Supporting Information for

A Near IR Fluorescent Probe for Enantioselective Recognition of Amino Acids in Aqueous Solution

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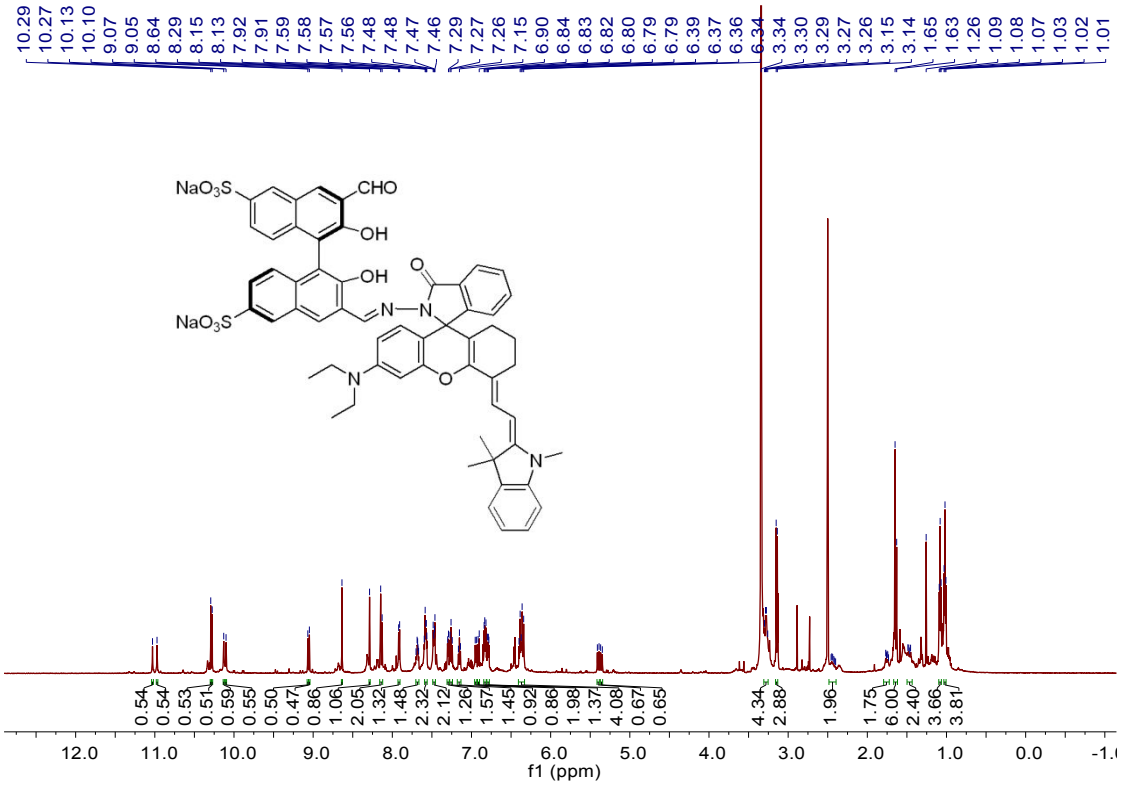
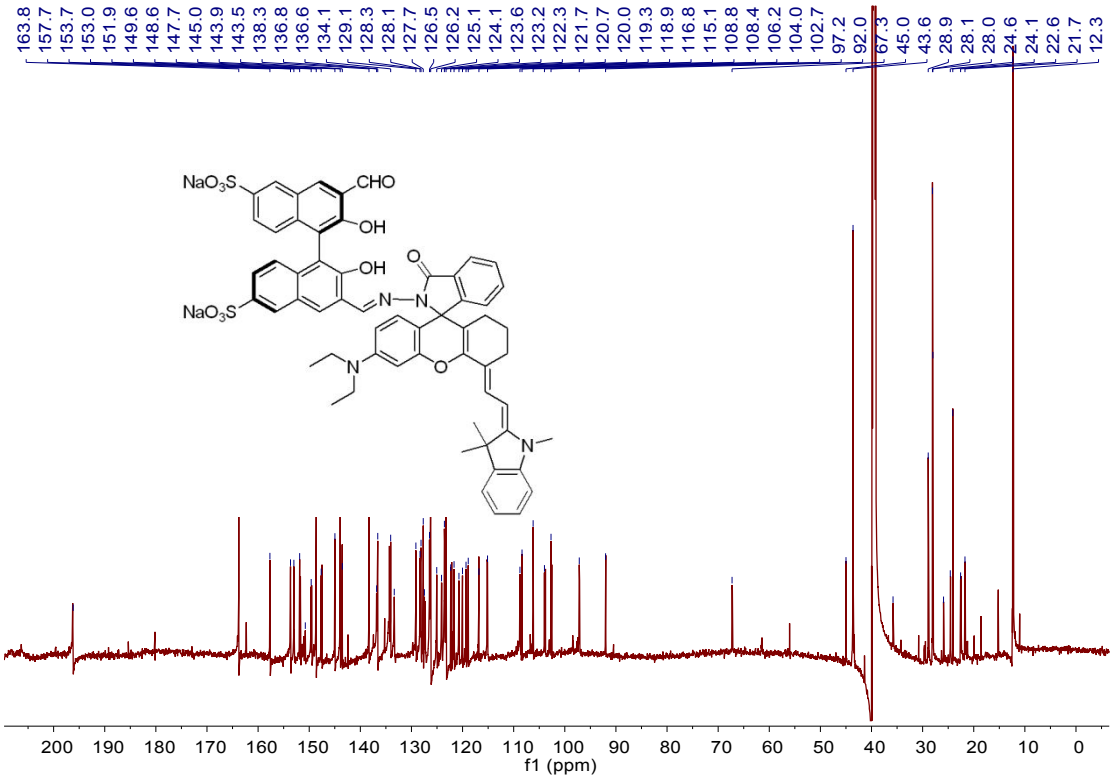
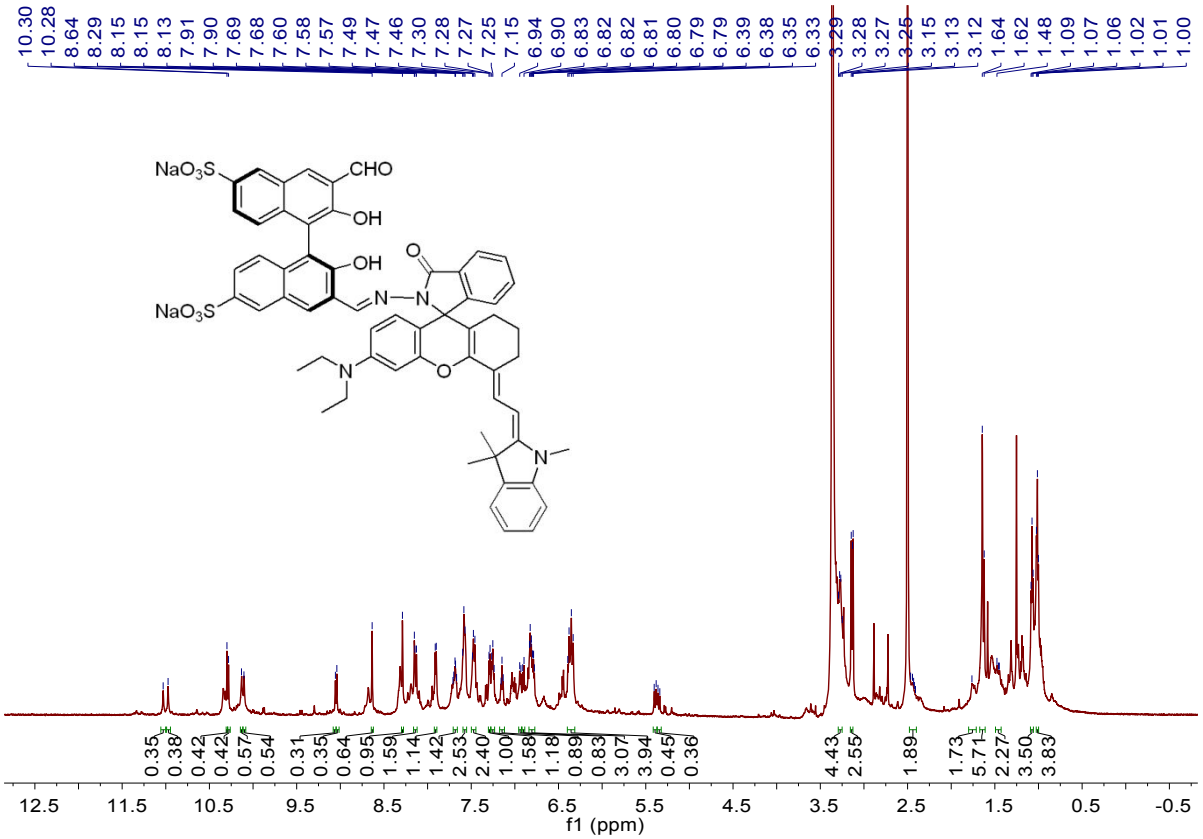
^{1}H NMR (600 MHz) spectra of (*R*)-**4** in DMSO-d_6



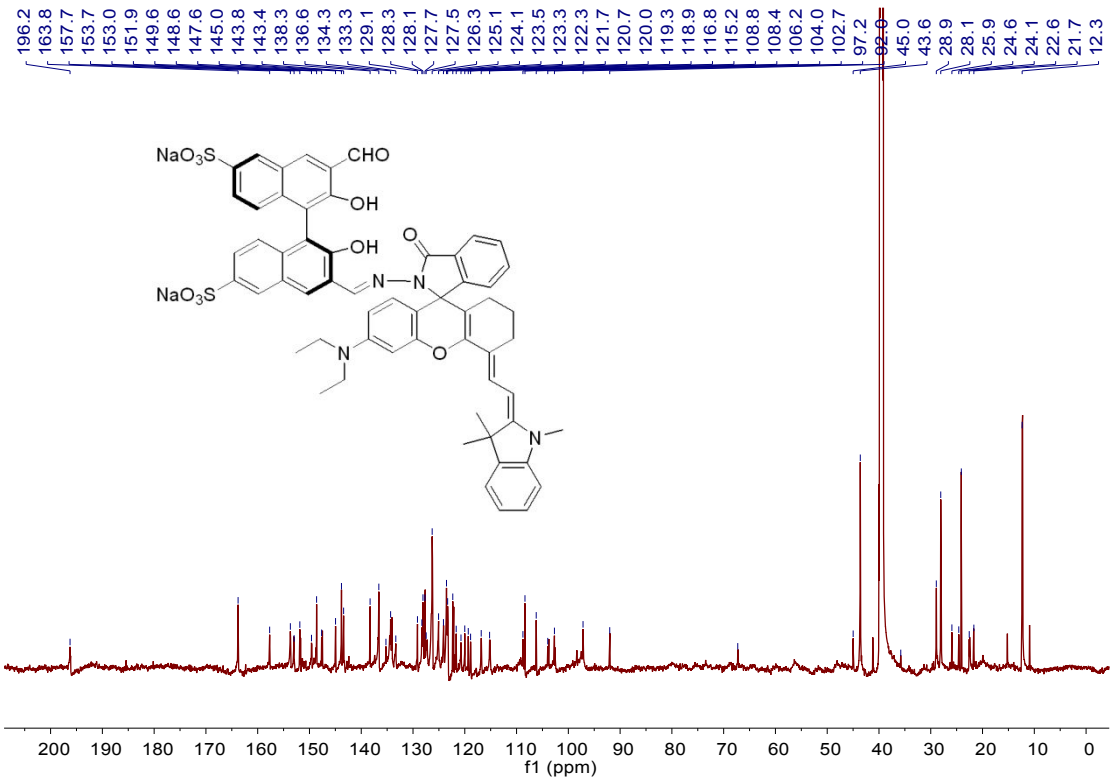
^{13}C{^{1}H} NMR (201 MHz) spectra of (*R*)-**4** in DMSO-d_6



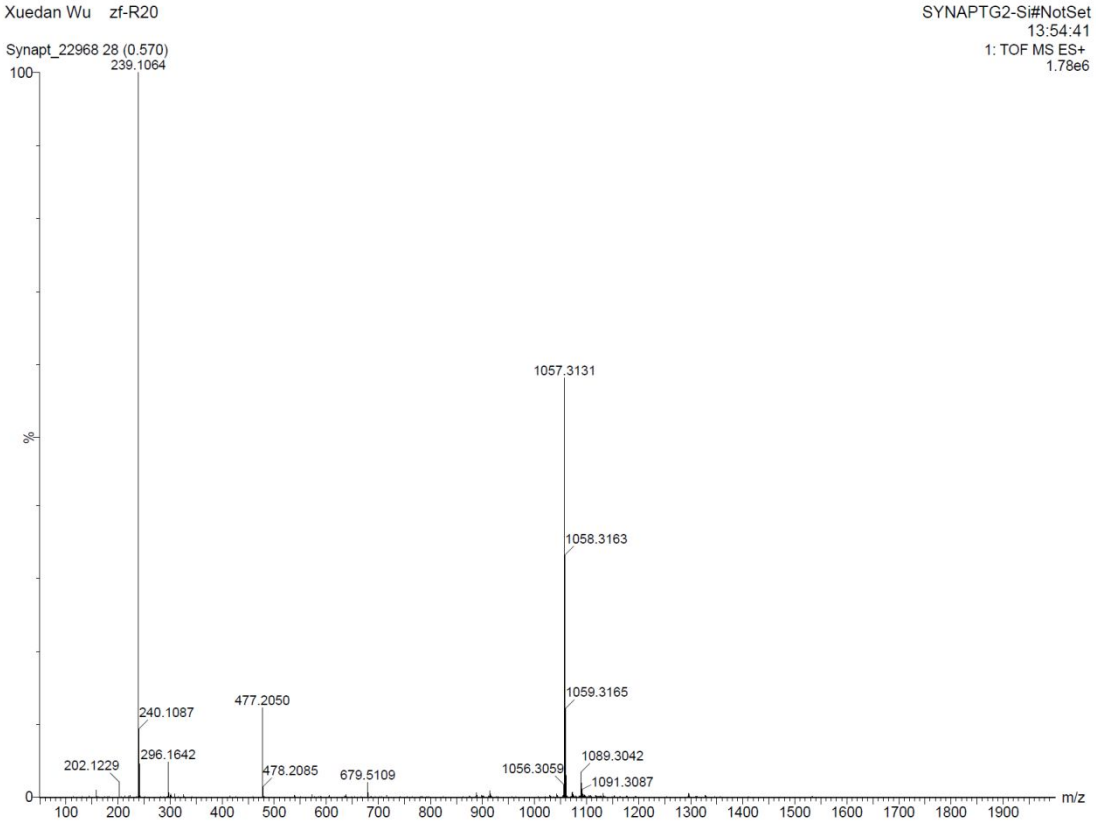
^{1}H NMR (600 MHz) spectra of (*S*)-**4** in DMSO-d_6



^{13}C{^{1}H} NMR (201 MHz) spectra of (*S*)-**4** in DMSO-d_6



HRMS of (*R*)-**4**



HRMS of (*S*)-**4**

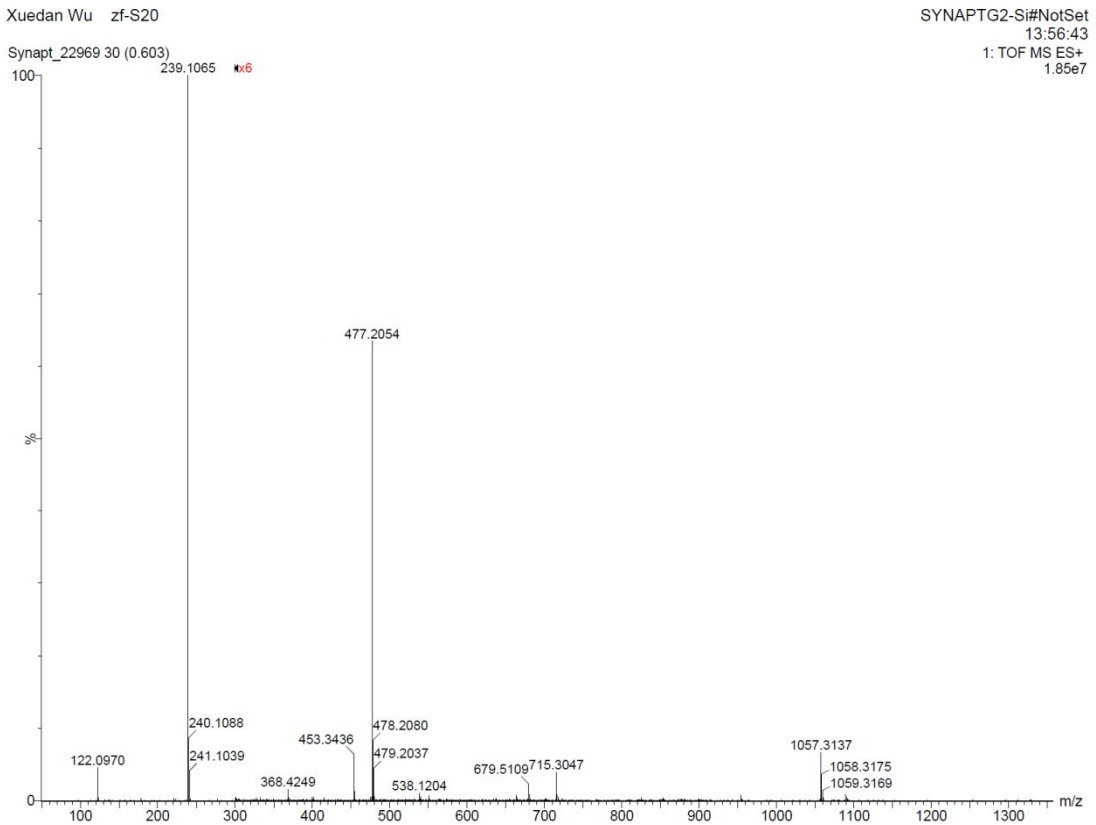
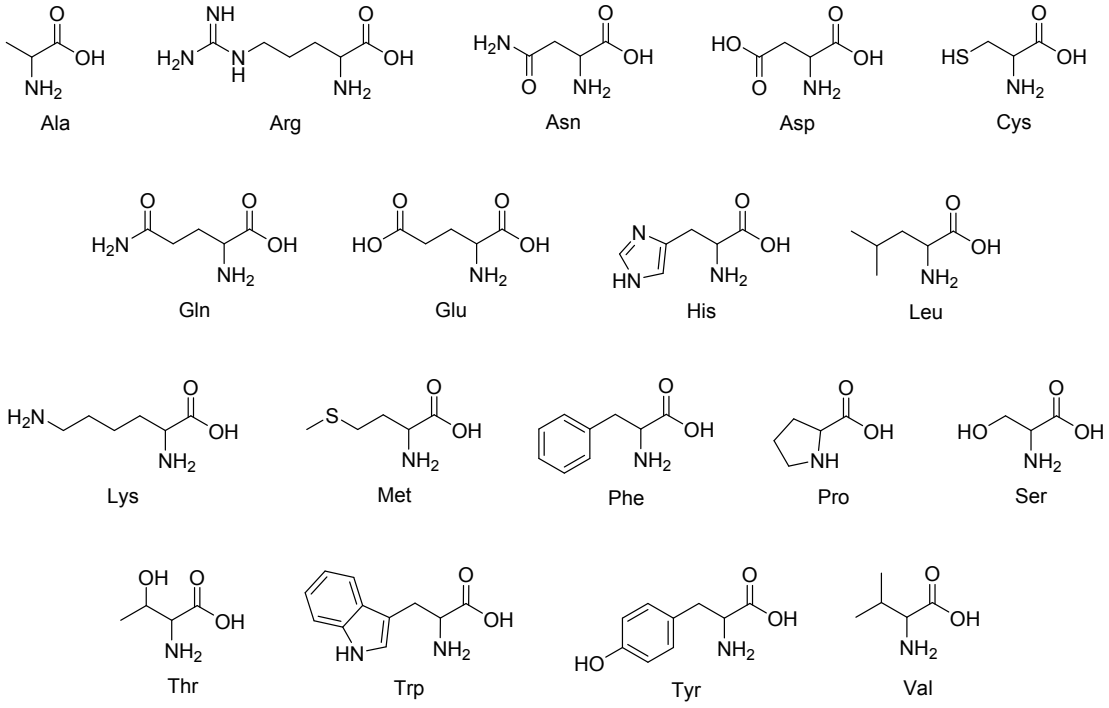


Figure S1. Structures of amino acids studied.



2. Fluorescence spectra of 4 with methionine

Figure S2. Fluorescence spectra of (*R*)-**4**+Zn^{2+} (2 equiv) (10 μM) with various equiv of D-Met or L-Met in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of methionine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

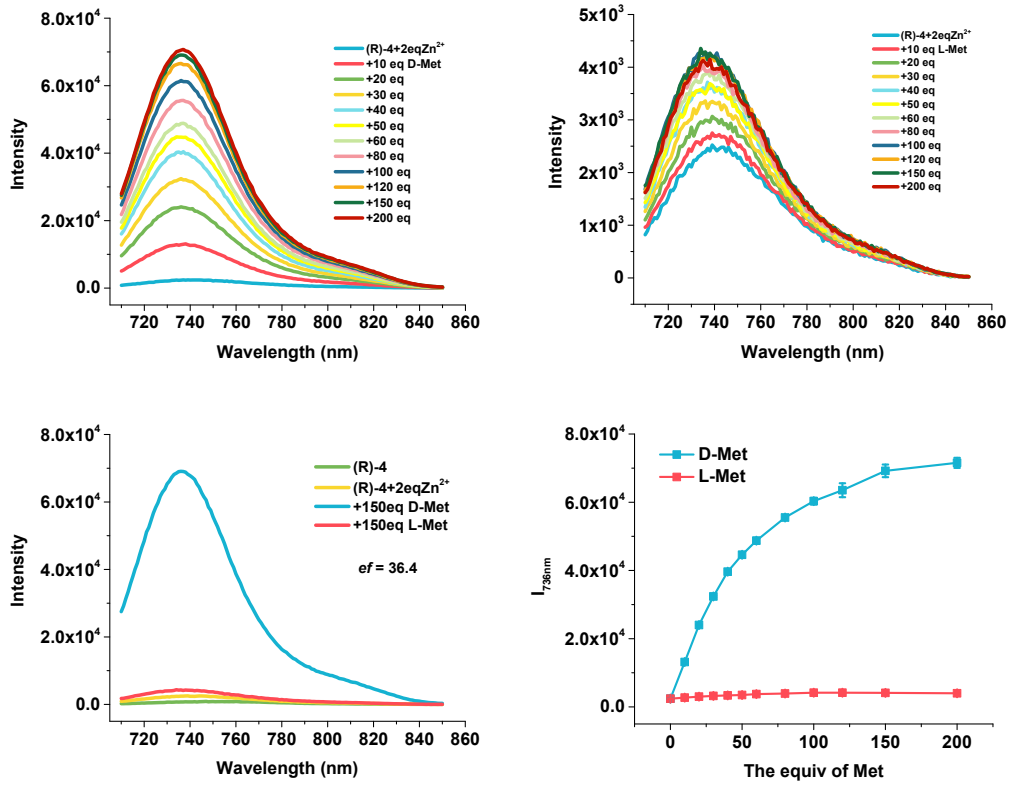


Figure S3. Fluorescence spectra of (*S*)-**4**+Zn^{2+} (2 equiv) (10 μM) with various equiv of D-Met or L-Met in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of methionine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

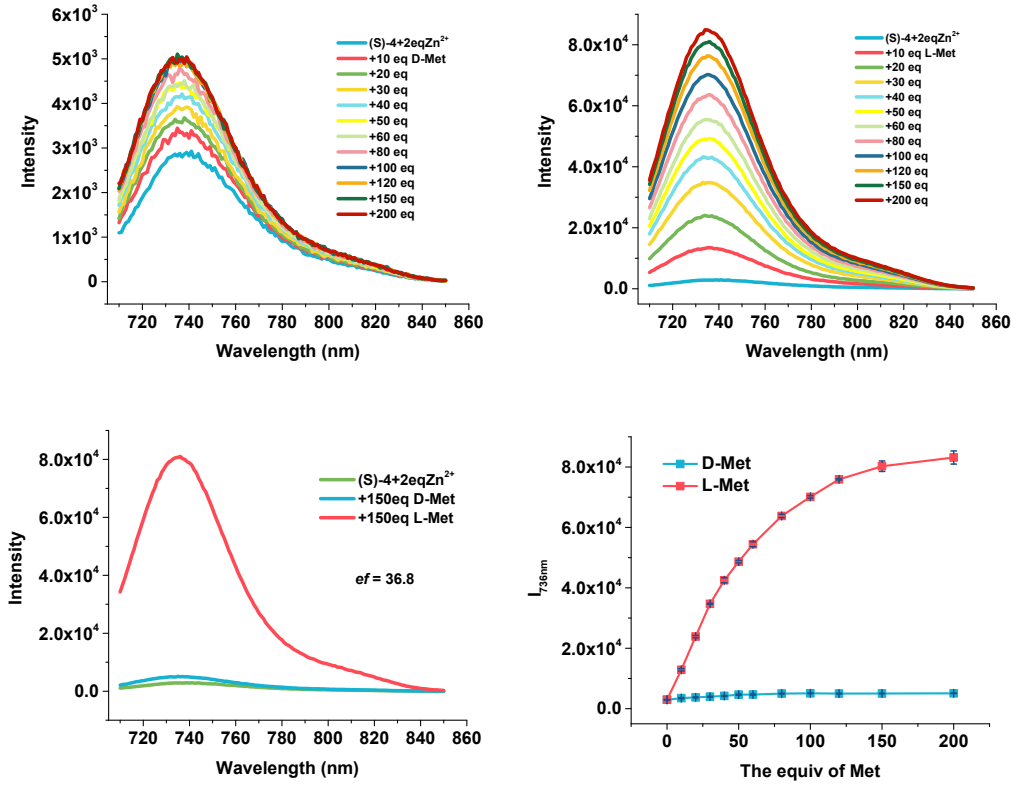


Figure S4. Fluorescence spectra of (*R*)-**4** and (*S*)-**4** (10 μM)+Zn^{2+} (2 equiv) (1.0×10^{-5} M) in the presence of the enantiomeric mixture of methionine (150 equiv) [from 0% to 100% D-Met]. Fluorescence intensity at 736 nm versus the enantiomeric purity of methionine. Spectra were recorded at rt after mixing at 37 °C for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

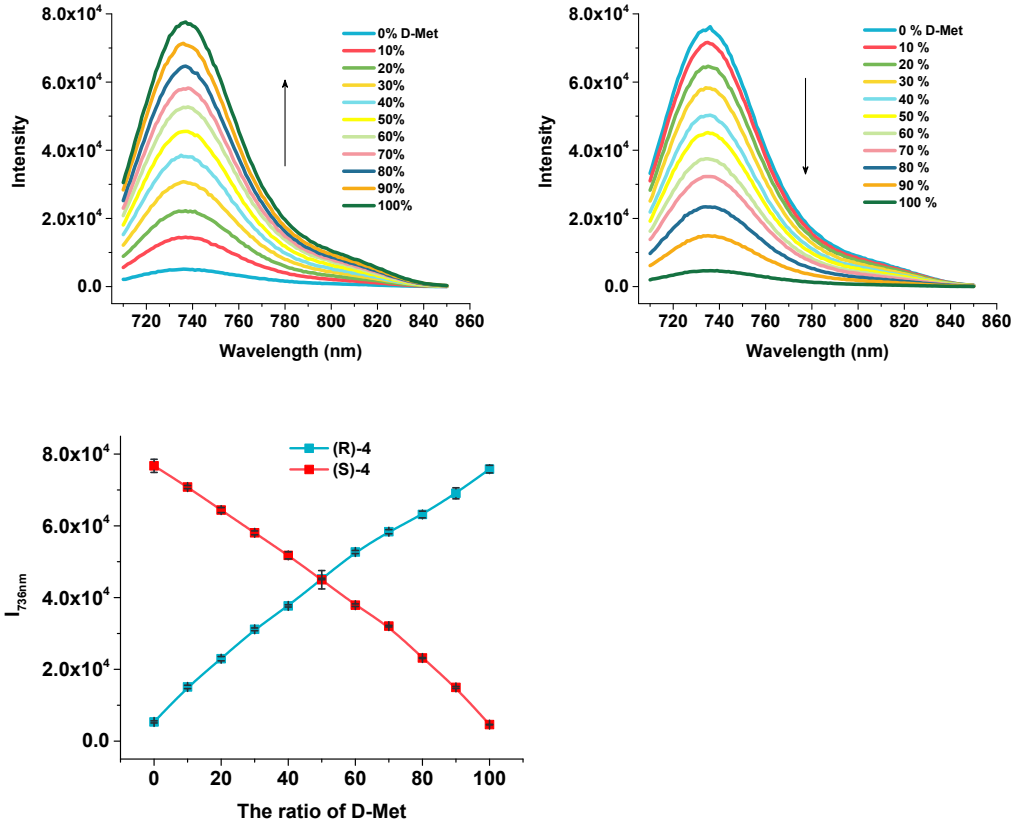


Figure S5. Fluorescence spectra of (*R*)-**4** (1.0×10^{-5} M) with various equiv of Zn^{2+} in 50 mM HEPES buffer (pH = 7.4)/1% DMSO in the presence of 150 equiv of D-Met or L-Met. Fluorescence intensity at 736 nm versus the equiv of $Zn(OAc)_2$. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

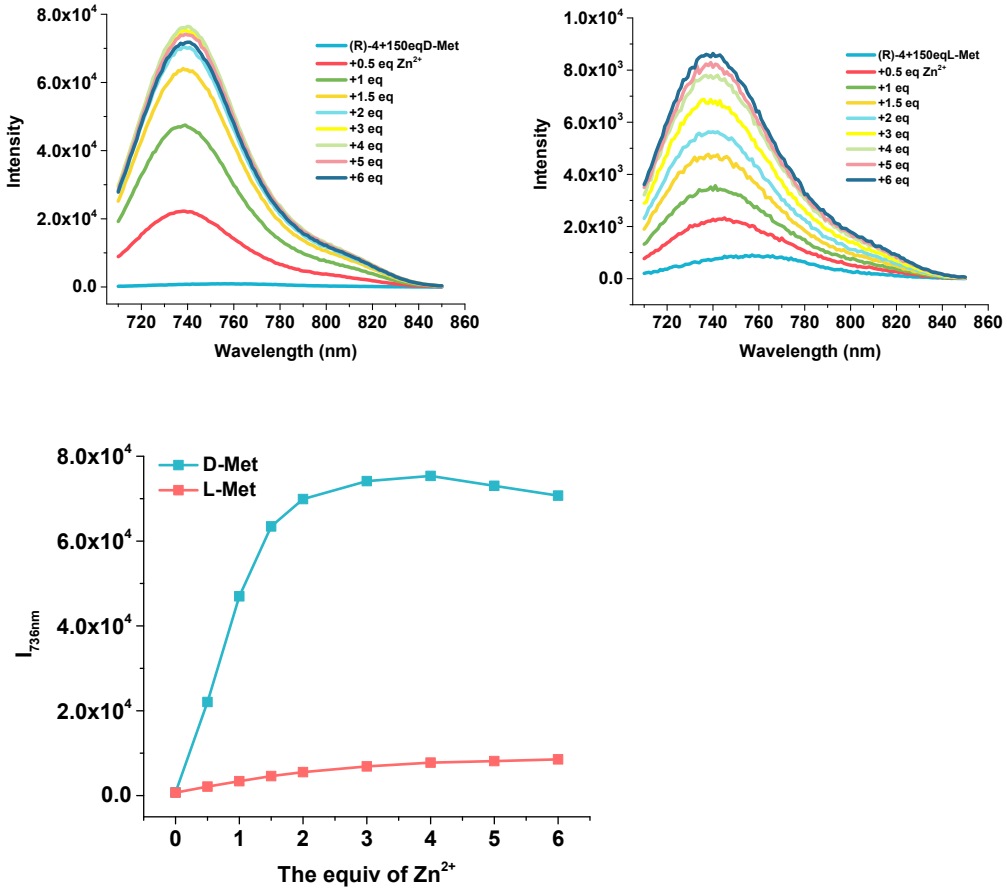
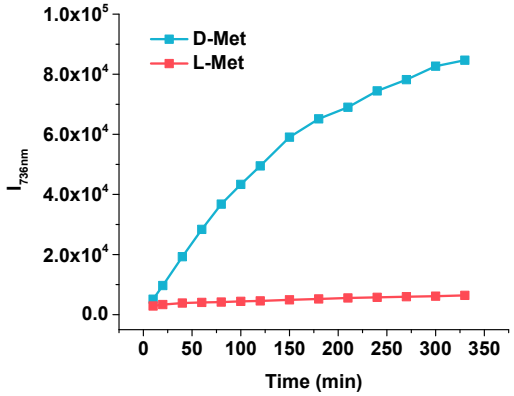


Figure S6. Time dependence fluorescence responses. (*R*)-**4** (1.0×10^{-5} M in 50 mM HEPES at pH = 7.4 / 1% DMSO) and Zn^{2+} (2 equiv) were placed in a 10 mL test tube, to which was added D- or L- Met (150 equiv). The resulting solutions were allowed to stand at 37 °C for 10, 20, 40, 60, 80, 100, 120, 150, 180, 210, 240, 270, 300 and 330 min respectively and each fluorescent spectrum was recorded at rt. This figure plots the fluorescent intensities at 736 nm versus the reaction time. (λ_{exc} = 690 nm, slits = 5/5 nm)



3. Fluorescence spectra of (*R*)-4 with amino acids

Figure S7. Fluorescence spectra of (*R*)-**4** (10 μM)+Zn^{2+} (2 equiv) with various equiv of D- or L-Ala in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of alanine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

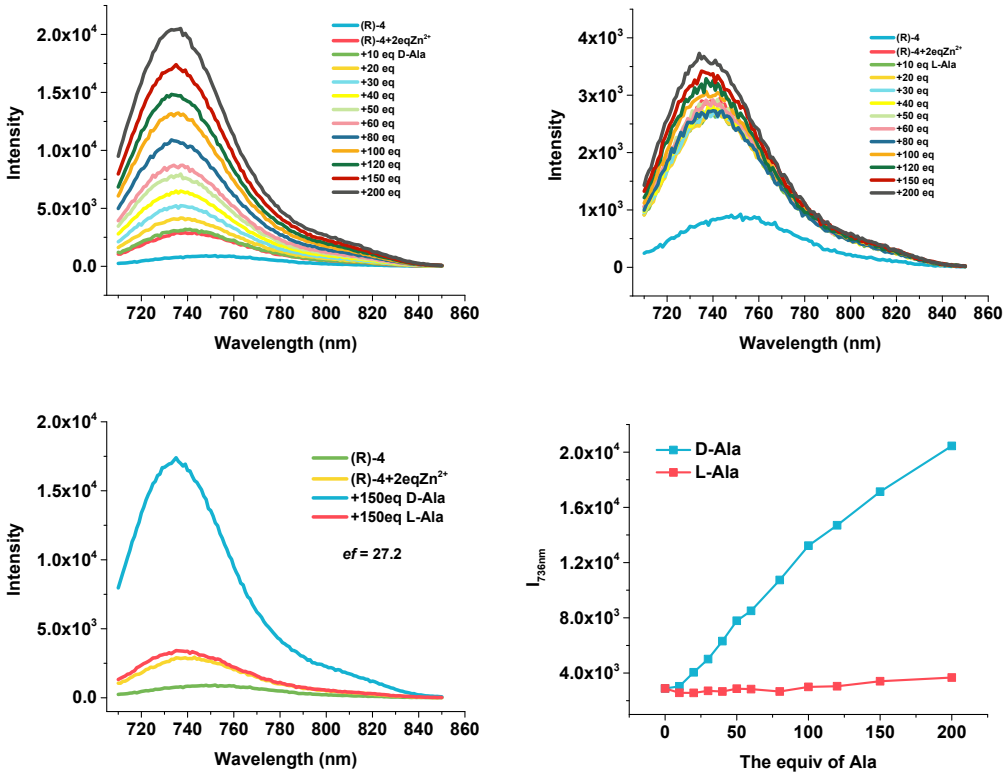
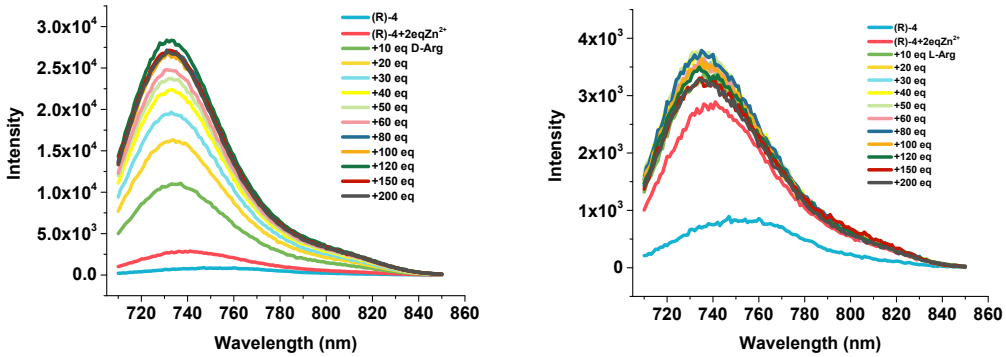
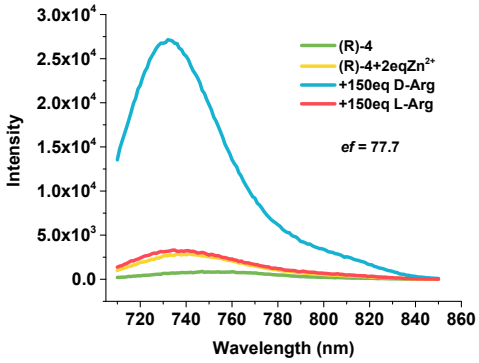


Figure S8. Fluorescence spectra of (*R*)-**4** (10 μM)+Zn^{2+}(2 equiv) with various equiv of D-Arg or L-Arg in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of arginine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)




3.0x10^4
2.5x10^4
2.0x10^4
1.5x10^4
1.0x10^4
5.0x10^3
0.0
Intensity
720 740 760 780 800 820 840 860
Wavelength (nm)
(R)-4
(R)-4+2eqZn2+
+150eq D-Arg
+150eq L-Arg
ef = 77.7

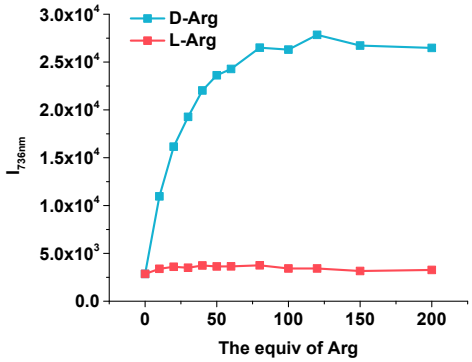

3.0x10^4
2.5x10^4
2.0x10^4
1.5x10^4
1.0x10^4
5.0x10^3
0.0
I736nm
0 50 100 150 200
The equiv of Arg
D-Arg
L-Arg

Figure S9. Fluorescence spectra of (*R*)-**4** (10 μM)+Zn^{2+} (2 equiv) with various equiv of D-Asn or L-Asn in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of Asparagine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

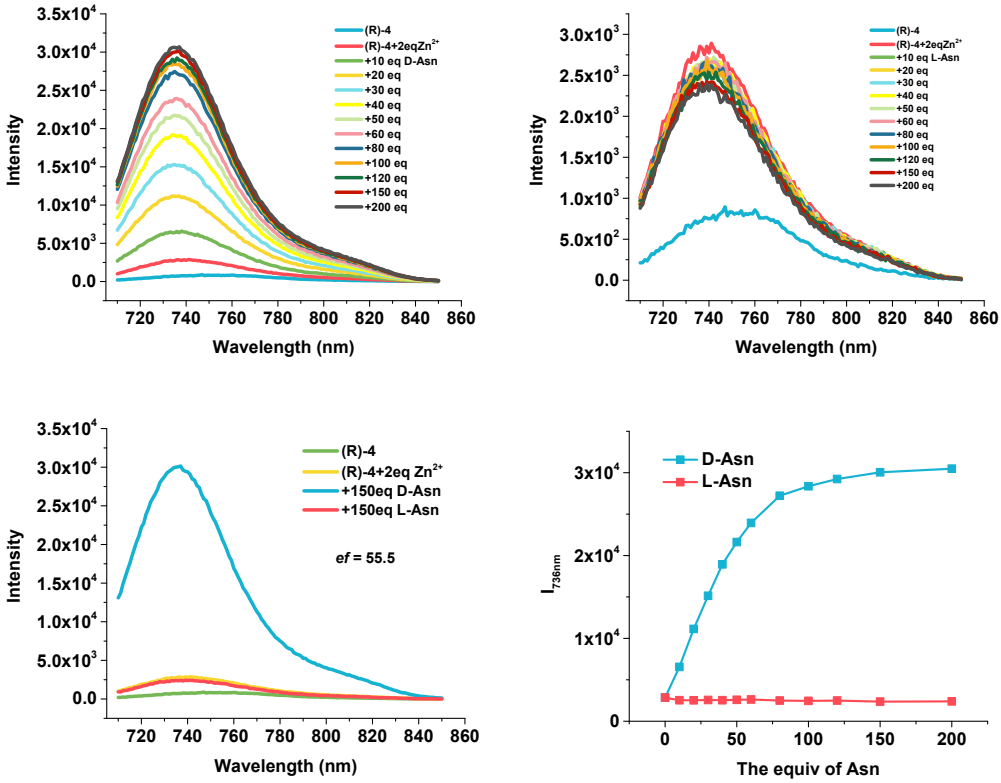


Figure S10. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+}(2 equiv) with various equiv of D-Gln or L-Gln in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of glutamine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

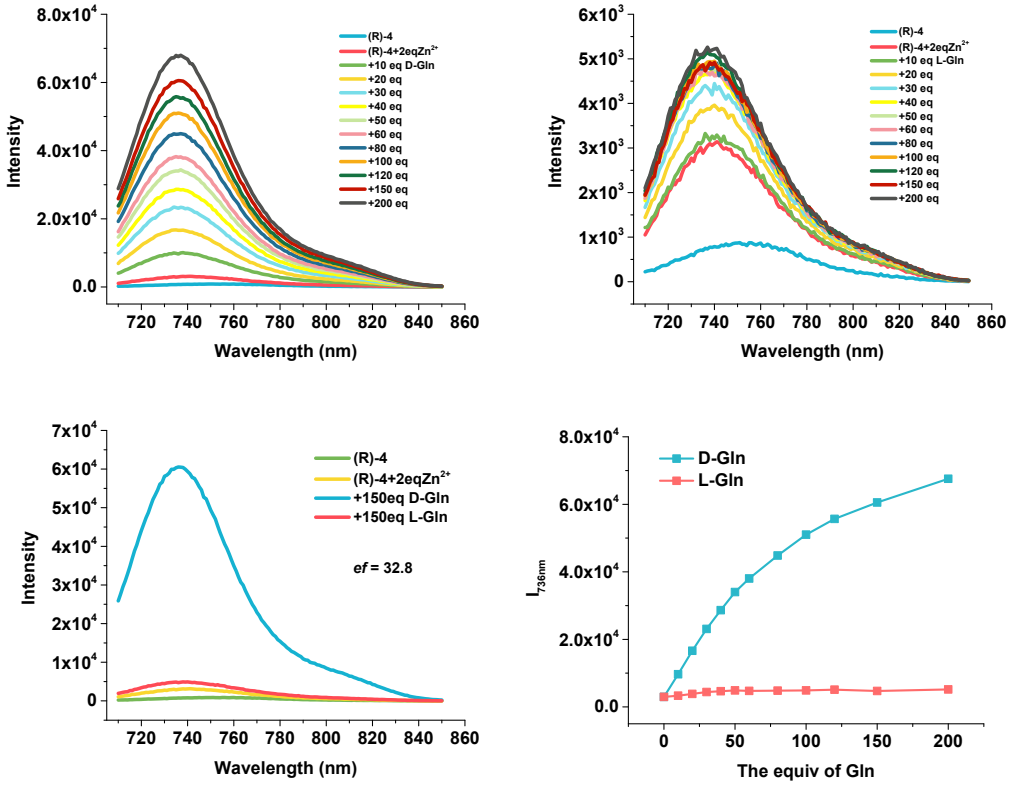


Figure S11. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-His or L-His in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of histidine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

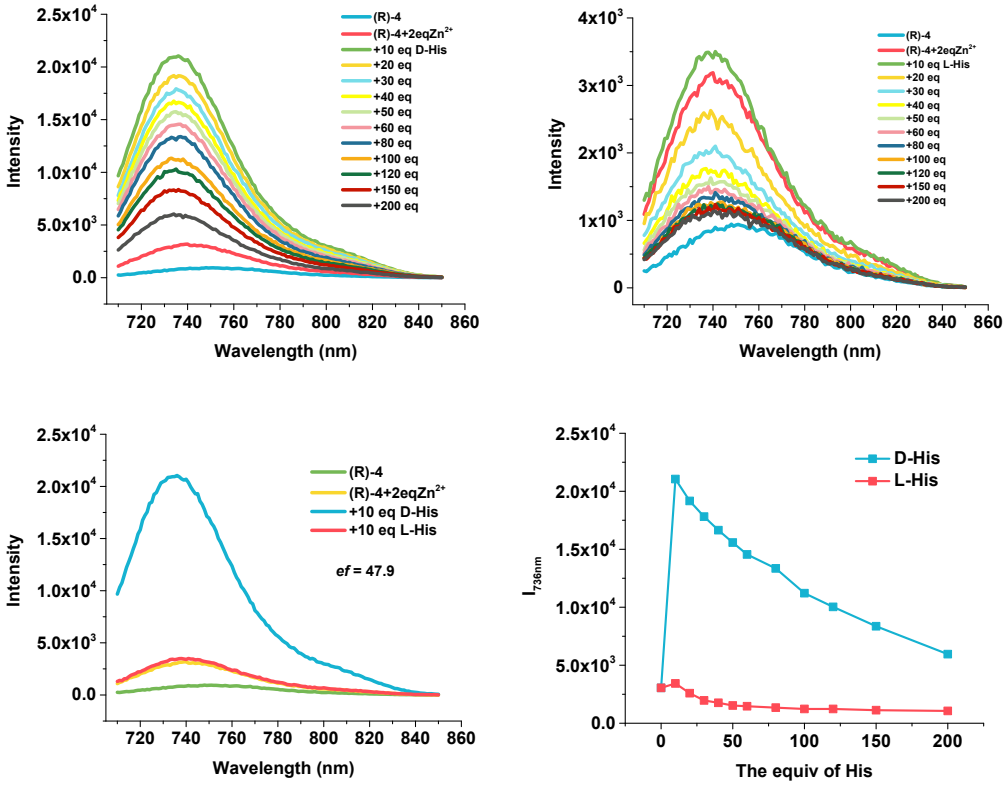


Figure S12. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Leu or L-Leu in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of Leucine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

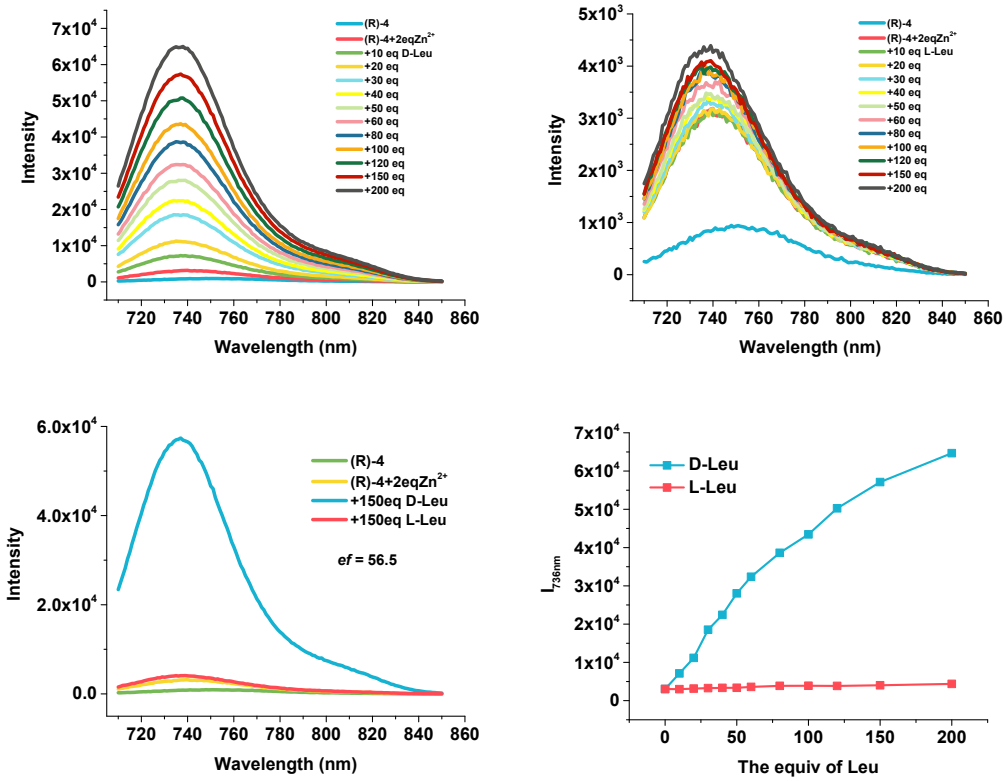


Figure S13. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Lys or L-Lys in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of Lysine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

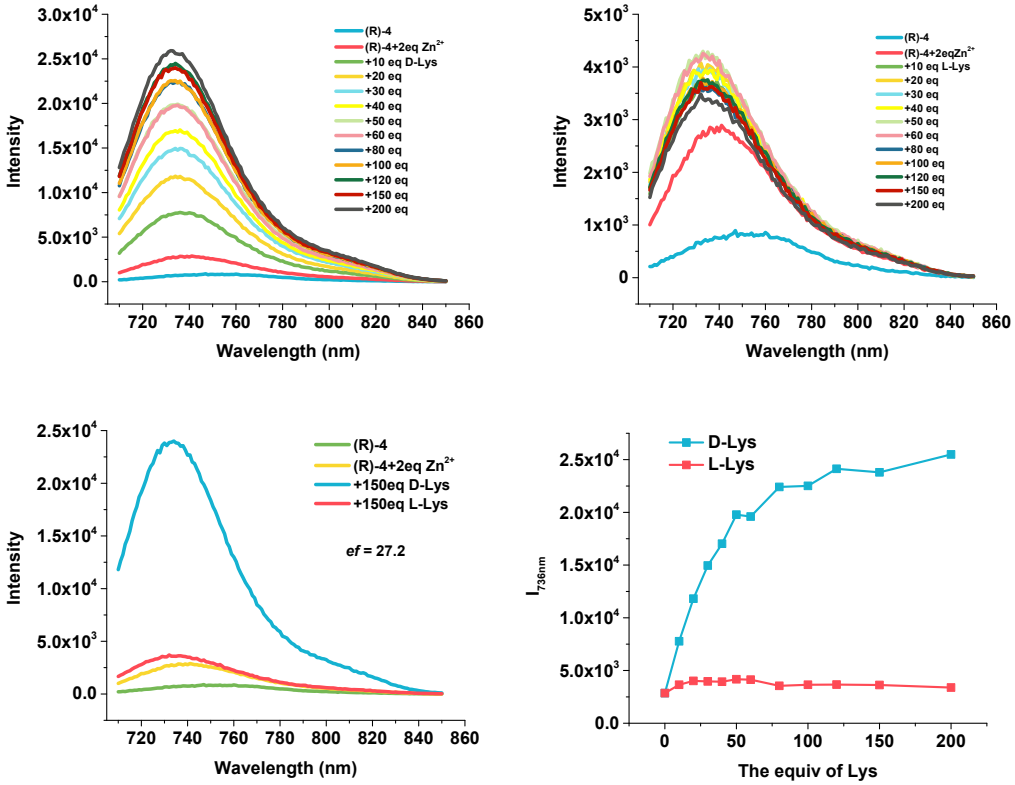


Figure S14. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Phe or L-Phe in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of phenylalanine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

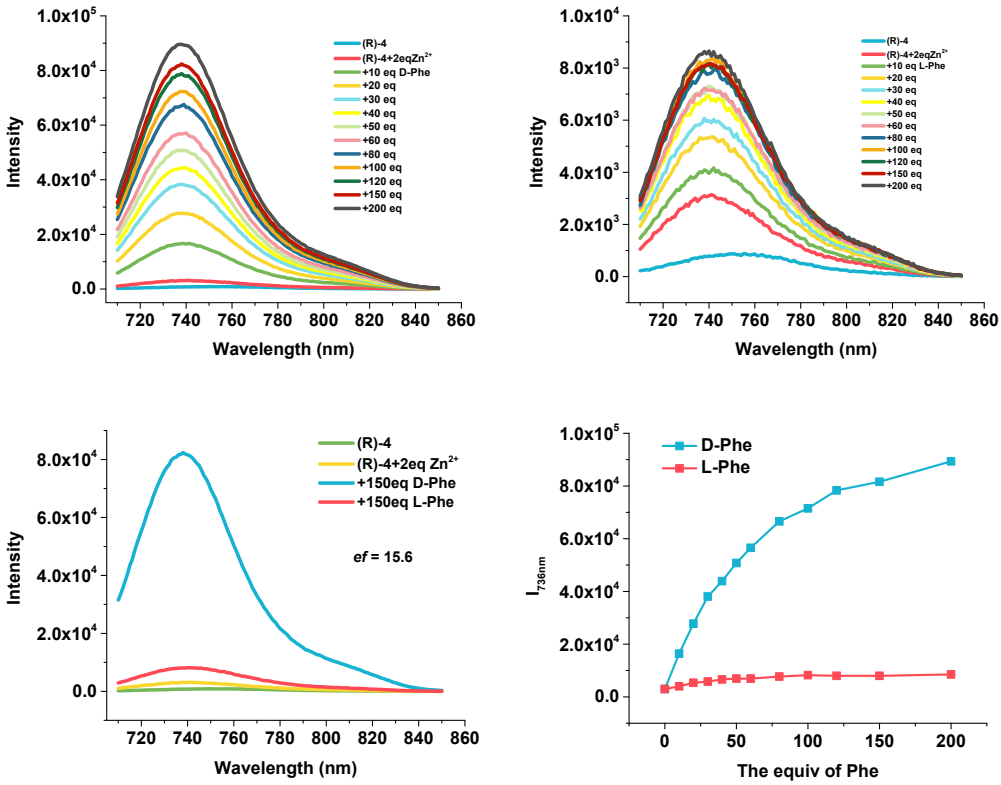


Figure S15. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Ser or L-Ser in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of Serine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

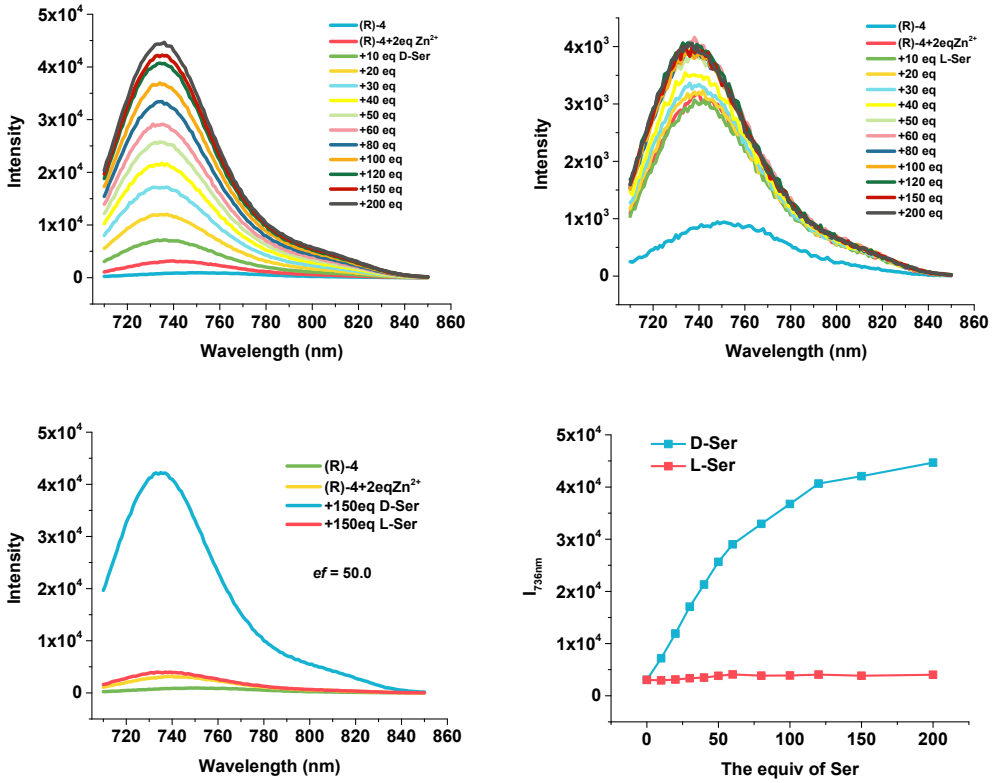


Figure S16. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv.) with various equiv of D-Thr or L-Thr in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of Threonine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

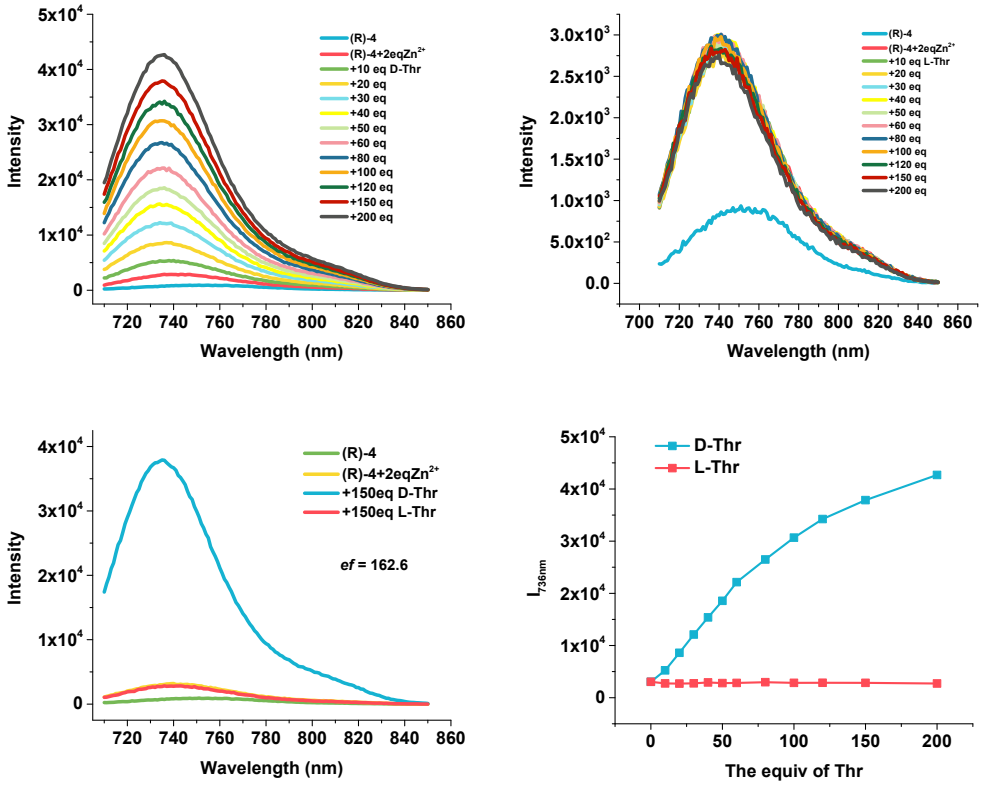


Figure S17. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Trp or L-Trp in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of tryptophan. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

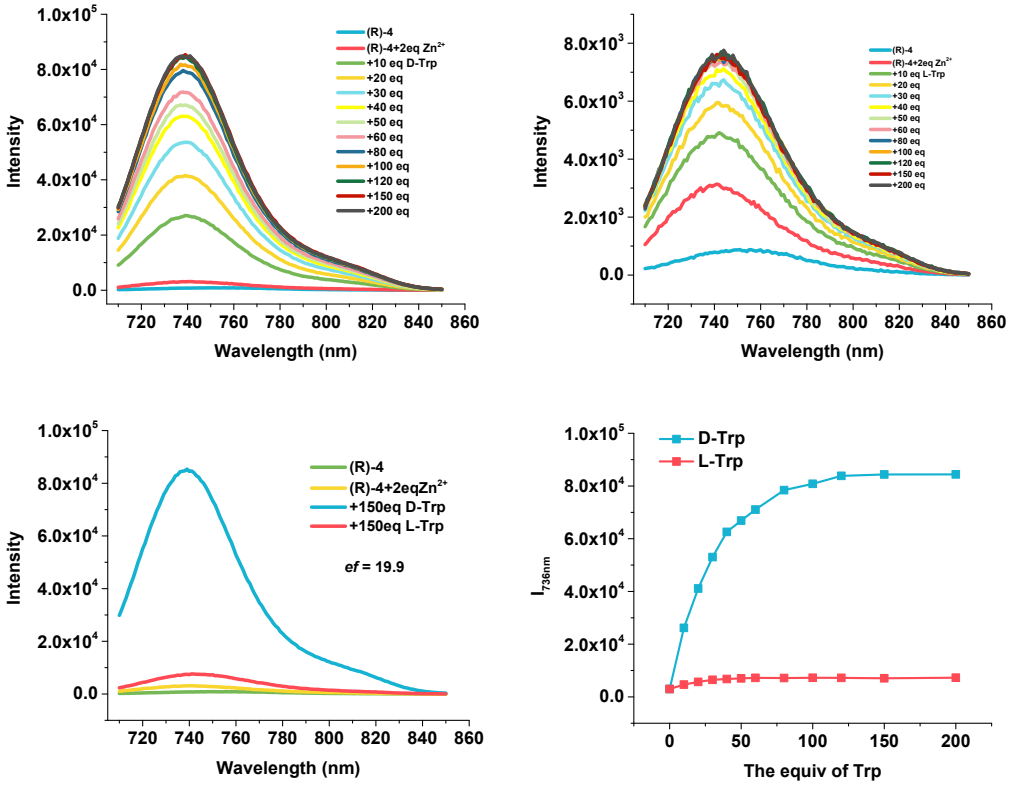


Figure S18. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Tyr or L-Tyr in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of tyrosine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)

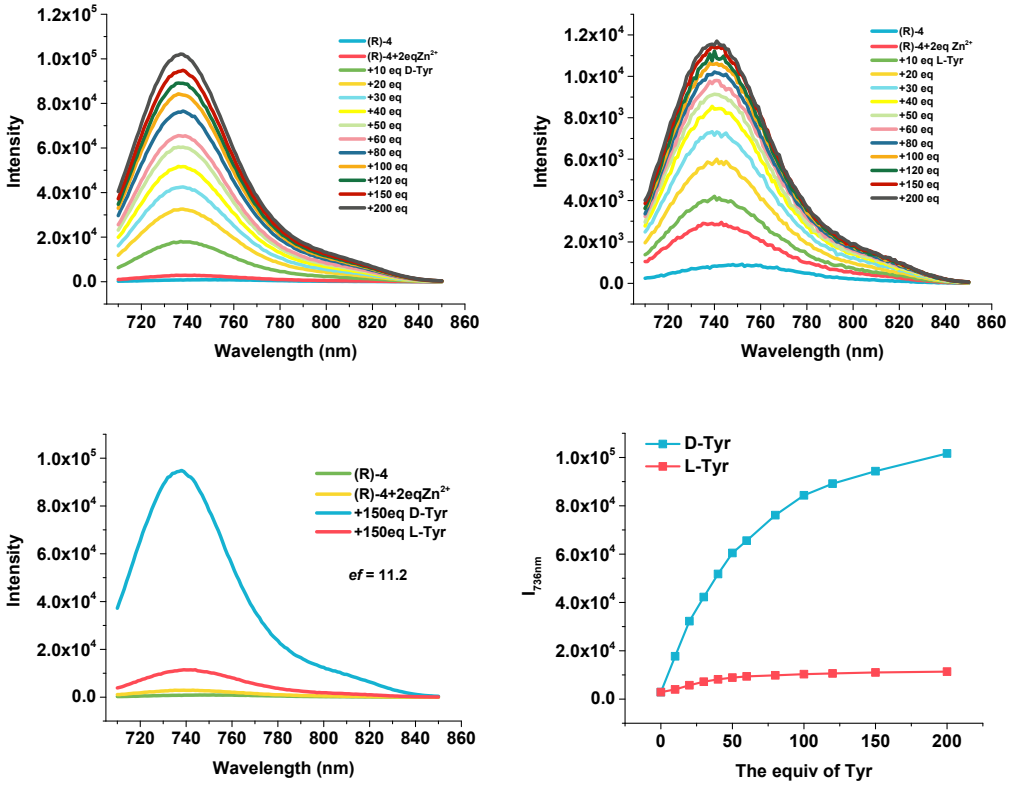
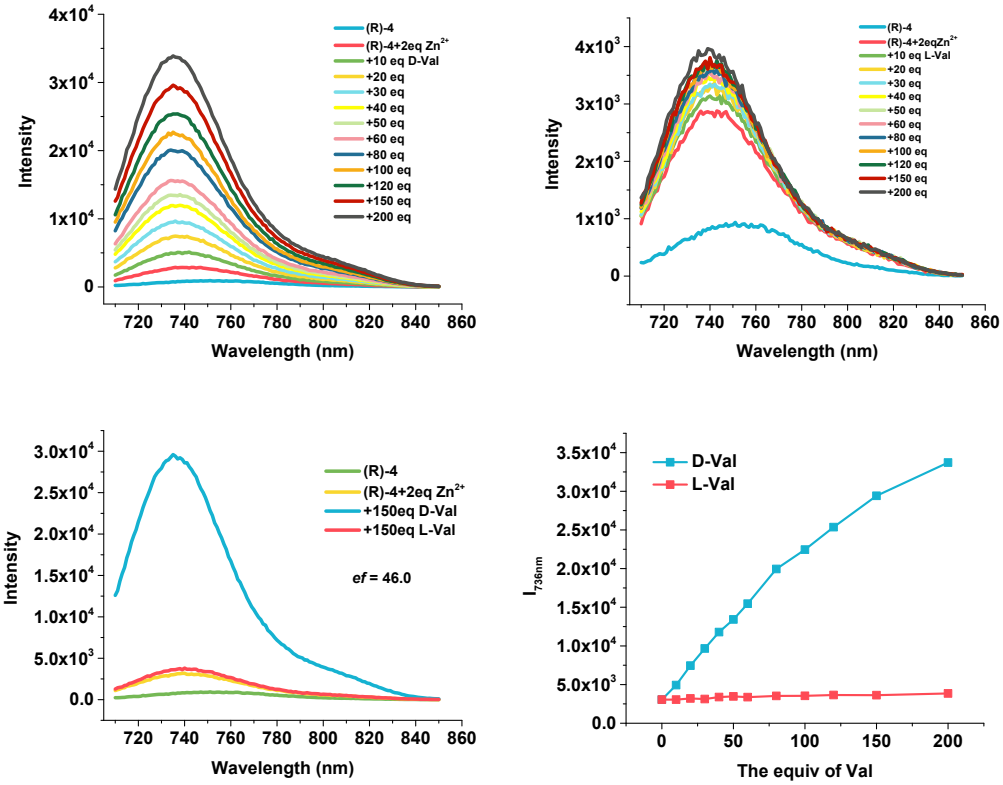


Figure S19. Fluorescence spectra of (*R*)-**4** (10 μM) + Zn^{2+} (2 equiv) with various equiv of D-Val or L-Val in 50 mM HEPES (pH = 7.4)/1% DMSO. Fluorescence intensity at 736 nm versus the equiv of valine. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm)



4. NMR and Mass spectroscopic studies of the reactions

Figure S20. ^{1}H NMR (600 MHz) titration of (*R*)-**4** (4 mM) + $ZnBr_2$ (1 equiv) with D- Met or L-Met in DMSO-d_6:HEPES buffer (3:1) (The ^{1}H NMR spectra were taken after the solution was allowed to stand at room temperature for 4 h. HEPES buffer: 50 mM at pD = 7.4 made with D_2O).

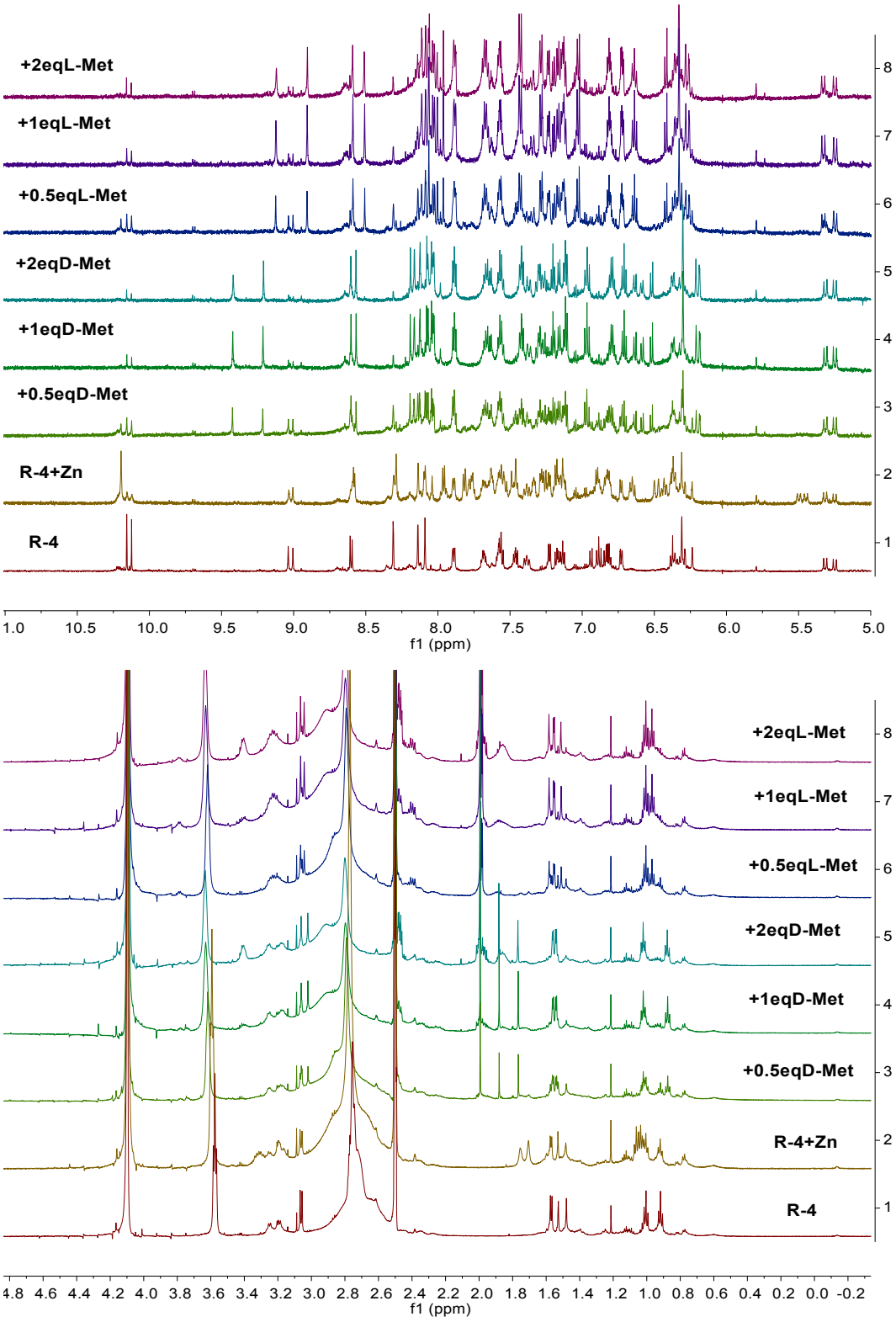


Figure S21. TOF mass spectra of (*R*)-**4** (2.0×10^{-5} M) + $Zn(OAc)_2$ (2 equiv) + D-Met (150 equiv).

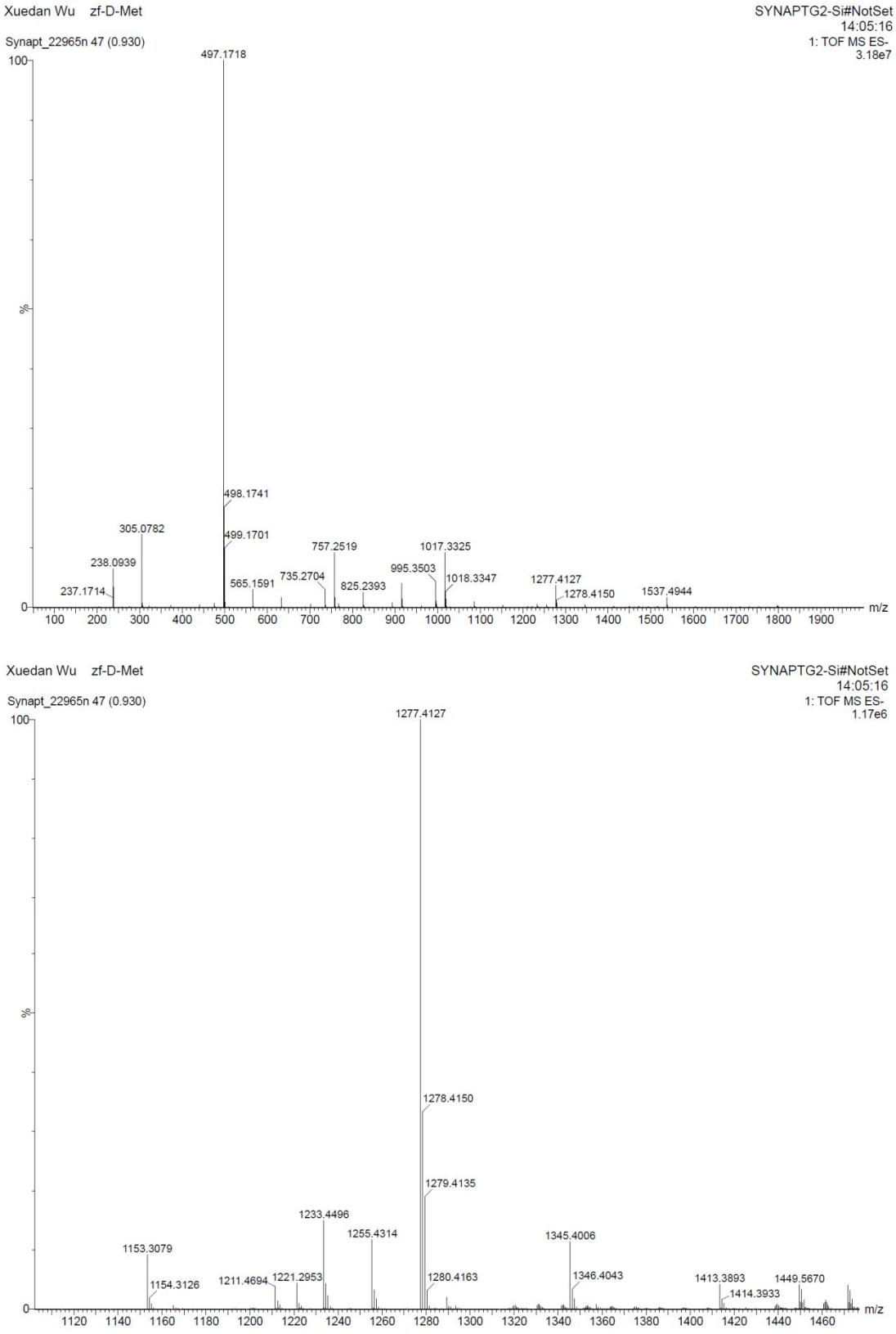
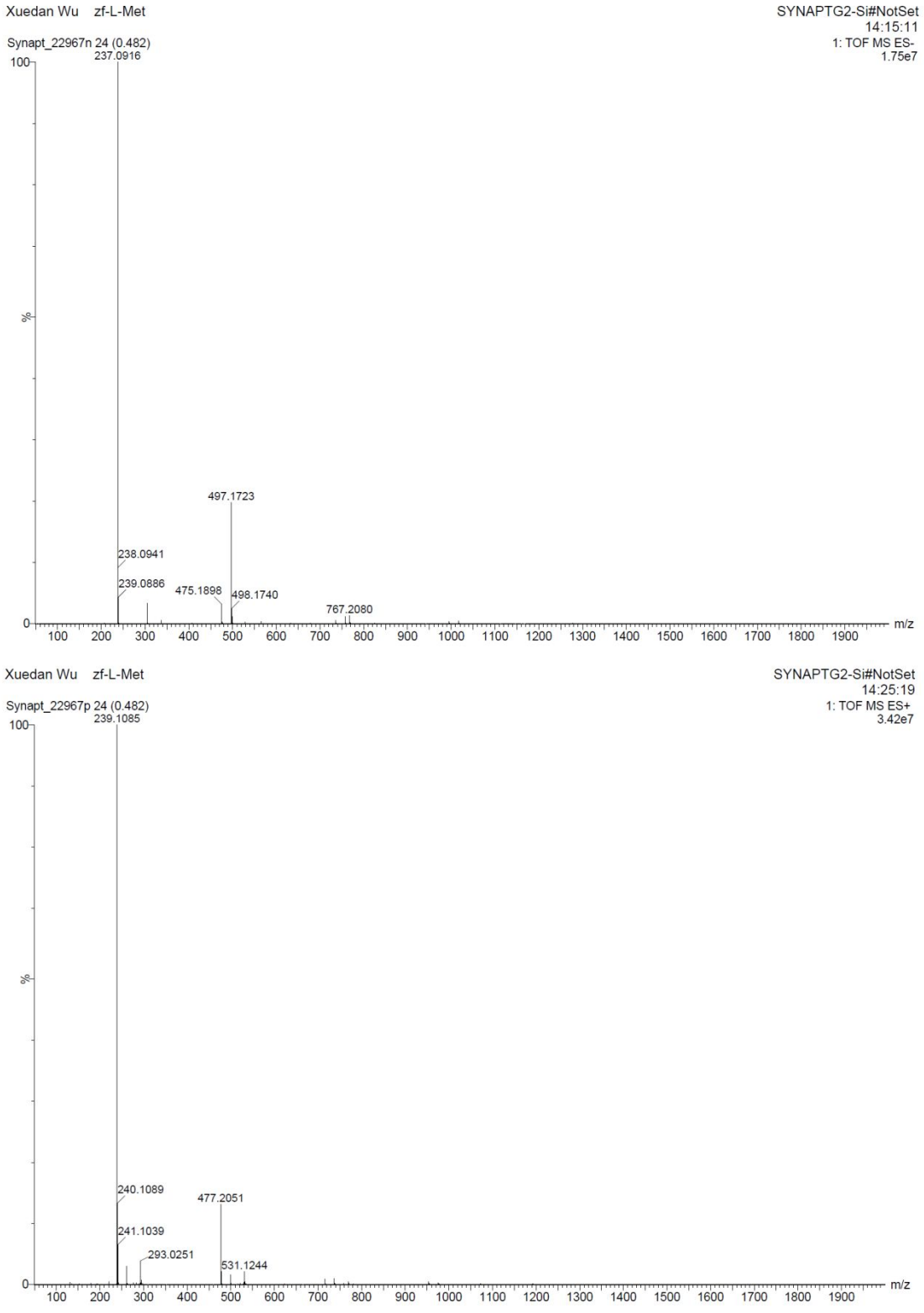
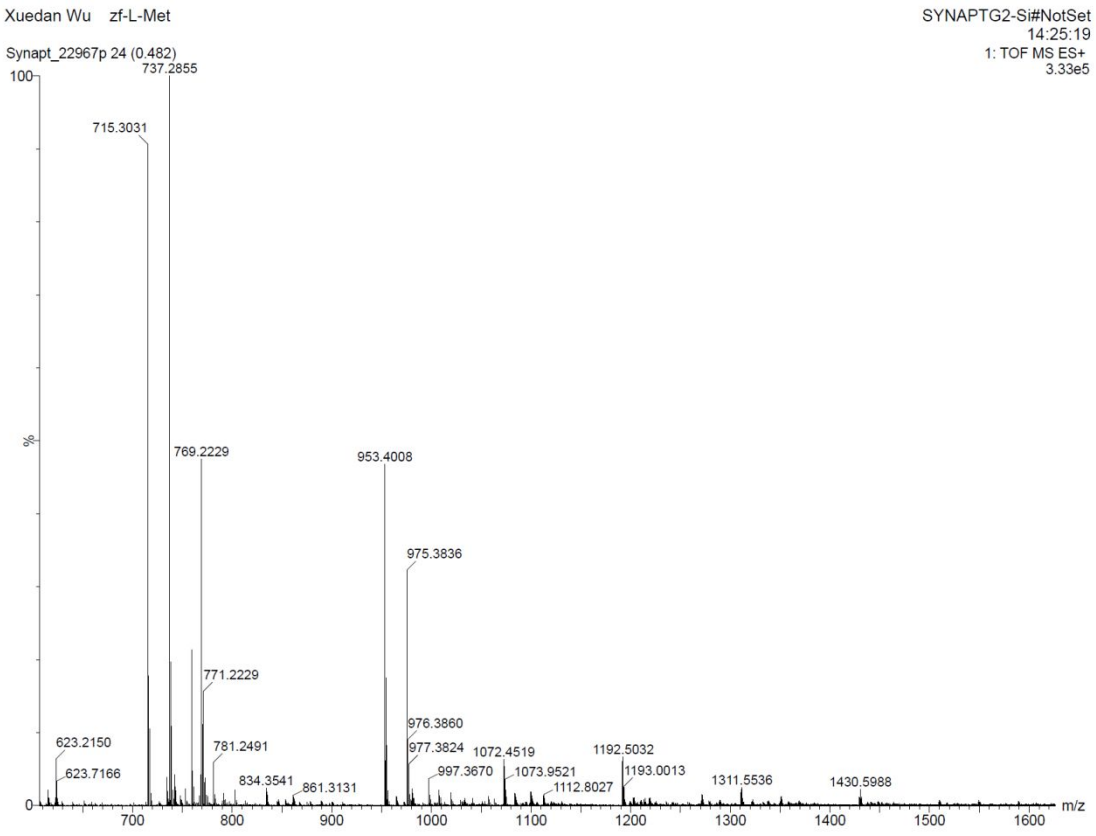


Figure S22. TOF mass spectra of (*R*)-**4** (2.0×10^{-5} M) + $Zn(OAc)_2$ (2 equiv) + L-Met (150 equiv).

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100
%
0
737.2855
715.3031
769.2229
953.4008
975.3836
771.2229
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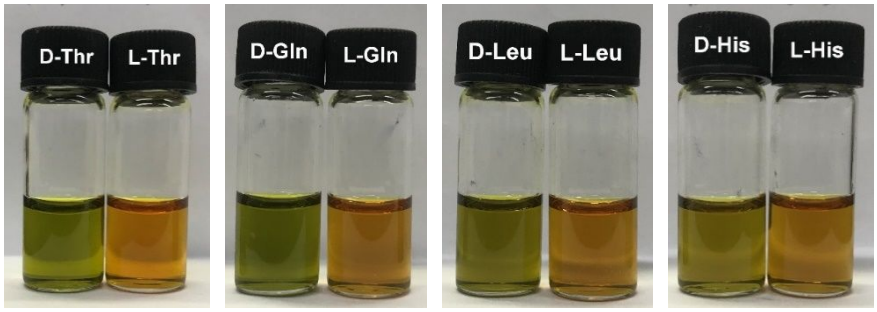
700
800
900
1000
1100
1200
1300
1400
1500
1600
m/z

5. Photographs of (*R*)-4 and $ZnBr_2$ with D- or L-amino acids

Figure S23. Photographs (in room light) of (*R*)-**4** (1 mM) + $ZnBr_2$ (1 equiv) with 1 equiv. of D- or L-amino acids in DMSO: HEPES buffer (3: 1).



6. Fluorescence spectra of (*R*)-4 with D-Met or L-Met in the presence of Zn^{2+} salts of various counter anions

Figure S24. Fluorescence spectra of (*R*)-4 (1.0×10^{-5} M) with several Zn^{2+} salts in 50 mM HEPES buffer (pH = 7.4)/1% DMSO in the presence of 150 equiv of D-Met or L-Met. Spectra were recorded at rt after mixing at 37 ℃ for 4 h. (λ_{exc} = 690 nm, slits = 5/5 nm, recorded on Hitech F-7000 spectrofluorometer).