Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Electrophilic activation of difunctional aminoboranes: B–N coupling versus intramolecular Cl/Me exchange

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Experimental Details

General procedures

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were performed under argon atmosphere using standard Schlenk techniques or an MBraun glovebox. Solvents (dichloromethane, *n*-pentane, *n*-hexane) were dried and degassed according to general purification methods. Solvents for NMR spectroscopy were dried and degassed prior to use. Heptamethyldisilazane, trimethylsilyl-trifluoromethanesulfonate Me_3SiOTf and silver tetrakis(perfluoro-*tert*-butoxy)aluminate $Ag[Al(OC(CF_3)_3)_4]$ were commercially purchased and used as received. Mesityllithium[1] and chloro(trimethylsilyl-(methyl)amino)-*n*-octylborane (**1a**)[2] were prepared as described in literature.

NMR spectra were recorded at 25 °C on a Bruker Avance III HD spectrometer operating at 300 MHz, on a Bruker Avance II-400 spectrometer, a Bruker Avance III HD spectrometer or on a Bruker Avance Neo 400 spectrometer operating at 400 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (^1H) or the deuterated solvent itself (^{13}C) and reported relative to external $SiMe_4$ (^1H, ^{13}C, ^{29}Si) or $BF_3{\cdot}OEt_2$ (^{11}B) standards. Mass spectra were obtained with the use of a Thermo Scientific Exactive Plus Orbitrap MS system employing atmospheric sample analysis probe (ASAP). All MS spectra obtained showed excellent congruence with the calculated isotopic distribution patterns. Elemental analyses were performed on an Elementar vario MICRO cube elemental analyzer.

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-Kα radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[3] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL[4] software and the SHELXLE graphical user interface.[5] Other structural information was extracted using OLEX2 software.[6]

Syntheses

Synthesis of dichloro-(2,4,6-trimethylphenyl)borane.[7] To a suspension of mesityllithium (2.52 g, 20.0 mmol, 1 equiv.) in *n*-hexane (200 mL) was added a solution of BCl_3 (1M in *n*-hexane, 50 mmol, 2.5 equiv.) at −78°C. The mixture was warmed to room temperature overnight. The formed salt was removed by filtration with *n*-pentane (3 x 15 mL) and the solvent was removed *in vacuo*. After distillation, a colorless liquid was obtained (2.05 g, 10.2 mmol, 51 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 (m, 2H, Ar-*H*), 2.35 (s, 6H, *o*-Mes-CH_3), 2.30 ppm (s, 3H, *p*-Mes-CH_3); ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): δ = 60.9 ppm (s).

Synthesis of 1b. To a solution of dichloro-(2,4,6-trimethylphenyl)borane (2.81 g, 13.99 mmol, 1 equiv.) in DCM (25 mL) was added heptamethyldisilazane (2.59 g, 14.76 mmol, 1.06 equiv.) dropwise at −78°C. After 30 min, the cooling bath was removed and the reaction was warmed to room temperature overnight. After removing the volatiles *in vacuo* and crystallization from *n*-hexane, colorless crystals were obtained (2.42 g, 9.04 mmol, 65 % yield).
^{1}H NMR (400 MHz, $CDCl_3$): (*Z*)-**1b**: δ = 6.86 (m, 2H, Mes-C*H*), 2.66 (s, 3H, N-CH_3), 2.32 (s, 3H, *p*-Mes-CH_3), 2.29 (s, 6H, *o*-Mes-CH_3), 0.43 ppm (s, 9H, Si-CH_3); (*E*)-**1b**: δ = 6.80 (m, 2H, Mes-C*H*), 3.04 (s, 3H, N-CH_3), 2.30 (s, 3H, *p*-Mes-CH_3), 2.29 (s, 6H, *o*-Mes-CH_3), −0.02 ppm (s, 9H, Si-CH_3); ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = 41.6 ppm (s); ^{29}Si{^{1}H} NMR (60 MHz, $CDCl_3$): (*Z*)-**1b**: δ = 14.3 ppm (s); (*E*)-**1b**: δ = 13.6 ppm (s); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*Z*)-**1b**: δ = 137.6 (s, *o*-Mes-*C*), 137.7 (s, *p*-Mes-*C*), 127.3 (s, Mes-CH), 35.2 (s, N-*C*H_3), 21.4 (s, *o*-Mes-*C*H_3), 21.3 (s, *p*-Mes-*C*H_3), 1.5 ppm (s, Si-*C*H_3); (*E*)-**1b**: δ = 138.0 (s, *o*-Mes-*C*), 137.8 (s, *o*-Mes-*C*), 127.2 (s, Mes-*C*H), 34.2 (s, N-*C*H_3), 22.1 (s, *p*-Mes-*C*H_3), 21.3 (s, *o*-Mes-*C*H_3), 0.1 ppm (s, Si-*C*H_3); HRMS (ASAP): m/z calcd.: 267.1376 [M]$^+$, found: 267.1371; elem. anal. calcd. (%) for $C_{13}H_{23}BClNSi$: C 58.33, H 8.66, N 5.23; found: C 58.56, H 8.96, N 5.28.

Synthesis of 2a.[8] To Me_3SiOTf (3.7 mg, 17 µmol, 5 mol%) was added a cold solution (−30 °C) of **1a** in DCM (0.7 mL, 0.48 M). Subsequently, the reaction was monitored via ^{11}B {^{1}H} NMR in a sealed J. Young tube and showed full conversion to compound **2a** after 24 h. After removing all volatiles *in vacuo* a colorless oil was obtained quantitatively.
^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.94 (s, 9H, N-CH_3), 1.36-1.29 (m, 36H, CH_2), 1.07-1.04 (m, 6H, B-CH_2), 0.89 (t, 9H, CH_3); ^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2): δ = 36.7 ppm (s).

Synthesis of 3a. To $Ag[Al(OC(CF_3)_3)_4]$ (17.6 mg, 16 µmol, 5 mol%) was added a cold solution (−30 °C) of **1a** in DCM (0.68 mL, 0.48 M). After 10 min, the ^{11}B {^{1}H} NMR revealed the formation of compound **3a**.
^{11}B{^{1}H} NMR (96 MHz, CH_2Cl_2): δ = 54.1 ppm (s).

Synthesis of 3b. To a solution of **1b** (25 mg, 90 µmol, 1 equiv.) in CD_2Cl_2 (0.3 mL) was added a solution of $Ag[Al(OC(CF_3)_3)_4]$ (5 mg, 4.5 µmol, 5 mol%) in CD_2Cl_2 (0.3 mL). Subsequently, the reaction was stored in the dark for 3 days, after which NMR spectra revealed full conversion to compound **3b**. The solvent was removed in vacuo and the residue was washed with *n*-hexane. After removing *n*-hexane *in vacuo* a colorless oil was obtained (18.3 mg, 68 µmol, 76 % yield).

^{1}H NMR (400 MHz, CD_2Cl_2): (*Z*)-**3b**: δ = 6.75 (m, 2H, Mes-C*H*), 2.99 (s, 3H, N-CH_3), 2.26 (s, 3H, *p*-Mes-CH_3), 2.17 (s, 6H, *o*-Mes-CH_3), 0.68 (s, 3H, B-CH_3), 0.13 ppm (s, 6H, Si-(CH_3)$_2$Cl); (*E*)-**3b**: δ = 6.79 (m, 2H, Mes-C*H*), 2.64 (s, 3H, N-CH_3), 2.27 (s, 3H, *p*-Mes-CH_3), 2.15 (s, 6H, *o*-Mes-CH_3), 0.75 (s, 3H, B-CH_3), 0.72 ppm (s, 6H, Si-(CH_3)$_2$Cl); ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = 52.7 ppm (s); ^{29}Si{^{1}H} NMR (60 MHz, CD_2Cl_2): (*Z*)-**3b**: δ = 20.2 ppm (s); (*E*)-**3b**: δ = 20.6 ppm (s); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): (*Z*)-**3b**: δ = 143.3 (s, *ipso*-Mes-*C*), 137.3 (s, *o*-Mes-*C*), 137.0 (s, *p*-Mes-*C*), 127.4 (s, Mes-*C*H), 33.6 (s, N-*C*H_3), 22.0 (s, *o*-Mes-*C*H_3), 21.3 (s, *p*-Mes-*C*H_3), 6.9 (br, B-*C*H_3), 3.4 ppm (s, Si-(*C*H_3)$_2$Cl); (*E*)-**3b**: δ = 143.3 (s, *ipso*-Mes-*C*), 136.6 (s, *p*-Mes-*C*), 136.6 (s, *o*-Mes-*C*), 127.4 (s, Mes-*C*H), 35.4 (s, N-*C*H_3), 21.3 (s, *p*-Mes-*C*H_3), 21.3 (s, *o*-Mes-*C*H_3), 8.5 (br, B-*C*H_3), 5.1 ppm (s, Si-(*C*H_3)$_2$Cl); HRMS (ASAP): m/z calcd.: 268.1454 $[M+H]^+$, found: 268.1449; elem. anal. calcd. (%) for C13H23BClNSi: C 58.33, H 8.66, N 5.23; found: C 58.48, H 8.79, N 5.08.

NMR spectra

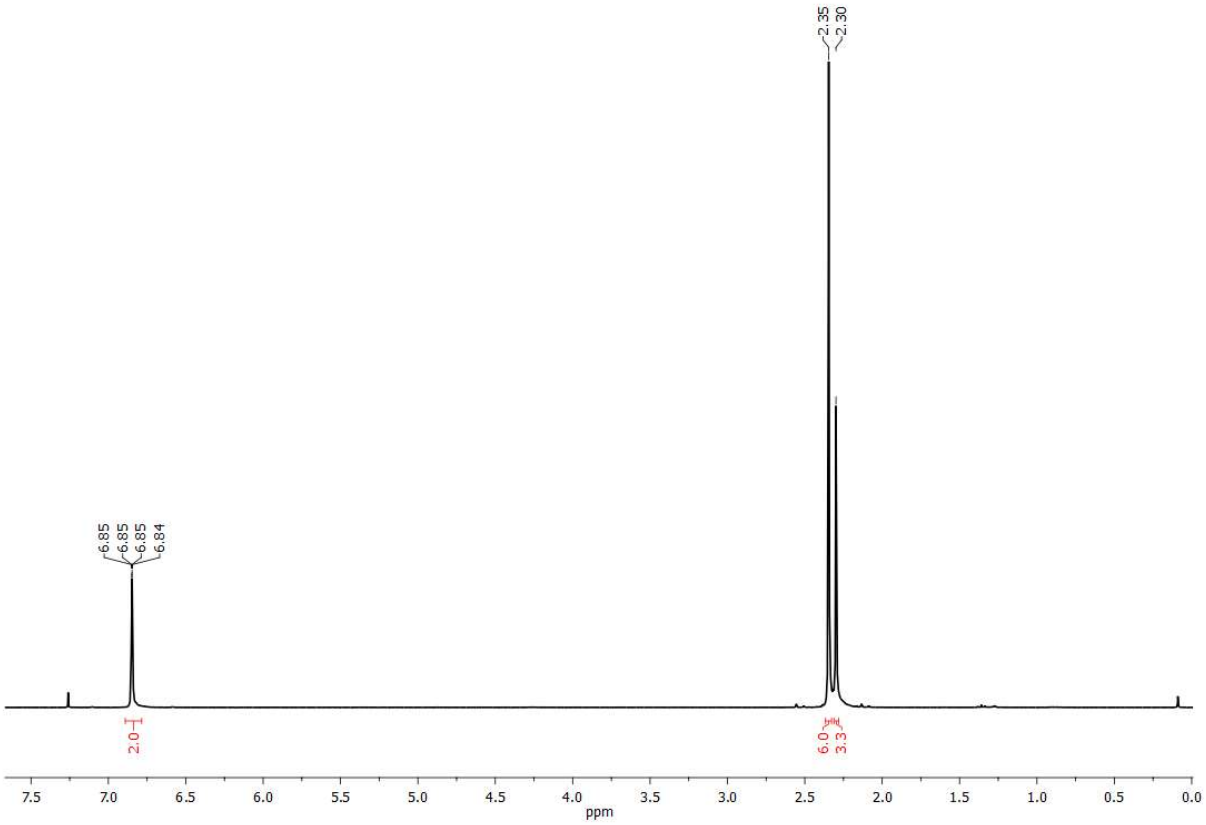

Figure S1. ^{1}H NMR spectrum (300 MHz) of $MesBCl_2$ in $CDCl_3$.

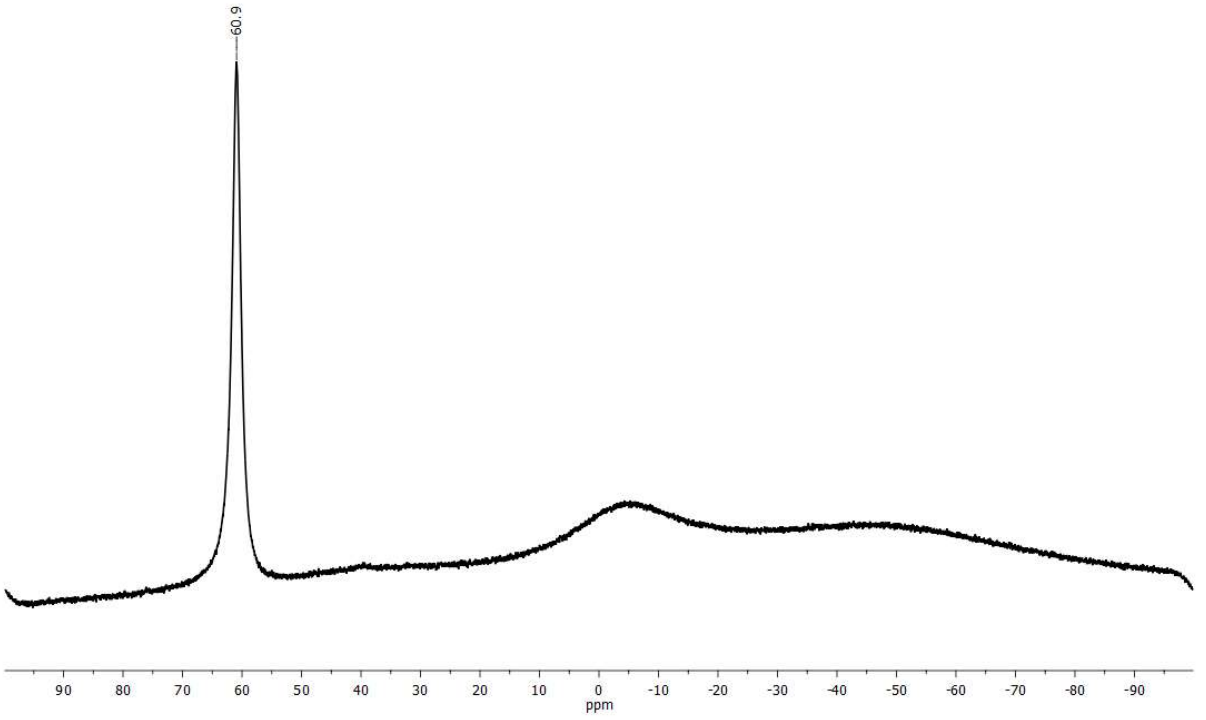

Figure S2. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of $MesBCl_2$ in $CDCl_3$.

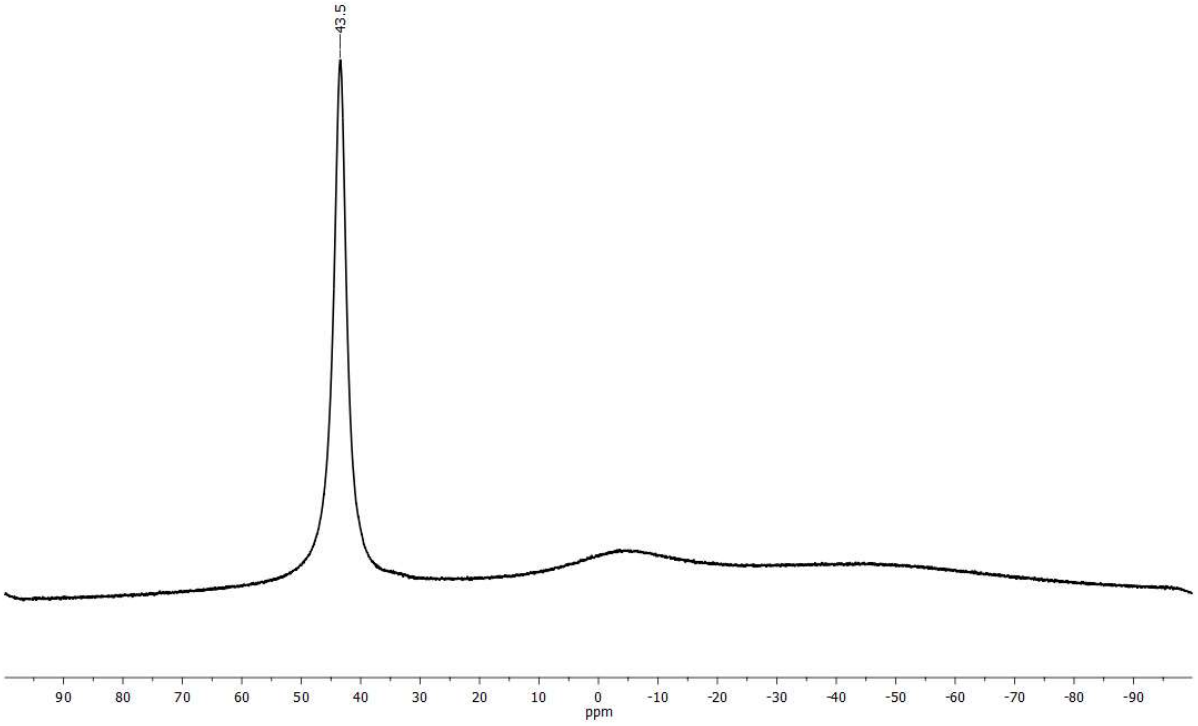

Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of **1a** in CH_2Cl_2.

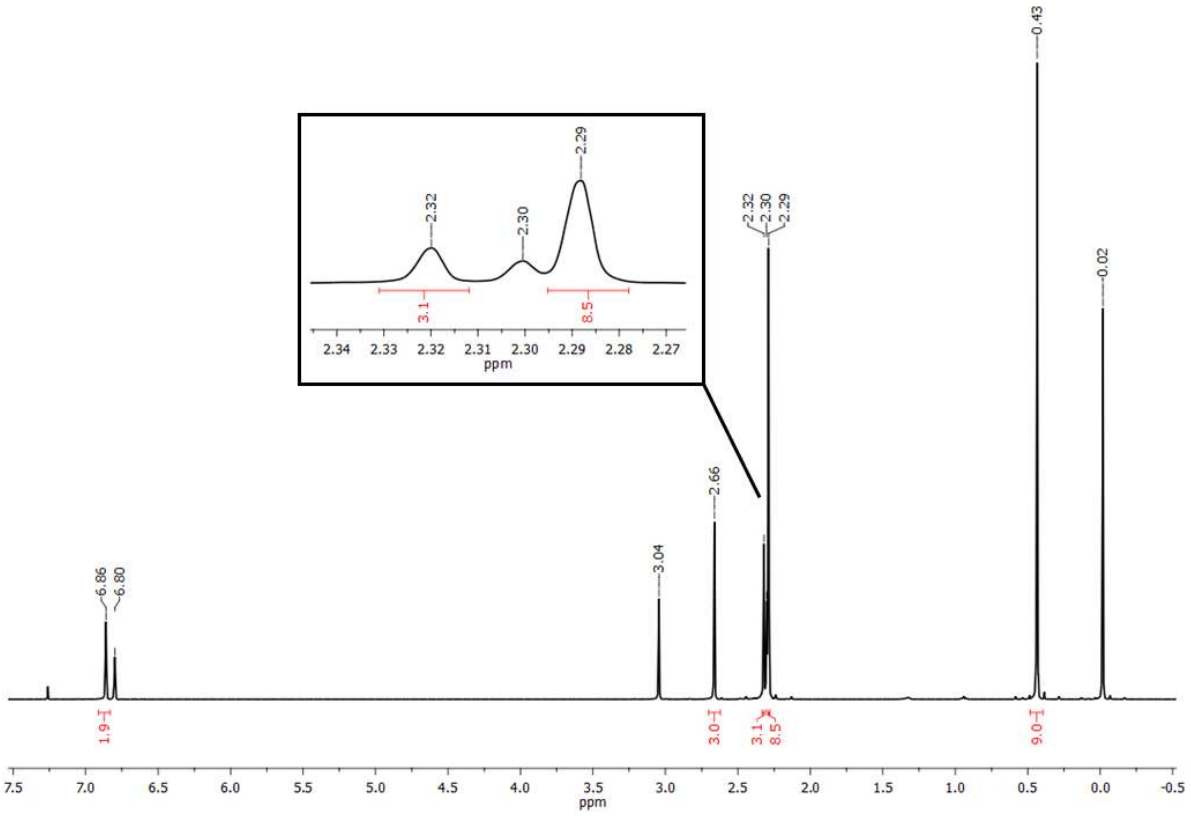

Figure S4. ^{1}H NMR spectrum (400 MHz) of **1b** in $CDCl_3$ with integrals for (*Z*)-**1b**.

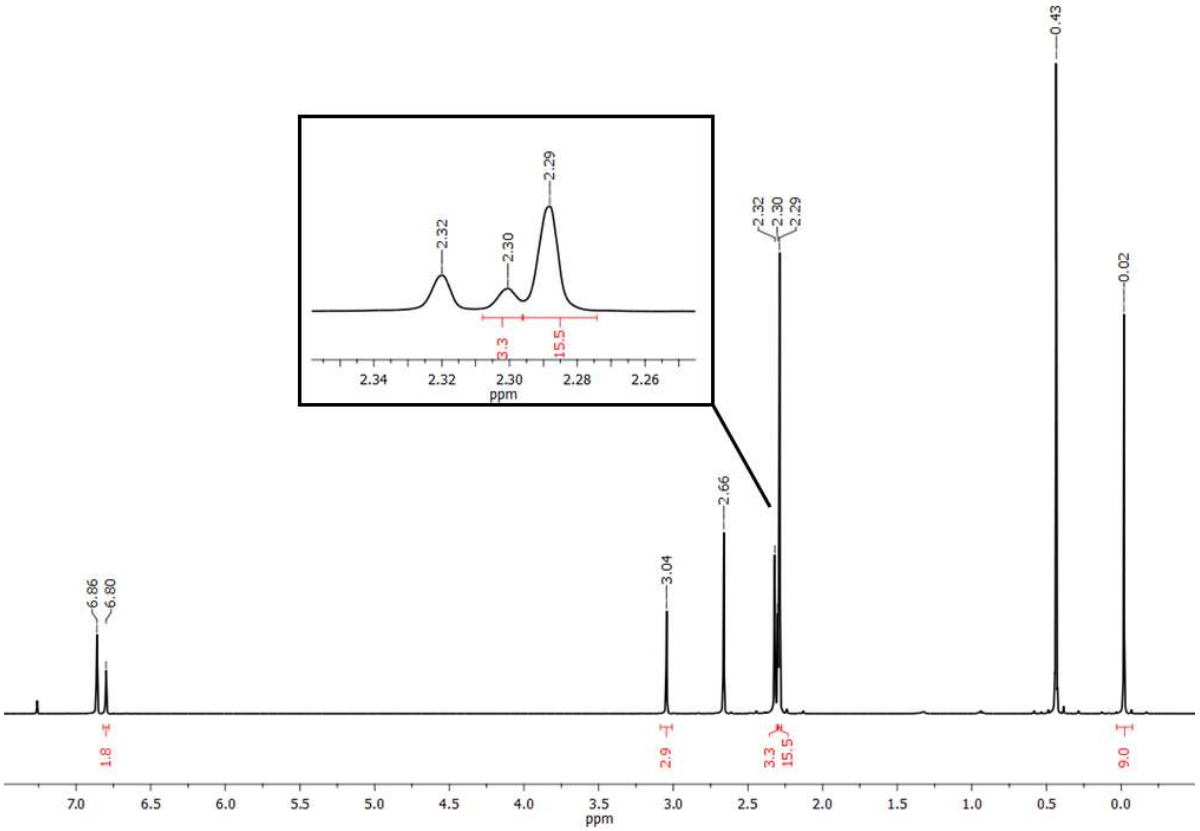

Figure S5. ^{1}H NMR spectrum (400 MHz) of **1b** in $CDCl_3$ with integrals for (*E*)-**1b**.

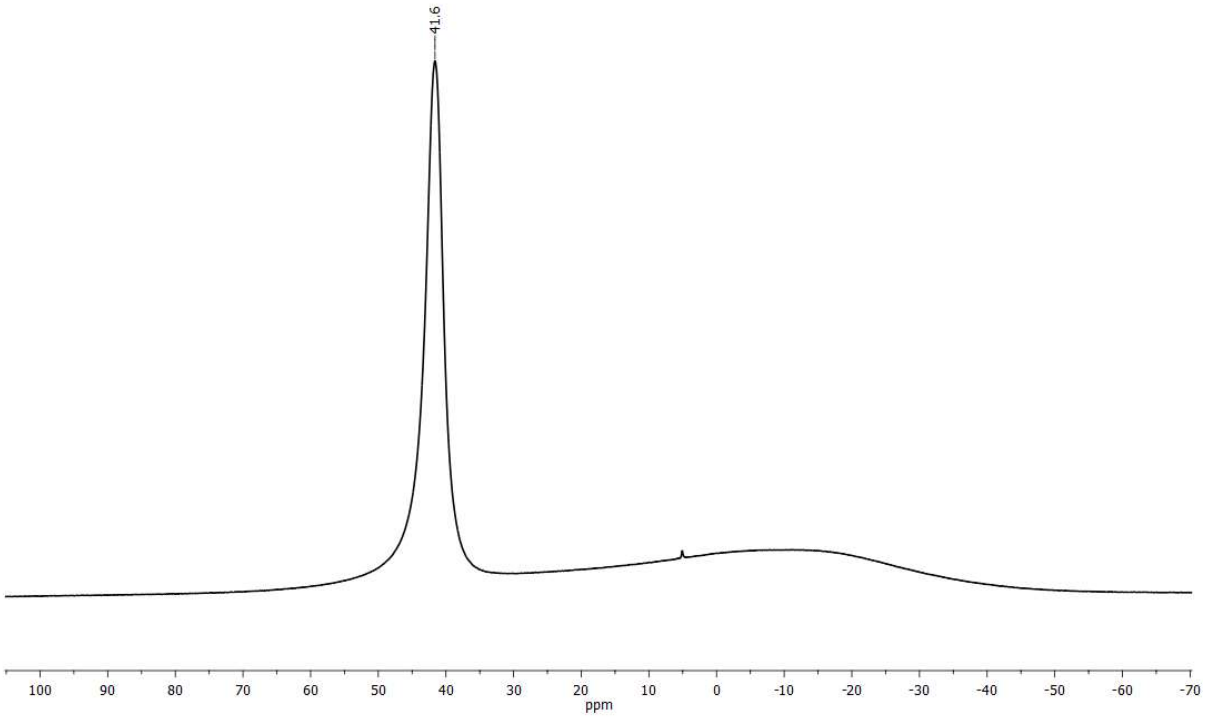

Figure S6. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz) of **1b** in $CDCl_3$.

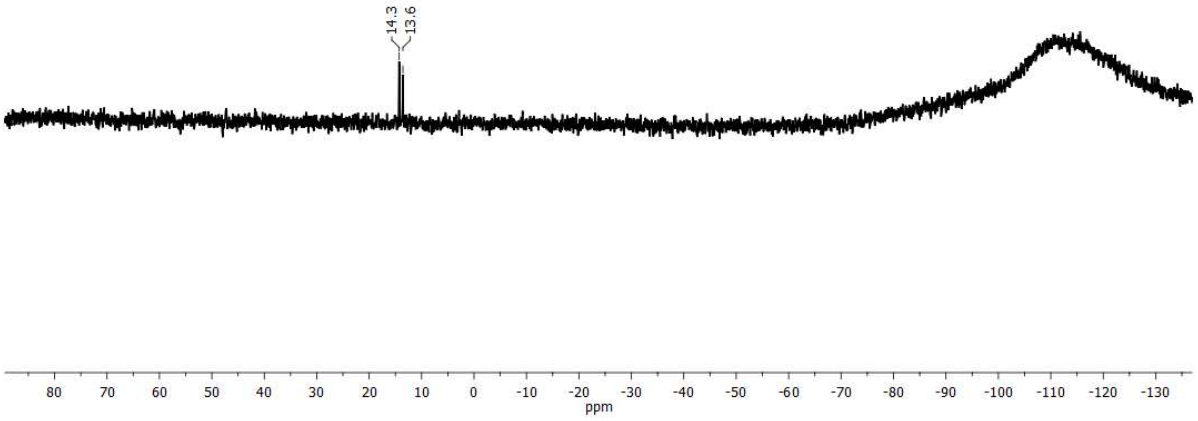

Figure S7. $^{29}Si\{^{1}H\}$ NMR spectrum (60 MHz) of **1b** in $CDCl_3$.

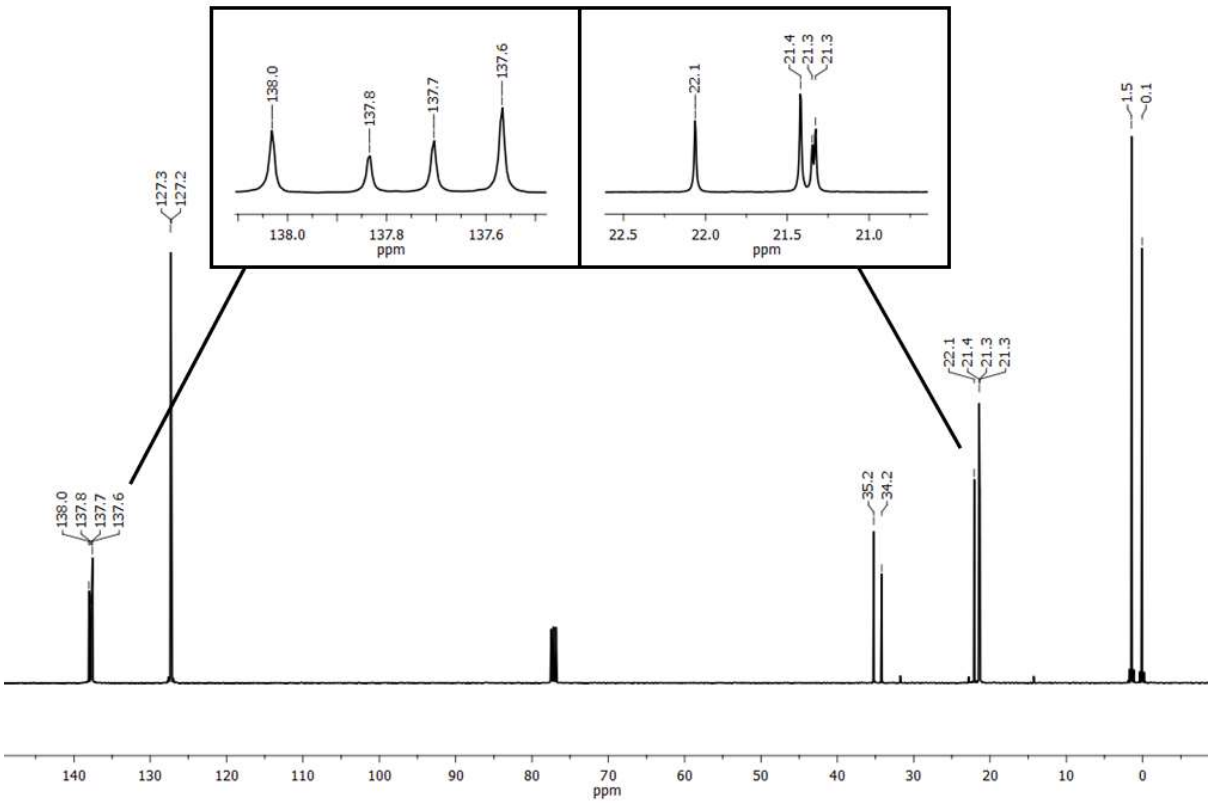

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **1b** in $CDCl_3$.

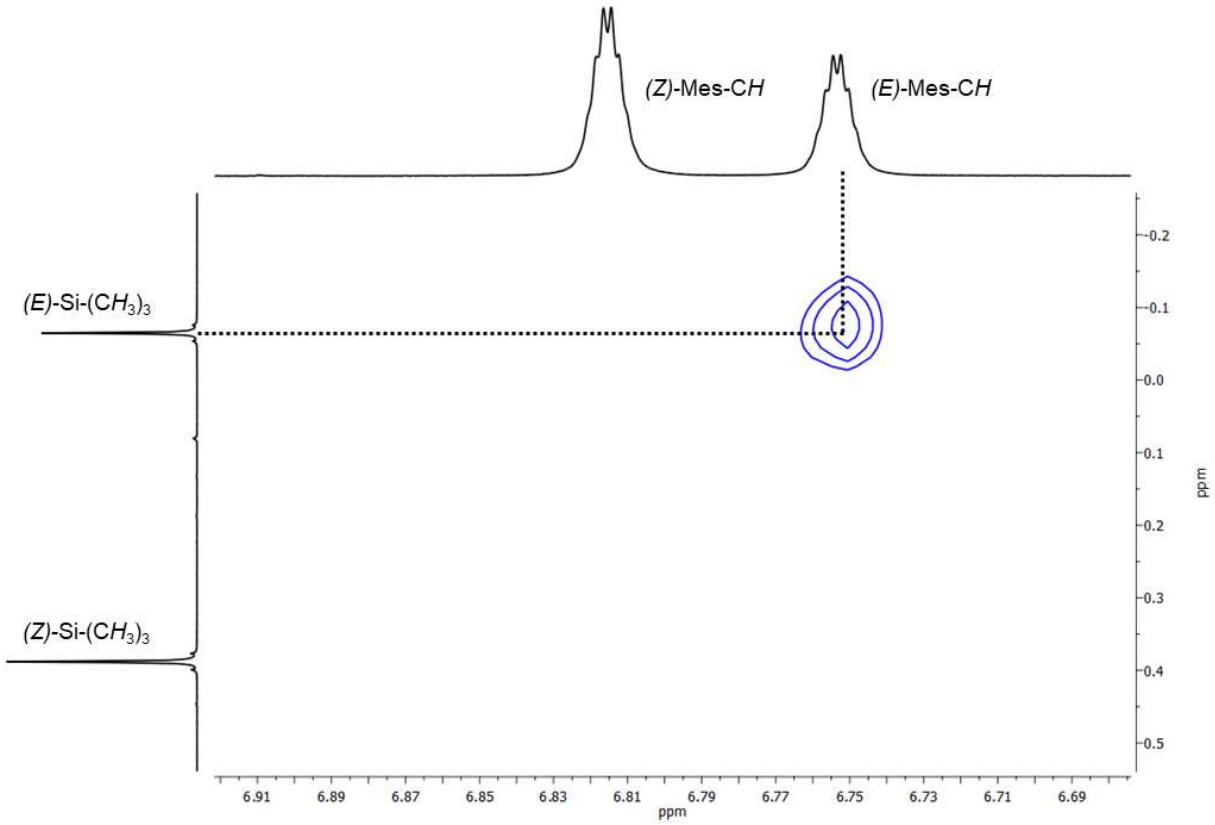

Figure S9. Detail of $^{1}H,^{1}H$ NOESY spectrum of **1b** in $CDCl_3$.

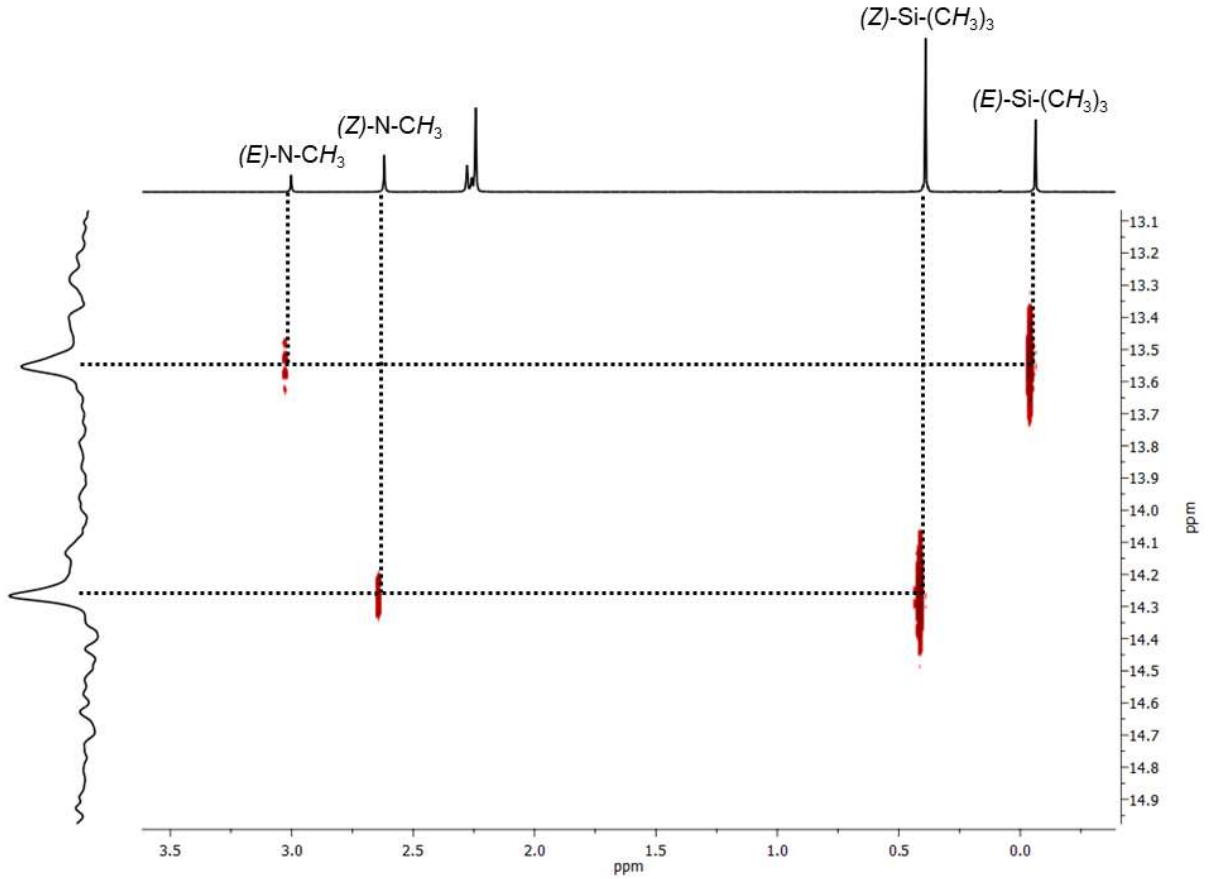

Figure S10. Detail of $^{1}H,^{29}Si$ HMQC spectrum of **1b** in $CDCl_3$.

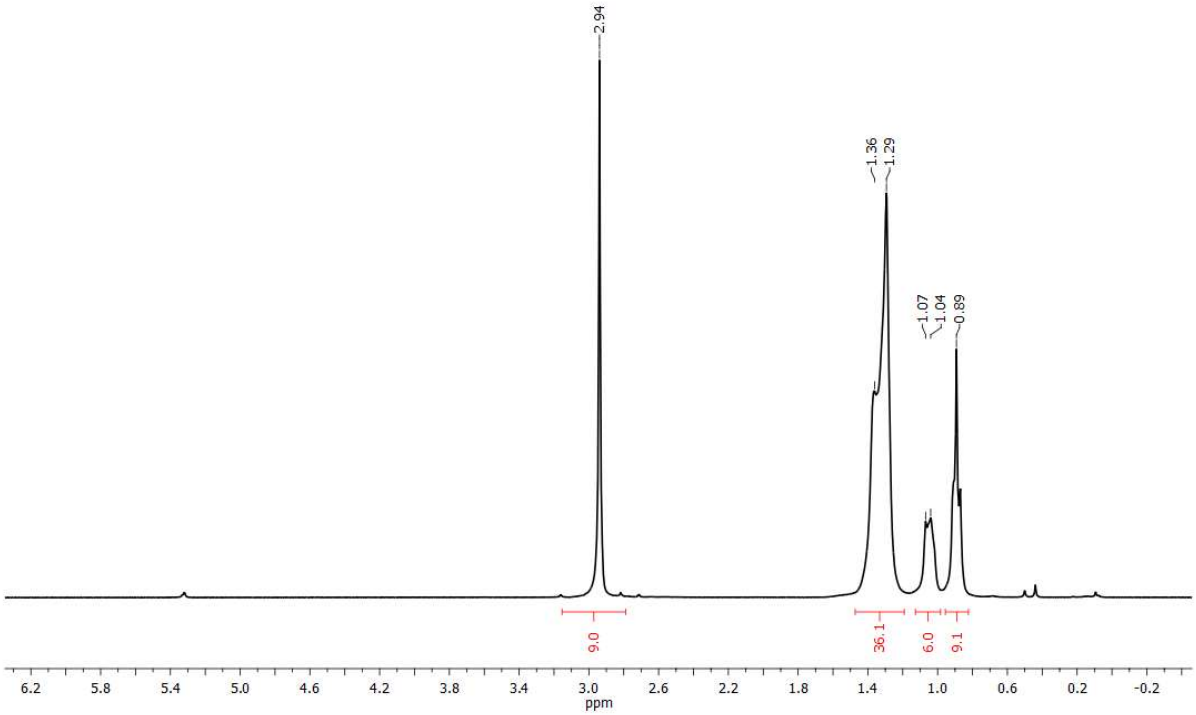

Figure S11. ^{1}H NMR spectrum (300 MHz) of **2a** in CD_2Cl_2.

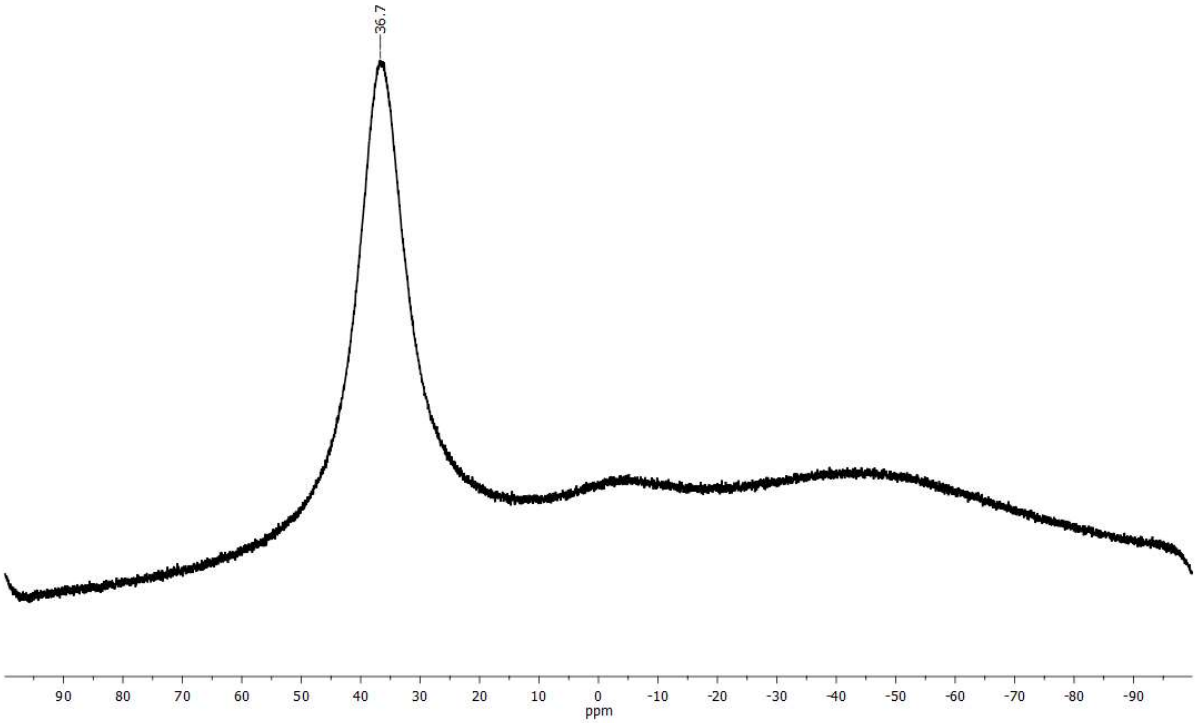

Figure S12. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of **2a** in CD_2Cl_2.

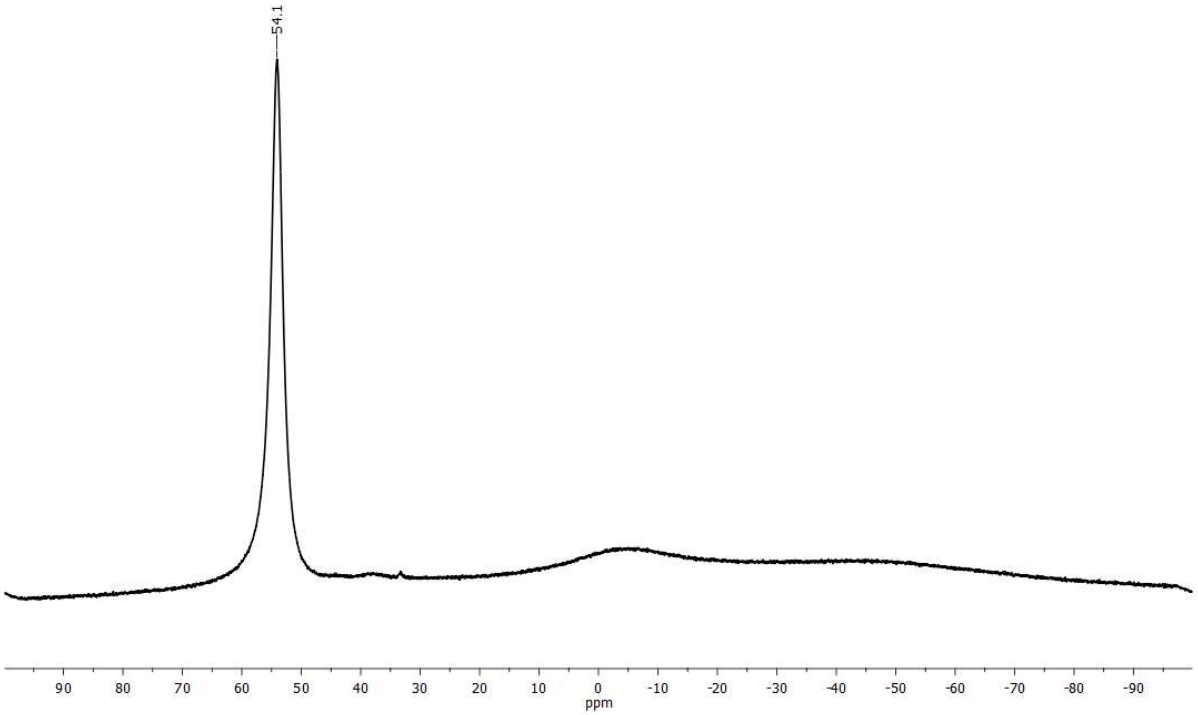

Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of the reaction of **1a** to **3a** in the presence of 5 mol% $Ag[Al(OC(CF_3)_3)_4]$ in CH_2Cl_2 after 10 min.

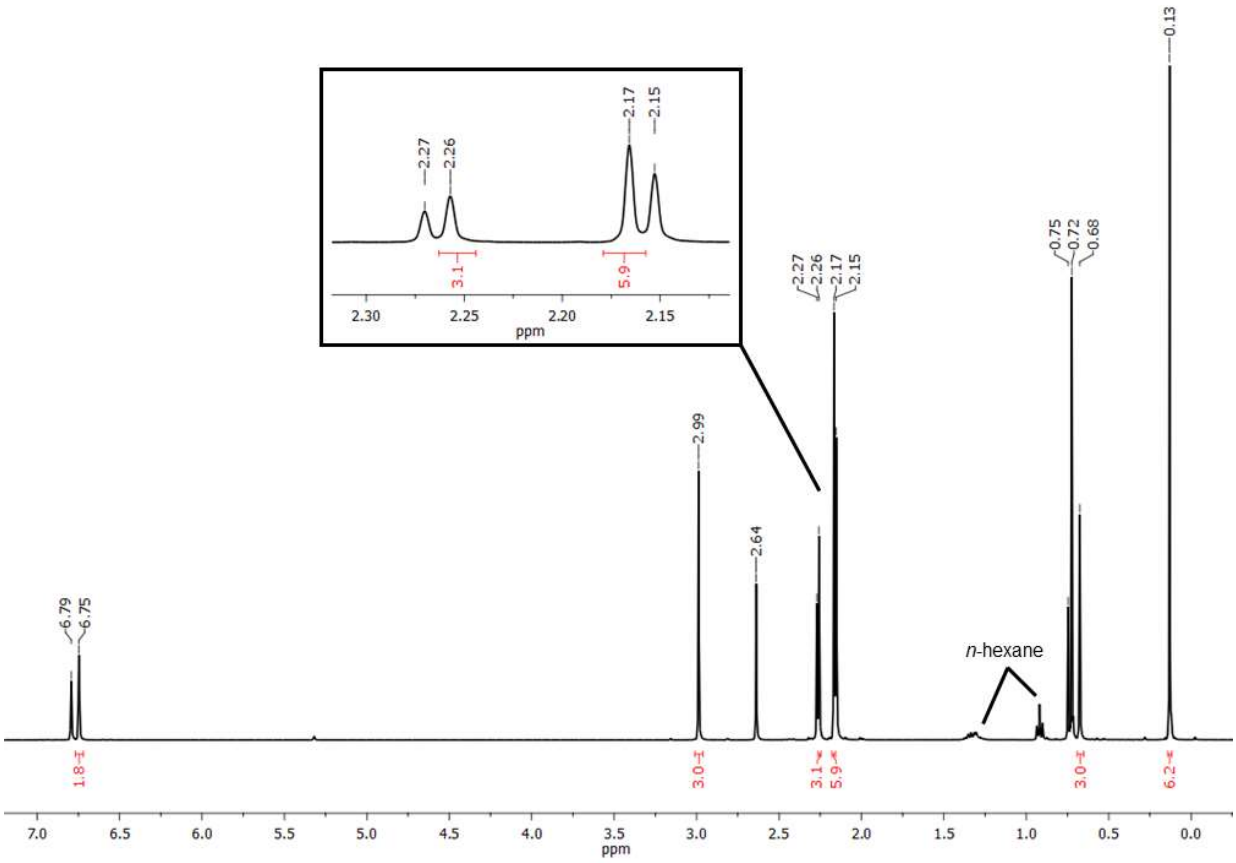

Figure S14. ^{1}H NMR spectrum (400 MHz) of **3b** in CD_2Cl_2 with integrals for (*Z*)-**3b**.

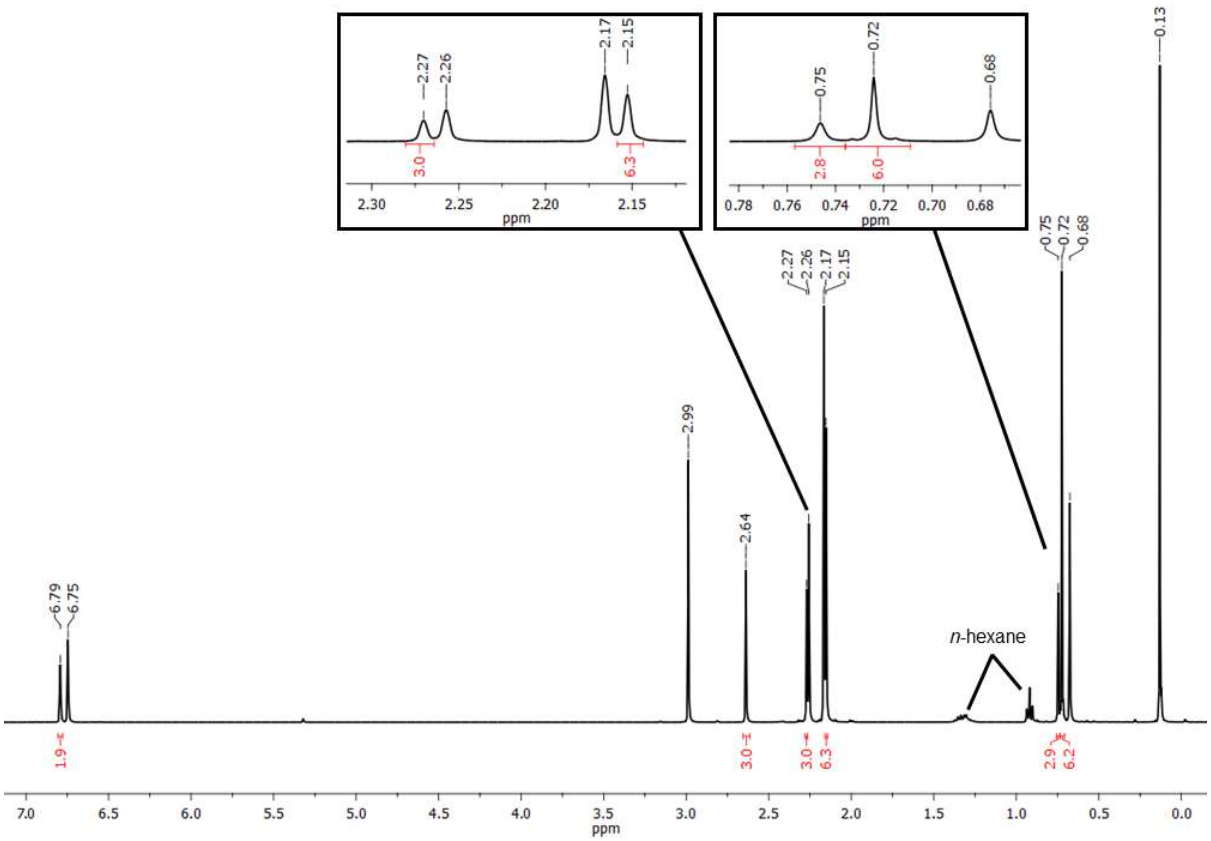

Figure S15. ^{1}H NMR spectrum (400 MHz) of **3b** in CD_2Cl_2 with integrals for (*E*)-**3b**.

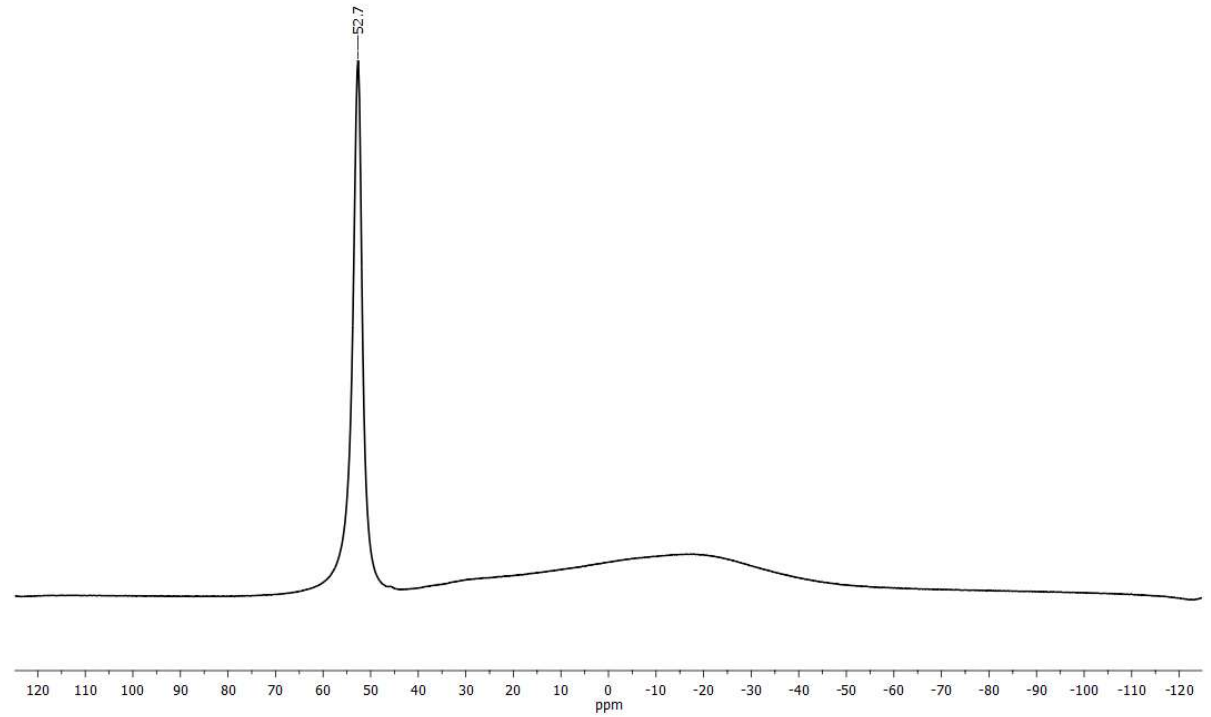

Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz) of **3b** in CD_2Cl_2.

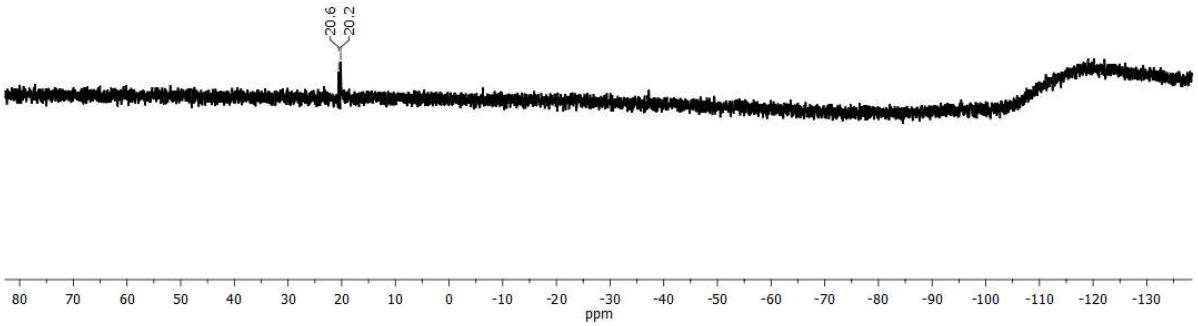

Figure S17. $^{29}Si\{^{1}H\}$ NMR spectrum (60 MHz) of **3b** in CD_2Cl_2.

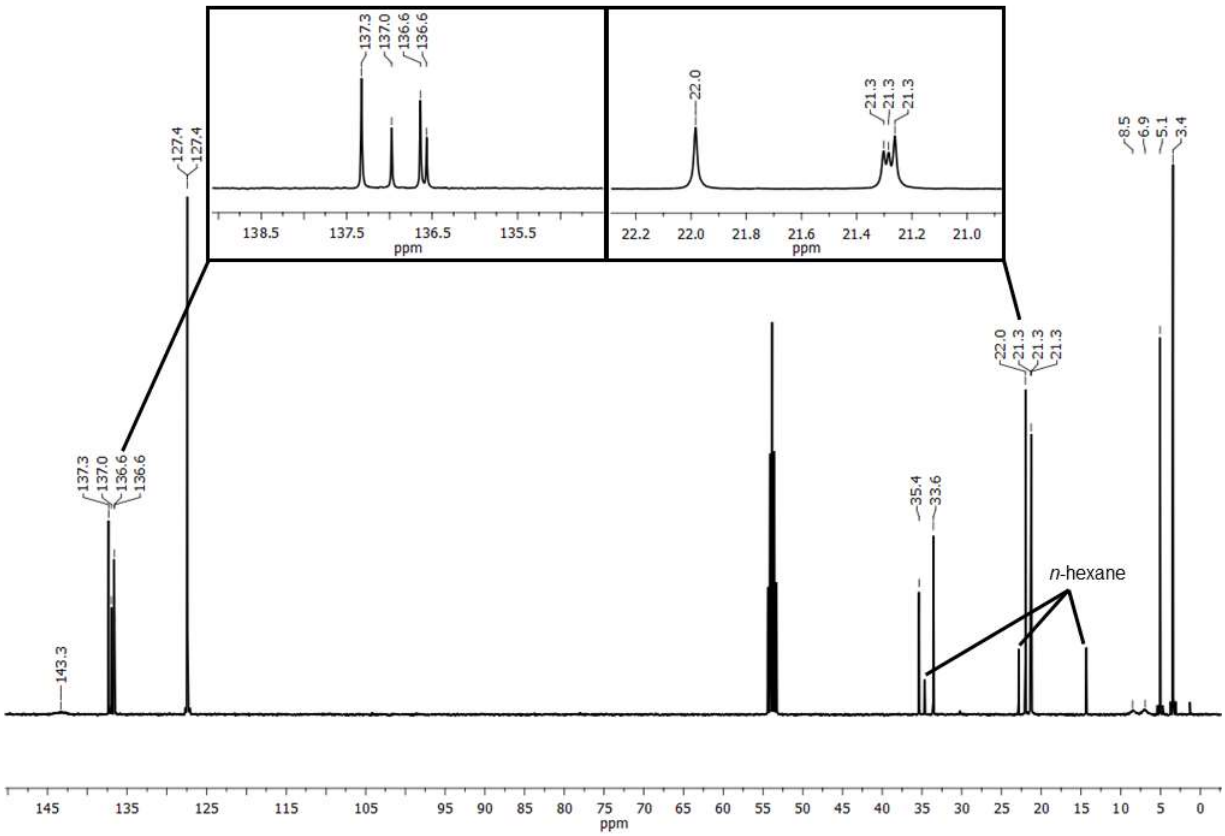

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz) of **3b** in CD_2Cl_2.

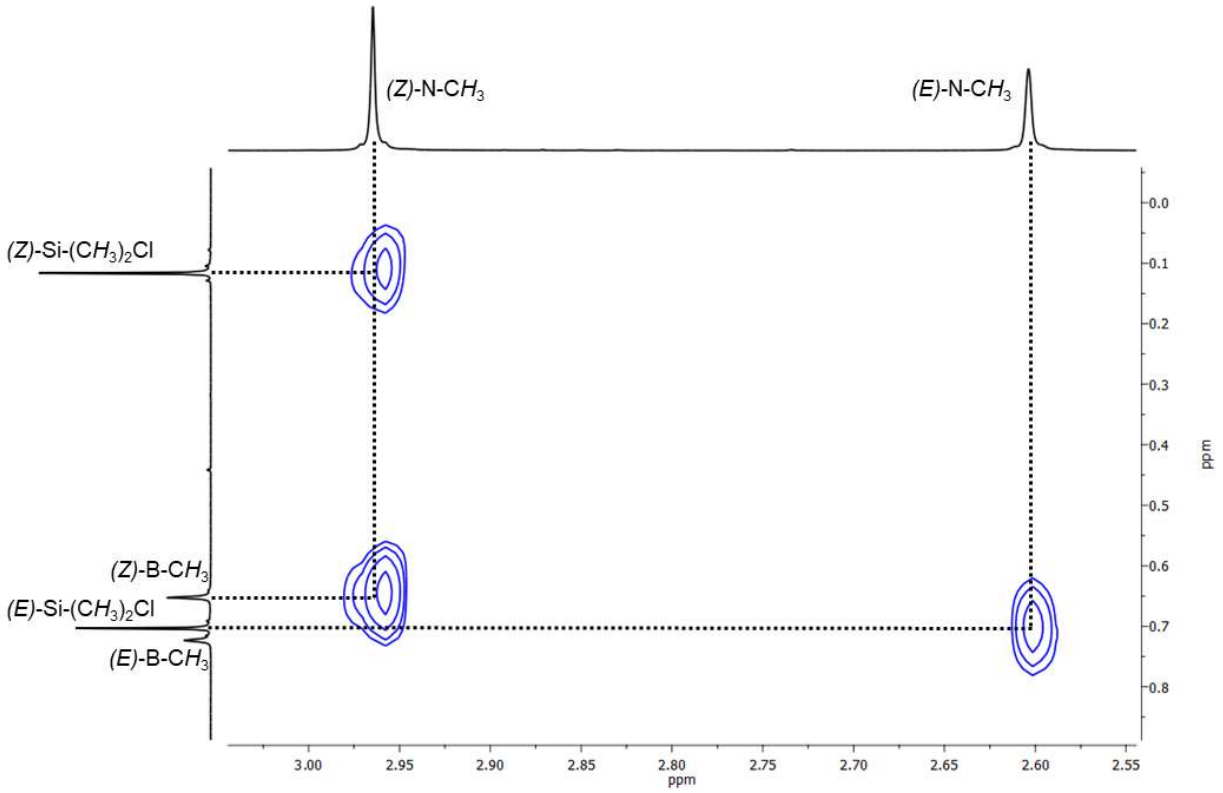

Figure S19. Detail of $^{1}H,^{1}H$ NOESY spectrum of **3b** in CD_2Cl_2.

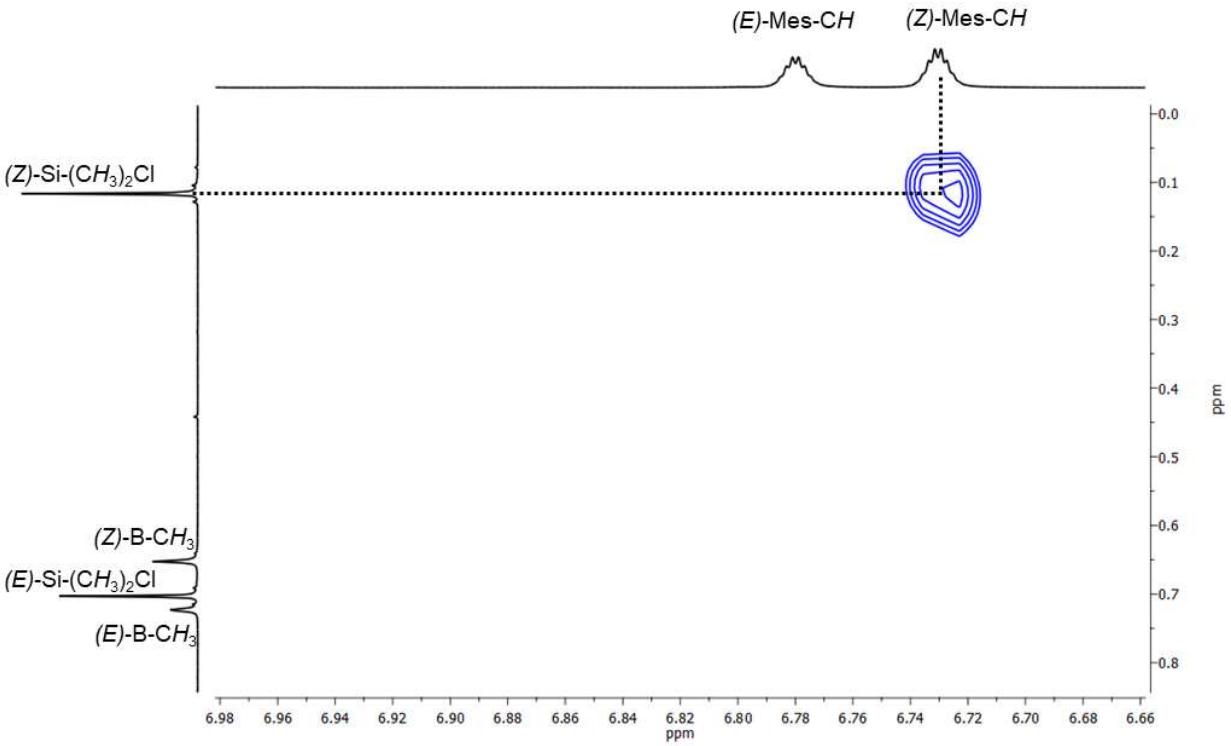

Figure S20. Detail of $^{1}H,^{1}H$ NOESY spectrum of **3b** in CD_2Cl_2.

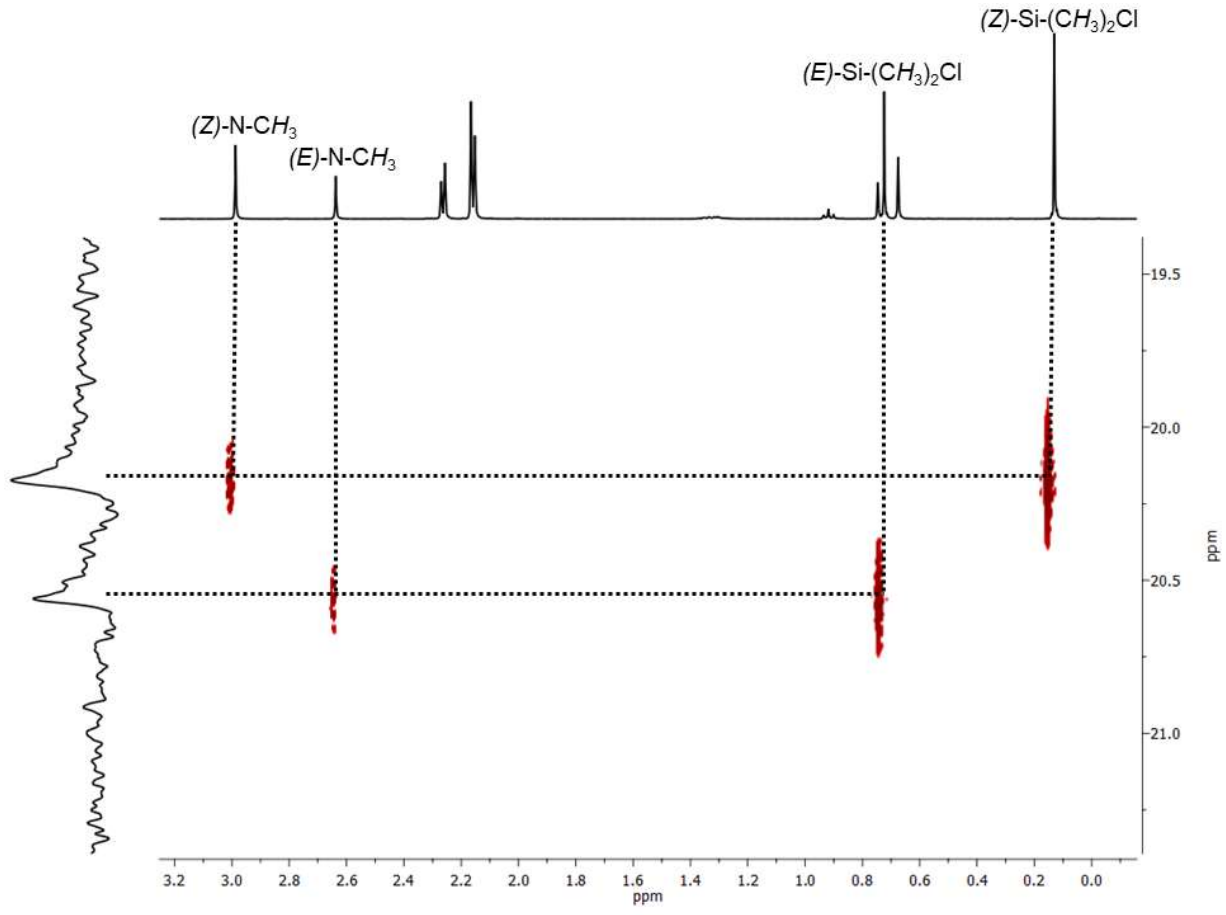

Figure S21. Detail of $^{1}H,^{29}Si$ HMQC spectrum of **3b** in CD_2Cl_2.

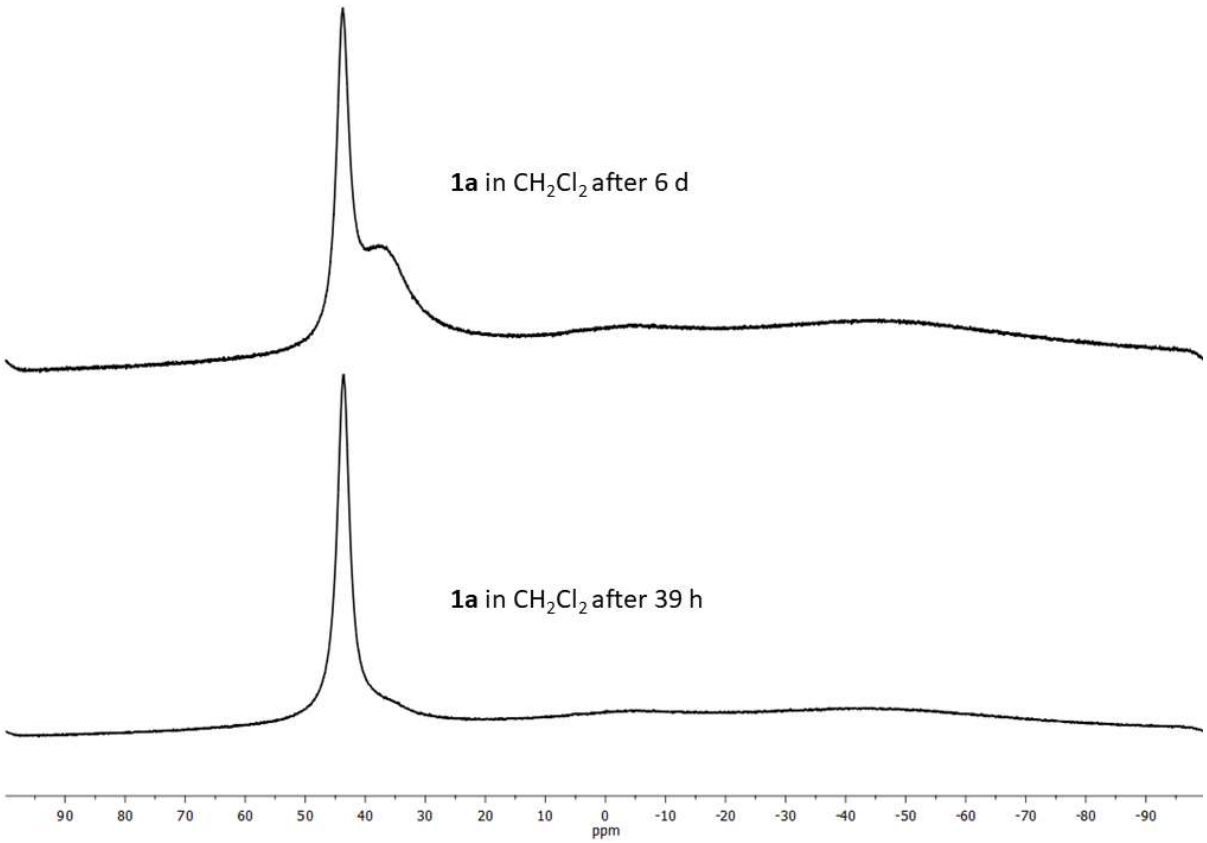

Figure S22. $^{11}B\{^{1}H\}$ NMR spectra (96 MHz) of **1a** in CH_2Cl_2 after 39 h and 6 d.

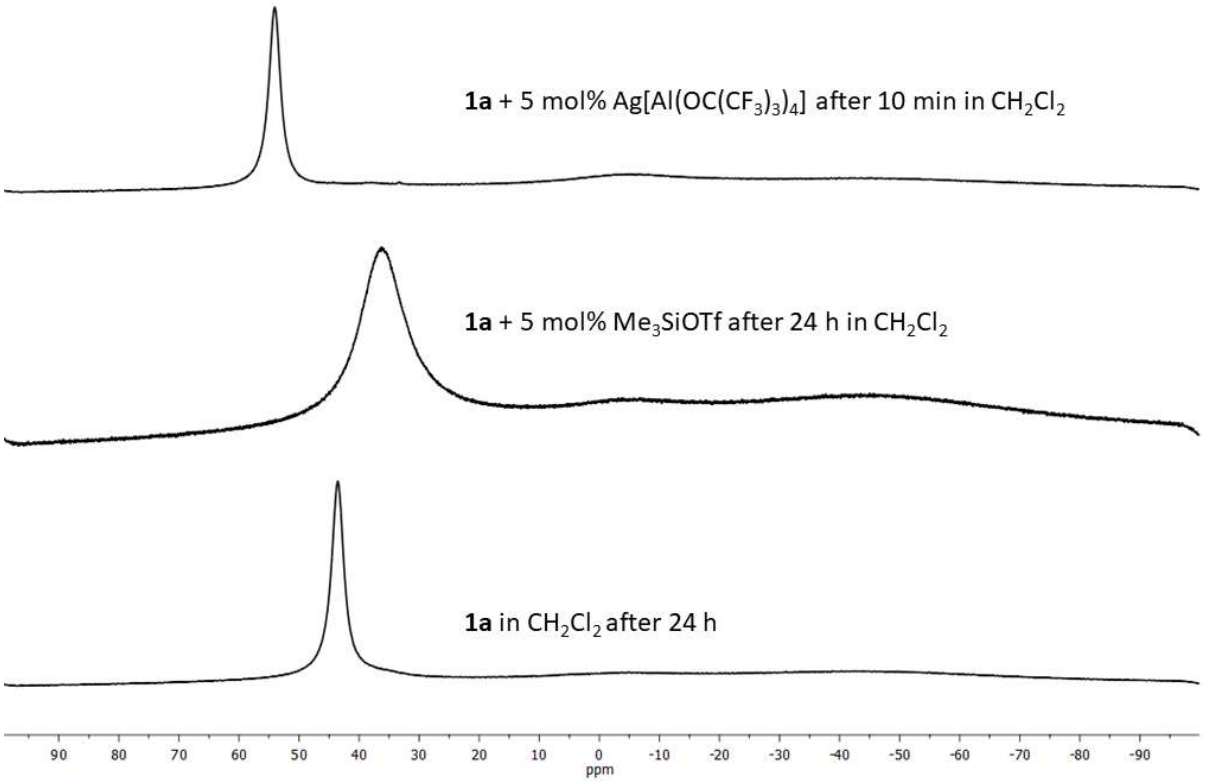

Figure S23. $^{11}B\{^{1}H\}$ NMR spectra (96 MHz) of **1a** in CH_2Cl_2 and of **1a** in the presence of 5 mol% Me_3SiOTf or $Ag[Al(OC(CF_3)_3)_4]$ in CH_2Cl_2.

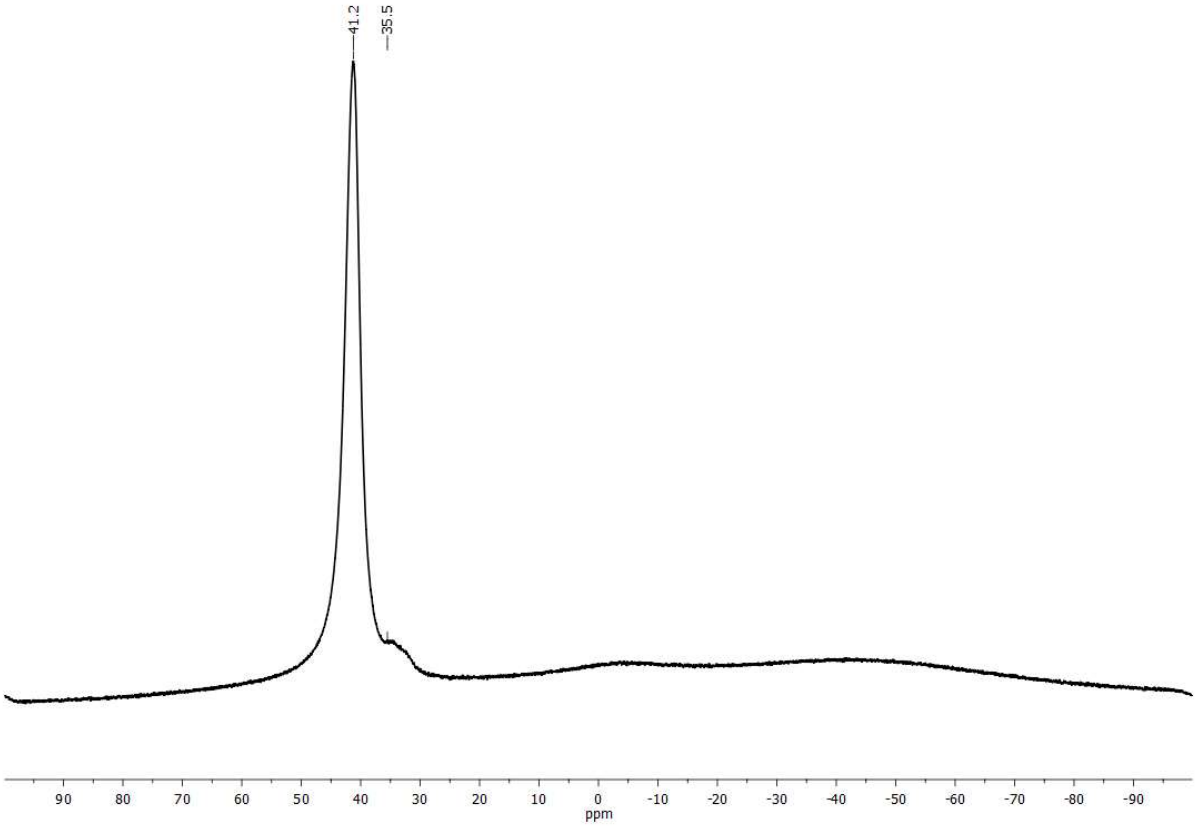

Figure S24. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of the reaction of **1b** in the presence of 5 mol% Me_3SiOTf in CD_2Cl_2 after 14 d.

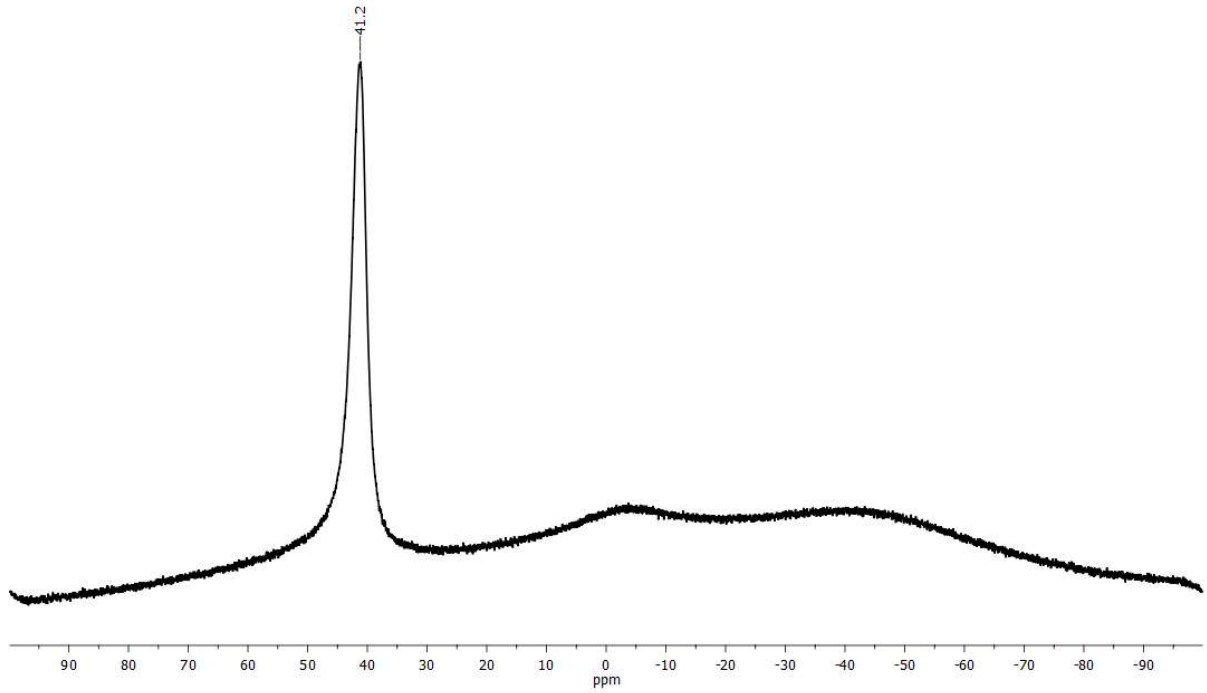

Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum (96 MHz) of the reaction of **1b** in the presence of 1 mol% $Ag[Al(OC(CF_3)_3)_4]$ in CD_2Cl_2 after 12 d.

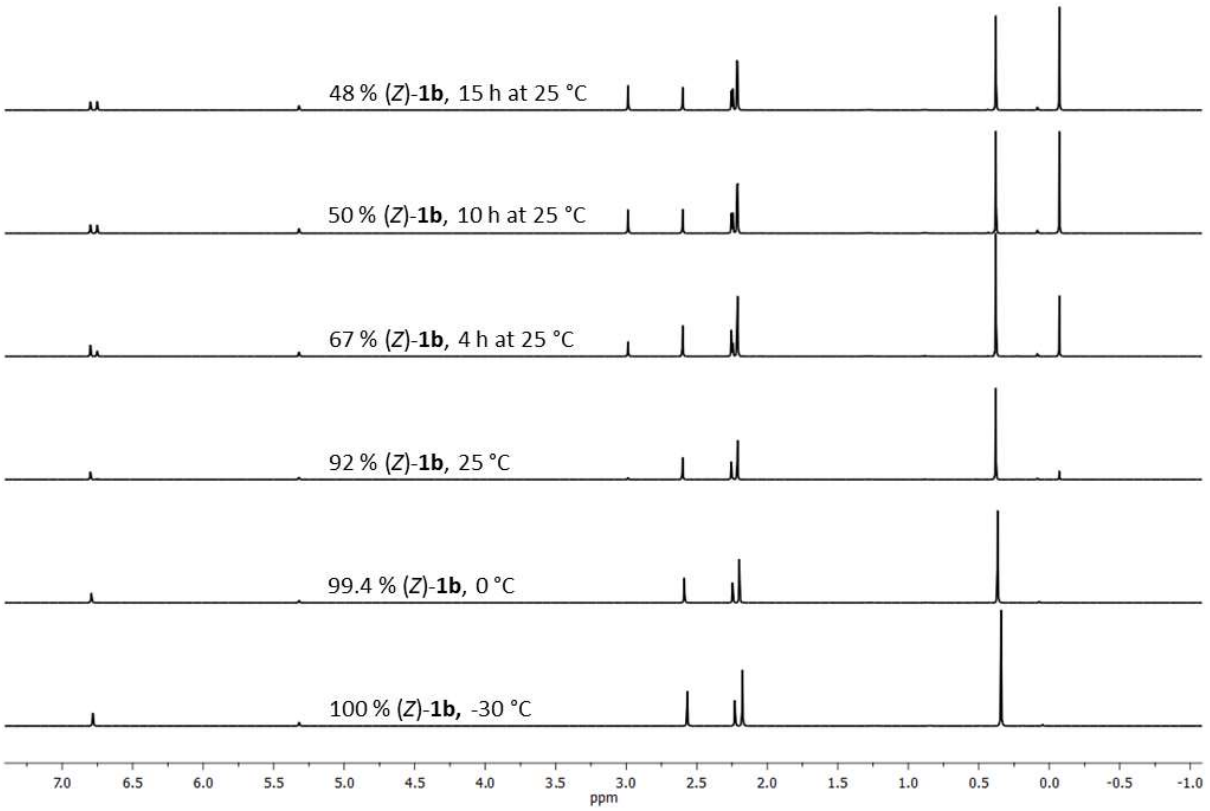

Figure S26. Isomerization of (*Z*)-**1b** to (*E/Z*)-**1b** between −30 °C and 25 °C in CD_2Cl_2.

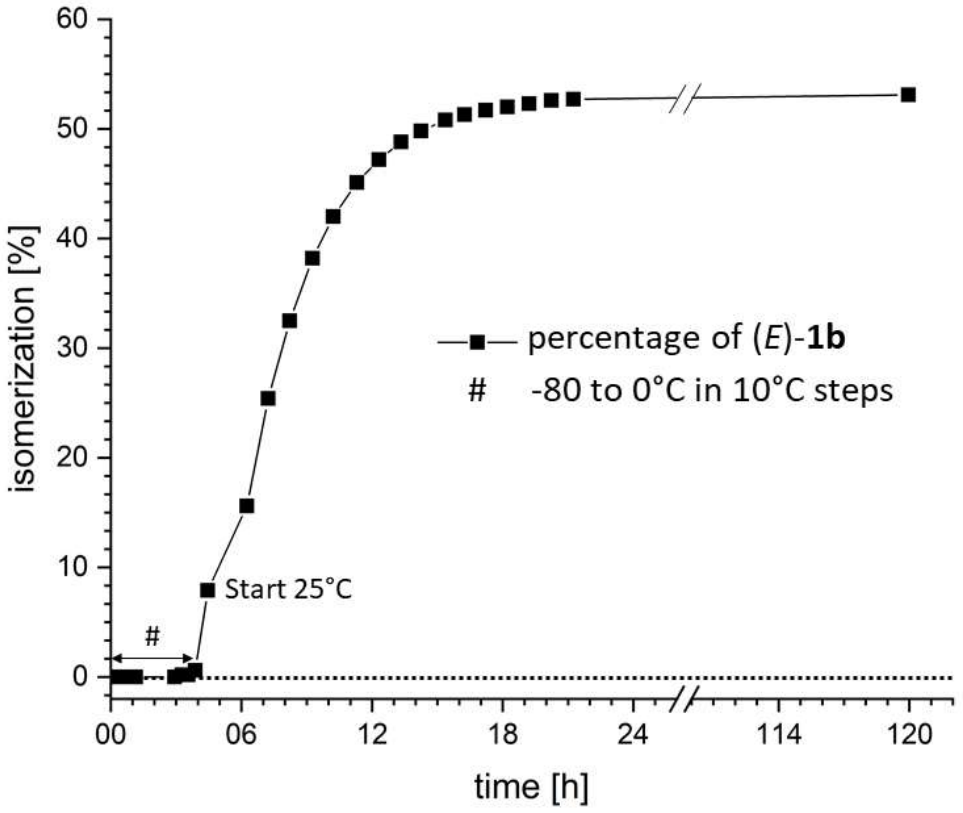

Figure S27. Progress of the isomerization of (*Z*)-**1b** to (*E/Z*)-**1b** between −80 °C and 25 °C in CD_2Cl_2.

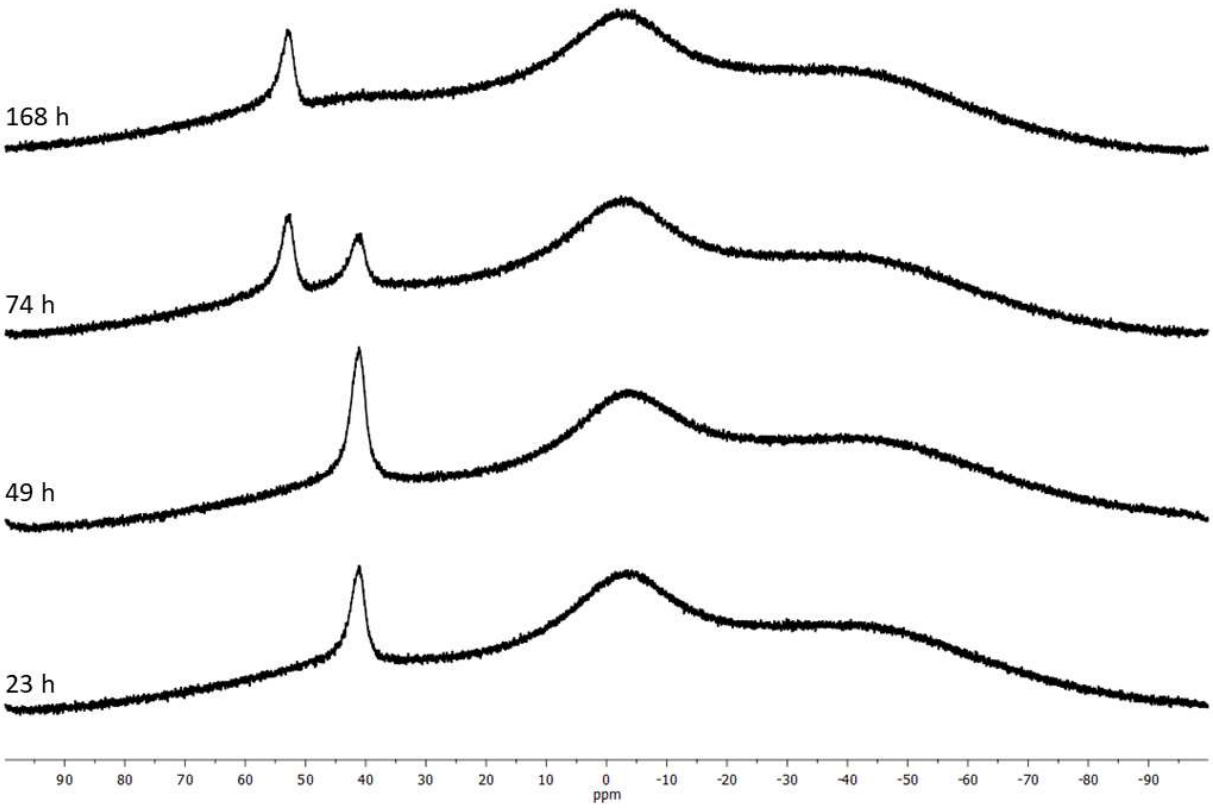

Figure S28. $^{11}B\{^1H\}$ NMR spectra (96 MHz) of a stirred reaction of **1b** in the presence of 5 mol% $Ag[Al(OC(CF_3)_3)_4]$ in CD_2Cl_2 (0.15 M).

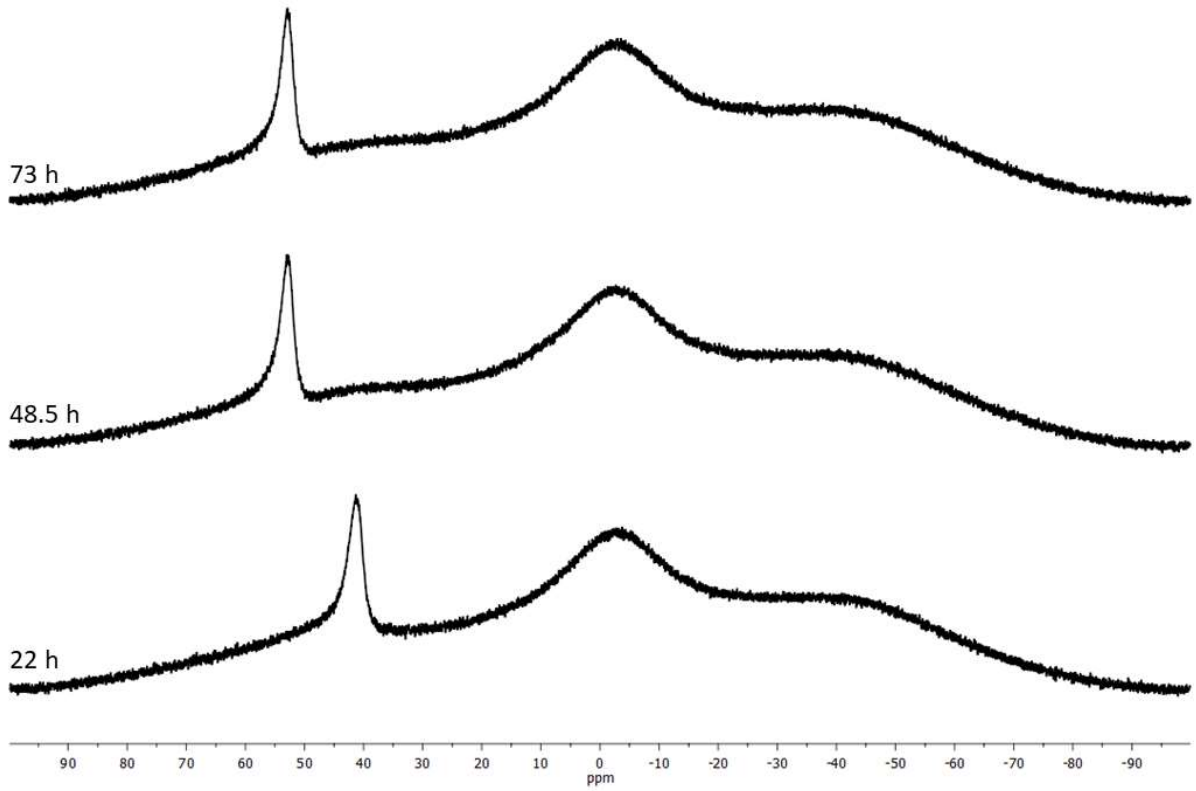

Figure S29. $^{11}B\{^{1}H\}$ NMR spectra (96 MHz) of a stirred reaction of **1b** in the presence of 5 mol% $Ag[Al(OC(CF_3)_3)_4]$ in CD_2Cl_2 (0.075 M).

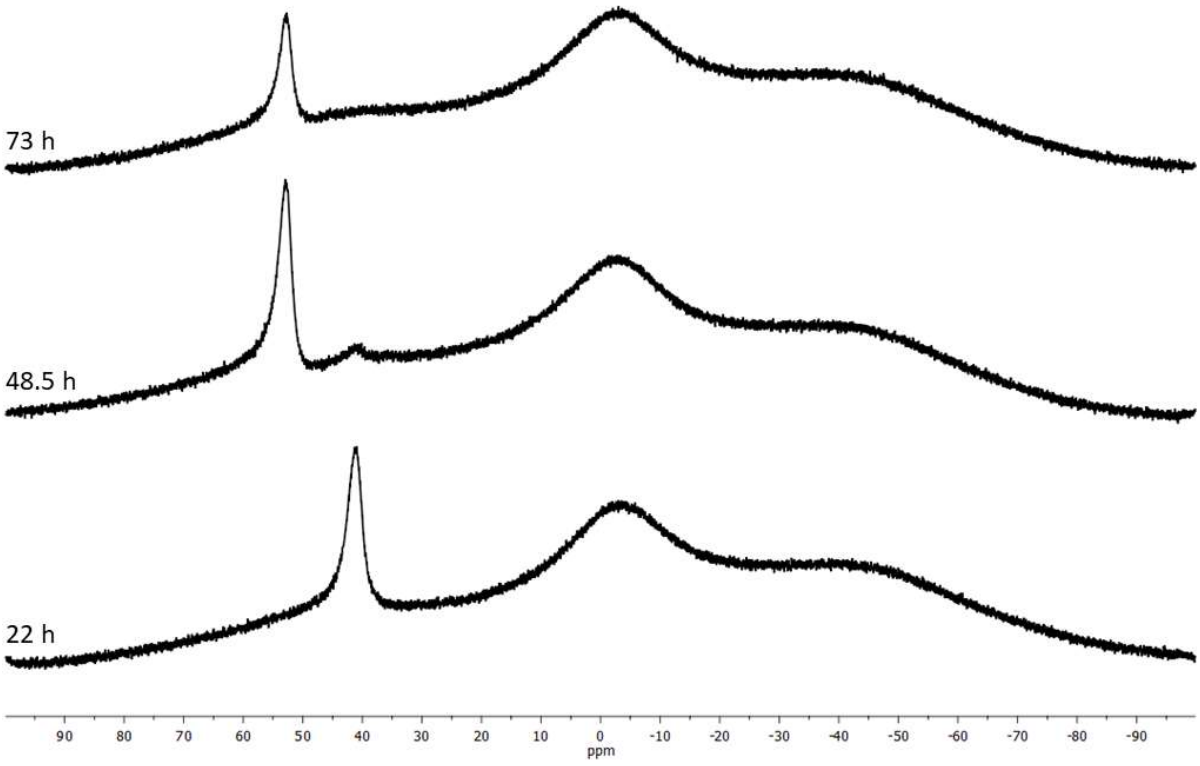

Figure S30. $^{11}B\{^{1}H\}$ NMR spectra (96 MHz) of a stirred reaction of **1b** in the presence of 5 mol% $Ag[Al(OC(CF_3)_3)_4]$ in CD_2Cl_2 (0.3 M).

Mass spectra

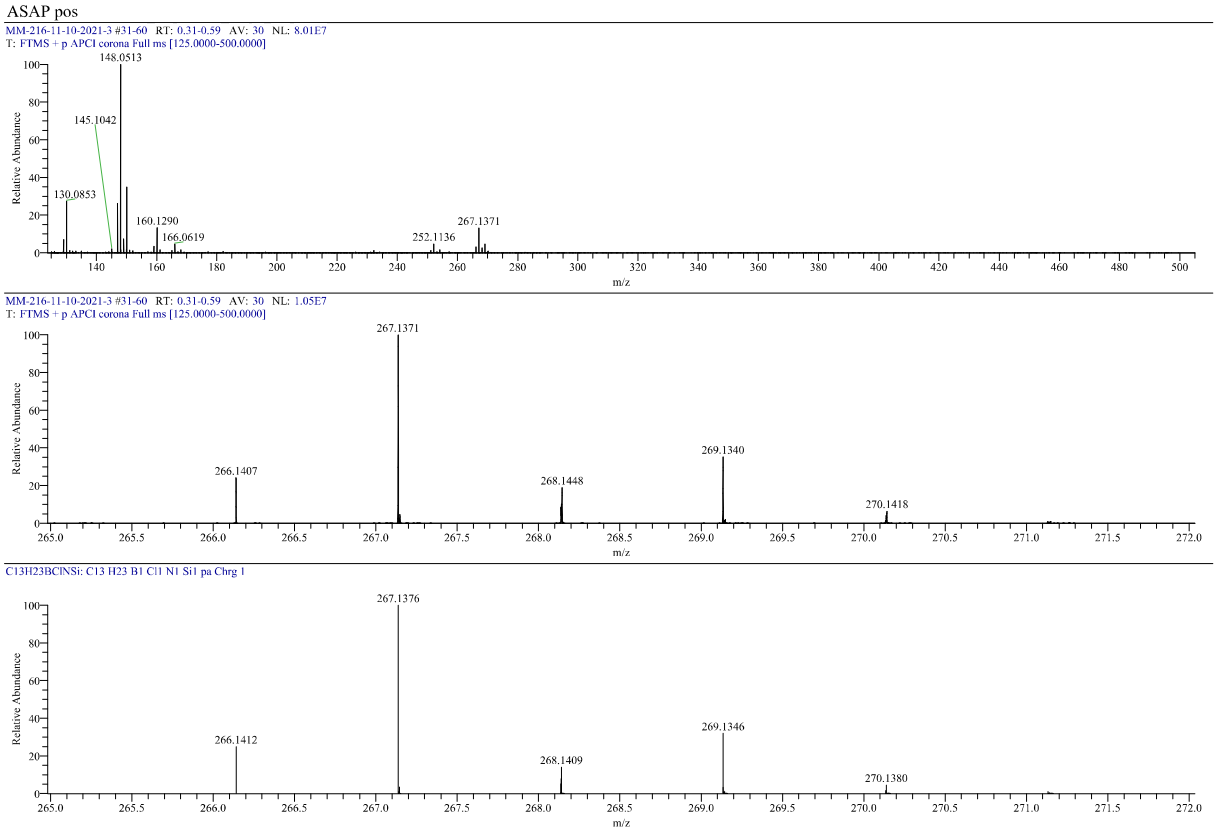

Figure S31. ASAP spectrum of **1b**.

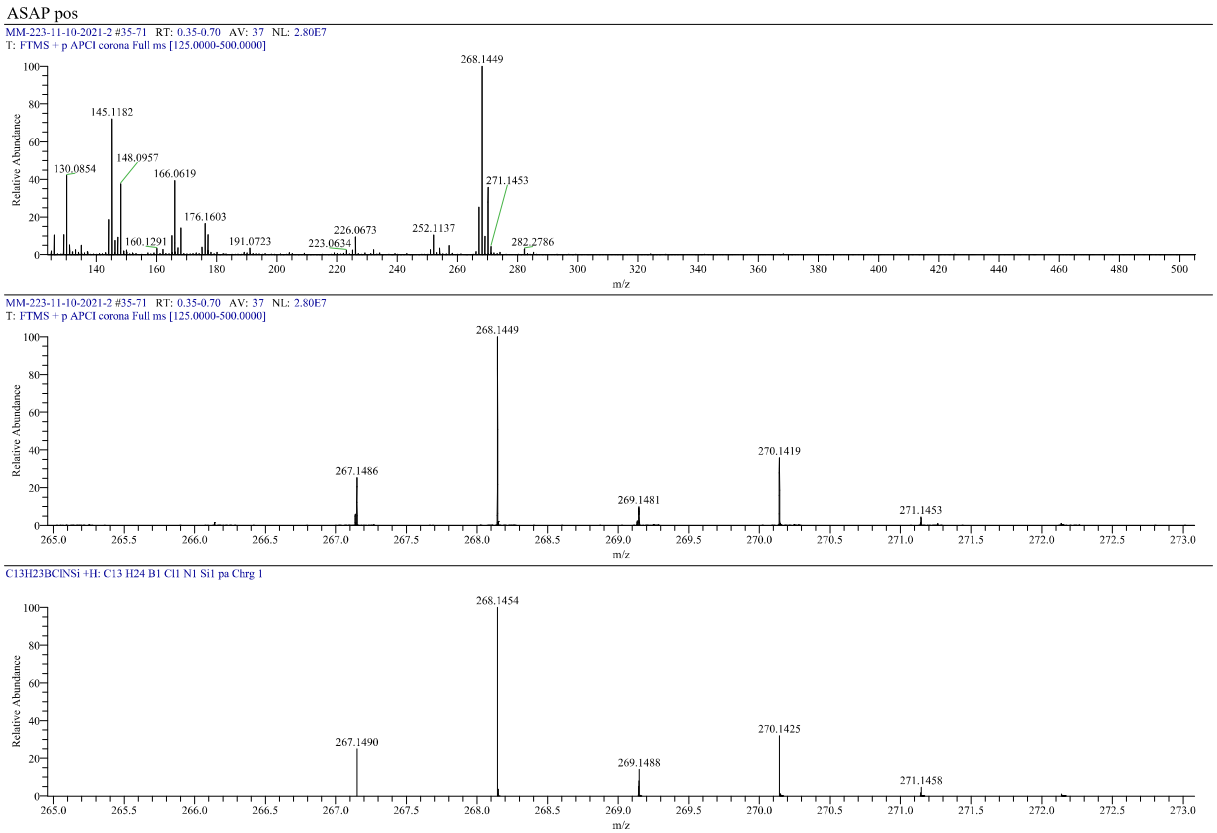

Figure S32. ASAP spectrum of **3b**.

Crystallographic Data

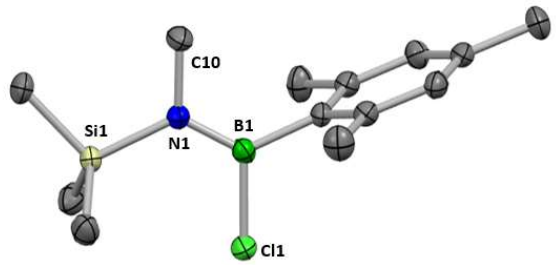

Figure S33. Molecular structure of (*Z*)-**1b** in the solid state (H atoms omitted for clarity).

Table S1. Crystal structure and refinement data for (*Z*)-1b

No.	**(*Z*)-1b**
CCDC number	2130024
Size / mm	0.170 x 0.343 x 0.467
Empiric Formula	C13 H23 B Cl N Si
M / g mol^{-1}	267.67
Crystal system	monoclinic
Space group	P 1 21/c 1
a / Å	8.256(4)
b / Å	11.579(6)
c / Å	16.616(8)
α / °	90.00
β / °	103.076(15)
γ / °	90.00
V / Å^3	1547.3(13)
Z	4
μ / mm^{-1}	0.305
T / K	98.42
$\theta_{min,max}$	2.163, 26.431
Completeness	0.989
Reflections: total/independent	3160, 2693
R_{int}	0.0922
Final *R*1 and *wR*2	0.0705, 0.2042
Largest peak, hole / e Å^{-3}	0.699, −0.649
ρ_{calc} / g cm^{-3}	1.149

Computational Data

DFT calculations were performed with the Gaussian 16, Revision C.01 program package[9] using the ωB97X-D[10] functional in combination with the 6-31+G(d,p)[11] basis sets for geometry optimizations in gas phase and the 6-311+G(d,p)[11a,11d,11h,12] basis sets for single-point energy calculations. The basis set SDD/ECP[13] was used for Ag atoms. Single-point energy calculations were performed with the PCM[14] solvation model mimicking dichloromethane (ε = 8.93) as solvent. To get a first insight, we investigated the geometrical structures and relative energies of possible intermediates. Their equilibrium geometries were determined by geometry optimization and proved by frequency computations. Scans along appropriate reaction coordinates were performed to compute possible reaction pathways between these minima. To compute the minimal energy path (MEP) all other coordinates have been optimized for each point. The connectivity between the obtained transition states and the corresponding intermediates was assessed by further geometry optimizations, visual inspection of the imaginary frequencies, and additional intrinsic reaction coordinate (IRC)[15] computations. Thermodynamic parameters were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. A concentration correction of $\Delta G^{0\rightarrow *} = RT\cdot\ln(24.46) = 1.89$ kcal mol^{-1} (T = 298.15 K) was added to the free energies of all calculated species. This was done to change the 1.00 atm gas phase values to the condensed phase standard state concentration of 1.00 mol·L^{-1}, which leads to a proper description of associative/dissociative steps. This is necessary because pure gas estimations overestimate the entropy penalty for the formation of complexes.[16]

Table S2. Relative energies of calculated species.

Molecules	Relative Energies [kJ mol^{-1}]
[(*Z*)-**1b**][Ag$^+$][(*Z*)-**1b**]	0
[(*Z*)-**1b^{Ag}**][(*Z*)-**1b**]	−30
[**4b**][AgCl][(*Z*)-**1b**]	+45
[**TS$_{4\rightarrow5}$**][AgCl][(*Z*)-**1b**]	+109
[(*E*)-**5b**][AgCl][(*Z*)-**1b**]	+98
[(*Z*)-**5b**][AgCl][(*Z*)-**1b**]	+32
[(*Z*,*E*)-**6b**][AgCl]	+85
[**TS$_{6\rightarrow3}$**][AgCl]	+105
[(*E*)-**3b**][Ag$^+$][(*Z*)-**1b**]	−5
[**TS$_{Rot3}$**][Ag$^+$][(*Z*)-**1b**]	+86
[**TS$_{Rot5}$**][AgCl][(*Z*)-**1b**]	+185

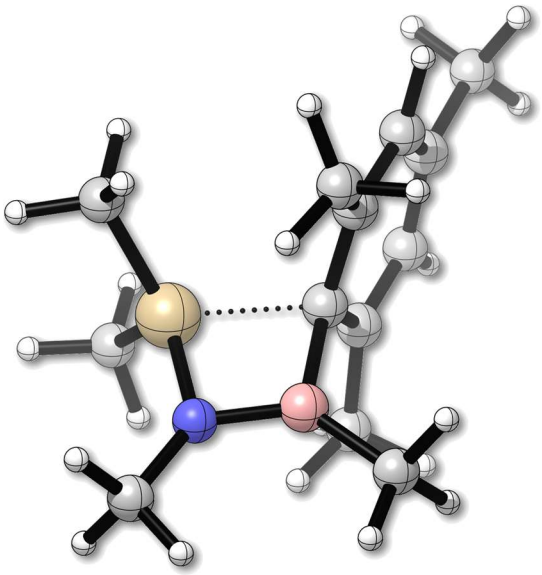

Figure S34. ωB97X-D/6-31+G(d,p)-optimized structure of (*Z*)-**5b**.

Cartesian coordinates (Å) and total energies (a.u.) of optimized stationary points

The molecular species were optimized at the ωB97X-D/6-31+G(d,p) level. The total energy is given as the sum of the electronic energy (ωB97X-D/6-311+G(d,p), PCM), the thermal correction to Gibbs Free Energy (ωB97X-D/6-31+G(d,p)), and the concentration correction (1.89 kcal/mol).

(*Z*)-**1b**:

Total energy: -1338.40525983326

B	3.075931000	-2.491253000	-0.073385000
N	2.098980000	-3.478685000	0.103692000
C	1.308484000	-3.895509000	-1.066122000
H	1.621834000	-3.340309000	-1.951409000
H	1.438591000	-4.963167000	-1.270404000
H	0.241246000	-3.709420000	-0.908018000
Si	1.719637000	-4.294214000	1.661944000
C	0.336772000	-5.527915000	1.334134000
H	0.622599000	-6.302305000	0.615400000
H	0.096115000	-6.030278000	2.278095000
H	-0.580158000	-5.050152000	0.975105000
C	3.212355000	-5.247023000	2.278918000
H	4.037540000	-4.586568000	2.555248000
H	2.939198000	-5.841072000	3.158493000

H	3.571301000	-5.936730000	1.507256000
C	1.098300000	-3.045599000	2.915563000
H	1.872159000	-2.329715000	3.202220000
H	0.249307000	-2.485476000	2.508780000
H	0.756758000	-3.561818000	3.820004000
C	3.398517000	-1.784686000	-1.443155000
C	4.363375000	-2.325226000	-2.310437000
C	2.719974000	-0.610853000	-1.813152000
C	4.639089000	-1.687804000	-3.520443000
C	3.016889000	0.004463000	-3.029611000
C	3.978340000	-0.517609000	-3.895292000
H	5.385998000	-2.114045000	-4.187442000
H	2.485340000	0.911881000	-3.309751000
C	5.090343000	-3.595641000	-1.936394000
H	5.656285000	-3.466964000	-1.007085000
H	4.387838000	-4.421891000	-1.776639000
H	5.792047000	-3.899077000	-2.717549000
C	1.667709000	-0.025359000	-0.900855000
H	0.862880000	-0.745041000	-0.711018000
H	2.095252000	0.246652000	0.070573000
H	1.218851000	0.872485000	-1.333367000
C	4.314446000	0.179793000	-5.189603000
H	5.122352000	0.905093000	-5.040891000
H	4.646408000	-0.531878000	-5.950929000
H	3.451696000	0.723692000	-5.584681000
Cl	4.068437000	-1.952094000	1.345538000

(*Z*)-**1b**^{Ag}:

Total energy (SDD/ECP for Ag): -1485.27118810326

B	-0.790987000	0.037122000	-0.011389000
N	-1.890542000	0.861594000	0.062200000
C	-1.663142000	2.315645000	0.176856000
H	-0.595691000	2.543886000	0.192221000
H	-2.112410000	2.844780000	-0.667605000
H	-2.107161000	2.704239000	1.096951000
Si	-3.643194000	0.328730000	0.028224000

C	-4.693483000	1.873834000	0.141684000
H	-4.543031000	2.557586000	-0.699119000
H	-5.744775000	1.564924000	0.120978000
H	-4.540348000	2.429665000	1.071559000
C	-3.966295000	-0.531604000	-1.601389000
H	-3.441736000	-1.485728000	-1.695718000
H	-5.038776000	-0.733196000	-1.699646000
H	-3.674352000	0.106413000	-2.442412000
C	-3.958450000	-0.756643000	1.519041000
H	-3.431490000	-1.712997000	1.473161000
H	-3.664494000	-0.245116000	2.441818000
H	-5.030068000	-0.973214000	1.591354000
C	0.731364000	0.499237000	0.004489000
C	1.368695000	0.907467000	-1.205780000
C	1.427577000	0.659828000	1.238644000
C	2.656254000	1.440263000	-1.156201000
C	2.725655000	1.190817000	1.232487000
C	3.349732000	1.593626000	0.051453000
H	3.129737000	1.759708000	-2.081515000
H	3.244108000	1.316696000	2.179557000
C	0.613651000	0.852979000	-2.512212000
H	0.045007000	-0.075204000	-2.627185000
H	-0.104783000	1.678776000	-2.563272000
H	1.287096000	0.946139000	-3.366495000
C	0.729930000	0.396263000	2.553565000
H	0.152004000	1.280638000	2.843977000
H	0.028994000	-0.442291000	2.501420000
H	1.446118000	0.194113000	3.352968000
C	4.732810000	2.187394000	0.060712000
H	5.420216000	1.586004000	-0.542371000
H	4.721659000	3.194599000	-0.366668000
H	5.136200000	2.253047000	1.073156000
Cl	-1.006270000	-1.797743000	-0.146750000
Ag	1.710472000	-1.687776000	-0.052895000

4b:

Total energy: -877.951005113263

B	0.400904000	0.046753000	0.667361000
N	1.707287000	0.048437000	0.876087000
C	2.316800000	0.085414000	2.226564000
H	2.932852000	-0.804049000	2.370685000
H	2.939196000	0.977260000	2.319613000
H	1.547573000	0.110524000	2.999236000
Si	2.825786000	-0.001944000	-0.596897000
C	3.853271000	1.548882000	-0.501033000
H	4.503291000	1.561557000	0.379109000
H	4.501951000	1.615828000	-1.381103000
H	3.228108000	2.447043000	-0.482407000
C	3.821126000	-1.566496000	-0.418788000
H	3.177350000	-2.448900000	-0.349967000
H	4.466407000	-1.694823000	-1.294515000
H	4.472491000	-1.544877000	0.460195000
C	1.677820000	-0.027161000	-2.070364000
H	1.028629000	-0.908720000	-2.088119000
H	1.049186000	0.867303000	-2.130610000
H	2.281542000	-0.056487000	-2.984106000
C	-1.042490000	0.021227000	0.384648000
C	-1.716829000	-1.233906000	0.287402000
C	-1.744933000	1.240289000	0.193533000
C	-3.067697000	-1.232250000	0.000152000
C	-3.103640000	1.184475000	-0.093096000
C	-3.778192000	-0.034050000	-0.191761000
H	-3.598015000	-2.177087000	-0.080941000
H	-3.651844000	2.110209000	-0.244297000
C	-0.973967000	-2.527447000	0.503810000
H	-0.074969000	-2.587248000	-0.119126000
H	-0.665355000	-2.633559000	1.549340000
H	-1.600763000	-3.386167000	0.258217000
C	-1.063650000	2.579240000	0.300620000
H	-1.440414000	3.128984000	1.168571000
H	0.022405000	2.497183000	0.406355000
H	-1.268560000	3.187537000	-0.584493000

C	-5.246819000	-0.083180000	-0.499012000
H	-5.428804000	-0.670466000	-1.404342000
H	-5.789884000	-0.569679000	0.317353000
H	-5.665939000	0.913718000	-0.644456000

$TS_{4\rightarrow5}$:

Total energy: -877.926654057263

B	0.590848000	0.001242000	0.095424000
N	1.679879000	-0.003173000	0.981070000
C	1.541694000	-0.007860000	2.438011000
H	2.016538000	-0.904679000	2.881999000
H	2.018933000	0.884730000	2.887951000
H	0.479445000	-0.007405000	2.755230000
Si	2.915060000	-0.000592000	-0.276288000
C	3.918562000	1.524908000	-0.394506000
H	4.574509000	1.621993000	0.496542000
H	4.595894000	1.518978000	-1.270396000
H	3.333477000	2.458898000	-0.447122000
C	3.914066000	-1.528141000	-0.405487000
H	3.326174000	-2.460003000	-0.464259000
H	4.590956000	-1.518152000	-1.281682000
H	4.570172000	-1.633298000	0.484519000
C	1.424181000	0.006126000	-1.564877000
H	0.852547000	-0.889327000	-1.892582000
H	0.853159000	0.904459000	-1.885883000
H	2.269764000	0.009109000	-2.328448000
C	-0.929415000	0.002852000	0.000992000
C	-1.621003000	-1.220103000	-0.026775000
C	-1.620019000	1.224882000	-0.025237000
C	-3.018179000	-1.212431000	-0.081851000
C	-3.018814000	1.218259000	-0.080478000
C	-3.723976000	0.003899000	-0.110155000
H	-3.569654000	-2.151974000	-0.102234000
H	-3.567168000	2.159604000	-0.099791000
C	-0.889411000	-2.522776000	-0.012914000
H	0.086429000	-2.483970000	0.484013000

H	-1.463986000	-3.305476000	0.512871000
H	-0.738444000	-2.900989000	-1.036031000
C	-0.890379000	2.528534000	-0.009253000
H	-1.451190000	3.299610000	0.547814000
H	0.100401000	2.484529000	0.456265000
H	-0.771716000	2.925825000	-1.029618000
C	-5.211821000	-0.006740000	-0.164377000
H	-5.590067000	-0.645493000	-0.978145000
H	-5.643378000	-0.401316000	0.770450000
H	-5.649944000	0.990193000	-0.316593000

(*E*)-**5b**:

Total energy: -877.930722751263

B	2.614670000	-2.709315000	-0.273437000
N	2.053072000	-3.975065000	-0.195933000
C	1.722541000	-4.908099000	-1.266128000
H	2.315262000	-5.820902000	-1.169860000
H	0.662426000	-5.167912000	-1.231417000
H	1.941583000	-4.440082000	-2.227641000
Si	1.997458000	-3.891600000	1.516446000
C	3.239870000	-4.884308000	2.455353000
H	4.235554000	-4.806019000	2.009749000
H	3.294612000	-4.578344000	3.504654000
H	2.949204000	-5.940930000	2.436994000
C	0.342993000	-3.634722000	2.296252000
H	-0.233933000	-4.564937000	2.241043000
H	0.430514000	-3.366054000	3.353564000
H	-0.228813000	-2.858843000	1.779249000
C	2.842697000	-1.987226000	1.288235000
H	2.660009000	-2.163314000	2.368371000
H	3.919958000	-1.801699000	1.254537000
H	2.294059000	-1.055606000	1.121075000
C	3.103208000	-1.859044000	-1.467915000
C	4.335729000	-2.177609000	-2.078373000
C	2.330735000	-0.792421000	-1.956881000
C	4.771273000	-1.419341000	-3.158627000

C	2.796960000	-0.058811000	-3.048545000
C	4.014363000	-0.353815000	-3.659265000
H	5.720573000	-1.661414000	-3.630478000
H	2.193344000	0.759514000	-3.433190000
C	5.170255000	-3.331012000	-1.570329000
H	5.401359000	-3.228587000	-0.502573000
H	4.656494000	-4.289308000	-1.708055000
H	6.123666000	-3.393518000	-2.098372000
C	1.013190000	-0.418146000	-1.317470000
H	0.517774000	-1.277970000	-0.851305000
H	1.148602000	0.355121000	-0.551312000
H	0.318075000	-0.012376000	-2.056077000
C	4.514971000	0.444976000	-4.833237000
H	5.461486000	0.937831000	-4.590386000
H	4.695654000	-0.203035000	-5.696159000
H	3.799389000	1.214434000	-5.130389000

(*Z*)-**5b**:

Total energy: -877.955903011263

B	2.565277000	-2.631704000	-0.564046000
N	2.101556000	-3.921877000	-0.267563000
C	1.693394000	-5.013278000	-1.139490000
H	2.317759000	-5.894913000	-0.971631000
H	0.650774000	-5.285305000	-0.954382000
H	1.791748000	-4.714843000	-2.184675000
Si	2.200300000	-3.711581000	1.457370000
C	3.468577000	-4.718729000	2.370796000
H	4.375122000	-4.910784000	1.795221000
H	3.746572000	-4.226626000	3.308796000
H	3.022599000	-5.685280000	2.631513000
C	0.602787000	-3.679558000	2.408270000
H	0.333241000	-4.709252000	2.669351000
H	0.725262000	-3.128764000	3.346814000
H	-0.229773000	-3.244050000	1.853962000
C	2.804395000	-1.917932000	-1.932962000
H	2.570512000	-2.540130000	-2.800457000

H	2.200913000	-1.004710000	-1.997532000
H	3.848562000	-1.594462000	-2.018306000
C	2.857153000	-1.880595000	0.891569000
C	1.906668000	-0.895042000	1.354457000
C	4.229144000	-1.737178000	1.323257000
C	2.281020000	0.025672000	2.316220000
C	4.554761000	-0.798746000	2.285457000
C	3.591653000	0.073883000	2.811928000
H	1.552387000	0.747172000	2.675734000
H	5.584772000	-0.714665000	2.621227000
C	0.525126000	-0.812623000	0.763978000
H	0.483389000	0.053910000	0.094692000
H	0.255867000	-1.689491000	0.171799000
H	-0.233339000	-0.663488000	1.536453000
C	5.327811000	-2.554319000	0.699284000
H	4.958189000	-3.395073000	0.108861000
H	5.899050000	-1.910390000	0.021349000
H	6.023969000	-2.932339000	1.452080000
C	3.962474000	1.055839000	3.881969000
H	3.340223000	1.952048000	3.837917000
H	3.811961000	0.596899000	4.866005000
H	5.012277000	1.348162000	3.812301000

(*Z*,*E*)-**6b**:

Total energy: -2216.340817213260

B	2.469251000	0.711232000	-0.169597000
N	3.774387000	0.793678000	0.239954000
C	4.163421000	2.089871000	0.849546000
H	3.319589000	2.779752000	0.850022000
H	4.493715000	1.939049000	1.879862000
H	4.978533000	2.546597000	0.284219000
Si	5.140239000	-0.413608000	0.047422000
C	6.652869000	0.320539000	0.865101000
H	6.508202000	0.516691000	1.931627000
H	7.465031000	-0.410044000	0.778285000
H	6.997272000	1.242333000	0.388213000

C	4.706887000	-2.011072000	0.926263000
H	3.903479000	-2.574989000	0.446492000
H	5.594715000	-2.653298000	0.934180000
H	4.435226000	-1.826689000	1.971136000
C	5.450267000	-0.645351000	-1.782082000
H	4.628602000	-1.142503000	-2.304264000
H	5.629412000	0.319395000	-2.268139000
H	6.348371000	-1.256074000	-1.925752000
C	1.270496000	1.691807000	-0.147767000
C	0.588669000	1.984900000	1.047867000
C	0.871483000	2.316098000	-1.350324000
C	-0.506494000	2.848095000	1.013030000
C	-0.218313000	3.180780000	-1.341739000
C	-0.938639000	3.439995000	-0.172219000
H	-1.034101000	3.066841000	1.938350000
H	-0.520907000	3.661497000	-2.268865000
C	1.026047000	1.430203000	2.382734000
H	1.808806000	0.672857000	2.289967000
H	1.420362000	2.231102000	3.016923000
H	0.183587000	0.983197000	2.920246000
C	1.597074000	2.047390000	-2.647558000
H	2.675056000	1.919767000	-2.499774000
H	1.220508000	1.139636000	-3.134180000
H	1.459165000	2.871069000	-3.351285000
C	-2.164876000	4.312535000	-0.191469000
H	-3.064005000	3.693101000	-0.286526000
H	-2.257361000	4.890442000	0.731681000
H	-2.149482000	5.008667000	-1.033247000
Cl	2.022009000	-0.993717000	-1.062941000
B	-2.220796000	-1.781988000	0.476537000
N	-1.084269000	-1.350451000	-0.288757000
C	-1.269775000	-0.298250000	-1.306999000
H	-1.403359000	0.673742000	-0.827514000
H	-0.410648000	-0.237748000	-1.975637000
H	-2.155062000	-0.511758000	-1.907386000
Si	0.394762000	-2.169564000	0.038348000
C	0.997723000	-2.119310000	1.797465000

H	0.354471000	-1.477976000	2.404375000
H	0.975890000	-3.127756000	2.222318000
H	2.025420000	-1.755788000	1.871583000
C	0.659540000	-3.765357000	-0.866636000
H	0.505509000	-3.644648000	-1.942696000
H	1.659160000	-4.174660000	-0.693502000
H	-0.074224000	-4.495750000	-0.508518000
C	-2.140304000	-2.979912000	1.514971000
H	-1.264775000	-3.639475000	1.510456000
H	-2.235896000	-2.578745000	2.532104000
H	-3.017642000	-3.619737000	1.370775000
C	-3.593463000	-1.035496000	0.282142000
C	-3.892722000	0.093329000	1.061355000
C	-4.524985000	-1.477263000	-0.674170000
C	-5.098615000	0.769154000	0.869531000
C	-5.721937000	-0.783335000	-0.844149000
C	-6.027990000	0.344700000	-0.079710000
H	-5.320524000	1.644754000	1.476443000
H	-6.434498000	-1.126892000	-1.591099000
C	-2.924726000	0.560288000	2.123972000
H	-2.971650000	-0.084208000	3.009942000
H	-1.892772000	0.551892000	1.754617000
H	-3.149653000	1.579206000	2.449935000
C	-4.229536000	-2.699975000	-1.512922000
H	-3.244220000	-2.637314000	-1.991515000
H	-4.237057000	-3.610504000	-0.902453000
H	-4.970629000	-2.832068000	-2.304518000
C	-7.341121000	1.062517000	-0.259579000
H	-7.291549000	2.087463000	0.116999000
H	-7.633326000	1.099438000	-1.312703000
H	-8.139878000	0.547625000	0.285010000

$TS_{6\rightarrow3}$:

Total energy: -2216.333177853260

B	-2.477250000	-1.153725000	-0.072626000
N	-3.779041000	-1.271902000	0.227366000
C	-4.162169000	-2.703645000	0.430647000
H	-3.304696000	-3.359130000	0.266792000
H	-4.524671000	-2.853599000	1.448217000
H	-4.948023000	-2.974008000	-0.277457000
Si	-5.123671000	-0.034015000	0.487809000
C	-6.519752000	-0.959650000	1.317273000
H	-6.241025000	-1.363170000	2.295418000
H	-7.333052000	-0.244518000	1.485815000
H	-6.928412000	-1.771071000	0.708596000
C	-4.473946000	1.274081000	1.651342000
H	-3.682959000	1.882055000	1.209929000
H	-5.294343000	1.943229000	1.933247000
H	-4.092312000	0.819041000	2.571409000
C	-5.663718000	0.589138000	-1.185029000
H	-4.894222000	1.175588000	-1.691940000
H	-5.945117000	-0.245007000	-1.836148000
H	-6.547976000	1.225206000	-1.067293000
C	-1.092966000	-1.727890000	-0.193641000
C	-0.209713000	-1.608657000	0.901942000
C	-0.689445000	-2.381839000	-1.380193000
C	1.066585000	-2.143917000	0.790179000
C	0.598170000	-2.900515000	-1.448134000
C	1.495027000	-2.773163000	-0.382062000
H	1.757640000	-2.057240000	1.622331000
H	0.921216000	-3.401987000	-2.356483000
C	-0.627612000	-0.870155000	2.147636000
H	-0.461602000	0.206916000	2.020362000
H	-1.687956000	-1.016780000	2.379569000
H	-0.050304000	-1.193856000	3.015874000
C	-1.628031000	-2.486304000	-2.555543000
H	-2.563378000	-2.987835000	-2.283193000
H	-1.885394000	-1.493138000	-2.941691000
H	-1.178237000	-3.053308000	-3.372541000

C	2.915048000	-3.249752000	-0.501324000
H	3.577079000	-2.391261000	-0.668606000
H	3.248648000	-3.735247000	0.419583000
H	3.039725000	-3.948477000	-1.331307000
Cl	-2.152889000	1.123218000	-1.000023000
B	2.019925000	1.789125000	0.508769000
N	0.931555000	1.539692000	-0.402972000
C	1.118704000	0.608035000	-1.535898000
H	1.898293000	-0.112144000	-1.294539000
H	0.204456000	0.052282000	-1.742753000
H	1.412836000	1.142648000	-2.444866000
Si	-0.513374000	2.500921000	-0.528312000
C	-1.158047000	3.347398000	0.994962000
H	-1.227902000	2.675056000	1.854140000
H	-0.535559000	4.200018000	1.275414000
H	-2.160466000	3.727317000	0.771517000
C	-0.504736000	3.585741000	-2.036122000
H	-0.291840000	3.015617000	-2.944533000
H	-1.461560000	4.098736000	-2.168397000
H	0.277399000	4.345282000	-1.923305000
C	1.934980000	2.923864000	1.621531000
H	1.770550000	3.914956000	1.179582000
H	1.136318000	2.764954000	2.354434000
H	2.873079000	2.985659000	2.177678000
C	3.350630000	0.932496000	0.409699000
C	3.707242000	0.092722000	1.489532000
C	4.220475000	1.002332000	-0.692798000
C	4.843922000	-0.706724000	1.409665000
C	5.363836000	0.197140000	-0.738435000
C	5.683564000	-0.679807000	0.292810000
H	5.093835000	-1.360039000	2.243820000
H	6.023697000	0.268163000	-1.600955000
C	2.906273000	0.077630000	2.772702000
H	3.242847000	0.874115000	3.445287000
H	1.838084000	0.231112000	2.602310000
H	3.029592000	-0.868482000	3.308304000
C	3.995116000	1.967682000	-1.835906000

H	3.131798000	2.618605000	-1.671111000
H	4.869041000	2.613764000	-1.962742000
H	3.845224000	1.438428000	-2.783195000
C	6.892294000	-1.576499000	0.219214000
H	7.564468000	-1.276328000	-0.588176000
H	7.456548000	-1.558009000	1.156080000
H	6.595029000	-2.615464000	0.037179000

(*E*)-**3b**:

Total energy: -1338.40713455326

B	0.103014000	0.133818000	0.703332000
N	1.114670000	0.005969000	-0.284347000
C	0.754373000	-0.170118000	-1.701244000
H	-0.330105000	-0.131146000	-1.809021000
H	1.192972000	0.617039000	-2.321803000
H	1.107097000	-1.132448000	-2.084532000
Si	2.821071000	0.044946000	0.166486000
C	3.271968000	-1.338872000	1.336481000
H	2.996801000	-2.301226000	0.893782000
H	4.351535000	-1.344768000	1.516969000
H	2.761057000	-1.247968000	2.298551000
C	3.353904000	1.741446000	0.737146000
H	3.158804000	2.475113000	-0.051173000
H	2.813809000	2.056923000	1.634233000
H	4.426393000	1.754174000	0.955275000
C	0.399296000	0.342403000	2.253911000
H	0.081402000	-0.559669000	2.793549000
H	1.424611000	0.560612000	2.562292000
H	-0.239057000	1.147372000	2.636219000
C	-1.430362000	0.053089000	0.303243000
C	-2.156484000	1.222984000	0.020938000
C	-2.092542000	-1.185965000	0.254653000
C	-3.515722000	1.143482000	-0.285921000
C	-3.452757000	-1.237476000	-0.053583000
C	-4.184417000	-0.080190000	-0.320981000
H	-4.065454000	2.056482000	-0.507654000

H	-3.953476000	-2.203318000	-0.091001000
C	-1.456316000	2.562663000	0.017999000
H	-1.004487000	2.782503000	0.992097000
H	-0.648939000	2.583225000	-0.723189000
H	-2.147645000	3.375915000	-0.217810000
C	-1.325836000	-2.463464000	0.510688000
H	-0.502844000	-2.579192000	-0.203906000
H	-0.885501000	-2.473548000	1.514317000
H	-1.970959000	-3.341626000	0.423879000
C	-5.661725000	-0.148649000	-0.617701000
H	-6.247938000	-0.084382000	0.306036000
H	-5.976288000	0.674566000	-1.265566000
H	-5.925630000	-1.088861000	-1.110465000
Cl	3.926518000	-0.328463000	-1.572464000

TS_{Rot3}:

Total energy: -1338.372666013260

B	0.235587000	1.131005000	0.821950000
N	1.450531000	1.005952000	-0.019086000
C	1.479485000	2.071775000	-1.033807000
H	0.835406000	1.846044000	-1.893485000
H	1.146860000	3.023272000	-0.601702000
H	2.495703000	2.231869000	-1.400623000
Si	2.565772000	-0.293337000	-0.139146000
C	3.001303000	-0.962723000	1.550522000
H	2.127207000	-1.235807000	2.144784000
H	3.630196000	-1.853136000	1.453933000
H	3.563467000	-0.200928000	2.101560000
C	4.107490000	0.233720000	-1.056891000
H	3.912618000	0.446750000	-2.111579000
H	4.560044000	1.117805000	-0.595114000
H	4.835975000	-0.582456000	-1.016200000
C	0.341685000	2.028188000	2.112502000
H	-0.612121000	2.398652000	2.497848000
H	0.764931000	1.366352000	2.886456000
H	1.057898000	2.849825000	2.003938000

C	-1.147373000	0.455182000	0.431418000
C	-2.095636000	1.211040000	-0.285323000
C	-1.492420000	-0.853945000	0.818936000
C	-3.317460000	0.639986000	-0.648647000
C	-2.721576000	-1.394481000	0.443989000
C	-3.644493000	-0.669495000	-0.308481000
H	-4.036631000	1.241768000	-1.201656000
H	-2.970019000	-2.406670000	0.757619000
C	-1.834608000	2.649665000	-0.677661000
H	-2.772983000	3.204650000	-0.761887000
H	-1.214065000	3.172486000	0.057822000
H	-1.328419000	2.717310000	-1.646480000
C	-0.558363000	-1.688329000	1.661985000
H	0.239125000	-2.126372000	1.053259000
H	-0.098628000	-1.093444000	2.459382000
H	-1.092024000	-2.512568000	2.142597000
C	-4.951277000	-1.286150000	-0.738779000
H	-5.717324000	-0.523007000	-0.903007000
H	-4.828512000	-1.839620000	-1.676528000
H	-5.325913000	-1.988866000	0.011204000
Cl	1.798483000	-1.908851000	-1.259342000

TS_{Rot5}:

Total energy: -877.897654831263

B	0.492964000	1.275397000	-0.384648000
N	1.708438000	0.747102000	0.309560000
C	2.278522000	1.718314000	1.286000000
H	3.034981000	1.244743000	1.916927000
H	2.742917000	2.560523000	0.767520000
H	1.493943000	2.092341000	1.947570000
Si	2.560209000	-0.674258000	0.075272000
C	3.365161000	-1.458689000	1.542520000
H	4.366896000	-1.036909000	1.689184000
H	2.788184000	-1.309243000	2.458019000
H	3.496237000	-2.532016000	1.372551000
C	3.295115000	-1.104825000	-1.563192000

H	3.263818000	-2.181443000	-1.757395000
H	2.821450000	-0.572414000	-2.391319000
H	4.351842000	-0.810269000	-1.536473000
C	0.650252000	2.695971000	-1.044318000
H	1.645633000	2.795770000	-1.493806000
H	-0.096967000	2.888687000	-1.816789000
H	0.564247000	3.511806000	-0.315355000
C	-0.844198000	0.452600000	-0.294925000
C	-0.898732000	-0.963294000	-0.349307000
C	-2.055706000	1.128697000	0.008870000
C	-2.077803000	-1.662489000	-0.121250000
C	-3.222011000	0.393916000	0.242505000
C	-3.265681000	-0.994915000	0.177699000
H	-2.081823000	-2.747984000	-0.187638000
H	-4.134779000	0.932139000	0.484442000
C	0.303236000	-1.778848000	-0.729860000
H	0.787154000	-1.424968000	-1.640780000
H	1.031143000	-1.841139000	0.136456000
H	0.073594000	-2.836785000	-0.880275000
C	-2.167986000	2.632102000	0.138825000
H	-3.146194000	2.903395000	0.539468000
H	-1.416601000	3.051115000	0.812820000
H	-2.063318000	3.130851000	-0.828126000
C	-4.549001000	-1.749659000	0.391566000
H	-4.366174000	-2.729260000	0.840343000
H	-5.232841000	-1.196430000	1.039223000
H	-5.057155000	-1.912874000	-0.564853000

Ag^+:

Total energy (SDD/ECP): -146.854492474263

Ag	-0.201774000	0.000000000	-1.767258000

AgCl:

Total energy (SDD/ECP for Ag): -607.291749383263

Ag	0.000000000	0.000000000	0.614540000
Cl	0.000000000	0.000000000	-1.699023000

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