Supporting information for:

Copper Complexes of Silicon Pyridine-2-olates *R*Si(pyO)$_3$ (*R* = Me, Ph, Bn, Allyl) and Ph$_2$Si(pyO)$_2$

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Contents

Compound **1c** (BnSi(pyO)$_3$, $C_{22}H_{19}N_3O_3Si$). A Schlenk flask was charged with magnetic stirring bar and 2-hydroxypyridine (3.00 g, 31.6 mmol), then evacuated and set under Ar atmosphere prior to adding THF (40 mL) and triethylamine (3.80 g, 37.6 mmol). The resultant mixture was stirred in an ice bath, and benzyltrichlorosilane (2.50 g, 11.1 mmol) was added dropwise via syringe through a septum. Upon completed addition of silane, stirring in ice bath was continued for 1 h, whereupon the flask was stored at 5 °C for 2 h. Thereafter, the triethylamine hydrochloride precipitate was removed by filtration and washed with THF (20 mL). From the combined filtrate and washings, the solvent was removed under reduced pressure (condensation into a cold trap) to afford a colorless solid. This crude product was dissolved into hot THF (6 mL), filtered hot (to remove some turbidity), and then hexane (3 mL) was added to the hot filtrate, which was then allowed to crystallize upon cooling to room temperature. After 3 h, the flask was transferred into a fridge and was stored at 5 °C overnight to complete crystallization. From the coarse crystalline product the supernatant was removed by decantation, the crystals were washed with a mixture of THF (2 mL) and hexane (2 mL) and dried in vacuum. Yield: 2.97 g (7.40 mmol, 70%). Elemental analysis calculated for $C_{22}H_{19}N_3O_3Si$ (401.49 g·mol^{-1}): C, 65.81%; H, 4.77%; N, 10.47%; found C, 65.75%; H, 4.80%; N, 10.45%. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.07 (m, 3H, H^6), 7.49 (ddd, 3H, 8.2, 7.3, 2.1 Hz, H^4), 7.10-6.97 (mm, 5H, Ph), 6.84 (m, 3H, H^5), 6.76 (d, 3H, 8.2 Hz, H^3), 3.11 (s, 2H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 160.4 (C^2), 147.2 (C^6), 139.2 (C^4), 136.0 (Ph-i), 129.0, 128.0 (Ph-o/m), 124.8 (Ph-p), 118.1 (C^5), 113.0 (C^3), 22.6 (CH_2); ^{29}Si{^{1}H} NMR ($CDCl_3$): δ (ppm) −54.7.

Compound **1d** (AllylSi(pyO)$_3$, $C_{18}H_{17}N_3O_3Si$). A Schlenk flask was charged with magnetic stirring bar and 2-hydroxypyridine (3.00 g, 31.6 mmol), then evacuated and set under Ar atmosphere prior to adding THF (40 mL) and triethylamine (4.00 g, 39.6 mmol). The resultant mixture was stirred in an ice bath, and allyltrichlorosilane (2.00 g, 11.4 mmol) was added dropwise via syringe through a septum. Upon completed addition of silane, stirring in ice bath was continued for 1 h, whereupon the flask was stored at 5 °C overnight. Thereafter, the triethylamine hydrochloride precipitate was removed by filtration and washed with THF (15 mL). From the combined filtrate and washings, the solvent was removed under reduced pressure (condensation into a cold trap) to afford a beige oil. This crude product was dissolved into hot THF (2 mL) and hexane (2 mL), filtered hot (to remove some turbidity), and then further hexane (2 mL) was added to the hot filtrate, which was then stored at 5 °C for 6 h and at −24 °C overnight for crystallization. From the crystalline product the supernatant was removed by decantation at −10 °C (flask stored in an ice/ethanol bath), the crystals were washed with a cold (−10 °C) mixture of THF (2 mL) and hexane (2 mL) and dried in vacuum. Yield: 2.70 g (7.68 mmol, 73%). Elemental analysis calculated for $C_{18}H_{17}N_3O_3Si$ (351.43 g·mol^{-1}): C, 61.52%; H, 4.88%; N, 11.96%; found C, 61.41%; H, 4.69%; N, 11.95%. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.07 (m, 3H, H^6), 7.54 (m, 3H, H^4), 6.90-6.80 (mm, 6H, H^{3,5}), 5.92 (m, 1H, incl. 17.1, 10.1, 7.8 Hz, Allyl =CH), 4.91 (m, 1H, incl. $^3J_{HH(trans)}$ 17.1 Hz, $=CH_2$), 4.86 (m, 1H, incl. $^3J_{HH(cis)}$ 10.1 Hz, $=CH_2$), 2.52 (m, 2H, incl. 7.8 Hz, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 160.5 (C^2), 147.3 (C^6), 139.2 (C^4), 131.1 (Allyl =CH), 118.1 (C^5), 115.6 (Allyl CH_2), 113.0 (C^3), 20.8 (CH_2); ^{29}Si{^{1}H} NMR ($CDCl_3$): δ (ppm) −53.4.

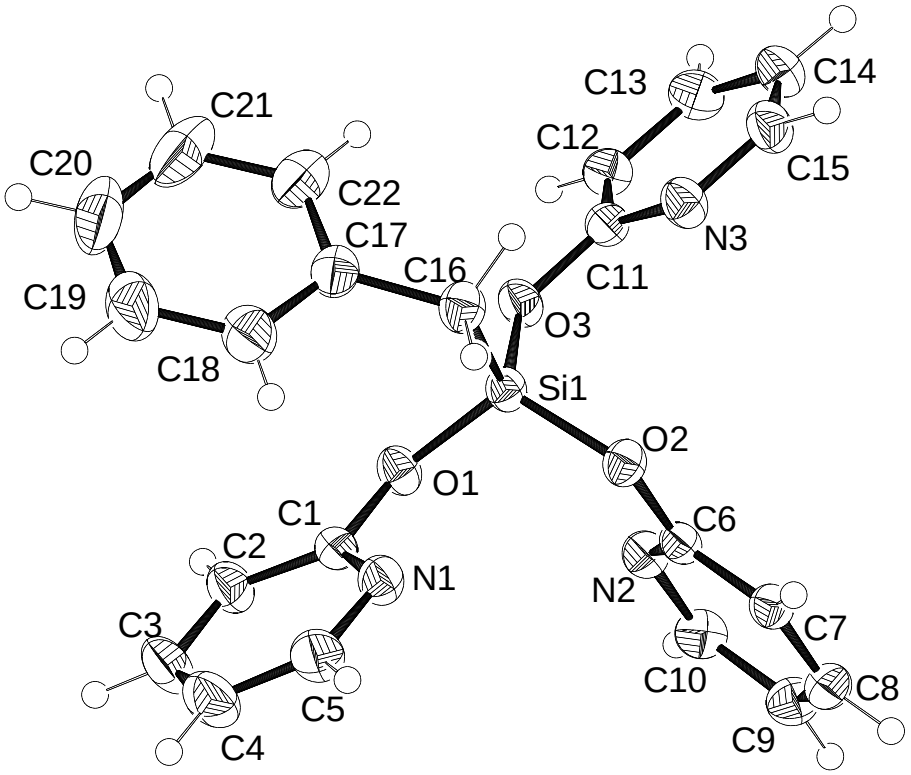

Figure S1. Molecular structure of **2c** in the crystal (ORTEP representation with thermal displacement ellipsoids at the 50% probability level).

Table S1. Bond lengths [Å] of **2c** in the crystal.

Bond	Bond Length [Å]	Bond	Bond Length [Å]
Si(1)-O(2)	1.6405(12)	C(4)-C(5)	1.374(3)
Si(1)-O(3)	1.6410(12)	C(6)-C(7)	1.391(2)
Si(1)-O(1)	1.6457(12)	C(7)-C(8)	1.377(2)
Si(1)-C(16)	1.8564(18)	C(8)-C(9)	1.392(2)
O(1)-C(1)	1.3655(19)	C(9)-C(10)	1.384(2)
O(2)-C(6)	1.3635(19)	C(11)-C(12)	1.393(2)
O(3)-C(11)	1.3648(19)	C(12)-C(13)	1.377(2)
N(1)-C(1)	1.323(2)	C(13)-C(14)	1.391(3)
N(1)-C(5)	1.348(2)	C(14)-C(15)	1.379(3)
N(2)-C(6)	1.328(2)	C(16)-C(17)	1.515(2)
N(2)-C(10)	1.346(2)	C(17)-C(22)	1.383(3)
N(3)-C(11)	1.325(2)	C(17)-C(18)	1.393(3)
N(3)-C(15)	1.347(2)	C(18)-C(19)	1.386(3)
C(1)-C(2)	1.389(2)	C(19)-C(20)	1.367(4)
C(2)-C(3)	1.383(3)	C(20)-C(21)	1.365(4)
C(3)-C(4)	1.390(3)	C(21)-C(22)	1.397(3)

Table S2. Bond angles [deg] of **2c** in the crystal.

Atoms	Bond Angle [deg.]	Atoms	Bond Angle [deg.]
O(2)-Si(1)-O(3)	114.13(6)	O(2)-C(6)-C(7)	118.11(14)
O(2)-Si(1)-O(1)	113.84(6)	C(8)-C(7)-C(6)	117.56(15)
O(3)-Si(1)-O(1)	97.74(6)	C(7)-C(8)-C(9)	119.62(16)
O(2)-Si(1)-C(16)	107.35(7)	C(10)-C(9)-C(8)	118.13(16)
O(3)-Si(1)-C(16)	111.60(7)	N(2)-C(10)-C(9)	123.30(15)
O(1)-Si(1)-C(16)	112.13(7)	N(3)-C(11)-O(3)	117.89(14)
C(1)-O(1)-Si(1)	124.80(10)	N(3)-C(11)-C(12)	124.62(15)
C(6)-O(2)-Si(1)	127.29(10)	O(3)-C(11)-C(12)	117.48(14)
C(11)-O(3)-Si(1)	128.64(10)	C(13)-C(12)-C(11)	117.61(15)
C(1)-N(1)-C(5)	116.60(15)	C(12)-C(13)-C(14)	119.47(16)
C(6)-N(2)-C(10)	117.01(14)	C(15)-C(14)-C(13)	117.92(16)
C(11)-N(3)-C(15)	116.32(15)	N(3)-C(15)-C(14)	124.04(16)
N(1)-C(1)-O(1)	116.84(14)	C(17)-C(16)-Si(1)	110.61(11)
N(1)-C(1)-C(2)	125.13(15)	C(22)-C(17)-C(18)	118.20(19)
O(1)-C(1)-C(2)	118.02(14)	C(22)-C(17)-C(16)	121.15(18)
C(3)-C(2)-C(1)	116.94(16)	C(18)-C(17)-C(16)	120.58(18)
C(2)-C(3)-C(4)	119.43(17)	C(19)-C(18)-C(17)	120.5(2)
C(5)-C(4)-C(3)	118.60(18)	C(20)-C(19)-C(18)	120.8(3)
N(1)-C(5)-C(4)	123.29(17)	C(21)-C(20)-C(19)	119.4(2)
N(2)-C(6)-O(2)	117.52(14)	C(20)-C(21)-C(22)	120.7(3)
N(2)-C(6)-C(7)	124.37(15)	C(17)-C(22)-C(21)	120.4(2)

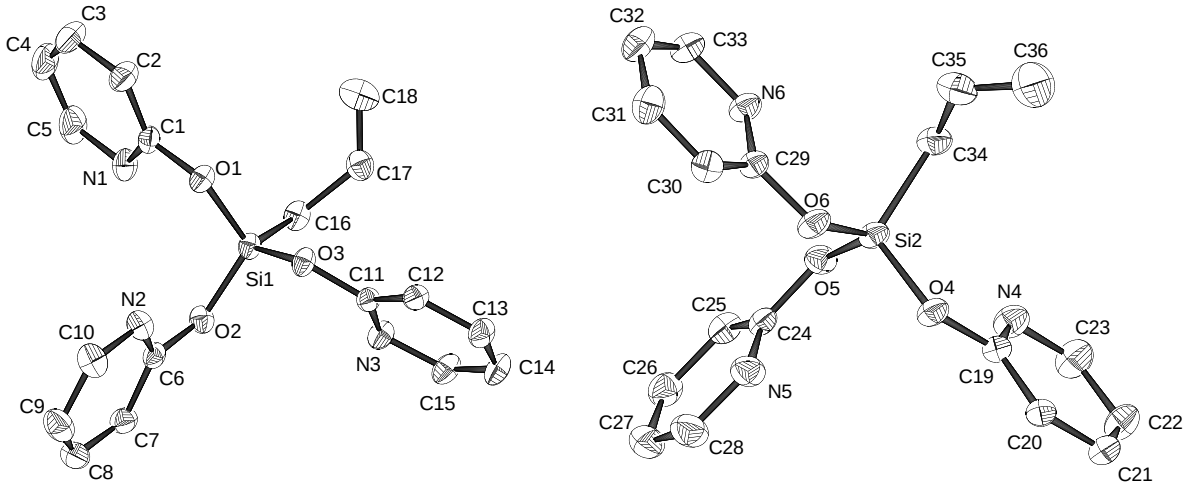

Figure S2. Molecular structure of **2d** in the crystal (ORTEP representation of the two independent molecules of the asymmetric unit with thermal displacement ellipsoids at the 30% probability level, hydrogen atoms are not depicted for clarity). The allyl groups (C17, C18 as well as C35, C36) are disordered over two positions with site occupancy ratios of 0.917(5):0.083(5) and 0.740(8):0.260(8), respectively. Only the predominant part of this disorder is shown.

Table S3. Bond lengths [Å] of **2d** in the crystal.

Bond	Bond Length [Å]	Bond	Bond Length [Å]
Si(1)-O(1)	1.6459(15)	Si(2)-O(5)	1.6326(18)
Si(1)-O(2)	1.6488(16)	Si(2)-O(6)	1.6464(17)
Si(1)-O(3)	1.6489(15)	Si(2)-O(4)	1.6469(16)
Si(1)-C(16)	1.839(3)	Si(2)-C(34)	1.840(2)
O(1)-C(1)	1.358(3)	O(4)-C(19)	1.371(3)
O(2)-C(6)	1.363(3)	O(5)-C(24)	1.370(3)
O(3)-C(11)	1.367(3)	O(6)-C(29)	1.364(3)
N(1)-C(1)	1.318(3)	N(4)-C(19)	1.316(3)
N(1)-C(5)	1.346(3)	N(4)-C(23)	1.348(3)
N(2)-C(6)	1.318(3)	N(5)-C(24)	1.323(3)
N(2)-C(10)	1.340(3)	N(5)-C(28)	1.347(3)
N(3)-C(11)	1.317(3)	N(6)-C(29)	1.327(3)
N(3)-C(15)	1.348(3)	N(6)-C(33)	1.346(3)
C(1)-C(2)	1.385(3)	C(19)-C(20)	1.384(3)
C(2)-C(3)	1.376(4)	C(20)-C(21)	1.379(4)
C(3)-C(4)	1.378(5)	C(21)-C(22)	1.374(4)
C(4)-C(5)	1.361(5)	C(22)-C(23)	1.370(4)
C(6)-C(7)	1.389(3)	C(24)-C(25)	1.375(3)
C(7)-C(8)	1.377(4)	C(25)-C(26)	1.376(4)
C(8)-C(9)	1.380(4)	C(26)-C(27)	1.381(4)
C(9)-C(10)	1.375(4)	C(27)-C(28)	1.368(4)
C(11)-C(12)	1.381(3)	C(29)-C(30)	1.386(3)
C(12)-C(13)	1.370(3)	C(30)-C(31)	1.372(4)
C(13)-C(14)	1.383(3)	C(31)-C(32)	1.391(4)
C(14)-C(15)	1.372(4)	C(32)-C(33)	1.362(4)
C(16)-C(17)	1.511(4)	C(34)-C(35)	1.490(5)
C(17)-C(18)	1.292(4)	C(35)-C(36)	1.313(6)

Table S4. Bond angles [deg] of **2c** in the crystal.

Atoms	Bond Angle [deg.]	Atoms	Bond Angle [deg.]
O(1)-Si(1)-O(2)	115.06(9)	O(5)-Si(2)-O(6)	112.50(9)
O(1)-Si(1)-O(3)	97.82(8)	O(5)-Si(2)-O(4)	113.32(9)
O(2)-Si(1)-O(3)	110.80(9)	O(6)-Si(2)-O(4)	98.34(8)
O(1)-Si(1)-C(16)	110.60(10)	O(5)-Si(2)-C(34)	106.25(10)
O(2)-Si(1)-C(16)	107.62(9)	O(6)-Si(2)-C(34)	113.84(10)
O(3)-Si(1)-C(16)	114.95(10)	O(4)-Si(2)-C(34)	112.74(11)
C(1)-O(1)-Si(1)	125.99(14)	C(19)-O(4)-Si(2)	125.43(14)
C(6)-O(2)-Si(1)	126.13(14)	C(24)-O(5)-Si(2)	129.50(14)
C(11)-O(3)-Si(1)	123.93(13)	C(29)-O(6)-Si(2)	126.46(14)
C(1)-N(1)-C(5)	116.5(2)	C(19)-N(4)-C(23)	116.2(2)
C(6)-N(2)-C(10)	116.7(2)	C(24)-N(5)-C(28)	116.0(2)
C(11)-N(3)-C(15)	116.5(2)	C(29)-N(6)-C(33)	116.5(2)
N(1)-C(1)-O(1)	117.19(19)	N(4)-C(19)-O(4)	117.1(2)
N(1)-C(1)-C(2)	124.5(2)	N(4)-C(19)-C(20)	124.9(2)
O(1)-C(1)-C(2)	118.3(2)	O(4)-C(19)-C(20)	118.0(2)
C(3)-C(2)-C(1)	117.3(3)	C(21)-C(20)-C(19)	117.4(2)
C(2)-C(3)-C(4)	119.7(3)	C(22)-C(21)-C(20)	119.1(2)
C(5)-C(4)-C(3)	118.3(3)	C(23)-C(22)-C(21)	118.8(3)
N(1)-C(5)-C(4)	123.8(3)	N(4)-C(23)-C(22)	123.5(3)
N(2)-C(6)-O(2)	117.3(2)	N(5)-C(24)-O(5)	116.8(2)
N(2)-C(6)-C(7)	124.4(2)	N(5)-C(24)-C(25)	125.0(2)
O(2)-C(6)-C(7)	118.4(2)	O(5)-C(24)-C(25)	118.3(2)
C(8)-C(7)-C(6)	117.4(2)	C(24)-C(25)-C(26)	117.6(2)
C(7)-C(8)-C(9)	119.8(2)	C(25)-C(26)-C(27)	119.4(3)
C(10)-C(9)-C(8)	117.7(3)	C(28)-C(27)-C(26)	118.2(3)
N(2)-C(10)-C(9)	124.0(3)	N(5)-C(28)-C(27)	123.9(3)
N(3)-C(11)-O(3)	116.65(18)	N(6)-C(29)-O(6)	117.10(19)
N(3)-C(11)-C(12)	124.6(2)	N(6)-C(29)-C(30)	124.4(2)
O(3)-C(11)-C(12)	118.74(19)	O(6)-C(29)-C(30)	118.52(19)
C(13)-C(12)-C(11)	117.8(2)	C(31)-C(30)-C(29)	117.6(2)
C(12)-C(13)-C(14)	119.3(2)	C(30)-C(31)-C(32)	119.3(2)
C(15)-C(14)-C(13)	118.3(2)	C(33)-C(32)-C(31)	118.4(2)
N(3)-C(15)-C(14)	123.4(2)	N(6)-C(33)-C(32)	123.8(2)
C(17)-C(16)-Si(1)	111.42(17)	C(35)-C(34)-Si(2)	113.7(2)
C(18)-C(17)-C(16)	126.5(3)	C(36)-C(35)-C(34)	123.4(4)

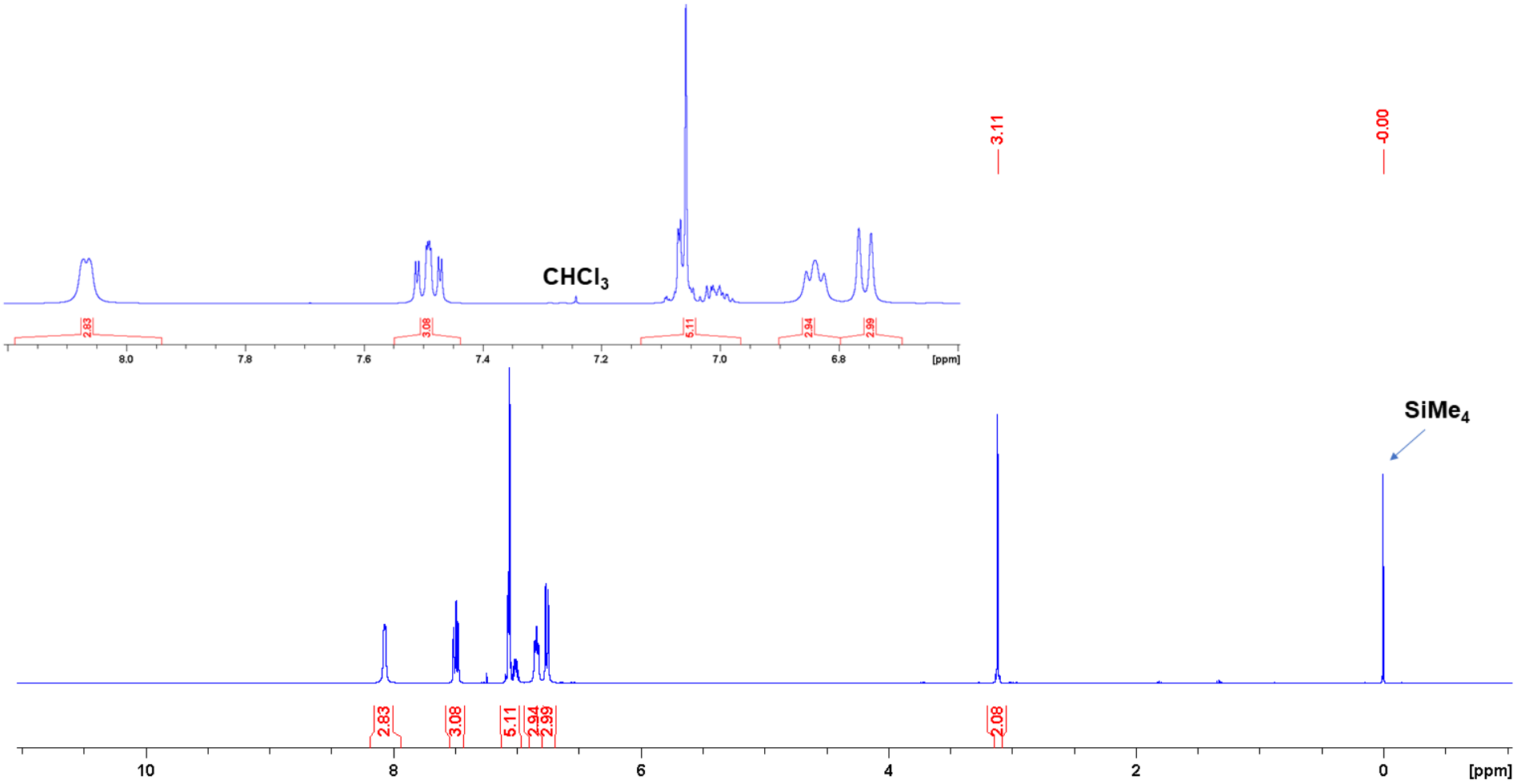

Figure S3. ^{1}H NMR spectrum of BnSi(pyO)$_3$ (**1c**) in $CDCl_3$ (full spectrum and magnified inset of group of signals).

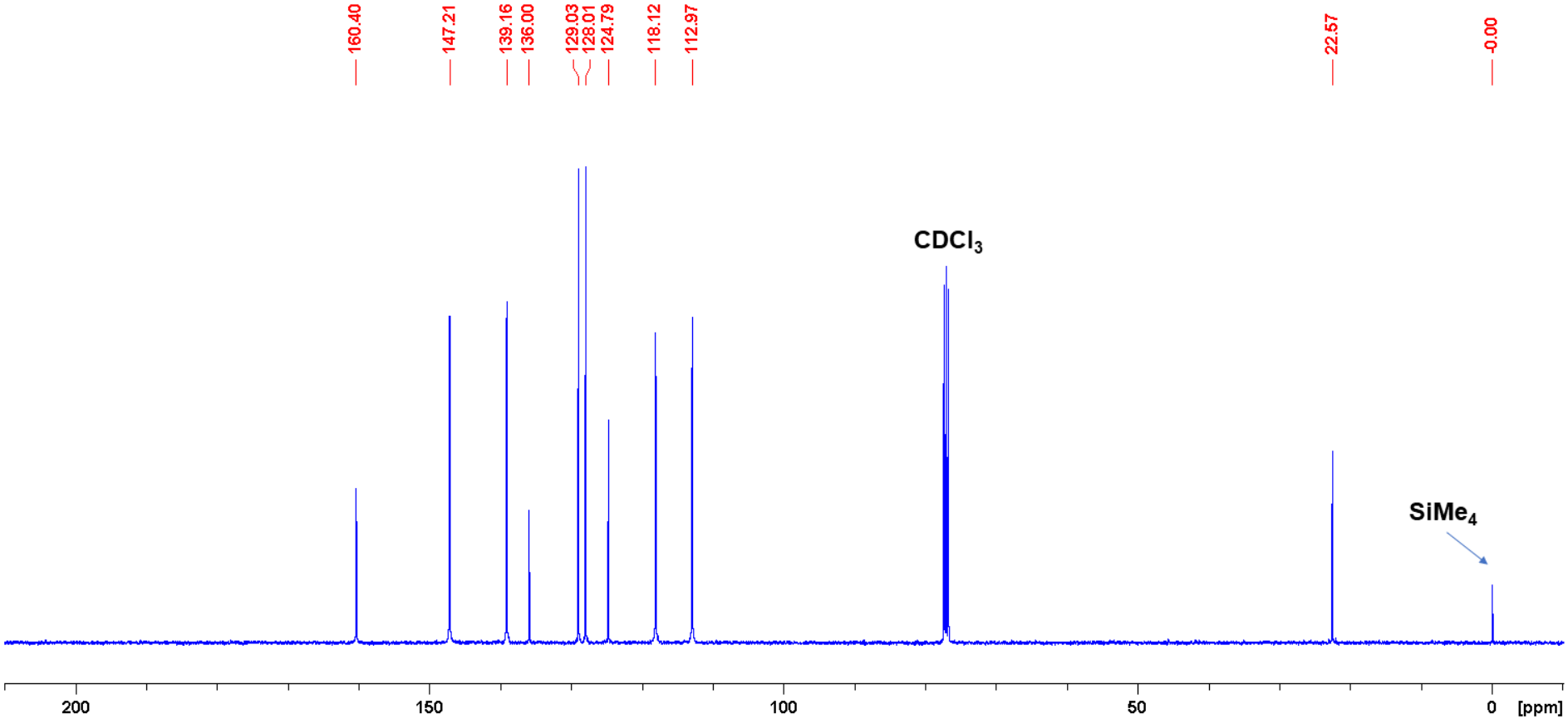

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of $BnSi(pyO)_3$ (**1c**) in $CDCl_3$.

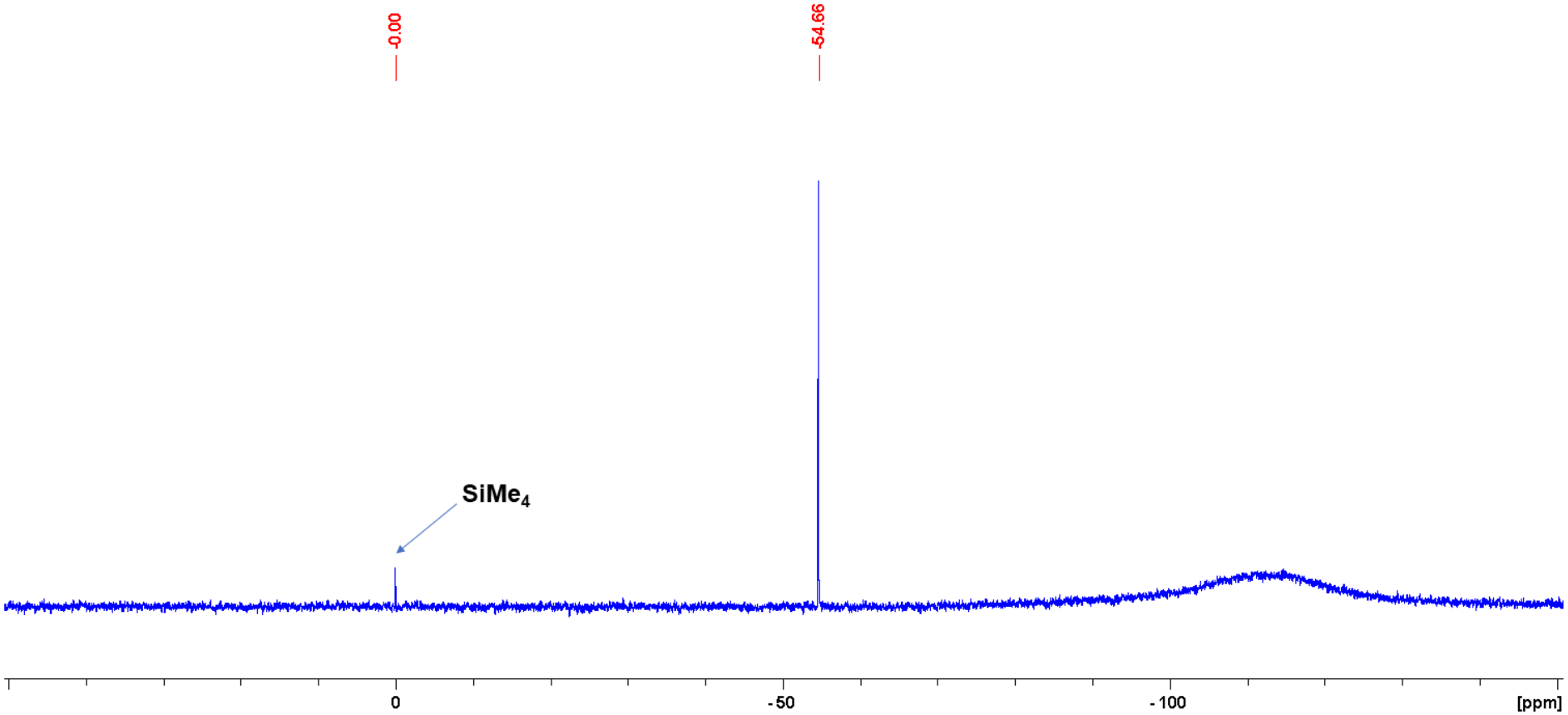

Figure S5. $^{29}Si\{^{1}H\}$ NMR spectrum of $BnSi(pyO)_3$ (**1c**) in $CDCl_3$.

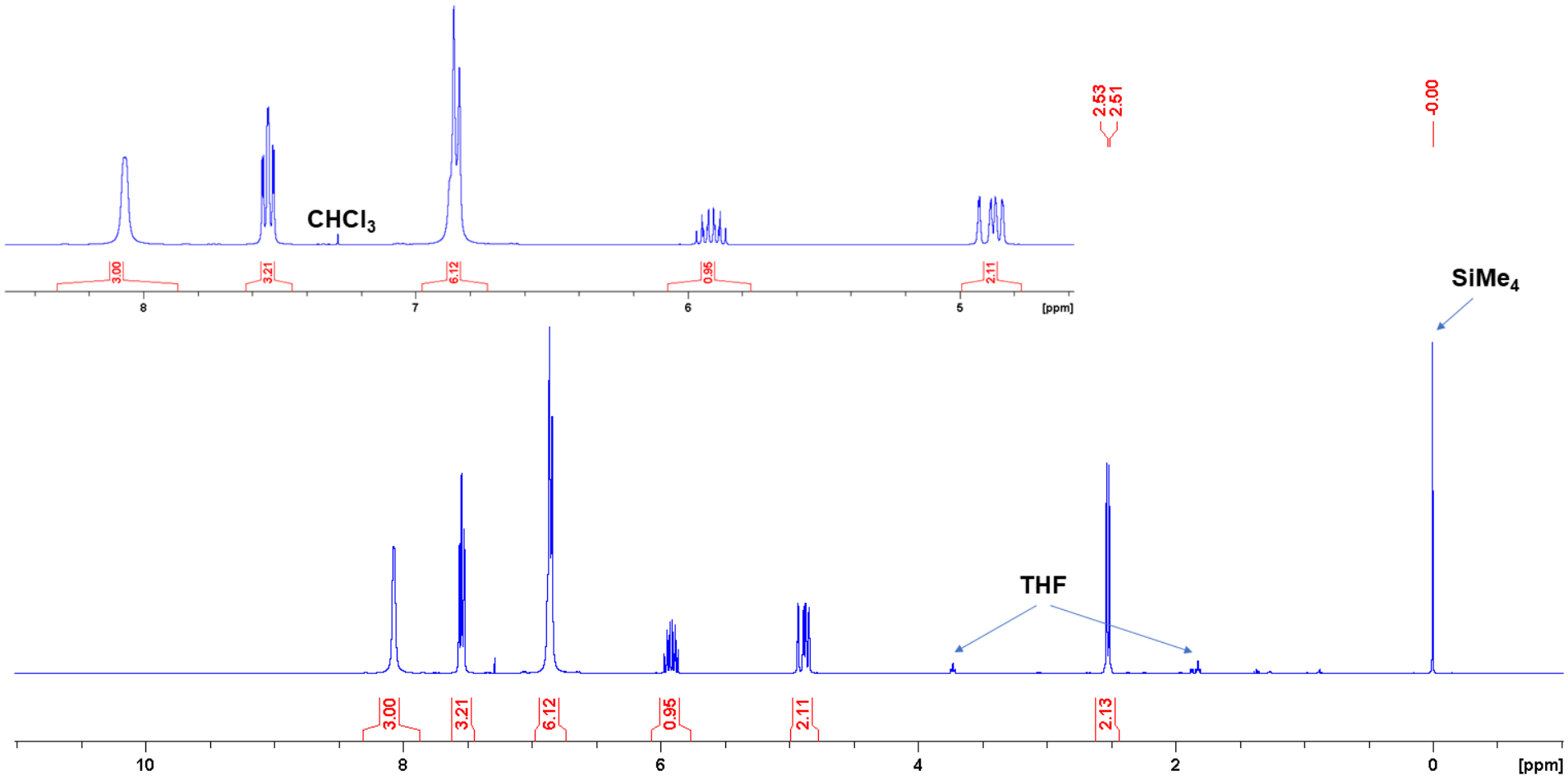

Figure S6. ^{1}H NMR spectrum of AllylSi(pyO)$_3$ (**1d**) in $CDCl_3$ (full spectrum and magnified inset of group of signals).

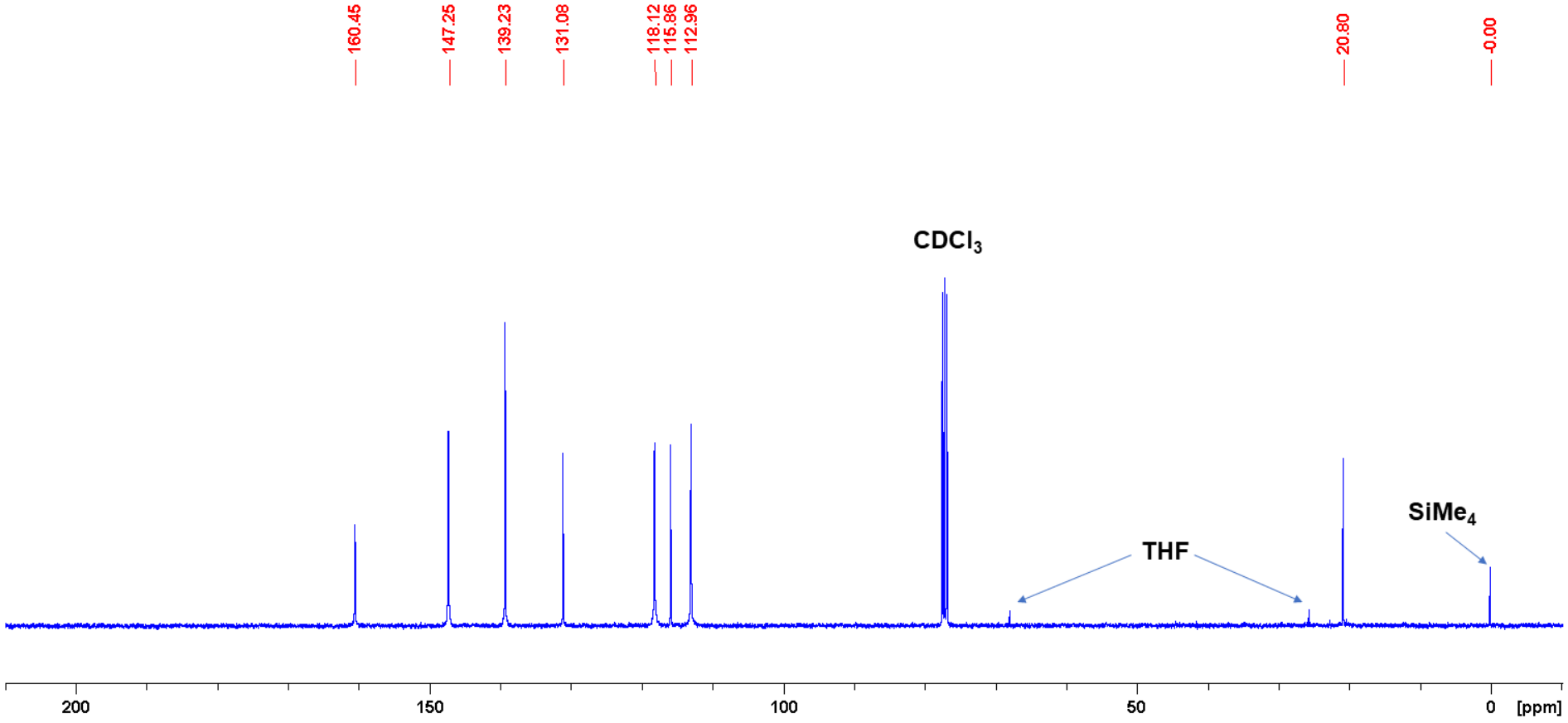

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of AllylSi(pyO)$_3$ (**1d**) in $CDCl_3$.

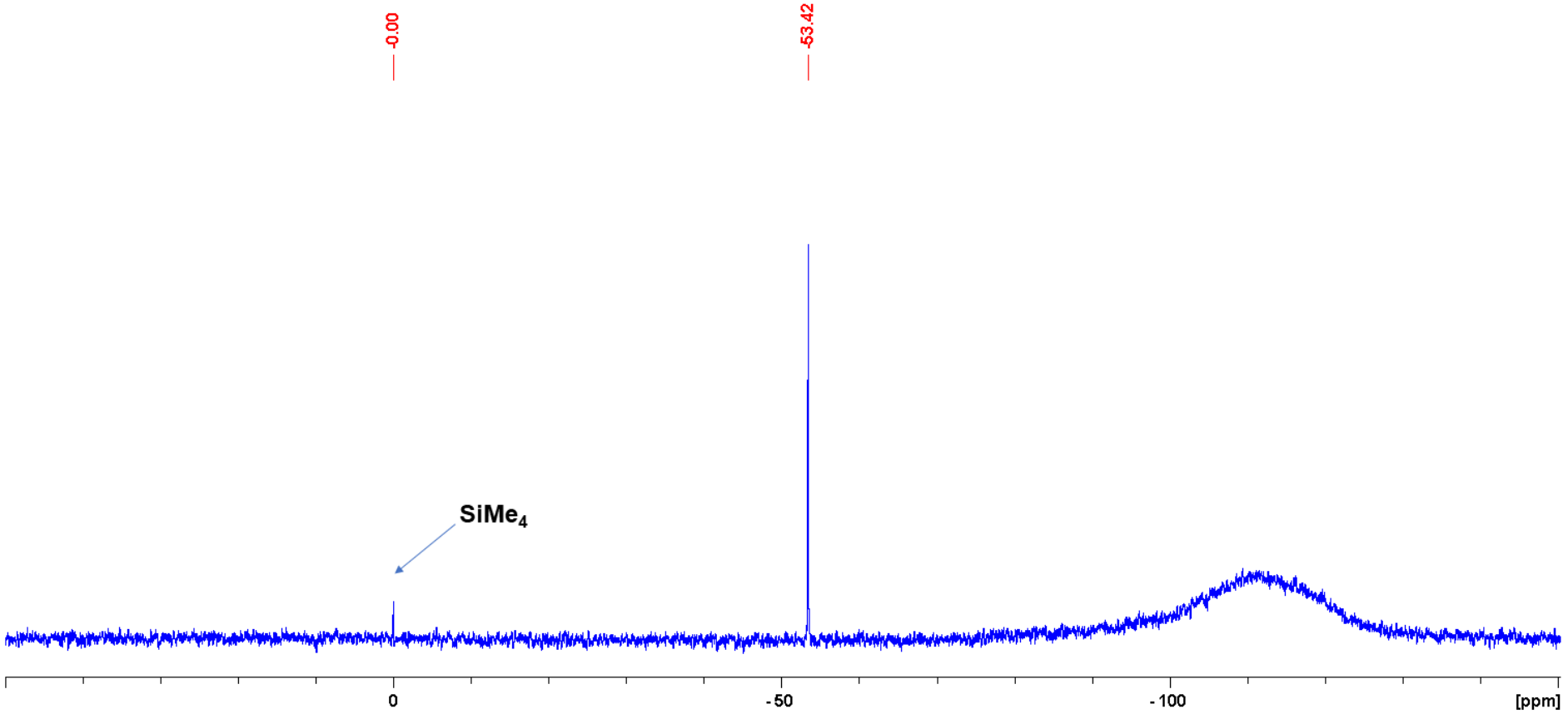

Figure S8. $^{29}Si\{^{1}H\}$ NMR spectrum of AllylSi(pyO)$_3$ (**1d**) in $CDCl_3$.

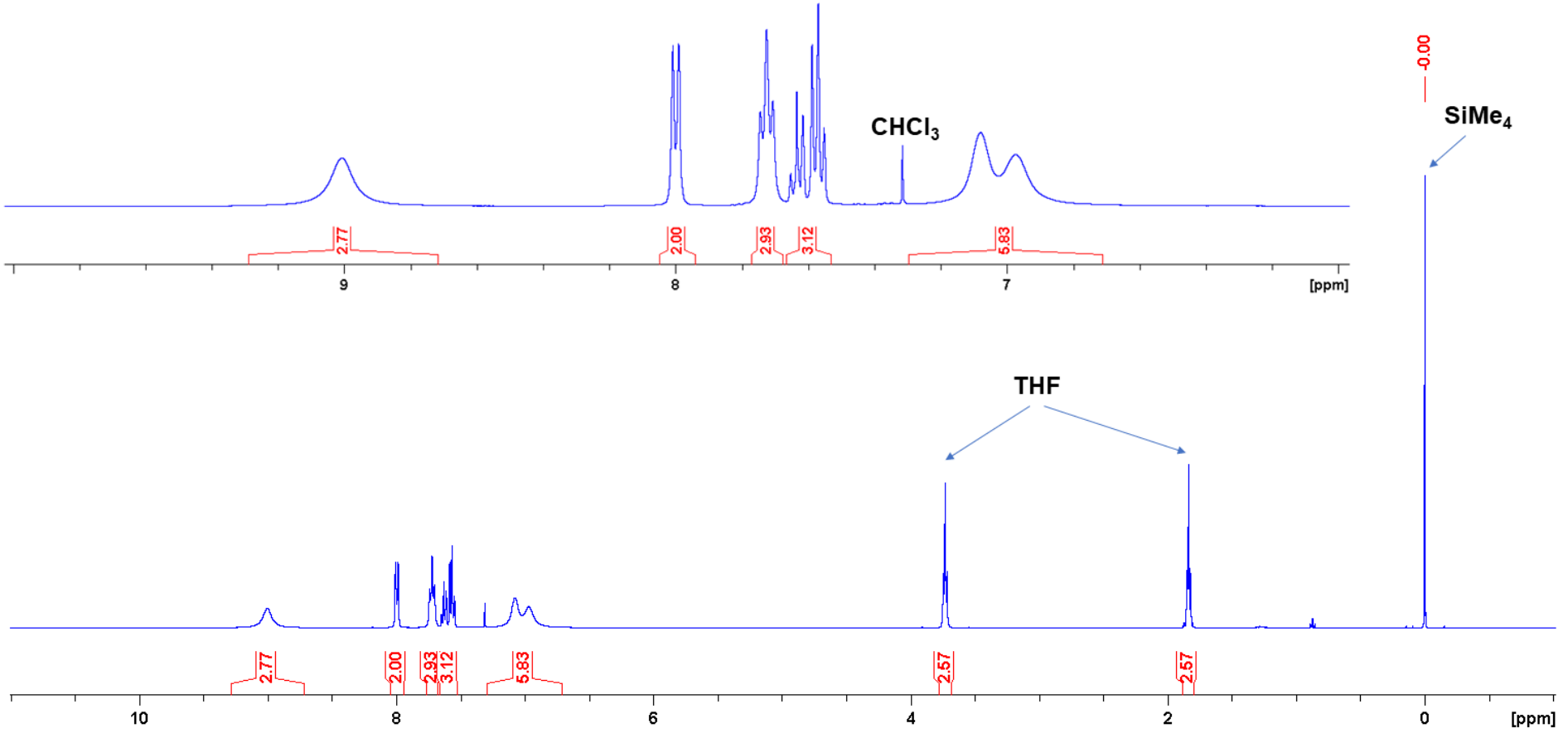

Figure S9. ^{1}H NMR spectrum of the THF solvate of PhSi(μ^2-pyO)$_3$CuCl [(**2b**)$_2$·(THF)] in $CDCl_3$ (full spectrum and magnified inset of group of signals).

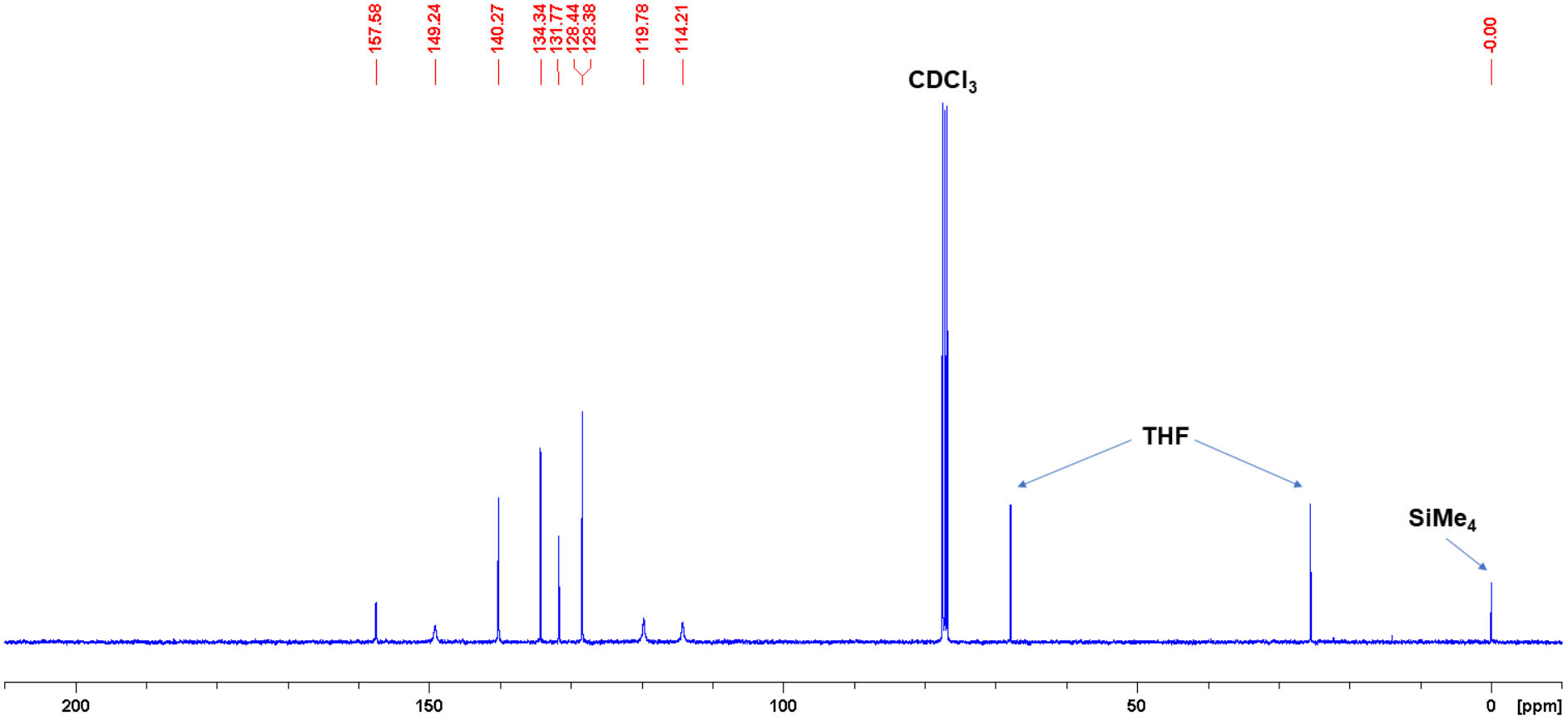

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of the THF solvate of PhSi(μ^2-pyO)$_3$CuCl [(**2b**)$_2$·(THF)] in $CDCl_3$.

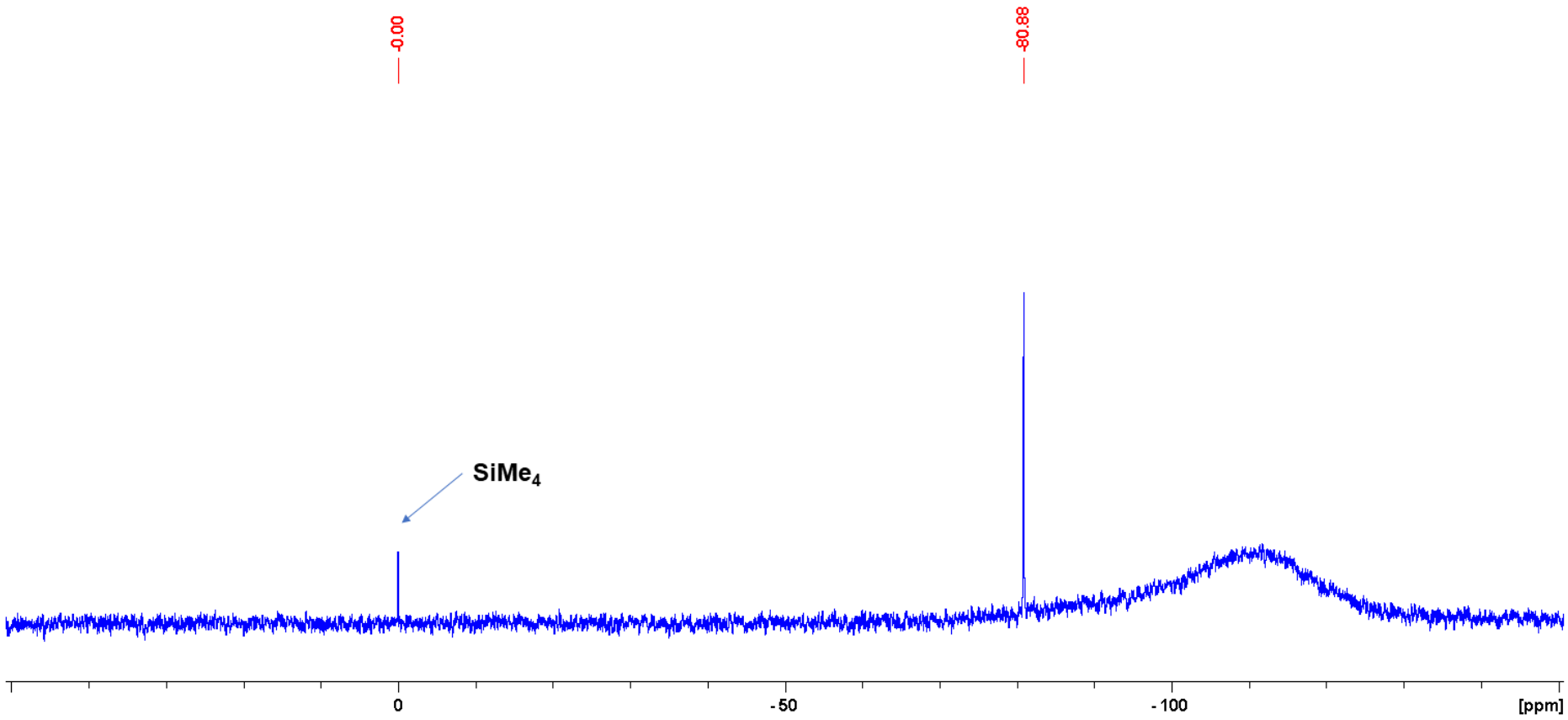

Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum of the THF solvate of PhSi(μ^2-pyO)$_3$CuCl [(**2b**)$_2$·(THF)] in $CDCl_3$.

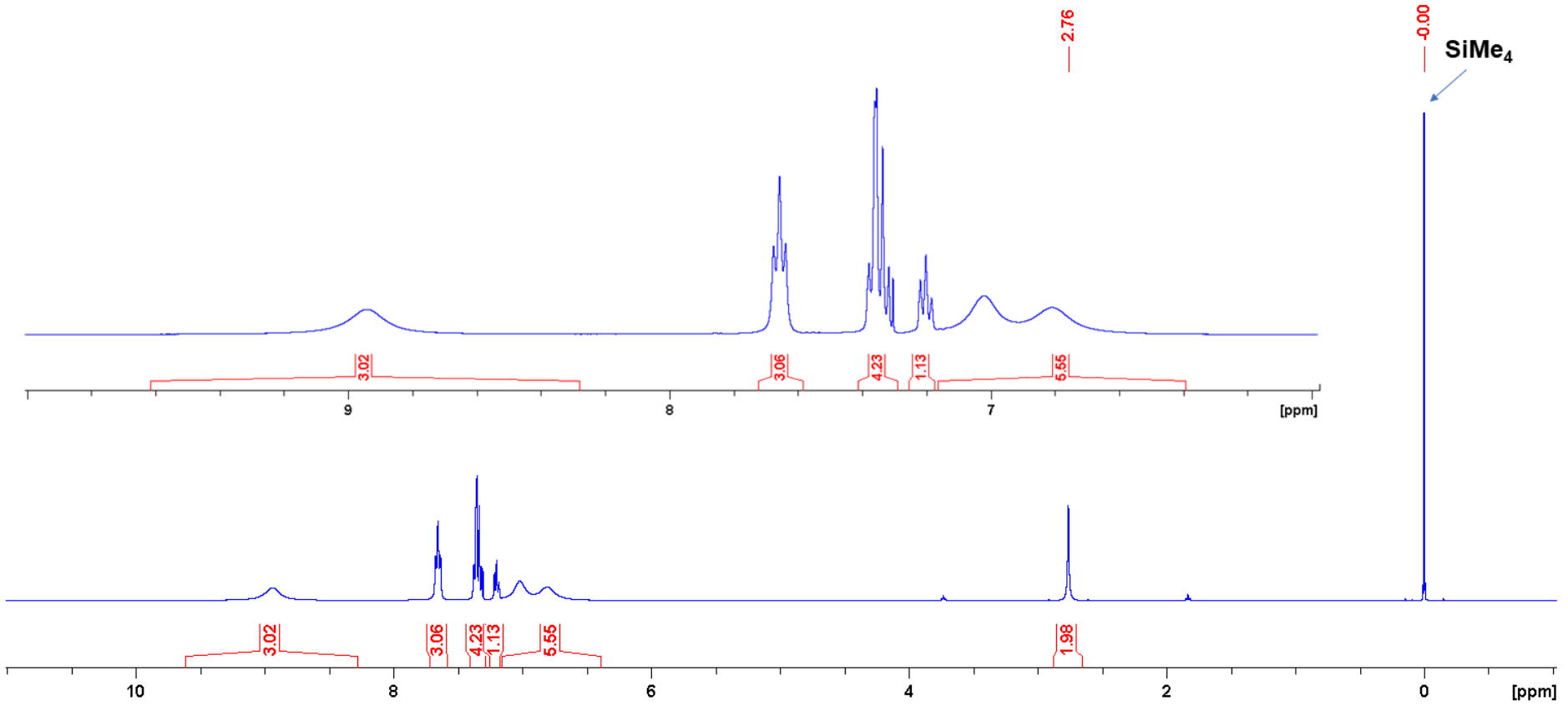

Figure S12. ^{1}H NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) in $CDCl_3$ (full spectrum and magnified inset of group of signals).

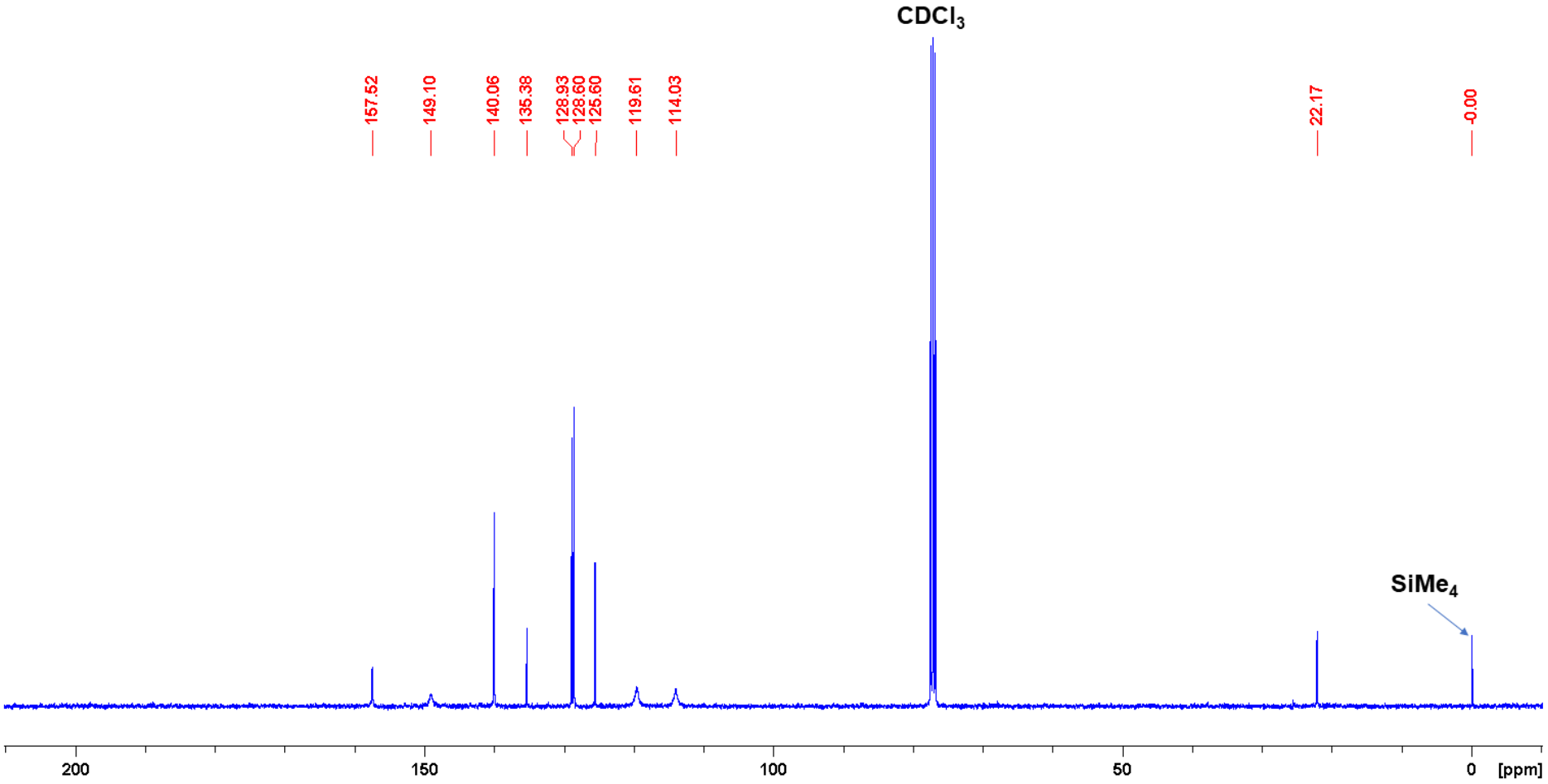

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) in $CDCl_3$.

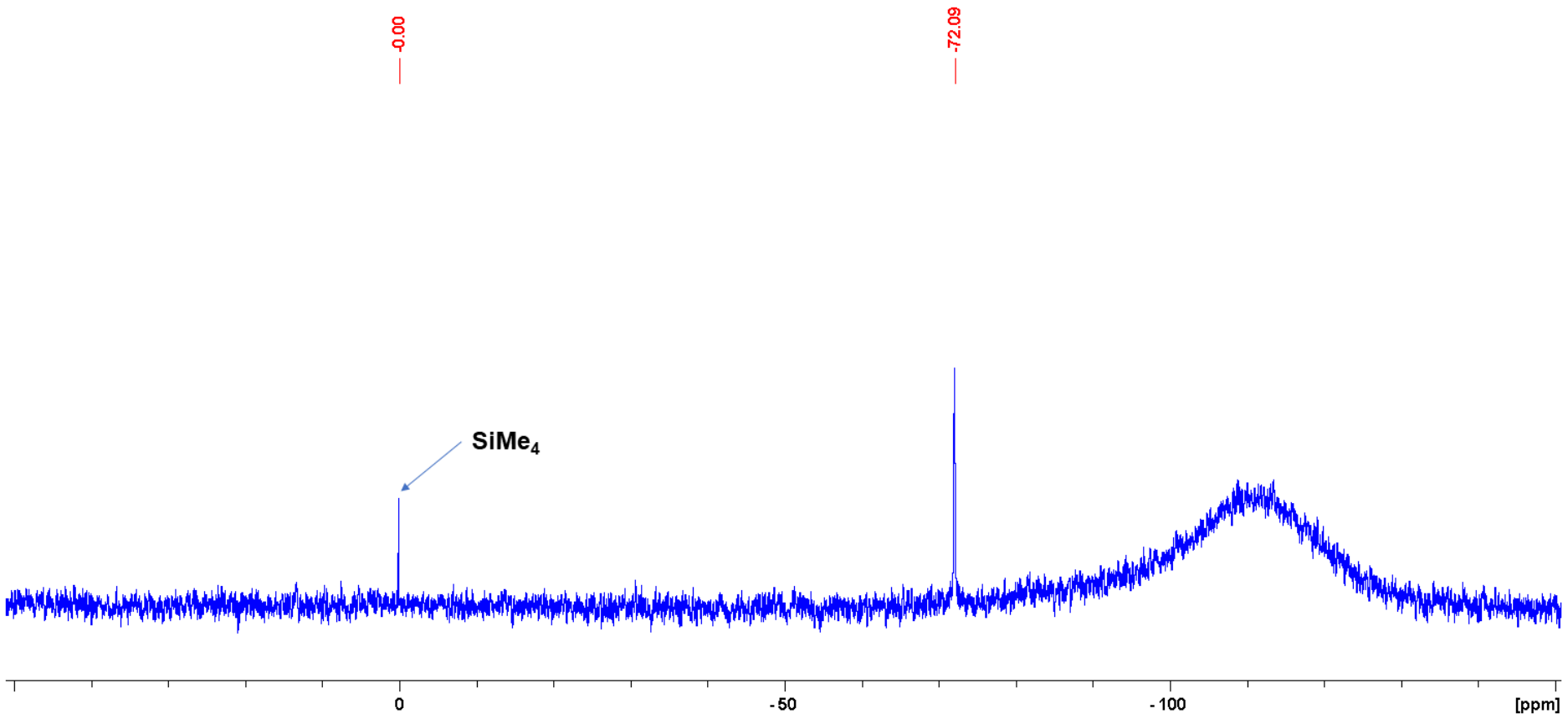

Figure S14. $^{29}Si\{^{1}H\}$ NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) in $CDCl_3$.

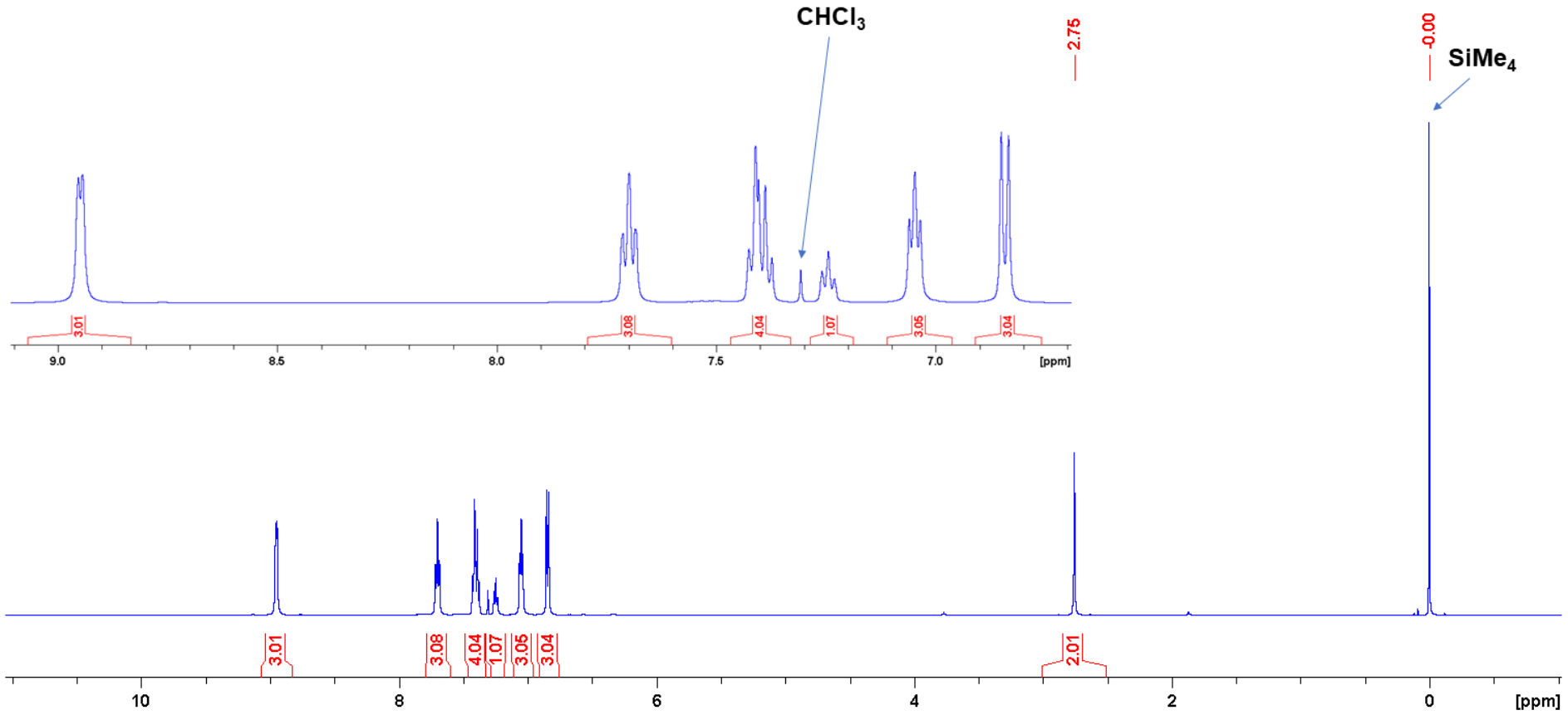

Figure S15. ^{1}H NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) in $CDCl_3$ at –30 °C (full spectrum and magnified inset of group of signals).

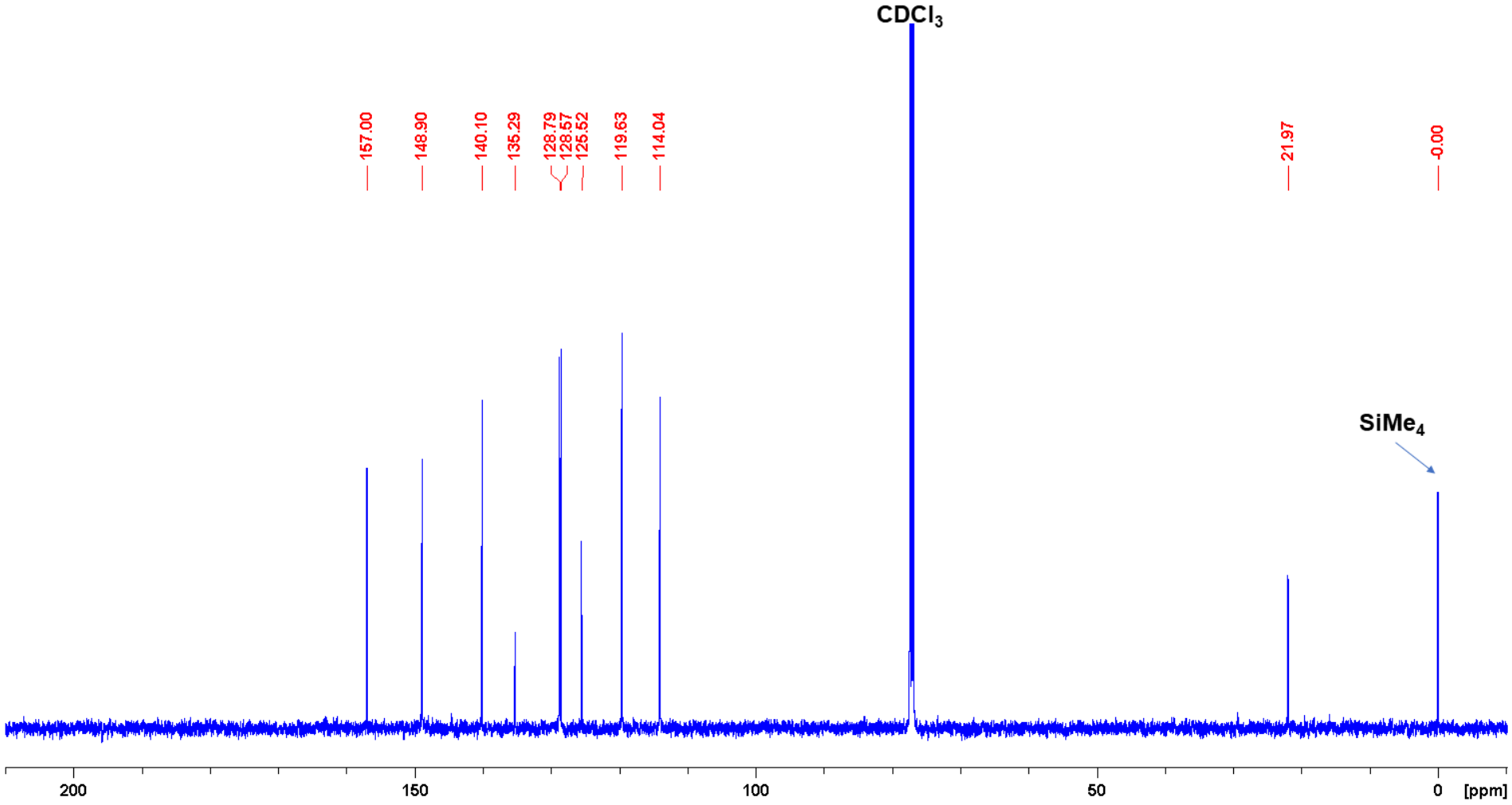

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) in $CDCl_3$ at –30 °C.

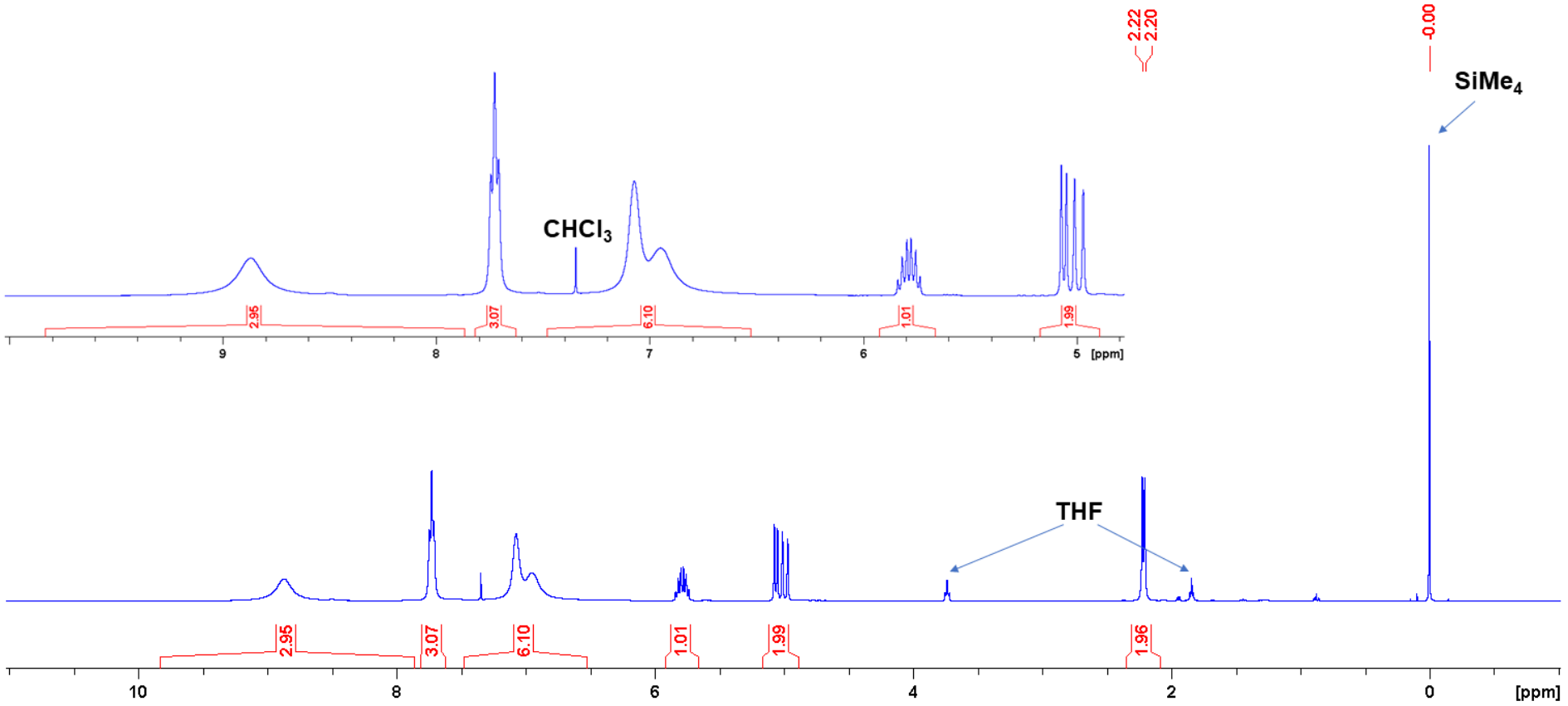

Figure S17. ^{1}H NMR spectrum of (κO-pyO)Si(μ^2-pyO)$_2$(Allyl)CuCl (**2d'**) in $CDCl_3$ (full spectrum and magnified inset of group of signals).

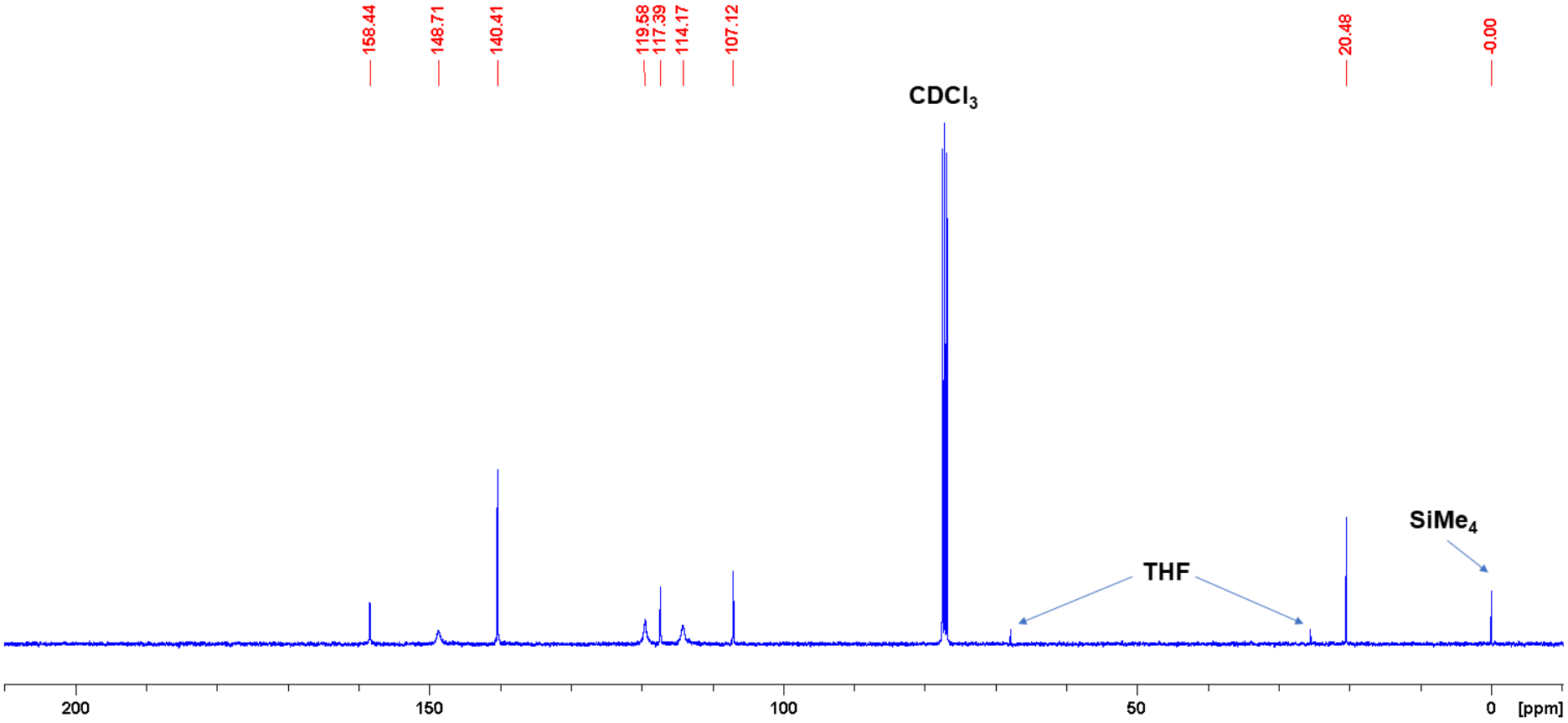

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of (κO-pyO)Si(μ^2-pyO)$_2$(Allyl)CuCl (**2d'**) in $CDCl_3$.

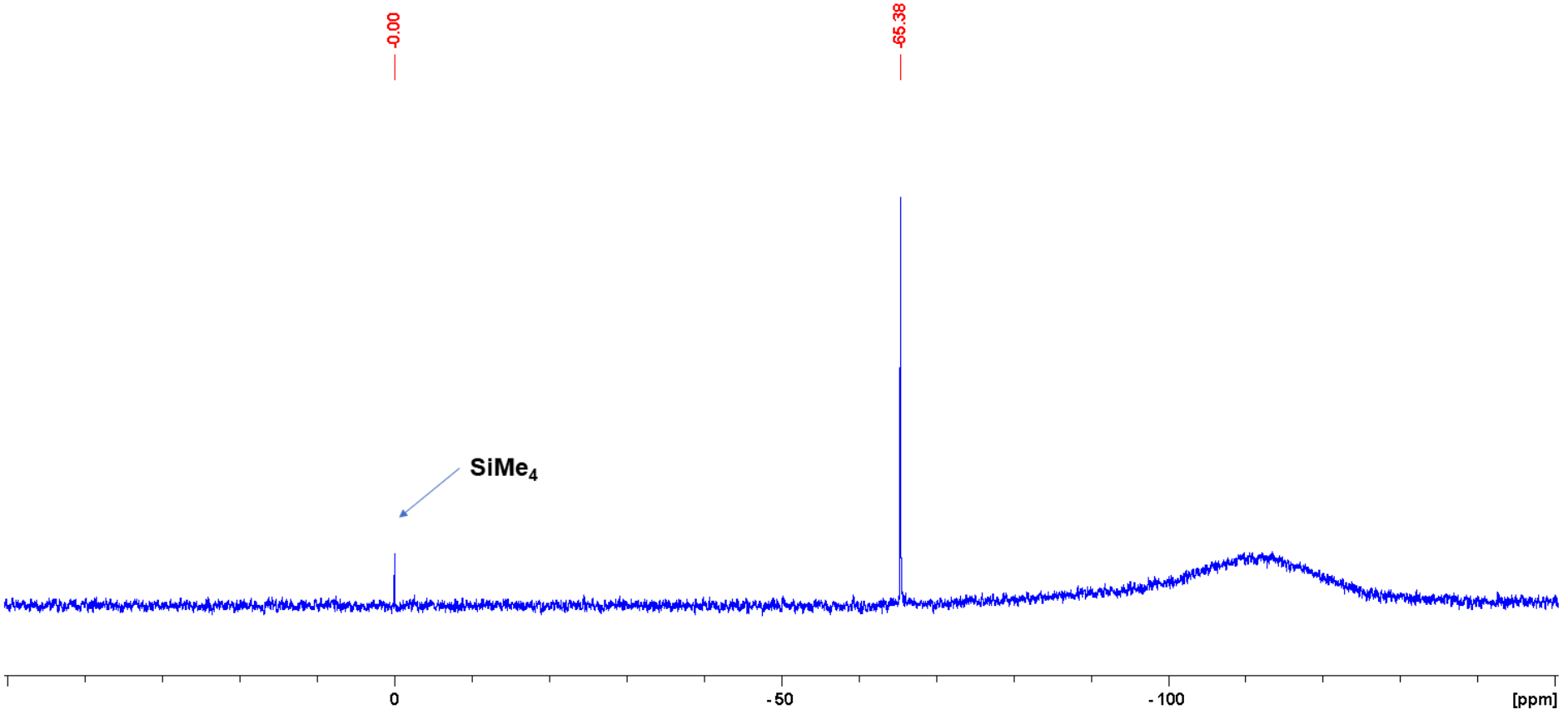

Figure S19. $^{29}Si\{^{1}H\}$ NMR spectrum of (κO-pyO)Si(μ^2-pyO)$_2$(Allyl)CuCl (**2d'**) in $CDCl_3$.

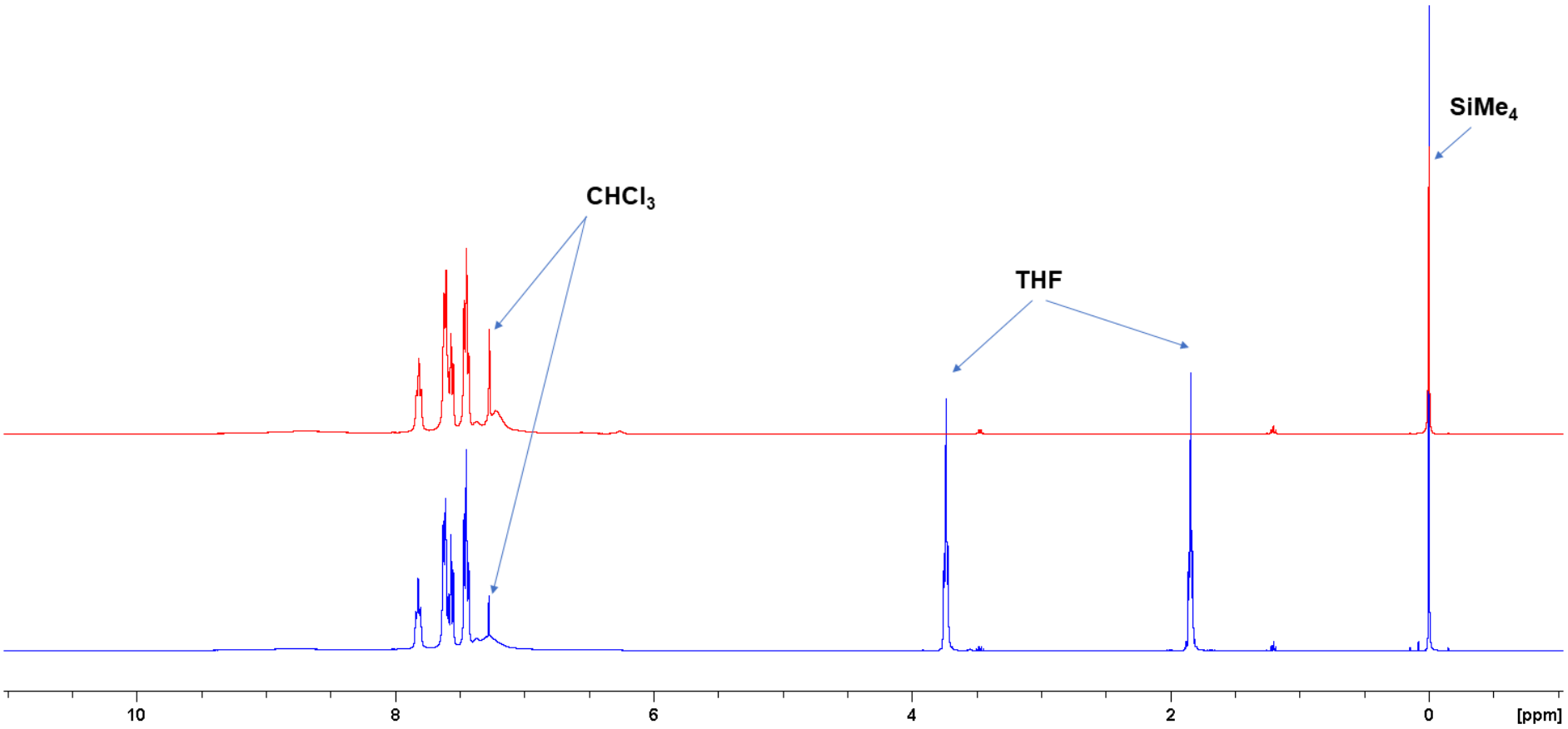

Figure S20. ^{1}H NMR spectra of the chloroform solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_3$ [(**5^3**)·$(CHCl_3)$] (top) and of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5^4**)·$(THF)_2$)] (bottom) in $CDCl_3$.

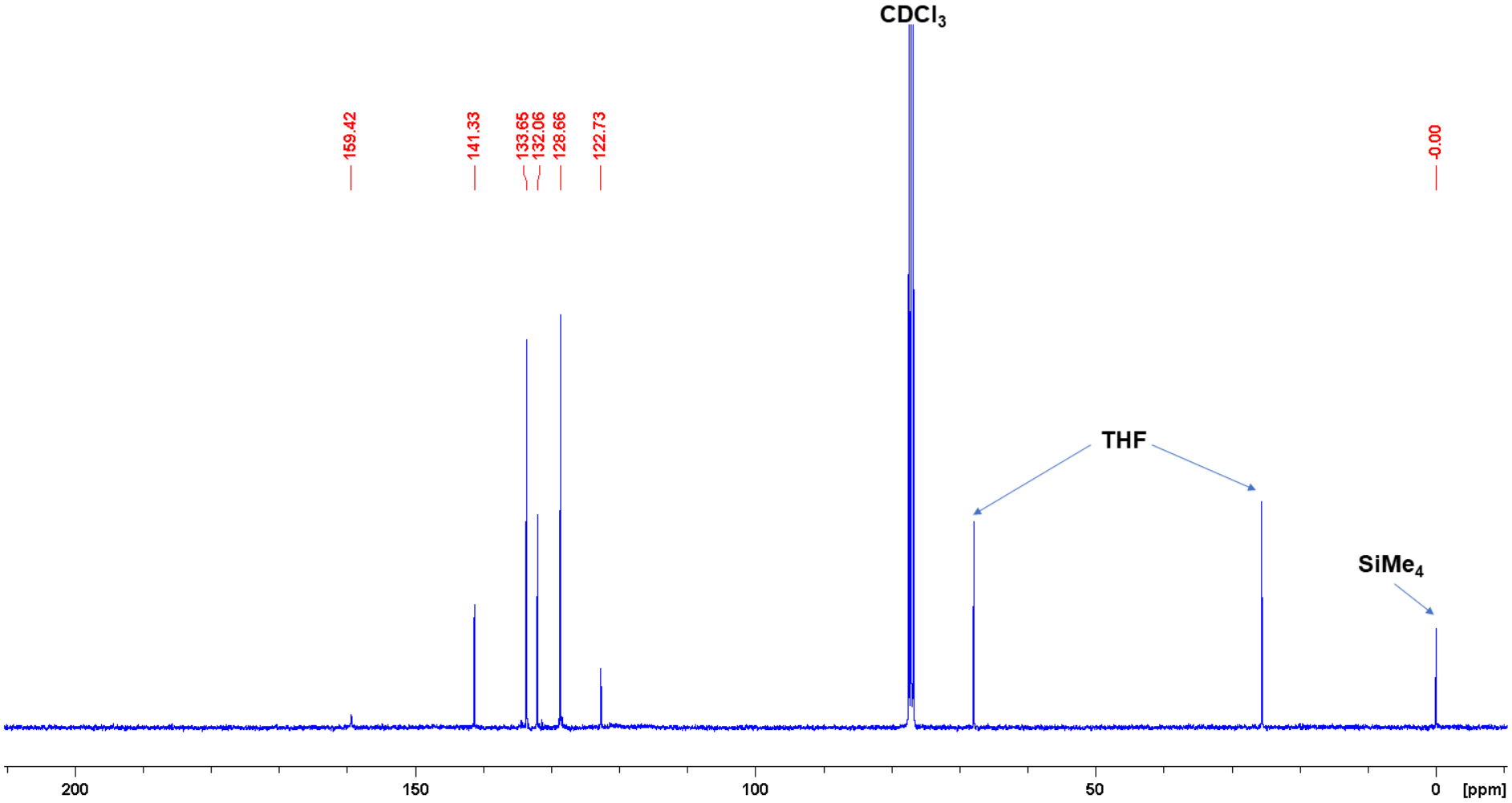

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5**^{4})·$(THF)_2$)] in $CDCl_3$.

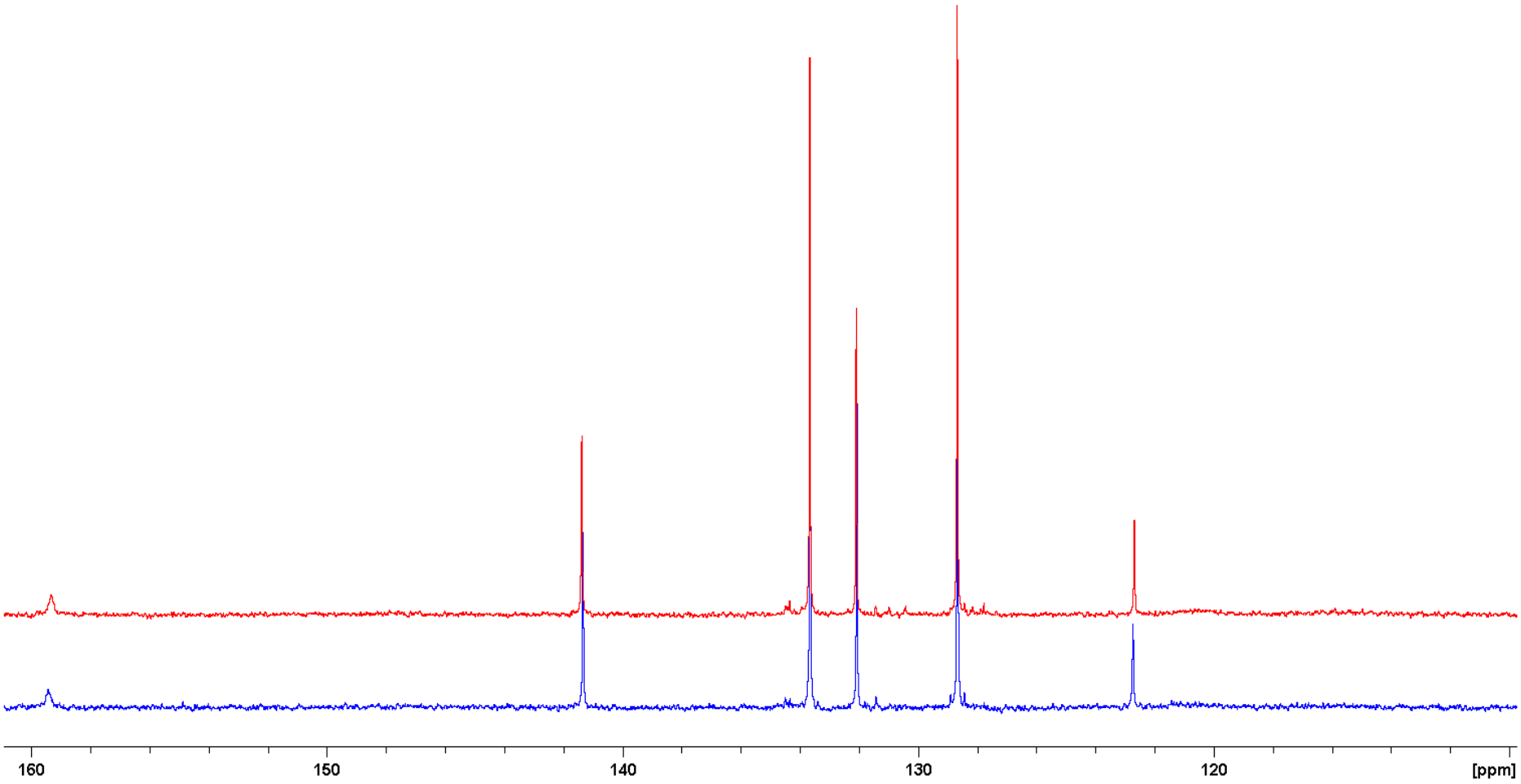

Figure S22. Magnified section of the $^{13}C\{^{1}H\}$ NMR spectrum of the chloroform solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_3$ [(**5**^{3})·$(CHCl_3)$] (top) and of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5**^{4})·$(THF)_2$)] (bottom) in $CDCl_3$.

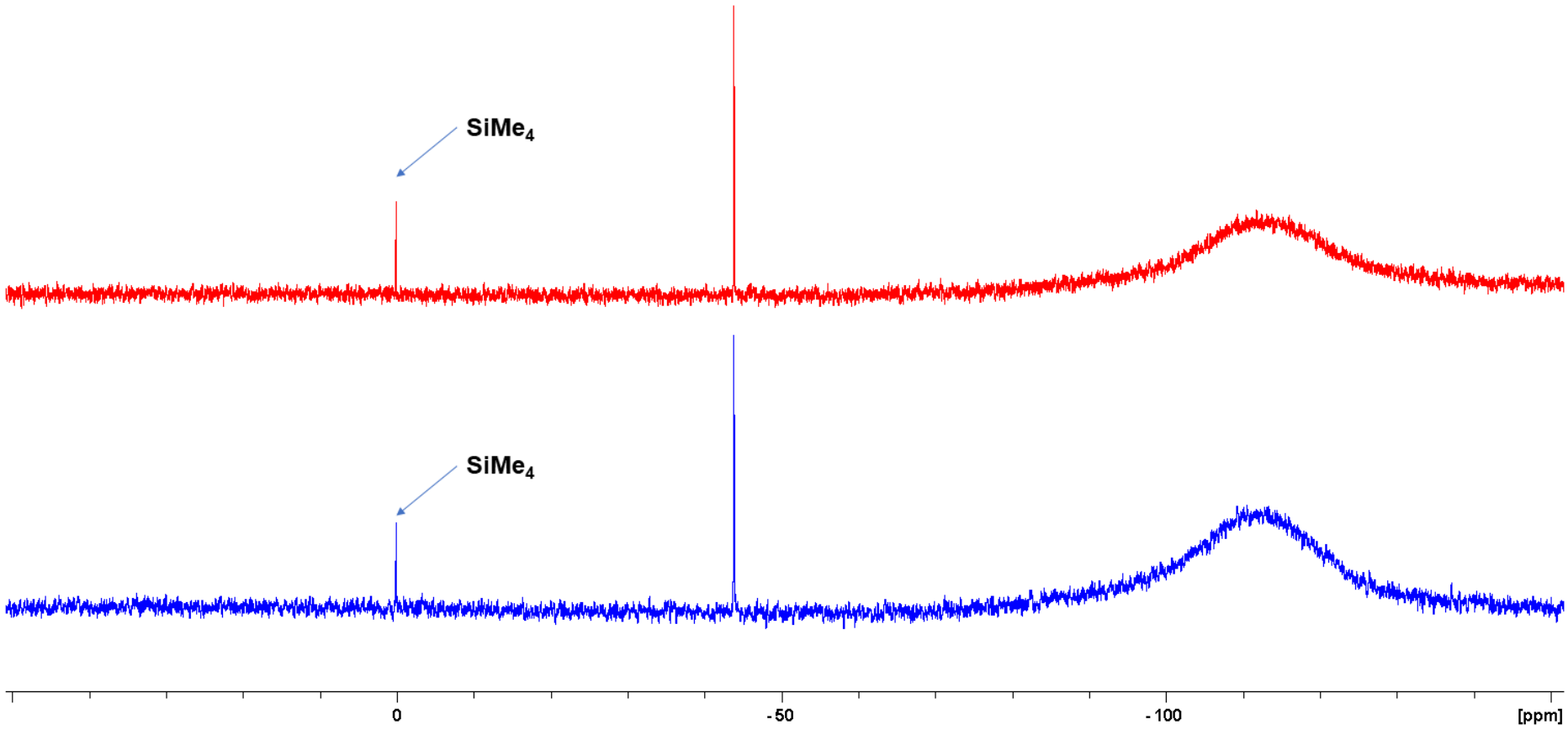

Figure S23. $^{29}Si\{^{1}H\}$ NMR spectrum of the chloroform solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_3$ [(**5^3**)·$(CHCl_3)$] (top) and of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5^4**)·$(THF)_2$)] (bottom) in $CDCl_3$.

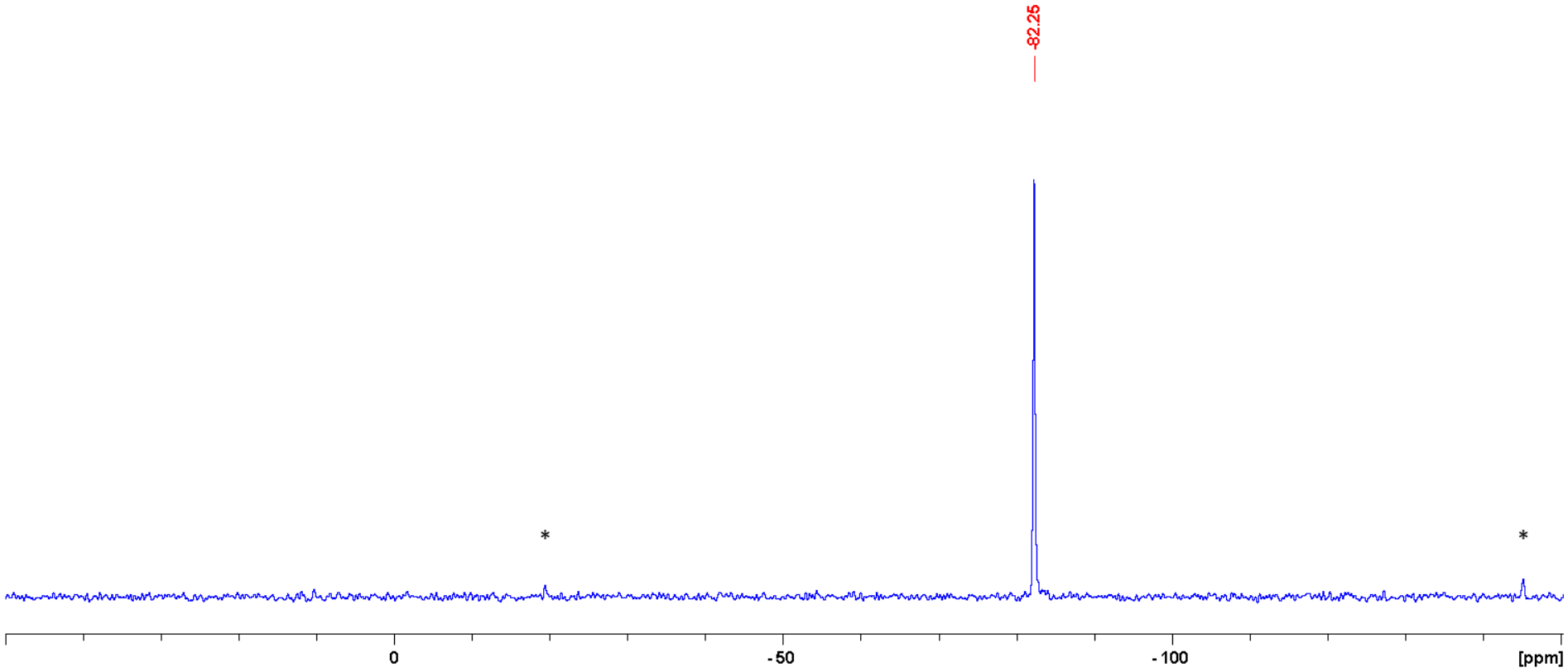

Figure S24. ^{29}Si CP/MAS NMR spectrum of the THF solvate of PhSi(μ^2-pyO)$_3$CuCl [(**2b**)$_2$·(THF)] recorded at ν_{spin} = 5 kHz. Spinning side bands are asterisked.

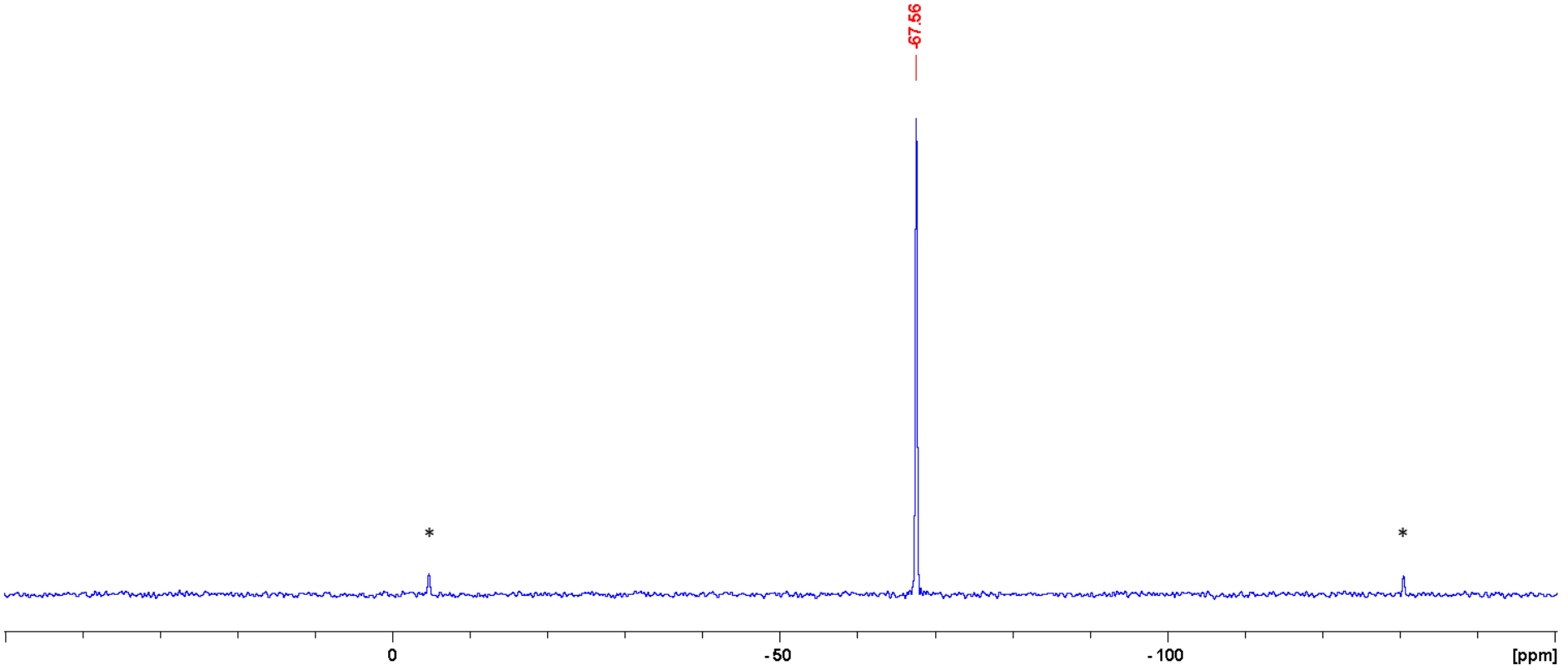

Figure S25. ^{29}Si CP/MAS NMR spectrum of BnSi(μ^2-pyO)$_3$CuCl (**2c**) recorded at ν_{spin} = 5 kHz. Spinning side bands are asterisked.

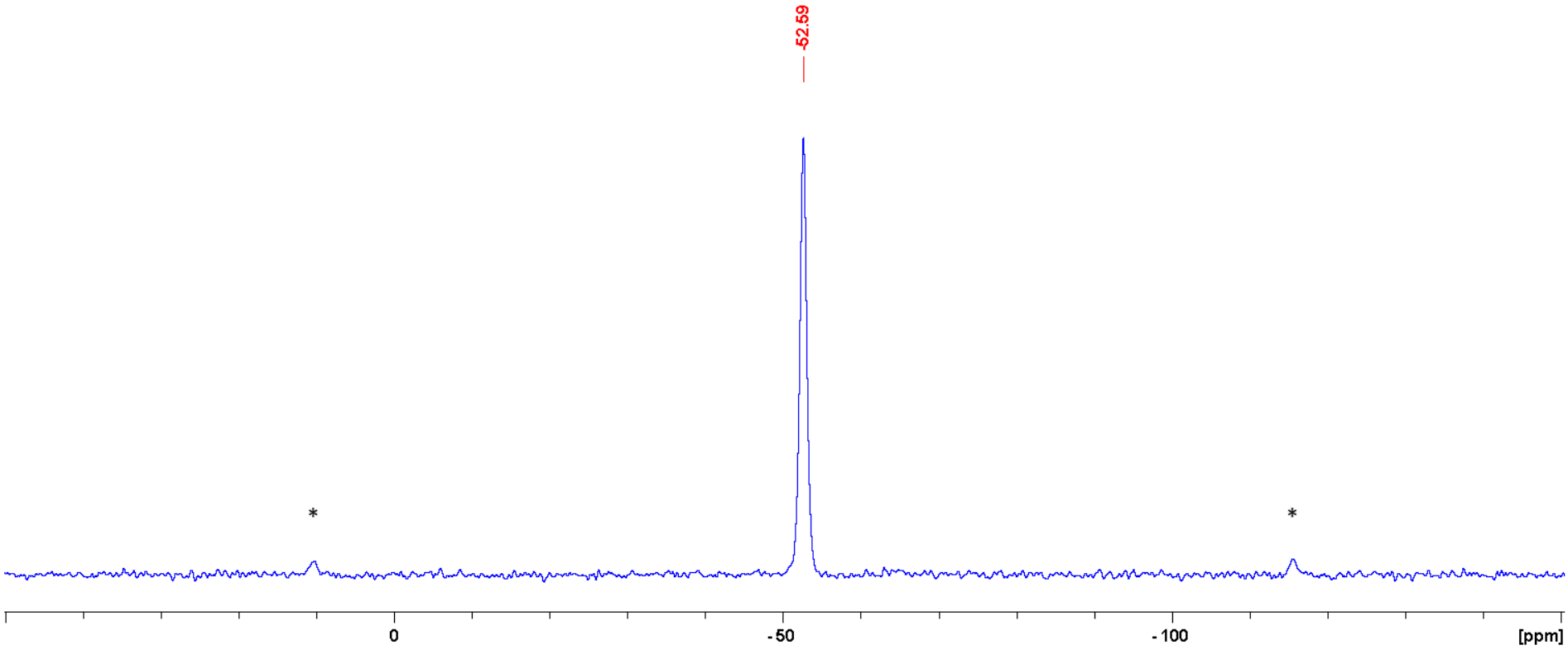

Figure S26. ^{29}Si CP/MAS NMR spectrum of (κO-pyO)Si(μ^2-pyO)$_2$(Allyl)CuCl (**2d'**) recorded at ν_{spin} = 5 kHz. Spinning side bands are asterisked.

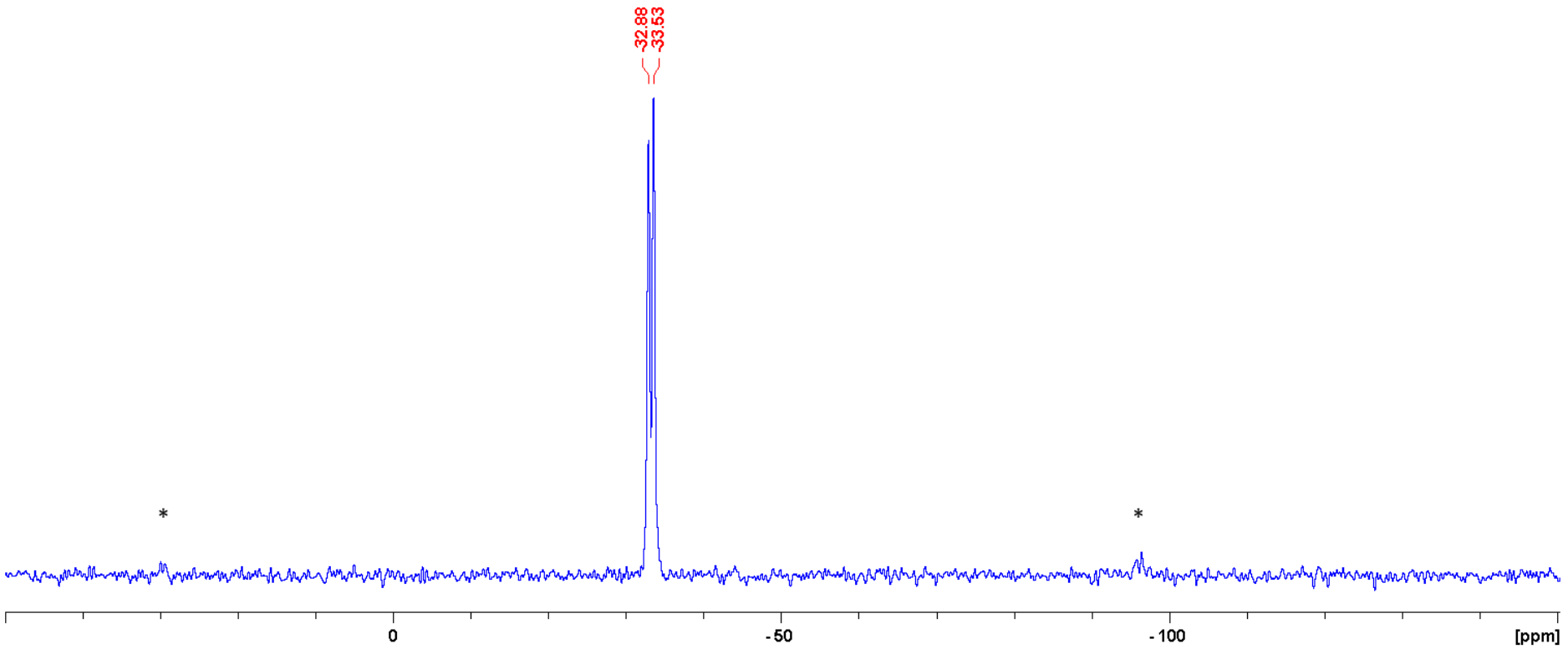

Figure S27. ^{29}Si CP/MAS NMR spectrum of the chloroform solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_3$ [(**5^3**)·($CHCl_3$)] recorded at ν_{spin} = 5 kHz. Spinning side bands are asterisked.

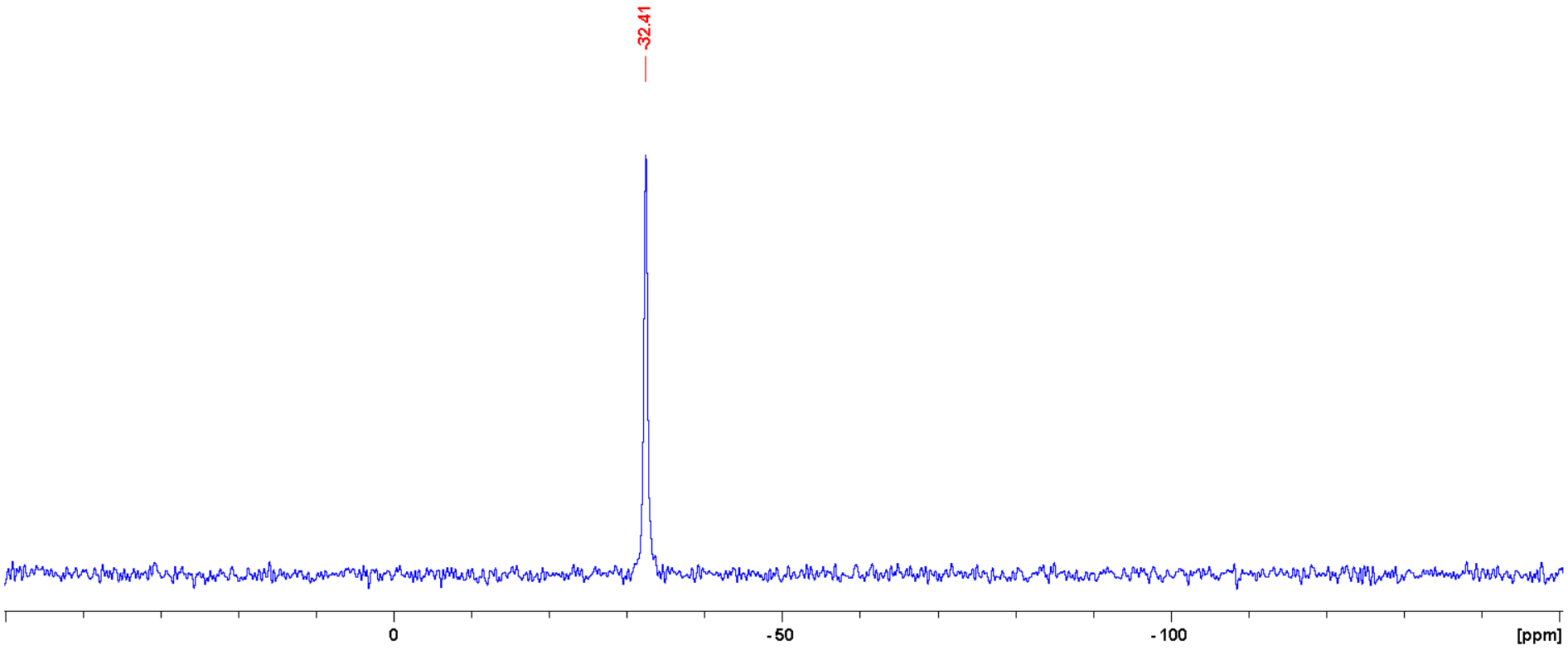

Figure S28. ^{29}Si CP/MAS NMR spectrum of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5^4**)·$(THF)_2$)] recorded at ν_{spin} = 5 kHz.

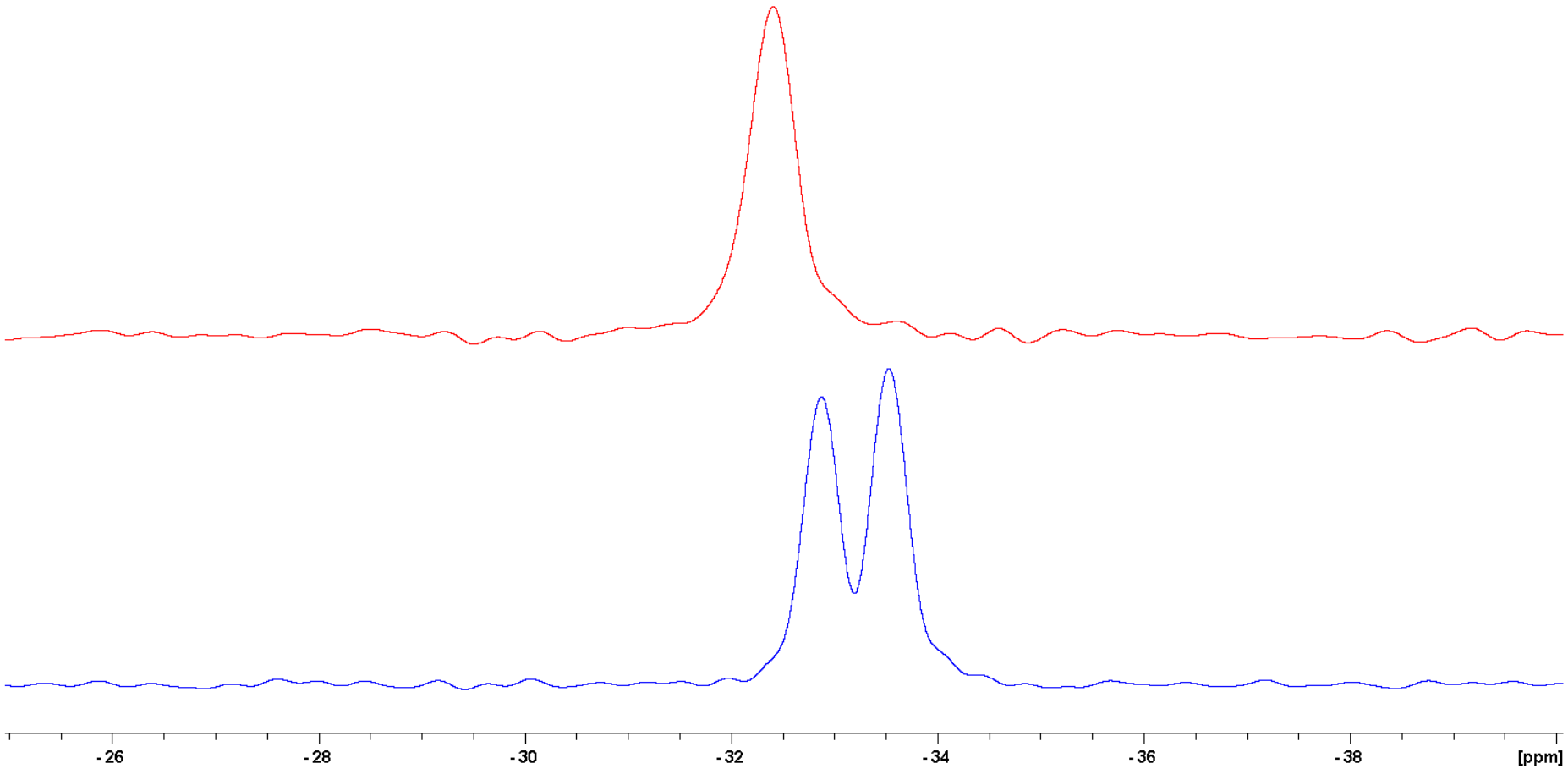

Figure S29. Magnified signals at the isotropic chemical shifts from the ^{29}Si CP/MAS NMR spectra of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_3$ [(**5^3**)·($CHCl_3$)] (bottom) and of the THF solvate of $[Ph_2Si(\mu^2\text{-}pyO)_2]_2(CuCl)_4$ [(**5^4**)·$(THF)_2$)] (top).

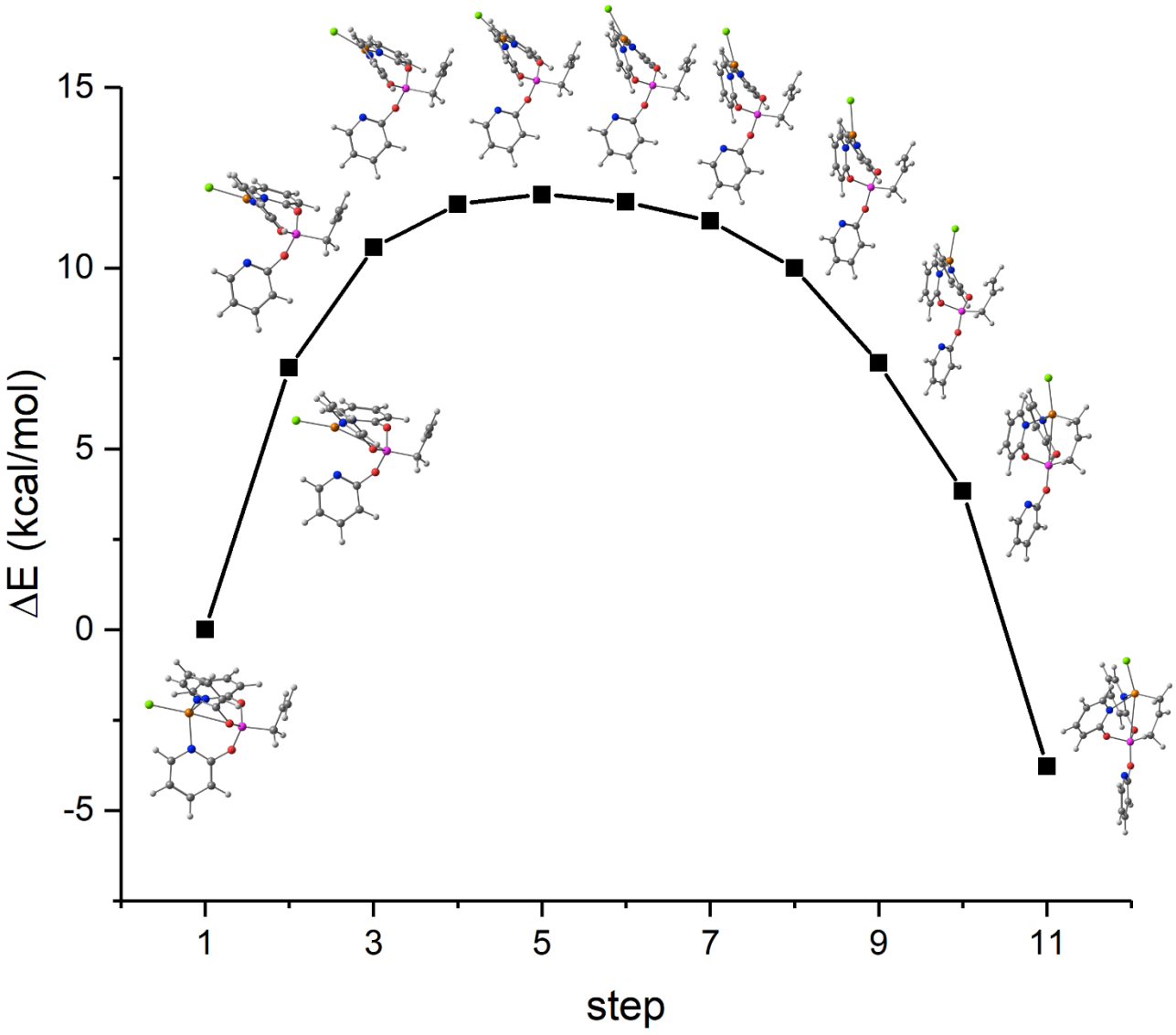

Figure S30. Graphical representation of the "Nudged Elastic Band" (NEB) scan of the interconversion of isomers **2d** (step 1) and **2d'** (step 11) in 9 intermediate steps. For each step the relative energy and the molecular conformation are given.

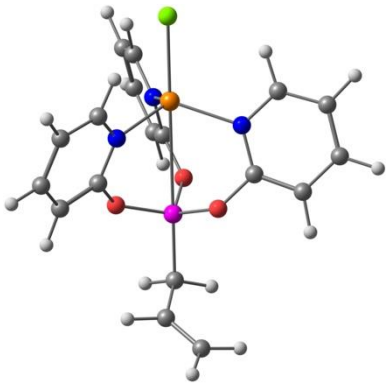

Figure S31. Optimized molecular structure of **2d**.

PBE0:

final single point energy: -3501.810698882165 a.u.

final Gibbs free energy: -3501.53597493 a.u.

B2T-PLYP:

final single point energy: -3502.055768088580 a.u.

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

Cu	-0.15830683639692	0.03228701304606	-0.00021690970085
Cl	-0.18018383284339	0.11684027146990	2.35432132701249
Si	-0.12679425075381	-0.08793393361932	-3.12645614742738
O	-0.33595847288793	1.49136037710099	-2.72656593508756
N	-1.18915150080069	1.67095612691630	-0.60545826038013
C	-1.10815204423972	2.14265913809920	-1.84117602053817
C	-1.76006429375324	3.29635717259492	-2.26001930277139
H	-1.64837750986887	3.62882031032812	-3.28287367190396
C	-2.53527707687609	3.97535507926984	-1.34293366709036
H	-3.05853952622485	4.87714787295703	-1.63632664367472
C	-2.63512499568718	3.48616298513077	-0.04542455357308
H	-3.23152921768511	3.98806163530074	0.70421018026634
C	-1.94764524777860	2.33711319281017	0.27770436144525
H	-1.96900207034419	1.91311917882162	1.27477595866111
O	-1.38333240313466	-1.02268896774252	-2.64075170457674
N	-1.10975518917046	-1.69677092389835	-0.46626397741521
C	-1.57707579960050	-1.94135658614256	-1.68208120931875
C	-2.28625352661737	-3.09154961705393	-2.00793327714845
H	-2.64390200253694	-3.22626518526942	-3.01946448939045
C	-2.50417886371071	-4.02490942356683	-1.01584780206799
H	-3.05153169430155	-4.93329229549104	-1.23581797499629
C	-2.01264701054142	-3.78344310175520	0.26206460859614
H	-2.16234477535341	-4.48817357029750	1.06860891359447
C	-1.32587279577201	-2.61148011813258	0.49061665186113
H	-0.93264363956698	-2.35372851150078	1.46703010078754
O	1.32126983470882	-0.67800008625089	-2.62653103812707
N	1.80019620701361	0.05315107388986	-0.50578166057277
C	2.22811721407905	-0.31221130126444	-1.70588812833101
C	3.57357710170270	-0.36429023342538	-2.05069608676097
H	3.85556017215552	-0.67585574978754	-3.04696616957532
C	4.50483743616631	-0.00951731865512	-1.09678940465819
H	5.56154424374625	-0.03706481565916	-1.33290323370682
C	4.06842334034120	0.38272368786175	0.16350627371282
H	4.76470154232126	0.66744656444981	0.94048280018541
C	2.71410998604858	0.39769600098561	0.41389432435911
H	2.30902870107451	0.67522769922783	1.37990611085823
C	-0.09871389764942	-0.15438772958083	-4.97156056900453
H	0.75540542479026	0.45104485861185	-5.29430258405818
H	0.09876758203471	-1.18877008442686	-5.26675222362621
C	-1.36487969747626	0.34783906217956	-5.57842868458637
H	-1.54223809150553	1.41743164303013	-5.49386324110687
C	-2.27683966670846	-0.41036132942984	-6.17467776291726
H	-2.14069000908890	-1.48219026272709	-6.27874548681159
H	-3.18717055530759	0.01708957559510	-6.57719050143536

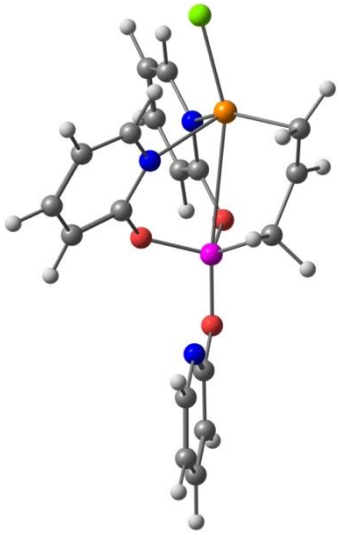

Figure S32. Optimized molecular structure of **2d'.**

PBE0:

final single point energy: -3501.816723111214 a.u.

final Gibbs free energy: -3501.54008371 a.u.

B2T-PLYP:

final single point energy: -3502.060962415792 a.u.

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

Cu	-0.03161672519962	0.05790040780608	0.01894107114295
Cl	0.07446505922937	0.07709831727514	2.29962318040681
Si	-0.96892993705083	-0.72713927884963	-2.99391473218179
O	-1.65445176089155	0.74901565799522	-2.70522791500683
O	-1.83576889533129	-1.81369948605192	-2.11206218108070
O	-1.40937899044516	-0.90431416996931	-4.58748295803889
N	-1.83244743995397	0.93746941338469	-0.41620359149778
N	-0.59127742922939	-2.17503919532276	-0.23041934426989
N	-0.35745193565687	-2.91377022429025	-4.55341214485306
C	-2.31678673761417	1.18988301126366	-1.63026419389538
C	-3.48155052422795	1.92193324267802	-1.84122705096727
H	-3.81446485022951	2.09378262372021	-2.85536452499872
C	-4.17257581446871	2.39368963461285	-0.74676158364229
H	-5.08278190779653	2.96489864990495	-0.88281476758036
C	-3.68735772444980	2.11906597513445	0.52623145661510
H	-4.19759110385501	2.46313405096945	1.41535608233355
C	-2.52346534371467	1.39414930047447	0.64229554491040
H	-2.08981060507105	1.15613293442747	1.60630655595533
C	-1.39498461398255	-2.65812303729399	-1.16240696063442
C	-1.82358621427022	-3.98072743009393	-1.19447385995619
H	-2.48377913776990	-4.31029584425207	-1.98481284577831
C	-1.37192698728527	-4.82898899154293	-0.20400720495957
H	-1.68141756337820	-5.86713037712173	-0.19656664411520
C	-0.51675439815505	-4.33751072935516	0.77579550113690
H	-0.14071817438996	-4.97084221027253	1.56779213961603
C	-0.15760583367537	-3.00659604066725	0.72210327081122
H	0.48539441513139	-2.55901032133882	1.47090918328976
C	-1.04130779482467	-2.02002659800264	-5.24573377591334
C	-1.38952485270500	-2.17670722576888	-6.58351846876393
H	-1.95060189743551	-1.40625733686537	-7.09450899660495
C	-0.99097497042958	-3.34097936775648	-7.20955301150278
H	-1.24024450015020	-3.50711588234232	-8.25067604634769
C	-0.27061424598256	-4.29410845073593	-6.49635312434915
H	0.05560010081912	-5.21630147623127	-6.95795573150036
C	0.02197161194198	-4.03295555188448	-5.17190793355189
H	0.58178318227195	-4.74312492614130	-4.57267772784490
C	0.85190177689547	-0.66934265829118	-2.69436620120112
H	1.19378829473784	-1.66994701718665	-2.42548638420249
H	1.33508662458445	-0.40968206683885	-3.64361546613018
C	1.20817710840661	0.32855338067519	-1.63226248205965
H	1.05466367557380	1.37327848355016	-1.88769434893704
C	1.93929551920125	0.02501384836622	-0.51584872389265
H	2.29607475771024	-0.98495197665570	-0.34367814970959
H	2.37600210211667	0.80845388188512	0.09131015975042

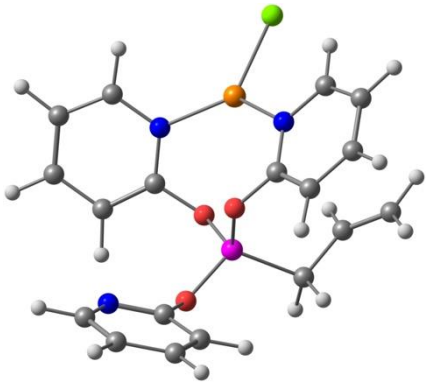

Figure S33. Optimized molecular structure of **2d-TS.**

PBE0:

final single point energy: -3501.797479055886 a.u.

final Gibbs free energy: -3501.52325900 a.u.

B2T-PLYP:

final single point energy: -3502.044045622440 a.u.

Table S7. Atomic coordinates for optimized structure of **2d-TS**.

Cu	-0.49894066387061	0.74799152399855	2.72578230102231
Cl	-0.23520487809424	1.16690257478804	4.91333019614156
Si	0.66243394931591	0.87072812634699	-0.63118976021584
O	-0.01229802491355	2.14526064340252	0.15610141108420
O	0.15869106339827	-0.56615273616123	-0.00692355600127
O	0.05048889403525	0.86966379054806	-2.14839970421210
N	-1.71814999788496	1.82306976262038	1.62579089140181
N	0.50778150508733	-0.90319758050780	2.23042693339081
N	-1.78824091346824	-0.08242783546357	-3.07051536071242
C	-1.31439308960628	2.32297941587075	0.46255071878474
C	-2.14808739534395	3.02588248671786	-0.39353848340318
H	-1.75703204445518	3.40106947933391	-1.32893539525553
C	-3.46217521332405	3.21531054557812	-0.01256873669606
H	-4.14134164454650	3.75869061371936	-0.65755195783156
C	-3.89559316089302	2.70500459121609	1.20452206116437
H	-4.91399902902274	2.83735006004269	1.54311593284256
C	-2.99416962604904	2.02061404191925	1.99031692355258
H	-3.27757371782263	1.60992787907577	2.95122481009347
C	0.67878309464676	-1.31776008989514	0.98067142169921
C	1.33421488751883	-2.49718919658649	0.65546966288312
H	1.42899737093665	-2.78207647287628	-0.38347054383672
C	1.85353870300229	-3.25975919117808	1.68194668891846
H	2.37765095858576	-4.18178289844493	1.46223692720789
C	1.69972867219175	-2.82601186675018	2.99276029676345
H	2.09567664494757	-3.39016812790813	3.82598783632278
C	1.02016743096709	-1.64910531996877	3.21994554384082
H	0.86588340335674	-1.25665424598134	4.21843031436876
C	-0.49291277762411	-0.16109960245191	-2.84594074018305
C	0.31489351287311	-1.19727708568096	-3.30292951117820
H	1.37656510724309	-1.19638202317279	-3.09251604653439
C	-0.28573863833535	-2.20985973140269	-4.02575265998240
H	0.30634725298428	-3.03787651717398	-4.39640084917442
C	-1.65141609084180	-2.14822933929581	-4.27046228566821
H	-2.16029918089637	-2.91983124150506	-4.83260127979551
C	-2.35287444618860	-1.06448648021235	-3.77508952523944
H	-3.42071004438884	-0.97379760311068	-3.94540858228646
C	2.48751133544410	1.10772921610197	-0.56506796364931
H	2.95524877714526	0.25985673124476	-1.07442045109436
H	2.70404019119170	2.00497483656453	-1.15614385483993
C	3.00253407210713	1.25134114196684	0.83069934520136
H	2.69466561380518	2.14780152098040	1.36233006474860
C	3.76798128389260	0.36246124770965	1.45019264967593
H	4.08767622088545	-0.55106537235748	0.95935535037989
H	4.08965163200798	0.51758132833915	2.47263696630170

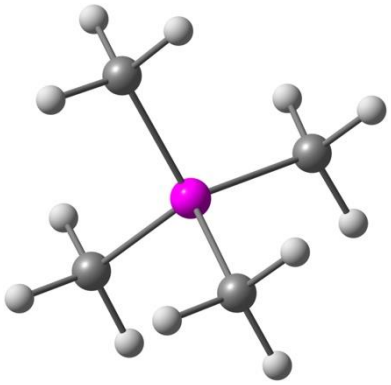

Figure S34. Optimized molecular structure of tetrametylsilane**.**

PBE0:

final single point energy: -450.025994878474 a.u.
final Gibbs free energy: -449.91131301 a.u.

Table S8. Atomic coordinates for optimized structure of tetrametylsilane.

Si	0.00712380499160	-0.00938451924514	-0.02075740880057
C	-1.53606549601940	-0.70684250177735	0.78421427771561
H	-1.56192420465589	-1.79610039645058	0.69805443755793
H	-1.57298619562357	-0.45297084308981	1.84657504448331
H	-2.43892932783988	-0.31113640939925	0.31235969794108
C	1.52227205748933	-0.72792016535119	0.81826348846505
H	1.53516808554058	-0.47788477592985	1.88212942976521
H	1.53763915801517	-1.81710819118996	0.72900366911012
H	2.44122791902612	-0.34109109688325	0.37078543792105
C	0.01848623120203	1.85741857404280	0.15453395010097
H	0.00825958882349	2.15294017976880	1.20666411462309
H	0.91077031309155	2.28782890228971	-0.30705710927756
H	-0.85618883725074	2.30090495920005	-0.32788028317615
C	0.02242368632071	-0.46353993659454	-1.84003918238511
H	0.91401020976084	-0.06995808844540	-2.33462729542087
H	0.01481263875275	-1.54811511663416	-1.97429553357287
H	-0.85301984962468	-0.05555289131087	-2.35155933605029

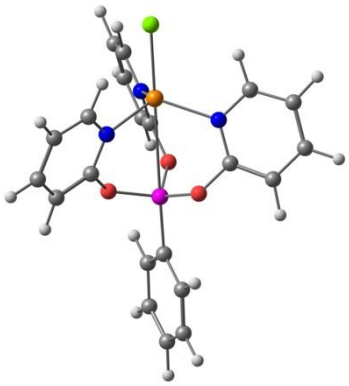

Figure S35. Optimized molecular structure of **2b.**

PBE0:

final single point energy: -3616.139243380901 a.u.
final Gibbs free energy: -3615.84495997 a.u.

Table S9. Atomic coordinates for optimized structure of **2b**.

Cu	-0.09884257102471	-0.16685116679036	-0.03209014388758
Cl	-0.16070702249620	-0.25640842060208	2.30929697806820
Si	-0.00504152286314	-0.03375142684180	-3.16290104346327
O	-0.02473417131735	-1.62224951005703	-2.76383550102546
O	1.31807208600831	0.77640210347992	-2.63517267320973
O	-1.39674594790845	0.71664008498132	-2.71915899072991
N	0.68550213707326	-1.94582610467007	-0.60884276524026
N	1.05192338320889	1.44324765377162	-0.45623656404069
N	-2.02956379451892	0.04599742787341	-0.61825964789831
C	0.57805548604695	-2.39794802065172	-1.84930767211138
C	1.03194549162020	-3.65016328896386	-2.24623184387651
H	0.91068568077724	-3.95855843555338	-3.27546864750579
C	1.62879063311522	-4.45529573053010	-1.29827504070251
H	1.99433483347248	-5.43737143046584	-1.57304535990388
C	1.75284553615278	-3.99010566727219	0.00589018244747
H	2.21246009701081	-4.58999204078335	0.77953176028184
C	1.26864718392390	-2.73554786918090	0.30489686047984
H	1.31530869144550	-2.31953464803660	1.30472070045925
C	1.57649488213113	1.65600236914239	-1.65356255118846
C	2.40867700812471	2.73151835961573	-1.94089675617536
H	2.80813348290176	2.84270369515524	-2.93940343896559
C	2.69307840493507	3.62254705829073	-0.92694584482964
H	3.33678104959986	4.47299831151727	-1.11634261870841
C	2.14375361867715	3.41372338552579	0.33285442589083
H	2.34355407982639	4.08629896651568	1.15598892300970
C	1.33373094908391	2.31599251049420	0.52288734741894
H	0.88800431331667	2.08369325912817	1.48306361333077
C	-2.36951672108560	0.46193558928297	-1.82931224494491
C	-3.68681788401073	0.67708913272573	-2.21826417218788
H	-3.89465617277494	1.02141263341086	-3.22185464712669
C	-4.68481966035898	0.43641548010552	-1.29709894608930
H	-5.72205380473245	0.59190228086190	-1.56751831563656
C	-4.34118553068398	-0.00705430313978	-0.02509891731647
H	-5.09216704530578	-0.20592186206512	0.72732511859611
C	-3.00775715611088	-0.18645752157810	0.26969567232124
H	-2.66991840935078	-0.51124669433203	1.24696312609760
C	0.07653978252154	0.02982766525031	-5.00001037953391
C	0.56645550239003	1.16705730887797	-5.64587496181293
H	0.94044817028735	2.00158961490932	-5.06289775617113
C	0.58925245401003	1.24238356981303	-7.03015815215461
H	0.97530011577433	2.13014374024536	-7.51721097332195
C	0.12273627172714	0.17840084444930	-7.78968572737742
H	0.14225836236894	0.23536487517514	-8.87167402660856
C	-0.36508744253624	-0.95968187445548	-7.16269933063988
H	-0.72631225492802	-1.79267828479406	-7.75394000981353
C	-0.38802244600077	-1.03265920087375	-5.77789458514975
H	-0.76685017352359	-1.92827031896128	-5.29860698005340

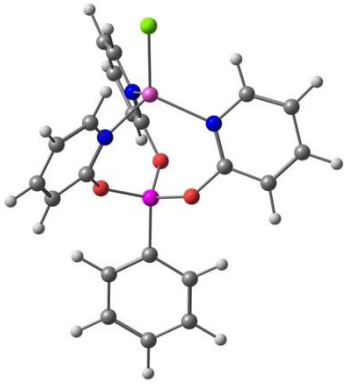

Figure S36. Optimized molecular structure of **2b-Li.**

PBE0:

final single point energy: -1960.985097569343 a.u.
final Gibbs free energy: -1960.68904966 a.u.

Table S10. Atomic coordinates for optimized structure of **2b-Li**.

Li	-0.12925029470051	-0.15769792898725	0.19856854892242
Cl	-0.16987294253514	-0.21579920038515	2.44704642649710
Si	-0.03592507560044	-0.03709576079612	-3.17739623714798
O	-0.03765686099483	-1.61806864256046	-2.74539880102575
O	1.28794305401905	0.70347025710714	-2.56696588468816
O	-1.43006196997438	0.66968334334461	-2.69434995519733
N	0.76840088121432	-1.84480552048357	-0.61011289071493
N	0.91587667253247	1.50154022312916	-0.45530911051378
N	-2.03198079152390	-0.08541772253077	-0.61458576154558
C	0.64642561878357	-2.33372662576737	-1.83148045386485
C	1.16145108508495	-3.56554329358952	-2.22101978411203
H	1.02046913725398	-3.90739889678647	-3.23699878248124
C	1.84319441323764	-4.30791950217926	-1.27858030904062
H	2.25857529896836	-5.27213985965115	-1.54534761536428
C	1.98883340857530	-3.80423919896398	0.00850471724956
H	2.51468915529262	-4.35540631909693	0.77601180636510
C	1.43498009045075	-2.57373500256098	0.29478553290482
H	1.49635095575703	-2.13683809315210	1.28550160374882
C	1.48931021069829	1.65522905220867	-1.63466288521408
C	2.31474530557771	2.72694193704108	-1.95508251926411
H	2.75589006980376	2.78891143070612	-2.94022585706202
C	2.53528623080167	3.68262803853687	-0.98383442323697
H	3.17172510133875	4.53318339915413	-1.19562561089966
C	1.93343607223779	3.54014842830424	0.26065690645984
H	2.08400871682916	4.26554726972935	1.04836358719510
C	1.13618534970563	2.43545450625650	0.47846910091263
H	0.65740003790529	2.25463695602989	1.43441448457217
C	-2.39378560381197	0.32412186746416	-1.81661047113418
C	-3.71849443815984	0.44770599044422	-2.22040180555217
H	-3.94429052195484	0.79560277653639	-3.21896104014764
C	-4.70345080344551	0.11328971705424	-1.31339529067701
H	-5.74704939540302	0.19564326670049	-1.59173669638609
C	-4.34004939982968	-0.32791636847893	-0.04669033669246
H	-5.08131975864399	-0.59793374236225	0.69287599698945
C	-2.99671621304323	-0.40873764571106	0.25655298517189
H	-2.64990842090515	-0.72673668285609	1.23362384909861
C	0.04257216080025	0.09135138980273	-5.00707673175538
C	1.26960753682156	0.23166166962297	-5.65945321293954
H	2.18464991609376	0.29957484201325	-5.08217926914689
C	1.33138731781303	0.29337896894829	-7.04329312080218
H	2.28917379584074	0.40482198115725	-7.53714326156443
C	0.16600548442442	0.21634003252354	-7.79336130097480
H	0.21366658359410	0.26778082167421	-8.87462908635293
C	-1.06090516194427	0.07868371110305	-7.15891096397052
H	-1.97149558825125	0.02320486643557	-7.74318569892575
C	-1.12145964411832	0.01698832498400	-5.77510136942002
H	-2.08559682061570	-0.08265496111269	-5.28893152927204

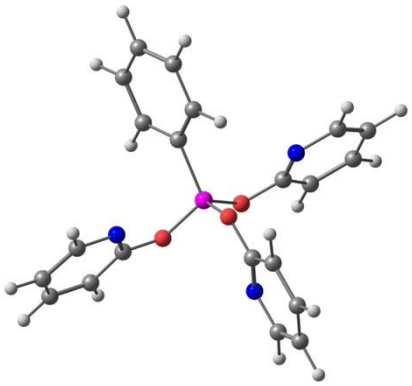

Figure S37. Optimized molecular structure of **1b.**

PBE0:

final single point energy: -1491.004138181560 a.u.
final Gibbs free energy: -1490.71020326 a.u.

Table S11. Atomic coordinates for optimized structure of **1b**.

Si	0.02620078296233	0.06469081049695	0.10919221618262
O	-0.83300935968386	1.34241437626984	0.72059696099773
O	1.60578044415389	0.02716284254362	0.56402413341344
O	-0.88148186429661	-1.13613087713928	0.80539946270799
N	0.57497285212106	2.90269132506331	-0.16628363316518
N	1.26782897266877	0.08889894984610	2.82210798351735
N	0.43385657131609	-2.79819829542536	-0.03246870808922
C	-0.51788673244483	2.63308347648378	0.52356193911954
C	-1.35631002736576	3.60996042981179	1.05726182916084
H	-2.23665320228256	3.32079698895039	1.61495966108409
C	-1.01516637207325	4.92997984674415	0.84660604826332
H	-1.63909143243146	5.72097173977461	1.24532839700582
C	0.13247145572652	5.23281604068144	0.12088767483889
H	0.43099808557096	6.25607401927588	-0.06344956566489
C	0.88996793389056	4.18346903663180	-0.36225348188177
H	1.79373342850330	4.36865984545487	-0.93374556111683
C	2.10923018882414	0.00355032675243	1.80933211669426
C	3.49068582537010	-0.10530521543269	1.95658156229770
H	4.12344114488433	-0.17103383097526	1.08201096104884
C	3.99826202138359	-0.12412862080731	3.23916988069490
H	5.06674781086972	-0.20749216106262	3.39814305845454
C	3.12690718192763	-0.03569246427358	4.31978512569675
H	3.48771352483075	-0.04714887897443	5.33954359862378
C	1.77493596593968	0.06839033562726	4.05542176131870
H	1.05625032239337	0.13983531291940	4.86546849776651
C	-0.63344618515143	-2.44701103243222	0.66118576898382
C	-1.50760098952540	-3.35966403053071	1.24915639493511
H	-2.36445957149590	-3.00564716067352	1.80599620213131
C	-1.23226121800188	-4.70198878939960	1.09071616612185
H	-1.88576688363788	-5.44469688277075	1.53257605854960
C	-0.11283550627624	-5.09015700031090	0.36113176260358
H	0.13352888636358	-6.13345133268033	0.21637222304334
C	0.68447231312180	-4.09977601752163	-0.17849978173208
H	1.56802760450172	-4.35194201527235	-0.75604571456866
C	-0.01735319373205	0.04035162370989	-1.72915462268638
C	1.06979275815958	-0.39135930072890	-2.48942256091801
H	1.97272516239834	-0.72472855512539	-1.99230458562741
C	1.00438153822009	-0.40016970451135	-3.87403522993546
H	1.85662207083099	-0.73546030611946	-4.45329447746695
C	-0.15229864638418	0.01895960568146	-4.51804691461287
H	-0.20328501490941	0.01132167671552	-5.60056461680820
C	-1.24262848032818	0.44867238267003	-3.77491502635618
H	-2.14595446811625	0.77792435522173	-4.27460025514630
C	-1.17343736935480	0.46050943203492	-2.38967241201127
H	-2.02897518644092	0.80728881580644	-1.81950608846857