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N-Isopropyl-*N'*,*N'*-diphenyl-*N*-(silylmethyl)ureas: synthesis and structure

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Experimental

^{1}H, ^{13}C, ^{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 internal standards. 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. The solvents were purified by standard procedures prior to use.[S1]

N-Isopropyl-N',N'-diphenyl-N-(triethoxysilylmethyl)urea 1.

Diphenylcarbamoyl chloride (2.17 g, 9.0 mmol) was added dropwise to the solution of amine $Pr^iNHCH_2Si(OEt)_3$ (2.21 g, 9.0 mmol) and excess Et_3N in benzene (20 ml) with stirring. The reaction mixture was refluxed for 2 days. Then the precipitate was filtered, the solvent was removed. White crystals were obtained by recrystallization from hexane. Yield 3.32 g (86 %). White powder. ^{1}H NMR (CDCl$_3$, δ ppm): 7.28 – 7.12 (m, 10H, Ph), 4.22 (septet, 1H, -$\underline{CH}(CH_3)_2$, ^3J = 6 Hz), 3.92 (m, 6H, Et), 2.63 (s, 2H, CH$_2$), 1.25 (t, 9H, Et, ^3J = 7 Hz), 0.92 (d, 6H, -$CH\underline{(CH_3)}_2$, ^3J = 6 Hz). ^{13}C (CDCl$_3$, δ, ppm): 160.49 (C=O), 145.33 (Ph), 129.05 (Ph), 124.54 (Ph), 124.03 (Ph), 58.79 (-$\underline{CH_2}CH_3$), 50.09 (-$\underline{CH}(CH_3)_2$), 27.03 (CH$_2$), 19.91 (-$CH(\underline{CH_3})_2$), 18.30 (-$CH_2\underline{CH_3}$). ^{29}Si (CDCl$_3$, δ, ppm): -54.36. IR (film from chloroform, ν, cm^{-1}): 1659 (C=O).

N-Isopropyl-N’,N’-diphenyl-N-[(diethoxy(methyl)silylmethyl]urea 2. Diphenylcarbamoyl chloride (2.14 g, 9.2 mmol) was added dropwise to the solution of amine $Pr^iNHCH_2Si(OEt)_2Me$ (1.90 g, 9.2 mmol) and excess Et_3N in benzene (20 ml) with stirring. The reaction mixture was refluxed for 2 days. Then the precipitate was filtered, the solvent was removed. Substance was washed by pentane, hexane and toluene. Yield 3.49 g (94 %). Yellow oil. ^{1}H NMR ($CDCl_3$, δ ppm): 7.27 – 7.09 (m, 10H, Ph), 4.23 (septet, 1H, $-\underline{CH}(CH_3)_2$, ^3J = 7 Hz), 3.81 (q, 4H, Et), 2.51 (s, 2H, CH_2), 1.24 (t, 6H, Et, ^3J = 7 Hz), 0.88 (d, 6H, $-CH\underline{(CH_3)}_2$, ^3J = 6 Hz), 0.36 (s, 3H, Me). ^{13}C ($CDCl_3$, δ, ppm): 160.90 (C=O), 145.26 (Ph), 129.16 (Ph), 124.52 (Ph), 124.16 (Ph), 58.33 ($-\underline{CH_2}CH_3$), 50.16 ($-\underline{CH}(CH_3)_2$), 29.99 (CH_2), 19.92 ($-CH(\underline{CH_3})_2$), 18.48 ($-CH_2\underline{CH_3}$), -3.17 (Me). ^{29}Si ($CDCl_3$, δ, ppm): -12.44. IR (film from chloroform, ν, cm^{-1}): 1654 (C=O).

N-Isopropyl-N’,N’-diphenyl-N-[(ethoxy(dimethyl)silylmethyl]urea 3. Diphenylcarbamoyl chloride (5.32 g, 23.0 mmol) was added dropwise to the solution of amine $Pr^iNHCH_2Si(OEt)Me_2$ (4.03 g, 23.0 mmol) and excess Et_3N in benzene (20 ml) with stirring. After that, the reaction mixture was refluxed for 2 days. Then the precipitate was filtered, the solvent was removed. Substance was washed by several solvents such as pentane, hexane and toluene. Yield 3.49 g (94 %). Yellow oil. ^{1}H NMR ($CDCl_3$, δ ppm): 7.30 – 7.06 (m, 10H, Ph), 4.25 (septet, 1H, $-CH(\underline{CH_3})_2$, ^3J = 7 Hz), 3.69 (q, 2H, Et), 2.52 (s, 2H, CH_2), 1.19 (t, 3H, Et, ^3J = 7 Hz), 0.87 (d, 6H, $-CH(CH_3)_2$, ^3J = 6 Hz), 0.3 (s, 6H, $-(CH_3)_2$). ^{13}C (CDCl3, δ, ppm): 160.56 (C=O), 144.95 (Ph), 129.02 (Ph), 124.19 (Ph), 124.04 (Ph), 57.99 ($-\underline{CH}(CH3)_2$), 49.74 ($-\underline{CH_2}CH_3$), 31.81 (CH_2), 19.74 ($-CH(\underline{CH_3})_2$), 18.46 ($-CH_2\underline{CH_3}$), -1.19 (Me). ^{29}Si (CDCl3, δ, ppm): 11.43. IR (film from chloroform, ν, cm^{-1}): 1648 (C=O).

N-Isopropyl-N’,N’-diphenyl-N-[(trifluorosilyl)methyl]urea 4. Reagent $BF_3 \cdot Et_2O$ (0.66 g, 4.6 mmol) was added dropwise to a solution of compound **1** (2.00 g, 4.6 mmol) in benzene (10 ml) with stirring, and the mixture was refluxed for 1 day. The solvent was removed and the substance was dried in vacuum. White crystals were obtained by recrystallization from chloroform and hexane. Yield 1.52 g (93 %). White crystals. ^{1}H NMR ($CDCl_3$, δ ppm): 7.25 (m, 2H, Ph), 7.06 (m, 8H, Ph), 3.83 (septet, 1H, $-CH(\underline{CH_3})_2$, ^3J = 7 Hz), 2.68 (s, 2H, CH_2), 0.97 (d, 6H, -CH(CH3)2, ^3J = 6 Hz). ^{13}C (CDCl3, δ, ppm): 163.61 (C=O), 141.0 (Ph), 129.87 (Ph), 126.95 (Ph), 125.46 (Ph), 47.83 ($-\underline{CH}(CH3)_2$), 26.53 (t, $-CH_2$, ^3J = 30 Hz), 18.42 ($-CH(\underline{CH_3})_2$). ^{29}Si (CDCl3, δ, ppm): -105.11 (q. ^1J = 211.7 Hz). IR (film from chloroform, ν, cm^{-1}): 1561 (C=O). Found, %: C, 57.84; H, 5.34; N, 8.15. $C_{17}H_{19}F_3N_2OSi$. Calculated, %: C, 57.94; H, 5.43; N, 7.95.

N-Isopropyl-N',N'-diphenyl-N-[difluoro(methyl)silylmethyl]urea 5. Reagent $BF_3{\cdot}Et_2O$ (0.71 g, 5.0 mmol) was added dropwise to a solution of compound **2** (7.6 mmol, 3.06 g.) in benzene (10 ml) with stirring. Then, mixture was refluxed for 1 day. The solvent was removed and the substance was dried in vacuum. White crystals were obtained by recrystallization from chloroform and hexane. Yield 2.5 g (95 %). White crystals. ^1H NMR (CDCl$_3$, δ ppm): 7.37 – 7.01 (m, 10H, Ph), 3.97 (septet, 1H, -CH(CH$_3$)$_2$, ^3J = 7 Hz), 2.56 (s, 2H, CH$_2$), 0.95 (d, 6H, -CH(CH$_3$)$_2$, ^3J = 6 Hz), 0.33 (s, 3H, -CH$_3$). ^{13}C (CDCl$_3$, δ, ppm): 162.89 (C=O), 143.50 (Ph), 129.50 (Ph), 125.88 (Ph), 124.72 (Ph), 48.58 (-CH(CH$_3$)$_2$), 29.07 (t, -CH$_2$, ^3J = 30 Hz), 19.14 (-CH(CH$_3$)$_2$), 0.39 (t, -CH$_3$, ^3J = 22 Hz). ^{29}Si (CDCl$_3$, δ, ppm): -53.95 (t. ^1J = 260 Hz). IR (film from chloroform, ν, cm^{-1}): 1592 (C=O). Found, %: C, 62.50; H, 6.72; N, 7.92. $C_{18}H_{22}F_2N_2OSi$. Calculated, %: C, 62.04; H, 6.36; N, 8.04.

N-Isopropyl-N',N'-diphenyl-N-[fluoro(dimethyl)silylmethyl]urea 6. Reagent $BF_3{\cdot}Et_2O$ (0.38 g, 2.7 mmol) was added dropwise to a solution of compound **3** (8.0 mmol, 3.00 g.) in benzene (10 ml) with stirring. The mixture was refluxed for 1 day. The solvent was removed and the substance was dried in vacuum. White crystals were obtained by recrystallization from chloroform and hexane Yield 2.7 g (98 %). White crystals. ^1H NMR (CDCl$_3$, δ ppm): 7.33 – 6.97 (m, 10H, Ph), 4.10 (septet, 1H, -CH(CH$_3$)$_2$, ^3J = 7 Hz), 2.45 (s, 2H, CH$_2$), 0.88 (d, 6H, -CH(CH$_3$)$_2$, ^3J = 6 Hz), 0.32 (s, 3H, -CH$_3$). ^{13}C (CDCl$_3$, δ, ppm): 161.74 (C=O), 143.91 (Ph), 129.02 (Ph), 124.56 (Ph), 123.75 (Ph), 48.57 (-CH(CH$_3$)$_2$), 30.04 (CH$_2$), 19.07 (-CH(CH$_3$)$_2$), 0.84 (s, -CH$_3$). ^{29}Si (CDCl$_3$, δ, ppm): -10.13. IR (film from chloroform, ν, cm^{-1}): 1611 (C=O). Found, %: C, 65.80; H, 7.25; N, 8.07. $C_{19}H_{25}FN_2OSi$. Calculated, %: C, 66.24; H, 7.31; N,8.15.

Single crystal X-ray analysis of compounds 4-6

Table S1. Crystal data, details of intensity measurements, and structure refinement for compounds **4-6**.

Parameter	Compound		
	4	**5**	**6**
Formula	$C_{17}H_{19}F_3N2OSi$	$C_{18}H_{22}F_2N_2OSi$	$C_{19}H_{25}FN_2OSi$
M / g·mol^{-1}	352.43	348.46	344.50
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	P 2_1/n	P$2_12_12_1$	Pbca
a / Å	9.112 (2)	8.483 (1)	7.865 (1)
b / Å	10.210 (2)	10.195 (1)	19.928 (2)
c / Å	19.596 (4)	21.258 (1)	25.227 (2)
α, β, γ / °	90, 100.66 (1), 90	90, 90, 90	90, 90, 90
Volume / Å^3	1791.7 (7)	1838.5(1)	3954.1(6)
Z	4	4	8
F(000)	736	736	1472
$d_{calc.}$ / g·cm^{-3}	1.307	1.259	1.157
μ/ mm^{-1}	0.166	0.153	0.135
2*Θ* range / °	4.22-60.24	4.4-50.8	3.2-50.8
Crystal size / mm	0.30 × 0.05 × 0.05	0.40 × 0.35 × 0.22	0.7 × 0.34 × 0.06
Crystal habit	colorless needle	colorless prism	colorless plate
Index ranges	*h* = -12≤11, *k* = -14≤14, *l* = -27≤27	*h* = -10≤10, *k* = -12≤12, *l* = -24≤25	*h* = -9≤9, *k* = -23≤24, *l* = -30≤30
Refl. Collected	32085	18454	47389
Ind. Reflections	5269	3371	3629
T_{min} /T_{max}	0.7460 / 0.5524	0.862 / 0.928	0.815 / 0.862
N of parameters	219	220	221
R_1/wR_2 [I >2σ(I)]	0.0597 / 0.1566	0.0319 / 0.0933	0.0422 / 0.1277
R_1/wR_2 (all data)	0.1297 / 0.1581	0.0366 / 0.0974	0.0583 / 0.1144
S	0.982	1.004	1.004
$\Delta\rho_{max}$, $\Delta\ \rho_{min}$ (e Å^{-3})	0.351 / -0.454	0.135 / -0.146	0.210 / -0.268

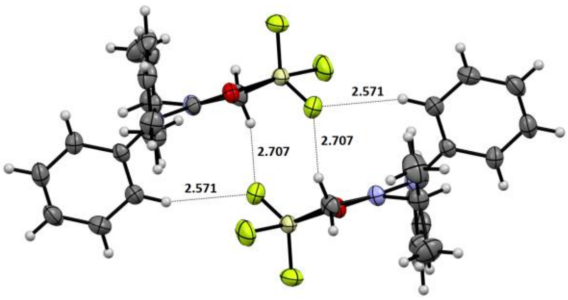
Crystal data for urea **4** were collected at 293(2) K on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[S2] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX programs set.[S2] The X-ray diffraction experiment for **5** and **6** was carried out at 296(2) K on a Bruker KAPPA APEX II diffractometer (graphite-monochromated Mo Kα radiation). Reflection intensities were corrected for absorption by SADABS-2016 program.[S3] The structure of compounds was solved by direct methods using the SHELXT-2014 program[S4] and refined by anisotropic (isotropic for all H atoms) full-matrix least-squares method against F^2 of all reflections by SHELXL-2018.[S4] The positions of the hydrogen atoms were calculated geometrically and refined in riding model.

Crystallographic data for **4-6** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC **2223501**, **2222921** and **2222920**. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033 or e-mail: deposit@ccdc.cam.ac.uk; internet: www.ccdc.cam.ac.uk).

Table S2. Selected bond lengths, bond and torsion angles in compounds **4-6**

Compound	Bond	*l*, Å	Angle	φ, °	Torsion angle	θ, °
4	Si1-O1	1.892(1)	F1-Si1-O1	174.2(1)	Si1-O1-C3-N1	1.4(2)
	Si1-F1	1.635(1)	F1-Si1-C8	92.9(1)	Si1-O1-C3-N2	-178.4(1)
	Si1-C8	1.865(2)	F2-Si1-O1	89.7(1)	C3-N1-C2-C9	141.6(2)
	Si1-F2	1.586(1)	F2-Si1-C8	116.4(1)	C2-N1-C3-O1	155.9(2)
	Si1-F3	1.596(1)	F3-Si1-O1	85.5(1)	F1-Si1-C8-N1	177.9(2)
	O1-C3	1.274(2)	F3-Si1-C8	130.9(1)	O1-Si1-C8-N1	-6.8(1)
	N1-C2	1.483(2)	F3-Si1-F1	93.2(1)	C3-N1-C2-C1	-93.3(2)
	N2-C3	1.366(2)	C3-O1-Si1	114.2(1)	C2-N1-C8-Si1	-155.0(2)
	C1-C2	1.516(3)	C3-N1-C2	126.3(2)	C5-C4-C16-C17	-0.7(3)
5	Si1-O1	2.050(2)	F1-Si1-O1	173.4(1)	Si1-O1-C3-N1	-3.4(3)
	Si1-F1	1.638(2)	F1-Si1-C8	93.6(1)	Si1-O1-C3-N2	176.9(2)
	Si1-C8	1.870(3)	F2-Si1-O1	83.8(1)	C3-N1-C2-C9	130.6(3)
	Si1-C18	1.835(4)	F2-Si1-C8	117.9(2)	C2-N1-C3-N2	-15.8(3)
	Si1-F2	1.593(2)	F2-Si1-F1	96.1(1)	F1-Si1-C8-N1	171.7(2)
	O1-C3	1.248(3)	C3-O1-Si1	112.1(1)	F2-Si1-C8-N1	-89.5(2)
	N1-C2	1.473(3)	C3-N1-C2	125.6(2)	C3-N1-C2-C1	-104.3(3)
	N2-C3	1.391(3)	O1-C3-N2	120.0(2)	O1-Si1-C8-N1	-11.7(2)
	C1-C2	1.523(4)	C1-C2-C9	112.1(2)	C7-C6-C5-C4	0.5(5)
6	Si1-O1	2.219(1)	F1-Si1-O1	171.9(1)	Si1-O1-C3-N1	2.3(2)
	Si1-F1	1.656(1)	F1-Si1-C8	93.5(1)	Si1-O1-C3-N2	-178.1(1)
	Si1-C8	1.864(2)	C8-Si1-O1	78.4(1)	C2-N1-C3-O1	165.9(2)
	Si1-C18	1.838(3)	C3-O1-Si1	109.9(1)	C2-N1-C3-N2	-13.7(3)
	Si1-C19	1.840(3)	C3-N1-C2	125.5(2)	F1-Si1-C8-N1	175.9(2)
	O1-C3	1.244(2)	C3-N2-C4	116.9(1)	C3-N1-C2-C1	118.8(2)
	N1-C2	1.485(2)	O1-C3-N1	120.3(2)	O1-Si1-C8-N1	-4.0(2)
	N2-C3	1.401(2)	N1-C3-N2	119.2(2)	C4-C5-C6-C7	0.4(3)
	C1-C2	1.505(3)	C1-C2-C9	111.8(2)	C3-N2-C4-C5	124.5(2)

In the crystal molecules of urea **4** form dimeric structure by short contacts between the fluorine atom and the hydrogen atoms of the CH$_2$-groups of neighboring molecules (Figure S1). The lengths of intermolecular F···H-C bonds are 2.571 Å and 2.707 Å. In addition there are T-stacking between C$_{Ar}$-H hydrogen and π-system of phenyl ring of neighboring molecules (Figure S2).



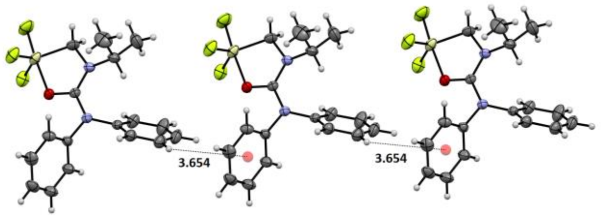


Figure S1. Short contacts F···HC in the crystal of urea **4**.

Figure S2. T-stacking in the crystal of compound **4**.

Crystal structure of compound **5** forms by short contacts F···H-C_{Ar} of length 2.477 Å, that less than sum of WdW radii (2.720 Å)[S5] (Figure S3). Crystal structure of compound **6** forms by short contacts F···H-C_{Ar} 2.792 Å, 2.832 Å and 2.890 Å (Figure S4).

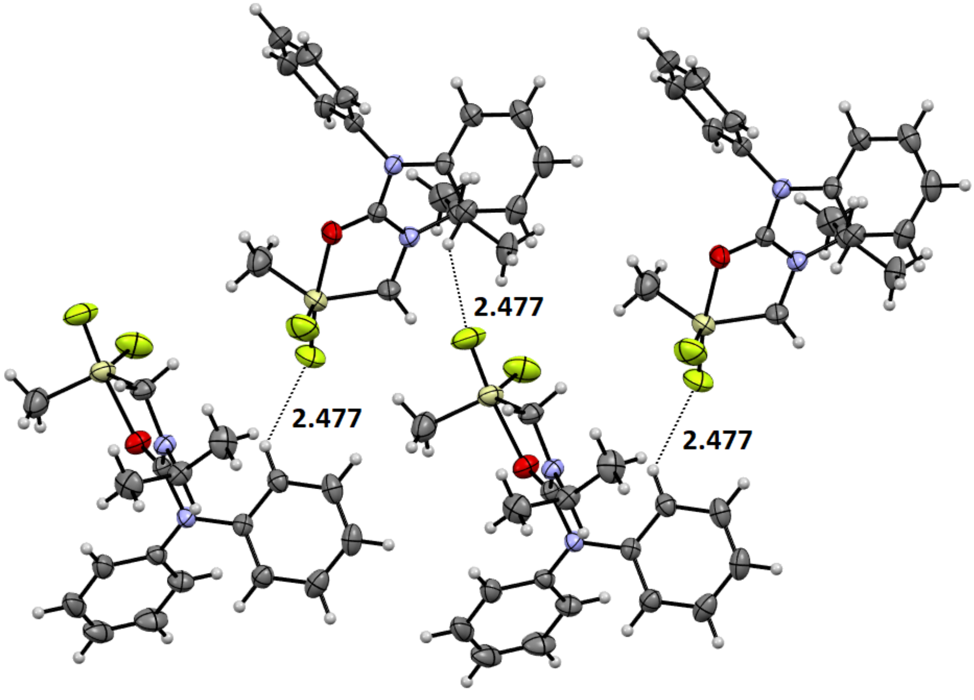


Figure S3. Short contacts F···H-C in the crystal of compound **5**.

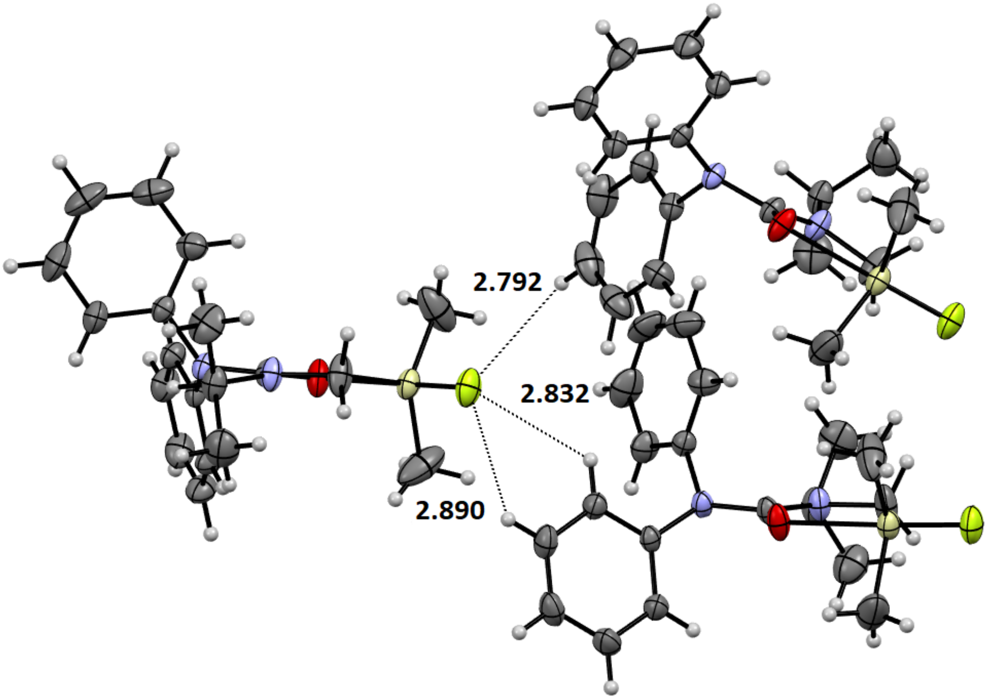


Figure S4. Intermolecular distances F···H-C in the crystal of compound **6**.

References

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S4 G.M. Sheldrick, *Acta Crystallogr*., 2015, **A71**, 3.

S5 R. S. Rowland and R. Taylor, *J. Phys. Chem*., 1996, **100**, 7384.

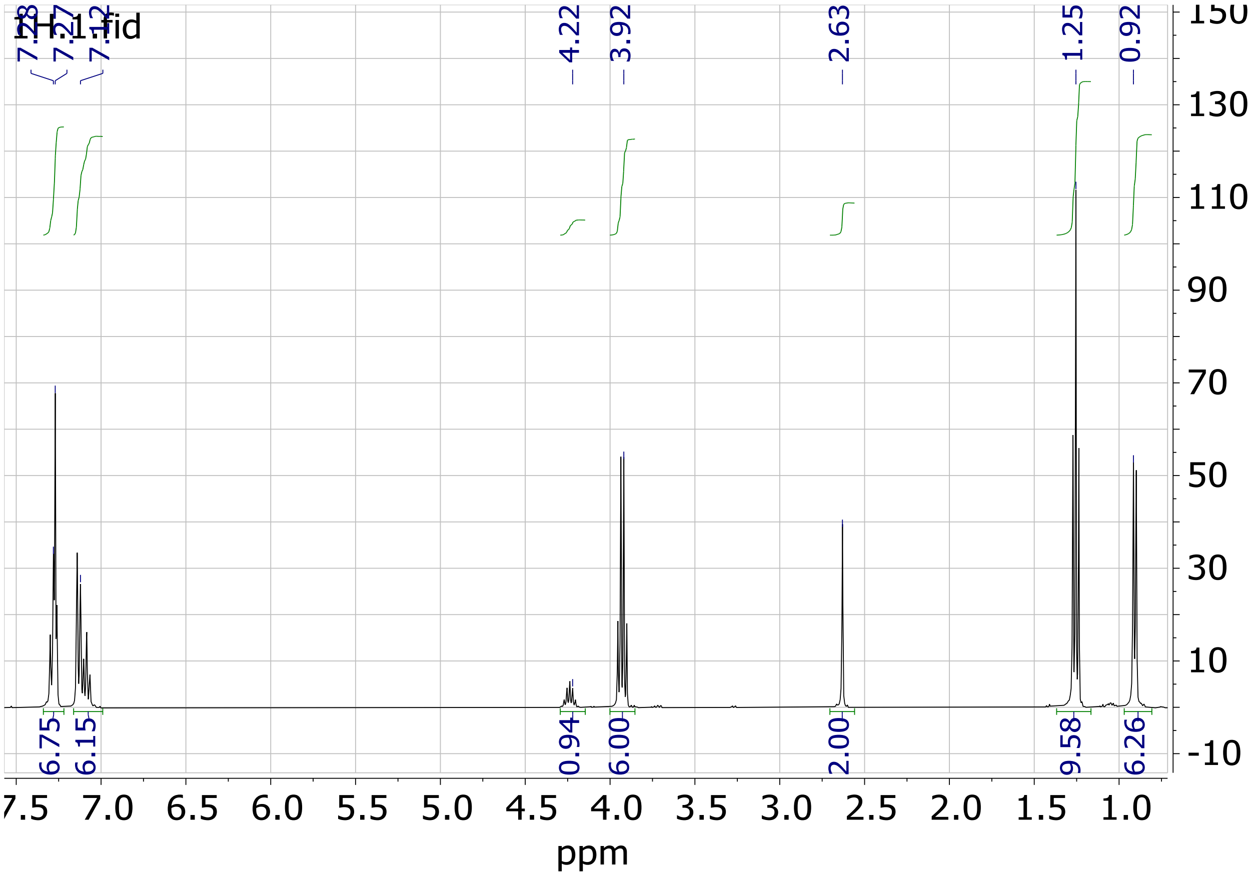

Figure S5. The NMR ^{1}H spectrum of compound 1.

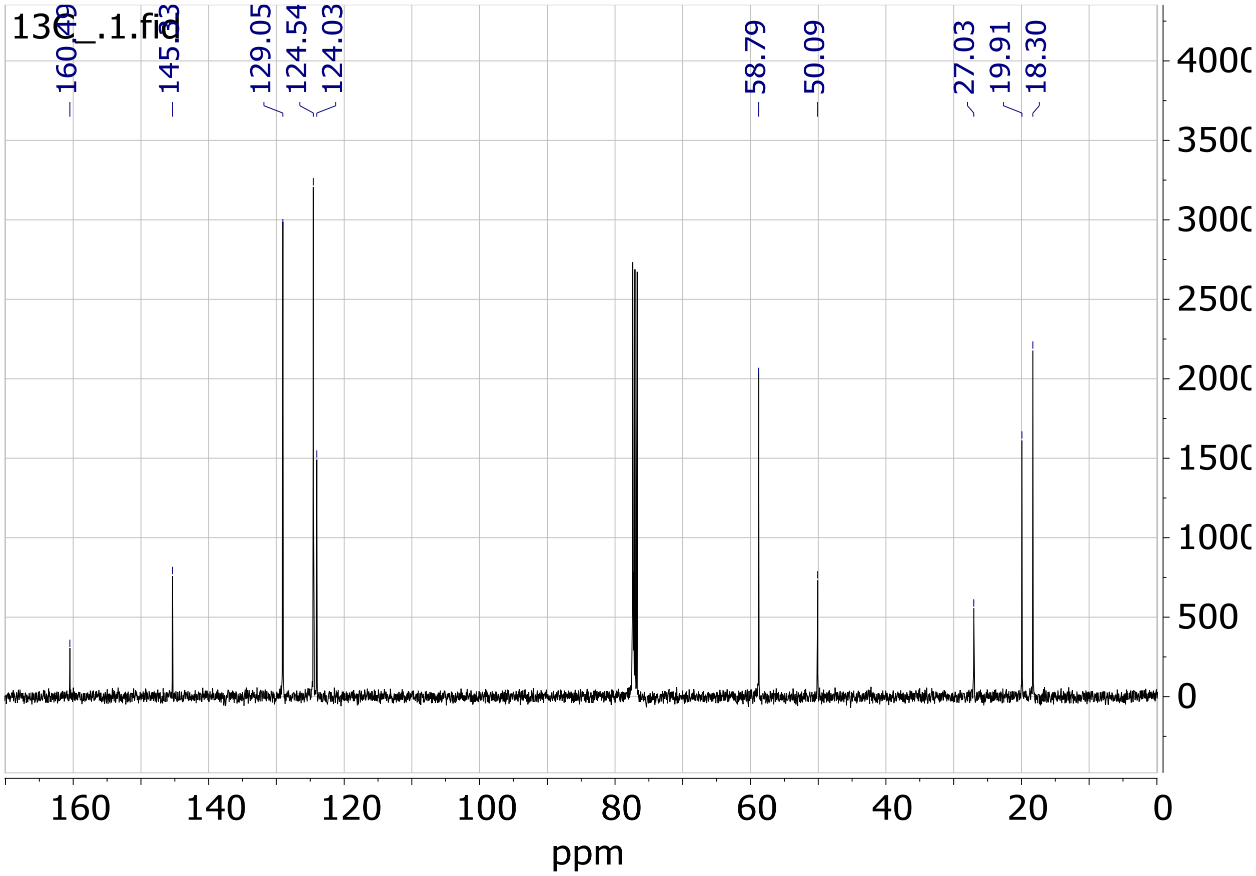

Figure S6. The NMR ^{13}C spectrum of compound 1.

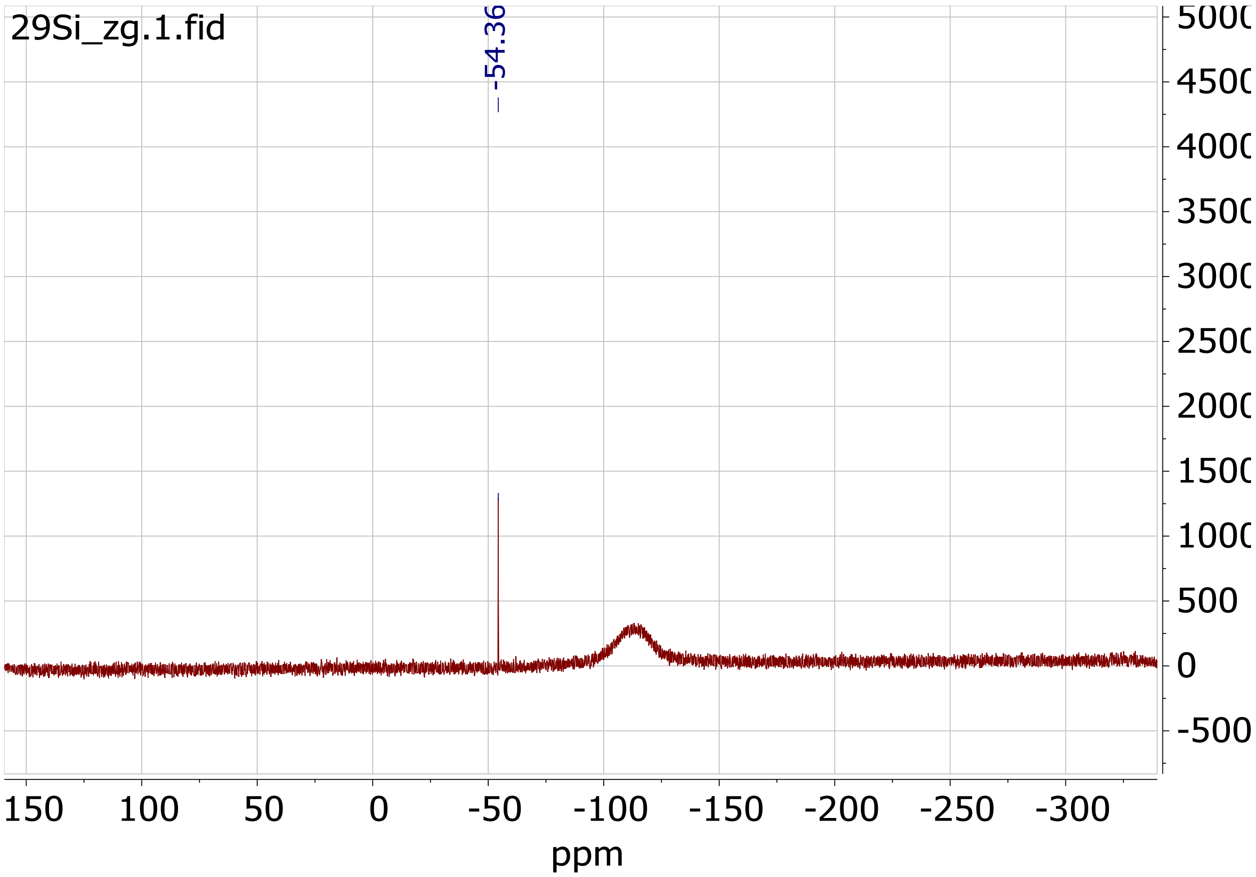

Figure S7. The NMR ^{29}Si spectrum of compound 1.

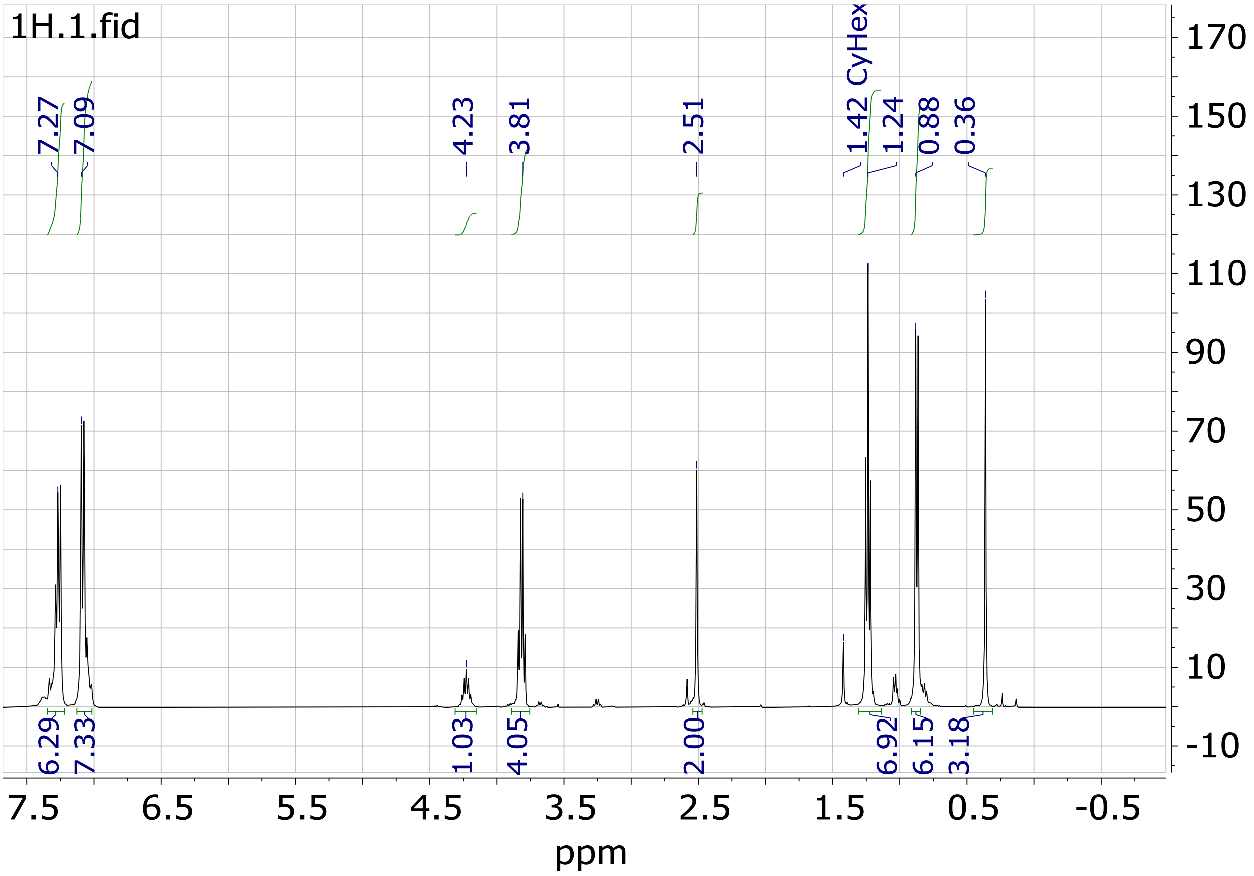

Figure S8. The NMR ^{1}H spectrum of compound 2.

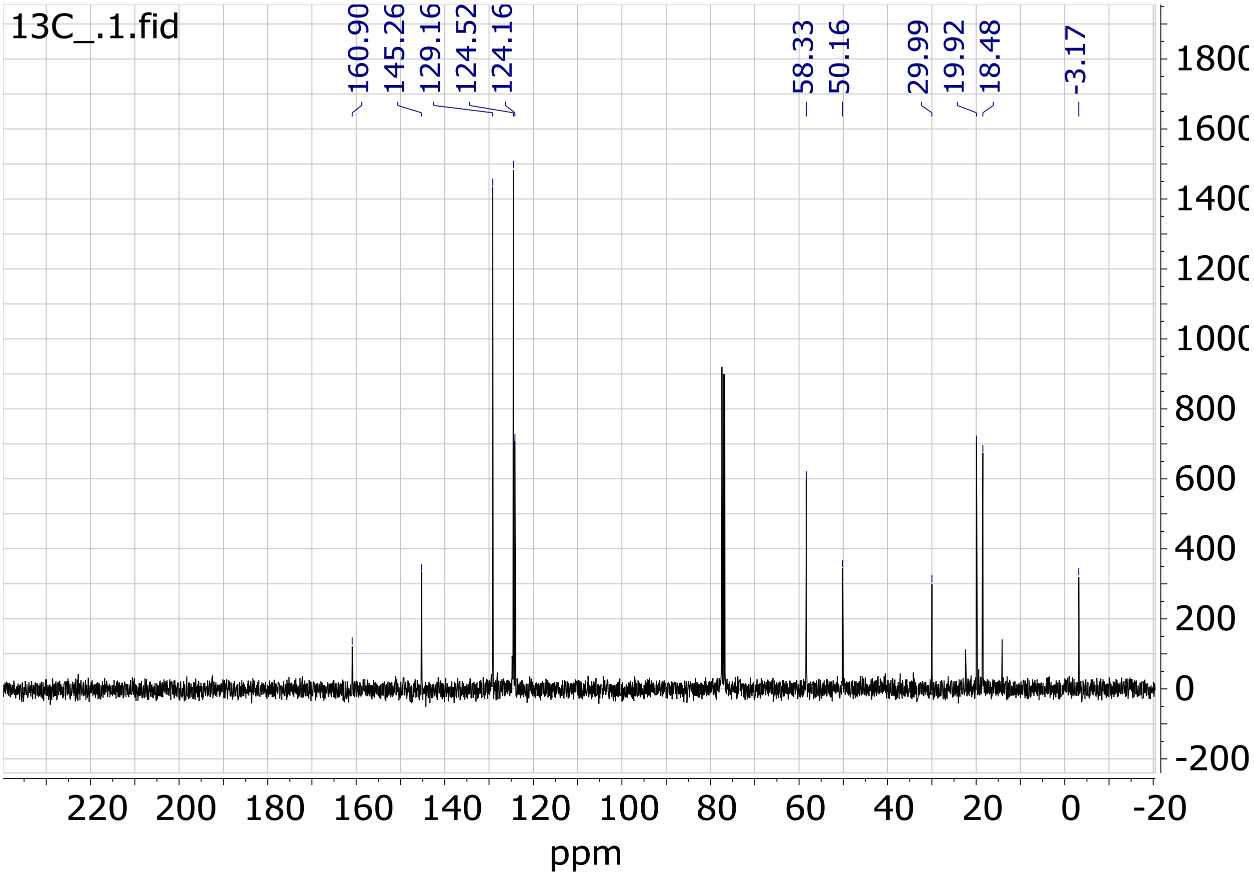

Figure S9. The NMR ^{13}C spectrum of compound 2.

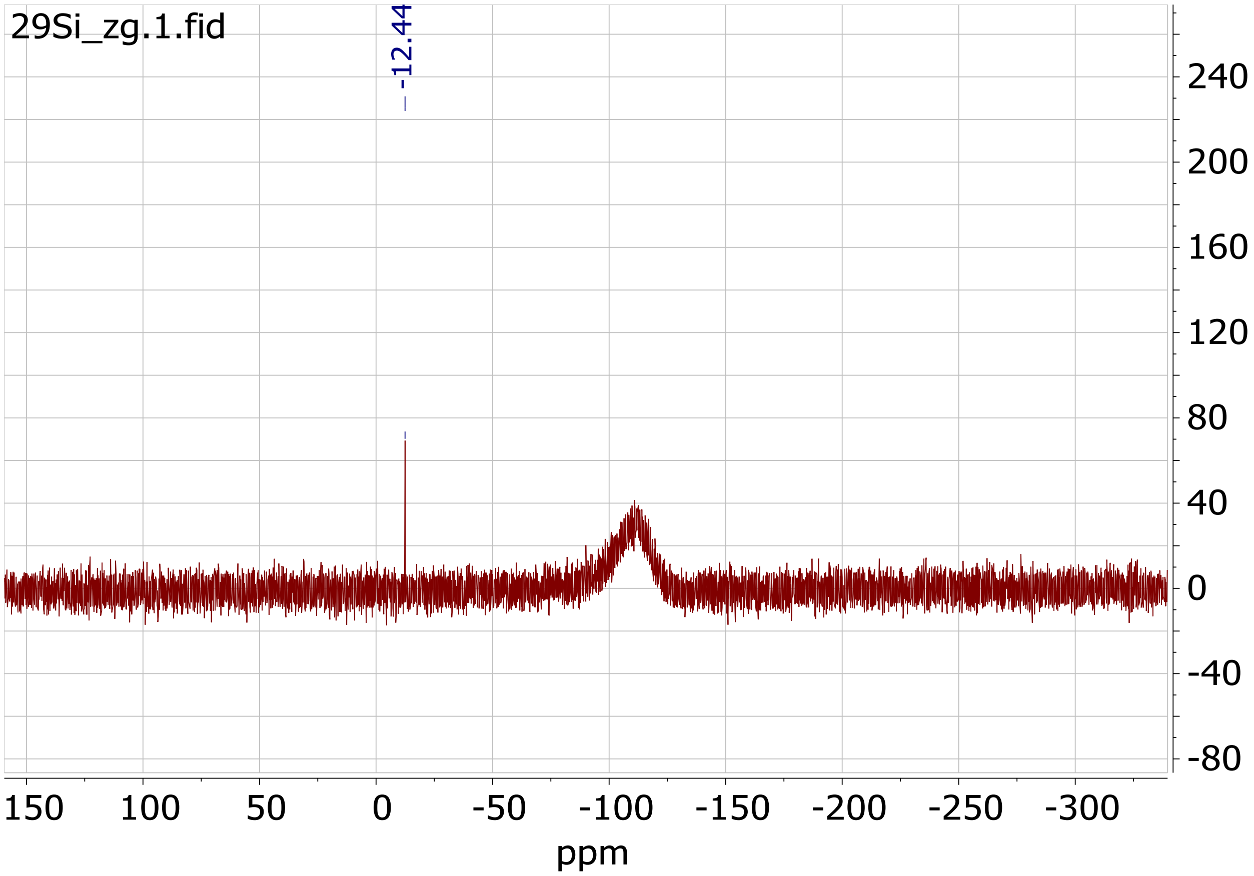

Figure S10. The NMR ^{29}Si spectrum of compound 2.

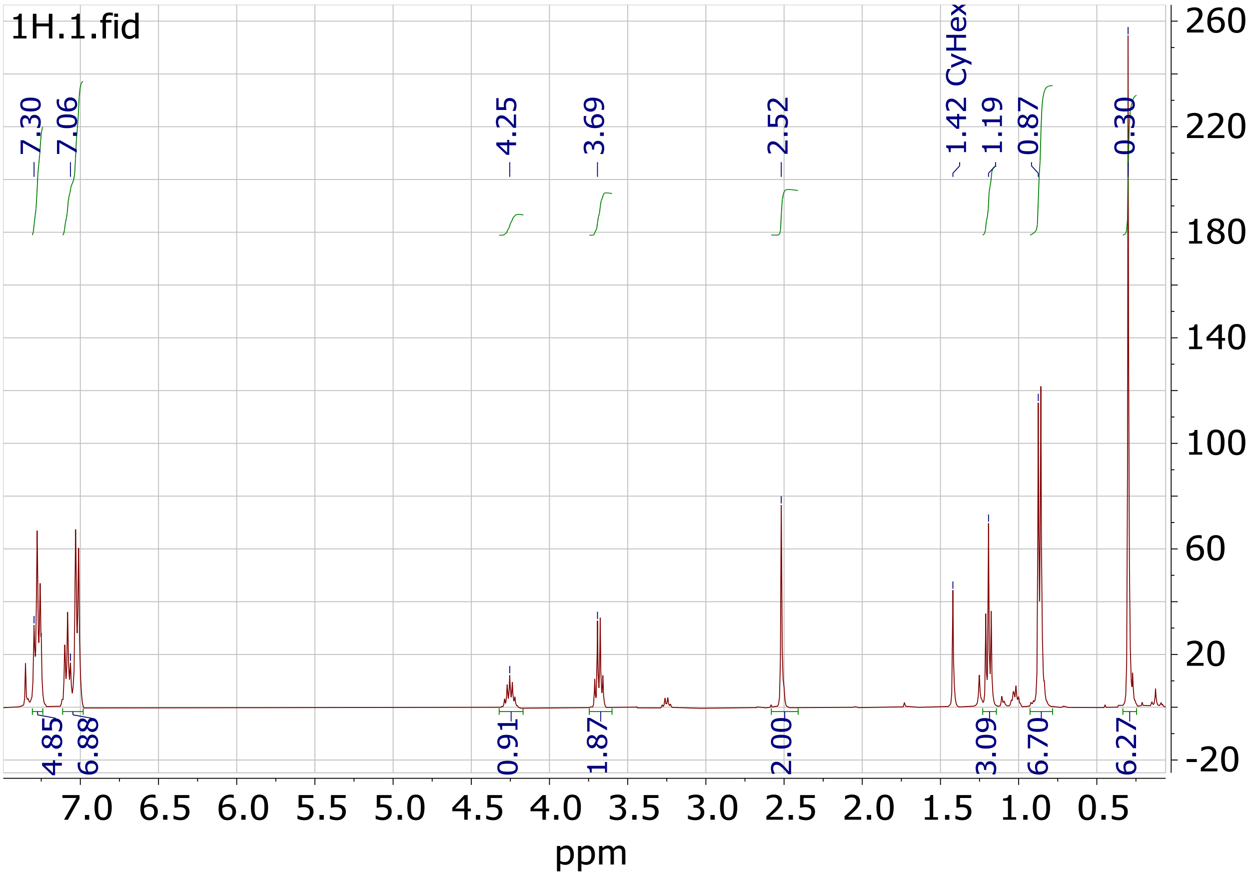

Figure S11. The NMR ^1H spectrum of compound 3.

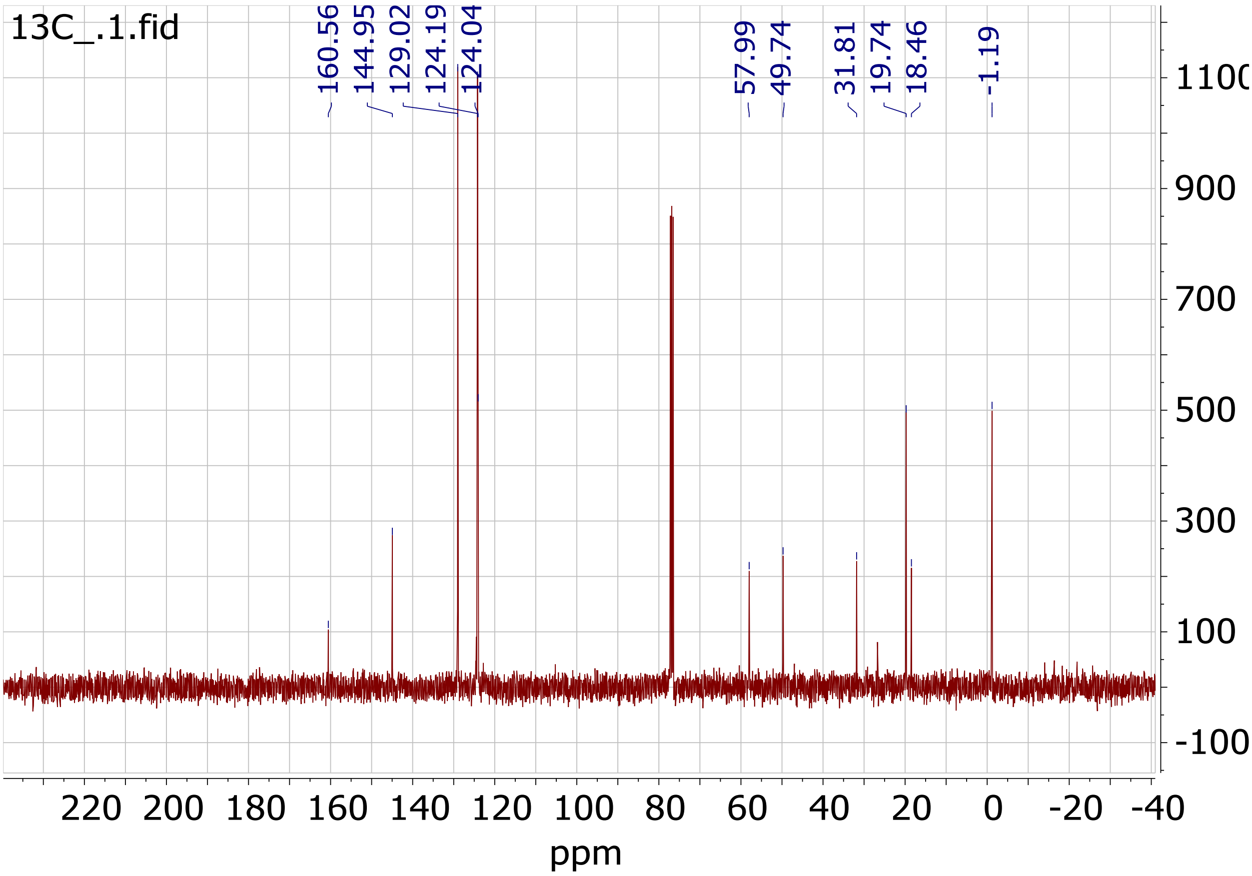

Figure S12. The NMR ^{13}C spectrum of compound 3.

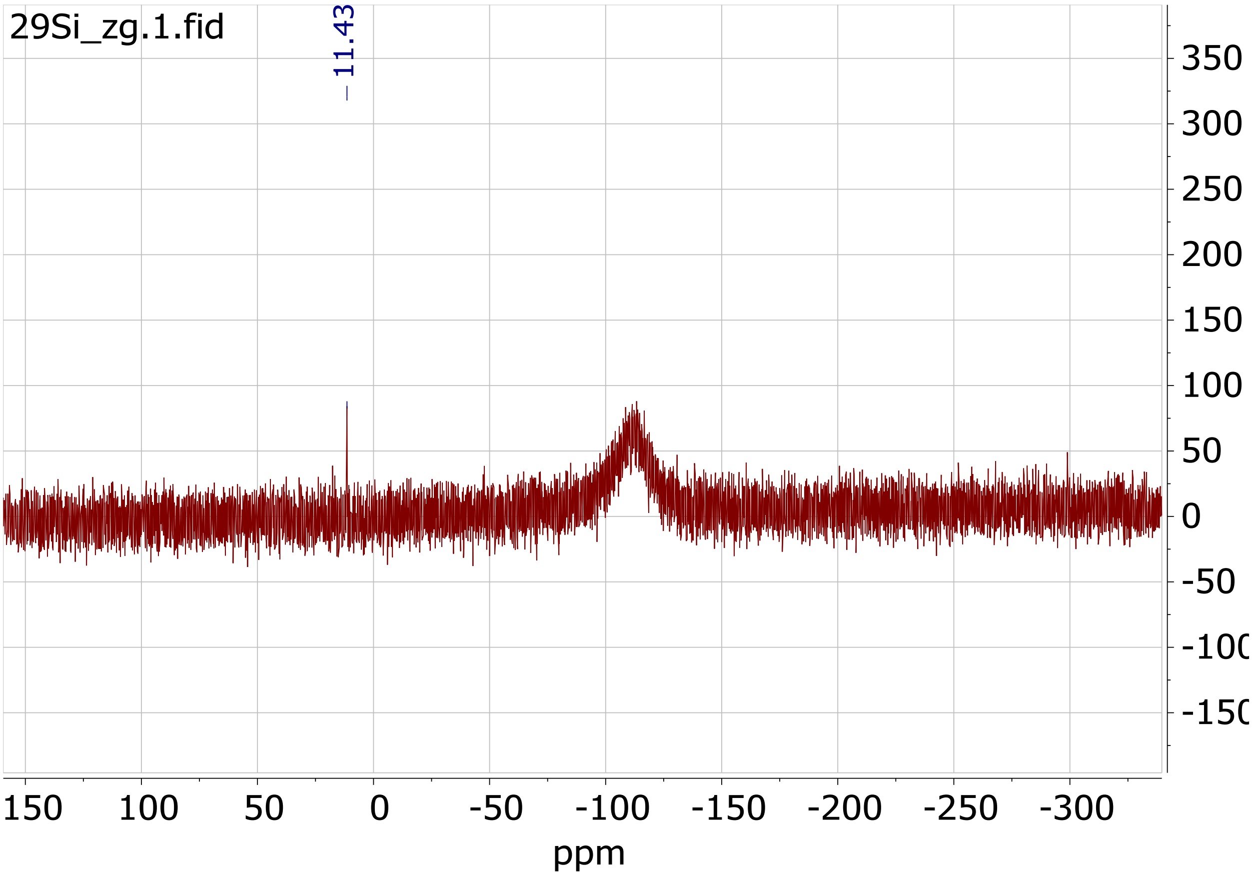

Figure S13. The NMR ^{29}Si spectrum of compound 3.

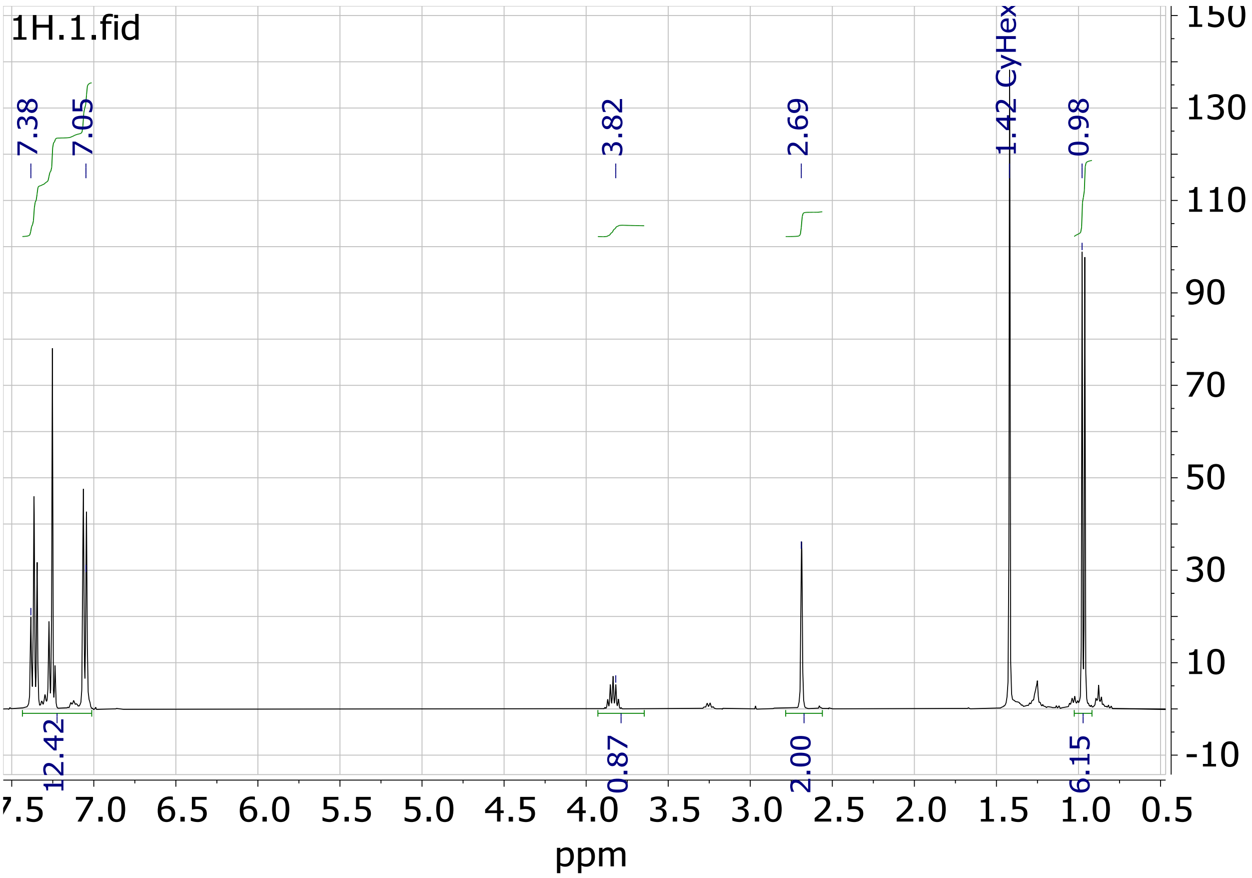

Figure S14. The NMR ^{1}H spectrum of compound 4.

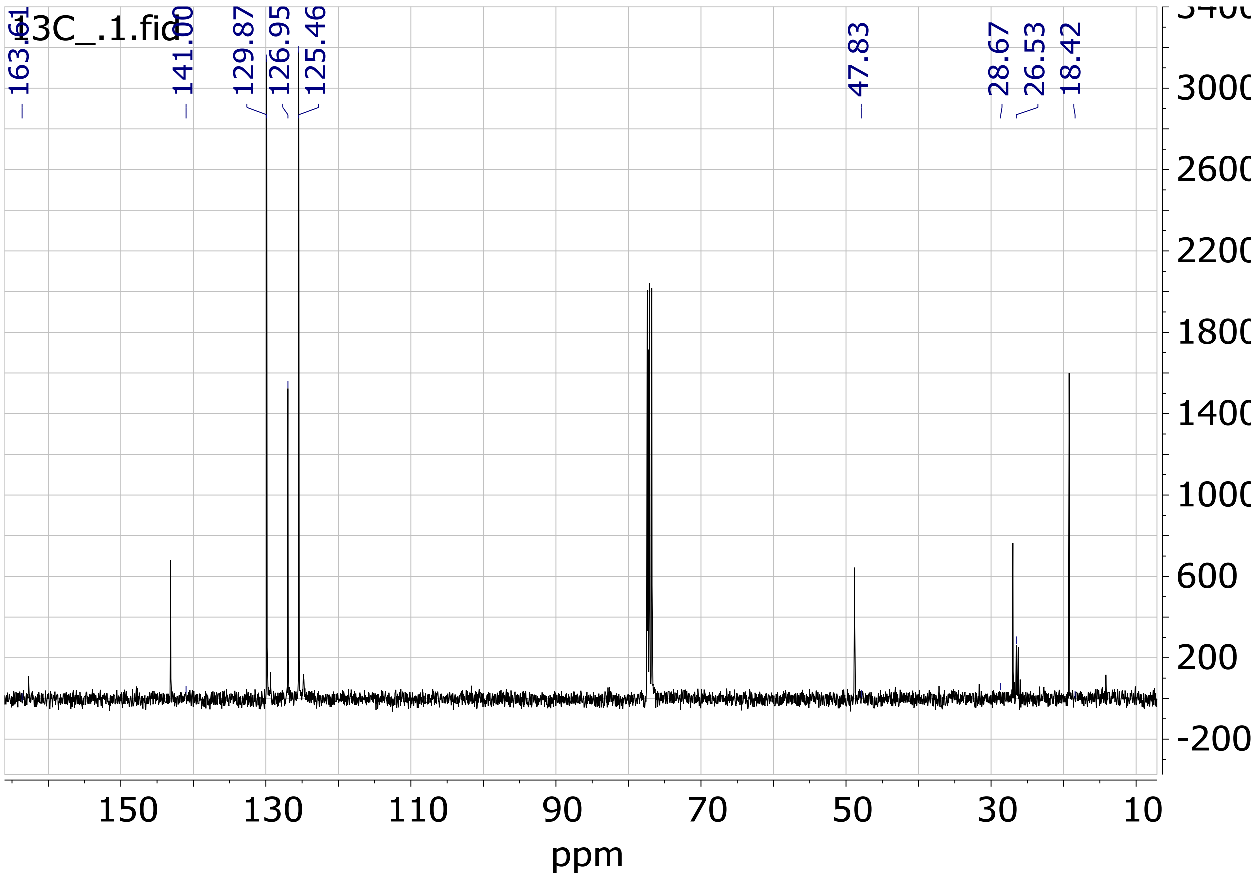

Figure S15. The NMR ^{13}C spectrum of compound 4.

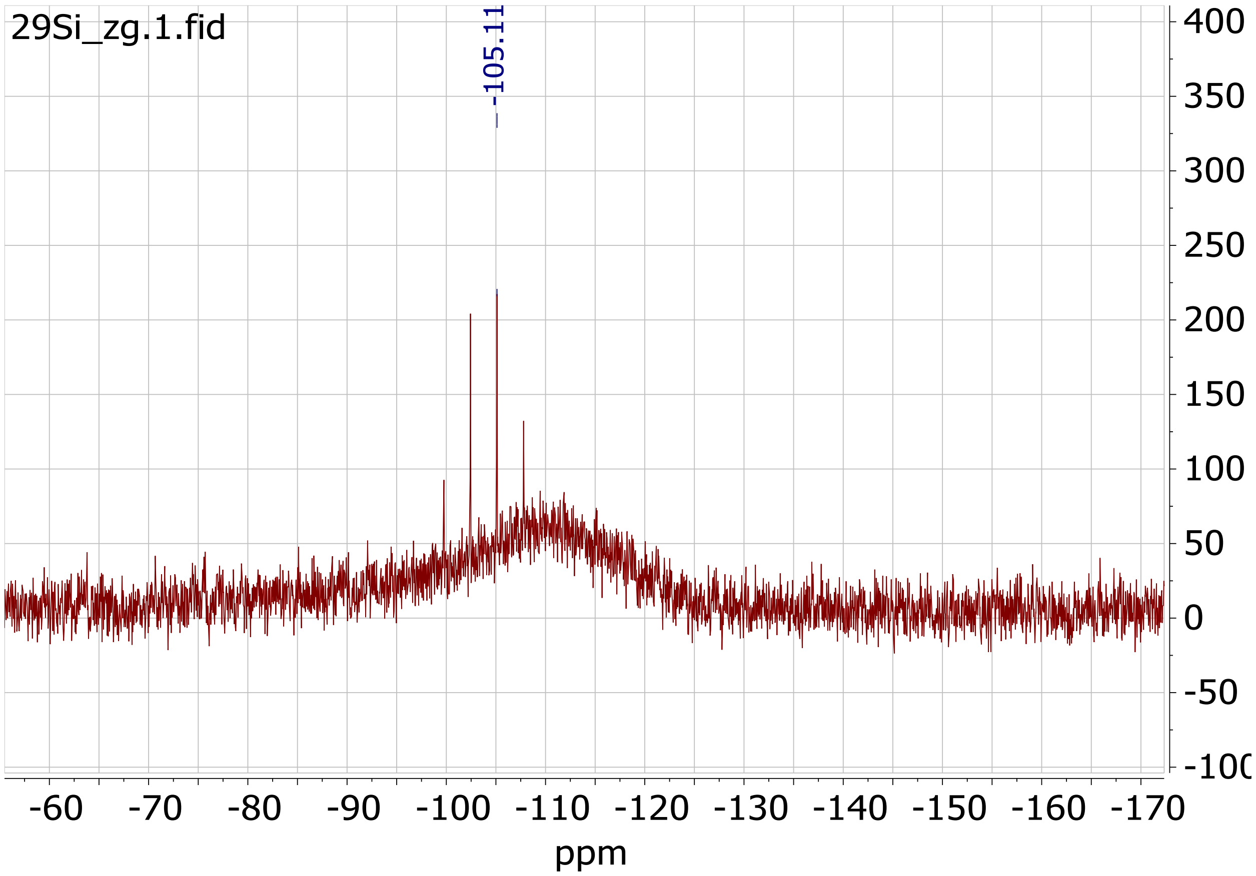

Figure S16. The NMR ^{29}Si spectrum of compound 4.

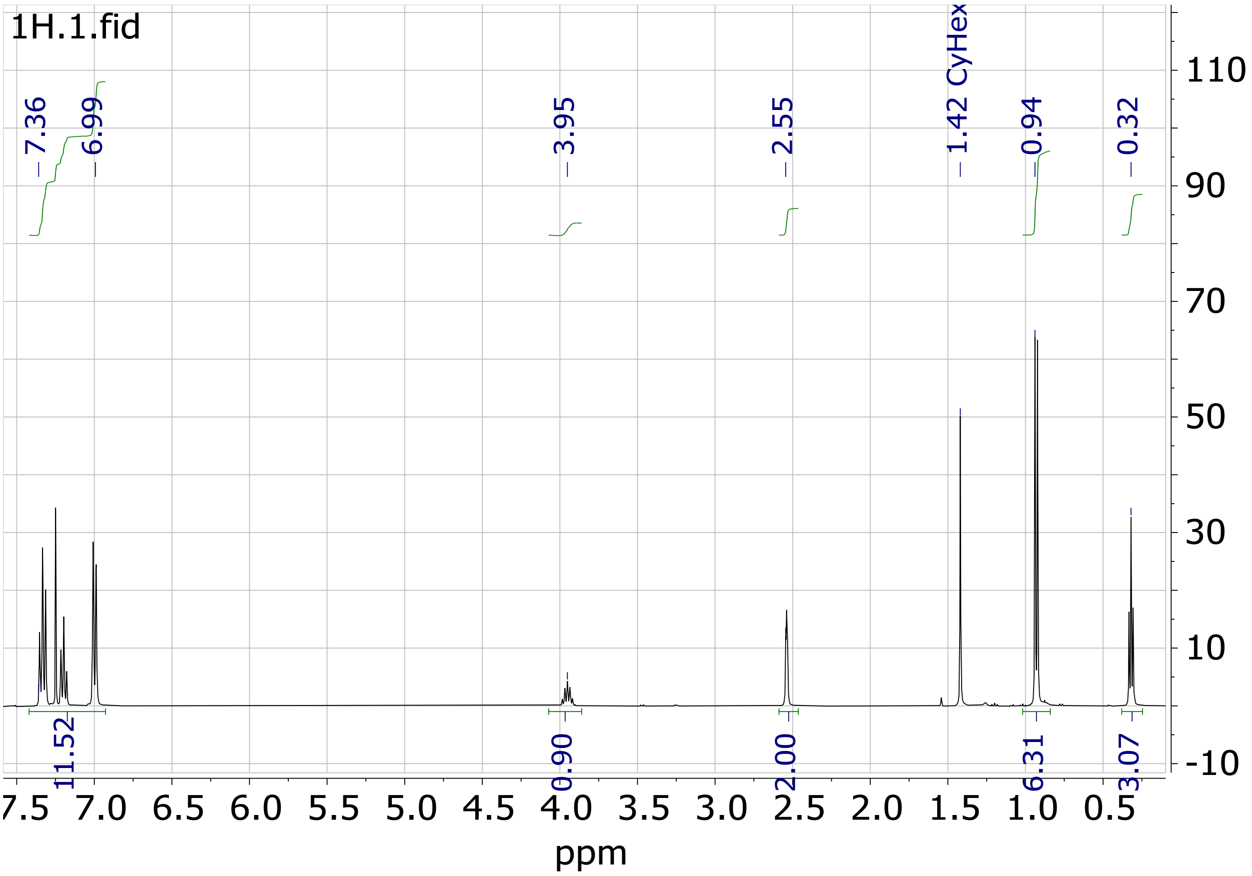

Figure S17. The NMR ^{1}H spectrum of compound 5.

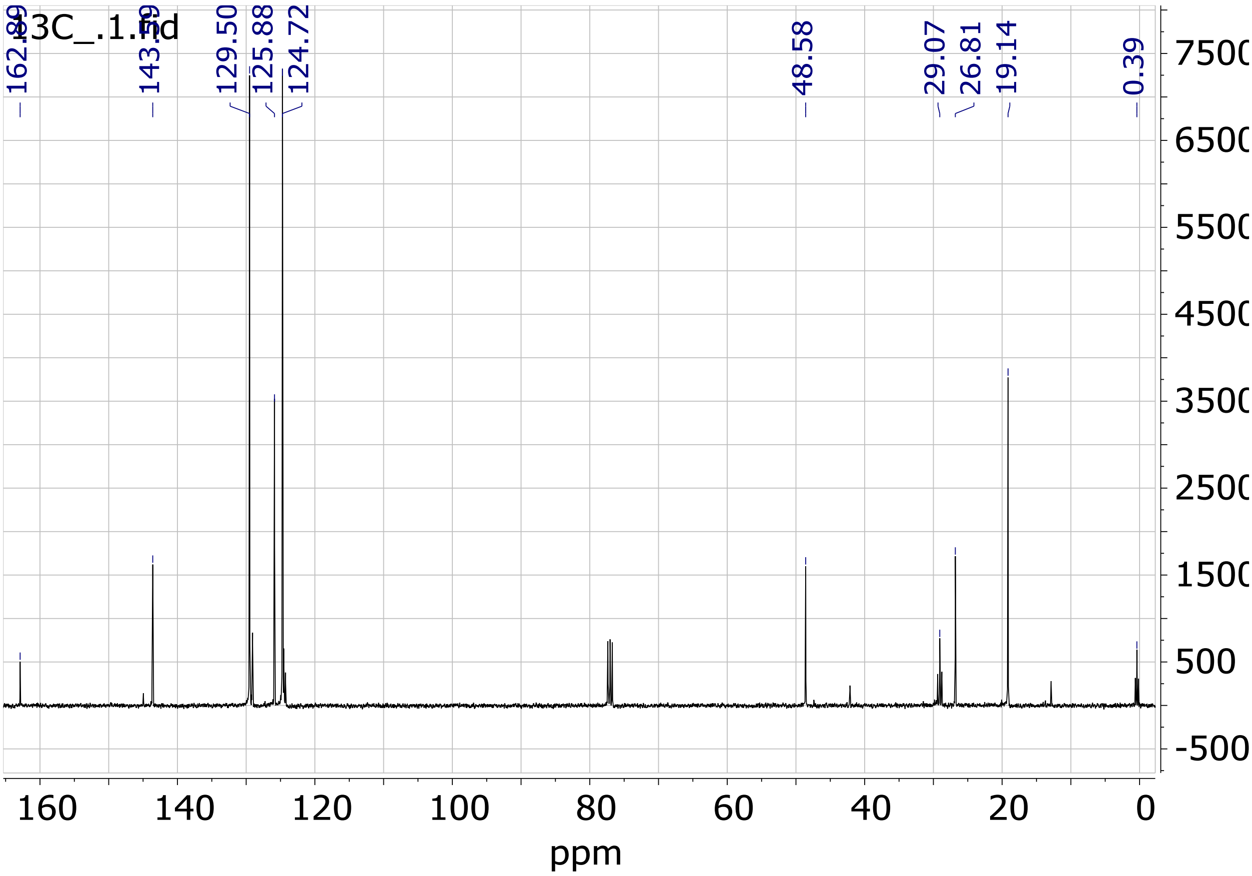

Figure S18. The NMR ^{13}C spectrum of compound 5.

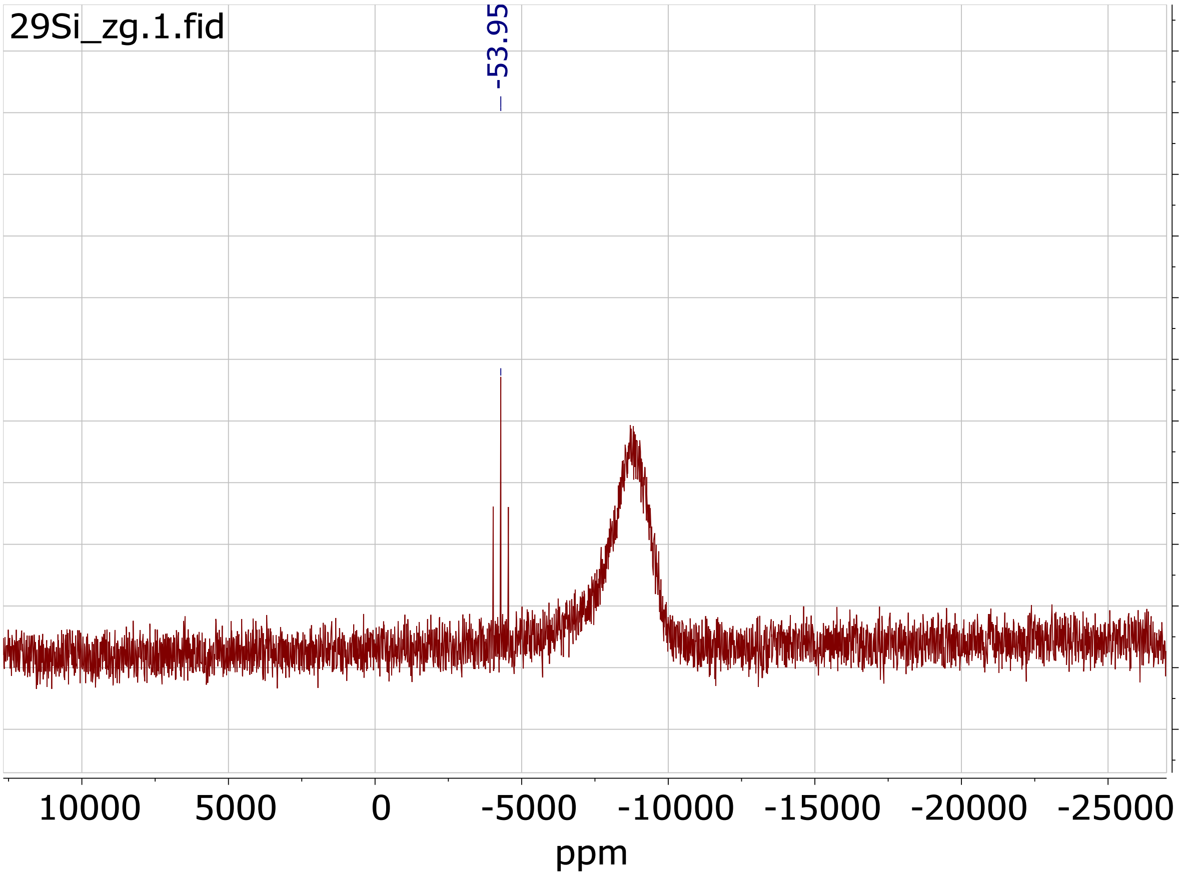

Figure S19. The NMR ^{29}Si spectrum of compound 5.

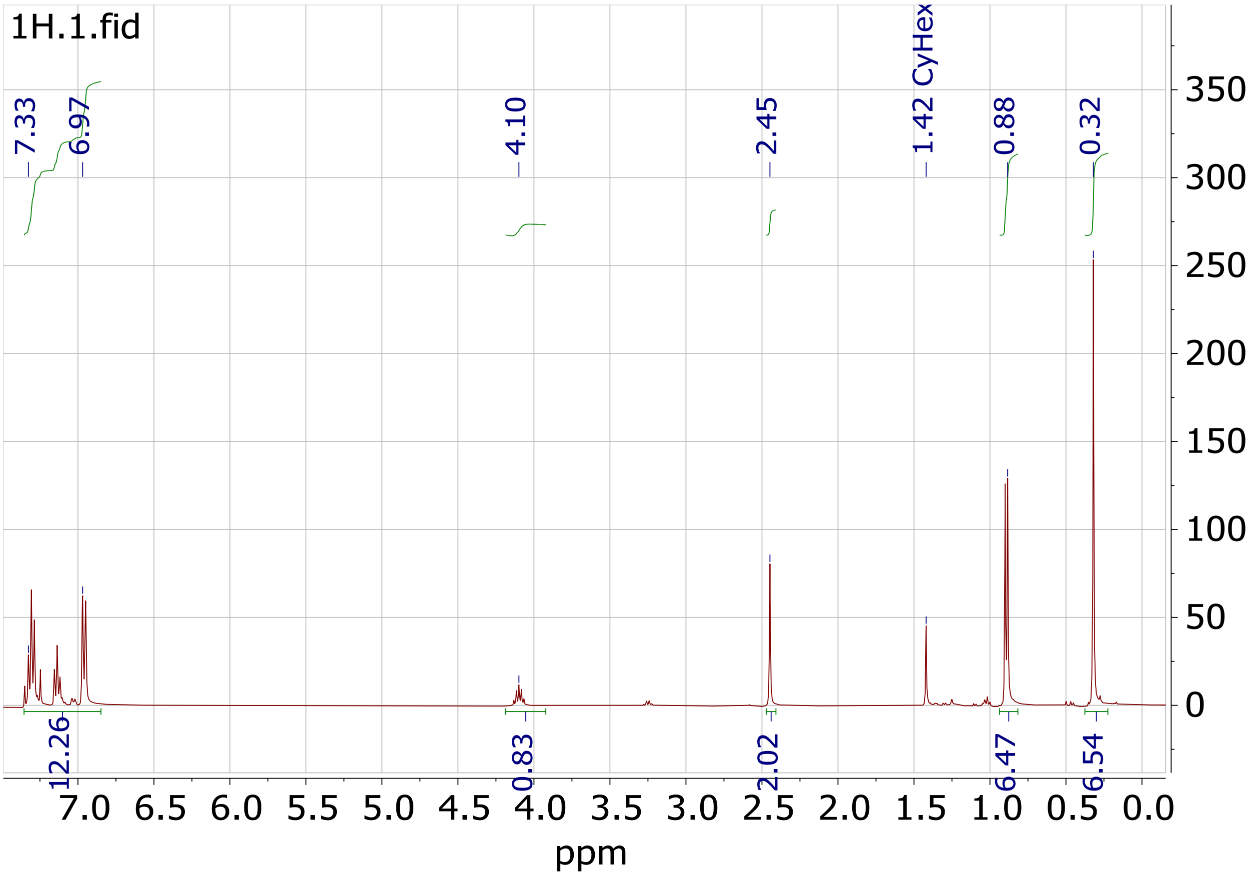

Figure S20. The NMR ^{1}H spectrum of compound 6.

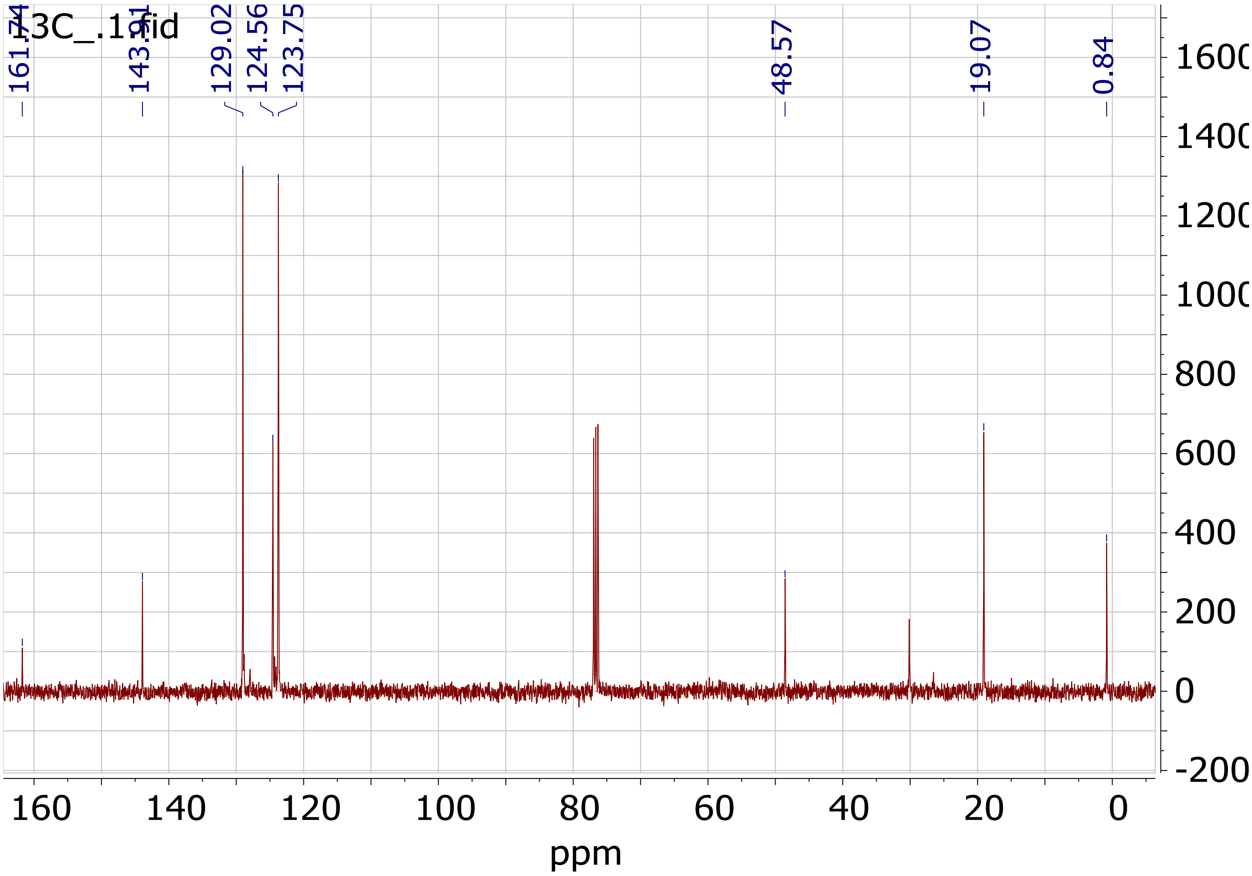

Figure S21. The NMR ^{3}H spectrum of compound 6.

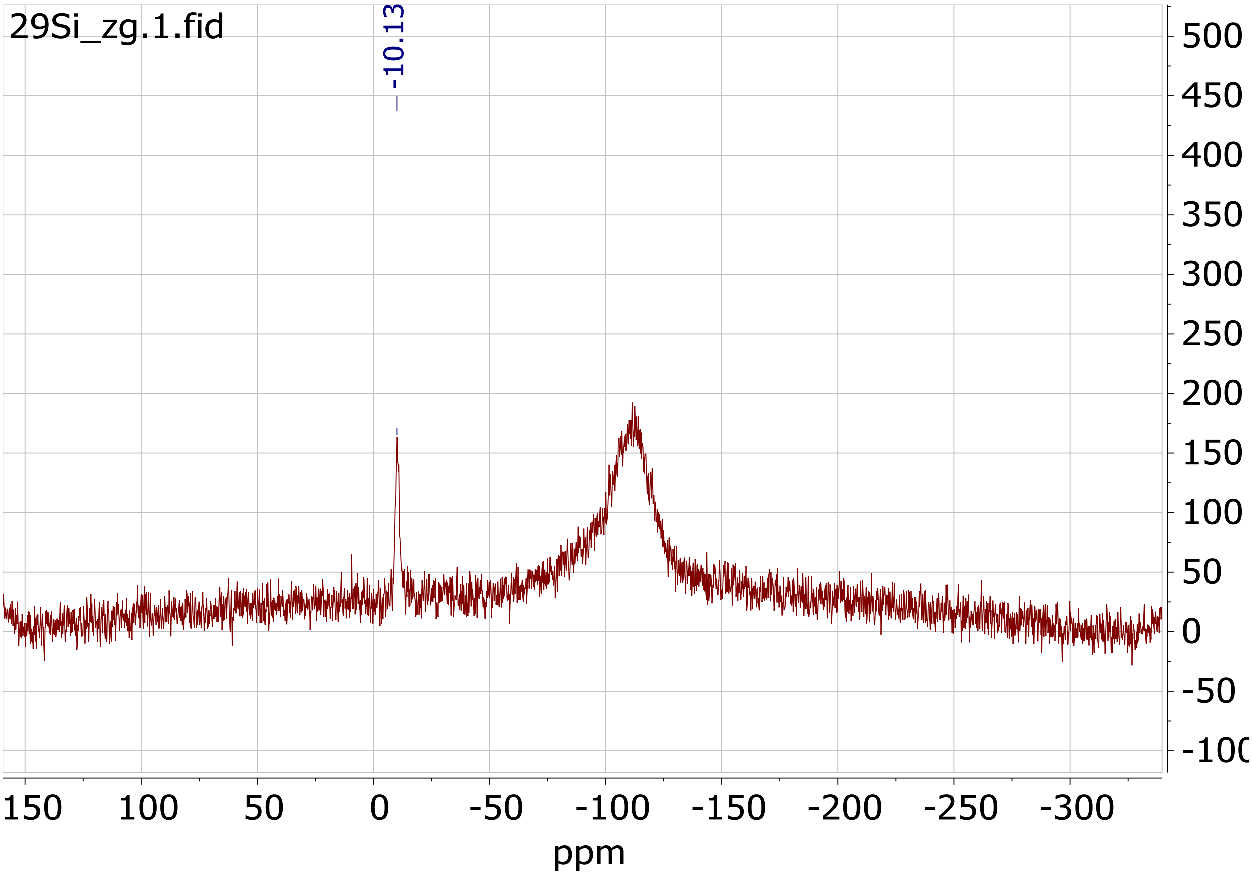

Figure S22. The NMR ^{29}Si spectrum of compound 6.

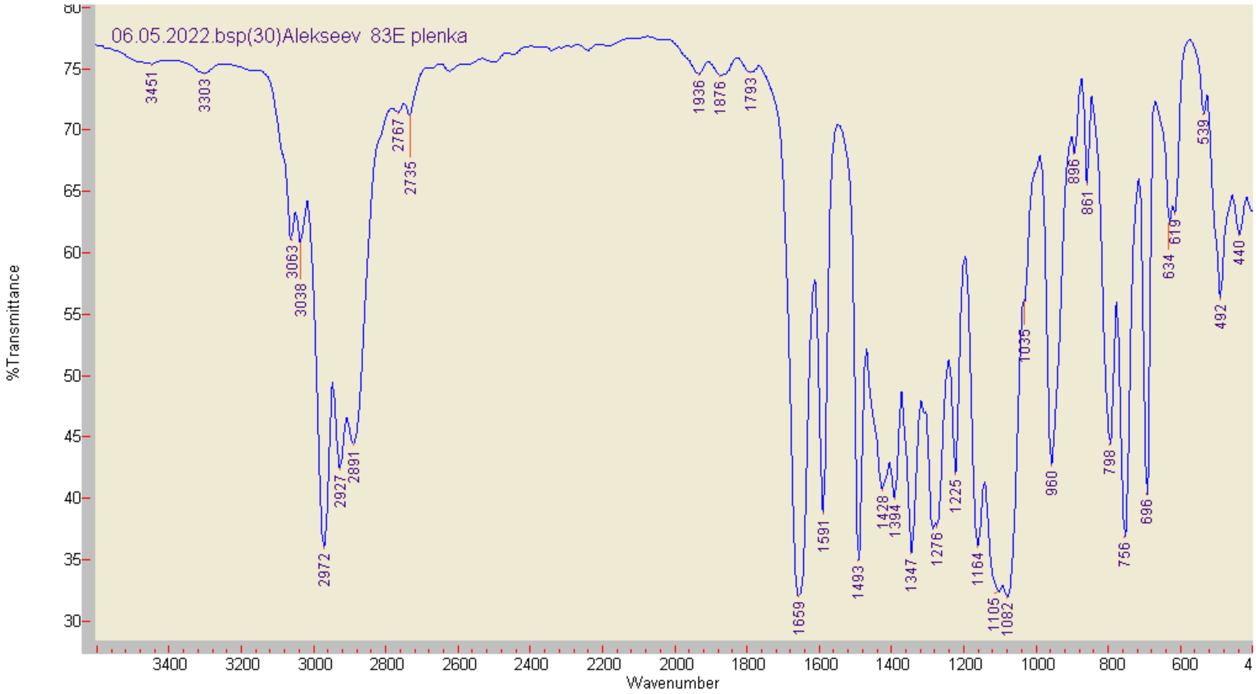

Figure S23. The IR spectrum of compound 1.

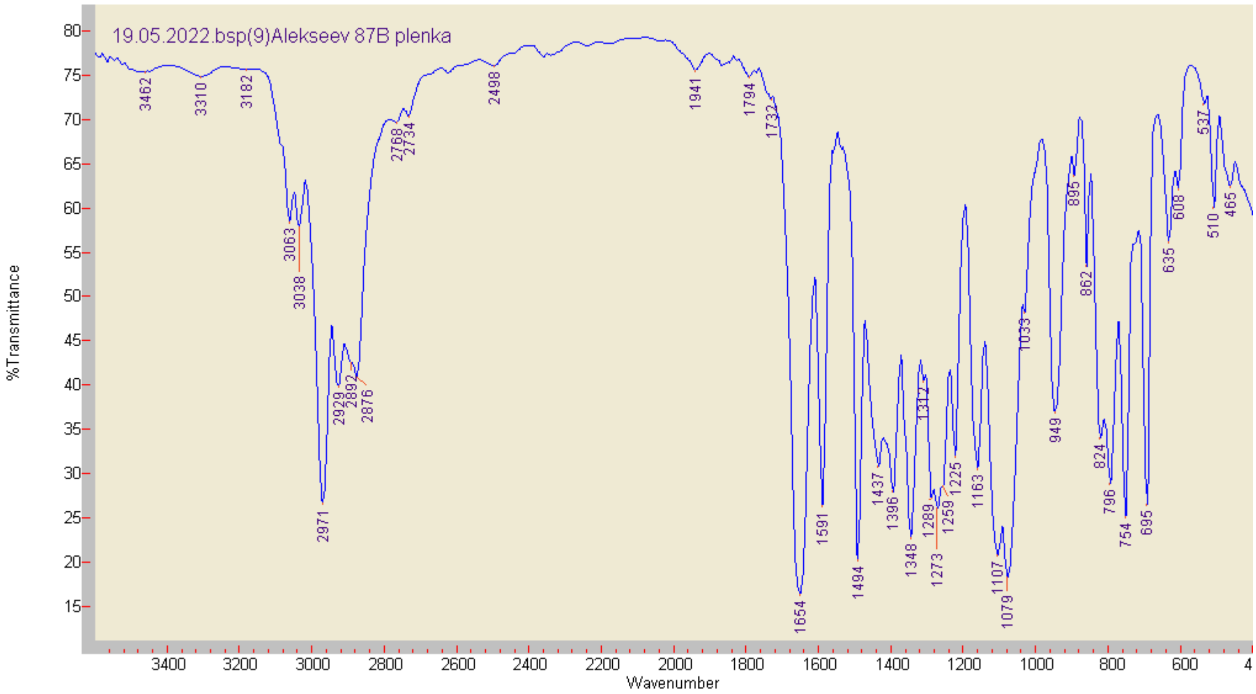

Figure S24. The IR spectrum of compound 2.

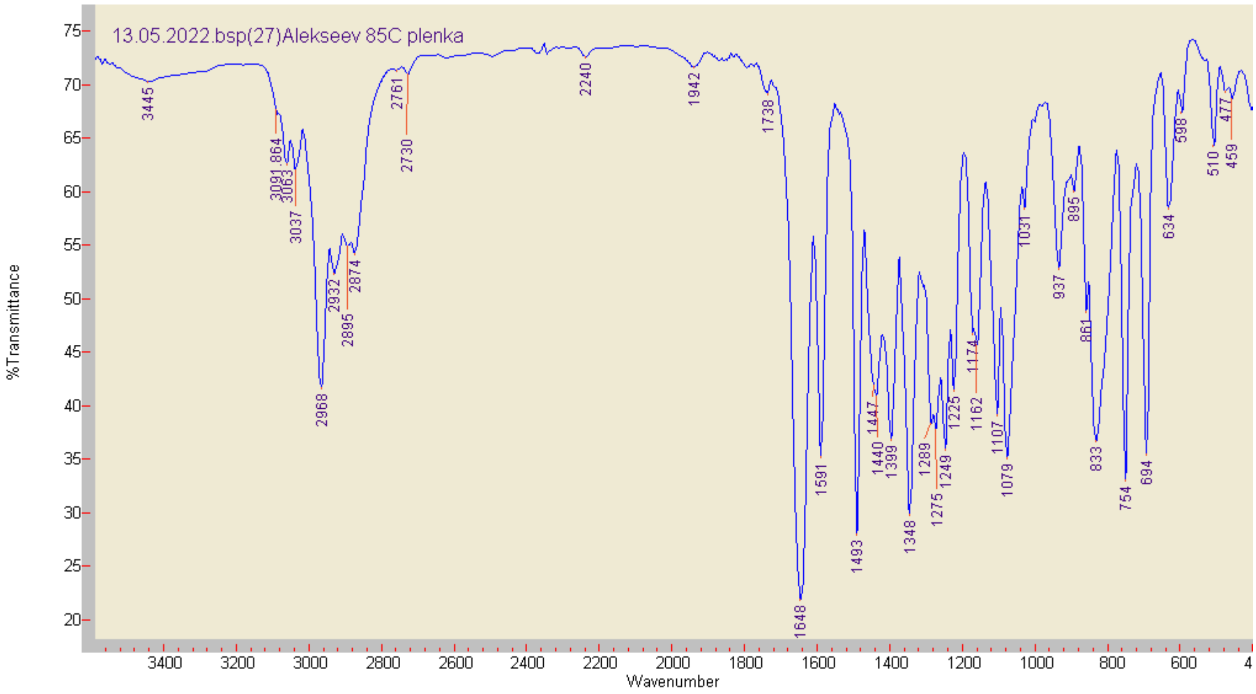

Figure S25. The IR spectrum of compound 3.

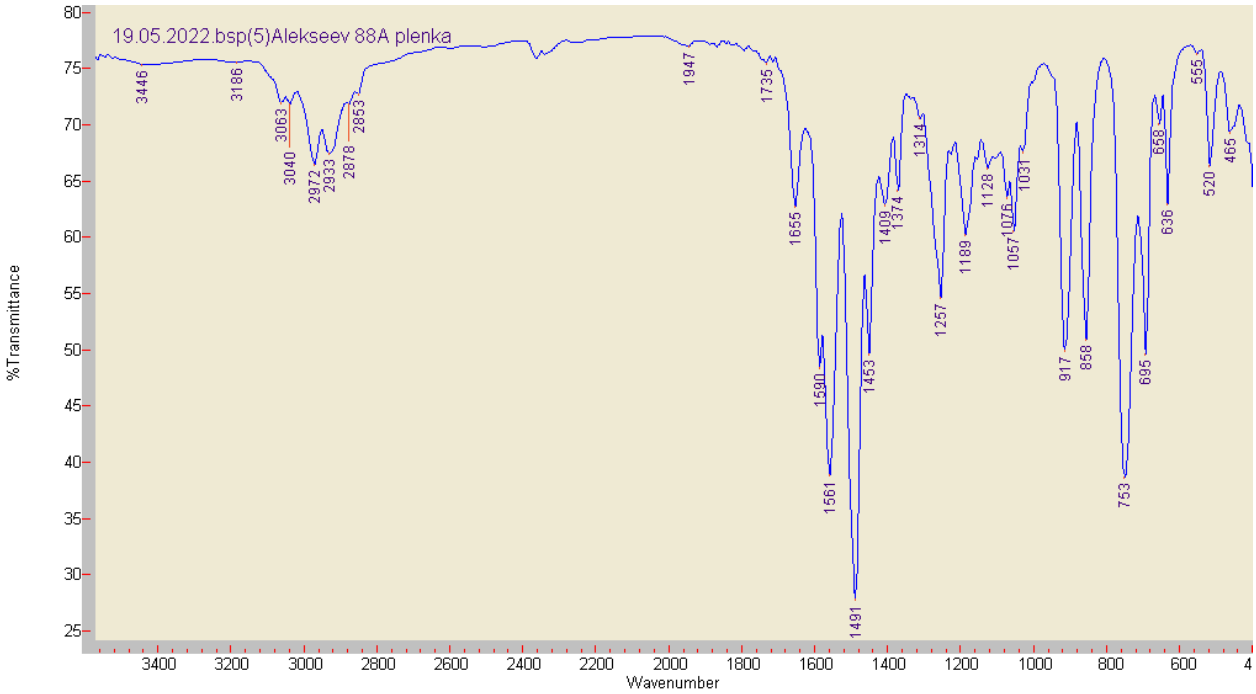

Figure S26. The IR spectrum of compound 4.

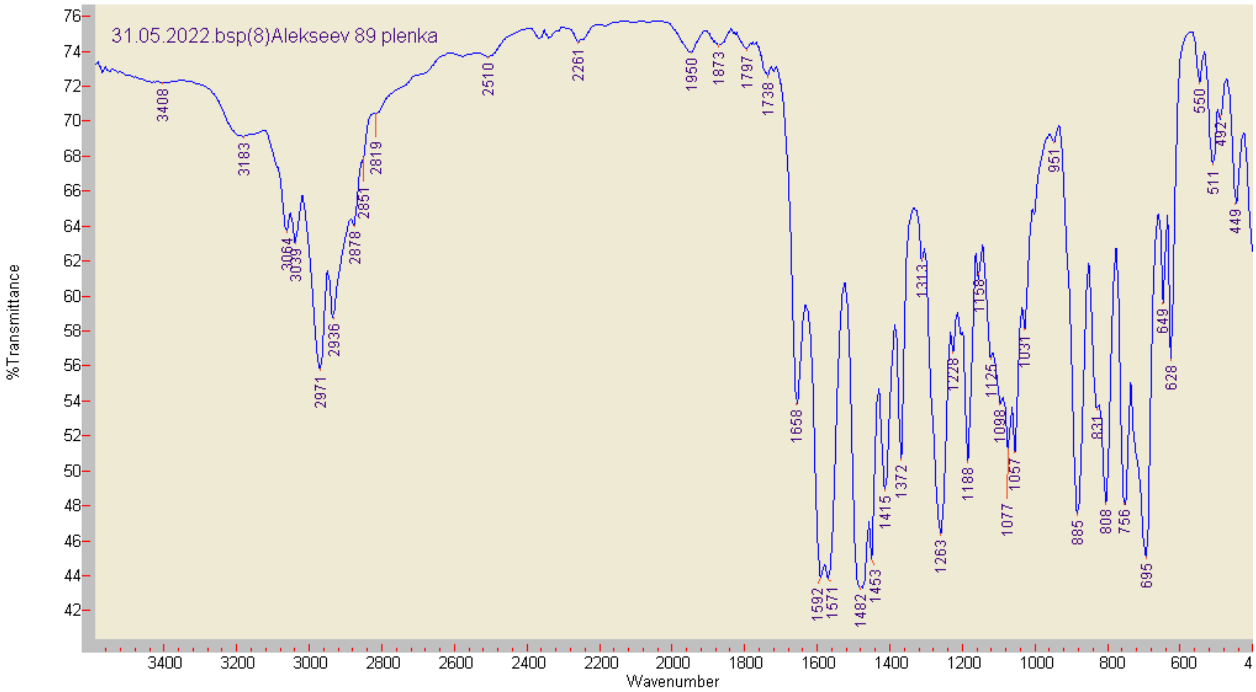

Figure S27. The IR spectrum of compound 5.

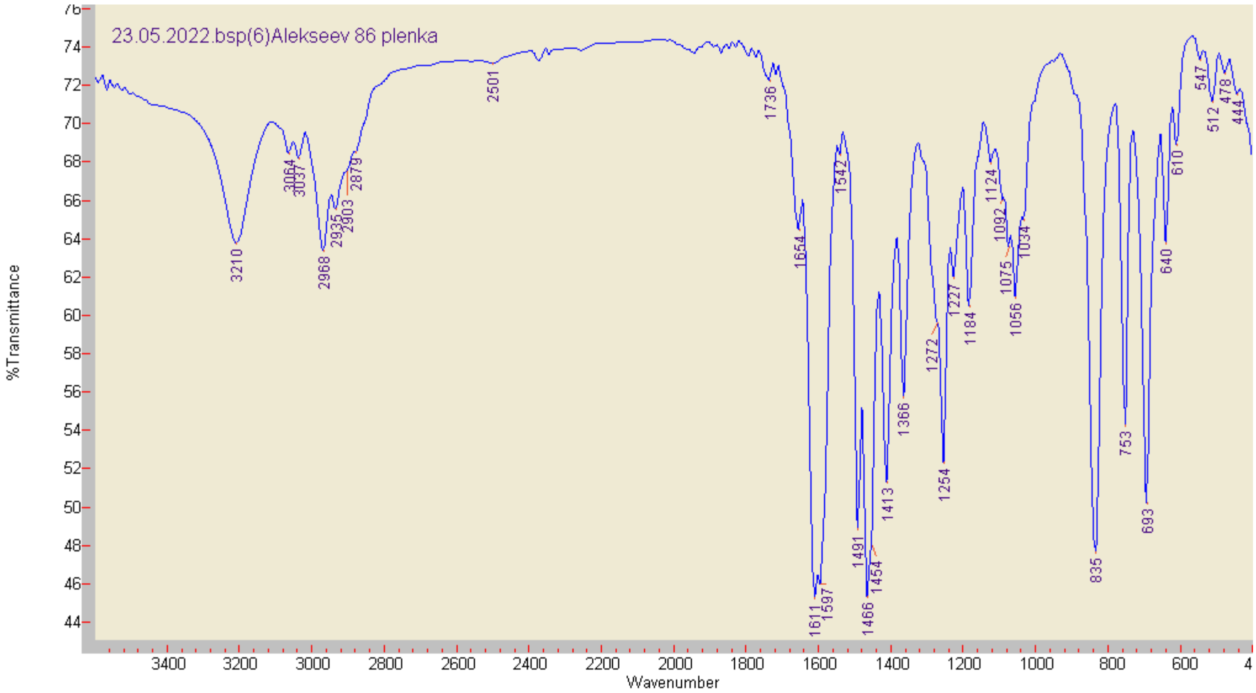

Figure S28. The IR spectrum of compound 6.