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# Cooperative N-H bond activation by amido-Ge(II) cations

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## Supporting Information

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## 1. Representative NMR spectra of key compounds

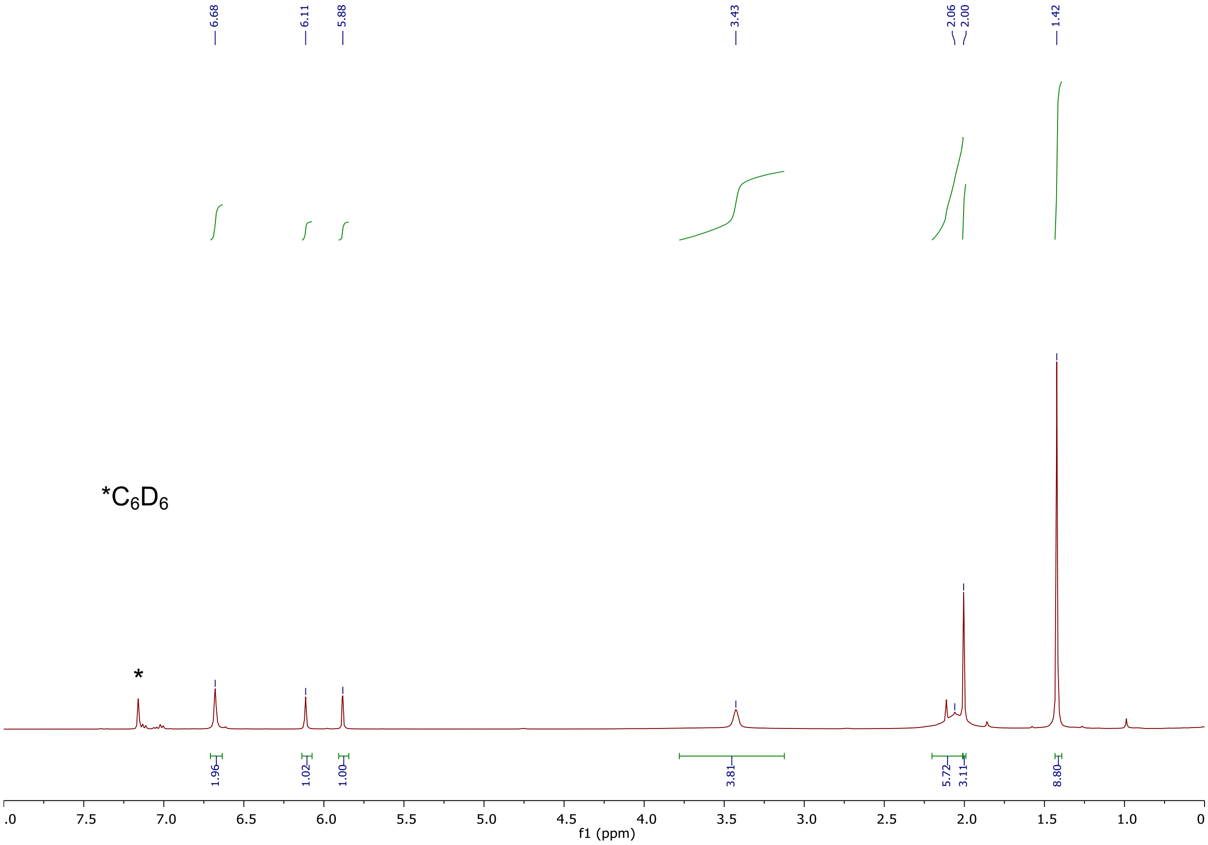


**Figure s1**: $^1$H NMR spectrum of **1** in benzene-d$_6$.

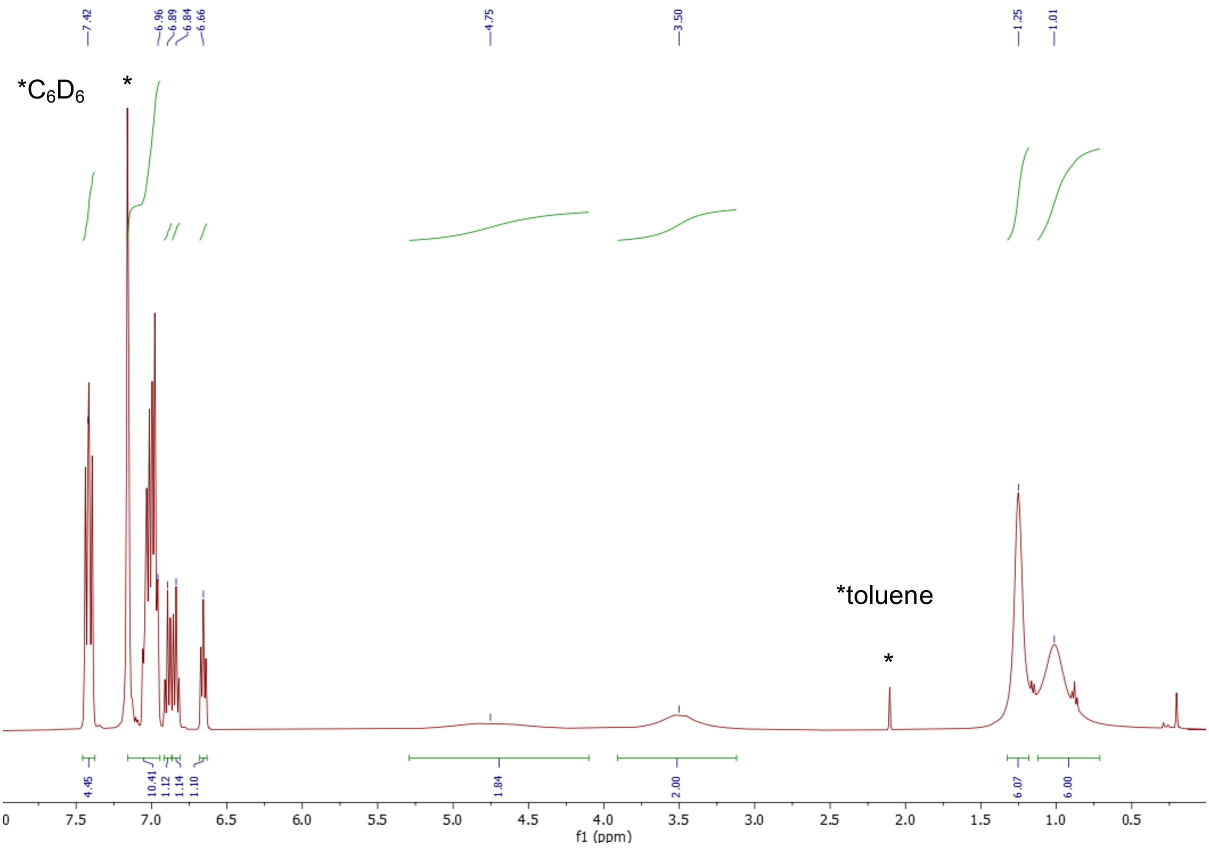


**Figure s2**: $^{1}$H NMR spectrum of **2** in benzene-$d_6$ at 298 K.

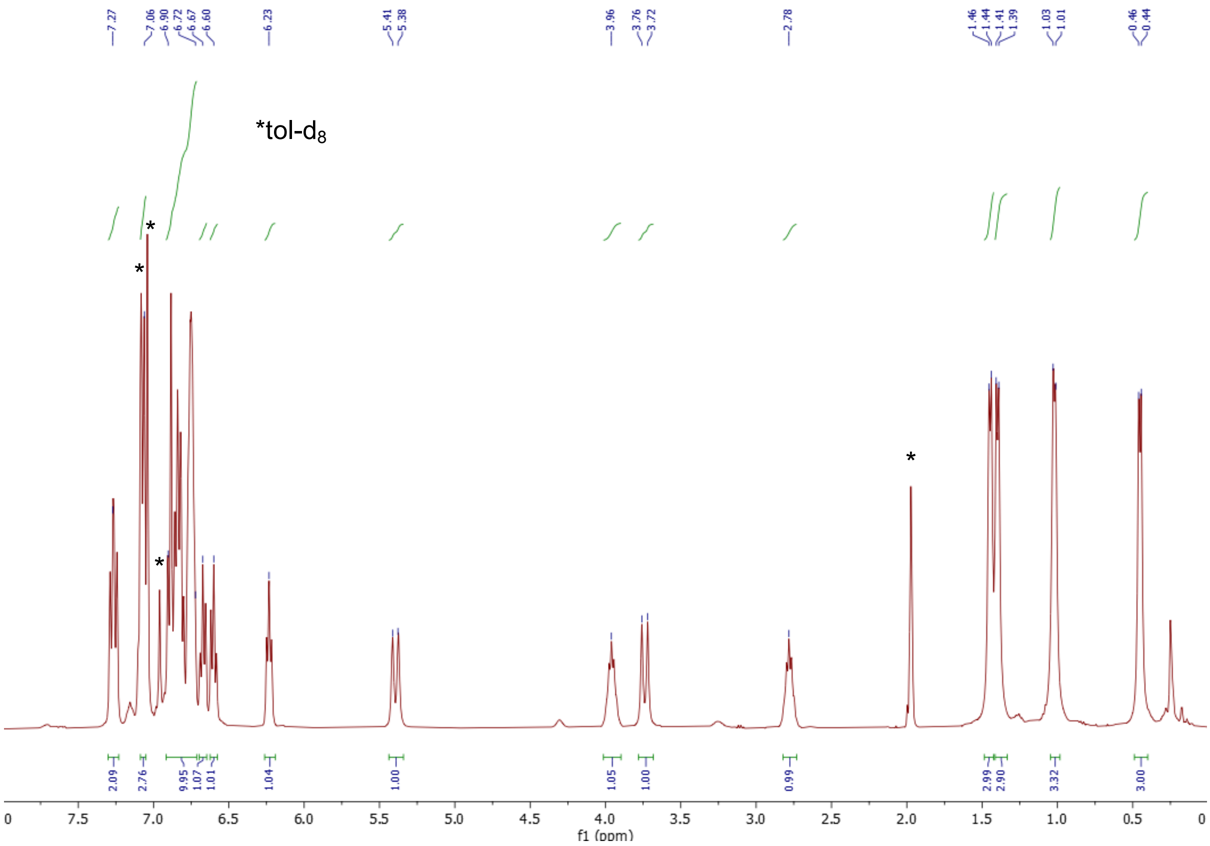


**Figure s3**: $^1$H NMR spectrum of **2** in toluene-$d_8$ at 193 K.

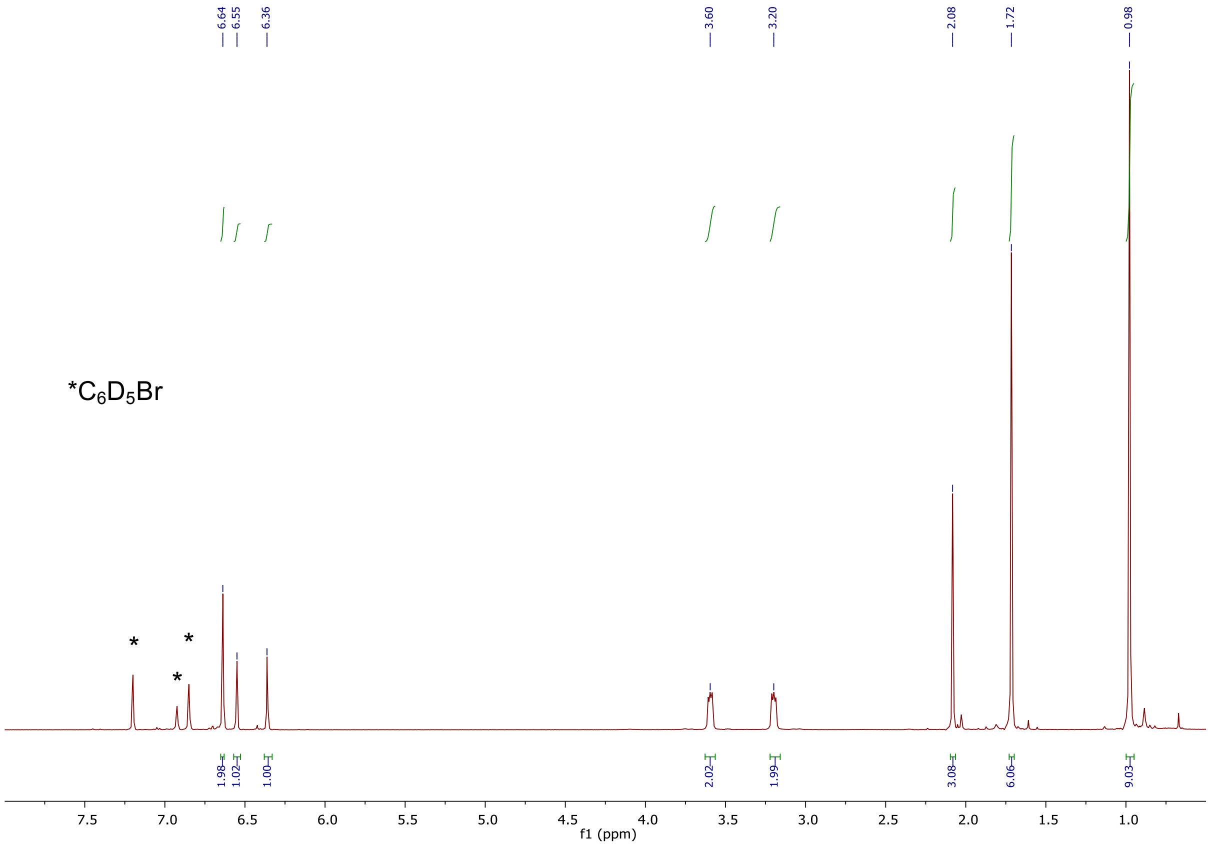


**Figure s4**: $^1$H NMR spectrum of **3** in bromobenzene-d$_5$.

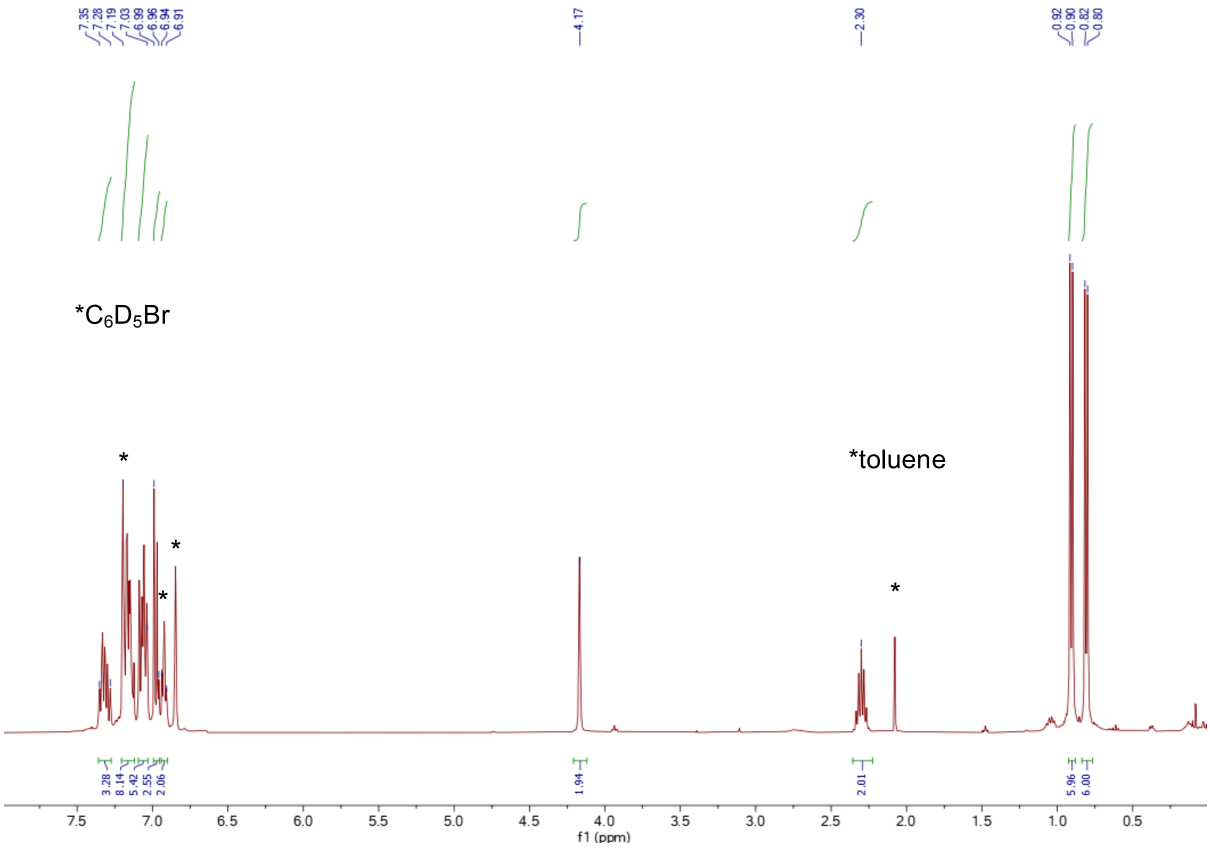


**Figure s5**: $^{1}$H NMR spectrum of **4** in bromobenzene-d$_5$.

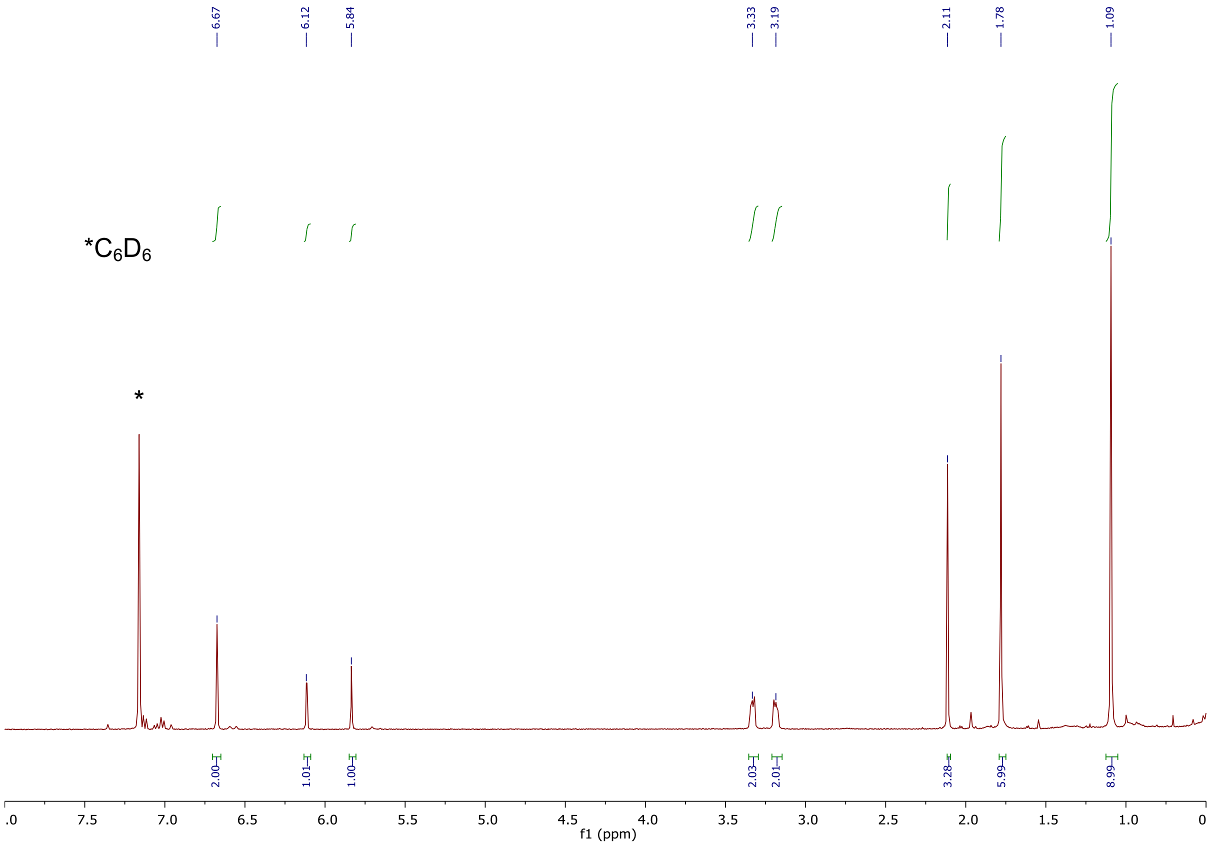


**Figure s6**: $^1$H NMR spectrum of **5** in benzene-d$_6$.

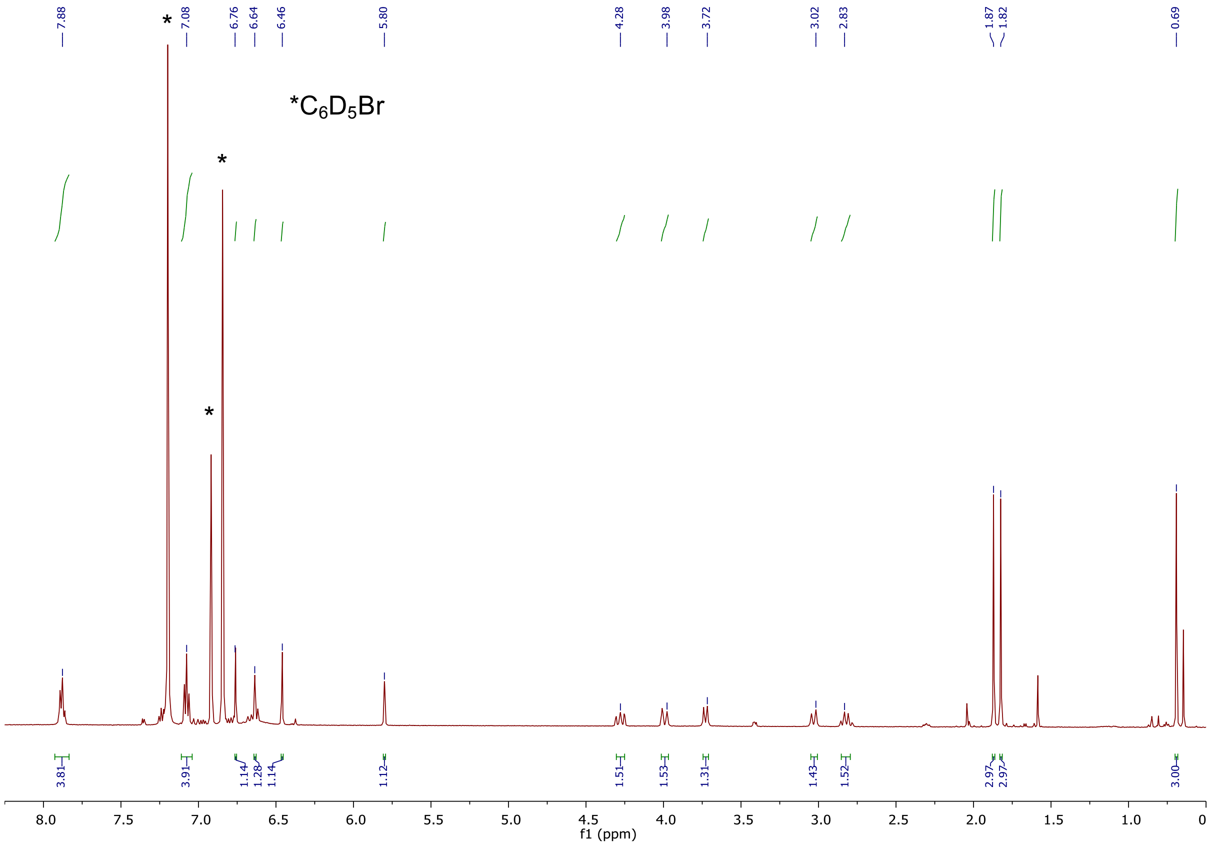


**Figure s7**: $^1$H NMR spectrum of **6** in bromobenzene-d$_5$.

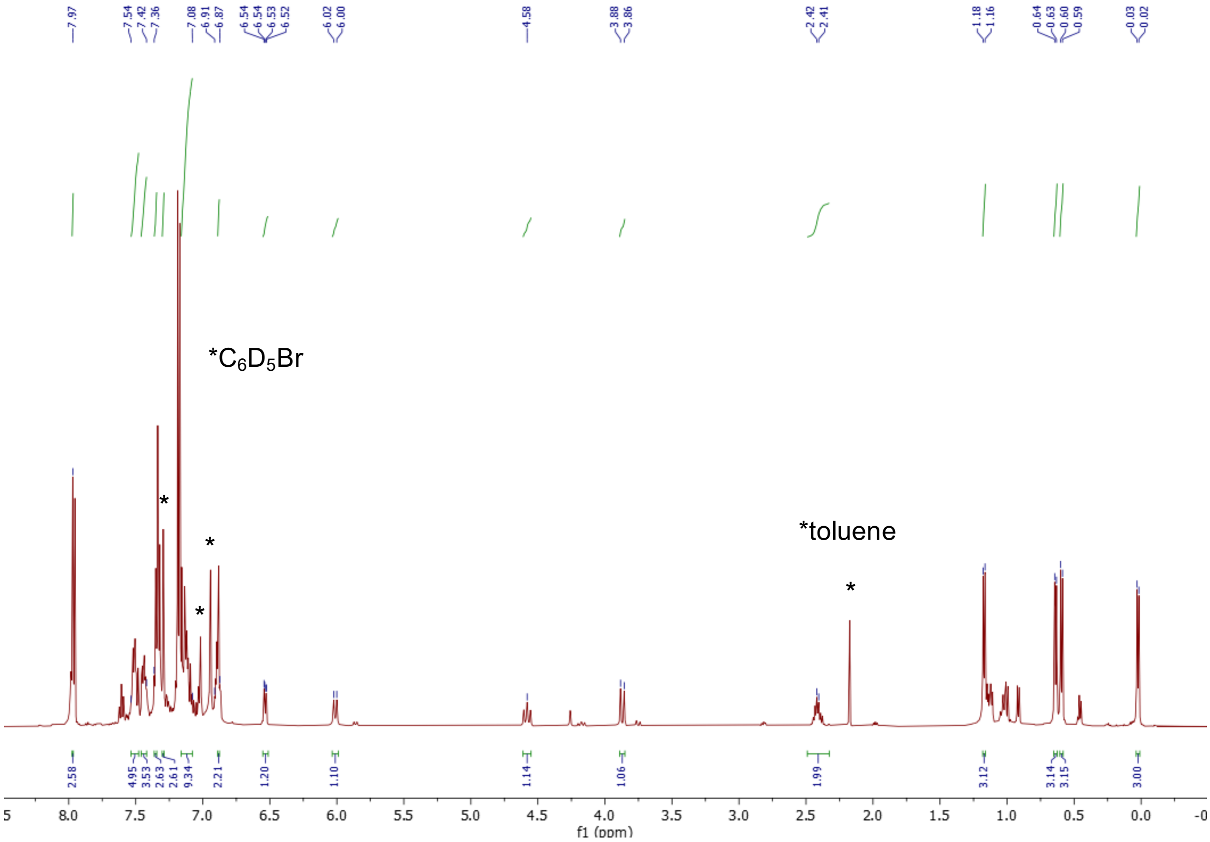


**Figure s8**: $^1$H NMR spectrum of **7** in bromobenzene-d$_5$ (contains ca 10% protio ligand).

## 2. Additional synthetic and characterizing data

Li($L^2$): To a solution of ($L^2$)H [s1] (1.00 g, 2.21 mmol) in diethyl ether (20 mL) was added dropwise at –78 °C, $^n$BuLi (1.66 mL of a 1.6 M solution in hexane, 2.66 mmol). The colour of solution instantly changed from colourless to yellow. The reaction mixture was slowly warmed to room temperature and stirred overnight, over which time an off-white suspension was formed. The resulting white solid was isolated by filtration, washed with hexane (15 mL) and dried in vacuo. It was used for subsequent chemistry without further purification. Yield: 750 mg, 74%. $^1$H NMR (400 MHz, THF-$d_8$, 298 K): $\delta_H$ 1.03 (12H, d, $^3J_{HH}$ = 6.8 Hz, Dipp $^i$Pr CH(C$\underline{H}_3$)$_2$), 3.84 (2H, q, $^3J_{HH}$ = 6.8 Hz, Dipp $^i$Pr C$\underline{H}$(CH$_3$)$_2$), 4.67 (1H, br d, methylene CH), 4.68 (1H, br d, methylene CH), 6.20 (1H, t, $^3J_{HH}$ = 7.4 Hz, Dipp *para* CH), 6.62 (1H, br m, phenyl CH), 6.64 (2H, d, $^3J_{HH}$ = 7.4 Hz, Dipp *meta* CH), 6.89 (1H, br m, phenyl backbone CH), 7.16-7.26 (11H, overlapping m, PPh$_2$ and phenyl backbone CH), 8.10 (1H, br m, phenyl backbone CH). $^{13}$C{$^1$H} NMR (126 MHz, THF-$d_8$, 298 K): $\delta_C$ 25.3 (Dipp $^i$Pr $\underline{C}$H(CH$_3$)$_2$), 28.0 (CH$_3$ of $^t$Bu), 60.8 (d, $^3J_{CP}$ = 25.1 Hz, methylene C), 113.2 (Dipp *para* C), 122.9 (Dipp *meta* C), 125.0 (phenyl backbone C), 128.2 (PPh$_2$), 128.9 (br d, $^3J_{CP}$ = 3.9 Hz, phenyl backbone C), 129.5 (m, phenyl backbone C), 132.1 (m, phenyl backbone C), 133.2 (phenyl backbone C), 133.9 (PPh$_2$), 134.6 (br d, PPh$_2$), 139.0 (m, PPh$_2$), 141.5 (Dipp $^i$Pr $\underline{C}$H(CH$_3$)$_2$), 155.7 (d, $^1J_{CP}$ = 21.9 Hz, phenyl backbone C), 162.2 (Dipp *ipso* C). $^7$Li NMR (104 MHz, THF-$d_8$, 298 K): $\delta_{Li}$ 0.2 (s). $^{31}$P NMR (104 MHz, THF-$d_8$, 298 K): $\delta_P$ -15.9 (s).

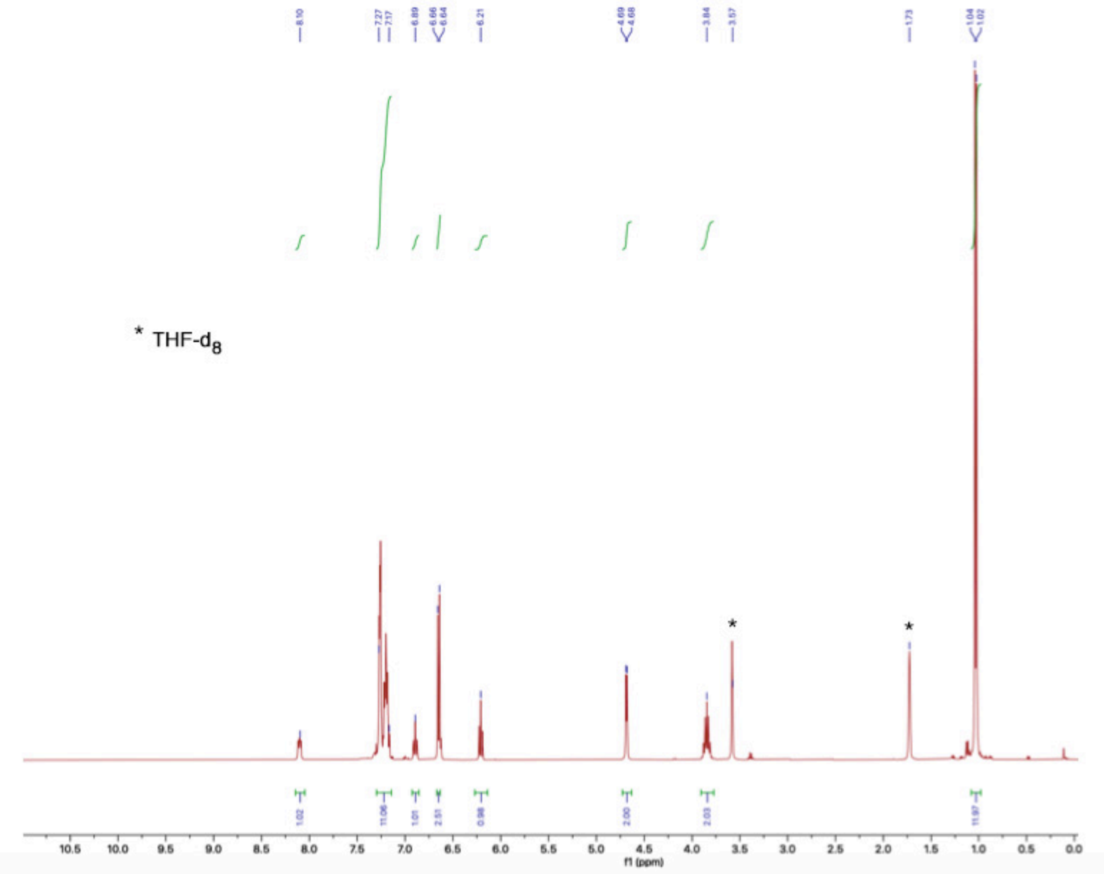
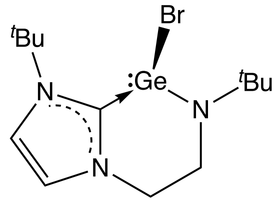


**Figure s9**: $^1$H NMR spectrum of Li($L^2$) in THF-$d_8$.



**(L$^{tBu}$)GeBr**: To a mixture of [(L$^{tBu}$)H$_2$]Br [s2] (580 mg, 1.91 mmol) and Ge{N(SiMe$_3$)$_2$}$_2$ [s3] (750 mg, 1.91 mmol) was added toluene (15 mL) at –78 °C. The reaction mixture was warmed to room temperature and then heated to 80 °C for 12 h, over which time a colourless solution was formed. Volatiles were removed *in vacuo*, and the product isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene stored at −30 °C. Yield: 660 mg, 93%. $^1$H NMR (400 MHz, benzene-d$_6$, 298 K): $\delta_H$ 1.39 (9H, s, $^t$Bu), 1.50 (9H, s, $^t$Bu), 3.54 (4H, br s, CH$_2$), 5.94 (1H, br d, imidazolylidene backbone CH), 6.21 (1H, br d, imidazolylidene backbone CH). $^{13}$C{$^1$H} NMR (126 MHz, benzene-d$_6$, 298 K): $\delta_C$ 30.7 (CH$_3$ of $^t$Bu), 31.2 (CH$_3$ of $^t$Bu), 43.8 (CH$_2$), 53.1 (CH$_2$), 56.6 (quaternary C of $^t$Bu), 60.5 (quaternary C of $^t$Bu), 117.9 (imidazolylidene CH), 120.3 (imidazolylidene), 168.6 (imidazolylidene C). Elemental microanalysis: calc. for $C_{13}H_{24}BrGeN_3$: C 41.65% H 6.45% N 11.21%; meas. C 41.73% H 6.80% N 11.29%. Crystallographic data: $C_{13}H_{24}BrGeN_3$ ($M_r$ = 374.89): monoclinic, $P2_1/c$, $a$ = 7.3994(2), $b$ = 10.027(2), $c$ = 21.820(4) Å, β = 91.18(3)°, $V$ = 1618.6(6) Å$^3$, $Z$ = 4, $\rho_c$ = 1.538 g cm$^{-3}$, $T$ = 150 K, λ = 1.54184 Å. $R_1$ = 0.0977 for 3274 observed unique reflections [$I > 2\sigma(I)$], w$R_2$ = 0.2661 for all 3374 unique reflections. Max. and min. residual electron densities 2.55, −1.27 e Å$^{-3}$. CCDC ref: 1952091.

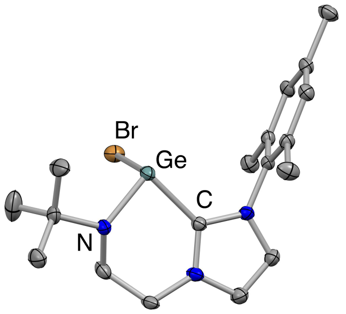


**Figure s10**: Molecular structure of (L$^{tBu}$)GeBr as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level and hydrogen atoms omitted for clarity. Key bond lengths (Å) and angles (°): Ge-C 2.07(1), Ge-N 1.866(9), Ge-Br 2.609(2), Br-Ge-C 94.3(3), Br-Ge-N 98.5(3), C-Ge-N 90.5(4).

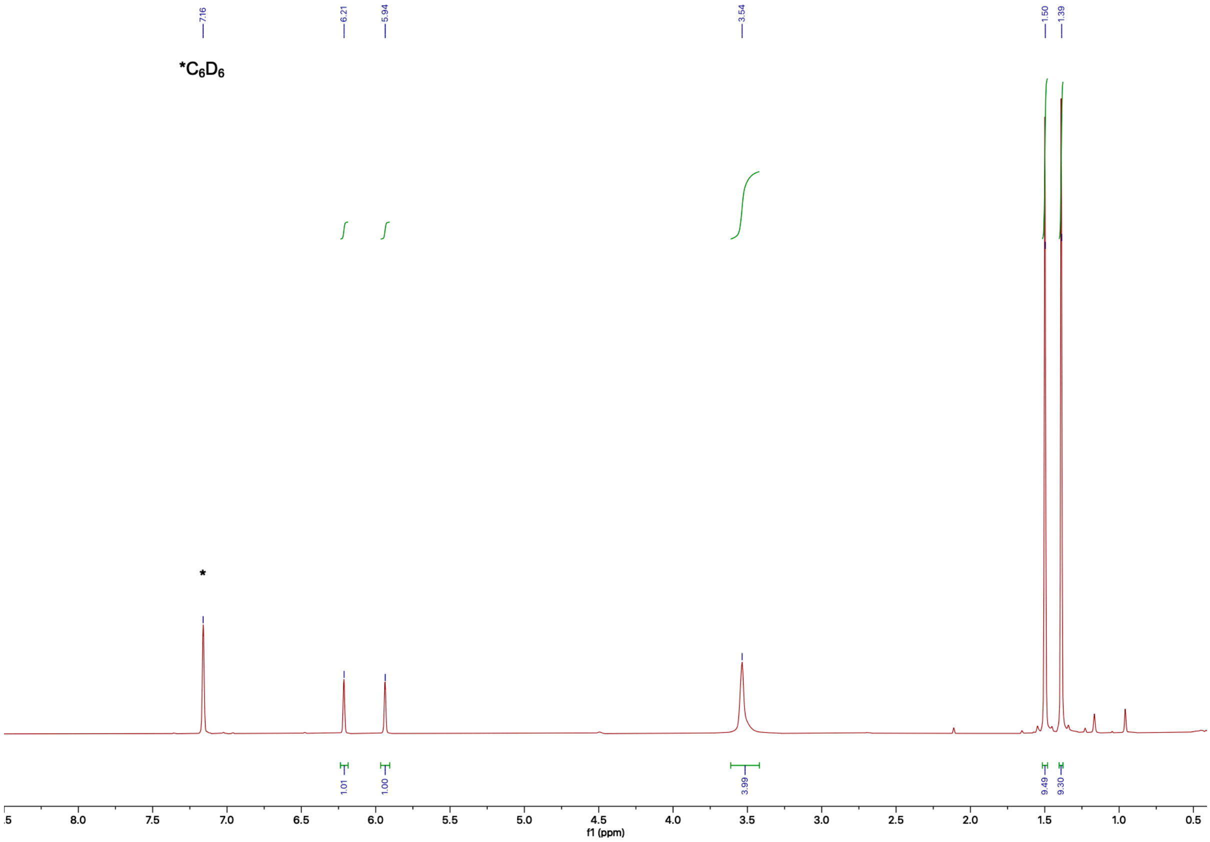
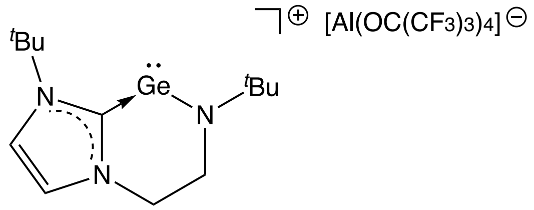


**Figure s11**: $^1$H NMR spectrum of (L$^{tBu}$)GeBr in benzene-d$_6$.



**[(L$^{tBu}$)Ge][Al(OC(CF$_3$)$_3$)$_4$]**: To a suspension of Li[Al(OC(CF$_3$)$_3$)$_4$] [s4] (390 mg, 0.40 mmol) in bromobenzene (5 mL) was added a solution of (L$^{tBu}$)GeBr (150 mg, 0.40 mmol) at room temperature. The reaction mixture was slowly warmed to room temperature and stirred for 12 h, over which time a yellow solution and a white precipitate were formed. Volatiles were removed in *vacuo* and compound 3 isolated as an oily yellow solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in bromobenzene stored at −30 °C. Yield: 200 mg, 40%. $^1$H NMR (400 MHz, benzene-d$_6$, 298 K): $\delta_H$ 1.04 (9H, s, $^t$Bu), 1.27 (9H, s, $^t$Bu), 3.05 (2H, br t, CH$_2$), 3.41 (2H, br t, CH$_2$), 6.42 (1H, s, imidazolylidene backbone CH), 6.66 (1H, s, imidazolylidene backbone CH). $^{13}$C{$^1$H} NMR (126 MHz, bromobenzene-d$_5$, 298 K): $\delta_C$ 30.5 (CH$_3$ of $^t$Bu), 31.7 (CH$_3$ of $^t$Bu), 45.0 (CH$_2$), 51.8 (CH$_2$), 61.0 (quaternary C of $^t$Bu), 61.2 (quaternary C of $^t$Bu), 79.5 (quaternary C of C(CF$_3$)$_3$), 120.1 (imidazolylidene backbone CH), 121.0 (imidazolylidene backbone CH), 121.9 (q, $^1J_{CF}$ = 294 Hz, CF$_3$ of C(CF$_3$)$_3$), 164.5 (imidazolylidene C). $^{19}$F NMR (376 MHz, bromobenzene-d$_5$, 298 K): $\delta_F$ 74.6. $^{27}$Al NMR (104 MHz, bromobenzene-d$_5$, 298 K): $\delta_{Al}$ 35.4. Elemental microanalysis: calc. for $C_{29}H_{24}AlF_{36}GeN_3O_4$: C 27.60% H 1.92% N 3.33% meas. C 27.51% H 2.02% N 3.38%. Crystallographic data: $C_{29}H_{24}AlF_{36}GeN_3O_4$ ($M_r$ = 1262.08): triclinic, *P*-1, $a$ = 10.2433(6), $b$ = 14.4020(8), $c$ = 16.1962(9) Å, α = 95.690(5)°, β = 107.389(5)°, γ = 100.633(5)°, $V$ = 2210.4(2) Å$^3$, $Z$ = 2, $\rho_c$ = 1.896 g cm$^{-3}$, $T$ = 150 K, λ = 1.54184 Å. $R_1$ = 0.0778 for 7732 observed unique reflections [$I > 2\sigma(I)$], w$R_2$ = 0.2304 for all 9104 unique reflections. Max. and min. residual electron densities 1.67, -1.17 e Å$^{-3}$. CCDC ref: 1952093.

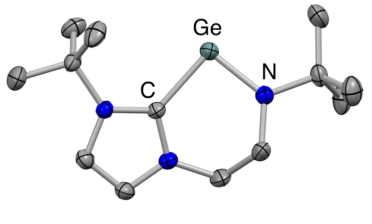


**Figure s12**: Molecular structures of the cationic components of [(L$^{tBu}$)Ge][Al(OC(CF$_3$)$_3$)$_4$] as determined by X-ray crystallography. Thermal ellipsoids set at the 40% probability level; anions and hydrogen atoms omitted for clarity. Key bond lengths (Å) and angles (°): Ge-N 1.823(5), Ge-C 2.049(4), C-Ge-N 93.1(2)

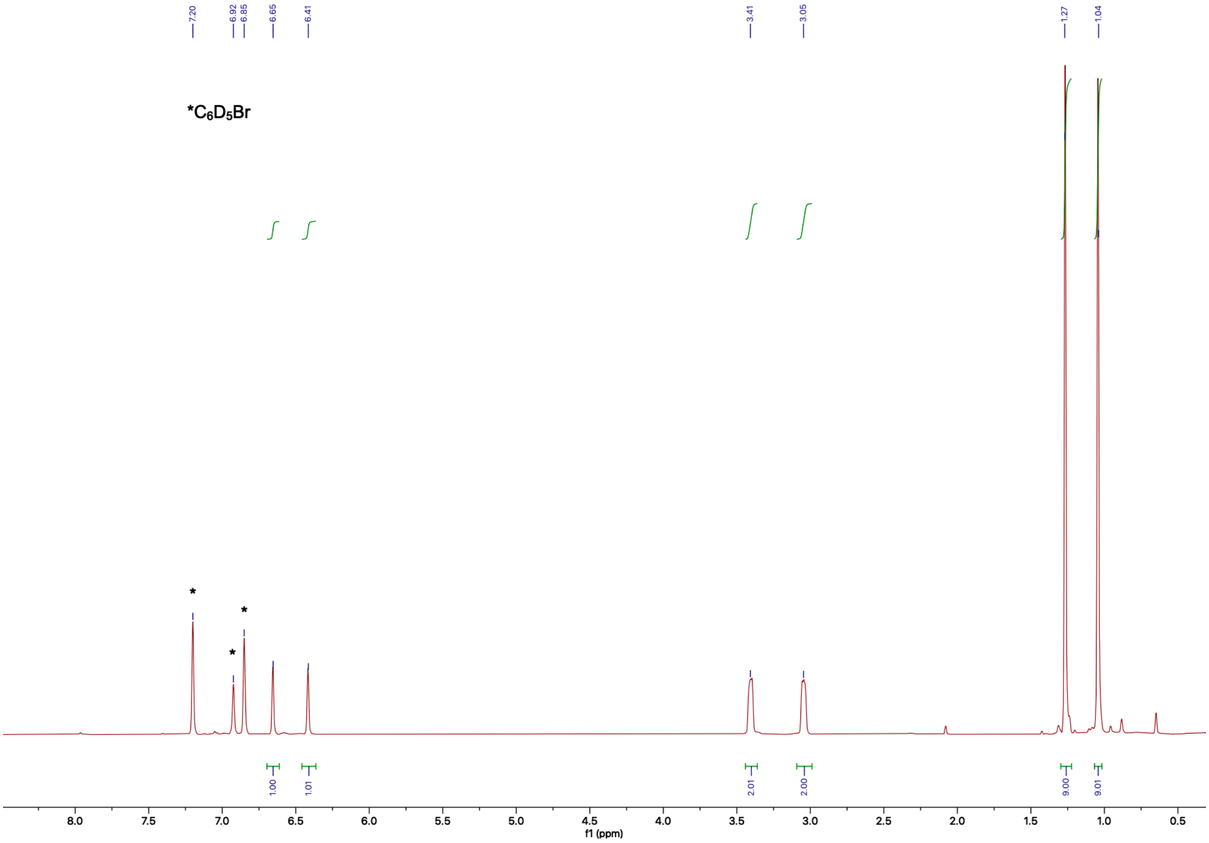


**Figure s13**: $^1$H NMR spectrum of $[(L^{tBu})Ge][Al(OC(CF_3)_3)_4]$ in bromobenzene-$d_5$.

## 3. DFT optimized *xyz*-coordinates for the cationic components of 3 and 3·$NH_3$

**3**

48

| | | | |
|---|---|---|---|
| C | 1.24422 | 2.80486 | 0.04735 |
| C | -0.01997 | 3.30077 | 0.01049 |
| N | -0.85890 | 2.21980 | -0.03216 |
| C | -0.15790 | 1.07968 | -0.03197 |
| N | 1.13465 | 1.43907 | 0.01597 |
| C | -2.31228 | 2.22964 | -0.10452 |
| C | -2.89928 | 1.06026 | 0.65245 |
| N | -2.57271 | -0.24595 | 0.09455 |
| Ge | -0.89028 | -0.79881 | -0.37236 |
| C | 2.22616 | 0.50672 | 0.04971 |
| C | -3.71104 | -1.19965 | 0.04735 |
| C | -4.31118 | -1.36062 | 1.44425 |
| C | -3.23015 | -2.56134 | -0.43052 |
| C | -4.76687 | -0.69377 | -0.93685 |
| H | 2.19857 | 3.30048 | 0.10407 |
| H | -0.37886 | 4.31638 | 0.02154 |
| H | -2.58954 | 1.12217 | 1.70259 |
| H | -3.97994 | 1.20362 | 0.64154 |
| H | -2.61514 | 2.20598 | -1.15512 |
| H | -2.66281 | 3.16318 | 0.33665 |
| H | -5.19246 | 0.26757 | -0.64358 |
| H | -5.59308 | -1.40472 | -0.98798 |
| H | -4.34011 | -0.59335 | -1.93684 |
| H | -3.55631 | -1.71993 | 2.14708 |
| H | -5.12248 | -2.08951 | 1.41370 |
| H | -4.72835 | -0.42964 | 1.83122 |
| H | -2.80039 | -2.51670 | -1.43538 |
| H | -4.07890 | -3.24526 | -0.46999 |
| H | -2.49001 | -2.99634 | 0.24709 |
| C | 2.81165 | 0.12496 | -1.15555 |
| C | 3.85763 | -0.78515 | -1.09391 |
| C | 4.31343 | -1.30119 | 0.11445 |
| C | 3.69069 | -0.89275 | 1.28918 |
| C | 2.64036 | 0.01438 | 1.28560 |
| C | 2.32126 | 0.65271 | -2.46756 |
| H | 4.32829 | -1.10180 | -2.01860 |
| C | 5.46461 | -2.25527 | 0.15194 |
| H | 4.03214 | -1.29183 | 2.23841 |
| C | 1.97852 | 0.43711 | 2.56057 |
| H | 0.93062 | 0.12441 | 2.59477 |
| H | 2.48274 | -0.00598 | 3.41799 |
| H | 1.99449 | 1.52263 | 2.68651 |
| H | 5.39543 | -2.93019 | 1.00578 |
| H | 5.51691 | -2.85271 | -0.75892 |
| H | 6.40867 | -1.70956 | 0.24087 |
| H | 2.94407 | 0.28868 | -3.28320 |
| H | 1.29437 | 0.33123 | -2.66841 |
| H | 2.33061 | 1.74481 | -2.49975 |

**3·$NH_3$**

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| | | | |
|---|---|---|---|
| C | 1.24216 | 2.87112 | -0.30201 |
| C | -0.02647 | 3.34544 | -0.26166 |
| N | -0.84947 | 2.25328 | -0.14148 |
| C | -0.13425 | 1.12209 | -0.11550 |
| N | 1.15247 | 1.50304 | -0.21566 |

| | | | |
|---|---|---|---|
| C | -2.30091 | 2.27536 | -0.00913 |
| C | -2.78576 | 1.07459 | 0.77845 |
| N | -2.58087 | -0.18276 | 0.09584 |
| Ge | -0.88956 | -0.77043 | -0.40695 |
| C | 2.25123 | 0.58722 | -0.14141 |
| C | -3.76468 | -1.06021 | -0.00332 |
| C | -4.29080 | -1.40694 | 1.39077 |
| C | -3.38895 | -2.35489 | -0.70950 |
| C | -4.86203 | -0.38063 | -0.82457 |
| H | 2.18809 | 3.37998 | -0.37590 |
| H | -0.40301 | 4.35388 | -0.29743 |
| H | -2.31065 | 1.10036 | 1.77158 |
| H | -3.84966 | 1.23817 | 0.95728 |
| H | -2.75084 | 2.28363 | -1.00504 |
| H | -2.56728 | 3.19992 | 0.50599 |
| H | -5.21563 | 0.54524 | -0.36609 |
| H | -5.72802 | -1.03861 | -0.91856 |
| H | -4.49584 | -0.15054 | -1.82724 |
| H | -3.52428 | -1.92789 | 1.97088 |
| H | -5.16225 | -2.06079 | 1.32020 |
| H | -4.59619 | -0.51984 | 1.94948 |
| H | -3.01232 | -2.17251 | -1.71864 |
| H | -4.27039 | -2.99276 | -0.79148 |
| H | -2.63103 | -2.91882 | -0.15642 |
| C | 2.66730 | -0.06758 | -1.29918 |
| C | 3.69929 | -0.98917 | -1.17469 |
| C | 4.30653 | -1.25857 | 0.04650 |
| C | 3.86504 | -0.57057 | 1.17282 |
| C | 2.84317 | 0.36799 | 1.10345 |
| C | 2.02714 | 0.19685 | -2.62509 |
| H | 4.03789 | -1.51276 | -2.06251 |
| C | 5.43369 | -2.23745 | 0.14022 |
| H | 4.33778 | -0.75999 | 2.13118 |
| C | 2.42103 | 1.13108 | 2.32296 |
| H | 1.33750 | 1.25945 | 2.38258 |
| H | 2.76108 | 0.63017 | 3.22924 |
| H | 2.85418 | 2.13529 | 2.32586 |
| H | 5.50589 | -2.67040 | 1.13854 |
| H | 5.31950 | -3.04687 | -0.58187 |
| H | 6.38587 | -1.74245 | -0.07217 |
| H | 2.63090 | -0.21920 | -3.43047 |
| H | 1.03660 | -0.26521 | -2.68011 |
| H | 1.90233 | 1.26561 | -2.81049 |
| N | -0.09996 | -1.32836 | 1.63871 |
| H | -0.33092 | -2.30172 | 1.80790 |
| H | -0.46928 | -0.78224 | 2.40986 |
| H | 0.91432 | -1.24591 | 1.63972 |

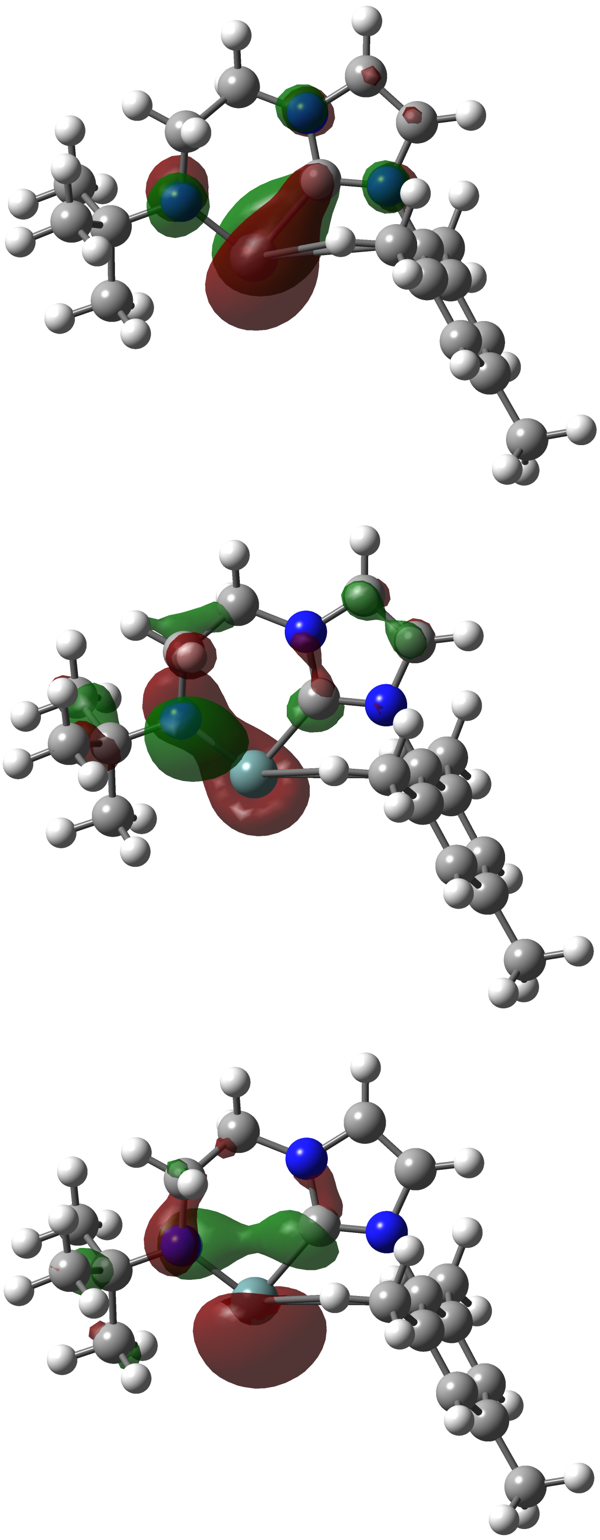

**Figure s14:** LUMO (top), HOMO-2 (centre) and HOMO-3 (lower) for the cationic component of **3**. The respective energies are: -5.51 eV/-532 kJ mol$^{-1}$, -10.22 eV/-986 kJ mol$^{-1}$ and -10.48 eV/-1011 kJ mol$^{-1}$.

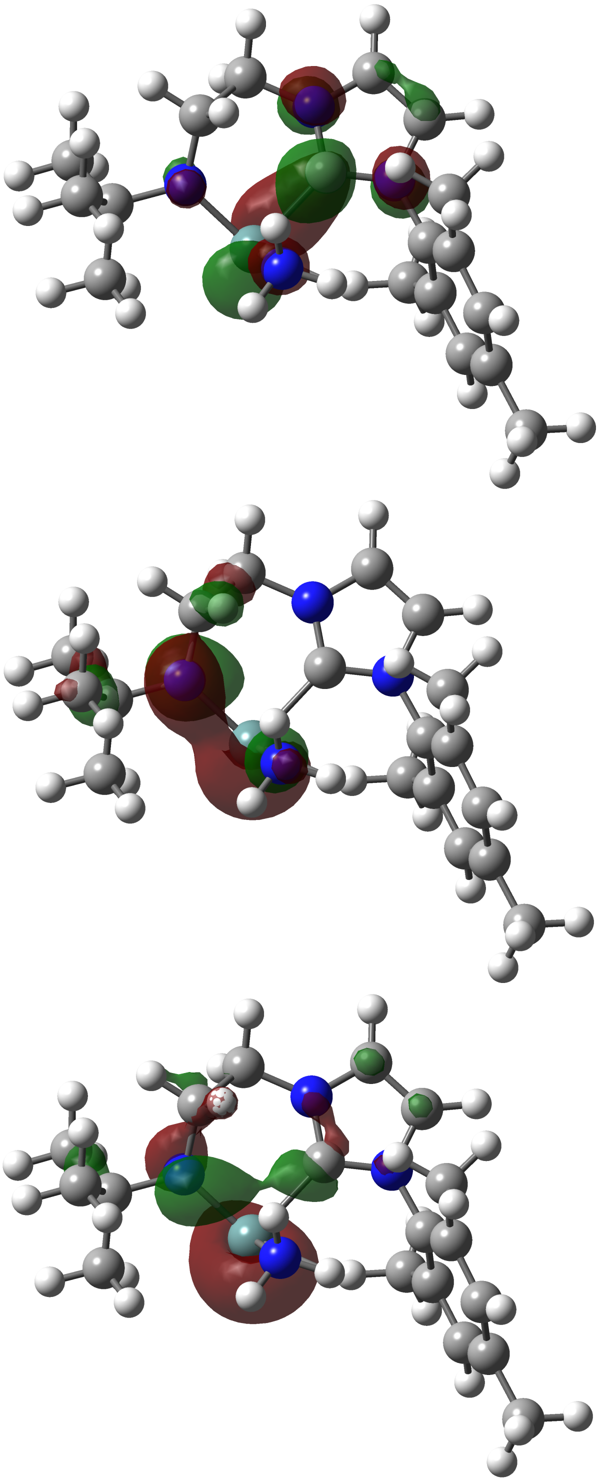

**Figure s15:** LUMO (top), HOMO (centre) and HOMO-1 (lower) for the cationic component of **3**·$NH_3$. The respective energies are: -4.17 eV/-402 kJ mol$^{-1}$, -9.18 eV/-886 kJ mol$^{-1}$ and -9.44 eV/-911 kJ mol$^{-1}$.

## 4. References for supporting information

s1 B. Liu, D. Cui, J. Ma, X. Chen and X. Jing, *Chem.-Eur. J.*, 2007, **13**, 834–845.

s2 P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem. Int. Ed.,* 2003, **42**, 5981–5984.

s3 D. H. Harris and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1974, 895-896.

s4 I. Krossing, *Chem.-Eur. J.,* 2001, **7**, 490-502.