Benzodithiophene based π-conjugated macrocycle: synthesis, morphology and electrochemical characterizaion

Anjan Bedi,* Sanjio S. Zade*
Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur 741246, India.
[*] email: sanjiozade@iiserkol.ac.in, anjan.bedi@gmail.com

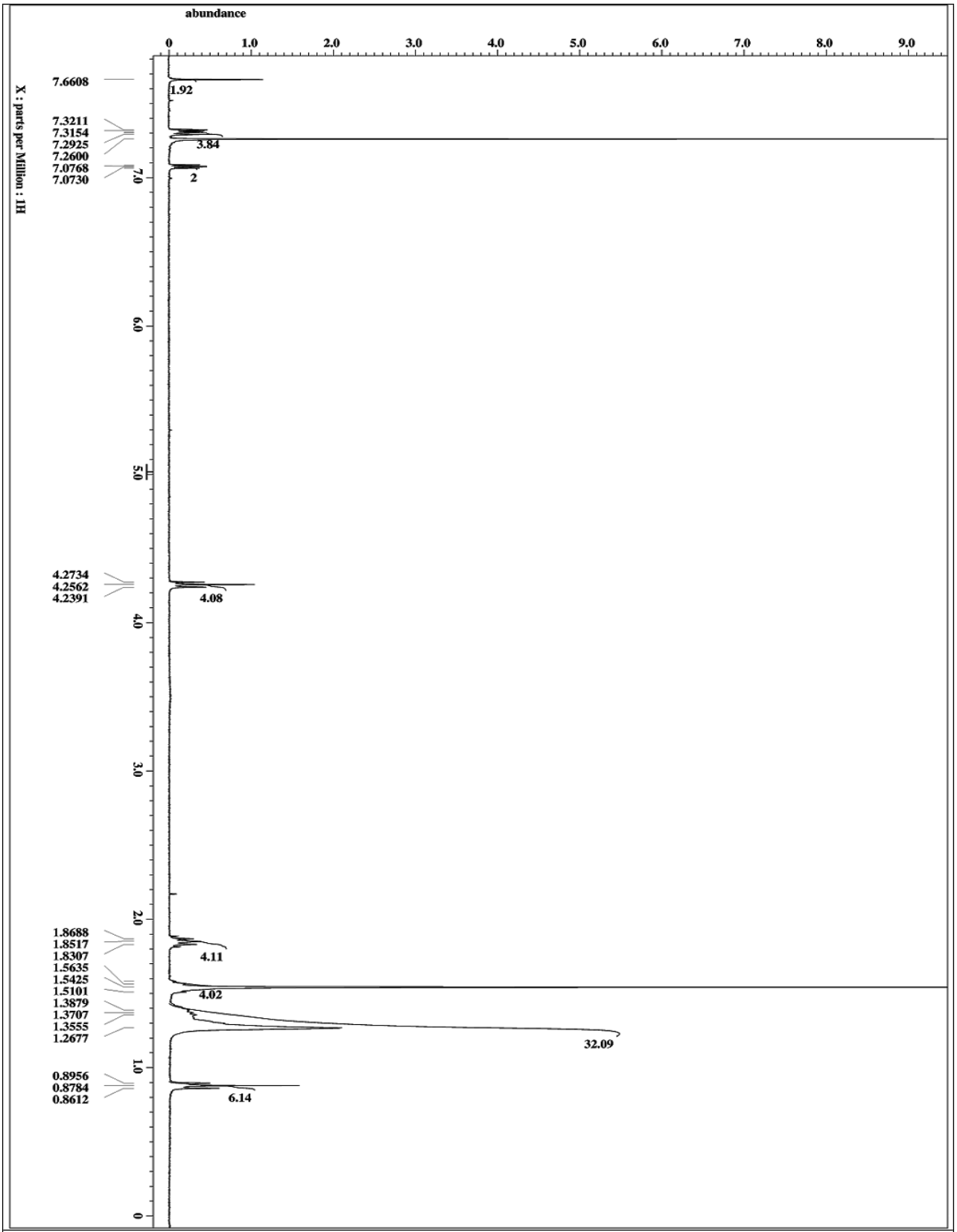


Fig. S1 ^{1}H NMR of compound **3**

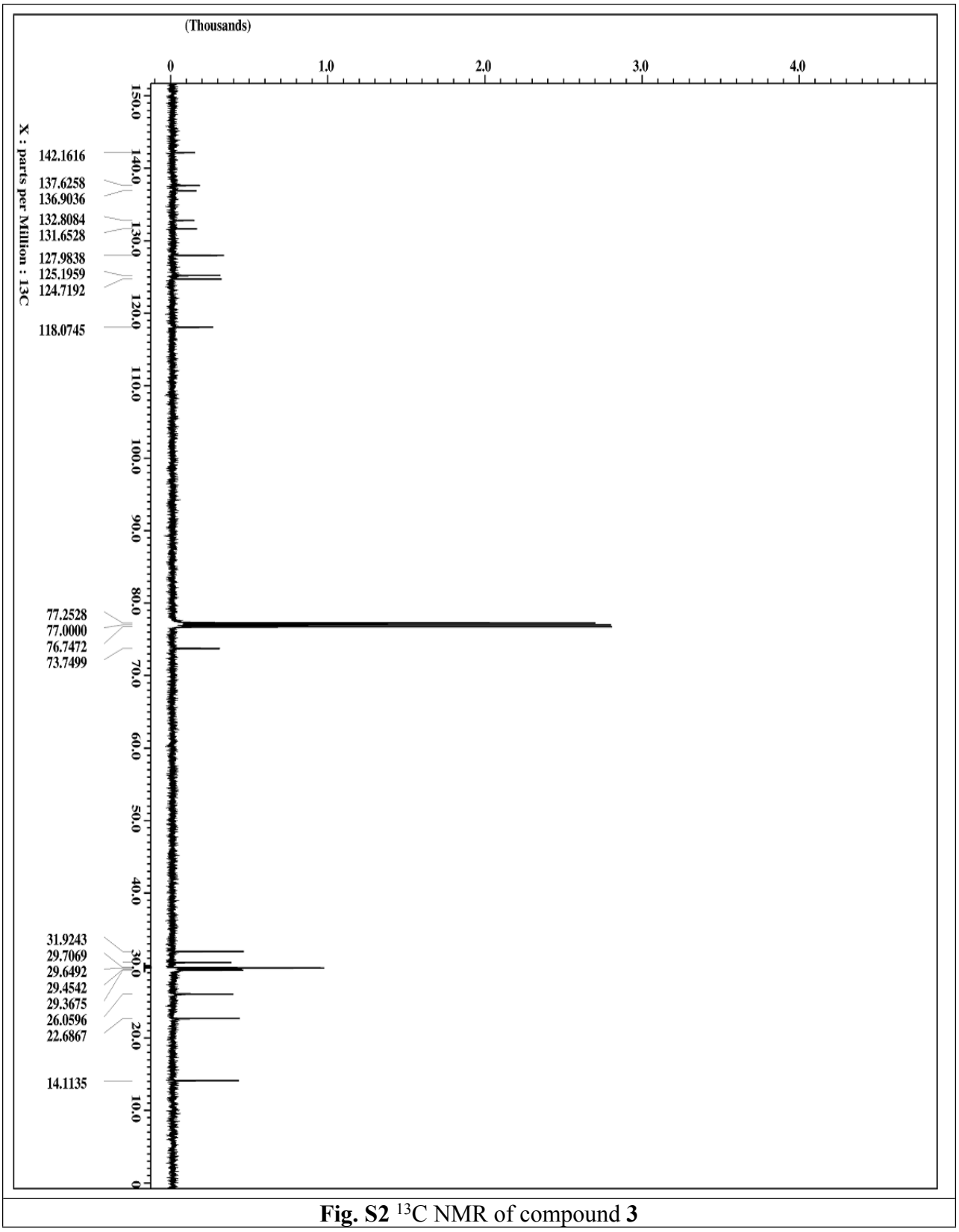


Fig. S2 ^{13}C NMR of compound **3**

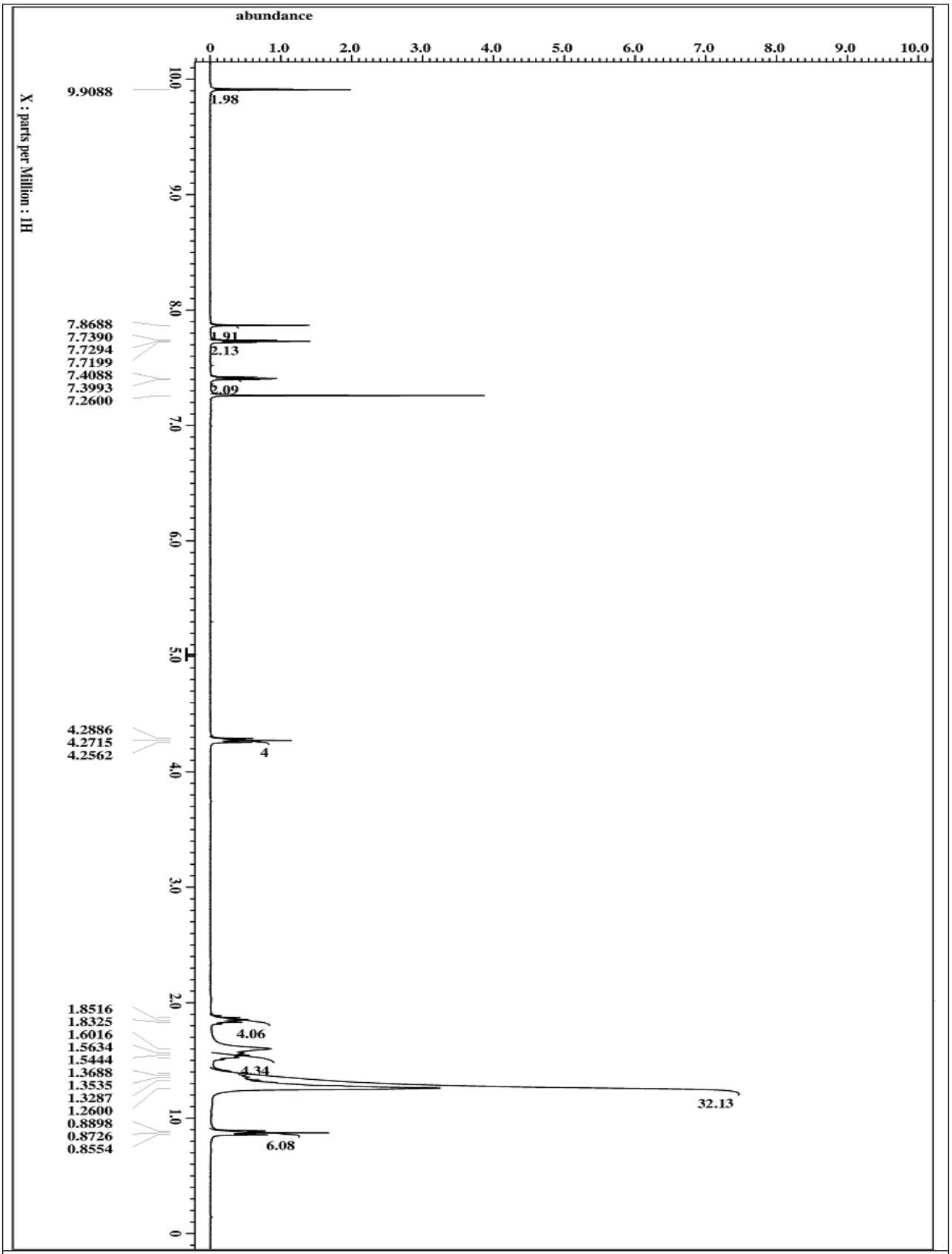


Fig. S3 ^{1}H NMR of compound **4**

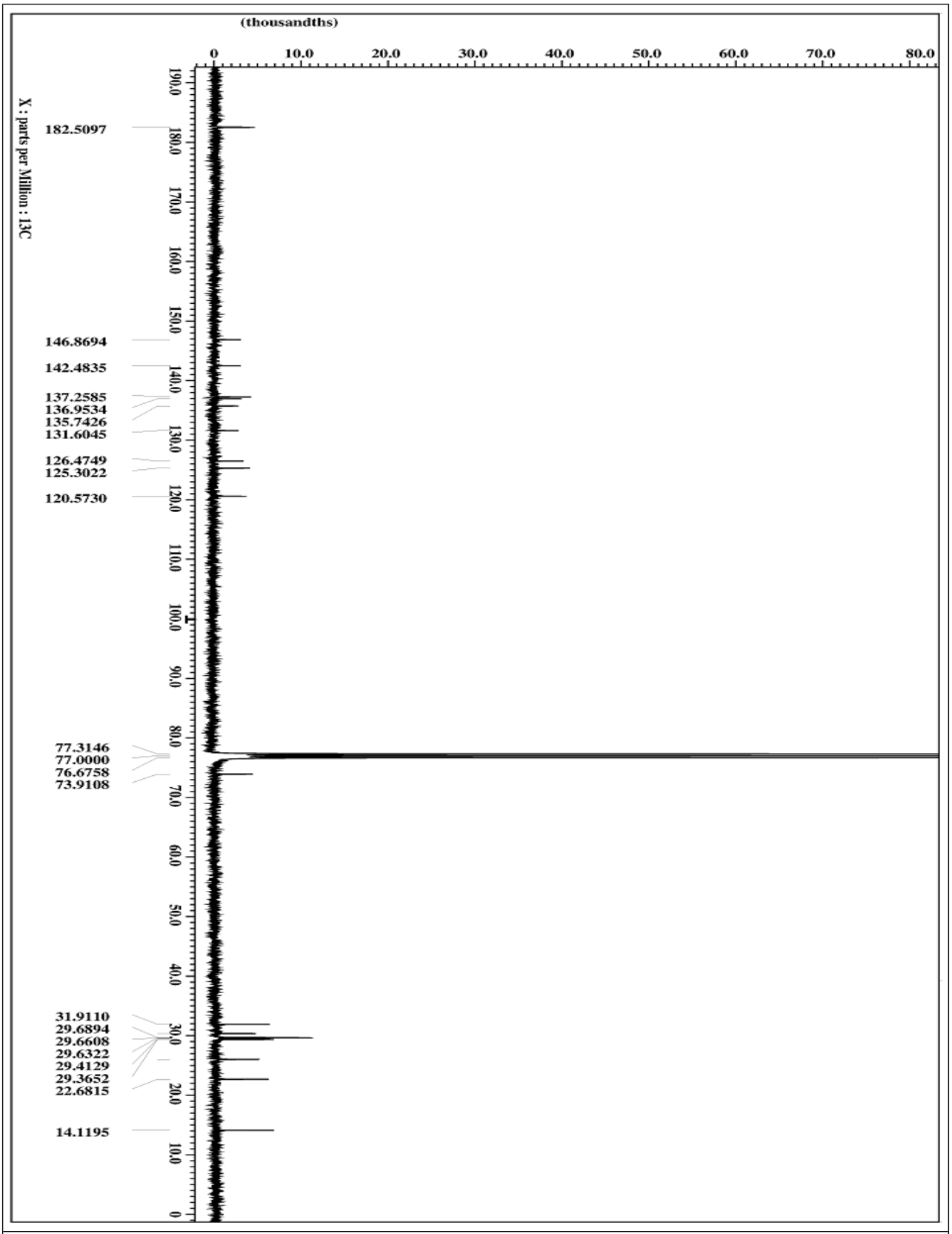


Fig. S4 ^{13}C NMR of compound **4**

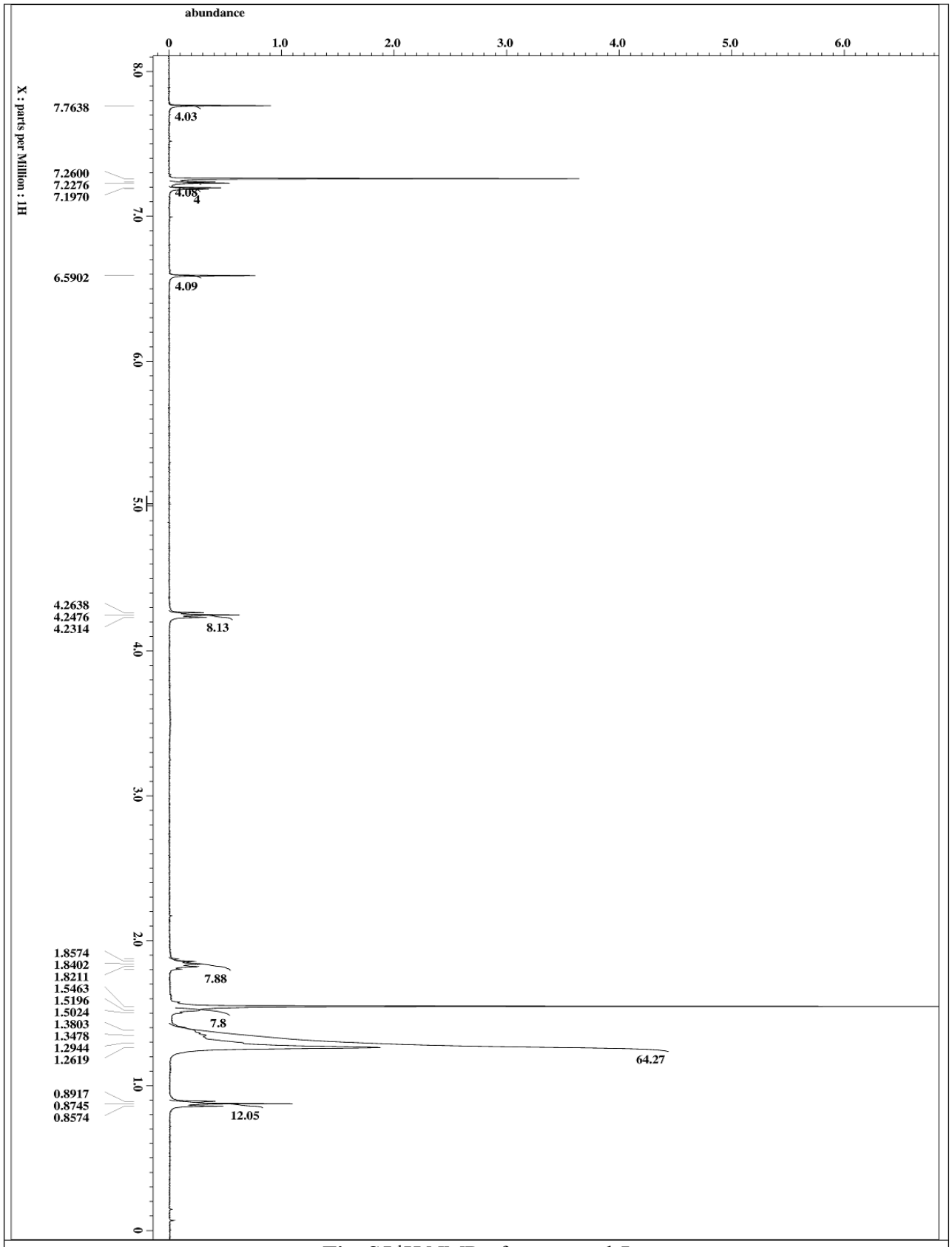


Fig. S5 ^{1}H NMR of compound **5**

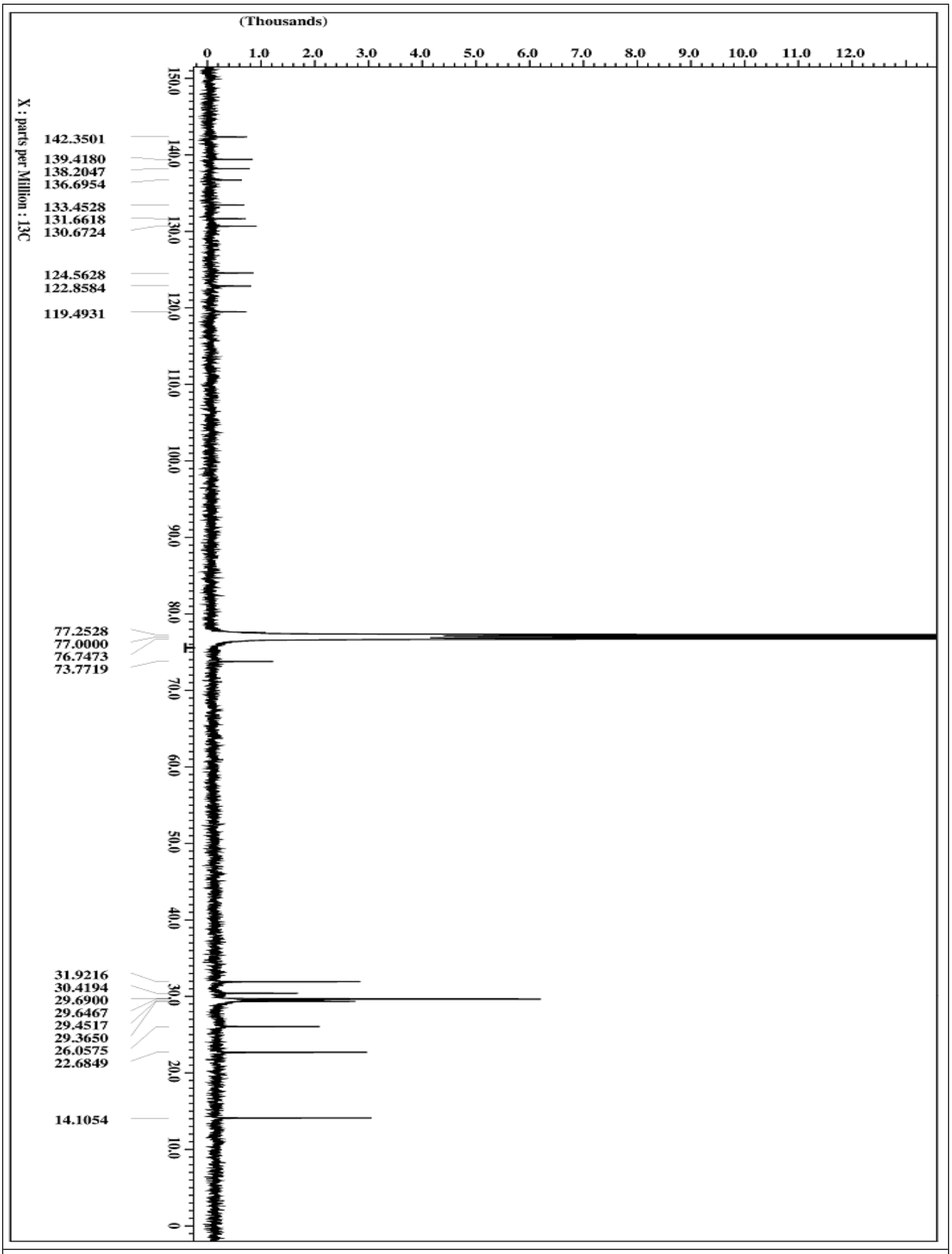


Fig. S6 ^{13}C NMR of compound **5**

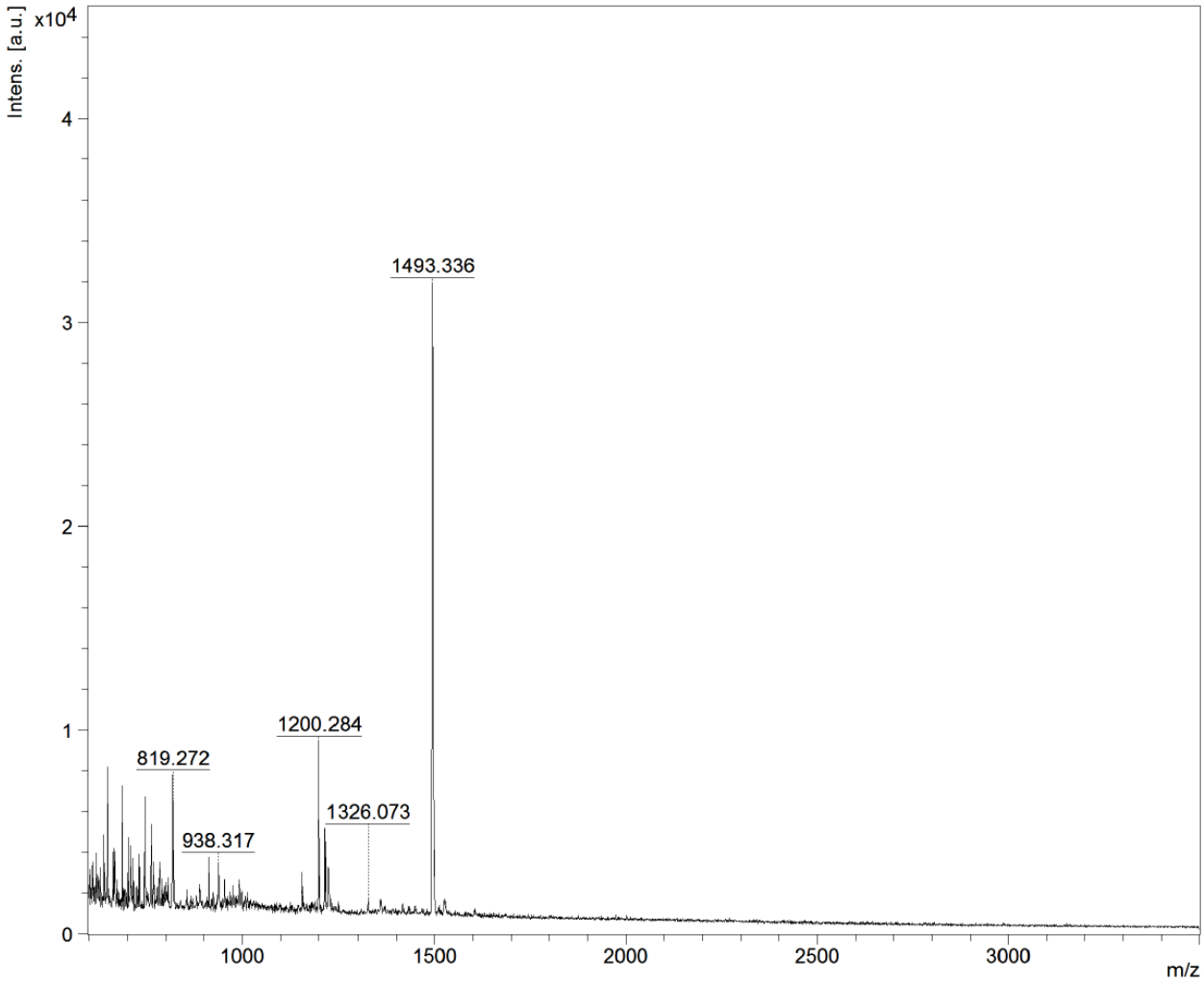


Fig. S7 MALDI-TOF Mass spectrometry of **5**

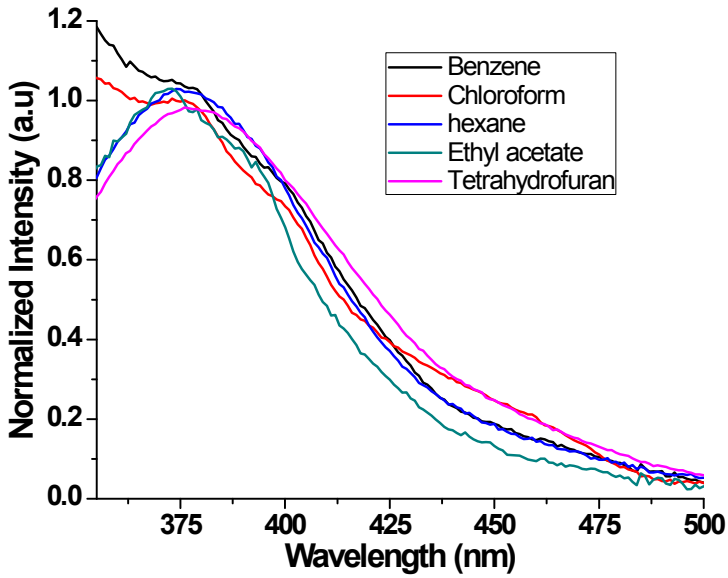
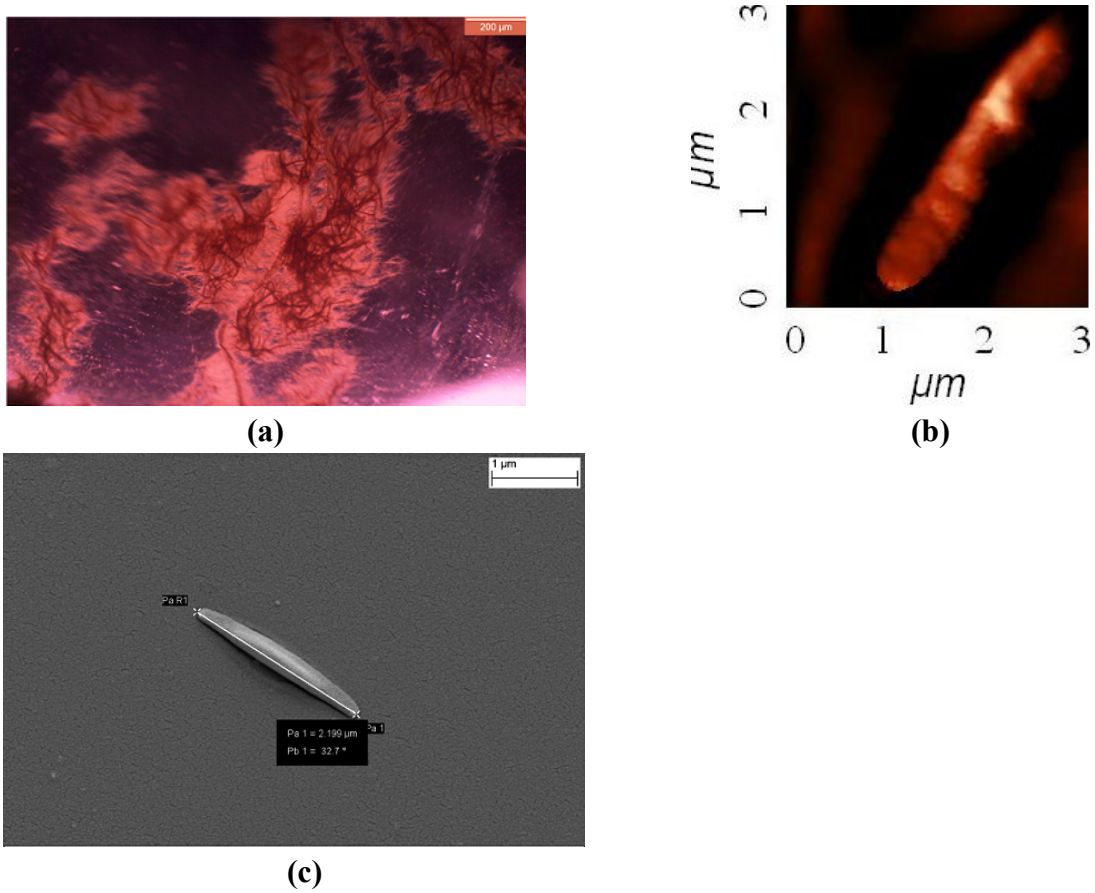


Fig. S8 UV-vis spectra of the macrocycle (**5**) in various solvents.



(a) **(b)**

(c)

Fig. S9 (a) Micrograph on a glass plate using a light microscope with 1000× magnification. (b) AFM topography of a single fibre obtained on SiO_2 surface. (c) SEM images of single microfiber of the macrocycle on a silicon wafer with 44000 × magnification (right).

Table S1 NICS (0 to 2 and 0 to -2) value calculated at B3LYP/6-311+G(d,p) on the optimized structure of macrocycle **5** at B3LYP/6-31G(d).[a]

Position of Bq	0	1	2	-1	-2
NICS value	1.7	1.6	1.2	1.3	0.7

[a] The coordinates of Bq(0) to get NICS(0) was calculated by averaging the coordinates of four hydrogen and four sulfur atoms of the inside periphery of the macrocycle **5**. Bq(1, 2, -1, -2) were placed with respect to Bq(0).

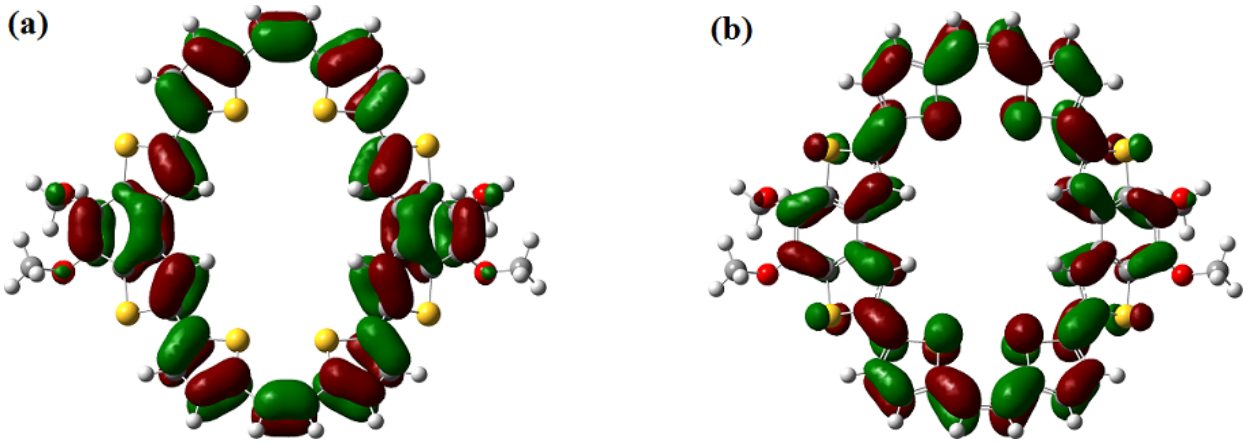


Fig. S10 Optimized structure of the frontier orbitals; (a) HOMO and (b) LUMO of the macrocycle.

Fluorescence decay:

The fluorescence decay for compound **5** was also studied to confirm the formation of the excimer. This needed a single exponential fit in solution but required a double exponential fit in solid state. In solution, a sole component of **5** with a lifetime (τ_1, x^2= 1.26) of 1.15 ns was present. But, in film two components were present with lifetime of 445 ps (τ_1, 37%, x^2 = 1.17) and 1.12 ns (τ_2, 63%, x^2 = 1.17). As the higher lifetime is believed to be found from the excimer species, the excimers dominated the fluorescent behavior of the compound in solid to shift the λ_{max}^{em} by 200 nm to the lower energy.

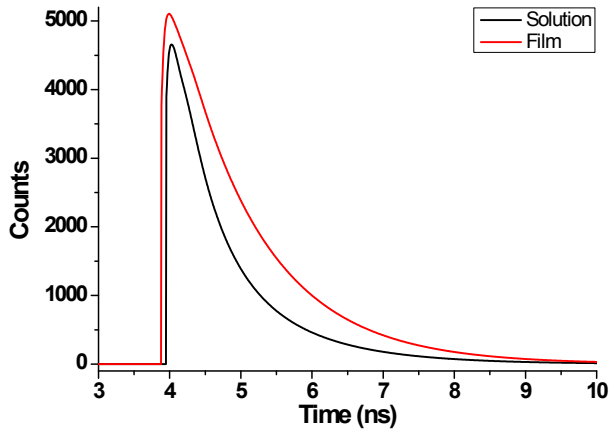


Fig. S11 Decay of fluorescence for compound **5** in solution (49.06 μM) and thin film on ITO-coated glass.

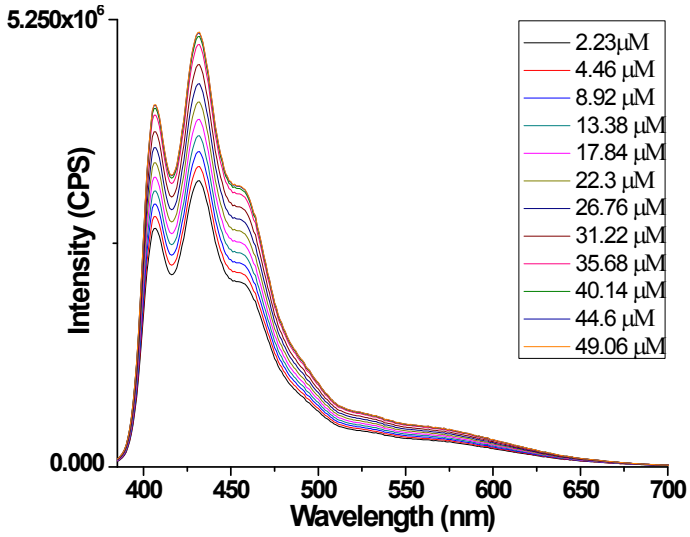


Fig. S12 Concentration dependent fluorescence spectra of **5** in THF.

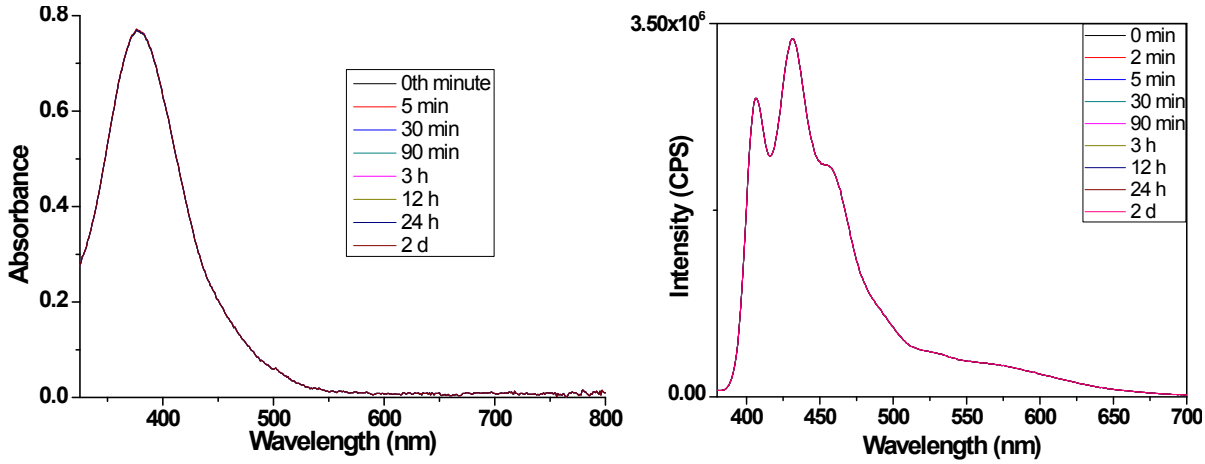


Fig. S13 Time-dependent absorption (left) and fluoroscence (right) spectra of macrocycle **5** in THF.

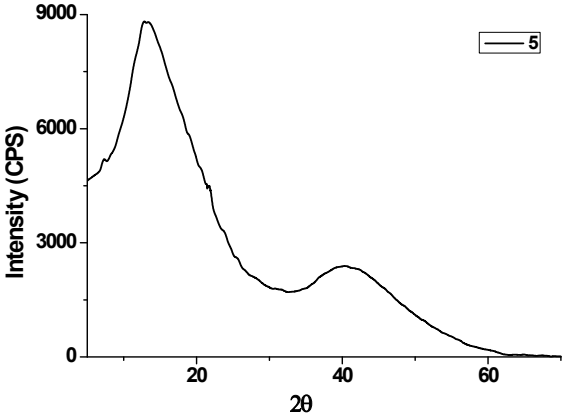


Fig. S14 Powder XRD pattern of compound **5**

Coordinates for optimized geometry of 5 at B3LYP/6-31G(d)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.701480	1.364236	0.815192
2	6	0	-4.595882	0.710376	0.227023
3	6	0	-3.657474	1.643719	-0.319830
4	6	0	-4.032895	2.955895	-0.169483
5	6	0	-6.785758	0.685042	1.396778
6	6	0	-4.599742	-0.713365	0.206384
7	6	0	-5.698393	-1.378830	0.794448
8	6	0	-6.773375	-0.711058	1.406377
9	6	0	-4.033287	-2.951277	-0.226025
10	6	0	-3.662619	-1.636085	-0.360482
11	1	0	-2.756061	1.350814	-0.847503
12	1	0	-2.765428	-1.333248	-0.889738
13	16	0	-5.562420	-3.115525	0.652647
14	16	0	-5.565369	3.103454	0.706552
15	6	0	-3.385557	-4.150147	-0.712340
16	6	0	-3.984283	-5.347956	-1.054680
17	16	0	-1.648835	-4.249806	-0.937808
18	6	0	-3.072622	-6.319645	-1.508622
19	1	0	-5.056704	-5.501861	-1.004085
20	6	0	-1.746629	-5.907842	-1.515281
21	1	0	-3.363920	-7.313963	-1.831018
22	6	0	-3.385043	4.163181	-0.633770
23	6	0	-3.983942	5.366598	-0.955858
24	16	0	-1.648367	4.267178	-0.857180
25	6	0	-3.072583	6.346082	-1.393080
26	1	0	-5.056329	5.519613	-0.902236
27	6	0	-1.746489	5.934664	-1.406597
28	1	0	-3.363995	7.345749	-1.698374
29	16	0	1.648363	4.267183	-0.857172
30	6	0	3.072577	6.346092	-1.393062
31	6	0	3.385040	4.163188	-0.633761
32	6	0	3.983937	5.366609	-0.955839
33	1	0	3.363987	7.345760	-1.698351
34	6	0	4.032893	2.955901	-0.169479
35	1	0	5.056323	5.519627	-0.902213
36	6	0	3.657474	1.643725	-0.319830
37	16	0	5.565367	3.103460	0.706557
38	6	0	4.595883	0.710383	0.227021
39	1	0	2.756061	1.350821	-0.847503
40	6	0	5.701481	1.364242	0.815191
41	6	0	4.599745	-0.713359	0.206376
42	6	0	6.785760	0.685048	1.396776
43	6	0	5.698398	-1.378824	0.794436
44	6	0	3.662623	-1.636078	-0.360493
45	6	0	6.773378	-0.711053	1.406367
46	16	0	5.562427	-3.115519	0.652629
47	6	0	4.033292	-2.951269	-0.226040
48	1	0	2.765431	-1.333239	-0.889748
49	6	0	3.385564	-4.150139	-0.712358
50	6	0	3.984291	-5.347945	-1.054704
51	16	0	1.648841	-4.249800	-0.937823

52	6	0	3.072630	-6.319636	-1.508646
53	1	0	5.056712	-5.501849	-1.004112
54	6	0	1.746635	-5.907839	-1.515289
55	1	0	3.363929	-7.313952	-1.831046
56	8	0	-7.798665	-1.456626	1.938415
57	8	0	-7.799671	1.419803	1.964983
58	8	0	7.799663	1.419811	1.964992
59	8	0	7.798671	-1.456616	1.938411
60	6	0	-9.059457	1.338994	1.278724
61	1	0	-9.743797	1.985039	1.832462
62	1	0	-8.960817	1.705549	0.250027
63	1	0	-9.437637	0.312287	1.269734
64	6	0	-7.916567	-1.385238	3.368720
65	1	0	-6.996765	-1.740393	3.848279
66	1	0	-8.131914	-0.363283	3.695044
67	1	0	-8.745160	-2.045109	3.633869
68	6	0	9.059471	1.338984	1.278775
69	1	0	9.437643	0.312274	1.269810
70	1	0	8.960866	1.705528	0.250071
71	1	0	9.743796	1.985032	1.832528
72	6	0	7.916522	-1.385261	3.368722
73	1	0	8.131847	-0.363309	3.695077
74	1	0	6.996708	-1.740436	3.848241
75	1	0	8.745114	-2.045127	3.633886
76	6	0	-0.681181	6.816336	-1.814271
77	1	0	-1.102358	7.747198	-2.192450
78	6	0	0.681176	6.816338	-1.814268
79	1	0	1.102351	7.747201	-2.192446
80	6	0	1.746484	5.934668	-1.406590
81	6	0	-0.681162	-6.782414	-1.937783
82	1	0	-1.102327	-7.706736	-2.331694
83	6	0	0.681169	-6.782413	-1.937786
84	1	0	1.102333	-7.706735	-2.331698

The optimized energy for the macrocycle (**5**) was obtained to be − 5179.86 a.u.

Reference 23 in full

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