Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Singlet carbenes as mimics for transition metals: Synthesis of an air stable organic mixed valence compound [$M_2(C_2)^{+\bullet}$; M = cyclic(alkyl)(amino)carbene]

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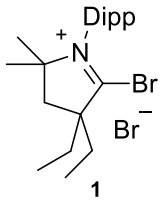
Supporting Information

Contents:

1. Experimental details

General: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk techniques unless otherwise specified. Dry, oxygen-free solvents were employed. EPR spectra were recorded on Bruker EMX. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) and Varian Inova 500 spectrometers (500 MHz for ^{1}H, 125 MHz for ^{13}C). All spectra were obtained in the indicated solvent at 25 °C. Chemical shifts are given in ppm and are referenced to the corresponding solvent residual peak (^{1}H, ^{13}C).[1] NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sx* = sextet, *sept* = septet, *m* = multiplet, *br* = broad signal. Melting points were measured with a Büchi melting point apparatus system. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. CAAC^{Et} was prepared following a literature procedure[2] while all other starting materials were purchased from commercial sources.



1

Bromine (0.46 g, 2.9 mmol) was added dropwise to a solution of CAAC^{Et} (1.0 g, 3.2 mmol) in hexane (25 mL) at -78ºC. The solution was allowed to warm up to room temperature and stirred for 12 hours. The resulting pale yellow precipitate was recovered by filtration, washed with diethyl ether (3 x 20 mL) and dried under vacuum overnight. **1** was isolated as a pale yellow solid (1.2 g, 90%). m.p.: 160 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) = 7.60 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 2.66 (s, 2H), 2.52 (sept, *J* =6.8 Hz, 2H), 2.19-1.91 (m, 4H), 1.35 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.65 (s, 6H), 1.15 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) = 191.1 (N*C*-Br), 144.1(C_{ortho}), 132.4 (C_{para}), 129.5 (C_{ipso}), 126.3 (C_{meta}), 84.6 (NC_{quat}), 61.7 (C_{quat}), 40.0 (C_{H2}), 32.1 (C_{H2}), 30.0 (C_{H}), 29.3 (C_{H}), 26.4 (C_{H3}), 23.5 (C_{H3}), 9.1 (C_{H3}). HRMS (ESI-TOFMS): m/z calculated for $[C_{22}H_{35}NBr]^{+}$ 392.1953, found 192.1956

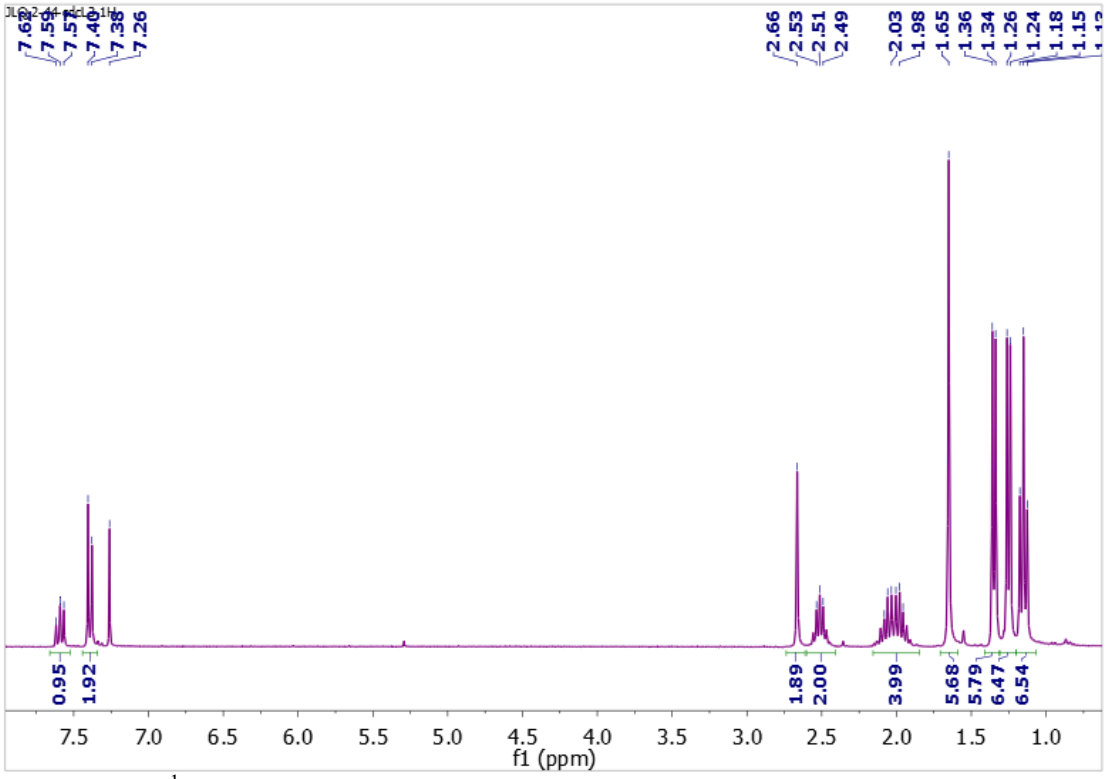


Figure S1. ^{1}H NMR of **1** in $CDCl_3$.

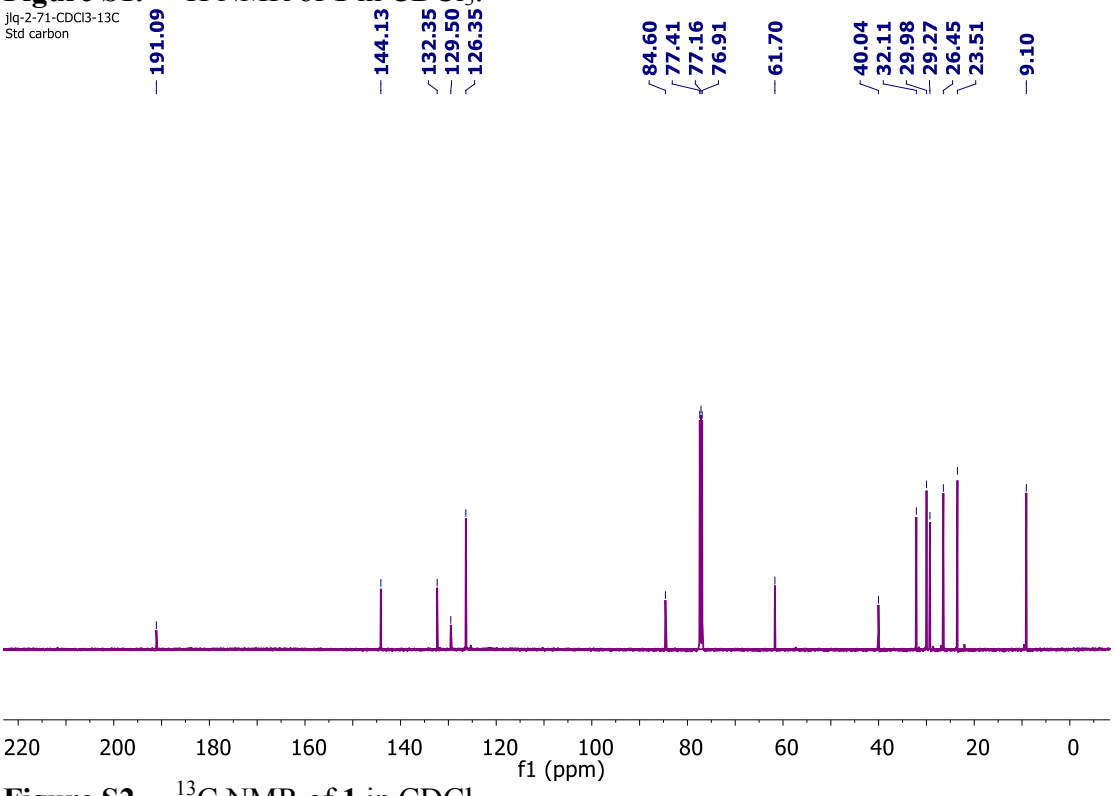
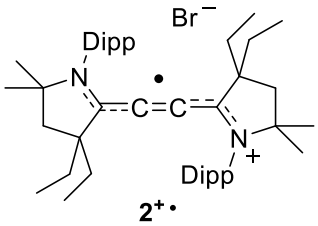


Figure S2. ^{13}C NMR of **1** in $CDCl_3$.



n-BuLi (0.89 mL, 2.5 M in hexane, 2.2 mmol) was added dropwise to a solution of trimethylsilylacetylene (258.8 mg, 2.6 mmol) in THF (10 mL) at -78ºC. After 1 hour at -78ºC, a suspension of **1** (700 mg, 1.48 mmol) in THF (10 mL) was added and the reaction mixture was maintained at -78ºC for another hour. Then, the solution was allowed to slowly warm up to room temperature and stirred for an additional 12 hours. Volatiles were removed under vacuum and the residue was washed with diethyl ether (3x10 mL). The resulting solid was extracted with CH_2Cl_2 (2 x 20 mL). After evaporation of the solvent, the radical cation $\mathbf{2}^{+\bullet}$ was isolated as a red solid (220 mg, 40%). m.p.: 250 ºC (dec.) Single crystals were obtained by slow vapor diffusion of diethyl ether into a saturated solution of $\mathbf{2}^{+\bullet}$ in THF.

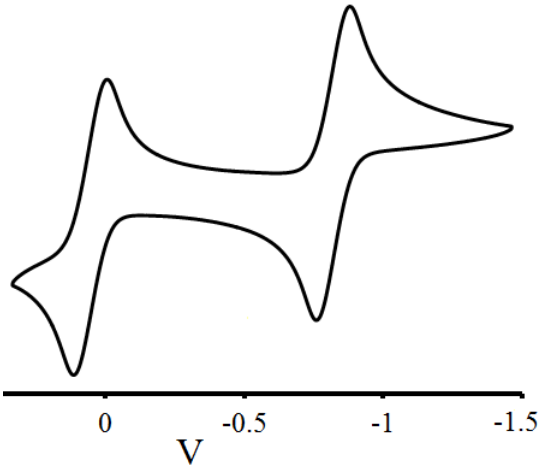


Figure S3. Cyclic voltammogram of a THF solution of radical cation ($\mathbf{2}^{+\bullet}$) (0.1 M nBu$_4$NPF$_6$ as electrolyte, scan rate 100 mV.S^{-1}, potential versus Fc+/Fc).

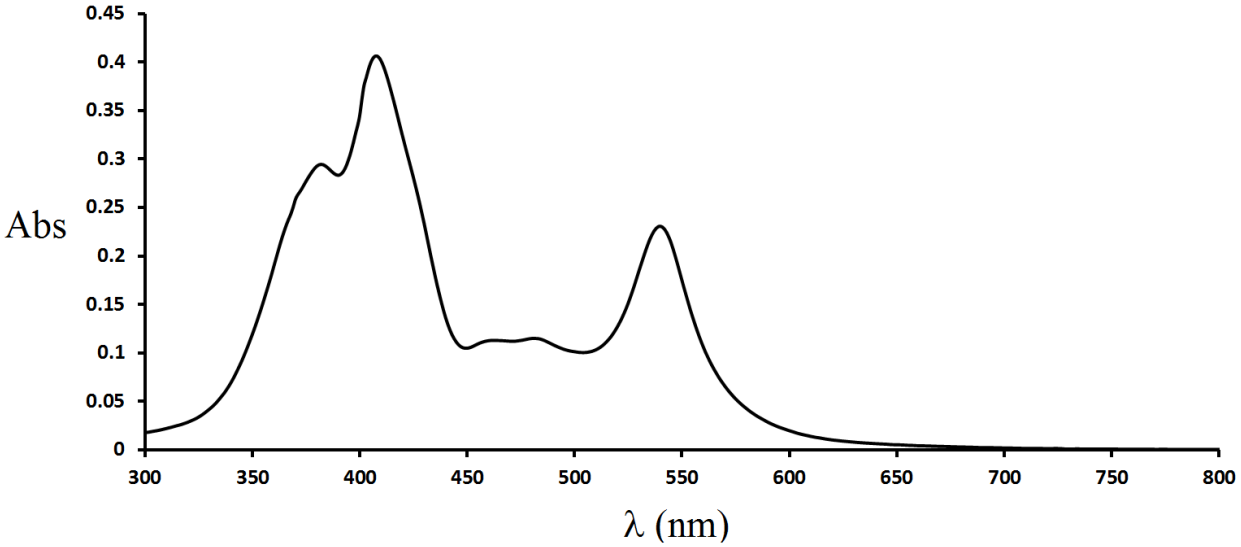


Figure S4. UV-Vis spectrum of radical cation ($\mathbf{2}^{+\bullet}$) in methylene chloride (5.5×10^{-4} mol.L^{-1})

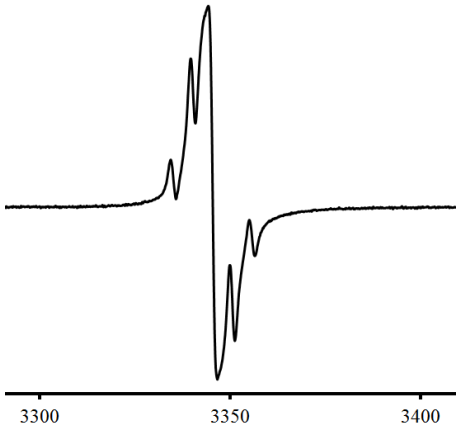
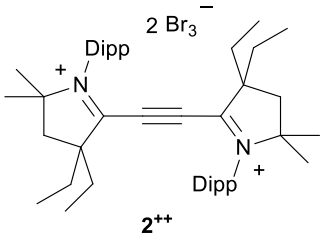


Figure S5. X-Band EPR of radical cation ($\mathbf{2}^{+\bullet}$) in THF at room temperature.



$\mathbf{2}^{++}$

Bromine (146 mg, 0.9 mmol) was added dropwise to a solution of $\mathbf{2}^{+\bullet}$ (75 mg, 0.1 mmol) in $CHCl_3$ (5 mL). The resulting yellow precipitate was recovered by filtration and washed with diethyl ether (3x5 ml). $\mathbf{2}^{++}$ was isolated as a yellow solid (59 mg, 53 %). m.p.: 200 °C(dec.). Single crystals are obtained by vapor diffusion of diethyl ether into a saturated solution of $\mathbf{2}^{++}$ in CH_3CN.

^{1}H NMR (CD_3CN, 300 MHz) = 7.64 (t, J = 7.8 Hz, 2H), 7.47 (d, J = 7.8 Hz, 4 H), 2.55 (s, 4H), 2.44 (sept, J = 6.6 Hz, 4H), 1.88-1.68 (m, 8H), 1.56 (s, 12H), 1.27 (d, J = 6.7 Hz, 12H), 1.07 (t, J = 7.4 Hz, 12H), 0.79 (br, 12H); ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz) = 178.8 (N*C*-C_E), 145.0 (C_{ortho}), 134.1 (C_{para}), 129.5 (C_{ipso}), 127.9 (C_{meta}), 96.7 (C_E), 88.4 (NC_{quat}), 63.1 (C_{quat}), 40.5 (C_{H2}), 32.4 (C_{H2}), 30.6 (C_H), 29.3 (C_{H2}), 27.1 (C_{H3}), 23.0 (C_{H3}), 10.0 (C_{H3}). HRMS (ESI-TOFMS): m/z calculated for $[C_{46}H_{70}N_2]^{2+}$ 325.2764, found 325.2764

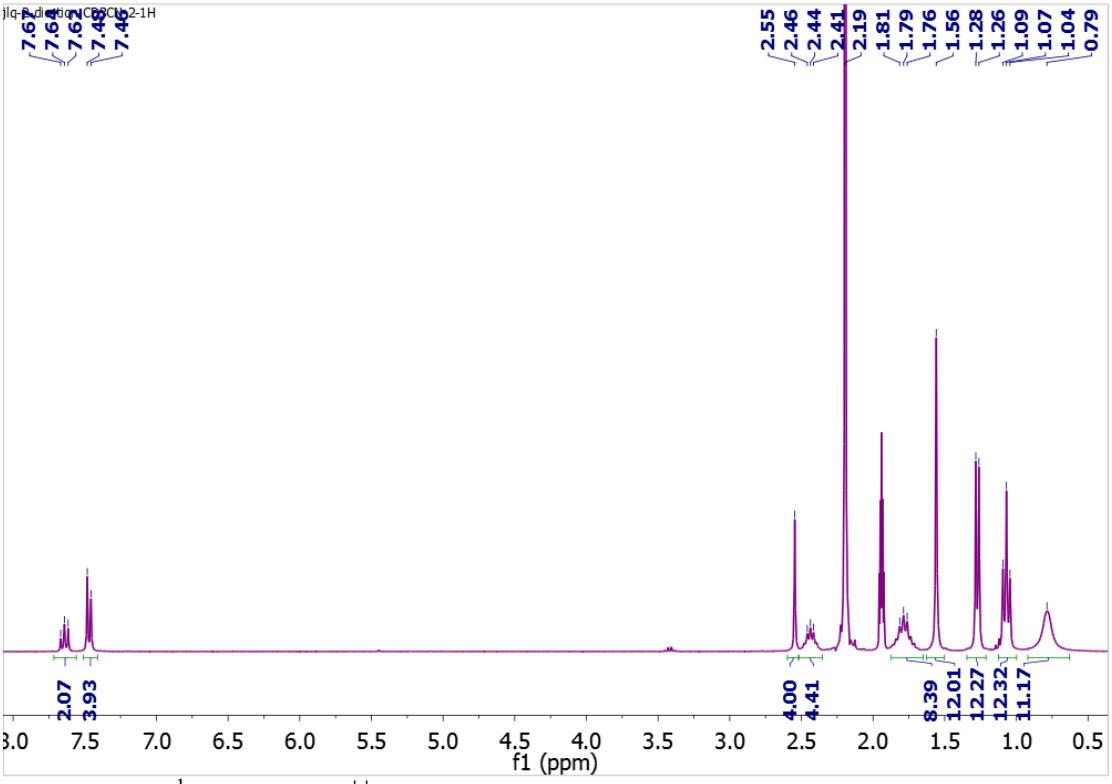


Figure S6. ^{1}H NMR of $\mathbf{2}^{++}$ in CD_3CN.

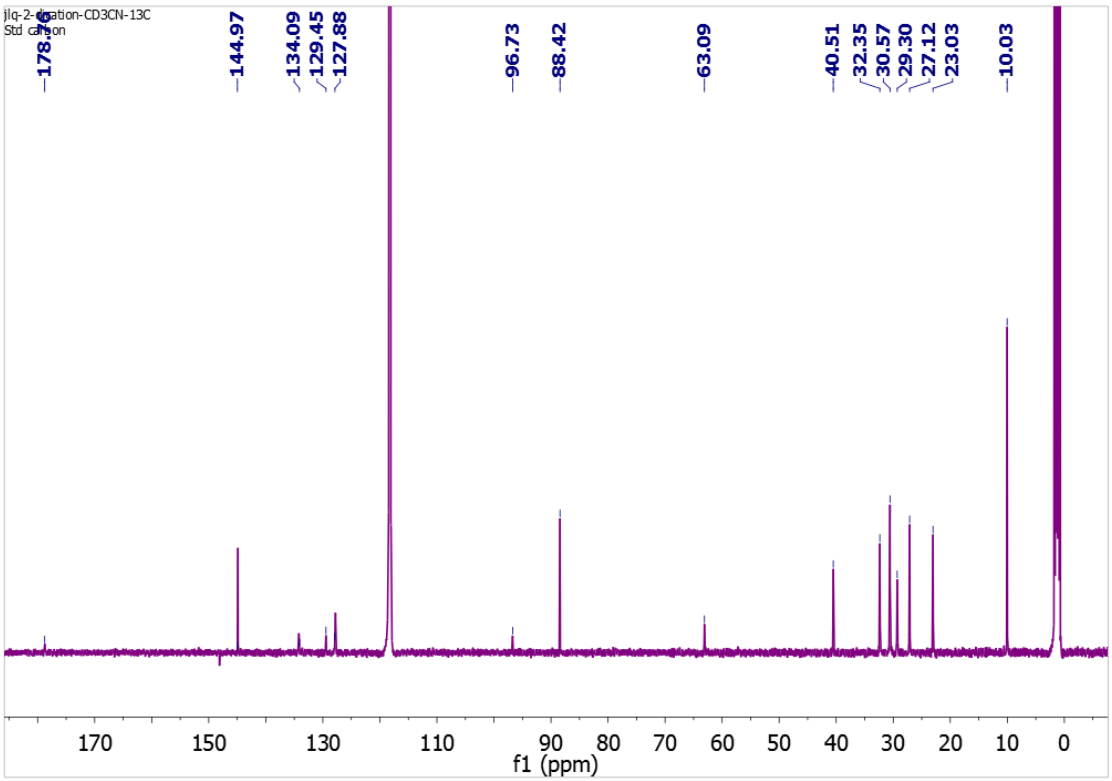
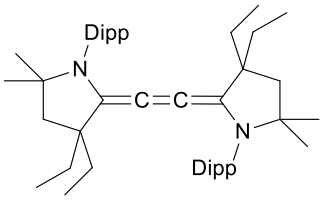


Figure S7. ^{13}C NMR of $\mathbf{2}^{++}$ in CD_3CN.



2

In a glovebox, zinc dust (15 mg, 0.23 mmol) was added to a solution of $\mathbf{2}^{+\bullet}$ (30 mg, 0.04 mmol) in THF (2 mL). The solution was stirred at room temperature for 10 min and then volatiles were removed under vacuum. The neutral product **2** was extracted with diethyl ether (2 x 10 mL). After evaporation of the solvent, **2** was recovered as yellow solid (15 mg, 56%). Single crystals were obtained by slow evaporation of a saturated diethyl ether solution.

^1H NMR (C_6D_6, 500 MHz) = 8.60 (b, 6H), 3.45 (sept, J = 6.8 Hz, 4H), 1.78 (s, 4H), 1.35 (d, J = 6.5 Hz, 12H), 1.27 (d, J = 7.0 Hz, 12H), 1.18 (s, 12H), 0.89 (t, J = 7.4 Hz, 12H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) = 150.9 (C_{ortho}), 141.0 (C_{quart}), 136.3 (C_{ipso}), 124.5 (C_{meta}), 63.9 (C_{quat}), 49.0 (C_{quat}), 46.2 (C_{H2}), 33.4 (C_{H2}), 30.7 (C_{H3}), 28.7 (C_H), 26.9 (C_{H3}), 24.4 (C_{H2}), 10.4 (C_{H3}).

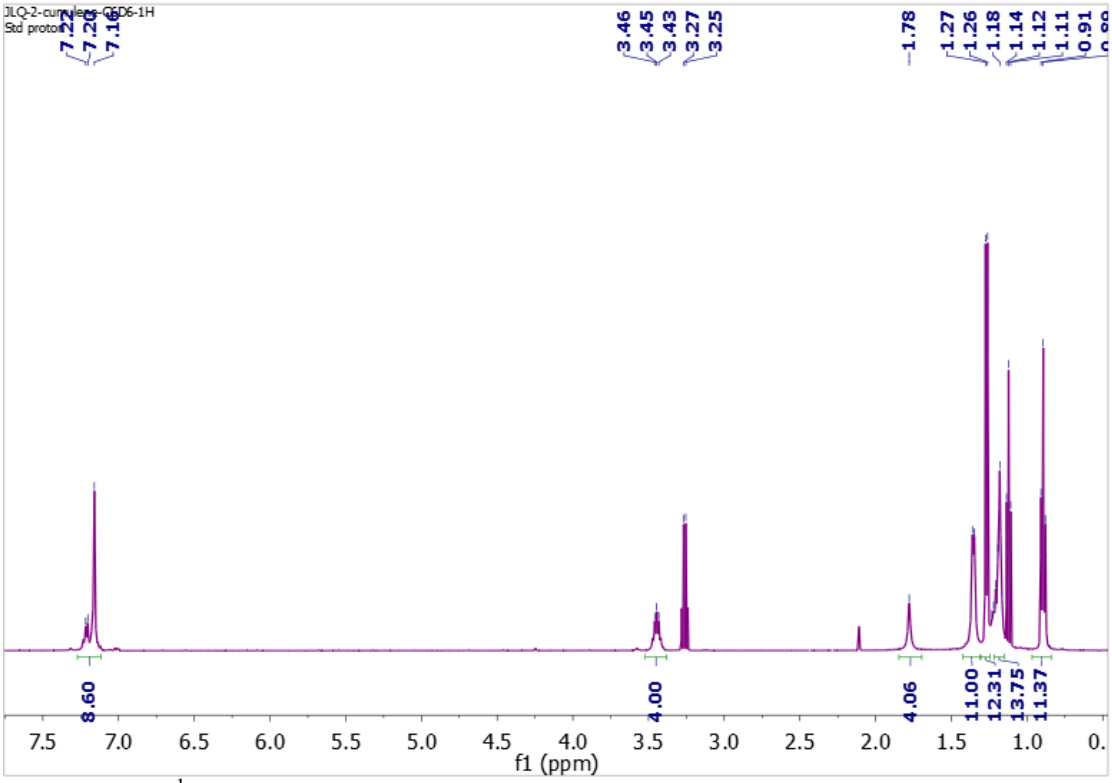


Figure S8. ^{1}H NMR of **2** in C_6D_6.

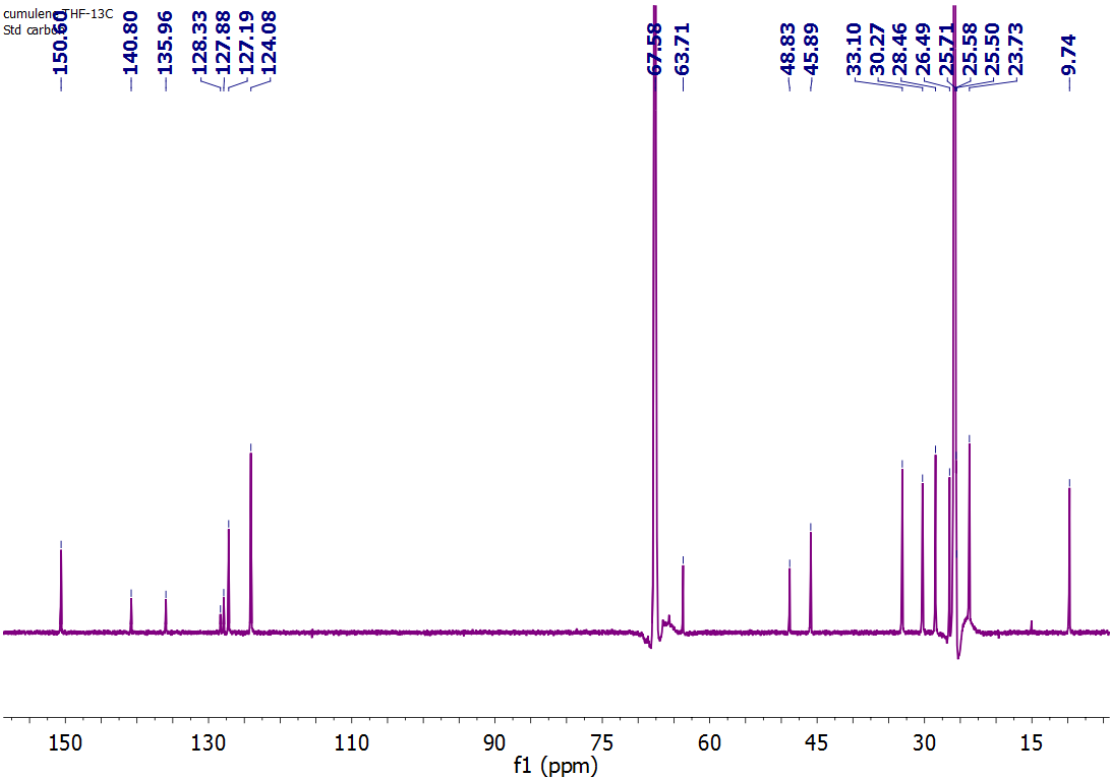


Figure S9. ^{13}C NMR of **2** in C_4H_8O.

2. Crystallographic details

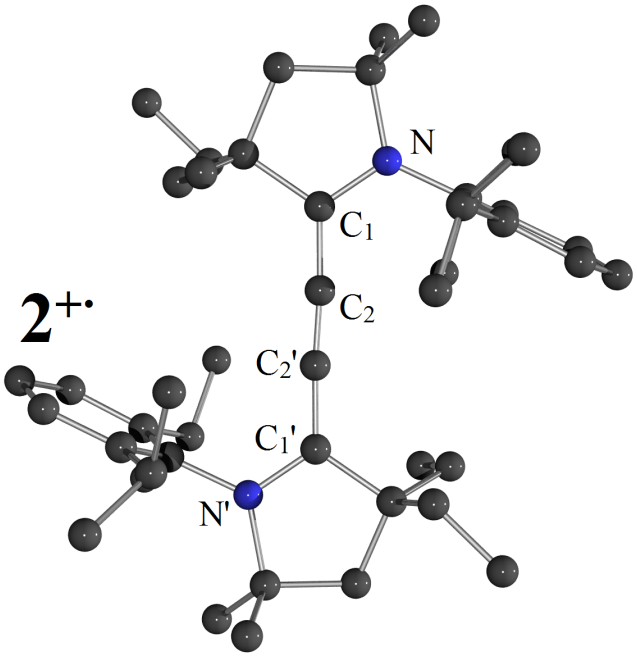


Figure S10 Structure of dication $\mathbf{2}^{+\bullet}$ in the solid state. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

Table S1 Crystal data and structure refinement for $\mathbf{2}^{+\bullet}$.

Empirical formula	C46 H73 Br N2 O	
Molecular formula	C46 H70 N2, 0.5(Br2 H6 O2)	
Formula weight	749.97	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.3761(9) Å	α= 90°.
	b = 13.3939(13) Å	β= 101.929(2)°.
	c = 16.9447(17) Å	γ = 90°.
Volume	2082.0(4) $Å^3$	
Z	2	
Density (calculated)	1.196 Mg/m^3	
Absorption coefficient	1.023 mm^{-1}	

F(000)	812
Crystal size	0.117 x 0.103 x 0.053 mm^3
Crystal color, habit	Red Plate
Theta range for data collection	1.955 to 26.510°.
Index ranges	-11<=h<=11, -16<=k<=15, -21<=l<=21
Reflections collected	20297
Independent reflections	4277 [R(int) = 0.0879]
Completeness to theta = 25.000°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6414
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4277 / 5 / 252
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1034
R indices (all data)	R1 = 0.0886, wR2 = 0.1123
Extinction coefficient	n/a
Largest diff. peak and hole	0.323 and -0.544 e.$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{2}^{+\bullet}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	10445(2)	1847(1)	4115(1)	12(1)
C(19)	6444(3)	1330(2)	4389(1)	23(1)
C(18)	7272(2)	2034(2)	3935(1)	16(1)
C(13)	7996(2)	1484(2)	3338(1)	14(1)
C(12)	9517(2)	1406(2)	3409(1)	13(1)
C(1)	10711(2)	1364(2)	4820(1)	12(1)
C(2)	10215(2)	416(2)	4925(1)	12(1)
C(17)	10138(2)	882(2)	2854(1)	13(1)
C(21)	11759(2)	706(2)	2952(1)	17(1)
C(23)	12329(3)	1045(2)	2213(1)	25(1)
C(20)	6249(3)	2855(2)	3518(1)	21(1)
C(14)	7121(3)	1020(2)	2674(1)	17(1)
C(15)	7713(3)	531(2)	2102(1)	18(1)
C(16)	9199(3)	464(2)	2190(1)	16(1)
C(5)	11112(2)	2877(2)	4160(1)	16(1)
C(11)	12416(3)	2926(2)	3755(2)	28(1)
C(4)	11582(3)	3014(2)	5076(1)	16(1)
C(3)	11677(2)	1978(2)	5477(1)	14(1)
C(8)	13222(2)	1523(2)	5637(1)	20(1)
C(9)	14407(3)	2173(2)	6134(2)	30(1)
C(10)	10001(3)	3650(2)	3774(2)	27(1)
C(22)	12133(3)	-385(2)	3132(2)	29(1)
C(6)	11088(3)	1956(2)	6258(1)	19(1)
C(7)	9608(3)	2433(2)	6217(2)	28(1)
Br(1)	4670(1)	5098(1)	4977(1)	34(1)
O(1S)	7815(5)	4423(3)	5126(2)	45(1)

Bond lengths [Å] and angles [°] for $\mathbf{2}^{+\bullet}$

N(1)-C(12)	1.452(3)	C(5)-C(10)	1.518(3)
N(1)-C(1)	1.336(3)	C(11)-H(11A)	0.9800
N(1)-C(5)	1.510(3)	C(11)-H(11B)	0.9800
C(19)-H(19A)	0.9800	C(11)-H(11C)	0.9800
C(19)-H(19B)	0.9800	C(4)-H(4A)	0.9900
C(19)-H(19C)	0.9800	C(4)-H(4B)	0.9900
C(19)-C(18)	1.526(3)	C(4)-C(3)	1.540(3)
C(18)-H(18)	1.0000	C(3)-C(8)	1.543(3)
C(18)-C(13)	1.520(3)	C(3)-C(6)	1.536(3)
C(18)-C(20)	1.533(3)	C(8)-H(8A)	0.9900
C(13)-C(12)	1.410(3)	C(8)-H(8B)	0.9900
C(13)-C(14)	1.394(3)	C(8)-C(9)	1.522(3)
C(12)-C(17)	1.394(3)	C(9)-H(9A)	0.9800
C(1)-C(2)	1.375(3)	C(9)-H(9B)	0.9800
C(1)-C(3)	1.523(3)	C(9)-H(9C)	0.9800
C(2)-C(2)#1	1.230(4)	C(10)-H(10A)	0.9800
C(17)-C(21)	1.513(3)	C(10)-H(10B)	0.9800
C(17)-C(16)	1.394(3)	C(10)-H(10C)	0.9800
C(21)-H(21)	1.0000	C(22)-H(22A)	0.9800
C(21)-C(23)	1.529(3)	C(22)-H(22B)	0.9800
C(21)-C(22)	1.519(3)	C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800	C(6)-H(6A)	0.9900
C(23)-H(23B)	0.9800	C(6)-H(6B)	0.9900
C(23)-H(23C)	0.9800	C(6)-C(7)	1.516(3)
C(20)-H(20A)	0.9800	C(7)-H(7A)	0.9800
C(20)-H(20B)	0.9800	C(7)-H(7B)	0.9800
C(20)-H(20C)	0.9800	C(7)-H(7C)	0.9800
C(14)-H(14)	0.9500	Br(1)-Br(1)#2	0.6623(15)
C(14)-C(15)	1.379(3)	O(1S)-H(1SB)	0.877(19)
C(15)-H(15)	0.9500	O(1S)-H(1S)	0.868(18)
C(15)-C(16)	1.373(3)	O(1S)-H(1SA)	0.896(19)
C(16)-H(16)	0.9500		
C(5)-C(11)	1.523(3)	C(12)-N(1)-C(5)	125.77(16)
C(5)-C(4)	1.533(3)	C(1)-N(1)-C(12)	120.64(18)

C(1)-N(1)-C(5)	113.48(17)	H(23A)-C(23)-H(23C)	109.5
H(19A)-C(19)-H(19B)	109.5	H(23B)-C(23)-H(23C)	109.5
H(19A)-C(19)-H(19C)	109.5	C(18)-C(20)-H(20A)	109.5
H(19B)-C(19)-H(19C)	109.5	C(18)-C(20)-H(20B)	109.5
C(18)-C(19)-H(19A)	109.5	C(18)-C(20)-H(20C)	109.5
C(18)-C(19)-H(19B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(18)-C(19)-H(19C)	109.5	H(20A)-C(20)-H(20C)	109.5
C(19)-C(18)-H(18)	107.7	H(20B)-C(20)-H(20C)	109.5
C(19)-C(18)-C(20)	109.9(2)	C(13)-C(14)-H(14)	119.2
C(13)-C(18)-C(19)	112.32(19)	C(15)-C(14)-C(13)	121.6(2)
C(13)-C(18)-H(18)	107.7	C(15)-C(14)-H(14)	119.2
C(13)-C(18)-C(20)	111.30(18)	C(14)-C(15)-H(15)	120.0
C(20)-C(18)-H(18)	107.7	C(16)-C(15)-C(14)	120.1(2)
C(12)-C(13)-C(18)	124.24(19)	C(16)-C(15)-H(15)	120.0
C(14)-C(13)-C(18)	118.9(2)	C(17)-C(16)-H(16)	119.4
C(14)-C(13)-C(12)	116.8(2)	C(15)-C(16)-C(17)	121.3(2)
C(13)-C(12)-N(1)	117.54(19)	C(15)-C(16)-H(16)	119.4
C(17)-C(12)-N(1)	119.9(2)	N(1)-C(5)-C(11)	112.26(18)
C(17)-C(12)-C(13)	122.42(19)	N(1)-C(5)-C(4)	100.98(16)
N(1)-C(1)-C(2)	123.81(19)	N(1)-C(5)-C(10)	111.18(18)
N(1)-C(1)-C(3)	111.39(19)	C(11)-C(5)-C(4)	111.19(19)
C(2)-C(1)-C(3)	124.76(18)	C(10)-C(5)-C(11)	108.6(2)
C(2)#1-C(2)-C(1)	175.5(3)	C(10)-C(5)-C(4)	112.53(19)
C(12)-C(17)-C(21)	123.64(19)	C(5)-C(11)-H(11A)	109.5
C(12)-C(17)-C(16)	117.7(2)	C(5)-C(11)-H(11B)	109.5
C(16)-C(17)-C(21)	118.6(2)	C(5)-C(11)-H(11C)	109.5
C(17)-C(21)-H(21)	107.8	H(11A)-C(11)-H(11B)	109.5
C(17)-C(21)-C(23)	112.14(18)	H(11A)-C(11)-H(11C)	109.5
C(17)-C(21)-C(22)	110.88(19)	H(11B)-C(11)-H(11C)	109.5
C(23)-C(21)-H(21)	107.8	C(5)-C(4)-H(4A)	110.0
C(22)-C(21)-H(21)	107.8	C(5)-C(4)-H(4B)	110.0
C(22)-C(21)-C(23)	110.2(2)	C(5)-C(4)-C(3)	108.47(17)
C(21)-C(23)-H(23A)	109.5	H(4A)-C(4)-H(4B)	108.4
C(21)-C(23)-H(23B)	109.5	C(3)-C(4)-H(4A)	110.0
C(21)-C(23)-H(23C)	109.5	C(3)-C(4)-H(4B)	110.0
H(23A)-C(23)-H(23B)	109.5	C(1)-C(3)-C(4)	101.12(16)

C(1)-C(3)-C(8)	108.03(18)	C(6)-C(7)-H(7B)	109.5
C(1)-C(3)-C(6)	110.76(19)	C(6)-C(7)-H(7C)	109.5
C(4)-C(3)-C(8)	113.60(19)	H(7A)-C(7)-H(7B)	109.5
C(6)-C(3)-C(4)	113.52(18)	H(7A)-C(7)-H(7C)	109.5
C(6)-C(3)-C(8)	109.42(17)	H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	108.5	H(1SB)-O(1S)-H(1S)	109(3)
C(3)-C(8)-H(8B)	108.5	H(1S)-O(1S)-H(1SA)	106(3)
H(8A)-C(8)-H(8B)	107.5		
C(9)-C(8)-C(3)	115.0(2)		
C(9)-C(8)-H(8A)	108.5		
C(9)-C(8)-H(8B)	108.5		
C(8)-C(9)-H(9A)	109.5		
C(8)-C(9)-H(9B)	109.5		
C(8)-C(9)-H(9C)	109.5		
H(9A)-C(9)-H(9B)	109.5		
H(9A)-C(9)-H(9C)	109.5		
H(9B)-C(9)-H(9C)	109.5		
C(5)-C(10)-H(10A)	109.5		
C(5)-C(10)-H(10B)	109.5		
C(5)-C(10)-H(10C)	109.5		
H(10A)-C(10)-H(10B)	109.5		
H(10A)-C(10)-H(10C)	109.5		
H(10B)-C(10)-H(10C)	109.5		
C(21)-C(22)-H(22A)	109.5		
C(21)-C(22)-H(22B)	109.5		
C(21)-C(22)-H(22C)	109.5		
H(22A)-C(22)-H(22B)	109.5		
H(22A)-C(22)-H(22C)	109.5		
H(22B)-C(22)-H(22C)	109.5		
C(3)-C(6)-H(6A)	108.2		
C(3)-C(6)-H(6B)	108.2		
H(6A)-C(6)-H(6B)	107.4		
C(7)-C(6)-C(3)	116.18(19)		
C(7)-C(6)-H(6A)	108.2		
C(7)-C(6)-H(6B)	108.2		
C(6)-C(7)-H(7A)	109.5		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1 #2 -x+1,-y+1,-z+1

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**$^{+\bullet}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	14(1)	10(1)	11(1)	2(1)	2(1)	-2(1)
C(19)	24(2)	24(1)	24(1)	3(1)	10(1)	3(1)
C(18)	16(1)	17(1)	17(1)	0(1)	6(1)	0(1)
C(13)	17(1)	10(1)	15(1)	4(1)	6(1)	0(1)
C(12)	14(1)	12(1)	11(1)	4(1)	2(1)	-2(1)
C(1)	12(1)	14(1)	14(1)	1(1)	6(1)	3(1)
C(2)	11(1)	18(1)	8(1)	0(1)	1(1)	3(1)
C(17)	14(1)	9(1)	17(1)	4(1)	6(1)	-1(1)
C(21)	13(1)	19(1)	19(1)	-1(1)	5(1)	2(1)
C(23)	20(2)	30(2)	27(1)	1(1)	13(1)	0(1)
C(20)	21(1)	21(1)	22(1)	1(1)	7(1)	4(1)
C(14)	12(1)	16(1)	21(1)	3(1)	2(1)	-2(1)
C(15)	20(1)	14(1)	17(1)	0(1)	-1(1)	-5(1)
C(16)	20(1)	13(1)	17(1)	1(1)	8(1)	-1(1)
C(5)	16(1)	12(1)	18(1)	2(1)	2(1)	-4(1)
C(11)	39(2)	23(1)	29(1)	-6(1)	18(1)	-15(1)
C(4)	18(1)	13(1)	16(1)	-1(1)	3(1)	-1(1)
C(3)	18(1)	10(1)	13(1)	1(1)	1(1)	0(1)
C(8)	19(1)	18(1)	19(1)	-1(1)	-1(1)	4(1)
C(9)	21(2)	28(2)	35(2)	-6(1)	-5(1)	5(1)
C(10)	30(2)	16(1)	29(1)	7(1)	-7(1)	-5(1)
C(22)	31(2)	22(1)	37(2)	4(1)	10(1)	10(1)
C(6)	26(2)	17(1)	14(1)	-1(1)	6(1)	-4(1)
C(7)	32(2)	27(2)	30(1)	-5(1)	20(1)	-4(1)
Br(1)	51(1)	32(1)	20(1)	-3(1)	9(1)	-17(1)
O(1S)	88(4)	19(2)	27(2)	-4(2)	10(2)	-9(2)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $\mathbf{2}^{+\bullet}$.

	x	y	z	U(eq)
H(19A)	5658	1002	4005	35
H(19B)	6029	1711	4781	35
H(19C)	7114	823	4672	35
H(18)	8058	2362	4341	19
H(21)	12267	1109	3424	20
H(23A)	11874	644	1744	37
H(23B)	13389	957	2315	37
H(23C)	12090	1751	2105	37
H(20A)	5390	2550	3175	31
H(20B)	6761	3265	3185	31
H(20C)	5942	3276	3926	31
H(14)	6092	1041	2615	20
H(15)	7092	239	1646	21
H(16)	9595	127	1791	20
H(11A)	13133	2420	3991	43
H(11B)	12861	3590	3836	43
H(11C)	12093	2799	3176	43
H(4A)	10864	3435	5277	19
H(4B)	12543	3350	5208	19
H(8A)	13200	878	5920	24
H(8B)	13485	1381	5112	24
H(9A)	14535	2776	5828	44
H(9B)	15325	1800	6256	44
H(9C)	14124	2363	6639	44
H(10A)	9631	3476	3207	40
H(10B)	10463	4309	3807	40
H(10C)	9191	3664	4058	40
H(22A)	11833	-579	3632	44
H(22B)	13187	-481	3196	44
H(22C)	11620	-800	2686	44

H(6A)	11033	1252	6425	22
H(6B)	11802	2297	6685	22
H(7A)	8913	2165	5753	42
H(7B)	9687	3157	6158	42
H(7C)	9267	2285	6713	42
H(1SB)	7670(60)	3850(20)	5350(30)	67
H(1S)	7000(30)	4750(40)	5020(40)	67
H(1SA)	8400(50)	4730(40)	4850(30)	67

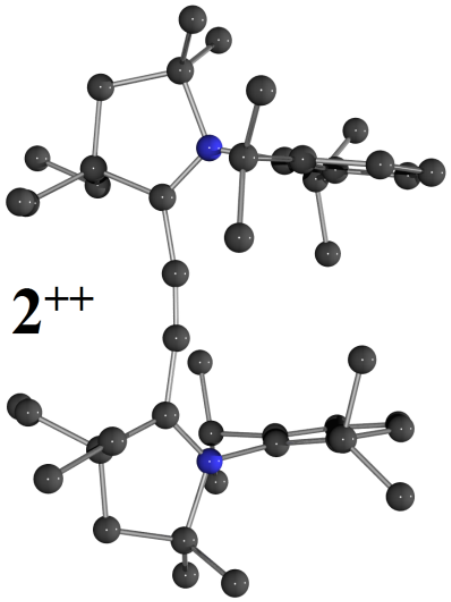


Figure S11 Structure of dication $\mathbf{2}^{++}$ in the solid state. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

Table S2 Crystal data and structure refinement for $\mathbf{2}^{++}$

Identification code	$\mathbf{2}^{++}$	
Empirical formula	C46 H70 Br6 N2	
Molecular formula	C46 H70 N2, 2(Br3)	
Formula weight	1130.50	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 14.2658(9) Å	α= 90°.

	b = 19.7423(12) Å	β= 104.823(2)°.
	c = 17.2861(13) Å	γ = 90°.
Volume	4706.4(5) $Å^3$	
Z	4	
Density (calculated)	1.595 Mg/m^3	
Absorption coefficient	5.151 mm^{-1}	
F(000)	2280	
Crystal size	0.121 x 0.109 x 0.067 mm^3	
Crystal color, habit	Yellow Plate	
Theta range for data collection	2.396 to 30.513°.	
Index ranges	-19<=h<=18, -27<=k<=26, -24<=l<=24	
Reflections collected	22939	
Independent reflections	6532 [R(int) = 0.0293]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0998 and 0.0604	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6532 / 0 / 253	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0520	
R indices (all data)	R1 = 0.0425, wR2 = 0.0565	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.531 and -0.368 $e.Å^{-3}$	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**$^{++}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	7029(1)	6715(1)	7460(1)	9(1)
C(1)	6324(1)	7144(1)	7282(1)	9(1)
C(2)	5396(1)	7032(1)	7443(1)	11(1)
C(3)	6544(1)	7775(1)	6862(1)	10(1)
C(4)	7655(1)	7710(1)	7002(1)	13(1)
C(5)	7945(1)	6972(1)	7231(1)	11(1)
C(6)	5979(1)	7700(1)	5970(1)	14(1)

C(7)	6148(1)	8283(1)	5438(1)	21(1)
C(8)	6236(1)	8426(1)	7224(1)	13(1)
C(9)	6607(1)	8490(1)	8131(1)	18(1)
C(10)	8118(1)	6553(1)	6536(1)	17(1)
C(11)	8820(1)	6908(1)	7944(1)	15(1)
C(12)	6988(1)	6043(1)	7806(1)	10(1)
C(13)	6668(1)	5501(1)	7278(1)	12(1)
C(14)	6720(1)	4857(1)	7622(1)	16(1)
C(15)	7070(1)	4761(1)	8433(1)	17(1)
C(16)	7358(1)	5308(1)	8940(1)	15(1)
C(17)	7314(1)	5968(1)	8639(1)	11(1)
C(18)	6212(1)	5582(1)	6388(1)	14(1)
C(19)	5120(1)	5434(1)	6208(1)	21(1)
C(20)	6680(1)	5122(1)	5876(1)	21(1)
C(21)	7560(1)	6557(1)	9224(1)	13(1)
C(22)	6781(1)	6636(1)	9687(1)	18(1)
C(23)	8560(1)	6462(1)	9806(1)	18(1)
Br(1)	5000	3467(1)	7500	21(1)
Br(2)	4720(1)	3429(1)	5982(1)	32(1)
Br(3)	9774(1)	5123(1)	5987(1)	24(1)
Br(4)	10000	5122(1)	7500	17(1)

Bond lengths

[Å] and angles [°] for **2**$^{++}$.

N(1)-C(1)	1.290(2)	C(4)-H(4B)	0.9900
N(1)-C(5)	1.545(2)	C(4)-C(5)	1.539(2)
N(1)-C(12)	1.463(2)	C(5)-C(10)	1.530(2)
C(1)-C(2)	1.437(2)	C(5)-C(11)	1.519(2)
C(1)-C(3)	1.516(2)	C(6)-H(6A)	0.9900
C(2)-C(2)#1	1.196(3)	C(6)-H(6B)	0.9900
C(3)-C(4)	1.546(2)	C(6)-C(7)	1.530(2)
C(3)-C(6)	1.553(2)	C(7)-H(7A)	0.9800
C(3)-C(8)	1.542(2)	C(7)-H(7B)	0.9800
C(4)-H(4A)	0.9900	C(7)-H(7C)	0.9800

C(8)-H(8A)	0.9900	C(22)-H(22B)	0.9800
C(8)-H(8B)	0.9900	C(22)-H(22C)	0.9800
C(8)-C(9)	1.525(2)	C(23)-H(23A)	0.9800
C(9)-H(9A)	0.9800	C(23)-H(23B)	0.9800
C(9)-H(9B)	0.9800	C(23)-H(23C)	0.9800
C(9)-H(9C)	0.9800	Br(1)-Br(2)#1	2.5531(3)
C(10)-H(10A)	0.9800	Br(1)-Br(2)	2.5531(3)
C(10)-H(10B)	0.9800	Br(3)-Br(4)	2.5523(3)
C(10)-H(10C)	0.9800	Br(4)-Br(3)#2	2.5522(3)
C(11)-H(11A)	0.9800		
C(11)-H(11B)	0.9800	C(1)-N(1)-C(5)	112.49(13)
C(11)-H(11C)	0.9800	C(1)-N(1)-C(12)	125.62(14)
C(12)-C(13)	1.405(2)	C(12)-N(1)-C(5)	121.84(13)
C(12)-C(17)	1.402(2)	N(1)-C(1)-C(2)	123.60(15)
C(13)-C(14)	1.398(2)	N(1)-C(1)-C(3)	114.15(14)
C(13)-C(18)	1.518(2)	C(2)-C(1)-C(3)	122.22(14)
C(14)-H(14)	0.9500	C(2)#1-C(2)-C(1)	170.99(10)
C(14)-C(15)	1.375(3)	C(1)-C(3)-C(4)	100.77(13)
C(15)-H(15)	0.9500	C(1)-C(3)-C(6)	106.21(13)
C(15)-C(16)	1.384(3)	C(1)-C(3)-C(8)	112.02(13)
C(16)-H(16)	0.9500	C(4)-C(3)-C(6)	113.51(14)
C(16)-C(17)	1.399(2)	C(8)-C(3)-C(4)	113.10(14)
C(17)-C(21)	1.521(2)	C(8)-C(3)-C(6)	110.66(13)
C(18)-H(18)	1.0000	C(3)-C(4)-H(4A)	110.0
C(18)-C(19)	1.537(2)	C(3)-C(4)-H(4B)	110.0
C(18)-C(20)	1.535(2)	H(4A)-C(4)-H(4B)	108.4
C(19)-H(19A)	0.9800	C(5)-C(4)-C(3)	108.40(13)
C(19)-H(19B)	0.9800	C(5)-C(4)-H(4A)	110.0
C(19)-H(19C)	0.9800	C(5)-C(4)-H(4B)	110.0
C(20)-H(20A)	0.9800	C(4)-C(5)-N(1)	100.83(12)
C(20)-H(20B)	0.9800	C(10)-C(5)-N(1)	109.89(13)
C(20)-H(20C)	0.9800	C(10)-C(5)-C(4)	113.41(14)
C(21)-H(21)	1.0000	C(11)-C(5)-N(1)	109.78(13)
C(21)-C(22)	1.534(2)	C(11)-C(5)-C(4)	113.49(14)
C(21)-C(23)	1.533(2)	C(11)-C(5)-C(10)	109.14(14)
C(22)-H(22A)	0.9800	C(3)-C(6)-H(6A)	108.8

C(3)-C(6)-H(6B)	108.8	C(17)-C(12)-N(1)	118.55(14)
H(6A)-C(6)-H(6B)	107.7	C(17)-C(12)-C(13)	123.72(15)
C(7)-C(6)-C(3)	113.79(14)	C(12)-C(13)-C(18)	124.26(15)
C(7)-C(6)-H(6A)	108.8	C(14)-C(13)-C(12)	116.24(16)
C(7)-C(6)-H(6B)	108.8	C(14)-C(13)-C(18)	119.33(15)
C(6)-C(7)-H(7A)	109.5	C(13)-C(14)-H(14)	119.2
C(6)-C(7)-H(7B)	109.5	C(15)-C(14)-C(13)	121.66(16)
C(6)-C(7)-H(7C)	109.5	C(15)-C(14)-H(14)	119.2
H(7A)-C(7)-H(7B)	109.5	C(14)-C(15)-H(15)	119.7
H(7A)-C(7)-H(7C)	109.5	C(14)-C(15)-C(16)	120.62(16)
H(7B)-C(7)-H(7C)	109.5	C(16)-C(15)-H(15)	119.7
C(3)-C(8)-H(8A)	108.5	C(15)-C(16)-H(16)	119.6
C(3)-C(8)-H(8B)	108.5	C(15)-C(16)-C(17)	120.89(17)
H(8A)-C(8)-H(8B)	107.5	C(17)-C(16)-H(16)	119.6
C(9)-C(8)-C(3)	115.25(14)	C(12)-C(17)-C(21)	124.21(15)
C(9)-C(8)-H(8A)	108.5	C(16)-C(17)-C(12)	116.79(15)
C(9)-C(8)-H(8B)	108.5	C(16)-C(17)-C(21)	118.90(15)
C(8)-C(9)-H(9A)	109.5	C(13)-C(18)-H(18)	108.2
C(8)-C(9)-H(9B)	109.5	C(13)-C(18)-C(19)	109.53(15)
C(8)-C(9)-H(9C)	109.5	C(13)-C(18)-C(20)	112.63(15)
H(9A)-C(9)-H(9B)	109.5	C(19)-C(18)-H(18)	108.2
H(9A)-C(9)-H(9C)	109.5	C(20)-C(18)-H(18)	108.2
H(9B)-C(9)-H(9C)	109.5	C(20)-C(18)-C(19)	109.82(14)
C(5)-C(10)-H(10A)	109.5	C(18)-C(19)-H(19A)	109.5
C(5)-C(10)-H(10B)	109.5	C(18)-C(19)-H(19B)	109.5
C(5)-C(10)-H(10C)	109.5	C(18)-C(19)-H(19C)	109.5
H(10A)-C(10)-H(10B)	109.5	H(19A)-C(19)-H(19B)	109.5
H(10A)-C(10)-H(10C)	109.5	H(19A)-C(19)-H(19C)	109.5
H(10B)-C(10)-H(10C)	109.5	H(19B)-C(19)-H(19C)	109.5
C(5)-C(11)-H(11A)	109.5	C(18)-C(20)-H(20A)	109.5
C(5)-C(11)-H(11B)	109.5	C(18)-C(20)-H(20B)	109.5
C(5)-C(11)-H(11C)	109.5	C(18)-C(20)-H(20C)	109.5
H(11A)-C(11)-H(11B)	109.5	H(20A)-C(20)-H(20B)	109.5
H(11A)-C(11)-H(11C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(11B)-C(11)-H(11C)	109.5	H(20B)-C(20)-H(20C)	109.5
C(13)-C(12)-N(1)	117.65(14)	C(17)-C(21)-H(21)	108.3

C(17)-C(21)-C(22)	110.52(14)
C(17)-C(21)-C(23)	111.17(14)
C(22)-C(21)-H(21)	108.3
C(23)-C(21)-H(21)	108.2
C(23)-C(21)-C(22)	110.30(15)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Br(2)-Br(1)-Br(2)#1	176.610(14)
Br(3)#2-Br(4)-Br(3)	179.881(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+2,y,-z+3/2

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $\mathbf{2}^{++}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	8(1)	10(1)	9(1)	-1(1)	3(1)	-1(1)
C(1)	9(1)	11(1)	7(1)	-2(1)	1(1)	-1(1)
C(2)	14(1)	8(1)	10(1)	-1(1)	2(1)	0(1)
C(3)	8(1)	11(1)	12(1)	2(1)	3(1)	0(1)
C(4)	9(1)	13(1)	19(1)	4(1)	5(1)	0(1)
C(5)	9(1)	13(1)	14(1)	1(1)	6(1)	-1(1)
C(6)	14(1)	16(1)	13(1)	1(1)	4(1)	0(1)
C(7)	22(1)	27(1)	14(1)	7(1)	3(1)	0(1)
C(8)	15(1)	10(1)	16(1)	0(1)	5(1)	1(1)
C(9)	22(1)	15(1)	18(1)	-3(1)	5(1)	-1(1)
C(10)	15(1)	21(1)	19(1)	-2(1)	10(1)	-1(1)
C(11)	9(1)	16(1)	20(1)	3(1)	4(1)	-1(1)
C(12)	7(1)	8(1)	14(1)	2(1)	4(1)	1(1)
C(13)	8(1)	12(1)	17(1)	-2(1)	5(1)	1(1)
C(14)	14(1)	11(1)	24(1)	-4(1)	7(1)	-1(1)
C(15)	17(1)	10(1)	26(1)	5(1)	9(1)	3(1)
C(16)	14(1)	15(1)	16(1)	3(1)	5(1)	2(1)
C(17)	8(1)	12(1)	14(1)	0(1)	4(1)	0(1)
C(18)	15(1)	13(1)	16(1)	-4(1)	4(1)	-1(1)
C(19)	14(1)	21(1)	25(1)	-7(1)	1(1)	1(1)
C(20)	20(1)	24(1)	20(1)	-10(1)	5(1)	-1(1)
C(21)	14(1)	14(1)	11(1)	1(1)	3(1)	0(1)
C(22)	19(1)	18(1)	16(1)	-2(1)	5(1)	0(1)
C(23)	16(1)	22(1)	14(1)	-1(1)	-1(1)	2(1)
Br(1)	12(1)	11(1)	40(1)	0	9(1)	0
Br(2)	38(1)	21(1)	38(1)	2(1)	13(1)	2(1)
Br(3)	32(1)	22(1)	19(1)	-2(1)	8(1)	-4(1)

Br(4)	19(1)	12(1)	20(1)	0	5(1)	0

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**$^{++}$.

	x	y	z	U(eq)
H(4A)	7847	7835	6509	16
H(4B)	7989	8019	7437	16
H(6A)	6172	7270	5760	17
H(6B)	5277	7672	5938	17
H(7A)	5905	8706	5611	32
H(7B)	5805	8190	4881	32
H(7C)	6844	8326	5481	32
H(8A)	6469	8821	6974	16
H(8B)	5519	8447	7082	16
H(9A)	6366	8109	8388	28
H(9B)	6375	8916	8306	28
H(9C)	7317	8487	8280	28
H(10A)	8210	6076	6697	26
H(10B)	8699	6719	6394	26
H(10C)	7557	6594	6074	26
H(11A)	8713	7176	8391	23
H(11B)	9398	7075	7798	23
H(11C)	8913	6432	8105	23
H(14)	6509	4476	7288	19
H(15)	7113	4316	8648	21
H(16)	7590	5234	9499	18
H(18)	6297	6063	6238	17
H(19A)	5021	4958	6327	31
H(19B)	4816	5524	5641	31
H(19C)	4826	5725	6540	31
H(20A)	7385	5185	6032	32
H(20B)	6429	5239	5310	32

H(20C)	6526	4648	5959	32
H(21)	7573	6981	8911	15
H(22A)	6154	6732	9311	26
H(22B)	6957	7011	10069	26
H(22C)	6734	6216	9977	26
H(23A)	8534	6089	10174	28
H(23B)	8749	6880	10113	28
H(23C)	9038	6357	9504	28

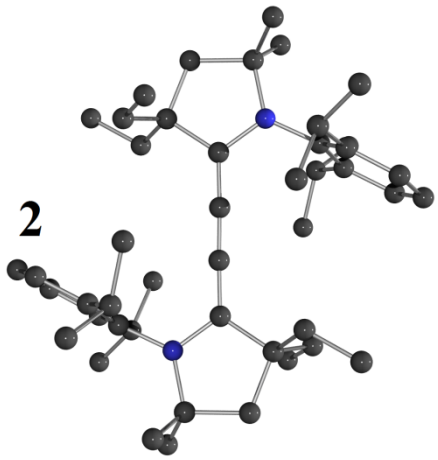


Figure S12 Structure of cumulene **2** in the solid state. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity

Table S3 Crystal data and structure refinement for **2**

Identification code	**2**	
Empirical formula	C46 H70 N2	
Molecular formula	C46 H70 N2	
Formula weight	651.04	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5494(5) Å	α= 86.558(2)°.
	b = 12.1924(6) Å	β= 84.548(2)°.
	c = 17.6614(8) Å	γ = 76.620(2)°.
Volume	1989.92(17) Å^3	

Z	2
Density (calculated)	1.087 Mg/m^3
Absorption coefficient	0.061 mm^{-1}
F(000)	720
Crystal size	0.174 x 0.121 x 0.115 mm^3
Crystal color, habit	Colorless Block
Theta range for data collection	2.035 to 25.364°.
Index ranges	-11<=h<=11, -13<=k<=14, -21<=l<=21
Reflections collected	24096
Independent reflections	7306 [R(int) = 0.0273]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6868
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7306 / 0 / 449
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0910
R indices (all data)	R1 = 0.0467, wR2 = 0.0956
Extinction coefficient	n/a
Largest diff. peak and hole	0.250 and -0.197 e.$Å^{-3}$

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	901(1)	2633(1)	646(1)	14(1)
C(1)	783(1)	3781(1)	726(1)	13(1)
C(2)	234(1)	4594(1)	228(1)	14(1)
C(3)	1391(1)	3980(1)	1457(1)	15(1)
C(4)	1972(1)	2765(1)	1779(1)	20(1)
C(5)	1576(1)	1902(1)	1278(1)	16(1)
C(6)	203(1)	4716(1)	1983(1)	18(1)
C(7)	-1084(2)	4211(1)	2246(1)	26(1)
C(8)	2626(1)	4599(1)	1254(1)	20(1)
C(9)	3453(2)	4765(1)	1921(1)	31(1)

C(10)	537(2)	1258(1)	1717(1)	26(1)
C(11)	2920(2)	1031(1)	995(1)	25(1)
C(12)	582(1)	2274(1)	-63(1)	13(1)
C(13)	-808(1)	2098(1)	-140(1)	16(1)
C(14)	-1121(1)	1822(1)	-850(1)	20(1)
C(15)	-119(1)	1741(1)	-1473(1)	21(1)
C(16)	1229(1)	1942(1)	-1397(1)	19(1)
C(17)	1600(1)	2218(1)	-700(1)	15(1)
C(18)	-1988(1)	2252(1)	512(1)	19(1)
C(19)	-3216(1)	3275(1)	359(1)	26(1)
C(20)	-2579(2)	1187(1)	677(1)	27(1)
C(21)	3072(1)	2489(1)	-665(1)	18(1)
C(22)	3177(1)	3579(1)	-1120(1)	23(1)
C(23)	4303(1)	1508(1)	-936(1)	25(1)
N(1A)	5515(1)	2318(1)	4688(1)	14(1)
C(1A)	5271(1)	392(1)	4843(1)	14(1)
C(2A)	5891(1)	1188(1)	4505(1)	13(1)
C(3A)	7152(1)	984(1)	3896(1)	14(1)
C(4A)	7505(1)	2162(1)	3764(1)	18(1)
C(5A)	6427(1)	3026(1)	4265(1)	17(1)
C(6A)	8396(1)	101(1)	4229(1)	18(1)
C(7A)	9790(1)	-212(1)	3713(1)	24(1)
C(8A)	6753(1)	537(1)	3165(1)	17(1)
C(9A)	5458(1)	1276(1)	2800(1)	22(1)
C(10A)	7220(2)	3575(1)	4794(1)	27(1)
C(11A)	5526(2)	3971(1)	3787(1)	28(1)
C(12A)	4404(1)	2671(1)	5288(1)	14(1)
C(13A)	4740(1)	2559(1)	6052(1)	16(1)
C(14A)	3625(1)	2867(1)	6620(1)	20(1)
C(15A)	2201(1)	3238(1)	6453(1)	21(1)
C(16A)	1874(1)	3301(1)	5705(1)	19(1)
C(17A)	2947(1)	3019(1)	5113(1)	15(1)
C(18A)	6251(1)	2050(1)	6292(1)	18(1)
C(19A)	6282(1)	927(1)	6735(1)	21(1)
C(20A)	6796(2)	2852(1)	6770(1)	26(1)
C(21A)	2501(1)	3033(1)	4309(1)	18(1)

C(22A)	1746(1)	2072(1)	4218(1)	21(1)
C(23A)	1532(2)	4165(1)	4080(1)	26(1)

Bond lengths [Å] and angles [°] for **2**

N(1)-C(1)	1.3923(15)	C(11)-H(11C)	0.9800
N(1)-C(5)	1.4854(15)	C(12)-C(13)	1.4120(16)
N(1)-C(12)	1.4342(14)	C(12)-C(17)	1.4092(16)
C(1)-C(2)	1.3316(16)	C(13)-C(14)	1.3936(17)
C(1)-C(3)	1.5189(16)	C(13)-C(18)	1.5204(17)
C(2)-C(2)#1	1.264(2)	C(14)-H(14)	0.9500
C(3)-C(4)	1.5506(16)	C(14)-C(15)	1.3809(18)
C(3)-C(6)	1.5436(16)	C(15)-H(15)	0.9500
C(3)-C(8)	1.5450(16)	C(15)-C(16)	1.3854(18)
C(4)-H(4A)	0.9900	C(16)-H(16)	0.9500
C(4)-H(4B)	0.9900	C(16)-C(17)	1.3933(17)
C(4)-C(5)	1.5479(16)	C(17)-C(21)	1.5241(16)
C(5)-C(10)	1.5303(17)	C(18)-H(18)	1.0000
C(5)-C(11)	1.5284(17)	C(18)-C(19)	1.5323(18)
C(6)-H(6A)	0.9900	C(18)-C(20)	1.5331(17)
C(6)-H(6B)	0.9900	C(19)-H(19A)	0.9800
C(6)-C(7)	1.5206(18)	C(19)-H(19B)	0.9800
C(7)-H(7A)	0.9800	C(19)-H(19C)	0.9800
C(7)-H(7B)	0.9800	C(20)-H(20A)	0.9800
C(7)-H(7C)	0.9800	C(20)-H(20B)	0.9800
C(8)-H(8A)	0.9900	C(20)-H(20C)	0.9800
C(8)-H(8B)	0.9900	C(21)-H(21)	1.0000
C(8)-C(9)	1.5276(18)	C(21)-C(22)	1.5294(17)
C(9)-H(9A)	0.9800	C(21)-C(23)	1.5341(17)
C(9)-H(9B)	0.9800	C(22)-H(22A)	0.9800
C(9)-H(9C)	0.9800	C(22)-H(22B)	0.9800
C(10)-H(10A)	0.9800	C(22)-H(22C)	0.9800
C(10)-H(10B)	0.9800	C(23)-H(23A)	0.9800
C(10)-H(10C)	0.9800	C(23)-H(23B)	0.9800
C(11)-H(11A)	0.9800	C(23)-H(23C)	0.9800
C(11)-H(11B)	0.9800	N(1A)-C(2A)	1.3906(15)

N(1A)-C(5A)	1.4866(15)	C(15A)-H(15A)	0.9500
N(1A)-C(12A)	1.4356(15)	C(15A)-C(16A)	1.3797(18)
C(1A)-C(1A)#2	1.266(2)	C(16A)-H(16A)	0.9500
C(1A)-C(2A)	1.3328(16)	C(16A)-C(17A)	1.3922(17)
C(2A)-C(3A)	1.5231(16)	C(17A)-C(21A)	1.5183(16)
C(3A)-C(4A)	1.5489(16)	C(18A)-H(18A)	1.0000
C(3A)-C(6A)	1.5428(17)	C(18A)-C(19A)	1.5303(17)
C(3A)-C(8A)	1.5430(16)	C(18A)-C(20A)	1.5352(17)
C(4A)-H(4AA)	0.9900	C(19A)-H(19D)	0.9800
C(4A)-H(4AB)	0.9900	C(19A)-H(19E)	0.9800
C(4A)-C(5A)	1.5459(16)	C(19A)-H(19F)	0.9800
C(5A)-C(10A)	1.5287(17)	C(20A)-H(20D)	0.9800
C(5A)-C(11A)	1.5295(18)	C(20A)-H(20E)	0.9800
C(6A)-H(6AA)	0.9900	C(20A)-H(20F)	0.9800
C(6A)-H(6AB)	0.9900	C(21A)-H(21A)	1.0000
C(6A)-C(7A)	1.5242(17)	C(21A)-C(22A)	1.5334(17)
C(7A)-H(7AA)	0.9800	C(21A)-C(23A)	1.5295(18)
C(7A)-H(7AB)	0.9800	C(22A)-H(22D)	0.9800
C(7A)-H(7AC)	0.9800	C(22A)-H(22E)	0.9800
C(8A)-H(8AA)	0.9900	C(22A)-H(22F)	0.9800
C(8A)-H(8AB)	0.9900	C(23A)-H(23D)	0.9800
C(8A)-C(9A)	1.5241(17)	C(23A)-H(23E)	0.9800
C(9A)-H(9AA)	0.9800	C(23A)-H(23F)	0.9800
C(9A)-H(9AB)	0.9800		
C(9A)-H(9AC)	0.9800	C(1)-N(1)-C(5)	114.23(9)
C(10A)-H(10D)	0.9800	C(1)-N(1)-C(12)	118.17(9)
C(10A)-H(10E)	0.9800	C(12)-N(1)-C(5)	126.86(9)
C(10A)-H(10F)	0.9800	N(1)-C(1)-C(3)	110.56(9)
C(11A)-H(11D)	0.9800	C(2)-C(1)-N(1)	124.97(10)
C(11A)-H(11E)	0.9800	C(2)-C(1)-C(3)	124.46(10)
C(11A)-H(11F)	0.9800	C(2)#1-C(2)-C(1)	176.07(16)
C(12A)-C(13A)	1.4080(16)	C(1)-C(3)-C(4)	102.81(9)
C(12A)-C(17A)	1.4155(17)	C(1)-C(3)-C(6)	110.18(9)
C(13A)-C(14A)	1.3928(17)	C(1)-C(3)-C(8)	108.65(9)
C(13A)-C(18A)	1.5229(17)	C(6)-C(3)-C(4)	114.43(10)
C(14A)-H(14A)	0.9500	C(6)-C(3)-C(8)	109.17(10)
C(14A)-C(15A)	1.3845(18)	C(8)-C(3)-C(4)	111.34(10)

C(3)-C(4)-H(4A)	109.7	C(5)-C(10)-H(10B)	109.5
C(3)-C(4)-H(4B)	109.7	C(5)-C(10)-H(10C)	109.5
H(4A)-C(4)-H(4B)	108.2	H(10A)-C(10)-H(10B)	109.5
C(5)-C(4)-C(3)	109.87(9)	H(10A)-C(10)-H(10C)	109.5
C(5)-C(4)-H(4A)	109.7	H(10B)-C(10)-H(10C)	109.5
C(5)-C(4)-H(4B)	109.7	C(5)-C(11)-H(11A)	109.5
N(1)-C(5)-C(4)	102.27(9)	C(5)-C(11)-H(11B)	109.5
N(1)-C(5)-C(10)	112.26(10)	C(5)-C(11)-H(11C)	109.5
N(1)-C(5)-C(11)	112.13(10)	H(11A)-C(11)-H(11B)	109.5
C(10)-C(5)-C(4)	111.67(10)	H(11A)-C(11)-H(11C)	109.5
C(11)-C(5)-C(4)	111.14(10)	H(11B)-C(11)-H(11C)	109.5
C(11)-C(5)-C(10)	107.42(10)	C(13)-C(12)-N(1)	119.58(10)
C(3)-C(6)-H(6A)	108.4	C(17)-C(12)-N(1)	119.69(10)
C(3)-C(6)-H(6B)	108.4	C(17)-C(12)-C(13)	120.37(10)
H(6A)-C(6)-H(6B)	107.4	C(12)-C(13)-C(18)	122.41(10)
C(7)-C(6)-C(3)	115.58(10)	C(14)-C(13)-C(12)	118.46(11)
C(7)-C(6)-H(6A)	108.4	C(14)-C(13)-C(18)	119.07(11)
C(7)-C(6)-H(6B)	108.4	C(13)-C(14)-H(14)	119.2
C(6)-C(7)-H(7A)	109.5	C(15)-C(14)-C(13)	121.53(11)
C(6)-C(7)-H(7B)	109.5	C(15)-C(14)-H(14)	119.2
C(6)-C(7)-H(7C)	109.5	C(14)-C(15)-H(15)	120.2
H(7A)-C(7)-H(7B)	109.5	C(14)-C(15)-C(16)	119.61(11)
H(7A)-C(7)-H(7C)	109.5	C(16)-C(15)-H(15)	120.2
H(7B)-C(7)-H(7C)	109.5	C(15)-C(16)-H(16)	119.4
C(3)-C(8)-H(8A)	108.4	C(15)-C(16)-C(17)	121.19(11)
C(3)-C(8)-H(8B)	108.4	C(17)-C(16)-H(16)	119.4
H(8A)-C(8)-H(8B)	107.5	C(12)-C(17)-C(21)	122.66(10)
C(9)-C(8)-C(3)	115.30(10)	C(16)-C(17)-C(12)	118.78(11)
C(9)-C(8)-H(8A)	108.4	C(16)-C(17)-C(21)	118.52(10)
C(9)-C(8)-H(8B)	108.4	C(13)-C(18)-H(18)	107.6
C(8)-C(9)-H(9A)	109.5	C(13)-C(18)-C(19)	111.48(10)
C(8)-C(9)-H(9B)	109.5	C(13)-C(18)-C(20)	111.76(10)
C(8)-C(9)-H(9C)	109.5	C(19)-C(18)-H(18)	107.6
H(9A)-C(9)-H(9B)	109.5	C(19)-C(18)-C(20)	110.50(11)
H(9A)-C(9)-H(9C)	109.5	C(20)-C(18)-H(18)	107.6
H(9B)-C(9)-H(9C)	109.5	C(18)-C(19)-H(19A)	109.5
C(5)-C(10)-H(10A)	109.5	C(18)-C(19)-H(19B)	109.5

C(18)-C(19)-H(19C)	109.5	C(2A)-C(3A)-C(8A)	112.04(9)
H(19A)-C(19)-H(19B)	109.5	C(6A)-C(3A)-C(4A)	112.44(10)
H(19A)-C(19)-H(19C)	109.5	C(8A)-C(3A)-C(4A)	112.57(9)
H(19B)-C(19)-H(19C)	109.5	C(8A)-C(3A)-C(6A)	109.21(9)
C(18)-C(20)-H(20A)	109.5	C(3A)-C(4A)-H(4AA)	109.7
C(18)-C(20)-H(20B)	109.5	C(3A)-C(4A)-H(4AB)	109.7
C(18)-C(20)-H(20C)	109.5	H(4AA)-C(4A)-H(4AB)	108.2
H(20A)-C(20)-H(20B)	109.5	C(5A)-C(4A)-C(3A)	109.88(9)
H(20A)-C(20)-H(20C)	109.5	C(5A)-C(4A)-H(4AA)	109.7
H(20B)-C(20)-H(20C)	109.5	C(5A)-C(4A)-H(4AB)	109.7
C(17)-C(21)-H(21)	107.7	N(1A)-C(5A)-C(4A)	102.47(9)
C(17)-C(21)-C(22)	111.45(10)	N(1A)-C(5A)-C(10A)	112.38(10)
C(17)-C(21)-C(23)	111.51(10)	N(1A)-C(5A)-C(11A)	111.45(10)
C(22)-C(21)-H(21)	107.7	C(10A)-C(5A)-C(4A)	110.91(10)
C(22)-C(21)-C(23)	110.62(10)	C(10A)-C(5A)-C(11A)	107.61(11)
C(23)-C(21)-H(21)	107.7	C(11A)-C(5A)-C(4A)	112.06(10)
C(21)-C(22)-H(22A)	109.5	C(3A)-C(6A)-H(6AA)	108.2
C(21)-C(22)-H(22B)	109.5	C(3A)-C(6A)-H(6AB)	108.2
C(21)-C(22)-H(22C)	109.5	H(6AA)-C(6A)-H(6AB)	107.4
H(22A)-C(22)-H(22B)	109.5	C(7A)-C(6A)-C(3A)	116.18(10)
H(22A)-C(22)-H(22C)	109.5	C(7A)-C(6A)-H(6AA)	108.2
H(22B)-C(22)-H(22C)	109.5	C(7A)-C(6A)-H(6AB)	108.2
C(21)-C(23)-H(23A)	109.5	C(6A)-C(7A)-H(7AA)	109.5
C(21)-C(23)-H(23B)	109.5	C(6A)-C(7A)-H(7AB)	109.5
C(21)-C(23)-H(23C)	109.5	C(6A)-C(7A)-H(7AC)	109.5
H(23A)-C(23)-H(23B)	109.5	H(7AA)-C(7A)-H(7AB)	109.5
H(23A)-C(23)-H(23C)	109.5	H(7AA)-C(7A)-H(7AC)	109.5
H(23B)-C(23)-H(23C)	109.5	H(7AB)-C(7A)-H(7AC)	109.5
C(2A)-N(1A)-C(5A)	114.23(9)	C(3A)-C(8A)-H(8AA)	108.4
C(2A)-N(1A)-C(12A)	119.00(9)	C(3A)-C(8A)-H(8AB)	108.4
C(12A)-N(1A)-C(5A)	126.58(9)	H(8AA)-C(8A)-H(8AB)	107.4
C(1A)#2-C(1A)-C(2A)	177.74(16)	C(9A)-C(8A)-C(3A)	115.58(10)
N(1A)-C(2A)-C(3A)	110.43(9)	C(9A)-C(8A)-H(8AA)	108.4
C(1A)-C(2A)-N(1A)	124.46(10)	C(9A)-C(8A)-H(8AB)	108.4
C(1A)-C(2A)-C(3A)	125.05(10)	C(8A)-C(9A)-H(9AA)	109.5
C(2A)-C(3A)-C(4A)	102.94(9)	C(8A)-C(9A)-H(9AB)	109.5
C(2A)-C(3A)-C(6A)	107.44(9)	C(8A)-C(9A)-H(9AC)	109.5

H(9AA)-C(9A)-H(9AB)	109.5
H(9AA)-C(9A)-H(9AC)	109.5
H(9AB)-C(9A)-H(9AC)	109.5
C(5A)-C(10A)-H(10D)	109.5
C(5A)-C(10A)-H(10E)	109.5
C(5A)-C(10A)-H(10F)	109.5
H(10D)-C(10A)-H(10E)	109.5
H(10D)-C(10A)-H(10F)	109.5
H(10E)-C(10A)-H(10F)	109.5
C(5A)-C(11A)-H(11D)	109.5
C(5A)-C(11A)-H(11E)	109.5
C(5A)-C(11A)-H(11F)	109.5
H(11D)-C(11A)-H(11E)	109.5
H(11D)-C(11A)-H(11F)	109.5
H(11E)-C(11A)-H(11F)	109.5
C(13A)-C(12A)-N(1A)	120.19(10)
C(13A)-C(12A)-C(17A)	120.01(10)
C(17A)-C(12A)-N(1A)	119.46(10)
C(12A)-C(13A)-C(18A)	123.20(10)
C(14A)-C(13A)-C(12A)	118.63(11)
C(14A)-C(13A)-C(18A)	118.06(11)
C(13A)-C(14A)-H(14A)	119.2
C(15A)-C(14A)-C(13A)	121.66(11)
C(15A)-C(14A)-H(14A)	119.2
C(14A)-C(15A)-H(15A)	120.3
C(16A)-C(15A)-C(14A)	119.31(11)
C(16A)-C(15A)-H(15A)	120.3
C(15A)-C(16A)-H(16A)	119.3
C(15A)-C(16A)-C(17A)	121.49(11)
C(17A)-C(16A)-H(16A)	119.3
C(12A)-C(17A)-C(21A)	122.49(10)
C(16A)-C(17A)-C(12A)	118.78(11)
C(16A)-C(17A)-C(21A)	118.64(11)
C(13A)-C(18A)-H(18A)	108.1
C(13A)-C(18A)-C(19A)	110.25(10)
C(13A)-C(18A)-C(20A)	112.23(10)
C(19A)-C(18A)-H(18A)	108.1
C(19A)-C(18A)-C(20A)	110.01(10)
C(20A)-C(18A)-H(18A)	108.1
C(18A)-C(19A)-H(19D)	109.5
C(18A)-C(19A)-H(19E)	109.5
C(18A)-C(19A)-H(19F)	109.5
H(19D)-C(19A)-H(19E)	109.5
H(19D)-C(19A)-H(19F)	109.5
H(19E)-C(19A)-H(19F)	109.5
C(18A)-C(20A)-H(20D)	109.5
C(18A)-C(20A)-H(20E)	109.5
C(18A)-C(20A)-H(20F)	109.5
H(20D)-C(20A)-H(20E)	109.5
H(20D)-C(20A)-H(20F)	109.5
H(20E)-C(20A)-H(20F)	109.5
C(17A)-C(21A)-H(21A)	107.8
C(17A)-C(21A)-C(22A)	110.86(10)
C(17A)-C(21A)-C(23A)	112.14(10)
C(22A)-C(21A)-H(21A)	107.8
C(23A)-C(21A)-H(21A)	107.8
C(23A)-C(21A)-C(22A)	110.14(10)
C(21A)-C(22A)-H(22D)	109.5
C(21A)-C(22A)-H(22E)	109.5
C(21A)-C(22A)-H(22F)	109.5
H(22D)-C(22A)-H(22E)	109.5
H(22D)-C(22A)-H(22F)	109.5
H(22E)-C(22A)-H(22F)	109.5
C(21A)-C(23A)-H(23D)	109.5
C(21A)-C(23A)-H(23E)	109.5
C(21A)-C(23A)-H(23F)	109.5
H(23D)-C(23A)-H(23E)	109.5
H(23D)-C(23A)-H(23F)	109.5
H(23E)-C(23A)-H(23F)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -x+1,-y,-z+1

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	17(1)	11(1)	13(1)	0(1)	-4(1)	-3(1)
C(1)	12(1)	13(1)	13(1)	-1(1)	1(1)	-4(1)
C(2)	16(1)	14(1)	13(1)	-5(1)	0(1)	-5(1)
C(3)	18(1)	14(1)	14(1)	0(1)	-4(1)	-4(1)
C(4)	27(1)	17(1)	17(1)	0(1)	-8(1)	-3(1)
C(5)	21(1)	14(1)	16(1)	1(1)	-6(1)	-3(1)
C(6)	23(1)	16(1)	14(1)	-2(1)	-2(1)	-5(1)
C(7)	28(1)	24(1)	25(1)	-3(1)	8(1)	-8(1)
C(8)	19(1)	23(1)	21(1)	-3(1)	-3(1)	-8(1)
C(9)	32(1)	36(1)	32(1)	-4(1)	-10(1)	-19(1)
C(10)	33(1)	23(1)	25(1)	10(1)	-9(1)	-11(1)
C(11)	29(1)	20(1)	22(1)	-1(1)	-8(1)	5(1)
C(12)	17(1)	9(1)	14(1)	-1(1)	-4(1)	-2(1)
C(13)	18(1)	12(1)	18(1)	-1(1)	-3(1)	-4(1)
C(14)	19(1)	20(1)	23(1)	-2(1)	-6(1)	-7(1)
C(15)	27(1)	22(1)	16(1)	-4(1)	-7(1)	-6(1)
C(16)	22(1)	18(1)	16(1)	-2(1)	1(1)	-3(1)
C(17)	18(1)	10(1)	17(1)	0(1)	-2(1)	-2(1)
C(18)	17(1)	22(1)	19(1)	-2(1)	-1(1)	-8(1)
C(19)	20(1)	30(1)	28(1)	-4(1)	0(1)	-3(1)
C(20)	28(1)	30(1)	27(1)	0(1)	1(1)	-16(1)
C(21)	16(1)	21(1)	18(1)	-2(1)	0(1)	-5(1)
C(22)	21(1)	24(1)	24(1)	-2(1)	4(1)	-8(1)
C(23)	18(1)	27(1)	28(1)	-4(1)	1(1)	-3(1)
N(1A)	14(1)	12(1)	16(1)	-2(1)	2(1)	-5(1)
C(1A)	13(1)	14(1)	14(1)	-4(1)	1(1)	-1(1)
C(2A)	13(1)	13(1)	13(1)	-1(1)	-3(1)	-4(1)
C(3A)	14(1)	15(1)	14(1)	-1(1)	1(1)	-5(1)
C(4A)	17(1)	18(1)	19(1)	-1(1)	2(1)	-8(1)

C(5A)	16(1)	16(1)	20(1)	0(1)	2(1)	-8(1)
C(6A)	16(1)	21(1)	17(1)	-1(1)	-1(1)	-2(1)
C(7A)	16(1)	28(1)	25(1)	-2(1)	0(1)	0(1)
C(8A)	18(1)	19(1)	15(1)	-3(1)	0(1)	-6(1)
C(9A)	24(1)	25(1)	19(1)	-1(1)	-5(1)	-7(1)
C(10A)	32(1)	28(1)	28(1)	-8(1)	6(1)	-20(1)
C(11A)	23(1)	20(1)	37(1)	9(1)	5(1)	-5(1)
C(12A)	15(1)	9(1)	17(1)	-2(1)	1(1)	-4(1)
C(13A)	17(1)	12(1)	18(1)	-3(1)	-2(1)	-4(1)
C(14A)	23(1)	22(1)	15(1)	-5(1)	-2(1)	-4(1)
C(15A)	19(1)	22(1)	20(1)	-6(1)	4(1)	-1(1)
C(16A)	14(1)	19(1)	24(1)	-2(1)	-1(1)	-2(1)
C(17A)	18(1)	12(1)	18(1)	-1(1)	-2(1)	-4(1)
C(18A)	16(1)	20(1)	18(1)	-3(1)	-3(1)	-4(1)
C(19A)	18(1)	24(1)	21(1)	0(1)	-3(1)	-3(1)
C(20A)	26(1)	27(1)	27(1)	-4(1)	-10(1)	-9(1)
C(21A)	16(1)	21(1)	17(1)	0(1)	-2(1)	-5(1)
C(22A)	22(1)	25(1)	19(1)	-1(1)	-5(1)	-8(1)
C(23A)	29(1)	24(1)	27(1)	5(1)	-10(1)	-6(1)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for GB_MM33_0m.

	x	y	z	U(eq)
H(4A)	3035	2617	1788	24
H(4B)	1547	2686	2308	24
H(6A)	643	4873	2438	21
H(6B)	-154	5447	1711	21
H(7A)	-1489	3997	1803	39
H(7B)	-1822	4769	2529	39
H(7C)	-770	3541	2577	39
H(8A)	3320	4168	866	24
H(8B)	2215	5349	1020	24
H(9A)	4264	5102	1732	47
H(9B)	3822	4033	2177	47

H(9C)	2805	5266	2282	47
H(10A)	-322	1796	1925	40
H(10B)	1018	802	2134	40
H(10C)	249	764	1372	40
H(11A)	2668	580	609	37
H(11B)	3292	534	1423	37
H(11C)	3662	1419	772	37
H(14)	-2045	1685	-906	24
H(15)	-354	1550	-1952	25
H(16)	1914	1892	-1828	22
H(18)	-1550	2395	978	22
H(19A)	-2827	3954	278	39
H(19B)	-3938	3369	798	39
H(19C)	-3668	3158	-95	39
H(20A)	-3112	1073	252	40
H(20B)	-3227	1274	1145	40
H(20C)	-1775	533	740	40
H(21)	3185	2606	-120	21
H(22A)	3070	3487	-1657	34
H(22B)	4119	3745	-1070	34
H(22C)	2409	4202	-924	34
H(23A)	4233	823	-630	37
H(23B)	5233	1692	-880	37
H(23C)	4230	1384	-1473	37
H(4AA)	8502	2121	3894	21
H(4AB)	7444	2405	3221	21
H(6AA)	8623	391	4703	22
H(6AB)	8050	-595	4368	22
H(7AA)	9612	-584	3266	36
H(7AB)	10529	-727	3993	36
H(7AC)	10125	472	3548	36
H(8AA)	7601	441	2786	20
H(8AB)	6553	-218	3287	20
H(9AA)	5234	890	2371	33
H(9AB)	5685	1995	2616	33
H(9AC)	4622	1419	3177	33
H(10D)	6517	4026	5160	41
H(10E)	7764	4063	4493	41

H(10F)	7888	2986	5068	41
H(11D)	5087	3641	3404	41
H(11E)	6149	4441	3534	41
H(11F)	4765	4435	4119	41
H(14A)	3847	2821	7136	24
H(15A)	1457	3446	6849	26
H(16A)	895	3542	5591	23
H(18A)	6923	1896	5821	21
H(19D)	5600	1054	7189	32
H(19E)	7258	609	6887	32
H(19F)	6006	400	6411	32
H(20D)	6718	3583	6496	39
H(20E)	7808	2530	6861	39
H(20F)	6211	2954	7258	39
H(21A)	3398	2908	3953	21
H(22D)	2399	1348	4337	32
H(22E)	1489	2086	3693	32
H(22F)	869	2169	4567	32
H(23D)	623	4291	4404	39
H(23E)	1329	4158	3547	39
H(23F)	2023	4773	4141	39

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3. Computational details

The geometry optimization of the molecules have been carried out using the DFT functional B3LYP with 6-311(d,p) basis sets using the program package Gaussian 09.[3] The nature of the stationary points was verified by calculation of the vibrational frequencies.

Coordinates of the optimized radical cation (**2**$^{+\bullet}$) in the doublet state:

N	2.88084300	0.78969300	0.02251700
C	2.13015200	-1.42705500	-3.21823200
H	2.23961200	-2.51020200	-3.31855600
H	2.05975800	-1.00726100	-4.22553800
H	1.18954200	-1.22733300	-2.70313700
C	3.32701200	-0.80606400	-2.47259100
H	3.12633100	0.26030200	-2.39561800
C	3.47000700	-1.36472600	-1.05795000

C	3.24667800	-0.61567600	0.12162000
C	1.59582700	1.19414300	-0.01548800
C	0.51521200	0.34320000	-0.00845300
C	3.32719000	-1.21355900	1.40230900
C	3.02118800	-0.48871700	2.71317600
H	2.83400600	0.56046500	2.48758500
C	4.19652000	-0.55768200	3.70738600
H	4.35698000	-1.57810300	4.06392800
H	3.98562300	0.06237500	4.58287200
H	5.13213300	-0.21214100	3.26524800
C	4.61174900	-0.98821100	-3.30430500
H	4.79674500	-2.04206900	-3.52668200
H	5.49439300	-0.60103500	-2.79247800
H	4.51802800	-0.46594300	-4.26014900
C	3.81654400	-2.71265500	-0.91925200
H	3.99989800	-3.30455000	-1.80796000
C	3.93050400	-3.30880200	0.32757800
H	4.20978300	-4.35311200	0.40816800
C	3.67936300	-2.56481900	1.47103100
H	3.75699400	-3.04206300	2.44039900
C	3.87950800	1.93827400	0.01741300
C	4.81160300	1.88358900	1.23471700
H	4.27138800	1.97960400	2.17547500
H	5.51197400	2.71925700	1.16850900
H	5.39687700	0.96275700	1.25052600
C	2.95249000	3.18053600	0.06525500
H	3.20021200	3.86671100	-0.74444300
H	3.12172200	3.72113600	0.99670400
C	1.47037400	2.71994600	-0.01856500
C	0.67093500	3.14825200	1.24694400
H	-0.32551700	2.70485000	1.18514700
H	1.15505300	2.70358000	2.12357900
C	0.53100900	4.65887200	1.46807100
H	1.49786300	5.16833200	1.49661900
H	0.04069600	4.84511500	2.42655600
H	-0.07670600	5.13464800	0.69633300
C	4.75507500	1.92269400	-1.24269600
H	5.36267000	1.01885700	-1.29403500
H	5.43695400	2.77506800	-1.19705900
H	4.17163100	2.01219600	-2.15742700
C	1.74087500	-1.03226200	3.37391300
H	0.88002900	-0.93320800	2.71208200
H	1.52830000	-0.47943600	4.29326200
H	1.84695600	-2.08728800	3.63983900

C	0.73925600	3.23560900	-1.28612800
H	-0.29186600	2.87070900	-1.25135600
H	0.67839100	4.32419300	-1.20500400
C	1.36070000	2.88270700	-2.63858200
H	1.44333500	1.80320400	-2.78660400
H	2.35396800	3.32045000	-2.76302700
H	0.73927600	3.27380100	-3.44711600
N	-2.88082800	-0.78968700	-0.02245900
C	-2.13001900	1.42711900	3.21814400
H	-2.23946000	2.51027200	3.31842800
H	-2.05953700	1.00737200	4.22546400
H	-1.18946000	1.22736300	2.70296900
C	-3.32695600	0.80611600	2.47264100
H	-3.12629000	-0.26025600	2.39568700
C	-3.47006000	1.36472700	1.05799200
C	-3.24673600	0.61566100	-0.12156900
C	-1.59579100	-1.19408600	0.01554600
C	-0.51521500	-0.34309400	0.00851000
C	-3.32731000	1.21351800	-1.40227000
C	-3.02119700	0.48868500	-2.71311700
H	-2.83390100	-0.56046800	-2.48750400
C	-4.19650000	0.55747600	-3.70737400
H	-4.35702700	1.57785200	-4.06401400
H	-3.98552000	-0.06264000	-4.58279700
H	-5.13209700	0.21189400	-3.26523600
C	-4.61160300	0.98830800	3.30448100
H	-4.79659100	2.04218100	3.52679800
H	-5.49429700	0.60107800	2.79278100
H	-4.51777400	0.46611700	4.26035600
C	-3.81661900	2.71264800	0.91927700
H	-3.99994900	3.30456200	1.80797700
C	-3.93062700	3.30877100	-0.32756200
H	-4.20992000	4.35307600	-0.40816100
C	-3.67950400	2.56477200	-1.47100800
H	-3.75714200	3.04200400	-2.44038100
C	-3.87944200	-1.93830400	-0.01732000
C	-4.81173200	-1.88354400	-1.23447800
H	-4.27166000	-1.97942600	-2.17533300
H	-5.51204300	-2.71926000	-1.16824300
H	-5.39706500	-0.96274700	-1.25009600
C	-2.95237100	-3.18052700	-0.06540900
H	-3.20003200	-3.86689300	0.74415100
H	-3.12157000	-3.72095200	-0.99696700
C	-1.47028100	-2.71988400	0.01847500

C	-0.67083500	-3.14806200	-1.24705900
H	0.32573000	-2.70494400	-1.18507200
H	-1.15477700	-2.70303500	-2.12361200
C	-0.53134200	-4.65866100	-1.46857400
H	-1.49834900	-5.16782500	-1.49725400
H	-0.04107800	-4.84480000	-2.42710500
H	0.07622700	-5.13481600	-0.69695500
C	-4.75484500	-1.92285500	1.24290700
H	-5.36245900	-1.01903900	1.29439600
H	-5.43670500	-2.77524300	1.19728100
H	-4.17127800	-2.01241600	2.15754900
C	-1.74093100	1.03237300	-3.37382200
H	-0.88009100	0.93340100	-2.71197200
H	-1.52827500	0.47957900	-4.29317200
H	-1.84711100	2.08739500	-3.63973600
C	-0.73916800	-3.23564800	1.28600400
H	0.29190900	-2.87061300	1.25134800
H	-0.67817100	-4.32421300	1.20471200
C	-1.36076600	-2.88305500	2.63846300
H	-1.44343100	-1.80358900	2.78672300
H	-2.35404300	-3.32084500	2.76268300
H	-0.73942700	-3.27432500	3.44697700

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stolz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

[2] J. K. Mahoney, D. Martin, C. E. Moore, A. L. Rheingold and G. Bertrand, *J. Am. Chem. Soc.*, 2013, **135**, 18766-18769.

[3] Gaussian 09, 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, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.