Supporting Information

Figure S1. $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of compound 1
Figure S2. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of compound 1
Figure S3. HMQC (DMSO-$d_6$) spectrum of compound 1
Figure S4. $^1$H-$^1$H COSY (DMSO-$d_6$) spectrum of compound 1
Figure S5. HMBC spectrum (DMSO-$d_6$) of compound 1
Figure S6. HRMSIMS spectrum of compound 1
Figure S7. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 3
Figure S8. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 3
Figure S9. HMQC (CDCl$_3$) spectrum of compound 3
Figure S10. $^1$H-$^1$H COSY (CDCl$_3$) spectrum of compound 3
Figure S11. HMBC (CDCl$_3$) spectrum of compound 3
Figure S12. NOESY (CDCl$_3$) spectrum of compound 3
Figure S13. HRMSIMS spectrum of compound 3
Figure S14. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 4
Figure S15. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 4
Figure S16. HMQC (CDCl$_3$) spectrum of compound 4
Figure S17. $^1$H-$^1$H COSY (CDCl$_3$) spectrum of compound 4
Figure S18. HMBC (CDCl$_3$) spectrum of compound 4
Figure S19. HRMSIMS spectrum of compound 4
Figure S20. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 13a-1/13b-1
Figure S21. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 13a-1/13b-1
Figure S22. ESIMS spectrum of compounds 13a-1/13b-1
Figure S23. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 13a-2/13b-2
Figure S24. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 13a-2/13b-2
Figure S25. ESIMS spectrum of compounds 13a-2/13b-2
Figure S26. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 13a-3/13b-3
Figure S27. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 13a-3/13b-3
Figure S28. ESIMS spectrum of compounds 13a-3/13b-3
Figure S29. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 14a/14b
Figure S30. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 14a/14b
Figure S31. ESIMS spectrum of compounds 14a/14b
Figure S32. The determination of the absolute configuration of 1 by Marfey’s Method
S1. The spectroscopic data of 13a-1/13b-1, 13a-2/13b-2, 13a-3/13b-3, 14a/14b
Figure S1. $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of compound 1.

Figure S2. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of compound 1.
Figure S3. HMQC (DMSO-$d_6$) spectrum of compound 1.

Figure S4. $^1$H-$^1$H COSY (DMSO-$d_6$) spectrum of compound 1.
Figure S5. HMBC spectrum (DMSO-$d_6$) of compound 1.

Figure S6. HRESIMS spectrum of compound 1.
Figure S7. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 3.

Figure S8. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 3.
Figure S9. HMQC (CDCl$_3$) spectrum of compound 3.

Figure S10. $^1$H-$^1$H COSY (CDCl$_3$) spectrum of compound 3.
Figure S11. HMBC (CDCl$_3$) spectrum of compound 3.

Figure S12. NOESY (CDCl$_3$) spectrum of compound 3.
Figure S13. HRESIMS spectrum of compound 3.

Figure S14. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 4.
Figure S15. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 4.

Figure S16. HMQC (CDCl$_3$) spectrum of compound 4.
Figure S17. $^1$H–$^1$H COSY (CDCl$_3$) spectrum of compound 4.

Figure S18. HMBC (CDCl$_3$) spectrum of compound 4.
Figure S19. HRESIMS spectrum of compound 4.

Figure S20. $^1$H NMR (400 MHz, Acetone-$_d_6$) spectrum of compounds 13a-1/13b-1.
Figure S21. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 13a-1/13b-1.

Figure S22. ESIMS spectrum of compounds 13a-1/13b-1.
Figure S23. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 13a-2/13b-2.

Figure S24. $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 13a-2/13b-2.
Figure S25. ESIMS spectrum of compounds 13a-2/13b-2.

Figure S26. $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 13a-3/13b-3.
**Figure S27.** \(^{13}\)C NMR (100 MHz, Acetone-\(d_6\)) spectrum of compounds 13a-3/13b-3.

**Figure S28.** ESIMS spectrum of compounds 13a-3/13b-3.
**Figure S29.** $^1$H NMR (400 MHz, Acetone-$d_6$) spectrum of compounds 14a/14b.

**Figure S30.** $^{13}$C NMR (100 MHz, Acetone-$d_6$) spectrum of compounds 14a/14b.
Figure S31. ESIMS spectrum of compounds 14a/14b.
Figure S32. The determination of the absolute configuration of 1 by Marfey’s Method (A–G) (HPLC analysis solvents: A, H$_2$O + 0.1% TFA, B, MeCN; linear gradient: 0 min, 25% B; 40 min, 60% B; 45 min, 100% B; temperature, 30 °C; flow rate, 1 mL/min; UV detection at $\lambda$ 340 nm; FDAA, 14.2 min).

(A) FDAA derivatives of standard L- and D-Phe

(B) FDAA derivative of standard L-Phe

(C) FDAA derivatives of (S)-2-amino-3-(4-methoxyphenyl)-1-propanol and (R)-2-amino-3-(4-methoxyphenyl)-1-propanol (14a)
Figure S32. Cont.

(D) FDAA derivative of (S)-2-amino-3-(4-methoxyphenyl)-1-propanol (14b)

(E) FDAA derivatives of the hydrolysates from 1

(F) Co-injection of FDAA derivatives of the hydrolysates from 1 with FDAA derivative of standard L-Phe

(G) Co-injection of FDAA derivatives of the hydrolysates from 1 with FDAA derivative of (S)-2-amino-3-(4-methoxyphenyl)-1-propanol (14b)
S1. The Spectroscopic Data of 13a-1, 13b-1, 13a-2, 13b-2, 13a-3, 13b-3, 14a and 14b

(S/R)-3-(4-Hydroxyphenyl)-2-[(ethoxycarbonyl)amino] propionic acid (13a-1) and (S)-3-(4-hydroxyphenyl)-2-[(ethoxycarbonyl)amino] propionic acid (13b-1): $^1$H NMR (400 MHz, acetone-$d_6$, $\delta$, ppm, J/Hz): 7.11 (2H, d, $J = 7.6$ Hz), 6.76 (2H, d, $J = 7.6$ Hz), 6.19 (1H, d, $J = 8.0$ Hz), 4.42 (1H, m), 3.99 (2H, q, $J = 7.0$ Hz), 3.11 (1H, dd, $J = 13.9, 4.4$ Hz), 2.91 (1H, dd, $J = 13.9, 5.2$ Hz), 1.14 (3H, t, $J = 7.0$ Hz). $^{13}$C NMR (100 MHz, acetone-$d_6$, $\delta$, ppm): 172.6 (C), 172.6 (C), 156.2 (C), 130.2 (CH), 130.2 (CH), 128.0 (C), 115.1 (CH), 115.1 (CH), 60.1 (CH$_2$), 55.4 (CH$_2$), 36.5 (CH$_2$), 14.0 (CH$_3$). ESIMS: 252.1 [M − H]$^-$.

Methyl (S/R)-2-[(ethoxycarbonyl)amino]-3-(4-methoxyphenyl) propanoate (13a-2) and methyl (S)-2-[(ethoxycarbonyl)amino]-3-(4-methoxyphenyl) propanoate (13b-2): $^1$H NMR (400 MHz, acetone-$d_6$, $\delta$, ppm, J/Hz): 7.18 (2H, d, $J = 7.8$ Hz), 6.85 (2H, d, $J = 7.8$ Hz), 6.41 (1H, d, $J = 7.6$ Hz), 4.40 (1H, dd, $J = 14.0, 7.6$ Hz), 3.99 (2H, q, $J = 6.9$ Hz), 3.75 (3H, s), 3.66 (3H, s), 3.07 (1H, dd, $J = 13.9, 5.0$ Hz), 2.94 (1H, dd, $J = 13.9, 8.9$ Hz), 1.14 (3H, t, $J = 6.9$ Hz). $^{13}$C NMR (100 MHz, acetone-$d_6$, $\delta$, ppm): 172.4 (C), 172.4 (C), 158.1 (C), 130.2 (CH), 130.2 (CH), 129.0 (C), 113.7 (CH), 113.7 (CH), 60.3 (CH$_2$), 55.6 (CH), 54.6 (CH$_3$), 51.5 (CH$_3$), 36.6 (CH$_2$), 14.1 (CH$_3$). ESIMS: 282.3 [M + H]$^+$.

(S/R)-2-[(Ethoxycarbonyl)amino]-3-(4-methoxyphenyl) propan-1-ol (13a-3) and (S)-2-[(ethoxycarbonyl)amino]-3-(4-methoxyphenyl) propan-1-ol (13b-3): $^1$H NMR (400 MHz, acetone-$d_6$, $\delta$, ppm, J/Hz): 7.21 (2H, d, $J = 7.6$ Hz), 6.86 (2H, d, $J = 7.6$ Hz), 6.11 (1H, d, $J = 7.8$ Hz), 4.15 (1H, m), 4.02 (2H, q, $J = 7.0$ Hz), 3.76 (3H, s), 3.38 (2H, m), 2.91 (1H, dd, $J = 13.6, 6.4$ Hz), 2.76 (1H, dd, $J = 13.6, 7.8$ Hz), 1.16 (3H, t, $J = 7.0$ Hz). $^{13}$C NMR (100 MHz, acetone-$d_6$, $\delta$, ppm): 159.1 (C), 157.3 (C), 131.8 (C), 131.1 (CH), 131.1 (CH), 114.5 (CH), 114.5 (CH), 64.1 (CH$_2$), 60.8 (CH$_2$), 55.6 (CH), 55.5 (CH$_3$), 37.1 (CH$_2$), 15.1 (CH$_3$). ESIMS: 252.1 [M − H]$^-$.

(S/R)-2-Amino-3-(4-methoxyphenyl)-1-propanol (14a) and (S)-2-amino-3-(4-methoxyphenyl)-1-propanol (14b): $^1$H NMR (400 MHz, acetone-$d_6$, $\delta$, ppm, J/Hz): 7.17 (2H, d, $J = 7.5$ Hz), 6.84 (2H, d, $J = 7.5$ Hz), 3.75 (3H, s), 3.55 (1H, m), 3.74 (1H, t, $J = 7.4$ Hz), 3.29 (1H, t, $J = 7.4$ Hz), 2.84 (1H, dd, $J = 13.5, 6.5$ Hz), 2.67 (1H, dd, $J = 13.5, 7.4$ Hz). $^{13}$C NMR (100 MHz, acetone-$d_6$, $\delta$, ppm): 159.2 (C), 132.2 (C), 130.7 (CH), 130.7 (CH), 114.5 (CH), 114.5 (CH), 71.0 (CH$_2$), 60.5 (CH), 55.4 (CH$_3$), 39.1 (CH$_2$). ESIMS: 182.2 [M + H]+$^+$.