Supplementary Information

Elucidation of a detection mechanism of fluorescent sensor based on photo-induced electron transfer for water

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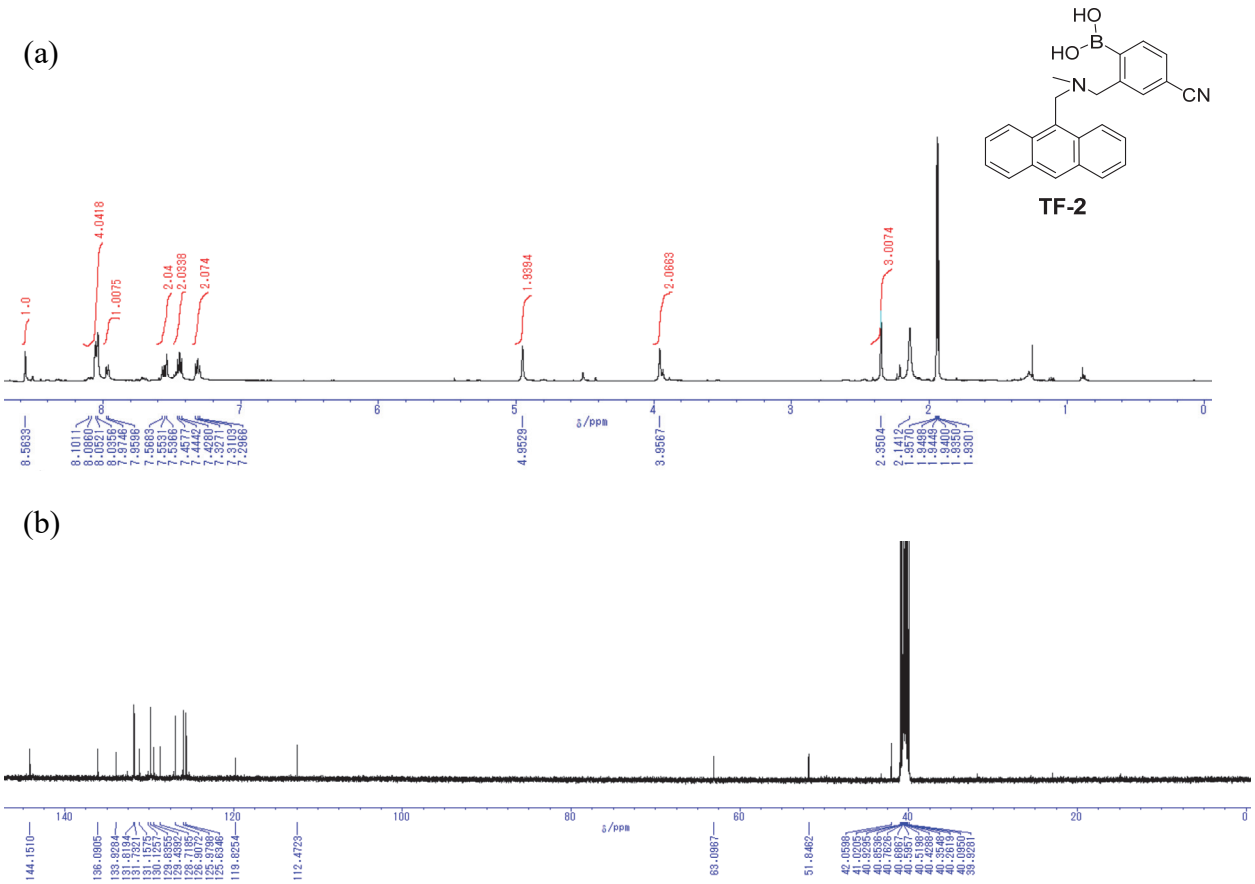

Fig. S1 (a) ^{1}H NMR (500 MHz) spectrum of **TF-2** in acetonitrile-d_3. (b) ^{13}C NMR (125 MHz) spectrum of **TF-2** in DMSO-d_6.

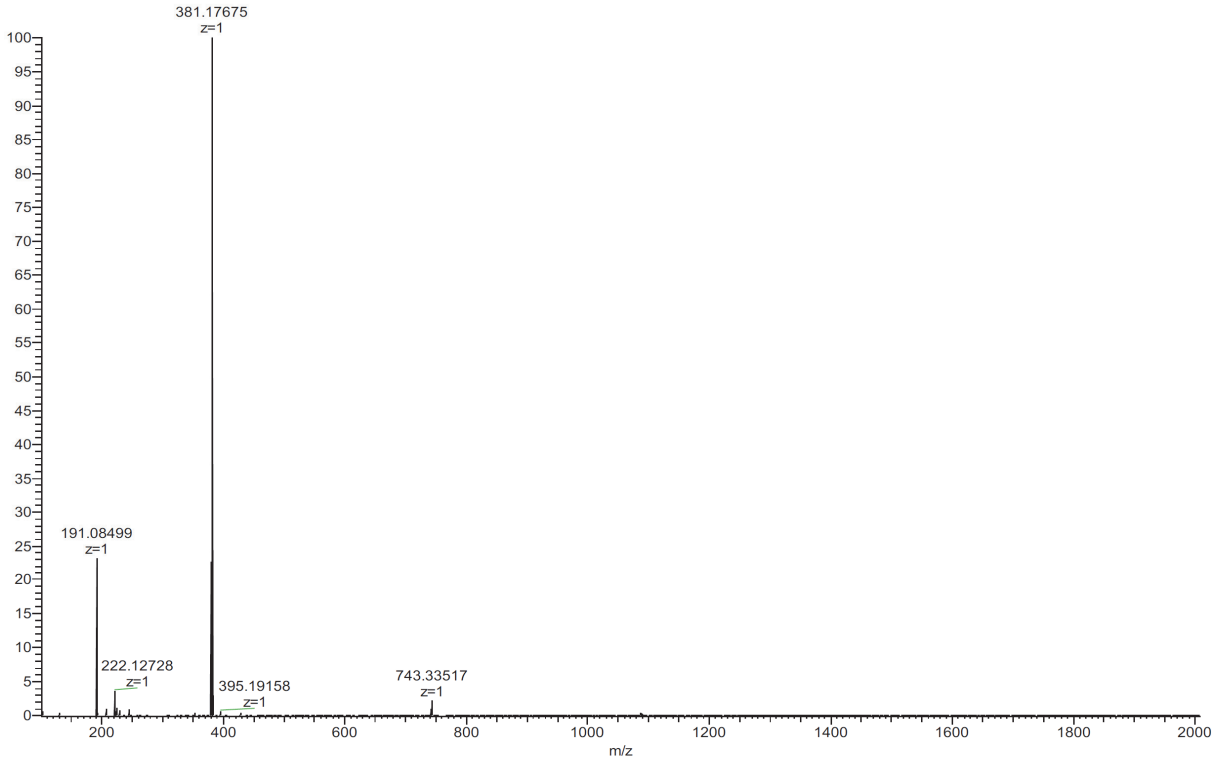

Fig. S2 HRMS (ESI) spectrum of **TF-2**.

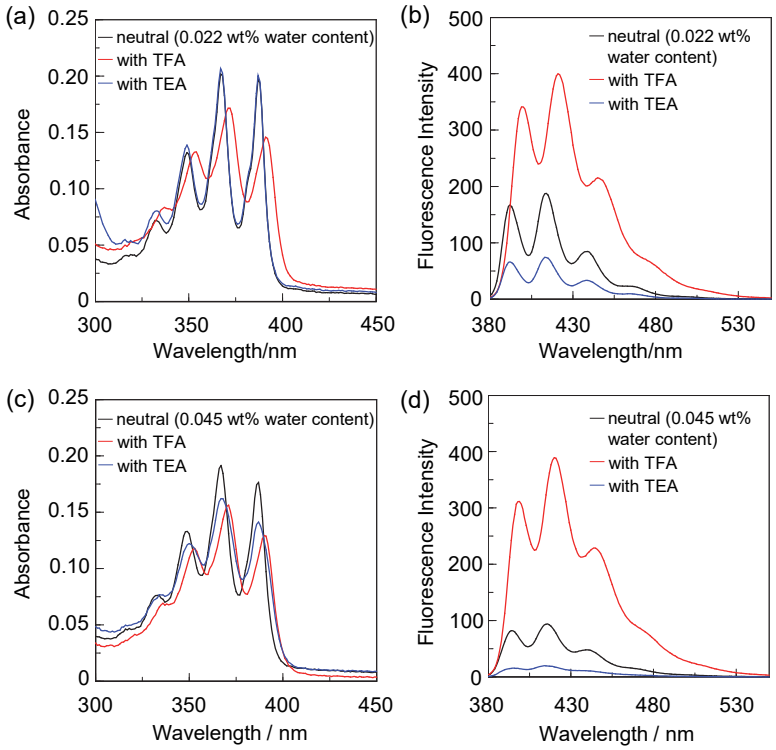

Fig. S3 (a) Photoabsorption and (b) fluorescence spectra (λ^{ex} = 366 nm) of **TF-2** (2.0 × 10^{-5} M) in neutral THF (0.022 wt% water content) and in THF containing CF_3COOH (TFA) (0.2 M) or triethylamine (TEA) (0.2 M). (a) Photoabsorption and (b) fluorescence spectra (λ^{ex} = 366 nm) of **TF-2** (2.0 × 10^{-5} M) in neutral ethanol (0.045 wt% water content) and in ethanol containing TFA (0.2 M) or TEA (0.2 M).

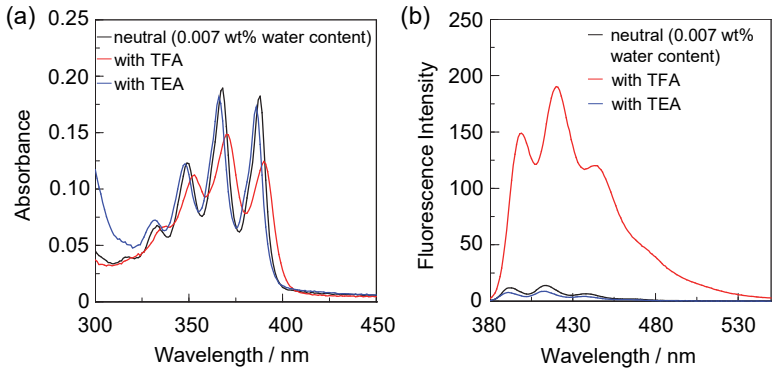

Fig. S4 (a) Photoabsorption and (b) fluorescence spectra (λ^{ex} = 370 nm) of **OF-2** (2.0 × 10^{-5} M) in neutral acetonitrile (0.007 wt% water content) and in acetonitrile containing CF_3COOH (TFA) (0.2 M) or triethylamine (TEA) (0.2 M).

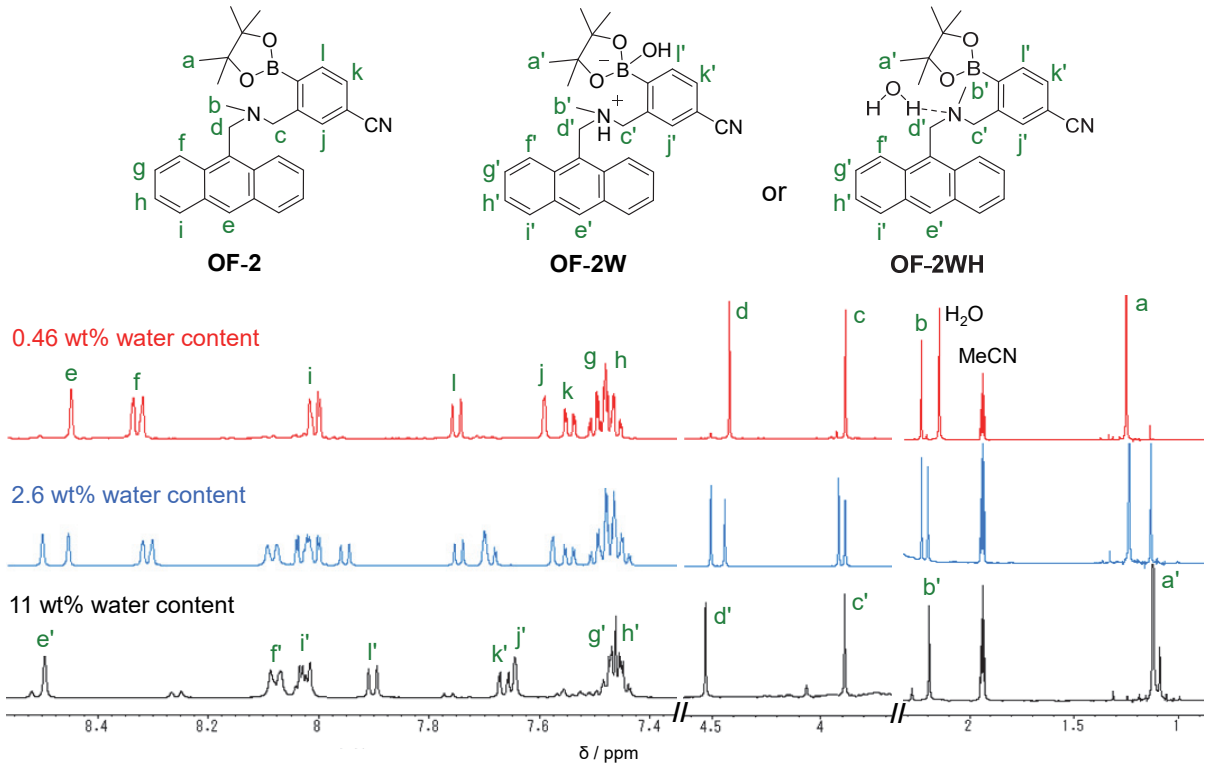

Fig. S5 ^{1}H NMR spectra of **OF-2** (2.0×10^{-2} M) in acetonitrile-d_3 with 0.46 wt%, 2.6 wt% and 11 wt% water content.

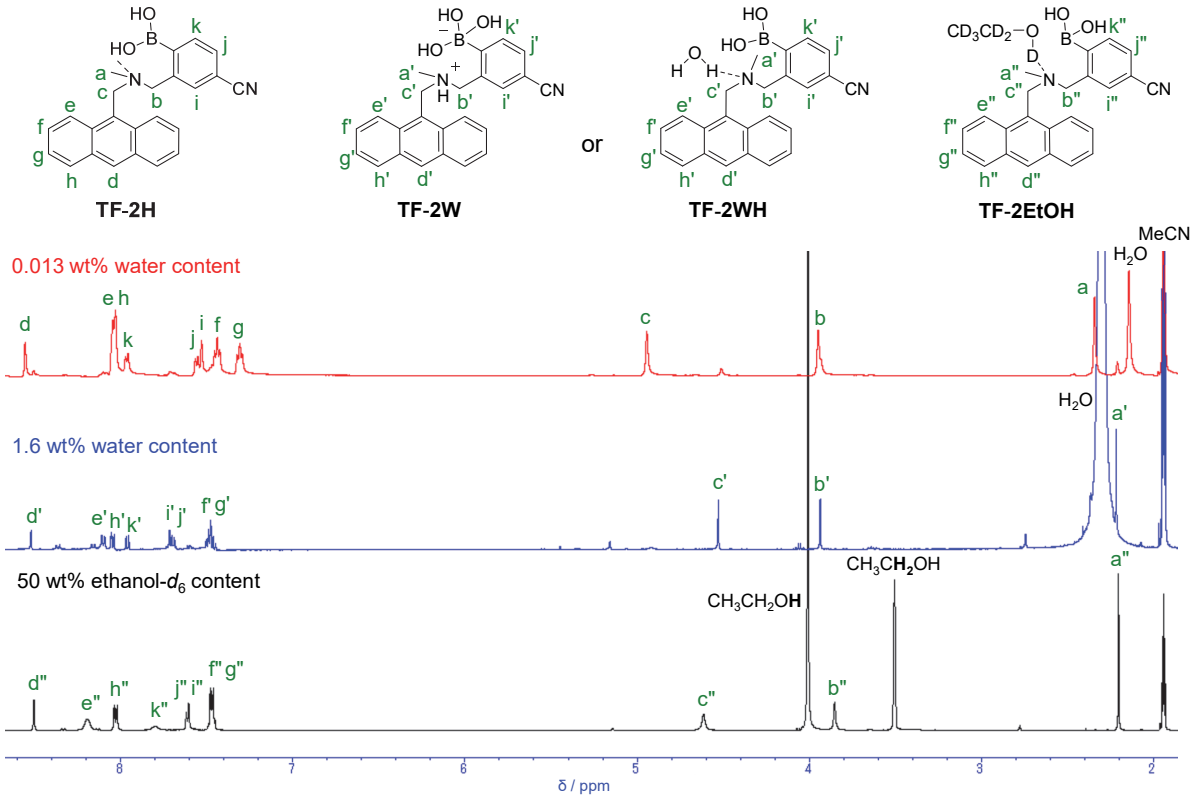

Fig. S6 ^{1}H NMR spectra of **TF-2** (2.0×10^{-2} M) in acetonitrile-d_3 with 0.013 wt% and 1.6 wt% water content and 50 wt% ethanol-d_6 content.

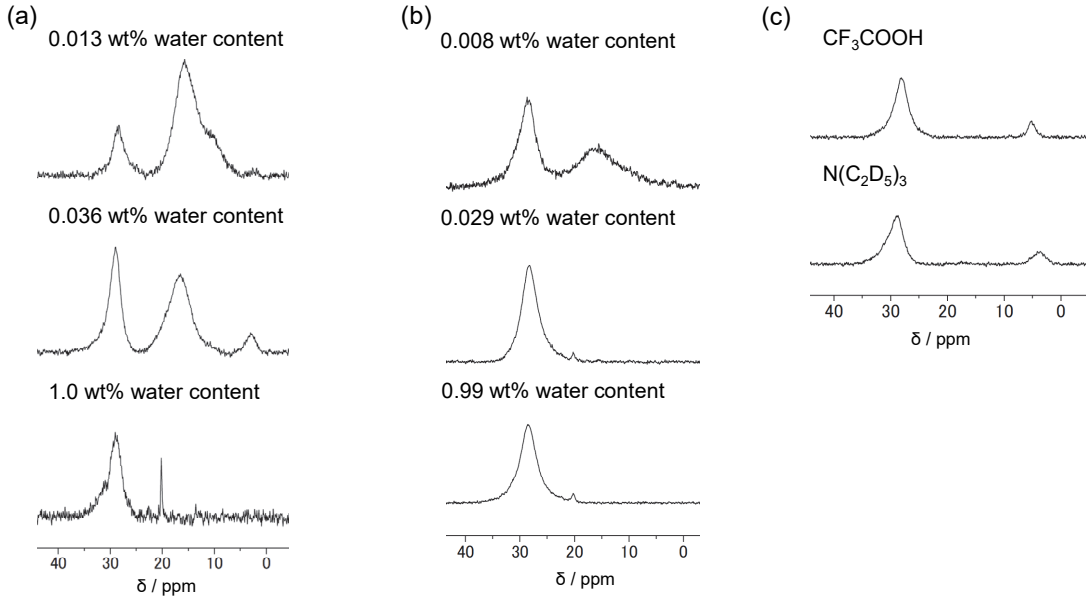

Fig. S7 ^{11}B NMR spectra of **TF-2** (2.0×10^{-2} M) in (a) acetonitrile-d_3 with 0.013 wt%, 0.036 wt% and 1.0 wt% water content, (b) THF-d_8 with 0.008 wt%, 0.029 wt% and 0.99 wt% water content, and (c) acetonitrile-d_3 with CF_3COOH (2.0 M) or $N(C_2D_5)_3$ (2.0 M).

Table S1 Crystal data and structure refinement parameters for **TF-2 (**CCDC 2192821).

Compound	**TF-2**
Molecular formula	$C_{24}H_{21}N_2O_2B$
Formula weight	380.24
Number of reflection used for unit cell determination (2θ range/°)	6435 (4.76-55.4)
Temperature/K	173(2)
Crystal System	monoclinic
Space group	$P2_1/c$
a/Å	12.7784(15)
b/Å	10.4451(12)
c/Å	15.3432(18)
α/°	
β/°	104.3580(10)
γ/°	
V/Å^3	1983.9(4)
Z	4
D_c/g cm^{-3}	1.273
F(000)	800.0
Radiation	Mo-Kα (λ = 0.71073 Å)
Crystal size/mm^3	0.20×0.17×0.06
Range of induces *h*; *k*; *l*	-16, 16; -13, 13; -20, 20
Reflections collected (unique)	4786
Reflection observed with $I_0>2\sigma I_0$	3874
Number of parameters	265
Final R indexes [$I_0>2\sigma I_0$]	R_1 = 0.0426, wR_2 =0.0975
Final R indexes [all data]	R_1 = 0.0534, wR_2 =0.1045
Goodness-of-fit on F^2	0.979
Max. Shift/Error in final cycle	0.00
Max. peak in final diff. map/e Å^{-3}	0.282
Min. peak in final diff. map/e Å^{-3}	-0.238

Table S2 Geometrical coordinates of the optimized **OF-2** by DFT at the B3LYP/6-31G(d,p) level.

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	-2.0580709	-0.2056343	1.2099493
2	C	0	-0.7514045	-0.1479518	1.7949184
3	H	0	0.0342839	0.3917148	1.2843139
4	C	0	-0.4670387	-0.782374	2.9766883
5	H	0	0.536122	-0.7205625	3.3879281
6	C	0	-1.4660718	-1.5276266	3.6638306
7	H	0	-1.2225493	-2.0221768	4.5995978
8	C	0	-2.727489	-1.6166766	3.1410393
9	H	0	-3.5021064	-2.1819219	3.6527593
10	C	0	-3.0646185	-0.9680865	1.9120497
11	C	0	-4.3538036	-1.0521795	1.3810069
12	H	0	-5.111179	-1.6238793	1.9124888
13	C	0	-4.6951286	-0.4181063	0.1849895
14	C	0	-6.0205435	-0.5208832	-0.3431393
15	H	0	-6.7495761	-1.102008	0.2155489
16	C	0	-6.3667147	0.090031	-1.5162872
17	H	0	-7.3764203	0.0044116	-1.9063821
18	C	0	-5.3930354	0.8432932	-2.2300675
19	H	0	-5.6691711	1.3248014	-3.163681
20	C	0	-4.1136204	0.9687329	-1.7559857
21	H	0	-3.4026233	1.5457356	-2.3336174
22	C	0	-3.6962044	0.3513423	-0.5290392
23	C	0	-2.3838602	0.4552528	-0.0015468
24	C	0	-1.3210419	1.2968978	-0.6885134
25	H	0	-1.7879597	2.0069444	-1.3894374
26	H	0	-0.8269103	1.9177435	0.0656015
27	C	0	-0.7903251	-0.3313504	-2.4340789
28	H	0	-1.2318503	0.2409538	-3.271472
29	H	0	-1.5626946	-0.9929369	-2.0363059
30	H	0	0.0234201	-0.9447809	-2.8295042
31	C	0	0.7899584	1.4018431	-1.8796528
32	H	0	0.3707213	2.2374117	-2.4720246
33	H	0	1.4084209	0.8056885	-2.5555384
34	C	0	1.6700428	1.9563325	-0.7754959
35	C	0	1.6729043	3.3249859	-0.510399

36	H	0	1.0576463	3.9930832	-1.1054321
37	C	0	2.4607911	3.8582459	0.5242248
38	C	0	3.2443555	3.0047381	1.3130737
39	H	0	3.8457372	3.4130582	2.1182101
40	C	0	3.2365822	1.6384813	1.0473001
41	H	0	3.8432426	0.9770615	1.658437
42	C	0	2.4738772	1.0897237	0.0024781
43	C	0	2.4530888	5.2704784	0.7744659
44	N	0	-0.2664937	0.5174016	-1.3663719
45	N	0	2.4474397	6.4164989	0.9755239
46	C	0	2.8325504	-2.6752403	0.2177161
47	C	0	3.0709177	-2.4166567	-1.3204042
48	B	0	2.5993587	-0.4521397	-0.2534303
49	O	0	2.8819699	-1.3235902	0.7674071
50	O	0	2.5670481	-1.0560302	-1.4871338
51	C	0	1.4377095	-3.2272102	0.5334152
52	H	0	1.2753123	-3.189279	1.6133144
53	H	0	0.6557918	-2.6273322	0.0613401
54	H	0	1.3343687	-4.2656826	0.2050363
55	C	0	3.9046327	-3.5133336	0.9096429
56	H	0	3.6680519	-3.6026815	1.973474
57	H	0	3.9419768	-4.5225045	0.4866466
58	H	0	4.8939181	-3.0612401	0.8208181
59	C	0	4.5534103	-2.3811056	-1.7134317
60	H	0	5.0028807	-3.3778469	-1.6817602
61	H	0	4.640827	-1.9968447	-2.7331784
62	H	0	5.1252159	-1.7218499	-1.0545557
63	C	0	2.2998322	-3.338232	-2.2617068
64	H	0	2.4991498	-3.0534134	-3.2987601
65	H	0	2.6167929	-4.3781568	-2.1316611
66	H	0	1.2235112	-3.2795402	-2.0935443

Table S3 Geometrical coordinates of the optimized **TF-2** by DFT at the B3LYP/6-31G(d,p) level.

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	B	0	2.6387425	1.6177721	1.7278803
2	C	0	-1.6126904	1.0427043	-0.6368494
3	C	0	-0.3886961	1.7706239	-0.7961478
4	H	0	0.5537546	1.2904757	-0.5686191
5	C	0	-0.37893	3.0721344	-1.2259363
6	H	0	0.5672552	3.5933024	-1.3370489
7	C	0	-1.5918669	3.7519968	-1.526359
8	H	0	-1.5629039	4.7839615	-1.8626102
9	C	0	-2.7862459	3.098901	-1.3921668
10	H	0	-3.7225499	3.6008111	-1.621148
11	C	0	-2.8388319	1.7394307	-0.9528947
12	C	0	-4.0582476	1.0696427	-0.8317563
13	H	0	-4.9788333	1.5969598	-1.0707226
14	C	0	-4.1258677	-0.2617242	-0.4175769
15	C	0	-5.3863211	-0.9287781	-0.3084365
16	H	0	-6.2838793	-0.3691799	-0.5579764
17	C	0	-5.4668101	-2.2320956	0.0967764
18	H	0	-6.4294374	-2.728014	0.1746631
19	C	0	-4.2761868	-2.9422195	0.4167156
20	H	0	-4.3417091	-3.9779217	0.7370333
21	C	0	-3.0494591	-2.3383826	0.3255264
22	H	0	-2.1708151	-2.9167936	0.5818704
23	C	0	-2.9063455	-0.9731872	-0.0942513
24	C	0	-1.6584141	-0.307213	-0.2038801
25	C	0	-0.358352	-1.0267961	0.1052626
26	H	0	-0.4947247	-2.1153321	0.0431811
27	H	0	0.3817262	-0.7796282	-0.6594349
28	C	0	-0.6253787	-1.0331918	2.5484175
29	H	0	-0.7636527	-2.1224845	2.6461154
30	H	0	-1.6042008	-0.5693986	2.422005
31	H	0	-0.1806385	-0.6556963	3.4734598
32	C	0	1.5681503	-1.3148482	1.5833799
33	H	0	1.480913	-2.4101024	1.4838458
34	H	0	1.884206	-1.1160484	2.6130088
35	C	0	2.6370932	-0.8074595	0.6286566

36	C	0	3.1595242	-1.7004959	-0.3090269
37	H	0	2.7751388	-2.7143746	-0.3654595
38	C	0	4.1867844	-1.3131515	-1.1841459
39	C	0	4.7064327	-0.0134149	-1.110385
40	H	0	5.5052678	0.2880513	-1.7795647
41	C	0	4.1897193	0.8705478	-0.1687992
42	H	0	4.6031299	1.8714378	-0.0982957
43	C	0	3.1531879	0.5113182	0.7108832
44	C	0	4.7006804	-2.2491062	-2.1416531
45	N	0	0.2430924	-0.6742083	1.4182397
46	N	0	5.1149685	-3.0100255	-2.9182077
47	O	0	3.5388885	2.5985044	2.0597185
48	H	0	3.1225095	3.2494779	2.6400608
49	O	0	1.3859104	1.6570821	2.2413767
50	H	0	0.8033416	0.9451672	1.8651319