Supporting Information for

Balancing transmetalation and CF_2 α-elimination barriers in organobismuth-catalyzed olefin difluorocarbenation

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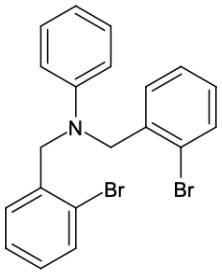
1. General Comments on Experimental Details

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques or an Innovative Technology Inc. glovebox. All reagents and solvents were purchased from commercial suppliers. Solvents were purified through an alumina column solvent system and further dried with molecular sieves. Column chromatography was performed with 35-70 mesh silica gel using flash column techniques or Combiflash© NextGen System. Distillation was performed with Kugelrohr Buchi B-585 glass oven. The ^{1}H, ^{13}C and ^{19}F NMR characterization of novel compounds was performed with Agilent DD2 600 MHz. The previously reported compounds were recorded with Agilent DD2 300 MHz. The reactions in the reaction studies section were monitored by Agilent DD2 300 MHz via ^{1}H and ^{19}F NMR. Chemical shifts for ^{1}H, ^{13}C and ^{19}F and are given in parts per million (ppm); ^{1}H and ^{13}C were referenced internally according to the residual solvent resonances. Coupling constants are given in Hertz (Hz) and the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; brs, broad singlet; app, apparent. **1-CF$_3$**, **A-CF$_3$**, and **B-CF$_3$** were synthesized according to our procedures [Louis-Goff 2022]. 10-Fluoro-5-((trifluoromethyl)imino)-5,10-dihydro-5,l4-dibenzo[*b*,*e*][1,4]thiabismine-5-oxide (**4-F**) was synthesized according to a previously reported procedure by Planas and coworkers [Planas 2020]. Chlorobis(2,4,6-triisopropylphenyl)bismuthine (**C-Cl**) was synthesized according to a procedure by Matano and coworkers [Matano 1992].

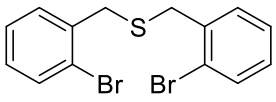
2. Syntheses of ligands L2, L3, L5, L6 and L7

N,*N*-bis(2-bromobenzyl)aniline (**L2**)



N,*N*-bis(2-bromobenzyl)aniline (**L2**) was prepared from a modified procedure [Zhang 2021]. In a Schlenk flask equipped with a Teflon valve, 2-bromobenzyl bromide (15.00 g; 60.02 mmol), potassium carbonate (7.84 g; 56.73 mmol) and aniline (2.40 g; 25.77 mmol) were combined and suspended in 120 mL of DMF and stirred overnight for 16 h at 120°C. After the reaction was completed, the mixture was poured into water (150 mL) and extracted with EtOAc (60 mL x 3). The combined organic layers were washed with water (70 mL x 4) and a saturated brine solution (70 mL x 1), then dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo*. The crude product was purified by recrystallization using a mixture of solvents hexane:EtOAc (20:1). The final product (7.22 g; 16.75 mmol) was obtained as a white solid in 65% yield. The NMR spectra of **L2** are consistent with the original report [Zhang 2021].

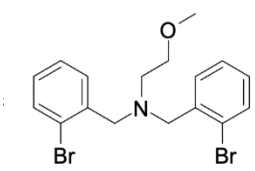
bis(2-bromobenzyl)sulfane (**L3**)



Bis(2-bromobenzyl)sulfane (**L3**) was prepared via modified procedures previously reported [Zhang 2009, Liu 2018]. 2-Bromobenzyl bromide (53.8 g, 0.215 mol) was placed into a Schlenk flask equipped with a Teflon valve and dissolved in 80 mL of DMF. Sodium sulfide nonahydrate (26.41 g, 0.110 mol) was added to this solution and the reaction mixture was then stirred at 100 °C for 16 hours. After, the solvent was removed *in vacuo*. Brine (40 mL) was added to the residue and the mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$ and filtered through a silica gel plug. After that, the filtrate was concentrated *in vacuo*, and the obtained crude product was recrystallized from chloroform

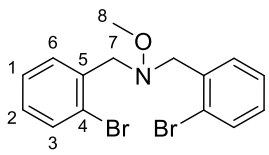
layered with hexanes affording the product **L3** as a pale-yellow powder (27.16 g, 72.99 mmol) in 68% yield. The NMR spectra of **L3** are consistent with the original report [Liu 2018].

N,*N*-bis(2-bromobenzyl)-2-methoxyethan-1-amine (***L5***)



N,*N*-bis(2-bromobenzyl)-2-methoxyethan-1-amine (**L5**) was prepared from a modified procedure [Toma 2017]. A water solution (50 mL of water) of NaOH (7.35 g; 183.76 mmol) was added to a 500 mL round bottom and cooled down to 0°C. Then, 2-bromobenzylbromide (21.00 g; 84.02 mmol) was dissolved in DCM (200 mL) and added to the NaOH solution. Finally, 2-methoxyethanamine (3.00 g; 39.94 mmol) was added and the reaction mixture was stirred at 0°C for 6 hours. Then, the organic phase was separated and washed with water solution of NH_4Cl (1.0 M, 3 x 70 mL) and then dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 1.0 M HCl solution, and the solution was washed with Et_2O (3 x 20 mL). Then, the solution was neutralized with water solution of NaOH (2.0 M, 20 mL) and the desired compound was extracted with DCM (3 x 50 mL). The combined organic layers were then dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo*. The obtained white oil was distilled in Kugelrohr distillation apparatus to give the product **L5** as a dark-brown oil (6.270 g, 15.176 mmol) in 38% yield. The NMR spectra of **L5** are consistent with the original report [Toma 2017].

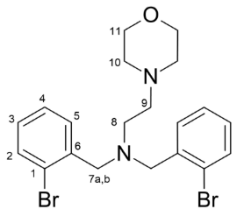
N,*N*-bis(2-bromobenzyl)-*O*-methylhydroxylamine (***L6***)



A solution of *O*-methylhydroxylamine hydrochloride (370 mg, 4.43 mmol) in 15 mL of dimethylformamide (DMF) was added dropwise to a mixture of bromobenzylbromide (5.00 g, 20.0 mmol), triethyl amine (2.02 g, 20.0 mmol), and NaI (20 mg, 0.13 mmol) in a Schlenk flask equipped with a Teflon valve. The reaction mixture was stirred at 120 °C for 2 days and then cooled to room temperature. The reaction mixture was then quenched with water, and the crude product was extracted with Et_2O (4 x 10 mL) and the combined organic phase was washed with D.I. water (2 x 10 mL), brine (1 x 10 mL), dried over $MgSO_4$ and filtered through celite and concentrated *in vacuo*. The crude oil was then run through a silica column with a gradient of pure hexanes for 10 minutes, and a slow increase to 1:19 hexanes: ethyl acetate over 15 minutes. The pure fractions were combined and concentrated *in vacuo* affording the product **L6** as a yellowish oil (1.65 g, 4.28 mmol) in 97% yield.

Yellowish oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 30°C): δ 7.56 (dd, J = 7.6, 0.8 Hz, 2H, H_3), 7.54 (dd, J = 7.6, 1.4 Hz, 2H, H_6), 7.29 (ddd, J = 7.6, 7.6, 0.8 Hz, 2H, H_2), 7.14 (ddd, J = 7.6, 7.6, 1.4 Hz, 2H, H_1), 4.05 (s, 4H, H_7), 3.16 (s, 3H, H_8). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C)**:** δ 136.8 (C_4), 132.7 (C_3), 132.0 (C_6), 128.8 (C_1), 127.0 (C_2), 125.0 (C_5) 61.9 (C_7), 61.1 (C_8). **HRMS Calc. for $C_{15}H_{15}Br_2NO$ [M+H]$^+$**: 382.9508, **Found**: 382.952.

N,N-bis(2-bromobenzyl)-2-morpholinoethan-1-amine (***L7***)



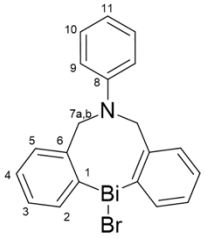
In a Schlenk flask equipped with a Teflon valve, 2-bromobenzyl bromide (4.23 g, 16.92 mmol), potassium carbonate (2.34 g; 16.93 mmol), 4-(2-aminoethyl)morpholine (1.00 g; 7.68 mmol) and 60 mL of DMF were combined and the reaction mixture was stirred overnight (16 h) at 120°C. After the reaction was completed, the reaction mixture was poured into water (60 mL) and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water (4 x 40 mL) and brine (1 x 40 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo*. The obtained yellow oil was distilled in Kugelrohr apparatus to give the product **L7** as a dark-brown oil (1.91 g, 4.08 mmol) in 53% yield.

Dark-brown oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 30°C): δ 7.62 (dd, *J* = 1.3, 7.7 Hz, 2H, H_2), 7.50 (dd, *J* = 1.0, 8.0 Hz, 2H, H_5), 7.28-7.25 (m, 2H, H_4), 7.08 (app dt, 2H, H_3), 3.79 (s, 4H, H_{7ab}), 3.67 (app t, 4H, H_{11}), 2.70 (app t, 2H, H_8), 2.54 (app t, 2H, H_9), 2.39 (m, 4H, H_{10}). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C): δ 138.6(C_6), 132.6(C_2), 130.4(C_5), 128.2(C_3), 127.2(C_4), 124.1(C_1), 66.8(C_{11}), 58.5(C_{7ab}), 56.7(C_9), 53.9(C_{10}), 51.1(C_8). **HRMS Calc. for $C_{20}H_{24}Br_2N_2O$ [M]$^+$**: 466.02554, **Found**: 466.02544.

3. Syntheses of organobismuths 2, 3, 4, 5, 6, 7 and C

General comment for the synthesis of Bi-CF_3 complexes: In many cases, the TMS-CF_3 reagent had to be added in portions followed by checking the reaction conversion with ^{19}F NMR. This is due to a fast side reaction, CF_2 dimerization, forming CF_2=CF_2.

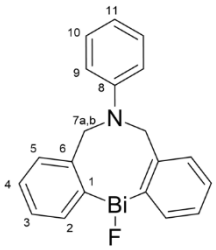
2-Br



$(2\text{-}BrC_6H_4CH_2)_2PhN$ (**L2**) (5.36 g, 12.43 mmol) was dissolved in 15 mL of THF and added dropwise into a mixture of magnesium powder (0.79 g; 32.50 mmol) and THF (25 mL) in a Schlenk flask equipped with a Teflon valve under nitrogen atmosphere. Then, anthracene (0.05 g, 0.28 mmol) was added, and the reaction was stirred at RT for 16 h overnight. The formed suspension was filtered through a cotton plug to remove excess magnesium powder and the filtrate was added dropwise into a well agitated THF (35 mL) solution of $BiBr_3$ (7.81 g; 17.41 mmol) in a separate Schlenk flask. The reaction mixture was stirred under nitrogen at RT for 16 h overnight, then filtered through celite, the celite was washed with DCM (3 x 30 mL), and then the combined filtrate was concentrated *in vacuo*. The obtained solid was dissolved in DCM (80 mL) and filtered through a silica gel plug. The plug was washed with DCM (3 x 30 mL) and the filtrate was concentrated *in vacuo*. Lastly, the formed solid residue was washed with EtOAc (3 x 25 ml) and dried *in vacuo* affording the product **2-Br** with entrapped DCM in ratio ~1:0.1 as a light-green solid (2.09 g, 3.67 mmol) in 30% yield.

^{1}H NMR (600 MHz, $CDCl_3$, 21°C): δ 8.84 (dd, *J* = 7.5 Hz, 2H, H_2), 7.55 (t, *J* = 7.4 Hz, 2H, H_3), 7.51(d, *J* = 7.4 Hz, 2H, H_5), 7.42 (dt, *J* = 1.9, 7.4, 2H, H_4), 7.34-7.31 (m, 2H, H_{10}), 7.22 (d, *J* = 7.9 Hz, 2H, H_9), 7.15 (t, *J* = 7.4 Hz, 1H, H_{11}), 4.85 (d, *J* = 15.0 Hz, 2H, H_{7a}), 4.62 (d, *J* = 15.0 Hz, 2H, H_{7b}). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 21°C): δ 169.6 (C_1), 148.4 (C_8), 147.9 (C_6), 140.3 (C_2), 132.0 (C_3), 129.8 (C_{10}), 128.4 (C_4), 128.0 (C_5), 125.1 (C_{11}), 119.1 (C_9), 63.1 (C_{7ab}). **Anal. Calc. for $BiC_{20}H_{17}BrN{\cdot}0.1CH_2Cl_2$**: C, 42.45; H, 3.05; N, 2.46. **Found**: C, 42.28; H, 3.22; N, 2.63.

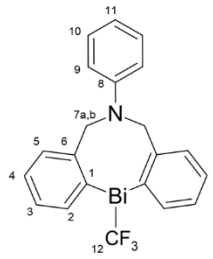
2-F



AgF (270 mg; 2.14 mmol) was added under nitrogen atmosphere to a stirred solution of PhN(2-Br$C_6H_4CH_2)_2$BiBr **2-Br** (1.00 g; 1.79 mmol) in DCM (20 mL) in a Schlenk flask equipped with a Teflon valve. The reaction flask was sealed, covered in aluminium foil, and stirred overnight (16 h) at 60°C. After that, the reaction mixture was filtered through celite with DCM, the celite was washed with DCM (3 x 10 mL) and the combined filtrates were concentrated *in vacuo*. The crude product was purified by recrystallization using a mixture of solvent DCM:Pentane (1:2), affording the final product **2-F** (0.64 g, 1.28 mmol) as off-grey crystals in 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$, 30°C): δ 8.24 (d, J = 7.3 Hz, 2H, H_2), 7.60 (app t, 2H, H_3), 7.51(d, J = 7.5 Hz, 2H, H_5), 7.34-7.30 (m, 4H, $H_{10,4}$), 7.20 (d, J = 8.2 Hz, 2H, H_9), 7.13 (t, J = 7.4 Hz, 1H, H_{11}), 4.83 (d, J = 15.0 Hz, 2H, H_{7a}), 4.56 (d, J = 15.0 Hz, 2H, H_{7b}). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C): δ 181.6 (d, J = 11.4 Hz, C_1), 148.8 (C_8), 148.0 (C_6), 135.5 (d, J = 2.9 Hz, C_2), 130.8 (C_3), 129.7 (C_{10}), 128.4 (C_5), 128.1 (C_4), 124.7 (C_{11}), 118.7 (C_9), 63.2 (C_{7ab}). **^{19}F NMR** (564 MHz, $CDCl_3$, 30°C): δ -200.4. **Anal. Calc. for BiC$_{20}$H$_{17}$FN**: C, 48.11; H, 3.43; N, 2.81. **Found**: C, 47.01; H, 3.51; N, 2.67. An attempt to obtain EA has failed perhaps due to contamination of the product with an inorganic salt (AgF or AgBr).

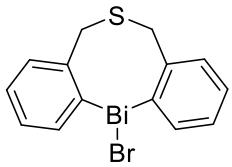
2-CF$_3$



In a Schlenk flask equipped with a Teflon valve, PhN(2-Br$C_6H_4CH_2)_2$BiF (**2-F**) (290 mg; 0.58 mmol) was dissolved in 10 mL of DCM under nitrogen atmosphere. The TMS-CF_3 (130 mg; 0.91 mmol) was added to the solution and the reaction mixture was sealed and stirred at 60°C for 1 day. After that, the reaction mixture was concentrated *in vacuo* to dryness and the solid was crystalized by slow evaporation of acetonitrile (10 mL), affording PhN(2-Br$C_6H_4CH_2)_2$BiCF_3 (**2-CF$_3$**) (0.26 g, 0.47 mmol) as light-brown crystals in 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$, 30°C): δ 8.24 (d, J = 7.3 Hz, 2H, H_2), 7.44-7.42 (m, 4H, $H_{3,5}$), 7.38-7.35(m, 2H, H_4), 7.28-7.25 (m, 2H, H_{10}), 7.10 (d, J = 8.1 Hz, 2H, H_9), 7.02 (t, J = 7.3 Hz, 1H, H_{11}), 4.72 (d, J = 15.2 Hz, 2H, H_{7a}), 4.42 (d, J = 15.2 Hz, 2H, H_{7b}). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C): δ 157.6 (C_1), 148.2 (C_6), 146.4 (C_8), 145.4 (q, $^1J_{CF}$ = 395 Hz, C_{12}), 139.3 (C_2), 130.8 (C_3), 129.4 (C_{10}), 128.7 (C_5), 128.3 (C_4), 122.8 (C_{11}), 117.9 (C_9), 59.7 (C_{7ab}). **^{19}F NMR** (564 MHz, $CDCl_3$, 30°C): δ -37.6. **Anal. Calc. for BiC$_{21}$H$_{17}$F$_3$N**: C, 45.91; H, 3.12; N, 2.55. **Found**: C, 45.97; H, 3.02; N, 2.63.

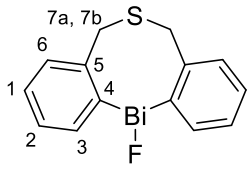
3-Br



3-Br was prepared from a modified procedure [Toma 2016]. The ligand **L3** (4.12 g, 11.07 mmol) was dissolved in Et_2O (180 mL) in a 350 mL Schlenk flask equipped with a Teflon valve and the solution was cooled down to -84 °C. *n*-BuLi (2.40 M, 23.25 mmol, 9.69 mL) was added slowly (over 5 minutes) to the cooled solution. The mixture was stirred at -84 °C for 5 minutes and warmed to room temperature where it stirred for an additional 3.5 hours. Then the solution was cooled down to -84 °C and a solution of $BiBr_3$ (5.47 g, 12.18 mmol) in THF (30 mL) was added to the lithiated ligand. The reaction was allowed to warm

to room temperature overnight. Then the reaction mixture was quenched with water (100 mL) and extracted with toluene (100 mL x 2). The combined organic phases were then dried over $MgSO_4$, filtered over celite, and the filtrate was then concentrated *in vacuo*. The crude product was then dissolved in ethyl acetate (10 mL) and the product **3-Br** was precipitated with hexanes (60 mL) as a yellow solid (1.77 g, 3.54 mmol) in 32% yield. The NMR spectra of **3-Br** are consistent with the original report [Toma 2016].

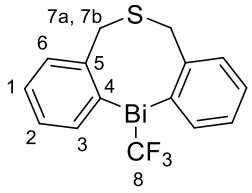
3-F



Under nitrogen atmosphere, **3-CF_3** (25 mg, 0.051 mmol) and cyclooctene (110 mg, 1.00 mmol) were dissolved in 0.5 mL deuterated toluene and transferred to a J-Young NMR tube. Fluorobenzene (48 mg, 0.50 mmol) was added as an internal standard. The reaction NMR tube was then heated at 120 °C and monitored by ^{1}H NMR and ^{19}F NMR. Upon complete conversion of **3-CF_3**, the solution was removed from the NMR tube and solvent, excess cyclooctene, and difluorocyclopropane product were removed *in vacuo* to afford **3-F** (21 mg, 0.043 mmol) as a colorless solid in 86% yield. Crystals suitable for single crystal X-ray crystallography were obtained from slow evaporation of a DCM solution.

White crystalline solid. **^{1}H NMR** (600 MHz, C_6D_6, 30°C): δ 8.75 (d, J = 7.5 Hz, 2H, H_3), 7.30-7.28 (m, 2H, H_2), 6.97-6.94 (m, 4H, $H_{1,6}$), 3.52 (d, J = 15.4 Hz, 2H, H_{7a}), 3.42 (d, J = 15.4 Hz, 2H, H_{7b}). **$^{13}C\{^{1}H\}$ NMR** (150 MHz, C_6D_6, 30°C)**:** δ 180.6 (C_4), 147.1 (C_5), 136.2 (C_3), 130.8 (C_6), 129.9 (C_2), 127.6 (C_1), 41.0 ($C_{7a,b}$). **^{19}F NMR** (564 MHz, C_6D_6, 30°C): δ -178.2. **Anal. Calc. for $BiC_{15}H_{12}SF$**: C, 38.19; H, 2.75. **Found**: C, 39.099; H, 2.738. An attempt to obtain EA has failed perhaps due to contamination of the product with grease or silicon grease.

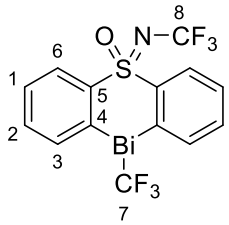
3-CF_3



Under nitrogen atmosphere, **3-Br** (100 mg, 0.20 mmol) and CsF (91 mg, 0.60 mmol) were combined and suspended in THF (2 mL). To this stirring suspension, $TMSCF_3$ (0.15 mL, 1.01 mmol) was added and the mixture was stirred at RT for 4-5 hours. Then, $TMSCF_3$ (0.15 mL, 1.01 mmol) was added again and the reaction was stirred at RT for 1 additional hour. The reaction was monitored by ^{1}H NMR and ^{19}F NMR. Upon complete conversion of the starting bismuth bromide, the solvent was removed *in vacuo*. The obtained solid was dissolved in DCM (5 mL), filtered over Celite, and the filtrate was concentrated *in vacuo*. Then the product was recrystallized from Et_2O (3 mL) by slow evaporation of Et_2O at -30 °C affording the product **3-CF_3** as white crystals (23 mg, 0.04 mmol, 23%).

^{1}H NMR (600 MHz, $CDCl_3$, 60°C) δ 8.30 (d, J = 7.5 Hz, 2H, H_3), 7.45 (d, J = 7.5 Hz, 2H, H_6), 7.41 (app t, J = 7.5 Hz, 2H, H_2), 7.35 (app t, J = 7.5 Hz, 2H, H_1), 4.08 (d, J = 14.8 Hz, 2H, H_{7a}), 3.93 (d, J = 14.8 Hz, 2H, H_{7b}). **$^{13}C\{^{1}H\}$ NMR** (150 MHz, $CDCl_3$, 60°C) δ 160.8 (C_4), 149.0 (q, J = 397.3 Hz, C_8), 145.4 (C_5), 139.4 (C_3), 131.7 (C_6), 130.2 (C_2), 128.4 (C_1), 37.9($C_{7a,b}$). **^{19}F NMR** (564 MHz, $CDCl_3$, 60°C) δ -37.3 (s, $^{12}CF_3$), -37.44 (d, $^{1}J_{CF}$ = 394 Hz, $^{13}CF_3$). **Anal. Calc. for $BiC_{15}H_{12}SF_3$**: C, 36.75; H, 2.47. **Found**: C, 37.12; H, 2.48.

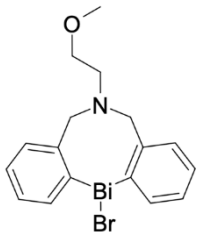
4-CF₃



Under nitrogen atmosphere, the bismuth fluoride **4-F** (220 mg, 0.430 mmol) was suspended in 5 mL of toluene in a 25 mL pressure flask. (triphenylphosphinio)difluoroacetate (176 mg, 0.494 mmol) was added to the suspension and the mixture was then stirred at 90 °C overnight (15 h) and monitored by ^{1}H NMR and ^{19}F NMR. After complete full conversion of the starting **4-F**, the mixture was allowed to cool down to room temperature, and the reaction mixture was filtered over celite, and the celite plug was washed with ethyl acetate (3 x15 mL). The volatiles were removed *in vacuo* and the crude product was purified by column chromatography using hexane/dichloromethane (7/3-1/1) as eluent affording the product **4-CF₃** (85 mg, 0.15 mmol) as white solid in 35% yield. Crystals suitable for single crystal XRD were obtained by recrystallization in a mixture of dichloromethane layered with hexane.

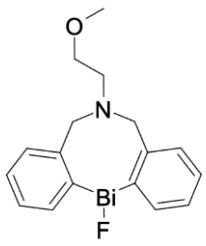
^{1}H NMR (600 MHz, $CDCl_3$, 40°C) δ 8.50 – 8.45 (m, 4H, $H_{3,6}$), 7.67 (app t, J = 7.7 Hz, 2H, H_2), 7.55 (app t, J = 7.7 Hz, 2H, H_1). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 40°C) δ 160.3 (C_4), 157.5 (q, J = 385.6 Hz, C_7), 139.4 (C_5), 136.7 (C_3), 134.7 (C_2), 129.4 (C_1), 129.1 (C_6), 121.6 (q, J = 259.9 Hz, C_8). **^{19}F NMR** (564 MHz, $CDCl_3$, 40°C) δ -38.5 (3F, F_7), -42.0 (3F, F_8). **Anal. Calc. for $BiC_{14}H_8NOSF_6$**: C, 29.96; H, 1.44; N, 2.50. **Found**: C, 30.31; H, 1.63; N, 2.46.

5-Br



5-Br was prepared from a modified procedure [Toma 2017]. (2-$BrC_6H_4CH_2)_2N(CH_2)_2OCH_3$ (**L5**) (6.28 g; 15.20 mmol) and 30 mL of THF was added to a Schlenk flask equipped with a Teflon valve under nitrogen atmosphere. The solution was cooled down to -78°C and freshly titrated solution of *n*-BuLi (1.45M, 33.45 mmol; volume 23.07 mL) was added dropwise. The mixture was stirred at -78°C for 2 hours. Then, a THF (40 mL) solution of $BiCl_3$ (5.26 g; 16.68 mmol) was added at -78°C. The mixture was slowly warmed up to RT and stirred overnight (16 h). Then, the reaction mixture was concentrated *in vacuo*. The residue was diluted with saturated aqueous $NaHCO_3$ (150 mL) and extracted with DCM (3 x 120 mL). The combined organic layer was filtered through a cotton. Then the filtrated was washed with brine (200 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* to give a solid residue. The solid was washed with EtOAc (3 x 10 mL) and concentrated *in vacuo* to afford the product **5-Br** (5.59 g, 10.31 mmol) as a white solid in 68% yield. The NMR spectra of **5-Br** are consistent with the original report [Toma 2017].

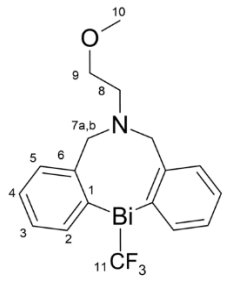
5-F



5-F was prepared from a modified procedure [Toma 2017]. AgF (98 mg; 0.77 mmol) was added under nitrogen atmosphere to a stirred DCM (15 mL) solution of $CH_3O(CH_2)_2N(CH_2C_6H_4)_2BiBr$ (**5-Br**) (350 mg; 0.65 mmol) in a Schlenk flask equipped with a Teflon valve. The reaction flask was sealed, covered with aluminum foil and stirred overnight (16 h) at 60°C. After that, the reaction mixture was filtered through celite with DCM, the celite was washed with DCM (3 x 5 mL) and the combined filtrates were concentrated *in vacuo*. The crude product was purified by

recrystallization using a mixture of solvent DCM:Pentane (1:2), affording the final product **5-F** (170 mg, 0.35 mmol), which was obtained as white crystals in 55% yield. The NMR spectra of **5-F** are consistent with the original report [Toma 2017].

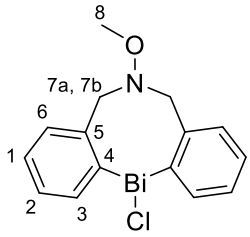
5-CF$_3$



$CH_3O(CH_2)_2N(CH_2C_6H_4)_2BiF$ (**5-F**) (81 mg; 1.68 mmol) and 10 mL of THF was added to a 100 mL round bottom flask under nitrogen atmosphere. Then, CsF (460 mg; 3.03 mmol) and TMS-CF_3 (280 mg; 1.97 mmol) were added to the mixture and the reaction mixture was stirred for 2 hours. A second portion of CsF (460 mg, 3.03 mmol) and TMS-CF_3 (280 mg; 1.97 mmol) was added, and the reaction mixture was stirred for 1 hour. Finally, a third portion of TMS-CF_3 (280 mg; 1.97 mmol) was added, and the reaction was stirred overnight (16 h). The next day three more additions of TMS-CF_3 (280 mg; 1.97 mmol) were added each an hour apart. After that, the reaction mixture was concentrated *in vacuo* to dryness. The solid was dissolved in DCM (15 mL) and the reaction mixture was filtered through celite and washed with DCM (3 x 10 mL). The combined filtrate was concentrated *in vacuo*. The obtained solid was crystalized with DCM:Pentane (1:2) affording product **5-CF$_3$** (540 mg, 1.02 mmol) as white crystals in 60% yield.

^{1}H NMR (600 MHz, $CDCl_3$, 30°C): δ 8.28 (d, J = 7.4 Hz, 2H, H_2), 7.38 (app dt, 2H, H_5), 7.32-7.26 (m, 4H, $H_{3,4}$), 4.01 (d, J = 14.8 Hz, 2H, H_{7a}), 3.95 (d, J = 14.8 Hz, 2H, H_{7b}), 3.41 (app t, 2H, H_9), 3.05 (s, 3H, H_{10}), 2.98 (app t, 2H, H_8). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C): δ 159.0(C_1), 148.7 (q, $^1J_{CF}$ = 396.7 Hz, C_{11}), 146.7(C_6), 138.9(C_2), 130.3(C_5), 128.4(C_3), 127.8(C_4), 69.0(C_9), 61.6(C_{7ab}), 58.2(C_{10}), 56.0(C_8). **^{19}F NMR** (564 MHz, $CDCl_3$, 30°C): δ -38.1. **Anal. Calc. for $BiC_{18}H_{19}F_3NO$**: C, 40.69; H, 3.60; N, 2.64. **Found**: C, 40.62; H, 3.47; N, 2.38.

6-Cl

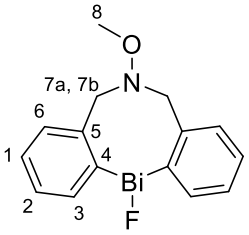


Under nitrogen atmosphere, the ligand **L6** (680 mg, 1.77 mmol) was dissolved in 10 mL THF and transferred into a pressure flask. The solution was cooled to -78 °C and 1.56M *n*BuLi (3.54 mmol, 2.27 mL) hexane solution was added dropwise and stirred for 10 minutes. A solution of $BiCl_3$ (613 mg, 1.94 mmol) in 20 mL of THF was added dropwise to the lithiated solution at -78 °C and stirred for 30 minutes. The cooled solution was then allowed to warm to RT and stirred overnight. The reaction was quenched with saturated $NaHCO_3$ aqueous solution (20 mL) and the total volume of solvent was reduced *in vacuo* to 30 mL. The product was extracted with $CHCl_3$ (4 x 10 mL), and the combined organic layers were dried over $MgSO_4$, filtered through celite, and the filtrate was concentrated *in vacuo*. The obtained solid was then run through a silica column with a gradient of pure hexanes for 5 minutes, and a slow increase to 1:3 hexane: ethyl acetate over 25 minutes. The pure fractions were combined and concentrated *in vacuo* affording the product **6-Cl** (307 mg, 0.654 mmol) as a colorless solid in 37% yield.

White crystalline solid. **^{1}H NMR** (600 MHz, $CDCl_3$, 30°C): δ 8.64 (d, J = 7.4 Hz, 2H, H_3), 7.52 (dd, J = 7.4, 7.4 Hz, 2H, H_2), 7.47 (d, J=7.4 Hz, 2H, H_6), 7.33 (dd, J = 7.4, 7.4, Hz, 2H, H_1), 4.56 (d, J = 15.2 Hz, 2H, H_{7a}), 4.43 (d, J = 15.2 Hz, 2H, H_{7b}), 3.66 (s, 3H, H_8). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C)**:** δ 170.3

(C_4), 146.8 (C_5), 138.2 (C_3), 131.3 (C_2), 128.4 (C_6), 127.8 (C_1) 67.0 ($C_{7a,b}$), 64.0 (C_8). **Anal. Calc. for $BiC_{15}H_{15}NOCl$:** C, 38.36; H, 3.22; N, 2.98. **Found:** C, 38.68; H, 3.14; N, 2.96.

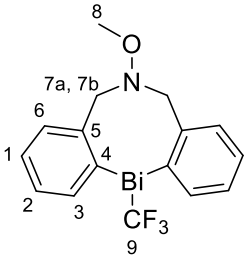
6-F



Under nitrogen atmosphere, **6-CF_3** (25 mg, 0.050 mmol), cyclooctene (110 mg, 1.00 mmol), deuterated toluene (0.5 mL), and fluorobenzene (internal standard) (48 mg, 0.50 mmol) were placed into a J-Young NMR tube. The NMR tube was sealed, and then the reaction mixture was heated at 120 °C and monitored by ^{1}H NMR and ^{19}F NMR. Approximately after 15 h, the full conversion based on ^{19}F NMR was observed. The solution was removed from the NMR tube and the volatiles (solvent, excess cyclooctene, and difluorocyclopropane product) were removed *in vacuo* affording the product **6-F** (20 mg, 0.044 mmol) as a colorless solid in 88% yield. Crystals suitable for single crystal X-ray crystallography were obtained from slow evaporation of a DCM solution.

White crystalline solid. **^{1}H NMR** (600 MHz, $CDCl_3$, 30°C): δ 8.20 (d, J = 7.3 Hz, 2H, H_3), 7.55 (dd, J = 7.5, 7.3, 2H, H_1), 7.45 (d, J = 7.5, 2H, H_6), 7.28 (dd, J = 7.5, 7.3 Hz, 2H, H_2), 4.53 (d, J = 14.9 Hz, 2H, H_{7a}), 4.39 (d, J = 14.9 Hz, 2H, H_{7b}), 3.64 (s, 3H, H_8). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C)**:** δ 177.8 (C_5), 146.8 (C_4), 135.7 (C_3), 130.5 (C_1), 128.3 (C_2), 128.1 (C_6), 67.3 ($C_{7a,b}$), 63.8 (C_8). **^{19}F NMR** (564 MHz, $CDCl_3$, 30°C): δ -189.2. **Anal. Calc. for $BiC_{16}H_{15}NOF_3$:** C, 39.75; H, 3.34; N, 3.09. **Found:** C, 39.94; H, 3.08; N, 3.10.

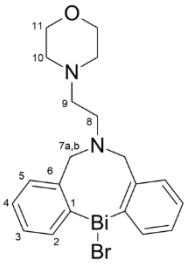
6-CF_3



Under nitrogen atmosphere, **6-Cl** (307 mg, 0.654 mmol) was dissolved in 10 mL of THF and CsF (198 mg, 1.303 mmol) and $TMSCF_3$ (279 mg, 1.96 mmol) were added to this solution. The reaction mixture was stirred for 10 hours, and then additional $TMSCF_3$ (279 mg, 1.96 mmol) was added and the solution was stirred for 3 hours. The full conversion of **6-Cl** was confirmed by ^{1}H NMR, and the solvent was removed *in vacuo*. The solid was dissolved in DCM (volume) and filtered over celite. The filtrate was concentrated *in vacuo*, and the solid was washed over a glass frit filter with a cold methanol (3 x 5 mL). The solid was washed with DCM (volume) through the frit and the filtrate was concentrated *in vacuo* affording the **6-CF_3** (182 mg, 0.362 mmol) as a colorless solid in 55% yield. Crystals suitable for Xray were obtained by recrystallization in DCM/Hexane diffusion at -19 °C.

White crystalline solid. **^{1}H NMR** (600 MHz, $CDCl_3$, 60°C): δ 8.27 (d, J = 7.3 Hz, 2H, H_3), 7.42 (ddd, J = 7.4, 7.4, 0.96 Hz, 2H, H_2), 7.38-7.37 (m, 2H, H_6), 7.33 (ddd, J = 7.4, 7.4, 0.96 Hz, 2H, H_1), 4.33 (d, J = 14.9 Hz, 2H, H_{7a}), 4.19 (d, J = 14.9 Hz, 2H, H_{7b}), 3.61 (s, 3H, H_8). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 60°C)**:** δ 157.1 (C_4), 153.2 (q, $^1J_{CF}$ = 397, C_9), 145.7 (C_5), 138.6 (C_3), 130.5 (C_2), 128.7 (C_6), 128.2 (C_1) 63.5 ($C_{7a,b}$), 63.0 (C_8). **^{19}F NMR** (564 MHz, $CDCl_3$, 60°C): δ -37.82 (s, $^{12}CF_3$), -37.96 (d, $^1J_{CF}$ = 397 Hz, $^{13}CF_3$). **Anal. Calc. for $BiC_{16}H_{15}NOF_3$:** C, 38.18; H, 3.00; N, 2.78. **Found:** C, 38.46; H, 2.84; N, 2.78.

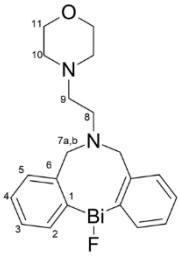
7-Br



$O(CH_2)_4N(CH_2)_2N(CH_2C_6H_4Br)_2$ **L7** (0.79 g; 1.69 mmol) and 30 mL of THF was added to a Schlenk flask equipped with a Teflon valve under nitrogen atmosphere. The solution was cooled down to -78°C and freshly titrated solution of *n*-BuLi (1.45M, 3.87 mmol; volume 2.67 mL) was added dropwise to the solution. The reaction mixture was stirred at -78°C for 2 hours. Then, a THF (20 mL) solution of $BiCl_3$ (0.53 g; 1.7 mmol) was added at -78°C to the reaction mixture. The reaction mixture was slowly warmed up to RT and stirred overnight (16 h). Then, the reaction mixture was filtered through celite, the celite was washed with DCM (3 x 20 mL), and the combined filtrate was concentrated *in vacuo*. The obtained solid was dissolved in DCM (20 mL) and filtered through a silica gel plug (this filtrate was discarded). Then the silica gel plug was washed with 1:1 DCM:MeOH (3 x 20 mL) and the combined filtrate was concentrated *in vacuo*. Then the obtained solid was washed with MeOH (10 mL) dissolved in DCM (20 mL) and the solution was washed with saturated aqueous solution of NaBr (20 mL). The organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* affording the product **7-Br** with entrapped DCM in ratio ~1:1.4 as a white solid (0.64 g, 0.89 mmol) in 53% yield. The sample for EA was crystallized in DCM:Hexane (1:2) and dried *in vacuo*. However, the DCM could be only partially removed to the ~1:0.5 ratio of **7-Br**: DCM (^{1}H NMR of the EA sample is also provided).

^{1}H NMR (600 MHz, $CDCl_3$, 30°C): δ 8.85 (d, *J* = 7.4 Hz, 2H, C_2), 7.45 (app t, 2H, H_3), 7.41 (d, *J* = 7.4 Hz, 2H, H_5), 7.32 (app t, 2H, H_4), 4.32 (d, *J* = 14.9 Hz, 2H, H_{7a}), 4.10 (d, *J* = 14.9 Hz, 2H, H_{7b}), 3.61 (app t, 4H, H_{11}), 3.13-3.12 (m, 2H, H_8), 2.35-2.33 (m, 2H, H_9), 1.95 (app t, 4H, H_{10}). **^{13}C{^{1}H} NMR** (150 MHz, $CDCl_3$, 30°C): δ 172.6(C_1), 147.6(C_6), 139.9(C_2), 131.3(C_3), 127.8(C_4), 127.0(C_5), 66.7(C_{11}), 66.4(C_{7ab}), 56.6(C_8), 54.3(C_9), 53.4(C_{10}). **Anal. Calc. for $BiC_{20}H_{24}BrN_2O\cdot0.5CH_2Cl_2$**: C, 38.49; H, 3.94; N, 4.38. **Found**: C, 38.32; H, 3.76; N, 4.27. **HRMS Calc. for $BiC_{20}H_{24}BrN_2O$ [M]$^+$**: 596.08759. **Found**: 596.08696.

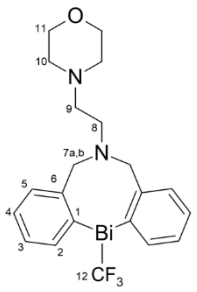
7-F



$O(CH_2)_4N(CH_2)_2N(CH_2C_6H_4)_2BiCF_3$ (**7-CF_3**) (0.32 g; 0.55 mmol), cyclooctene (3. 64 g, 33.03 mmol), and 15 mL of THF were added to a 50 mL Schlenk flask equipped with a Teflon valve under nitrogen atmosphere. The reaction flask was sealed and stirred for 2 days at 120°C. Then, the reaction mixture was concentrated *in vacuo*, and the residue was dissolved in MeCN and filtered through a cotton plug. The filtrate was then concentrated *in vacuo* and the residue was crystalized by slow evaporation of a MeCN (5 mL) solution to obtain the product **7-F** as white crystals (0.19 g, 0.35 mmol) in 65% yield.

^{1}H NMR (600 MHz, CD_3CN, 30°C): δ 8.06(d, *J* = 7.3 Hz, 2H, H_2), 7.45-7.43 (m, 4H, $H_{3,4}$), 7.24 (app dt, 2H, H_5), 4.16 (d, *J*= 15.2 Hz, 2H, H_{7a}), 4.12 (d, *J* = 15.2 Hz, 2H, H_{7b}), 3.54 (app t, 4H, H_{11}), 3.04 (app t, 2H, H_8), 2.24-2.22 (m, 2H, H_9), 1.92-1.90 (m, 4H, H_{10}). **^{13}C{^{1}H} NMR** (150 MHz, CD_3CN, 30°C): δ 183.3(C_1), 150.0(C_6), 135.7(C_2), 130.3(C_3), 128.6(C_4), 128.4(C_5), 67.3(C_{11}), 66.6(C_{7ab}), 57.0(C_8), 55.3(C_9), 54.2(C_{10}). **^{19}F NMR** (564 MHz, CD_3CN, 30°C): δ -174.6. **Anal. Calc. for $BiC_{20}H_{24}FN_2O$**: C, 44.78; H, 4.51; N, 5.22. **Found:** C, 44.80; H, 4.40; N, 5.14.

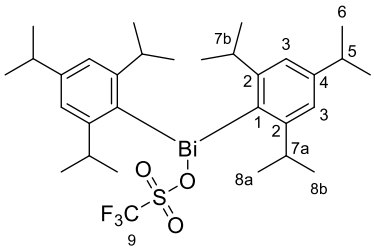
7-CF₃



$O(CH_2)_4N(CH_2)_2N(CH_2C_6H_4)_2BiBr$ (**7-Br**) (0.78 g; 1.31 mmol) and 15 mL of THF were added to a 100 mL round bottom flask under nitrogen atmosphere. Next, CsF (0.40 g; 2.63 mmol) and $TMSCF_3$ (0.56 g; 3.94 mmol) were added to the solution and the reaction mixture was stirred for 2 hours. Then, a second addition of CsF (0.40 g; 2.63 mmol) and $TMSCF_3$ (0.56 g; 3.94 mmol) were added to the reaction mixture and was stirred for 1 hour. A third addition of $TMSCF_3$ (0.56 g; 3.94 mmol) was added to the reaction, and the reaction mixture was stirred overnight (16 h). The following day three more additions of $TMSCF_3$ (0.56 g; 3.94 mmol) were added to the reaction mixture (each addition was followed by one hour of stirring). Then, the reaction mixture was concentrated *in vacuo*. The obtained residue was extracted with benzene (20 mL), the extract was filtered through celite, and the celite was washed with benzene (2 x 15 mL). The combined filtrates were concentrated *in vacuo*. The solid residue was washed with cold EtOH (10 mL) and crystalized by slow evaporation of benzene (3 mL) solution affording the product **7-CF₃** with entrapped C_6H_6 in ratio ~1:1.4 as white crystals (0.50 g, 0.72 mmol) in 55% yield. The sample for EA was further extensively dried *in vacuo* and the C_6H_6 could be only partially removed to a 1:0.4 ratio of **7-CF₃**: C_6H_6 (^{1}H NMR of the EA sample is also provided).

^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 8.65 (d, J = 7.4 Hz, 2H, H_2), 7.17-7.15 (m, 2H, H_3), 7.05 (app dt, 2H, H_4), 6.92 (d, J = 7.5 Hz, 2H, H_5), 3.48-3.45(m, 6H, $H_{7a,11}$), 3.14 (d, J = 14.8 Hz, 2H, H_{7b}), 2.13-2.11 (m, 2H, H_8), 1.69-1.68 (m, 2H, H_9), 1.61 (app t, 4H, H_{10}). **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, 30°C): δ 161.0(C_1), 151 (q, $^1J_{CF}$ = 399.5 Hz, C_{12}), 146.8(C_6), 139.3(C_2), 130.6(C_3), 128.5(C_5), 127.3(C_4), 66.9(C_{11}), 62.3(C_{7ab}), 55.1(C_9), 53.9(C_8), 53.5(C_{10}). **^{19}F NMR** (564 MHz, C_6D_6, 30°C): δ -37.4. **Anal. Calc**. **for $BiC_{21}H_{24}F_3N_2O$:0.4C_6H_6**: C, 45.50; H, 4.31; N, 4.54. **Found**: C, 45.89; H, 4.30; N, 4.42. **HRMS Calc. for $BiC_{21}H_{24}F_3N_2O$ [M]$^+$**: 586.16446. **Found**: 586.1644.

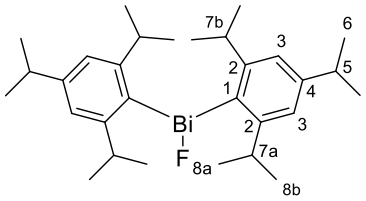
C-OTf



Under nitrogen atmosphere, **C-Cl** (2.00 g, 3.07 mmol) was dissolved in 20 mL pentane. AgOTf (0.87 g, 3.38 mmol) was added to the stirring solution and the reaction was stirred in the absence of light for 72 hours. The formed suspension was then filtered through celite, the celite was washed with pentane (3 x 5 mL), and the combined filtrates were concentrated *in vacuo* to afford the product **C-OTf** (2.17 g, 2.84 mmol) as a yellow solid in 92% yield. **C-OTf** was checked by NMR and carried to the next step.

^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 7.64 (s, 4H, H_3), 2.82 (sept, J = 6.5 Hz, 4H, $H_{7a,b}$), 2.61 (sept, J = 6.9 Hz, 2H, H_5), 1.11 (d, J = 6.5 Hz, 24H, $H_{8a,b}$), 1.09 (d, J = 6.9 Hz, 12H, H_6). **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, 30°C)**:** δ 206.2 (C_1), 157.1 (C_2), 150.6 (C_4), 128.8 (C_3) 119.0 (C_9) (q, $^1J_{CF}$ = 319, C_9), 37.6 ($C_{7a,b}$), 35.1 (C_5) 24.2 ($C_{8a,b}$), 23.8 (C_6). **^{19}F NMR** (564 MHz, C_6D_6, 30°C): δ -77.4 (s, $^{12}CF_3$), -77.51 (d, $^1J_{CF}$ = 319 Hz, $^{13}CF_3$).

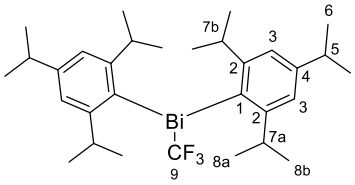
C-F



Under nitrogen atmosphere, **C-OTf** (1.27 g, 1.57 mmol) and NaF (330 mg, 7.86 mmol) were combined and dissolved in 30 mL of THF in a Schlenk flask equipped with a Teflon valve. The solution was stirred for 14 hours at 60 °C. After the full conversion of the starting **C-OTf** based on ^{1}H NMR and ^{19}F NMR, the solvent was removed *in vacuo* and the product was dissolved in pentane, filtered through celite, and the filtrate was concentrated *in vacuo* affording the product **C-F** (825 mg, 1.30 mmol) as a white crystalline solid in 83% yield. Crystallization by slow evaporation of pentane under nitrogen atmosphere provided suitable crystals for single crystal X-ray crystallography.

^{1}H NMR (600 MHz, C_6D_6, 30°C): δ 7.44 (s, 2H, H_3), 3.27 (sept, J = 6.8 Hz, 2H, $H_{7a,b}$), 2.71 (sept, J = 6.8 Hz, 1H, H_5), 1.18 (d, J = 6.8 Hz, 12H, $H_{8a,b}$), 1.13 (d, J = 6.8 Hz, 6H, H_6). **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, 30°C)**:** δ 188.6 (C_1), 156.8 (C_2), 149.8 (C_4), 126.2 (C_3), 35.9 ($C_{7a,b}$), 35.0 (C_5) 25.0 (C_6), 24.5 (C_{8a}), 24.1 (C_{8b}). **^{19}F NMR** (564 MHz, C_6D_6, 30°C): δ -216.02. **Anal. Calc. for $BiC_{30}H_{46}F$:** C, 56.77; H, 7.31. **Found:** C, 57.31; H, 7.40. An attempt to obtain EA has failed perhaps due to contamination of the product with grease or silicon grease.

C-CF$_3$



Under nitrogen atmosphere, chlorobis(2,4,6-triisopropylphenyl)bismuthine **C-Cl** (250 mg, 0.384 mmol) and CsF (87 mg, 0.57 mmol) were combined and dissolved in 7 mL THF. To the solution was added $TMSCF_3$ (71 µl, 0.50 mmol) and the reaction was stirred overnight. A second addition of $TMSCF_3$ (71 µl, 0.50 mmol) was added to the reaction and stirred for an additional 2 hours. A third addition of $TMSCF_3$ (71 µl, 0.50 mmol) was added to the reaction and stirred for 1 hour. After full consumption of **C-Cl** was confirmed by ^{1}H NMR, the solvent was removed *in vacuo*. The solid was then redissolved in pentane, filtered through celite, and concentrated *in vacuo* to afford the product **C-CF$_3$** (237 mg, 0.346 mmol) as a white solid in 90% yield. Crystals suitable for single crystal X-ray crystallography were obtained through slow evaporation of a pentane solution.

White crystalline solid. **^{1}H NMR** (600 MHz, C_6D_6, 30°C): δ 7.28 (s, 4H, H_3), 2.98 (sept, J = 6.7 Hz, 4H, $H_{7a,b}$), 2.70 (sept, J = 6.9 Hz, 2H, H_5), 1.16 (d, J = 6.9 Hz, 12H, H_6), 1.11 (d, J = 6.7 Hz, 12H, H_{8a}), 1.09 (d, J = 6.7 Hz, 12H, H_{8b}). **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, 30°C)**:** δ 165.2 (C_1), 155.9 (C_2), 149.9 (C_4), 132.6 (q, $^{1}J_{CF}$ = 397, C_9), 124.4 (C_3), 40.0 ($C_{7a,b}$), 34.6 (C_5) 24.7 (C_{8a}), 24.3 (C_{8b}) 24.1 (C_6). **^{19}F NMR** (564 MHz, C_6D_6, 30°C): δ -34.07 (s, $^{12}CF_3$), -34.21 (d, $^{1}J_{CF}$ = 397 Hz, $^{13}CF_3$). **Anal. Calc. for $BiC_{31}H_{46}F_3$:** C, 54.38; H, 6.77. **Found:** C, 54.57; H, 6.69.

4. Reactivity Studies

CF_2 α-Elimination

Attention, Hazard: heating DCM above its boiling point is dangerous. The following experiments with DCM were conducted in very small scale (NMR tubes) with appropriate precaution.

Under nitrogen atmosphere, trifluoromethyl bismuth complex (0.050 mmol) was placed into a J-Young NMR tube. Then the cyclooctene (110 mg, 1.0 mmol), deuterated dichloromethane (0.75 mL), and fluorobenzene (internal standard) (4.7 μL, 0.050 mmol) were added. The reaction was mixed, then heated to 120 °C, and monitored by ^{1}H and ^{19}F NMR at time points 0 min, 30 min, 90 min, 150 min, 180 min, 210 min, 270 min, and 390 min.

Transmetalation

Under nitrogen atmosphere, bismuth fluoride complex (0.050 mmol) was placed into a J-Young NMR tube. Then the toluene-d_8 (0.5 mL), TMS-CF_3 (89 μL, 0.60 mmol) and fluorobenzene (internal standard) (47 μL, 0.50 mmol) were added. The reaction was stirred at RT and monitored by ^{1}H and ^{19}F NMR at time points 0 min, 5 mins, and 14 hours. In the second study, **1-F**, **5-F**, **7-F** were monitored at time points 10 min, 50 min, 90 min, 140 min, 200 min, 310 min, 420 min, 630 min, and 820 min.

Catalytic Study

Under nitrogen atmosphere, trifluoromethyl bismuth complex (0.050 mmol) was placed into a J-Young NMR tube. Then the *trans*-stilbene (90 mg, 0.50 mmol), toluene-d_8 (0.5 mL), $TMSCF_3$ (89 μL, 0.60 mmol) and fluorobenzene (internal standard) (47 μL, 0.50 mmol) were added. The reaction was heated to 100 °C and monitored by ^{1}H and ^{19}F NMR at time points 0 min, 30 min, 2 h, 5 h, and 21 h.

5. References

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[Toma 2016] Toma, A.; Raţ, C. I.; Silvestru, A.; Rüffer, T.; Lang, H.; Mehring, M. Heterocyclic bismuth(III) compounds with transannular S→Bi interactions. An experimental and theoretical approach *J. Organomet. Chem.* **2016**, 806, 5-11. https://doi.org/10.1016/j.jorganchem.2016.01.019

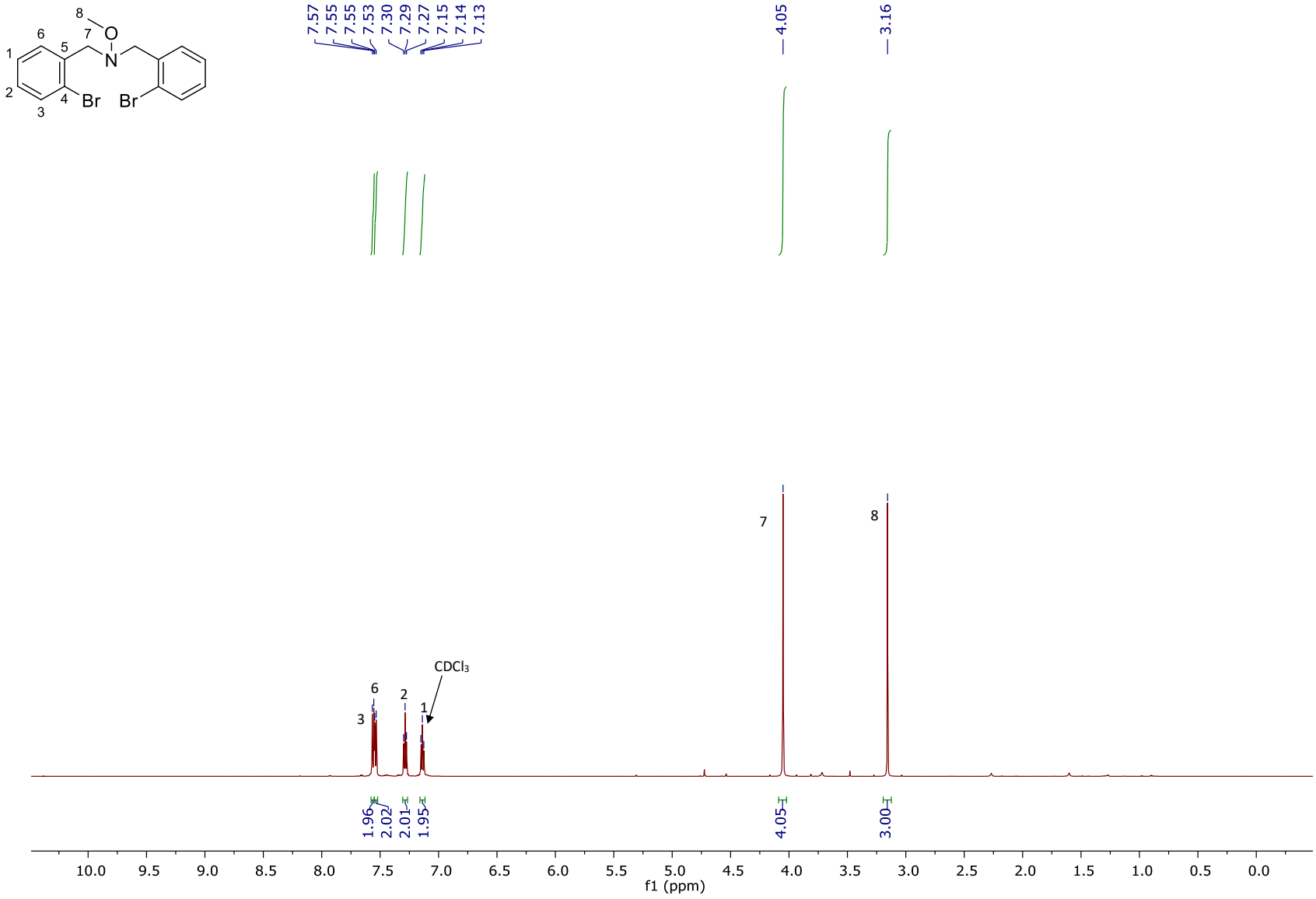


Figure S1. ^{1}H NMR of **L6** (600 MHz, $CDCl_3$, 30°C)

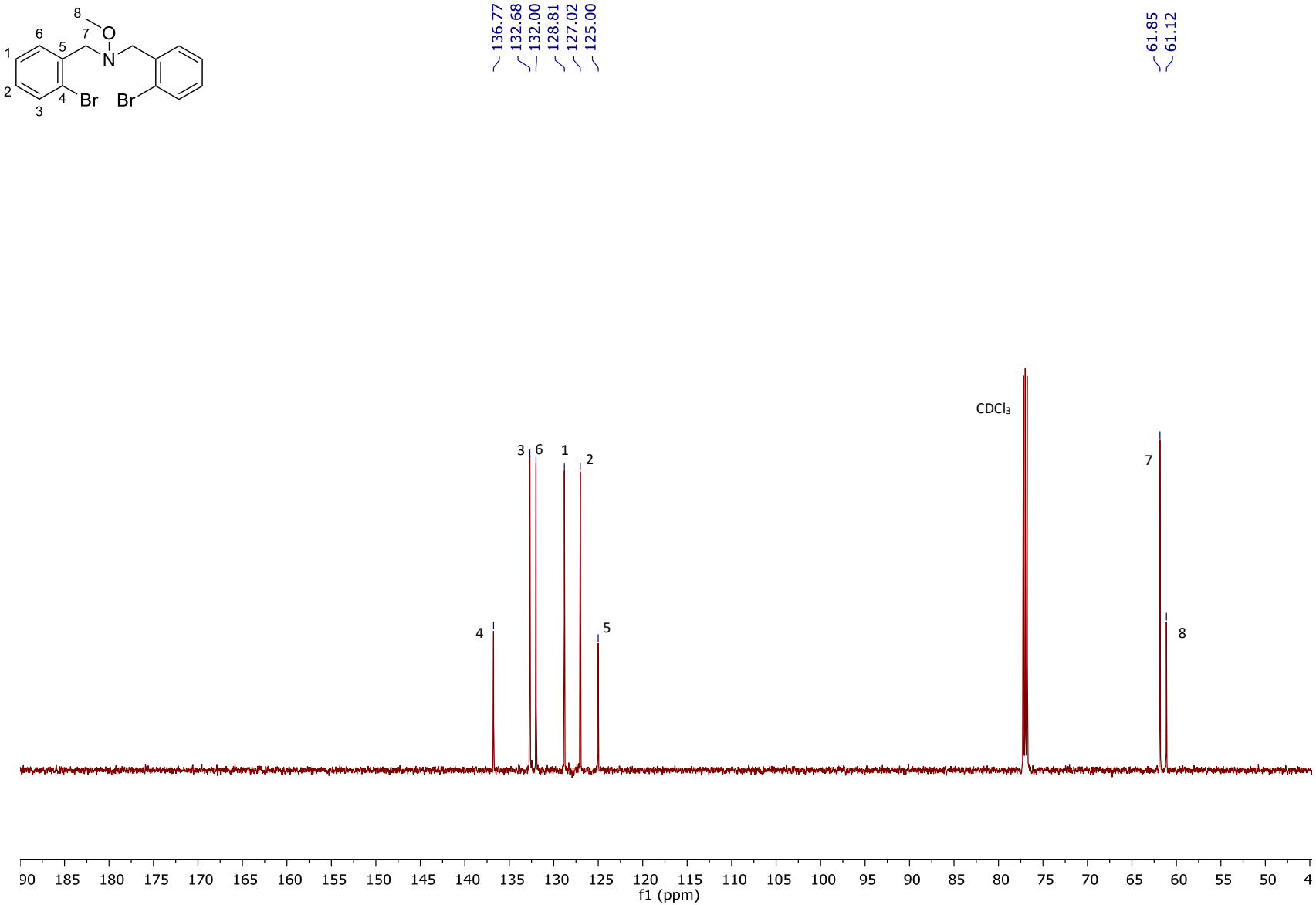


Figure S2. $^{13}C\{^{1}H\}$ NMR of **L6** (150 MHz, $CDCl_3$, 30°C)

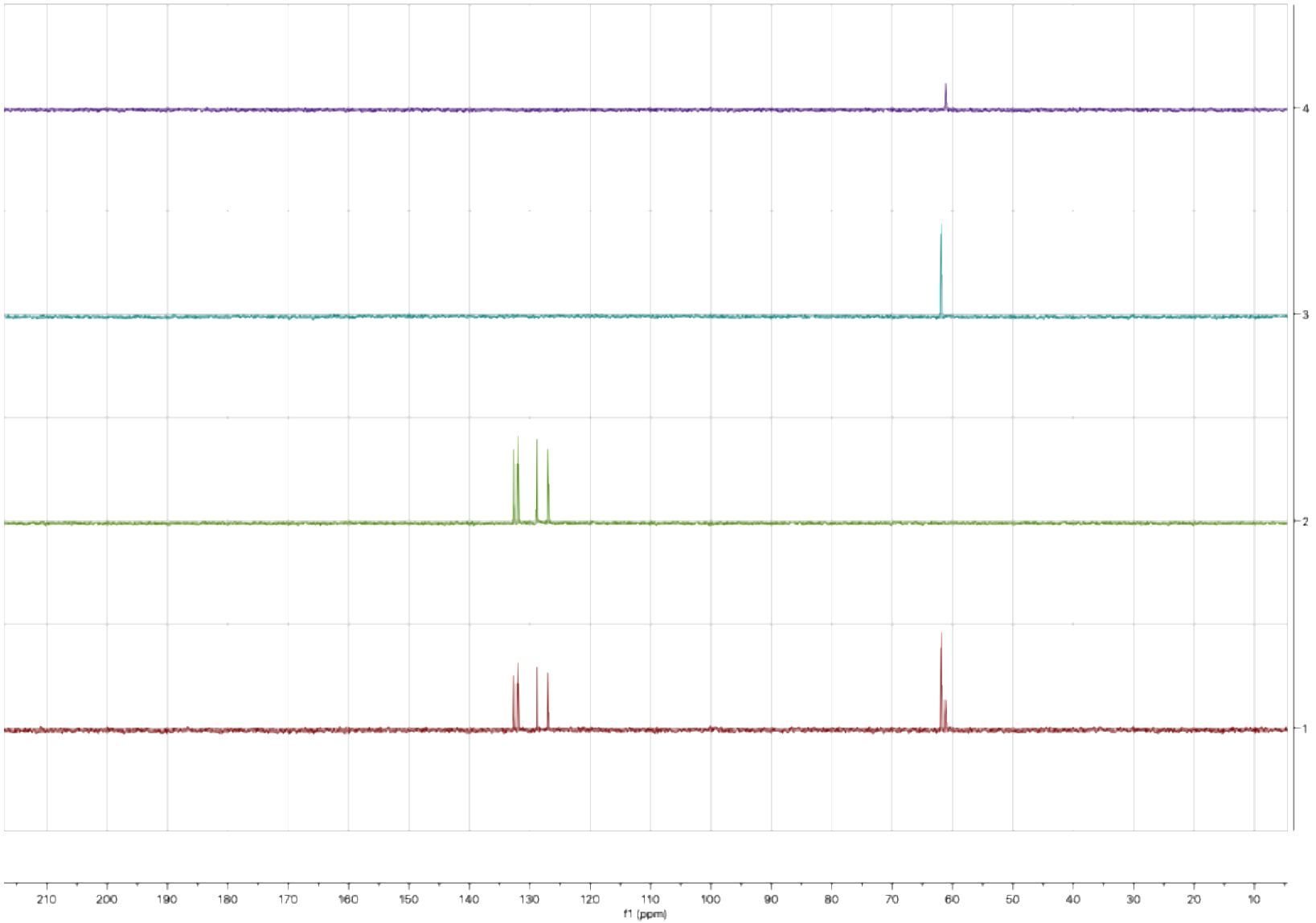


Figure S3. $^{13}C\{^{1}H\}$ DEPT of **L6** in $CDCl_3$

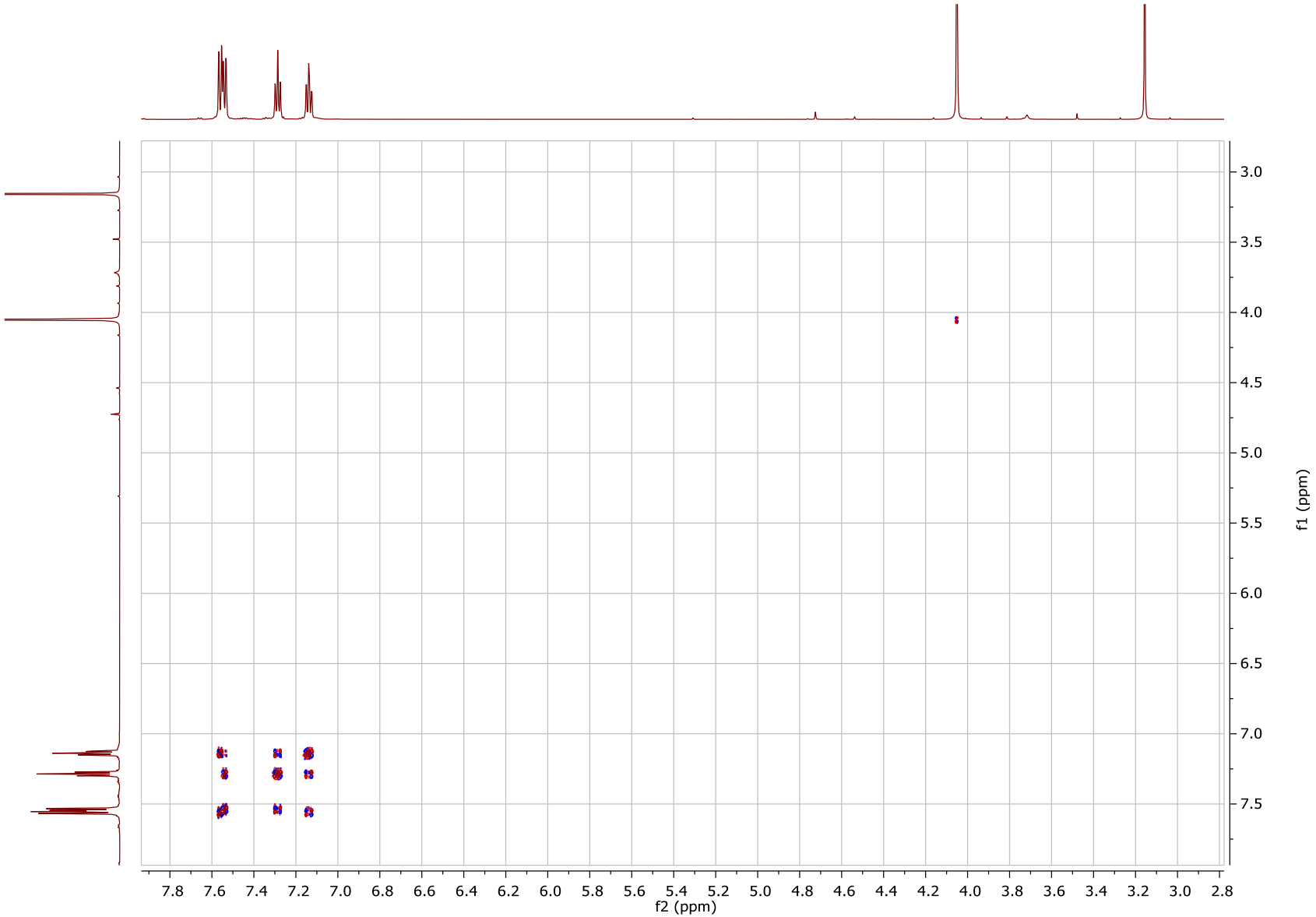


Figure S4. COSY of **L6** in $CDCl_3$

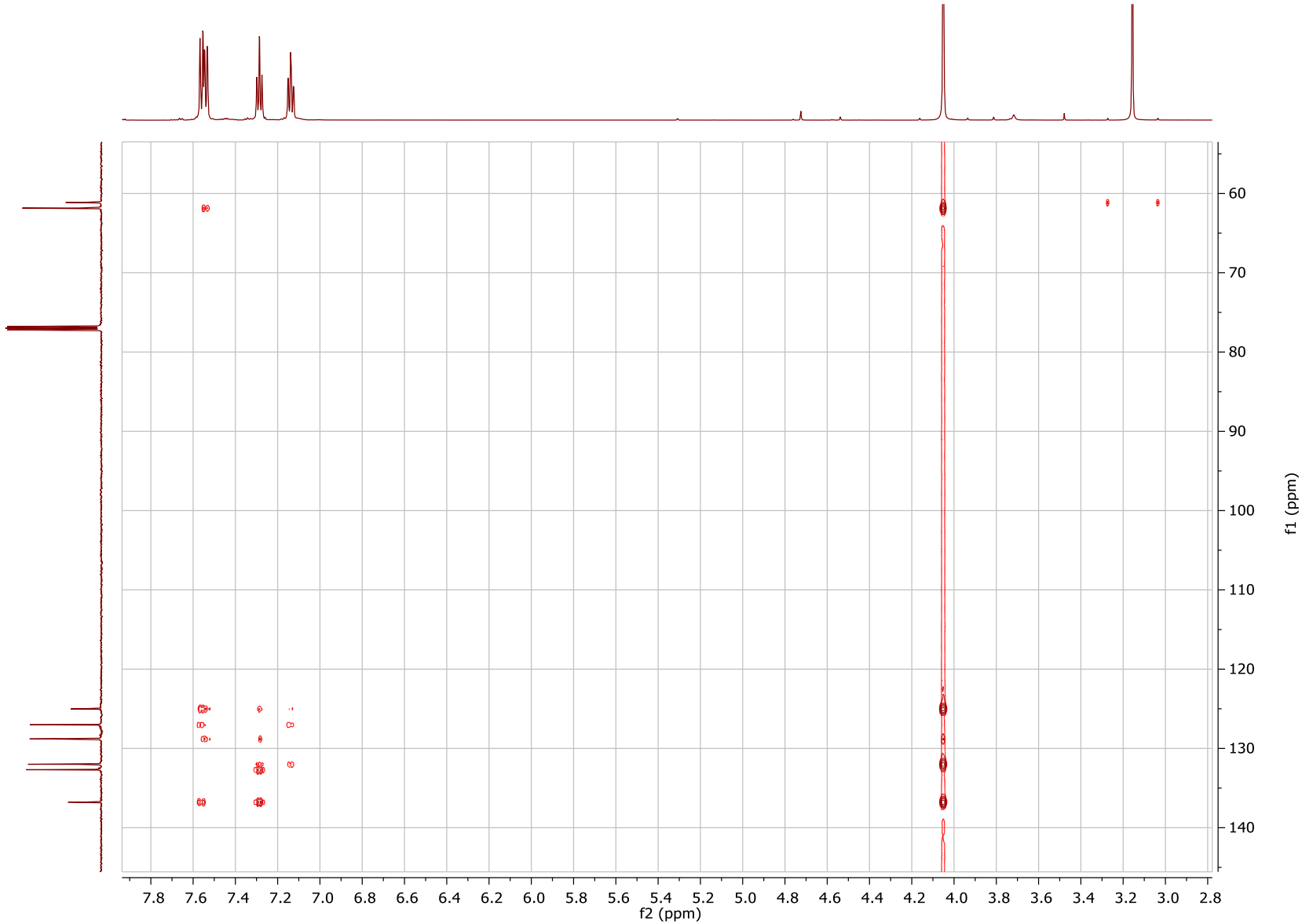


Figure S5. HMBC of **L6** in $CDCl_3$

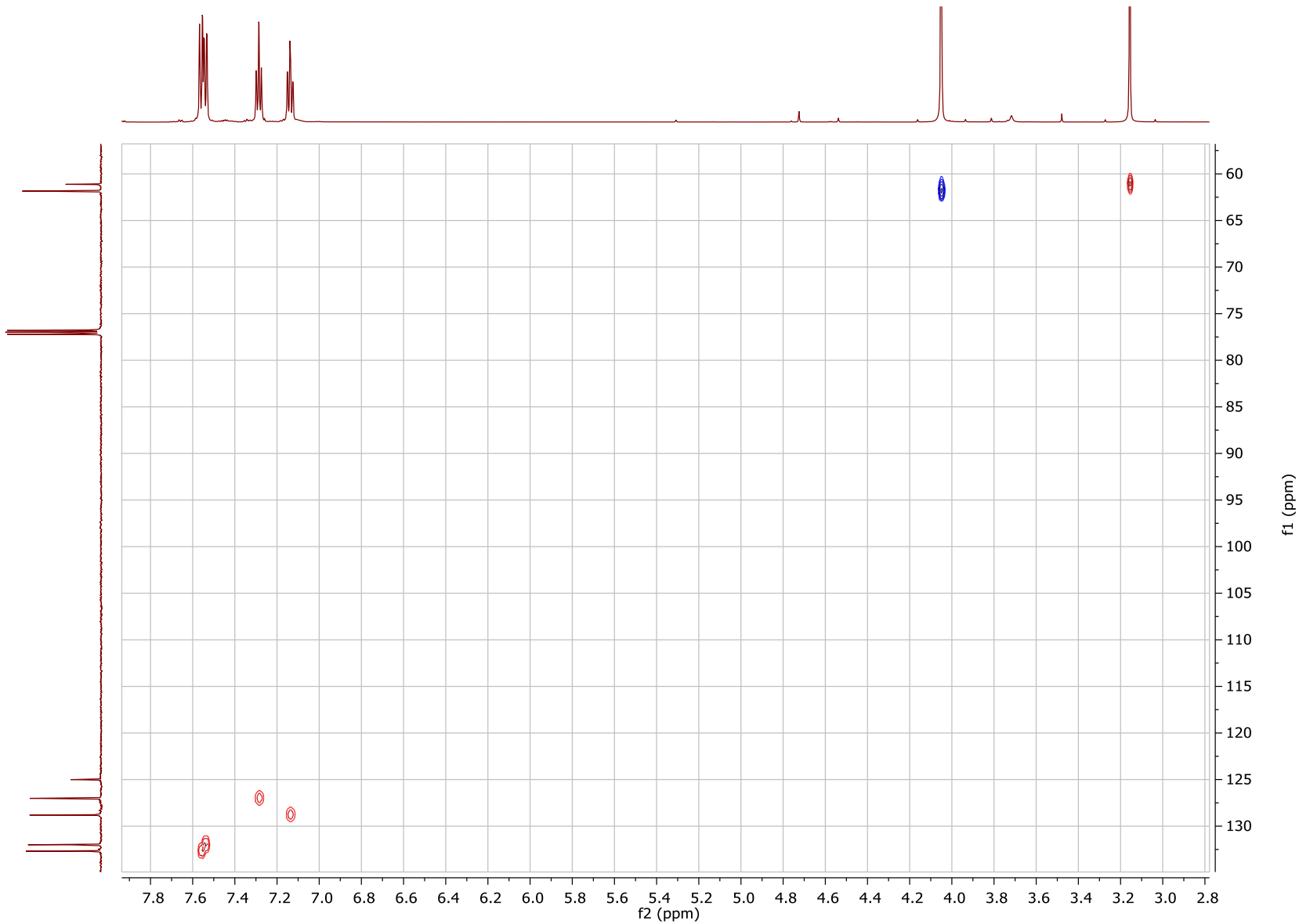
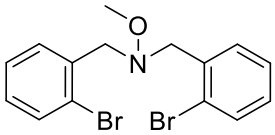


Figure S6. HSQC of **L6** in $CDCl_3$



Qualitative Compound Identification Report

Data File	TLG-4-010-CHCl 3.d	Sample Name	TLG-4-010
Sample Type	Sample	Position	P1-C3
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Acq Method	20_100forHRMS.m	Acquired Time	5/21/2025 4:39:15 PM (UTC-10:00)
IRM Calibration Status	Success	DA Method	Landon.m
Comment			
Sample Group		Info.	
Stream Name	LC 1	Acquisition Time (Local)	5/21/2025 4:39:15 PM (UTC-10:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.06.01 (B6157)	QTOF Driver Version	6.00.01
QTOF Firmware Version	20.643	Tune Mass Range Max.	3200

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	Hits (DB)
Cpd 1: C15 H15 Br2 N O; 2.406	2.406	382.9508	10240	C15 H15 Br2 N O	382.952	-3.22	1

Compound Label	*m/z*	RT	Algorithm	Mass
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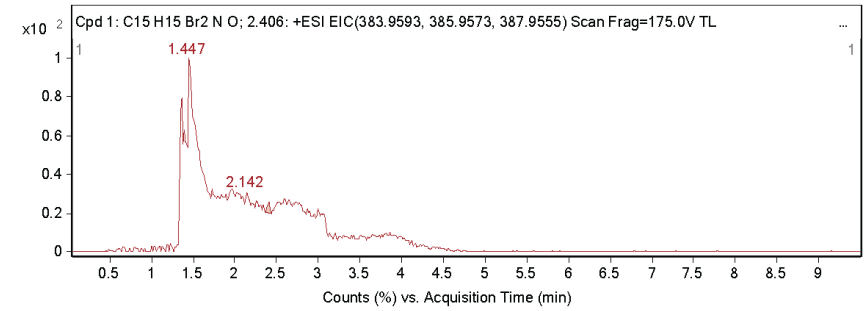
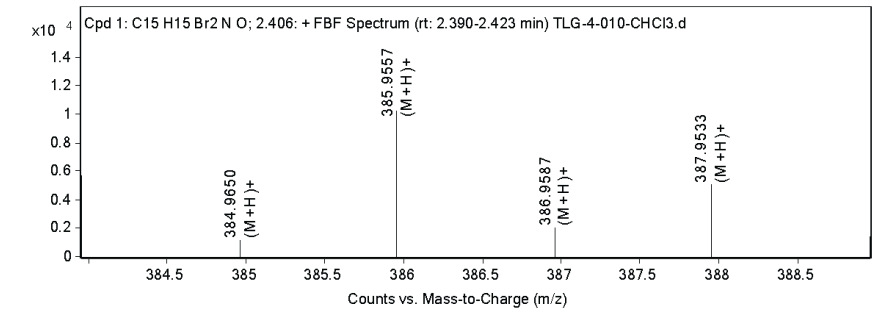
Compound Chromatograms

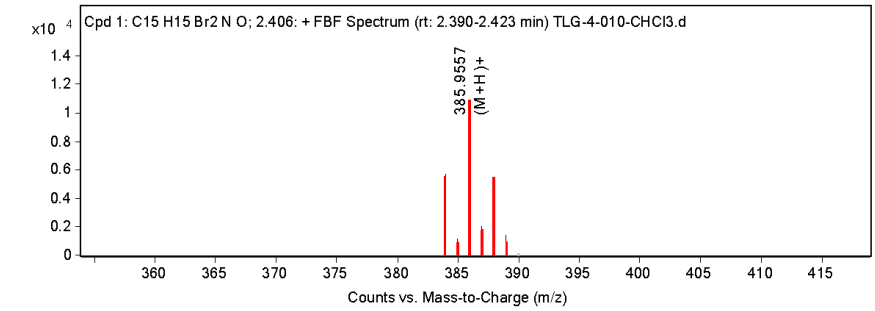


MS Spectrum



MS Zoomed Spectrum

Qualitative Compound Identification Report



MS Spectrum Peak List

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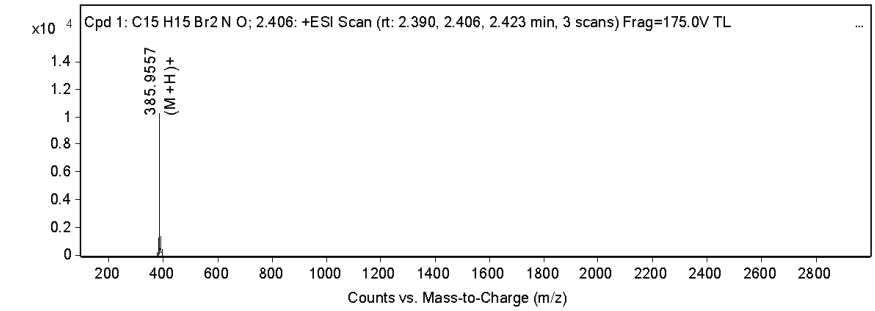
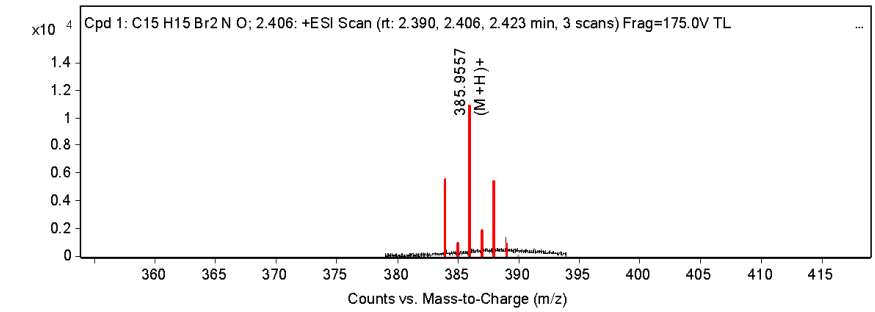
383.9585	1	5713.73	(M+H)+
384.965	1	1102.1	(M+H)+
385.9557	1	10239.86	(M+H)+
386.9587	1	2006.7	(M+H)+
387.9533	1	5025.55	(M+H)+
388.9599	1	1352.6	(M+H)+

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	z	Abund	Ion
383.9585	383.9593	2.06	1	5713.73	(M+H)+
384.965	384.9626	-6.3	1	1102.1	(M+H)+
385.9557	385.9573	4.18	1	10239.86	(M+H)+
385.9558				10232.07	
386.9587	386.9605	4.73	1	2006.7	(M+H)+
387.9533	387.9555	5.72	1	5025.55	(M+H)+
388.9599	388.9586	-3.43	1	1352.6	(M+H)+

--- End Of Report ---

Figure S7. HRMS of **L6**

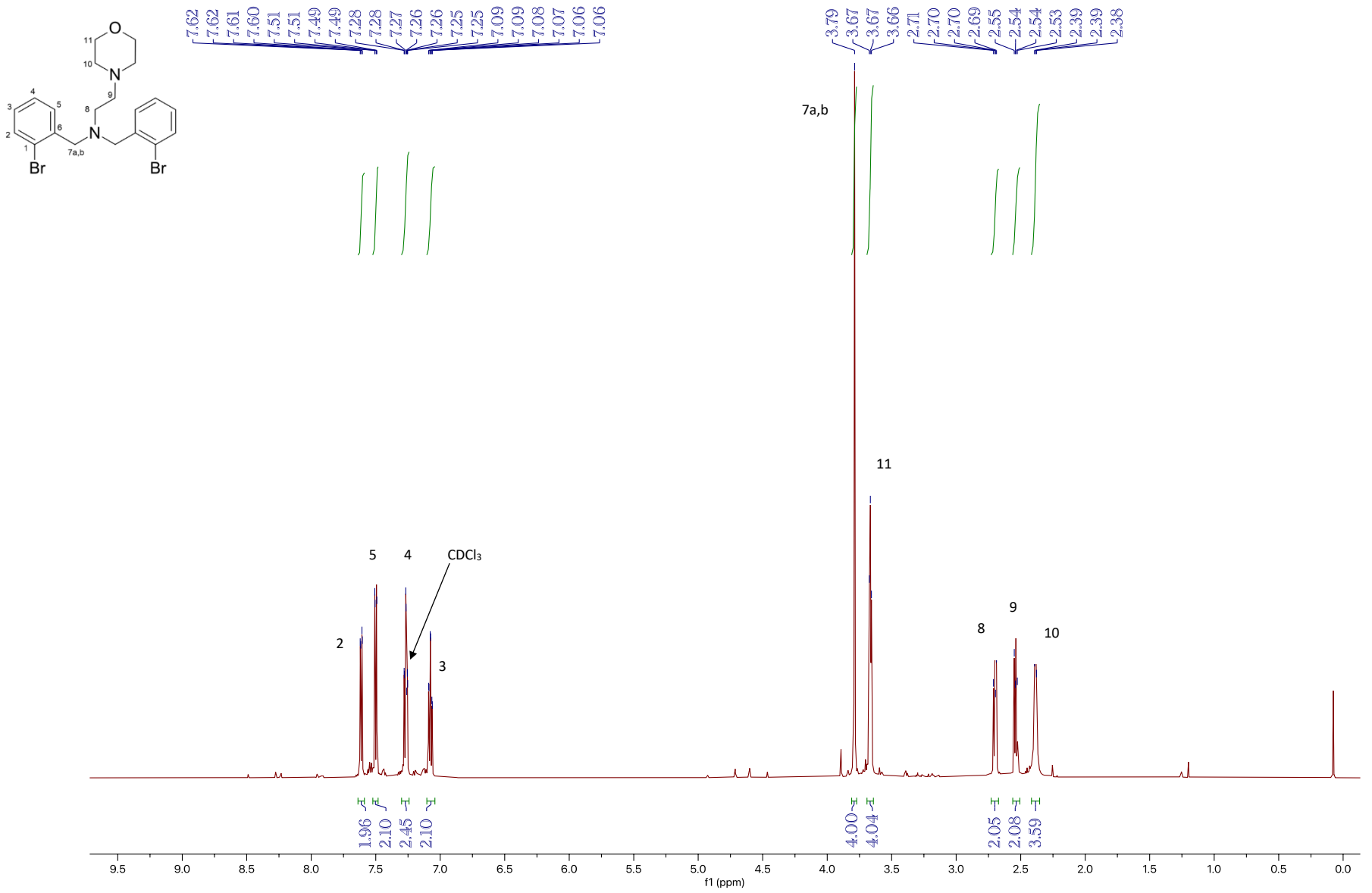


Figure S8. ^{1}H NMR of **L7** (600 MHz, $CDCl_3$, 30°C)

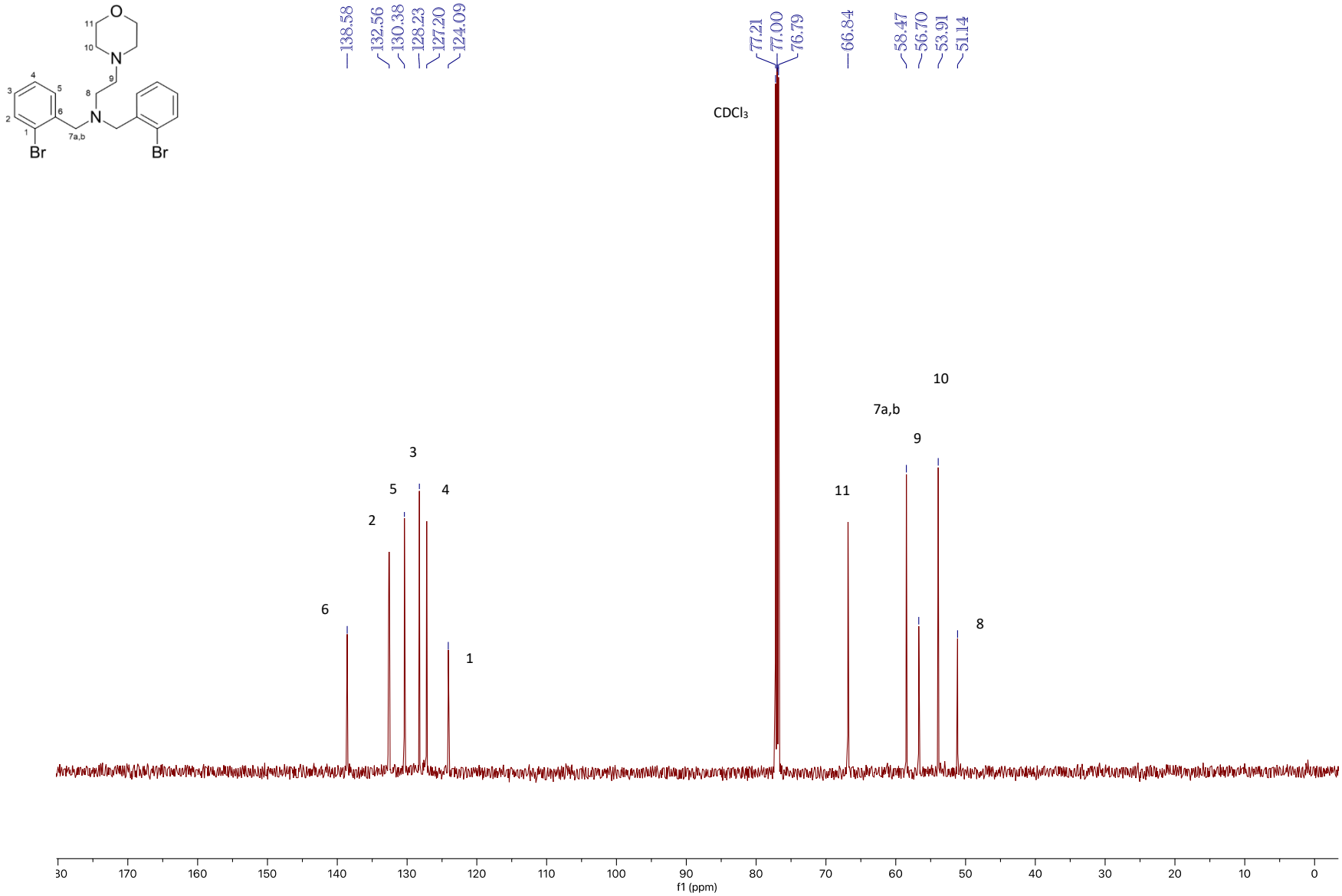


Figure S9. $^{13}C\{^{1}H\}$ NMR of **L7** (150 MHz, $CDCl_3$, 30°C)

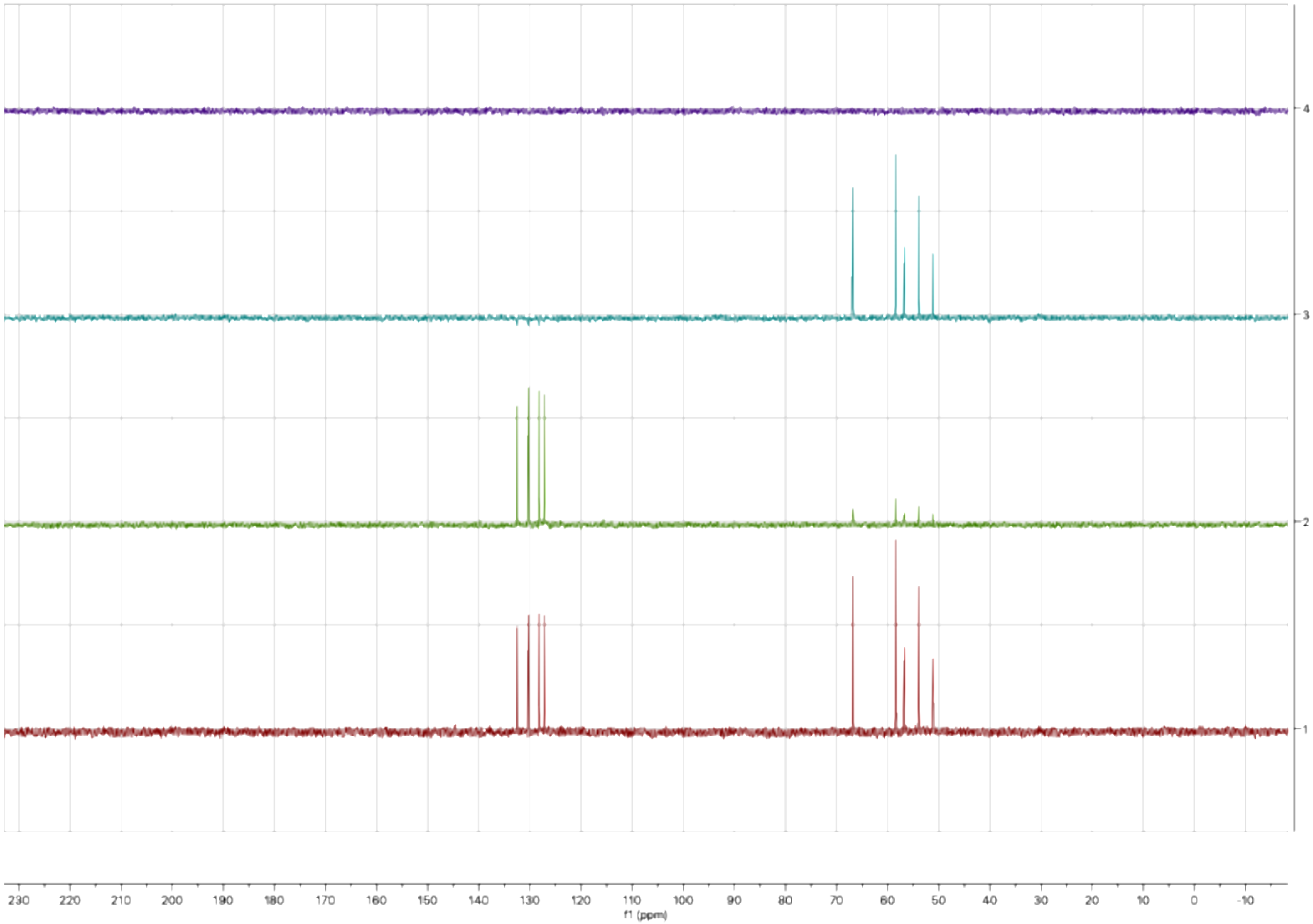


Figure S10. $^{13}C\{^{1}H\}$ DEPT of **L7** in $CDCl_3$

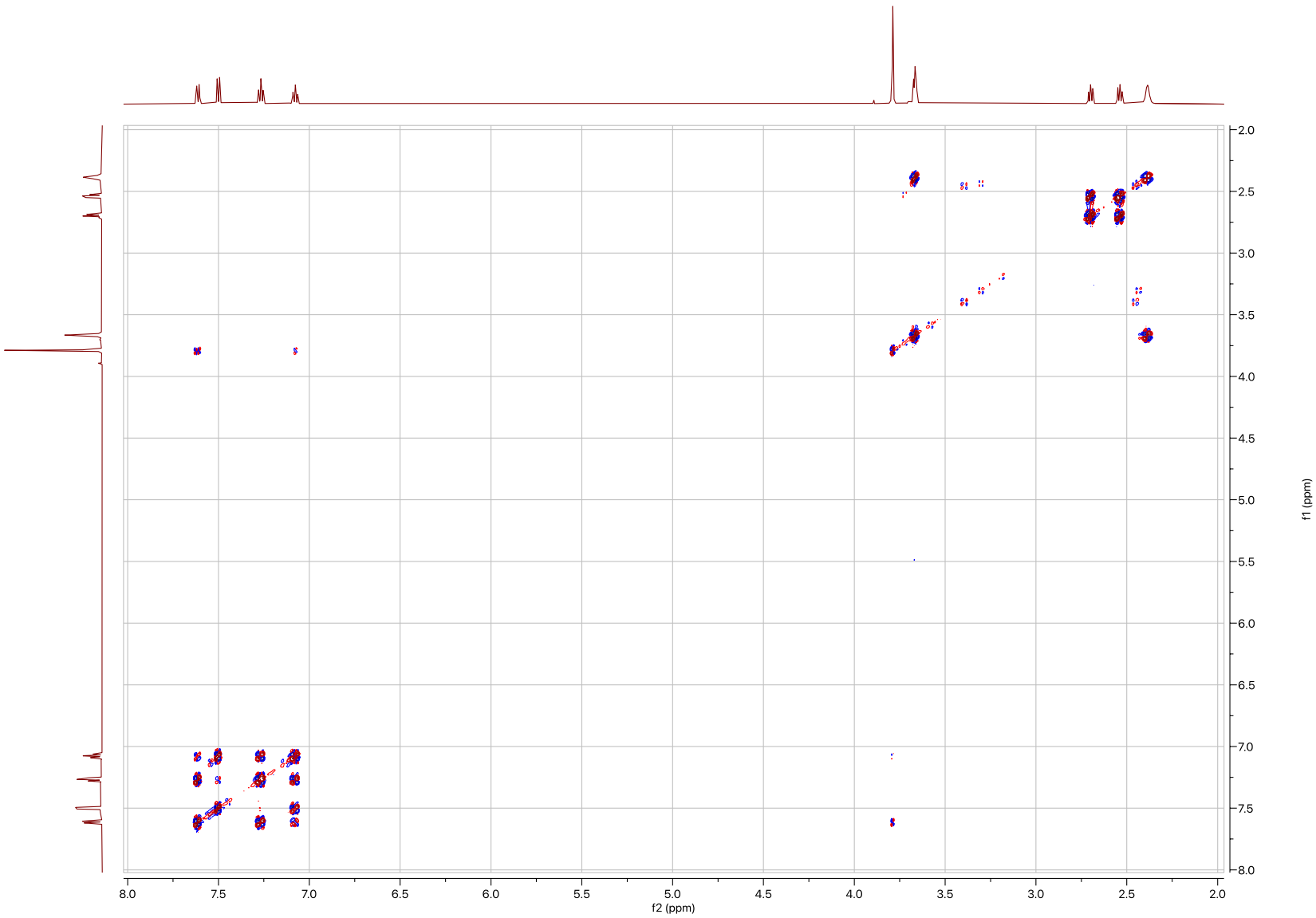


Figure S11. COSY of **L7** in $CDCl_3$

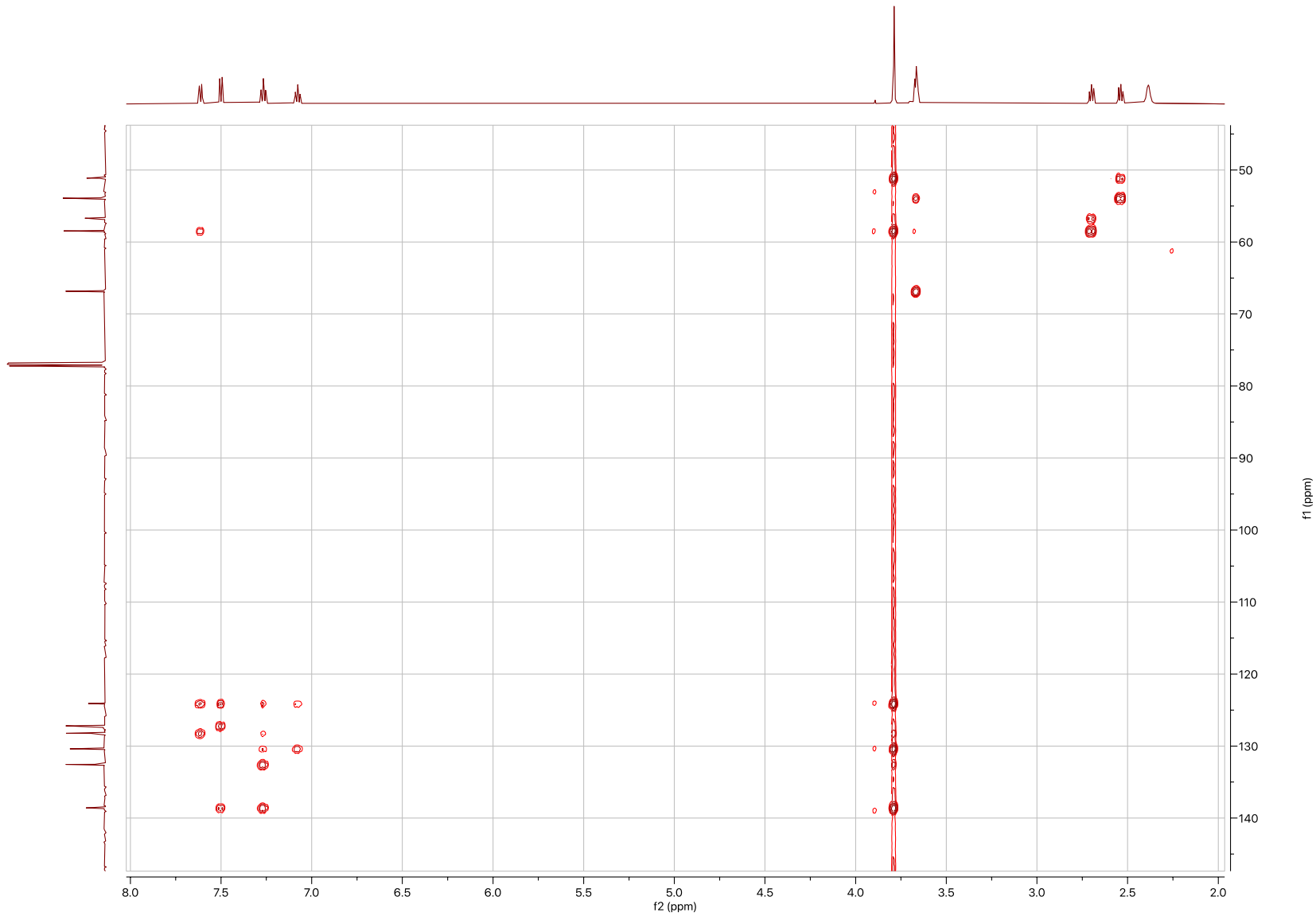


Figure S12. HMBC of **L7** in $CDCl_3$

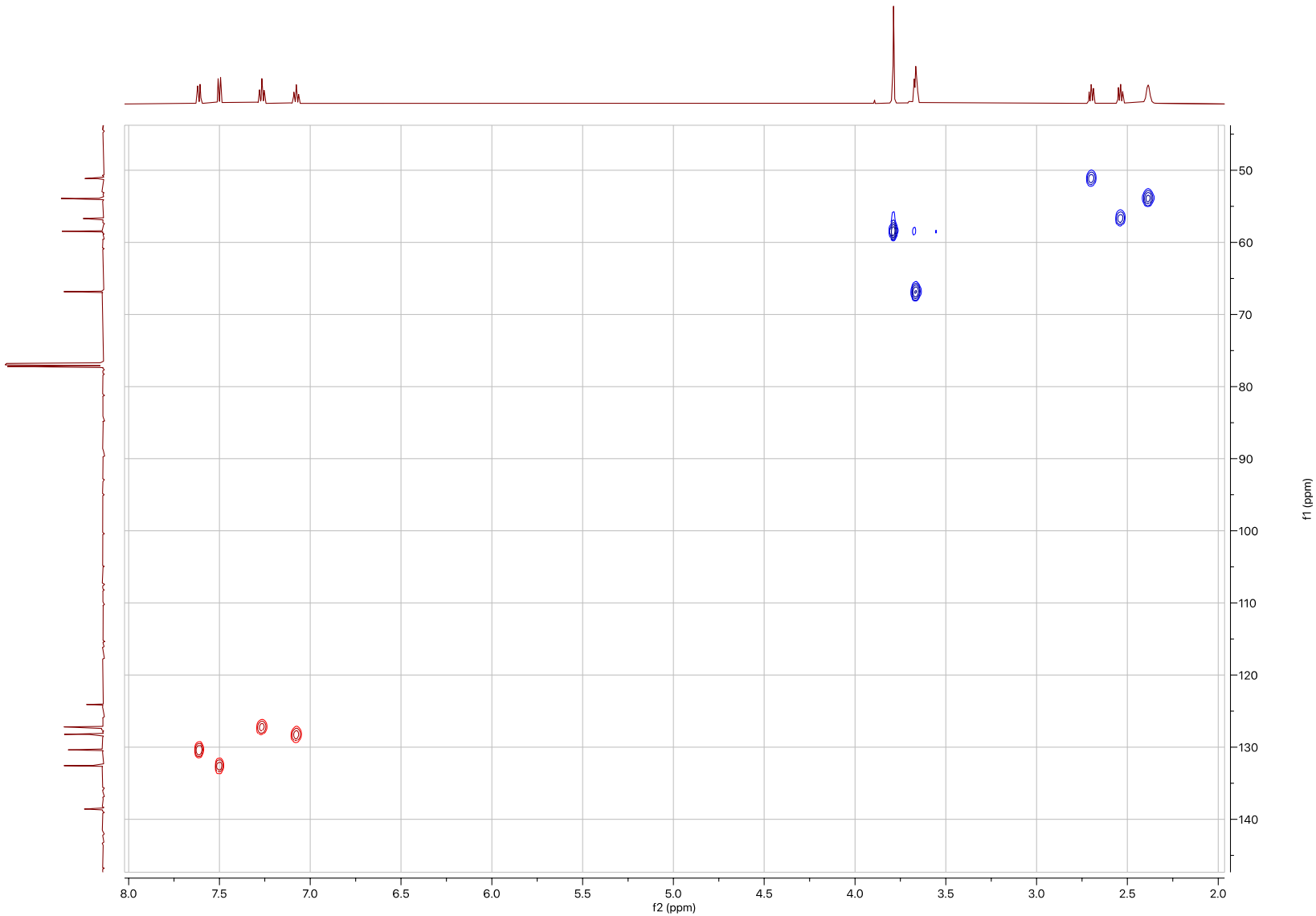
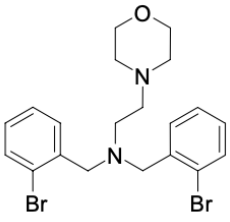


Figure S13. HSQC of **L7** in $CDCl_3$



Qualitative Compound Report

Data File	MV-277.d	**Sample Name**	
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IRM Calibration Status	Success	**DA Method**	Tius_Analysis_Method_LB.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6157)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
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Compound Label	*m/z*	RT	Algorithm	Mass
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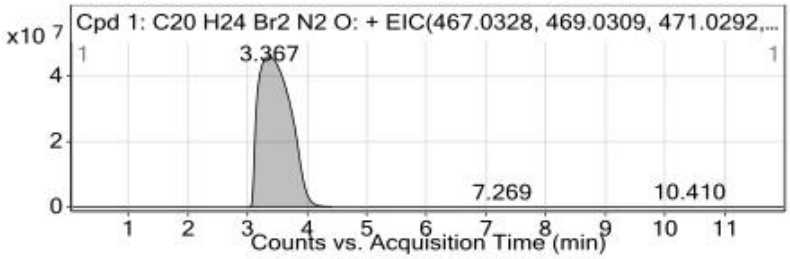
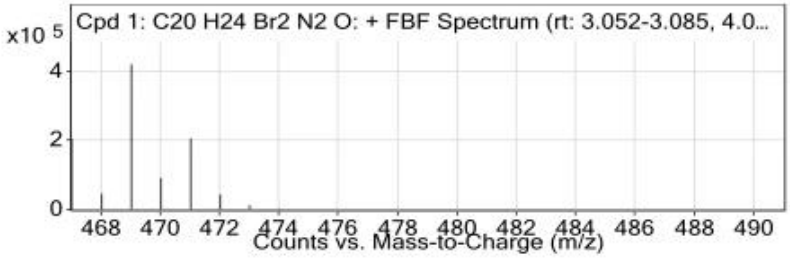
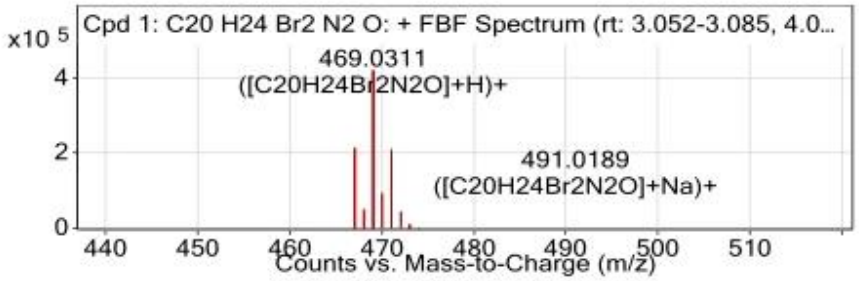


MS Spectrum



MS Zoomed Spectrum

Qualitative Compound Report



MS Spectrum Peak List

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469.0311	1	420879.19	C20H24Br2N2O	(M+H)+
470.0343	1	91599.75	C20H24Br2N2O	(M+H)+
471.029	1	205945.19	C20H24Br2N2O	(M+H)+
472.0316	1	44026.46	C20H24Br2N2O	(M+H)+
473.0175	1	12105.49	C20H24Br2N2O	(M+H)+
474.0132	1	2032.86	C20H24Br2N2O	(M+H)+
475.0168	1	457.23	C20H24Br2N2O	(M+H)+
491.0189	1	230.13	C20H24Br2N2O	(M+Na)+

--- End Of Report ---

Figure S14. HRMS of **L7**

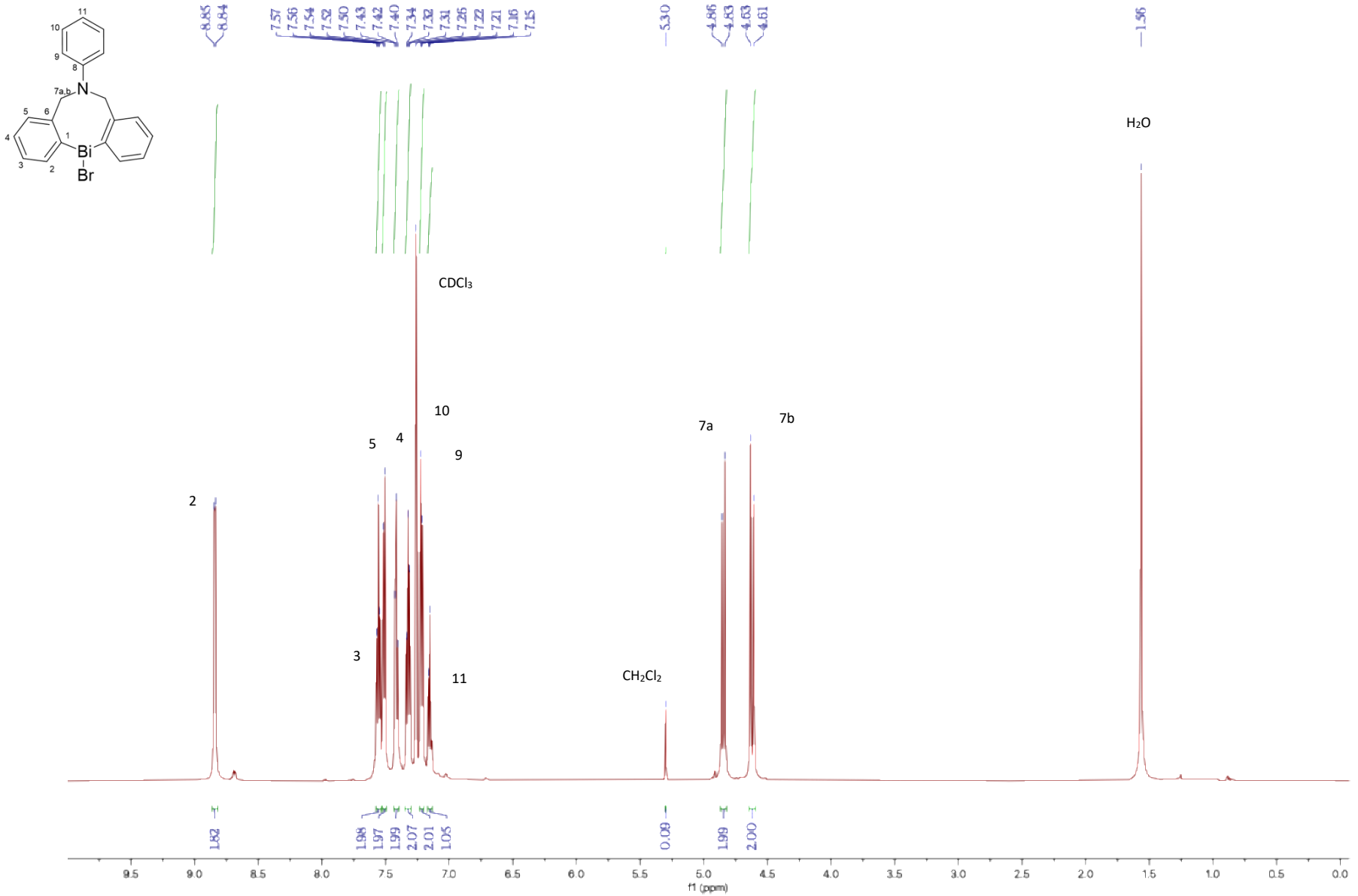


Figure S15. ^{1}H NMR of **2-Br** (600 MHz, $CDCl_3$, 21°C)

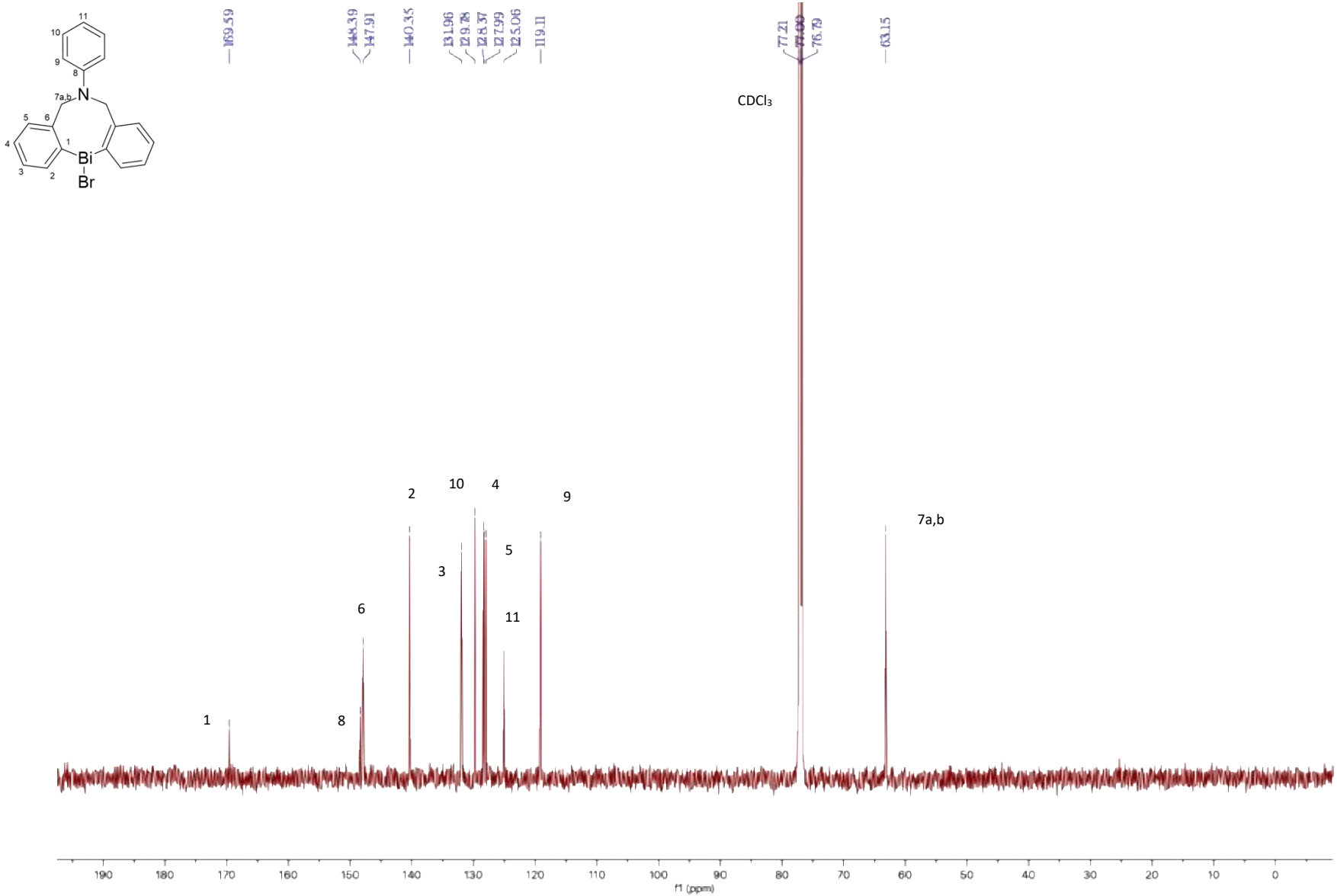


Figure S16. $^{13}C\{^{1}H\}$ NMR of **2-Br** (150 MHz, $CDCl_3$, 21°C)

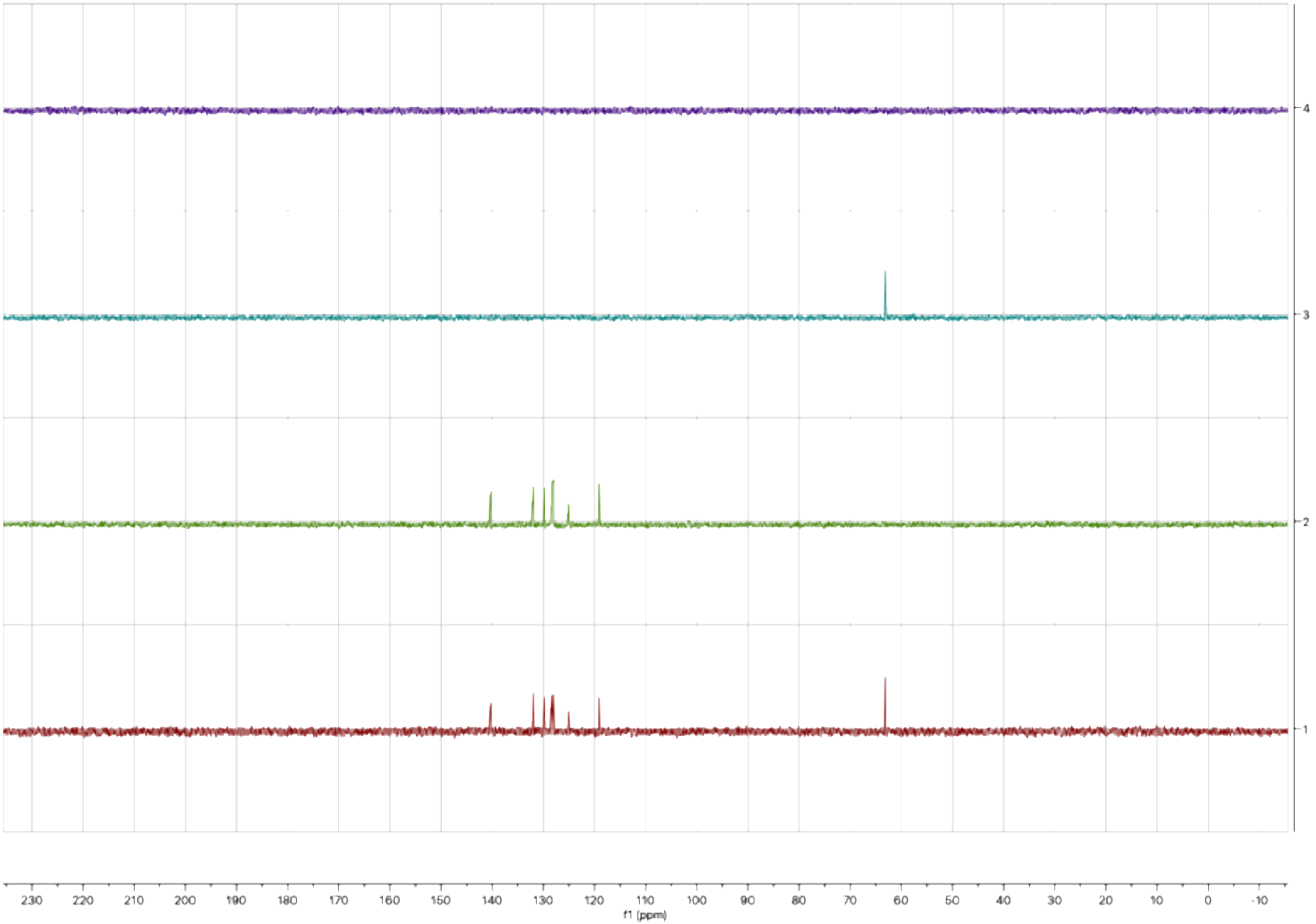


Figure S17. $^{13}C\{^{1}H\}$ DEPT NMR of **2-Br** in $CDCl_3$

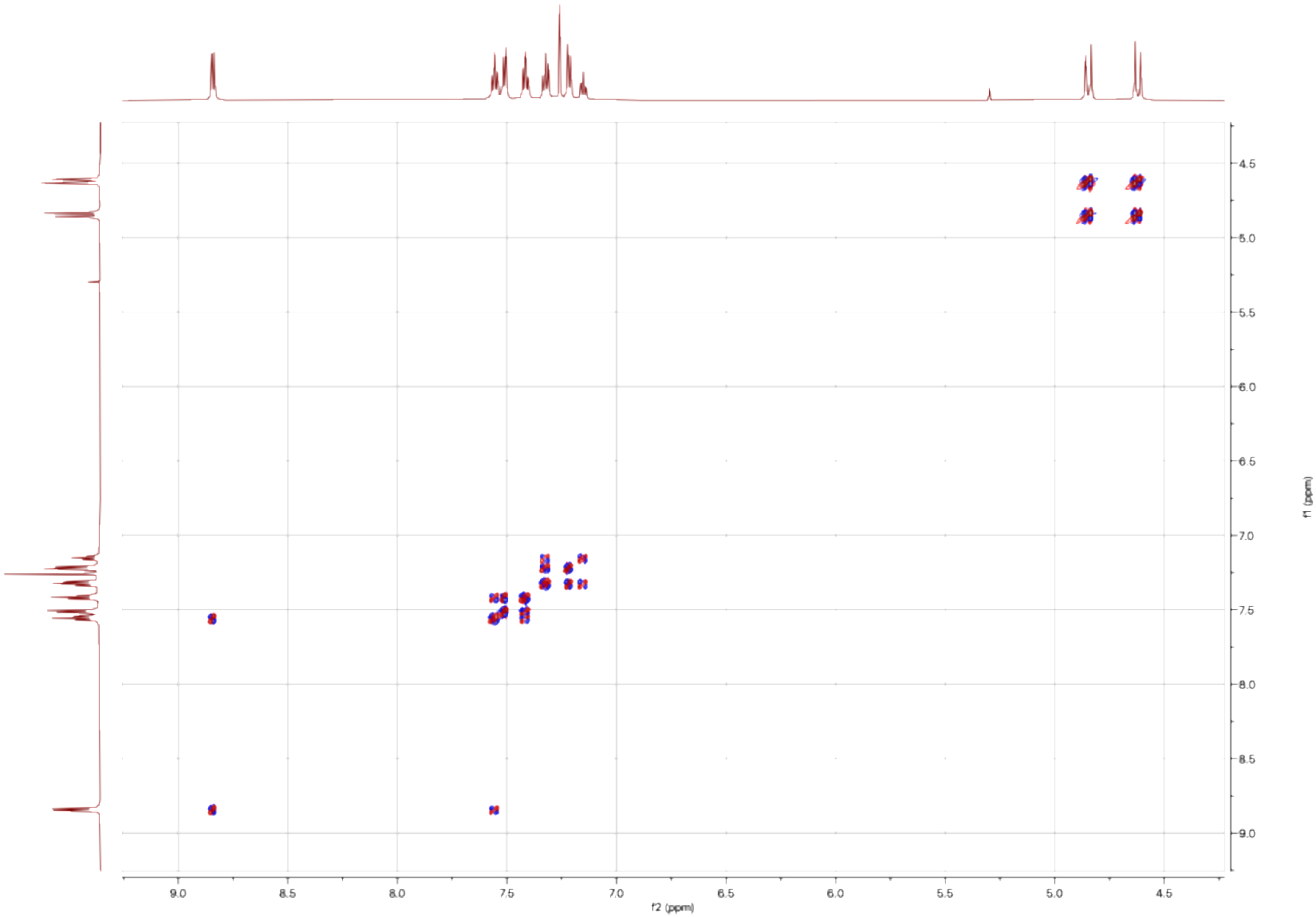


Figure S18. COSY NMR of **2-Br** in $CDCl_3$

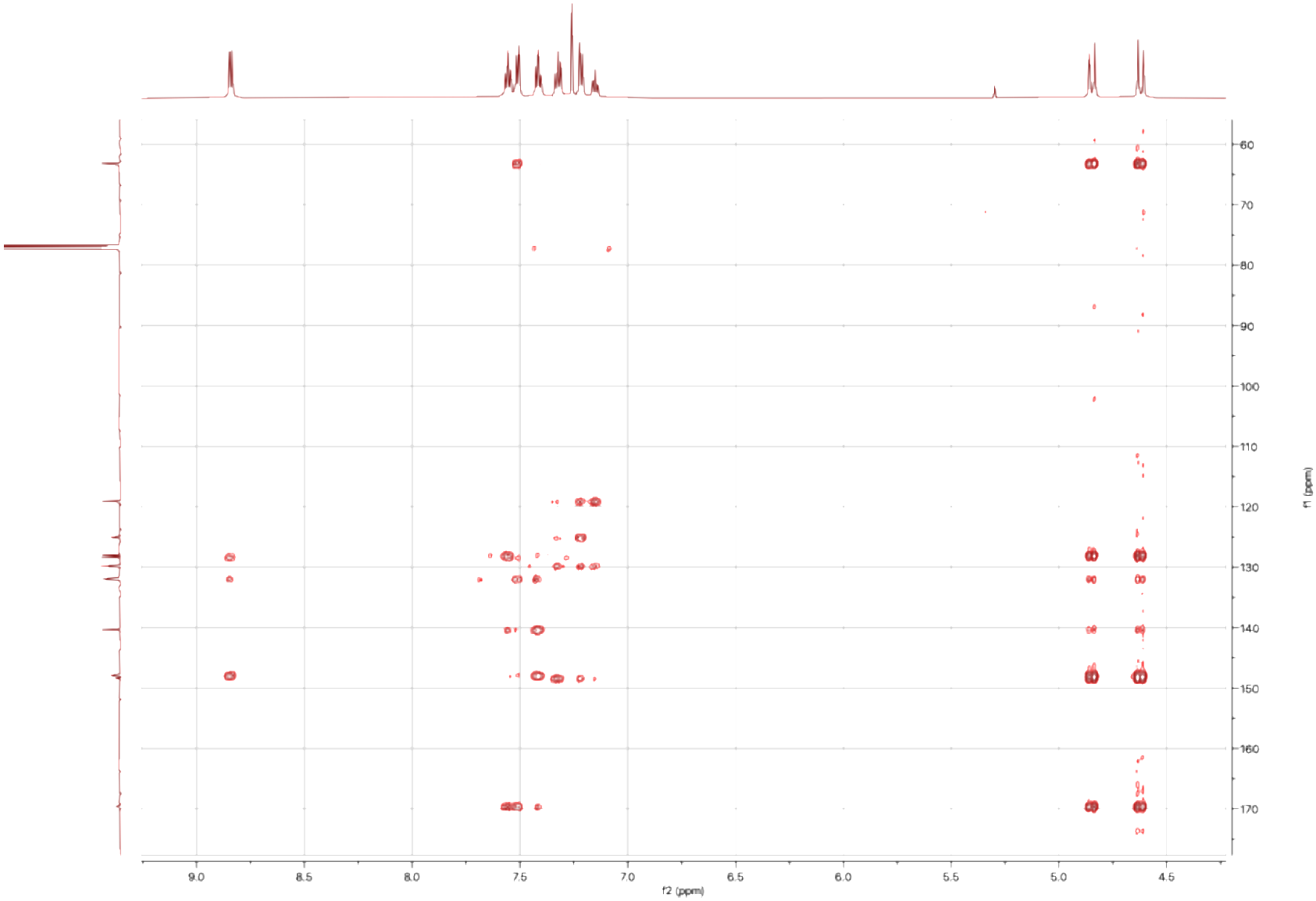


Figure S19. HMBC NMR of **2-Br** in $CDCl_3$

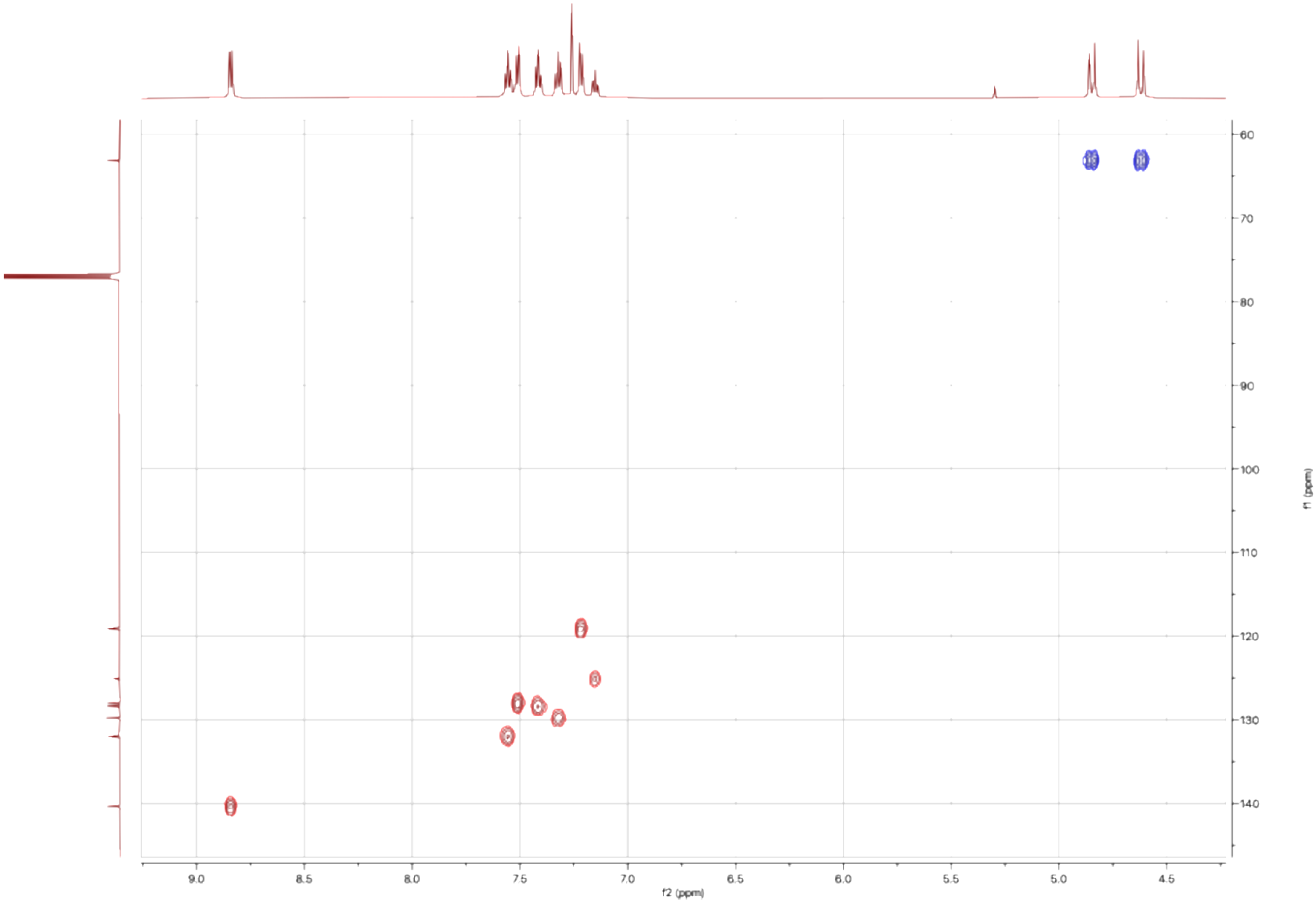
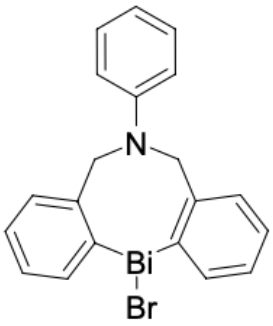


Figure S20. HSQC NMR of **2-Br** in $CDCl_3$



Chemical Formula: $C_{20}H_{17}BiBrN \cdot 0.1CH_2Cl_2$

Elemental Analysis: C, 42.45; H, 3.05; N, 2.46.

CENTC Elemental Analysis Facility
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Rochester, NY 14627 USA
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Date of report	2/16/2024 5:45:04PM
User ID	Administrator
Comments	MV_170 [Hyvl]

DATE & TIME	2/16/2024 11:15:21 AM	P_ID	EA LAB
SAMPLE ID	24056	USER ID	Administrator
WEIGHT (mg)	1.883	MODE	CHN

CARBON	42.283%
HYDROGEN	3.220%
NITROGEN	2.628%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

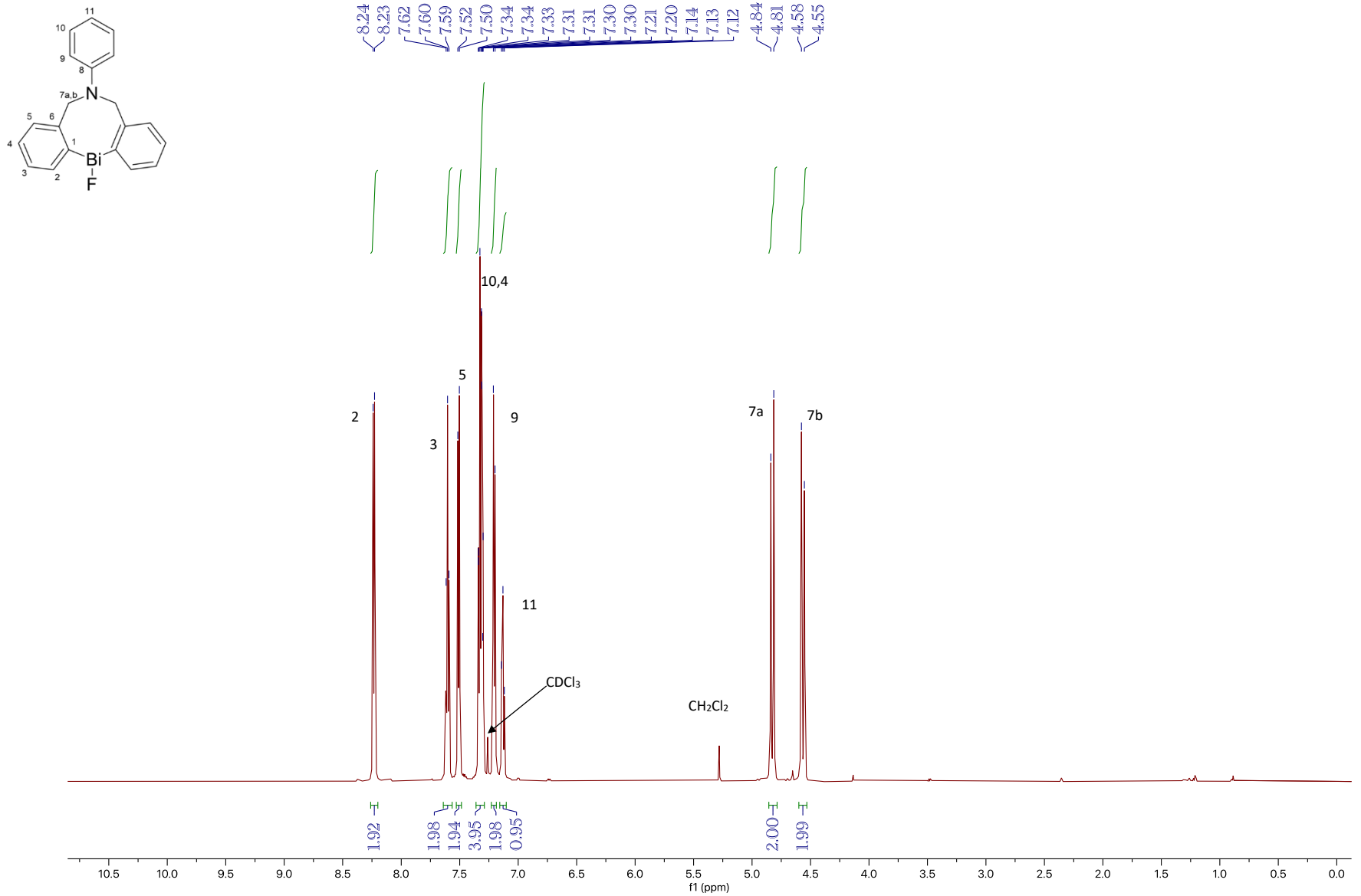


Figure S21. ^{1}H NMR of **2-F** (600 MHz, $CDCl_3$, 30°C)

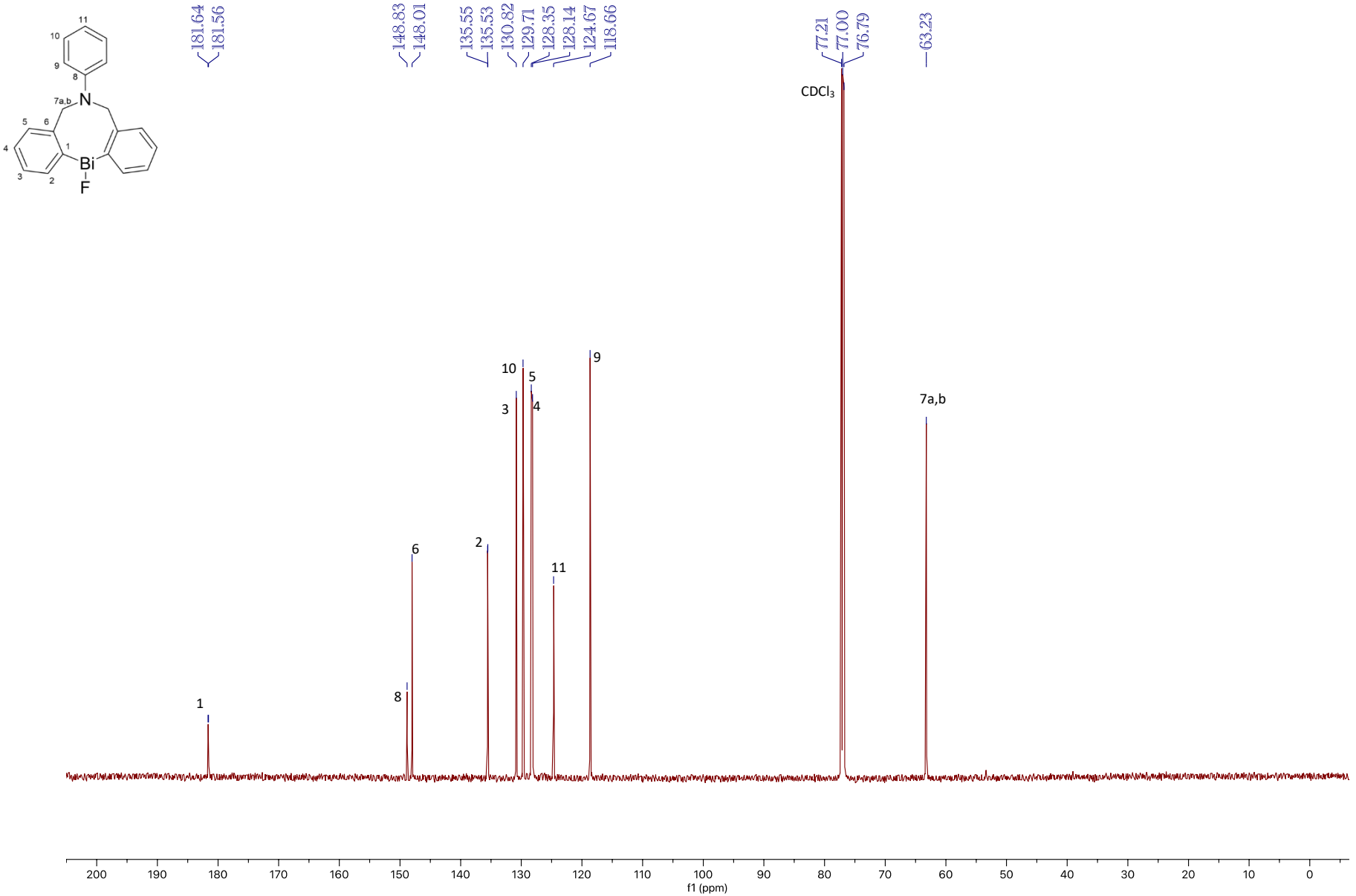


Figure S22. $^{13}C\{^{1}H\}$ NMR of **2-F** (150 MHz, $CDCl_3$, 30°C)

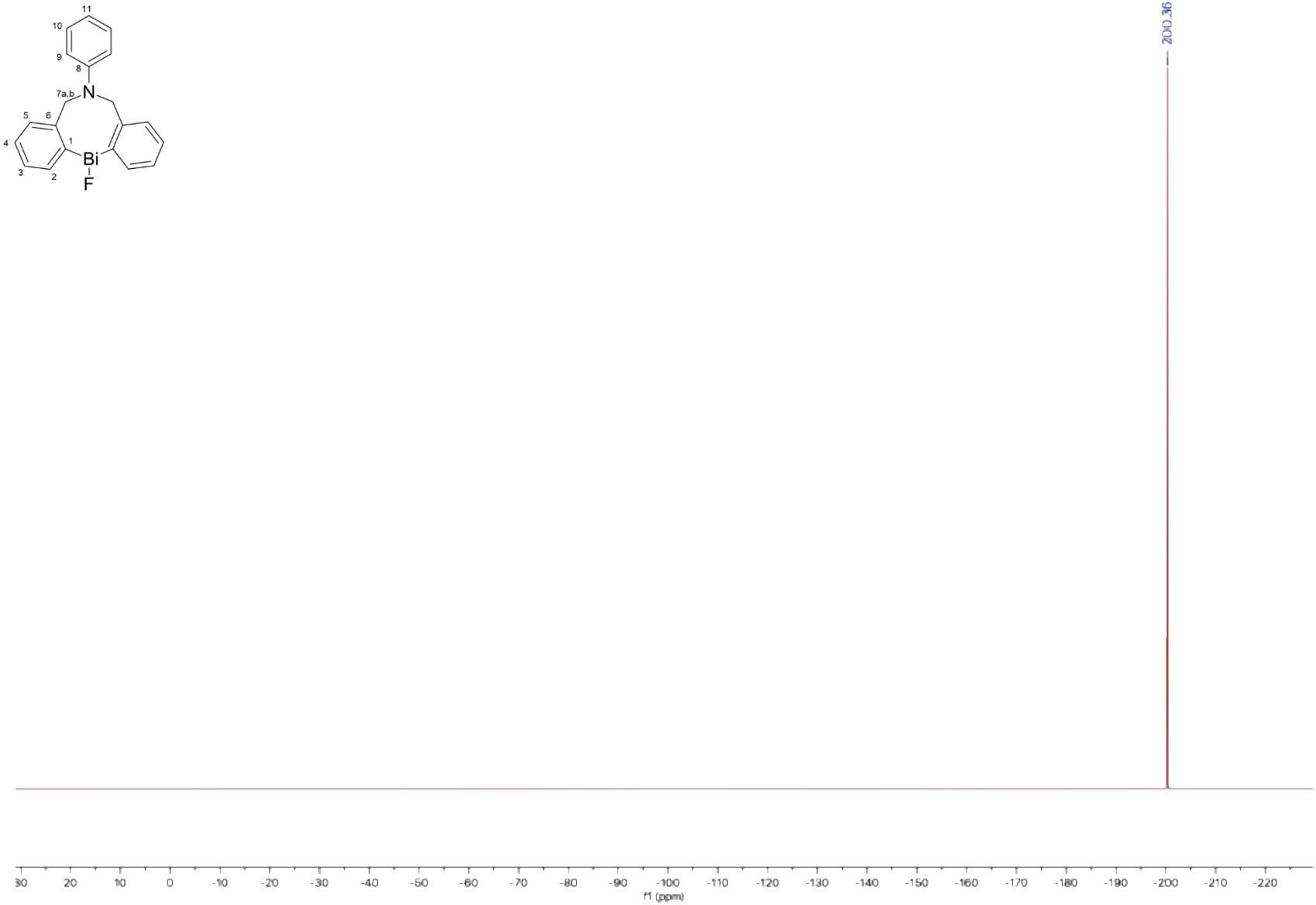


Figure S23. ^{19}F NMR of **2-F** (564 MHz, $CDCl_3$, 30°C)

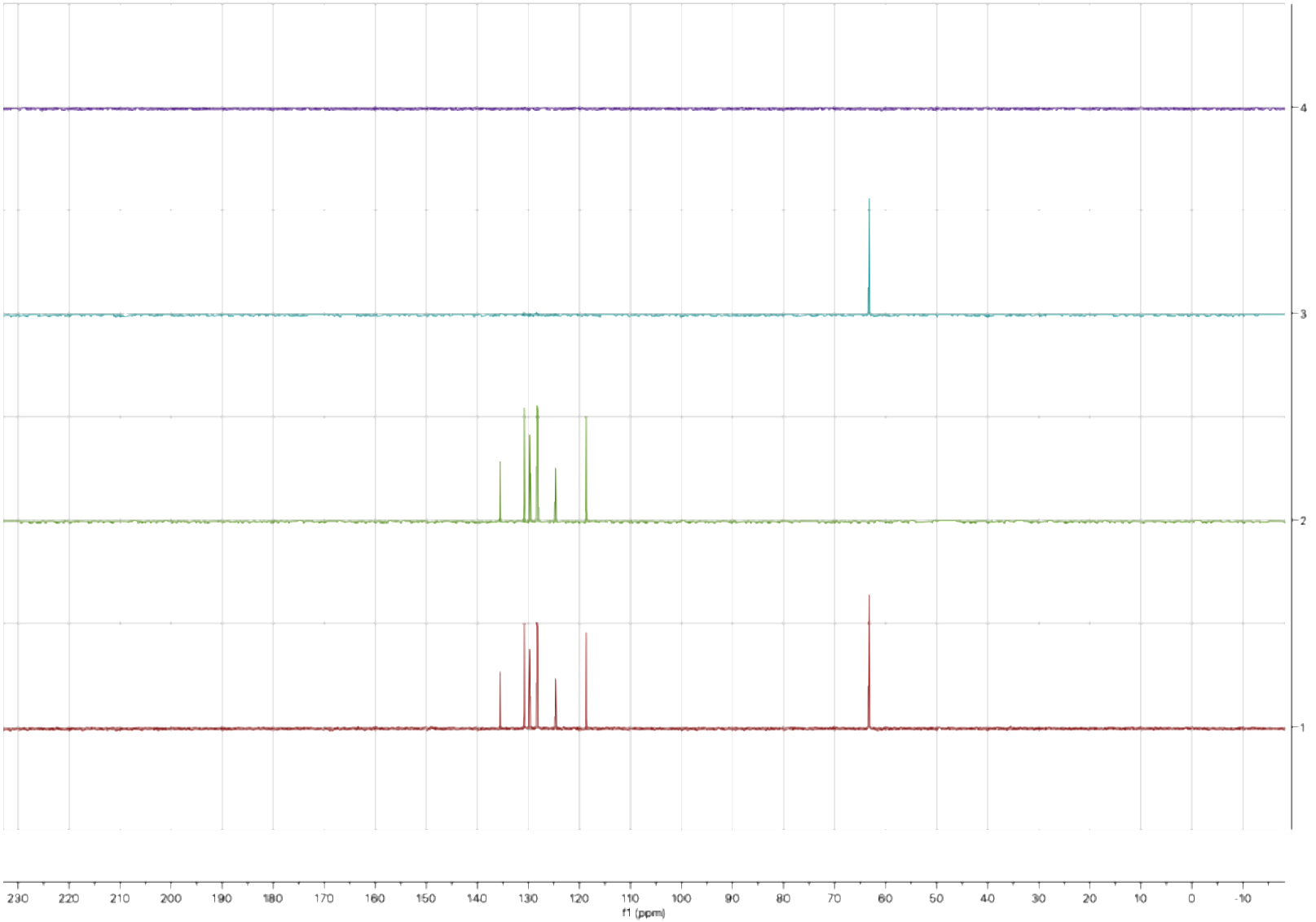


Figure S24. $^{13}C\{^{1}H\}$ DEPT of **2-F** in $CDCl_3$

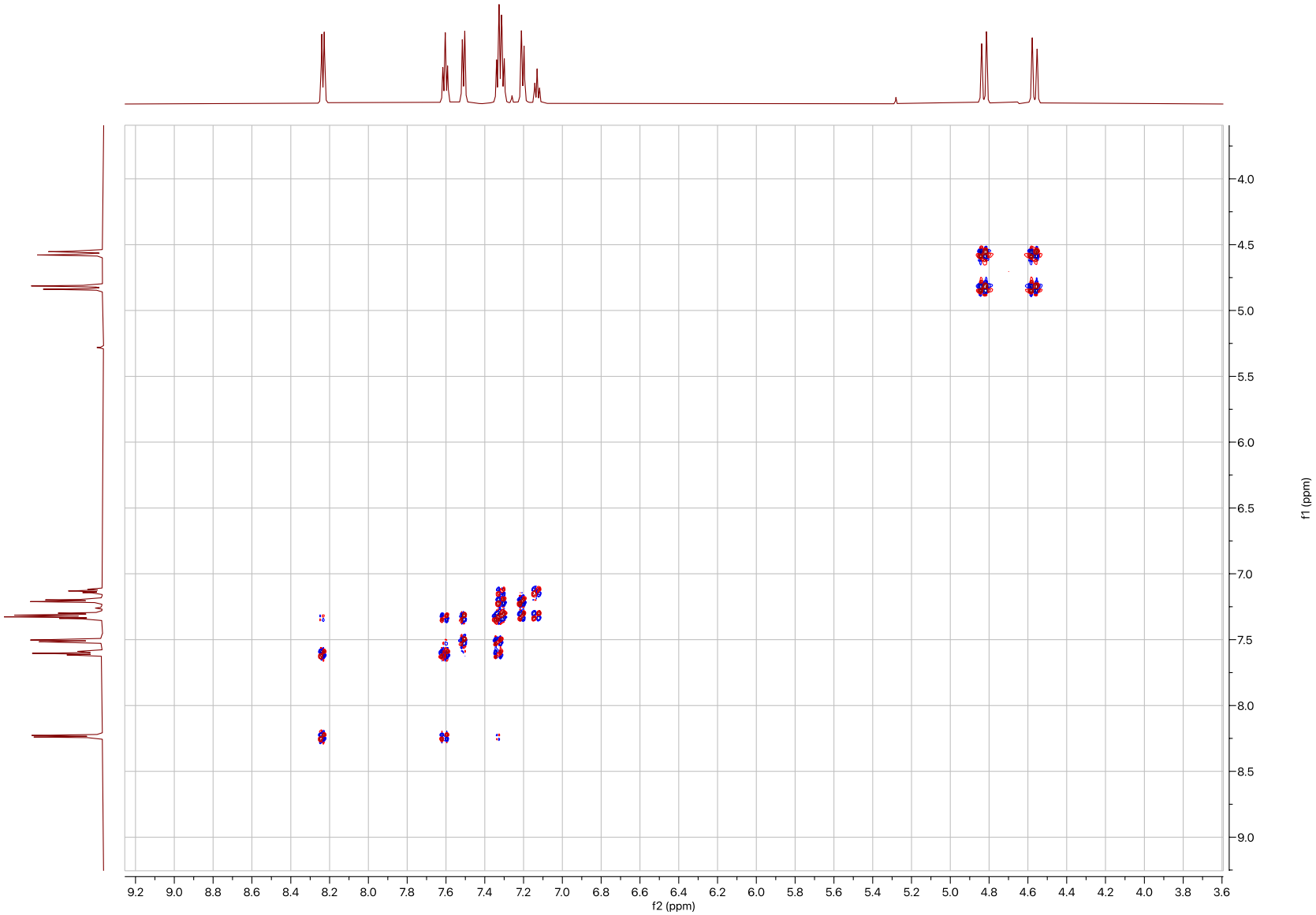


Figure S25. COSY of **2-F** in $CDCl_3$

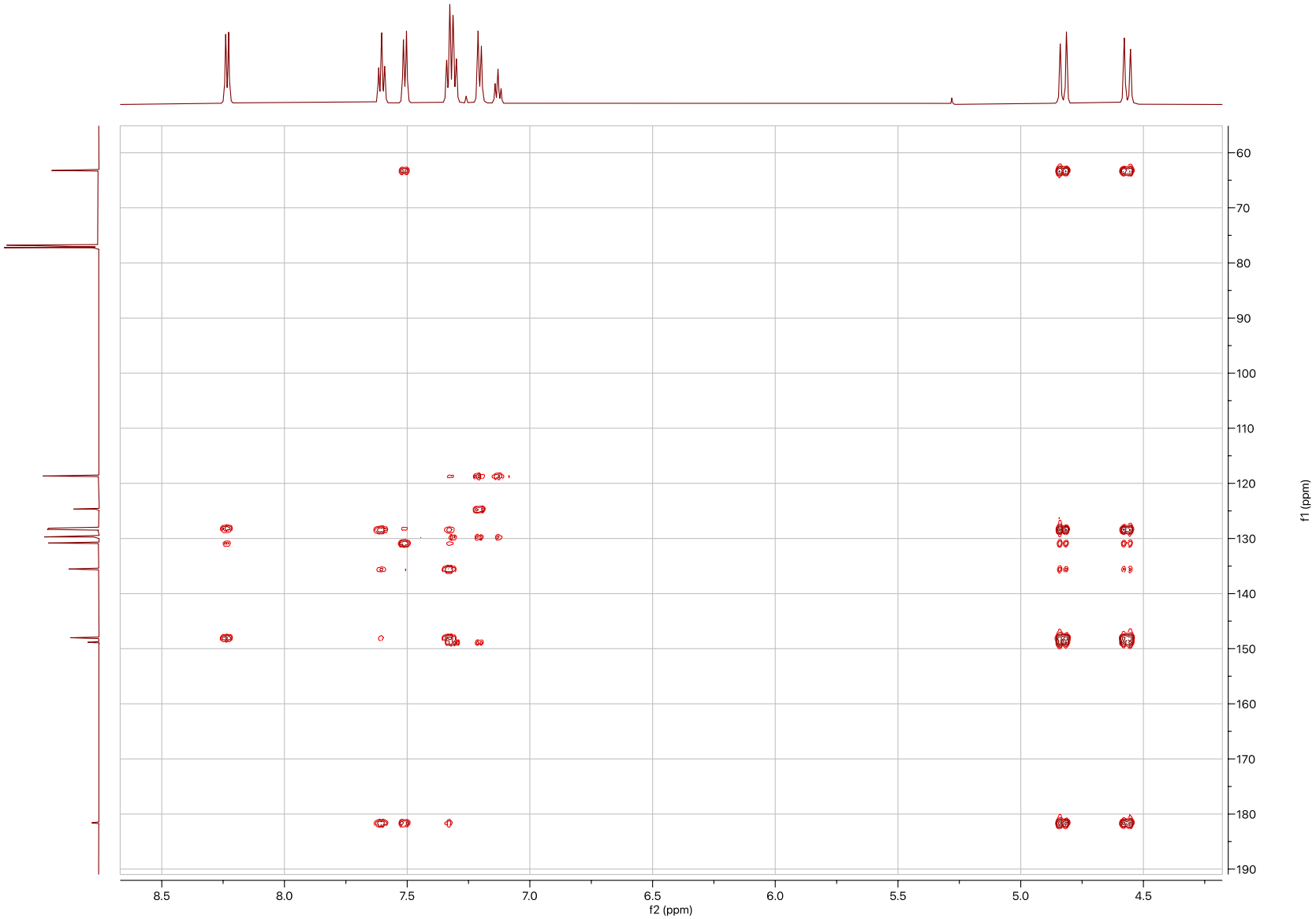


Figure S26. HMBC of **2-F** in $CDCl_3$

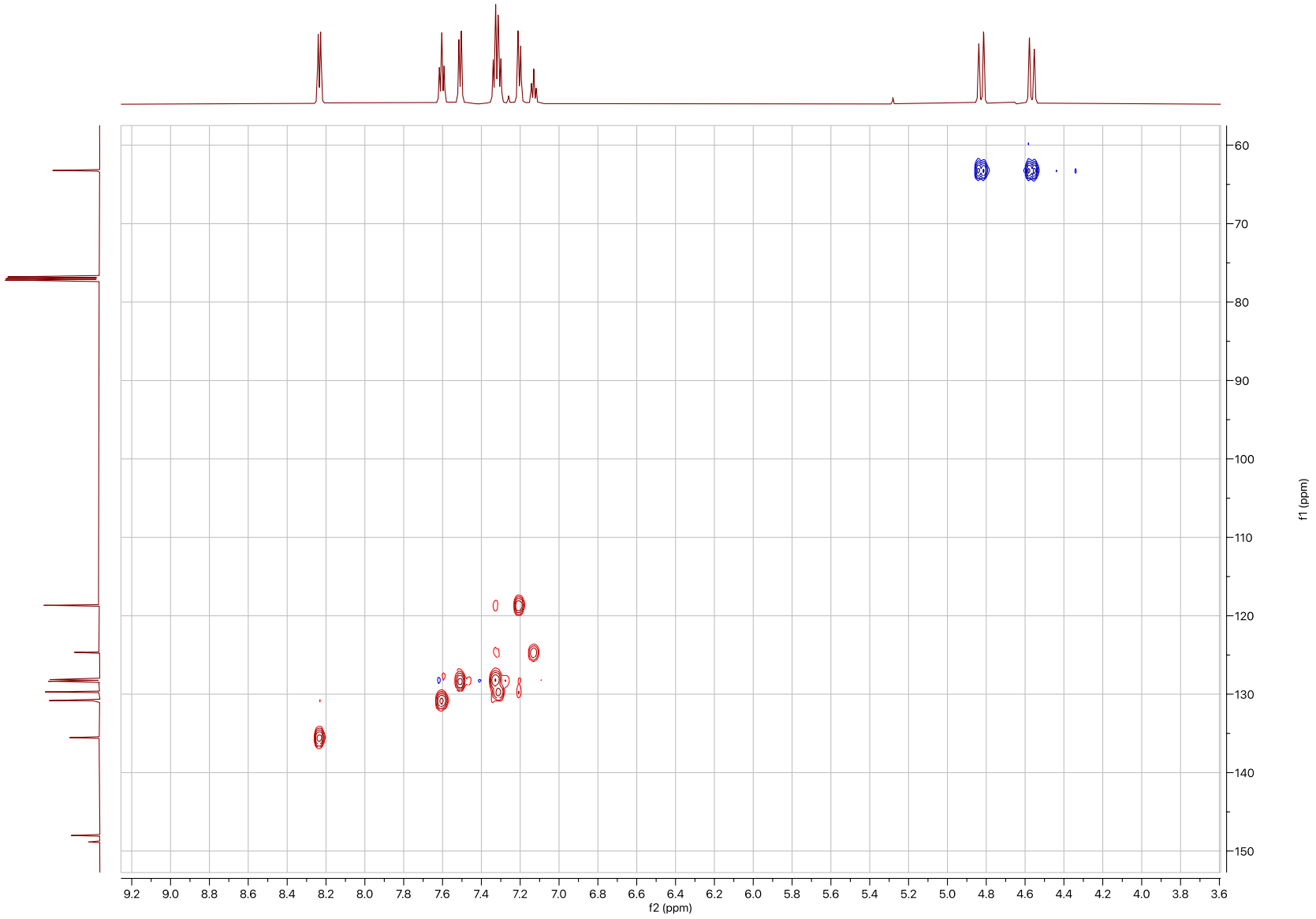
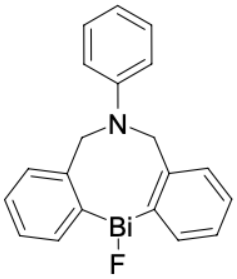


Figure S27. HSQC of **2-F** in $CDCl_3$



Chemical Formula: $BiC_{20}H_{17}FN$

Molecular Weight: 499.34

Elemental Analysis: C: 48.11; H: 3.43; N: 2.81

CENTC Elemental Analysis Facility
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Date of report	4/12/2024 6:05:12PM
User ID	Administrator
Comments	MV_299 [Hyvl]

DATE & TIME	4/12/2024 3:03:15 PM	P_ID	EA LAB
SAMPLE ID	24196	USER ID	Administrator
WEIGHT (mg)	2.546	MODE	CHN

CARBON	47.005%
HYDROGEN	3.511%
NITROGEN	2.673%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

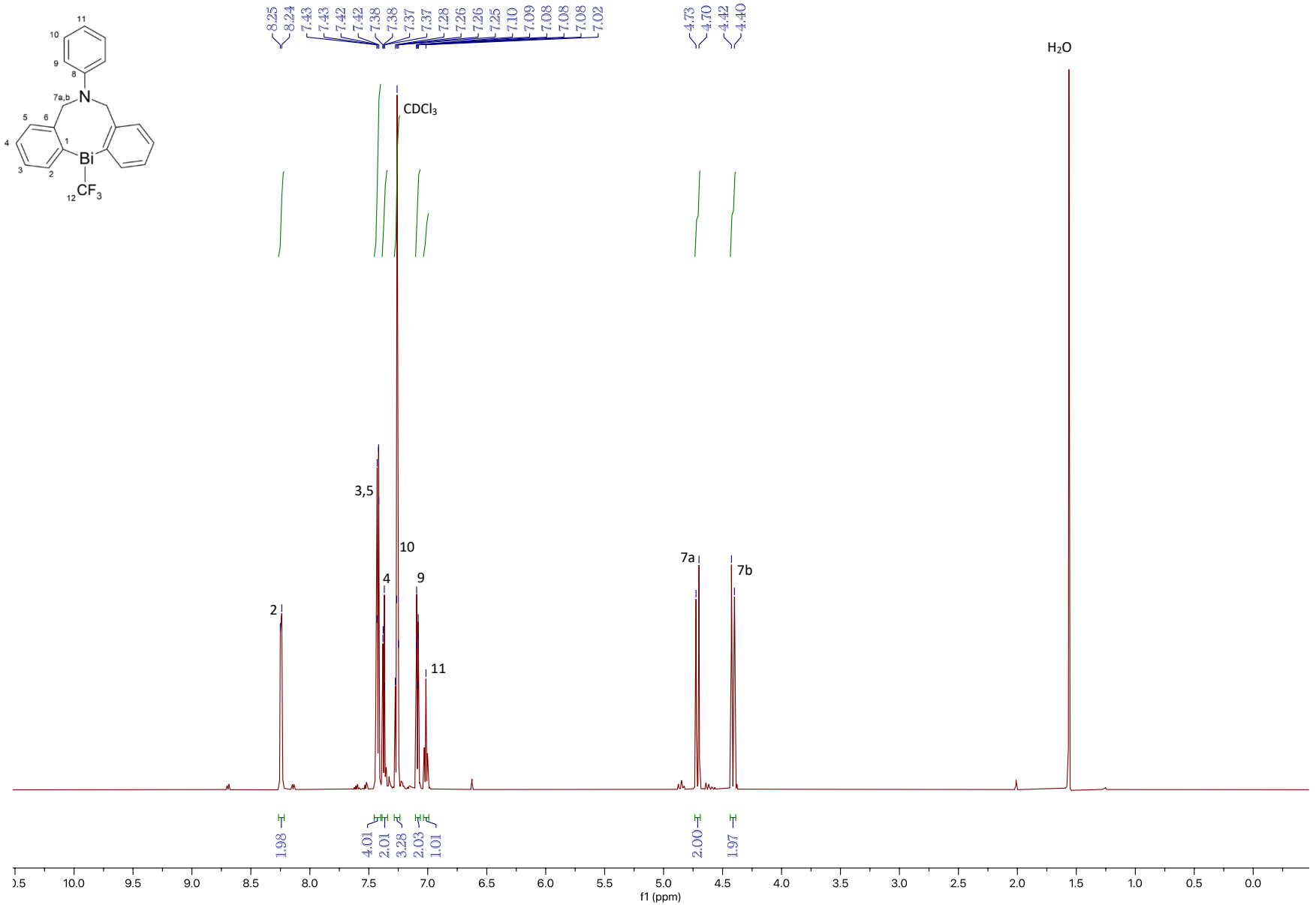


Figure S28. ^{1}H NMR of **2-CF$_3$** (600 MHz, $CDCl_3$, 30°C)

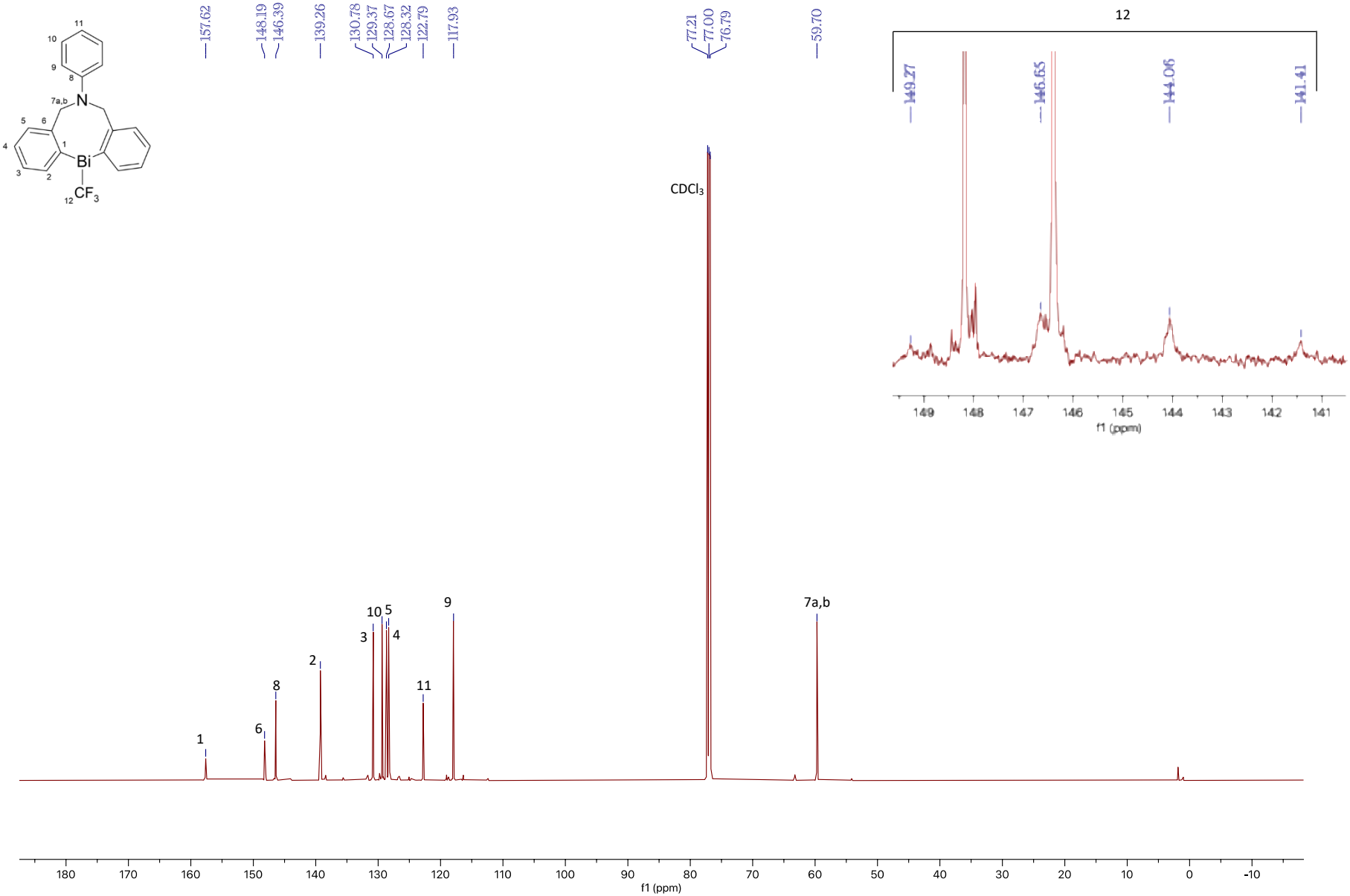


Figure S29. $^{13}C\{^{1}H\}$ NMR of **2-CF$_3$** (150 MHz, $CDCl_3$, 30°C)

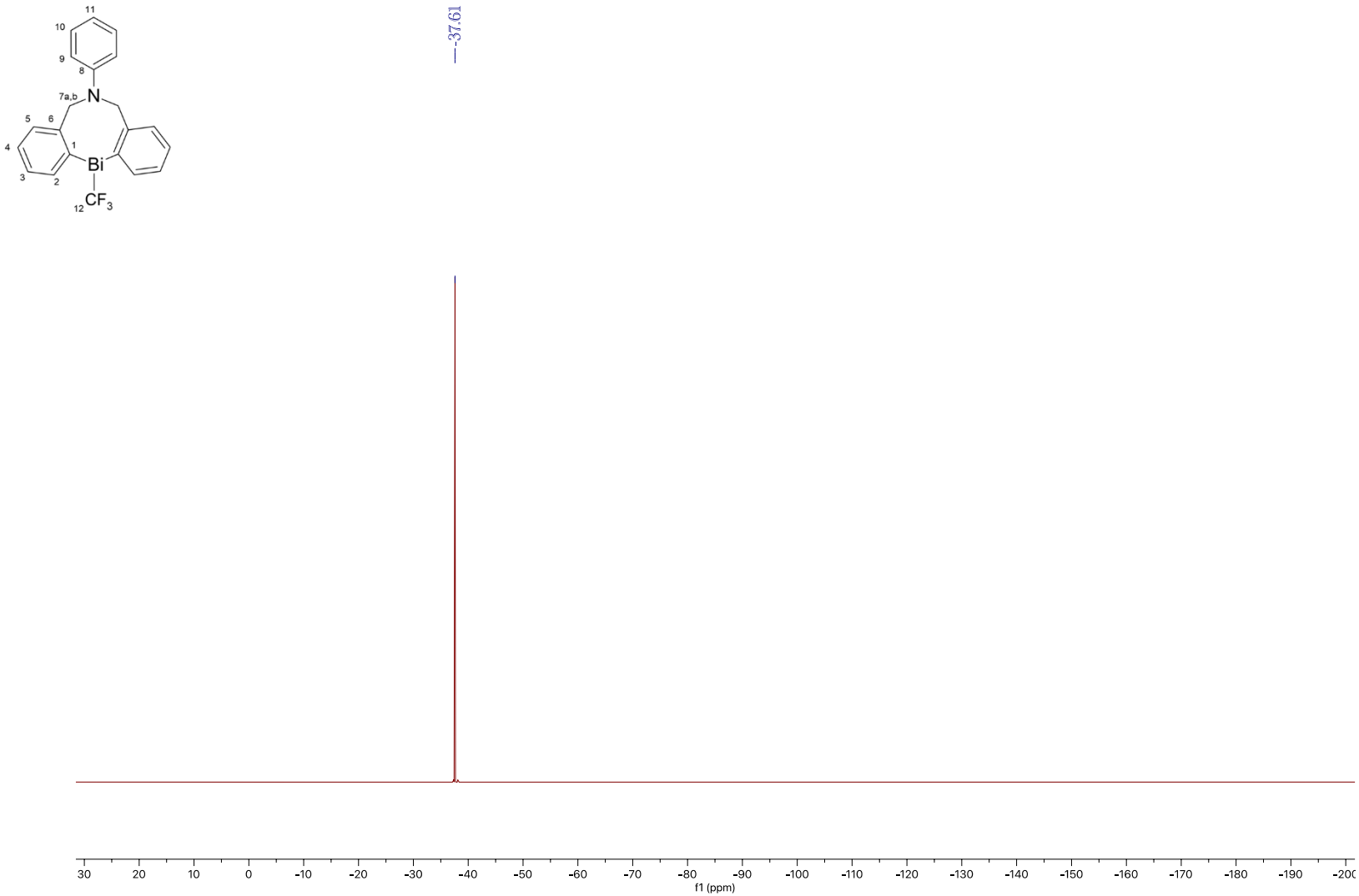


Figure S30. ^{19}F NMR of **2-CF_3** (564 MHz, $CDCl_3$, 30°C)

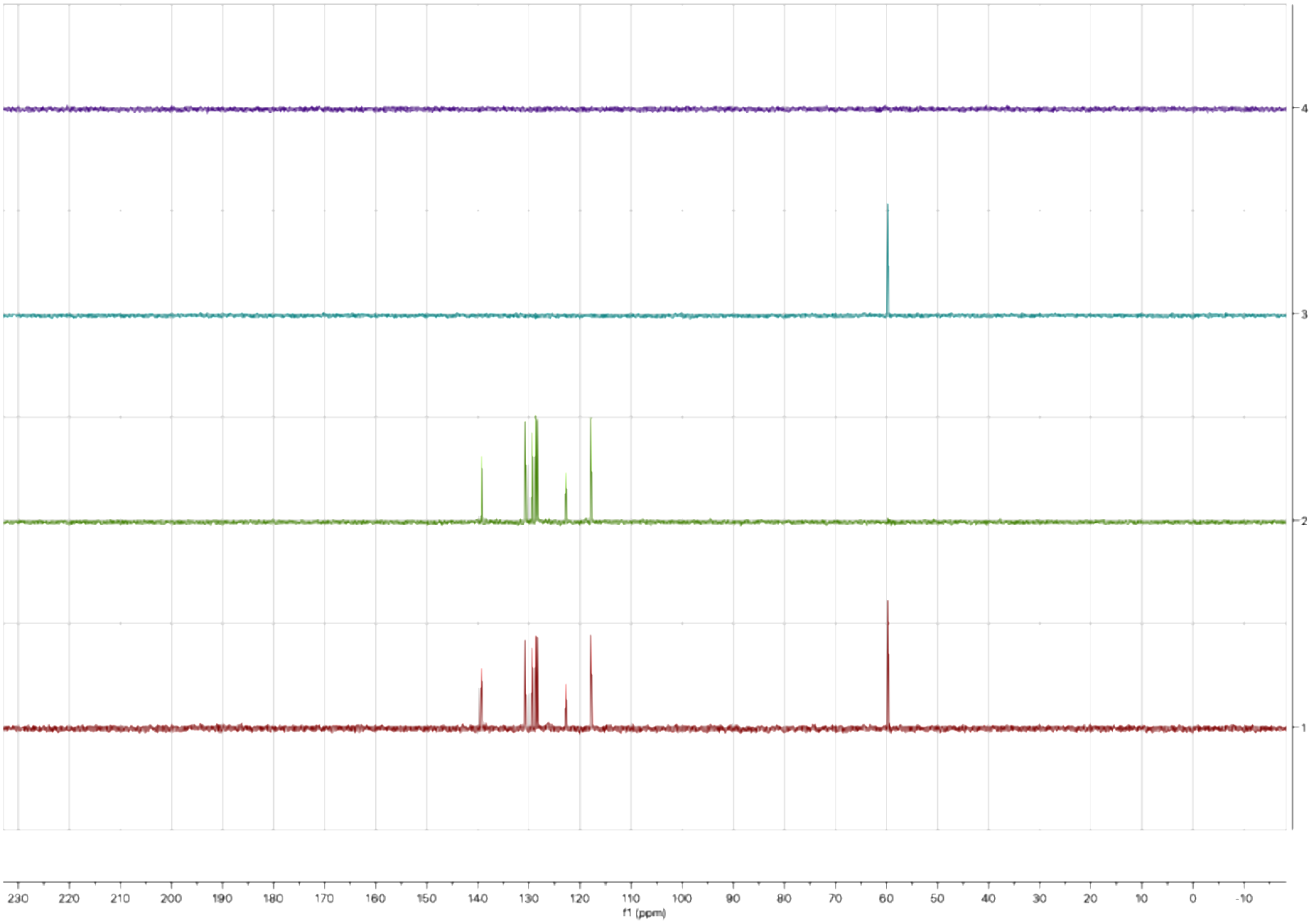


Figure S31. $^{13}C\{^{1}H\}$ DEPT of **2-CF_3** in $CDCl_3$

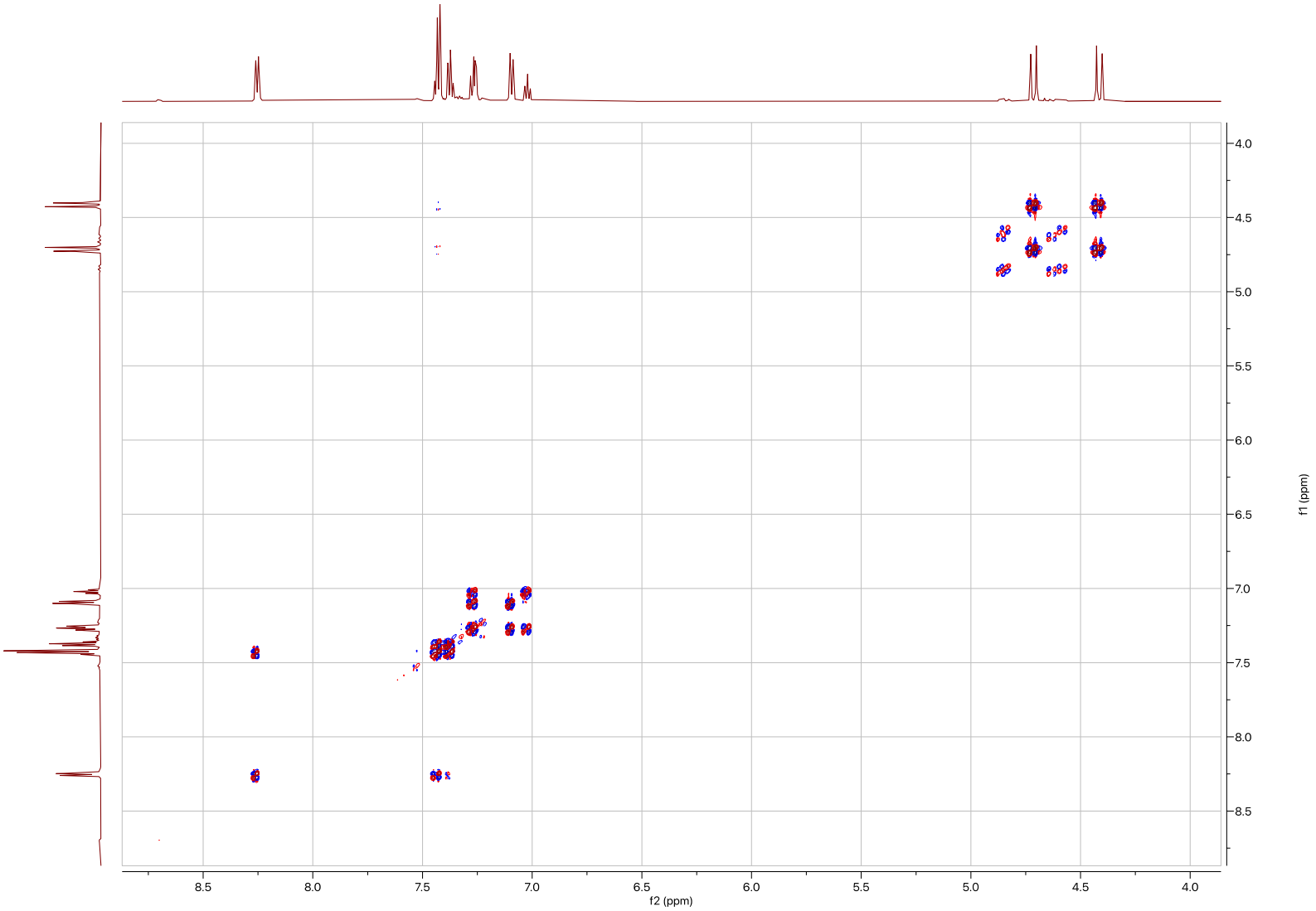


Figure S32. COSY of **2-CF_3** in $CDCl_3$

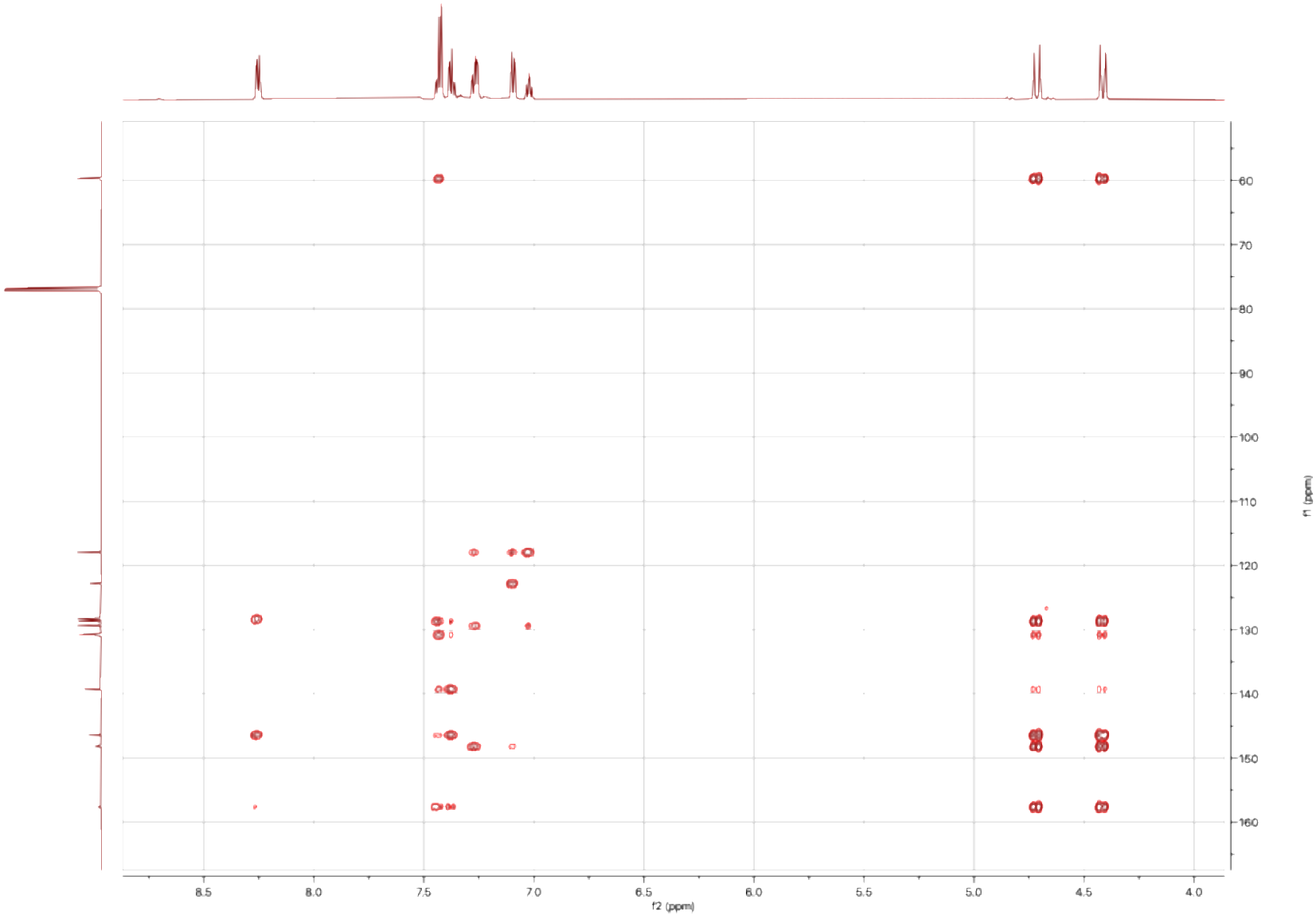


Figure S33. HMBC of **2-CF_3** in $CDCl_3$

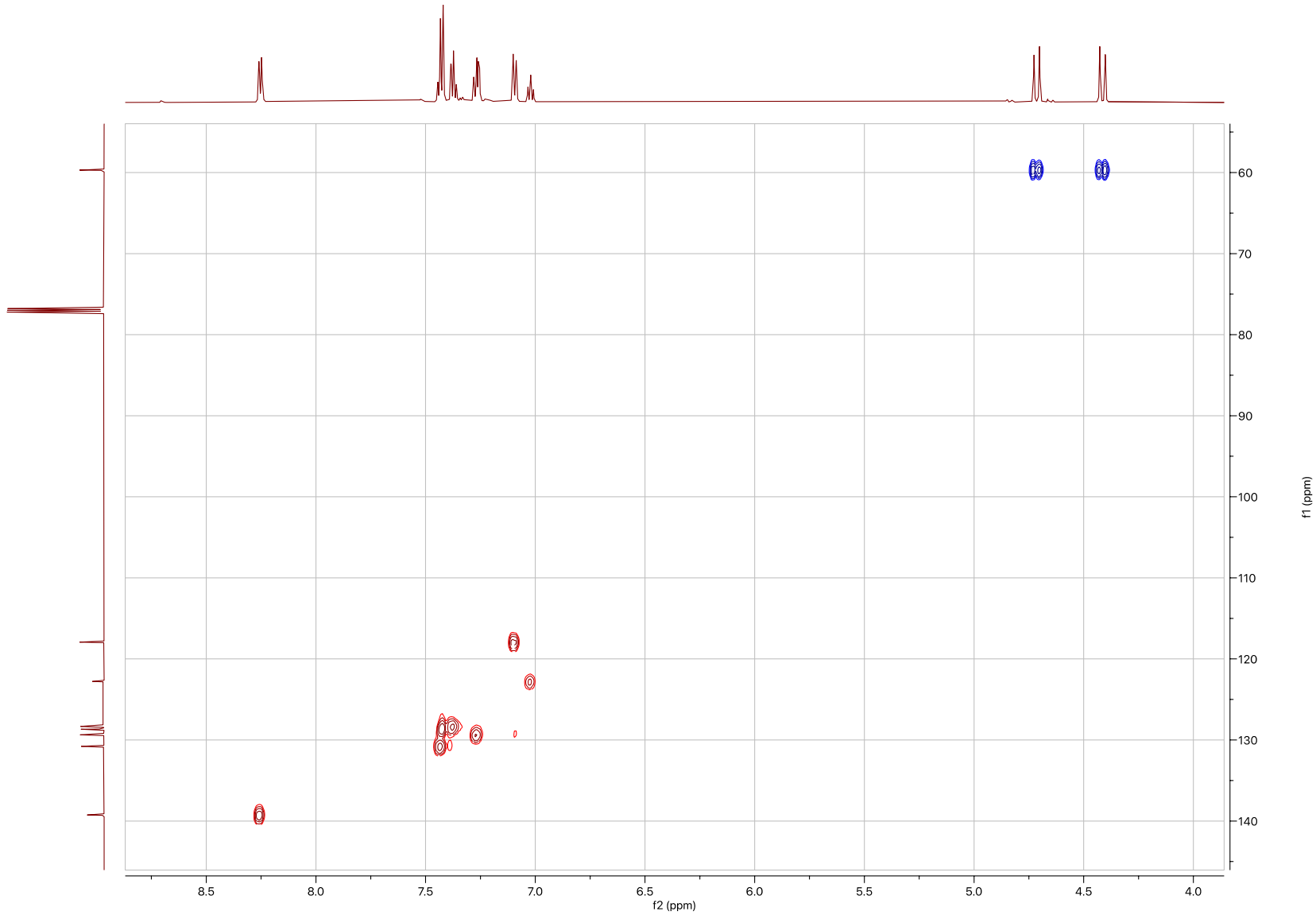
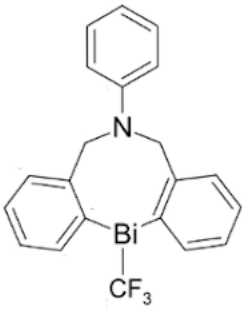


Figure S34. HSQC of **2-CF$_3$** in $CDCl_3$



Chemical Formula: $BiC_{21}H_{17}F_3N$

Molecular Weight: 549.35

Elemental Analysis: C: 45.91; H: 3.12 N: 2.55

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Date of report	12/15/2023 5:19:46PM
User ID	Administrator
Comments	MV_215 [Hyvl]

DATE & TIME	12/15/2023 2:13:37 PM	P_ID	EA LAB
SAMPLE ID	23686	USER ID	Administrator
WEIGHT (mg)	2.557	MODE	CHN

CARBON	45.966%
HYDROGEN	3.021%
NITROGEN	2.630%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

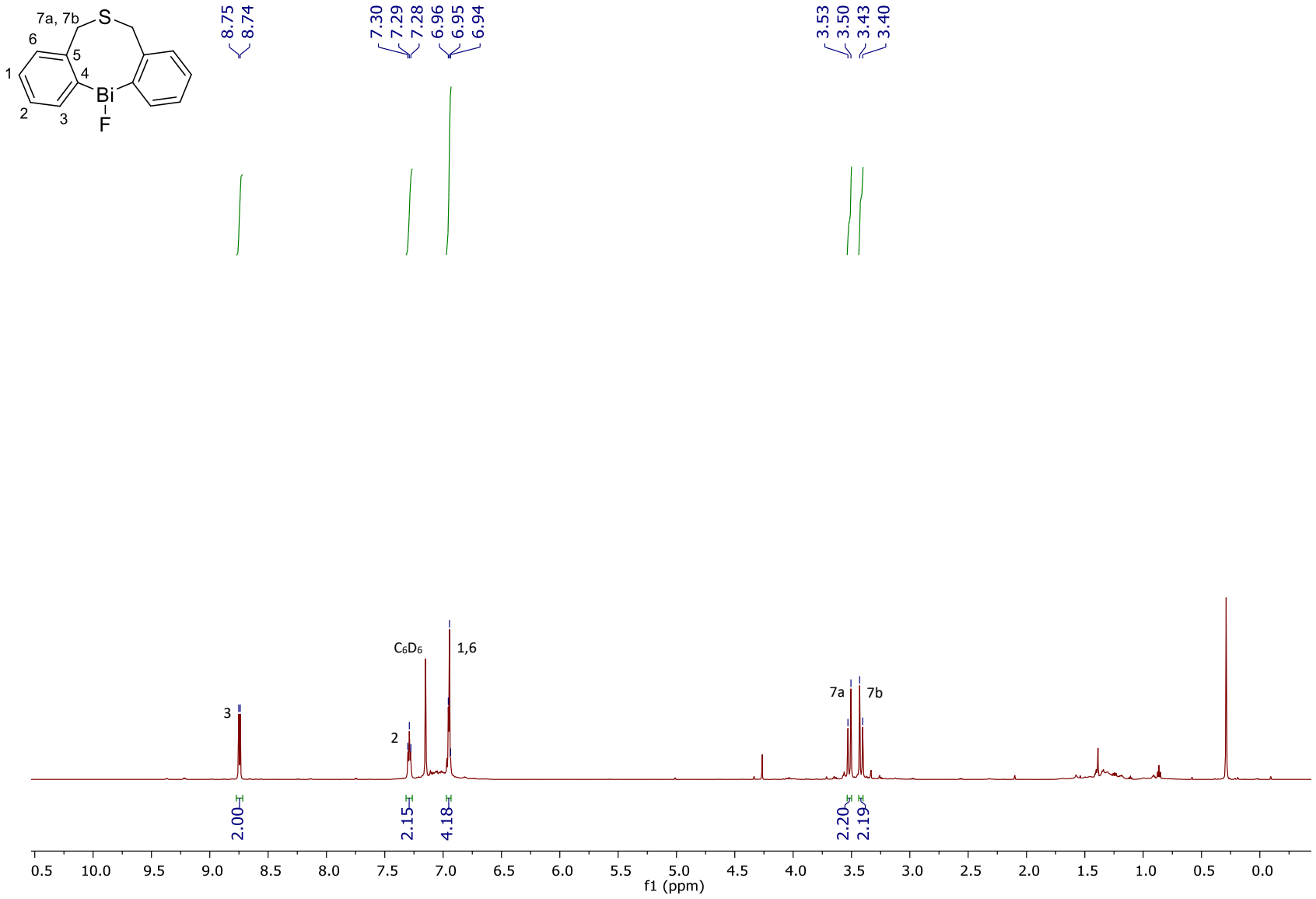


Figure S35. ^{1}H NMR of **3-F** (600 MHz, C_6D_6, 30°C)

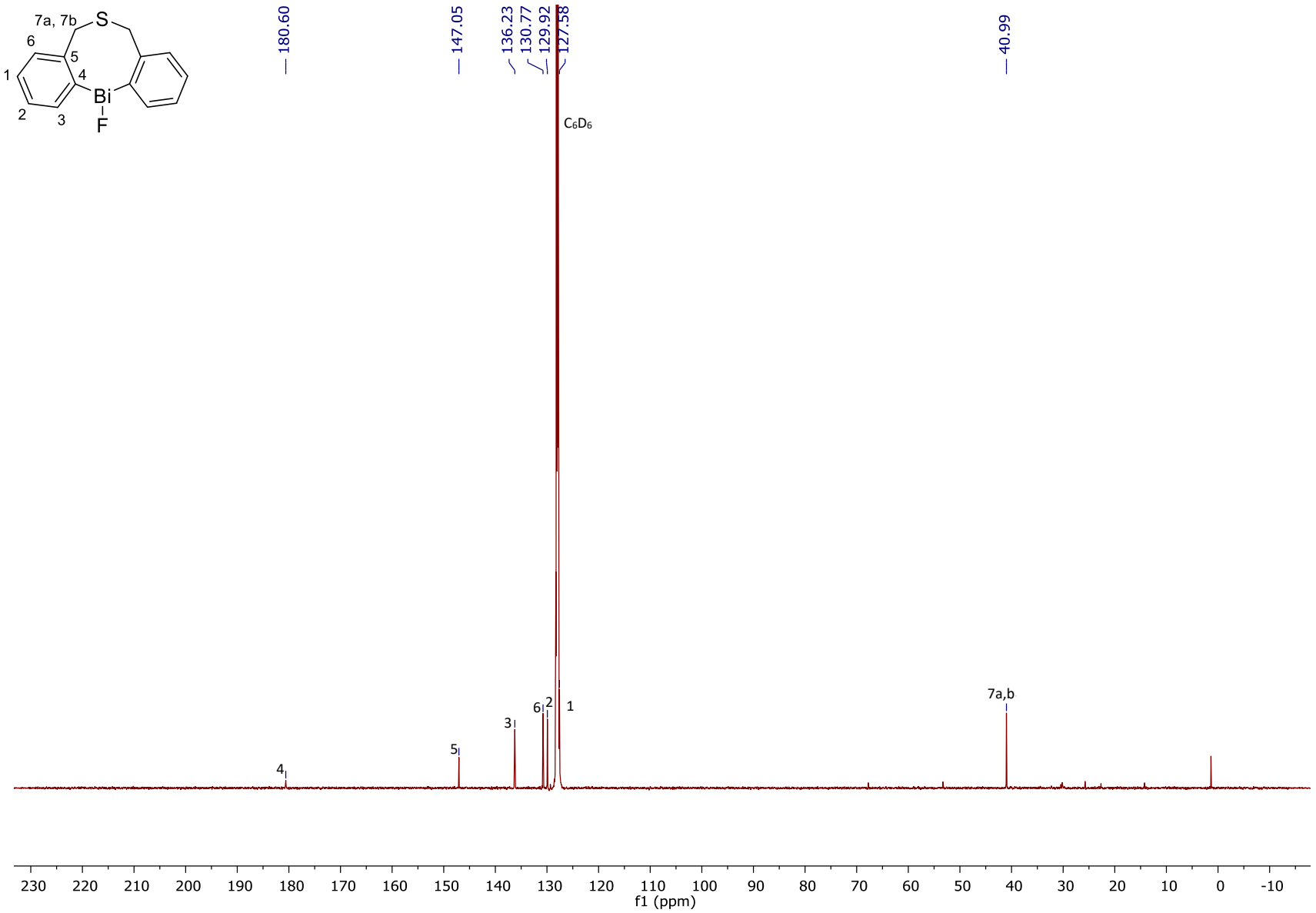


Figure S36. $^{13}C\{^{1}H\}$ NMR of **3-F** (150 MHz, C_6D_6, 30°C)

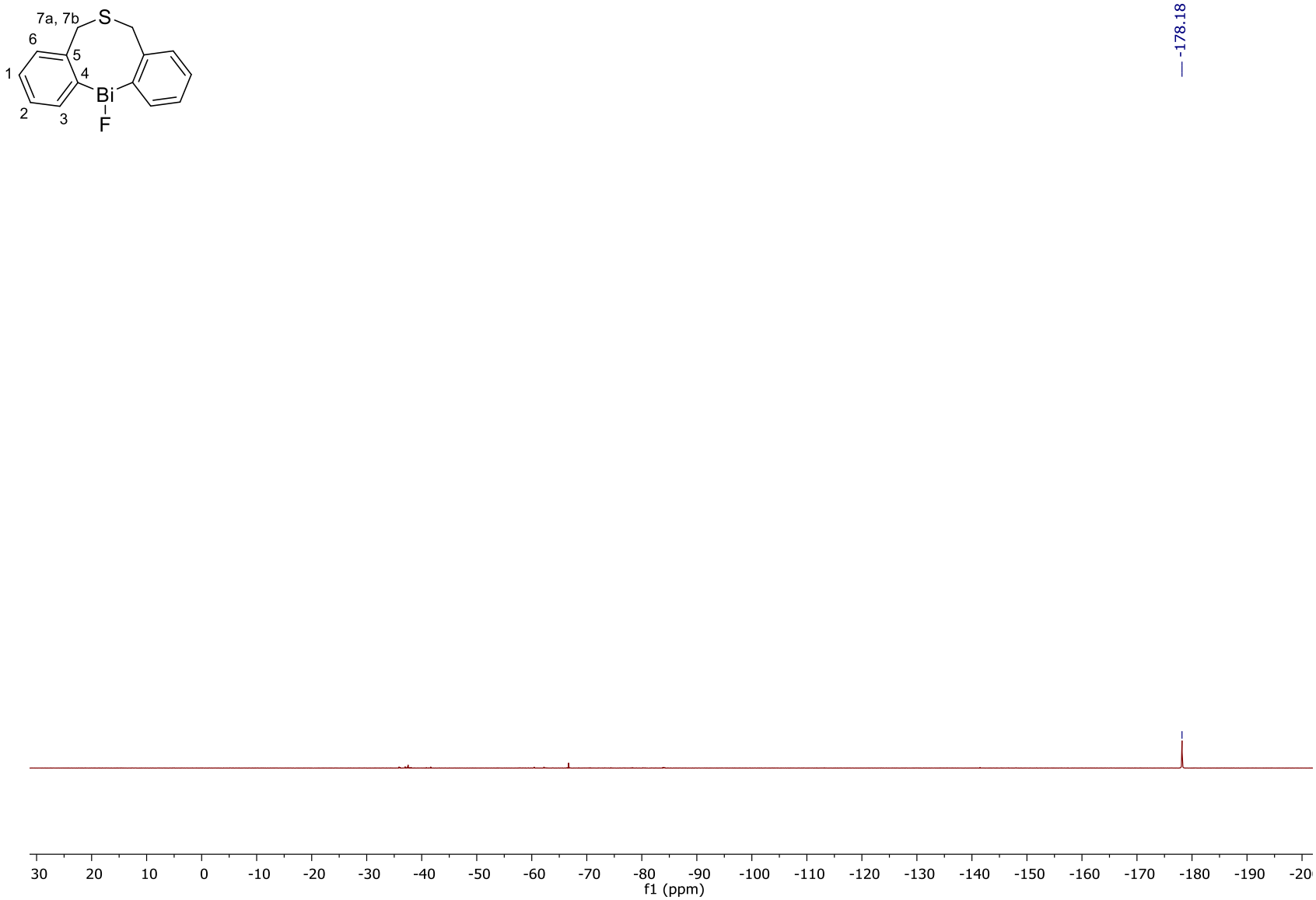


Figure S37. ^{19}F NMR of **3-F** (564 MHz, C_6D_6, 30°C)

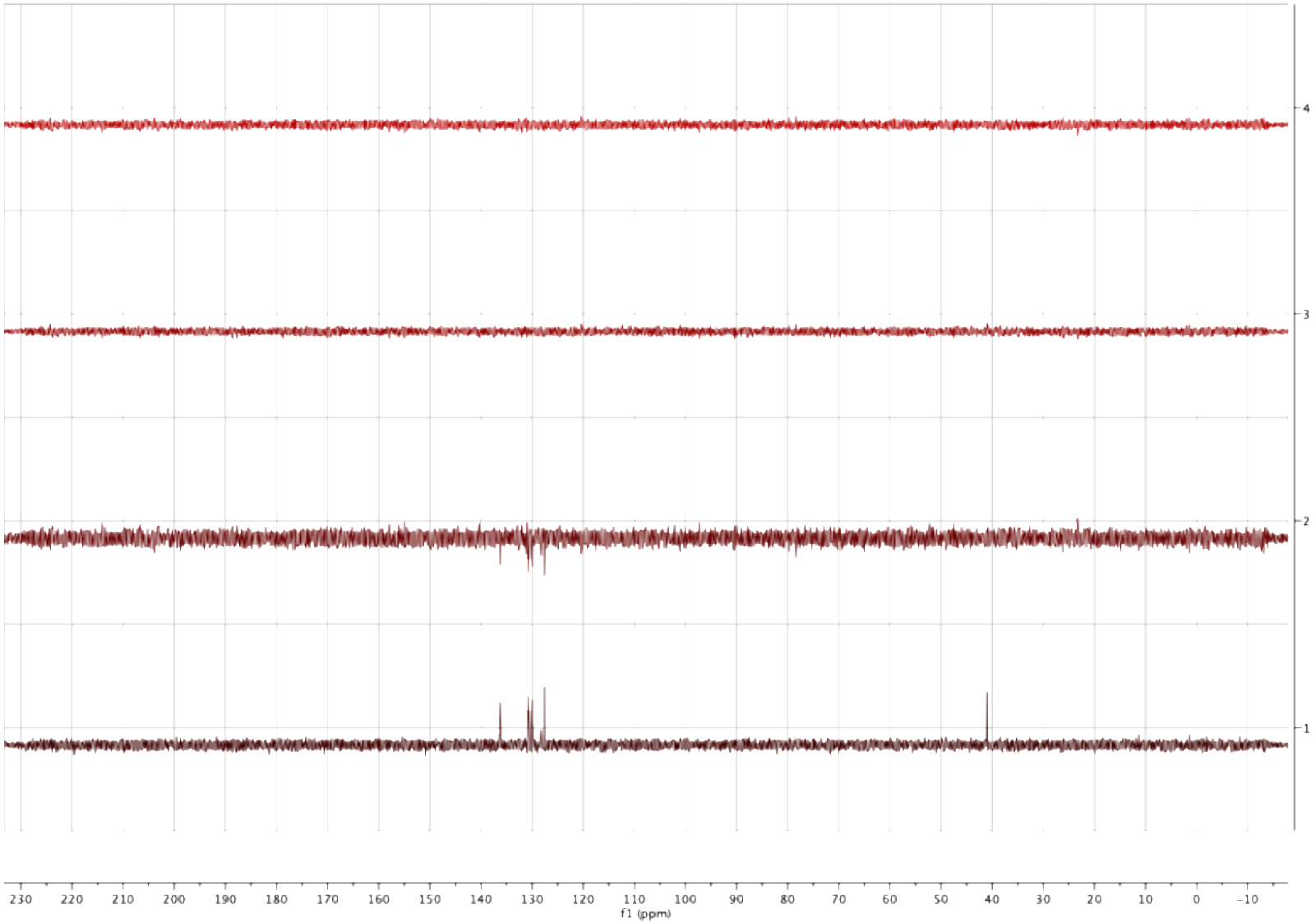


Figure S38. $^{13}C\{^{1}H\}$ DEPT of **3-F** in C_6D_6

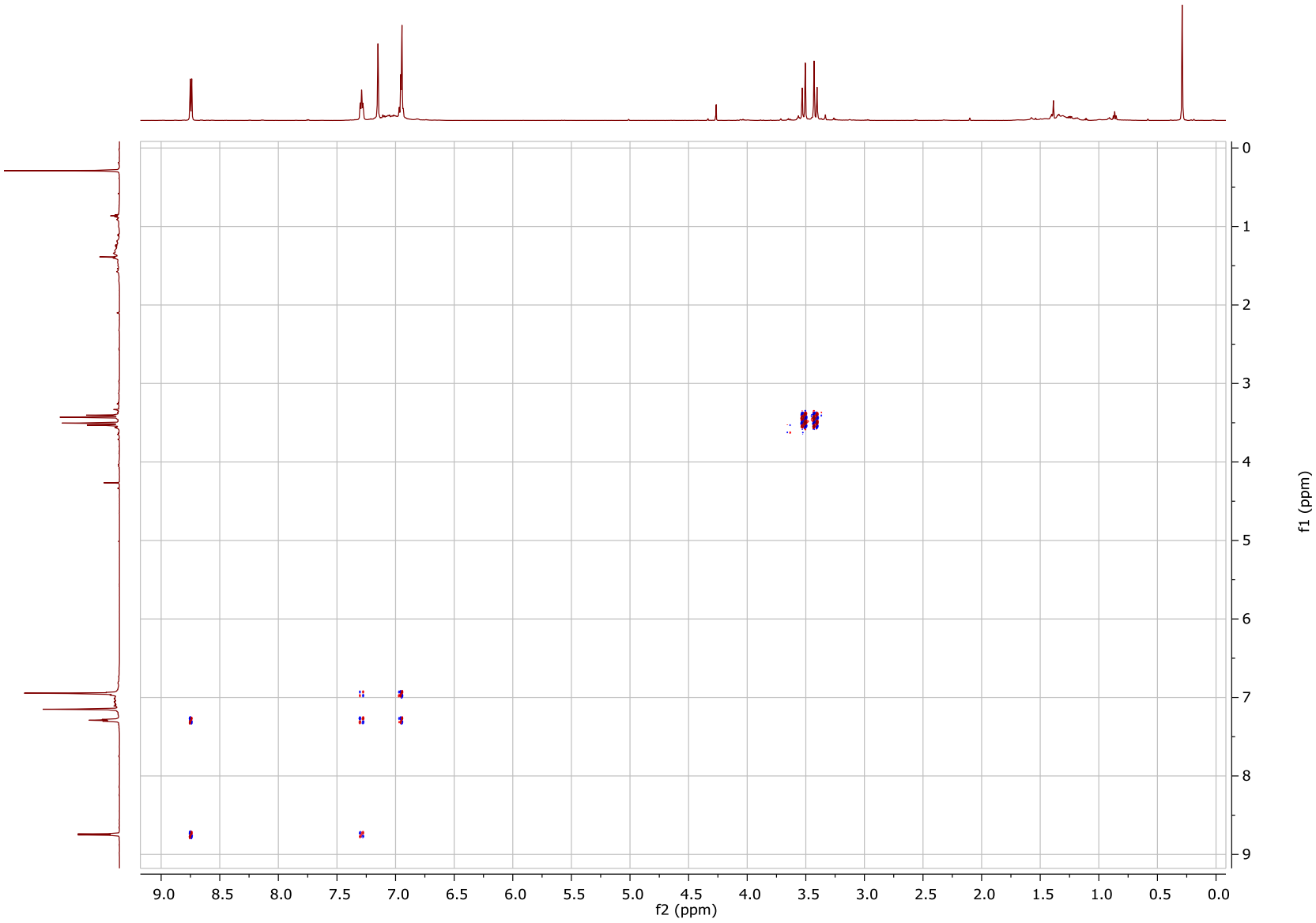


Figure S39. COSY of **3-F** in C_6D_6

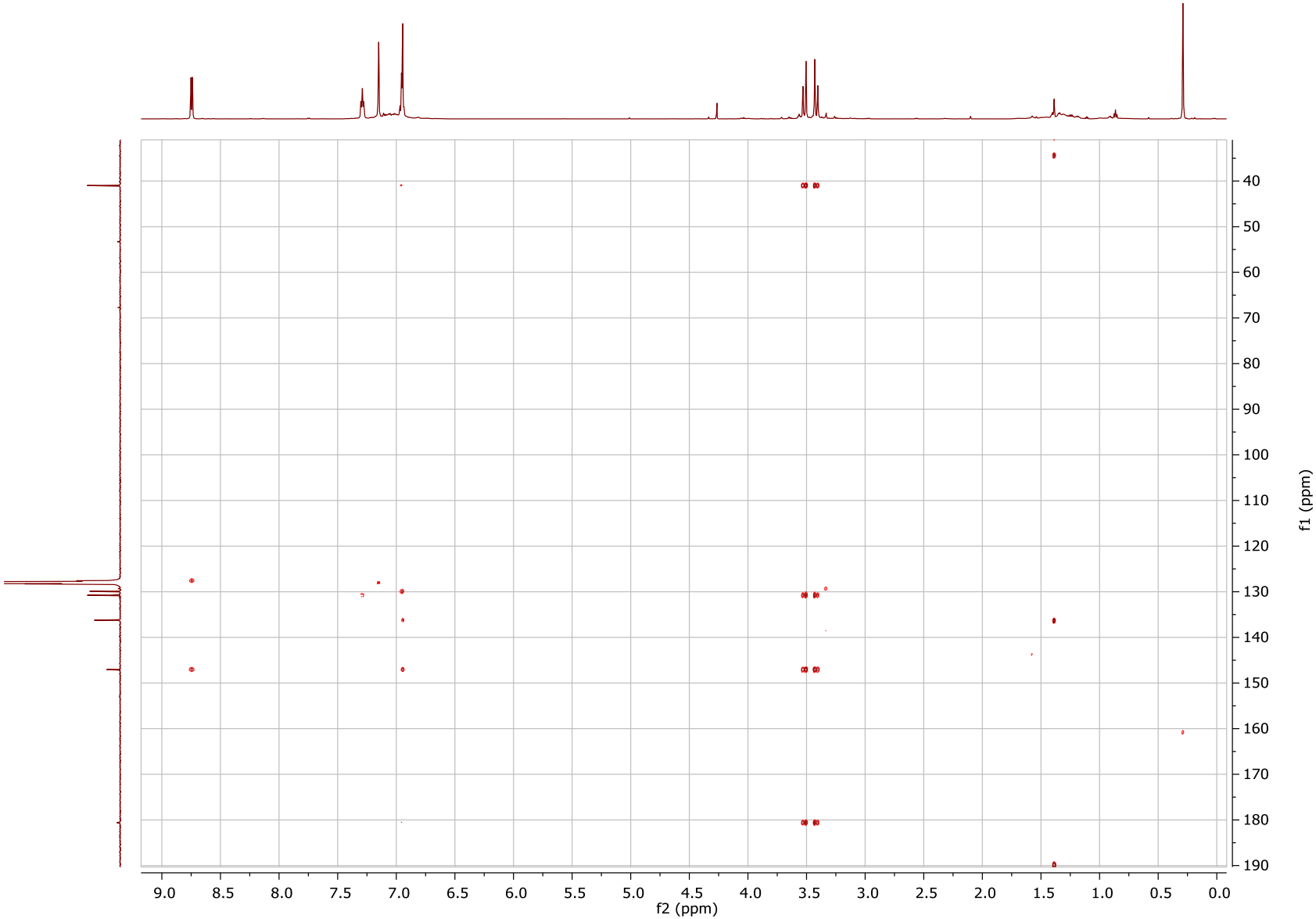


Figure S40. HMBC of **3-F** in C_6D_6

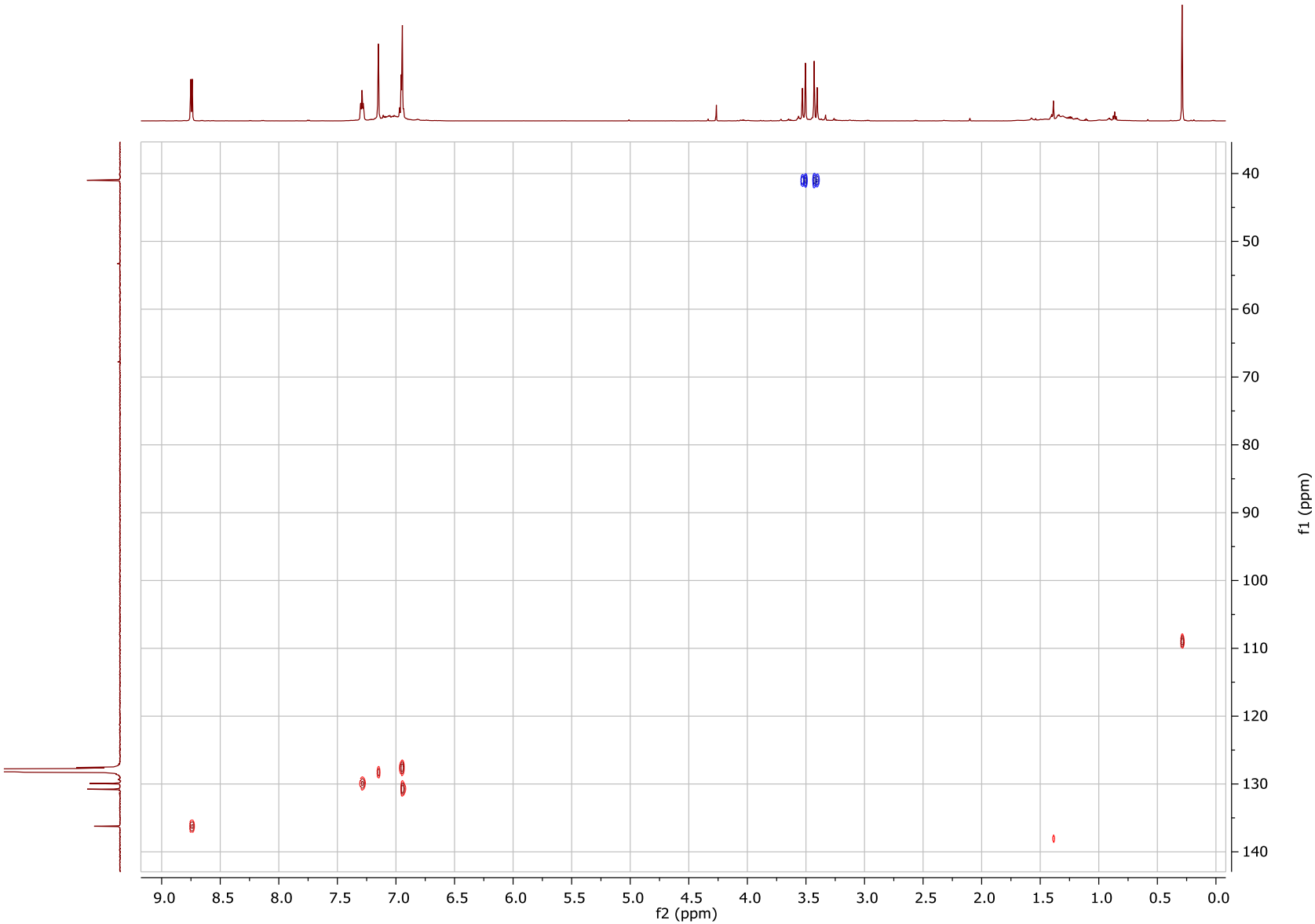
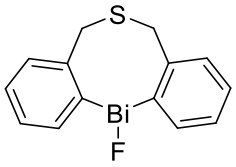


Figure S41. HSQC of **3-F** in C_6D_6



Chemical Formula: $BiC_{14}H_{12}SF$

Molecular Weight: 440.29

Elemental Analysis: C: 38.19; H: 2.75

CENTC Elemental Analysis Facility
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Date of report	2/16/2024 5:46:57PM
User ID	Administrator
Comments	TLG_4_173 [Hyvl]

DATE & TIME	2/16/2024 4:20:59 PM	P_ID	EA LAB
SAMPLE ID	24062	USER ID	Administrator
WEIGHT (mg)	2.145	MODE	CHN

CARBON	39.099%
HYDROGEN	2.738%
NITROGEN	-.129%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

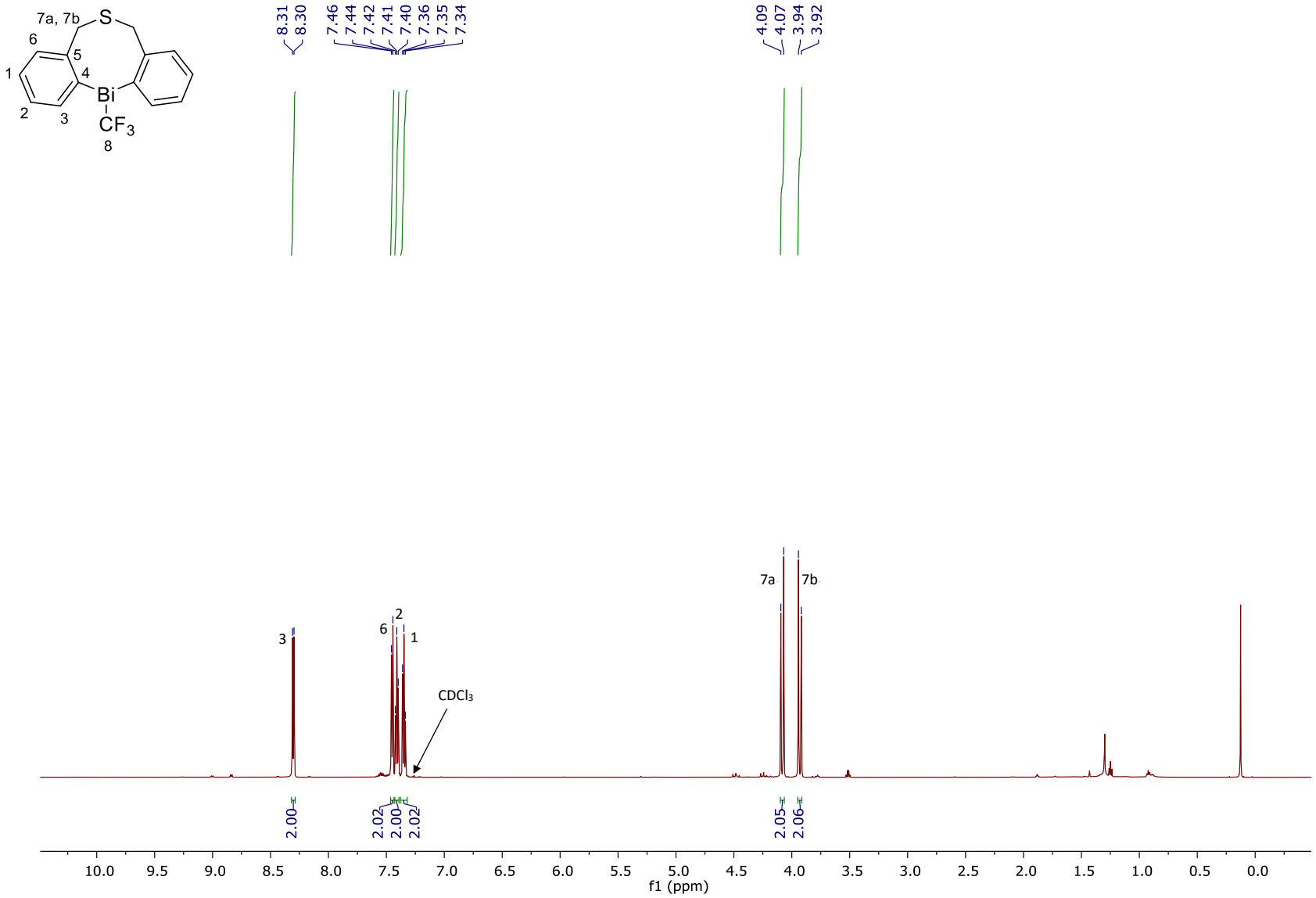


Figure S42. ^{1}H NMR of **3-CF$_3$** in (600 MHz, $CDCl_3$, 60°C)

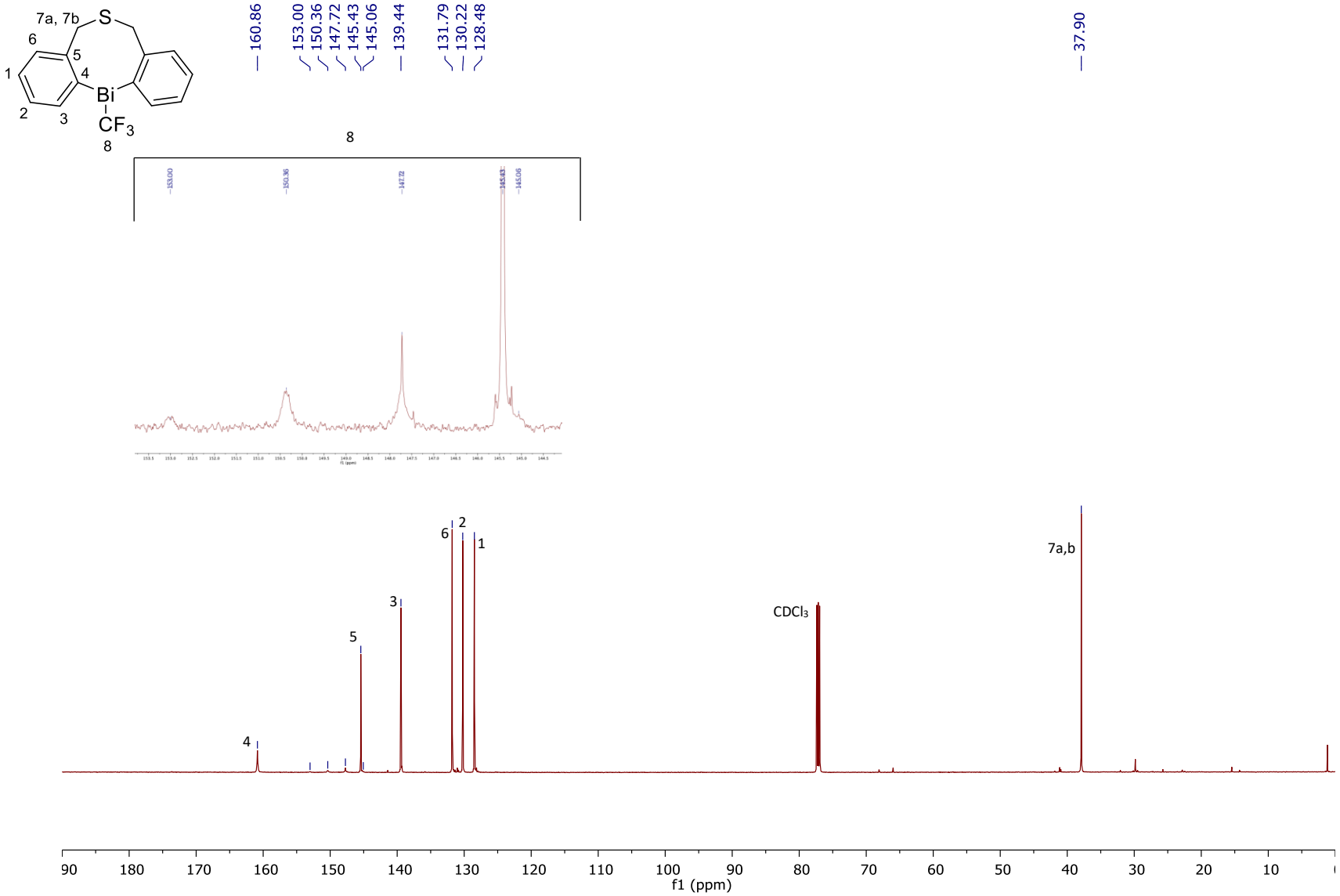


Figure S43. $^{13}C\{^{1}H\}$ NMR of **3-CF$_3$** (150 MHz, $CDCl_3$, 60°C)

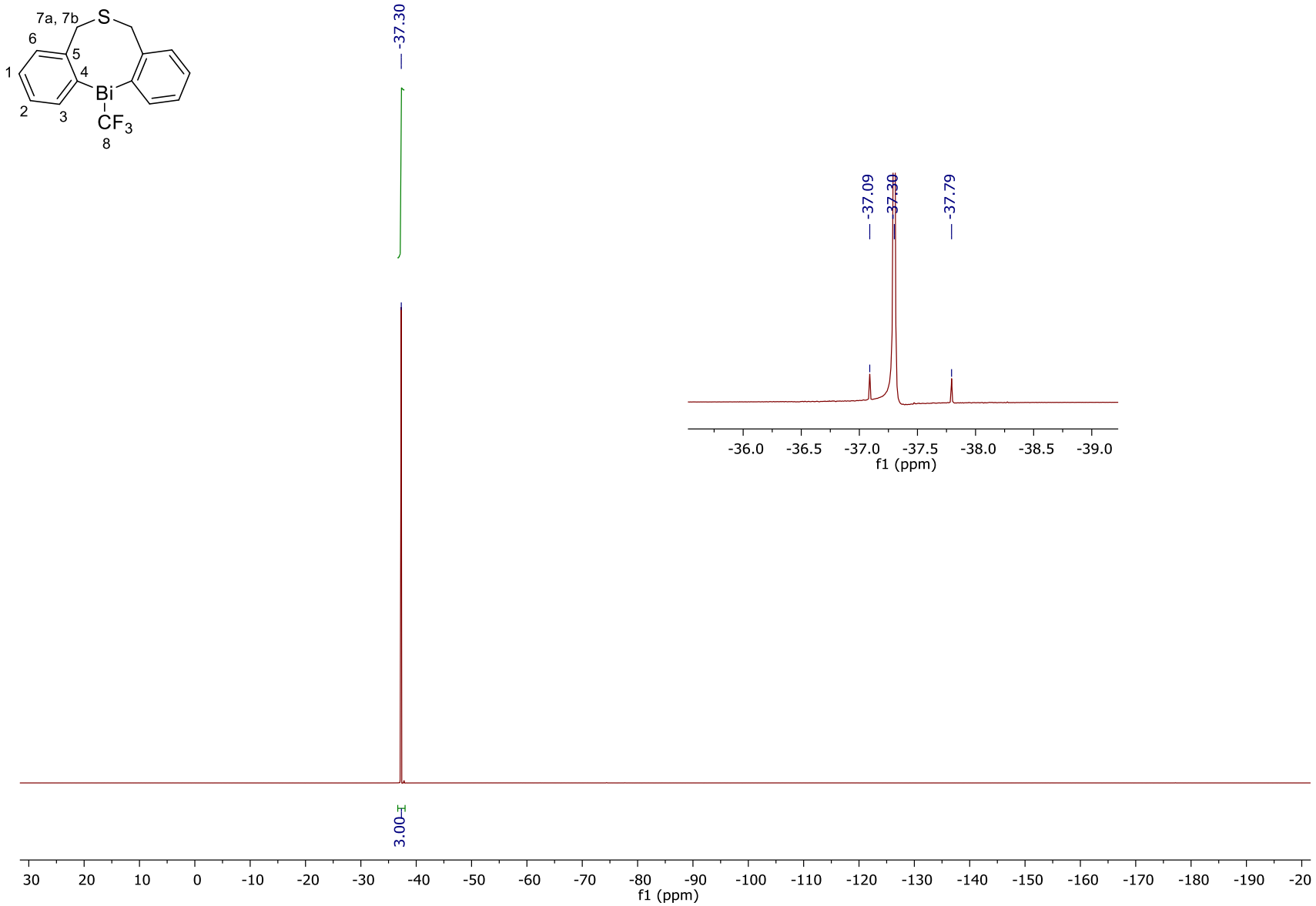


Figure S44. ^{19}F NMR of **3-CF_3** (564 MHz, $CDCl_3$, 60°C)

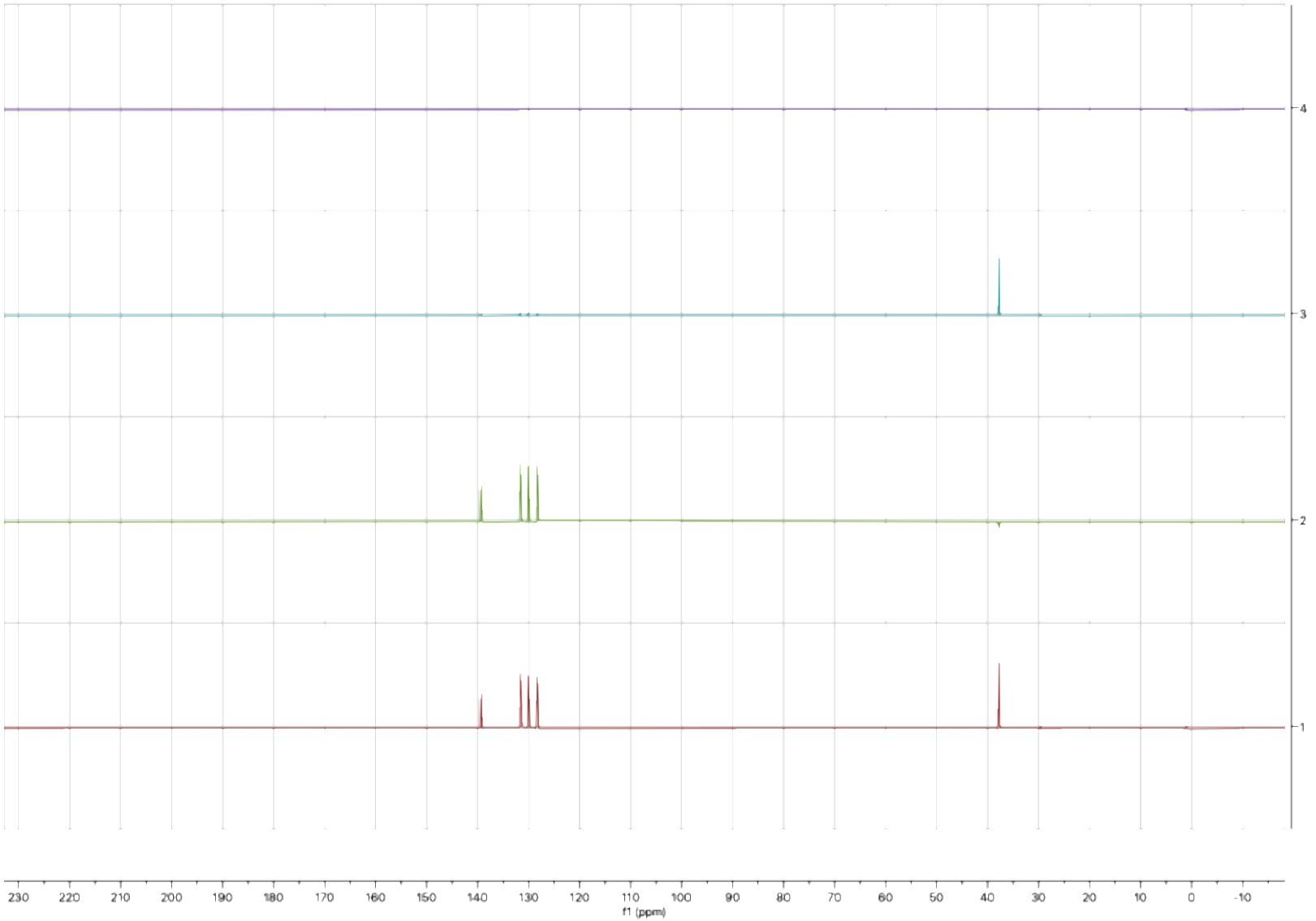


Figure S45. $^{13}C\{^{1}H\}$ DEPT of **3-CF$_3$** in $CDCl_3$

Figure S46. COSY of **3-CF_3** in $CDCl_3$

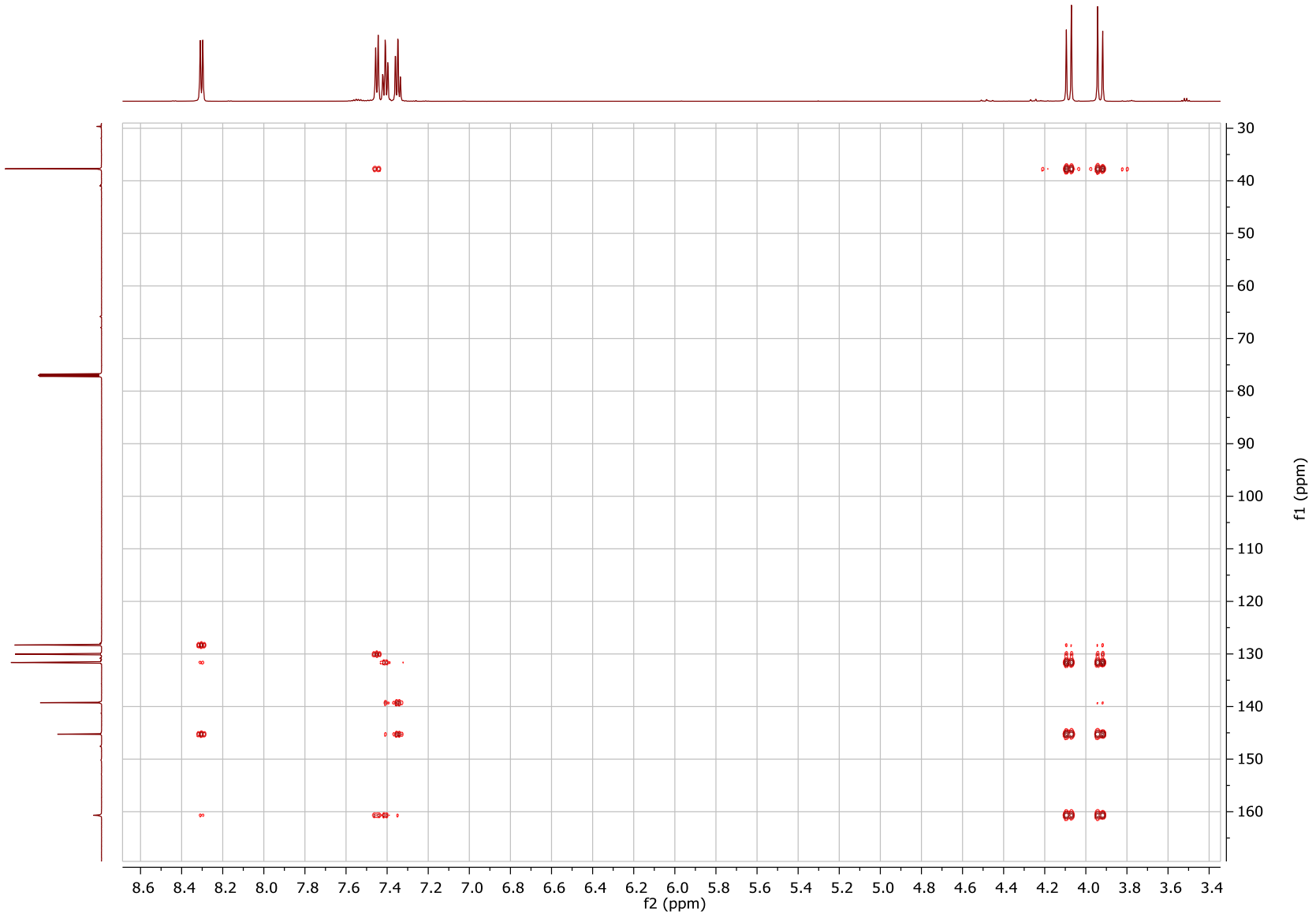


Figure S47. HMBC of **3-CF_3** in $CDCl_3$

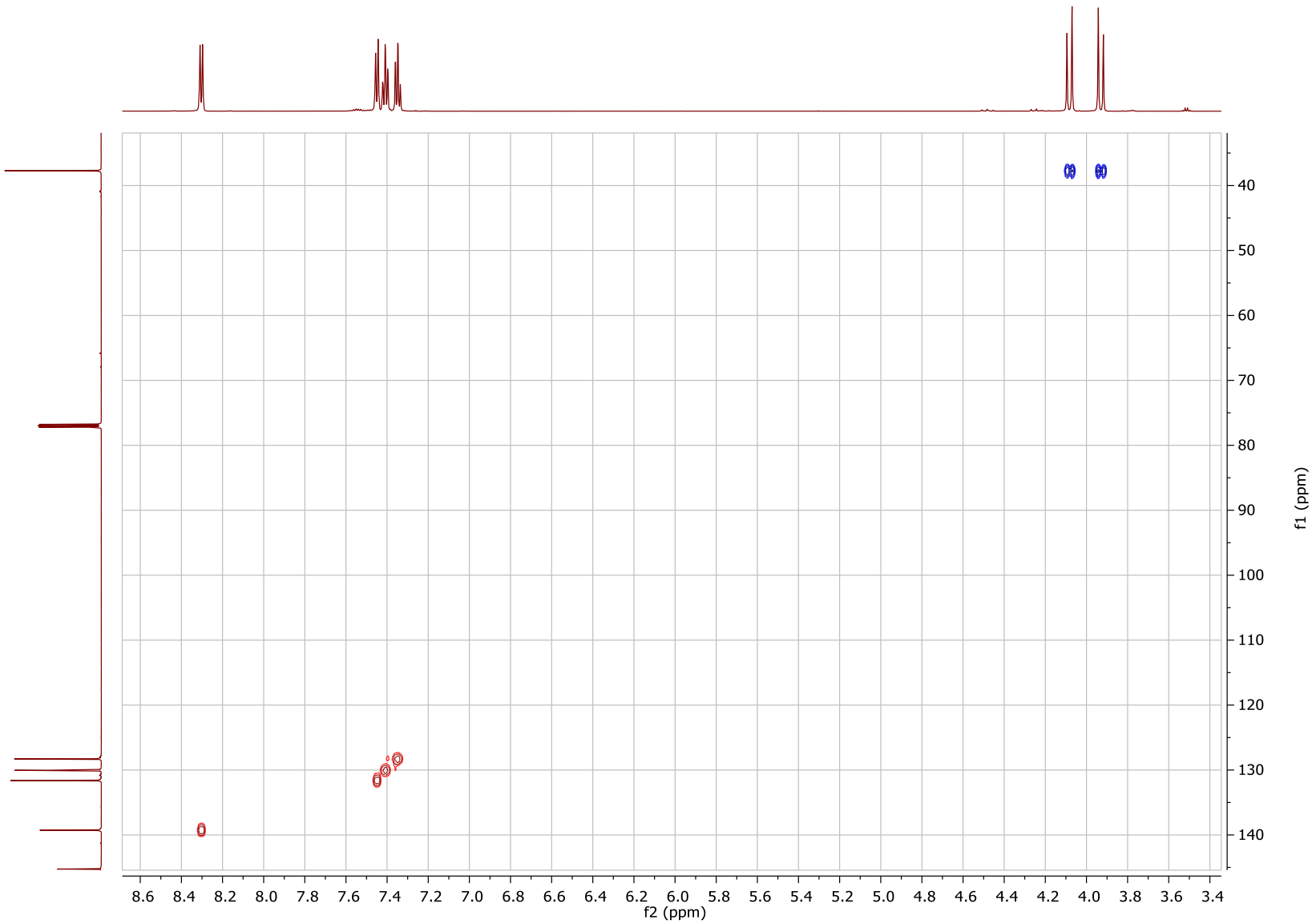
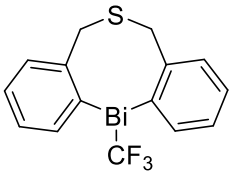


Figure S48. HSQC of **3-CF_3** in $CDCl_3$



Chemical Formula: $BiC_{15}H_{12}SF_3$

Molecular Weight: 490.30

Elemental Analysis: C: 36.75; H: 2.47

CENTC Elemental Analysis Facility
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Date of report	9/10/2021 1:58:41PM
User ID	Administrator
Comments	HVT 3_20 [Hyvl]

DATE & TIME	9/10/2021 1:42:11 PM	P_ID	EA LAB
SAMPLE ID	21510	USER ID	Administrator
WEIGHT (mg)	2.345	MODE	CHN

CARBON	37.115%
HYDROGEN	2.476%
NITROGEN	0.007%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

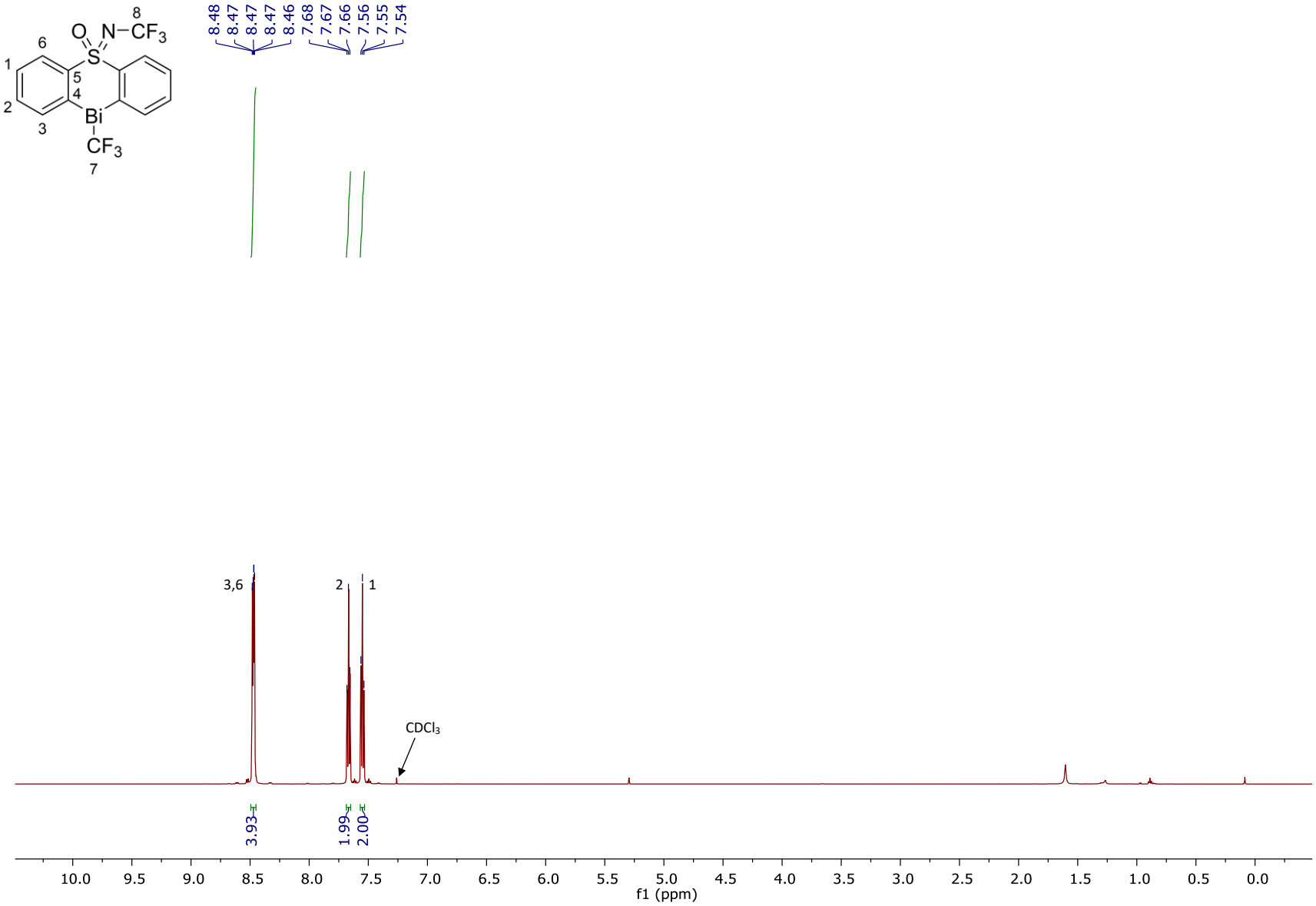


Figure S49. ^{1}H NMR of **4-CF$_3$** (600 MHz, $CDCl_3$, 40°C)

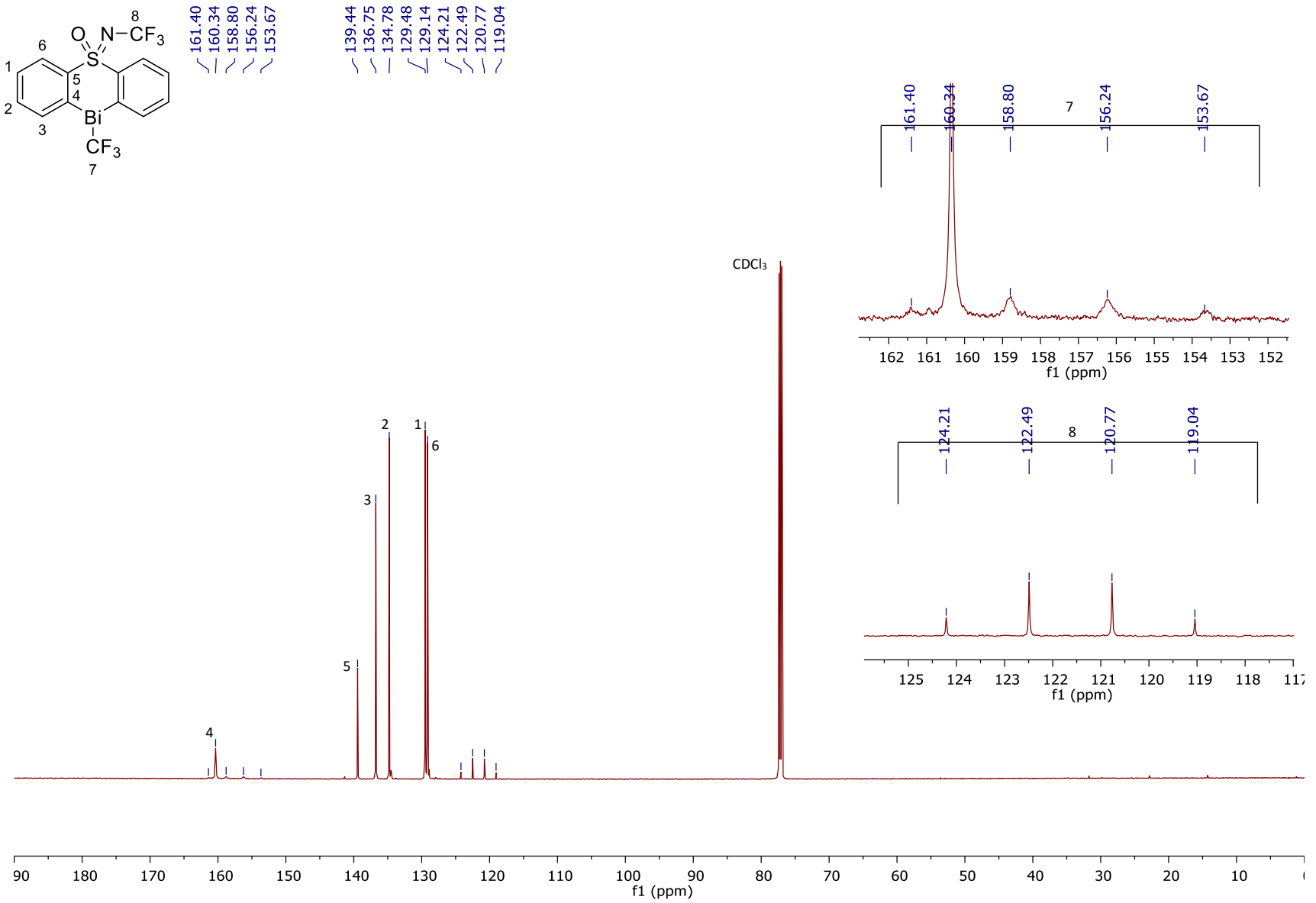


Figure S50. $^{13}C\{^{1}H\}$ NMR of **4-CF$_3$** (600 MHz, $CDCl_3$, 40°C)

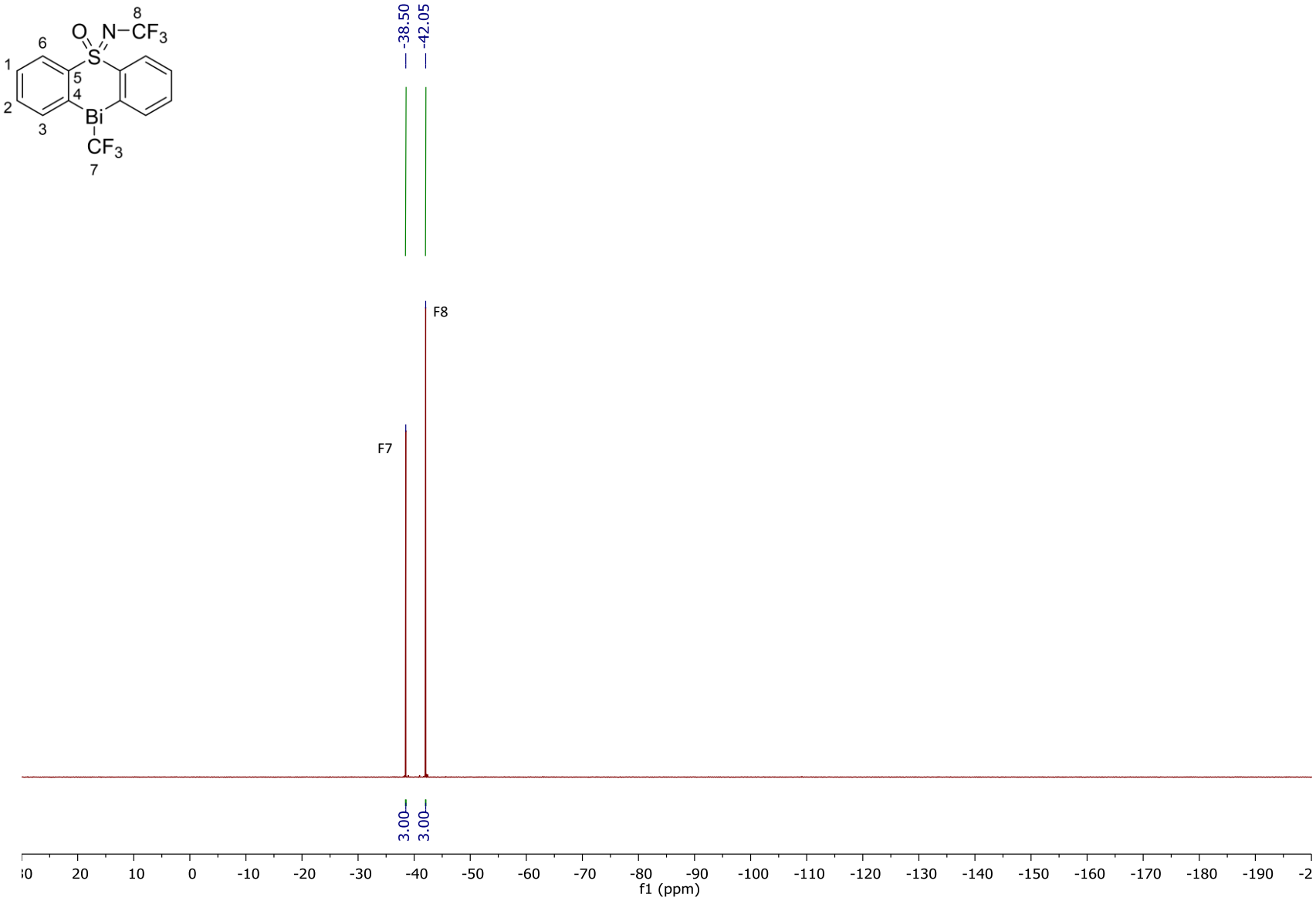


Figure S51. ^{19}F NMR of **4-CF_3** (564 MHz, $CDCl_3$, 40°C)

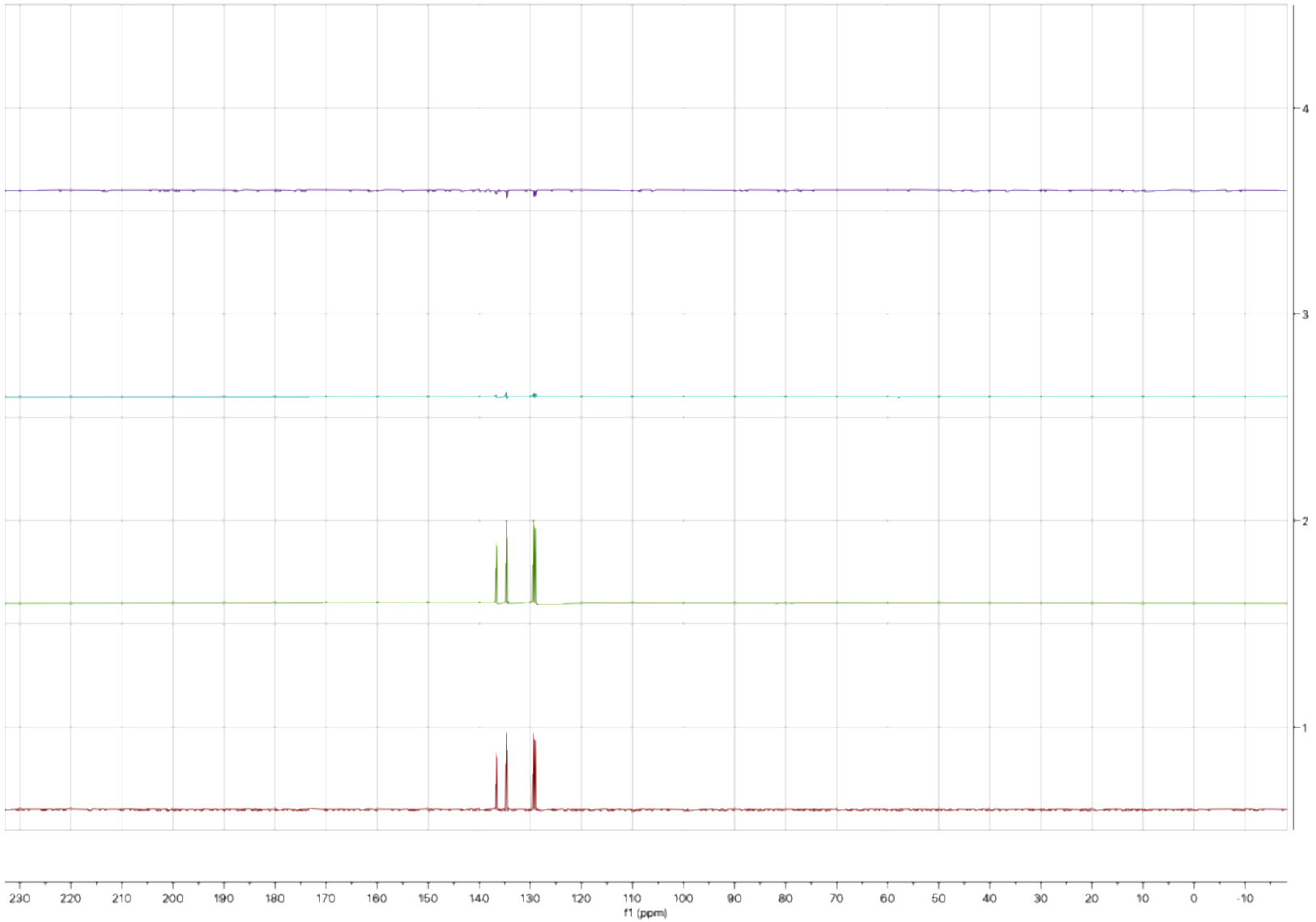


Figure S52. $^{13}C\{^{1}H\}$ DEPT of **4-CF_3** in $CDCl_3$

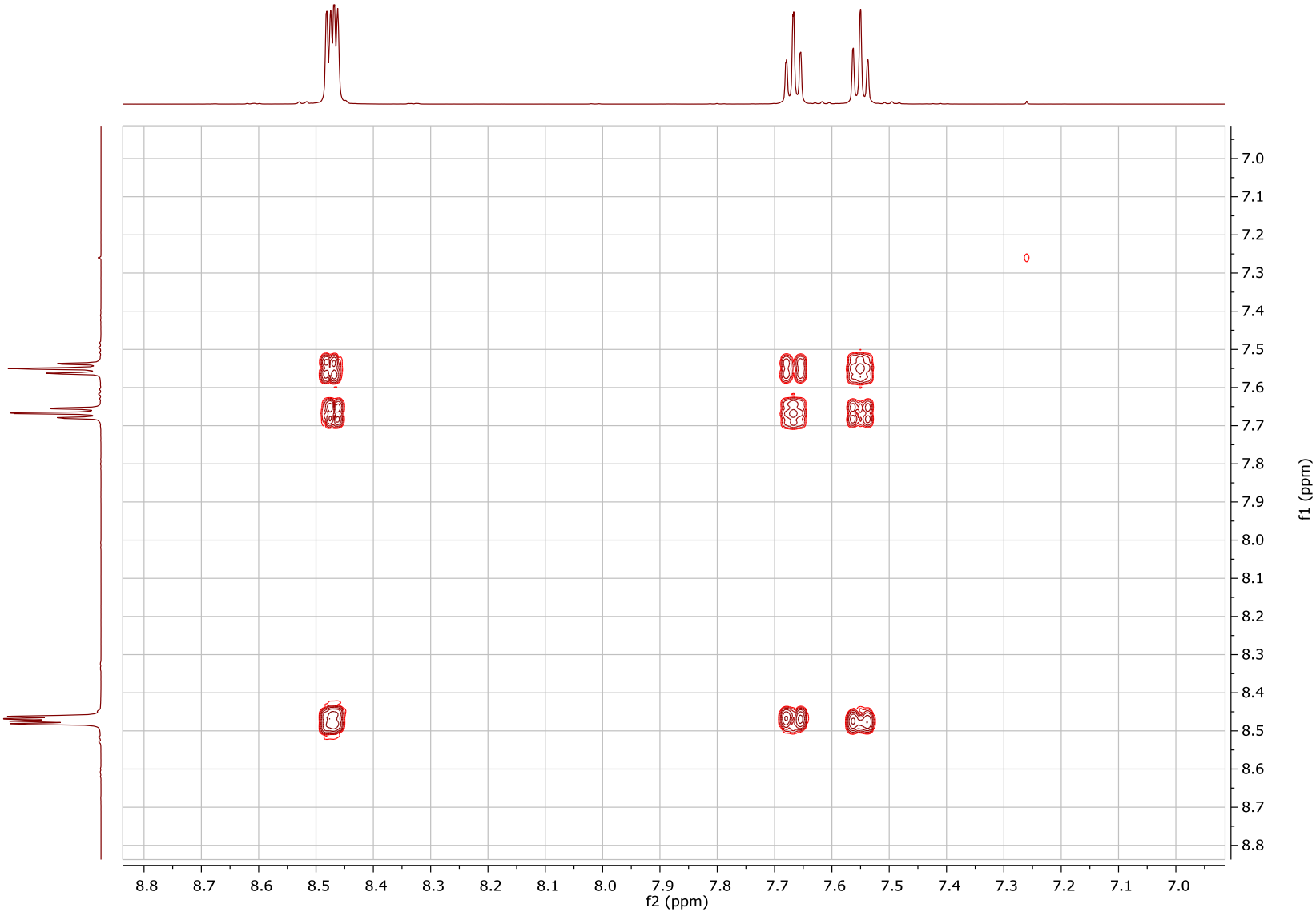


Figure S53. COSY of **4-CF_3** in $CDCl_3$

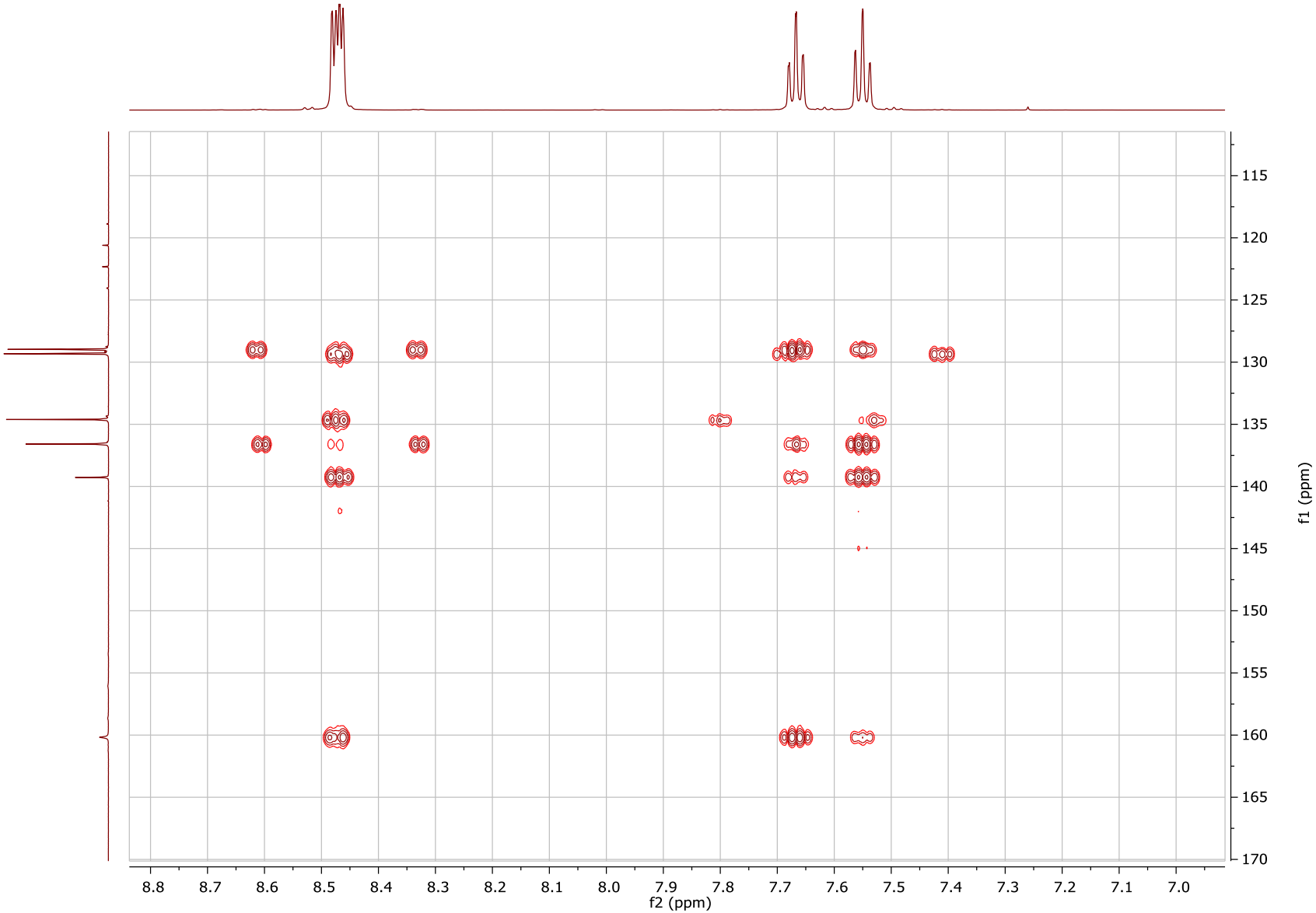


Figure S54. HMBC of **4-CF_3** in $CDCl_3$

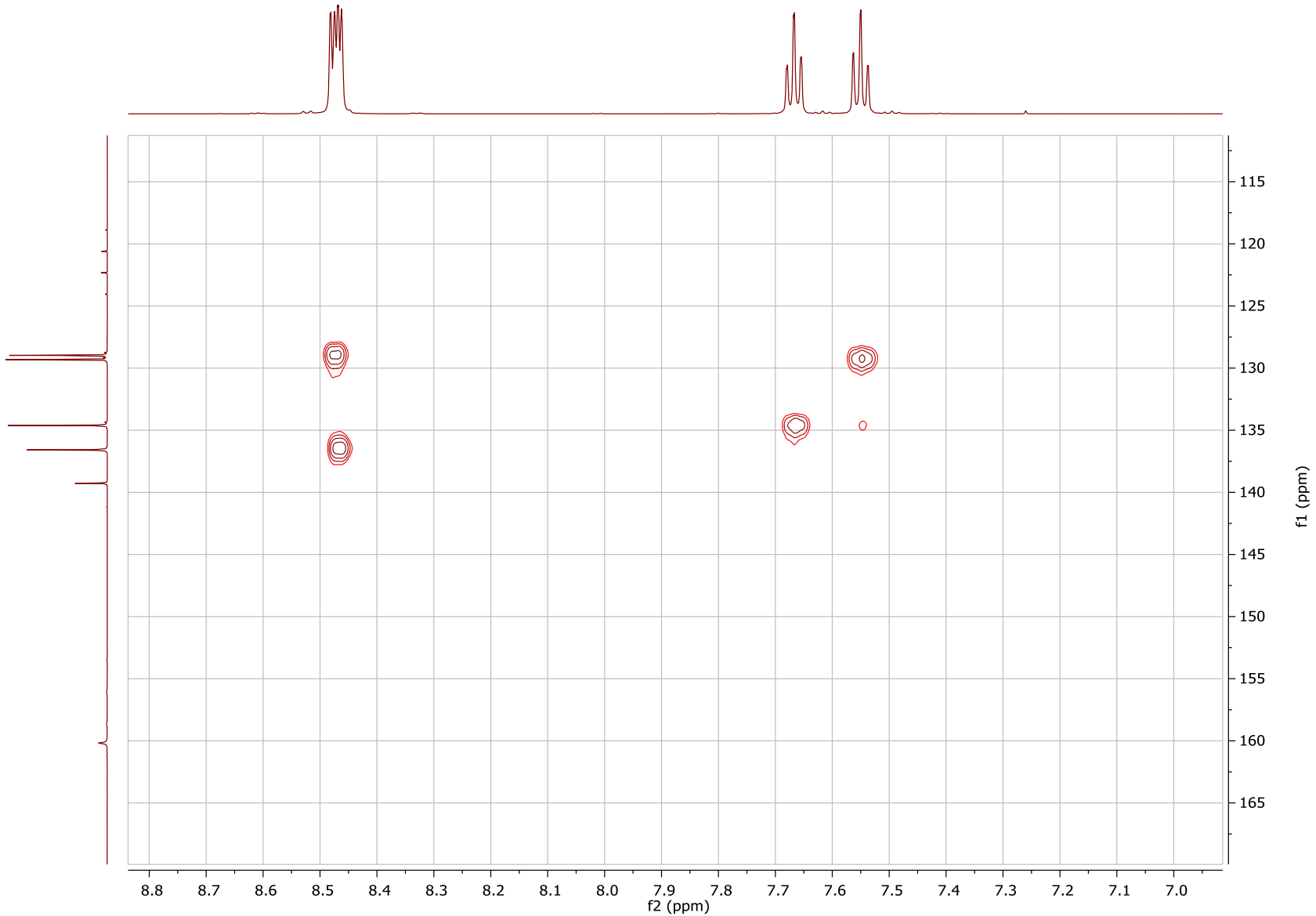
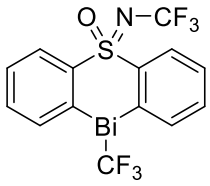


Figure S55. HSQC of **4-CF_3** in $CDCl_3$



Chemical Formula: $BiC_{14}H_8NOSF_6$

Molecular Weight: 561.25

Elemental Analysis: C: 29.96; H: 1.44; N, 2.50

CENTC Elemental Analysis Facility
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Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	6/4/2021 3:15:07PM
User ID	Administrator
Comments	HVT2_126 [Hyvl]

DATE & TIME	6/4/2021 1:40:07 PM	P_ID	EA LAB
SAMPLE ID	21317	USER ID	Administrator
WEIGHT (mg)	2.055	MODE	CHN

CARBON	30.308%
HYDROGEN	1.632%
NITROGEN	2.459%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

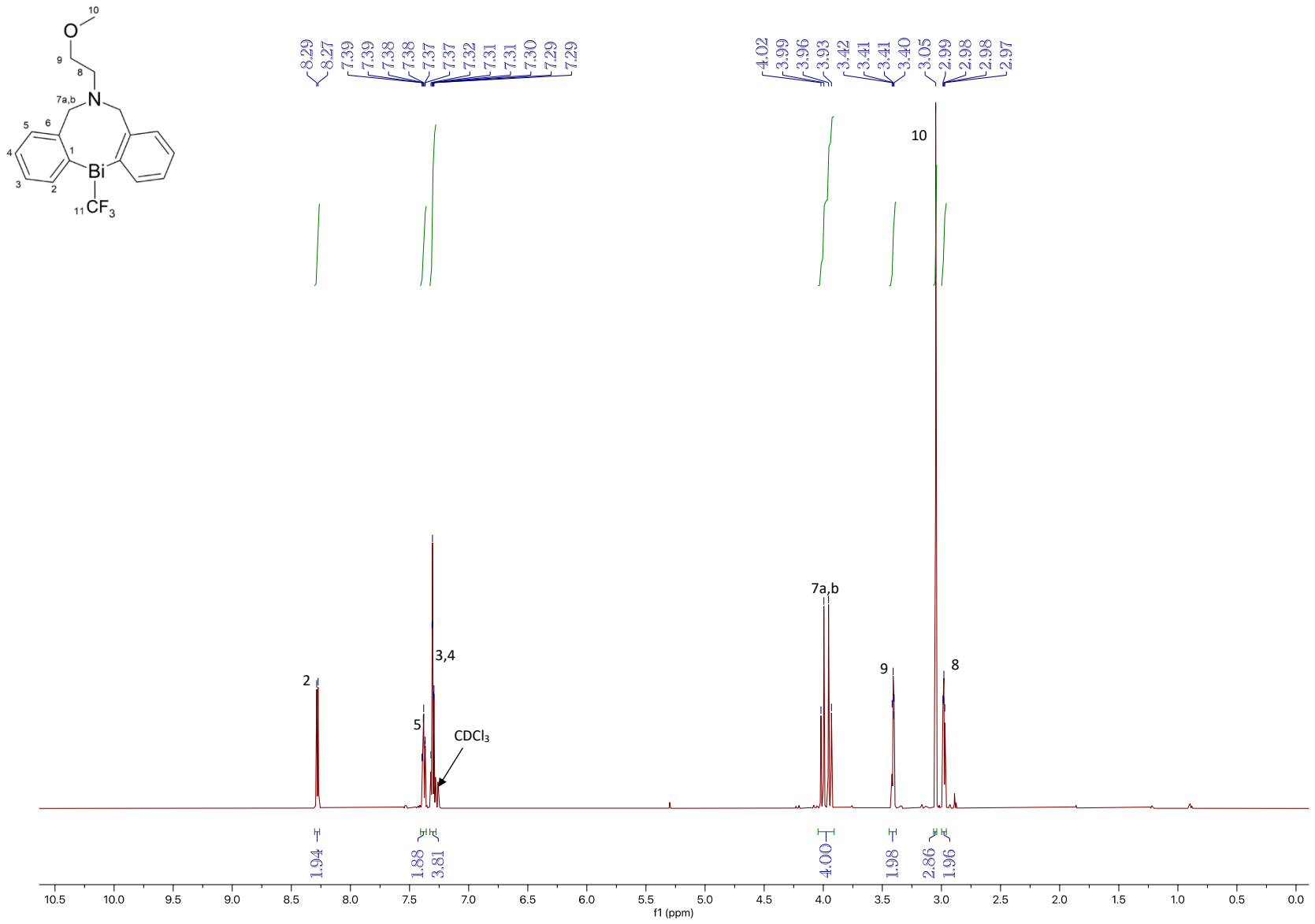


Figure S56. ^{1}H NMR of **5-CF$_3$** (600 MHz, $CDCl_3$, 30°C)

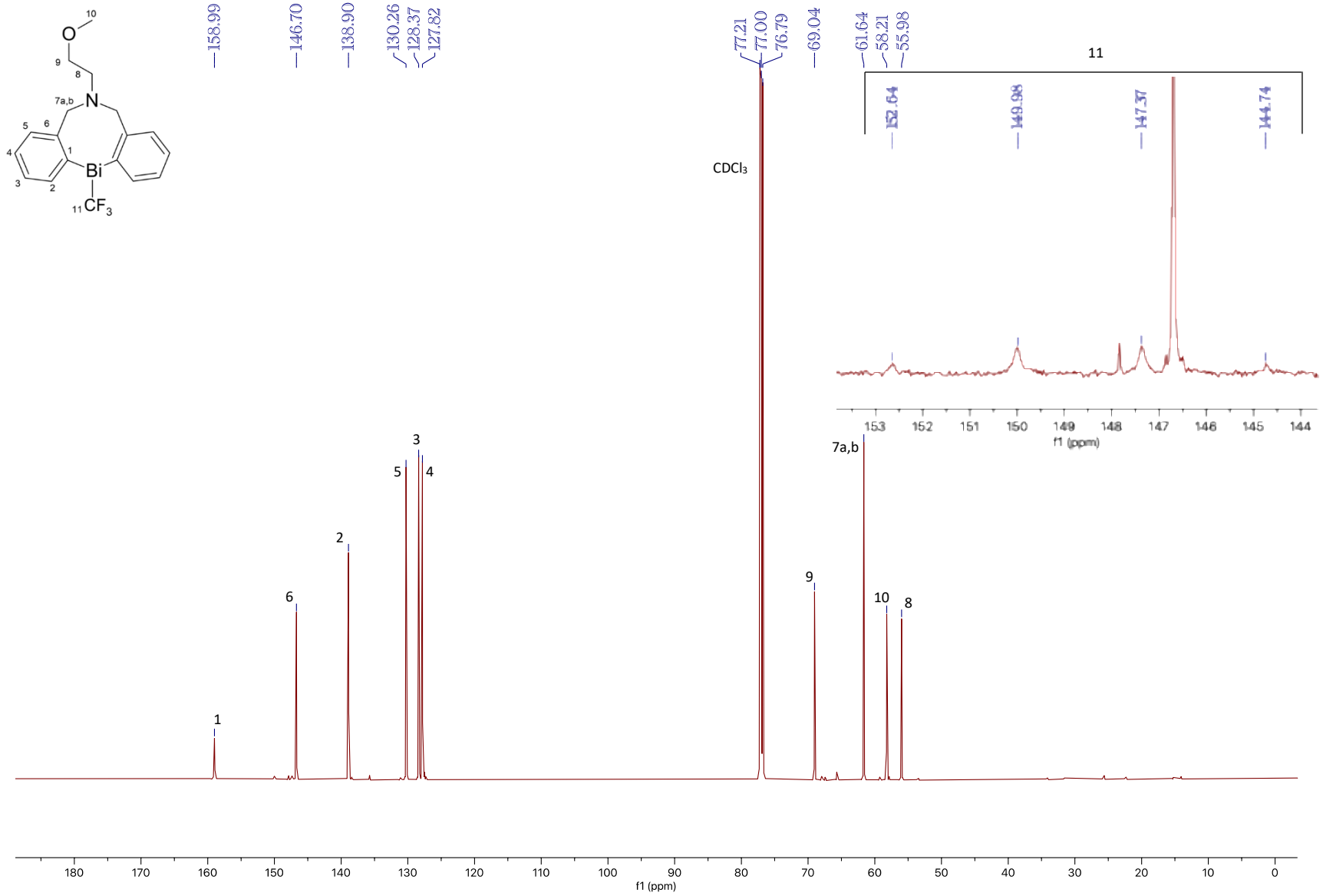


Figure S57. $^{13}C\{^{1}H\}$ NMR of **5-CF$_3$** (150 MHz, $CDCl_3$, 30°C)

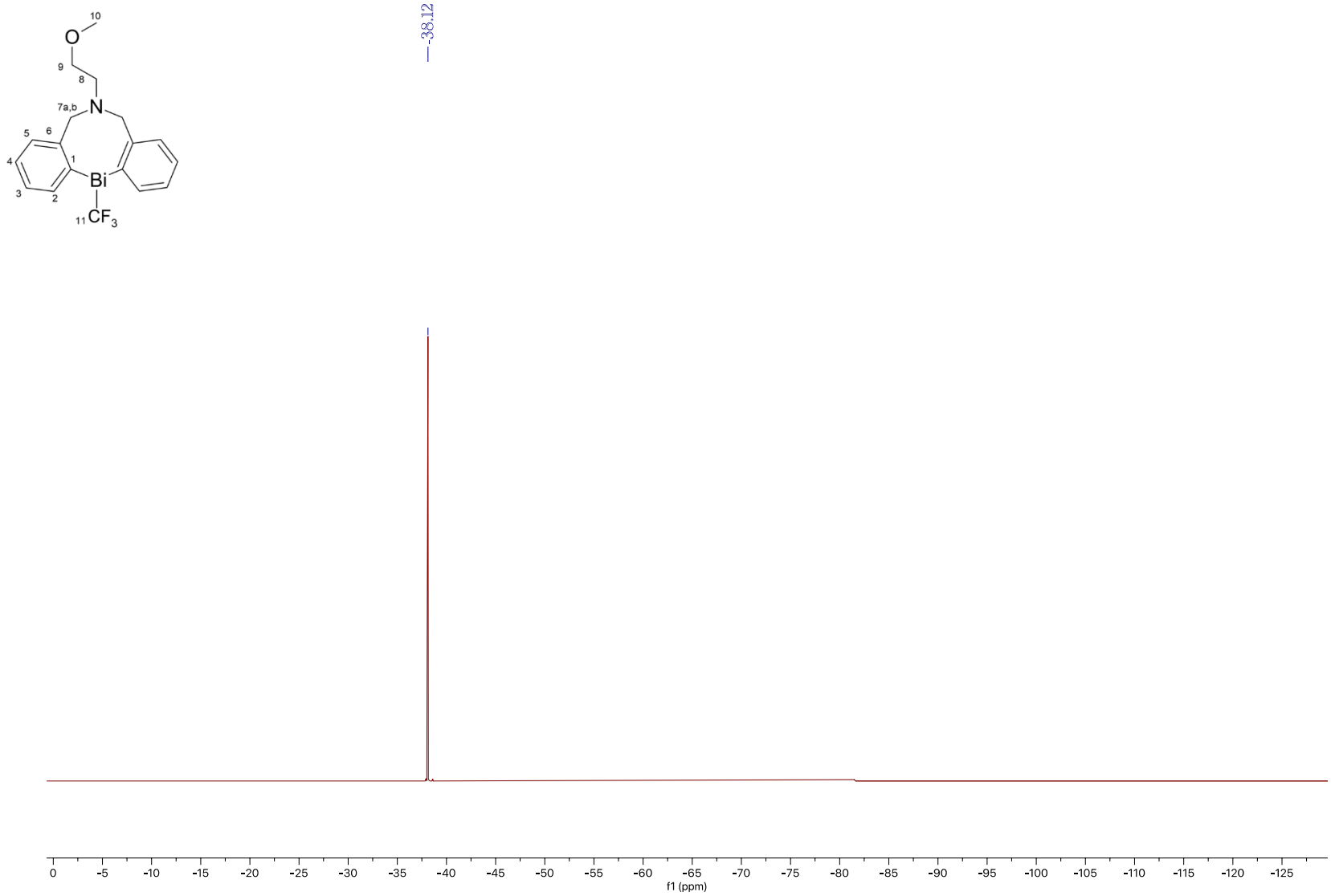


Figure S58. ^{19}F NMR of **5-CF$_3$** (564 MHz, $CDCl_3$, 30°C)

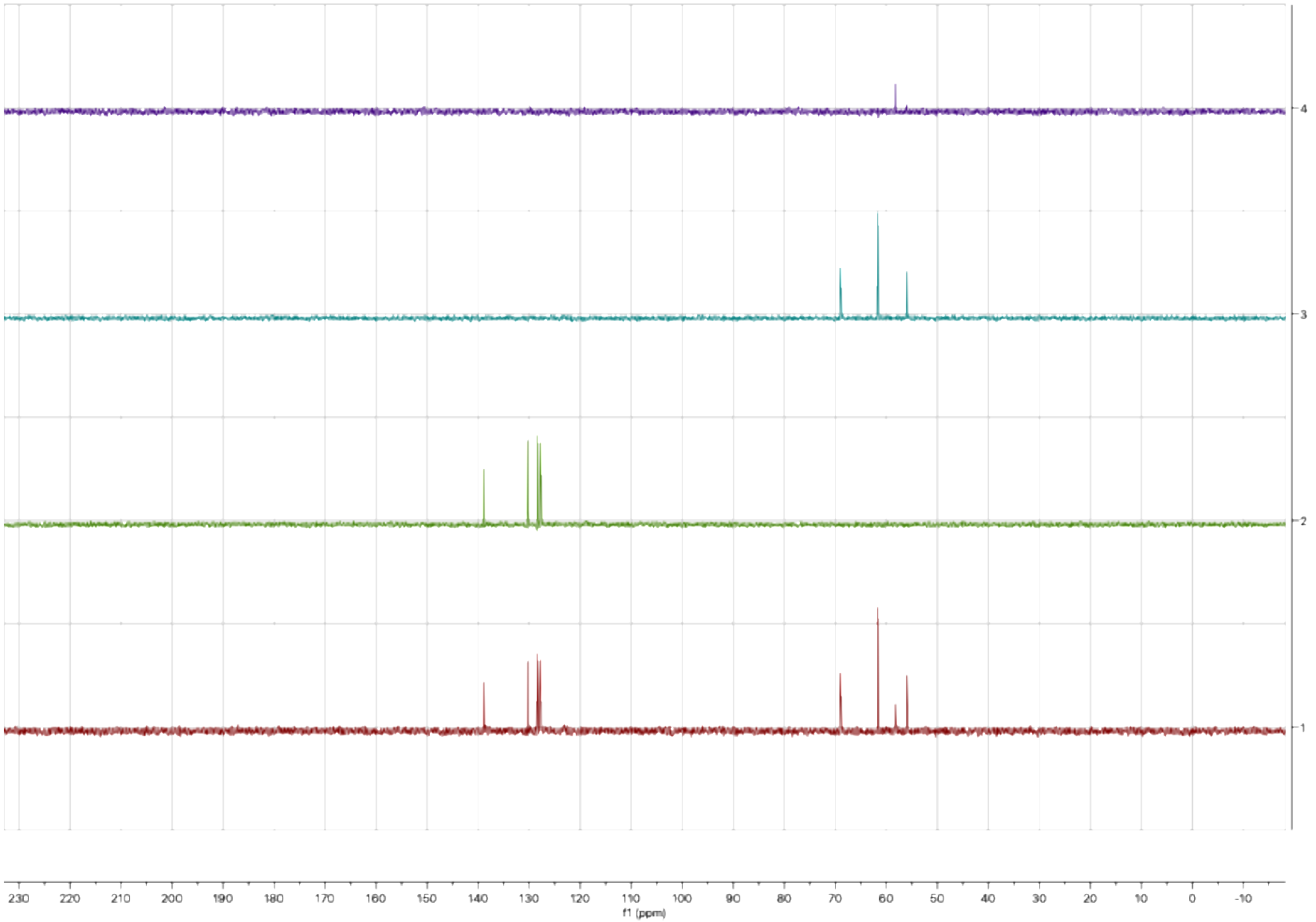


Figure S59. $^{13}C\{^{1}H\}$ DEPT of **5-CF$_3$** in $CDCl_3$

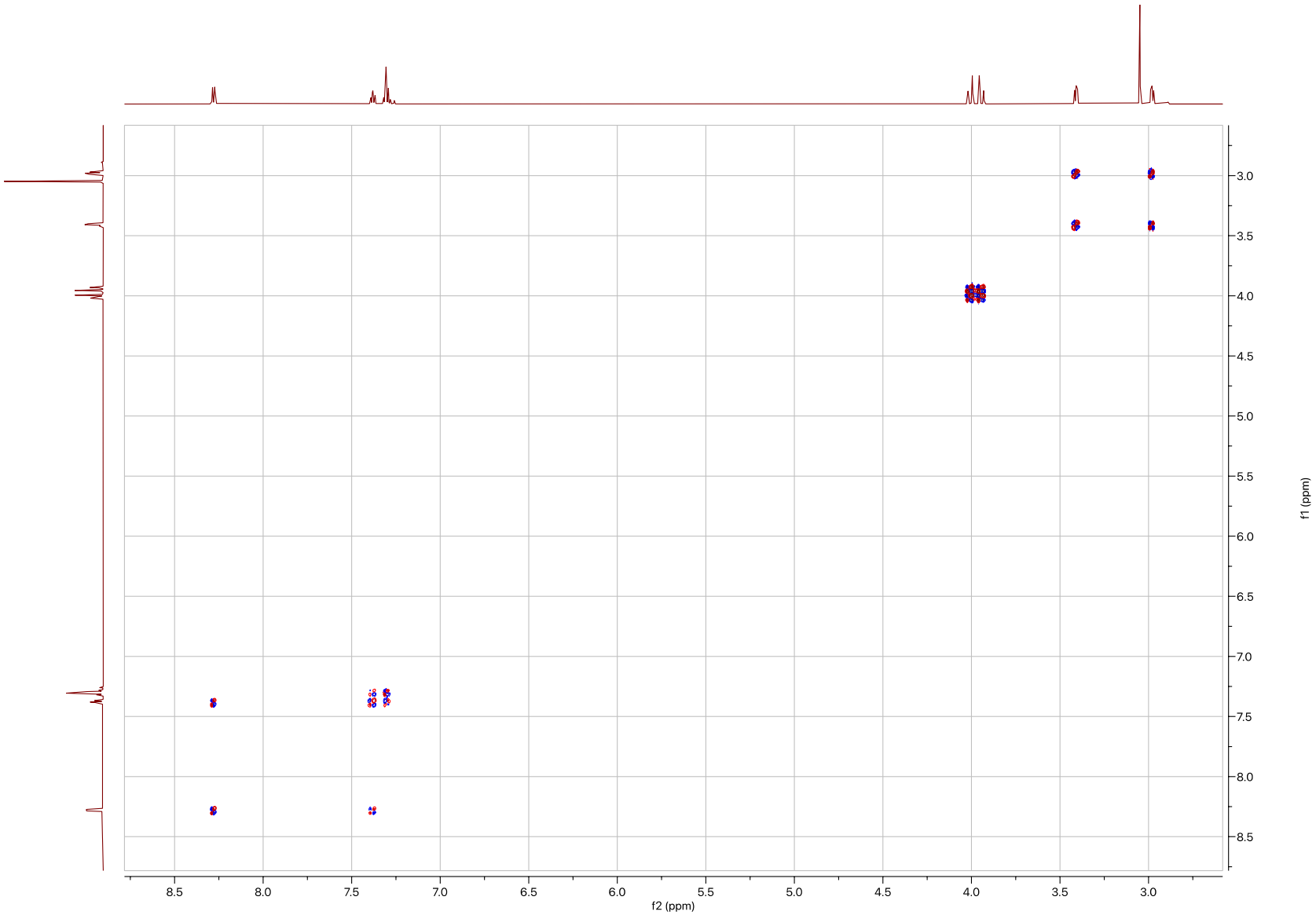


Figure S60. COSY of **5-CF_3** in $CDCl_3$

Figure S61. HMBC of **5-CF_3** in $CDCl_3$

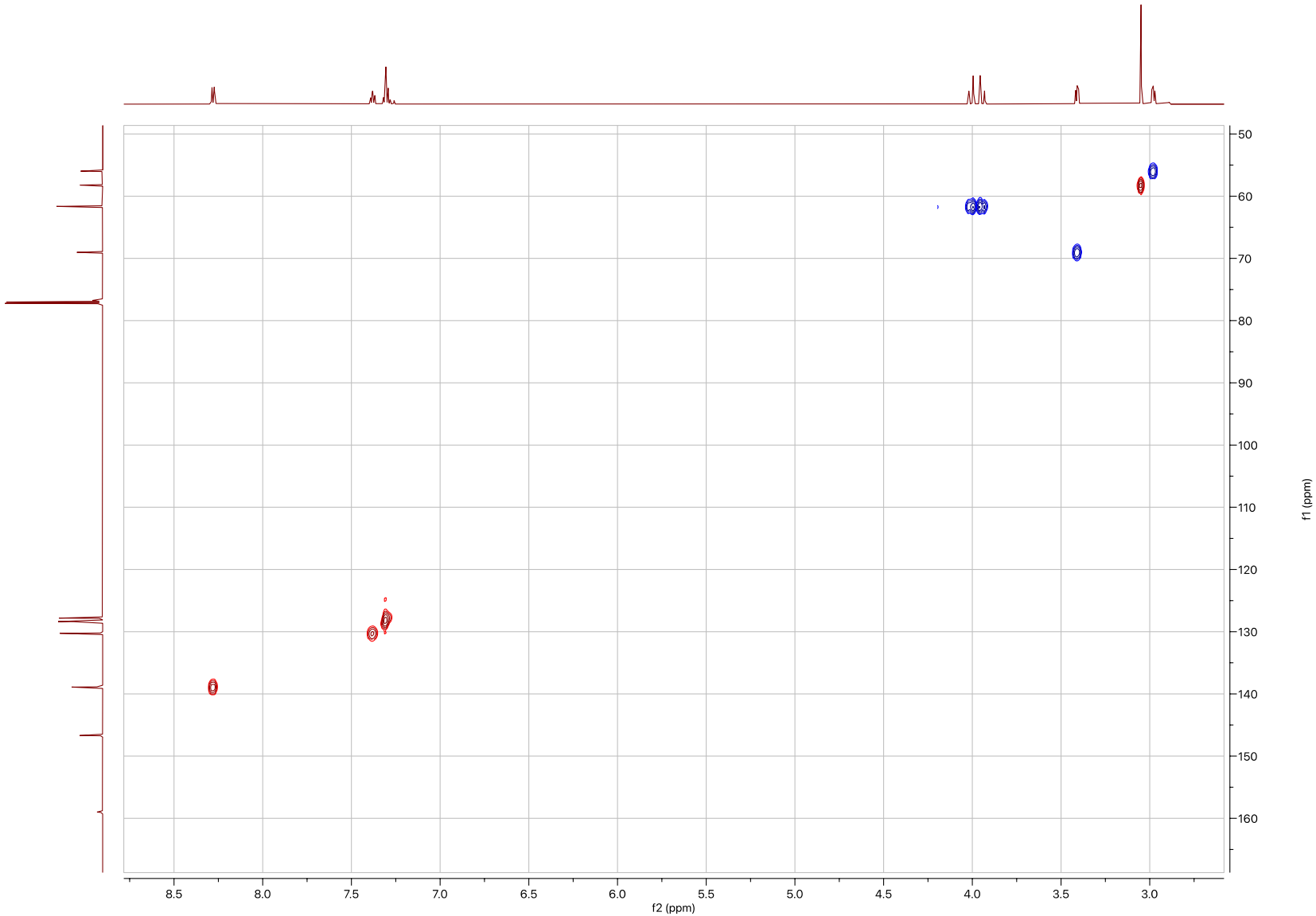
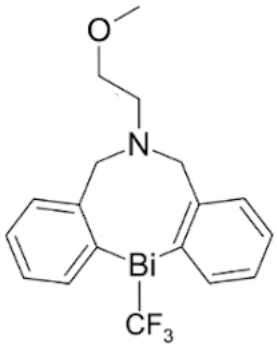


Figure S62. HSQC of **5-CF_3** in $CDCl_3$



Chemical Formula: $BiC_{18}H_{19}F_3NO$

Molecular Weight: 531.33

Elemental Analysis: C: 40.69; H: 3.60; N, 2.64

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Date of report	2/16/2024 5:47:17PM
User ID	Administrator
Comments	TLG_4_196 [Hyvl]

DATE & TIME	2/16/2024 3:29:20 PM	P_ID	EA LAB
SAMPLE ID	24063	USER ID	Administrator
WEIGHT (mg)	2.155	MODE	CHN

CARBON	40.623%
HYDROGEN	3.466%
NITROGEN	2.383%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

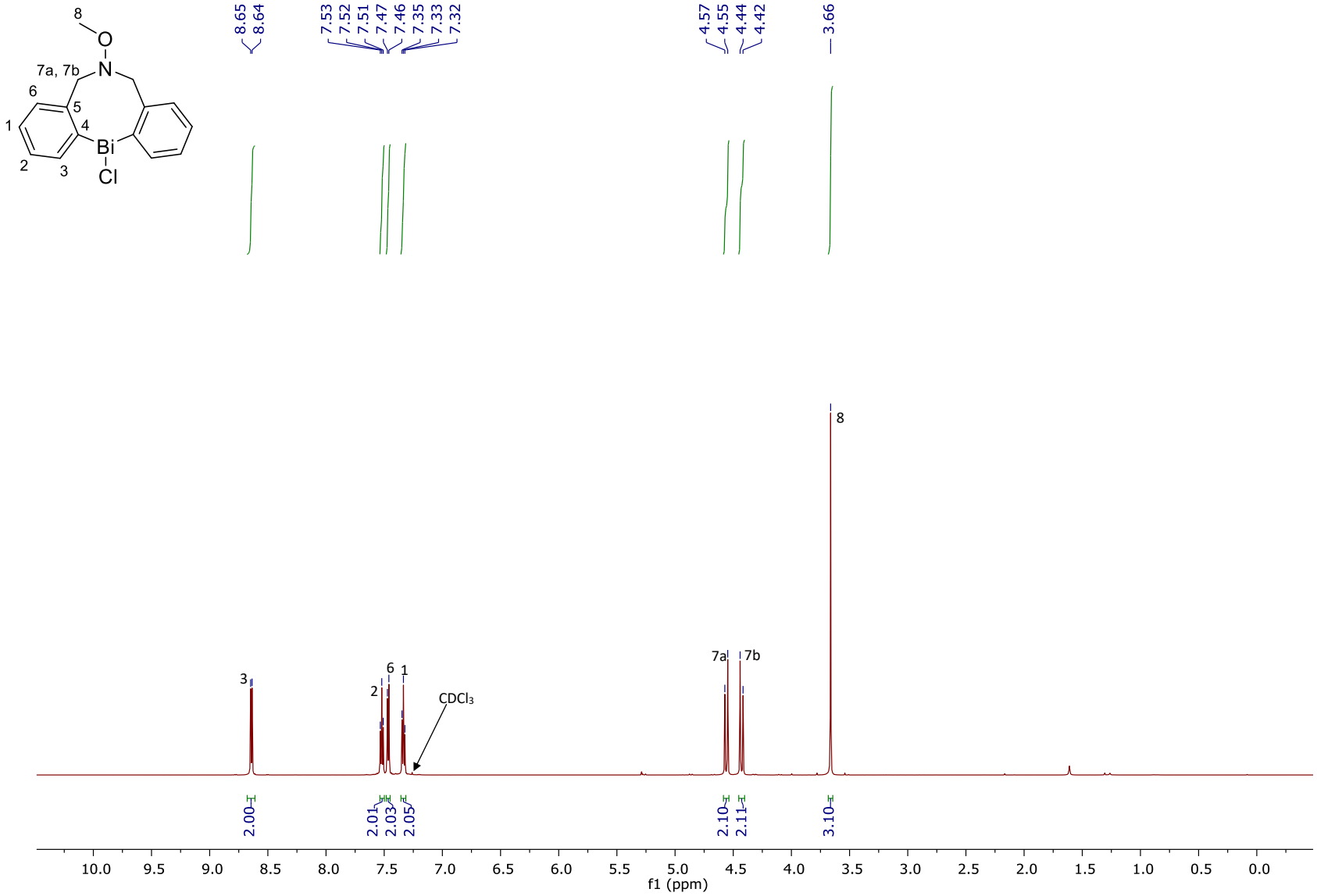


Figure S63. ^{1}H NMR of **6-Cl** (600 MHz, $CDCl_3$, 30°C)

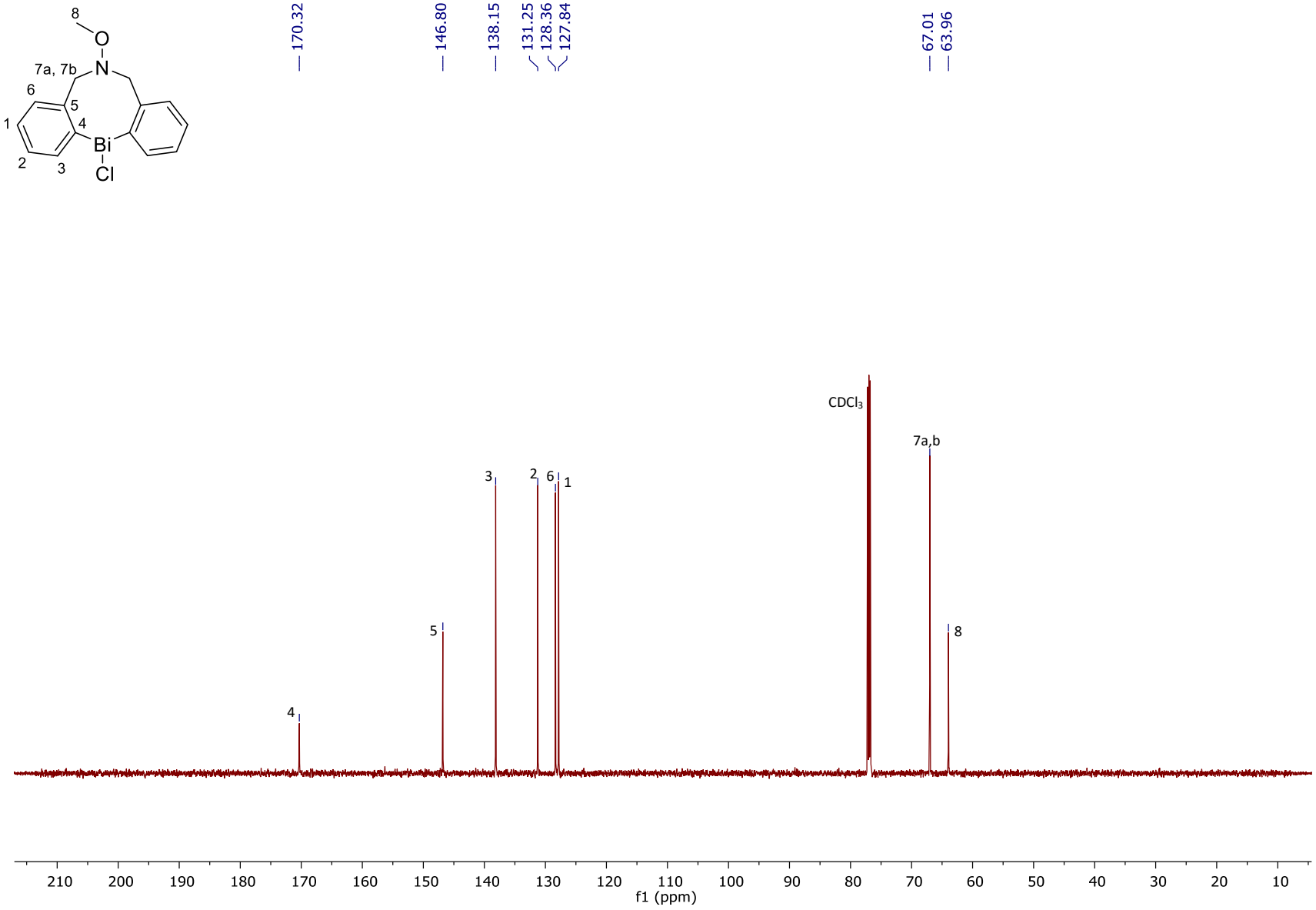


Figure S64. $^{13}C\{^{1}H\}$ NMR of **6-Cl** (150 MHz, $CDCl_3$, 30°C)

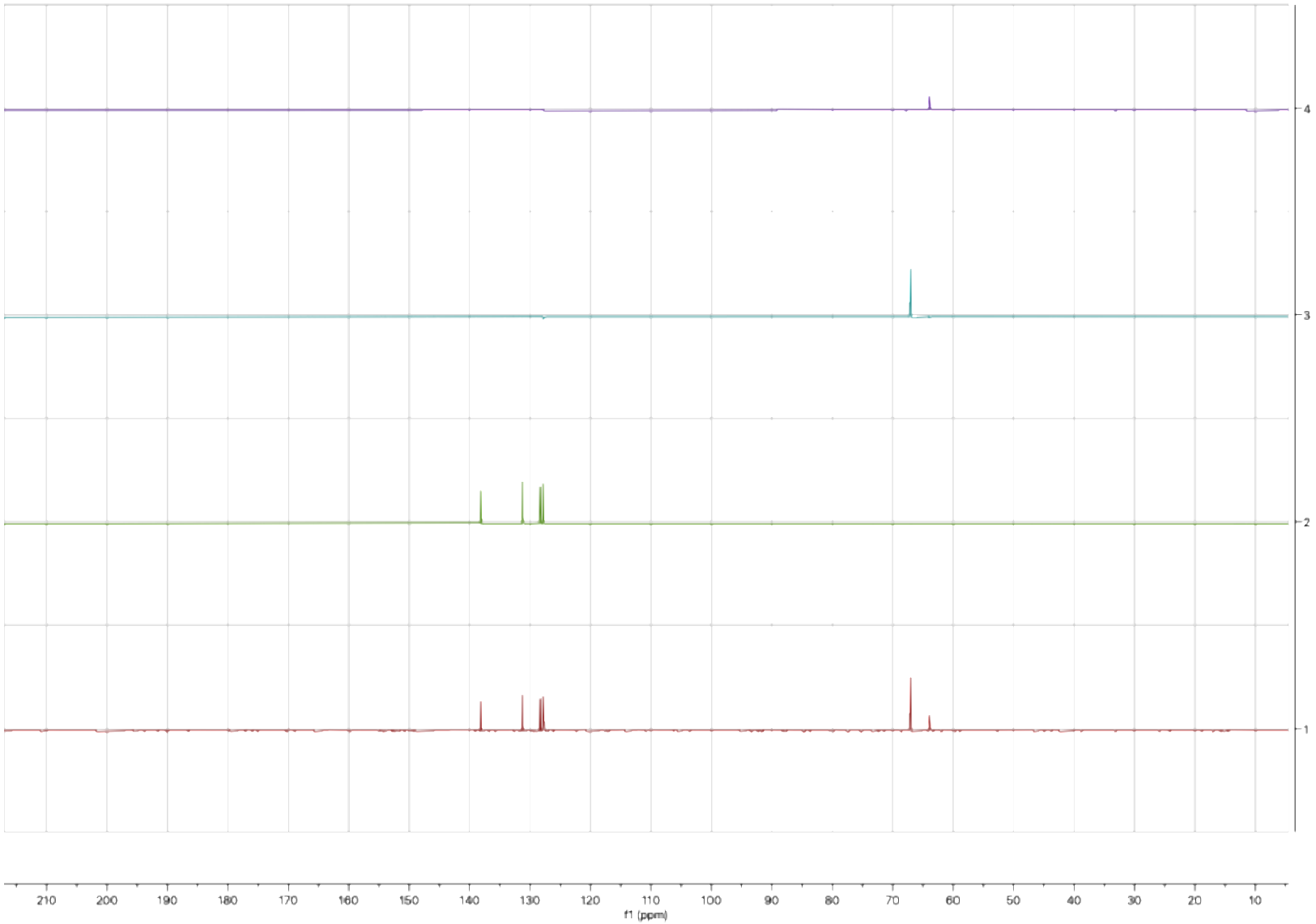


Figure S65. $^{13}C\{^{1}H\}$ DEPT of **6-Cl** in $CDCl_3$

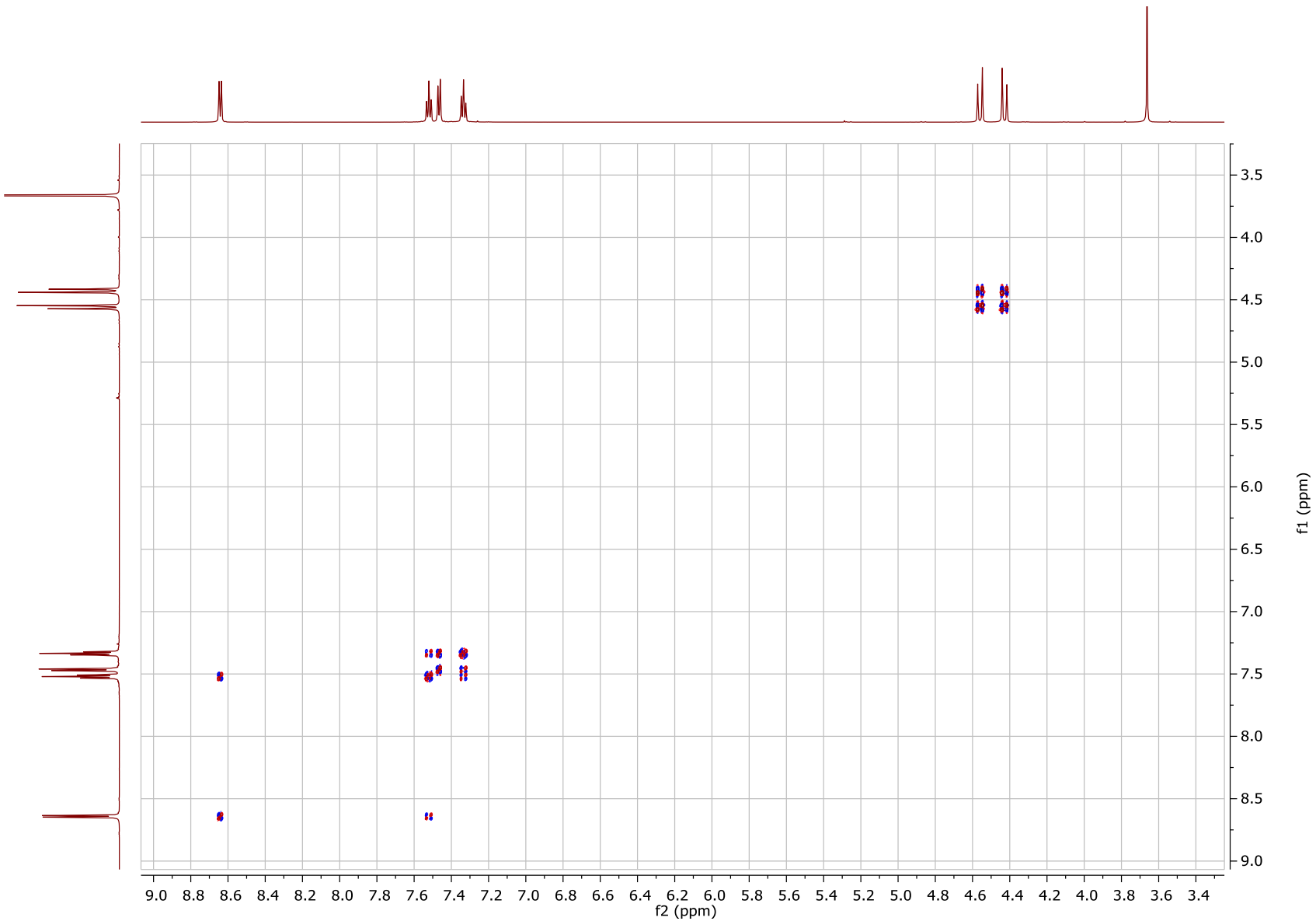


Figure S66. COSY of **6-Cl** in $CDCl_3$

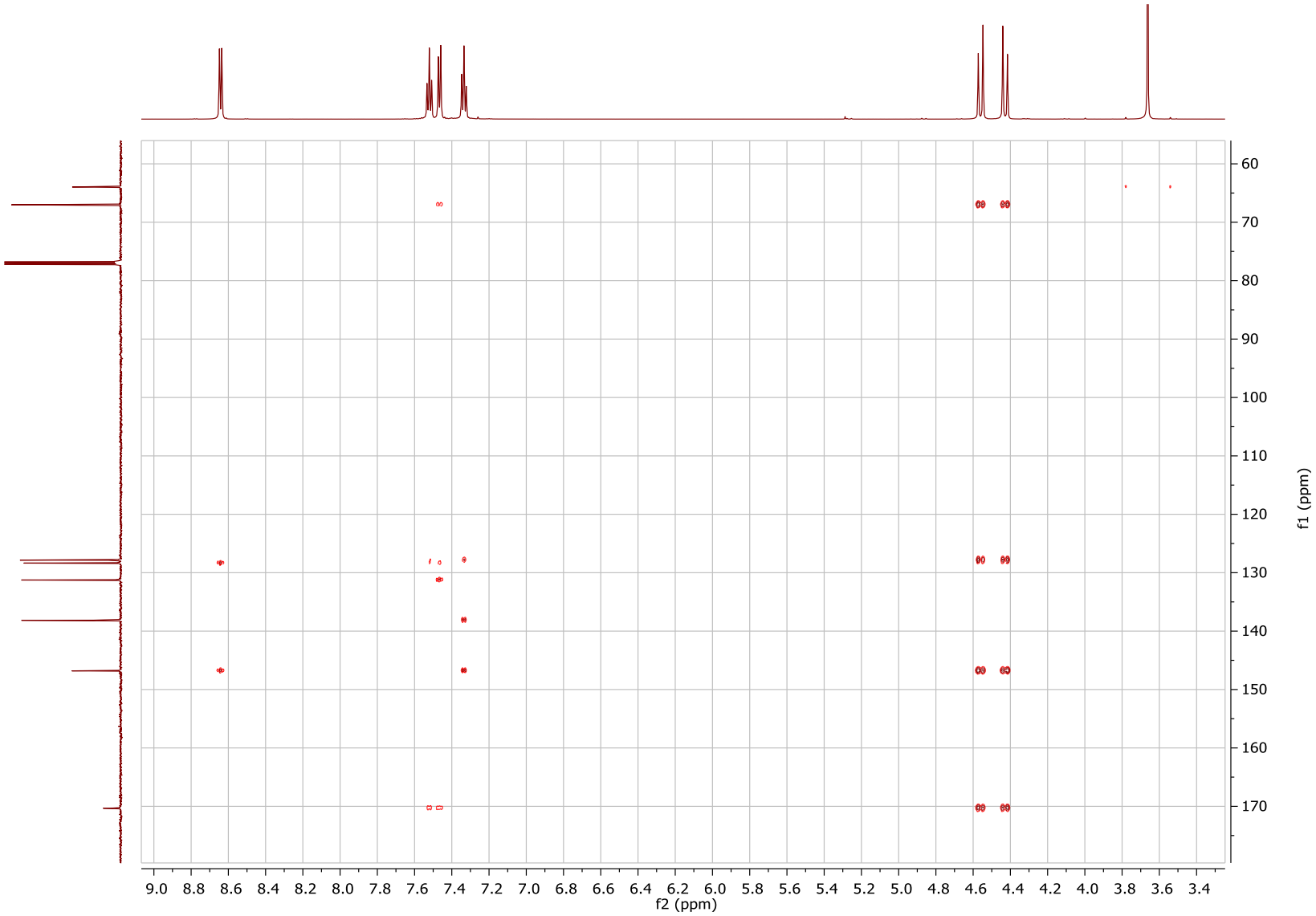


Figure S67. HMBC of **6-Cl** in $CDCl_3$

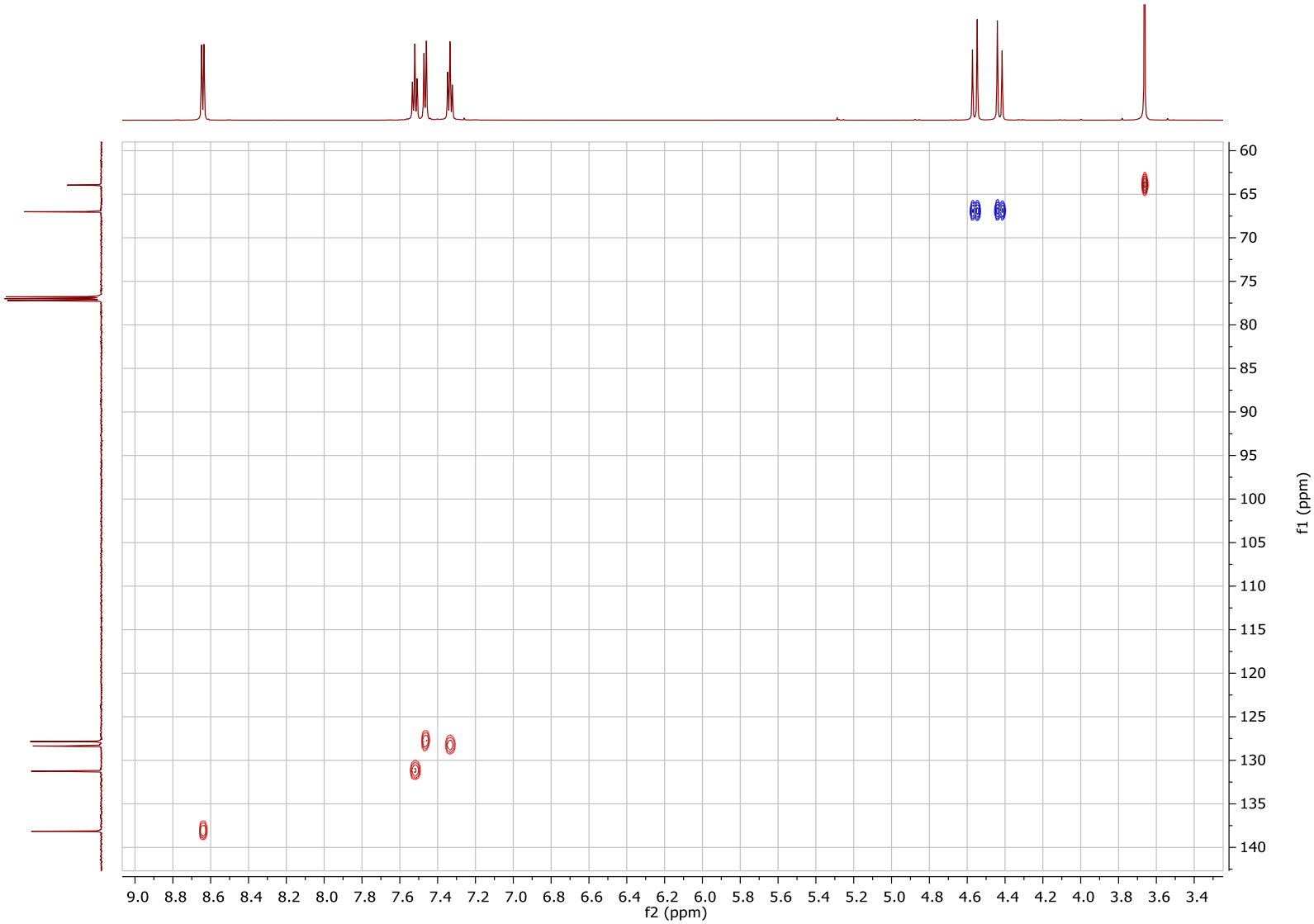
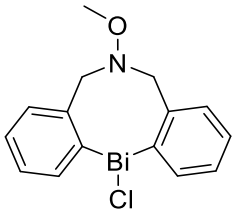


Figure S68. HSQC of **6-Cl** in $CDCl_3$



Chemical Formula: $BiC_{15}H_{15}NOCl$

Molecular Weight: 469.72

Elemental Analysis: C: 38.36; H: 3.22; N: 2.98

CENTC Elemental Analysis Facility
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Date of report	2/10/2023 6:52:55PM
User ID	Administrator
Comments	TLG_4_005X [Hyvl]

DATE & TIME	2/10/2023 12:18:17 PM	P_ID	EA LAB
SAMPLE ID	23077	USER ID	Administrator
WEIGHT (mg)	2.444	MODE	CHN

CARBON	38.683%
HYDROGEN	3.141%
NITROGEN	2.962%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

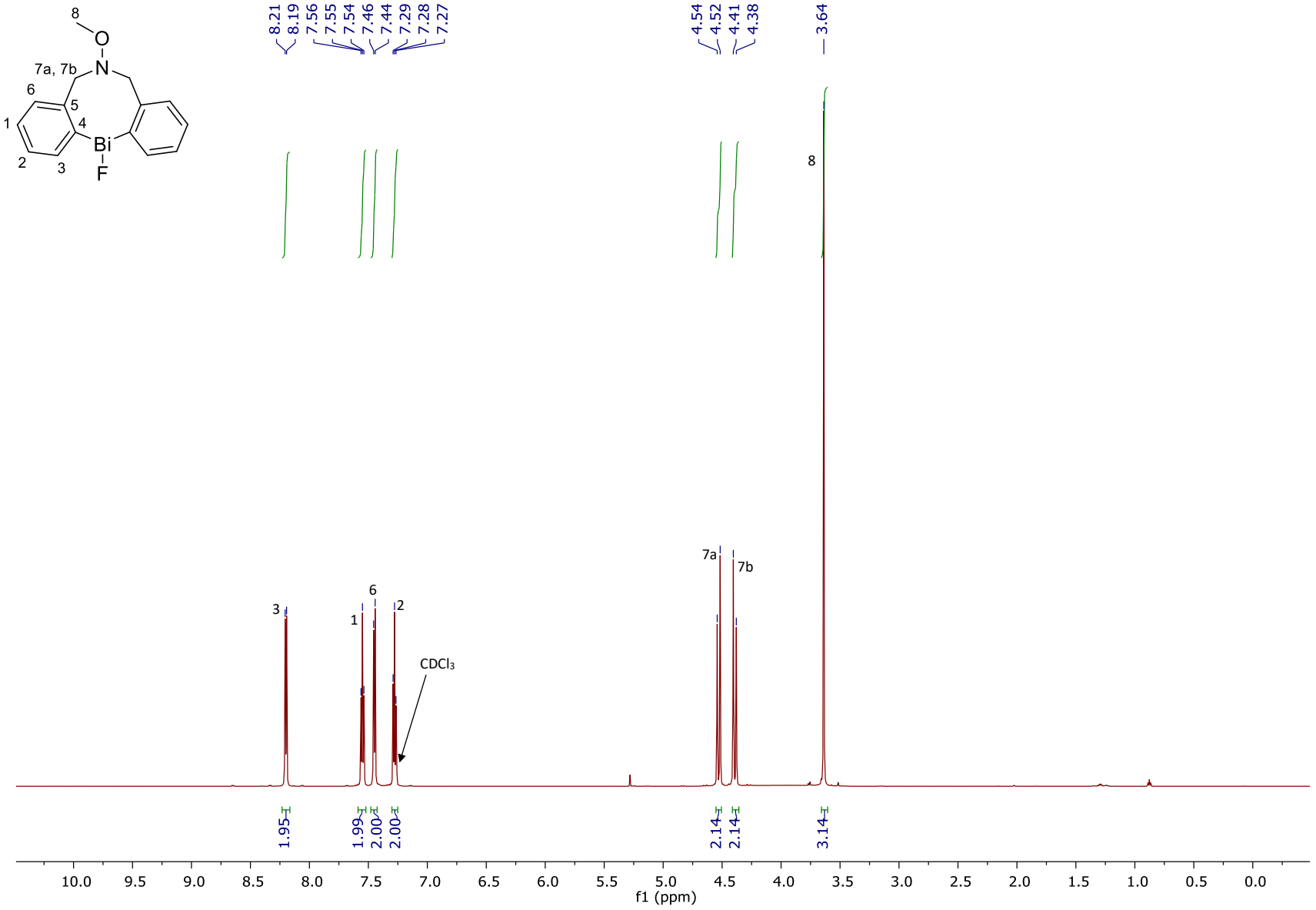


Figure S69. ^{1}H NMR of **6-F** (600 MHz, $CDCl_3$, 30°C)

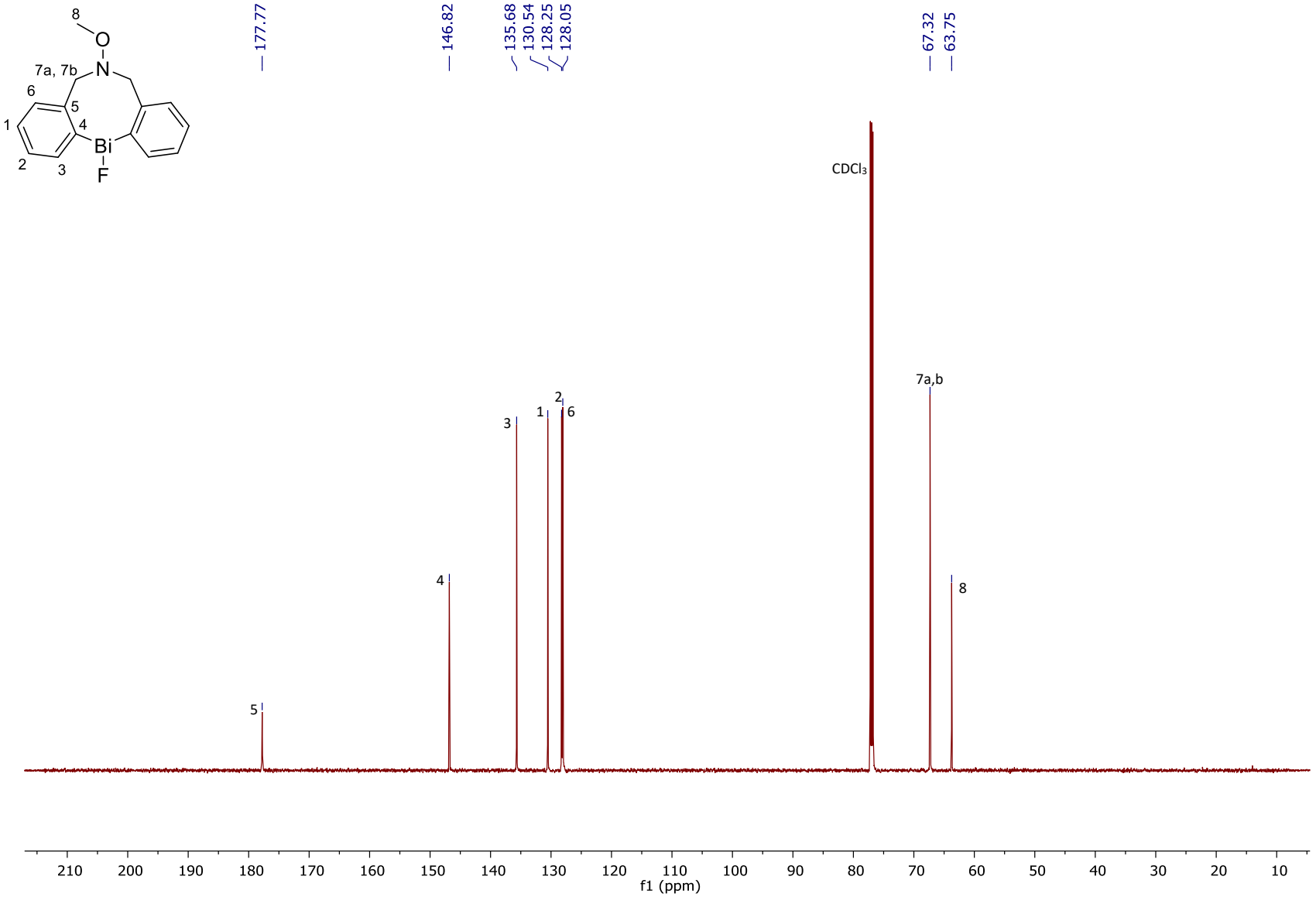


Figure S70. $^{13}C\{^{1}H\}$ NMR of **6-F** (150 MHz, $CDCl_3$, 30°C)

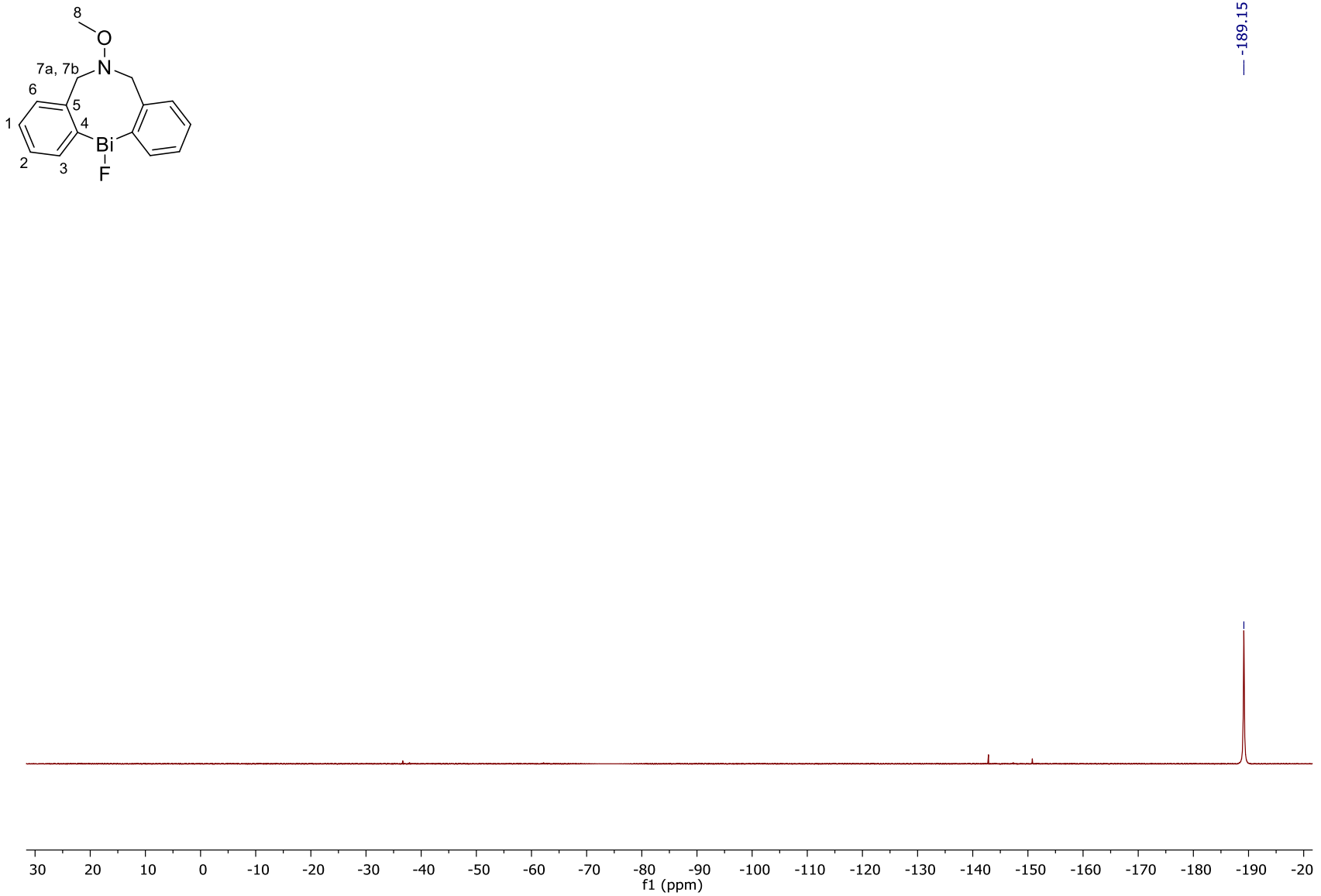


Figure S71. ^{19}F NMR of **6-F** (564 MHz, $CDCl_3$, 30°C)

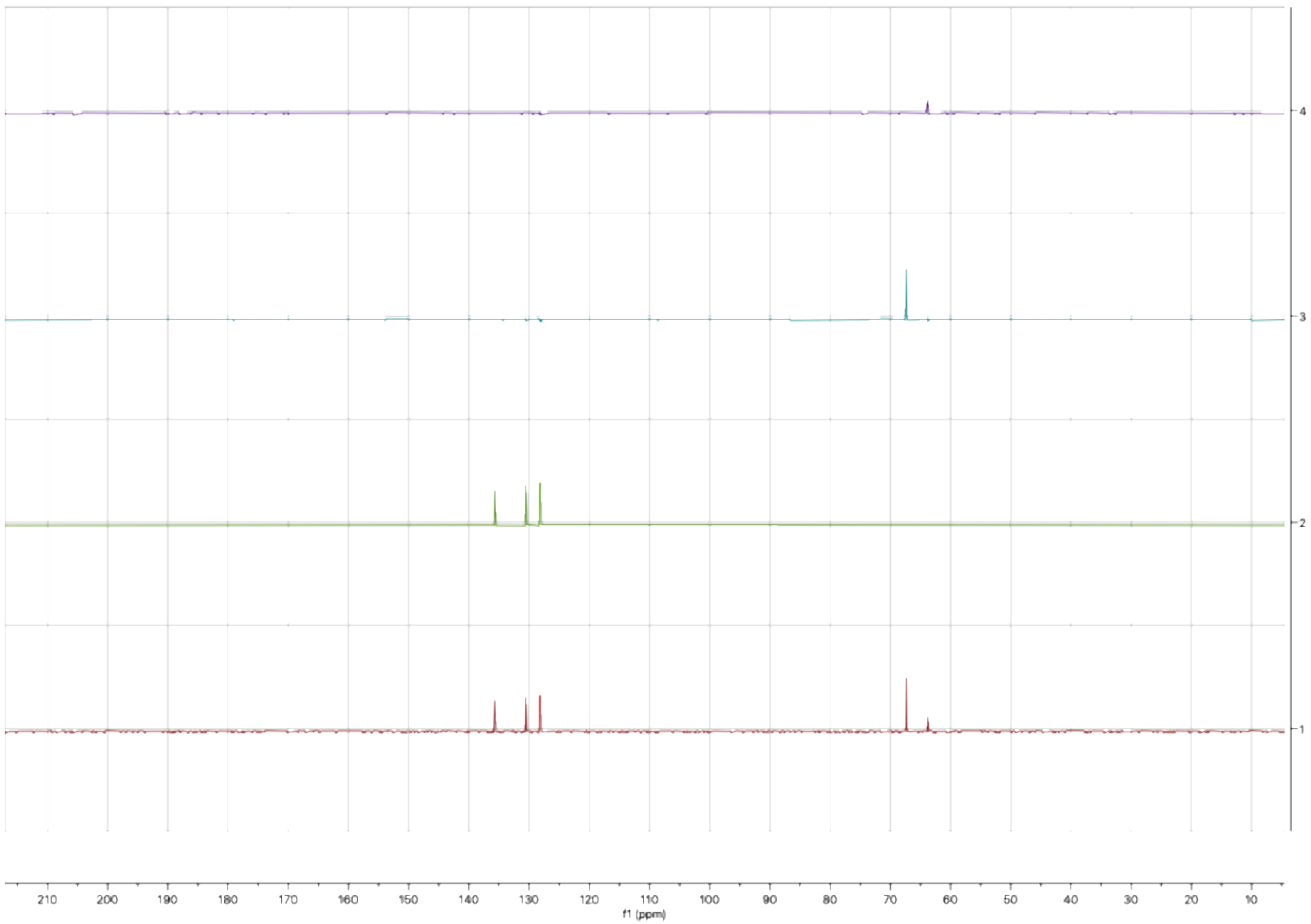


Figure S72. $^{13}C\{^{1}H\}$ DEPT of **6-F** in $CDCl_3$

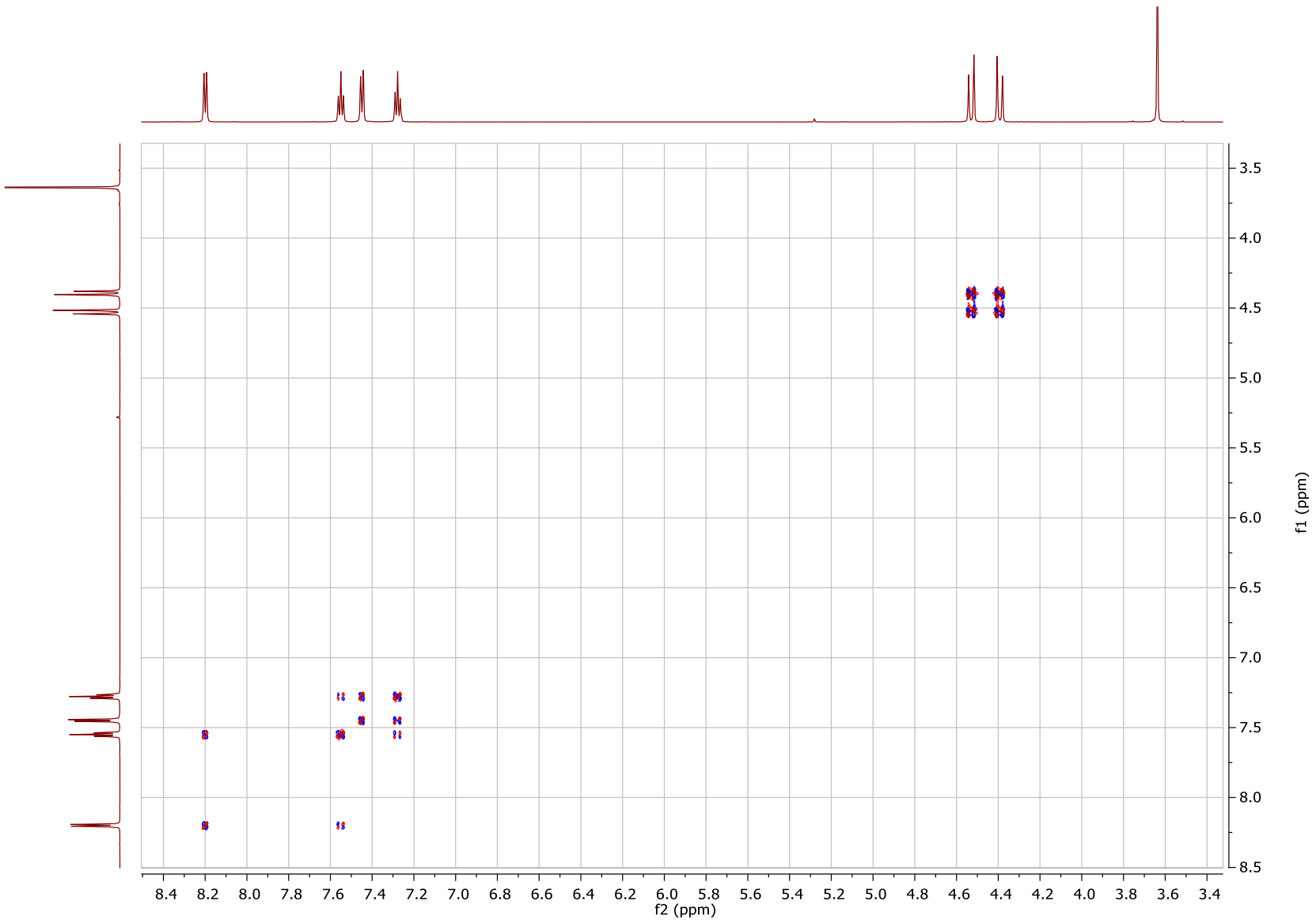


Figure S73. COSY of **6-F** in $CDCl_3$

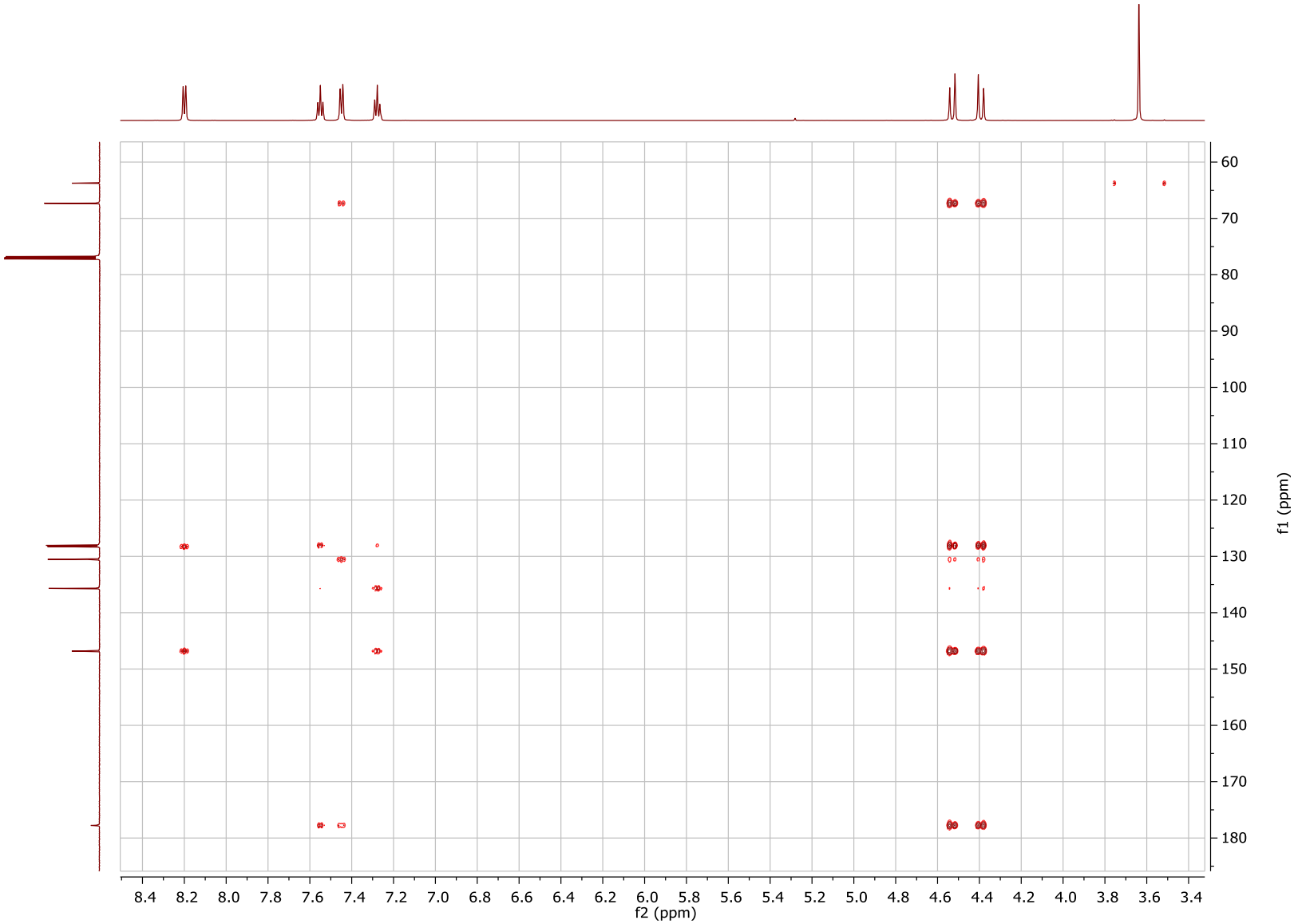


Figure S74. HMBC of **6-F** in $CDCl_3$

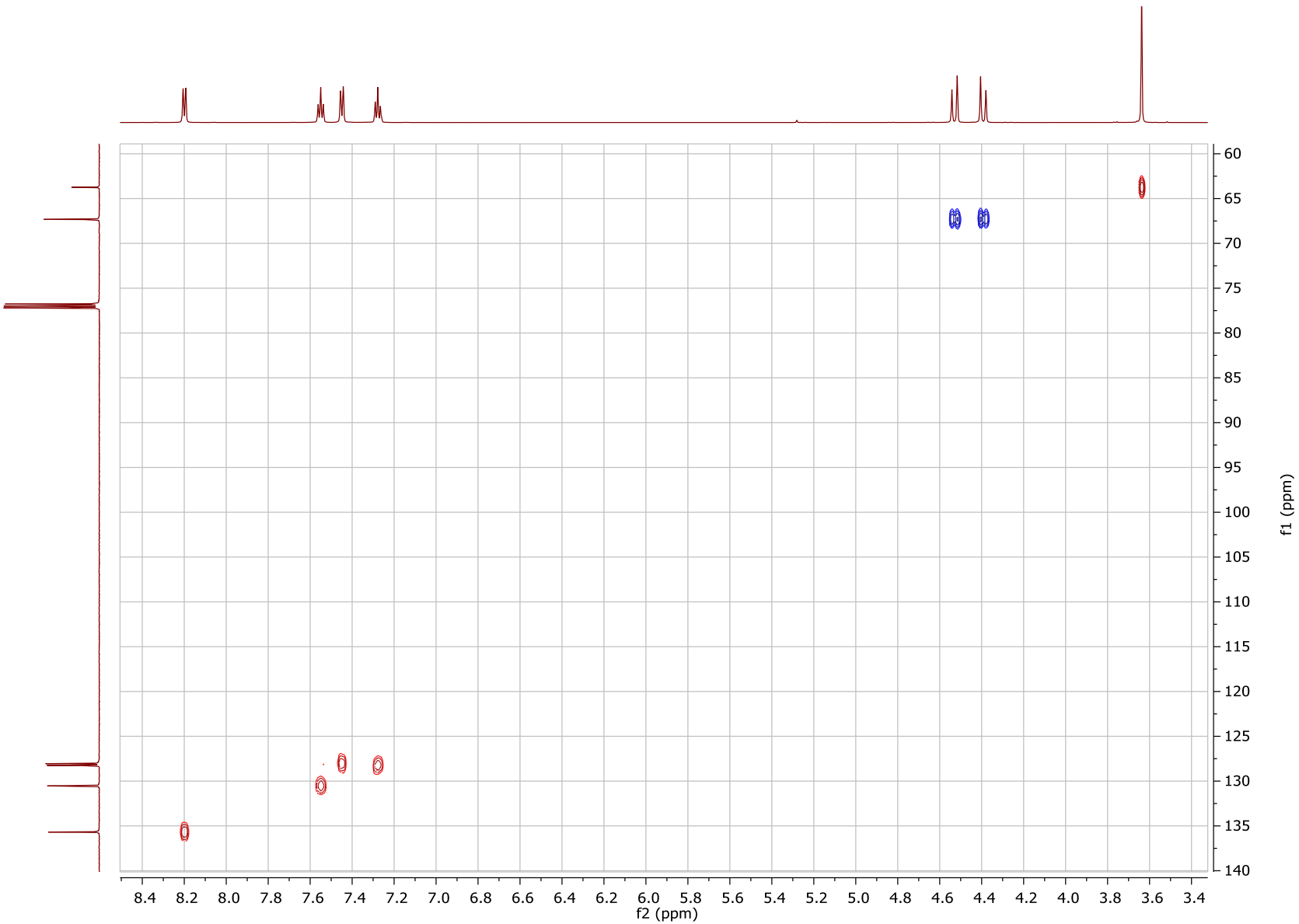
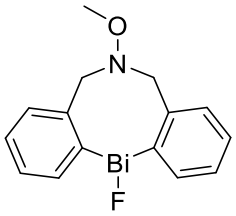


Figure S75. HSQC of **6-F** in $CDCl_3$



Chemical Formula: $BiC_{15}H_{15}NOF$

Molecular Weight: 453.27

Elemental Analysis: C: 39.75; H: 3.34; N: 3.09

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
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Date of report	2/3/2023 6:09:41PM
User ID	Administrator
Comments	TLG_4_122B [Hyvl]

DATE & TIME	2/3/2023 6:05:48 PM	P_ID	EA LAB
SAMPLE ID	23068	USER ID	Administrator
WEIGHT (mg)	2.302	MODE	CHN

CARBON	39.935%
HYDROGEN	3.079%
NITROGEN	3.095%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

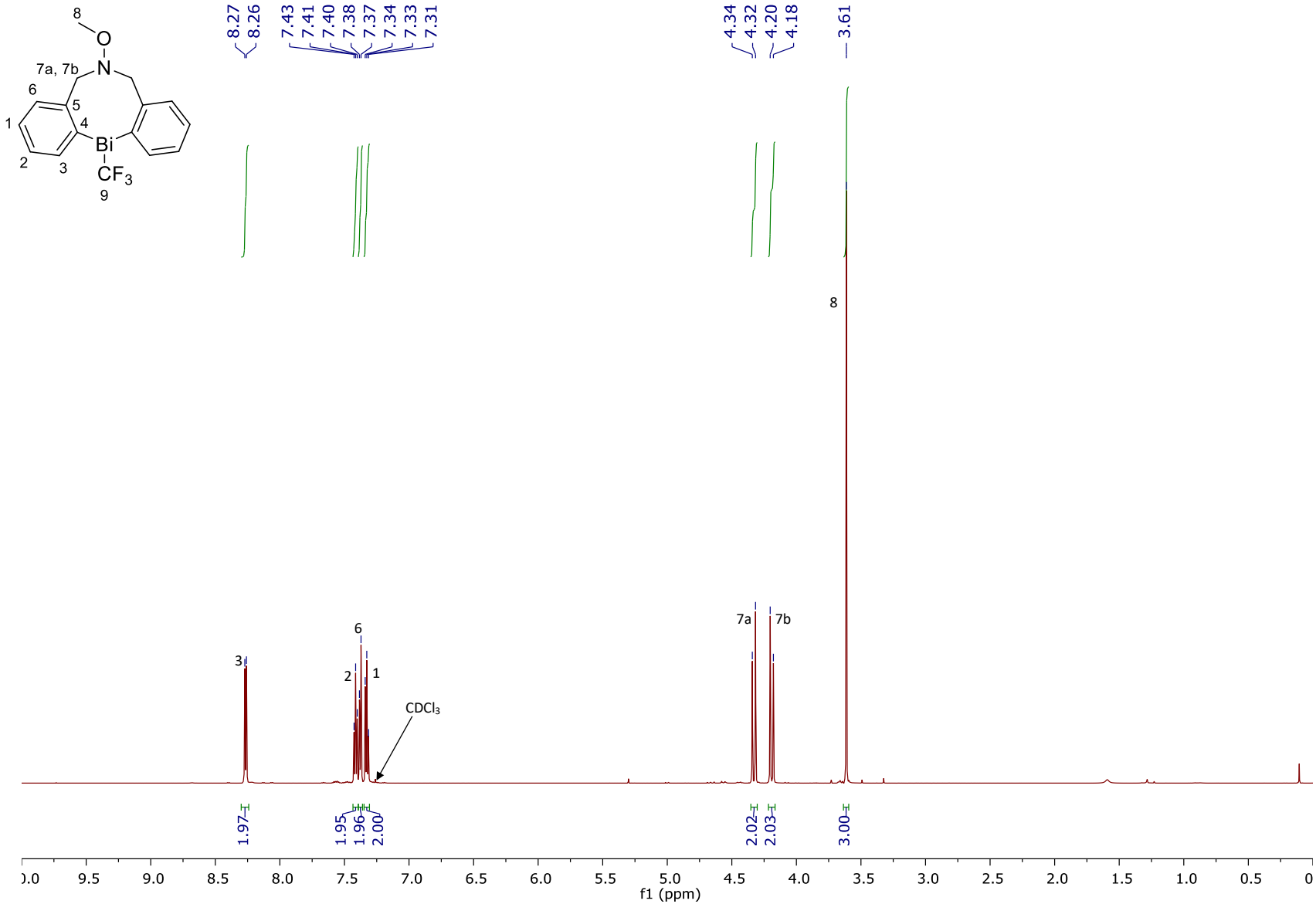


Figure S76. ^{1}H NMR of **6-CF$_3$** (600 MHz, $CDCl_3$, 60°C)

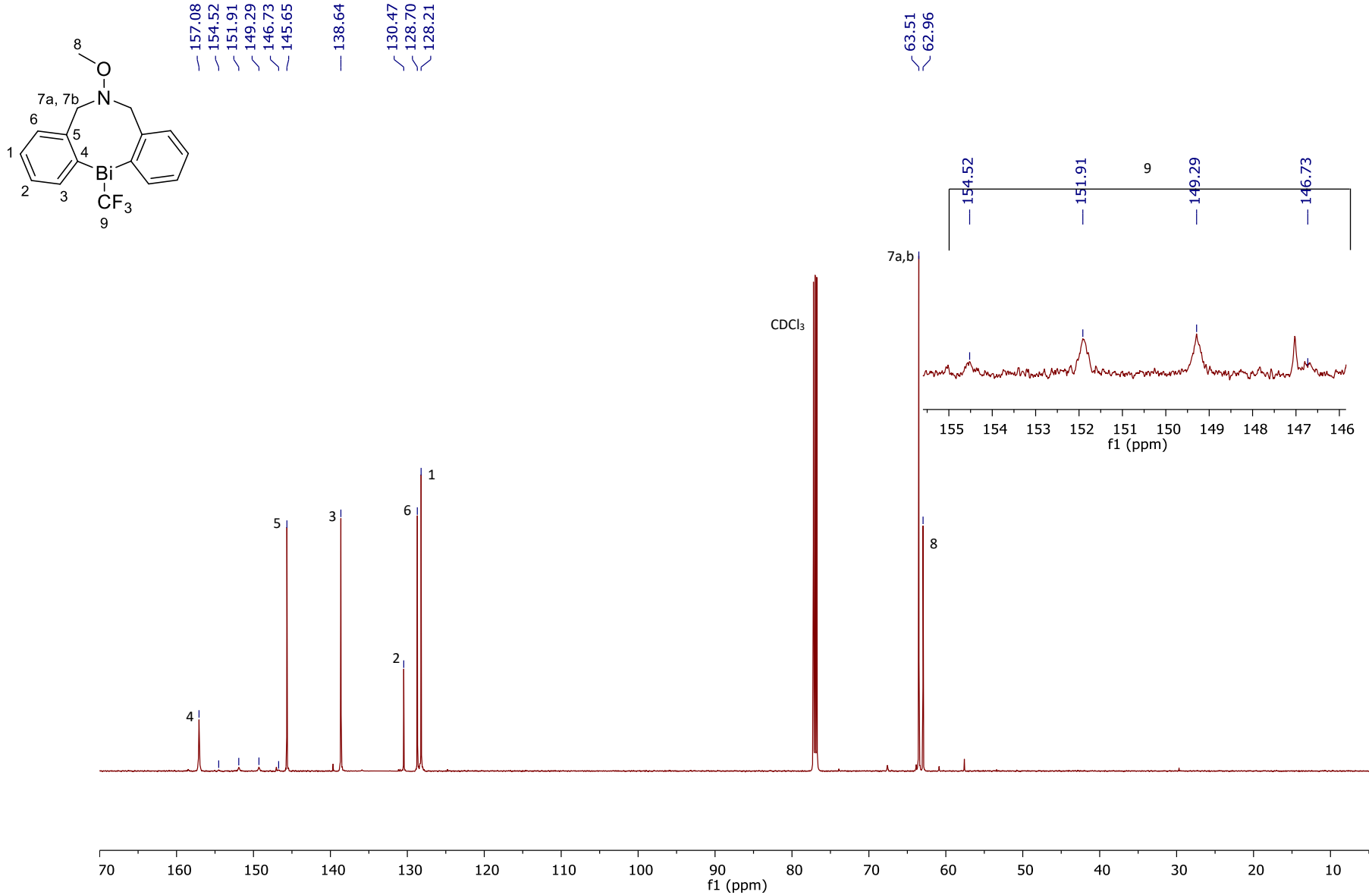


Figure S77. $^{13}C\{^{1}H\}$ NMR of **6-CF$_3$** (150 MHz, $CDCl_3$, 60°C)

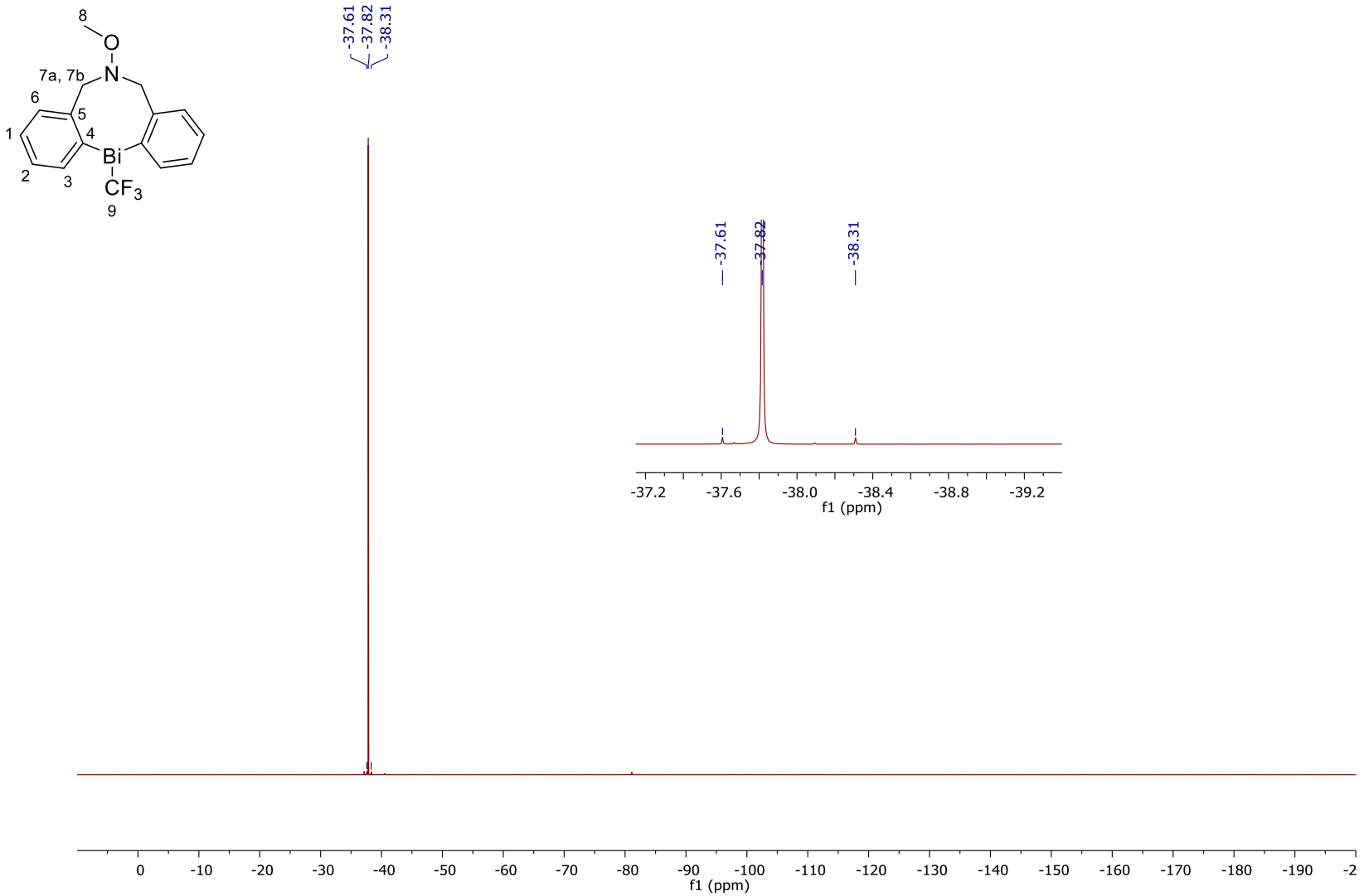


Figure S78. ^{19}F NMR of **6-CF_3** (564 MHz, $CDCl_3$, 60°C)

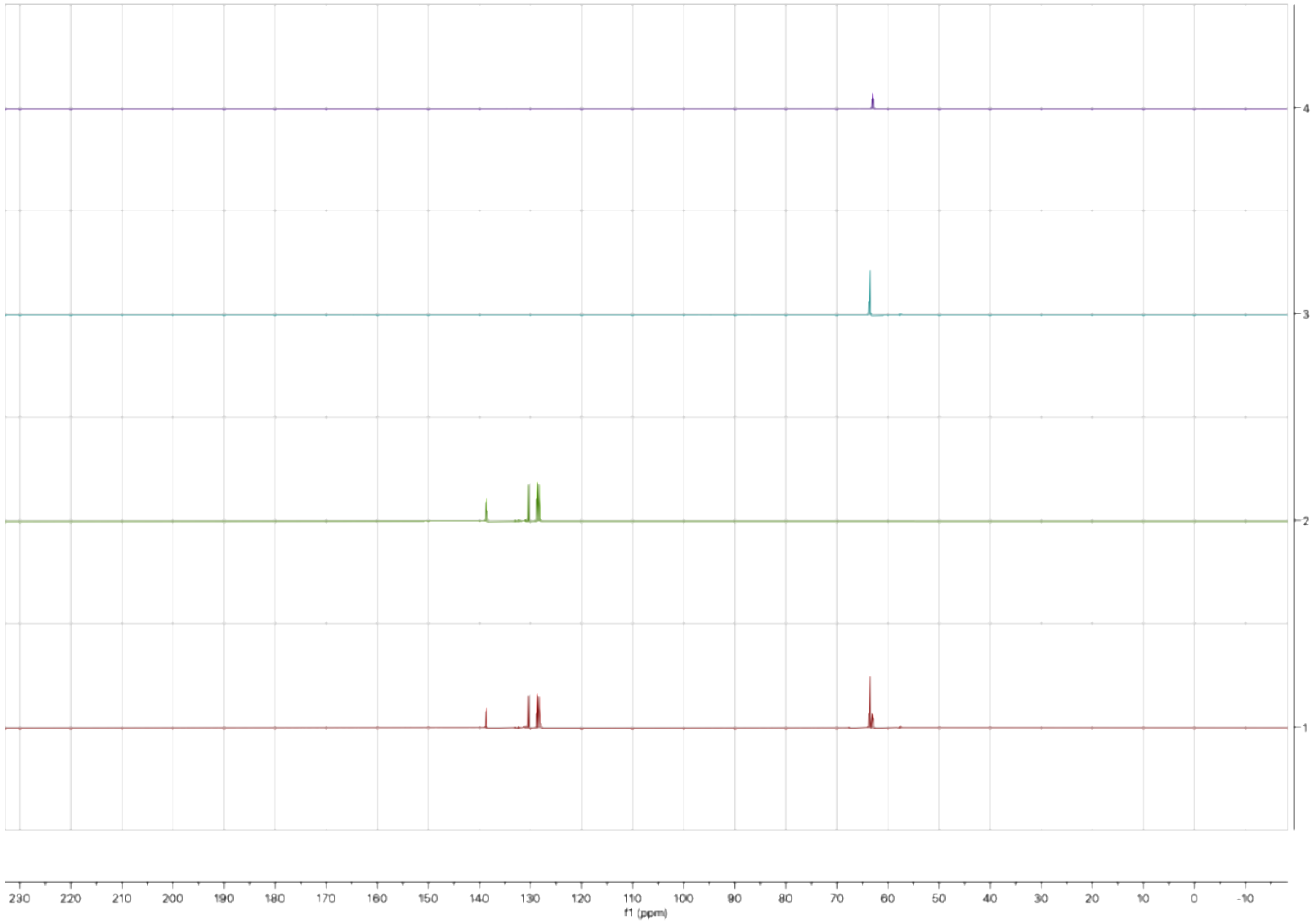


Figure S79. $^{13}C\{^{1}H\}$ DEPT of **6-CF$_3$** in $CDCl_3$

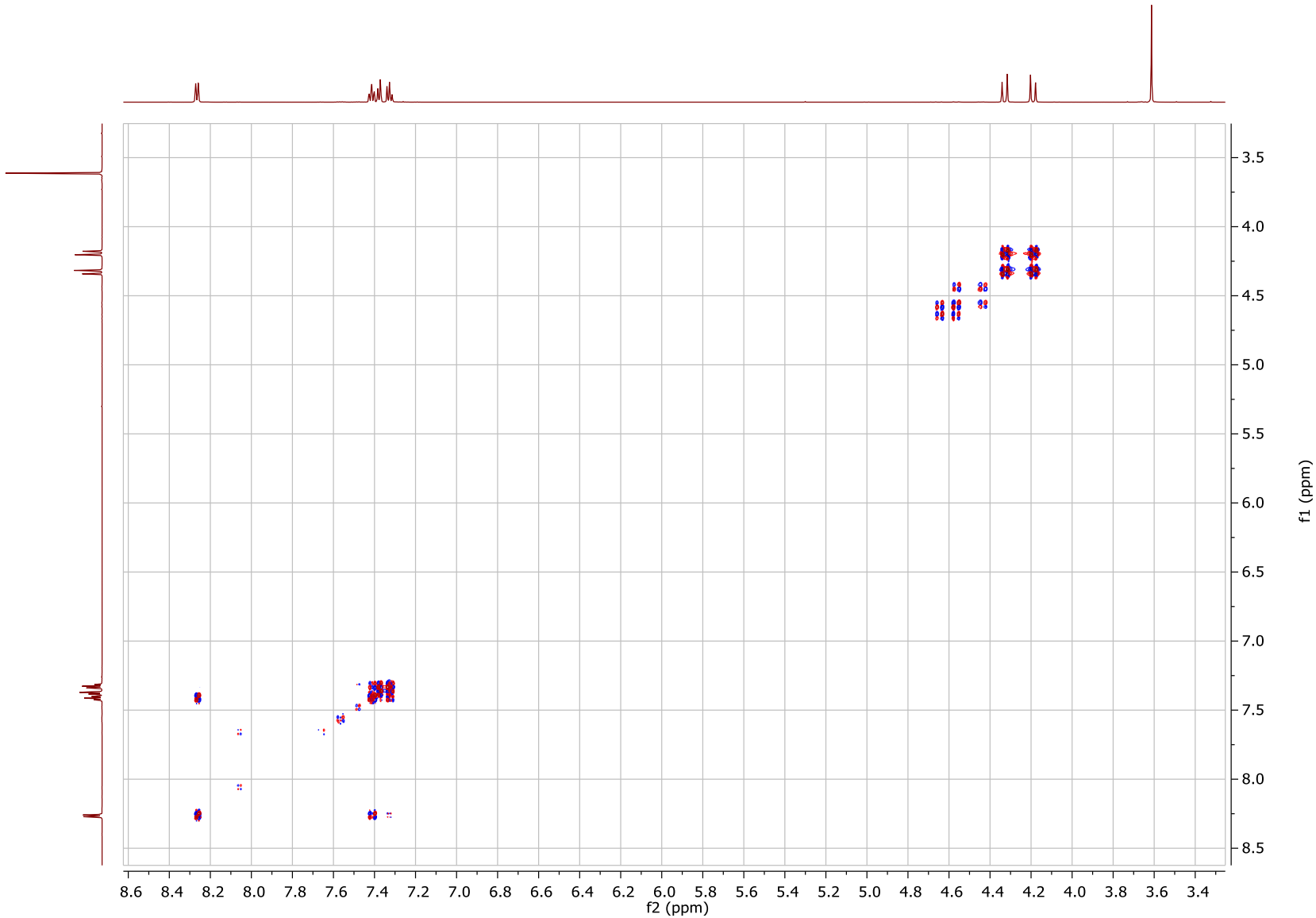


Figure S80. COSY of **6-CF_3** in $CDCl_3$

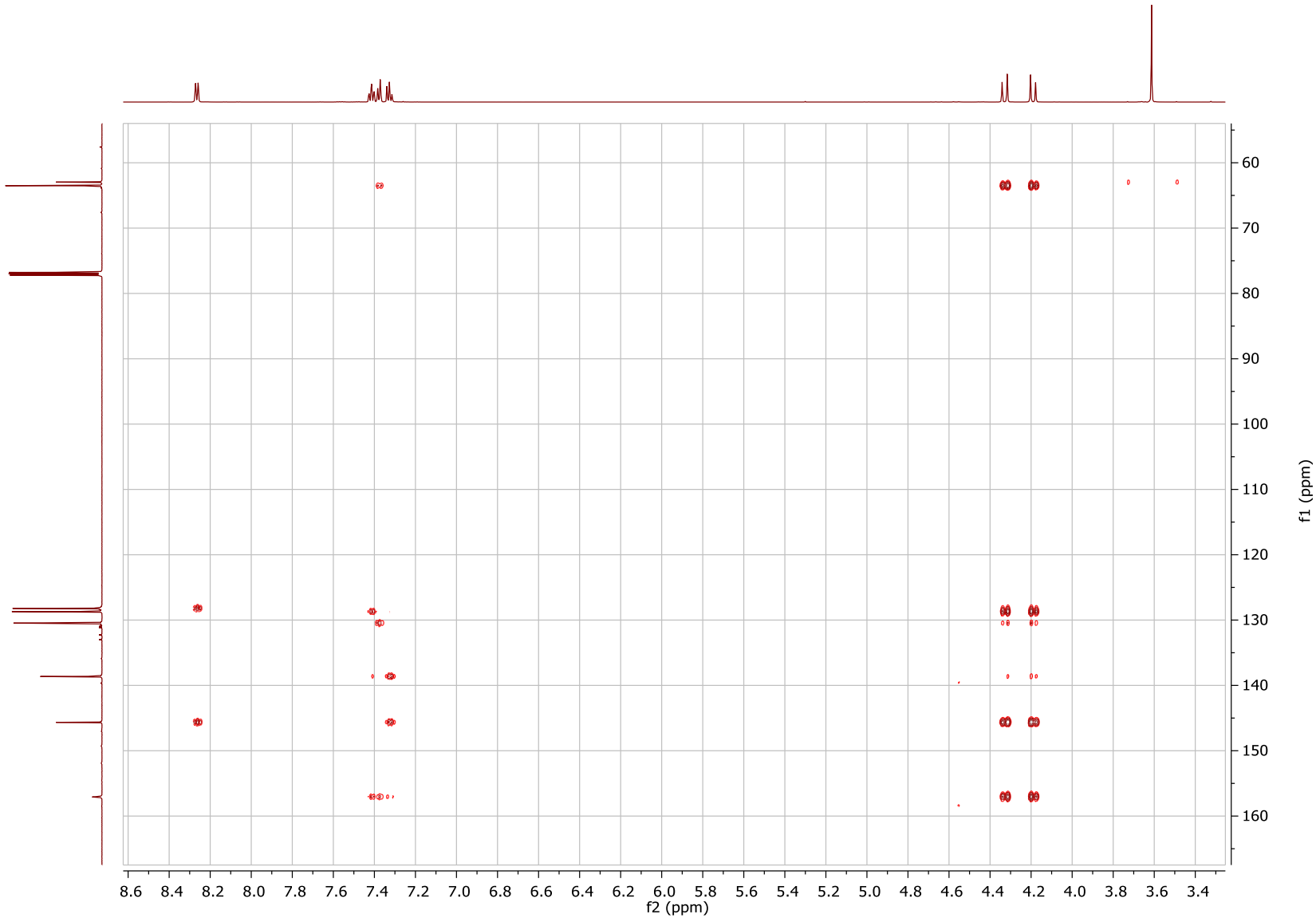


Figure S81. HMBC of **6-CF_3** in $CDCl_3$

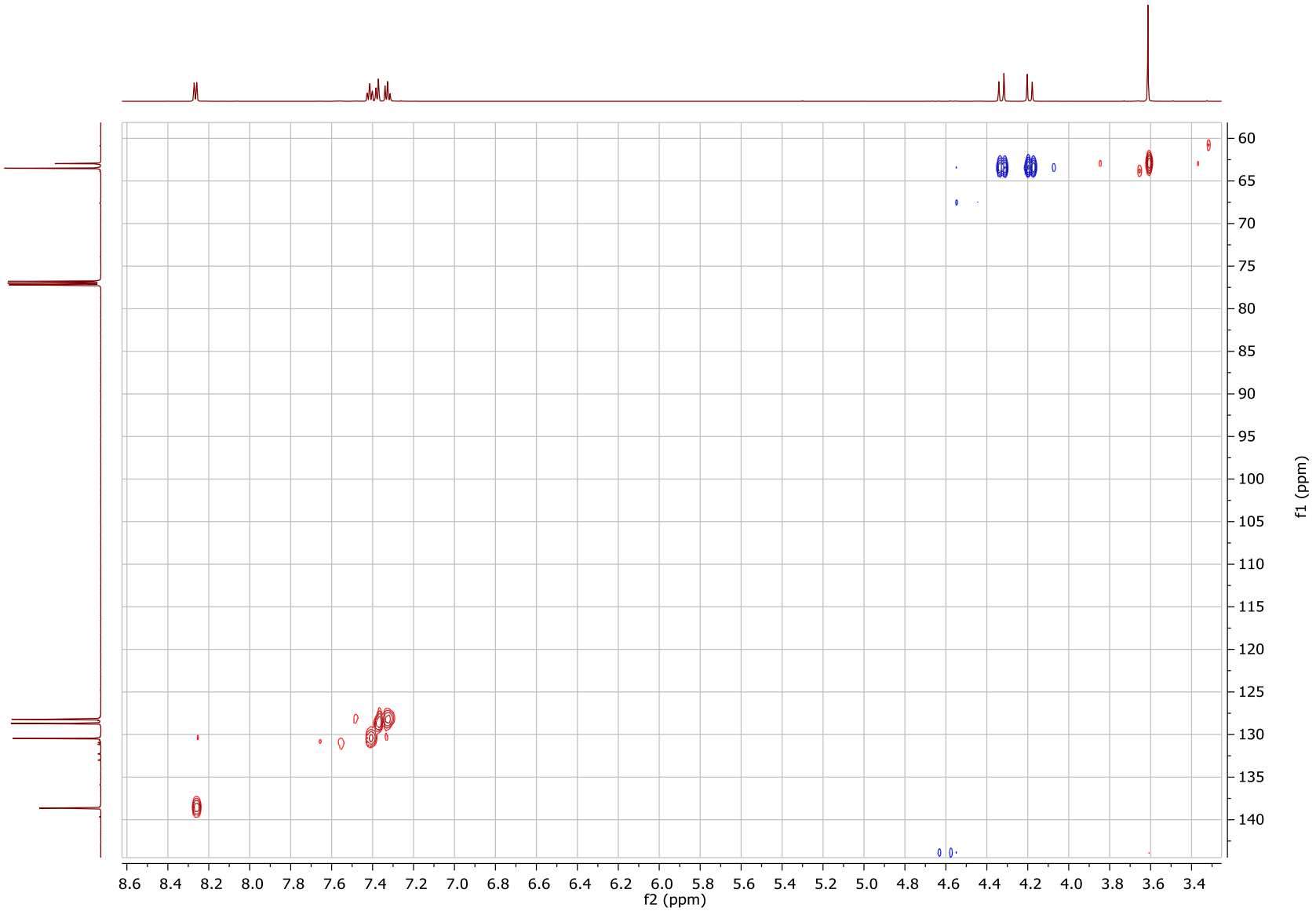
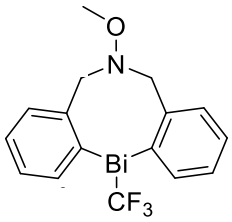


Figure S82. HSQC of **6-CF_3** in $CDCl_3$



Chemical Formula: $BiC_{16}H_{15}NOF_3$

Molecular Weight: 503.28

Elemental Analysis: C: 38.18; H: 3.00; N, 2.78

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
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Date of report	2/3/2023 6:08:36PM
User ID	Administrator
Comments	TLG_4_009 [Hyvl]

DATE & TIME	2/3/2023 6:00:52 PM	P_ID	EA LAB
SAMPLE ID	23066	USER ID	Administrator
WEIGHT (mg)	2.485	MODE	CHN

CARBON	38.461%
HYDROGEN	2.840%
NITROGEN	2.777%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

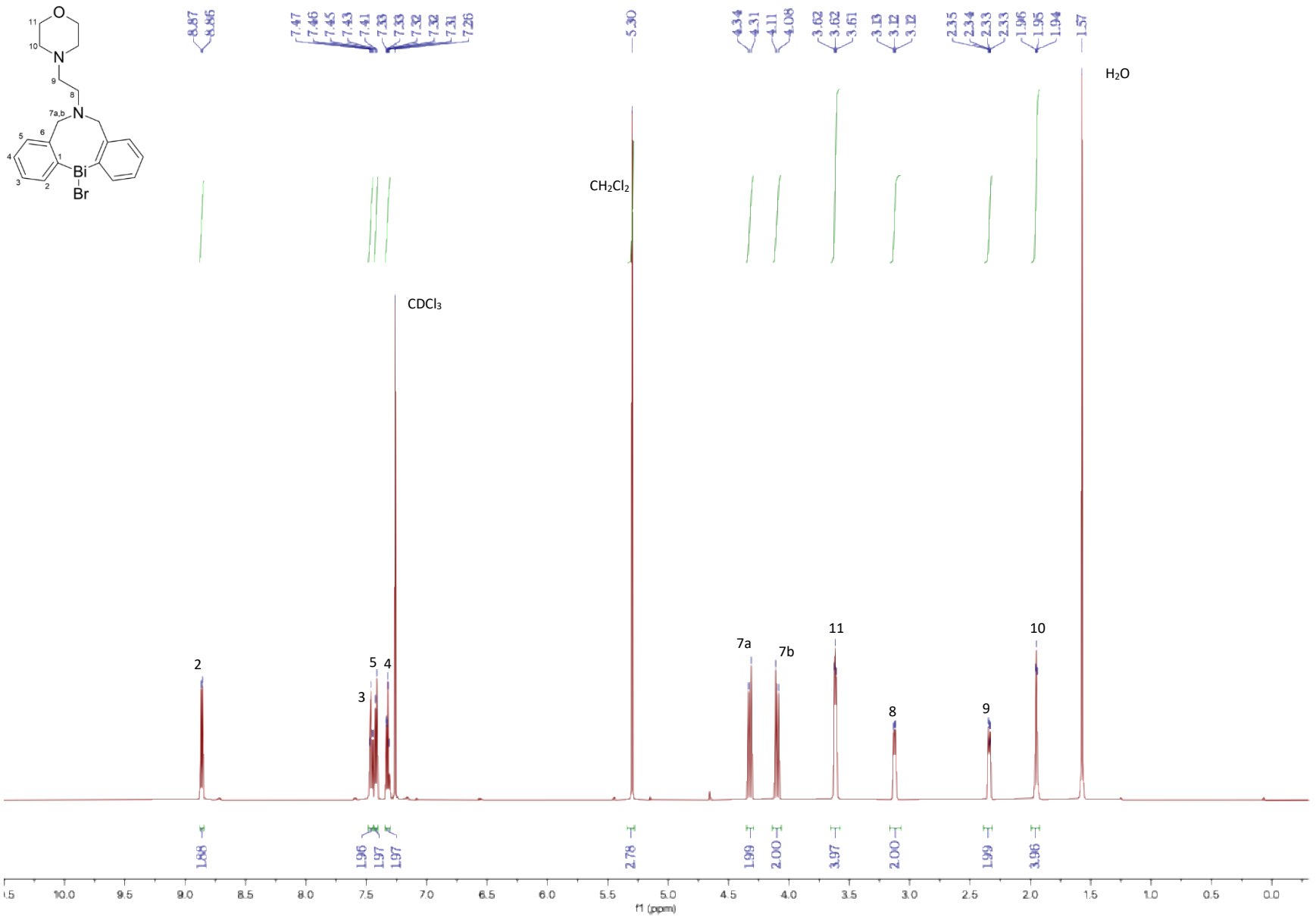


Figure S83. ^{1}H NMR of **7-Br** (600 MHz, $CDCl_3$, 30°C)

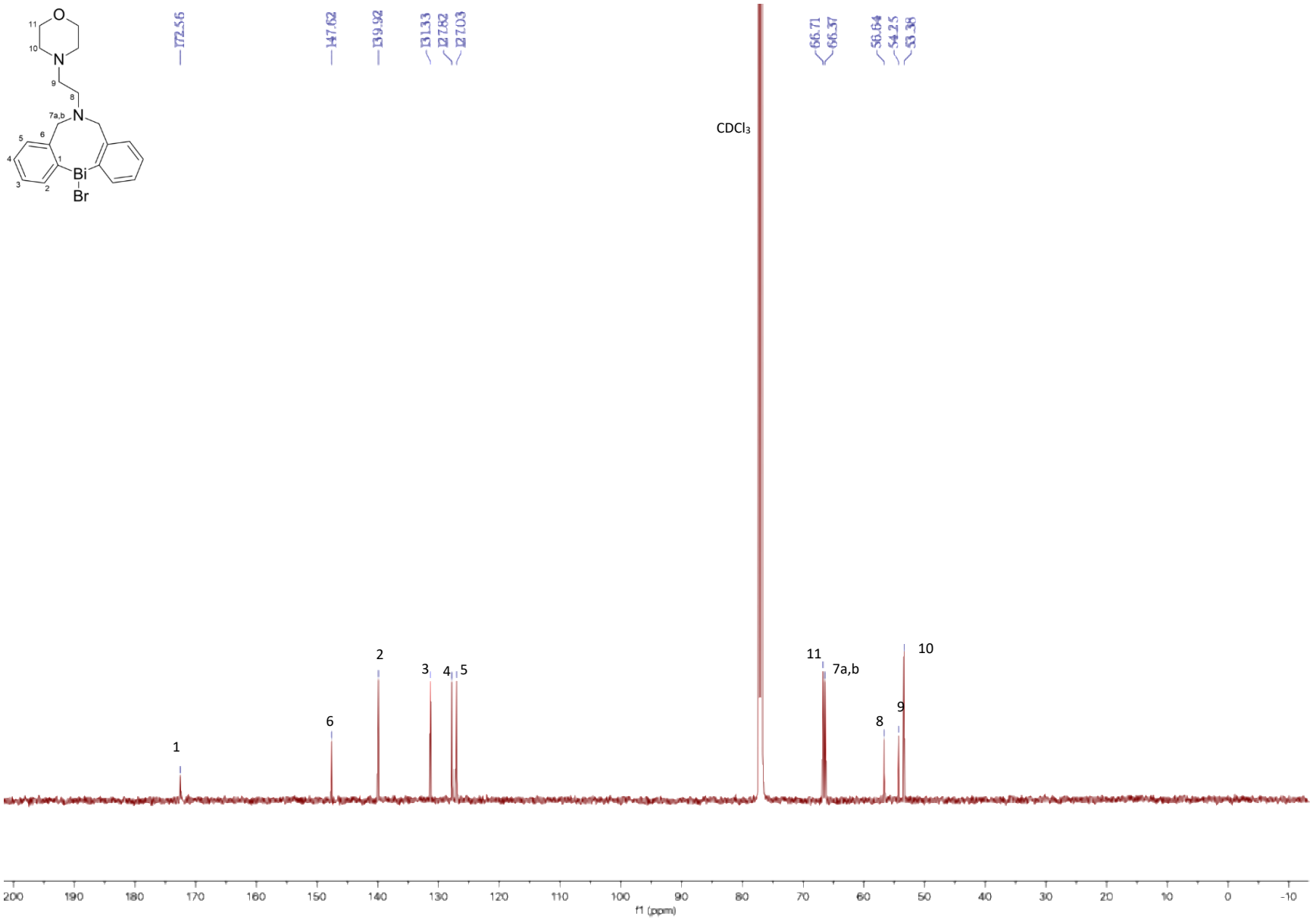


Figure S84. $^{13}C\{^{1}H\}$ NMR of **7-Br** (150 MHz, $CDCl_3$, 30°C)

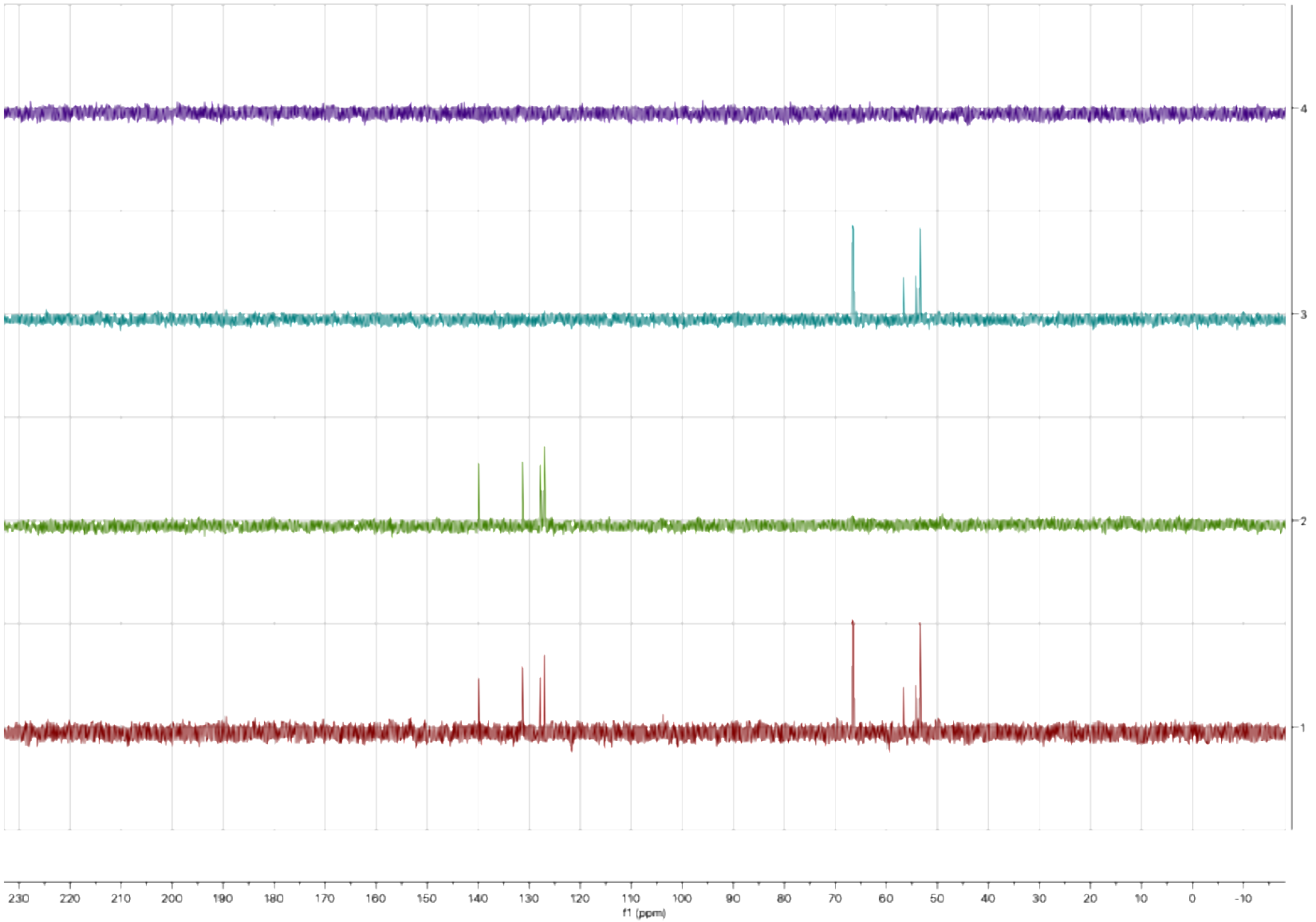


Figure S85. $^{13}C\{^{1}H\}$ DEPT of **7-Br** in $CDCl_3$

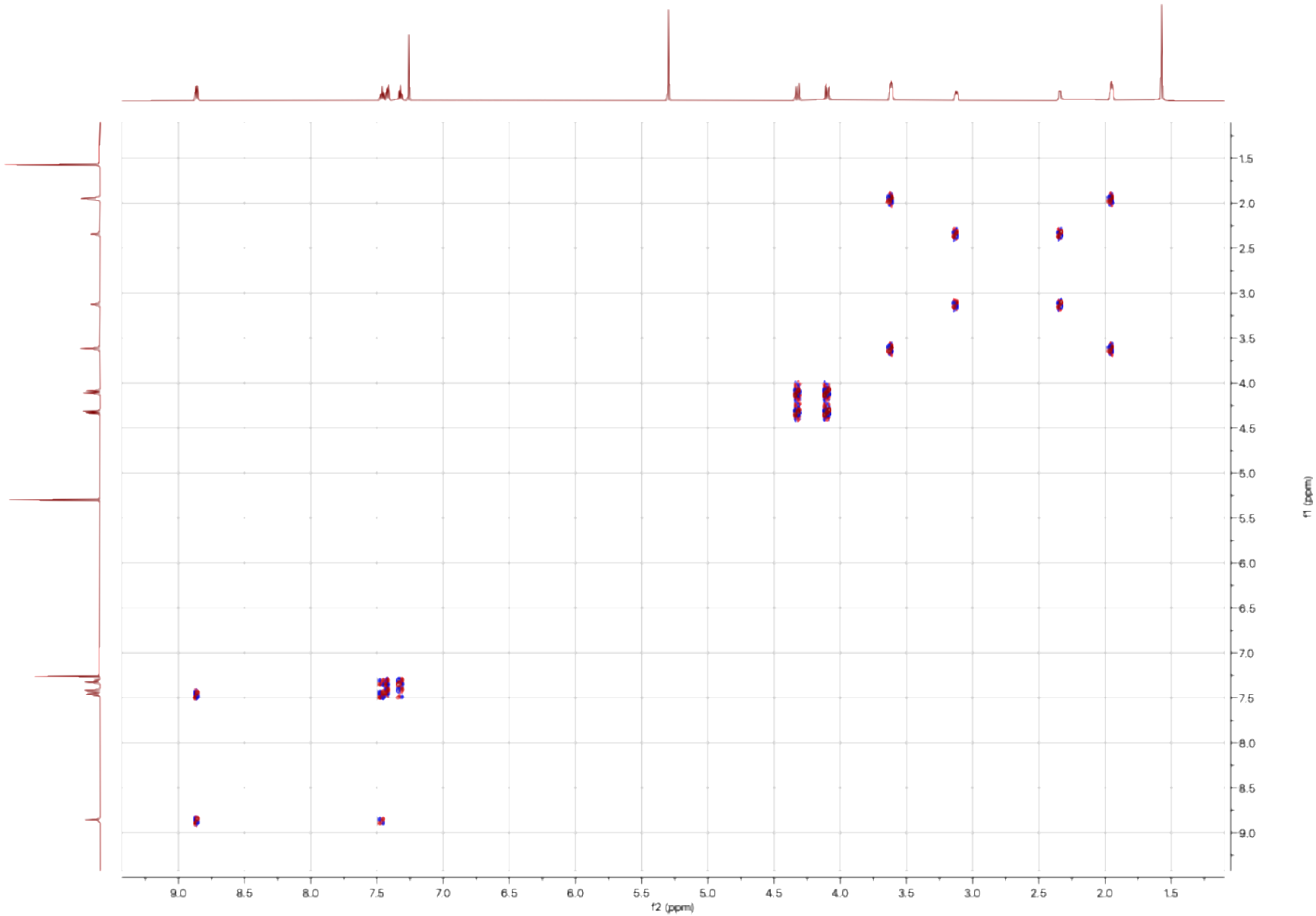


Figure S86. COSY of **7-Br** in $CDCl_3$

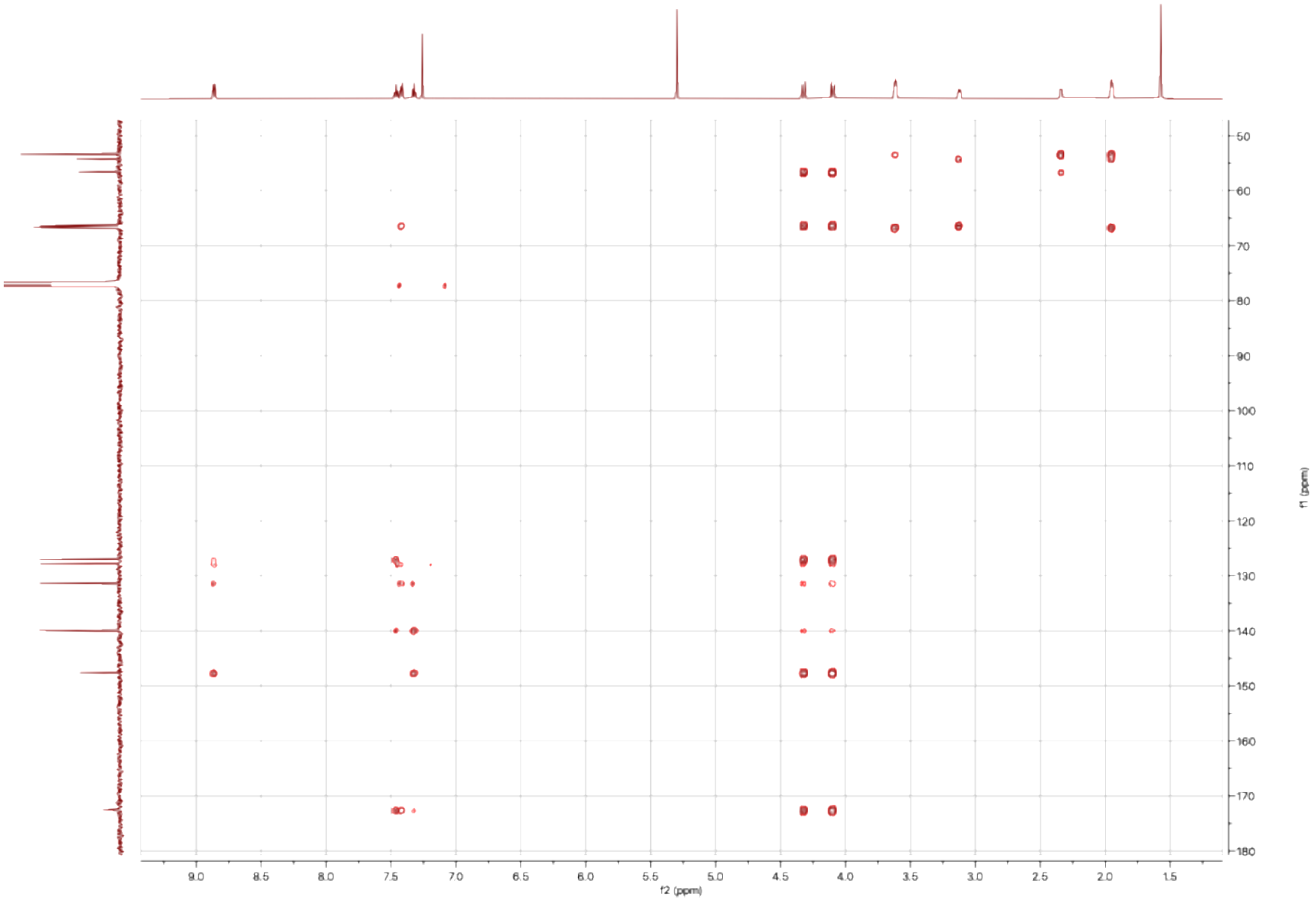


Figure S87. HMBC of **7-Br** in $CDCl_3$

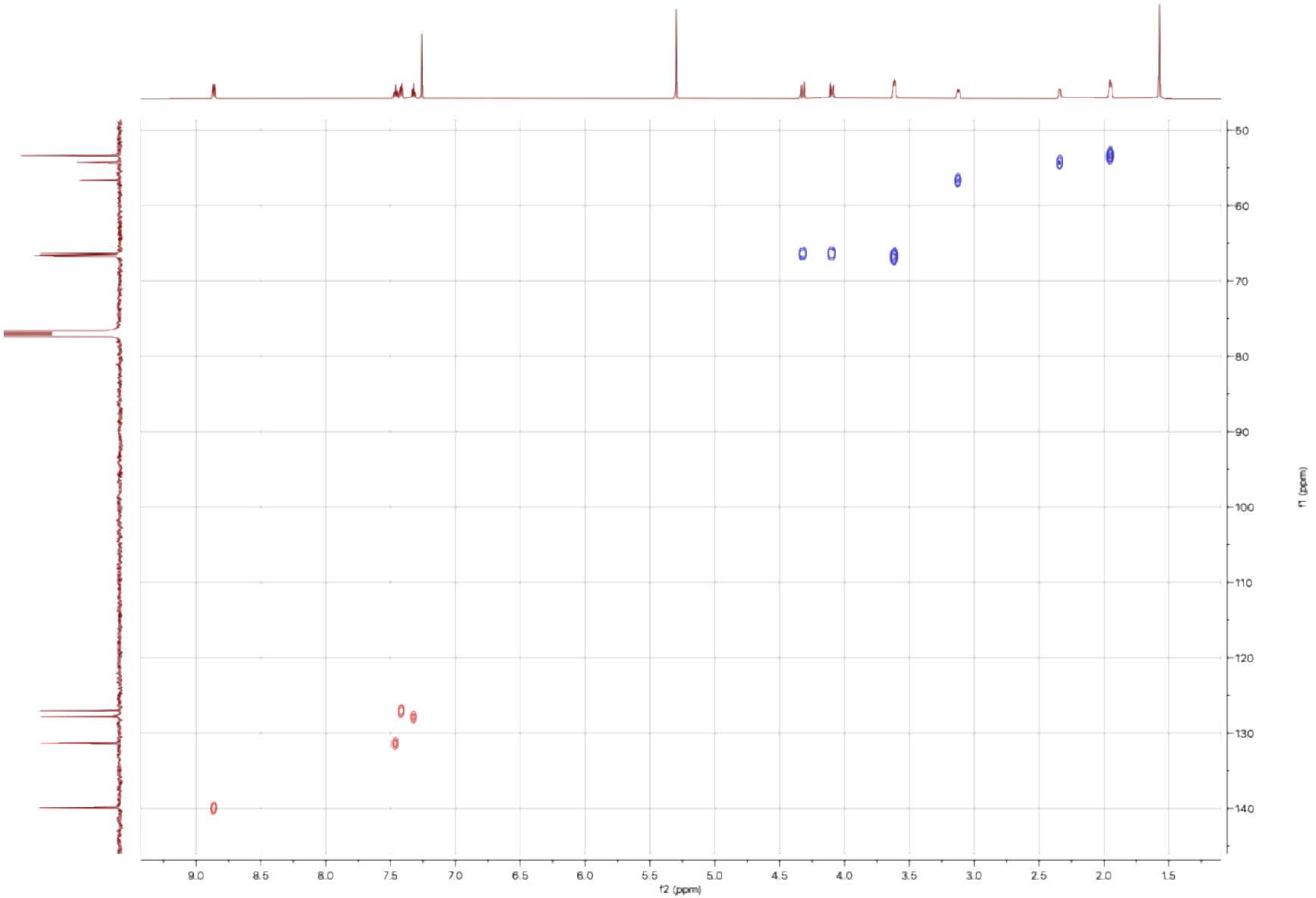
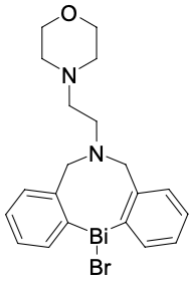


Figure S88. HSQC of **7-Br** in $CDCl_3$



Chemical Formula: $BiC_{20}H_{24}BrN_2O \cdot 0.5CH_2Cl_2$

Elemental Analysis: C, 38.49; H, 3.94; N, 4.38.

CENTC Elemental Analysis Facility
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Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	2/16/2024 5:45:22PM
User ID	Administrator
Comments	MV_248 [Hyvl]

DATE & TIME	2/16/2024 11:20:21 AM	P_ID	EA LAB
SAMPLE ID	24057	USER ID	Administrator
WEIGHT (mg)	2.279	MODE	CHN

CARBON	38.315%
HYDROGEN	3.759%
NITROGEN	4.267%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

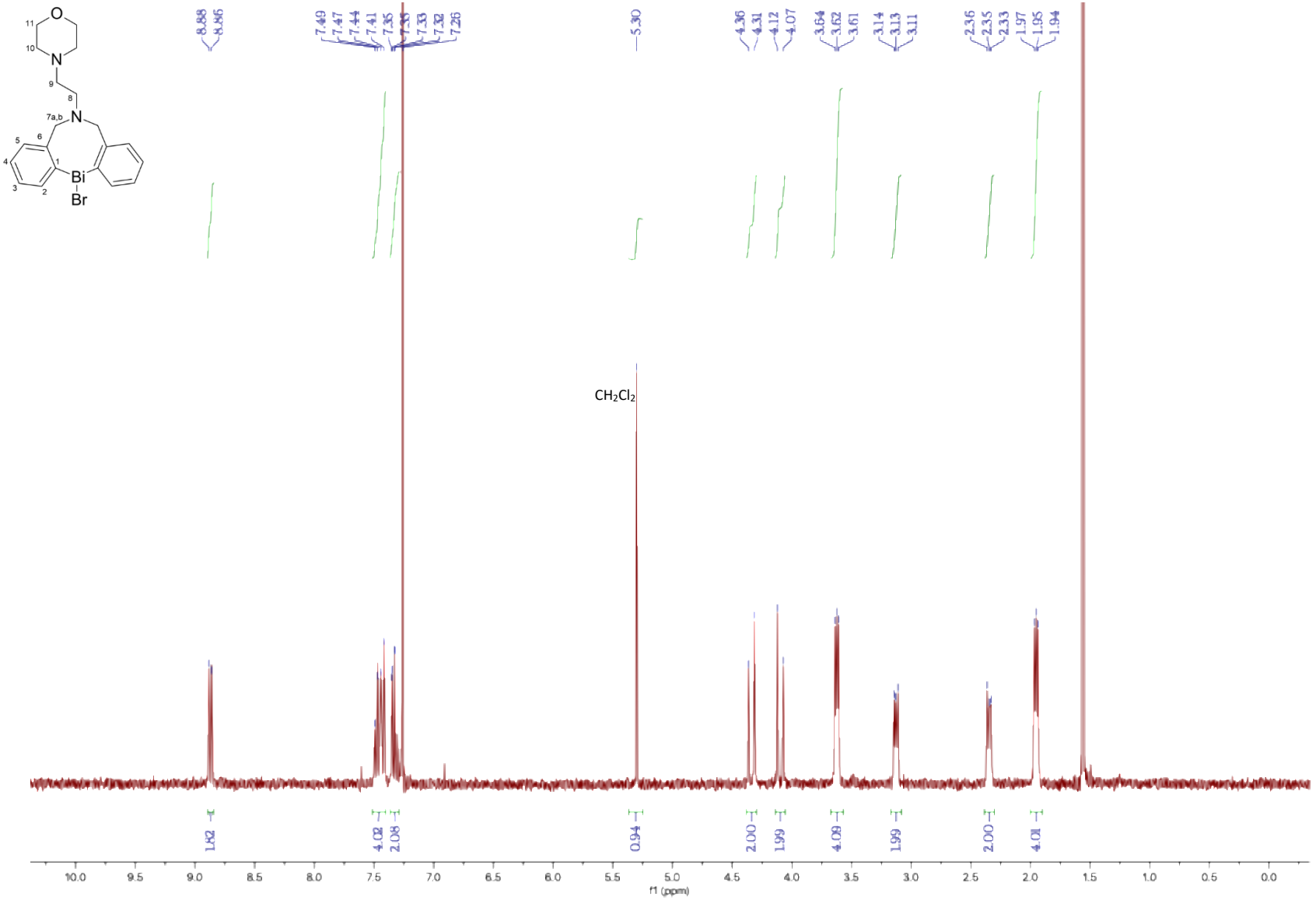
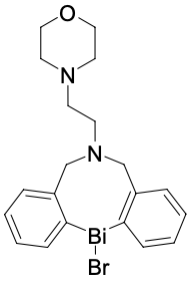


Figure S89. ^{1}H NMR of **7-Br** (300 MHz, $CDCl_3$, 21°C) sample used for EA.



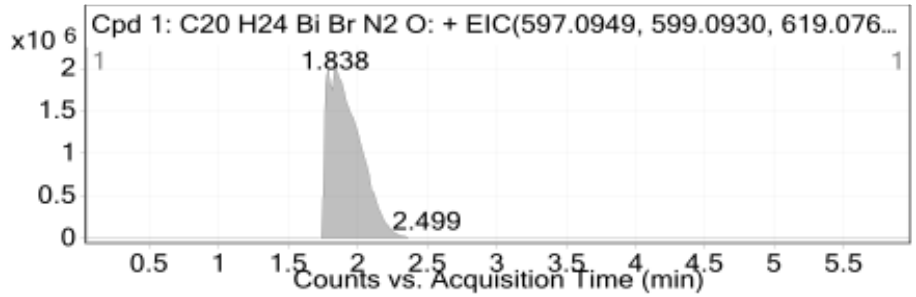
Qualitative Compound Report

	A-MV-3-47_Dinj.d	**Sample Name**	Unavailable
	Unavailable	**Position**	Unavailable
Name	Unavailable	**User Name**	Unavailable
		Acquired Time	Unavailable
tion Status	Success	**DA Method**	Tius_Analysis_Method_LB.m
	Sample information is unavailable		

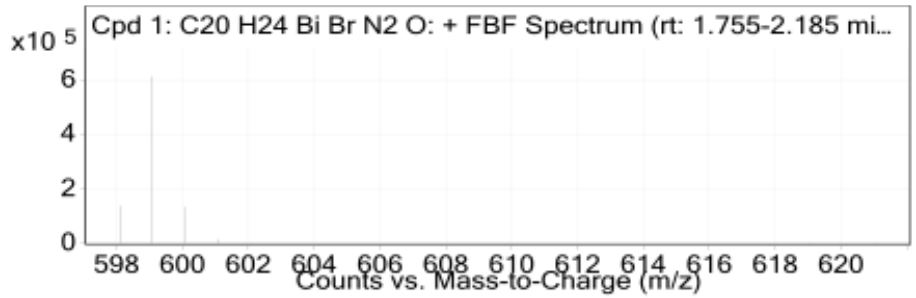
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C20 H24 Bi Br N2 O	1.838	596.08696	617952	C20 H24 Bi Br N2 O	596.08759	-1.04

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C20 H24 Bi Br N2 O	597.0943	1.838	Find By Formula	596.08696

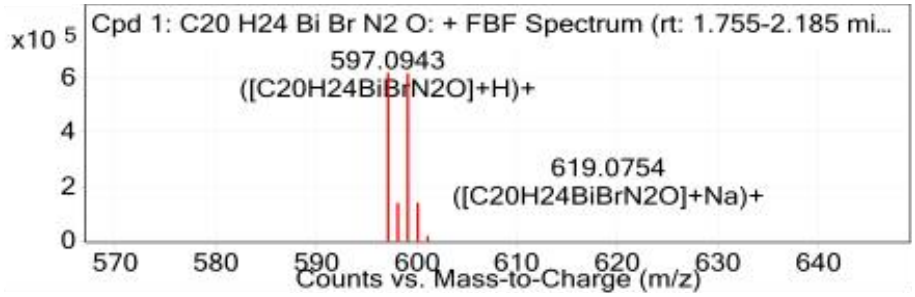


MS Spectrum



MS Zoomed Spectrum

Qualitative Compound Report



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
597.0943	1	617951.56	C20H24BiBrN2O	(M+H)+
598.0971	1	137021.58	C20H24BiBrN2O	(M+H)+
599.0925	1	611227.75	C20H24BiBrN2O	(M+H)+
600.0951	1	132668.38	C20H24BiBrN2O	(M+H)+
601.099	1	15046.43	C20H24BiBrN2O	(M+H)+
602.1036	1	1177.05	C20H24BiBrN2O	(M+H)+
619.0754	1	1802.92	C20H24BiBrN2O	(M+Na)+
620.0808	1	81.33	C20H24BiBrN2O	(M+Na)+
621.073	1	1638.03	C20H24BiBrN2O	(M+Na)+
622.0764	1	137.78	C20H24BiBrN2O	(M+Na)+

--- End Of Report ---

Figure S90. HRMS of **7-Br**

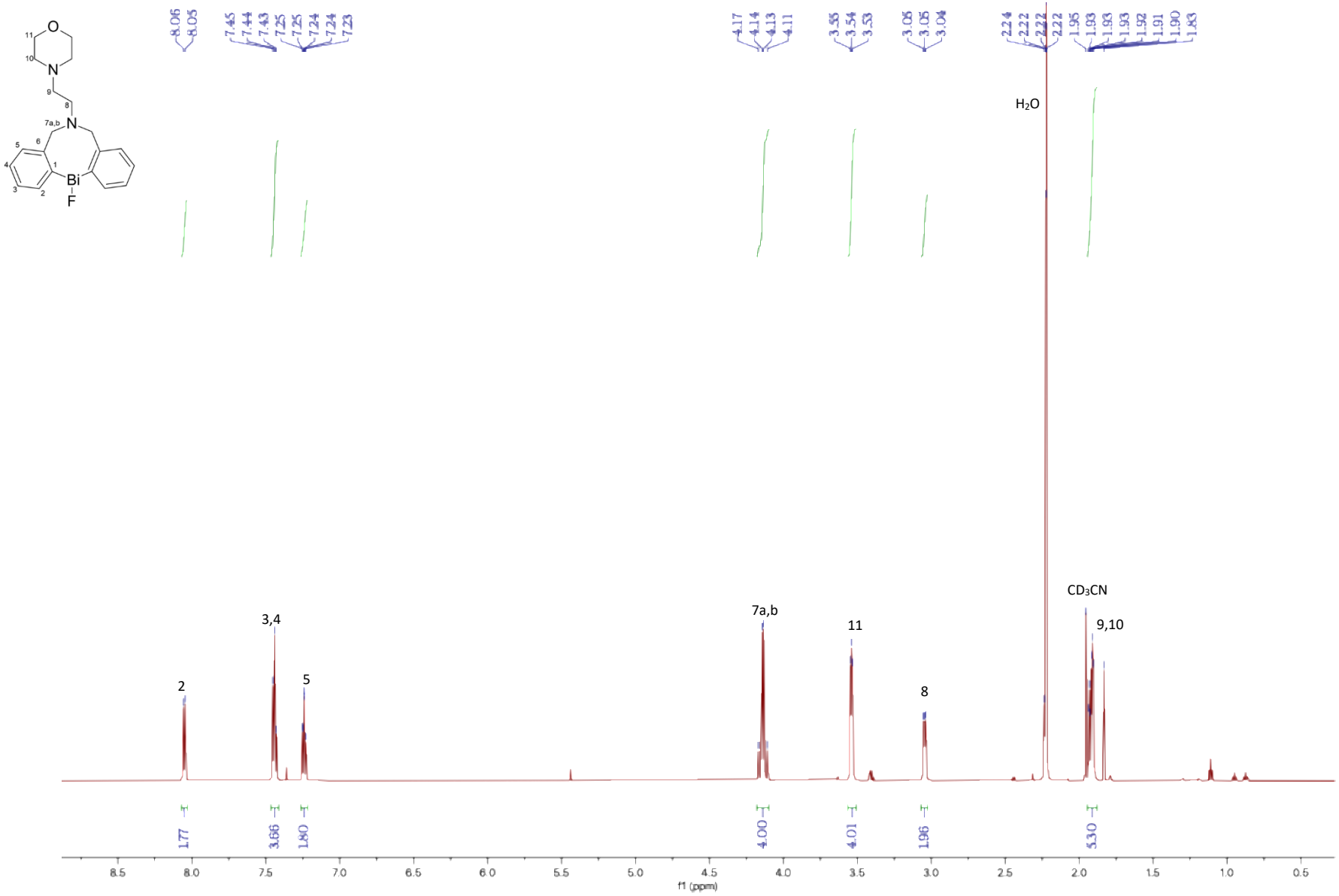


Figure S91. ^{1}H NMR of **7-F** (600 MHz, CD_3CN, 30°C)

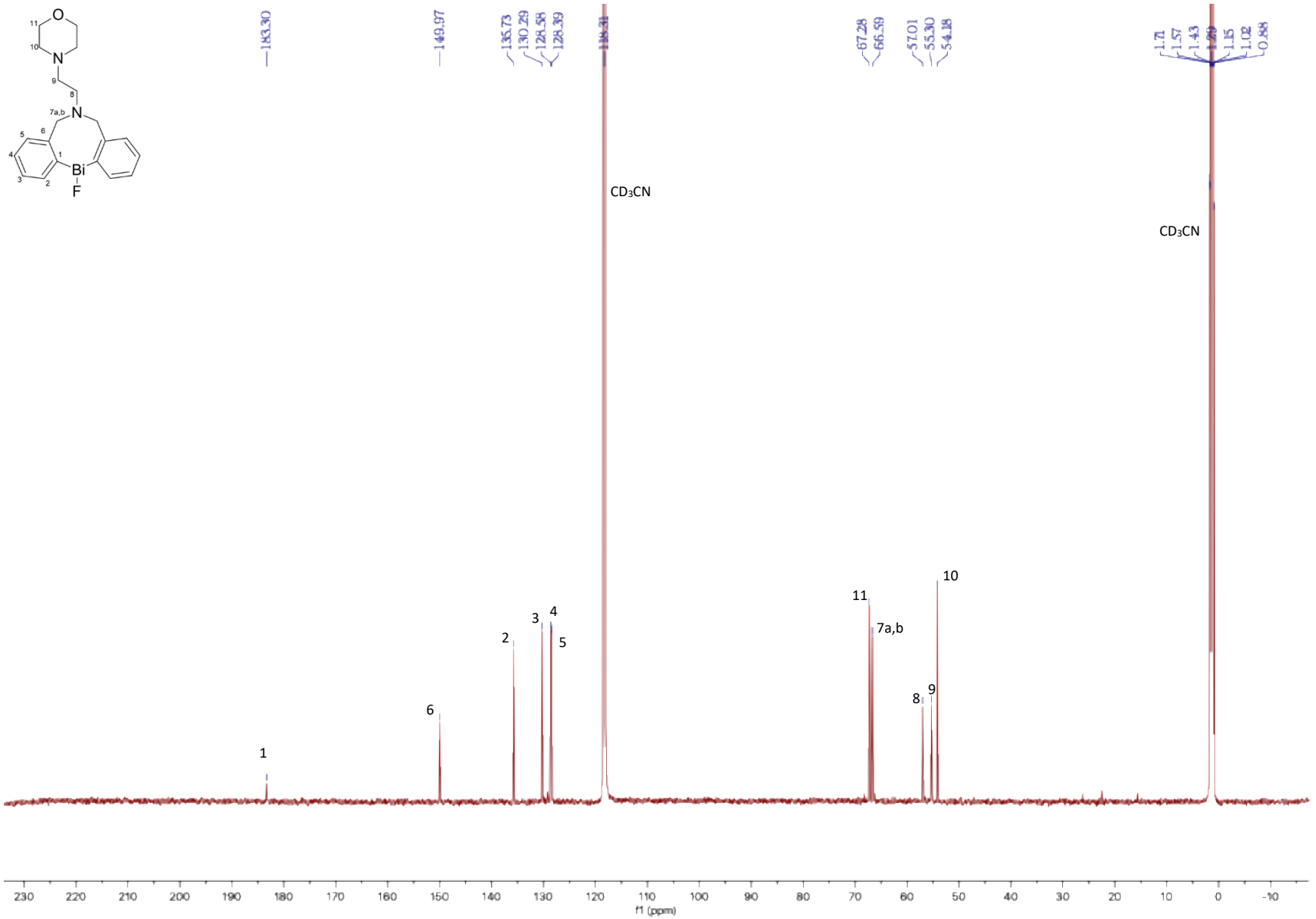


Figure S92. $^{13}C\{^{1}H\}$ NMR of **7-F** (150 MHz, CD_3CN, 30°C)

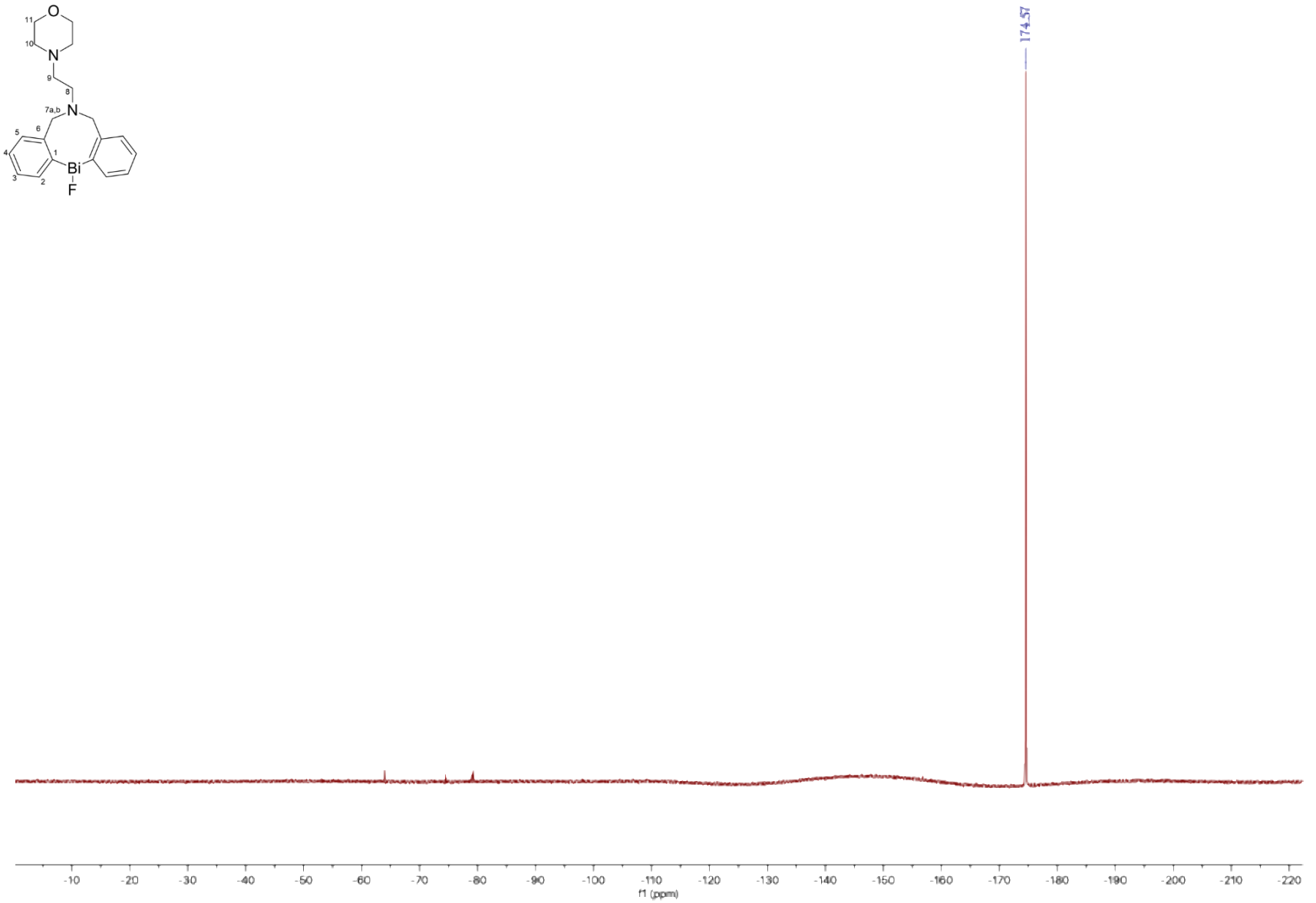


Figure S93. ^{19}F NMR of **7-F** (564 MHz, CD_3CN, 30°C)

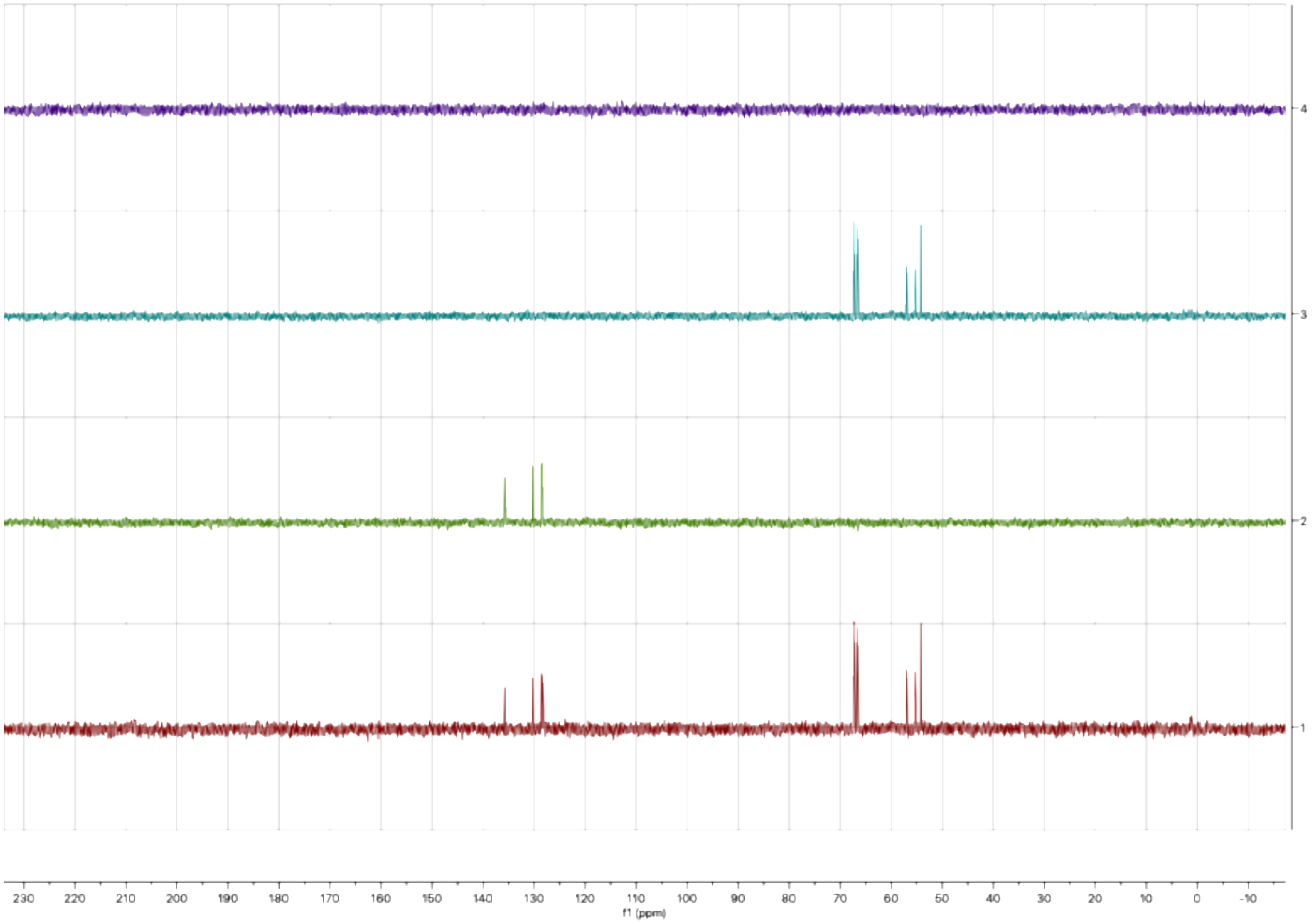


Figure S94. $^{13}C\{^{1}H\}$ DEPT of **7-F** in CD_3CN

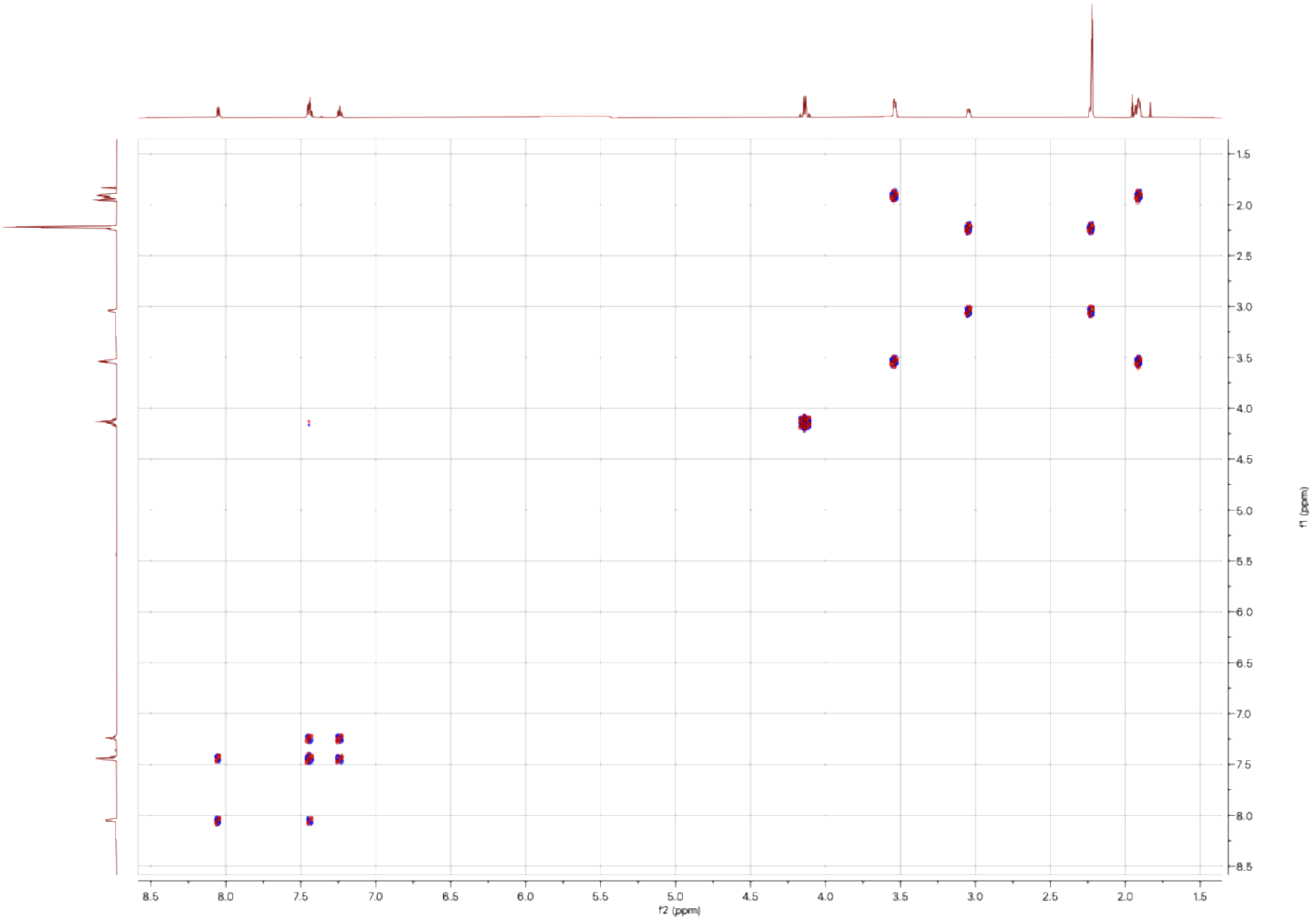


Figure S95. COSY of **7-F** in CD_3CN

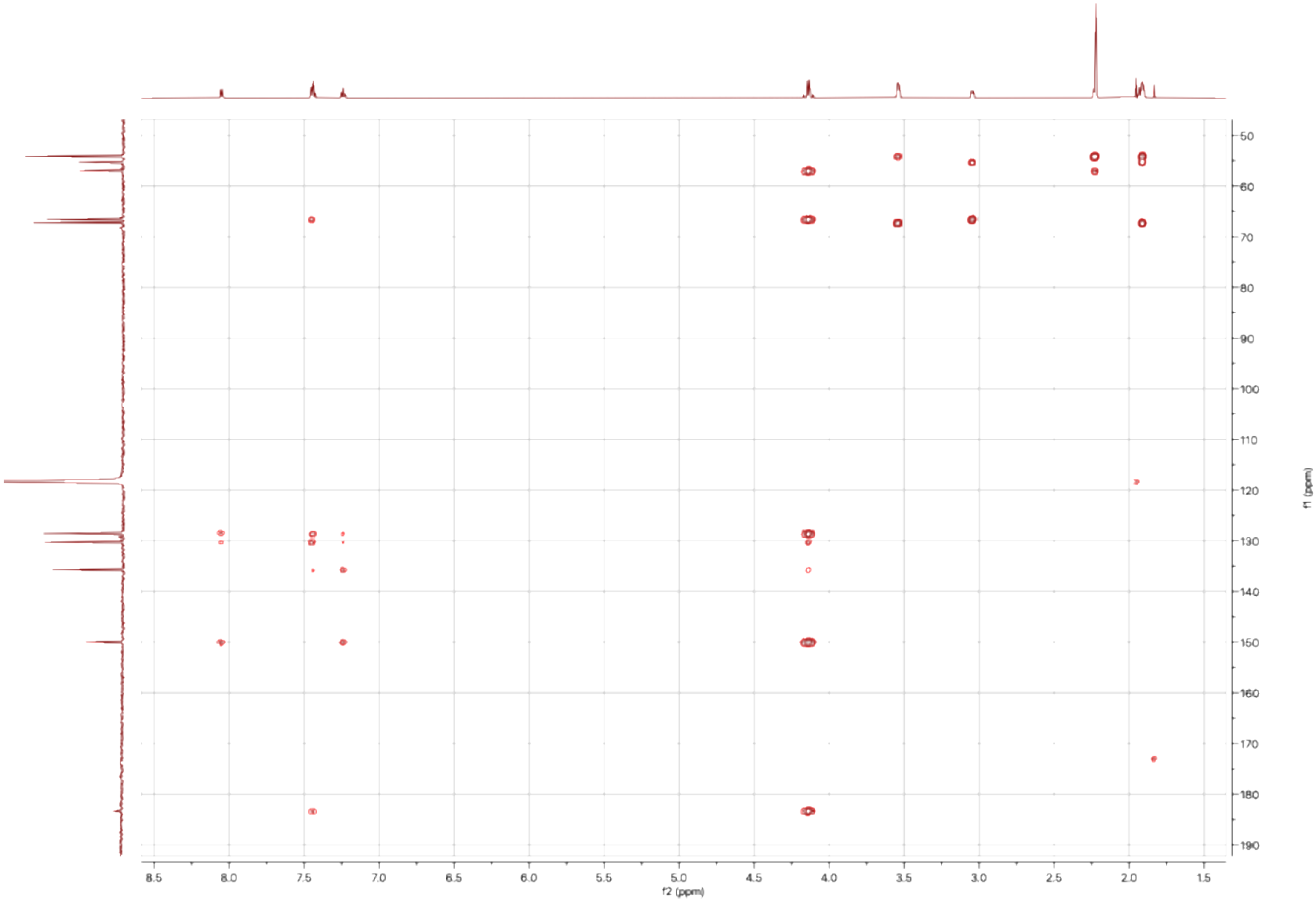


Figure S96. HMBC of **7-F** in CD_3CN

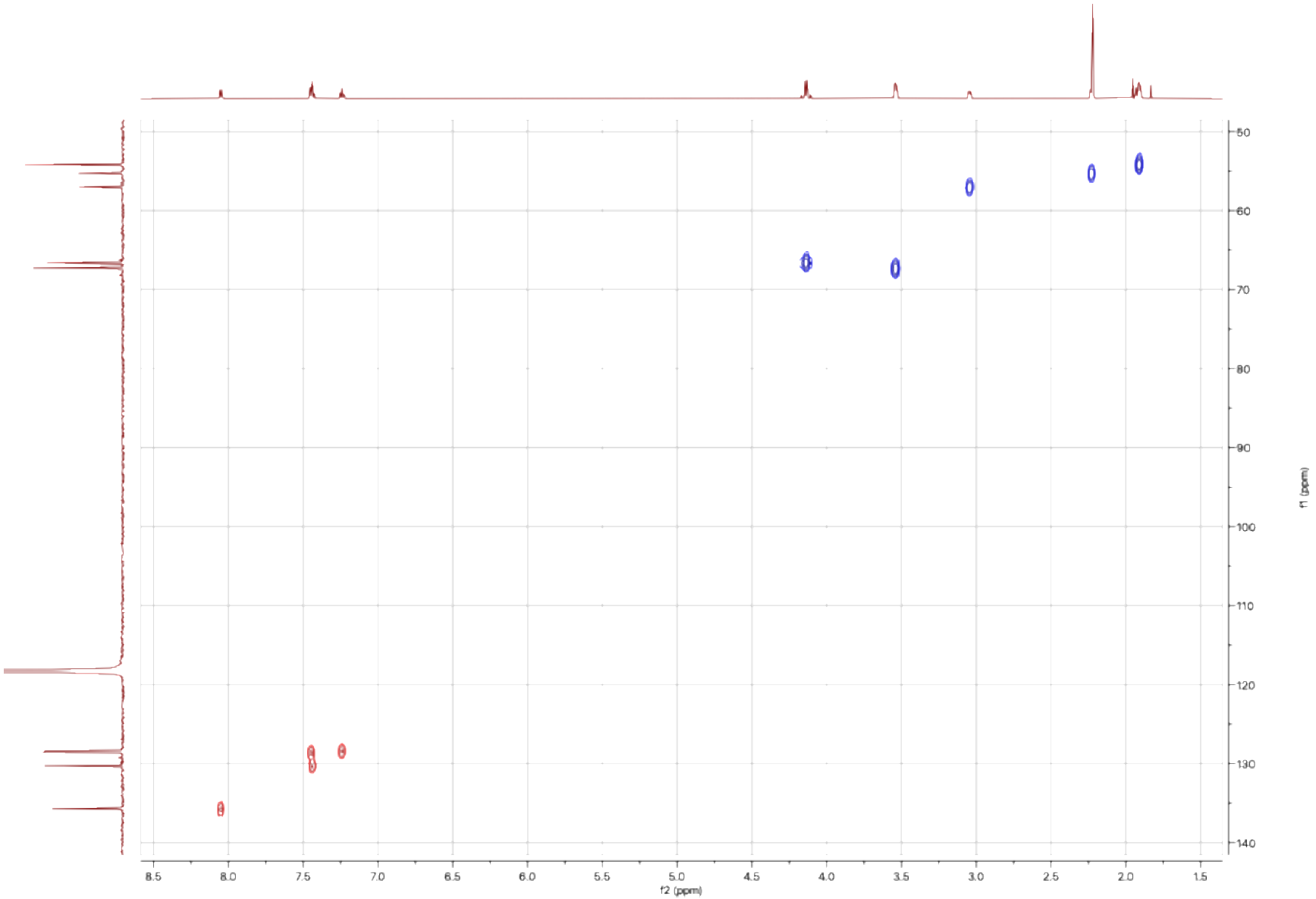
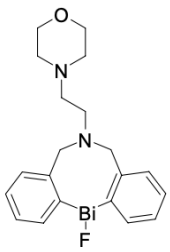


Figure S97. HSQC of **7-F** in CD_3CN



Chemical Formula: $BiC_{20}H_{24}FN_2O$

Molecular Weight: 536.40

Elemental Analysis: C: 44.78; H: 4.51; N: 5.22

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	2/16/2024 5:46:42PM
User ID	Administrator
Comments	MV_262 [Hyvl]

DATE & TIME	2/16/2024 3:19:18 PM	P_ID	EA LAB
SAMPLE ID	24061	USER ID	Administrator
WEIGHT (mg)	1.990	MODE	CHN

CARBON	44.795%
HYDROGEN	4.404%
NITROGEN	5.144%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

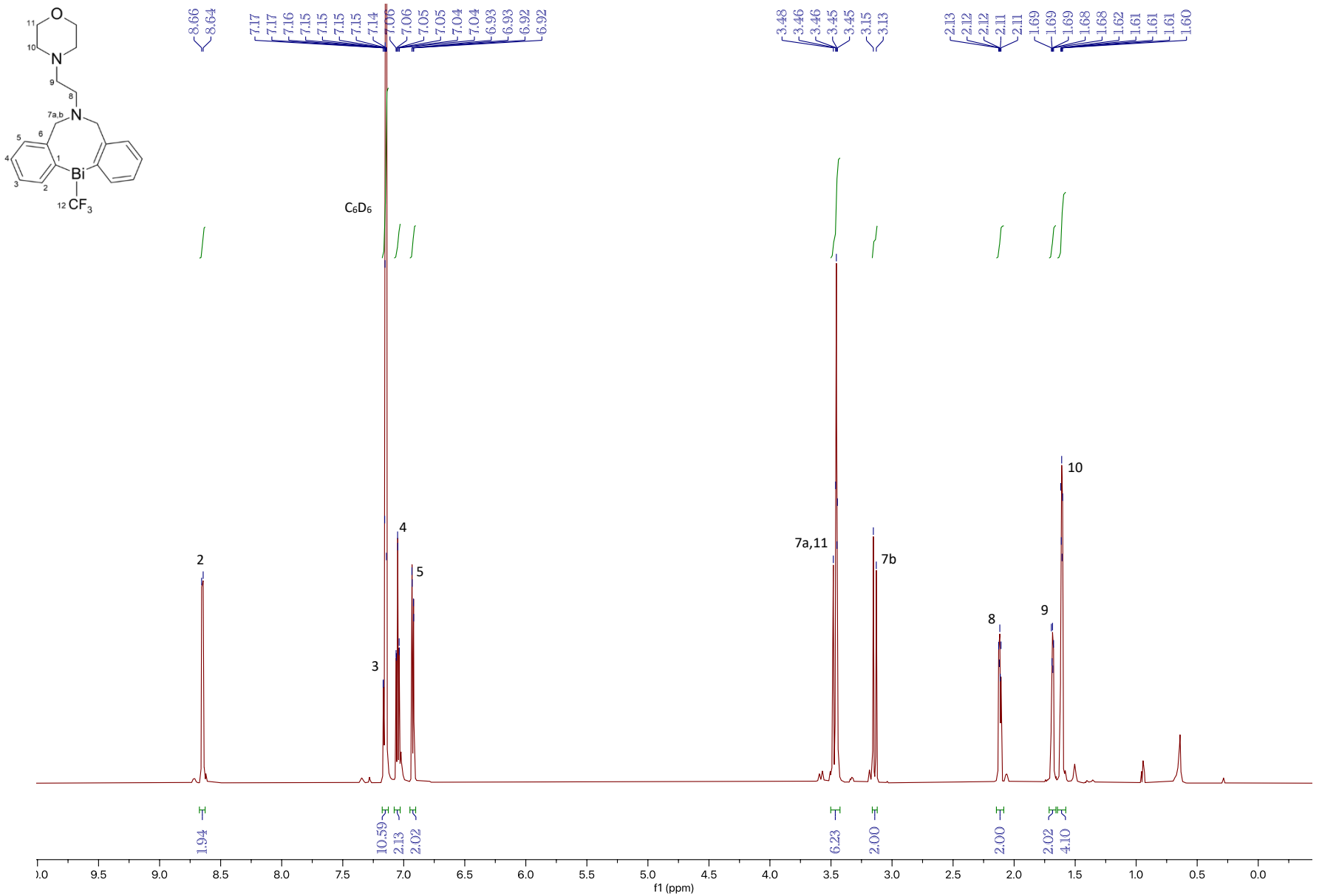


Figure S98. ^{1}H NMR of **7-CF$_3$** (600 MHz, C_6D_6, 30°C)

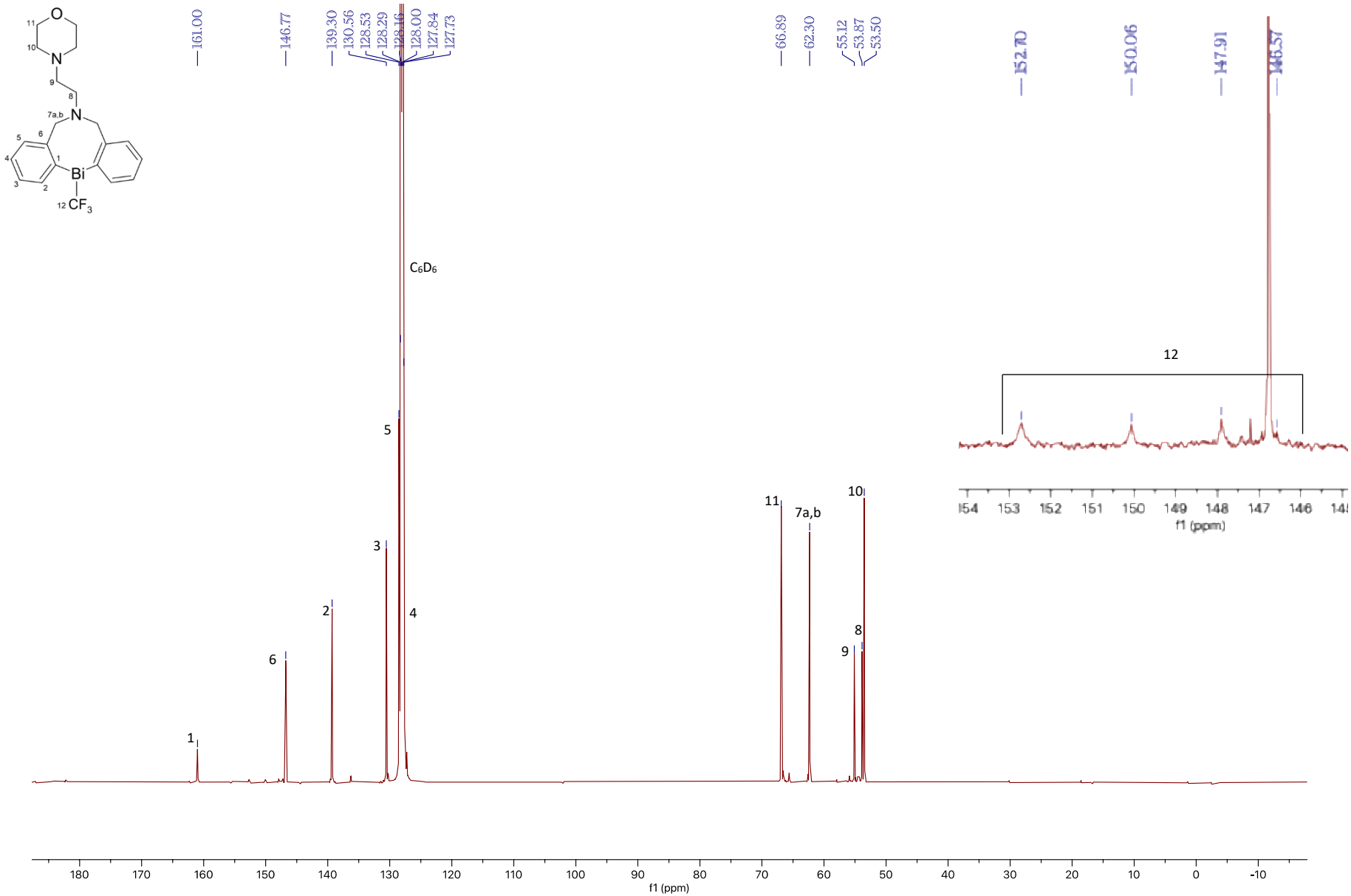


Figure S99. $^{13}C\{^{1}H\}$ NMR of **7-CF$_3$** (150 MHz, C_6D_6, 30°C)

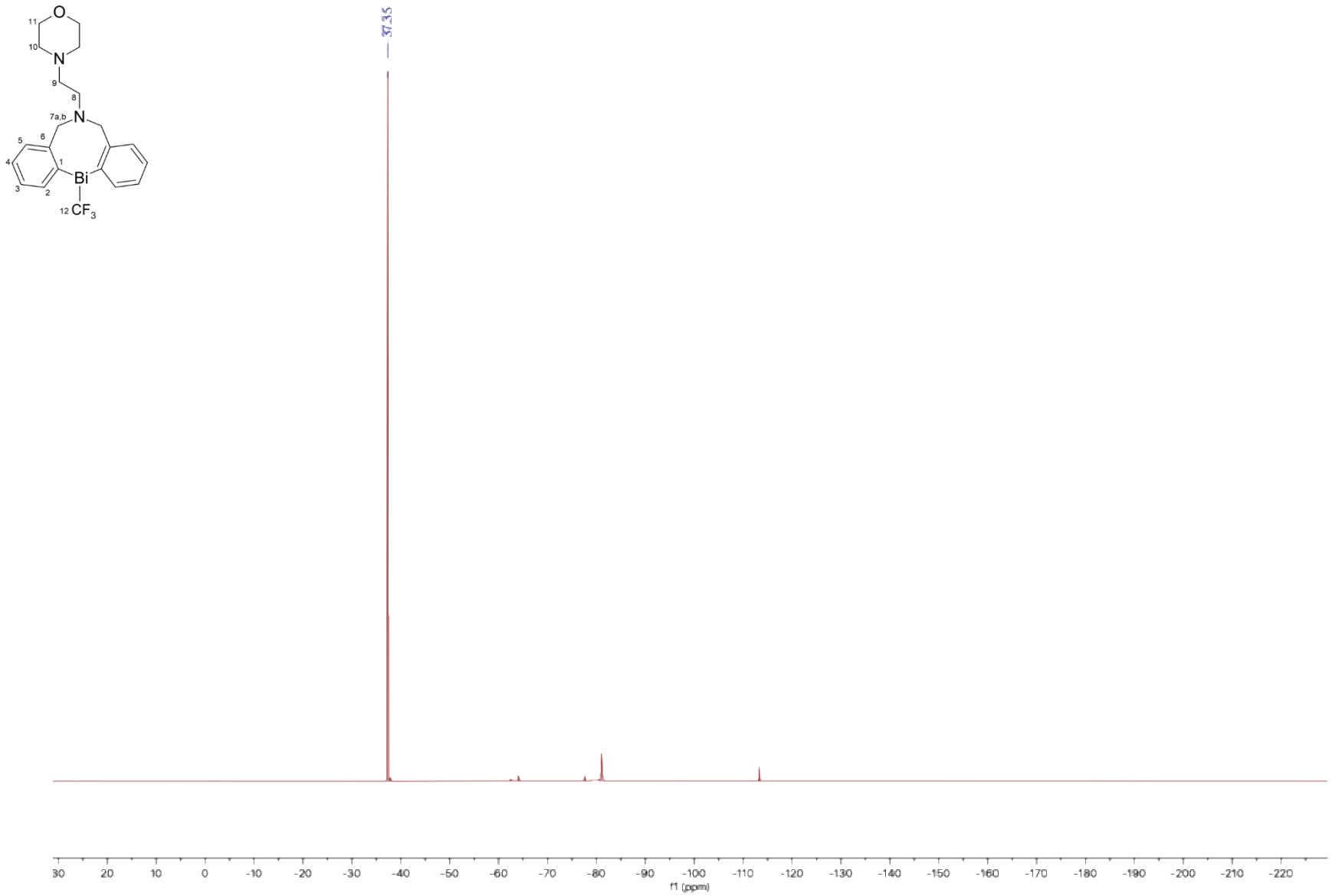


Figure S100. ^{19}F NMR of **7-CF$_3$** (564 MHz, C_6D_6, 30°C)

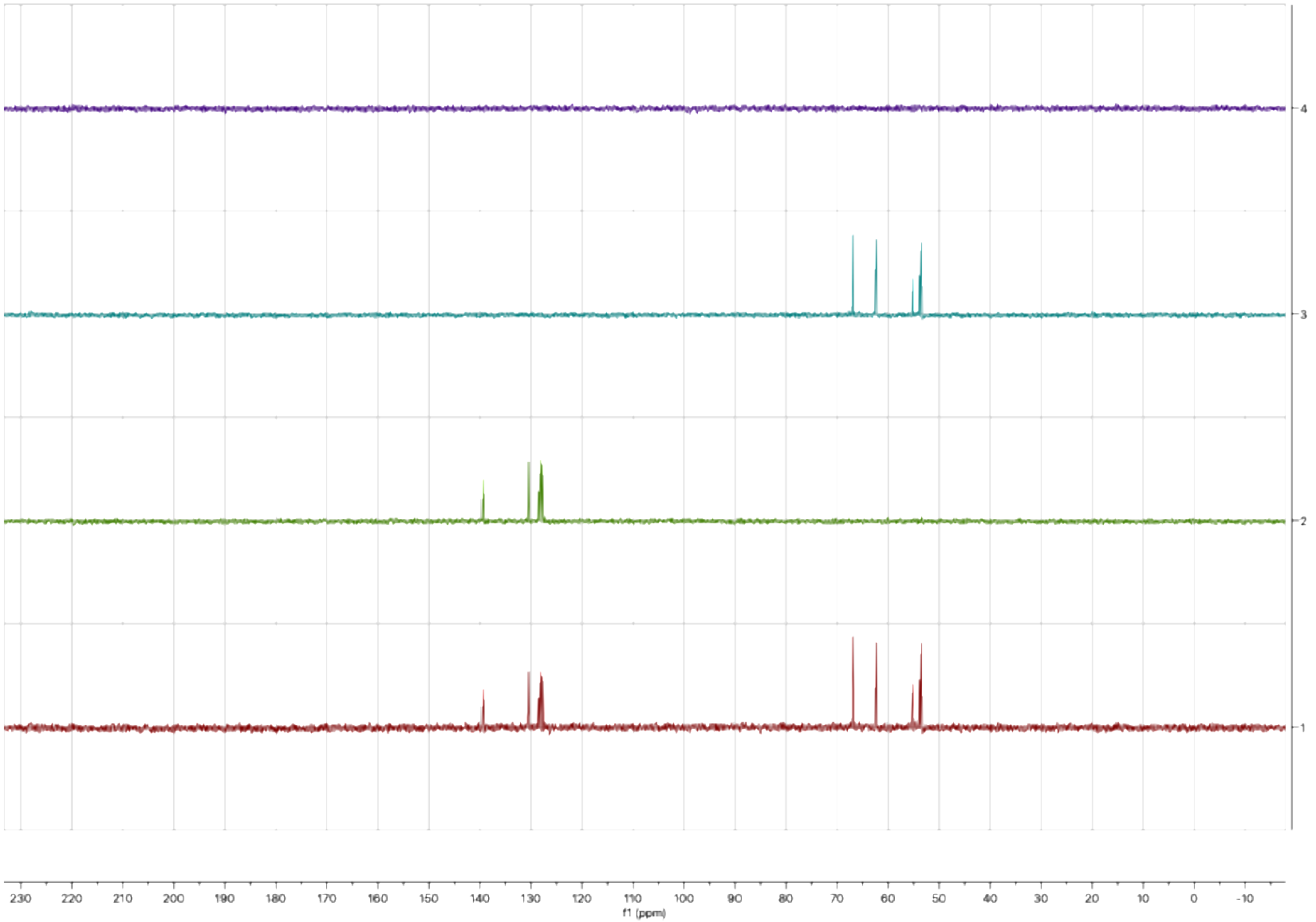


Figure S101. $^{13}C\{^{1}H\}$ DEPT of **7-CF_3** in C_6D_6

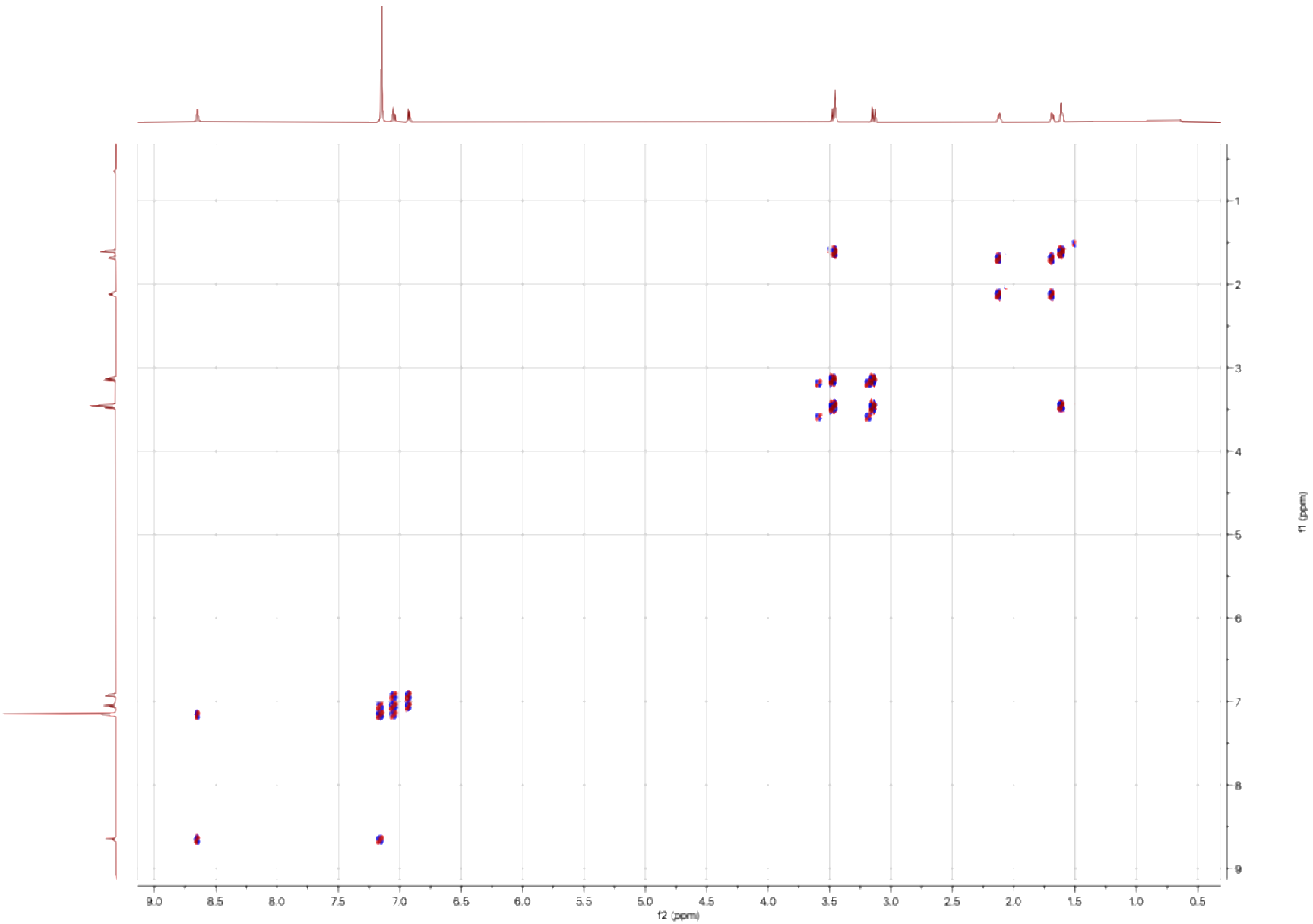
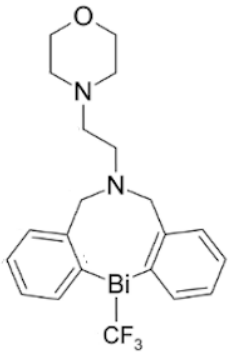


Figure S102. COSY of **7-CF_3** in C_6D_6

Figure S103. HMBC of **7-CF_3** in C_6D_6

Figure S104. HSQC of **7-CF_3** in C_6D_6



Chemical Formula: $C_{21}H_{24}BiF_3N_2O \cdot 0.4C_6H_6$

Elemental Analysis: C, 45.50; H, 4.31; N, 4.54.

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	4/12/2024 6:04:21PM
User ID	Administrator
Comments	MV_274 [Hyvl]

DATE & TIME	4/12/2024 1:33:51 PM	P_ID	EA LAB
SAMPLE ID	24195	USER ID	Administrator
WEIGHT (mg)	2.131	MODE	CHN

CARBON	45.886%
HYDROGEN	4.301%
NITROGEN	4.423%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

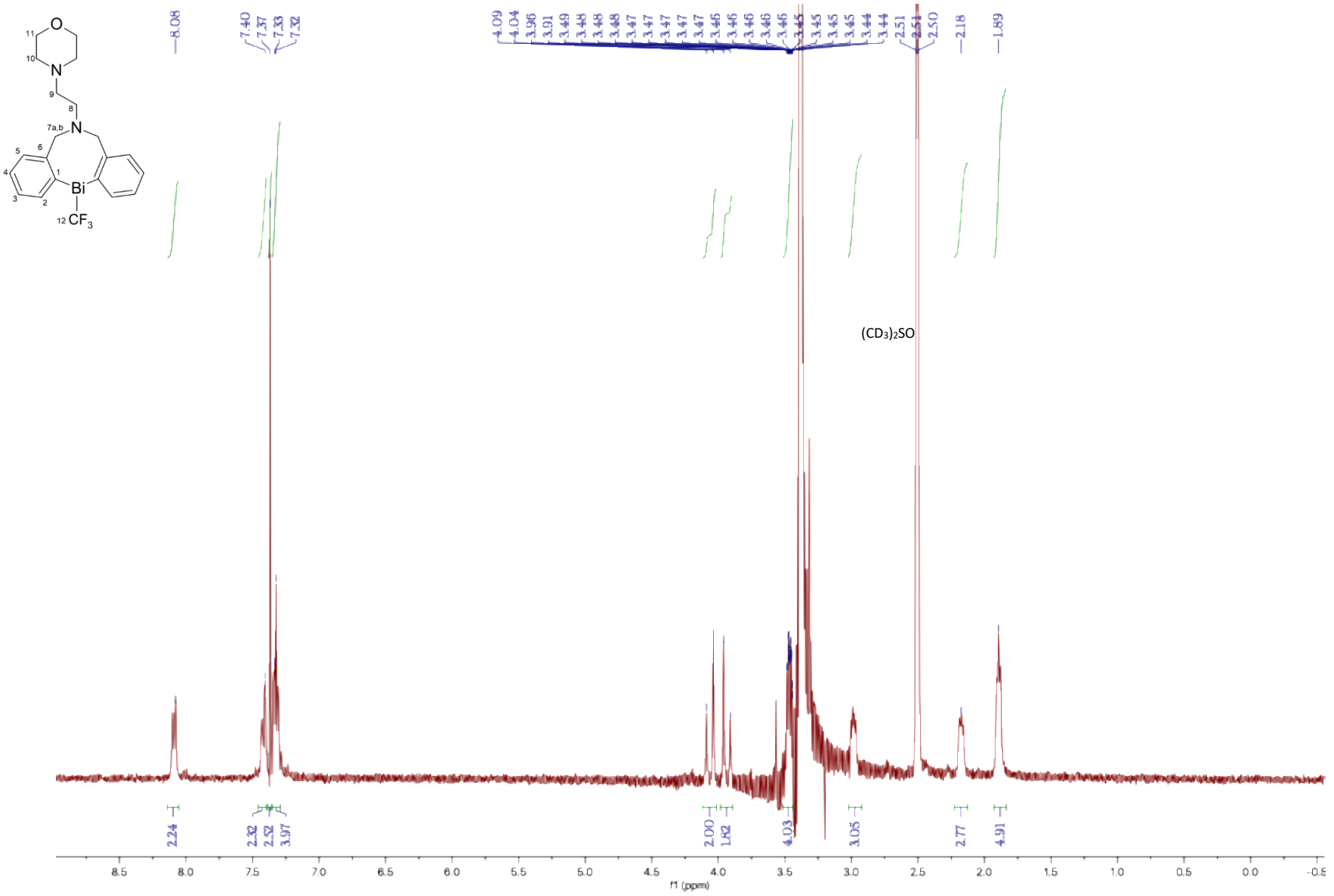
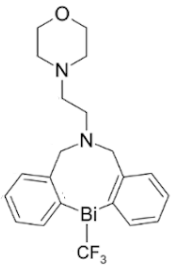


Figure S105. ^{1}H NMR for EA of **7-CF$_3$** (300 MHz, $(CD_3)_2SO$, 21°C)



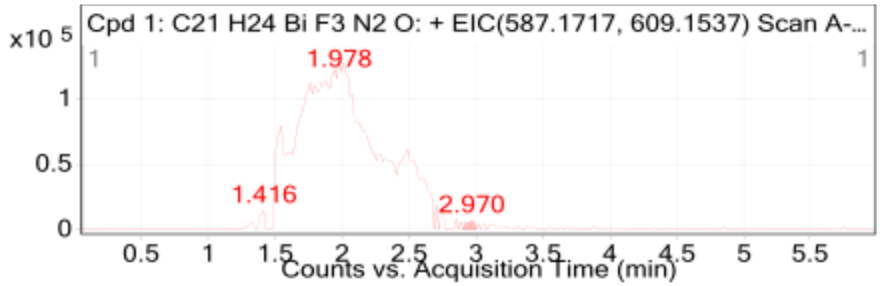
Qualitative Compound Report

Data File	A-MV-3-50-Dinj.d	**Sample Name**	Unavailable
Sample Type	Unavailable	**Position**	Unavailable
Instrument Name	Unavailable	**User Name**	Unavailable
Acq Method		**Acquired Time**	Unavailable
IRM Calibration Status	Success	**DA Method**	Tius_Analysis_Method_LB.m
Comment	Sample information is unavailable		

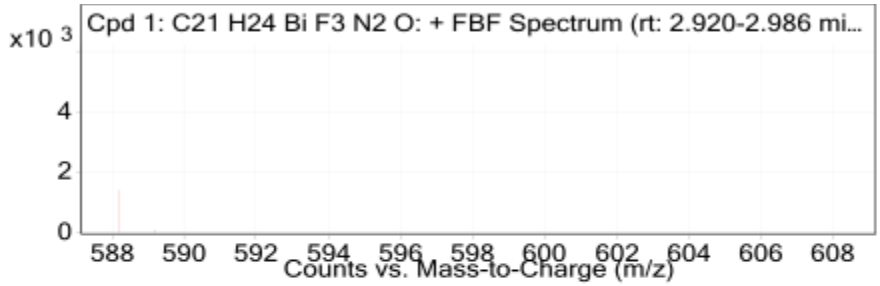
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C21 H24 Bi F3 N2 O	2.97	586.1644	5374	C21 H24 Bi F3 N2 O	586.16446	-0.1

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C21 H24 Bi F3 N2 O	587.1722	2.97	Find By Formula	586.1644

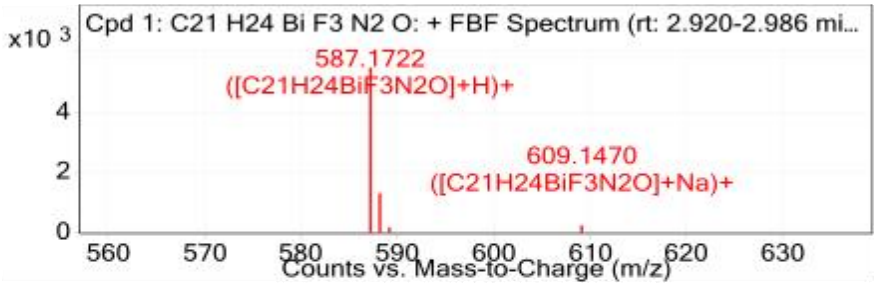


MS Spectrum



MS Zoomed Spectrum

Qualitative Compound Report



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
587.1722	1	5373.58	C21H24BiF3N2O	(M+H)+
588.1739	1	1406.08	C21H24BiF3N2O	(M+H)+
589.1781	1	108.34	C21H24BiF3N2O	(M+H)+
609.147	1	216.07	C21H24BiF3N2O	(M+Na)+

--- End Of Report ---

Figure S106. HRMS of **7-CF_3**

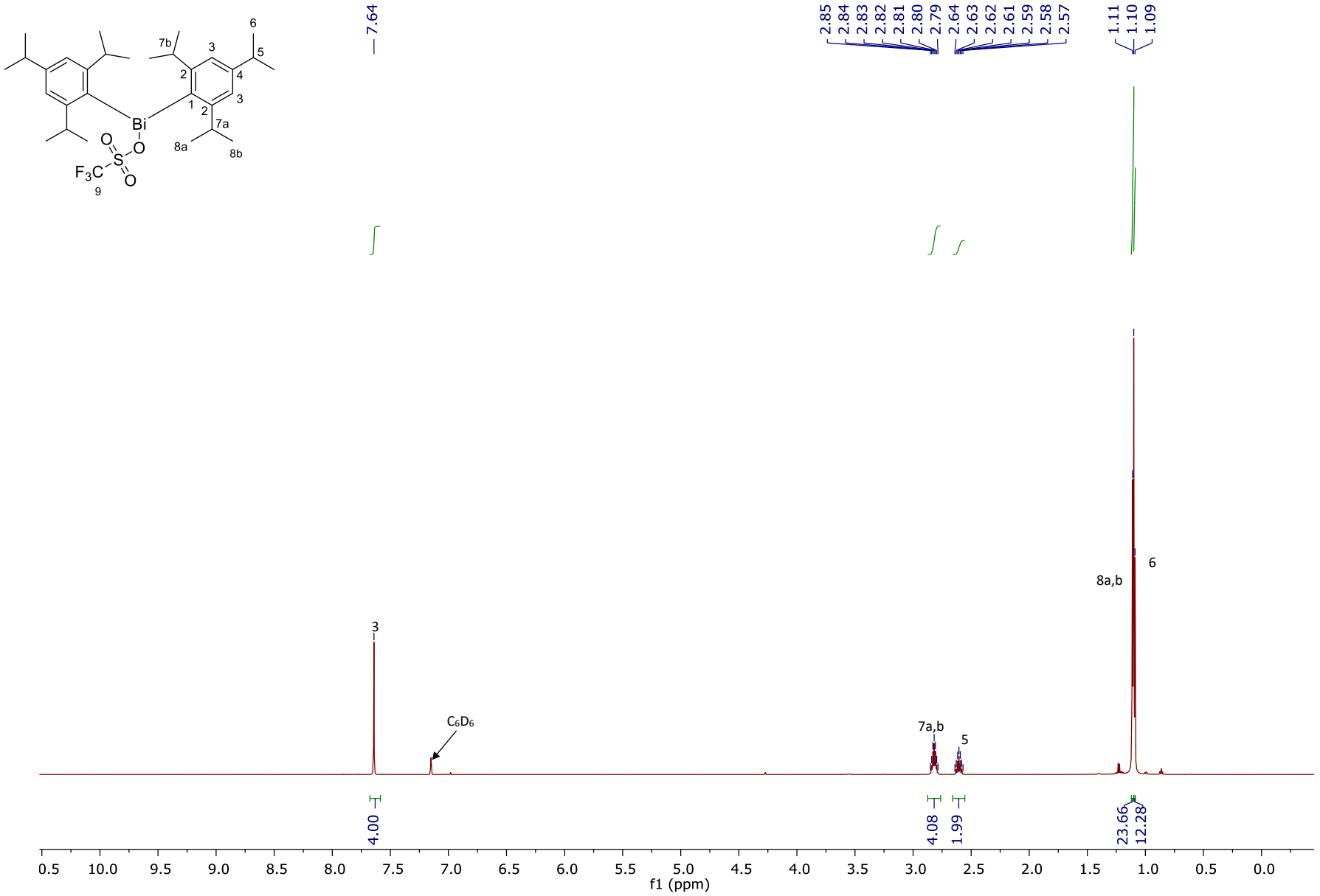


Figure S107. ^{1}H NMR of **C-OTf** (600 MHz, C_6D_6, 30°C)

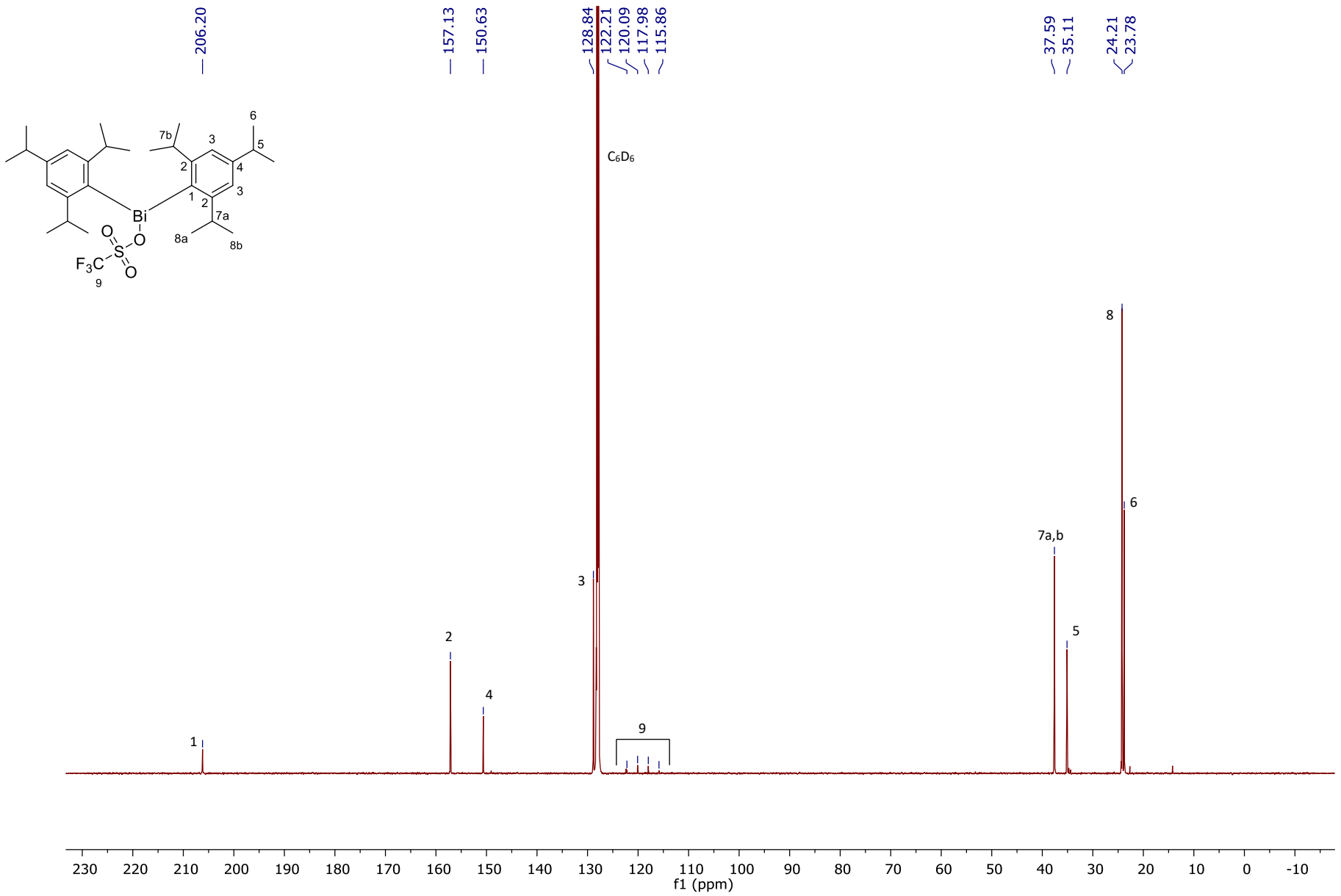


Figure S108. $^{13}C\{^{1}H\}$ NMR of **C-OTf** (150 MHz, C_6D_6, 30°C)

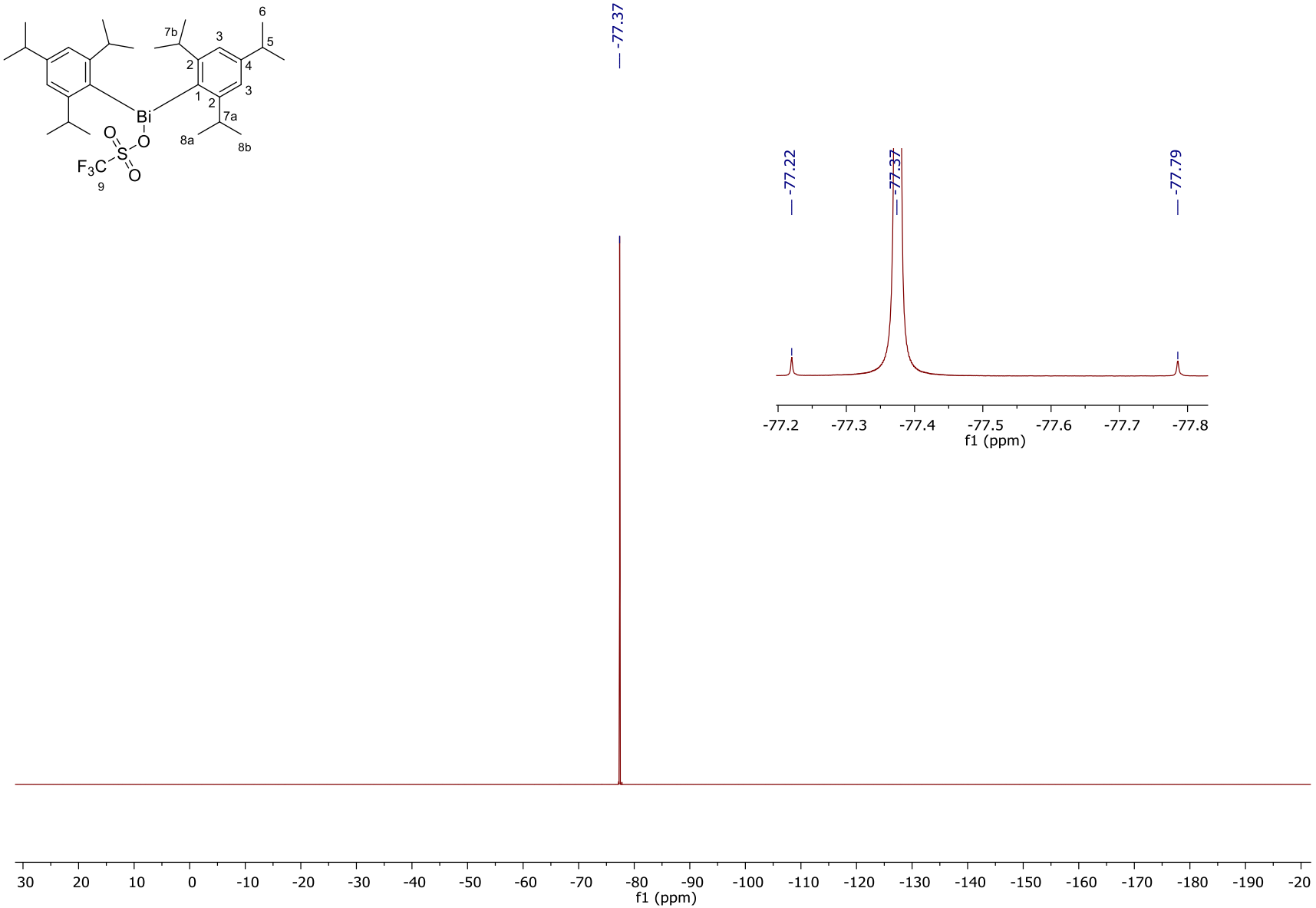


Figure S109. ^{19}F NMR of **C-OTf** (564 MHz, C_6D_6, 30°C)

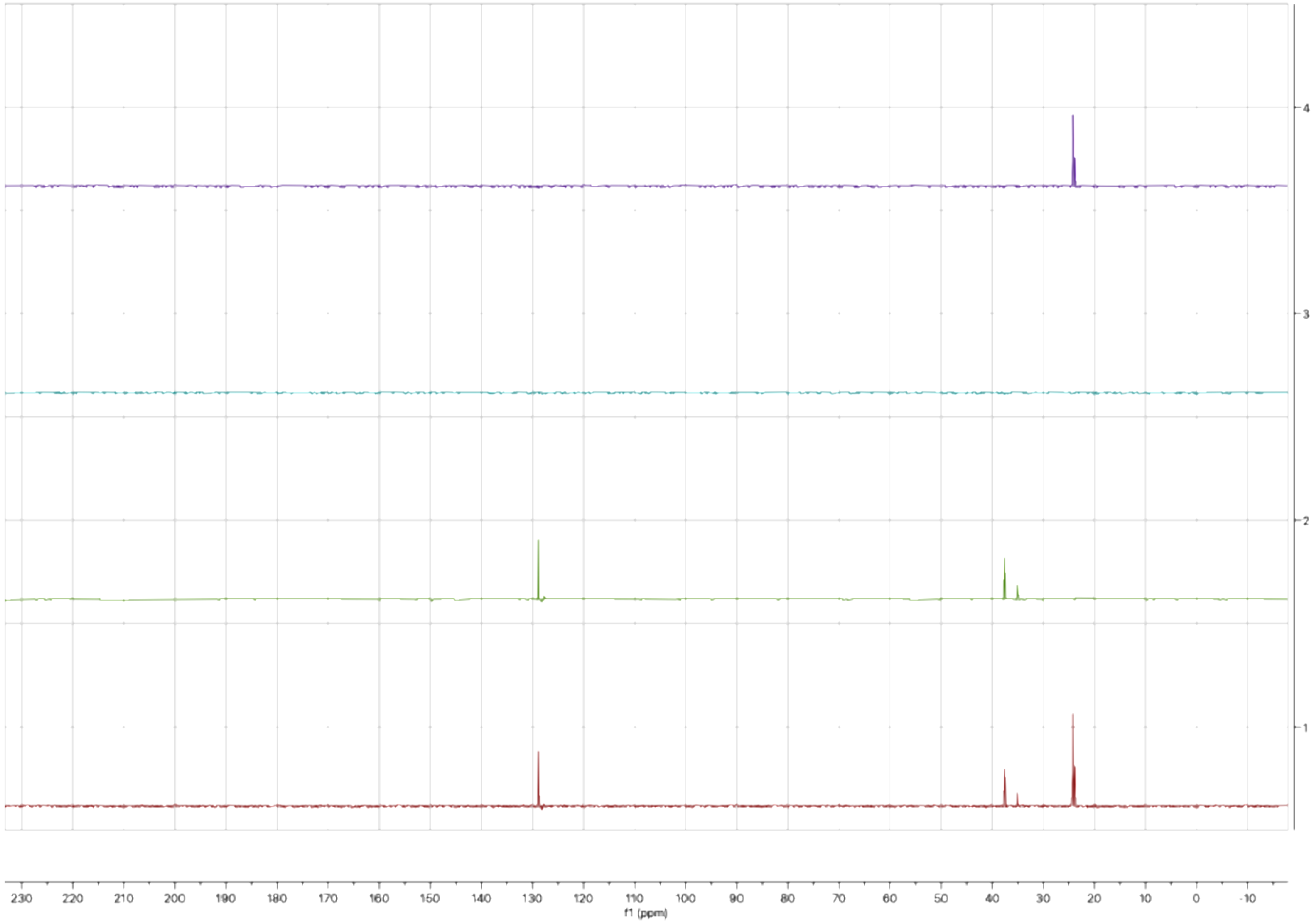


Figure S110. $^{13}C\{^{1}H\}$ DEPT of **C-OTf** in C_6D_6

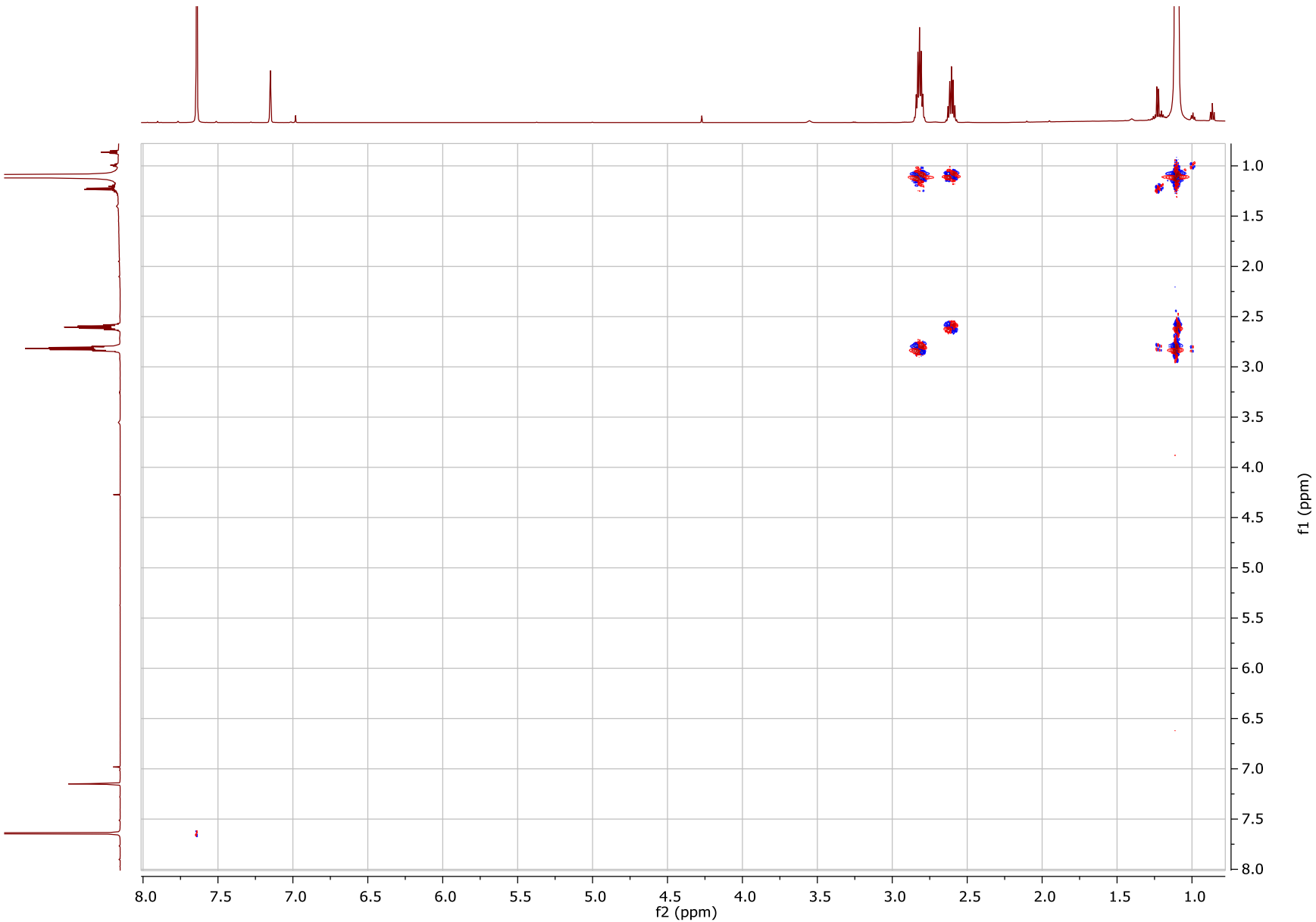


Figure S111. COSY of **C-OTf** in C_6D_6

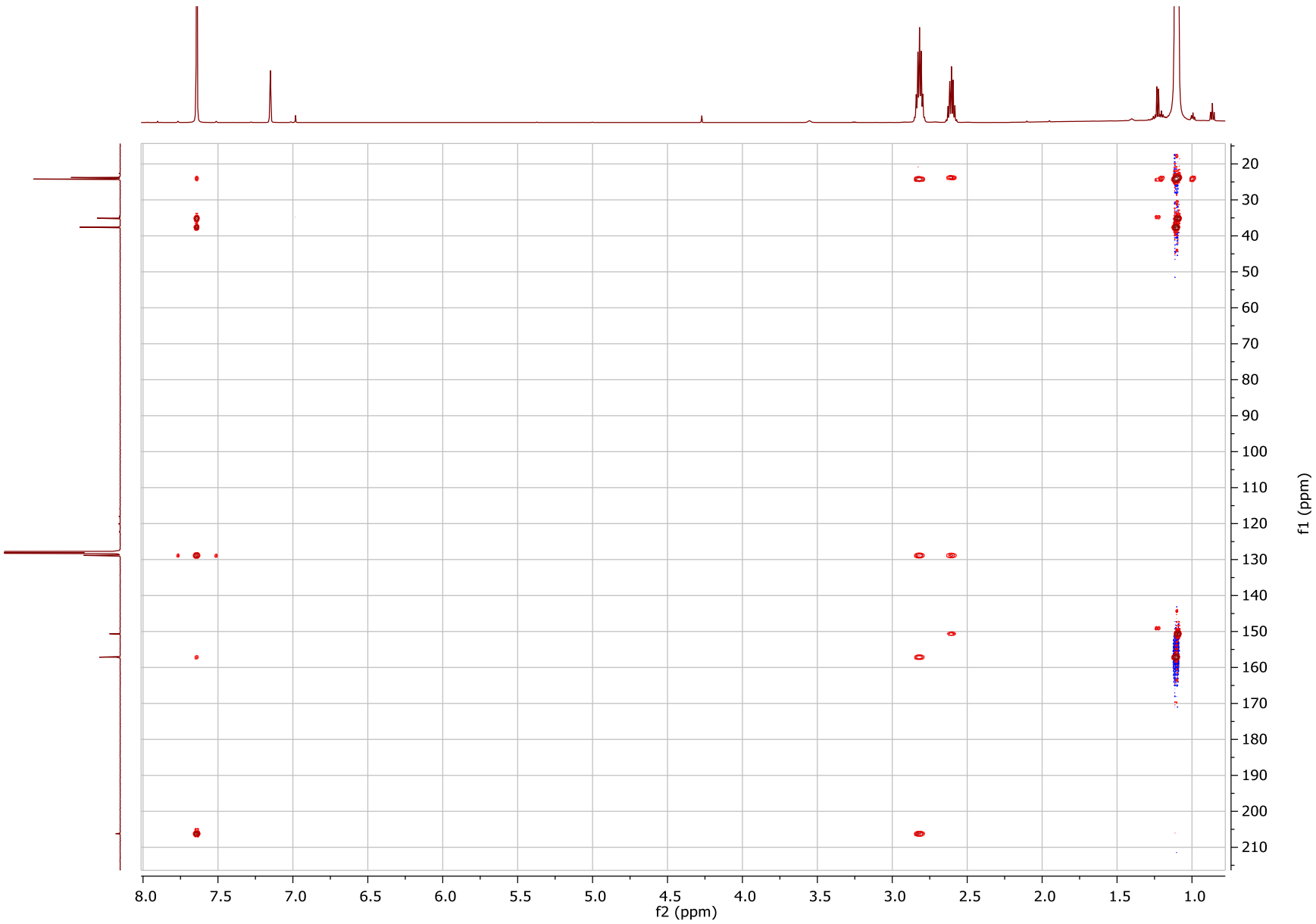


Figure S112. HMBC of **C-OTf** in C_6D_6

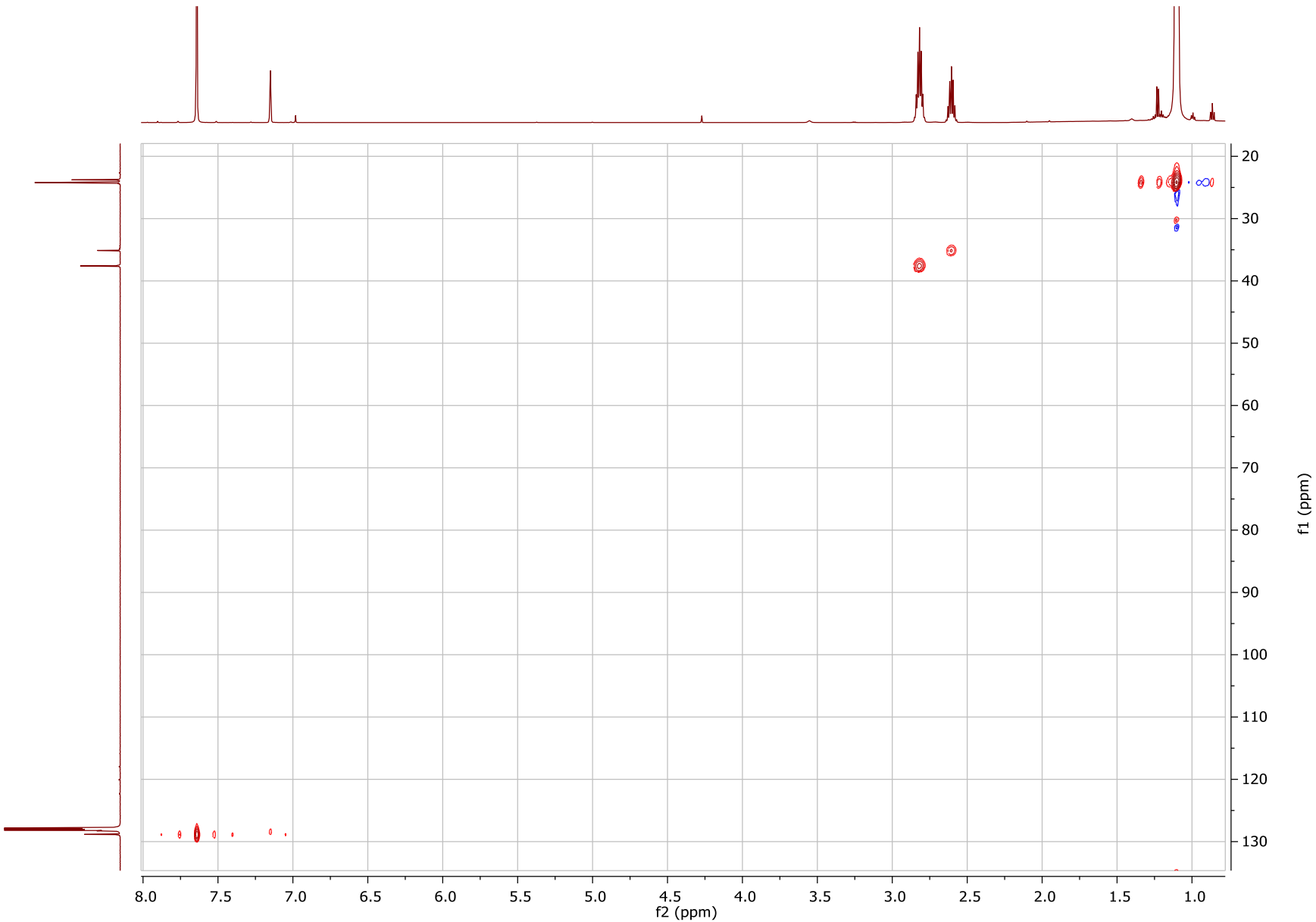


Figure S113. HSQC of **C-OTf** in C_6D_6

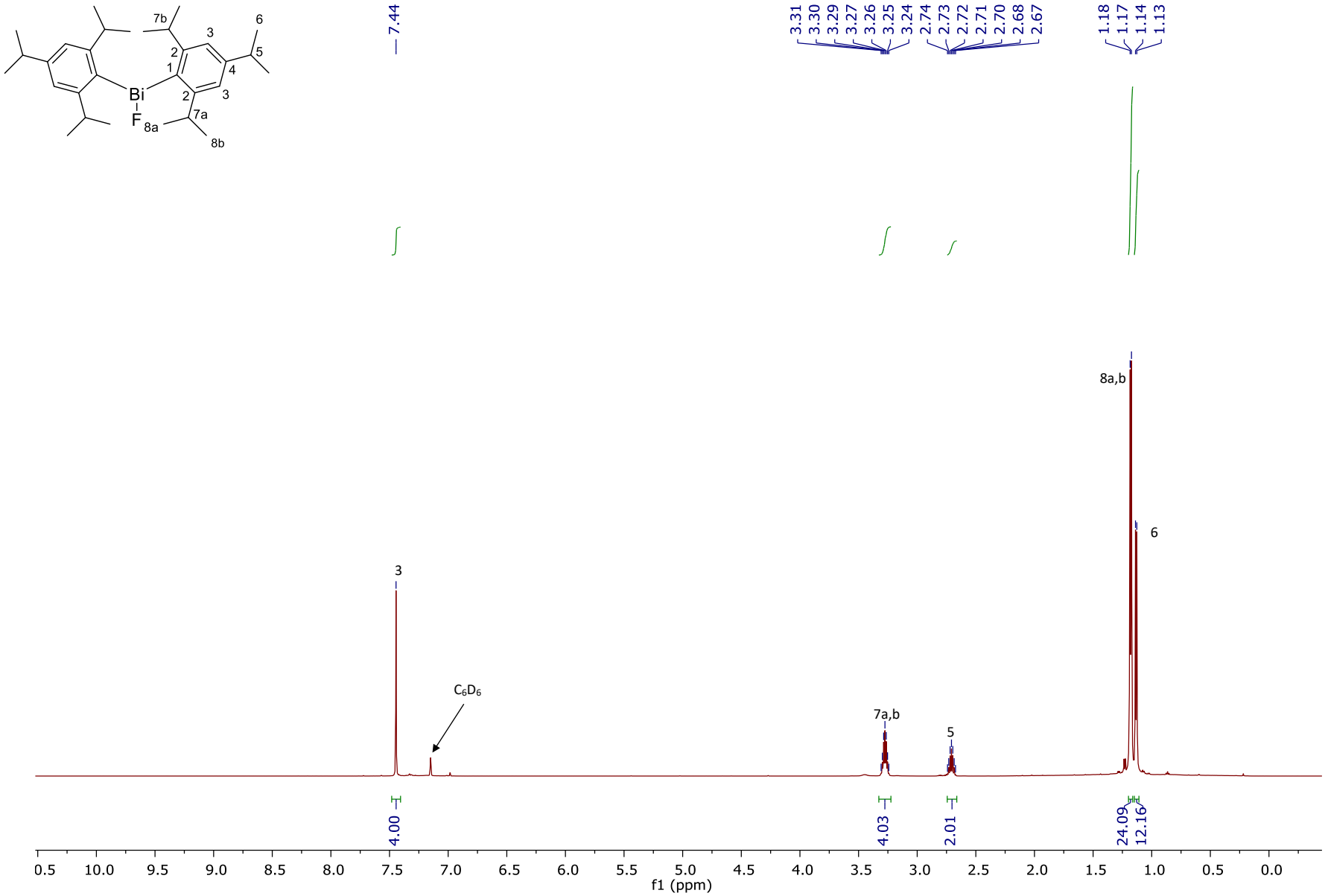


Figure S114. ^{1}H NMR of **C-F** (600 MHz, C_6D_6, 30°C)

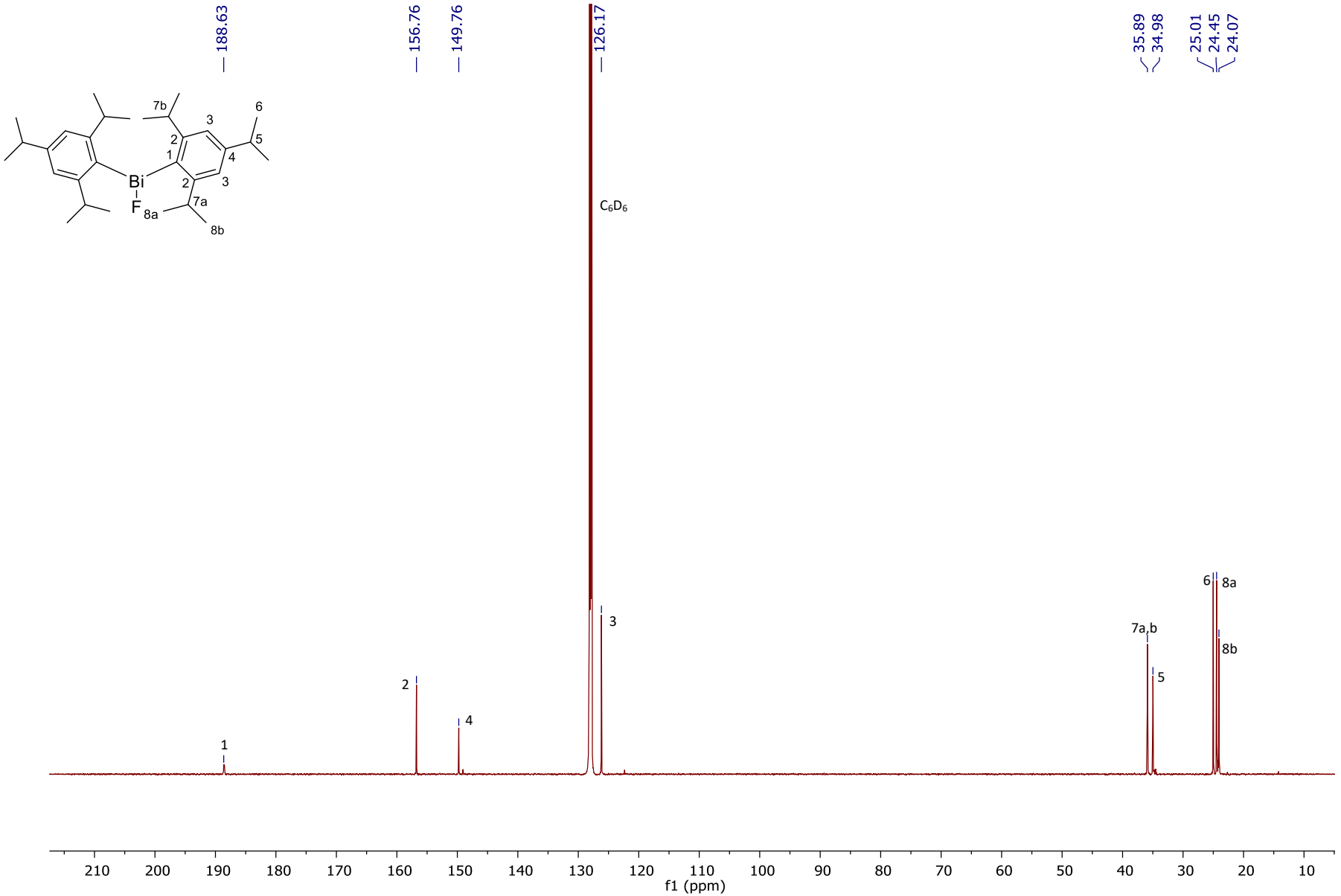


Figure S115. $^{13}C\{^{1}H\}$ NMR of **C-F** (150 MHz, C_6D_6, 30°C)

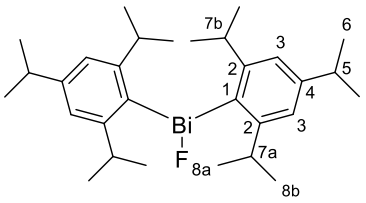


Figure S116. ^{19}F NMR of **C-F** (564 MHz, C_6D_6, 30°C)

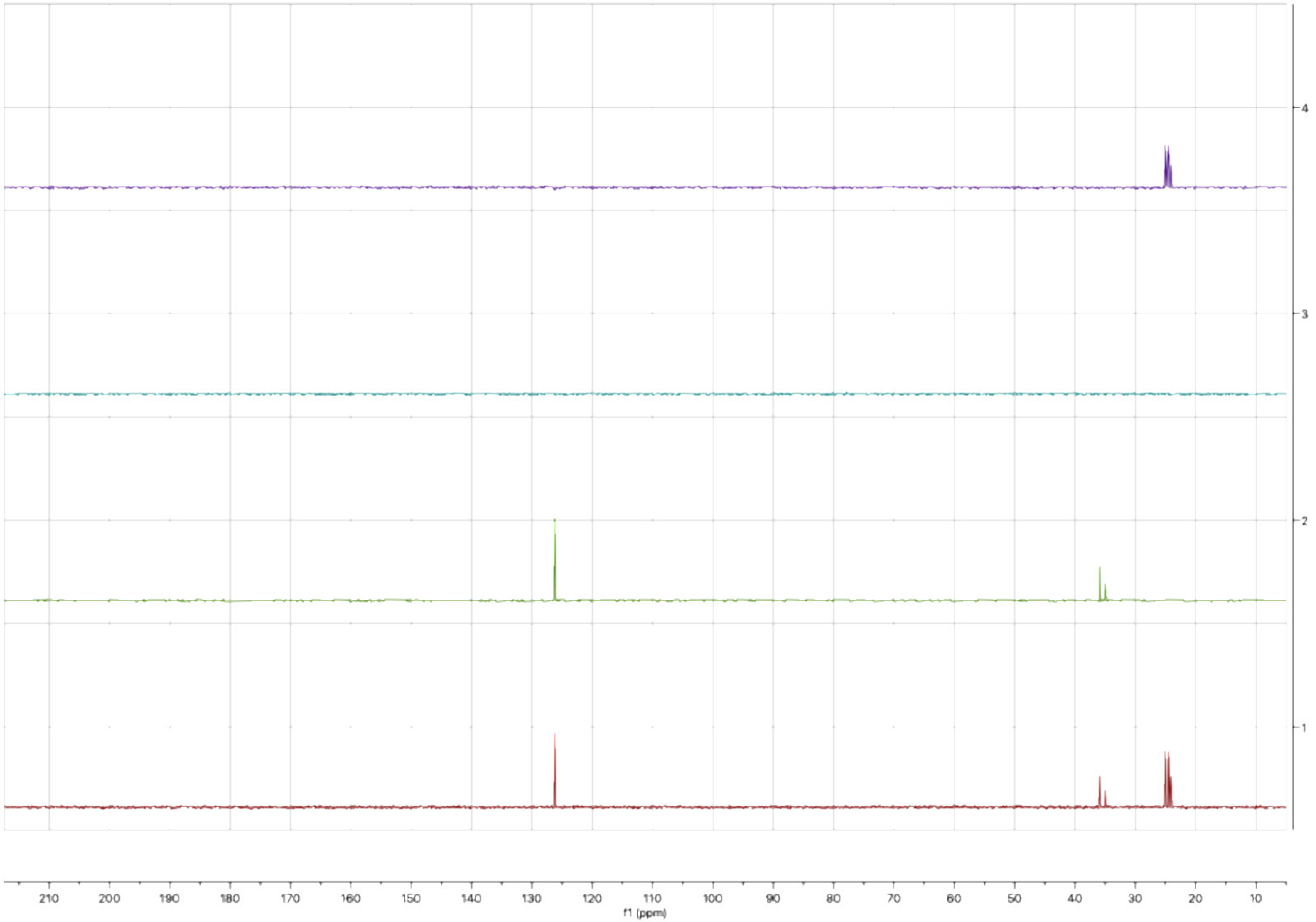


Figure S117. $^{13}C\{^{1}H\}$ DEPT of **C-F** in C_6D_6

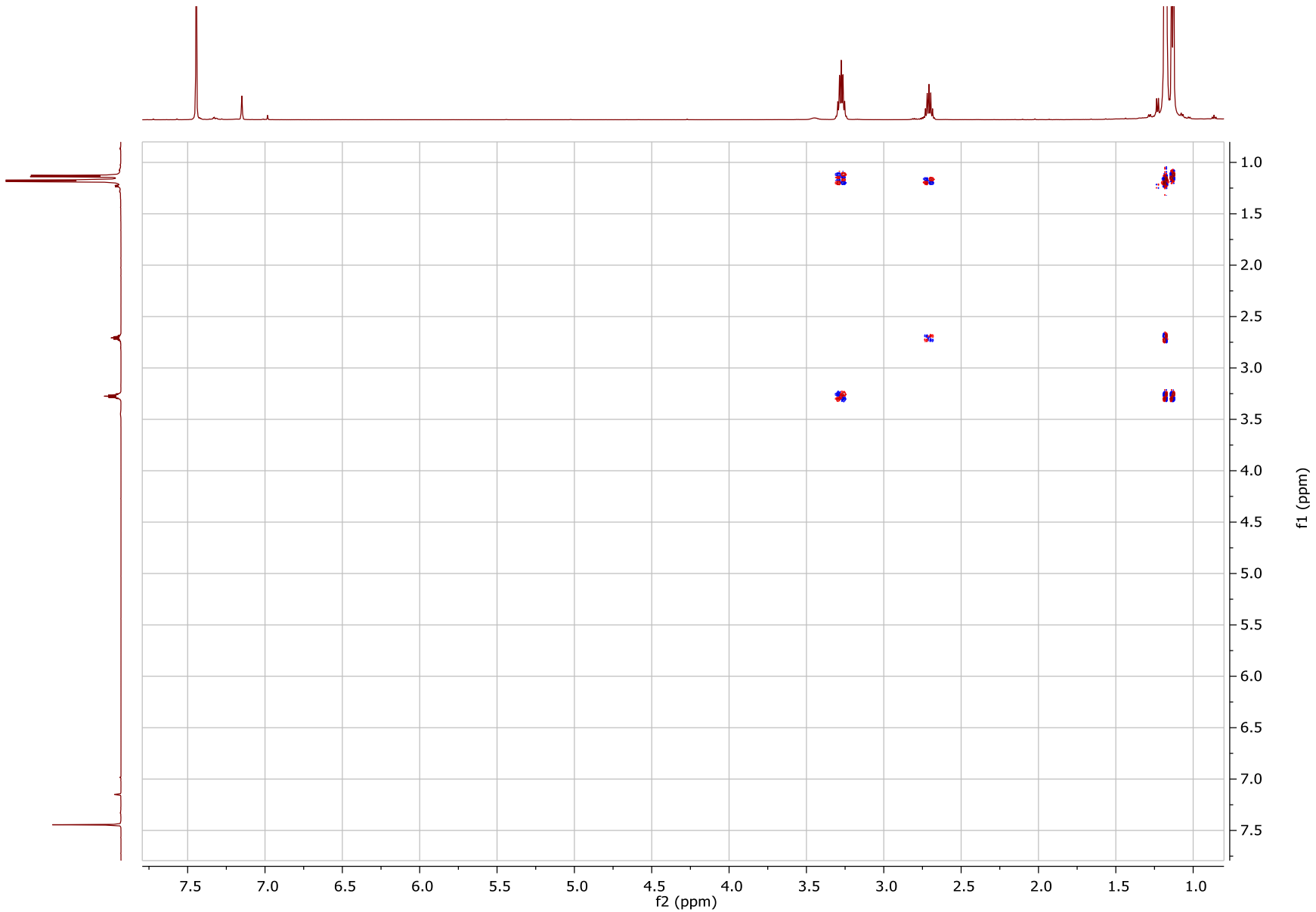


Figure S118. COSY of **C-F** in C_6D_6

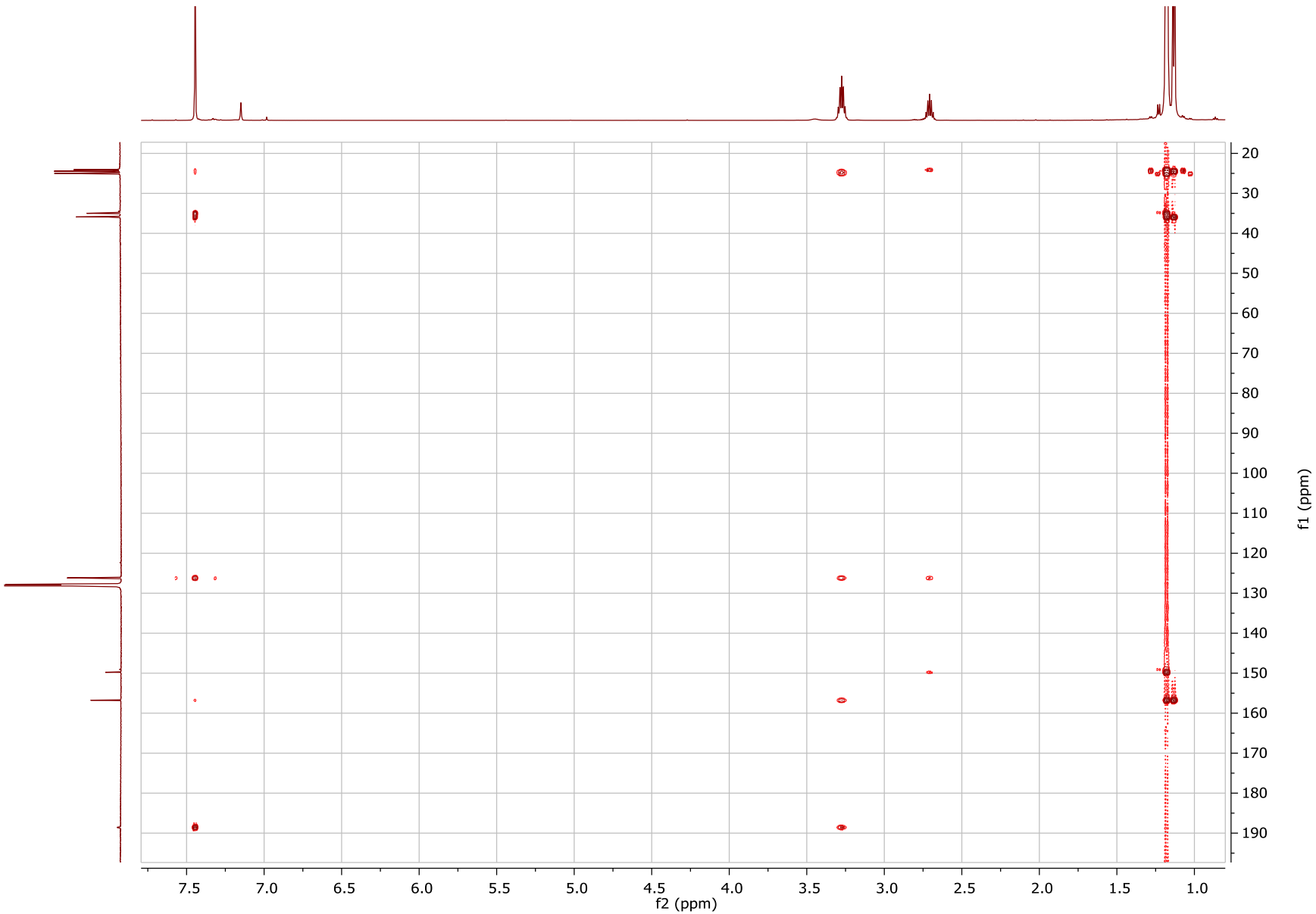


Figure S119. HMBC of **C-F** in C_6D_6

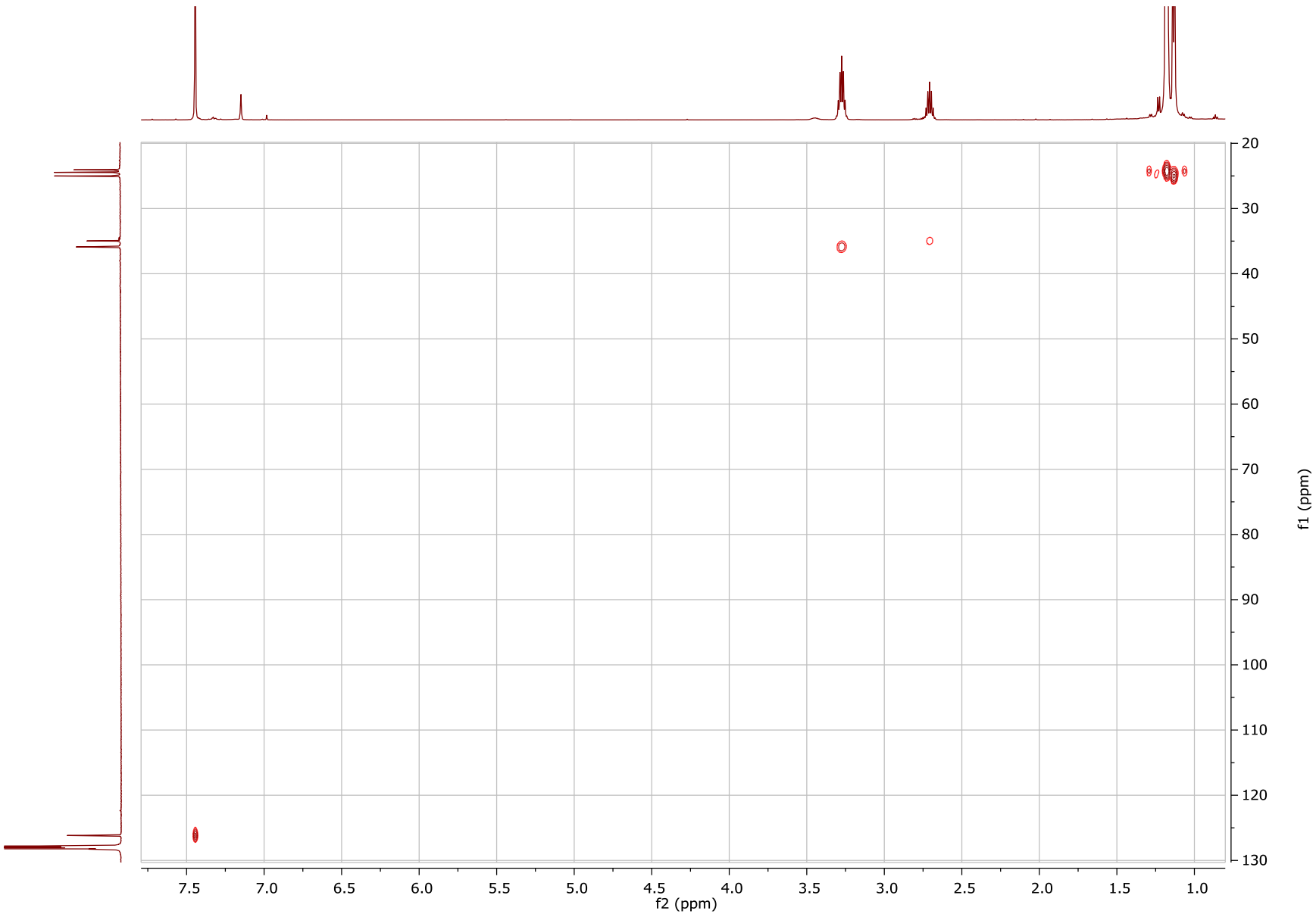
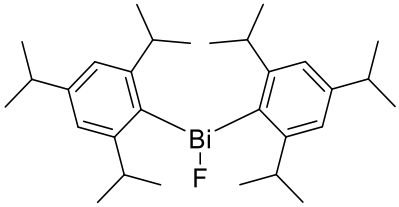


Figure S120. HSQC of **C-F** in C_6D_6



Chemical Formula: $BiC_{30}H_{46}F$

Molecular Weight: 634.68

Elemental Analysis: C: 56.77; H: 7.31

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	2/10/2023 7:04:57PM
User ID	Administrator
Comments	TLG_4_142B [Hyvl]

DATE & TIME	2/10/2023 4:30:03 PM	P_ID	EA LAB
SAMPLE ID	23089	USER ID	Administrator
WEIGHT (mg)	2.065	MODE	CHN

CARBON	57.306%
HYDROGEN	7.395%
NITROGEN	-.134%

Special Handling

The sample was transferred under argon and was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. Air-sensitive samples were handled in a VAC Atmospheres glovebox.

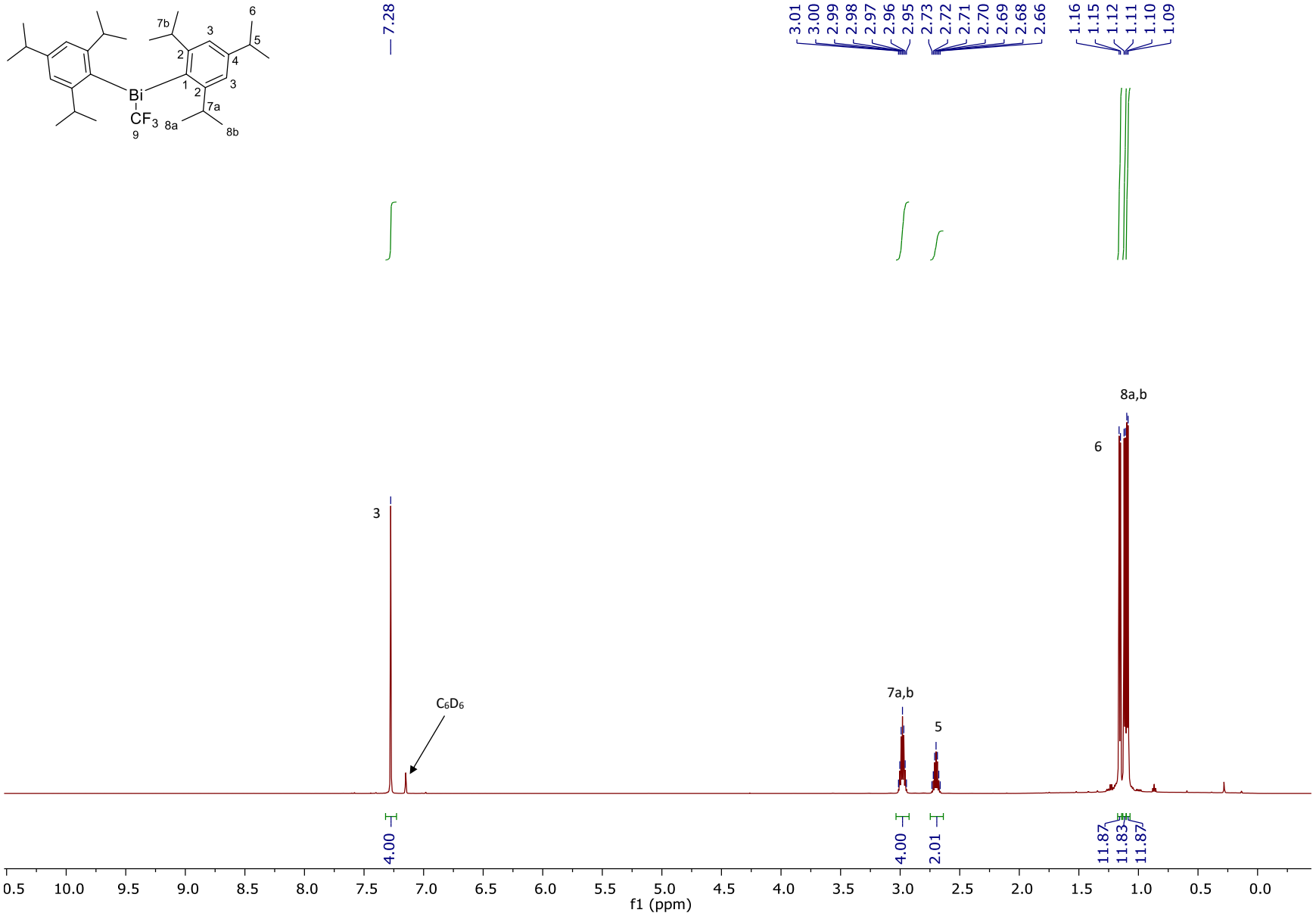


Figure S121. ^{1}H NMR of **C-CF$_3$** (600 MHz, C_6D_6, 30°C)

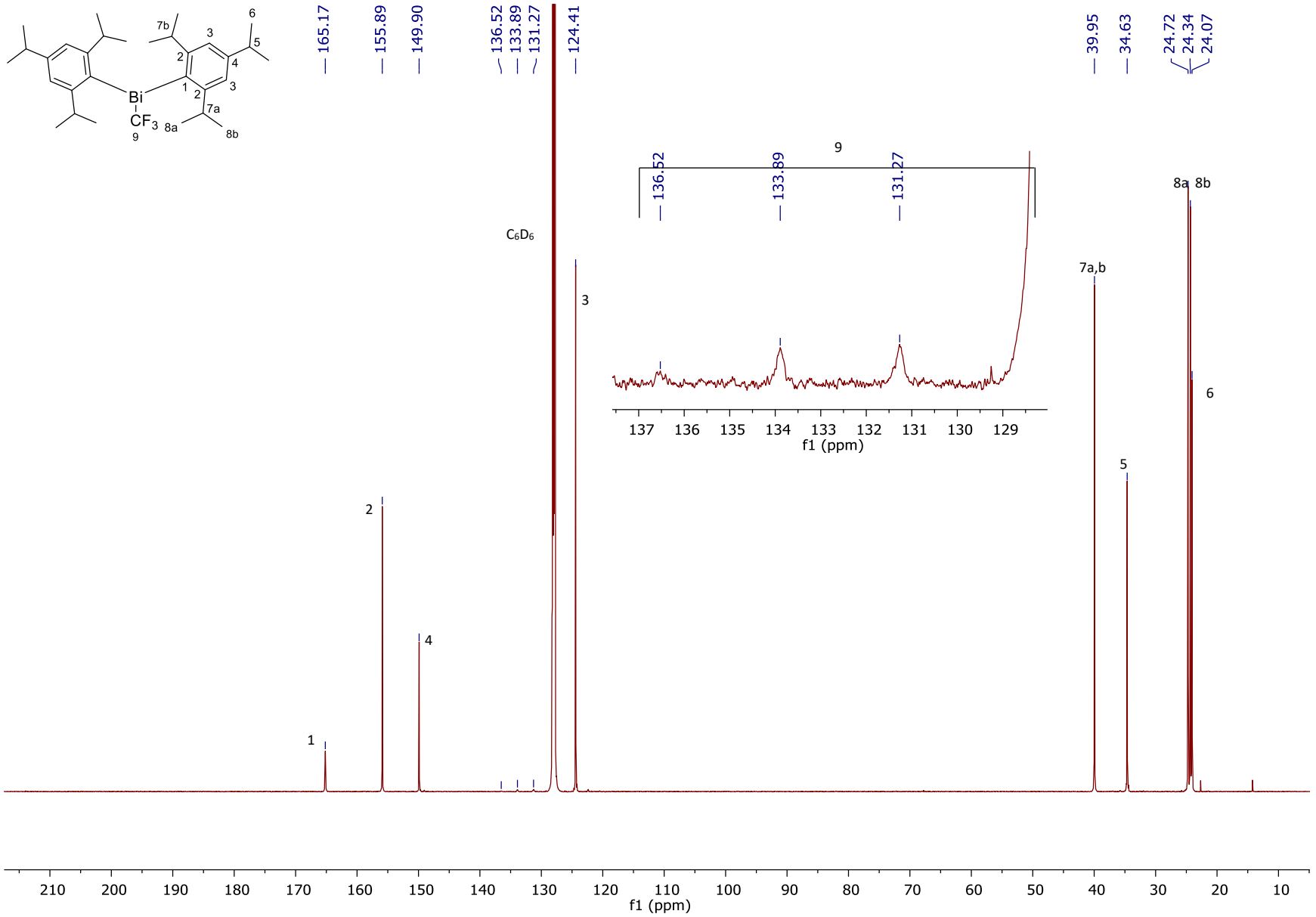


Figure S122. $^{13}C\{^{1}H\}$ NMR of **C-CF₃** (150 MHz, C_6D_6, 30°C)

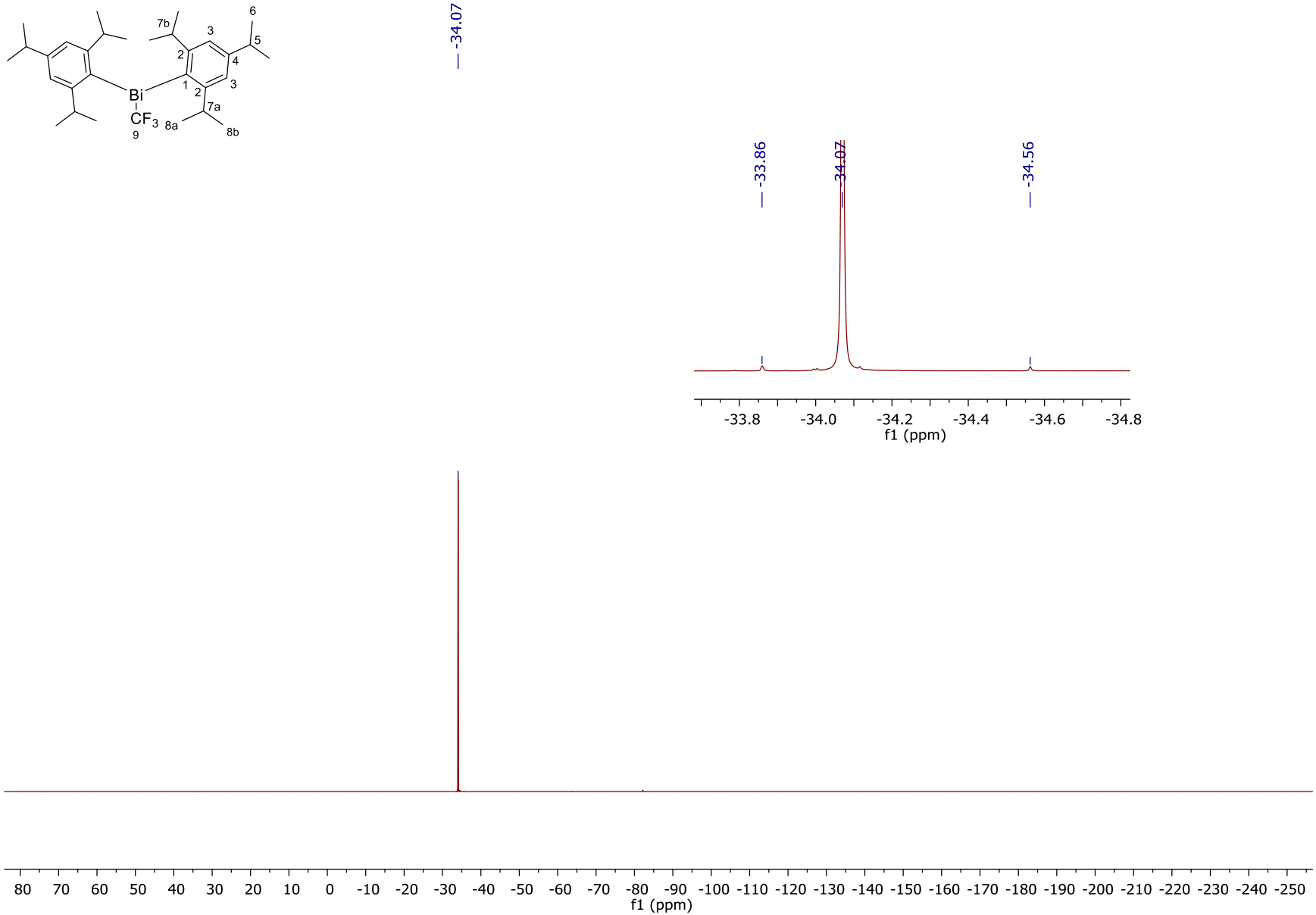


Figure S123. ^{19}F NMR of **C-CF$_3$** (564 MHz, C_6D_6, 30°C)

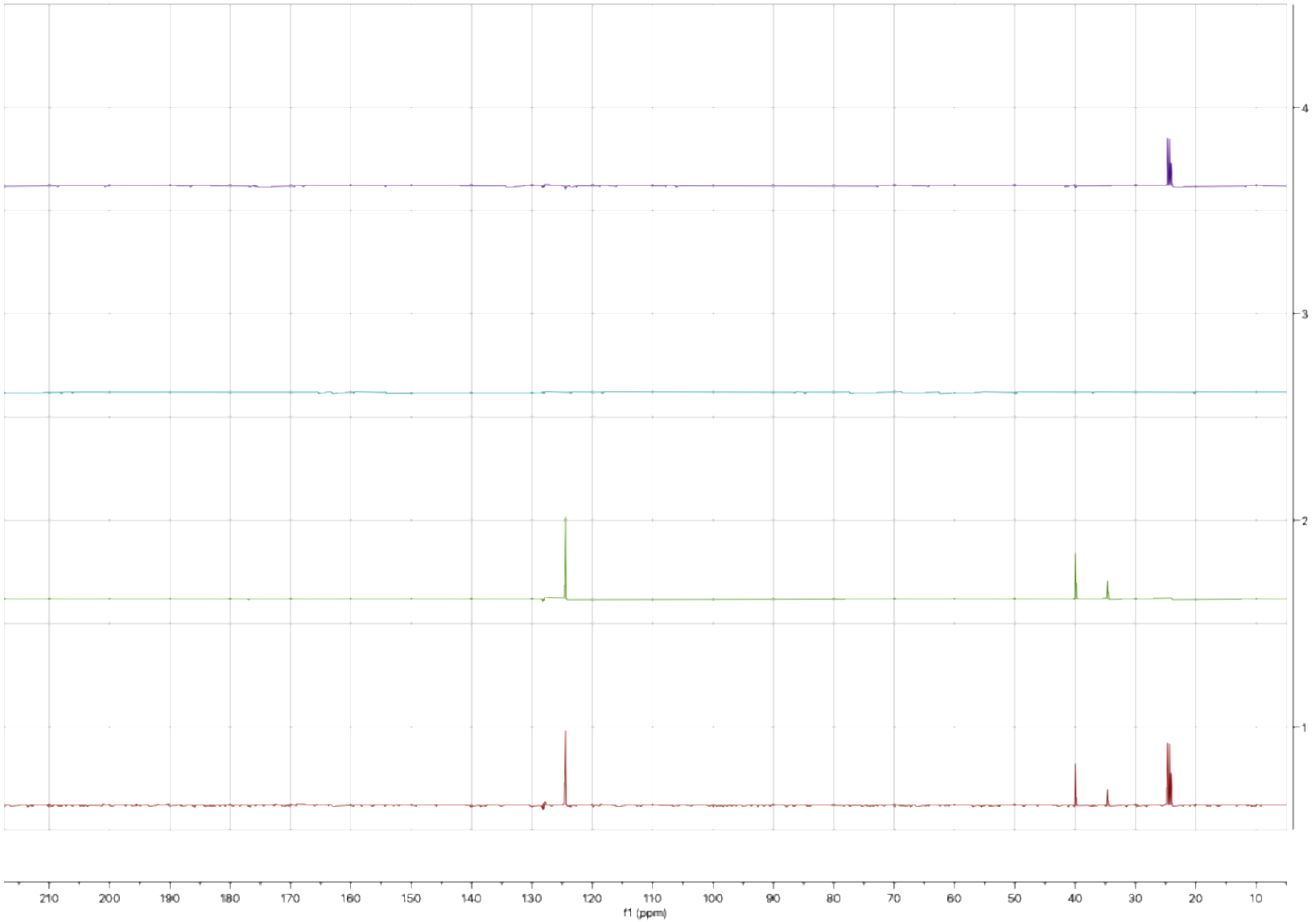


Figure S124. $^{13}C\{^{1}H\}$ DEPT of **C-CF$_3$** in C_6D_6

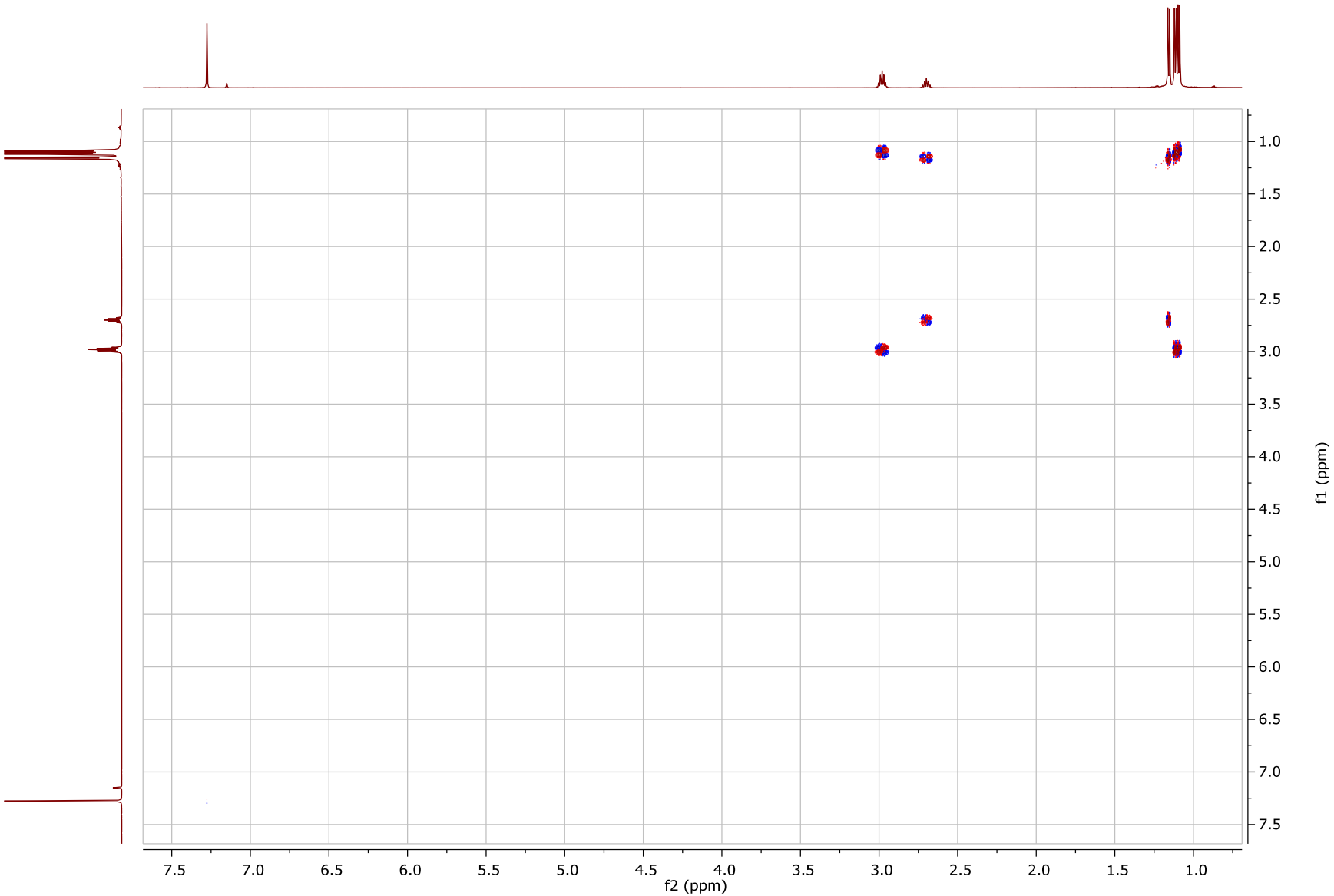


Figure S125. COSY of **C-CF$_3$** in C_6D_6

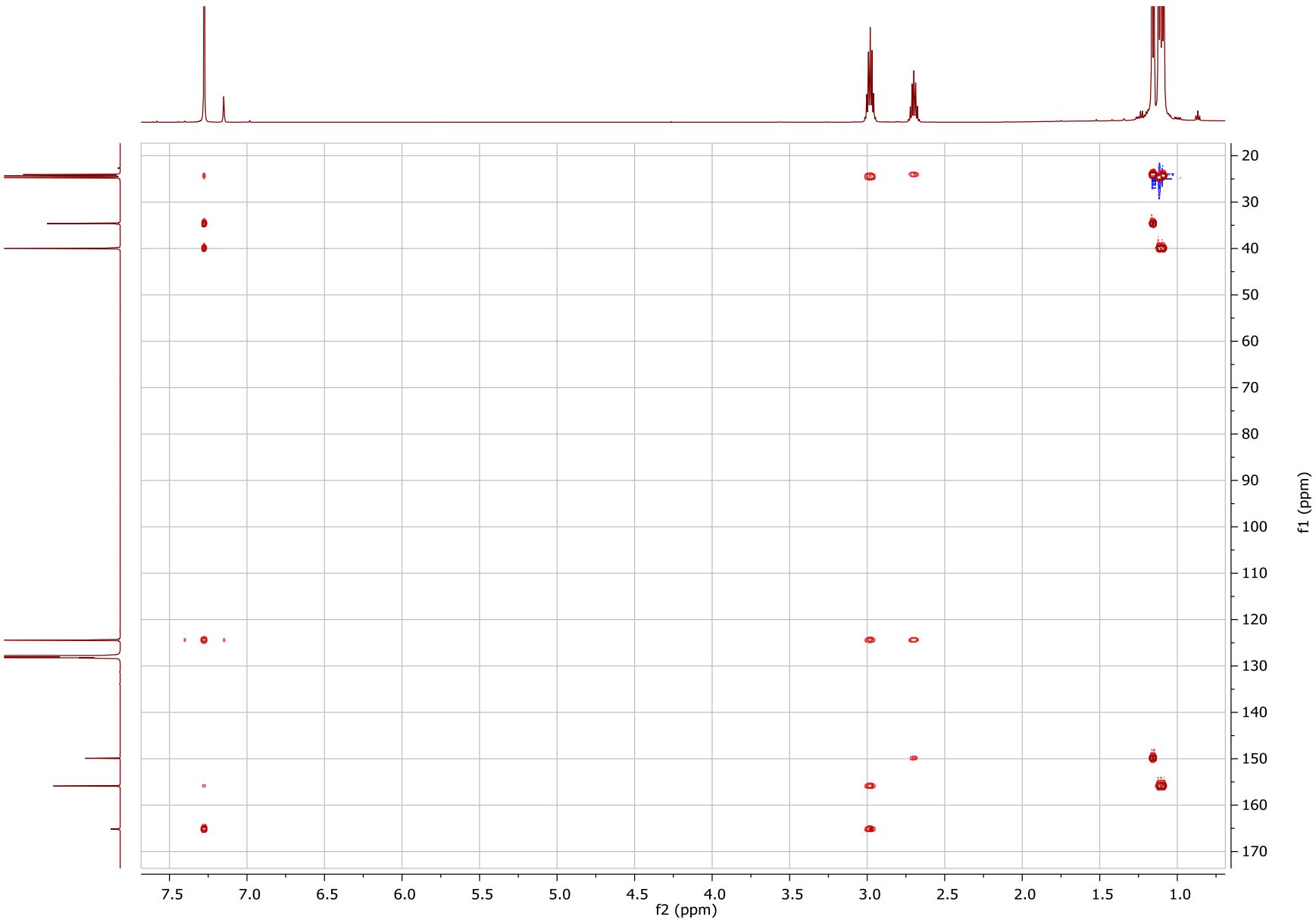


Figure S126. HMBC of **C-CF$_3$** in C_6D_6

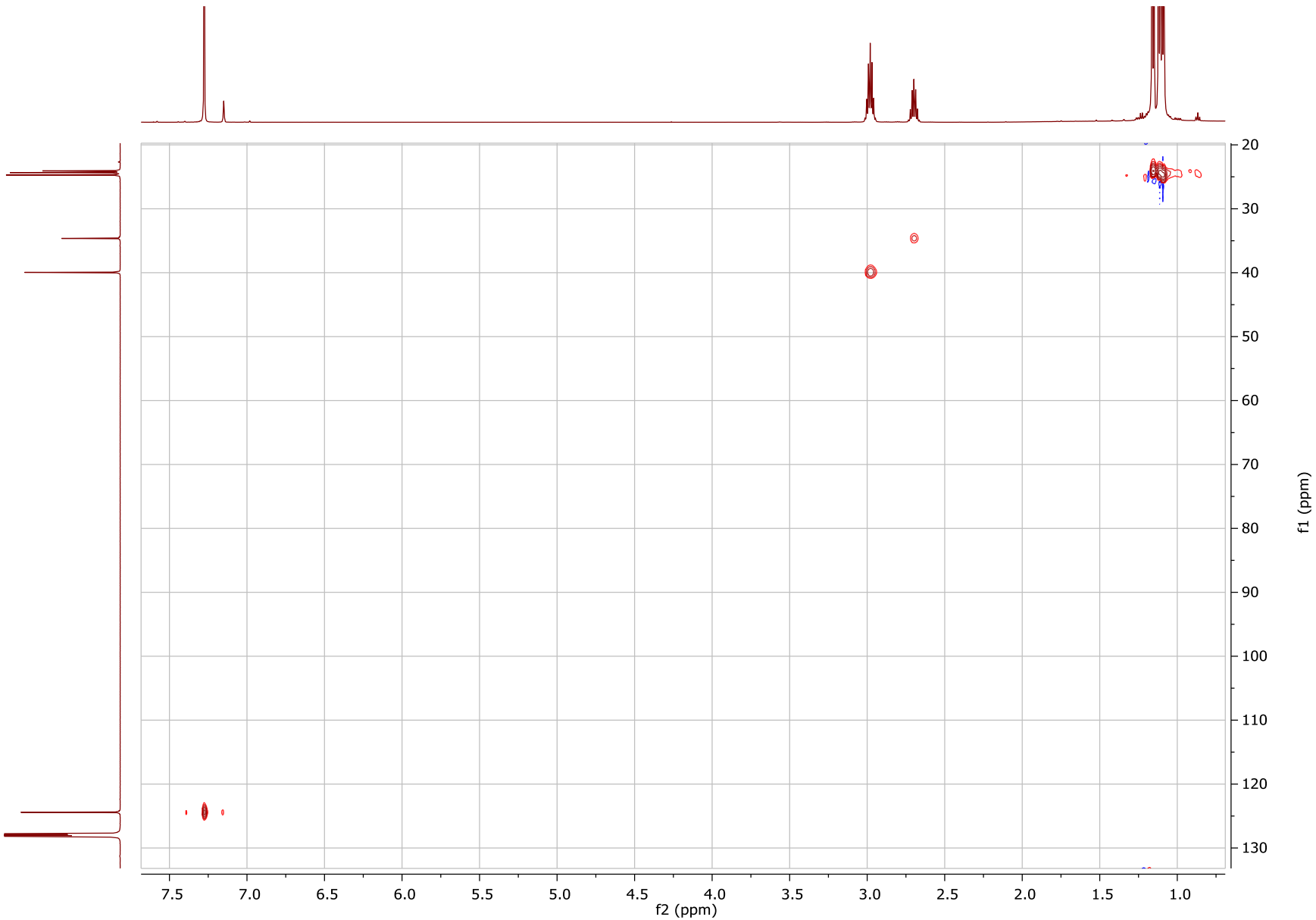
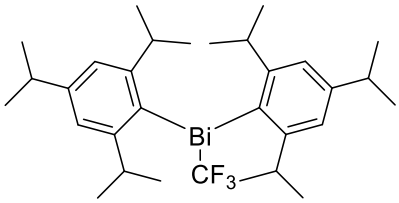


Figure S127. HSQC of **C-CF$_3$** in C_6D_6



Chemical Formula: $BiC_{31}H_{46}F_3$

Molecular Weight: 684.68

Elemental Analysis: C: 54.38; H: 6.77

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	2/10/2023 6:53:26PM
User ID	Administrator
Comments	TLG_4_167 [Hyvl]

DATE & TIME	2/10/2023 12:18:19 PM	P_ID	EA LAB
SAMPLE ID	23079	USER ID	Administrator
WEIGHT (mg)	2.578	MODE	CHN

CARBON	54.573%
HYDROGEN	6.694%
NITROGEN	0.020%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Table S1. Final Energies, Enthalpy and Entropy Corrections for DFT Calculations in **Scheme 5**.

Name	Formula	Energy(DZ)	Energy(TZ)	D0	NumNegative	ZPE	EnthalpyCorr (T=273, p=1.0)	EntropyCorr (T=273, p=1.0)	EnthalpyCorr (T=393, p=1.0)	EntropyCorr (T=393, p=1.0)	E	H(273K)	G(273K)	H(393K)	G(393K)
F-anion	F	-99.76373744	-99.92176862	0	0	0	0.001297	0.012774	0.003111	0.019522	-99.9217686	-99.9204716	-99.9290302	-99.91865762	-99.9317374
CF2_carbene	CF2	-237.7086823	-237.7874946	-0.00009288	0	0.00597267	0.009604072	0.024791016	0.011537737	0.037986557	-237.781615	-237.777983	-237.794593	-237.7760498	-237.801501
						A									
A_CCC_Bi+	C15H14Bi	-794.4259648	-794.6120435	-0.02222399	0	0.24314416	0.255910655	0.050598009	0.267963887	0.08707319	-794.391123	-794.378357	-794.412257	-794.3663036	-794.424643
A_CCC_BiCF3	C16H14BiF3	-1132.312817	-1132.57515	-0.02904507	0	0.25648667	0.273292778	0.059958901	0.288458611	0.104243543	-1132.34771	-1132.3309	-1132.37107	-1132.315736	-1132.38558
A_CCC_BiCF3_ElimTS	C16H14BiF3	-1132.25599	-1132.517429	-0.02799896	1	0.25379792	0.270641261	0.060111587	0.285743896	0.104391275	-1132.29163	-1132.27479	-1132.31506	-1132.259684	-1132.32963
A_CCC_BiF	C15H14BiF	-894.5414461	-894.7324014	-0.02448603	0	0.24498913	0.258931551	0.052938992	0.271927589	0.091563924	-894.511898	-894.497956	-894.533425	-894.4849599	-894.546308
						B									
B_pTol2_Bi+	C14H14Bi	-756.3255596	-756.505417	-0.01776223	0	0.23273688	0.247462043	0.058808915	0.259704287	0.099134417	-756.290442	-756.275717	-756.315119	-756.2634749	-756.329895
B_pTol2_BiCF3	C15H14BiF3	-1094.209611	-1094.467672	-0.02377019	0	0.24610879	0.264789141	0.06831098	0.280100923	0.116456521	-1094.24533	-1094.22665	-1094.27242	-1094.211341	-1094.28937
B_pTol2_BiCF3_ElimTS	C15H14BiF3	-1094.151546	-1094.409988	-0.02327263	1	0.24342506	0.262234587	0.068404417	0.277501754	0.116541913	-1094.18984	-1094.17103	-1094.21686	-1094.155759	-1094.23384
B_pTol2_BiF	C14H14BiF	-856.4341708	-856.619885	-0.01902633	0	0.23478193	0.250586456	0.061019893	0.263732478	0.103391471	-856.404129	-856.388325	-856.429208	-856.3751788	-856.444451
						C									
C_supermesityl_Bi+	C30H46Bi	-1385.429512	-1385.776514	-0.07752289	0	0.67855081	0.712605574	0.0987529	0.743007746	0.178106105	-1385.17549	-1385.14143	-1385.2076	-1385.111029	-1385.23036
C_supermesityl_BiCF3	C31H46BiF3	-1723.301587	-1723.726658	-0.08793735	0	0.69311699	0.731260236	0.107777757	0.764768485	0.194786245	-1723.12148	-1723.08334	-1723.15555	-1723.049827	-1723.18033
C_supermesityl_BiCF3_ElimTS	C31H46BiF3	-1723.246356	-1723.674359	-0.08715873	1	0.69005448	0.728559916	0.109338795	0.762035018	0.196998304	-1723.07146	-1723.03296	-1723.10622	-1722.999483	-1723.13147
C_supermesityl_BiF	C30H46BiF	-1485.532452	-1485.886307	-0.08076565	0	0.68154286	0.717091899	0.101932308	0.748455065	0.183828143	-1485.28553	-1485.24998	-1485.31828	-1485.218617	-1485.34178
						1									
1_CNC_tBu_Bi+	C18H21BiN	-967.782713	-968.0142366	-0.03930174	0	0.34398772	0.360982218	0.058533267	0.377452575	0.103718722	-967.709551	-967.692556	-967.731773	-967.6760858	-967.745577
1_CNC_tBu_BiCF3	C19H21BiF3N	-1305.626925	-1305.936011	-0.04669896	0	0.35523987	0.377027448	0.070796077	0.396736091	0.125219296	-1305.62747	-1305.60568	-1305.65312	-1305.585974	-1305.66987
1_CNC_tBu_BiCF3_ElimTS	C19H21BiF3N	-1305.580738	-1305.889848	-0.045338	1	0.35373008	0.375109349	0.06890505	0.394668971	0.122321153	-1305.58146	-1305.56008	-1305.60624	-1305.540517	-1305.62247
1_CNC_tBu_BiF	C18H21BiFN	-1067.860947	-1068.098946	-0.04162616	0	0.34405327	0.362971135	0.064152346	0.380497624	0.113066471	-1067.79652	-1067.7776	-1067.82058	-1067.760075	-1067.83583
						2									
2_CNC_Ph_Bi+	C20H17BiN	-1041.594056	-1041.834524	-0.03417557	0	0.31252236	0.329091038	0.059874965	0.345059736	0.105048225	-1041.55618	-1041.53961	-1041.57972	-1041.52364	-1041.59402
2_CNC_Ph_BiCF3	C21H17BiF3N	-1379.446341	-1379.765271	-0.04152669	0	0.32540759	0.346069255	0.069165399	0.365162013	0.122131892	-1379.48139	-1379.46073	-1379.50707	-1379.441635	-1379.52346
2_CNC_Ph_BiCF3_ElimTS	C21H17BiF3N	-1379.398017	-1379.716232	-0.04037406	1	0.32298714	0.343638462	0.069097945	0.362651479	0.121942597	-1379.43362	-1379.41297	-1379.45926	-1379.393955	-1379.47566
2_CNC_Ph_BiF	C20H17BiFN	-1141.679279	-1141.926575	-0.03669541	0	0.31351187	0.331632658	0.063855648	0.348598499	0.111966051	-1141.64976	-1141.63164	-1141.67442	-1141.614672	-1141.68969
						3									
3_CSC_BiF	C14H12BiS	-1153.360948	-1153.556612	-0.02184462	0	0.2160828	0.229024402	0.050883202	0.241115734	0.087537339	-1153.36237	-1153.34943	-1153.38352	-1153.337341	-1153.39599
3_CSC_BiCF3	C15H12BiF3S	-1491.214463	-1491.483592	-0.02897124	0	0.22884578	0.246032014	0.060623864	0.26125402	0.105276472	-1491.28372	-1491.26653	-1491.30715	-1491.251309	-1491.32184
3_CSC_BiCF3_ElimTS	C15H12BiF3S	-1491.167388	-1491.436156	-0.02770038	1	0.22629526	0.243546638	0.06110009	0.258708481	0.105893685	-1491.23756	-1491.22031	-1491.26125	-1491.205148	-1491.2761
3_CSC_BiF	C14H12BiFS	-1253.449956	-1253.64715	-0.02421444	0	0.21757714	0.231861498	0.053632939	0.244908763	0.092632907	-1253.45379	-1253.4395	-1253.47544	-1253.426456	-1253.48852
						4									
4_SONCF3C_Bi+	C13H8BiF3NOS	-1542.259104	-1542.602509	-0.02612246	0	0.18287131	0.199042392	0.059791753	0.213283075	0.102923194	-1542.44576	-1542.42959	-1542.46965	-1542.415348	-1542.48431
4_SONCF3C_BiCF3	C14H8BiF6NOS	-1880.126449	-1880.547691	-0.03306592	0	0.19625237	0.216397855	0.06871901	0.233716197	0.119427223	-1880.3845	-1880.36436	-1880.4104	-1880.347041	-1880.42706
4_SONCF3C_BiCF3_ElimTSX3								not found							
4_SONCF3C_BiF	C13H8BiF4NOS	-1642.357145	-1642.707434	-0.02811478	0	0.18474547	0.202094125	0.061465418	0.217277318	0.10645281	-1642.5508	-1642.53345	-1642.57464	-1642.518271	-1642.58959
						5									
5_CNC_CH2CH2OMe_Bi+	C17H19BiNO	-1003.683997	-1003.926519	-0.035747	0	0.3216392	0.338571185	0.059740431	0.354289576	0.104569825	-1003.64063	-1003.62369	-1003.66372	-1003.607976	-1003.67804
5_CNC_CH2CH2OMe_BiCF3	C18H19BiF3NO	-1341.522834	-1341.844161	-0.04341056	0	0.3336507	0.354808264	0.069267229	0.373642012	0.121983472	-1341.55392	-1341.53276	-1341.57917	-1341.513929	-1341.59566
5_CNC_CH2CH2OMe_BiCF3_ElimTS	C18H19BiF3NO	-1341.479044	-1341.799769	-0.04231194	1	0.33148867	0.352579925	0.069010658	0.371337468	0.121526025	-1341.51059	-1341.4895	-1341.53574	-1341.470744	-1341.55217
5_CNC_CH2CH2OMe_BiF	C17H19BiFNO	-1103.757204	-1104.007473	-0.03830109	0	0.32181818	0.34049358	0.065101002	0.35719813	0.113461166	-1103.72396	-1103.70528	-1103.7489	-1103.688576	-1103.76459
						6									
6_CNC_OMe_Bi+	C15H15BiNO	-924.9909067	-925.2140386	-0.02727002	0	0.26382974	0.278507607	0.054497259	0.292250969	0.094689704	-924.977479	-924.962801	-924.999314	-924.9490576	-925.0125
6_CNC_OMe_BiCF3	C16H15BiF3NO	-1262.842502	-1263.142802	-0.03423732	0	0.27535677	0.294646034	0.065670801	0.31160208	0.114591164	-1262.90168	-1262.88239	-1262.92639	-1262.865437	-1262.94221
6_CNC_OMe_BiCF3_ElimTS	C16H15BiF3NO	-1262.795791	-1263.095663	-0.03302543	1	0.2728467	0.292261543	0.066102555	0.309162994	0.115151125	-1262.85584	-1262.83643	-1262.88072	-1262.819526	-1262.89668
6_CNC_OMe_BiF	C15H15BiFNO	-1025.075944	-1025.305126	-0.02940079	0	0.26470666	0.280824109	0.057541391	0.295551197	0.100242953	-1025.06982	-1025.0537	-1025.09226	-1025.038975	-1025.10614
						7									
7_CNC_CH2CH2morpholine_Bi+	C20H24BiN2O	-1175.788043	-1176.073015	-0.04877623	1	0.40345535	0.421911076	0.062368524	0.440175158	0.111341467	-1175.71834	-1175.69988	-1175.74167	-1175.681616	-1175.75621
7_CNC_CH2CH2morpholine_BiCF3	C21H24BiF3N2O	-1513.624044	-1513.988292	-0.05673077	0	0.41513238	0.438800119	0.076407571	0.460590167	0.13574099	-1513.62989	-1513.60622	-1513.65742	-1513.584432	-1513.67538
7_CNC_CH2CH2morpholine_BiCF3_ElimTS	C21H24BiF3N2O	-1513.579762	-1513.944168	-0.0556841	1	0.4127594	0.436489593	0.077020458	0.458209139	0.136542043	-1513.58709	-1513.56336	-1513.61497	-1513.541643	-1513.63313
7_CNC_CH2CH2morpholine_BiF	C20H24BiFN2O	-1275.858975	-1276.151934	-0.05148823	0	0.40374566	0.424591681	0.06938253	0.444233209	0.123079764	-1275.79968	-1275.77883	-1275.82532	-1275.759189	-1275.84165

Table S2. Barriers and Bond Dissociation Gibbs Free Energies for DFT Calculations in **Scheme 5**.

	H(273K)	G(273K)	H(393K)	G(393K)	$\Delta G_{ElimTS-Dissociation}$
A					
Elim TS	35.2	35.1	35.2	35.1	
Bi-F + CF2	34.5	27.0	34.3	23.7	11.4
BDGE Bi-F	125.0	120.6	125.5	119.2	
B					
Elim TS	34.9	34.9	34.9	34.8	
Bi-F + CF2	37.9	30.5	37.7	27.2	7.6
BDGE Bi-F	120.6	116.1	121.1	114.7	
C					
Elim TS	31.6	31.0	31.6	30.7	
Bi-F + CF2	34.7	26.8	34.6	23.2	
BDGE Bi-F	118.0	114.0	118.6	112.8	
1					
Elim TS	28.6	29.4	28.5	29.7	
Bi-F + CF2	31.4	23.8	31.3	20.4	9.3
BDGE Bi-F	103.3	100.3	103.7	99.5	
2					
Elim TS	30.0	30.0	29.9	30.0	
Bi-F + CF2	32.1	23.9	31.9	20.3	9.7
BDGE Bi-F	107.7	104.0	108.2	102.9	
3					
Elim TS	29.0	28.8	29.0	28.7	
Bi-F + CF2	30.8	23.3	30.6	20.0	8.7
BDGE Bi-F	106.4	102.2	107.0	100.9	
4					
Elim TS	-	-	-	-	
Bi-F + CF2	33.2	25.8	33.1	22.6	-
BDGE Bi-F	115.1	110.4	115.6	108.9	
5					
Elim TS	27.1	27.3	27.1	27.3	
Bi-F + CF2	31.1	22.4	30.9	18.6	8.7
BDGE Bi-F	101.1	98.0	101.6	97.2	
6					
Elim TS	28.8	28.7	28.8	28.6	
Bi-F + CF2	31.8	24.8	31.6	21.7	6.9
BDGE Bi-F	106.9	102.9	107.5	101.6	
7					
Elim TS	26.9	26.6	26.9	26.5	
Bi-F + CF2	31.0	23.5	30.9	20.2	6.3
BDGE Bi-F	99.4	97.0	99.7	96.4	

X-ray Crystallography

X-ray structural analysis: Crystal data and refinement details are presented in Tables S3 to S70. Candidate data crystals were selected, sectioned, mounted using viscous oil onto plastic mesh or loops, and cooled to the data collection temperature. Data were collected on various Bruker-AXS area detector diffractometers with either graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å) focused with Goebel mirrors. Unit cell parameters were obtained from fast scan data frames, 1°/s ω, of an Ewald hemisphere. The unit-cell parameters and systematic absences in the diffraction data were uniquely consistent with $P2_1/c$ for **2-CF$_3$**, **5-CF$_3$**, **7-CF$_3$**, **6-F**, and **7-F**; and with $P2_1/n$ for **4-CF$_3$**, **C-CF$_3$**, and **3-F**. No symmetry higher than triclinic was observed for **3-CF$_3$**, and **6-CF$_3$**; and, the centrosymmetric option, *P*-1, yielded chemically reasonable and computationally stable results of refinement. Two symmetry independent compound molecules were located in the asymmetric unit of **6-CF$_3$**. The data were treated with multi-scan absorption corrections (SADABS[1] embedded in various versions of Apex[2]). The structures were solved in Olex2[3] using either direct methods[4] or intrinsic phasing methods.[5] Nonhydrogen atoms were refined with anisotropic displacement parameters. Details on the mixed H-atom treatments are contained in each CIF. Atomic scattering factors are contained in the SHELXTL program library.[6] The structures have been deposited at the Cambridge Structural Database under CCDC 2504497 for **2-CF$_3$**, 2504520 for **5-CF$_3$**, 2504522 for **7-CF$_3$**, 2504525 for **6-F**, 2504526 for **7-F**; 2504513 for **4-CF$_3$**, 2504553 for **C-CF$_3$**, 2504524 for **3-F**, 2504512 for **3-CF$_3$**, and 2504521 for **6-CF$_3$**.

[1] Sheldrick, G.M. (2010) SADABS. University of Gottingen, Gottingen, Germany.
[2] Apex 6 [Computer Software]; Bruker AXS Inc.: Madison, WI, USA, 2024.
[3] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. "Olex2: A complete structure solution, refinement and analysis program" *J. Appl. Cryst*., **2009,** *42,* 339-341. DOI: 10.1107/S0021889808042726
[4] Sheldrick, G. M. "A short history of SHELX" *Acta Cryst.* **2008,** *A64*, 112-122. DOI: 10.1107/S0108767307043930
[5] Sheldrick, G.M. "SHELXT: Integrated space-group and crystal-structure determination" *Acta Cryst.* **2015**, *A71*, 3–8. DOI: 10.1107/S2053273314026370
[6] Sheldrick, G.M. "Crystal structure refinement with SHELXL" *Acta Cryst.* **2015**, *C71*, 3–8. DOI: 10.1107/S2053229614024218

Table S3. Crystal data and structure refinement for 2-CF_3.

Identification code	hyvl108_0m_a
Empirical formula	$C_{21}H_{17}BiF_3N$
Formula weight	532.45
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5151(13)
b/Å	9.3054(10)
c/Å	16.450(2)
α/°	90
β/°	92.005(3)
γ/°	90
Volume/Å^3	1761.6(4)
Z	4
ρ_{calc}g/cm^3	2.008
μ/mm^{-1}	10.040
F(000)	973.0
Crystal size/mm^3	0.31 × 0.28 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.54 to 56.672
Index ranges	$-8 \leq h \leq 15$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected	18306
Independent reflections	4392 [R_{int} = 0.0589, R_{sigma} = 0.0516]
Data/restraints/parameters	4392/0/235
Goodness-of-fit on F^2	0.939
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0800
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.0848
Largest diff. peak/hole / e Å^{-3}	1.10/-1.29

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	7213.6(2)	4839.9(2)	5118.3(2)	12.14(7)
F3	8407(3)	1849(4)	5191(2)	32.0(8)
F2	7788(3)	2254(4)	6396(2)	32.2(8)
F1	6585(3)	1567(4)	5440(2)	32.3(8)
C15	8729(4)	5568(6)	5920(3)	12.9(9)
C18	9052(4)	9124(6)	3832(4)	22.4(11)
N1	7016(3)	7705(5)	5350(3)	15.0(8)

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C19	8317(5)	9480(6)	3178(3)	20.5(10)
C1	7497(5)	2430(6)	5593(3)	22.1(11)
C20	7141(5)	9289(6)	3257(3)	22.0(11)
C7	5353(4)	6655(6)	6052(3)	16.0(10)
C9	7717(4)	7975(5)	6108(3)	16.4(10)
C21	6692(4)	8754(6)	3971(3)	19.8(10)
C6	4456(4)	6968(6)	6577(3)	19.0(10)
C8	5764(4)	7803(6)	5482(3)	17.9(10)
C4	4424(4)	4518(6)	7028(3)	19.8(10)
C16	7438(4)	8370(5)	4625(3)	14.2(9)
C11	9704(4)	7444(6)	6695(3)	19.1(10)
C17	8633(4)	8577(6)	4541(3)	20.1(11)
C10	8744(4)	6954(6)	6231(3)	15.3(9)
C5	3999(4)	5897(6)	7066(3)	20.8(11)
C2	5806(4)	5252(5)	6024(3)	14.6(9)
C12	10651(5)	6540(7)	6855(3)	24.4(12)
C3	5330(4)	4191(6)	6512(3)	17.4(10)
C14	9687(4)	4667(6)	6071(3)	19.1(10)
C13	10642(5)	5157(6)	6544(4)	21.3(11)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	11.17(10)	15.11(11)	10.12(10)	-1.15(6)	-0.16(6)	0.84(6)
F3	23.6(17)	26.6(18)	46(2)	-7.0(16)	2.7(15)	7.1(14)
F2	28.8(17)	37(2)	30.2(19)	10.6(15)	-7.6(15)	-0.2(15)
F1	20.8(16)	22.3(17)	53(2)	-3.5(16)	-5.8(16)	-2.4(13)
C15	5.9(18)	23(2)	10(2)	4.5(18)	0.6(15)	-0.1(17)
C18	17(2)	21(3)	30(3)	3(2)	2(2)	2(2)
N1	11.9(18)	17(2)	16(2)	0.7(16)	0.5(15)	-1.0(15)
C19	28(3)	23(3)	11(2)	2(2)	1.9(19)	1(2)
C1	18(2)	27(3)	21(3)	-3(2)	-4(2)	7(2)
C20	22(2)	26(3)	17(2)	2(2)	-7(2)	-2(2)
C7	10(2)	21(3)	17(2)	-2.6(19)	-0.4(17)	-5.4(18)
C9	17(2)	16(2)	16(2)	-4.1(19)	-1.8(18)	-2.0(18)
C21	16(2)	22(3)	21(3)	3(2)	-5(2)	-2.3(19)
C6	12(2)	26(3)	19(3)	-9(2)	-2.8(19)	6.6(19)

Table S5. Anisotropic Displacement Parameters ($Å^2×10^3$) for 2-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	11(2)	22(3)	21(3)	2(2)	3.9(18)	4.4(18)
C4	16(2)	28(3)	15(2)	5(2)	1.4(19)	-4(2)
C16	15(2)	12(2)	15(2)	-0.8(18)	-0.4(18)	-1.0(17)
C11	14(2)	27(3)	16(2)	4(2)	-1.5(18)	-6.9(19)
C17	13(2)	25(3)	22(3)	3(2)	-1.5(19)	1.0(19)
C10	12(2)	24(3)	10(2)	7.0(18)	0.7(17)	-2.5(18)
C5	14(2)	34(3)	15(2)	-6(2)	1.2(18)	1(2)
C2	11(2)	22(3)	11(2)	-3.2(18)	-1.7(17)	-3.0(17)
C12	17(2)	36(3)	20(3)	5(2)	-5(2)	-7(2)
C3	14(2)	23(3)	15(2)	-0.6(19)	-3.6(18)	-8.3(19)
C14	16(2)	23(3)	18(3)	2(2)	3.9(19)	2.9(19)
C13	10(2)	34(3)	20(3)	8(2)	3(2)	3.5(19)

Table S6. Bond Lengths for 2-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	C15	2.255(4)	C20	C21	1.390(8)
Bi1	N1	2.704(4)	C7	C6	1.400(7)
Bi1	C1	2.393(6)	C7	C8	1.509(7)
Bi1	C2	2.272(5)	C7	C2	1.407(7)
F3	C1	1.370(6)	C9	C10	1.525(7)
F2	C1	1.361(6)	C21	C16	1.400(7)
F1	C1	1.339(6)	C6	C5	1.395(8)
C15	C10	1.388(7)	C4	C5	1.376(8)
C15	C14	1.401(7)	C4	C3	1.401(7)
C18	C19	1.385(7)	C16	C17	1.401(7)
C18	C17	1.377(8)	C11	C10	1.398(6)
N1	C9	1.483(6)	C11	C12	1.395(8)
N1	C8	1.468(6)	C2	C3	1.397(7)
N1	C16	1.443(6)	C12	C13	1.385(8)
C19	C20	1.377(8)	C14	C13	1.401(8)

Table S7. Bond Angles for 2-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C15	Bi1	N1	71.84(15)	C6	C7	C8	119.4(5)
C15	Bi1	C1	89.81(18)	C6	C7	C2	119.7(5)
C15	Bi1	C2	96.99(17)	C2	C7	C8	120.8(5)
C1	Bi1	N1	152.74(16)	N1	C9	C10	113.7(4)

Table S7. Bond Angles for 2-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	Bi1	N1	71.07(16)	C20	C21	C16	120.3(5)
C2	Bi1	C1	92.09(19)	C5	C6	C7	120.6(5)
C10	C15	Bi1	119.6(3)	N1	C8	C7	112.2(4)
C10	C15	C14	119.4(4)	C5	C4	C3	120.2(5)
C14	C15	Bi1	120.8(4)	C21	C16	N1	122.1(4)
C17	C18	C19	121.6(5)	C17	C16	N1	120.0(4)
C9	N1	Bi1	103.9(3)	C17	C16	C21	117.9(5)
C8	N1	Bi1	99.8(3)	C12	C11	C10	120.3(5)
C8	N1	C9	111.9(4)	C18	C17	C16	120.6(5)
C16	N1	Bi1	105.9(3)	C15	C10	C9	122.0(4)
C16	N1	C9	115.7(4)	C15	C10	C11	120.3(5)
C16	N1	C8	117.1(4)	C11	C10	C9	117.7(5)
C20	C19	C18	118.2(5)	C4	C5	C6	119.9(5)
F3	C1	Bi1	108.0(4)	C7	C2	Bi1	116.9(4)
F2	C1	Bi1	117.2(4)	C3	C2	Bi1	124.1(4)
F2	C1	F3	104.8(4)	C3	C2	C7	118.9(5)
F1	C1	Bi1	113.8(3)	C13	C12	C11	119.6(5)
F1	C1	F3	106.2(4)	C2	C3	C4	120.7(5)
F1	C1	F2	106.0(5)	C15	C14	C13	120.1(5)
C19	C20	C21	121.4(5)	C12	C13	C14	120.2(5)

Table S8. Torsion Angles for 2-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	C15	C10	C9	5.2(6)	C6	C7	C8	N1	145.9(4)
Bi1	C15	C10	C11	-176.8(4)	C6	C7	C2	Bi1	177.8(3)
Bi1	C15	C14	C13	177.4(4)	C6	C7	C2	C3	1.2(7)
Bi1	N1	C9	C10	31.1(5)	C8	N1	C9	C10	137.9(4)
Bi1	N1	C8	C7	45.0(4)	C8	N1	C16	C21	-16.6(7)
Bi1	N1	C16	C21	93.5(5)	C8	N1	C16	C17	166.9(5)
Bi1	N1	C16	C17	-82.9(5)	C8	C7	C6	C5	175.1(4)
Bi1	C2	C3	C4	-176.9(4)	C8	C7	C2	Bi1	2.2(6)
C15	C14	C13	C12	-0.8(8)	C8	C7	C2	C3	-174.4(4)
C18	C19	C20	C21	0.0(9)	C16	N1	C9	C10	-84.5(5)
N1	C9	C10	C15	-28.6(7)	C16	N1	C8	C7	158.6(4)
N1	C9	C10	C11	153.3(4)	C11	C12	C13	C14	-0.1(9)
N1	C16	C17	C18	175.8(5)	C17	C18	C19	C20	0.7(9)
C19	C18	C17	C16	-0.3(9)	C10	C15	C14	C13	0.9(8)
C19	C20	C21	C16	-1.2(9)	C10	C11	C12	C13	0.8(8)

Table S8. Torsion Angles for 2-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C20	C21	C16	N1	-174.9(5)	C5	C4	C3	C2	-0.6(7)
C20	C21	C16	C17	1.6(8)	C2	C7	C6	C5	-0.7(7)
C7	C6	C5	C4	-0.6(7)	C2	C7	C8	N1	-38.4(6)
C7	C2	C3	C4	-0.6(7)	C12	C11	C10	C15	-0.6(8)
C9	N1	C8	C7	-64.4(5)	C12	C11	C10	C9	177.5(5)
C9	N1	C16	C21	-152.0(5)	C3	C4	C5	C6	1.2(7)
C9	N1	C16	C17	31.5(6)	C14	C15	C10	C9	-178.3(5)
C21	C16	C17	C18	-0.8(8)	C14	C15	C10	C11	-0.2(7)

Table S9. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H18	9865.28	9260.36	3789.04	27
H19	8616.69	9846.39	2688.85	25
H20	6624.28	9527.25	2814.88	26
H9A	7207.35	7886.18	6578.18	20
H9B	8011.52	8974.11	6098.71	20
H21	5876.21	8649.06	4013.85	24
H6	4156.21	7917.55	6600.68	23
H8A	5334.46	7712.08	4952.42	22
H8B	5587.1	8760.35	5709.51	22
H4	4102.08	3784.47	7352.7	24
H11	9712	8396.96	6902.15	23
H17	9158.52	8337.65	4978.55	24
H5	3394.62	6120.16	7424	25
H12	11298.49	6871.41	7176.53	29
H3	5623.3	3237.94	6493.7	21
H14	9688.56	3721.38	5853.48	23
H13	11285.78	4539.33	6650.95	26

Table S10. Crystal data and structure refinement for 3-CF_3.

Identification code	hyvl112
Empirical formula	$C_{15}H_{12}BiF_3S$
Formula weight	490.29
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	8.7437(5)
b/Å	9.1594(5)
c/Å	10.8034(6)
α/°	102.249(2)
β/°	102.9270(10)
γ/°	114.5380(10)
Volume/Å^3	720.28(7)
Z	2
ρ_{calc}g/cm^3	2.261
μ/mm^{-1}	12.402
F(000)	456.0
Crystal size/mm^3	0.29 × 0.26 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.12 to 54.354
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 10, -13 ≤ l ≤ 13
Reflections collected	9272
Independent reflections	3198 [R_{int} = 0.0418, R_{sigma} = 0.0355]
Data/restraints/parameters	3198/0/181
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0186, wR_2 = 0.0439
Final R indexes [all data]	R_1 = 0.0195, wR_2 = 0.0443
Largest diff. peak/hole / e Å^{-3}	1.35/-0.79

Table S11. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for hyvl112. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	4026.0(2)	4712.2(2)	2745.6(2)	17.26(5)
S1	7999.3(10)	7073.3(10)	4263.9(9)	29.92(18)
F1	291(2)	2975(3)	326.0(19)	34.8(4)
F2	455(2)	5112(3)	1759(2)	32.4(4)
F3	-44(3)	2813(3)	2223(2)	41.1(5)
C1	8179(4)	7000(4)	2609(4)	31.3(8)
C2	6803(4)	7237(4)	1681(3)	21.8(6)
C3	7384(4)	8344(4)	966(3)	30.2(7)
C4	6191(5)	8543(4)	39(3)	30.0(7)
C5	4367(5)	7651(4)	-182(3)	27.8(7)
C6	3772(4)	6594(4)	557(3)	20.3(6)

Table S11. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for hyvl112. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C7	4968(3)	6378(3)	1500(3)	16.7(5)
C8	4305(4)	6832(3)	4471(3)	20.4(6)
C9	2849(4)	6534(4)	4902(3)	23.8(6)
C10	3008(4)	7704(4)	6054(3)	26.3(7)
C11	4635(5)	9187(4)	6782(3)	29.0(7)
C12	6072(4)	9503(4)	6347(3)	26.9(7)
C13	5934(4)	8349(4)	5195(3)	22.8(6)
C14	7532(4)	8831(4)	4738(3)	26.4(7)
C15	954(4)	3891(4)	1678(3)	23.4(6)

Table S12. Anisotropic Displacement Parameters (Å^2×10^3) for hyvl112. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	16.46(7)	9.36(7)	18.50(7)	1.27(5)	0.65(5)	4.16(5)
S1	19.4(3)	19.1(4)	37.8(5)	7.8(3)	-4.5(3)	5.8(3)
F1	20.4(9)	40.0(11)	25.5(10)	-5.1(8)	0.8(7)	9.8(8)
F2	25.9(9)	38.7(11)	33.5(11)	4.3(8)	7.7(8)	21.8(9)
F3	26.4(10)	38.1(12)	44.6(13)	12.3(10)	16.4(9)	2.1(9)
C1	15.9(14)	21.8(16)	37.4(19)	-11.6(14)	1.0(13)	7.3(13)
C2	21.0(14)	16.7(14)	20.4(14)	-3.9(11)	7.7(11)	7.4(12)
C3	26.2(15)	19.2(16)	35.3(18)	-3.5(13)	19.5(14)	4.1(13)
C4	41.6(19)	19.7(16)	25.6(16)	4.6(13)	21.2(15)	8.9(14)
C5	39.1(18)	24.1(17)	17.5(15)	2.7(13)	8.5(13)	16.0(15)
C6	22.7(14)	16.2(14)	18.9(14)	-0.1(11)	6.9(11)	9.9(12)
C7	17.4(13)	11.7(12)	14.9(13)	-2.8(10)	4.5(10)	5.7(11)
C8	28.1(15)	12.0(13)	14.0(13)	3.6(11)	2.7(11)	6.3(12)
C9	30.0(16)	16.7(14)	20.1(14)	7.1(12)	6.4(12)	8.1(13)
C10	37.0(17)	22.7(16)	19.9(15)	7.9(13)	12.8(13)	13.2(14)
C11	50(2)	19.2(15)	17.2(14)	4.6(12)	11.5(14)	16.9(15)
C12	38.5(17)	14.6(14)	16.9(14)	3.4(12)	5.3(13)	6.7(13)
C13	29.3(15)	14.3(14)	16.5(14)	4.3(11)	3.9(12)	5.9(12)
C14	28.9(16)	13.3(14)	21.4(15)	-0.8(12)	4.9(13)	1.6(13)
C15	21.4(14)	25.2(16)	19.3(14)	1.7(12)	7.2(12)	10.4(12)

Table S13. Bond Lengths for 3-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	S1	3.0236(7)	C3	C4	1.375(5)
Bi1	C7	2.267(3)	C4	C5	1.390(5)
Bi1	C8	2.274(3)	C5	C6	1.393(4)
Bi1	C15	2.383(3)	C6	C7	1.397(4)
S1	C1	1.819(4)	C8	C9	1.394(4)
S1	C14	1.819(3)	C8	C13	1.402(4)
F1	C15	1.367(3)	C9	C10	1.396(4)

Table S13. Bond Lengths for 3-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	C15	1.353(3)	C10	C11	1.389(5)
F3	C15	1.358(4)	C11	C12	1.379(5)
C1	C2	1.506(4)	C12	C13	1.396(4)
C2	C3	1.402(4)	C13	C14	1.511(4)
C2	C7	1.406(4)			

Table S14. Bond Angles for 3-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	Bi1	S1	74.40(7)	C6	C7	C2	118.5(3)
C7	Bi1	C8	95.36(10)	C9	C8	Bi1	118.3(2)
C7	Bi1	C15	93.03(10)	C9	C8	C13	119.0(3)
C8	Bi1	S1	72.96(8)	C13	C8	Bi1	122.3(2)
C8	Bi1	C15	90.73(10)	C8	C9	C10	120.9(3)
C15	Bi1	S1	157.99(8)	C11	C10	C9	119.8(3)
C1	S1	Bi1	85.82(10)	C12	C11	C10	119.6(3)
C1	S1	C14	103.41(15)	C11	C12	C13	121.3(3)
C14	S1	Bi1	89.00(10)	C8	C13	C14	122.4(3)
C2	C1	S1	115.1(2)	C12	C13	C8	119.3(3)
C3	C2	C1	118.3(3)	C12	C13	C14	118.2(3)
C3	C2	C7	119.2(3)	C13	C14	S1	112.6(2)
C7	C2	C1	122.5(3)	F1	C15	Bi1	113.36(18)
C4	C3	C2	121.5(3)	F2	C15	Bi1	119.13(19)
C3	C4	C5	119.6(3)	F2	C15	F1	104.5(2)
C4	C5	C6	119.7(3)	F2	C15	F3	105.5(2)
C5	C6	C7	121.4(3)	F3	C15	Bi1	108.29(19)
C2	C7	Bi1	119.7(2)	F3	C15	F1	104.9(2)
C6	C7	Bi1	121.7(2)				

Table S15. Torsion Angles for 3-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	S1	C1	C2	46.3(2)	C4	C5	C6	C7	-1.4(5)
Bi1	S1	C14	C13	44.2(2)	C5	C6	C7	Bi1	178.5(2)
Bi1	C8	C9	C10	172.5(2)	C5	C6	C7	C2	-0.9(4)
Bi1	C8	C13	C12	-172.1(2)	C7	C2	C3	C4	-3.4(5)
Bi1	C8	C13	C14	11.1(4)	C8	C9	C10	C11	0.1(4)
S1	C1	C2	C3	134.8(3)	C8	C13	C14	S1	-47.1(4)
S1	C1	C2	C7	-45.9(4)	C9	C8	C13	C12	1.5(4)
C1	S1	C14	C13	129.7(2)	C9	C8	C13	C14	-175.3(3)
C1	C2	C3	C4	176.0(3)	C9	C10	C11	C12	1.0(5)
C1	C2	C7	Bi1	4.5(4)	C10	C11	C12	C13	-0.8(5)
C1	C2	C7	C6	-176.1(3)	C11	C12	C13	C8	-0.5(4)
C2	C3	C4	C5	1.1(5)	C11	C12	C13	C14	176.5(3)
C3	C2	C7	Bi1	-176.2(2)	C12	C13	C14	S1	136.0(2)
C3	C2	C7	C6	3.2(4)	C13	C8	C9	C10	-1.4(4)

Table S15. Torsion Angles for 3-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C4	C5	C6	1.3(5)	C14	S1	C1	C2	-41.7(3)

Table S16. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H1A	9389.33	7899.84	2737.46	38
H1B	8072.64	5883.16	2159.68	38
H3	8630.91	8971.87	1124.32	36
H4	6609.89	9285.05	-446.58	36
H5	3530.99	7761.76	-833.27	33
H6	2526.84	6007.1	415.74	24
H9	1733.62	5522.13	4405.53	29
H10	2007.23	7486.72	6339.27	32
H11	4757.95	9979.91	7574.37	35
H12	7177.72	10526.16	6841.51	32
H14A	8601.74	9806.99	5477.27	32
H14B	7305.53	9206.11	3953.39	32

Table S17. Crystal data and structure refinement for **4-CF_3**.

Identification code	HVT2-172	
Empirical formula	C14 H8 Bi F6 N O S	
Formula weight	561.25	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.5658(6) Å	□= 90°.
	b = 9.3066(6) Å	□= 93.575(3)°.
	c = 19.3565(12) Å	□ = 90°.
Volume	1540.07(18) $Å^3$	
Z	4	
Density (calculated)	2.421 Mg/m^3	
Absorption coefficient	11.651 mm^{-1}	
F(000)	1040	
Crystal size	0.31 x 0.28 x 0.27 mm^3	
Theta range for data collection	3.236 to 27.102°.	
Index ranges	-9<=h<=10, -11<=k<=10, -24<=l<=24	
Reflections collected	11393	
Independent reflections	3337 [R(int) = 0.0242]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	None	
Max. and min. transmission	0.4912 and 0.3022	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3337 / 0 / 244	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0166, wR2 = 0.0342	
R indices (all data)	R1 = 0.0197, wR2 = 0.0350	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.499 and -0.619 $e.Å^{-3}$	

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4-CF_3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Bi(1)	5750(1)	7050(1)	5792(1)	16(1)
S(1)	1747(1)	7181(1)	5631(1)	15(1)
O(1)	64(2)	7211(2)	5620(1)	21(1)
F(3)	8169(2)	7283(2)	7051(1)	30(1)
F(2)	6330(2)	5867(2)	7332(1)	31(1)
C(7)	4153(3)	8331(3)	6449(1)	15(1)
F(1)	8048(2)	5116(2)	6650(1)	31(1)
C(4)	2129(3)	9862(3)	7261(1)	19(1)
C(6)	4748(3)	9195(3)	6987(1)	16(1)
C(3)	1498(3)	8988(3)	6733(1)	16(1)
C(2)	2528(3)	8245(3)	6336(1)	14(1)
N(1)	2610(3)	7554(3)	4973(1)	17(1)
C(5)	3731(4)	9967(3)	7388(1)	19(1)
C(1)	2455(4)	8915(3)	4684(2)	22(1)
C(12)	1905(4)	2961(3)	6003(2)	26(1)
C(14)	2473(4)	5427(3)	5801(1)	17(1)
C(13)	1373(4)	4346(3)	5856(1)	21(1)
C(9)	4084(3)	5196(3)	5889(1)	18(1)
C(11)	3491(4)	2697(3)	6096(2)	27(1)
C(8)	7154(3)	6275(4)	6791(2)	22(1)
C(10)	4583(4)	3804(3)	6039(1)	22(1)
F(4)	2154(12)	8857(7)	4026(3)	50(2)
F(5)	3870(7)	9522(7)	4771(5)	62(2)
F(6')	1133(6)	9056(6)	4265(3)	74(2)
F(6)	1480(11)	9746(8)	4941(5)	60(3)
F(5')	2383(7)	10053(5)	5095(3)	50(2)
F(4')	3563(7)	9223(5)	4259(3)	58(2)

Table S19. Bond lengths [Å] and angles [°] for **4-CF$_3$**.

Bi(1)-C(7)	2.265(3)
Bi(1)-C(9)	2.254(3)
Bi(1)-C(8)	2.327(3)
S(1)-O(1)	1.440(2)
S(1)-C(2)	1.782(3)
S(1)-N(1)	1.552(2)
S(1)-C(14)	1.771(3)
F(3)-C(8)	1.355(4)
F(2)-C(8)	1.352(3)
C(7)-C(6)	1.387(4)
C(7)-C(2)	1.397(4)
F(1)-C(8)	1.359(4)
C(4)-H(4)	0.9500
C(4)-C(3)	1.388(4)
C(4)-C(5)	1.383(4)
C(6)-H(6)	0.9500
C(6)-C(5)	1.400(4)
C(3)-H(3)	0.9500
C(3)-C(2)	1.390(4)
N(1)-C(1)	1.388(4)
C(5)-H(5)	0.9500
C(1)-F(4)	1.285(6)
C(1)-F(5)	1.338(6)
C(1)-F(6')	1.357(5)
C(1)-F(6)	1.263(8)
C(1)-F(5')	1.328(6)
C(1)-F(4')	1.325(5)
C(12)-H(12)	0.9500
C(12)-C(13)	1.391(4)
C(12)-C(11)	1.381(5)
C(14)-C(13)	1.387(4)
C(14)-C(9)	1.396(4)
C(13)-H(13)	0.9500
C(9)-C(10)	1.389(4)

C(11)-H(11)	0.9500
C(11)-C(10)	1.400(5)
C(10)-H(10)	0.9500

C(7)-Bi(1)-C(8)	89.74(10)
C(9)-Bi(1)-C(7)	87.05(10)
C(9)-Bi(1)-C(8)	89.47(10)
O(1)-S(1)-C(2)	109.17(13)
O(1)-S(1)-N(1)	120.78(13)
O(1)-S(1)-C(14)	111.10(13)
N(1)-S(1)-C(2)	109.17(13)
N(1)-S(1)-C(14)	100.32(13)
C(14)-S(1)-C(2)	105.00(13)
C(6)-C(7)-Bi(1)	121.4(2)
C(6)-C(7)-C(2)	117.8(2)
C(2)-C(7)-Bi(1)	120.83(19)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(5)-C(4)-C(3)	120.6(3)
C(7)-C(6)-H(6)	120.0
C(7)-C(6)-C(5)	120.1(3)
C(5)-C(6)-H(6)	120.0
C(4)-C(3)-H(3)	121.1
C(4)-C(3)-C(2)	117.8(3)
C(2)-C(3)-H(3)	121.1
C(7)-C(2)-S(1)	118.3(2)
C(3)-C(2)-S(1)	118.6(2)
C(3)-C(2)-C(7)	123.0(2)
C(1)-N(1)-S(1)	119.8(2)
C(4)-C(5)-C(6)	120.7(3)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
F(4)-C(1)-N(1)	111.7(4)
F(4)-C(1)-F(5)	105.5(6)
F(5)-C(1)-N(1)	105.7(3)
F(6')-C(1)-N(1)	112.6(3)

F(6)-C(1)-N(1)	116.6(4)
F(6)-C(1)-F(4)	108.7(6)
F(6)-C(1)-F(5)	108.0(6)
F(5')-C(1)-N(1)	119.5(3)
F(5')-C(1)-F(6')	102.3(4)
F(4')-C(1)-N(1)	113.1(3)
F(4')-C(1)-F(6')	102.2(4)
F(4')-C(1)-F(5')	105.2(4)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(11)-C(12)-C(13)	119.9(3)
C(13)-C(14)-S(1)	116.8(2)
C(13)-C(14)-C(9)	123.4(3)
C(9)-C(14)-S(1)	119.9(2)
C(12)-C(13)-H(13)	120.9
C(14)-C(13)-C(12)	118.2(3)
C(14)-C(13)-H(13)	120.9
C(14)-C(9)-Bi(1)	119.8(2)
C(10)-C(9)-Bi(1)	122.9(2)
C(10)-C(9)-C(14)	117.3(3)
C(12)-C(11)-H(11)	119.5
C(12)-C(11)-C(10)	121.0(3)
C(10)-C(11)-H(11)	119.5
F(3)-C(8)-Bi(1)	112.35(19)
F(3)-C(8)-F(1)	105.5(2)
F(2)-C(8)-Bi(1)	117.54(18)
F(2)-C(8)-F(3)	105.1(2)
F(2)-C(8)-F(1)	105.1(2)
F(1)-C(8)-Bi(1)	110.34(18)
C(9)-C(10)-C(11)	120.3(3)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9

Symmetry transformations used to generate equivalent atoms:

Table S20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 4-CF_3. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Bi(1)	14(1)	20(1)	14(1)	2(1)	3(1)	4(1)
S(1)	15(1)	16(1)	14(1)	0(1)	-1(1)	0(1)
O(1)	14(1)	25(1)	23(1)	-1(1)	-2(1)	-2(1)
F(3)	17(1)	39(1)	32(1)	4(1)	-4(1)	-4(1)
F(2)	18(1)	55(1)	21(1)	14(1)	2(1)	-2(1)
C(7)	16(2)	16(1)	14(1)	2(1)	2(1)	1(1)
F(1)	22(1)	35(1)	37(1)	7(1)	0(1)	12(1)
C(4)	17(2)	24(2)	17(1)	-2(1)	5(1)	3(1)
C(6)	10(1)	20(1)	18(1)	2(1)	-1(1)	-1(1)
C(3)	12(1)	18(1)	18(1)	2(1)	2(1)	-1(1)
C(2)	16(2)	12(1)	14(1)	1(1)	0(1)	-2(1)
N(1)	21(1)	18(1)	13(1)	2(1)	1(1)	2(1)
C(5)	23(2)	20(1)	14(1)	-4(1)	3(1)	-4(1)
C(1)	20(2)	25(2)	19(1)	3(1)	0(1)	0(1)
C(12)	39(2)	19(2)	22(2)	-1(1)	7(1)	-5(1)
C(14)	25(2)	17(1)	9(1)	-2(1)	1(1)	3(1)
C(13)	27(2)	21(2)	16(1)	-2(1)	2(1)	-6(1)
C(9)	23(2)	21(1)	10(1)	-2(1)	2(1)	2(1)
C(11)	46(2)	16(2)	19(1)	1(1)	6(1)	6(1)
C(8)	11(1)	33(2)	23(1)	7(1)	4(1)	3(1)
C(10)	30(2)	23(2)	13(1)	1(1)	2(1)	6(1)
F(4)	95(6)	37(3)	15(2)	15(2)	-12(3)	-7(4)
F(5)	28(3)	40(4)	115(6)	45(5)	-21(4)	-16(3)
F(6')	55(3)	60(3)	98(5)	48(3)	-56(3)	-28(3)
F(6)	83(6)	28(4)	75(7)	26(4)	55(6)	36(4)
F(5')	108(5)	16(2)	26(2)	-1(2)	10(3)	4(3)
F(4')	69(4)	36(2)	75(3)	30(3)	58(3)	20(2)

Table 21. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4-CF_3.

	x	y	z	U(eq)
H(4)	1454	10393	7536	23
H(6)	5846	9264	7084	19
H(3)	398	8899	6647	19
H(5)	4147	10568	7751	23
H(12)	1179	2197	6040	32
H(13)	285	4547	5795	26
H(11)	3847	1750	6200	32
H(10)	5670	3602	6103	26

Table S22. Crystal data and structure refinement for 5-CF_3.

Identification code	hyvl002
Empirical formula	$C_{18}H_{19}NOF_3Bi$
Formula weight	531.32
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.2635(3)
b/Å	12.7354(4)
c/Å	12.9743(4)
α/°	90
β/°	115.7490(10)
γ/°	90
Volume/Å^3	1825.13(9)
Z	4
ρ_{calc}g/cm^3	1.934
μ/mm^{-1}	19.265
F(000)	1008.0
Crystal size/mm^3	0.123 × 0.108 × 0.081
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.004 to 136.36
Index ranges	$-13 \leq h \leq 14$, $-15 \leq k \leq 14$, $-15 \leq l \leq 14$
Reflections collected	30139
Independent reflections	3209 [R_{int} = 0.0436, R_{sigma} = 0.0214]
Data/restraints/parameters	3209/0/218
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0203, wR_2 = 0.0475
Final R indexes [all data]	R_1 = 0.0225, wR_2 = 0.0485
Largest diff. peak/hole / e Å^{-3}	0.55/-0.81

Table S23. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	7717.1(2)	5283.6(2)	4116.7(2)	41.71(7)
F1	7749(3)	3616(2)	2352(3)	94.1(10)
F2	8059(3)	5074(2)	1738(2)	69.9(7)
F3	9495(2)	4346(2)	3154(2)	81.2(8)
O1	6928(5)	4883(4)	6096(4)	106.5(15)
N1	6885(3)	6846(2)	4943(3)	49.8(7)
C1	8859(3)	6735(3)	4334(3)	43.7(8)

Table S23. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C2	9626(3)	6869(3)	3803(4)	55.6(10)
C3	10339(4)	7769(4)	4022(4)	72.0(13)
C4	10287(5)	8522(4)	4761(5)	82.0(15)
C5	9543(4)	8386(4)	5286(5)	73.6(13)
C6	8825(4)	7506(3)	5084(3)	53.9(10)
C7	8022(4)	7371(4)	5690(4)	62.5(11)
C8	5982(3)	5896(3)	2701(3)	47.3(9)
C9	5359(4)	5329(4)	1707(4)	64.6(12)
C10	4267(4)	5696(6)	885(4)	86.1(17)
C11	3801(4)	6620(6)	1034(5)	89.7(19)
C12	4408(4)	7190(4)	2029(4)	72.2(14)
C13	5501(3)	6830(3)	2874(3)	52.9(10)
C14	6174(4)	7491(3)	3927(4)	59.9(11)
C15	6123(4)	6571(4)	5526(4)	71.7(13)
C16	6687(6)	5814(5)	6505(5)	87.1(16)
C17	7644(9)	4200(8)	6982(8)	173(5)
C18	8295(4)	4555(3)	2721(4)	53.1(10)

Table S24. Anisotropic Displacement Parameters (Å^2×10^3) for 5-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	50.58(10)	37.92(9)	39.71(10)	1.22(5)	22.49(7)	1.71(6)
F1	133(3)	57.4(16)	126(3)	-34.2(17)	89(2)	-24.7(17)
F2	84.4(18)	82.8(17)	45.2(14)	4.4(12)	30.7(13)	3.5(14)
F3	73.2(17)	93(2)	76.4(18)	-3.9(16)	32.2(15)	30.7(15)
O1	141(4)	107(3)	109(3)	44(3)	89(3)	46(3)
N1	55.5(18)	49.7(18)	47.5(18)	-8.4(15)	25.6(16)	2.8(15)
C1	42.6(18)	44(2)	39.2(19)	2.7(16)	12.5(16)	-1.1(15)
C2	48(2)	59(2)	54(2)	8(2)	16.8(19)	0.2(19)
C3	57(3)	79(3)	81(3)	10(3)	32(2)	-13(2)
C4	72(3)	57(3)	107(4)	-9(3)	29(3)	-24(2)
C5	73(3)	54(3)	86(3)	-17(2)	27(3)	-16(2)
C6	54(2)	48(2)	52(2)	-2.7(18)	14.7(19)	-1.6(18)
C7	77(3)	57(3)	54(2)	-13(2)	29(2)	0(2)
C8	39.9(18)	60(2)	41(2)	-0.5(18)	16.7(16)	-5.1(17)
C9	53(2)	84(3)	56(3)	-13(2)	22(2)	-15(2)
C10	53(3)	138(5)	57(3)	-12(3)	15(2)	-20(3)

Table S24. Anisotropic Displacement Parameters ($Å^2×10^3$) for 5-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	41(2)	151(6)	62(3)	26(4)	8(2)	6(3)
C12	50(2)	96(4)	74(3)	21(3)	30(2)	21(2)
C13	45(2)	65(3)	52(2)	9(2)	23.5(18)	5.6(19)
C14	63(2)	51(2)	67(3)	1(2)	30(2)	15(2)
C15	81(3)	75(3)	81(3)	-7(3)	57(3)	9(3)
C16	101(4)	110(5)	73(3)	0(3)	59(3)	-8(4)
C17	179(8)	195(9)	191(9)	137(8)	124(8)	85(7)
C18	65(3)	45(2)	56(2)	-4.2(18)	32(2)	2.2(19)

Table S25. Bond Lengths for 5-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	N1	2.665(3)	C2	C3	1.395(6)
Bi1	C1	2.262(4)	C3	C4	1.377(7)
Bi1	C8	2.261(4)	C4	C5	1.367(8)
Bi1	C18	2.399(4)	C5	C6	1.378(6)
F1	C18	1.353(5)	C6	C7	1.514(6)
F2	C18	1.351(5)	C8	C9	1.383(6)
F3	C18	1.355(5)	C8	C13	1.389(6)
O1	C16	1.381(7)	C9	C10	1.382(7)
O1	C17	1.405(8)	C10	C11	1.359(9)
N1	C7	1.469(5)	C11	C12	1.383(8)
N1	C14	1.474(5)	C12	C13	1.390(6)
N1	C15	1.476(5)	C13	C14	1.508(6)
C1	C2	1.396(5)	C15	C16	1.503(7)
C1	C6	1.395(5)			

Table S26. Bond Angles for 5-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Bi1	N1	70.37(12)	C5	C6	C7	119.9(4)
C1	Bi1	C18	92.31(14)	N1	C7	C6	110.7(3)
C8	Bi1	N1	71.29(12)	C9	C8	Bi1	121.4(3)
C8	Bi1	C1	97.61(13)	C9	C8	C13	119.8(4)
C8	Bi1	C18	90.14(14)	C13	C8	Bi1	118.7(3)
C18	Bi1	N1	151.95(12)	C10	C9	C8	120.1(5)
C16	O1	C17	112.2(7)	C11	C10	C9	120.6(5)
C7	N1	Bi1	100.7(2)	C10	C11	C12	119.9(5)
C7	N1	C14	111.1(3)	C11	C12	C13	120.5(5)

Table S26. Bond Angles for 5-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C15	113.6(3)	C8	C13	C12	119.1(4)
C14	N1	Bi1	103.7(2)	C8	C13	C14	121.4(3)
C14	N1	C15	109.3(3)	C12	C13	C14	119.4(4)
C15	N1	Bi1	117.8(3)	N1	C14	C13	112.2(3)
C2	C1	Bi1	123.4(3)	N1	C15	C16	115.1(4)
C6	C1	Bi1	117.2(3)	O1	C16	C15	108.8(4)
C6	C1	C2	119.3(4)	F1	C18	Bi1	110.2(3)
C3	C2	C1	119.8(4)	F1	C18	F3	104.8(3)
C4	C3	C2	120.0(4)	F2	C18	Bi1	120.7(3)
C5	C4	C3	120.1(4)	F2	C18	F1	103.2(3)
C4	C5	C6	121.2(5)	F2	C18	F3	103.6(3)
C1	C6	C7	120.4(4)	F3	C18	Bi1	112.8(3)
C5	C6	C1	119.7(4)				

Table S27. Torsion Angles for 5-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	N1	C7	C6	45.9(4)	C6	C1	C2	C3	-0.4(6)
Bi1	N1	C14	C13	37.3(4)	C7	N1	C14	C13	144.6(3)
Bi1	N1	C15	C16	55.5(5)	C7	N1	C15	C16	-61.8(5)
Bi1	C1	C2	C3	-177.2(3)	C8	C9	C10	C11	0.8(8)
Bi1	C1	C6	C5	177.3(3)	C8	C13	C14	N1	-33.8(5)
Bi1	C1	C6	C7	-1.7(5)	C9	C8	C13	C12	-1.4(6)
Bi1	C8	C9	C10	176.4(4)	C9	C8	C13	C14	-177.8(4)
Bi1	C8	C13	C12	-177.3(3)	C9	C10	C11	C12	-1.5(9)
Bi1	C8	C13	C14	6.3(5)	C10	C11	C12	C13	0.8(8)
N1	C15	C16	O1	-60.8(6)	C11	C12	C13	C8	0.7(7)
C1	C2	C3	C4	0.1(7)	C11	C12	C13	C14	177.2(4)
C1	C6	C7	N1	-36.1(5)	C12	C13	C14	N1	149.7(4)
C2	C1	C6	C5	0.2(6)	C13	C8	C9	C10	0.7(7)
C2	C1	C6	C7	-178.7(4)	C14	N1	C7	C6	-63.5(4)
C2	C3	C4	C5	0.4(8)	C14	N1	C15	C16	173.5(4)
C3	C4	C5	C6	-0.5(9)	C15	N1	C7	C6	172.8(4)
C4	C5	C6	C1	0.2(7)	C15	N1	C14	C13	-89.2(4)
C4	C5	C6	C7	179.2(5)	C17	O1	C16	C15	169.6(6)
C5	C6	C7	N1	145.0(4)					

Table S28. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H2	9660.01	6358.79	3305.01	67
H3	10849.8	7860.4	3668.95	86
H4	10759.78	9124.66	4902.93	98
H5	9519.62	8896.88	5788.16	88
H7A	8442.92	6957.44	6378.39	75
H7B	7845.49	8053.59	5913.46	75
H9	5674.81	4699.16	1592.97	78
H10	3846.42	5306.35	222.28	103
H11	3074.97	6869.3	468.33	108
H12	4082.52	7818.19	2133.48	87
H14A	6712.58	7966.68	3787.41	72
H14B	5597.19	7910.76	4075.34	72
H15A	5371.88	6270.69	4966.54	86
H15B	5922.48	7211.48	5810.5	86
H16A	7431.45	6106.03	7083.99	105
H16B	6138.64	5686.14	6849.86	105
H17A	7687.5	3528.57	6666.48	259
H17B	7290.22	4119.5	7507.88	259
H17C	8444.35	4486.55	7377.92	259

Table S29. Crystal data and structure refinement for 6-CF_3.

Identification code	hyvl104_0m_a
Empirical formula	$C_{16}H_{15}BiF_3NO$
Formula weight	503.27
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.3263(7)
b/Å	9.3742(6)
c/Å	17.9914(13)
α/°	89.902(2)
β/°	77.349(2)
γ/°	88.952(2)
Volume/Å^3	1534.48(19)
Z	4
ρ_{calc}g/cm^3	2.178
μ/mm^{-1}	11.522
F(000)	944.0
Crystal size/mm^3	0.33 × 0.29 × 0.27
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.346 to 54.568
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 12, -14 ≤ l ≤ 23
Reflections collected	21237
Independent reflections	6816 [R_{int} = 0.0643, R_{sigma} = 0.0684]
Data/restraints/parameters	6816/0/393
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.0964
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.0999
Largest diff. peak/hole / e Å^{-3}	1.51/-2.05

Table S30. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	4815.8(2)	2552.4(2)	737.3(2)	10.50(8)
Bi1'	7741.1(2)	6274.2(2)	4569.8(2)	11.11(8)
F2'	6873(4)	9640(4)	4688(2)	23.6(9)
O1	8707(5)	1872(5)	-243(2)	19.2(10)
F1	1774(4)	1589(4)	1667(2)	22.0(8)
N1	7763(5)	2740(5)	331(3)	10.2(10)
F2	2443(4)	3258(4)	2323(2)	22.4(8)

Table S30. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F3	1592(4)	3790(4)	1338(2)	21.0(8)
F3'	8314(4)	9034(4)	5428(2)	24.9(9)
N1'	7990(6)	4539(5)	3354(3)	13.1(10)
O1'	9075(5)	3406(5)	3157(3)	20.7(10)
F1'	6024(5)	8544(4)	5741(2)	28.3(9)
C3'	8280(7)	5513(7)	2705(3)	17.5(13)
C7	5130(7)	7086(6)	1577(3)	15.7(13)
C16	5809(7)	1539(6)	1649(3)	13.3(12)
C9'	9154(6)	7316(6)	3533(3)	9.6(11)
C6	6545(7)	7484(7)	1206(3)	17.8(13)
C11	7329(7)	1628(6)	1614(3)	11.5(12)
C8	4617(7)	5734(6)	1433(3)	12.2(8)
C12	7938(7)	895(6)	2144(3)	15.7(13)
C14	5574(8)	9(6)	2754(4)	19.0(14)
C12'	4065(7)	4996(7)	3468(4)	16.6(13)
C15	4946(7)	716(6)	2217(3)	13.8(12)
C1'	7156(7)	8551(7)	5135(3)	15.2(12)
C10	8294(6)	2592(6)	1045(3)	12.9(12)
C1	2498(6)	2857(6)	1606(3)	12.3(12)
C2	8199(9)	465(7)	-217(4)	28.1(17)
C9	5513(6)	4785(6)	935(3)	12.2(8)
C5	7427(7)	6548(6)	709(4)	14.9(12)
C4'	9279(6)	6710(6)	2821(3)	12.5(12)
C7'	11009(7)	8998(7)	2992(4)	20.0(14)
C4	6918(6)	5189(6)	561(3)	11.9(12)
C10'	6515(7)	3895(6)	3479(3)	15.1(13)
C2'	9587(9)	2950(8)	3798(4)	31.3(17)
C14'	3205(7)	7148(7)	4133(4)	17.7(13)
C16'	5597(7)	6200(6)	4178(3)	13.2(12)
C3	7903(6)	4183(6)	28(3)	12.9(12)
C13	7072(7)	106(6)	2714(4)	17.9(13)
C11'	5364(7)	5061(6)	3729(3)	13.5(12)
C6'	11145(7)	8395(7)	2279(4)	18.6(13)
C8'	10030(6)	8473(6)	3611(4)	13.3(12)
C13'	2981(7)	6057(7)	3662(4)	18.3(13)
C5'	10265(7)	7239(7)	2194(4)	17.8(13)
C15'	4507(7)	7246(6)	4389(3)	14.5(12)

Table S31. Anisotropic Displacement Parameters ($Å^2×10^3$) for 6-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	11.88(13)	10.94(12)	9.37(13)	0.86(9)	-3.61(9)	-2.84(8)
Bi1'	14.64(13)	11.75(12)	7.35(12)	-0.16(9)	-3.30(9)	0.43(9)
F2'	33(2)	14.2(18)	23(2)	-4.9(15)	-6.0(17)	8.1(16)
O1	24(3)	16(2)	13(2)	-6.7(18)	6.4(18)	3.0(18)
F1	20(2)	17.7(19)	28(2)	5.5(16)	-4.4(16)	-9.7(15)
N1	9(2)	10(2)	9(2)	1.8(18)	2.1(19)	-2.7(18)
F2	17(2)	33(2)	17.7(19)	-5.2(16)	-5.8(15)	-5.5(16)
F3	15.4(19)	20.0(19)	27(2)	8.1(16)	-4.4(16)	1.9(15)
F3'	32(2)	22(2)	24(2)	-10.4(16)	-12.7(18)	-2.5(17)
N1'	15(3)	9(2)	14(3)	-5.6(19)	-1(2)	3.1(19)
O1'	20(2)	20(2)	21(2)	-7.6(19)	-2.2(19)	6.1(18)
F1'	29(2)	31(2)	20(2)	-9.9(17)	5.5(17)	-0.9(18)
C3'	22(3)	23(3)	7(3)	-2(2)	-1(2)	-3(3)
C7	23(3)	13(3)	10(3)	0(2)	-1(2)	0(2)
C16	17(3)	13(3)	10(3)	-3(2)	-3(2)	4(2)
C9'	9(3)	12(3)	8(3)	1(2)	-4(2)	0(2)
C6	22(3)	20(3)	12(3)	-1(2)	-5(3)	-7(3)
C11	19(3)	5(3)	11(3)	-4(2)	-3(2)	5(2)
C8	12(2)	12(2)	14(2)	3.6(16)	-4.3(17)	-1.8(16)
C12	19(3)	17(3)	13(3)	-8(2)	-7(2)	7(2)
C14	29(4)	12(3)	14(3)	2(2)	0(3)	2(3)
C12'	18(3)	17(3)	16(3)	1(2)	-6(3)	-6(2)
C15	18(3)	13(3)	9(3)	2(2)	0(2)	0(2)
C1'	18(3)	19(3)	6(3)	-4(2)	0(2)	2(2)
C10	12(3)	12(3)	15(3)	-3(2)	-4(2)	1(2)
C1	11(3)	11(3)	16(3)	-1(2)	-5(2)	-4(2)
C2	39(4)	15(3)	25(4)	-8(3)	4(3)	-4(3)
C9	12(2)	12(2)	14(2)	3.6(16)	-4.3(17)	-1.8(16)
C5	14(3)	14(3)	17(3)	5(2)	-6(2)	-4(2)
C4'	10(3)	18(3)	11(3)	1(2)	-4(2)	1(2)
C7'	17(3)	14(3)	29(4)	2(3)	-4(3)	3(2)
C4	13(3)	15(3)	9(3)	0(2)	-4(2)	0(2)
C10'	20(3)	11(3)	15(3)	-6(2)	-3(2)	-6(2)
C2'	35(4)	33(4)	26(4)	1(3)	-8(3)	15(3)
C14'	15(3)	17(3)	20(3)	5(3)	-1(3)	4(2)
C16'	16(3)	17(3)	7(3)	1(2)	-3(2)	-5(2)

Table S31. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3	11(3)	15(3)	11(3)	3(2)	2(2)	-1(2)
C13	28(4)	14(3)	12(3)	2(2)	-5(3)	2(3)
C11'	16(3)	16(3)	7(3)	1(2)	0(2)	-1(2)
C6'	17(3)	16(3)	20(3)	7(3)	1(3)	2(2)
C8'	14(3)	10(3)	18(3)	0(2)	-8(2)	4(2)
C13'	12(3)	25(3)	18(3)	9(3)	-4(3)	-3(2)
C5'	22(3)	19(3)	12(3)	-1(2)	-4(3)	2(3)
C15'	18(3)	12(3)	12(3)	-1(2)	0(2)	2(2)

Table S32. Bond Lengths for 6-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	N1	2.694(5)	C16	C11	1.409(8)
Bi1	C16	2.254(6)	C16	C15	1.395(8)
Bi1	C1	2.387(6)	C9'	C4'	1.384(8)
Bi1	C9	2.255(6)	C9'	C8'	1.395(8)
Bi1'	N1'	2.695(5)	C6	C5	1.378(9)
Bi1'	C9'	2.266(6)	C11	C12	1.387(8)
Bi1'	C1'	2.368(6)	C11	C10	1.516(8)
Bi1'	C16'	2.263(6)	C8	C9	1.393(8)
F2'	C1'	1.356(7)	C12	C13	1.381(9)
O1	N1	1.442(6)	C14	C15	1.395(9)
O1	C2	1.407(8)	C14	C13	1.388(9)
F1	C1	1.370(6)	C12'	C11'	1.393(8)
N1	C10	1.480(7)	C12'	C13'	1.394(9)
N1	C3	1.455(7)	C9	C4	1.395(8)
F2	C1	1.334(7)	C5	C4	1.414(8)
F3	C1	1.365(7)	C4'	C5'	1.387(8)
F3'	C1'	1.385(7)	C7'	C6'	1.382(9)
N1'	O1'	1.443(6)	C7'	C8'	1.372(9)
N1'	C3'	1.462(8)	C4	C3	1.496(8)
N1'	C10'	1.484(8)	C10'	C11'	1.515(8)
O1'	C2'	1.404(8)	C14'	C13'	1.377(9)
F1'	C1'	1.341(7)	C14'	C15'	1.395(9)
C3'	C4'	1.515(8)	C16'	C11'	1.389(8)
C7	C6	1.399(9)	C16'	C15'	1.392(8)
C7	C8	1.407(8)	C6'	C5'	1.399(9)

Table S33. Bond Angles for 6-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	Bi1	N1	71.00(18)	C11'	C12'	C13'	120.6(6)
C16	Bi1	C1	91.4(2)	C14	C15	C16	120.5(6)
C1	Bi1	N1	153.21(17)	F2'	C1'	Bi1'	118.2(4)
C9	Bi1	N1	69.69(18)	F2'	C1'	F3'	103.8(5)
C9	Bi1	C16	95.3(2)	F3'	C1'	Bi1'	110.2(4)
C9	Bi1	C1	92.9(2)	F1'	C1'	Bi1'	113.5(4)
C9'	Bi1'	N1'	70.50(18)	F1'	C1'	F2'	105.9(5)
C9'	Bi1'	C1'	89.8(2)	F1'	C1'	F3'	103.7(5)
C9'	Bi1'	C16'	99.1(2)	N1	C10	C11	112.1(5)
C1'	Bi1'	N1'	149.44(18)	F1	C1	Bi1	108.7(4)
C16'	Bi1'	N1'	69.10(19)	F2	C1	Bi1	120.0(4)
C16'	Bi1'	C1'	92.3(2)	F2	C1	F1	104.9(5)
C2	O1	N1	110.5(4)	F2	C1	F3	105.5(5)
O1	N1	Bi1	125.1(3)	F3	C1	Bi1	112.1(4)
O1	N1	C10	107.8(4)	F3	C1	F1	104.3(4)
O1	N1	C3	104.9(4)	C8	C9	Bi1	122.4(4)
C10	N1	Bi1	105.8(3)	C8	C9	C4	119.8(5)
C3	N1	Bi1	100.5(3)	C4	C9	Bi1	117.8(4)
C3	N1	C10	112.7(5)	C6	C5	C4	120.9(6)
O1'	N1'	Bi1'	124.5(3)	C9'	C4'	C3'	120.5(5)
O1'	N1'	C3'	105.1(4)	C9'	C4'	C5'	120.5(6)
O1'	N1'	C10'	107.9(4)	C5'	C4'	C3'	118.9(5)
C3'	N1'	Bi1'	103.8(3)	C8'	C7'	C6'	120.8(6)
C3'	N1'	C10'	112.9(5)	C9	C4	C5	119.3(5)
C10'	N1'	Bi1'	102.7(3)	C9	C4	C3	120.7(5)
C2'	O1'	N1'	111.1(5)	C5	C4	C3	120.0(5)
N1'	C3'	C4'	111.9(5)	N1'	C10'	C11'	108.5(5)
C6	C7	C8	119.5(6)	C13'	C14'	C15'	121.7(6)
C11	C16	Bi1	120.4(4)	C11'	C16'	Bi1'	118.7(4)
C15	C16	Bi1	120.1(4)	C15'	C16'	Bi1'	121.6(4)
C15	C16	C11	119.3(5)	C15'	C16'	C11'	119.7(6)
C4'	C9'	Bi1'	119.8(4)	N1	C3	C4	110.2(5)
C4'	C9'	C8'	119.0(5)	C14	C13	C12	120.1(6)
C8'	C9'	Bi1'	120.8(4)	C12'	C11'	C10'	118.0(5)
C5	C6	C7	119.9(6)	C16'	C11'	C12'	120.1(6)
C16	C11	C10	121.3(5)	C16'	C11'	C10'	121.9(6)
C12	C11	C16	119.4(5)	C7'	C6'	C5'	119.1(6)
C12	C11	C10	119.2(5)	C7'	C8'	C9'	120.6(6)

Table S33. Bond Angles for 6-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	C8	C7	120.6(6)	C14'	C13'	C12'	118.5(6)
C11	C12	C13	121.0(6)	C4'	C5'	C6'	120.0(6)
C13	C14	C15	119.7(6)	C16'	C15'	C14'	119.3(6)

Table S34. Torsion Angles for 6-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	N1	C10	C11	32.0(5)	C6	C5	C4	C3	-179.1(6)
Bi1	N1	C3	C4	46.8(5)	C11	C16	C15	C14	1.2(9)
Bi1	C16	C11	C12	-174.6(4)	C11	C12	C13	C14	1.5(9)
Bi1	C16	C11	C10	9.9(7)	C8	C7	C6	C5	-0.5(9)
Bi1	C16	C15	C14	175.8(4)	C8	C9	C4	C5	1.5(9)
Bi1	C9	C4	C5	-176.0(4)	C8	C9	C4	C3	179.5(5)
Bi1	C9	C4	C3	2.1(7)	C12	C11	C10	N1	152.9(5)
Bi1'	N1'	O1'	C2'	23.1(6)	C15	C16	C11	C12	0.1(8)
Bi1'	N1'	C3'	C4'	38.2(5)	C15	C16	C11	C10	-175.5(5)
Bi1'	N1'	C10'	C11'	43.8(5)	C15	C14	C13	C12	-0.2(9)
Bi1'	C9'	C4'	C3'	10.9(7)	C10	N1	C3	C4	-65.4(6)
Bi1'	C9'	C4'	C5'	-172.7(4)	C10	C11	C12	C13	174.3(5)
Bi1'	C9'	C8'	C7'	172.5(4)	C2	O1	N1	Bi1	-37.9(6)
Bi1'	C16'	C11'	C12'	-179.0(4)	C2	O1	N1	C10	87.2(6)
Bi1'	C16'	C11'	C10'	-1.7(7)	C2	O1	N1	C3	-152.5(5)
Bi1'	C16'	C15'	C14'	-179.9(4)	C9	C4	C3	N1	-39.6(8)
O1	N1	C10	C11	-103.9(5)	C5	C4	C3	N1	138.4(5)
O1	N1	C3	C4	177.7(5)	C4'	C9'	C8'	C7'	-0.4(9)
N1'	C3'	C4'	C9'	-37.5(8)	C7'	C6'	C5'	C4'	-0.3(9)
N1'	C3'	C4'	C5'	146.0(6)	C10'	N1'	O1'	C2'	-97.1(6)
N1'	C10'	C11'	C12'	143.1(5)	C10'	N1'	C3'	C4'	148.7(5)
N1'	C10'	C11'	C16'	-34.2(7)	C3	N1	C10	C11	140.9(5)
O1'	N1'	C3'	C4'	-93.9(6)	C13	C14	C15	C16	-1.1(9)
O1'	N1'	C10'	C11'	176.9(4)	C11'	C12'	C13'	C14'	-1.7(9)
C3'	N1'	O1'	C2'	142.2(5)	C11'	C16'	C15'	C14'	-1.3(9)
C3'	N1'	C10'	C11'	-67.3(6)	C6'	C7'	C8'	C9'	0.1(9)
C3'	C4'	C5'	C6'	176.6(6)	C8'	C9'	C4'	C3'	-176.2(5)
C7	C6	C5	C4	0.6(9)	C8'	C9'	C4'	C5'	0.3(9)
C7	C8	C9	Bi1	175.9(4)	C8'	C7'	C6'	C5'	0.2(9)
C7	C8	C9	C4	-1.5(9)	C13'	C12'	C11'	C10'	-178.3(5)
C16	C11	C12	C13	-1.4(9)	C13'	C12'	C11'	C16'	-0.9(9)
C16	C11	C10	N1	-31.5(7)	C13'	C14'	C15'	C16'	-1.4(9)

Table S34. Torsion Angles for 6-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C9'	C4'	C5'	C6'	0.0(9)	C15'	C14'	C13'	C12'	2.9(9)
C6	C7	C8	C9	1.0(9)	C15'	C16'	C11'	C12'	2.4(9)
C6	C5	C4	C9	-1.1(9)	C15'	C16'	C11'	C10'	179.7(5)

Table S35. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H3'A	7337.42	5924.97	2628.99	21
H3'B	8742.52	4972.58	2238.95	21
H7	4520.53	7723.58	1923.56	19
H6	6897.1	8397.38	1296.77	21
H8	3651.07	5466.57	1677.88	15
H12	8965.57	936.69	2114.42	19
H14	4978.53	-536.73	3144.31	23
H12'	3917.85	4220.69	3155.05	20
H15	3924.24	636.13	2237.97	17
H10A	8316.96	3546.34	1275.65	15
H10B	9310.15	2195.94	925.01	15
H2A	8826.68	-98.76	-623.88	42
H2B	7185.76	471.27	-285.72	42
H2C	8232.19	41.18	277.93	42
H5	8390.21	6820.52	462.97	18
H7'	11599.23	9784.95	3054.91	24
H10C	6421.1	3149.31	3876.36	18
H10D	6377.02	3447.1	3002.54	18
H2'A	8752.45	2672.39	4201.57	47
H2'B	10107.12	3729.73	3980.73	47
H2'C	10259.7	2130.72	3659.08	47
H14'	2452.71	7851.88	4287.39	21
H3A	7636.64	4204.52	-475.31	15
H3B	8935.43	4485.65	-41.95	15
H13	7502.63	-371.16	3080.3	22
H6'	11825.34	8760.45	1852.89	22
H8'	9949.07	8901.31	4096.95	16
H13'	2106.9	6027.91	3472.76	22
H5'	10344.27	6816.7	1706.66	21
H15'	4647.71	8019.54	4704.68	17

Table S36. Crystal data and structure refinement for 7-CF_3.

Identification code	hyvl109_0m_a
Empirical formula	$C_{21}H_{24}BiF_3N_2O$
Formula weight	586.40
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.1393(7)
b/Å	13.2160(9)
c/Å	17.0483(11)
α/°	90
β/°	94.660(2)
γ/°	90
Volume/Å^3	2276.9(3)
Z	4
ρ_{calc}g/cm^3	1.711
μ/mm^{-1}	7.779
F(000)	1128.0
Crystal size/mm^3	0.10 × 0.10 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.904 to 55.13
Index ranges	$-13 \leq h \leq 5$, $-17 \leq k \leq 9$, $-19 \leq l \leq 22$
Reflections collected	15187
Independent reflections	5225 [R_{int} = 0.0571, R_{sigma} = 0.0653]
Data/restraints/parameters	5225/0/280
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0382, wR_2 = 0.0957
Final R indexes [all data]	R_1 = 0.0434, wR_2 = 0.0991
Largest diff. peak/hole / e Å^{-3}	1.67/-1.03

Table S37. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	3316.8(2)	5161.4(2)	6217.9(2)	13.79(8)
F1	1012(3)	6771(2)	6080.1(18)	35.4(7)
F2	2813(3)	7632(2)	6297.7(18)	35.8(7)
F3	2265(3)	7021(2)	5142.4(17)	33.7(7)
O1	-465(3)	3284(3)	6810.7(19)	29.1(8)
N1	5151(3)	4028(3)	6908(2)	16.6(7)
N2	2339(3)	3306(3)	7192(2)	16.8(7)

Table S37. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-CF_3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C11	3487(4)	5586(3)	7504(2)	14.5(8)
C17	3576(4)	2875(3)	7552(3)	19.9(9)
C10	4524(5)	5165(3)	7981(3)	16.2(10)
C2	5314(4)	5771(3)	5924(2)	18.3(9)
C12	2529(4)	6160(3)	7845(2)	18.2(9)
C16	4736(4)	2972(3)	7038(3)	22.4(10)
C23	987(6)	9541(5)	5488(3)	35.6(13)
C18	1393(4)	3476(4)	7792(3)	21.6(9)
C24	1191(6)	10489(5)	5179(3)	36.5(13)
C15	4613(5)	5345(4)	8800(3)	21.4(9)
C4	6790(5)	7033(4)	5453(3)	29.4(12)
C1	2306(5)	6773(3)	5924(3)	22.3(9)
C13	2613(5)	6328(3)	8656(3)	22.8(10)
C3	5530(5)	6727(4)	5616(2)	22.9(10)
C8	6186(4)	4046(4)	6346(3)	19.8(9)
C9	5615(4)	4554(4)	7637(3)	17.3(8)
C21	1713(5)	2649(4)	6581(3)	22.3(10)
C20	436(5)	3112(4)	6226(3)	27.1(11)
C14	3658(5)	5918(4)	9123(3)	23.9(10)
C7	6392(5)	5111(3)	6046(3)	20.8(10)
C22	-214(6)	9045(4)	5313(3)	36.1(13)
C19	130(5)	3929(4)	7419(3)	27.3(11)
C5	7844(5)	6369(4)	5598(3)	28.5(11)
C6	7650(5)	5425(4)	5897(3)	23.3(10)

Table S38. Anisotropic Displacement Parameters (Å^2×10^3) for 7-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	14.18(11)	14.12(13)	12.43(12)	0.88(5)	-2.81(7)	-1.12(5)
F1	24.5(15)	38.9(18)	42.2(18)	8.8(15)	-0.4(13)	8.8(14)
F2	47.6(18)	19.7(15)	37.9(17)	-2.3(13)	-10.3(14)	1.0(14)
F3	41.9(17)	31.4(16)	26.3(15)	8.4(13)	-6.8(13)	5.1(14)
O1	17.7(16)	45(2)	24.7(18)	-1.1(16)	2.1(13)	-6.2(15)
N1	17.3(17)	19.3(19)	12.7(17)	-1.2(14)	-1.1(14)	4.2(15)
N2	15.5(17)	21.6(19)	13.3(17)	1.7(15)	1.2(14)	0.5(15)
C11	15.6(19)	13(2)	15(2)	2.3(16)	-0.9(16)	-2.4(16)
C17	25(2)	14(2)	20(2)	2.7(17)	-1.4(18)	4.6(18)

Table S38. Anisotropic Displacement Parameters ($Å^2×10^3$) for 7-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	20(2)	14(2)	14(2)	0.1(16)	0.0(19)	-0.2(16)
C2	21(2)	20(2)	14(2)	0.2(17)	-0.7(17)	-6.2(18)
C12	15.4(19)	20(2)	19(2)	5.9(17)	-0.8(17)	4.0(17)
C16	18(2)	21(2)	28(2)	-0.7(19)	0.9(19)	3.5(18)
C23	49(3)	29(3)	30(3)	6(2)	7(3)	5(3)
C18	25(2)	23(2)	17(2)	-1.3(18)	6.4(19)	-1.3(19)
C24	42(3)	29(3)	39(3)	3(3)	10(3)	-2(3)
C15	24(2)	25(2)	15(2)	0.4(18)	-2.0(18)	0.1(19)
C4	44(3)	29(3)	16(2)	-6(2)	9(2)	-16(2)
C1	27(2)	19(2)	20(2)	0.7(18)	-3.3(19)	4.2(19)
C13	27(2)	16(2)	27(2)	-0.7(18)	8(2)	2.9(18)
C3	29(2)	27(2)	12(2)	-2.4(18)	-0.9(18)	-7(2)
C8	12.4(19)	28(3)	19(2)	-0.2(19)	1.1(17)	3.8(18)
C9	16(2)	20(2)	16(2)	-0.2(18)	0.0(17)	1.9(18)
C21	25(2)	24(2)	19(2)	-6.1(19)	5.6(19)	-4.0(19)
C20	21(2)	39(3)	22(2)	-4(2)	1.2(19)	-9(2)
C14	32(2)	26(2)	14(2)	3.3(18)	2.9(19)	2(2)
C7	19(2)	27(2)	17(2)	-6.6(18)	6(2)	-4.7(18)
C22	54(3)	20(3)	38(3)	8(2)	25(3)	4(2)
C19	21(2)	39(3)	23(2)	0(2)	3.3(19)	4(2)
C5	26(2)	41(3)	19(2)	-6(2)	4(2)	-14(2)
C6	19(2)	36(3)	14(2)	-6(2)	-0.7(18)	-4(2)

Table S39. Bond Lengths for 7-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	N1	2.594(3)	C10	C15	1.412(7)
Bi1	C11	2.256(4)	C10	C9	1.525(6)
Bi1	C2	2.273(4)	C2	C3	1.393(6)
Bi1	C1	2.399(5)	C2	C7	1.400(7)
F1	C1	1.359(5)	C12	C13	1.397(6)
F2	C1	1.380(5)	C23	C24	1.381(8)
F3	C1	1.370(5)	C23	C22	1.394(9)
O1	C20	1.424(6)	C18	C19	1.507(7)
O1	C19	1.437(6)	C24	$C22^1$	1.388(9)
N1	C16	1.480(6)	C15	C14	1.380(7)
N1	C8	1.477(5)	C4	C3	1.389(7)
N1	C9	1.468(5)	C4	C5	1.389(8)

Table S39. Bond Lengths for 7-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C17	1.465(5)	C13	C14	1.382(7)
N2	C18	1.475(5)	C8	C7	1.518(6)
N2	C21	1.462(6)	C21	C20	1.514(7)
C11	C10	1.392(6)	C7	C6	1.384(6)
C11	C12	1.395(6)	C5	C6	1.368(7)
C17	C16	1.528(6)			

[1]-X,2-Y,1-Z

Table S40. Bond Angles for 7-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	Bi1	N1	73.00(13)	N1	C16	C17	114.0(4)
C11	Bi1	C2	97.29(15)	C24	C23	C22	119.9(6)
C11	Bi1	C1	88.81(15)	N2	C18	C19	110.2(4)
C2	Bi1	N1	71.69(14)	C23	C24	C22[1]	120.8(6)
C2	Bi1	C1	90.72(16)	C14	C15	C10	119.8(5)
C1	Bi1	N1	152.32(14)	C3	C4	C5	119.2(5)
C20	O1	C19	110.1(3)	F1	C1	Bi1	111.1(3)
C16	N1	Bi1	114.2(3)	F1	C1	F2	104.0(4)
C8	N1	Bi1	102.6(2)	F1	C1	F3	103.7(4)
C8	N1	C16	109.8(3)	F2	C1	Bi1	119.8(3)
C9	N1	Bi1	106.2(2)	F3	C1	Bi1	113.2(3)
C9	N1	C16	113.3(3)	F3	C1	F2	103.5(4)
C9	N1	C8	110.2(3)	C14	C13	C12	119.3(4)
C17	N2	C18	110.6(3)	C4	C3	C2	120.9(5)
C21	N2	C17	112.0(4)	N1	C8	C7	111.0(4)
C21	N2	C18	108.4(3)	N1	C9	C10	112.5(4)
C10	C11	Bi1	117.6(3)	N2	C21	C20	110.6(4)
C10	C11	C12	119.5(4)	O1	C20	C21	111.2(4)
C12	C11	Bi1	122.6(3)	C15	C14	C13	121.0(4)
N2	C17	C16	113.6(4)	C2	C7	C8	120.0(4)
C11	C10	C15	119.7(4)	C6	C7	C2	120.4(5)
C11	C10	C9	121.6(4)	C6	C7	C8	119.6(5)
C15	C10	C9	118.6(4)	C24[1]	C22	C23	119.3(5)
C3	C2	Bi1	125.1(3)	O1	C19	C18	111.2(4)
C3	C2	C7	118.4(4)	C6	C5	C4	120.6(4)
C7	C2	Bi1	116.5(3)	C5	C6	C7	120.3(5)
C11	C12	C13	120.7(4)				

[1]-X,2-Y,1-Z

Table S41. Torsion Angles for 7-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	N1	C16	C17	-60.1(4)	C12	C13	C14	C15	-0.2(7)
Bi1	N1	C8	C7	44.2(4)	C16	N1	C8	C7	166.0(4)
Bi1	N1	C9	C10	31.7(4)	C16	N1	C9	C10	-94.5(4)
Bi1	C11	C10	C15	-175.1(3)	C18	N2	C17	C16	-162.5(4)
Bi1	C11	C10	C9	8.2(6)	C18	N2	C21	C20	57.3(5)
Bi1	C11	C12	C13	174.1(3)	C24	C23	C22	C24[1]	0.5(10)
Bi1	C2	C3	C4	-179.9(3)	C15	C10	C9	N1	153.3(4)
Bi1	C2	C7	C8	1.0(6)	C4	C5	C6	C7	1.1(7)
Bi1	C2	C7	C6	-178.7(4)	C3	C2	C7	C8	-177.3(4)
N1	C8	C7	C2	-35.3(6)	C3	C2	C7	C6	3.0(7)
N1	C8	C7	C6	144.4(4)	C3	C4	C5	C6	0.1(7)
N2	C17	C16	N1	65.4(5)	C8	N1	C16	C17	-174.6(4)
N2	C18	C19	O1	58.5(5)	C8	N1	C9	C10	142.1(4)
N2	C21	C20	O1	-58.5(5)	C8	C7	C6	C5	177.6(4)
C11	C10	C15	C14	1.5(7)	C9	N1	C16	C17	61.7(5)
C11	C10	C9	N1	-30.0(6)	C9	N1	C8	C7	-68.5(5)
C11	C12	C13	C14	-0.1(7)	C9	C10	C15	C14	178.2(4)
C17	N2	C18	C19	179.4(4)	C21	N2	C17	C16	76.4(5)
C17	N2	C21	C20	179.6(4)	C21	N2	C18	C19	-57.4(5)
C10	C11	C12	C13	1.1(7)	C20	O1	C19	C18	-58.0(5)
C10	C15	C14	C13	-0.5(7)	C7	C2	C3	C4	-1.7(7)
C2	C7	C6	C5	-2.7(7)	C22	C23	C24	C22[1]	-0.5(10)
C12	C11	C10	C15	-1.8(7)	C19	O1	C20	C21	57.7(5)
C12	C11	C10	C9	-178.4(4)	C5	C4	C3	C2	0.2(7)

[1]-X,2-Y,1-Z

Table S42. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H17A	3433.27	2150.24	7663.71	24
H17B	3809.15	3219.3	8060.02	24
H12	1812.47	6438.54	7521.42	22
H16A	5499.66	2592.02	7288.83	27
H16B	4486.92	2654.46	6521.42	27
H23	1665.62	9227.69	5820.75	43
H18A	1789.09	3938.52	8203.27	26
H18B	1196.93	2825.41	8045.99	26

Table S42. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7-CF_3.

Atom	*x*	*y*	*z*	U(eq)
H24	2008.43	10826.01	5303.56	44
H15	5329.24	5072.31	9127.21	26
H4	6928.55	7687.3	5245.29	35
H13	1959.29	6720.04	8884.96	27
H3	4804.93	7177.37	5515.81	27
H8A	5924.42	3594.79	5896.89	24
H8B	7026.56	3789.38	6608.66	24
H9A	6349.47	5013.99	7529.05	21
H9B	5964.48	4049.85	8030.34	21
H21A	1526.85	1980.57	6809.53	27
H21B	2323.98	2545.08	6163.22	27
H20A	630.25	3762.33	5970.54	33
H20B	23.25	2654.07	5817.19	33
H14	3718.34	6033.62	9674.46	29
H22	-362.7	8395.85	5527.48	43
H19A	-498.21	4032.58	7826.54	33
H19B	322.73	4597.27	7192.06	33
H5	8709.08	6573.67	5489.35	34
H6	8381.82	4983.24	6002.55	28

Table S43. Crystal data and structure refinement for C-CF_3.

Identification code	hyvl02_0m
Empirical formula	$C_{31}H_{46}BiF_3$
Formula weight	684.66
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.9497(8)
b/Å	17.0078(11)
c/Å	13.8407(10)
α/°	90
β/°	98.688(2)
γ/°	90
Volume/Å^3	3013.4(3)
Z	4
ρ_{calc}g/cm^3	1.509
μ/mm^{-1}	5.886
F(000)	1368.0
Crystal size/mm^3	0.29 × 0.27 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.82 to 54.314
Index ranges	-14 ≤ h ≤ 16, -20 ≤ k ≤ 21, -17 ≤ l ≤ 17
Reflections collected	20579
Independent reflections	6673 [R_{int} = 0.0660, R_{sigma} = 0.0746]
Data/restraints/parameters	6673/0/328
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.0933
Final R indexes [all data]	R_1 = 0.0480, wR_2 = 0.0990
Largest diff. peak/hole / e Å^{-3}	1.26/-0.75

Table S44. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for C-CF_3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	5949.7(2)	3179.3(2)	3445.8(2)	12.49(7)
F2	6223(2)	3294.7(15)	1271(2)	24.6(6)
F3	6452(2)	2120.8(15)	1838(2)	26.3(6)
F1	7729(2)	2946.1(18)	2013(2)	28.3(6)
C29	8631(3)	2742(2)	4276(3)	14.6(9)
C1	6820(3)	4187(2)	4306(3)	13.0(8)
C7	6003(3)	3653(2)	5767(3)	15.1(9)

Table S44. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for C-CF$_3$. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
C2	6670(3)	4233(2)	5291(3)	13.3(8)
C3	7130(3)	4859(2)	5856(3)	15.3(9)
C21	8315(3)	1486(2)	5120(3)	13.7(8)
C17	6795(3)	2179(2)	4331(3)	9.9(8)
C26	8174(3)	178(2)	5975(3)	14.5(9)
C6	7381(3)	4768(2)	3894(3)	13.6(8)
C9	4947(3)	4021(3)	5879(3)	22.4(10)
C31	9148(4)	3208(2)	5165(4)	22.0(11)
C23	4956(3)	1641(3)	4455(3)	17.0(9)
C5	7824(3)	5373(2)	4491(3)	14.8(9)
C16	6712(3)	2889(2)	2052(3)	16.2(9)
C18	6152(3)	1598(2)	4667(3)	11.4(8)
C10	8185(3)	6135(3)	6065(3)	18.2(9)
C30	9445(3)	2380(3)	3716(3)	20.4(10)
C22	7878(3)	2129(2)	4561(3)	12.6(8)
C19	6622(3)	965(2)	5203(3)	13.2(8)
C4	7715(3)	5438(2)	5468(3)	13.4(8)
C25	4427(3)	1379(3)	5317(4)	25.4(11)
C27	8442(4)	-441(3)	5266(3)	24.1(10)
C20	7704(3)	900(2)	5431(3)	11.5(8)
C8	6553(4)	3318(3)	6737(4)	28.2(12)
C24	4538(4)	1179(3)	3537(4)	29.3(12)
C13	7523(4)	4773(2)	2823(3)	19.2(9)
C15	7043(4)	5511(3)	2301(3)	23.7(10)
C11	8483(4)	5975(3)	7143(3)	26.9(11)
C12	7431(5)	6840(3)	5898(5)	38.9(16)
C14	8672(4)	4704(3)	2697(4)	30.5(12)
C28	9139(3)	373(3)	6728(3)	23.8(11)

Table S45. Anisotropic Displacement Parameters (Å^2×10^3) for C-CF$_3$. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Bi1	11.88(11)	9.96(11)	15.38(11)	1.74(6)	1.32(7)	0.09(5)
F2	36.3(17)	24.1(14)	13.1(14)	6.0(11)	2.7(12)	7.1(12)
F3	41.6(17)	11.0(12)	25.9(15)	-3.0(11)	3.5(12)	0.4(12)
F1	19.2(15)	42.8(16)	24.2(16)	-7.8(13)	7.4(11)	0.3(13)
C29	15(2)	11(2)	18(2)	1.0(16)	2.8(16)	-0.6(17)

Table S45. Anisotropic Displacement Parameters ($Å^2×10^3$) for C-CF_3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	10(2)	10.6(19)	18(2)	-2.6(16)	2.5(16)	1.4(16)
C7	18(2)	12(2)	17(2)	1.2(17)	6.2(17)	1.2(17)
C2	11(2)	14(2)	17(2)	4.4(16)	6.7(16)	4.1(16)
C3	18(2)	14(2)	15(2)	2.7(17)	5.1(17)	2.7(17)
C21	14(2)	12(2)	15(2)	0.3(17)	3.1(16)	-2.1(17)
C17	14(2)	5.7(18)	11(2)	2.9(15)	6.5(15)	0.8(16)
C26	13(2)	15(2)	17(2)	4.7(17)	5.1(16)	-0.6(17)
C6	14(2)	13(2)	14(2)	2.8(16)	4.6(16)	-0.1(16)
C9	20(2)	22(2)	25(3)	0.6(19)	2.5(19)	-4.9(19)
C31	19(3)	19(2)	27(3)	-6.7(18)	2(2)	-6.7(17)
C23	14(2)	14(2)	22(2)	0.3(18)	-0.3(17)	-2.5(17)
C5	17(2)	10.1(19)	18(2)	2.6(16)	5.5(16)	-3.0(16)
C16	23(2)	12(2)	13(2)	-0.6(17)	0.1(17)	-3.7(18)
C18	11(2)	8.2(18)	15(2)	-4.0(16)	1.8(15)	-0.3(16)
C10	18(2)	21(2)	16(2)	-3.7(18)	6.0(17)	-9.5(18)
C30	17(2)	15(2)	31(3)	1.2(19)	10.8(19)	-0.9(18)
C22	15(2)	6.3(18)	17(2)	-2.9(16)	4.3(16)	-0.5(16)
C19	14(2)	11.9(19)	14(2)	0.2(16)	4.0(16)	-3.3(16)
C4	12(2)	14(2)	14(2)	3.5(17)	1.1(15)	-0.1(17)
C25	15(2)	32(3)	32(3)	8(2)	12(2)	0(2)
C27	30(3)	16(2)	27(3)	3.0(19)	7(2)	8(2)
C20	14(2)	10.6(19)	10(2)	-0.5(16)	2.7(15)	1.7(16)
C8	24(3)	32(3)	30(3)	17(2)	9(2)	1(2)
C24	21(3)	32(3)	33(3)	-1(2)	-4(2)	-4(2)
C13	25(2)	13(2)	21(2)	-3.6(17)	9.2(19)	-5.2(18)
C15	37(3)	21(2)	13(2)	1.7(19)	2.5(19)	-9(2)
C11	30(3)	27(3)	22(3)	0(2)	-1(2)	-13(2)
C12	52(4)	15(3)	42(4)	-10(2)	-18(3)	2(2)
C14	31(3)	35(3)	31(3)	-6(2)	21(2)	-7(2)
C28	16(2)	31(3)	23(3)	12(2)	-2.3(18)	0.1(19)

Table S46. Bond Lengths for C-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	C1	2.284(4)	C17	C18	1.415(6)
Bi1	C17	2.278(4)	C17	C22	1.392(6)
Bi1	C16	2.349(4)	C26	C27	1.514(6)
F2	C16	1.356(5)	C26	C20	1.519(5)

Table S46. Bond Lengths for C-CF_3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F3	C16	1.370(5)	C26	C28	1.538(6)
F1	C16	1.330(5)	C6	C5	1.388(6)
C29	C31	1.530(6)	C6	C13	1.521(6)
C29	C30	1.530(6)	C23	C18	1.534(6)
C29	C22	1.520(6)	C23	C25	1.528(6)
C1	C2	1.407(6)	C23	C24	1.522(6)
C1	C6	1.399(6)	C5	C4	1.386(6)
C7	C2	1.525(6)	C18	C19	1.395(5)
C7	C9	1.533(6)	C10	C4	1.519(6)
C7	C8	1.532(6)	C10	C11	1.508(6)
C2	C3	1.400(6)	C10	C12	1.541(7)
C3	C4	1.397(6)	C19	C20	1.393(6)
C21	C22	1.408(6)	C13	C15	1.534(6)
C21	C20	1.381(6)	C13	C14	1.529(6)

Table S47. Bond Angles for C-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Bi1	C16	110.53(15)	C24	C23	C25	110.9(4)
C17	Bi1	C1	96.93(16)	C4	C5	C6	123.1(4)
C17	Bi1	C16	93.29(14)	F2	C16	Bi1	110.2(3)
C31	C29	C30	111.4(4)	F2	C16	F3	104.1(3)
C22	C29	C31	111.5(4)	F3	C16	Bi1	104.9(3)
C22	C29	C30	111.9(3)	F1	C16	Bi1	124.0(3)
C2	C1	Bi1	114.7(3)	F1	C16	F2	106.1(3)
C6	C1	Bi1	124.3(3)	F1	C16	F3	105.9(3)
C6	C1	C2	120.8(4)	C17	C18	C23	122.1(4)
C2	C7	C9	110.6(3)	C19	C18	C17	118.9(4)
C2	C7	C8	113.7(4)	C19	C18	C23	119.0(4)
C8	C7	C9	111.5(4)	C4	C10	C12	109.5(4)
C1	C2	C7	123.5(4)	C11	C10	C4	114.8(4)
C3	C2	C1	118.3(4)	C11	C10	C12	110.5(4)
C3	C2	C7	118.1(4)	C21	C22	C29	117.0(4)
C4	C3	C2	122.0(4)	C17	C22	C29	124.2(4)
C20	C21	C22	122.0(4)	C17	C22	C21	118.8(4)
C18	C17	Bi1	116.0(3)	C18	C19	C20	121.7(4)
C22	C17	Bi1	123.7(3)	C3	C4	C10	122.4(4)
C22	C17	C18	120.3(4)	C5	C4	C3	117.4(4)
C27	C26	C20	110.9(3)	C5	C4	C10	120.1(4)

Table S47. Bond Angles for C-CF_3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C27	C26	C28	110.3(4)	C21	C20	C26	122.1(4)
C20	C26	C28	112.6(4)	C21	C20	C19	118.5(4)
C1	C6	C13	123.2(4)	C19	C20	C26	119.4(4)
C5	C6	C1	118.3(4)	C6	C13	C15	111.3(4)
C5	C6	C13	118.5(4)	C6	C13	C14	112.0(4)
C25	C23	C18	113.3(4)	C14	C13	C15	110.0(4)
C24	C23	C18	110.8(4)				

Table S48. Torsion Angles for C-CF_3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	C1	C2	C7	1.3(5)	C5	C6	C13	C14	62.6(5)
Bi1	C1	C2	C3	-176.6(3)	C18	C17	C22	C29	-177.0(4)
Bi1	C1	C6	C5	176.4(3)	C18	C17	C22	C21	0.9(6)
Bi1	C1	C6	C13	-3.2(6)	C18	C19	C20	C21	0.5(6)
Bi1	C17	C18	C23	-0.4(5)	C18	C19	C20	C26	-177.1(4)
Bi1	C17	C18	C19	179.2(3)	C30	C29	C22	C21	56.5(5)
Bi1	C17	C22	C29	1.6(6)	C30	C29	C22	C17	-125.5(4)
Bi1	C17	C22	C21	179.5(3)	C22	C21	C20	C26	175.8(4)
C1	C2	C3	C4	0.8(6)	C22	C21	C20	C19	-1.7(6)
C1	C6	C5	C4	-1.6(6)	C22	C17	C18	C23	178.3(4)
C1	C6	C13	C15	118.6(4)	C22	C17	C18	C19	-2.1(6)
C1	C6	C13	C14	-117.8(5)	C25	C23	C18	C17	-141.0(4)
C7	C2	C3	C4	-177.2(4)	C25	C23	C18	C19	39.4(5)
C2	C1	C6	C5	2.7(6)	C27	C26	C20	C21	-83.6(5)
C2	C1	C6	C13	-176.9(4)	C27	C26	C20	C19	93.8(5)
C2	C3	C4	C5	0.3(6)	C20	C21	C22	C29	179.1(4)
C2	C3	C4	C10	177.8(4)	C20	C21	C22	C17	1.0(6)
C17	C18	C19	C20	1.3(6)	C8	C7	C2	C1	130.2(4)
C6	C1	C2	C7	175.5(4)	C8	C7	C2	C3	-52.0(5)
C6	C1	C2	C3	-2.3(6)	C24	C23	C18	C17	93.5(5)
C6	C5	C4	C3	0.1(6)	C24	C23	C18	C19	-86.1(5)
C6	C5	C4	C10	-177.4(4)	C13	C6	C5	C4	178.0(4)
C9	C7	C2	C1	-103.4(5)	C11	C10	C4	C3	30.7(6)
C9	C7	C2	C3	74.4(5)	C11	C10	C4	C5	-151.9(4)
C31	C29	C22	C21	-69.0(5)	C12	C10	C4	C3	-94.2(5)
C31	C29	C22	C17	108.9(5)	C12	C10	C4	C5	83.2(5)
C23	C18	C19	C20	-179.0(4)	C28	C26	C20	C21	40.5(5)
C5	C6	C13	C15	-61.0(5)	C28	C26	C20	C19	-142.0(4)

Table S49. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C-CF$_3$.

Atom	*x*	*y*	*z*	U(eq)
H29	8211.18	3122.9	3826.19	18
H7	5854.6	3199.55	5306.98	18
H3	7041.24	4892.39	6523.67	18
H21	9053.02	1453.75	5287.7	16
H26	7633.13	-49.69	6337.57	17
H9A	5061.24	4489.75	6292.64	34
H9B	4527.61	3639.34	6181.19	34
H9C	4577.74	4168.86	5233.62	34
H31A	9603.31	2858.66	5603.44	33
H31B	8607.85	3426.41	5513.14	33
H31C	9563.37	3636.87	4948.89	33
H23	4764.62	2204.59	4322.98	20
H5	8220.69	5760.55	4215.94	18
H10	8837.37	6286.3	5806.72	22
H30A	9830.26	2799.28	3440.88	31
H30B	9094.17	2048.7	3186.08	31
H30C	9932.92	2058.47	4161.93	31
H19	6193.53	567.85	5417.98	16
H25A	4502.54	809.13	5402.09	38
H25B	3683.84	1515.82	5189.35	38
H25C	4756.4	1645.36	5913.22	38
H27A	7831.57	-541.22	4771.39	36
H27B	8646.78	-928.64	5622.67	36
H27C	9022.5	-255.1	4946.98	36
H8A	7166.14	3014.81	6621.76	42
H8B	6070.08	2973.56	7020.64	42
H8C	6772.93	3749.61	7190.17	42
H24A	4826.28	1397.33	2979.36	44
H24B	3774.45	1216.32	3414.71	44
H24C	4745.28	626.66	3627.07	44
H13	7146.93	4305.6	2502.34	23
H15A	6285.66	5510.03	2299.6	36
H15B	7187.13	5516.02	1625.93	36
H15C	7348.06	5980.3	2643.3	36
H11A	7851.57	5870.85	7433.37	40
H11B	8845.5	6434.06	7460.4	40

Table S49. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C-CF$_3$.

Atom	*x*	*y*	*z*	U(eq)
H11C	8945.33	5516.43	7235.97	40
H12A	7279.09	6955.93	5197.56	58
H12B	7754.31	7299.95	6247.08	58
H12C	6779.76	6711.25	6143.47	58
H14A	9048.07	5177.03	2956.07	46
H14B	8725.12	4649.47	2000.8	46
H14C	8980.24	4241.38	3051.63	46
H28A	9382.2	-103.33	7090.23	36
H28B	8953.63	771.62	7184.05	36
H28C	9695.8	576.67	6389.85	36

Table S50. Crystal data and structure refinement for 3-F.

Identification code	hyvl100_0m_a
Empirical formula	$C_{14}H_{12}BiFS$
Formula weight	440.28
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.7248(7)
b/Å	8.8059(5)
c/Å	12.0826(7)
α/°	90
β/°	95.804(2)
γ/°	90
Volume/Å^3	1241.10(13)
Z	4
ρ_{calc}g/cm^3	2.356
μ/mm^{-1}	14.359
F(000)	816.0
Crystal size/mm^3	0.29 × 0.28 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.614 to 54.448
Index ranges	$-15 \leq h \leq 14$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$
Reflections collected	11106
Independent reflections	2772 [R_{int} = 0.0580, R_{sigma} = 0.0507]
Data/restraints/parameters	2772/0/154
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0325, wR_2 = 0.0809
Final R indexes [all data]	R_1 = 0.0350, wR_2 = 0.0826
Largest diff. peak/hole / e Å^{-3}	2.24/-1.21

Table S51. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3-F. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	3275.7(2)	6801.7(2)	8046.7(2)	11.0(1)
S1	5441.9(12)	8336.9(14)	8361.0(12)	14.8(3)
F1	2090(3)	5040(4)	7429(3)	18.2(7)
C1	3837(5)	6980(6)	6324(4)	12.4(10)
C2	3331(4)	6042(6)	5484(4)	14.5(10)
C3	3712(5)	6067(6)	4429(4)	16.9(11)
C4	4616(5)	7018(7)	4202(5)	18.7(12)

Table S51. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3-F. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C5	5108(5)	7959(6)	5042(5)	16.4(11)
C6	4726(5)	7958(6)	6098(5)	13.7(11)
C7	5233(4)	9093(6)	6962(4)	13.5(10)
C8	6310(5)	6653(6)	8186(6)	18.0(12)
C9	5770(4)	5165(6)	8498(4)	12.1(10)
C10	6501(5)	3945(6)	8753(5)	17.3(11)
C11	6084(5)	2511(7)	8972(4)	17.0(11)
C12	4918(5)	2308(6)	8948(4)	15.2(11)
C13	4174(5)	3517(6)	8729(4)	13.2(10)
C14	4586(4)	4957(6)	8481(4)	10.5(10)

Table S52. Anisotropic Displacement Parameters (Å^2×10^3) for 3-F. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	9.68(13)	11.20(14)	12.80(14)	0.93(6)	4.46(8)	0.87(6)
S1	17.4(7)	12.2(6)	14.7(7)	-1.7(5)	1.8(5)	-1.6(5)
F1	13.9(15)	14.3(16)	25.9(17)	4.6(13)	-1.3(13)	-6.6(12)
C1	13(2)	16(3)	9(2)	0.8(19)	3.8(19)	4.6(19)
C2	13(2)	16(3)	14(2)	0(2)	0.1(19)	2(2)
C3	22(3)	12(3)	15(3)	-2(2)	-3(2)	6(2)
C4	18(3)	26(3)	13(3)	2(2)	4(2)	7(2)
C5	18(3)	16(3)	16(3)	4(2)	7(2)	5(2)
C6	15(3)	13(2)	13(3)	6(2)	1(2)	6(2)
C7	13(2)	12(2)	17(3)	1(2)	7.8(19)	-2.0(19)
C8	14(3)	10(3)	30(3)	0(2)	1(2)	-1.4(19)
C9	10(2)	16(3)	10(2)	-1(2)	3.2(18)	-1.3(19)
C10	16(3)	17(3)	20(3)	4(2)	3(2)	2(2)
C11	17(3)	17(3)	18(3)	6(2)	5(2)	7(2)
C12	27(3)	7(2)	12(3)	4(2)	1(2)	-3(2)
C13	15(2)	16(2)	9(2)	1(2)	4.4(19)	-3(2)
C14	10(2)	11(2)	11(2)	-2.9(19)	2.3(18)	1.8(18)

Table S53. Bond Lengths for 3-F.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	S1	2.8683(14)	C4	C5	1.390(8)
Bi1	F1	2.165(3)	C5	C6	1.394(8)
Bi1	C1	2.251(5)	C6	C7	1.522(7)

Table S53. Bond Lengths for 3-F.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	C14	2.261(5)	C8	C9	1.520(7)
S1	C7	1.810(5)	C9	C10	1.389(7)
S1	C8	1.823(6)	C9	C14	1.399(7)
C1	C2	1.394(7)	C10	C11	1.388(8)
C1	C6	1.401(8)	C11	C12	1.376(8)
C2	C3	1.392(8)	C12	C13	1.385(8)
C3	C4	1.399(8)	C13	C14	1.400(7)

Table S54. Bond Angles for 3-F.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	Bi1	S1	155.86(9)	C1	C6	C7	121.2(5)
F1	Bi1	C1	88.20(17)	C5	C6	C1	119.5(5)
F1	Bi1	C14	87.86(16)	C5	C6	C7	119.2(5)
C1	Bi1	S1	75.64(14)	C6	C7	S1	113.9(4)
C1	Bi1	C14	90.55(18)	C9	C8	S1	114.9(4)
C14	Bi1	S1	74.71(13)	C10	C9	C8	117.4(5)
C7	S1	Bi1	90.89(17)	C10	C9	C14	119.4(5)
C7	S1	C8	102.4(3)	C14	C9	C8	123.2(5)
C8	S1	Bi1	95.66(18)	C11	C10	C9	121.6(5)
C2	C1	Bi1	119.3(4)	C12	C11	C10	118.8(5)
C2	C1	C6	119.5(5)	C11	C12	C13	120.7(5)
C6	C1	Bi1	121.1(4)	C12	C13	C14	120.8(5)
C3	C2	C1	120.3(5)	C9	C14	Bi1	124.0(4)
C2	C3	C4	120.5(5)	C9	C14	C13	118.6(5)
C5	C4	C3	118.7(5)	C13	C14	Bi1	117.4(4)
C4	C5	C6	121.3(6)				

Table S55. Torsion Angles for 3-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	S1	C7	C6	-41.4(4)	C5	C6	C7	S1	-142.3(4)
Bi1	S1	C8	C9	-27.5(4)	C6	C1	C2	C3	0.5(8)
Bi1	C1	C2	C3	-176.1(4)	C7	S1	C8	C9	-119.7(4)
Bi1	C1	C6	C5	175.3(4)	C8	S1	C7	C6	54.6(4)
Bi1	C1	C6	C7	-8.6(7)	C8	C9	C10	C11	-175.4(5)
S1	C8	C9	C10	-158.4(4)	C8	C9	C14	Bi1	-2.1(7)
S1	C8	C9	C14	25.1(7)	C8	C9	C14	C13	176.8(5)
C1	C2	C3	C4	0.8(8)	C9	C10	C11	C12	-0.8(8)
C1	C6	C7	S1	41.6(6)	C10	C9	C14	Bi1	-178.6(4)

Table S55. Torsion Angles for 3-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	C6	C5	-1.3(8)	C10	C9	C14	C13	0.3(7)
C2	C1	C6	C7	174.8(5)	C10	C11	C12	C13	-1.2(8)
C2	C3	C4	C5	-1.4(8)	C11	C12	C13	C14	2.8(8)
C3	C4	C5	C6	0.6(8)	C12	C13	C14	Bi1	176.7(4)
C4	C5	C6	C1	0.7(8)	C12	C13	C14	C9	-2.3(8)
C4	C5	C6	C7	-175.5(5)	C14	C9	C10	C11	1.2(8)

Table 56. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3-F.

Atom	*x*	*y*	*z*	U(eq)
H2	2722.78	5382.98	5631.28	17
H3	3355.1	5433.89	3859.01	20
H4	4887.4	7020.52	3487.8	22
H5	5717.12	8616.11	4894.01	20
H7A	4718.95	9985.42	6957.74	16
H7B	5981.07	9448.07	6746.91	16
H8A	6471.34	6593.78	7398.29	22
H8B	7052.98	6773.58	8644.78	22
H10	7305.3	4094.41	8778.19	21
H11	6595.02	1685.88	9136.25	20
H12	4620.93	1329.2	9081.64	18
H13	3373.59	3367.48	8748.37	16

Table S57. Crystal data and structure refinement for 6-F.

Identification code	hyvl101_0ma_a
Empirical formula	$C_{15}H_{15}BiFNO$
Formula weight	453.26
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.847(2)
b/Å	14.652(3)
c/Å	9.803(3)
α/°	90
β/°	104.388(8)
γ/°	90
Volume/Å^3	1369.9(6)
Z	4
ρ_{calc}g/cm^3	2.198
μ/mm^{-1}	12.872
F(000)	848.0
Crystal size/mm^3	0.3 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.27 to 54.192
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 18, -6 ≤ l ≤ 12
Reflections collected	4678
Independent reflections	2861 [R_{int} = 0.0501, R_{sigma} = 0.0798]
Data/restraints/parameters	2861/0/173
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.1137
Largest diff. peak/hole / e Å^{-3}	2.44/-1.51

Table S58. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 6-F. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	3217.5(3)	7395.0(2)	8199.8(3)	11.23(13)
F1	3202(4)	8761(3)	7470(5)	18.6(10)
O1	2809(5)	4930(3)	8477(5)	15.2(11)
N1	3386(6)	5632(4)	7735(6)	11.3(12)
C1	1620(7)	7029(5)	6190(7)	12.4(14)
C2	671(8)	7712(5)	5542(9)	13.7(16)
C3	-298(8)	7495(5)	4271(9)	15.1(17)

Table S58. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 6-F. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C4	-315(7)	6632(6)	3686(8)	21.6(18)
C5	641(7)	5973(5)	4351(7)	14.1(15)
C6	1631(7)	6185(5)	5599(7)	10.1(14)
C7	2757(7)	5481(5)	6215(7)	15.6(16)
C8	4935(7)	5475(5)	8081(8)	14.1(15)
C9	5581(7)	6212(5)	7386(7)	11.1(14)
C10	6692(7)	5983(6)	6818(7)	17.2(17)
C11	7308(7)	6652(5)	6148(8)	17.8(16)
C12	6788(9)	7541(5)	6045(9)	16.0(17)
C13	5695(7)	7762(5)	6637(8)	14.1(15)
C14	5072(7)	7086(5)	7317(7)	13.1(15)
C15	1922(8)	5332(5)	9253(8)	21.0(18)

Table S59. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 6-F. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	12.0(2)	9.54(19)	11.96(19)	-1.39(9)	2.64(12)	-0.36(9)
F1	26(2)	6(2)	25(2)	1.9(18)	9.7(18)	-1.8(17)
O1	19(3)	14(3)	17(3)	5(2)	12(2)	-1(2)
N1	16(3)	10(3)	10(3)	4(2)	7(2)	1(2)
C1	16(4)	12(4)	11(3)	4(3)	7(3)	-4(3)
C2	8(4)	11(4)	23(4)	-5(3)	6(3)	-2(3)
C3	5(4)	23(4)	17(4)	11(3)	2(3)	-1(3)
C4	14(4)	33(5)	17(4)	9(3)	3(3)	-4(3)
C5	19(4)	14(4)	12(4)	2(3)	8(3)	-6(3)
C6	12(3)	9(3)	11(3)	3(3)	7(3)	-4(3)
C7	17(4)	16(4)	14(4)	-11(3)	5(3)	-4(3)
C8	9(3)	14(4)	20(4)	3(3)	6(3)	3(3)
C9	10(3)	12(4)	9(3)	-1(3)	-2(2)	1(3)
C10	12(4)	24(5)	14(4)	-2(3)	1(3)	0(3)
C11	16(4)	16(4)	23(4)	-3(3)	8(3)	-1(3)
C12	26(5)	15(4)	8(4)	-2(3)	7(3)	-15(3)
C13	10(4)	12(4)	20(4)	1(3)	3(3)	0(3)
C14	10(3)	13(4)	16(4)	-3(3)	3(3)	-1(3)
C15	26(4)	13(4)	30(5)	1(3)	18(3)	4(3)

Table S60. Bond Lengths for 6-F.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	F1	2.124(4)	C3	C4	1.387(11)
Bi1	N1	2.635(6)	C4	C5	1.392(10)
Bi1	C1	2.259(7)	C5	C6	1.397(9)
Bi1	C14	2.252(8)	C6	C7	1.524(9)
O1	N1	1.454(7)	C8	C9	1.500(10)
O1	C15	1.421(8)	C9	C10	1.387(10)
N1	C7	1.481(8)	C9	C14	1.371(10)
N1	C8	1.496(8)	C10	C11	1.399(11)
C1	C2	1.407(10)	C11	C12	1.394(10)
C1	C6	1.367(10)	C12	C13	1.381(12)
C2	C3	1.405(11)	C13	C14	1.415(11)

Table S61. Bond Angles for 6-F.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	Bi1	N1	149.43(18)	C3	C4	C5	120.1(7)
F1	Bi1	C1	89.1(2)	C4	C5	C6	120.0(7)
F1	Bi1	C14	89.9(2)	C1	C6	C5	119.6(6)
C1	Bi1	N1	71.1(2)	C1	C6	C7	121.8(6)
C14	Bi1	N1	69.2(2)	C5	C6	C7	118.5(6)
C14	Bi1	C1	94.2(2)	N1	C7	C6	112.2(6)
C15	O1	N1	110.0(5)	N1	C8	C9	108.1(5)
O1	N1	Bi1	123.9(4)	C10	C9	C8	118.3(7)
O1	N1	C7	106.3(5)	C14	C9	C8	120.3(7)
O1	N1	C8	106.3(5)	C14	C9	C10	121.5(7)
C7	N1	Bi1	106.9(4)	C9	C10	C11	119.7(8)
C7	N1	C8	110.6(6)	C12	C11	C10	119.6(8)
C8	N1	Bi1	102.5(4)	C13	C12	C11	120.0(7)
C2	C1	Bi1	117.7(5)	C12	C13	C14	120.5(7)
C6	C1	Bi1	120.4(5)	C9	C14	Bi1	119.3(6)
C6	C1	C2	121.8(7)	C9	C14	C13	118.7(7)
C3	C2	C1	117.9(7)	C13	C14	Bi1	121.9(6)
C4	C3	C2	120.5(7)				

Table S62. Torsion Angles for 6-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	N1	C7	C6	-28.8(6)	C6	C1	C2	C3	1.3(11)
Bi1	N1	C8	C9	-46.2(6)	C7	N1	C8	C9	67.5(7)
Bi1	C1	C2	C3	178.2(6)	C8	N1	C7	C6	-139.7(6)

Table S62. Torsion Angles for 6-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	C1	C6	C5	-179.6(5)	C8	C9	C10	C11	179.3(6)
Bi1	C1	C6	C7	-3.5(9)	C8	C9	C14	Bi1	-1.8(8)
O1	N1	C7	C6	105.3(6)	C8	C9	C14	C13	-179.2(6)
O1	N1	C8	C9	-177.6(5)	C9	C10	C11	C12	-0.6(10)
N1	C8	C9	C10	-142.2(6)	C10	C9	C14	Bi1	178.0(5)
N1	C8	C9	C14	37.6(9)	C10	C9	C14	C13	0.6(10)
C1	C2	C3	C4	0.4(12)	C10	C11	C12	C13	1.7(11)
C1	C6	C7	N1	24.8(10)	C11	C12	C13	C14	-1.7(11)
C2	C1	C6	C5	-2.8(11)	C12	C13	C14	Bi1	-176.8(6)
C2	C1	C6	C7	173.3(7)	C12	C13	C14	C9	0.5(10)
C2	C3	C4	C5	-0.6(12)	C14	C9	C10	C11	-0.5(10)
C3	C4	C5	C6	-0.9(11)	C15	O1	N1	Bi1	11.6(6)
C4	C5	C6	C1	2.5(11)	C15	O1	N1	C7	-112.6(6)
C4	C5	C6	C7	-173.7(7)	C15	O1	N1	C8	129.5(6)
C5	C6	C7	N1	-159.1(6)					

Table S63. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 6-F.

Atom	*x*	*y*	*z*	U(eq)
H2	684.99	8300.21	5952.11	16
H3	-947.37	7943.6	3807.3	18
H4	-979.32	6490.3	2830.34	26
H5	619.98	5379.61	3956.43	17
H7A	2338.52	4863.19	6078.71	19
H7B	3503.27	5510.11	5701.11	19
H8A	5139.78	4869.09	7732.34	17
H8B	5326.67	5493.49	9113.27	17
H10	7034.12	5373.82	6883.97	21
H11	8075.98	6500.95	5764.47	21
H12	7183.9	7994.22	5569.33	19
H13	5359.5	8371.61	6587.21	17
H15A	1173.01	5674.46	8611.95	32
H15B	2472.14	5747.3	9963.56	32
H15C	1509.92	4852.5	9719.93	32

Table S64. Crystal data and structure refinement for 7-F.

Identification code	hyvl001
Empirical formula	$C_{20}H_{24}BiFN_2O$
Formula weight	536.39
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.1835(3)
b/Å	16.0674(6)
c/Å	14.7898(6)
α/°	90
β/°	105.9510(10)
γ/°	90
Volume/Å^3	1869.80(12)
Z	4
ρ_{calc}g/cm^3	1.905
μ/mm^{-1}	18.668
F(000)	1032.0
Crystal size/mm^3	0.105 × 0.103 × 0.072
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.302 to 136.474
Index ranges	$-9 \leq h \leq 9$, $-14 \leq k \leq 19$, $-16 \leq l \leq 17$
Reflections collected	22526
Independent reflections	3318 [R_{int} = 0.0350, R_{sigma} = 0.0231]
Data/restraints/parameters	3318/0/227
Goodness-of-fit on F^2	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0194, wR_2 = 0.0484
Final R indexes [all data]	R_1 = 0.0195, wR_2 = 0.0485
Largest diff. peak/hole / e Å^{-3}	0.66/-0.59

Table S65. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-F. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Bi1	5346.3(2)	3535.5(2)	5070.3(2)	41.88(8)
F1	3817(4)	3528.3(14)	6038.4(16)	71.2(7)
O1	10357(4)	1753(2)	6468(3)	94.3(12)
N1	5701(4)	3443.0(16)	3395.4(19)	41.5(6)
N2	8374(3)	2307.3(17)	4674(2)	47.0(6)
C1	3326(4)	4326.2(19)	4103(2)	45.1(7)
C2	1864(5)	4597(2)	4320(3)	57.8(9)

Table S65. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 7-F. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C3	693(5)	5096(2)	3690(4)	71.6(13)
C4	993(5)	5339(3)	2861(4)	72.3(12)
C5	2430(5)	5072(2)	2637(3)	60.5(10)
C6	3605(4)	4567(2)	3258(2)	46.2(7)
C7	5185(5)	4286(2)	3015(2)	50.9(8)
C8	4266(4)	2309.4(18)	4501(2)	36.4(6)
C9	3906(4)	1688(2)	5071(2)	42.8(7)
C10	3505(4)	891(2)	4725(3)	51.2(8)
C11	3433(5)	712(2)	3804(3)	52.3(8)
C12	3765(5)	1326(2)	3225(2)	46.2(8)
C13	4184(4)	2124.0(19)	3565(2)	37.7(6)
C14	4440(4)	2811(2)	2915(2)	44.9(7)
C15	7427(5)	3264(3)	3309(3)	59.2(9)
C16	8117(5)	2418(3)	3661(3)	61.1(10)
C17	8606(5)	1429(2)	4911(3)	59.6(10)
C18	8935(6)	1302(3)	5949(3)	74.5(13)
C19	10113(6)	2617(3)	6257(4)	85.1(15)
C20	9845(5)	2772(3)	5232(3)	66.3(11)

Table S66. Anisotropic Displacement Parameters (Å^2×10^3) for 7-F. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi1	54.46(11)	37.71(11)	31.73(9)	-3.02(4)	8.93(6)	-13.90(5)
F1	99.2(18)	79.3(17)	45.6(12)	-9.2(10)	37.6(13)	-24.9(12)
O1	89(2)	60.9(18)	99(2)	17.4(18)	-32.5(19)	-3.4(17)
N1	49.6(15)	40.1(15)	36.9(14)	6.4(11)	15.3(12)	-2.7(11)
N2	40.5(13)	39.7(15)	59.6(17)	5.0(13)	11.9(12)	-1.9(11)
C1	53.2(17)	29.8(16)	52.0(18)	-4.8(14)	13.8(14)	-9.6(13)
C2	62(2)	38.4(19)	80(3)	-11.8(18)	31.0(19)	-14.6(16)
C3	51(2)	48(2)	115(4)	-20(2)	21(2)	-7.5(17)
C4	60(2)	51(2)	90(3)	-7(2)	-6(2)	3.9(18)
C5	74(2)	43(2)	55(2)	2.7(16)	1.3(18)	-1.4(18)
C6	53.8(18)	32.3(16)	48.1(18)	1.0(14)	6.8(14)	-5.5(14)
C7	66(2)	42.9(19)	46.1(18)	12.8(15)	19.2(16)	-2.4(16)
C8	38.1(14)	32.7(15)	36.9(15)	0.7(12)	8.0(12)	-4.1(12)
C9	50.6(17)	38.5(17)	41.4(17)	3.1(14)	16.0(14)	-4.7(14)
C10	56.4(19)	36.8(18)	62(2)	7.4(16)	19.8(16)	-6.6(15)

Table S66. Anisotropic Displacement Parameters ($Å^2×10^3$) for 7-F. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	57.7(19)	34.1(17)	64(2)	-7.1(16)	14.1(16)	-6.1(14)
C12	55.5(19)	38.9(17)	41.0(18)	-6.9(14)	8.1(14)	0.1(14)
C13	42.0(15)	34.5(16)	33.8(14)	-0.5(13)	5.7(12)	-1.5(12)
C14	59.9(19)	42.7(18)	30.5(15)	-1.5(13)	9.8(13)	-1.6(15)
C15	60(2)	65(2)	62(2)	14.6(19)	31.9(18)	2.7(19)
C16	60(2)	64(2)	68(2)	8.7(19)	33.8(19)	12.6(18)
C17	54(2)	44(2)	76(3)	1.1(17)	10.2(19)	-3.5(15)
C18	74(3)	56(2)	79(3)	16(2)	-4(2)	-13(2)
C19	77(3)	56(3)	92(3)	0(2)	-28(2)	-9(2)
C20	45.8(18)	46(2)	99(3)	10(2)	5.3(19)	-5.6(16)

Table S67. Bond Lengths for 7-F.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi1	F1	2.145(2)	C3	C4	1.371(7)
Bi1	N1	2.576(3)	C4	C5	1.375(6)
Bi1	C1	2.257(3)	C5	C6	1.393(5)
Bi1	C8	2.228(3)	C6	C7	1.504(5)
O1	C18	1.407(5)	C8	C9	1.390(4)
O1	C19	1.425(5)	C8	C13	1.398(4)
N1	C7	1.483(4)	C9	C10	1.385(5)
N1	C14	1.483(4)	C10	C11	1.378(5)
N1	C15	1.481(5)	C11	C12	1.381(5)
N2	C16	1.465(5)	C12	C13	1.385(4)
N2	C17	1.454(4)	C13	C14	1.516(4)
N2	C20	1.463(5)	C15	C16	1.509(5)
C1	C2	1.391(5)	C17	C18	1.498(6)
C1	C6	1.385(5)	C19	C20	1.491(7)
C2	C3	1.392(6)			

Table S68. Bond Angles for 7-F.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	Bi1	N1	151.89(10)	C4	C5	C6	120.2(4)
F1	Bi1	C1	88.06(11)	C1	C6	C5	120.2(3)
F1	Bi1	C8	90.23(10)	C1	C6	C7	119.8(3)
C1	Bi1	N1	71.30(10)	C5	C6	C7	120.0(3)
C8	Bi1	N1	73.93(9)	N1	C7	C6	111.0(3)
C8	Bi1	C1	96.47(11)	C9	C8	Bi1	122.3(2)

Table S68. Bond Angles for 7-F.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	O1	C19	109.7(3)	C9	C8	C13	119.1(3)
C7	N1	Bi1	102.51(19)	C13	C8	Bi1	118.0(2)
C14	N1	Bi1	104.65(17)	C10	C9	C8	120.6(3)
C14	N1	C7	110.8(3)	C11	C10	C9	119.9(3)
C15	N1	Bi1	117.2(2)	C10	C11	C12	120.1(3)
C15	N1	C7	108.9(3)	C11	C12	C13	120.5(3)
C15	N1	C14	112.4(3)	C8	C13	C14	119.7(3)
C17	N2	C16	109.7(3)	C12	C13	C8	119.8(3)
C17	N2	C20	109.1(3)	C12	C13	C14	120.4(3)
C20	N2	C16	112.3(3)	N1	C14	C13	113.2(2)
C2	C1	Bi1	123.8(3)	N1	C15	C16	114.8(3)
C6	C1	Bi1	117.1(2)	N2	C16	C15	113.4(3)
C6	C1	C2	119.1(3)	N2	C17	C18	110.7(3)
C1	C2	C3	120.2(4)	O1	C18	C17	112.2(4)
C4	C3	C2	120.2(4)	O1	C19	C20	111.0(4)
C3	C4	C5	120.2(4)	N2	C20	C19	110.9(3)

Table S69. Torsion Angles for 7-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Bi1	N1	C7	C6	-43.9(3)	C7	N1	C15	C16	-179.4(3)
Bi1	N1	C14	C13	-33.8(3)	C8	C9	C10	C11	-1.1(5)
Bi1	N1	C15	C16	65.0(4)	C8	C13	C14	N1	35.2(4)
Bi1	C1	C2	C3	178.9(3)	C9	C8	C13	C12	-0.7(4)
Bi1	C1	C6	C5	-178.5(2)	C9	C8	C13	C14	175.3(3)
Bi1	C1	C6	C7	1.2(4)	C9	C10	C11	C12	0.2(5)
Bi1	C8	C9	C10	-169.3(2)	C10	C11	C12	C13	0.4(5)
Bi1	C8	C13	C12	170.3(2)	C11	C12	C13	C8	-0.2(5)
Bi1	C8	C13	C14	-13.7(4)	C11	C12	C13	C14	-176.1(3)
O1	C19	C20	N2	58.4(5)	C12	C13	C14	N1	-148.9(3)
N1	C15	C16	N2	-64.5(5)	C13	C8	C9	C10	1.3(5)
N2	C17	C18	O1	-57.2(5)	C14	N1	C7	C6	67.2(4)
C1	C2	C3	C4	-1.5(6)	C14	N1	C15	C16	-56.3(4)
C1	C6	C7	N1	33.6(4)	C15	N1	C7	C6	-168.7(3)
C2	C1	C6	C5	-0.2(5)	C15	N1	C14	C13	94.4(3)
C2	C1	C6	C7	179.5(3)	C16	N2	C17	C18	177.9(3)
C2	C3	C4	C5	1.8(6)	C16	N2	C20	C19	-177.6(3)
C3	C4	C5	C6	-1.3(6)	C17	N2	C16	C15	165.3(3)
C4	C5	C6	C1	0.5(5)	C17	N2	C20	C19	-55.8(4)

Table S69. Torsion Angles for 7-F.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C5	C6	C7	-179.2(3)	C18	O1	C19	C20	-58.6(6)
C5	C6	C7	N1	-146.7(3)	C19	O1	C18	C17	58.2(6)
C6	C1	C2	C3	0.7(5)	C20	N2	C16	C15	-73.3(4)
C7	N1	C14	C13	-143.6(3)	C20	N2	C17	C18	54.5(4)

Table S70. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7-F.

Atom	*x*	*y*	*z*	U(eq)
H2	1668.71	4444.56	4887.77	69
H3	-294.98	5264.96	3831.45	86
H4	223.75	5684.43	2450.01	87
H5	2618.05	5228.09	2067.99	73
H7A	4976.94	4279.39	2336.87	61
H7B	6098.67	4676.26	3272.1	61
H9	3935.2	1808.44	5689.98	51
H10	3283.65	476.27	5114.51	61
H11	3159.95	177.12	3570.98	63
H12	3707.95	1203.32	2602.78	55
H14A	4811.64	2565.91	2405.67	54
H14B	3359.43	3084.13	2641.71	54
H15A	8200.1	3684.99	3654.4	71
H15B	7408.57	3311.52	2652.18	71
H16A	7334	1995.03	3328.46	73
H16B	9192.04	2334.77	3517.34	73
H17A	9555.44	1213.48	4708.73	72
H17B	7594.65	1123.04	4581.77	72
H18A	7941.86	1474.48	6138.49	89
H18B	9116.72	713.98	6091.12	89
H19A	11101.3	2924.66	6611.98	102
H19B	9134.45	2813.9	6444.24	102
H20A	9667.72	3361.87	5105.07	80
H20B	10851.26	2604.83	5052.79	80