Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting information for

Optimisation of Dynamic Nuclear Polarisation using “off-the-shelf” Gd(III)-based polarising agents

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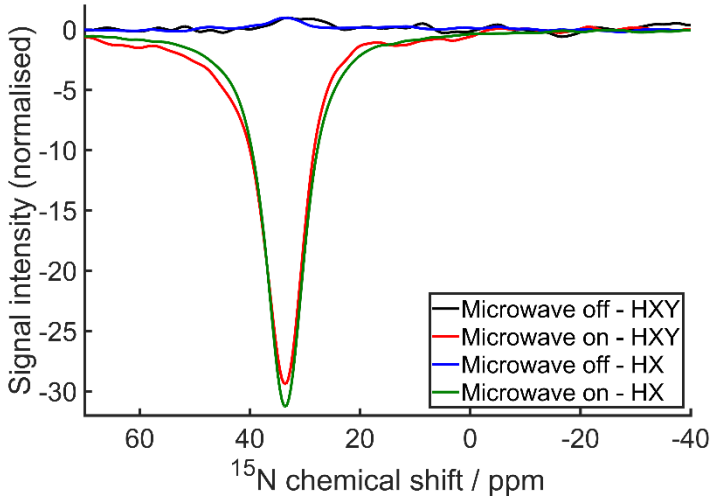

Figure S1: Comparison of the DNP-enhanced ^{15}N NMR spectra of 2-^{13}C,^{15}N-glycine with 20 mM $GdBr_3$, using a triple resonance (HXY) or double resonance (HX) probe.

Table S1: List of peaks found in the HRMS spectra of all Gd(III) compounds in 3/2 v/v glycerol/H_2O Peaks arising from the fragmentation of glycerol are not shown.

Species	m/z (calculated)	m/z (observed)
$Gd(NO_3)_3 \cdot 6H_2O$		
$[GdO]^+$	173.9190	173.9185
$[Gd^{3+} + 2 \times \text{glycerol} - 2 \times H^+]^+$	340.0031	340.0026
$[Gd^{3+} + 2 \times \text{glycerol} + NO^{3-} - H^+]^+$	402.9988	402.9981
$GdCl_3 \cdot 6H_2O$		
$[GdO]^+$	173.9190	173.9188
$[Gd^{3+} + 2 \times \text{glycerol} - 2 \times H^+]^+$	340.0031	340.0034
$[Gd^{3+} + 2 \times \text{glycerol} + Cl^- - H^+]^+$	375.9798	375.9793
$Gd_2(SO_4)_3 \cdot 8H_2O$		
$[GdO]^+$	173.9190	173.9184
$[Gd^{3+} + 2 \times \text{glycerol} - 2 \times H^+]^+$	340.0031	340.0022
$[Gd^{3+} + 2 \times \text{glycerol} + SO_4^{2-}]^+$	437.9705	437.9605
$GdBr_3 \cdot 13H_2O$		
$[GdO]^+$	173.9190	173.9179
$[Gd^{3+} + 2 \times \text{glycerol} - 2 \times H^+]^+$	340.0031	340.0021
$[Gd^{3+} + 2 \times \text{glycerol} + Br^- - H^+]^+$	419.9293	419.9267
$Gd(OAc)_3 \cdot 4H_2O$		
$[GdO]^+$	173.9190	173.9181
$[2 \times Gd^{3+} + 2 \times \text{glycerol} - 4 \times H^+]^{2+}$	247.9558	247.9546
$[2 \times Gd^{3+} + 6 \times H_2O + 2 \times OAc^- - 2 \times H^+]^{2+}$	269.9613	269.9684
$[2 \times Gd^{3+} + 10 \times H_2O + OAc^- - 3 \times H^+]^{2+}$	275.9718	275.9689
$[2 \times Gd^{3+} + 3 \times \text{glycerol} - 4 \times H^+]^{2+}$	293.9795	293.9806
$[Gd^{3+} + 2 \times \text{glycerol} - 2 \times H^+]^+$	340.0031	340.0027
$[2 \times Gd^{3+} + \text{glycerol} + 12 \times H_2O + OAc^- - 3 \times H^+]^{2+}$	340.0061	340.0027
$[2 \times Gd^{3+} + 2 \times \text{glycerol} + 7 \times H_2O + OAc^- - 3 \times H^+]^{2+}$	341.0033	341.0043
$[2 \times Gd^{3+} + 2 \times \text{glycerol} + H_2O + 2 \times OAc^- - 3 \times H^+]^+$	632.9566	632.9554
$[2 \times Gd^{3+} + \text{glycerol} + 2 \times H_2O + 4 \times OAc^- - H^+]^+$	678.9621	678.9617
$Gd(NO_3)_3 \cdot 6H_2O$ + glycine		
$[GdO]^+$	173.9190	173.9181
$[Gd^{3+} + \text{glycine} + \text{glycerol} - 2 \times H^+]^+$	322.9878	322.9862

$[Gd^{3+} + 2 \times glycerol - 2 \times H^+]^+$	340.0031	340.0014
$[Gd^{3+} + 3 \times glycine - 2 \times H^+]^+$	381.0045	381.0030
$[Gd^{3+} + 2 \times glycine + glycerol - 2 \times H^+]^+$	398.0199	398.0180
$[Gd^{3+} + glycine + 2 \times glycerol - 2 \times H^+]^+$	415.0352	415.0333
$GdCl_3 \cdot 6H_2O$ + glycine		
$[GdO]^+$	173.9190	173.9184
$[Gd^{3+} + glycine + glycerol - 2 \times H^+]^+$	322.9878	322.9871
$[Gd^{3+} + 2 \times glycerol - 2 \times H^+]^+$	340.0031	340.0026
$[Gd^{3+} + 3 \times glycine - 2 \times H^+]^+$	381.0045	381.0041
$[Gd^{3+} + 2 \times glycine + glycerol - 2 \times H^+]^+$	398.0199	398.0195
$[Gd^{3+} + glycine + 2 \times glycerol - 2 \times H^+]^+$	415.0352	415.0348
$Gd_2(SO_4)_3 \cdot 8H_2O$ + glycine		
$[GdO]^+$	173.9190	173.9181
$[Gd^{3+} + glycine + glycerol - 2 \times H^+]^+$	322.9878	322.9866
$[Gd^{3+} + 2 \times glycerol - 2 \times H^+]^+$	340.0031	340.0017
$[Gd^{3+} + 3 \times glycine - 2 \times H^+]^+$	381.0045	381.0030
$[Gd^{3+} + 2 \times glycine + glycerol - 2 \times H^+]^+$	398.01985	398.0183
$[Gd^{3+} + glycine + 2 \times glycerol - 2 \times H^+]^+$	415.0352	415.0337
$GdBr_3 \cdot 13H_2O$ + glycine		
	173.9190	173.9184
$[Gd^{3+} + glycine + glycerol - 2 \times H^+]^+$	322.9878	322.9865
$[Gd^{3+} + 2 \times glycerol - 2 \times H^+]^+$	340.0031	340.0017
$[Gd^{3+} + 3 \times glycine - 2 \times H^+]^+$	381.0045	381.0030
$[Gd^{3+} + 2 \times glycine + glycerol - 2 \times H^+]^+$	398.0199	398.0183
$[Gd^{3+} + glycine + 2 \times glycerol - 2 \times H^+]^+$	415.0352	415.0338
$Gd(OAc)_3 \cdot 4H_2O$ + glycine		
$[GdO]^+$	173.9190	173.9182
$[Gd^{3+} + glycine + glycerol - 2 \times H^+]^+$	322.9878	322.9863
$[Gd^{3+} + 2 \times glycerol - 2 \times H^+]^+$	340.0031	340.0020
$[Gd^{3+} + 3 \times glycine - 2 \times H^+]^+$	381.0045	381.0031
$[Gd^{3+} + 2 \times glycine + glycerol - 2 \times H^+]^+$	398.0199	398.0186
$[Gd^{3+} + glycine + 2 \times glycerol - 2 \times H^+]^+$	415.0352	415.0340

Table S2: ^1H, ^{13}C, and ^{15}N DNP enhancement factors, build-up time constants, contribution factors, and overall sensitivity improvements for 1.5 M 2-^{13}C,^{15}N-glycine in 6/3/1 v/v/v glycerol-d_8/D_2O/H_2O at ~105 K at 14.1 T, for various concentrations of $Gd(NO_3)_3$

$[Gd(NO_3)_3]$ / mM	Nuclide	ε	$T_{B,ON}$ / s	θ	ε_θ
2	^1H	−1.8 ± 0.1	22.0 ± 0.2	1.03 ± 0.04	−3.2 ± 0.2
	^{13}C	−4.1 ± 0.1	1187 ± 112		−4.5 ± 0.4
	^{15}N	-[a]	-[a]		-[a]
10	^1H	−2.7 ± 0.1	9.7 ± 0.7	0.69 ± 0.03	−4.8 ± 0.3
	^{13}C	−14 ± 0.2	442 ± 18		−17 ± 1
	^{15}N	−24 ± 3	1426 ± 135		−30 ± 4
20	^1H	−4.5 ± 0.1	4.8 ± 0.2	0.43 ± 0.02	−7.2 ± 0.3
	^{13}C	−23 ± 3	222 ± 7		−24 ± 3
	^{15}N	−27 ± 2	304 ± 31		−47 ± 5
40	^1H	-2.8 ± 0.3	1.8 ± 0.3	0.26 ± 0.04	-4.4 ± 0.9
	^{13}C	-15 ± 2	114 ± 9		-13 ± 3
	^{15}N	-37 ± 4	124 ± 6		-61 ± 12
60	^1H	-2.0 ± 0.3	1.3 ± 0.5	0.20 ± 0.01	-2.8 ± 0.6
	^{13}C	-6.5 ± 1.0	67 ± 11		-5.8 ± 1.1
	^{15}N	-33 ± 3	58 ± 6		-60 ± 12
100	^1H	−2.7 ± 0.6	0.7 ± 0.2	0.07 ± 0.01	−1.8 ± 0.5
	^{13}C	−12 ± 1	36 ± 5		−5.1 ± 0.6

	^{15}N	−21 ± 1	22 ± 2		−22 ± 2

[a] Not measured.

Table S3: Electron spin-lattice and spin-spin relaxation times of various Gd(III) compounds and concentrations in 3/2 v/v glycerol/H_2O at 100 K (except where noted), measured at X-band and Q-band, with and without 1.5 M glycine.

Gd(III) compound	Conc. / mM	T_{1e} / ns				T_{2e} / ns			
		X-band		Q-band		X-band		Q-band	
with (w) or without (w/o) glycine		w/o	w	w/o	w	w/o	w	w/o	w
$Gd(NO_3)_3$	2	455 ± 6	472 ± 3	640 ± 31	545 ± 1	230 ± 2	231 ± 1	264 ± 3	253 ± 2
	10	403 ± 4	433 ± 2	470 ± 2	470 ± 1	96.5 ± 0.6	115 ± 2	103.8 ± 0.3	93 ± 1
	20	312 ± 21	369 ± 3	398 ± 7	429 ± 11	72 ± 1	54 ± 1	59 ± 1	49 ± 2
	40	228 ± 37	263 ± 56	383 ± 8	470 ± 7	38 ± 4*	41 ± 3*	45 ± 6*	60 ± 1*
	60	148 ± 95	175 ± 85	332 ± 23	193 ± 38	48 ± 6*	53 ± 1*	40 ± 14*	36 ± 1*
	100	274 ± 17†	237 ± 11†	335 ± 4†	231 ± 15†	36 ± 2†	28 ± 1†	30 ± 6†	44 ± 2†
$GdCl_3$	20	315 ± 7	417 ± 2	350 ± 2	443 ± 2	59 ± 1	66 ± 1	54.7 ± 0.2	52 ± 2
$Gd_2(SO_4)_3$	10	347 ± 6	378 ± 3	394 ± 4	404 ± 1	66 ± 3	60 ± 1	64.5 ± 0.2	59 ± 1
$GdBr_3$	20	327 ± 8	331 ± 4	361 ± 11	362 ± 3	61 ± 5	48 ± 1	48 ± 2	48 ± 2
$Gd(OAc)_3$	20	313 ± 10	295 ± 3	346 ± 1	391 ± 2	58 ± 2	58 ± 1	50 ± 2	55 ± 1

** Measured at 80 K*

† Measured at 30 K

Table S4: ^{1}H, ^{13}C, and ^{15}N DNP enhancement factors, build-up time constants, contribution factors, and overall sensitivity improvements for 1.5 M 2-^{13}C,^{15}N-glycine in 6/3/1 v/v/v glycerol-d_8/D_2O/H_2O at ~105 K at 14.1 T, for various Gd(III)-based polarizing agents.

Gd(III) compound	Nuclide	ε	$T_{B,ON}$ / s	θ	ε_θ
$Gd(NO_3)_3$	^{1}H	−4.5 ± 0.1	4.8 ± 0.2	0.43 ± 0.02	−7.2 ± 0.3
	^{13}C	−23 ± 3	222 ± 7		−24 ± 2
	^{15}N	−27 ± 2	304 ± 31		−48 ± 5
$GdCl_3$	^{1}H	−4.7 ± 0.3	4.6 ± 0.2	0.44 ± 0.02	−7.8 ± 0.6
	^{13}C	−20 ± 1	244 ± 8		−21 ± 3
	^{15}N	−30 ± 1	331 ± 14		−51 ± 3
$Gd_2(SO_4)_3$	^{1}H	−3.1 ± 0.4	4.2 ± 1.0	0.39 ± 0.02	−4.8 ± 0.8
	^{13}C	−17 ± 1	253 ± 15		−15 ± 2
	^{15}N	−27 ± 2	405 ± 51		−36 ± 4
$GdBr_3$	^{1}H	−3.4 ± 0.2	3.8 ± 0.2	0.44 ± 0.02	−6.3 ± 0.8
	^{13}C	−13 ± 1	184 ± 11		−15 ± 1
	^{15}N	−29 ± 1	278 ± 28		−53 ± 5
$Gd(OAc)_3$	^{1}H	-0.39 ± 0.03	2.9 ± 0.6	0.46 ± 0.02	−0.85 ± 0.10
	^{13}C	−9.7 ± 0.2	162 ± 24		−13 ± 2
	^{15}N	−17 ± 1	229 ± 14		−35 ± 3

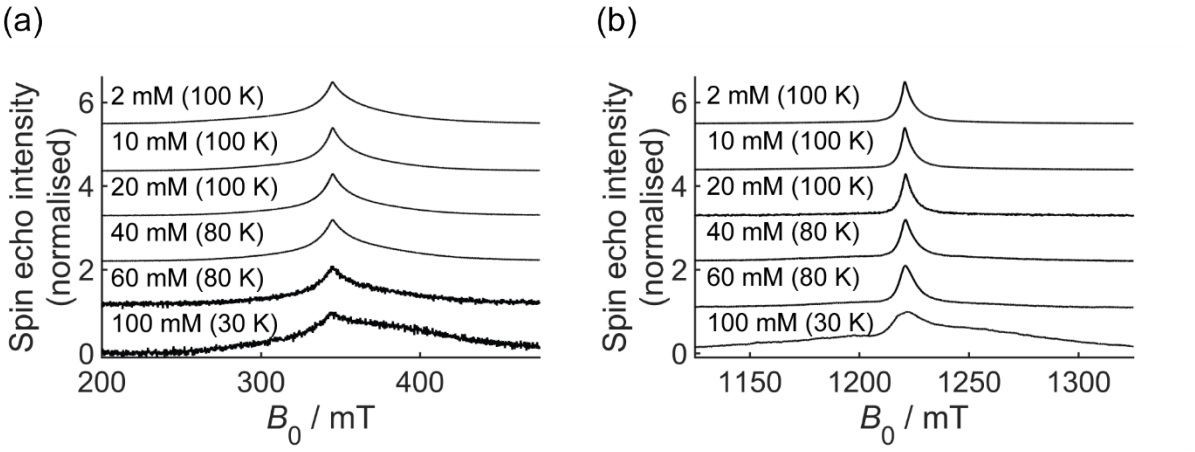

Figure S2: Echo-detected field-swept EPR spectra of various concentrations of $Gd(NO_3)_3$ in 3/2 v/v glycerol/H_2O with 1.5 M glycine, measured at (a) X-band and (b) Q-band.

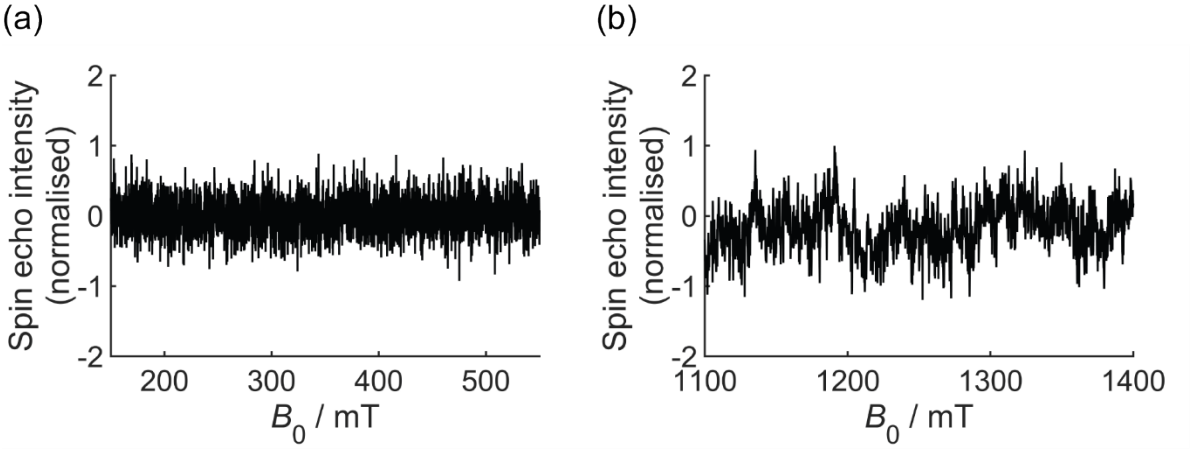

Figure S3: Echo-detected field-swept EPR spectra of 3/2 v/v glycerol/H_2O, measured at (a) X-band and (b) Q-band at 30 K.

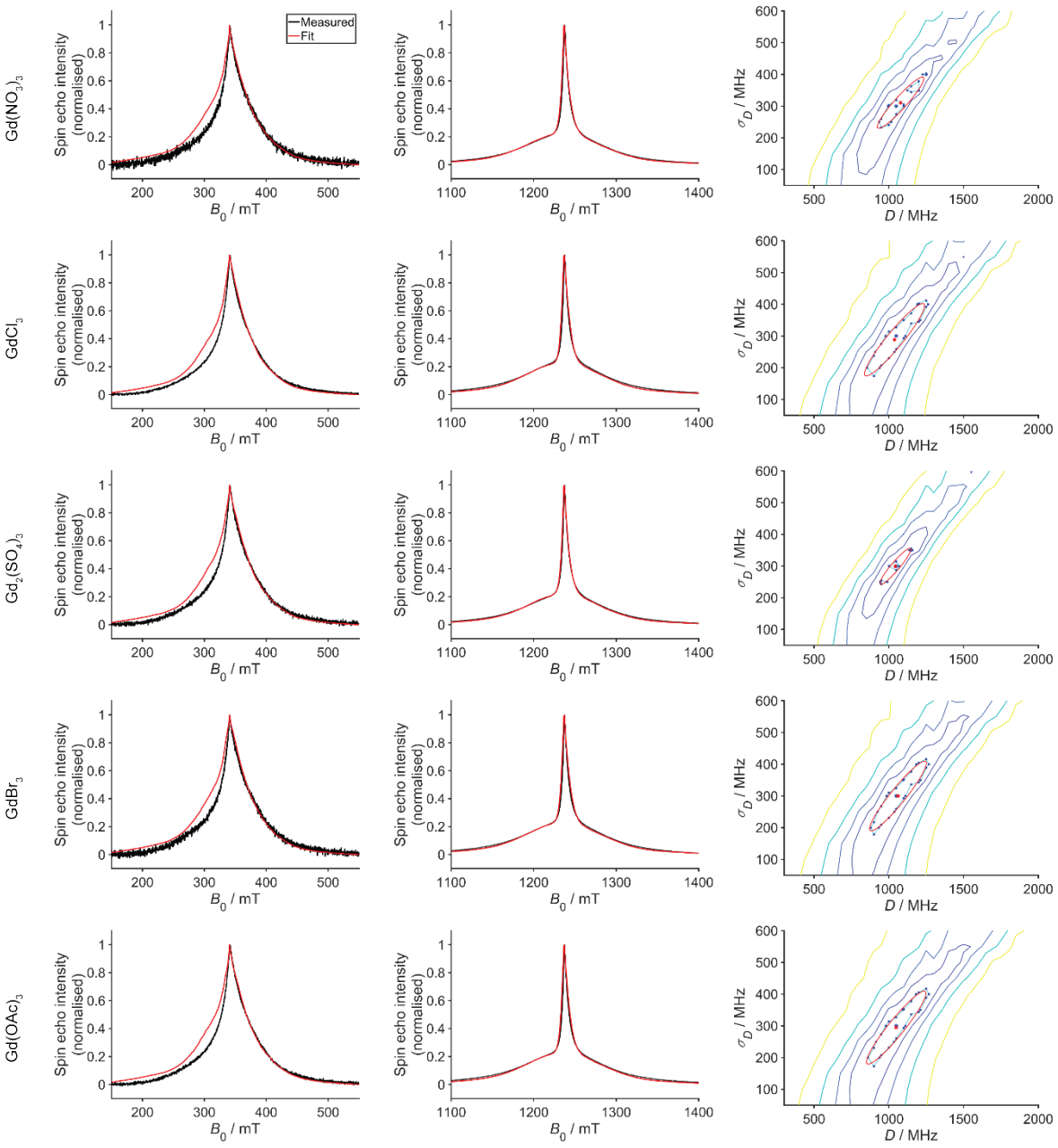

Figure S4: Fits to the echo detected field swept X-band and Q-band EPR spectra, along with contour plots, for 25 μM of all Gd(III) compounds in 3/2 v/v glycerol/H_2O at 10 K.

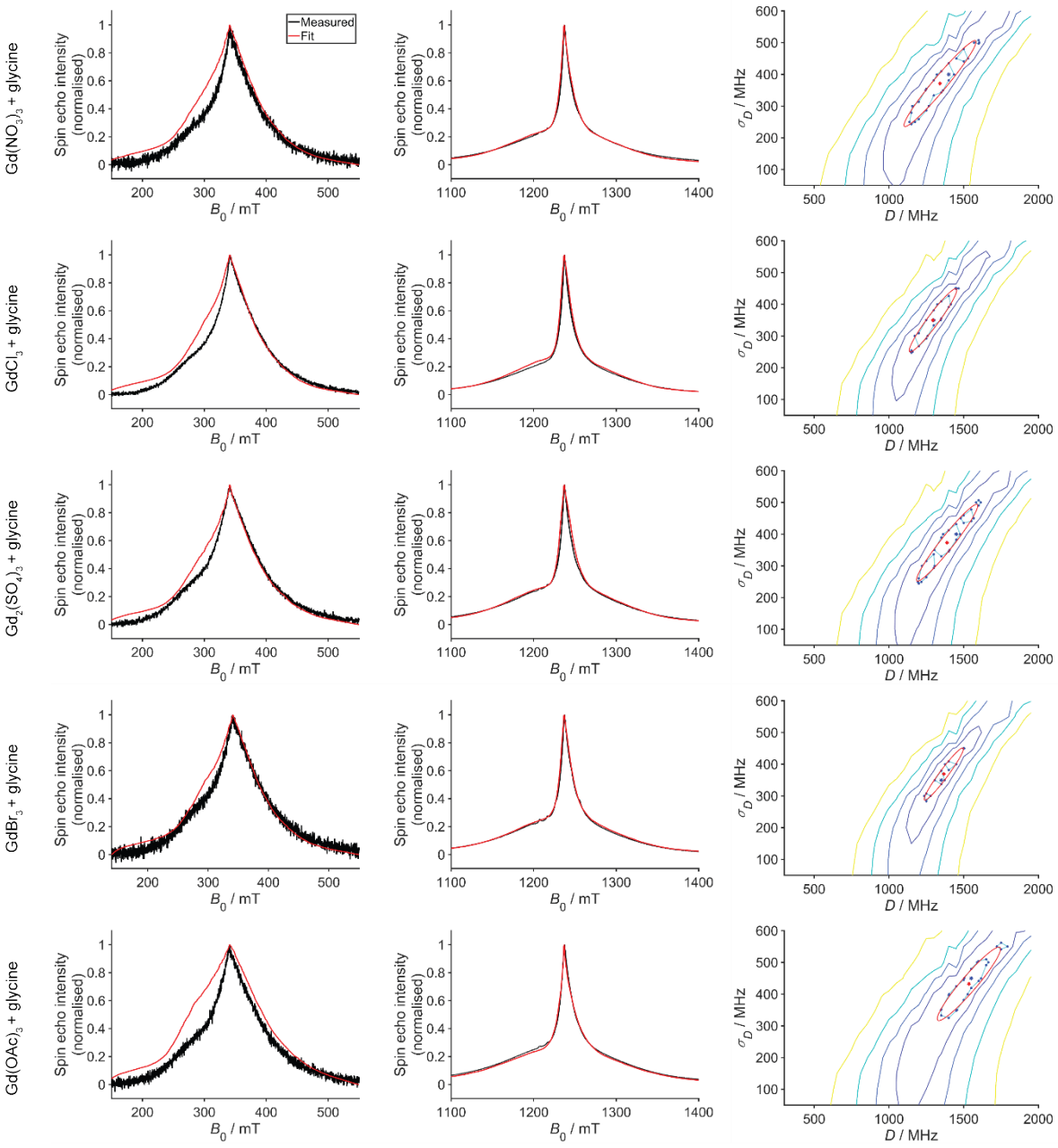

Figure S5: Fits to the echo detected field swept X-band and Q-band EPR spectra, along with contour plots, for 25 μM of all Gd(III) compounds in 3/2 v/v glycerol/H_2O at 10 K, with 1.5 M glycine added.