

Supporting Information

Synthesis of an alanine-based colorimetric sensors and enantioselective recognition of aspartate and malate anions

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Additional spectra

Figure SI-1. Color change of complex **1** upon addition of hydroxide anion in mixture solvent (DMSO/H₂O = 4/1, v/v): (a) **1** only; (b) **1** + 1.0 equiv. of hydroxide.

Figure SI-2a. The 2D NOESY spectrum of receptor **1**

Figure SI-2b. The 2D NOESY spectrum of receptor **2**

SI-Table 1. Bond lengths^a of receptors **1-2** with D- and L-aspartate anions from *ab initio* HF/6-31G(D) calculations

Figure SI-3. Dilution experiment by ¹H NMR of **1** in the presence of 1.0 equiv. of D-aspartate in the solution (DMSO-*d*₆/ H₂O = 4/1). (a) [**1**] = [D-aspartate] = 10 mM; (b) [**1**] = [D-aspartate] = 5 mM; (c) [**1**] = [D-aspartate] = 3 mM; (d) [**1**] = [D-aspartate] = 1 mM.

Figure SI-4. Dilution experiment by ¹H NMR of **1** in the presence of 1.0 equiv. of L-aspartate in the solution (DMSO-*d*₆/ H₂O = 4/1). (a) [**1**] = [L-aspartate] = 10 mM; (b) [**1**] = [L-aspartate] = 5 mM; (c) [**1**] = [L-aspartate] = 3 mM; (d) [**1**] = [L-aspartate] = 1 mM.

Figure SI-5. ¹H NMR spectra change of **1** operated in the solution (DMSO-*d*₆/H₂O = 4/1) after addition of 2.0 equivalents of anions: (a) **1** only; (b) **1**+ L-malate; (c) **1**+ D-malate.

Figure SI-6. Dilution experiment by ¹H NMR of **1** in the presence of 1.0 equiv. of D-malate in the solution (DMSO-*d*₆/ H₂O = 4/1). (a) [**1**] = [L-malate] = 10 mM; (b) [**1**] = [L-malate] = 5 mM; (c) [**1**] = [L-malate] = 3 mM; (d) [**1**] = [L-malate] = 1 mM.

Figure SI-7. A series of spectra taken over the course of the titration of a 5×10⁻⁵M DMSO/H₂O (4/1, v/v) in **1** with a standard solution of D-malate at 25°C. The titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-8. A series of spectra taken over the course of the titration of a 5×10^{-5} M DMSO/H₂O (4/1, v/v) in **1** with a standard solution of L-malate at 25°C. The titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-9. A series of spectra taken over the course of the titration of a 5×10^{-5} M DMSO/H₂O (4/1, v/v) in **2** with a standard solution of L-aspartate at 25°C. The titration profile (insert) indicates the formation of a 1:1 complex.

Figure SI-10. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/H₂O = 4/1) upon addition of various quantities of D-aspartate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

Figure SI-11. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/H₂O = 4/1) upon addition of various quantities of L-aspartate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

Figure SI-12. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of D-aspartate in the solution (DMSO-*d*₆/H₂O = 4/1). (a) [**2**] = [D-aspartate] = 10 mM; (b) [**2**] = [D-aspartate] = 5 mM; (c) [**2**] = [D-aspartate] = 1 mM.

Figure SI-13. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of L-aspartate in the solution (DMSO-*d*₆/H₂O = 4/1). (a) [**2**] = [L-aspartate] = 10 mM; (b) [**2**] = [L-aspartate] = 5 mM; (c) [**2**] = [L-aspartate] = 1 mM.

Figure SI-14. ¹H NMR spectra change of **2** operated in the solution (DMSO-*d*₆/H₂O = 4/1) after addition of 2.0 equivalents of anions: (a) **2** only; (b) **2**+ L-aspartate; (c) **2**+ D-aspartate.

Figure SI-15. Color changes of complex **2** upon addition of various anions in DMSO/H₂O (4/1, v/v): (a) **2** only; (b) **2** + 2.0 equiv. of L-malate; (c) **2** + 2.0 equiv. of D-malate.

Figure SI-16. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/H₂O = 4/1) upon addition of various quantities of D-malate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

Figure SI-17. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/H₂O = 4/1) upon addition of various quantities of L-malate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

Figure SI-18. ¹H NMR spectra change of **2** operated in the solution (DMSO-*d*₆/H₂O = 4/1) after addition of 2.0 equivalents of anions: (a) **2** only; (b) **2**+ L-malate; (c) **2**+ D-malate.

Figure SI-19. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of D-malate in the solution (DMSO-*d*₆/H₂O = 4/1). (a) [**2**] = [D-malate] = 10 mM; (b) [**2**] = [D-malate] = 5 mM; (c) [**2**] = [D-malate] = 1 mM.

Figure SI-20. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of L-malate in the solution (DMSO-*d*₆/H₂O = 4/1). (a) [**2**] = [L-malate] = 10 mM; (b) [**2**]

= [L-malate] = 5 mM; (c) [2] = [L-malate] = 1 mM.

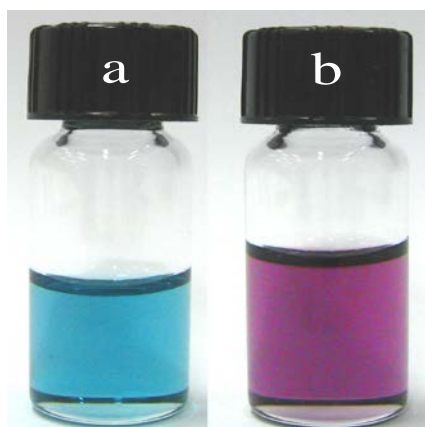


Figure SI-1. Color change of complex **1** upon addition of hydroxide anion in mixture solvent (DMSO/H₂O = 4/1, v/v): (a) **1** only; (b) **1** + 1.0 equiv. of hydroxide.

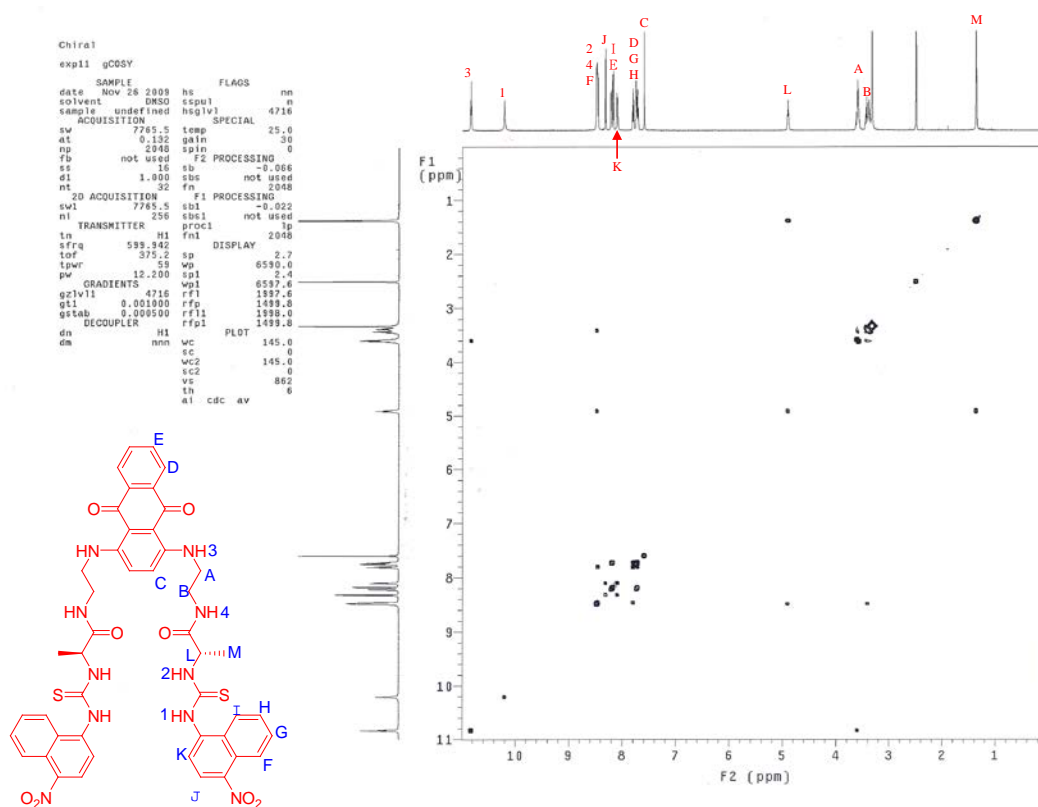


Figure SI-2a. The 2D NOESY spectrum of receptor **1**

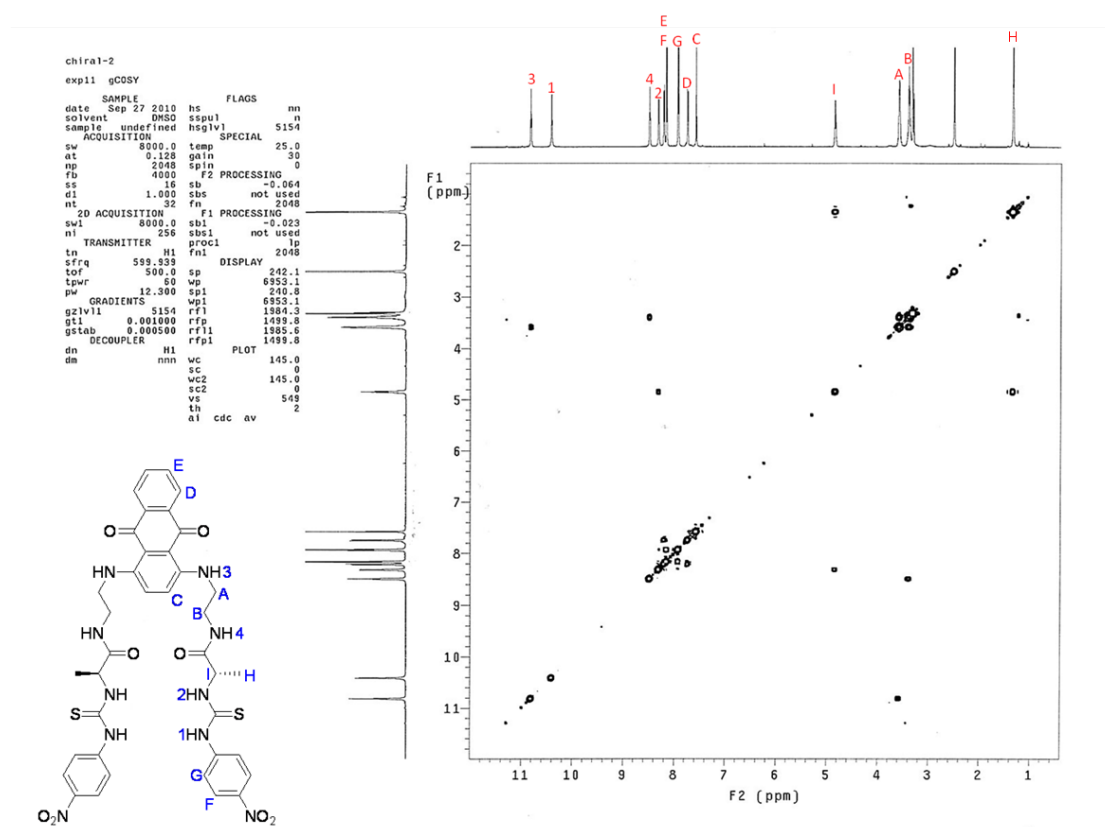
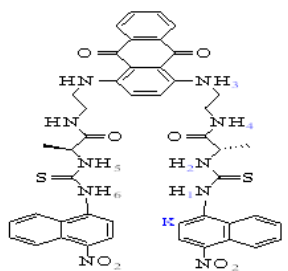
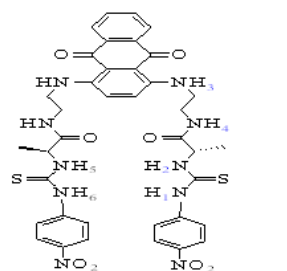


Figure SI-2b. The 2D NOESY spectrum of receptor 2.

SI-Table 1. Bond lengths^a of receptors **1-2** with D- and L-aspartate anions from *ab initio* HF/6-31G(D) calculations



1



2

compound ^c	Anion ^c	H(1)...L ^c	H(2)...L ^c	H(5)...L ^c	H(6)...L ^c
1 ^c	D-aspartate ^c	0.9795(O1) ^c	2.5285(O2) ^c	2.5485(O3) ^c	1.9485(O4) ^c
	L-aspartate ^c	1.9535(O1) ^c	1.8885(O2) ^c	2.6225(O3) ^c	1.9595(O4) ^c
	D-malate ^c	0.9795(O1) ^c	2.5665(O2) ^c	2.4875(O3) ^c	1.9285(O4) ^c
	L-malate ^c	1.7995(O1) ^c	1.8625(O2) ^c	2.8215(O3) ^c	2.0425(O4) ^c
2 ^c	D-aspartate ^c	1.8315(O1) ^c	1.9345 (O2) ^c	2.8245(O3) ^c	1.8685(O4) ^c
	L-aspartate ^c	1.8125(O1) ^c	1.9335(O2) ^c	2.7665(O3) ^c	1.8375(O4) ^c
	D-malate ^c	1.8135(O1) ^c	1.8785 (O2) ^c	2.1775(O3) ^c	1.8135(O4) ^c
	L-malate ^c	1.8105(O1) ^c	1.8455(O2) ^c	2.8015(O3) ^c	1.9155(O4) ^c

^a The unit of computed distances is Å.

^b Four oxygen atoms(O1、O2、O3 and O4) of guest form hydrogen bonds with the receptors where O1 is hydrogen-bonded to H1 and O2 to H2 and O3 to H5 and O4 to H6. Footnote text.

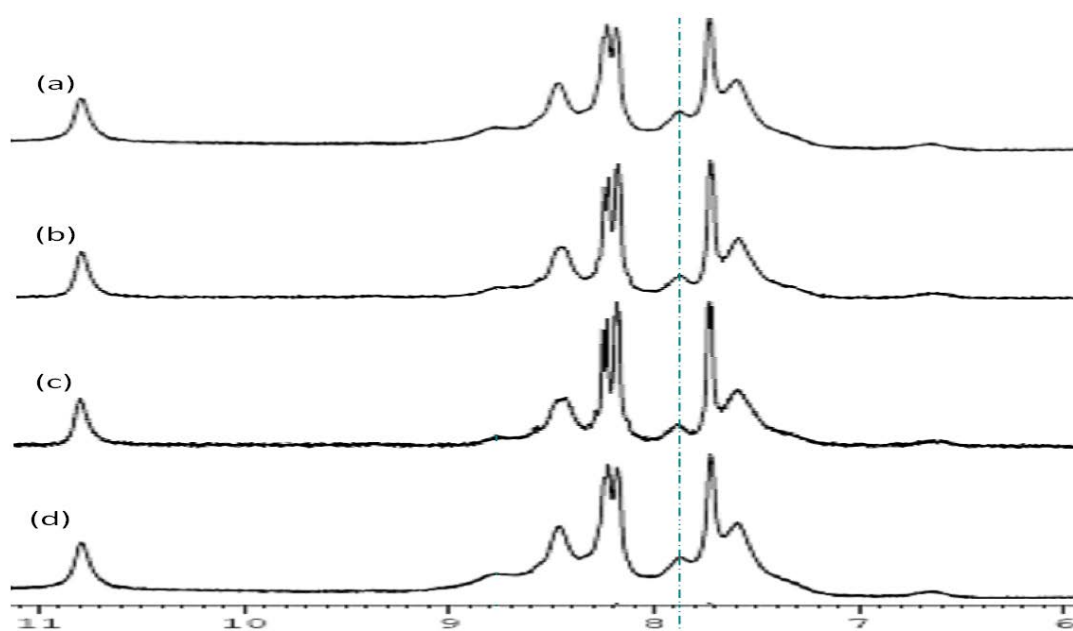


Figure SI-3. Dilution experiment by ¹H NMR of **1** in the presence of 1.0 equiv. of D-aspartate in the solution (DMSO-*d*₆/ H₂O = 4/1). (a) [1] = [D-aspartate] = 10 mM; (b) [1] = [D-aspartate] = 5 mM; (c) [1] = [D-aspartate] = 3 mM; (d) [1] = [D-aspartate] = 1 mM.

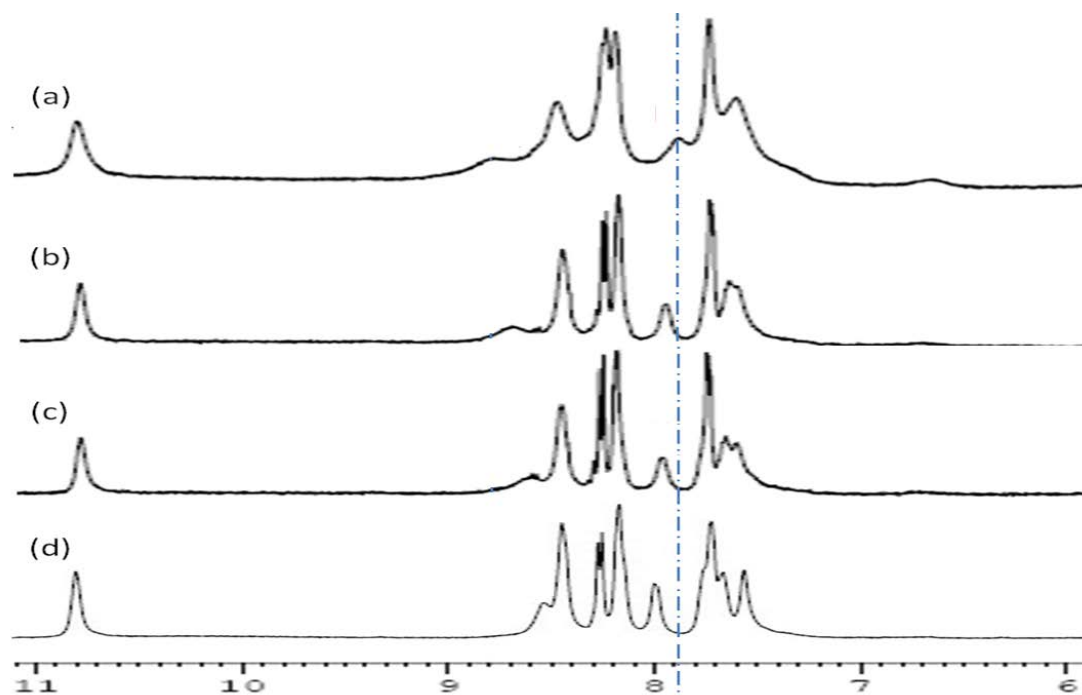


Figure SI-4. Dilution experiment by ^1H NMR of **1** in the presence of 1.0 equiv. of L-aspartate in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O} = 4/1$). (a) $[\mathbf{1}] = [\text{L-aspartate}] = 10 \text{ mM}$; (b) $[\mathbf{1}] = [\text{L-aspartate}] = 5 \text{ mM}$; (c) $[\mathbf{1}] = [\text{L-aspartate}] = 3 \text{ mM}$; (d) $[\mathbf{1}] = [\text{L-aspartate}] = 1 \text{ mM}$.

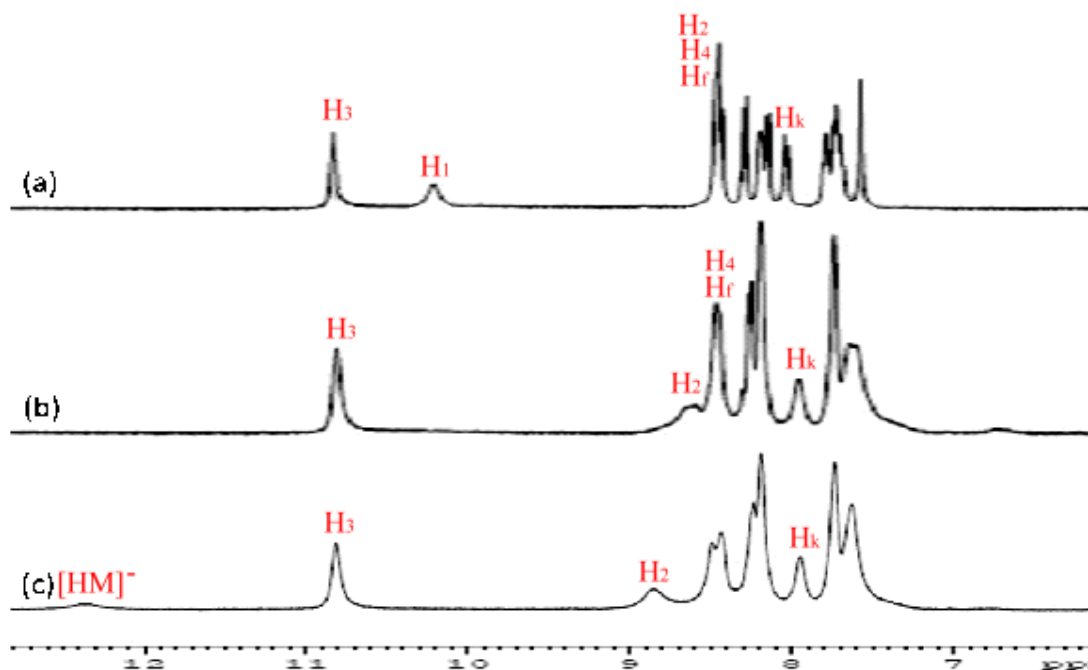


Figure SI-5. ^1H NMR spectra change of **1** operated in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O} = 4/1$) after addition of 2.0 equivalents of anions: (a) **1** only; (b) **1**+ L-malate; (c) **1**+ D-malate.

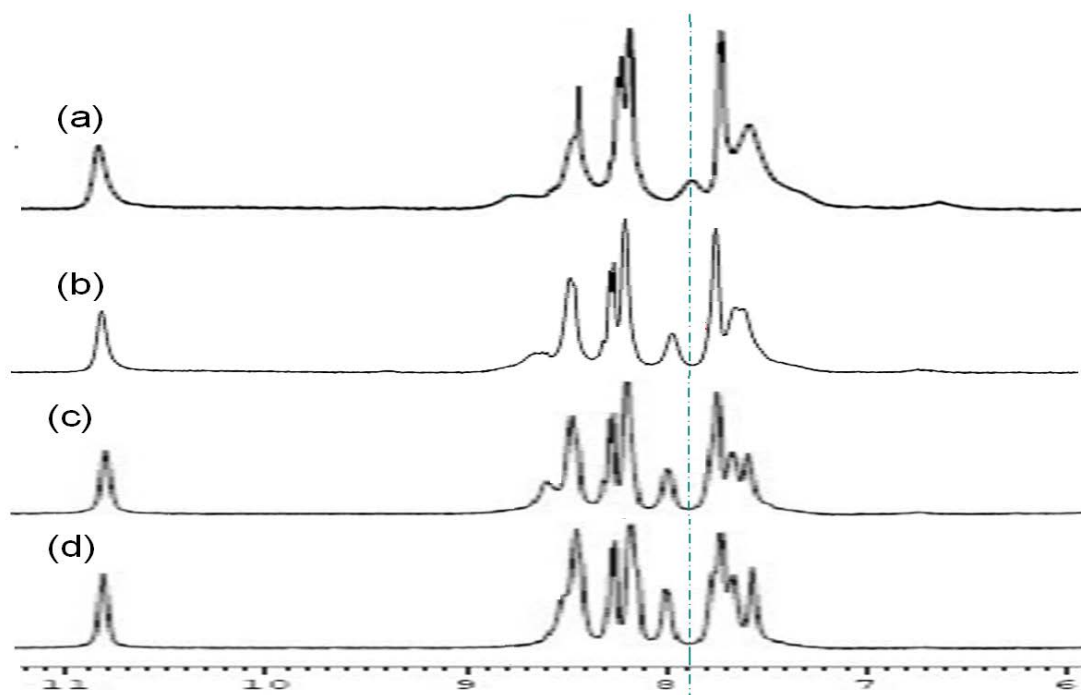


Figure SI-6. Dilution experiment by ^1H NMR of **1** in the presence of 1.0 equiv. of D-malate in the solution (DMSO- d_6 / H_2O = 4/1). (a) $[\mathbf{1}] = [\text{L-malate}] = 10$ mM; (b) $[\mathbf{1}] = [\text{L-malate}] = 5$ mM; (c) $[\mathbf{1}] = [\text{L-malate}] = 3$ mM; (d) $[\mathbf{1}] = [\text{L-malate}] = 1$ mM.

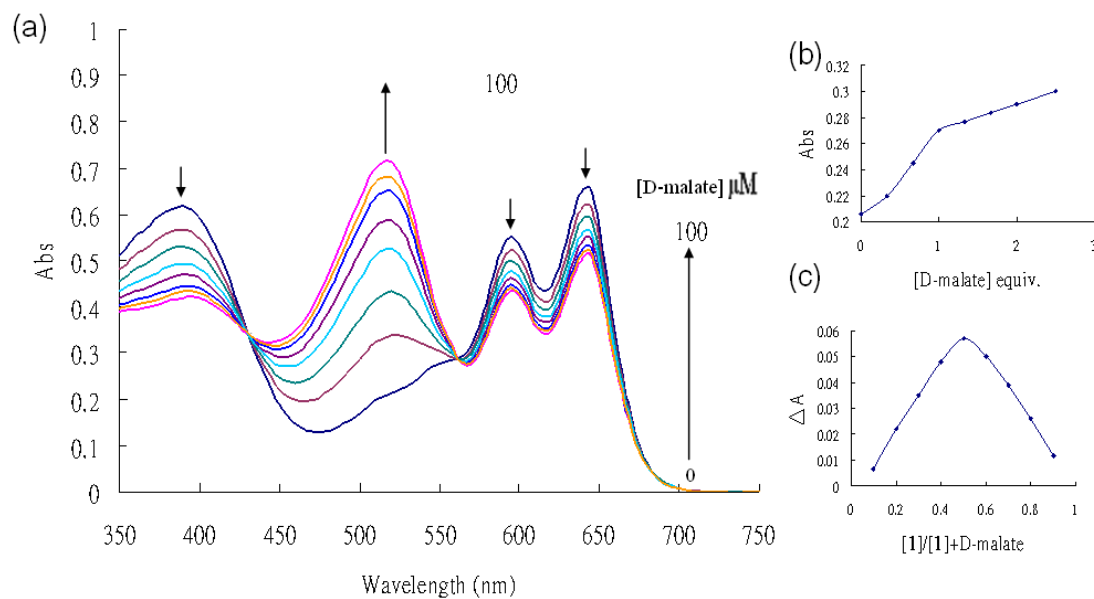


Figure SI-7. A series of spectra taken over the course of the titration of a 5×10^{-5} M DMSO/ H_2O (4/1, v/v) in **1** with a standard solution of D-malate at 25°C . The titration profile (insert) indicates the formation of a 1:1 complex.

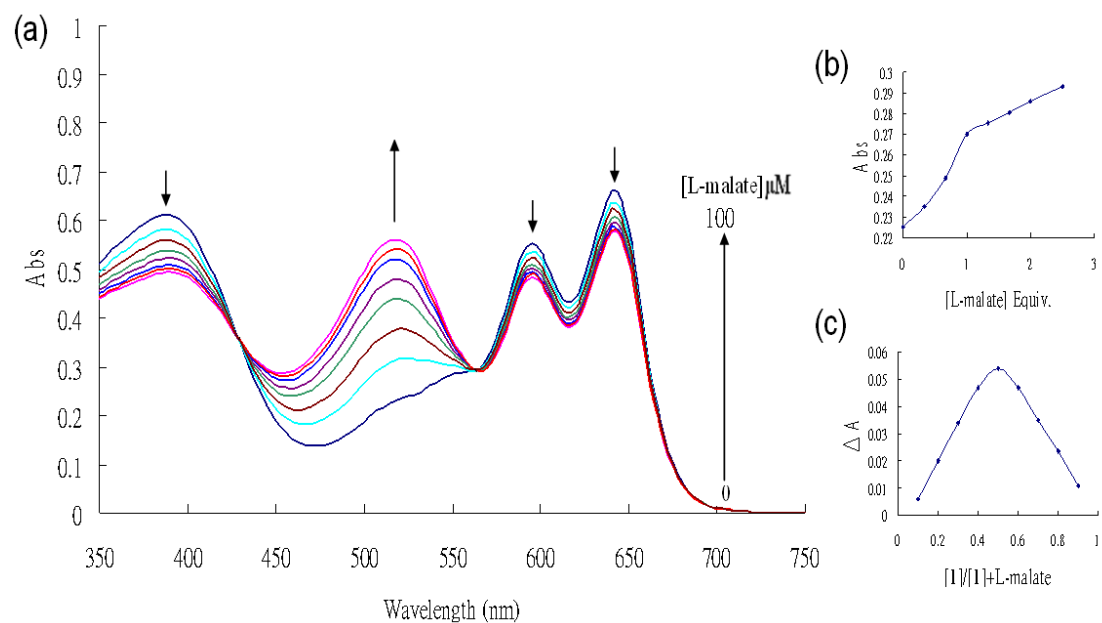


Figure SI-8. A series of spectra taken over the course of the titration of a $5 \times 10^{-5} \text{M}$ DMSO/ H_2O (4/1, v/v) in **1** with a standard solution of L-malate at 25°C . The titration profile (insert) indicates the formation of a 1:1 complex.

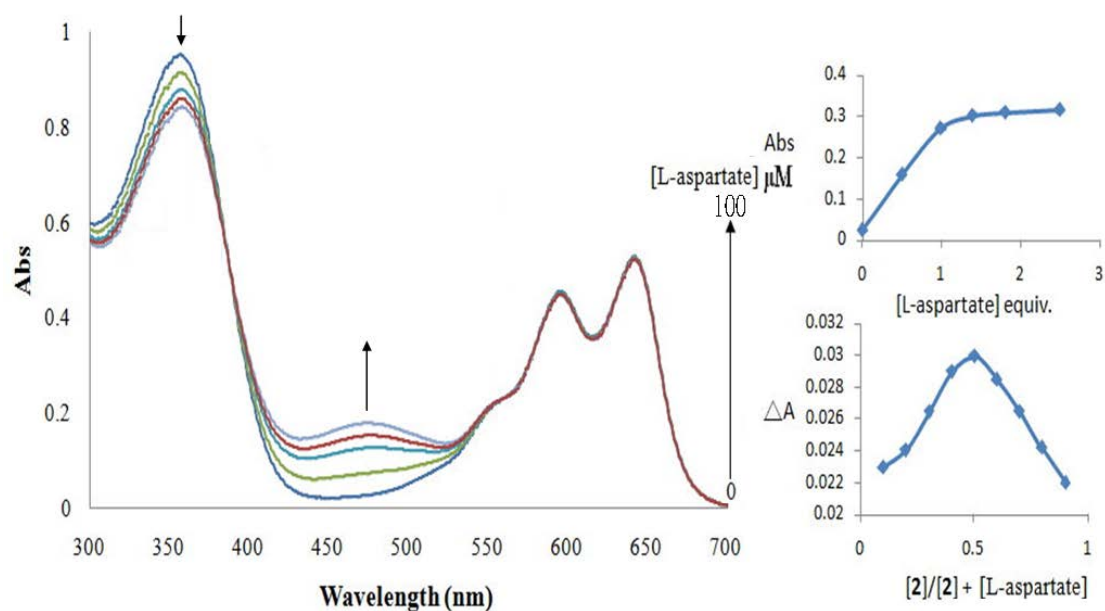


Figure SI-9. A series of spectra taken over the course of the titration of a $5 \times 10^{-5} \text{M}$ DMSO/ H_2O (4/1, v/v) in **2** with a standard solution of L-aspartate at 25°C . The titration profile (insert) indicates the formation of a 1:1 complex.

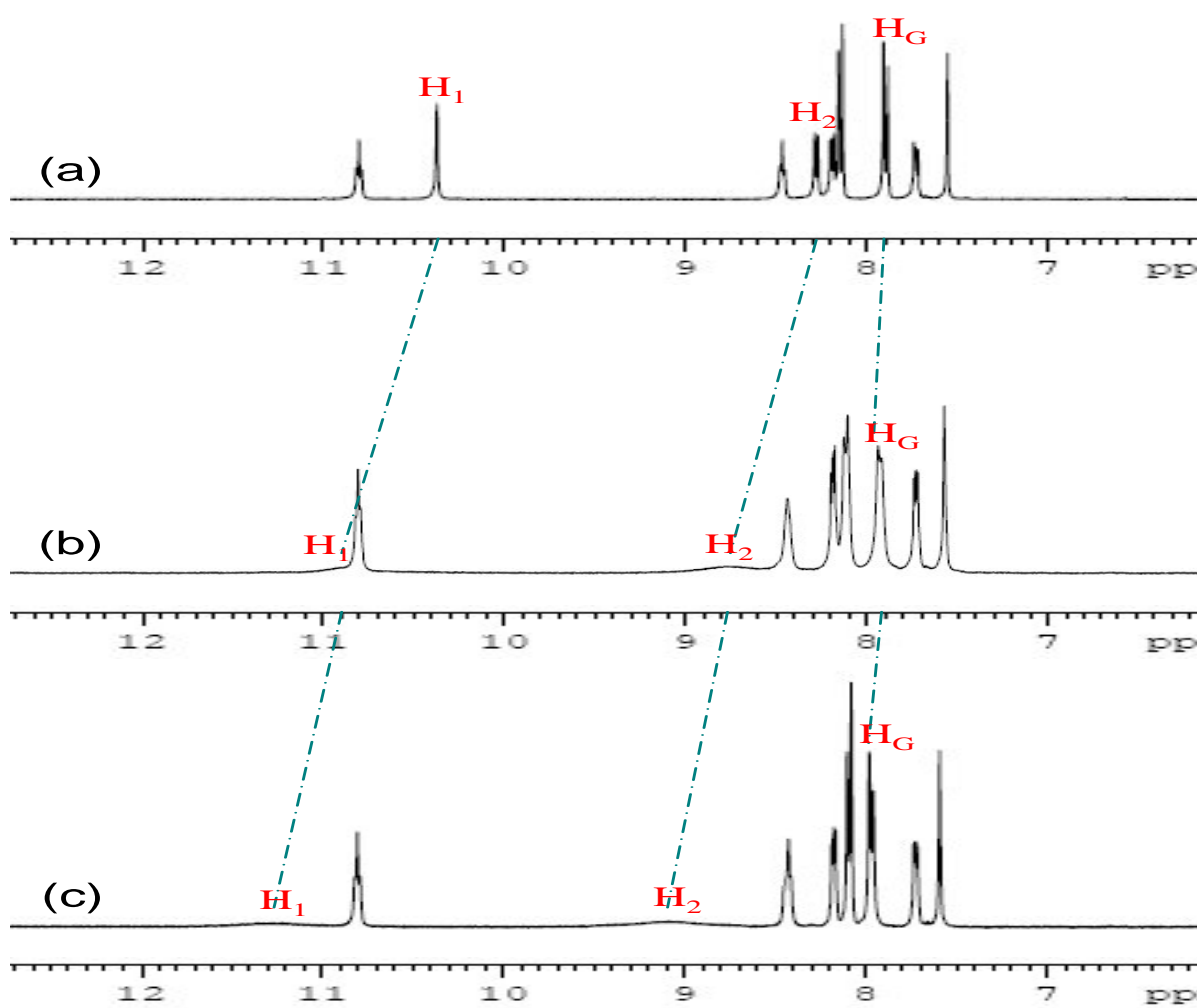


Figure SI-10. ^1H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O} = 4/1$) upon addition of various quantities of D-aspartate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

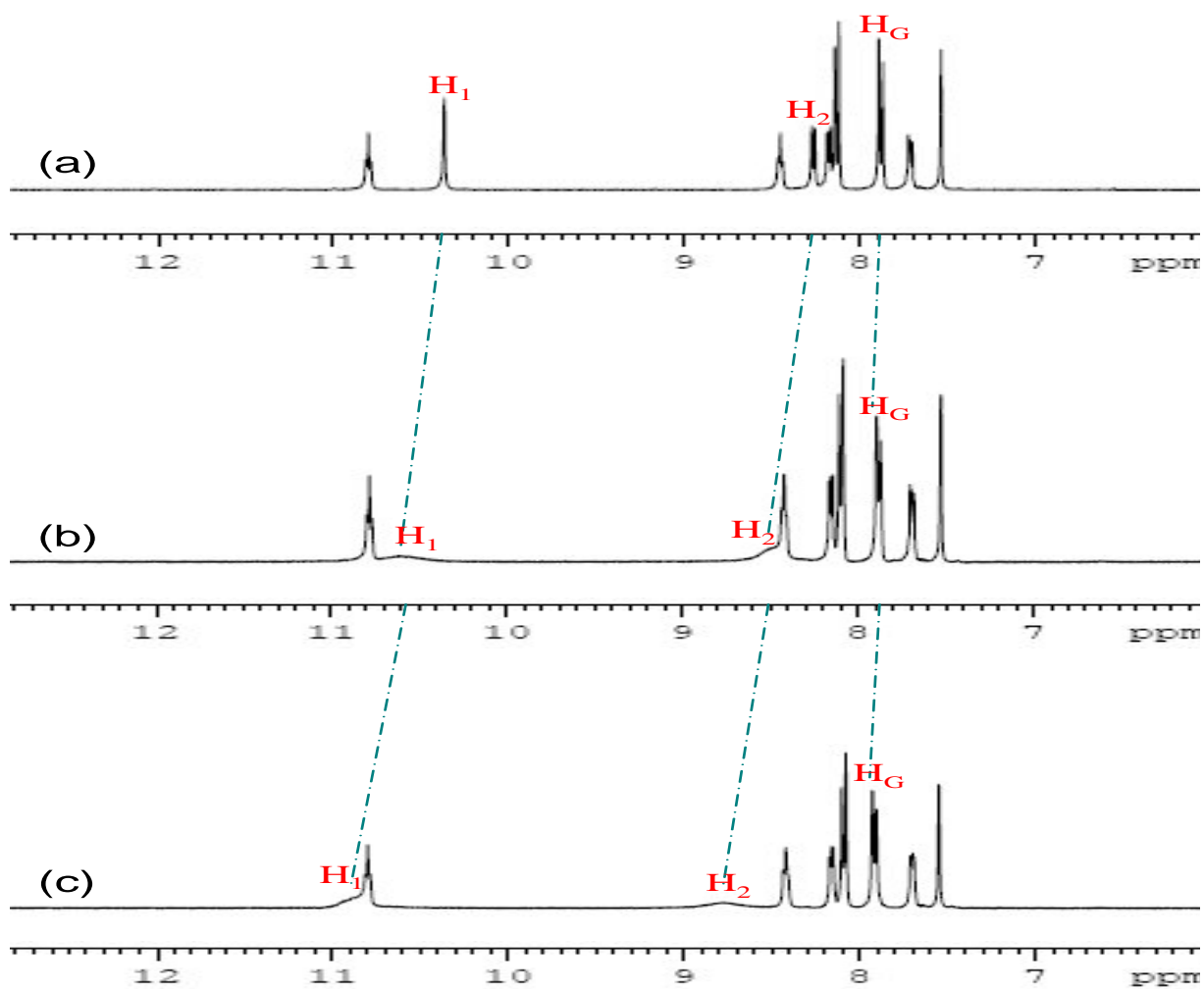


Figure SI-11. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/ H₂O = 4/1) upon addition of various quantities of L-aspartate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

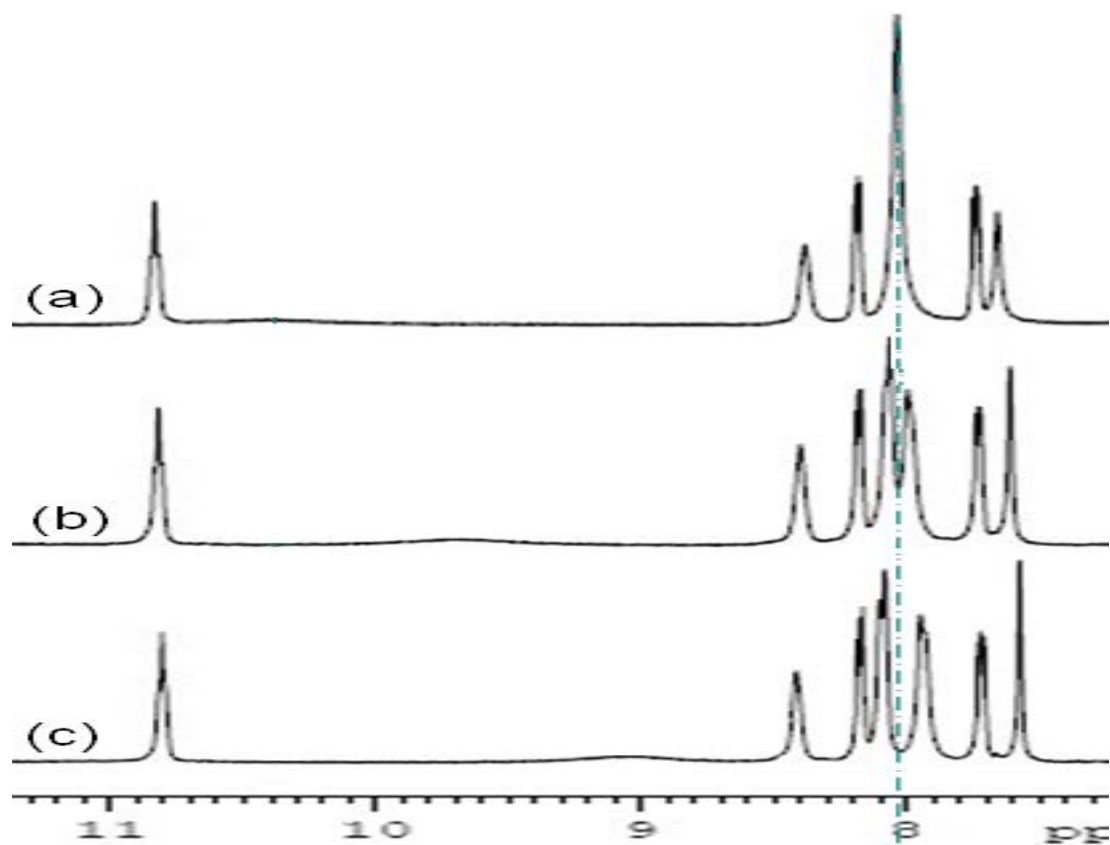


Figure SI-12. Dilution experiment by ^1H NMR of **2** in the presence of 1.0 equiv. of D-aspartate in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O} = 4/1$). (a) $[\mathbf{2}] = [\text{D-aspartate}] = 10 \text{ mM}$; (b) $[\mathbf{2}] = [\text{D-aspartate}] = 5 \text{ mM}$; (c) $[\mathbf{2}] = [\text{D-aspartate}] = 1 \text{ mM}$.

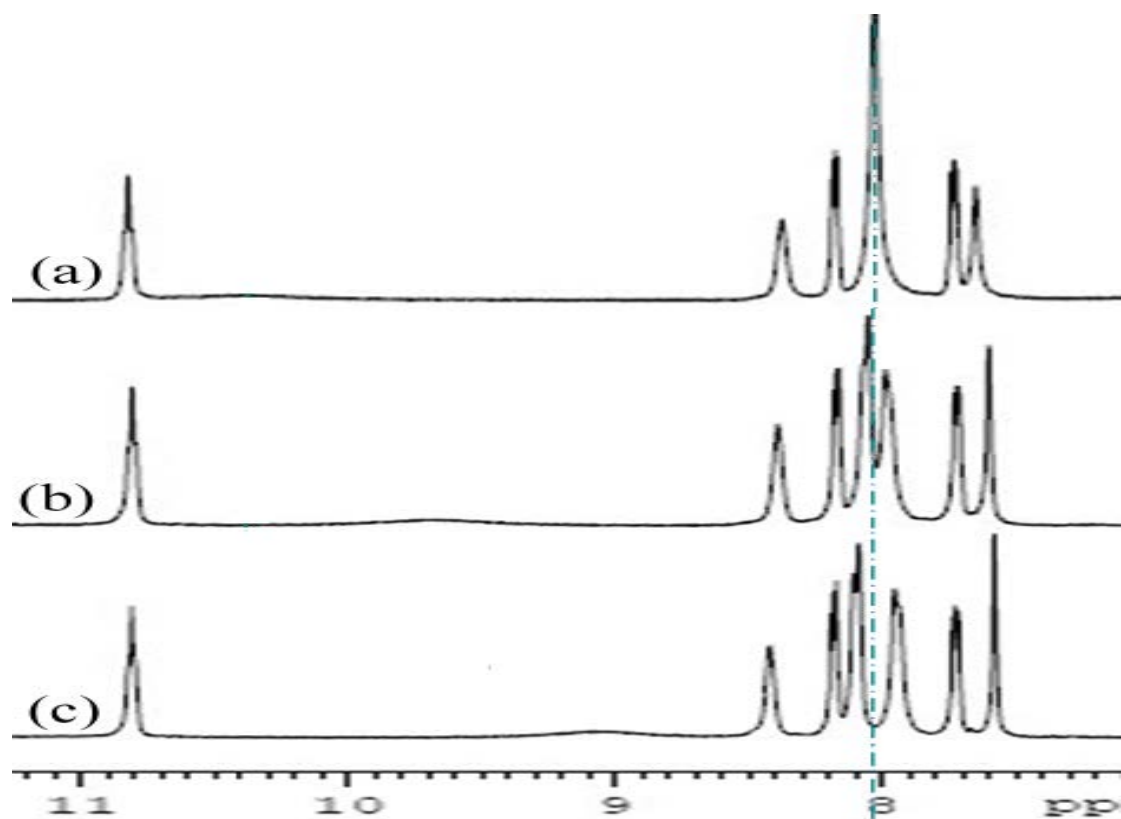


Figure SI-13. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of L-aspartate in the solution (DMSO-*d*₆/ H₂O = 4/1). (a) [2] = [L-aspartate] = 10 mM; (b) [2] = [L-aspartate] = 5 mM; (c) [2] = [L-aspartate] = 1 mM.

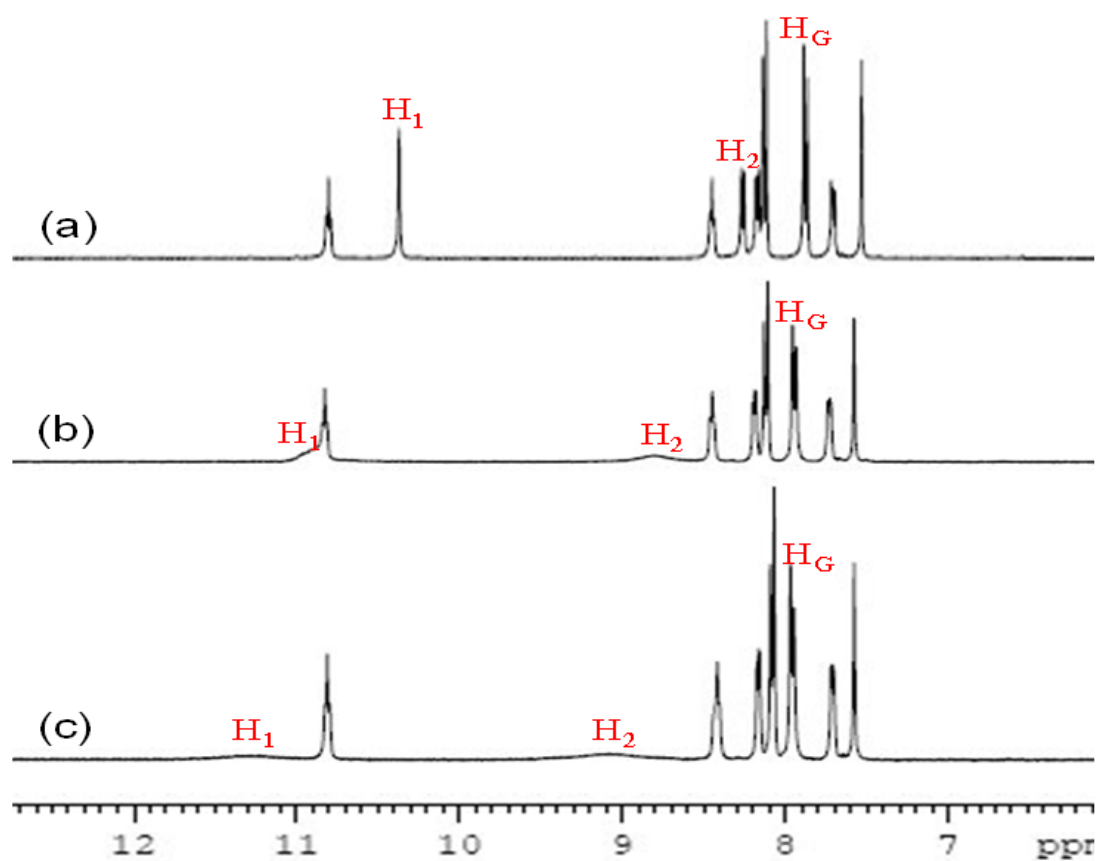


Figure SI-14. ^1H NMR spectra change of **2** operated in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O}=4/1$) after addition of 2.0 equivalents of anions: (a) **2** only; (b) **2**+ L-aspartate; (c) **2**+ D-aspartate.



Figure SI-15. Color changes of complex **2** upon addition of various anions in $\text{DMSO}/\text{H}_2\text{O}$ (4/1, v/v): (a) **2** only; (b) **2** + 2.0 equiv. of L-malate; (c) **2** + 2.0 equiv. of D-malate.

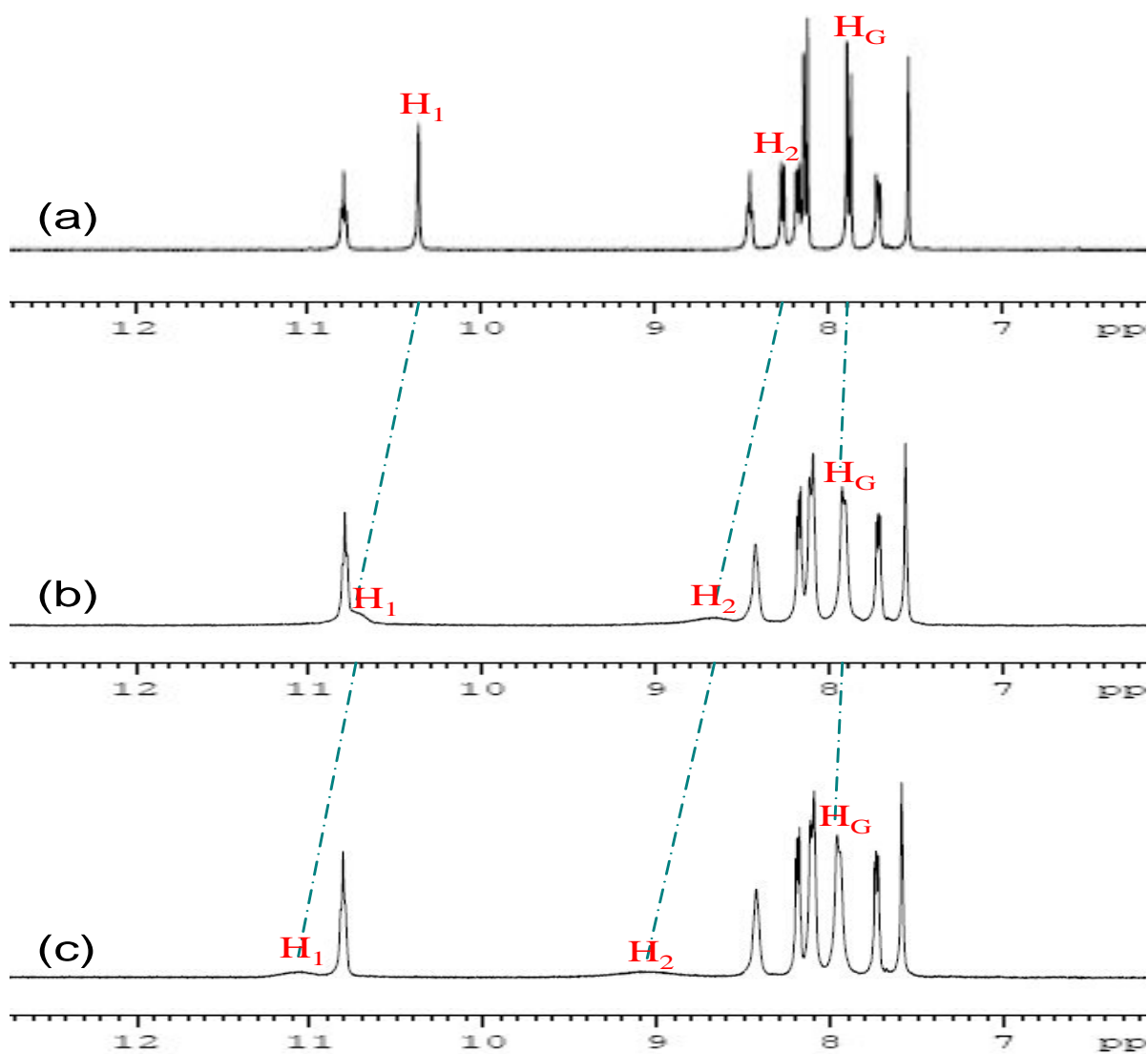


Figure SI-16. ¹H NMR (400Hz) spectra of sensor **2** (10 mM) in the solution (DMSO-*d*₆/ H₂O = 4/1) upon addition of various quantities of D-malate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

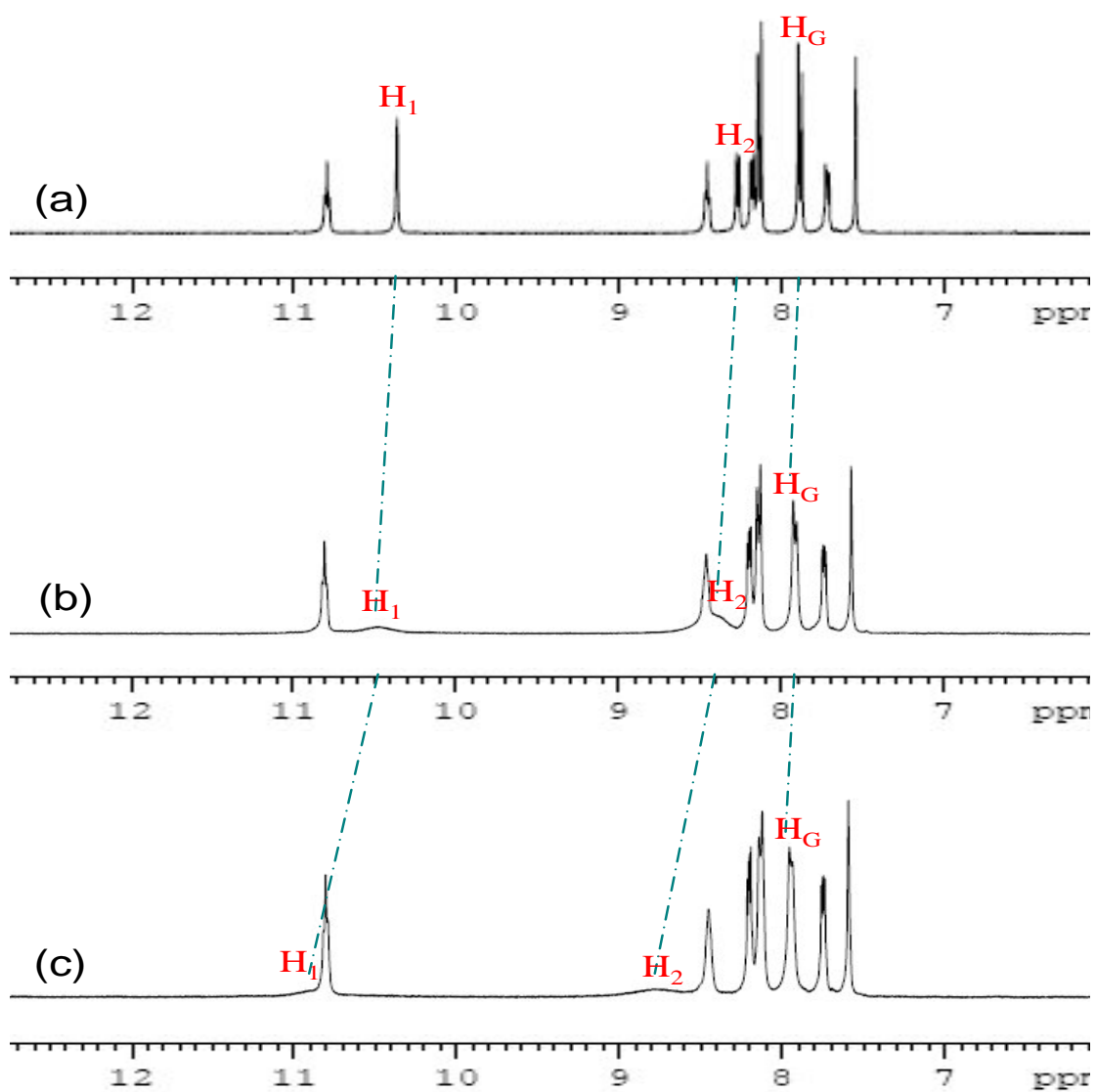


Figure SI-17. ^1H NMR (400Hz) spectra of sensor 2 (10 mM) in the solution (DMSO- d_6 / H_2O = 4/1) upon addition of various quantities of L-malate: (a) 0 eq.; (b) 0.2 eq.; (c) 1.0 eq.

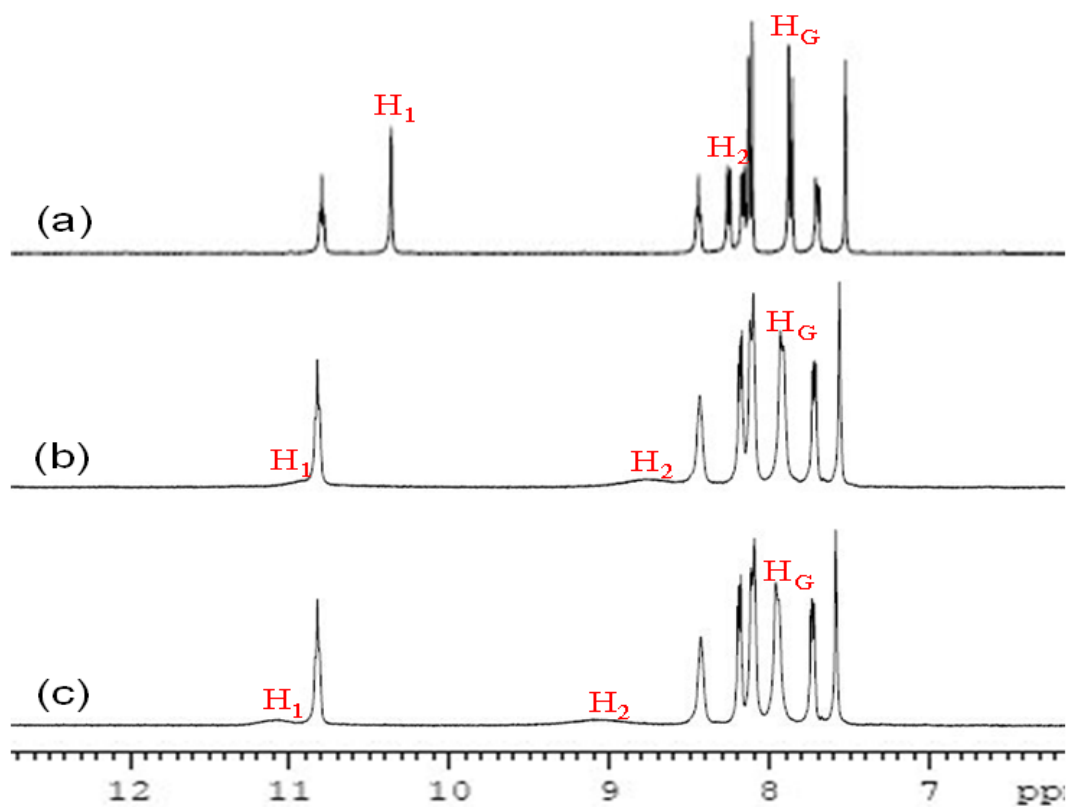


Figure SI-18. ^1H NMR spectra change of **2** operated in the solution ($\text{DMSO-}d_6/\text{H}_2\text{O}=4/1$) after addition of 2.0 equivalents of anions: (a) **2** only; (b) **2**+ L-malate; (c) **2**+ D-malate.

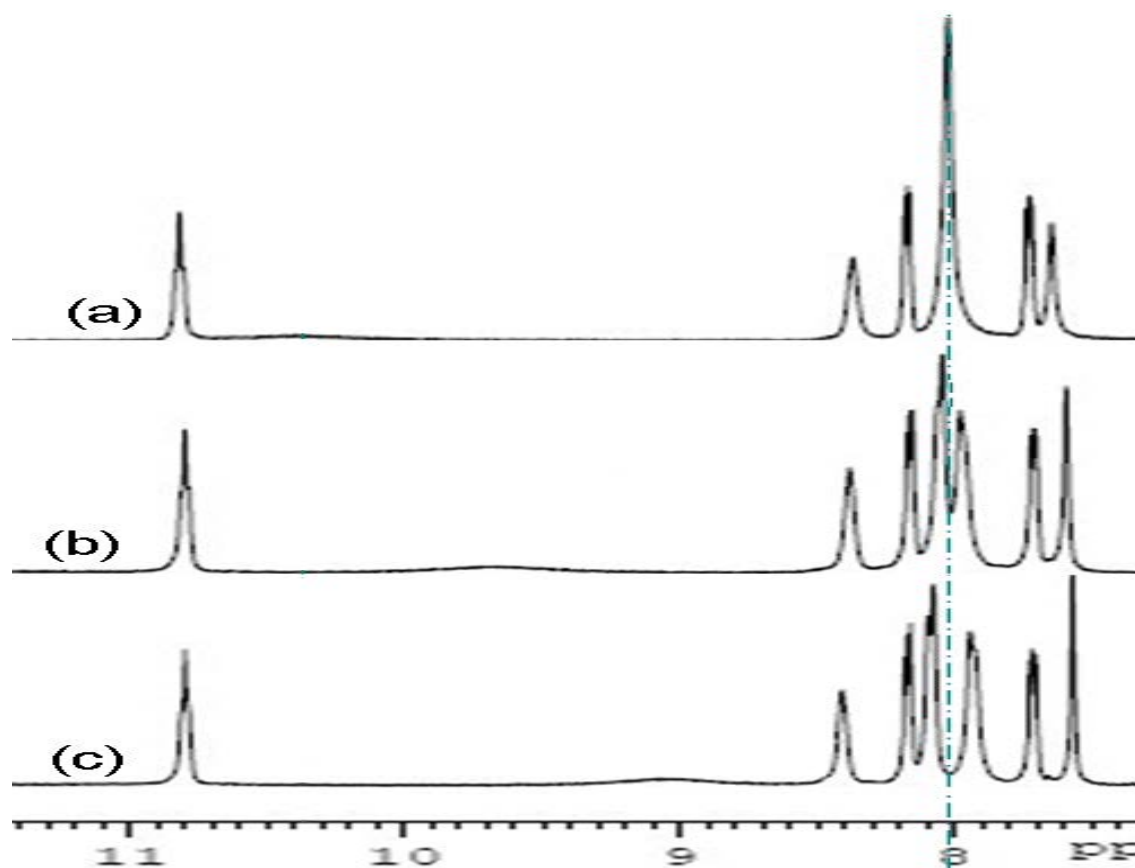


Figure SI-19. Dilution experiment by ¹H NMR of **2** in the presence of 1.0 equiv. of D-malate in the solution (DMSO-*d*₆/H₂O = 4/1). (a) [**2**] = [D-malate] = 10 mM; (b) [**2**] = [D-malate] = 5 mM; (c) [**2**] = [D-malate] = 1 mM.

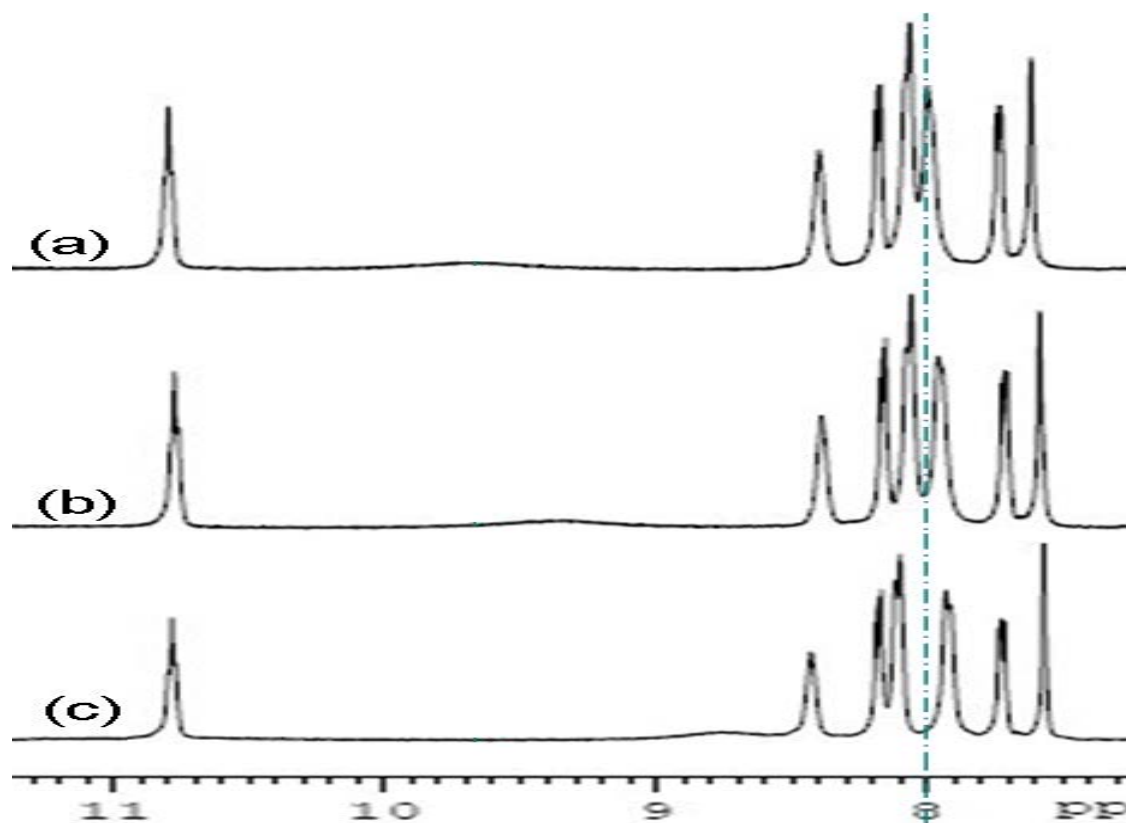


Figure SI-20. Dilution experiment by ^1H NMR of **2** in the presence of 1.0 equiv. of L-malate in the solution (DMSO- d_6 / $\text{H}_2\text{O} = 4/1$). (a) $[\mathbf{2}] = [\text{L-malate}] = 10 \text{ mM}$; (b) $[\mathbf{2}] = [\text{L-malate}] = 5 \text{ mM}$; (c) $[\mathbf{2}] = [\text{L-malate}] = 1 \text{ mM}$.