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Supporting information

Novel synthesis of lower rim α-hydrazinotetrazolocalix[4]arenes via an Ugi-azide multicomponent reaction

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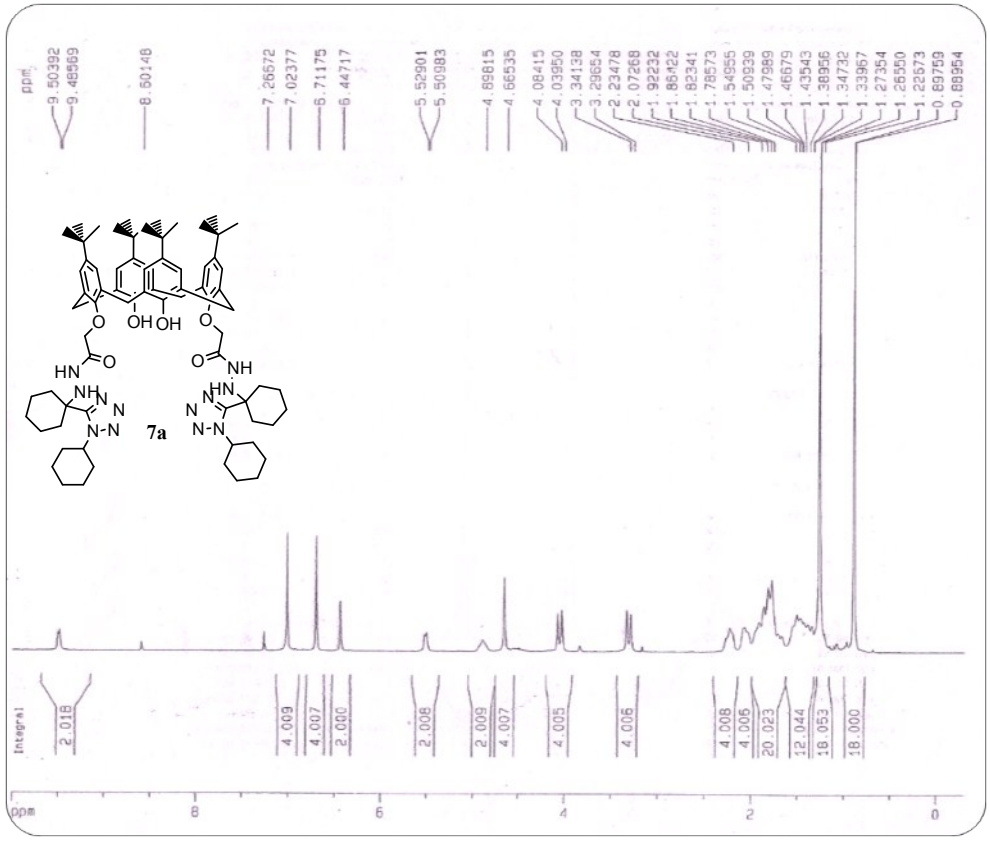
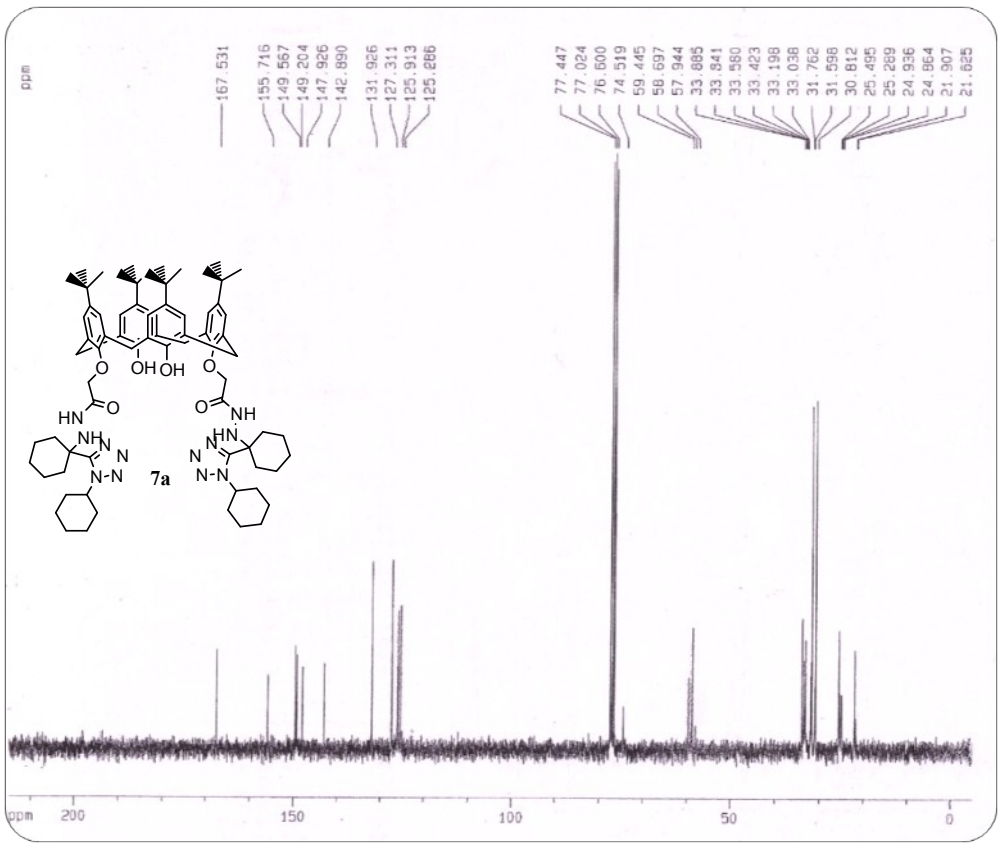
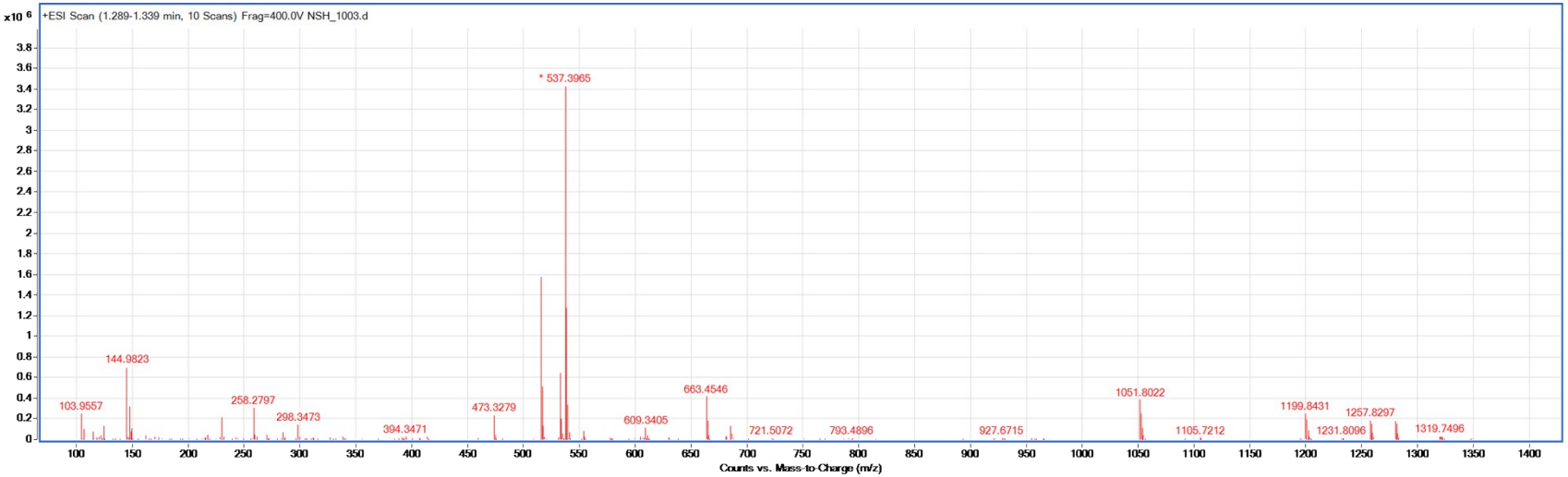
Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7a**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7a**	C74 H104 N12 O6	1256.8202	1257.8275	1279.8094	1257.8297	-1.79	1279.8117	-1.83



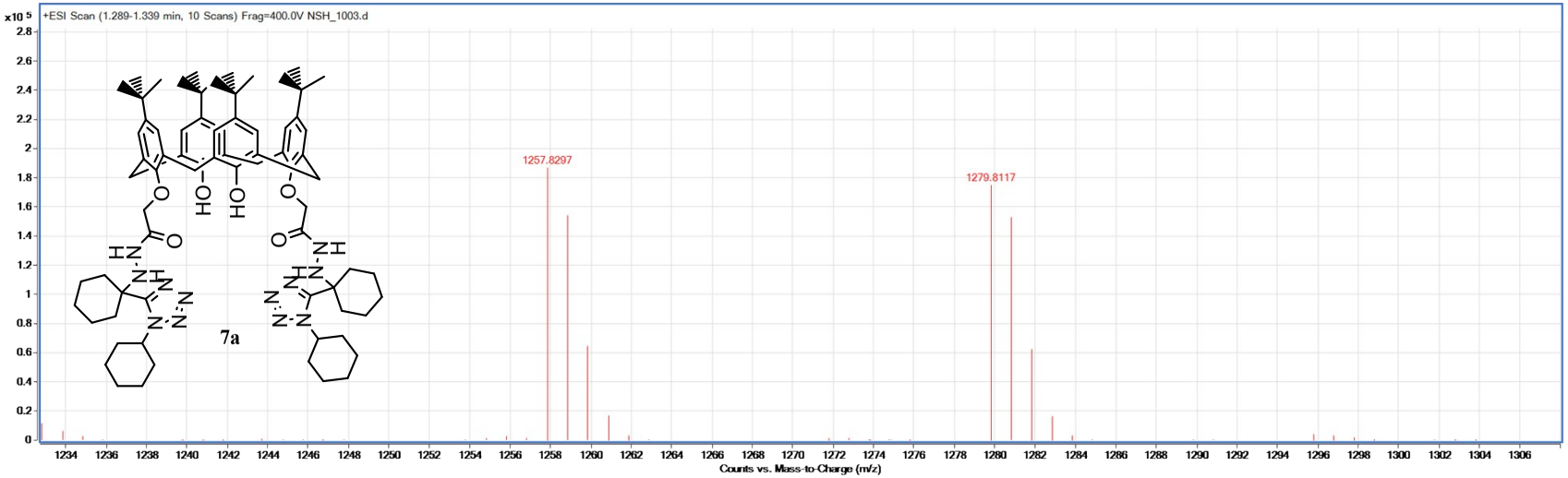
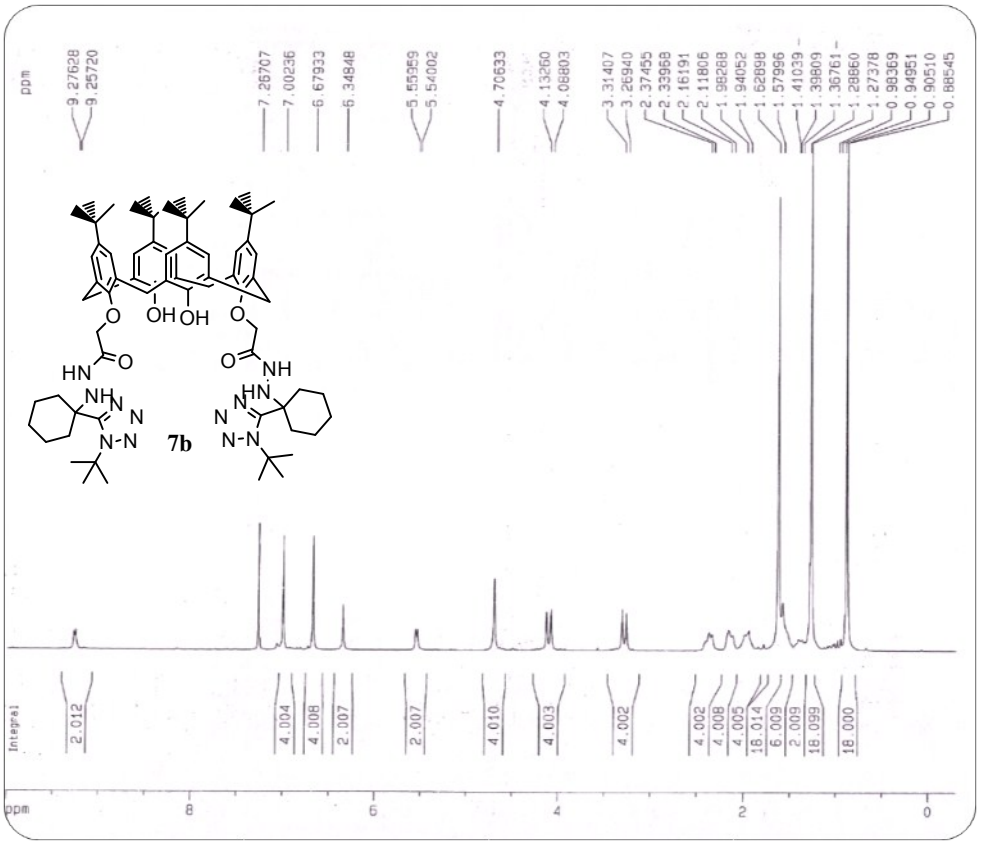
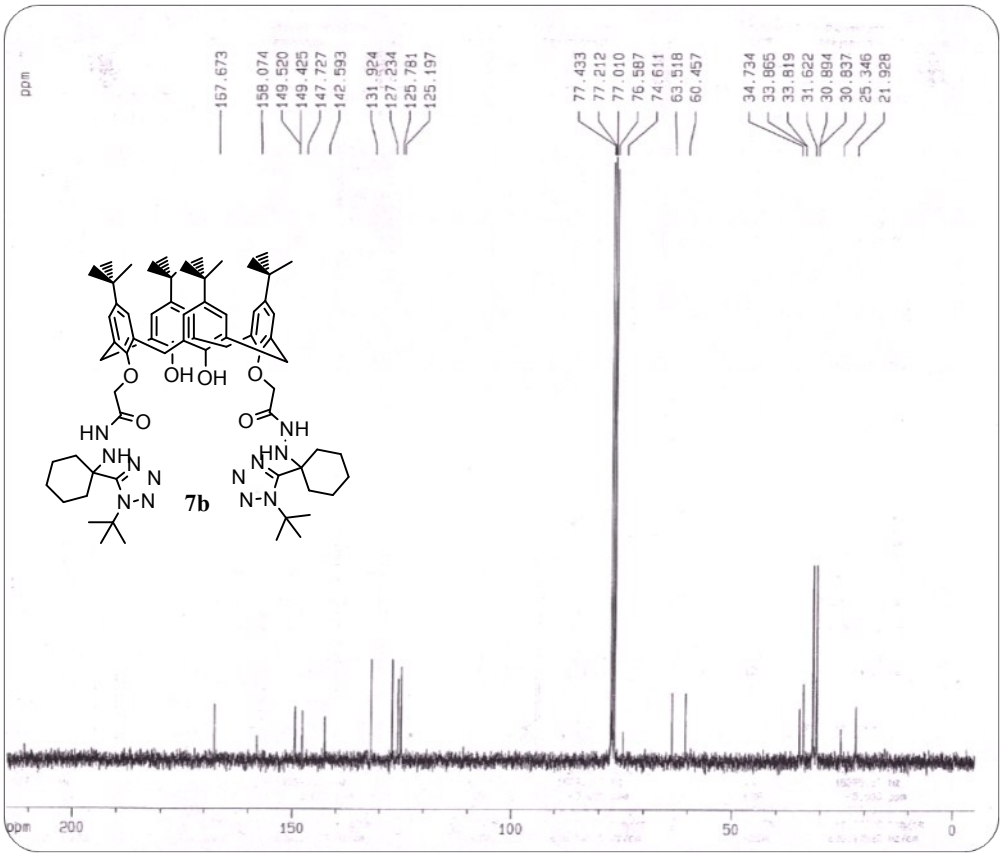
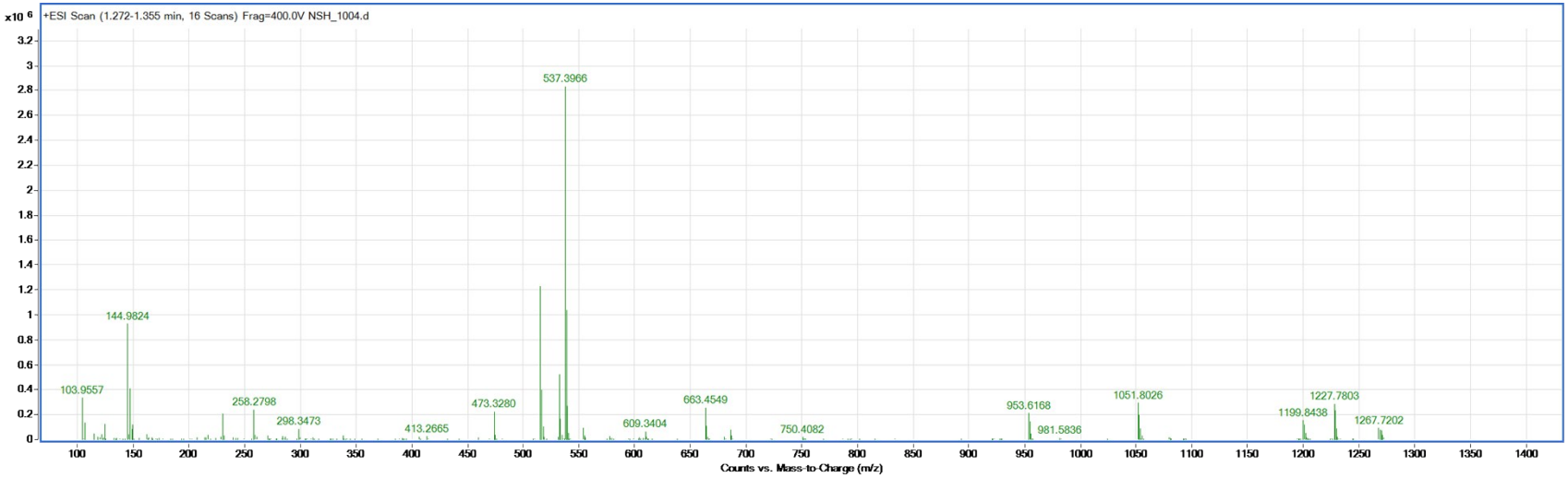


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7b**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7b**	C70 H100 N12 O6	1204.7889	1205.7962	1227.7781	ND	-	1227.7803	-1.83



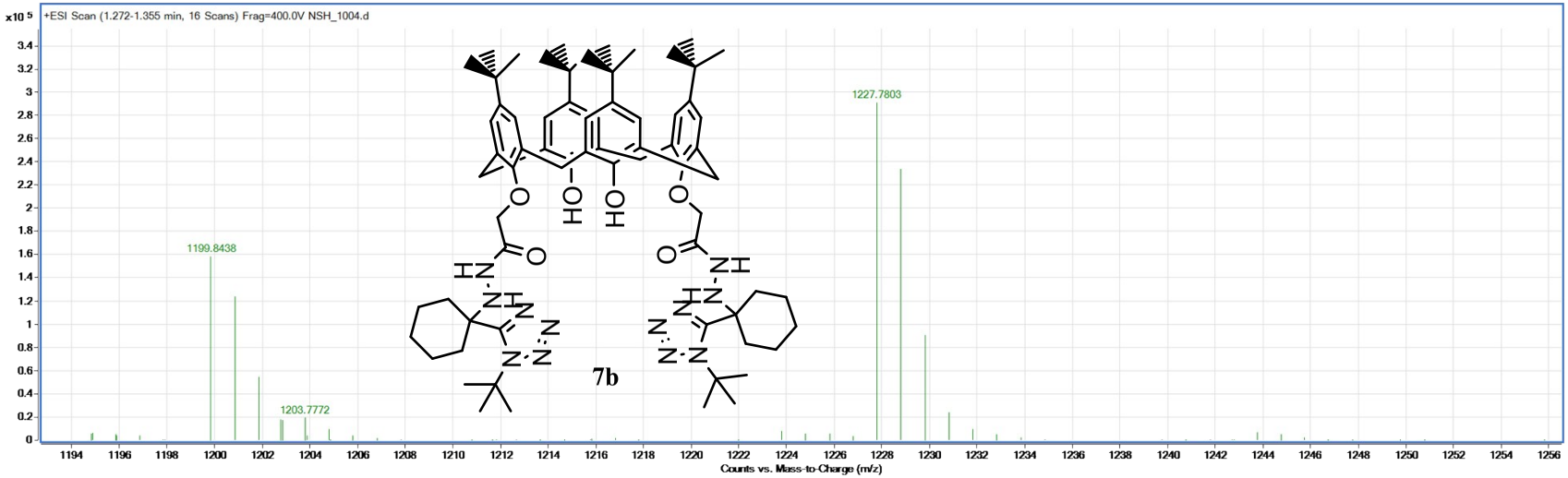
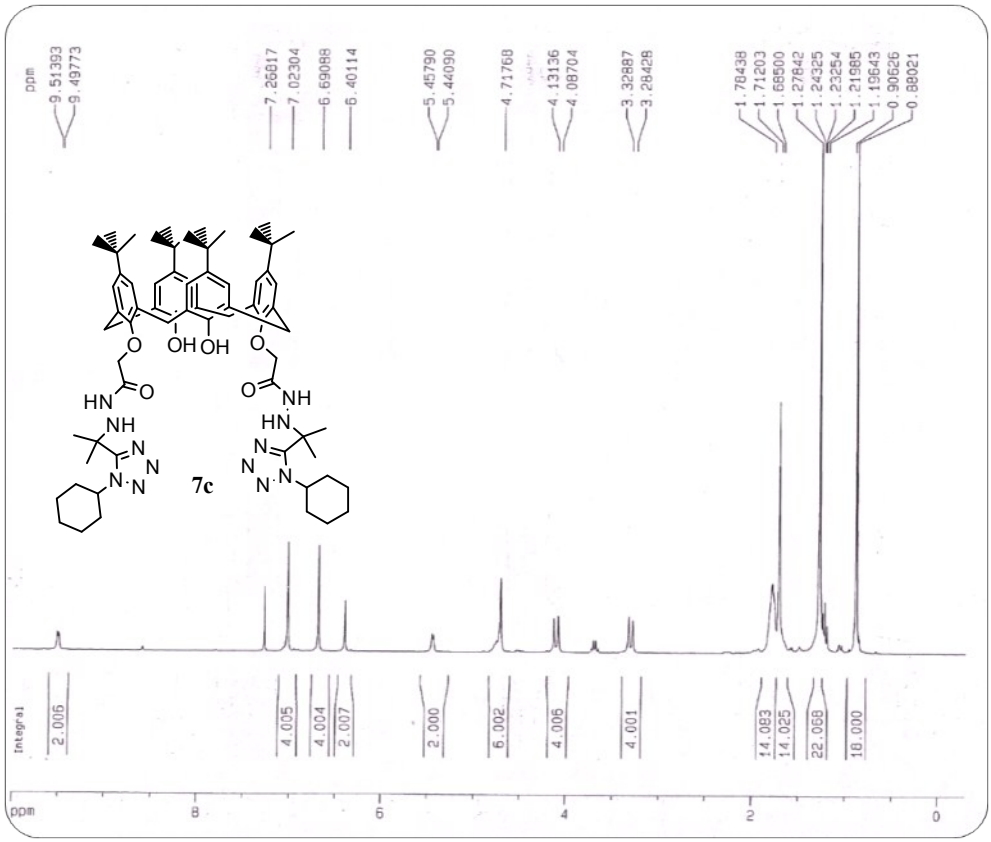
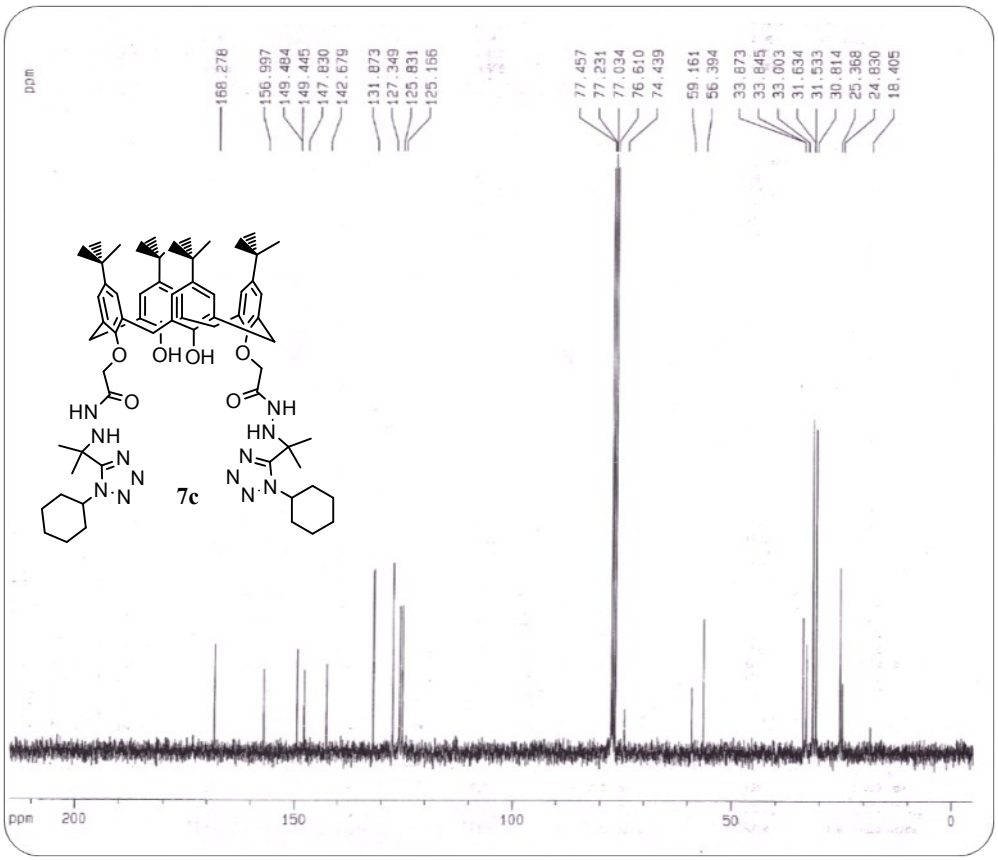
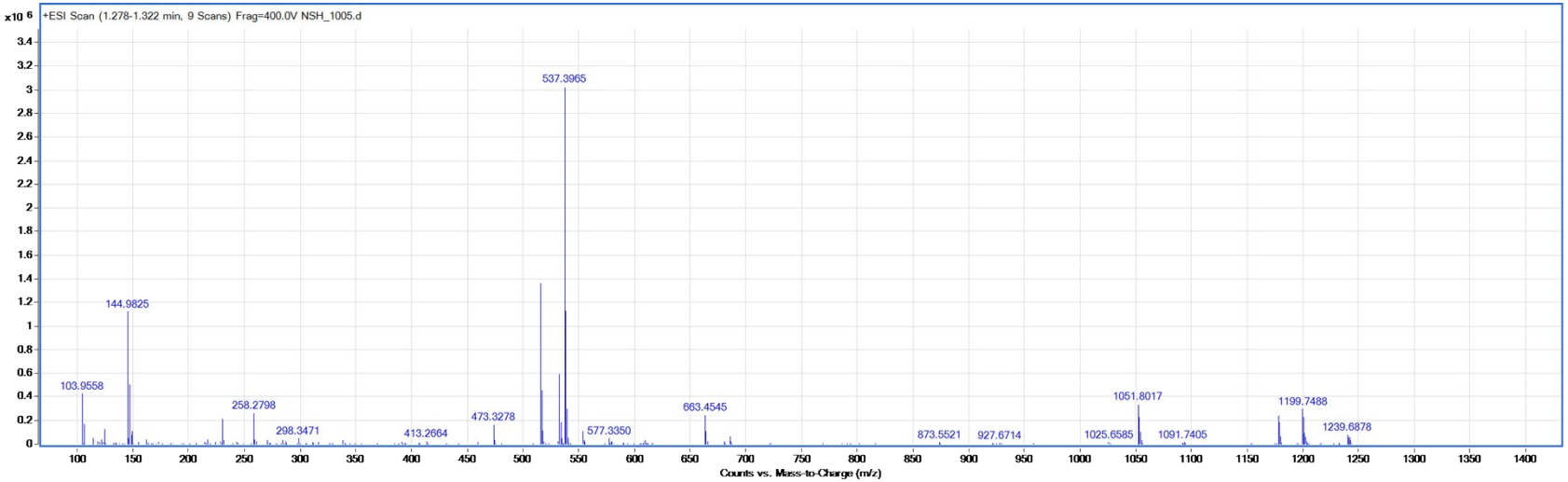


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7c**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7c**	C68 H96 N12 O6	1176.7576	1177.7649	1199.7468	1177.7665	-1.40	1199.7488	-1.7



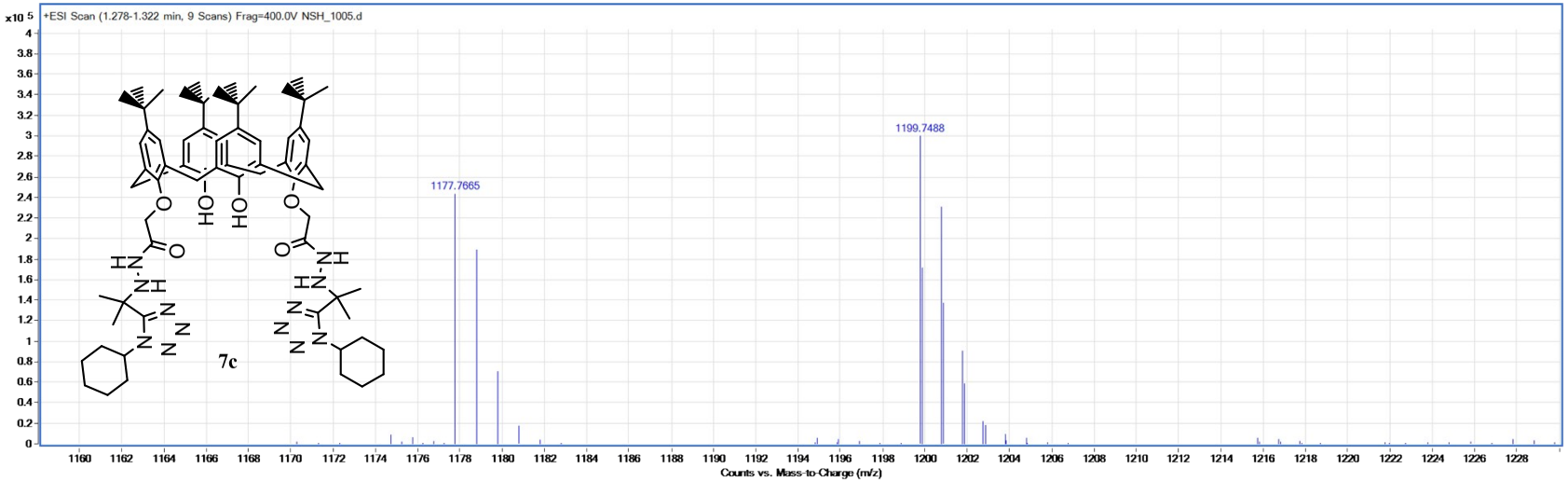
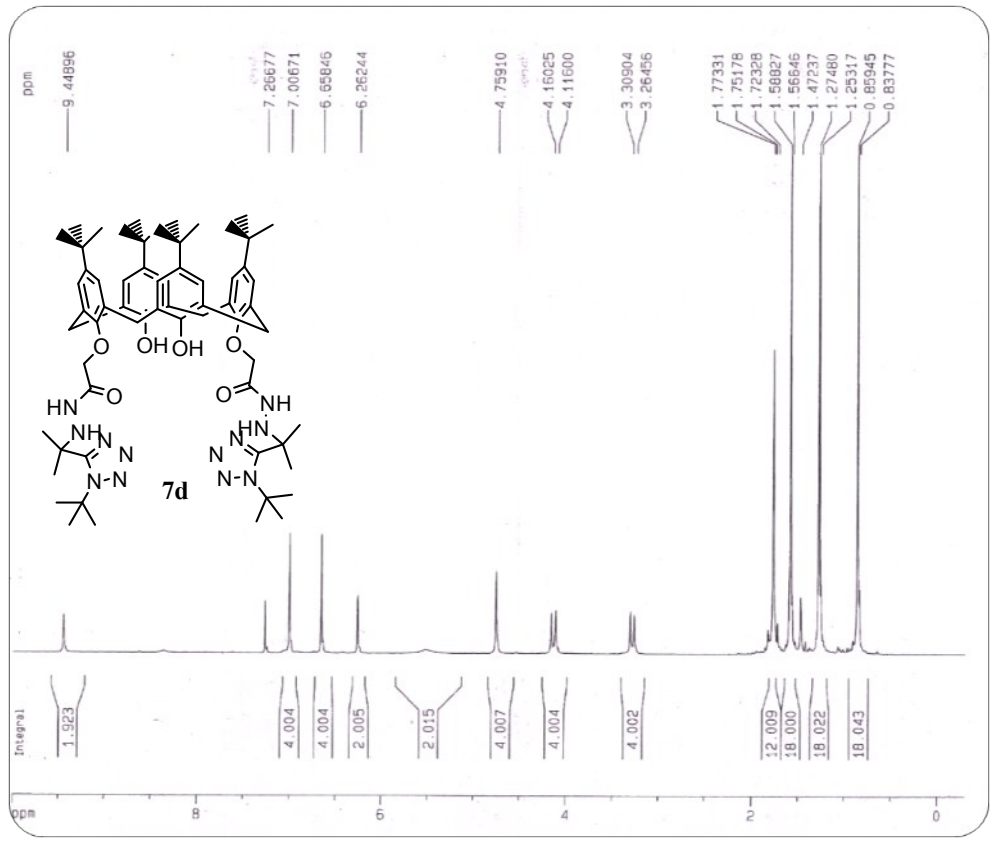
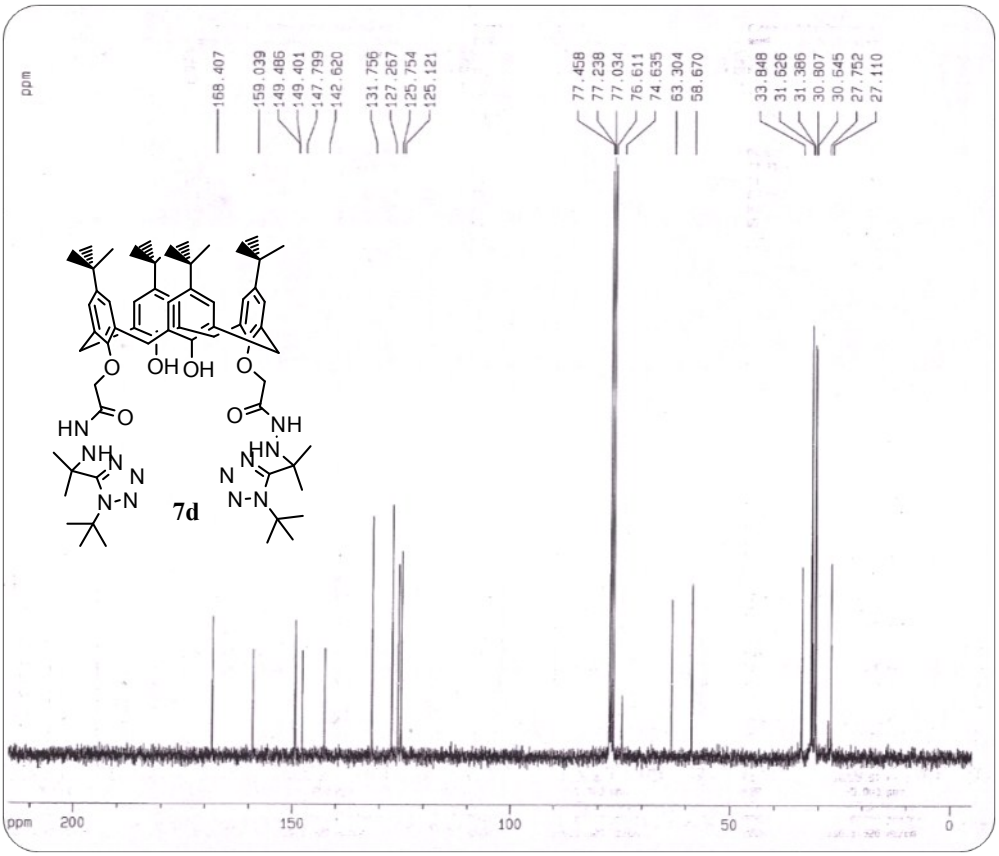
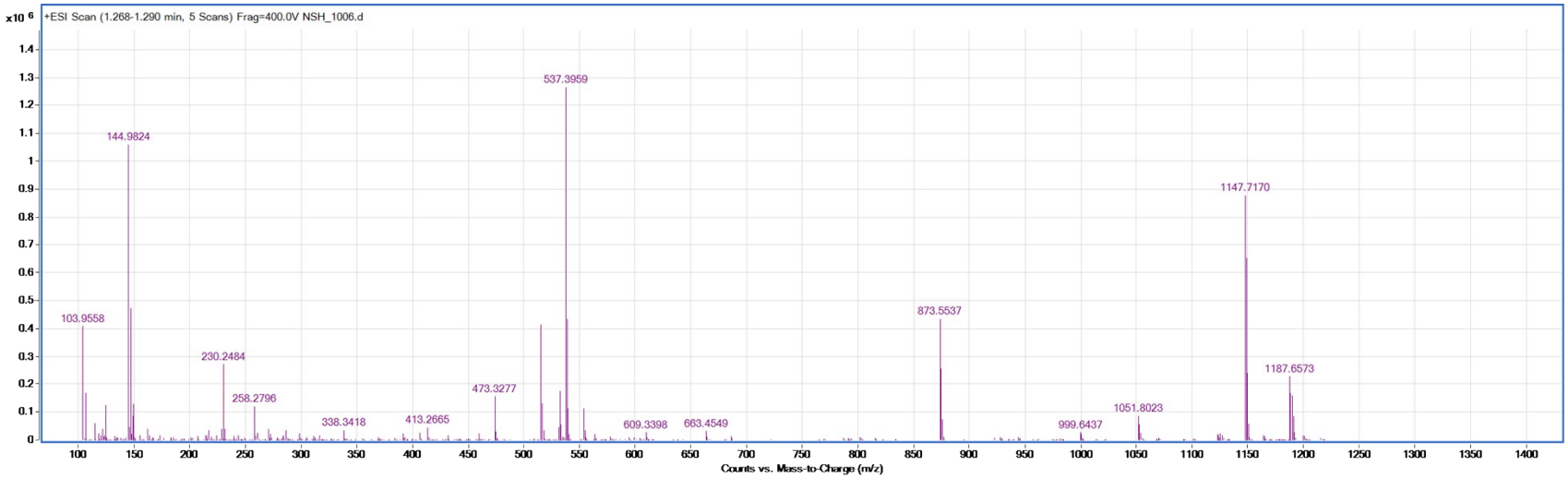


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7d**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7d**	C64 H92 N12 O6	1124.7263	1125.7336	1147.7155	1125.7328	0.76	1147.717	-1.33



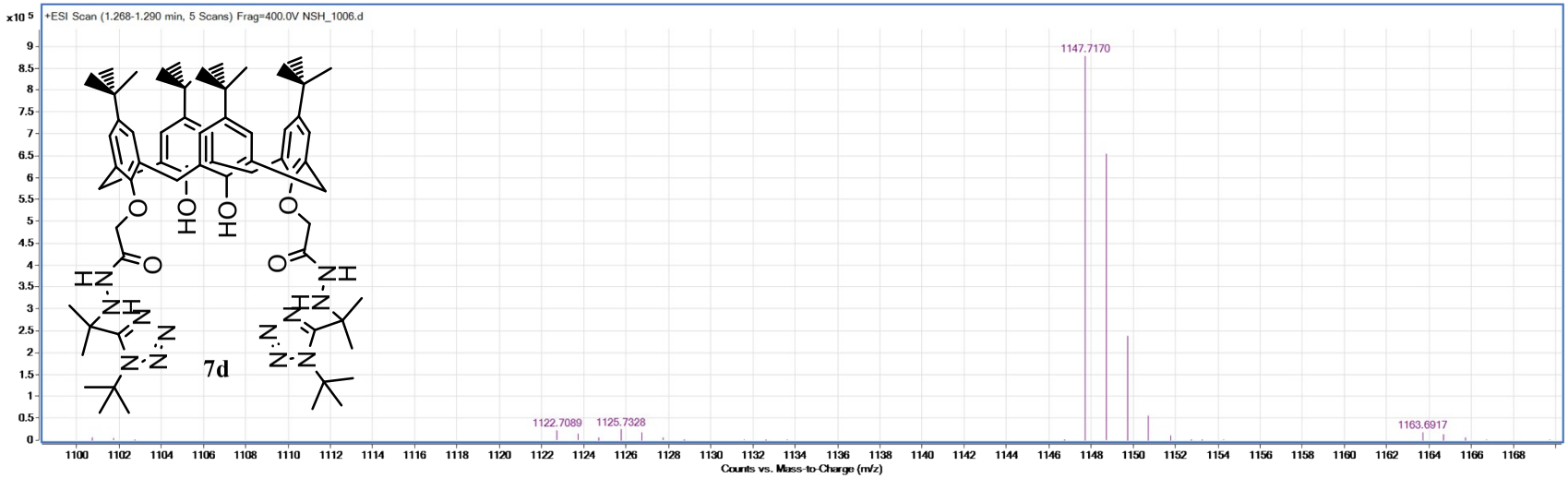
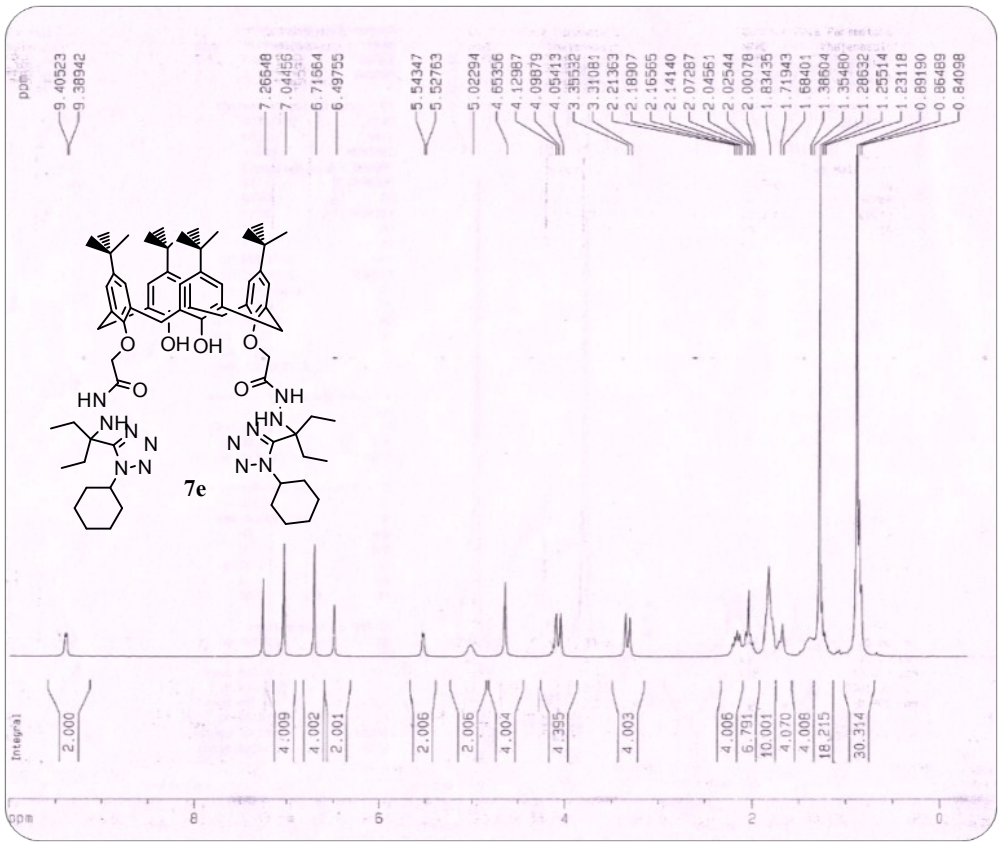
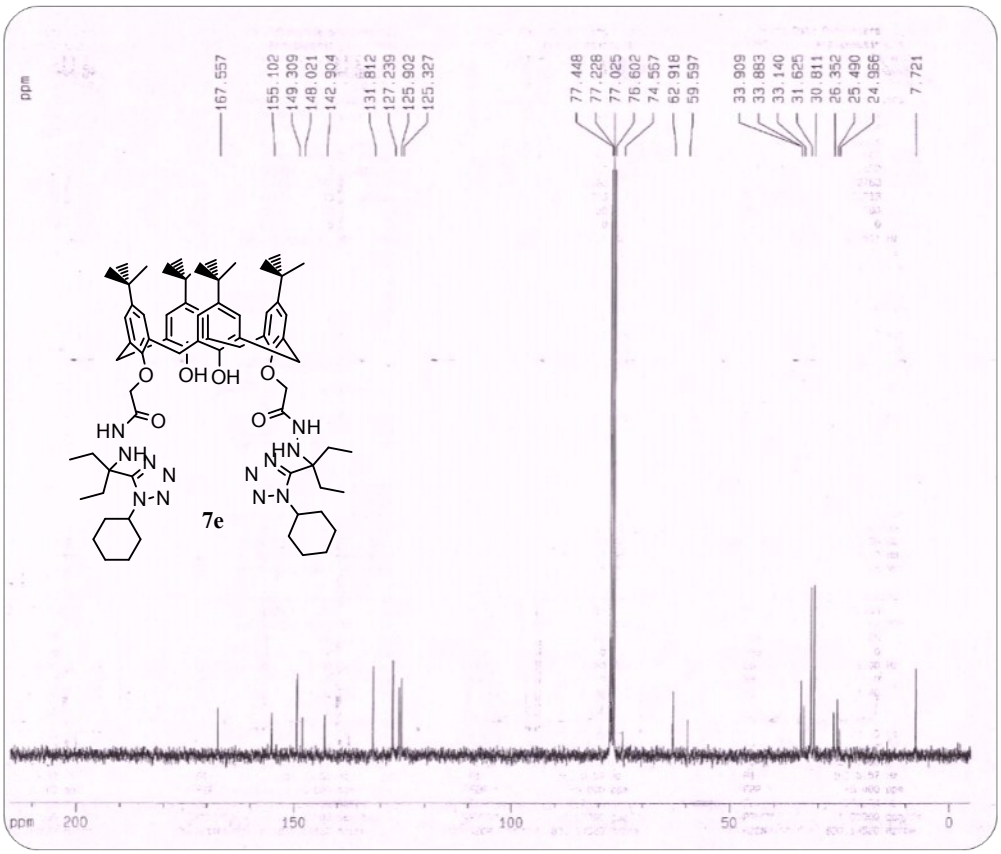
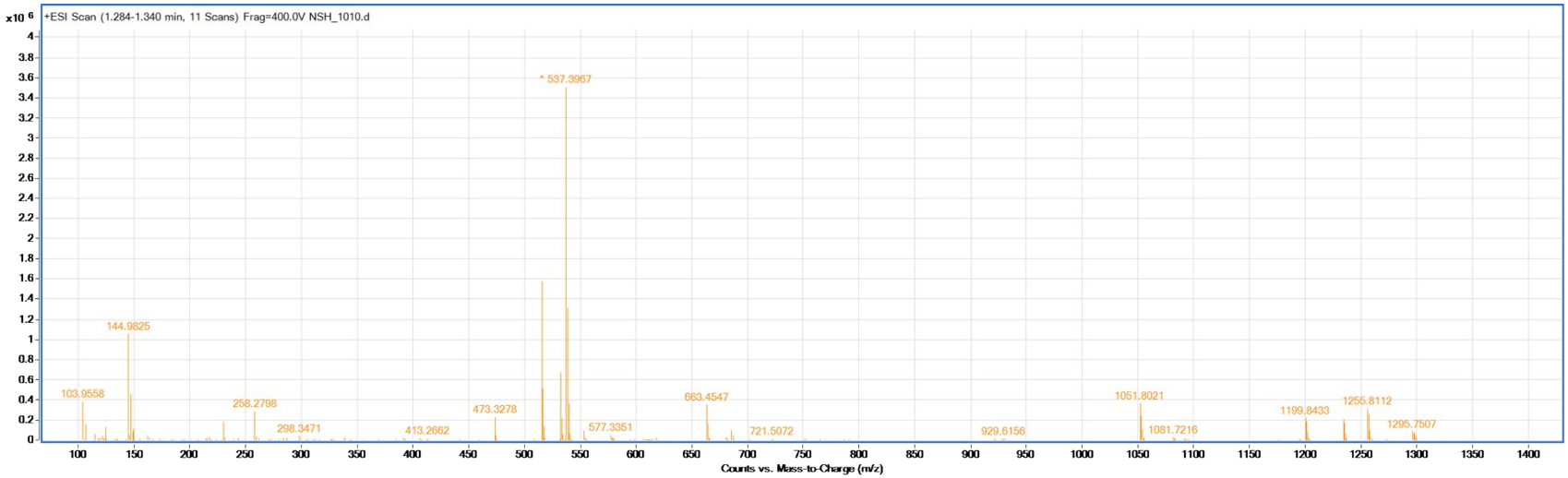


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7e**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7e**	C72 H104 N12 O6	1232.8202	1233.8275	1255.8094	1233.8293	-1.50	1255.8112	-1.46



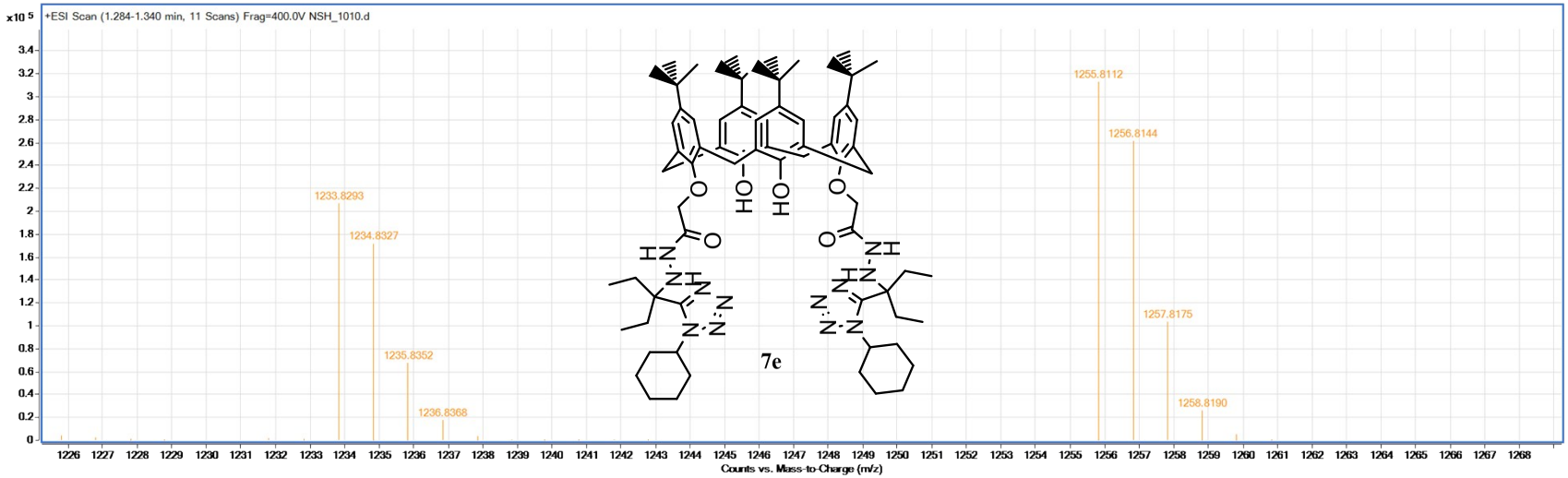
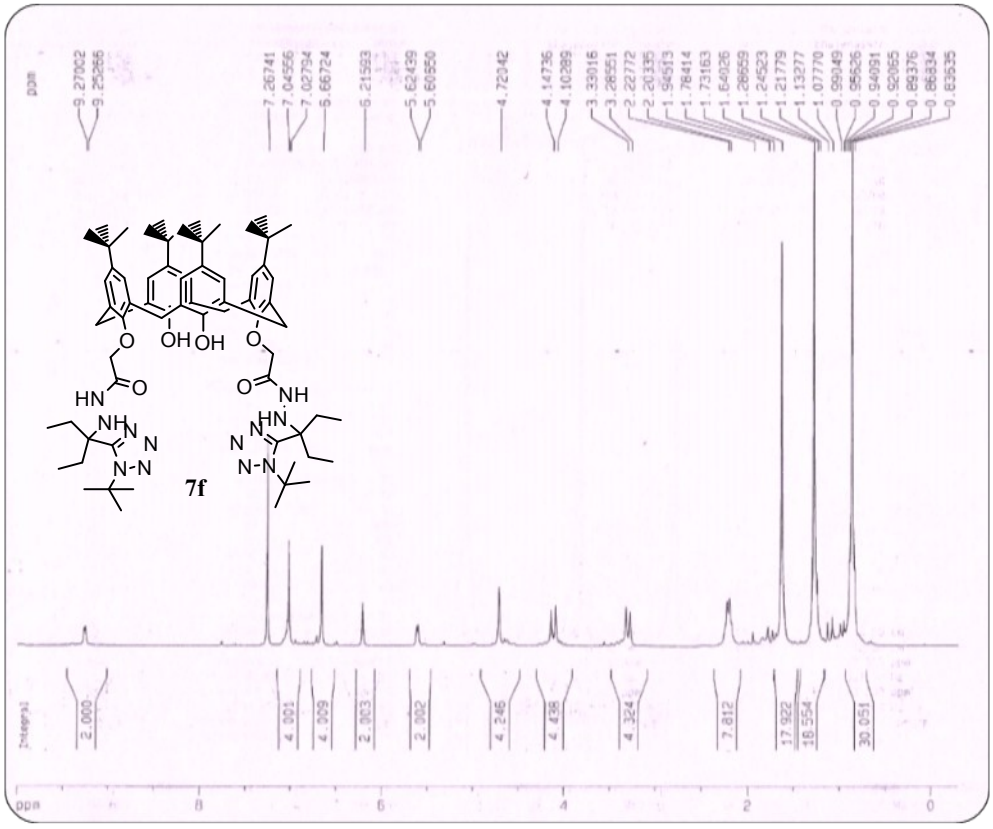
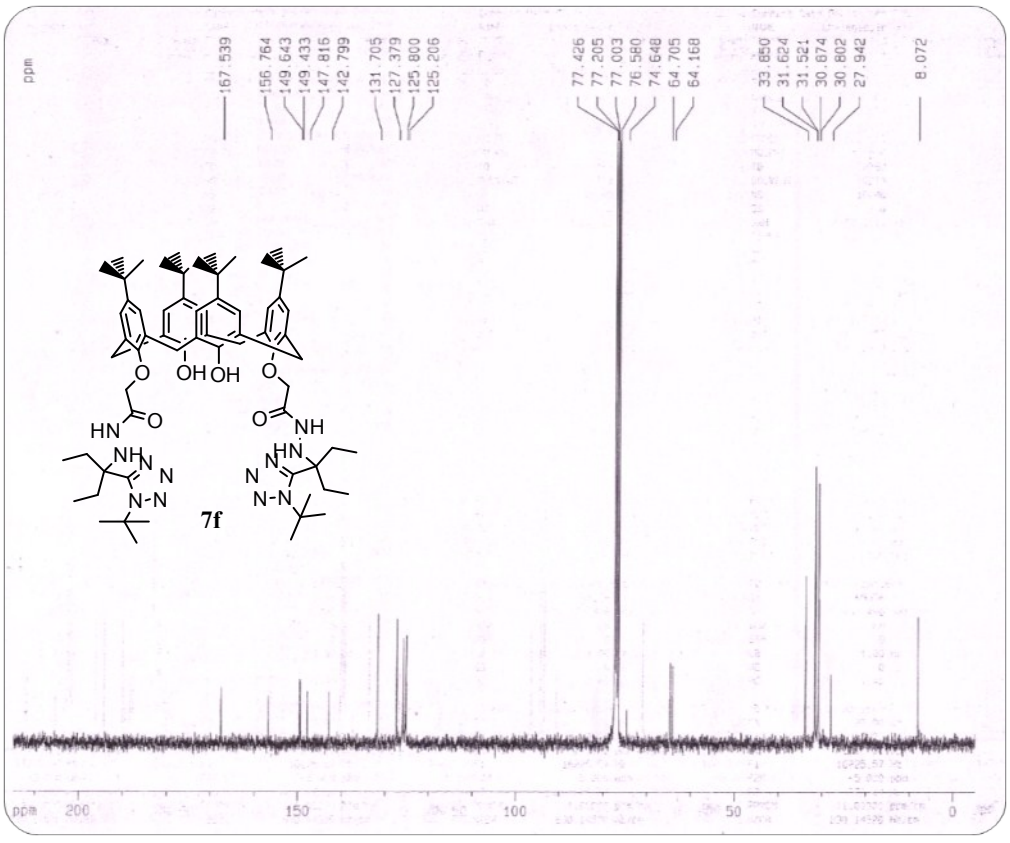
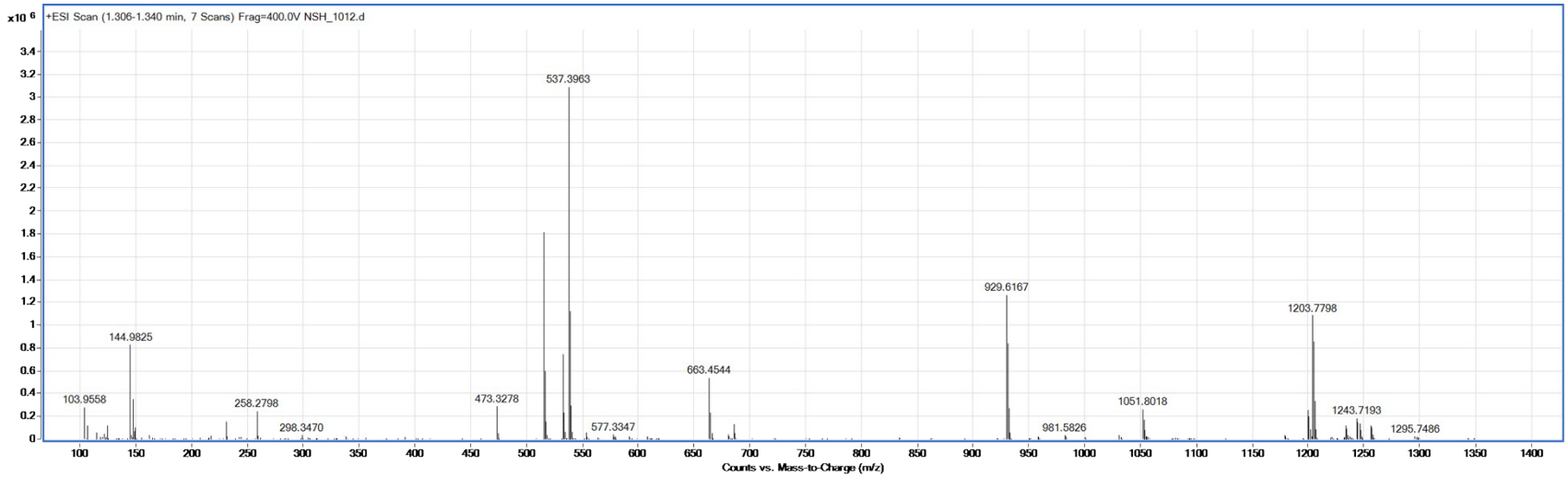


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7f**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7f**	C68 H100 N12 O6	1180.7889	1181.7962	1203.7781	ND	-	1203.7798	-1.44



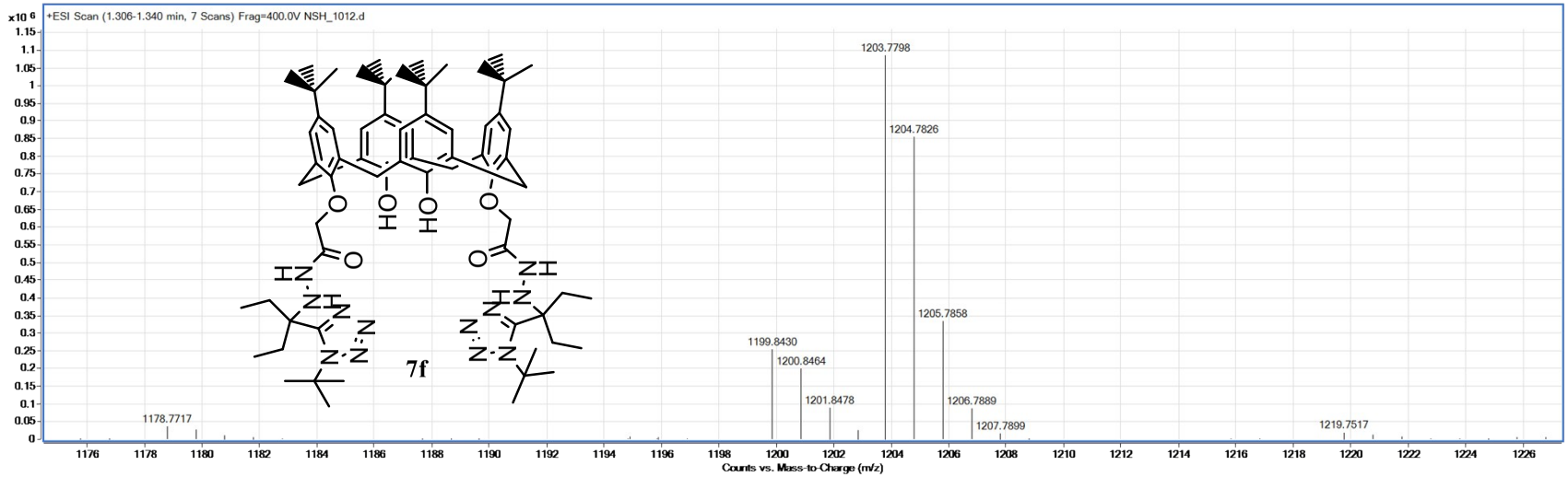
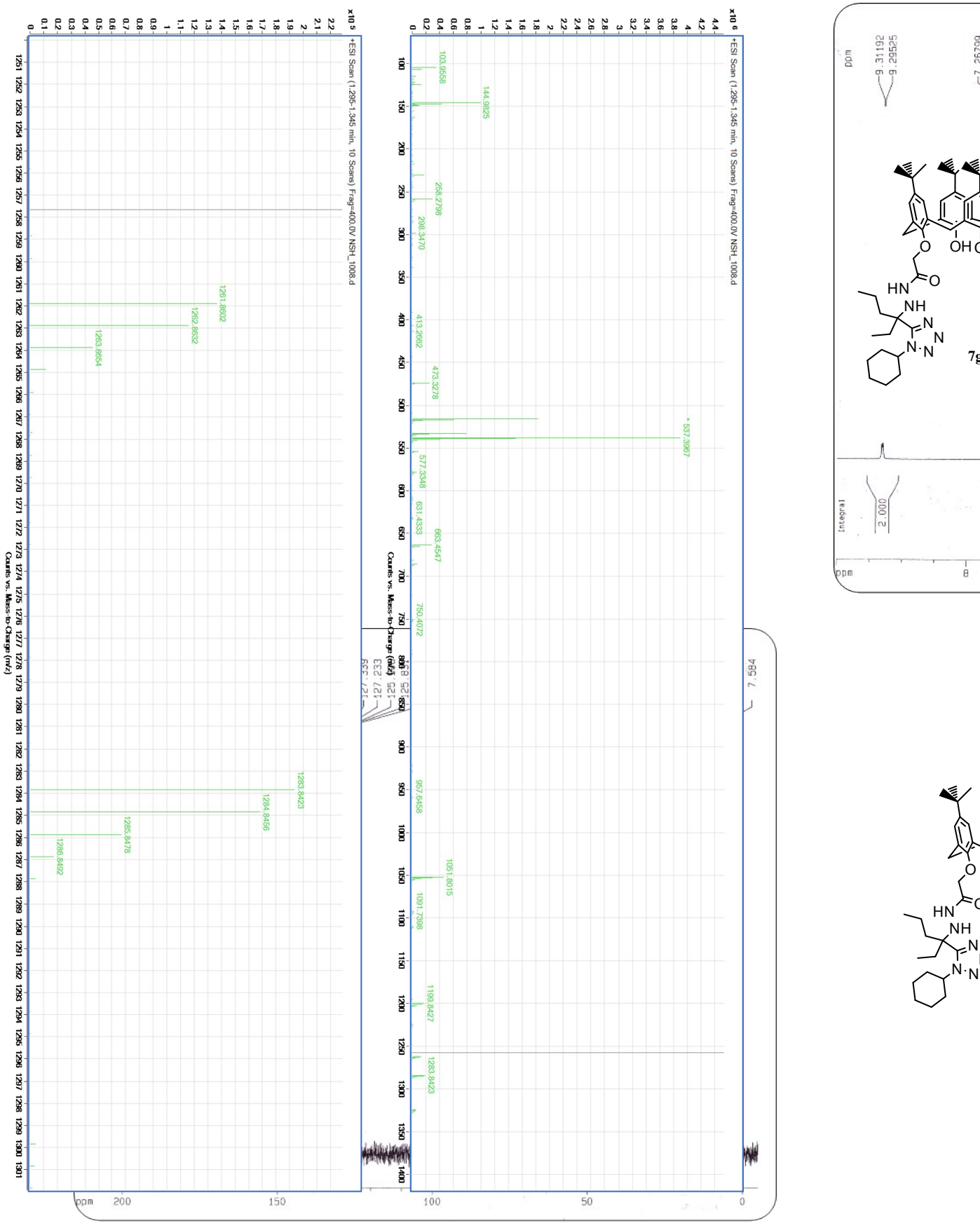
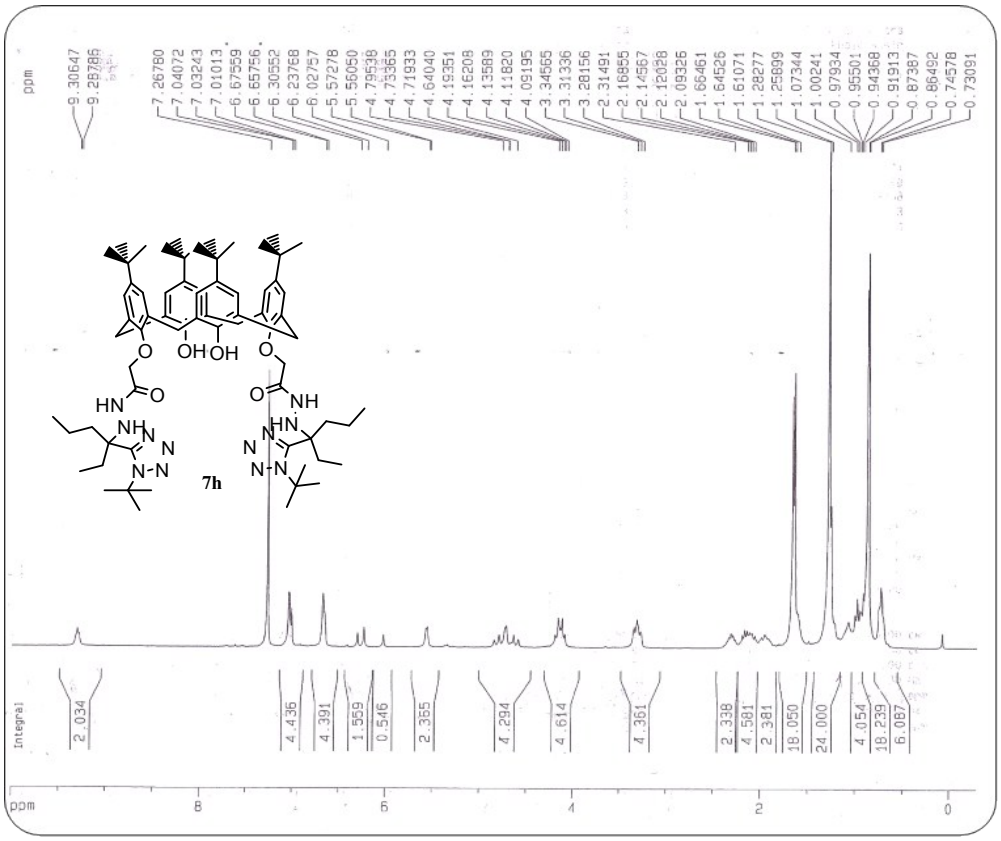


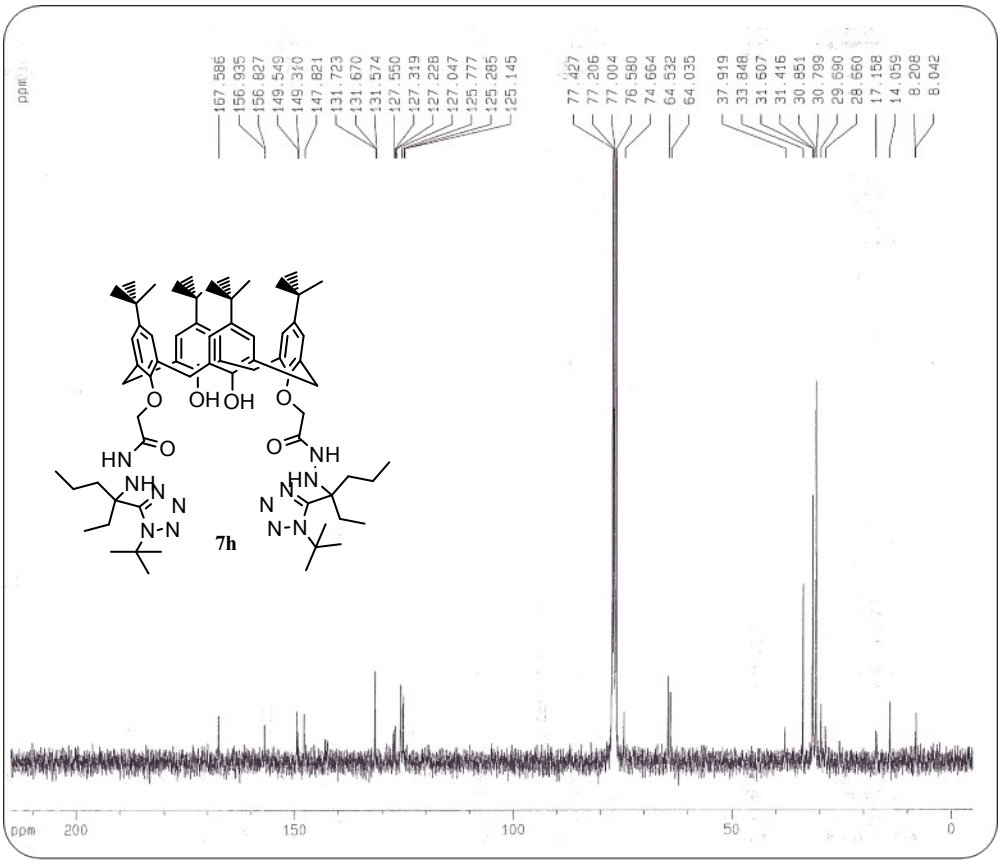
Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7g**



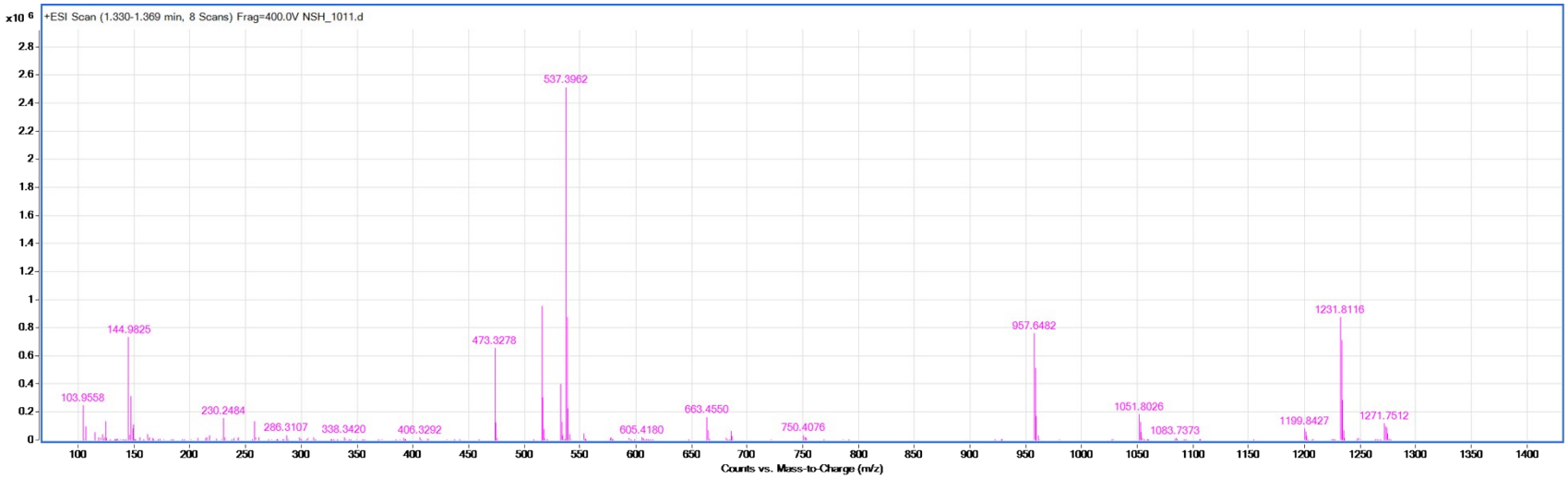
Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7g**	C74 H108 N12 O6	1260.8515	1261.8588	1283.8407	1261.8602	-1.15	1283.8426	-1.27

Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7h**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7h**	C70 H104 N12 O6	1208.8202	1209.8275	1231.8094	ND	-	1231.8116	-1.82



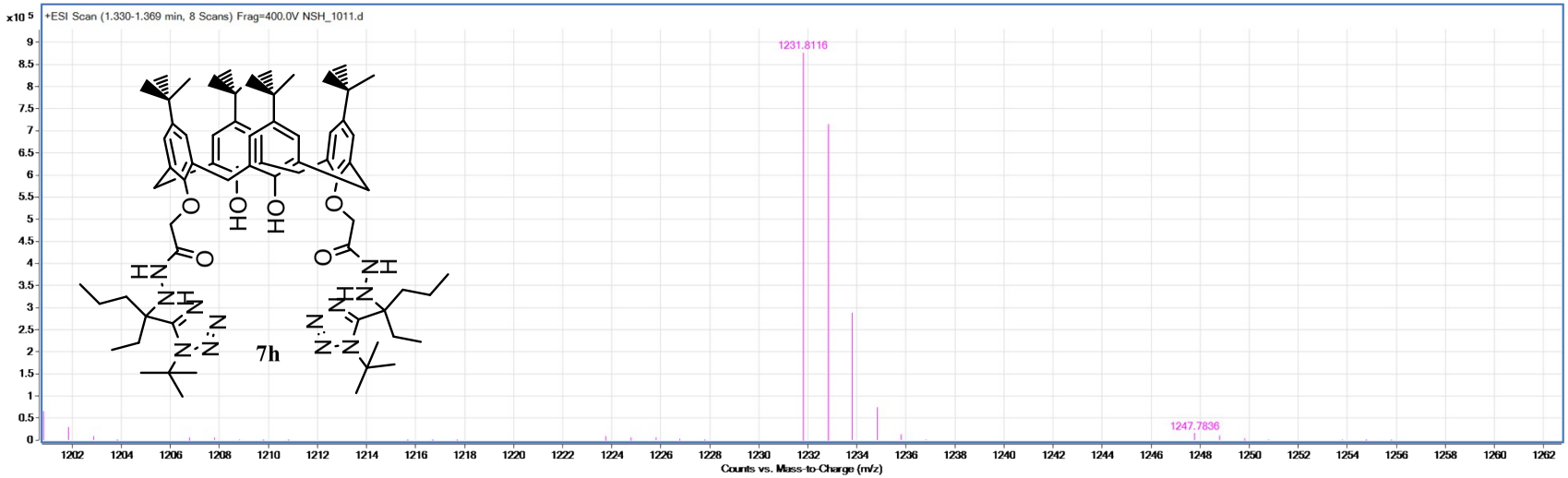
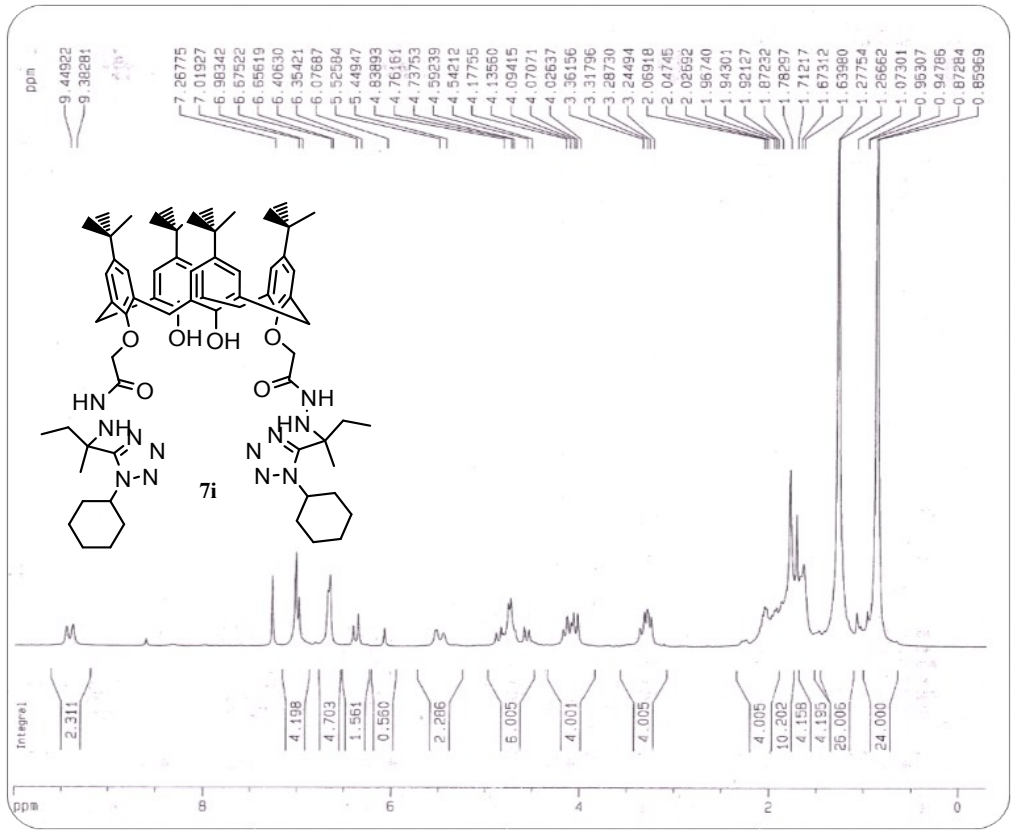
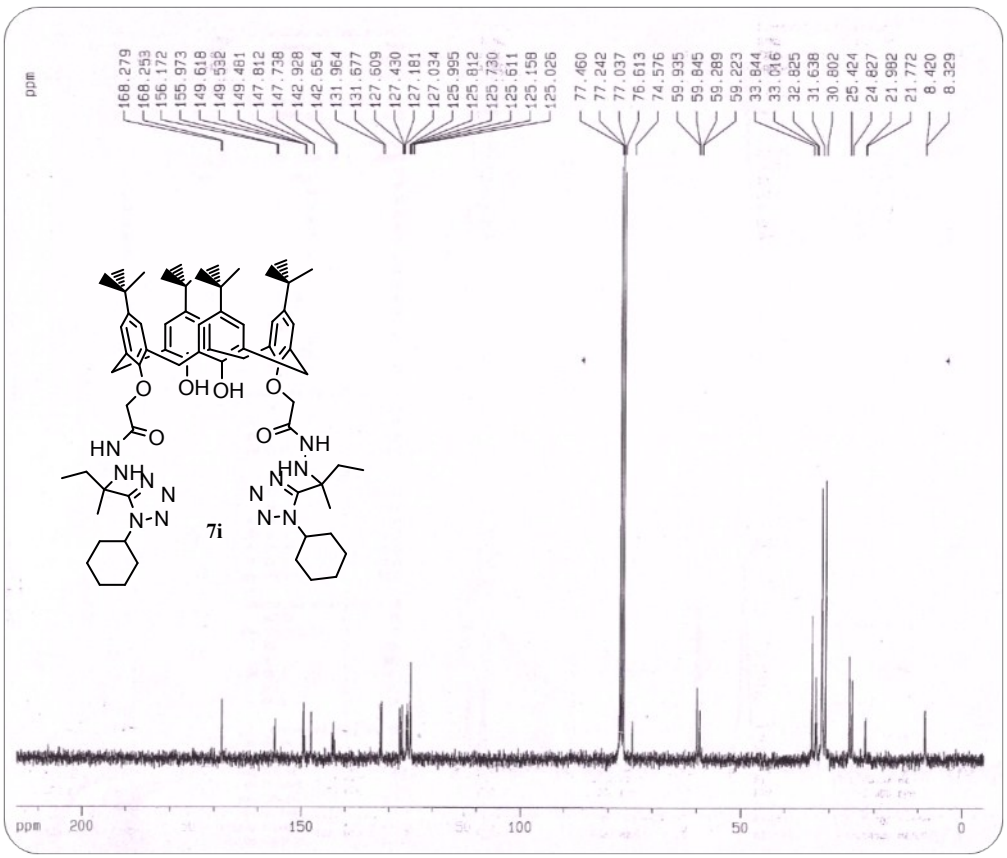
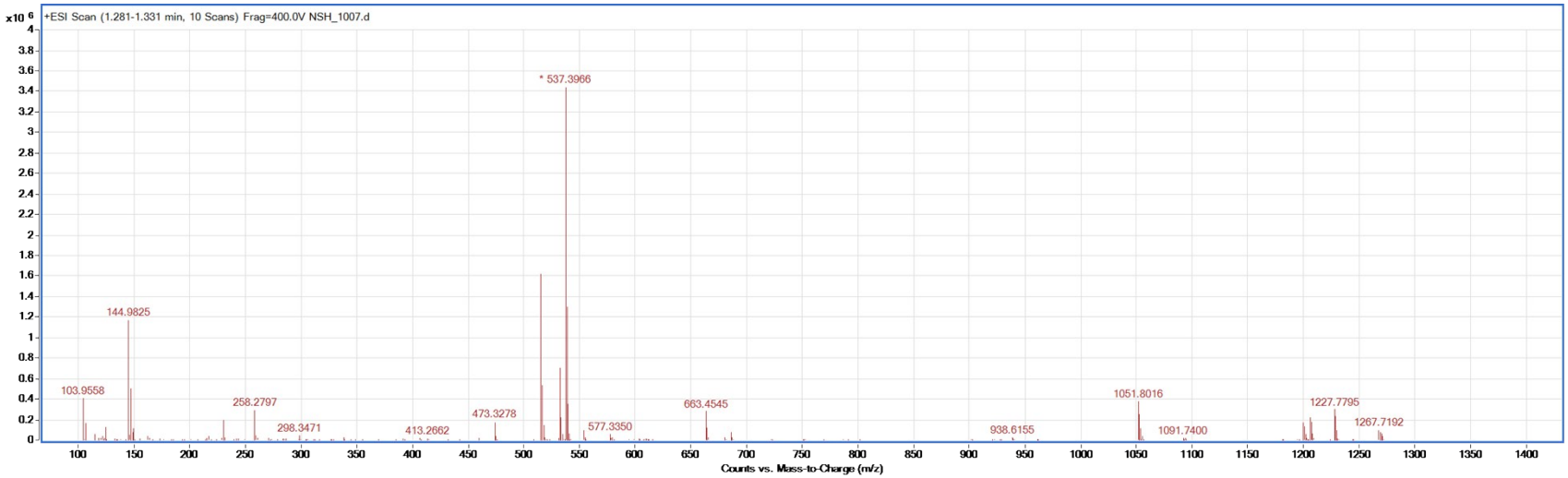


Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7i**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7i**	C70 H100 N12 O6	1204.7889	1205.7962	1227.7781	1205.7976	-1.20	1227.7795	-1.16



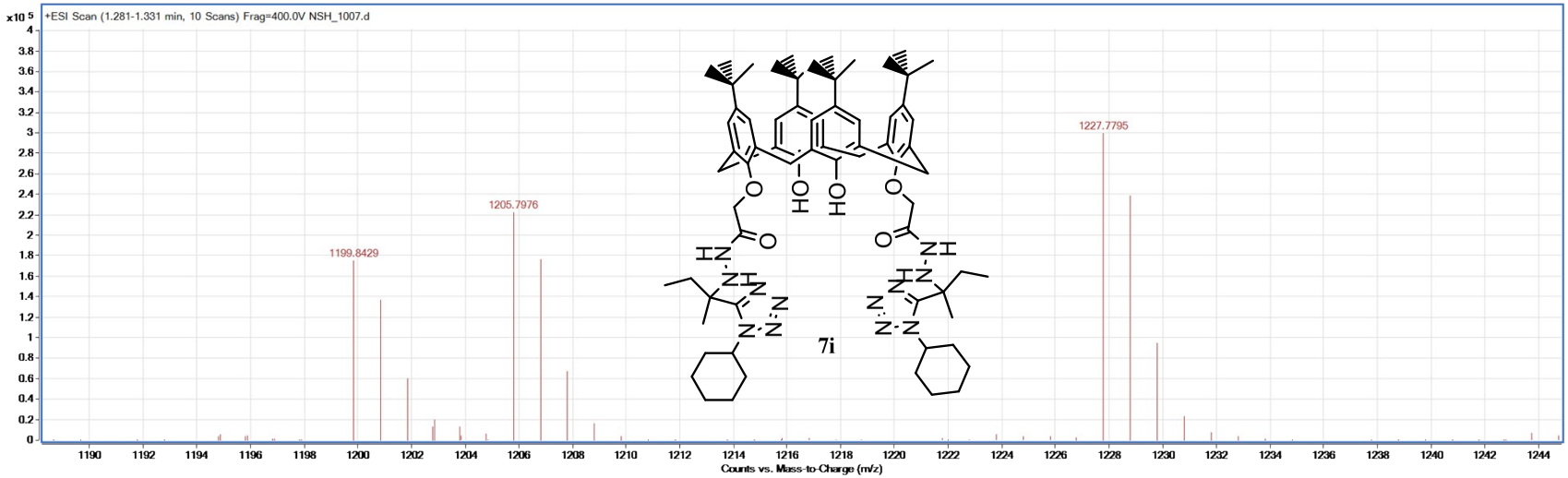
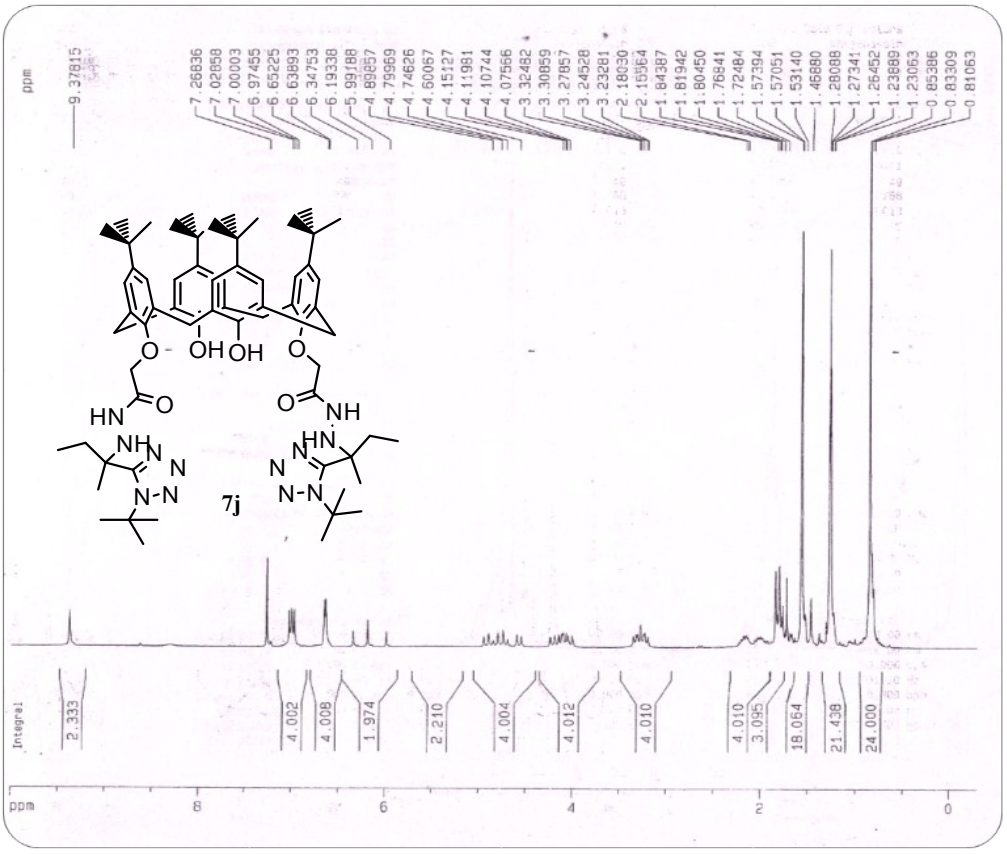
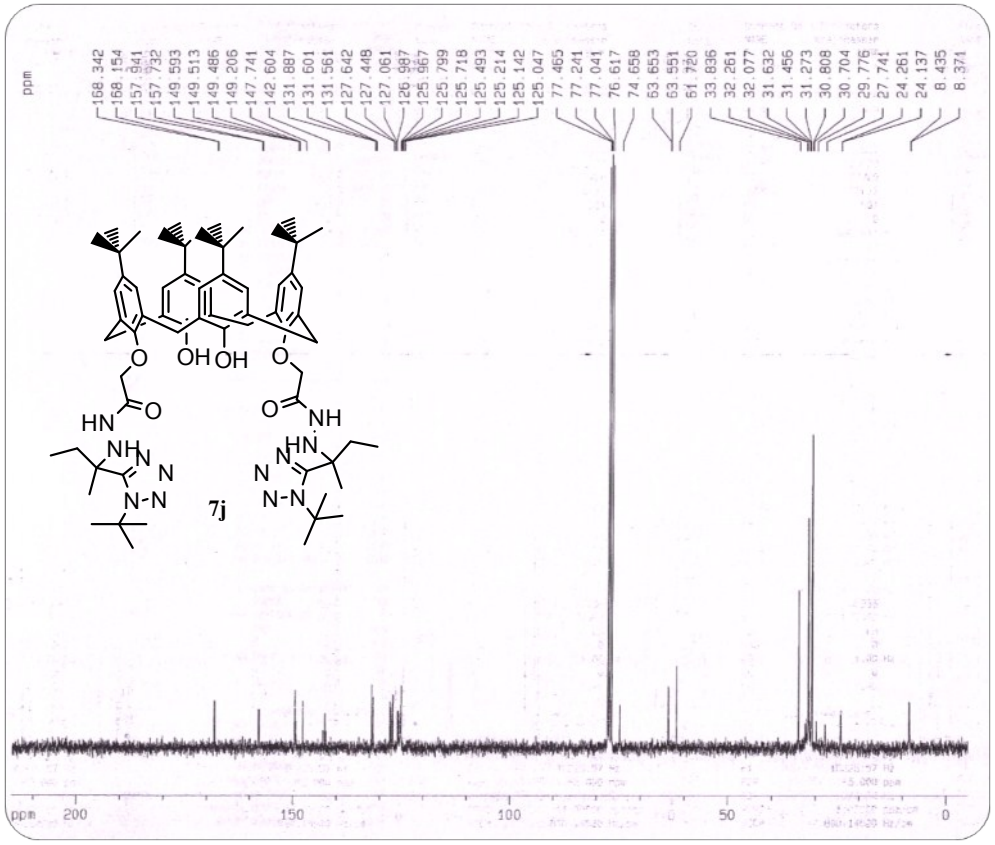
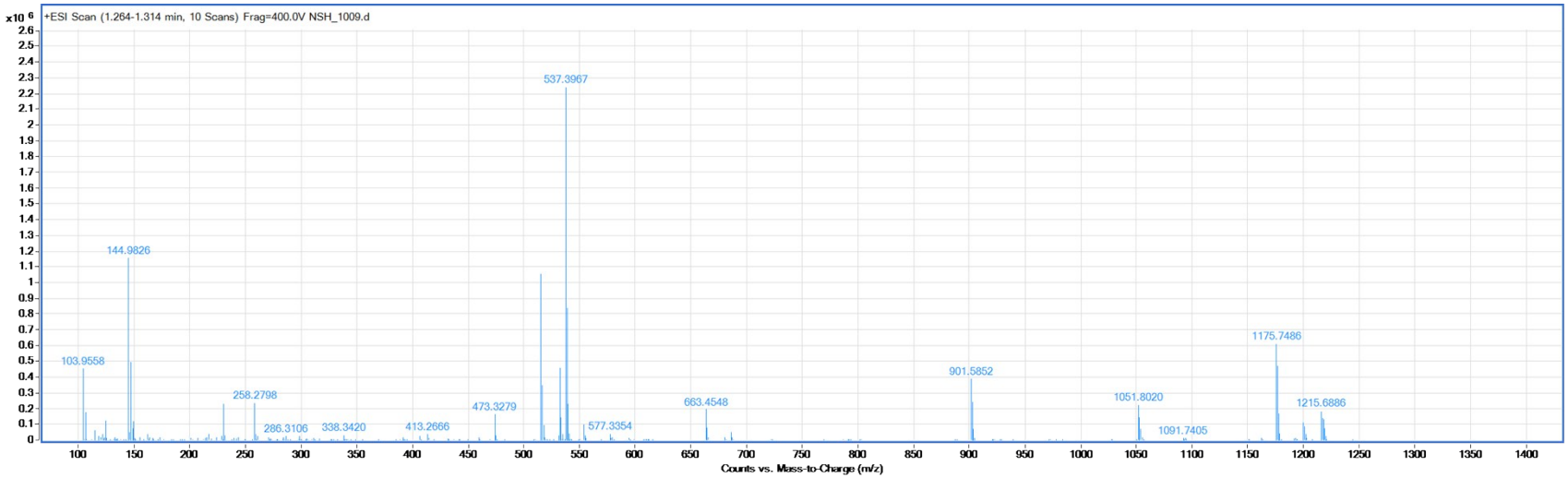


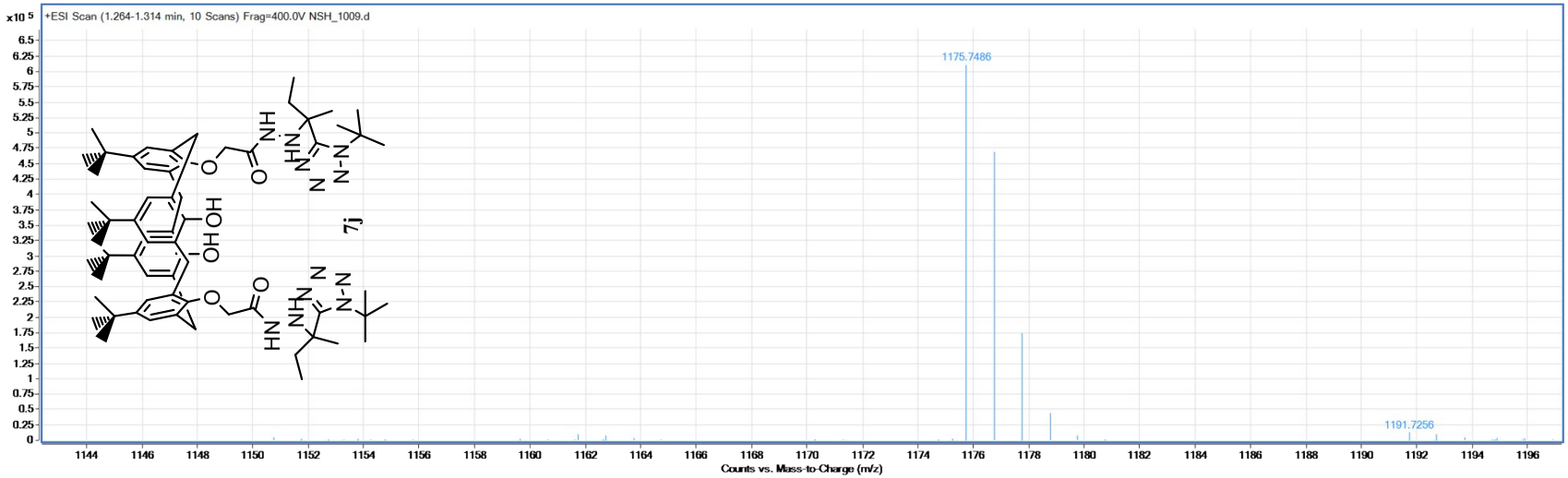
Figure S1 ^{1}H NMR and ^{13}C NMR spectra of **7j**





Compound	Nominal formula	Calculated masses			Ions detected (m/z)			
		Molecule	[M+H]+	[M+Na]+	[M+H]+	Error (ppm)	[M+Na]+	Error (ppm)
Compound **7j**	C66 H96 N12 O6	1152.7576	1153.7649	1175.7468	ND	-	1175.7486	-1.56





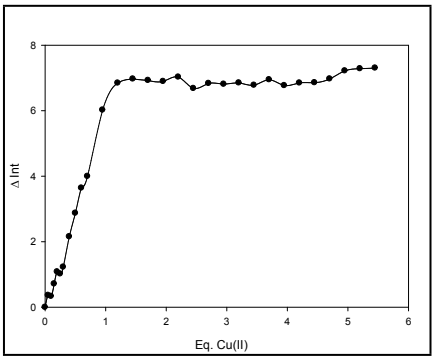
Fluorescence response of 7a-7j to various metal ions at 612 nm in CH_3CN:

$C_{\text{Compound 7a}} = 10^{-4}$ mol/l, $V_{\text{Compound 7a}} = 2000$ μL, $C_{Cu(ClO4)2} = 10^{-3}$ mol/l

Volume of $Cu(ClO_4)_2$ μL	$C_{\text{Compound 7a}}$ mol/l	$C_{Cu^{2+}}$ mol/l	ratio $C_{Cu^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.0001	0	0	28.0717	0
10	9.95025E-05	4.98E-06	0.05	27.7095	0.3622
20	9.90099E-05	9.9E-06	0.1	27.738	0.3337
30	9.85222E-05	1.48E-05	0.15	27.3601	0.7116
40	9.80392E-05	1.96E-05	0.2	26.9906	1.0811
50	9.7561E-05	2.44E-05	0.25	27.0544	1.0173
60	9.70874E-05	2.91E-05	0.3	26.8477	1.224
80	9.61538E-05	3.85E-05	0.4	25.9192	2.1525
100	9.52381E-05	4.76E-05	0.5	25.2006	2.8711
120	9.43396E-05	5.66E-05	0.6	24.4325	3.6392
140	9.34579E-05	6.54E-05	0.7	24.0772	3.9945
190	9.13242E-05	8.68E-05	0.95	22.0518	6.0199
240	8.92857E-05	0.000107	1.2	21.2266	6.8451
290	8.73362E-05	0.000127	1.45	21.1031	6.9686
340	8.54701E-05	0.000145	1.7	21.1464	6.9253
390	8.3682E-05	0.000163	1.95	21.1763	6.8954
440	8.19672E-05	0.00018	2.2	21.0429	7.0288
490	8.03213E-05	0.000197	2.45	21.391	6.6807
540	7.87402E-05	0.000213	2.7	21.238	6.8337
590	7.72201E-05	0.000228	2.95	21.2608	6.8109
640	7.57576E-05	0.000242	3.2	21.223	6.8487
690	7.43494E-05	0.000257	3.45	21.2927	6.779
740	7.29927E-05	0.00027	3.7	21.1255	6.9462
790	7.16846E-05	0.000283	3.95	21.303	6.7687
840	7.04225E-05	0.000296	4.2	21.2238	6.8479
890	6.92042E-05	0.000308	4.45	21.2163	6.8554
940	6.80272E-05	0.00032	4.7	21.101	6.9707
990	6.68896E-05	0.000331	4.95	20.8539	7.2178
1040	6.57895E-05	0.000342	5.2	20.7883	7.2834
1090	6.47249E-05	0.000353	5.45	20.7684	7.3033

Graphical representation of the titration curve:

K_a = **422000** M^{-1}

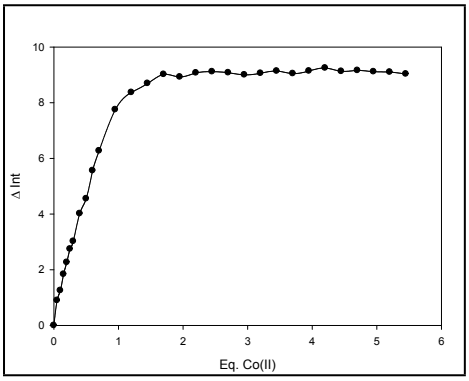


$C_{\text{Compound 7a}} = 10^{-4}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Co(ClO4)2} = 10^{-3}$ mol/l

Volume of $Co(ClO_4)_2$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Co^{2+}}$ mol/l	ratio $C_{Co^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.0001	0	0	29.4114	0
10	9.95E-05	4.98E-06	0.05	28.5138	0.8976
20	9.9E-05	9.9E-06	0.1	28.1576	1.2538
30	9.85E-05	1.48E-05	0.15	27.5738	1.8376
40	9.8E-05	1.96E-05	0.2	27.1452	2.2662
50	9.76E-05	2.44E-05	0.25	26.6668	2.7446
60	9.71E-05	2.91E-05	0.3	26.3909	3.0205
80	9.62E-05	3.85E-05	0.4	25.3934	4.018
100	9.52E-05	4.76E-05	0.5	24.8603	4.5511
120	9.43E-05	5.66E-05	0.6	23.85	5.5614
140	9.35E-05	6.54E-05	0.7	23.139	6.2724
190	9.13E-05	8.68E-05	0.95	21.6608	7.7506
240	8.93E-05	0.000107	1.2	21.0401	8.3713
290	8.73E-05	0.000127	1.45	20.718	8.6934
340	8.55E-05	0.000145	1.7	20.3909	9.0205
390	8.37E-05	0.000163	1.95	20.4848	8.9266
440	8.2E-05	0.00018	2.2	20.3393	9.0721
490	8.03E-05	0.000197	2.45	20.2968	9.1146
540	7.87E-05	0.000213	2.7	20.3325	9.0789
590	7.72E-05	0.000228	2.95	20.4088	9.0026
640	7.58E-05	0.000242	3.2	20.3527	9.0587
690	7.43E-05	0.000257	3.45	20.274	9.1374
740	7.3E-05	0.00027	3.7	20.3643	9.0471
790	7.17E-05	0.000283	3.95	20.2701	9.1413
840	7.04E-05	0.000296	4.2	20.1637	9.2477
890	6.92E-05	0.000308	4.45	20.2817	9.1297
940	6.8E-05	0.00032	4.7	20.2502	9.1612
990	6.69E-05	0.000331	4.95	20.296	9.1154
1040	6.58E-05	0.000342	5.2	20.3099	9.1015
1090	6.47E-05	0.000353	5.45	20.3793	9.0321

Graphical representation of the titration curve:

K_a = **599000** M^{-1}

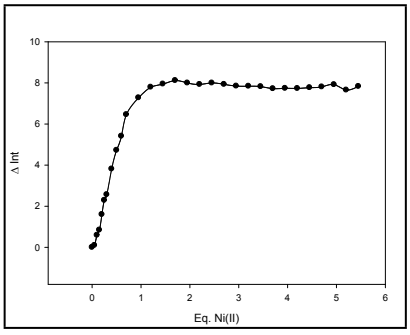


$C_{\text{Compound 7a}} = 10^{-4}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Ni(ClO4)2} = 10^{-3}$ mol/l

Volume of $Ni(ClO_4)_2$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Ni^{2+}}$ mol/l	ratio $C_{Ni^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.0001	0	0	27.0572	0
10	9.95E-05	4.98E-06	0.05	26.9589	0.0983
20	9.9E-05	9.9E-06	0.1	26.4687	0.5885
30	9.85E-05	1.48E-05	0.15	26.2148	0.8424
40	9.8E-05	1.96E-05	0.2	25.4589	1.5983
50	9.76E-05	2.44E-05	0.25	24.7688	2.2884
60	9.71E-05	2.91E-05	0.3	24.49411	2.56309
80	9.62E-05	3.85E-05	0.4	23.2449	3.8123
100	9.52E-05	4.76E-05	0.5	22.336	4.7212
120	9.43E-05	5.66E-05	0.6	21.6474	5.4098
140	9.35E-05	6.54E-05	0.7	20.5982	6.459
190	9.13E-05	8.68E-05	0.95	19.7811	7.2761
240	8.93E-05	0.000107	1.2	19.2648	7.7924
290	8.73E-05	0.000127	1.45	19.1111	7.9461
340	8.55E-05	0.000145	1.7	18.9404	8.1168
390	8.37E-05	0.000163	1.95	19.0602	7.997
440	8.2E-05	0.00018	2.2	19.1292	7.928
490	8.03E-05	0.000197	2.45	19.0601	7.9971
540	7.87E-05	0.000213	2.7	19.1271	7.9301
590	7.72E-05	0.000228	2.95	19.2099	7.8473
640	7.58E-05	0.000242	3.2	19.2182	7.839
690	7.43E-05	0.000257	3.45	19.238	7.8192
740	7.3E-05	0.00027	3.7	19.3356	7.7216
790	7.17E-05	0.000283	3.95	19.3216	7.7356
840	7.04E-05	0.000296	4.2	19.3261	7.7311
890	6.92E-05	0.000308	4.45	19.2885	7.7687
940	6.8E-05	0.00032	4.7	19.2516	7.8056
990	6.69E-05	0.000331	4.95	19.1396	7.9176
1040	6.58E-05	0.000342	5.2	19.4048	7.6524
1090	6.47E-05	0.000353	5.45	19.2275	7.8297

Graphical representation of the titration curve:

K_a = **17000000** M^{-1}

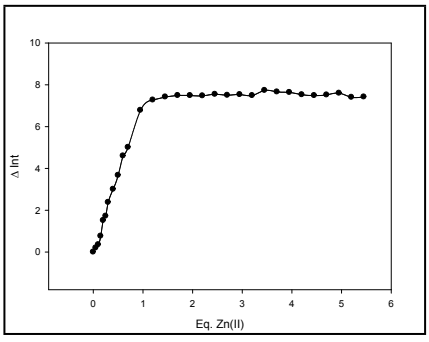


$C_{\text{Compound 7a}} = 10^{-4}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Zn(ClO4)2} = 10^{-3}$ mol/l

Volume of $Zn(ClO_4)_2$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Zn^{2+}}$ mol/l	ratio $C_{Zn^{2+}} / C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.0001	0	0	28.0224	0
10	9.95E-05	4.98E-06	0.05	27.8248	0.1976
20	9.9E-05	9.9E-06	0.1	27.669	0.3534
30	9.85E-05	1.48E-05	0.15	27.2607	0.7617
40	9.8E-05	1.96E-05	0.2	26.5106	1.5118
50	9.76E-05	2.44E-05	0.25	26.3053	1.7171
60	9.71E-05	2.91E-05	0.3	25.6449	2.3775
80	9.62E-05	3.85E-05	0.4	25.0174	3.005
100	9.52E-05	4.76E-05	0.5	24.3523	3.6701
120	9.43E-05	5.66E-05	0.6	23.423	4.5994
140	9.35E-05	6.54E-05	0.7	23.0141	5.0083
190	9.13E-05	8.68E-05	0.95	21.2407	6.7817
240	8.93E-05	0.000107	1.2	20.7484	7.274
290	8.73E-05	0.000127	1.45	20.6019	7.4205
340	8.55E-05	0.000145	1.7	20.5324	7.49
390	8.37E-05	0.000163	1.95	20.5367	7.4857
440	8.2E-05	0.00018	2.2	20.5484	7.474
490	8.03E-05	0.000197	2.45	20.4759	7.5465
540	7.87E-05	0.000213	2.7	20.521	7.5014
590	7.72E-05	0.000228	2.95	20.4877	7.5347
640	7.58E-05	0.000242	3.2	20.5349	7.4875
690	7.43E-05	0.000257	3.45	20.2902	7.7322
740	7.3E-05	0.00027	3.7	20.3611	7.6613
790	7.17E-05	0.000283	3.95	20.3848	7.6376
840	7.04E-05	0.000296	4.2	20.4954	7.527
890	6.92E-05	0.000308	4.45	20.5361	7.4863
940	6.8E-05	0.00032	4.7	20.5039	7.5185
990	6.69E-05	0.000331	4.95	20.4212	7.6012
1040	6.58E-05	0.000342	5.2	20.6196	7.4028
1090	6.47E-05	0.000353	5.45	20.6024	7.42

Graphical representation of the titration curve:

K_a = **1430000** M^{-1}

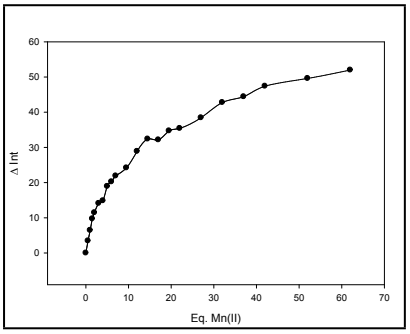


$C_{\text{Compound 7a}} = 10^{-5}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Mn(ClO4)2} = 10^{-3}$ mol/l

Volume of $Mn(ClO_4)_2$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Mn^{2+}}$ mol/l	ratio $C_{Mn^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.00001	0	0	109.944	0
10	9.95E-06	4.98E-06	0.5	106.481	3.463
20	9.9E-06	9.9E-06	1	103.489	6.455
30	9.85E-06	1.48E-05	1.5	100.227	9.717
40	9.8E-06	1.96E-05	2	98.4847	11.4593
60	9.71E-06	2.91E-05	3	95.8304	14.1136
80	9.62E-06	3.85E-05	4	95.1029	14.8411
100	9.52E-06	4.76E-05	5	91.0004	18.9436
120	9.43E-06	5.66E-05	6	89.7039	20.2401
140	9.35E-06	6.54E-05	7	88.0288	21.9152
190	9.13E-06	8.68E-05	9.5	85.7394	24.2046
240	8.93E-06	0.000107	12	81.0573	28.8867
290	8.73E-06	0.000127	14.5	77.5552	32.3888
340	8.55E-06	0.000145	17	77.7853	32.1587
390	8.37E-06	0.000163	19.5	75.2313	34.7127
440	8.2E-06	0.00018	22	74.527	35.417
540	7.87E-06	0.000213	27	71.5114	38.4326
640	7.58E-06	0.000242	32	67.1674	42.7766
740	7.3E-06	0.00027	37	65.5336	44.4104
840	7.04E-06	0.000296	42	62.5433	47.4007
1040	6.58E-06	0.000342	52	60.3417	49.6023
1240	6.17E-06	0.000383	62	57.9559	51.9881

Graphical representation of the titration curve:

$K_a = \mathbf{7767}\ M^{-1}$

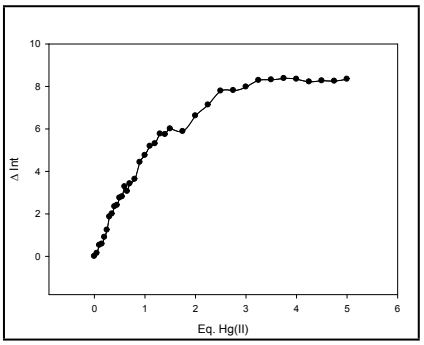


$C_{\text{Compound 7a}} = 10^{-4}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Hg(ClO4)2} = 10^{-3}$ mol/l

Volume of $Hg(ClO_4)_2$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Hg^{2+}}$ mol/l	ratio $C_{Hg^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.0001	0	0	29.431	0
10	9.95E-05	4.98E-06	0.05	29.2892	0.1418
20	9.9E-05	9.9E-06	0.1	28.9085	0.5225
30	9.85E-05	1.48E-05	0.15	28.8504	0.5806
40	9.8E-05	1.96E-05	0.2	28.533	0.898
50	9.76E-05	2.44E-05	0.25	28.1934	1.2376
60	9.71E-05	2.91E-05	0.3	27.5697	1.8613
70	9.66E-05	3.38E-05	0.35	27.4309	2.0001
80	9.62E-05	3.85E-05	0.4	27.0898	2.3412
90	9.57E-05	4.31E-05	0.45	27.0259	2.4051
100	9.52E-05	4.76E-05	0.5	26.6792	2.7518
110	9.48E-05	5.21E-05	0.55	26.623	2.808
120	9.43E-05	5.66E-05	0.6	26.1508	3.2802
130	9.39E-05	6.1E-05	0.65	26.3716	3.0594
140	9.35E-05	6.54E-05	0.7	26.0106	3.4204
160	9.26E-05	7.41E-05	0.8	25.8009	3.6301
180	9.17E-05	8.26E-05	0.9	25.0008	4.4302
200	9.09E-05	9.09E-05	1	24.6737	4.7573
220	9.01E-05	9.91E-05	1.1	24.2454	5.1856
240	8.93E-05	0.000107	1.2	24.1238	5.3072
260	8.85E-05	0.000115	1.3	23.6666	5.7644
280	8.77E-05	0.000123	1.4	23.6913	5.7397
300	8.7E-05	0.00013	1.5	23.4245	6.0065
350	8.51E-05	0.000149	1.75	23.5476	5.8834
400	8.33E-05	0.000167	2	22.8144	6.6166
450	8.16E-05	0.000184	2.25	22.3016	7.1294
500	0.00008	0.0002	2.5	21.6454	7.7856
550	7.84E-05	0.000216	2.75	21.6202	7.8108
600	7.69E-05	0.000231	3	21.4534	7.9776
650	7.55E-05	0.000245	3.25	21.1446	8.2864
700	7.41E-05	0.000259	3.5	21.1182	8.3128
750	7.27E-05	0.000273	3.75	21.054	8.377
800	7.14E-05	0.000286	4	21.0884	8.3426
850	7.02E-05	0.000298	4.25	21.2129	8.2181
900	6.9E-05	0.00031	4.5	21.1649	8.2661
950	6.78E-05	0.000322	4.75	21.1797	8.2513
1000	6.67E-05	0.000333	5	21.087	8.344

Graphical representation of the titration curve:

K_a = **15100** M^{-1}

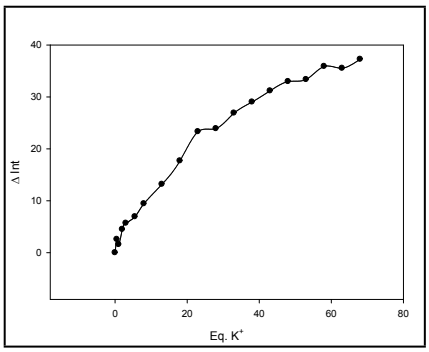


$C_{\text{Compound 7a}} = 10^{-5}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{K(ClO4)} = 10^{-3}$ mol/l

Volume of $K(ClO_4)$ µL	$C_{\text{Compound 7a}}$ mol/l	C_{K^+} mol/l	ratio $C_{K^+}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.00001	0	0	116.945	0
10	9.95E-06	4.98E-06	0.5	114.37	2.575
20	9.9E-06	9.9E-06	1	115.356	1.589
40	9.8E-06	1.96E-05	2	112.449	4.496
60	9.71E-06	2.91E-05	3	111.266	5.679
110	9.48E-06	5.21E-05	5.5	110.017	6.928
160	9.26E-06	7.41E-05	8	107.515	9.43
260	8.85E-06	0.000115	13	103.775	13.17
360	8.47E-06	0.000153	18	99.2604	17.6846
460	8.13E-06	0.000187	23	93.6251	23.3199
560	7.81E-06	0.000219	28	93.0449	23.9001
660	7.52E-06	0.000248	33	90.0451	26.8999
760	7.25E-06	0.000275	38	87.9231	29.0219
860	6.99E-06	0.000301	43	85.7729	31.1721
960	6.76E-06	0.000324	48	83.9735	32.9715
1060	6.54E-06	0.000346	53	83.5951	33.3499
1160	6.33E-06	0.000367	58	81.0567	35.8883
1260	6.13E-06	0.000387	63	81.424	35.521
1360	5.95E-06	0.000405	68	79.6893	37.2557

Graphical representation of the titration curve:

K_a = **1560** M^{-1}

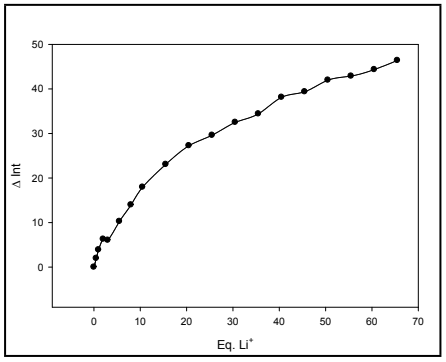


$C_{\text{Compound 7a}} = 10^{-5}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Li(ClO4)} = 10^{-3}$ mol/l

Volume of $Li(ClO_4)$ µL	$C_{\text{Compound 7a}}$ mol/l	C_{Li^+} mol/l	ratio $C_{Li^+}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.00001	0	0	118.097	0
10	9.95E-06	4.98E-06	0.5	116.134	1.963
20	9.9E-06	9.9E-06	1	114.22	3.877
40	9.8E-06	1.96E-05	2	111.812	6.285
60	9.71E-06	2.91E-05	3	112.044	6.053
110	9.48E-06	5.21E-05	5.5	107.843	10.254
160	9.26E-06	7.41E-05	8	104.133	13.964
210	9.05E-06	9.5E-05	10.5	100.139	17.958
310	8.66E-06	0.000134	15.5	95.0316	23.0654
410	8.3E-06	0.00017	20.5	90.8363	27.2607
510	7.97E-06	0.000203	25.5	88.4845	29.6125
610	7.66E-06	0.000234	30.5	85.5987	32.4983
710	7.38E-06	0.000262	35.5	83.6997	34.3973
810	7.12E-06	0.000288	40.5	79.956	38.141
910	6.87E-06	0.000313	45.5	78.7356	39.3614
1010	6.64E-06	0.000336	50.5	76.1206	41.9764
1110	6.43E-06	0.000357	55.5	75.2107	42.8863
1210	6.23E-06	0.000377	60.5	73.7461	44.3509
1310	6.04E-06	0.000396	65.5	71.7094	46.3876

Graphical representation of the titration curve:

K_a = **2480** M^{-1}

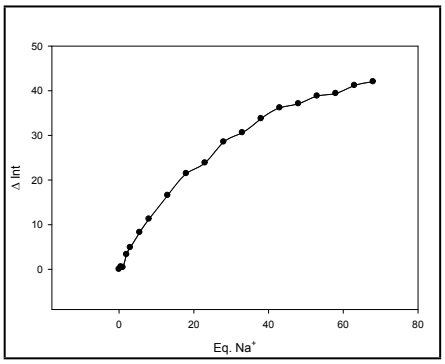


$C_{\text{Compound 7a}} = 10^{-5}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Na(ClO4)} = 10^{-3}$ mol/l

Volume of $Na(ClO_4)$ µL	$C_{\text{Compound 7a}}$ mol/l	C_{Na^+} mol/l	ratio $C_{Na^+}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.00001	0	0	112.327	0
10	9.95E-06	4.98E-06	0.5	111.784	0.543
20	9.9E-06	9.9E-06	1	111.91	0.417
40	9.8E-06	1.96E-05	2	109.01	3.317
60	9.71E-06	2.91E-05	3	107.441	4.886
110	9.48E-06	5.21E-05	5.5	104.074	8.253
160	9.26E-06	7.41E-05	8	101.068	11.259
260	8.85E-06	0.000115	13	95.7676	16.5594
360	8.47E-06	0.000153	18	90.8754	21.4516
460	8.13E-06	0.000187	23	88.4908	23.8362
560	7.81E-06	0.000219	28	83.7973	28.5297
660	7.52E-06	0.000248	33	81.7158	30.6112
760	7.25E-06	0.000275	38	78.5752	33.7518
860	6.99E-06	0.000301	43	76.1528	36.1742
960	6.76E-06	0.000324	48	75.2479	37.0791
1060	6.54E-06	0.000346	53	73.5115	38.8155
1160	6.33E-06	0.000367	58	72.944	39.383
1260	6.13E-06	0.000387	63	71.1503	41.1767
1360	5.95E-06	0.000405	68	70.31	42.017

Graphical representation of the titration curve:

K_a = **1640** M^{-1}



$C_{\text{Compound 7a}} = 10^{-5}$ mol/l, $V_{\text{Compound 7a}} = 2000$ µL, $C_{Ba(ClO4)} = 10^{-3}$ mol/l

Volume of $Ba(ClO_4)$ µL	$C_{\text{Compound 7a}}$ mol/l	$C_{Ba^{2+}}$ mol/l	ratio $C_{Ba^{2+}}/C_{\text{Compound 7a}}$	Fluorescenc Emission	Relative Emission Difference
0	0.00001	0	0	118.827	0
10	9.95E-06	4.98E-06	0.5	112.643	6.184
20	9.9E-06	9.9E-06	1	112.634	6.193
30	9.85E-06	1.48E-05	1.5	110.801	8.026
50	9.76E-06	2.44E-05	2.5	109.159	9.668
70	9.66E-06	3.38E-05	3.5	105.229	13.598
120	9.43E-06	5.66E-05	6	103.768	15.059
170	9.22E-06	7.83E-05	8.5	100.487	18.34
270	8.81E-06	0.000119	13.5	93.6235	25.2035
370	8.44E-06	0.000156	18.5	89.0758	29.7512
470	8.1E-06	0.00019	23.5	85.5567	33.2703
570	7.78E-06	0.000222	28.5	83.2423	35.5847
670	7.49E-06	0.000251	33.5	79.7273	39.0997
770	7.22E-06	0.000278	38.5	79.4311	39.3959
870	6.97E-06	0.000303	43.5	76.0323	42.7947
970	6.73E-06	0.000327	48.5	72.6436	46.1834
1070	6.51E-06	0.000349	53.5	72.6981	46.1289
1170	6.31E-06	0.000369	58.5	70.3869	48.4401
1270	6.12E-06	0.000388	63.5	68.3988	50.4282
1370	5.93E-06	0.000407	68.5	68.0929	50.7341

Graphical representation of the titration curve:

K_a = **4290** M^{-1}

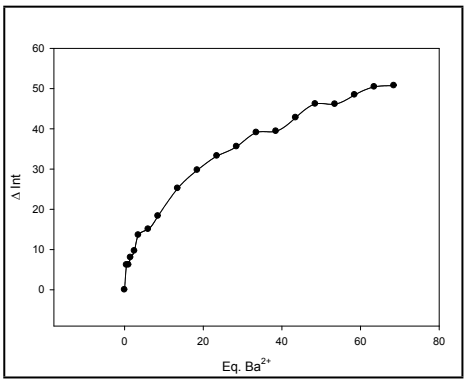


Figure S11 The ^{1}H NMR spectra of **7a** and Ni(II)-**7a**

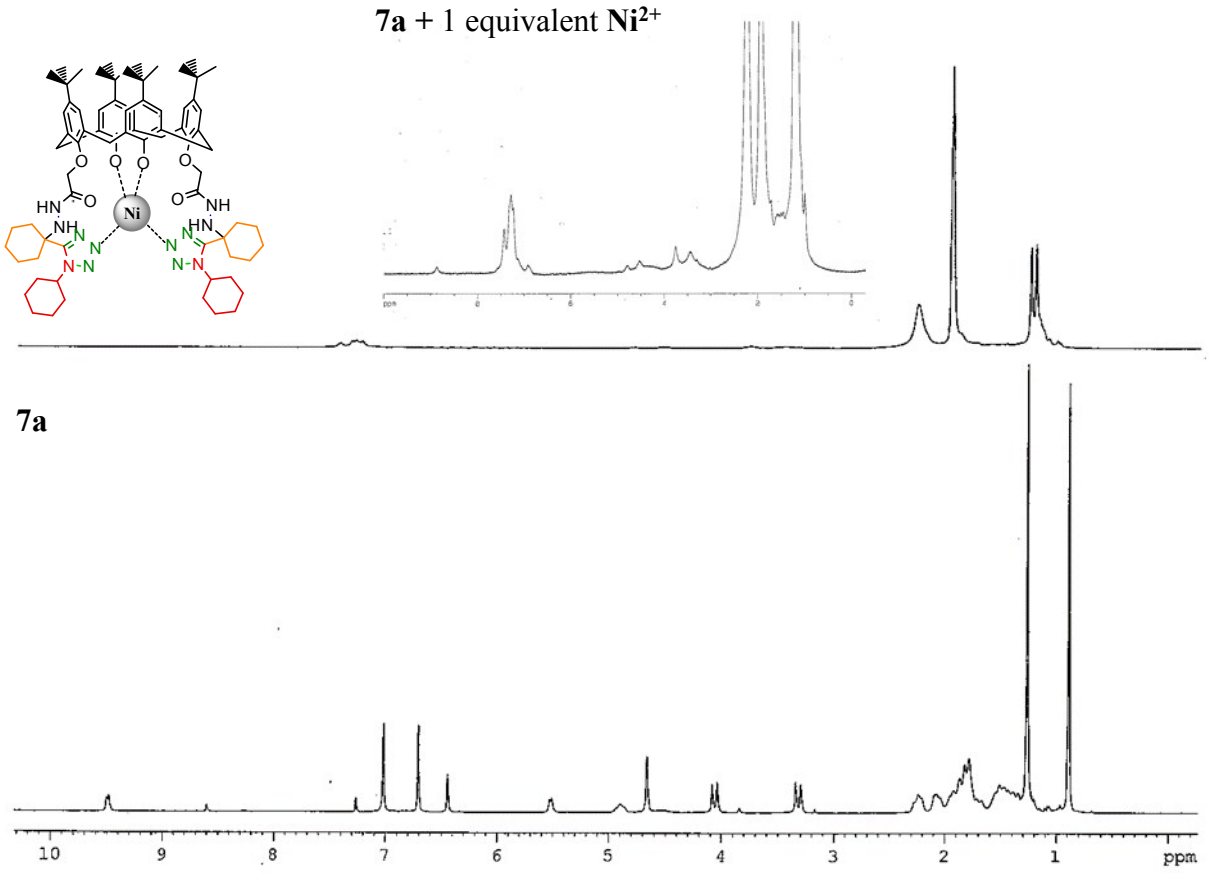
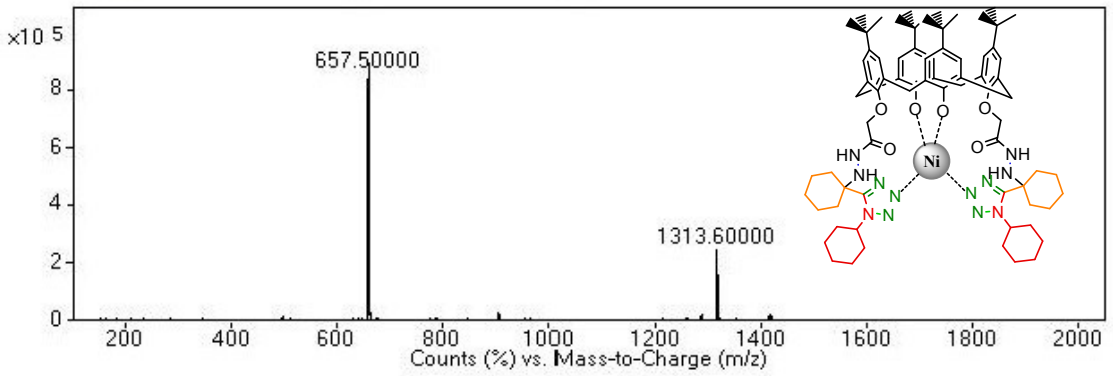
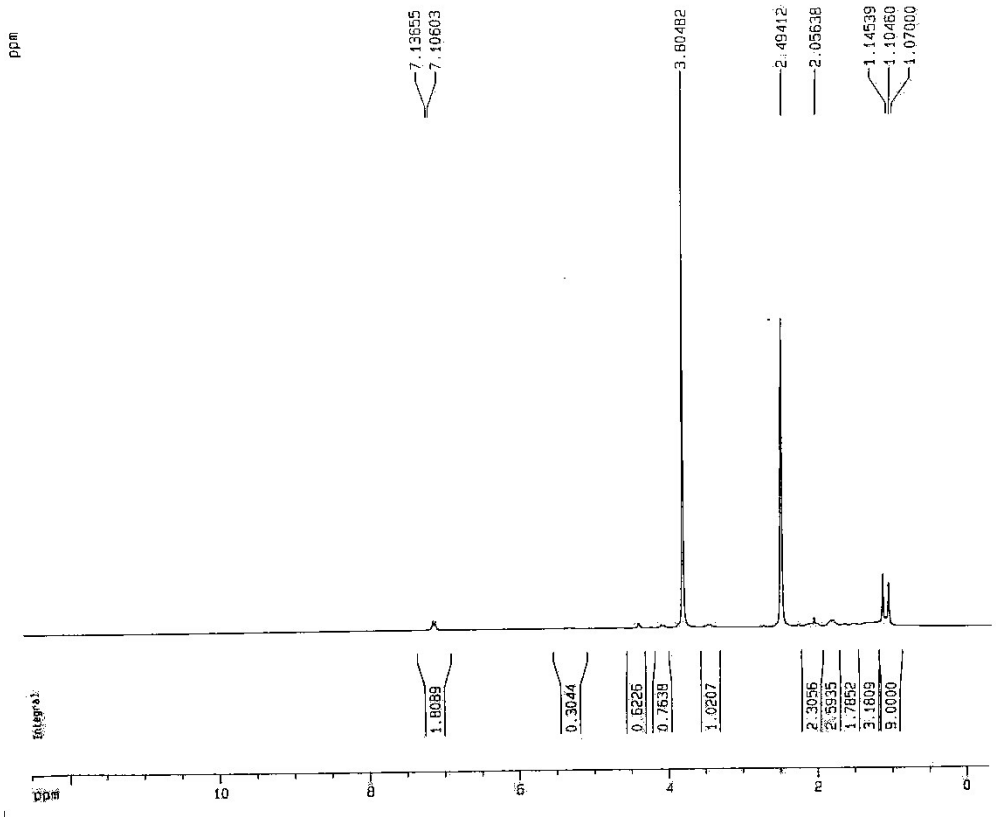


Figure S12 ESI-MS spectra of Ni(II)-**7a** in CH_3CN

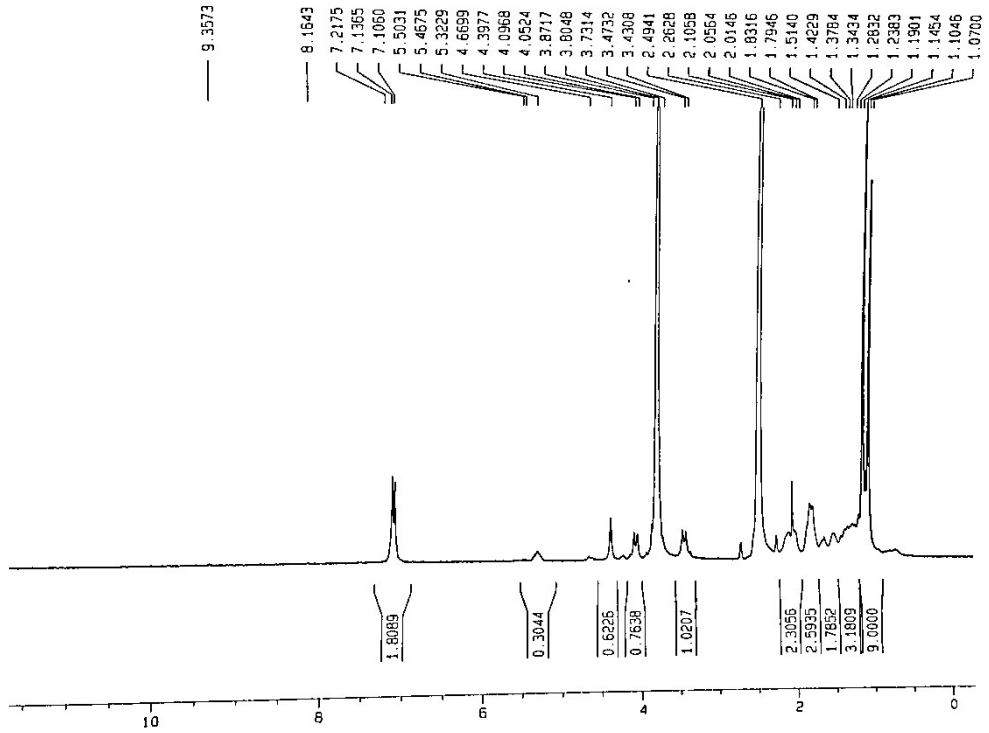
The below mass spectra using electrospray ionisation was recorded with an Agilent 6410 Triple Quadrupole LC/MS.



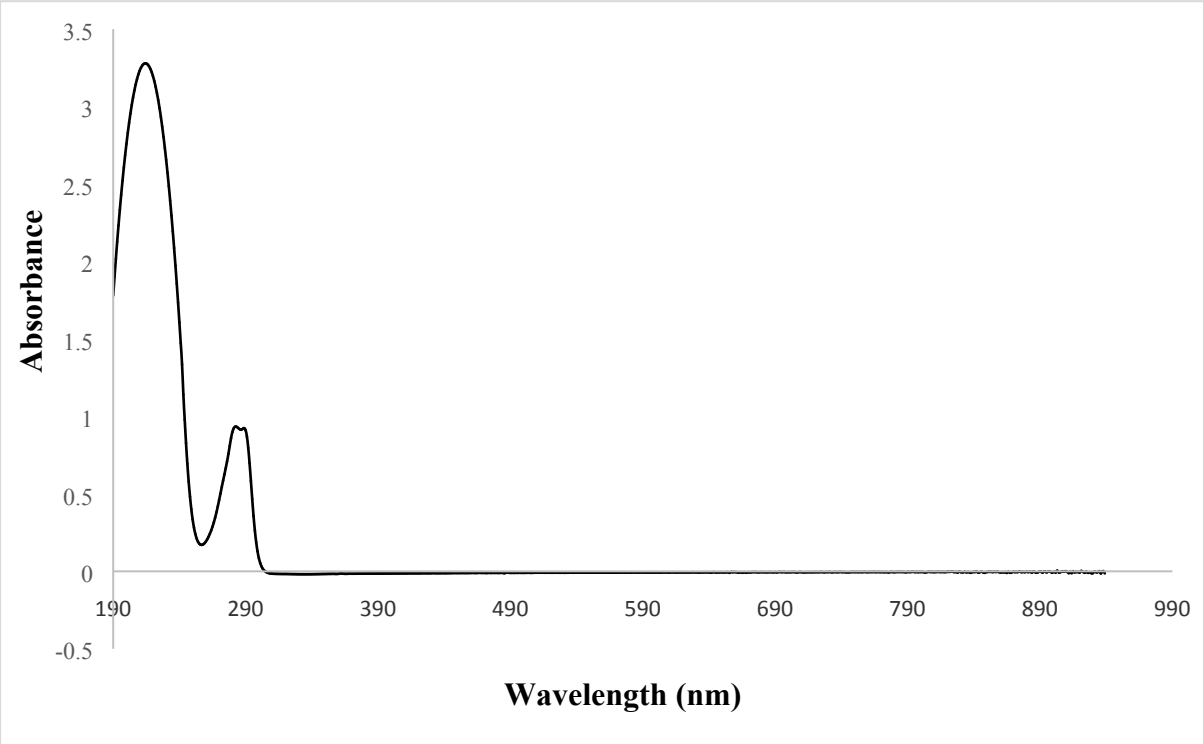
The ^{1}H NMR spectra of **7a** in DMSO-D_2O (**Figure S13**)



Zoomed and expanded spectra of spectra of **7a** in DMSO-D_2O



Full UV/Vis spectrum of compound **7a (Figure S14)**



Fluorescence intensity changes of compound **7c** in MeCN upon addition of 1 equiv. of various metal perchlorates; λex = 280 nm (**Figure S15**).

The binding sites of all the synthesized α-hydrazino tetrazolocalix[4]arenes are the same and alkyl substituents do not have significant effects on binding affinity. Therefore, metal ion binding properties of one of the α-hydrazino tetrazolocalix[4]arenes (**7a**) as the model compound were investigated. In order to prove this the effectiveness of another synthesized α-hydrazino tetrazolocalix[4]arene derivative toward the Ni(II) recognition in CH_3CN has also been investigated.