Supporting Information

Triarylborane substituted naphthalimide as fluoride and cyanide ion sensor

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Experimental:

All the chemicals were purchased from commercial sources and used without further purification. Triethylamine was received from commercial source, and distilled on KOH prior to use. ^{1}H NMR and ^{13}C NMR spectra were performed on 400 MHz and 100 MHz Bruker Ultra shield (Avance–III) Nano Bay spectrometer. All the spectra were recorded at 298K.^{1}H NMR data are reported as follows: s: singlet, d: doublet, t: triplet, bs: broad singlet and coupling constants, *J*, are given in Hz. Chemical shifts in ^{1}H NMR and ^{13}C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm) and $CDCl_3$ (77.00) as standards. TLC analysis was carried out using silica gel 60 F_{254} plates. UV–vis absorption spectra of all compounds were recorded in THF on a carry–100 Bio UV–visible Spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from Horibayovin (model: FM–100). The excitation and emission slits were 2/2 nm for the emission measurements. All the measurements were done at 298K. For UV–visi and fluorescence titrations the anion (F^-, Cl^-, Br^-, I^-, NO_2^- and CN^-) stock solutions were prepared in THF in the order of 10^{-3}M. The triarylborane naphthalimide **3** stock solution was prepared (C=1mM) in THF. Working solutions of **3** and anions were freshly prepared from stock solutions. The fluorescence quantum yield (Φ) was calculated using Diphenylanthracene (Φ=0.9) as reference. Column chromatography was performed on Merck silica gel (230-400 mesh). The anions were used in their tetrabutylammonium salts.The relative fluorescence quantum efficiency, (Φ), is evaluated by employing 9,10-diphenyl anthracene as standard (Φ =0.9) following the equation 1.

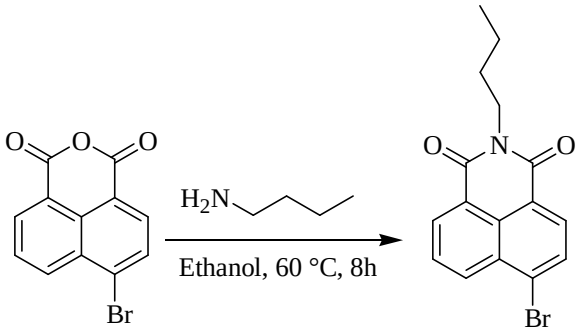
$$\Phi = \Phi_{std} \left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \text{..... 1}$$

Where Φ_{unk}, Φ_{std}, I_{unk}, I_{std}, A_{std}, A_{unk}, η_{unk} and η_{std} are the fluorescence quantum efficiency, the integral of the emission intensities, the absorbance at the excitation wavelength and the refractive indexes of the corresponding solvents of the unknown samples and the standard respectively.

The binding constant of the complex formed in solution has been estimated by using the standard Benesi−Hildebrand equation 2.

$$\frac{1}{I - I_o} = \frac{1}{I_1 - I_o} + \frac{1}{(I_1 - I_o)K_a[M]} \qquad \text{Eq. 2}$$

Where I_0 is the intensity before addition of anion, I is the intensity in the presence of F^-/ CN^-, I_1 is intensity upon saturation with anion, and K_a is the association constant of the complex formed.



1 **2**

Scheme S1: Synthesis of 4-Bromonaphthalimide **2**

Synthesis of 4-Bromonaphthalimide 2: 4–Bromo–1,8–naphthalimide (1 g, 3.62 mmol) was dissolved in 15 mL ethanol. Then n–butyl amine (0.29 g, 3.98 mmol) was added, and the mixture was stirred at 60°C for 8 h. The mixture was cooled to room temperature and evaporated in vacuum to obtain the residue. Then the residue was purified on silica gel column chromatography employing hexane: ethyl acetate (19:1, V/V) to provide 2. Yield: 1.06 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J*=6.52, 1H, aromatic), 8.55 (d, *J*=8.28, 1H, aromatic), 8.40 (d, *J*=7.78, 1H, aromatic), 8.03 (d, *J*=7.78, 1H, aromatic), 7.84 (t, *J*=7.52, 1H, aromatic), 4.16 (t, *J*=7.52, 2H, –NCH_2), 1.74–1.67 (m, 2H, –CH_2), 1.49–1.39 (m, 2H, –CH_2), 0.97 (t, *J*=7.27, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 163.6, 163.6, 133.2, 132.0, 131.1, 131.0, 130.5, 130.1, 128.9, 128.0, 123.1, 122.2, 40.3, 30.1, 20.3, 13.8. Mass spectral data: m/z (M+Na) =354.01 (M+1).

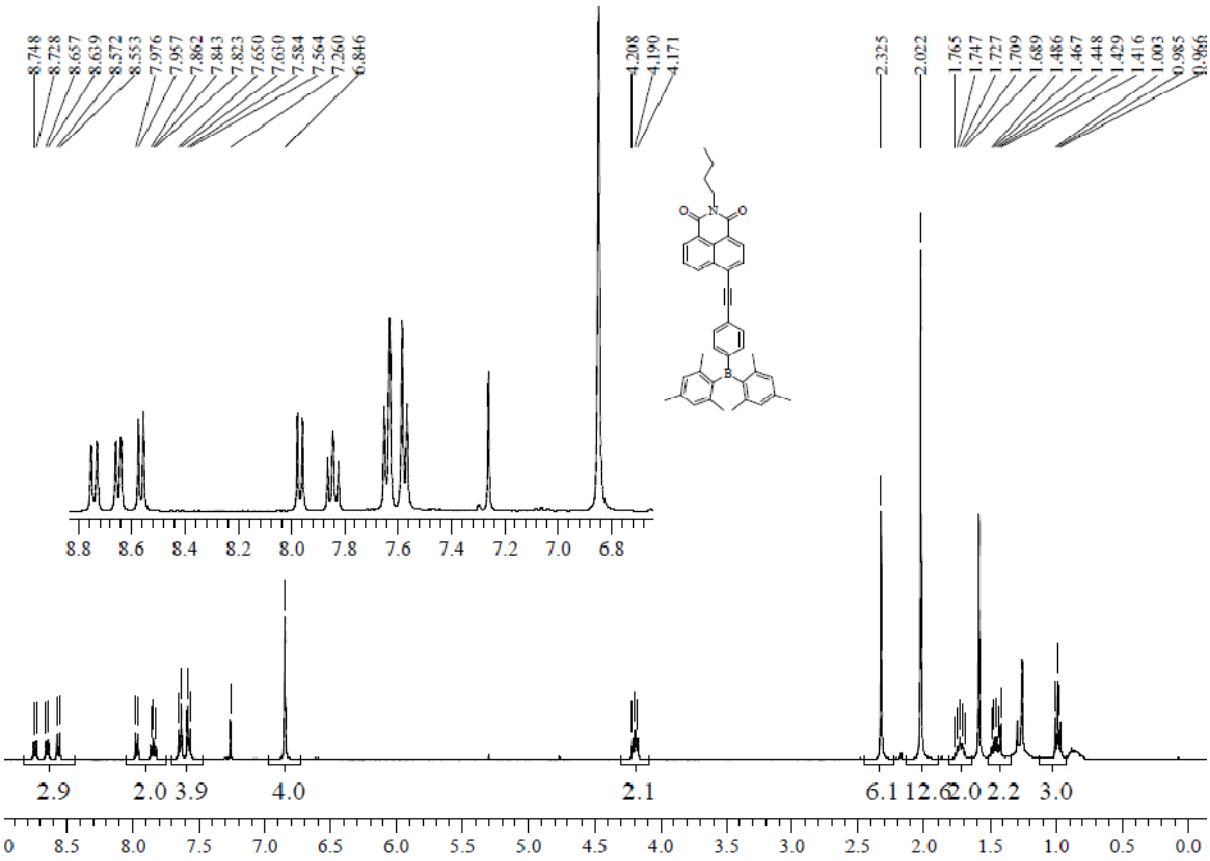


Figure S1: ^{1}H-NMR spectrum of **3**

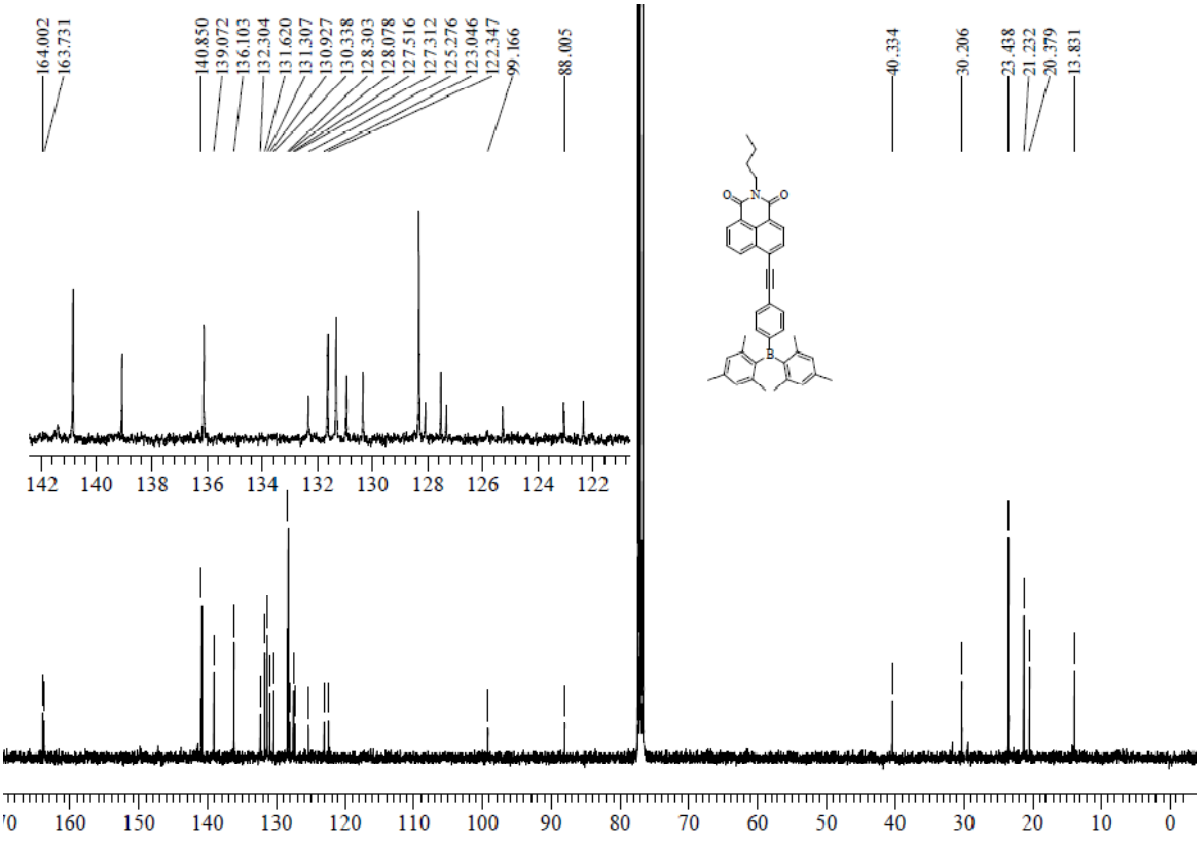


Figure S2: ^{13}C-NMR spectrum of **3**

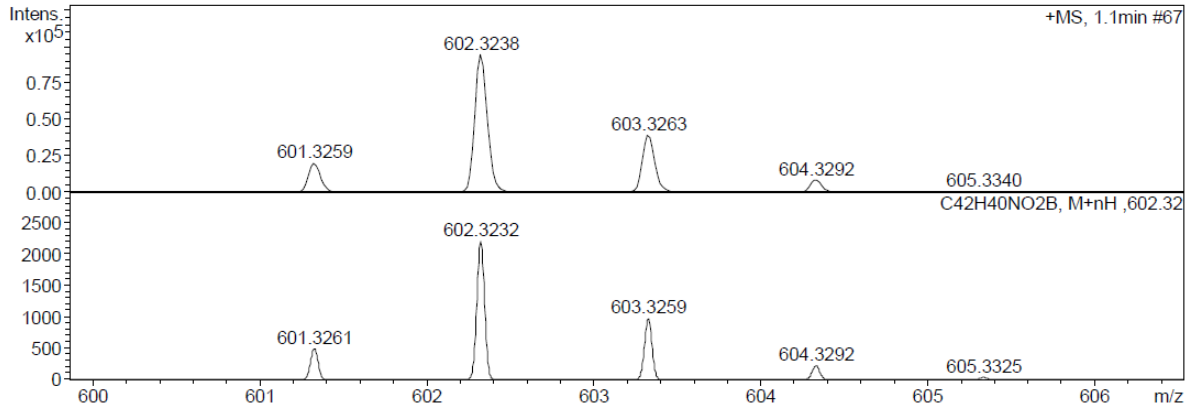


Figure S3: HRMS of **3.**

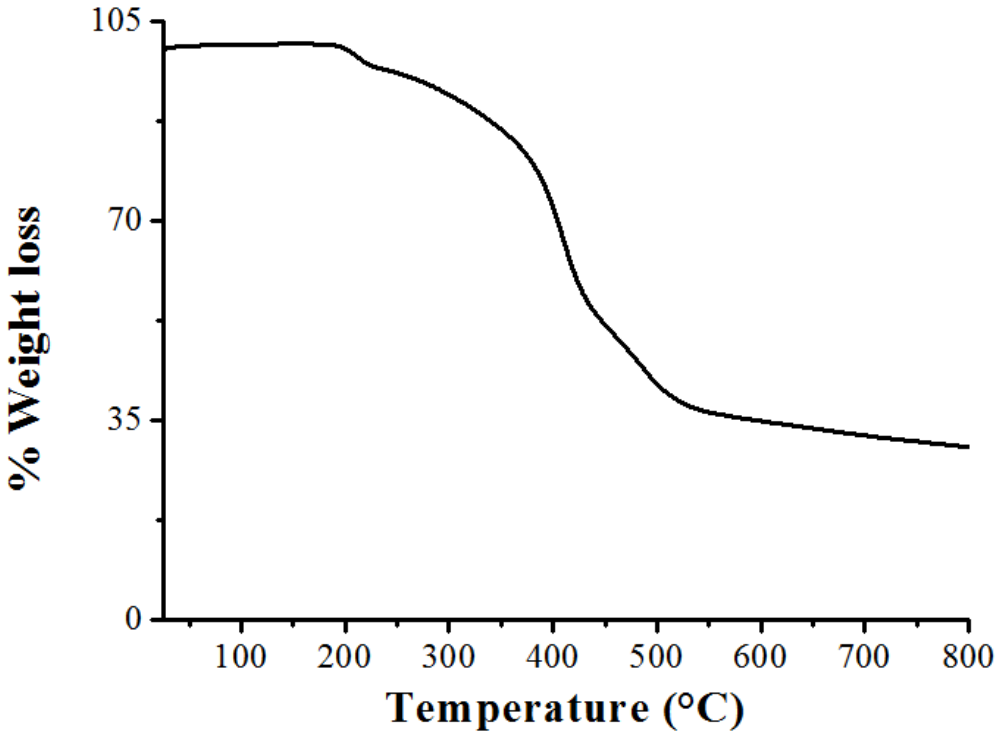
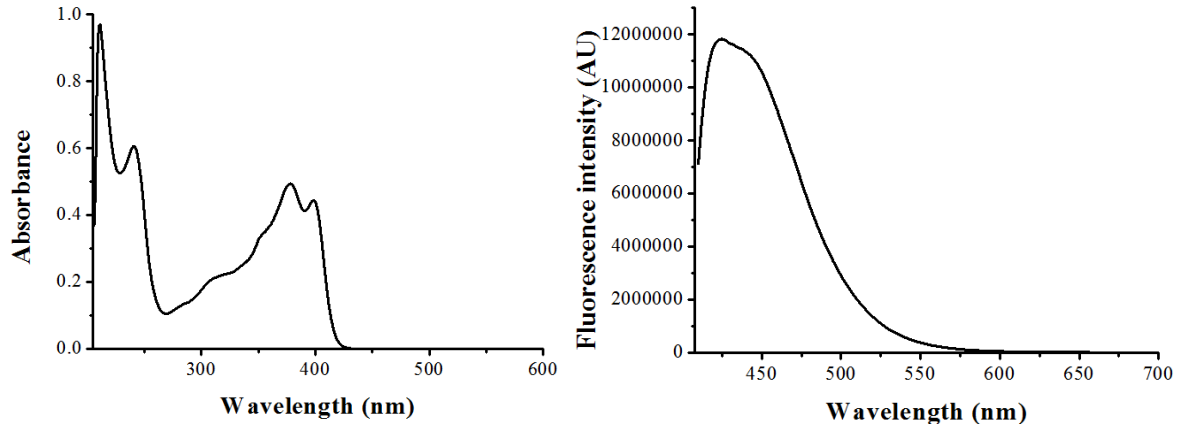


Figure S4: TGA plot of the **3**.



(a) **(b)**

Figure S5: The absorption (a) and fluorescence spectra (b) of triarylborane naphthalimide **3** (1.66×10^{-5} M) in THF solvent (λ_{ex} 398 nm).

Anion Binding Studies:

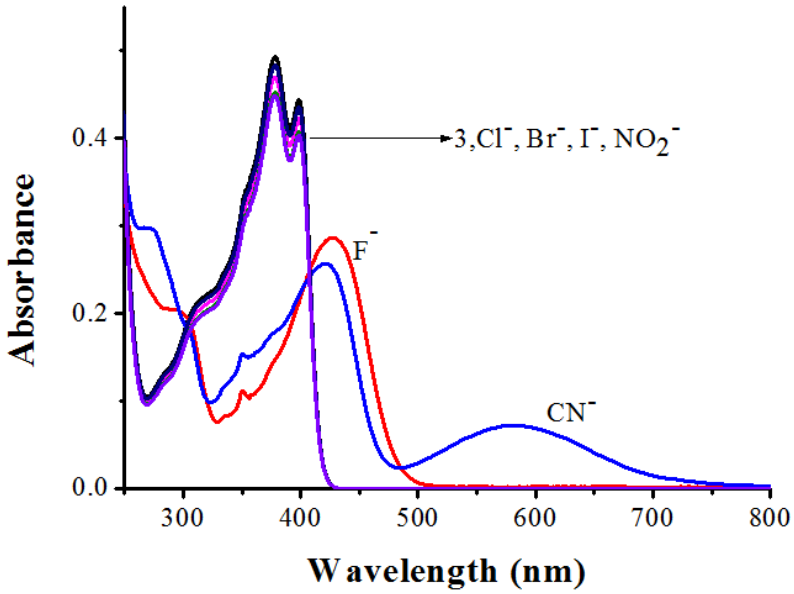


Figure S6: Effect of anions on the absorption spectrum of **3** (3.66 µM) in THF solvent.

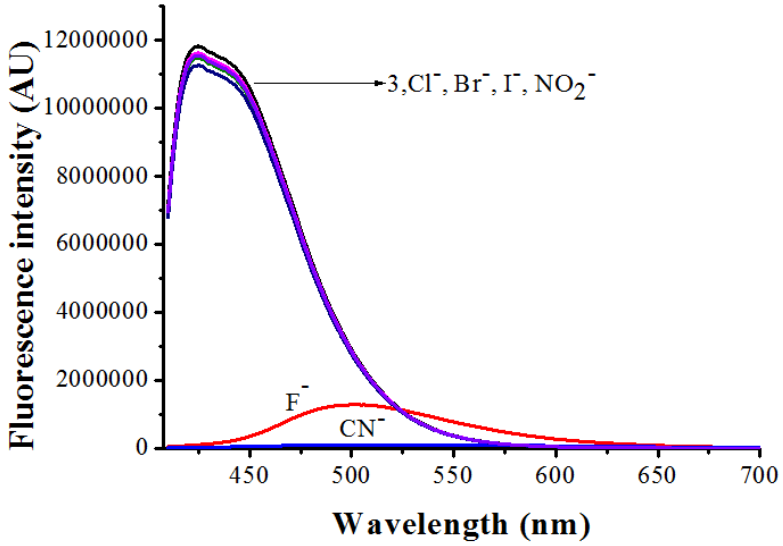


Figure S7: Effect of anions on the fluorescence spectrum of **3** (1.66 x 10^{-5} M) (λ_{ex} 398nm) in THF solvent.

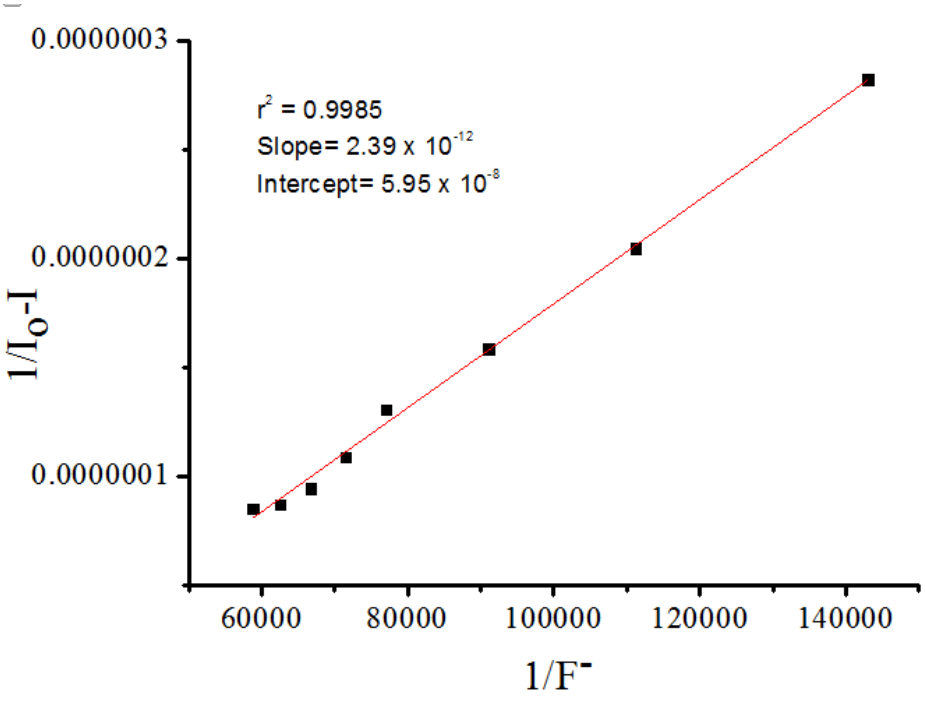


Figure S8: Benesi–Hildebrand plot of **3** by plotting $1/(I_0-I)$ as a function of $1/[F^-]$ for the calculation of binding constant (K). Here I refer to the fluorescence intensity of **3** at 424 nm at a given F^- concentration and I_o corresponds to the initial fluorescence intensity of **3** at 424 nm in the absence of F^-.

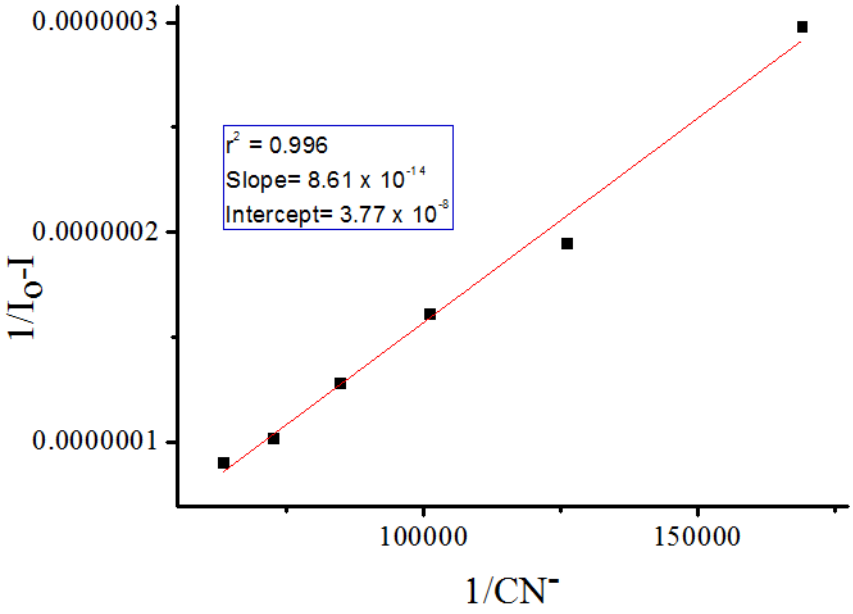


Figure S9: Benesi–Hildebrand plot of **3** by plotting $1/(I_0-I)$ as a function of $1/[CN^-]$ for the calculation of binding constant (K). Here I refer to the fluorescence intensity of **3** at 424 nm at a given CN^- concentration and I_o corresponds to the initial fluorescence intensity of **3** at 424 nm in the absence of CN^-.

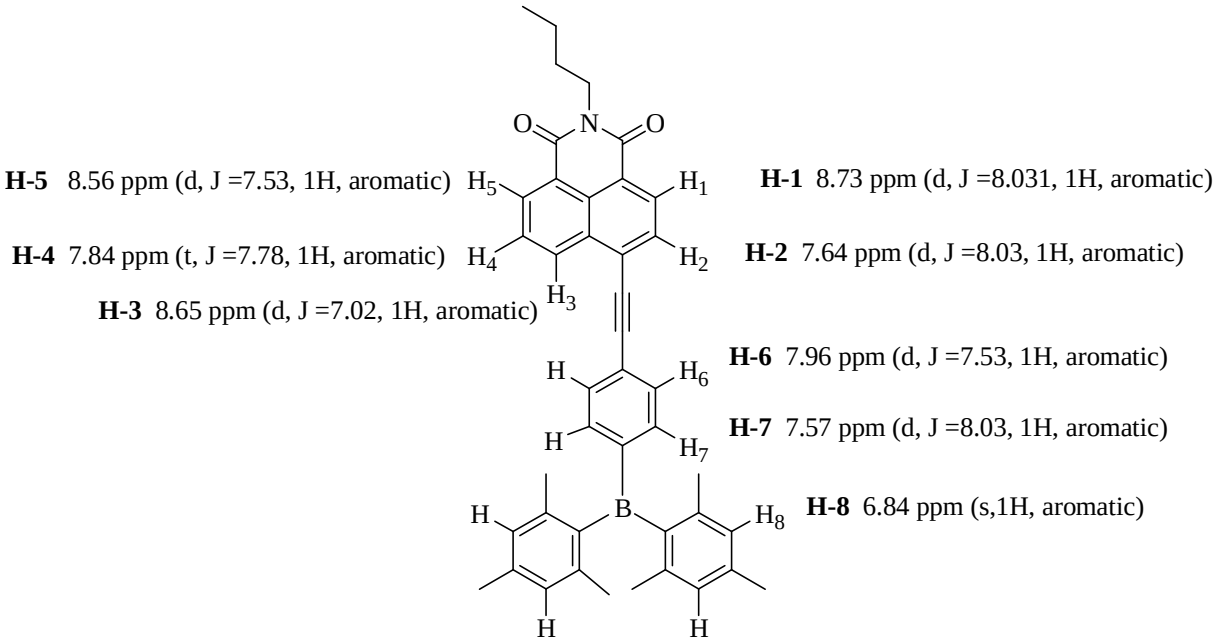


Figure S10: Aromatic proton assignment of **3**

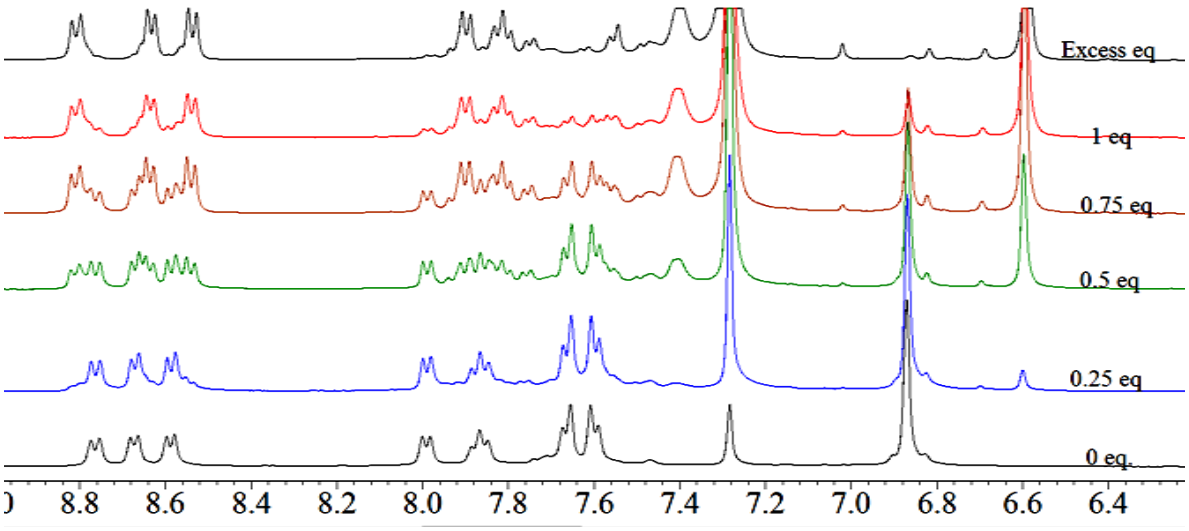


Figure S11: ^{1}H–NMR titration spectra of triarylborane naphthalimide **3** with TBAF in $CDCl_3$.

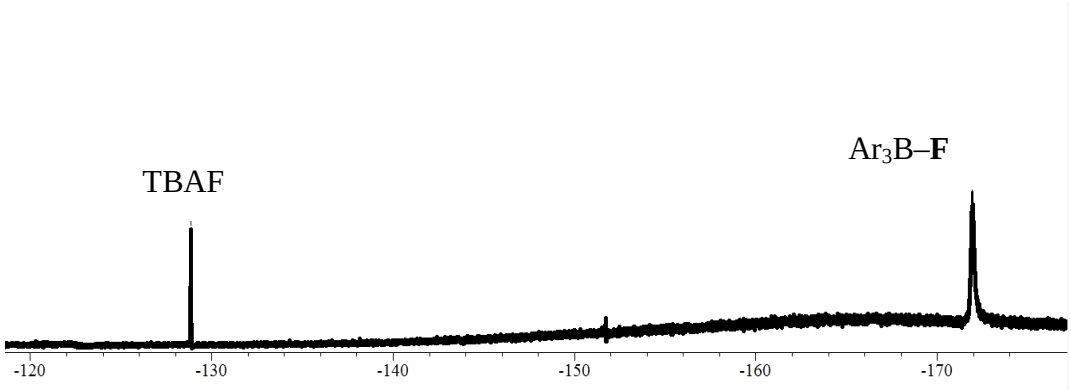


Figure S12: The ^{19}F NMR spectrum of **3** with 5 eq of TBAF in $CDCl_3$.

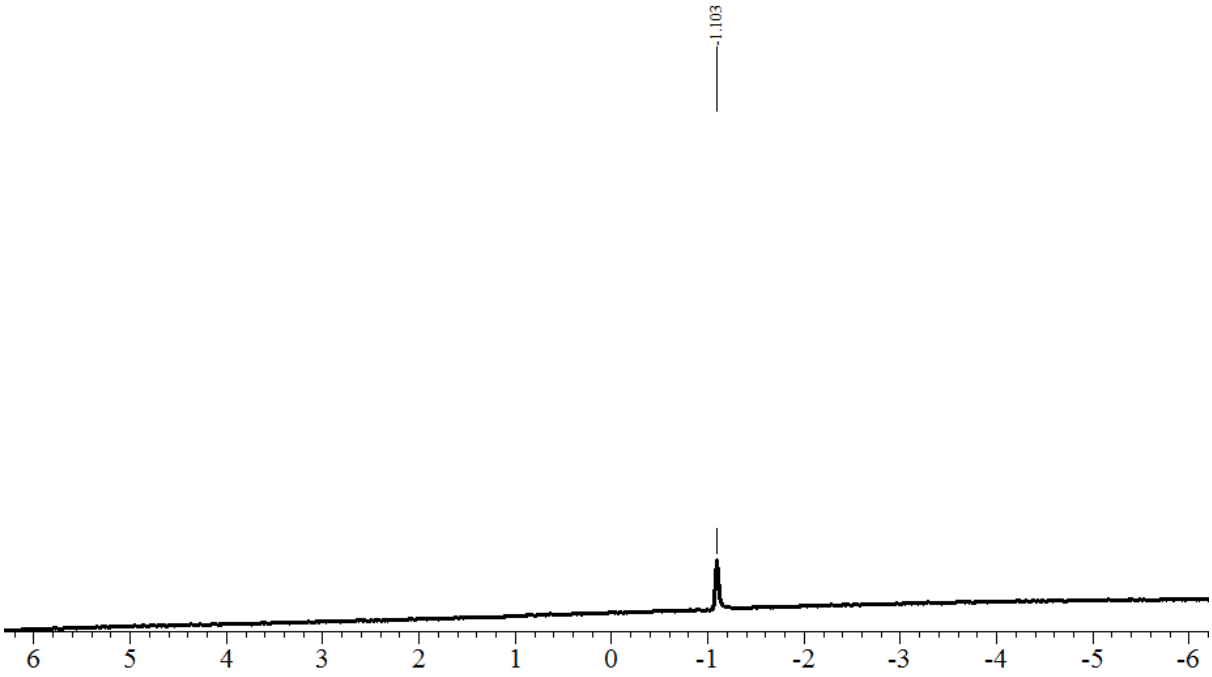


Figure S13: The ^{11}B NMR spectrum of **3** with 5 eq of TBAF in $CDCl_3$.

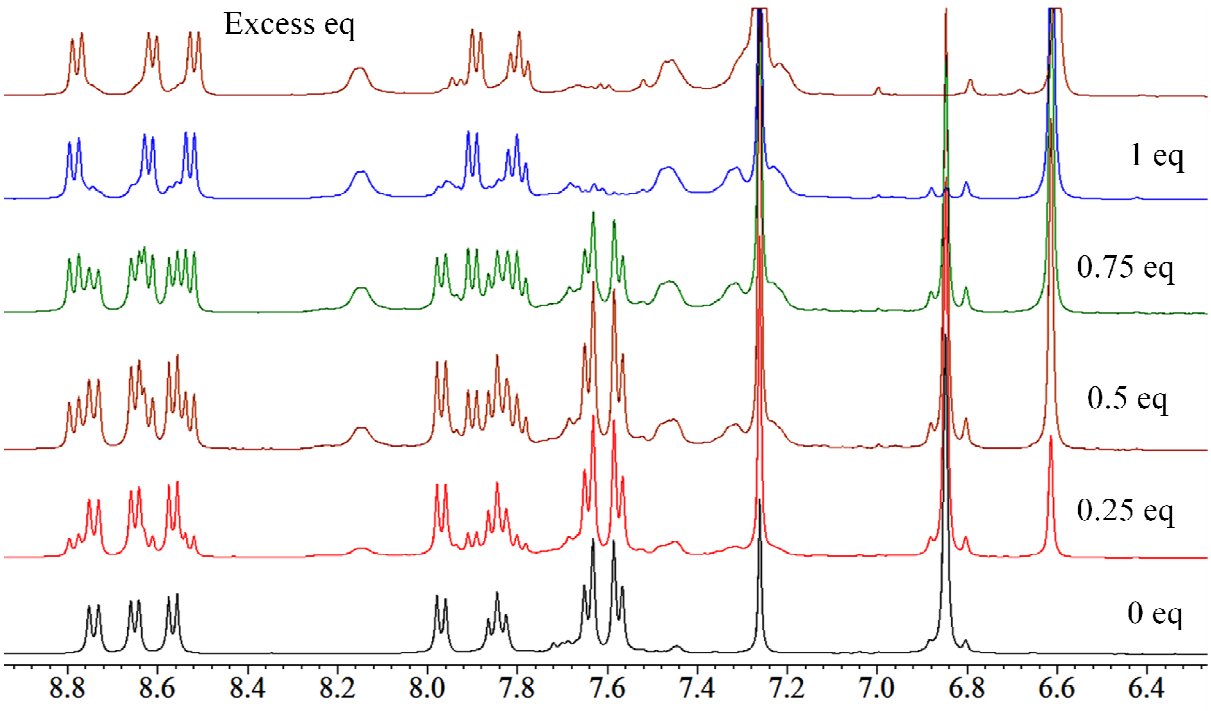


Figure S14: ^{1}H–NMR titration spectra of triarylborane naphthalimide **3** with TBACN in $CDCl_3$.

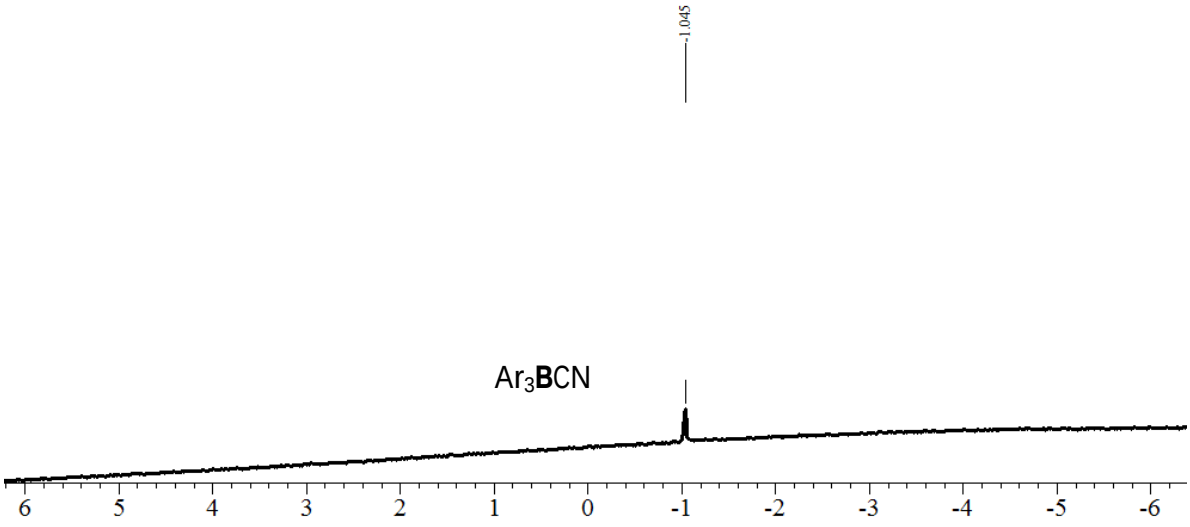


Figure S15: The ^{11}B NMR spectrum of **3** with 5 eq of TBACN in $CDCl_3$.

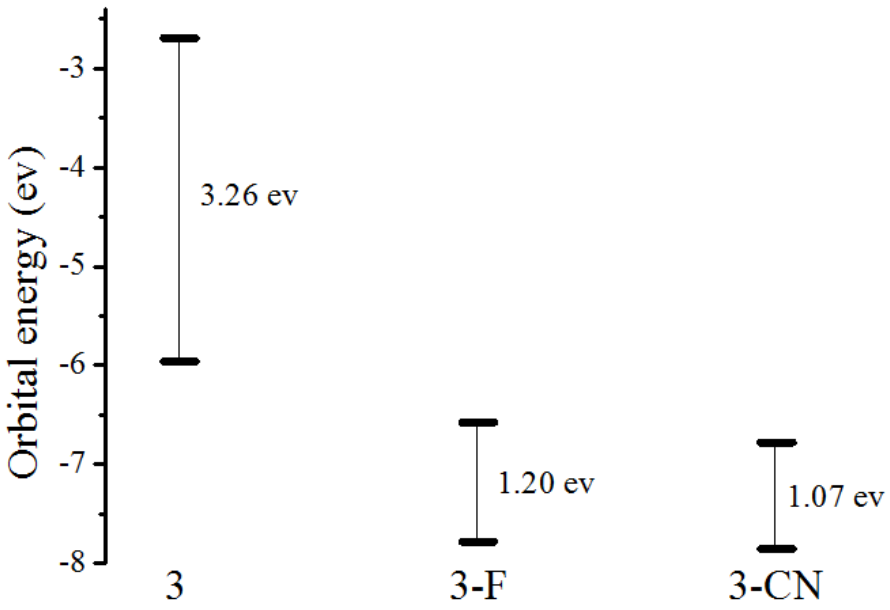


Figure S16: The energy level diagram of the frontier molecular orbitals (HOMO to LUMO) of the triarylborane naphthalimide **3** and **3–F** and **3–CN** calculated using B3LYP level of DFT theory.

DFT data of 3:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.243035	0.413582	0.567893
2	6	0	4.094275	-0.580945	-0.030864
3	6	0	3.590961	-1.680197	-0.769342
4	6	0	3.819076	1.471644	1.273516
5	6	0	5.507519	-0.453027	0.122691
6	6	0	6.051535	0.634436	0.851195
7	6	0	5.210084	1.580240	1.413384
8	6	0	7.518227	0.775521	1.017334
9	6	0	7.840520	-1.301795	-0.315266
10	6	0	6.367368	-1.418257	-0.461828
11	6	0	5.841132	-2.478144	-1.178711
12	6	0	4.446604	-2.607745	-1.330435
13	1	0	4.044162	-3.444029	-1.894432
14	1	0	6.524259	-3.198763	-1.615949
15	1	0	3.171559	2.218350	1.721205
16	1	0	5.650462	2.404786	1.964016
17	8	0	8.022896	1.710277	1.627063
18	8	0	8.615356	-2.103355	-0.821442
19	7	0	8.319852	-0.222698	0.442978
20	1	0	2.516555	-1.779194	-0.887733
21	6	0	9.780753	-0.099294	0.605911
22	1	0	9.950939	0.365901	1.578180

23	1	0	10.183352	-1.113350	0.611046
24	6	0	10.431069	0.730679	-0.506150
25	1	0	10.211394	0.262879	-1.474325
26	1	0	9.978381	1.730335	-0.514560
27	6	0	11.948914	0.851533	-0.322029
28	1	0	12.393640	-0.153338	-0.297804
29	1	0	12.161510	1.305526	0.656130
30	6	0	12.617778	1.678846	-1.424504
31	1	0	13.700259	1.749676	-1.268874
32	1	0	12.451039	1.230874	-2.411701
33	1	0	12.216831	2.699394	-1.451604
34	6	0	1.830473	0.330051	0.450125
35	6	0	0.616878	0.273314	0.362832
36	6	0	-0.801679	0.224740	0.271994
37	6	0	-1.456099	-0.925000	-0.216892
38	6	0	-1.581523	1.329653	0.674109
39	6	0	-2.842996	-0.965594	-0.282976
40	1	0	-0.863620	-1.780062	-0.528771
41	6	0	-2.965697	1.282112	0.570962
42	1	0	-1.085158	2.216889	1.055635
43	6	0	-3.641068	0.135237	0.098172
44	1	0	-3.328058	-1.868823	-0.642644
45	1	0	-3.547700	2.149942	0.869997
46	5	0	-5.213041	0.086111	0.007369
47	6	0	-5.930168	-1.325035	0.060395
48	6	0	-6.752970	-1.761120	-1.018993
49	6	0	-5.748254	-2.215221	1.149763
50	6	0	-7.327035	-3.032602	-0.994867
51	6	0	-6.355362	-3.478908	1.140337
52	6	0	-7.142792	-3.913163	0.077471
53	1	0	-7.938104	-3.348507	-1.838859
54	1	0	-6.207178	-4.136952	1.995372
55	6	0	-6.006447	1.446629	-0.149909
56	6	0	-7.031032	1.806101	0.769902
57	6	0	-5.710437	2.357473	-1.198308
58	6	0	-7.697473	3.026590	0.638463
59	6	0	-6.424212	3.556590	-1.312246
60	6	0	-7.417569	3.916867	-0.402361
61	1	0	-8.464240	3.287472	1.365973
62	1	0	-6.194403	4.228004	-2.138130
63	6	0	-4.647501	2.089650	-2.249656
64	1	0	-3.672177	2.489045	-1.945567
65	1	0	-4.502620	1.025401	-2.450875
66	1	0	-4.915766	2.572736	-3.195505
67	6	0	-7.413824	0.914869	1.935039
68	1	0	-8.200794	1.382077	2.535497
69	1	0	-7.780638	-0.059585	1.597346
70	1	0	-6.564693	0.724116	2.602454
71	6	0	-8.187123	5.208043	-0.549632
72	1	0	-9.177563	5.032531	-0.990653
73	1	0	-8.349454	5.691313	0.420559
74	1	0	-7.661191	5.916558	-1.197823
75	6	0	-4.988195	-1.837459	2.406995
76	1	0	-4.329319	-0.978867	2.268759
77	1	0	-5.686855	-1.587970	3.217046
78	1	0	-4.376224	-2.674493	2.762391
79	6	0	-7.006734	-0.895911	-2.237599
80	1	0	-7.454637	0.065763	-1.969683

81	1	0	-6.081574	-0.676903	-2.785455
82	1	0	-7.682306	-1.401043	-2.935157
83	6	0	-7.772312	-5.285934	0.068838
84	1	0	-8.842568	-5.233881	-0.164642
85	1	0	-7.310762	-5.931603	-0.689741
86	1	0	-7.662731	-5.783551	1.037704

Total Energy = -1854.69 HF

DFT data of 3–F:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.415034	-0.288379	0.424995
2	6	0	-4.376865	0.747126	0.157532
3	6	0	-4.017312	2.058455	-0.240664
4	6	0	-3.852295	-1.557446	0.806027
5	6	0	-5.762436	0.434283	0.296928
6	6	0	-6.165901	-0.865930	0.689951
7	6	0	-5.219100	-1.843989	0.938216
8	6	0	-7.608698	-1.201231	0.835996
9	6	0	-8.187645	1.120958	0.170460
10	6	0	-6.738361	1.429574	0.035945
11	6	0	-6.352239	2.698678	-0.352471
12	6	0	-4.984538	3.011214	-0.489094
13	1	0	-4.693362	4.011243	-0.794335
14	1	0	-7.121861	3.437434	-0.547400
15	1	0	-3.118031	-2.330786	1.003708
16	1	0	-5.557850	-2.830391	1.234738
17	8	0	-7.981482	-2.320304	1.160283
18	8	0	-9.052692	1.951668	-0.066045
19	7	0	-8.527030	-0.174736	0.587891
20	1	0	-2.965601	2.301807	-0.349355
21	6	0	-9.963022	-0.496606	0.723211
22	1	0	-10.046312	-1.230307	1.525972
23	1	0	-10.464475	0.425775	1.017704
24	6	0	-10.566327	-1.047558	-0.572780
25	1	0	-10.430304	-0.308237	-1.371462
26	1	0	-10.016936	-1.950555	-0.864903
27	6	0	-12.056650	-1.375790	-0.420111
28	1	0	-12.599143	-0.470078	-0.118154
29	1	0	-12.187521	-2.098532	0.396299
30	6	0	-12.674686	-1.938076	-1.703640
31	1	0	-13.736950	-2.163452	-1.567840
32	1	0	-12.588959	-1.224080	-2.530293
33	1	0	-12.174508	-2.863126	-2.011004
34	6	0	-2.021151	-0.037157	0.306384
35	6	0	-0.823071	0.158037	0.211395
36	6	0	0.577510	0.363967	0.099874
37	6	0	1.114714	1.657226	-0.057818
38	6	0	1.473105	-0.723371	0.151639
39	6	0	2.486557	1.849359	-0.172320
40	1	0	0.447165	2.511667	-0.080958
41	6	0	2.843451	-0.522852	0.032041
42	1	0	1.083254	-1.726707	0.283049

43	6	0	3.372996	0.761610	-0.148997
44	1	0	2.865150	2.861456	-0.277049
45	1	0	3.496909	-1.385964	0.096435
46	5	0	5.566539	-0.306098	-1.055335
47	6	0	4.911701	1.036363	-0.213209
48	6	0	5.222689	2.197766	-1.105541
49	6	0	5.418371	1.156708	1.189841
50	6	0	5.988023	3.247625	-0.639692
51	6	0	6.126348	2.270059	1.586318
52	6	0	6.426362	3.321468	0.697494
53	1	0	6.212397	4.074895	-1.306889
54	1	0	6.455007	2.351017	2.618162
55	6	0	6.603512	-1.357041	-0.604178
56	6	0	7.851077	-1.044891	-0.001753
57	6	0	6.277476	-2.740247	-0.811068
58	6	0	8.680458	-2.066944	0.462950
59	6	0	7.127808	-3.721124	-0.304767
60	6	0	8.326202	-3.412309	0.351964
61	1	0	9.640756	-1.805981	0.901274
62	1	0	6.861367	-4.765252	-0.446047
63	6	0	5.073472	-3.211248	-1.602963
64	1	0	4.136581	-2.722277	-1.328061
65	1	0	5.218803	-3.021851	-2.671484
66	1	0	4.934236	-4.286271	-1.473330
67	6	0	8.403195	0.362734	0.057168
68	1	0	9.384399	0.389830	-0.428488
69	1	0	7.777392	1.088479	-0.463776
70	1	0	8.550336	0.702755	1.087515
71	6	0	9.209350	-4.504888	0.895106
72	1	0	9.325623	-5.317474	0.171443
73	1	0	10.202428	-4.130371	1.153720
74	1	0	8.771242	-4.942205	1.800241
75	6	0	5.127989	0.086092	2.197997
76	1	0	5.434628	-0.897265	1.828813
77	1	0	5.650124	0.283282	3.135590
78	1	0	4.054410	0.029609	2.405245
79	6	0	4.715281	2.261594	-2.521508
80	1	0	5.435608	1.795168	-3.204141
81	1	0	3.768022	1.741432	-2.651035
82	1	0	4.603556	3.302825	-2.832196
83	6	0	7.219068	4.500024	1.167403
84	1	0	8.289964	4.282354	1.050415
85	1	0	7.005038	5.396248	0.580986
86	1	0	7.047058	4.706544	2.226522
87	9	0	4.936885	-0.462555	-2.215295

Total Energy = -1954.38 HF

DFT data of 3–CN:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.526718	-0.377356	-0.557174
2	6	0	4.361999	0.426588	0.294069
3	6	0	3.863937	1.181986	1.384331

4	6	0	4.097317	-1.098358	-1.607049
5	6	0	5.763801	0.459526	0.027172
6	6	0	6.304026	-0.283434	-1.051742
7	6	0	5.477309	-1.050970	-1.853120
8	6	0	7.765025	-0.254781	-1.337299
9	6	0	8.083017	1.280772	0.588867
10	6	0	6.618726	1.236750	0.849322
11	6	0	6.099341	1.960246	1.906382
12	6	0	4.715063	1.931305	2.171181
13	1	0	4.318684	2.503948	3.003584
14	1	0	6.778383	2.543382	2.518692
15	1	0	3.457287	-1.702193	-2.241115
16	1	0	5.919897	-1.610946	-2.669322
17	8	0	8.254974	-0.899108	-2.254391
18	8	0	8.848026	1.925923	1.290624
19	7	0	8.557320	0.548294	-0.509792
20	1	0	2.799460	1.160559	1.593104
21	6	0	10.009756	0.586366	-0.781168
22	1	0	10.130276	0.469425	-1.858766
23	1	0	10.359280	1.574504	-0.479791
24	6	0	10.777997	-0.507048	-0.032290
25	1	0	10.602895	-0.391717	1.044125
26	1	0	10.381251	-1.486324	-0.326371
27	6	0	12.283341	-0.450620	-0.320337
28	1	0	12.669732	0.537700	-0.037890
29	1	0	12.450146	-0.548129	-1.401346
30	6	0	13.070269	-1.537083	0.418336
31	1	0	14.140104	-1.472896	0.197122
32	1	0	12.948566	-1.445492	1.503365
33	1	0	12.730035	-2.537839	0.129783
34	6	0	2.123335	-0.449871	-0.346663
35	6	0	0.918358	-0.526795	-0.188016
36	6	0	-0.487042	-0.637276	-0.025259
37	6	0	-1.192276	0.203786	0.855256
38	6	0	-1.221575	-1.607924	-0.739946
39	6	0	-2.572565	0.092728	1.008476
40	1	0	-0.651321	0.950239	1.426288
41	6	0	-2.595938	-1.712397	-0.585109
42	1	0	-0.699689	-2.283778	-1.408629
43	6	0	-3.302689	-0.858159	0.282918
44	1	0	-3.051485	0.754900	1.716880
45	1	0	-3.124914	-2.483356	-1.137717
46	5	0	-5.584877	0.326962	0.946349
47	6	0	-6.481000	1.271560	0.102827
48	6	0	-7.821601	0.934038	-0.200356
49	6	0	-5.974484	2.535298	-0.322487
50	6	0	-8.598034	1.804531	-0.970801
51	6	0	-6.780656	3.361117	-1.101753
52	6	0	-8.095041	3.015900	-1.447609
53	1	0	-9.630928	1.537895	-1.182757
54	1	0	-6.375831	4.309680	-1.445629
55	6	0	-4.841738	-1.114741	0.410554
56	6	0	-5.438006	-1.362094	-0.939976
57	6	0	-5.117864	-2.182160	1.431291
58	6	0	-6.307387	-2.410565	-1.142430
59	6	0	-6.032677	-3.176841	1.156388
60	6	0	-6.631796	-3.317549	-0.113985
61	1	0	-6.743396	-2.556777	-2.126800

62	1	0	-6.241760	-3.925847	1.914115
63	6	0	-4.354949	-2.231966	2.717892
64	1	0	-3.306842	-2.474043	2.503776
65	1	0	-4.346881	-1.278647	3.250243
66	1	0	-4.758927	-2.999134	3.380165
67	6	0	-5.112476	-0.458562	-2.094600
68	1	0	-4.654090	-1.046801	-2.897982
69	1	0	-6.030116	-0.019302	-2.497777
70	1	0	-4.424713	0.341862	-1.830333
71	6	0	-7.600947	-4.428154	-0.366382
72	1	0	-8.614654	-4.080540	-0.121618
73	1	0	-7.607860	-4.732512	-1.415475
74	1	0	-7.398419	-5.296079	0.265419
75	6	0	-4.578368	2.998962	0.032024
76	1	0	-3.800506	2.320434	-0.335957
77	1	0	-4.377243	3.982888	-0.396770
78	1	0	-4.450805	3.087293	1.117120
79	6	0	-8.495624	-0.288611	0.384469
80	1	0	-8.991515	-0.888253	-0.385804
81	1	0	-7.805727	-0.937665	0.931933
82	1	0	-9.267651	0.015396	1.100043
83	6	0	-8.942673	3.948692	-2.273834
84	1	0	-9.873661	3.473088	-2.590841
85	1	0	-9.204040	4.846040	-1.701188
86	1	0	-8.407206	4.284219	-3.167665
87	6	0	-5.316255	0.756598	2.396639
88	7	0	-5.205815	1.119547	3.499237

Total Energy = -1947.31 HF