Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Synthesis and redox activity of carbene-coordinated group 13 metal radicals

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Content

1. Experimental Section

2. Spectroscopic Characterization (NMR, IR)

Figure S1. ^{1}H NMR spectrum of **1**.
Figure S2. ^{13}C{^{1}H} NMR spectrum of **1**.
Figure S3. ^{1}H NMR spectrum of **5**.
Figure S4. ^{19}F NMR spectrum of **5**.
Figure S5. ^{1}H NMR spectrum of **6**.
Figure S6. ^{13}C{^{1}H} NMR spectrum of **6**.
Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **6**.
Figure S8. ^{1}H-^{13}C HSQC NMR spectrum of **6**.
Figure S9. ^{1}H-^{13}C HMBC NMR spectrum of **6**.
Figure S10. ^{19}F NMR spectrum of **6**.
Figure S11. ^{11}B NMR spectrum of **6**.
Figure S12. IR spectrum of **1**.
Figure S13. IR spectrum of **3**.
Figure S14. IR spectrum of **4**.
Figure S15. IR spectrum of **6**.

3. Crystallographic Details

Table S1. Crystal data and structure refinement of **3**-**6** and **5S**.

Table S2. Selected bond lengths [Å] and angles [°] of the $C_{cAAC}M(X_2)C_{IPr}$ unit of **3**–**6** (calc. values).

Figure S16 and S20. Molecular structures of **3**-**6** and **5S**.

4. EPR measurement

Figure S21. Simulated EPR spectra for various amounts of Al and N hyperfine coupling in the frozen solution regime.
Figure S22. Room temperature EPR spectrum of **3**.

5. Cyclic Voltammetry measurement

Figure S23. Cyclic voltammogram for **3**, **4** and **6**.

6. Computational Details

Figure S24. Biorthogonalized HOMO, SOMO and LUMO of **3** and **4** as well as the HOMO, LUMO and LUMO+1 of **5** and **6**.
Table S3. Calculated X–Y bond lengths, X and Y, NPA atomic charges, natural spin density, Wiberg bond indices (WBI), and NBO analysis of **3**.
Table S4. Calculated X–Y bond lengths, X and Y, NPA atomic charges, natural spin density, Wiberg bond indices (WBI), and NBO analysis of **4**.
Table S5. Calculated X–Y bond lengths, X and Y, NPA atomic charges, natural spin density, Wiberg bond indices (WBI), and NBO analysis of **5**.
Table S6. Calculated X–Y bond lengths, X and Y, NPA atomic charges, natural spin density, Wiberg bond indices (WBI), and NBO analysis of **6**.
Table S7. Cartesian coordinates of **3** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.
Table S8. Cartesian coordinates of **4** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.
Table S9. Cartesian coordinates of **5** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.
Table S10. Cartesian coordinates of **6** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.
Table S11. Cartesian coordinates of **3** [Å] optimized at the BP86/def2-TZVP level of theory.
Table S12. Cartesian coordinates of **4** [Å] optimized at the BP86/def2-TZVP level of theory.

7. References

1. Experimental Section

General procedure. All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. Toluene and *n*-hexane were dried by Braun solvent drying system and degassed to use. Fluorobenzene and deuterated dichloromethane were dried by stirring with CaH_2. The NMR (^1H, ^{13}C, ^{19}F and ^{11}B) spectra were recorded on Bruker Avance II 600 MHz and 500 MHz spectrometers. Elemental analysis was performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen. IR spectra were reported by a Bruker ALPHA-T FT-IR spectrometer equipped with a single-reflection ATR sampling module. Cyclic voltammetry (CV) studies were performed in a glovebox using a Metrohm Autolab PGSTAT 204 potentiostat with a three electrodes setup consisting of a Pt disc (d = 1 mm) working electrode, Pt wire counter electrode, and Ag wire pseudo-reference electrode, and ferrocene as internal standard. Positive feedback compensation was utilized to reduce solvent resistance effects. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. $^{i\text{Pr}}$NHC,[1] cAAC,[2] and (cAAC)$GaCl_3$[3] were prepared according to the literatures.

Synthesis of 1: A mixture of $^{\text{Me}}$cAAC (285 mg, 1 mmol) and $AlBr_3$ (267 mg, 1 mmol) was suspended in 20 mL of *n*-hexane, and stirred overnight, yielding a colourless solid that was isolated by filtration. Yield: 586 mg (90%). Mp: 220 °C. Anal. Calcd (%) for $C_{20}H_{31}NAlBr_3$ (Mr = 552.16): C, 43.5; H, 5.66; N, 2.54. Found: C, 43.2; H, 5.01; N, 2.72. ^{1}H NMR (500 MHz, d^8-toluene, 298K, ppm): δ = 0.83 (s, 6 H, CH_3),1.03 (d, $^3J_{HH}$ = 5 Hz, 6 H, CHMe_2), 1.34 (s, 2 H, CH_2), 1.48 (d, $^3J_{HH}$ = 8 Hz, 6 H, CHMe_2), 1.65 (s, 6 H, CH_3), 2.55 (sept, $^3J_{HH}$ = 5 Hz, 2 H, CHMe$_2$), 6.95−7.12 (m, 3 H, C_6H_3).^{13}C NMR (125 MHz, d^8-toluene, 298K, ppm): δ = 24.9, 27.0, 28.6, 29.2, 30.1, 50.8, 56.3, 82.3, 126.1, 131.0, 133.0, 145.4. **ATR-IR**: *v* 2955, 2921, 2861, 1452, 1366, 1258, 1093, 1047, 1011, 801, 774 cm^{-1}.

Synthesis of 3: $^{\text{Me}}$cAAC($AlBr_3$) (276 mg, 0.5 mmol) was dissolved in 40 mL of toluene, and the solution was transferred to a stirred, cooled (–70 °C) mixture of $^{i\text{Pr}}$NHC (90 mg, 0.5 mmol) and KC_8 (135 mg, 1 mmol), and then the temperature was slowly raised up to room temperature. The suspension was stirred for 12 h, filtered and the resulting dark red filtrate concentrated to 4 mL and kept at 4 °C, yielding dark orange crystals after 24 h. Yield: 86 mg (26%). Melting point: Mp: 131 °C (dec.). Anal. Calcd (%) for $C_{31}H_{51}N_3AlBr_2$ (Mr = 652.55): C, 57.1; H, 7.88; N, 6.44. Found: C, 57.2; H, 7.66; N, 6.67. **ATR-IR**: *v* 2962, 2927, 2855, 1447, 1369, 1354, 1319, 1188, 1128, 1108, 903, 806, 770, 492 cm^{-1}.

Synthesis of 4: $^{\text{Me}}$cAAC($GaCl_3$) (231 mg, 0.5 mmol) was dissolved in 50 mL toluene, and the solution was transferred to a mixture of $^{i\text{Pr}}$NHC (90 mg, 0.5 mmol) and KC_8 (135 mg, 1 mmol) at -70 ^{o}C under stirring. The temperature was slowly raised up to room temperature and keep the stirring overnight. After filtration, the dark red filtrate was concentrated to 5 mL and kept at 4 ^{o}C. After 1 day, dark orange crystals were obtained. Yield: 97 mg (32%). Melting point: Mp: 124 ^{o}C (dec.). Anal. Calcd (%) for $C_{31}H_{51}N_3GaCl_2$ (Mr = 606.39): C, 61.4; H, 8.48; N, 6.93. Found: C, 60.9; H, 8.40; N, 6.55. **ATR-IR**: *v* 2965, 2939, 2863, 1441, 1375, 1360, 1329, 1199, 1133, 906, 809 ,774 cm^{-1}.

Synthesis of 5 and 5S: Compound **3** (69 mg, 0.11 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (97 mg, 0.11 mmol) were dissolved in benzene (5 mL) at ambient temperature, immediately giving a yellow solution that was stirred for

1 h. The solvent was removed in vacuo and the residue washed with *n*-hexane (5×2 mL) two times. The resulting pale brown solid was dissolved in fluorobenzene, and *n*-hexane was layered on the top. After keeping at ambient temperature for 2 days, tiny colourless crystals were formed, which still contained some by-products even after several recrystallization attempts, probably due to the instability of **5** in solution state. Therefore, **5** was only characterised by ^{1}H and ^{19}F NMR spectroscopy. **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 1.38 (d, $^{3}J_{HH}$ = 4.0 Hz, 6H, CH*Me*$_2$), 1.39 (d, $^{3}J_{HH}$ = 8.0 Hz, 6H, CH*Me*$_2$), 1.47 (s, 6H, C*Me*$_2$), 1.54 (d, $^{3}J_{HH}$ = 8.0 Hz, 12H, CH*Me*$_2$), 1.56 (s, 6H, C*Me*$_2$), 2.15 (s, 2H, C*H*$_2$), 2.36 (s, 6H, C*Me*), 2.74 (sept, $^{3}J_{HH}$ = 8.0 Hz, 2H, C*H*Me$_2$), 5.40 (sept, $^{3}J_{HH}$ = 8.0 Hz, 2H, C*H*Me$_2$), 7.37-7.65 (m, 3H, C$_6$*H*$_3$). **^{19}F NMR (376 MHz, CD_2Cl_2)** δ = -133.1(m, 8F, *o*-*F*), -163.8 (t, $^{3}J_{FF}$ = 22.6 Hz, 4F, *p*-*F*), -167.6 (m, 8F, *m*-*F*). (Note: [cAAC-H][B(C$_6$F$_5$)$_4$] (**5S**) was identified as one of the side-products by single crystal X-ray diffraction).

Synthesis of 6: Compound **4** (70 mg, 0.12 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (107 mg, 0.12 mmol) were dissolved in toluene (5 mL) under stirring at ambient temperature, yielding a yellow solution that was stirred for 12 h. After removing the solvent in vacuo, the residue was washed with *n*-hexane (5×2 mL) two times and the resulting yellow solid was dried. Yield: 122 mg (82%). Single crystal suitable for X-ray diffraction were obtained by layering *n*-hexane on the top of fluorobenzene solution. Melting point: 236 °C (dec.). Anal. calcd. (%) for $C_{55}H_{51}N_3GaCl_2BF_{20}$ (Mr = 1285.44): C, 51.4; H, 4.00; N, 3.26. Found: C, 52.0; H, 3.84; N, 3.11. **^{1}H NMR (600 MHz, CD_2Cl_2)** δ = 1.35 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H, CH*Me*$_2$), 1.38 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H, CH*Me*$_2$), 1.48 (s, 6H, C*Me*$_2$), 1.53 (s, 6H, C*Me*$_2$), 1.54 (d, $^{3}J_{HH}$ = 6.0 Hz, 12H, CH*Me*$_2$), 2.20 (s, 2H, C*H*$_2$), 2.34 (s, 6H, C*Me*), 2.70 (sept, $^{3}J_{HH}$ = 6.0 Hz, 2H, C*H*Me$_2$), 5.27 (sept, $^{3}J_{HH}$ = 6.0 Hz, 2H, C*H*Me$_2$), 7.38 (d, $^{3}J_{HH}$ = 6.0 Hz, 2H, *m*-Ar*H*), 7.54 (t, $^{3}J_{HH}$ = 6.0 Hz, 1H, *p*-Ar*H*). **^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2)** δ = 11.2, 21.9, 25.6, 27.4, 29.4, 29.7, 29.8, 50.2, 55.7, 87.2, 126.6, 130.8, 131.5,136.0, 137.7, 145.3, 147.9, 149.5, 153.0 (carbene carbon in $^{i\text{Pr}}$NHC), 225.1 (carbene carbon in $^{\text{Me}}$cAAC). **^{19}F NMR (565 MHz, CD_2Cl_2)** δ = -133.1(m, 8F, *o*-*F*), -163.8 (t, $^{3}J_{FF}$ = 33.9 Hz, 4F, *p*-*F*), -167.6 (m, 8F, *m*-*F*). **^{11}B NMR (192 MHz, CD_2Cl_2)** δ = -16.7. ATR-IR: *v* 2987, 1642, 1511, 1461, 1387, 1374, 1272, 1084, 978, 774, 755, 683, 659, 574 cm^{-1}.

2. Spectroscopic Characterization (NMR, IR)

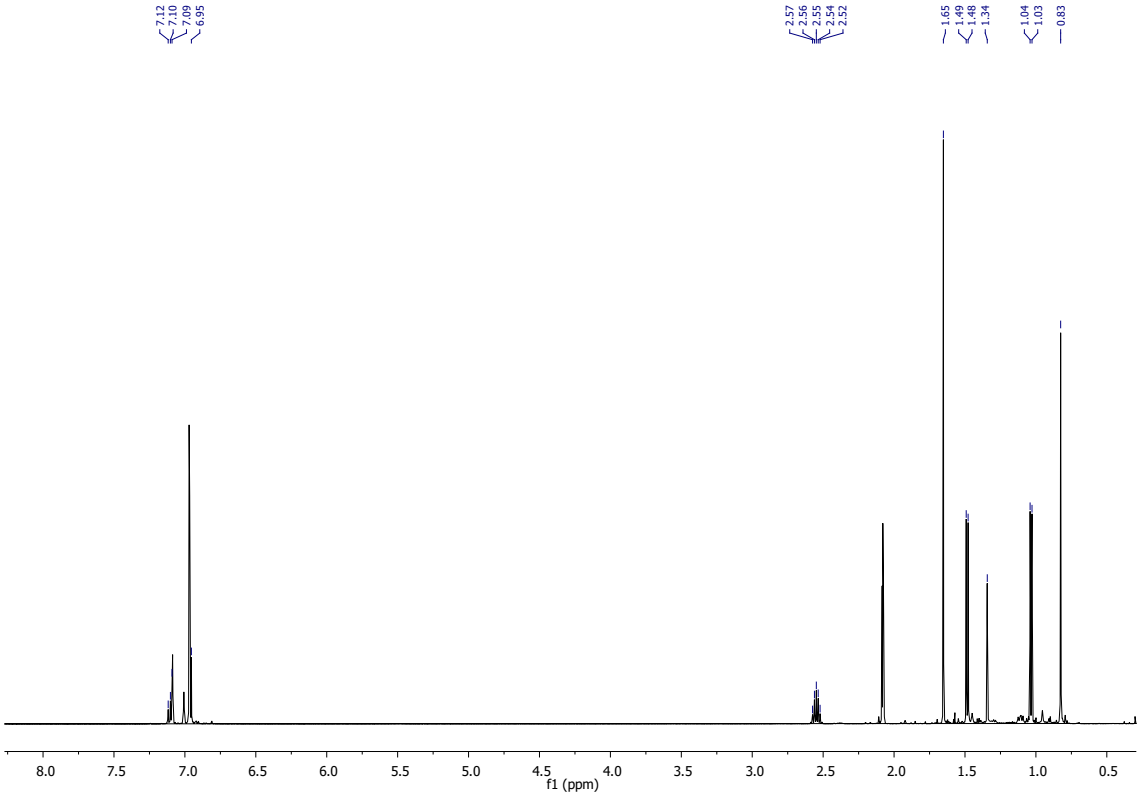

Figure S1. ^{1}H NMR spectrum of **1** in d^{8}-toluene at 298K.

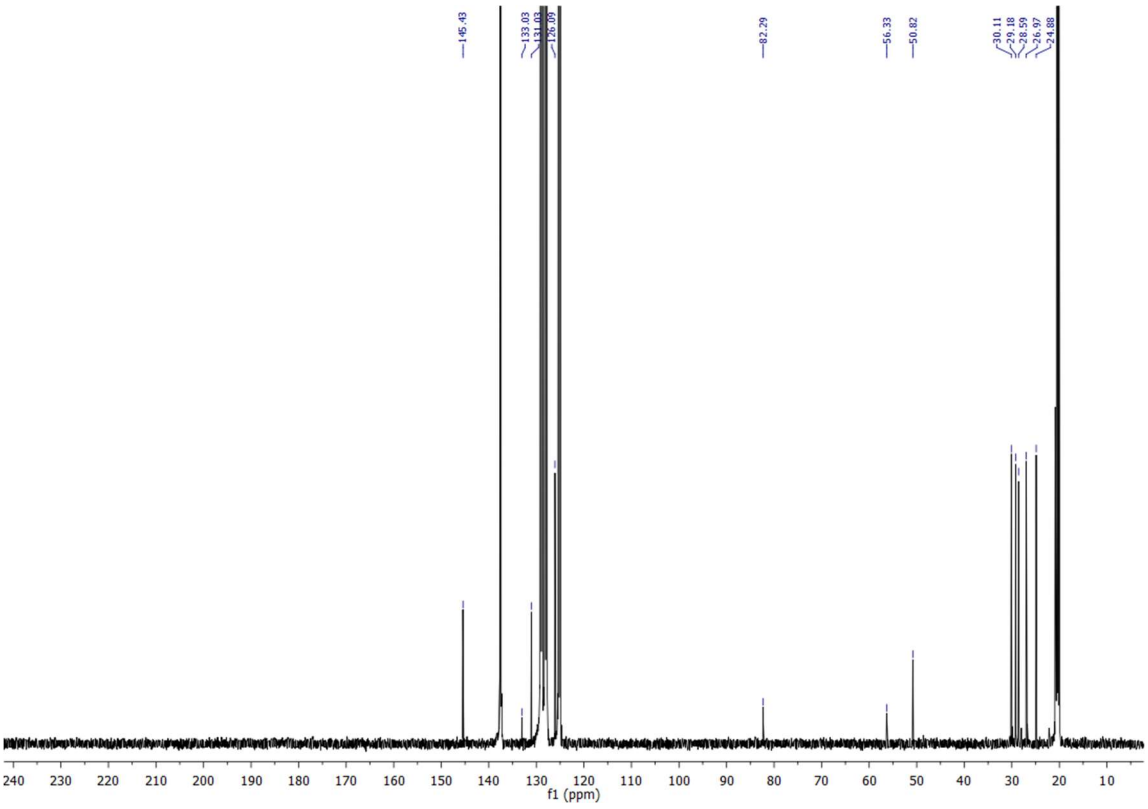

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1** in d^{8}-toluene at 298K.

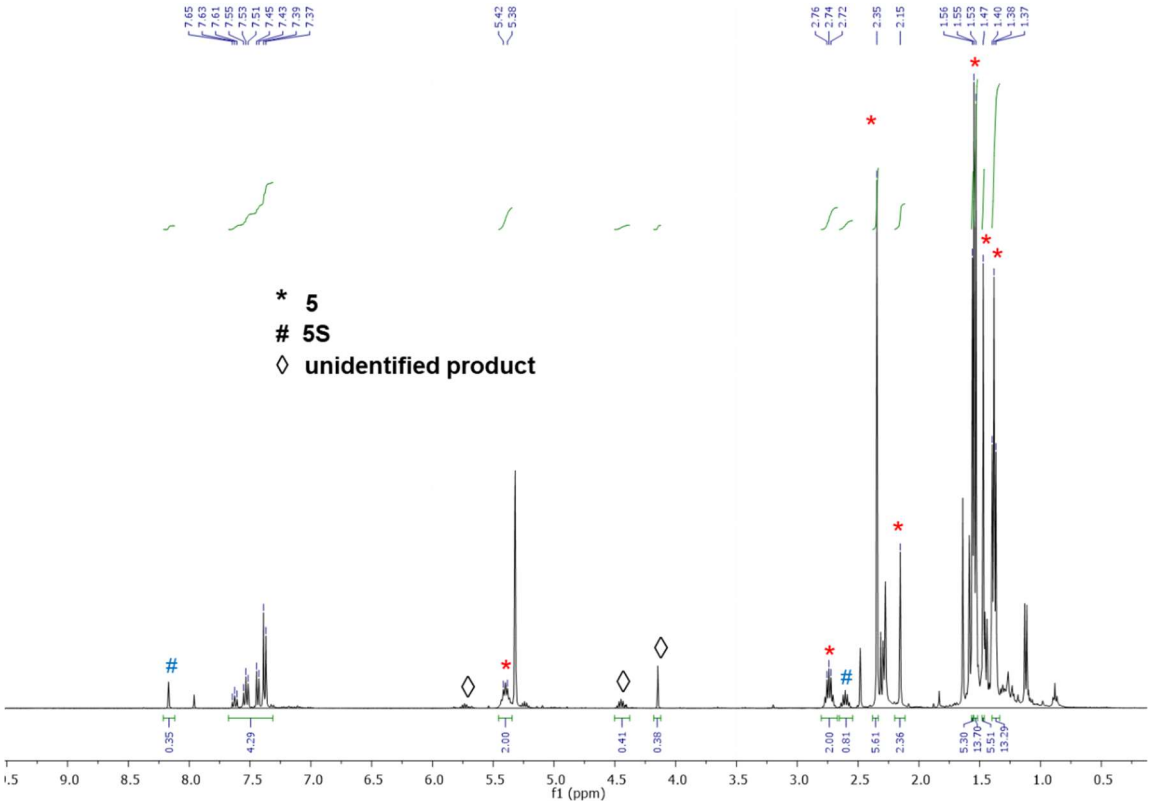

Figure S3. ^{1}H NMR spectrum of **5** in CD_2Cl_2 at 298K.

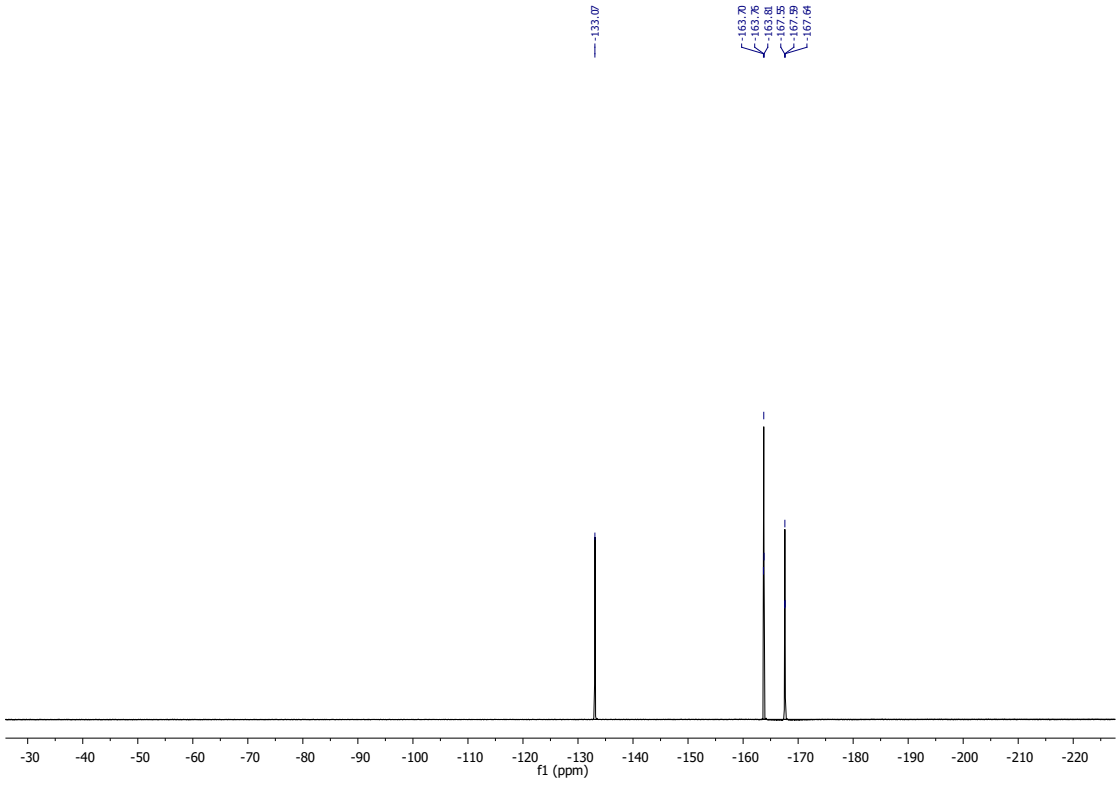

Figure S4. ^{19}F NMR spectrum of **5** in CD_2Cl_2 at 298K.

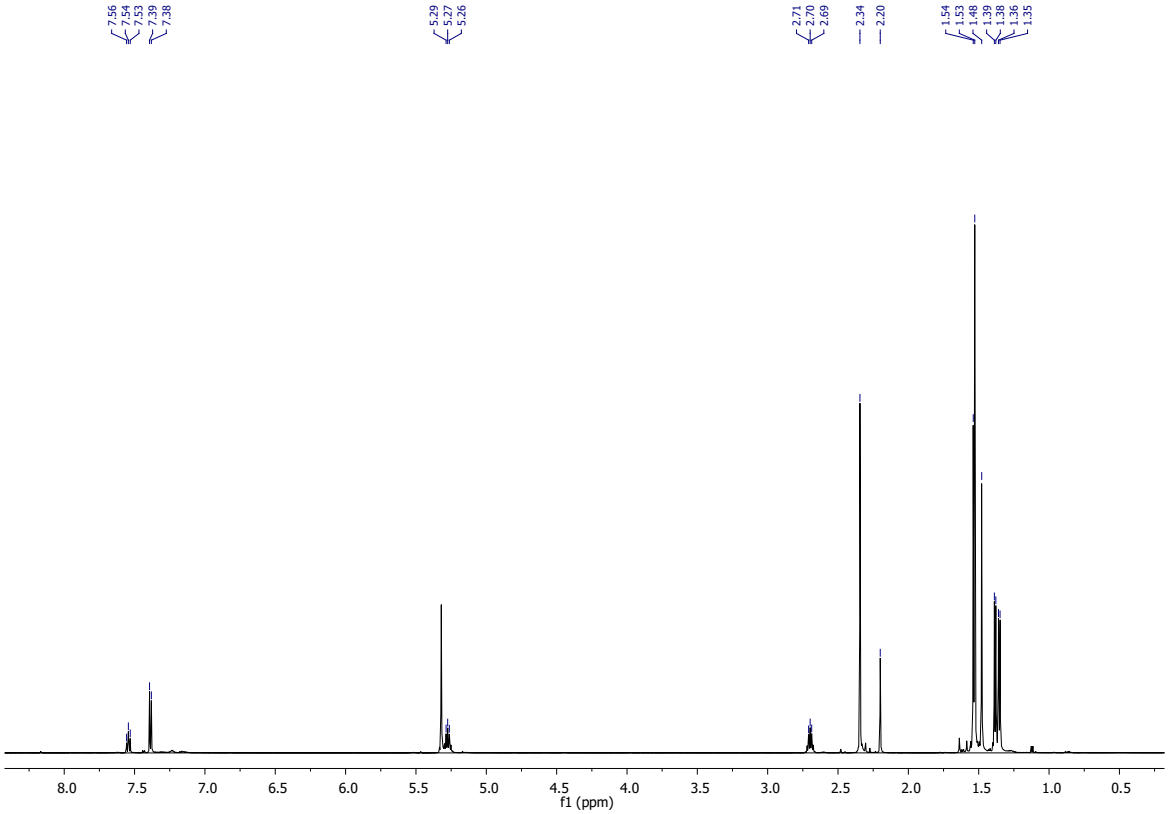

Figure S5. ^{1}H NMR spectrum of **6** in CD_2Cl_2 at 298K.

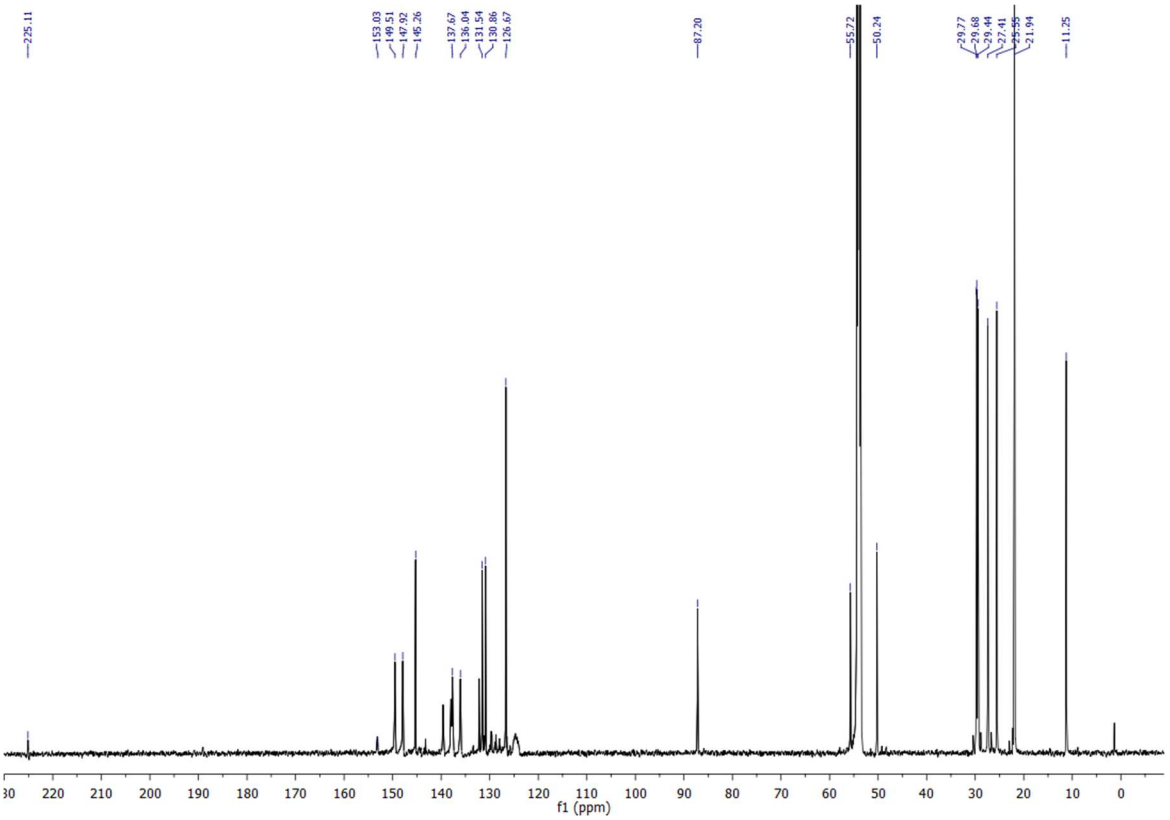

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 298K.

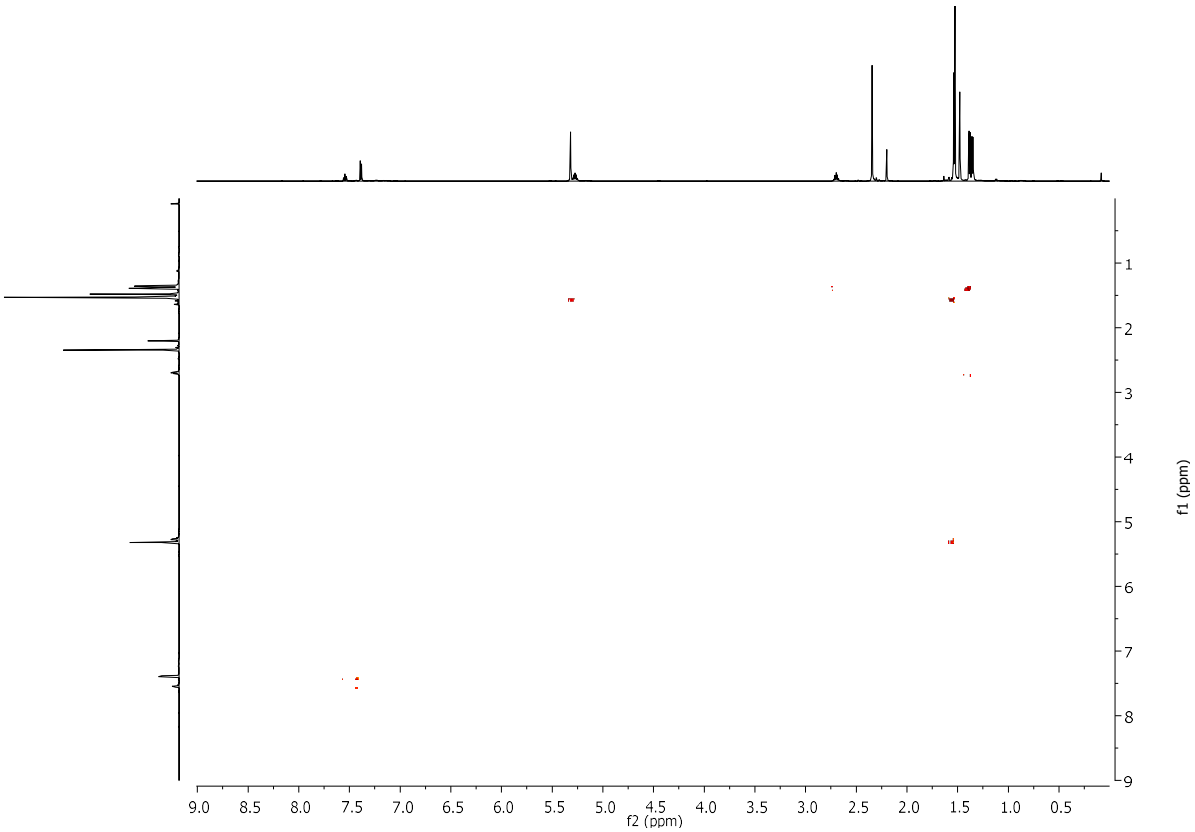

Figure S7. ^{1}H-^{1}H COSY NMR spectrum of **6** in CD_2Cl_2 at 298K.

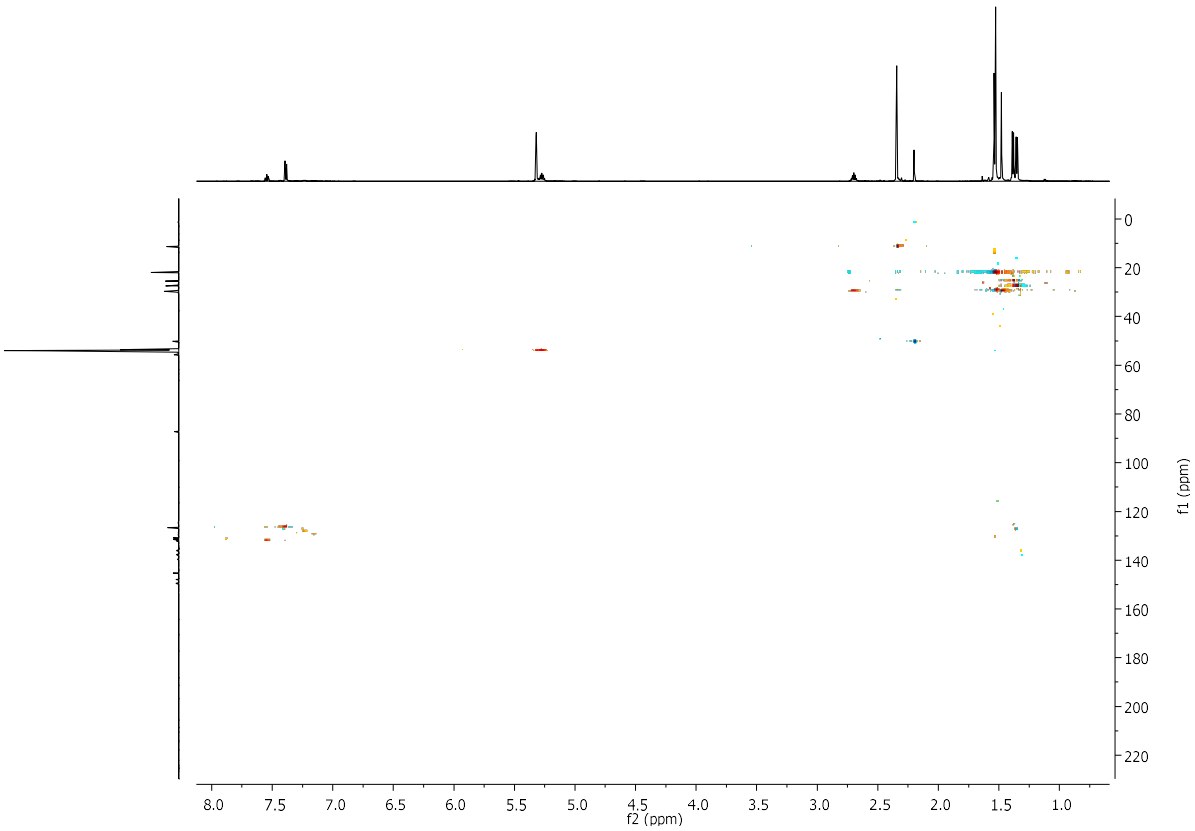

Figure S8. ^{1}H-^{13}C HSQC NMR spectrum of **6** in CD_2Cl_2 at 298K.

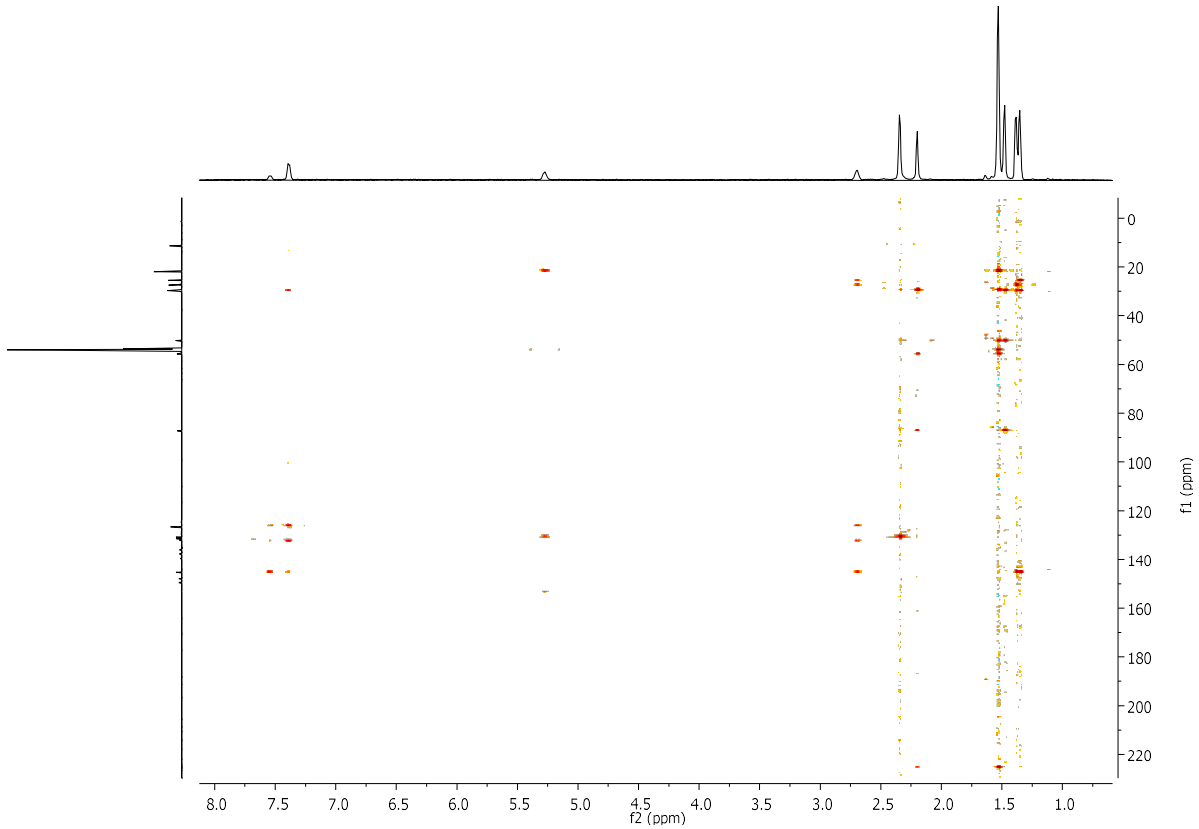

Figure S9. ^{1}H-^{13}C HMBC NMR spectrum of **6** in CD_2Cl_2 at 298K.

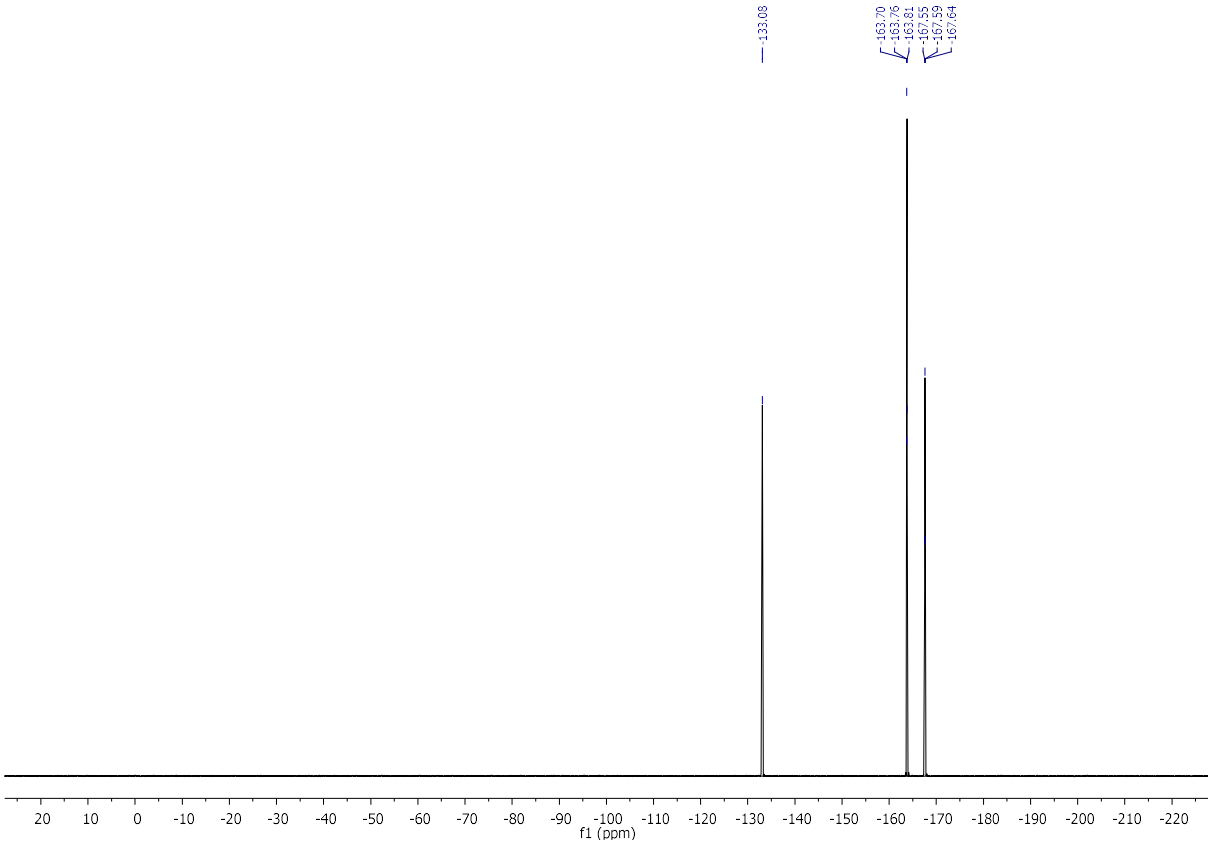

Figure S10. ^{19}F NMR spectrum of **6** in CD_2Cl_2 at 298K.

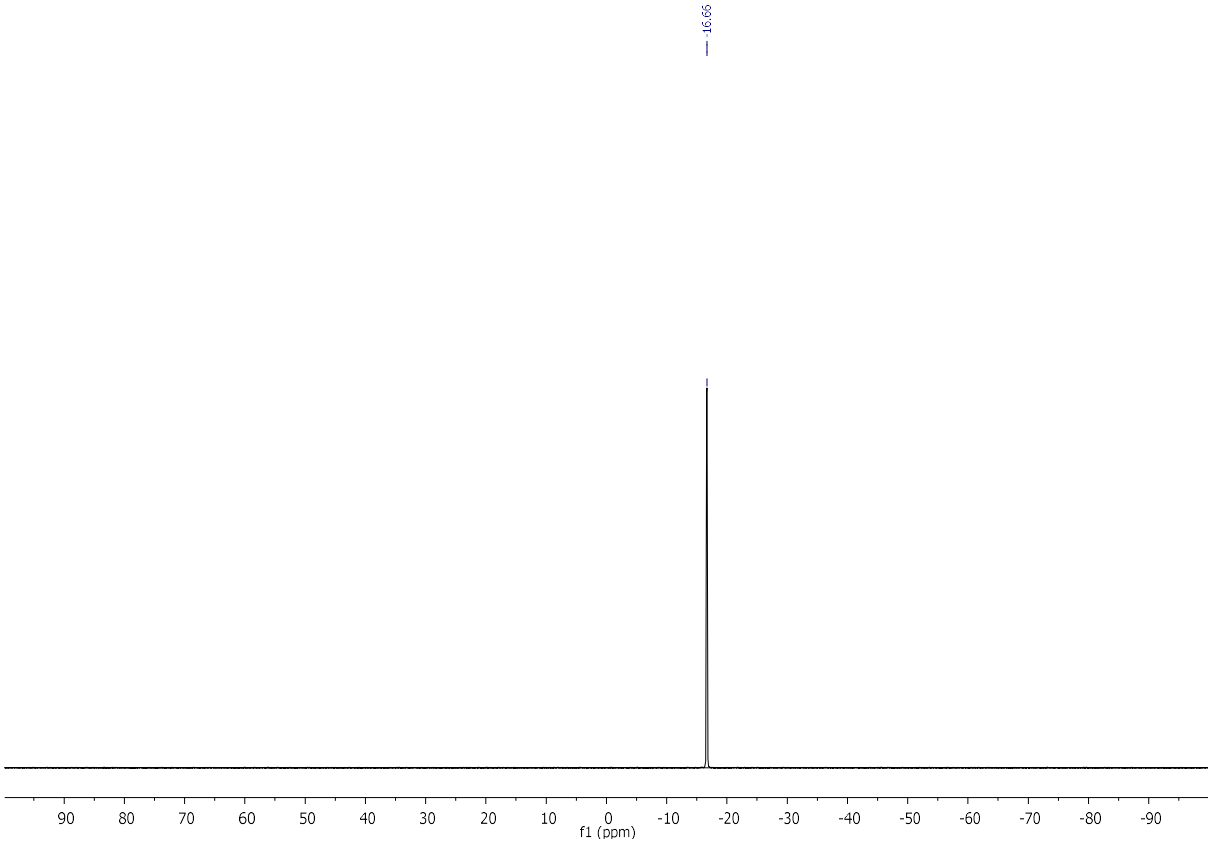

Figure S11. ^{11}B NMR spectrum of **6** in CD_2Cl_2 at 298K.

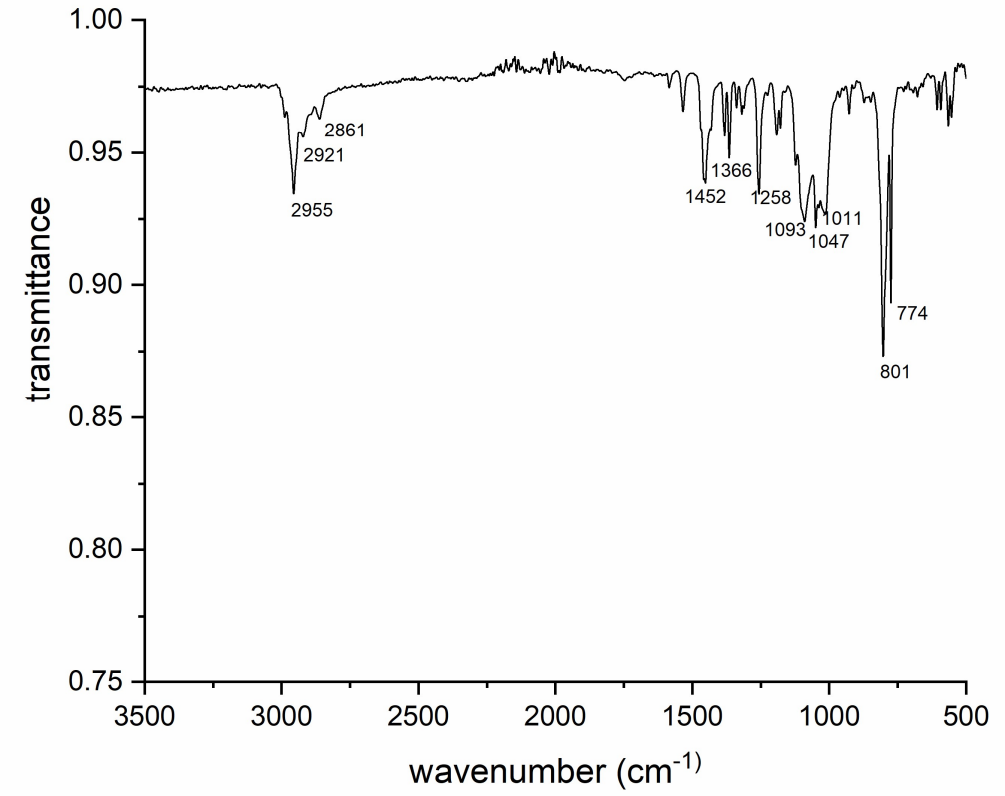

Figure S12. Infrared resonance spectrum of **1**.

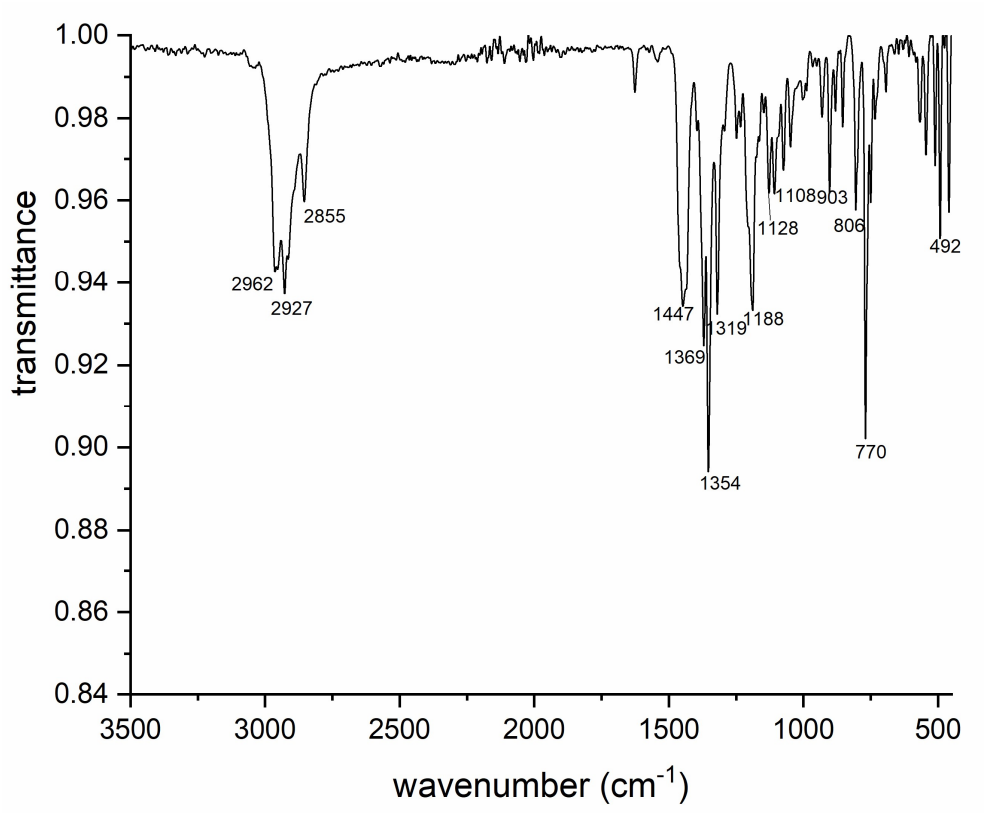

Figure S13. Infrared resonance spectrum of **3**.

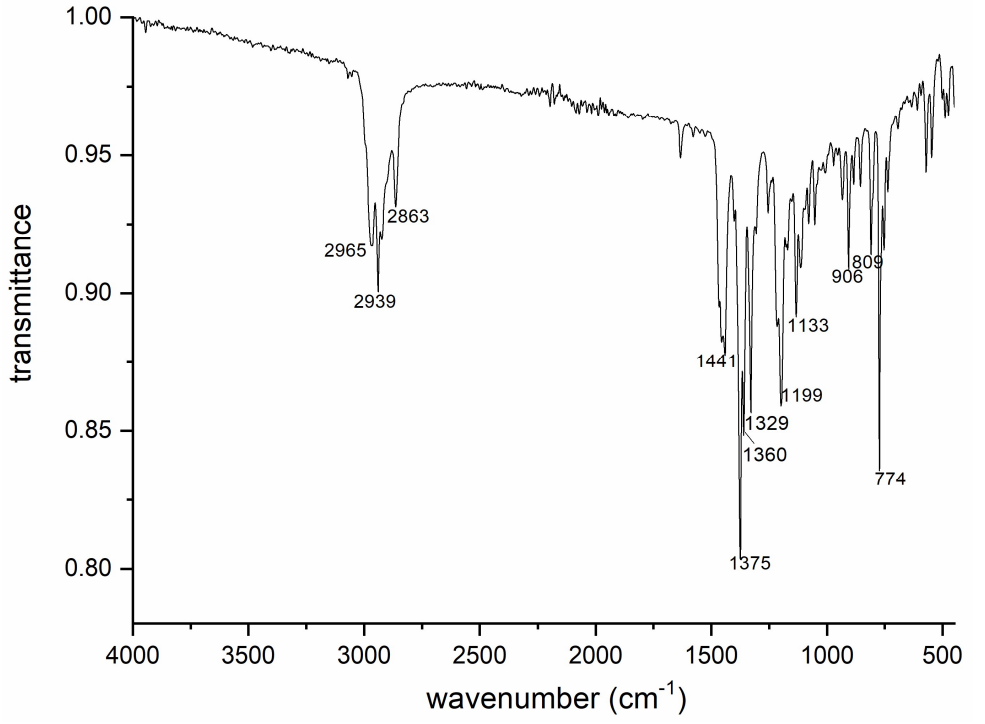

Figure S14. Infrared resonance spectrum of **4**.

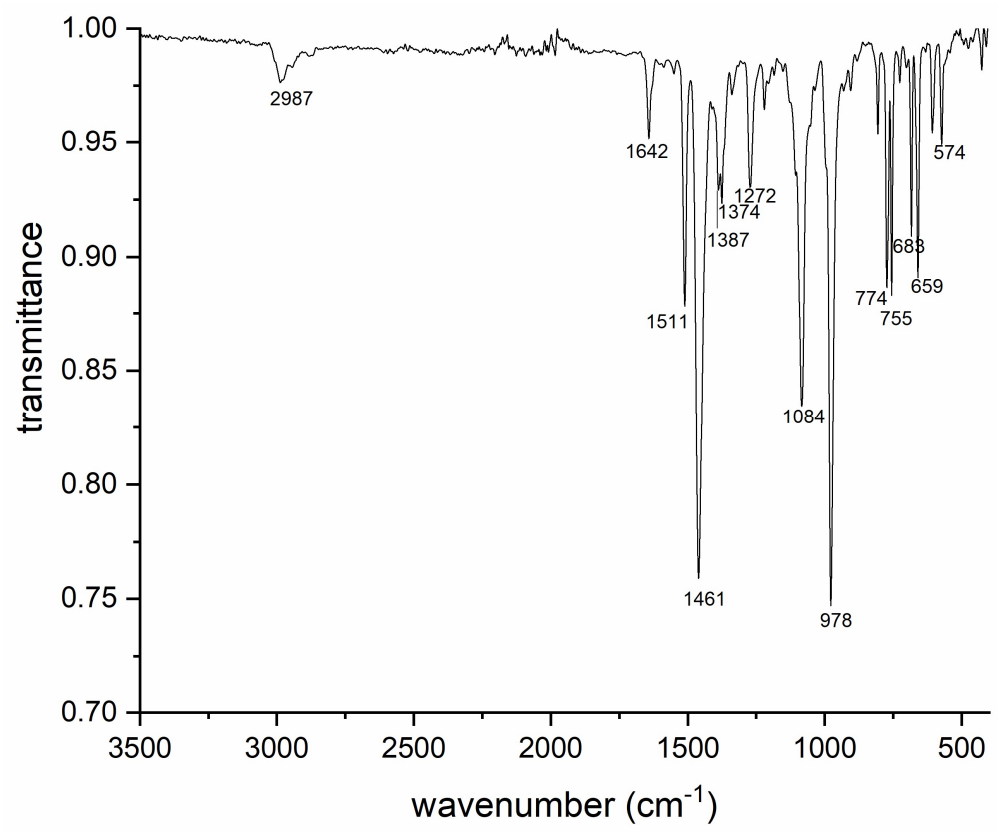

Figure S15. Infrared resonance spectrum of **6**.

3. Crystallographic Details

The crystals were mounted on nylon loops in inert oil. Data of **3**, **4**, **5**, **5S** were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated $Mo_{K\alpha}$ radiation, l = 0.71073 Å) those of **6** on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated $Cu_{K\alpha}$ radiation, l = 1.54178 Å, microfocus source) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)[4] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2017)[5,6]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX3). Hydrogen atoms were refined using a riding model or rigid methyl groups. The crystal of **4** was a two component non-merohedral twin and the model was refined against de-twinned HKLF4 data.

CCDC-2129477 (**3**), -2129478 (**4**), -2129479 (**5**), -2129480 (**5S**), and -2129481 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystallographic data of compounds **3**-**6**.

Ident. code	**3**	**4**	**5**	**5S**	**6**
Emp. formula	$C_{31}H_{51}Br_2AlN_3$	$C_{31}H_{51}Cl_2GaN_3$	$C_{55}H_{51}BBr_2F_{20}AlN_3$	$C_{44}H_{32}BF_{20}N$	$C_{55}H_{51}BCl_2F_{20}GaN_3$
M	652.54	606.36	1331.59	965.51	1285.41
Crystal size [mm]	0.344 × 0.202 × 0.178	0.470 × 0.450 × 0.320	0.392 × 0.184 × 0.171	0.737 × 0.388 × 0.133	0.184 × 0.130 × 0.027
T [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Cryst. system	monoclinic	monoclinic	monoclinic	Orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a [Å]	14.9332(16)	15.157(6)	17.3212(16)	14.3008(19)	9.3349(4)
b [Å]	10.7999(12)	10.928(4)	17.0220(16)	14.7881(19)	19.9338(9)
c [Å]	20.545(2)	20.000(7)	19.1672(18)	19.075(3)	29.6976(13)
α [°]	90	90	90	90	90
β [°]	90.806(2)	90.064(7)	101.493(3)	90	93.9233(14)
γ [°]	90	90	90	90	90
V [Å^3]	3313.1(6)	3313(2)	5538.0(9)	4034.1(9)	5513.2(4)
Z	4	4	4	4	4
D_{calc} [g·cm^{-3}]	1.308	1.216	1.597	1.590	1.549
μ([mm^{-1}])	2.496	1.015	1.588	0.157	2.552
Transmissions	0.75/0.57	0.75/0.59	0.75/0.61	0.75/0.66	0.75/0.61
F(000)	1364	1292	2680	1952	2608
Index ranges	$-24 \le h \le 24$ $18 \le k \le 18$ $-34 \le l \le 34$	$-21 \le h \le 21$ $0 \le k \le 15$ $0 \le l \le 29$	$-26 \le h \le 26$ $-26 \le k \le 26$ $-29 \le l \le 29$	$-22 \le h \le 22$ $-22 \le k \le 22$ $-29 \le l \le 29$	$-11 \le h \le 11$ $-24 \le k \le 25$ $-37 \le l \le 38$
ϑ_{max} [°]	36.385	32.524	33.336	33.288	80.893
Refl. collected	179562	85326	218986	144712	213348
Independ. refl.	16101	10289	21310	15513	12053
R_{int}	0.0564	0.0496	0.0576	0.0498	0.0396
Ref. params.	348	348	753	603	753
R_1 [$I > 2\sigma(I)$]	0.0346	0.0659	0.0331	0.0411	0.0262
wR_2 [$I > 2\sigma(I)$]]	0.0761	0.1394	0.0743	0.0954	0.0698
R_1 [all data]	0.0575	0.1228	0.0546	0.0538	0.0277
wR_2 [all data]	0.0843	0.1555	0.0818	0.1031	0.0710
x(Flack)				-0.05(7)	
GooF	1.025	1.074	1.019	1.051	1.027
$\Delta\rho_{final}$ (max/min) [e·Å^{-3}]	1.823/-1.491	0.546/-0.438	0.640/-0.671	0.629/-0.263	0.349/-0.432

Table S2. Selected bond lengths [Å] and angles [°] of the $C_{cAAC}M(X_2)C_{IPr}$ unit of **3**–**6** (calc. values).

	3	**4**	**5**	**6**
M-X_1	2.3603(4) (2.3708)	2.221(1) (2.237)	2.2824(4) (2.2895)	2.1798(3) (2.1982)
M-X_2	2.3462(4) (2.3407)	2.249(2) (2.2692)	2.2934(5) (2.3171)	2.2042(3) (2.2209)
M-C_{cAAC}	1.941(1) (1.941)	1.932(3) (1.958)	2.055(1) (2.055)	2.037(1) (2.063)
M-C_{IPr}	2.078(1) (2.106)	2.059(3) (2.115)	2.047(1) (2.065)	2.026(1) (2.070)
X-M-X	101.08(2) (104.88)	100.68(5) (105.89)	106.79(2) (109.61)	106.63(2) (110.73)
C-M-C	113.20(5) (110.61)	116.78(1) (112.47)	117.12(5) (109.89)	117.59(5) (112.65)

For **3** and **5** M: Al; X: Br. For **4** and **6** M: Ga; X: Cl. M06-2X/def2-SVP(D3zero)

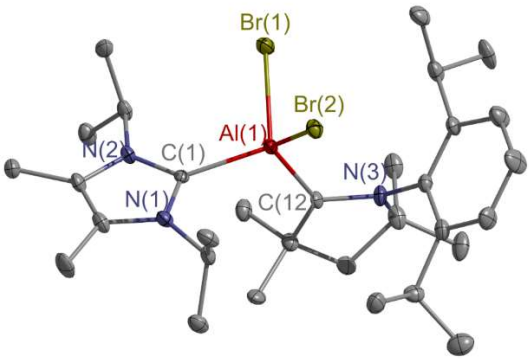

Figure S16. Molecular structure of **3** thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Br(1)-Al(1) 2.3603(4), Br(2)-Al(1) 2.3462(4), Al(1)-C(12) 1.9411(12), Al(1)-C(1) 2.0783(12), N(1)-C(1) 1.3637(15), N(2)-C(1) 1.3598(15), N(3)-C(12) 1.4048(15); C(12)-Al(1)-C(1), 113.20(5), C(12)-Al(1)-Br(2) 113.75(4), C(1)-Al(1)-Br(2) 107.08(3), C(12)-Al(1)-Br(1) 112.89(4), C(1)-Al(1)-Br(1) 107.97(4), Br(2)-Al(1)-Br(1) 101.083(15), C(1)-N(1)-C(2) 110.77(10), N(2)-C(1)-N(1) 104.67(10), N(3)-C(12)-Al(1) 124.33(9).

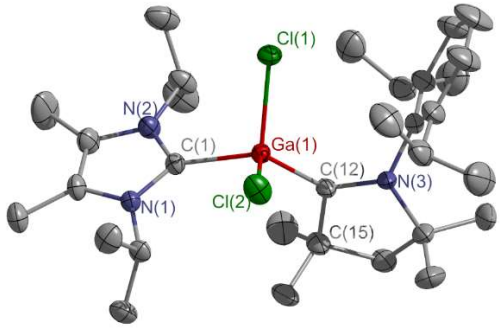

Figure S17. Molecular structure of **4** thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-C(12) 1.932(3), Ga(1)-C(1) 2.059(3), Ga(1)-Cl(1) 2.2209(10), Ga(1)-Cl(2) 2.2492(12), N(1)-C(1) 1.351(4), N(2)-C(1) 1.350(4), N(3)-C(12) 1.383(4); C(12)-Ga(1)-C(1) 116.78(13), C(12)-Ga(1)-Cl(1) 114.70(10), C(1)-Ga(1)-Cl(1) 104.69(9), C(12)-Ga(1)-Cl(2) 112.54(11), C(1)-Ga(1)-Cl(2) 105.81(9), Cl(1)-Ga(1)-Cl(2) 100.68(5), N(2)-C(1)-N(1) 105.2(3), N(3)-C(12)-Ga(1) 125.0(2).

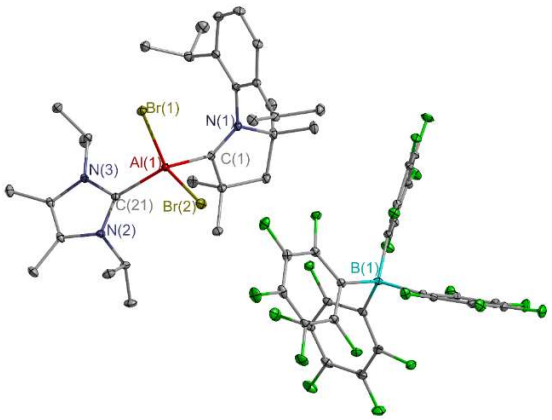

Figure S18. Molecular structure of **5** thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Br(1)-Al(1) 2.2824(4), Br(2)-Al(1) 2.2934(5), Al(1)-C(21) 2.0471(13), Al(1)-C(1) 2.0549(13), N(1)-C(1) 1.3042(17); C(21)-Al(1)-C(1) 117.12(5), C(21)-Al(1)-Br(1) 105.91(4), C(1)-Al(1)-Br(1) 113.62(4), C(21)-Al(1)-Br(2) 113.63(4), C(1)-Al(1)-Br(2) 99.47(4), Br(1)-Al(1)-Br(2) 106.787(18), N(1)-C(1)-Al(1) 131.24(10), N(3)-C(21)-N(2) 105.19(11).

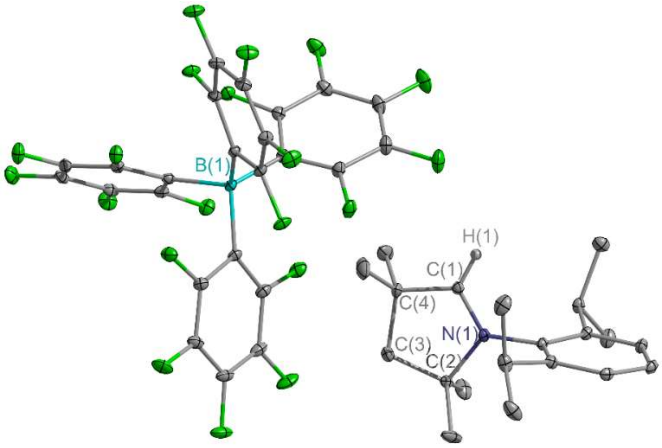

Figure S19. Molecular structure of **5S** thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): N(1)-C(1) 1.278(2), N(1)-C(2) 1.543(2), C(1)-C(4) 1.490(2), C(2)-C(3) 1.548(3), C(3)-C(4) 1.541(3); C(1)-N(1)-C(2) 112.39(14), N(1)-C(1)-C(4)114.67(16).

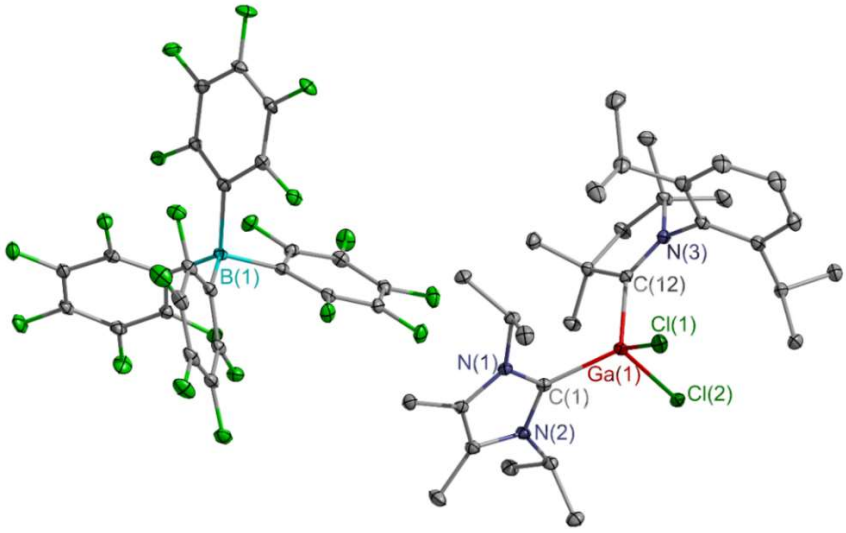

Figure S20. Molecular structure of **6** thermal ellipsoids at 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Ga(1)-C(1) 2.0263(13), Ga(1)-C(12) 2.0367(12), Ga(1)-Cl(1) 2.1798(3), Ga(1)-Cl(2) 2.2042(3), N(3)-C(12) 1.2980(16); C(1)-Ga(1)-C(12) 117.59(5), C(1)-Ga(1)-Cl(1) 108.63(4), C(12)-Ga(1)-Cl(1) 114.22(4), C(1)-Ga(1)-Cl(2) 111.90(4), C(12)-Ga(1)-Cl(2) 96.92(3), Cl(1)-Ga(1)-Cl(2) 106.632(14), N(3)-C(12)-Ga(1) 129.76(9), N(1)-C(1)-N(2) 105.81(11).

4. EPR measurement

Experimental procedure. For EPR measurements, 1 mM samples of **3** and **4** in toluene were prepared in a glovebox and frozen in custom 4 mm (OD) quartz EPR tubes. Continuous-wave (CW) X-band EPR spectra at 77 K (~9.45 GHz) were collected with a Bruker MS 5000 spectrometer. For **3** the spectrum was obtained with 100 kHz field modulation frequency, 5 G modulation amplitude, 0.5 mW microwave power and a scan time of 60 s, which was repeated three times and averaged. For **4**, the spectrum was obtained with 100 kHz field modulation frequency, 0.1 G modulation amplitude, 0.02 mW microwave power and a scan time of 300 s. An effective time constant of 0.05 sec was applied digitally to the ~30 k point spectrum. The EPR data were processed and analysed in Matlab R2019b and simulated using the EasySpin package (v. 6.0.0-dev.34).[7]

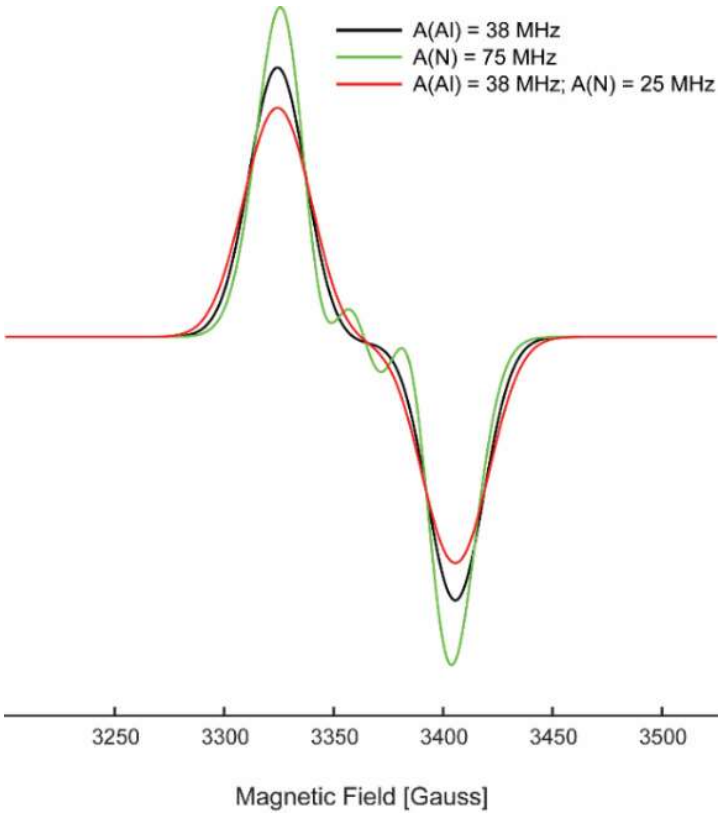

Figure S21. Simulated EPR spectra for various amounts of Al and N hyperfine coupling in the frozen solution regime. Simulations were obtained using a 27 Gauss peak-to-peak linewidth and a microwave frequency of 9.43 GHz.

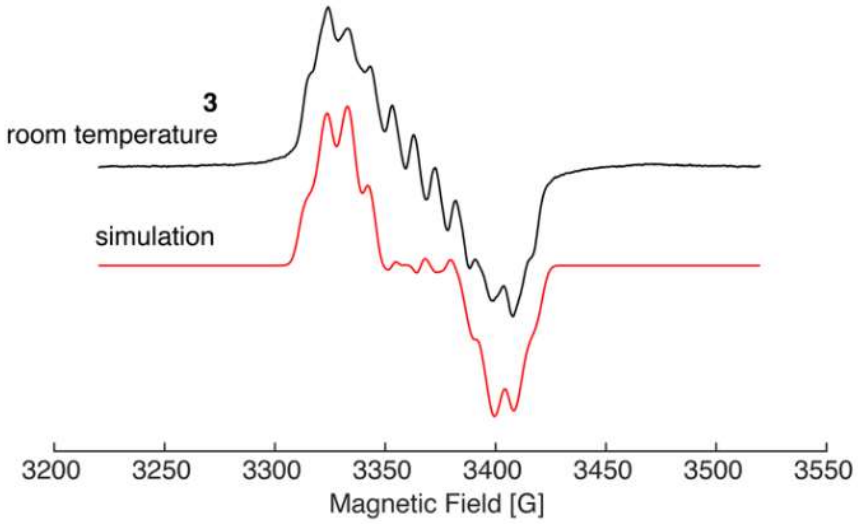

Figure S22. Room temperature EPR spectrum of **3**. Simulations were obtained with the following parameters: a_{iso}(^{27}Al) = 35.0 MHz; a_{iso}(^{14}N) = 25.0 MHz; a_{iso}(^{79}Br) = 10 MHz; a_{iso}(^{81}Br) = 10 MHz; lw = 6.6 Gauss (fwhm). All isotopologoues of bromine (^{79}Br and ^{81}Br) were calculated in their natural abundance weights. The weak isotropic bromine coupling is resemblant of the weak halide coupling observed in other carbene radicals coordinated to main group centers.[8]

5. Cyclic Voltammetry measurement

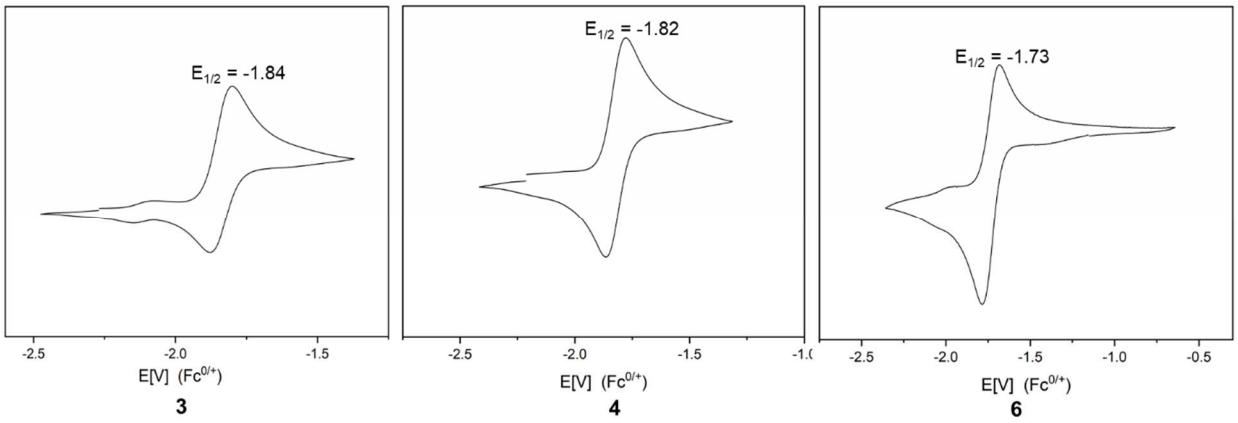

Figure S23. Cyclic voltammograms of **3**, **4** (1mM in 1,2-difluorobenzene**)** and **6** (1 mM in THF) containing [*n*-Bu_4N][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (50 mM) as electrolyte at 100 mV s^{-1} scan rate.

6. Computational Details

The ORCA quantum chemistry package version 4.0.x[9-12] was used for the DFT calculations of spin densities and Mulliken spin population. Unrestricted (UKS) geometry optimization of the radical species **3** and **4** was carried out at the BP86 level of theory[13] with def2- variants of Alrich's all-electron Gaussian triple-ζ valence polarized recontracted basis set (def2-TZVP)[14] and Weigend's "universal" Coulomb fitting basis (def2/J) on all atoms.[15] Single point energy calculations employed the TPSSh functional,[16] the resolution of identity (RI-J) algorithm for the computation of the Coulomb terms and the 'chain of spheres exchange' (COSX) algorithm for the calculation of the exchange terms.[17] A tight self-consistent field (SCF) convergence threshold of $1x10^{-8}$ au was chosen by use of the "TightSCF" keyword. An increased grid was used during the SCF iterations (Grid4), and for the final energy evaluation after SCF convergence Grid7 was used. Using ORCA version 5.0.0. the cations **5** and **6** were–optimized on the M06-2X level of theory omitting the counter ions with the def2-SVP[14] basis set utilizing Grimmes empirical dispersion correction (D3zero).[18] For comparison **3** and **4** were reoptimized analogous. To accelerate the calculations with ultrafine grid settings, default "verytightSCF" and the "DefGrid3" with increased radical grid (7.0), the RI-J and COSX[17] approximation was utilized with the def-2J auxiliary basis sets.[19] Vibrational frequency calculations were carried out for all optimized structures to verify the stationary point as minima (no imaginary frequencies were found). Single point calculations were performed on optimized geometries using def2-TZVP basis set[14] for the M06-2X density functional and reported data refer to this level of theory. Natural bond orbital analysis was performed using the NBO 6.0 program.[20]

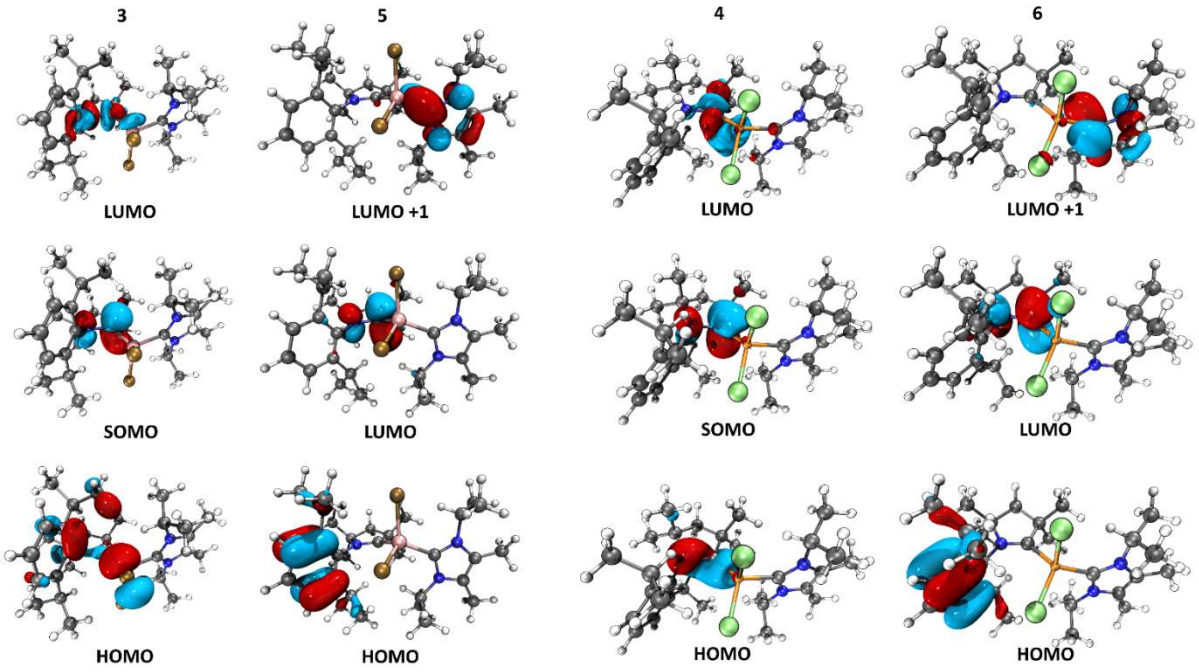

Fig. S24. Biorthogonalized HOMO, SOMO and LUMO of **3** and **4** as we as the HOMO, LUMO and LUMO+1 of **5** and **6**, isovalue 0.05. Biorthogonalizations were performed for the openshell systems using Multiwfn program 3.8.[21] VMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute

for Advanced Science and Technology at the University of Illinois at Urbana-Champaign and used to plot grid-data.[22]

Table S3. Calculated X–Y bond lengths (r, Å) (exp.), X and Y, NPA atomic charges (q, |e|), Natural spin density (ρ_s, |e|), Wiberg bond indices (WBI), occupation numbers (ON, |e|) of the σ XY bonds according to NBO analysis for α and β spin orbitals for the C-Al$(Br)_2$-C skeleton of **3**.

X-Y	r(X-Y)	q(X)	q(Y)	ρ_s(X)	ρ_s(Y)	WBI	ON(α)[a]	ON(β)[a]
Al-C_{cAAC}	1.9412 (1.941(1))	1.40	-0.44	0.04	0.68	0.55	0.97 15.1/84.9	0.97 15.6/84.4
Al-C_{NHC}	2.1055 (2.078(1))	1.40	0.03	0.04	0.00	0.46	0.97 15.0/85.0	0.97 14.7/85.3
Al-Br_1	2.3708 (2.3603(4))	1.40	-0.54	0.04	0.02	0.67	0.99 15.6/84.4	0.99 16.4/83.6
Al-Br_2	2.3407 (2.3462(4))	1.40	-0.52	0.04	0.00	0.71	0.99 16.6/83.4	0.99 16.4/83.6
C_{cAAC}-N	1.3950 (1.405(2))	-0.44	-0.48	0.68	0.20	1.23	0.99 35.4/64.6	σ 0.99 34.5/65.5 π 0.96 23.0/77.0

[a]: Squared polarization coefficients c_X ($|c_X|^2$) of the σXY bond NBOs.

Table S4. Calculated X–Y bond lengths (r, Å) (exp.), X and Y, NPA atomic charges (q, |e|), Natural spin density (ρ_s, |e|), Wiberg bond indices (WBI), occupation numbers (ON, |e|) of the σ XY bonds according to NBO analysis for α and β spin orbitals for the C-Ga$(Cl)_2$-C skeleton of **4**.

X-Y	r(X-Y)	q(X)	q(Y)	ρ_s(X)	ρ_s(Y)	WBI	ON(α)[a]	ON(β)[a]
Ga-C_{cAAC}	1.9588 1.932(3))	1.42	-0.39	0.03	0.69	0.61	0.97 17.9/82.1	0.97 18.7/81.3
Ga-C_{NHC}	2.1150 (2.059(3))	1.42	0.06	0.03	0.00	0.50	0.97 16.5/83.5	0.97 16.2/83.8
Ga-Cl_1	2.2379 (2.221(1))	1.42	-0.58	0.03	0.00	0.63	0.99 15.2/84.8	0.99 15.0/85.0
Ga-Cl_2	2.2692 (2.249(2))	1.42	-0.59	0.03	0.02	0.59	0.99 14.0/86.0	0.98 15.2/84.8
C_{cAAC}-N	1.3902 (1.383(4))	-0.39	-0.48	0.69	0.21	1.23	0.99 35.4/64.4	σ 0.99 34.6/65.4 π 0.96 23.4/76.6

[a]: Squared polarization coefficients c_X ($|c_X|^2$) of the σXY bond NBOs.

Table S5. Calculated X–Y bond lengths (r, Å) (exp.), X and Y, NPA atomic charges (q, |e|), Natural spin density (ρ_s, |e|), Wiberg bond indices (WBI), occupation numbers (ON, |e|) of the σ XY bonds according to NBO analysis for α and β spin orbitals for the C-Al$(Br)_2$-C skeleton of **5**.

X-Y	r(X-Y)	q(X)	q(Y)	WBI	ON[a]
Al-C_{cAAC}	2.0552 (2.055(1))	1.36	0.02	0.42	Lp C 1.68[b]
Al-C_{NHC}	2.0647 (2.047(1))	1.36	-0.03	0.49	Lp C 1.65[b]
Al-Br_1	2.2895 (2.2824(4))	1.36	-0.46	0.79	1.99 18.7/81.3
Al-Br_2	2.3171 (2.2934(5))	1.36	-0.47	0.73	1.98 20.2/81.8
C_{cAAC}-N	1.2971 (1.304(2))	0.02	-0.34	1.62	σ 1.98 34.3/65.7 π 1.96 28.6/71.4

[a]: Squared polarization coefficients c_X ($|c_X|^2$) of the σXY bond NBOs. [b]: The accepted lewis strucure consisted of 3 parts, two carbenes and the $AlBr_2$, but by second order perturbation theory analysis a strong interaction of the lone pair on the C_{CAAC} and on the C_{NHC} with the Lewis vacant orbital at Al was found with 154 and 180 kcal/mol, respectively.

Table S6. Calculated X–Y bond lengths (r, Å) (exp.), X and Y, NPA atomic charges (q, |e|), Natural spin density (ρ_s, |e|), Wiberg bond indices (WBI), occupation numbers (ON, |e|) of the σ XY bonds according to NBO analysis for α and β spin orbitals for the C-Ga$(Cl)_2$-C skeleton of **6**.

X-Y	r(X-Y)	q(X)	q(Y)	WBI	ON[a]
Ga-C_{cAAC}	2.0631 (2.037(1))	1.40	0.06	0.47	1.93 15.6/84.4
Ga-C_{NHC}	2.0699 (2.026(1))	1.40	0.01	0.54	1.94 18.1/81.9
Ga-Cl_1	2.1982 (2.1798(3))	1.40	-0.53	0.69	1.97 16.6/83.5
Ga-Cl_2	2.2209 (2.2042(3))	1.40	-0.54	0.65	1.97 16.1/83.9
C_{cAAC}-N	1.2930 (1.298(2))	0.06	-0.34	1.63	σ 1.98 34.4/65.6 π 1.96 28.9/71.1

[a]: Squared polarization coefficients c_X ($|c_X|^2$) of the σXY bond NBOs.

Table S7. Cartesian coordinates of **3** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.

Br	3.090632516	8.48986272	10.50250584	C	4.652587741	7.714559762	4.928178732
Br	1.363495424	8.139107197	7.209494885	C	4.057398944	6.722322274	4.147300051
Al	2.915204787	9.469195918	8.350525388	H	3.881696084	6.909211737	3.085535427
N	1.390473658	12.02801301	7.547785832	C	3.690422477	5.499159266	4.69787953
N	1.911910879	12.17207344	9.631927581	H	3.225332464	4.733164388	4.075277596
N	5.414518138	8.52458783	7.107797962	C	3.923555163	5.259683997	6.044553567
C	2.019515512	11.36440066	8.548665563	H	3.637358659	4.299038434	6.476774901
C	0.871752111	13.22996608	7.999251528	C	4.501369546	6.231468324	6.870006235
C	1.198978552	13.31853943	9.324534981	C	5.047731922	9.021913382	4.261814891
C	1.24488354	11.49200071	6.178923524	H	5.642441219	9.594420366	4.98556528
H	1.886612433	10.60406415	6.170441725	C	3.810444534	9.857271468	3.930081923
C	1.772196019	12.44867286	5.115554544	H	4.096124368	10.82418112	3.485352212
H	1.812383705	11.91165362	4.158265675	H	3.235681348	10.04461836	4.845800876
H	2.790272102	12.78526302	5.355798124	H	3.158122208	9.328578243	3.217049077
H	1.12518035	13.3234142	4.974650203	C	5.90445988	8.804893734	3.010678261
C	-0.179504424	11.01799305	5.912599845	H	5.326260536	8.327819548	2.205363784
H	-0.18926393	10.43757203	4.979475576	H	6.773157724	8.164050167	3.219755855
H	-0.88457625	11.85402285	5.801648377	H	6.269889788	9.769221007	2.626324611
H	-0.518285674	10.35511033	6.718623339	C	4.722704279	5.895505158	8.33330493
C	2.435810223	11.82766045	10.9698583	H	4.986933339	6.828161899	8.851451678
H	3.132363389	11.00602242	10.78348755	C	5.879293535	4.897858983	8.481496709
C	1.327036714	11.28584085	11.86278974	H	5.601635044	3.925382853	8.045307763
H	0.567574538	12.04968233	12.08672324	H	6.121293474	4.736488259	9.543143462
H	1.762578608	10.94203239	12.81124941	H	6.788654961	5.238575127	7.965614294
H	0.844233347	10.42300039	11.38490363	C	3.464142065	5.332976182	9.002274682
C	3.239132079	12.95823545	11.60894418	H	2.596434524	5.985746747	8.838499868
H	3.885485382	13.45639829	10.87205444	H	3.623854767	5.247217258	10.08735303
H	3.886925355	12.52197063	12.3816785	H	3.223113102	4.32936047	8.618411322
H	2.60827411	13.71103884	12.09775954	C	5.216724515	11.98674239	6.81922248
C	0.137312121	14.23412608	7.17149053	H	5.122632131	11.66723587	5.770170484
H	0.824088494	14.84749381	6.570713432	H	5.955880271	12.80368975	6.872385683
H	-0.421644173	14.90949793	7.829936807	H	4.243098225	12.39085495	7.14319219
H	-0.581831287	13.7637117	6.491446176	C	5.671717953	11.32290352	9.164179206
C	0.880356515	14.4246728	10.27645312	H	6.406429159	12.13785012	9.269135808
H	1.751699645	15.06619292	10.46876685	H	5.921143711	10.52938387	9.881107987
H	0.519998972	14.04298409	11.23979302	H	4.687651268	11.73012646	9.443465019
H	0.089660469	15.05357068	9.850887657	C	7.725497344	7.981800541	6.324350602
C	4.669311686	9.62433396	7.533539632	H	7.509852033	8.334136915	5.306451213
C	6.865609792	8.700848031	7.356878644	H	7.551791088	6.896163123	6.354707822
C	6.99421784	10.23299916	7.268767559	H	8.788104112	8.16719134	6.538697499
H	7.193880282	10.51685136	6.222825876	C	7.233814396	8.208521888	8.766116041
H	7.829623213	10.61172525	7.876479895	H	7.242455919	7.112126683	8.810367854
C	5.628737009	10.80807632	7.71607277	H	6.503956713	8.567253733	9.505727979
C	4.861922088	7.474656102	6.307803049	H	8.235396608	8.567644999	9.047438553

Table S8. Cartesian coordinates of **4** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.

Br	6.889297208	2.278913983	9.427138981	H	11.74776647	2.025149109	6.551060765
Br	10.58207479	1.572520804	9.237307522	C	9.065727948	2.56599252	4.415832675
Al	8.62159214	1.772548807	8.018434821	H	9.621157135	2.414973467	3.478829369
N	9.116542011	4.56925357	6.907080756	H	8.295874839	3.330962249	4.238013362
N	8.731968076	-1.113127447	6.86673037	H	8.56567962	1.619680221	4.668077883
N	7.001350604	-0.029190677	6.173067708	C	10.83817792	6.379969283	6.660832387
C	9.2113453	3.284269205	6.757035051	H	11.45698375	6.902171958	5.917353029
C	10.05466352	2.965357299	5.527568464	H	11.50884444	5.868852653	7.362477605
C	10.76644742	4.295011375	5.232540664	H	10.24682913	7.131108206	7.202130573
H	11.77749824	4.26632813	5.664017468	C	9.039699624	6.160806002	4.967213367
H	10.86957268	4.480660421	4.154687961	H	9.673732952	6.707733563	4.256196509
C	9.947906475	5.39302839	5.92013738	H	8.439686493	6.896115102	5.518124746
C	8.27266162	5.286255346	7.86074389	H	8.371749035	5.505475299	4.39345223
C	8.809648862	5.691874432	9.102251664	C	8.124537482	0.095793508	6.920985104
C	8.022799857	6.522224255	9.907939335	C	7.984197294	-2.003113319	6.118511531
H	8.418361941	6.84740523	10.87104974	C	6.889372858	-1.312079951	5.666652757
C	6.755962467	6.930839316	9.518746682	C	9.995205608	-1.430861999	7.573112845
H	6.169001173	7.588510538	10.16056095	H	10.43965933	-0.45339662	7.773017955
C	6.227683866	6.469282365	8.3211108	C	9.708258786	-2.092962175	8.91432925
H	5.212966994	6.754652324	8.03967842	H	9.231994923	-3.076588126	8.79179594
C	6.957383513	5.63274015	7.471951965	H	9.053961813	-1.457921935	9.528581079
C	10.13935395	5.228095134	9.682232733	H	10.6516604	-2.233854605	9.459074532
H	10.63589946	4.568627187	8.953473054	C	10.99701864	-2.192137044	6.709477709
C	11.07981874	6.39056891	10.0289009	H	10.79961708	-3.269451926	6.666861876
H	11.26739356	7.064665329	9.184658029	H	11.9932247	-2.062179562	7.1533875
H	12.04514531	5.995696167	10.37648112	H	11.03136406	-1.793412989	5.685164153
H	10.6620033	6.993668178	10.84798295	C	6.000304931	1.045069964	5.996540561
C	9.882709448	4.41063314	10.95864031	H	6.496345299	1.951114062	6.380011428
H	9.143901244	3.615214318	10.80034584	C	4.765338629	0.77234076	6.849387756
H	9.510170866	5.06502243	11.76069063	H	4.044715236	1.591047841	6.725682042
H	10.81761847	3.9483695	11.30595754	H	5.031351664	0.700604471	7.911455838
C	6.223137727	5.088054506	6.250878025	H	4.26942116	-0.158261671	6.543197956
H	6.908353687	4.435604955	5.685697066	C	5.661491195	1.290797099	4.52561386
C	5.033594793	4.236959515	6.718544735	H	6.545189287	1.205935843	3.879111683
H	4.535353677	3.767172839	5.857223182	H	5.260996001	2.307958546	4.41975403
H	4.285068256	4.868239366	7.218594732	H	4.89136732	0.600761575	4.160176263
H	5.339009545	3.464760145	7.435875045	C	8.329211414	-3.435874132	5.876472957
C	5.694331498	6.179348629	5.310643173	H	7.443542585	-3.96542879	5.508139455
H	6.471854651	6.866086121	4.958281829	H	8.652613401	-3.934454017	6.798470574
H	4.923687773	6.780095713	5.814691579	H	9.124233946	-3.548922083	5.126997356
H	5.221856222	5.71843592	4.430744772	C	5.806721633	-1.805817182	4.763270171
C	11.05943547	1.82629349	5.719739714	H	5.933823391	-1.431578866	3.737805627
H	11.64513429	1.713235056	4.795740307	H	4.807150929	-1.519897985	5.110172853
H	10.55291236	0.867136443	5.907943312	H	5.841026602	-2.900159129	4.721911687

Table S9. Cartesian coordinates of **5** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.

Ga	3.075849246	6.660048657	8.110775302	C	4.619502262	9.968684523	6.70271753
Cl	1.542947245	7.860073801	7.006929241	C	4.094195851	10.99986405	5.91412503
Cl	3.21553347	7.582465767	10.17928246	H	3.821019816	11.94354275	6.390488049
N	1.956104019	4.027346786	9.455240225	C	3.901330826	10.84228934	4.54943831
N	1.597245208	4.071824654	7.331687454	H	3.487061057	11.65754915	3.954108834
N	5.545106317	7.674371773	6.831009689	C	4.227328412	9.630927538	3.949003669
C	2.174693699	4.760630225	8.341865252	H	4.05990665	9.498290411	2.877825248
C	1.210765773	2.897106007	9.157839163	C	4.761204227	8.57823391	4.693853616
C	0.986149552	2.923315084	7.807998237	C	4.766369573	10.21177752	8.193355758
C	2.437328525	4.423589177	10.79536076	H	5.060692515	9.261829052	8.66139507
H	3.17818545	5.203539575	10.59616562	C	3.439197506	10.6473357	8.825709122
C	3.157448766	3.292289975	11.52364688	H	3.156597154	11.65807045	8.491415763
H	3.834877507	2.751773069	10.84663857	H	3.531799314	10.66365038	9.921367055
H	2.471742571	2.574725063	11.99147008	H	2.627137485	9.955684201	8.565182566
H	3.765579653	3.734098638	12.32476737	C	5.847651979	11.26384607	8.471952441
C	1.321204877	5.067770927	11.60695242	H	6.796014099	11.02922612	7.967045036
H	0.922075248	5.938786111	11.07069056	H	6.039312565	11.34744583	9.552486418
H	1.730224602	5.424309462	12.56237963	H	5.52284718	12.25215537	8.110524019
H	0.504199851	4.362504695	11.82064457	C	5.038667613	7.262027197	3.989216567
C	1.635871502	4.522581653	5.924831167	H	5.564396483	6.60939392	4.698922987
H	2.383145872	5.327262537	5.928168014	C	5.914277712	7.419224436	2.742676869
C	0.299471594	5.10410904	5.479675377	H	6.150923553	6.432697444	2.315934302
H	0.430399399	5.578513272	4.4965617	H	6.859947127	7.93242252	2.967767602
H	-0.039628007	5.875046938	6.181014364	H	5.39975965	7.999829058	1.962530901
H	-0.469360963	4.324025436	5.380338015	C	3.710902214	6.588060381	3.625047443
C	2.146703104	3.438800019	4.978904085	H	3.199770851	7.151185844	2.828151061
H	2.444960999	3.919929811	4.037821633	H	3.039343825	6.570646089	4.495318307
H	1.374929895	2.696939029	4.736920761	H	3.879227624	5.562162974	3.260483397
H	3.025708031	2.923495013	5.389326265	C	5.392228105	4.187966942	6.584602703
C	0.770394069	1.866163879	10.14483605	H	4.431872553	3.779390579	6.939614932
H	-0.032282006	1.261690054	9.706030951	H	6.143383901	3.382570393	6.643151298
H	0.380113514	2.322470336	11.0631312	H	5.270632572	4.480173226	5.530020399
H	1.588010595	1.186269054	10.42302707	C	5.864102046	4.91591227	8.906898462
C	0.257683317	1.918616108	6.976769556	H	4.884740729	4.511013557	9.211993774
H	-0.399776195	2.396067715	6.240238025	H	6.117398776	5.727755026	9.600567765
H	-0.36735374	1.29331244	7.62531356	H	6.604836967	4.108176043	9.023224596
H	0.948755165	1.255112619	6.437718199	C	7.397536493	8.021181599	8.44624392
C	4.828561341	6.556365158	7.242423664	H	8.414538409	7.687136717	8.702044273
C	7.003365972	7.514697985	7.05009405	H	6.697247834	7.651343693	9.207817871
C	7.146264149	5.983709125	6.961391531	H	7.380814823	9.11757902	8.483164538
H	8.004674409	5.613779495	7.542037307	C	7.830777988	8.237354919	5.994317696
H	7.312246146	5.703387919	5.908365148	H	7.584814762	7.881951203	4.984572105
C	5.800725589	5.393796072	7.445119583	H	8.899881338	8.055489202	6.177321136
C	4.972775204	8.751508359	6.083236765	H	7.653264049	9.322354859	6.029486042

Table S10. Cartesian coordinates of **6** [Å] for the optimized geometry at the M06-2X/def2-SVP level of theory.

Ga	2.599923192	12.38025435	13.81162665	C	4.367711563	13.2391837	10.07718314
Cl	3.774619511	10.7821613	12.86397855	C	4.778407922	12.40430141	9.034778916
Cl	0.446564716	11.84051695	13.87584896	H	5.829247719	12.40037473	8.741188383
N	4.686721617	12.96043573	15.94722509	C	3.88485892	11.56642335	8.380560016
N	2.772175809	12.66786994	16.90117881	H	4.227535076	10.9289448	7.564935092
N	2.517023619	14.2164353	11.3845358	C	2.562491798	11.51717506	8.796722243
C	3.377687151	12.73725056	15.6963109	H	1.874801229	10.81895718	8.317607241
C	4.916431847	13.00893268	17.31181987	C	2.085428334	12.33110342	9.830017365
C	3.700906453	12.81366861	17.91643606	C	5.454127226	14.00547592	10.82332854
C	5.718492076	13.06949949	14.8926701	H	4.981884362	14.61492212	11.61017671
H	5.146415017	13.16428629	13.95638909	C	6.392441535	12.99938488	11.50604088
C	6.549909634	11.79393463	14.81215163	H	6.961861826	12.43661612	10.75211013
H	5.912103939	10.92886583	14.59070496	H	5.836856906	12.26707973	12.10575949
H	7.094549135	11.61059303	15.74802251	H	7.123275668	13.52484469	12.13933391
H	7.29029427	11.89226564	14.00719237	C	6.289325946	14.92643604	9.925549239
C	6.566616371	14.33113406	15.04317436	H	6.858780064	14.3372313	9.192497098
H	7.052839307	14.54575063	14.08225636	H	7.019359415	15.48116142	10.5330158
H	7.362680338	14.20734881	15.7871019	H	5.685969172	15.65364086	9.37007671
H	5.957735879	15.2032261	15.31899493	C	0.650472287	12.10832556	10.28688497
C	1.321569568	12.41463753	17.07697094	H	0.427953064	12.79491881	11.11865864
H	0.889218714	12.64914382	16.10080471	C	0.505398633	10.6728299	10.81794033
C	1.062140579	10.93906028	17.34919906	H	0.57113187	9.952649915	9.988798758
H	-0.021323238	10.76469399	17.394206	H	-0.472175701	10.54654416	11.30361793
H	1.502328639	10.61361084	18.30279235	H	1.286144589	10.42301091	11.54732239
H	1.470014659	10.31880846	16.53899046	C	-0.375734254	12.32941117	9.168128538
C	0.669912602	13.35449872	18.08698833	H	-0.300958627	13.31940565	8.701764265
H	1.027828638	14.38724399	17.96536798	H	-1.392924573	12.21181382	9.568168584
H	0.824801711	13.04372407	19.12673688	H	-0.249468717	11.5788093	8.374396817
H	-0.41317441	13.35062991	17.90499597	C	1.033438812	15.25074309	14.43419593
C	6.233280836	13.27016647	17.96677286	H	0.732010679	16.2480377	14.7859059
H	7.045477805	12.68637101	17.51831809	H	1.453321688	14.7101612	15.29674813
H	6.173096473	12.99312784	19.0252112	H	0.14166284	14.71182399	14.08734522
H	6.506330556	14.33361665	17.91734224	C	3.362017092	16.0034463	13.90728044
C	3.399880261	12.76110995	19.3781245	H	4.139484691	16.15125253	13.14363028
H	2.732463078	11.92601838	19.62384551	H	3.766365519	15.34959823	14.69505889
H	2.935853199	13.68986166	19.73709338	H	3.135964398	16.97944686	14.36051276
H	4.331715858	12.6148887	19.93581582	C	0.966309251	15.39594342	9.814651401
C	2.463975448	14.0937714	12.6705858	H	0.617845541	16.39228108	9.50774066
C	2.059512922	15.57848826	10.85758686	H	0.109792922	14.84656578	10.22544777
C	1.521554554	16.230431	12.13955637	H	1.340763452	14.87383652	8.923358887
H	1.807948284	17.28896137	12.20512216	C	3.228556852	16.33315261	10.23682338
H	0.423211233	16.18156096	12.14348811	H	3.619114512	15.79074608	9.366212182
C	2.069635039	15.40763624	13.31814045	H	4.045714023	16.51118209	10.94809159
C	2.999073929	13.22363227	10.4290049	H	2.860597661	17.30840289	9.889934654

Table S11. Cartesian coordinates of **3** [Å] optimized at the BP86/def2-TZVP level of theory.

Al	0.02414569006580	0.07088943954349	0.00475363013462
Br	-0.04294338170184	2.08747517554463	1.27236008901115
Br	-0.07672368733614	-1.62255026204246	1.62090672470825
N	-2.14918500857929	-1.29130153125892	-1.68252733974259
N	-2.68862745240979	0.78614433874108	-1.40490840380577
N	2.88321813575152	0.05018608860355	-0.59321369559606
C	-1.70937680796202	-0.12354607661099	-1.12533184794371
C	-3.39663926935251	-1.12453291407563	-2.27873538391806
C	-3.73976293364751	0.19429086769534	-2.10018379686937
C	-1.36504007756654	-2.55001279297285	-1.63643594718232
H	-0.38981076140405	-2.23620384320659	-1.23393184610062
C	-1.13376189078855	-3.13150798115960	-3.03142770843427
H	-0.35003470867663	-3.89609217100135	-2.96363302840036
H	-0.79507831821977	-2.36292064734796	-3.73633220713968
H	-2.03040293799561	-3.61714247870863	-3.43485656661654
C	-1.98087780263979	-3.55804228567979	-0.66860038657546
H	-1.28557659931603	-4.39834984350590	-0.53983504017253
H	-2.93085440357107	-3.96272980002167	-1.04408839117383
H	-2.13928955736692	-3.10107355539354	0.31495085479575
C	-2.61057052684509	2.20707023866625	-0.99128359218536
H	-1.57805108423718	2.32155855746257	-0.63951215586529
C	-3.51750584460987	2.48303708196481	0.20560542624870
H	-4.58420355073178	2.39705867555841	-0.04517762904915
H	-3.33325965564407	3.50338321277314	0.56772754080593
H	-3.28385618853370	1.79230065332425	1.02562628183234
C	-2.80960634705266	3.17314204891441	-2.15887264385904
H	-2.22761113869463	2.86009852856237	-3.03635501019713
H	-2.44484809301732	4.16282510876229	-1.85263096666262
H	-3.86075749088217	3.28480149686322	-2.45225446986674
C	-4.17568444168556	-2.17936935729164	-2.98754812349628
H	-3.79063351101156	-2.36970771760595	-4.00003093627635
H	-5.21914190181210	-1.85602536622255	-3.08911934434703
H	-4.17593991368806	-3.13165439712907	-2.44402313996793
C	-4.97425777941147	0.89033728837047	-2.56169155268471
H	-4.79852275733068	1.49316761904954	-3.46465155303676
H	-5.38752618245905	1.55328392038561	-1.79173345978179
H	-5.74362356337498	0.14774434491719	-2.80700859240344
C	1.59273375959836	0.09296055635602	-1.12685024279362
C	3.84956086780640	0.88291954264535	-1.38467556343933
C	3.19691240336855	0.80358472649327	-2.77796922856598
H	3.55079058618734	-0.11074708099895	-3.27974335573376
H	3.46384969756002	1.66066756548811	-3.41232697848398
C	1.67051422875423	0.69343424034233	-2.53573248307614
C	3.31619420765346	-0.89413737582611	0.39058474389474
C	3.39864193747531	-2.26948675729818	0.04931745049731
C	3.95818962146565	-3.16183910838757	0.96877992335000
H	4.04306847983248	-4.21660845312842	0.70104307400970
C	4.41644132193418	-2.73365583237530	2.21237209632237
H	4.86201090087684	-3.44405335850813	2.91063149754574
C	4.27064208540981	-1.39760024551695	2.56407489982317
H	4.58156127106397	-1.06574603493048	3.55616474300926
C	3.70983567469169	-0.46494709884976	1.68112941231571
C	2.89284909656881	-2.82636997220224	-1.27086482329965
H	2.34837504752407	-2.01735278817734	-1.77618307694286
C	1.89387901833840	-3.96707544862085	-1.02192703737838

H	1.45131582374081	-4.30319811204534	-1.97124032839669
H	1.09566294107812	-3.64231132724300	-0.34056278042975
H	2.38394817671470	-4.83964297644320	-0.56574800526934
C	4.02844771827480	-3.30427629990030	-2.18779337241931
H	4.60853074466433	-4.11013266917837	-1.71312087908674
H	4.72614435665761	-2.49160814127860	-2.42967817582794
H	3.62243250263840	-3.69377549768161	-3.13424557030463
C	3.48467340320031	0.94868033957421	2.18385565249507
H	2.96029276333036	1.50229379228984	1.39421111425166
C	4.80667176985799	1.66376449104977	2.50650014991658
H	5.31197157490797	1.18275319429187	3.35785628998846
H	4.62375872722306	2.71460785218424	2.77677582046774
H	5.50634105148134	1.64312425520504	1.65903380338347
C	2.57166106311752	0.94305102431703	3.42214257970948
H	1.63800955455825	0.40349578861342	3.22113695897523
H	2.31429180205917	1.97295632860804	3.70884532081312
H	3.06921447425690	0.46422439239128	4.27921849801722
C	1.02660846716568	-0.22933420900814	-3.58697743238402
H	1.46163670043024	-1.23752790468097	-3.55107790985462
H	1.16883686874496	0.17232619206749	-4.60418724470236
H	-0.05548923514164	-0.31180487326329	-3.40954351348693
C	0.95789820087754	2.05917149575494	-2.63795575803946
H	1.08107160415668	2.49180778125996	-3.64450517865779
H	1.32461248140826	2.78032082164482	-1.89938305181213
H	-0.12004900899770	1.93015320745979	-2.46220671263904
C	5.26407096431554	0.31205868431880	-1.36385622473617
H	5.29303525071497	-0.71011864241905	-1.76024014238403
H	5.66899830111243	0.28988343733063	-0.34304054556124
H	5.92228945092855	0.94196620396377	-1.97909738878225
C	3.87717279901245	2.33776309083517	-0.87372413099906
H	4.49127004126110	2.43077035719080	0.02851508562361
H	2.86799744434785	2.69165858117247	-0.63114695056380
H	4.30650952853053	2.99869288864621	-1.64147303454450

Table S12. Cartesian coordinates of **4** [Å] optimized at the BP86/def2-TZVP level of theory.

Ga	0.07066106163470	-0.10306892056856	-0.00760424040625
Cl	-0.00596043189805	1.54672575990004	1.49713769863161
Cl	0.25051524254535	-1.99427370660849	1.24710930111784
N	-2.74414737185907	-1.07691013078556	-0.99603904761675
N	-2.41759800989637	1.02578341149779	-1.40005987347573
N	2.85706315145978	0.10311765384071	-0.87856199478150
C	-1.81997424262555	-0.08389866618072	-0.88242098552348
C	-3.92615106442446	-0.59211764270291	-1.55479640494957
C	-3.71879538585741	0.74191866285356	-1.81241718049721
C	-2.48875759262246	-2.46700802020083	-0.54731531060234
C	-2.75795908740134	-3.49559665664553	-1.64502383817422
C	-3.20495937298996	-2.75771800638341	0.76959387793481
C	-1.73245736454683	2.33899695879293	-1.47927879612512
C	-2.27264939110518	3.31473811046243	-0.43644824828099
C	-1.74177328139246	2.90949037296042	-2.89710080532231
C	-5.14929771400176	-1.39993636345671	-1.82400551163492
C	-4.66714459538531	1.71336338491457	-2.42750351796287
C	1.53291291983399	-0.00549328879358	-1.29524609776678
C	3.79032707012073	-0.67694258685970	-1.75622911678268
C	2.98488268087033	-0.70326491456476	-3.07156638342802
C	1.48805770718756	-0.66911537296466	-2.66989101722495
C	3.31662062765498	1.09741925576665	0.04462270958097
C	3.77595200873682	0.73074558739104	1.33087606454769
C	4.31925115744055	1.72105778273170	2.16098703566271
C	4.38780020038480	3.04919722967090	1.75827556215986
C	3.88164912938063	3.41024449768584	0.51202957492660
C	3.33979337715352	2.45741452353174	-0.35612646603106
C	3.65424733686293	-0.67864670464520	1.87792809217722
C	2.81294135714411	-0.69458103918917	3.16551536780713
C	5.03276892330206	-1.30838578152929	2.13716627985831
C	2.77033103763598	2.93457080708874	-1.68002030598840
C	3.81486014787285	3.62741677273825	-2.56760435089205
C	1.57856740093781	3.87037365180988	-1.42327369303311
C	0.67362716953056	0.17132716123554	-3.67154648843267
C	0.85757206124323	-2.07845388496646	-2.63716179388402
H	2.38832200233036	2.05359822250653	-2.21120990710789
H	-0.69042178775161	2.10427400134705	-1.22015413253101
H	3.12002193719342	-1.28022412515758	1.13080760147289
H	-1.41394572109098	-2.48045148606051	-0.32923585181648
H	3.22581924719367	0.20218782472431	-3.65039183049345
H	3.23439685909888	-1.57482189870805	-3.69297733378629
C	3.99946087594576	-2.10083392937726	-1.20585367946277
H	3.05140670351324	-2.54073535525829	-0.87361887358871
H	4.43351479782620	-2.74669827271564	-1.98383254579070
H	4.68501772149086	-2.09715486812403	-0.35119758970113
C	5.14280105812522	0.01110263932153	-1.91436874230359
H	5.78534042938222	-0.58862107672553	-2.57469991886847
H	5.03413440408544	1.01098167244833	-2.35193988824379
H	5.65051452824480	0.11625916371125	-0.94580278583286
H	1.04464148012905	1.20457880212238	-3.71577253093773
H	1.34197853703724	-2.73629193256918	-1.90701166390715
H	-0.38449231846356	0.19799998374365	-3.37227443743264
H	-0.20425219380440	-2.00594173553567	-2.35993199871825
H	0.72360586015475	-0.26139121446449	-4.68451820545549
H	0.91047317043266	-2.55401795722297	-3.63026016082862

H	1.07184733522898	4.12095744499891	-2.36759966612889
H	3.36835387208179	3.91864014786760	-3.53070625057934
H	1.90908914749848	4.81306786048015	-0.96208366810340
H	4.20306512030150	4.53964976556199	-2.09062135084192
H	0.86377913395730	3.40103670463703	-0.73440252505319
H	4.67259916953735	2.97302276456785	-2.77474056102350
H	2.62704448366539	-1.73057472959869	3.48298658484411
H	5.55597155632436	-0.77884894719773	2.94801713043909
H	1.84216233757496	-0.20942908224774	3.00809548093530
H	5.68062254936932	-1.26550708429448	1.24993450165676
H	3.33254498659317	-0.17431678330302	3.98478721225346
H	4.92806233181556	-2.36167703876658	2.43760414967018
H	4.67855711889657	1.44085194073026	3.15257014806302
H	4.81610570504292	3.80479740402002	2.41900148661554
H	3.91132821311373	4.45679906156378	0.20228425771554
H	-4.67197084823903	2.67616261608428	-1.90210902131325
H	-4.43492452122229	1.90808566079751	-3.48478956966366
H	-5.68548809791695	1.30743092524604	-2.38442235367244
H	-5.40424356601428	-2.05654222688010	-0.98299871647142
H	-6.00153370516342	-0.72973820540615	-1.99160307370431
H	-5.04294082870703	-2.02858877592660	-2.72020049294471
H	-2.91690298860398	-2.01785000395889	1.52699261231166
H	-4.29908737735264	-2.75951442636539	0.66386290863077
H	-2.89583866434219	-3.74604554228083	1.13533139384786
H	-1.01654531279766	3.73167149538960	-2.94312127066298
H	-2.72000919254280	3.31756365551569	-3.17881281931765
H	-1.44291382484539	2.15468239547211	-3.63511951768592
H	-2.22897304594714	2.86760587071067	0.56332886445181
H	-3.30252345959192	3.62759714839835	-0.65838591331062
H	-1.64158630382835	4.21380385177769	-0.43004574317048
H	-3.82610163344691	-3.69533037637959	-1.79693266510332
H	-2.31700892015138	-3.17980308205148	-2.60039921781148
H	-2.28257257928848	-4.44218008199536	-1.35476980212592

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