

Supporting Information

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S1 Crystallographic details

Suitable single crystals were mounted on a hair or on a MiTiGen mount in perfluorinated inert oil. The intensity measurements were performed at 100 K on an Oxford Diffraction Nova A and a Rigaku XtaLAB Synergy S Single Source diffractometer using mirror-focused CuK α radiation or on an Oxford Diffraction Eos using monochromated MoK α radiation. The diffractometer software CrysAlisPRO was employed.^[1] Absorption corrections were based on multiscans. The structures were refined anisotropically on F^2 using SHELXL-2017/1 or -2018/3.^[2] Hydrogen atoms were included using a riding model or rigid methyl groups. Further details are given in Table S1-11.

Solvent content: Sulfur species **4** contains three coordinated THF molecules per asymmetric unit; all three are ordered. Oxygen species **6** contains three coordinated THF molecules per asymmetric unit; two are ordered, one is disordered over two positions. Species **7** contains four coordinated THF molecules and one co-crystallized THF molecule per asymmetric unit; all THF molecules are disordered over two positions. Selenium species **8** contains three coordinated Et₂O molecules per asymmetric unit; all three are disordered over two positions. Tellurium species **9** contains two coordinated THF and two coordinated Et₂O molecules per asymmetric unit; all coordinated solvent molecules are ordered. Oxygen species **10** contains one toluene molecule per asymmetric unit, which is disordered over two positions. Selenium species **12** contains one toluene molecule per asymmetric unit; it is ordered. Disulfide **13** contains one THF and two *n*hexane molecules per asymmetric unit; all solvent molecules are ordered. Diselenide **14** contains one chlorobenzene and one *n*hexane molecule per asymmetric unit; the chlorobenzene molecule is ordered, the *n*hexane molecule is disordered over two positions.

Exceptions and special details: The disordered solvent molecules were refined using appropriate restraints to improve stability of refinement, but the dimensions are not entirely satisfactory and should be interpreted with caution. The solvent molecules in molecular structure **14'** could not be modeled and the residual electron density was removed with SQUEEZE. The used solvent for crystallization was toluene and there were several positions possible for the disordered molecule. Refinement with disorder models was insufficient due to the many positions.

Complete data have been deposited with the Cambridge Crystallographic Data Centre under the CCDC numbers 2013320–2013330 for compounds **4** and **6–14**. These data can be obtained free of charge from <http://www.ccdc.cam.ac.uk/>.

S1.1 (THF)₃Li[(IDipp)=S] (**4**)**Table S1.** Crystallographic data for compound **4**.

Compound	4	
Identification code	2013320	
Empirical formula	C ₃₉ H ₅₉ LiN ₂ O ₃ S	
Formula weight	642.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at offset/far, HyPix (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3854(2) Å	$\alpha = 73.147(2)^\circ$
	b = 10.9362(2) Å	$\beta = 78.248(2)^\circ$
	c = 18.6719(4) Å	$\gamma = 69.152(2)^\circ$
Volume	1884.72(7) Å ³	
Z	2	
Density (calculated)	1.133 Mg/m ³	
Absorption coefficient	0.123 mm ⁻¹	
F(000)	700	
Crystal habitus	prism (colourless)	
Crystal size	0.337 x 0.105 x 0.089 mm ³	
Theta range for data collection	2.578 to 31.140°	
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 15, -25 ≤ l ≤ 25	
Reflections collected	100742	
Independent reflections	10317 [R(int) = 0.0638]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.459	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10317 / 0 / 423	
Goodness-of-fit on F ²	1.054	
Final R indices [I > 2σ(I)]	R1 = 0.0374, wR2 = 0.0976	
R indices (all data)	R1 = 0.0432, wR2 = 0.1006	
Largest diff. peak and hole	0.461 and -0.227 e.Å ⁻³	
Crystallisation Details:	A saturated solution of Li[IDippS] · 3thf in thf was layered with hexane at room temperature.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	-	

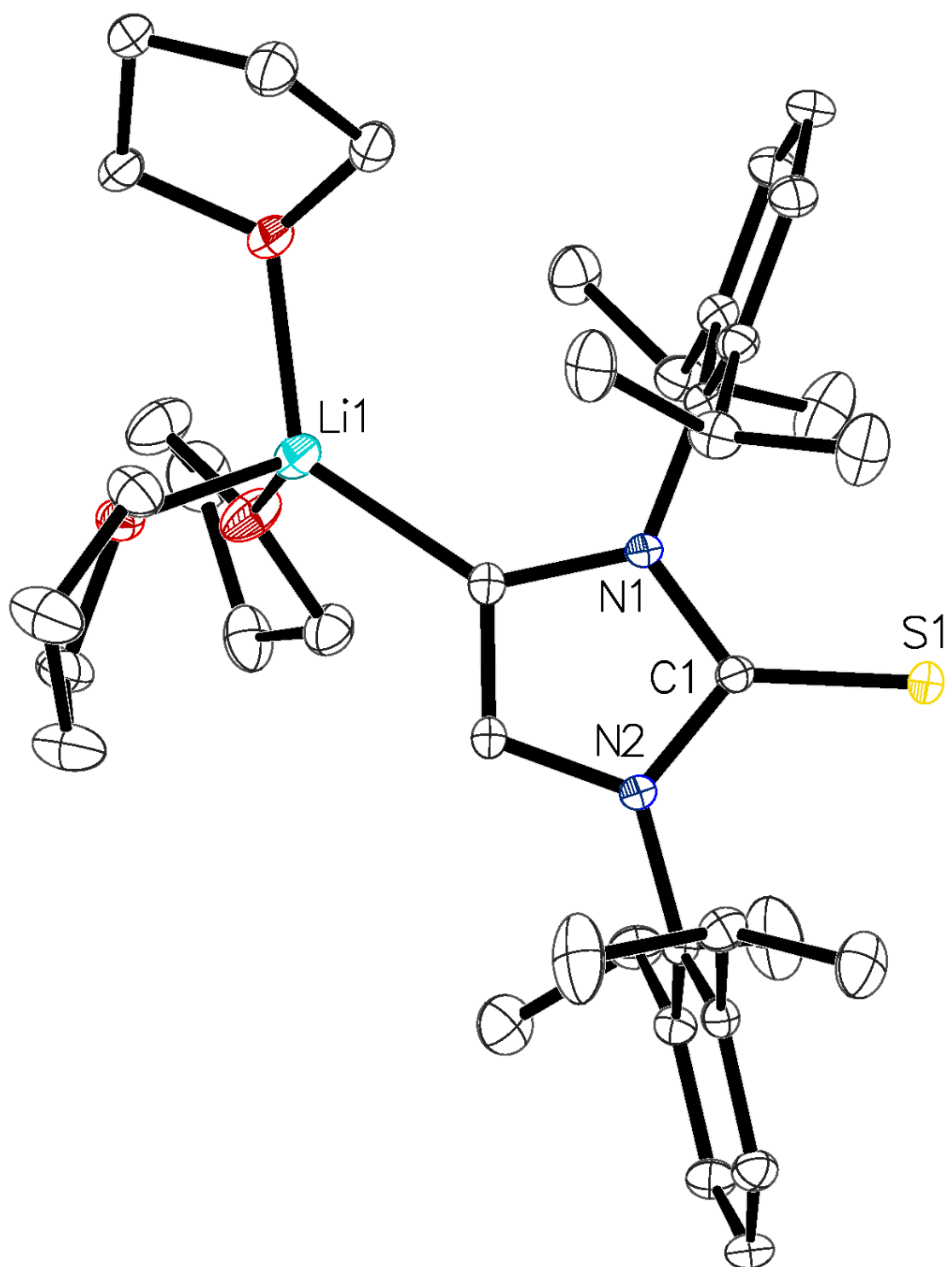


Figure S1. Molecular structure of **4** with thermal displacement parameters drawn at 50% probability; hydrogen atoms are omitted for clarity.

S1.2 [(WCA-IDipp)O]Li(THF)₃ (6·3THF)**Table S 2.** Crystallographic data for compound 6·3THF.

Compound	6·3THF	
Identification code	2013321	
Empirical formula	C ₅₇ H ₅₉ BF ₁₅ LiN ₂ O ₄	
Formula weight	1138.81	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at home/near, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	<i>P2₁/n</i>	
Unit cell dimensions	a = 10.6547(2) Å	$\alpha = 90^\circ$
	b = 36.0847(4) Å	$\beta = 109.136(2)^\circ$
	c = 14.6984(2) Å	$\gamma = 90^\circ$
Volume	5338.85(15) Å ³	
Z	4	
Density (calculated)	1.417 Mg/m ³	
Absorption coefficient	1.067 mm ⁻¹	
F(000)	2360	
Crystal habitus	plate (colorless)	
Crystal size	0.286 x 0.225 x 0.126 mm ³	
Theta range for data collection	2.449 to 77.764°	
Index ranges	-13 ≤ h ≤ 13, -45 ≤ k ≤ 45, -16 ≤ l ≤ 18	
Reflections collected	112445	
Independent reflections	11276 [R(int) = 0.0463]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.56647	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11276 / 0 / 760	
Goodness-of-fit on F ²	1.048	
Final R indices [I > 2σ(I)]	R1 = 0.0438, wR2 = 0.1159	
R indices (all data)	R1 = 0.0464, wR2 = 0.1177	
Largest diff. peak and hole	0.478 and -0.446 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-OLi(thf) ₃ in THF was layered with hexane at ambient temperature.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	Two methyl groups in an isopropyl moiety and one carbon atom in the molecule are disordered and were refined over two positions. No restraints were applied.	

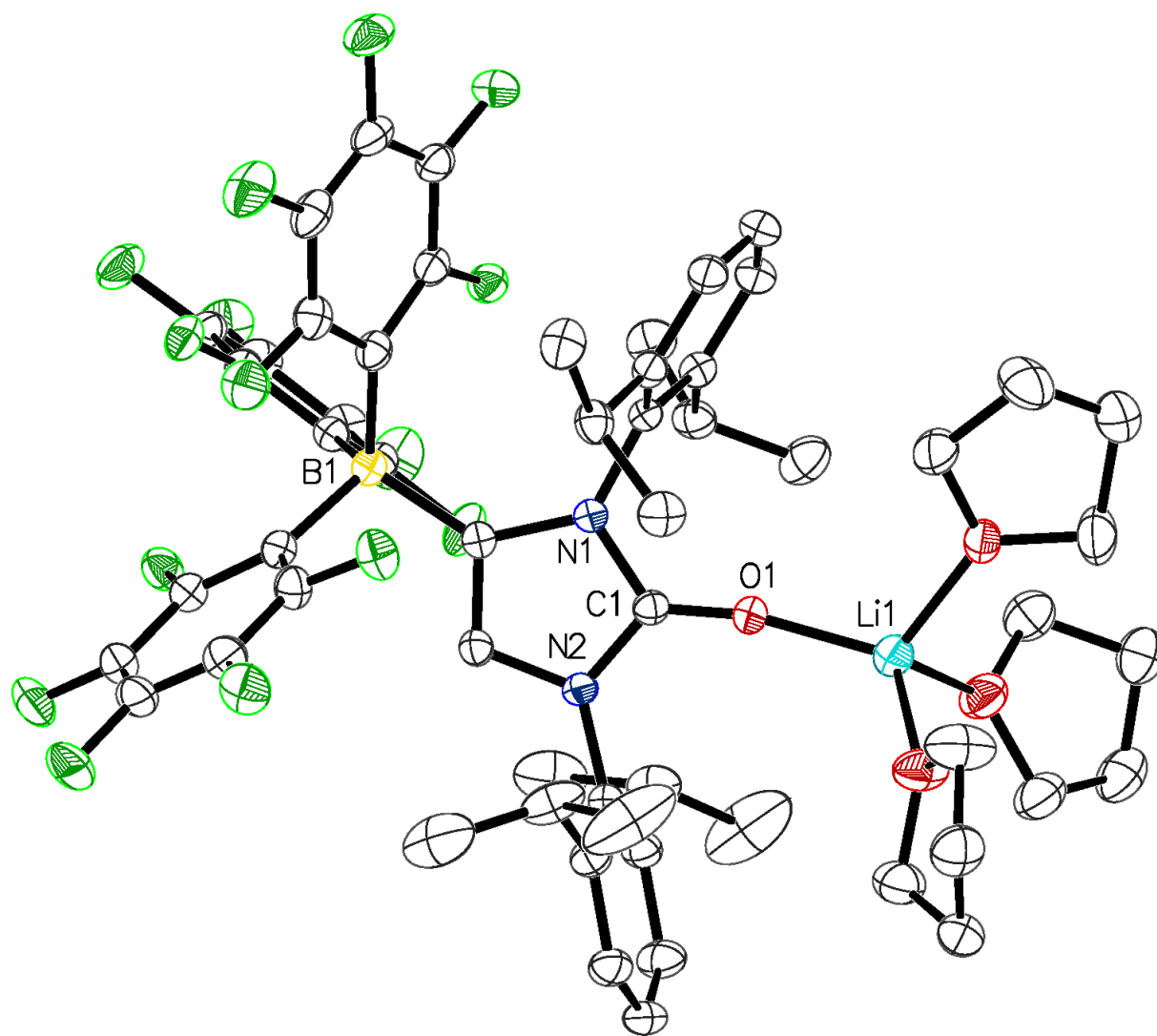


Figure S2. Molecular structure of 6·3THF with thermal displacement parameters drawn at 50% probability; hydrogen atoms, the second position of a disordered THF molecule and the second position of a disordered isopropyl group are omitted for clarity.

S1.3 [(WCA-IDipp)S]Li(THF)₃ (7·5THF)**Table S 3.** Crystallographic data for compound 7·5THF.

Compound	7·5THF	
Identification code	2013322	
Empirical formula	C ₆₅ H ₇₅ BF ₁₅ LiN ₂ O ₅ S	
Formula weight	1299.08	
Temperature	101(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Xcalibur, Atlas, Nova (ω scan)	
Crystal system	Monoclinic	
Space group	<i>P2₁/c</i>	
Unit cell dimensions	a = 10.71830(10) Å	$\alpha = 90^\circ$
	b = 26.7113(2) Å	$\beta = 119.9080(10)^\circ$
	c = 25.5331(3) Å	$\gamma = 90^\circ$
Volume	6336.61(12) Å ³	
Z	4	
Density (calculated)	1.362 Mg/m ³	
Absorption coefficient	1.278 mm ⁻¹	
F(000)	2712	
Crystal habitus	irregular (colourless)	
Crystal size	0.301 x 0.172 x 0.145 mm ³	
Theta range for data collection	3.309 to 76.232°	
Index ranges	-13 ≤ h ≤ 12, -33 ≤ k ≤ 33, -32 ≤ l ≤ 32	
Reflections collected	129565	
Independent reflections	13234 [R(int) = 0.0509]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.977 and 0.959	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13234 / 790 / 941	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0497, wR2 = 0.1297	
R indices (all data)	R1 = 0.0592, wR2 = 0.1381	
Largest diff. peak and hole	1.031 and -0.809 e.Å ⁻³	
Crystallisation Details:	A saturated THF solution of WCA-IDipp-SLi was layered with hexane at ambient temperatures.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	All THF molecules are disordered and were refined over two positions.	

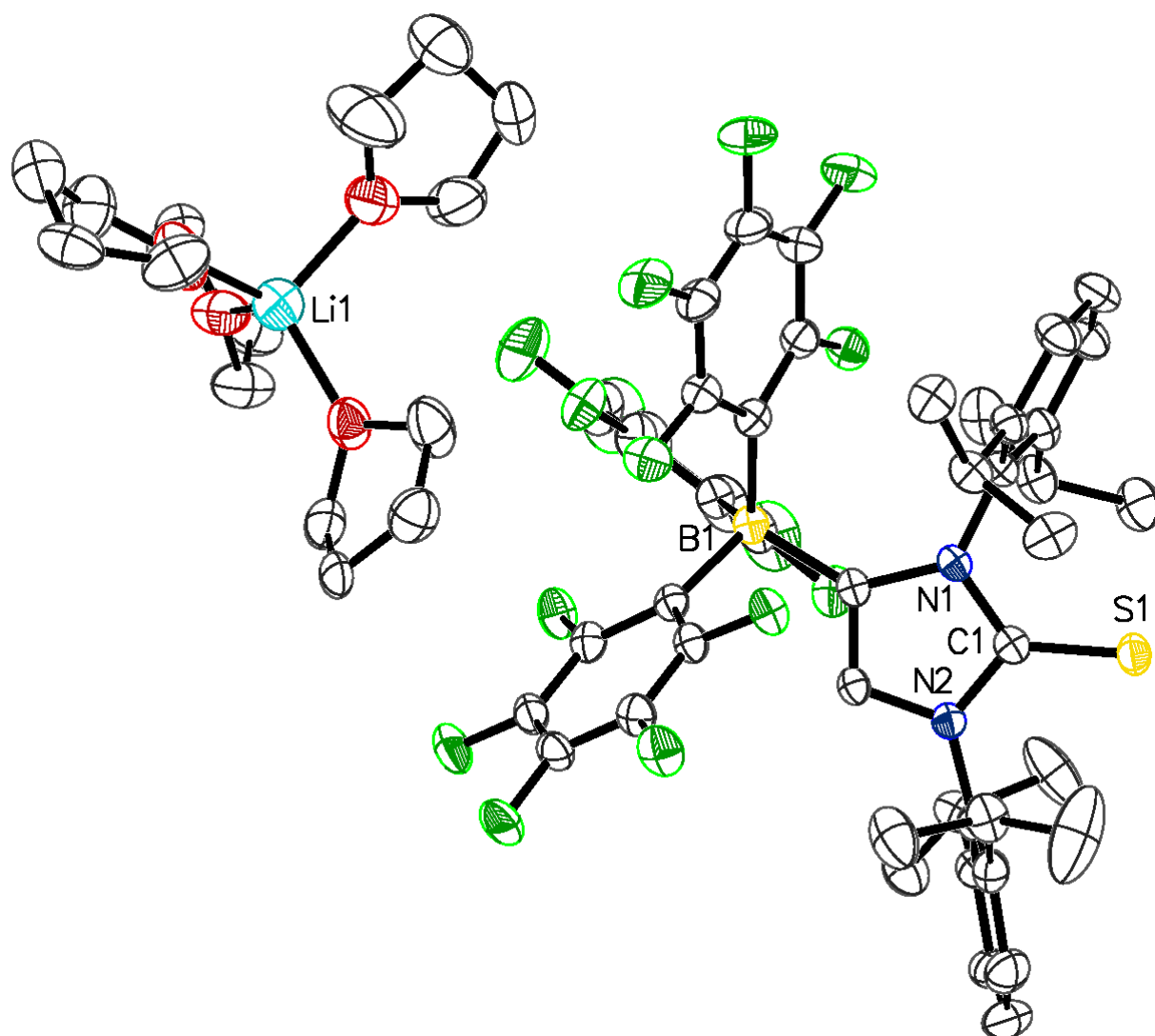


Figure S3. Molecular structure of 7·5THF with thermal displacement parameters drawn at 50% probability; hydrogen atoms, second positions of the disordered THF molecules and one co-crystallized THF molecule are omitted for clarity.

S1.4 [(WCA-IDipp)Se]Li(OEt₂)₃ (8·3Et₂O)**Table S 4.** Crystallographic data for compound 8·3Et₂O.

Compound	8·3Et ₂ O	
Identification code	2013323	
Empirical formula	C ₅₇ H ₆₅ BF ₁₅ LiN ₂ O ₃ Se	
Formula weight	1207.82	
Temperature	100(2) K	
Wavelength	0.7107 Å	
Instrument (scan mode)	Xcalibur, Eos (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.6670(4) Å	α = 94.150(2)°
	b = 14.6160(4) Å	β = 90.650(2)°
	c = 16.7800(4) Å	γ = 113.000(2)°
Volume	2849.54(14) Å ³	
Z	2	
Density (calculated)	1.408 Mg/m ³	
Absorption coefficient	0.753 mm ⁻¹	
F(000)	1244	
Crystal habitus	irregular (colourless)	
Crystal size	0.529 x 0.372 x 0.301 mm ³	
Theta range for data collection	2.153 to 31.088°	
Index ranges	-18 ≤ h ≤ 18, -20 ≤ k ≤ 20, -24 ≤ l ≤ 24	
Reflections collected	253747	
Independent reflections	16941 [R(int) = 0.0445]	
Completeness to theta = 25.241°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.959 and 0.936	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16941 / 90 / 802	
Goodness-of-fit on F ²	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0623, wR2 = 0.1540	
R indices (all data)	R1 = 0.0808, wR2 = 0.1671	
Largest diff. peak and hole	1.354 and -0.872 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-SeLi in Et ₂ O was layered with hexane at ambient temperatures.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	The three Et ₂ O molecules which coordinate to the Li cation are disordered and were refined over two positions. The major component was refined anisotropically, the minor component isotropically.	

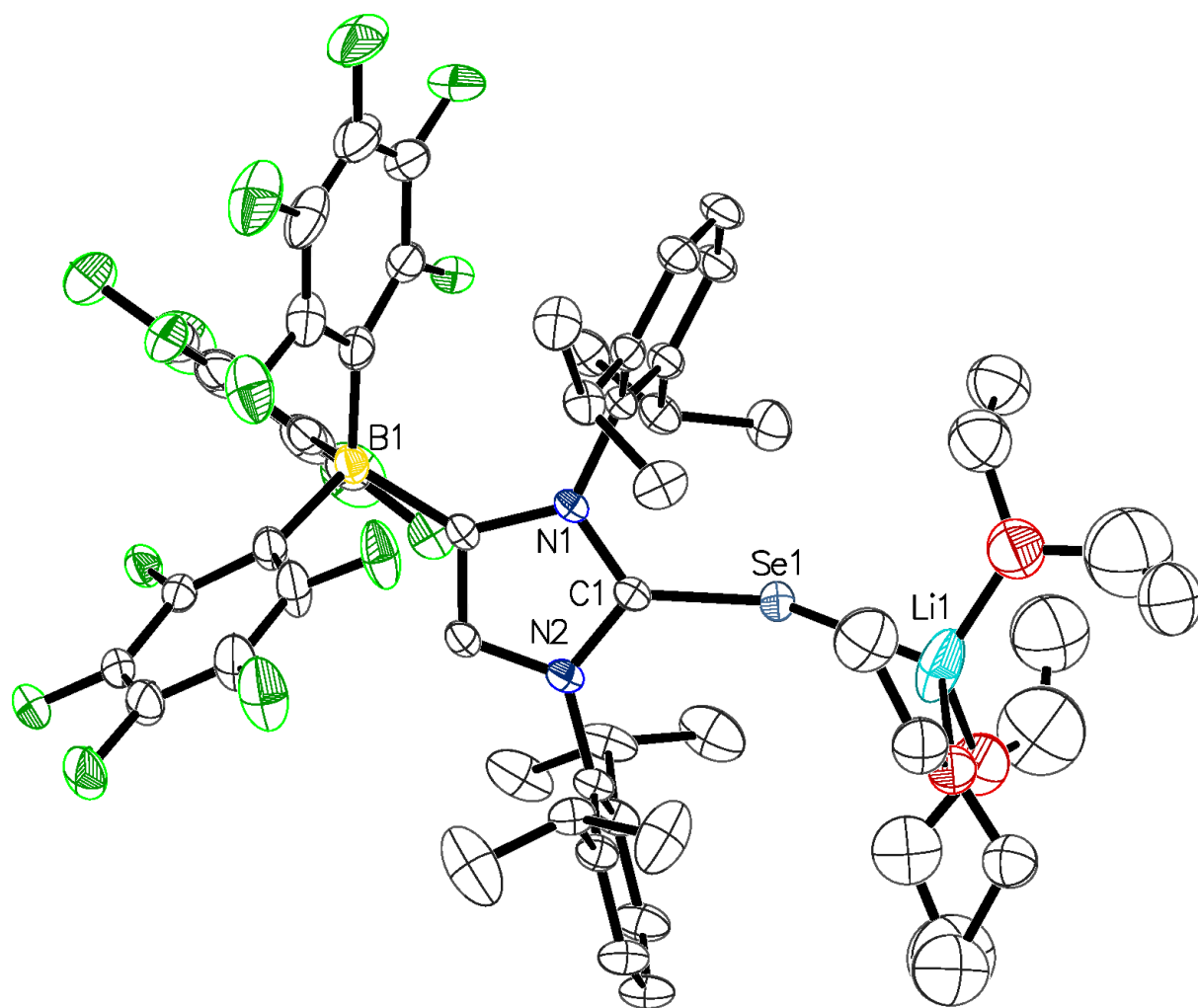


Figure S4. Molecular structure of $8 \cdot 3\text{Et}_2\text{O}$ with thermal displacement parameters drawn at 50% probability; hydrogen atoms and the second positions of the disordered Et_2O molecules are omitted for clarity.

S1.5 [(WCA-IDipp)Te]Li(OEt₂)₃ (9·2Et₂O·2THF).**Table S 5.** Crystallographic data for compound 9·2Et₂O·2THF.

Compound	9·2Et ₂ O·2THF	
Identification code	2013324	
Empirical formula	C ₆₁ H ₇₁ BF ₁₅ LiN ₂ O ₄ Te	
Formula weight	1326.54	
Temperature	100(2) K	
Wavelength	1.5418 Å	
Instrument (scan mode)	Xcalibur, Atlas, Nova (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.1800(4) Å	$\alpha = 100.740(2)^\circ$
	b = 14.5110(4) Å	$\beta = 103.210(2)^\circ$
	c = 16.9900(4) Å	$\gamma = 92.730(2)^\circ$
Volume	3094.17(15) Å ³	
Z	2	
Density (calculated)	1.424 Mg/m ³	
Absorption coefficient	4.596 mm ⁻¹	
F(000)	1356	
Crystal habitus	irregular (yellow)	
Crystal size	0.406 x 0.161 x 0.125 mm ³	
Theta range for data collection	3.460 to 76.539°	
Index ranges	-16 ≤ h ≤ 16, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	
Reflections collected	114871	
Independent reflections	12929 [R(int) = 0.0570]	
Completeness to theta = 67.680°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.468	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	12929 / 120 / 779	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R1 = 0.0431, wR2 = 0.1179	
R indices (all data)	R1 = 0.0436, wR2 = 0.1184	
Largest diff. peak and hole	1.695 and -0.990 e.Å ⁻³	
Crystallisation Details:	A saturated solution of [WCA-IDipp=Te][Li(THF) _n] in Et ₂ O was layered with hexane at ambient temperatures in the dark. The compound is highly light-sensitive.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	Atoms in the Li coordinating THF and Et ₂ O molecules were restrained with ISOR 0.005 due to misshapen thermal ellipsoids.	

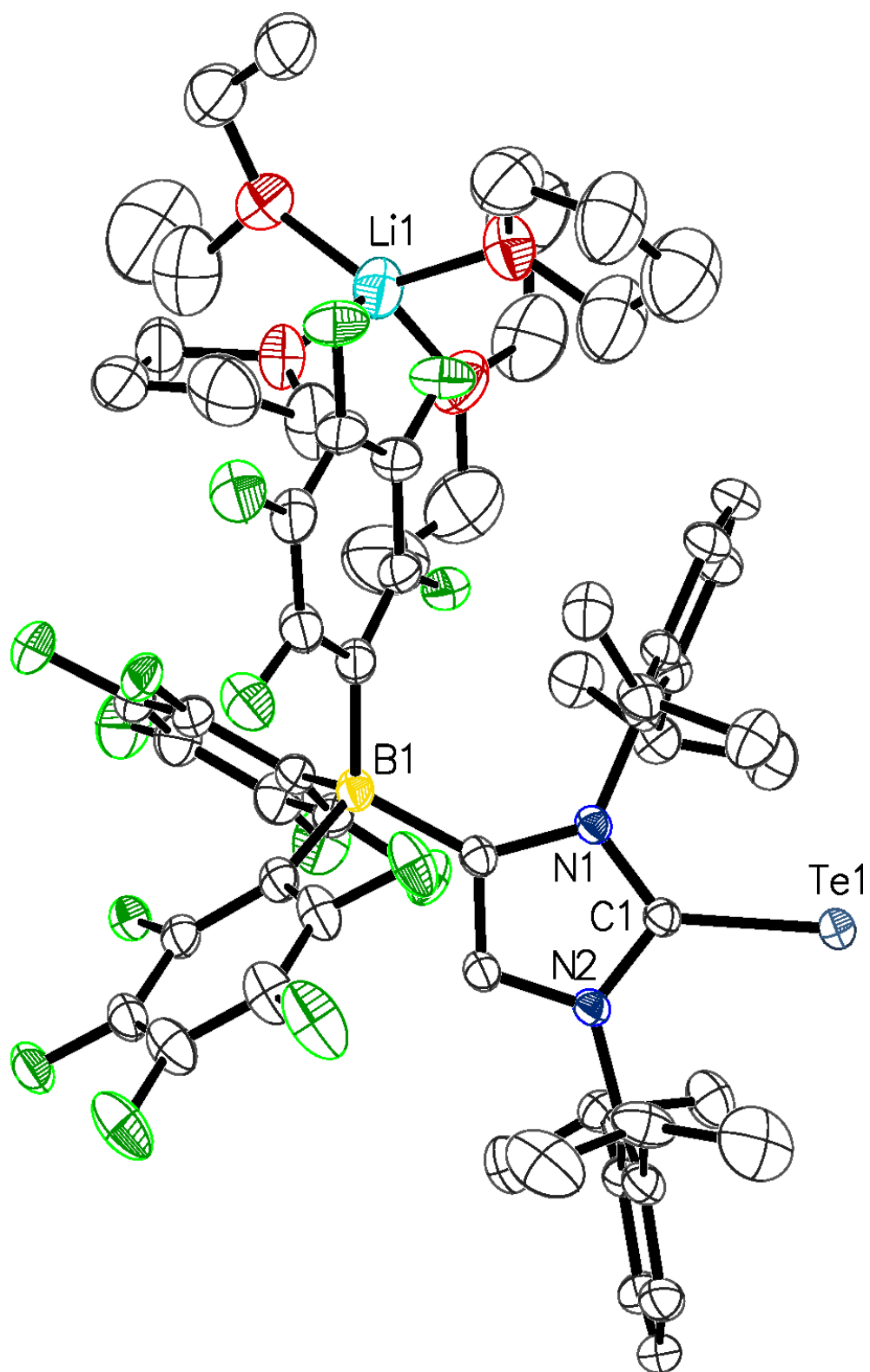


Figure S5. Molecular structure of 9·2Et₂O·2THF with thermal displacement parameters drawn at 50% probability; hydrogen atoms are omitted for clarity.

S1.6 (WCA-IDipp)OH (10·toluene)**Table S 6.** Crystallographic data for compound **10**-toluene.

Compound	10 -toluene	
Identification code	2013325	
Empirical formula	C ₅₂ H ₄₄ BF ₁₅ N ₂ O	
Formula weight	1008.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at offset/far, HyPix (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2374(2) Å	α = 88.932(2)°
	b = 11.4752(2) Å	β = 85.317(2)°
	c = 20.0948(4) Å	γ = 81.974(2)°
Volume	2329.67(8) Å ³	
Z	2	
Density (calculated)	1.438 Mg/m ³	
Absorption coefficient	0.127 mm ⁻¹	
F(000)	1036	
Crystal habitus	irregular (colourless)	
Crystal size	0.466 x 0.303 x 0.262 mm ³	
Theta range for data collection	2.637 to 30.508°	
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28	
Reflections collected	210091	
Independent reflections	14218 [R(int) = 0.0562]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.263	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14218 / 0 / 715	
Goodness-of-fit on F ²	1.025	
Final R indices [I > 2σ(I)]	R1 = 0.0467, wR2 = 0.1268	
R indices (all data)	R1 = 0.0518, wR2 = 0.1308	
Largest diff. peak and hole	1.357 and -0.499 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-OH in toluene was layered with nhexane at ambient temperatures under inert conditions.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	A toluene molecule is disordered over two positions and was refined as such. The hydrogen atom bound to the oxygen atom was located in the difference electron density map and its position was fixed. The displacement parameters were refined.	

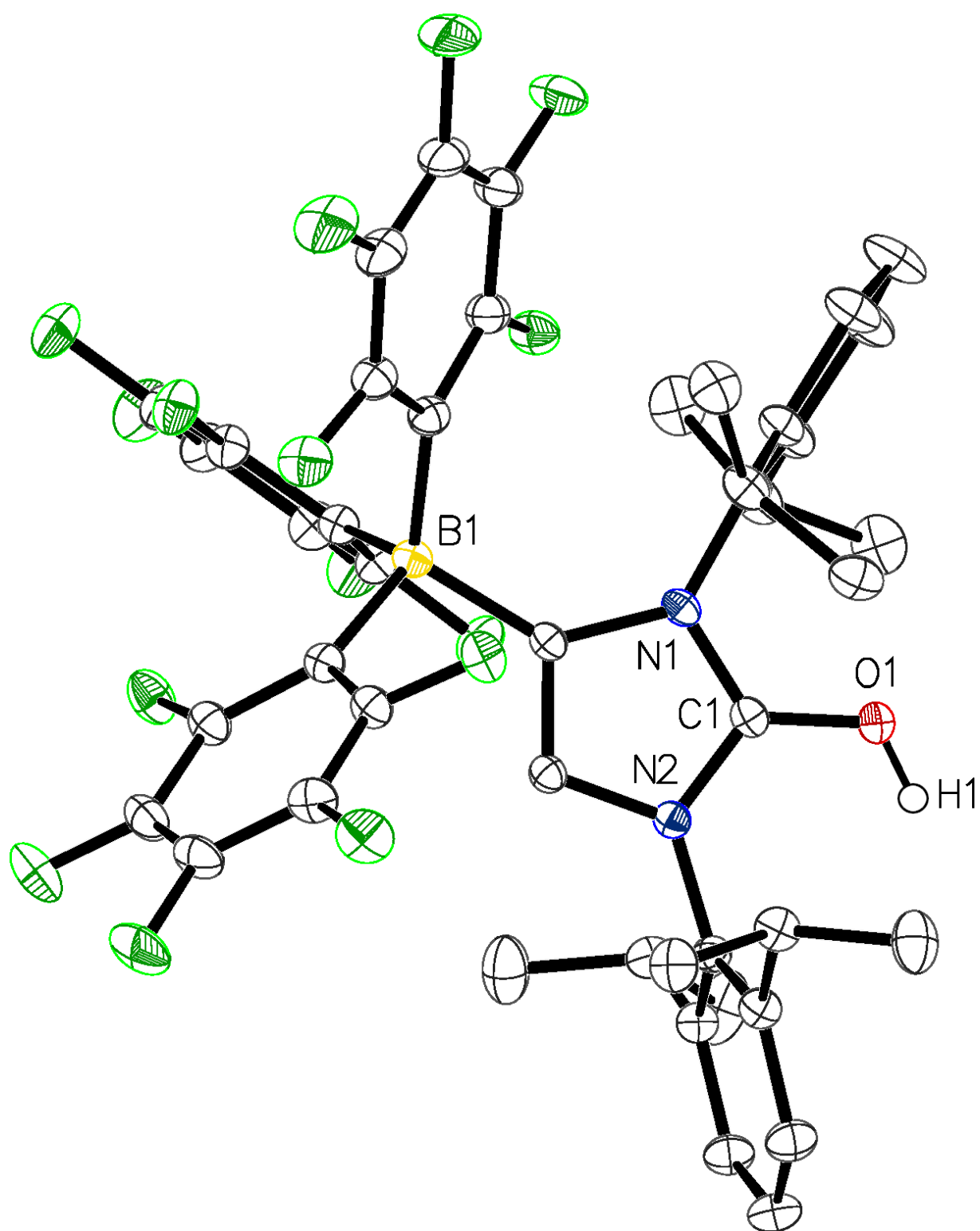


Figure S6. Molecular structure of **10**-toluene with thermal displacement parameters drawn at 50% probability; hydrogen atoms (except the oxygen bound) and one disordered toluene molecule are omitted for clarity.

S1.7 (WCA-IDipp)SH (11)**Table S 7.** Crystallographic data for compound **11**.

Compound	11	
Identification code	2013326	
Empirical formula	C ₄₅ H ₃₆ BF ₁₅ N ₂ S	
Formula weight	932.63	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at home/near, HyPix (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.5249(6) Å	$\alpha = 73.171(6)^\circ$
	b = 12.2429(9) Å	$\beta = 74.186(6)^\circ$
	c = 18.9300(9) Å	$\gamma = 65.396(8)^\circ$
Volume	2090.2(3) Å ³	
Z	2	
Density (calculated)	1.482 Mg/m ³	
Absorption coefficient	1.617 mm ⁻¹	
F(000)	952	
Crystal habitus	plate (colourless)	
Crystal size	0.170 x 0.078 x 0.027 mm ³	
Theta range for data collection	2.477 to 77.958°	
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -21 ≤ l ≤ 23	
Reflections collected	29949	
Independent reflections	8670 [R(int) = 0.0660]	
Completeness to theta = 67.684°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.719	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8670 / 0 / 589	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0542, wR2 = 0.1376	
R indices (all data)	R1 = 0.0787, wR2 = 0.1517	
Largest diff. peak and hole	0.473 and -0.422 e.Å ⁻³	
Crystallisation Details:	Decomposition product of a saturated solution of WCA-IDipp-SLi + FeCl ₂ (NCMe) ₂ layered with nhexane at ambient temperatures under inert conditions.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	Thy hydrogen atom bound to the sulfur atom (H1) was refined freely. No restraints or constraints were applied.	

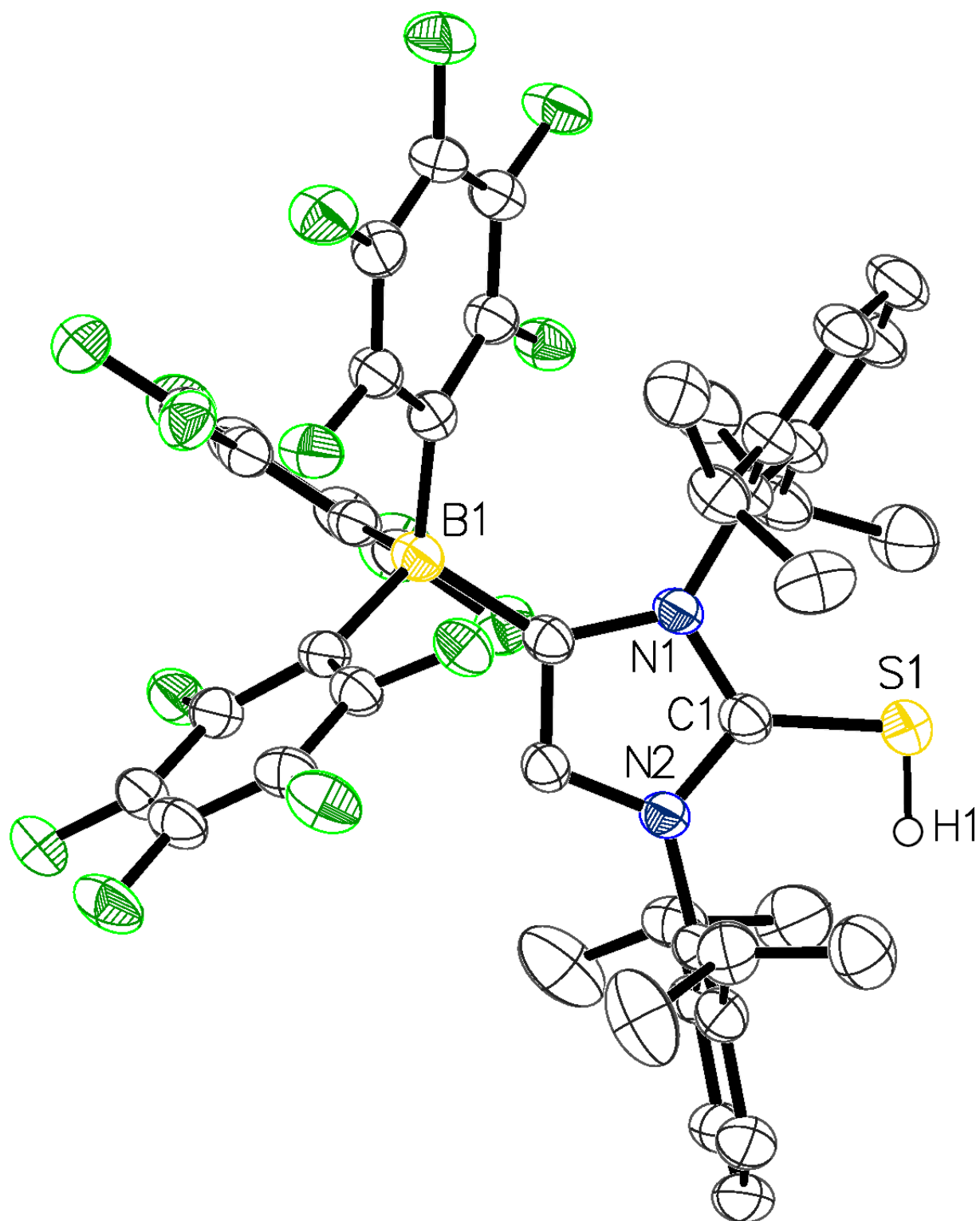


Figure S 7. Molecular structure of **11** with thermal displacement parameters drawn at 50% probability; hydrogen atoms (except the sulfur bound) are omitted for clarity.

S1.8 (WCA-IDipp)SeH (12·toluene)**Table S 8.** Crystallographic data for compound **12**·toluene.

Compound	12 ·toluene	
Identification code	2013327	
Empirical formula	C ₅₂ H ₄₄ BF ₁₅ N ₂ Se	
Formula weight	1071.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at offset/far, HyPix (ω scan)	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	a = 15.0020(4) Å	$\alpha = 90^\circ$
	b = 17.0336(4) Å	$\beta = 111.308(4)^\circ$
	c = 19.9857(4) Å	$\gamma = 90^\circ$
Volume	4758.0(2) Å ³	
Z	4	
Density (calculated)	1.496 Mg/m ³	
Absorption coefficient	0.887 mm ⁻¹	
F(000)	2176	
Crystal habitus	irregular (colourless)	
Crystal size	0.236 x 0.215 x 0.138 mm ³	
Theta range for data collection	2.630 to 40.249°	
Index ranges	-27 ≤ h ≤ 27, -30 ≤ k ≤ 30, -36 ≤ l ≤ 36	
Reflections collected	313659	
Independent reflections	29944 [R(int) = 0.0726]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.439	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	29944 / 0 / 650	
Goodness-of-fit on F ²	1.018	
Final R indices [I > 2σ(I)]	R1 = 0.0537, wR2 = 0.1255	
R indices (all data)	R1 = 0.0950, wR2 = 0.1437	
Largest diff. peak and hole	3.071 and -1.713 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-SEH in toluene was layered with nhexane at ambient temperatures under inert conditions.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	The hydrogen atom bound to the Se atom was located in the difference electron density map and its position was fixed. The displacement parameters were refined.	

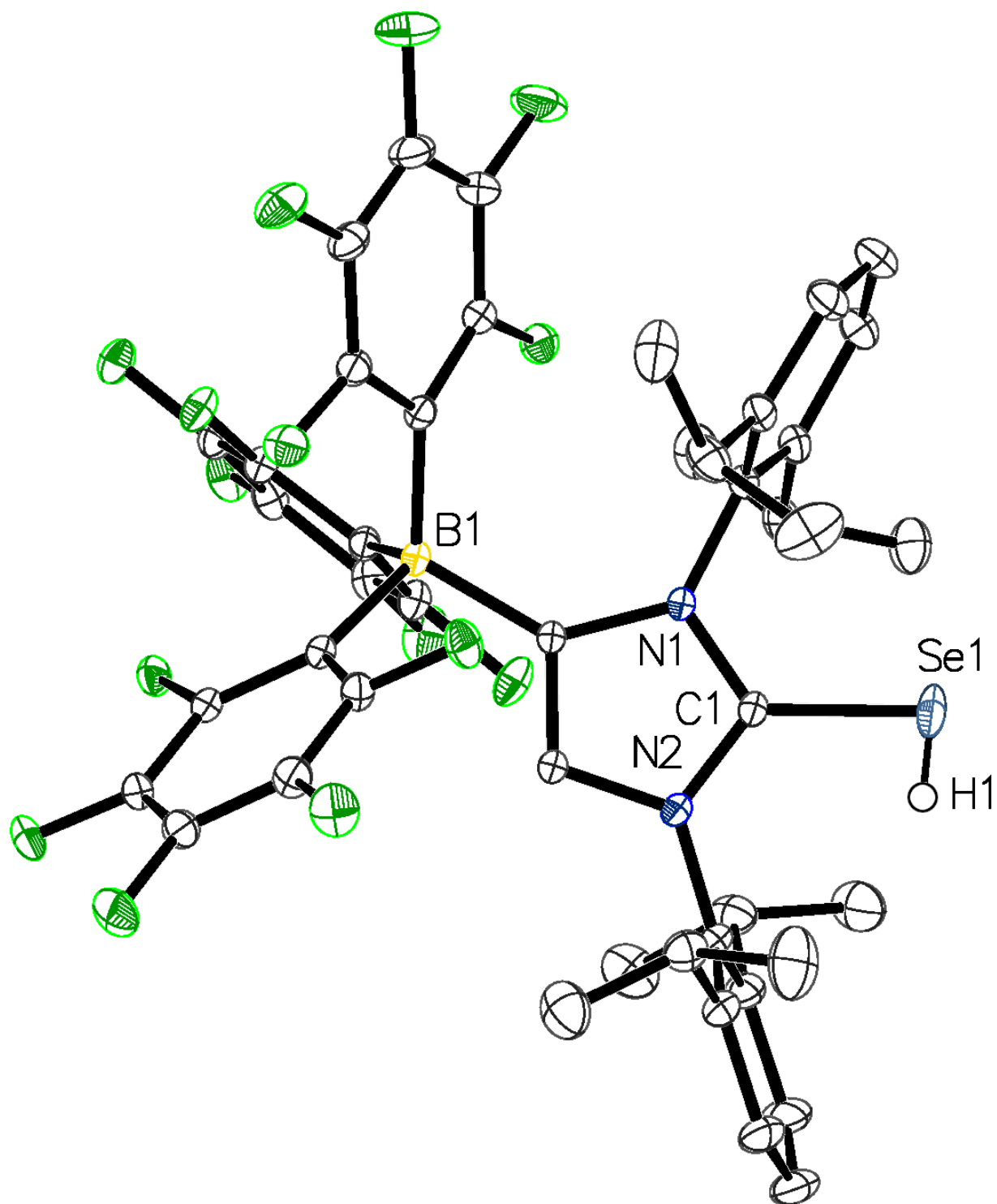


Figure S 8. Molecular structure of 12-toluene with thermal displacement parameters drawn at 50% probability; hydrogen atoms (except the selenium bound) and one toluene molecule are omitted for clarity.

S1.9 (WCA-IDipp)₂S₂ (**13**·2 *n*-hexane·THF)**Table S 9.** Crystallographic data for compound **13**·2 *n*-hexane·THF.

Compound	13 ·2 <i>n</i> -hexane·THF	
Identification code	2013328	
Empirical formula	C ₁₀₆ H ₁₀₆ B ₂ F ₃₀ N ₄ OS ₂	
Formula weight	2107.68	
Temperature	100(2) K	
Wavelength	0.7107 Å	
Instrument (scan mode)	Xcalibur, Eos (ω scan)	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 17.0630(8) Å	α = 91.180(4)°
	b = 17.1310(10) Å	β = 90.880(4)°
	c = 19.4910(10) Å	γ = 119.760(6)°
Volume	4942.7(5) Å ³	
Z	2	
Density (calculated)	1.416 Mg/m ³	
Absorption coefficient	0.163 mm ⁻¹	
F(000)	2180	
Crystal habitus	irregular (orange)	
Crystal size	0.583 x 0.481 x 0.337 mm ³	
Theta range for data collection	2.375 to 26.371°	
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -24 ≤ l ≤ 24	
Reflections collected	22760	
Independent reflections	22760 [R(int) = ?]	
Completeness to theta = 25.241°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.94743	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	22760 / 102 / 1327	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0812, wR2 = 0.2169	
R indices (all data)	R1 = 0.0959, wR2 = 0.2232	
Largest diff. peak and hole	0.622 and -0.635 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-S-S-IDipp-WCA in THF was layered with hexane at ambient temperatures.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	The crystal was a two-component twin. Therefore, the solution was refined as such with a BASF of 0.4354.	

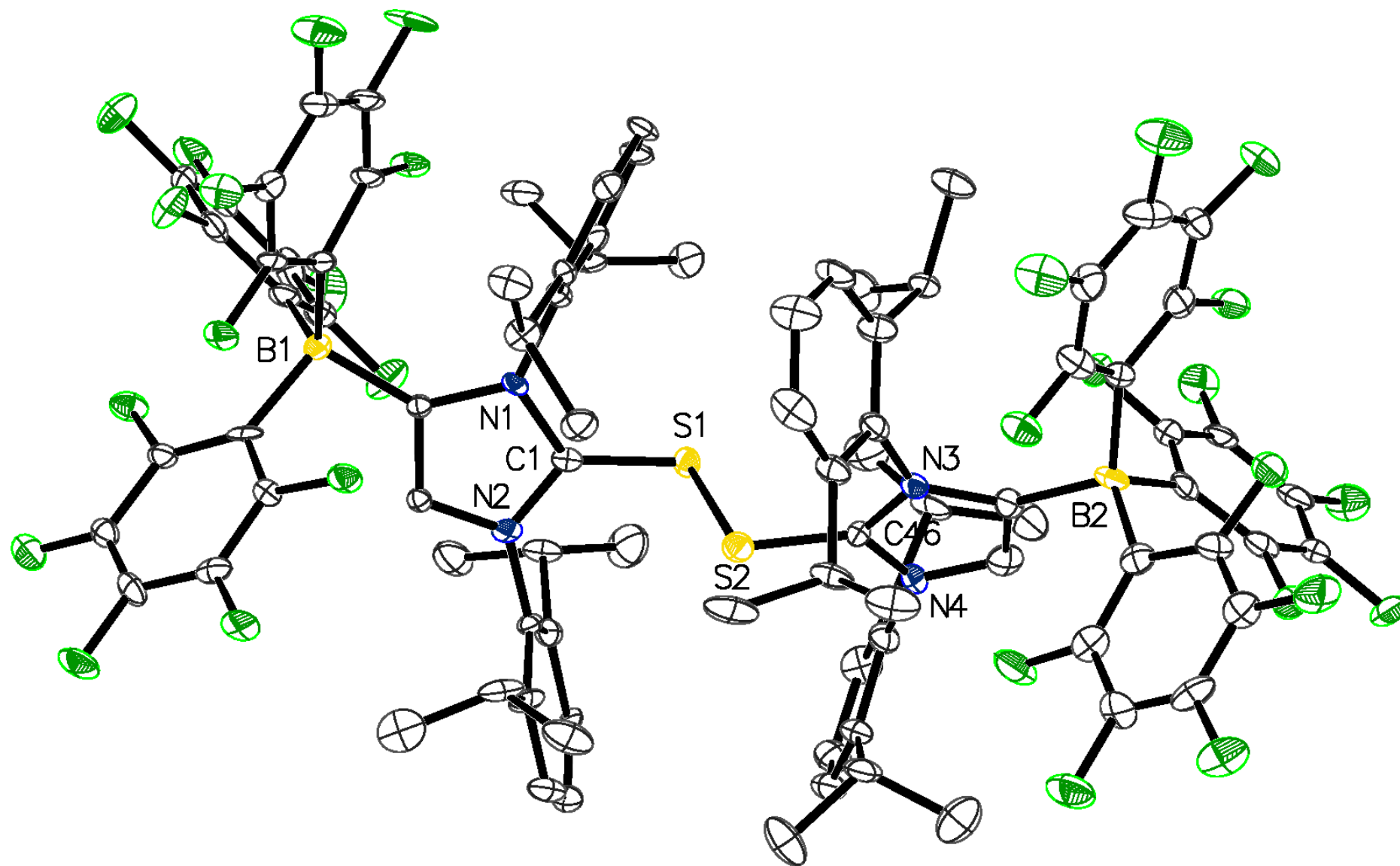


Figure S 9. Molecular structure of 13·2 *n*-hexane-THF with thermal displacement parameters drawn at 50% probability; hydrogen atoms, two co-crystallized *n*-hexane and one THF molecule are omitted for clarity.

S1.10 (WCA-IDipp)₂Se₂ (**14**·*n*-hexane·PhCl)**Table S 10.** Crystallographic data for compound **14**·*n*-hexane·PhCl.

Compound	14 · <i>n</i> -hexane·PhCl	
Identification code	2013329	
Empirical formula	C ₁₀₂ H ₈₉ B ₂ ClF ₃₀ N ₄ Se ₂	
Formula weight	2155.76	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at home/near, HyPix (ω scan)	
Crystal system	Orthorhombic	
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 12.56245(6) Å	$\alpha = 90^\circ$
	b = 26.01067(13) Å	$\beta = 90^\circ$
	c = 29.40849(13) Å	$\gamma = 90^\circ$
Volume	9609.45(8) Å ³	
Z	4	
Density (calculated)	1.490 Mg/m ³	
Absorption coefficient	2.172 mm ⁻¹	
F(000)	4376	
Crystal habitus	block (orange)	
Crystal size	0.269 x 0.132 x 0.075 mm ³	
Theta range for data collection	2.268 to 77.130°	
Index ranges	-15 ≤ h ≤ 15, -31 ≤ k ≤ 32, -36 ≤ l ≤ 37	
Reflections collected	273369	
Independent reflections	19811 [R(int) = 0.0479]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.443	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19811 / 253 / 1344	
Goodness-of-fit on F ²	1.066	
Final R indices [I > 2σ(I)]	R1 = 0.0479, wR2 = 0.1339	
R indices (all data)	R1 = 0.0485, wR2 = 0.1346	
Absolute structure parameter	-0.006(2)	
Largest diff. peak and hole	1.855 and -1.057 e.Å ⁻³	
Crystallisation Details:	A saturated solution of WCA-IDipp-Se-Se-IDipp-WCA in chlorobenzene was layered with hexane at ambient temperatures.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details	One <i>n</i> -hexane molecule is disordered and was refined over two positions. Several SADI and ISOR restraints were applied. One chlorobenzene molecule was refined with the restraints FLAT and ISOR.	

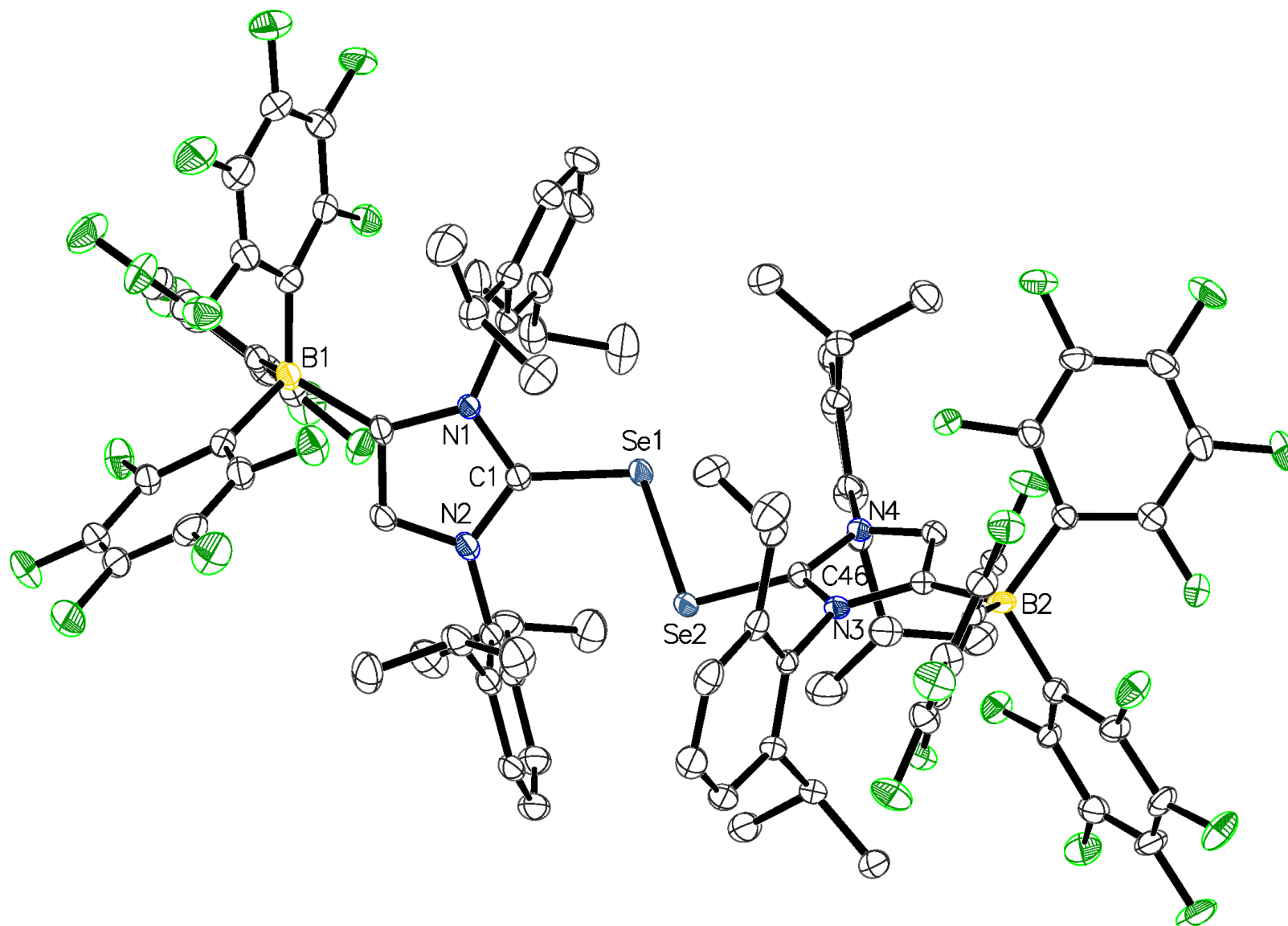


Figure S10. Molecular structure of 14-*n*-hexane-PhCl with thermal displacement parameters drawn at 50% probability; hydrogen atoms, one co-crystallized chlorobenzene and one *n*-hexane molecule are omitted for clarity.

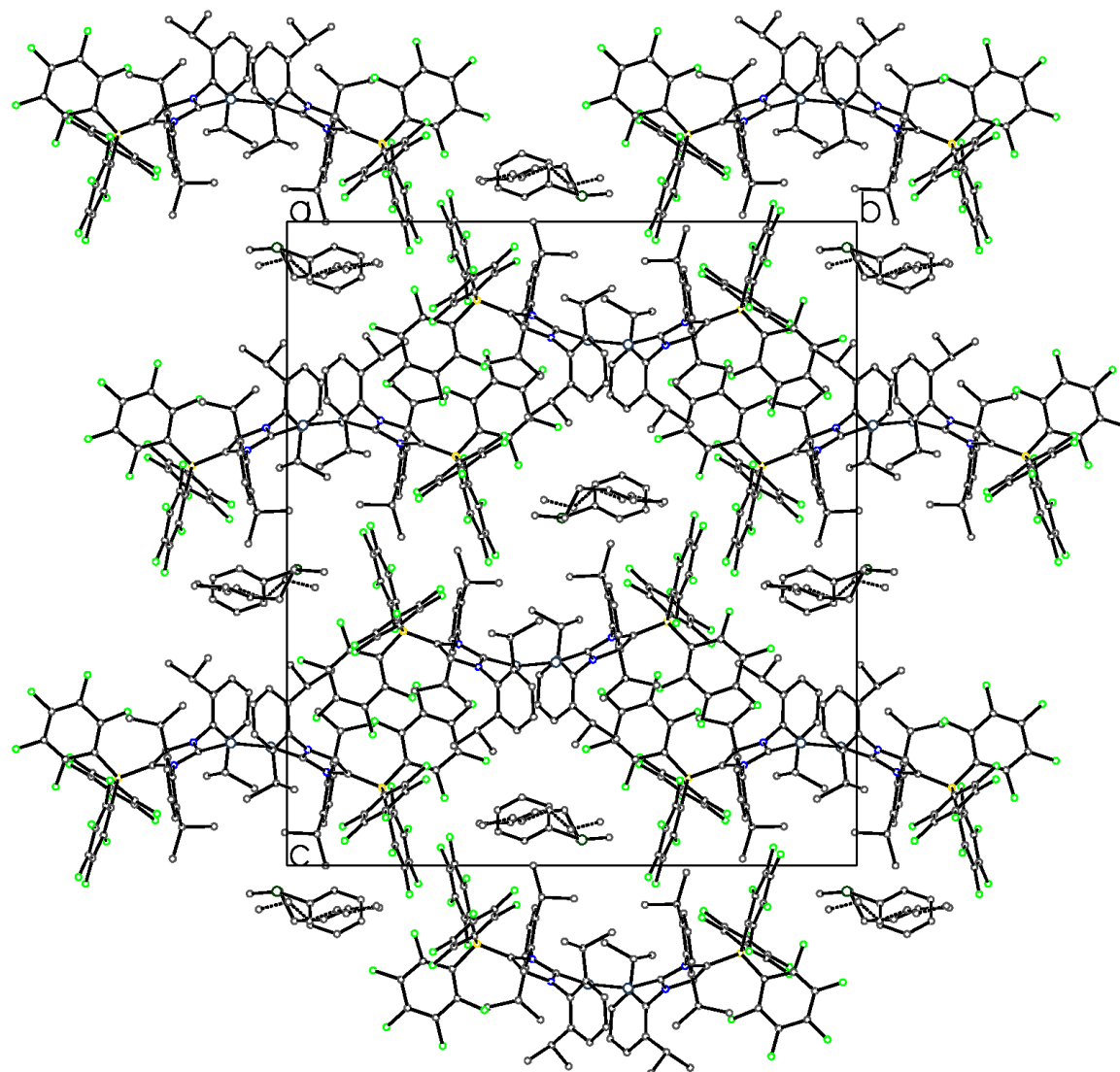


Figure S11. Packing diagram of **14-*n*-hexane-PhCl**. The view is along the *a* axis.

S1.11 (WCA-IDipp)₂Se₂ (14')**Table S 11.** Crystallographic data for compound **14'**.

Compound	14'	
Identification code	2013330	
Empirical formula	C ₉₀ H ₇₀ B ₂ F ₃₀ N ₄ Se ₂	
Formula weight	1957.04	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at home/near, HyPix (ω scan)	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.08186(4) Å	α = 101.7487(2)°
	b = 13.56275(5) Å	β = 108.1065(3)°
	c = 15.67500(4) Å	γ = 95.1486(3)°
Volume	2162.535(12) Å ³	
Z	1	
Density (calculated)	1.503 Mg/m ³	
Absorption coefficient	2.074 mm ⁻¹	
F(000)	986	
Crystal habitus	irregular (pink)	
Crystal size	0.243 x 0.198 x 0.138 mm ³	
Theta range for data collection	3.059 to 77.484°	
Index ranges	-14 ≤ h ≤ 13, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	
Reflections collected	90726	
Independent reflections	9039 [R(int) = 0.0188]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.336	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9039 / 132 / 672	
Goodness-of-fit on F ²	1.030	
Final R indices [I > 2σ(I)]	R1 = 0.0352, wR2 = 0.0861	
R indices (all data)	R1 = 0.0355, wR2 = 0.0862	
Largest diff. peak and hole	0.729 and -0.572 e.Å ⁻³	
Crystallisation Details:	A saturated solution of 13 in toluene was layered with <i>n</i> hexane at ambient temperatures.	
Solution	SHELXT-2014/5 (Sheldrick 2015)	
Refinement	SHELXL-2018/3 (Sheldrick 2018)	
Interface	OLEX2 v1.2	
Measurement and Refinement Details:	One methyl group from the isopropyl group adjacent to the borate moiety is disordered and was refined over two positions. No restraints were applied. One pentafluorophenyl moiety is disordered and was refined over two positions. One ISOR restraint was applied. Residual electron density was removed with SQUEEZE. The used solvent for crystallization was toluene and there were several positions possible for the disordered molecule. Refinement with disorder models were insufficient due to the many positions, hence the removal of the electron density.	

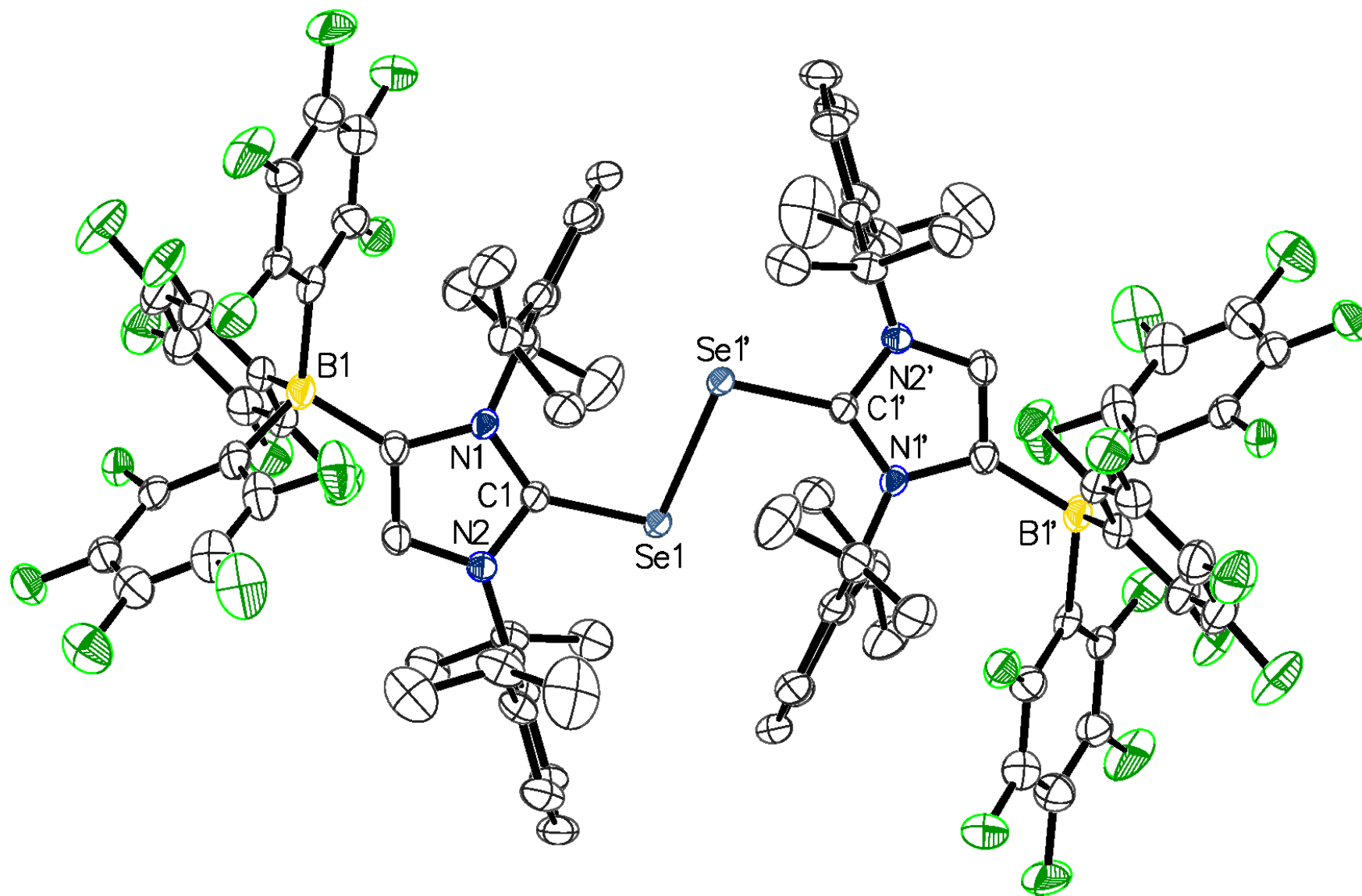


Figure S12. Molecular structure of **14'** with thermal displacement parameters drawn at 50% probability; hydrogen atoms are omitted for clarity.

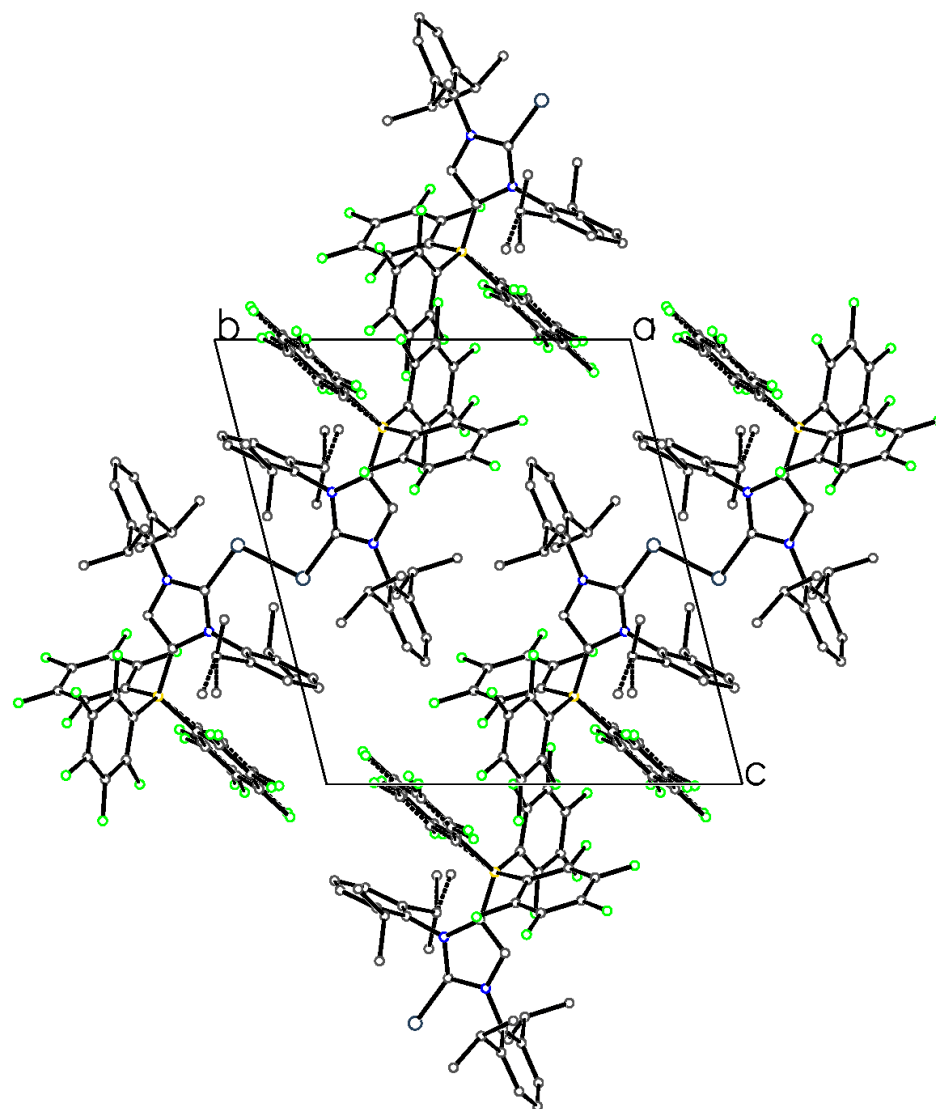


Figure S13. Packing diagram of 14'. The view is along the a axis.

S2 ^1H , ^{11}B , ^{13}C , ^{19}F and ^{77}Se NMR Spectra

S2.1 $(\text{THF})_3\text{Li}[(\text{IDipp})=\text{S}]$ (**4**)

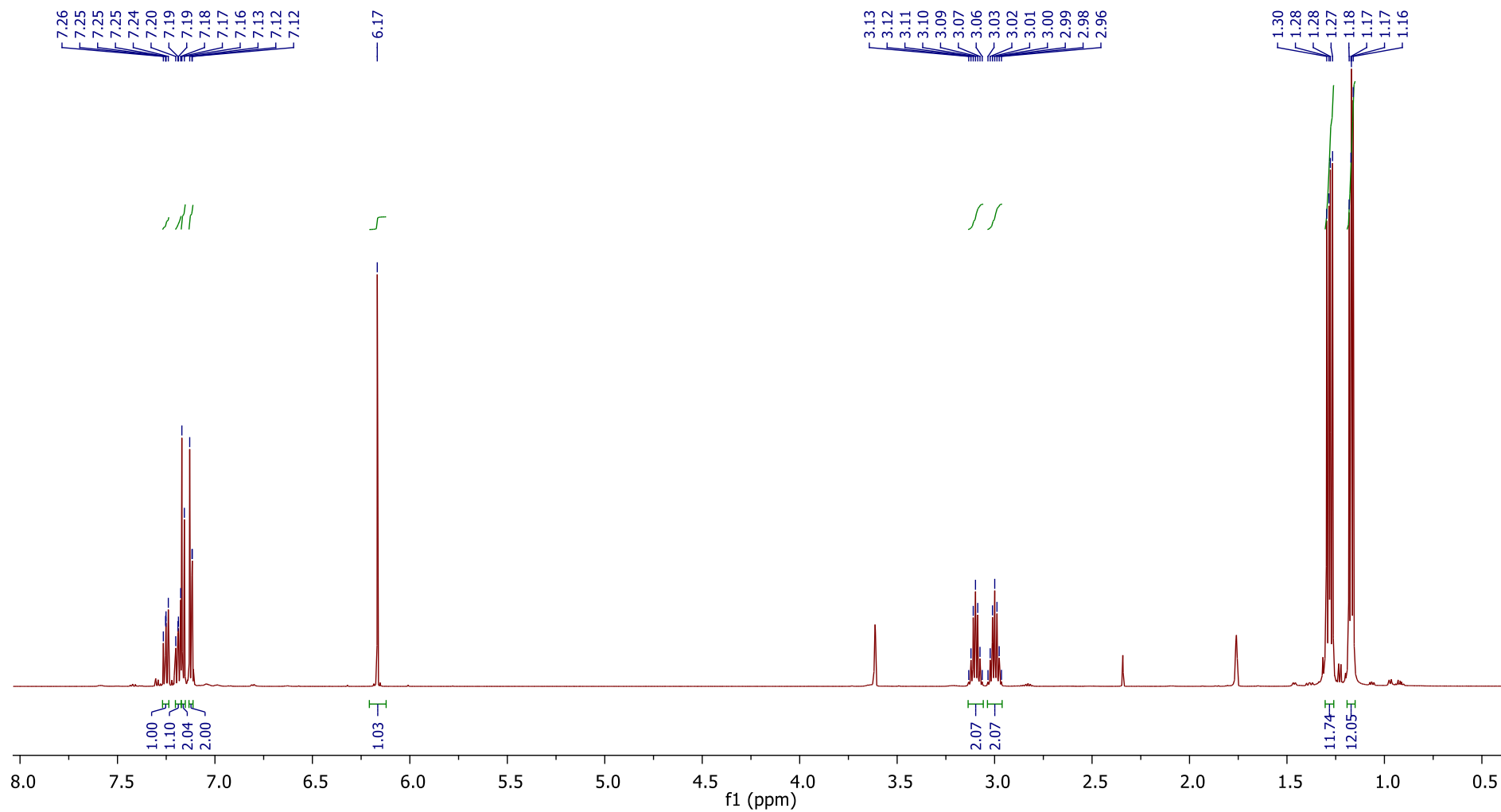


Figure S14. ^1H NMR spectrum (600 MHz, $\text{THF}-d_8$, 298K) of $(\text{THF})_3\text{Li}[(\text{IDipp})=\text{S}]$ (**4**).

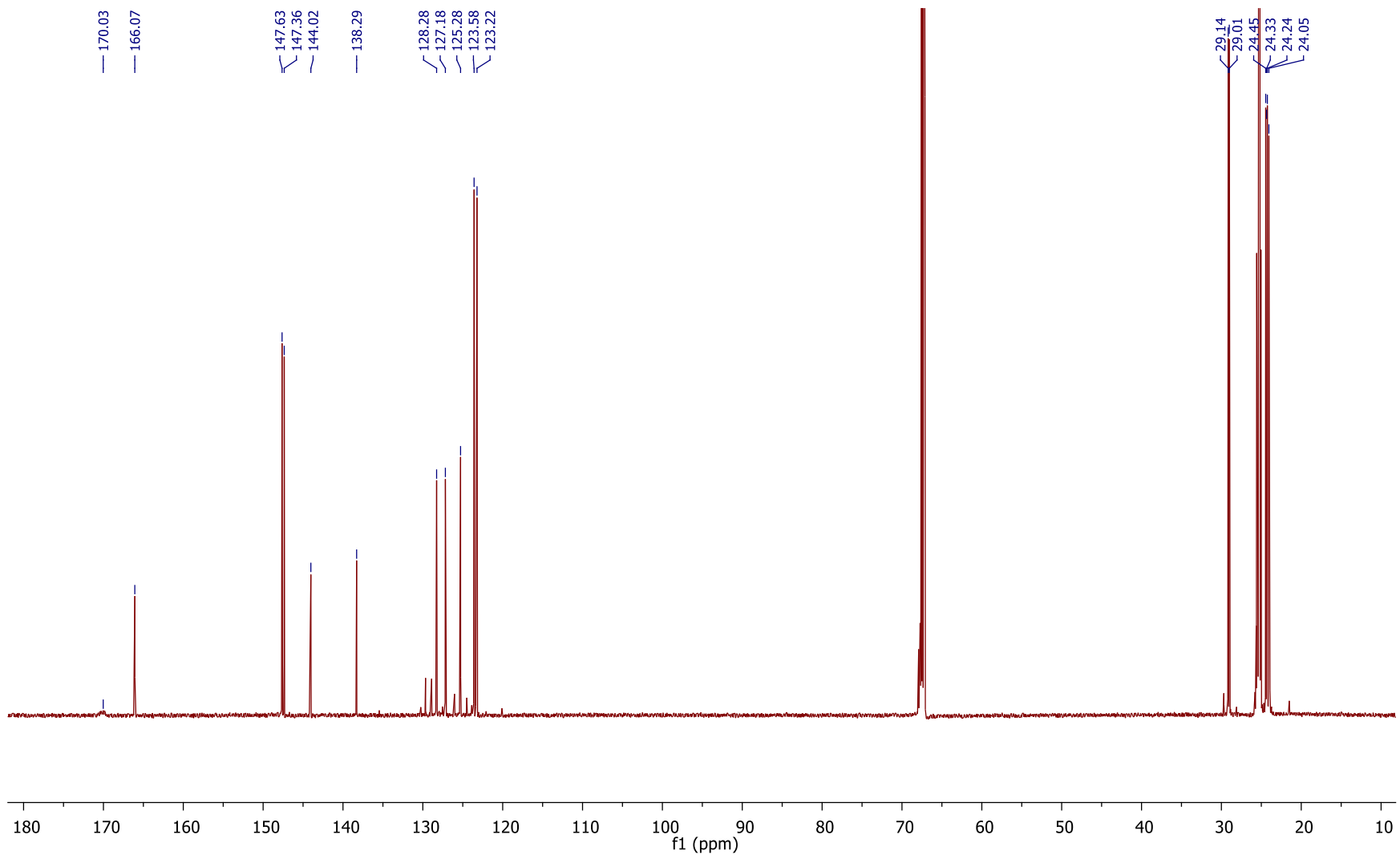


Figure S15. ^{13}C NMR spectrum (152 MHz, $\text{THF-}d_8$, 298K) of $(\text{THF})_3\text{Li}[(\text{IDipp})=\text{S}]$ (**4**). Note: There are two signals in the ^{13}C NMR spectrum, which give a cross peak in the ^1H - ^{13}C -HMBC spectrum to the backbone proton signal at 6.17 ppm in the ^1H NMR spectrum. One is the signal at 170 ppm and the other one is the signal at 166 ppm. These two signals correspond to either the CLi or CS. The CLi carbon atom has carbene character, and the signal should have lower intensity than the corresponding CS signal. Therefore, the signal at 170 ppm was assigned to CLi and the signal at 166 ppm was assigned to CS.

S2.2 [(WCA-IDipp)O]Li·3THF (6·3THF)

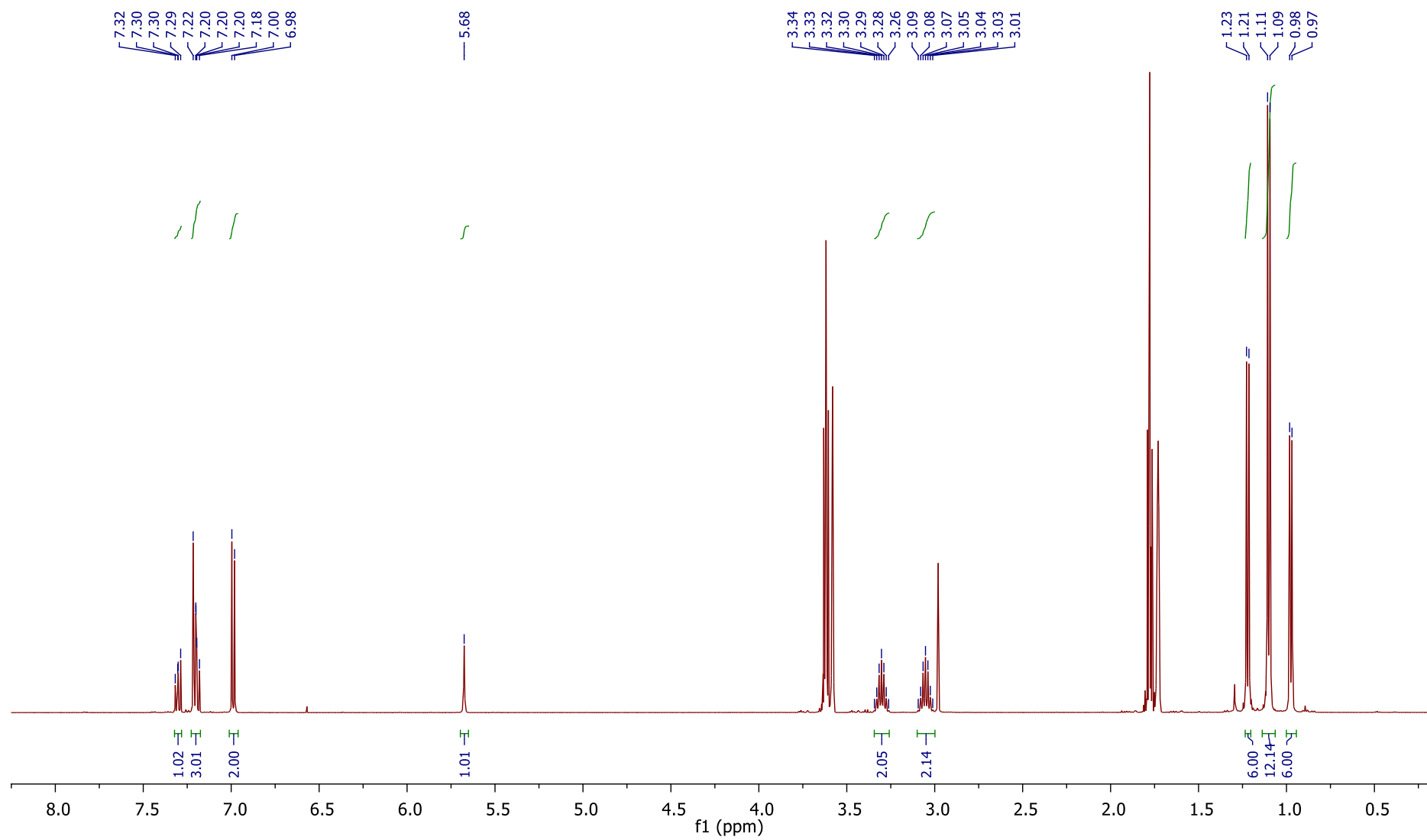


Figure S16. ^1H NMR spectrum (500 MHz, $\text{THF-}d_8$, 298K) of [(WCA-IDipp)O]Li·3THF (6·3THF).

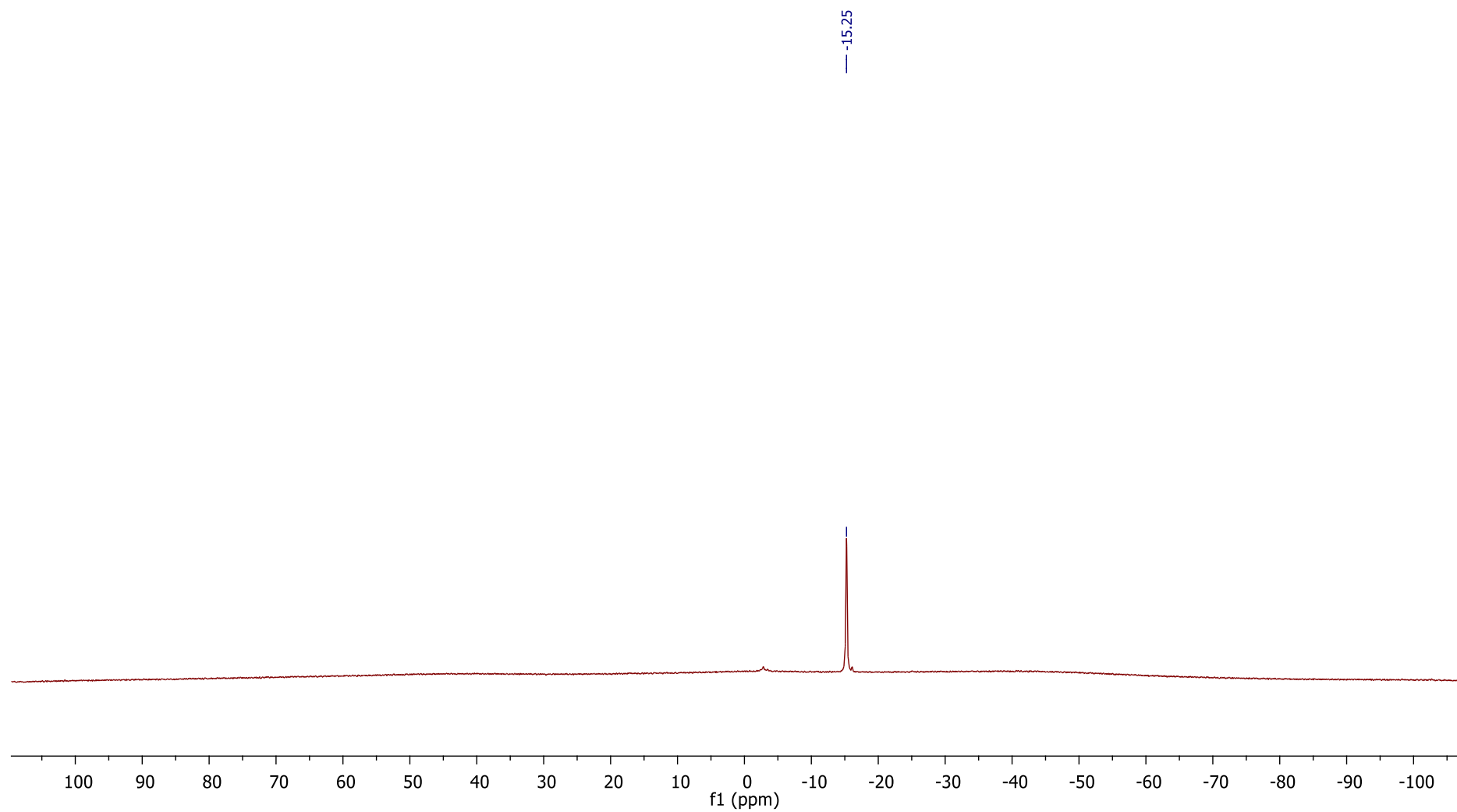


Figure S 17. ^{11}B NMR spectrum (96 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{O}]\text{Li}\cdot 3\text{THF}$ (**6** $\cdot 3\text{THF}$).

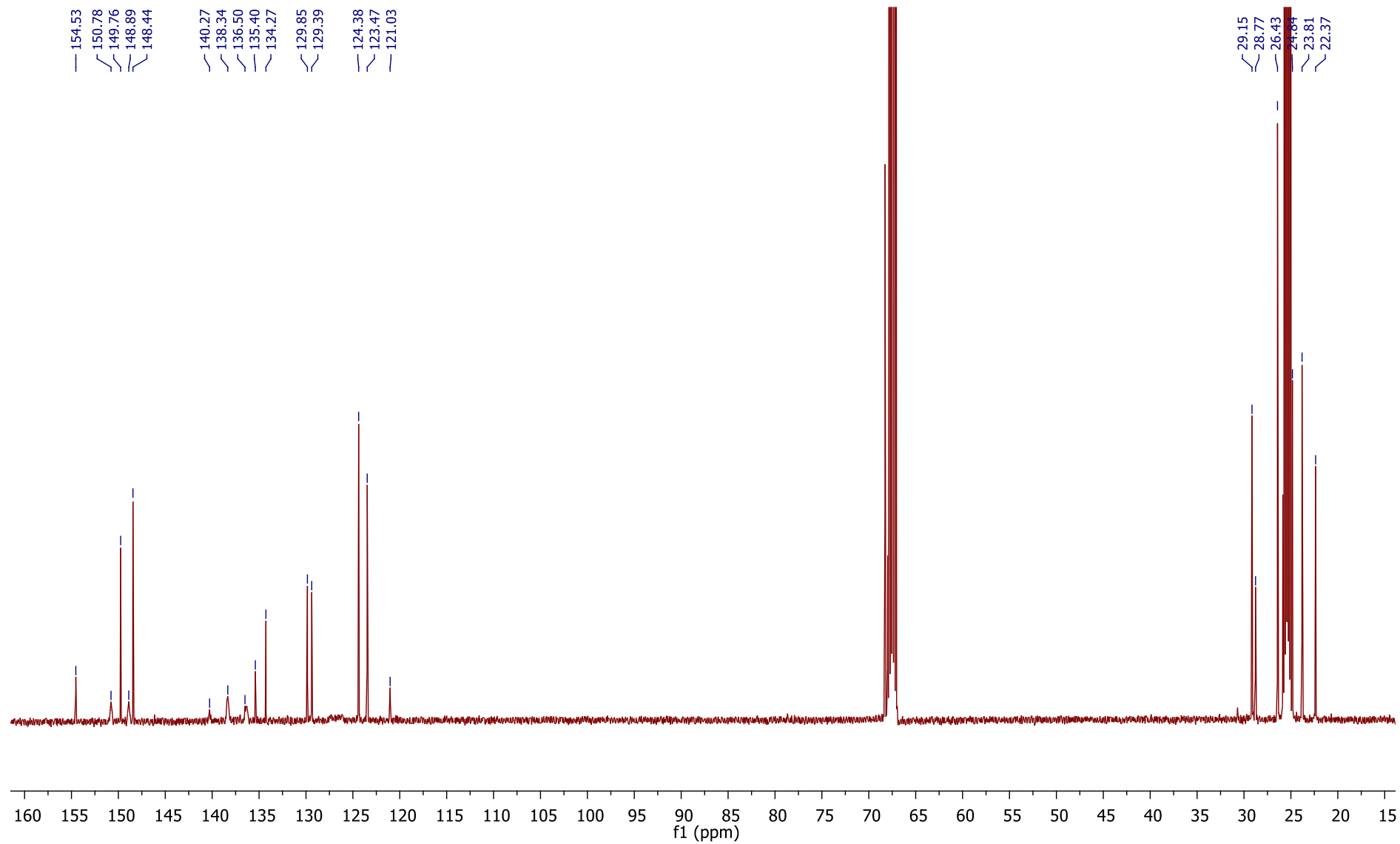


Figure S 18. ^{13}C NMR spectrum (126 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{O}]\text{Li}\cdot 3\text{THF}$ (**6** $\cdot 3\text{THF}$).

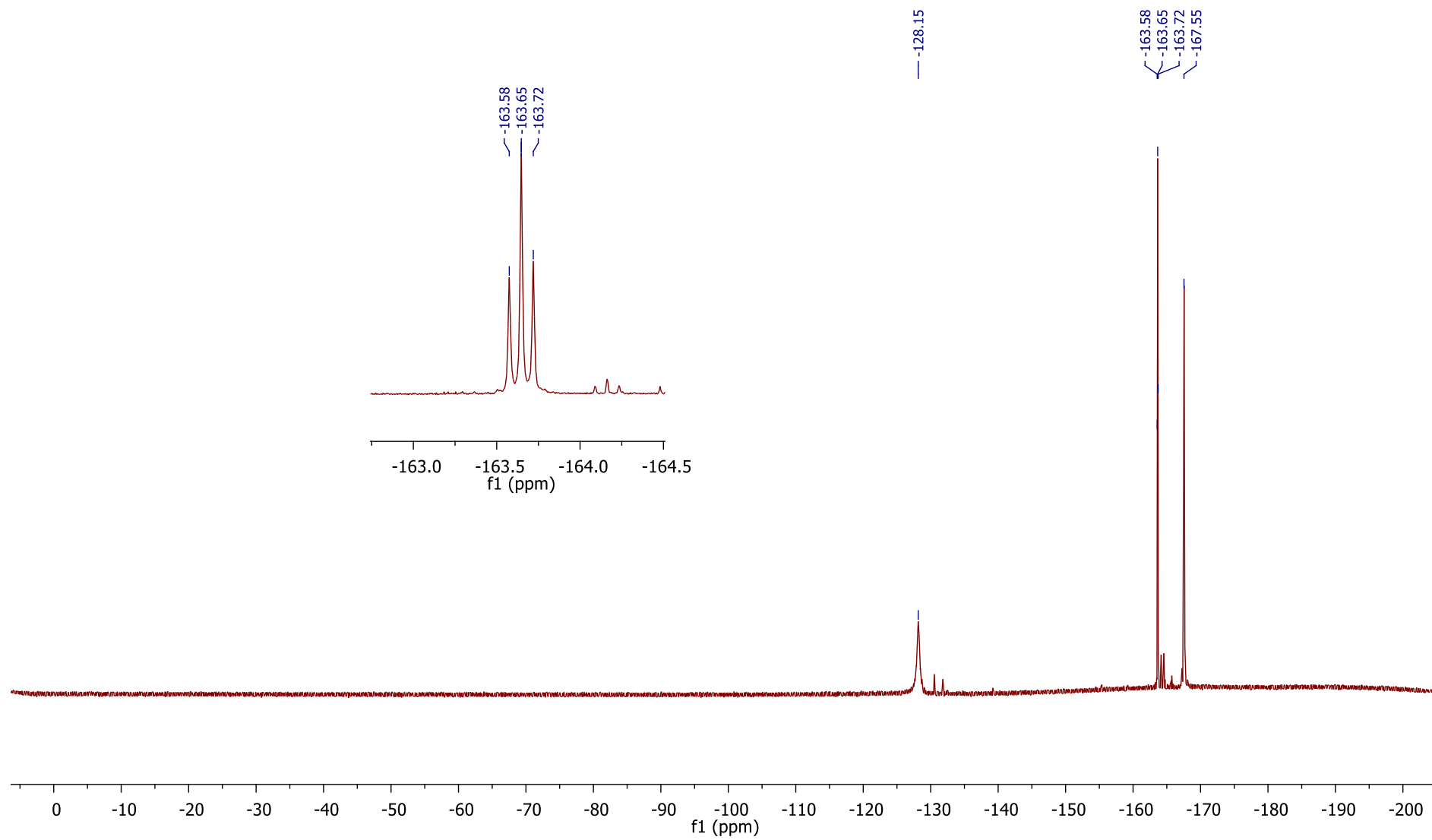


Figure S19. ^{19}F NMR spectrum (283 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{O}]\text{Li}\cdot 3\text{THF}$ (**6** \cdot 3THF).

S2.3 [(WCA-IDipp)S]Li·5THF (7·5THF)

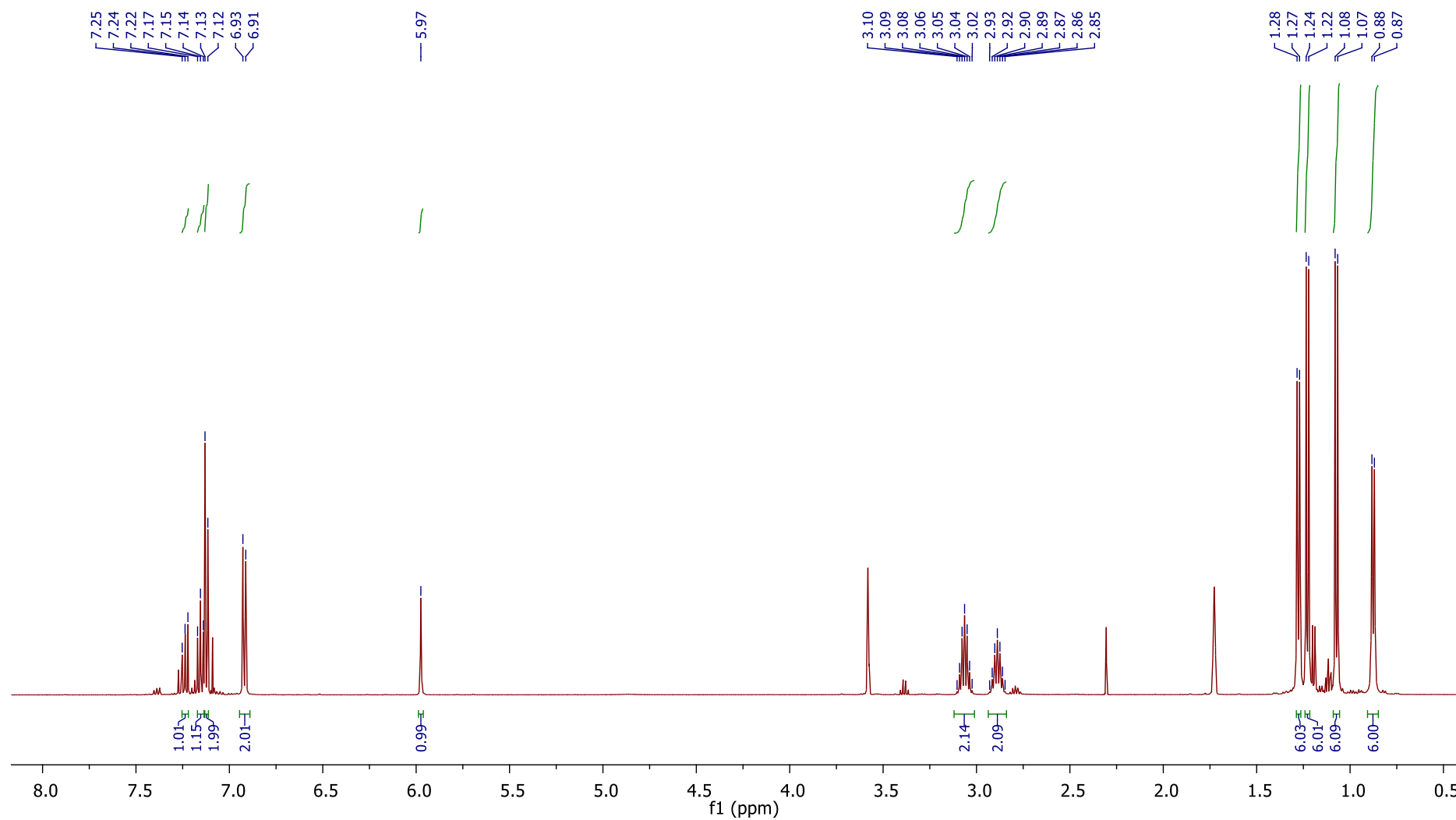


Figure S 20. ^1H NMR spectrum (500 MHz, THF- d_8 , 298K) of [(WCA-IDipp)S]Li·5THF (7·5THF).

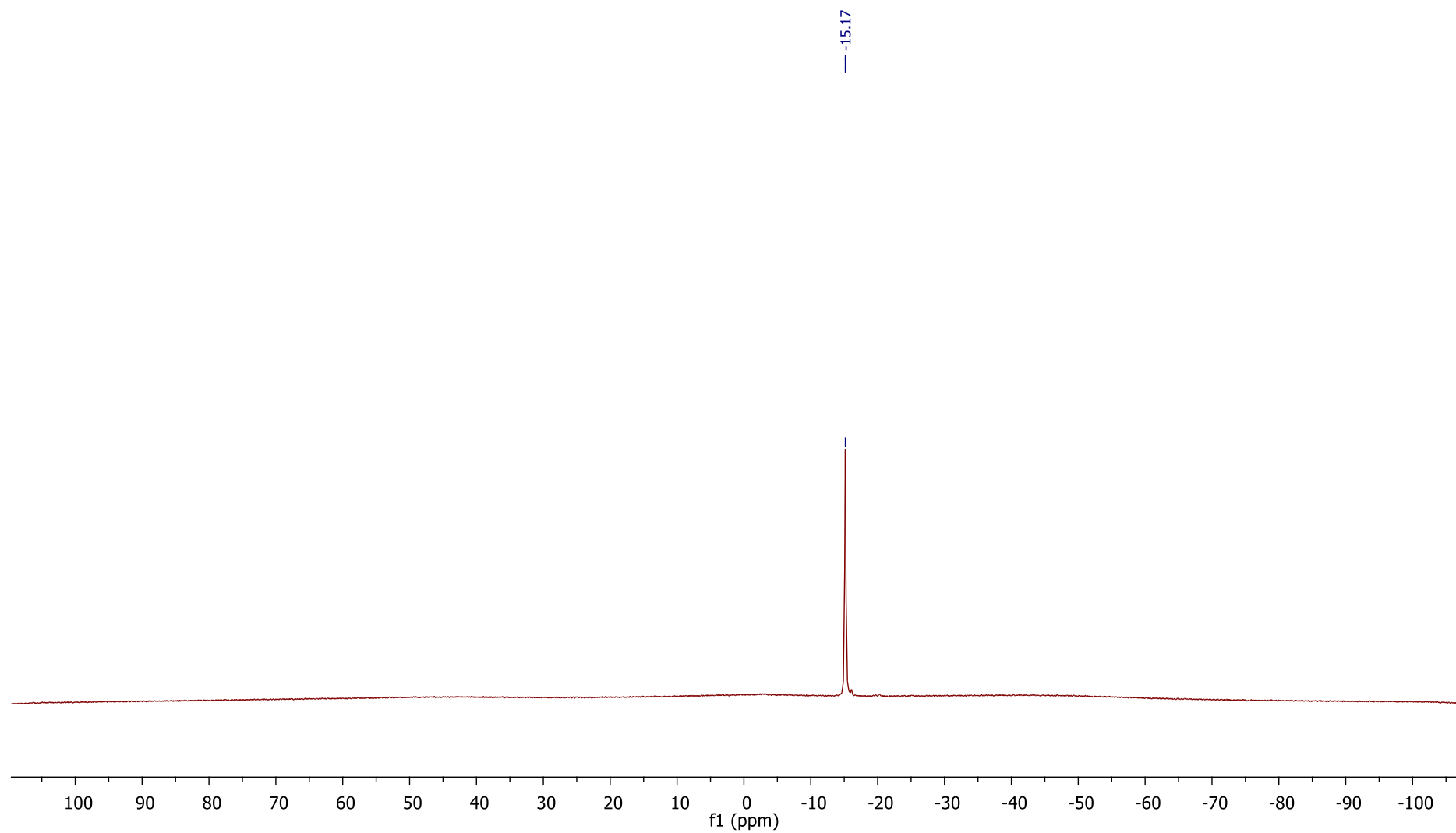


Figure S 21. ^{11}B NMR spectrum (96 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{S}]\text{Li}\cdot 5\text{THF}$ (**7** $\cdot 5\text{THF}$).

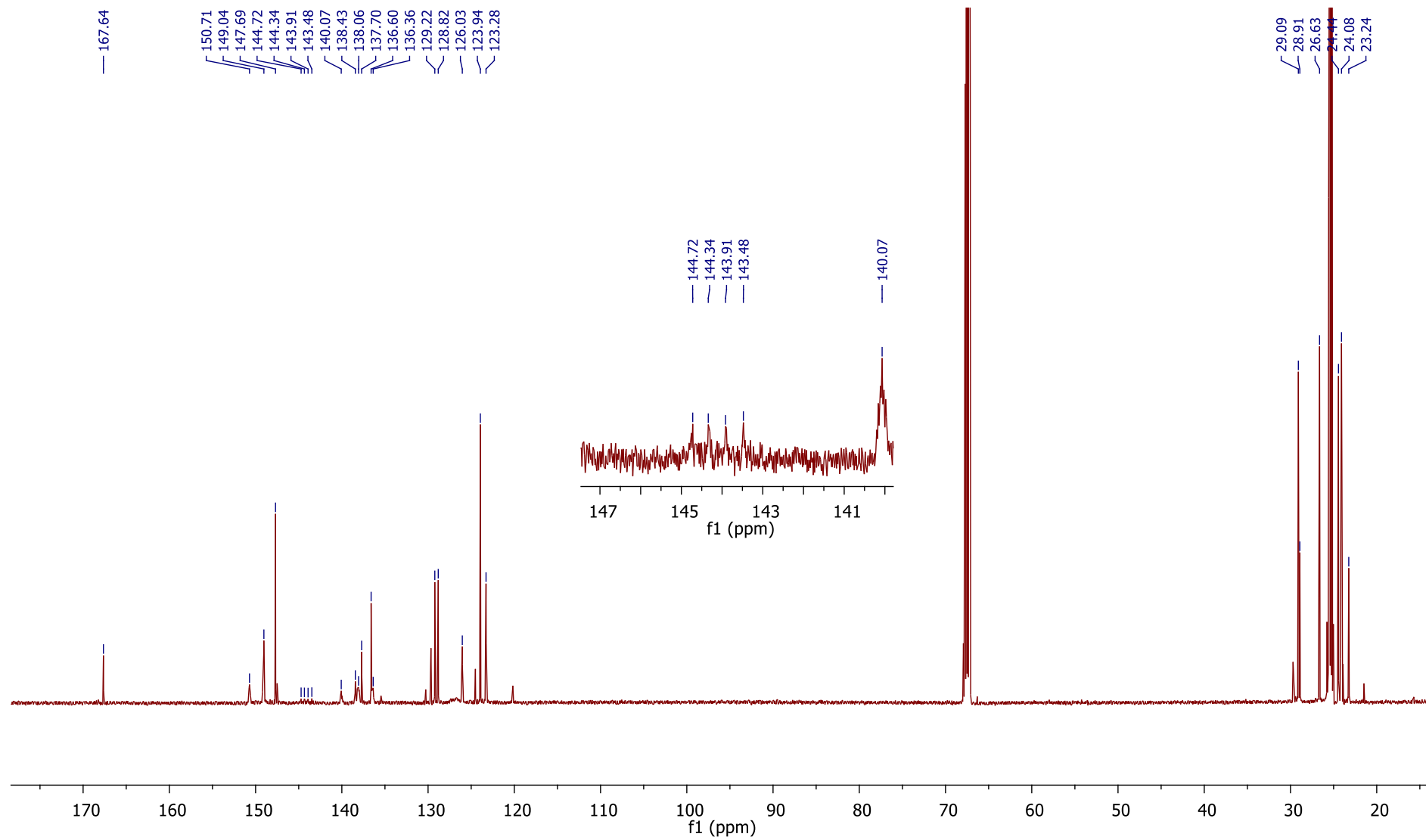


Figure S 22. ^{13}C NMR spectrum (151 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{S}]\text{Li-5THF}$ (7:5THF).

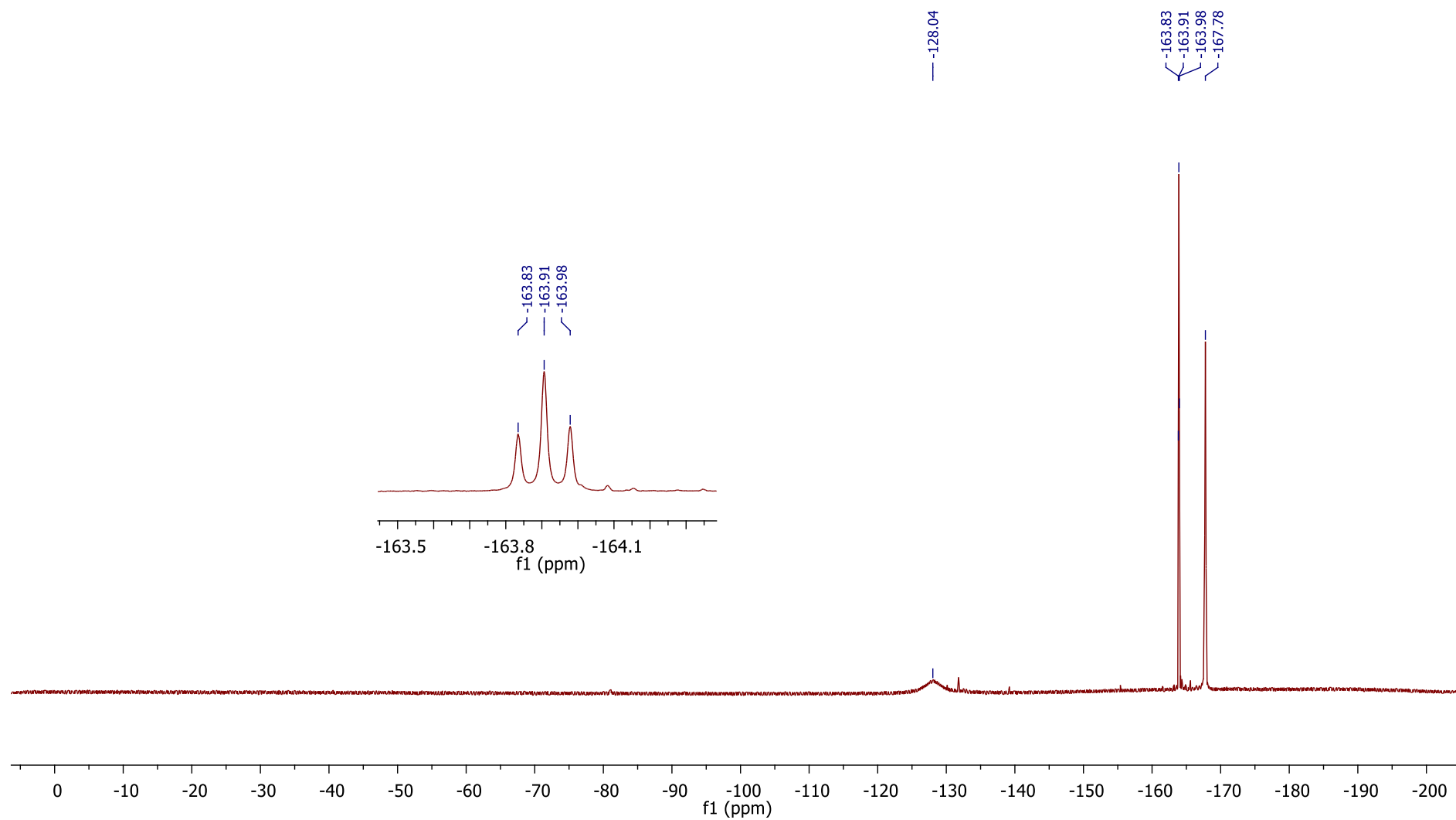


Figure S 23. ^{19}F NMR spectrum (283 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{S}]\text{Li}\cdot 5\text{THF}$ (7·5THF).

S2.4 [(WCA-IDipp)Se]Li·3Et₂O (8·3Et₂O)

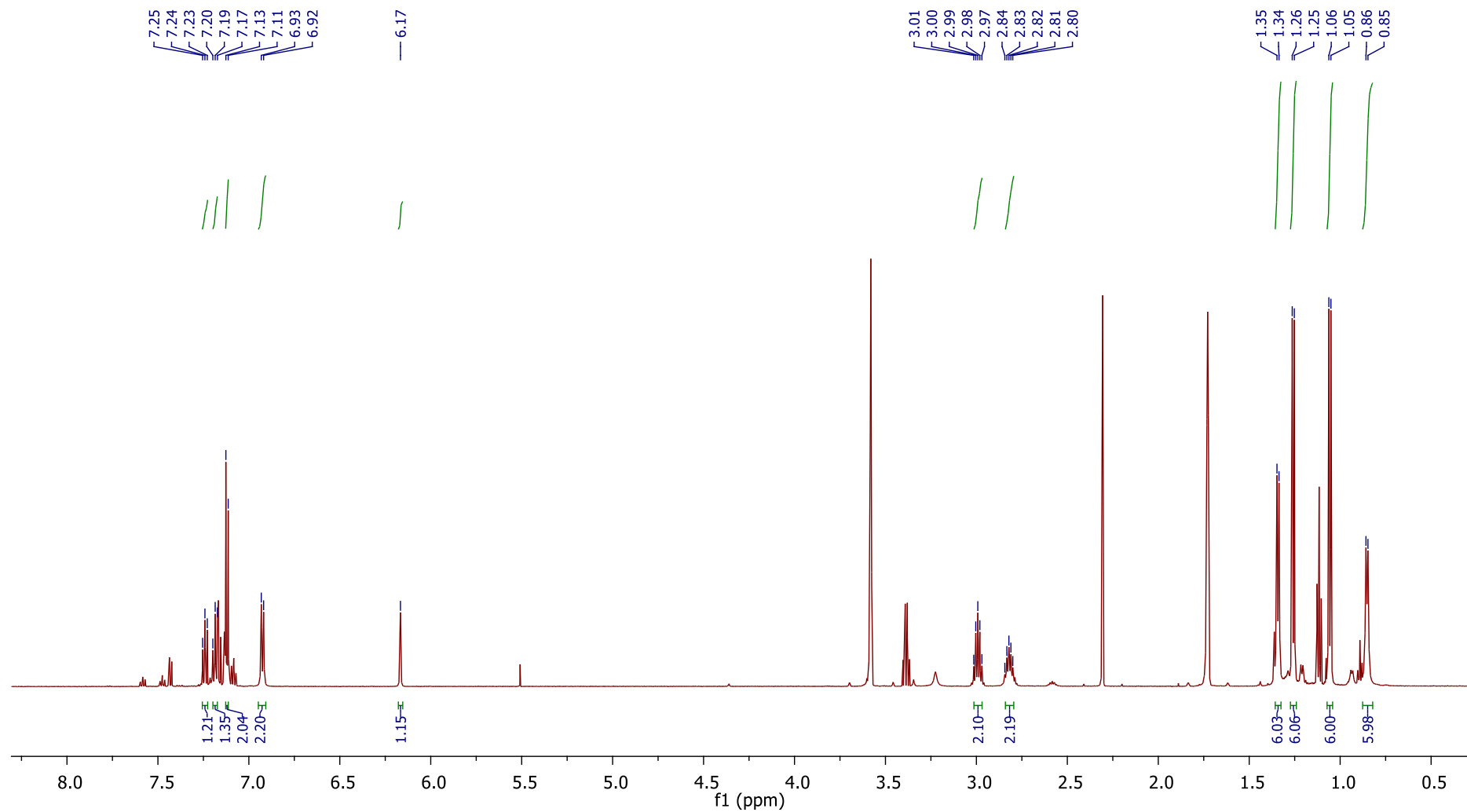


Figure S 24. ¹H NMR spectrum (600 MHz, THF-*d*₈, 298K) of [(WCA-IDipp)Se]Li·3Et₂O (8·3Et₂O).

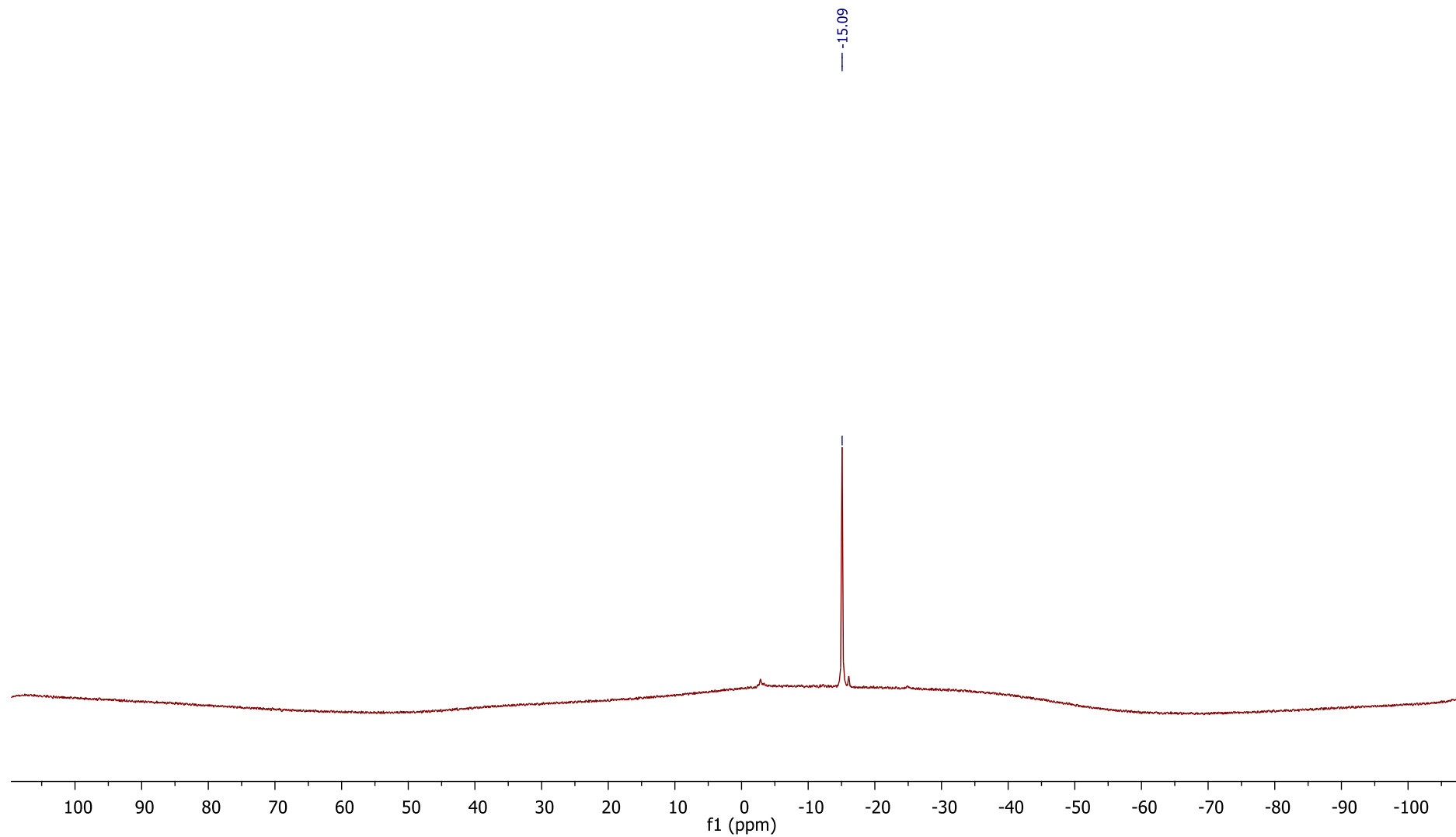


Figure S 25. ^{11}B NMR spectrum (96 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Se}]\text{Li}\cdot 3\text{Et}_2\text{O}$ (**8** $\cdot 3\text{Et}_2\text{O}$).

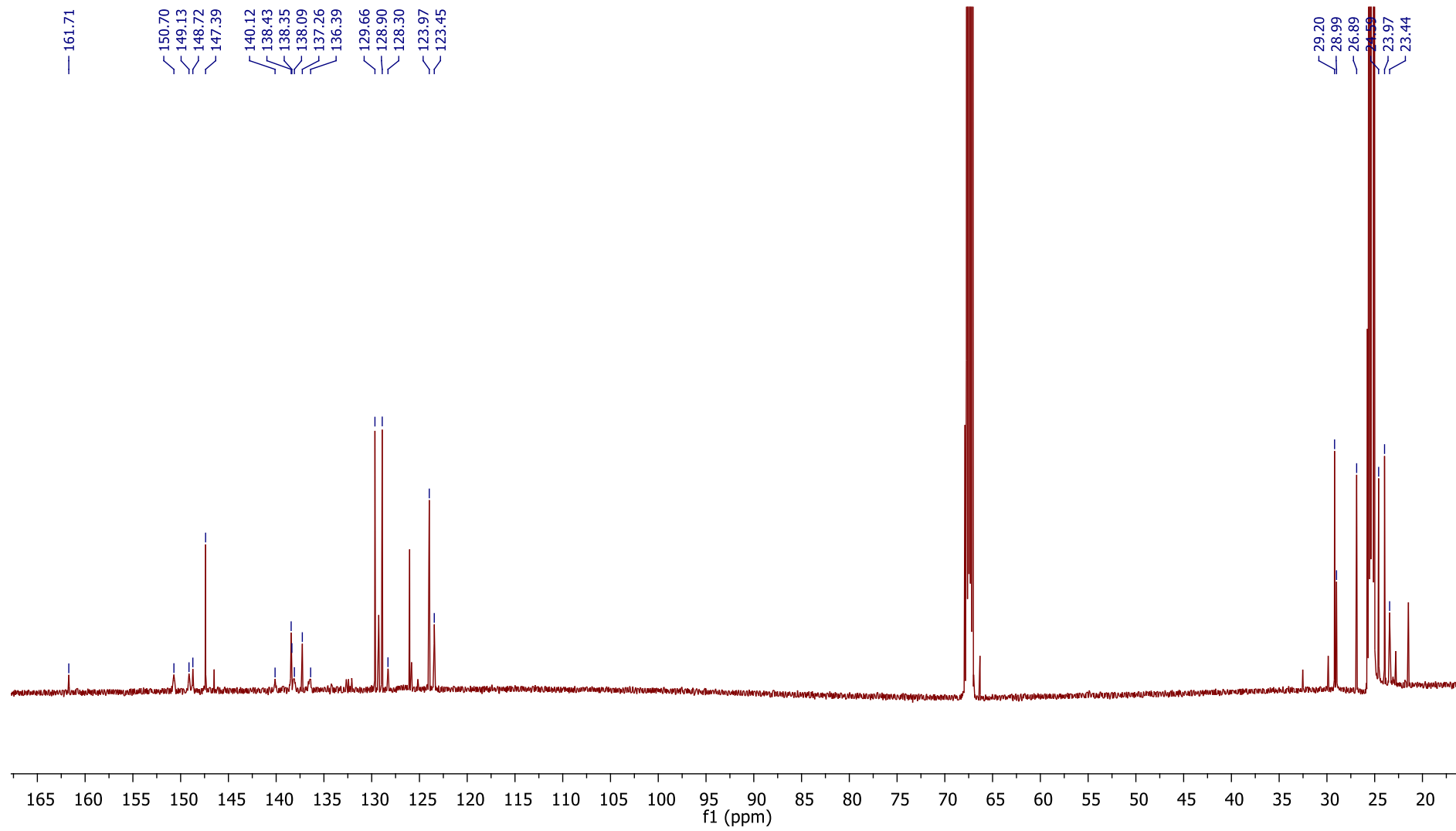


Figure S 26. ^{13}C NMR spectrum (151 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Se}]\text{Li}\cdot 3\text{Et}_2\text{O}$ (**8** $\cdot 3\text{Et}_2\text{O}$).

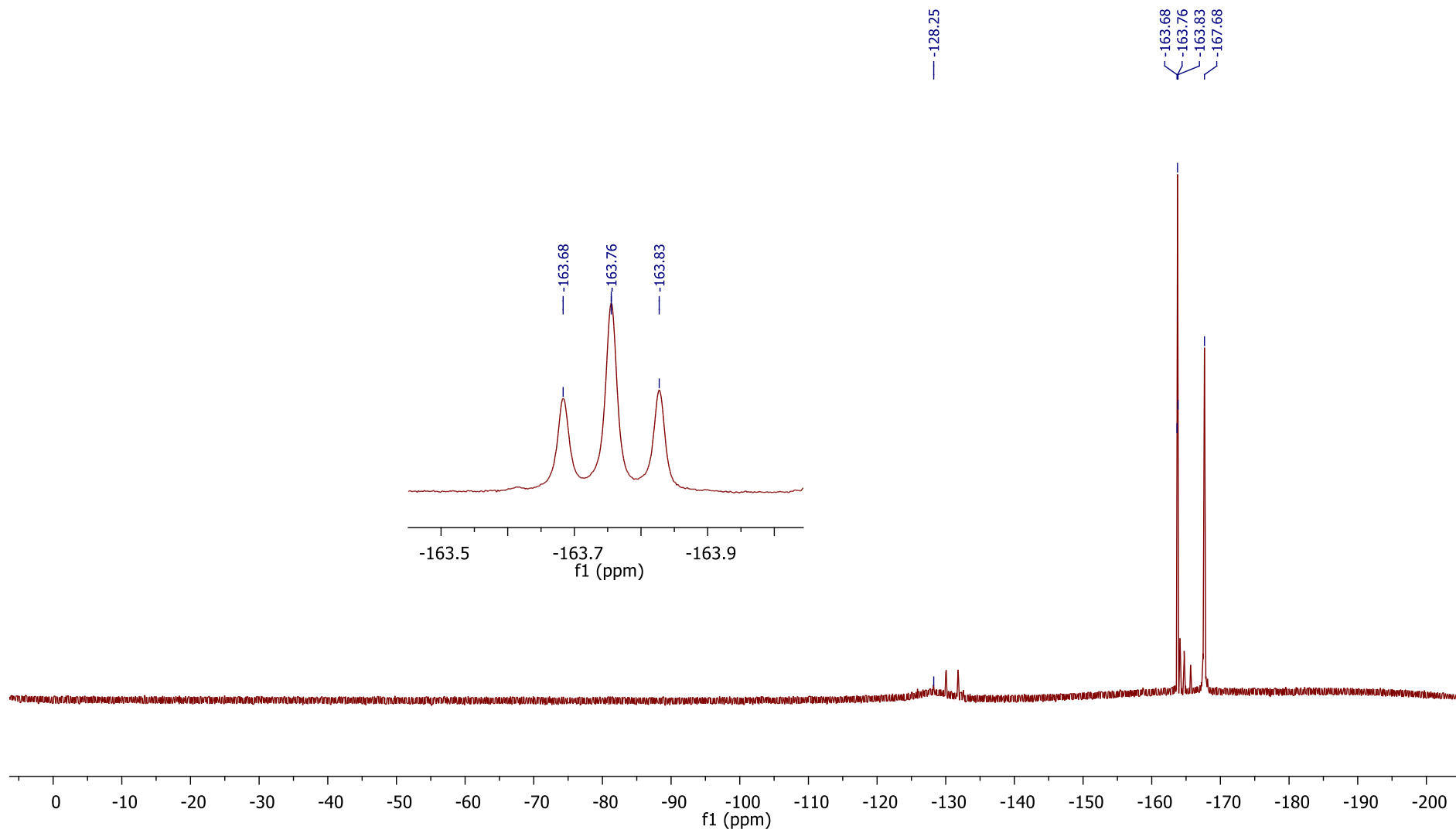


Figure S 27. ^{19}F NMR spectrum (283 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Se}]\text{Li}\cdot 3\text{Et}_2\text{O}$ (**8** $\cdot 3\text{Et}_2\text{O}$).

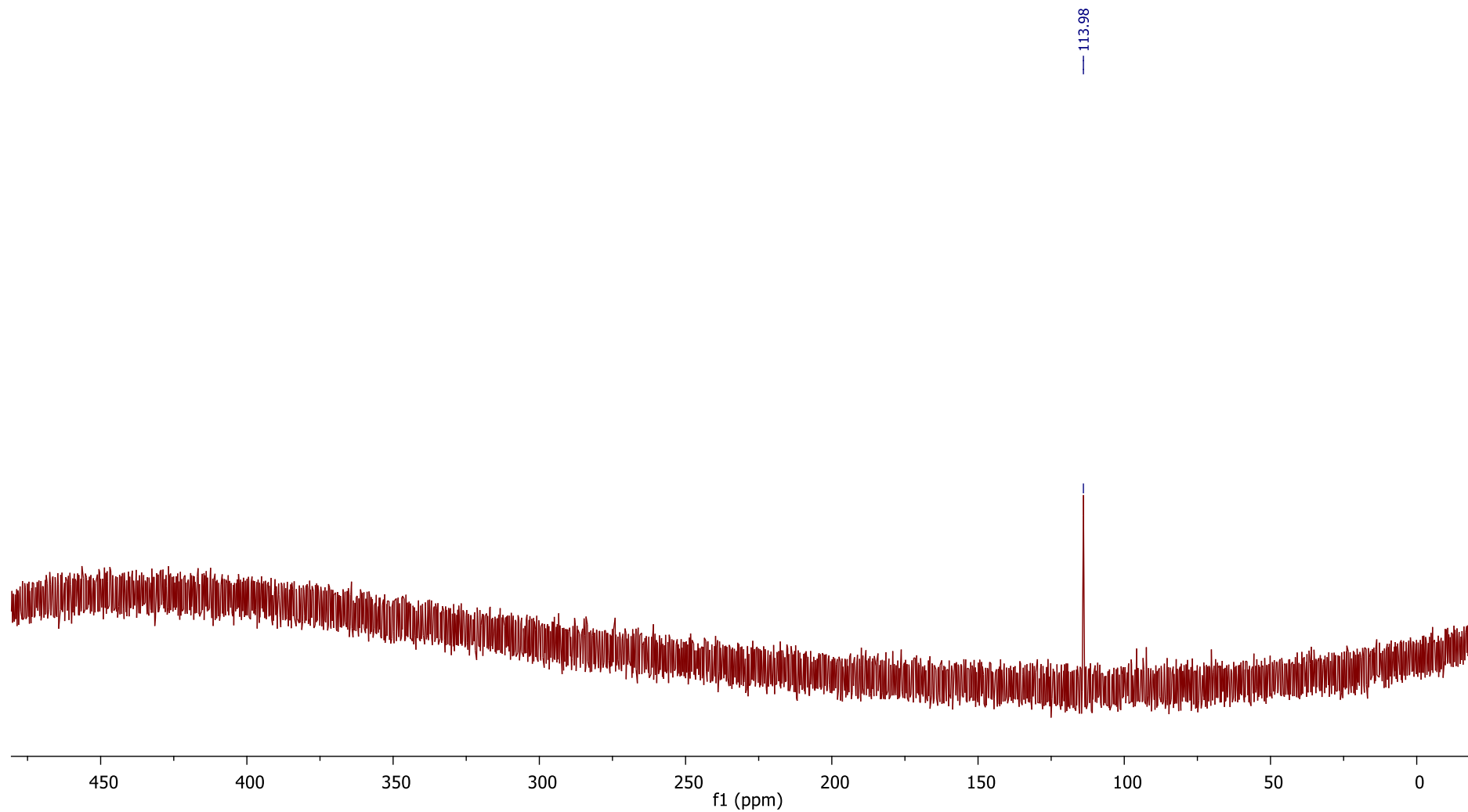


Figure S 28. ^{77}Se NMR spectrum (76 MHz, THF- d_8 , 298 K) of $[(\text{WCA-IDipp})\text{Se}]\text{Li}\cdot 3\text{Et}_2\text{O}$ (**8** $\cdot 3\text{Et}_2\text{O}$).

S2.5 [(WCA-IDipp)Te]Li·2Et₂O·2THF (9·2Et₂O·2THF)

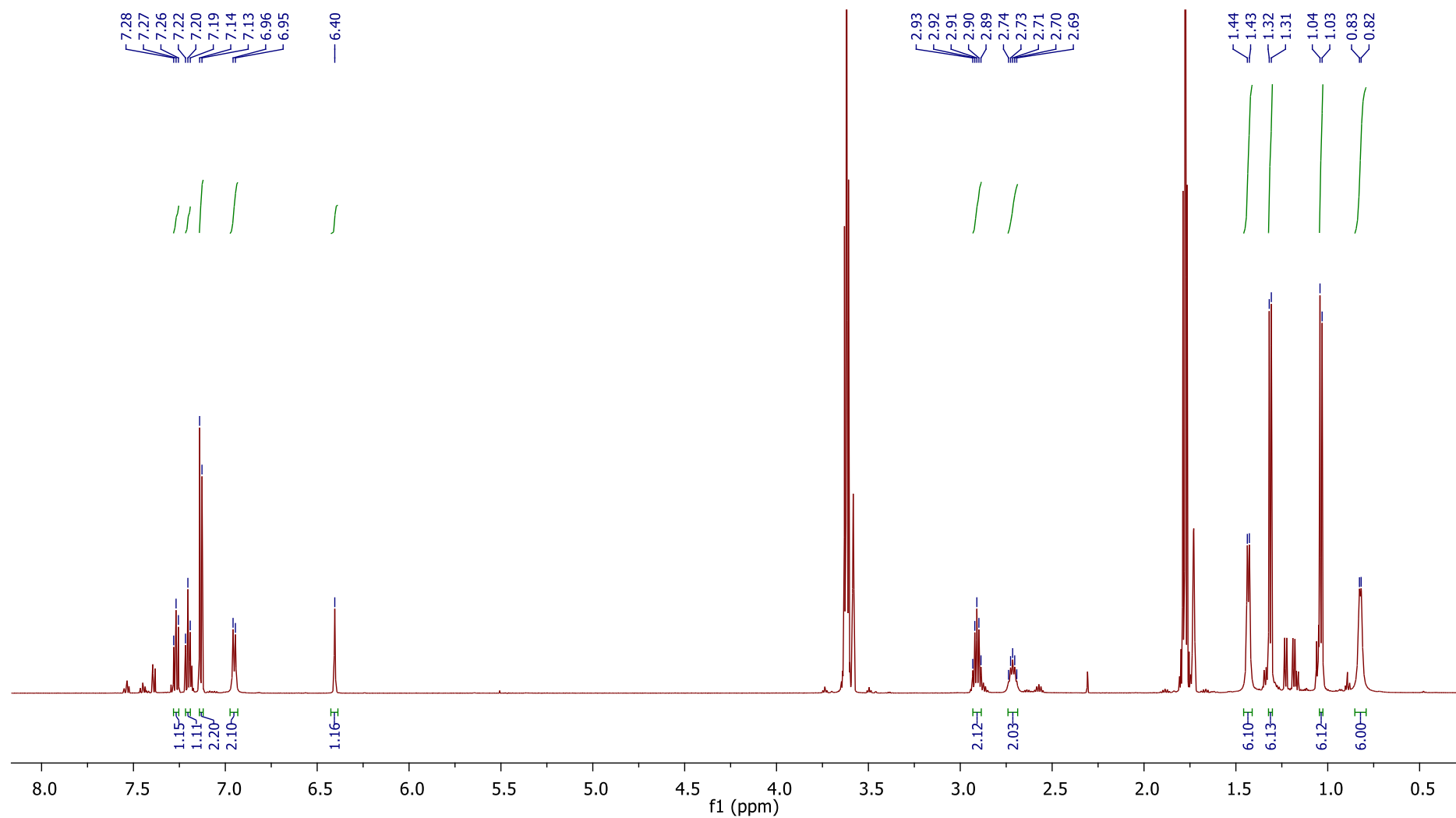


Figure S 29. ¹H NMR spectrum (600 MHz, THF-*d*₈, 298K) of [(WCA-IDipp)Te]Li·2Et₂O·2THF (9·2Et₂O·2THF)

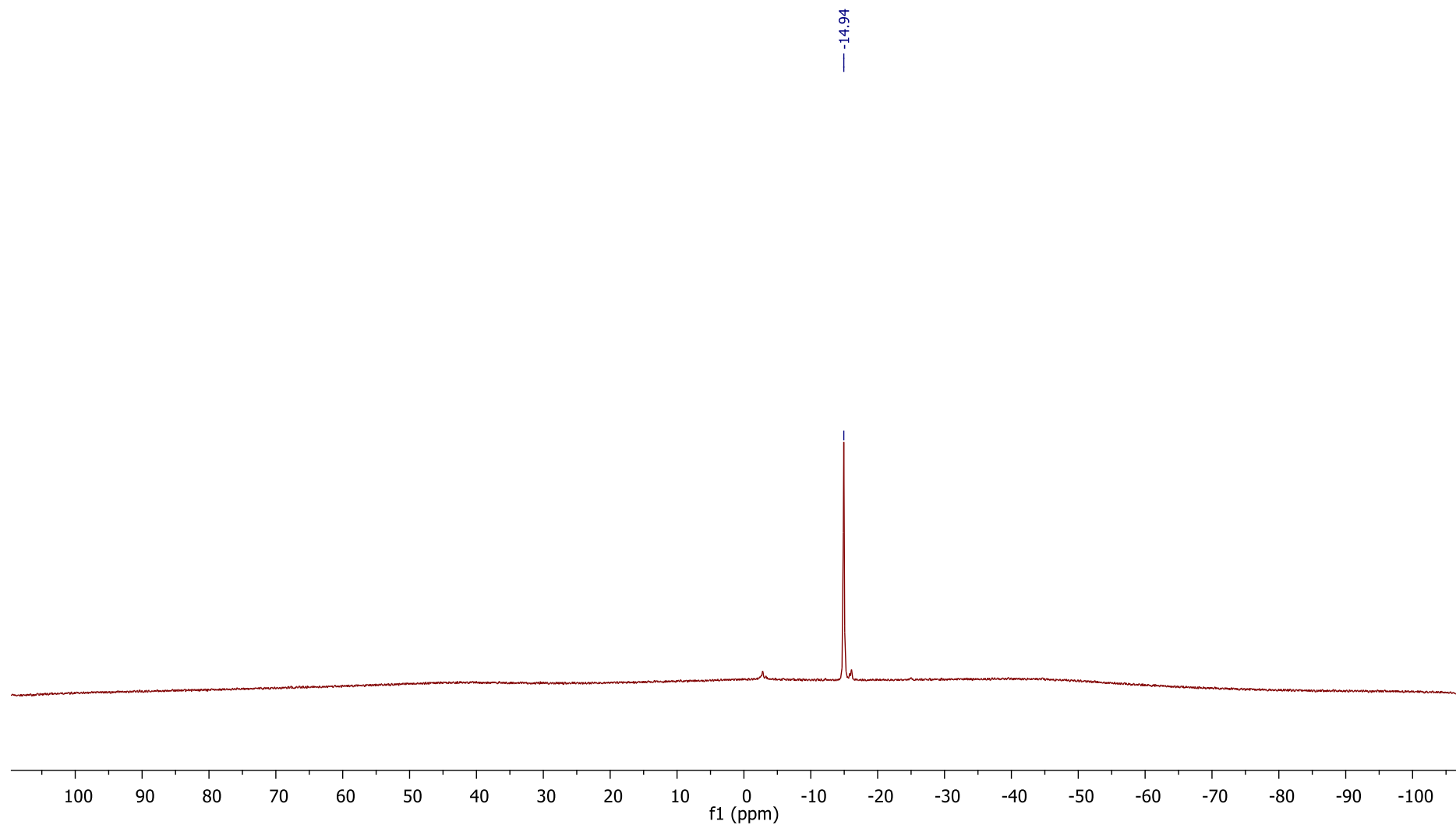


Figure S 30. ^{11}B NMR spectrum (96 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Te}]\text{Li}\cdot 2\text{Et}_2\text{O}\cdot 2\text{THF}$ ($9\cdot 2\text{Et}_2\text{O}\cdot 2\text{THF}$)

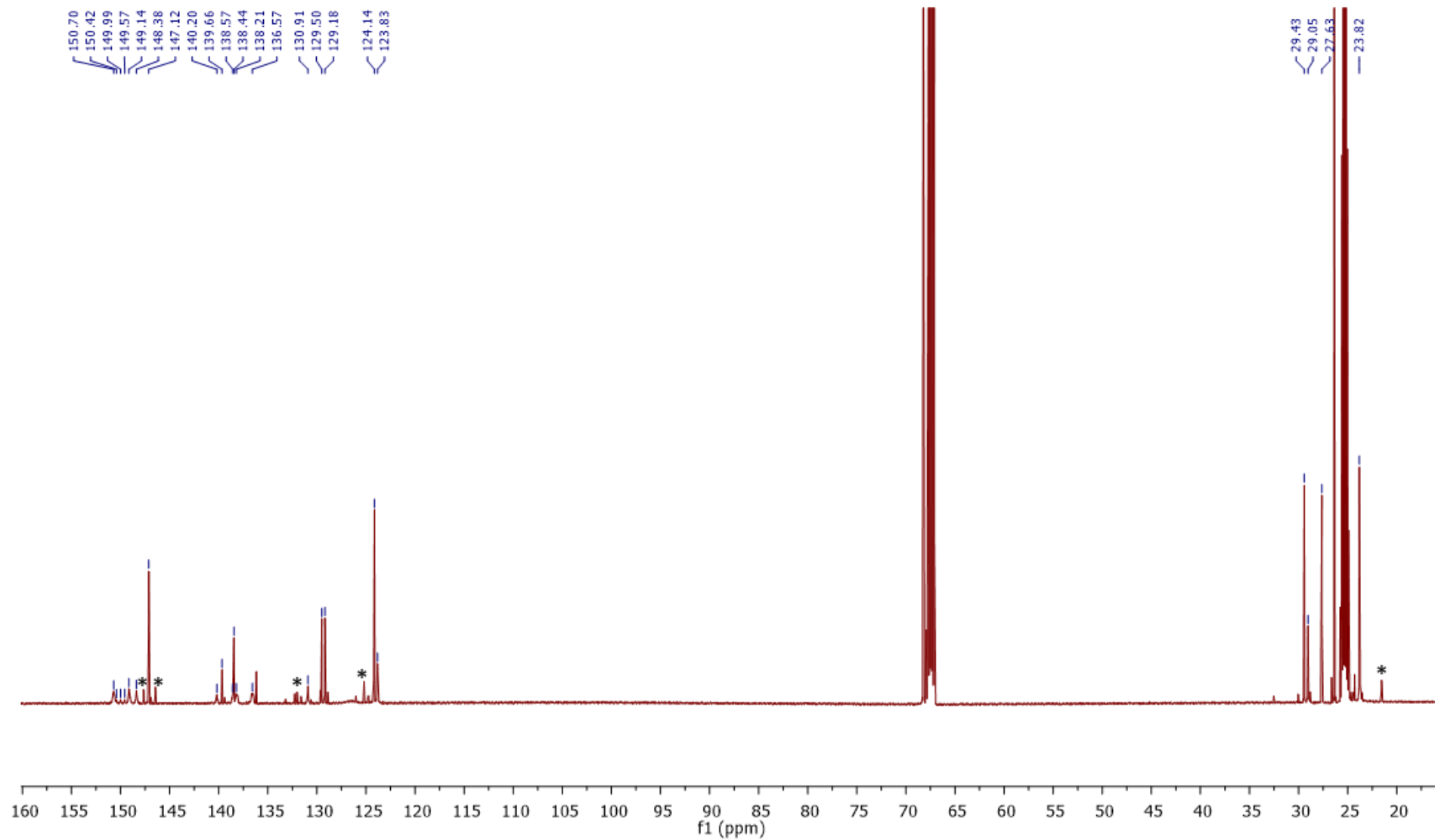


Figure S 31. ^{13}C NMR spectrum (151 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Te}]\text{Li}\cdot 2\text{Et}_2\text{O}\cdot 2\text{THF}$ (**9** $\cdot 2\text{Et}_2\text{O}\cdot 2\text{THF}$). Signals marked with * correspond to the decomposition product of **9**. **9** decomposes over time upon light exposure.

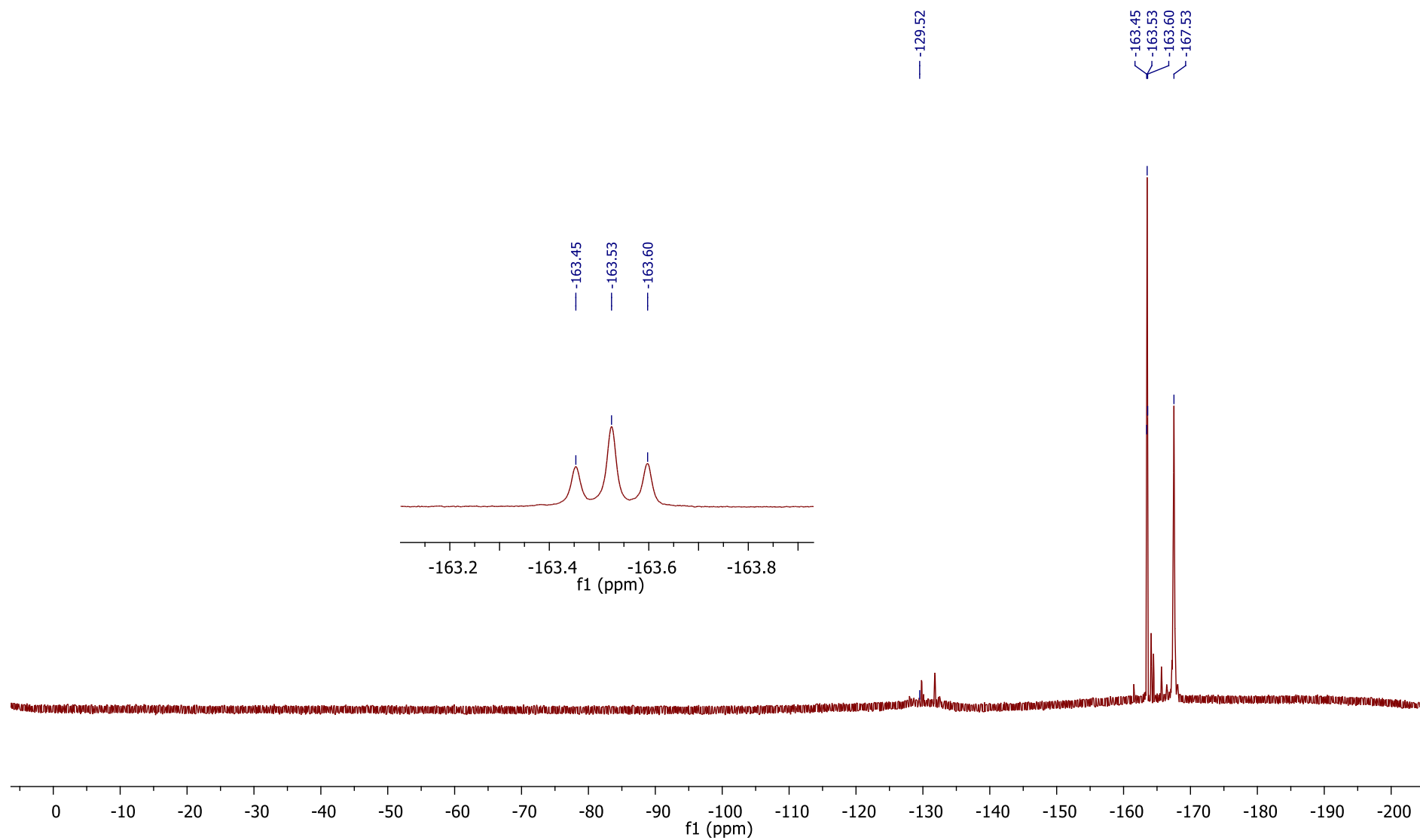


Figure S 32. ^{19}F NMR spectrum (283 MHz, $\text{THF-}d_8$, 298K) of $[(\text{WCA-IDipp})\text{Te}]\text{Li}\cdot 2\text{Et}_2\text{O}\cdot 2\text{THF}$ (9·2Et₂O·2THF)

S2.6 (WCA-IDipp)OH (**10**)

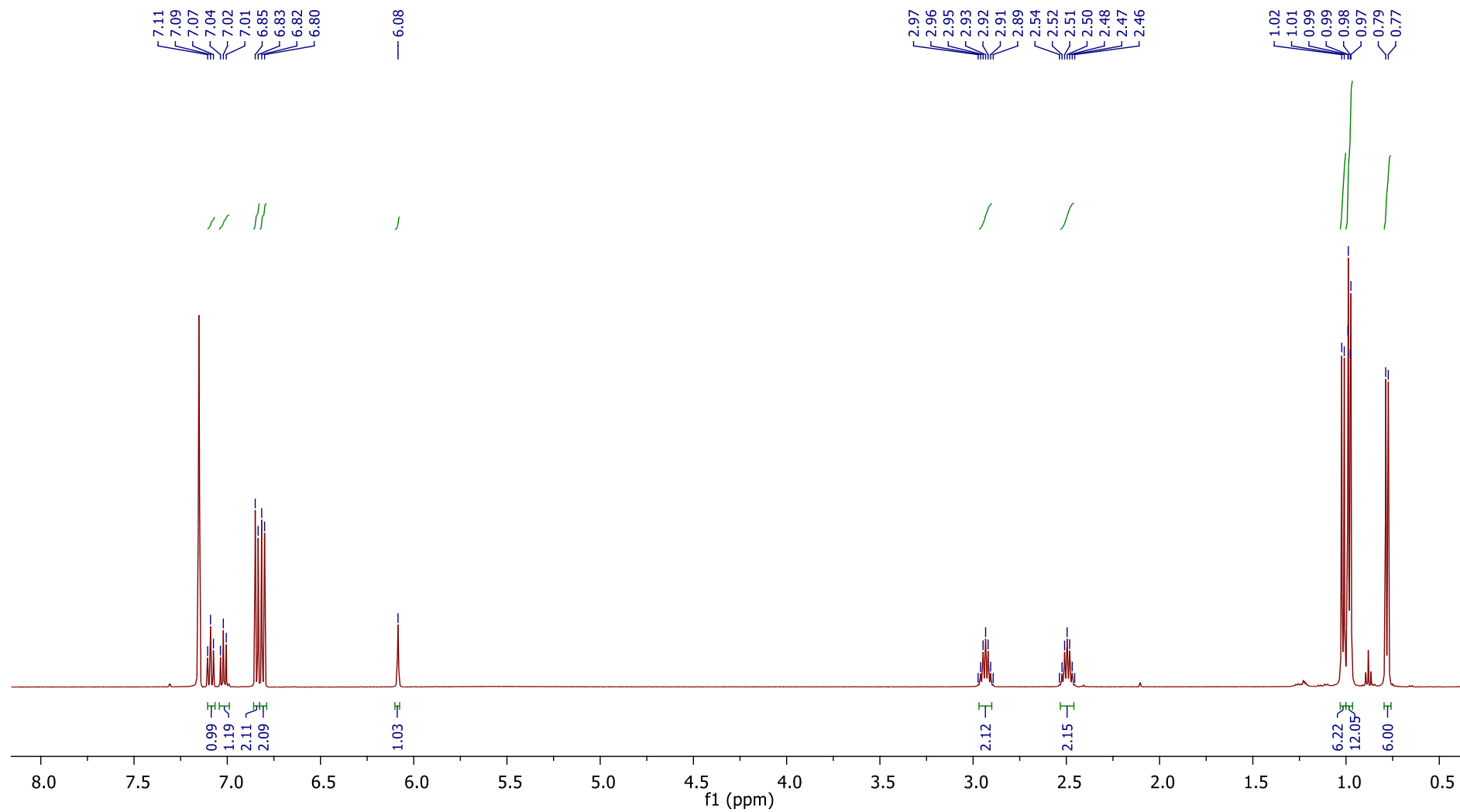


Figure S 33. ¹H NMR spectrum (500 MHz, C₆D₆, 298K) of (WCA-IDipp)OH (**10**).

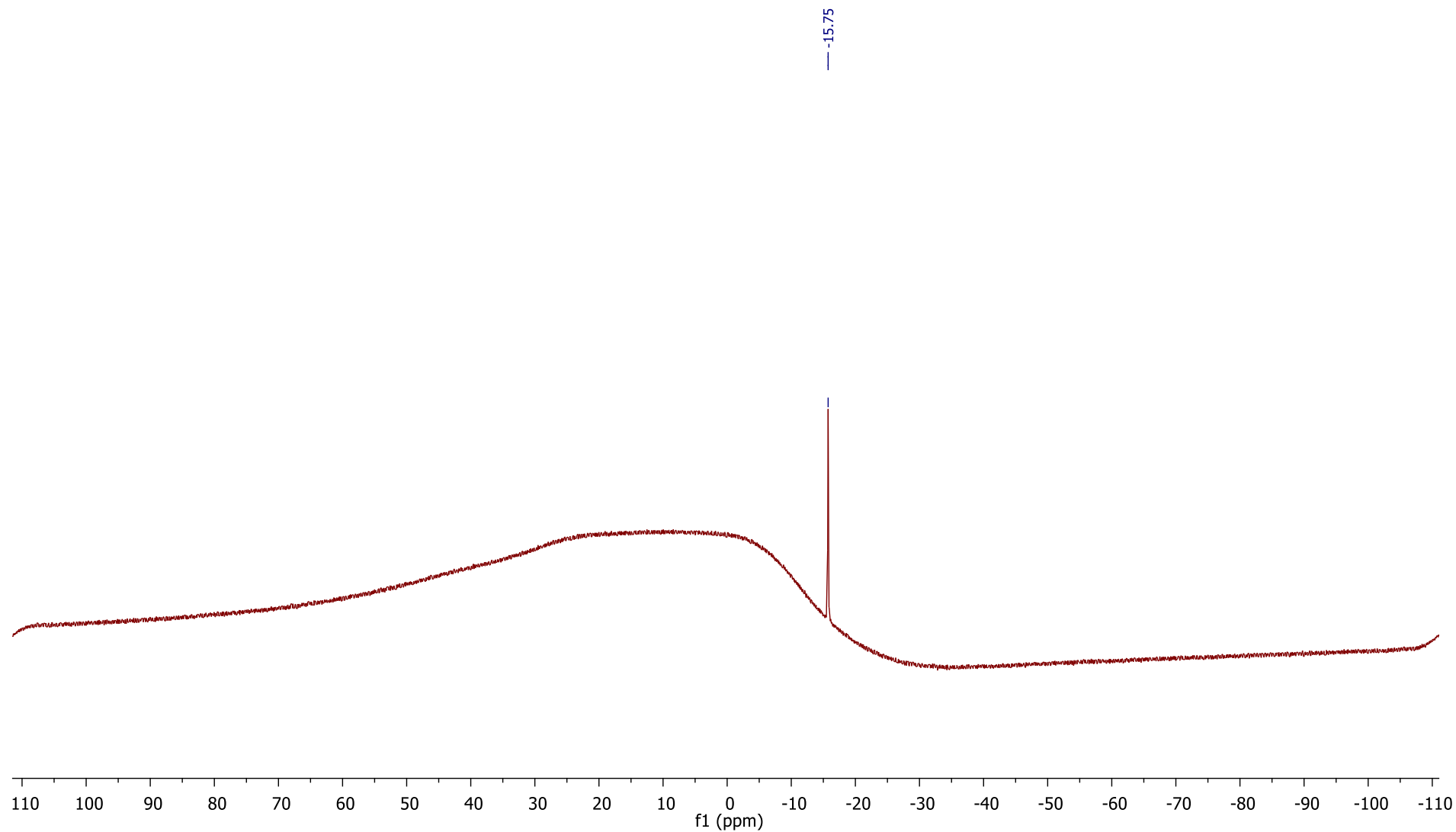


Figure S 34. ^{11}B NMR spectrum (161 MHz, C_6D_6 , 298K) of (WCA-IDipp)OH (**10**).

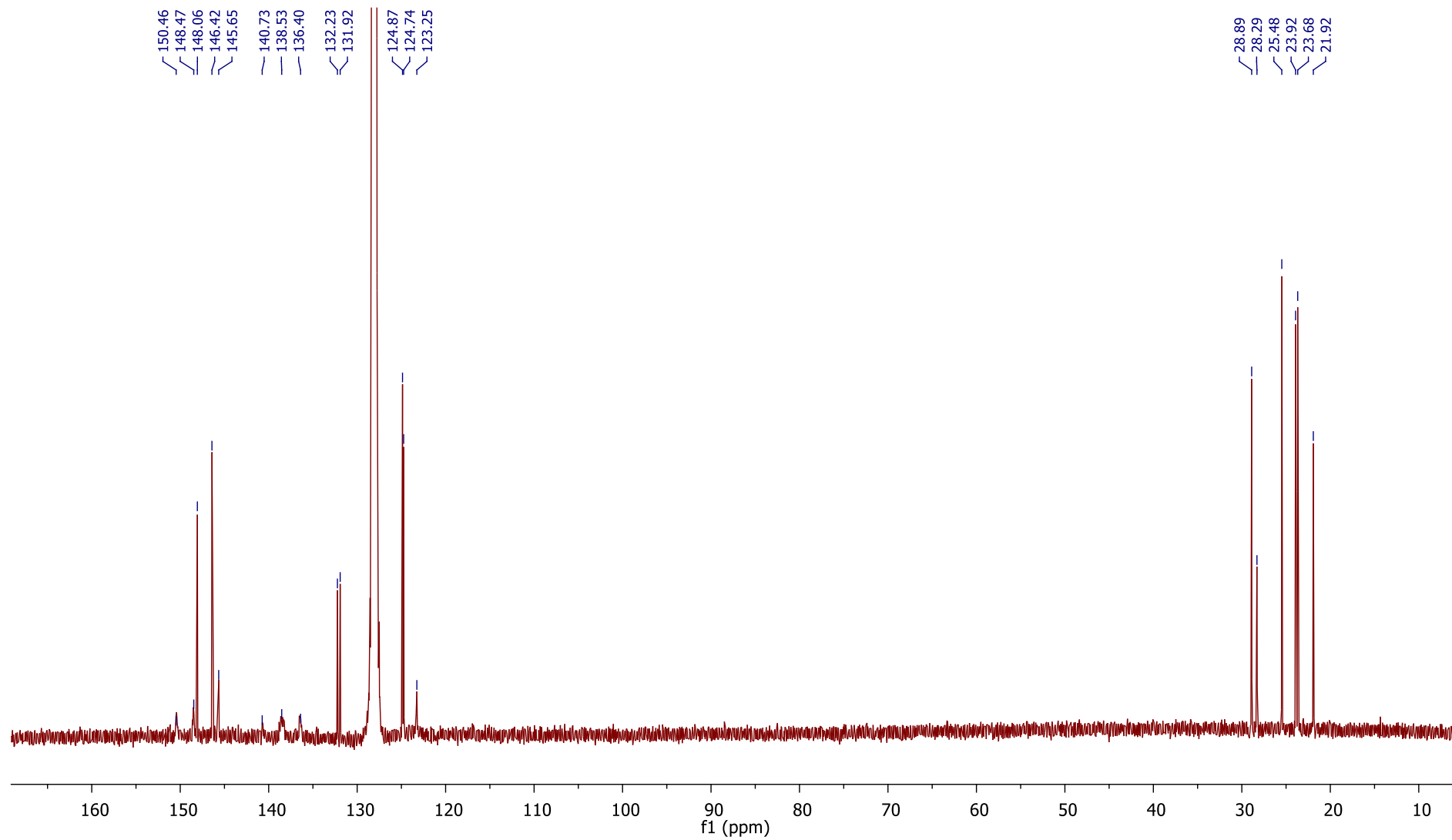


Figure S 35. ^{13}C NMR spectrum (126 MHz, C_6D_6 , 298K) of (WCA-IDipp)OH (10).

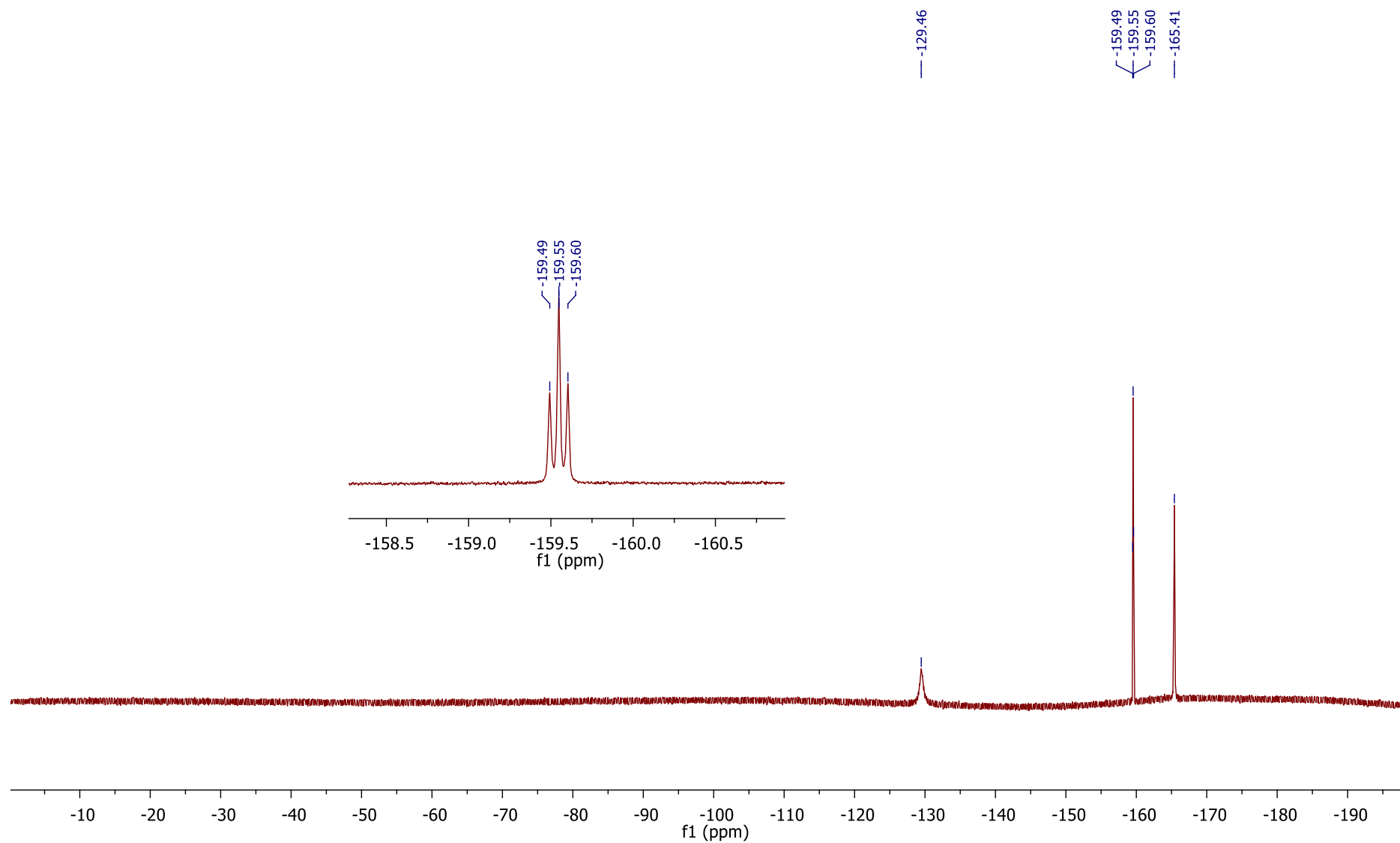


Figure S 36. ^{19}F NMR spectrum (377 MHz, C_6D_6 , 298K) of (WCA-IDipp)OH (10).

S2.7 (WCA-IDipp)SH (**11**)

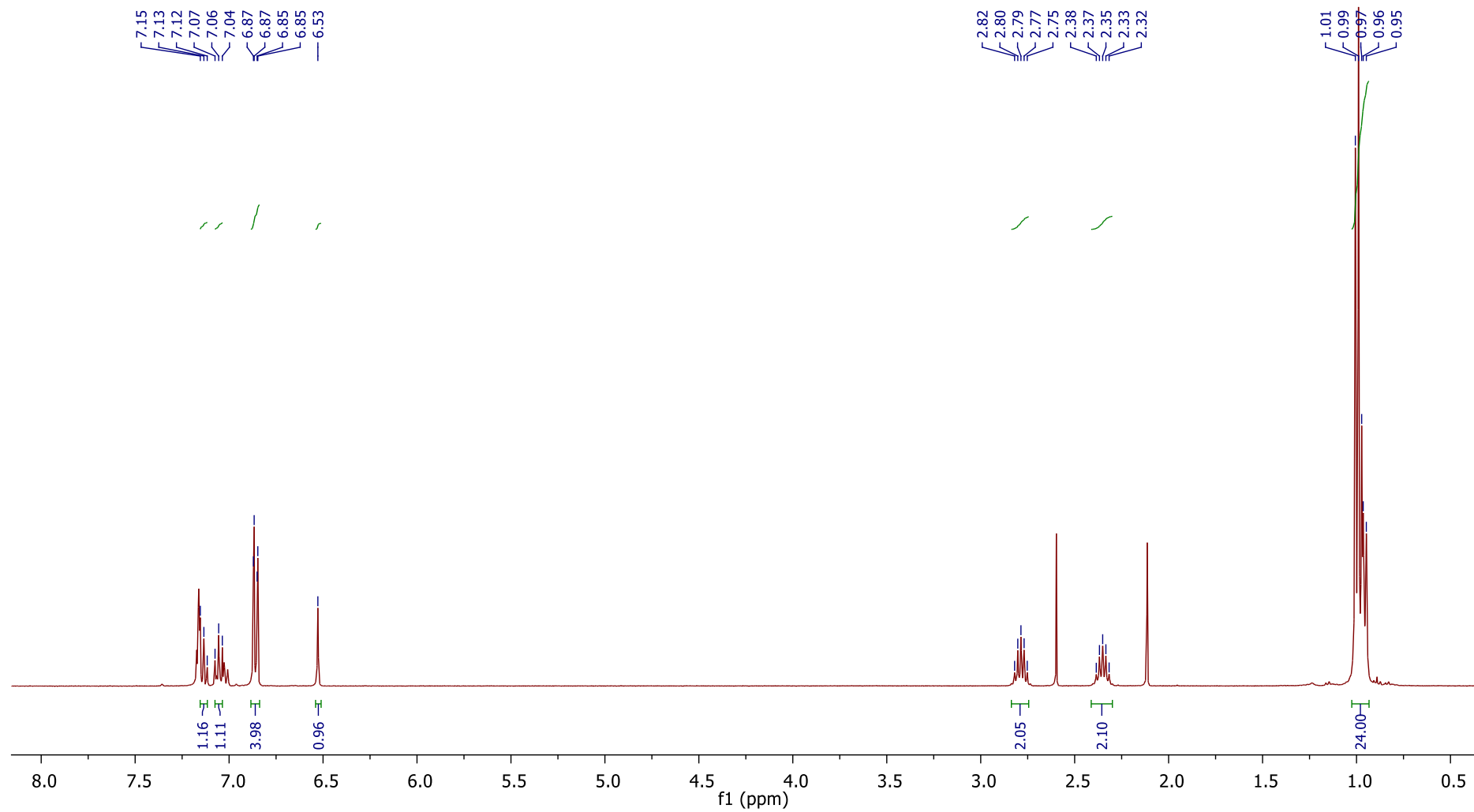


Figure S 37. ^1H NMR spectrum (400 MHz, C_6D_6 , 298K) of (WCA-IDipp)SH (**11**).

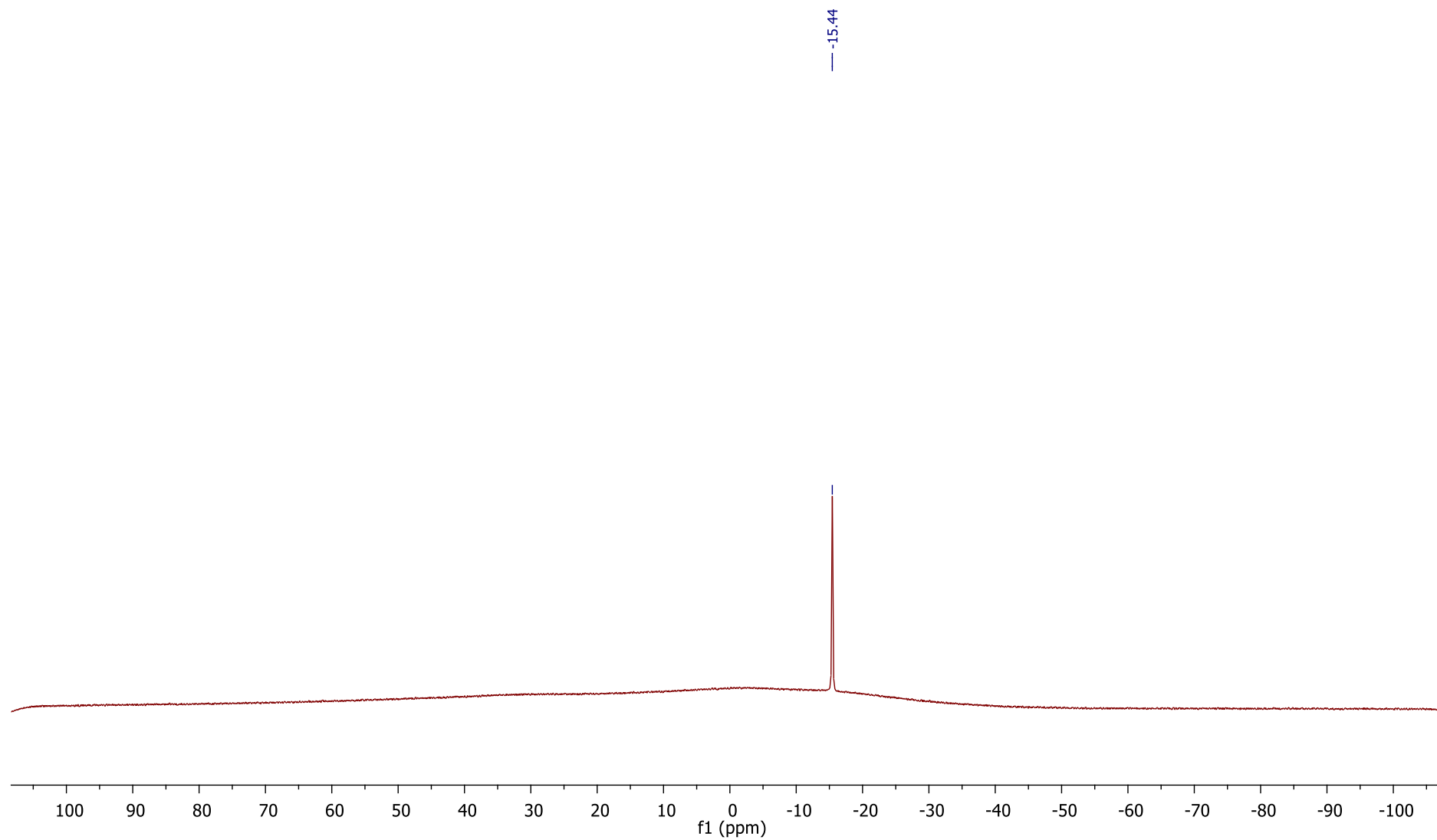


Figure S 38. ^{11}B NMR spectrum (128 MHz, C_6D_6 , 298K) of (WCA-IDipp)SH (**11**).

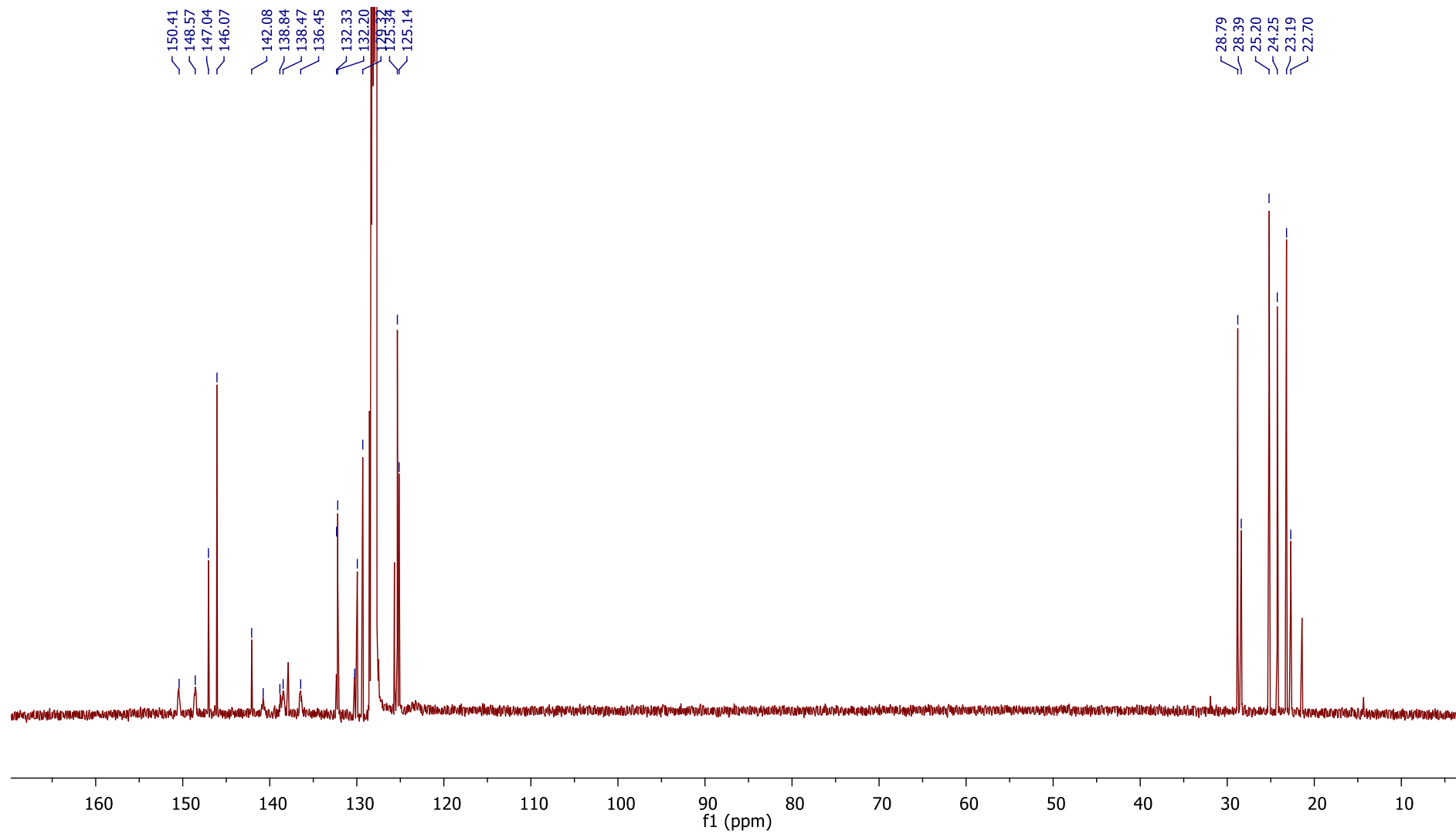


Figure S 39. ¹³C NMR spectrum (126 MHz, C₆D₆, 298K) of (WCA-IDipp)SH (**11**).

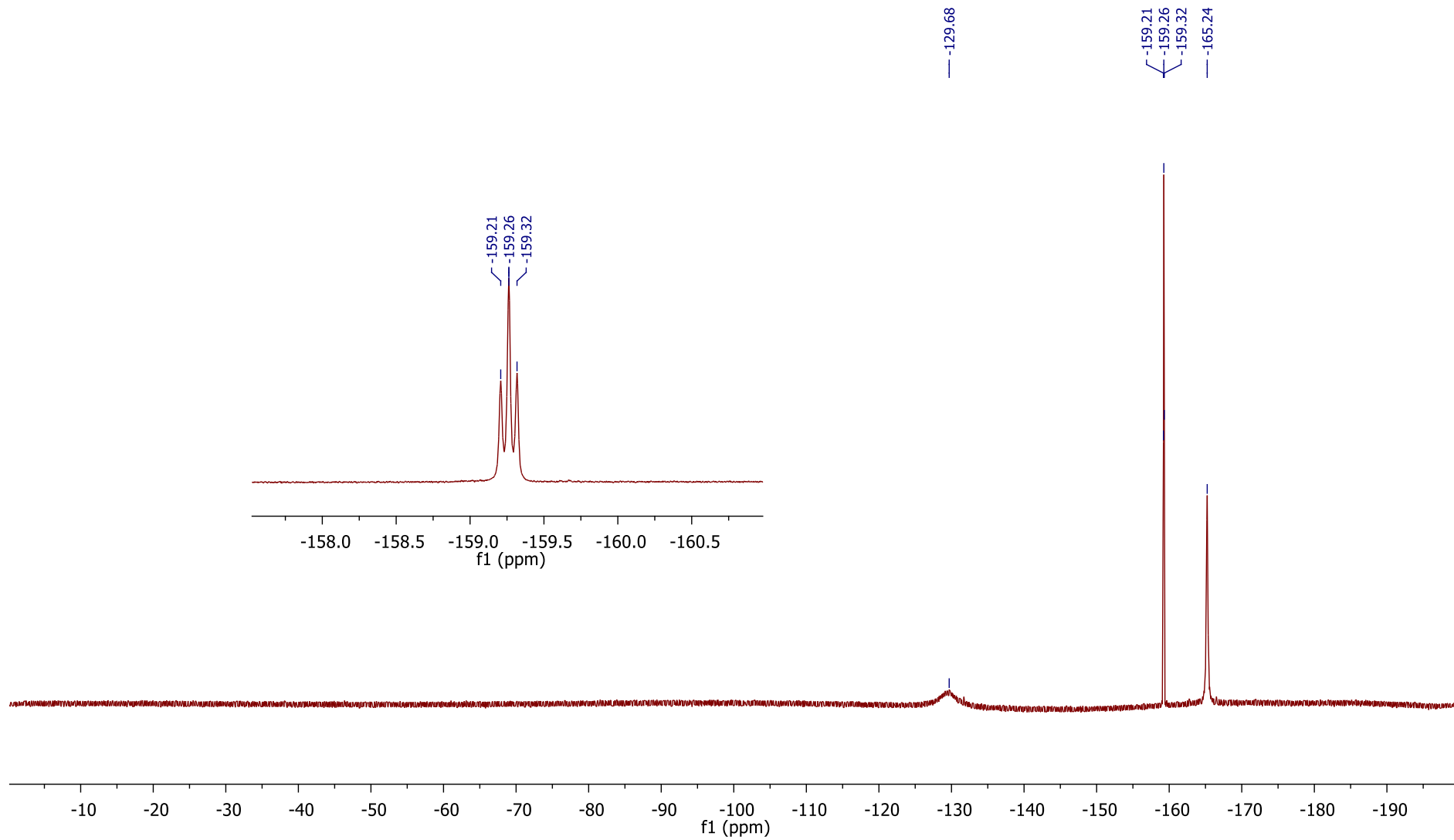


Figure S 40. ^{19}F NMR spectrum (377 MHz, C_6D_6 , 298K) of (WCA-IDipp)SH (**11**).

S2.8 (WCA-IDipp)SeH (12)

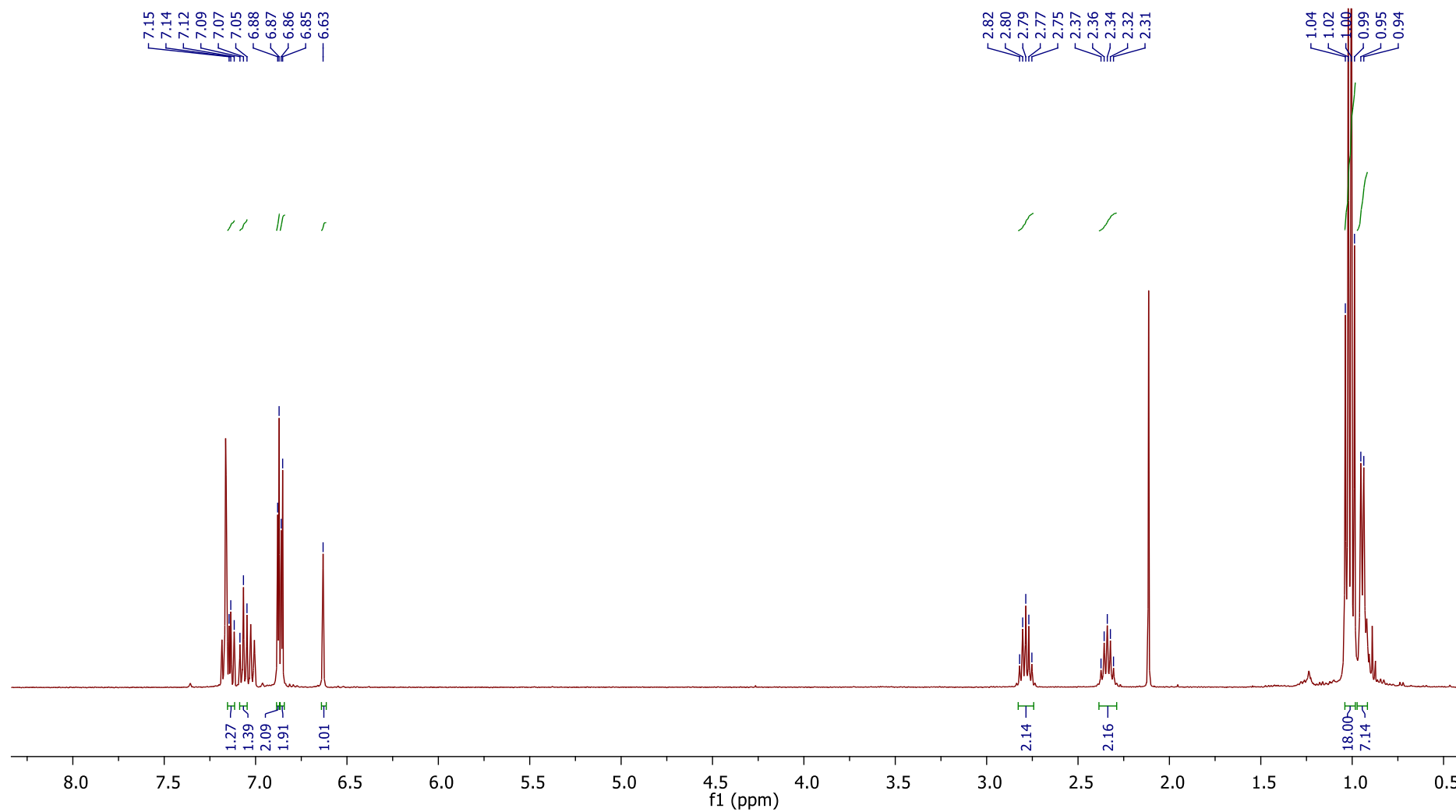


Figure S 41. ^1H NMR spectrum (400 MHz, C_6D_6 , 298K) of (WCA-IDipp)SeH (12).

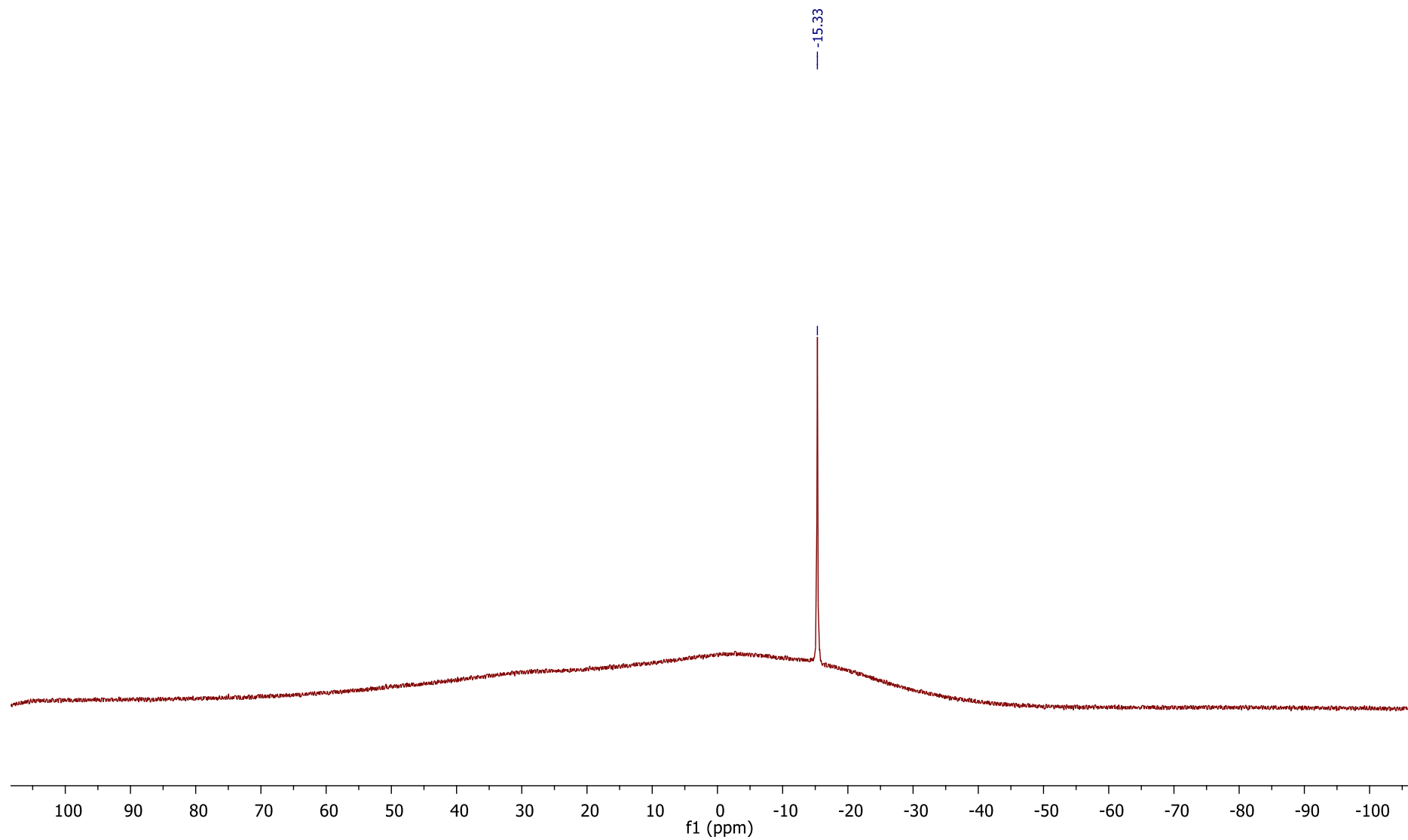


Figure S 42. ^{11}B NMR spectrum (128 MHz, C_6D_6 , 298K) of (WCA-IDipp)SeH (**12**).

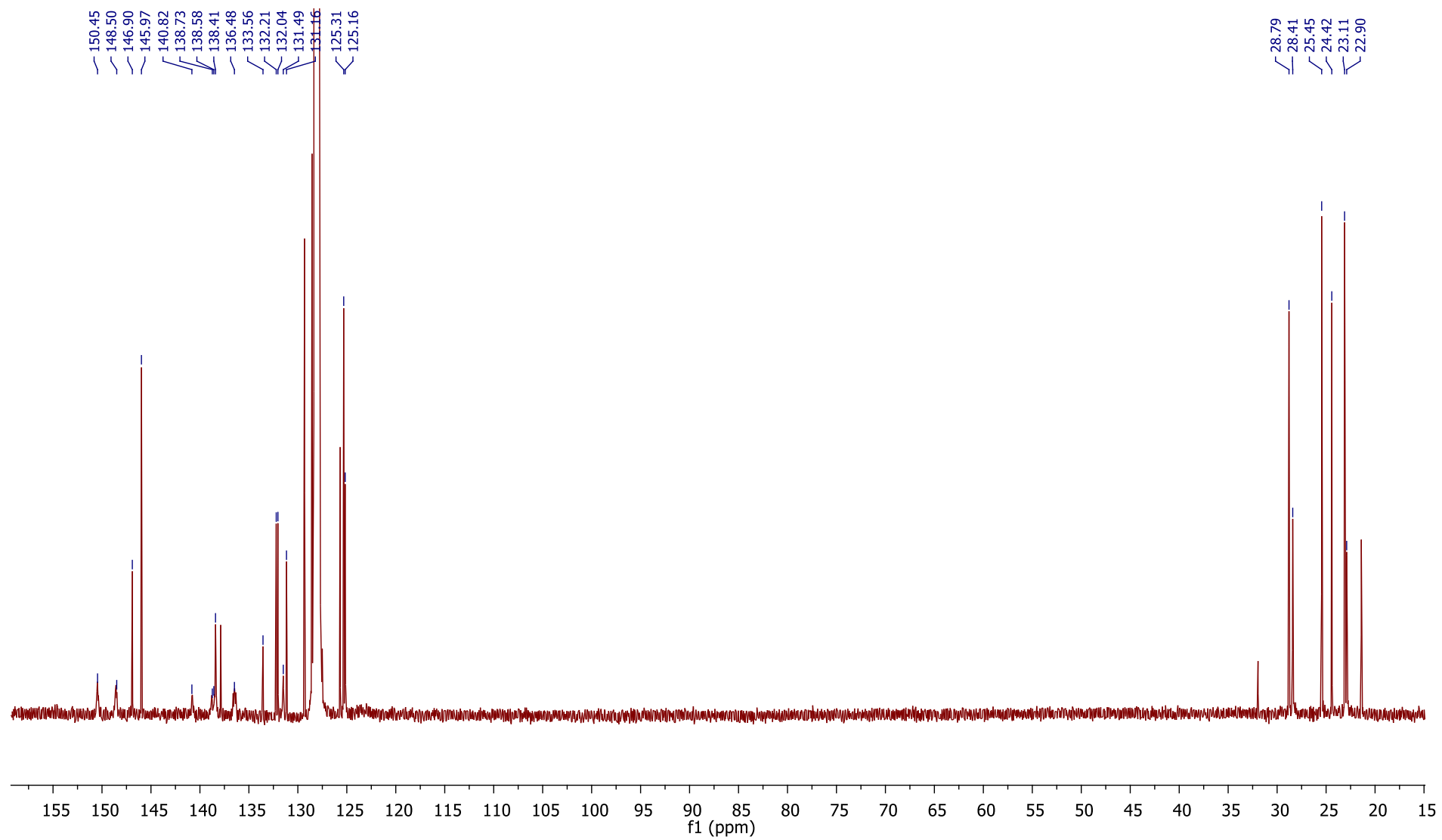


Figure S 43. ¹³C NMR spectrum (126 MHz, C₆D₆, 298K) of (WCA-IDipp)SeH (**12**).

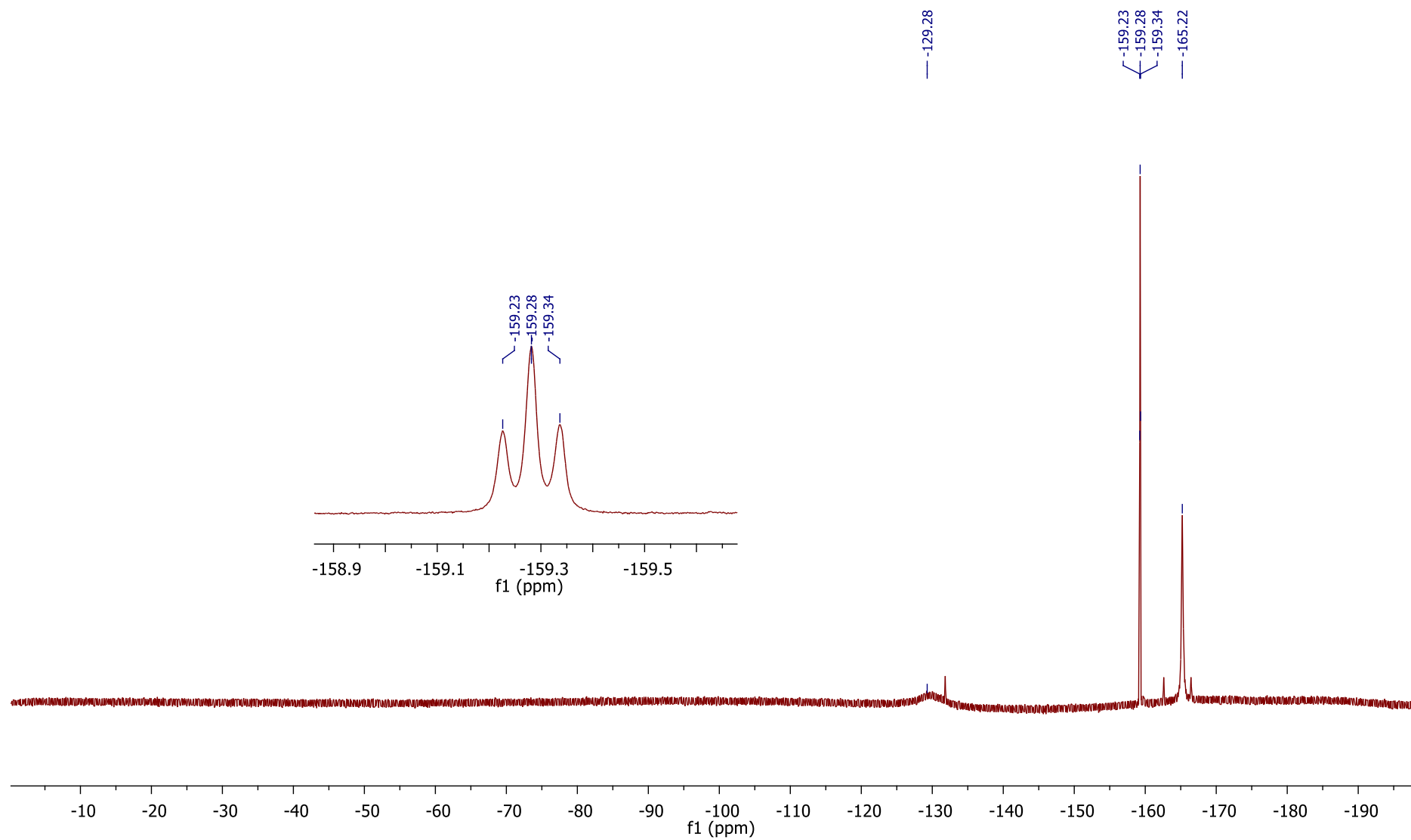


Figure S 44. ^{19}F NMR spectrum (377 MHz, C_6D_6 , 298K) of (WCA-IDipp)SeH (12).

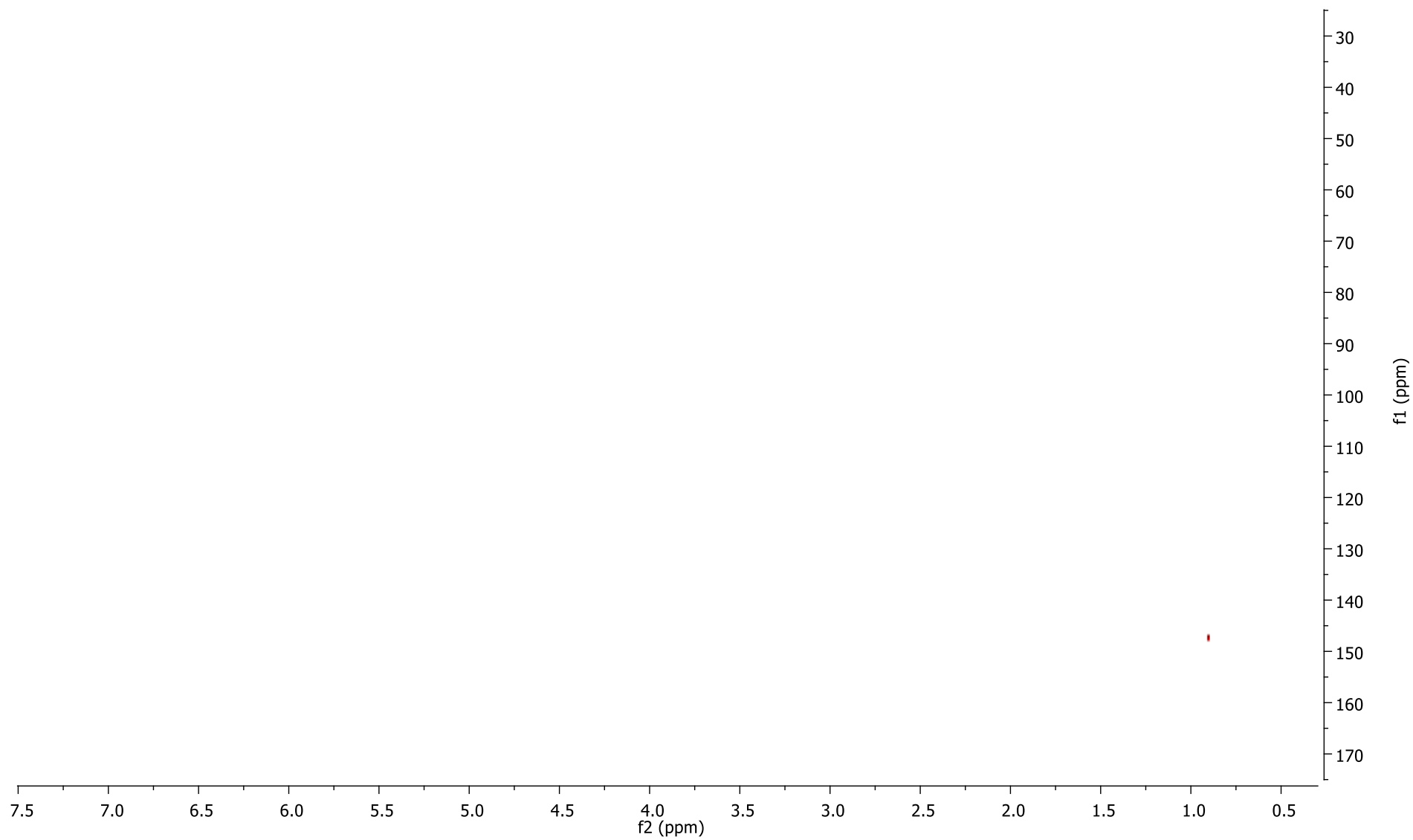


Figure S 45. ^1H , ^{77}Se -HMBC NMR (500 & 95 MHz, C_6D_6 , 298K) spectrum of (WCA-IDipp)SeH (**12**).

S2.9 (WCA-IDipp)₂S₂ (**13**)

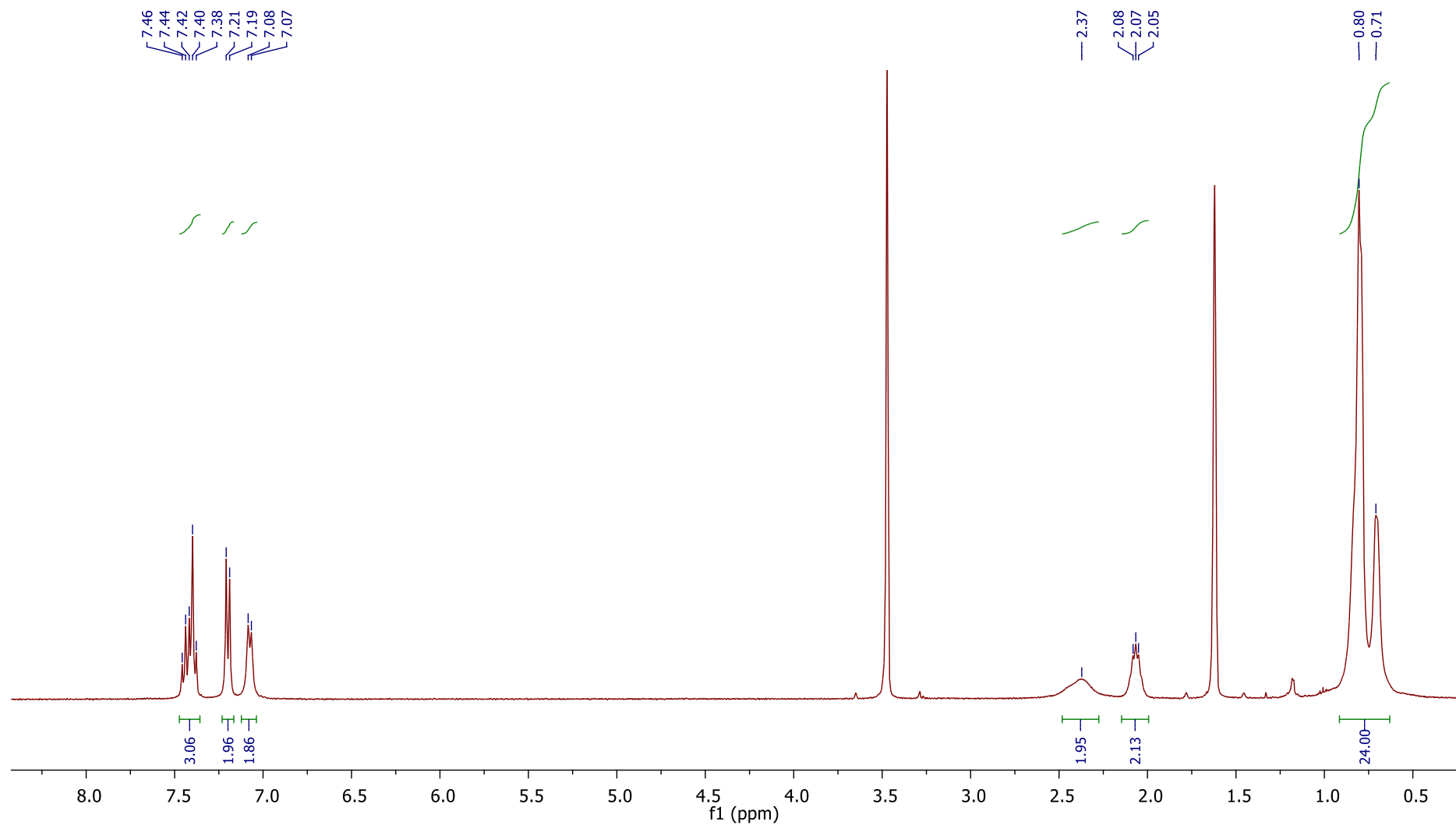


Figure S 46. ¹H NMR spectrum (400 MHz, THF-*d*₈, 298K) of (WCA-IDipp)₂S₂ (**13**).

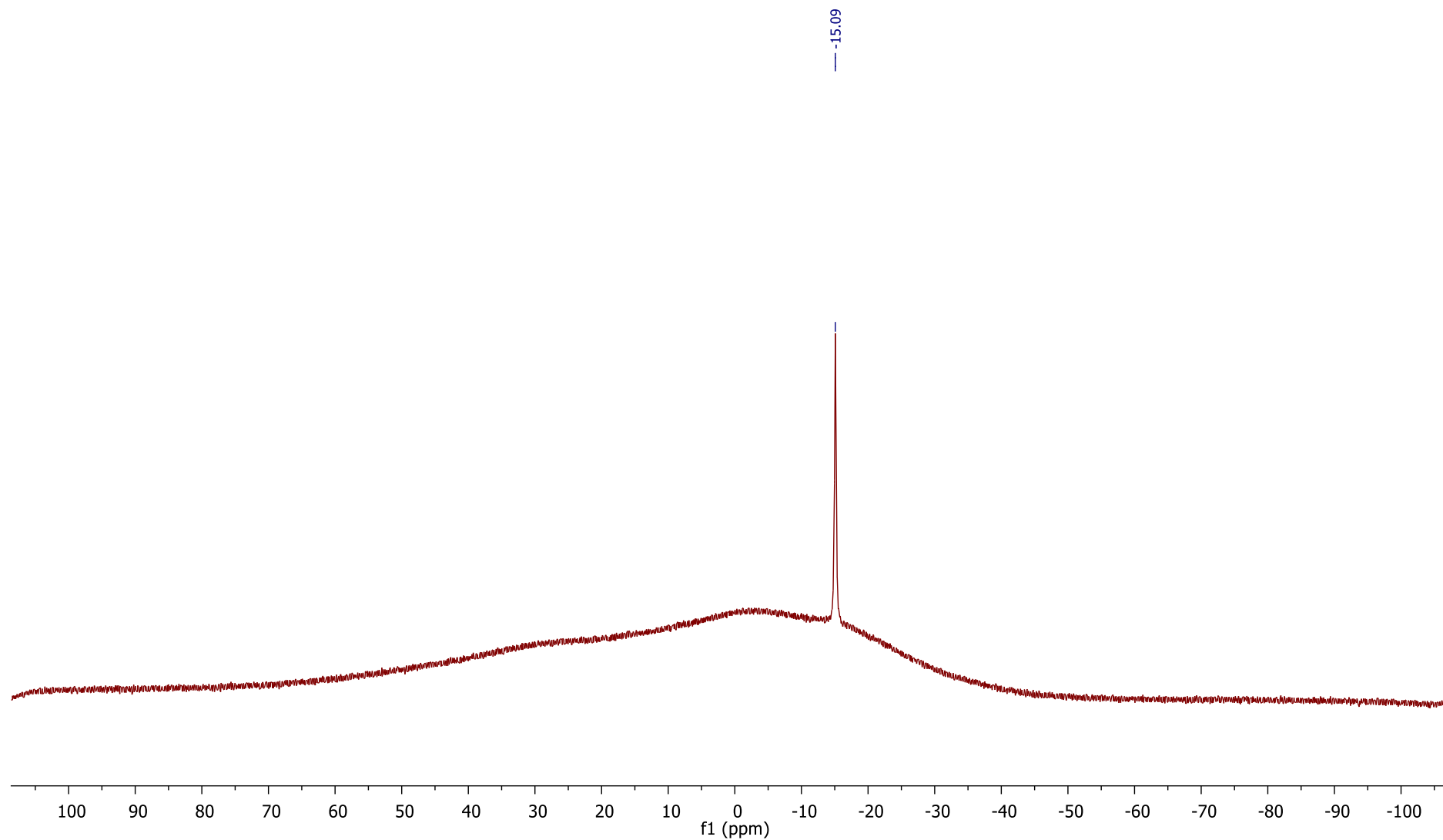


Figure S 47. ^{11}B NMR spectrum (128 MHz, THF- d_8 , 298K) of (WCA-IDipp) $_2$ S $_2$ (**13**).

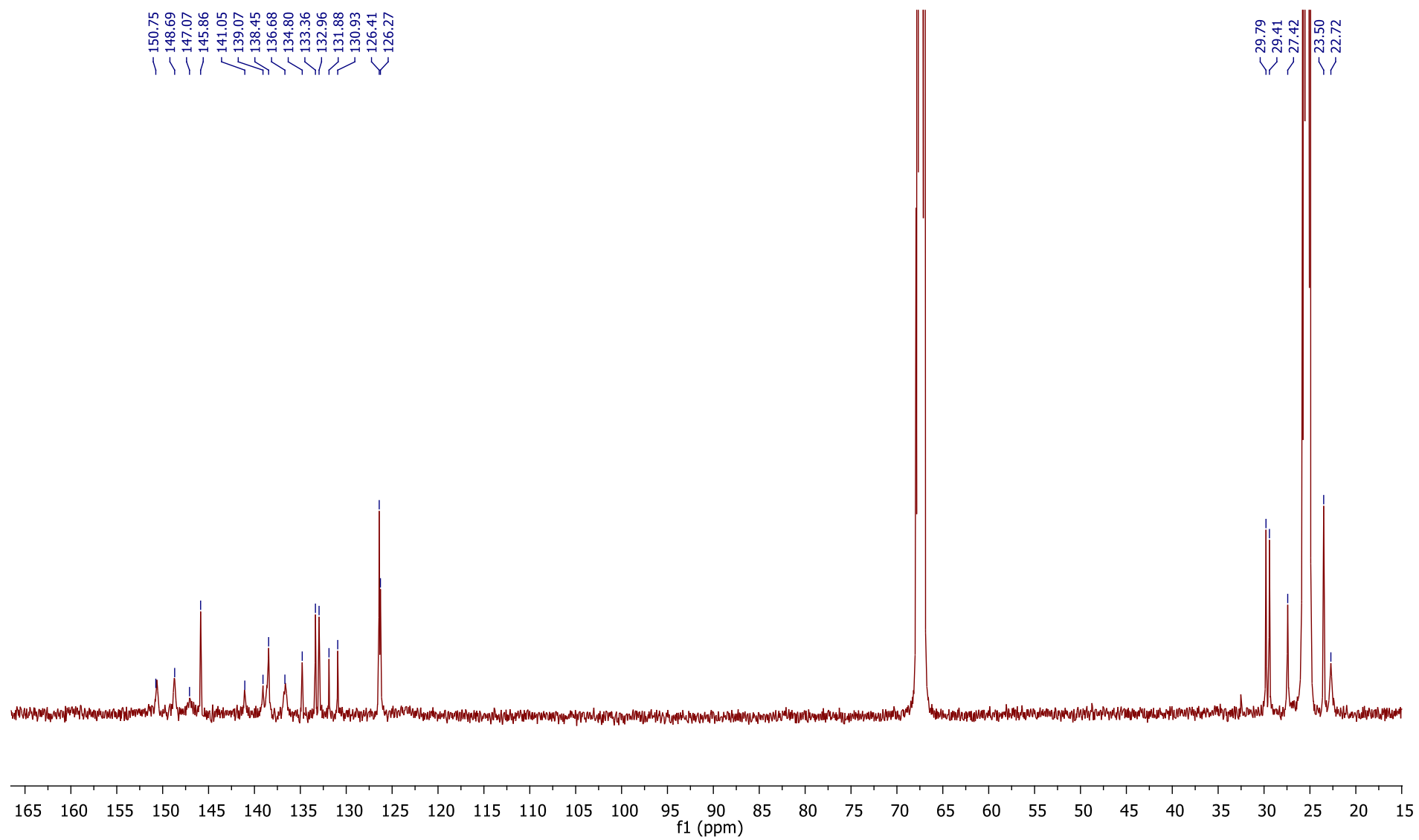


Figure S 48. ^{13}C NMR spectrum (126 MHz, $\text{THF-}d_8$, 298K) of $(\text{WCA-IDipp})_2\text{S}_2$ (**13**).

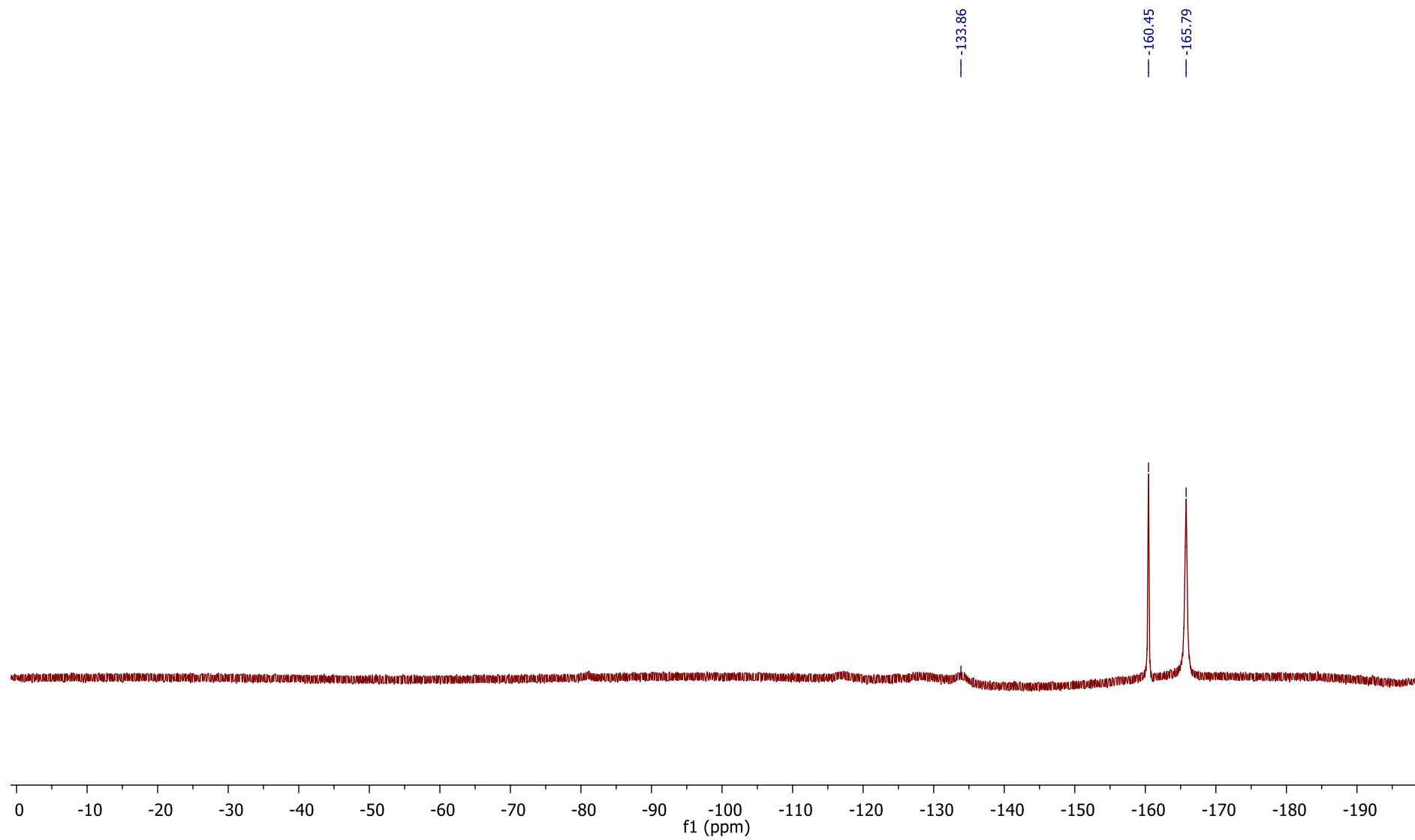


Figure S 49. ^{19}F NMR spectrum (377 MHz, $\text{THF-}d_8$, 298K) of $(\text{WCA-IDipp})_2\text{S}_2$ (**13**).

S2.10 (WCA-IDipp)₂Se₂ (**14**)

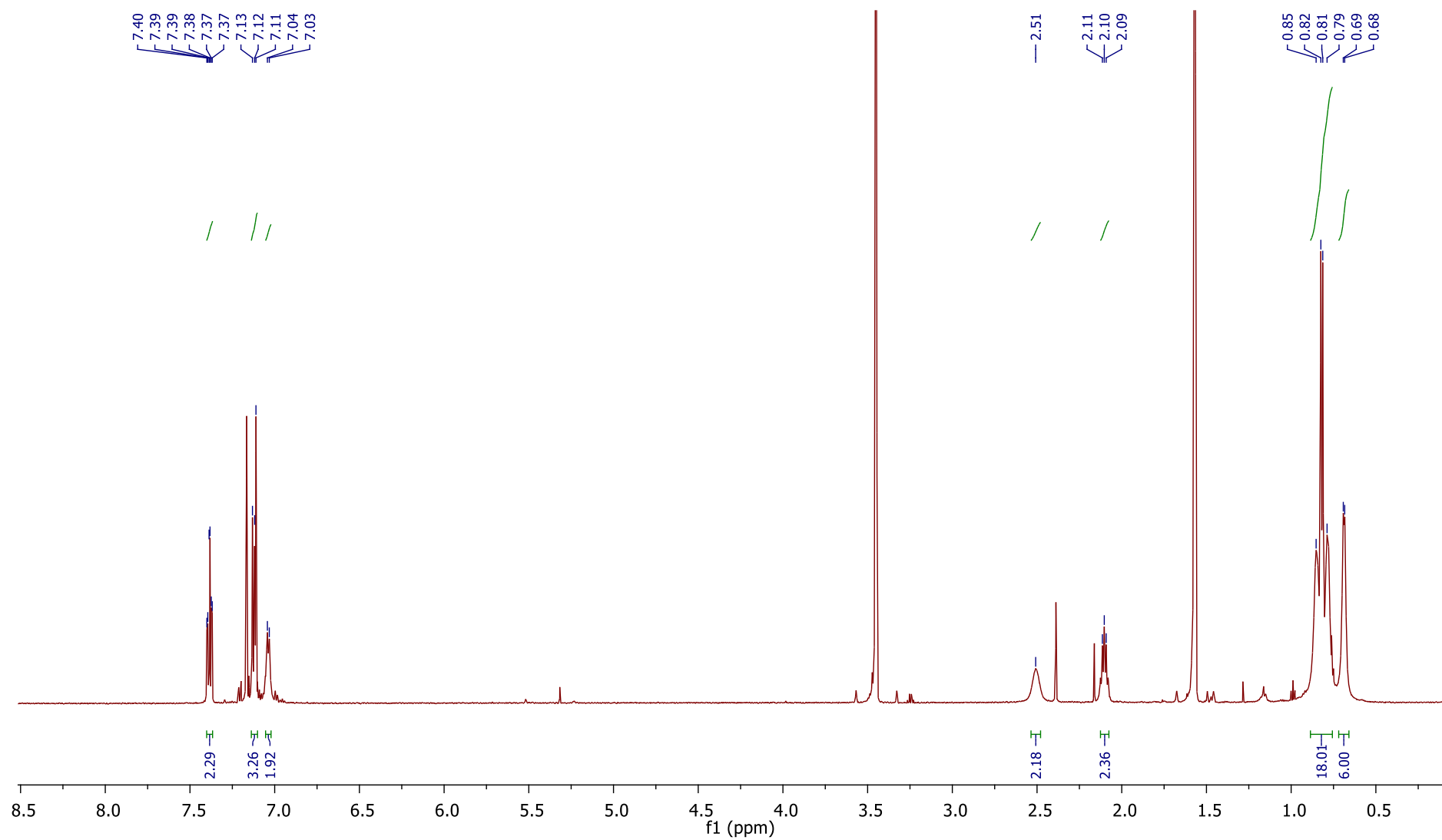


Figure S 50. ¹H NMR spectrum (600 MHz, THF-*d*₈, 298K) of (WCA-IDipp)₂Se₂ (**14**).

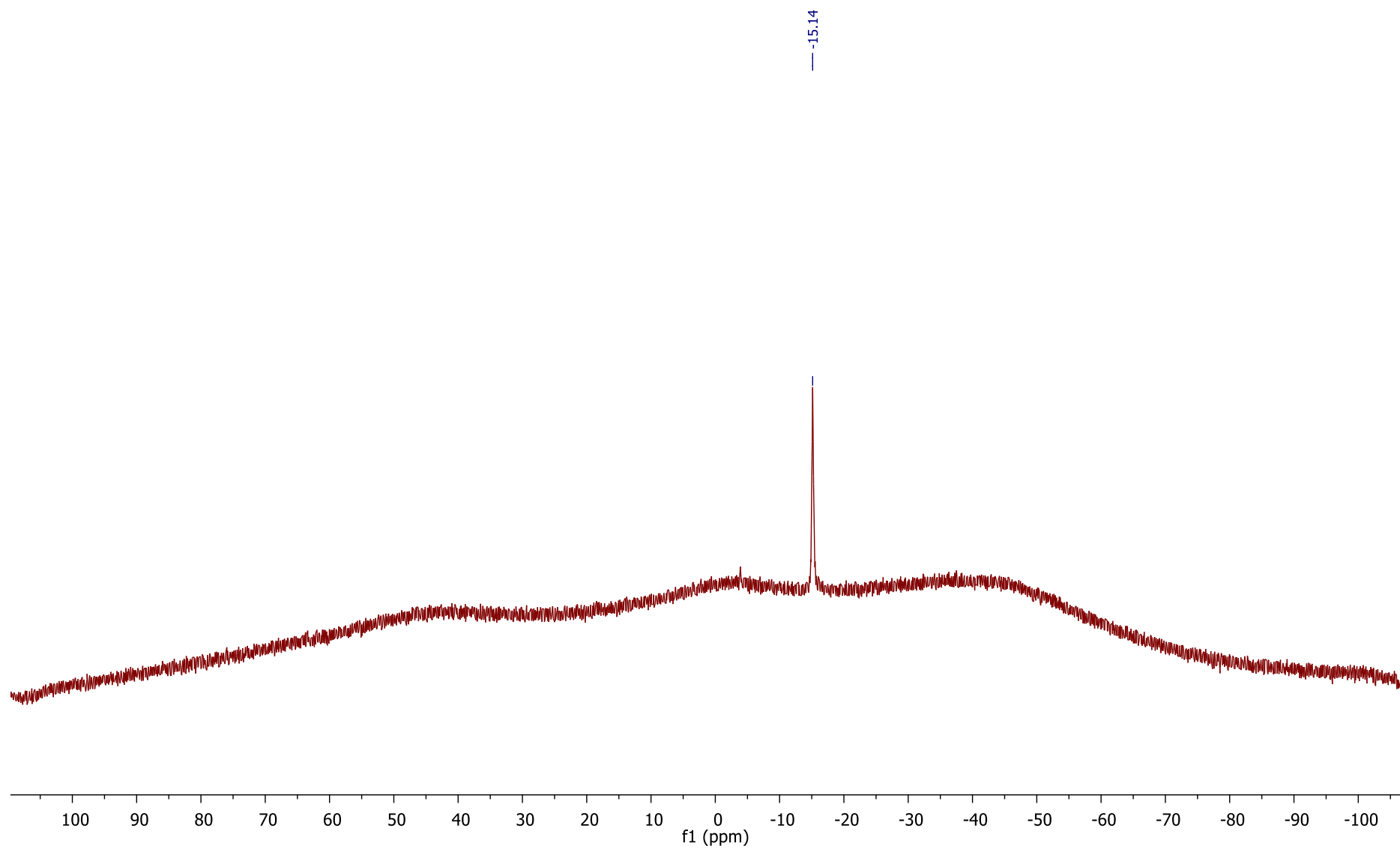


Figure S 51. ^{11}B NMR spectrum (96 MHz, $\text{THF-}d_8$, 298K) of $(\text{WCA-IDipp})_2\text{Se}_2$ (**14**).

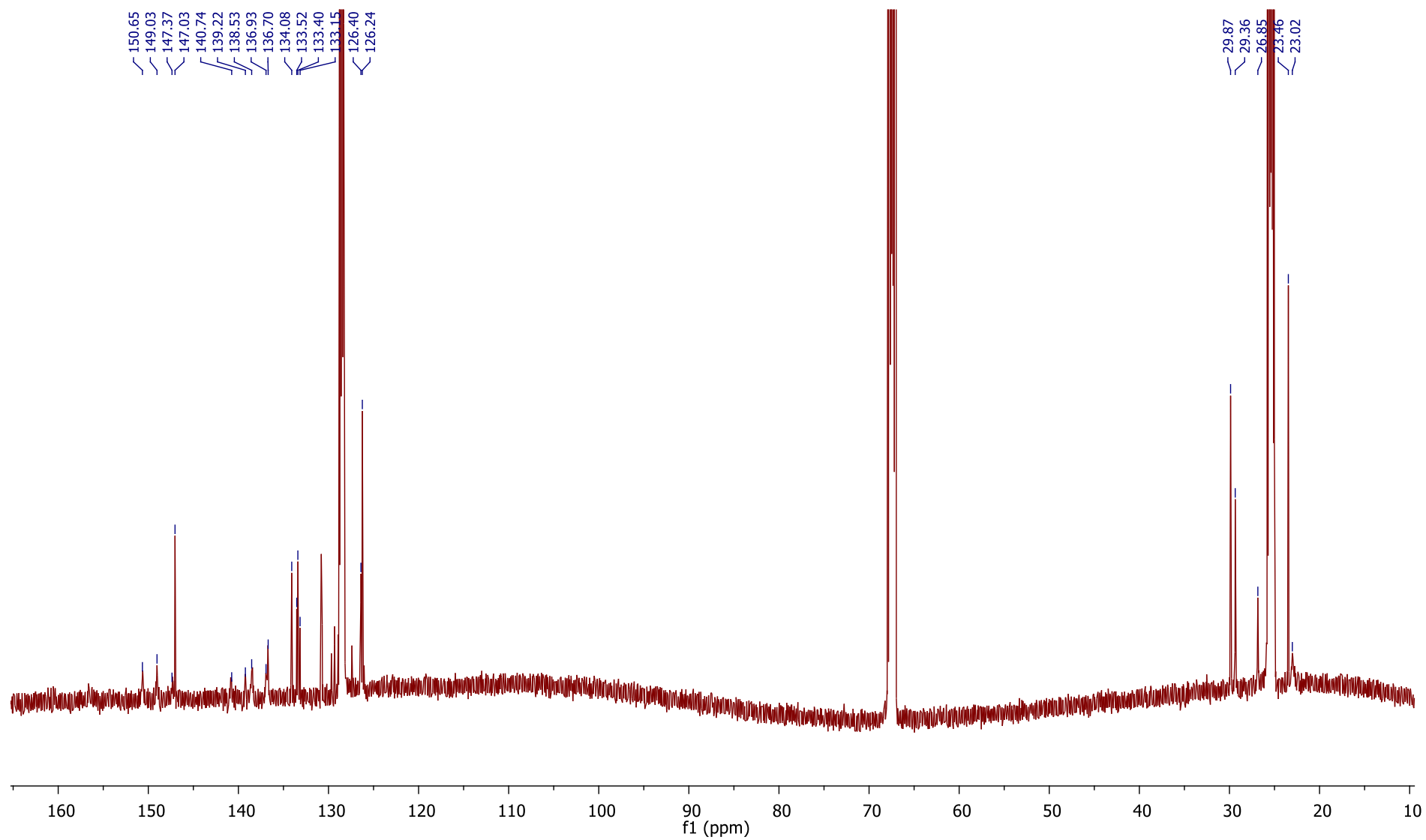


Figure S 52. ^{13}C NMR spectrum (151 MHz, $\text{THF-}d_8$, 298K) of $(\text{WCA-IDipp})_2\text{Se}_2$ (**14**).

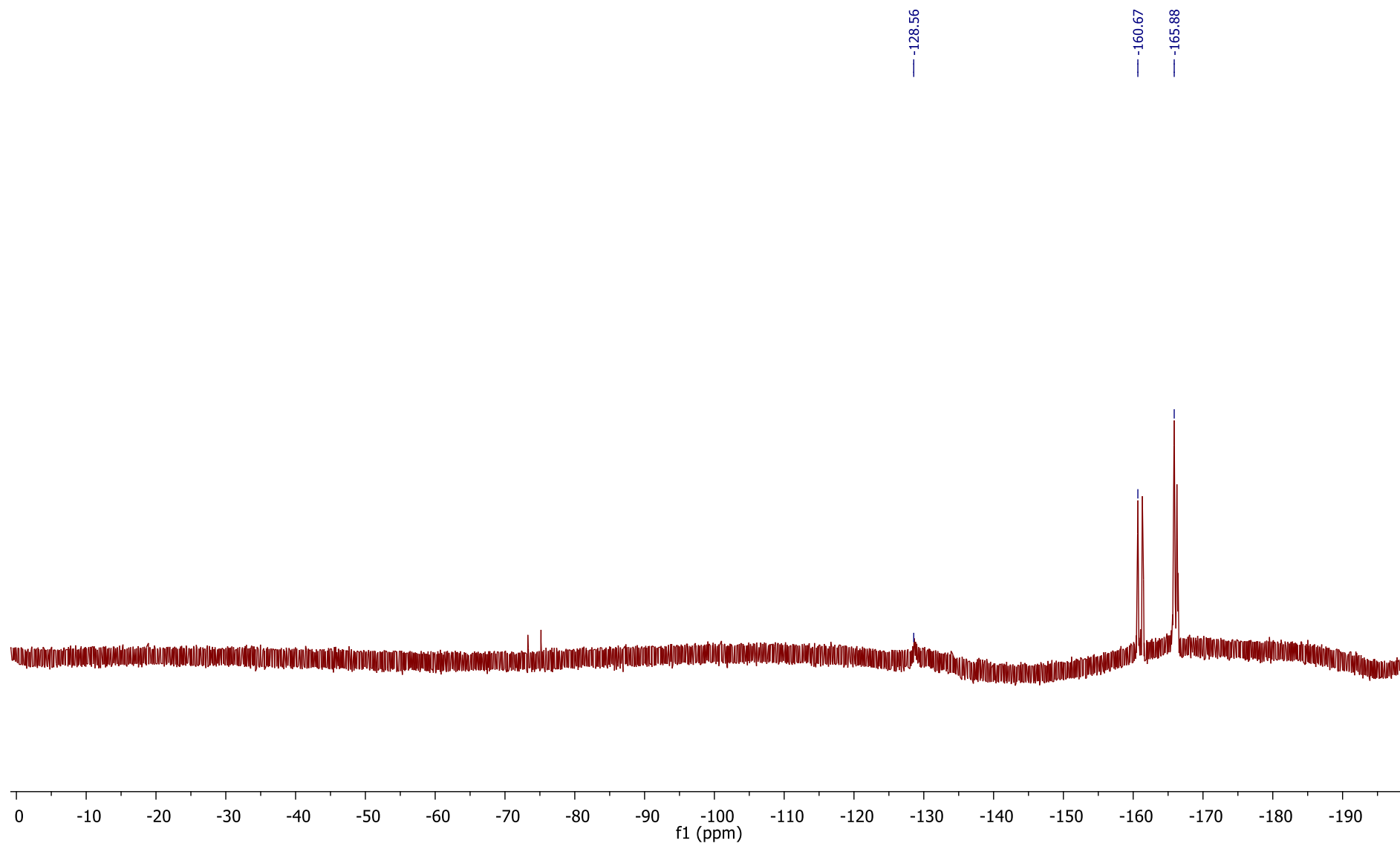


Figure S 53. ^{19}F NMR spectrum (377 MHz, $\text{THF-}d_8$, 298K) of $(\text{WCA-IDipp})_2\text{Se}_2$ (**14**).

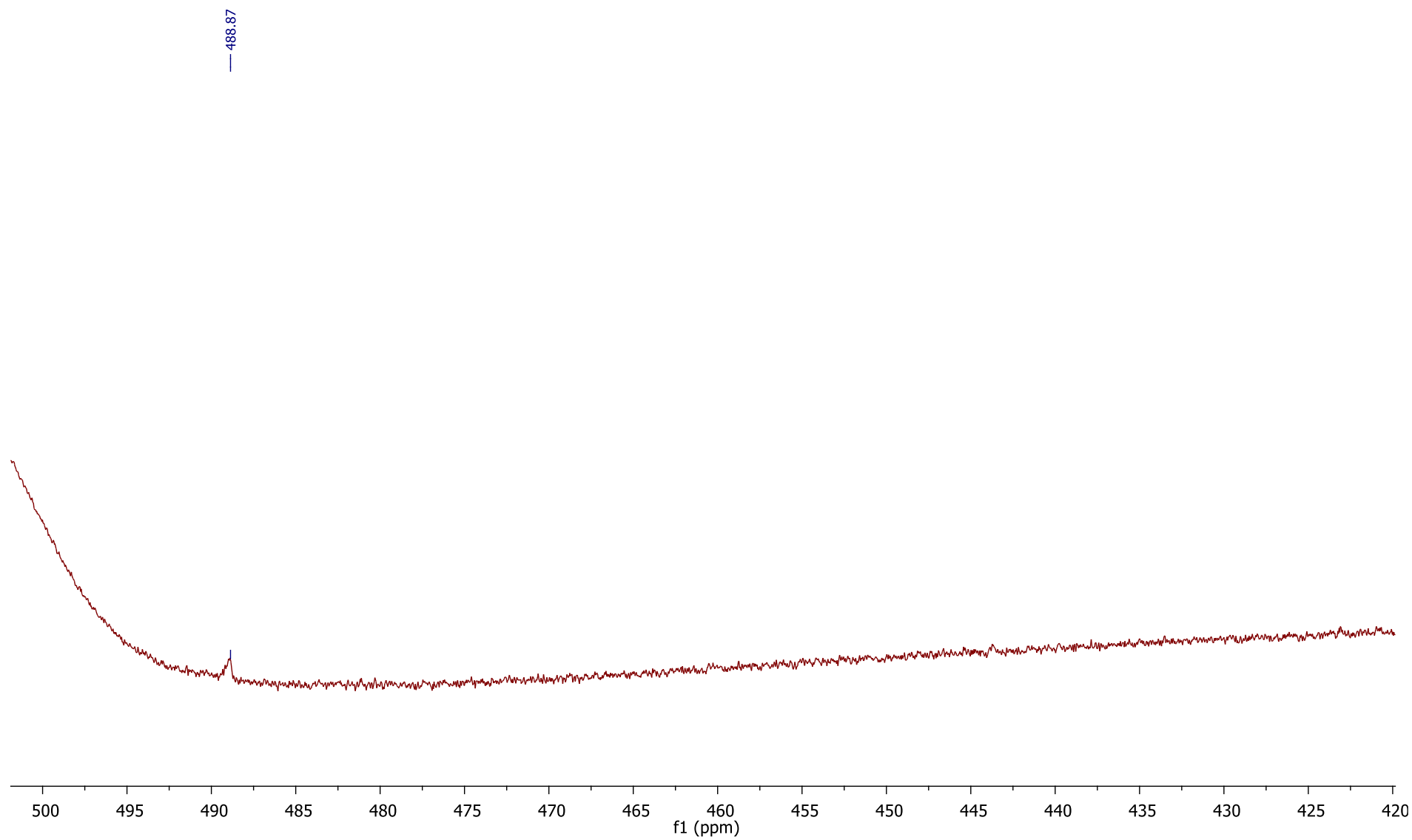


Figure S 54. ^{77}Se NMR spectrum (75 MHz, $\text{THF-}d_8$, 298 K) of $(\text{WCA-IDipp})_2\text{Se}_2$ (**14**).

S3 Computational Details

All computations were performed using the density functional method B97-D^[3] (S. Grimme) as implemented in the Gaussian09 program.^[4] For all main group elements (C, H, B, F, P and As) the all-electron triple- ζ basis set (6-311G**) was used.^[5] Natural Bond Orbital (NBO) analysis (Wiberg Bond Index, WBI) was carried out using NBO version 3,^[6] which is part of the Gaussian09 program package.

Table S3.1 Energies for all optimized structures of the adducts (WCA^a-IDipp)EH (E = O, S, Se) and (IDipp)EH (E = N, P, As)

Compound	E_{0K}^b [Ha]	E_{298K}^c [Ha]	H_{298K}^c [Ha]	G_{298K}^c [Ha]
(WCA-IDipp)OH (10)	-3441.684434	-3441.622764	-3441.621820	-3441.781032
(WCA-IDipp)SH (11)	-3764.698570	-3764.636505	-3764.635561	-3764.794647
(WCA-IDipp)SeH (12)	-5769.229240	-5769.166543	-5769.165599	-5769.328550
(IDipp)NH (II)	-1214.297694	-1214.266311	-1214.265366	-1214.358301
(IDipp)PH (III)	-1500.919742	-1500.887217	-1500.886273	-1500.982810
(IDipp)AsH (IV)	-3396.537302	-3396.504296	-3396.503352	-3396.602261

^a weakly coordinating anionic (WCA) borate moiety B(C₆F₅)₃.

^b DFT energy incl. ZPE.

^c standard conditions T = 298.15 K and p = 1 atm.

Table S3.2 NBO analysis of (WCA-IDipp)OH (**10**)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								s	p	d
(WCA-IDipp)OH (9)	1.	σ (C-O)	C	1.09	0.76	0.58	34	30	70	0
			O		-0.63					
	2.	σ (O-H)	O	0.73	---	0.87	75	20	80	0
			H		0.50					
	186.	LP(O)	O	---	---	---	100	46	54	0
	187.	LP(O)	O	---	---	---	100	0	100	0
	1248.	σ^* (C-O)	C	---	---	-0.82	66	30	70	0
			O		---					
	1249.	σ^* (O-H)	O	---	---	0.50	75	20	80	0
			H		---					

Table S3.3 NBO analysis of (WCA-IDipp)SH (11)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								S	p	d
(WCA-IDipp)SH (10)	1.	$\sigma(\text{C-S})$	C	1.14	0.30	0.74	55	33	67	0
			S		0.11	0.67	45	18	81	1
	2.	$\sigma(\text{S-H})$	S	0.94	---	0.76	75	13	87	0
			H		0.16	0.65	42	100	0	0
	191.	LP(S)	S	---	---	---	100	69	31	0
	192.	LP(S)	S	---	---	---	100	0	100	0
	1255.	$\sigma^*(\text{C-S})$	C	---	---	-0.67	45	33	67	0
			S		---	0.74	55	18	81	1
	1249.	$\sigma^*(\text{S-H})$	S	---	---	0.65	42	13	87	0
			H		---	-0.76	75	100	0	0

Table S3.4 NBO analysis of (WCA-IDipp)SeH (12)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								S	p	d
(WCA-IDipp)SeH (11)	1.	$\sigma(\text{C-Se})$	C	1.08	0.26	0.77	59	33	67	0
			Se		0.21	0.64	41	14	86	0
	2.	$\sigma(\text{Se-H})$	Se	0.95	---	0.75	56	11	89	0
			H		0.11	0.67	44	100	0	0
	200.	LP(Se)	Se	---	---	---	100	76	24	0
	201.	LP(Se)	Se	---	---	---	100	0	100	0
	1273.	$\sigma^*(\text{C-Se})$	C	---	---	-0.64	41	33	67	0
			Se		---	0.77	59	14	86	0
	1274.	$\sigma^*(\text{Se-H})$	Se	---	---	0.67	44	11	89	0
			H		---	-0.75	56	100	0	0

Table S3.5 NBO analysis of (IDipp)NH (II)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								s	p	d
(IDipp)NH (II)	7.	$\sigma(\text{C-N})$	C	1.65	0.60	0.66	43	40	60	0
			N		-0.80	0.76	57	40	60	0
	8.	$\pi(\text{C-N})$	C	---	---	0.59	34	0	100	0
			N		---	0.81	66	0	100	0
	77.	$\sigma(\text{N-H})$	N	0.85	---	0.82	67	20	80	0
			H		0.34	0.58	33	100	0	0
	110.	LP(N)	N	---	---	---	100	40	60	0
	692.	$\sigma^*(\text{C-N})$	C	---	---	0.76	57	40	60	0
			N		---	-0.66	43	40	60	0
	693.	$\pi^*(\text{C-N})$	C	---	---	0.81	66	0	100	0
			N		---	-0.59	34	0	100	0
	762.	$\sigma^*(\text{N-H})$	N	---	---	-0.58	33	20	80	0
			H		---	0.82	67	100	0	0

Table S3.6 NBO analysis of (IDipp)PH (III)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								s	p	d
(IDipp)PH (III)	7.	$\sigma(\text{C-P})$	C	1.37	0.10	0.82	67	43	57	0
			P		-0.04	0.57	33	18	81	1
	8.	$\pi(\text{C-P})$	C	---	---	0.59	35	0	100	0
			P		---	0.81	65	0	100	0
	77.	$\sigma(\text{P-H})$	P	0.96	---	0.69	48	14	86	0
			H		-0.02	0.72	52	100	0	0
	114.	LP(P)	P	---	---	---	100	69	31	0
	700.	$\sigma^*(\text{C-P})$	C	---	---	0.57	33	43	57	0
			P		---	-0.82	67	18	81	1
	701.	$\pi^*(\text{C-P})$	C	---	---	0.81	65	0	100	0
			P		---	-0.59	35	0	100	0
	770	$\sigma^*(\text{P-H})$	P	---	---	0.72	52	14	86	0
H			---		-0.69	48	100	0	0	

Table S3.7 NBO analysis of (IDipp)AsH (IV)

	bond no.	type	element	WBI	NBO charge	coefficient	localization [%]	AO contribution [%]		
								S	p	d
(IDipp)AsH (IV)	7.	$\sigma(\text{C-As})$	C	1.28	0.11	0.83	69	42	58	0
			As		-0.04	0.55	31	13	87	0
	76.	$\sigma(\text{As-H})$	As	0.96	---	0.69	47	12	88	0
			H		-0.04	0.73	53	0	100	0
	123.	LP(As)	As	---	---	---	100	76	24	0
	124.	LP(As)	As	---	---	---	100	0	100	0
	719.	$\sigma^*(\text{C-As})$	C	---	---	0.55	31	42	58	0
			As		---	-0.83	69	13	87	0
	788.	$\sigma^*(\text{As-H})$	As	---	---	0.73	53	12	88	0
			H		---	-0.69	47	0	100	0

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