Supporting Information

A New Chiral Shift Reagent for Determination of Enantiomeric Excess and Absolute Configuration of Cyanohydrins

Lomary S. Moon, Ravinder. S. Jolly,* Yoganjaneyulu Kasetti and Prasad V. Bharatam

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6. ^{1}H NMR spectra of aldehyde and ketone cyanohydrins in presence of (*S*)-mandelate-DMAPH$^+$ ion-pair corresponding to Entries 1-14, Table 1and 1-5, Table 2 of main paper

Methods

NMR Data. Mandelic acid (2.74 mg, 18 μmol) and CDCl3 (0.6 mL) were mixed in 5 mm NMR tube and DMAP (1.73 mg, 18 μmol) added to it. Mandelic acid has poor solubility in CDCl3, but it readily goes into solution upon addition of DMAP. 18 μmol of chiral cyanohydrin was added and 1H NMR data was collected on Jeol ACX 300 MHz spectrometer. Chemical shifts (ppm) are internally referenced to TMS signal (0 ppm).

Association Constant *K*a. 20 mM solution of mandelate/DMAP$^+$ ion-pair in CDCl3 was placed in nineteen 5 mm NMR tubes. One tube was set aside. A predetermined quantity of a concentrated solution of mandelonitrile in CDCl3 was added to each of remaining eighteen tubes so that finally solutions with desired relative amounts (equiv) of the mandelonitrile versus ionpair were obtained. Volume and concentrations changes were taken into account during analysis. The concentration of ion-pair was always maintained at 20 mM. 1H NMR data was collected on Jeol ACX 300 MHz spectrometer. Plots of concentration versus chemical shift are shown in Figure S1 and S2. The association constants were calculated by nonlinear regression methods.

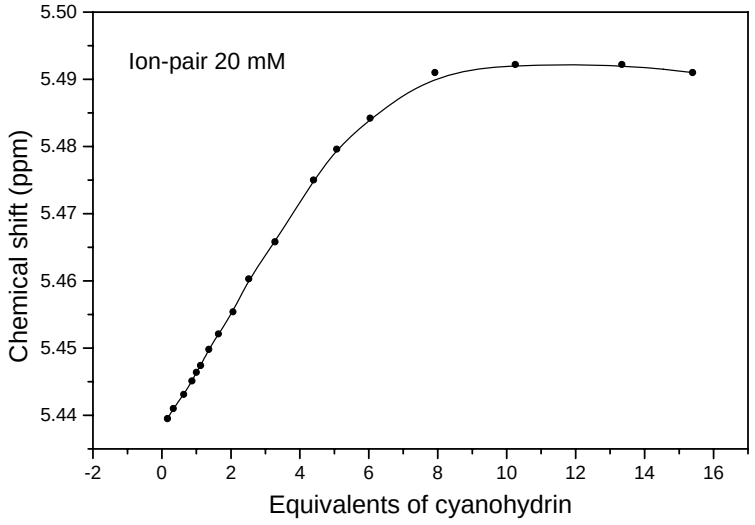


Figure S1. ^{1}H NMR titration data obtained for the complexation of (*R*)-mandelate-DMAPH$^+$ ion-pair as host and (*R*)-mandelonitrile as guest. Chemical shift values for α-H of mandelonitrile.

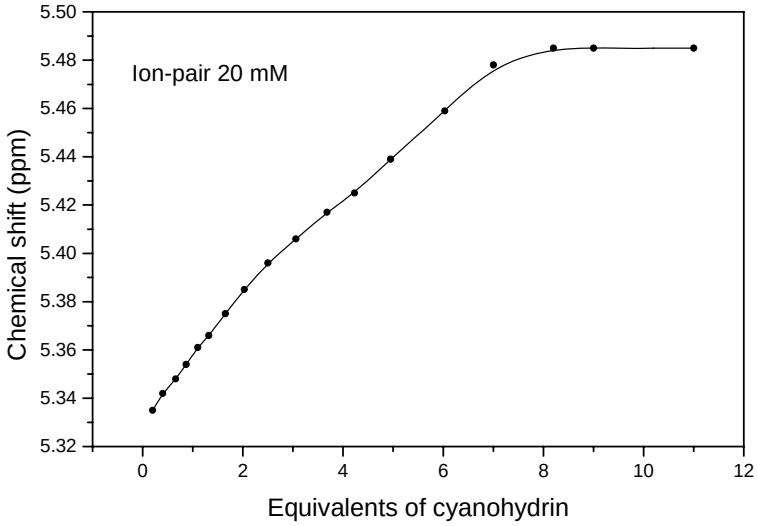


Figure S2. ^{1}H NMR titration data obtained for the complexation of (*S*)-mandelate-DMAPH^{+} ion-pair as host and (*R*)-mandelonitrile as guest. Chemical shift values for α-H of mandelonitrile.

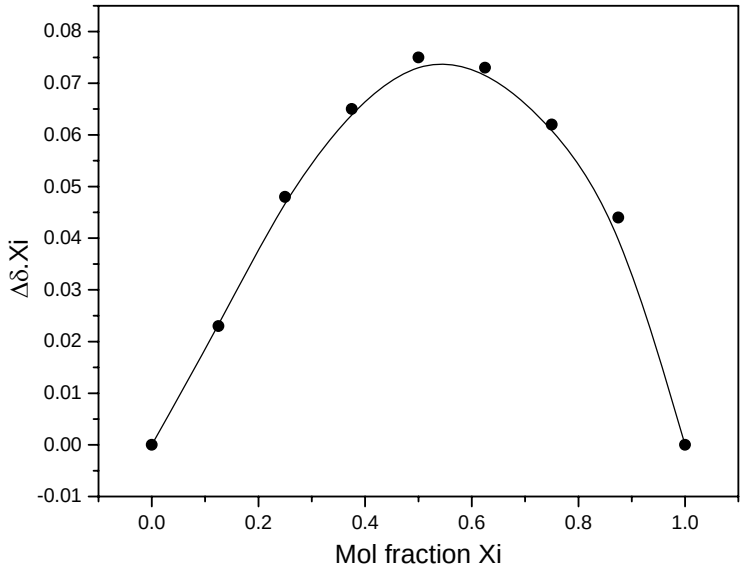
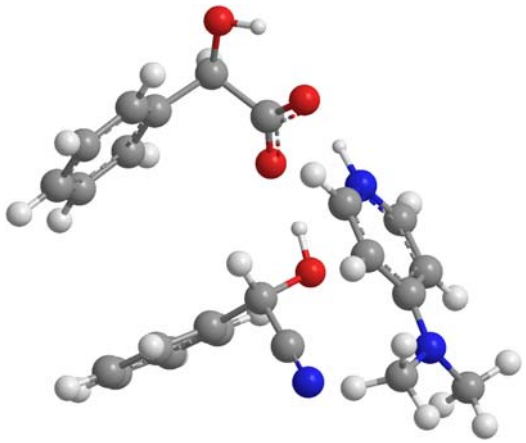


Figure S3. Job's plot for the complexation of mandelate-DMAPH^{+} ion-pair with mandelonitrile. $\Delta\delta$ is shift (ppm) for α-H of mandelonitrile.

(i) Coordinates for (*S*)-mandelonitrile/(*R*)-mandelate/DMAPH$^+$ (Gausian03)[S1] complex.



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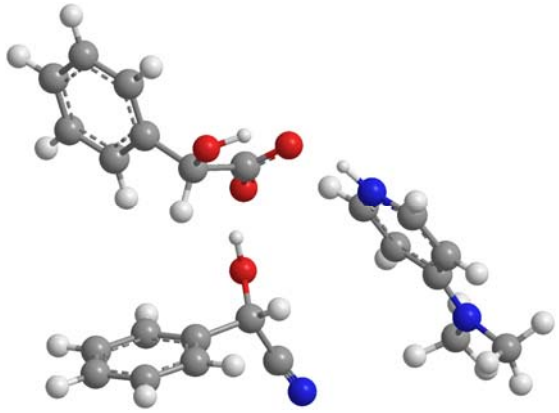
C	0	-0.3559	-1.5802	-0.2635
C	0	-1.4970	-1.0283	0.2207
C	0	-2.0953	0.0705	-0.4522
N	0	-3.1872	0.6894	0.0193
C	0	-3.6553	0.4308	1.3905
C	0	-3.6967	1.8952	-0.6529
H	0	5.6202	-1.0850	-2.2465
C	0	4.8986	-1.5224	-1.5707
C	0	3.5174	-0.9281	-1.8706
C	0	5.2126	-1.1256	-0.1396
O	0	2.5958	-1.7890	-2.0601
O	0	3.3944	0.3065	-1.8646
H	0	-1.8183	1.3291	-2.1874
H	0	0.2470	0.2601	-2.8850
H	0	1.2045	-1.4784	-1.6994
H	0	0.1282	-2.3953	0.2322
H	0	-1.9178	-1.4160	1.1184
H	0	-4.5738	0.9746	1.5538
H	0	-3.8621	-0.6211	1.5386
H	0	-2.9173	0.7684	2.1090
H	0	-4.6334	2.1788	-0.1994
H	0	-3.8793	1.6956	-1.7011
H	0	-2.9944	2.7139	-0.5519
C	0	4.8963	-1.9860	0.8950
C	0	5.0759	-1.5877	2.2078
C	0	5.5954	-0.3370	2.4920
C	0	5.9220	0.5223	1.4562
C	0	5.7259	0.1292	0.1448
O	0	4.8334	-2.9341	-1.7206
H	0	3.9178	-3.1318	-1.9813

C	0	4.2174	4.7507	0.3813
C	0	4.5518	4.7394	1.7210
C	0	3.9222	3.8544	2.5830
C	0	2.9841	2.9678	2.0909
C	0	2.6677	2.9635	0.7427
C	0	3.2738	3.8619	-0.1099
C	0	1.6892	1.9338	0.1988
O	0	1.5754	1.9619	-1.2196
C	0	0.3497	2.1908	0.7570
N	0	-0.6867	2.3704	1.1933
H	0	4.6902	5.4474	-0.2844
H	0	5.3002	5.4097	2.0961
H	0	4.1636	3.8518	3.6253
H	0	2.5028	2.2734	2.7544
H	0	3.0097	3.8457	-1.1468
H	0	2.0066	0.9560	0.5433
H	0	2.2804	1.3588	-1.5966
H	0	4.5190	-2.9590	0.6589
H	0	4.8101	-2.2502	3.0082
H	0	5.7494	-0.0334	3.5091
H	0	6.3042	1.5019	1.6670
H	0	5.9392	0.8088	-0.6573

(ii) Coordinates for (*S*)-mandelonitrile/(*S*)-mandelate/DMAPH$^+$ (Gausian03)[S1] complex.



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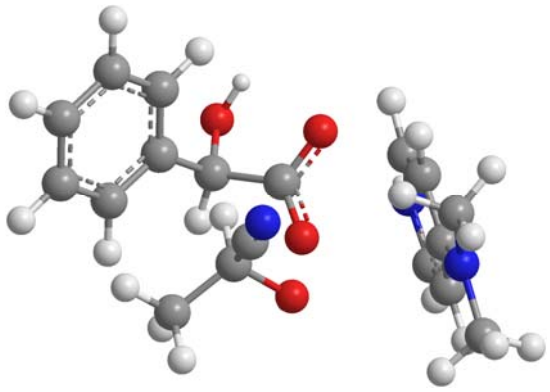
C	0	-0.3113	0.0709	-1.5031
N	0	0.0908	-1.0895	-0.9636
C	0	-0.6849	-1.7459	-0.0904
C	0	-1.8970	-1.2593	0.2915
C	0	-2.3466	-0.0092	-0.2185
N	0	-3.4928	0.5574	0.2067
C	0	-4.2805	-0.0643	1.2695

C	0	-3.9023	1.8755	-0.2900
C	0	6.7307	1.9728	-2.1584
C	0	7.6598	1.1274	-2.7498
C	0	7.5920	-0.2353	-2.5103
C	0	6.6037	-0.7532	-1.6837
C	0	5.6714	0.0875	-1.0920
C	0	5.7448	1.4554	-1.3345
C	0	4.6118	-0.4602	-0.1560
C	0	3.2283	-0.5013	-0.7940
H	0	4.5278	0.1988	0.6971
O	0	2.6714	-1.6374	-0.8817
O	0	2.6846	0.5762	-1.1424
H	0	-1.7663	1.5648	-1.5994
H	0	0.3789	0.5482	-2.1588
H	0	1.0622	-1.4009	-1.1038
H	0	-0.2874	-2.6560	0.3025
H	0	-2.4720	-1.8130	0.9949
H	0	-5.0584	0.6147	1.5663
H	0	-4.7392	-0.9865	0.9393
H	0	-3.6722	-0.2669	2.1390
H	0	-4.8807	2.0979	0.0963
H	0	-3.9622	1.8824	-1.3682
H	0	-3.2198	2.6477	0.0335
H	0	6.7781	3.0279	-2.3310
H	0	8.4255	1.5272	-3.3840
H	0	8.3105	-0.8931	-2.9570
H	0	6.5655	-1.8003	-1.4763
H	0	5.0298	2.1103	-0.8820
O	0	4.9520	-1.7543	0.3143
H	0	4.2789	-2.3775	0.0580
C	0	4.2861	4.7357	1.6901
C	0	4.5594	4.1835	2.9341
C	0	3.7291	3.2004	3.4482
C	0	2.6282	2.7732	2.7199
C	0	2.3476	3.3287	1.4790
C	0	3.1826	4.3134	0.9658
C	0	1.1630	2.8342	0.6637
O	0	1.4116	2.8469	-0.7283
C	0	-0.0590	3.6350	0.8717
N	0	-1.0406	4.2001	1.0085
H	0	4.9346	5.4830	1.2817
H	0	5.4135	4.5114	3.4899
H	0	3.9445	2.7590	4.4007
H	0	2.0012	1.9985	3.1165
H	0	2.9774	4.7227	0.0005
H	0	0.9248	1.8299	0.9913
H	0	2.0092	2.1330	-0.9801

(iii) Coordinates for (*S*)-lactonitrile/(*R*)-mandelate/DMAPH$^+$ (Gausian03)[S1] complex.



C	0	-1.3652	0.4957	-1.9773
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C	0	-0.2346	-1.6528	-0.6746
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C	0	-1.8288	0.2033	-0.6720
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C	0	-3.2698	0.5737	1.3159
C	0	-3.4105	2.1142	-0.7742
H	0	4.9557	-0.6203	-2.2473
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C	0	3.0035	-1.3261	-1.6606
C	0	4.8466	-0.8826	-0.0784
O	0	2.3789	-2.3743	-1.3943
O	0	2.3505	-0.3277	-2.0284
H	0	-1.7784	1.3253	-2.5699
H	0	-0.0268	-0.0587	-3.5996
H	0	0.9122	-1.9417	-2.4489
H	0	0.1881	-2.5420	-0.1824
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H	0	-3.7047	-0.4513	1.3237
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C	0	5.6978	0.7630	1.4959
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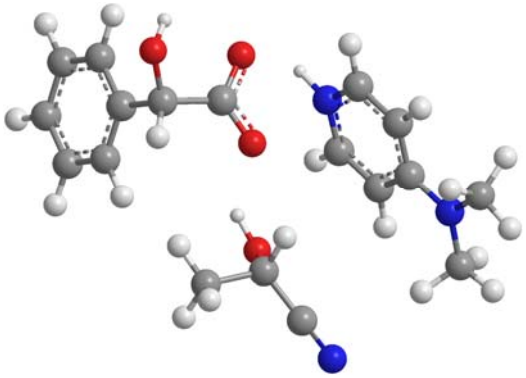
C	0	1.8442	1.6887	0.5178

O	0	1.1460	1.6511	-0.7134
C	0	0.8717	1.7448	1.6297
N	0	0.1207	1.7696	2.5116
H	0	3.4149	2.8942	1.4428
H	0	2.2782	3.8298	0.4046
H	0	2.3982	0.7262	0.6043
H	0	1.7363	1.4267	-1.4311
H	0	4.1756	-2.7482	0.8153
H	0	4.7226	-2.0669	3.1363
H	0	5.6976	0.1895	3.5889
H	0	6.1232	1.7608	1.6912
H	0	5.5826	1.0822	-0.6364

(iv) Coordinates for (*S*)-lactonitrile/(*S*)-mandelate/DMAPH$^+$ (Gausian03)[S1] complex.



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C	0	-0.0333	0.1608	-2.0489
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C	0	-0.1481	-1.6974	-0.6025
C	0	-1.2702	-1.1633	0.0281
C	0	-1.8147	0.0800	-0.3752
N	0	-2.9608	0.6274	0.2392
C	0	-3.5834	-0.1131	1.3581
C	0	-3.4801	1.9193	-0.2599
C	0	6.1846	1.9414	-2.0606
C	0	6.9518	1.0551	-2.8184
C	0	6.8521	-0.3171	-2.5844
C	0	5.9916	-0.7985	-1.5955
C	0	5.2270	0.0809	-0.8192
C	0	5.3282	1.4541	-1.0712
C	0	4.2880	-0.4288	0.2476
C	0	2.9271	-0.6703	-0.3705
H	0	4.1972	0.2935	1.0893
O	0	2.7255	-1.7183	-1.0200
O	0	1.9965	0.1559	-0.2789
H	0	-1.5087	1.6861	-1.8568
H	0	0.4687	0.6533	-2.8960
H	0	1.2970	-1.4694	-2.1466

H	0	0.2522	-2.6796	-0.3074
H	0	-1.7191	-1.7627	0.8342
H	0	-4.4590	0.4428	1.7605
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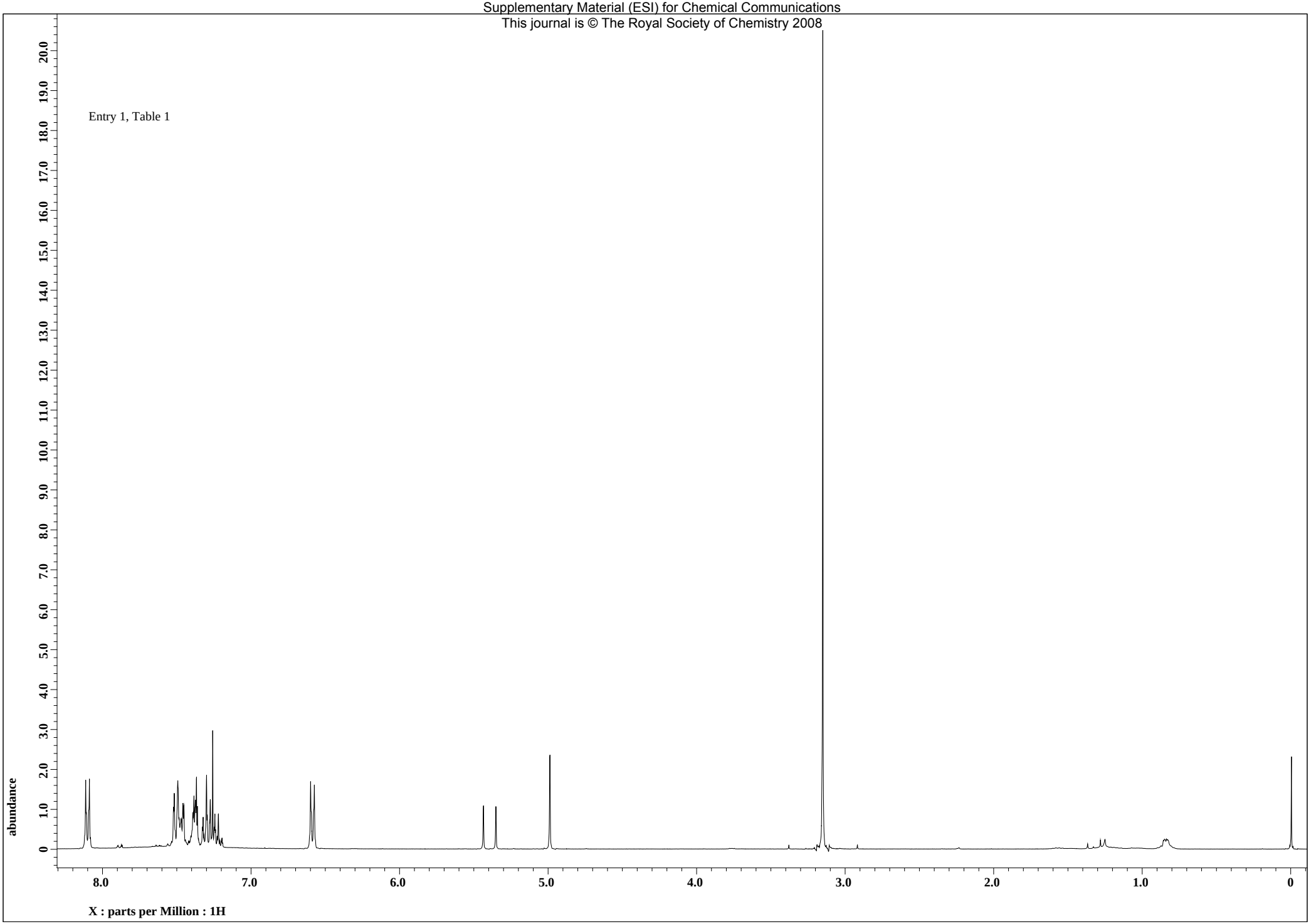
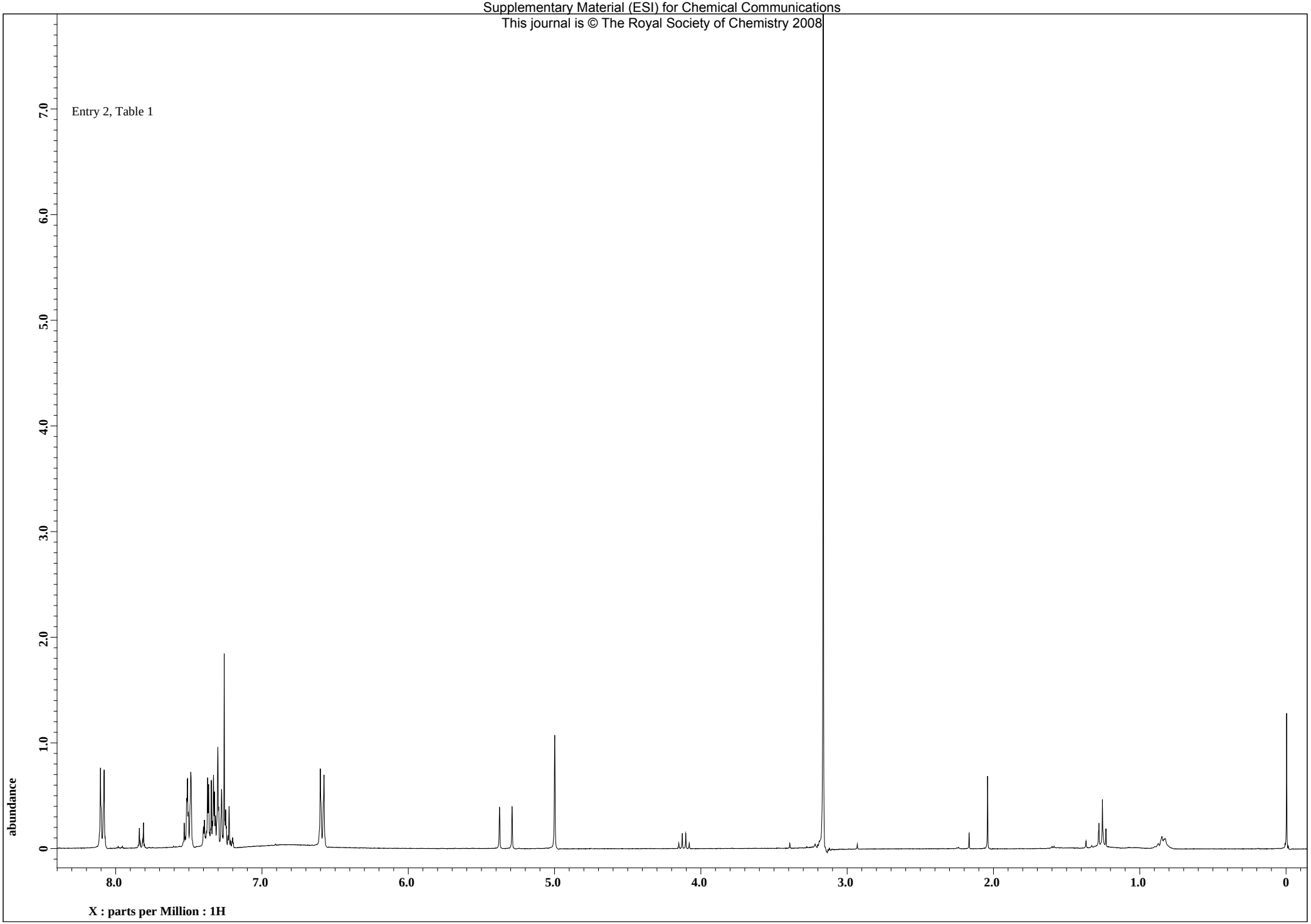
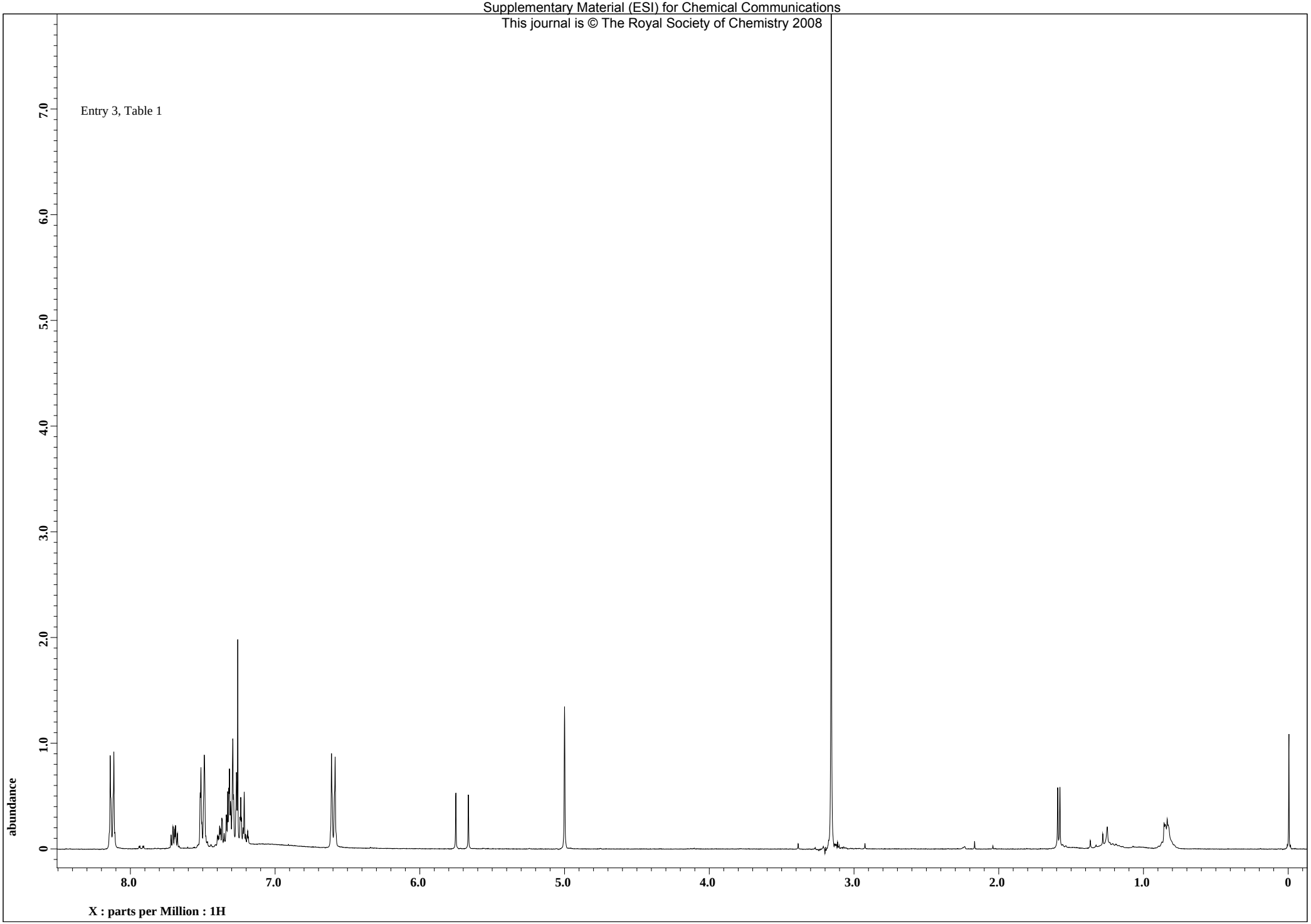
H	0	-3.8068	1.8322	-1.3208
H	0	-2.7228	2.7261	-0.1473
H	0	6.2534	3.0258	-2.2453
H	0	7.6283	1.4361	-3.6005
H	0	7.4503	-1.0215	-3.1851
H	0	5.9236	-1.8870	-1.4435
H	0	4.7232	2.1658	-0.4872
O	0	4.7649	-1.6528	0.7978
H	0	4.6723	-2.3152	0.1092
C	0	2.2903	3.4641	1.3783
H	0	3.1209	2.7290	1.2777
C	0	1.0282	2.9621	0.6872
O	0	1.3087	2.7441	-0.6844
C	0	-0.1189	3.8856	0.8169
N	0	-1.0228	4.5996	0.9421
H	0	2.1128	3.6261	2.4662
H	0	2.6314	4.4290	0.9378
H	0	0.7161	1.9833	1.1185
H	0	1.9555	2.0471	-0.7904

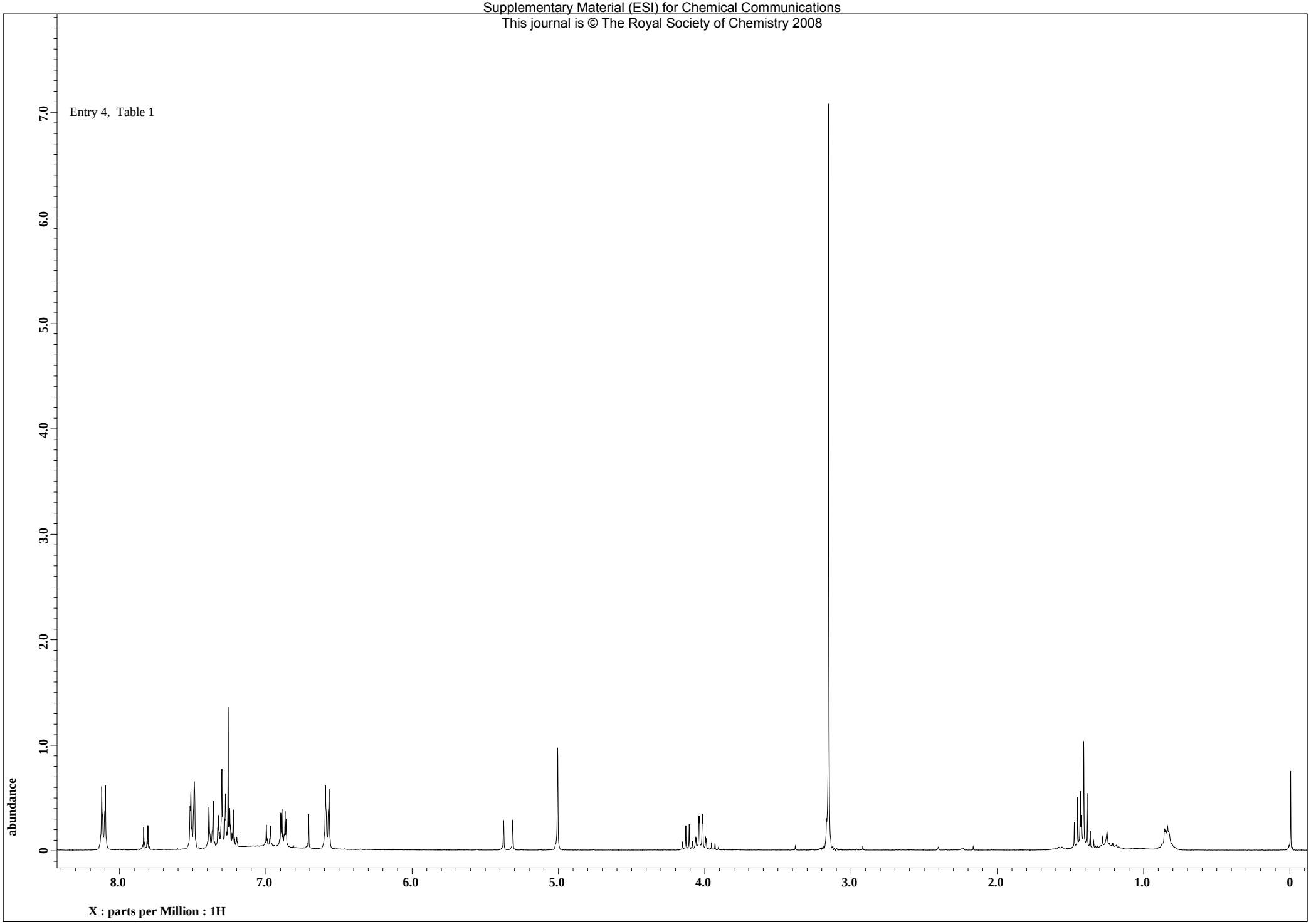
Reference

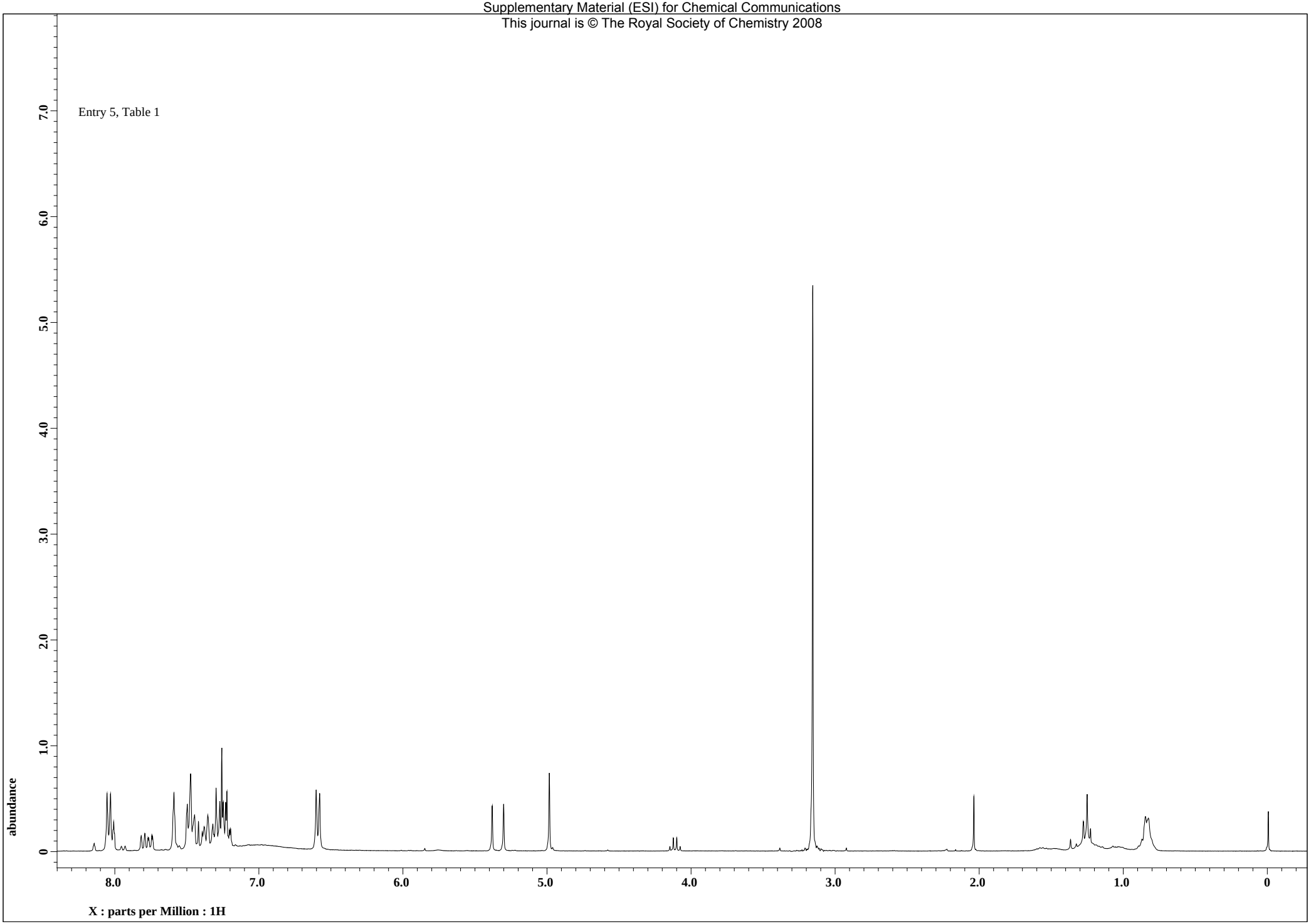
[S1]. Gaussian03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

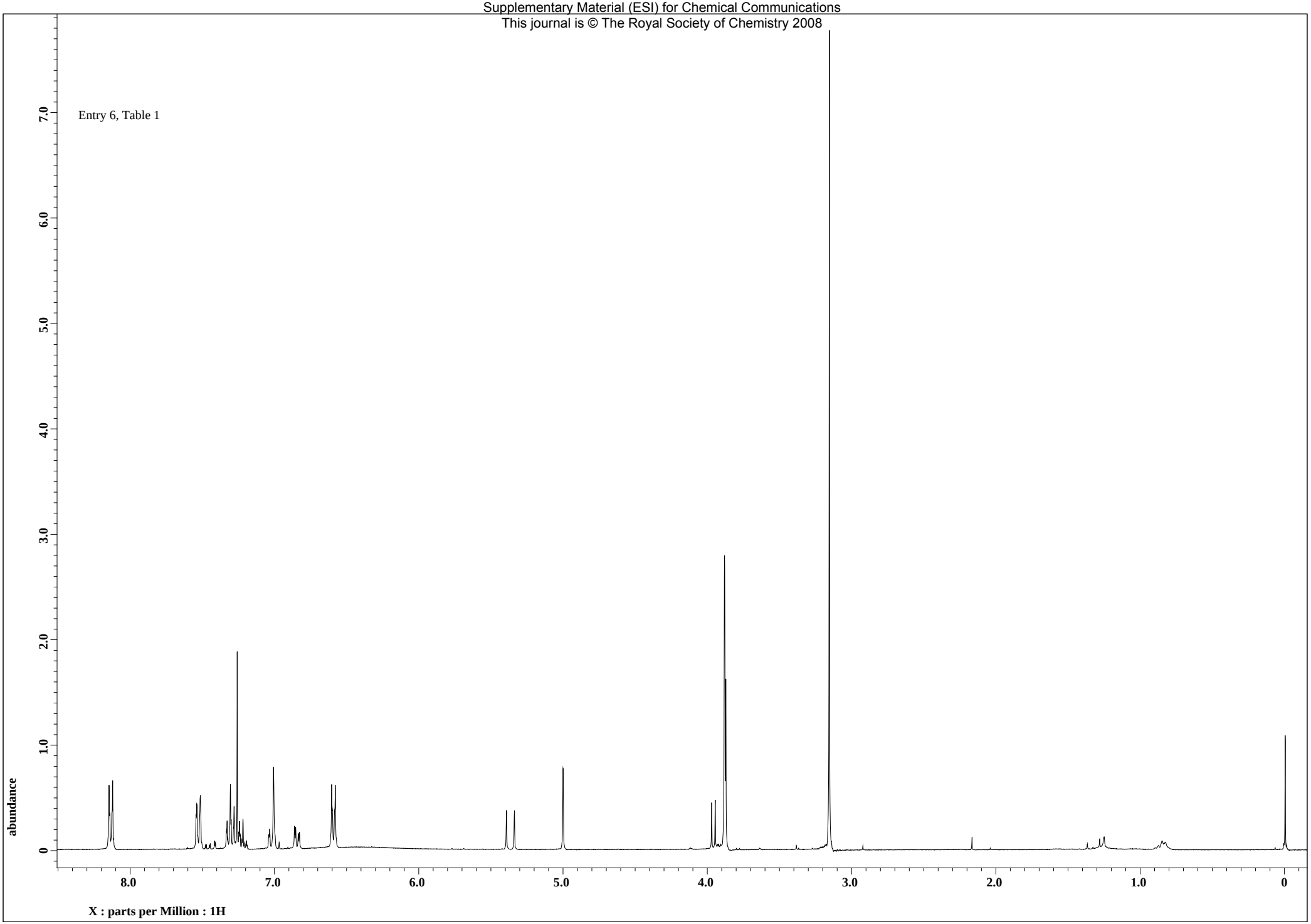


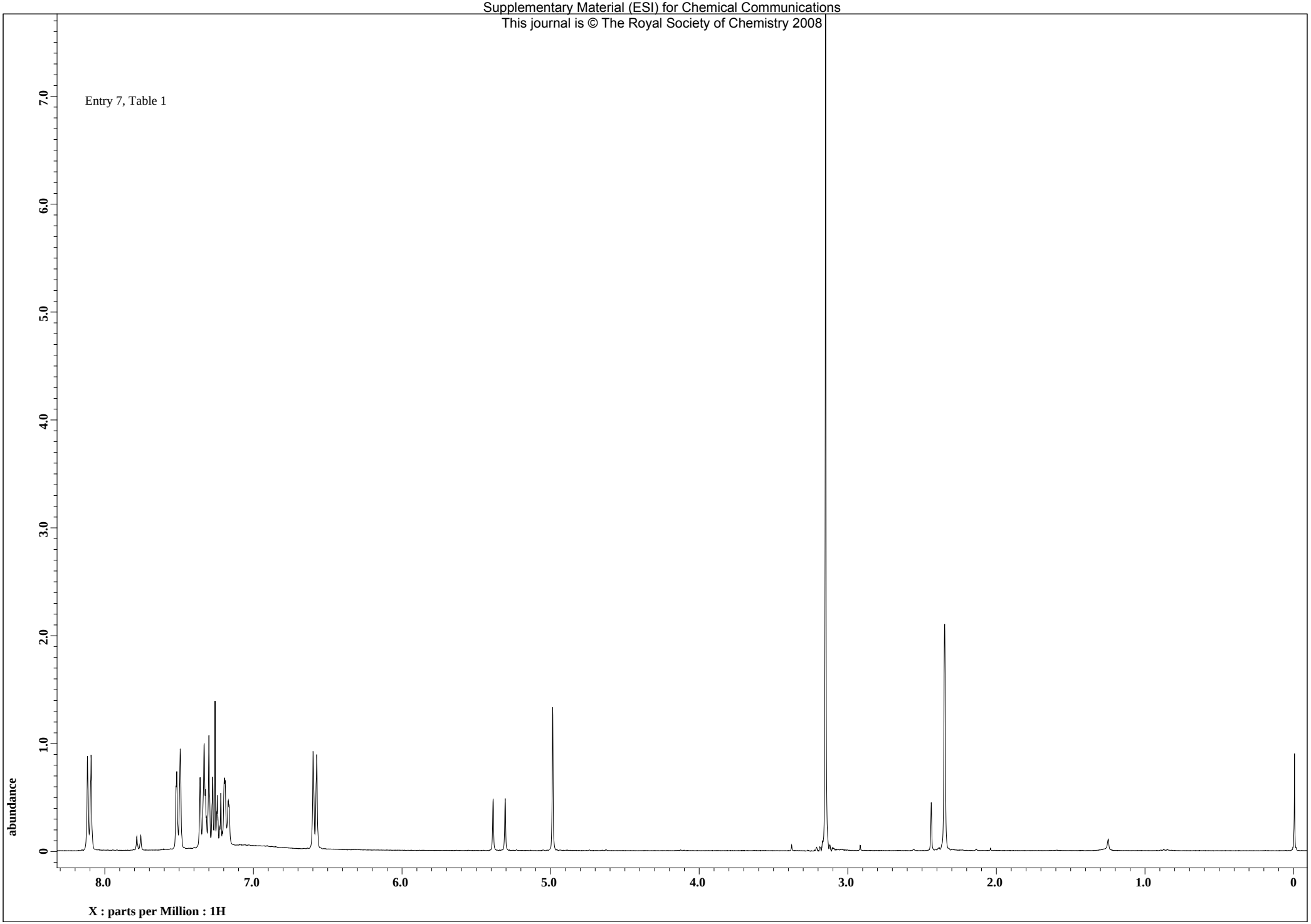


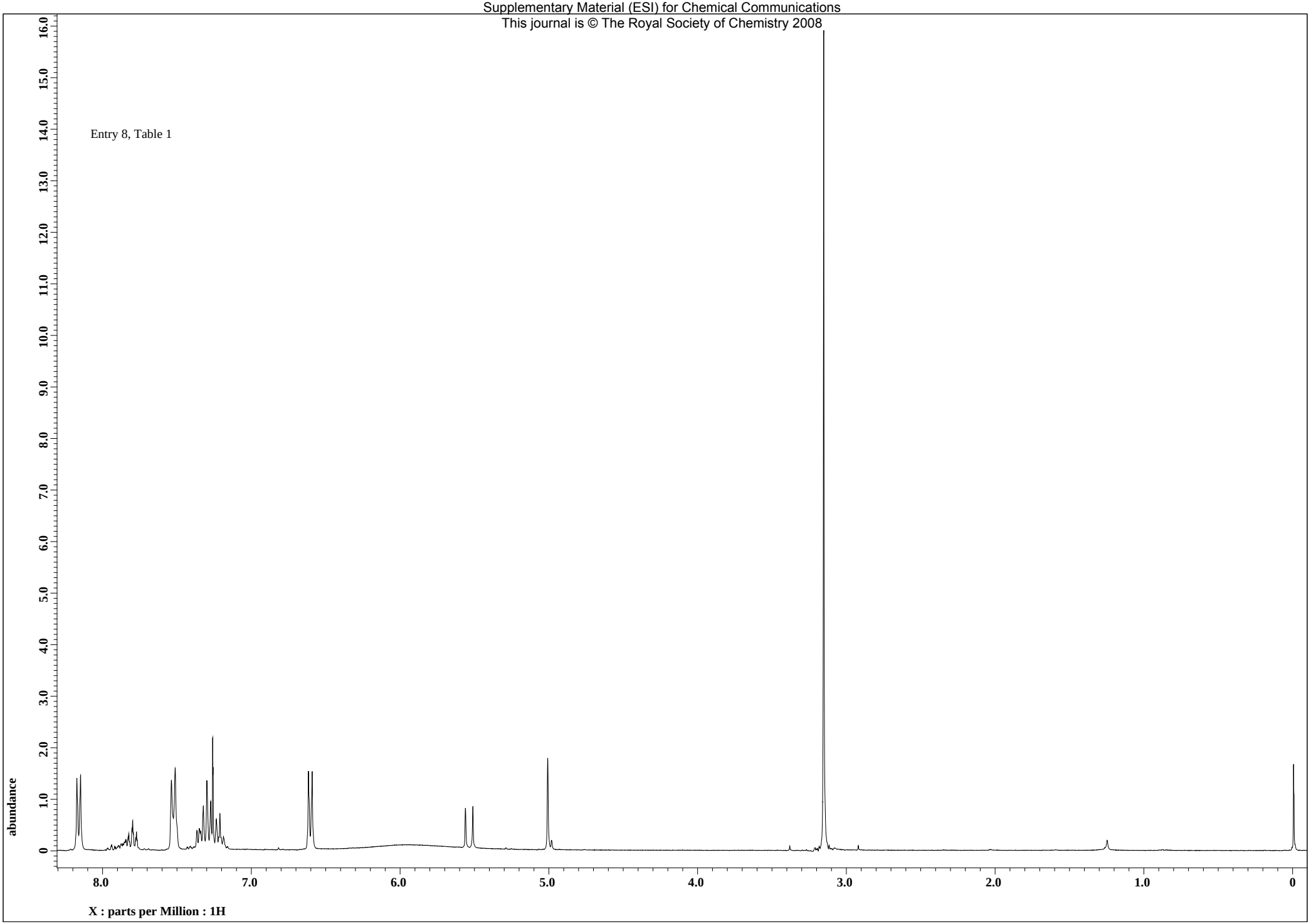


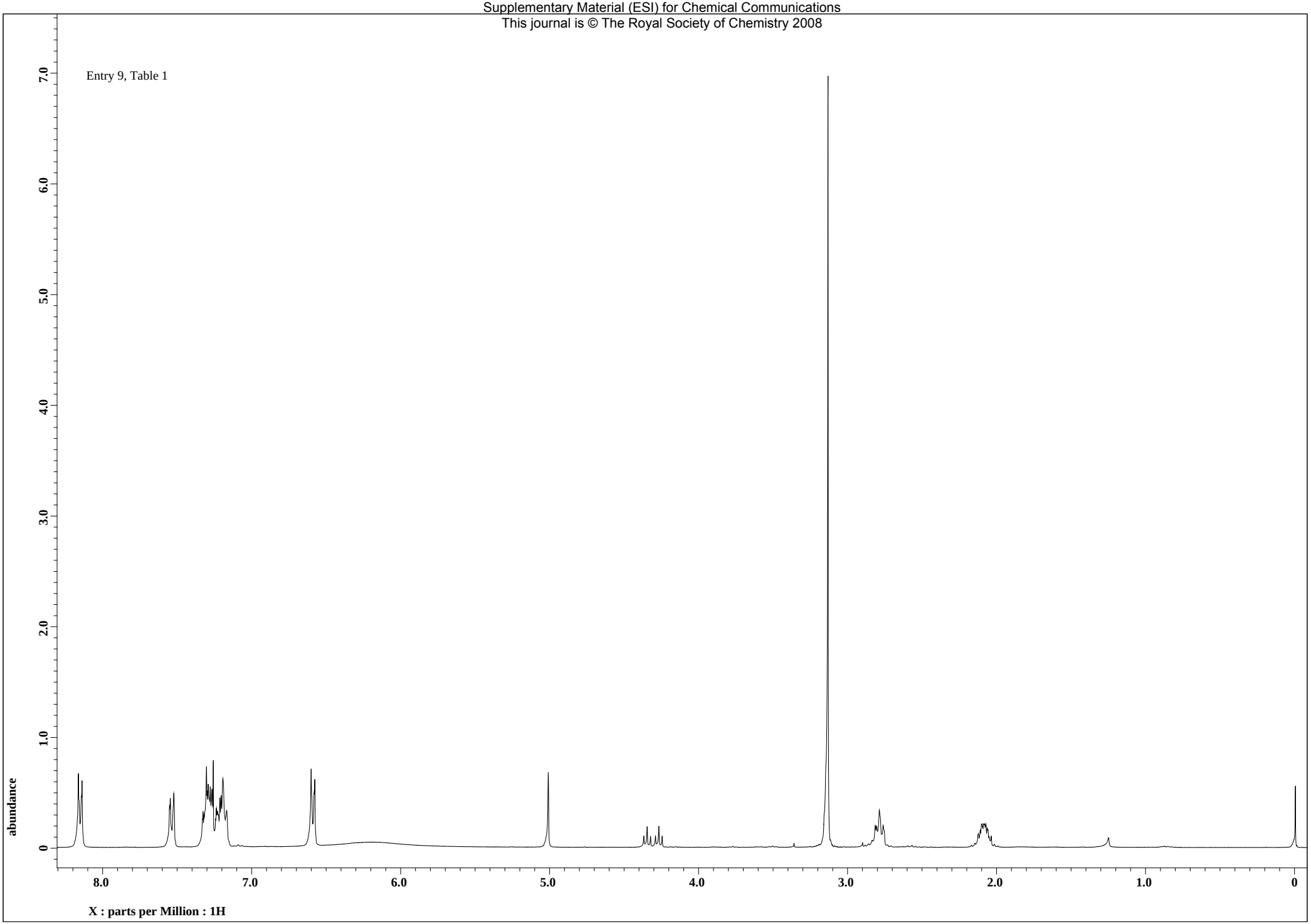


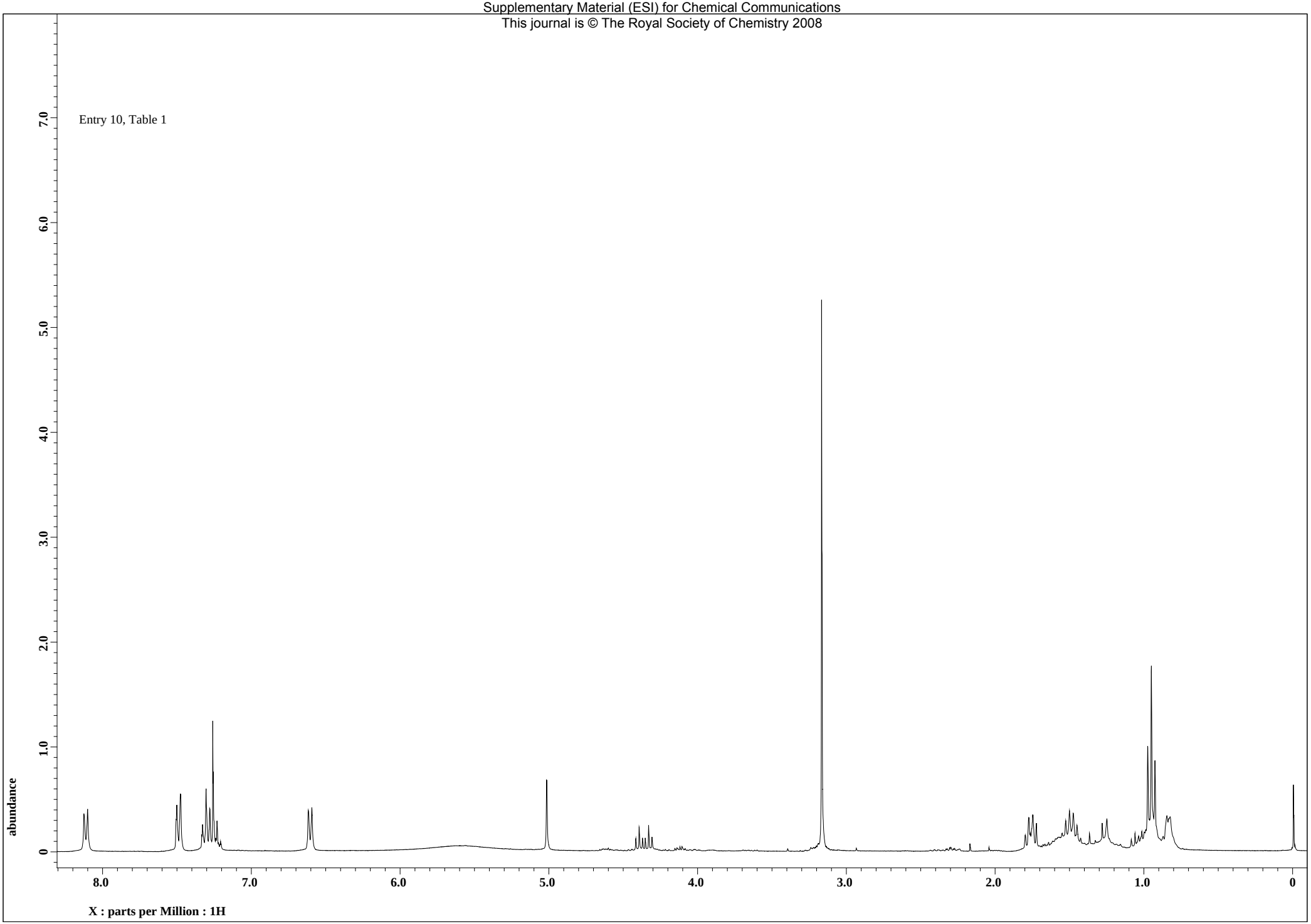


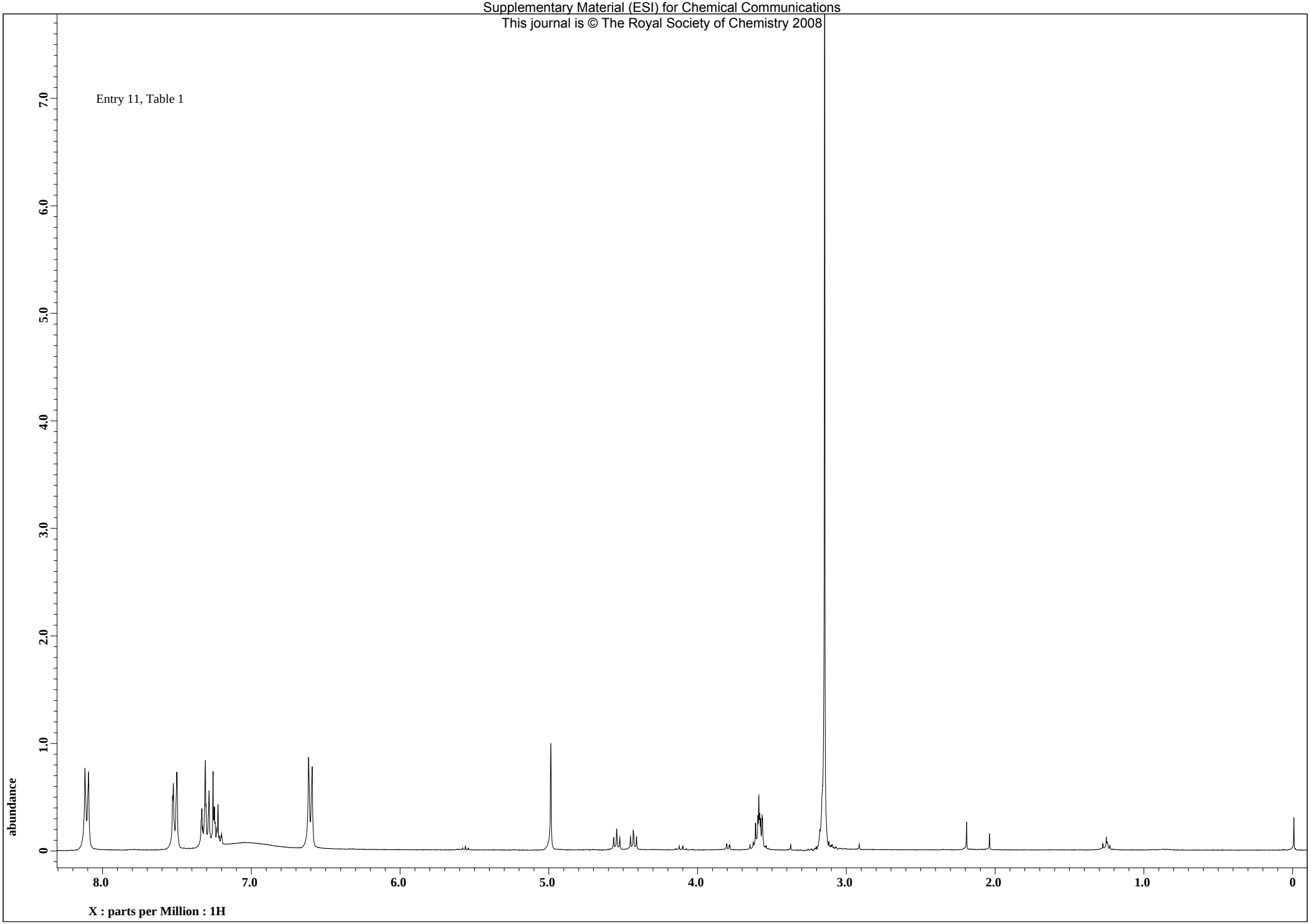


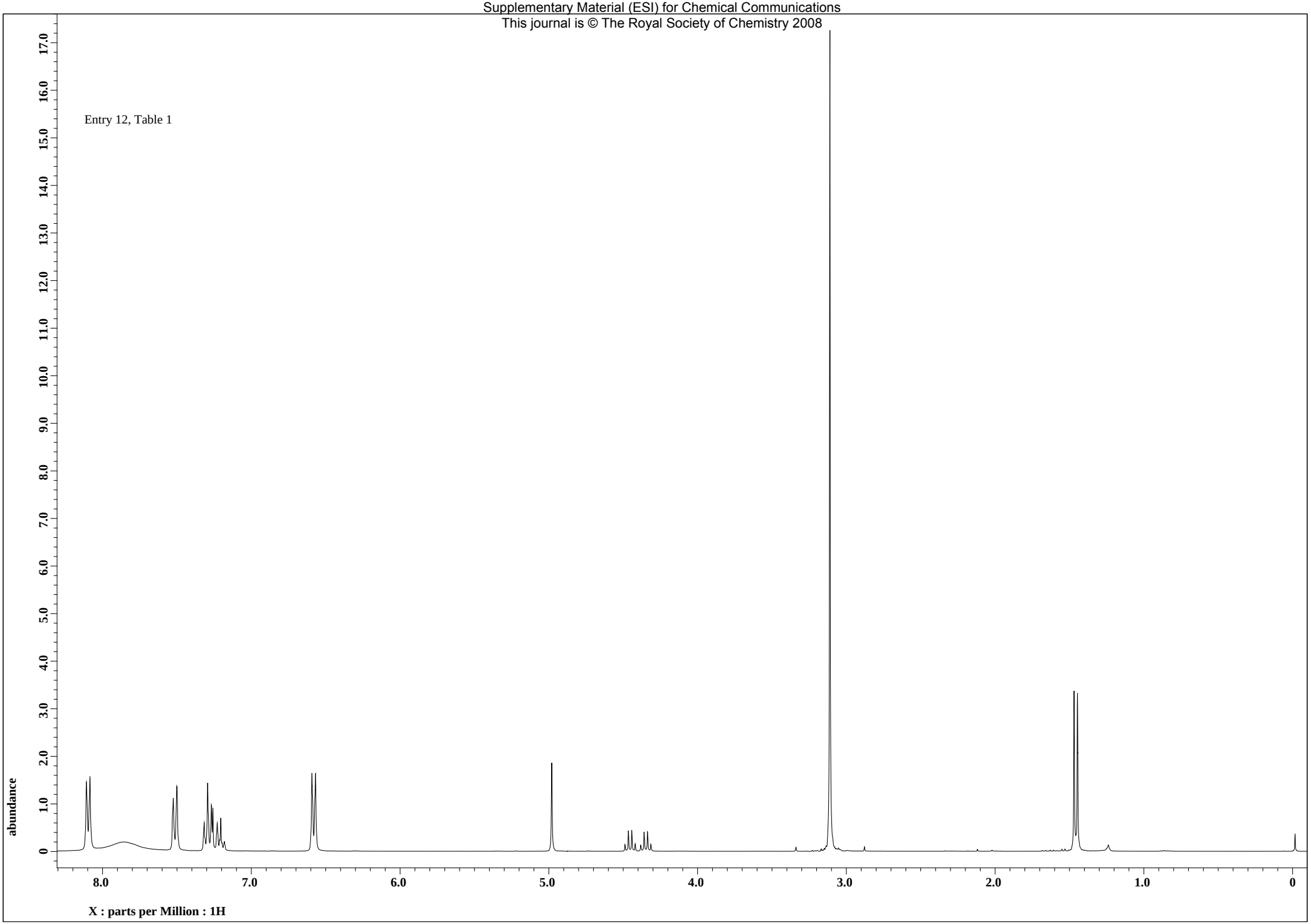


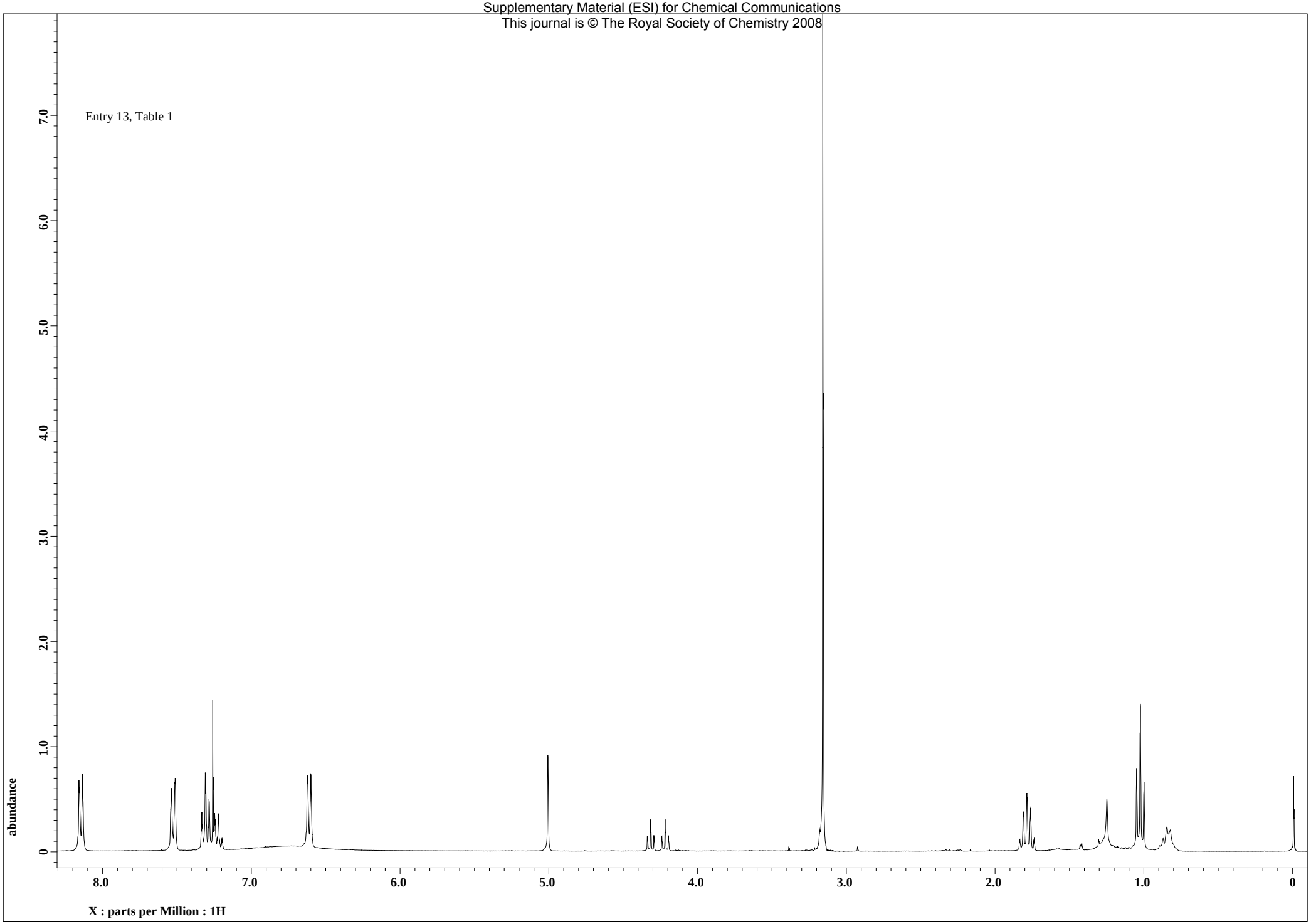


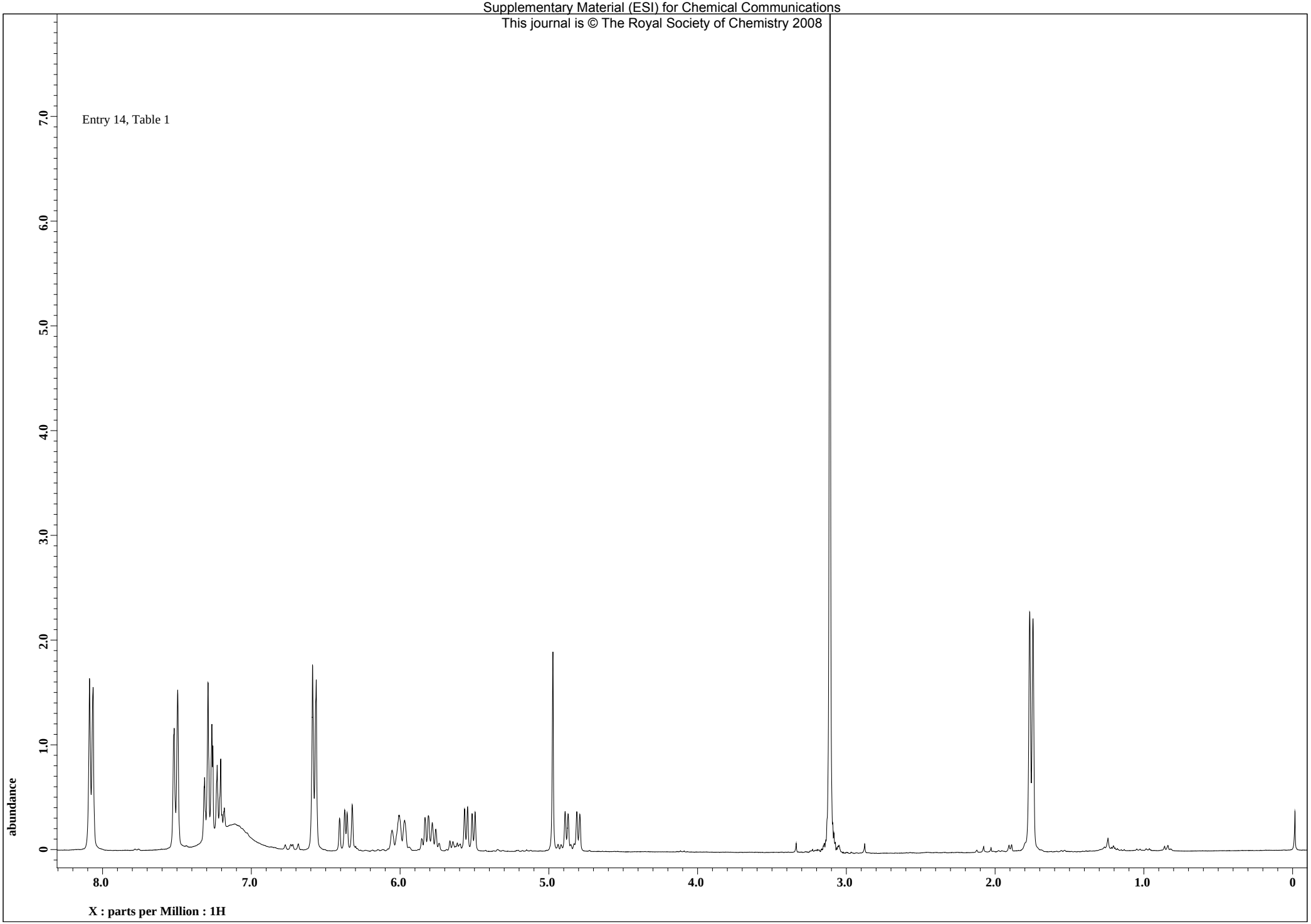




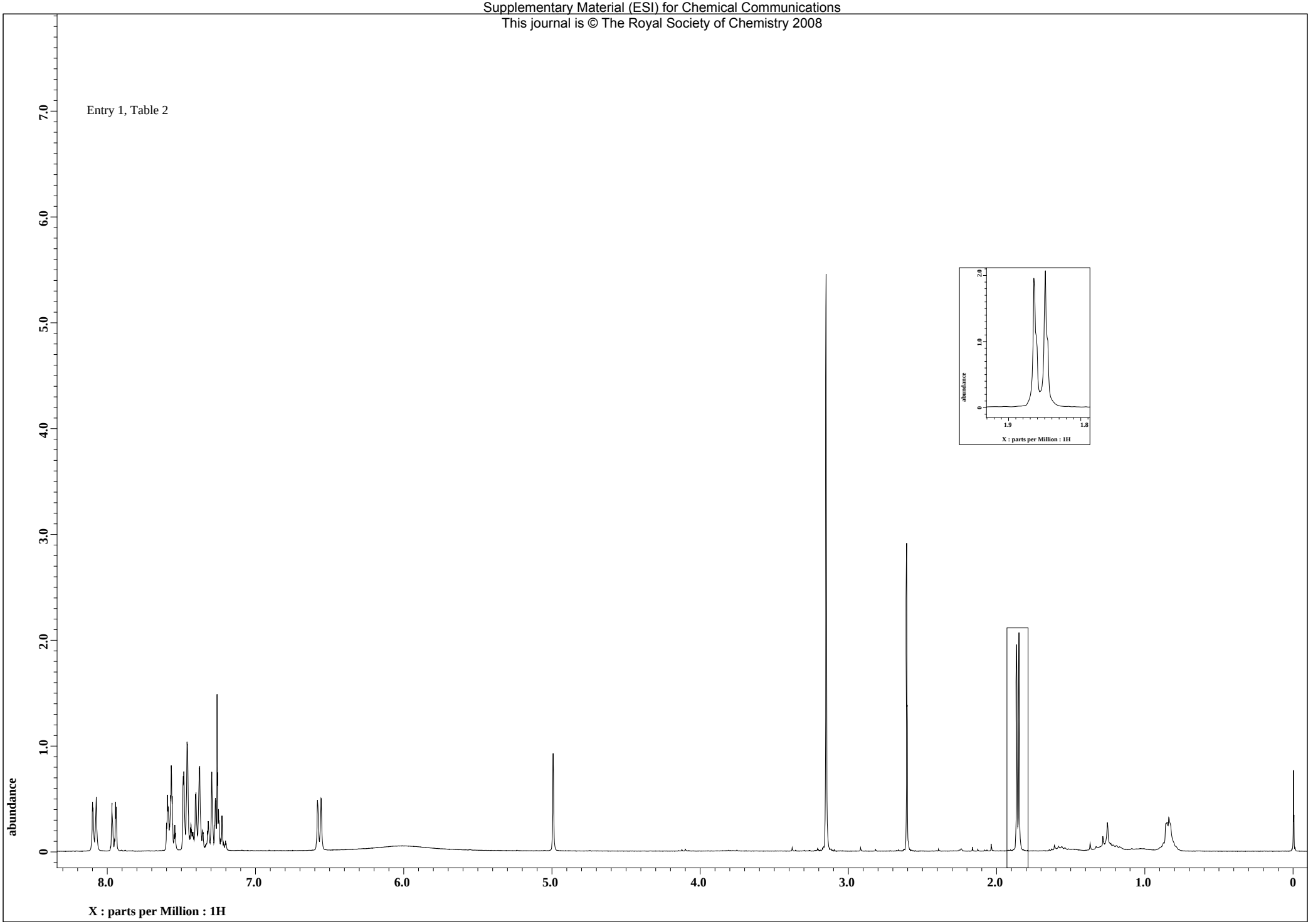




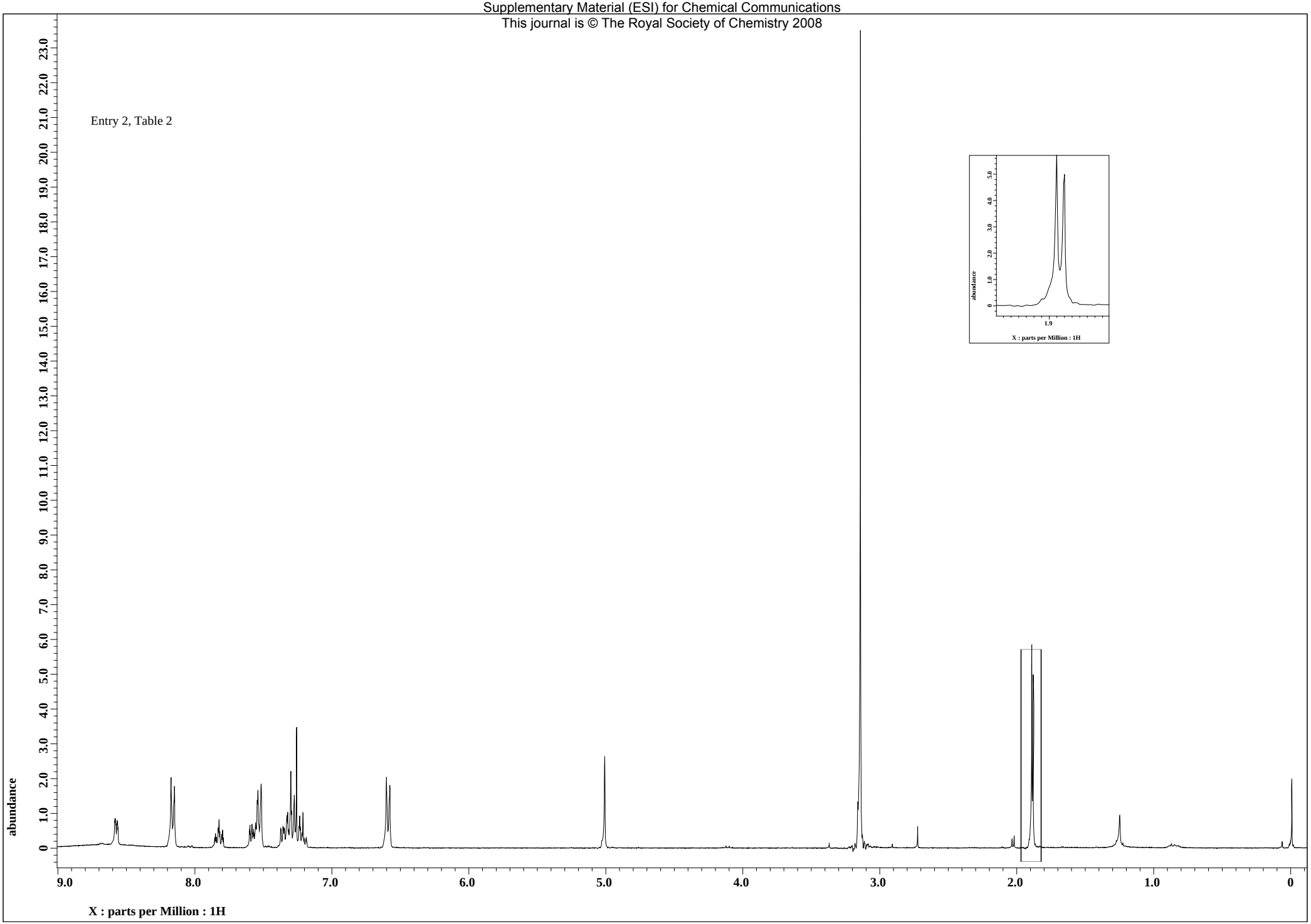


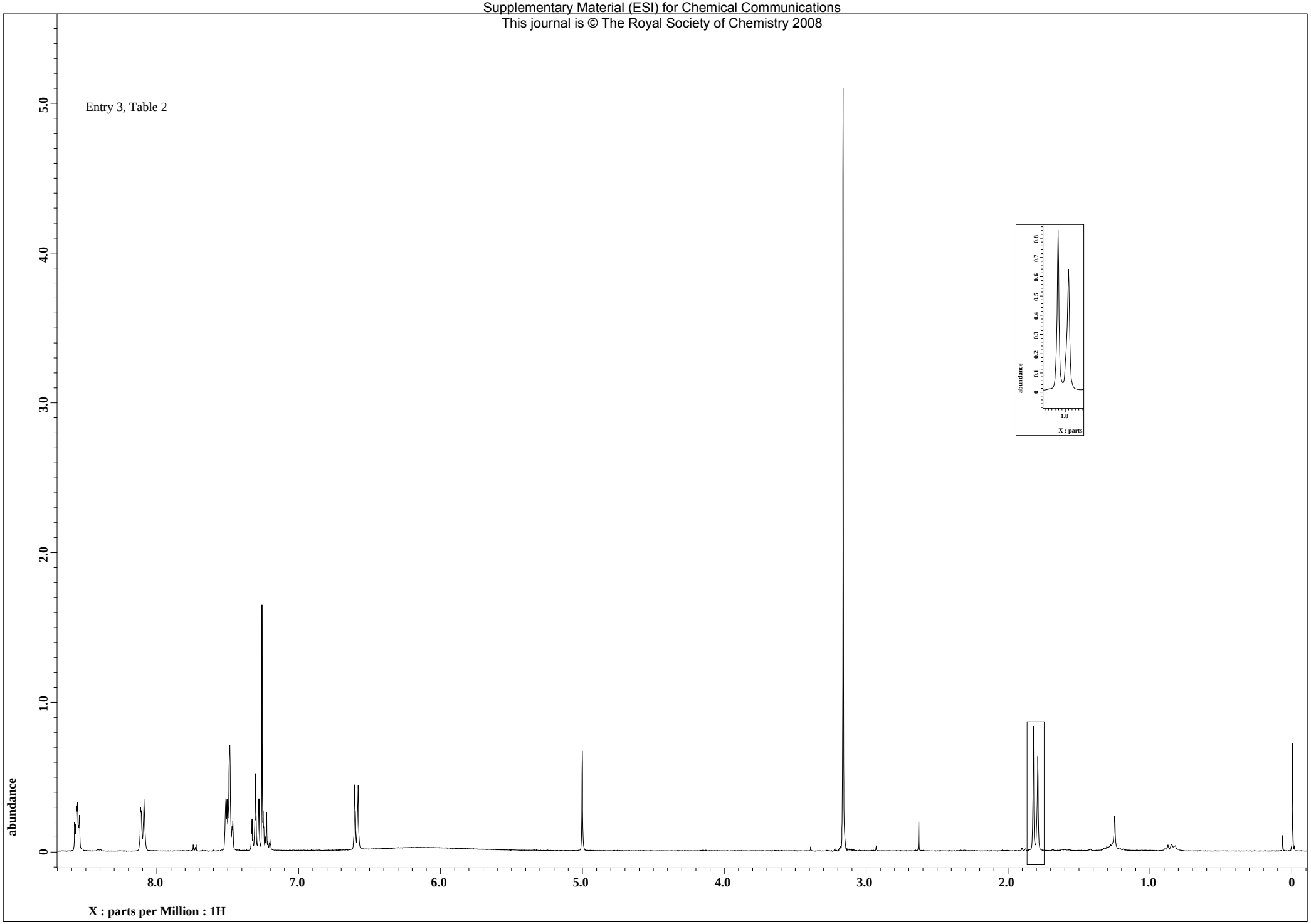


Entry 1, Table 2



Entry 2, Table 2





Entry 4, Table 2