## Electronic Supporting Information

# Ytterbium complex with 2-(tosylamino)-benzylidene-N-(2-halobenzoyl)-hydrazones for solution-processable NIR OLEDs

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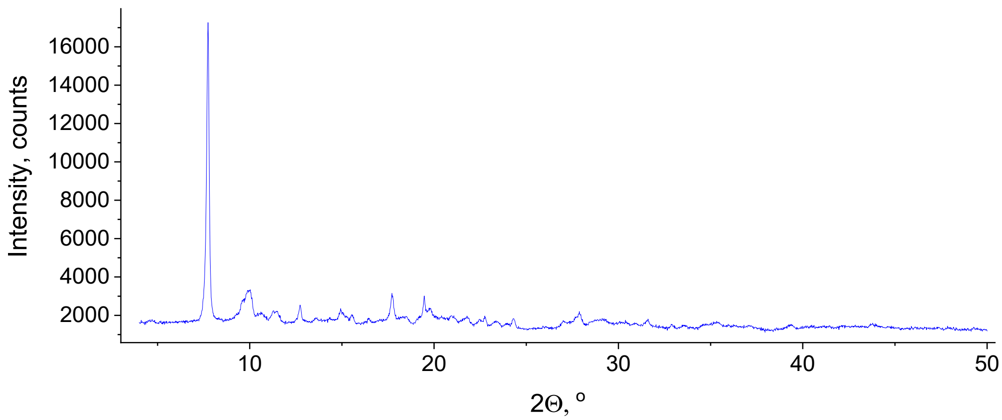
## Contents

# XRD data



Intensity, counts
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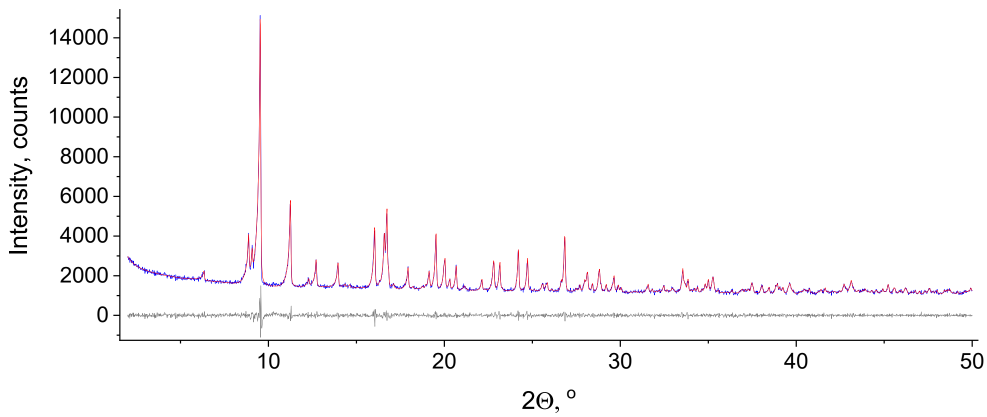
6000
4000
2000
10
20
30
40
50
2Θ, °


a)



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2Θ, °


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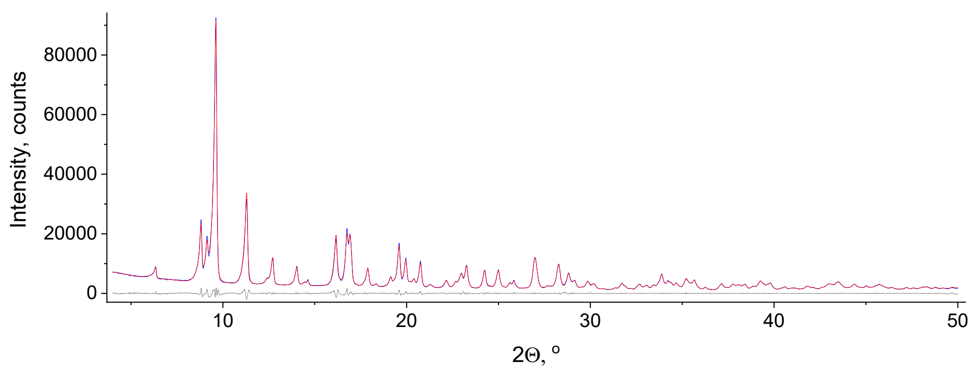

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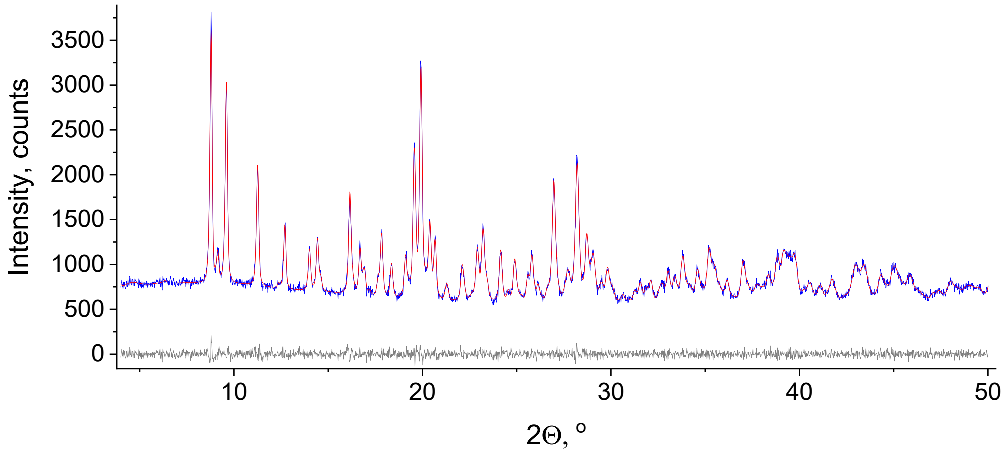


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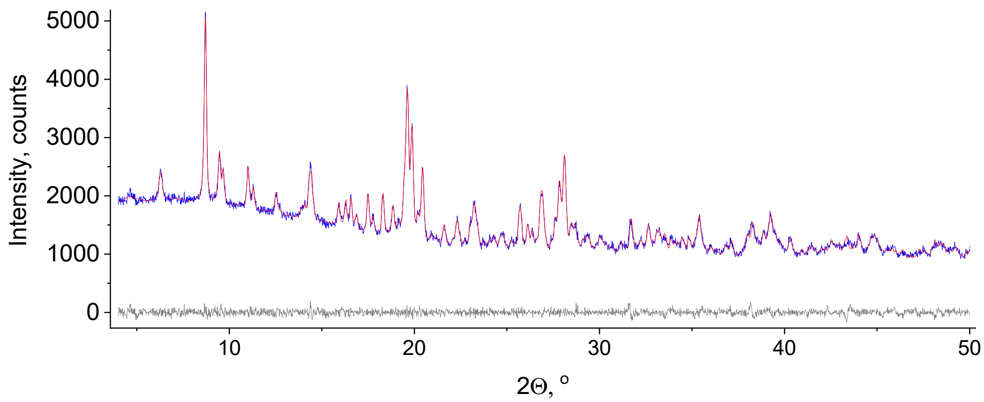



e)

**Figure S1.** PXRD patterns of a) $Yb(L^{F})(HL^{F})$, b) $Gd(L^{Cl})(HL^{Cl})$, c) $Yb(L^{Cl})(HL^{Cl})$, d) $Yb(L^{Br})(H^{Br})$, e) $Yb(L^{I})(H^{I})$: experimental curve (blue), fitting curve (red), difference (grey).

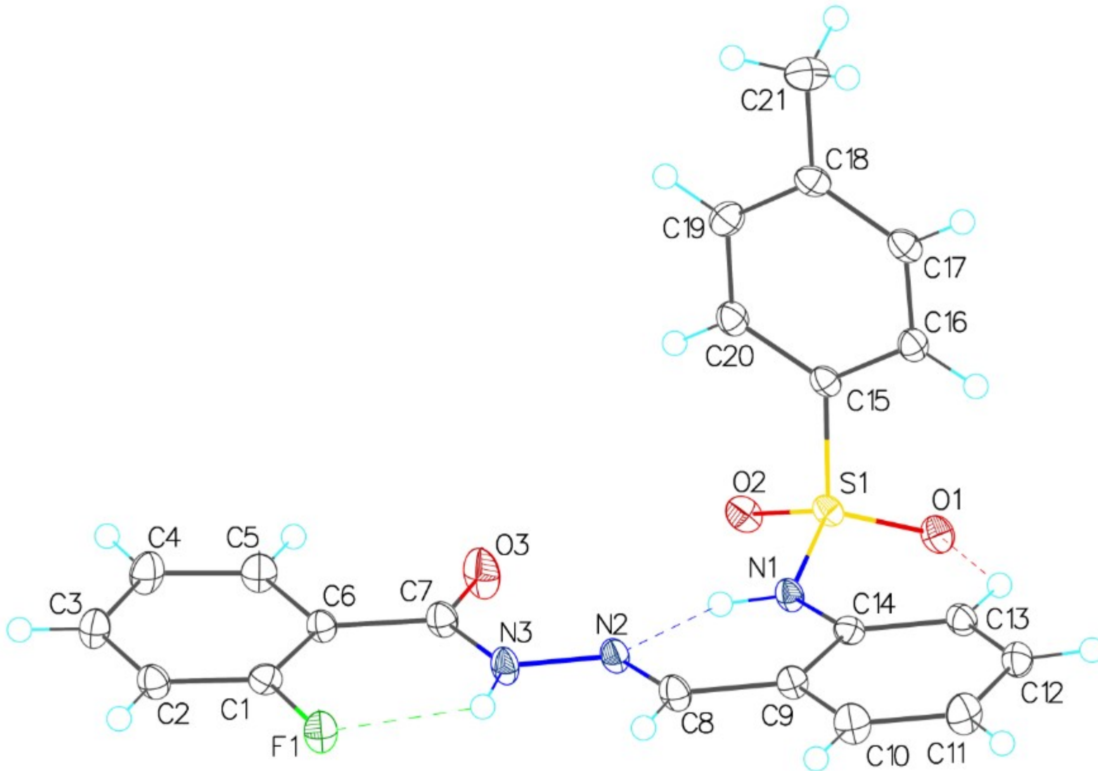
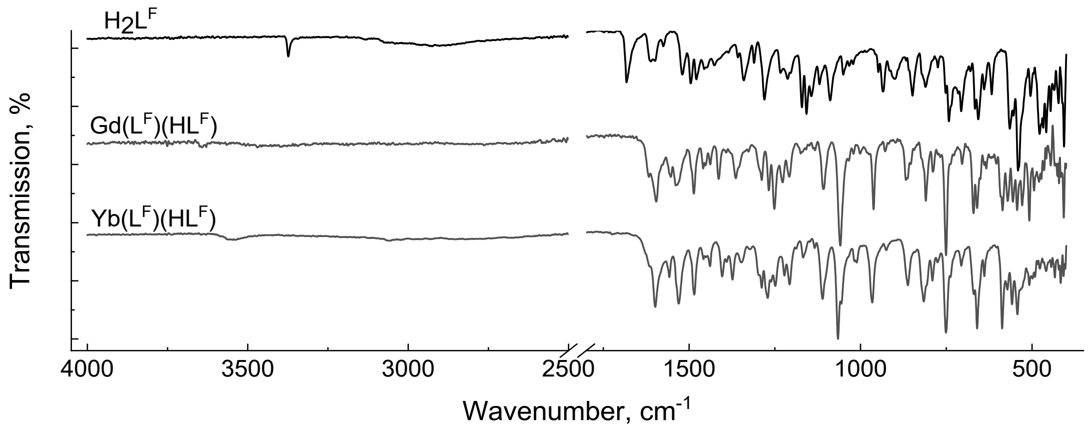



**Figure S2**. The single-crystal X-ray structure of $H_2L^F$, atoms are represented by thermal displacement ellipsoids (p=50%).

**Crystal Data** for $C_{21}H_{18}FN_3O_3S$ (M =411.44 g/mol): triclinic, space group P-1 (no. 2), a = 8.2778(15) Å, b = 10.4591(19) Å, c = 11.303(3) Å, α = 108.611(3)°, β = 93.498(5)°, γ = 94.266(4)°, V = 921.1(3) Å3, Z = 2, T = 120 K, μ(MoKα) = 0.216 mm-1, Dcalc = 1.483 g/cm$^3$, 12341 reflections measured (3.82° ≤ 2Θ ≤ 61.34°), 5653 unique (Rint = 0.0726, Rsigma = 0.0661) which were used in all calculations. The final R1 was 0.0500 (>2sigma(I)) and wR2 was 0.1433 (all data).

# IR specrtroscopy data

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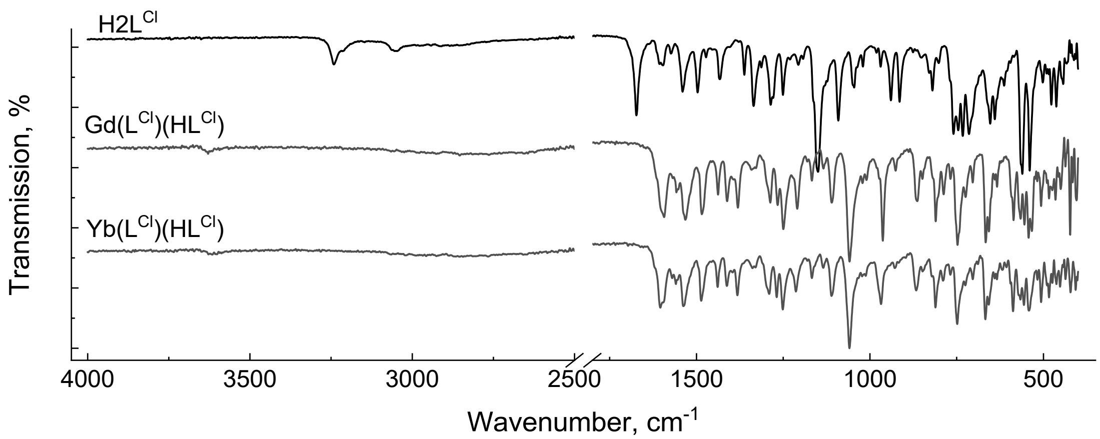


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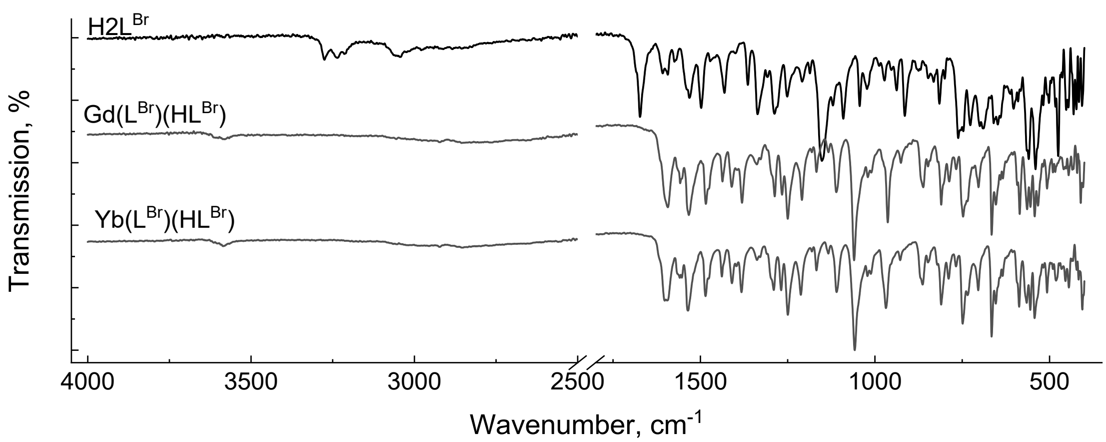


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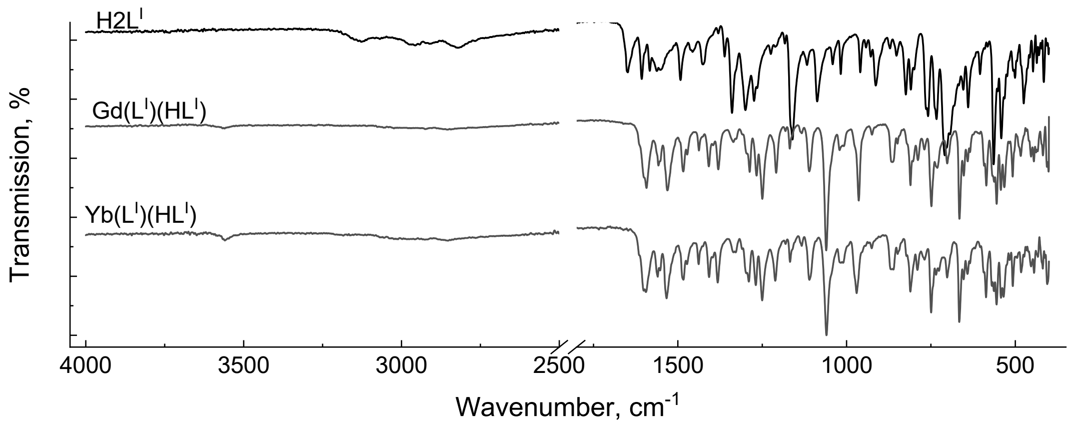
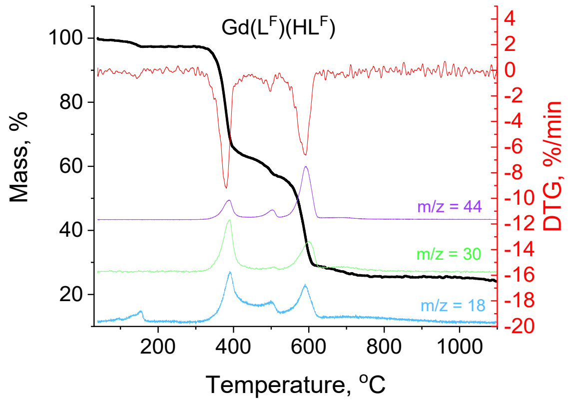



d)

**Figure S3.** IR spectra of a) $H_2L^F$ (1), $Gd(L^F)(HL^F)$ (2), $Yb(L^F)(HL^F)$ (3); b) $H_2L^{Cl}$ (1), $Gd(L^{Cl})(HL^{Cl})$ (2), $Yb(L^{Cl})(HL^{Cl})$ (3); c) $H_2L^{Br}$ (1), $Gd(L^{Br})(HL^{Br})$ (2), $Yb(L^{Br})(HL^{Br})$ (3) and d) $H_2L^I$ (1), $Gd(L^I)(HL^I)$ (2), $Yb(L^I)(HL^I)$ (3).

# TGA data

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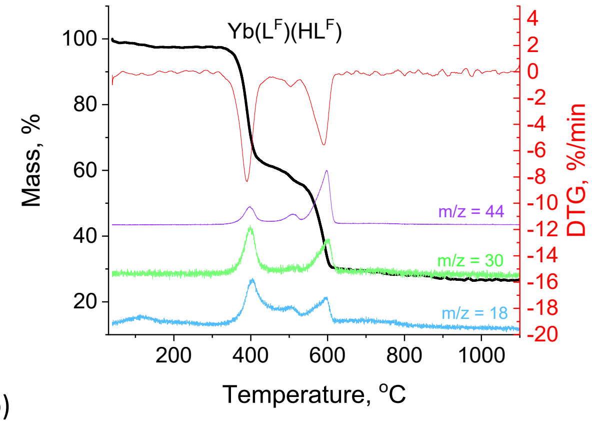


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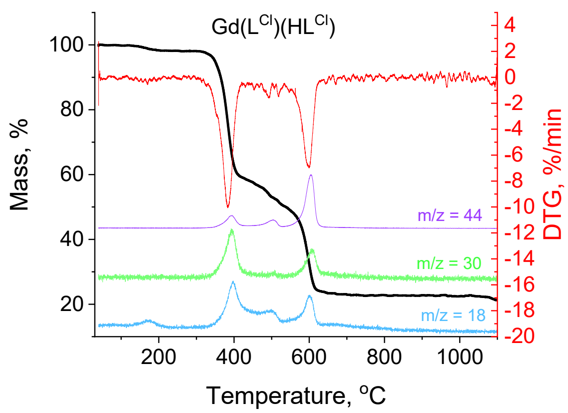
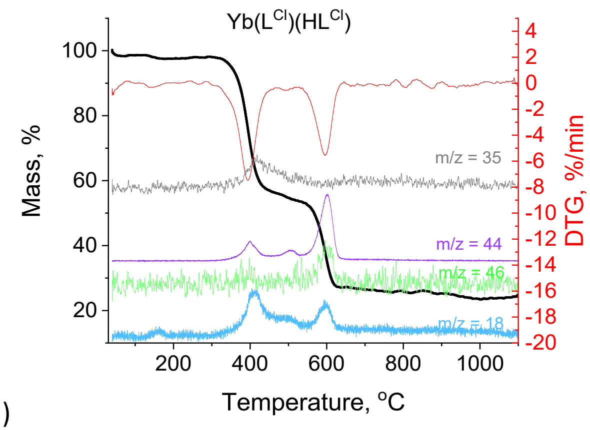



c)

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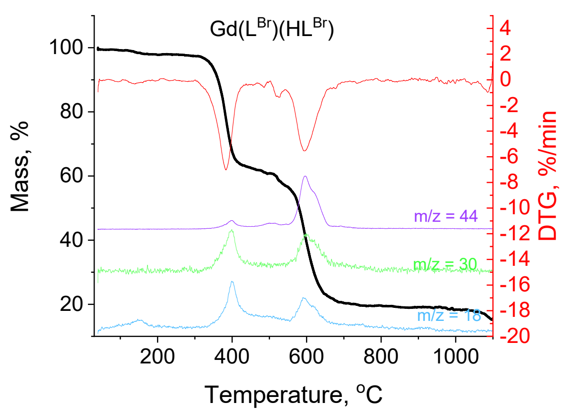


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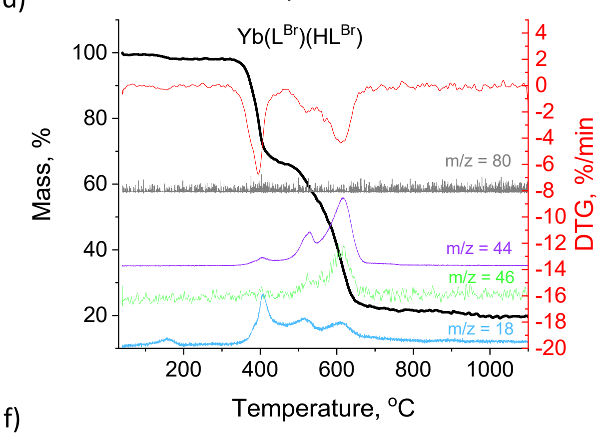


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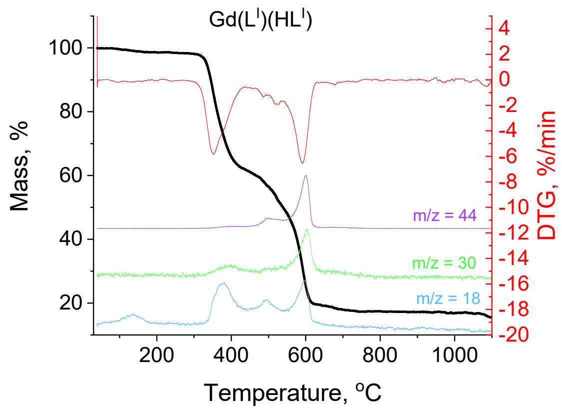
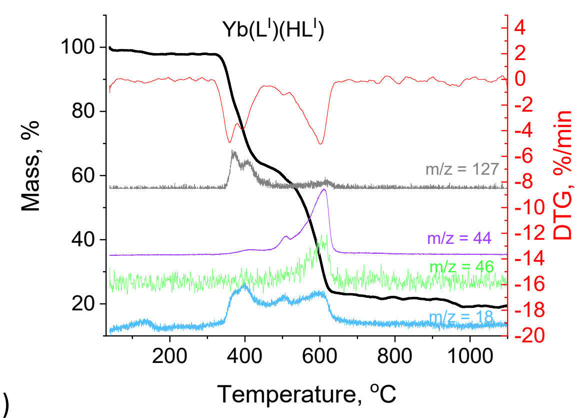



g)




h)

**Figure S4.** TGA and DTG data of a) Gd($L^F$)($HL^F$), b) Yb($L^F$)($HL^F$), c) Gd($L^{Cl}$)($HL^{Cl}$), d) Yb($L^{Cl}$)($HL^{Cl}$), e) Gd($L^{Br}$)($HL^{Br}$), f) Yb($L^{Br}$)($HL^{Br}$), g) Gd($L^I$)($HL^I$), h) Yb($L^I$)($HL^I$) Ionic currents are shown in blue (m/Z = 18), green (m/Z = 30) and violet (m/Z = 44).

# Photophysical properties

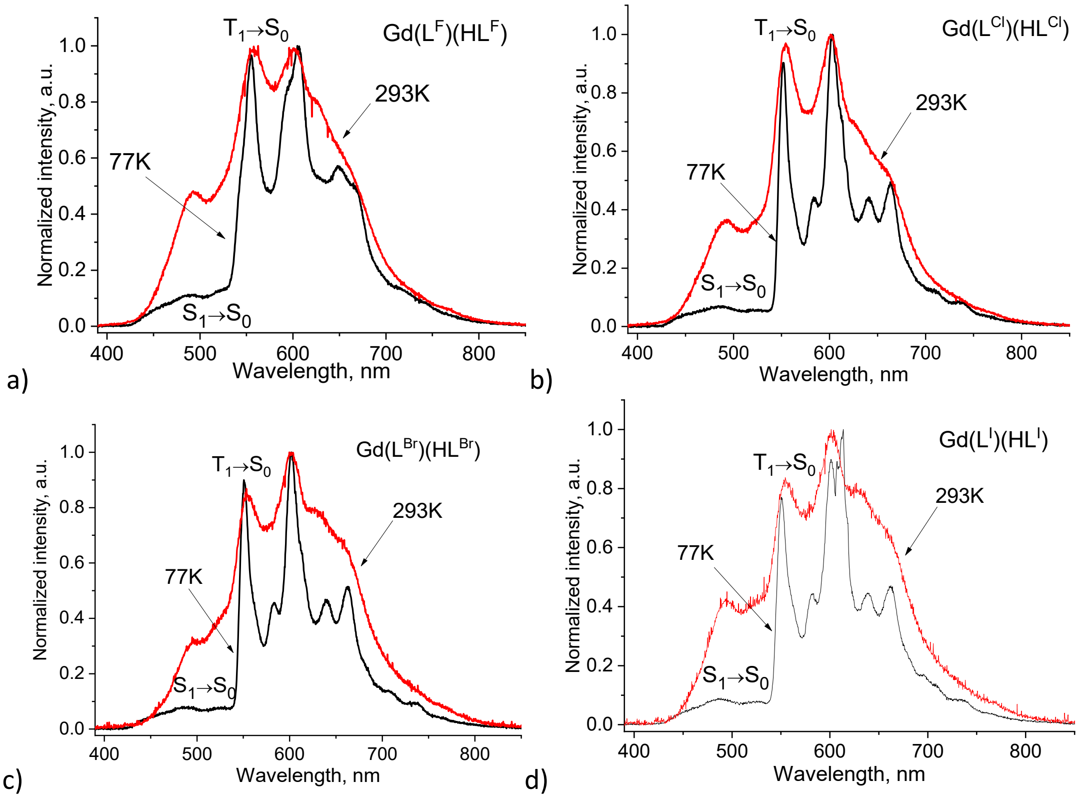



**Figure S5**. Luminescence spectra of gadolinium complex powders at 77 and 298 K ($\lambda_{ex}$ = 337 nm).

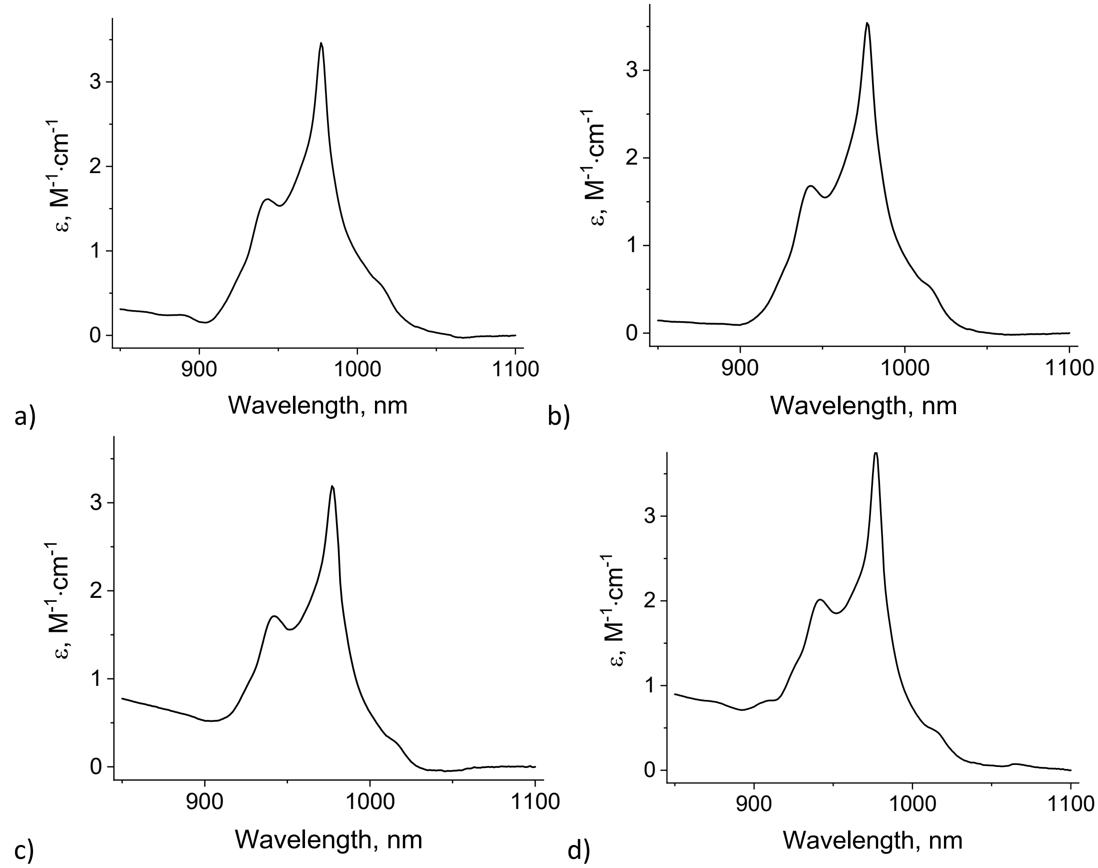



**Figure S6**. Light absorption coefficient versus wavelength of a) Yb($L^F$)($HL^F$), b) Yb($L^{Cl}$)($HL^{Cl}$), c) Yb($L^{Br}$)($HL^{Br}$) and d) Yb($L^I$)($HL^I$). Absorption spectra of the ligands and Yb(L)(HL) were obtained in DMSO solution (c = 2.5·$10^{-2}$ M, l = 10.0 mm) in the range 800 – 1100 nm.

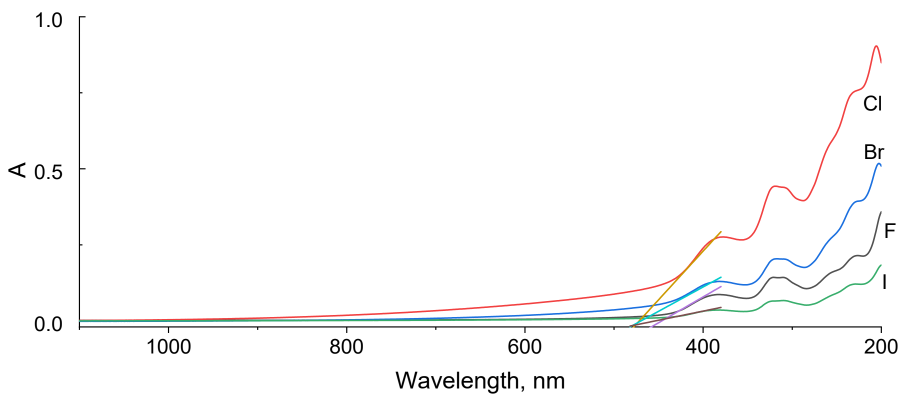



**Figure S7.** Absorption spectra of films of Yb($L^F$)($HL^F$), Yb($L^{Cl}$)($HL^{Cl}$), Yb($L^{Br}$)($HL^{Br}$) and Yb($L^I$)($HL^I$).

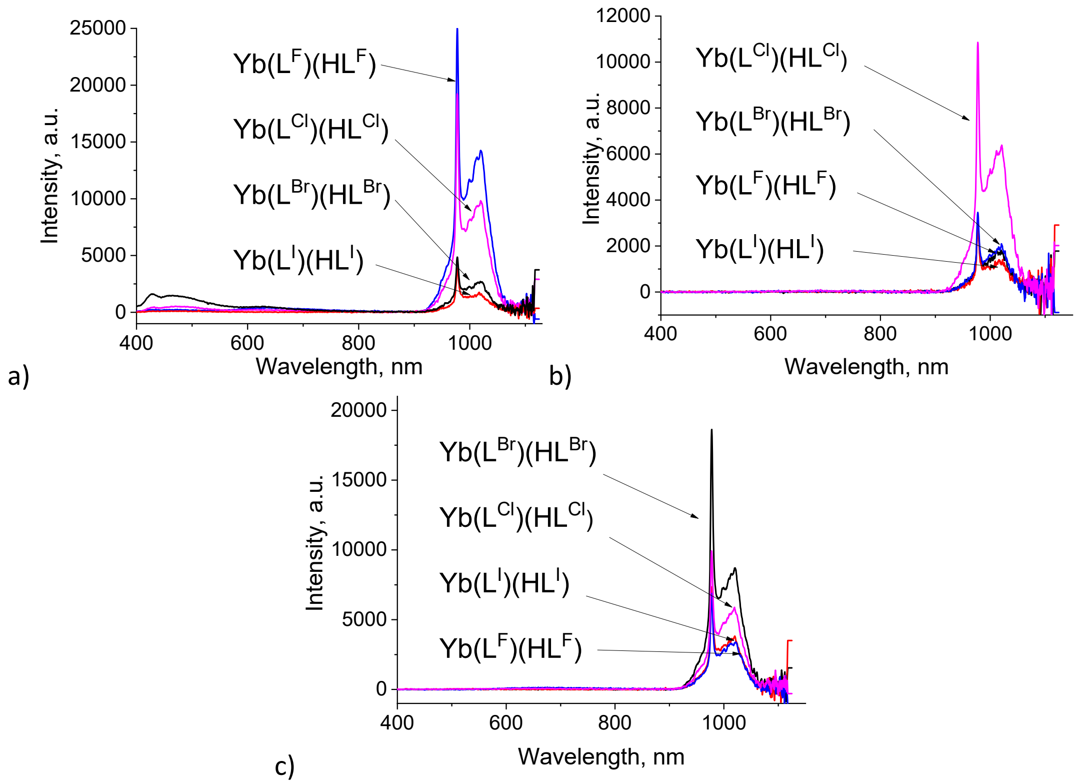
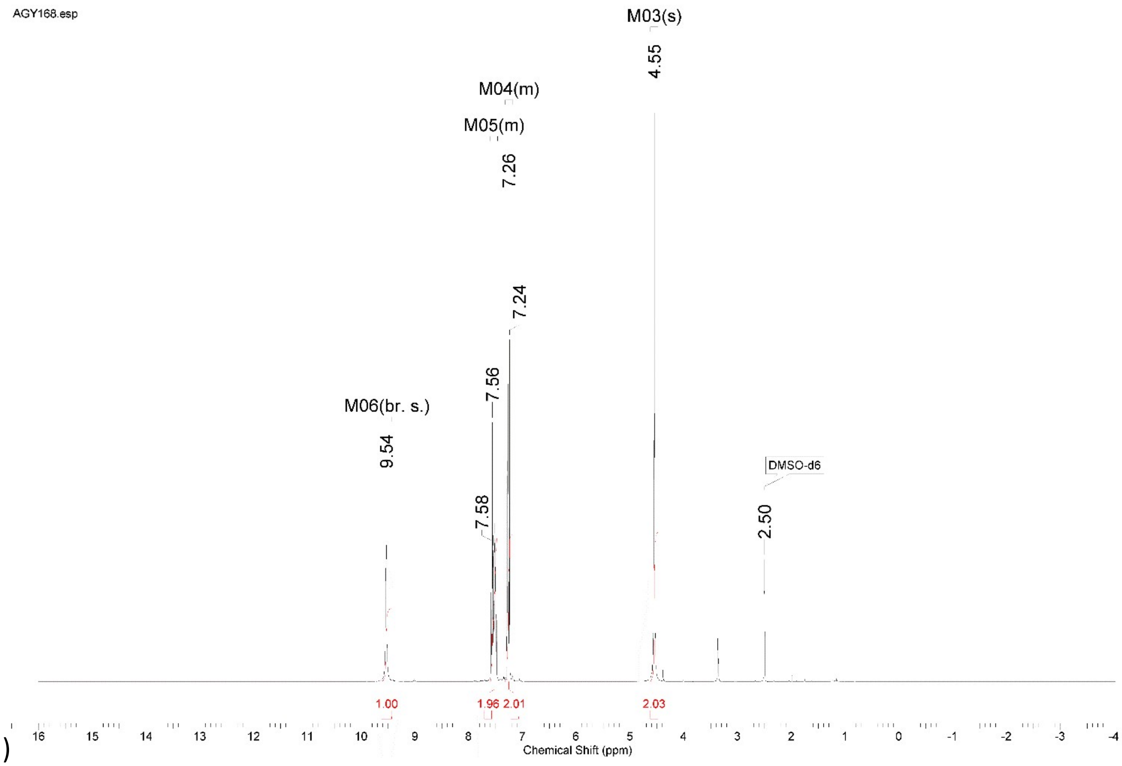



**Figure S8.** Electroluminescence spectra of OLEDs in different experiment: a) 1st; b) 2nd, and c) 3rd.

# NMR data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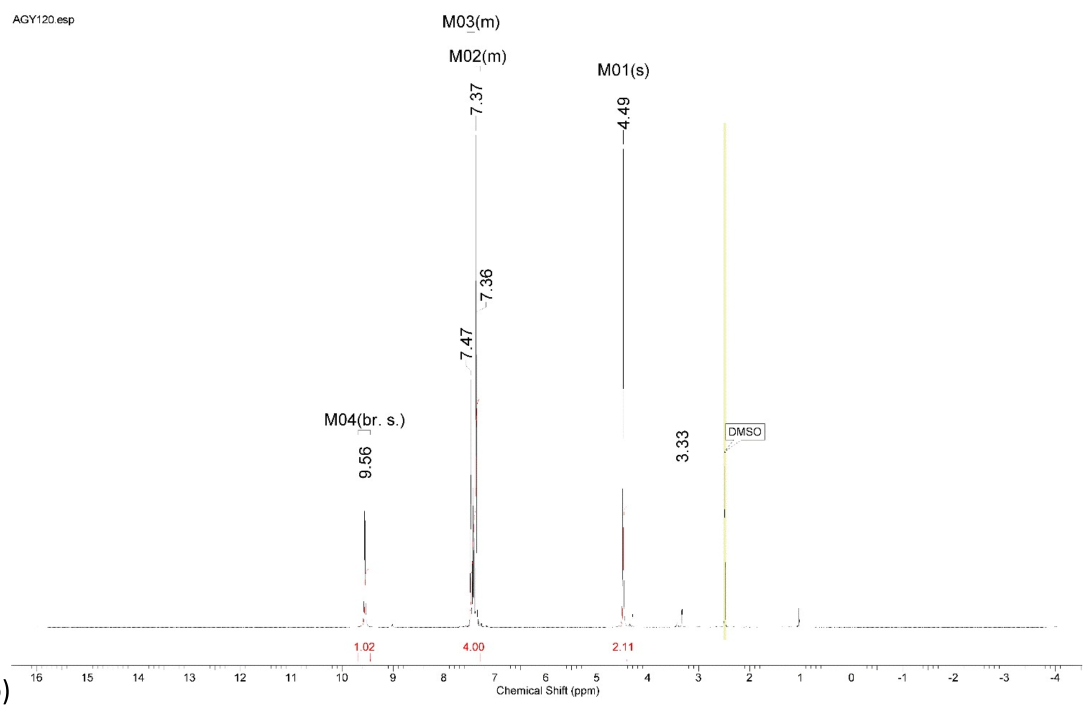
4.55
M04(m)
M05(m)
7.26
7.24
7.56
M06(br. s.)
9.54
7.58
DMSO-d6
2.50
1.00
1.96
2.01
2.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
Chemical Shift (ppm)

a)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M02(m)
M01(s)
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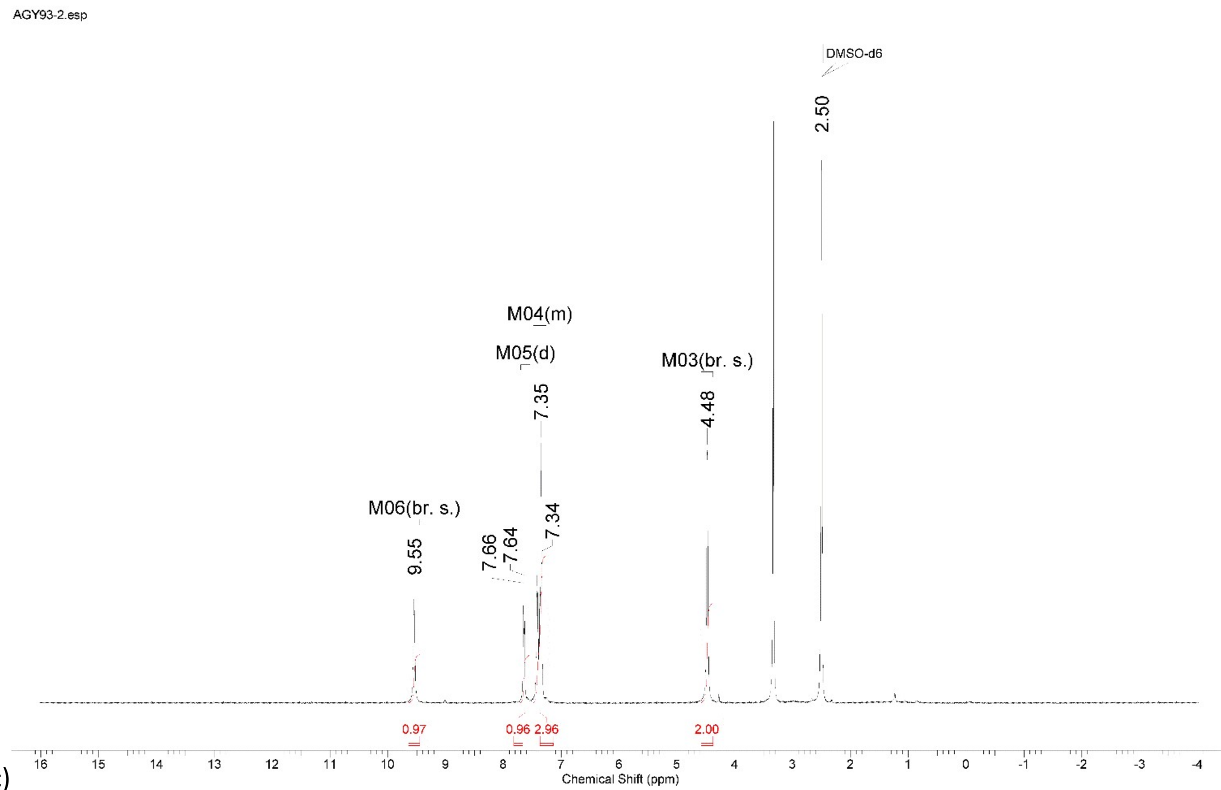
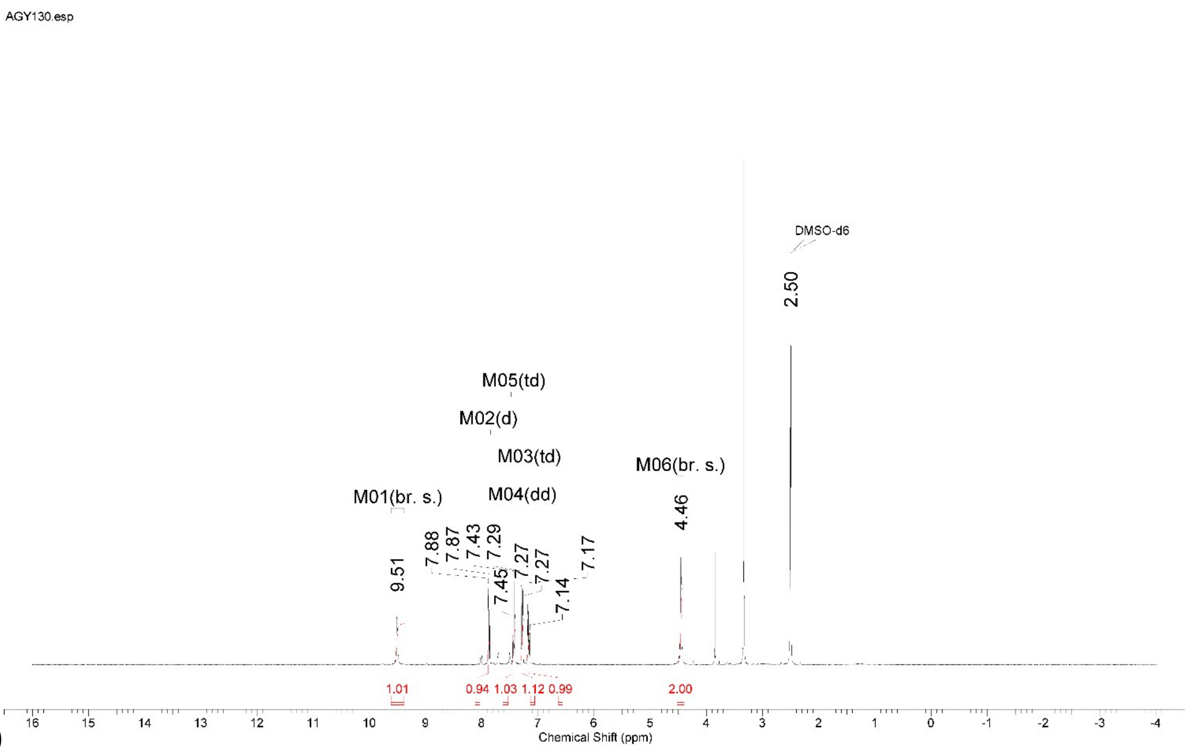
4.49
7.36
7.47
M04(br. s.)
9.56
3.33
DMSO
1.02
4.00
2.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
Chemical Shift (ppm)

b)




c)




d)

**Figure S9.** NMR spectra of a) 2-Fluorobenzohydrazide, b) 2-Chlorobenzohydrazide, c) 2-Bromobenzohydrazide, d) 2-Iodobenzohydrazide.

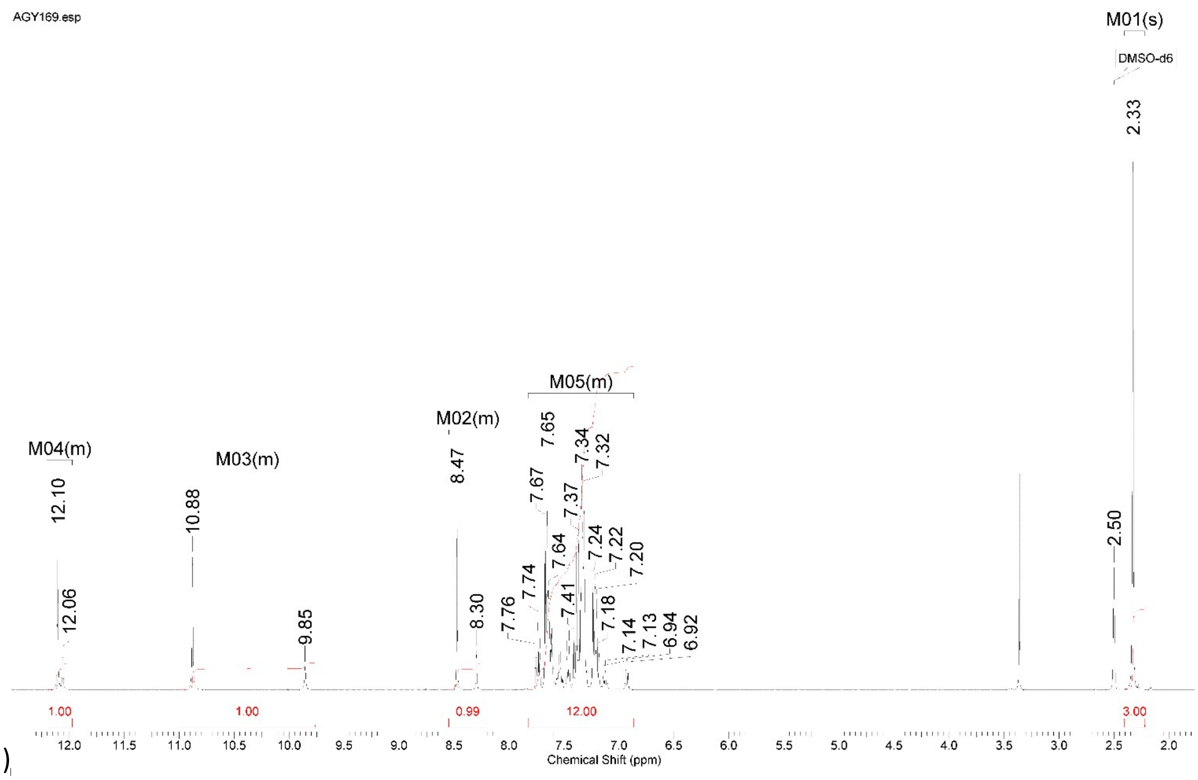
$^{1}H$, $^{13}C$ NMR spectra were recorded at 25 °C using Bruker Avance 400 spectrometer with the operating frequency of 400 and 101 MHz, respectively. Chemical shifts are reported in ppm relative to residual solvent signals.

a) 2-Fluorobenzohydrazide. Yield 79%. White powder. $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm 4.54 (s, 2 H) 7.17 - 7.31 (m, 2 H) 7.45 - 7.59 (m, 2 H) 9.53 (br. s., 1 H).

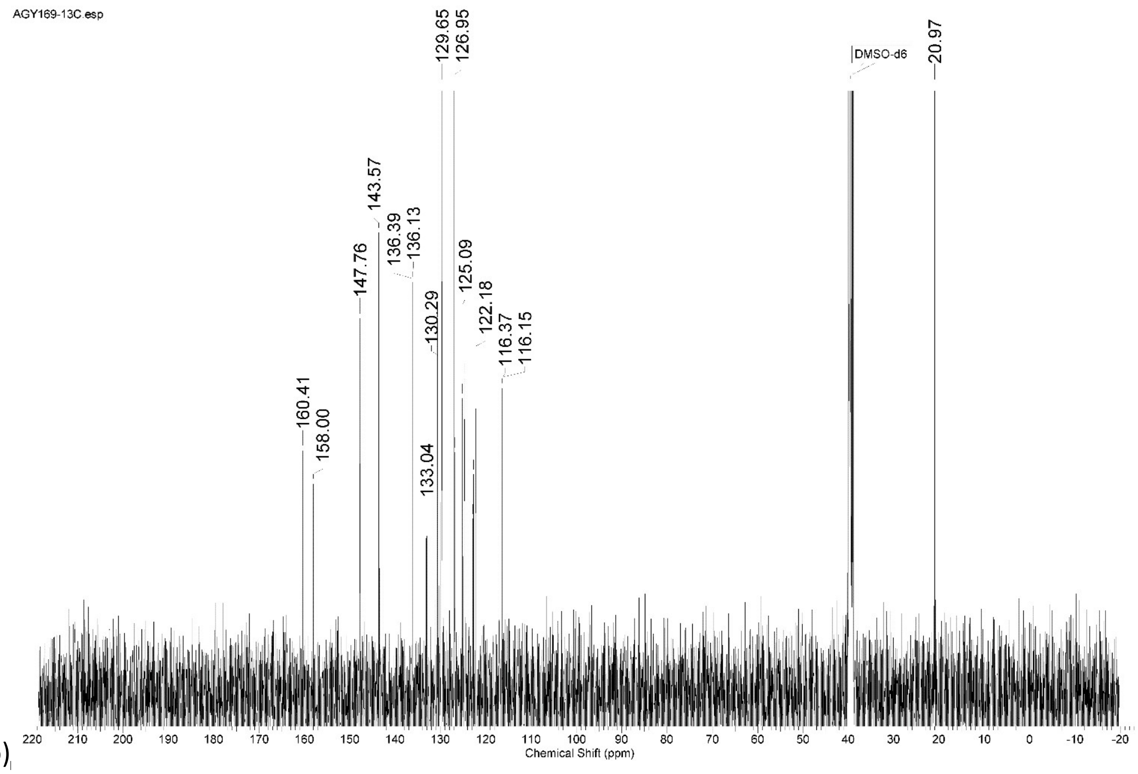
b) 2-Chlorobenzohydrazide. Yield 43%. White powder. $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm 4.49 (s, 2 H) 7.29 - 7.40 (m, 2 H) 7.40 - 7.55 (m, 2 H) 9.56 (br. s., 1 H).

c) 2-Bromobenzohydrazide. Yield 53%. White powder. $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm 4.48 (br. s., 2 H) 7.26 - 7.48 (m, 3 H) 7.65 (d, *J*=7.58 Hz, 1 H) 9.55 (br. s., 1 H).

d) 2-Iodobenzohydrazide. Yield 62%. White powder. $^{1}H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ ppm 4.46 (br. s., 2 H) 7.16 (td, *J*=7.64, 1.59 Hz, 1 H) 7.28 (dd, *J*=7.52, 1.53 Hz, 1 H) 7.43 (td, *J*=7.46, 0.98 Hz, 1 H) 7.88 (d, *J*=7.82 Hz, 1 H) 9.51 (br. s., 1)




a)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136.13
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125.09
130.29
122.18
116.37
116.15
160.41
158.00
133.04
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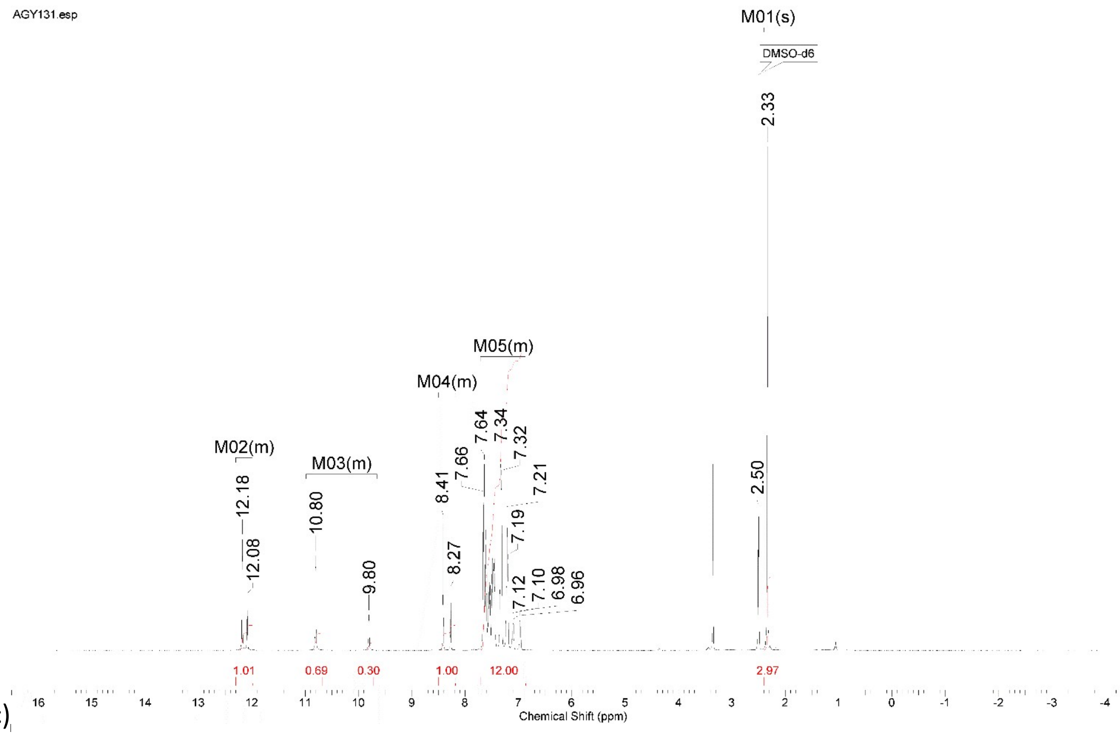
Chemical Shift (ppm)

b)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DMSO-d6
2.33
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M04(m)
M02(m)
M03(m)
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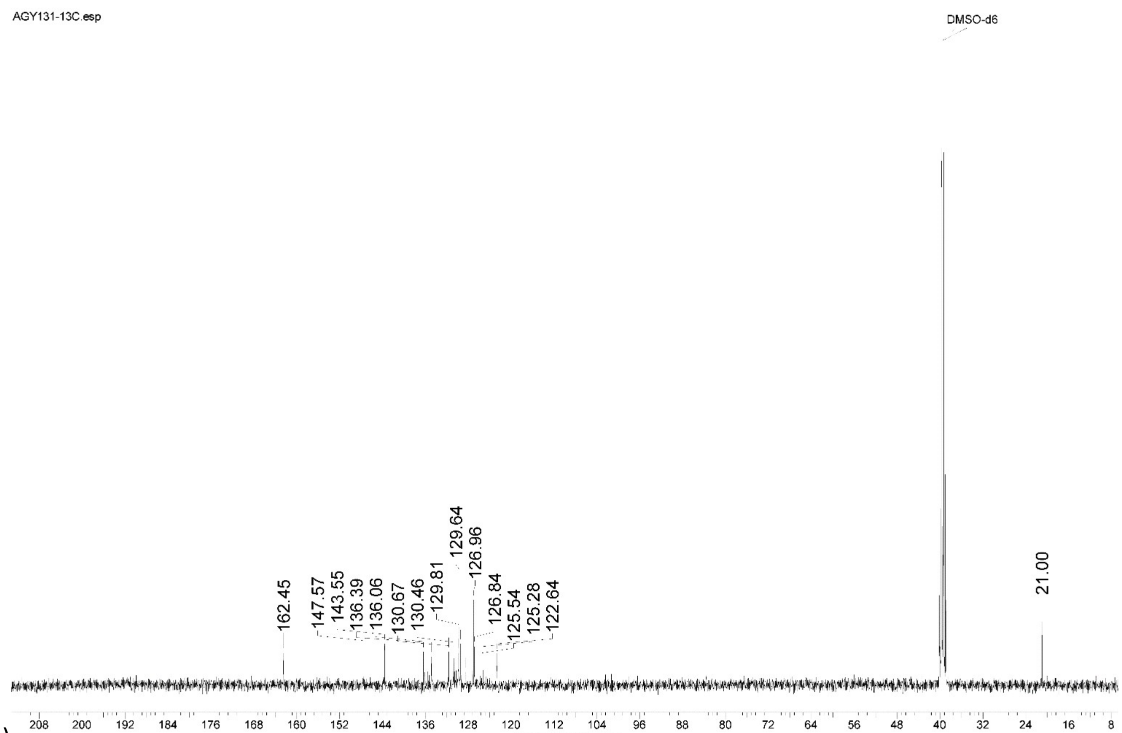
12.08
10.80
9.80
8.41
8.27
7.66
7.64
7.34
7.32
7.21
7.19
7.12
7.10
6.98
6.96
2.50
1.01
0.69
0.30
1.00
12.00
2.97
Chemical Shift (ppm)

c)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130.46
129.81
129.64
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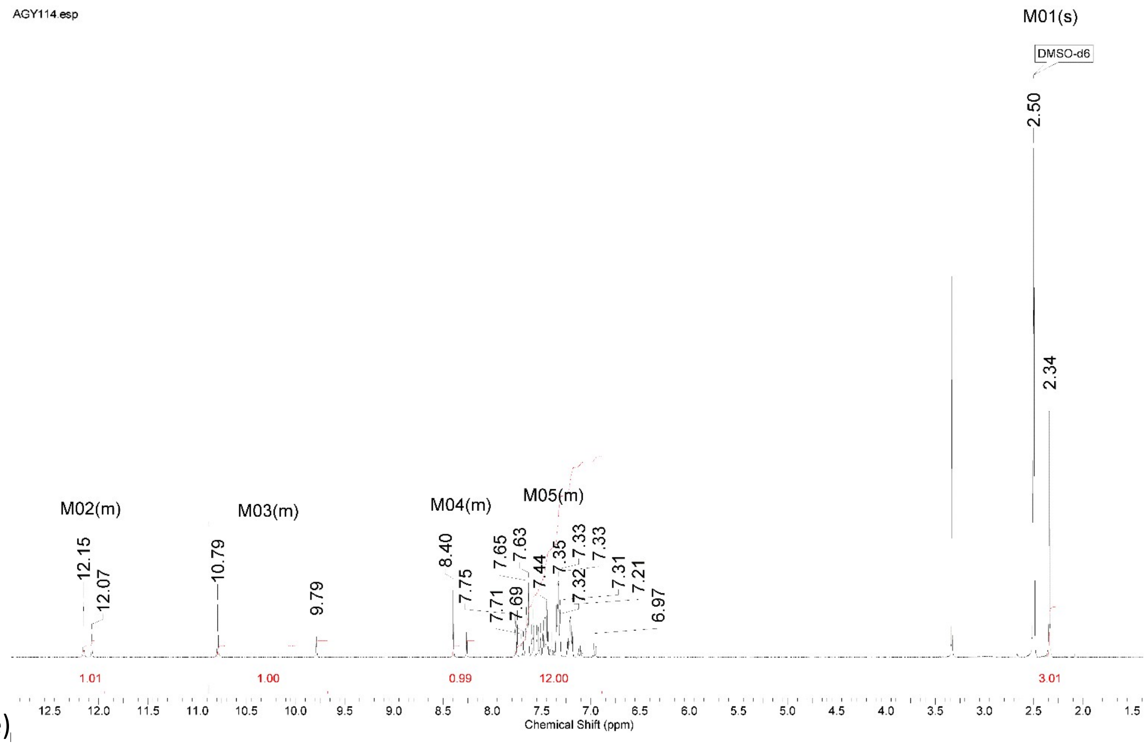
126.84
125.54
125.28
122.64
21.00
Chemical Shift (ppm)

d)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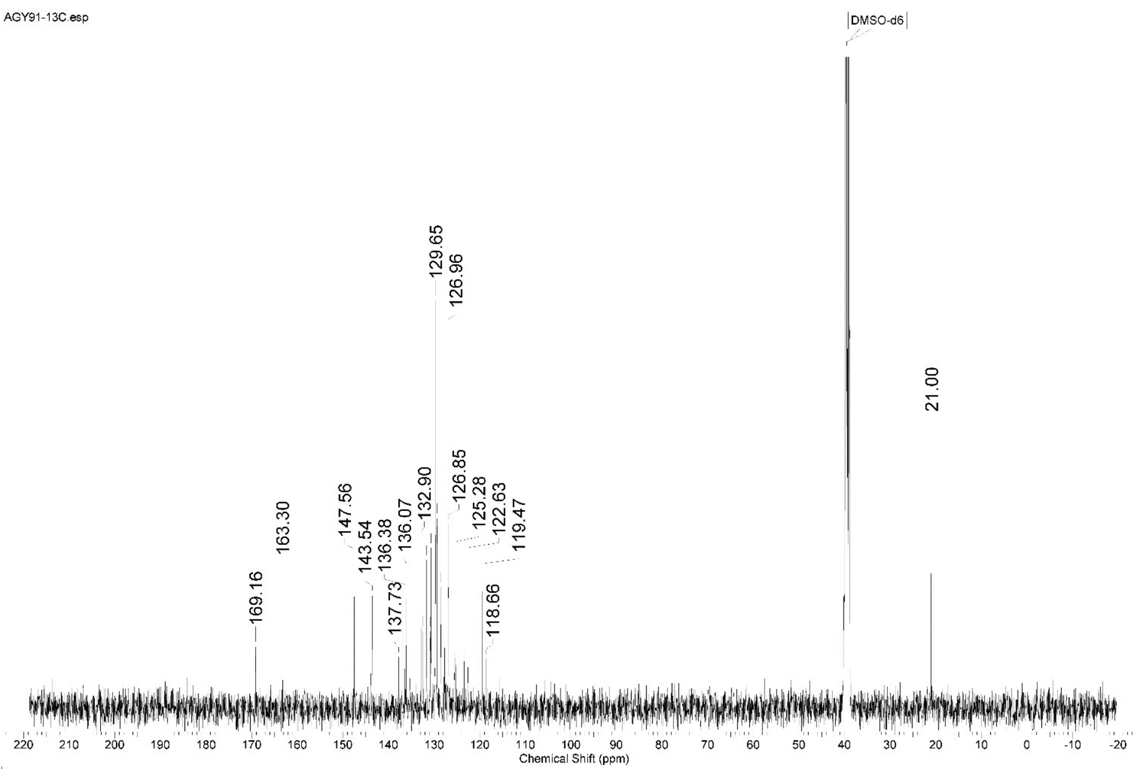
DMSO-d6
2.50
2.34
M02(m)
12.15
12.07
M03(m)
10.79
9.79
M04(m)
8.40
7.75
M05(m)
7.71
7.69
7.65
7.63
7.44
7.35
7.33
7.33
7.32
7.31
7.21
6.97
1.01
1.00
0.99
12.00
3.01
Chemical Shift (ppm)

e)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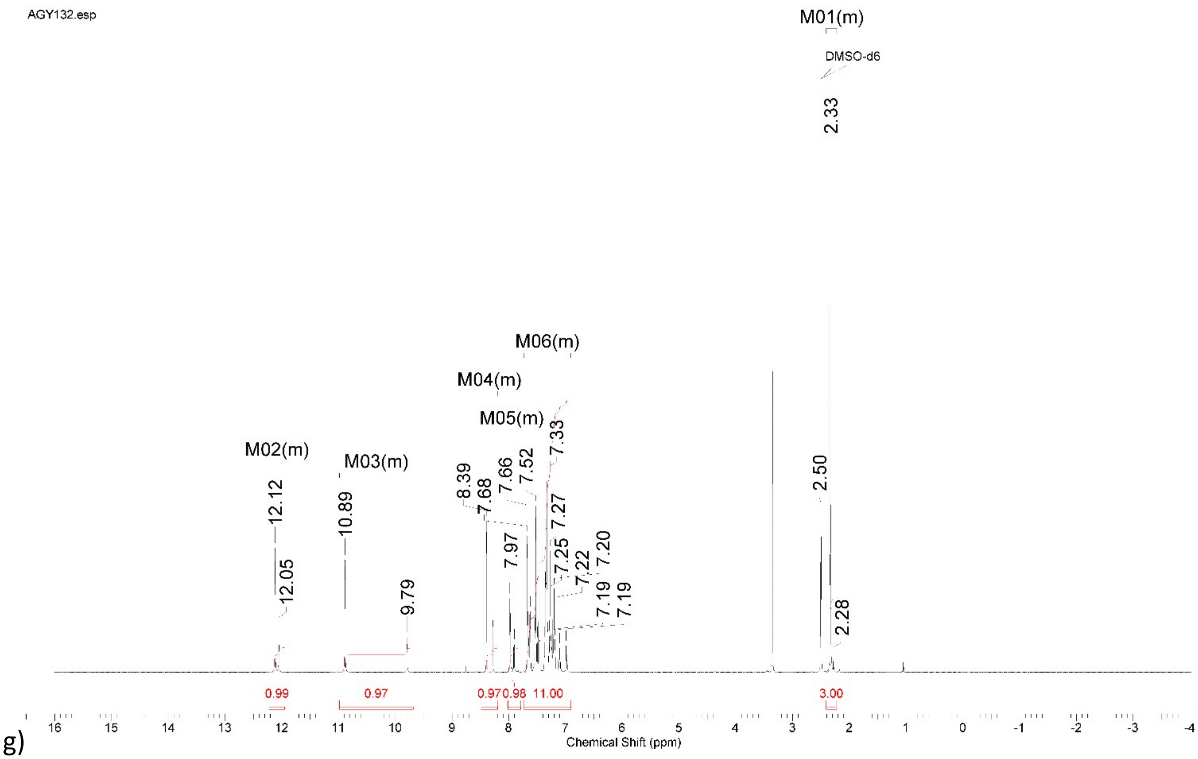
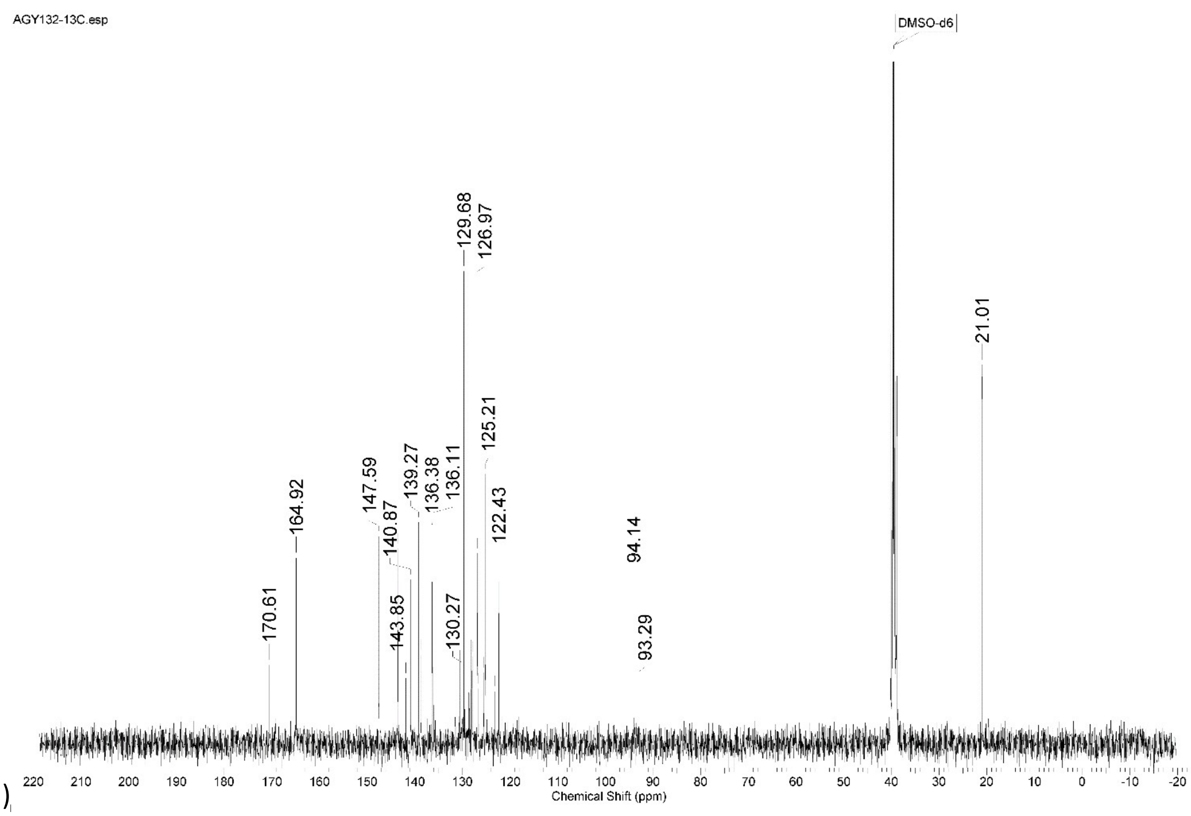
126.96
21.00
169.16
163.30
147.56
143.54
136.38
137.73
136.07
132.90
126.85
125.28
122.63
119.47
118.66
Chemical Shift (ppm)

f)




g)




h)

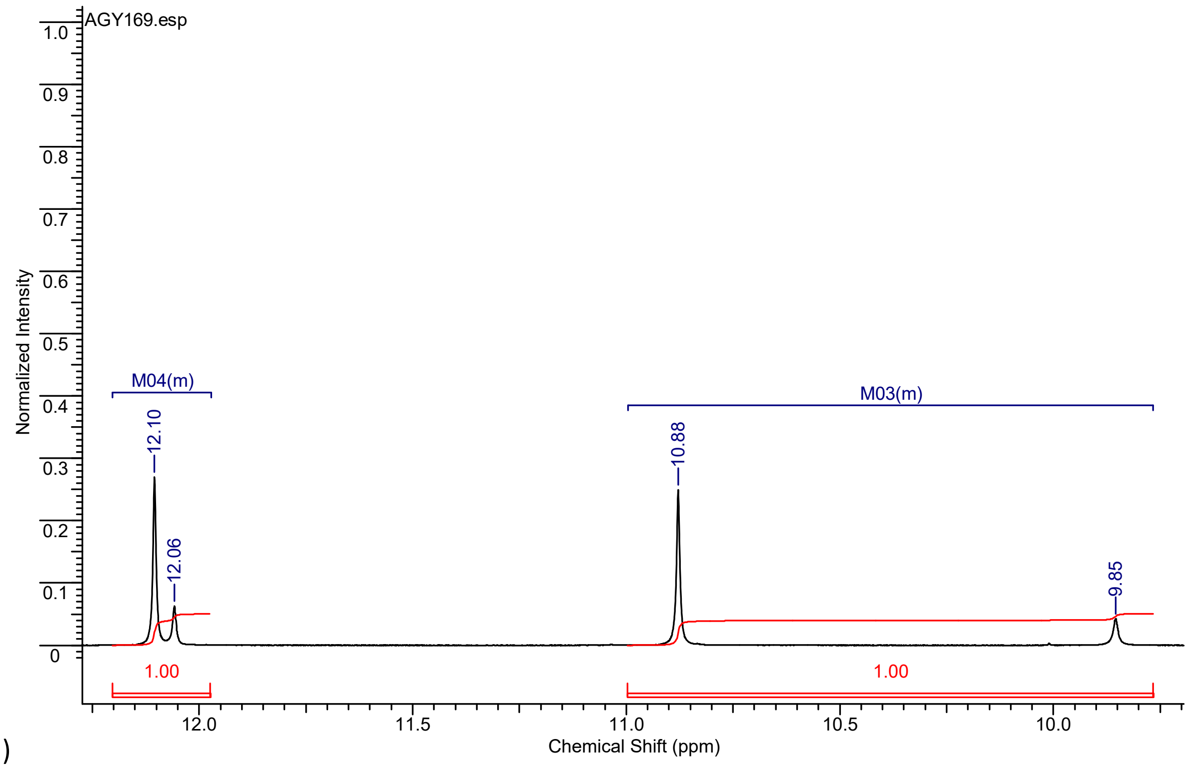
**Figure S10.** NMR spectra of a) $H_2L^F$, b) $H_2L^F$ (13C), c) $H_2L^{Cl}$, d) $H_2L^{Cl}$ (13C), e) $H_2L^{Br}$, f) $H_2L^{Br}$ (13C), g) $H_2L^I$, h) $H_2L^I$ (13C).

a-b) $H_2L^F$: Yield 94%. Colorless crystals. X-Ray quality crystal was obtained by slow evaporation of ethanolic solution. $^1H$ NMR (400 MHz, DMSO-$d_6$) δ ppm 2.33 (s, 3 H) 6.87 - 7.83 (m, 12 H) 8.21 - 8.55 (m, 1 H) 9.77 - 11.00 (m, 1 H) 11.97 - 12.20 (m, 1 H). $^{13}C$ NMR (101 MHz, DMSO-$d_6$) δ ppm 20.97, 116.15, 116.37, 122.18, 122.71, 122.86, 124.70, 125.09, 125.22, 125.96, 126.83, 126.95, 129.65, 130.08, 130.29, 130.65, 133.04, 133.12, 136.13, 136.39, 143.57, 147.76, 158.00, 160.41, 160.48.

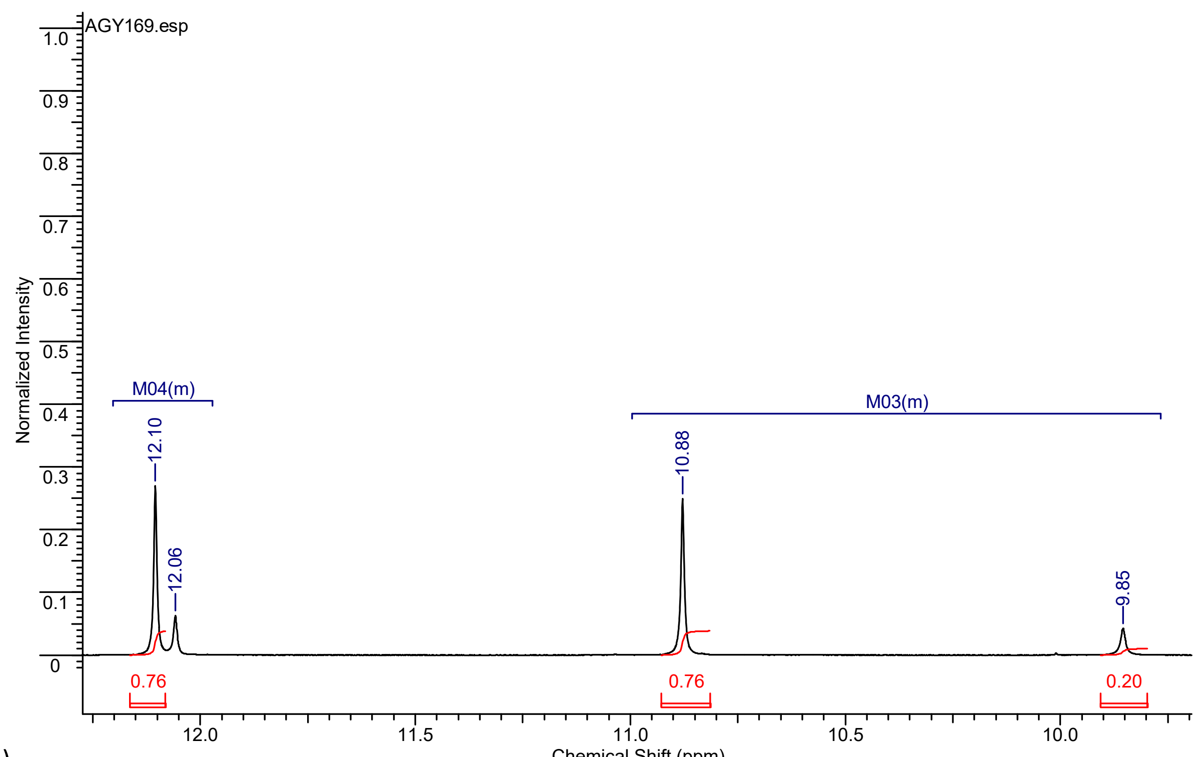
c-d) $H_2L^{Cl}$: Yield 74%. Colorless crystals. $^1H$ NMR (400 MHz, DMSO-$d_6$) δ ppm 2.33 (s, 3 H) 6.87 - 7.71 (m, 12 H) 8.18 - 8.50 (m, 1 H) 9.65 - 10.98 (m, 1 H) 11.99 - 12.30 (m, 1 H). $^{13}C$ NMR (101 MHz, DMSO-$d_6$) δ ppm 21.00, 122.64, 123.66, 125.28, 125.54, 125.70, 126.84, 126.96, 127.20, 127.33, 128.42, 128.53, 129.34, 129.41, 129.64, 129.81, 129.89, 130.29, 130.46, 130.67, 131.59, 134.87, 135.31, 135.57, 136.06, 136.16, 136.39, 143.55, 147.57, 162.45.

e-f) $H_2L^{Br}$: Yield 90%. Colorless crystals. $^1H$ NMR (400 MHz, DMSO-$d_6$) δ ppm 2.34 (s, 3 H) 6.89 - 7.87 (m, 12 H) 8.19 - 8.46 (m, 1 H) 9.67 - 10.88 (m, 1 H) 11.94 - 12.23 (m, 1 H). $^{13}C$ NMR (101 MHz, DMSO-$d_6$) δ ppm 21.00, 118.66, 119.47, 122.63, 123.46, 125.28, 125.52, 125.64, 126.85, 126.96, 127.65, 127.78, 128.53, 129.37, 129.65, 129.91, 130.29, 130.67, 130.85, 131.68, 132.43, 132.90, 135.32, 136.07, 136.16, 136.38, 137.01, 137.73, 143.54, 143.92, 147.56, 163.30, 169.16.

g-h) $H_2L^I$: Yield 76%. Colorless crystals. $^1H$ NMR (400 MHz, DMSO-$d_6$) δ ppm 2.23 - 2.41 (m, 3 H) 6.91 - 7.73 (m, 11 H) 7.83 - 8.06 (m, 1 H) 8.20 - 8.49 (m, 1 H) 9.68 - 10.98 (m, 1 H) 11.95 - 12.22 (m, 1 H). $^{13}C$ NMR (101 MHz, DMSO-$d_6$) δ ppm 21.01, 93.29, 94.14, 122.43, 123.27, 125.21, 125.57, 126.77, 126.90, 126.97, 127.95, 128.04, 128.16, 128.64, 128.71, 129.63, 129.68, 130.12, 130.27, 130.65, 131.52, 135.33, 136.11, 136.17, 136.38, 138.69, 139.27, 140.87, 141.85, 143.50, 143.54, 143.85, 147.59, 164.92, 170.61.

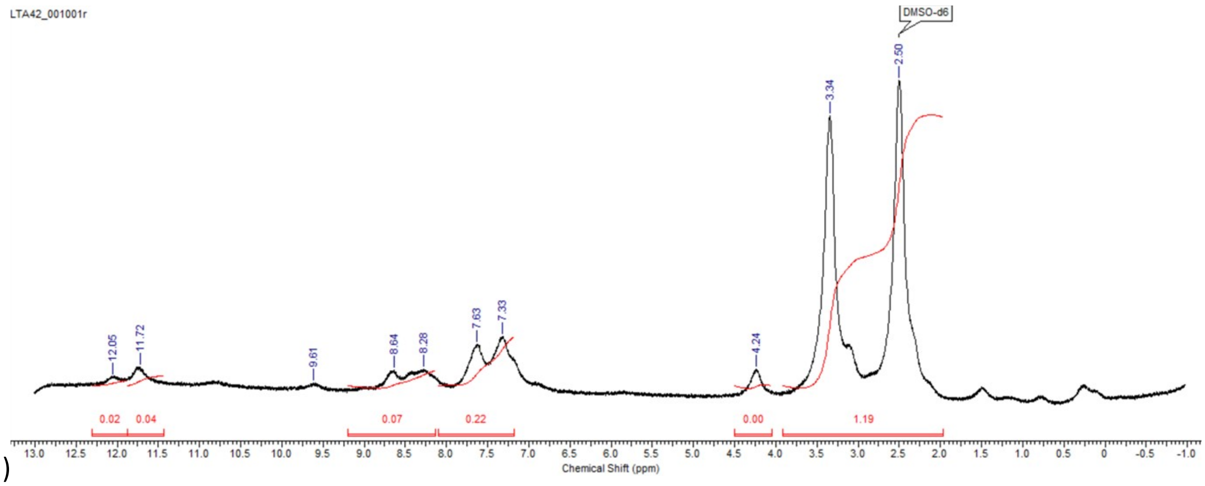



a)

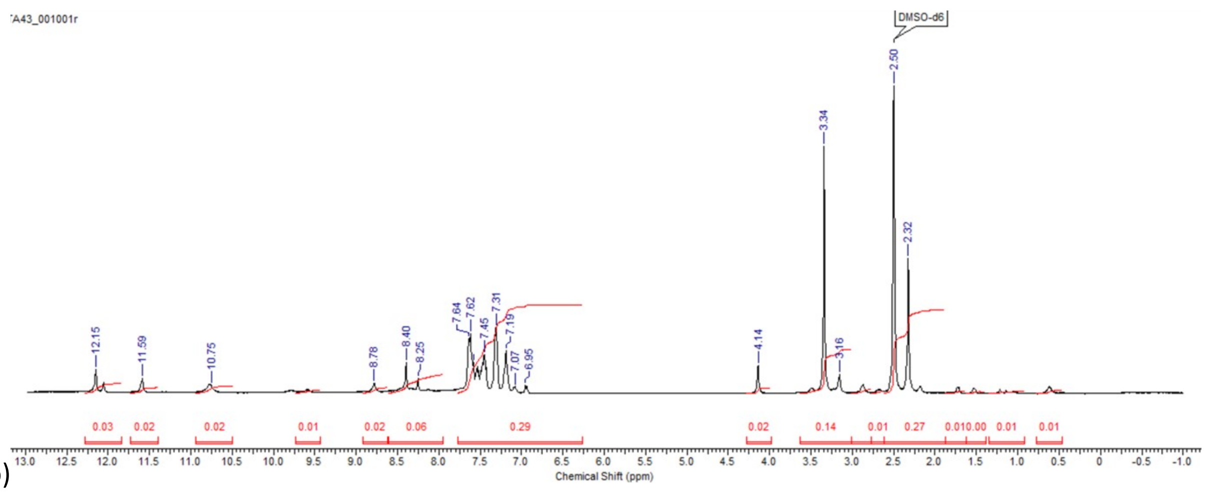



b)

**Figure S11.** Zoomed part of the $^{1}H$ NMR spectrum of $H_2L^F$.


LTA42_001001r
DMSO-d6
2.50
3.34
12.05
11.72
9.61
8.64
8.28
7.63
7.33
4.24
0.02
0.04
0.07
0.22
0.00
1.19
Chemical Shift (ppm)

a)


'A43_001001r
DMSO-d6
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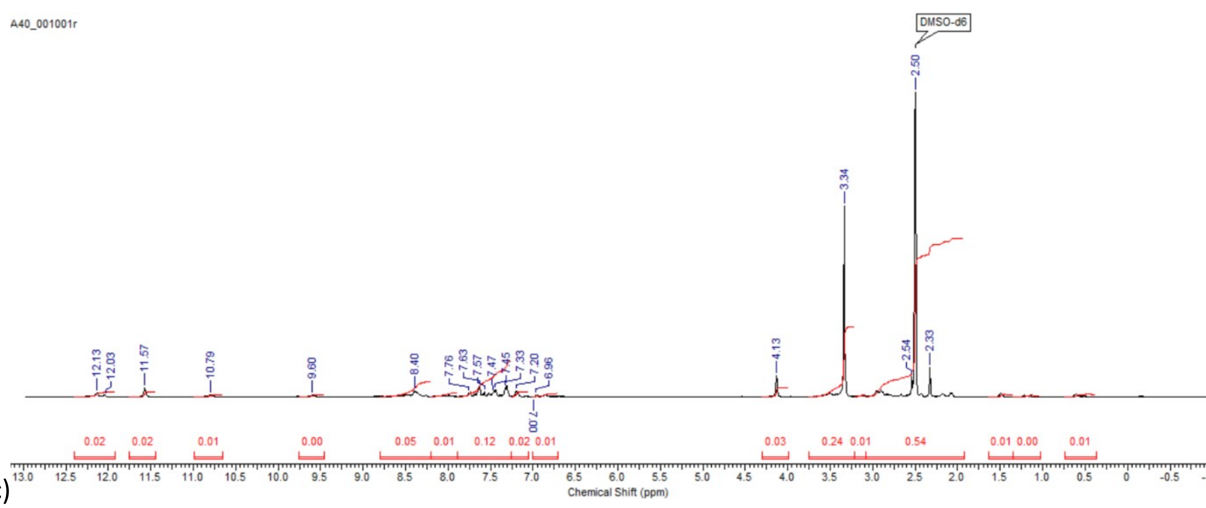
3.34
2.32
12.15
11.59
10.75
8.78
8.40
8.25
7.64
7.62
7.45
7.31
7.19
7.07
6.95
4.14
3.16
0.03
0.02
0.02
0.01
0.02
0.06
0.29
0.02
0.14
0.01
0.27
0.010.00
0.01
0.01
Chemical Shift (ppm)

b)


A40_001001r
DMSO-d6
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3.34
12.13
12.03
11.57
10.79
9.60
8.40
7.76
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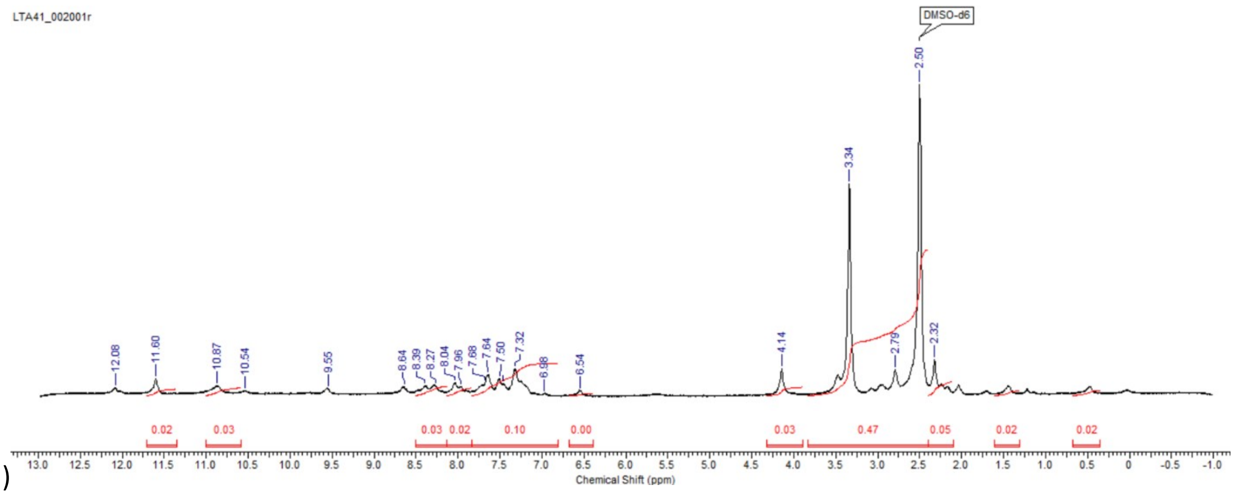
7.57
7.47
7.45
7.33
7.20
6.96
7.00
4.13
2.54
2.33
0.02
0.02
0.01
0.00
0.05
0.01
0.12
0.02
0.01
0.03
0.24
0.01
0.54
0.01
0.00
0.01
Chemical Shift (ppm)

c)




d)

**Figure S12.** $^1$H NMR spectra of a) Yb($L^F$)($HL^F$), b) Yb($L^{Cl}$)($HL^{Cl}$), c) Yb($L^{Br}$)($HL^{Br}$), d) Yb($HL^I$)($HL^I$).

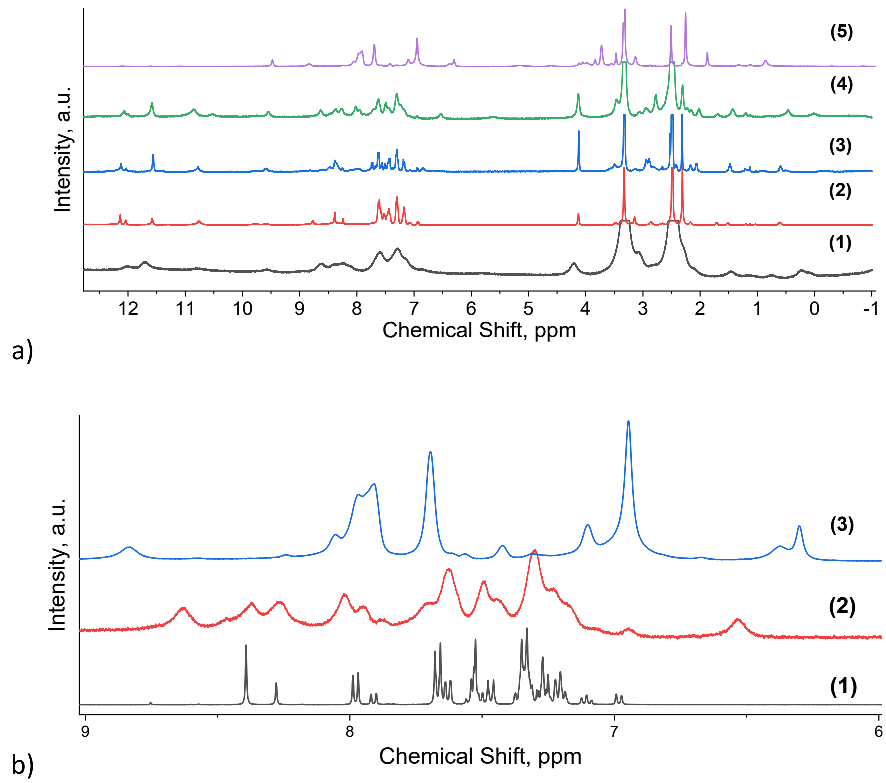
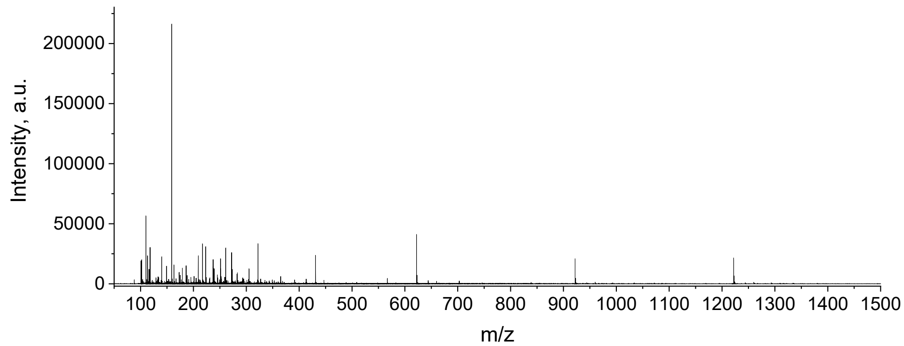
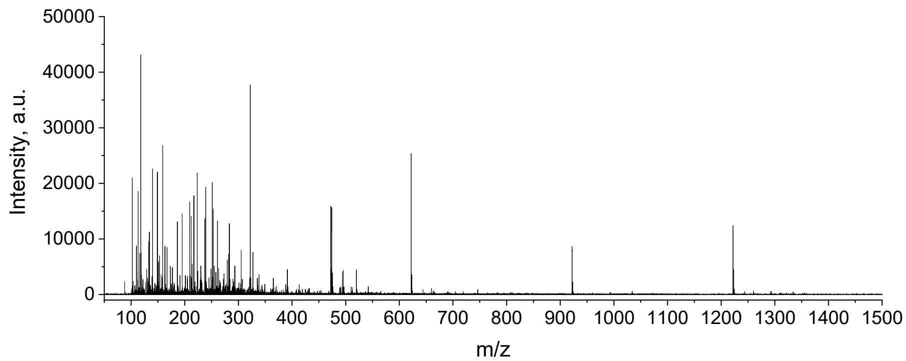



**Figure S13.** a) $^1$H NMR spectra of spectra of a) Yb(L$^F$)(HL$^F$) (1), Yb(L$^{Cl}$)(HL$^{Cl}$) (2), Yb(L$^{Br}$)(HL$^{Br}$) (3), Yb(L$^I$)(HL$^I$) (4) and the reference complex K[Yb(L)$_2$] from [17] (5) and b) zoomed part of the $^1$H NMR spectra of HL$^I$ (1), Yb(L$^I$)(HL$^I$) (2), KYb(L$^H$)$_2$ (3).

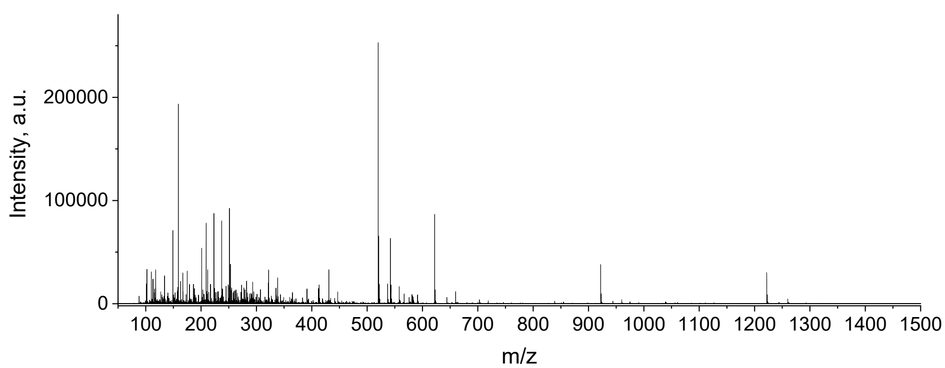
# Mass-spectroscopy data



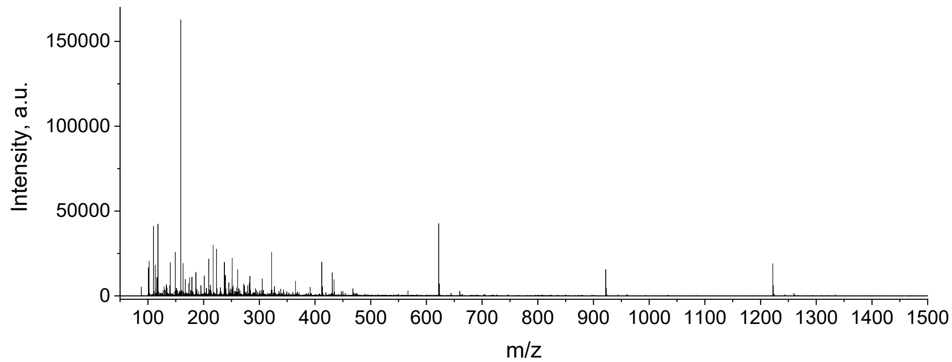

a)




b)

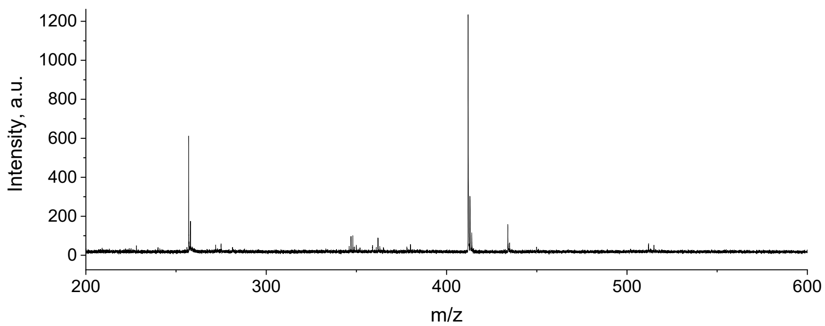



c)

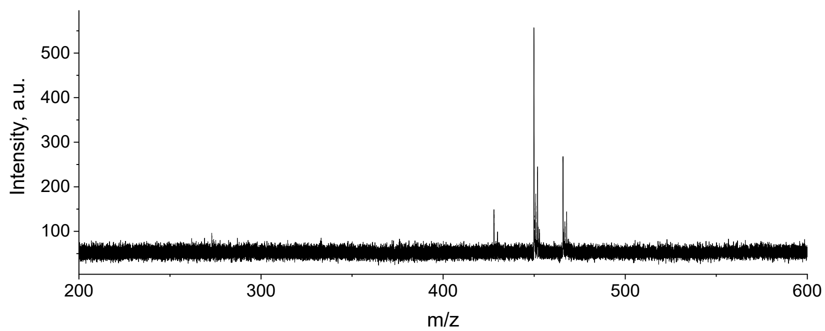



d)

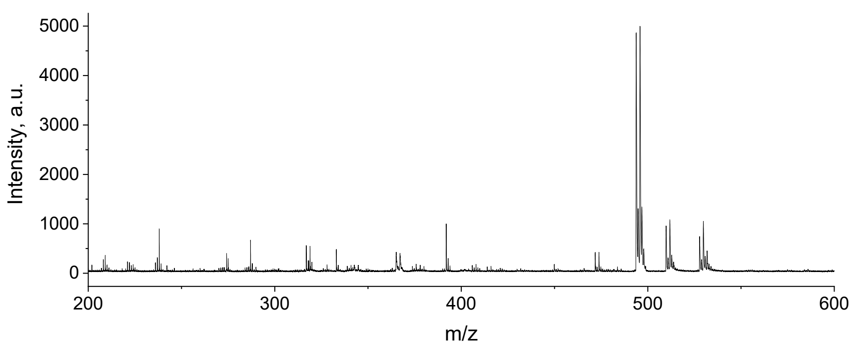
**Figure S14.** ES MS spectra of a) Yb($L^F$)($HL^F$), b) Yb($L^{Cl}$)($HL^{Cl}$), c) Yb($L^{Br}$)($HL^{Br}$), d) Yb($HL^I$)($HL^I$).



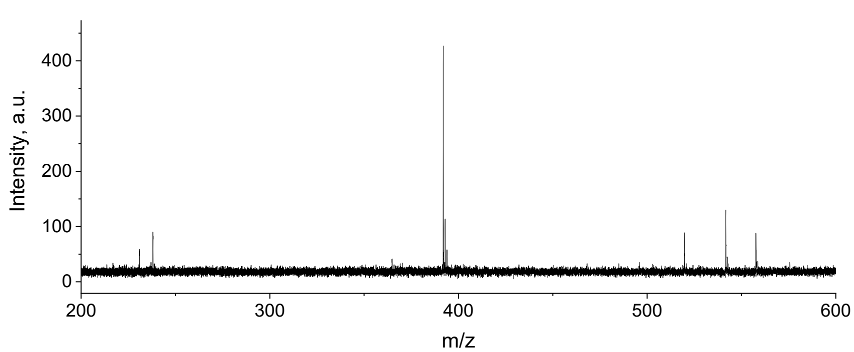
a)



b)



c)



d)

**Figure 15.** MALDI spectra of a) $H_2L^F$, b) $H_2L^{Cl}$, c) $H_2L^{Br}$, d) $H_2L^I$.

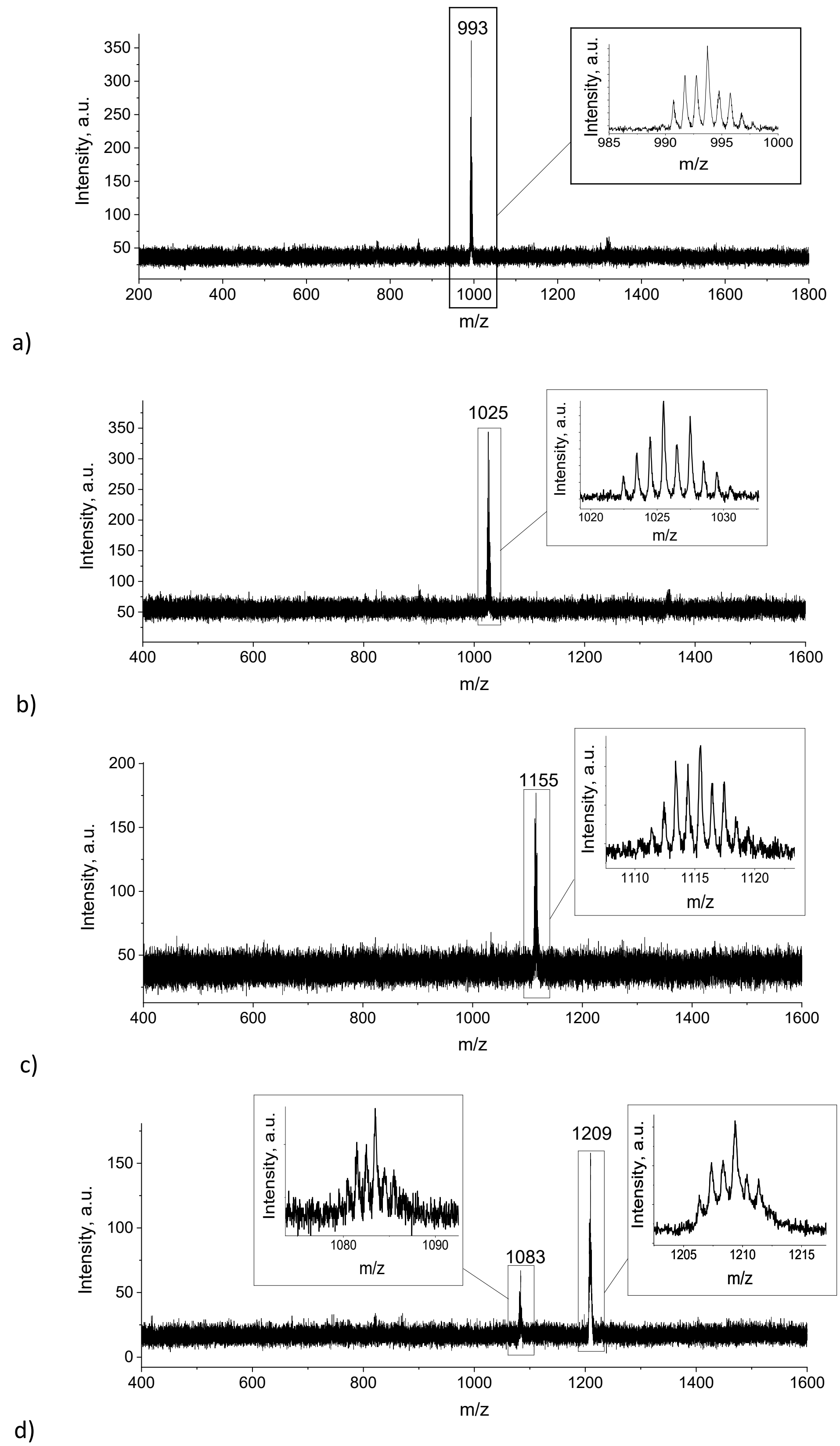



**Figure 16.** MALDI spectra of a) Yb($L^F$)($HL^F$), b) Yb($L^{Cl}$)($HL^{Cl}$), c) Yb($L^{Br}$)($HL^{Br}$), d) Yb($L^I$)($HL^I$).