Supporting Information

Phenyl-capped cyclopenta[*c*]chalcogenophenes: synthesis, crystal structures, electrochemistry and theoretical insights

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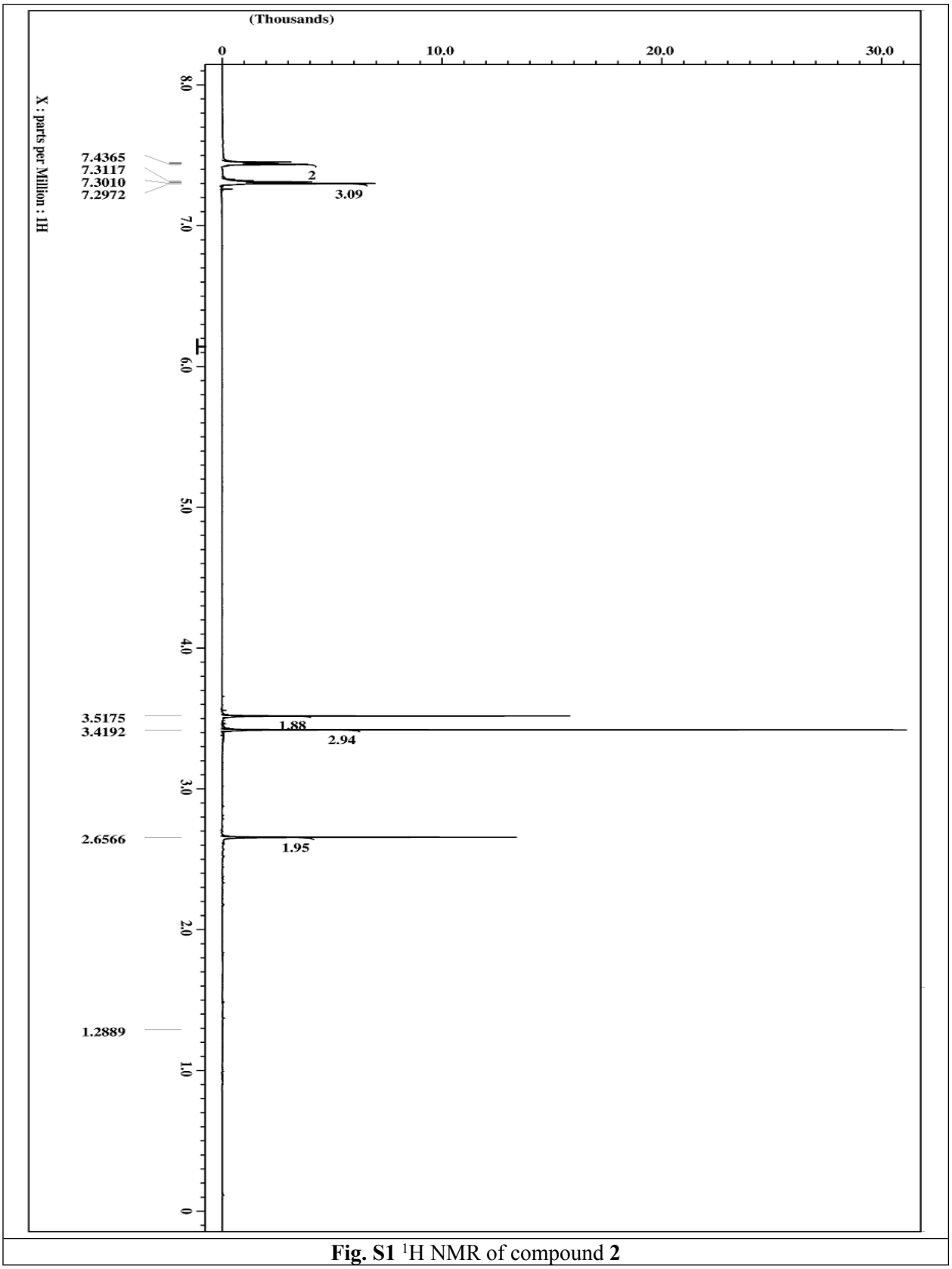

Fig. S1 ^{1}H NMR of compound **2**

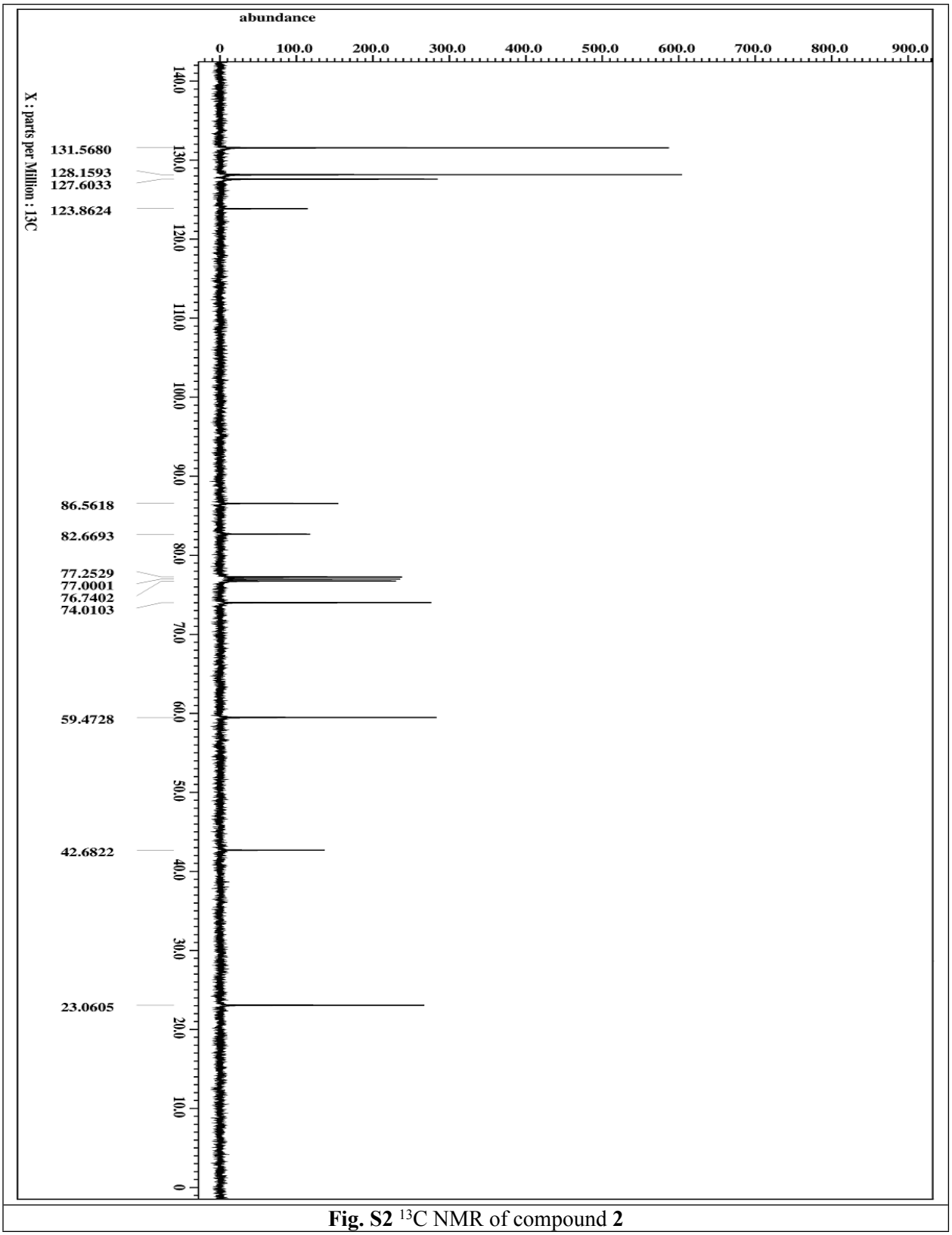

Fig. S2 ^{13}C NMR of compound **2**

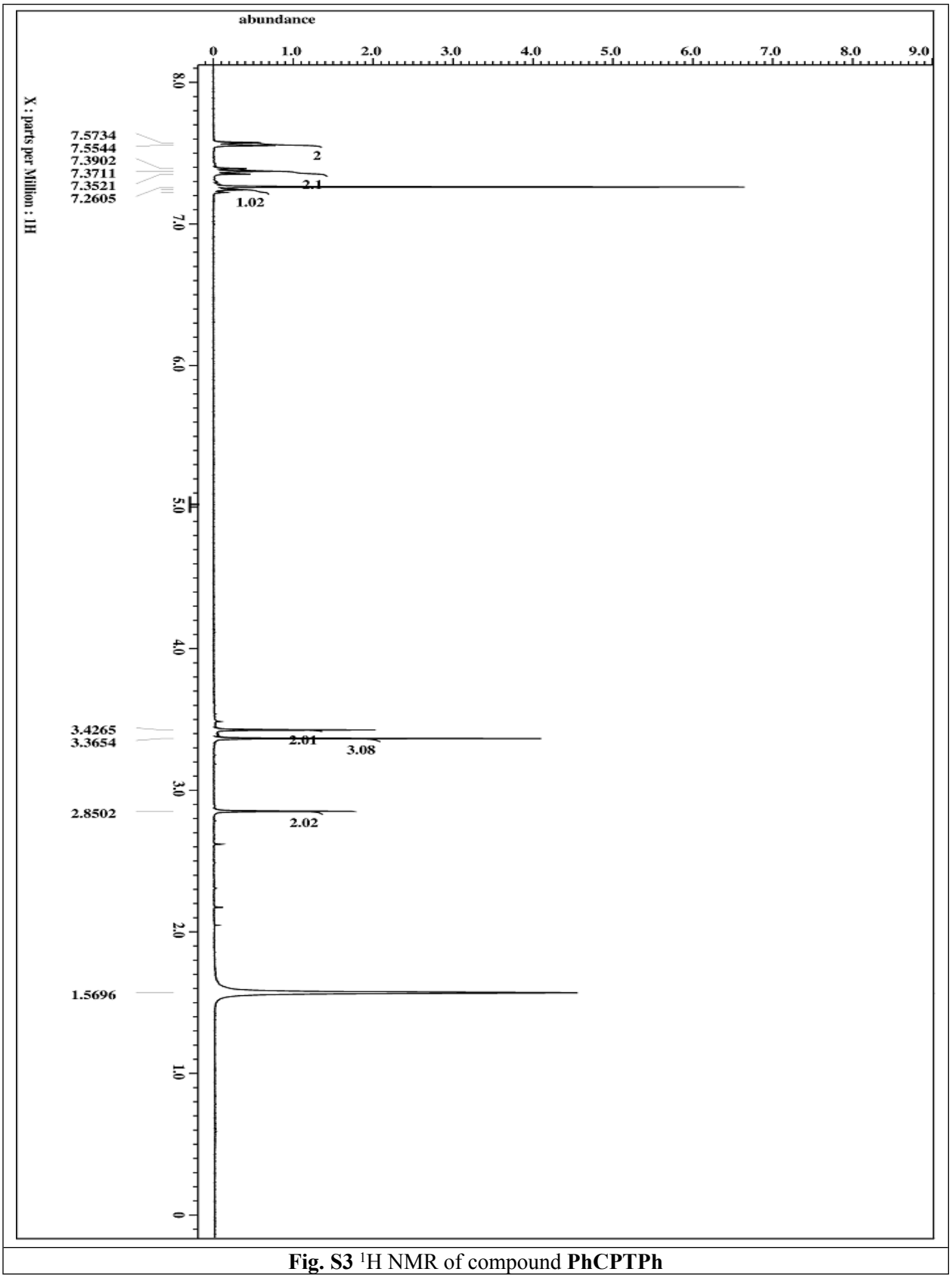

Fig. S3 ^{1}H NMR of compound **PhCPTPh**

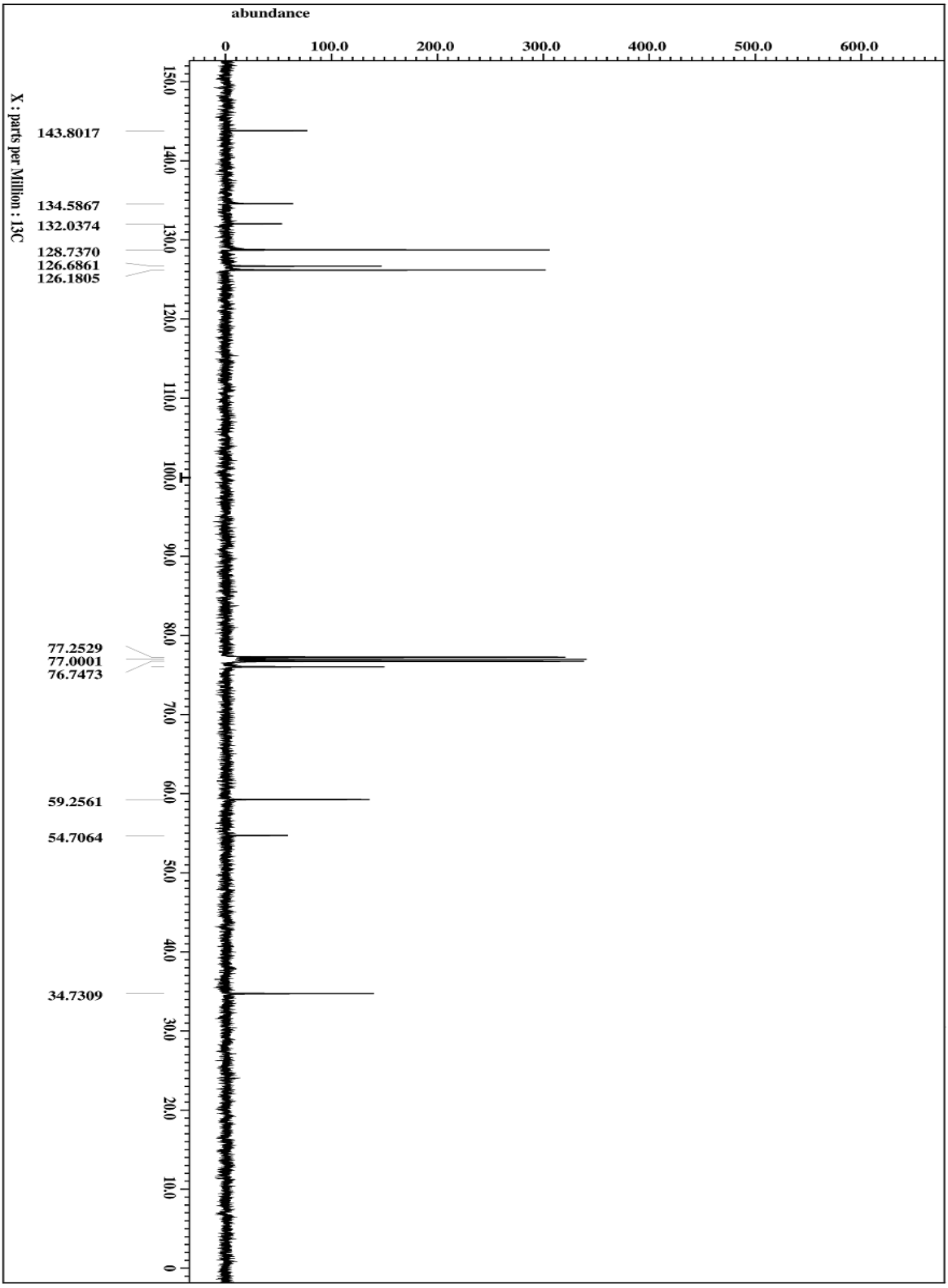

Fig. S4 ^{13}C NMR of compound **PhCPTPh**

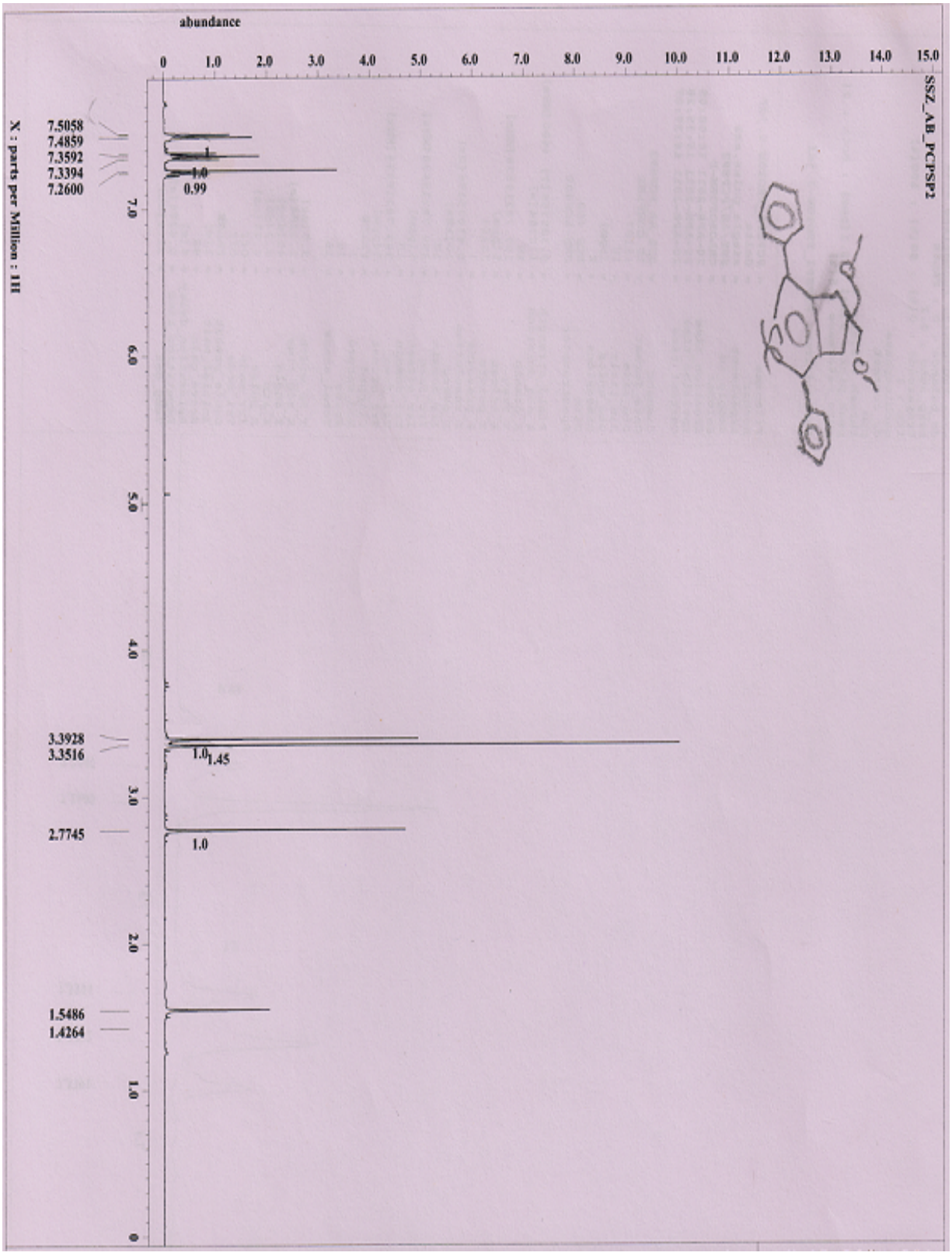

Fig. S5 ^{1}H NMR of compound **PhCPSPh**

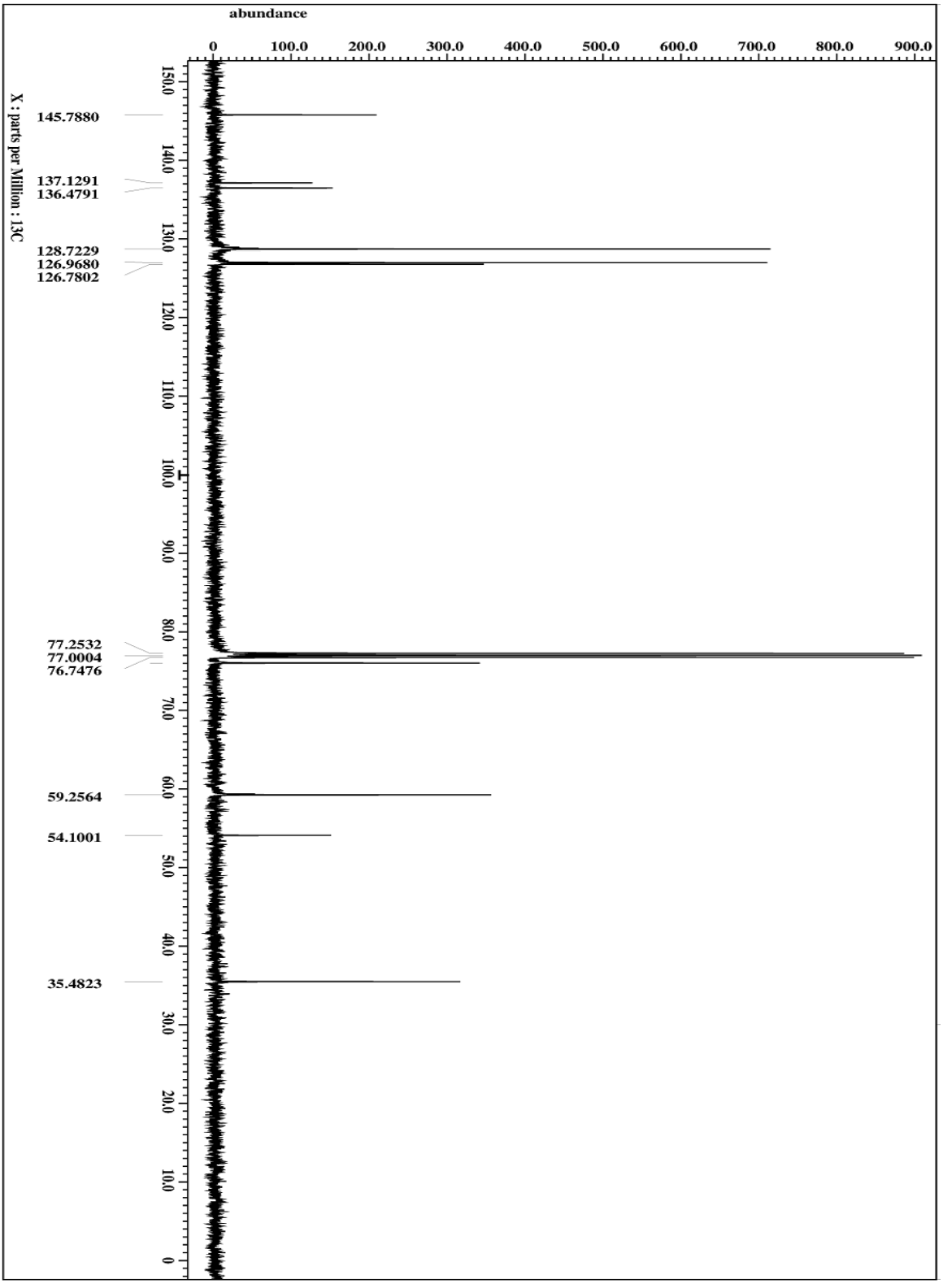

Fig. S6 ^{13}C NMR of compound **PhCPSPh**

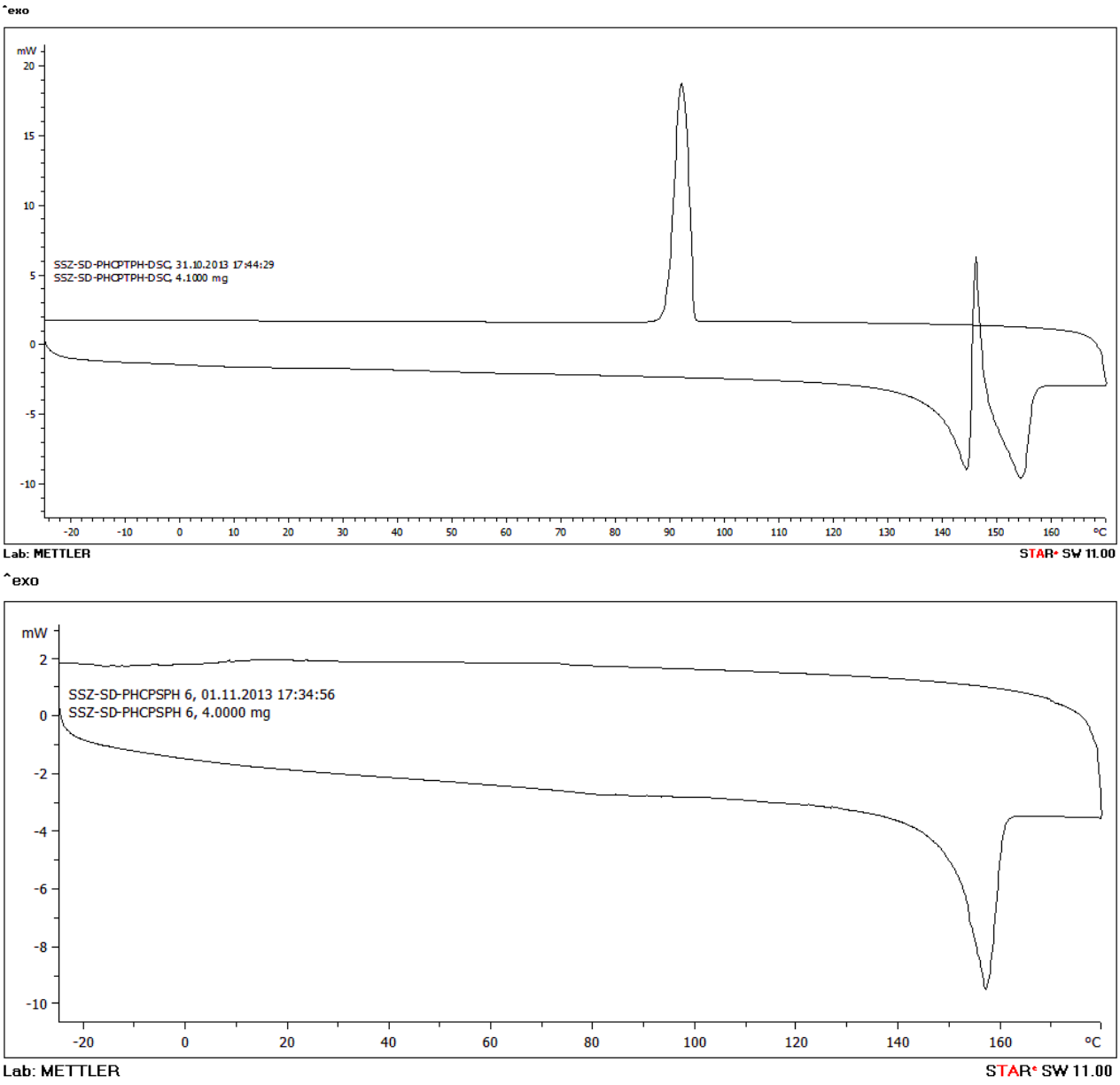

Fig. S7. DSC thermogram of **PhCPTPh** (above) and **PhCPSPh** (below)

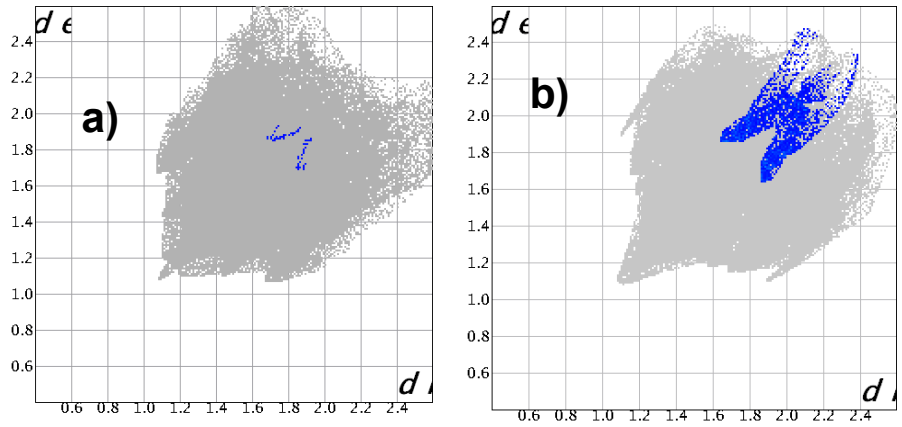

Fig S8. Fingerprint plot of the compound, a) PhCPTPh and (b) PhCPSPh The outline of the full fingerprint is shown in gray while C…S and C…Se interaction shown in blue.

Table S1 Relative contribution of different interactions to the total Hirshfeld surface

PhCPTPh		**PhCPSPh**	
Contact	%	Contact	%
H…H	57.9	H…H	61.3
C…H	30.6	C…H	26.7
O…H	5.4	O…H	5.3
S…H	5.1	Se…H	3.6
S…C	0.1	Se…C	2.7

Table S2. Important short contacts in the crystals

Number of types	**PhCPTPh**		**PhCPSPh**	
	anticipating atoms	bond length (Å)	anticipating atoms	bond length (Å)
1	C6···H20B	2.898	C23···Se1	3.514
2	S1···C14	3.488	H20···H20	2.377
3	O1···H23A	2.634	C1···C12	3.353
4	C13···H2	2.896	C7···H12B	2.897
5	C4···H18B	2.849	–	–
6	O2···H4	2.651	–	–

Table S3. Crystallographic data and refinement parameters for **PhCPTPh** and **PhCPSPh**

Parameters	**PhCPTPh**	**PhCPSPh**
Empirical formula	$C_{23}H_{24}O_2S$	$C_{23}H_{24}O_2Se$
Formula weight	364.49	411.38
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
T (K)	153 K	273 K
a (Å)	40.4991(18)	34.8342(19)
b (C)	5.9278(1)	5.7765(3)
c (Å)	16.1917(6)	22.9523(12)
α (°)	90	90
β (°)	106.414(6)	123.607(1)
γ (°)	90	90
Z	8	8
V (Å^3)	3728.7(2)	3846.5(4)
D_x (g/cm^3)	1.299	1.421
Radiation	MoK\α	MoK\α
μ(Mo Kα)/mm^{-1}	0.188	1.966
F(0 0 0)	1552.0	1696
Crystal size/mm	0.39 × 0.31 × 0.20	0.40 × 0.31 × 0.21
θ range for data collection (°)	2.26–31.41	2.81–33.71
Limiting indices	$-47 \le h \le 48$, $-7 \le k \le 7$, $-14 \le l \le 13$	$-44 \le h \le 44$, $-6 \le k \le 7$, $-27 \le l \le 29$
Reflections collected	15721	20054
Independent reflections	3273	4203
Observed reflections	3049	3049
Goodness-of-fit on F^2	1.09	1.079
R_1 and wR_2 indices [I > 2σ(I)]	$R1$ = 0.0356, w$R2$ = 0.0860	$R1$ = 0.0239, w$R2$ = 0.0547
R_1 and wR_2 (all data)	$R1$ = 0.0381, w$R2$ = 0.0879	$R1$ = 0.0307, w$R2$ = 0.0572
CCDC deposition number	995427	998094

Coordinates for optimized geometry of PhCPTPh

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.899591	-1.285386	-0.284814
2	6	0	-3.504055	-2.353813	0.405474
3	1	0	-2.882808	-3.051381	0.960457
4	6	0	-4.887015	-2.516160	0.406551
5	1	0	-5.327790	-3.348512	0.948949
6	6	0	-5.704813	-1.611342	-0.273573
7	1	0	-6.784129	-1.736076	-0.268596
8	6	0	-5.121164	-0.545950	-0.961694
9	1	0	-5.745306	0.160734	-1.502559
10	6	0	-3.737193	-0.386553	-0.973424
11	1	0	-3.297761	0.428500	-1.538657
12	6	0	-1.444454	-1.104680	-0.291026
13	6	0	-0.692943	0.037928	-0.440727
14	6	0	-1.002897	1.506179	-0.599114
15	1	0	-1.836867	1.854200	0.017242
16	1	0	-1.254667	1.742565	-1.644331
17	6	0	0.335029	2.208133	-0.194769
18	6	0	0.325437	2.522530	1.310181
19	1	0	0.234572	1.586150	1.886334
20	1	0	1.276134	3.002243	1.587033
21	6	0	-0.832812	3.728240	2.970541
22	1	0	-0.968658	2.839610	3.607897
23	1	0	-1.695825	4.388196	3.093765
24	1	0	0.073638	4.257670	3.305355
25	6	0	0.550094	3.490832	-0.999521
26	1	0	0.503659	3.263873	-2.079457
27	1	0	-0.247679	4.214784	-0.772369
28	6	0	2.080212	5.249491	-1.341581
29	1	0	2.081237	5.121447	-2.436480
30	1	0	3.070438	5.587105	-1.023773
31	1	0	1.338666	6.023334	-1.086143
32	6	0	1.448282	1.143784	-0.469056
33	1	0	1.866619	1.293575	-1.474430
34	1	0	2.288188	1.233041	0.228818
35	6	0	0.713904	-0.170476	-0.367415
36	6	0	1.083782	-1.479453	-0.160618
37	6	0	2.416415	-2.072711	-0.011443
38	6	0	3.542233	-1.463914	-0.599547
39	1	0	3.415668	-0.565247	-1.193957
40	6	0	4.812897	-2.016001	-0.452266
41	1	0	5.665116	-1.527584	-0.917726
42	6	0	4.992395	-3.194408	0.274517
43	1	0	5.983585	-3.625492	0.385033
44	6	0	3.884588	-3.814695	0.856055
45	1	0	4.009843	-4.731007	1.426983
46	6	0	2.614649	-3.260087	0.719462
47	1	0	1.766263	-3.740890	1.198694
48	8	0	-0.761548	3.384109	1.603919
49	8	0	1.818107	4.034710	-0.673956
50	16	0	-0.363907	-2.480646	-0.080059

Coordinates for optimized geometry of cation radical of PhCPTPh

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.930449	-1.174973	-0.251292
2	6	0	-3.575442	-2.368538	0.172169
3	1	0	-2.986429	-3.199611	0.548477
4	6	0	-4.955180	-2.478720	0.140623
5	1	0	-5.431529	-3.394333	0.476197
6	6	0	-5.735049	-1.407415	-0.317551
7	1	0	-6.816930	-1.496363	-0.341571
8	6	0	-5.120646	-0.223828	-0.745075
9	1	0	-5.724512	0.601694	-1.108294
10	6	0	-3.739828	-0.102456	-0.712890
11	1	0	-3.279859	0.810073	-1.068603
12	6	0	-1.497333	-1.058368	-0.223144
13	6	0	-0.676351	0.085932	-0.352656
14	6	0	-0.938333	1.560333	-0.507307
15	1	0	-1.724594	1.941119	0.150323
16	1	0	-1.240664	1.785735	-1.540854
17	6	0	0.437432	2.219884	-0.168393
18	6	0	0.449783	2.661281	1.307133
19	1	0	0.369596	1.779350	1.968740
20	1	0	1.407483	3.157711	1.521067
21	6	0	-0.660995	4.078125	2.836413
22	1	0	-0.765058	3.286774	3.594364
23	1	0	-1.526561	4.741827	2.890184
24	1	0	0.250211	4.654474	3.052434
25	6	0	0.722724	3.418678	-1.078831
26	1	0	0.611813	3.120806	-2.137097
27	1	0	-0.004370	4.219231	-0.875741
28	6	0	2.393768	5.019845	-1.552955
29	1	0	2.342081	4.848088	-2.638815
30	1	0	3.421164	5.268626	-1.278565
31	1	0	1.736943	5.864535	-1.298784
32	6	0	1.498332	1.086936	-0.359802
33	1	0	1.986638	1.177510	-1.339284
34	1	0	2.295181	1.140930	0.389369
35	6	0	0.688884	-0.180021	-0.273714
36	6	0	1.001873	-1.545217	-0.082003
37	6	0	2.281147	-2.191279	0.041132
38	6	0	3.475841	-1.516804	-0.327224
39	1	0	3.430714	-0.512158	-0.727247
40	6	0	4.705200	-2.148397	-0.215192
41	1	0	5.608186	-1.623128	-0.509798
42	6	0	4.783073	-3.460326	0.268528
43	1	0	5.748486	-3.949211	0.357499
44	6	0	3.616058	-4.144519	0.636560
45	1	0	3.676661	-5.159649	1.015656
46	6	0	2.383448	-3.524065	0.523193
47	1	0	1.490333	-4.059308	0.831584
48	8	0	-0.633273	3.539198	1.524438
49	8	0	2.041658	3.853752	-0.825799
50	16	0	-0.486862	-2.486554	-0.004168

Coordinates for optimized geometry of PhCPSPh

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.935966	-0.972568	-0.288257
2	6	0	-3.593195	-1.959203	0.472744
3	1	0	-3.002147	-2.650814	1.067731
4	6	0	-4.982600	-2.044891	0.491800
5	1	0	-5.463995	-2.814578	1.089389
6	6	0	-5.754889	-1.141162	-0.241341
7	1	0	-6.839358	-1.205479	-0.223297
8	6	0	-5.119643	-0.155575	-0.998975
9	1	0	-5.708944	0.548497	-1.580792
10	6	0	-3.728976	-0.073273	-1.027136
11	1	0	-3.249768	0.677995	-1.645918
12	6	0	-1.474425	-0.876937	-0.304302
13	6	0	-0.666964	0.220813	-0.459440
14	6	0	-0.947141	1.696610	-0.622121
15	1	0	-1.786131	2.057601	-0.020359
16	1	0	-1.176619	1.934771	-1.672126
17	6	0	0.394279	2.376084	-0.201905
18	6	0	0.387280	2.658521	1.309192
19	1	0	0.284967	1.711450	1.865400
20	1	0	1.343263	3.121267	1.596750
21	6	0	-0.757927	3.842738	2.993698
22	1	0	-0.903894	2.942547	3.612351
23	1	0	-1.613575	4.509597	3.130618
24	1	0	0.154286	4.354879	3.339740
25	6	0	0.626340	3.672340	-0.979445
26	1	0	0.575927	3.469128	-2.063960
27	1	0	-0.161092	4.402357	-0.736137
28	6	0	2.180345	5.416740	-1.285608
29	1	0	2.179406	5.312074	-2.383040
30	1	0	3.175123	5.734228	-0.961252
31	1	0	1.449325	6.194940	-1.013446
32	6	0	1.487742	1.301798	-0.499507
33	1	0	1.883241	1.449817	-1.514591
34	1	0	2.344847	1.378601	0.178319
35	6	0	0.743215	-0.008321	-0.388835
36	6	0	1.143277	-1.302764	-0.174099
37	6	0	2.490792	-1.855698	-0.019685
38	6	0	3.596152	-1.260217	-0.658060
39	1	0	3.442827	-0.400969	-1.302344
40	6	0	4.879539	-1.779135	-0.498870
41	1	0	5.715259	-1.303033	-1.005219
42	6	0	5.092928	-2.909012	0.292766
43	1	0	6.094030	-3.313927	0.412586
44	6	0	4.006416	-3.515129	0.927427
45	1	0	4.158424	-4.392918	1.550035
46	6	0	2.724459	-2.993325	0.777745
47	1	0	1.889757	-3.457201	1.297216
48	8	0	-0.689948	3.526514	1.620258
49	8	0	1.902146	4.191684	-0.643885
50	34	0	-0.389087	-2.412853	-0.074569

Coordinates for optimized geometry of cation radical of PhCPSPh

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.976186	-0.765394	-0.269649
2	6	0	-3.717245	-1.869082	0.233648
3	1	0	-3.194868	-2.714276	0.673351
4	6	0	-5.101307	-1.867829	0.210994
5	1	0	-5.649405	-2.715035	0.610617
6	6	0	-5.792474	-0.769706	-0.319965
7	1	0	-6.878115	-0.770143	-0.338247
8	6	0	-5.084452	0.326562	-0.827487
9	1	0	-5.620203	1.171575	-1.248275
10	6	0	-3.697967	0.336589	-0.801975
11	1	0	-3.166950	1.179573	-1.223796
12	6	0	-1.539530	-0.775465	-0.245088
13	6	0	-0.629680	0.294838	-0.384902
14	6	0	-0.815395	1.782525	-0.541710
15	1	0	-1.598797	2.199225	0.096954
16	1	0	-1.080038	2.020807	-1.582998
17	6	0	0.580215	2.375145	-0.175180
18	6	0	0.601981	2.766927	1.314221
19	1	0	0.481984	1.868388	1.946687
20	1	0	1.577627	3.216833	1.549072
21	6	0	-0.460542	4.175743	2.884582
22	1	0	-0.602010	3.364004	3.614463
23	1	0	-1.298703	4.872157	2.956447
24	1	0	0.471807	4.706688	3.125504
25	6	0	0.923482	3.589539	-1.043586
26	1	0	0.805072	3.332638	-2.111716
27	1	0	0.232423	4.415135	-0.816438
28	6	0	2.669427	5.126428	-1.458041
29	1	0	2.617530	4.991978	-2.549177
30	1	0	3.705186	5.319131	-1.170221
31	1	0	2.050104	5.991925	-1.180636
32	6	0	1.585047	1.202485	-0.400076
33	1	0	2.048240	1.282837	-1.393052
34	1	0	2.404302	1.214415	0.325935
35	6	0	0.726573	-0.033580	-0.308353
36	6	0	1.027303	-1.397153	-0.104531
37	6	0	2.304410	-2.045095	0.017051
38	6	0	3.497066	-1.413690	-0.426902
39	1	0	3.453020	-0.437900	-0.892723
40	6	0	4.720611	-2.056678	-0.312442
41	1	0	5.620915	-1.565589	-0.668026
42	6	0	4.796402	-3.335991	0.251742
43	1	0	5.757648	-3.832600	0.343061
44	6	0	3.632387	-3.977633	0.697373
45	1	0	3.691114	-4.966508	1.140719
46	6	0	2.405922	-3.346371	0.579433
47	1	0	1.515037	-3.843054	0.953944
48	8	0	-0.445765	3.681129	1.555286
49	8	0	2.259540	3.955177	-0.770772
50	34	0	-0.582041	-2.392098	0.004338