**SUPPORTING INFORMATION** (Ms. ID: om-2016-00426q)

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# Amidinatogermylene Metal Complexes as Homogeneous Catalysts in Alcoholic Media

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**Table S1.** Crystal, measurement and refinement data for the compounds studied by XRD

| | **2** | **5** | **6** |
|---|---|---|---|
| formula | $C_{27}H_{44}ClGeN_2Rh$ | $C_{29}H_{46}Cl_2GeN_2Ru$ | $2(C_{29}H_{47}Cl_2GeIrN_2)$ |
| fw | 607.59 | 667.3 | 1518.75 |
| cryst syst | Monoclinic | monoclinic | Monoclinic |
| space group | *P*21/c | P21/n | *P*21/c |
| *a*, Å | 16.7872(2) | 9.2077(1), | 24.1428(2) |
| *b*, Å | 12.2820(2) | 20.0025(4) | 9.3753(1) |
| *c*, Å | 13.9392(2) | 16.7333(3) | 27.3016(2) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 106.677(2) | 90.978(1) | 95.134(1) |
| $\gamma$, deg | 90 | 90 | 90 |
| *V*, Å$^3$ | 2753.10(7) | 3081.44(9) | 6154.8(1) |
| Z | 4 | 4 | 4 |
| *F*(000) | 1256 | 1376 | 3024 |
| $D_{calcd}$, g cm$^{-3}$ | 1.466 | 1.438 | 1.639 |
| μ, mm$^{-1}$ | 1.805 (Mo Kα) | 6.900 (Cu Kα) | 11.185 (Cu Kα) |
| cryst size, mm | 0.19 x 0.13 x 0.10 | 0.12 x 0.10 x 0.08 | 0.26 x 0.16 x 0.09 |
| *T*, K | 120.0(1) | 150(2) | 155(2) |
| $\theta$ range, deg | 3.32 to 31.50 | 3.44 to 69.00 | 3.25 to 68.99 |
| min./max. *h*, *k*, *l* | –23/24, –17/18, –20/19 | –10/11, –23/23, –14/19 | –29/27, –8/11, –32/32 |
| no. collected reflns | 40344 | 14539 | 29901 |
| no. unique reflns | 8550 | 5640 | 11357 |
| no. reflns with $I > 2\sigma(I)$ | 7168 | 5094 | 10591 |
| no. params/restraints | 298/0 | 328/0 | 659/0 |
| GOF (on $F^2$) | 1.040 | 1.036 | 1.042 |
| $R_1$ (on $F$, $I > 2\sigma(I)$) | 0.031 | 0.043 | 0.024 |
| $wR_2$ (on $F^2$, all data) | 0.063 | 0.108 | 0.059 |
| min./max. $\Delta\rho$, e Å$^{-3}$ | –0.489/0.597 | –1.476/2.145 | –1.411/0.948 |
| CCDC dep. no. | 1480090 | 1480091 | 1480092 |

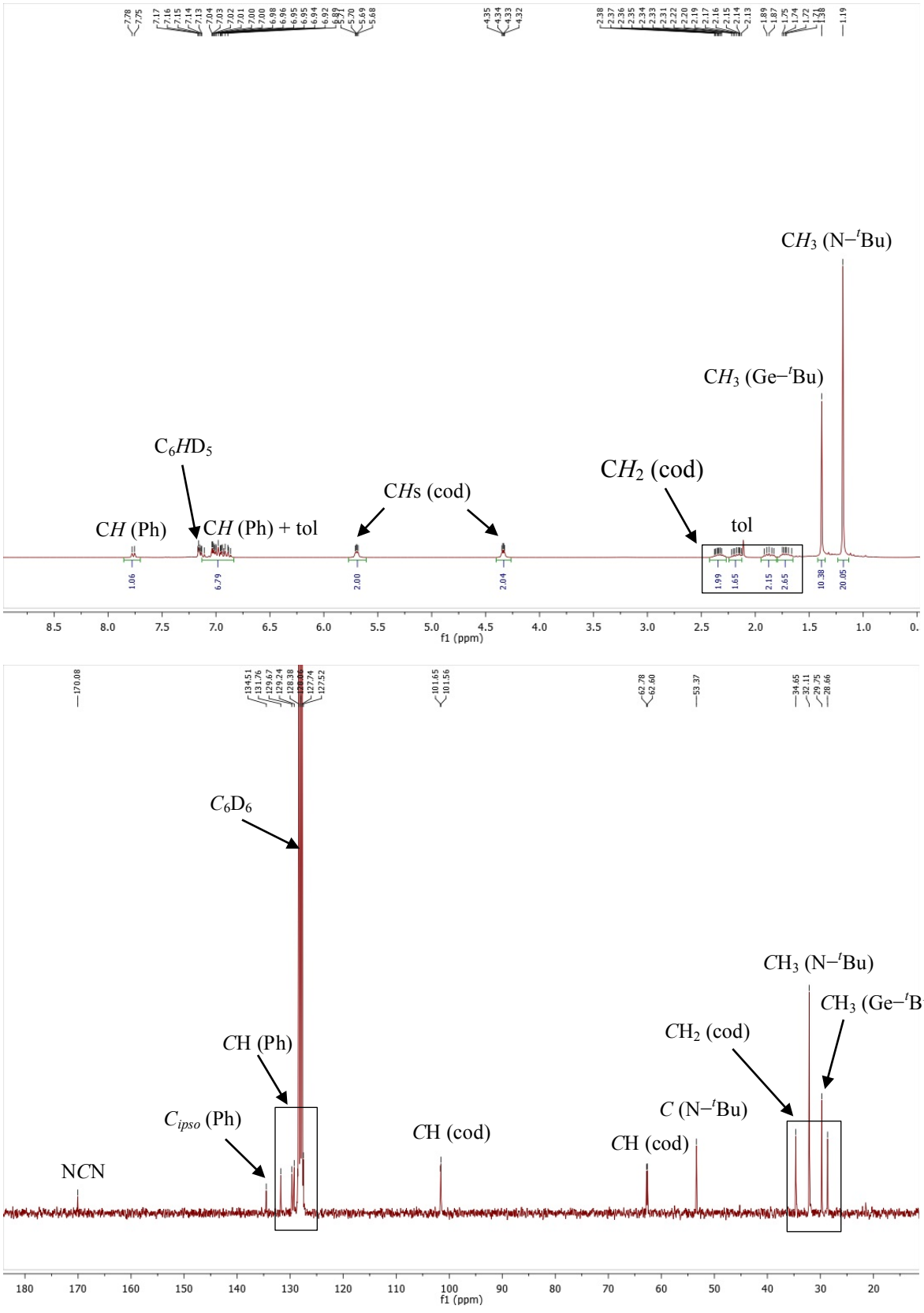


**Figure S1.** $^{1}$H (top; 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom; 75.5 MHz) NMR spectra of **2** ($C_6D_6$, 25 °C).

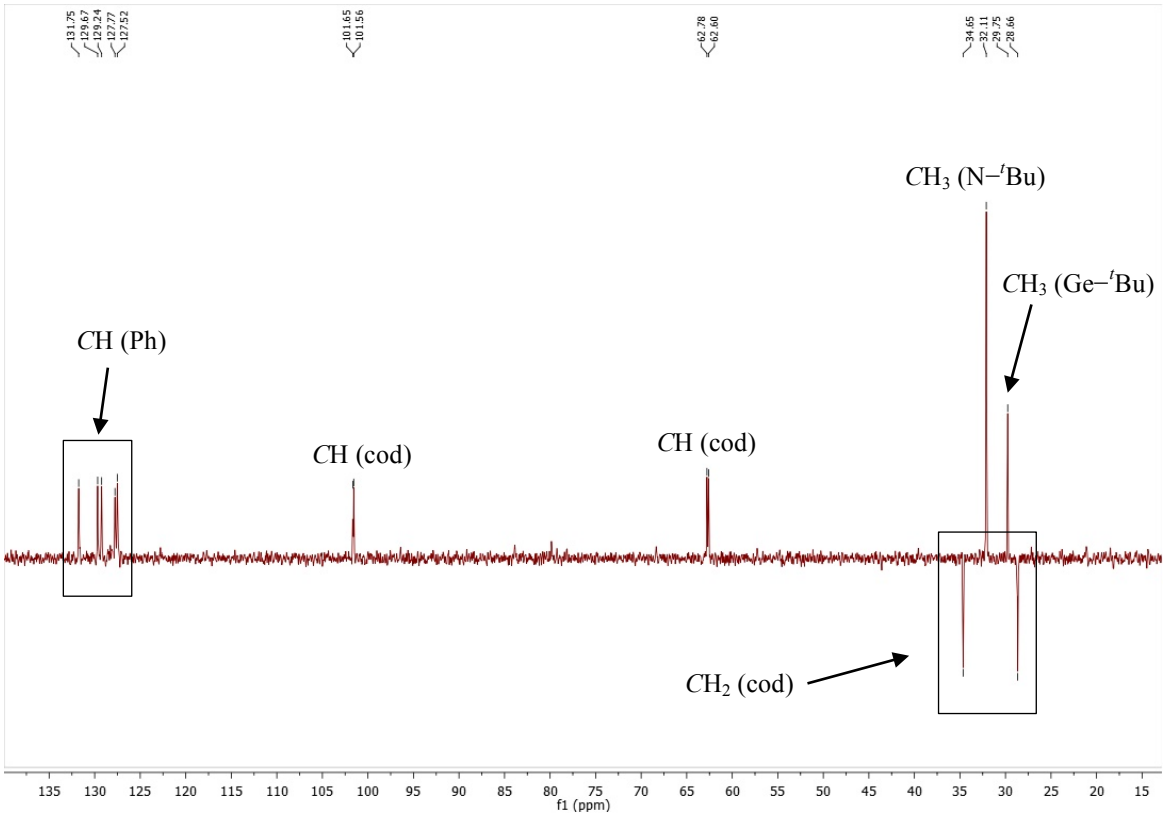


**Figure S2.** $^{13}C\{^{1}H\}$-DEPT 135 (75.5 MHz) NMR spectrum of **2** ($C_6D_6$, 25 °C).

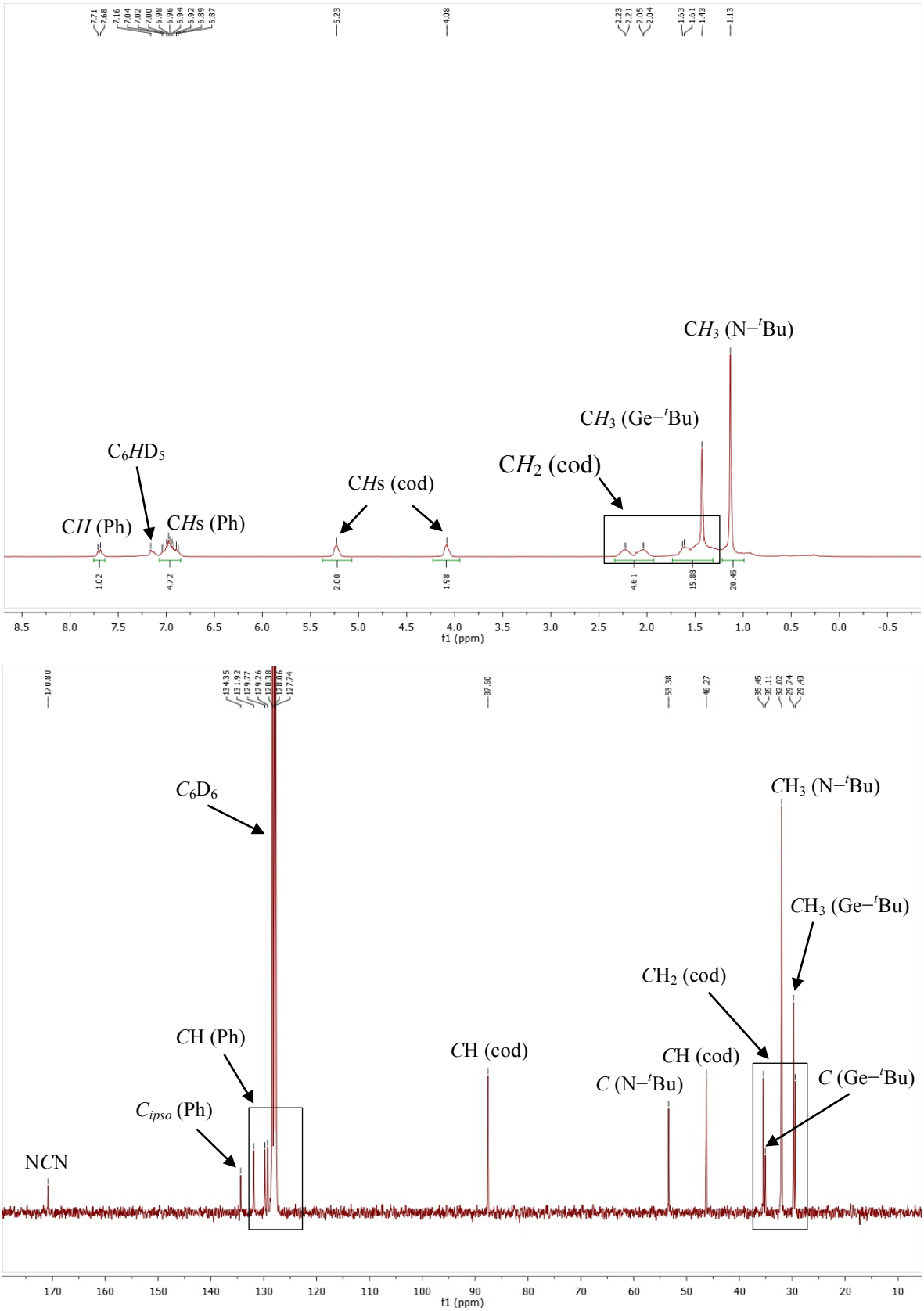


**Figure S3.** $^{1}$H (top; 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom; 75.5 MHz) NMR spectra of **3** ($C_6D_6$, 25 ºC).

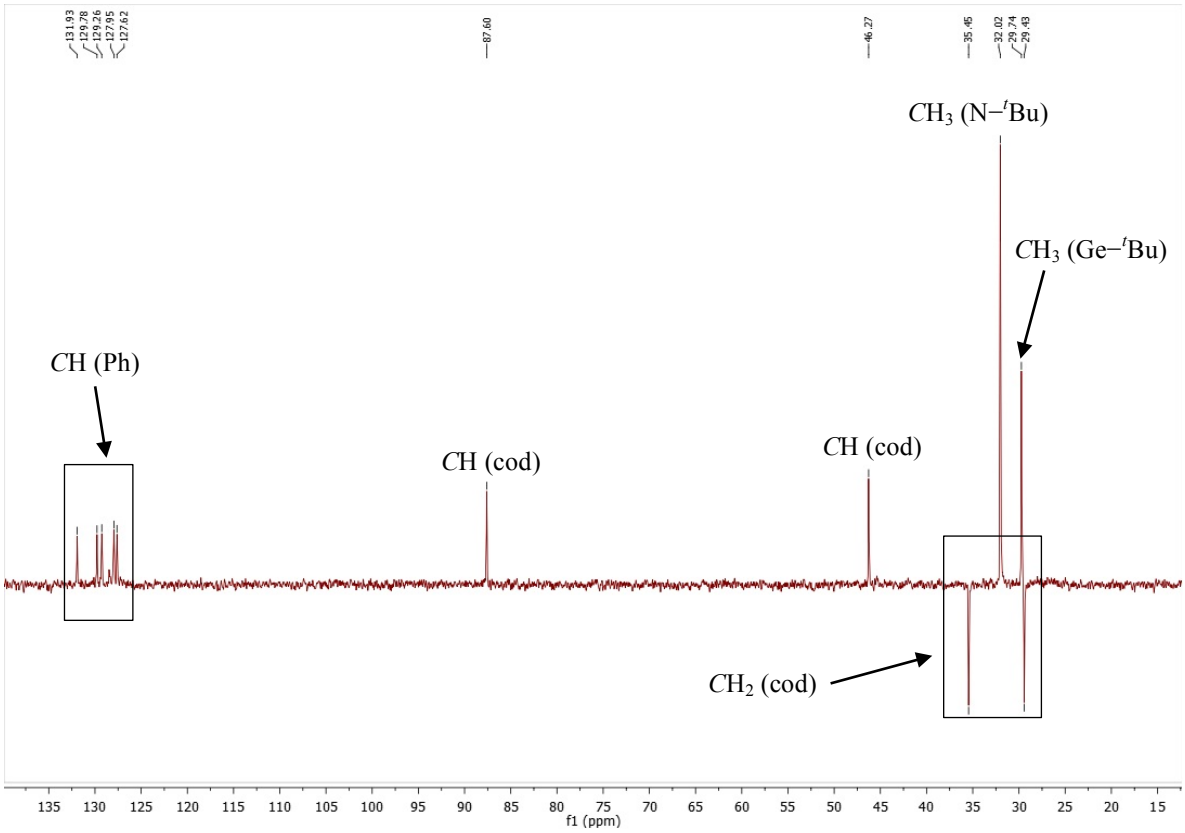


**Figure S4.** $^{13}C\{^{1}H\}$-DEPT 135 (75.5 MHz) NMR spectrum of **3** ($C_6D_6$, 25 ºC).

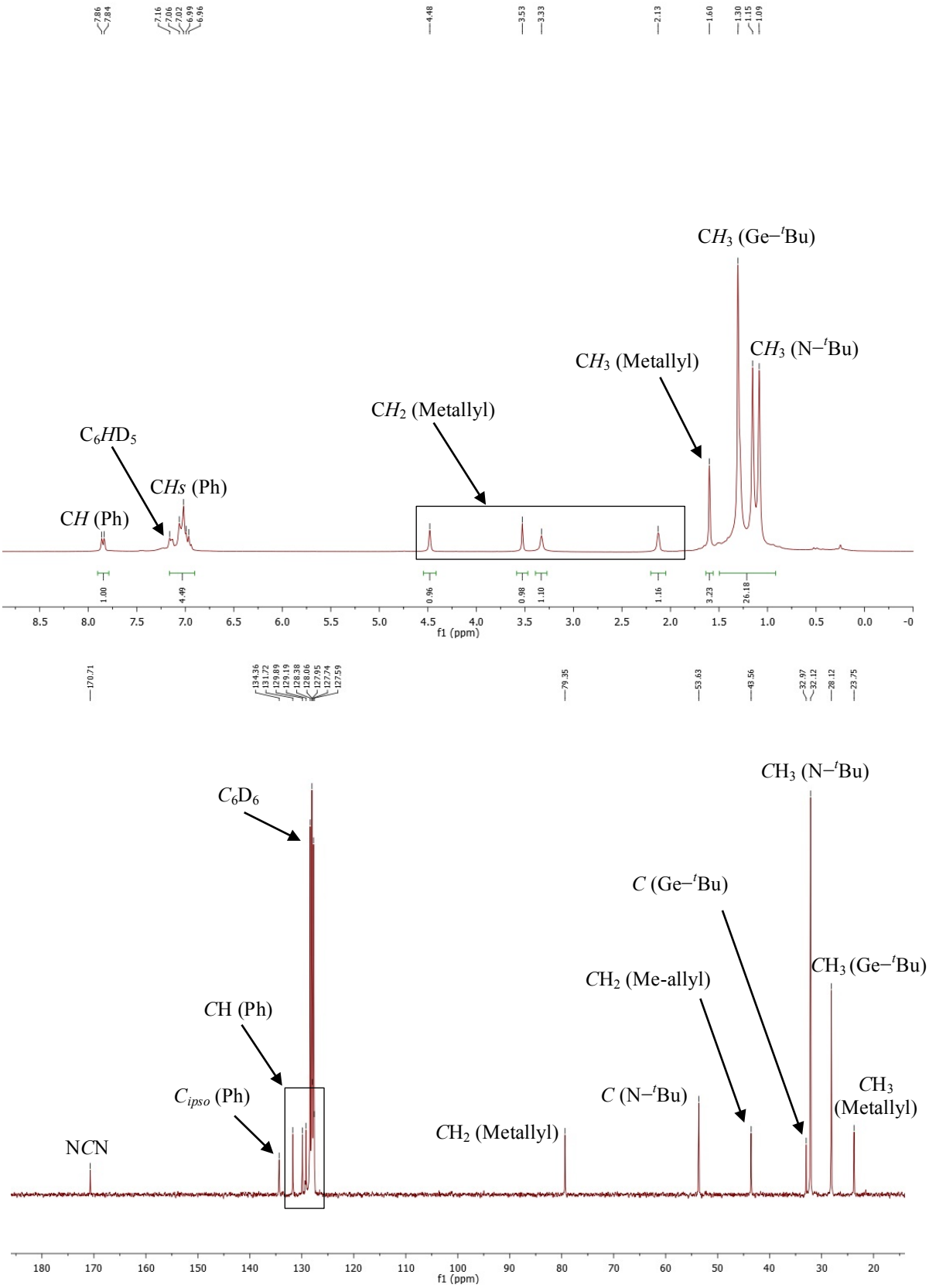


**Figure S5.** $^{1}$H (top; 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom; 75.5 MHz) NMR spectra of **4** ($C_6D_6$, 25 °C).

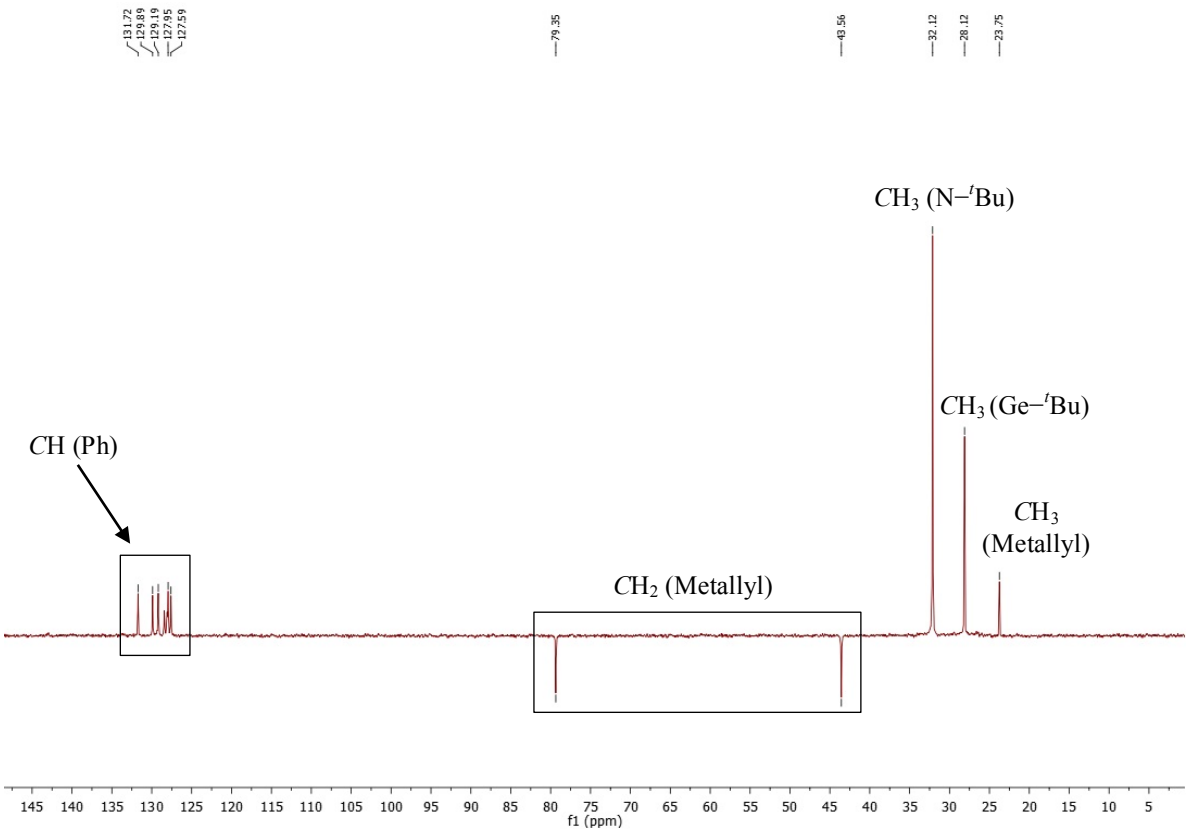


**Figure S6.** $^{13}C\{^{1}H\}$-DEPT 135 (75.5 MHz) NMR spectrum of **4** ($C_6D_6$, 25 °C).

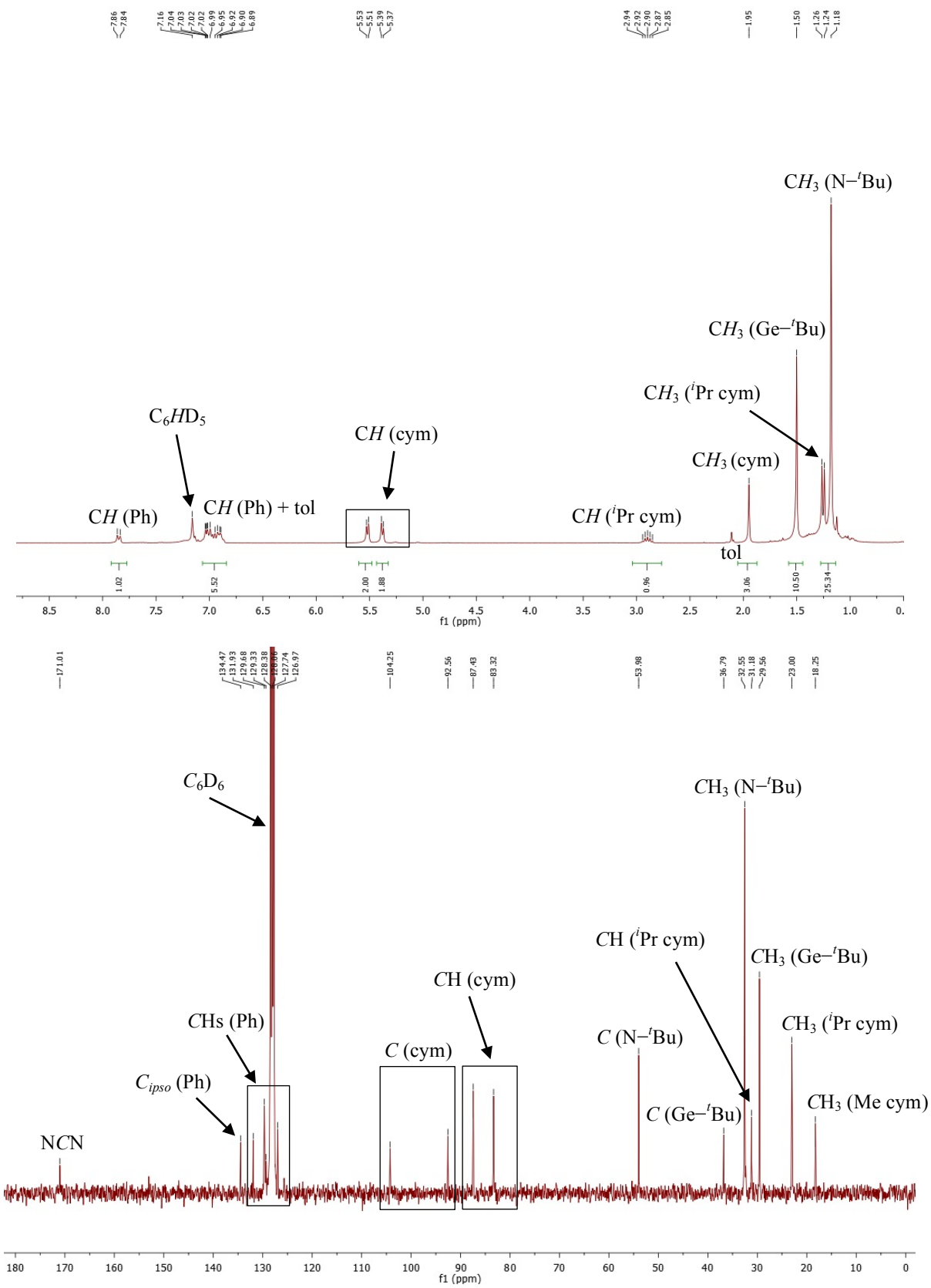


**Figure S7.** $^{1}$H (top; 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom; 75.5 MHz) NMR spectra of **5** ($C_6D_6$, 25 °C).

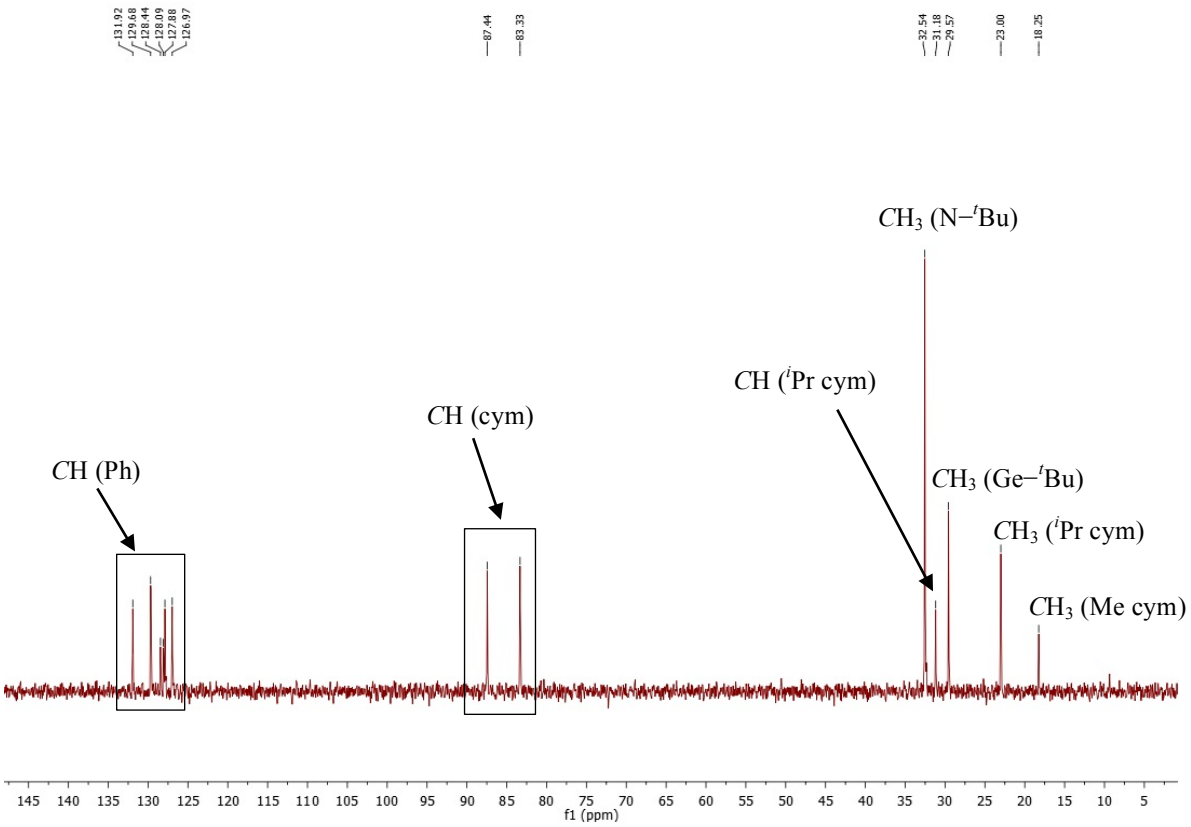


**Figure S8.** $^{13}C\{^{1}H\}$-DEPT 135 (75.5 MHz) NMR spectrum of **5** ($C_6D_6$, 25 ºC).

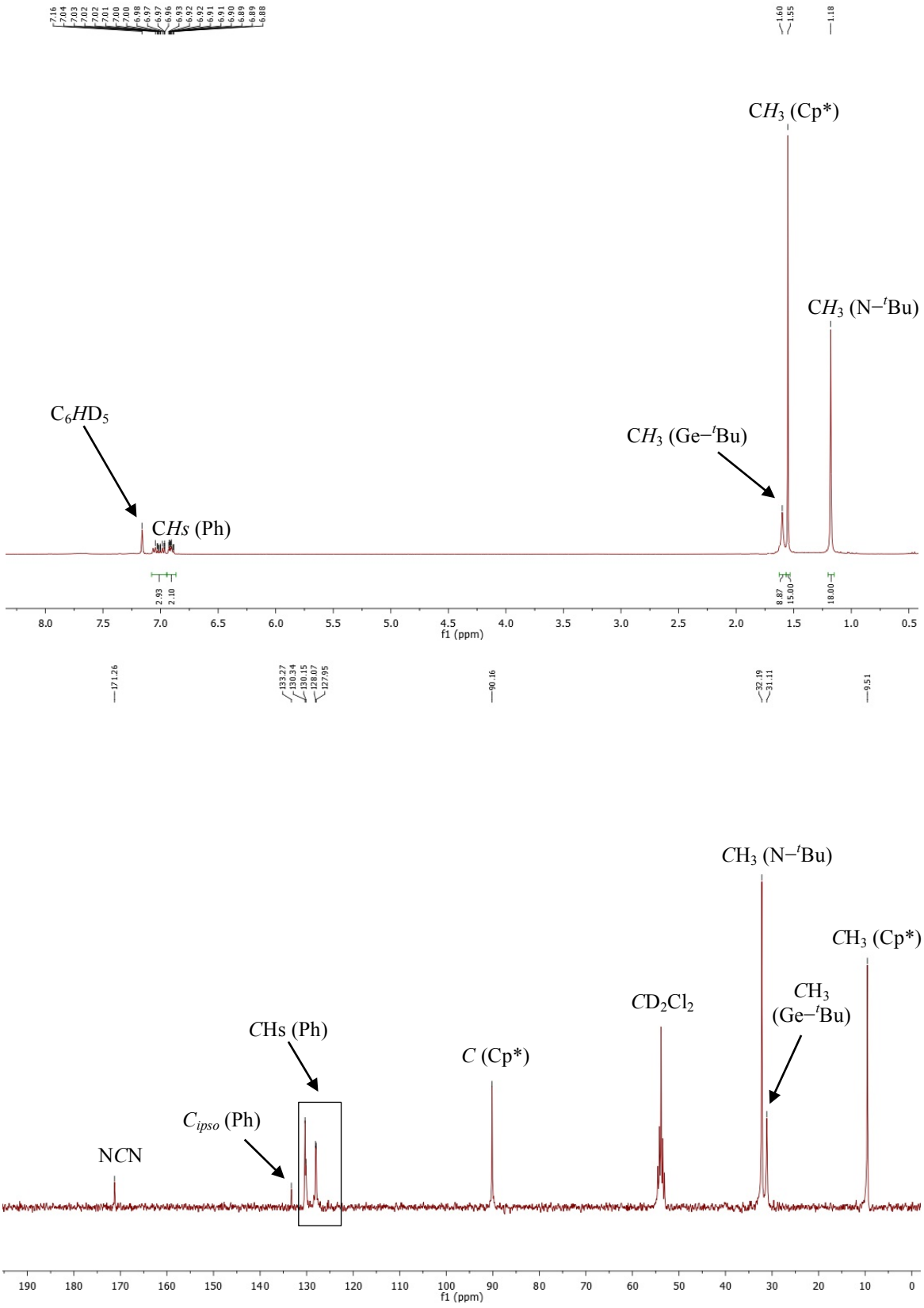


**Figure S9.** $^{1}$H (top; 300.1 MHz, $C_6D_6$) and $^{13}C\{^{1}H\}$ (bottom; 75.5 MHz, $CD_2Cl_2$) NMR spectra of **6** (25 °C).

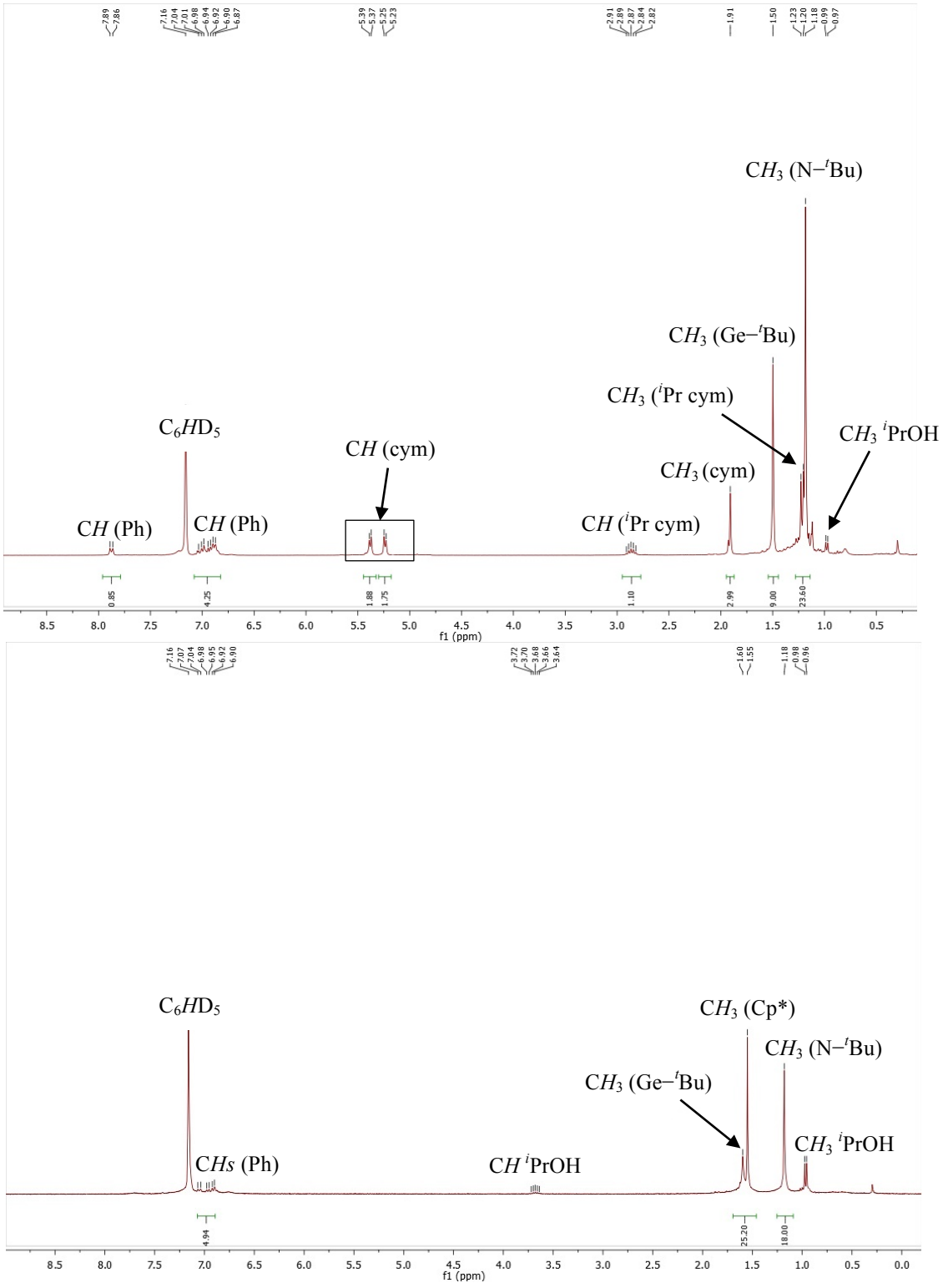


**Figure S10.** $^{1}$H NMR spectra (300.1 MHz, $C_6D_6$, 25 ºC) of **5** (top) and **6** (bottom) after one day in isopropanol under air.

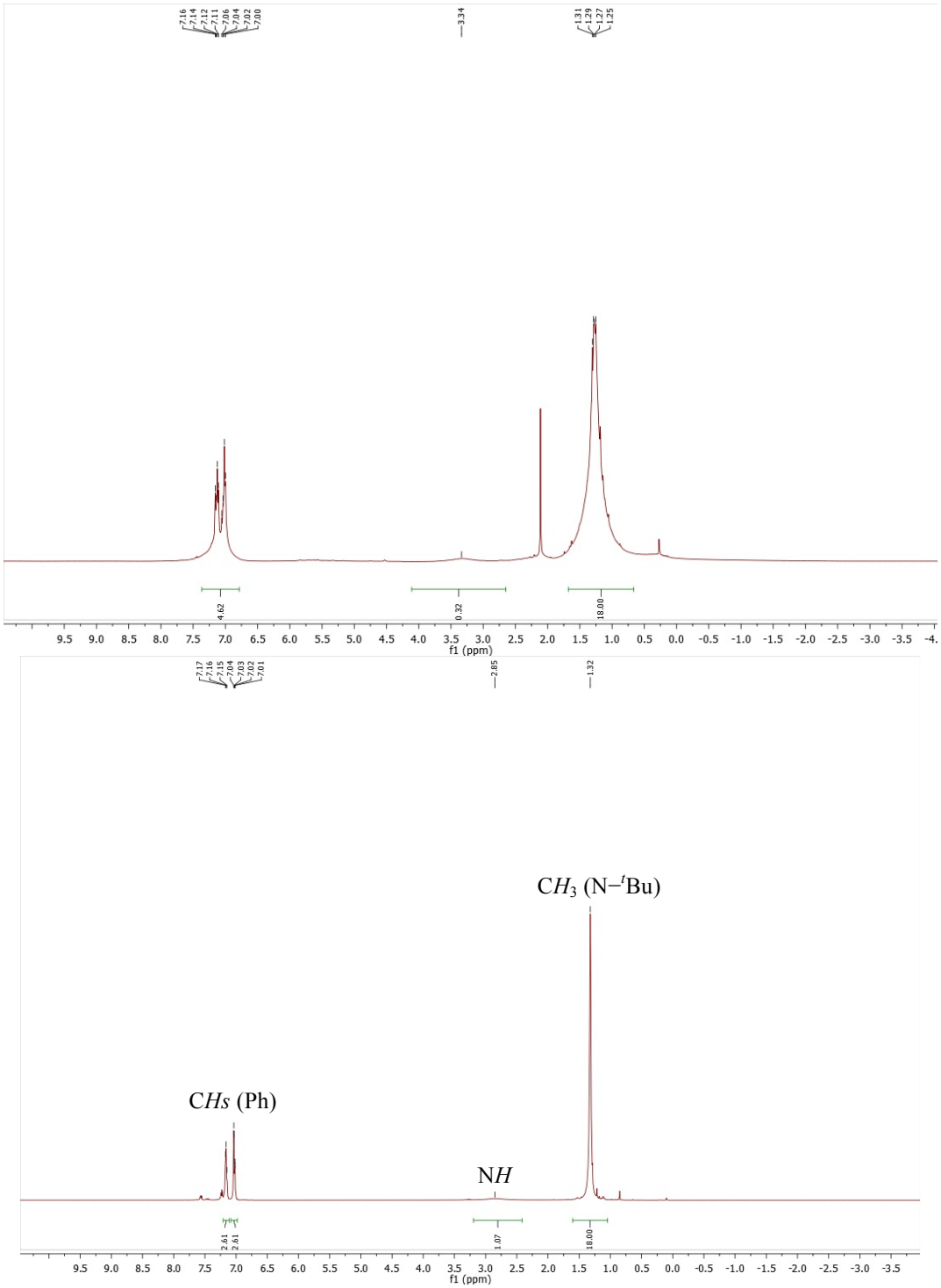


**Figure S11.** $^{1}$H NMR spectra (300.1 MHz, $C_6D_6$, 25 ºC) of **3** after one day in toluene under air (top) and of pure $^{t}Bu_2$bzamH (bottom).

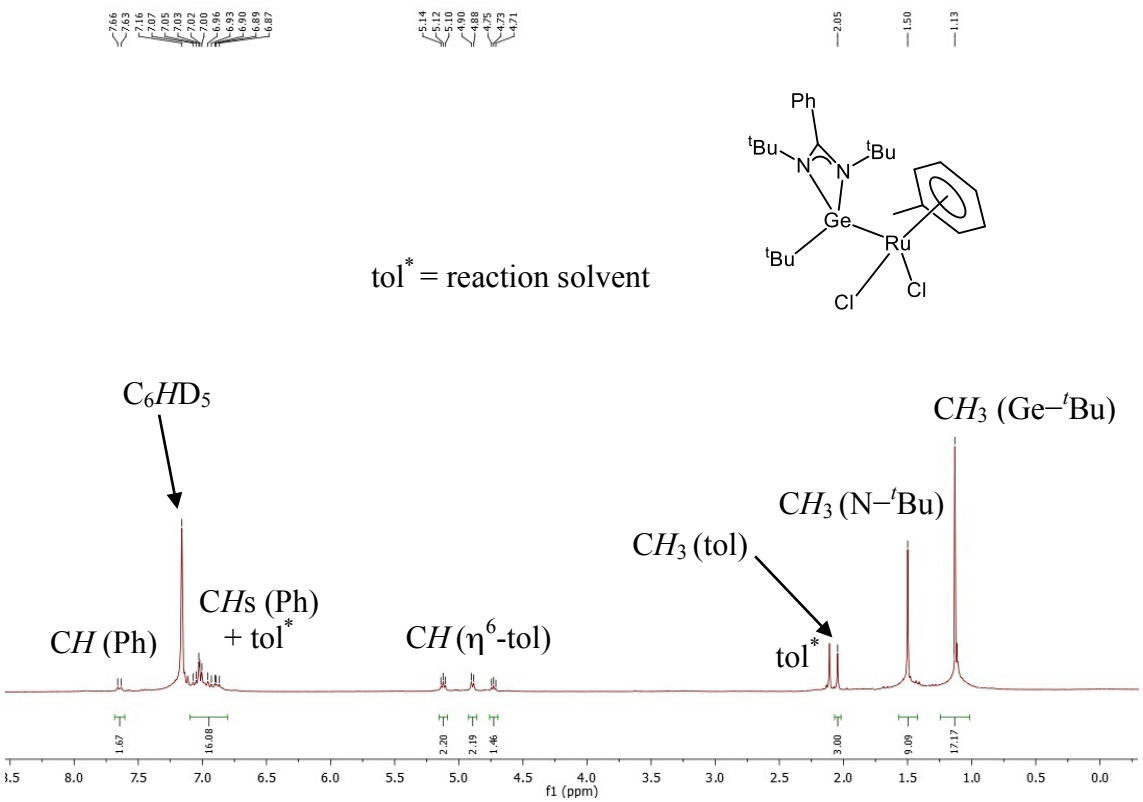


**Figure S12.** $^{1}$H NMR spectra (300.1 MHz, $C_6D_6$, 25 ºC) of the solid obtained by solvent evaporation after heating complex **5** in toluene at reflux temperature for 24 h.