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N-(Chlorodimethylsilyl)methyl anilides: synthesis and structure

Anastasiya S. Soldatenko, Irina V. Sterkhova and Nataliya F. Lazareva

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Experimental

1.1. Material and methods

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.61 and 79.5 MHz, respectively) with cyclohexane or $(Me_3Si)_2O$ as an internal standard. FTIR spectra were taken on a FT-IR Varian 3100 spectrometer.

All reactions and other manipulations were carried out in thoroughly dried glassware in argon atmosphere. Elemental analysis is performed on the Thermo Scientific Flash 2000 Automatic CHNS Analyzer. Melting points were determined using the Boetius Block apparatus. *N*-Aryl-*N*-trimethylsilyl amides **1a-c** were synthesized according to the procedures described in the literature.[S1] The solvents were purified by standard procedures prior to use.[S2]

***N*-(Chlorodimethylsilyl)methyl-*N*-(4-methylphenyl)acetamide 3a.**

A. Chloro(chloromethyl)dimethylsilane **2a** (0.369 g, 2.58 mmol) was added dropwise to a solution of *N*-(4-methylphenyl)-*N*-(trimethylsilyl)acetamide **1a** (0.571 g, 2.58 mmol) in chloroform (7 ml). The reaction mixture was kept at room temperature for 10 h. Chloroform and side products were removed in a vacuum, and the precipitate was recrystallized from benzene. Yield: 0.630 g (2.46 mmol, 95%). M. p. = 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.69 (s, 6H, Me-Si); 1.97 (s, 3H, Me-C); 2.39 (s, 3H, Me-Ph), 3.13 (s, 2H, CH_2); 7.08-7.10 (d, 2H, Ph, ^{3}J = 7.9 Hz), 7.26-7.28 (d,

2H, Ph, ^{3}J = 7.9 Hz). ^{13}C ($CDCl_3$, δ, ppm): 7.48 (Me-Si); 18.67 (4-Me-C_6H_4); 21.41 (Me-C=O); 46.56 (NCH_2); 125.73, 131.00, 138.34 (4-Me-C), 139.37(C-N) (Ph); 174.04 (C=O). ^{29}Si ($CDCl_3$, δ, ppm): -34.50. IR (film, cm^{-1}): 438, 564, 606, 714, 738, 823, 839, 996, 1047, 1107, 1175, 1213, 1251, 1280, 1300, 1384, 1404, 1451, 1513, 1577, 1610, 1648, 1686, 2802, 2860, 2903, 2922, 2955, 2986, 3031, 3052, 3124. Found, %: C, 56.76; H, 6.72; N 5.34. $C_{12}H_{18}ClNOSi$. Calculated, %: %: C, 56.34; H, 7.09; N 5.48.

B. Chloromethyl(fluoro)dimethylsilane **2b** 0.506 g (3.99 mmol) was added dropwise to a solution of *N*-(4-methylphenyl)-*N*-(trimethylsilyl)acetamide **1a** (0.884 g, 3.99 mmol in chloroform (8 ml). The mixture was kept at room temperature for 48 h. Chloroform and side products were removed in a vacuum, and the precipitate was recrystallized from benzene. Yield: 1.020 g (3.98 mmol, 90%).

N-**(Chlorodimethylsilyl)methyl-*N*-(4-chlorophenyl)acetamide 3b.**

A. Chloro(chloromethyl)dimethylsilane **2a** (0.548 g, 3.83 mmol) was added dropwise to a solution of *N*-(4-chlorophenyl)-*N*-(trimethylsilyl)acetamide **1b** (0.927 g, 3.83 mmol) in chloroform (8 ml). The mixture was kept at room temperature for 3 h. Chloroform and side products were removed in a vacuum, and the precipitate was recrystallized from benzene. Yield: 0.92 g (3.33 mmol, 87%). M. p. = 143-145 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.65 (s, 6H, Me-Si); 1.97 (s, 3H, Me-C=O); 3.08 (s, 2H, CH_2); 7.16-7.18 (d, 2H, Ph, ^{3}J = 8.5 Hz) 7.44-7.46 (d, 2H, Ph, ^{3}J = 8.5 Hz). ^{13}C ($CDCl_3$, δ, ppm): 6.61 (Me-Si); 18.66 (Me-C=O); 45.79 (NCH_2); 127.27, 130.33, 134.73(C-Cl), 139.46(C-N) (Ph); 173.32 (C=O). ^{29}Si ($CDCl_3$, δ, ppm): -31.84. IR (film, cm^{-1}): 419, 486, 515, 557, 603, 660, 688, 741, 837, 913, 995, 1016, 1046, 1093, 1171, 1215, 1253, 1289, 1385, 1405, 1490, 1583, 1649, 2803, 2854, 2908, 2958, 2982, 3035, 3052, 3086. Found, %: C, 47.98; H, 5.18; N 4.93. $C_{11}H_{15}Cl_2NOSi$. Calculated, %: C, 47.83; H, 5.47; N 5.07.

B. Chloromethyl(fluoro)dimethylsilane **2b** (0.397 g, 3.14 mmol) was added dropwise to a solution of *N*-(4-chlorophenyl)-*N*-(trimethylsilyl)acetamide **1b** 0.759 g (3.14 mmol) chloroform (8 ml). The mixture was kept at room temperature for 24 h. Chloroform and side products were removed in a vacuum, and the precipitate was recrystallized from benzene. Yield: 0.730 g (2.64 mmol, 84%).

N-**(Chlorodimethylsilyl)methyl-*N*-phenylbenzamide 3c.**

A. Chloro(chloromethyl)dimethylsilane **2a** (0.143 g, 1 mmol) was added dropwise to a solution of *N*-phenyl-*N*-(trimethylsilyl)benzamide **1c** (0.269 g, 1 mmol) in chloroform (10 ml). The reaction mixture was kept at room temperature for 48 h. Chloroform and side products were removed in vacuum, and the precipitate was recrystallized from benzene. Yield: 0.264 g (0.87 mmol, 87%). M. p. = 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.79 (s, 6H, Me-Si); 3.41 (s, 2H, CH_2); 7.03-7.53 (m, PhC=O + Ph-N). ^{13}C ($CDCl_3$, δ, ppm): 6.92 (Me-Si); 47.45 (NCH_2); 125.76, 128.02, 128.10, 128.22, 129.38, 129.62, 131.84, 141.58 (PhC=O + Ph-N); 171.25 (C=O). ^{29}Si ($CDCl_3$, δ, ppm): -32.27. IR (film, cm^{-1}): 440, 520, 583, 698, 732, 792, 838, 912, 1053, 1253, 1307, 1378, 1447, 1494, 1549,1593, 1633, 2901, 2957. Found, %: C, 63.46; H, 6.09; N 4.48. $C_{16}H_{18}ClNOSi$. Calculated, %: C, 63.24; H, 5.97; N 4.61.

B. Chloromethyl(fluoro)dimethylsilane **2b** (0.215 g, 1.5 mmol) was added dropwise to a solution of *N*-phenyl-*N*-(trimethylsilyl)benzamide **1c** (0.404 g, 1.5 mmol) in chloroform (15 ml). The mixture was kept at the room temperature for 240 h. Chloroform and side products were removed in vacuum, and the precipitate was recrystallized from benzene. Yield: 0.283 g (0.93 mmol, 62%).

Single crystals of compound **3c** were prepared from the melt when the melt was slowly cooled to room temperature (at a rate of ~ 20 deg h^{-1}).

X-ray study and refinement

Crystal data were collected on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[S3] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set.[S3] **CCDC 2156048 (3a)**, **2156049 (3b)** and **1845007 (3c)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

X-Ray single crystal structure analysis

Single crystals of **3a,b** were obtained by re-crystallization from benzene solution, single crystals of **3c** were obtained from melt. In order to investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of single crystals **3a-c** was carried out. The molecular structures are depicted in Figure S1. Crystal data, data collection and structure refinement details are summarized in Table S1. Principal bond distances, bond angles and torsion angles are presented in Table S2.

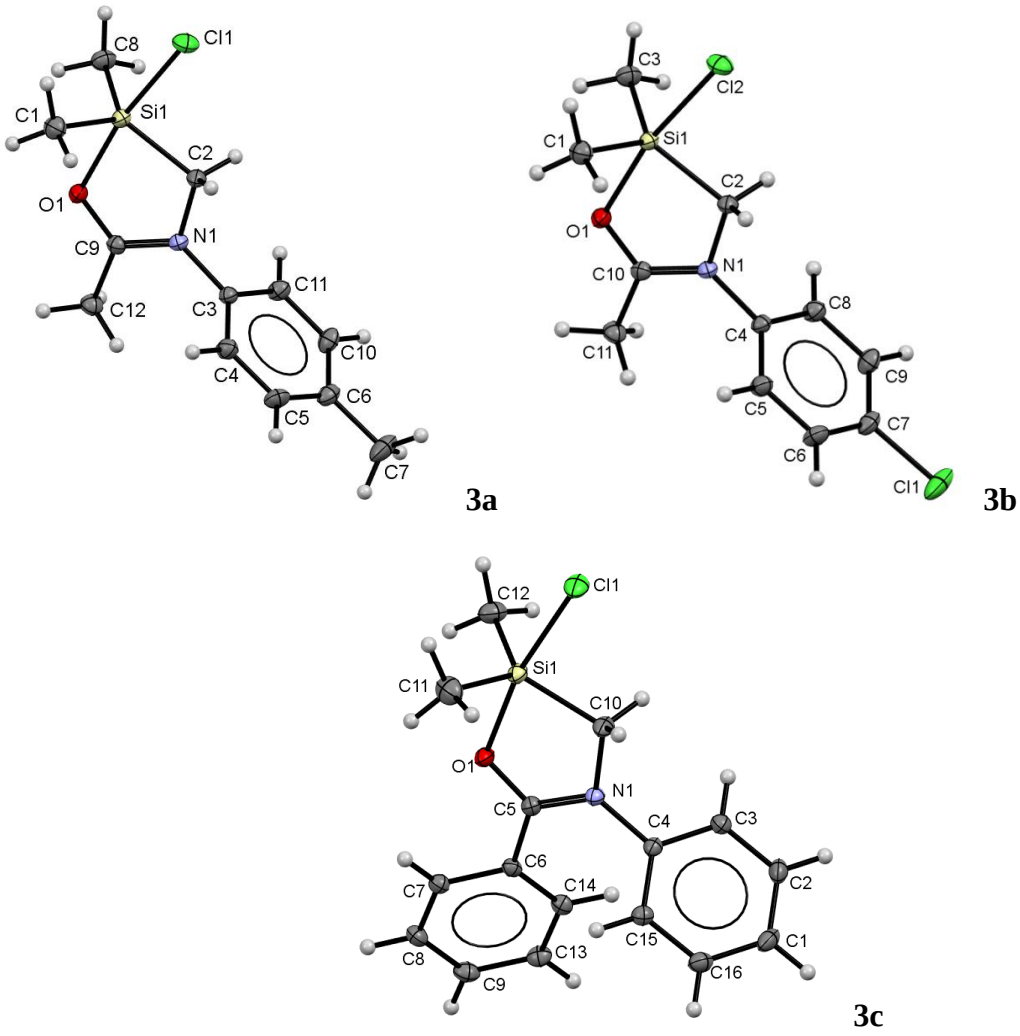

Figure S1. Molecular structures of compounds **3a,b** (ORTEP, 20% thermal ellipsoids) and **3c** (ORTEP, 50% thermal ellipsoids)

Table S1. Crystal Data, Details of Intensity Measurements, and Structure Refinement for compounds **3a-c.**

Compound	**3a**	**3b**	**3c**
Empirical formula	$C_{12}H_{18}ClNOSi$	$C_{11}H_{13}Cl_2NOSi$	$C_{16}H_{18}ClNOSi$
Formula weight, $g \cdot mol^{-1}$	255.81	274.21	303.85
Crystal system	monoclinic	monoclinic	tetragonal
Space group	C 2/c	C 2/c	P 4_1
a , Å	17.3707(11)	17.4552(8)	10.5266(4)
b , Å	10.0019(6)	9.8986(5)	10.5266(4)
c , Å	16.2210(9)	16.0718(8)	13.9411(7)
α , °	90	90	90
β , °	99.797(2)	99.984(2)	90
γ , °	90	90	90
Volume, $Å^3$	2777.1(3)	2734.9(2)	1544.80(14)
Z	8	8	4
D calc., $g \cdot cm^{-3}$	1.224	1.332	1.381
Abs. coefficient, mm^{-1}	0.343	0.542	0.185
Radiation (λ / Å)	MoKα (0.71073)	MoKα (0.71073)	MoKα (0.71073)
Temperature, K	293(2)	293(2)	100(2)
2Θ range, °	4.72 – 60.68	4.74 – 60.02	4.84 – 60.13
Crystal size, mm	0.25 × 0.40 × 0.40	0.45 × 0.50 × 0.50	0.29 × 0.32 × 0.34
Crystal habit	colorless prism	colorless prism	colorless prism
F(000)	1088	1136	640
Reflections collected	45061	25787	45285
Independent reflections	4133	3843	4363
Max. and min. trans.	0.7460 / 0.6396	0.7460 / 0.5042	0.9600 / 0.7600
N. of ref. parameters	150	168	183
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0485 / 0.1125	0.0494 / 0.1132	0.0257 / 0.0658
R_1 / wR_2 (all data)	0.1158 / 0.1288	0.1031 / 0.1274	0.0289 / 0.0677
Goodness-of-fit on F^2	1.021	1.032	1.058
L. diff. peak / hole, $e \cdot Å^{-3}$	0.282 / -0.256	0.316 / -0.443	0.228 / -0.186
Weight scheme, $P=(F_o^2+2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)+ (0.0650P)^2]$	$w = 1/[\sigma^2(F_o^2)+ (0.0702 P)^2+ 0.4458 P]$	$w = 1/[\sigma^2(F_o^2)+ (0.0392 P)^2+ 0.2603 P]$

Table S2. Selected bond lengths, bond and torsion angles in compounds **3a-c**

Compound	Bond	*l*, Å	Angle	φ, ˚	Torsion angle	θ, ˚
3a	Cl1-Si1	2.273(1)	C1-Si1-C8	118.2(1)	C9-N1-C2-Si1	3.9(2)
	Si1-C1	1.858(2)	C1-Si1-C2	119.4(1)	C3-N1-C2-Si1	-179.1(1)
	Si1-C8	1.862(2)	C8-Si1-C2	121.5(1)	C1-Si1-C2-N1	82.9(2)
	Si1-C2	1.894(2)	C1-Si1-O1	90.5(1)	C8-Si1-C2-N1	-86.4(2)
	Si1-O1	2.010(1)	C8-Si1-O1	88.3(1)	O1-Si1-C2-N1	-3.2(1)
	O1-C9	1.270(2)	C2-Si1-O1	82.2(1)	Cl1-Si1-C2-N1	178.3(1)
	N1-C9	1.329(2)	C1-Si1-Cl1	95.3(1)	C9-N1-C3-C4	-83.8(2)
	N1-C3	1.443(2)	C8-Si1-Cl1	95.3(1)	C2-N1-C3-C4	99.4(2)
	N1-C2	1.472(2)	C2-Si1-Cl1	88.7(1)	C9-N1-C3-C11	98.9(2)
	C3-C4	1.373(2)	O1-Si1-Cl1	170.7(1)	C2-N1-C3-C11	-77.9(2)
	C3-C11	1.377(2)	C9-O1-Si1	113.9(1)	C11-C3-C4-C5	-0.5(3)
	C4-C5	1.385(3)	C9-N1-C3	124.5(1)	N1-C3-C4-C5	-177.8(2)
	C6-C7	1.508(3)	C9-N1-C2	115.9(1)	C3-C4-C5-C6	0.4(3)
3b	Cl2-Si1	2.278(1)	C1-Si1-C3	118.2(1)	C1-Si1-C2-N1	84.5(2)
	Si1-C1	1.853(2)	C1-Si1-C2	120.1(1)	C3-Si1-C2-N1	-85.4(2)
	Si1-C3	1.861(2)	C3-Si1-C2	121.0(1)	O1-Si1-C2-N1	-1.9(1)
	Si1-C2	1.894(1)	C1-Si1-O1	90.9(1)	Cl2-Si1-C2-N1	179.4(1)
	Si1-O1	2.011(1)	C3-Si1-O1	88.5(1)	Si1-C2-N1-C10	2.8(2)
	Cl1-C7	1.735(2)	C2-Si1-O1	82.1(1)	Si1-C2-N1-C4	178.6(1)
	O1-C10	1.261(2)	C1-Si1-Cl2	95.2(1)	C10-N1-C4-C8	101.8(2)
	C2-N1	1.475(2)	C3-Si1-Cl2	95.5(1)	C2-N1-C4-C8	-73.6(2)
	N1-C10	1.323(2)	C2-Si1-Cl2	88.1(1)	C10-N1-C4-C5	-81.7(2)
	N1-C4	1.444(2)	O1-Si1-Cl2	170.1(1)	C2-N1-C4-C5	102.9(2)
	C4-C8	1.376(3)	C10-O1-Si1	114.0(1)	C8-C4-C5-C6	0.2(3)
	C4-C5	1.380(3)	N1-C2-Si1	110.2(1)	N1-C4-C5-C6	-176.3(2)
	C10-C11	1.491(3)	C10-N1-C4	125.3(1)	C4-C5-C6-C7	0.0(3)
3c	Cl1-Si1	2.299(1)	C12-Si1-C11	117.5(1)	C16-C1-C2-C3	-0.9(3)
	Si1-C12	1.860(2)	C12-Si1-C10	123.0(1)	C1-C2-C3-C4	0.3(3)
	Si1-C11	1.860(2)	C12-Si1-O1	90.2(1)	C2-C3-C4-C15	1.0(3)
	Si1-C10	1.888(2)	C10-Si1-O1	82.1(1)	C2-C3-C4-N1	177.6(2)
	Si1-O1	1.976(1)	C12-Si1-Cl1	94.4(1)	C5-N1-C4-C15	-53.9(2)
	O1-C5	1.272(2)	O1-Si1-Cl1	169.4(1)	C10-N1-C4-C15	122.9(2)
	N1-C5	1.332(2)	C5-O1-Si1	114.7(1)	C5-N1-C4-C3	129.5(2)
	C1-C2	1.385(3)	C5-N1-C4	127.3(1)	C10-N1-C4-C3	-53.6(2)
	C1-C16	1.391(3)	C5-N1-C10	114.5(1)	Si1-O1-C5-N1	1.9(2)
	C2-C3	1.392(3)	C4-N1-C10	118.1(1)	Si1-O1-C5-C6	-175.6(1)
	C3-C4	1.394(2)	C2-C1-C16	120.1(2)	C4-N1-C5-O1	172.7(2)
	C4-C15	1.392(2)	C3-C4-N1	118.3(2)	C4-N1-C5-C6	-10.0(3)
	C5-C6	1.481(2)	O1-C5-N1	117.4(2)	O1-C5-C6-C14	148.2(2)
	C6-C7	1.402(2)	N1-C5-C6	124.9(2)	N1-C5-C6-C14	-29.1(3)

The silicon atoms in the molecules of compounds **3a-c** have a distorted trigonal-bipyramidal configuration, which is typical for such structures.[S4-S9] The equatorial vertices contain carbon atoms, while the axial vertices contain oxygen and chlorine atoms. The exit of the silicon atom from the equatorial plane towards the Cl atom is 0.100, 0.095, and 0.064 Å in the molecules of amides **3a-c**, respectively. The degrees of bipyramidality of TBP (η_a and η_e, %), estimated by the Tamao formulas,[S10] are shown in Table S3. The value of the Cl-Si-O angle differs from the unfolded (180º) by almost 10º (170.7(1), 170.1(1) and 169.4(1)º in amides **3a-c**). The five-membered heterocycle in molecules **3a-c** is almost planar; the departure of the Si atom from the cycle plane is 0.078 Å, 0.044, and 0.050 Å, respectively. The lengths of the Si-Cl bonds consist of 2.273(1), 2.278(1) and 2.299(1) Å in compounds **3a-c**, respectively. The length of the Si-O bond in compounds **2a,b** almost coincide (2.010(1) and 2.011(1) Å)) and are on 0.035 Å longer in comparison with compound **3c** (1.976(1) Å). These differences connected with different thermal conditions of X-ray experiment: compounds **3a,b** were analyzed by X-ray diffraction at 293 K whereas compound **3c** at 100 K. We recently discussed the effect of temperature on the Si←O dative bond length[S11] and found that as the temperature increases, the dative interaction weakens and the bond length increases. The Si-Cl and Si-O bonds lengths are typical for [3+2] TBP coordination.[S12] The value of the Si-Cl bond length in similar structures ranges from 2.264 to 2.335 Å, and the Si-O coordination bond length is 1.921 to 1.990 Å. Average distances Si-C equatorial bonds are 1.899 and 1.869 Å in compounds **3a,b** respectively. The sum of Si-Cl and Si-O bonds in the compounds is almost the same and amounts to 4.283, 4.289 and 4.275 Å for amides **3a-c**, respectively, which is close to the average value of the sum of these bonds in similar structures (4.264 Å).[S4-S9] The crystal structure of amides 1-3 is formed due to short contacts between chlorine and hydrogen atoms of neighboring molecules (Figure S2). The lengths of H···Cl halogen bonds in the crystals of compounds **3a-c** are 2.803-2.884 Å.

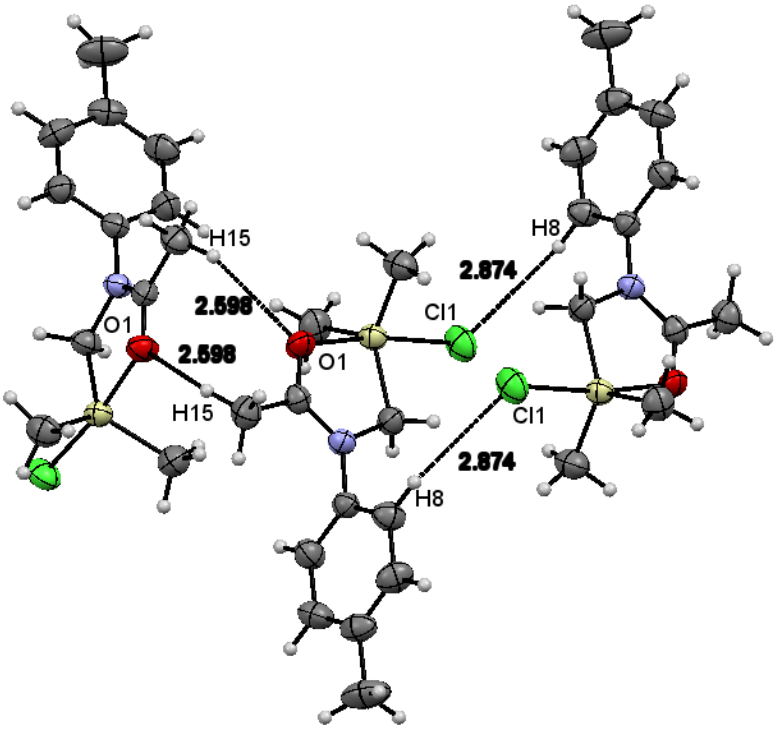

Figure S2. Short contacts in the crystals of compound **3a.**

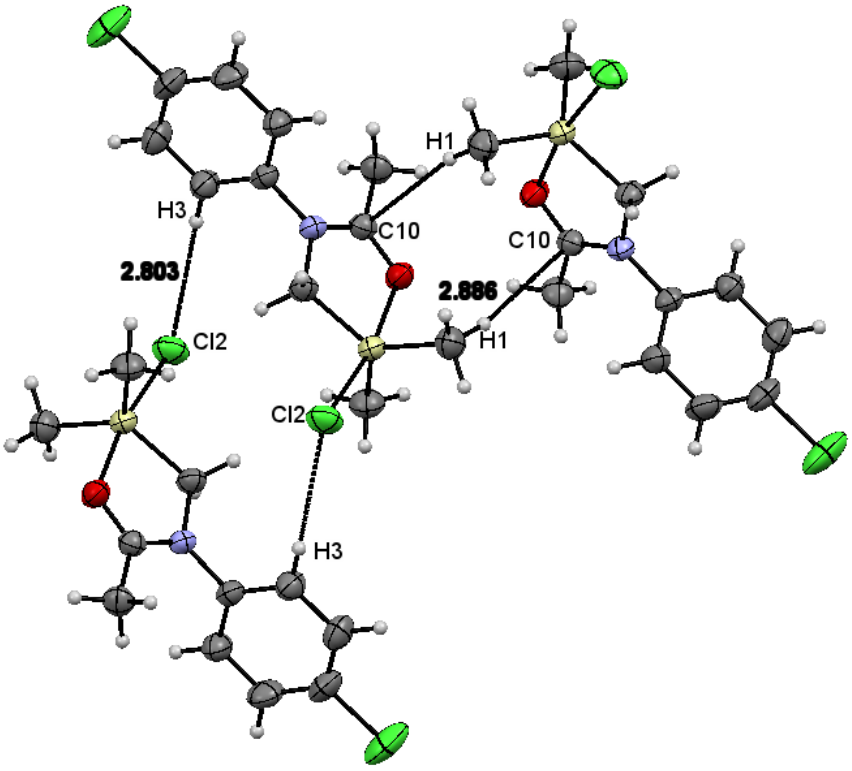

Figure S3. Short contacts in the crystals of compound **3b.**

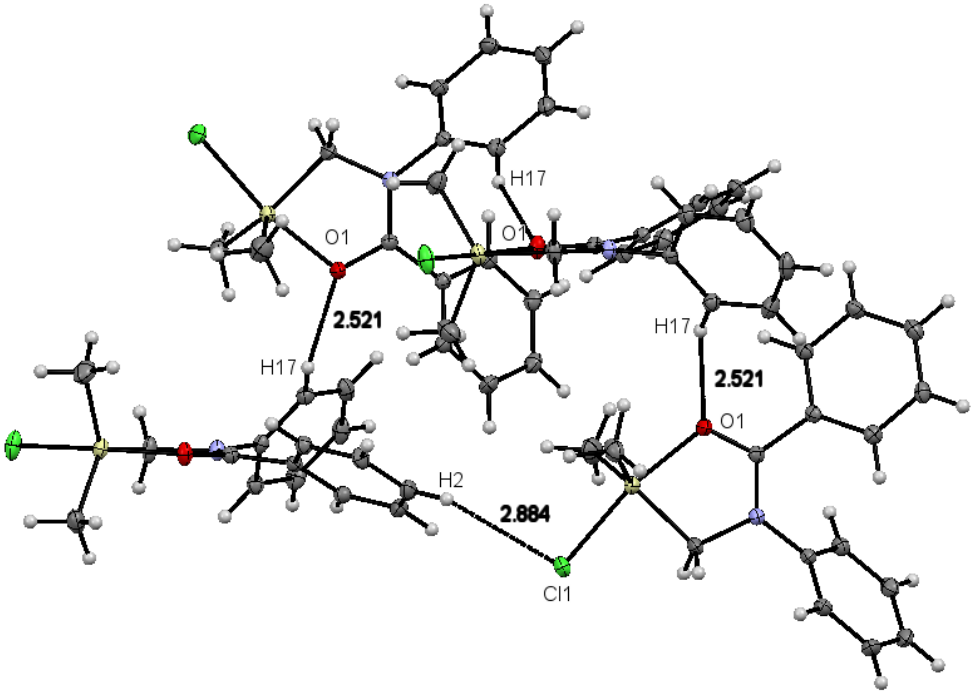

Figure S4. Short contacts in the crystals of compound **3c**

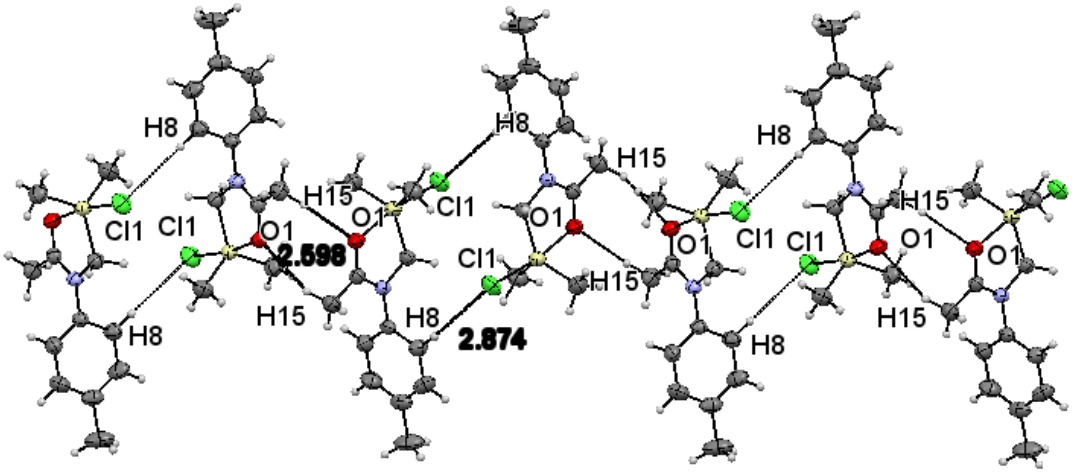

Figure S5. Crystal structure of compound **3a**.

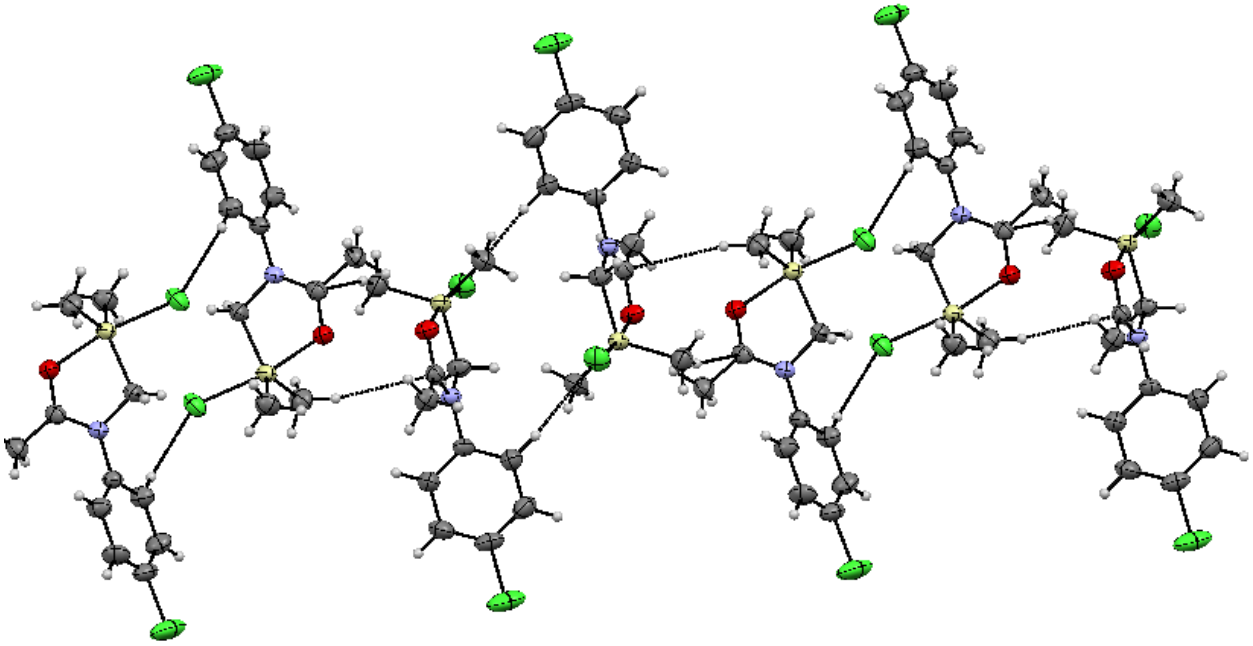

Figure S6. Crystal structure of compound **3b.**

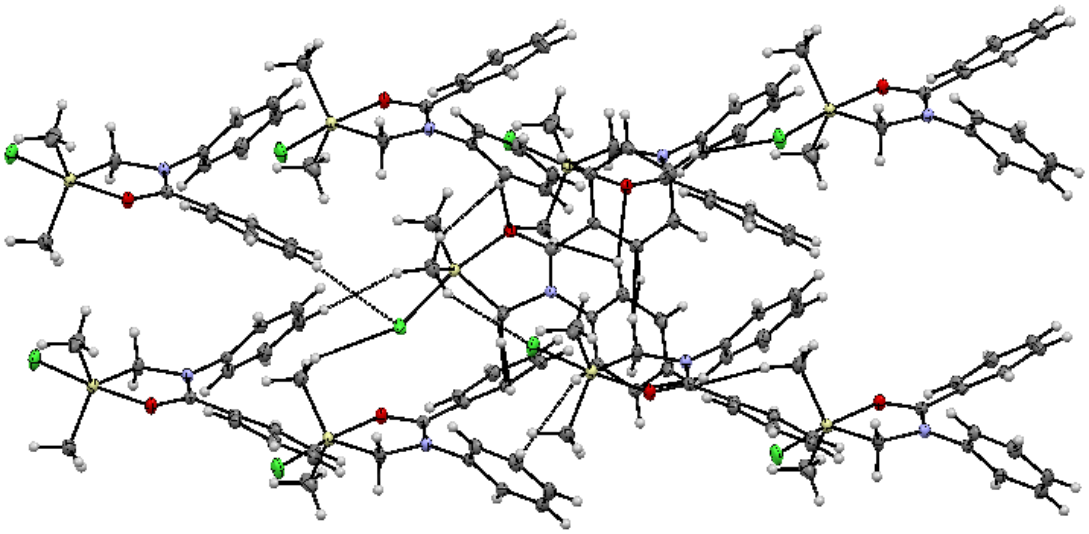

Figure S7. Crystal structure of compound **3c.**

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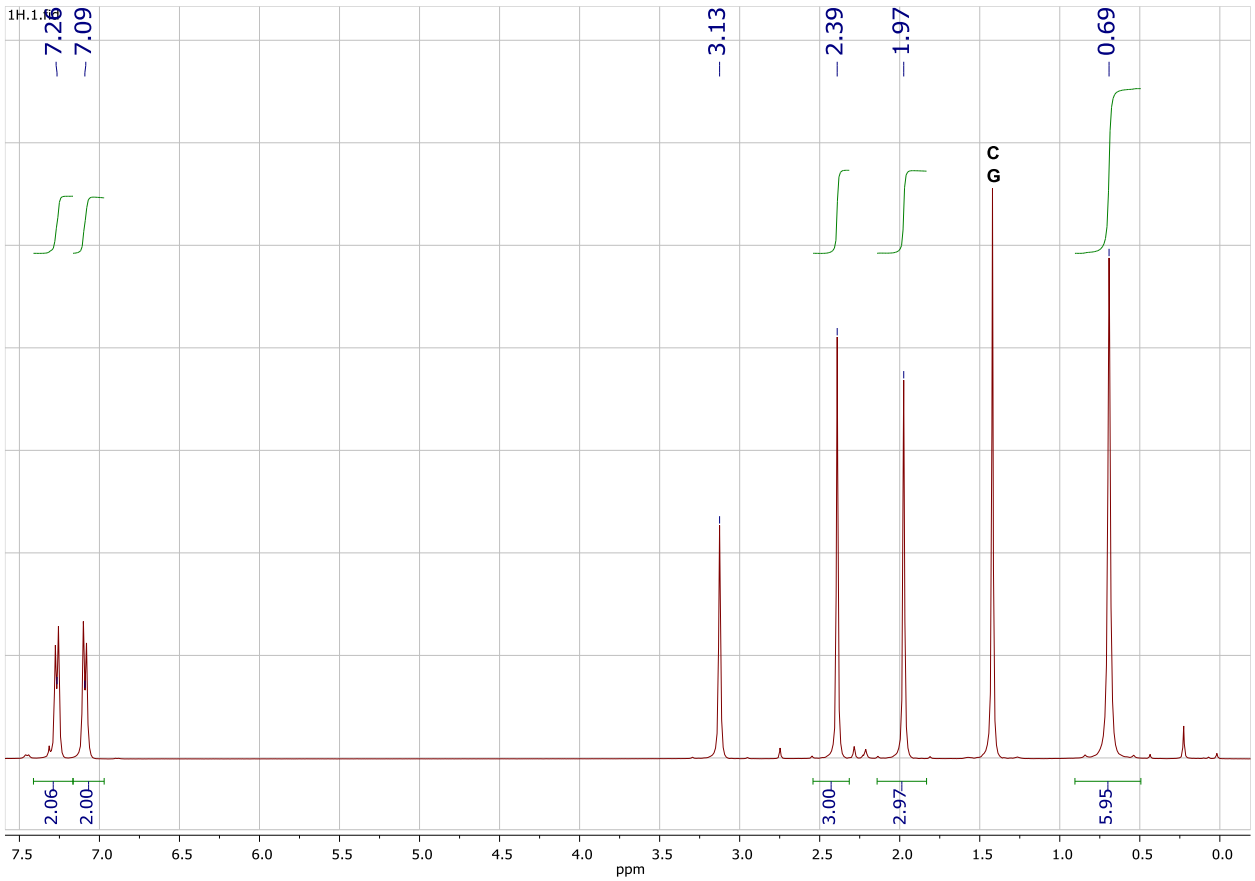

Figure S8. NMR ^{1}H spectrum of compound **3a**.

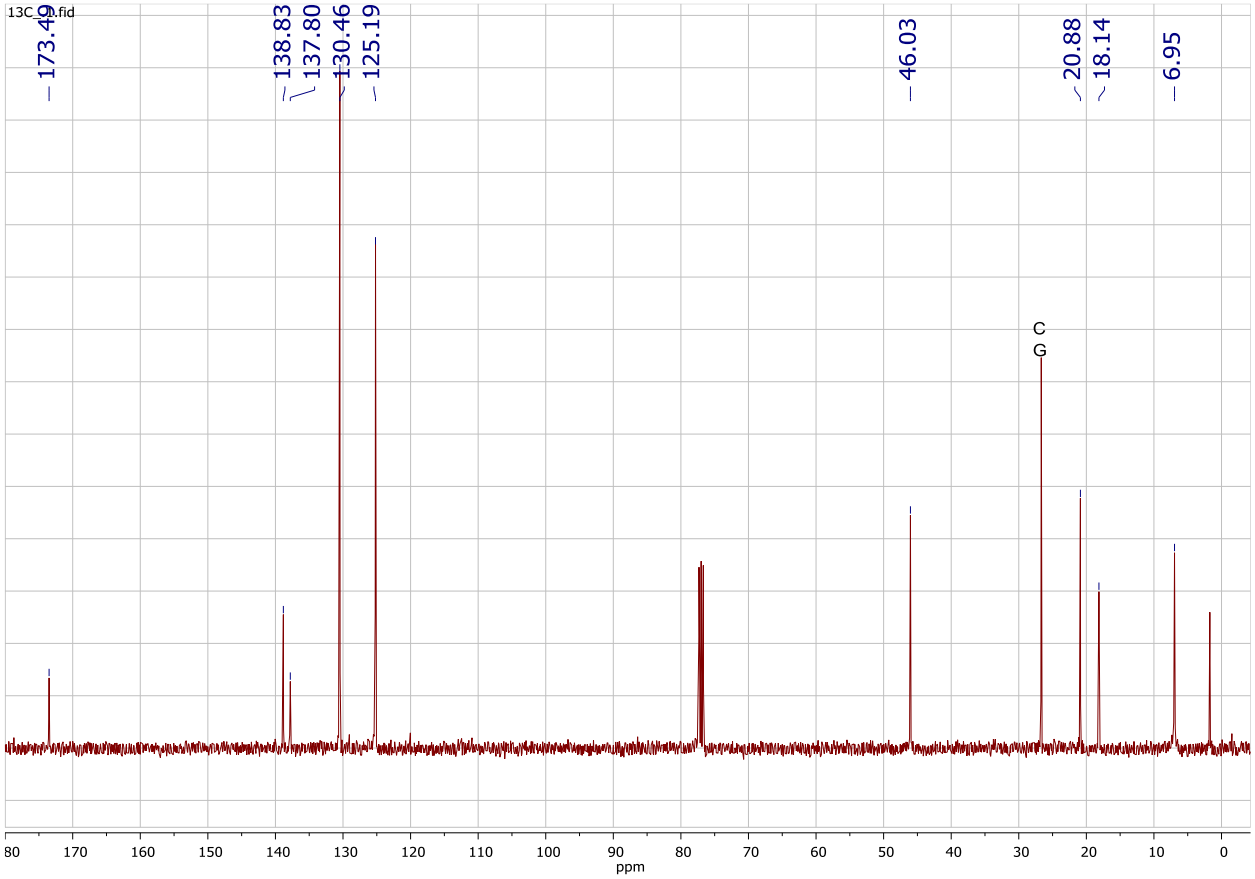

Figure S9. NMR ^{13}C spectrum of compound **3a.**

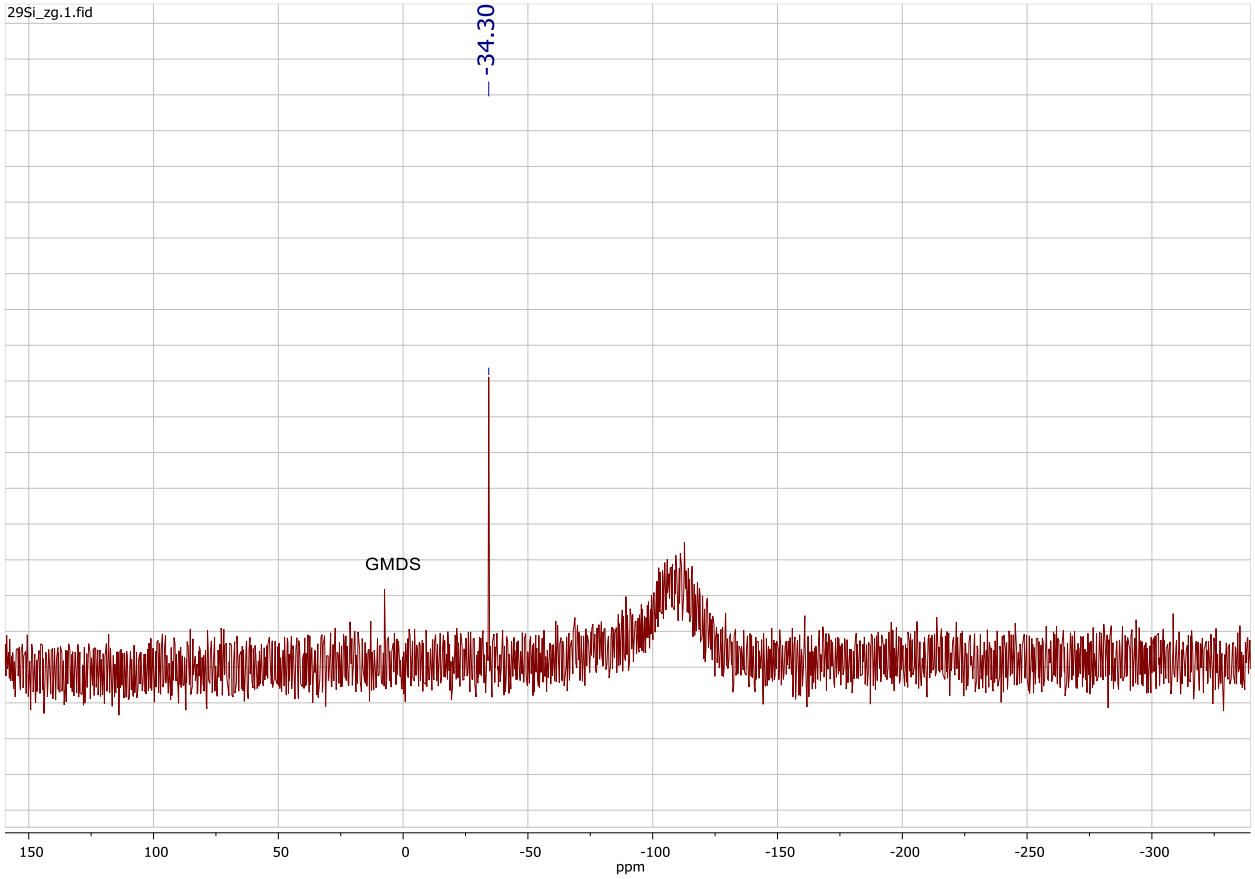

Figure S10. NMR ^{29}Si spectrum of compound **3a.**

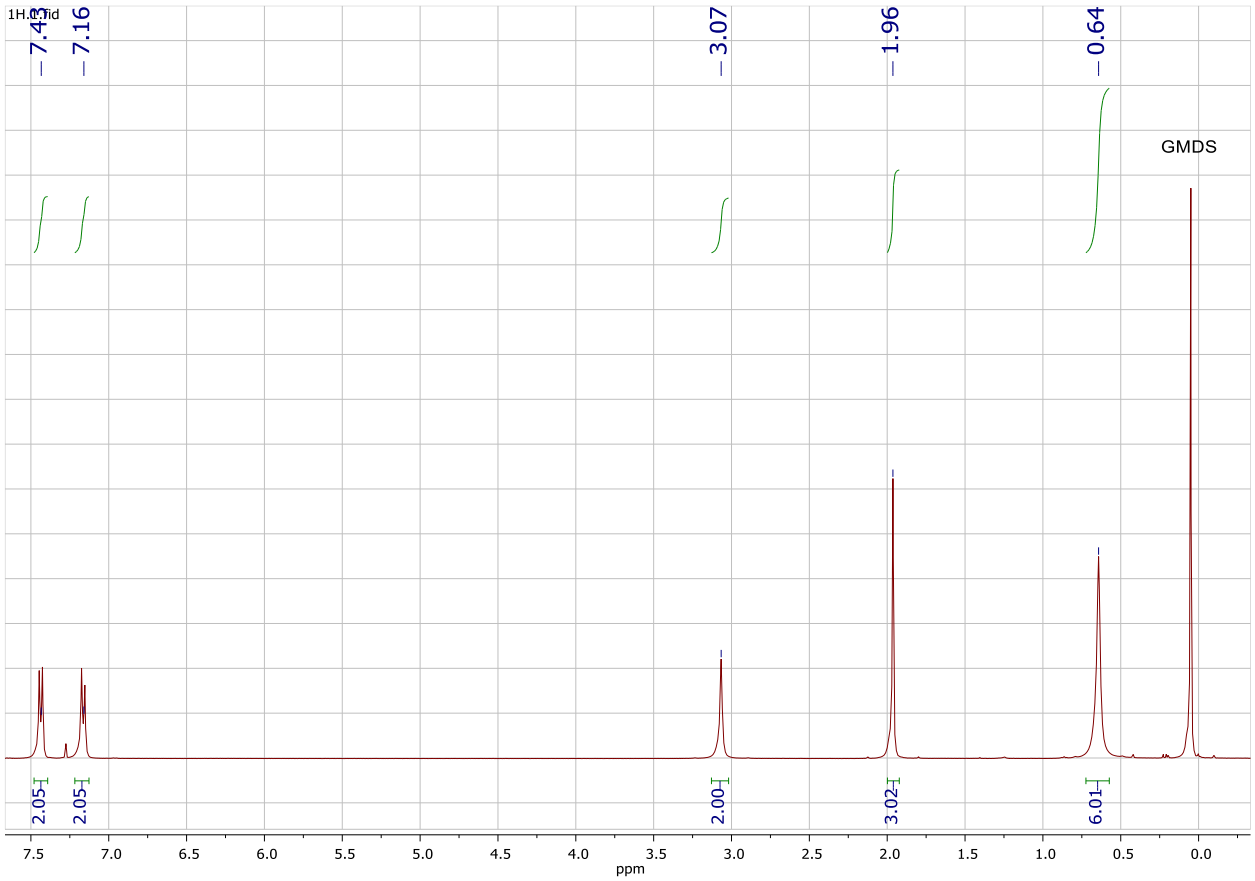

Figure S11. NMR ^{1}H spectrum of compound **3b**.

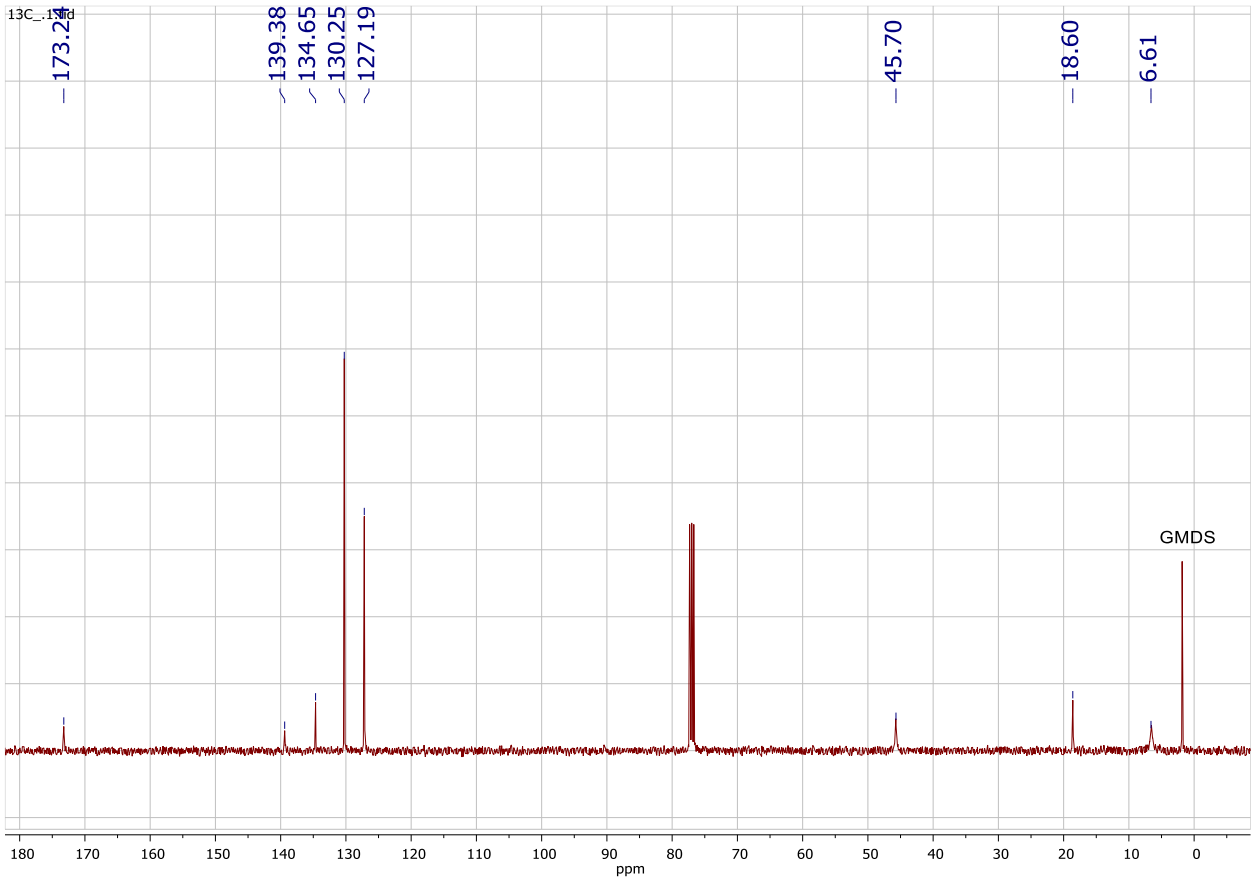

Figure S12. NMR ^{13}C spectrum of compound compound **3b.**

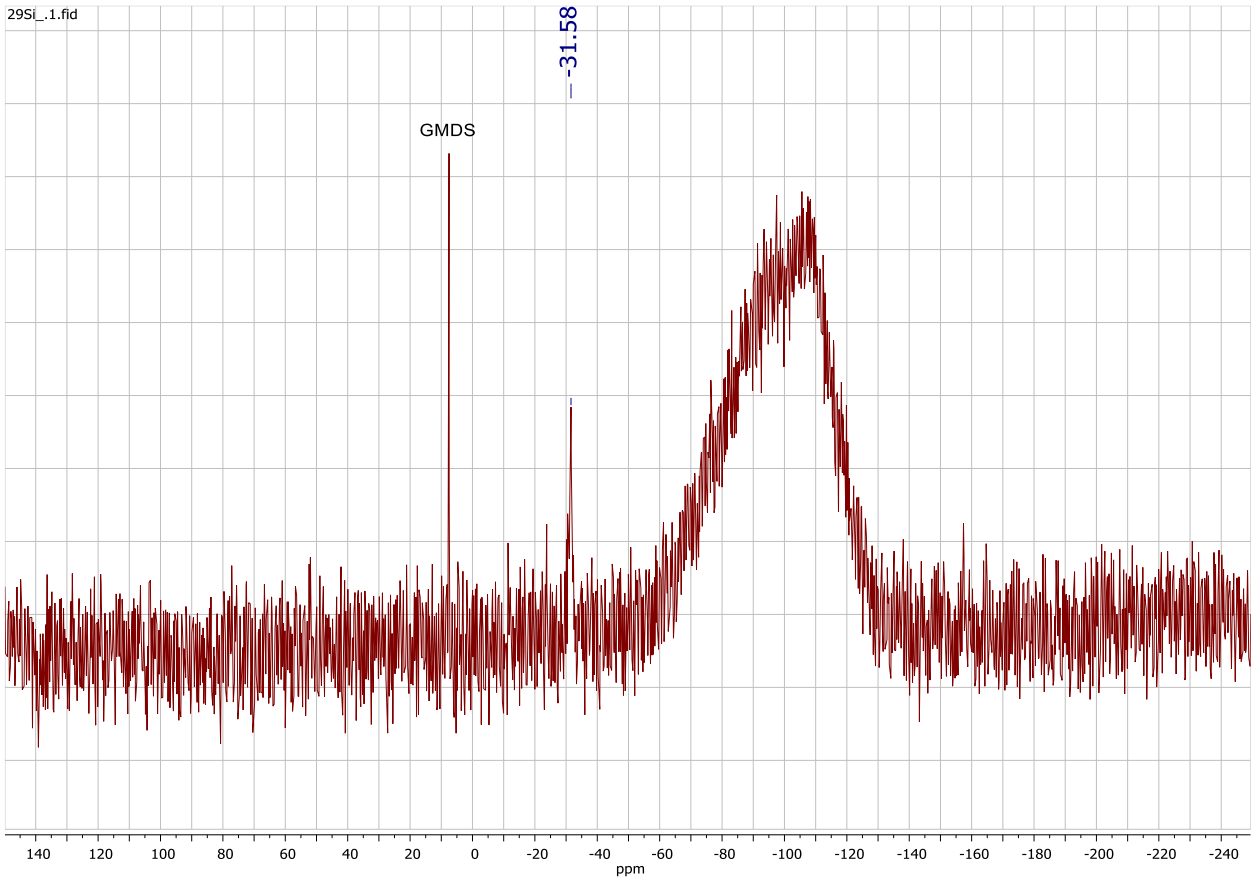

Figure S13. NMR ^{29}Si spectrum of compound **3b.**

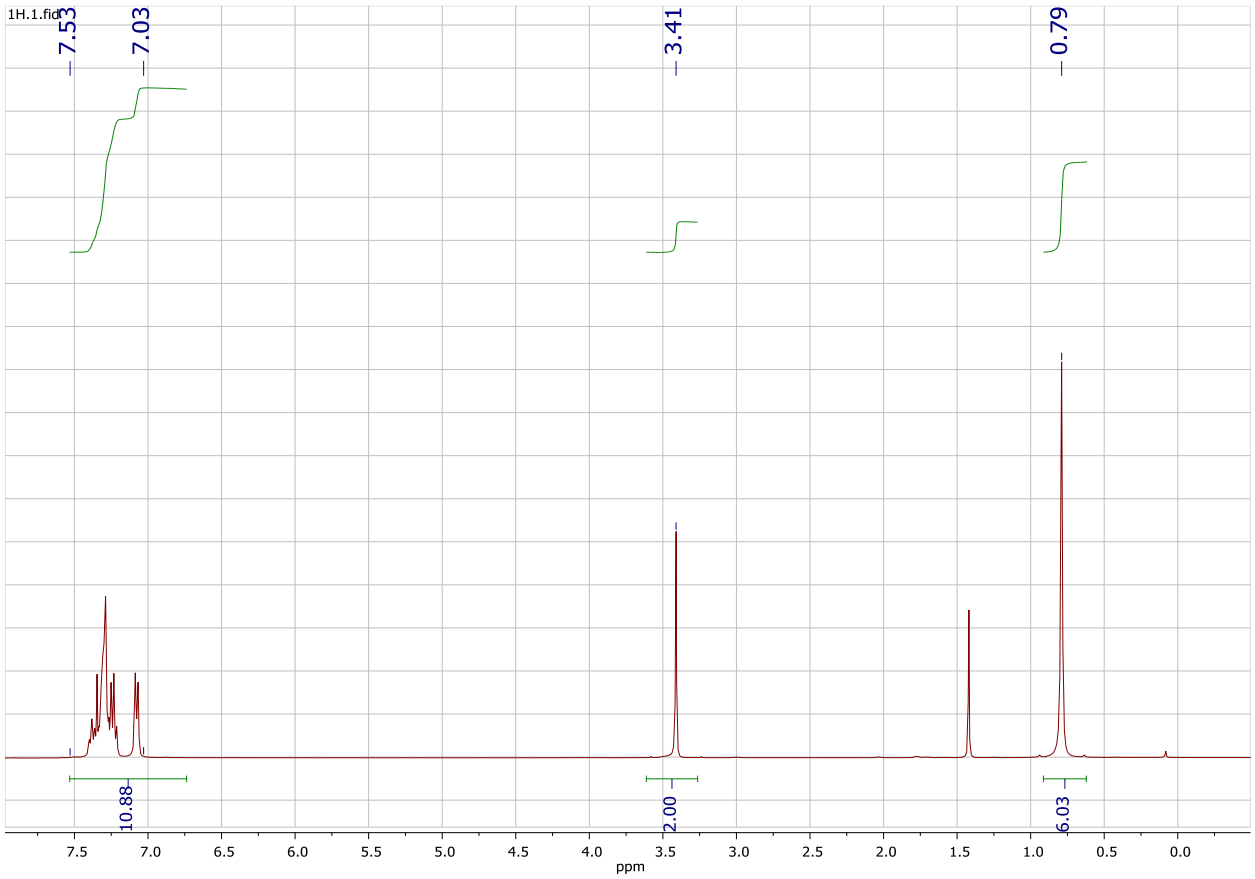

Figure S14. NMR ^{1}H spectrum of compound **3c.**

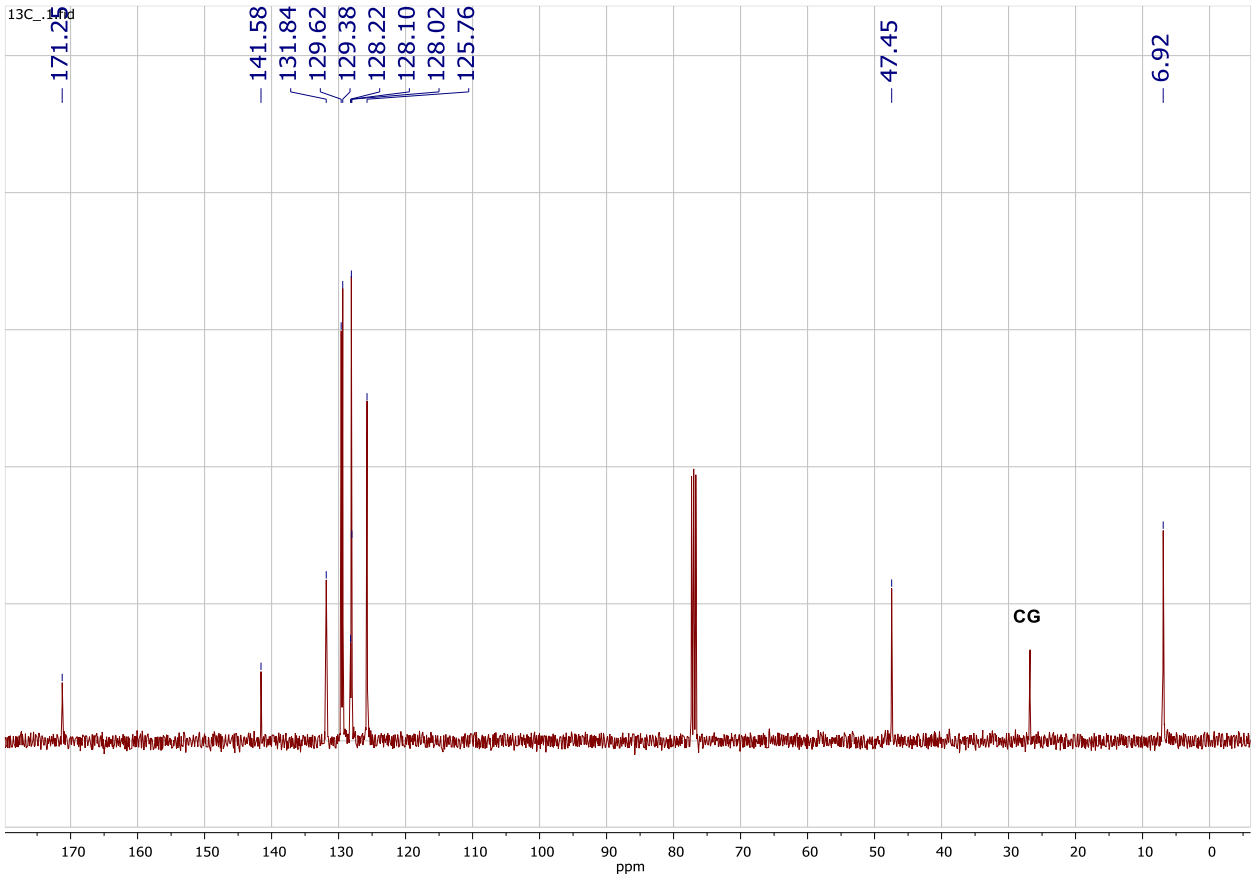

Figure S15. NMR ^{13}C spectrum of compound **3c**.

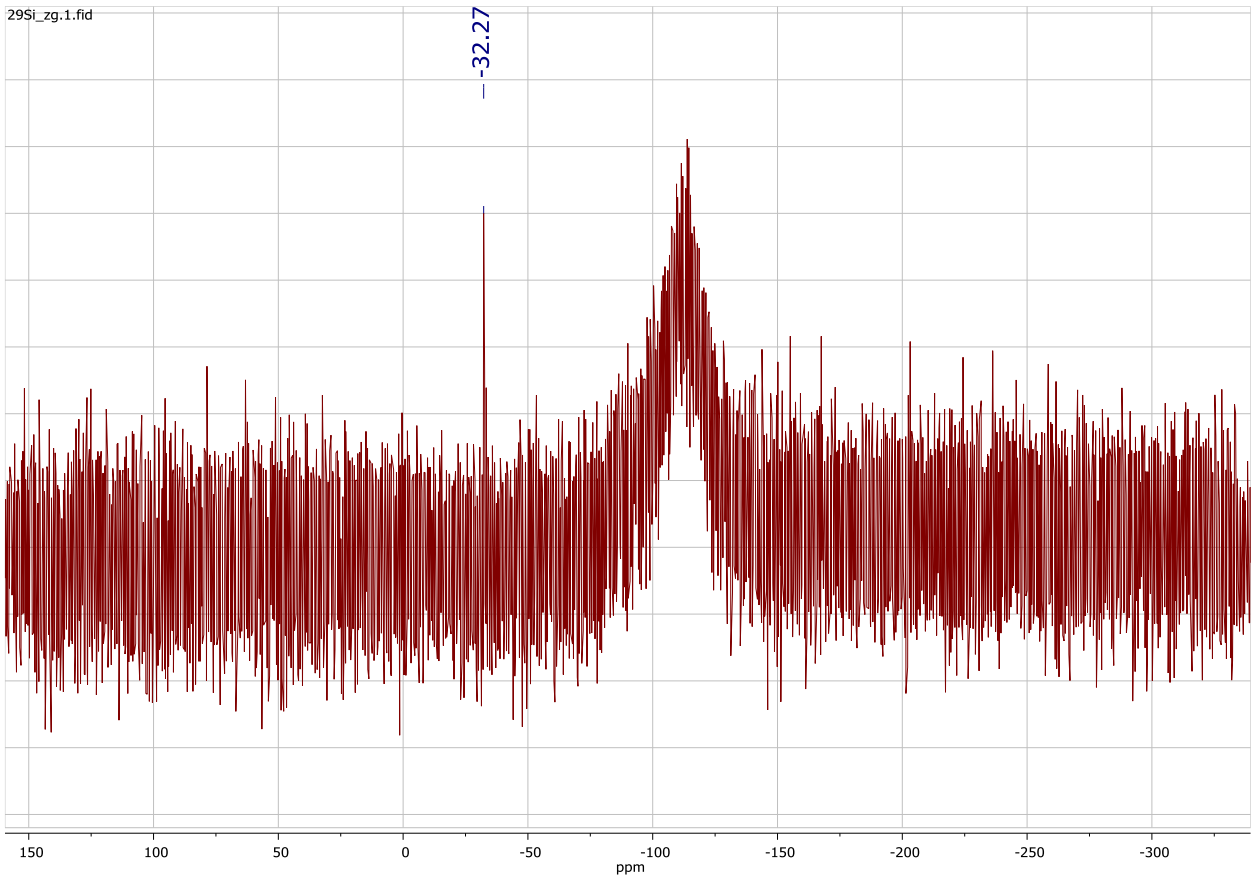

Figure S16. NMR ^{29}Si spectrum of compound **3c.**

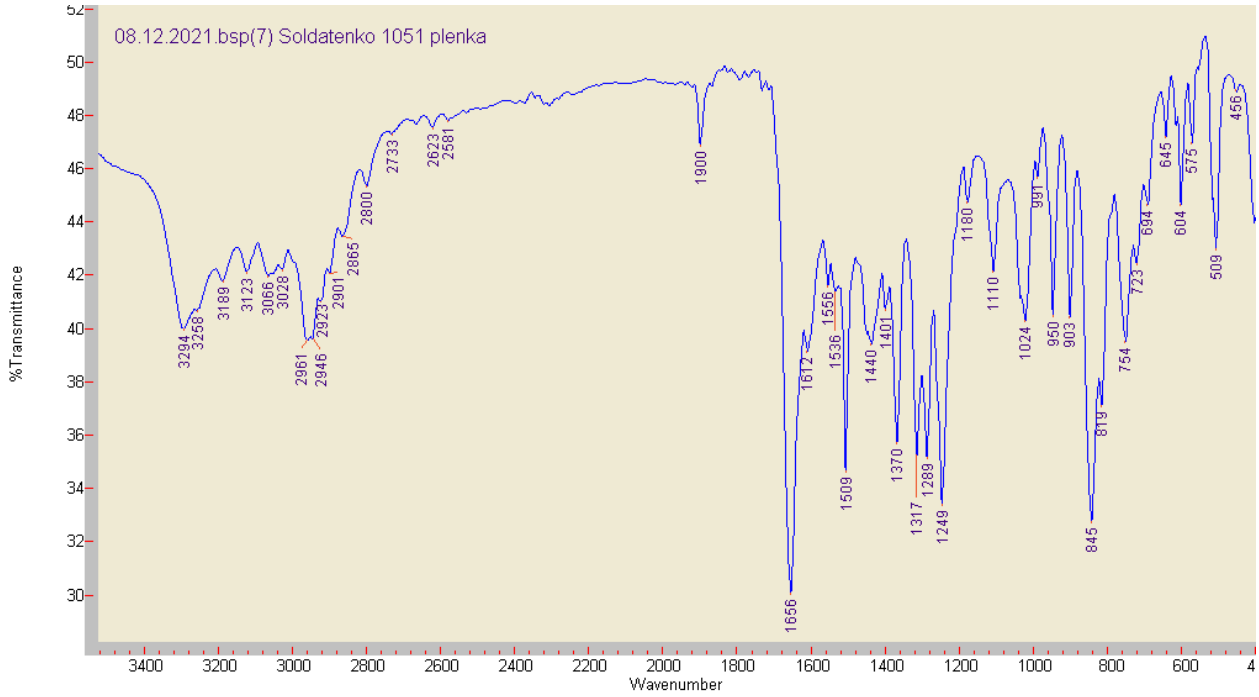

Figure S17. IR spectrum of compound **3a.**

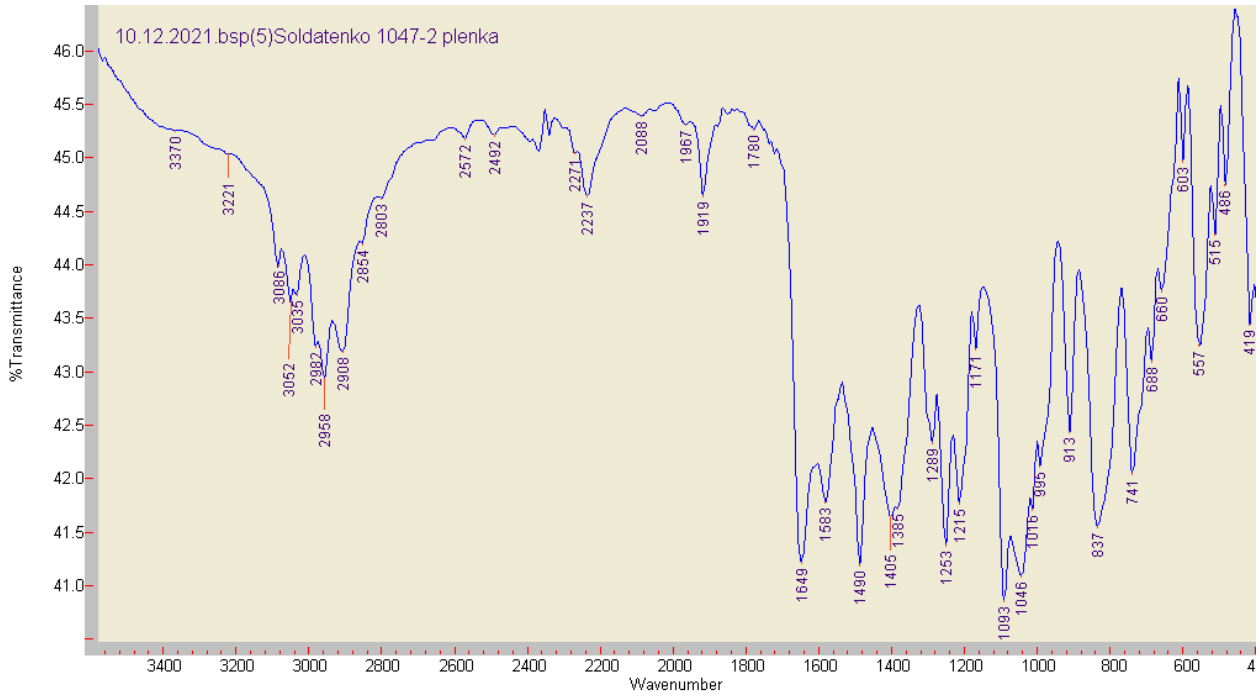

Figure S18. IR spectrum of compound **3b.**

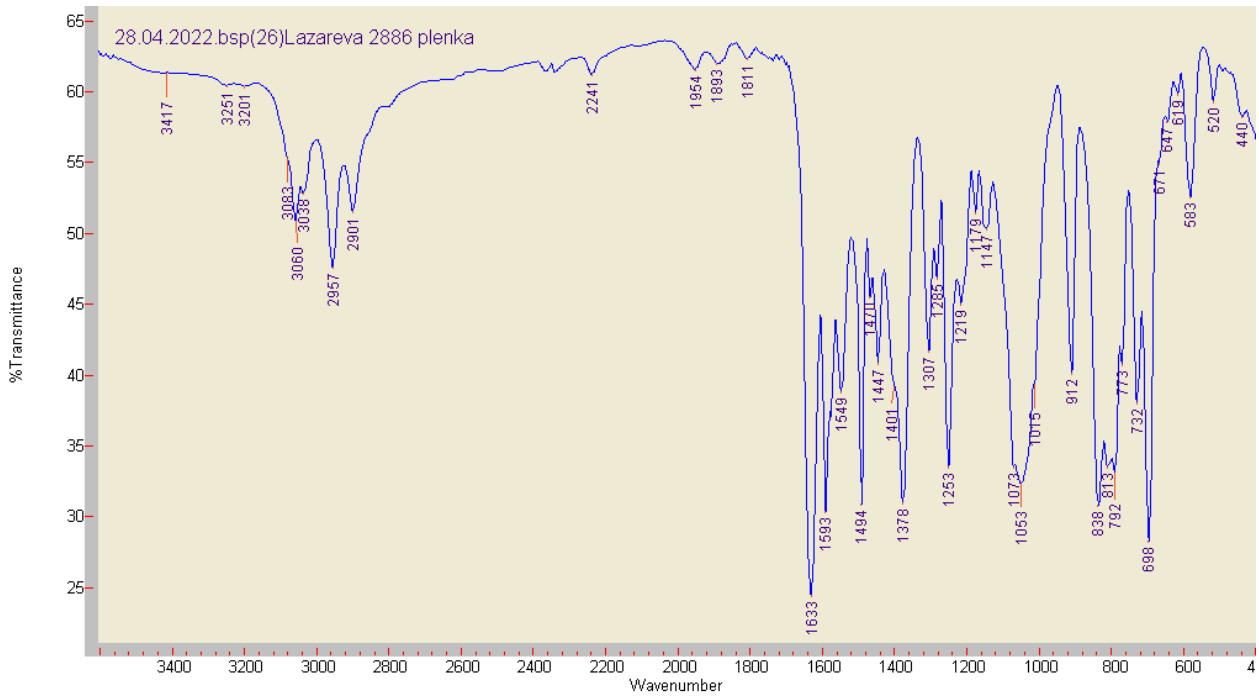

Figure S19. IR spectrum of compound **3c.**

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