Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Luong Phong Ho, Matthias Tamm*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. Fax: +49 (531) 391 5387; Tel: +49 (531) 391 5309; E-Mail: m.tamm@tu-bs.de

Content

S1 Materials and Methods

Unless otherwise indicated, all starting materials were obtained from commercial sources (Sigma-Aldrich, Alfa-Aeser, Roth, TCI, VWR or Fischer Chemical) and were used without further purification. Elemental analyses were carried out on a Vario Micro Cube System. All operations with air and moisture sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 200B) or on a high vacuum line using Schlenk techniques. The ^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVII 300 (300 MHz) and Bruker AV-II 600 (600 MHz). The chemical shifts are expressed in parts per million (ppm) with the residual solvent signal as internal standard for ^{1}H and ^{13}C NMR spectra. All other spectra were calibrated using external references. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet) and br (broad). ^{11}B, ^{13}C and ^{19}F NMR spectra were measured broadband proton decoupled. *n*-Pentane, *n*-Hexane, and benzene were purified by distillation over sodium/benzophenone. Deuterated solvents were purified by stirring the degassed solvents with Na/K alloy overnight and were subsequently filtered and distilled under reduced pressure. All solvents were stored over molecular sieves (4 Å) in argon atmosphere prior to use. (WCA-IDipp)Li(toluene) (**1**)[1] and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine[2] were prepared according to literature procedures.

S2 Synthetic Procedures

S2.1 (WCA-IDipp)BiCl$_2$·C$_6$H$_6$ (2)

(WCA-IDipp)Li(toluene) (2 g, 2 mmol, 1 eq.) was suspended in 50 mL benzene and BiCl$_3$ (632 mg, 2 mmol, 1 eq.) was added as solid at once. The resulting suspension quickly turned pink and became clearer. Stirring was continued overnight at room temperature. Afterwards, the mixture was filtered through Celite, leaving purple colored LiCl on the Celite and a pink solution. The solvent was removed in *vacuo*, giving a pink solid, which was washed with 3 × 5 mL *n*-hexane. Subsequent removal of residual solvent in *vacuo* yielded the product as a pale pink solid (1.763 g, 1.40 mmol, 70%). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated benzene solution.

^{1}H NMR (600 MHz; C$_6$D$_6$): δ = 7.09-7.06 (m, 1H, *p*-Dipp), 7.05-7.02 (m, 1H, *p*-Dipp), 6.93 (d, $^3J(^1H, ^1H)$ = 7.8 Hz, 2H, *m*-Dipp), 6.85 (s, 1H, $\underline{H}$C=CB), 6.74 (d, J = 7.8 Hz, 2H, *m*-Dipp), 2.92 (sept, $^3J(^1H, ^1H)$ = 6.7 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 2.55 (sept, $^3J(^1H, ^1H)$ = 6.7 Hz, 2H, C$\underline{H}$(CH$_3$)$_2$), 1.31 (d, $^3J(^1H, ^1H)$ = 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 0.91–0.85 (m, 18H, 3 × CH(C$\underline{H}_3$)$_2$) ppm.

^{13}C NMR (151 MHz; C$_6$D$_6$): δ = 212.2 (s, N-C-N), 155.0-153.8 (m, HC=$\underline{C}$B), 149.9-149.7 (m, =CF), 148.3-148.1 (m, =CF), 147.8 (s, *o*-Dipp), 145.9 (s, *o*-Dipp), 140.3-140.2 (m, =CF), 138.7-138.5 (m, =CF), 138.0-137.8 (m, =CF), 137.4 (s, H$\underline{C}$=CB), 136.4-136.2 (m, =CF), 133.4 (s, *ipso*-Dipp), 132.3 (s, *p*-Dipp), 131.4 (s, *p*-Dipp), 131.0 (s, *ipso*-Dipp), 125.3 (s, *m*-Dipp), 123.6 (s, *m*-Dipp), 29.1 (s, $\underline{C}$H(CH$_3$)$_2$), 27.6 (s, $\underline{C}$H(CH$_3$)$_2$), 27.1 (s, CH($\underline{C}$H$_3$)$_2$), 26.7 (s, CH($\underline{C}$H$_3$)$_2$), 22.5 (s, CH($\underline{C}$H$_3$)$_2$), 21.9 (s, CH($\underline{C}$H$_3$)$_2$) ppm.

^{11}B NMR (96 MHz; C$_6$D$_6$): δ = –15.4 (s, 1B) ppm.

^{19}F NMR (282 MHz; C$_6$D$_6$): δ = –130.82 – –131.55 (m, 6F, *m*-Ar-F), –158.59 (t, $^3J(^{19}F, ^{19}F)$ = 20.7 Hz, 3F, *p*-Ar-F), –164.44 – –164.81 (m, 6F, *o*-Ar-F) ppm.

EA - Anal. calc. for C$_{45}$H$_{35}$BBiCl$_2$F$_{15}$N$_2$·C$_7$H$_8$: C, 49.12; H, 3.41; N, 2.20. Found: C, 49.57; H, 3.461; N, 2.65.

S2.2 (WCA-IDipp)$_2$Bi$_2$ (3)

A solution of (WCA-IDipp)BiCl$_2$·C$_6$H$_6$ (50 mg, 0.040 mmol, 1 eq.) in 0.5 mL benzene was frozen at –30°C under inert atmosphere in a narrow scintillation vial. Subsequently, four layers each consisting of 0.5 mL benzene were frozen atop of each other. A solution of 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (9 mg, 0.040 mmol, 1 eq.) in 0.5 mL *n*-pentane was cooled to –30°C under inert atmosphere and carefully added on top of the frozen benzene layers. The vial was then allowed to warm undisturbed to room temperature overnight, upon which purple prism shaped crystals formed. The supernatant solution was carefully removed via decantation and the residual crystals were washed with 3×2 mL *n*-pentane. Subsequent removal of residual solvent in *vacuo* yielded the product as a purple solid (13 mg, 0.006 mmol, 29%).

^{1}H-NMR (600 MHz; THF-*d*$_8$): δ = 7.64 (t, $^3J(^1H, ^1H)$ = 7.8 Hz, 2H, *p*-Dipp), 7.31 (d, $^3J(^1H, ^1H)$ = 7.5 Hz, 4H, *m*-Dipp), 7.26-7.24 (m, 6H, *m*-Dipp & *p*-Dipp), 7.19 (s, 2H, $\underline{H}$C=CB), 2.78 (t, $^3J(^1H, ^1H)$ = 6.8 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 2.28 (t, $^3J(^1H, ^1H)$ = 6.9 Hz, 4H, C$\underline{H}$(CH$_3$)$_2$), 1.15 (d, $^3J(^1H, ^1H)$ = 6.9 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.13 (t, $^3J(^1H, ^1H)$ = 6.9 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 1.05 (d, J = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$), 0.91 (d, $^3J(^1H, ^1H)$ = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_2$) ppm.

^{11}B-NMR (96 MHz; THF-*d*$_8$): δ = –16.0 (s, 2B) ppm.

^{13}C NMR (126 MHz, THF) δ = 151.0 – 150.4 (m, =CF), 149.5 (s, *o*-Dipp), 148.9 – 148.6 (m, =CF), 147.4 (s, HC=$\underline{C}$B) 146.6 (s, *o*-Dipp), 141.2 – 140.4 (m, =CF),139.5 (s, *ipso*-Dipp), 139.0 – 138.4 (m, 2 × =CF), 136.9 – 136.4 (m, =CF), 135.5 (s, *p*-Dipp), 135.4 (s, *ipso*-Dipp), 134.8 –

134.5 (m, $\mathrm{H}\underline{C}\mathrm{{=}CB}$), 132.6 (s, *p*-Dipp), 127.8 (s, *m*-Dipp), 126.2 (s, *m*-Dipp), 33.5 (s, $\mathrm{CH}(\underline{C}\mathrm{H}_3)_2$), 29.6 (s, $\underline{C}\mathrm{H}(\mathrm{CH}_3)_2$), 28.8 (s, $\underline{C}\mathrm{H}(\mathrm{CH}_3)_2$), 22.7 (s, $\mathrm{CH}(\underline{C}\mathrm{H}_3)_2$) ppm.

Two signals corresponding to two $\mathrm{CH}(\underline{C}\mathrm{H}_3)_2$ groups are overlayed with the residual solvent signal of the THF-d_8. The signal corresponding to N–C–N was not observed.

^{19}F-NMR (282 MHz; THF-d_8): δ = –129.13 – –129.88 (m, 12F, *o*-F), –162.18 (t, $^3J(^{19}\mathrm{F}, ^{19}\mathrm{F})$ = 20.2 Hz, 6F, *p*-F), –167.05 – –167.36 (m, 12F, *m*-F) ppm.

EA - Anal. calc. for $C_{90}H_{72}B_2Bi_2F_{30}N_4$: C, 48.71; H, 3.27; N, 2.52. Found: C, 48.14; H, 3.285; N, 2.97.

UV-Vis (THF): λ_{max} = 366 nm (3153 M^{-1} cm^{-1}), 532 (5090 M^{-1} cm^{-1}) nm.

S3 Crystallographic details

Suitable single crystals were mounted on a hair in perfluorinated inert oil. The intensity measurements were performed at 100 K on an Rigaku XtaLAB Synergy S Single Source diffractometer using mirror-focussed Mo*K*α radiation. The diffractometer software CrysAlisPRO was employed.[3] Absorption corrections were based on multiscans. The structures were refined anisotropically on F^2 using SHELXL-2018.[4] Hydrogen atoms were included using a riding model or rigid methyl groups. Further details are given in Table S1-2.

Solvent content: The chloride species **2** contain two non-coordinated benzene molecules which are each disordered over two positions. One benzene molecule is coordinated to the bismuth atom and is ordered. The overall composition is three benzene molecules per asymmetric unit.

The dibismuthene **3** crystallizes with one molecule of benzene per asymmetric unit, which is formally ordered but display high *U* values.

Exceptions and special details: The solvent molecules in **2** and **3** were refined using appropriate restraints to improve stability of refinement.

Complete data have been deposited with the Cambridge Crystallographic Data Centre under the CCDC numbers 2050051-2050052 for compounds **2** and **3**. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/.

S3.1 (WCA-IDipp)BiCl$_2$·C$_6$H$_6$ (2)

Table S1. Crystallographic data for compound 2**.**

Compound	**2**	
Identification code (CCDC)	2050051	
Empirical formula	$C_{63}H_{53}BBiCl_2F_{15}N_2$	
Formula weight	1413.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at offset/far, HyPix (w scan)	
Crystal system	Monoclinic	
Space group	*P*2$_1$/*c*	
Unit cell dimensions	a = 15.9856(4) Å	a= 90°
	b = 12.4306(2) Å	b= 97.483(2)°
	c = 29.7067(6) Å	g = 90°
Volume	5852.8(2) Å^3	
Z	4	
Density (calculated)	1.604 Mg/m^3	
Absorption coefficient	3.194 mm^{-1}	
F(000)	2808	
Crystal habitus	prism (colorless)	
Crystal size	0.191 x 0.185 x 0.062 mm^3	
Theta range for data collection	1.761 to 28.280°	
Index ranges	-21<=h<=19, -16<=k<=16, -39<=l<=39	
Reflections collected	312494	
Independent reflections	14524 [R(int) = 0.0640]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14524 / 199 / 876	
Goodness-of-fit on F^2	1.242	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1108	
R indices (all data)	R1 = 0.0557, wR2 = 0.1126	
Largest diff. peak and hole	2.095 and -1.438 e.Å^{-3}	
Solution	SHELXS-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)	
Refinement	SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)	
Interface	OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)	

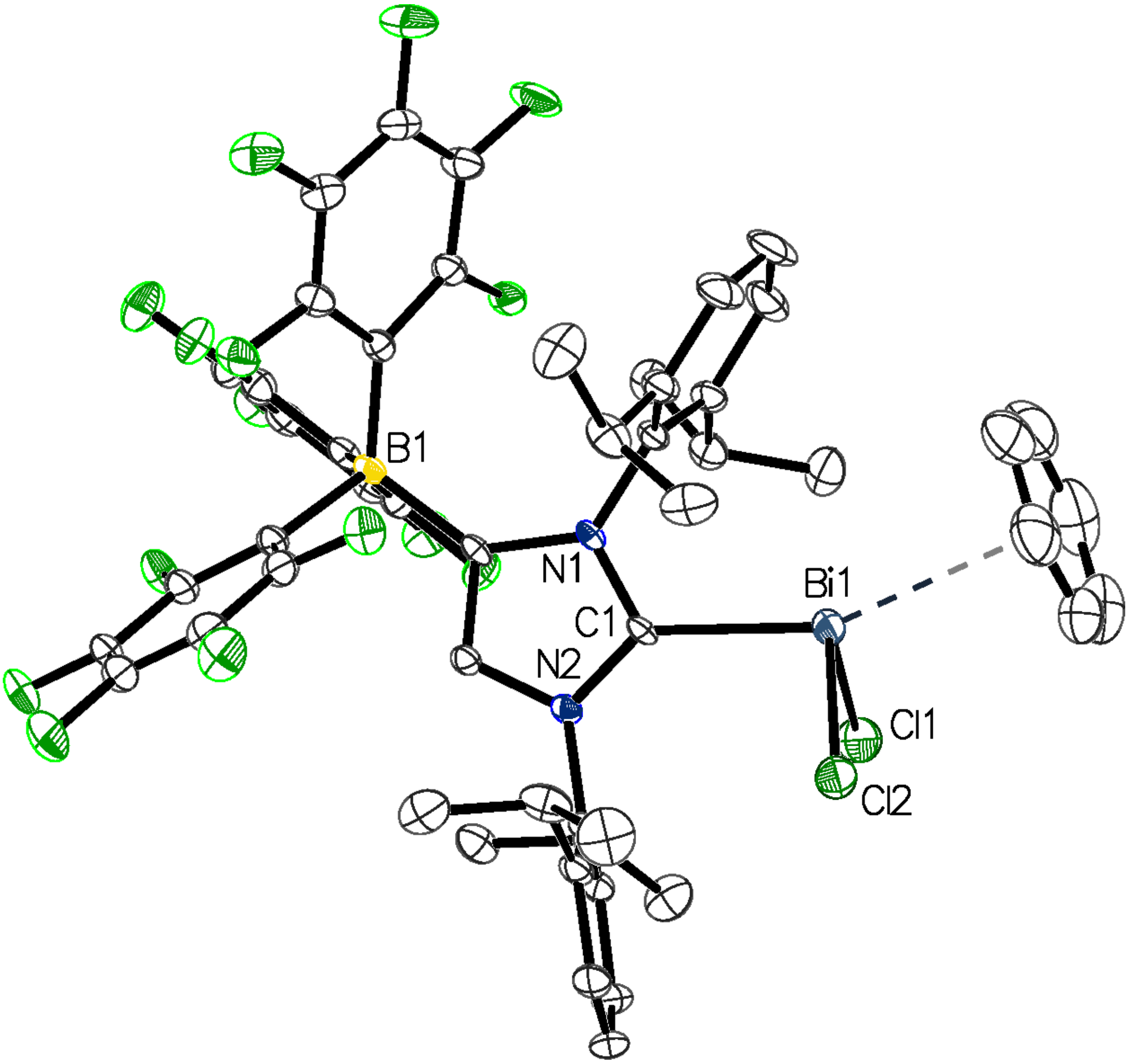


Figure S1. Molecular structure of (WCA-IDipp)BiCl$_2$·C$_6$H$_6$ (**2**·C$_6$H$_6$); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and non-coordinated solvent molecules are omitted for clarity.

S3.2 (WCA-IDipp)$_2$Bi$_2$ (3)

Table S2 Crystallographic data for compound **3.**

Compound	**3**	
Identification code (CCDC)	2050052	
Empirical formula	C51H41BBiF15N2	
Formula weight	1186.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Instrument (scan mode)	XtaLAB Synergy, Single source at offset/far, HyPix (w scan)	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 15.4427(2) Å	a= 90°
	b = 12.47520(10) Å	b= 96.8350(10)°
	c = 24.6006(2) Å	g = 90°
Volume	4705.64(8) Å3	
Z	4	
Density (calculated)	1.675 Mg/m3	
Absorption coefficient	3.845 mm-1	
F(000)	2336	
Crystal habitus	prism (clear purple)	
Crystal size	0.419 x 0.127 x 0.047 mm3	
Theta range for data collection	1.482 to 35.949°	
Index ranges	-25<=h<=25, -20<=k<=18, -40<=l<=40	
Reflections collected	375218	
Independent reflections	21102 [R(int) = 0.0690]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.386	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	21102 / 42 / 639	
Goodness-of-fit on F2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0556, wR2 = 0.1292	
R indices (all data)	R1 = 0.0840, wR2 = 0.1401	
Largest diff. peak and hole	4.361 and -1.194 e.Å-3	
Solution	SHELXS-2014/5 (G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8)	
Refinement	SHELXL-2018/3 (G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122)	
Interface	OLEX2 v1.2 (O. V. Dolomanov et al., J. Appl. Cryst., 2009, 42, 339-341)	

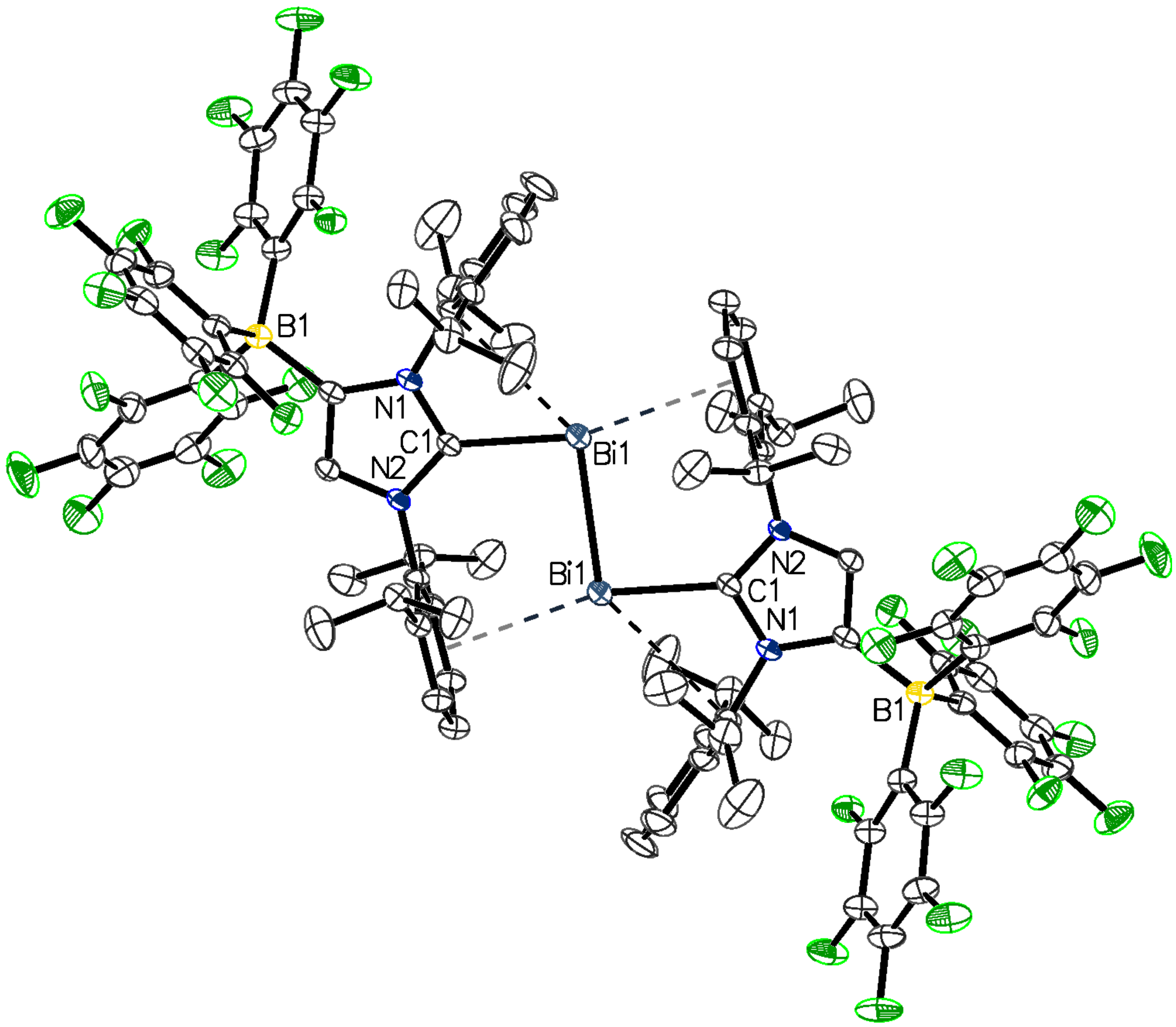


Figure S2. Molecular structure of (WCA-IDipp)$_2$Bi$_2$ (**3**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and non-coordinated solvent molecules are omitted for clarity.

S4 ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra

S4.1 (WCA-IDipp)BiCl$_2$·C$_6$H$_6$ (2)

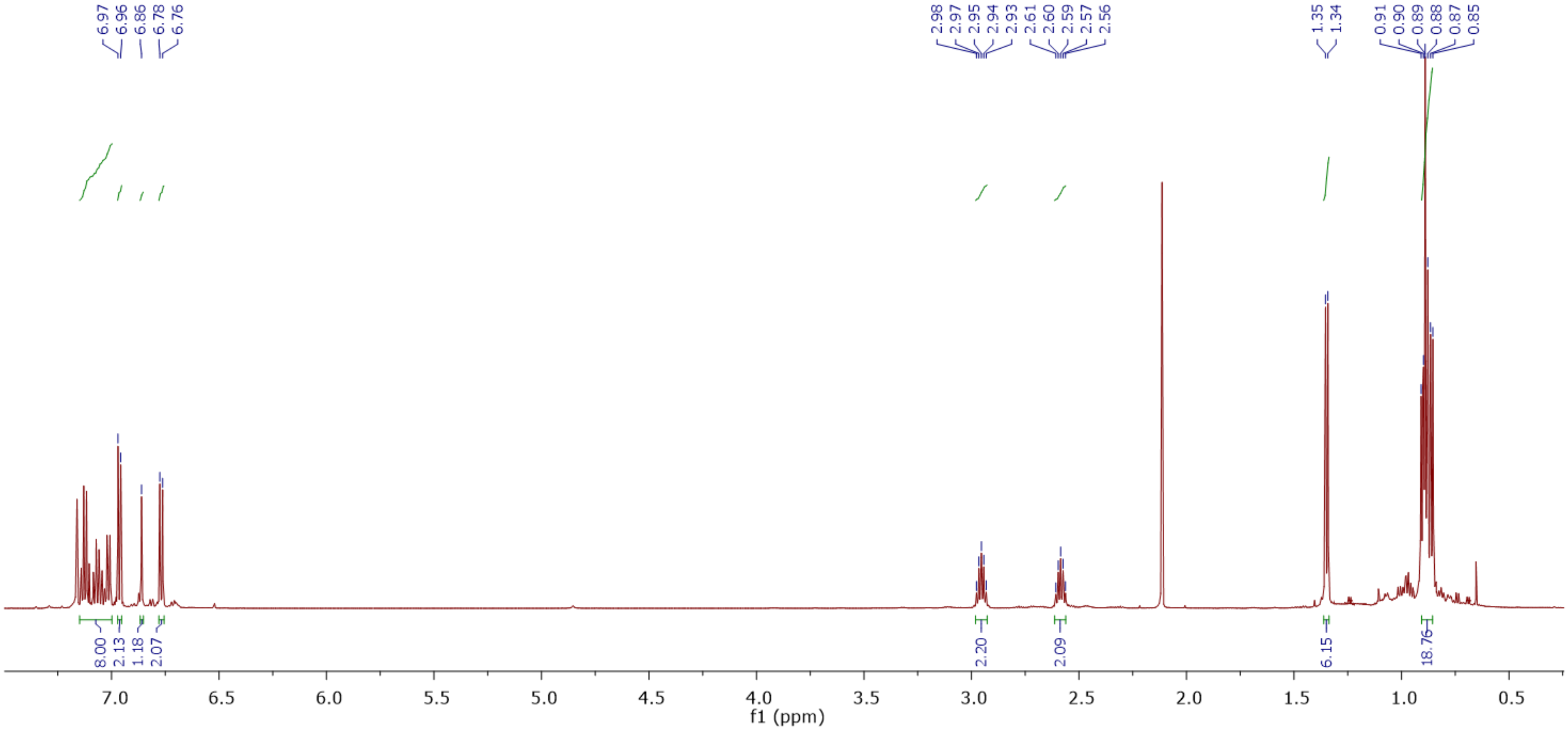


Figure S3. ^{1}H NMR spectrum (600 MHz; C$_6$D$_6$, 278 K) of (WCA-IDipp)BiCl$_2$ (**2**).

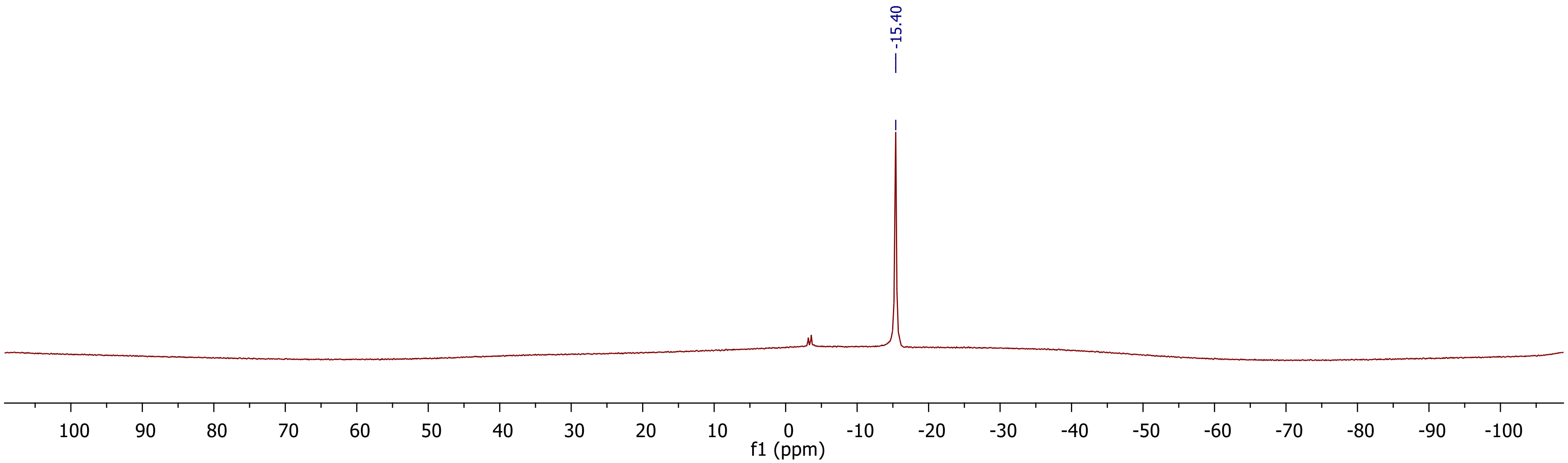


Figure S4. ^{11}B NMR spectrum (96 MHz; C_6D_6, 278 K) of (WCA-IDipp)$BiCl_2$ (**2**).

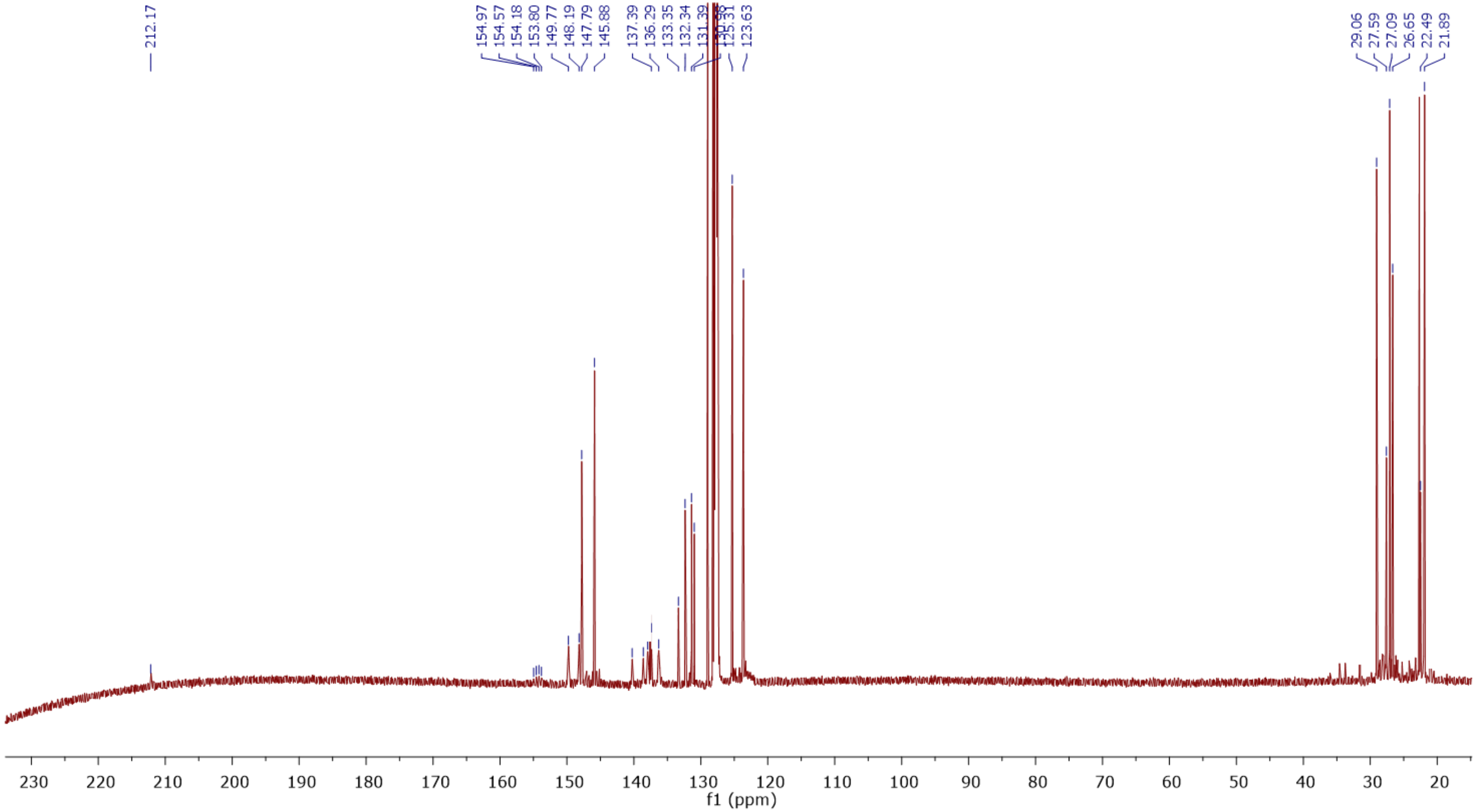


Figure S5. ^{13}C NMR spectrum (151 MHz, C_6D_6, 278 K) of (WCA-IDipp)BiCl$_2$ (**2**).

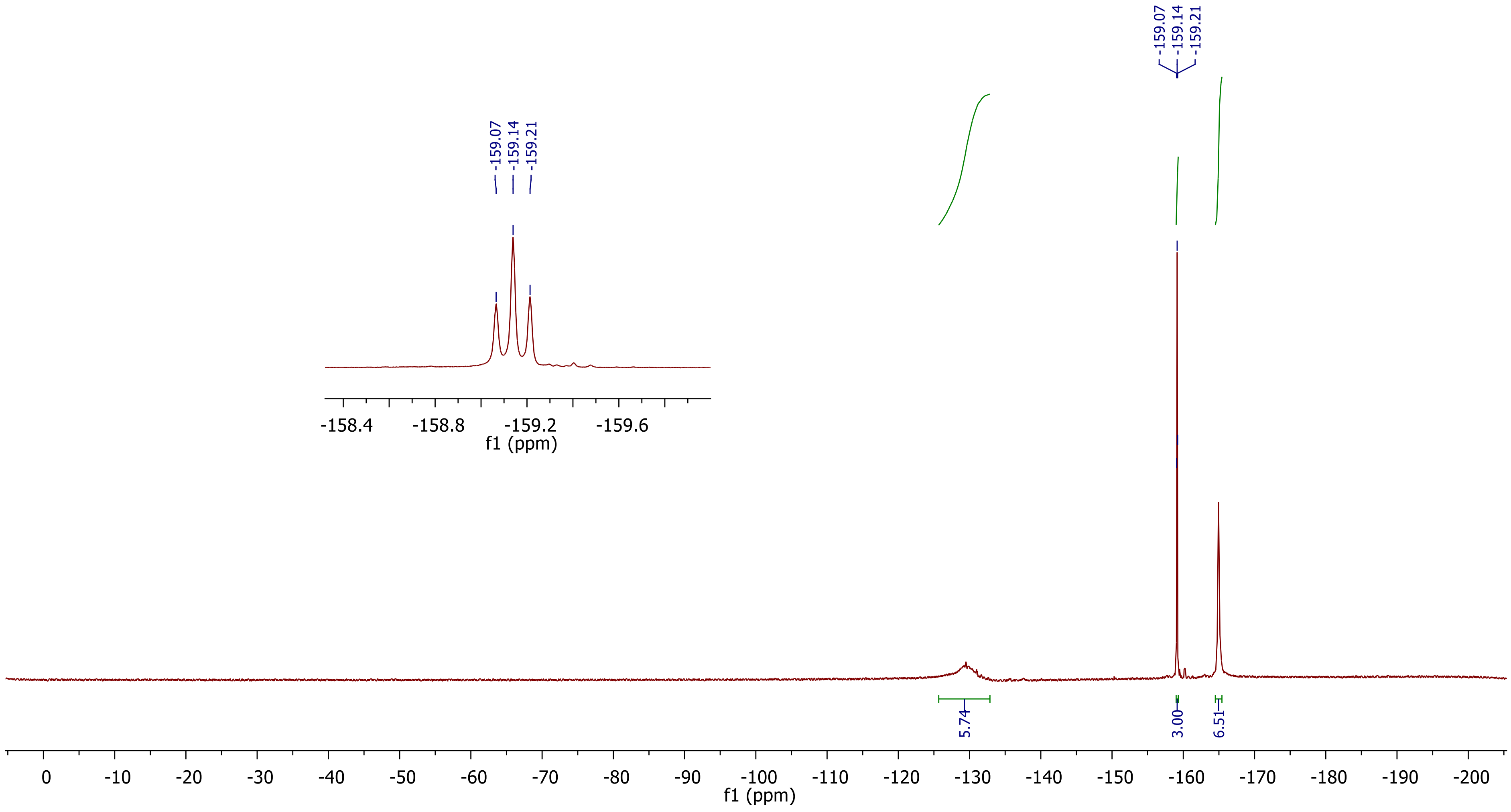


Figure S6. ^{19}F NMR spectrum (282 MHz, C_6D_6, 278 K) of (WCA-IDipp)BiCl$_2$ (**2**).

S4.2 (WCA-IDipp)$_2$Bi$_2$ (3)

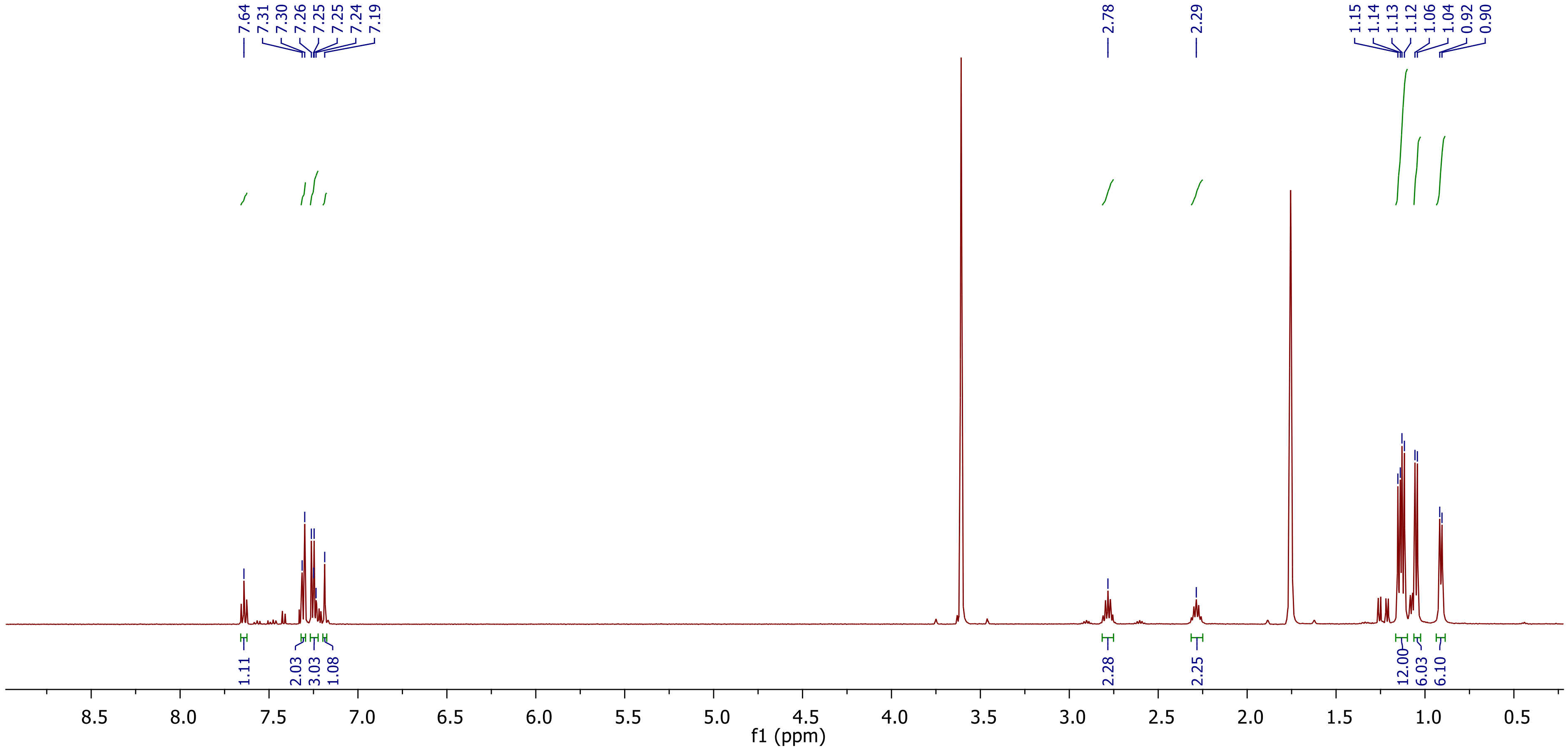


Figure S7. ^{1}H NMR spectrum (600 MHz, THF-d_8, 278 K) of (WCA-IDipp)$_2$Bi$_2$ (**3**).

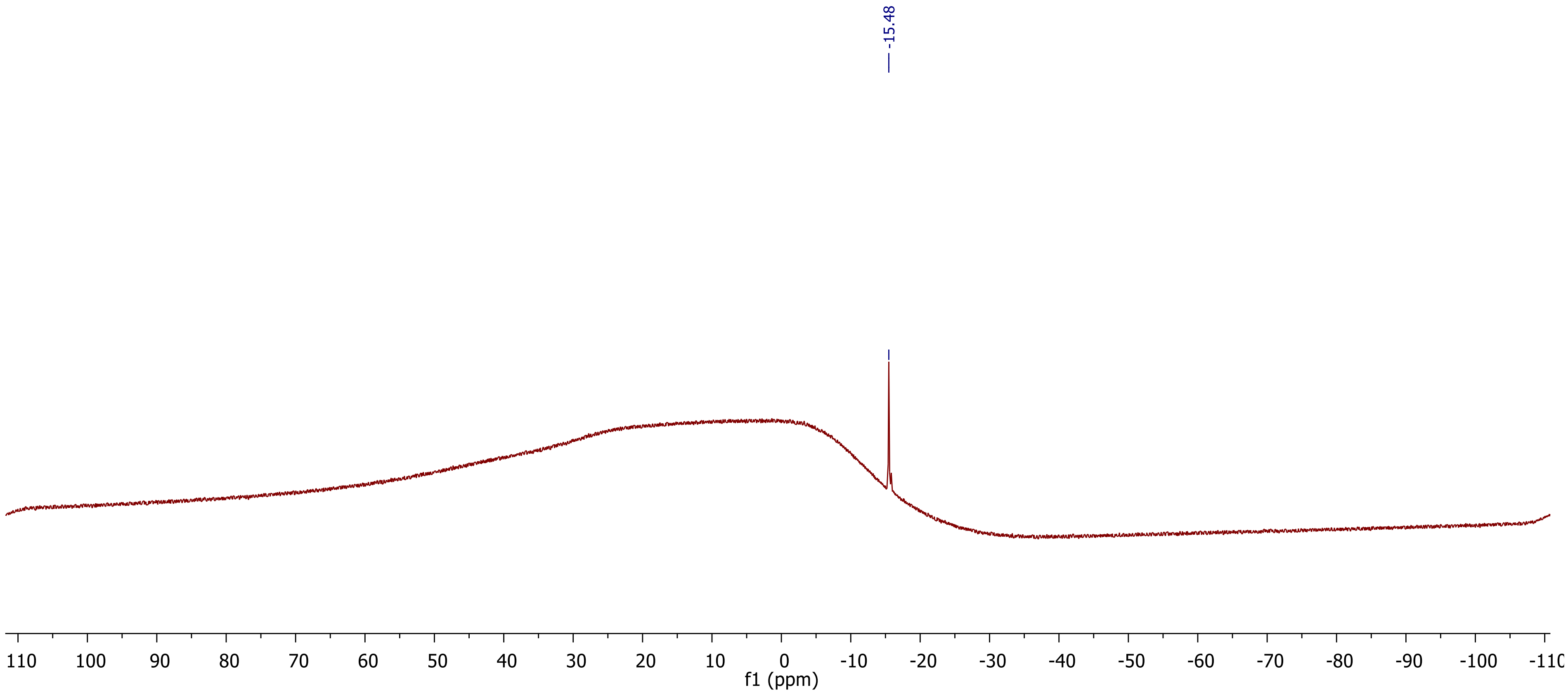


Figure S8. ^{11}B NMR spectrum (96 MHz, THF-d_8, 278 K) of (WCA-IDipp)$_2$Bi$_2$ (**3**).

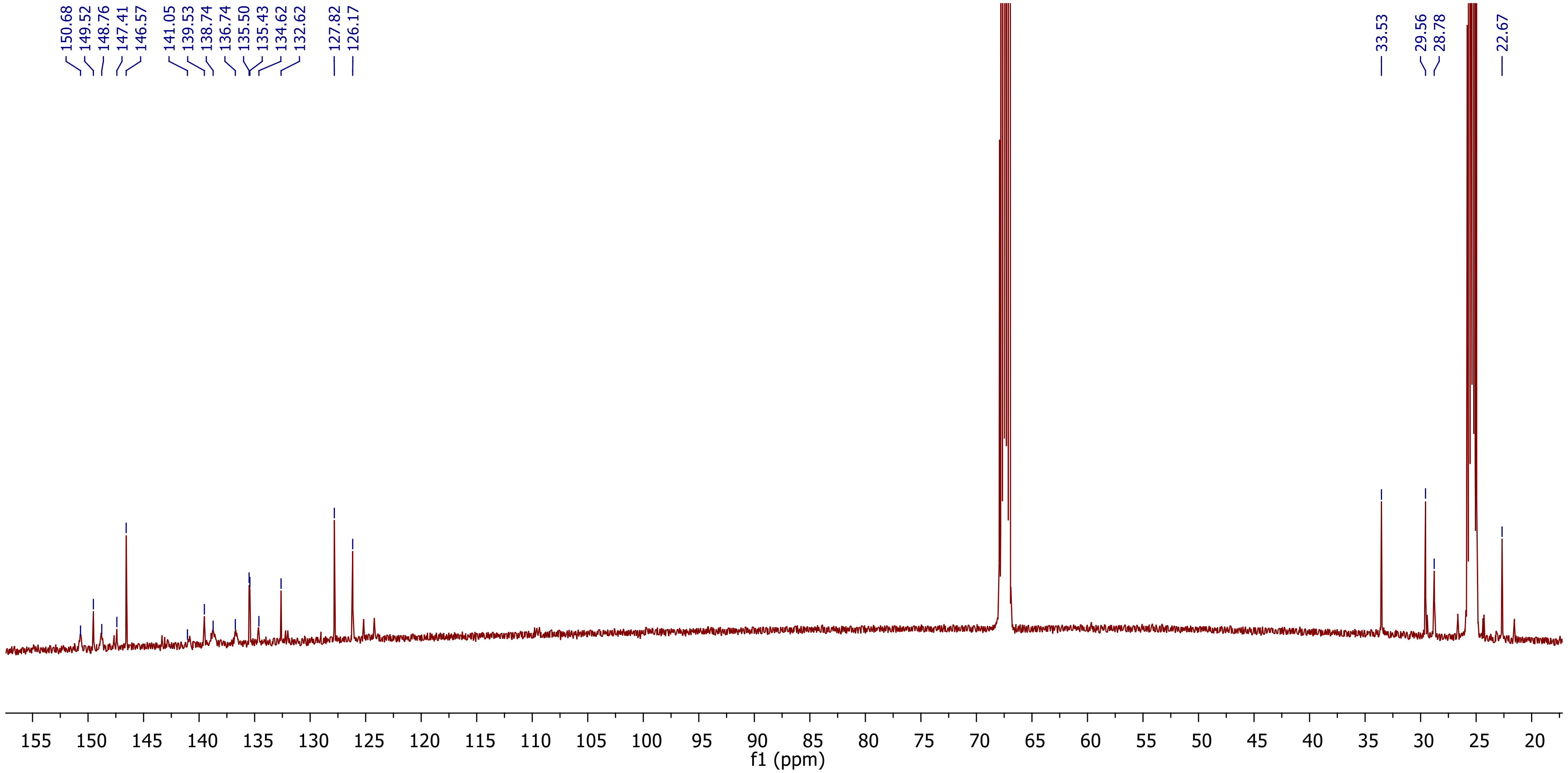


Figure S9. ^{13}C NMR spectrum (151 MHz, C_6D_6, 278 K) of (WCA-IDipp)$_2$Bi$_2$ (**3**).

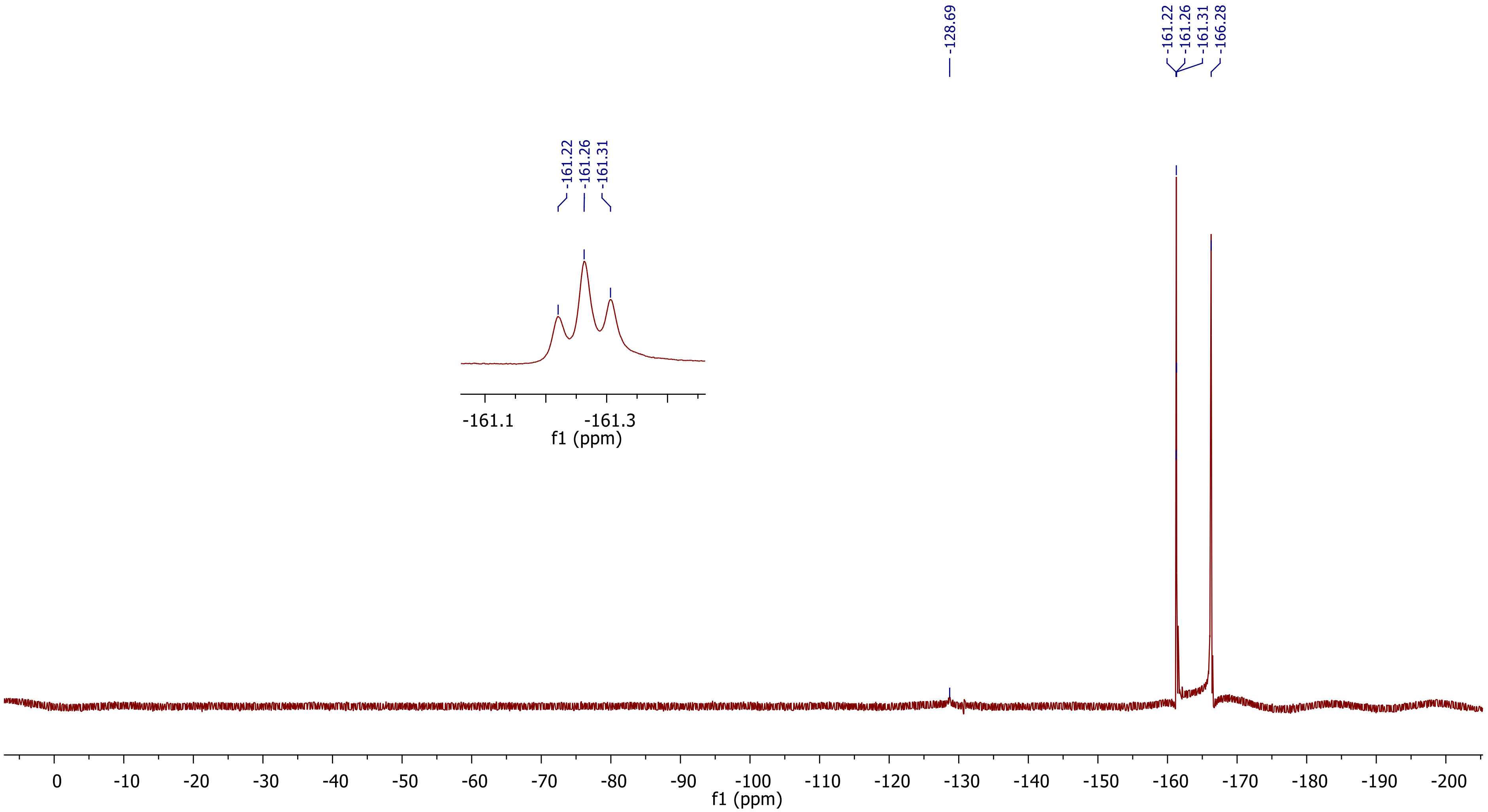


Figure S10. ^{19}F NMR spectrum (282 MHz, THF-d_8, 278 K) of (WCA-IDipp)$_2$Bi$_2$ (**3**).

S5 UV/Vis spectra of (WCA-IDipp)$_2$Bi$_2$ (3)

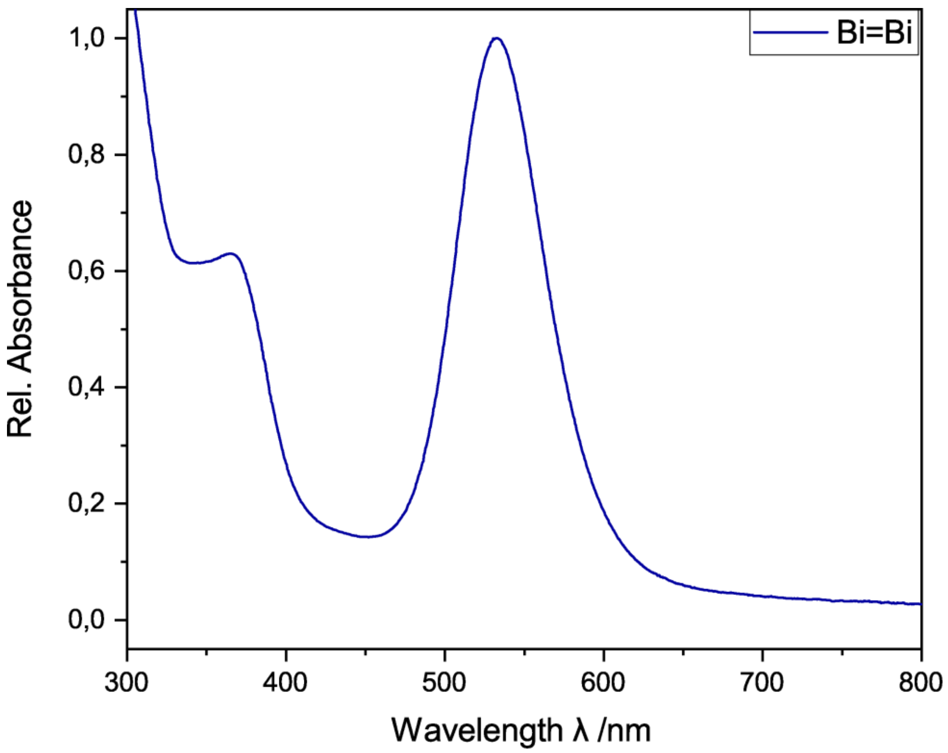
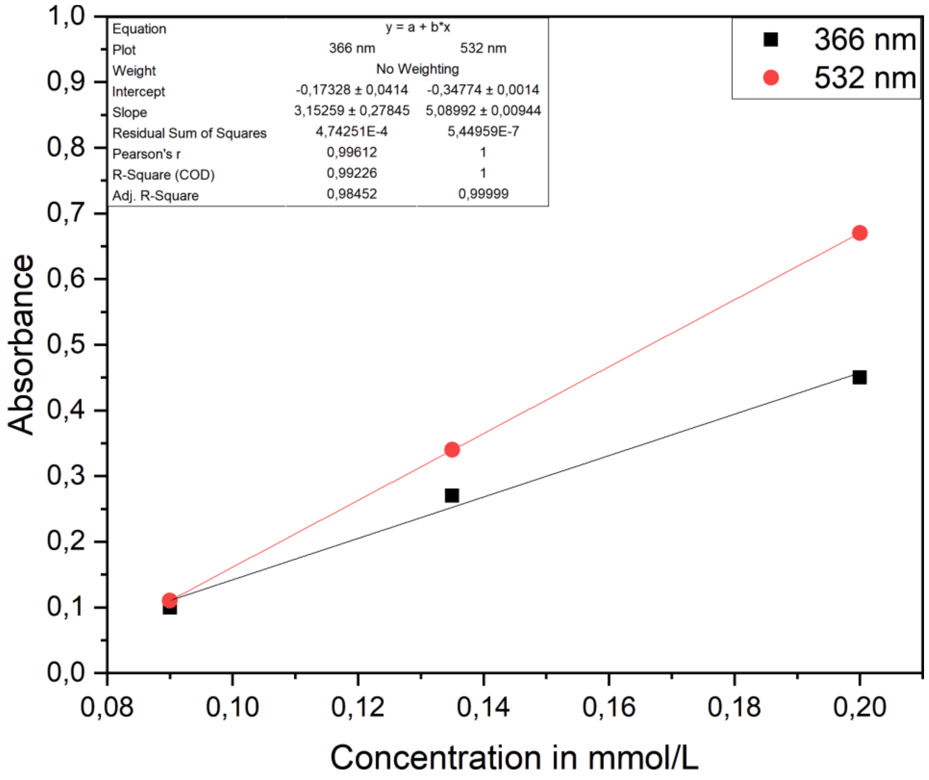


Figure S11. UV/Vis spectrum of (WCA-IDipp)$_2$Bi$_2$ (**3**, $2 \cdot 10^{-4}$ M) in THF at room temperature.



Equation	y = a + b*x	
Plot	366 nm	532 nm
Weight	No Weighting	
Intercept	-0,17328 ± 0,0414	-0,34774 ± 0,0014
Slope	3,15259 ± 0,27845	5,08992 ± 0,00944
Residual Sum of Squares	4,74251E-4	5,44959E-7
Pearson's r	0,99612	1
R-Square (COD)	0,99226	1
Adj. R-Square	0,98452	0,99999

Figure S12. Absorbances at 366 and 532 nm for a dilution series with linear fits.

S6 References

[1] L. P. Ho, A. Nasr, P. G. Jones, A. Altun, F. Neese, G. Bistoni and M. Tamm, *Chem. Eur. J.*, 2018, **24**, 18922–18932.
[2] a) R. A. Sulzbach and A. F. M. Iqbal, *Angew. Chem.*, 1971, **83**, 145; b) P. K. Majhi, H. Ikeda, T. Sasamori, H. Tsurugi, K. Mashima and N. Tokitoh, *Organometallics*, 2017, **36**, 1224–1226.
[3] CrysAlisPRO, Oxford Diffraction/Agilent Technologies UK Ltd, Yarnton, England.
[4] Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.