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Supporting Information

Serendipitous isolation of triazinone based air stable organic radical: synthesis, crystal structure and computation

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1. Experimental Section

1.1. Materials and methods

All the reactions were performed under ultrahigh pure nitrogen atmosphere unless mentioned elsewhere. All the deuterated NMR solvents were purchased from Acros Organics, and the other commercially procured chemicals were used as received. The NMR spectra were recorded by Bruker AV-400 400 MHz spectrometer using tetramethylsilane as internal standard in case of $CDCl_3$ solvent. The electron spin resonance (ESR) spectra were recorded on a (JEOL) JESFA200 ESR spectrometer. The IR spectra (with KBr pellets) were recorded over the range 400–4000 cm^{-1} with a JASCO FT/IT-5300 spectrometer. Elemental analysis was performed by FLASH EA series 1112 CHNS analyzer.

Synthesis of $[\mathbf{1^{2+}(PF_6)_2^{2-}\cdot 2H_2O \equiv 1(PF_6)_2\cdot 2H_2O}]$: Cyanuric chloride (100 mg, 0.54 mmol) was dissolved in dry CH_3CN (15 mL) in 25 mL round bottom flask. To this mixture were added 4,4'-bipyridine (250 mg, 1.67 mmol) and resulting reaction mixture was refluxed for 3 hrs with stirring at 80ºC under dry N_2 atmosphere and then cooled to room temperature. This afforded green colored precipitate, which was filtered off and dried in air. The resulting product was dissolved in water by slightly warming and the clear solution was filtered. To this filtrate, NH_4PF_6 were added economically until the precipitation was completed. This product was filtered off, and dried in air. The yield 176 mg (81% based of 4,4'-bipyridine). IR (KBr pellet) (ν/cm^{-1}): 3657, 3400, 3130, 2557, 2146, 1631, 1570, 1496, 1444, 1391, 1337, 1207, 1163, 1033, 997, 837, 760, 652, 630, 557, 491. ^{1}H NMR (400 MHz, DMSO-d_6): ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85 (d, J = 7.2 Hz, 4H), 6.53 (br s, 4H), 6.31 (d, J = 6.8 Hz, 4H), 5.85 (d, J = 4.4 Hz, 4H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 165.0, 163.4, 157.1, 149.5, 146.5, 141.9, 125.8, 123.8. Anal. Calcd for $C_{23}H_{20}F_{12}N_7O_3P_2$: C, 37.70; H, 2.75; N, 13.39. Found: C, 38.32; H, 2.98; N, 12.84.

Synthesis of $[\mathbf{1^{+\bullet}PF_6^- \equiv 1^{\bullet}PF_6}]$: Cyanuric chloride (100 mg, 0.54 mmol) was dissolved in dry CH_3CN (15 mL) in 25 mL round bottom flask. To this mixture were added 4,4'-bipyridine (250 mg, 1.67 mmol) and resulting reaction mixture was refluxed for 48 hrs

with stirring at 80ºC under dry N_2 atmosphere and then cooled to room temperature, affording pale green color precipitate, that was filtered off and dried in air. The resulting product was dissolved in water by slightly warming and the clear solution was obtained by its filtering. To this filtrate, NH_4PF_6 were added economically until the precipitation was completed. This product was filtered off, and dried in air. The yield is 100 mg (32%). IR (KBr pellet) (ν/cm^{-1}): 3445, 3134, 3086, 3057, 1618, 1552, 1496, 1388, 1338, 1288, 1159, 810. Anal. Calcd for $C_{23}H_{16}F_6N_7OP$: C, 50.08; H, 2.93; N, 17.79. Found: C, 51.22; H, 2.71; N, 18.41.

2. NMR studies

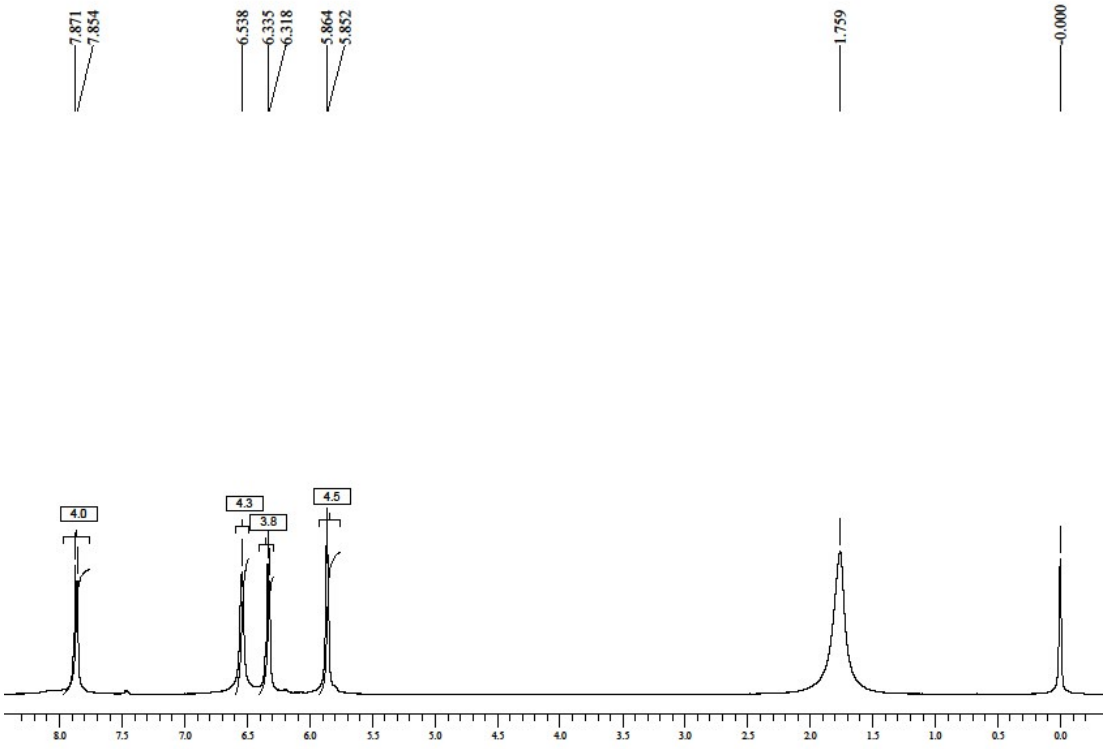

Fig. S1 ^{1}H NMR spectrum for compound **1(PF$_6$)$_2$·2H$_2$O].**

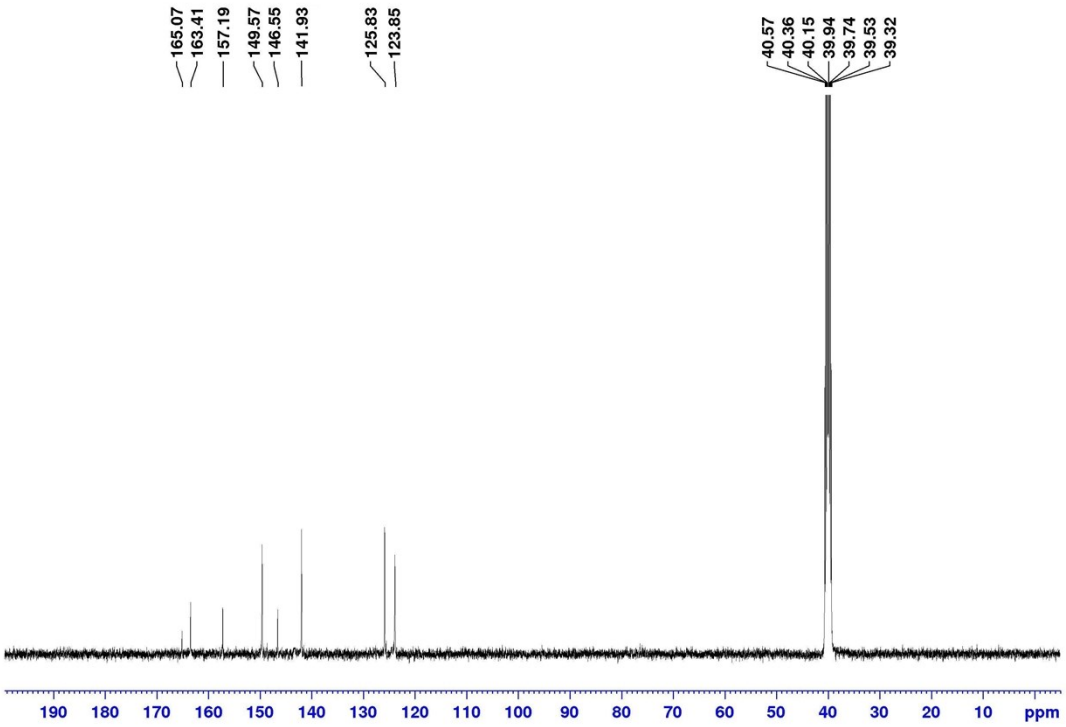

Fig. S2 ^{13}C NMR spectrum for compound **1(PF$_6$)$_2$·2H$_2$O].**

3. Single crystal X-ray crystallographic analysis

Crystal data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo-Kα) = 0.71073 Å], graphite monochromator; 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction by SAINTPLUS,[1] absorption correction using an empirical method SADABS,[2] structure solution using SHELXS-97[3] and refined using SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their respective parent atoms. A summary of the crystallographic data and structural determination for **1(PF$_6$)$_2$·2H$_2$O** and **1$^{\bullet}$PF$_6$** are provided in SI Table 1. The complete bond lengths and angles for the compounds **1(PF$_6$)$_2$·2H$_2$O** and **1$^{\bullet}$PF$_6$** have been provided in SI (Table 2).

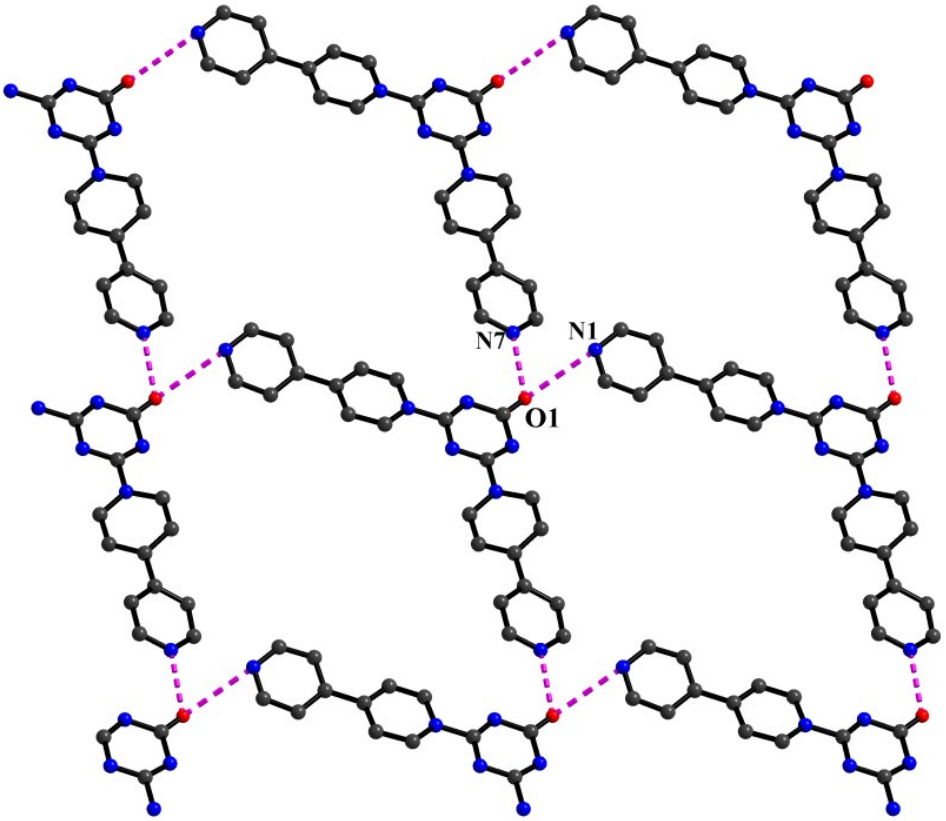

Fig. S3 Infinite 2D network in the crystal structure of **1**$(PF_6)_2 \cdot 2H_2O$, formed by bifurcated N···O=C non-covalent interactions. Hydrogen atoms, the counter anions, and the solvents are eliminated for clarity; color code, gray, carbon; blue, nitrogen; red, oxygen.

Table S1. Crystal data and structural refinement for compounds **$1(PF_6)_2 \cdot 2H_2O$** and **$1^{\bullet}PF_6$**

	$1(PF_6)_2 \cdot 2H_2O$	**$1^{\bullet}PF_6$**
Empirical formula	$C_{23}H_{21}F_{12}N_7O_3P_2$	$C_{23}H_{16}F_6N_7OP$
Formula weight	728.37	551.40
T [K]	100(2)	100(2)
λ [Å]	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	P2(1)/c
a [Å]	8.633(4)	5.036(2)
b [Å]	12.422(6)	19.412(9)
c [Å]	13.653(6)	23.741(10)
α [deg]	87.328(8)	90
β [deg]	89.110(7)	87.874(10)
γ [deg]	79.874(8)	90
V [Å^3]	1439.9(12)	2319.2(18)
Z	2	4
D_{calc} [Mg m^{-3}]	1.680	1.579
μ [mm^{-1}]	0.270	0.201
F[000]	730	1120
Crystal size [mm^3]	0.30 x 0.10 x 0.04	0.28 x 0.08 x 0.06
θ range for data collection [deg]	2.833 to 22.497	1.355 to 25.00
Reflections collected/unique	9540/3377	14864/4044
R (int)	0.0972	0.1317
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3377 / 0 / 424	4044 / 0 / 343
Goodness-of-fit on F^2	0.989	0.972
R_1/wR_2 [$I > 2\sigma(I)$]	0.0809/0.1874	0.0683/0.1395
R_1/wR_2 (all data)	0.1513/0.2247	0.1620/0.1747
Largest diff. Peak/hole [e Å^{-3}]	0.450 /-0.302	0.378/-0.321

Table S2. Selected bond lengths [Å] and angles [°] for compound **1(PF$_6$)$_2$·2H$_2$O**

N(6)-C(9)	1.351(8)	N(4)-C(11)-N(5)	128.8(6)
N(6)-C(8)	1.386(9)	N(4)-C(11)-N(6)	118.2(6)
N(6)-C(11)	1.435(9)	N(5)-C(11)-N(6)	113.0(6)
N(3)-C(13)	1.276(8)	N(3)-C(13)-N(5)	129.5(6)
N(3)-C(25)	1.414(9)	N(3)-C(13)-N(2)	118.5(6)
N(4)-C(11)	1.299(8)	N(5)-C(13)-N(2)	112.0(6)
N(4)-C(25)	1.393(9)	C(10)-C(9)-N(6)	119.8(7)
O(1)-C(25)	1.188(8)	C(10)-C(6)-C(7)	115.2(7)
N(2)-C(14)	1.306(10)	C(10)-C(6)-C(5)	123.6(7)
N(2)-C(15)	1.336(9)	C(15)-C(16)-C(18)	120.3(7)
N(5)-C(13)	1.341(9)	N(6)-C(8)-C(7)	118.3(6)
C(9)-C(10)	1.342(9)	C(9)-C(10)-C(6)	123.6(7)
C(6)-C(10)	1.401(10)	C(23)-C(19)-C(20)	116.8(7)
C(7)-C(8)	1.388(10)	C(23)-C(19)-C(18)	122.6(7)
C(19)-C(20)	1.408(10)	C(20)-C(19)-C(18)	120.5(7)
C(19)-C(18)	1.508(9)	C(1)-C(3)-C(5)	119.8(7)
N(7)-C(1)	1.299(9)	C(16)-C(18)-C(17)	117.3(7)
N(7)-C(2)	1.329(9)	C(16)-C(18)-C(19)	121.2(6)
C(3)-C(1)	1.365(11)	C(17)-C(18)-C(19)	121.5(7)
C(3)-C(5)	1.386(9)	C(21)-N(1)-C(22)	116.7(7)
C(18)-C(17)	1.381(10)	N(2)-C(15)-C(16)	122.2(7)
N(1)-C(22)	1.331(12)	C(2)-C(4)-C(5)	122.4(7)
C(5)-C(4)	1.400(10)	N(2)-C(14)-C(17)	122.1(8)
C(9)-N(6)-C(8)	121.2(6)	N(7)-C(1)-C(3)	122.2(7)
C(8)-N(6)-C(11)	117.6(6)	N(7)-C(2)-C(4)	119.1(8)
C(14)-N(2)-C(15)	118.8(6)	N(1)-C(21)-C(20)	124.4(8)
C(14)-N(2)-C(13)	121.8(6)	O(1)-C(25)-N(4)	121.8(6)
C(15)-N(2)-C(13)	119.4(6)	O(1)-C(25)-N(3)	121.2(6)
C(13)-N(5)-C(11)	109.9(6)	N(4)-C(25)-N(3)	116.9(7)

Table S3. Selected bond lengths [Å] and angles [°] for compound **1•PF$_6$**

N(4)-C(4)	1.344(5)	C(21)-C(23)	1.362(7)
N(4)-C(2)	1.466(5)	N(4)-C(5)	1.353(5)
N(6)-C(14)	1.326(5)	N(2)-C(2)	1.284(5)
N(6)-C(3)	1.458(5)	O(1)-C(1)	1.224(4)
N(3)-C(2)	1.326(5)	N(6)-C(15)	1.329(5)
N(1)-C(1)	1.398(5)	N(3)-C(3)	1.319(5)
C(7)-C(8)	1.386(5)	N(1)-C(3)	1.290(5)
C(8)-C(9)	1.471(6)	C(7)-C(4)	1.368(6)
C(9)-C(10)	1.366(7)	C(8)-C(6)	1.392(6)
N(7)-C(22)	1.305(7)	N(7)-C(23)	1.316(6)
C(22)-C(20)	1.377(7)	N(5)-C(12)	1.319(7)
N(5)-C(13)	1.326(6)	C(13)-C(10)	1.379(7)
C(4)-N(4)-C(5)	120.1(4)	C(3)-N(1)-C(1)	115.0(4)
C(14)-N(6)-C(3)	120.7(3)	N(2)-C(2)-N(4)	116.3(4)
C(3)-N(3)-C(2)	109.7(3)	N(4)-C(5)-C(6)	120.4(4)
N(2)-C(2)-N(3)	131.0(4)	C(10)-C(9)-C(8)	122.2(4)
N(3)-C(2)-N(4)	112.7(3)	C(16)-C(17)-C(18)	116.4(4)
N(1)-C(3)-N(3)	130.5(4)	C(18)-C(17)-C(19)	122.0(4)
N(3)-C(3)-N(6)	112.5(3)	N(1)-C(3)-N(6)	116.9(4)
O(1)-C(1)-N(2)	120.7(4)	O(1)-C(1)-N(1)	120.1(4)
C(5)-C(6)-C(8)	121.5(4)	N(1)-C(1)-N(2)	119.2(3)
C(15)-C(16)-C(17)	120.6(4)	N(4)-C(4)-C(7)	120.5(4)
N(6)-C(14)-C(18)	121.0(4)	C(12)-C(11)-C(9)	119.4(5)
C(20)-C(19)-C(21)	115.7(4)	N(6)-C(15)-C(16)	121.1(4)
C(21)-C(19)-C(17)	122.1(4)	C(22)-N(7)-C(23)	114.9(5)
N(7)-C(22)-C(2)	125.0(5)	C(14)-C(18)-C(17)	120.8(4)
C(12)-N(5)-C(13)	115.5(5)	C(19)-C(20)-C(22)	119.7(5)
N(5)-C(12)-C(11)	124.7(5)	N(5)-C(13)-C(10)	123.9(6)
C(15)-N(6)-C(3)	119.2(3)	C(9)-C(10)-C(13)	120.2(5)

4. Computational Details:

The geometry optimizations of the molecules have been carried out using the DFT, M062X Minnesota functionals with DZVP basis set. Gaussian-09 program package is used for this purpose. The nature of the stationary points was verified by calculation of the vibrational frequencies.

Coordinates of the optimized geometry of 1^{2+}:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.000181	-3.619587	0.190508
2	9	0	1.161195	-2.479387	-0.180442
3	9	0	1.164828	-4.661688	0.597613
4	9	0	-1.161116	-2.479598	-0.180198
5	9	0	-1.164180	-4.661909	0.597852
6	9	0	0.000286	-3.012899	1.740422
7	9	0	0.000070	-4.118964	-1.342335
8	15	0	-0.000191	3.663223	0.911224
9	9	0	1.152861	2.614851	1.491767
10	9	0	-0.000194	4.465970	2.300993
11	9	0	-1.163529	4.590282	0.285371
12	9	0	-0.000110	2.749521	-0.513250
13	9	0	1.163114	4.590334	0.285421
14	9	0	-1.153135	2.614702	1.491767
15	7	0	2.344298	-0.072126	0.659014
16	7	0	-1.206327	-0.540128	2.649892
17	7	0	1.206332	-0.540088	2.649909
18	8	0	-0.000003	-0.994935	4.514477
19	7	0	-2.344287	-0.072196	0.658984
20	7	0	0.000005	0.032479	0.700833
21	6	0	1.108926	-0.194129	1.400365
22	6	0	-1.108920	-0.194157	1.400352
23	6	0	2.432191	0.803684	-0.372309
24	1	0	1.562599	1.417154	-0.565988
25	6	0	4.700107	0.077202	-0.776364
26	6	0	4.555575	-0.824101	0.292293
27	1	0	5.365561	-1.476304	0.587406

28	6	0	-4.555561	-0.824214	0.292303
29	1	0	-5.365539	-1.476412	0.587453
30	6	0	3.377199	-0.885448	0.993016
31	1	0	3.198837	-1.558395	1.817870
32	6	0	3.603040	0.893215	-1.089380
33	1	0	3.645500	1.596816	-1.909007
34	6	0	-5.960211	0.158416	-1.542222
35	7	0	8.359977	0.314284	-2.994815
36	6	0	6.717181	-0.986744	-1.815512
37	1	0	6.385374	-1.968856	-1.501129
38	6	0	-4.700111	0.077041	-0.776392
39	7	0	-8.360006	0.314017	-2.994811
40	6	0	5.960200	0.158616	-1.542204
41	6	0	-3.603051	0.893045	-1.089451
42	1	0	-3.645521	1.596609	-1.909108
43	6	0	-3.377182	-0.885514	0.993024
44	1	0	-3.198813	-1.558417	1.817911
45	6	0	6.439446	1.384037	-2.019986
46	1	0	5.914206	2.310211	-1.820342
47	6	0	-2.432198	0.803564	-0.372381
48	1	0	-1.562622	1.417043	-0.566115
49	6	0	7.894717	-0.854110	-2.545459
50	1	0	8.490610	-1.730552	-2.781287
51	6	0	-6.439464	1.383815	-2.020056
52	1	0	-5.914222	2.309999	-1.820460
53	6	0	-6.717196	-0.986956	-1.815468
54	1	0	-6.385387	-1.969054	-1.501042
55	6	0	7.637798	1.405478	-2.727623
56	1	0	8.036159	2.346289	-3.095085
57	6	0	-7.637823	1.405223	-2.727680
58	1	0	-8.036189	2.346018	-3.095181
59	6	0	-7.894742	-0.854356	-2.545406
60	1	0	-8.490638	-1.730809	-2.781185
61	6	0	0.000001	-0.707110	3.309144

Coordinates of the optimized radical cation ($2^{+\bullet}$) in the doublet state:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.000049	2.253241	-0.000112
2	9	0	-0.527752	1.040271	1.005691
3	9	0	0.527647	1.040223	-1.005861
4	9	0	0.549449	3.347364	-1.019075
5	9	0	-0.549540	3.347412	1.018805
6	9	0	1.441561	2.197409	0.769849
7	9	0	-1.441655	2.197384	-0.770078
8	7	0	-2.337806	-1.772767	-0.060695
9	7	0	-1.196173	-3.825046	-0.006655
10	8	0	0.000047	-5.753077	-0.000109
11	7	0	2.337824	-1.772729	0.060657
12	7	0	0.000008	-1.787160	-0.000018
13	7	0	1.196227	-3.825024	0.006589
14	6	0	-1.111658	-2.510722	-0.017414
15	6	0	-4.660780	-1.650669	0.381556
16	1	0	-5.553034	-2.125976	0.772938
17	6	0	-4.682863	-0.310513	-0.064155
18	6	0	-2.322118	-0.489110	-0.518247
19	1	0	-1.370227	-0.099987	-0.864551
20	6	0	-5.919180	0.486900	-0.027317
21	6	0	4.682881	-0.310473	0.064227
22	6	0	1.111687	-2.510701	0.017371
23	6	0	0.000033	-4.462707	-0.000004
24	6	0	-3.484224	0.245827	-0.532758
25	1	0	-3.427192	1.257099	-0.917060
26	6	0	-3.492546	-2.362835	0.372375
27	1	0	-3.407671	-3.387933	0.711601
28	6	0	3.484209	0.245884	0.532727
29	1	0	3.427149	1.257167	0.916998
30	6	0	-5.863308	1.866570	0.198718
31	1	0	-4.922928	2.379270	0.378041
32	6	0	3.492590	-2.362807	-0.372328
33	1	0	3.407740	-3.387916	-0.711525

34	6	0	2.322106	-0.489055	0.518160
35	1	0	1.370186	-0.099913	0.864361
36	6	0	5.919206	0.486931	0.027462
37	7	0	8.258464	2.021699	-0.055344
38	6	0	8.303961	0.706757	0.168901
39	1	0	9.290752	0.278950	0.323815
40	6	0	4.660824	-1.650639	-0.381455
41	1	0	5.553104	-2.125957	-0.772766
42	7	0	-8.258417	2.021691	0.055637
43	6	0	7.173085	-0.106317	0.210721
44	1	0	7.281394	-1.165599	0.423000
45	6	0	-7.060188	2.580201	0.238518
46	1	0	-7.051277	3.650231	0.427058
47	6	0	-8.303943	0.706747	-0.168586
48	1	0	-9.290749	0.278947	-0.323421
49	6	0	5.863364	1.866598	-0.198598
50	1	0	4.923003	2.379305	-0.377998
51	6	0	-7.173078	-0.106339	-0.210475
52	1	0	-7.281413	-1.165624	-0.422729
53	6	0	7.060254	2.580217	-0.238320
54	1	0	7.051366	3.650244	-0.426877

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5. References

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