Electronic Supplementary Information

Aromatic fluorine atom-induced highly amine-sensitive trimethine cyanine dye showing colorimetric and ratiometric fluorescence change

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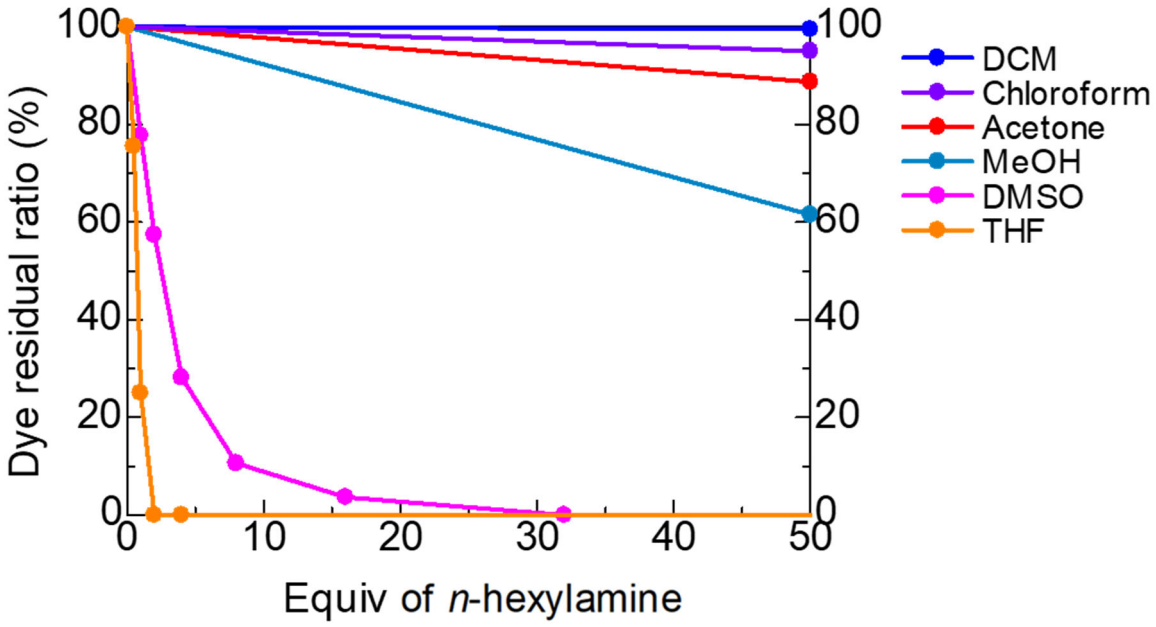


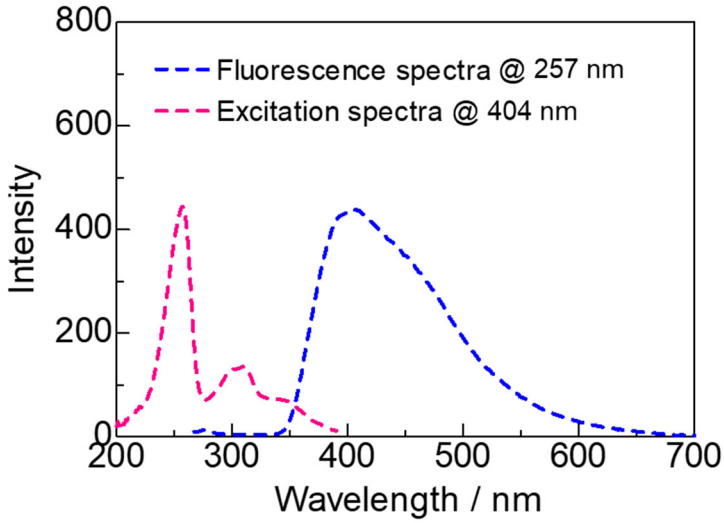
Figure S1. Dye residual ratio calculated from molar absorption coefficient (ε) at 579 nm of dye **2a** solusion (5 x 10^{-6} M) in adding *n*-hexylamine.

Table S1. DN and AN value of solvents.

Solvent	AN	DN (kcal mol^{-1})
DCM	20	1
Chloroform	23	4
Acetone	13	17
MeOH	42	19
DMSO	19	30
THF	8	20

[a] Gutmann Acceptor number (AN) and Donor number (DN).

a)



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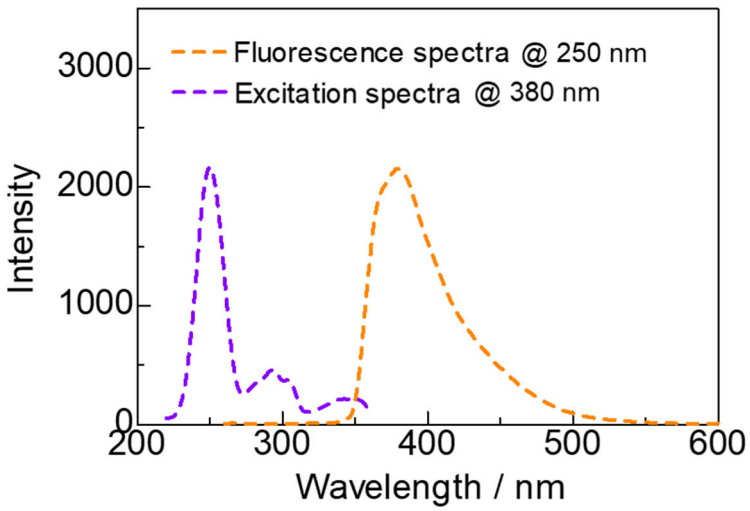
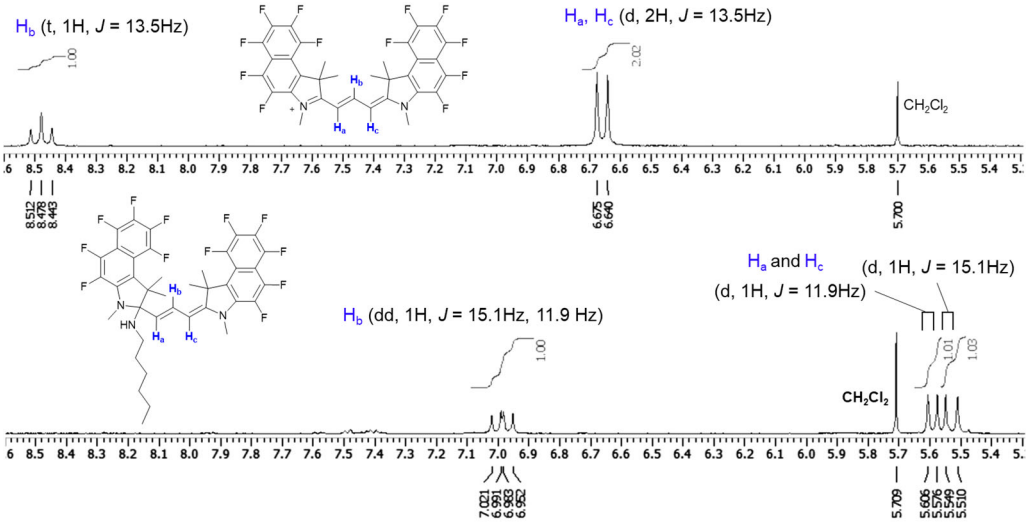


Fig. S2. a) Fluorescence and excitation spectra of dye **2a** and b) **2b** (5×10^{-6} M) in THF completely reacted with *n*-hexylamine.

a)



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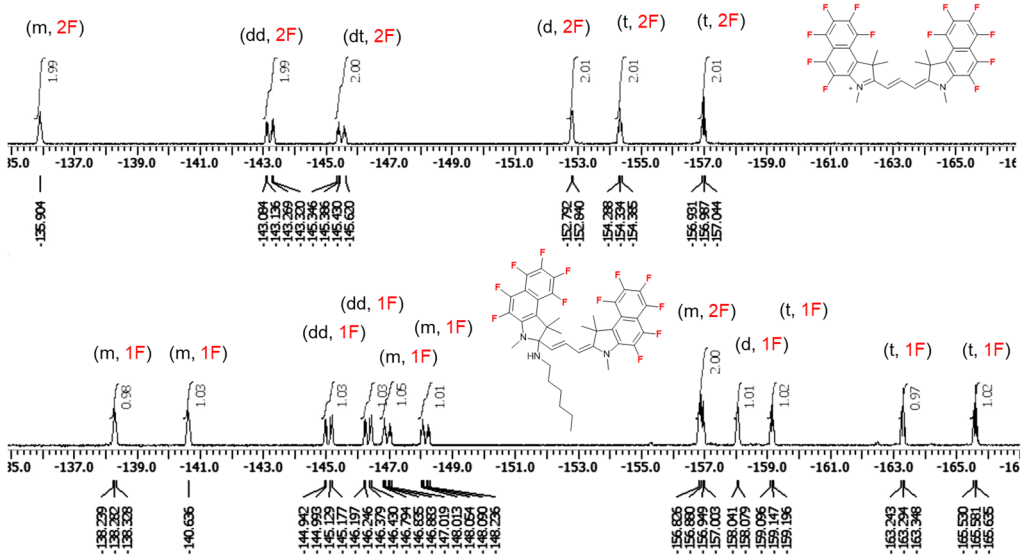


c)

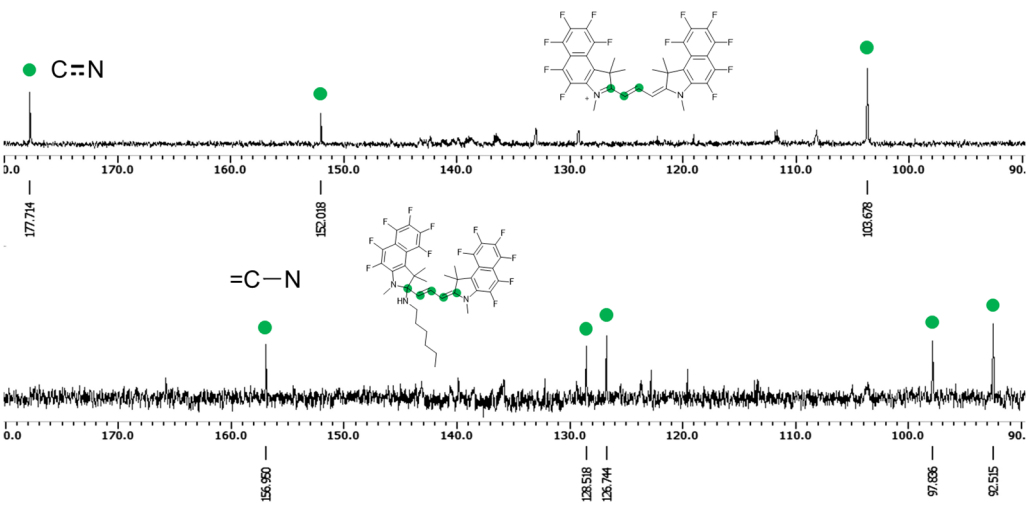


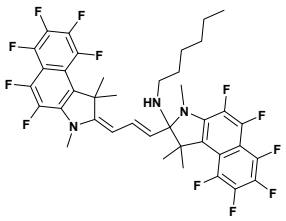
Fig. S3. a) ^{1}H, b) ^{19}F, and c) ^{13}C NMR analysis for the reaction of dye **2a** (1×10^{-5} mol) with *n*-hexylamine (20 equiv) in DMSO-d6.

a)

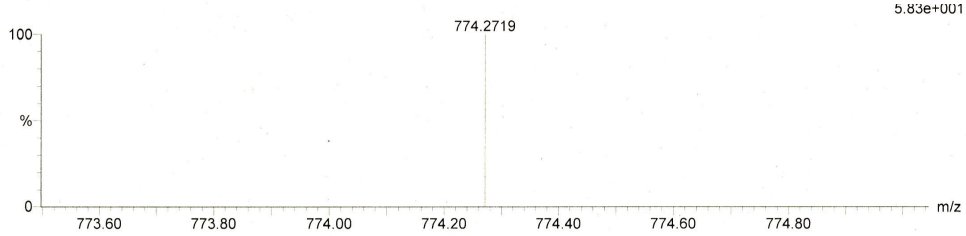
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 33-39 H: 21-36 N: 2-3 F: 11-12
20210716_2 18 (0.637)
1: TOF MS ES+



5.83e+001



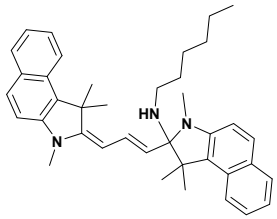
Minimum:				-1.5			
Maximum:		50.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
774.2719	774.2718	0.1	0.1	17.5	17.7	0.0	C39 H36 N3 F12

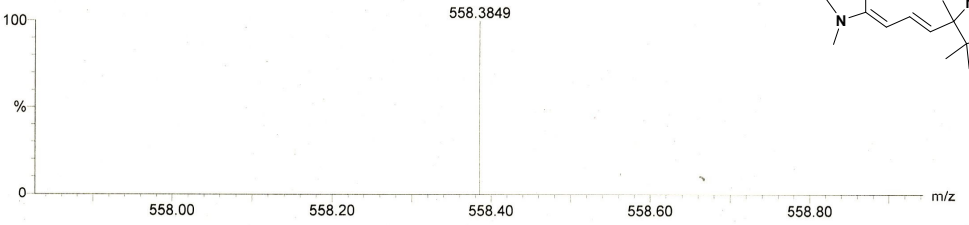
b)

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 39-39 H: 48-48 N: 3-3 Na: 0-1
20220214_2 22 (0.774)
1: TOF MS ES+



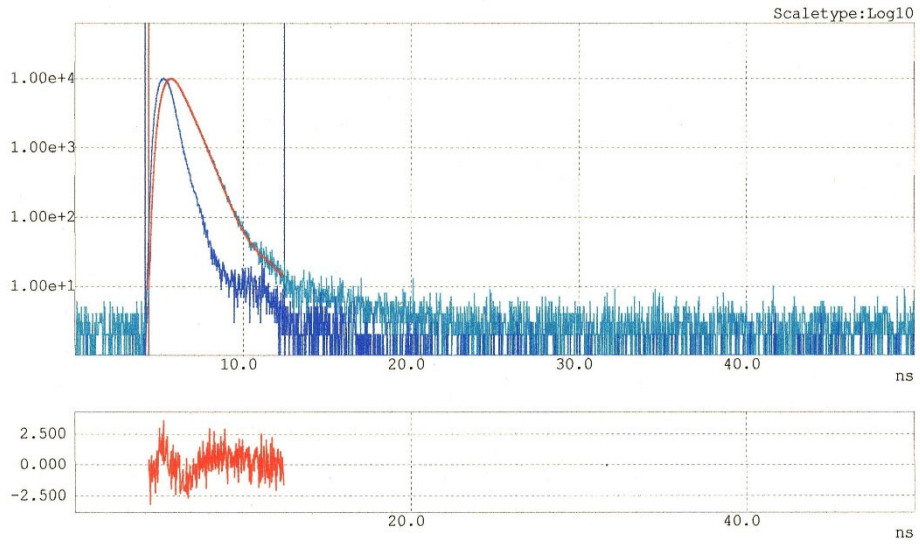


Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
558.3849	558.3848	0.1	0.2	17.5	23.7	0.0	C39 H48 N3

Fig. S4. a) MS analysis for amine-added dyes **2a** and b) **2b**.

The results of fluorescence lifetime

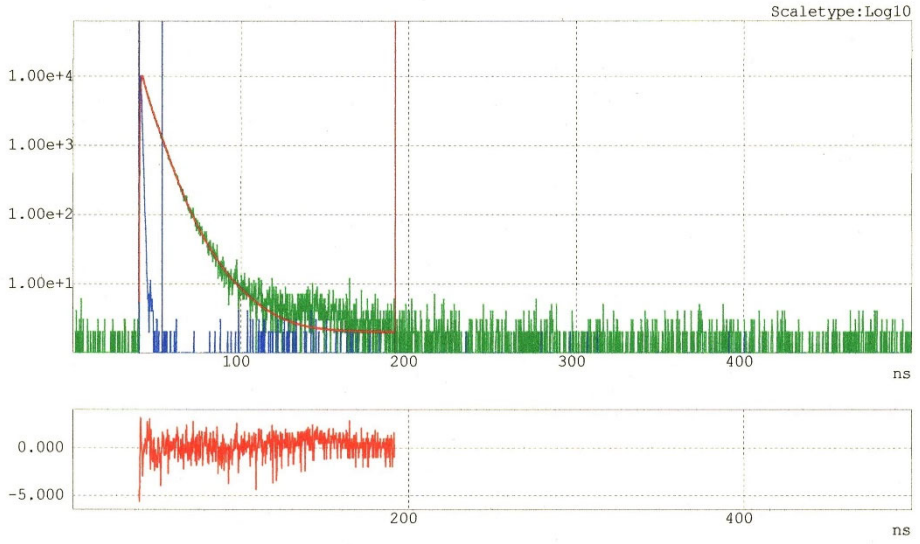
1. Dye **2a** (5 x 10^{-6} M) in THF.



Excitation Wavelength /nm : 470
Time Range /ns : 50 ns
Stop Condtion : Peak Count 10000
Frequency : 5 MHz

Name	EMML	CH1	Meas. Time	<r>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
1	526	1.322	775.1	0.677118	0.677118					556.343					3

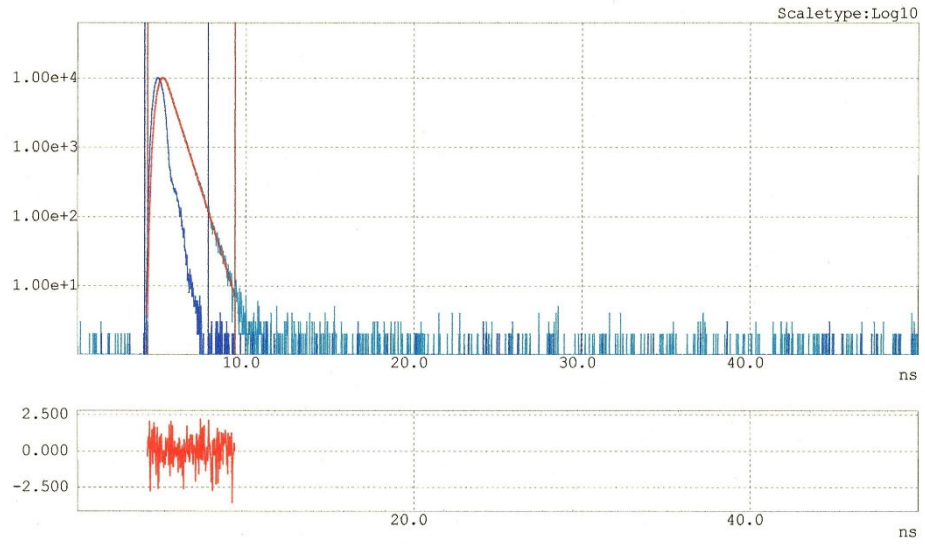
2. Dye **2a** (5 x 10^{-6} M) in THF with *n*-hexylamine (2 equiv).



Excitation Wavelength /nm : 280
Time Range /ns : 500 ns
Stop Condtion : Peak Count 10000
Frequency : 500 kHz

Name	EMML	CH1	Meas. Time	<r>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
0	404	1.39029	318.6	6.08041	0.993043	5.83555	14.6132			1424.64	2113.5	61.9387			2

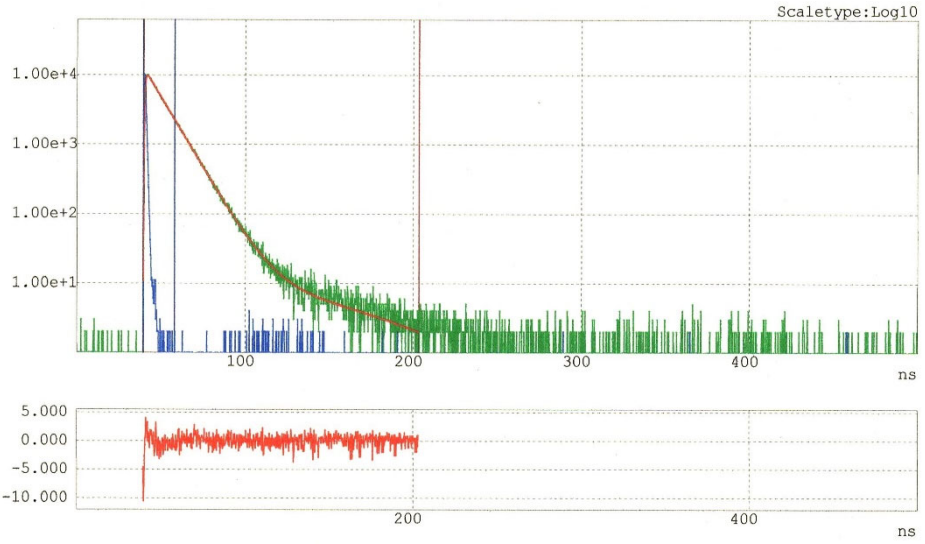
3. Dye **2b** (5 x 10^{-6} M) in THF.



Excitation Wavelength /nm : 590
Time Range /ns : 50 ns
Stop Condtion : Peak Count 10000
Frequency : 5 MHz

Name	EMWL	CH1	Meas. Time	<τ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
1	617	1.03879	139.4	0.521284	0.366574	0.589888				272.344	447.812				-1

4. Dye **2b** (5 x 10^{-6} M) in THF with *n*-hexylamine (6400 equiv).



Excitation Wavelength /nm : 280
Time Range /ns : 500 ns
Stop Condtion : Peak Count 10000
Frequency : 500 kHz

Name	EMWL	CH1	Meas. Time	<τ>	Tau1	Tau2	Tau3	Tau4	Tau5	A1	A2	A3	A4	A5	Background
0	380	1.48219	142.1	12.5490	10.6124	110.079				2624.16	5.80465				-3

Computational Details.

All calculations were performed using the computational chemistry software package Gaussian 16 ver. C.01 [1]. Computational resources in the form of super computers were provided by Research Center for Computational Science, Okazaki, Japan.

Ground state geometries of compound **2a**, **2b** were calculated by DFT at the RB3LYP/6-31+G(d,p) scrf=(solvent=dichloromethane) level.

At the optimized structures, no imaginary frequency was found through the frequency analysis. All coordinates are reported as XYZ Cartesian coordinates. And computed E (RB3LYP) and sum of electronic and thermal Energies of optimized structures are shown.

2a

E (RB3LYP) = -2577.625224 a.u.

Sum of electronic and thermal Energies= -2577.105643 a.u.

Imaginary Frequency = 0

Table S2. Cartesian coordinates of the optimized **2a**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-4.774293	1.679121	0.113635
C	-4.470385	0.326227	0.028708
C	-7.129699	1.214178	0.096221
C	-6.109535	2.128579	0.145227
C	-7.717549	-2.467815	-0.114018
C	-6.39228	-2.934096	-0.14786
C	-7.955656	-1.119263	-0.03362
C	-5.517185	-0.64266	-0.019877
C	-6.892559	-0.180418	0.015315
C	-5.340403	-2.052482	-0.102301
N	-3.603706	2.453804	0.147685
F	-4.107832	-2.601618	-0.138989
F	-6.169158	-4.253266	-0.224546
F	-8.72643	-3.347827	-0.159563
F	-9.23736	-0.713067	-0.001876
F	-8.385876	1.691996	0.124729
F	-6.43154	3.436279	0.215262
C	-2.940127	0.194919	-0.002834
C	-2.449846	-0.41239	-1.345305
H	-2.818832	0.177788	-2.188852
H	-1.35994	-0.421335	-1.391677
H	-2.799661	-1.436685	-1.458139
C	-2.407165	-0.556135	1.248391
H	-2.739138	-0.057855	2.1634
H	-2.765246	-1.58366	1.263404
H	-1.316505	-0.581564	1.254173
C	-2.503949	1.663284	0.069525
C	-1.220919	2.214996	0.049669
H	-1.156294	3.297585	0.070494
C	-3.538674	3.917438	0.256423
H	-3.104668	4.337972	-0.654453

H	-4.534484	4.319885	0.394101
H	-2.923325	4.189931	1.116578
C	4.774294	1.679122	-0.113637
C	4.470386	0.326228	-0.02871
C	7.1297	1.214178	-0.096234
C	6.109536	2.12858	-0.145234
C	7.717546	-2.467817	0.114009
C	6.392276	-2.934095	0.147862
C	7.955655	-1.119265	0.033605
C	5.517186	-0.642658	0.019873
C	6.89256	-0.180418	-0.015327
C	5.3404	-2.052479	0.102305
N	3.603706	2.453803	-0.147679
F	4.107828	-2.601609	0.139009
F	6.169152	-4.253264	0.224556
F	8.726425	-3.34783	0.159551
F	9.237361	-0.713072	0.001853
F	8.385877	1.691996	-0.124746
F	6.431541	3.436279	-0.215266
C	2.94013	0.194917	0.002839
C	2.449864	-0.412407	1.345308
H	2.818846	0.17777	2.188858
H	1.359958	-0.421368	1.391686
H	2.799693	-1.436699	1.458133
C	2.407165	-0.556131	-1.248388
H	2.739126	-0.057842	-2.163395
H	2.765255	-1.583654	-1.263411
H	1.316505	-0.58157	-1.254161
C	2.50395	1.663282	-0.069508
C	3.538672	3.917437	-0.256418
H	3.104717	4.337977	0.65448
H	4.534475	4.319881	-0.394155
H	2.923276	4.189928	-1.11654
C	0	1.533904	0.000011
H	-0.000001	0.452585	0.000002
C	1.220919	2.214995	-0.049639
H	1.156296	3.297585	-0.07045

2b

E (RB3LYP) = -1386.857547 a.u.

Sum of electronic and thermal Energies= -1386.250611 a.u.

Imaginary Frequency = 0

Table S3. Cartesian coordinates of the optimized **2b**.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	4.789846	1.298894	-0.072853
C	4.451362	-0.041172	-0.009714
C	7.124263	0.81666	-0.063018
C	6.122905	1.761442	-0.099119
C	7.627154	-2.881807	0.096161
C	6.284639	-3.333637	0.124224
C	7.892986	-1.531113	0.034932
C	5.471224	-1.031601	0.027173
C	6.839779	-0.576295	-0.001204
C	5.237192	-2.437193	0.091056
N	3.615191	2.084655	-0.101136
C	2.929019	-0.162516	0.010734
C	2.437767	-0.809493	1.331719
H	2.797733	-0.245401	2.196623
H	1.34751	-0.843293	1.376574
H	2.808566	-1.832679	1.416098
C	2.411509	-0.9215	-1.239199
H	2.743836	-0.428653	-2.156985
H	2.79223	-1.944532	-1.247403
H	1.32099	-0.971085	-1.253474
C	2.503744	1.314039	-0.046215
C	1.224542	1.879063	-0.034018
H	1.170765	2.963316	-0.048685
C	3.602645	3.543591	-0.173531
H	3.182193	3.967429	0.742964
H	4.618345	3.910238	-0.29548
H	3.01029	3.871391	-1.031537
C	-4.789838	1.298902	0.072879
C	-4.451363	-0.041162	0.009658
C	-7.124255	0.816655	0.063607
C	-6.122893	1.761443	0.099469

C	-7.627165	-2.881814	-0.095435
C	-6.284654	-3.333638	-0.123818
C	-7.892989	-1.531121	-0.03415
C	-5.471229	-1.031596	-0.026977
C	-6.839779	-0.576298	0.001728
C	-5.237204	-2.437188	-0.090908
N	-3.61518	2.084666	0.100939
C	-2.929025	-0.162497	-0.011216
C	-2.43814	-0.809315	-1.332416
H	-2.798328	-0.245107	-2.197151
H	-1.347898	-0.843134	-1.377571
H	-2.808979	-1.832484	-1.416827
C	-2.411153	-0.921625	1.238478
H	-2.743197	-0.428875	2.156418
H	-2.791887	-1.944653	1.24668
H	-1.320626	-0.971222	1.252414
C	-2.503742	1.314054	0.045805
C	-3.602624	3.543599	0.17342
H	-3.182386	3.967495	-0.743147
H	-4.618296	3.910234	0.295627
H	-3.010071	3.871347	1.031307
C	-0.000001	1.204482	-0.000246
H	-0.000008	0.122533	-0.000235
C	-1.224538	1.879072	0.033561
H	-1.170752	2.963324	0.048294
H	-6.366361	2.816072	0.143152
H	-8.162635	1.134134	0.081268
H	-8.918752	-1.172839	-0.012154
H	-8.440561	-3.600269	-0.122147
H	-6.077392	-4.398532	-0.172135
H	-4.223698	-2.817248	-0.114365
H	4.223683	-2.817258	0.114276
H	6.077371	-4.398532	0.172499
H	8.440547	-3.600258	0.123074
H	8.918752	-1.172825	0.013182
H	8.162646	1.134143	-0.080425
H	6.366378	2.816073	-0.142729

Reference

[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.