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Electronic Supplementary Material

to

Maximizing the Relaxivity of HSA-Bound Gadolinium Complexes by Simoultaneous Optimization of Rotation and Water Exchange

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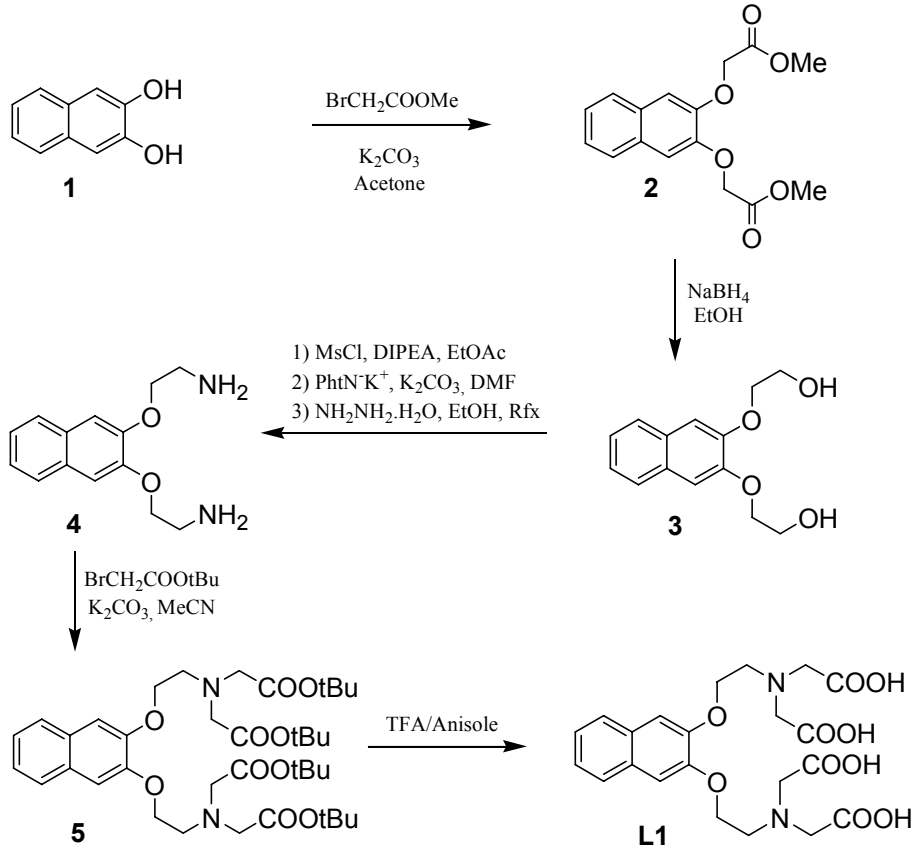
Reaction schemes and characterization of ligands **L1** and **L2**.

NMR spectra were recorded with a Jeol ECP-300 spectrometer, operating at 300 MHz and 75.4 MHz for ^{1}H and ^{13}C, respectively. Mass spectra were performed on a ThermoFinningan LCQ-deca XP-PLUS, operating in ESI-MS mode.

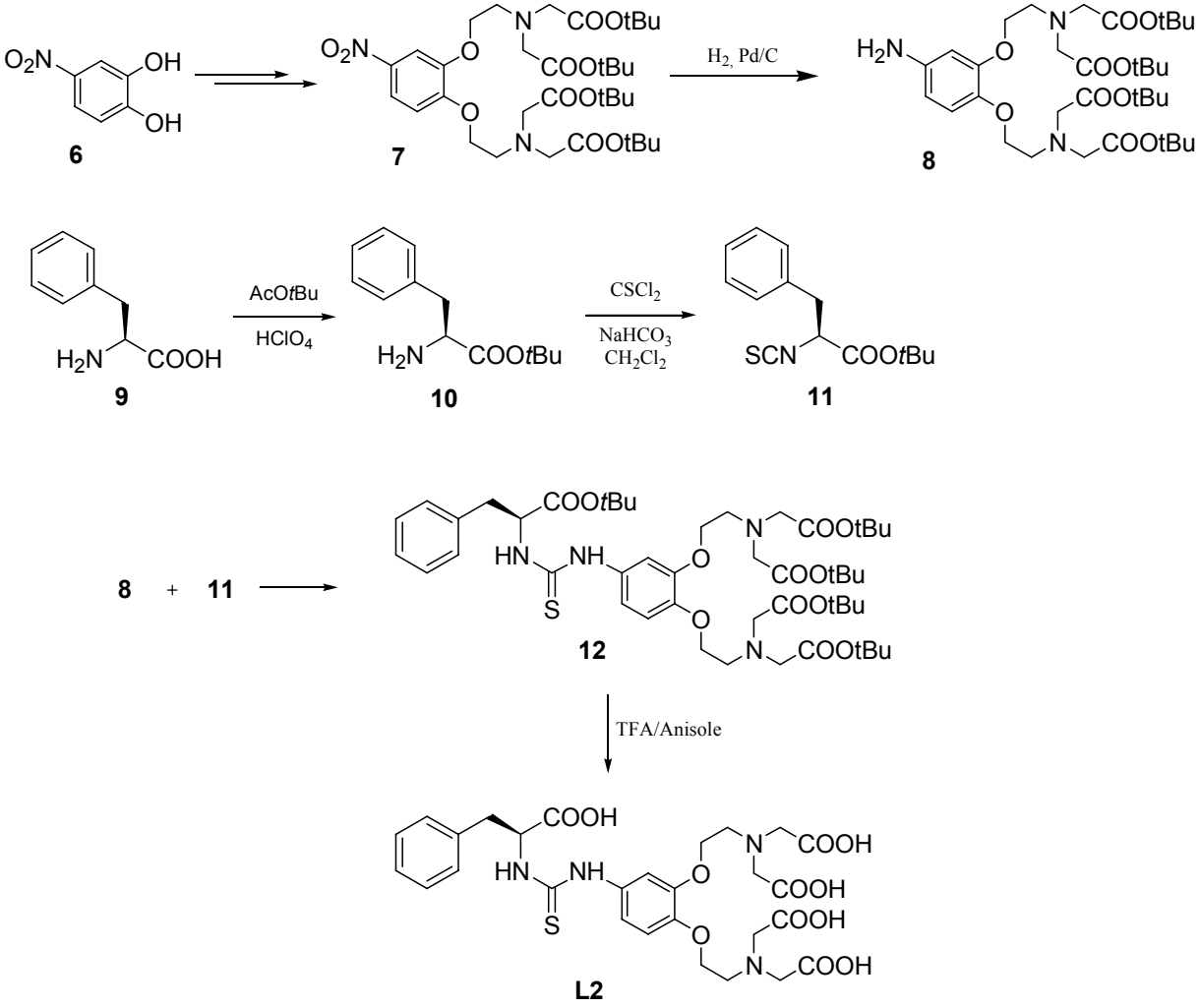


Scheme S1

Ligand L1

Amorphous white solid. M.p. 151-152°C (dec). ^{1}H-NMR (D_2O, 298 K) δ: 7.65 [m, 2H], 7.25 [m, 2H], 7.23 [s, 2H], 4.25 [t, 4H, J = 5.4 Hz], 3.78 [s, 8H], 3.35 [t, 4H, J = 4.8 Hz]. ^{13}C-NMR (D_2O, 298 K) δ: 169.9 [C], 147.0 [C], 129.1 [C], 126.6 [CH], 125.0 [CH], 108.4 [CH], 63.1

[CH_2], 57.5 [CH_2], 54.6 [CH_2]. ESI-MS: Calcd. for $C_{22}H_{26}N_2O_{10}$: 478.1 u.m.a.. Found: 479.0 u.m.a. (MH^+).



Scheme S2

Ligand L2

White solid. Mp 158-159°C (dec). ^{1}H-NMR (DMSO-d_6, 298 K) δ: 10.52 [bs, 4H], 9.69 [bs, 1H], 7.31-6.88 [m, 8H], 6.33 [bd, 1H], 6.13 [bs, 1H], 5.22 [m, 1H], 4.03-3.84 [m, 4H], 3.55 [bs, 8H], 3.46 [m, 1H], 3.17-2.93 [m, 5H]. ^{13}C-NMR (DMSO-d_6, 298 K) δ: 173.9 [C], 173.2 [2xC], 148.6 [C], 148.2 [C], 134.8 [C], 130.3 [CH], 129.5 [C], 128.6 [CH], 126.2 [CH], 121.4 [CH], 113.8 [CH], 113.0 [C], 68.4 [CH_2], 68.1 [CH_2], 60.4 [CH], 55.9 [2xCH_2], 53.2

[2xCH_2], 36.7 [CH_2]. ESI-MS (negative ion mode): Calcd. for $C_{28}H_{34}N_4O_{12}S$: 650.2 u.m.a..

Found: 649.2 u.m.a. ($M\text{-}H^+$).

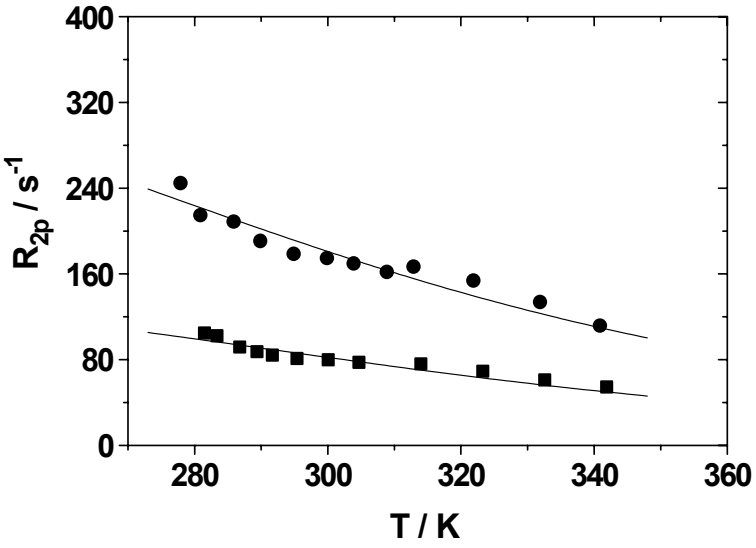


Figure S1. Temperature dependence of the paramagnetic contribution to the water ^{17}O NMR transverse relaxation rate (R_{2p}) for Gd**L1** (squares; 9 mM) and Gd**L2** (circles; 23 mM) at 2.12 T and pH=7.0.

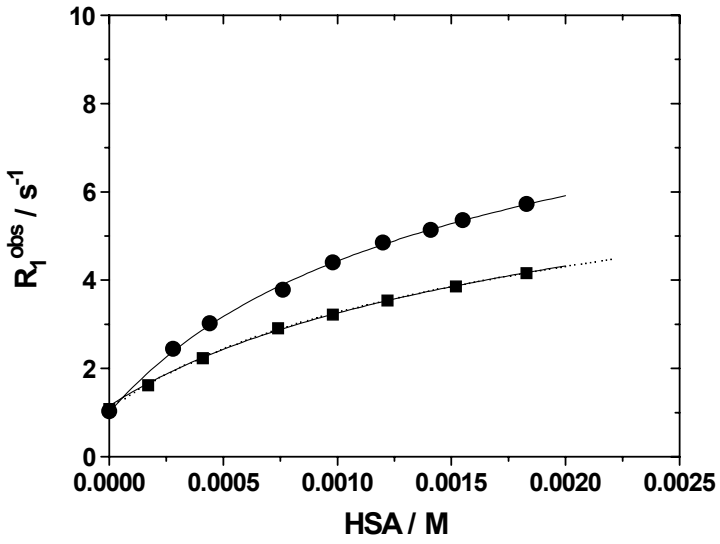


Figure S2. The water proton longitudinal relaxation rate of a solution of complexes Gd**L1** (circles; 0.11 mM) and Gd**L2** (squares; 0.10 mM) as a function of HSA concentration at 20 MHz, 298 K and pH = 7.0.