The Hexacoordinate Si Complex SiCl4(4-Azidopyridine) 2—Crystallographic Characterization of Two Conformers and Probing the Influence of SiCl4-Complexation on a Click Reaction with Phenylacetylene

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Supporting Information:

Content:

- Raman spectra of **2'** and **2''**
- ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of $CDCl_3$ solutions of **1** and **2'**
- $^{29}Si\{^{1}H\}$ NMR spectrum of a $CDCl_3$ solution of **2'**
- ^{13}C CP/MAS NMR spectra of **2'** and **2''**
- ^{13}C CP/MAS NMR spectra of two samples of **2'** (obtained from reaction in chloroform at room temperature and obtained from reaction in toluene at −78 °C)
- Graphics of the molecular structure and tables with bond lengths and angles of 1,4-**3** and 1,5-**3** in their crystal structures
- Graphics and tables with Cartesian coordinates of optimized molecular structures of **2'** and **2''** (as single molecules and in their crystal environment)
- Graphics of the orientation of the ^{29}Si CSA tensor principal axes in the molecular structures of **2'** and **2''**

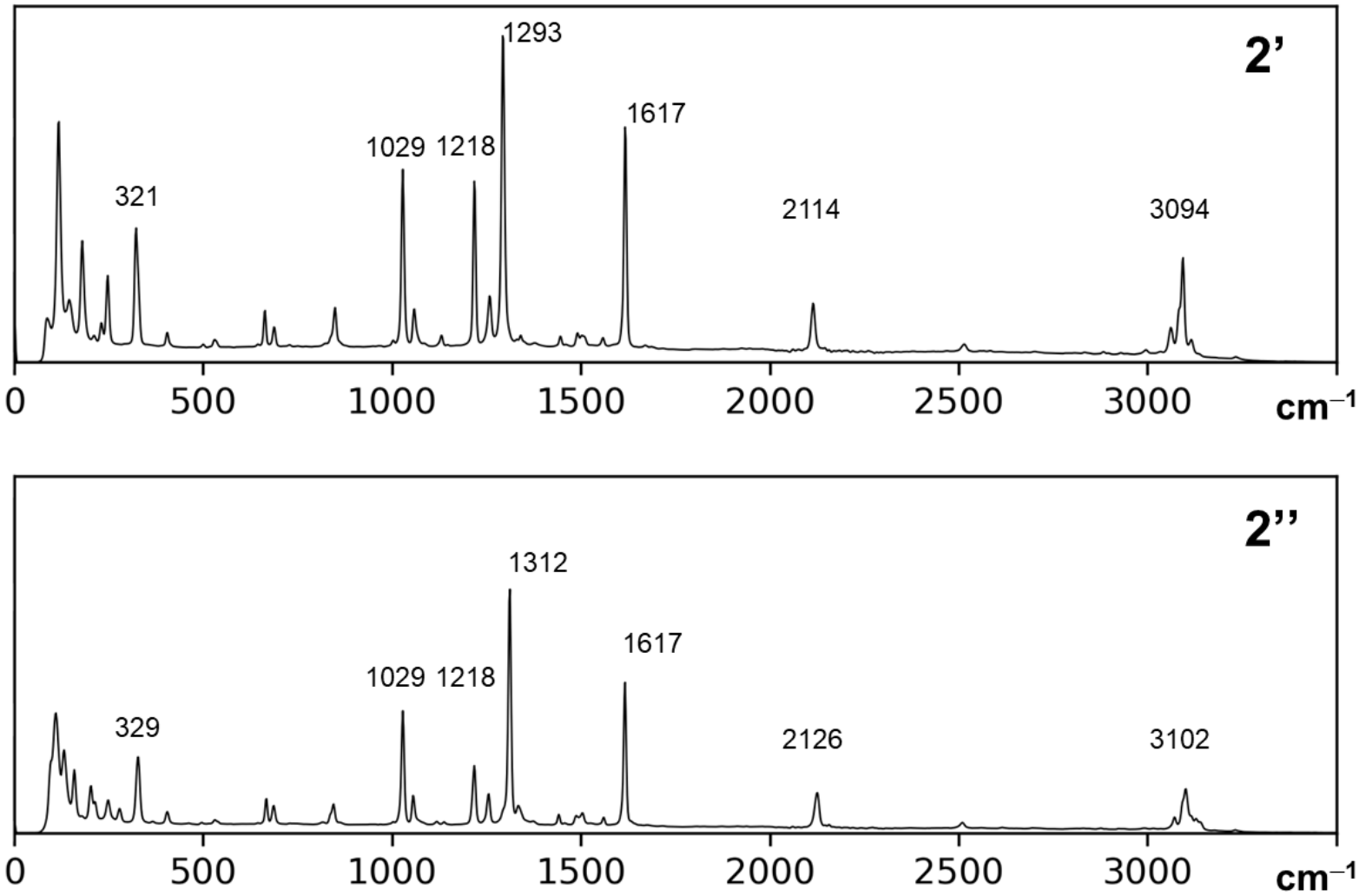

Figure S1. Raman spectra of **2’** and **2’’** (recorded from the solids in glass capillaries) with wavenumbers of selected bands.

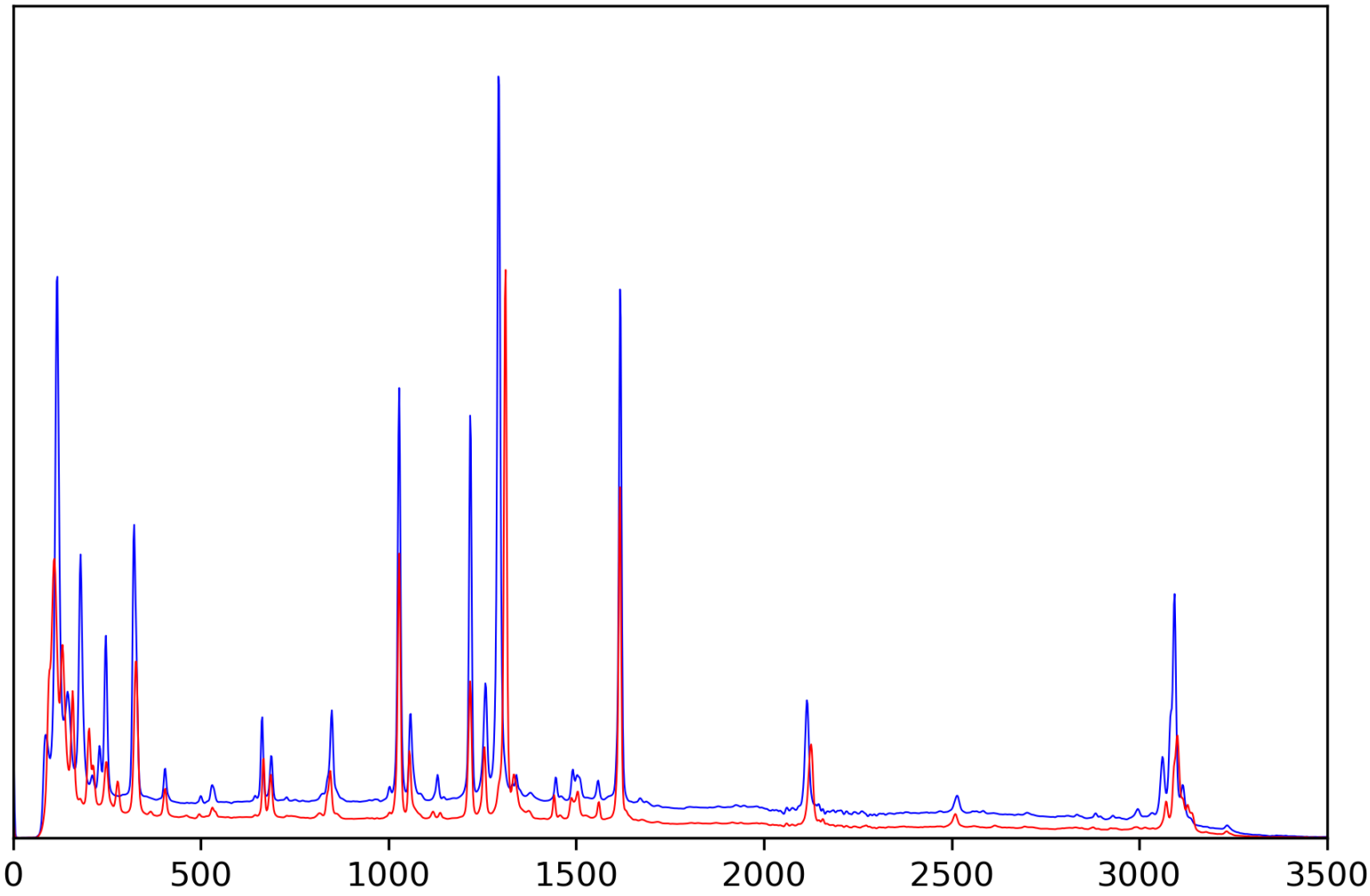

Figure S2. Overlay of the Raman spectra of **2'** (blue) and **2''** (red), which are shown as individual spectra in Figure S1. In addition to the band of the -N_3 stretch (2114 vs. 2126 cm^{-1}), the band at 1293 vs. 1312 cm^{-1} represents a suitable feature to distinguish **2'** from **2''**, respectively.

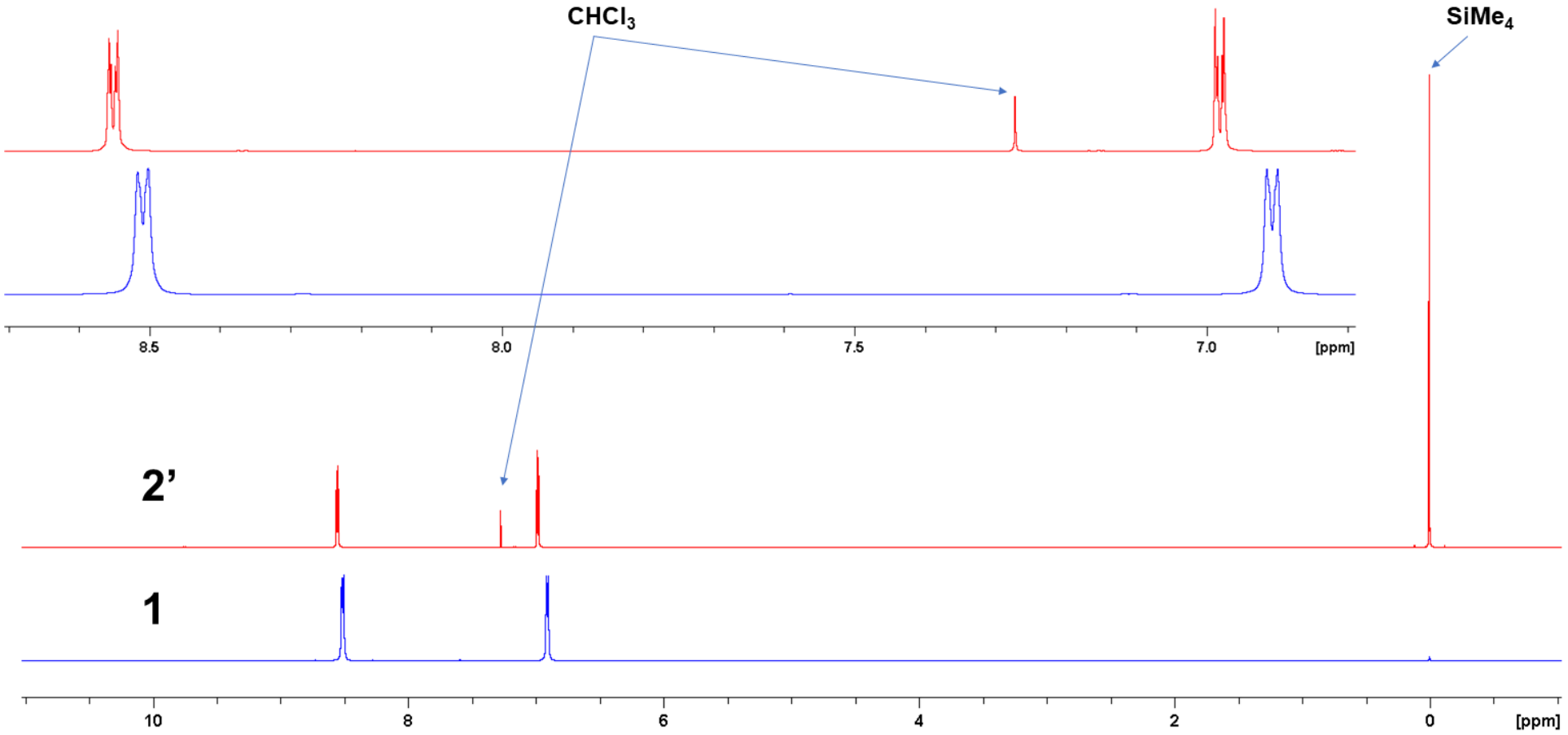

Figure S3. ^{1}H NMR spectra of a solution of **1** in $CDCl_3$ and of a solution of **2'** in $CDCl_3$ (full spectrum and magnified inset).

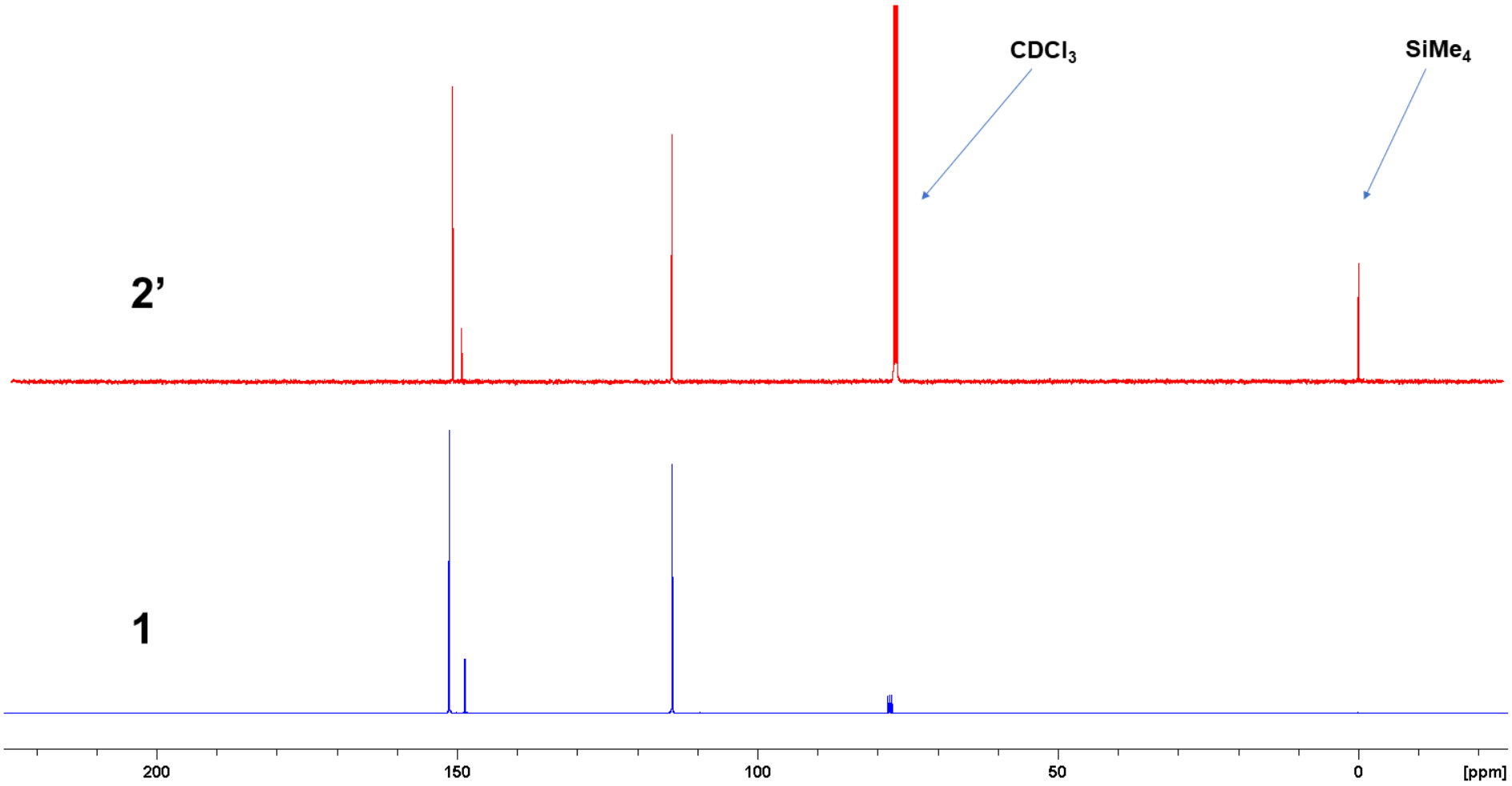

Figure S4. $^{13}C\{^{1}H\}$ NMR spectra of a solution of **1** in $CDCl_3$ and of a solution of **2'** in $CDCl_3$.

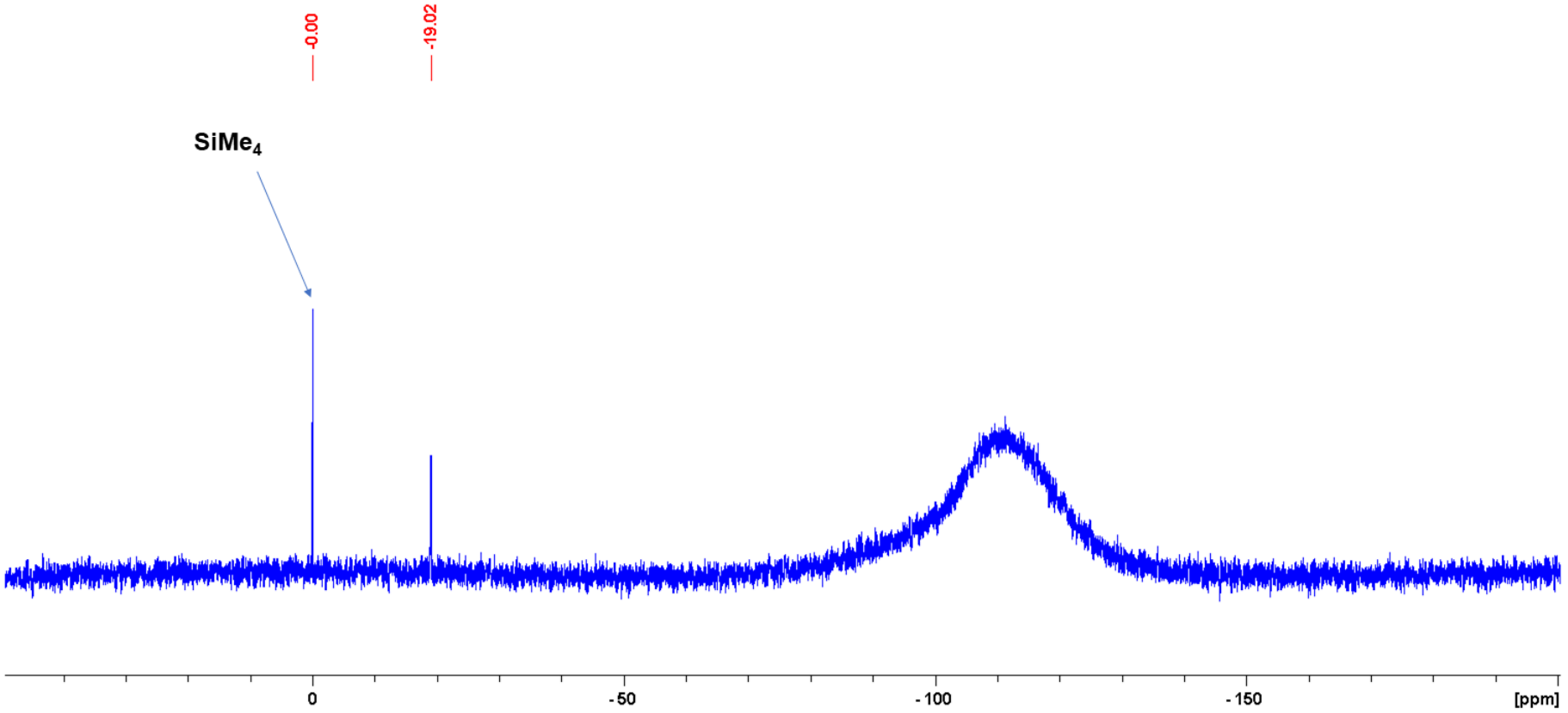

Figure S5. $^{29}Si\{^{1}H\}$ NMR spectrum of a solution of **2'** in $CDCl_3$.

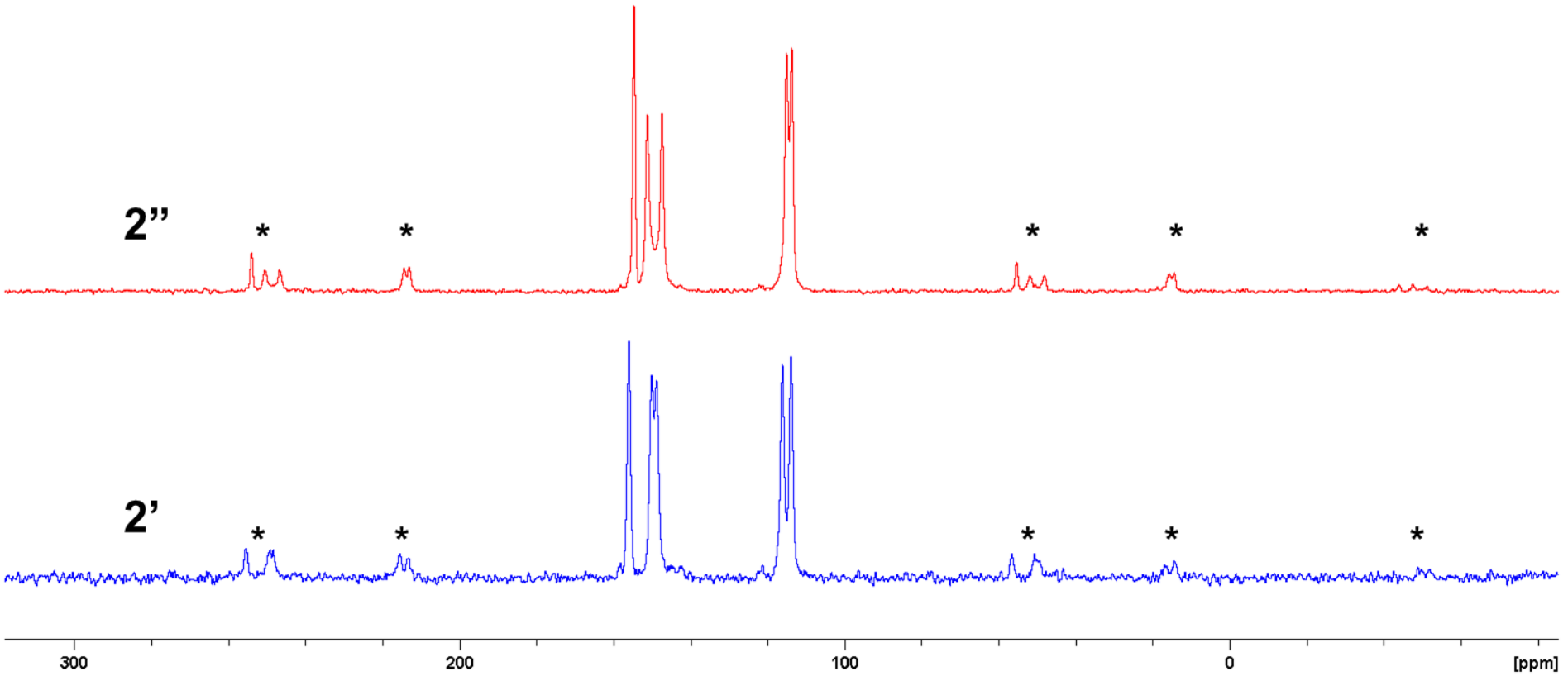

Figure S6. ^{13}C CP/MAS NMR spectra of **2'** and **2''** recorded at an MAS frequency of 10 kHz and with a CP contact time of τ = 2 ms. The groups of signals marked with an asterisk (*) are spinning side bands.

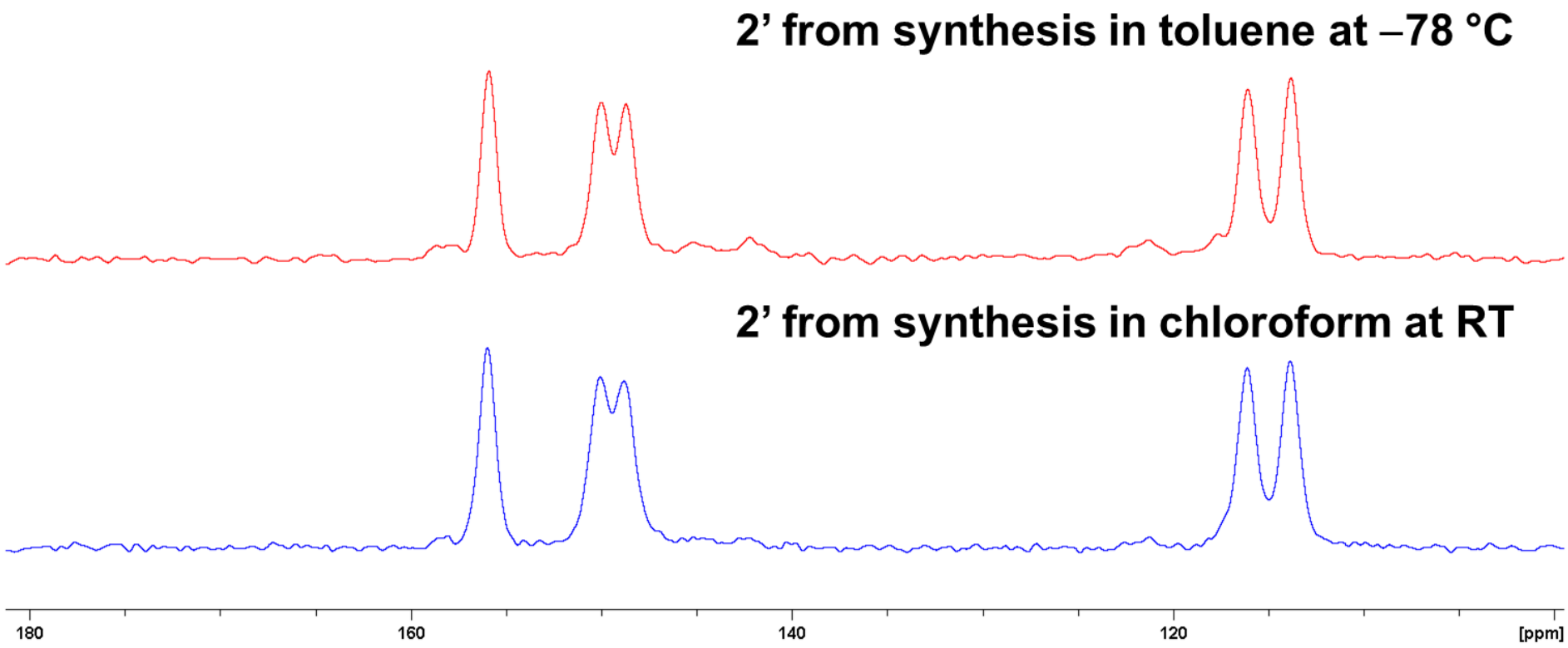

Figure S7. ^{13}C CP/MAS NMR spectra (section of isotropic chemical shift signals) of **2’** obtained from reaction in chloroform at room temperature and obtained from reaction in toluene at –78 °C. (Spectra were recorded at an MAS frequency of 10 kHz and with a CP contact time of τ = 2 ms.)

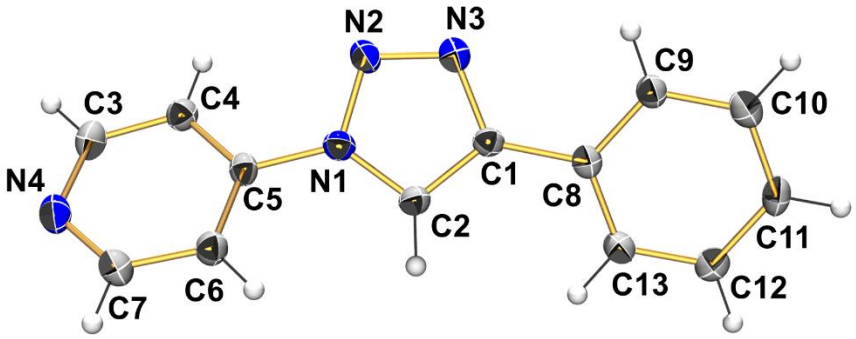

Figure S8. Molecular structure of 1,4-**3** with thermal displacement ellipsoids at the 50% probability level and labels of non-hydrogen atoms.

Table S1. Selected bond lengths (Å) and angles (deg) of 1,4-**3** in the crystal structure.

Bond	**Length**	**Bonds**	**Bond Angle**
N(1)-C(2)	1.355(3)	C(2)-N(1)-N(2)	110.64(17)
N(1)-N(2)	1.357(3)	C(2)-N(1)-C(5)	129.70(19)
N(1)-C(5)	1.430(3)	N(2)-N(1)-C(5)	119.65(17)
N(2)-N(3)	1.311(3)	N(3)-N(2)-N(1)	106.89(18)
N(3)-C(1)	1.366(3)	N(2)-N(3)-C(1)	109.55(19)
N(4)-C(7)	1.340(3)	C(7)-N(4)-C(3)	116.49(19)
N(4)-C(3)	1.343(3)	N(3)-C(1)-C(2)	108.01(18)
C(1)-C(2)	1.372(3)	N(3)-C(1)-C(8)	121.9(2)
C(1)-C(8)	1.460(3)	C(2)-C(1)-C(8)	130.1(2)
C(3)-C(4)	1.388(3)	N(1)-C(2)-C(1)	104.91(17)
C(4)-C(5)	1.380(3)	N(4)-C(3)-C(4)	123.9(2)
C(5)-C(6)	1.381(3)	C(5)-C(4)-C(3)	117.7(2)
C(6)-C(7)	1.386(3)	C(4)-C(5)-C(6)	120.1(2)
C(8)-C(13)	1.395(3)	C(4)-C(5)-N(1)	119.6(2)
C(8)-C(9)	1.399(3)	C(6)-C(5)-N(1)	120.2(2)
C(9)-C(10)	1.384(3)	C(5)-C(6)-C(7)	117.5(2)
C(10)-C(11)	1.384(3)	N(4)-C(7)-C(6)	124.3(2)
C(11)-C(12)	1.383(3)	C(13)-C(8)-C(9)	118.9(2)
C(12)-C(13)	1.387(3)	C(13)-C(8)-C(1)	121.3(2)
		C(9)-C(8)-C(1)	119.8(2)
		C(10)-C(9)-C(8)	120.4(2)
		C(9)-C(10)-C(11)	120.3(2)
		C(12)-C(11)-C(10)	119.8(2)
		C(11)-C(12)-C(13)	120.4(2)
		C(12)-C(13)-C(8)	120.2(2)

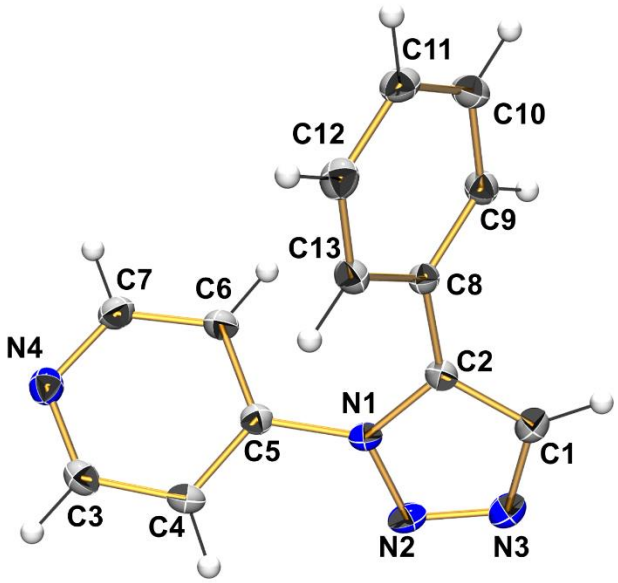

Figure S9. Molecular structure of 1,5-**3** with thermal displacement ellipsoids at the 50% probability level and labels of non-hydrogen atoms.

Table S2. Selected bond lengths (Å) and angles (deg) of 1,5-**3** in the crystal structure.

Bond	**Length**	**Bonds**	**Bond Angle**
N(1)-N(2)	1.3599(12)	N(2)-N(1)-C(2)	111.15(9)
N(1)-C(2)	1.3601(13)	N(2)-N(1)-C(5)	119.27(9)
N(1)-C(5)	1.4250(14)	C(2)-N(1)-C(5)	129.24(9)
N(2)-N(3)	1.3088(14)	N(3)-N(2)-N(1)	106.79(9)
N(3)-C(1)	1.3567(15)	N(2)-N(3)-C(1)	109.02(9)
N(4)-C(7)	1.3368(15)	C(7)-N(4)-C(3)	116.70(10)
N(4)-C(3)	1.3389(15)	N(3)-C(1)-C(2)	109.59(10)
C(1)-C(2)	1.3708(15)	N(1)-C(2)-C(1)	103.45(9)
C(2)-C(8)	1.4701(14)	N(1)-C(2)-C(8)	125.60(9)
C(3)-C(4)	1.3827(16)	C(1)-C(2)-C(8)	130.87(10)
C(4)-C(5)	1.3831(15)	N(4)-C(3)-C(4)	124.13(10)
C(5)-C(6)	1.3852(15)	C(3)-C(4)-C(5)	117.68(10)
C(6)-C(7)	1.3859(16)	C(4)-C(5)-C(6)	119.82(10)
C(8)-C(9)	1.3929(14)	C(4)-C(5)-N(1)	120.23(9)
C(8)-C(13)	1.3951(15)	C(6)-C(5)-N(1)	119.92(10)
C(9)-C(10)	1.3894(15)	C(5)-C(6)-C(7)	117.63(10)
C(10)-C(11)	1.3843(16)	N(4)-C(7)-C(6)	124.03(10)
C(11)-C(12)	1.3889(17)	C(9)-C(8)-C(13)	119.52(10)
C(12)-C(13)	1.3873(16)	C(9)-C(8)-C(2)	118.97(10)
		C(13)-C(8)-C(2)	121.46(9)
		C(10)-C(9)-C(8)	120.23(10)
		C(11)-C(10)-C(9)	120.11(10)
		C(10)-C(11)-C(12)	119.85(10)
		C(13)-C(12)-C(11)	120.40(11)
		C(12)-C(13)-C(8)	119.89(10)

Atomic coordinates and total energies:

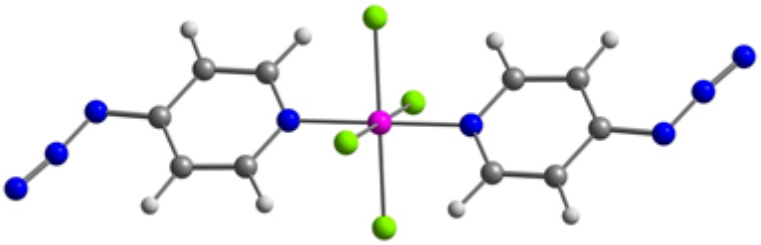

Figure S10. Optimized molecular structure of **2'**.

PBE0:

final single point energy: -2963.721207899691 a.u.
final Gibbs free energy: -2963.57161262 a.u.

Table S3. Atomic coordinates for optimized structure of **2'**.

Si	2.72384900	5.29550400	-0.13199800
Cl	1.14534100	3.77508700	-0.06065900
Cl	4.27354600	3.74422600	-0.06583800
Cl	4.30235700	6.81592200	-0.20334600
Cl	1.17415300	6.84678400	-0.19814900
C	2.73375000	6.67387100	3.83721000
C	2.72702100	5.51070900	4.60188100
C	2.72362600	4.28266000	3.94111000
C	2.72337100	4.26789800	2.56839000
C	2.73427200	6.56948200	2.46917400
C	2.71336500	4.02152500	-2.73317000
C	2.71390100	3.91713500	-4.10120600
C	2.72071300	5.08029600	-4.86587800
C	2.72417100	6.30834500	-4.20510800
C	2.72440700	6.32310800	-2.83238900
H	2.71826900	3.33652800	2.02235600
H	2.73875600	7.44836100	1.84388800
H	2.73744000	7.64640600	4.31018000
H	2.70881800	3.14264700	-2.10788300
H	2.71016000	2.94459900	-4.57417400
H	2.71974900	3.34329400	4.47715600
H	2.72811500	7.24771000	-4.74115600
H	2.72956000	7.25447900	-2.28635500
N	2.73260700	6.79102600	-7.66958100
N	2.72447200	5.66427500	5.98297300
N	2.72847900	5.38743800	1.83481800
N	2.71589000	4.64180300	6.67058900
N	2.71922100	5.20357000	-2.09881500
N	2.72328100	4.92672700	-6.24696900
N	2.71529400	3.79997300	7.40558200
N	2.73194300	5.94919700	-6.93458600

Figure S11. Optimized molecular structure of **2''**.

PBE0:

final single point energy: -2963.720885691764 a.u.
final Gibbs free energy: -2963.57146238 a.u.

Table S4. Atomic coordinates for optimized structure of **2''**.

Si	1.94516400	-2.36224200	1.57940700
Cl	4.14030900	-2.36138700	1.57902700
Cl	1.94579300	-0.17325300	1.57893400
Cl	-0.24882600	-2.36309100	1.57931500
Cl	1.94832600	-4.55123100	1.58040700
N	1.87901500	-2.43885300	7.70910100
N	2.61562000	-1.69366200	8.35751900
N	3.23156000	-1.08008500	9.06010100
N	1.94404000	-2.36282300	3.55236400
N	1.94388700	-2.36165600	-0.39355800
N	1.87791300	-2.28612900	-4.55029300
N	2.62018000	-3.02587600	-5.19882100
N	3.24076400	-3.63490200	-5.90149400
C	2.78238000	-1.51178100	5.61104900
C	2.74944400	-1.54284200	4.23873000
C	1.13823200	-3.18687500	4.23699700
C	1.10876600	-3.22102000	5.60781200
C	1.94509700	-2.36861100	6.32337600
C	1.13167400	-1.54358200	-1.07808400
C	1.10182000	-1.50967100	-2.44889600
C	1.94466900	-2.35586500	-3.16457700
C	2.78862500	-3.20646800	-2.45236400
C	2.75554900	-3.17566400	-1.08004100
H	0.49164300	-0.90379700	-0.49131900
H	3.38372600	-0.89514000	3.65426300
H	0.43208900	-0.83456900	-2.96202000
H	0.44436500	-3.90110100	6.12102700
H	3.45632400	-0.82532000	6.10537800
H	3.46785500	-3.88789200	-2.94678600
H	0.50320600	-3.83145500	3.65031400
H	3.39494600	-3.81858600	-0.49566500

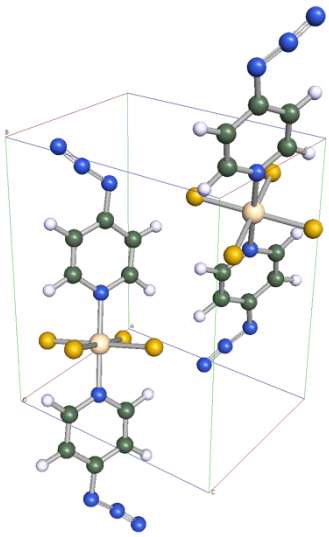

Figure S12. Optimized crystal structure of **2'** (perspective view of the optimized unit cell with the two molecules of **2'** contained therein).

PBE:

final single point energy: -5905.3937808735 a.u.

cell parameters: a = 7.332073 Å, b = 10.78938 Å, c = 9.203535 Å,
α = 90.0581187752°, β = 95.2484962287°, γ = 90.0916130243°,

Table S5. Atomic coordinates for optimized structure of **2'**.

Si	1.62492600	2.67282700	2.70245500
Si	4.86819600	8.05689100	7.28681400
Cl	-0.43972100	3.50950700	3.09617700
Cl	1.11429700	2.37039600	0.54701800
Cl	4.35600000	8.35737300	5.13154500
Cl	3.69053500	1.83736200	2.30618600
Cl	2.13237700	2.97514000	4.85834900
Cl	5.38278600	7.75544700	9.44086800
Cl	6.92932000	8.90052000	6.88851300
Cl	2.80572800	7.21403900	7.68555400
C	3.09205000	7.09999800	1.94458800
C	3.90035300	6.20520000	2.65508500
C	3.46794500	4.90616600	2.80884800
C	1.90344400	6.63046900	1.37339100
C	1.52542200	5.32477700	1.57356200
C	-0.20964100	0.42952800	2.59790700
C	-0.63386000	-0.87225800	2.75383100
C	0.17956100	-1.76155900	3.46540000
C	1.36543800	-1.28397700	4.03539900
C	1.73521400	0.02395100	3.83411900

C	5.14227800	4.10370300	5.94889400
C	4.76717200	5.40956400	6.15272900
C	6.32850900	3.62916500	6.52075500
C	7.13814800	4.52007800	7.23440500
C	6.70980200	5.82036800	7.39025900
C	3.01930800	10.28509300	7.17860000
C	2.58615400	11.58456900	7.32725700
C	3.39116300	12.48104800	8.03951300
C	4.57908100	12.01379000	8.61442300
C	4.96045600	10.70881000	8.41481800
H	-1.58408600	-1.19686500	2.33614800
H	4.05429000	4.16371000	3.33765000
H	0.59229800	4.92963500	1.18026300
H	2.03937800	-1.93983900	4.58669800
H	2.66633000	0.42562300	4.22578000
H	4.47163800	3.44718800	5.39455300
H	3.83519800	5.80819000	5.76026800
H	8.08686500	4.19719100	7.65679200
H	7.29712900	6.56019300	7.92156200
H	2.43318500	9.53960100	6.65384900
H	1.63612100	11.90160200	6.90291500
H	4.85239800	6.52235400	3.07438700
H	-0.79980600	1.16788900	2.06717400
H	5.24560100	12.67561600	9.16778600
H	1.23456900	7.29031800	0.82064400
H	5.89507700	10.31624200	8.80761100
N	0.53460600	-3.84741700	4.24786800
N	1.12966400	-4.63476400	4.85146400
N	5.52964900	6.26725900	6.87899000
N	6.72546100	2.28962700	6.43638700
N	5.97844700	1.54265300	5.73902400
N	5.38381700	0.75355000	5.13738700
N	4.20166900	9.84540200	7.69154300
N	0.96910100	0.87993800	3.10935800
N	2.28622700	4.46356700	2.29744000
N	3.49311100	8.43827700	1.86257800
N	2.74761500	9.19010800	1.16840700
N	-0.21303500	-3.10238200	3.54881200
N	2.15543500	9.98303100	0.56955600
N	2.98662100	13.81836400	8.12080200
N	3.72859300	14.57162500	8.81757000
N	4.31696400	15.36599500	9.41795800

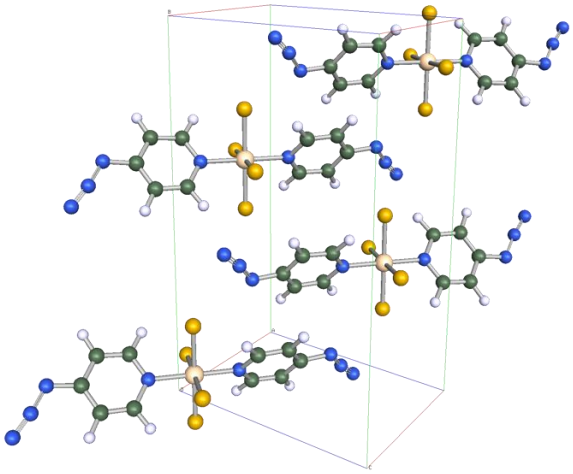

Figure S13. Optimized crystal structure of **2''** (perspective view of the optimized unit cell with the four molecules of **2''** contained therein).

PBE:

final single point energy: -11810.7336603415 a.u.

cell parameters: a = 8.17893 Å, b = 17.395311 Å, c = 10.93546 Å,
α = 89.9513496613°, β = 99.4572766531°, γ = 90.0341808038°,

Table S6. Atomic coordinates for optimized structure of **2''**.

Si	8.88041800	15.10784300	8.17346200
Si	-2.47811800	2.48939500	2.77109100
Si	1.60619900	11.18400300	2.76660500
Si	4.79625900	6.41378500	8.17733200
Cl	-2.47601800	4.72879100	2.77074400
Cl	1.61040100	13.42360800	2.75712400
Cl	4.79644200	8.65080300	8.16227300
Cl	0.00375100	11.16067100	4.33985000
Cl	3.19717500	6.45529500	9.75301800
Cl	1.60590300	8.94678900	2.78163800
Cl	3.20550900	11.14249400	1.19104300
Cl	-2.47734500	0.25197000	2.77024600
Cl	-4.07678200	2.45657400	4.34878000
Cl	4.79212500	4.17435300	8.18667200
Cl	-0.88099600	2.45623600	1.19393200
Cl	6.39841000	6.43737400	6.60393800
Cl	8.87987000	17.34529600	8.17508300
Cl	8.87817200	12.86813100	8.17414900
Cl	7.28302900	15.14076000	9.75054200
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C	3.43452100	5.47041000	5.80069300
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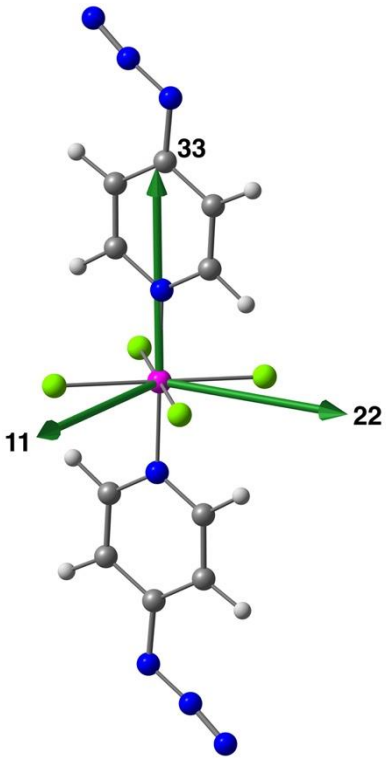

Figure S14. Graphical representation of the directions of the principal axes of the ^{29}Si CSA tensor of the optimized molecular structure of **2'** ($\delta_{11} > \delta_{22} > \delta_{33}$).

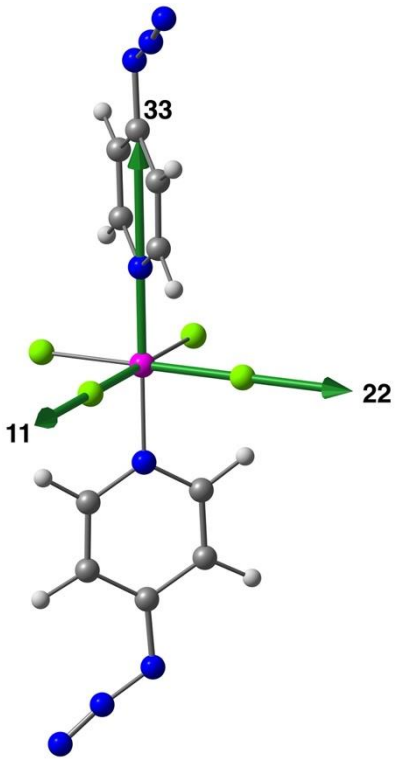

Figure S15. Graphical representation of the directions of the principal axes of the ^{29}Si CSA tensor of the optimized molecular structure of **2''** ($\delta_{11} > \delta_{22} > \delta_{33}$).

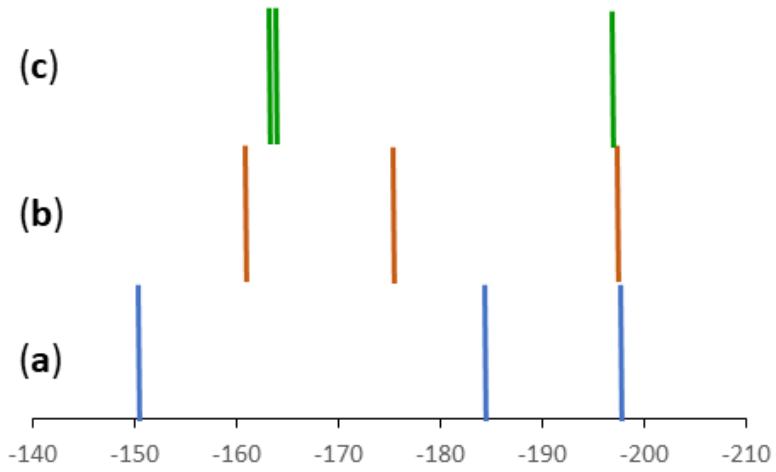

Figure S16. Graphical representation of the differences of the principal values of the ^{29}Si CSA tensor of (**a**) **2'** (experimental data), (**b**) **2''** (experimental data) and (**c**) the optimized molecular structure of **2''** ($\delta_{11} > \delta_{22} > \delta_{33}$).