Supporting Information

Figure S1. ¹H NMR (600 MHz, DMSO- d_6) spectrum of compound 1 Figure S2. ¹³C NMR (150 MHz, DMSO- d_6) spectrum of compound 1 Figure S3. HMQC (DMSO-*d*₆) spectrum of compound 1 Figure S4. ${}^{1}\text{H}-{}^{1}\text{H}$ 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. ¹H NMR (600 MHz, CDCl₃) spectrum of compound **3** Figure S8. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound 3 Figure S9. HMQC (CDCl₃) spectrum of compound 3 Figure S10. ¹H-¹H COSY (CDCl₃) spectrum of compound 3 Figure S11. HMBC (CDCl₃) spectrum of compound 3 Figure S12. NOESY (CDCl₃) spectrum of compound 3 Figure S13. HRESIMS spectrum of compound 3 Figure S14. ¹H NMR (600 MHz, CDCl₃) spectrum of compound 4 Figure S15. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound 4 Figure S16. HMQC (CDCl₃) spectrum of compound 4 Figure S17. ¹H-¹H COSY (CDCl₃) spectrum of compound 4 Figure S18. HMBC (CDCl₃) spectrum of compound 4 Figure S19. HRESIMS spectrum of compound 4 Figure S20. ¹H NMR (400 MHz, Acetone- d_6) spectrum of compounds 13a-1/13b-1 Figure S21. ¹³C 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. ¹H NMR (400 MHz, Acetone- d_6) spectrum of compounds 13a-2/13b-2 Figure S24. ¹³C 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. ¹H NMR (400 MHz, Acetone- d_6) spectrum of compounds 13a-3/13b-3 Figure S27. ¹³C 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. ¹H NMR (400 MHz, Acetone- d_6) spectrum of compounds 14a/14b Figure S30. ¹³C 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. ¹H NMR (600 MHz, DMSO- d_6) spectrum of compound 1.

Figure S2. ¹³C 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 S6. HRESIMS spectrum of compound 1.

Element	al Compositi	on Report									Page 1
Single N Toleranc Isotope c	lass Analysis e = 5.0 PPM cluster parame	/ DBE: m eters: Sepa	nin = -1.5 ration =	5, max = 50 1.0 Abur	0.0 ndance = 1	.0%					
Monoisoto 4 formula(e	pic Mass, Odd ar e) evaluated with	nd Even Elec 1 results with	tron lons hin limits (all results (u	p to 1000) for	r each mass)					
Z3121A 20110512-Z3 100-	3121A 85 (3.030) AM	(Cen,8, 80.00, I	Ht,5000.0,0.	00,1.00); Sm (N	/ld, 3.00); Cm (8	5:94)	559	2215			TOF MS ES+
-											259
%-	512.4988			537.2444	540.5376	5	56.2771	560.2321			
0	507.2278	515.1564	529.2	336 531 2396	541.539	7 5334 549.2019	1	561.2321568.57	575.2060	584.5742	, 591.2117.596.5951
Minimum	510.0	520.0	53	0.0	540.0	550.0	5	60.0 57	0.0	580.0	590.0 m/z
Maximum:		200.0	5.0	-1.5 50.0							
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula					
559.2215	559.2209	0.6	1.1	18.5	1	C33 H32	N2 0	5 Na			



Figure S7. ¹H NMR (600 MHz, CDCl₃) spectrum of compound 3.



Figure S9. HMQC (CDCl₃) spectrum of compound 3.

Figure S10. ¹H-¹H COSY (CDCl₃) spectrum of compound **3**.





Figure S11. HMBC (CDCl₃) spectrum of compound 3.

Figure S12. NOESY (CDCl₃) spectrum of compound 3.



Figure S13. HRESIMS spectrum of compound 3.









Figure S15. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound 4.

Figure S16. HMQC (CDCl₃) spectrum of compound 4.





Figure S17. ¹H-¹H COSY (CDCl₃) spectrum of compound **4**.

Figure S18. HMBC (CDCl₃) spectrum of compound 4.









1237 1046 7731 7543	1795	4001 33878 33878 33878 33878 99157 0957 0957 0957 0957 0957 0957 0957 09	1588 1413
6.23.	6.6	444 4 m m m m m m m m m m m m m m m m m	41.1-



Figure S21. ¹³C NMR (100 MHz, Acetone- d_6) spectrum of compounds 13a-1/13b-1.





		Mass Spe	ctrum List	Report	
Analysis Info				Acquisition Date	3/7/2013 3:02:25 PM
Analysis Name	D:\Data\zheng caiju	an\001.d			
Method	DEF MS.M		Operator	bruker	
Sample Name DL1				Instrument	HCT
Comment					
Acquisition Para	ameter				
Ion Source Type	ESI	Ion Polarity	Negative	Alternating Ion F	Polarity off
Mass Range Mode	Ultra Scan	Scan Begin	100 m/z	Scan End	500 m/z
Capillary Exit	-113.5 Volt	Skimmer	-40.0 Volt	Trap Drive	46.3
Accumulation Time	139 µs	Averages	3 Spectra	Auto MS/MS	off





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

Figure S24. ¹³C NMR (100 MHz, Acetone- d_6) spectrum of compounds 13a-2/13b-2.





Figure S25. ESIMS spectrum of compounds 13a-2/13b-2.





Figure S27. ¹³C 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. ¹H NMR (400 MHz, Acetone- d_6) spectrum of compounds 14a/14b.

Figure S30. ¹³C NMR (100 MHz, Acetone- d_6) spectrum of compounds 14a/14b.

1968	2281 7139	5859	504	114 921	283
	~132.	-114.	-71.0	60. 5 55. 4	-39.1



Mass Spectrum List Report						
Analysis Info				Acquisition Date	e 3/7/2013 3:11:22 PM	
Analysis Name Method Sample Name Comment	D:\Data\zheng caijı DEF_MS.M DL4	uan\004.d		Operator Instrument	bruker HCT	
Acquisition Para lon Source Type Mass Range Mode Capillary Exit Accumulation Time	ESI Ultra Scan 109.8 Volt 69 µs	lon Polarity Scan Begin Skimmer Averages	Positive 100 m/z 40.0 Volt 3 Spectra	Alternating loi Scan End Trap Drive Auto MS/MS	n Polarity off 500 m/z 31.7 off	
Intens. x10 ⁸					+MS, 0.1-0.5min #(18-17	
- - 5-	182.2					
-						
4-						
3-						
2-						
1-						
	165.1			363.2 40	05.3 	
0-4	150 200	250	300	350 400	0 450 n	

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, H₂O + 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 λ 340 nm; FDAA, 14.2 min).



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



(E) FDAA derivatives of the hydrolysates from 1

分钟

(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): ¹H NMR (400 MHz, acetone- d_6 , δ, 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). ¹³C NMR (100 MHz, acetone- d_6 , δ, 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 (CH₂), 55.4 (CH), 36.5 (CH₂), 14.0 (CH₃). 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): ¹H NMR (400 MHz, acetone- d_6 , δ , 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). ¹³C NMR (100 MHz, acetone- d_6 , δ , 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 (CH₂), 55.6 (CH), 54.6 (CH₃), 51.5 (CH₃), 36.6 (CH₂), 14.1 (CH₃). 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): ¹H NMR (400 MHz, acetone- d_6 , δ, 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). ¹³C NMR (100 MHz, acetone- d_6 , δ, ppm): 159.1 (C), 157.3 (C), 131.8 (C), 131.1 (CH), 131.1 (CH), 114.5 (CH), 114.5 (CH), 64.1 (CH₂), 60.8 (CH₂), 55.6 (CH), 55.5 (CH₃), 37.1 (CH₂), 15.1 (CH₃). 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): ¹H NMR (400 MHz, acetone- d_6 , δ, 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). ¹³C NMR (100 MHz, acetone- d_6 , δ, ppm): 159.2 (C), 132.2 (C), 130.7 (CH), 130.7 (CH), 114.5 (CH), 114.5 (CH), 71.0 (CH₂), 60.5 (CH), 55.4 (CH₃), 39.1 (CH₂). ESIMS: 182.2 [M + H]⁺.