Marbofloxacin combined with heavy rare-earth ions makes better candidates for veterinary drugs: Crystal structure and bio-activity studies

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Table S1. The selected bonds lengths for MB-Ln complexes.

Selected bond (Å)					
MB-Y		**MB-Tb**		**MB-Dy**	
Y−O1	2.292(5)	Tb1−O1	2.417(4)	Dy1−O3	2.312(4)
Y−O3	2.384(5)	Tb1−O2	2.325(5)	Dy1−O4	2.414(4)
Y−O5	2.319(5)	Tb1−O5	2.365(5)	Dy1−O7	2.332(5)
Y−O7	2.343(6)	Tb1−O6	2.342(5)	Dy1−O8	2.346(5)
Y−O9	2.334(5)	Tb1−O9	2.369(4)	Dy1−O11	2.325(5)
Y−O11	2.363(5)	Tb1−O10	2.355(5)	Dy1−O12	2.370(4)
Y−O13	2.295(6)	Tb1−O13	2.379(4)	Dy1−O15	2.345(5)
Y−O15	2.339(5)	Tb1−O14	2.359(5)	Dy1−O16	2.384(4)

MB-Ho		**MB-Er**		**MB-Tm**	
Ho1−O1	2.304(3)	Er1−O1	2.353(5)	Tm1−O1	2.327(6)
Ho1−O3	2.401(3)	Er1−O2	2.296(5)	Tm1−O2	2.287(6)
Ho1−O5	2.315(3)	Er1−O5	2.357(5)	Tm1−O5	2.377(5)
Ho1−O7	2.338(3)	Er1−O6	2.298(5)	Tm1−O6	2.271(6)
Ho1−O9	2.332(3)	Er1−O9	2.363(5)	Tm1−O9	2.329(5)
Ho1−O11	2.380(3)	Er1−O10	2.312(5)	Tm1−O10	2.320(6)
Ho1−O13	2.337(3)	Er1−O13	2.403(4)	Tm1−O14	2.314(6)
Ho1−O15	2.359(3)	Er1−O14	2.330(5)	Tm1−O15	2.338(5)

MB-Yb		**MB-Lu**		
Yb1−O1	2.276(3)	Lu1−O1	2.292(3)	
Yb1−O3	2.389(3)	Lu1−O2	2.268(3)	
Yb1−O5	2.282(3)	Lu1−O4	2.382(3)	
Yb1−O7	2.306(3)	Lu1−O5	2.269(2)	
Yb1−O9	2.292(3)	Lu1−O7	2.344(2)	
Yb1−O11	2.352(3)	Lu1−O8	2.285(2)	
Yb1−O13	2.301(3)	Lu1−O10	2.320(2)	

Yb1−O15	2.340(3)	Lu1−O11	2.296(3)	

Table S2. The selected bond angels for MB-Ln complexes.

Selected angles (°)					
MB-Y		**MB-Tb**		**MB-Dy**	
O1−Y−O3	71.81(17)	O10−Tb1−O9	71.07(16)	O11−Dy1−O8	72.96(17)
O1−Y−O5	141.51(17)	O9−Tb1−O13	78.53(15)	O7−Dy1−O12	74.86(15)
O5−Y−O3	76.97(17)	O5−Tb1−O13	142.00(18)	O7−Dy1−O8	72.41(16)
O5−Y−O7	71.62(18)	O14−Tb1−O1	76.91(15)	O3−Dy1−O8	78.78(16)
O7−Y−O3	76.8(2)	O2−Tb1−O1	71.06(16)	O3−Dy1−O4	71.93(15)
O7−Y−O11	142.56(18)	O2−Tb1−O6	139.47(14)	O3−Dy1−O15	113.40(15)
O9−Y−O3	77.27(18)	O6−Tb1−O5	71.53(17)	O7−Dy1−O15	79.90(16)
O9−Y−O11	71.29(16)	O10−Tb1−O5	73.25(16)	O16−Dy1−O4	116.50(14)

MB-Ho		**MB-Er**		**MB-Tm**	
O1−Ho1−O3	71.71(10)	O6−Er1−O5	71.08(16)	O6−Tm1−O5	72.4(2)
O5−Ho1−O3	76.30(11)	O1−Er1−O5	76.07(18)	O1−Tm1−O5	77.0(2)
O5−Ho1−O7	72.33(12)	O2−Er1−O1	73.94(18)	O2−Tm1−O1	72.6(2)
O1−Ho1−O7	79.93(11)	O2−Er1−O9	71.77(16)	O2−Tm1−O9	75.13(19)
O9−Ho1−O11	71.57(11)	O10−Er1−O9	73.21(17)	O6−Tm1−O10	78.6(2)
O13−Ho1−O11	76.79(11)	O10−Er1−O14	139.86(15)	O14−Tm1−O10	140.18(18)
O13−Ho1−O15	72.03(11)	O14−Er1−O13	71.28(18)	O14−Tm1−O15	71.78(18)
O1−Ho1−O15	141.87(10)	O6−Er1−O13	72.13(17)	O6−Tm1−O10	78.6(2)

MB-Yb		**MB-Lu**		
O1−Yb1−O3	72.26(11)	O2−Lu1−O1	72.91(9)	
O7−Yb1−O3	77.23(13)	O5−Lu1−O4	72.55(9)	
O5−Yb1−O7	73.08(12)	O1−Lu1−O10	112.78(10)	
O5−Yb1−O15	74.15(11)	O8−Lu1−O7	72.15(8)	
O13−Yb1−O15	72.12(11)	O1−Lu1−O11	72.21(10)	

O9−Yb1−O13	140.77(11)	O10−Lu1−O7	77.58(9)	
O9−Yb1−O11	72.21(11)	O8−Lu1−O4	75.86(8)	
O1−Yb1−O11	72.08(11)	O5−Lu1−O10	141.70(9)	

Table S3. The crystallographic data and refinement for the Gd(III) complex of marbofloxacin.

Compound	**MB-Gd**
Empirical formula	$C_{68}H_{77}F_4GdN_{16}O_{34}$
Formula weight	1895.71
Temperature/*K*	119.9(6)
Crystal system	triclinic
Space group	*P*-1
a/Å, *b*/Å, *c*/Å	15.0847(10), 17.9471(13), 21.4137(13)
α/°, *β*/°, *γ*/°	95.903(5), 107.495(6), 113.144(7)
Volume/Å^3	4920.1(6)
Z	2
*ρ*calc / g/cm^3	1.280
μ/mm $^{-1}$	0.762
F(000)	1938.0
Crystal size/mm^3	0.35 × 0.25 × 0.11
Radiation	Mo K*α* (*λ* = 0.71073)
2*θ* range for data collection/°	5.8 to 52.74
Index ranges	$-18 \le h \le 18$, $-22 \le k \le 22$, $-26 \le l \le 26$
Reflections collected	60772
Independent reflections	20094 [R_{int} = 0.1208, R_{sigma} = 0.1511]
Data/restraints/parameters	20094/0/1116
Goodness-of-fit on F^2	1.636
Final *R* indexes [*I*>=2*σ* (*I*)]	R_1 = 0.1893, wR_2 = 0.4465
Final *R* indexes [all data]	R_1 = 0.2703, wR_2 = 0.5230
Largest diff. peak/hole/e Å^{-3}	5.60/–3.17

Table S4. The selected bond and angels for the Gd(III) complex of marbofloxacin.

Selected bond (Å)		**Selected angles (°)**	
Gd−O3	2.341(11)	O3−Gd−O4	70.4(4)
Gd−O4	2.430(10)	O8−Gd−O4	77.8(4)
Gd−O7	2.344(12)	O7−Gd−O8	71.4 (4)
Gd−O8	2.388(10)	O7−Gd−O12	76.4(4)
Gd−O11	2.375(13)	O11−Gd−O12	70.2(4)
Gd−O12	2.383(11)	O15−Gd−O11	138.5(3)
Gd−O15	2.362(12)	O15−Gd−O16	71.3(3)
Gd−O16	2.400(9)	O3−Gd−O16	72.8(3)

The spectral characterizations for MB-Ln complexes:

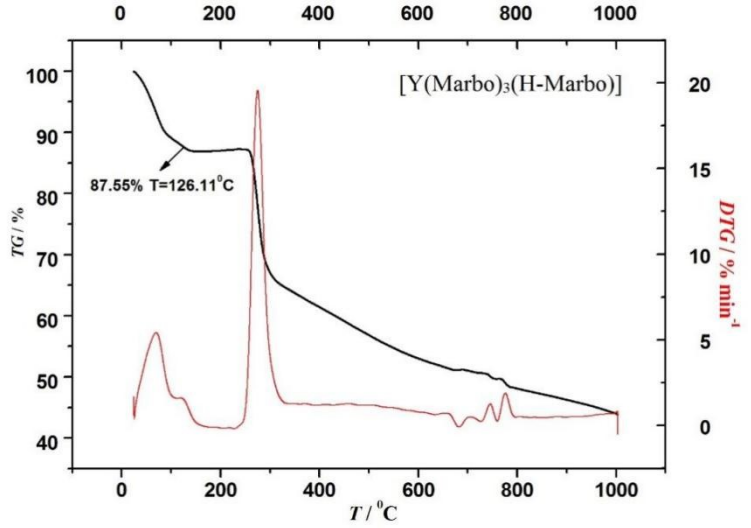

Figure S1. The TGA spectrum of MB-Y.

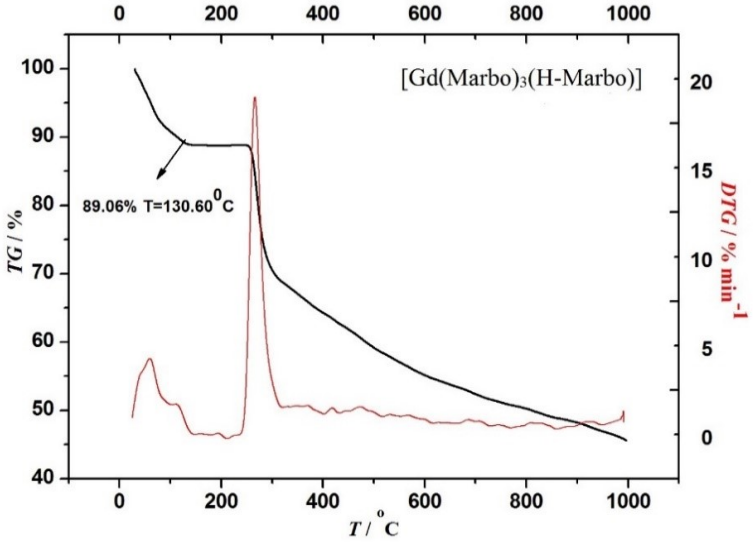

Figure S2. The TGA spectrum of MB-Gd.

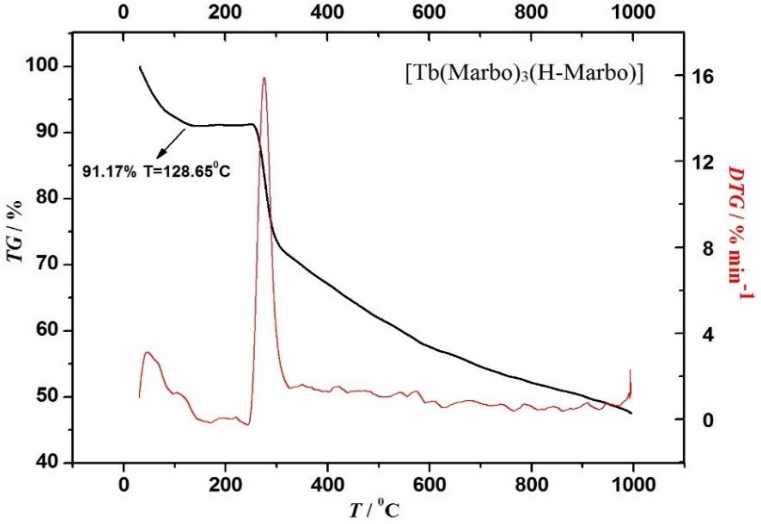

Figure S3. The TGA spectrum of MB-Tb.

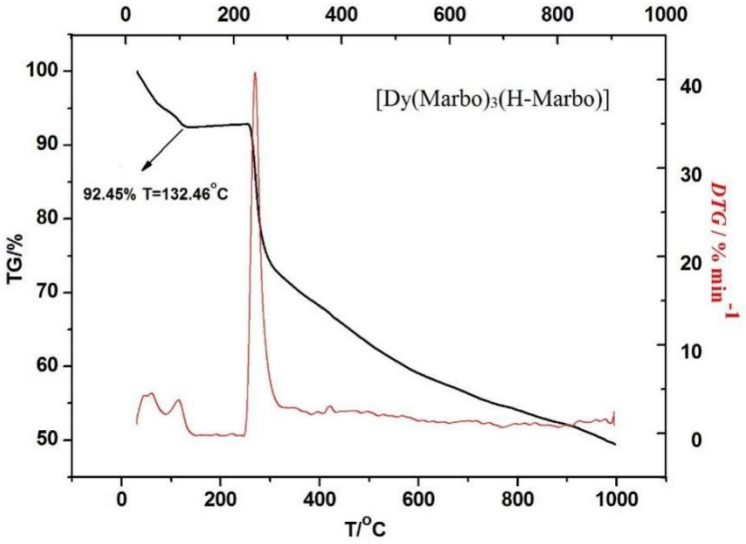

Figure S4. The TGA spectrum of MB-Dy.

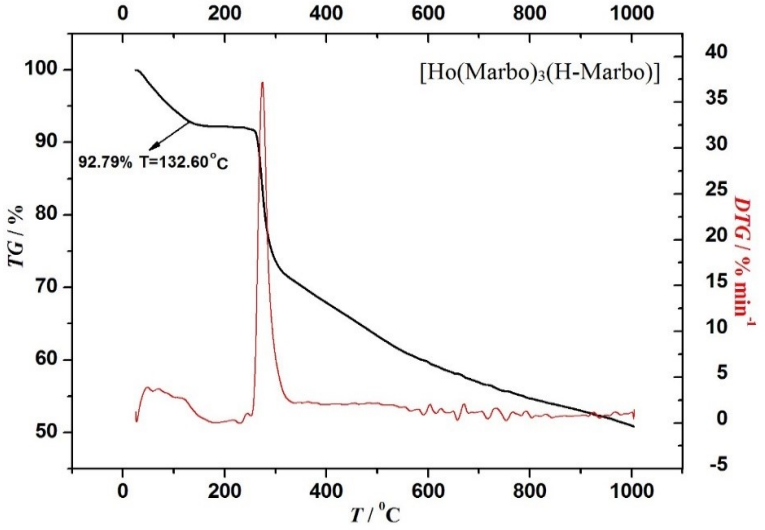

Figure S5. The TGA spectrum of MB-Ho.

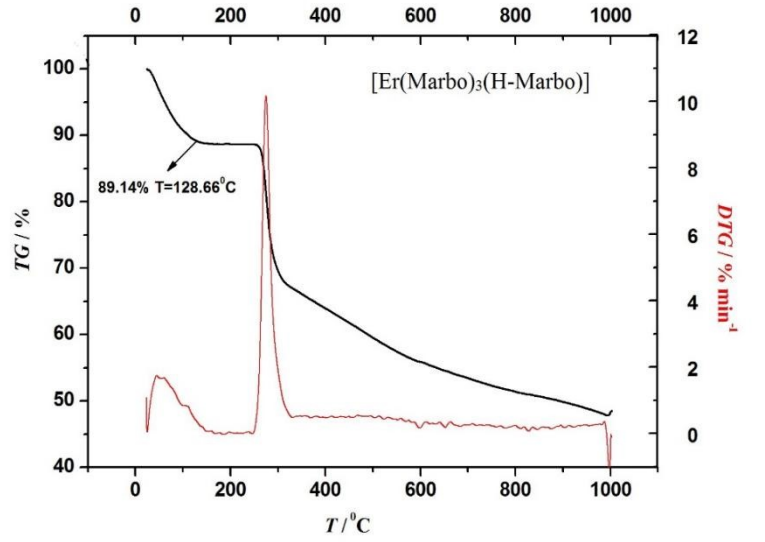

Figure S6. The TGA spectrum of MB-Er.

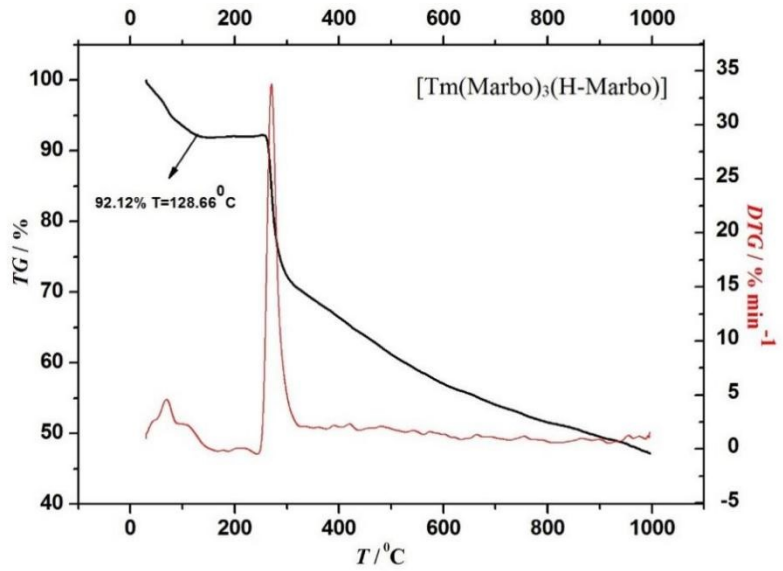

Figure S7. The TGA spectrum of MB-Tm.

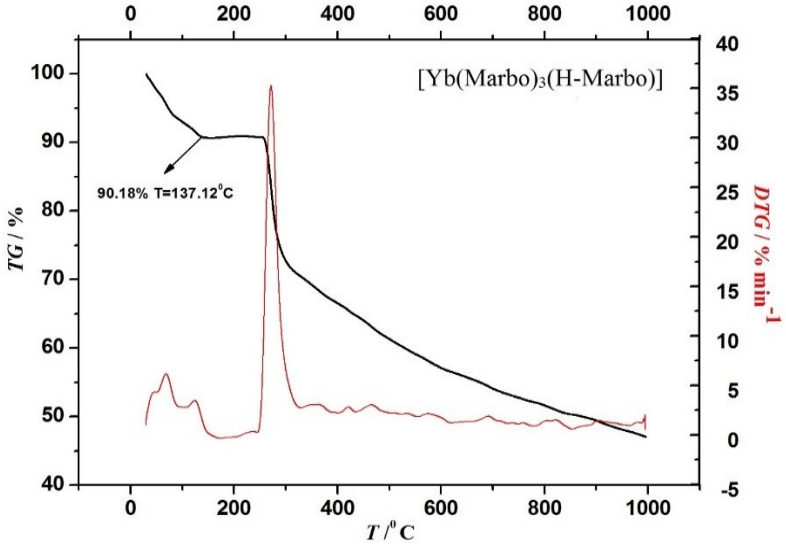

Figure S8. The TGA spectrum of MB-Yb.

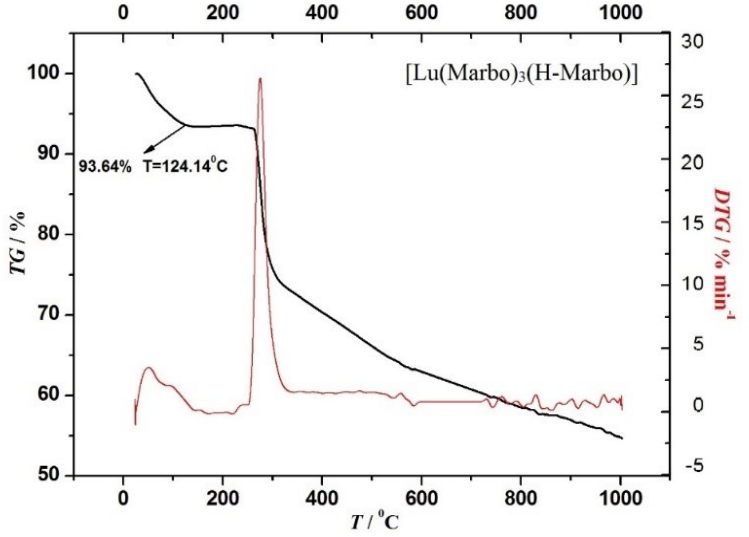

Figure S9. The TGA spectrum of MB-Lu.

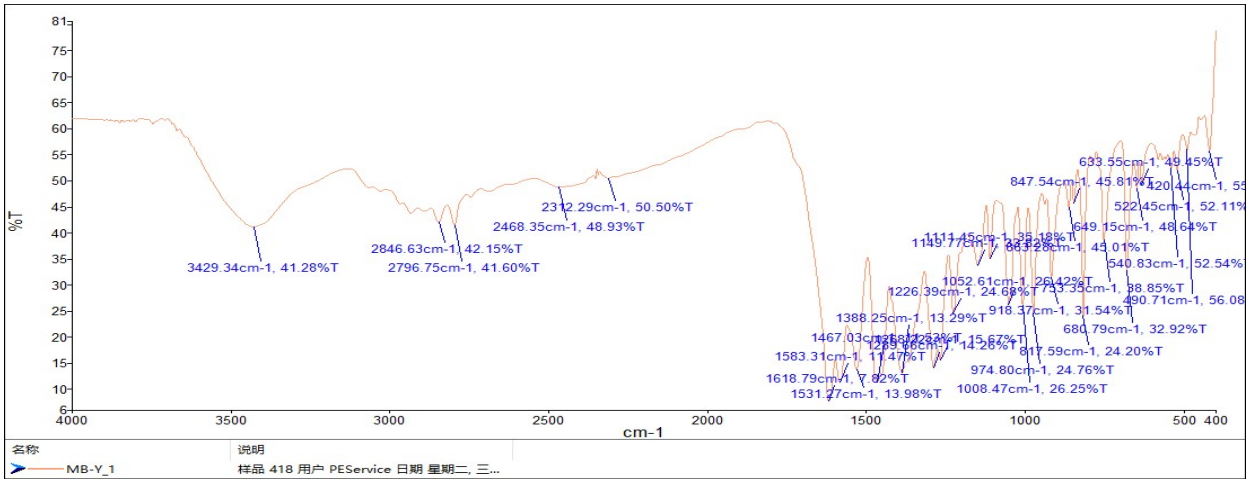

Figure S10. The IR spectrum of MB-Y.

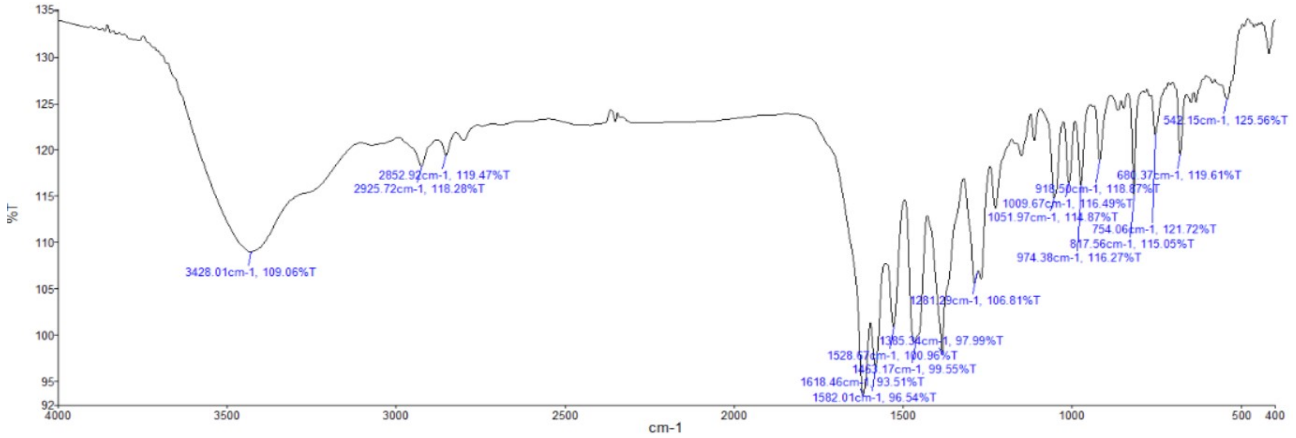

Figure S11. The IR spectrum of MB-Gd.

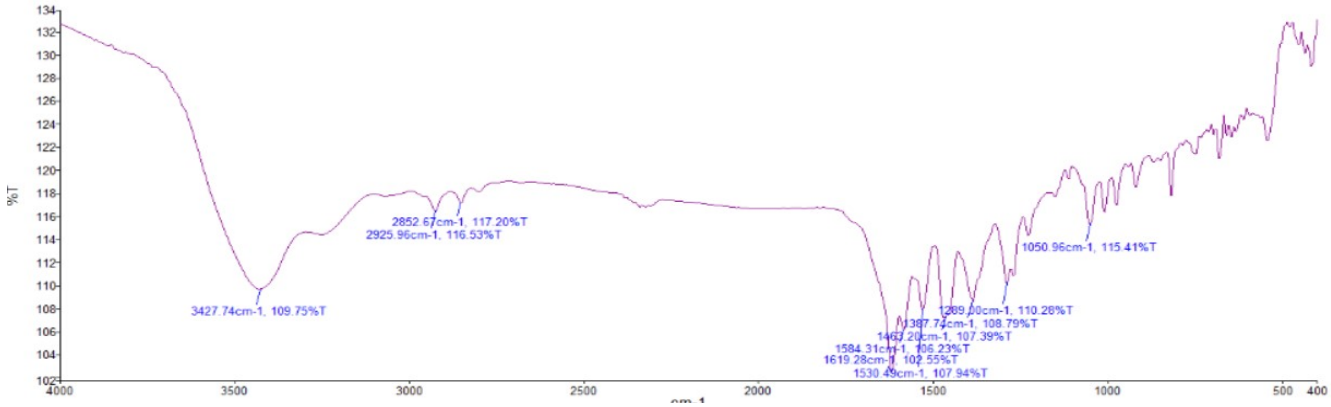

Figure S12. The IR spectrum of MB-Tb.

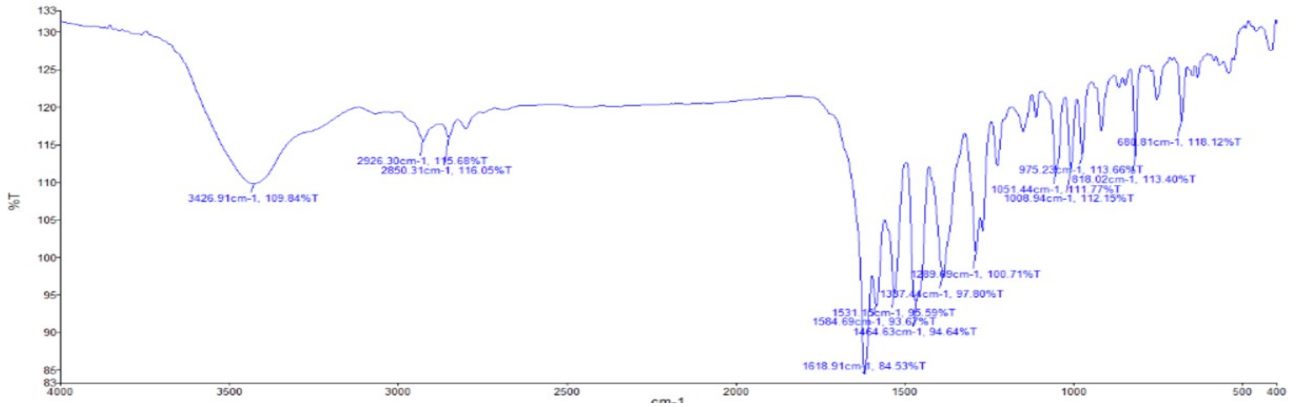

Figure S13. The IR spectrum of MB-Dy.

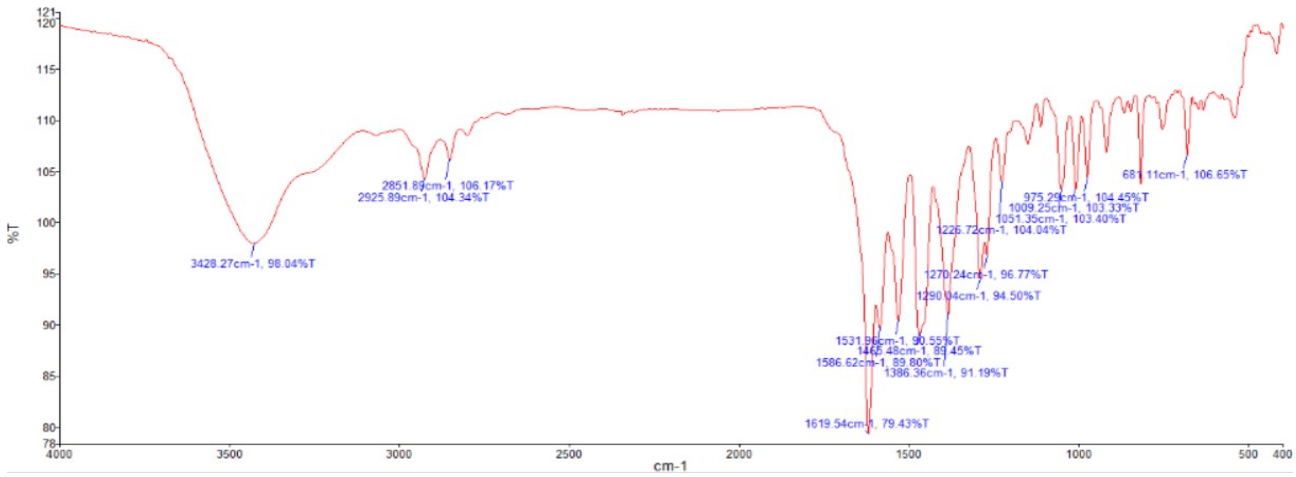

Figure S14. The IR spectrum of MB-Ho.

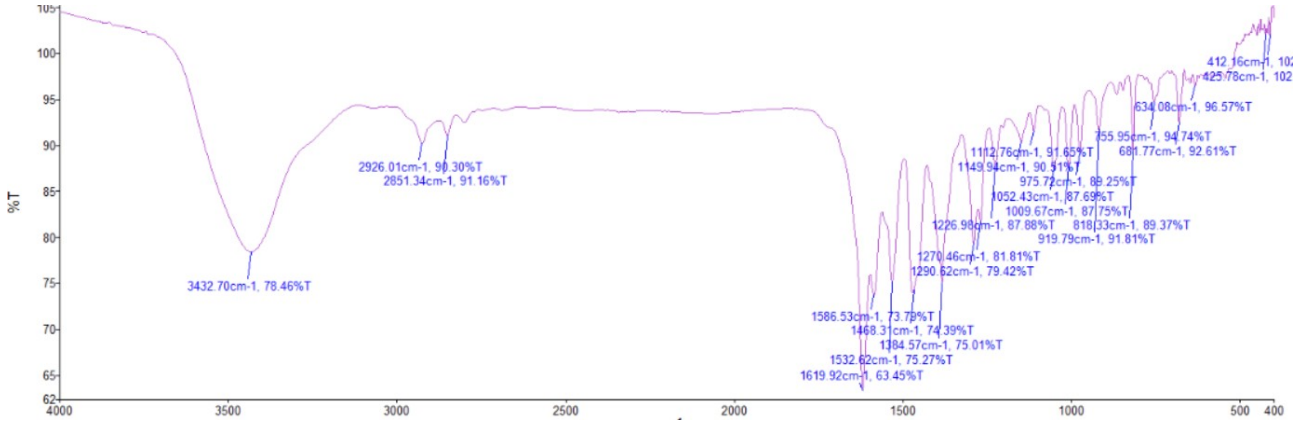

Figure S15. The IR spectrum of MB-Er.

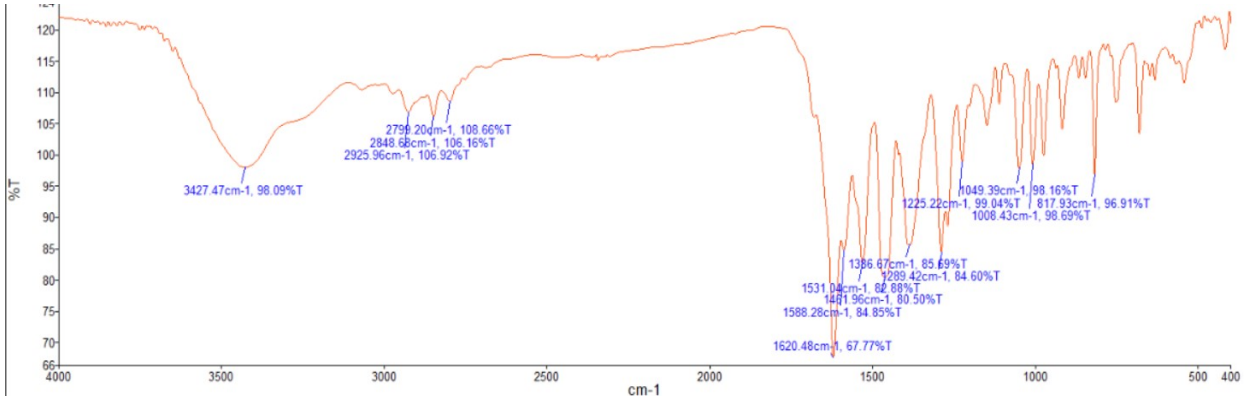

Figure S16. The IR spectrum of MB-Tm.

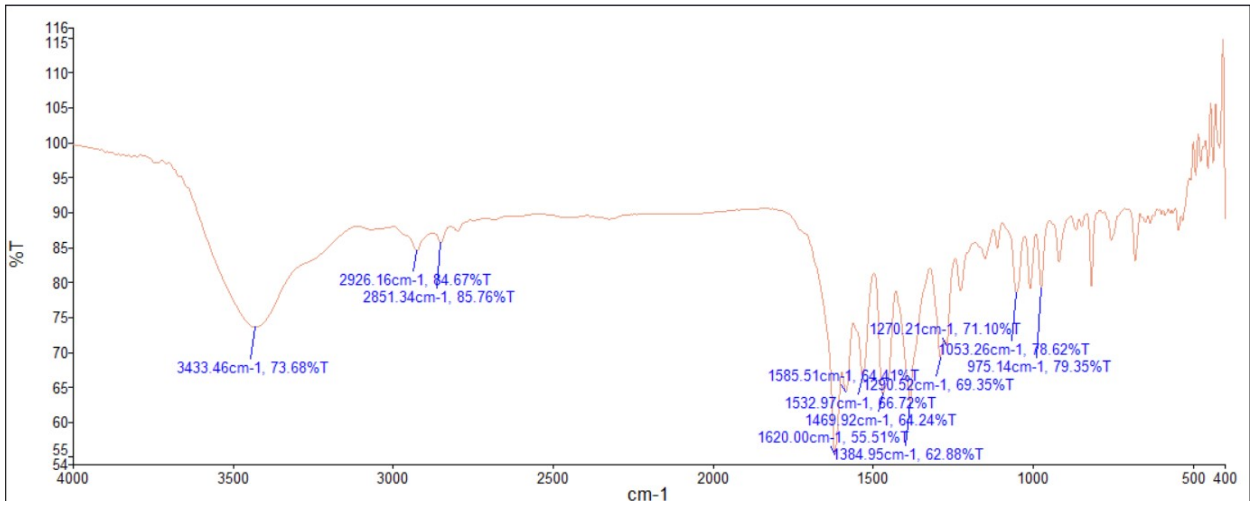

Figure S17. The IR spectrum of MB-Yb.

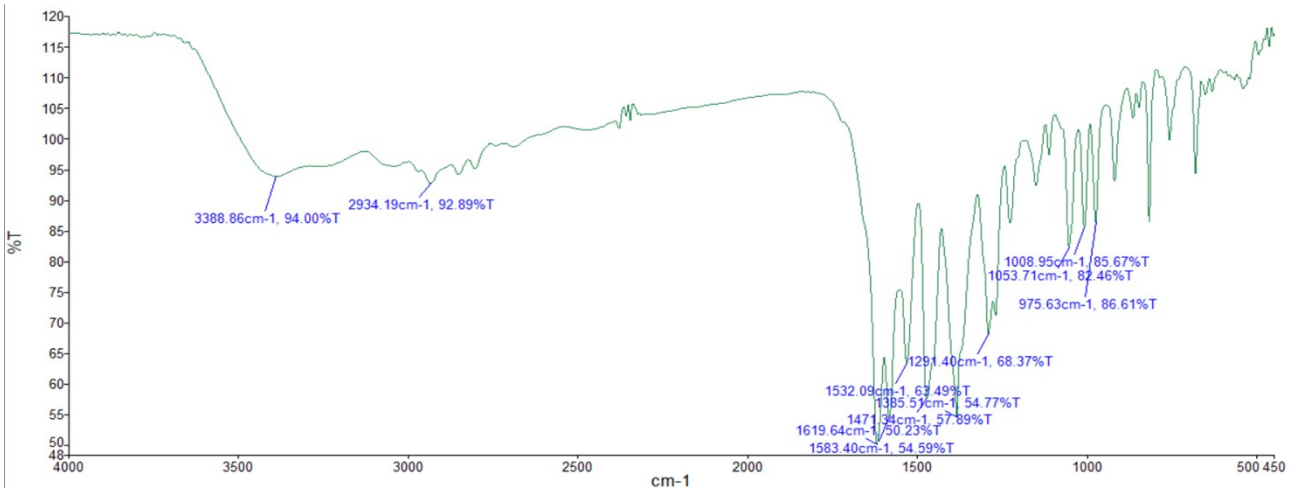

Figure S18. The IR spectrum of MB-Lu.

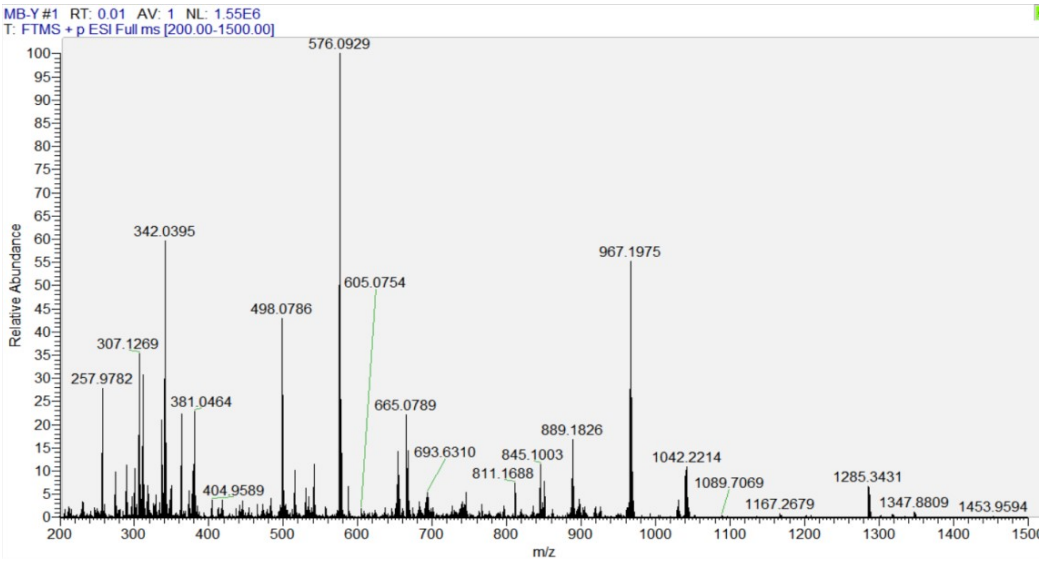

Figure S19. The HRMS of MB-Y.

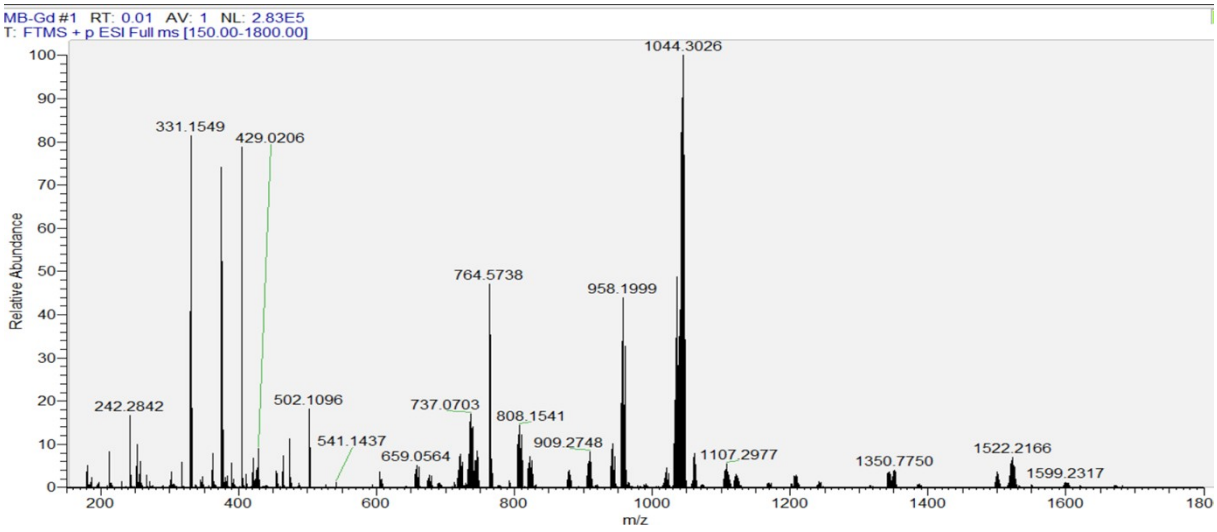

Figure S20. The HRMS of MB-Gd.

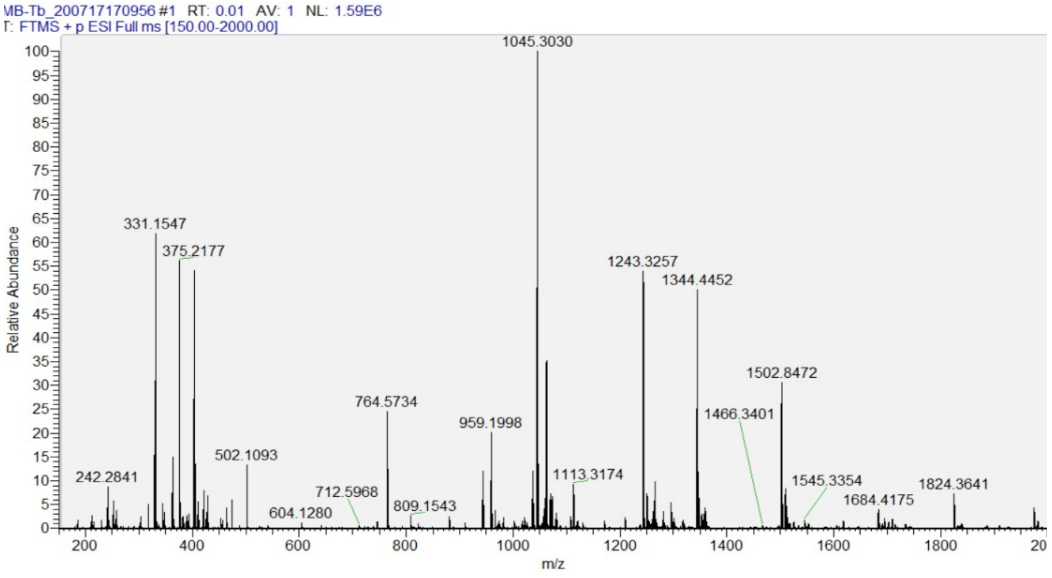

Figure S21. The HRMS of MB-Tb.

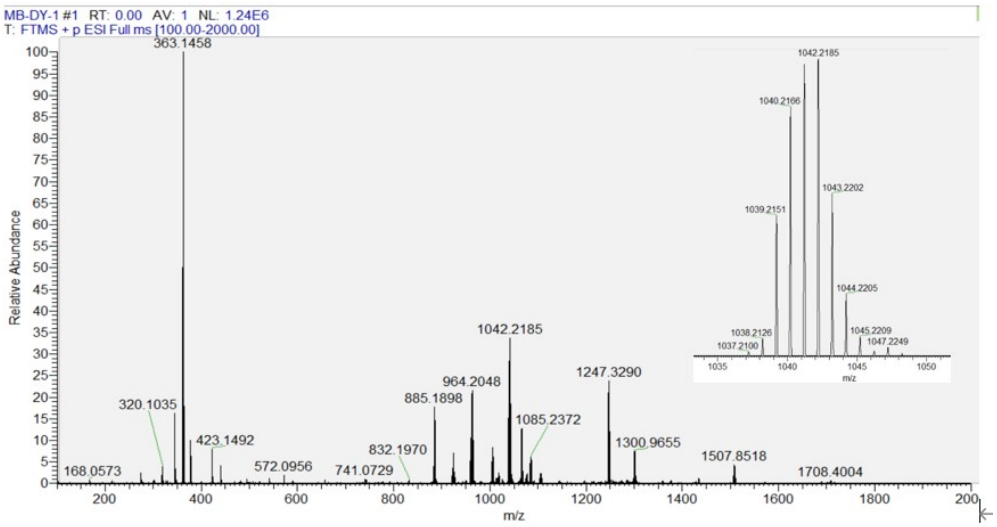

Figure S22. The HRMS of MB-Dy.

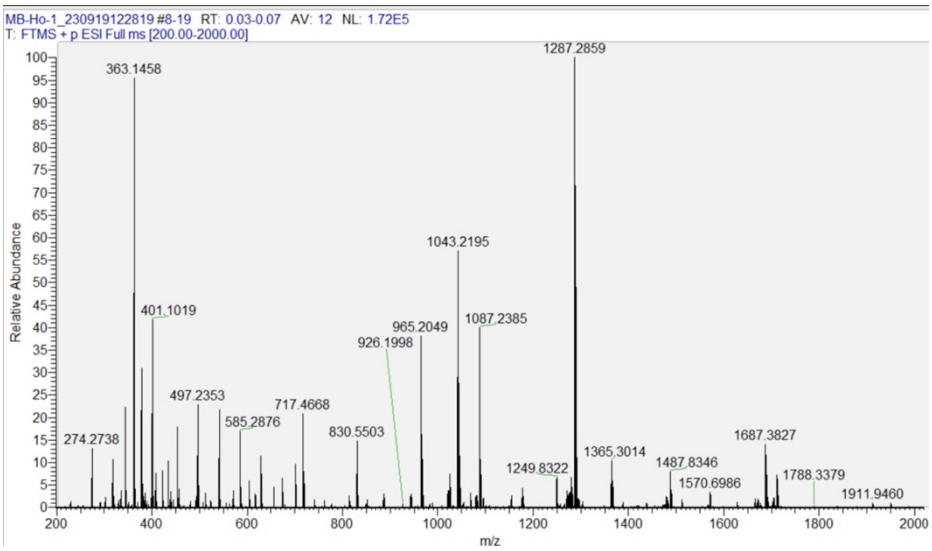

Figure S23. The HRMS of MB-Ho.

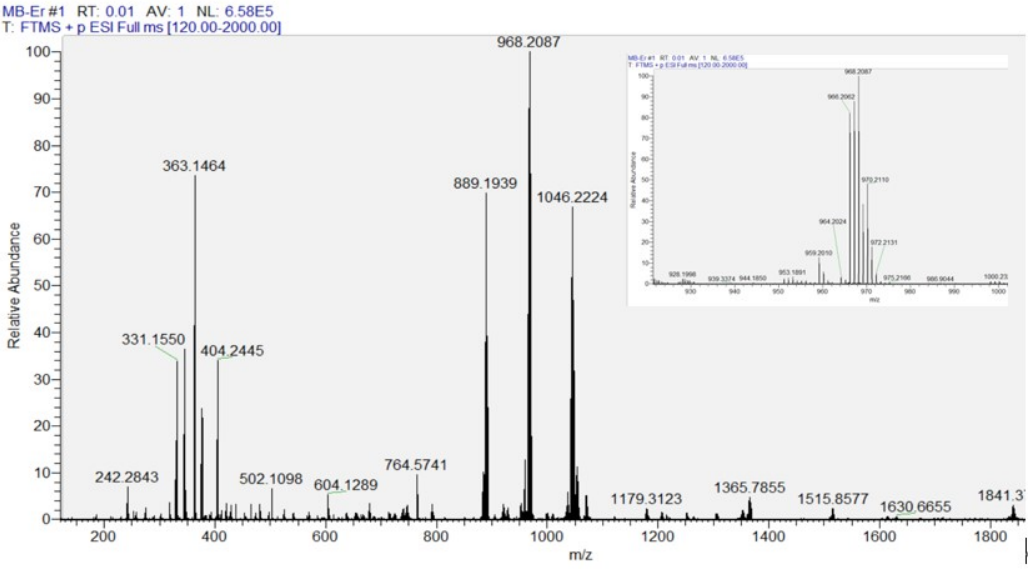

Figure S24. The HRMS of MB-Er.

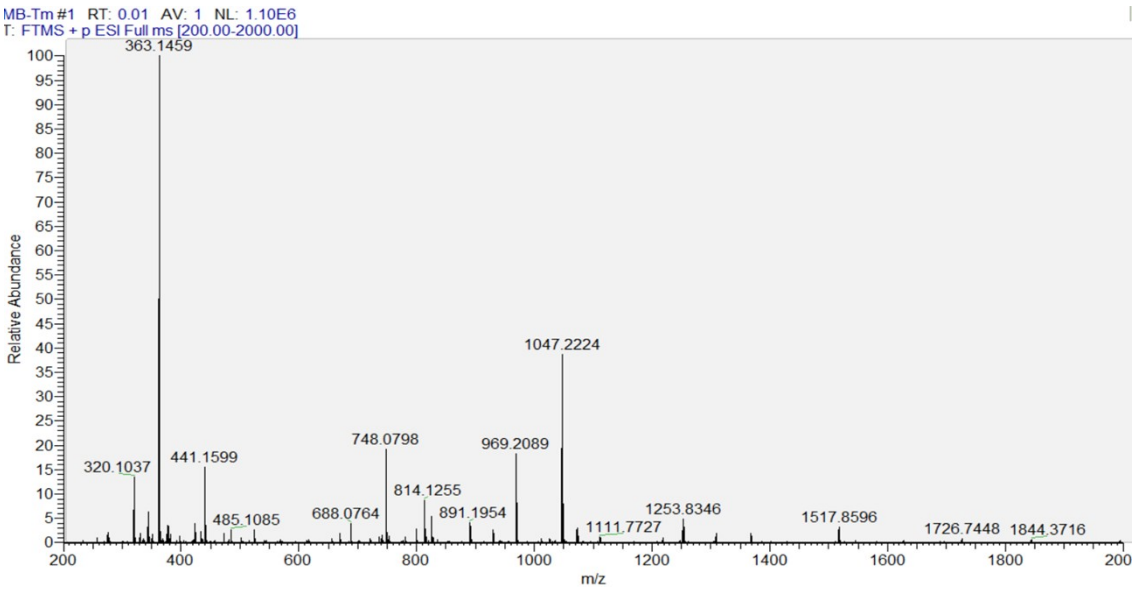

Figure S25. The HRMS of MB-Tm.

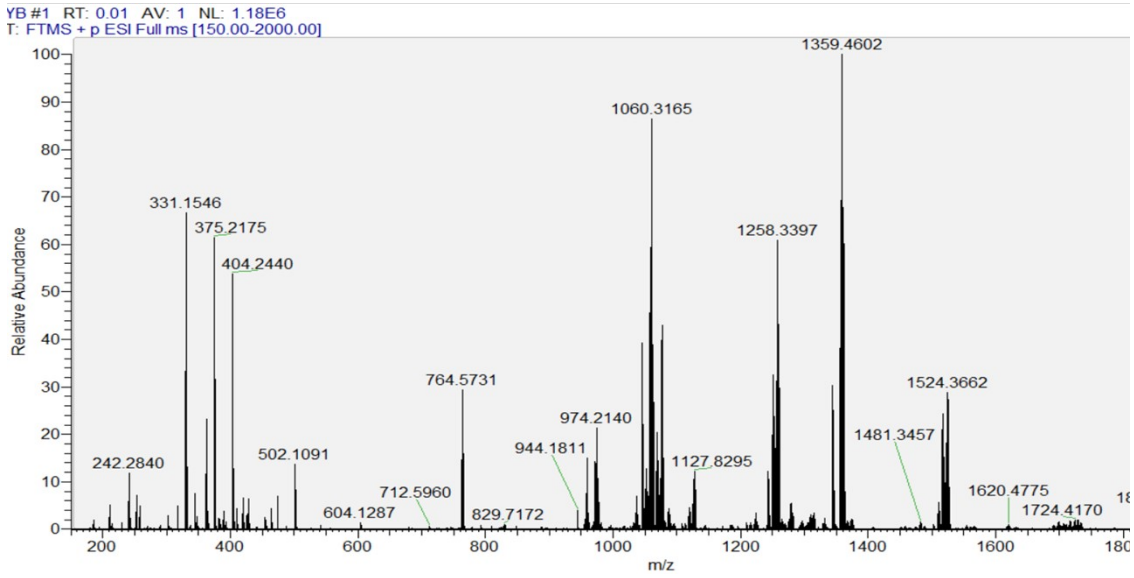

Figure S26. The HRMS of MB-Yb.

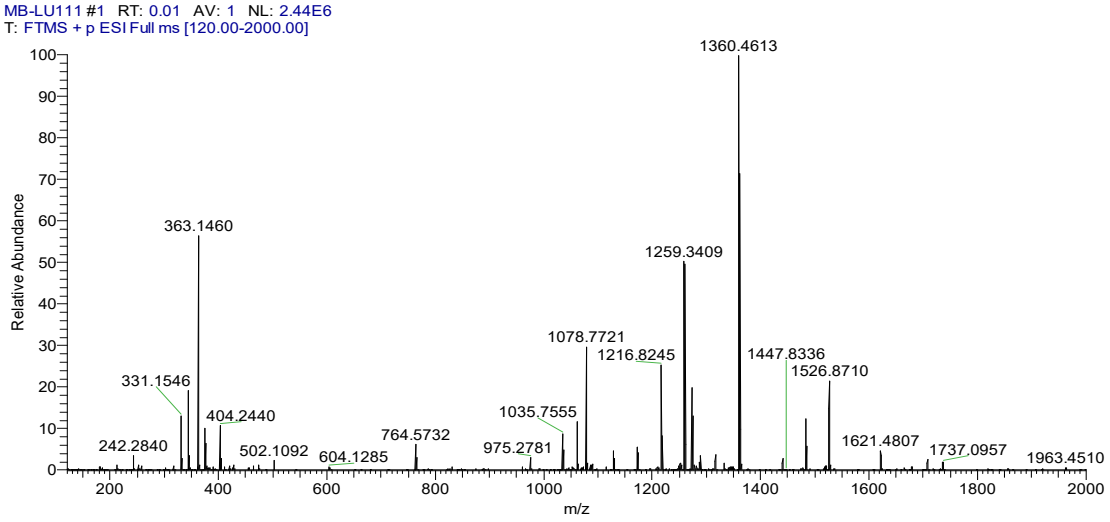

Figure S27. The HRMS of MB-Lu.

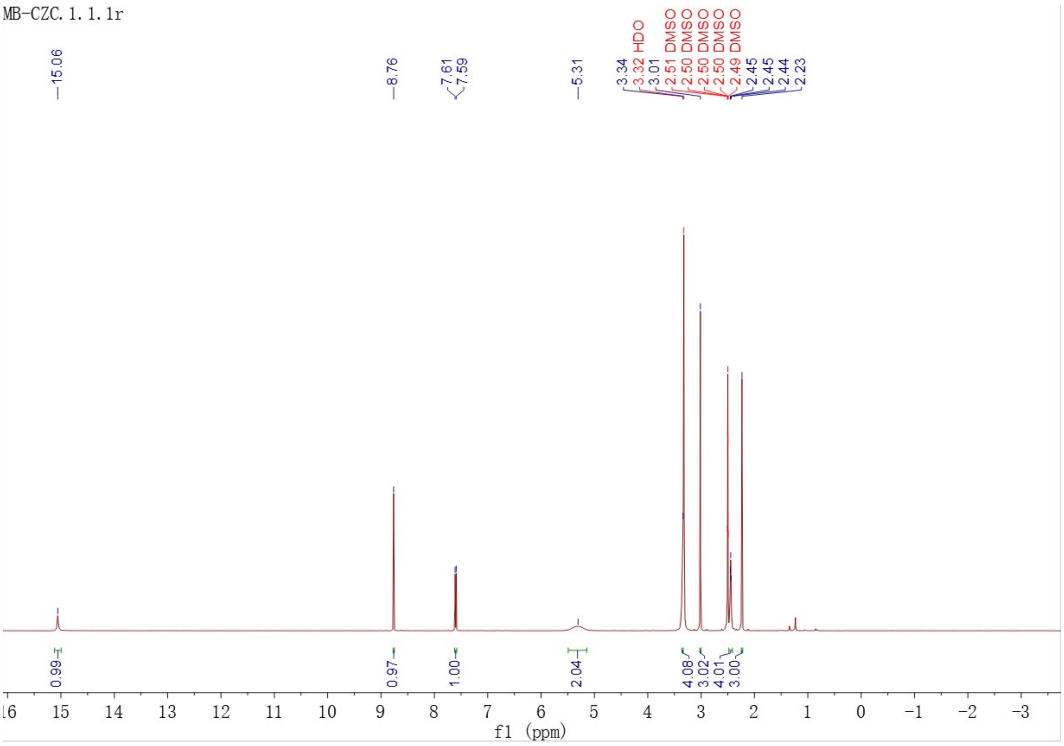

Figure S28. The ^{1}H-NMR spectrum of MB. (^{1}H-NMR (600 MHz, DMSO-d_6) δ 15.06 (s, 1H), 8.76 (s, 1H), 7.60 (d, J = 12.6 Hz, 1H), 5.31 (s, 2H), 3.34 (s, 4H), 3.01 (s, 3H), 2.45 (t, J = 4.8 Hz, 4H), 2.23 (s, 3H)).

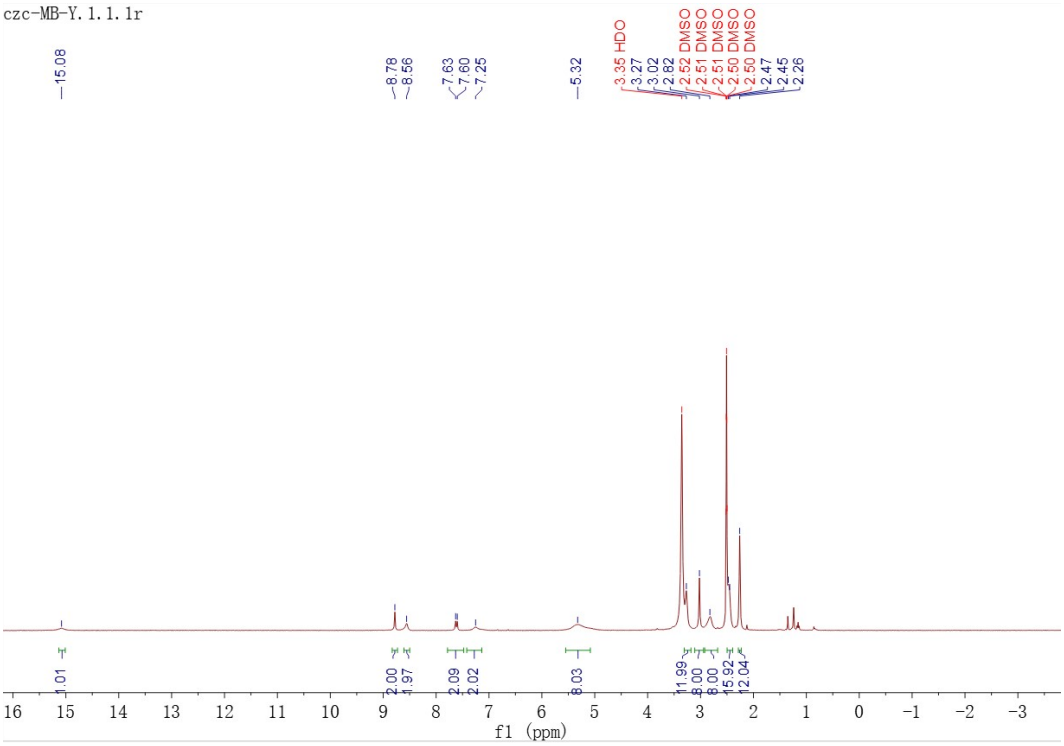

Figure S29. The ^{1}H-NMR spectrum of MB-Y for comparison with MB. (^{1}H-NMR (400 MHz, DMSO-d_6) δ 15.08 (s, 1H), 8.78 (s, 2H), 8.56 (s, 2H), 7.61 (d, J = 12.6 Hz, 2H), 7.25 (s, 2H), 5.32 (s, 8H), 3.27 (s, 12H), 3.02 (s, 8H), 2.82 (s, 8H), 2.46 (d, J = 10.5 Hz, 16H), 2.26 (s, 12H)).

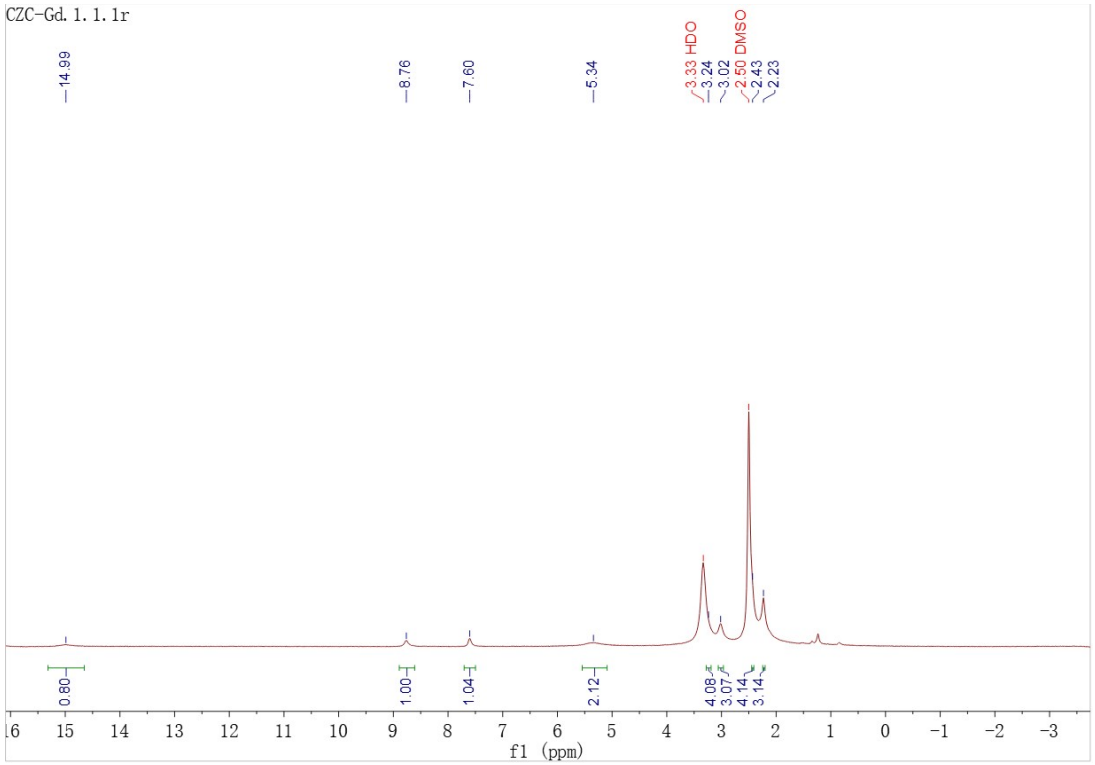

Figure S30. The ^{1}H-NMR spectrum of MB-Gd for comparison with MB. (^{1}H-NMR (600 MHz, DMSO-d_6) δ 14.99 (s, 1H), 8.76 (s, 1H), 7.60 (s, 1H), 5.34 (s, 2H), 3.24 (s, 4H), 3.02 (s, 3H), 2.43 (s, 4H), 2.23 (s, 3H)).

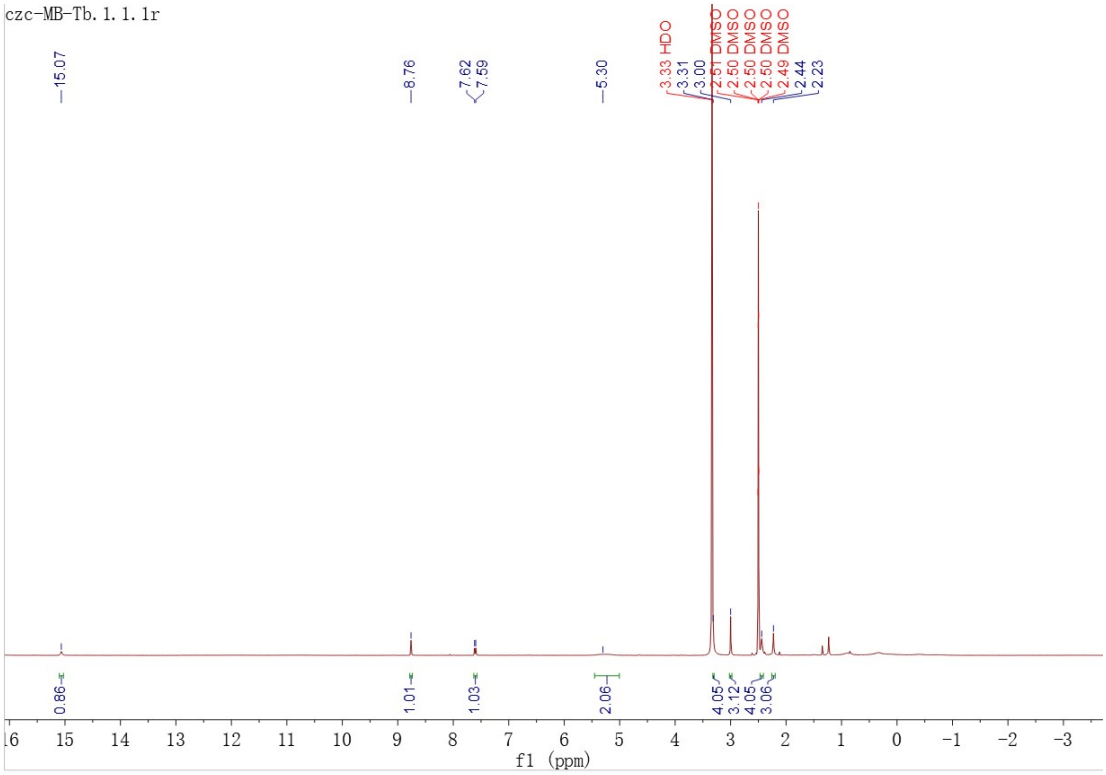

Figure S31. The ^{1}H-NMR spectrum of MB-Tb for comparison with MB. (^{1}H-NMR (600 MHz, DMSO-d_6) δ 15.07 (s, 1H), 8.76 (s, 1H), 7.61 (d, J = 12.5 Hz, 1H), 5.30 (s, 2H), 3.31 (s, 4H), 3.00 (s, 3H), 2.44 (s, 4H), 2.23 (s, 3H)).

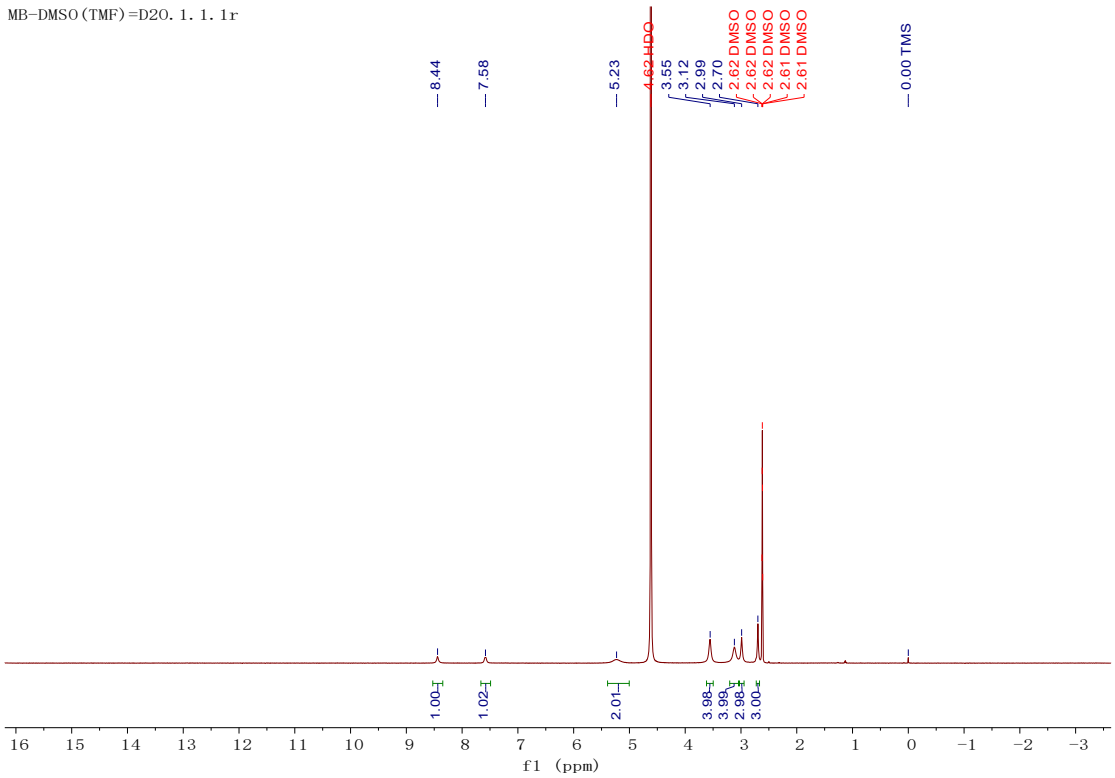

Figure S32. The ^{1}H-NMR spectrum of MB (1:1 proportion of deuterated DMSO-d_6 and D_2O). ^{1}H-NMR (600 MHz) δ 8.44 (s, 1H), 7.58 (s, 1H), 5.23 (s, 2H), 3.55 (s, 4H), 3.12 (s, 4H), 2.99 (s, 3H), 2.70 (s, 3H).

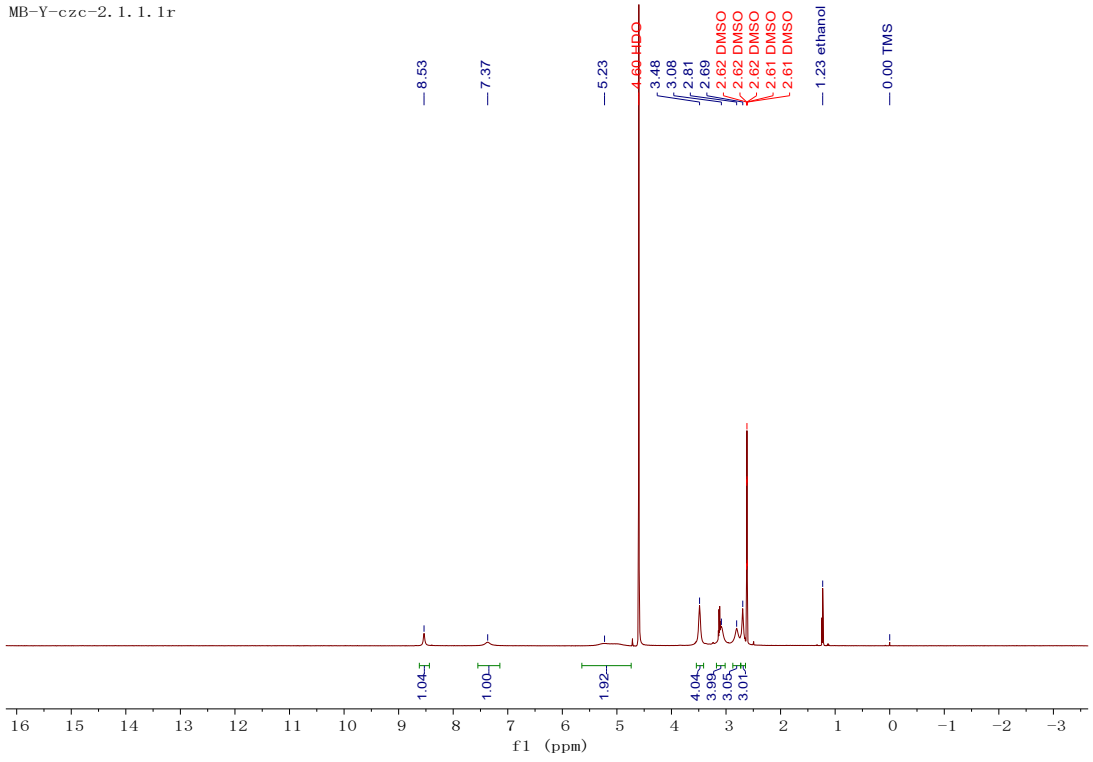

Figure S33. The ^{1}H-NMR spectrum of MB-Y for comparison with MB (1:1 proportion of deuterated DMSO-d_6 and D_2O). ^{1}H-NMR (600 MHz) δ 8.53 (s, 1H), 7.37 (s, 1H), 5.23 (s, 2H), 3.48 (s, 4H), 3.08 (s, 4H), 2.81 (s, 3H), 2.69 (s, 3H).

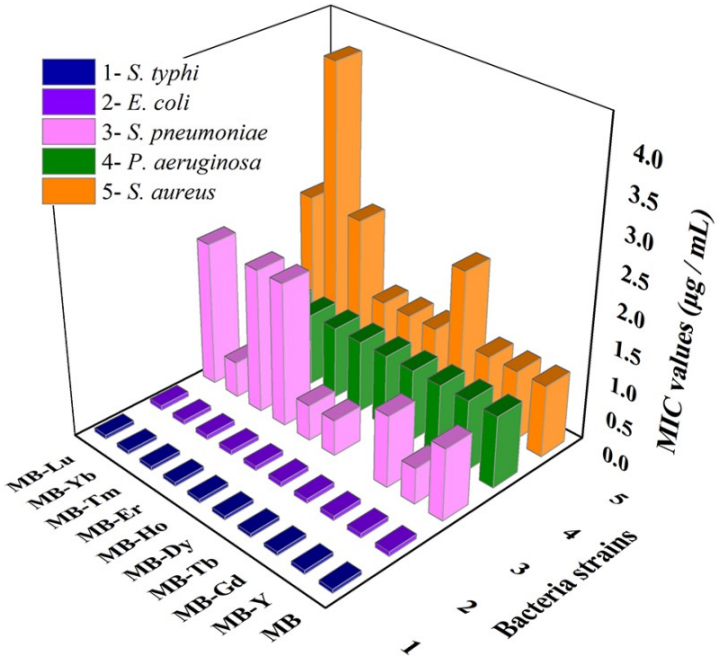

Figure S34. The antibacterial activity of the MB-Ln complexes presented by MIC values (μg/mL).

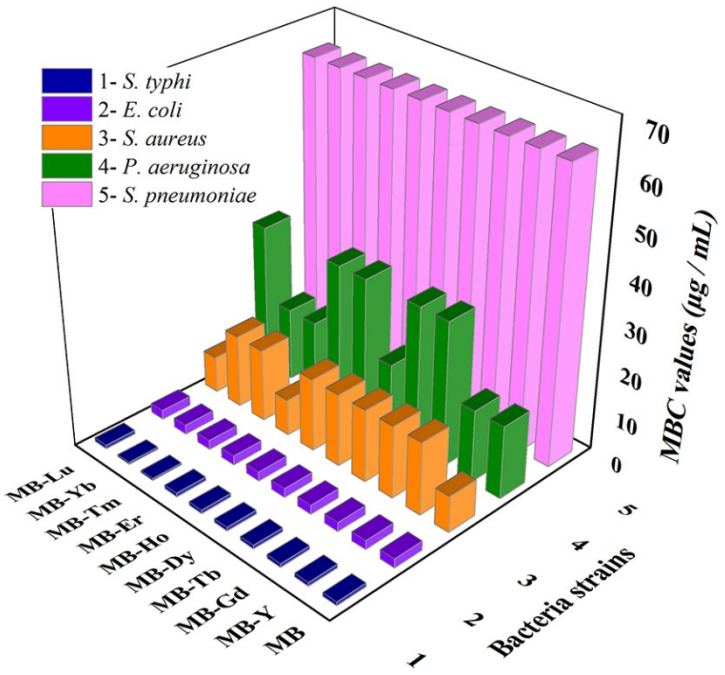

Figure S35. The antibacterial activity of the MB-Ln complexes presented by MBC values (μg/mL).