Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Symmetrical and Unsymmetrical Triphenylamine based Diketopyrrolopyrroles and their use as Donor for Solution Processed Bulk Heterojunction Organic Solar Cells

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Experimental part

General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under argon atmosphere. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on the BrukerAvance (III) 400 MHz instrument by using $CDCl_3$. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent

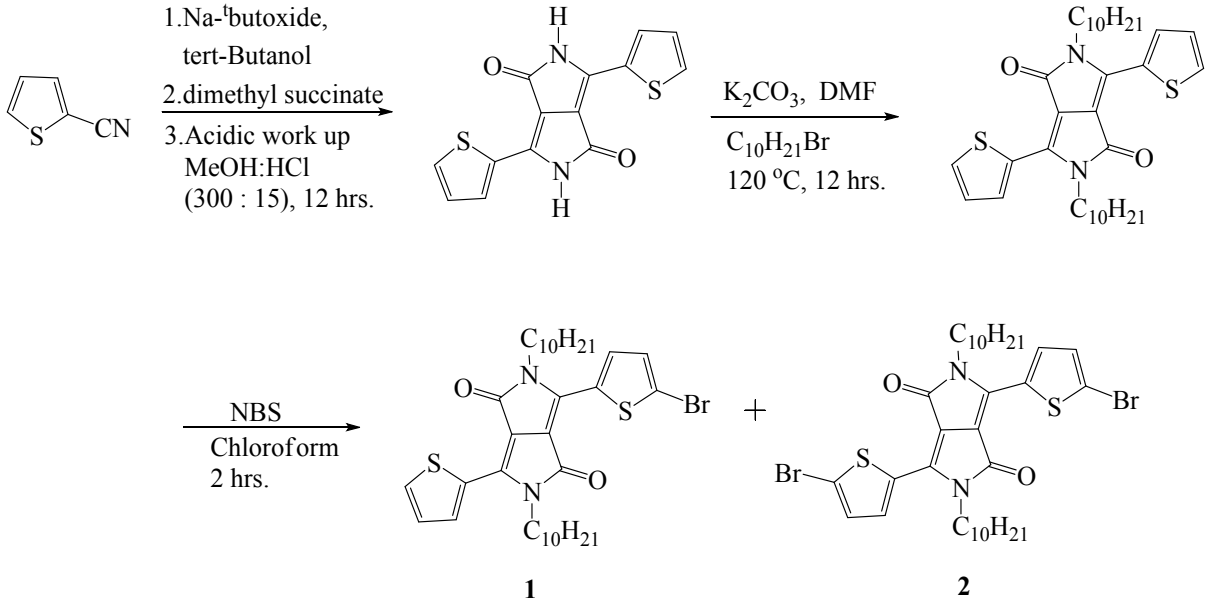
residual peak ($CDCl_3$, 7.26 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and the coupling constants, *J*, are given in Hz. ^{13}C NMR chemical shifts are reported relative to the solvent residual peak ($CDCl_3$, 77.02 ppm. Thermogravimetric analysis were performed on the Metler Toledo Thermal Analysis system. UV-visible absorption spectra were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Cyclic voltammograms(CVs) and differential pulse voltammograms (DPVs) were recorded on electrochemical analyzer using glassy carbon as working electrode, Pt wire as the counter electrode, and Saturated Ag/Ag^+ as the reference electrode. The scan rate was 100 mV s^{-1} for Cyclic voltammetry. A solution of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in dichloromethane (0.1 M) was used as the supporting electrolyte. All of the measurements were done at 25 °C. HRMS were recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer.

Experimental details

The SMOSCs were fabricated with a structure of ITO/PEDOT:PSS/**DPP3** or **DPP4**:$PC_{71}BM$/Al by using conventional solution spin casting technique. The indium tin oxide (ITO) coated glass substrates were cleaned sequentially by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol for 20 min. A layer of PEDOT:PSS was spin coated (3500 rpm, ~35 nm thick) onto ITO glass substrate and baked at 120° C for 20 min. The active layer was spin coated from the different weight ratios blends of **DPP3** or **DPP4** and $PC_{71}BM$ in chloroform and solvent additive (different concentration of 1,8–diiodooctane (DIO))/chloroform solution (concentration 15 mg/mL) at 1500 rpm for 25 sec on the top of ITO/PEDOT:PSS substrate. Finally 60 nm Al layer was deposited onto the active layer under high vacuum by a show mask to define the active layer 20 mm^2. All devices were fabricated and tested in ambient atmosphere without encapsulation. The hole-only and electron-only devices with ITO/ PEODT:PSS /active layer/ Au and ITO/ Al/active layer :$PC_{71}BM$/ Al architectures were also fabricated in an analogous way, in order to measure the hole and electron mobility, respectively. The current-voltage characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley© 238 source meter under simulated AM1.5G, 100 mW/cm^2. A xenon light source coupled with optical filter was used to give the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured illuminating the device through the light source and monochromator and the resulting current was measured using a Keithley electrometer under short circuit condition (V= 0V).

Synthesis of starting precursorsDPP**1** and DPP**2**

The starting precursorsmonobromodiketopyrrolopyrrole**1** and dibromodiketopyrrolopyrrole **2** were synthesized by reported procedures as shown in Scheme S1. Under argon atmosphere reaction of 2-thiophenecarbonnitrile with half equivalent of dimethyl succinate in presence of strong base sodium *tert*-butoxide in tert-butanol at 120 ^{o}C for 12 hours resulted in the formation of diketopyrrolopyrrole (DPP) in 65% yield. After completion of reaction worked up by methanol:hydrochloric acid (300ml methanol:15ml conc.HCl), filtered on Buchner funnel and finally washed with methanol yielded maroon solid. To make soluble, DPP was reacted with excess amount of 1-bromodecane in presence of base K_2CO_3 in *N,N* dimethylformamide (DMF) at 120 ^{o}C for 12 hours under argon atmosphere. The solvent was removed under vacuo and crude compound was purified by silica column chromatography (eluted with 50% dichloromethane in hexane) yielded 23% shiny crystalline solid. Then it was brominated with one equivalent and two equivalents of *N*- bromosuccinmide to give monobrominatedDPP**1** and dibrominatedDPP**2** respectively. Bromination carried out at room temperature in dry chloroform and compounds were purified by the use of silica-column chromatography, eluted with 30 – 80% of dichloromethane in hexane yielded 90% of pure compounds.



Scheme S1 Synthesis of alkyl-substituted bromodiketopyrrolopyrroles (DPP**1** and DPP**2**) as precursors.

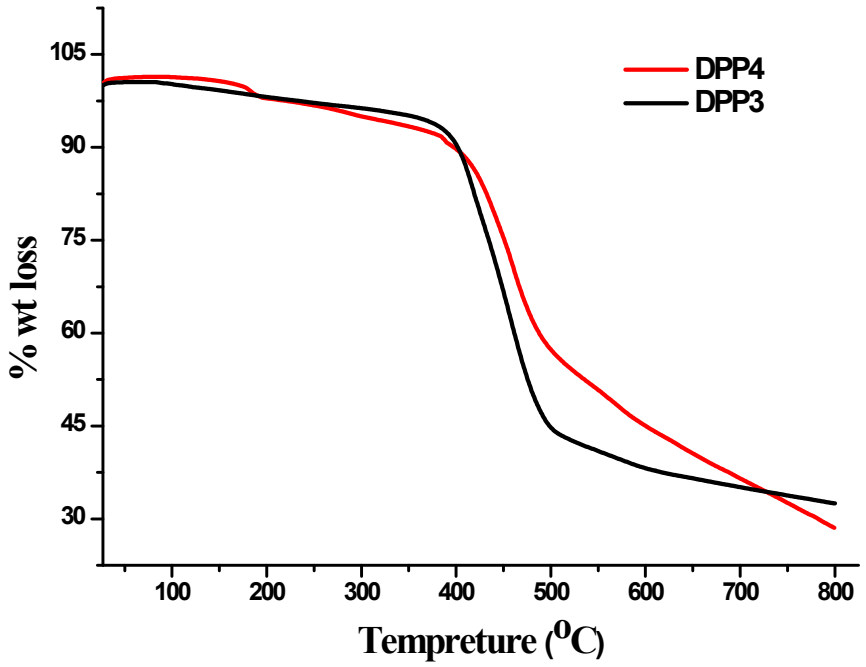


Fig.S1 TGA Curves of **DPP3** and **DPP4**

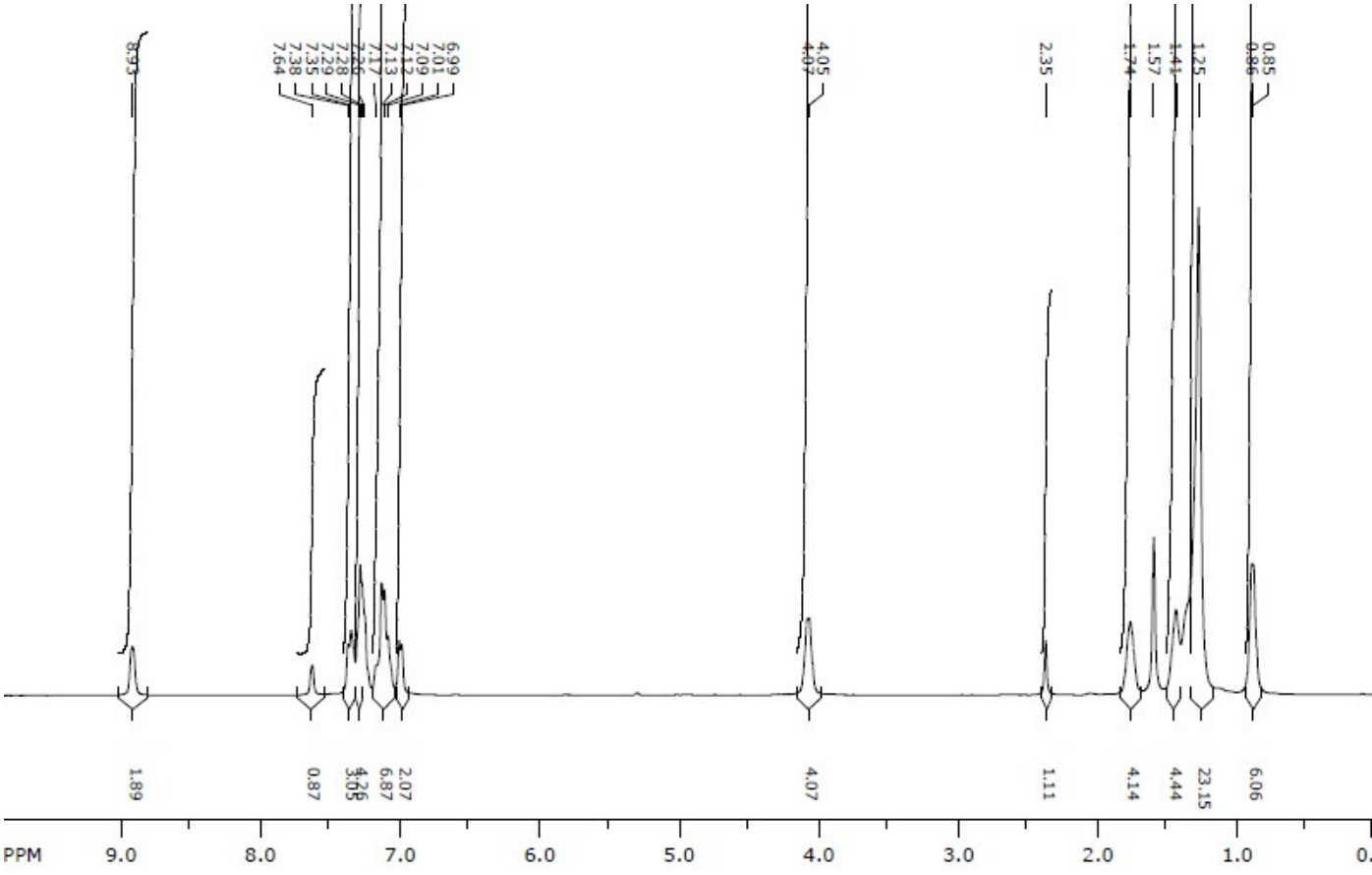


Fig.S2[1]H NMR Spectrum of **DPP3**

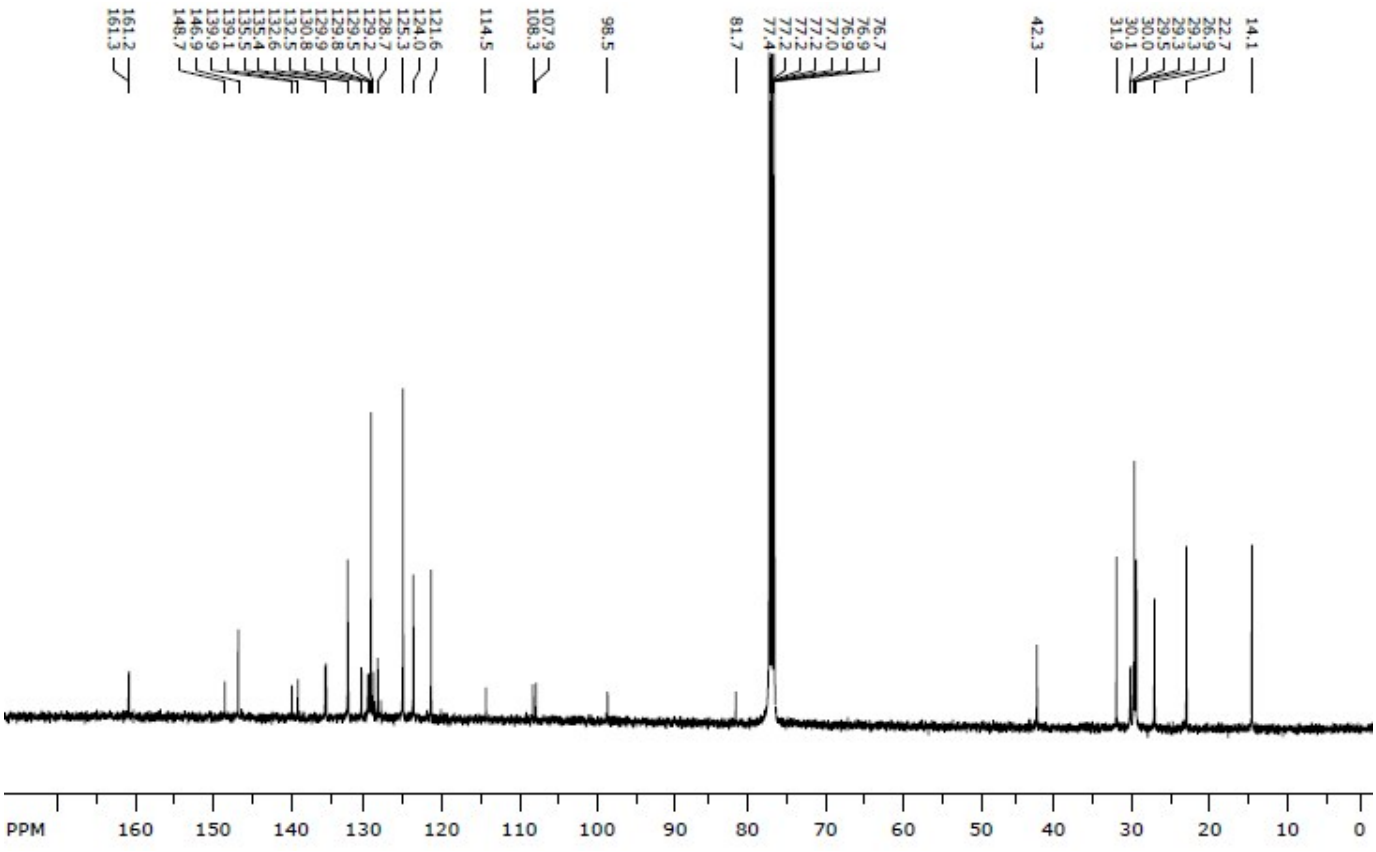


Fig.S3^{13}C NMR Spectrum of **DPP3**

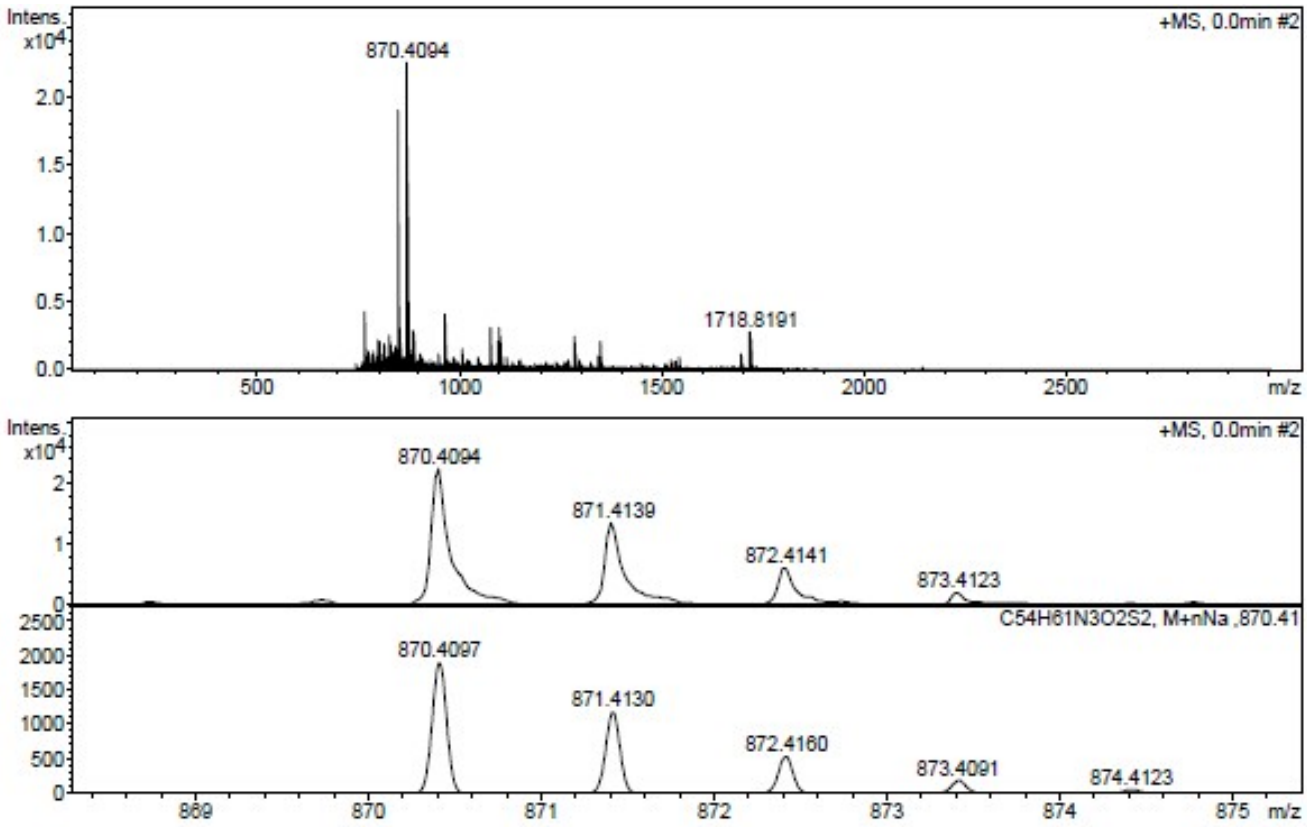


Fig. S4HRMS of **DPP3**

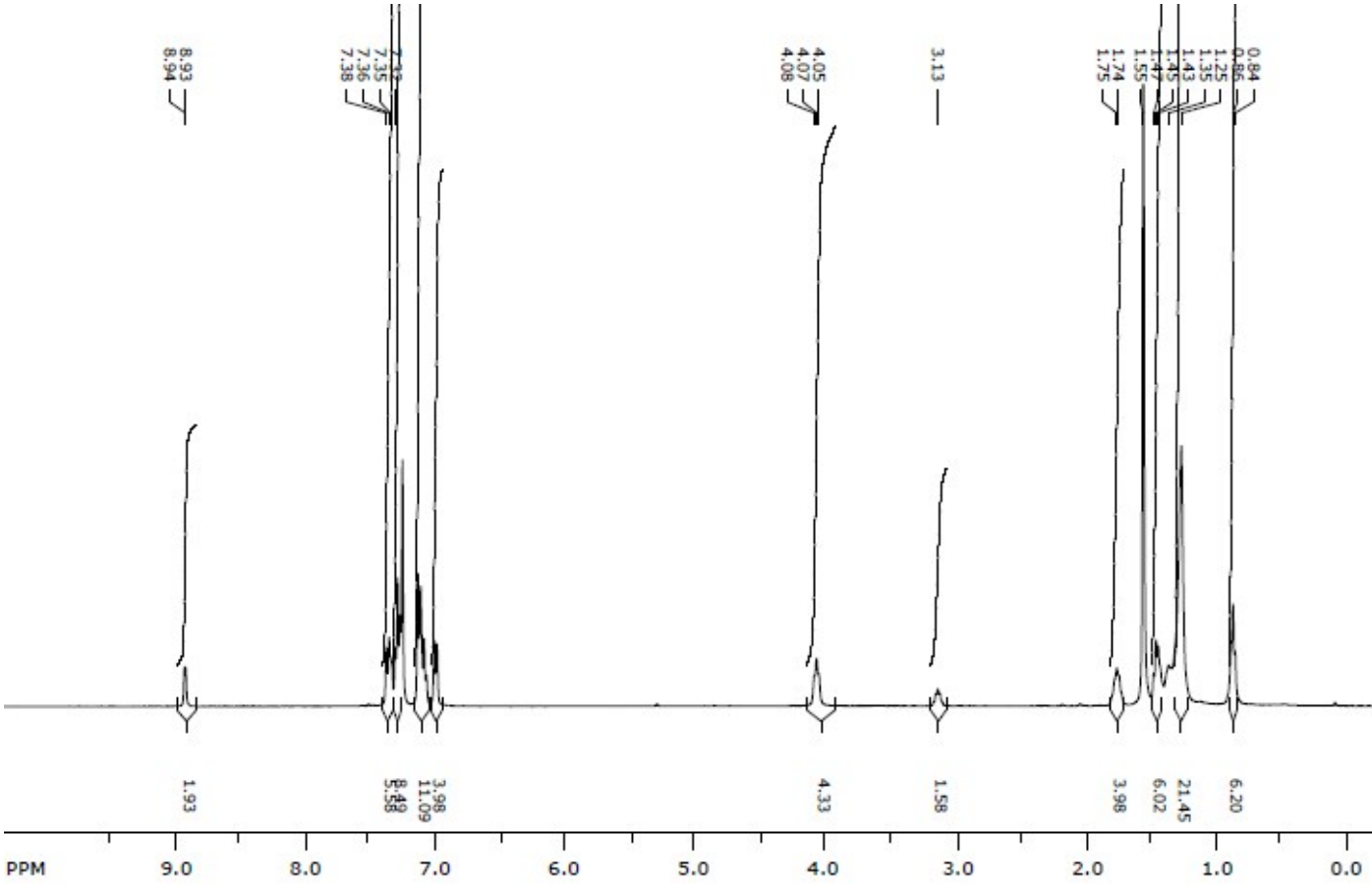


Fig.S5 ^{1}H NMR spectrum of **DPP4**

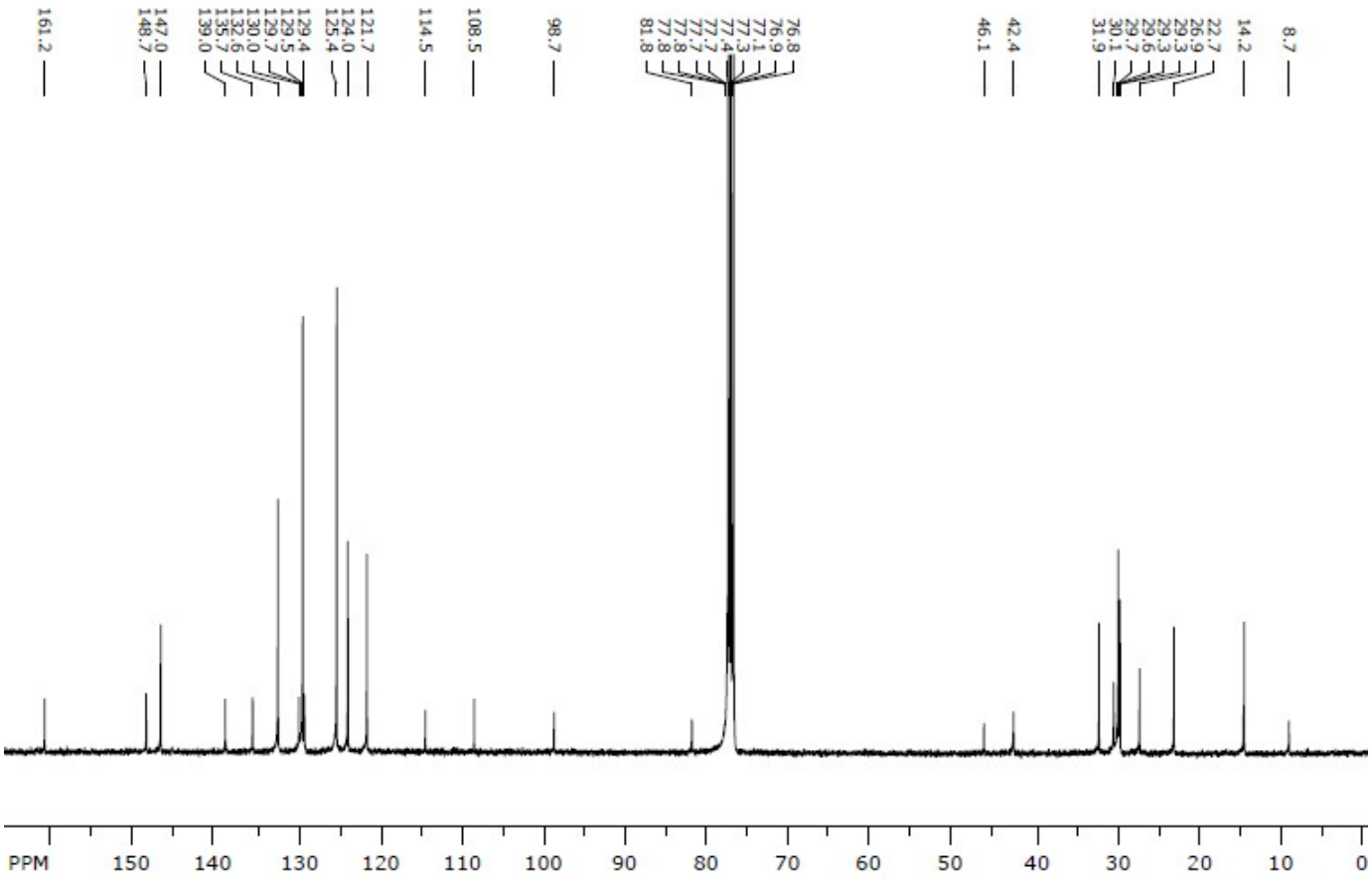


Fig.S6^{13}C NMR Spectrum of **DPP4**

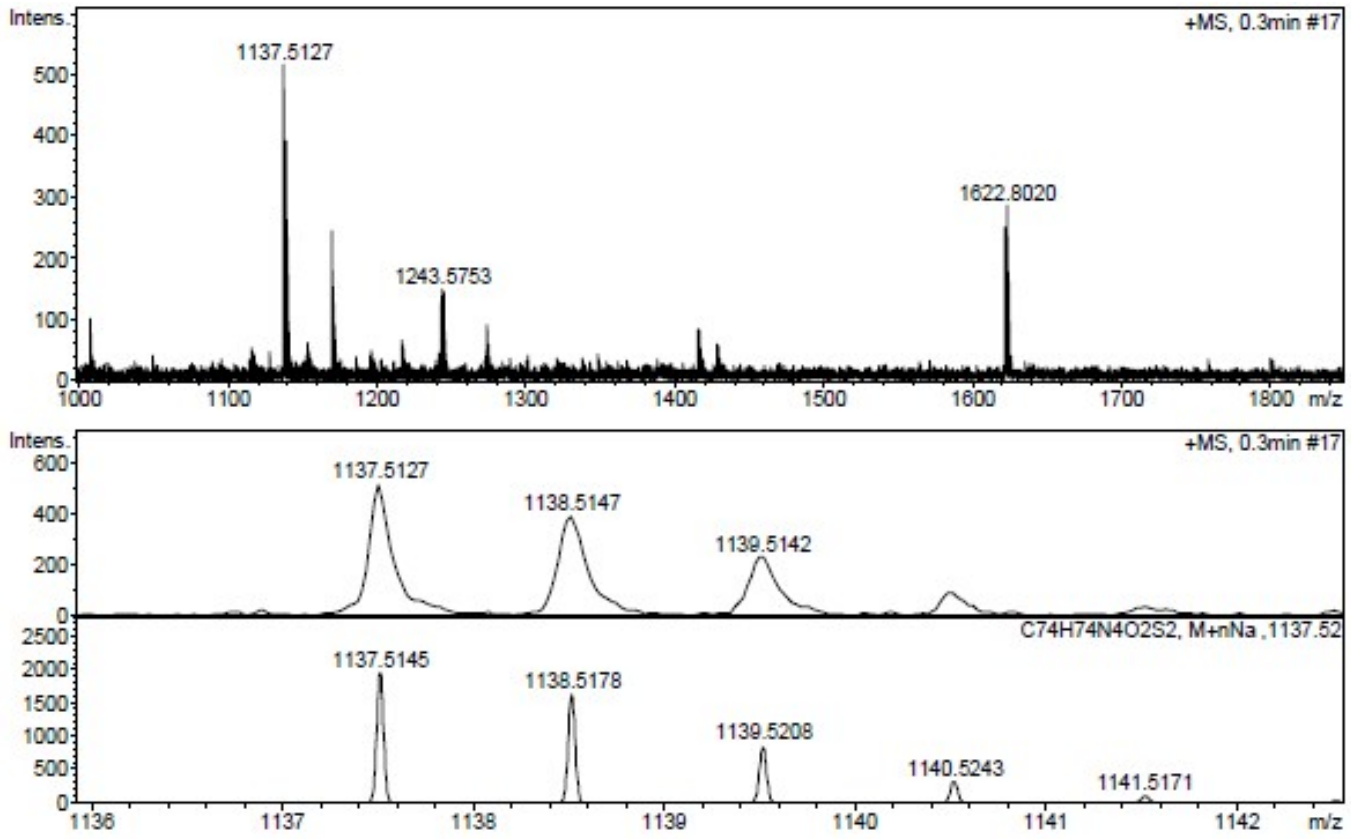


Fig.S7HRMS of **DPP4**

DFT Calculation data

Calculation method: B3LYP/6-31+G** for C, H, N, O, S with Gaussian 09.

DPP3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.579787	-1.515505	-0.422322
2	6	0	-4.239009	-1.404181	-0.346194
3	6	0	-4.748084	-0.156864	0.018996
4	6	0	-6.167708	-0.188785	-0.019136
5	6	0	-4.340187	1.177926	0.400804
6	6	0	-6.674491	1.067635	0.300396
7	6	0	-8.052162	1.498380	0.353180
8	6	0	-8.590847	2.778327	0.337586
9	16	0	-9.348778	0.306410	0.418131
10	6	0	-10.005470	2.801142	0.394782
11	1	0	-7.997295	3.676493	0.251364
12	6	0	-10.548742	1.543431	0.455349

13	1	0	-10.593163	3.711530	0.384606
14	1	0	-11.594655	1.272130	0.502418
15	6	0	-2.860206	-1.809604	-0.440602
16	6	0	-2.299090	-3.056812	-0.713784
17	16	0	-1.575902	-0.625403	-0.176684
18	6	0	-0.895210	-3.069626	-0.722808
19	1	0	-2.877554	-3.950287	-0.888462
20	6	0	-0.335202	-1.828120	-0.453969
21	1	0	-0.297066	-3.952080	-0.913624
22	6	0	-5.411127	-3.614290	-1.045904
23	1	0	-6.381454	-3.712500	-1.538247
24	1	0	-4.642158	-3.796936	-1.799818
25	6	0	-5.527619	3.257724	1.069835
26	1	0	-6.427058	3.441238	1.660340
27	1	0	-4.669482	3.295385	1.745996
28	6	0	-5.338154	4.303738	-0.032525
29	1	0	-5.304552	5.308062	0.402492
30	1	0	-4.394451	4.124029	-0.553067
31	1	0	-6.145854	4.274084	-0.770292
32	6	0	-5.336220	-4.610053	0.115654
33	1	0	-4.407949	-4.510703	0.685281
34	1	0	-6.174368	-4.446283	0.798018
35	1	0	-5.399719	-5.635636	-0.262968
36	7	0	-5.344797	-2.219323	-0.621564
37	7	0	-5.575035	1.888841	0.562151
38	8	0	-7.675299	-2.043555	-0.579653
39	8	0	-3.248633	1.706832	0.588545
40	6	0	1.021938	-1.486554	-0.380795
41	6	0	2.196798	-1.165919	-0.310237
42	6	0	3.562692	-0.795509	-0.225057
43	6	0	3.935312	0.529545	0.086248
44	6	0	4.589986	-1.737163	-0.446064
45	6	0	5.269593	0.893673	0.179594
46	1	0	3.161201	1.267303	0.270048
47	6	0	5.924790	-1.371321	-0.364782
48	1	0	4.326303	-2.759169	-0.697964
49	6	0	6.291118	-0.049288	-0.046053
50	1	0	5.531912	1.914334	0.434132
51	1	0	6.697242	-2.108493	-0.552360
52	7	0	7.649311	0.323555	0.043529
53	6	0	8.067596	1.623942	-0.364764
54	6	0	8.946238	2.368349	0.436545
55	6	0	7.616152	2.169696	-1.576216
56	6	0	9.367892	3.631881	0.027080
57	1	0	9.293936	1.950464	1.375420
58	6	0	8.029318	3.441269	-1.968727
59	1	0	6.943960	1.593457	-2.203246
60	6	0	8.909474	4.177798	-1.173408
61	1	0	10.048143	4.196765	0.657849
62	1	0	7.671700	3.850915	-2.908938
63	1	0	9.234590	5.165286	-1.485853
64	6	0	8.621899	-0.594057	0.535794
65	6	0	8.364050	-1.360657	1.683003
66	6	0	9.856458	-0.733353	-0.116472
67	6	0	9.320212	-2.256866	2.156410
68	1	0	7.415440	-1.249292	2.197545
69	6	0	10.813379	-1.618825	0.375416
70	1	0	10.058150	-0.144846	-1.005146

71	6	0	10.550738	-2.389035	1.509883
72	1	0	9.105956	-2.843248	3.045235
73	1	0	11.764275	-1.715479	-0.140544
74	1	0	11.296047	-3.082780	1.886267

Total Energy (HF) = -2576.5843083Hartree

DPP4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.114209	-1.377461	0.312294
2	6	0	-1.218083	-1.274107	0.129407
3	6	0	-0.709359	0.011532	-0.054741
4	6	0	0.706381	-0.015451	0.041785
5	6	0	-1.117175	1.373754	-0.324468
6	6	0	1.214987	1.270429	-0.141175
7	6	0	2.586312	1.705812	-0.096505
8	6	0	3.116483	2.991906	-0.008012
9	16	0	3.892022	0.520583	-0.118847
10	6	0	4.519898	3.034777	0.022246
11	1	0	2.512299	3.883382	0.066752
12	1	0	5.099122	3.946895	0.095984
13	6	0	-2.589698	-1.709041	0.086444
14	6	0	-3.120670	-2.995129	0.002813
15	16	0	-3.894749	-0.522999	0.105679
16	6	0	-4.524156	-3.037314	-0.026213
17	1	0	-2.517145	-3.887250	-0.069171
18	6	0	-5.110995	-1.780471	0.035146
19	1	0	-5.103927	-3.949381	-0.096239
20	6	0	-0.069608	-3.520405	0.729832
21	1	0	0.791637	-3.620206	1.395475
22	1	0	-0.964408	-3.762525	1.306492
23	6	0	0.066819	3.516637	-0.742014
24	1	0	0.963248	3.758827	-1.316085
25	1	0	-0.792509	3.615942	-1.410230
26	6	0	-0.125702	4.452586	0.454650
27	1	0	-0.163509	5.493429	0.116391
28	1	0	-1.069144	4.221458	0.955322
29	1	0	0.681290	4.357893	1.187628
30	6	0	0.119091	-4.455999	-0.467726
31	1	0	-0.689794	-4.360518	-1.198502
32	1	0	1.061330	-4.225309	-0.970873
33	1	0	0.157153	-5.497008	-0.129993
34	7	0	-0.118134	-2.108206	0.360787
35	7	0	0.115042	2.104595	-0.372202
36	8	0	2.205196	-1.913394	0.479356
37	8	0	-2.208160	1.909682	-0.491600
38	6	0	-6.475706	-1.461802	0.028705
39	6	0	-7.659256	-1.166592	0.026088
40	6	0	-9.037059	-0.831640	0.021313
41	6	0	-9.457578	0.512118	0.114539
42	6	0	-10.028855	-1.830449	-0.077355
43	6	0	-10.804289	0.841542	0.103491
44	1	0	-8.711159	1.296874	0.180066
45	6	0	-11.376014	-1.502894	-0.076912

46	1	0	-9.727588	-2.871044	-0.139695
47	6	0	-11.789933	-0.159803	0.010664
48	1	0	-11.104686	1.881618	0.162424
49	1	0	-12.121195	-2.287919	-0.139882
50	7	0	-13.161647	0.175012	0.006521
51	6	0	-13.639500	1.264282	0.791575
52	6	0	-14.549072	2.183782	0.247523
53	6	0	-13.215167	1.425388	2.119636
54	6	0	-15.026266	3.239237	1.022104
55	1	0	-14.877012	2.064358	-0.779644
56	6	0	-13.684050	2.494398	2.880490
57	1	0	-12.519698	0.711041	2.547504
58	6	0	-14.594167	3.404652	2.339408
59	1	0	-15.729705	3.943325	0.587134
60	1	0	-13.346123	2.606162	3.906652
61	1	0	-14.962832	4.232272	2.937384
62	6	0	-14.084587	-0.570976	-0.781895
63	6	0	-13.772127	-0.921873	-2.104594
64	6	0	-15.324107	-0.954364	-0.247351
65	6	0	-14.679679	-1.652193	-2.869092
66	1	0	-12.819242	-0.619515	-2.525958
67	6	0	-16.232319	-1.669079	-1.025768
68	1	0	-15.568218	-0.687227	0.775328
69	6	0	-15.915358	-2.026681	-2.337674
70	1	0	-14.423509	-1.915915	-3.891142
71	1	0	-17.187882	-1.958434	-0.598044
72	1	0	-16.622963	-2.589092	-2.938866
73	6	0	6.472372	1.460442	-0.035942
74	6	0	7.656075	1.165712	-0.032033
75	6	0	5.107556	1.778450	-0.043116
76	6	0	9.033888	0.831230	-0.024544
77	6	0	10.024719	1.827125	0.106704
78	6	0	9.456326	-0.509513	-0.146992
79	6	0	11.371481	1.498814	0.122770
80	1	0	9.722268	2.863813	0.212959
81	6	0	10.803257	-0.837879	-0.144827
82	1	0	8.711770	-1.290734	-0.259419
83	6	0	11.788122	0.159482	-0.006107
84	1	0	12.113889	2.280014	0.240142
85	1	0	11.103537	-1.873667	-0.255375
86	7	0	13.159349	-0.173538	0.002728
87	6	0	14.122466	0.714678	-0.558848
88	6	0	15.311471	0.995187	0.131213
89	6	0	13.900923	1.309861	-1.810296
90	6	0	16.260112	1.850737	-0.425430
91	1	0	15.485088	0.539219	1.100265
92	6	0	14.847346	2.178263	-2.350693
93	1	0	12.987539	1.088047	-2.352189
94	6	0	16.032933	2.451062	-1.665326
95	1	0	17.175710	2.058217	0.120810
96	1	0	14.661705	2.631395	-3.320211
97	1	0	16.771166	3.122338	-2.092938
98	6	0	13.603411	-1.403043	0.570716
99	6	0	14.551376	-2.189287	-0.101391
100	6	0	13.110008	-1.836776	1.810968
101	6	0	14.998353	-3.382922	0.461659
102	1	0	14.932701	-1.858639	-1.061681
103	6	0	13.549504	-3.040892	2.357354

104	1	0	12.384222	-1.227431	2.339151
105	6	0	14.497746	-3.818817	1.689963
106	1	0	15.732318	-3.980863	-0.070776
107	1	0	13.158068	-3.363815	3.317670
108	1	0	14.842732	-4.752832	2.122438

Total Energy (HF)=-3401.271158Hartree