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Synthesis and structure of (O→Si)-chelate fluorosilane, a novel complex of pentacoordinate silicon with *N*-acetylvaline

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Table S1. Selected bond lengths and bond angles (Å and °, respectively) in the molecule of fluorosilane **2**.

Si1–F1	1.6502(19)
Si1–O1	2.2792(19)
Si1–C1	1.850(3)
Si1–C2	1.852(3)
Si1–C3	1.887(3)
O1–C4	1.259(3)
O2–C7	1.198(3)
O3–H3	0.84(4)
O1•••O3/O1•••H3	2.661(2)/1.83
O3–C7	1.319(3)
O1–Si1–F1	170.48(10)
O3′–H3′•••O1	1.68

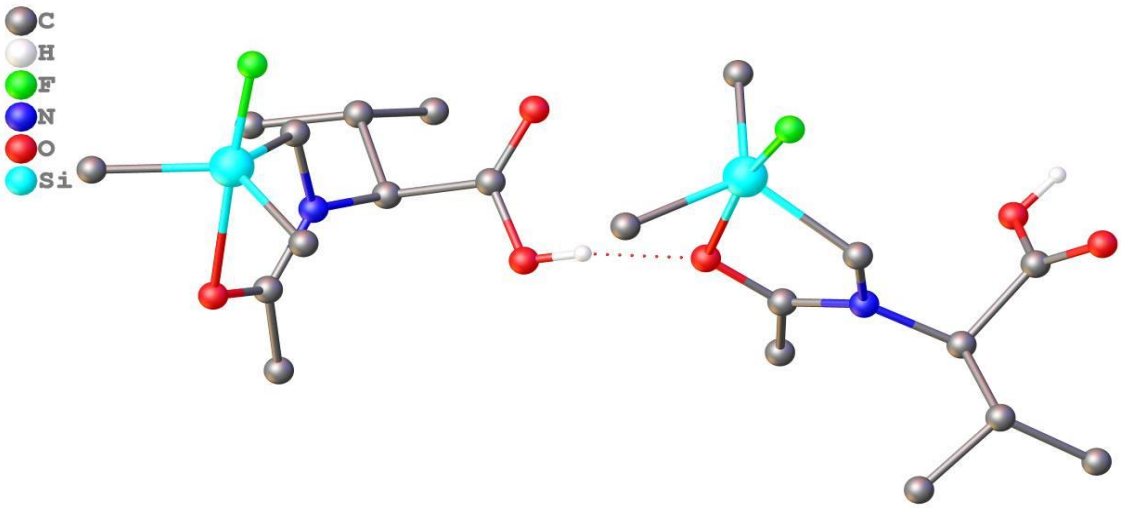


Figure S1. The hydrogen bond between the carboxyl group and the chelate ring O3′–H3′•••O1

Table S2. Selected topological parameters (atomic units), bond length and bond energies for **2-A**

Bond	Length, Å	$\rho(r)^*$	$\nabla^2\rho(r)$	$H^e(r)$	$V(r)$	Bond energy, kcal mol^{-1}
Si1–O1	2.230	0.042	0.053	–0.014	–0.041	–12.7
Si1–F1	1.687	0.105	0.713	–0.019	–0.217	–68.1
Si1–C1	1.871	0.123	0.229	–0.079	–0.215	–67.4
Si1–C2	1.872	0.123	0.228	–0.079	–0.214	–67.3
Si1–C3	1.908	0.115	0.220	–0.070	–0.195	–61.3

* Electron density at the BCP

Table S3. Selected topological parameters (atomic units), bond length and bond energies for **2-B**.

Bond	Length, Å	$\rho(r)$	$\nabla^2\rho(r)$	$H^e(r)$	$V(r)$	Bond energy, kcal mol^{-1}
Si1–O1	2.388	0.032	0.057	–0.005	–0.025	–7.9
Si1–F1	1.672	0.109	0.764	–0.019	–0.229	–71.9
Si1–C1	1.864	0.125	0.232	–0.081	–0.220	–68.9
Si1–C2	1.868	0.124	0.229	–0.080	–0.217	–68.0
Si1–C3	1.905	0.115	0.219	–0.071	–0.196	–61.4
Si1'–O1'	2.218	0.043	0.054	–0.014	–0.041	–13.0
Si1'–F1'	1.688	0.105	0.710	–0.019	–0.216	–67.8
Si1'–C1'	1.872	0.123	0.228	–0.079	–0.214	–67.3
Si1'–C2'	1.872	0.123	0.228	–0.079	–0.214	–67.2
Si1'–C3'	1.907	0.115	0.219	–0.070	–0.196	–61.4
O1•••H3'(O3')	1.646	0.050	0.147	0.006	–0.049	–15.4
O2'•••H1A(C1)	2.537	0.008	0.024	0.001	–0.005	–1.4

Atoms of the second molecule in dimer **2-B** with a shorter O→Si bond are designated with prime. For intermolecular interactions, the atoms covalently bonded to hydrogen atoms are shown in brackets.

Table S4. Selected topological parameters (atomic units), bond length and bond energies for **2-C**.

Bond	Length, Å	$\rho(r)$	$\nabla^2\rho(r)$	$H^e(r)$	$V(r)$	Bond energy, kcal mol^{-1}
Si1–O1	2.301	0.038	0.053	–0.009	–0.032	–10.0
Si1–F1	1.679	0.110	0.716	–0.026	–0.231	–72.5
Si1–C1	1.869	0.124	0.170	–0.077	–0.197	–61.8
Si1–C2	1.870	0.124	0.170	–0.077	–0.197	–61.7
Si1–C3	1.905	0.116	0.172	–0.069	–0.180	–56.6
O1•••$HCCl_3$	2.040	0.022	0.069	0.001	–0.016	–4.9

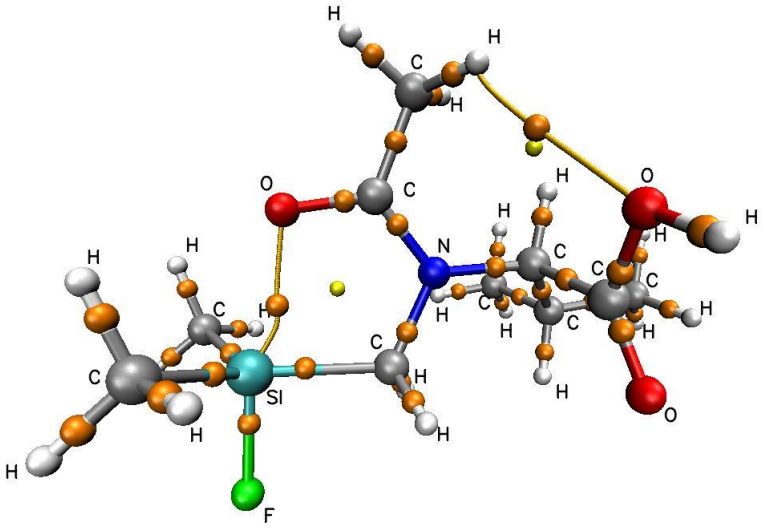


Figure S2. Molecular graph of monomer **2-A** optimised in the solvent medium (chloroform). BCP(3,–1) and BCP(3,+1) are shown in orange and yellow, respectively.

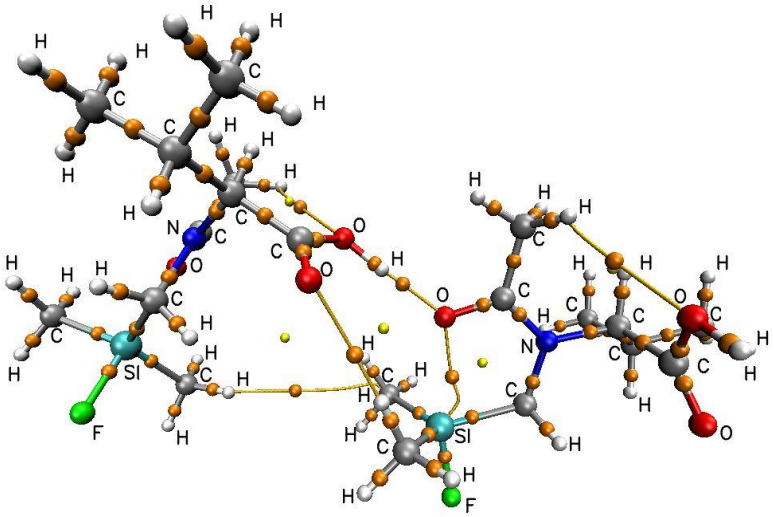


Figure S3. Molecular graph of dimer **2-B**. BCP(3,–1) and BCP(3,+1) are shown in orange and yellow, respectively.

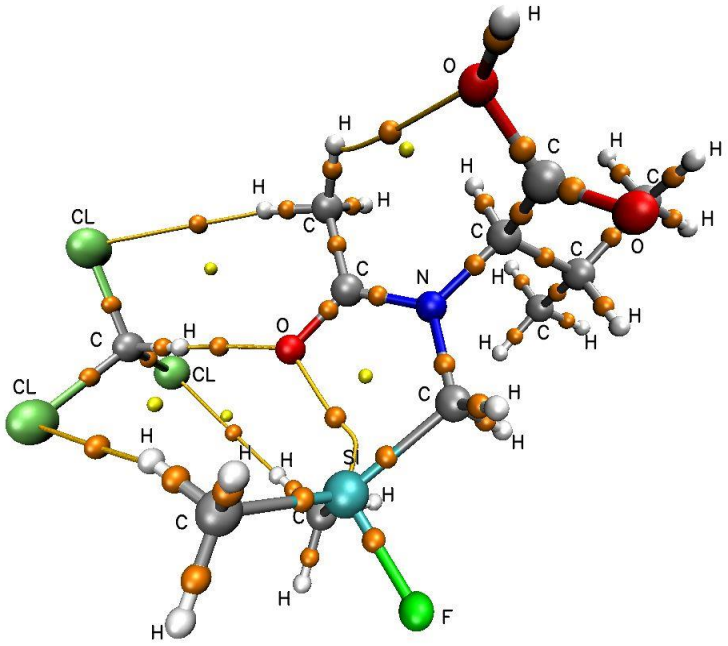


Figure S4. Molecular graph of associate **2-C**. BCP(3,–1) and BCP(3,+1) are shown in orange and yellow, respectively.

Experimental Section

IR spectra of solid samples were recorded on a Bruker Tensor-27 instrument equipped with an attenuated total reflection (ATR) module. ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectra in CD_3CN were recorded at 20 °C on a JEOL JNM-EX400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{19}F, 396 MHz; ^{29}Si, 79.5 MHz) instruments using standard pulse sequences. The ^{1}H, ^{13}C, ^{29}Si chemical shifts were measured using Me_4Si as internal reference. The ^{19}F chemical shifts were measured using $CFCl_3$ as external reference.

Disiloxane **1** was prepared as previously reported [A. A. Nikolin *et al*., *Russ. Chem. Bull.*, 2013, **62**, 1892].

(O→Si)-Chelate dimethyl-[*N*-(1-carboxy-2-methylpropyl)acetamidomethyl]fluoro-silane 2. Disiloxane **1** (0.46 g, 1 mmol) was refluxed with $BF_3{\cdot}Et_2O$ (0.14 g, 1 mmol) in acetonitrile (10 ml) for 3 h. The volatiles were then removed in vacuum, the residue was dissolved in boiling benzene and allowed to cool down. The precipitate formed was recrystallised from hot mixture of heptane and toluene (1:1). Yield 0.23 g (92%). The single crystal for X-ray study was obtained by repeated recrystallisation as above.

Found, %: C 48.15, H 8.11, N 5.46. $C_{10}H_{20}FNO_3Si$. Calculated, %: C 48.17, H 8.08, N 5.62. IR spectrum (ν, cm^{-1}): 1740 s (COOH); 1576 s, 1504 m (NC=O→Si). ^{1}H NMR spectrum (CD_3CN, δ, ppm): 0.31 and 0.33 (two s, 6H, $Si(CH_3)_2$); 0.85 (d, 3H, $(C\underline{H}_3)_2CH$, $^{3}J_{HH}$ = 6.6 Hz); 1.01 (d, 3H, $(C\underline{H}_3)_2CH$, $^{3}J_{HH}$ = 6.6 Hz); 2.11 (s, 3H, $(CO)CH_3$); 2.2–2.3 (m, 3H, $(CH_3)_2C\underline{H}$, $SiCH_2N$); 3.87 (d, 1H, $NC\underline{H}$, $^{3}J_{HH}$ = 6 Hz); 10.51–10.69 (broad s, 1H, COOH). ^{13}C NMR spectrum (CD_3CN, δ, ppm): 1.19 and 1.30 $Si(\underline{C}H_3)_2$, 18.73 and 19.31 $CH(\underline{C}H_3)_2$, 19.62 $\underline{C}H(CH_3)_2$, 27.66 $C(O)\underline{C}H_3$, 31.76 $N\underline{C}H_2Si$, 67.02 $N\underline{C}H_2$, 170.64 $\underline{C}(O)CH_3$, 174.49 $\underline{C}OOH$.

^{19}F NMR spectrum (CD_3CN, δ, ppm): −114.11.

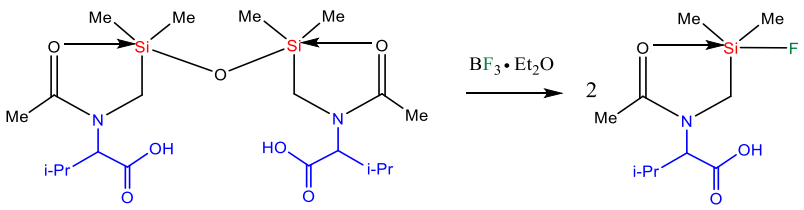
^{29}Si NMR spectrum (CD_3CN, δ, ppm): −21.7 ($^{1}J_{SiF}$ = 258 Hz).

X-ray diffraction study of a single crystal of fluorosilane **2** was carried out using Bruker Apex II diffractometer. The structure was solved by the direct method and refined by full-matrix technique against F^2 in the anisotropic-isotropic approximation. All calculations were carried out using SHELTXL software [G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112]. Figures were produced by Olex2 software [O. V. Dolomanov *et al*, *J. Appl. Cryst.*, 2009, **42**, 339]. The details of crystallographic data and structure refinement are summarised in Table S5.

Table S5. Crystal data for fluorosilane **2**.

Molecular formula	$C_{10}H_{20}FNO_3Si$
Formula weight	249.36
T, K	120
Space group	$Pca2_1$
Z	4
a, Å	12.7206(8)
b, Å	7.4105(5)
c, Å	14.9746(10)
α, °	90
β, °	90
γ, °	90
V, Å^3	1411.60(16)
d_{calc}, g cm^{-3}	1.173
μ, cm^{-1}	1.72
F(000)	536
$2\Theta_{max}$, °	50
No. of collected reflections	17538
No. of independent reflections	4363
No. of reflections with $I > 2\sigma(I)$	3466
No. of refined parameters	154
R_1 [$I > 2\sigma(I)$]	0.0411
wR_2 (all reflections)	0.0982
GOF	1.025
Residual electron density, e Å^{-3}(ρ_{min}/ρ_{max})	0.207/–0.182

Quantum-chemical calculations were carried out using Gaussian03 software.[16] The optimisation and calculation of second derivatives were performed using PBE0 functional and 6-311G(d,p) basis set. The PCM model was applied to account for nonspecific solvation. Electron density calculations were carried out using Multiwfn software [T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580.]



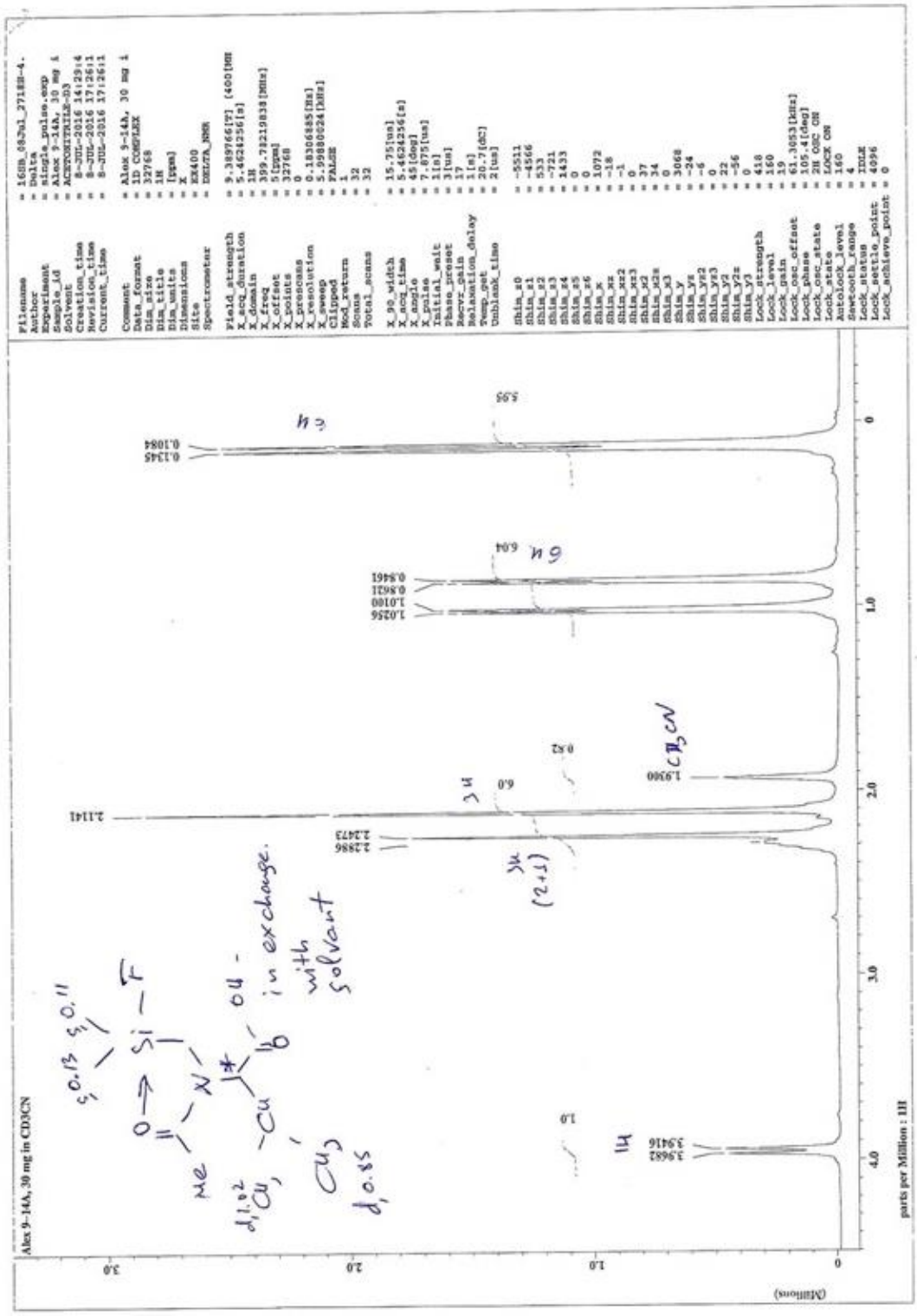


Figure S5. ^{1}H NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 400 MHz)

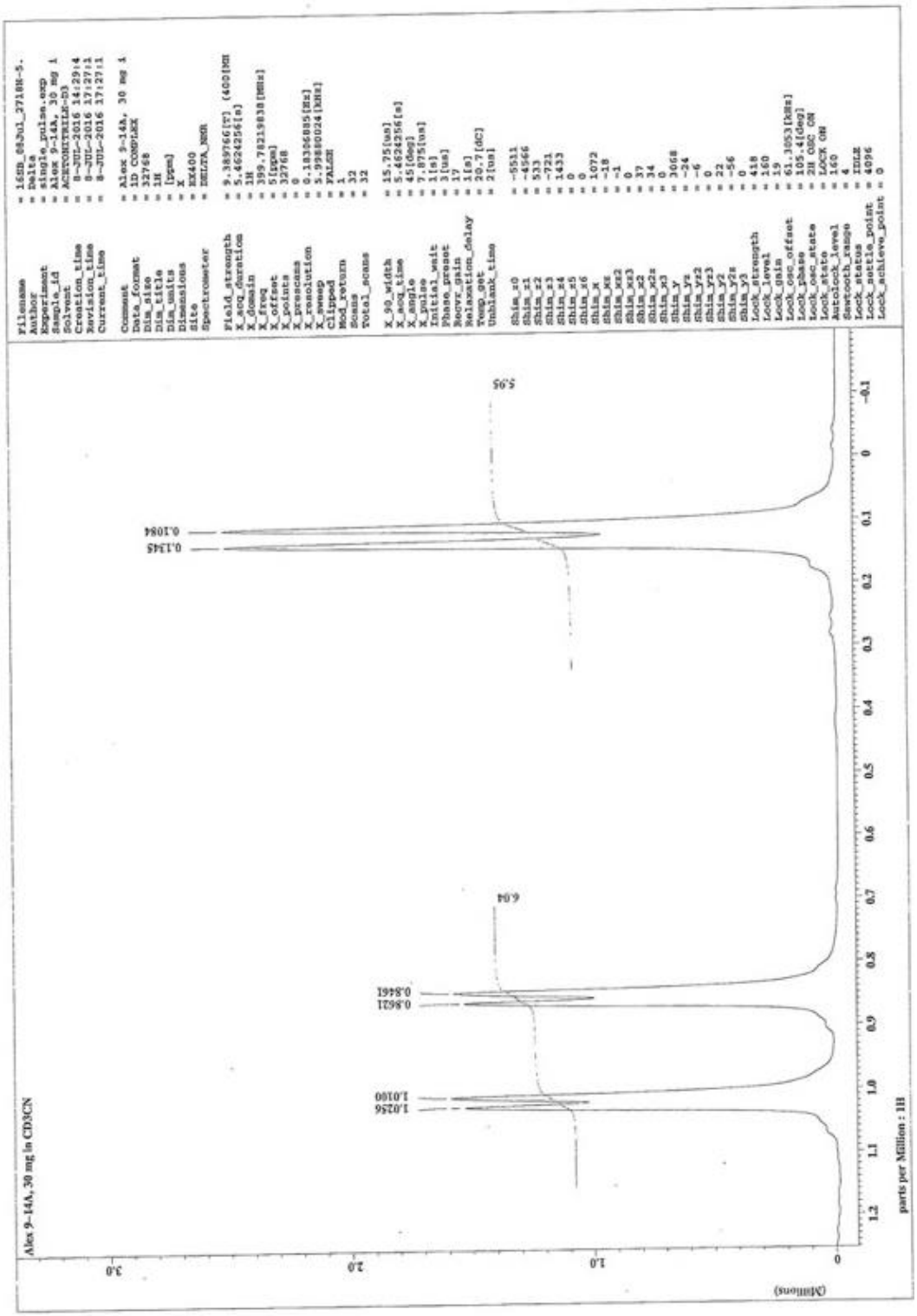


Figure S6. ^{1}H NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 400 MHz)

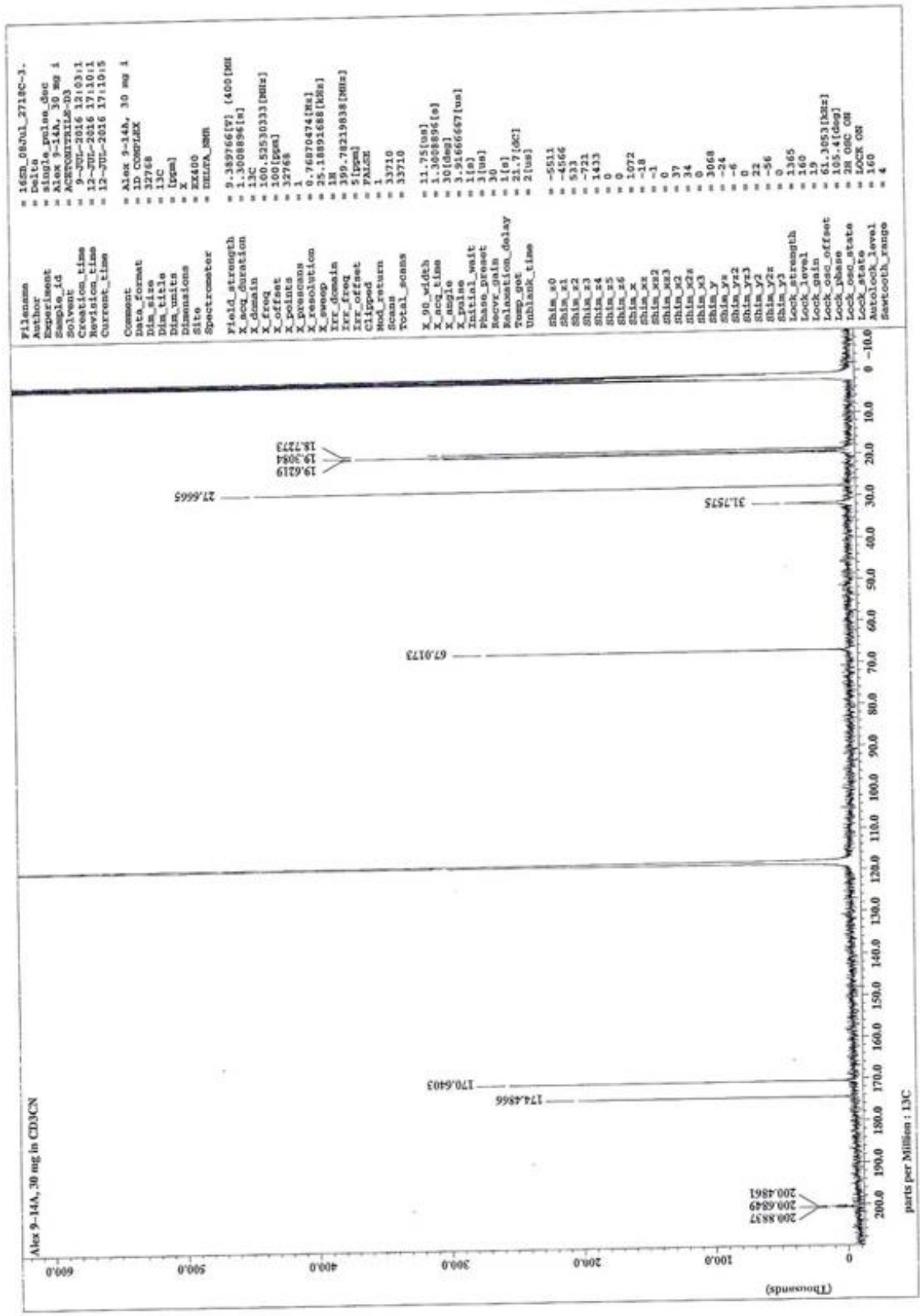


Figure S7. ^{13}C NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 100.6 MHz)

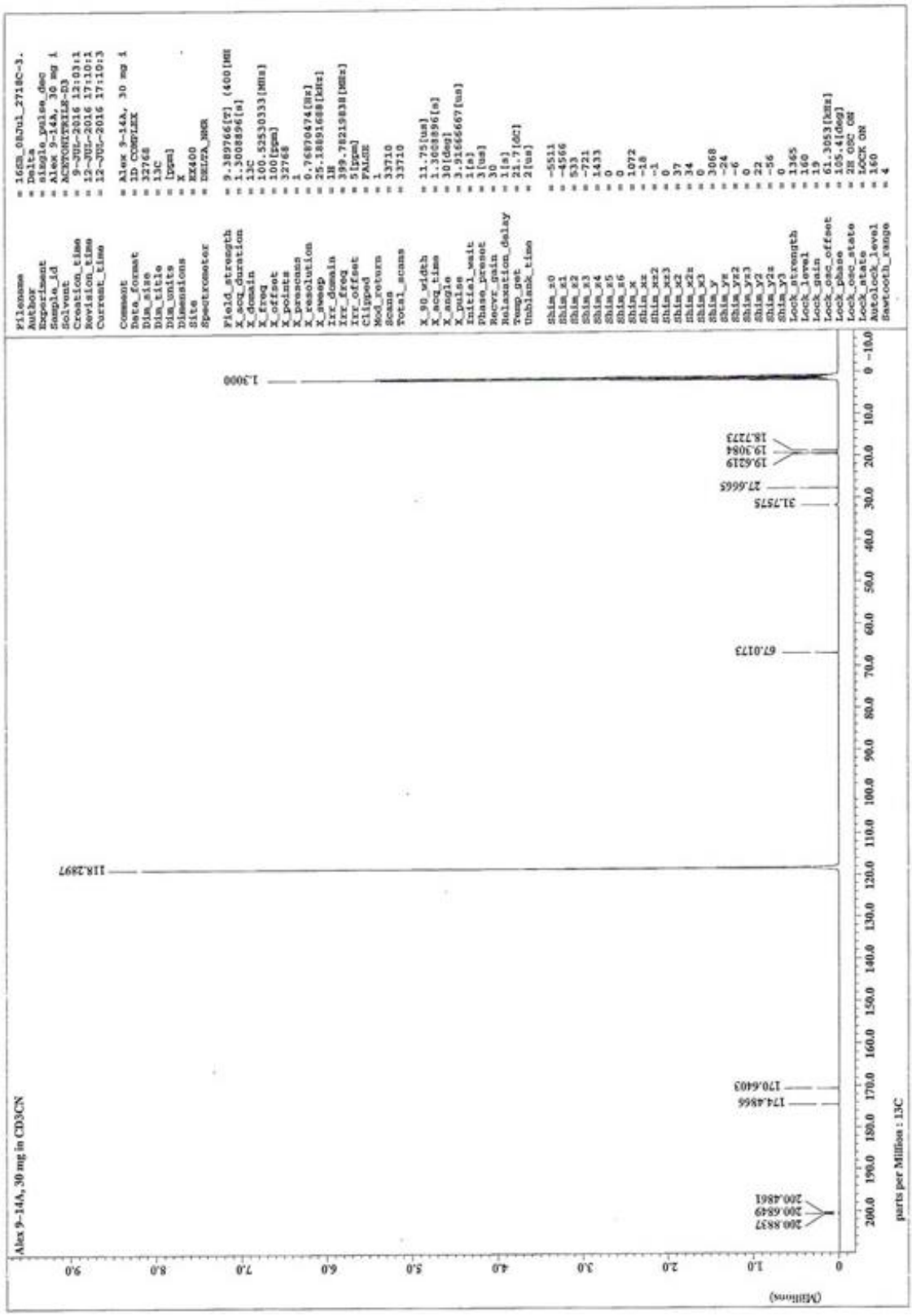


Figure S8. ^{13}C NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 100.6 MHz)

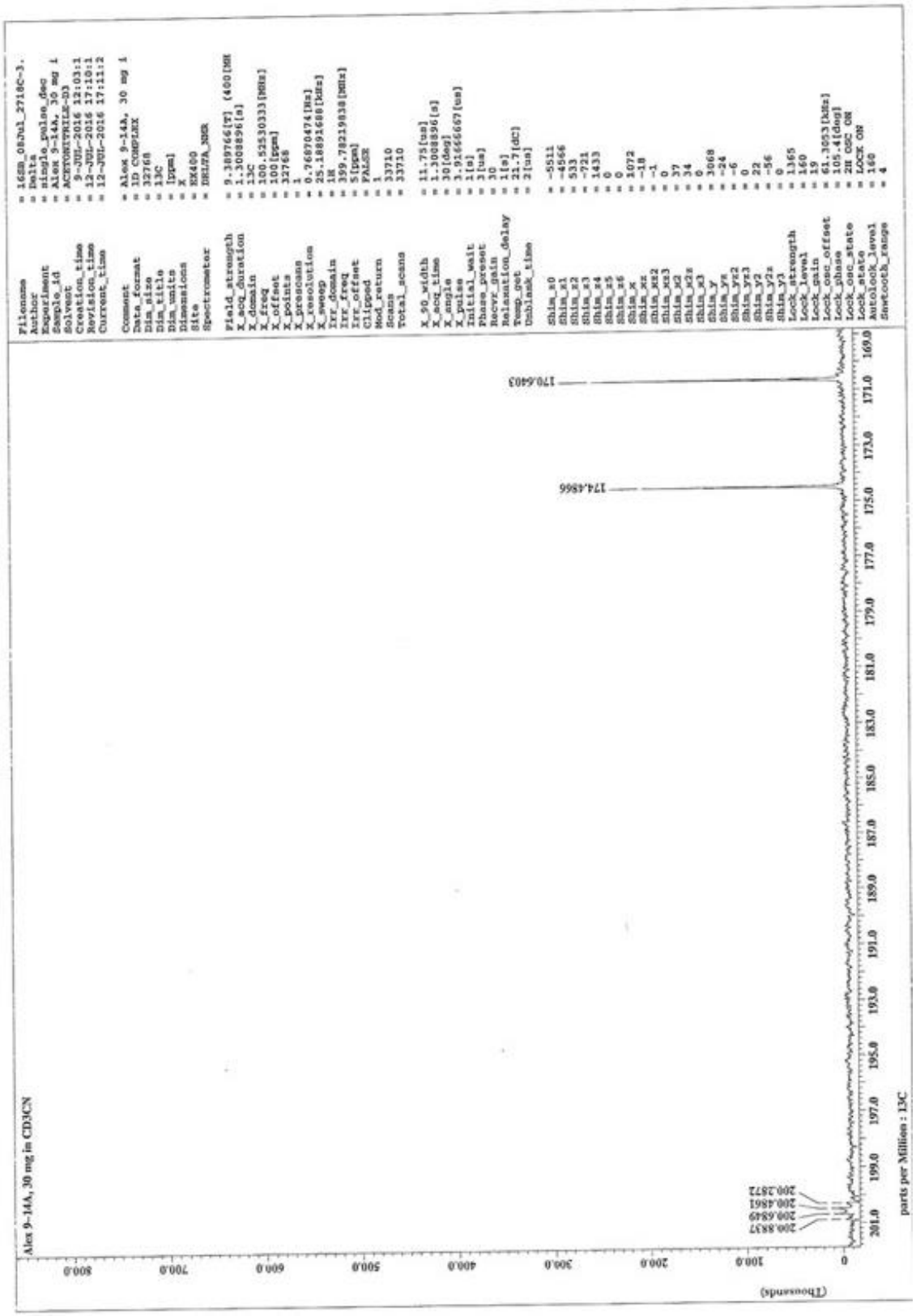


Figure S9. ^{13}C NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 100.6 MHz)

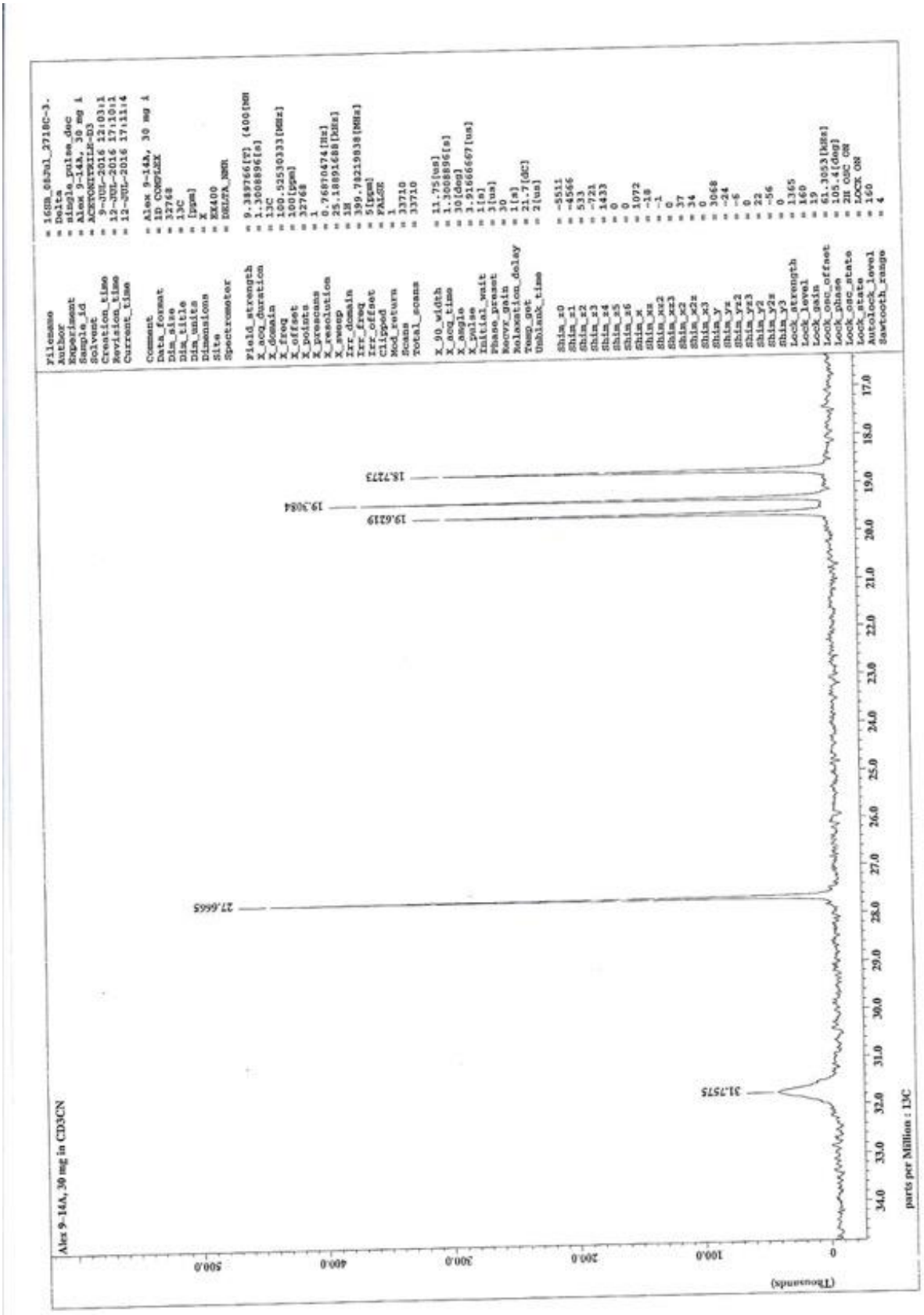


Figure S10. ^{13}C NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 100.6 MHz)

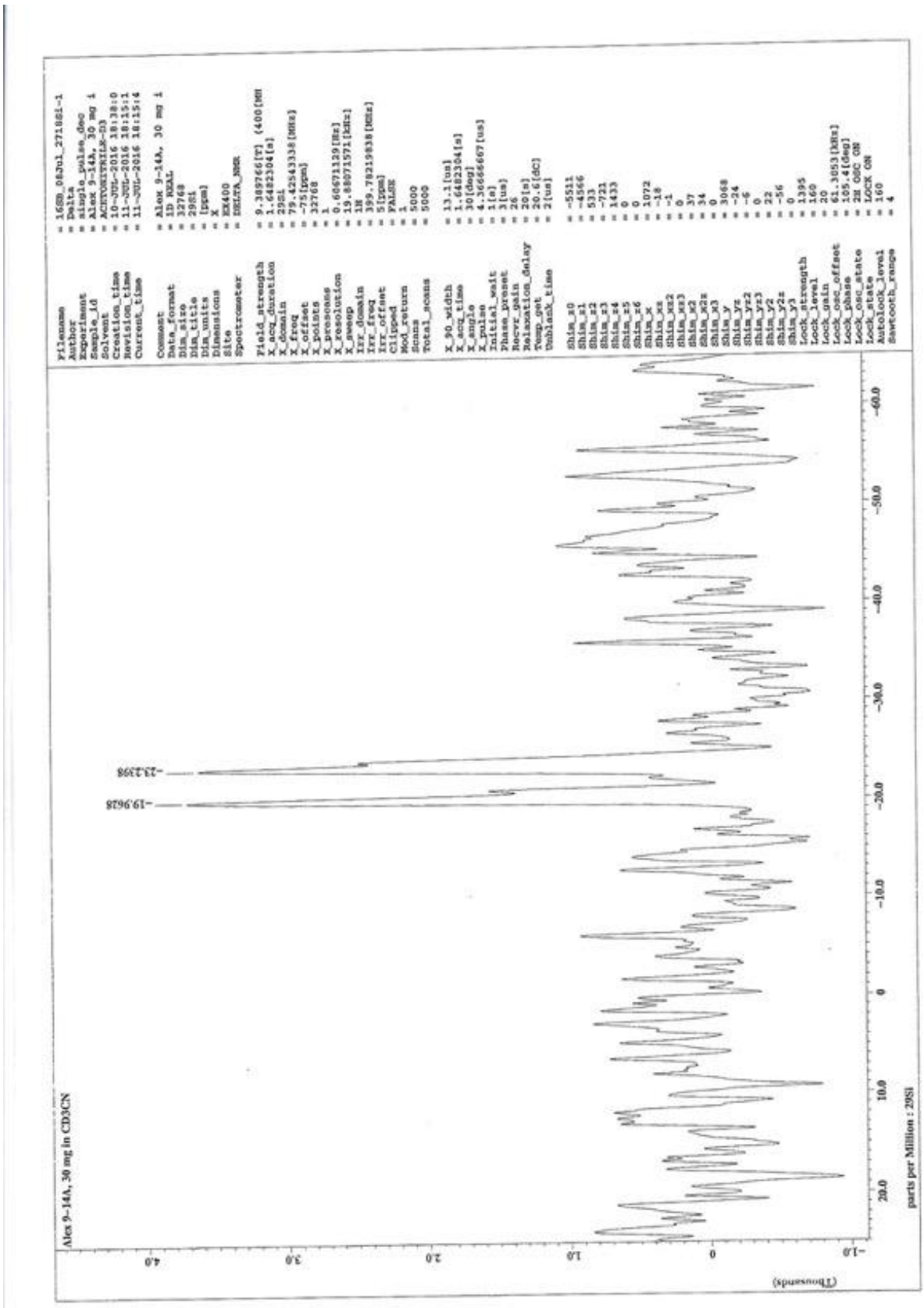


Figure S11. ^{29}Si NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 79.5 MHz)

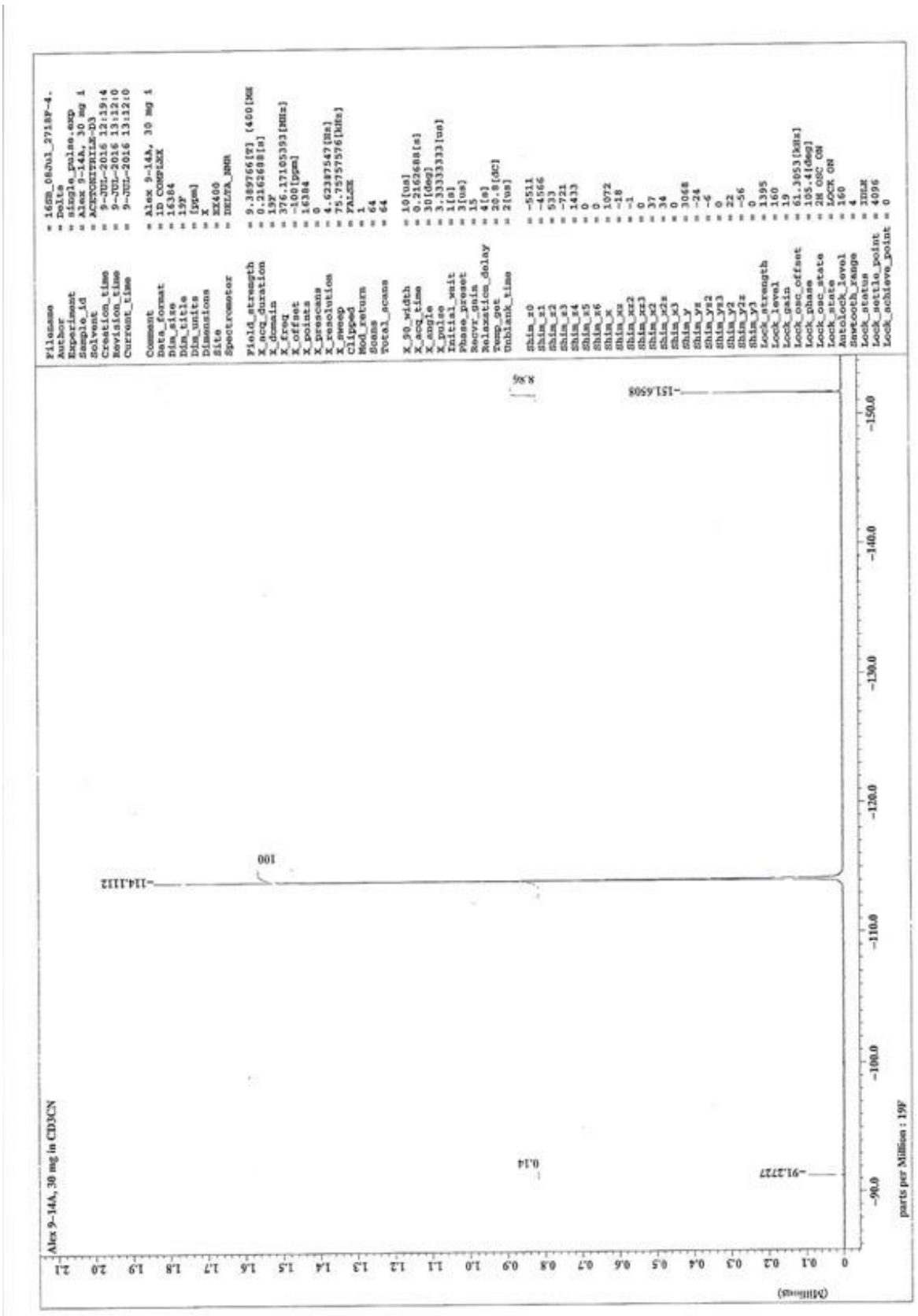


Figure S12. ^{19}F NMR of Comp. **2** in CD_3CN (JEOL JNM-EX400, 396 MHz)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 914a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 914a

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Temperature:     120 K
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Hall group	P 2c -2ac	P 2c -2ac
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Sum formula	C10 H20 F N O3 Si	C10 H20 F N O3 Si
Mr	249.36	249.36
Dx,g cm-3	1.173	1.173
Z	4	4
Mu (mm-1)	0.172	0.172
F000	536.0	536.0
F000'	536.60	
h,k,lmax	18,10,21	18,10,21
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Click on the hyperlinks for more details of the test.