Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

An air-stable *N*-heterocyclic carbene iminoxyl borate radical zwitterion

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Materials and Methods

1. General methods

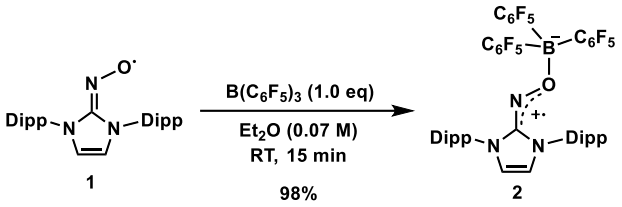
All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred. All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen.

2. Reagents

*I*PrNO (**1**) was synthesized according to a reference.[1] Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), trityl tetrakis(pentafluorophenyl)borate ($Ph_3C^+B(C_6F_5)_4^-$) and all other chemicals were purchased from commercial sources and used as received unless otherwise specified. 3Å molecular sieves were activated at 240 ˚C under dynamic vacuum for overnight prior to use. Diethyl ether, pentane, benzene, and tetrahydrofuran (THF) were distilled from deep purple sodium benzophenone ketyl, and stored over 3Å molecular sieves.

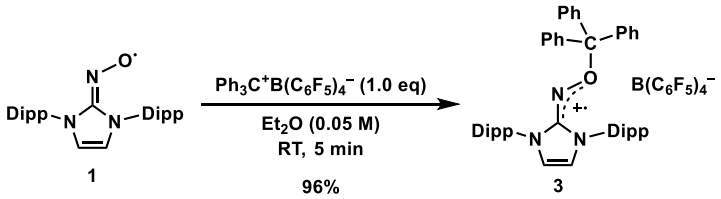
Experimental Details

Synthesis of 2



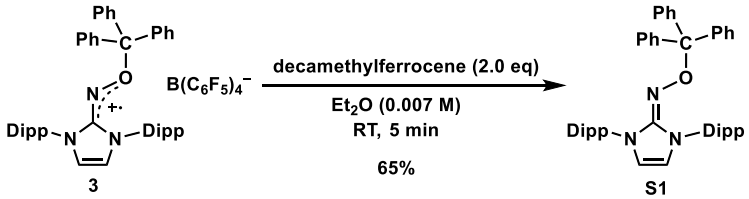
In a N_2 atmosphere glovebox, *I*PrNO (**1**, 60 mg, 0.14 mmol) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, 73 mg, 0.14 mmol) were placed in a 4 mL vial and subsequently dry diethyl ether (2 mL) was added to the vial. The solution became dark brown immediately. After 15 minutes, the reaction mixture was dried *in vacuo*, and the resulting dark brown solid was washed with dry pentane (1 × 0.5 mL) to afford 131 mg of the product (98%). Single crystals suitable for X-ray crystallography were obtained from recrystallization using pentane. Anal. Calcd for $C_{45}H_{36}N_3OBF_{15}$: C, 58.08; H, 3.90; N, 4.52. Found: C, 56.98; H, 3.78; N, 4.45.

Synthesis of 3



In a N_2 atmosphere glovebox, *I*PrNO (**1**, 20 mg, 0.048 mmol) and trityl tetrakis(pentafluorophenyl)borate ($Ph_3C^+B(C_6F_5)_4^-$, 44 mg, 0.048 mmol) were placed in a 4 mL vial and subsequently dry diethyl ether (1 mL) was added to the vial. The solution became dark brown immediately. After 5 minutes, dry pentane (3 mL) were added into the mixture to solidify the product. After 1 minute of sonication, the solution was decanted, and the remaining solid was dried *in vacuo* to afford 62 mg of the product as a dark brown solid (96%). Single crystals suitable for X-ray crystallography were obtained by layering dry pentane over the crude reaction mixture. Anal. Calcd for $C_{70}H_{51}N_3OBF_{20}$: C, 62.70; H, 3.83; N, 3.13. Found: C, 61.85; H, 3.71; N, 3.52. HRMS (FAB): m/z calcd for $[C_{46}H_{52}N_3O\ (M + H)^+]$ 662.4105, found 662.4107.

Reduction of 3



In a N_2 atmosphere glovebox, **3** (5.0 mg, 3.7 μmol) and decamethylferrocene (2.4 mg, 7.5 μmol)

were placed in a 4 mL vial and subsequently dry diethyl ether (0.5 mL) was added to the vial. Green solid was precipitated during the reaction. After 5 minutes, the reaction mixture was dried *in vacuo* and dissolved in dry pentane (0.5 mL). The mixture was filtered through a thin pad of dry Celite and eluted using dry pentane (2 × 0.5 mL). The filtrate was dried *in vacuo* and analyzed with ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard. ^{1}H NMR yield 65%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.96 (6 H, d, J = 6.9 Hz), 1.13 (6 H, d, J = 6.9 Hz), 1.20 (6 H, d, J = 6.9 Hz), 1.21 (6 H, d, J = 6.9 Hz), 3.08 (2 H, sept, J = 6.9 Hz), 3.41 (2 H, sept, J = 6.9 Hz), 5.71 (1 H, d, J = 2.6 Hz), 5.76 (1 H, d, J = 2.6 Hz), 6.97–7.04 (17 H, m), 7.13 (1 H, t, J = 7.7 Hz), 7.19 (2 H, d, J = 7.8 Hz), 7.36 (1 H, t, J = 7.7 Hz) ppm. ESI-MS: m/z calcd for [$C_{46}H_{52}N_3O$ $(M + H)^+$] 662.41, found 662.42.

X-ray Crystallography

CCDC 1823243 and CCDC 1823244 contains the supplementary crystallographic data for **2** and **3**, respectively. These data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

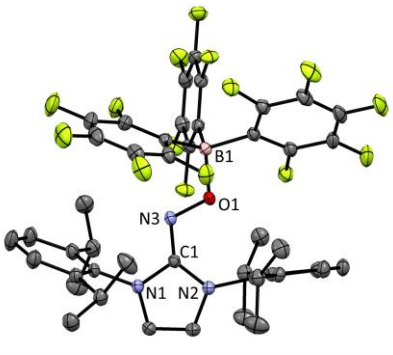
General information

A suitable crystal was coated with paratone-*N* oil and the diffraction data measured at 100 K either with synchrotron radiation on a 2D beamline at the Pohang Accelerator Laboratory, Korea. Using Olex2[2], The structure was solved by ShelXT[3] using Intrinsic Phasing and refined by ShelXL[4] using Least Squares minimization. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added to their geometrically ideal positions.

Crystal data and structure refinements

	2	**3**
Empirical formula	$C_{50}H_{48}BF_{15}N_3O$	$C_{70}H_{51}BF_{20}N_3O$
Formula weight	1002.72	1340.95
Temperature/K	100.0	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	14.812(3)	18.811(4)
b/Å	20.438(4)	12.397(3)
c/Å	15.737(3)	27.524(6)
α/°	90	90
β/°	94.18(3)	107.76(3)
γ/°	90	90
Volume/Å^3	4751.4(17)	6113(2)
Z	4	4
ρ_{calc}g/cm^3	1.402	1.457
μ/mm^{-1}	0.120	0.124
F(000)	2068.0	2740.0
Crystal size/mm^3	0.06 × 0.04 × 0.01	0.06 × 0.04 × 0.04
Radiation	synchrotron (λ = 0.700)	Synchrotron (λ = 0.700)
2Θ range for data collection/°	3.222 to 58.184	3.966 to 59.08
Index ranges	$-20 \le h \le 20$, $-28 \le k \le 28$, $-21 \le l \le 21$	$-25 \le h \le 25$, $-17 \le k \le 17$, $-38 \le l \le 38$
Reflections collected	34273	15989
Independent reflections	12560 [R_{int} = 0.0351, R_{sigma} = 0.0372]	15989 [R_{int} = 0.023, R_{sigma} = 0.0213]
Data/restraints/parameters	12560/0/641	15989/0/864
Goodness-of-fit on F^2	1.087	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1699	R_1 = 0.0450, wR_2 = 0.1326
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1788	R_1 = 0.0479, wR_2 = 0.1354

Selected structural data



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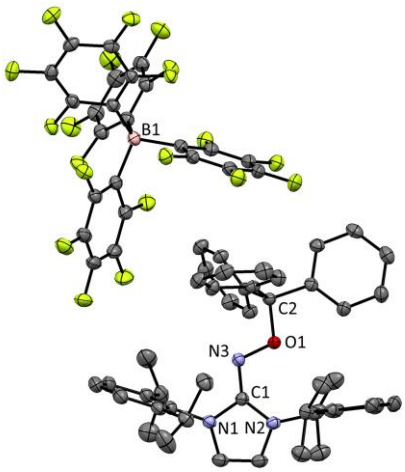


3

Table S1. Selected bond lengths (Å) and angles (°).

	2	**3**		**2**	**3**
C1–N1	1.367(2)	1.364(1)	N1–C1–N2	106.9(1)	107.70(9)
C1–N2	1.363(2)	1.361(1)	N2–C1–N3	134.0(1)	133.08(9)
C1–N3	1.339(2)	1.339(1)	N3–C1–N1	119.1(1)	119.18(9)
N3–O1	1.344(2)	1.361(1)	C1–N3–O1	111.5(1)	109.96(8)
O1–B1	1.536(2)	–	N3–O1–B1	112.4(1)	109.59(8)
O1–C2	–	1.497(1)	N3–O1–C2	–	–

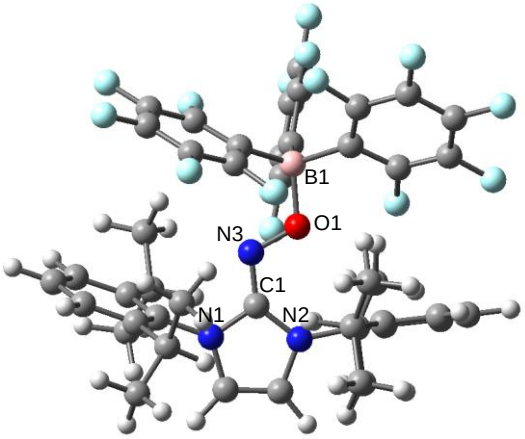
The thermal ellipsoids are set at a 50% probability level. A pentane molecule (in **2**) and hydrogen atoms were omitted for clarity.

DFT Calculation

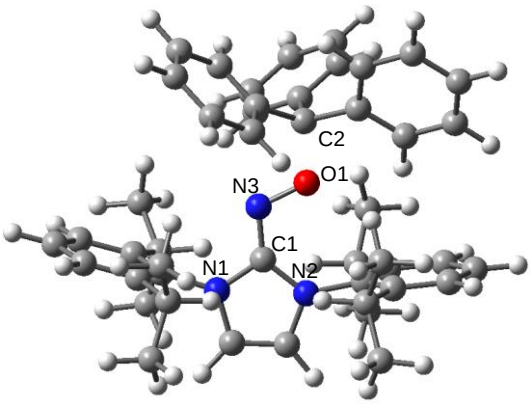
General information

Both geometry optimizations and frequency calculations were performed using Gaussian09 with B3LYP/6-31G(*d*, *p*) basis set.[5] In the geometry optimization, the default tight convergence in the SCF cycle was used without any orbital symmetry constraints. Solvation free energies were computed on gas phase-optimized geometries using SMD model.[6] Molecular orbitals were generated from the optimized geometry (B3LYP/6-31G(*d*, *p*)) using Multiwfn.[7] Wiberg bond indices (WBIs) were calculated from the optimized geometry with Löwdin orthogonalization method using Multiwfn. Spin density was calculated from the optimized geometry using natural bond orbital (NBO) method.

Metric comparison between DFT optimized and X-ray determined structures



2

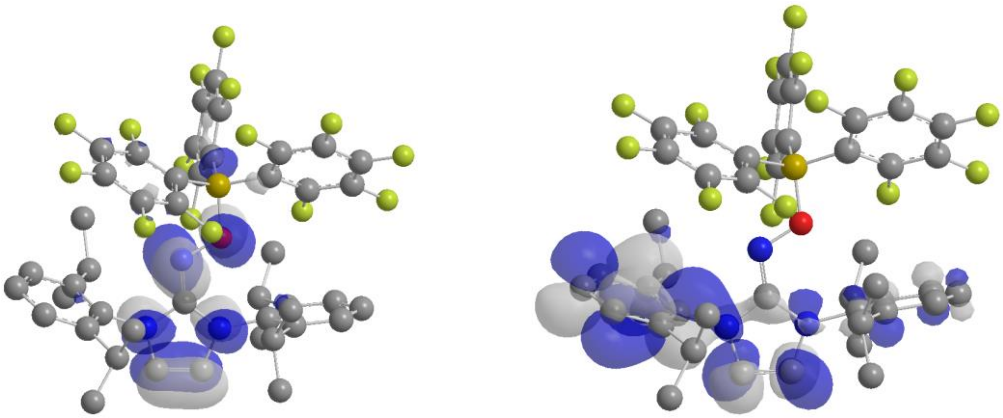


3

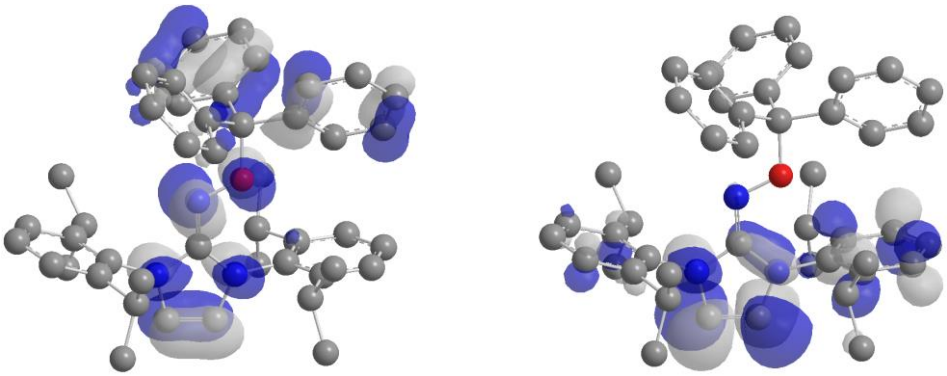
Bond length (Å)		C1–N1	C1–N2	C1–N3	N3–O1	O1–B1	O1–C2
2	**DFT**	1.37	1.37	1.34	1.32	1.56	–
	X-ray	1.37	1.36	1.34	1.34	1.54	–
3	**DFT**	1.38	1.38	1.34	1.34	–	1.54
	X-ray	1.36	1.36	1.34	1.36	–	1.50
Bond angle (°)		N1–C1–N2	N2–C1–N3	N3–C1–N1	C1–N3–O1	N3–O1–B1	N3–O1–C2
2	**DFT**	107.2	134.1	118.6	113.0	115.0	–
	X-ray	106.9	134.0	119.1	111.5	112.4	–
3	**DFT**	107.0	133.4	119.6	112.2	–	113.9
	X-ray	107.7	133.1	119.2	110.0	–	109.6

Molecular orbital

Only for cations; isosurface value = 0.03 a.u.; hydrogen atoms are omitted for clarity.



SOMO of **2** LUMO of **2**

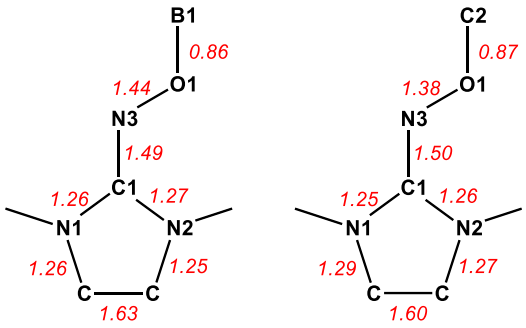


SOMO of **3** LUMO of **3**

Figure S1. SOMO and LUMOs of the radicals **2** and **3**.

Wiberg bond index

Selected WBIs are shown below:



2 **3**

Dissociation energy

The bond dissociation energies of the adducts with electron withdrawing C_6F_5 groups are much higher than the adducts with phenyl groups. $B(C_6F_5)_3$ and $C(C_6F_5)_3$ binds much stronger to oxygen atom than BPh_3 and CPh_3, because the electron withdrawing power of perfluorinated groups makes them more electrophilic.

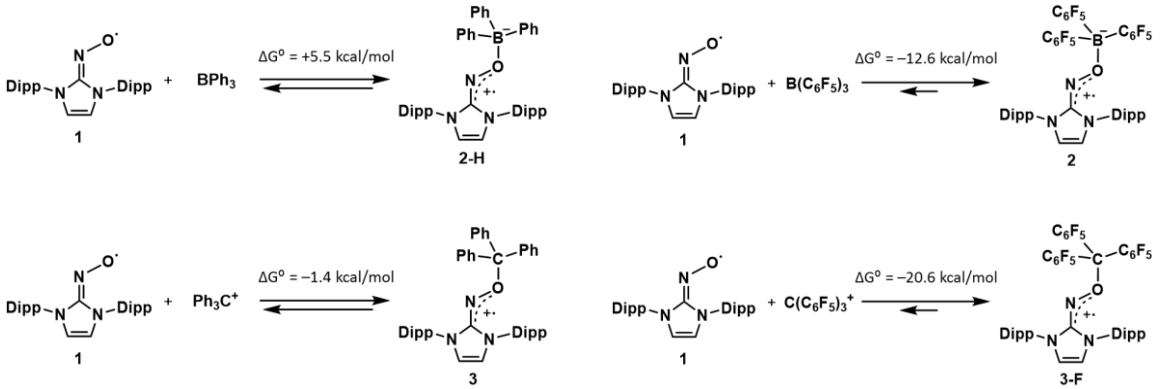
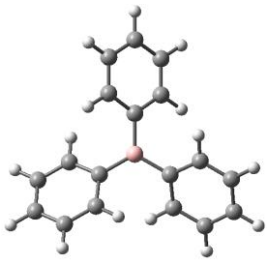


Figure S2. Solvation free energies (benzene) using SMD model were included for the calculation of ΔG^0.

Coordinates of optimized structures

The following optimized geometries were displayed in Cartesian coordinates (atomic unit). E° represents the electronic energy of the optimized structure, and G° represents the sum of electronic and thermal free energies in Hartree unit.

BPh_3 [E° = –719.8510977; G° = –719.617049; $G°_{(benzene)}$ = –719.6348058]



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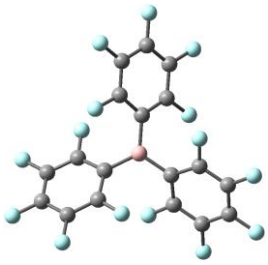
B	0.0031530057	-0.0014087578	0.0001245977	C	-0.1117828273	1.0935376753	-3.7348498688
C	0.2187377562	0.753522811	1.358927621	C	0.9435539782	2.0053584174	-3.8039303173
C	0.3393622151	0.7128204623	-1.356051028	C	1.7000991431	2.2778733874	-2.6622439467
C	-0.5507365819	-1.4696794178	-0.0021645337	C	1.390673648	1.6503928165	-1.4565416198
C	0.6011455374	0.0671404482	2.5323566182	C	-0.1553720517	-2.4068773452	-0.9818106328
C	0.8067961413	0.735723621	3.7381526762	C	-0.6366197634	-3.715143699	-0.9804344338
C	0.6061802749	2.1156474094	3.812907075	C	-1.5557200268	-4.1185542879	-0.0095988538
C	0.2140680842	2.8218014904	2.6737831182	C	-1.9774254454	-3.211879886	0.96517204
C	0.0383736686	2.1501094113	1.46497716	C	-1.4695079838	-1.9137178429	0.9740111639
C	-0.3969252104	0.4492456475	-2.532005649	H	0.7518760127	-1.0076279246	2.490821312

H	1.117188482	0.1824960345	4.6202491068	H	2.5256869783	2.9824375491	-2.7120147135
H	0.7547834261	2.6380912239	4.7539983176	H	1.9813712461	1.8786475683	-0.5741473564
H	0.0517048998	3.8947477252	2.7278499152	H	0.5518071802	-2.1038186592	-1.748388459
H	-0.2575451846	2.713280479	0.5847006931	H	-0.3013986835	-4.4184212215	-1.7377430265
H	-1.2153802459	-0.2636837284	-2.4946949295	H	-1.9414160671	-5.134391664	-0.0126367475
H	-0.7068367391	0.8821281023	-4.6189923045	H	-2.6962971616	-3.519353117	1.7196054145
H	1.175311579	2.5010118613	-4.7427108073	H	-1.7989092841	-1.2214525899	1.7433203984

$B(C_6F_5)_3$ [E° = –2208.2311075; G° = –2208.138939; $G°_{(benzene)}$ = –2208.14214]



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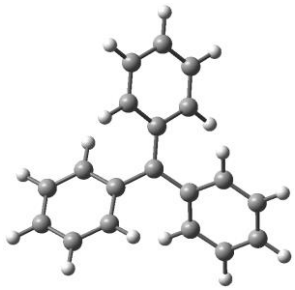
C	0.2148269237	0.7544261952	1.3604081296	C	-1.5477579763	-1.8938041774	0.9018247347
C	0.3476397	0.7090598059	-1.3537060938	F	0.9385404252	-1.2128606762	2.4912371574
C	-0.5642359365	-1.4642733062	-0.0026776659	F	1.3137592919	0.0915419176	4.8003268359
C	0.6607129293	0.1009771823	2.5201753361	F	0.794504752	2.7626141255	4.9690874947
C	0.8693286211	0.7554326842	3.7286512222	F	-0.1045525097	4.1236538382	2.7840560659
C	0.6089222806	2.1213531911	3.8169536105	F	-0.474913136	2.8478598623	0.458661334
C	0.1540211109	2.8150056804	2.6974782863	F	-1.5173143924	-0.2475599377	-2.4852271666
C	-0.0237512351	2.1306831911	1.5007664485	F	-0.91532762	0.9750217773	-4.7905779548
C	-0.4242874836	0.5329517285	-2.5128407535	F	1.2727291305	2.5935013013	-4.9570594509
C	-0.1376837171	1.1607743287	-3.7194780838	F	2.8561065746	2.9838829157	-2.7722149767
C	0.9770853879	1.9920005549	-3.8063865683	F	2.2697731121	1.7856147998	-0.4493138931
C	1.7819748915	2.1929572318	-2.6869505986	F	0.834985701	-2.1359067963	-1.8092211662
C	1.452286656	1.5640715343	-1.4919923709	F	-0.1301303896	-4.6344582284	-1.8026920805
C	-0.1198216356	-2.4358847415	-0.9131905997	F	-2.0626784052	-5.3557683071	-0.0195296956
C	-0.5996256045	-3.7403991586	-0.9269858211	F	-3.0164961591	-3.5383823688	1.7753479431
C	-1.5839651731	-4.1132027285	-0.0140724391	F	-2.0575085529	-1.0374137372	1.8025775805

Ph_3C^+ [E° = –732.8485709; G° = –732.609795; $G°_{(benzene)}$ = –732.6643809]



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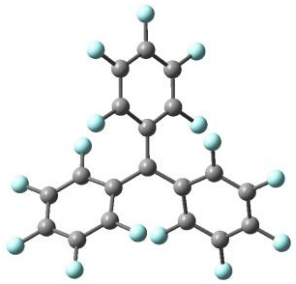
C	0.2025428874	0.6963865493	1.2552575699	C	0.1897814178	2.760635004	2.5510122244
C	0.3229006722	0.6549068491	-1.252348965	C	0.0136012326	2.1012317466	1.3432771738
C	-0.5183086569	-1.3537905246	-0.0023879653	C	-0.4361581887	0.392304799	-2.4237512714
C	0.5894572346	-0.0106933897	2.4245746827	C	-0.1363444474	1.0355735837	-3.6157163804
C	0.7921672052	0.6633986967	3.6199659802	C	0.9397232955	1.9286045544	-3.6781202204

C	1.7105199134	2.1907613043	-2.5394314198	H	-0.3249576034	2.649767716	0.4718058887
C	1.4010009697	1.5757270647	-1.3350956175	H	-1.2897547859	-0.2733338179	-2.3680942438
C	-0.1026823714	-2.2897965244	-0.9863388151	H	-0.7414406958	0.8505513031	-4.4968506287
C	-0.5949001492	-3.586738713	-0.9762780127	H	1.1781261338	2.4209900259	-4.6157480698
C	-1.5312923966	-3.9728538012	-0.0101056862	H	2.5548037836	2.869340185	-2.598445887
C	-1.9657365966	-3.0621733993	0.9601423924	H	2.0183655386	1.7541339049	-0.462190031
C	-1.4570004537	-1.7716472291	0.9779759314	H	0.6462332343	-2.0008921427	-1.7147216488
H	0.7805624945	-1.0759698812	2.364968736	H	-0.248072343	-4.3023182779	-1.7141379374
H	1.1172279493	0.1180680022	4.499585121	H	-1.9230656319	-4.9852409029	-0.0132416148
H	0.7339466694	2.5681225335	4.6280814762	H	-2.7053528027	-3.361741648	1.6949868341
H	0.013160785	3.829094658	2.6141416262	H	-1.8178284106	-1.0576673329	1.7093369108

$C(C_6F_5)_3^+$ [E° = –2221.1604301; G° = –2221.064169; $G°_{(benzene)}$ = –2221.105712]



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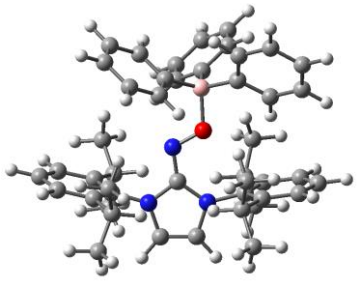
C	-0.0014776236	-0.0009440754	0.0013670541	C	-2.0441566088	-3.0520181946	0.9152415951
C	0.196789426	0.6954582331	1.2541508471	C	-1.5187920898	-1.7718601005	0.9276934976
C	0.3292370663	0.6502692696	-1.247999077	F	0.9008424116	-1.2816744188	2.3953128371
C	-0.5296172664	-1.3480472366	-0.0029292881	F	1.2844995334	0.0328747485	4.6911356586
C	0.6289788074	0.0210119249	2.430151747	F	0.7784578164	2.6942128389	4.8399884676
C	0.8447925403	0.6849837813	3.6249470884	F	-0.10678417	4.0625360384	2.6704758736
C	0.5934747646	2.0606666174	3.7037123996	F	-0.4755264983	2.7992701594	0.3440091274
C	0.145852712	2.7651225937	2.5788606574	F	-1.5329825411	-0.3106372417	-2.3951351503
C	-0.0270061131	2.0948781508	1.3806669765	F	-0.9110006694	0.9167384725	-4.6865035346
C	-0.4447149038	0.4555919962	-2.4257787884	F	1.2762995356	2.5162607135	-4.8273449174
C	-0.1468870837	1.0911508198	-3.6183986447	F	2.8499804862	2.9102835854	-2.6526719792
C	0.9758951271	1.9251677138	-3.6927909198	F	2.2511179546	1.7313642127	-0.3289693476
C	1.7805096014	2.1332502321	-2.565255143	F	0.8629229721	-2.0299246238	-1.820452279
C	1.4466626007	1.5226847144	-1.3691302723	F	-0.1186104754	-4.5161831887	-1.7998945308
C	-0.0902793561	-2.3252604171	-0.9392661327	F	-2.0463621288	-5.2068631964	-0.0198192735
C	-0.5768188639	-3.6206861087	-0.9377065221	F	-2.9914879133	-3.4023161681	1.7725794391
C	-1.5653549958	-3.984046666	-0.0142592192	F	-2.0184540544	-0.9133111799	1.8140097536

2-H [E° = –2009.8862785; G° = –2009.114692; $G°_{(benzene)}$ = –2009.157575]

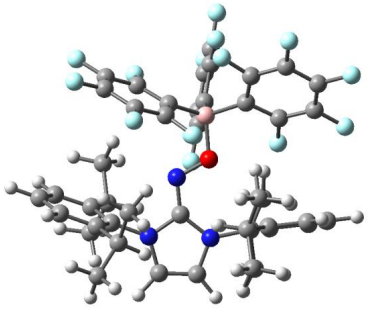


Charge = 0; Multiplicity = 2;

O	10.9763460164	4.3076034346	11.3278015162	N	10.3694507974	1.5766630865	11.1802137771

N	9.7162232972	3.9606407445	11.5297849866	H	12.932805329	7.0524459669	9.2063884237
N	8.2848079958	2.0978111181	11.6895663717	H	13.8149182398	1.4332920496	8.1407372535
C	9.5319473897	2.6326787668	11.4598519128	H	15.82736505	4.3246529272	10.9358475179
C	10.9821684542	6.251151764	9.6490162415	H	8.9415229952	5.5607063319	9.6930324216
C	13.7894755335	5.0090124194	11.0764321685	H	10.0972157897	-0.5537082735	11.0627278652
C	12.8775575008	5.9595293339	11.5767775831	H	11.0770736911	5.5760356116	13.9884811576
C	8.3525556134	0.7218038349	11.5620546019	H	12.7630528441	7.7620705773	12.7526832934
C	11.9439356025	6.8427186983	8.8099634766	H	16.7364644654	6.1958549298	12.3086361405
C	12.1412113279	1.5833371507	9.4817468365	H	8.4386783378	6.1266801511	7.3441134451
C	13.4986966085	1.4238854476	9.1788065076	H	11.2492231203	1.607665523	13.4235608867
C	15.1589709231	5.0831133975	11.3371886516	H	14.808641721	1.1446946189	12.2952999892
C	9.718545072	6.0051126527	9.0756406436	H	10.1856498855	7.167047392	5.9070486336
C	9.6325648658	0.4005548478	11.2476168455	H	10.1593445454	2.0046262859	8.8055916939
C	10.4189778408	6.3771480043	13.6577836704	H	15.1776270009	7.9193918024	13.2026607606
C	13.4249724853	7.0029065954	12.3457930739	H	8.6260020245	2.0883685201	14.0713819878
C	7.0892569551	2.8289321396	12.0565700855	H	9.4496334411	8.0496253538	10.8836268094
C	11.7815411956	1.5637182688	10.8427441074	H	12.435347577	7.6331281859	6.8656625646
C	15.6704018905	6.1305403686	12.1057307169	H	6.1343178395	1.6394269525	15.7963663272
C	10.3598808956	6.6909458257	12.2841942402	H	7.7317618224	0.9294985578	16.0662442546
C	9.4284020934	6.3266598802	7.7484042944	H	6.7934082643	0.4869431348	14.6293567222
C	12.3269654294	1.4283358363	13.3573977409	H	15.4940356373	1.1290815162	9.9237776574
C	6.2402493912	3.2907327606	11.0305874635	H	11.8788013591	0.1363780304	7.0897916321
C	14.0586482404	1.2577751813	11.5193017485	H	10.1904211863	0.5675150095	6.7846853702
C	10.4057009311	6.9129824149	6.9408382493	H	10.620806284	-0.3796477385	8.2192574431
C	12.7164024358	1.4133565021	11.8833426624	H	7.6328984486	2.9338874032	9.4541185042
C	11.125685677	1.7550648665	8.3562630585	H	4.3818257959	4.3071000399	10.6617391688
C	14.7950860702	7.0945602471	12.6059678107	H	9.7629936711	6.807619471	15.6658109442
C	6.8016304643	2.9933780832	13.423852184	H	8.2752844897	8.6792032857	14.9651372284
C	7.7138509037	2.4790195444	14.532555345	H	14.1082213569	2.4328963302	14.1486451135
C	9.5208587371	7.7595474167	11.9278583909	H	12.6588836617	2.6297544507	15.1404245442
C	11.665264169	7.1725775283	7.4800828803	H	12.8370609085	3.5386557114	13.6217036084
C	7.0536051927	1.3146843608	15.2975624606	H	5.3548624076	3.7971064166	14.7973596624
C	14.447013587	1.2544100325	10.1833562366	H	5.0876360989	4.3994102028	8.5965296152
C	10.9430240669	0.4415219064	7.570054052	H	6.5492676472	4.1168945679	7.6553253759
C	6.551063703	3.0691089788	9.5530012023	H	6.5998813764	5.201351893	9.0547783964
C	5.0612925105	3.9346269547	11.4202670043	H	8.6048077359	4.4322691934	14.9471687832
B	11.2907043038	5.8937056832	11.2171543413	H	8.8575637924	3.2241068179	16.2239389088
C	9.6806787733	7.074683211	14.6144460294	H	7.2848512519	4.0062433237	16.0459025556
C	8.8487028859	8.127795821	14.2242548434	H	8.1403720181	9.2924444702	12.5564157313
C	13.0238265983	2.5787202042	14.1089827997	H	11.6183325825	3.8531352507	7.9698313454
C	5.6079410452	3.6474493899	13.7527383182	H	10.704205362	3.0676783592	6.676928807
C	6.1725732877	4.2713652931	8.6711155638	H	12.4228647987	2.7166107572	6.8713016026
C	8.1395542339	3.6062561505	15.4904310554	H	12.0715090693	-0.7455811529	13.5283746345
C	8.7753578528	8.4690155204	12.8751833466	H	12.2830504959	0.0906984911	15.0767170682
C	11.495757541	2.9185820872	7.4180952912	H	13.6715128102	-0.17243818	14.0151164067
C	12.6036845575	0.0697298763	14.0298810718	H	6.1770059064	0.9018561655	9.60045916
C	5.8669283793	1.7863385377	9.035511561	H	6.1159610143	1.6166993228	7.982687067
C	4.7472051162	4.1119116003	12.7650479467	H	4.7775882997	1.8680404651	9.1160182696
H	13.4198737111	4.1916106902	10.4642213372	H	3.8280338769	4.6191904122	13.0426778482
H	7.484751523	0.1016466558	11.7127610944				

2 [E° = –3498.301681; G° = –3497.665299; $G°_{(benzene)}$ = –3497.693674]



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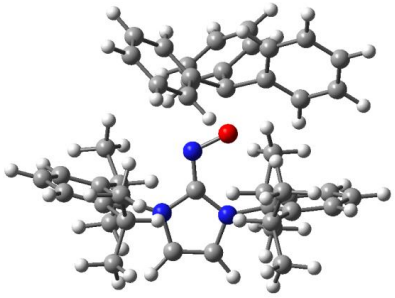
F	13.2344476705	4.3117739394	9.781829563	C	14.7056767668	7.0249032611	12.4741980127
F	9.7756875605	4.2671881355	8.786540045	C	6.9101025735	2.8920790705	13.5699121676
F	11.5612975699	9.2202473303	7.389249859	C	7.7888128721	2.1923475229	14.6046652935
F	11.8605189343	8.3980529597	9.921451688	C	9.0985116239	7.4532545055	11.8313743613
F	12.5760696809	7.8318425335	12.9163184991	C	11.1354756621	7.9996251785	7.7442321486
F	11.1678929369	5.3642122155	13.9075344347	C	6.9723631416	1.2307985077	15.4896193495
F	10.3538546175	7.5979462118	5.5403962123	C	14.490392646	1.2477150669	10.3147931378
O	10.94519203	4.3096647103	11.1921275038	C	10.9796468857	0.0177819146	7.7528794332
F	9.4611233302	5.1151065122	6.3112830046	C	6.6589556304	3.477231368	9.735813144
F	8.8211815487	7.8045025295	10.5561913477	C	5.2713735991	4.2395448272	11.7149382878
F	15.8614786499	4.4008199276	10.2508555817	B	11.14515286	5.8559131532	11.0589538903
F	16.8894231475	6.2194878972	12.0273457655	C	9.40965094	6.7735313262	14.4812013491
F	15.200502559	7.9287137633	13.3332927965	C	8.4017627299	7.6651711862	14.1264919242
F	9.551886161	6.3968659916	15.763995541	C	13.0603588006	2.7009862922	14.166929757
F	7.5847799552	8.1710842906	15.0596289245	C	5.7984709203	3.6319337983	13.9905361054
F	7.2661574495	8.8461989329	12.4244903288	C	6.6706675791	4.8780872909	9.0958284224
N	10.3659306057	1.5474784365	11.1267912408	C	8.5693863544	3.208671755	15.4611083217
N	9.723111682	3.9302881023	11.5268892564	C	8.2464160174	8.0056969077	12.7899737252
N	8.3068825992	2.0857497611	11.726279146	C	11.7101859473	2.3859156049	7.2196642455
C	9.5499058699	2.6024790815	11.4567841894	C	12.2639227046	0.2909196786	14.0759777446
C	10.8722417562	6.2831011579	9.4932227795	C	5.6612430893	2.5477794448	9.0159786424
C	13.6682160602	5.2034618297	10.7007350111	C	4.9867936865	4.295631922	13.0760927608
C	12.7524517671	6.0216834796	11.3687220002	H	7.4705794311	0.1071855182	11.7131031154
C	8.3442449724	0.7180297063	11.5562628091	H	13.9297552768	1.136632647	8.2483881461
C	11.291450301	7.5411574017	9.0482177499	H	10.0556521694	-0.5732041768	10.9784826329
C	12.2034469422	1.3890541577	9.5018939008	H	11.2043346002	2.0212471395	13.3864340241
C	13.5751807195	1.2382629166	9.2685869737	H	14.7758756385	1.4158945983	12.433468218
C	15.043931111	5.2398380604	10.9098201306	H	10.2784212602	1.8174870585	8.6922618144
C	10.2606347589	5.5081658415	8.5115057069	H	8.5277217949	1.5828705022	14.0753369685
C	9.6128156111	0.3850277661	11.1931788057	H	6.249693689	1.7678147625	16.1121792075
C	10.2372965676	6.2588916719	13.4926929723	H	7.6385301614	0.6808921149	16.1620406401
C	13.3327860082	6.9449533169	12.2416105587	H	6.4175013635	0.5025683065	14.8892310852
C	7.1662039999	2.8546763298	12.1852122133	H	15.5512498692	1.1461829741	10.1083943907
C	11.7933561657	1.5251444863	10.8410443455	H	11.9112648346	-0.427224407	7.3872200594
C	15.5690204254	6.1614995468	11.8088374465	H	10.279089564	0.0671444544	6.9127076678
C	10.1386694052	6.5738588782	12.1347630428	H	10.5591882679	-0.6633048012	8.5003298661
C	10.0763873377	5.9240720906	7.1943342303	H	7.65884769	3.0632744931	9.5902880798
C	12.2390567995	1.6660253569	13.3778228347	H	4.6351066551	4.76806704	11.0127527287
C	6.3728203002	3.5235427951	11.2328585544	H	14.099508067	2.3827409776	14.2985517691
C	14.0512331569	1.4029324439	11.6263422423	H	12.6306976625	2.832586183	15.1648493418
C	10.5207226246	7.1793866297	6.8014040487	H	13.055564433	3.6720793725	13.668494022
C	12.6917821781	1.542198722	11.9255542602	H	5.5718974923	3.6941667096	15.0499693999
C	11.2311603424	1.4260478517	8.3270207958	H	5.6669717295	5.3138354567	9.053944903

H	7.0451716636	4.8101554335	8.0699873037	H	11.6306275376	-0.4385648507	13.5599827962
H	7.3167049777	5.5676274538	9.6447523356	H	11.9088446591	0.3777211528	15.1083094673
H	9.2466382692	3.8145205635	14.8556621577	H	13.2810113122	-0.1142222213	14.1036141327
H	9.1687685368	2.6848541833	16.2136129208	H	5.6938640999	1.5296744126	9.4185178455
H	7.8954813854	3.8904270875	15.9891289874	H	5.8911292685	2.4971815725	7.9467508162
H	12.0481501482	3.3343905184	7.6406057544	H	4.6344104573	2.9139140667	9.1218177323
H	10.8938793001	2.594517344	6.521965786	H	4.1315234707	4.8655191147	13.4266250968
H	12.5375863635	1.9561119626	6.6451582222				

3 (only for cation) [E° = –2022.909931; G° = –2022.131888; $G°_{(benzene)}$ = –2022.198079]



Charge = +1; Multiplicity = 2;

O	11.0365409177	4.353252497	11.3046353505	C	11.6192169183	7.1457049397	7.5667811609
N	10.3962050415	1.6234408317	11.2150923368	C	7.0928079371	1.281763997	15.1423193288
N	9.7509249205	4.0195969562	11.481911188	C	14.4711523159	1.285080669	10.2123883383
N	8.3092378798	2.1768091366	11.697585225	C	10.9806669087	0.3814799598	7.6347172025
C	9.563332645	2.690956596	11.4571077675	C	6.5670330193	3.0888264866	9.5317718156
C	10.9582329565	6.2347717959	9.7238065994	C	5.088654907	4.0154022049	11.3788565733
C	13.6754214663	5.0142301965	11.0241669986	C	11.2780479216	5.8732728548	11.1796005329
C	12.7735934816	5.9791791446	11.4988677005	C	9.8057825416	6.8865372621	14.5512695608
C	8.3677097749	0.8074286287	11.6091568337	C	9.0354085849	8.0048873224	14.2178445743
C	11.9272440921	6.8039938245	8.8858008538	C	13.1291758258	2.4842051246	14.2040949852
C	12.1625742206	1.5964681815	9.5086399768	C	5.6210567237	3.76229954	13.7204305135
C	13.521442864	1.4430838998	9.2065059446	C	6.1636415939	4.253515959	8.6106742496
C	15.0422842551	5.1420529839	11.2674987982	C	7.9742826991	3.6102346531	15.6231920361
C	9.667305135	6.0261634929	9.2070788161	C	8.967897705	8.4201410534	12.8908350892
C	9.6538228769	0.4642655622	11.3097611563	C	11.4875769049	2.8609930339	7.4063787233
C	10.4951219436	6.191468993	13.5621283841	C	12.518822881	0.0255042835	13.9982933177
C	13.2767004386	7.0850600557	12.1974094844	C	5.8886963459	1.7829491365	9.0648737316
C	7.108069443	2.921701111	12.0460320012	C	4.7699487726	4.2166170264	12.7189904868
C	11.8121861727	1.5937413384	10.8726482078	H	13.313565192	4.1634320538	10.4603950155
C	15.5343138266	6.2437375857	11.9689348961	H	7.4957242212	0.1955584115	11.7709877414
C	10.4254936869	6.5969173085	12.218499991	H	12.9254049833	6.9924981	9.2603631655
C	9.3647665276	6.3607784618	7.8888581132	H	13.8364329457	1.4345376344	8.1683485324
C	12.3503870257	1.4328824245	13.3911737792	H	15.7223333942	4.3795998987	10.9005356099
C	6.2660240192	3.3591031883	11.0038882939	H	8.8961421137	5.6111638777	9.8460714903
C	14.0855903964	1.2912353037	11.5497995178	H	10.1077376909	-0.5007391221	11.1535544164
C	10.3407991276	6.9213999142	7.0616802878	H	11.1078410477	5.3377185262	13.8339685354
C	12.7438178466	1.4473481144	11.9172369025	H	12.6009959744	7.850681215	12.5597665291
C	11.1407918027	1.7210522784	8.3819032573	H	16.5995472182	6.3447978592	12.152440284
C	14.6471954028	7.2168600515	12.4269632199	H	8.3617246472	6.1933685293	7.5092827628
C	6.8150450474	3.0992751547	13.4115691055	H	11.2891354304	1.694102783	13.4657844323
C	7.7017170372	2.5609962989	14.5312213802	H	14.8363784137	1.1684123764	12.3230806407
C	9.65962975	7.7220087184	11.896422691	H	10.102080937	7.1871058037	6.0364795563

H	10.1693158828	1.9664662938	8.8244749613	H	5.3539667272	3.9210441048	14.7595444796
H	15.0171149046	8.0825916605	12.9673880837	H	5.0769672289	4.3530270528	8.5304569701
H	8.6724846939	2.290675437	14.1013413205	H	6.5431931875	4.0742116778	7.600300567
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H	10.6840120794	-0.4283149095	8.3091948403	H	11.925418807	-0.7219525264	13.4616818963
H	7.6499611142	2.9587885231	9.4238806651	H	12.2010350181	0.0217201501	15.0455609166
H	4.4093692483	4.3710172185	10.6126176895	H	13.5643486619	-0.2968550184	13.9659124297
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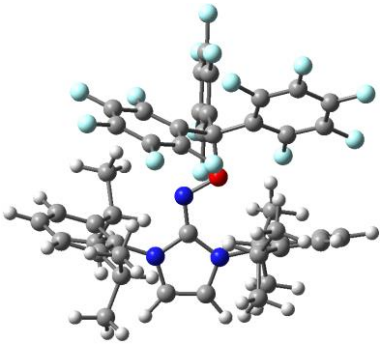
H	8.5042401955	8.5518202512	14.9906677596	H	6.1255570457	1.5825961062	8.0151833001
H	14.1969376922	2.2494181924	14.251687199	H	4.8005428957	1.8579817038	9.1568462075
H	12.7562426447	2.5141293001	15.2326758464	H	3.8492699916	4.7274435654	12.9832842629
H	13.0276979036	3.4812163929	13.7669676502				

3-F [E° = –3511.2550595; G° = –3510.614788; $G°_{(benzene)}$ = –3510.670111]



Charge = 1; Multiplicity = 2;

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F	11.2424250929	9.4237898858	7.7494824509	C	12.7116664286	6.019025728	11.2497220684
F	11.6350366043	8.471692069	10.2298941562	C	8.3647822902	0.8353521893	11.6132438597
F	12.6446981845	7.819458313	12.82277883	C	11.1504943534	7.6409376115	9.2921964069
F	11.5887094042	5.3259501311	13.8109627726	C	12.2231340945	1.359595198	9.558110876
F	10.1737353035	7.8114204819	5.8111182253	C	13.5959192034	1.2203299729	9.3174308296
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F	8.7760555621	7.6217113827	10.7214616762	C	9.6473148846	0.4790212247	11.2906520705
F	15.6985967594	4.4682506381	9.8106897074	C	10.5673698047	6.1462886434	13.5103237029
F	16.8622045051	6.2617471853	11.521772305	C	13.3435533719	6.9501904822	12.0832950924
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F	10.0676641746	6.2167425487	15.8147387349	C	11.8341845644	1.5838629521	10.8924649886
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C	10.3927319514	7.3375588562	7.0324291903	H	8.5973450762	1.9310963091	14.1249955251
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C	4.9396476656	4.3970413273	12.9155513843	H	11.7088622166	0.6129608552	15.1177718508
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H	10.0836084682	-0.4925051971	11.1259768282	H	5.9996918872	2.4779823763	7.8755681214
H	11.3407235873	2.3937508731	13.4174225842	H	4.7164183055	2.9202177743	9.0104489854
H	14.8347702913	1.5964292039	12.4503110041	H	4.0607498791	4.9545573968	13.2239445314
H	10.2682100991	1.6390033744	8.7366587095				

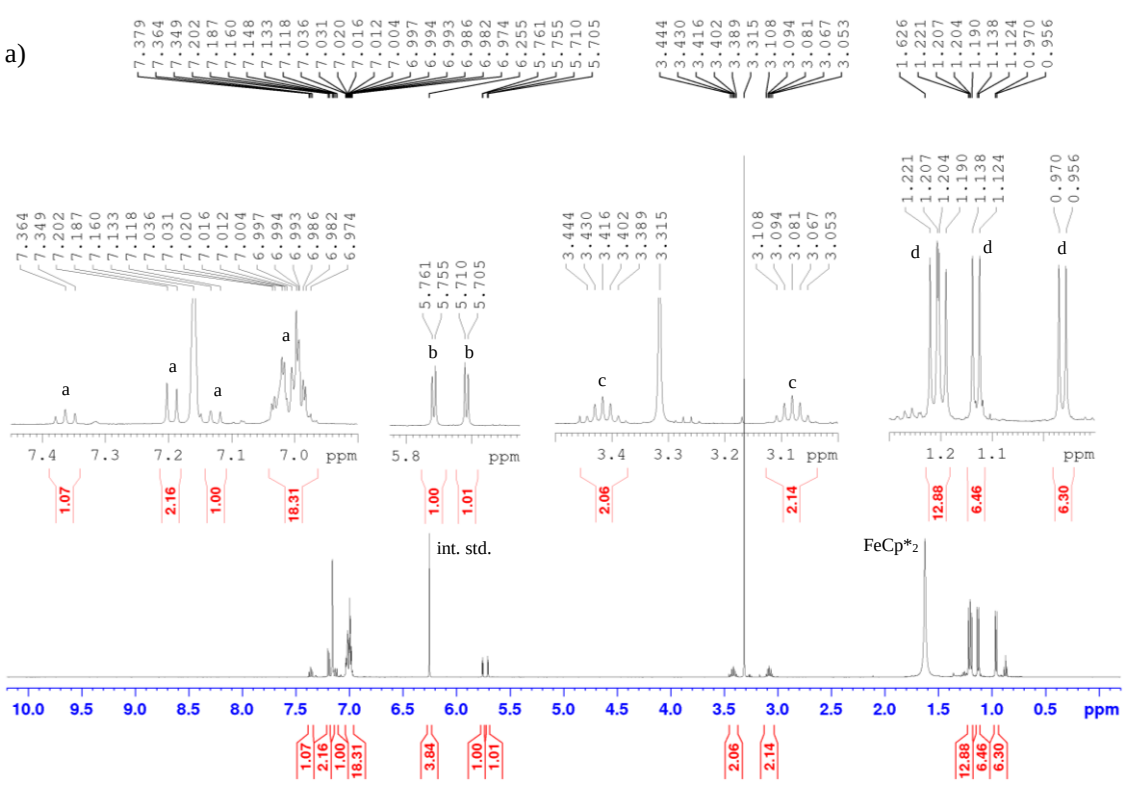
NMR

General information

^{1}H NMR spectra was recorded using a Bruker DRX 500 spectrometer operating at 500 MHz for ^{1}H acquisitions. Chemical shifts of ^{1}H acquisitions were referenced to the residual proton solvent peaks (^{1}H: C_6D_6, δ = 7.16 ppm).[8]

^{1}H spectrum of S1

a)



b)

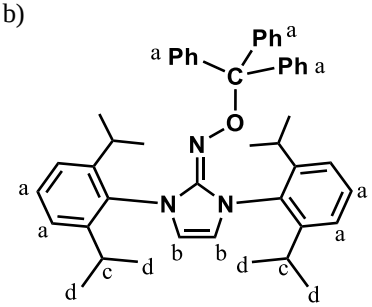


Figure S3. a) ^{1}H NMR spectrum and b) assignment of the signals for the compound **S1**.

EPR

General information

EPR spectra were recorded on a Bruker X-band A200 spectrometer using benzene solutions. Spectra processing and simulation were performed with Bruker WIN-EPR and EasySpin associated with DFT calculations.[9] Isotropic hyperfine coupling constants were initially computed using gaussian09 with B3LYP/6-31G(*d*, *p*) or EPRII basis sets,[10] and then rescaled to fit the experimental data.

EPR spectra

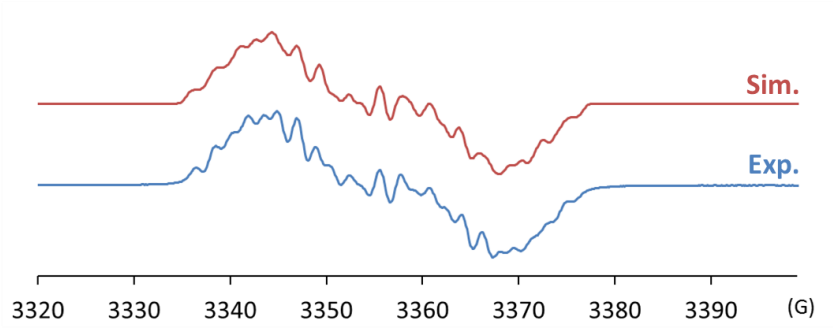


Figure S4. Experimental (bottom, blue) and simulated (top, red) EPR spectra of **2a** at microwave frequency = 9.4447 GHz. Simulated with the following parameters: g_{iso} = 2.0107; hyperfine coupling constants: $a(^{14}N)$ = 23.4, 9.1, 6.9 MHz, $a(^{11}B)$ = 6.7 MHz, $a(^{1}H)$ = 5.3, 3.6 MHz, $a(^{19}F)$ = 2.6, 1.7 MHz; Gaussian line width = 0.09 mT; Lorentzian line width = 0.01 mT.

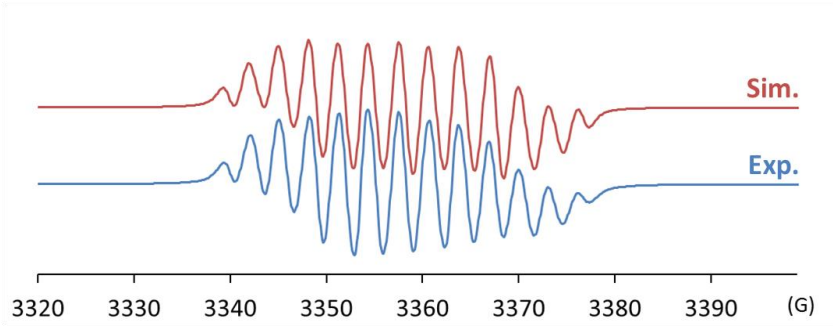


Figure S5. Experimental (bottom, blue) and simulated (top, red) EPR spectra of **2b** at microwave frequency = 9.4468 GHz. Simulated with the following parameters: g_{iso} = 2.0098; hyperfine coupling constants: $a(^{14}N)$ = 26.6, 9.3, 7.5 MHz, $a(^{1}H)$ = 10.2, 6.6 MHz; Gaussian line width = 0.06 mT; Lorentzian line width = 0.10 mT.

Comparison of the EPR spectra before and after silica filtration

Under ambient atmosphere, **2** (3.0 mg) was dissolved in benzene (0.5 mL) and the solution was filtered through silica. The filtrate was collected on an EPR tube, and the EPR spectrum was recorded under air.

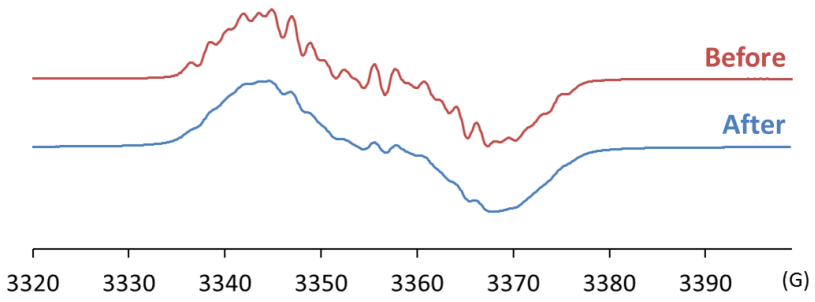


Figure S6. EPR spectra of **2a** before (top, red) and after (bottom, blue) silica filtration.

Crossover experiment (EPR)

In a N_2 atmosphere glovebox, **3** (5.0 mg) and $B(C_6F_5)_3$ (3.8 mg) was dissolved in benzene (1 mL). After 1 day, the solution was analyzed with EPR (green spectrum). Purple spectrum is the simulated EPR spectrum of 85:15 mixture of **2** and **3**. This experiment shows that **2** can be generated from **3** and $B(C_6F_5)_3$, which suggests the dissociation of **3** back to **1**.

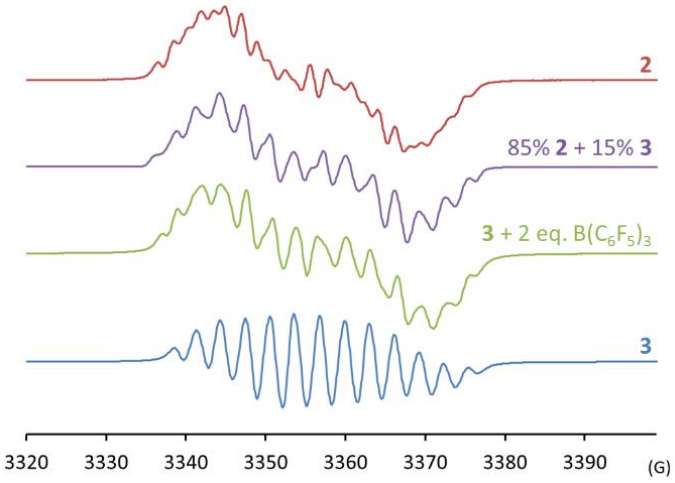


Figure S7. EPR spectrum from the crossover experiment (green) and fitted spectrum (purple).

UV-Vis Spectroscopy

General information

The UV-vis spectra were recorded at room temperature with Cary 6000i UV-Vis-NIR (Agilent Technologies). UV cell (quartz) with Teflon stopper was used to prevent decomposition of the sample.

UV-Vis spectra

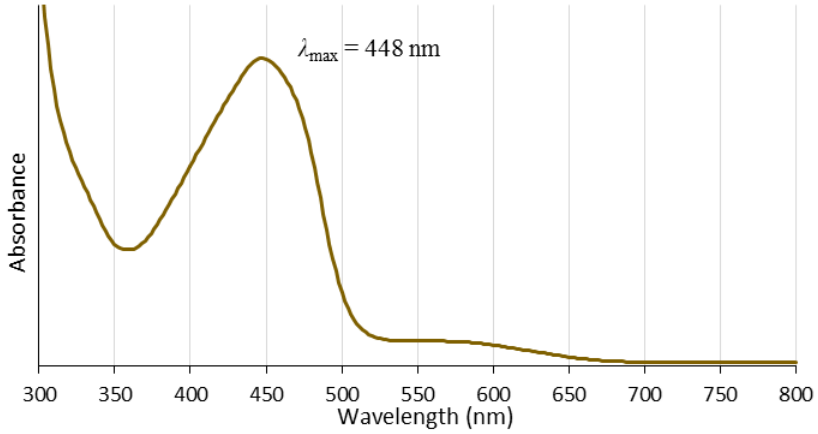


Figure S8. UV-Vis spectrum of **2**. Sample concentration = 0.36 mM (benzene solvent); Cell path = 10 mm.

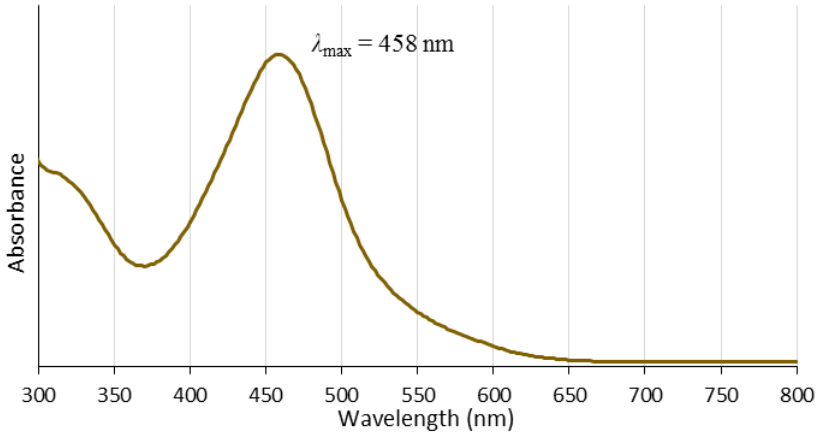


Figure S9. UV-Vis spectrum of **3**. Sample concentration = 0.25 mM (benzene solvent); Cell path = 10 mm.

UV-Vis monitoring

Under air, wet technical grade benzene (3 mL) was added into a UV cell (quartz) containing **2** (1.0 mg) or **3** (1.0 mg). Decay of the samples were monitored.

Monitoring of 2

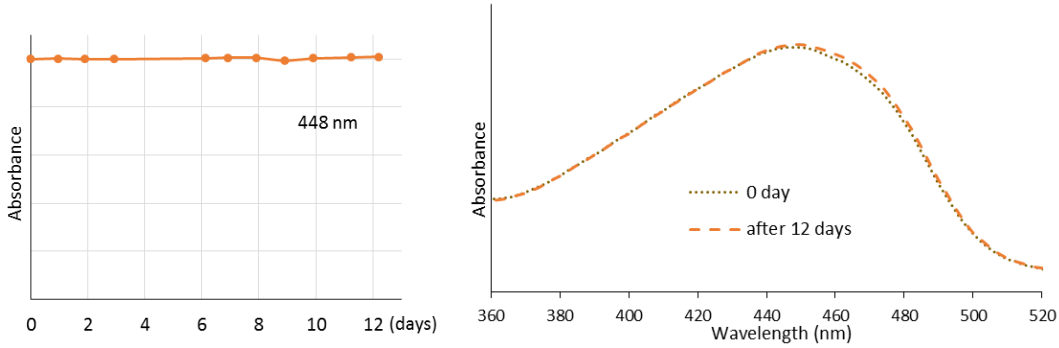


Figure S10. (Left) Absorbance at 448 nm during 12 days. (Right) Spectra before and after monitoring.

Monitoring of 3

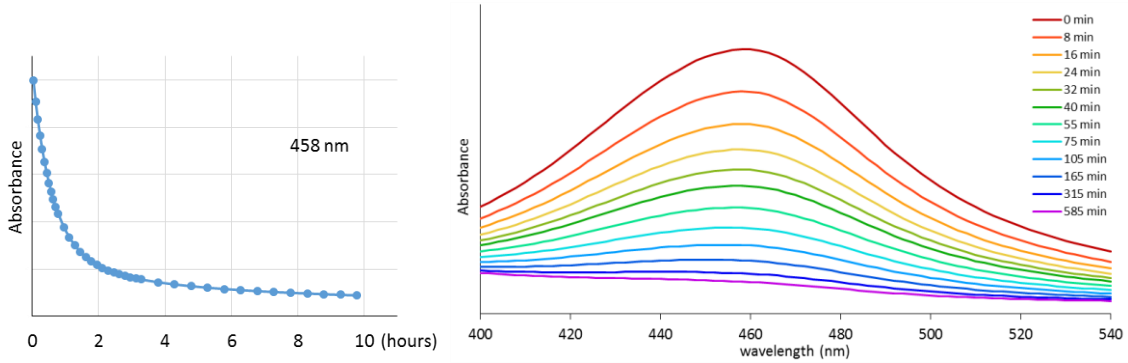
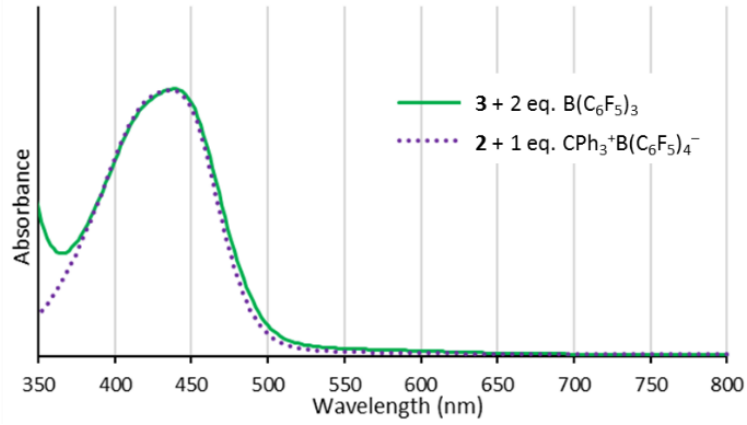


Figure S11. (Left) Absorbance at 458 nm during 10 hours. (Right) Selected spectra during monitoring.

Crossover experiment (UV)

The EPR sample for the crossover experiment was diluted and analyzed with UV-vis (green spectrum). Although the absorption peak was mainly governed by trityl cation (red spectrum), the presence of **2** was confirmed since the 1:1 mixture of **2** and $CPh_3^+B(C_6F_5)_4^-$ shows the same absorption (dotted purple), and the subtraction of trityl spectrum (red) from the green spectrum successfully generates the spectrum of **2** (dotted yellow).

a)



b)

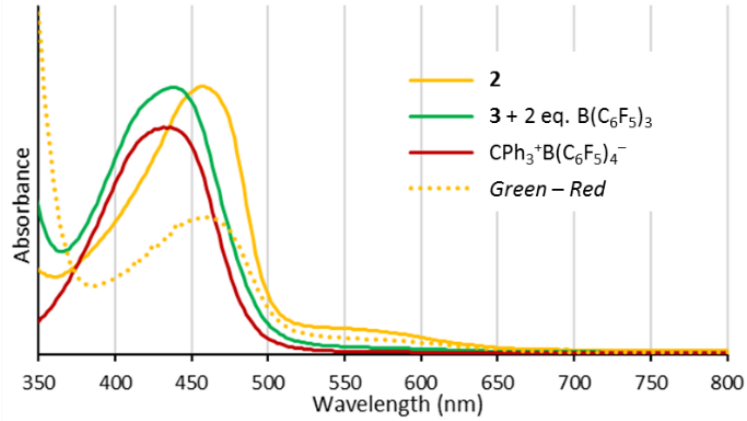


Figure S12. UV-Vis spectra for crossover experiments.

Cyclic Voltammetry

General information

Cyclic voltammograms were recorded at room temperature with a Princeton Applied Research (PAR) VersaSTAT 3 potentiostat. The working electrode was a glassy carbon disk (area = 0.02 cm^2), the reference electrode was Ag/AgCl (saturated), and the counter electrode was a platinum wire.

Cyclic voltammetry of 2

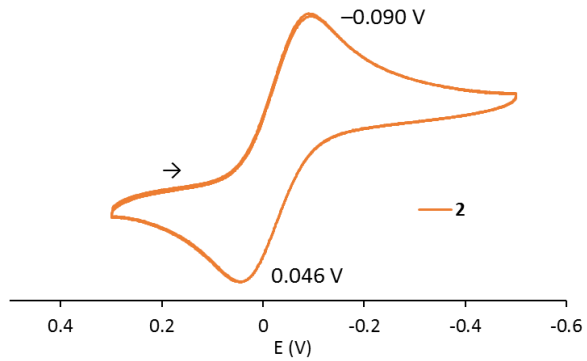


Figure S13. The solution of **2** (1.8 mM) was prepared using dry and degassed THF with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The cyclic voltammogram (potential versus saturated Ag/AgCl) was measured with scan rate of 0.1 V/s. The cyclic voltammogram of **2** in THF shows reversible one-electron redox potential at $E_{1/2}$ = –0.022 V versus Ag/AgCl (saturated) electrode.

Cyclic voltammetry of 3

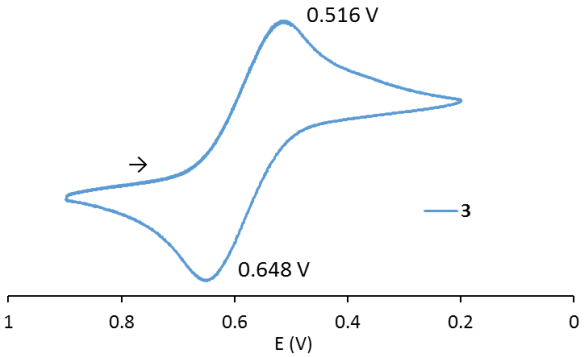


Figure S14. The solution of **3** (2.1 mM) was prepared using dry and degassed THF with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The cyclic voltammogram (potential versus saturated Ag/AgCl) was measured with scan rate of 0.5 V/s. The cyclic voltammogram of **3** in THF shows reversible one-electron redox potential at $E_{1/2}$ = 0.582 V versus Ag/AgCl (saturated) electrode.

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