

Electronic Supplementary Information

Chiral recognition of carboxylates by static library of thiourea receptors with amino acid arms

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S1 NMR spectra

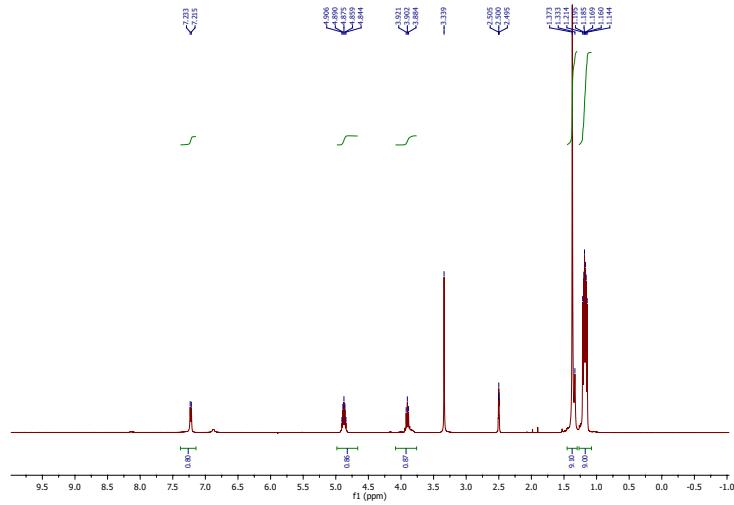


Figure S1: ^1H NMR spectrum of **8b** in DMSO-d_6 .

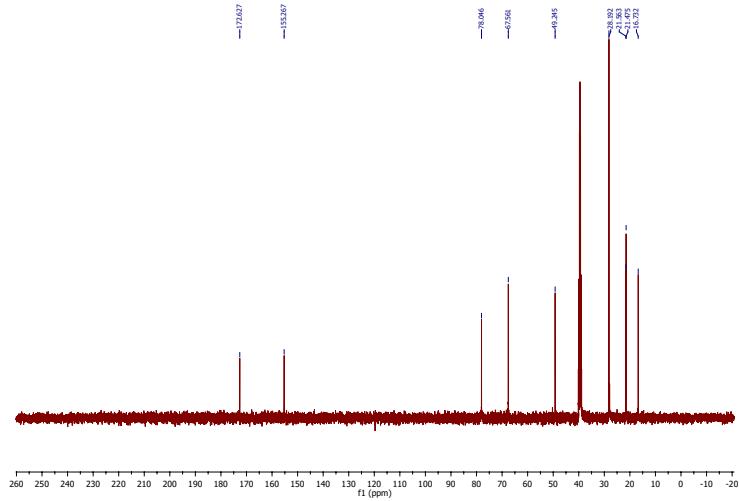


Figure S2: ^{13}C NMR spectrum of **8b** in DMSO-d_6 .

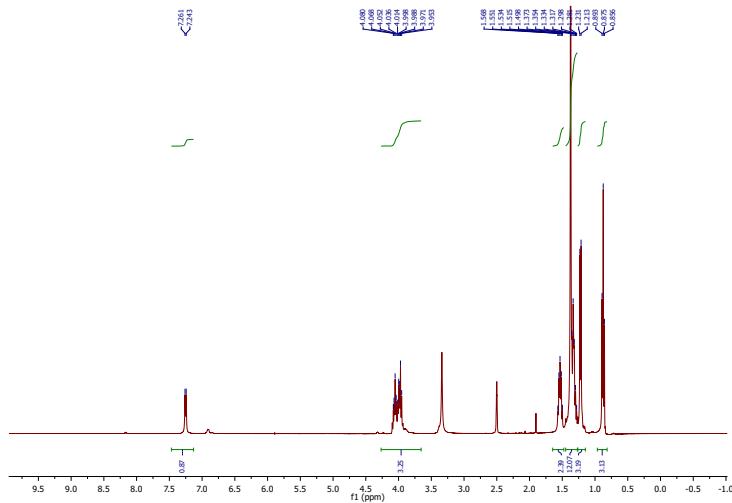


Figure S3: ^1H NMR spectrum of **8c** in DMSO-d_6 .

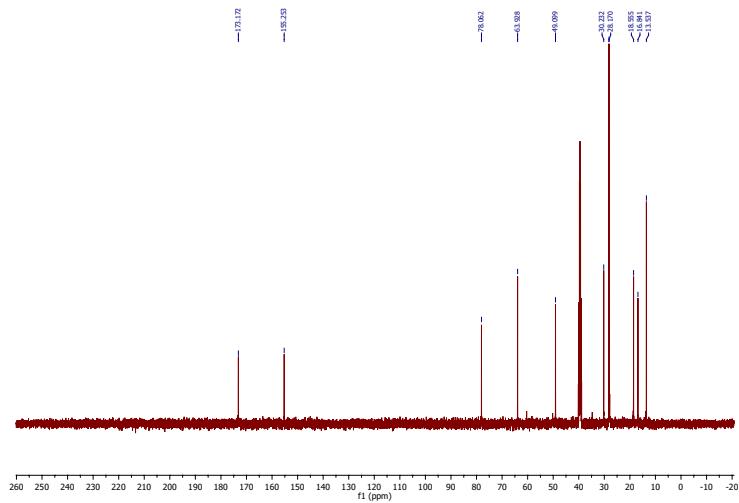


Figure S4: ^{13}C NMR spectrum of **8c** in DMSO-d_6 .

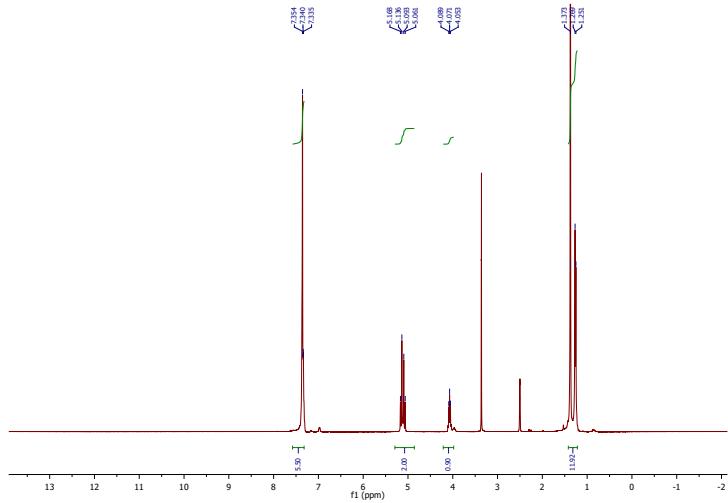


Figure S5: ^1H NMR spectrum of **8d** in DMSO-d_6 .

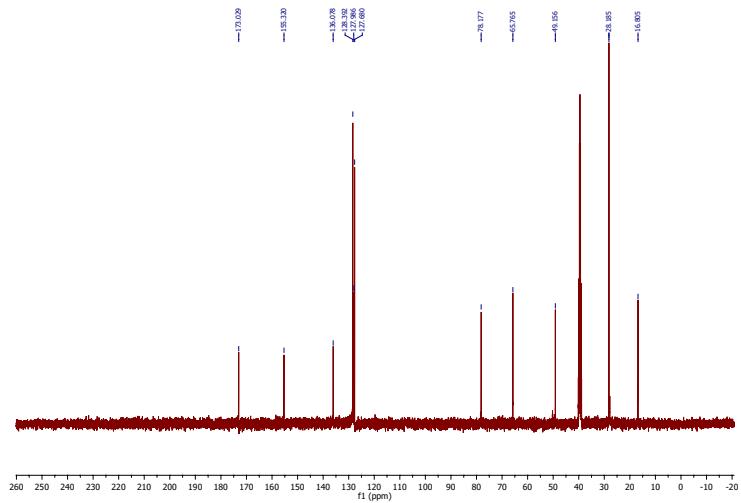


Figure S6: ^{13}C NMR spectrum of **8d** in DMSO-d_6 .

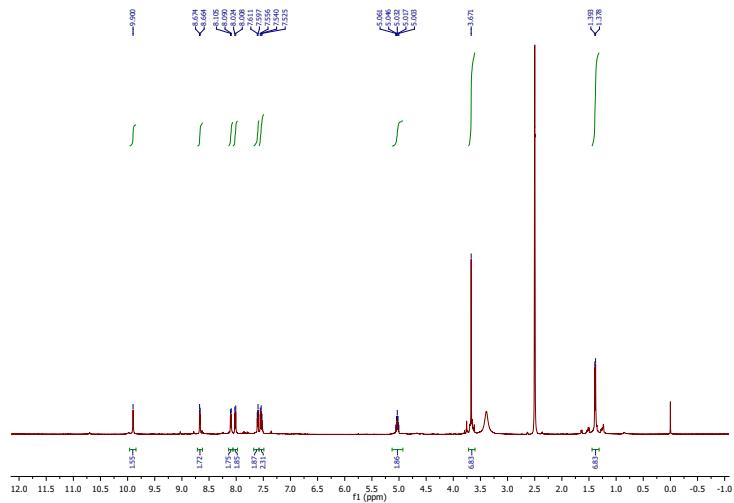


Figure S7: ^1H NMR spectrum of **1a** in DMSO-d_6 .

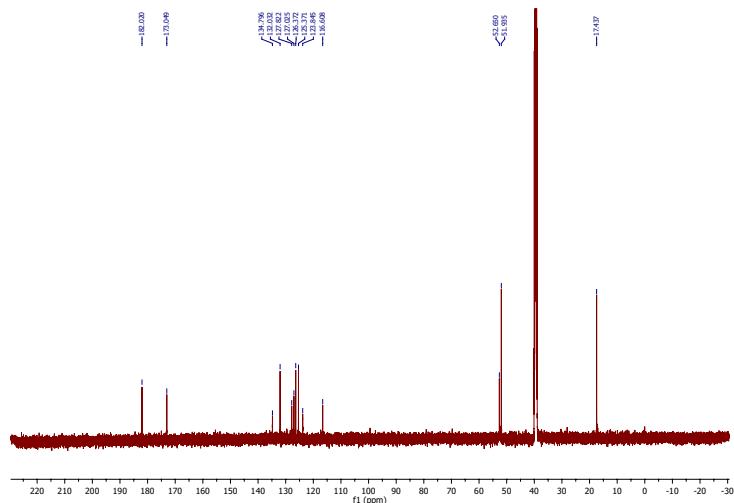


Figure S8: ^{13}C NMR spectrum of **1a** in DMSO-d_6 .

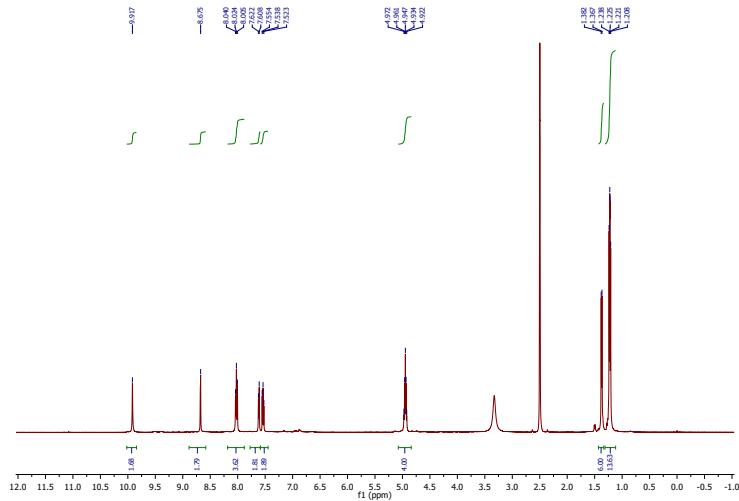


Figure S9: ^1H NMR spectrum of **1b** in DMSO-d_6 .

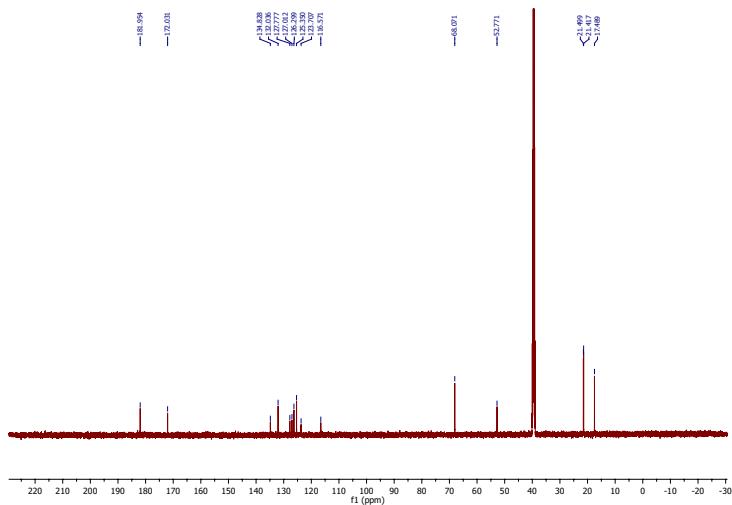


Figure S10: ^{13}C NMR spectrum of **1b** in DMSO-d_6 .

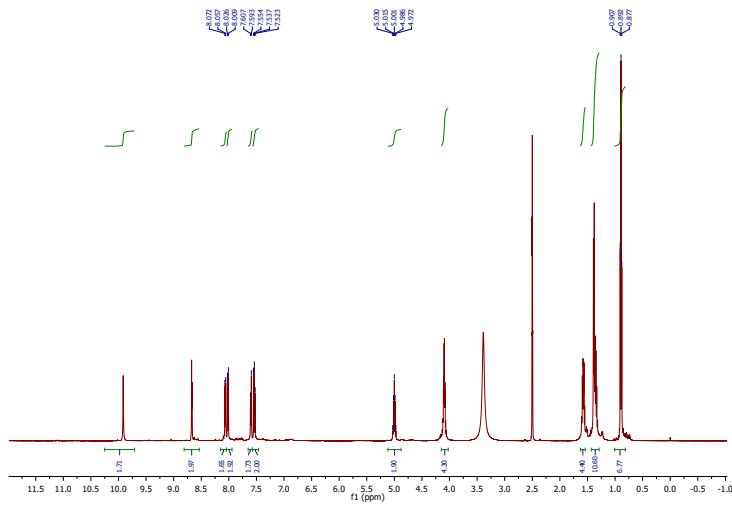


Figure S11: ^1H NMR spectrum of **1c** in DMSO-d_6 .

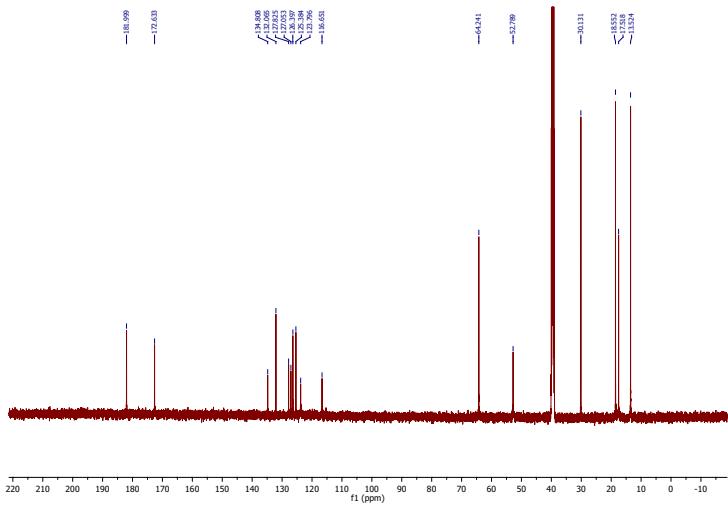


Figure S12: ^{13}C NMR spectrum of **1c** in DMSO-d_6 .

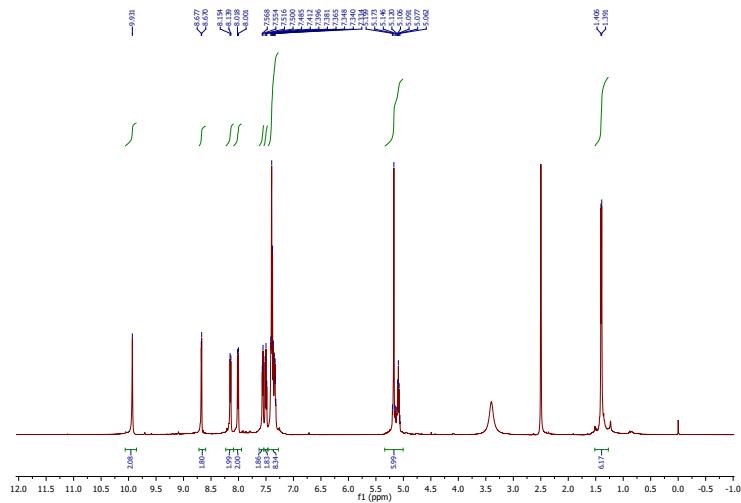


Figure S13: ^1H NMR spectrum of **1d** in DMSO-d_6 .

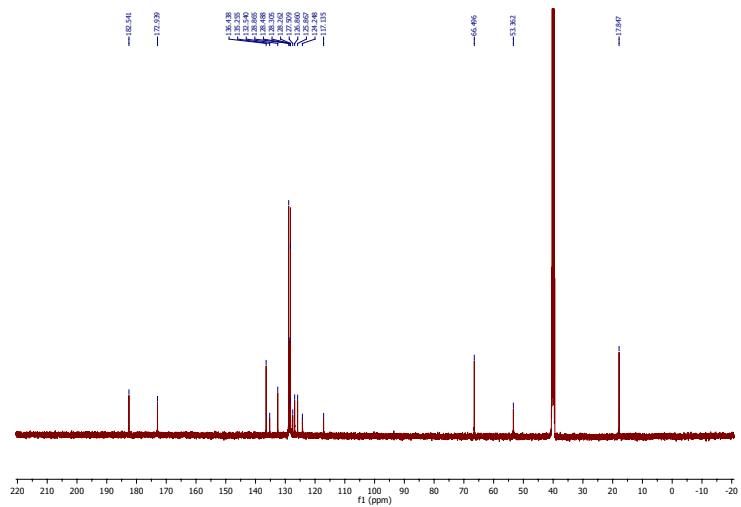


Figure S14: ^{13}C NMR spectrum of **1d** in DMSO-d_6 .

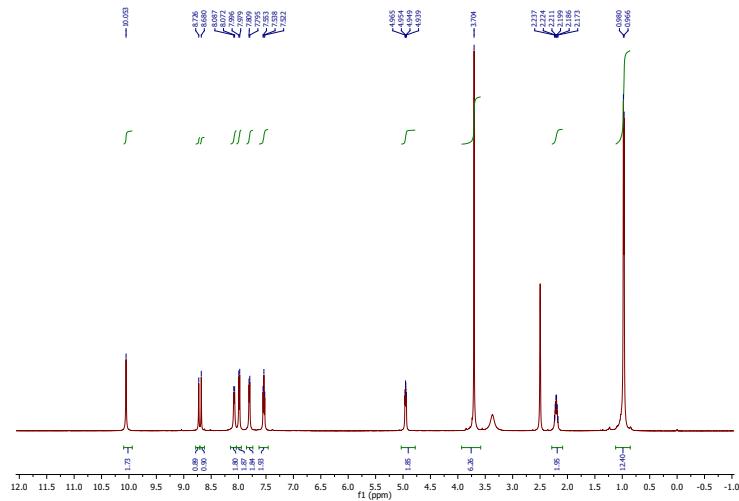


Figure S15: ^1H NMR spectrum of **1e** in DMSO-d_6 .

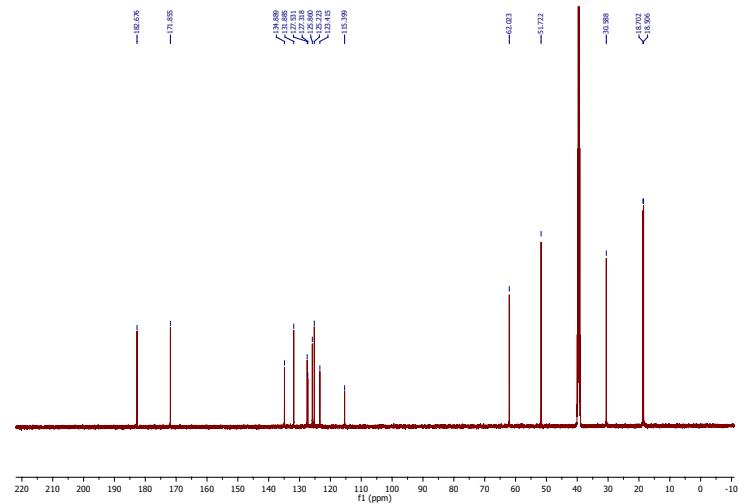


Figure S16: ^{13}C NMR spectrum of **1e** in DMSO-d_6 .

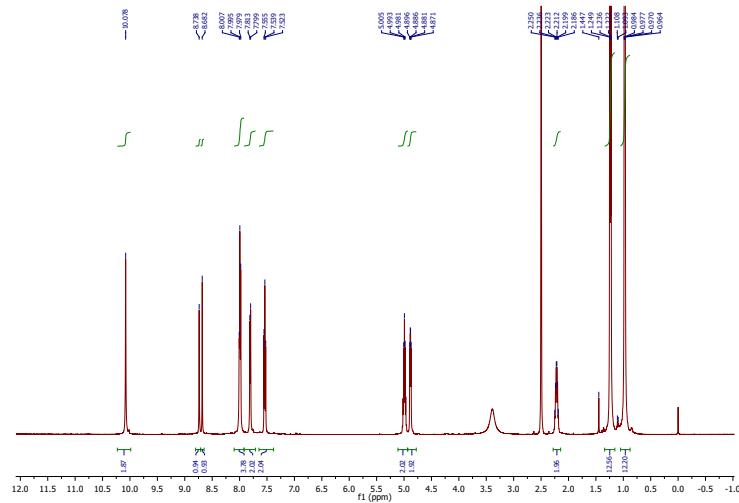


Figure S17: ^1H NMR spectrum of **1f** in DMSO-d_6 .

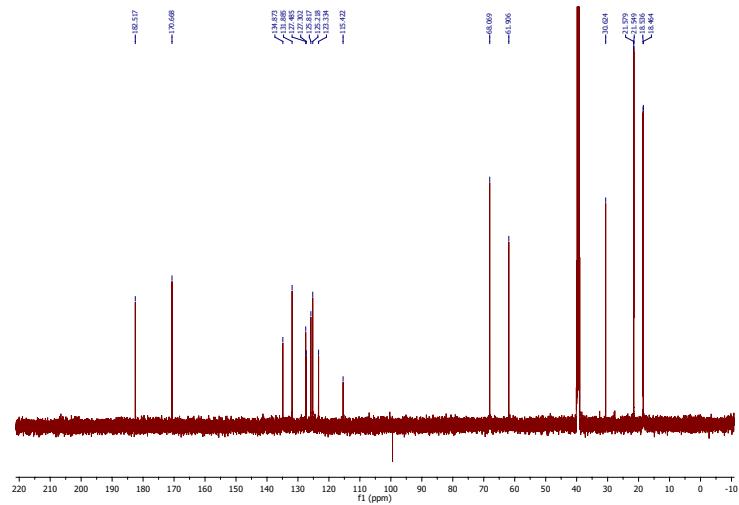


Figure S18: ^{13}C NMR spectrum of **1f** in DMSO-d_6 .

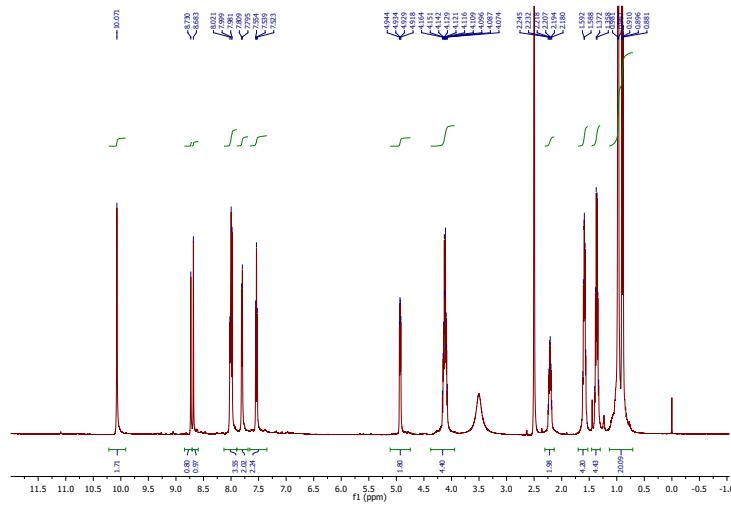


Figure S19: ^1H NMR spectrum of **1g** in DMSO-d_6 .

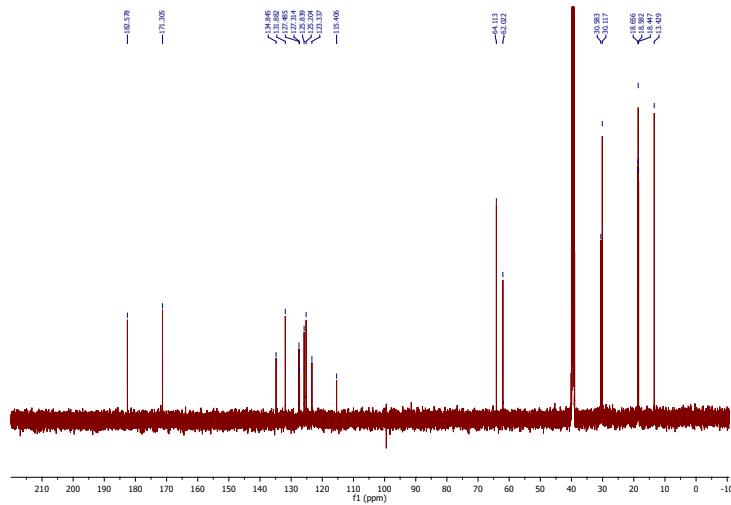


Figure S20: ^{13}C NMR spectrum of **1g** in DMSO-d_6 .

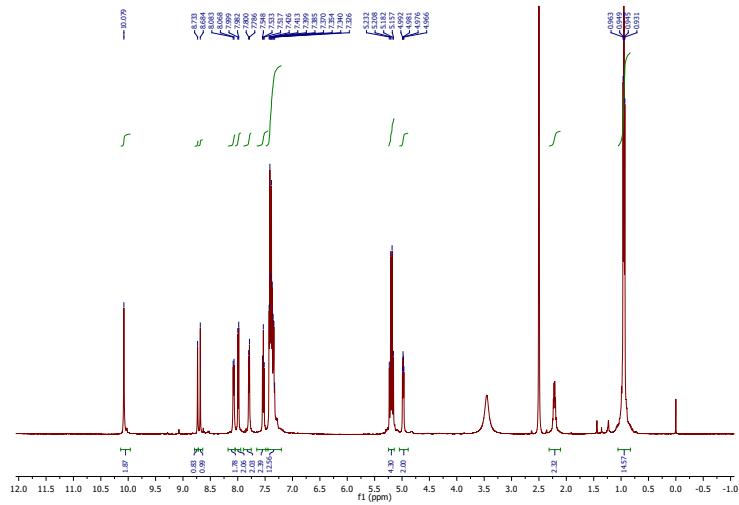


Figure S21: ^1H NMR spectrum of **1h** in DMSO-d_6 .

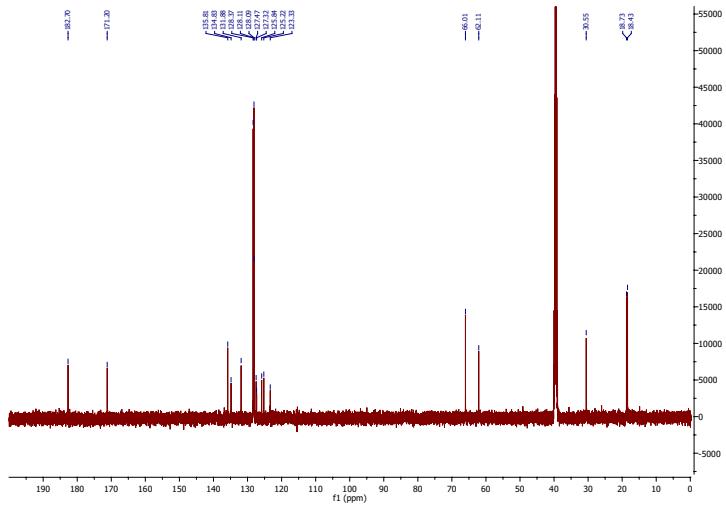


Figure S22: ^{13}C NMR spectrum of **1h** in DMSO-d_6 .

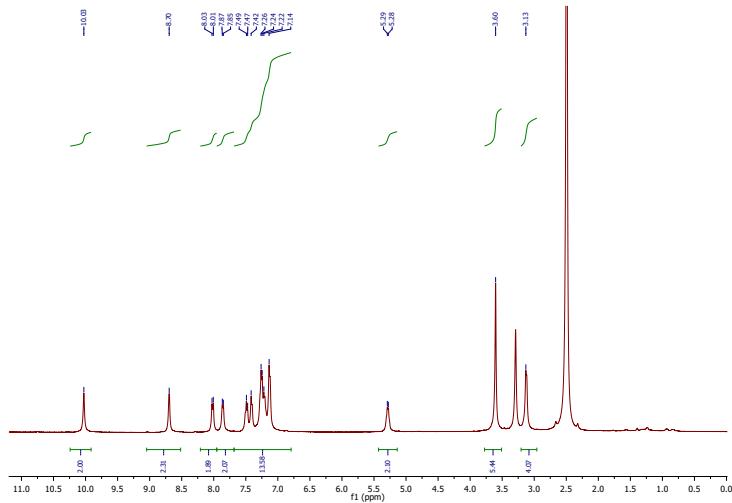


Figure S23: ^1H NMR spectrum of **1i** in DMSO-d_6 .

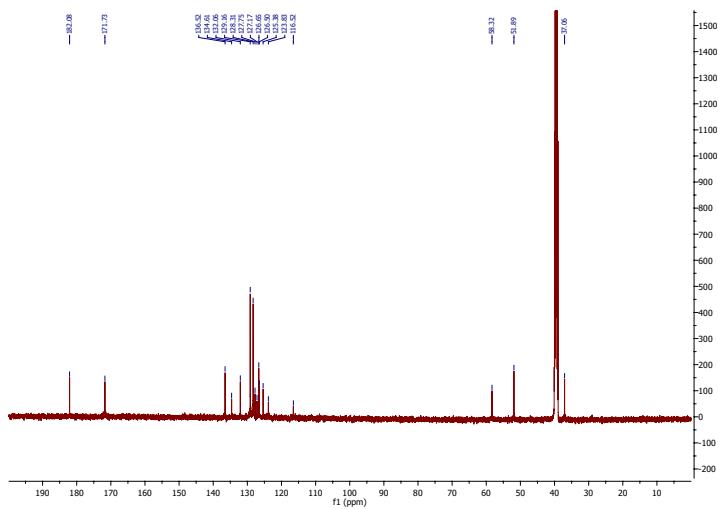


Figure S24: ^{13}C NMR spectrum of **1i** in DMSO-d_6 .

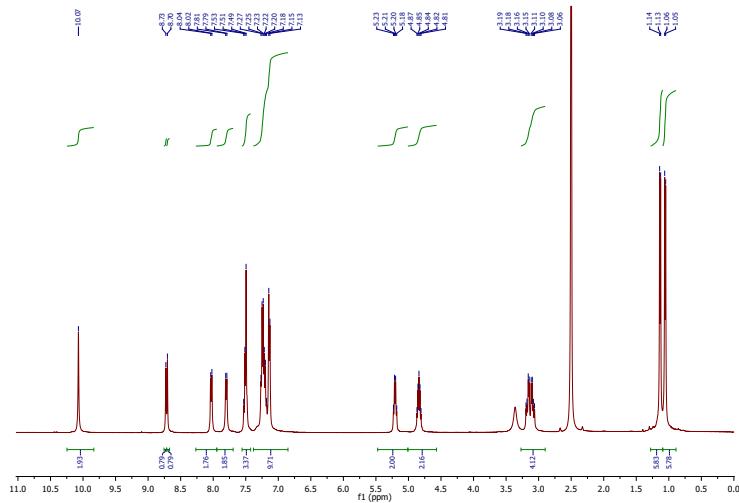


Figure S25: ^1H NMR spectrum of **1j** in DMSO-d_6 .

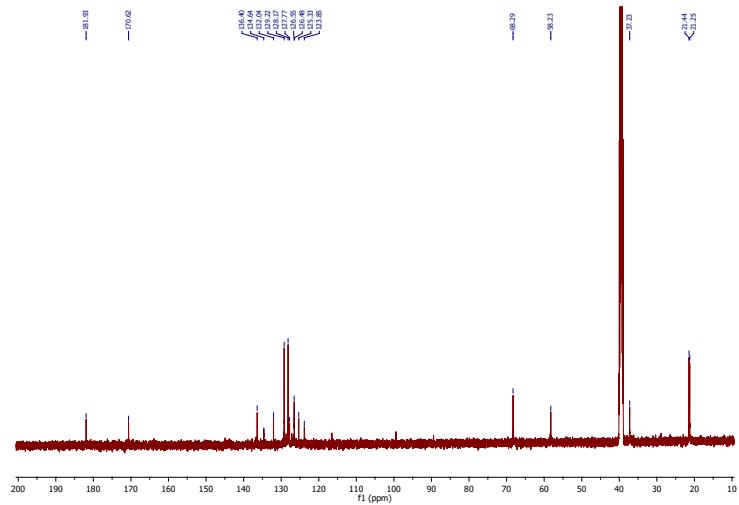


Figure S26: ^{13}C NMR spectrum of **1j** in DMSO-d_6 .

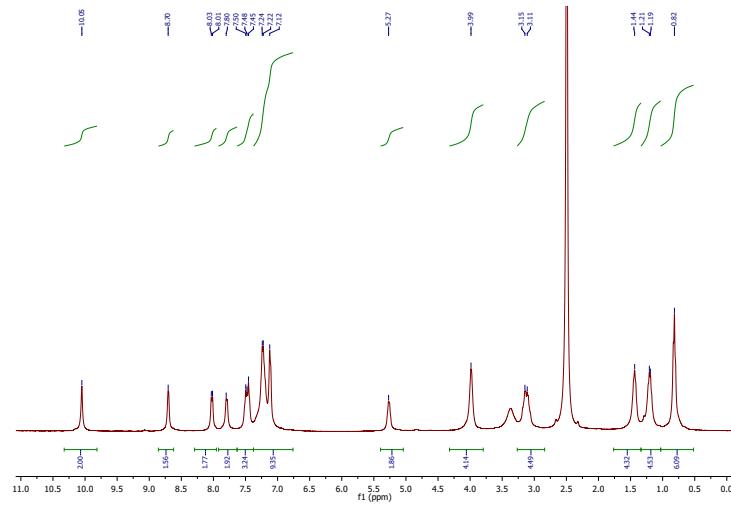


Figure S27: ^1H NMR spectrum of **1k** in DMSO-d_6 .

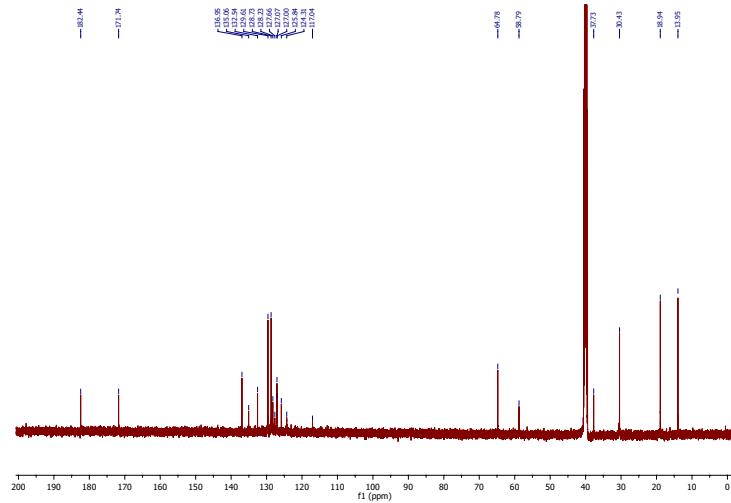


Figure S28: ^{13}C NMR spectrum of **1k** in DMSO-d_6 .

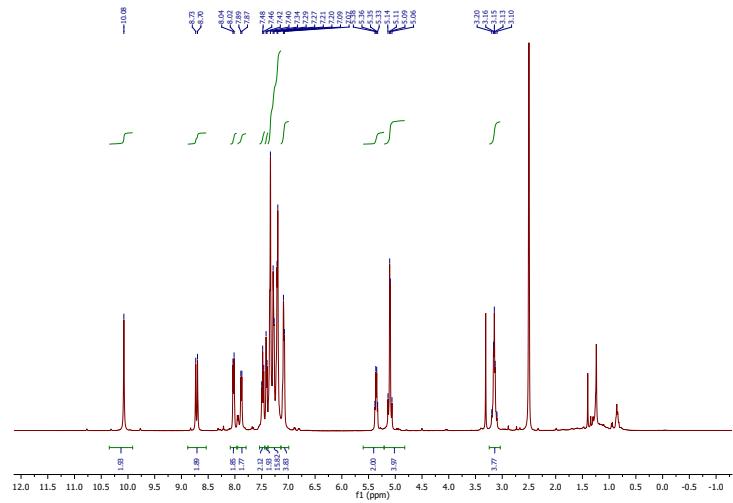
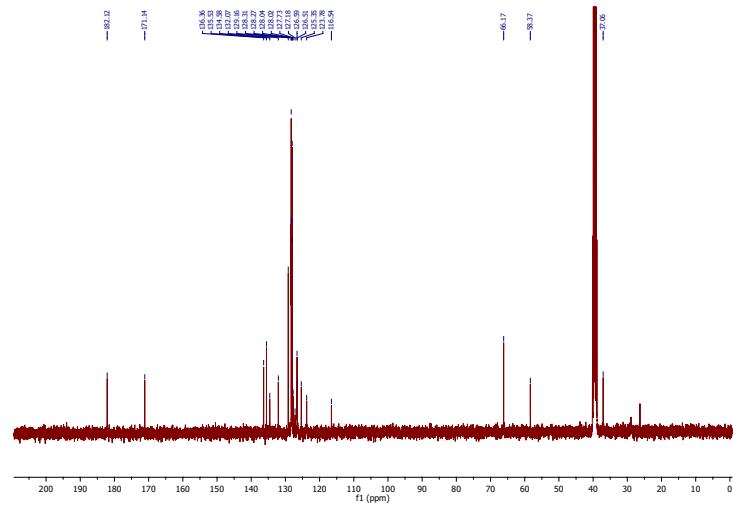


Figure S29: ^1H NMR spectrum of **1l** in DMSO-d_6 .



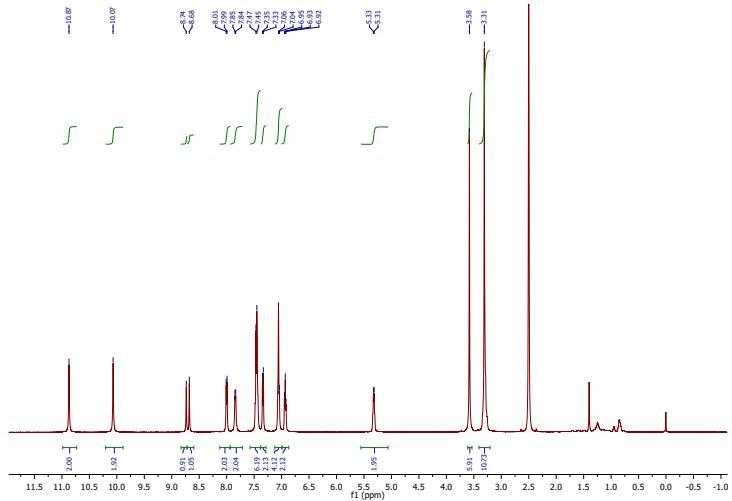


Figure S31: ^1H NMR spectrum of **1m** in DMSO-d_6 .

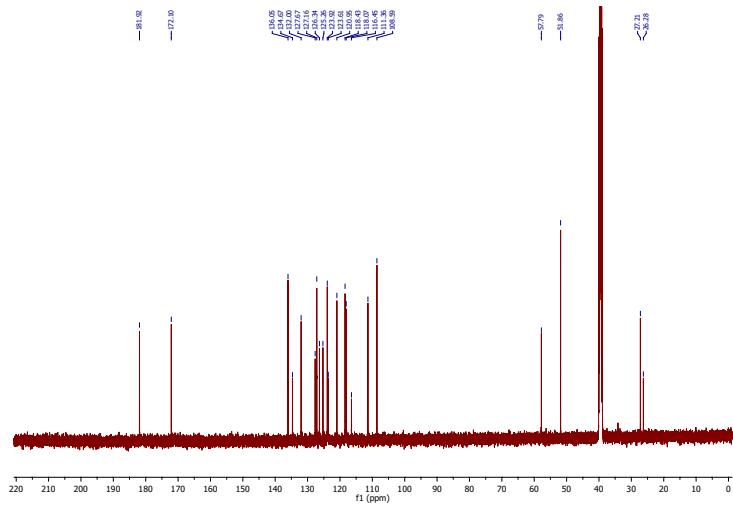
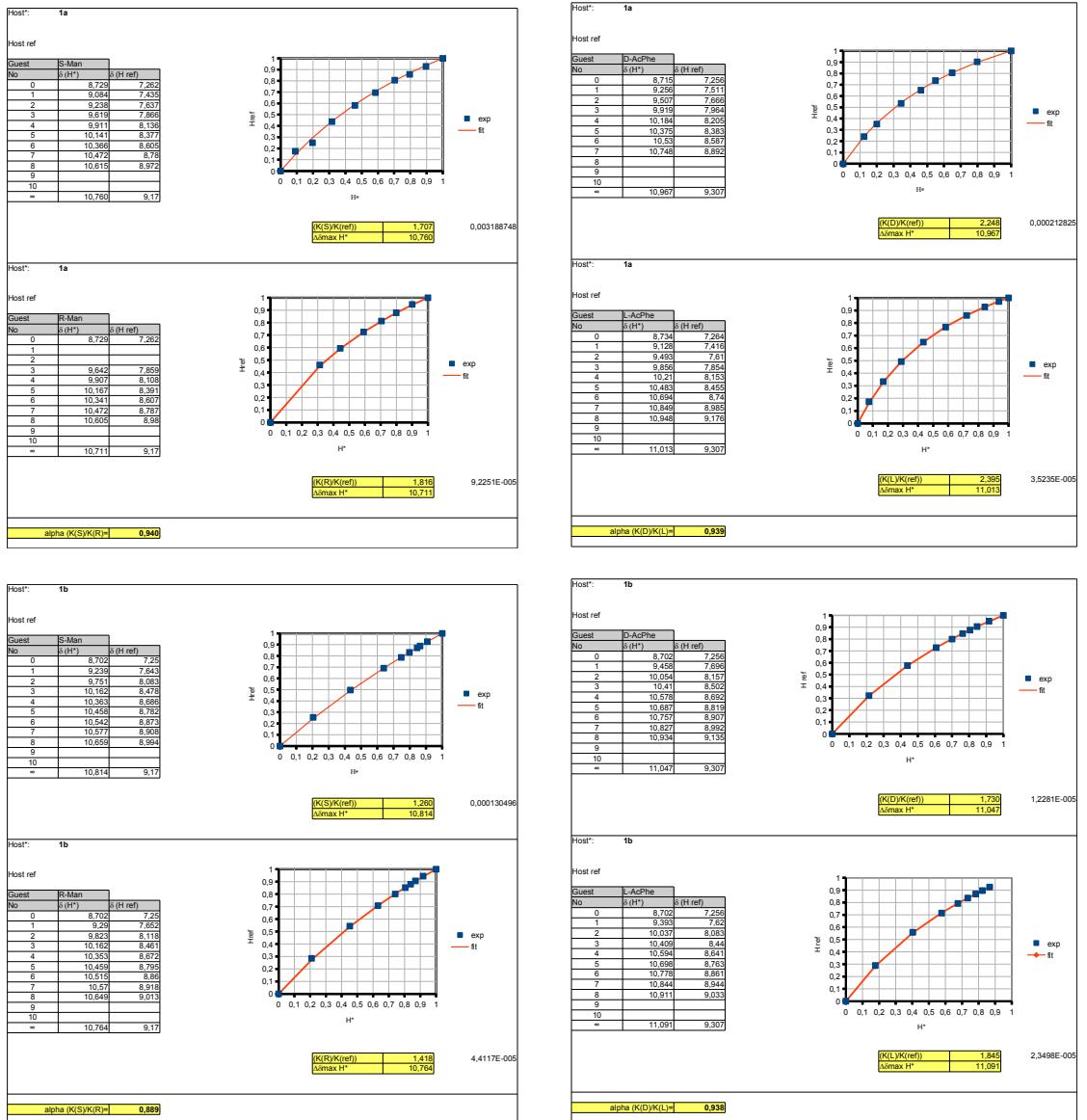
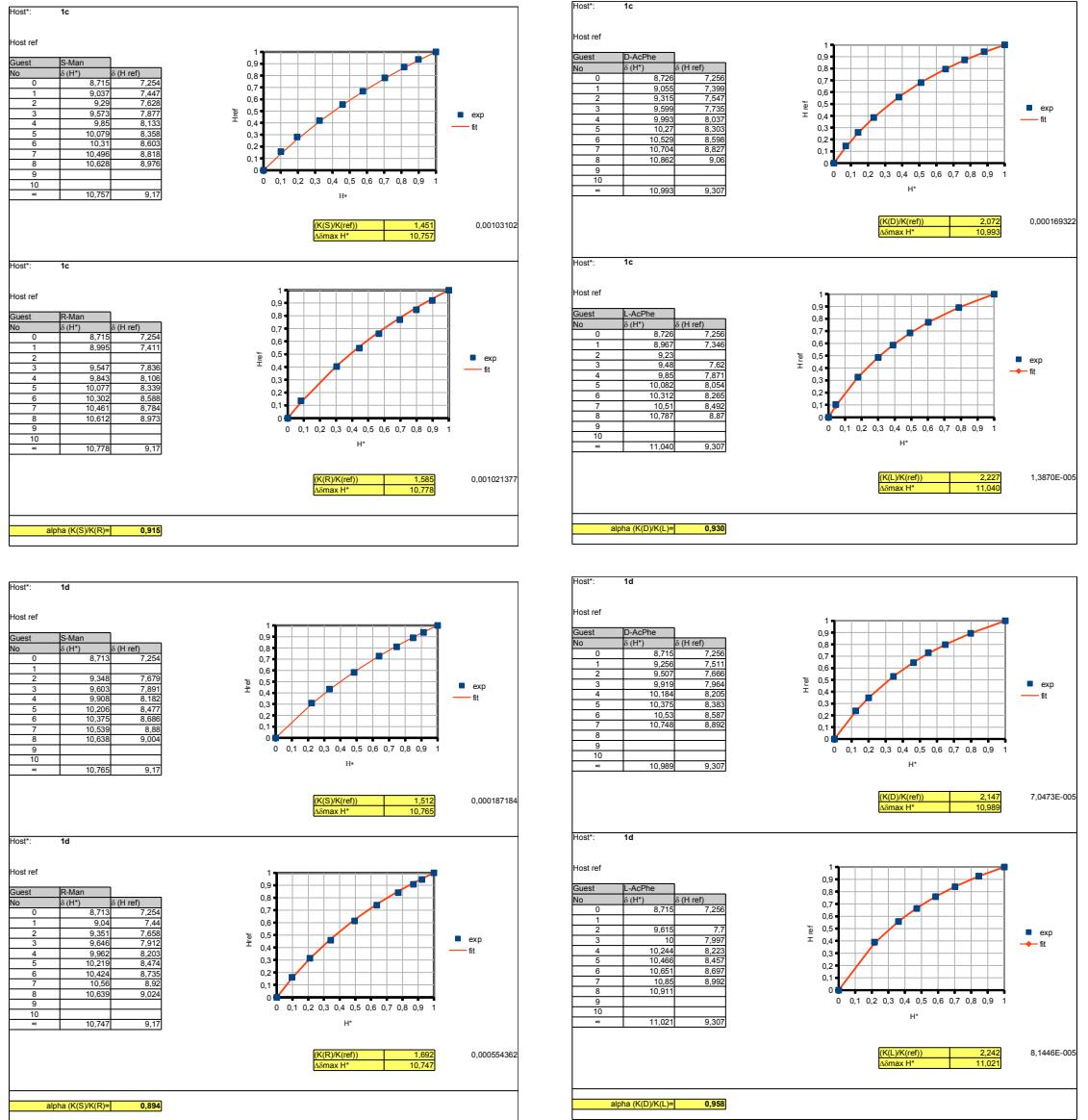
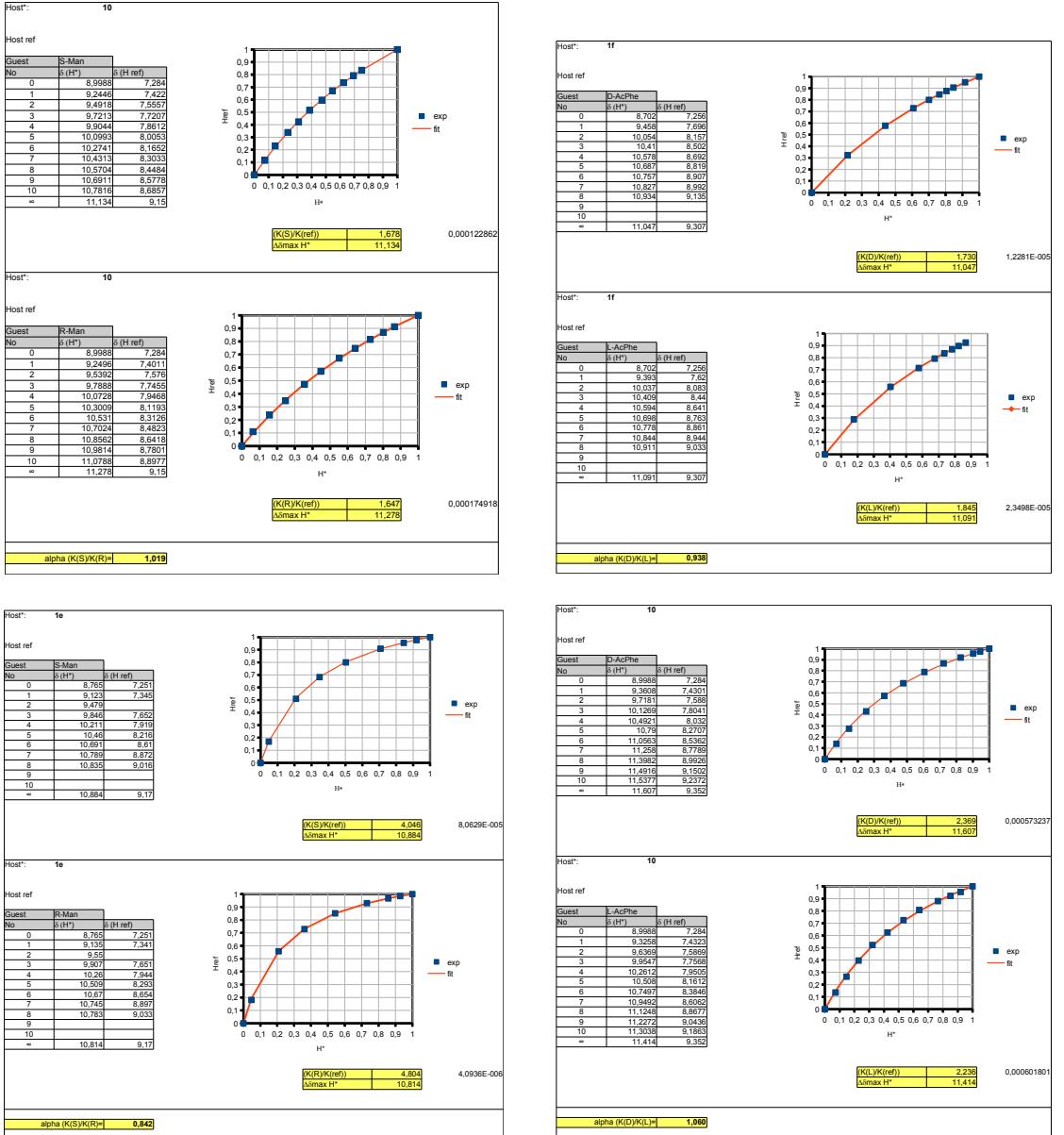


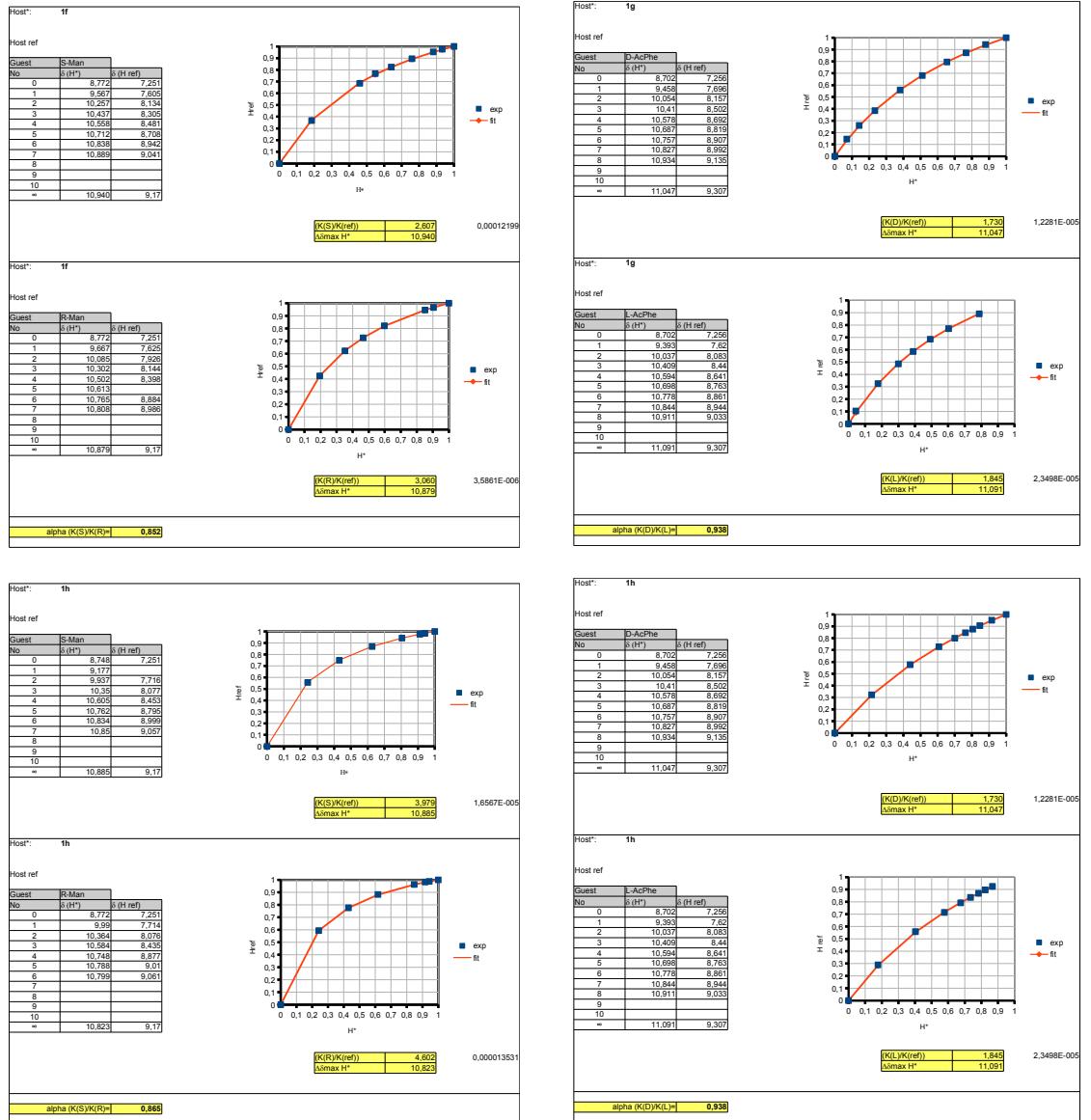
Figure S32: ^{13}C NMR spectrum of **1m** in DMSO-d_6 .

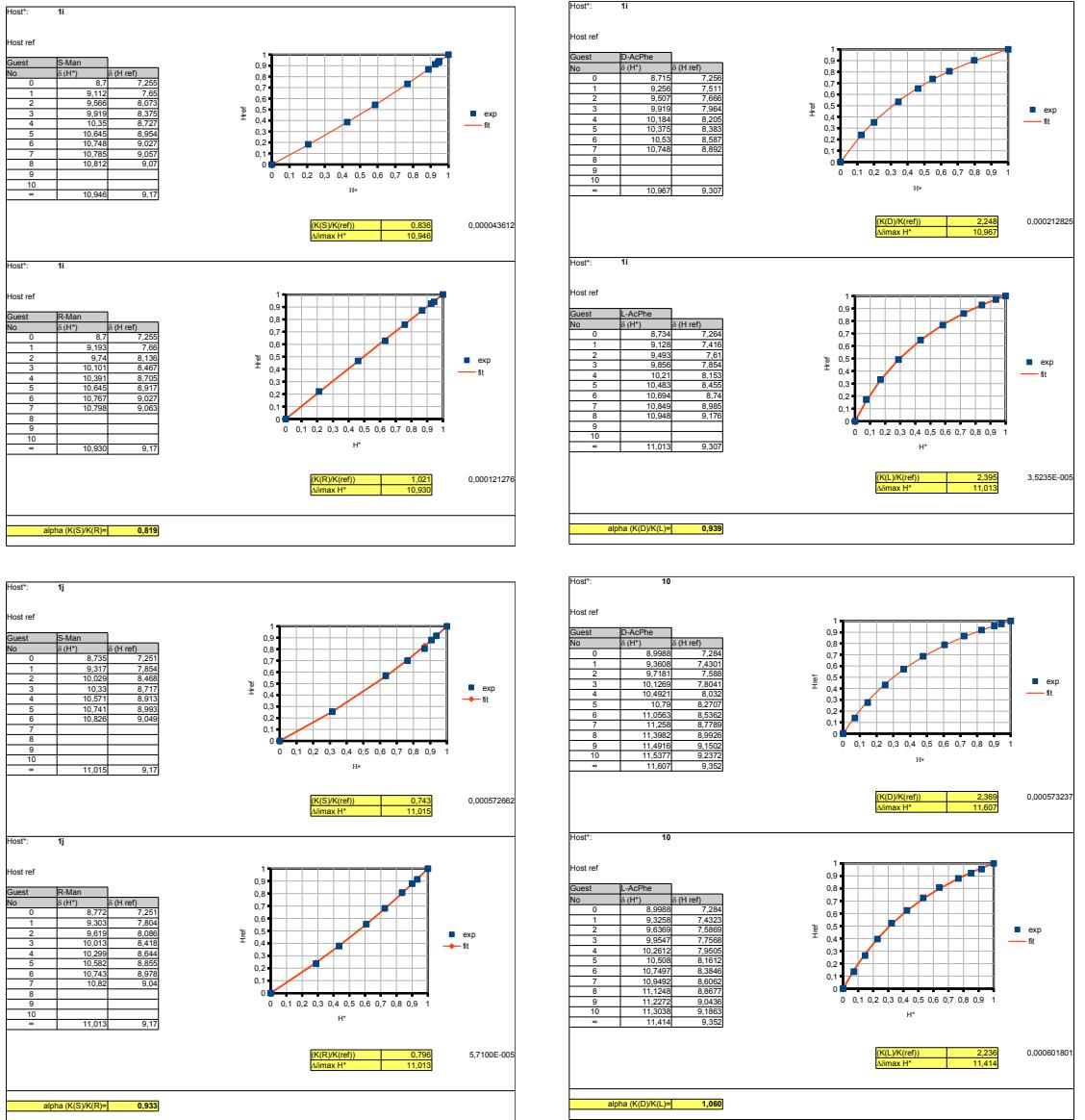
S2 Competitive Titrations

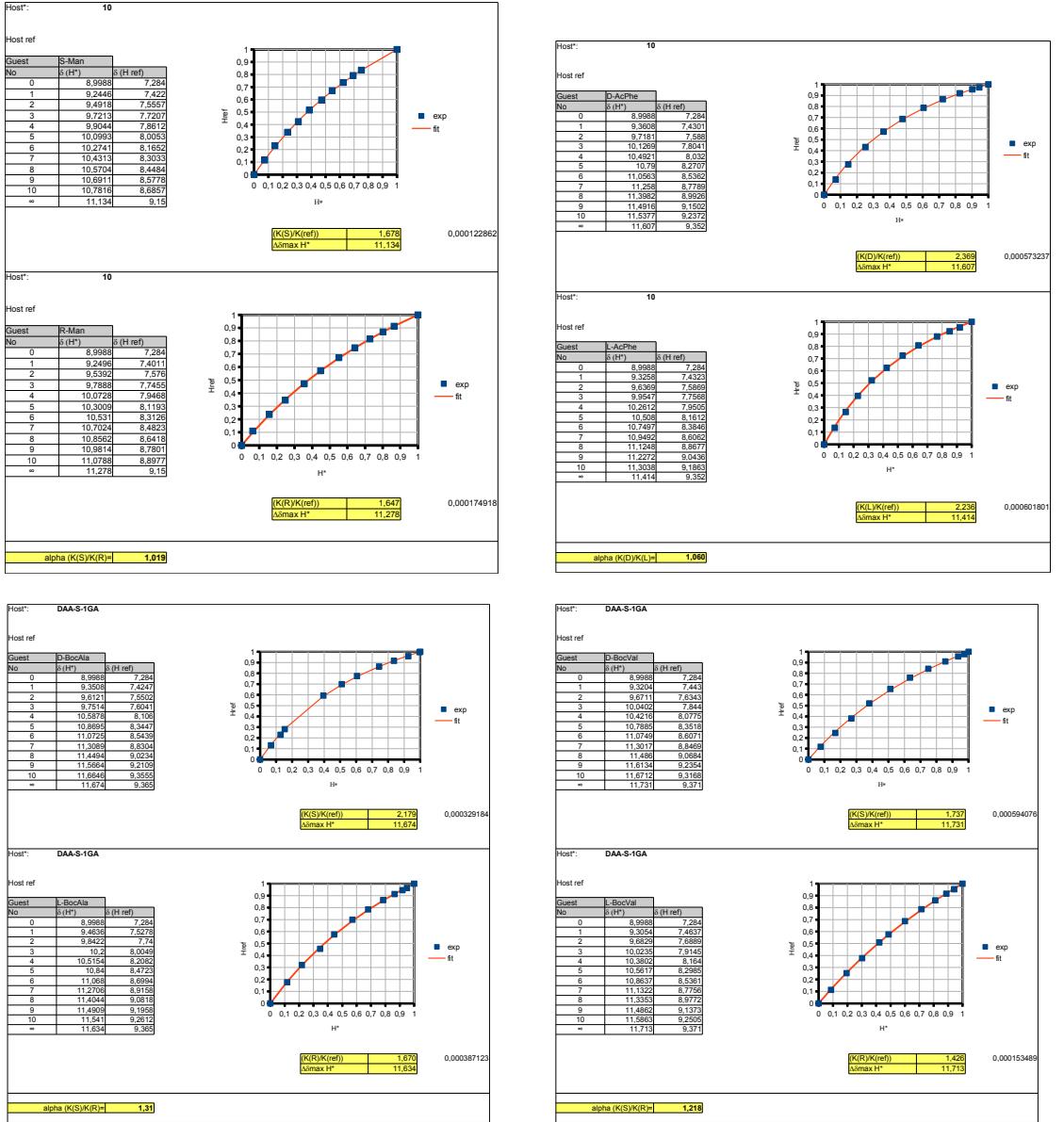


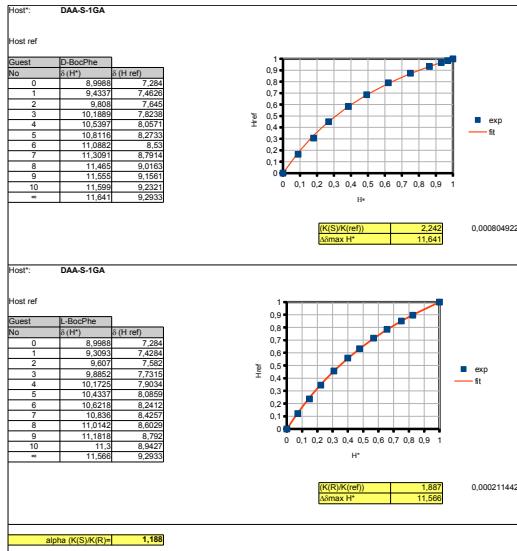








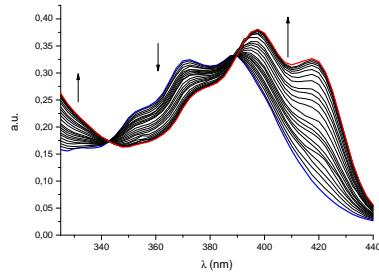




S3 UV-Vis titrations

S3.1 Procedure

To a solution of host **10** in MeCN (HPLC grade, $c = 5.0 \cdot 10^{-5}$, 2.5 mL) in 10 mm spectrophotometric cuvette, were added aliquots of solution of TBA salt of appropriate amino acid ($c = 5.0 \cdot 10^{-3}$) via a syringe pump. At least 20 titration points were recorded until host was saturated with guest c85%. Typical change of UV-Vis spectrum is presented in the Figure:

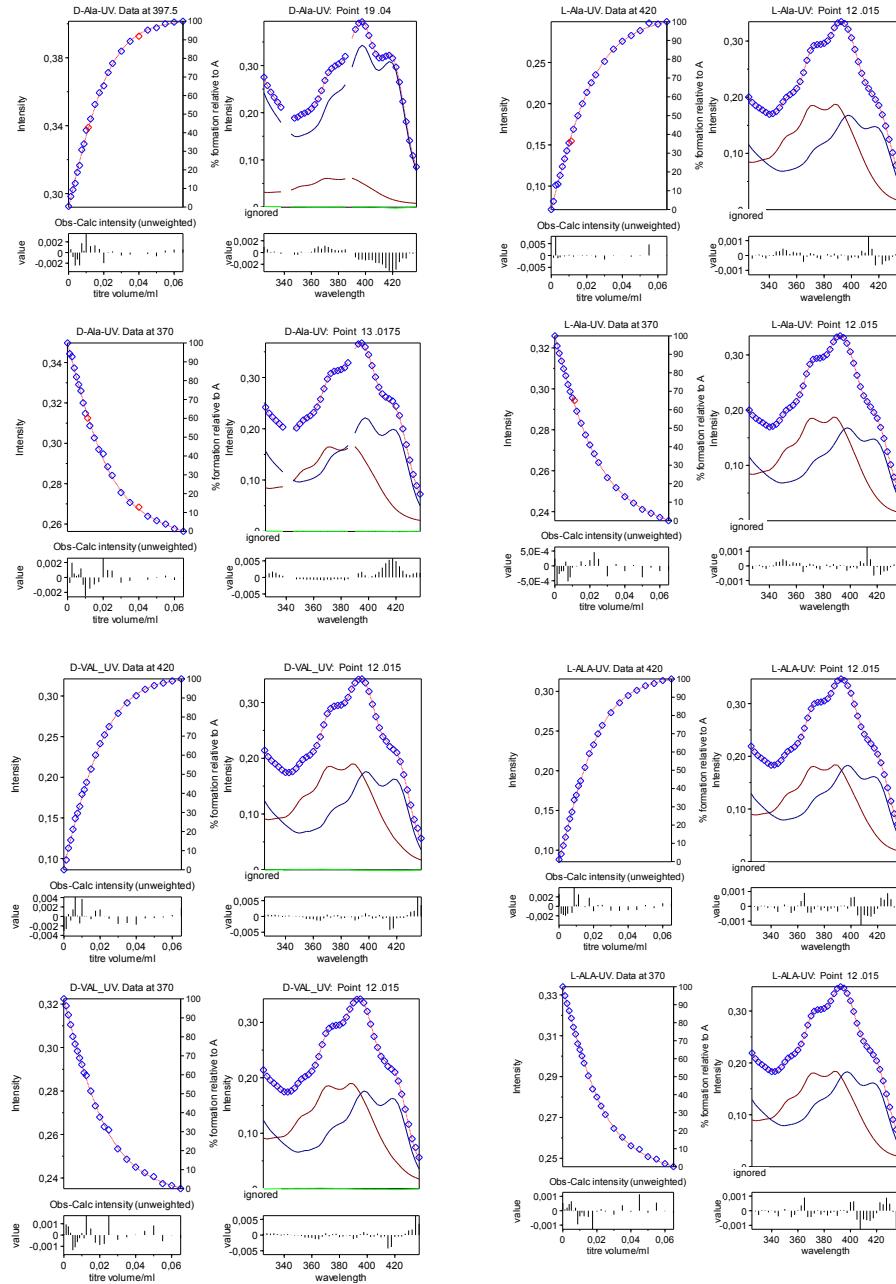


Data were fitted with HypSpec¹, which enables global fitting of absorption data at all wavelengths. The uncertainty of determination of association constants (K_a) is estimated to be $\pm 5\%$, uncertainty of enantioselectivities (α) $\pm 7\%$. The obtained results are presented in Table:

Guest	$K_a [M^{-1}]$	α
Boc-D-Ala	$1.19 \cdot 10^5$	1.40
Boc-L-Ala	$8.52 \cdot 10^4$	
Boc-D-Val	$1.19 \cdot 10^5$	1.02
Boc-L-Val	$1.16 \cdot 10^5$	

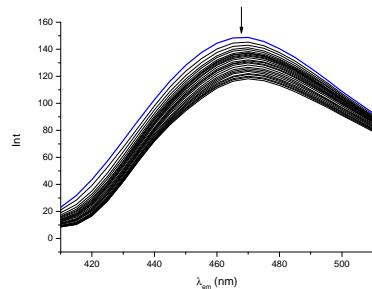
¹HypSpec by Peter Gans, *Protonic Software*

S3.2 Titration plots



S4 Fluorometry titrations

To a solution of host **10** in MeCN (HPLC grade, $c = 1.0 \cdot 10^{-5}$, 2.5 mL) in 10 mm fluorometer cuvette, were added aliquots of solution of TBA salt of appropriate amino acid ($c = 5.0 \cdot 10^{-3}$) via a syringe pump. At least 20 titration points were recorded until host was saturated with guest $\approx 85\%$. Typical change of emission spectrum ($\lambda_{ex}=360$ nm) is presented in the Figure:



Data were fitted with HypSpec, which enables global fitting of emission data at all wavelengths. The data could not be fit with any rational binding model, as the plateau could not be reached. Fine fitting with a 1 : 1 model was obtained when a contribution of the unbound guest to the fluorescence spectrum was assumed. The fitted "emission spectrum" of the unbound anion was found to be negative (green line on a plot), which means that quenching of receptors fluorescence is not trivial.

