Electronic Supporting Information B911982E

Spirocyclic Boronium Ions: Precursors to Persistent Neutral Radicals.

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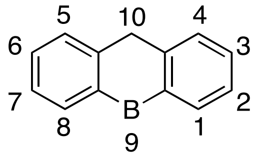
Experimental Details

General Considerations

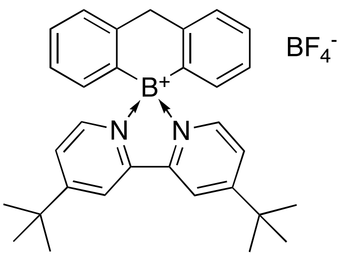
All solvents were purified before use. Dichloromethane and toluene were dried over CaH_2 and freshly distilled before use. Tetrahydrofuran, diethyl ether, and bromobenzene were distilled from sodium benzophenone. Commercially available compounds, (Aldrich), were purified by conventional means prior to use. Flash chromatography was carried out on SiliCycle Silia-P Flash Silica Gel (Ultra Pure Silica Gel) 40-63μm. Reactions were carried out under an inert argon atmosphere in a glove box or on a double manifold.

Instrumentation

Unless otherwise noted nuclear magnetic resonance spectroscopy ^{1}H, ^{11}B, ^{13}C and ^{19}F were preformed on a Bruker DRX-400 at 298K (^{1}H, 400.1 MHz; ^{11}B, 96.3 MHz; ^{13}C, 75.5 MHz; ^{19}F, 376.5 MHz). Chemical shifts are calibrated to the residual carbon and proton resonances of the solvent relative to $SiMe_4$ (δ 0.00 ppm), (^{1}H, δ 7.27; 13C, δ 77.23). ^{11}B NMR spectra were referenced relative to and external sample of BF_3OEt_2 (C_6D_6) (δ 0.0 ppm). Unambiguous spectral assignments were made when possible with the aid of 2D experiments including COSY, NOESY, HMBC, and HMQC in addition to DEPT 135. X-Ray crystallography was carried out on a Nonius Kappa CCD diffractometer (Dr. Masood Parvez, University of Calgary). EPR measurements were made on a Bruker EMX10/12, equipped with VT capabilities. DFT calculations were carried out using Gaussian 03.[i] The IUPAC numbering scheme for anthracene is in employed throughout:



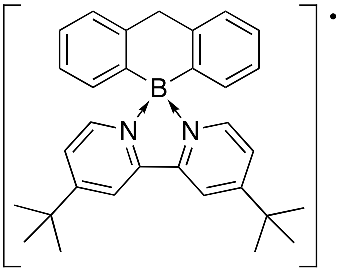
Synthesis of 9-bora-9-(4,4'-di-*tert*-butyl-2-2'-dipyridyl)-9,10-dihydroanthracene tetrafluoroborate, 1-^{t}Bu.



9-bora-9-chloro-9,10-dihydroanthracene (323 mg, 1.52 mmol) and 4,4'-di-*tert*-butyl-2-2'-dipyridyl (428 mg, 1.59 mmol) were placed in a flask and THF (30 mL) was added. The solids dissolved and after 15 minutes a very fine precipitate began to form. To this was added $AgBF_4$ (310 mg, 1.59 mmol) and the reaction was left to stir for several hours. The solution was filtered through a 0.2μm PTFE filter to give a pale amber liquid. Concentration of this liquid afforded 898 mg of off white solid which was pure enough for most applications. Material of analytical purity was obtained by, dissolved the white solid in a minimum volume of dichloromethane and cooling to -35°. The mother liquor was freed of solids and concentrated in vacuo to give a tacky material, which after sonicating in benzene gave a white solid 425 mg (53%). ^{1}H NMR (Bruker Advance 400 MHz, $CDCl_3$): δ = 9.33 (s, 2H, *m*-bipy), 8.05 (d, $^3J_{HH}$ = 6 Hz, 2H, *o*-bipy), 7.78 (d, $^3J_{HH}$ = 16 Hz, 2H, *m*-bipy), 7.48 (d, $^3J_{HH}$ = 7.6 Hz, 2H, $\mathbf{H}^{4,5}$), 7.35 (t, $^3J_{HH}$ = 6.4 Hz, 2H, $\mathbf{H}^{3,6}$), 7.08 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $\mathbf{H}^{2,7}$), 6.49 (d, $^3J_{HH}$ = 7.2 Hz, 2H, $\mathbf{H}^{1,8}$), 4.56 (s, 2H, $C\mathbf{H}_2$), 1.55 (s, 18H, *t*-Bu); $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$): δ = 5.5 (br, antrhr**B**bipy), -1 (s, $\mathbf{B}F_4$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 171.9, 146.5, 142.9, 142.6 ($\mathbf{C}^{m\text{-H(doublet)}}$), 130.8 ($\mathbf{C}^{1,8}$), 129.0 ($\mathbf{C}^{3,6}$), 128.6 ($\mathbf{C}^{4,5}$), 126.7 ($\mathbf{C}^{2,7}$), 125.8 ($\mathbf{C}^{o\text{-H}}$), 122.0 ($\mathbf{C}^{m\text{-H(singlet)}}$), 38.5 ($C\mathbf{H}_2$) 37.4 ($\mathbf{C}(CH_3)_3$), 30.4 ($C(\mathbf{C}H_3)_3$); $^{19}F\{^1H\}$ NMR (376.6, $CDCl_3$): δ = 151 ($B\mathbf{F}_4$); LRMS (EI): 444.2 (M^+-BF_4, 41%), 253 (100%); HRMS (EI): calculated for $C_{31}H_{34}BN_2$ (M^+-BF_4) 445.2815, found 445.2818; EA Calculated (C 69.96, H 6.44, N 5.26), found (C 68.97, H 6.55, N 5.09).

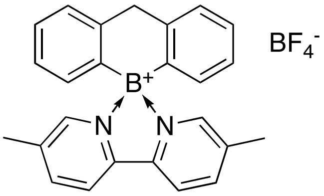
9-bora-9-(4,4'-di-*tert*-butyl-2-2'-dipyridyl)-9,10-dihydroanthracene radical, 2-^{t}Bu.

9-bora-9-(4,4'-di-*tert*-butyl-2-2'-dipyridyl)-9,10-dihydroanthracene tetrafluoroborate (340 mg, 0.6 mmol) was dissolved in THF (30 mL) and using a solid addition tube KC_8



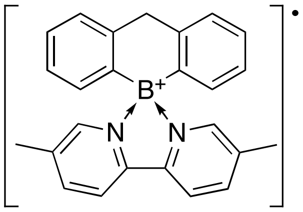
(86 mg) was slowly added. After 30 minutes the graphite was removed via filtration and all volatiles were removed in vacuo to give a dark solid. The solid residue was dissolved in toluene and filtered. Concentration of the toluene afforded a dark NMR silent powder, 206 mg (77%). HRMS (EI): calculated for $C_{31}H_{34}BN_2$ (M^+) 445.2815, found 445.2799; EA calculated (C 83.59, H 7.69, N 6.29), found (C 82.45, H 7.60, N 5.95).

9-bora-9-(5,5’-dimethyl-2-2’-dipyridyl)-9,10-dihydroanthracene tetrafluoroborate, 1-Me.



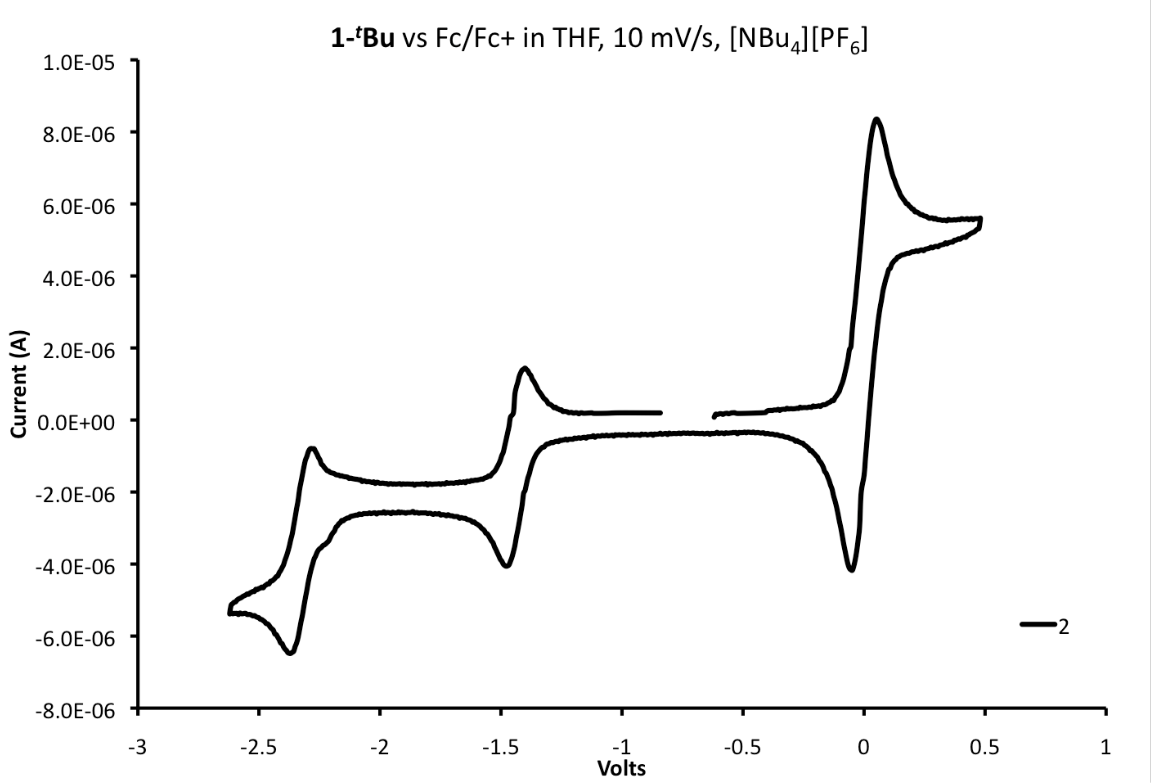
9-bora-9-chloro-9,10-dihydroanthracene (126 mg, 0.6mmol) and 5,5’-dimethyl-2-2’-dipyridyl (110 mg, 0.6 mmol) were placed in a flask and THF (30 mL) was added. The solids dissolved and after 15 minutes a very fine precipitate began to form. To this was added $AgBF_4$ (128 mg, 0.66 mmol) and the reaction was left to stir for several hours. The solution was filtered through a 0.2μm PTFE filter to give a pale amber liquid. Concentration of this liquid afforded 220 mg of off white solid. The crude material was dissolved in a minimum volume of dichloromethane and cooled to -35° to a white solid, 190 mg (66%). ^1H NMR (Bruker Advance 400 MHz, $CDCl_3$): $\delta = 9.14$ (d, $^3J_{HH} = 8Hz$, 2H, *m*-bipy), 8.48 (d, $^3J_{HH} = 8Hz$, 2H, *p*-bipy), 7.92 (s, 2H, *o*-bipy), 7.51 (d, $^3J_{HH} = 8Hz$, $\mathbf{H}^{4,5}$), 7.37 (t, $^3J_{HH} = 8Hz$, $\mathbf{H}^{3,6}$), 7.10 (t, $^3J_{HH} = 8Hz$, $\mathbf{H}^{2,7}$), 6.48 (d, $^3J_{HH} = 8Hz$, $\mathbf{H}^{1,8}$), 4.59 (s, 2H, $C\mathbf{H}_2$), 2.48 (s, 6H, $C\mathbf{H}_3$); $^{11}B\{^1H\}$ NMR (128.4 MHz, $CDCl_3$): $\delta = 5$ (br, antrhra**B**bipy), -1 (s, $\mathbf{B}F_4$); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 171.9$, 146.2 ($\mathbf{C}^{p\text{-H}}$), 144.17, 142.8, 142.7 ($\mathbf{C}^{o\text{-H}}$), 130.9 ($\mathbf{C}^{1,8}$), 129.3 ($\mathbf{C}^{3,6}$), 128.7 ($\mathbf{C}^{4,5}$), 127.0 ($\mathbf{C}^{2,7}$), 123.6 ($\mathbf{C}^{m\text{-H}}$), 38.5 ($C\mathbf{H}_2$) 19.0 ($\mathbf{C}H_3$); $^{19}F\{^1H\}$ NMR (376.6, $CDCl_3$): $\delta = 152$ ($B\mathbf{F}_4$); LRMS (EI): 361(M^+-BF_4, 90%), 360 (100%), 195(; HRMS (EI): calculated for $C_{25}H_{22}B_2N_2$, 361.1876, found 361.1864; EA $C_{25}H_{22}B_2F_4N_2{\bullet}CH_2Cl_2$ Calculated (C 58.59, H 4.54, N 5.26), found (C 58.82, H 4.82, N5.15).

9-bora-9-(5,5'-dimethyl-2-2'-dipyridyl)-9,10-dihydroanthracene radical, 2-Me.



9-bora-9-(5,5'-di-methyl-2-2'-dipyridyl)-9,10-dihydroanthracene tetrafluoroborate (180 mg, 0.4 mmol) was dissolved in THF (20 mL) and using a solid addition tube KC_8 (63 mg) was slowly added. After 30 minutes the graphite was removed via filtration and all volatiles were removed in vacuo to give a dark solid. The solid residue was dissolved in toluene, filtered, and evaporated to dryness. The remaining dark solids were layered with pentane and under sonication evaporated to dryness. This afforded a dark NMR silent powder, 90 mg (64%). LRMS (EI): 360.1 (M^+-BF_4, 100%); HRMS (EI): calculated for $C_{25}H_{22}BN_2$ (M^+) 361.1876, found 361.1875.

Cyclic Voltammetry



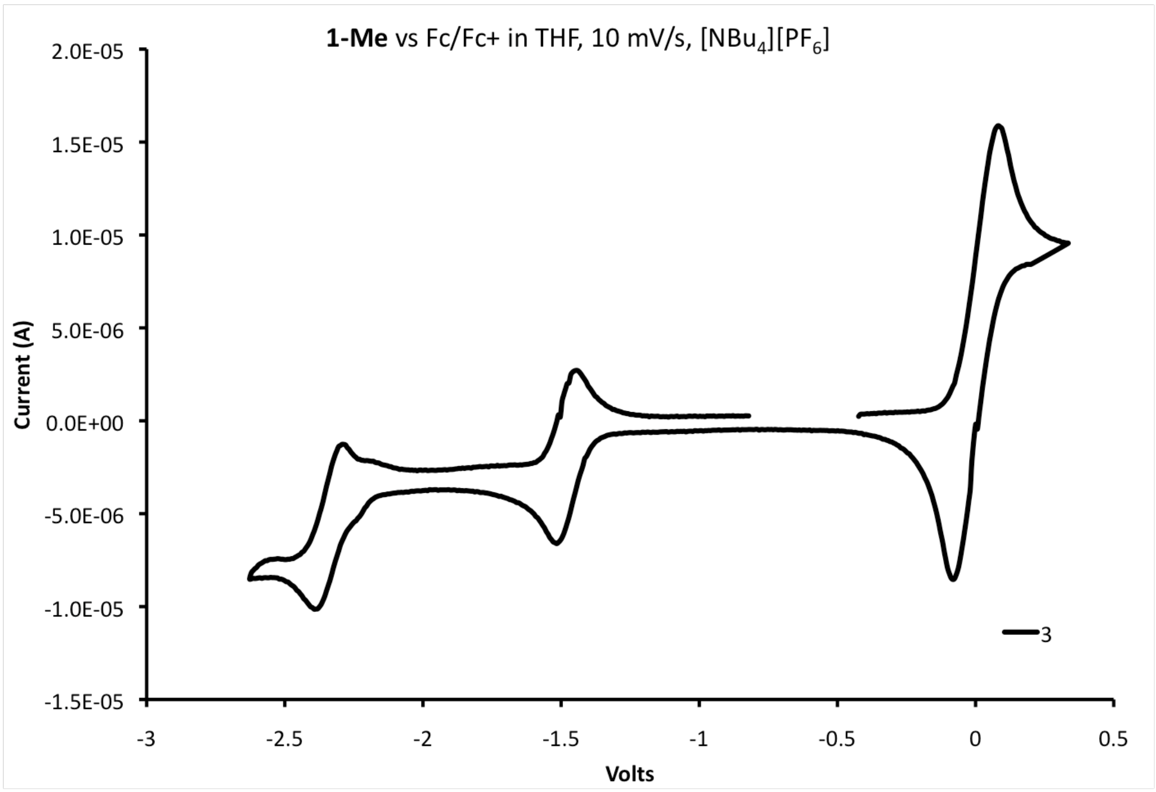


Table S1: Voltammetry summary (Volts).

Species	Radical[a]	Anion
1-^{t}Bu	-1.45 (**2-^{t}Bu**)	-2.31
1-Me	-1.50 (**2-Me**)	-2.35

[a] Test substrate 1 mM in 0.1 M [NBu_4][PF_6] THF solution; voltages reported against an internal standard of ferrocene/ferrocenium; Pt disc working electrode, Ag wire pseudo reference.

EPR Simulation

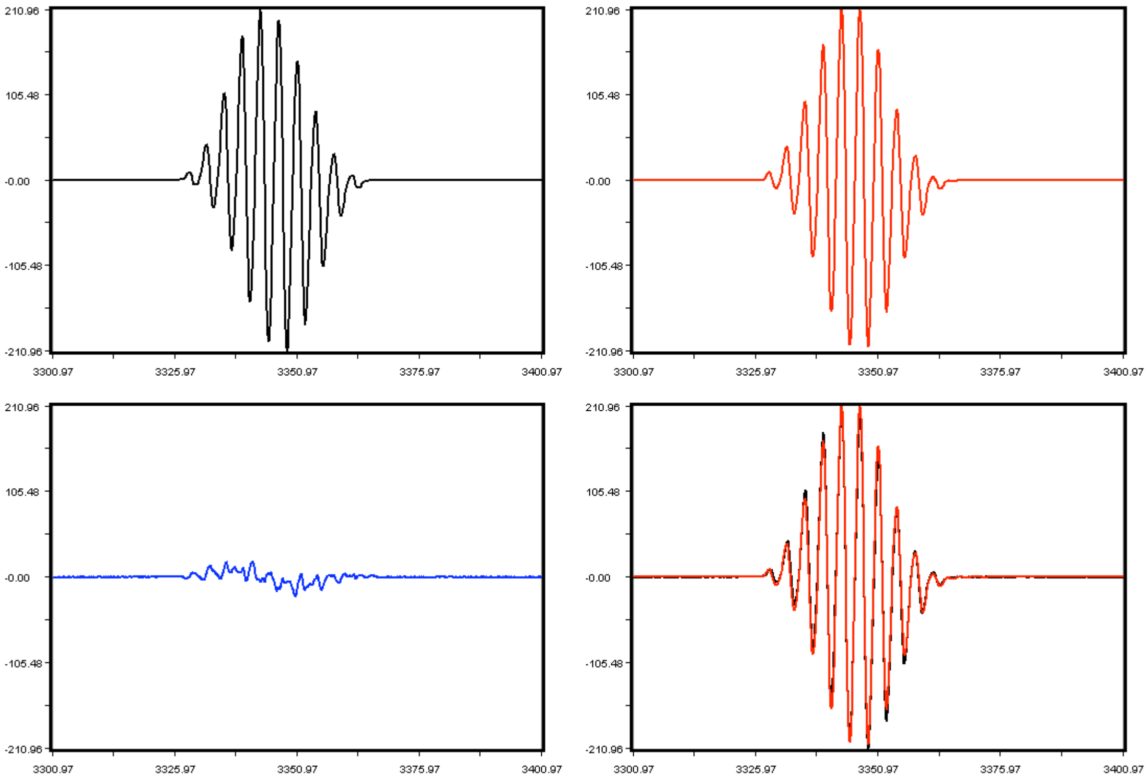
The HFCCs were calculated using DTF on molecular structures of **2-^{t}Bu** and **2-Me** which were optimized at the same level of theory, UB3LYP/6-31+G(d) (see below for atomic coordinates).[i] Using the calculated values as a starting point, the simulation was modified by hand until the goodness of fit (GOF) between experimental and simulation exceeded 95%. At this time the programs downhill simplex algorithm was utilized to arrive at the simulated values whose GOF are in excess of 99%.[ii]

Table S2: Calculated and simulated HFCCs (Gauss)

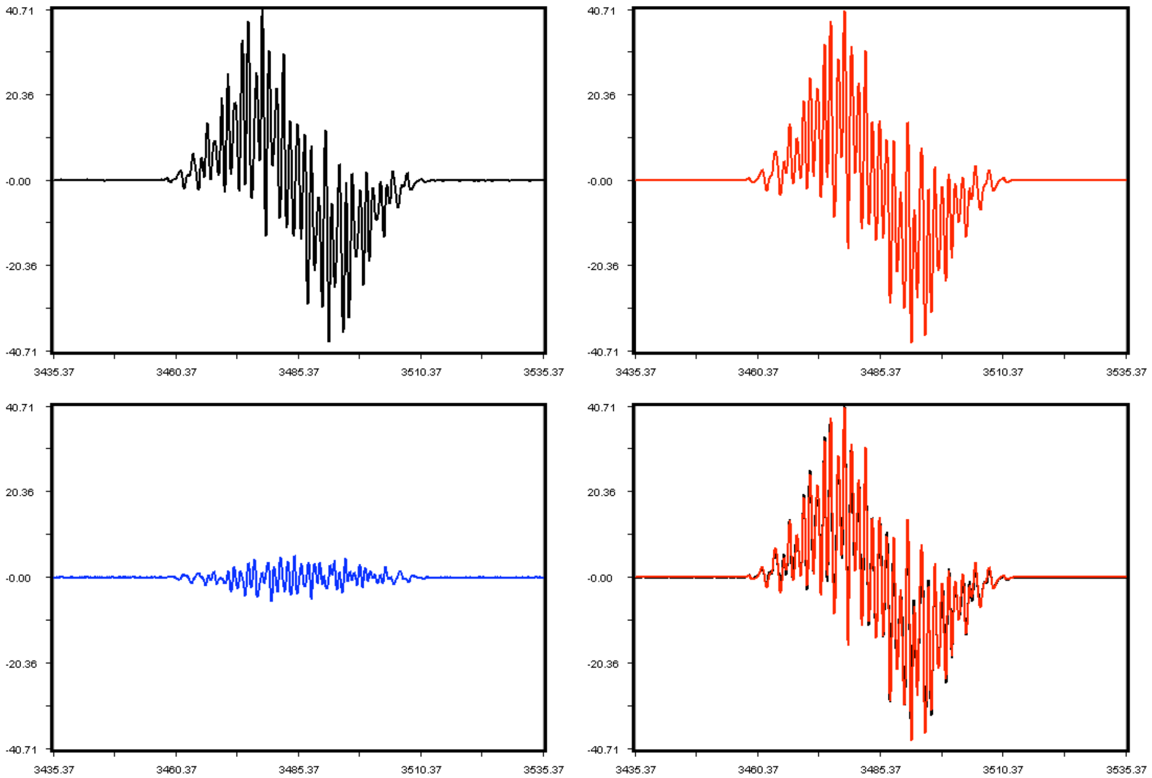
	2-^{t}Bu		**2-Me**	
Nuc.	Calc.[a]	Simulated [b]	Calc.[b]	Simulated [b]
$^{11}B_{.8}$	-3.789	3.891	-4.233	4.358
$^{10}B_{.2}$	-	1.213	-	1.250
$^{14}N_2$	3.451	3.576	3.867	4.105
$^{1}H_2$	-3.769	3.667	-2.522	2.341
$^{1}H_2$	-0.845	0.845	-0.132	0.145
$^{1}H_2$	0.451	0.451	-0.088	0.089
$^{1}H_n$[c]	0.241	0.237	3.371	2.940

[a] Geometries were optimized in the gas phase using UB3LYP/6-31+G(d), hyperfine coupling constants calculated using the same method/basis set, sign of coupling shown. [b] Simulated using Winsim2002 to > 99% correlation. [c] n = 18 for **2-^{t}Bu**; n = 6 for **2-Me**.

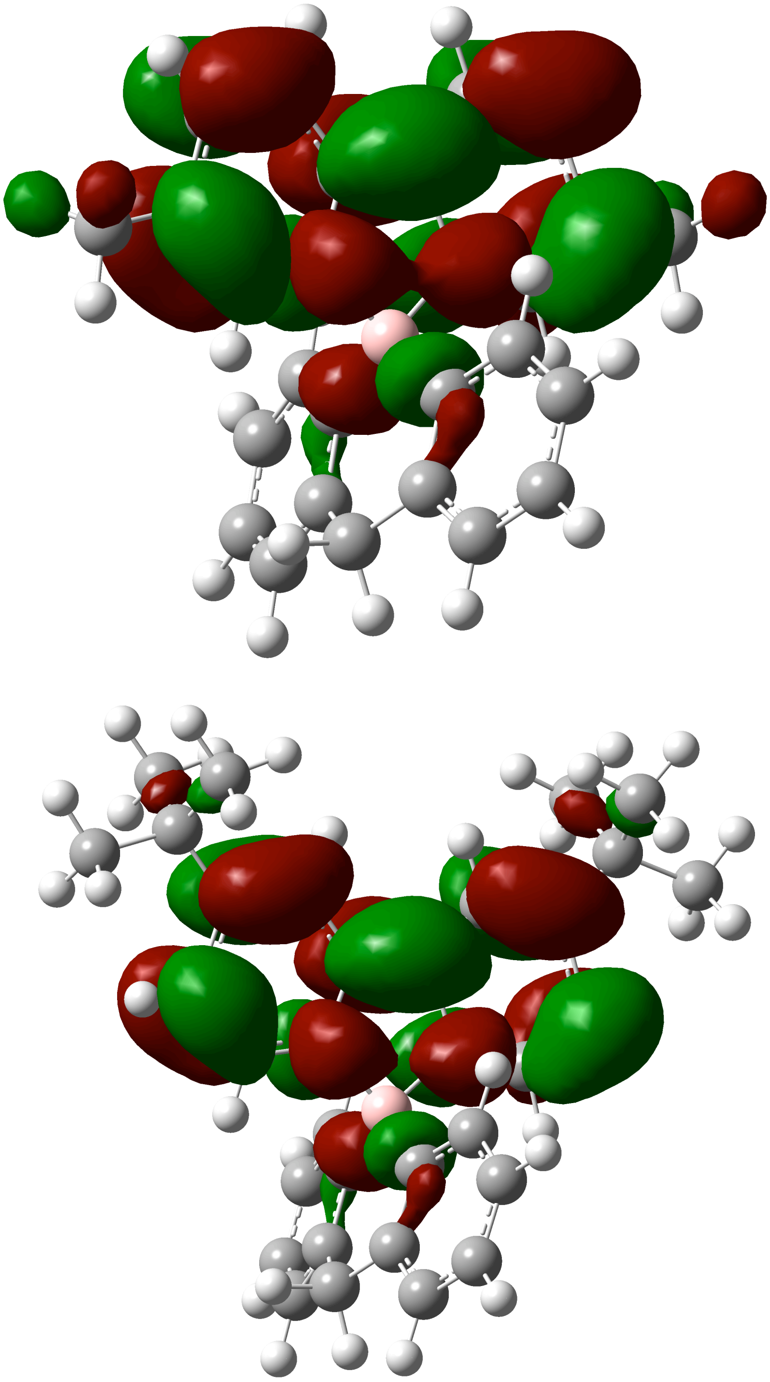
EPR of **2-^{t}Bu**. Clockwise from top left: experimental, simulated, residual, experimental & simulated overlay.



EPR of **2-Me**. Clockwise from top left: experimental, simulated, residual, experimental & simulated.



SOMO of **2-Me** (top) and **2-tBu** (bottom) showing the majority of the spin density on the bipyridyl framework, UB3LYP/6-31+G(d).



Optimized Structures of 2 (UB3LYP/6-31+G(d))—coordinates.

2-Me

N	0.342584	1.384294	-0.258417
N	-1.485995	-0.062504	0.081271
B	0.098154	-0.170500	0.040427
C	1.532279	2.007635	-0.420213
H	2.408809	1.372030	-0.335555
C	1.639313	3.359122	-0.675964
C	0.421092	4.104947	-0.767997
H	0.463272	5.172899	-0.968461
C	-0.797847	3.485345	-0.605771
H	-1.723620	4.049028	-0.675130
C	-0.842969	2.098372	-0.345797
C	-1.942974	1.229301	-0.141690
C	-3.332015	1.481808	-0.135308
H	-3.694661	2.490711	-0.309198
C	-4.208637	0.444466	0.091528
H	-5.279725	0.632005	0.097793
C	-3.726612	-0.885626	0.320648
C	-2.361023	-1.073212	0.303092
H	-1.91292	-2.048721	0.467522
C	2.977682	4.028856	-0.852123
H	3.799043	3.311734	-0.750085
H	3.131769	4.820483	-0.106411
H	3.065119	4.497211	-1.841822
C	-4.680005	-2.025618	0.569471
H	-4.143342	-2.967366	0.724915
H	-5.365403	-2.167738	-0.277133
H	-5.299742	-1.843894	1.458063
C	0.715730	-0.617191	1.463760
C	0.145857	-0.190333	2.679704
H	-0.733537	0.451747	2.654941
C	0.666747	-0.566955	3.917221
H	0.201303	-0.220425	4.837375
C	1.789796	-1.400293	3.964305
H	2.204622	-1.711822	4.920319
C	2.371139	-1.836291	2.774852
H	3.242289	-2.489522	2.810467
C	1.849096	-1.451729	1.527720
C	2.559051	-1.924376	0.272226
H	2.964206	-2.93052	0.443926

H	3.448481	-1.288534	0.119655
C	1.751360	-1.924633	-1.012813
C	2.184625	-2.738785	-2.073564
H	3.059686	-3.373145	-1.936680
C	1.510578	-2.751313	-3.293546
H	1.857539	-3.391236	-4.101760
C	0.382691	-1.941300	-3.465763
H	-0.154559	-1.942153	-4.411684
C	-0.050026	-1.138021	-2.411193
H	-0.933958	-0.517852	-2.553556
C	0.614427	-1.107283	-1.169002

2-^{t}Bu

N	0.486515	1.085804	0.000101
N	0.053808	-1.227778	-0.000080
B	1.326248	-0.277884	0.000052
C	0.956638	2.346553	0.000203
H	2.037475	2.448851	0.000252
C	0.122730	3.444799	0.000239
C	-1.298547	3.267777	0.000179
C	-1.771570	1.965987	0.000063
H	-2.838111	1.763119	-0.000010
C	-0.886063	0.866113	0.000024
C	-1.147460	-0.525573	-0.000088
C	-2.370980	-1.231329	-0.000193
H	-3.292391	-0.656491	-0.000198
C	-2.400469	-2.615786	-0.000291
C	-1.137662	-3.295575	-0.000287
C	0.036790	-2.575403	-0.000181
H	1.008548	-3.059532	-0.000172
C	2.211052	-0.443585	1.340122
C	1.614164	-0.697950	2.590936
H	0.530576	-0.789350	2.651058
C	2.365033	-0.842820	3.757115
H	1.872080	-1.039935	4.706623
C	3.758967	-0.739006	3.693295
H	4.361754	-0.858132	4.590825
C	4.372915	-0.489216	2.467177
H	5.458528	-0.414211	2.415470
C	3.615332	-0.337657	1.292985
C	4.345228	-0.022048	0.000237
H	5.316524	-0.534432	0.000254

H	4.597301	1.052651	0.000327
C	3.615474	-0.337474	-1.292635
C	4.373188	-0.488864	-2.466764
H	5.458794	-0.413864	-2.414926
C	3.759376	-0.738480	-3.692987
H	4.362263	-0.857477	-4.590467
C	2.365450	-0.842288	-3.756976
H	1.872602	-1.039268	-4.706566
C	1.614450	-0.697584	-2.590860
H	0.530869	-0.788976	-2.651116
C	2.211199	-0.443398	-1.339943
H	-1.077206	-4.375698	-0.000364
H	0.569866	4.429917	0.000321
C	-2.279327	4.454769	0.000157
C	-3.743222	-3.369796	-0.000409
C	-3.553658	-4.899485	-0.000463
H	-3.012537	-5.244977	-0.889118
H	-3.012716	-5.245057	0.888269
H	-4.533811	-5.390392	-0.000586
C	-1.552277	5.814169	0.000306
H	-0.923387	5.942605	0.889109
H	-0.923355	5.942800	-0.888444
H	-2.290787	6.624361	0.000374
C	-4.552177	-2.984555	-1.263287
H	-5.512364	-3.515804	-1.275544
H	-4.764628	-1.910516	-1.299395
H	-4.005383	-3.248864	-2.176064
C	-3.172437	4.386718	-1.262933
H	-3.759357	3.462489	-1.298267
H	-3.875085	5.229551	-1.276007
H	-2.566838	4.434044	-2.175573
C	-4.552336	-2.984669	1.262405
H	-5.512544	-3.515884	1.274470
H	-4.005674	-3.249101	2.175224
H	-4.764755	-1.910627	1.298605
C	-3.172708	4.386614	1.263049
H	-3.759672	3.462407	1.298185
H	-2.567303	4.433846	2.175821
H	-3.875338	5.229462	1.276043

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[i] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[ii] P.E.S.T. Winsim V.1.0, 2002; National Institute of Environmental Health Sciences National Institutes of Health, USA. http://epr.niehs.nis.gov/