Supporting Information for

Macrocyclic Chelates Bridged by a Diaza-crown Ether: Towards Multinuclear Bimodal Molecular Imaging Probes

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NMR CEST experiments

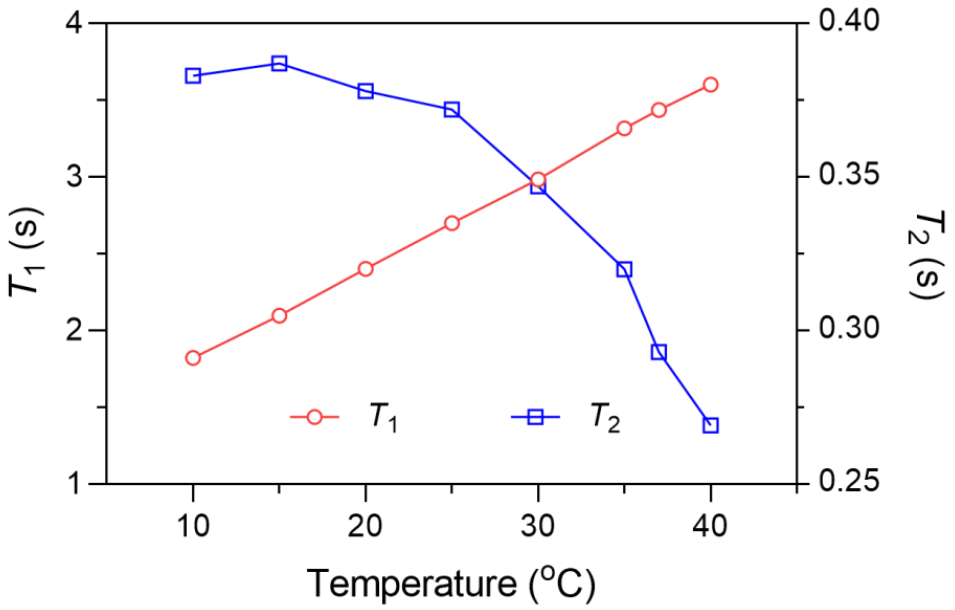
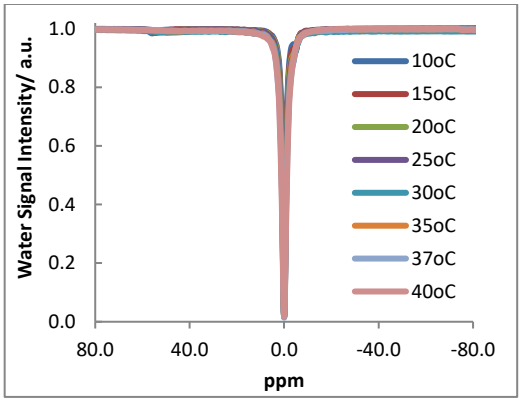
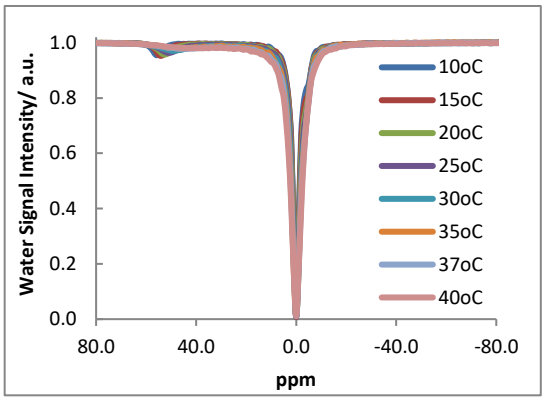


Figure S1. Change in T_1 and T_2 relaxation times for 5 mM **Eu$_2$L** with temperature at 300 MHz (50 mM HEPES, pH 7.4).



(**a**)



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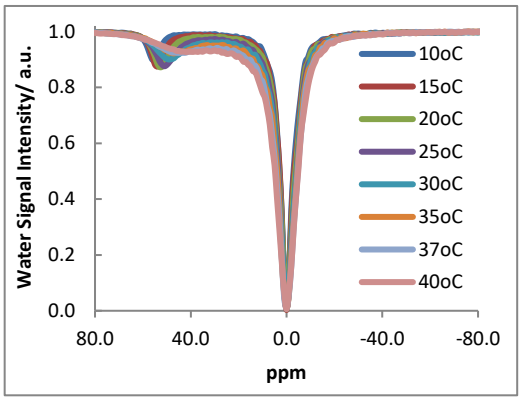

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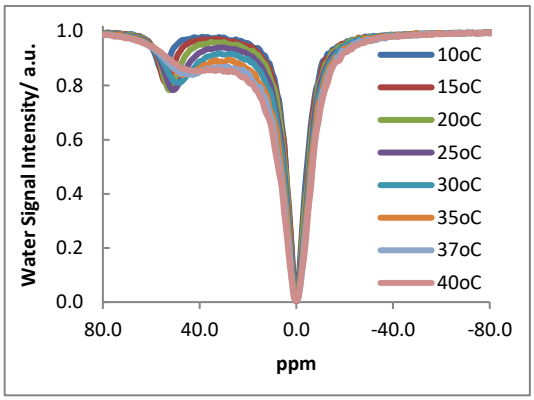

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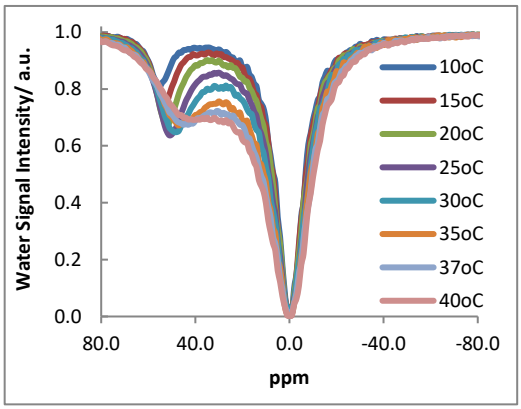

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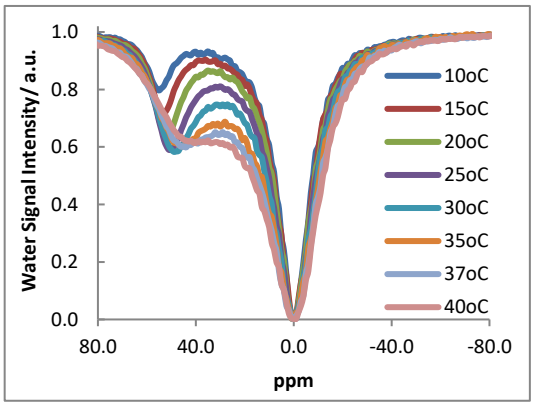


(**f**)

Figure S2. The CEST spectra of 5 mM **Eu$_2$L** at different temperatures and saturation power B_1: (a) 2.5 μT, (b) 5.0 μT, (c) 10 μT, (d) 15 μT, (e) 25 μT and (f) 30 μT.

Luminescence experiments

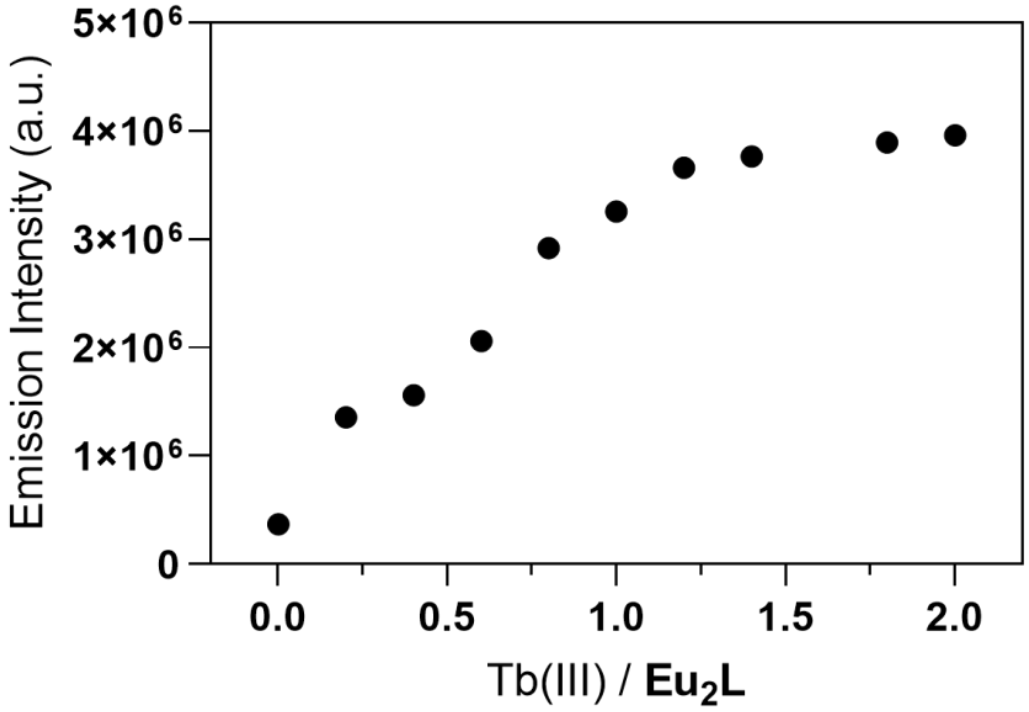
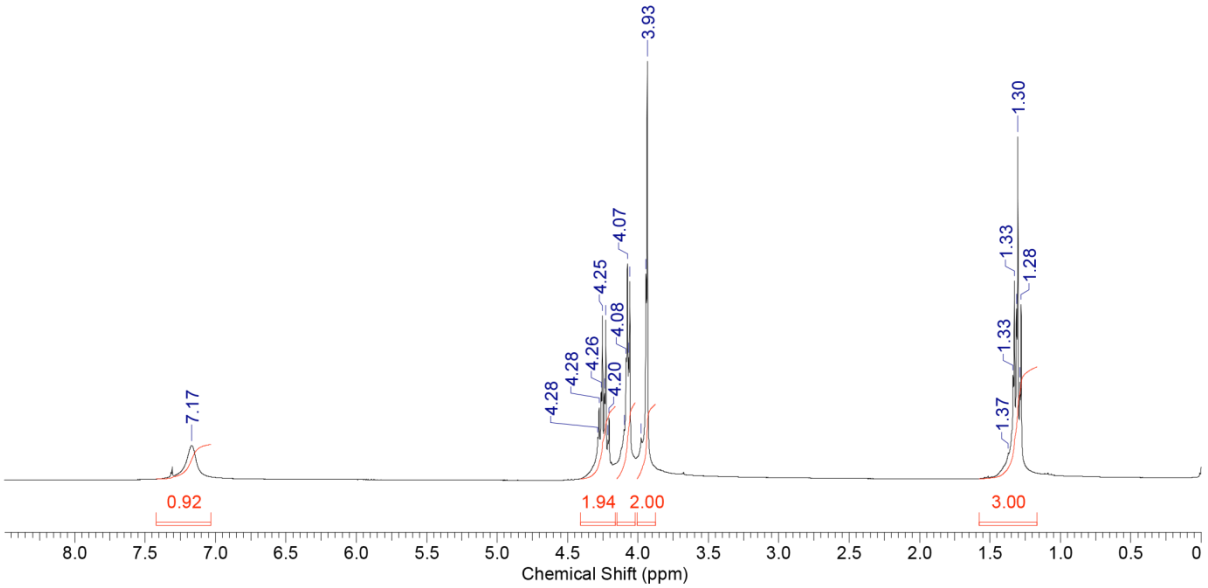
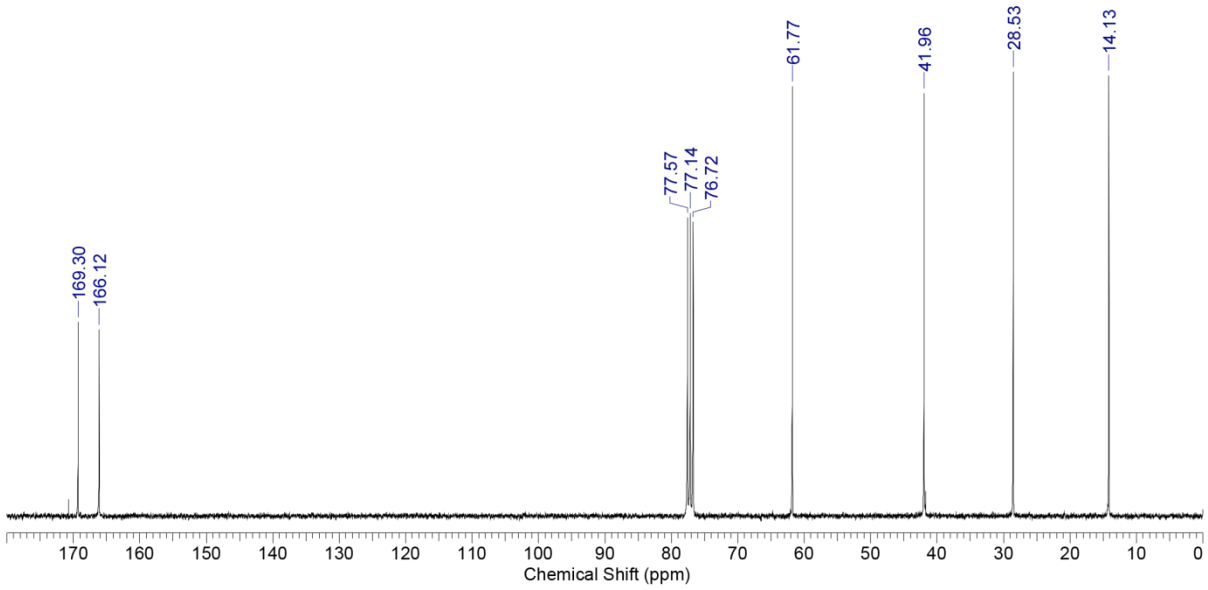


Figure S3. Emission intensity monitored at 545 nm of 0.2 mM **Eu$_2$L** upon titration with Tb^{3+} at 25 °C (50 mM HEPES, pH 7.4). The binding isotherm saturates after 1 equiv. of added Tb^{3+}, indicating formation of weak 1:1 complex between **Eu$_2$L** and Tb^{3+}.

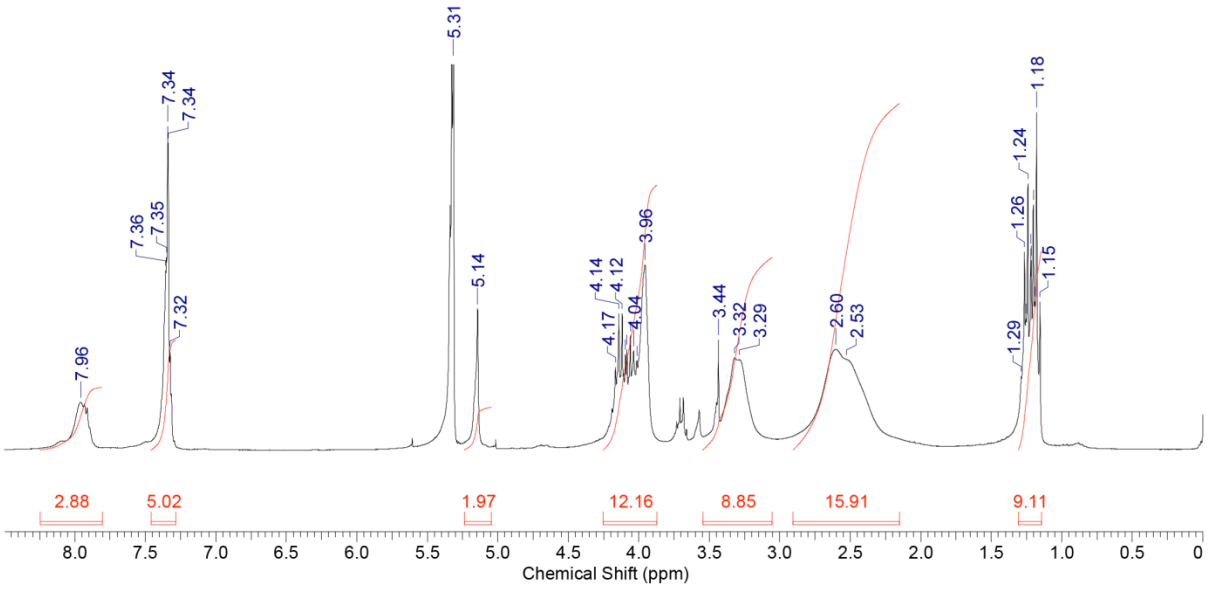
NMR spectra

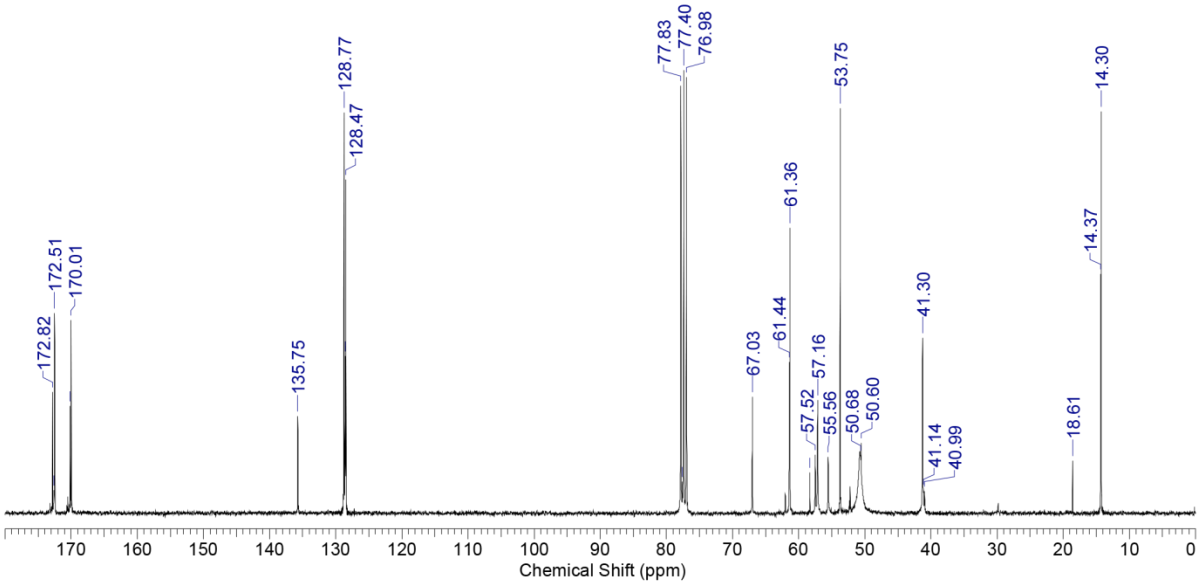
Compound **2**



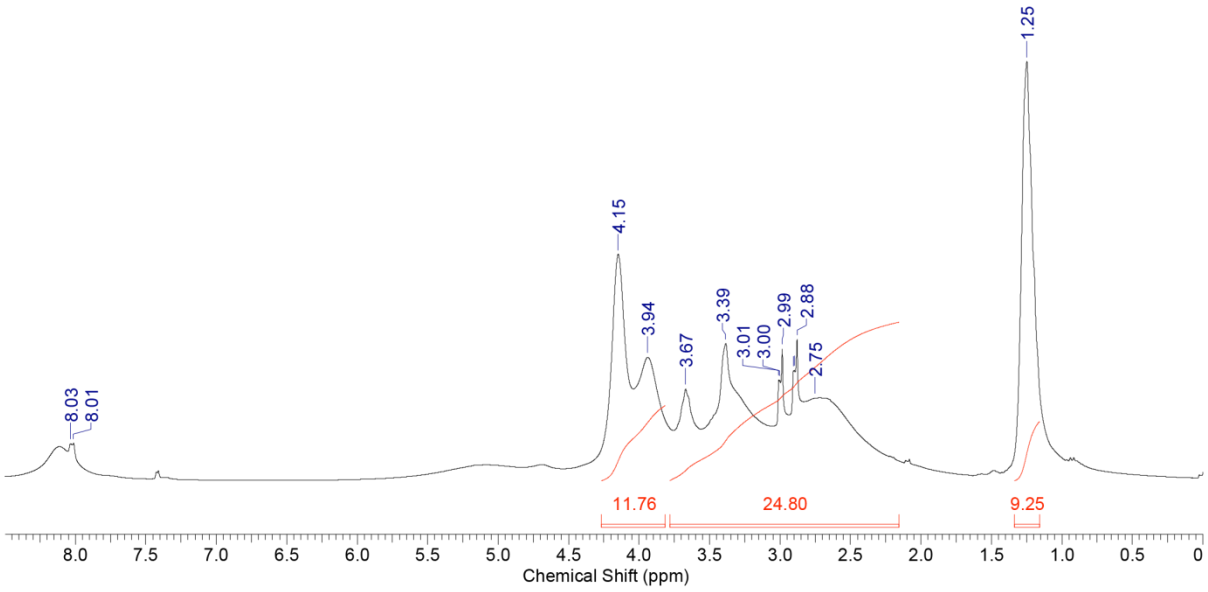


Compound **3**


7.96
7.36
7.35
7.34
7.34
7.32
5.31
5.14
4.17
4.14
4.12
4.04
3.96
3.44
3.32
3.29
2.60
2.53
1.29
1.26
1.24
1.18
1.15
2.88
5.02
1.97
12.16
8.85
15.91
9.11
Chemical Shift (ppm)


172.82
172.51
170.01
135.75
128.77
128.47
77.83
77.40
76.98
67.03
61.44
61.36
57.52
57.16
55.56
53.75
50.68
50.60
41.30
41.14
40.99
18.61
14.37
14.30
Chemical Shift (ppm)

Compound **4**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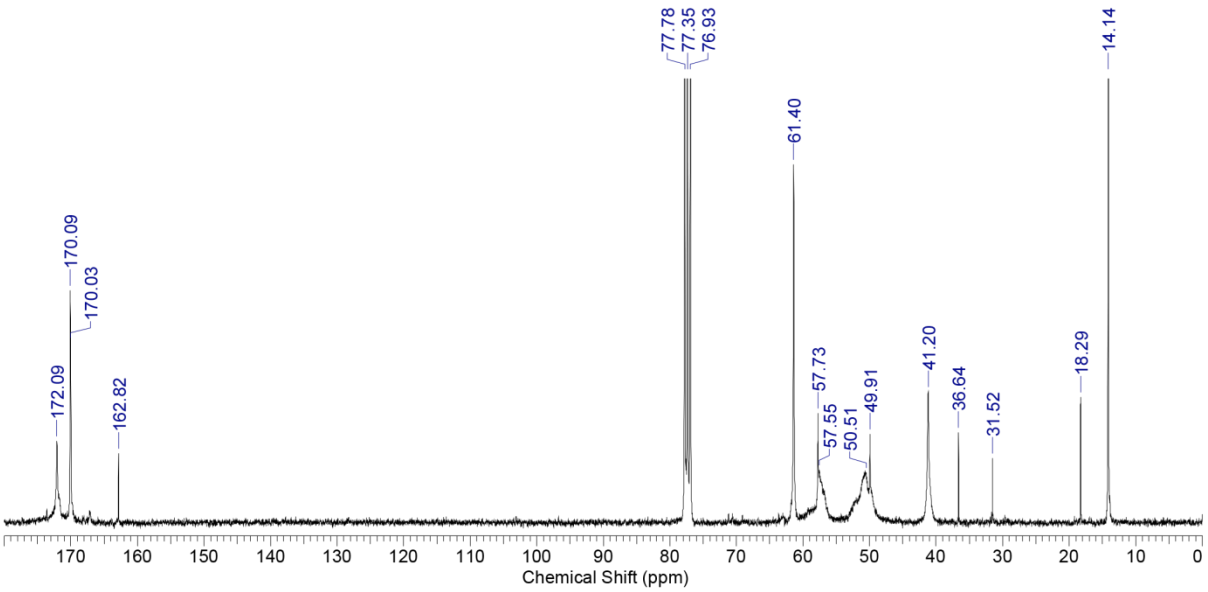
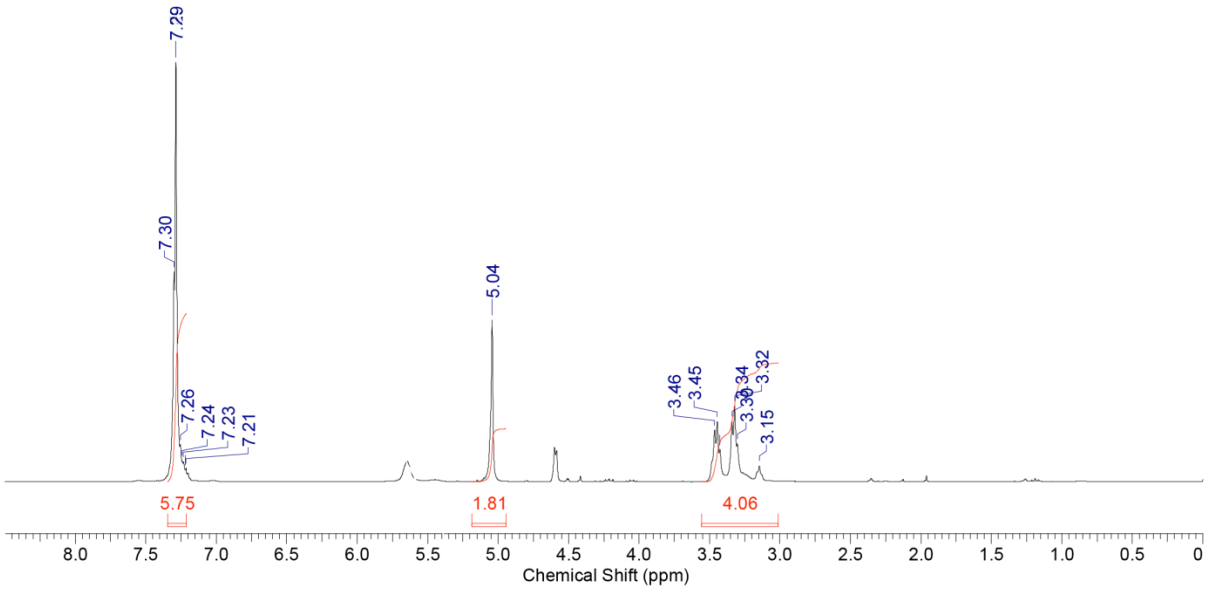
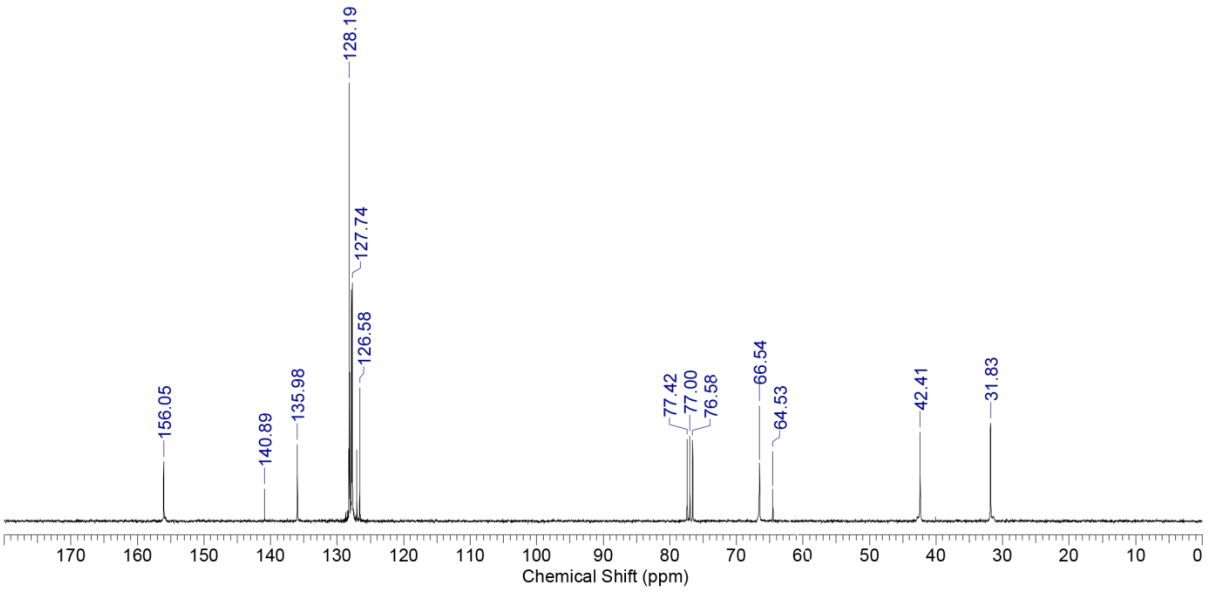
4.15
3.94
3.67
3.39
3.01
3.00
2.99
2.88
2.75
8.03
8.01
11.76
24.80
9.25
Chemical Shift (ppm)

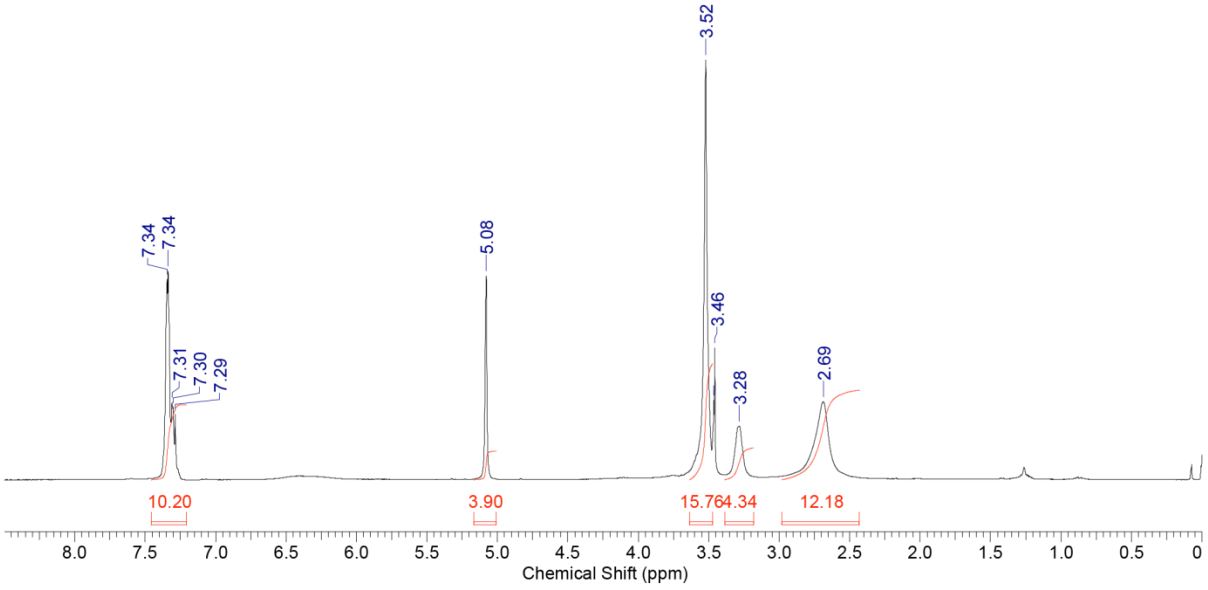

77.78
77.35
76.93
14.14
61.40
170.09
170.03
172.09
162.82
57.73
57.55
50.51
49.91
41.20
36.64
31.52
18.29
Chemical Shift (ppm)

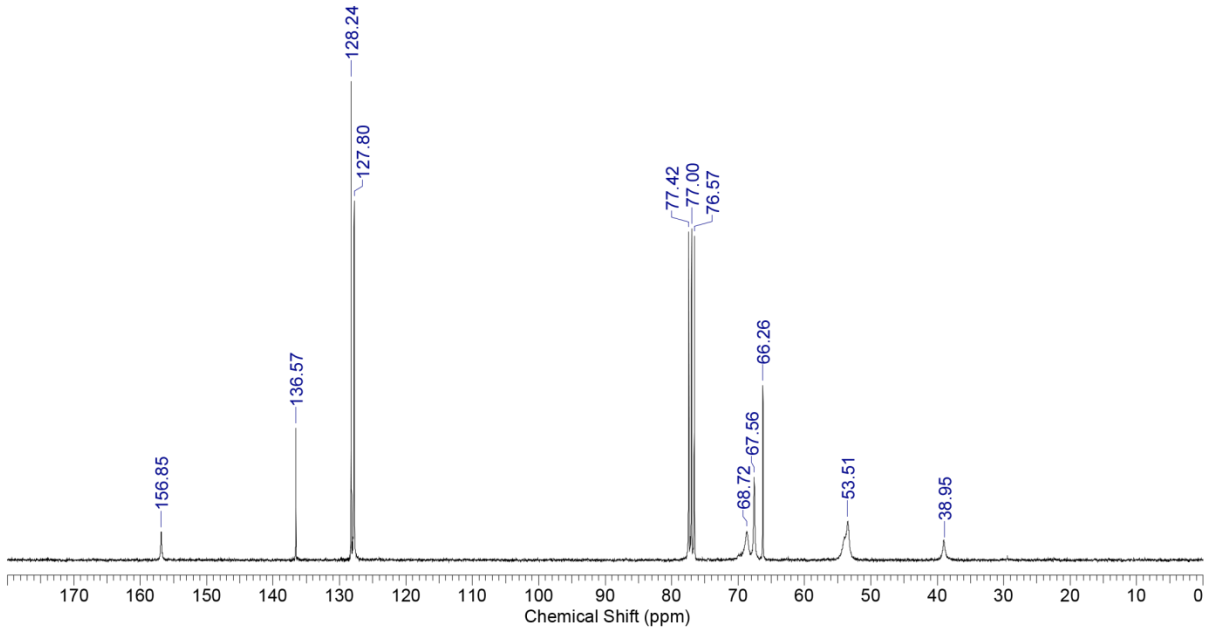
Compound **5**


7.29
7.30
7.26
7.24
7.23
7.21
5.04
3.46
3.45
3.34
3.32
3.30
3.15
5.75
1.81
4.06
Chemical Shift (ppm)

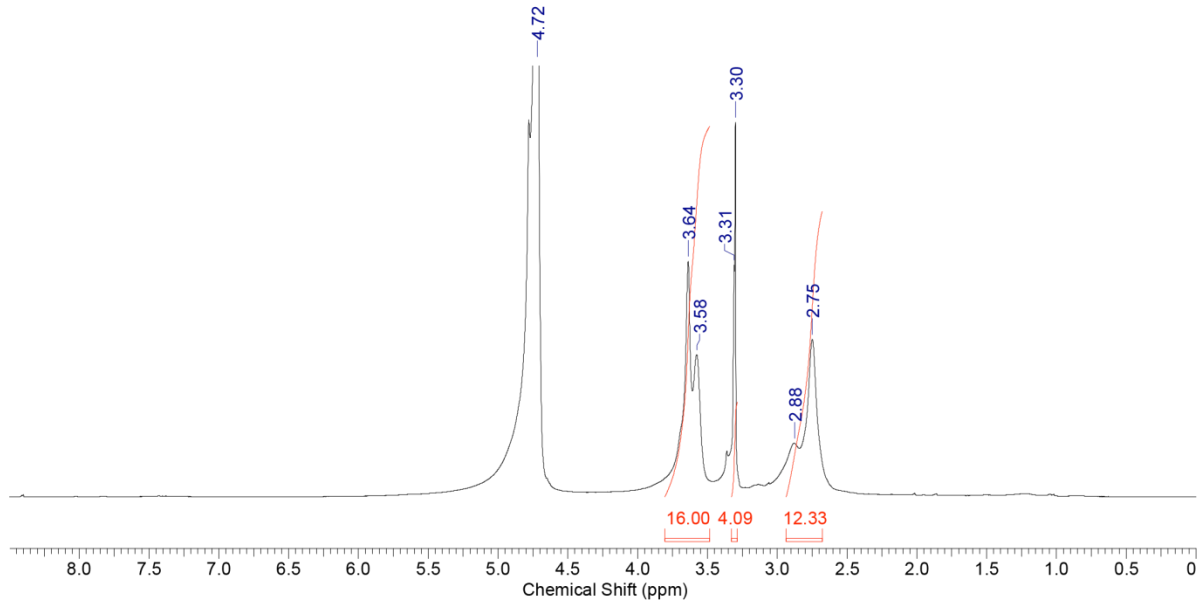

128.19
127.74
126.58
156.05
140.89
135.98
77.42
77.00
76.58
66.54
64.53
42.41
31.83
Chemical Shift (ppm)

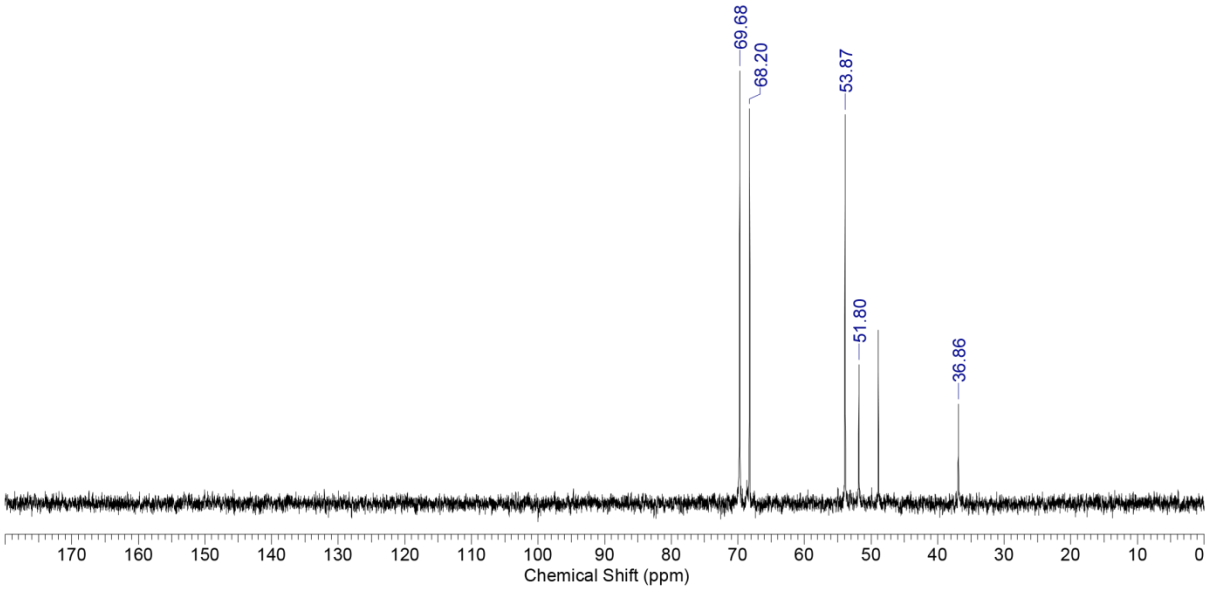
Compound **6**


7.34
7.34
7.31
7.30
7.29
5.08
3.52
3.46
3.28
2.69
10.20
3.90
15.76
4.34
12.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

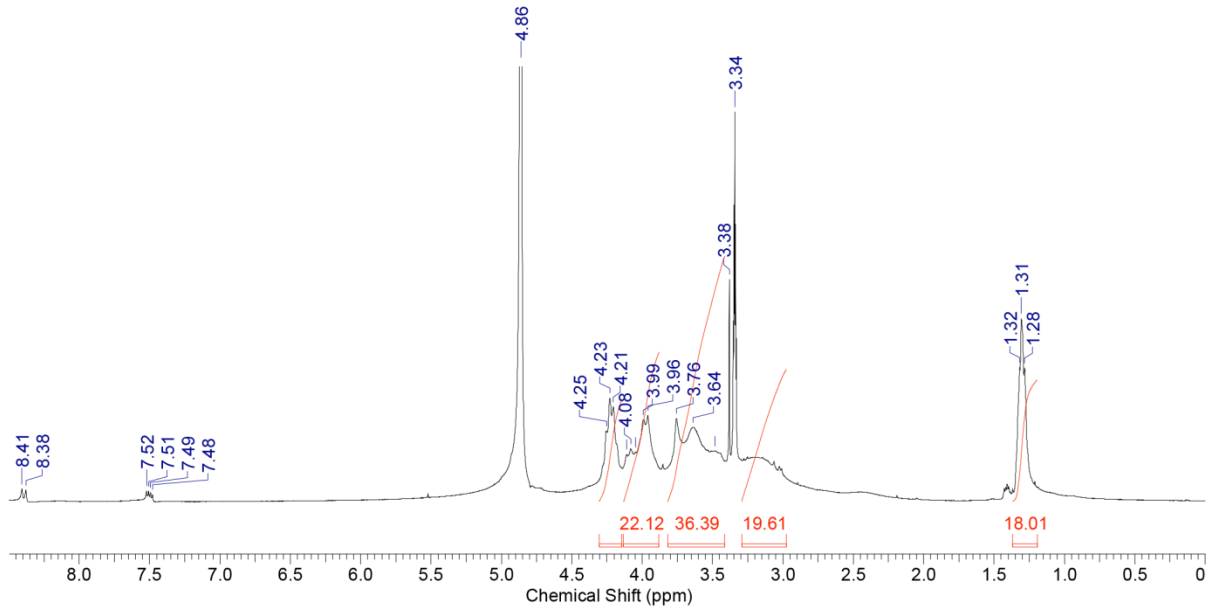

156.85
136.57
128.24
127.80
77.42
77.00
76.57
68.72
67.56
66.26
53.51
38.95
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

Compound **7**


4.72
3.64
3.30
3.31
3.58
2.88
2.75
16.00
4.09
12.33
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


69.68
68.20
53.87
51.80
36.86
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

Compound **8**


4.86
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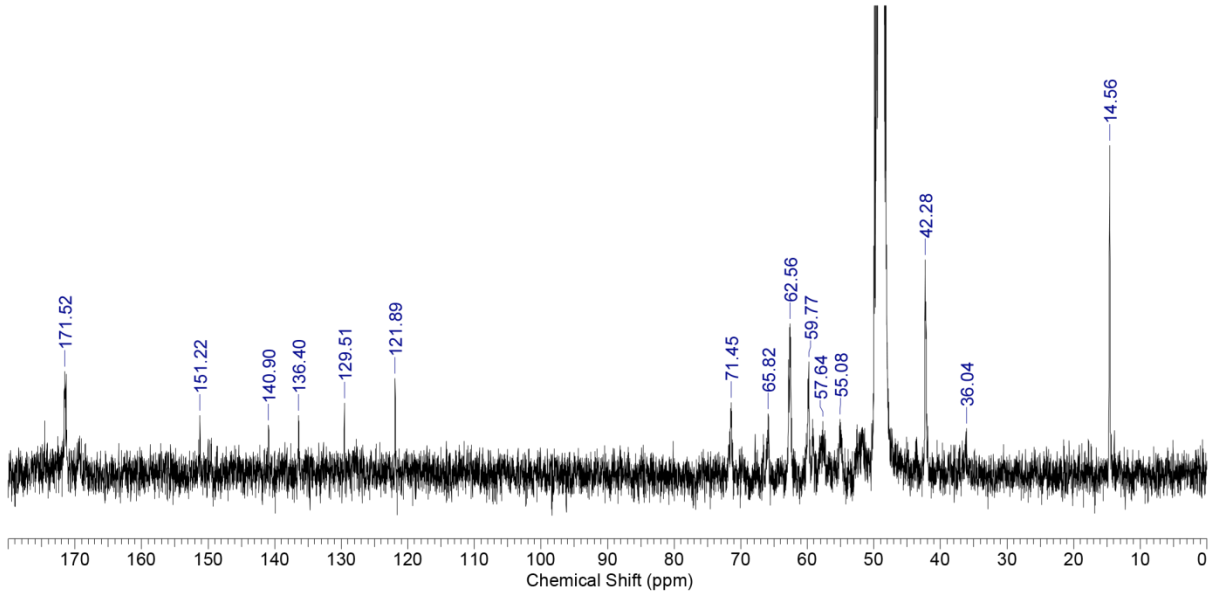
3.38
1.31
1.32
1.28
4.25
4.23
4.21
4.08
3.99
3.96
3.76
3.64
8.41
8.38
7.52
7.51
7.49
7.48
22.12
36.39
19.61
18.01
Chemical Shift (ppm)


171.52
151.22
140.90
136.40
129.51
121.89
71.45
65.82
62.56
59.77
57.64
55.08
42.28
36.04
14.56
Chemical Shift (ppm)

Compound **H_6L**