Stable GaN-Based Analogues of Thiele's and Chichibabin's Hydrocarbons

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1. Synthesis of compounds 1-4 and their NMR spectra

General considerations: All experiments were carried out under an argon or nitrogen atmosphere using standard Schlenk or dry glovebox techniques. Solvents were dried over Na metal, K metal, or CaH_2, and were distilled under nitrogen prior to use. Commercially available reagents were purchased from Energy Chemical and used as received. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained with a Bruker AVIII 400 MHz BBFO1 spectrometer at 298K. Chemical shifts (δ) are given in p.p.m. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. UV-vis spectra were recorded on the Lambda 750 spectrometer at room temperature. Element analyses were performed on an ElementarVario EL III instrument. EPR spectra were obtained using JEOL JES-X320 X-band apparatus. $Trip_2GaCl$ (Trip = 2,4,6-triisopropylphenyl) was synthesized according to the literature procedures.[S1]

Synthesis of compound 1

$Trip_2GaCl$ (1.54 g, 3.0 mmol) was added to the toluene solution of pyrazine (0.12 g, 1.5 mmol) at room temperature. The color of the solution changed from white to yellow and the mixture was stirred at room temperature overnight. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 ml) to afford **1** as a white powder (1.40 g, 85%). ^{1}H NMR (C_6D_6 , 400 MHz, 298 K): δ (ppm) = 8.01 (s, 4H, C*H*=C*H*), 7.12 (s, 8H, Ar-*H*), 3.13 (dt, 8H, $(CH_3)_2CH$), 2.79 (dt, 4H, $(CH_3)_2CH$), 1.29 (d, *J* = 6.2 Hz, 48H, $CH(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6 , 400 MHz, 298 K): δ 155.11 (Ar-*C*), 151.19 (Ar-*C*), 144.87 (Ar-*C*H), 143.07 (Ar-*C*H), 121.67 (Ar-*C*H), 39.20 ($(CH_3)_2CH$), 34.85 ($(CH_3)_2CH$), 25.22 ($(CH_3)_2CH$), 24.21 ($(CH_3)_2CH$). Elemental analysis for $C_{64}H_{96}Cl_2Ga_2N_2$(%): Calculated: C 69.64, H 8.77, N 2.54; Found: C 69.95, H 9.01, N 2.34.

Synthesis of compound 2

$Trip_2GaCl$ (1.54 g, 3.0 mmol) was added to the toluene solution of 4,4'-bipyridine (0.23 g, 1.5 mmol) at room temperature. The color of the solution changed from white to yellow and the mixture was stirred at room temperature overnight. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 ml) to afford **2** as a white powder (1.50 g, 84%). ^{1}H NMR (C_6D_6 , 300 MHz, 298 K): δ (ppm) = 8.75 (s, 4H, C*H*=C*H*), 7.27 (s, 8H, Ar-*H*), 6.27 (s, 4H, C*H*=C*H*), 3.56 (dt, 8H, $(CH_3)_2CH$), 2.97-2.82 (dt, 4H, $(CH_3)_2CH$), 1.27 (dd, J = 6.2 Hz, 72H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 400 MHz, 298 K): δ 156.18 (Ar-*C*), 150.00 (Ar-*C*), 149.15 (Ar-*C*), 146.97 (Ar-*C*H), 142.70 (Ar-*C*), 122.46 (Ar-*C*H), 121.78 (Ar-*C*H), 36.46 ($(CH_3)_2CH$), 34.82 ($(CH_3)_2CH$), 25.65 ($(CH_3)_2CH$), 24.36 ($(CH_3)_2CH$). Elemental analysis for $C_{70}H_{100}Cl_2Ga_2N_2$ (%): Calculated: C 71.26, H 8.54, N 2.37; Found: C 71.57, H 8.83, N 2.15.

Synthesis of compound 3

Potassium graphite (0.30 g, 2.2 mmol) was added to the toluene (60 mL) solution of **1** (1.10 g, 1.0 mmol) at room temperature. The color of the solution changed from yellow to deep red and the mixture was stirred for overnight. After filtration, removal of the solvent under vacuum, the residue was washed with cooled hexane (5 ml) to afford **3** as a deep red powder (0.36 g, 35%). ^{1}H NMR (C_6D_6 , 400 MHz, 298 K): δ (ppm) = 7.10 (s, 8H, Ar-*H*), 4.84 (s, 4H, C*H*=C*H*), 2.99 (dt, 8H, $(CH_3)_2CH$), 2.79 (dt, 4H, $(CH_3)_2CH$), 1.41 (s, 24H, $CH(CH_3)_2$), 1.22 (d, J = 7.0 Hz, 48H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 400 MHz, 298 K): δ 155.57 (Ar-*C*), 150.55 (Ar-*C*), 140.35 (Ar-*C*), 121.03 (Ar-*C*H), 120.24 (Ar-*C*H), 40.25 ($(CH_3)_2CH$), 34.87 ($(CH_3)_2CH$), 24.46 ($(CH_3)_2CH$), 24.29 ($(CH_3)_2CH$). UV-vis (THF): λ_{max} = 474 nm; Elemental analysis for $C_{64}H_{96}Ga_2N_2$(%): Calculated: C 74.42, H 9.37, N 2.71; Found: C 74.85, H 9.65, N 2.49.

Synthesis of compound 4

Potassium graphite (0.30 g, 2.2 mmol) was added to the toluene (60 mL) solution of **2** (1.18 g, 1.0 mmol) at -30 ^{o}C. The color of the solution changed from yellow to deep

purple and the mixture was stirred for 48h. After slowly warm up to room temperature, filtration, removal of the solvent under vacuum, the residue was washed with cooled hexane (5 ml) to afford **4** as a deep red powder (0.58 g, 56%). ^{1}H NMR (C_6D_6 , 400 MHz, 298 K): δ (ppm) = 7.12 (s, 8H, Ar-*H*), 6.39 (d, *J* = 7.5 Hz, 4H, C*H*=C*H*), 5.47 (d, *J* = 7.5 Hz, 4H, C*H*=C*H*), 2.91 (dt, 8H, $(CH_3)_2CH$), 2.79 (dt, 4H, $(CH_3)_2CH$), 1.30 (s, 24H, $CH(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 48H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6 , 400 MHz, 298 K): δ 155.61 (Ar-*C*), 151.24 (Ar-*C*), 139.79 (Ar-*C*), 132.70 (Ar-*C*H), 121.35 (Ar-*C*H), 109.17 (Ar-*C*H), 40.67 ($(CH_3)_2CH$), 34.84 ($(CH_3)_2CH$), 31.96 ($(CH_3)_2CH$), 24.20 ($(CH_3)_2CH$). UV-vis (THF): λ_{max} = 558 nm; Elemental analysis for $C_{78}H_{116}Ga_2N_2O_2$ (%): Calculated: C 74.75, H 9.33, N 2.55; Found: C 75.08, H 9.59, N 2.38.

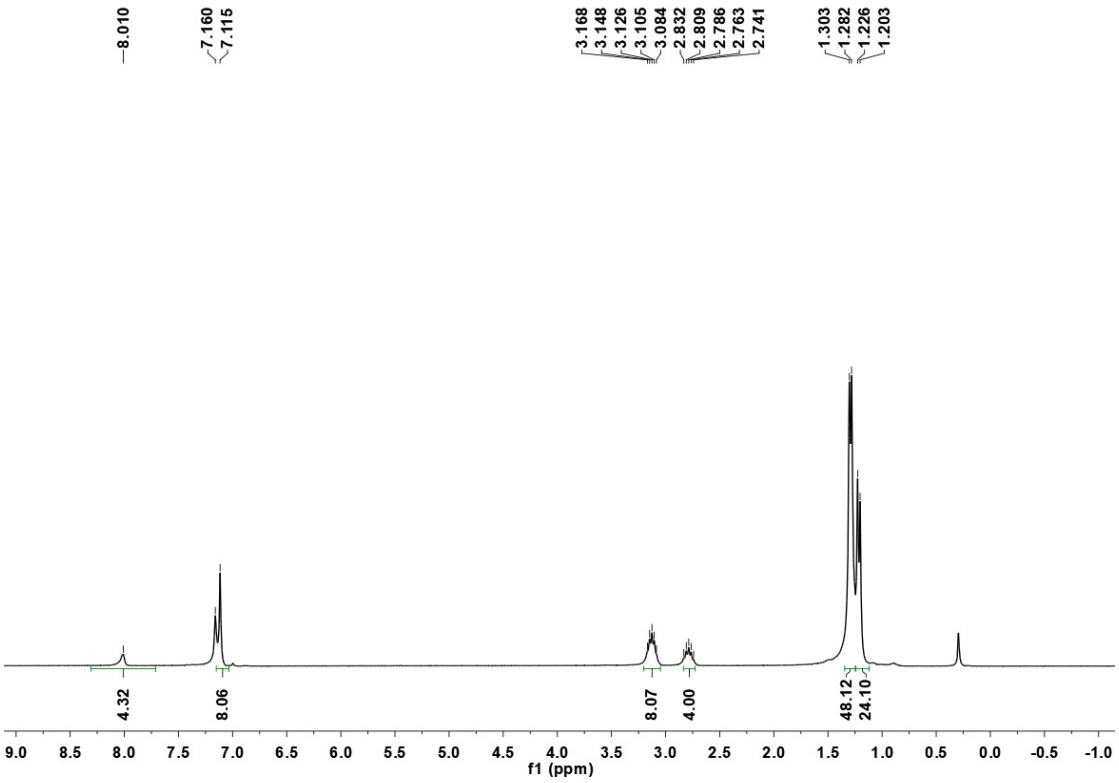


Fig. S1 ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K.

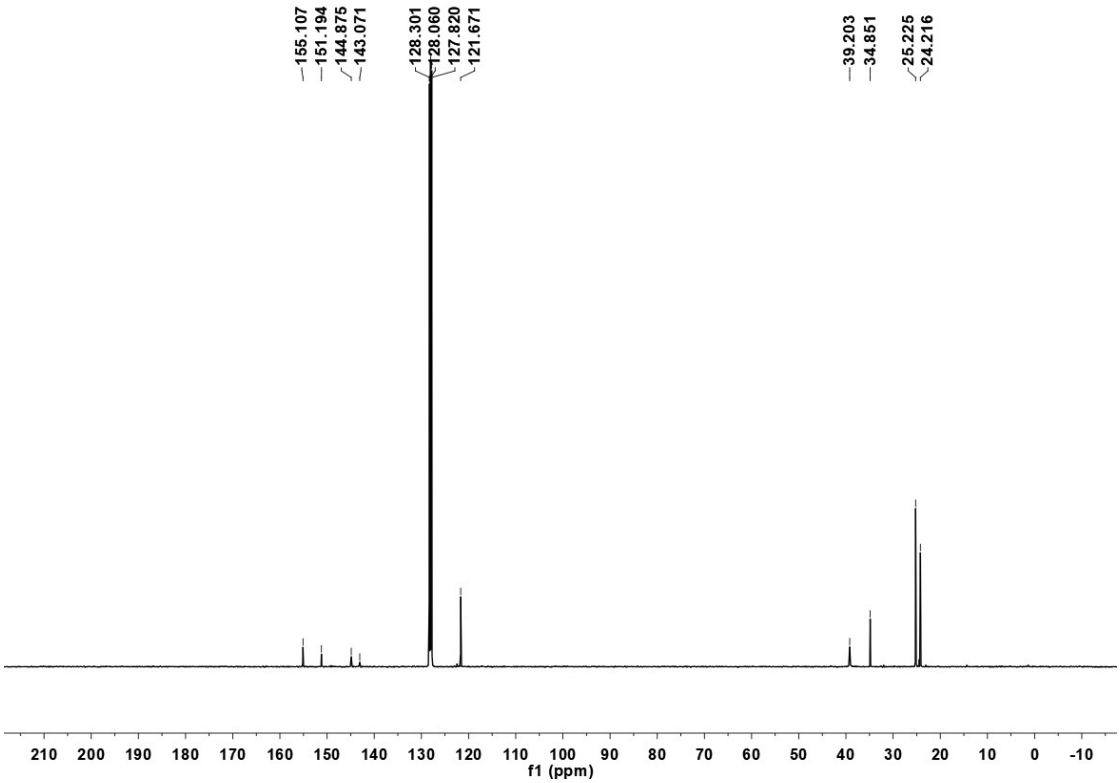


Fig. S2 ^{13}C{^{1}H} NMR spectrum of **1** in C_6D_6 at 298 K.

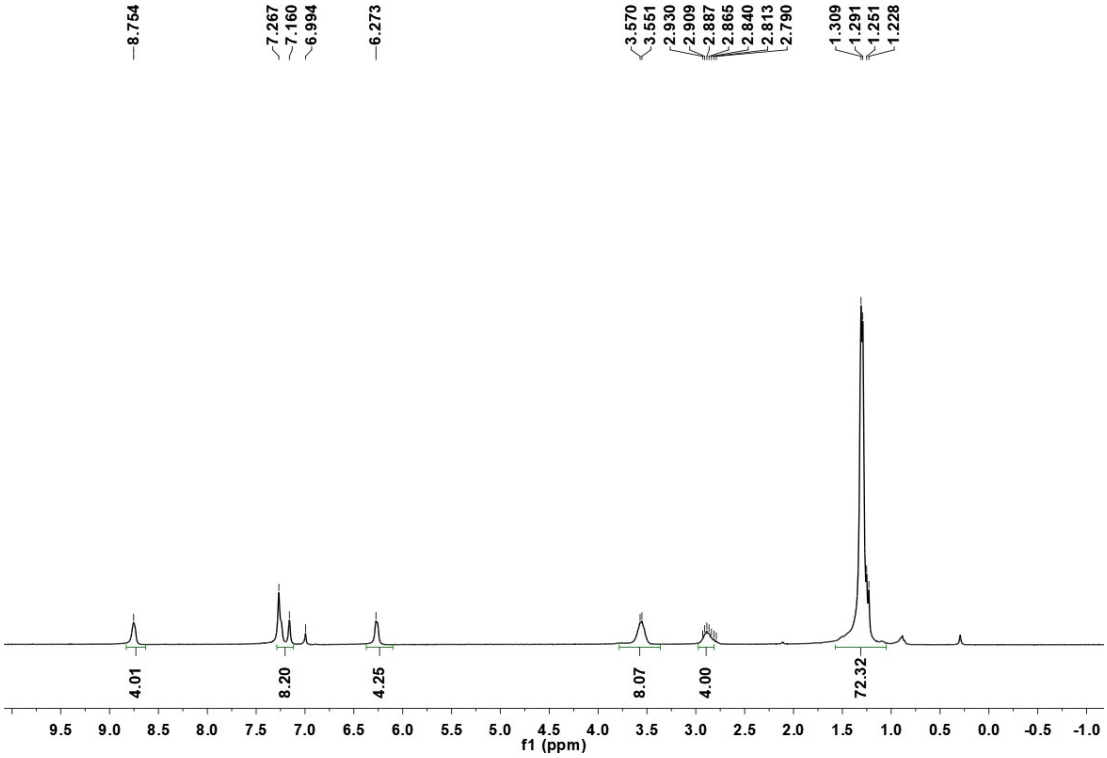


Fig. S3 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

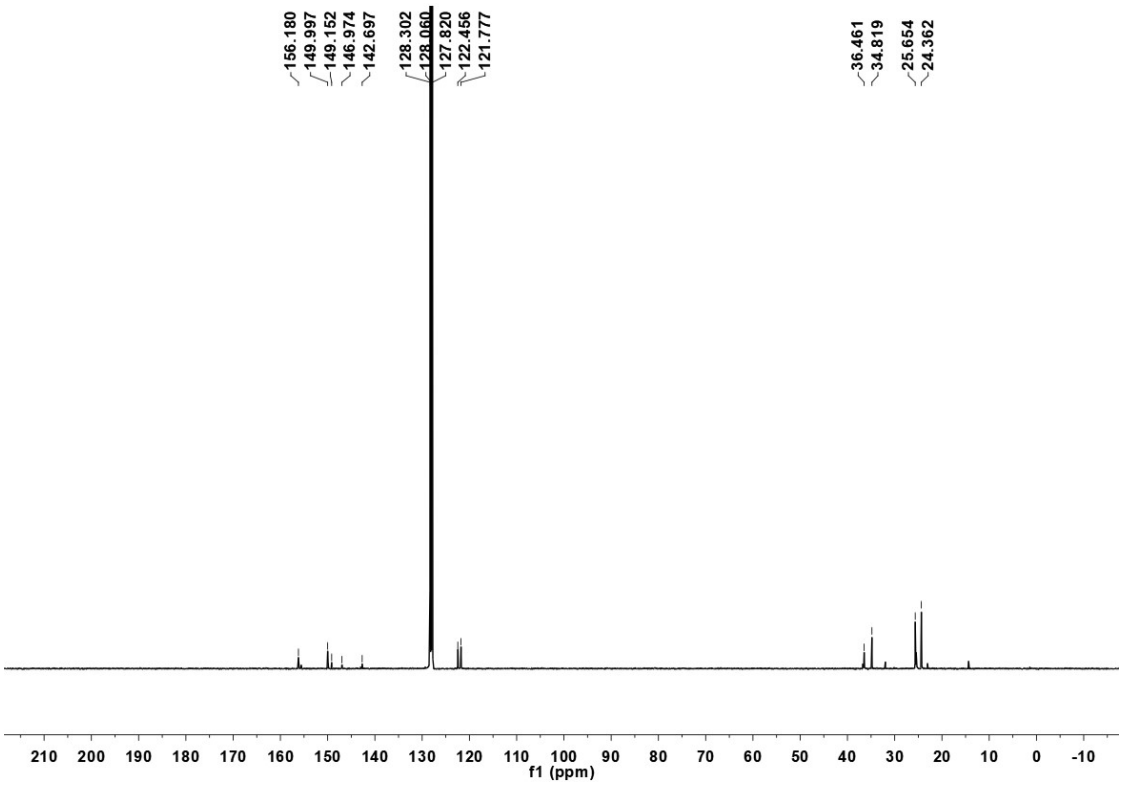


Fig. S4 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

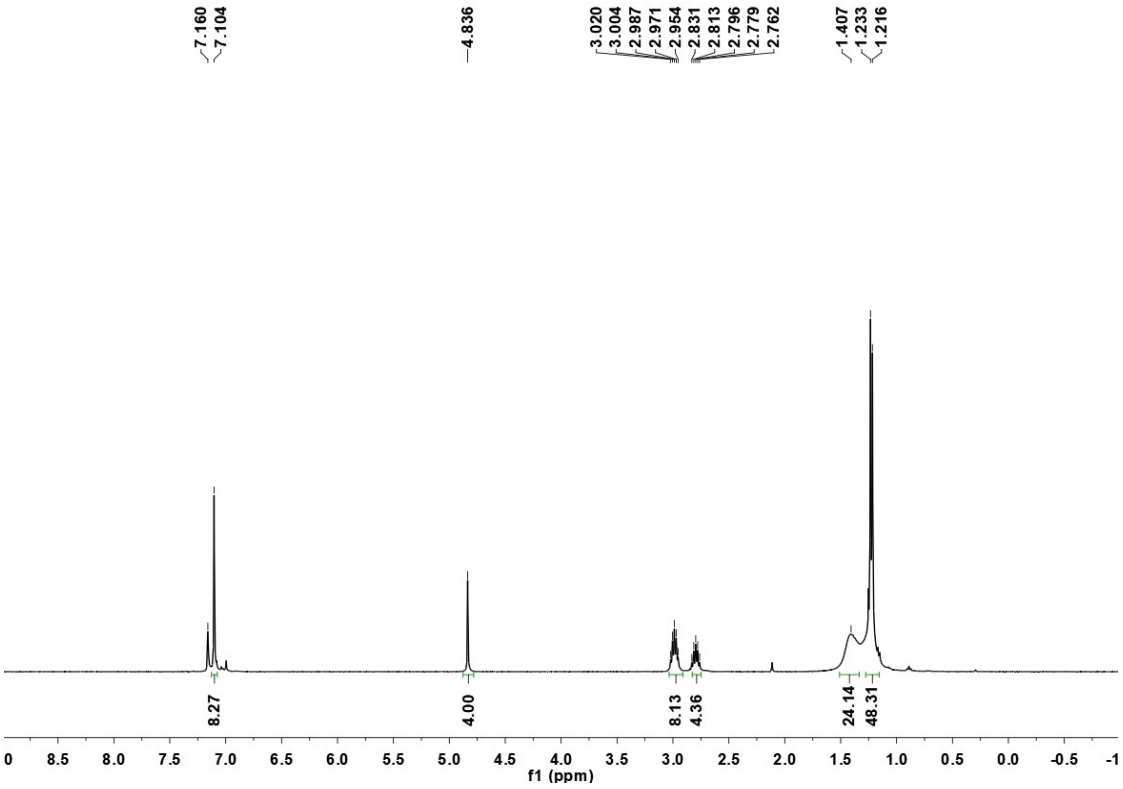


Fig. S5 ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K.

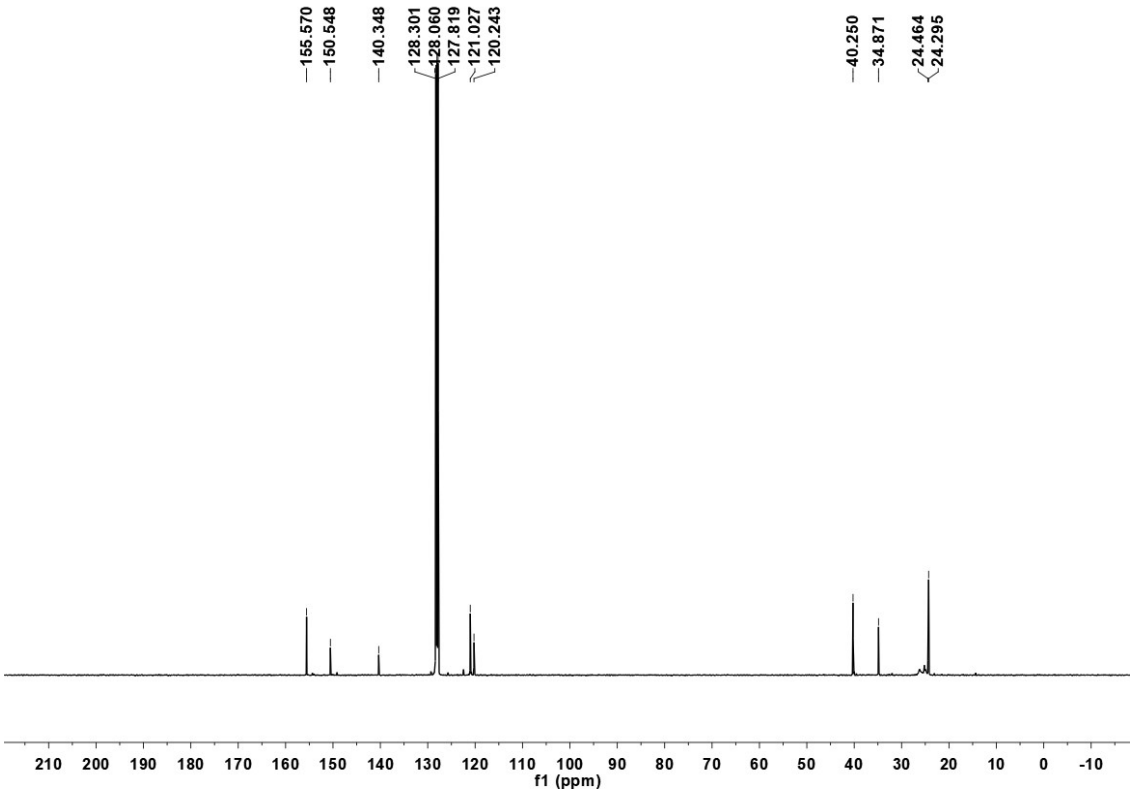


Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 298 K.

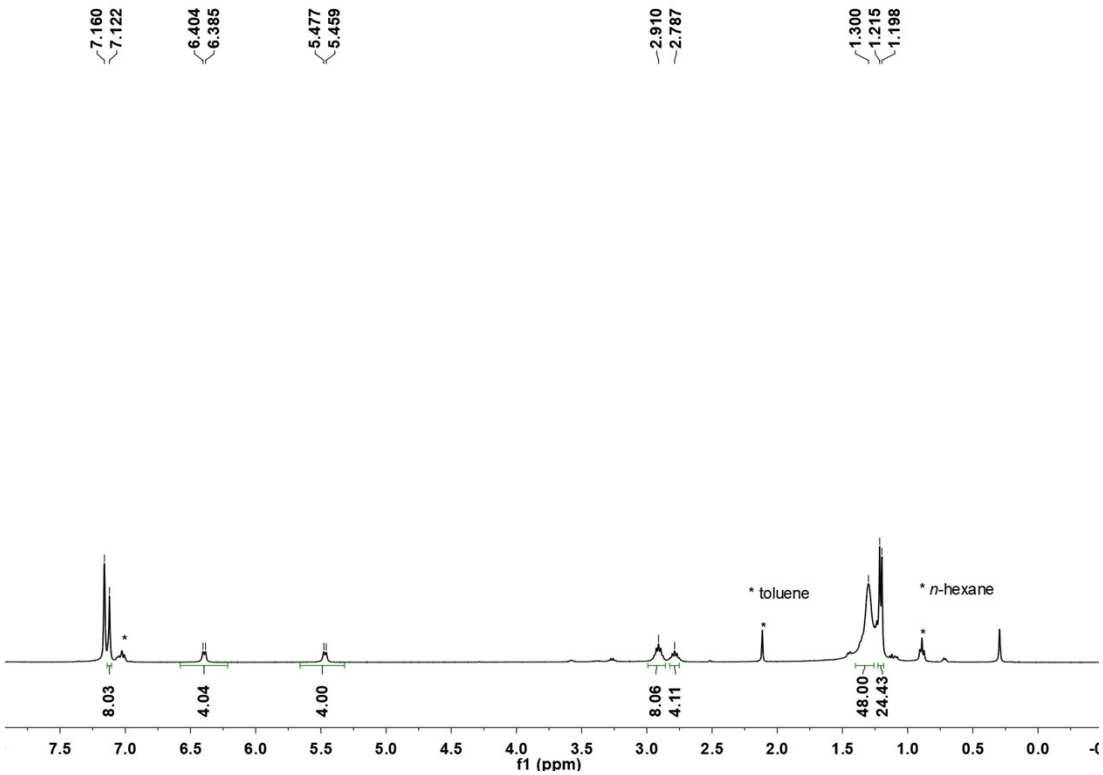


Fig. S7 ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K.

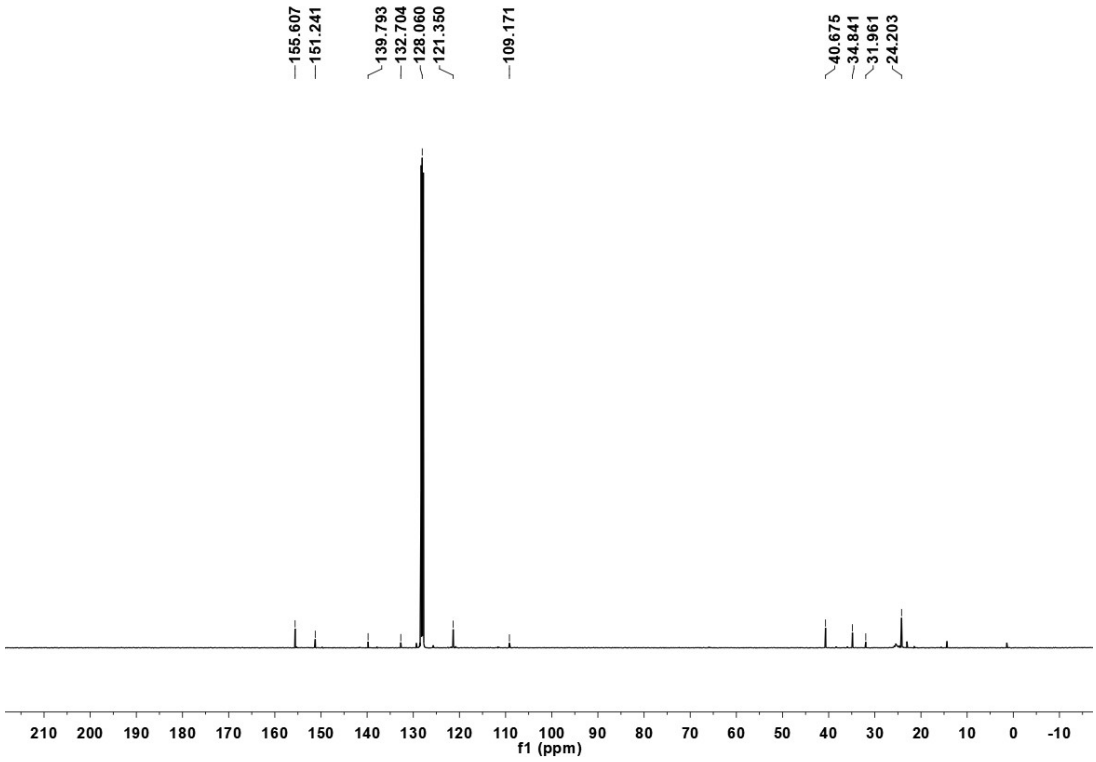


Fig. S8 ^{13}C{^{1}H} NMR spectrum of **4** in C_6D_6 at 298 K.

2. Crystal structural parameters for compounds 1-4

For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on a Bruker D8 CMOS detector at low temperatures. The structures were solved by direct methods and all refined on F^2 with the SHELX-2018/3 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Table S1. Summary of data collection and structure refinement.

Compounds	**1**	**2**	**3**	**4**
CCDC	2429370	2429371	2429372	2429373
Formula	$C_{35}H_{55}Br_{0.38}Cl_{0.62}GaN$	$C_{70}H_{100}Cl_2Ga_2N_2$	$C_{64}H_{96}Ga_2N_2$	$C_{86}H_{132}Ga_2N_2O_4$
Fw	611.46	1179.85	1032.86	1397.36
Crystal syst	monoclinic	tetragonal	triclinic	triclinic
Space group	C2/c	$I4_1/a$	P-1	P-1
Size, mm^3	0.22 × 0.16 × 0.08	0.13 × 0.12 × 0.10	0.18 × 0.16 × 0.13	0.13× 0.12 × 0.10
T, K	150.0	150.0	150.0	100.00
a, Å	32.7341(19)	18.6669(6)	9.926(5)	9.0948(5)
b, Å	23.0166(13)	18.6669(6)	12.299(11)	12.5381(7)
c, Å	9.2046(6)	39.267(3)	14.106(9)	18.2742(11)
α, deg	90	90	107.74(3)	81.321(2)
β, deg	92.844(2)	90	103.724(19)	80.234(2)
γ, deg	90	90	102.71(3)	73.737(2)
V, $Å^3$	6926.5(7)	13682.5(12)	1511.8(18)	1959.7(2)
Z	8	8	1	1
d_{calcd}, $g•cm^{-1}$	1.173	1.146	1.134	1.184
μ, mm^{-1}	1.302	0.904	0.928	0.737
Reflections collected	53102	68719	25050	29779
Independent reflections	7973	6037	5328	7175
[R_{int}]	0.0936	0.1184	0.0934	0.1013
R_1[I>2sigma(I)]	0.0492	0.0745	0.0572	0.0603
wR_2[I>2sigma(I)]	0.1313	0.1924	0.1530	0.1480
R_1[all data]	0.0812	0.1027	0.0742	0.0893
wR_2[all data]	0.1567	0.2151	0.1691	0.1699
GOF	1.033	1.054	1.065	1.047
Largest diff. Peak/hole, $e•Å^{-3}$	0.38/-0.86	2.17/-0.86	0.54/-0.77	0.48/-0.62

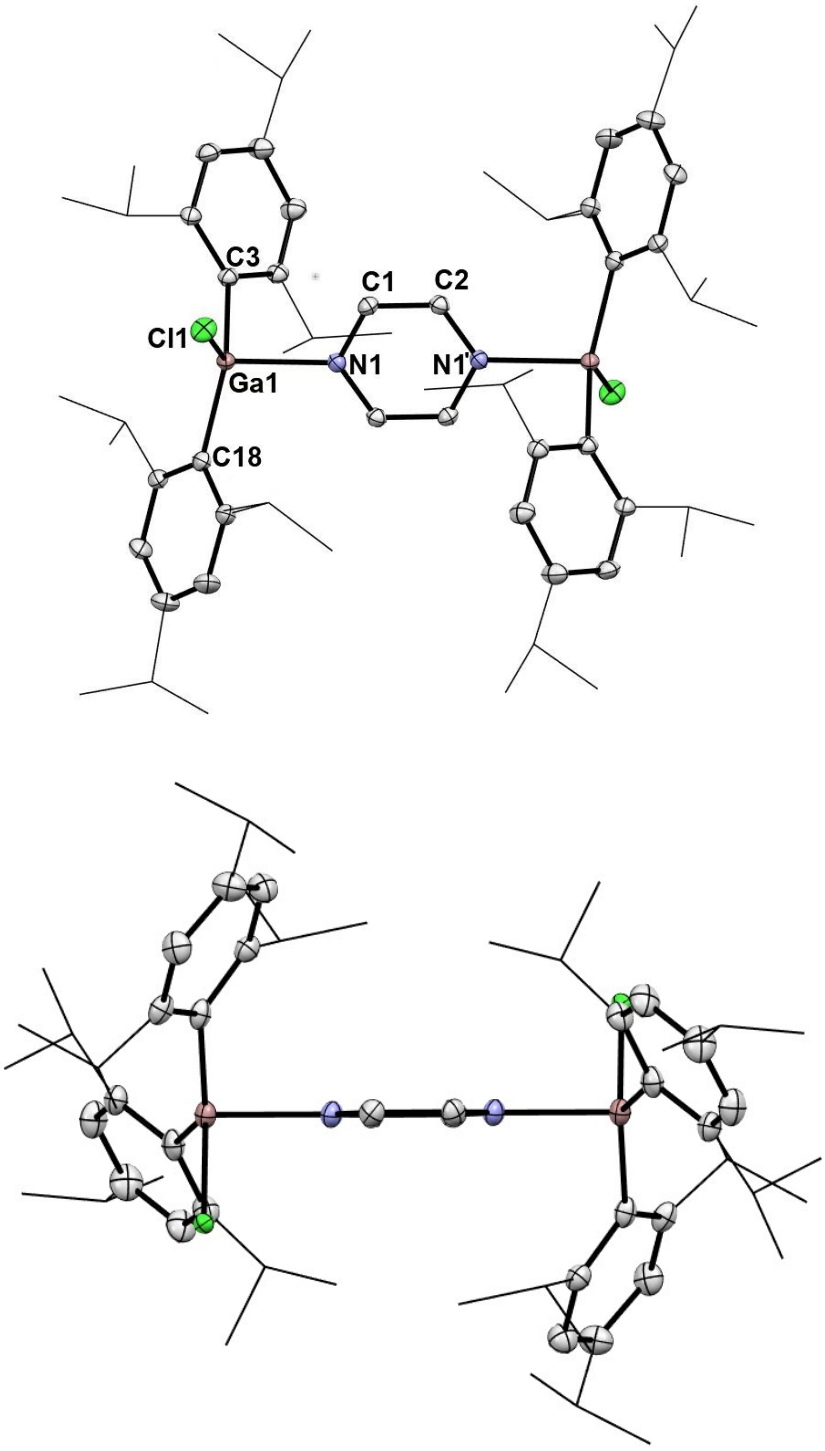


Fig. S9 Solid-state structure of **1** with side view. Hydrogen atoms are omitted and ^{i}Pr groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): Ga1–C3 2.006(3), Ga1–C18 1.999(3), Ga1–N1 2.150(2), Ga1–Cl1 2.197(9), N1–C1 1.333(3), C1–C2 1.384(4), C2–N1' 1.335(3), N1–Ga1–Cl1 94.5(3), C3–Ga1–N1 93.77(10), C3–Ga1–Cl1 110.4(4), C18–Ga1–N1 103.68(10), C3–Ga1–C18 133.75(11).

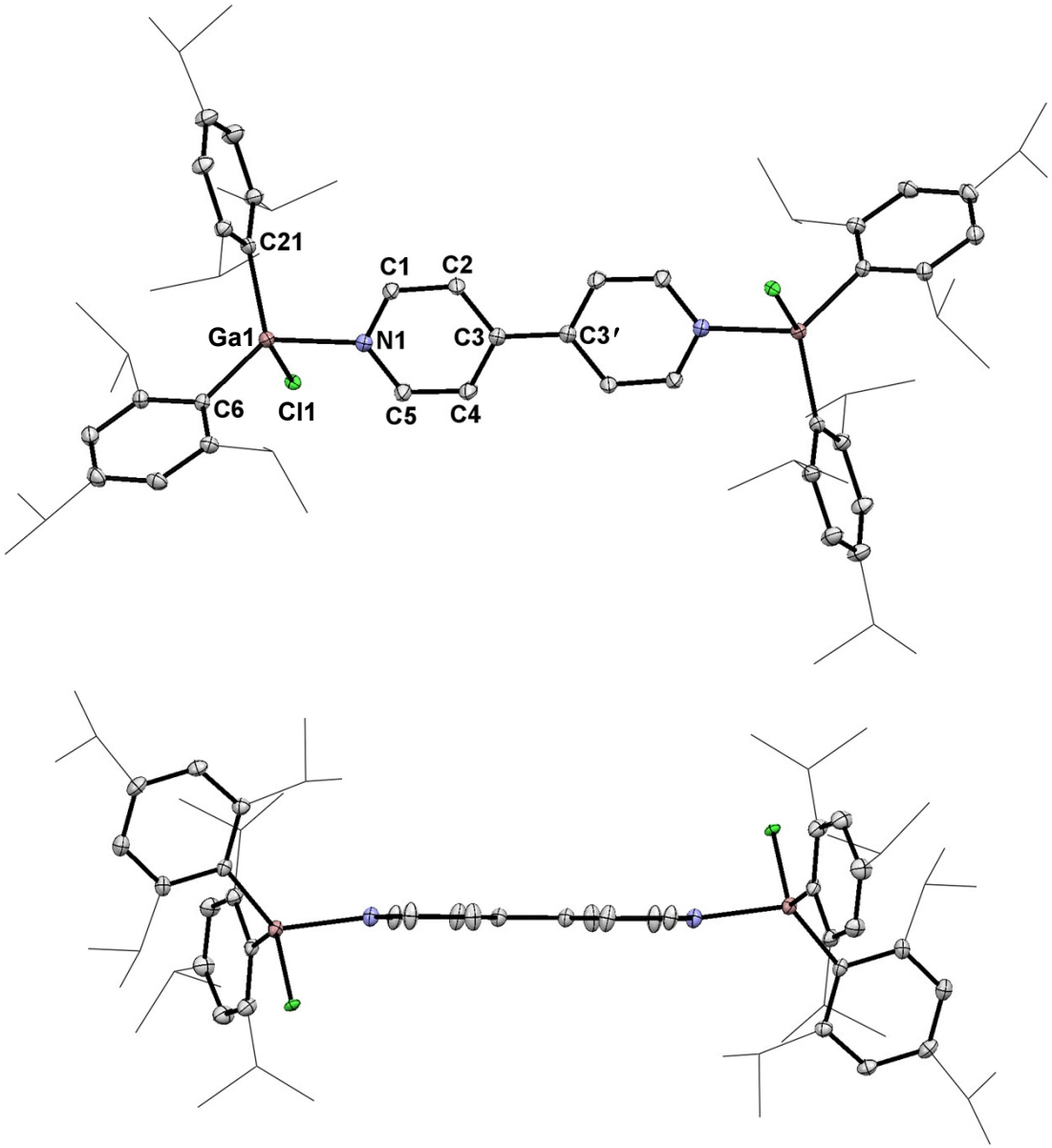


Fig. S10 Solid-state structure of **2** with side view. Hydrogen atoms are omitted and ^{i}Pr groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): Ga1–C6 1.988(6), Ga1–C21 1.997(6), Ga1–N1 2.099(5), Ga1–Cl1 2.3413(12), N1–C5 1.344(8), N1–C1 1.324(8), C4–C5 1.366(9), C1–C2 1.388(8), C3–C4 1.390(8), C3–C2 1.390(8), C3–C3' 1.479(11), N1–Ga1–Cl1 91.21(14), C6–Ga1–N1 121.4(2), C6–Ga1–Cl1 102.86(16), C21–Ga1–N1 123.81(18), C21–Ga1–C6 116.5(2).

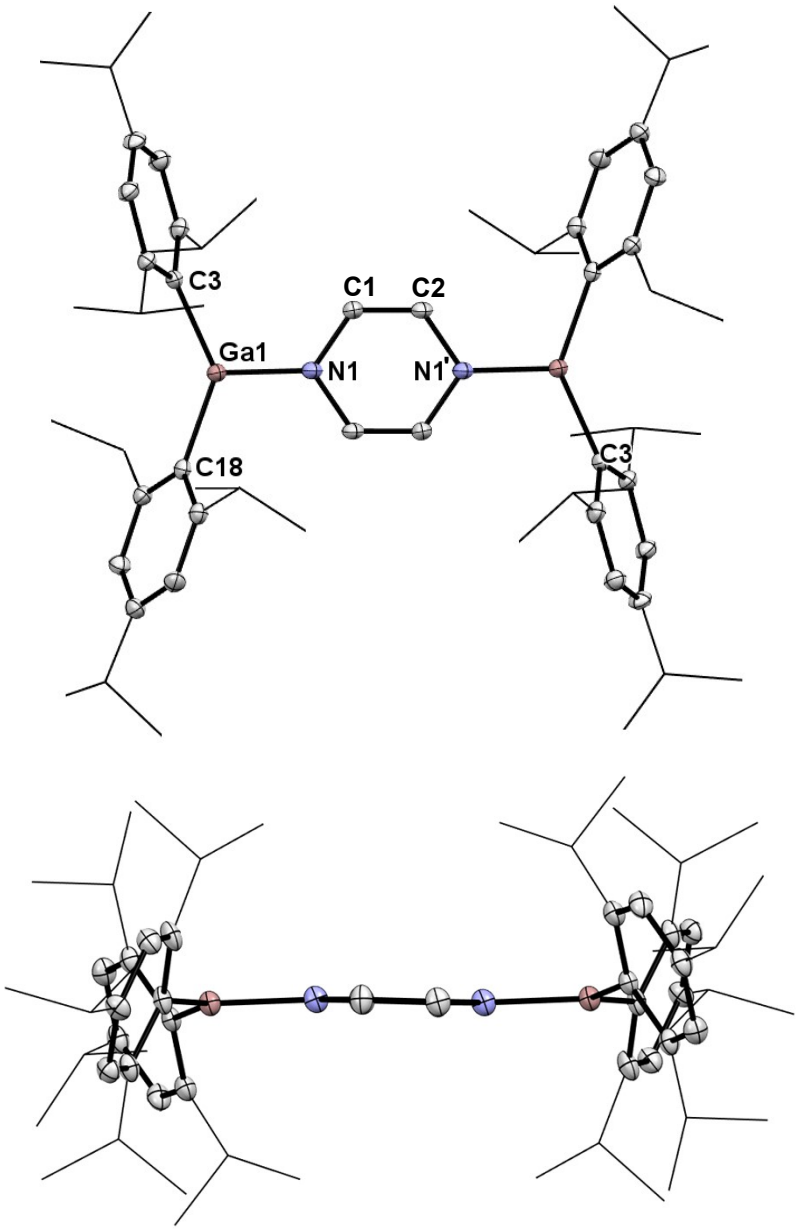


Fig. S11 Solid-state structure of **3** with side view. Hydrogen atoms are omitted and ^{i}Pr groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): Ga1–C3 1.988(7), Ga1–C18 1.973(4), Ga1–N1 1.843(3), N1–C1 1.424(5), C1–C2 1.323(5), C2–N1' 1.415(5), C3–Ga1–N1 113.4(6), C18–Ga1–N1 110.97(14), C3–Ga1–C18 135.4(6).

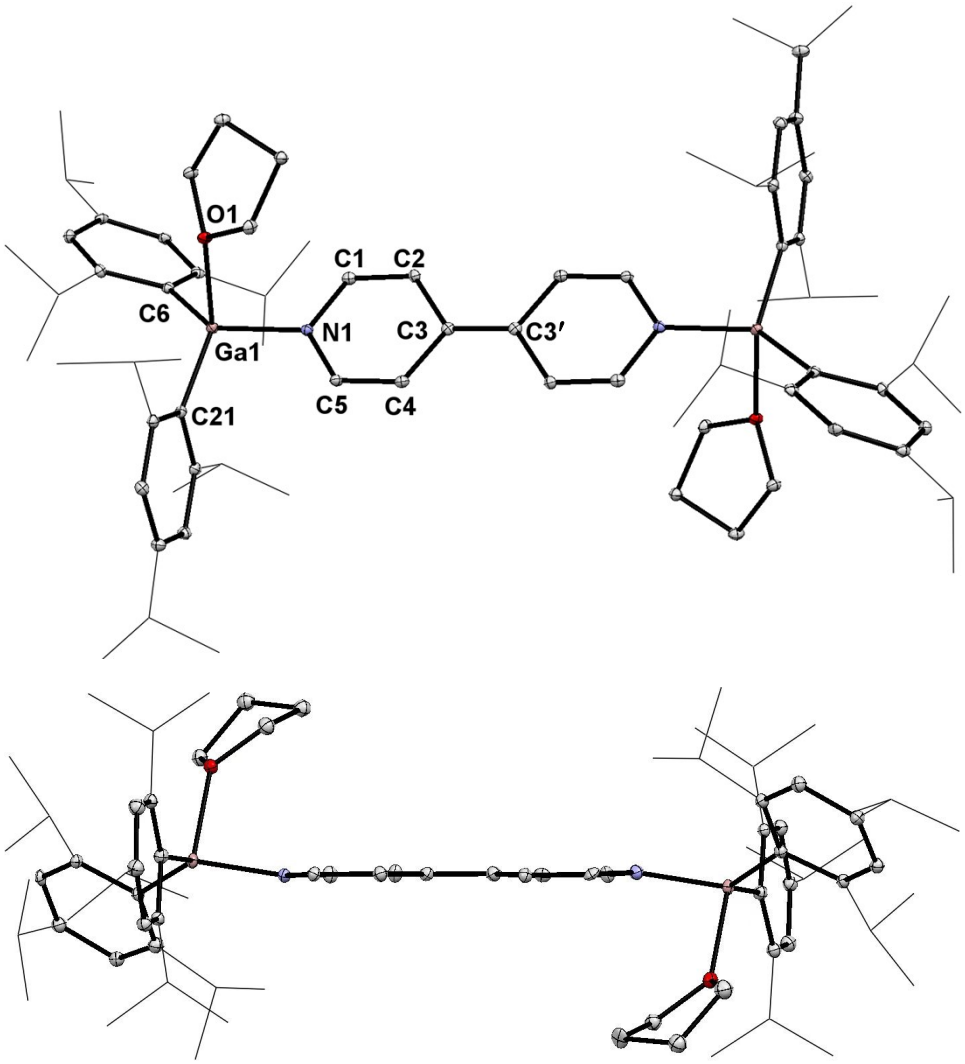


Fig. S12 Solid-state structure of **4** with side view. Hydrogen atoms are omitted and ^{i}Pr groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond distances (Å) and angles (°): Ga1–C6 1.988(4), Ga1–C21 1.991(4), Ga1–N1 1.915(3), Ga1–O1 2.162(3), N1–C1 1.391(5), N1–C5 1.389(5), C1–C2 1.355(5), C2–C3 1.458(5), C3–C4 1.451(5), C3–C3' 1.372(7), C4–C5 1.347(5), C6–Ga1–N1 123.52(14), C21–Ga1–N1 104.16(13), C6–Ga1–C21 123.32(15).

3. Cyclic voltammograms

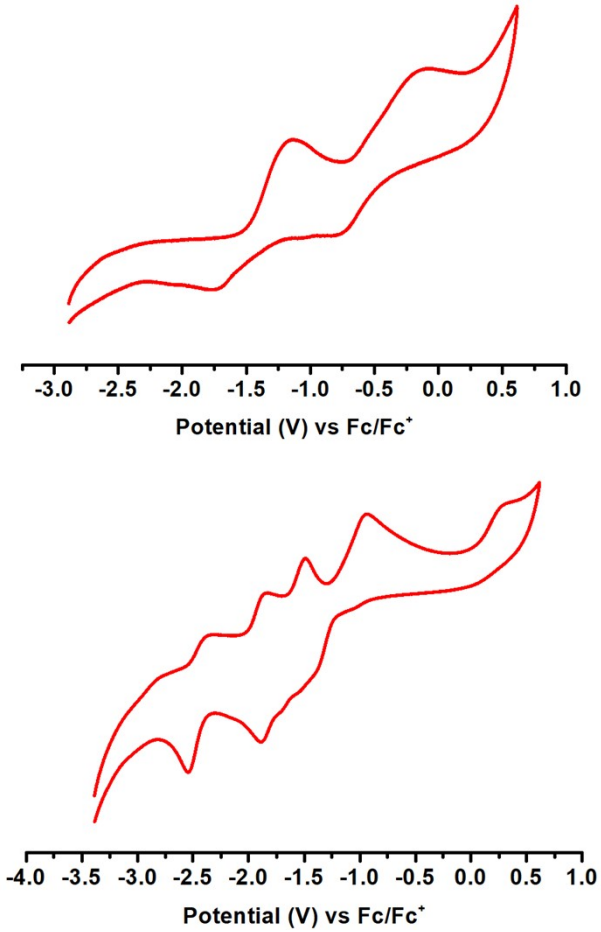


Fig. S13. The cyclic voltammograms of (a) **3** and (b) **4** in THF (0.1 M [^{n}Bu$_4$N][PF$_6$]) measured at a scan rate of 100 mV s^{-1}.

4. Theoretical calculations

The calculations were performed with the Gaussian 16[S2] program. For gometry optimizations and frequency calculations on the simplified model **3'**,**4'** (THF-free), and **4''** (THF-coordinated), in which the Trip groups were replaced with the phenyls, three electronic states (closed-shell singlet (CS), open-shell singlet (OS), and triplet (T) state) with the (U)BH&HLYP, functional and def2-SVP basis-sets were considered. TD-DFT, NICS, and NBO calculations were conducted under the BH&HLYP/def2-SVP level of theory. The calculated Kohn-Sham orbitals related to the observed transitions are shown in Table S2-S5. To gain further insight into the electronic structures, Multiwfn[S3] and VMD[S4] were also used.

DFT calculations reveal significant effects of the bridging framework and THF coordination on their electronic structures. As the bridging framework elongates in **4'** (THF-free bridged form), the HOMO energy rises markedly (+0.68 eV), while the LUMO undergoes a slight decrease (−0.24 eV), reducing the HOMO-LUMO gap from 4.40 eV (**3'**) to 3.48 eV (**4'**). Subsequent THF coordination in **4''** (THF-coordinated) elevates both the HOMO (+0.68 eV) and LUMO (+1.34 eV), restoring the gap to 4.30 eV – a value comparable to **3'**. These computational trends align with experimental observations: the stability of **3** and THF-bound **4** contrasts with the rapid color fading of THF-free **4'** in solution. Additionallly, natural bond orbital (NBO) analyses revealed that the Wiberg bond indexes (WBI) of Ga–N and C_o–$C_{o/m}$ bonds decrease progressively from **3'** to **4'** and further to **4''** (Ga–N: 0.59→0.53→0.43; C_o–$C_{o/m}$: 1.808→1.741→1.739), while N–C_o WBI increases from 1.02 (**3'**) to 1.07 (**4'**) and further to 1.08 (**4''**). THF coordination in **4''** reduces Ga–C WBI (0.62→0.56) while increasing Cp–Cp WBI (1.50→1.52).

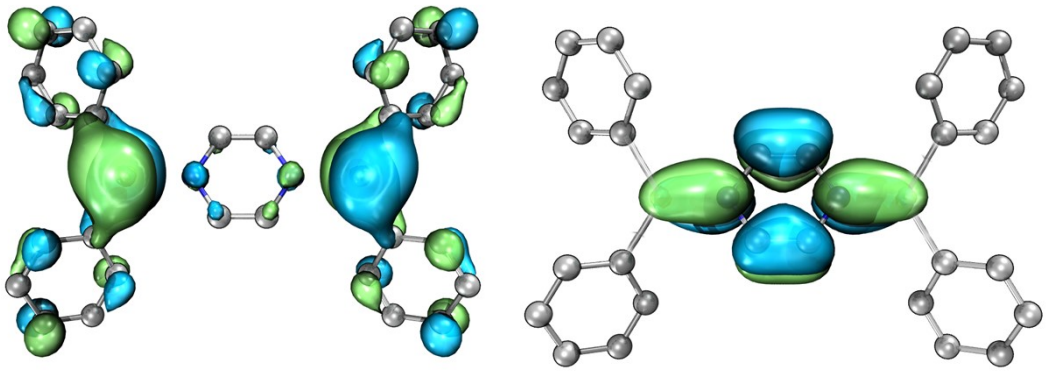


Fig. S13 The LUMO (left, −0.38 eV) and HOMO (right, −4.78 eV) of **3'-CS**.

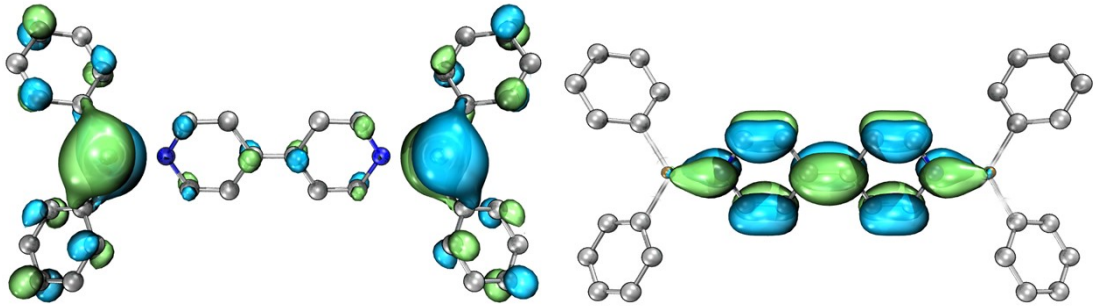


Fig. S14 The LUMO (left, −0.62 eV) and HOMO (right, −4.10 eV) of **4'-CS**.

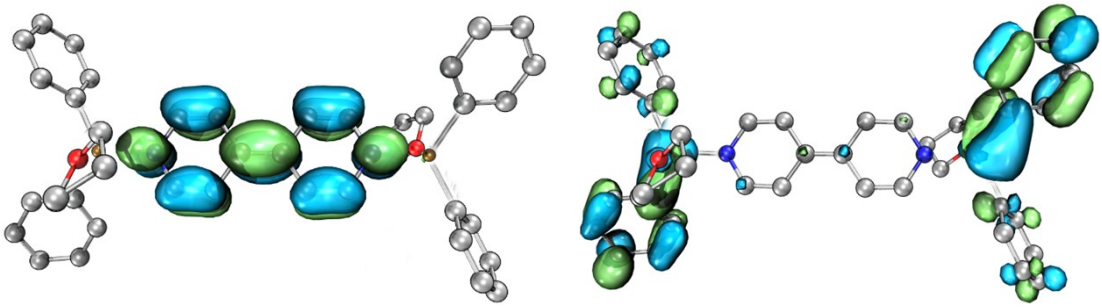
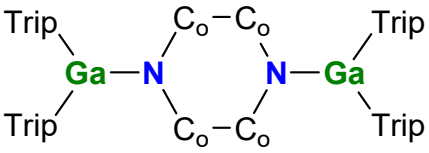


Fig. S15 The LUMO (left, 0.72 eV) and HOMO (right, −3.58 eV) of **4''-CS**.

Table S2. Electronic energies (E in Hartrees) and relative electronic energies ($\Delta E_{S\text{-}T}$ in kcal/mol) of compound **3** in closed-shell singlet (CS) and triplet (T) states.

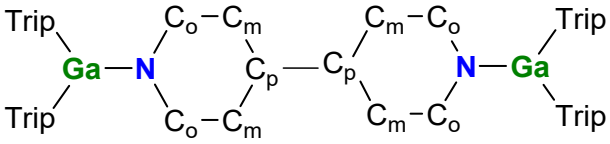
	E_{CS}	E_T	$\Delta E_{S\text{-}T}$
3'	-5038.055341	-5038.017589	23.69
4'	-5268.713231	-5268.687783	15.97

Table S3. Experimental and calculated bond lengths (avg., Å) of **3** at the (U)BH&HLYP / def2-SVP level.



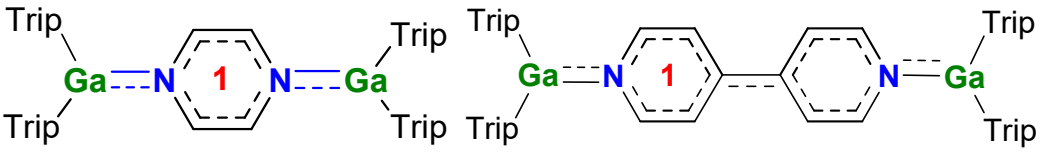
	3-Exp.	**3'-CS**	**3'-T**
Ga–C_{trip}	1.980(7)	1.959	1.945
Ga–N	1.843(3	1.847	1.903
N–Co	1.420(5)	1.407	1.382
Co–Co	1.323(5)	1.333	1.356
BLA	0.097(5)	0.074	0.026

Table S4. Experimental and calculated bond lengths (avg., Å) of **4** at the (U)BH&HLYP / def2-SVP level.



	4-Exp.	4′-CS	4′-T
Ga–C_{trip}	1.990(4)	1.956	1.948
Ga–N	1.915(3)	1.867	1.896
N–C_o	1.390(5)	1.389	1.380
C_o–C_m	1.351(5)	1.343	1.354
C_m–C_p	1.454(5)	1.454	1.429
C_p–C_p	1.372(7)	1.371	1.437
BLA	0.071(5)	0.079	0.050

Table S5. NICS(0), NICS(1) and NICS(1)ZZ values for the bridging rings in **3′** and **4′**.



	3′	4′
NICS (0)	16.2846	5.4655
NICS (1)	11.3864	1.9666
NICS (1)zz	36.9850	10.2270

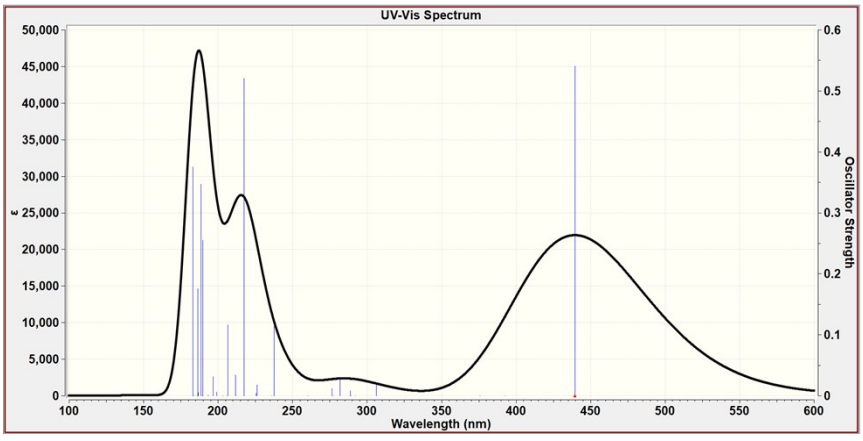


Fig. S16. Calculated UV-vis spectrum of **3′-CS**

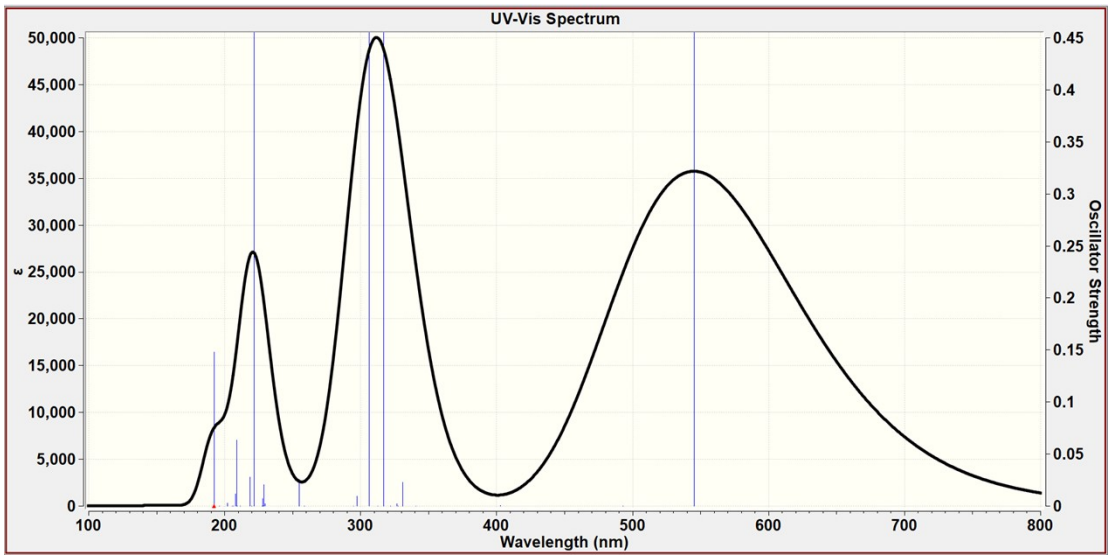


Fig. S17. Calculated UV-vis spectrum of **4′-CS**.

Coordinates for the optimized structure

3′-CS at the BH&HLYP/def2-SVP level

Ga	-3.29680000	0.00000000	0.00000500
C	-4.23303300	1.72076000	-0.04170800
C	-3.71746500	2.88252500	0.54578400
C	-4.42401200	4.07767600	0.52521300
H	-4.00353100	4.96284100	0.99102800
C	-5.66708300	4.14002300	-0.09040800
C	-6.20160100	3.00151600	-0.67736100
H	-7.17349100	3.04247000	-1.15800700
C	-5.49296900	1.80733100	-0.64639000
N	-1.44962200	-0.00000300	-0.00000400
C	-0.66654600	-1.12960200	0.29943800
H	-1.20040800	-2.03262400	0.56678500
C	0.66654900	-1.12959900	0.29944000
H	1.20041300	-2.03262000	0.56678900
C	-4.23303800	-1.72075800	0.04171500
C	-3.71746900	-2.88252400	-0.54577300
C	-4.42402000	-4.07767200	-0.52520800
H	-4.00353900	-4.96283900	-0.99102000
C	-5.66709700	-4.14001500	0.09040300
C	-6.20161600	-3.00150600	0.67735200
H	-7.17351000	-3.04245700	1.15799000
C	-5.49297900	-1.80732400	0.64638700
N	1.44962200	0.00000200	0.00000000
C	0.66654600	1.12960100	-0.29944300

H	1.20040800	2.03262300	-0.56679200
C	-0.66654900	1.12959900	-0.29944500
H	-1.20041300	2.03261900	-0.56679500
Ga	3.29680000	0.00000000	-0.00000600
C	4.23303300	-1.72076000	0.04170900
C	3.71746800	-2.88252400	-0.54578600
C	4.42401400	-4.07767500	-0.52521400
H	4.00353500	-4.96283900	-0.99103200
C	5.66708300	-4.14002200	0.09041200
C	6.20159900	-3.00151600	0.67736800
H	7.17348700	-3.04247000	1.15801700
C	5.49296700	-1.80733100	0.64639500
C	4.23303800	1.72075800	-0.04171500
C	3.71746700	2.88252500	0.54577000
C	4.42401900	4.07767300	0.52520500
H	4.00353500	4.96284000	0.99101500
C	5.66709700	4.14001500	-0.09040200
C	6.20161800	3.00150600	-0.67734700
H	7.17351400	3.04245500	-1.15798200
C	5.49298100	1.80732300	-0.64638200
H	-6.21899000	5.07385400	-0.11015900
H	-2.74922300	2.86121600	1.03643200
H	-5.93588100	0.92768200	-1.10476600
H	6.21900800	5.07384500	-0.11014600
H	5.93589500	0.92767200	-1.10475300
H	2.74922000	2.86122000	1.03640700
H	-6.21900700	-5.07384500	0.11014900
H	-2.74922300	-2.86121800	-1.03641400
H	-5.93589200	-0.92767400	1.10476000
H	5.93587800	-0.92768300	1.10477400
H	2.74922700	-2.86121400	-1.03643700
H	6.21899000	-5.07385400	0.11016300

3′-T at the UBH&HLYP/def2-SVP level

Ga	-3.17278400	-0.08083400	-0.01174200
C	-4.26794100	1.46142200	-0.46676800
C	-3.78684800	2.77544000	-0.41153100
C	-4.60904600	3.85342200	-0.70855200
H	-4.21705100	4.86335900	-0.65551300
C	-5.93156600	3.63812400	-1.07345500
C	-6.43119400	2.34436700	-1.13296200
H	-7.46411400	2.17236100	-1.41578300
C	-5.60786900	1.26940700	-0.82657700
N	-1.30361400	0.10364800	-0.31687600

C	-0.36284700	-0.67271900	0.33543700
H	-0.72829900	-1.39952300	1.04914700
C	0.96659900	-0.53084800	0.10741900
H	1.68101400	-1.15753200	0.62812000
C	-3.76055400	-1.78718300	0.71325000
C	-3.08006900	-2.98761000	0.47426900
C	-3.55077200	-4.19148300	0.97957800
H	-3.00988200	-5.11010200	0.77964800
C	-4.71184500	-4.21848300	1.74097900
C	-5.40438800	-3.04127000	1.98906700
H	-6.31242800	-3.05865500	2.58207100
C	-4.93502700	-1.84036500	1.47456500
N	1.46986600	0.37567400	-0.76830800
C	0.55489800	1.13775800	-1.41572900
H	0.93688500	1.86168800	-2.12670700
C	-0.78112500	1.01972200	-1.21057600
H	-1.48321200	1.63713400	-1.75575700
Ga	3.55589200	0.58831700	-1.03914400
C	4.13090400	-1.33456600	-0.90468100
C	3.90784000	-2.24746100	-1.94192000
C	4.29796300	-3.57705700	-1.84395600
H	4.11062800	-4.26029800	-2.66686000
C	4.93486500	-4.03172800	-0.69604100
C	5.17494100	-3.14768500	0.34653000
H	5.67470900	-3.49255300	1.24670000
C	4.77672400	-1.81901400	0.23908900
C	4.05406200	1.72260300	0.54202100
C	3.11931300	2.45121500	1.28607800
C	3.49728300	3.25445500	2.35528300
H	2.74500200	3.80378900	2.91360600
C	4.83545600	3.35615700	2.71105200
C	5.78670300	2.64959700	1.98694600
H	6.83650100	2.72226200	2.25435300
C	5.39700900	1.85024600	0.91947500
H	-6.57356200	4.47997800	-1.30943200
H	-2.75768900	2.97112700	-0.12681800
H	-6.02183300	0.26630700	-0.87268400
H	5.13517500	3.98283400	3.54476900
H	6.16568900	1.31222300	0.36996600
H	2.06405500	2.39449000	1.03213500
H	-5.07778300	-5.15853300	2.13967500
H	-2.17105000	-2.99444300	-0.11908500
H	-5.49649100	-0.93255900	1.67545900
H	4.97619900	-1.14656000	1.06911200

H	3.42074700	-1.91426500	-2.85499500
H	5.24586900	-5.06855100	-0.61714500

4′-CS at the UBH&HLYP/def2-SVP level

C	-2.83996100	-1.11369700	-0.36333000
H	-3.41321500	-1.98278400	-0.66468000
C	-1.49761300	-1.14718700	-0.37352800
H	-1.02910000	-2.07209200	-0.68263200
C	-0.68565000	-0.00000900	0.00005700
C	-1.49761200	1.14716900	0.37364700
H	-1.02909800	2.07206900	0.68276400
C	-2.83996000	1.11368400	0.36343600
H	-3.41321300	1.98277100	0.66478800
C	0.68564800	-0.00000800	0.00005200
C	1.49760900	-1.14718600	-0.37353800
H	1.02909500	-2.07209100	-0.68264100
C	2.83995700	-1.11369600	-0.36334400
H	3.41321000	-1.98278400	-0.66469600
C	2.83995900	1.11368600	0.36341900
H	3.41321300	1.98277500	0.66476500
C	1.49761100	1.14717100	0.37363400
H	1.02909800	2.07207300	0.68274900
C	-6.37657500	-1.72417000	-0.02335300
C	-5.84234000	-2.88092000	0.55753100
C	-6.54356700	-4.07912600	0.55440600
H	-6.10961200	-4.96077100	1.01423900
C	-7.79806000	-4.14906300	-0.03692500
C	-8.35011200	-3.01559600	-0.61745000
H	-9.33059900	-3.06345600	-1.07945500
C	-7.64754800	-1.81770400	-0.60379100
C	-6.37657900	1.72417700	0.02332900
C	-5.84229900	2.88094800	-0.55747200
C	-6.54353400	4.07914900	-0.55437300
H	-6.10954300	4.96081000	-1.01414000
C	-7.79808200	4.14906000	0.03684500
C	-8.35017900	3.01557100	0.61728500
H	-9.33070900	3.06341100	1.07920100
C	-7.64760600	1.81768500	0.60365500
C	6.37657400	1.72417500	0.02332700
C	7.64758800	1.81769200	0.60367900
C	8.35016000	3.01558000	0.61730900
H	9.33068000	3.06342700	1.07924500
C	7.79807400	4.14906100	0.03684200
C	6.54353900	4.07914100	-0.55440200

H	6.10955700	4.96079600	-1.01419000
C	5.84230600	2.88093900	-0.55750000
C	6.37657800	-1.72416900	-0.02335200
C	5.84233700	-2.88092800	0.55750800
C	6.54357100	-4.07913000	0.55438600
H	6.10961000	-4.96078200	1.01420100
C	7.79807800	-4.14905400	-0.03691500
C	8.35013700	-3.01557800	-0.61741600
H	9.33063500	-3.06342700	-1.07939800
C	7.64756500	-1.81769000	-0.60376200
Ga	-5.45360300	0.00000500	0.00000700
Ga	5.45360100	0.00000200	0.00000200
N	-3.58634800	-0.00000300	0.00004400
N	3.58634600	-0.00000300	0.00002900
H	-8.10328300	-0.94196900	-1.05691300
H	-4.86403700	-2.85342800	1.02720300
H	-8.34538400	-5.08573600	-0.04315600
H	-8.34541300	5.08572900	0.04305400
H	-4.86395500	2.85347600	-1.02705700
H	-8.10337500	0.94193300	1.05671000
H	8.34540400	5.08573100	0.04305100
H	4.86397100	2.85346000	-1.02710600
H	8.10335000	0.94194700	1.05675400
H	8.10330500	-0.94194700	-1.05686500
H	8.34540800	-5.08572400	-0.04314300
H	4.86402300	-2.85344700	1.02715800

4′-T at the UBH&HLYP/def2-SVP level

C	-2.68023900	-1.09872000	-0.23737800
H	-3.22207100	-1.94574100	-0.64040400
C	-1.33089000	-1.13037700	-0.12843000
H	-0.82935100	-2.03214600	-0.45192100
C	-0.59093000	-0.02028900	0.38415900
C	-1.40198500	1.09469100	0.75991600
H	-0.95925000	1.99322300	1.16737800
C	-2.74969300	1.07246400	0.62942300
H	-3.34822200	1.92330100	0.93154300
C	0.84023700	-0.02508900	0.50955800
C	1.63396300	-1.13207000	0.13556000
H	1.19154300	-2.03249200	-0.26702700
C	3.00143200	-1.09331700	0.27289800
H	3.61342200	-1.94106100	-0.01529200
C	2.93171200	1.02968200	1.11971700
H	3.48861500	1.87810700	1.50347100

C	1.56351000	1.07885300	1.01623300
H	1.06316600	1.98341400	1.33240500
C	-6.20880400	-1.74009600	-0.14311000
C	-5.69705500	-2.88803600	0.47451200
C	-6.37119100	-4.09956600	0.40989600
H	-5.95840600	-4.97511600	0.89939600
C	-7.57243200	-4.19004100	-0.28103900
C	-8.10051000	-3.06511300	-0.89945900
H	-9.03945000	-3.13080200	-1.43858700
C	-7.42720000	-1.85321300	-0.82453800
C	-6.20130800	1.73933900	-0.09215300
C	-5.57907300	2.88419900	-0.60521000
C	-6.24583900	4.10024700	-0.66077100
H	-5.74584700	4.97331400	-1.06616600
C	-7.55133900	4.19837600	-0.19750600
C	-8.18965900	3.07661300	0.31334400
H	-9.20997900	3.14829700	0.67444500
C	-7.52184300	1.86022000	0.35867600
C	6.20026900	1.71544400	0.06124400
C	7.17598400	2.59631200	0.53964100
C	7.49506500	3.77158400	-0.13030700
H	8.25949300	4.43211700	0.26740500
C	6.83511100	4.10297400	-1.30591900
C	5.85930200	3.24976600	-1.80346900
H	5.33862400	3.49818700	-2.72346500
C	5.55109000	2.07553800	-1.12604800
C	6.30942000	-1.69324000	0.08544900
C	6.20055100	-2.95270800	0.68631500
C	6.58570900	-4.11450400	0.02760800
H	6.48839200	-5.07675700	0.52118400
C	7.10459100	-4.04331200	-1.25860600
C	7.23391400	-2.80617500	-1.87526800
H	7.64370600	-2.74026300	-2.87858100
C	6.84095100	-1.65083500	-1.20892700
Ga	-5.33289200	-0.00337400	-0.03931000
Ga	5.77626000	0.00066400	1.02970700
N	-3.44470800	-0.01046700	0.13080700
N	3.65563100	-0.03476300	0.75875300
H	-7.86311100	-0.98445200	-1.30926500
H	-4.76088500	-2.84399400	1.02241000
H	-8.09790900	-5.13742500	-0.33525300
H	-8.07174600	5.14927900	-0.23706800
H	-4.55985000	2.83417200	-0.97562500
H	-8.04369700	0.99406400	0.75514000

H	7.07960500	5.02058200	-1.83133800
H	4.78457400	1.42643300	-1.54233100
H	7.70305400	2.36361900	1.46131700
H	6.95472400	-0.69451800	-1.71221200
H	7.41181200	-4.94698900	-1.77523600
H	5.81124200	-3.03334200	1.69838600

4″-CS at the BH&HLYP/def2-SVP level

Ga	5.46663900	-0.06521500	0.28229600
O	5.54367900	0.17474800	-1.82654700
N	3.57059400	-0.01599100	0.39316800
C	2.86000100	1.12653100	0.06643200
H	3.45262300	2.02609900	-0.06501500
C	1.52509700	1.17221900	-0.09270900
H	1.08653300	2.12915000	-0.34451300
C	0.68021300	-0.00390300	0.07429000
C	1.46147300	-1.18796400	0.41505100
H	0.97085300	-2.14015200	0.56974100
C	2.79861700	-1.15486700	0.55367500
H	3.34604100	-2.05783300	0.80163100
C	6.43230800	1.56004600	0.85889400
C	7.81392300	1.65012600	0.64855500
C	8.54550300	2.75598600	1.06227800
H	9.61543300	2.79653800	0.88470300
C	7.90821700	3.80419400	1.71280700
C	6.54253400	3.73374000	1.94924500
H	6.03861300	4.54329500	2.46736900
C	5.81818400	2.62479500	1.52736300
C	6.27065900	-1.86341300	0.45371200
C	7.08950000	-2.39410900	-0.54870500
C	7.69317300	-3.63899100	-0.41652300
H	8.32283700	-4.02358100	-1.21260700
C	7.49124300	-4.38977300	0.73284600
C	6.68668900	-3.88567200	1.74562300
H	6.52469000	-4.46413400	2.64943400
C	6.08893100	-2.63955300	1.60444600
C	5.99221500	1.36857400	-2.48799200
H	7.07259500	1.44684000	-2.36651000
H	5.52790000	2.22981500	-2.00217100
C	5.53653400	1.20814300	-3.92604100
H	5.37108700	2.17082300	-4.41295200
H	6.28603500	0.66212400	-4.50663500
C	4.26979900	0.37516400	-3.77465800

H	3.43122200	1.00071800	-3.45703300
H	3.97817900	-0.14544500	-4.68828000
C	4.64944800	-0.58252100	-2.66444600
H	3.80754600	-0.91265000	-2.05782400
H	5.19177200	-1.45629500	-3.03601500
N	-3.57059300	0.01599200	-0.39316300
C	-2.86000100	-1.12652900	-0.06642500
H	-3.45262200	-2.02609800	0.06502100
C	-1.52509600	-1.17221800	0.09271700
H	-1.08653200	-2.12914800	0.34452300
C	-0.68021300	0.00390500	-0.07428100
C	-1.46147300	1.18796500	-0.41504300
H	-0.97085300	2.14015300	-0.56973300
C	-2.79861600	1.15486800	-0.55366800
H	-3.34604000	2.05783400	-0.80162500
Ga	-5.46663900	0.06521400	-0.28229600
O	-5.54368400	-0.17474500	1.82654800
C	-6.43230400	-1.56004800	-0.85889400
C	-7.81391900	-1.65013200	-0.64855400
C	-8.54549600	-2.75599400	-1.06227900
H	-9.61542600	-2.79654800	-0.88470400
C	-7.90820700	-3.80420000	-1.71280800
C	-6.54252400	-3.73374200	-1.94924500
H	-6.03860200	-4.54329600	-2.46737000
C	-5.81817700	-2.62479600	-1.52736300
C	-6.27065900	1.86341100	-0.45371700
C	-7.08950700	2.39410700	0.54869600
C	-7.69318100	3.63898800	0.41651000
H	-8.32284900	4.02357800	1.21259000
C	-7.49124600	4.38976900	-0.73285800
C	-6.68668600	3.88566900	-1.74563100
H	-6.52468300	4.46413100	-2.64944200
C	-6.08892700	2.63955100	-1.60445000
C	-5.99221700	-1.36857200	2.48799300
H	-7.07259600	-1.44684200	2.36650900
H	-5.52789700	-2.22981200	2.00217500
C	-5.53653900	-1.20813700	3.92604300
H	-5.37109000	-2.17081500	4.41295500
H	-6.28604400	-0.66212100	4.50663400
C	-4.26980800	-0.37515300	3.77466100
H	-3.43122700	-1.00070300	3.45703900
H	-3.97819200	0.14545900	4.68828400
C	-4.64945800	0.58253000	2.66444800
H	-3.80755700	0.91266100	2.05782700

H	-5.19178700	1.45630100	3.03601400
H	7.95962300	-5.36255500	0.83993100
H	5.46761500	-2.27187700	2.41675800
H	7.26415400	-1.82604400	-1.45796600
H	8.34103500	0.83440100	0.15987700
H	8.47561100	4.66878000	2.04122400
H	4.75349500	2.59265800	1.73645500
H	-7.26416400	1.82604300	1.45795600
H	-5.46760600	2.27187500	-2.41675900
H	-7.95962600	5.36255000	-0.83994700
H	-8.47559900	-4.66878700	-2.04122500
H	-8.34103300	-0.83440800	-0.15987600
H	-4.75348800	-2.59265600	-1.73645500

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