Supporting Information

Highly Intense Fluorescent Diarylboron Diketonate

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Cyclic voltammograms of **1a**-**2b** and molecular orbital diagrams for the LUMO and of **2a** and **2b**……S2

General methods……. S3

The copies of NMR spectra of **1a**, **2a**, **1b**, **2b**……...S4-S7

Theoretical calculations of **1a**, **2a**, **1b**, **2b**……S8-S18

References…….….S18

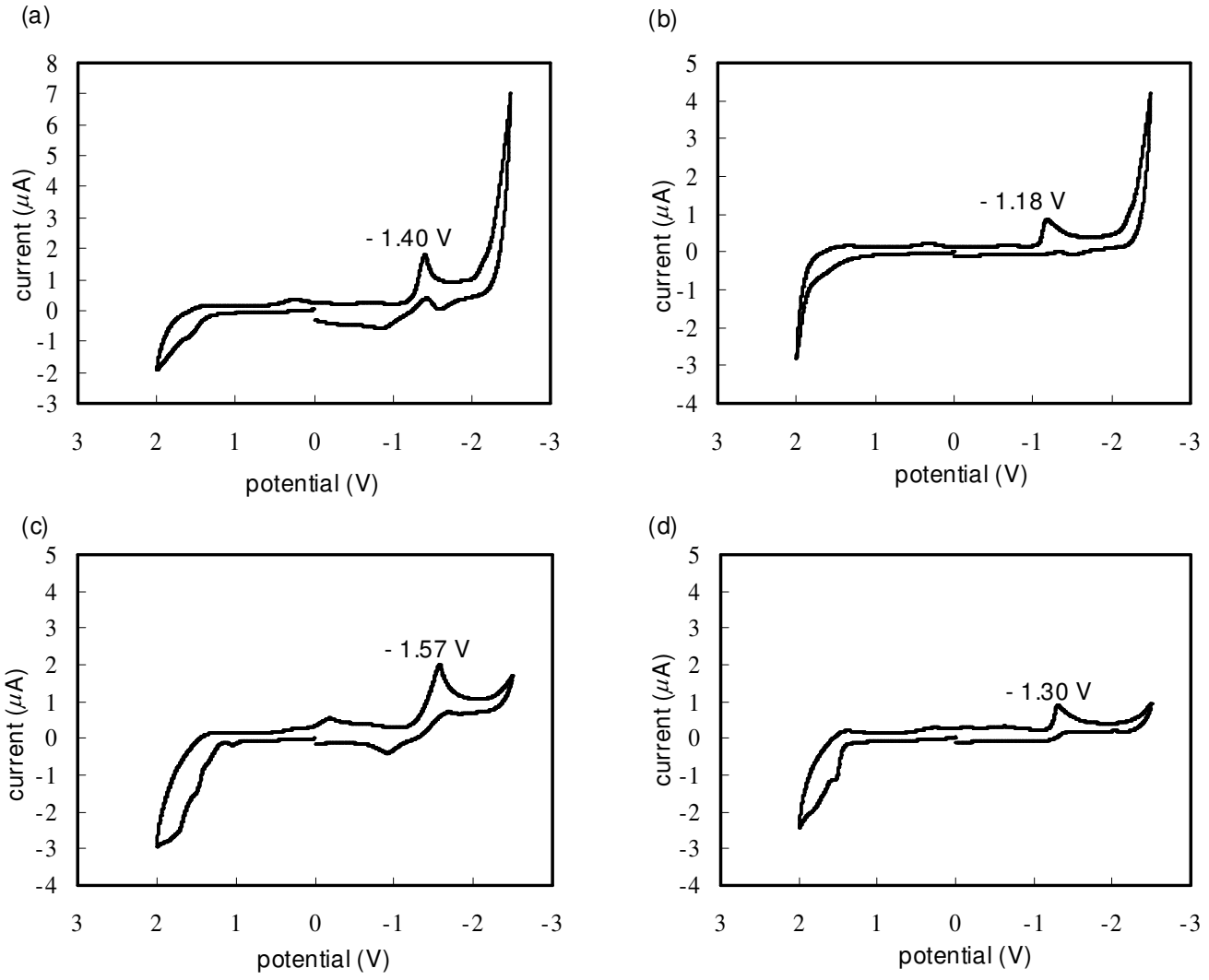


Figure 1S. Cyclic voltammograms of **1a** (a), **1b** (b), **2a** (c), and **2b** (d) measured in CH_3CN solution, containing 0.1 M *n*-Bu_4NClO_4 at r.t.

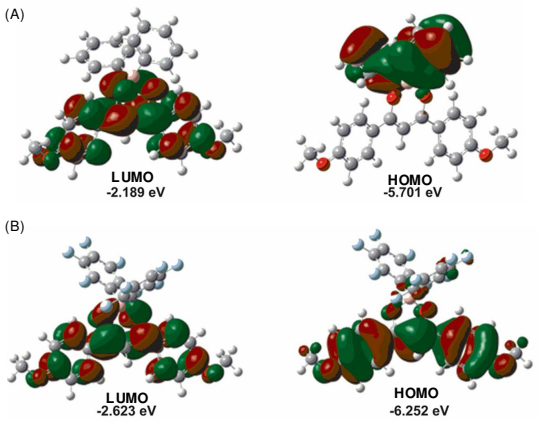


Figure 2S. Molecular orbital diagrams for the LUMO and of **2a** (A) and **2b** (B) (B3LYP/6-31G(d, p)//B3LYP/6-31G(d, p)).

Experimental Section

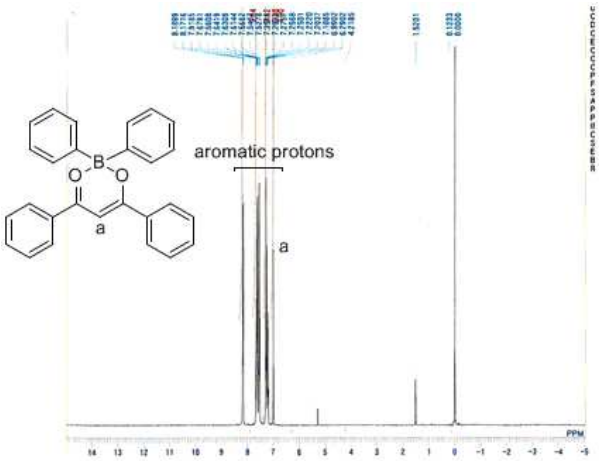
Measurements. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) spectra were recorded on JEOL JNM-EX400 spectrometers. ^{1}H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard in $CDCl_3$, and ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}OEt_2$ (sealed capillary). UV-vis spectra were recorded on a SHIMADZU UV-3600 spectrophotometer and fluorescence emission spectra on HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. FT-IR spectra were obtained using a Perkin-Elmer 1600 infrared spectrometer. X-ray crystallographic analysis was carried out by Rigaku R-AXIS RAPID-F graphite-monochromated Mo Kα radiation diffractometer with imaging plate. A symmetry-related absorption correction was carried out by using the program ABSCOR.[1] The analysis was carried out with direct methods (SHELX-97[2] or SIR92[3]) using Yadokari-XG.[4] The program ORTEP3[5] was used to generate the X-ray structural diagram.

Materials. Fluorobis(pentafluorophenyl)borane diethyl etherate ($(C_6H_5)_2BF{\cdot}OEt_2$) was synthesized from bromopentafluorobenzene according to the reported method.[6] 1,3-Biphenyl-1,3-propanedione, 1,3-bis(4-methoxyphenyl)-1,3-propanedione, triphenylborane (BPh_3), and boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) were used as received. Tetrahydrofuran (THF), diethyl ether, and triethylamine (NEt_3) were purified using a two-columm solid-state purification system.

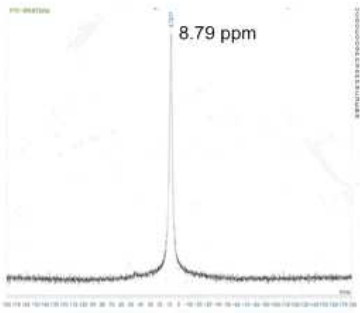
Cyclic voltammetry (CV) measurement.

CV was peformed with a BAS CV-50W Electrochemical Analyzer. The CV studies of **1a**-**2b** were carried out in acetonitrile 0.1 M *n*-Bu_4NClO as a scanning rate of 100 mVs^{-1} using Pt and Ag/Ag^+ electrodes. The values are expressed in potentials versus $Ag/AgNO_3$.

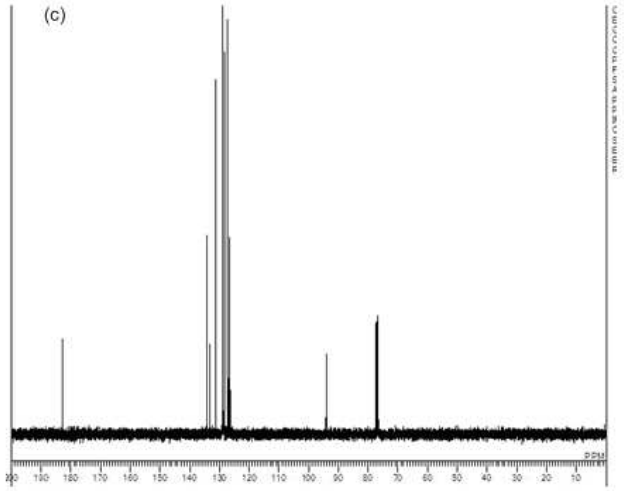
Supporting NMR spectra of 1a.



^{1}H NMR spectrum of **1a**

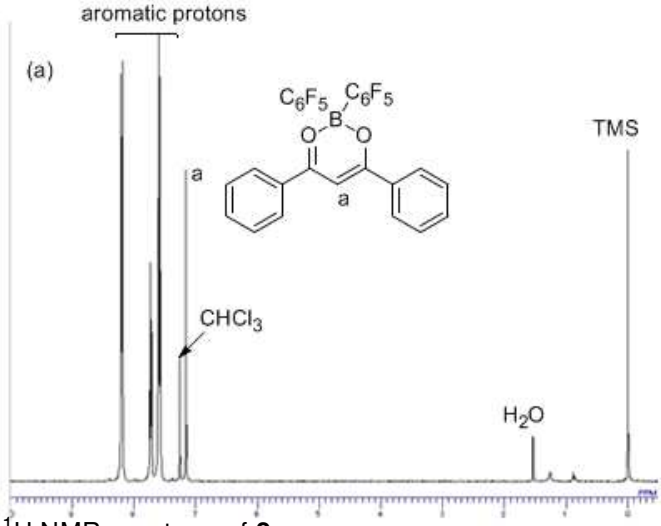


^{11}B NMR spectrum of **1a**

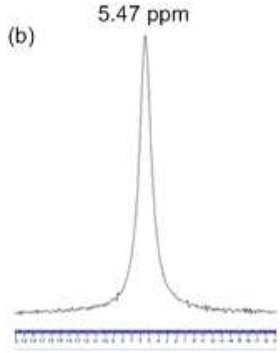


^{13}C NMR spectrum of **1a**

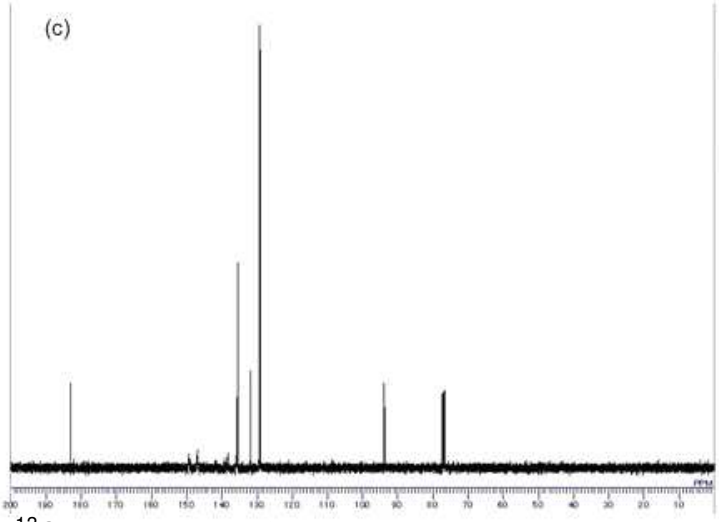
Supporting NMR spectra of 2a.



^{1}H NMR spectrum of **2a**

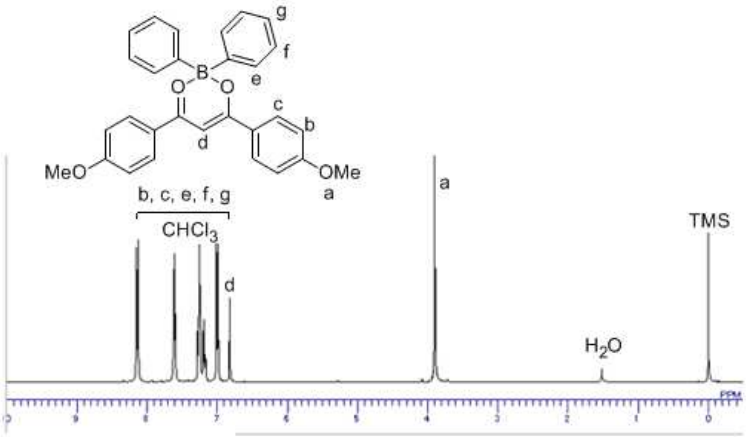


^{11}B NMR spectrum of **2a**

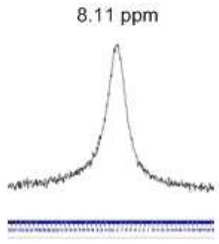


^{13}C NMR spectrum of **2a**

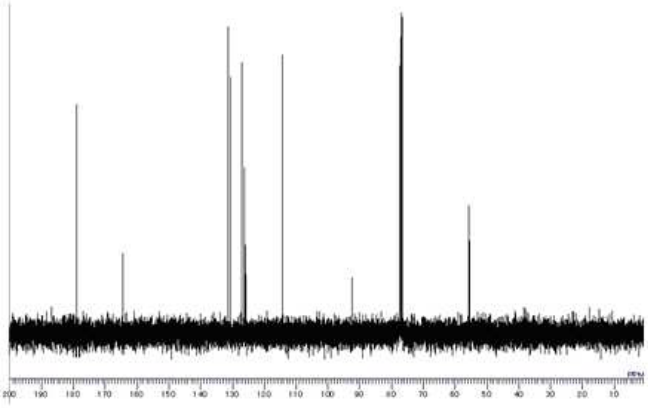
Supporting NMR spectra of 1b.



^{1}H NMR spectrum of **1b**

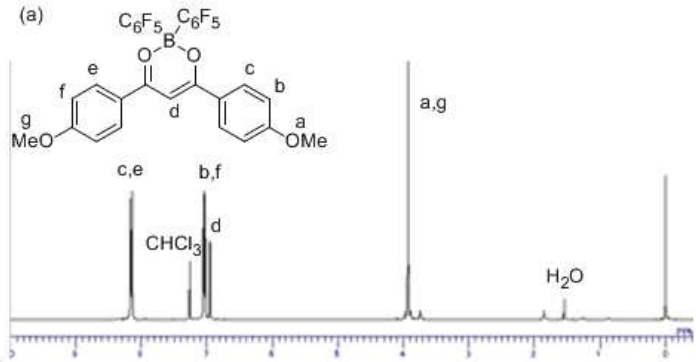


^{11}B NMR spectrum of **1b**

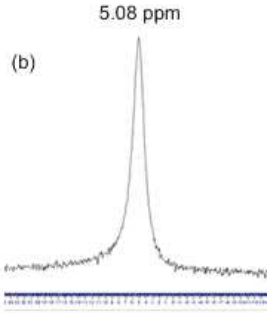


^{13}C NMR spectrum of **1b**

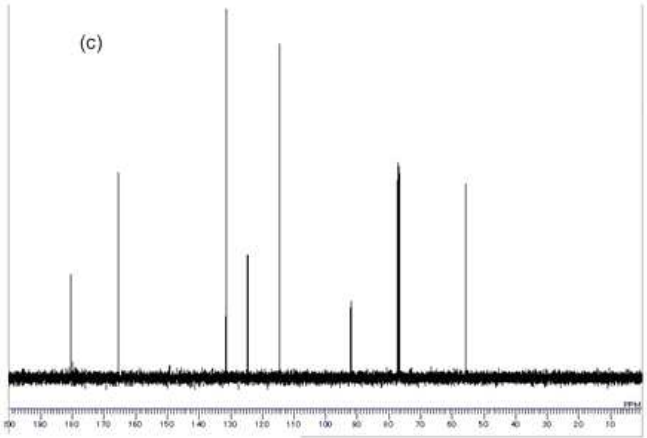
Supporting NMR spectrum of 2b.



^{1}H NMR spectrum of 2**1b**



^{11}B NMR spectrum of **2b**



^{13}C NMR spectrum of **2b**

Theoretical Calculations.

All calculations were carried out at DFT level using B3LYP exchange-correlation functional implemented in the Gaussian 03 (Revision D.01) suite of programs.[7] All calculations for the optimized structures were calculated with the 6-31G(d,p).

Gemetry (Cartesian Coordinates) of 1a

C	-0.52119	-1.49149	0.42979
C	0.88036	-1.49149	0.42979
C	1.55853	-0.26683	0.42979
O	0.92622	0.85466	0.28527
B	-0.53709	0.91756	-0.20062
O	-1.19689	-0.39939	0.27256
C	-1.26063	2.13073	0.56727
C	-0.97928	2.39930	1.91875
C	-1.62105	3.42436	2.61457
C	-2.57512	4.21325	1.96842
C	-2.87481	3.96740	0.62803
C	-2.22170	2.94115	-0.05841
C	-0.54673	0.95360	-1.81221
C	-1.49983	0.25216	-2.57011
C	-1.52293	0.31818	-3.96545
C	-0.58297	1.09473	-4.64356
C	0.37437	1.80353	-3.91460
C	0.38551	1.73258	-2.52112

C	3.01438	-0.14819	0.66561
C	3.55904	1.12081	0.92880
C	4.92374	1.26745	1.15806
C	5.76589	0.15415	1.11634
C	5.23629	-1.10929	0.84377
C	3.87052	-1.26182	0.62340
C	-1.32729	-2.70717	0.67857
C	-2.69244	-2.56675	0.98307
C	-3.47756	-3.68930	1.22796
C	-2.91634	-4.96646	1.16003
C	-1.56380	-5.11690	0.84553
C	-0.77242	-3.99634	0.61008
H	1.41796	-2.40536	0.62175
H	-4.52884	-3.56841	1.47039
H	-3.11751	-1.57106	1.02984
H	0.27098	-4.13195	0.34756
H	-1.12633	-6.10830	0.78023
H	-3.53083	-5.84209	1.34698
H	5.33173	2.25155	1.36701
H	2.89724	1.97840	0.95426
H	3.47993	-2.24718	0.39475
H	5.88868	-1.97587	0.79961

H	6.83140	0.27019	1.29094
H	-2.27266	-0.23821	-4.52257
H	-2.23672	-0.36256	-2.05880
H	1.13937	2.29012	-1.97015
H	1.11142	2.41168	-4.43317
H	-0.59558	1.14797	-5.72894
H	-1.37814	3.60959	3.65806
H	-0.23700	1.79638	2.43753
H	-2.45885	2.76854	-1.10477
H	-3.61340	4.57848	0.11531
H	-3.07763	5.01393	2.50481

Gemetry (Cartesian Coordinates) of 1b

C	-0.71410	-1.18371	0.33555
C	0.68723	-1.18371	0.33555
C	1.37167	0.03759	0.33555
O	0.74241	1.16352	0.18161
B	-0.71593	1.21488	-0.31717
O	-1.38376	-0.08336	0.16924
C	-1.45033	2.44992	0.40601
C	-0.96749	3.00663	1.60203
C	-1.63321	4.05036	2.24813
C	-2.81441	4.56368	1.71054

C	-3.31705	4.02796	0.52321
C	-2.63772	2.99041	-0.11712
C	-0.70252	1.24448	-1.93210
C	-1.37072	0.30220	-2.73039
C	-1.33873	0.36411	-4.12654
C	-0.62772	1.37970	-4.76459
C	0.04364	2.33362	-3.99529
C	-0.00100	2.26386	-2.60352
C	2.82441	0.14698	0.54121
C	3.46907	1.35918	0.24843
C	4.84118	1.51054	0.41805
C	5.60202	0.43549	0.89994
C	4.96967	-0.78210	1.20730
C	3.60486	-0.92052	1.02973
O	6.94225	0.46881	1.10658
C	7.64562	1.67342	0.82390
C	-1.52766	-2.38968	0.56258
C	-2.92802	-2.28376	0.54097
C	-3.74387	-3.39075	0.74797
C	-3.16257	-4.64536	0.98170
C	-1.76208	-4.76841	1.00794
C	-0.96233	-3.65855	0.80442

O	-3.85617	-5.79116	1.19359
C	-5.27868	-5.73876	1.18374
H	1.23465	-2.10749	0.42717
H	-4.81982	-3.26927	0.72493
H	-3.37195	-1.31192	0.36075
H	0.11384	-3.78501	0.83862
H	-1.33265	-5.74691	1.19323
H	5.30584	2.45758	0.17277
H	2.87653	2.18567	-0.12558
H	3.13795	-1.86190	1.29758
H	5.57475	-1.59641	1.59071
H	-1.86801	-0.38164	-4.71479
H	-1.93189	-0.49764	-2.25387
H	0.51618	3.02290	-2.02023
H	0.59630	3.13323	-4.48251
H	-0.59883	1.43143	-5.84980
H	-1.23097	4.46355	3.17006
H	-0.04741	2.61874	2.03201
H	-3.03271	2.59581	-1.05040
H	-4.23360	4.42432	0.09309
H	-3.33629	5.37607	2.20971
H	7.28480	2.50348	1.44286

H	8.68995	1.47170	1.06365
H	7.56283	1.94740	-0.23456
H	-5.66099	-5.40455	0.21196
H	-5.61535	-6.75836	1.37296
H	-5.66115	-5.07833	1.97094

Gemetry (Cartesian Coordinates) of 2a

C	-0.50818	-1.48469	0.65582
C	0.89142	-1.48469	0.65582
C	1.55923	-0.25327	0.65582
O	0.90732	0.85354	0.45084
B	-0.49367	0.83414	-0.11057
O	-1.17612	-0.38429	0.46426
C	-1.23201	2.19331	0.37459
C	-0.60044	3.42096	0.15777
C	-1.15365	4.64574	0.51756
C	-2.41152	4.67108	1.11365
C	-3.08715	3.47615	1.33520
C	-2.49593	2.26839	0.96272
C	-0.48818	0.68948	-1.74399
C	-1.70023	0.46555	-2.40348
C	-1.82094	0.36691	-3.78607
C	-0.68269	0.50382	-4.57627

C	0.54658	0.73547	-3.96905
C	0.62098	0.82541	-2.57914
C	2.99853	-0.09337	0.91750
C	3.60830	1.13760	0.61277
C	4.96955	1.31589	0.83685
C	5.73609	0.27628	1.36867
C	5.13662	-0.94658	1.68167
C	3.77616	-1.13206	1.45905
C	-1.33452	-2.68079	0.88968
C	-2.70204	-2.62896	0.56216
C	-3.50845	-3.74607	0.75533
C	-2.96605	-4.92106	1.28105
C	-1.61075	-4.97776	1.61704
C	-0.79806	-3.86545	1.42386
H	1.44009	-2.40760	0.75476
H	-4.56093	-3.70138	0.49370
H	-3.10641	-1.71256	0.14835
H	0.24665	-3.91295	1.71159
H	-1.19068	-5.88683	2.03584
H	-3.59805	-5.79113	1.43209
H	5.43493	2.26557	0.59256
H	3.00289	1.93138	0.19240

H	3.31697	-2.07680	1.72922
H	5.72895	-1.75167	2.10499
H	6.79865	0.41839	1.54204
F	-3.01163	0.14678	-4.36125
F	-2.83976	0.34197	-1.68584
F	1.85277	1.04275	-2.06948
F	1.64830	0.86483	-4.72227
F	-0.77148	0.41136	-5.90784
F	-0.49671	5.79259	0.29103
F	0.61074	3.45567	-0.44181
F	-3.21876	1.15930	1.20628
F	-4.30091	3.49306	1.90513
F	-2.96584	5.83662	1.46742

Gemetry (Cartesian Coordinates) of 2b

C	-0.67863	-1.20820	0.47188
C	0.72148	-1.20820	0.47188
C	1.39575	0.02014	0.47188
O	0.74118	1.13299	0.28012
B	-0.66092	1.12004	-0.26515
O	-1.34454	-0.09918	0.29365
C	-1.39306	2.47635	0.24850
C	-0.75894	3.70615	0.05321

C	-1.30416	4.92552	0.44306
C	-2.55695	4.94347	1.04957
C	-3.23522	3.74656	1.25076
C	-2.65195	2.54450	0.84814
C	-0.67486	1.00868	-1.90396
C	-1.89469	0.80506	-2.55533
C	-2.03055	0.73462	-3.93832
C	-0.90015	0.88048	-4.73788
C	0.33656	1.09216	-4.13886
C	0.42616	1.15402	-2.74818
C	2.82992	0.17578	0.71625
C	3.43705	1.41658	0.45303
C	4.79717	1.61091	0.66189
C	5.58341	0.55490	1.14814
C	4.98738	-0.69027	1.42225
C	3.63397	-0.87346	1.20902
O	6.91372	0.63111	1.38803
C	7.58577	1.86159	1.13724
C	-1.50539	-2.39646	0.69218
C	-2.88363	-2.32636	0.42184
C	-3.71068	-3.42791	0.60747
C	-3.16725	-4.63261	1.07974

C	-1.79035	-4.71486	1.35977
C	-0.97608	-3.61424	1.16854
O	-3.87672	-5.76460	1.29989
C	-5.27880	-5.75384	1.04935
H	1.26878	-2.13342	0.56551
H	-4.76697	-3.34252	0.38167
H	-3.29550	-1.39406	0.05188
H	0.07804	-3.69587	1.41281
H	-1.39396	-5.65330	1.73327
H	5.23538	2.57680	0.44035
H	2.82566	2.22548	0.07036
H	3.19358	-1.83588	1.44847
H	5.61239	-1.48914	1.80753
F	-3.22921	0.53314	-4.50546
F	-3.02822	0.67311	-1.82954
F	1.66494	1.35402	-2.24893
F	1.43153	1.23084	-4.90147
F	-1.00366	0.81602	-6.07078
F	-0.64317	6.07451	0.23625
F	0.44806	3.75078	-0.55473
F	-3.37926	1.43416	1.07460
F	-4.44484	3.75664	1.83110

F	-3.10436	6.10351	1.43315
H	7.18193	2.67031	1.75841
H	8.62954	1.68680	1.40146
H	7.51890	2.14392	0.07957
H	-5.49374	-5.54425	-0.00555
H	-5.63090	-6.75540	1.29978
H	-5.79094	-5.01762	1.68070

References

(1) Higashi, T. *ABSCOR. Program for Absorption Correction.*; Rigaku Corporation: Japan, 1995.

(2) Sheldrick, G. M. *SHELX-97. Programs for Crystal Structure Analysis*; University of Göttingen: Germany, 1997.

(3) Altomare, A.: Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliteri, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst*. **1999**, 32, 115.

(4) Wakita, Y. *Yadokari-XG. Program for Crystal Structure Analysis.*; 2000.

(5) Farrugia, L. *J. Appl. Cryst.* **1997**, *30*, 565.

(6) a) Yoshio, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559. (b) Duchateau, R.; Lancaster, S. J.; Thornton-Pett, M.; Bochamnn, M. *Organometallics*, **1997**, *16*, 4995.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. ; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y. ; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford CT, 2004.