Supplementary Material (ESI)

To Chelate Thallium(I) - Synthesis and Evaluation of Kryptofix-based Chelators for ^{201}Tl.

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Contents

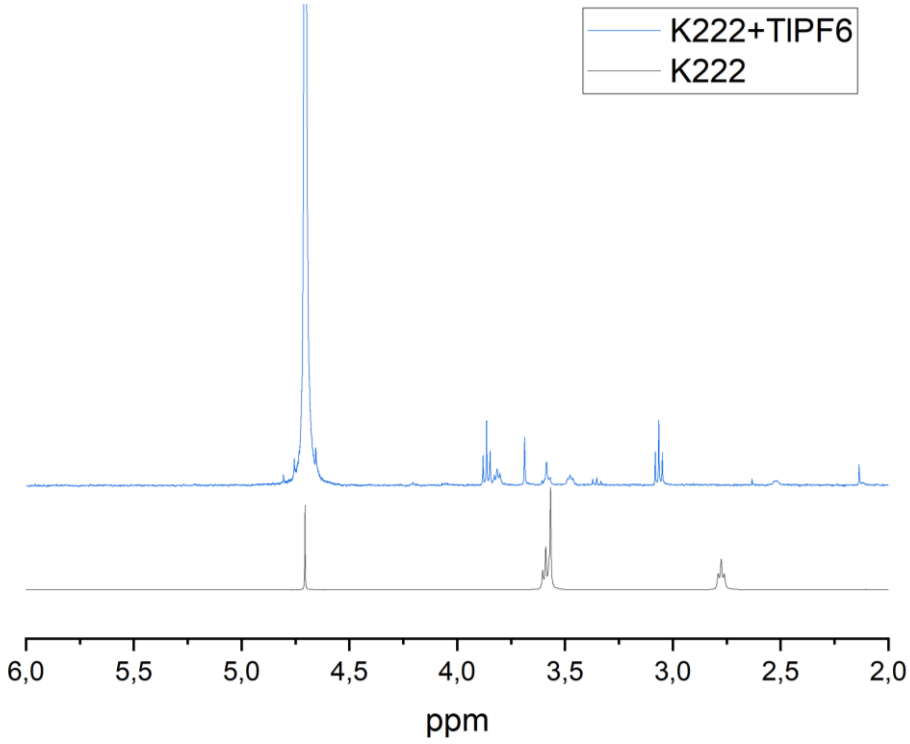


Figure S1. ^{1}H NMR spectrum of Kryptofix 222 before (black) and after (blue) addition of $TlPF_6$ in D_2O (400 MHz, 300 K)

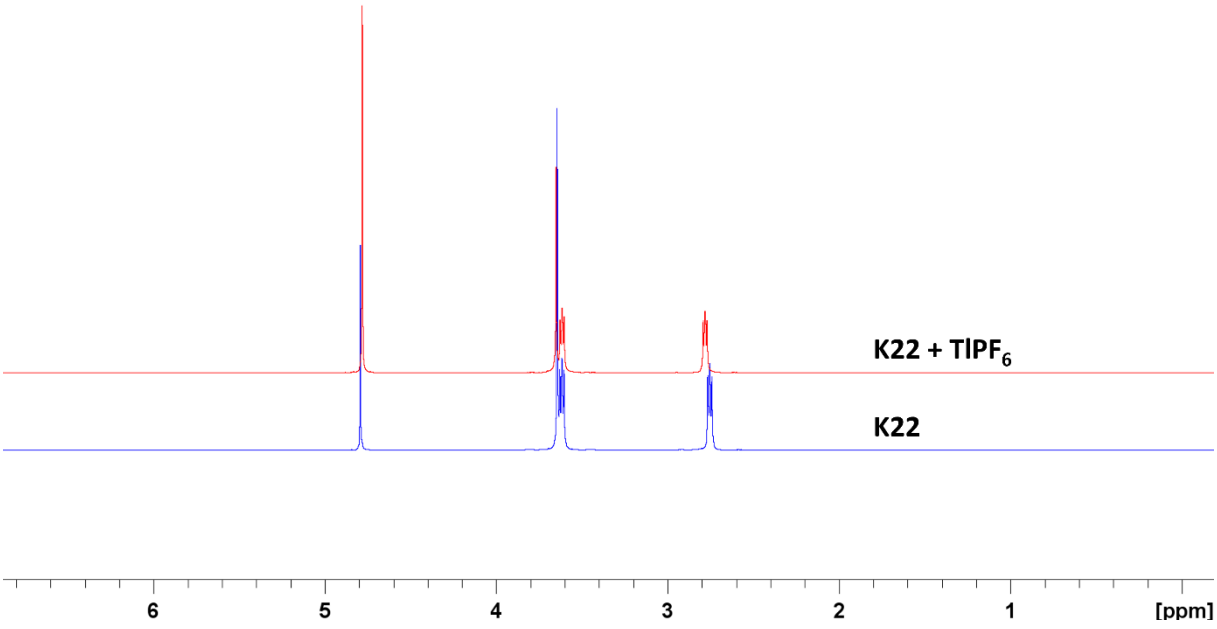


Figure S2. ^{1}H NMR spectrum of Kryptofix 22 before (blue) and after (red) addition of $TlPF_6$ in D_2O (400 MHz, 300 K).

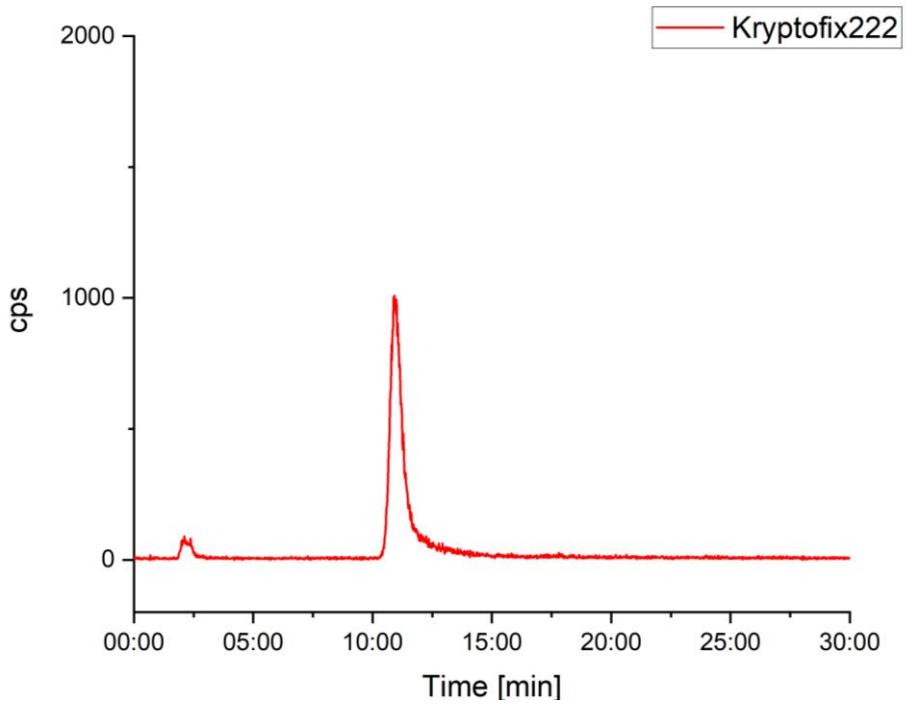


Figure S3. Radio-HPLC γ-trace after reaction of K222 with [^{201}Tl]Tl(I)Cl.

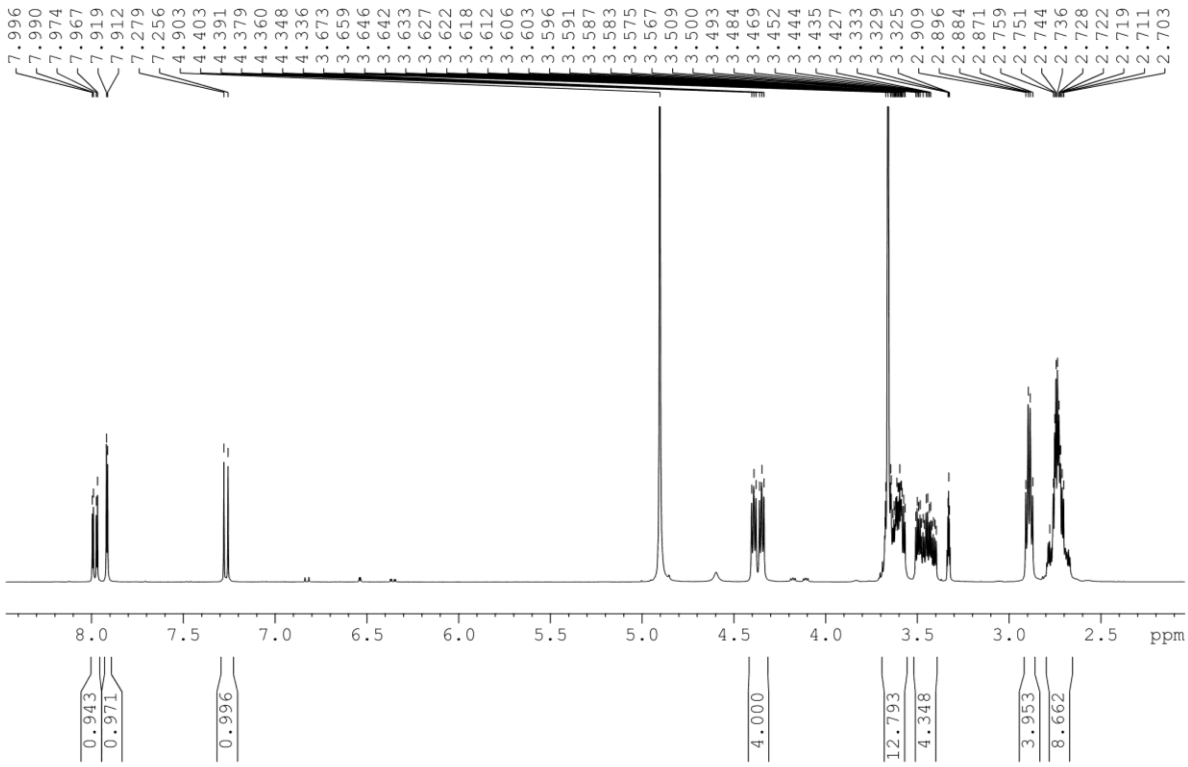


Figure S4. ^{1}H NMR spectrum of compound **5** in CD_3OD (400 MHz, 300 K)

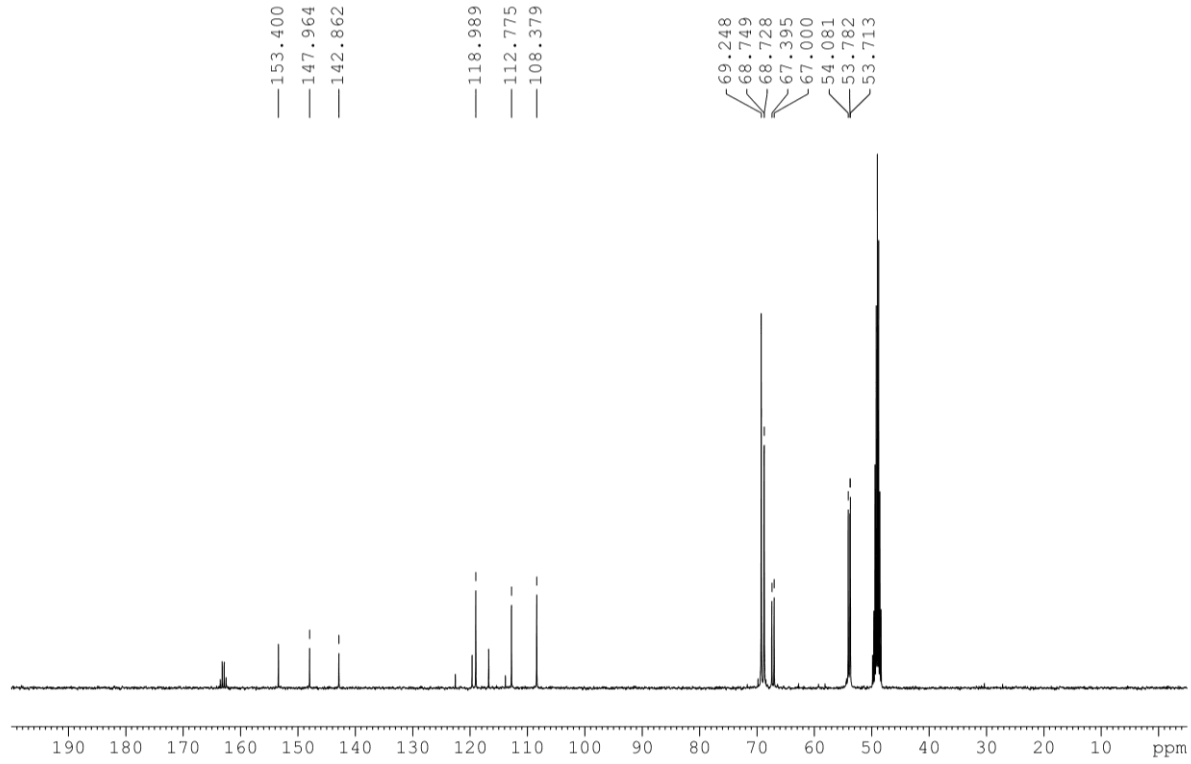


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in CD_3OD (101 MHz, 300 K).

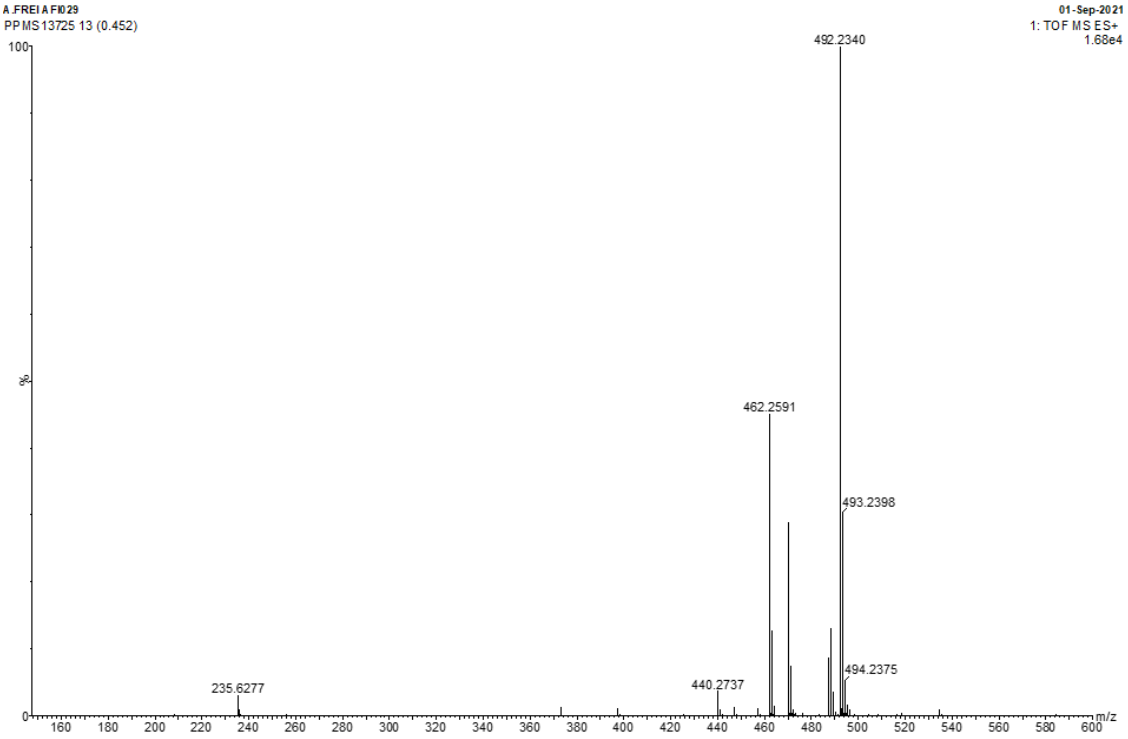


Figure S6. HR-MS spectrum of compound **5**

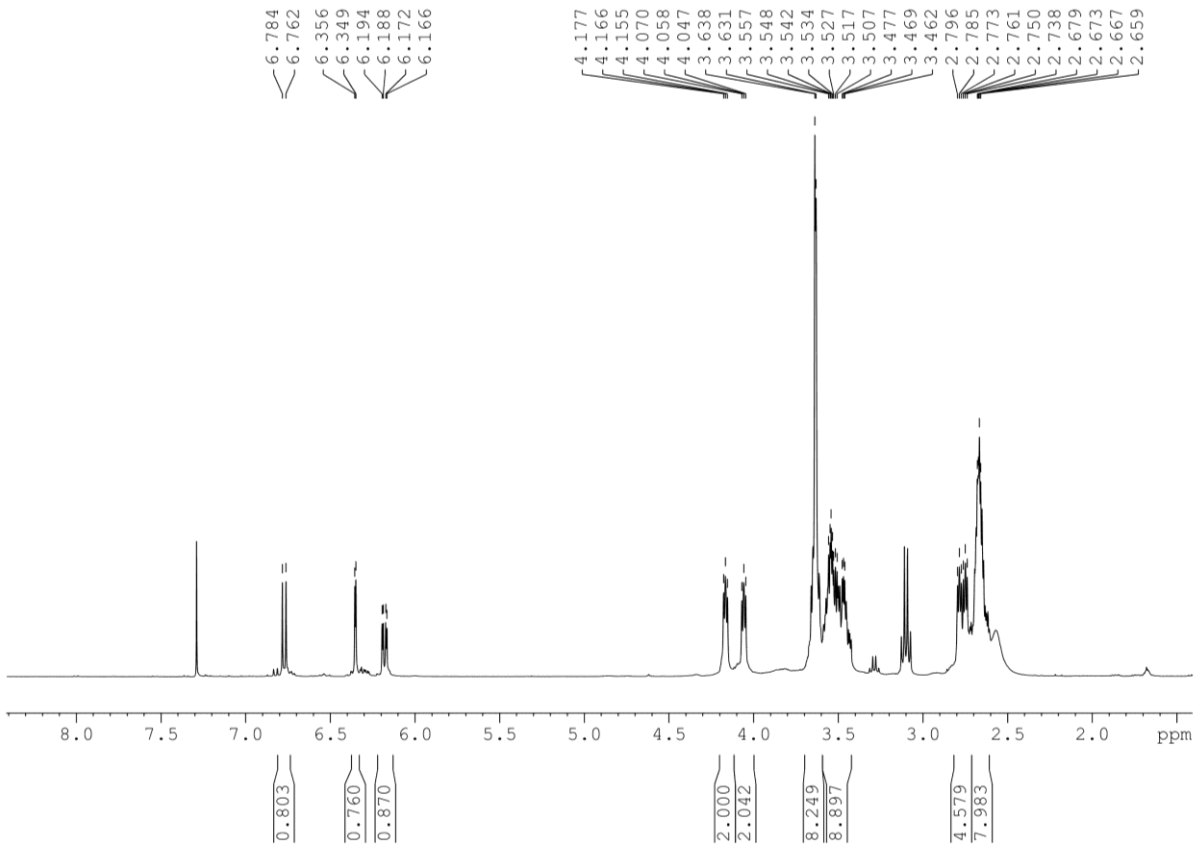


Figure S7. ^{1}H NMR spectrum of **K222-NH_2** in $CDCl_3$ (400 MHz, 300 K).

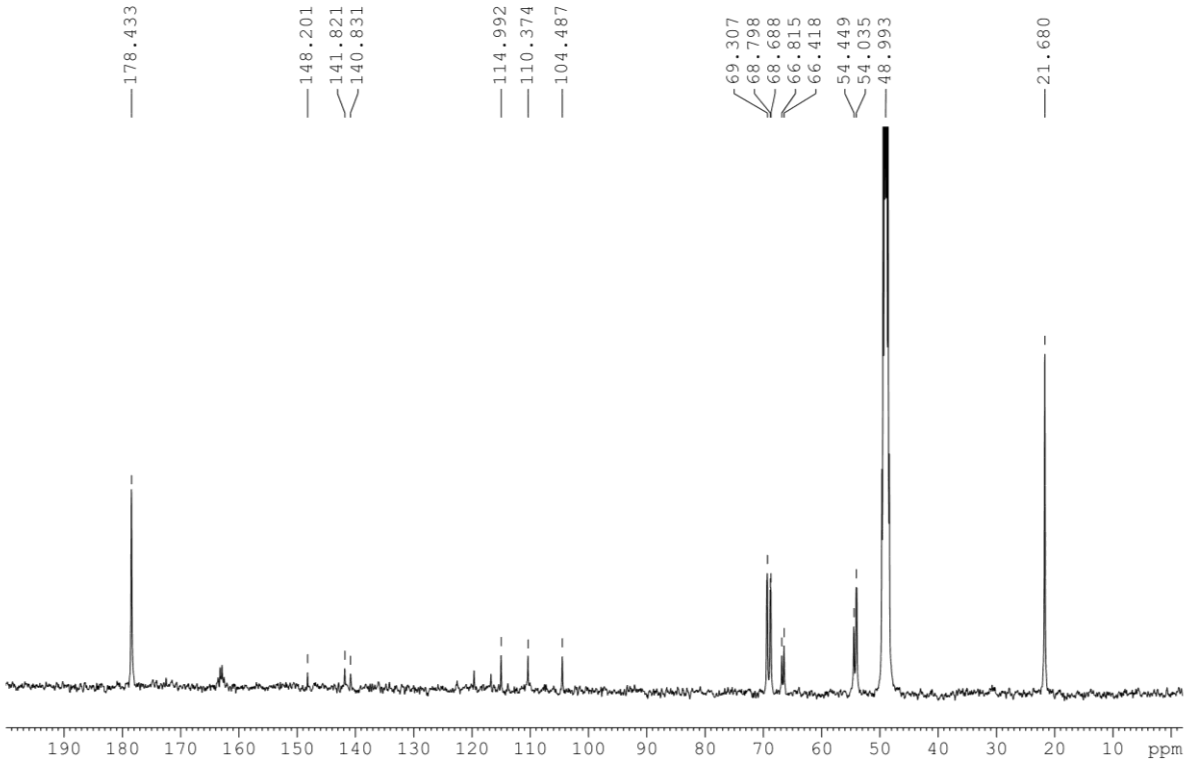


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **K222-NH_2** in CD_3OD (101 MHz, 300 K).

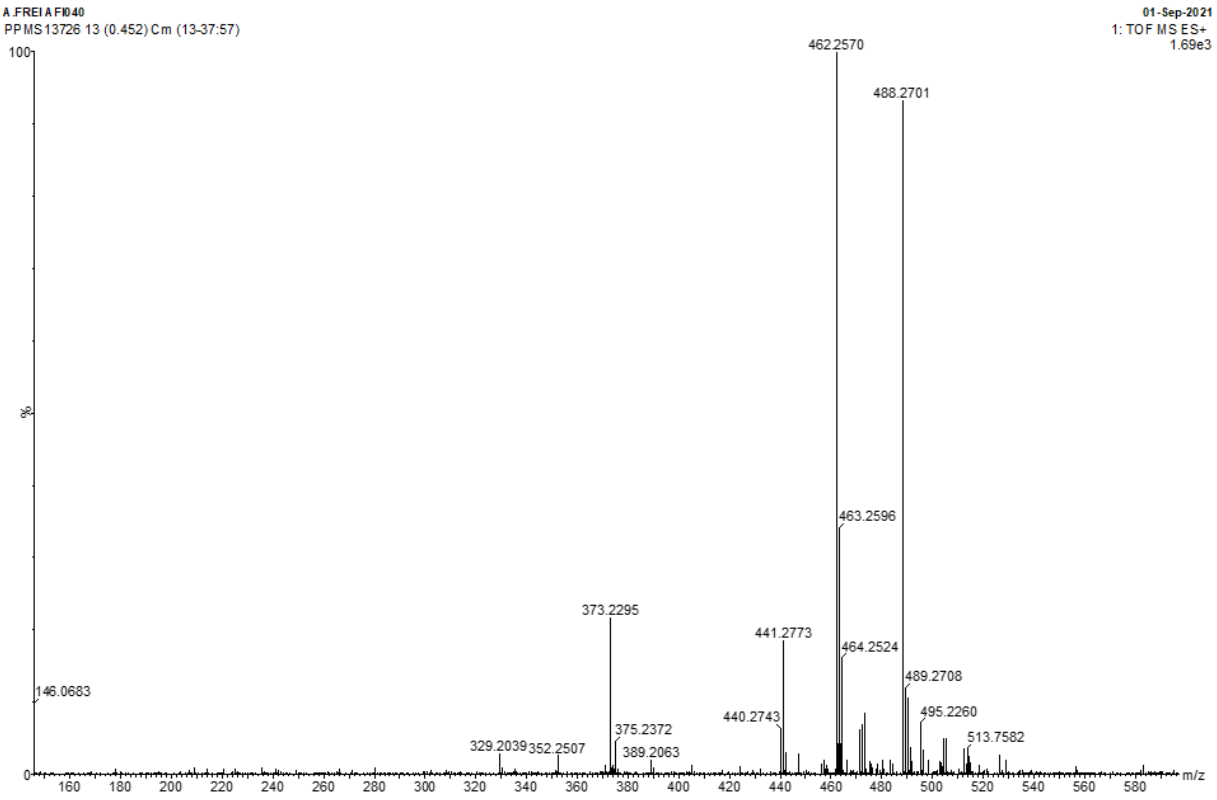


Figure S9. HR-MS spectrum of **K222-NH_2**

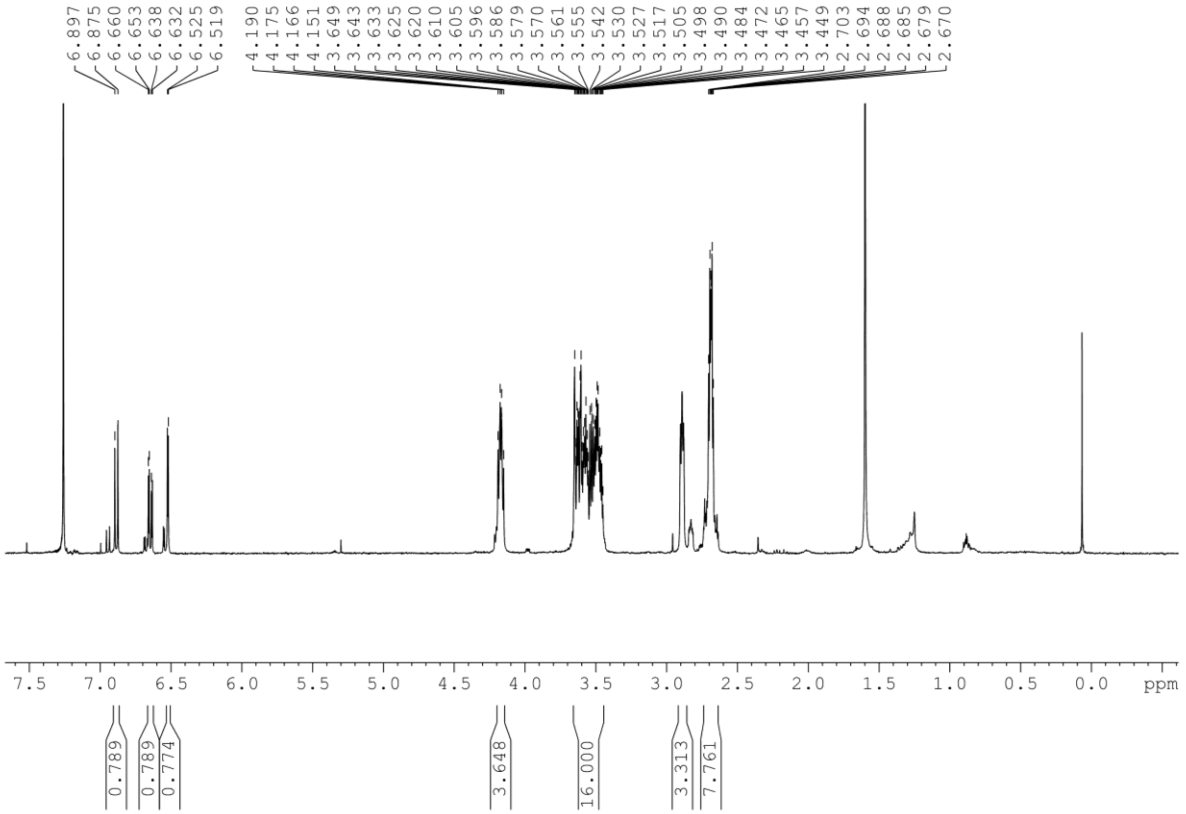


Figure S10. ^{1}H NMR spectrum of **K222-N_3** in $CDCl_3$ (400 MHz, 300 K)

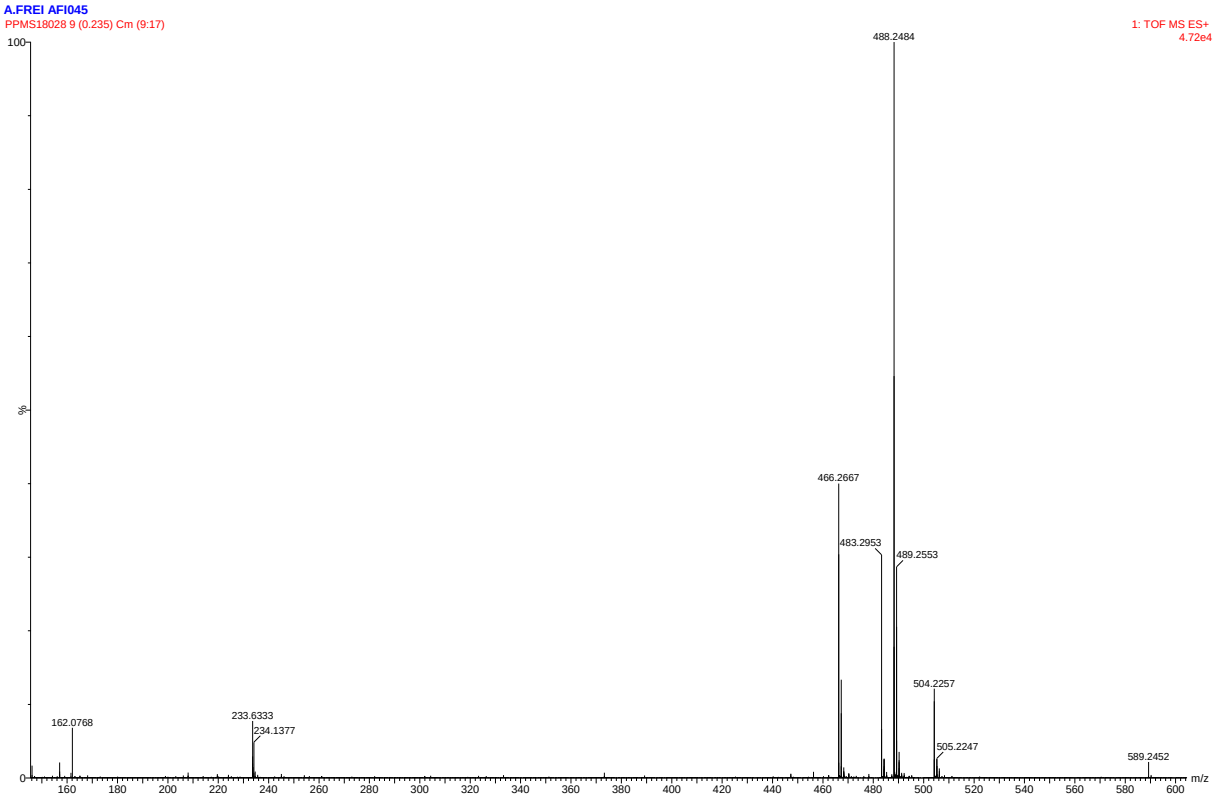


Figure S11. HR-MS spectrum of **K222-N_3**

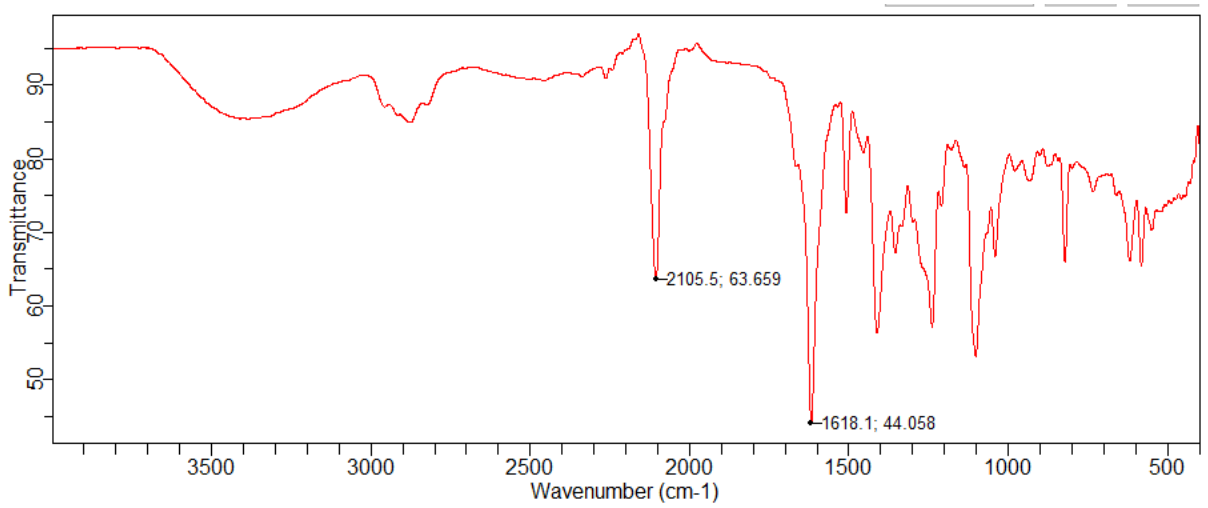


Figure S12. IR-spectrum of **K222-N_3**.

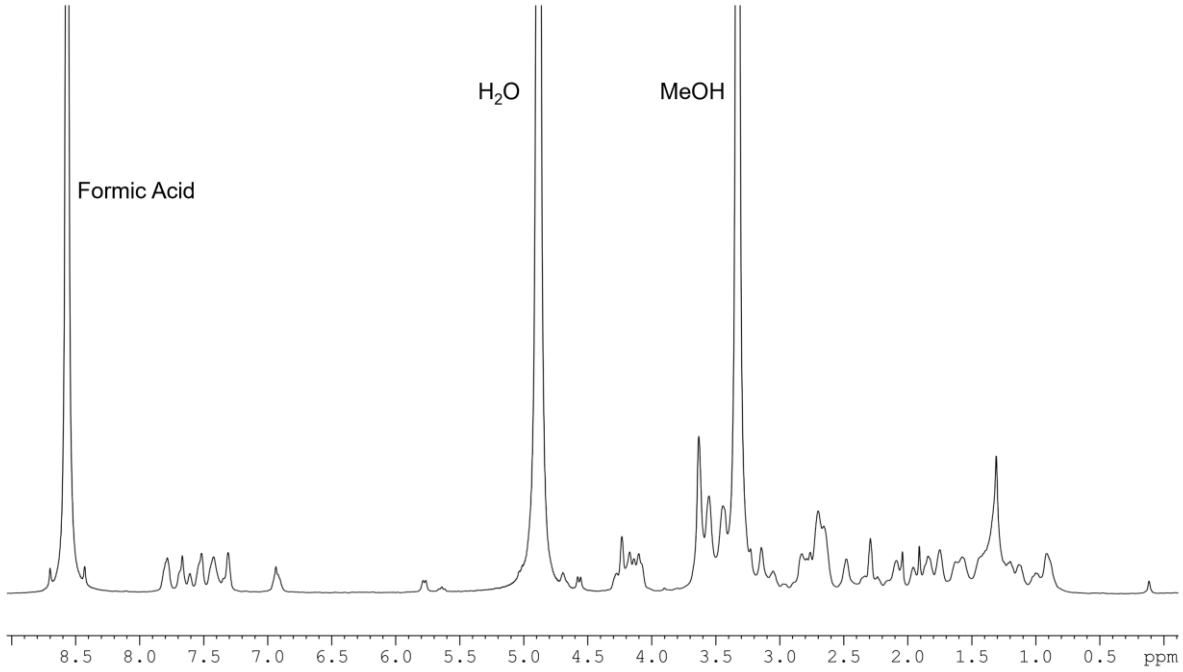


Figure S13. ^{1}H NMR spectrum of **K222-PSMA** in MeOD (400 MHz, 300 K)

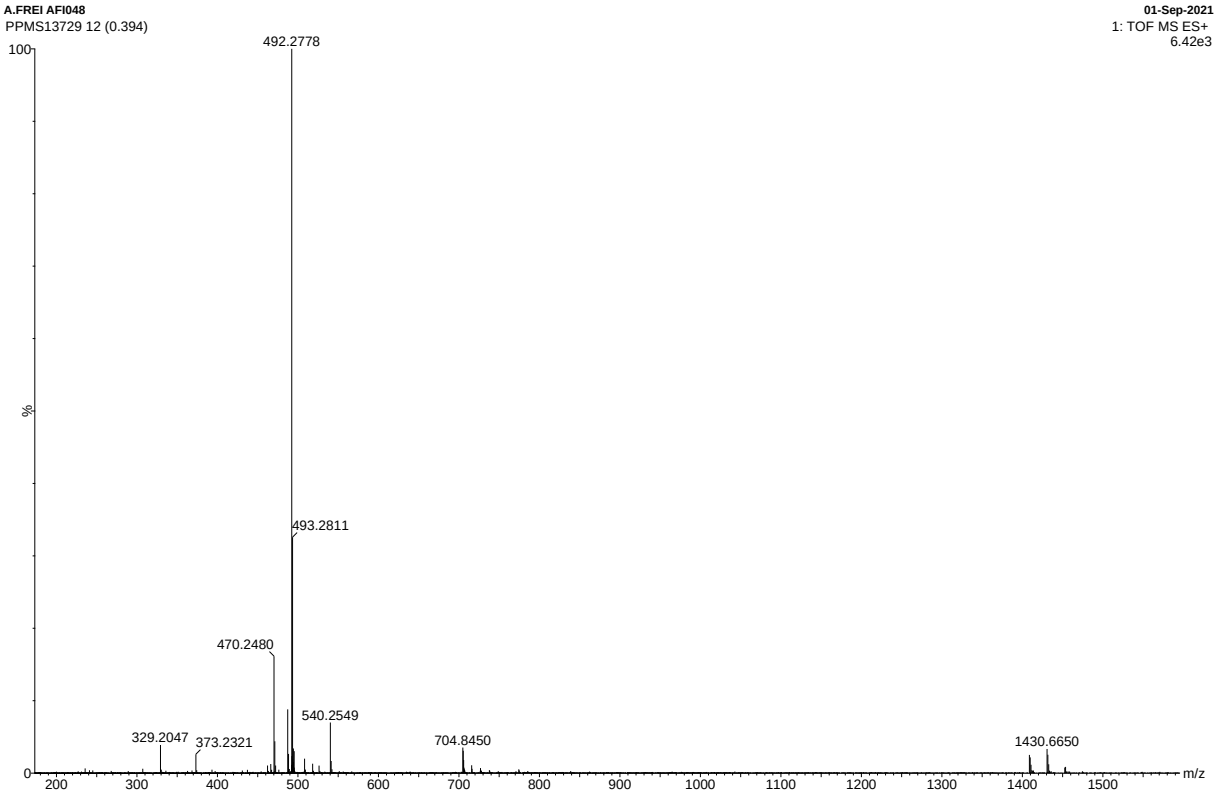


Figure S14. HR-MS spectrum of **K222-PSMA** (m/z = 1407.6751)

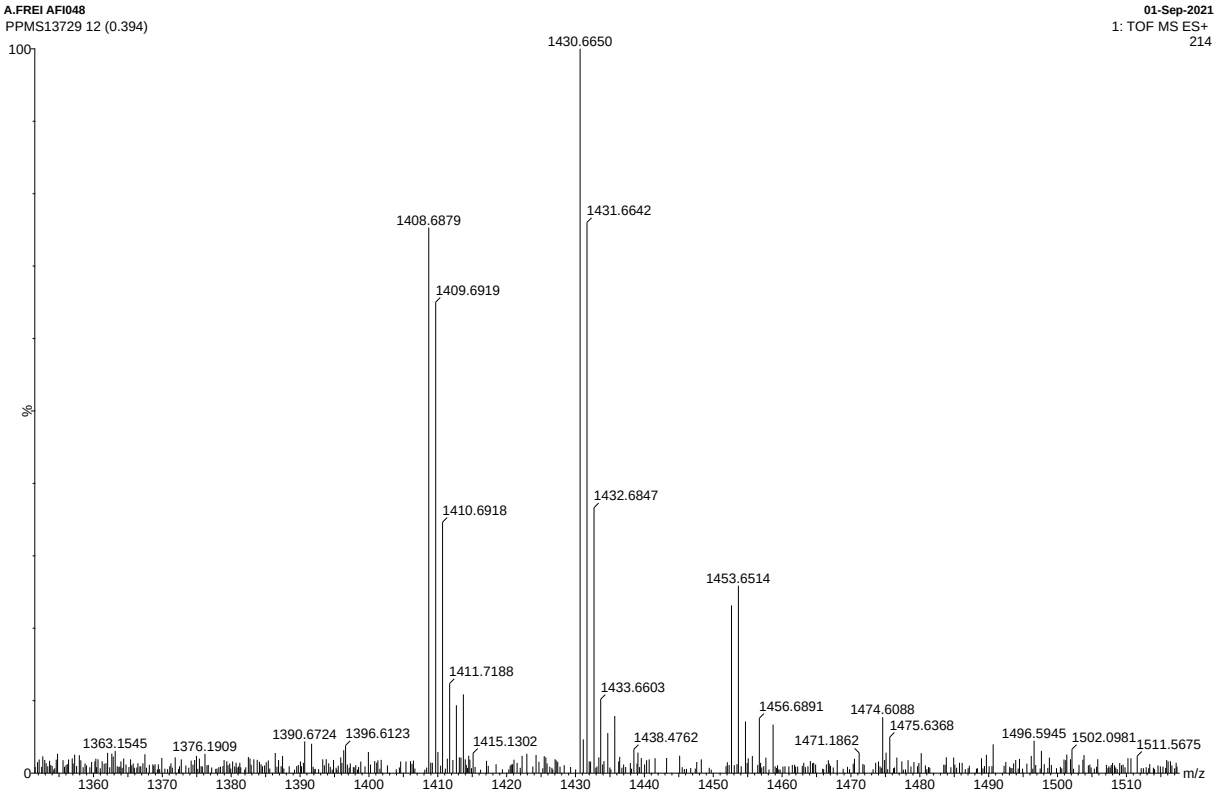


Figure S15. Detailed HR-MS spectrum of **K222-PSMA** (m/z = 1407.6751)

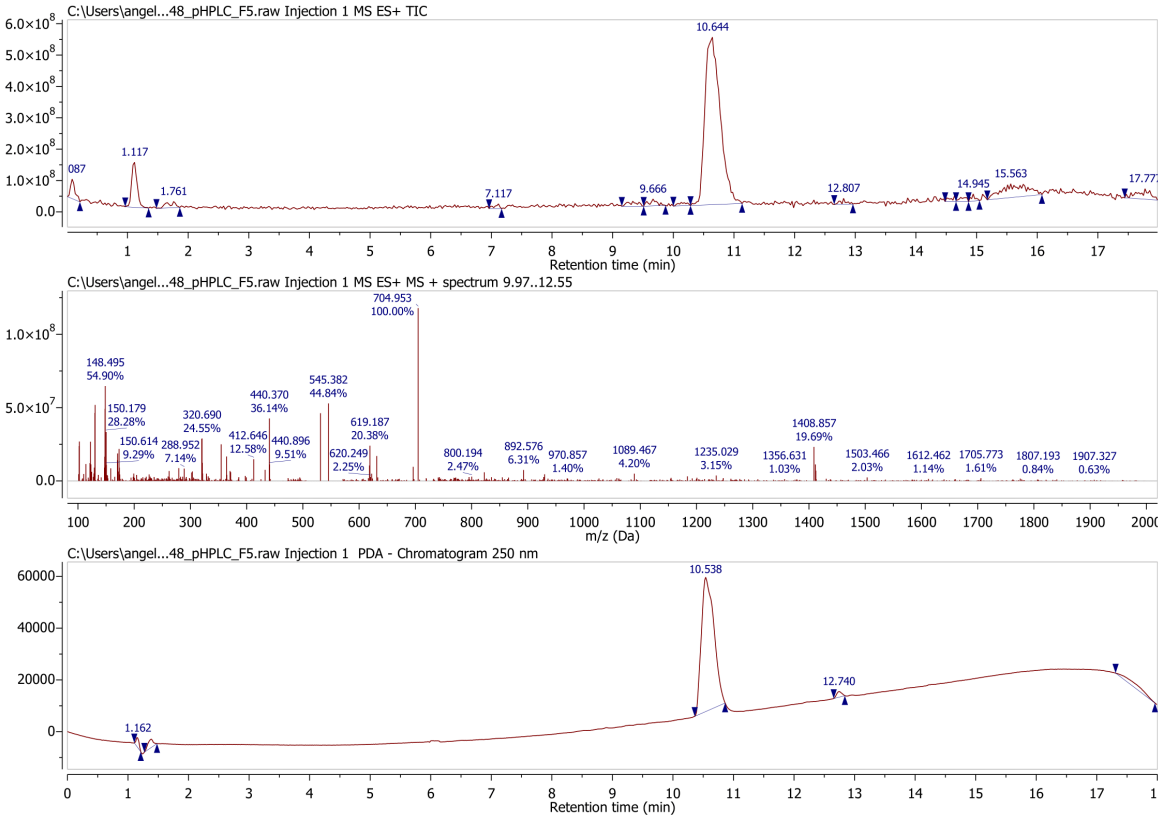


Figure S16. LC-MS trace of **K222-PSMA** after preparative HPLC purification.

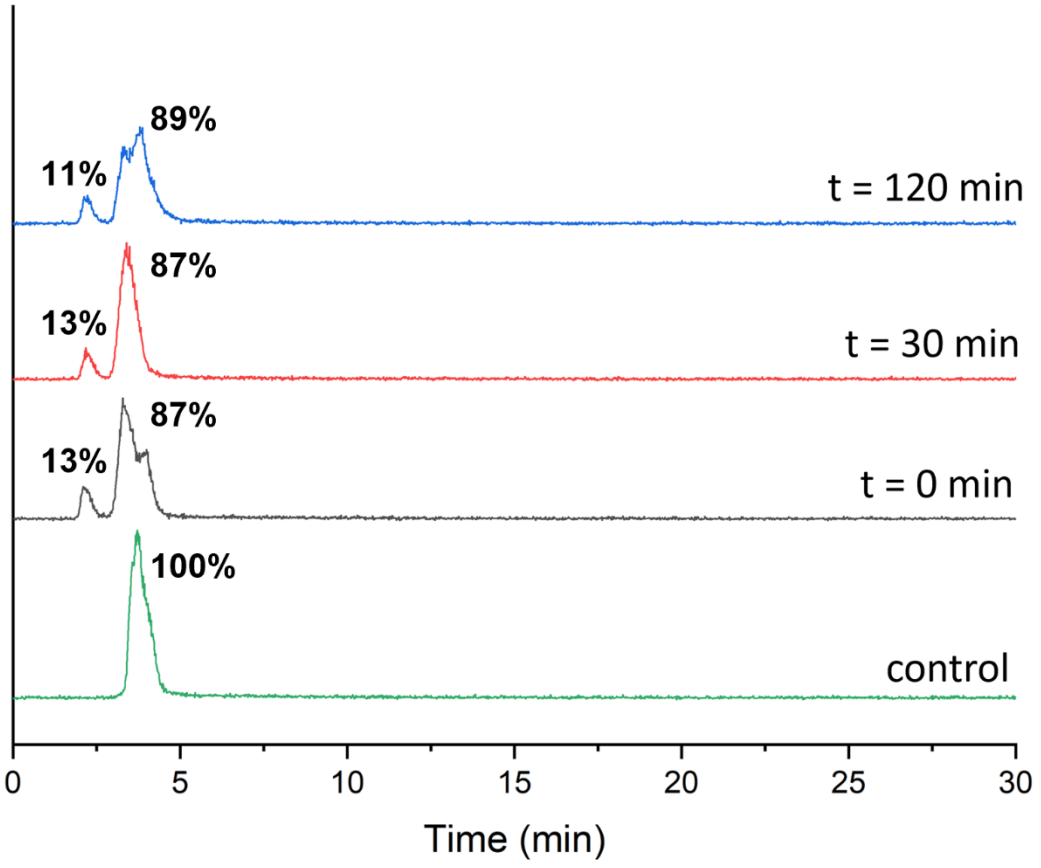


Figure S17. Stacked plot of the serum stability study of **K222-PSMA** in human serum. Radio-HPLC γ-traces are shown for three different time points and the control. Relative integrals of the first peak and the second peak are given in %.

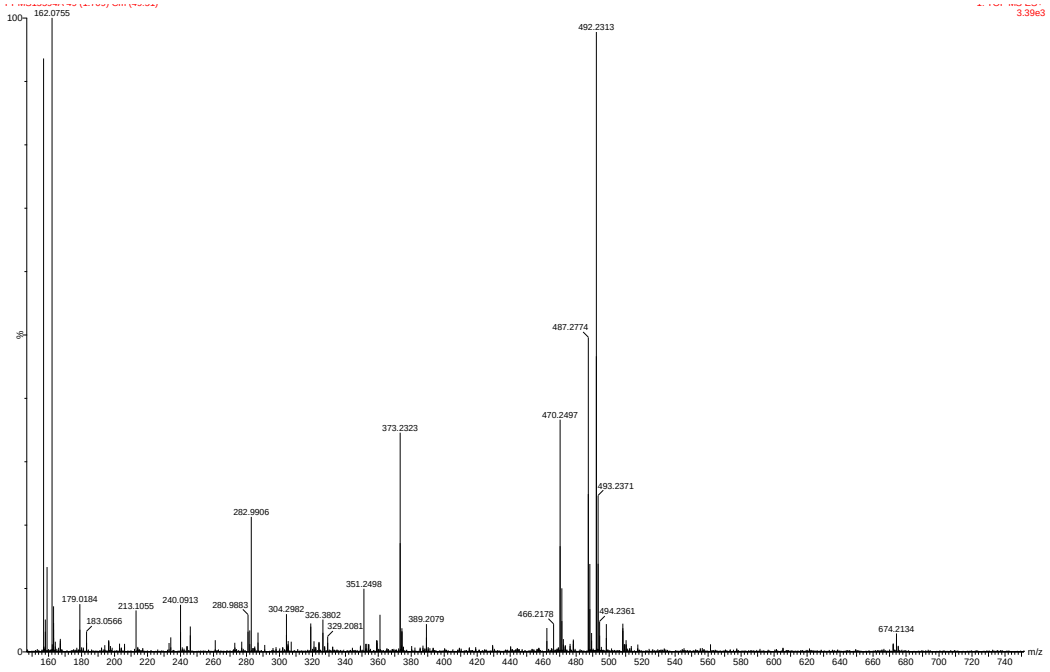
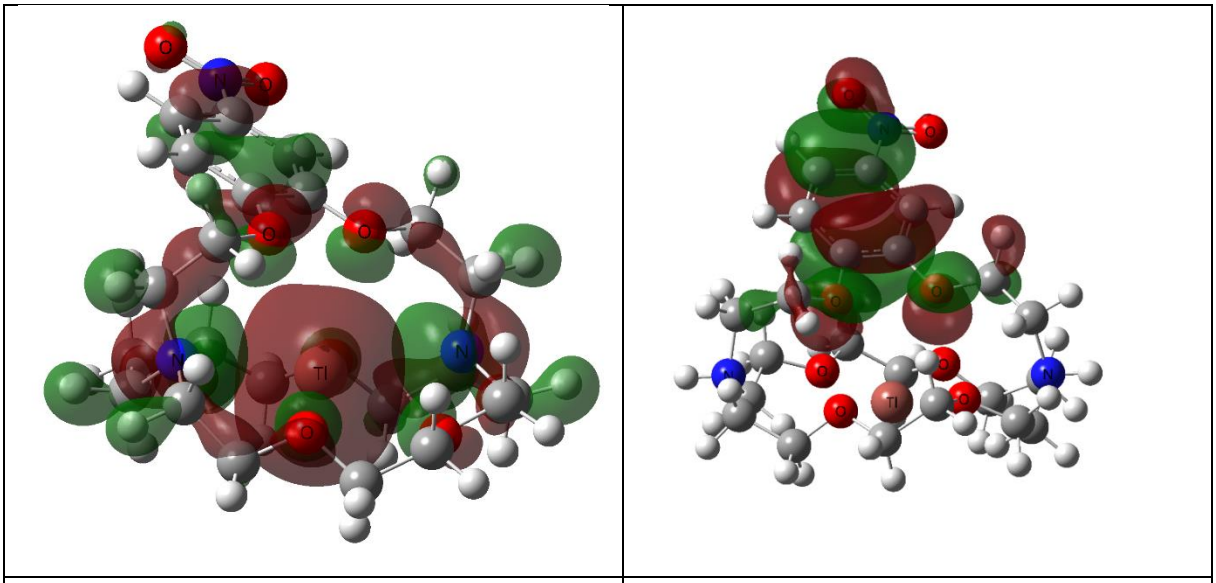


Figure S18. HR-ESI-MS spectrum of $[Tl(\mathbf{5})]^+$

	AR	stdev
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ (positive, 1 h)	4.70%	0.23%
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ (negative, 1 h)	4.93%	0.20%
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ (positive, 10 min)	2.75%	0.15%
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ (negative, 10 min)	2.88%	0.13%
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ + PMPA (positive, 1 h)	4.97%	0.13%
[^{201}Tl][Tl(**K222-PSMA**)]$^+$ + PMPA (negative, 1 h)	5.18%	0.08%
[^{201}Tl]TlCl (positive, 1 h)	6.09%	0.90%
[^{201}Tl]TlCl (negative, 1 h)	6.34%	0.14%

Table S1. Average (of three experiments) percentage added radioactivity measured for each experiment and calculated standard deviation.



Visualisation of the HOMO for Tl(**5**) in the unprotonated state

Visualisation of the HOMO for Tl(**5**) in the protonated state.

Figure S19. Comparison of the HOMO and orbital overlaps in the protonated and unprotonated **K22** macrocycle

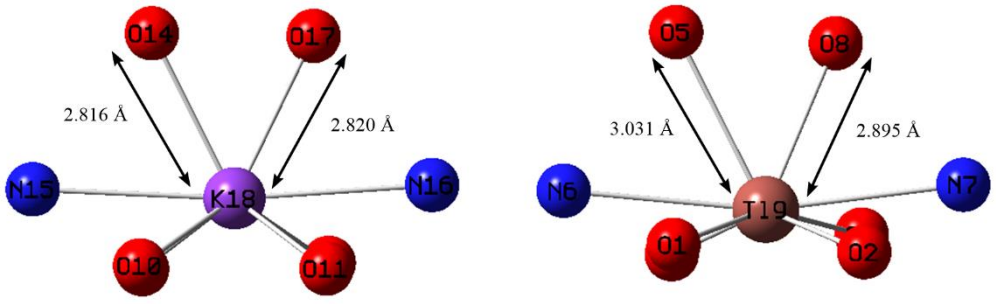


Figure S20. Visualisation of the calculated coordination environment for Tl(**5**)$^+$ and K(**5**)$^+$**.** Oxygens O14, O17,O5 and O8 are the ones belonging to the aromatic ring.

	Bond Lengths (Å) [σ]		
M-Crypt Complexes	**O-M Aliphatic**	**O-M Aromatic**	**N-M**
K(**K222**) (calcd.)	2.83 [0.023]	N/A	3.02 [0.001]
K(**K222**) (exp.)[1]	2.85 [0.025]	N/A	3.03 [0.005]
K(**5**)	2.79 [0.016]	2.82 [0.0015]	3.05 [0.03]
Tl(**5**)	2.86 [0.041]	2.96 [0.068]	3.05 [0.068]

Table S2. Comparison of coordination bond lengths between the experimental K(**K222**)$^+$ structure and calculated K(**K222**)$^+$**,** Tl(**5**)$^+$ and K(**5**)$^+$

References

[1] R. Alberto, K. Ortner, N. Wheatley, R. Schibli, A. P. Schubiger, *Journal of the American Chemical Society* **2001**, *123*, 3135-3136.