its key ROESY correlations.



Supplementary Figure 6. Proposed chemo-enzymatic pathway for the formation of compounds **21** through 8-6' phenoxy radical coupling.

Supplementary Material



Supplementary Figure 7. Structure of compound 3 and its key ROESY correlations.



Supplementary Figure 8. ¹H NMR spectrum of compound 1 in DMSO-*d*₆ at 600 Mhz.



Supplementary Figure 9. COSY NMR spectrum of compound 1 in DMSO-d₆

Supplementary Material



Supplementary Figure 10. Edited-HSQC NMR spectrum of compound 1 in DMSO-d₆

Supplementary Figure 11. HMBC NMR spectrum of compound 1 in DMSO-d6

Supplementary Figure 12. ROESY NMR spectrum of compound 1 in DMSO-d₆

Supplementary Figure 13. ¹H NMR spectrum of compound 2 in DMSO-d₆ at 600 MHz

Supplementary Figure 14. COSY NMR spectrum of compound 2 in DMSO-d₆

Supplementary Figure 15. Edited-HSQC NMR spectrum of compound 2 in DMSO-d6

Supplementary Figure 16. HMBC NMR spectrum of compound 2 in DMSO-d₆

Supplementary Figure 17. ¹H NMR spectrum of compound 3 in DMSO-d₆ at 600 MHz

Supplementary Material

Supplementary Figure 18. COSY NMR spectrum of compound 3 in DMSO-d₆

Supplementary Figure 19. ¹³C-DEPTQ NMR spectrum of compound 3 in DMSO-d₆ at 151 MHz

Supplementary Figure 20. Edited-HSQC NMR spectrum of compound 3 in DMSO-d6

Supplementary Figure 21. HMBC NMR spectrum of compound 3 in DMSO-d₆

Supplementary Material

Supplementary Figure 22. ROESY NMR spectrum of compound 3 in DMSO-d₆

Supplementary Figure 23. ¹H NMR spectrum of compound 4 in DMSO-d₆ at 600 MHz

Supplementary Figure 24. COSY NMR spectrum of compound 4 in DMSO-d₆

Supplementary Figure 25. Edited-HSQC NMR spectrum of compound 4 in DMSO-d6

Supplementary Figure 26. HMBC NMR spectrum of compound 4 in DMSO-d₆

Supplementary Figure 27. ROESY NMR spectrum of compound 4 in DMSO-d₆

Supplementary Figure 28. ¹H NMR spectrum of compound 5 in DMSO-d₆ at 600 MHz

Supplementary Figure 29. ¹³C-DEPTQ NMR spectrum of compound 5 in DMSO-*d*₆ at 151 MHz

Supplementary Figure 30. Edited-HSQC NMR spectrum of compound 5 in DMSO-d₆

Supplementary Figure 31. HMBC NMR spectrum of compound 5 in DMSO-d6

Supplementary Figure 32. ¹H NMR spectrum of compound 6 in DMSO-d₆ at 600 MHz

Supplementary Figure 33. COSY NMR spectrum of compound 6 in DMSO-d₆

Supplementary Figure 34. Edited-HSQC NMR spectrum of compound 6 in DMSO-d₆

Supplementary Figure 35. HMBC NMR spectrum of compound 6 in DMSO-d6

Supplementary Figure 36. ROESY NMR spectrum of compound 6 in DMSO-d6

Supplementary Figure 37. ¹H NMR spectrum of compound 7 in DMSO-*d*₆ at 600 MHz

Supplementary Material

Supplementary Figure 38. COSY NMR spectrum of compound 7 in DMSO-d₆

Supplementary Figure 39. ¹³C NMR spectrum of compound 7 in DMSO-*d*₆ at 151 MHz

Supplementary Figure 40. Edited-HSQC NMR spectrum of compound 7 in DMSO-d₆

Supplementary Figure 41. HMBC NMR spectrum of compound 7 in DMSO-d₆

Supplementary Material

Supplementary Figure 42. ROESY NMR spectrum of compound 7 in DMSO-d6

Supplementary Figure 43. ¹H NMR spectrum of compound 8 in DMSO-d₆ at 600 MHz

Supplementary Figure 44. COSY NMR spectrum of compound 8 in DMSO-d6

Supplementary Figure 45. Edited-HSQC NMR spectrum of compound 8 in DMSO-d₆

Supplementary Material

Supplementary Figure 46. HMBC NMR spectrum of compound 8 in DMSO-d₆

Supplementary Figure 47. ROESY NMR spectrum of compound 8 in DMSO-d6

Supplementary Figure 48. ¹H NMR spectrum of compound 9 in DMSO-d₆ at 600 MHz

Supplementary Figure 49. COSY NMR spectrum of compound 9 in DMSO-d₆

Supplementary Figure 50. ¹³C-DEPTQ NMR spectrum of compound 9 in DMSO-d₆ at 151 MHz

Supplementary Figure 51. Edited-HSQC NMR spectrum of compound 9 in DMSO-d6

Supplementary Figure 52. HMBC NMR spectrum of compound 9 in DMSO-d₆

Supplementary Figure 53. ROESY NMR spectrum of compound 9 in DMSO-d6

Supplementary Figure 54. ¹H NMR spectrum of compound 10 in DMSO-*d*₆ at 600 MHz

Supplementary Figure 55. COSY NMR spectrum of compound 10 in DMSO-d6

Supplementary Figure 56. ¹³C-DEPTQ NMR spectrum of compound 10 in DMSO-d₆ at 151 MHz

Supplementary Figure 57. Edited-HSQC NMR spectrum of compound 10 in DMSO-d₆

Supplementary Figure 58. HMBC NMR spectrum of compound 10 in DMSO-d₆

Supplementary Figure 59. ROESY NMR spectrum of compound 10 in DMSO-d6

Supplementary Figure 60. ¹H NMR spectrum of compound 11 in DMSO-d₆ at 600 MHz

Supplementary Figure 61. COSY NMR spectrum of compound 11 in DMSO-d6

Supplementary Figure 62. ¹³C-DEPTQ NMR spectrum of compound 11 in DMSO-*d*₆ at 151 MHz

Supplementary Figure 63. Edited-HSQC NMR spectrum of compound 11 in DMSO-d6


Supplementary Figure 64. HMBC NMR spectrum of compound 11 in DMSO-d6



Supplementary Figure 65. ROESY NMR spectrum of compound 11 in DMSO-d6



Supplementary Figure 66. ¹H NMR spectrum of compound 12 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 67. COSY NMR spectrum of compound 12 in DMSO-d₆



Supplementary Figure 68. ¹³C-DEPTQ NMR spectrum of compound 12 in DMSO-d₆ at 151 MHz



Supplementary Figure 69. Edited-HSQC NMR spectrum of compound 12 in DMSO-d6

Supplementary Material



Supplementary Figure 70. HMBC NMR spectrum of compound 12 in DMSO-d₆



Supplementary Figure 71. ROESY NMR spectrum of compound 12 in DMSO-d₆



Supplementary Figure 72. ¹H NMR spectrum of compound 13 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 73. COSY NMR spectrum of compound 13 in DMSO-d6



Supplementary Figure 74. ¹³C-DEPTQ NMR spectrum of compound 13 in DMSO-d₆ at 151 MHz



Supplementary Figure 75. Edited-HSQC NMR spectrum of compound 13 in DMSO-d6



Supplementary Figure 76. HMBC NMR spectrum of compound 13 in DMSO-d6



Supplementary Figure 77. ROESY NMR spectrum of compound 13 in DMSO-d6



Supplementary Figure 78. ¹H NMR spectrum of compound 14 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 79. COSY NMR spectrum of compound 14 in DMSO-d₆



Supplementary Figure 80. ¹³C-DEPTQ NMR spectrum of compound 14 in DMSO-d₆ at 151 MHz



Supplementary Figure 81. Edited-HSQC NMR spectrum of compound 14 in DMSO-d6



Supplementary Figure 82. HMBC NMR spectrum of compound 14 in DMSO-d₆



Supplementary Figure 83. ROESY NMR spectrum of compound 14 in DMSO-d₆



Supplementary Figure 84. ¹H NMR spectrum of compound 15 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 85. COSY NMR spectrum of compound 15 in DMSO-d₆



Supplementary Figure 86. ¹³C-DEPTQ NMR spectrum of compound 15 in DMSO-d₆ at 151 MHz



Supplementary Figure 87. Edited-HSQC NMR spectrum of compound 15 in DMSO-d6



Supplementary Figure 88. HMBC NMR spectrum of compound 15 in DMSO-d6



Supplementary Figure 89. ROESY NMR spectrum of compound 15 in DMSO-d6



Supplementary Figure 90. ¹H NMR spectrum of compound 16 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 91. COSY NMR spectrum of compound 16 in DMSO-d6



Supplementary Figure 92. ¹³C-DEPTQ NMR spectrum of compound 16 in DMSO-d₆ at 151 MHz



Supplementary Figure 93. Edited-HSQC NMR spectrum of compound 16 in DMSO-d6

Supplementary Material



Supplementary Figure 94. HMBC NMR spectrum of compound 16 in DMSO-d₆



Supplementary Figure 95. ROESY NMR spectrum of compound 16 in DMSO-d₆



Supplementary Figure 96. ¹H NMR spectrum of compound 17 in DMSO-d₆ at 600 MHz



Supplementary Figure 97. COSY NMR spectrum of compound 17 in DMSO-d6



Supplementary Figure 98. Edited-HSQC NMR spectrum of compound 17 in DMSO-d₆



Supplementary Figure 99. HMBC NMR spectrum of compound 17 in DMSO-d₆



Supplementary Figure 100. ROESY NMR spectrum of compound 17 in DMSO-d₆



Supplementary Figure 101. ¹H NMR spectrum of compound 18 in DMSO-d₆ at 600 MHz



Supplementary Figure 102. ¹H NMR spectrum of compound 19 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 103. COSY NMR spectrum of compound 19 in DMSO-d₆



Supplementary Figure 104. ¹³C-DEPTQ NMR spectrum of compound 19 in DMSO-d₆ at 151 MHz



Supplementary Figure 105. Edited-HSQC NMR spectrum of compound 19 in DMSO-d6



Supplementary Figure 106. HMBC NMR spectrum of compound 19 in DMSO-d₆



Supplementary Figure 107. ROESY NMR spectrum of compound 19 in DMSO-d₆



Supplementary Figure 108. ¹H NMR spectrum of compound 20 in DMSO-d₆ at 600 MHz



Supplementary Figure 109. COSY NMR spectrum of compound 20 in DMSO-d6



Supplementary Figure 110. ¹³C-DEPTQ NMR spectrum of compound 20 in DMSO-d₆ at 151 MHz



Supplementary Figure 111. Edited-HSQC NMR spectrum of compound 20 in DMSO-d6



Supplementary Figure 112. HMBC NMR spectrum of compound 20 in DMSO-d₆



Supplementary Figure 113. ROESY NMR spectrum of compound 20 in DMSO-d6



Supplementary Figure 114. ¹H NMR spectrum of compound 21 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 115. COSY NMR spectrum of compound 21 in DMSO-d6



Supplementary Figure 116. Edited-HSQC NMR spectrum of compound 21 in DMSO-d₆



Supplementary Figure 117. HMBC NMR spectrum of compound 21 in DMSO-d6



Supplementary Figure 118. ROESY NMR spectrum of compound 21 in DMSO-d6



Supplementary Figure 119. ¹H NMR spectrum of compound 22 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 120. COSY NMR spectrum of compound 22 in DMSO-d6



Supplementary Figure 121. ¹³C-DEPTQ NMR spectrum of compound 22 in DMSO-d₆ at 151 MHz



Supplementary Figure 122. Edited-HSQC NMR spectrum of compound 22 in DMSO-d₆



Supplementary Figure 123. HMBC NMR spectrum of compound 22 in DMSO-d6



Supplementary Figure 124. ROESY NMR spectrum of compound 22 in DMSO-d₆



Supplementary Figure 125. ¹H NMR spectrum of compound 23 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 126. COSY NMR spectrum of compound 23 in DMSO-d₆



Supplementary Figure 127. ¹³C-DEPTQ NMR spectrum of compound 23 in DMSO-d₆ at 151 MHz



Supplementary Figure 128. Edited-HSQC NMR spectrum of compound 23 in DMSO-d6



Supplementary Figure 129. HMBC NMR spectrum of compound 23 in DMSO-d6



Supplementary Figure 130. ROESY NMR spectrum of compound 23 in DMSO-d₆



Supplementary Figure 131. ¹H NMR spectrum of compound 24 in DMSO-*d*₆ at 600 MHz



Supplementary Figure 132. COSY NMR spectrum of compound 24 in DMSO-d₆



Supplementary Figure 133. ¹³C-DEPTQ NMR spectrum of compound 24 in DMSO-d₆ at 151 MHz



Supplementary Figure 134. Edited-HSQC NMR spectrum of compound 24 in DMSO-d₆



Supplementary Figure 135. HMBC NMR spectrum of compound 24 in DMSO-d6


Supplementary Figure 136. ROESY NMR spectrum of compound 24 in DMSO-d₆

Supplementary Table 1. Chromatographic conditions optimized at the UHPLC level and transferred to the analytical and semipreparative HPLC scale

Biotrans.	UHPLC (100 x 2.1 mm i.d., 1.7				HPLC (250 x 4.6 mm i.d., 5				Semipreparative HPLC (250 x 19 mm i.d.,			
reaction	Flow-rate (mL/min)	μm) %A	%B	Time (min)	Flow- rate (mL/min)	μm) %A	%B	Time (min)	Flow-rate (mL/min)	%A	%B	Time (min)
Caffeic acid	0.4	95	5	0	1	95	5	0	17	95	5	0
		95	5	0.05		40	60	60		40	60	60
		40	60	12.92		0	100	61		0	100	61
		0	100	13.14		0	100	70		0	100	70
		0	100	15.07								
Ferulic acid	0.4	70	30	0	1	70	30	0	17	70	30	0
		70	30	0.05		45	55	30		45	55	30
		45	55	6.49		35	65	60		35	65	60
		35	65	12.92		0	100	61		0	100	61
		0	100	13.14		0	100	70		0	100	70
		0	100	15.07								
Mixture caffeic/ferulic acid	0.4	80	20	0	1	80	20	0	17	80	20	0
		80	20	0.05		40	60	60		40	60	60
		40	60	12.92		0	100	61		0	100	61
		0	100	13.14		0	100	70		0	100	70
		0	100	15.07								