Electronic Supplementary Material (ESI) for Dalton Transactions.

Exploring Opportunities for Tuning Phenyltris(pyrazol-1-yl)borate Donation by Varying the Extent of Phenyl Substituent Fluorination

Supplementary Information

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Contents

I. General Procedures

All operations were performed under an atmosphere of 99.5% argon further purified by passage through a column of activated Aceto Corp. catalyst R3-11 and 10 Å molecular sieves. The plumbing components of the gas purification systems were made of glass and copper. Ultra-Torr® and Swagelock® fittings were employed to provide connections between glass and copper tubing that are impermeable to air. Solutions were routinely transferred via stainless steel cannulas. Gastight syringes equipped with stainless steel three-way stopcocks and needles were used to transfer solutions when necessary. Standard Schlenk techniques were employed with double manifold vacuum lines.[S1] Solids were handled in a glove box. Solvents were purified by standard procedures and stored under argon.

Literature procedures were employed to prepare $BrB(NMe_2)_2$, $Mo(CO)_3(CH_3CH_2CN)_3$, $Mo(CO)_3(C_5H_5N)_3$ and $[Mn(C_{10}H_8)(CO)_3][BF_4]$.[S2-S5] Ferrocene was purchased from Strem and sublimed prior to use. $Li[B(C_6F_5)_4]$ for the synthesis[S6] of $[NBu_4][B(C_6F_5)_4]$ was purchased from Boulder Scientific. Other reagents were obtained from Sigma-Aldrich and used as received. Alumina (activated, neutral, ~150 mesh) and Celite were treated similarly prior to the introduction of organometallic complexes. These substances (~10 cm^3) were first poured hot (oven-baked) onto a medium porosity frit. The filter flask was then evacuated and maintained under dynamic vacuum until the powder had cooled to ambient temperature.

Solution infrared spectra were acquired on a Nicolet Magna 550 FTIR spectrometer with samples sealed in 0.1 mm gastight NaCl cells. Nujol (mineral oil) mulls for IR spectra were prepared in the glove box. NMR samples were sealed under argon into 5 mm tubes and were analyzed on a Bruker 400 MHz FT-NMR spectrometer at ambient temperature. ^1H and ^{13}C chemical shifts are reported in parts per million (δ) and are given with reference to residual ^1H and ^{13}C solvent references relative to TMS. ^{31}P chemical shifts are reported in parts per million (δ) and are given with reference to 80% H_3PO_4. ^{11}B chemical shifts are reported in parts per million (δ) and are given with reference to $BF_3 \bullet OEt_2$. Melting points (uncorrected) were determined under argon in sealed capillary tubes on a Laboratory Devices Mel-Temp apparatus. Microanalyses were carried out by ALS Environmental Services, Tucson, AZ.

References

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II. Synthesis Descriptions and Characterization Data

$((3,5\text{-}CF_3)C_6H_3)B(NMe_2)_2$ (2)

Neat $BrB(NMe_2)_2$ (9.862 g, 55.1 mmol) was added to a solution of $((3,5\text{-}CF_3)C_6H_3)MgBr$ (freshly prepared from 3,5-bis(trifluoromethyl)bromobenzene (16.155 g, 55.1 mmol) and magnesium (1.377 g, 56.2 mmol)) in Et_2O (50 mL) at ambient temperature. The dark brown mixture was stirred (16 hr) at ambient temperature. The solvent was nearly completely removed *in vacuo* with the mixture maintained between 0 °C and -10 °C. Pentane (100 mL) was added and the dark brown suspension was triturated to extract a brown solution from a tan solid; this solid (containing $MgBr_2$) was separated by filtration. Roughly half the filtrate volume was removed *in vacuo* with the solution maintained 0 °C and -10 °C. The concentrated filtrate was distilled (3 torr, 75-77 °C) to afford an air sensitive colorless liquid (14.367 g, 46.0 mmol, 83%). This liquid degrades at ambient temperature under an argon atmosphere (changing from colorless to pale yellow over 24 hours at 25 °C), but can be confidently stored at -40 °C (as a solid) for at least one week. ^{11}B NMR (128 MHz, C_6D_6): δ 31.3 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ -62.6 (s, CF_3). ^1H NMR (400 MHz, C_6D_6): δ 7.82 (s, br, 1H, *p*-H), 7.73 (s, br, 2H, *o*-H), 2.31 (s, 12H, Me). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): 145.3 (s, br, *i*-C), 134.1 (m, *o*-C), 131.3 (q, $^2J_{CF}$ = 32.6 Hz, *m*-C), 124.9 (q, $^1J_{CF}$ = 270 Hz, CF_3), 122.0 (septet, $^3J_{CF}$ = 4.0 Hz, *p*-C), 40.9 (s, Me).

$K[((3,5\text{-}CF_3)C_6H_3)Bpz_3]$ (4)

Toluene (315 mL) and THF (125 mL) were added to **2** (12.15 g, 38.9 mmol) and pyrazole (5.36 g, 78.7 mmol); the resulting clear and colorless solution was stirred for 2 hr. This solution was added to potassium pyrazolate (4.17 g, 39.3 mmol). The ambient temperature suspension was heated to reflux (8 hr) affording a clear and colorless solution. The solvent was removed *in vacuo*, while maintaining the temperature at 40 °C, revealing a white solid. After drying *in vacuo* at ambient temperature (2 hr), pentane (250 mL) was added and the white solid was separated from a colorless filtrate. The solid was washed with pentane (4 * 25 mL) and dried *in vacuo* (1 hr). The white solid was heated in a Schlenk tube *in vacuo* via an oil bath (120 °C, 24 hr) and massed in the glove box as a nearly solvent-free salt (16.77 g, 93%). Anal. Calcd for $C_{17}H_{12}BF_6KN_6$: C, 43.98; H, 2.61; N, 18.10. Found: C, 44.12; H, 2.50; N, 18.30. Mp: 177 - 178 °C (dec). ^{11}B NMR (128 MHz, DMSO-d^6): δ 0.95 (s). $^{19}F\{^1H\}$ NMR (376 MHz, DMSO-d^6): δ -60.9 (s, CF_3). ^1H NMR (400 MHz, DMSO-d^6): 8.19 (s, br, 2H, *o*-H), 7.72 (s, br, 1H, *p*-H), 7.52 (app. d, J = 0.89 Hz, 3H, pzH-3/-5), 6.73 (app. d, J = 1.8 Hz, 3H, pzH-3/-5), 6.10 (t, J = 2.0 Hz, 3H, pzH-4). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d^6): 153.3 (s, br, *i*-C), 139.3 (s, pzC-3/-5), 134.5 (m, *o*-C), 133.2 (s, pzC-3/-5), 127.1 (q, $^2J_{CF}$ = 31.4 Hz, *m*-C), 124.9 (q, $^1J_{CF}$ = 273 Hz, CF_3), 118.4 (septet, $^3J_{CF}$ = 3.8 Hz, *p*-C), 103.1 (s, pzC-4).

$Tl[((3,5\text{-}CF_3)C_6H_3)Bpz_3]$ (6)

THF (30 mL) was added to **4** (0.562 g, 1.21 mmol) and thallium acetate (0.351 g, 1.33 mmol). The suspension was stirred at ambient temperature for 21 hr. The mixture was filtered through a Celite plug separating a white solid from a colorless filtrate. Removal of the solvent *in vacuo* revealed a white solid that was dried *in vacuo* for 3 hr (0.460 g, 60%). Anal. Calcd for $C_{17}H_{12}BF_6N_6Tl$: C, 32.44; H, 1.92; N, 13.35. Found: C, 32.75; H, 1.80; N, 13.09. Mp: 177 - 178 °C (dec). ^{11}B NMR (128 MHz, C_4D_8O): δ 1.17 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O): δ -63.2 (s, CF_3). ^1H NMR (400 MHz, C_4D_8O): 7.88 (s, br, 1H, *p*-H), 7.61 (m, 3H, pzH-3/-5), 7.37 (s, br, 2H, *o*-H), 7.32 (m, pzH-3/-5), 6.22 (m, 3H, pzH-4). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): 141.0 (s, pzC-3/-5), 134.6 (m, *o*-C), 136.7 (s, pzC-3/-5), 131.0 (q, $^2J_{CF}$ = 32.4

Hz, *m*-C), 125.1 (q, $^{1}J_{CF}$ = 273 Hz, CF_3), 121.8 (septet, $^{3}J_{CF}$ = 3.8 Hz, *p*-C), 105.0 (s, pzC-4), *i*-C not observed.

[Et_4N][$Mo(CO)_3$(((3,5-CF_3)C_6H_3)Bpz_3)] (8)

THF (50 mL) was added to **4** (0.423 g, 0.912 mmol) and $Mo(CO)_3(CH_3CH_2CN)_3$ (0.300 g, 0.869 mmol). The pale yellow solution was refluxed (1.5 hr), transferred to Et_4NBr (0.201 g, 0.956 mmol) and stirred at ambient temperature (2 hr). The suspension was filtered through alumina. Most of the solvent was removed *in vacuo* from the yellow filtrate, and Et_2O (40 mL) was added to generate a suspension. An off-white solid was isolated by filtration, washed with Et_2O (3 * 10 mL) and dried *in vacuo* for 3 hr. Et_2O diffusion into a CH_3CN solution provided pale yellow microcrystals (0.327 g, 51%). Anal. Calcd for $C_{28}H_{32}BF_6MoN_7O_3$: C, 45.73; H, 4.39; N, 13.33. Found: C, 45.79; H, 4.05; N, 13.14. Mp: 260 - 261 °C (dec). IR (CH_3CN): ν(CO) 1895 (s), 1761 (s) cm^{-1}; (THF): ν(CO) 1892 (s), 1762 (s), 1750 cm^{-1} (s, sh); (Nujol): ν(CO) 1894 (s), 1769 (s), 1749 (s), 1745 (s, sh) cm^{-1}. ^{11}B NMR (128 MHz, CD_3CN): δ -0.52 (s). $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): δ -63.1 (s, CF_3). ^{1}H NMR (400 MHz, CD_3CN): 8.46 (s, br, 2H, *o*-H), 8.16 (s, br, 1H, *p*-H), 7.85 (app. d, J = 1.8 Hz, 3H, pzH-3/-5), 7.38 (app. d, J = 2.4 Hz, pzH-3/-5), 6.14 (t, J = 2.2 Hz, 3H, pzH-4), 3.10 (m, 8H, Et_4N), 1.16 (m, 12H, Et_4N). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN): 231.8 (s, CO), 153.3 (s, br, *i*-C), 145.3 (s, pzC-3/-5), 136.0 (s, br, *o*-C), 135.9 (s, pzC-3/-5), 131.5 (q, $^{2}J_{CF}$ = 32.8 Hz, *m*-C), 125.1 (q, $^{1}J_{CF}$ = 273 Hz, CF_3), 123.2 (septet, $^{3}J_{CF}$ = 3.7 Hz, *p*-C), 105.8 (s, pzC-4), 53.1 (m, Et_4N), 7.7 (s, Et_4N), *i*-C not observed.

(((3,5-CF_3)C_6H_3)Bpz_3)$Mo(CO)_2$(2-methallyl)(10)

A 1.00 mL stock solution of 2-methylallyl bromide (0.230 g, 1.70 mmol) in CH_2Cl_2 was added to $Mo(CO)_3(C_5H_5N)_3$ (0.645 g, 1.55 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred (3 hr) while its color changed from yellow to pale orange; an IR spectrum ((CH_2Cl_2) ν(CO) 1938 (s), 1835 (m) cm^{-1}) indicated complete consumption of $Mo(CO)_3(C_5H_5N)_3$ and $Mo(CO)_2(C_5H_5N)_2$(2-methallyl)Br formation. This orange solution was added (along with a 10 mL CH_2Cl_2 rinse of the $Mo(CO)_2(C_5H_5N)_2$(2-methallyl)Br flask) to **4** (0.789 g, 1.70 mmol). The yellow suspension was stirred (14 hr) and then filtered through alumina. The CH_2Cl_2 was removed *in vacuo*, and the yellow solid was suspended in pentane (30 mL). This solid was collected by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo* (7 hr). The solid was dissolved in THF (20 mL) and the yellow solution was filtered through alumina. The filtrate solvent was removed *in vacuo* revealing a bright yellow solid (0.498 g, 51%) that was suspended in pentane (20 mL), isolated by filtration, washed with pentane (3 * 5 mL) and dried *in vacuo* (6 hr). Anal. Calcd for $C_{23}H_{19}BF_6MoN_6O_2$: C, 43.70; H, 3.03; N, 13.29. Found: C, 43.30; H, 2.66; N, 12.91. Mp: 232 - 234 °C (dec). IR (CH_2Cl_2): ν(CO) 1943 (s), 1851 (m) cm^{-1}; (THF): ν(CO) 1945 (s), 1857 (s); (Nujol): ν(CO) 1934 (s), 1842 (s), 1831 cm^{-1}. ^{11}B NMR (128 MHz, C_4D_8O): δ -0.97 (s). $^{19}F\{^{1}H\}$ NMR (376 MHz, C_4D_8O): δ -63.5 (s, CF_3). ^{1}H NMR (400 MHz, C_4D_8O): 8.45 (s, br, 2H, *o*-H), 8.29 (s, br, 3H, pzH-3/-5), 8.19 (s, br, 2H, *p*-H), 7.27 (s, br, 3H, pz-3/-5), 6.27 (s, 3H, pzH-4), 3.62 (s, 2H, allyl-C*H*H), 1.66 (s, 3H, allyl-CH_3), 1.36 (s, 2H, allyl-CH*H*). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_4D_8O): 228.2 (s, CO), 145.2 (s, br, pzC-3/-5), 137.7 (s, br, pzC-3/-5), 135.7 (m, *o*-C), 132.0 (q, $^{2}J_{CF}$ = 32.8 Hz, *m*-C), 124.9 (q, $^{1}J_{CF}$ = 274 Hz, CF_3), 123.2 (septet, $^{3}J_{CF}$ = 3.8 Hz, *p*-C), 106.6 (s, pzC-4), 84.2 (s, *C*CH_3), 59.9 (s, allyl-CH_2), 19.0 (s, allyl-CH_3), *i*-C not observed.

(((3,5-CF_3)C_6H_3)Bpz_3)$Mn(CO)_3$ (12)

THF (50 mL) was added to solid [$Mn(C_{10}H_8)(CO)_3$][BF_4] (0.468 g, 1.32 mmol) and **4** (0.645 g, 1.39 mmol); the colorless solution was stirred (16 hr) and then filtered through alumina. The solvent of the filtrate was removed *in vacuo*. Pentane (50 mL) was added and the colorless solution was cooled to -25 °C. The resulting suspension was filtered while maintaining the temperature between -30 °C and -25 °C to separate an ivory solid from a colorless filtrate. This solid (0.515 g, 69%) was washed with cold (-25 °C) pentane (4 * 10 mL) and dried *in vacuo* for 8 hr. Anal. Calcd for $C_{20}H_{12}BF_6MnN_6O_3$: C, 42.59; H, 2.14; N, 14.90. Found: C, 42.54; H, 0.24; N, 14.49. Mp: 221 - 223 °C (dec). IR (CH_2Cl_2): ν(CO) 2035 (s), 1932 (s) cm^{-1}; (THF): ν(CO) 2035 (s), 1932 (s); (Nujol): ν(CO) 2032 (s), 1934 (s), 1927 (s), 1889 (m, sh), 1845 (m, sh) cm^{-1}. ^{11}B NMR (128 MHz, C_4D_8O): δ -1.2 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O): δ -63.5 (s, CF_3). ^1H NMR (400 MHz, C_4D_8O): 8.53 (s, br, 2H, *o*-H), 8.23 (s, br, 2H, *p*-H), 8.11 (m, 3H, pzH-3/-5), 7.59 (m, 3H, pz-3/-5), 6.32 (app. t, J = 2.3 Hz, 3H, pzH-4). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): 222.3 (s, CO), 146.4 (s, pzC-3/-5), 136.7 (s, pzC-3/-5), 135.7 (m, *o*-C), 132.1 (q, $^2J_{CF}$ = 32.8 Hz, *m*-C), 124.9 (q, $^1J_{CF}$ = 274 Hz, CF_3), 123.5 (septet, $^3J_{CF}$ = 3.8 Hz, *p*-C), 107.2 (s, pzC-4), *i*-C not observed.

Fe(((3,5-CF_3)C_6H_3)Bpz_3)$_2$ (14)

THF (15 mL) was added to anhydrous $FeCl_2$ (0.063 g, 0.497 mmol) and **4** (0.462 g, 0.995 mmol). The mixture was stirred 18 hr while changing from pink to red-violet. More THF was added (10 mL), and the suspension was filtered through alumina. The solvent from the red-violet filtrate was removed *in vacuo* revealing a pale red solid. Pentane (30 mL) was added and the solid (0.240 g, 53%) was isolated by filtration, washed with pentane (3 * 5 mL) and dried in vacuo (6 hr). Anal. Calcd for $C_{34}H_{24}B_2F_{12}FeN_{12}$: C, 45.07; H, 2.67; N, 18.55. Found: C, 44.78; H, 2.73; N, 17.97. Mp: 307 - 308 °C (dec). ^{11}B NMR (128 MHz, C_4D_8O): δ -1.3 (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O): δ -63.3 (s, CF_3). ^1H NMR (400 MHz, C_4D_8O): 8.73 (s, 4H, *o*-H), 8.27 (s, 2H, *p*-H), 7.87 (s, 6H, pzH-3/-5), 7.11 (s, 6H, br, pz-3/-5), 6.44 (s, 6H, pzH-4). $^{13}C\{^1H\}$ NMR (101 MHz, C_4D_8O): 152.6 (s, pzC-3/-5), 140.8 (s, pzC-3/-5), 135.8 (m, *o*-C), 131.9 (q, $^2J_{CF}$ = 32.7 Hz, *m*-C), 125.1 (q, $^1J_{CF}$ = 274 Hz, CF_3), 123.2 (m, *p*-C), 109.1 (s, pzC-4), *i*-C not observed.

Cu(((3,5-CF_3)C_6H_3)Bpz_3)$_2$ (16)

THF (25 mL) was added to anhydrous $CuBr_2$ (0.132 g, 0.591 mmol) and **4** (0.549 g, 1.18 mmol); the dark blue mixture was stirred for 18 hr. The THF was removed *in vacuo*, and the blue residue was dissolved in CH_2Cl_2 (25 mL). The solution was filtered through alumina; the alumina plug was washed with CH_2Cl_2 (15 mL). The filtrate was concentrated *in vacuo* revealing a pale blue solid. Pentane (20 mL) was added to this solid (0.233 g, 43%) that was isolated by filtration, washed with pentane (4 * 5 mL) and dried in vacuo (5.5 hr). Anal. Calcd for $C_{34}H_{24}B_2CuF_{12}N_{12}$: C, 44.69; H, 2.65; N, 18.39. Found: C, 44.54; H, 1.07; N, 18.07. Mp: 221 - 222 °C (dec). No ^{11}B NMR resonance was observed (C_4D_8O). $^{19}F\{^1H\}$ NMR (376 MHz, C_4D_8O): δ -63.2 (s, CF_3). Evans Method (C_4D_8O): 2.0 μ_B.

III. Thermal Ellipsoid Drawings

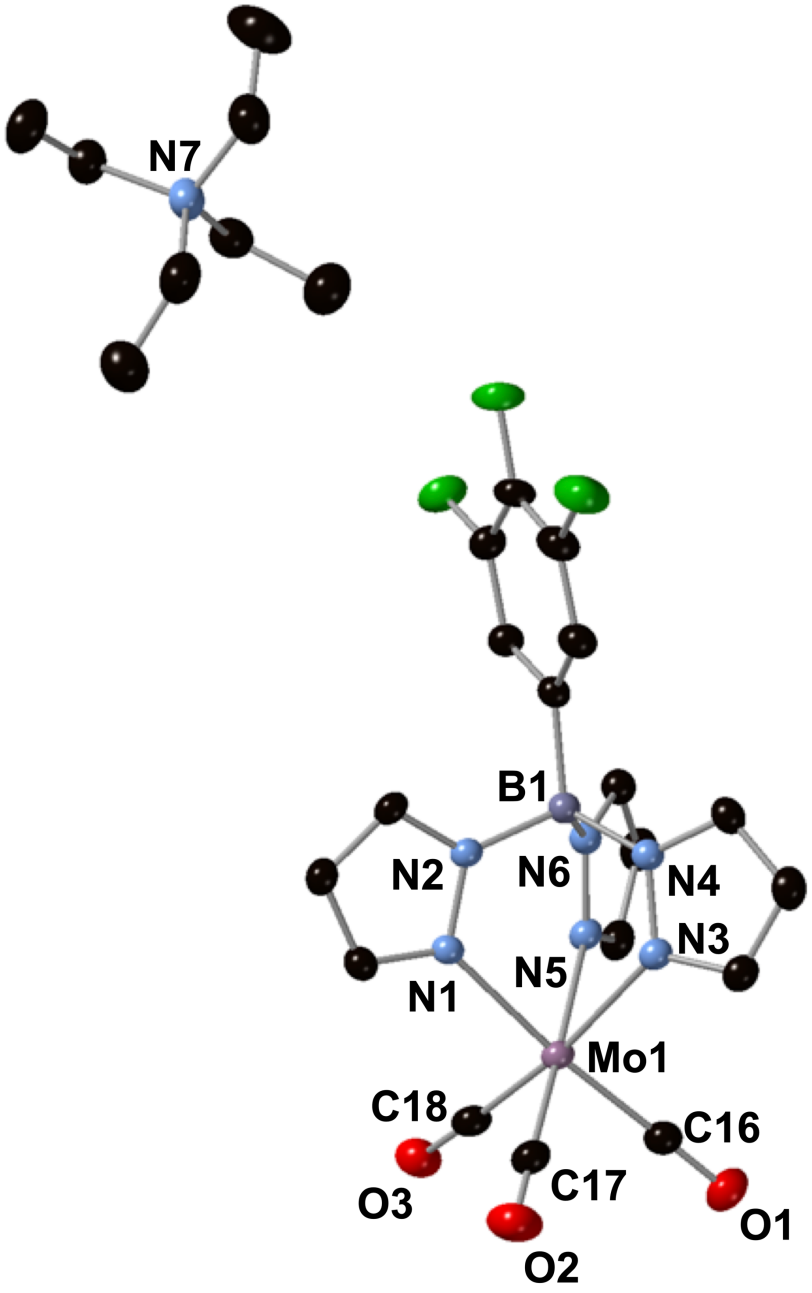


Fig. S1 Thermal ellipsoid (50%) drawing of **7**. Selected bond lengths (Å) and angles (°) Mo(1)–N(1) = 2.2297(15), Mo(1)–N(3) = 2.2908(15), Mo(1)–N(5) = 2.2463(16), Mo(1)–C(16) = 1.937(2), Mo(1)–C(17) = 1.937(2), Mo(1)–C(18) = 1.933(2), C(16)–O(1) = 1.176(2), C(17)–O(2) = 1.179(3), C(18)–O(3) = 1.175(2), C(18)-Mo(1)-C(17) = 87.37(8), C(18)-Mo(1)-C(16) = 89.75(8), C(17)-Mo(1)-C(16) = 84.84(8), C(18)-Mo(1)-N(1) = 95.58(7), C(17)-Mo(1)-N(1) = 97.37(7), C(18)-Mo(1)-N(5) = 92.68(7), C(16)-Mo(1)-N(5) = 96.69(7), N(1)-Mo-N(5) = 81.11(6), C(17)-Mo(1)-N(3) = 101.97(7), C(16)-Mo(1)-N(3) = 94.33(7), N(1)-Mo(1)-N(3) = 80.10(5), N(5)-Mo(1)-N(3) = 77.89(5).

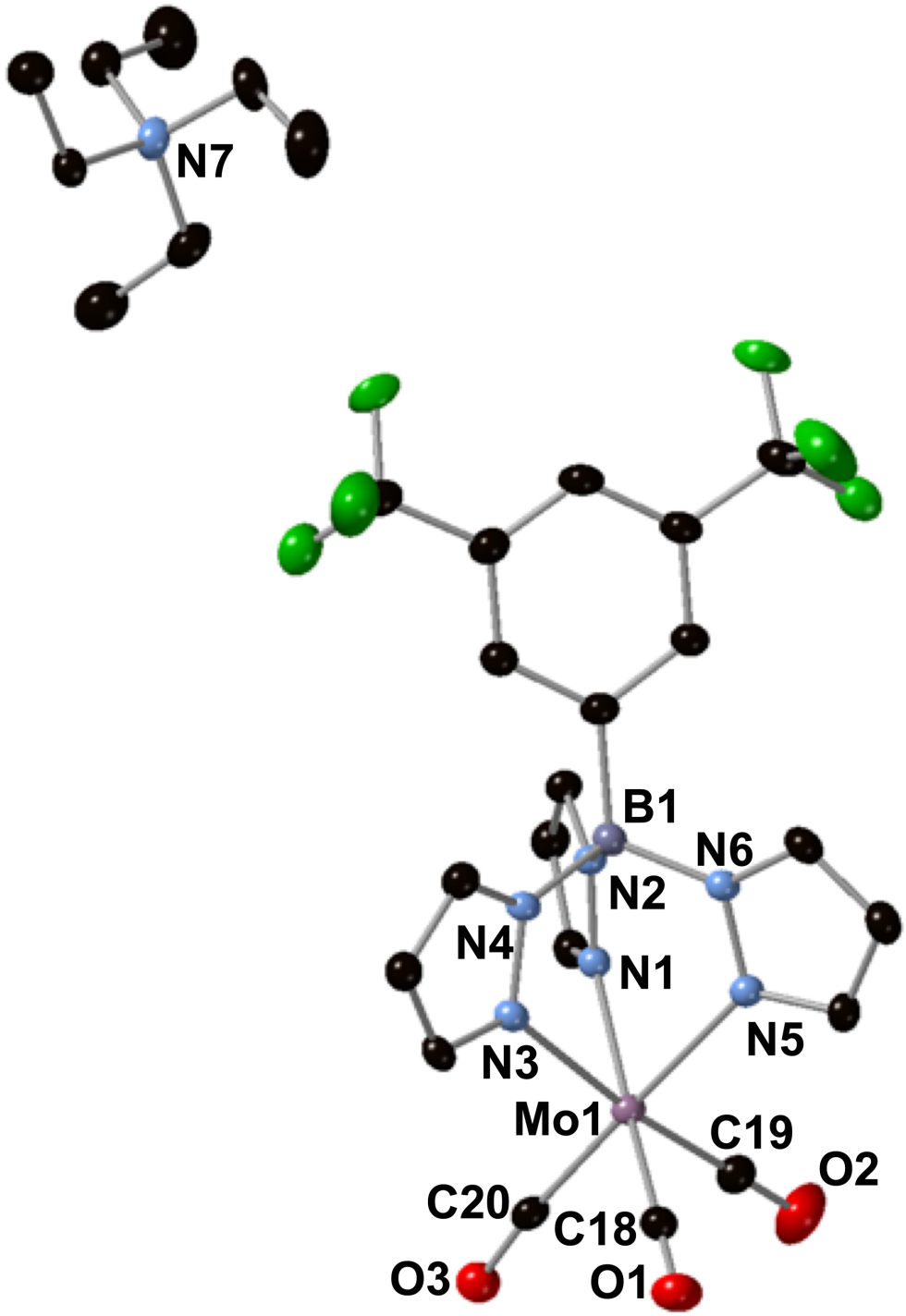


Fig. S2 Thermal ellipsoid (50%) drawing of **8**. Selected bond lengths (Å) and angles (°) Mo(1)–N(1) = 2.2413(18), Mo(1)–N(3) = 2.290(2), Mo(1)–N(5) = 2.2506(17), Mo(1)–C(18) = 1.929(2), Mo(1)–C(19) = 1.938(3), Mo(1)–C(20) = 1.933(2), C(18)–O(1) = 1.182(3), C(19)–O(2) = 1.167(3), C(20)–O(3) = 1.178(3), C(18)-Mo(1)-C(20) = 85.79(9), C(18)-Mo(1)-C(19) = 88.43(10), C(20)-Mo(1)-C(19) = 84.35(10), C(20)-Mo(1)-N(1) = 100.28(8), C(19)-Mo(1)-N(1) = 96.94(9), C(18)-Mo(1)-N(5) = 94.33(8), C(19)-Mo(1)-N(5) = 93.84(9), N(1)-Mo-N(5) = 79.76(6), C(18)-Mo(1)-N(3) = 95.28(9), C(20)-Mo(1)-N(3) = 100.95(9), N(1)-Mo(1)-N(3) = 78.89(7), N(5)-Mo(1)-N(3) = 80.86(7).

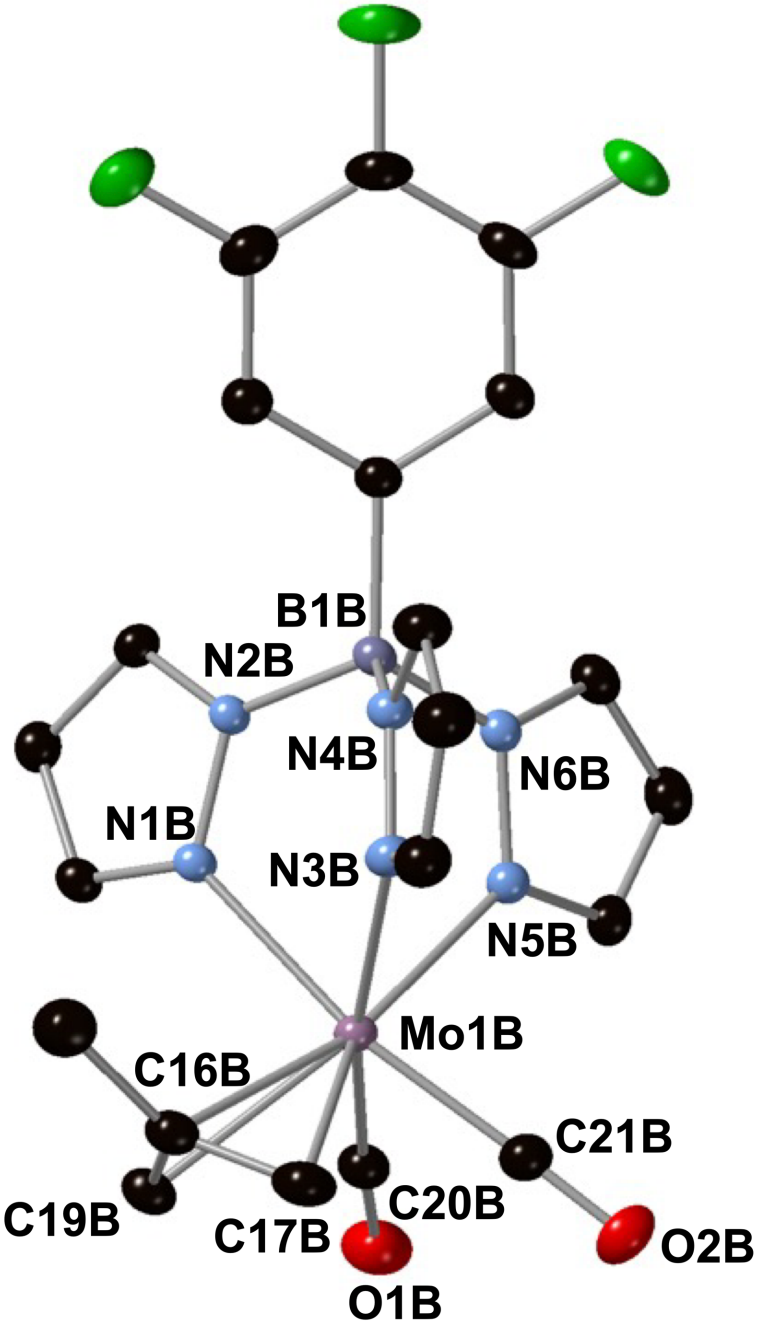


Fig. S3 Thermal ellipsoid (50%) drawing of **9(B)**. Selected bond lengths (Å) and angles (°) Mo(1B)–C(20B) = 1.9500(19), Mo(1B)–C(21B) = 1.9573(19), Mo(1B)–N(5B) = 2.2182(14), Mo(1B)–N(3B) = 2.2500(15), Mo(1B)–N(1B) = 2.2801(14), Mo(1B)–C(16B) = 2.2516(18), Mo(1B)–C(17B) = 2.3359(18), Mo(1B)–C(19B) = 2.3493(19), C(20B)–O(1B) = 1.159(2), C(21B)–O(2B) = 1.157(2), C(20B)-Mo(1B)-C(21B) = 78.94(8), C(20B)-Mo(1B)-C(5B) = 88.27(6), C(21B)-Mo(1B)-C(5B) = 89.11(7), C(21B)-Mo(1B)-C(3B) = 97.62(7), C(5B)-Mo(1B)-C(3B) = 79.34(5), C(20B)-Mo(1B)-C(16B) = 102.34(7), C(21B)-Mo(1B)-C(16B) = 102.43(7), N(3B)-Mo(1B)-C(16B) = 90.41(6), C(20B)-Mo(1B)-C(N1B) = 98.38(7), N(5B)-Mo(1B)-N(1B) = 78.19(5), N(3B)-Mo(1B)-N(1B) = 82.22(5), C(16B)-Mo(1B)-N(1B) = 90.44(6).

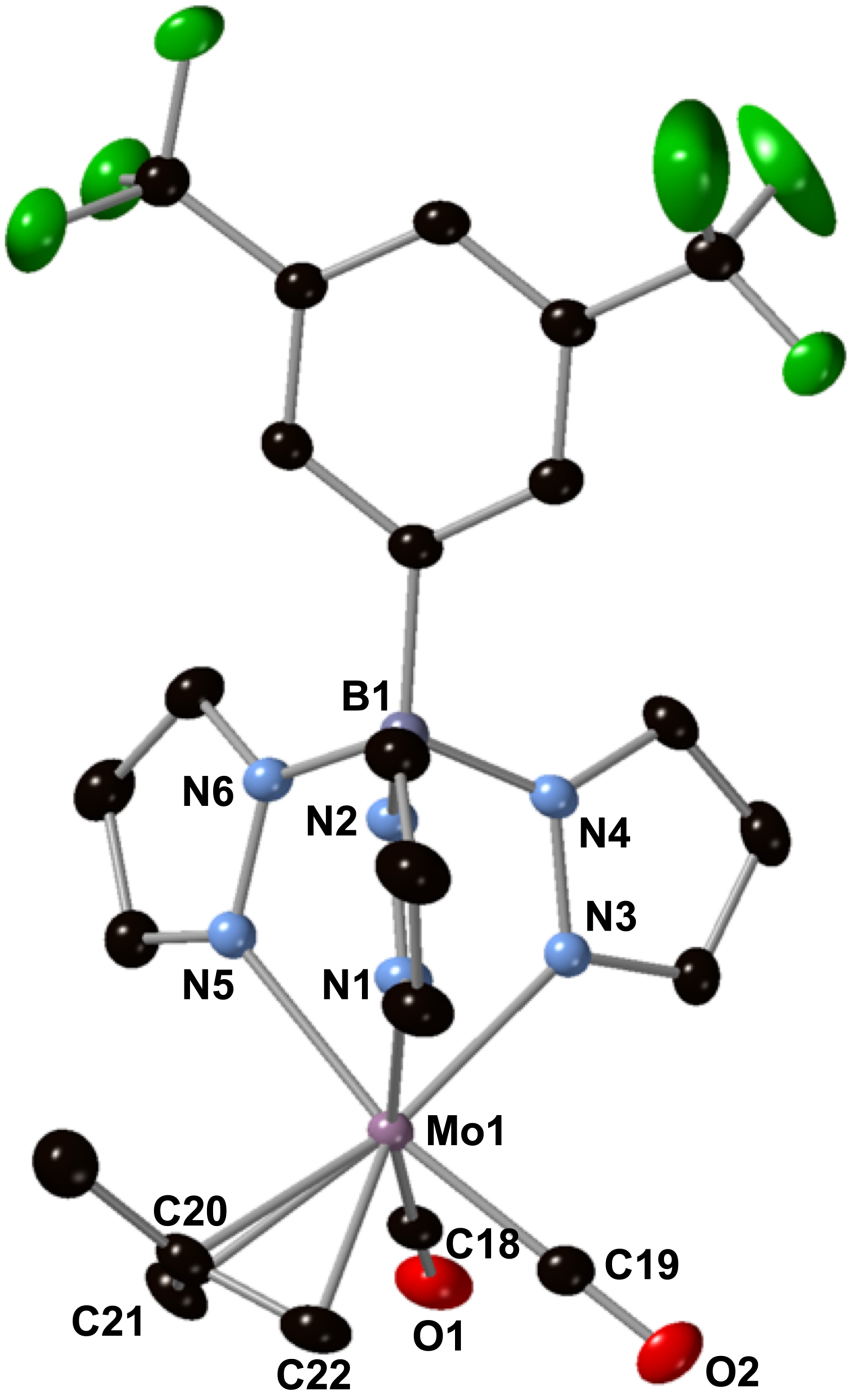


Fig. S4 Thermal ellipsoid (50%) drawing of **10**. Selected bond lengths (Å) and angles (°) Mo(1)–C(18) = 1.9439(15), Mo(1)–C(19) = 1.9576(16), Mo(1)–N(5) = 2.2869(12), Mo(1)–N(3) = 2.2105(12), Mo(1)–N(1) = 2.2443(12), Mo(1)–C(20) = 2.2432(15), Mo(1)–C(21) = 2.3423(15), Mo(1)–C(22) = 2.3309(15), C(18)–O(1) = 1.1627(15), C(19)–O(2) = 1.150(2), C(18)-Mo(1)-C(19) = 81.72(7), C(18)-Mo(1)-N(3) = 88.82(5), C(19)-Mo(1)-N(3) = 86.97(6), C(18)-Mo(1)-C(20) = 102.90(6), C(19)-Mo(1)-C(20) = 102.79(7), C(19)-Mo(1)-N(1) = 97.95(6), N(3)-Mo(1)-N(1) = 77.60(4), C(20)-Mo(1)-N(1) = 90.45(5), C(18)-Mo(1)-N(5) = 93.97(5), N(3)-Mo(1)-N(5) = 79.56(4), C(20)-Mo(1)-N(5) = 91.19(5), N(1)-Mo(1)-N(5) = 83.10(4).

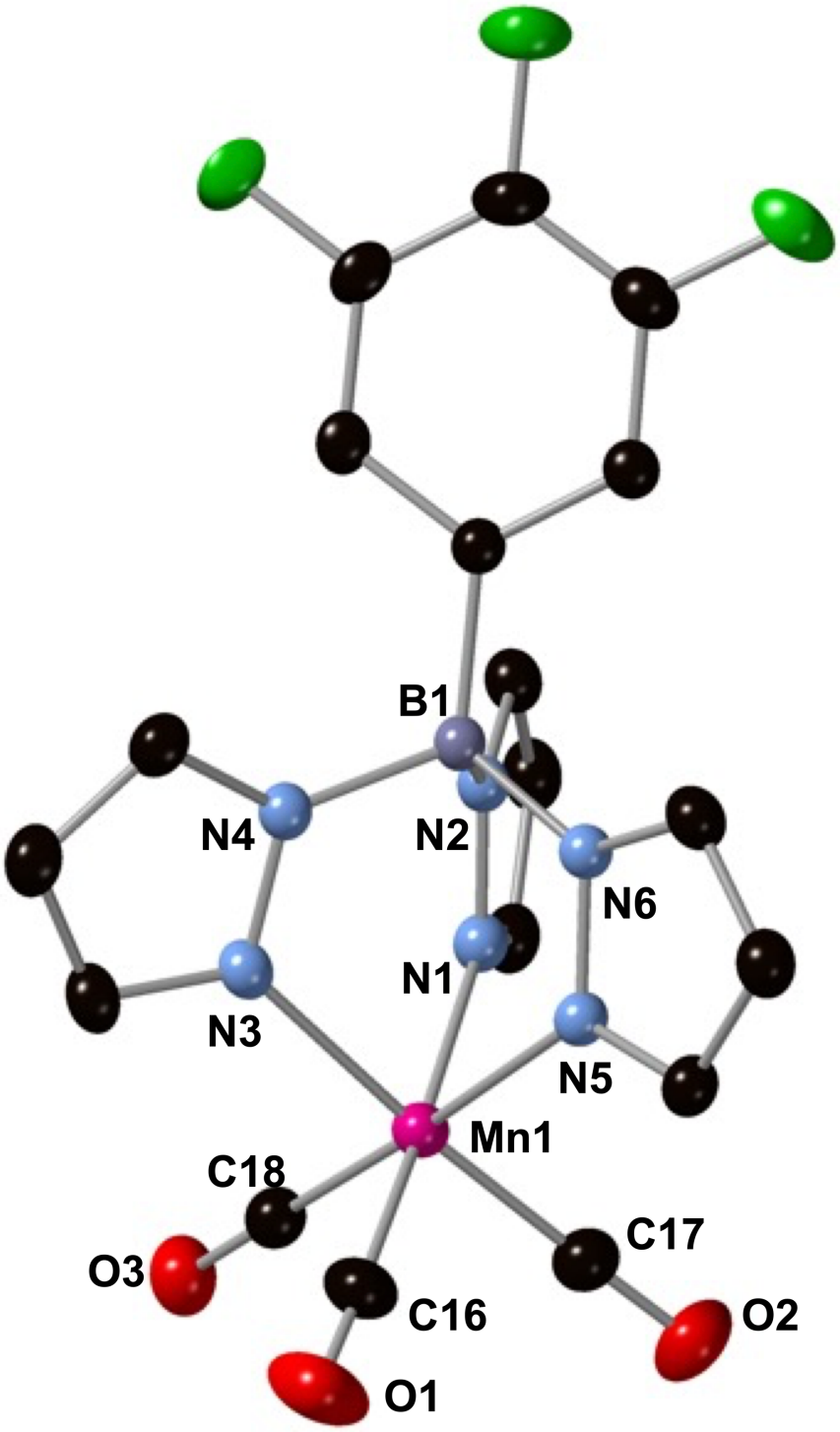


Fig. S5 Thermal ellipsoid (50%) drawing of **11**. Selected bond lengths (Å) and angles (°) Mn(1)–C(16) = 1.8100(16), Mn(1)–C(17) = 1.8064(16), Mn(1)–C(18) = 1.8067(15), Mn(1)–N(1) = 2.0216(12), Mn(1)–N(3) = 2.0592(12), Mn(1)–N(5) = 2.0485(11), C(16)–O(1) = 1.1437(19), C(17)–O(2) = 1.1472(19), C(18)–O(3) = 1.1459(18), C(17)-Mn(1)-C(18) = 91.25(6), C(17)-Mn(1)-C(16) = 90.85(7), C(18)-Mn(1)-C(16) = 89.00(7), C(17)-Mn(1)-N(1) = 92.38(6), C(18)-Mn(1)-N(1) = 92.44(6), C(17)-Mn(1)-N(5) = 90.65(6), C(16)-Mn(1)-N(5) = 93.23(6), N(1)-Mn(1)-N(5) = 85.23(5), C(18)-Mn(1)-N(3) = 92.72(6), C(16)-Mn(1)-N(3) = 91.15(6), N(1)-Mn(1)-N(3) = 85.52(5), N(5)-Mn(1)-N(3) = 85.31(4).

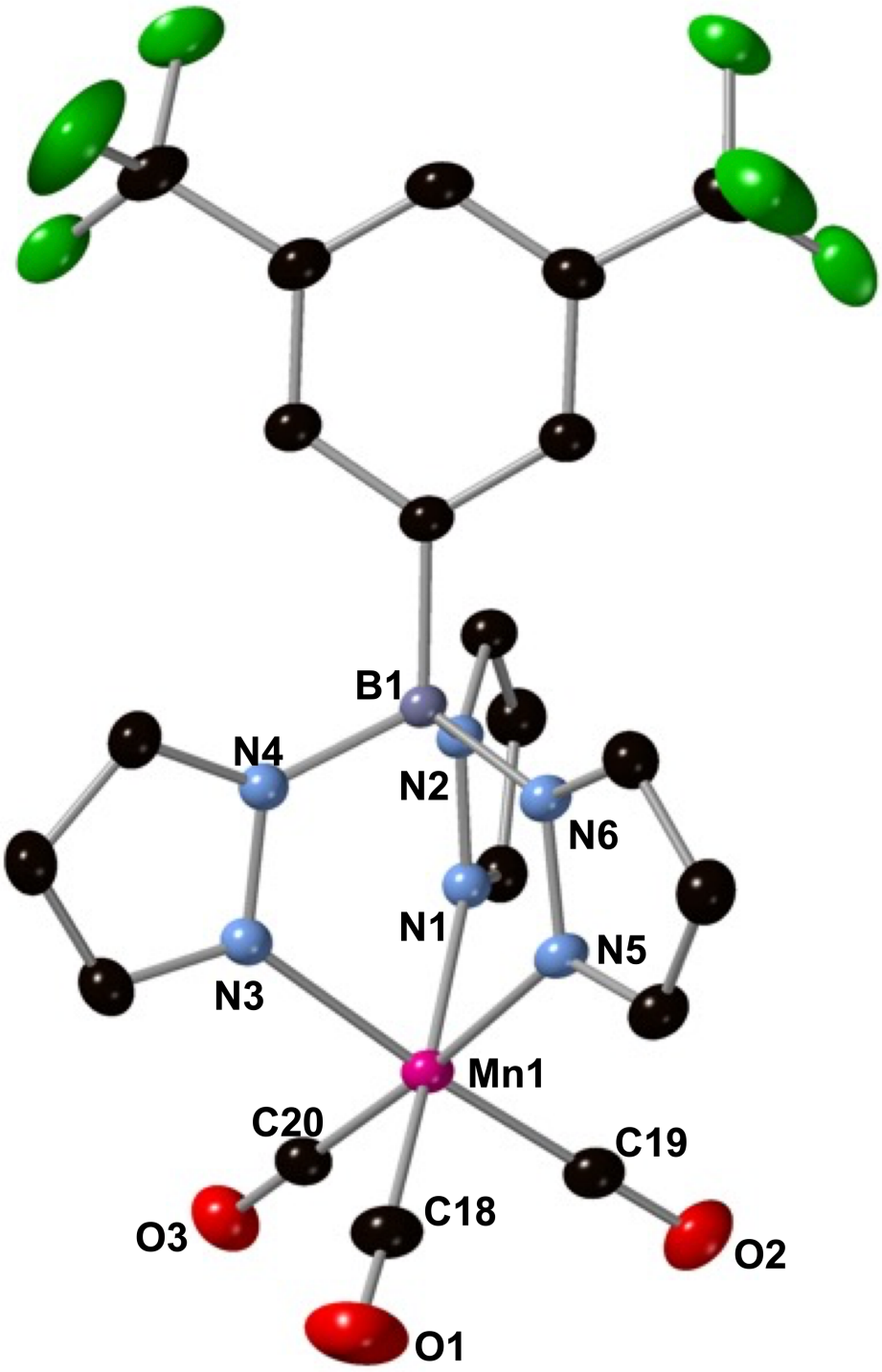


Fig. S6 Thermal ellipsoid (50%) drawing of **12**. Selected bond lengths (Å) and angles (°) Mn(1)–C(18) = 1.817(3), Mn(1)–C(19) = 1.804(2), Mn(1)–C(20) = 1.795(2), Mn(1)–N(1) = 2.0178(19), Mn(1)–N(3) = 2.0518(18), Mn(1)–N(5) = 2.0542(19), C(18)–O(1) = 1.143(3), C(19)–O(2) = 1.146(3), C(20)–O(3) = 1.152(3), C(20)-Mn(1)-C(19) = 89.54(10), C(20)-Mn(1)-C(18) = 90.09(11), C(19)-Mn(1)-C(18) = 92.03(12), C(20)-Mn(1)-N(1) = 91.38(9), C(19)-Mn(1)-N(1) = 90.83(10), C(20)-Mn(1)-N(3) = 92.70(9), C(18)-Mn(1)-N(3) = 91.33(10), N(1)-Mn(1)-N(3) = 85.75(7), C(19)-Mn(1)-N(5) = 93.32(9), C(18)-Mn(1)-N(5) = 92.23(10), N(1)-Mn(1)-N(5) = 86.15(7), N(3)-Mn(1)-N(5) = 84.30(7).

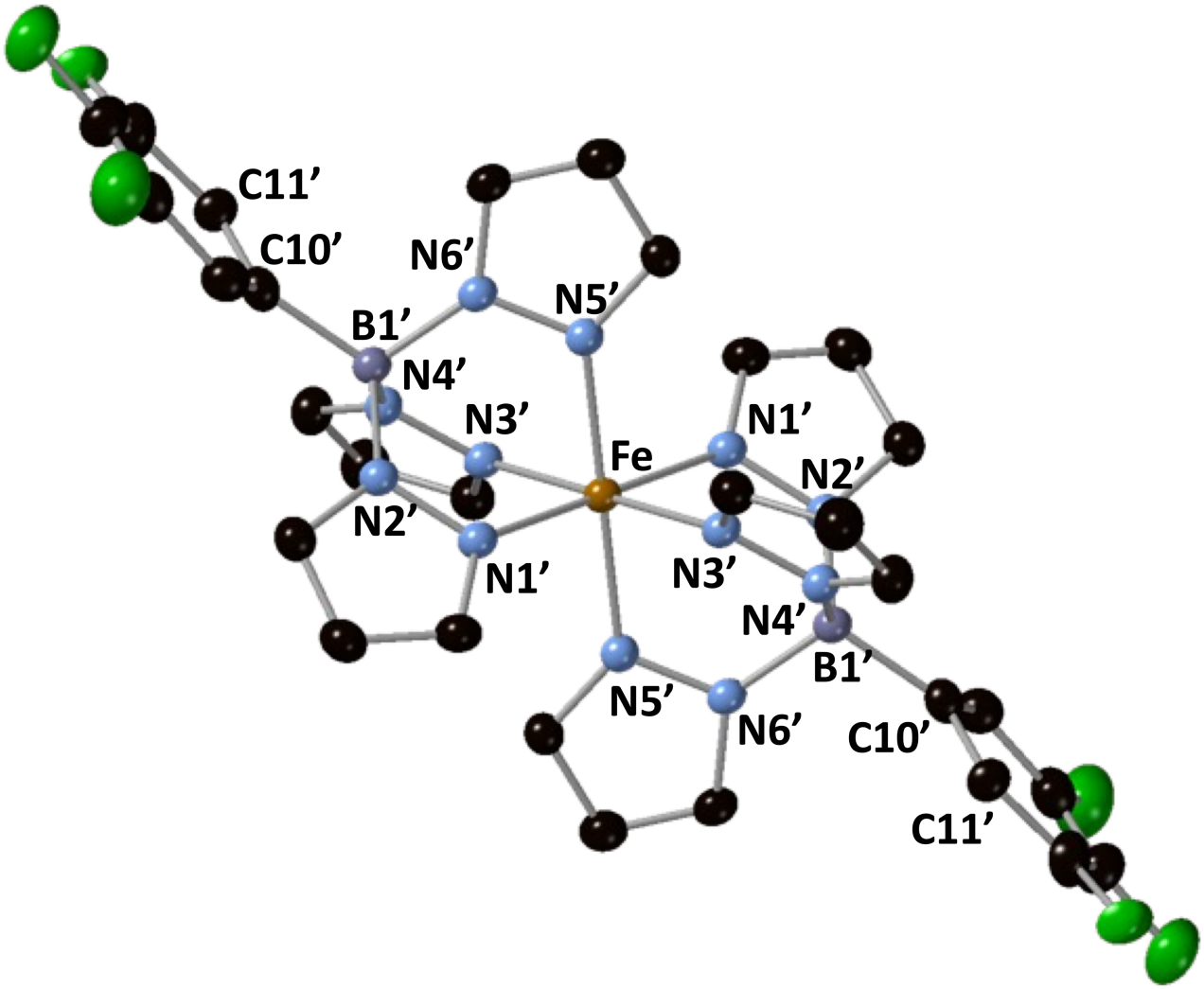


Fig. S7 Thermal ellipsoid (50%) drawing of **13** (minor form). Selected bond lengths (Å) and angles (º) Fe–N(1') = 2.008(18), Fe–N(3') = 1.950(16), Fe–N(5') = 1.988(15), Ave N–Fe–N = 90(2), N(6')-B1'-C(10')-C(11') (Dihedral) = -84(3), C(10')-B1'-N(4') = 116.7(9), C(10')-B1'-N(6') = 107.3(8), C(10')-B1'-N(2') = 112.6(9).

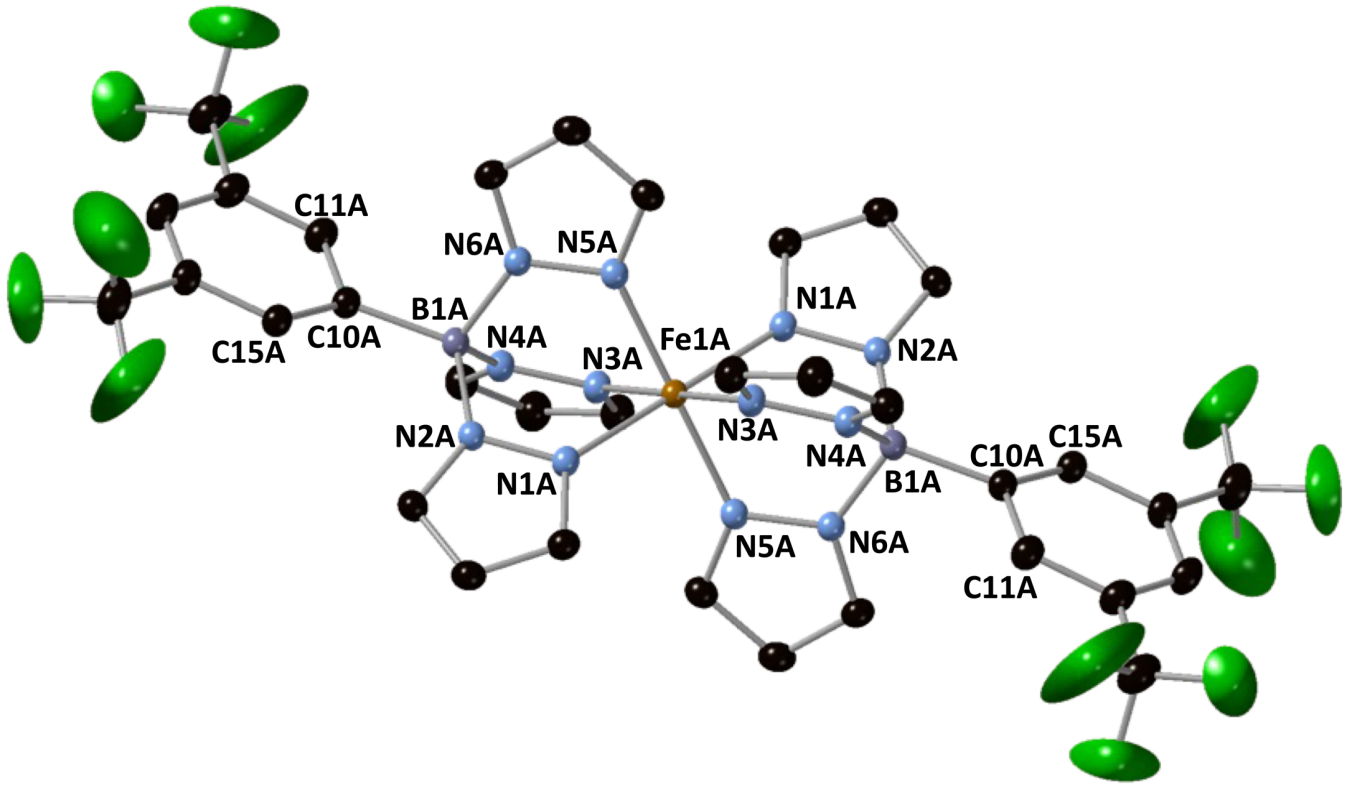


Fig. S8 Thermal ellipsoid (50%) drawing of **14A**. Selected bond lengths (Å) and angles (°) Fe(1A)–N(1A) = 1.9684(14), Fe(1A)–N(3A) = 1.9786(14), Fe(1A)–N(5A) = 1.9494(15), Ave N–Fe–N = 90(2), N(6A)-B(1A)-C(10A)-C(15A) (Dihedral) = 94.04(19), C(10A)-B(1A)-N(4A) = 114.17(14), C(10A)-B(1A)-N(6A) = 106.58(13), C(10A)-B(1A)-N(2A) = 116.27(14).

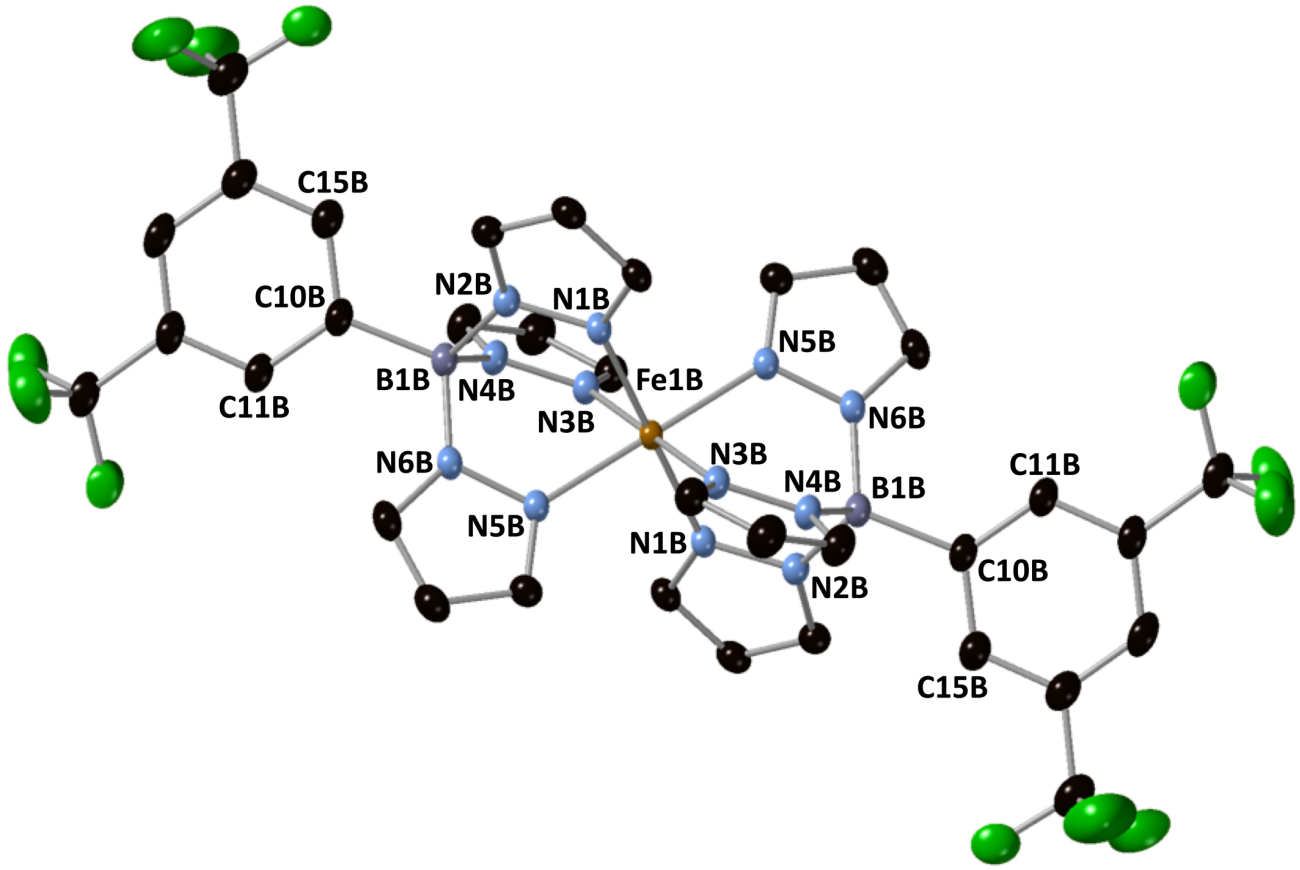


Fig. S9 Thermal ellipsoid (50%) drawing of **14B**. Selected bond lengths (Å) and angles (°) Fe(1B)–N(1B) = 1.9665(15), Fe(1B)–N(3B) = 1.9476(15), Fe(1B)–N(5B) = 1.9606(14), Ave N–Fe–N = 90(2), N(4B)-B(1B)-C(10B)-C(11B) (Dihedral) = 96.4(2), C(10B)-B(1B)-N(4B) = 107.92(14), C(10B)-B(1B)-N(6B) = 115.60(15), C(10B)-B(1B)-N(2B) = 113.33(14).

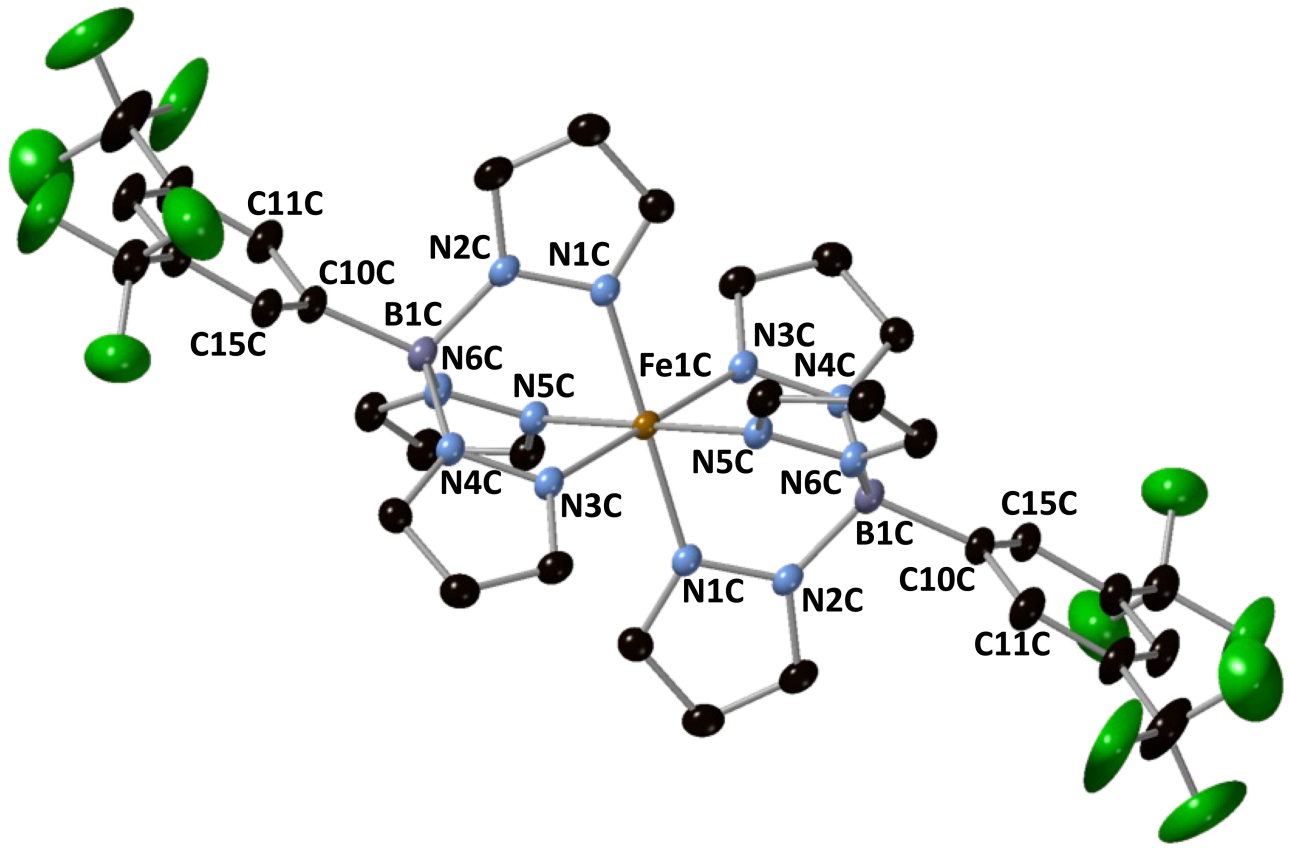


Fig. S10 Thermal ellipsoid (50%) drawing of **14C**. Selected bond lengths (Å) and angles (°) Fe(1C)–N(1C) = 1.9493(14), Fe(1C)–N(3C) = 1.9722(15), Fe(1C)–N(5C) = 1.9708(14), Ave N–Fe–N = 90(2), N(2C)-B(1C)-C(10C)-C(15C) (Dihedral) = 89.1(2), C(10C)-B(1C)-N(4C) = 115.76(14), C(10C)-B(1C)-N(6C) = 114.09(14), C(10C)-B(1C)-N(2C) = 107.42(14).

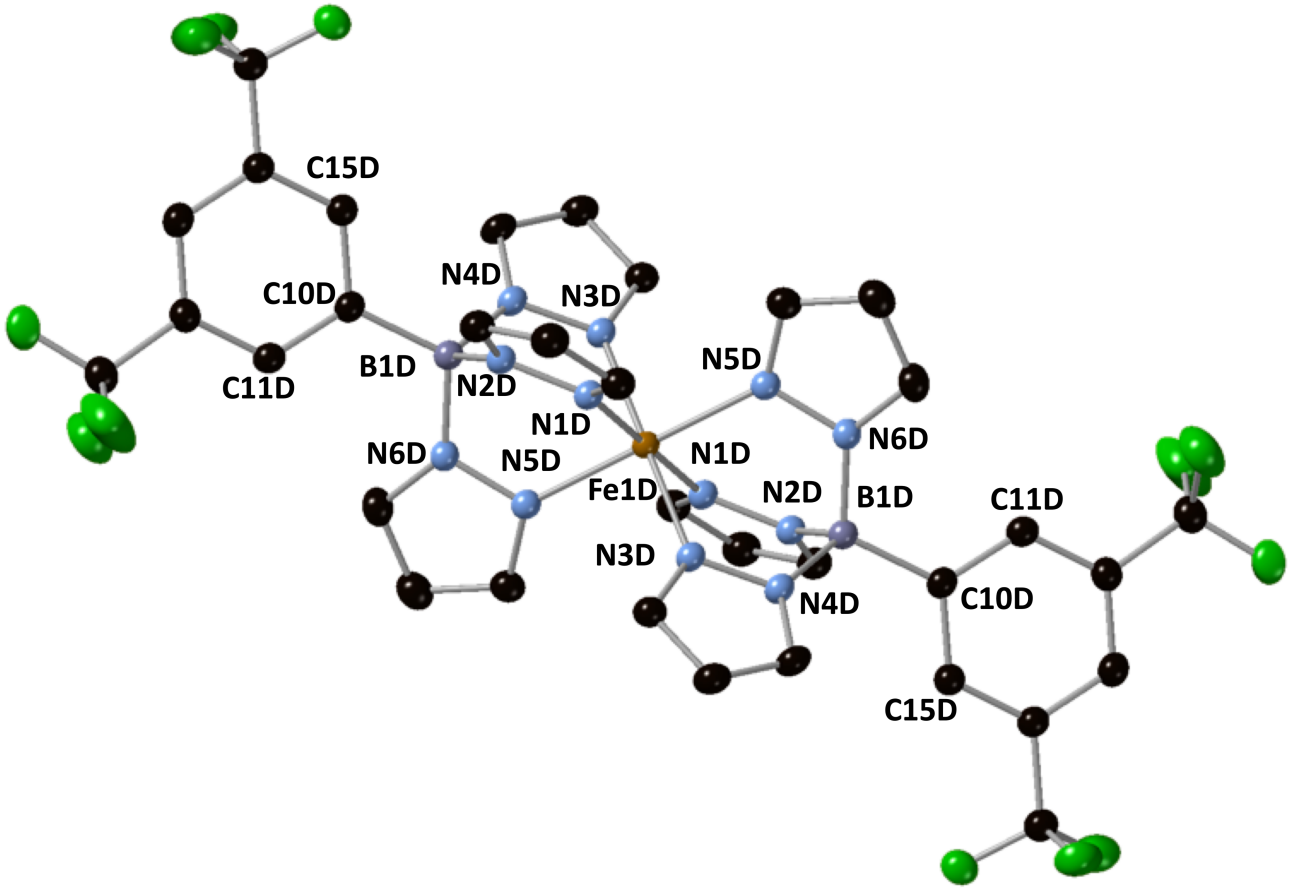


Fig. S11 Thermal ellipsoid (50%) drawing of **14D**. Selected bond lengths (Å) and angles (°) Fe(1D)–N(1D) = 1.9490(15), Fe(1D)–N(3D) = 1.9780(15), Fe(1D)–N(5D) = 1.9727(15), Ave N–Fe–N = 90(2), N(2D)-B(1D)-C(10D)-C(11D) (Dihedral) = -93.9(2), C(10D)-B(1D)-N(4D) = 114.50(14), C(10D)-B(1D)-N(6D) = 115.57(15), C(10D)-B(1D)-N(2D) = 107.49(14).

IV. X-ray Crystallographic and Refinement Details

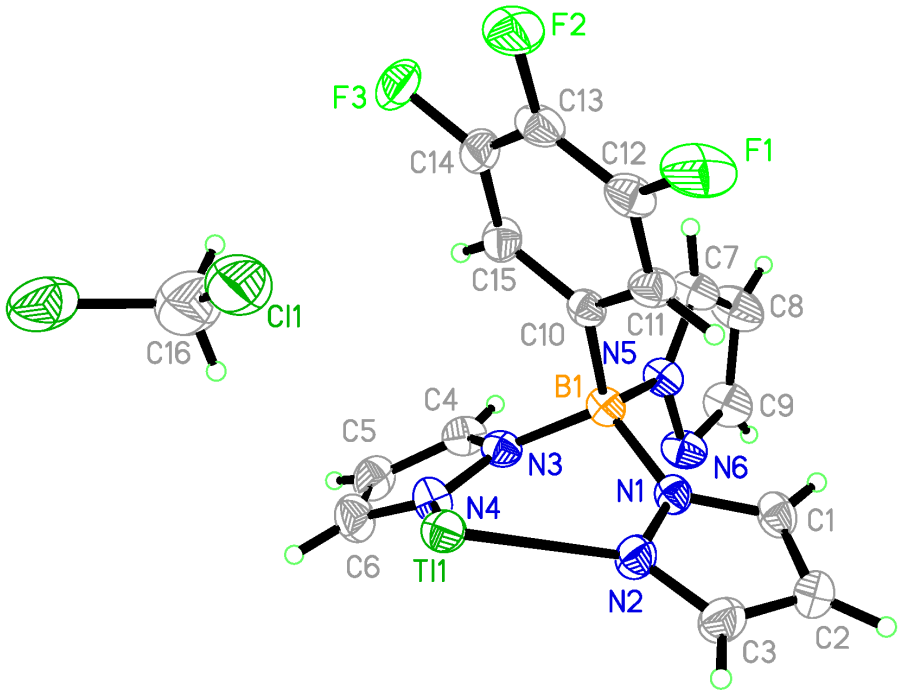
REFERENCE NUMBER: 22091z

CRYSTAL STRUCTURE REPORT

$C_{15}\ H_{11}\ B\ F_3\ N_6\ Tl \cdot \frac{1}{2}(C\ H_2\ Cl_2)$

Report prepared for:
Prof. P. Fischer - Macalester University

June 9, 2022



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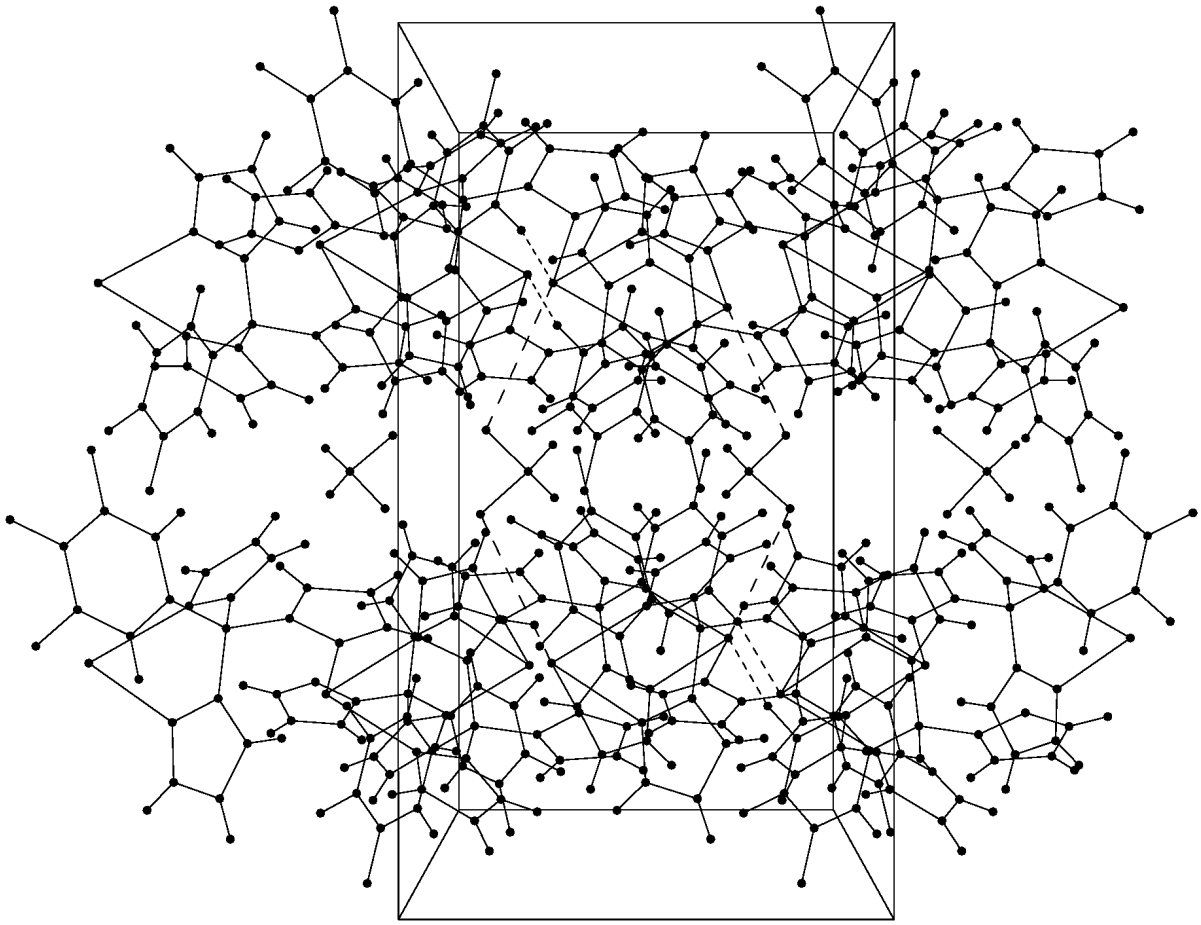


Data collection

A crystal (approximate dimensions 0.160 x 0.150 x 0.070 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 479 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 4 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2942 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick 2008)[4] and refined using SHELXL-2014 (Sheldrick 2014).[4] The space group *C*2/c was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided all non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0272$ and $wR2 = 0.0499$ (F^2, obs. data).

Structure description

The structure is the one suggested as a hemi-solvate of DCM. The DCM is located on a two-fold axis. The structure is polymeric.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22091z.

Identification code	22091z	
Empirical formula	$C_{15.50}H_{12}BClF_3N_6Tl$	
Formula weight	589.94	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	a = 18.9101(19) Å	α = 90°
	b = 10.4677(12) Å	β = 90.289(4)°
	c = 19.1159(17) Å	γ = 90°
Volume	3783.9(7) Å^3	
Z	8	
Density (calculated)	2.071 Mg/m^3	
Absorption coefficient	8.720 mm^{-1}	
F(000)	2216	
Crystal color, morphology	Colourless, Plate	
Crystal size	0.160 x 0.150 x 0.070 mm^3	
Theta range for data collection	2.224 to 30.537°	
Index ranges	$-18 \le h \le 26$, $-14 \le k \le 12$, $-26 \le l \le 27$	
Reflections collected	17512	
Independent reflections	5784 [R(int) = 0.0353]	
Observed reflections	4672	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.4920 and 0.3775	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5784 / 0 / 249	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0499	
R indices (all data)	R1 = 0.0413, wR2 = 0.0541	
Largest diff. peak and hole	0.882 and -0.834 e.Å^{-3}	

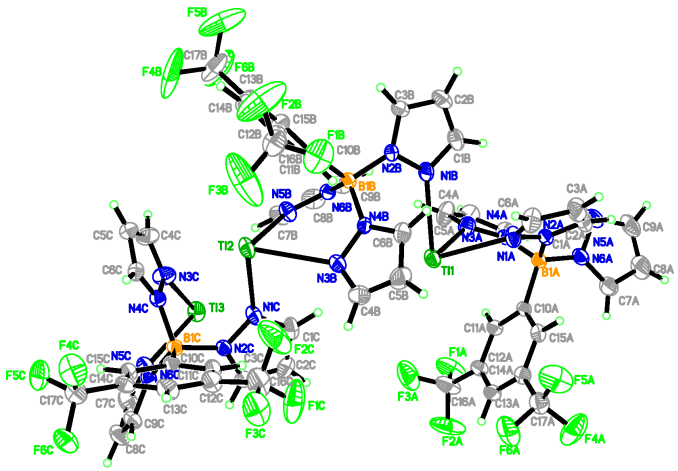
REFERENCE NUMBER: 22113z

CRYSTAL STRUCTURE REPORT

$Tl^{+}\ [C_{17}\ H_{12}\ B\ F_{6}\ N_{6}]^{-}$

Report prepared for:
Prof. P. Fischer

July 25, 2022



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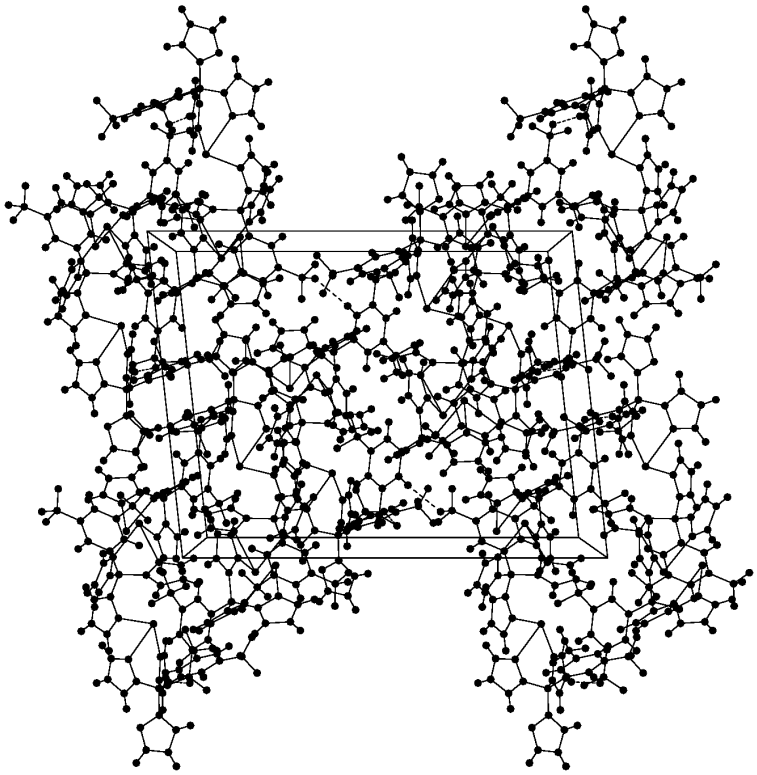


Data collection

A crystal (approximate dimensions 0.200 x 0.090 x 0.090 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 1524 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2873 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group $P2_1/n$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0263 and $wR2$ = 0.0520 (F^2, obs. data).

Structure description

The structure is the one suggested. There are three formula units per asymmetric unit. The structure is polymeric where each Tl^+ is coordinated to three pz nitrogen atoms, with either 1 or 2 coming from the same ligand.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22113z.

Identification code	22113z	
Empirical formula	$C_{17}H_{12}BF_6N_6Tl$	
Formula weight	629.51	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 17.4697(8) Å	α = 90°
	b = 16.3093(7) Å	β = 96.179(2)°
	c = 22.5734(11) Å	γ = 90°
Volume	6394.2(5) $Å^3$	
Z	12	
Density (calculated)	1.962 Mg/m^3	
Absorption coefficient	7.645 mm^{-1}	
F(000)	3552	
Crystal color, morphology	Brown, Needle	
Crystal size	0.200 x 0.090 x 0.090 mm^3	
Theta range for data collection	1.878 to 30.524°	
Index ranges	$-24 \le h \le 24$, $-23 \le k \le 18$, $-32 \le l \le 32$	
Reflections collected	98282	
Independent reflections	19523 [R(int) = 0.0430]	
Observed reflections	15290	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.4611	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19523 / 0 / 838	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	$R1$ = 0.0263, $wR2$ = 0.0520	
R indices (all data)	$R1$ = 0.0444, $wR2$ = 0.0572	
Largest diff. peak and hole	1.153 and -0.823 e.$Å^{-3}$	

REFERENCE NUMBER: 22111z

CRYSTAL STRUCTURE REPORT

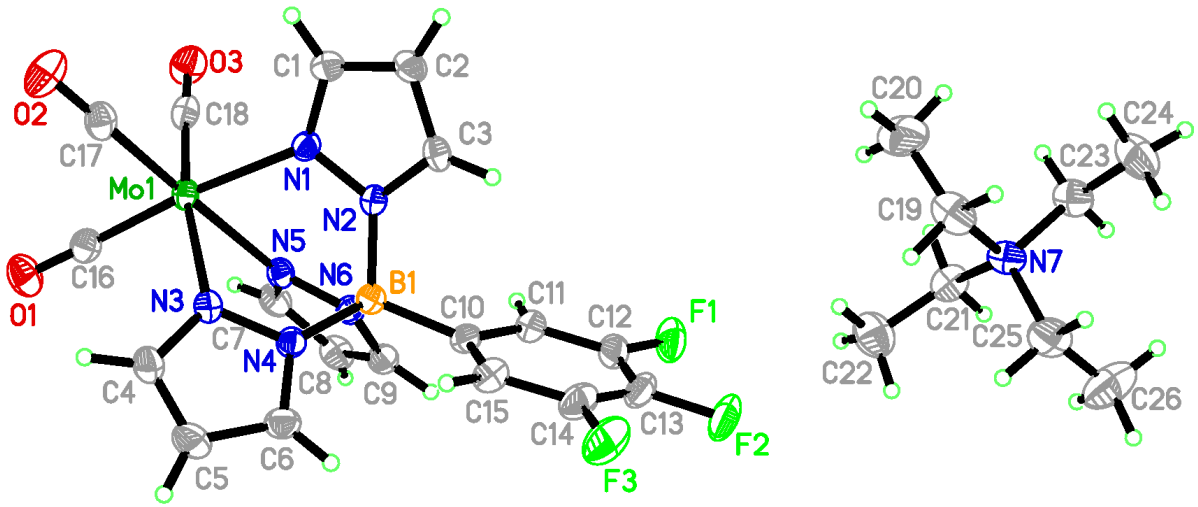
$C_{26}\ H_{31}\ B\ F_3\ Mo\ N_7\ O_3$

or

$[C_8H_{20}N]^+\ [C_{18}H_{11}BF_3MoN_6O_3]^-$

Report prepared for:
Prof. P. Fischer

July 25, 2022



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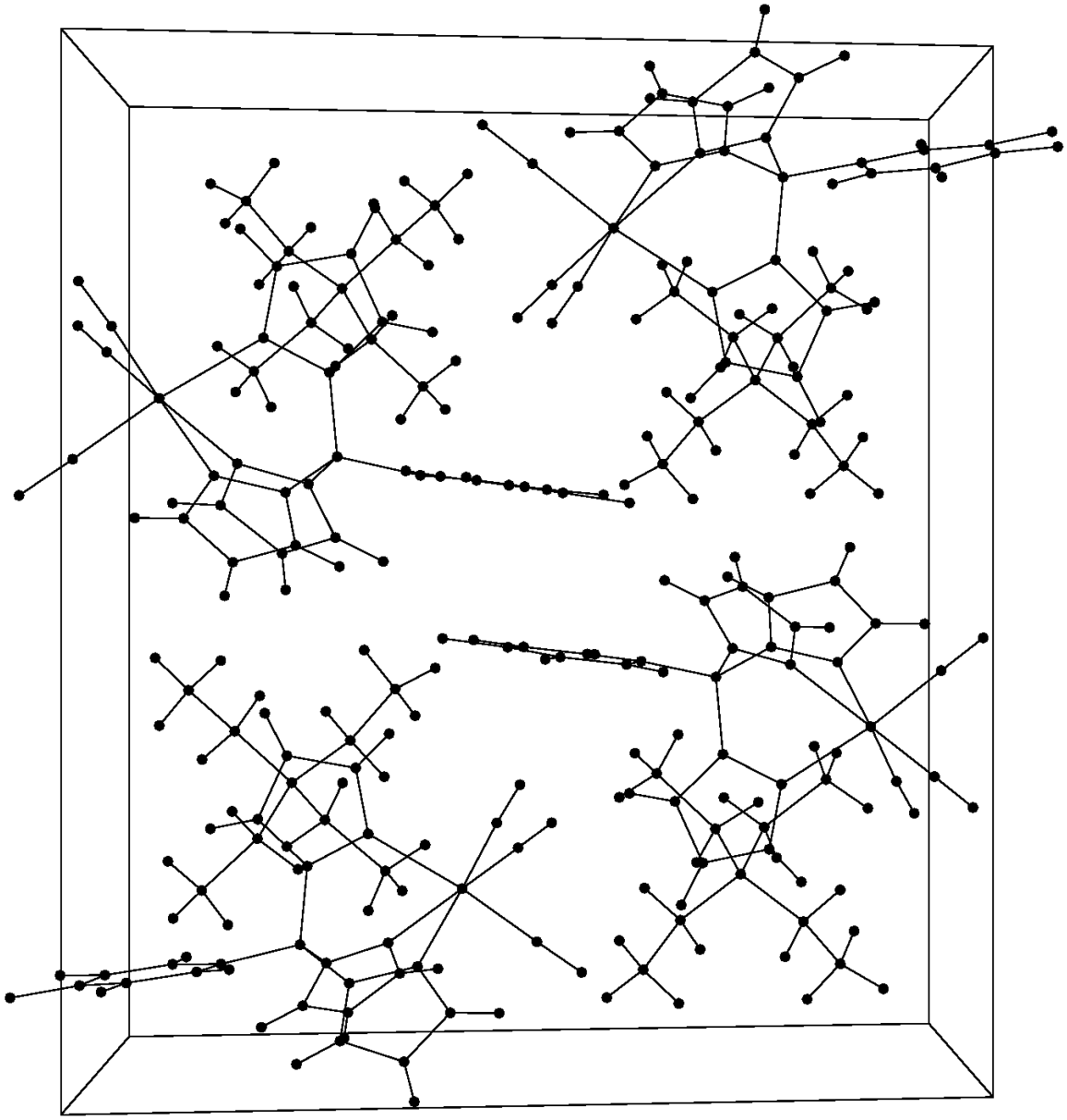


Data collection

A crystal (approximate dimensions 0.190 x 0.160 x 0.160 mm^3) was placed onto the tip of a 150 μmm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 580 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2912 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0354 and $wR2$ = 0.0777 (F^2, obs. data).

Structure description

The structure is the one suggested.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22111z.

Identification code	22111z	
Empirical formula	$C_{26}H_{31}BF_3MoN_7O_3$	
Formula weight	653.33	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.0744(4) Å	α = 90°
	b = 18.9906(8) Å	β = 96.281(2)°
	c = 16.6747(6) Å	γ = 90°
Volume	2856.3(2) Å^3	
Z	4	
Density (calculated)	1.519 Mg/m^3	
Absorption coefficient	0.520 mm^{-1}	
F(000)	1336	
Crystal color, morphology	yellow, Block	
Crystal size	0.190 x 0.160 x 0.160 mm^3	
Theta range for data collection	2.145 to 30.564°	
Index ranges	$-12 \le h \le 9$, $-22 \le k \le 27$, $-23 \le l \le 23$	
Reflections collected	29927	
Independent reflections	8704 [R(int) = 0.0441]	
Observed reflections	6715	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.6335	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8704 / 0 / 374	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	$R1$ = 0.0354, $wR2$ = 0.0777	
R indices (all data)	$R1$ = 0.0520, $wR2$ = 0.0874	
Largest diff. peak and hole	0.403 and -0.608 e.Å^{-3}	

REFERENCE NUMBER: 22112z

CRYSTAL STRUCTURE REPORT

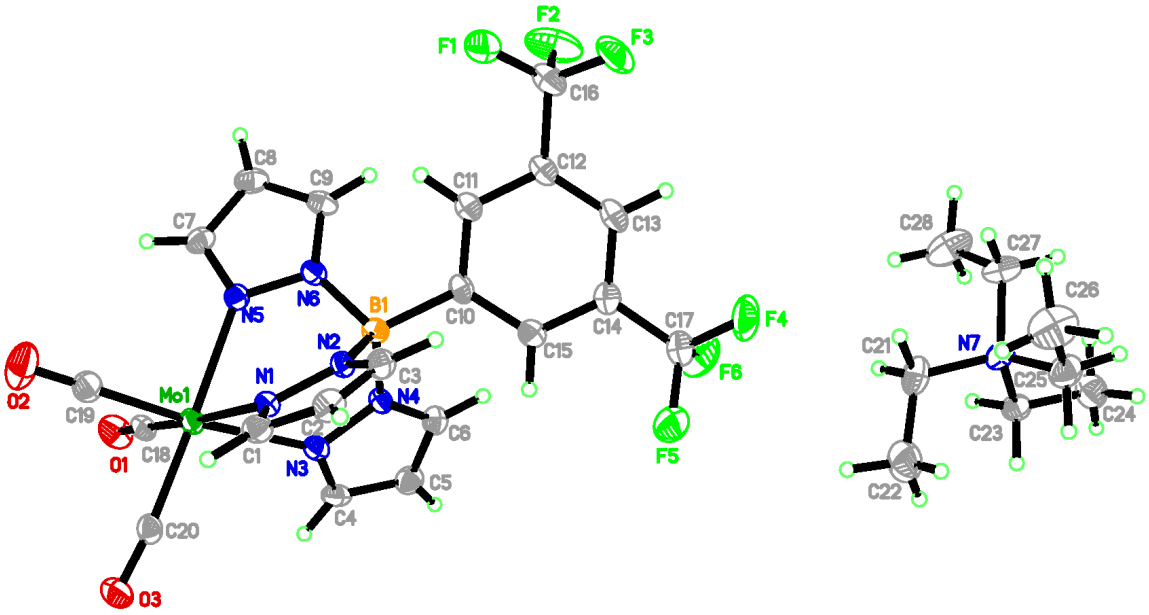
$C_{28}\ H_{32}\ B\ F_6\ Mo\ N_7\ O_3$

or

$[C_8H_{20}N]^+\ [C_{20}H_{12}BF_6MoN_6O_3]^-$

Report prepared for:
Prof. P. Fischer

July 25, 2022



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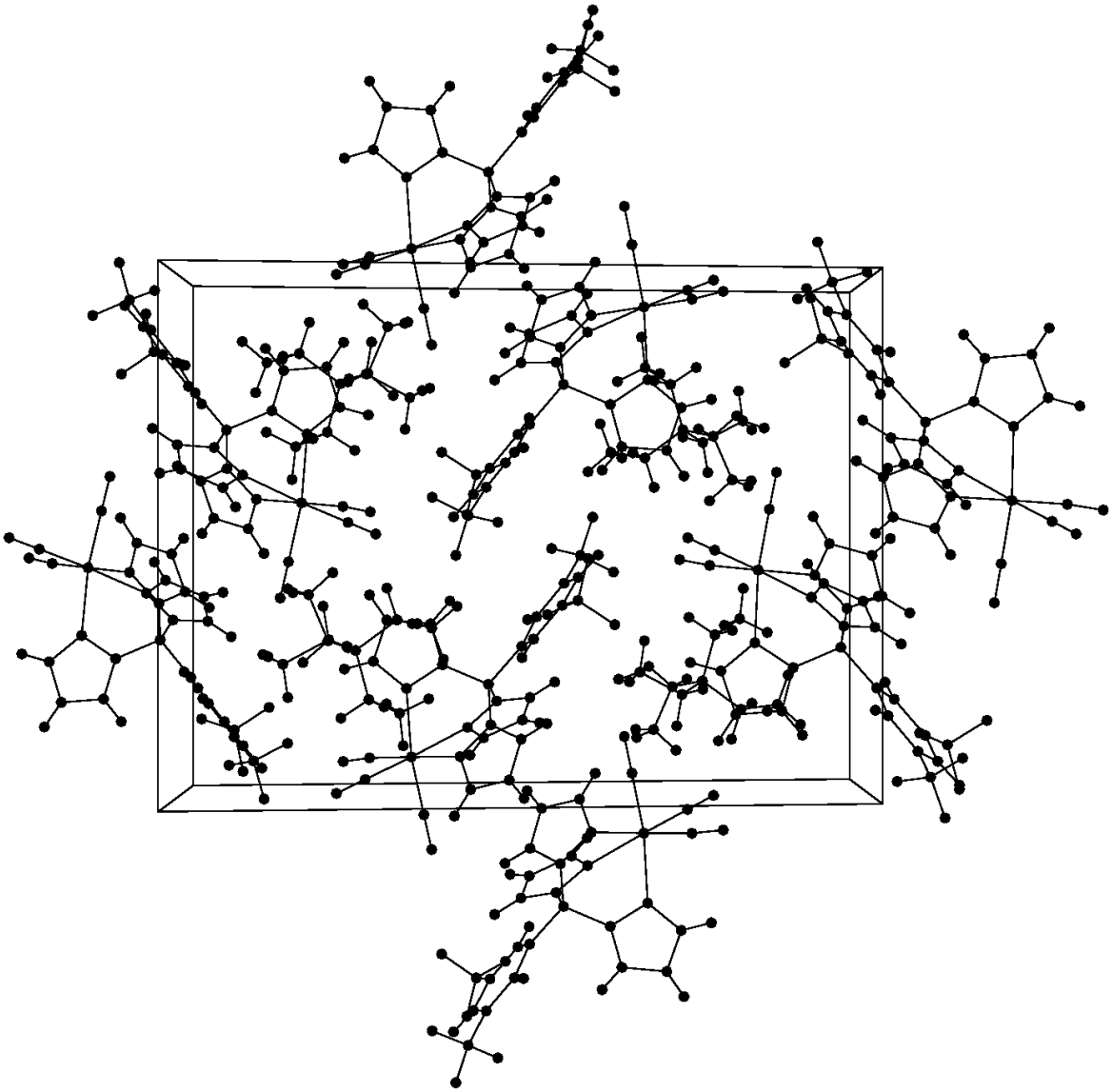


Data collection

A crystal (approximate dimensions 0.120 x 0.110 x 0.060 mm^3) was placed onto the tip of a 150μm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 660 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2871 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group $P2_1/n$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0429 and $wR2$ = 0.0831 (F^2, obs. data).

Structure description

The structure is the one suggested. The TEA is disordered about a local center in an approximate 0.72:0.28 ratio. One of the two disordered images was selected for the drawings for the sake of clarity.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22112z.

Identification code	22112z	
Empirical formula	C_{28} H_{32} B F_6 Mo N_7 O_3	
Formula weight	735.35	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.0815(6) Å	α = 90°
	b = 15.9381(10) Å	β = 96.793(3)°
	c = 21.3866(14) Å	γ = 90°
Volume	3073.8(3) Å^3	
Z	4	
Density (calculated)	1.589 Mg/m^3	
Absorption coefficient	0.507 mm^{-1}	
F(000)	1496	
Crystal color, morphology	Yellow, Block	
Crystal size	0.120 x 0.110 x 0.060 mm^3	
Theta range for data collection	1.918 to 30.542°	
Index ranges	$-12 \le h \le 11$, $-22 \le k \le 22$, $-29 \le l \le 30$	
Reflections collected	29027	
Independent reflections	9326 [R(int) = 0.0575]	
Observed reflections	6630	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7461 and 0.6342	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9326 / 118 / 445	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	$R1$ = 0.0429, $wR2$ = 0.0831	
R indices (all data)	$R1$ = 0.0676, $wR2$ = 0.0947	
Largest diff. peak and hole	0.570 and -0.639 e.Å^{-3}	

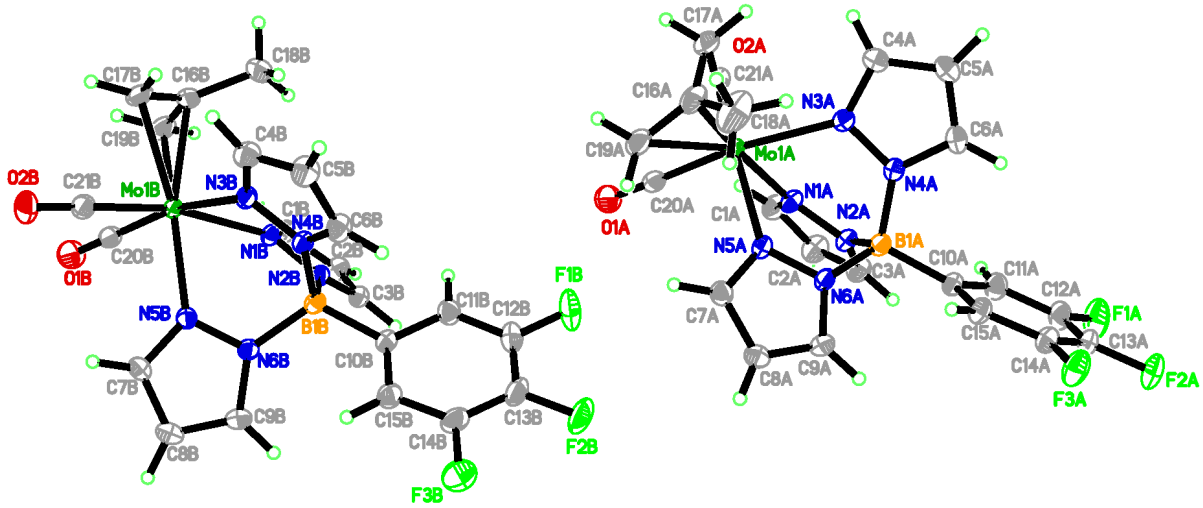
REFERENCE NUMBER: 22106z

CRYSTAL STRUCTURE REPORT

$C_{21}H_{18}BF_3MoN_6O_2$

Report prepared for:
Prof. P. Fischer

July 13, 2022



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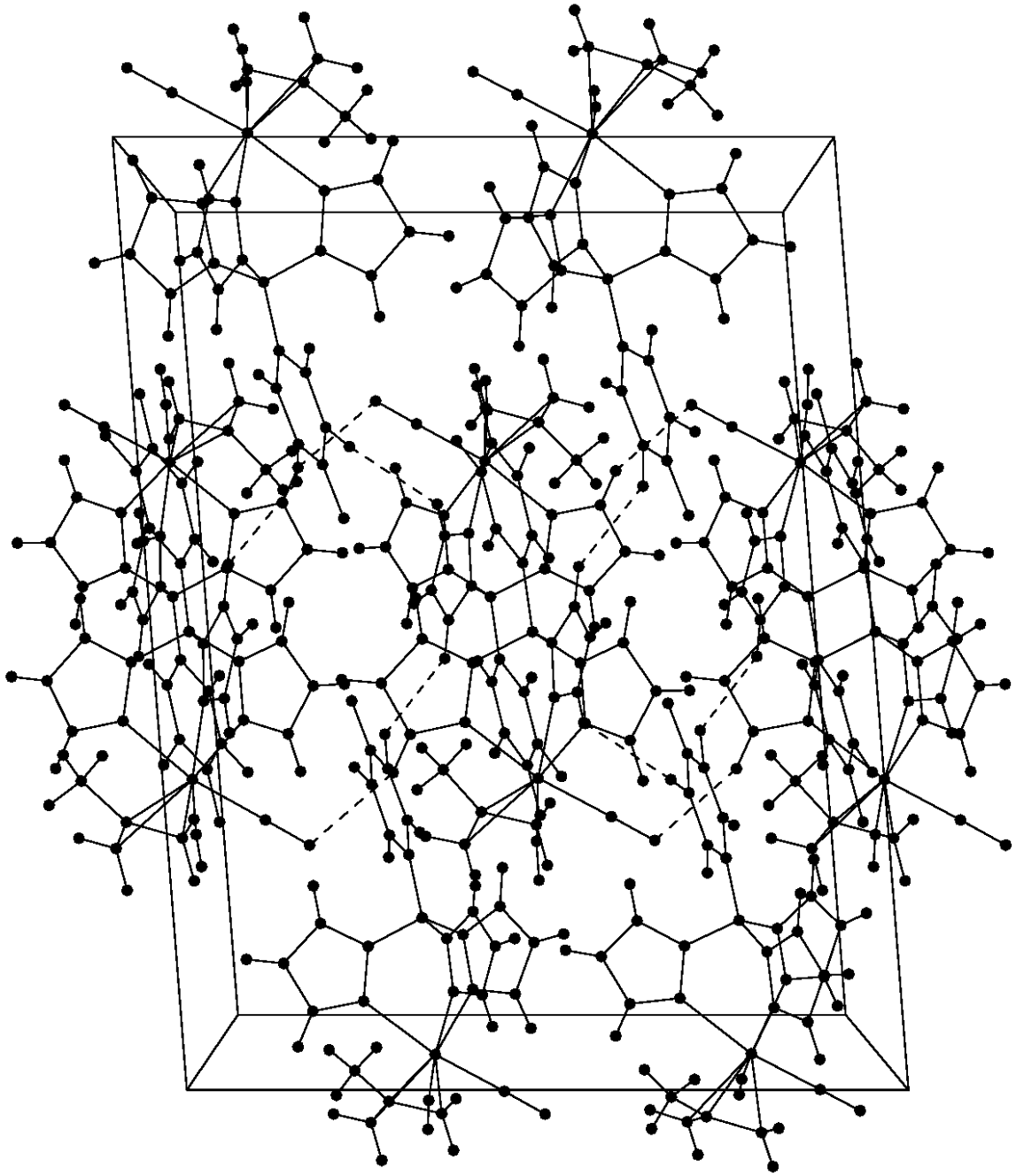


Data collection

A crystal (approximate dimensions 0.160 x 0.120 x 0.025 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from ?? reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2905 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick, 2018)[4] and refined using SHELXL-2018/3 (Sheldrick, 2018).[4] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0297$ and $wR2 = 0.0670$ (F^2, obs. data).

Structure description

The structure is the one suggested. There are two molecules in the asymmetric unit: Z'=2. The absolute structure of these is inverted. There appears to be a pseudo-symmetric glide relating these.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2013, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22106za.

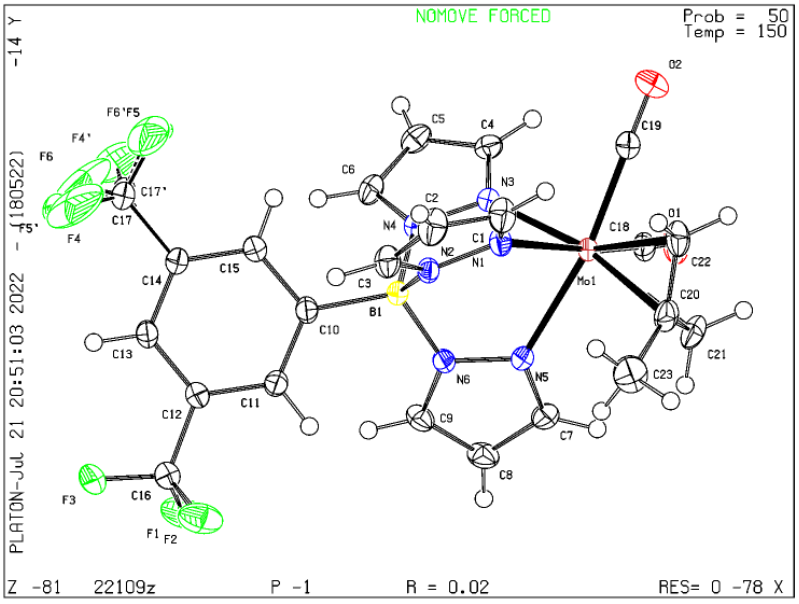
Identification code	22106z	
Empirical formula	$C_{21}H_{18}BF_3MoN_6O_2$	
Formula weight	550.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 20.9464(7) Å	α = 90°
	b = 13.3844(5) Å	β = 94.4542(14)°
	c = 15.8056(5) Å	γ = 90°
Volume	4417.8(3) Å^3	
Z, Z'	8, 2	
Density (calculated)	1.654 Mg/m^3	
Absorption coefficient	0.651 mm^{-1}	
F(000)	2208	
Crystal color, morphology	Yellow, Plate	
Crystal size	0.160 x 0.120 x 0.025 mm^3	
Theta range for data collection	1.996 to 30.537°	
Index ranges	$-29 \le h \le 28$, $-19 \le k \le 15$, $-20 \le l \le 22$	
Reflections collected	45071	
Independent reflections	13478 [R(int) = 0.0322]	
Observed reflections	11086	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7457 and 0.6102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13478 / 0 / 615	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	$R1$ = 0.0297, $wR2$ = 0.0670	
R indices (all data)	$R1$ = 0.0421, $wR2$ = 0.0738	
Largest diff. peak and hole	0.511 and -0.865 e.Å^{-3}	

REFERENCE NUMBER: 22109z

CRYSTAL STRUCTURE REPORT

$C_{23}H_{19}BF_6MoN_6O_2$

Report prepared for: Paul Fischer
July 21, 2022



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Data collection

A crystal (approximate dimensions 0.190 x 0.150 x 0.100 mm) was placed onto the tip of a 0.15 mm MiTeGen loop and mounted on a Bruker Photon-II CMOS diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 736 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 2 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.75 Å. Four major sections of frames were collected with 0.30∫ steps in ω at four different ϕ settings and a detector position of -28∫ in 2θ. The intensity data were corrected for absorption and decay.[2] Final cell constants were calculated from the xyz centroids of 1887 strong reflections from the actual data collection after integration.[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT 2018/2 (Sheldrick, 2018)[4] and refined using SHELXL-2018/3 (Sheldrick, 2018).[5] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0235$ and $wR2 = 0.0586$ (F^2, all data).

Structure description

The structure is the one suggested. The reflection -2 -1 2 was omitted due to suspected interference from the beam stop. The molecule contains a disordered CF_3 group. This group has been modeled in two parts made up of atoms C17, F4, F5, F6 and C17', F4', F5', F6' with occupancies of 53.4% and 46.6% respectively. Atoms C17 and C17' were modeled using the EADP constraint. Atoms C17, C17', F4, F4', F5, F5', F6, F6' were all modeled using SADI restraints. C17, F4, F5, F6 and C17', F4', F5', F6' were modeled using strong RIGU restraints. In total, 66 restraints were added.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Alex Lovstedt as a coauthor or 2) acknowledge Alex Lovstedt and the X-Ray Crystallographic Laboratory.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2016).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2016).

[3] SAINT, Bruker Analytical X-ray Systems, Madison, WI (2016).

[4] SHELXTL 2018/2, Bruker Analytical X-Ray Systems, Madison, WI (2016); G. M. Sheldrick, *Acta Cryst.* **A71**, 3-8 (2015).

[5] SHELXL 2018/3; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \ / \ \Sigma\ [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^2)^2] \ / \ (n-p)]^{1/2}$$

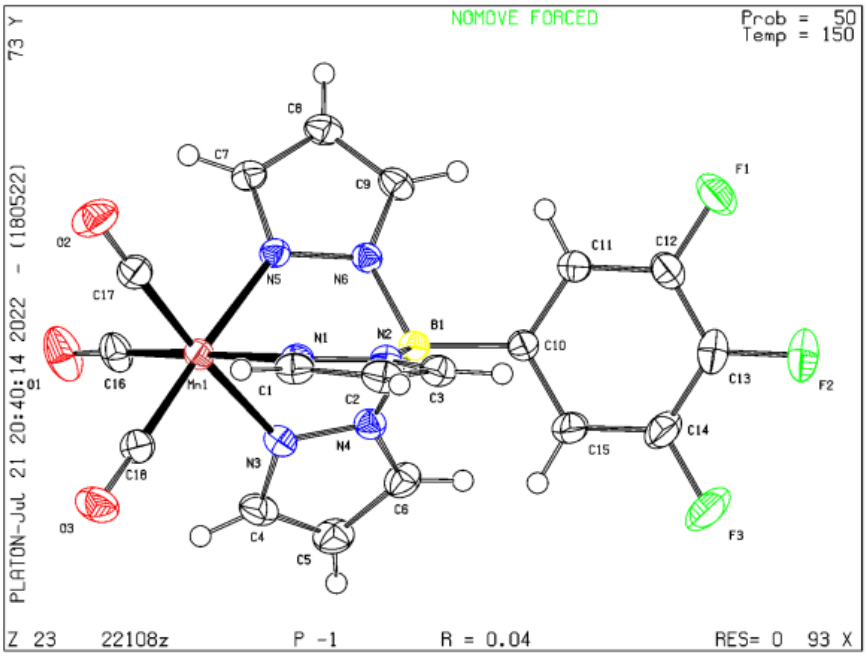
Table 1. Crystal data and structure refinement for 22109.

Identification code	22109	
Empirical formula	C_{23} H_{19} B F_6 Mo N_6 O_2	
Formula weight	632.19	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.6506(4) Å	α = 107.215(2) º
	b = 13.0055(8) Å	β = 108.4390(10) º
	c = 13.0165(8) Å	γ = 101.553(2) º
Volume	1255.28(12) $Å^3$	
Z	2	
Density (calculated)	1.673 Mg/m^3	
Absorption coefficient	0.601 mm^{-1}	
F(000)	632	
Crystal color, morphology	yellow, block	
Crystal size	0.190 x 0.150 x 0.100 mm^3	
Theta range for data collection	1.951 to 29.216 º	
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 17$, $-17 \le l \le 17$	
Reflections collected	64683	
Independent reflections	6785 [R(int) = 0.0440]	
Observed reflections	6396	
Completeness to theta = 25.242 º	99.8%	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6785 / 66 / 384	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0235, wR2 = 0.0570	
R indices (all data)	R1 = 0.0257, wR2 = 0.0586	
Largest diff. peak and hole	0.670 and -0.470 e.$Å^{-3}$	

REFERENCE NUMBER: 22108z

CRYSTAL STRUCTURE REPORT

$C_{18}H_{11}BF_3MnN_6O_3$



Report prepared for: Paul Fischer

July 21, 2022

Alex Lovstedt

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Data collection

A crystal (approximate dimensions 0.100 x 0.070 x 0.040 mm was placed onto the tip of a 0.15 mm MiTeGen loop and mounted on a Bruker Photon-III CMOS diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 272 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 15 seconds and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.70 Å. Four major sections of frames were collected with 0.30∫ steps in ω at four different ϕ settings and a detector position of -28∫ in 2θ. The intensity data were corrected for absorption and decay.[2] Final cell constants were calculated from the xyz centroids of 9877 strong reflections from the actual data collection after integration.[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick 2008)[4] and refined using SHELXL-2018/3 (Sheldrick, 2018).[5] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0353 and $wR2$ = 0.0937 (F^2, all data).

Structure description

The structure is the one suggested. The reflection 0 -1 1 was omitted due to suspected interference from the beam stop.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Alex Lovstedt as a coauthor or 2) acknowledge Alex Lovstedt and the X-Ray Crystallographic Laboratory.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2016).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2016).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2016).

[4] SHELXTL 2018/2, Bruker Analytical X-Ray Systems, Madison, WI (2016); G. M. Sheldrick, *Acta Cryst.* **A71**, 3-8 (2015).

[5] SHELXL 2018/3; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

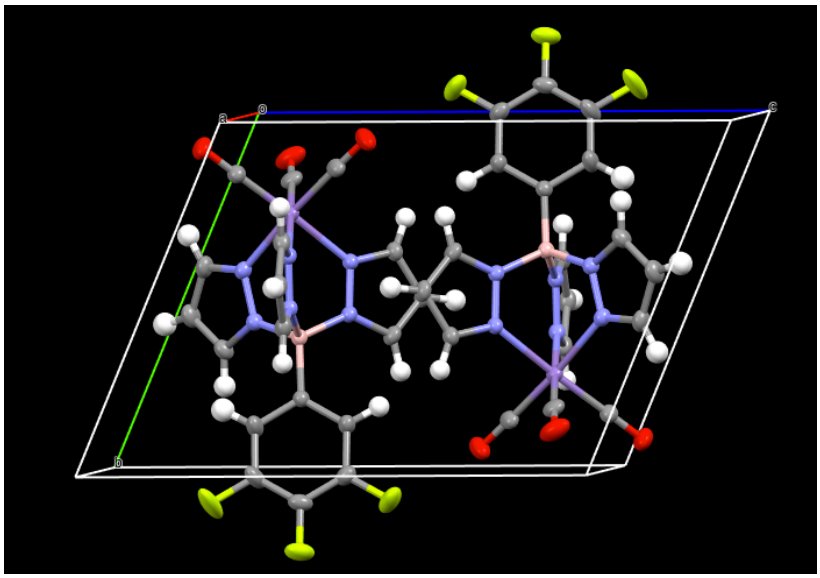
$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o{}^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c{}^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

where $w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c{}^2)^2] \,/\, (n-p)]^{1/2}$$



An image showing the unit cell packing of 22108. The red, green, and blue axes are the a, b, and c axes respectively.

Table 1. Crystal data and structure refinement for 22108.

Identification code	22108z	
Empirical formula	C18 H11 B F3 Mn N6 O3	
Formula weight	482.08	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0619(6) Å	α = 112.867(2) º
	b = 10.3783(7) Å	β = 92.257(2) º
	c = 13.2434(11) Å	γ = 103.333(2) º
Volume	983.12(13) Å^3	
Z	2	
Density (calculated)	1.629 Mg/m^3	
Absorption coefficient	0.734 mm^{-1}	
F(000)	484	
Crystal color, morphology	white, Block	
Crystal size	0.100 x 0.070 x 0.040 mm^3	
Theta range for data collection	2.210 to 32.050 º	
Index ranges	$-12 \le h \le 11$, $-11 \le k \le 15$, $-19 \le l \le 19$	
Reflections collected	25684	
Independent reflections	6818 [R(int) = 0.0350]	
Observed reflections	5566	
Completeness to theta = 25.242 º	99.9%	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6818 / 0 / 289	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0867	
R indices (all data)	R1 = 0.0477, wR2 = 0.0937	
Largest diff. peak and hole	0.447 and -0.548 e.Å^{-3}	

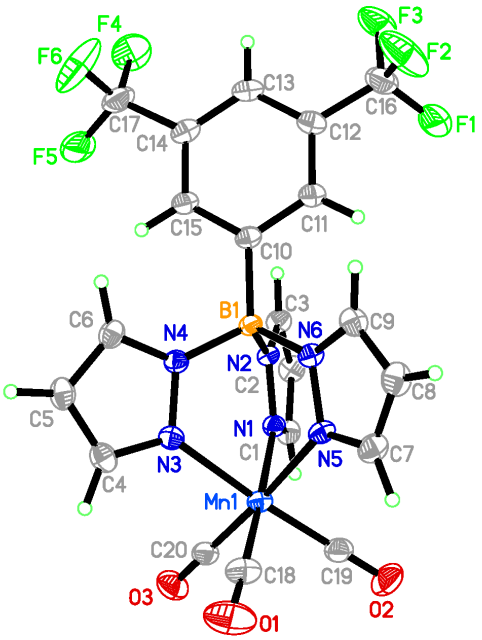
REFERENCE NUMBER: 22127z

CRYSTAL STRUCTURE REPORT

$C_{20}H_{12}BF_6MnN_6O_3$

Report prepared for:
Prof. P. Fischer

September 12, 2022



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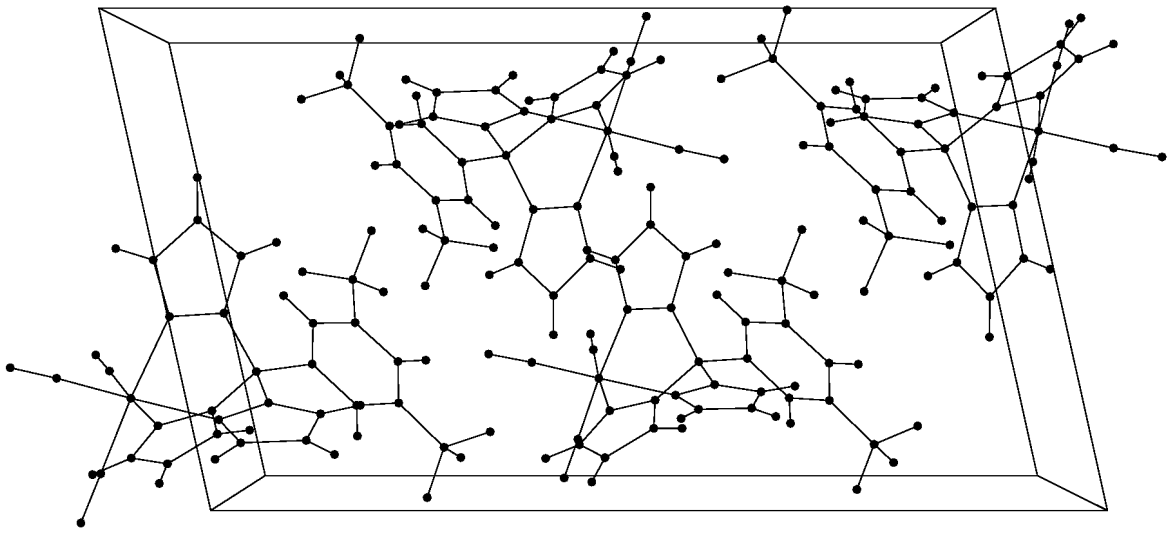


Data collection

A crystal (approximate dimensions 0.110 x 0.080 x 0.040 mm^3) was placed onto the tip of a 150 μm diameter glass capillary and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from two sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 502 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.75 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (TWINABS).[2] Final cell constants were calculated from 2924 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick, 2018)[4] and refined using SHELXL-2018/3 (Sheldrick, 2018).[4] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0438$ and $wR2 = 0.0912$ (F^2, obs. data).

Structure description

The structure is the one suggested. All specimens examined were cracked leading to difficult data collections. The sample was originally collected as 22107, but this could not be effectively integrated as a twin by non-merohedry. See the CIF for details of twinning.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2016).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2016).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2016).

[4] SHELXTL 2018/2, Bruker Analytical X-Ray Systems, Madison, WI (2016); G. M. Sheldrick, *Acta Cryst.* **A71**, 3-8 (2015).

[5] SHELXL 2018/3; G. M. Sheldrick, *Acta Cryst.* **C71**, 3-8 (2015).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

where $w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22127z.

Identification code	22127z	
Empirical formula	C20 H12 B F6 Mn N6 O3	
Formula weight	564.11	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.7733(8) Å	α = 90°
	b = 9.5312(6) Å	β = 102.577(3)°
	c = 20.5338(12) Å	γ = 90°
Volume	2248.9(2) Å^3	
Z	4	
Density (calculated)	1.666 Mg/m^3	
Absorption coefficient	0.674 mm^{-1}	
F(000)	1128	
Crystal color, morphology	Colorless, Plate	
Crystal size	0.110 x 0.080 x 0.040 mm^3	
Theta range for data collection	2.366 to 28.282°	
Index ranges	$-15 \le h \le 15$, $0 \le k \le 12$, $0 \le l \le 27$	
Reflections collected	5604	
Independent reflections	5604 [R(int) = 0.0774]	
Observed reflections	4820	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.746070 and 0.670767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5604 / 0 / 335	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0912	
R indices (all data)	R1 = 0.0576, wR2 = 0.1010	
Largest diff. peak and hole	0.589 and -0.466 e.Å^{-3}	

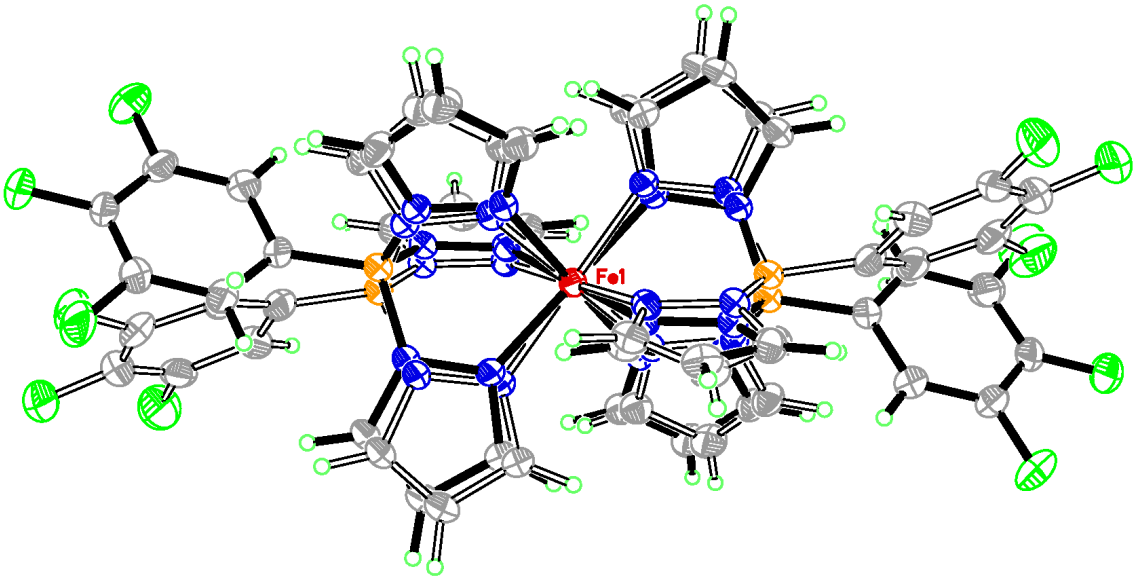
REFERENCE NUMBER: 22110z

CRYSTAL STRUCTURE REPORT

$C_{30}H_{22}B_2F_6FeN_{12}$

Report prepared for:
Prof. P. Fischer

July 25, 2022



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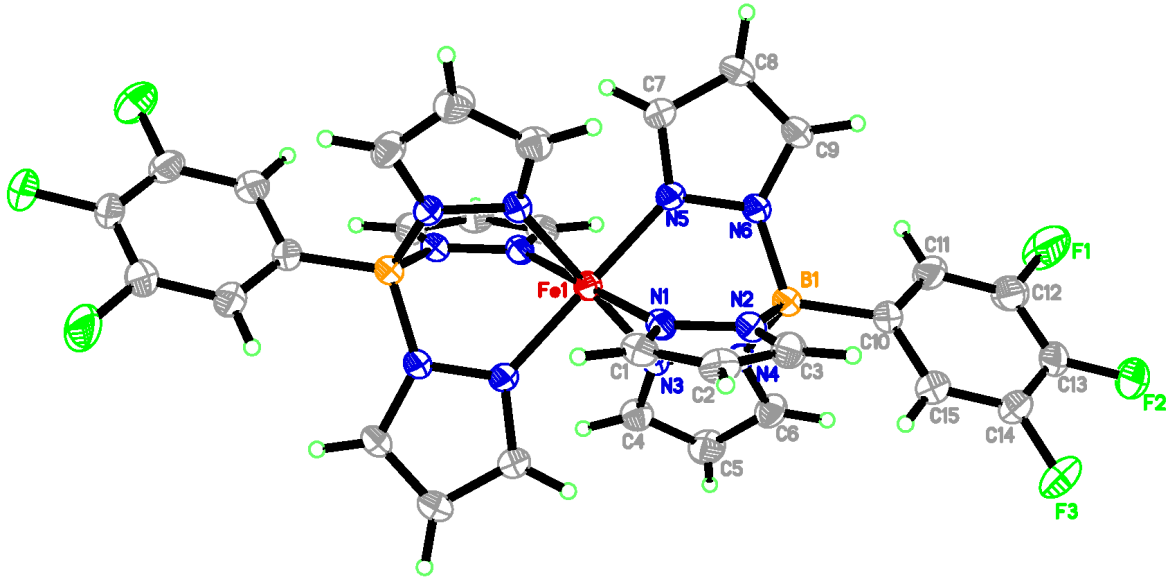
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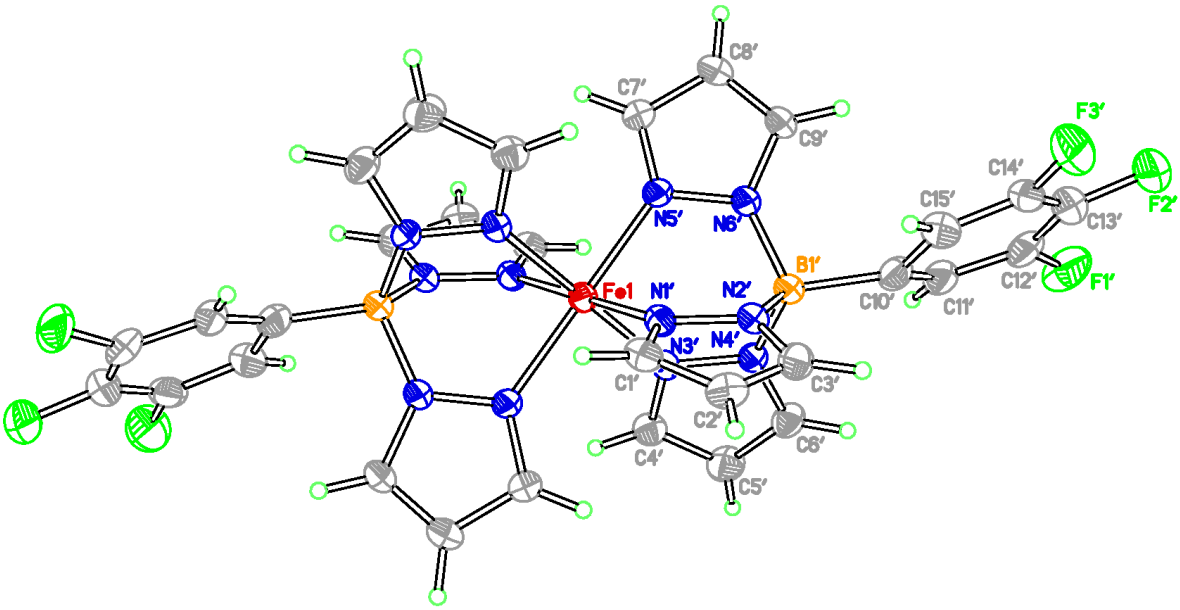
F3

Major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C12′
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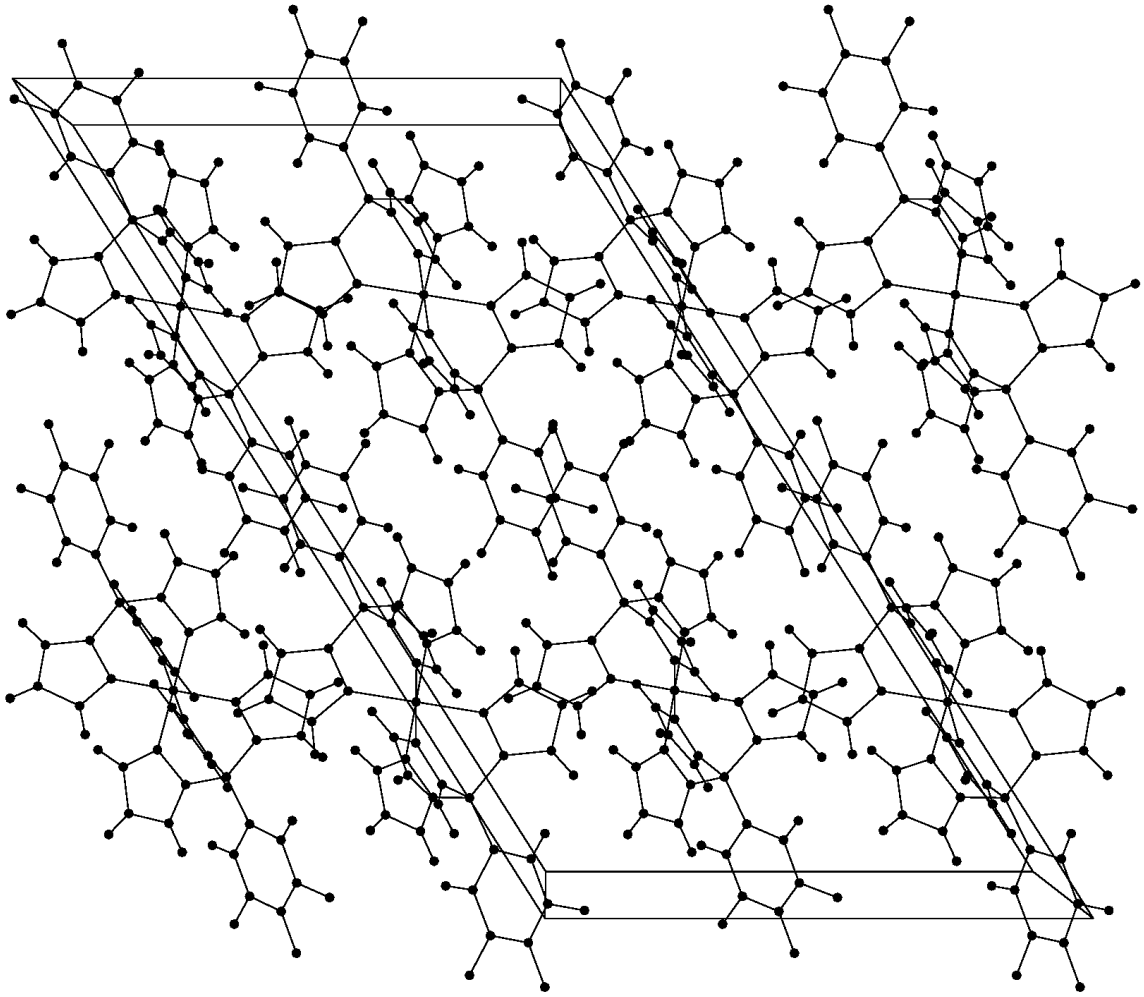
Minor



Data collection

A crystal (approximate dimensions 0.170 x 0.065 x 0.025 mm^3) was placed onto the tip of a 150μm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 269 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 20 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2997 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group *C*2/c was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0390 and $wR2$ = 0.0900 (F^2, obs. data).

Structure description

The structure is the one suggested. The ligand is disordered in an approximate 4:1 ratio. Both drawings are provided.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22110z.

Identification code	22110z	
Empirical formula	C_{30} H_{22} B_2 F_6 Fe N_{12}	
Formula weight	742.06	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 27.4242(11) Å	α = 90°
	b = 9.1455(4) Å	β = 122.375(2)°
	c = 15.1202(5) Å	γ = 90°
Volume	3202.8(2) Å^3	
Z	4	
Density (calculated)	1.539 Mg/m^3	
Absorption coefficient	0.550 mm^{-1}	
F(000)	1504	
Crystal color, morphology	Red, Needle	
Crystal size	0.170 x 0.065 x 0.025 mm^3	
Theta range for data collection	2.394 to 30.547°	
Index ranges	$-28 \le h \le 39$, $-13 \le k \le 10$, $-21 \le l \le 20$	
Reflections collected	12223	
Independent reflections	4838 [*R*(int) = 0.0333]	
Observed reflections	3609	
Completeness to theta = 25.242°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.5644 and 0.4597	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4838 / 264 / 350	
Goodness-of-fit on F^2	1.029	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0390, *wR*2 = 0.0900	
R indices (all data)	*R*1 = 0.0589, *wR*2 = 0.0999	
Largest diff. peak and hole	0.311 and -0.470 e.Å^{-3}	

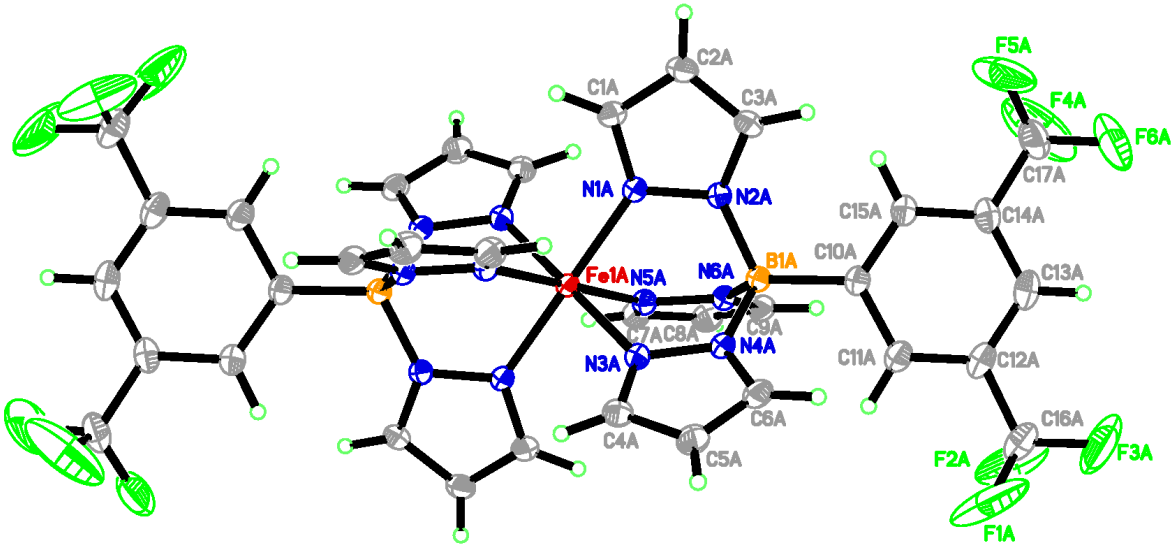
REFERENCE NUMBER: 22120zz

CRYSTAL STRUCTURE REPORT

$C_{34}\ H_{24}\ B_2\ F_{12}\ Fe\ N_{12}$

Report prepared for:
Prof. P. Fischer

July 26, 2022



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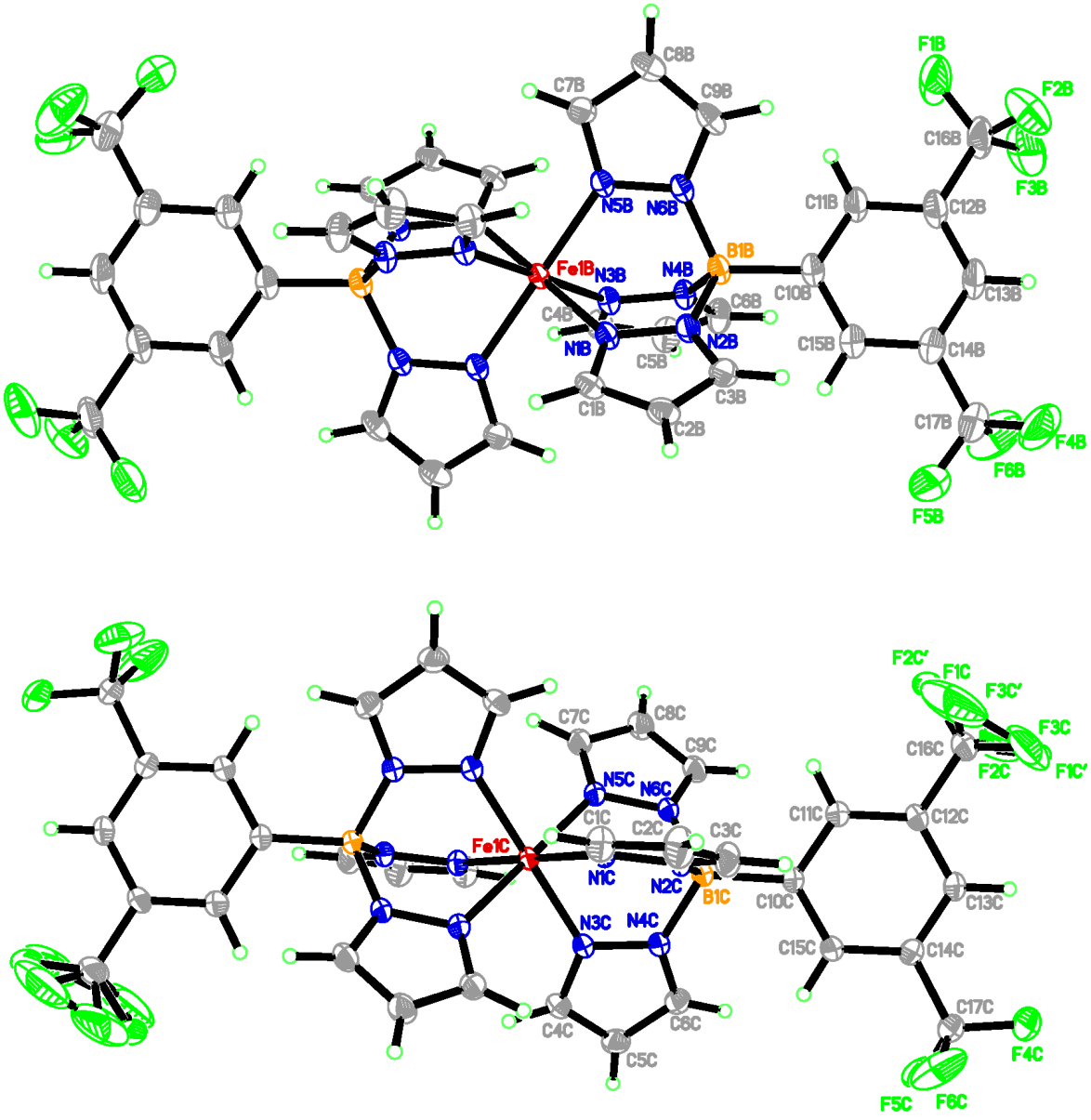
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C1B
C2B
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F5B

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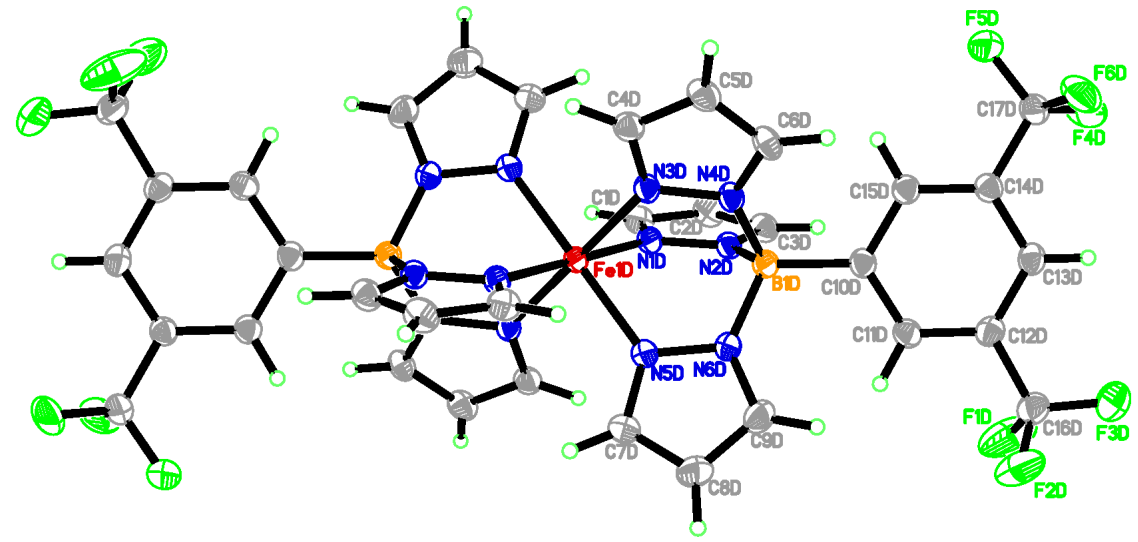
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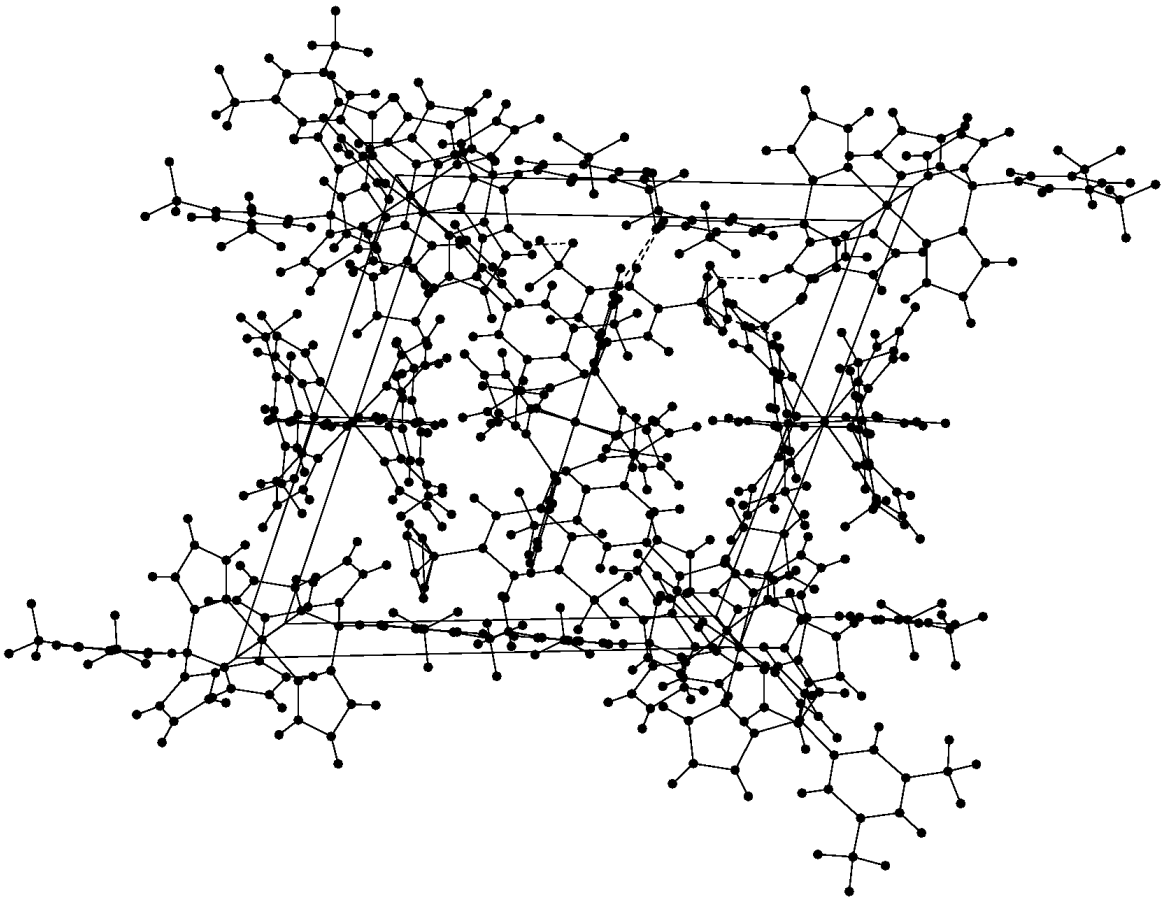


Data collection

A crystal (approximate dimensions 0.190 x 0.150 x 0.035 mm^3) was placed onto the tip of a 150 μm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 584 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 30 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2941 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group P -1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0459 and $wR2$ = 0.1179 (F^2, obs. data).

Structure description

The structure is the one suggested. There are four molecules in the asymmetric unit each with its metal atom located on different inversion centers: 4 x ½ the formula unit. One -CF_3 group was modelled as being rotationally disordered.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o{}^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ \Sigma\ [w(F_o^2\ )^2]]^{1/2}$$

$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c{}^2)^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22120zz.

Identification code	22120zz	
Empirical formula	C_{34} H_{24} B_2 F_{12} Fe N_{12}	
Formula weight	906.12	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.6527(16) Å	α = 104.507(4)°
	b = 16.2542(16) Å	β = 105.302(4)°
	c = 16.687(2) Å	γ = 103.887(4)°
Volume	3745.3(7) $Å^3$	
Z	4	
Density (calculated)	1.607 Mg/m^3	
Absorption coefficient	0.509 mm^{-1}	
F(000)	1824	
Crystal color, morphology	Red, Plate	
Crystal size	0.190 x 0.150 x 0.035 mm^3	
Theta range for data collection	2.085 to 30.569°	
Index ranges	$-21 \le h \le 22$, $-23 \le k \le 20$, $-23 \le l \le 23$	
Reflections collected	155918	
Independent reflections	22921 [R(int) = 0.0395]	
Observed reflections	18614	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6478 and 0.6290	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22921 / 30 / 1115	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1179	
R indices (all data)	R1 = 0.0599, wR2 = 0.1292	
Largest diff. peak and hole	1.273 and -0.820 e.$Å^{-3}$	

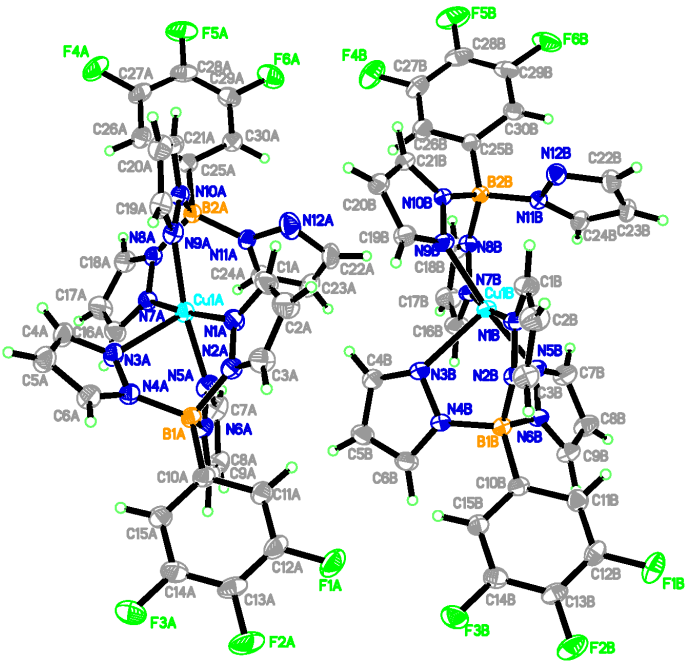
REFERENCE NUMBER: 22105z

CRYSTAL STRUCTURE REPORT

$C_{30}H_{22}B_2CuF_6N_{12}$

Report prepared for:
Prof. P. Fischer

July 24, 2022



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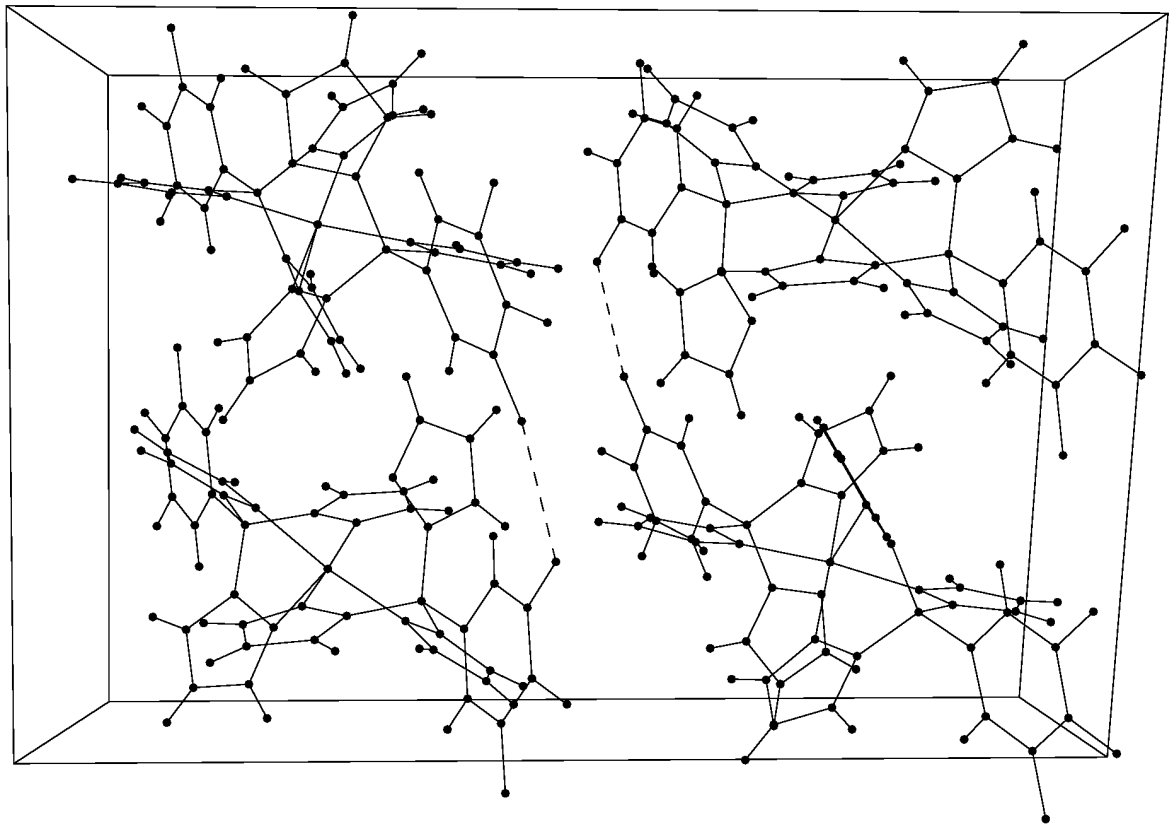


Data collection

A crystal (approximate dimensions 0.160 x 0.120 x 0.025 mm^3) was placed onto the tip of a 150 μm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 238 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 20 seconds and a detector distance of 5.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.83 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2792 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXS-97 (Sheldrick 2008)[4] and refined using SHELXL-2014 (Sheldrick 2014).[4] The space group P-1 was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0383 and $wR2$ = 0.0963 (F^2, obs. data).

Structure description

The structure is the one suggested. There are two independent molecules in the asymmetric unit. These have a pseudo-glide relationship parallel to (1 0 -3) except for the uncoordinated pz-group, which violates the putative glide.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R_1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22105z.

Identification code	22105z	
Empirical formula	$C_{30}H_{22}B_2CuF_6N_{12}$	
Formula weight	749.75	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.5103(7) Å	α = 91.514(3)°
	b = 14.6077(13) Å	β = 92.467(3)°
	c = 21.4716(19) Å	γ = 102.182(3)°
Volume	3217.2(5) Å^3	
Z	4	
Density (calculated)	1.548 Mg/m^3	
Absorption coefficient	0.758 mm^{-1}	
F(000)	1516	
Crystal color, morphology	Blue, Plate	
Crystal size	0.160 x 0.120 x 0.025 mm^3	
Theta range for data collection	1.985 to 30.576°	
Index ranges	$-15 \le h \le 14$, $-20 \le k \le 20$, $-30 \le l \le 30$	
Reflections collected	127609	
Independent reflections	19685 [R(int) = 0.0463]	
Observed reflections	15391	
Completeness to theta = 25.242°	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5645 and 0.5259	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19685 / 0 / 919	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0963	
R indices (all data)	R1 = 0.0561, wR2 = 0.1071	
Largest diff. peak and hole	0.628 and -0.646 e.Å^{-3}	

REFERENCE NUMBER: 22122z

CRYSTAL STRUCTURE REPORT

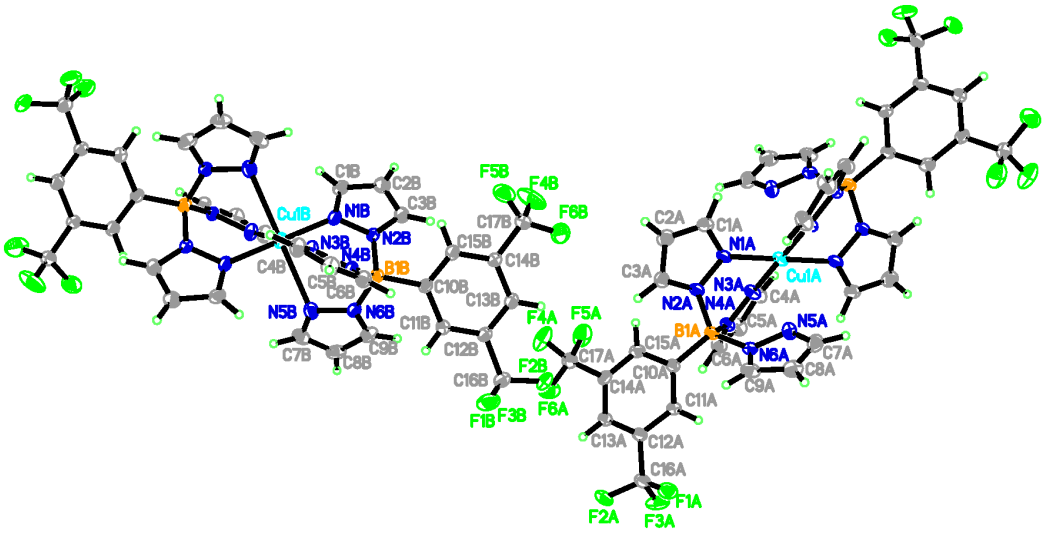
$C_{34}H_{24}B_2CuF_{12}N_{12}$

or

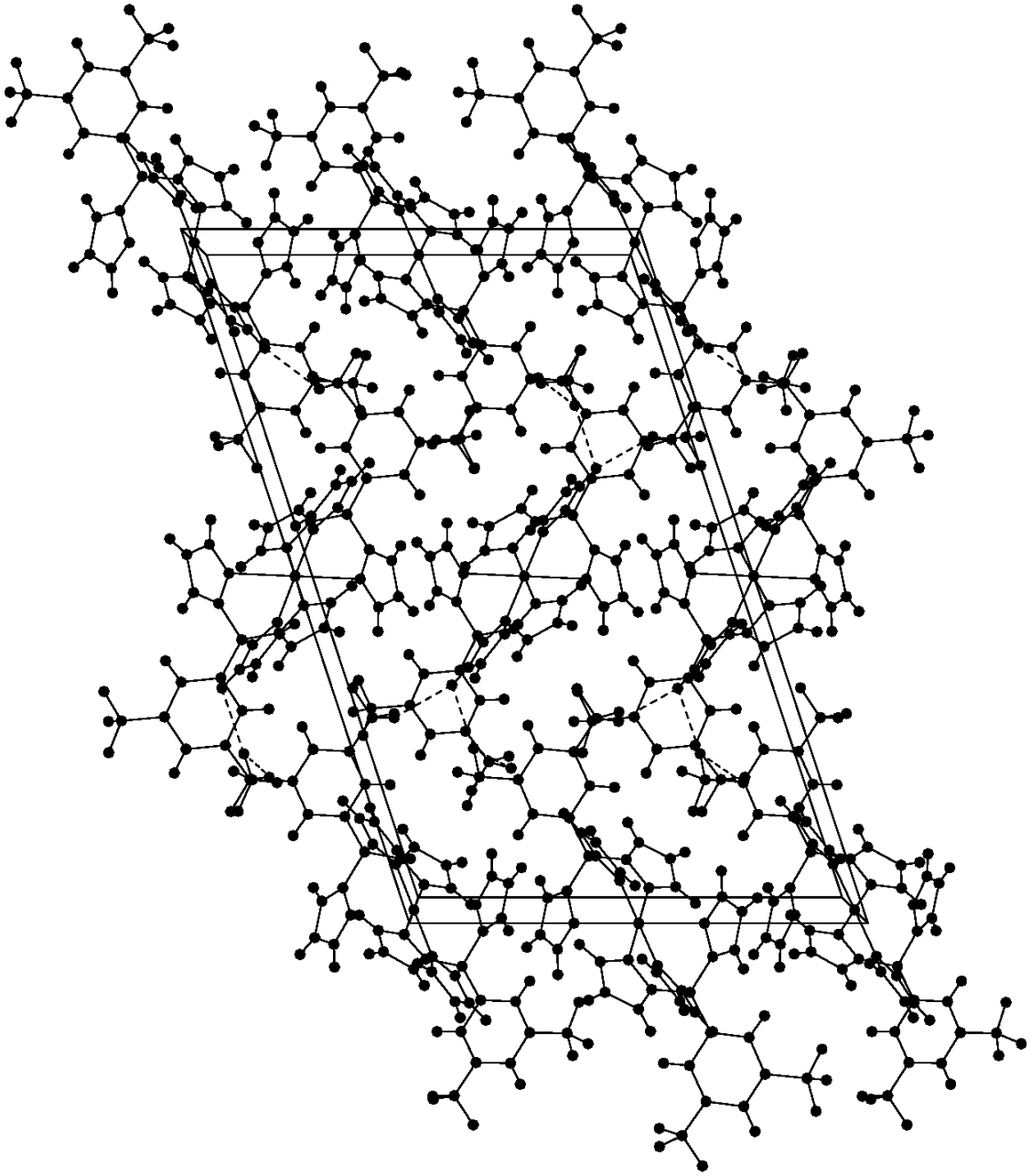
$2(C_{34}H_{24}B_2CuF_{12}N_{12})$½

Report prepared for:
Prof. P. Fischer

July 26, 2022



Victor G. Young, Jr.
X-Ray Crystallographic Laboratory
Department of Chemistry
University of Minnesota
207 Pleasant St. S.E.
Minneapolis, MN 55455



Data collection

A crystal (approximate dimensions 0.100 x 0.090 x 0.045 mm^3) was placed onto the tip of a 150 μm diameter MiTeGen Dual-Thickness Microloop and mounted on a Bruker PHOTON-III CPAD diffractometer for a data collection at 150(2) K.[1] A preliminary set of cell constants was calculated from reflections harvested from three sets of frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced an initial orientation matrix determined from 642 reflections. The data collection was carried out using MoKα radiation (parabolic mirrors) with a frame time of 10 seconds and a detector distance of 4.0 cm. A strategy program was used to assure complete coverage of all unique data to a resolution of 0.70 Å. All major sections of frames were collected with 1.20º steps in ω or ϕ at different detector positions in 2θ. The intensity data were corrected for absorption and decay (SADABS).[2] Final cell constants were calculated from 2848 strong reflections from the actual data collection after integration (SAINT).[3] Please refer to Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SHELXT-2018/2 (Sheldrick 2015)[4] and refined using SHELXL-2018/3 (Sheldrick 2015).[4] The space group $P2_1/c$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1$ = 0.0455 and $wR2$ = 0.1078 (F^2, obs. data).

Structure description

The structure is the one suggested. There are two molecules in the asymmetric unit each with its metal atom located on different inversion centers: 2 x ½ the formula unit. The specimen selected was a twin by pseudo-merohedry. The twin lattice symmetry appeared to be C-orthorhombic, however a correct solution was determined in P-monoclinic in space group $P2_1/c$ with a nearly equal twin mass ratio.

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 192 Kolthoff Hall, Department of Chemistry, University of Minnesota. All calculations were performed using Pentium computers using the current SHELXTL suite of programs. All publications arising from this report MUST either 1) include Victor G. Young, Jr. as a coauthor or 2) acknowledge Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory. The Bruker-AXS D8 Venture diffractometer was purchased through a grant from NSF/MRI (#1229400) and the University of Minnesota.

[1] APEX3, Bruker Analytical X-ray Systems, Madison, WI (2014).

[2] SADABS, Bruker Analytical X-ray Systems, Madison, WI (2014).

[3] SAINT Bruker Analytical X-ray Systems, Madison, WI (2014).

[4] SHELXTL 2014, Bruker Analytical X-Ray Systems, Madison, WI (2013); G. M. Sheldrick, *Acta Cryst.* **A64**, 112-122 (2008).

Some equations of interest:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o^{\ 2}|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^{\ 2})^2] \ / \ \Sigma\ [w(F_o^{\ 2}\ )^2]]^{1/2}$$

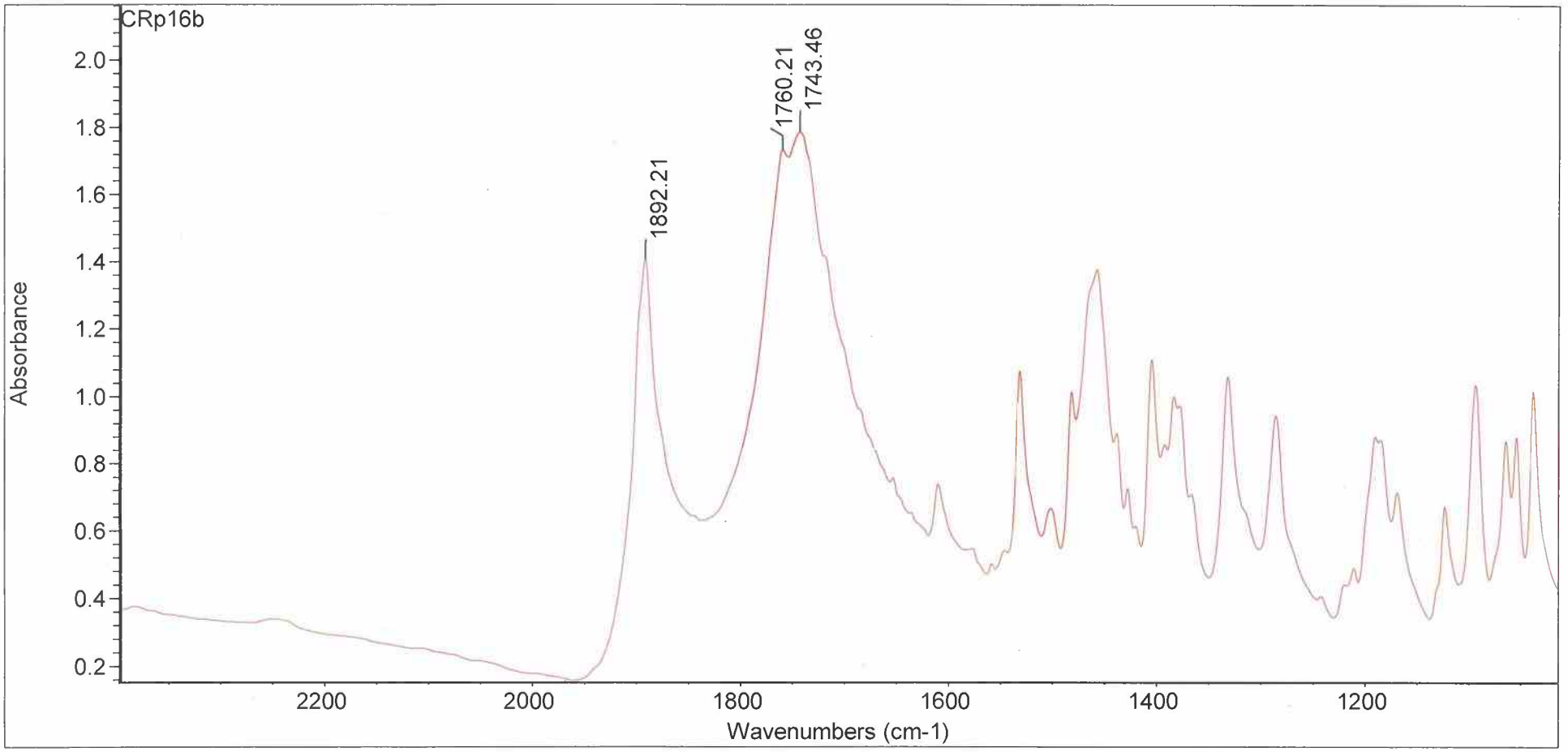
$$\text{where } w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$$

$$\text{GooF} = S = [\Sigma[w(F_o^2-F_c^{\ 2})^2] \ / \ (n-p)]^{1/2}$$

Table 1. Crystal data and structure refinement for 22122z.

Identification code	22122z	
Empirical formula	$C_{34}H_{24}B_2CuF_{12}N_{12}$	
Formula weight	913.81	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 26.450(2) Å	α = 90°
	b = 8.7643(6) Å	β = 108.226(3)°
	c = 16.5941(11) Å	γ = 90°
Volume	3653.8(5) Å^3	
Z	4	
Density (calculated)	1.661 Mg/m^3	
Absorption coefficient	0.706 mm^{-1}	
F(000)	1836	
Crystal color, morphology	Blue, Block	
Crystal size	0.100 x 0.090 x 0.045 mm^3	
Theta range for data collection	2.324 to 30.544°	
Index ranges	$-37 \le h \le 26$, $-12 \le k \le 12$, $-23 \le l \le 23$	
Reflections collected	36238	
Independent reflections	11040 [R(int) = 0.0418]	
Observed reflections	8969	
Completeness to theta = 25.242°	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6478 and 0.4636	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11040 / 0 / 554	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	$R1$ = 0.0455, $wR2$ = 0.1078	
R indices (all data)	$R1$ = 0.0607, $wR2$ = 0.1157	
Largest diff. peak and hole	0.862 and -0.875 e.Å^{-3}	

V. IR Spectra



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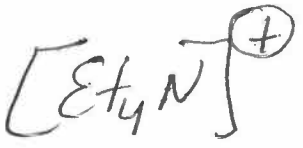
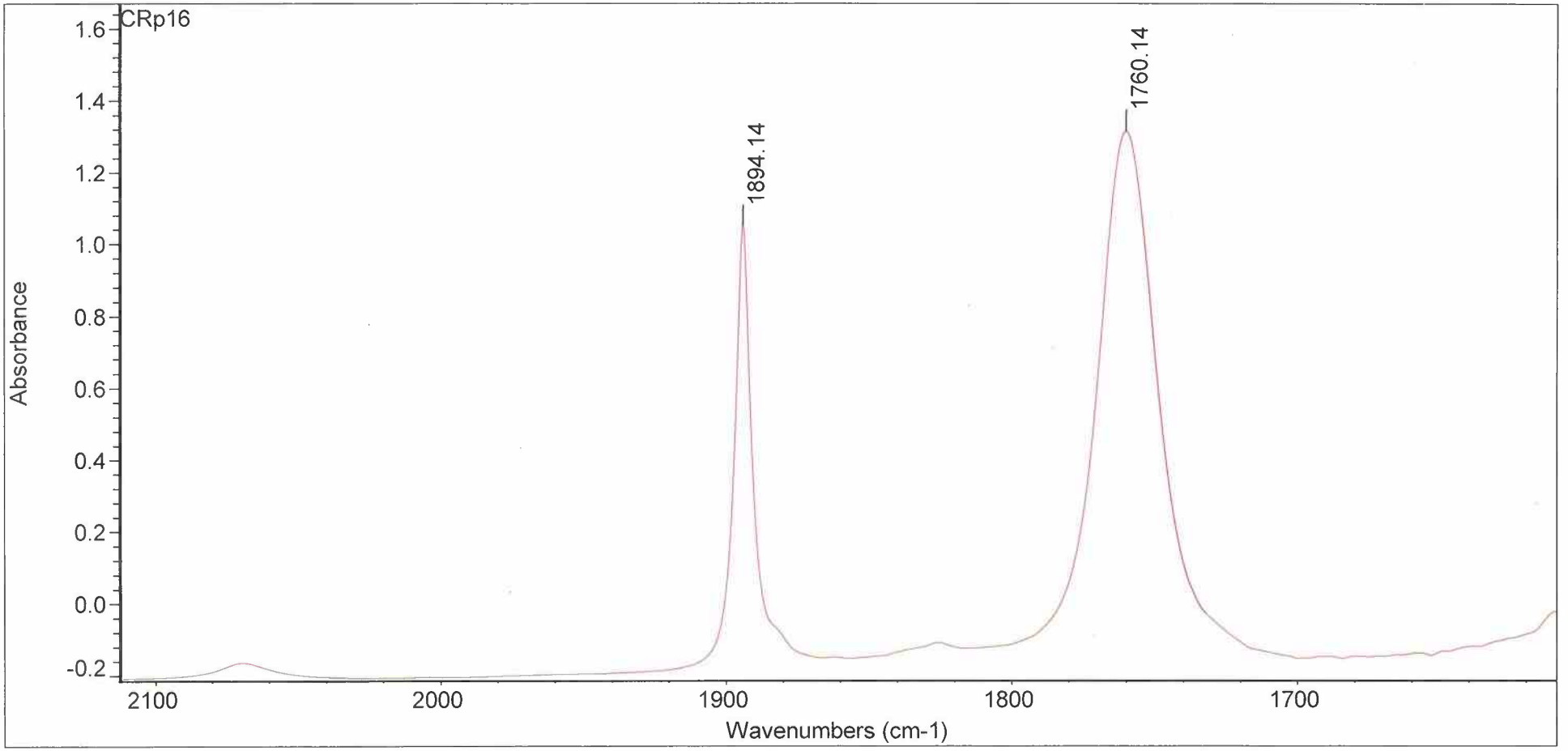
FIND PEAKS:

Spectrum:	CRp16b			
Region:	2397.89	1014.25		
Absolute threshold:	1.396			
Sensitivity:	74			
Peak list:				
	Position:	1743.46	Intensity:	1.786
	Position:	1760.21	Intensity:	1.732
	Position:	1892.21	Intensity:	1.407

nujol mull IR (7)



mull

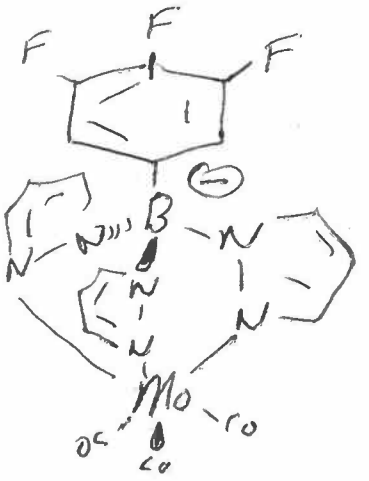


Fri Jul 15 15:42:03 2022 (GMT-05:00)
FIND PEAKS:

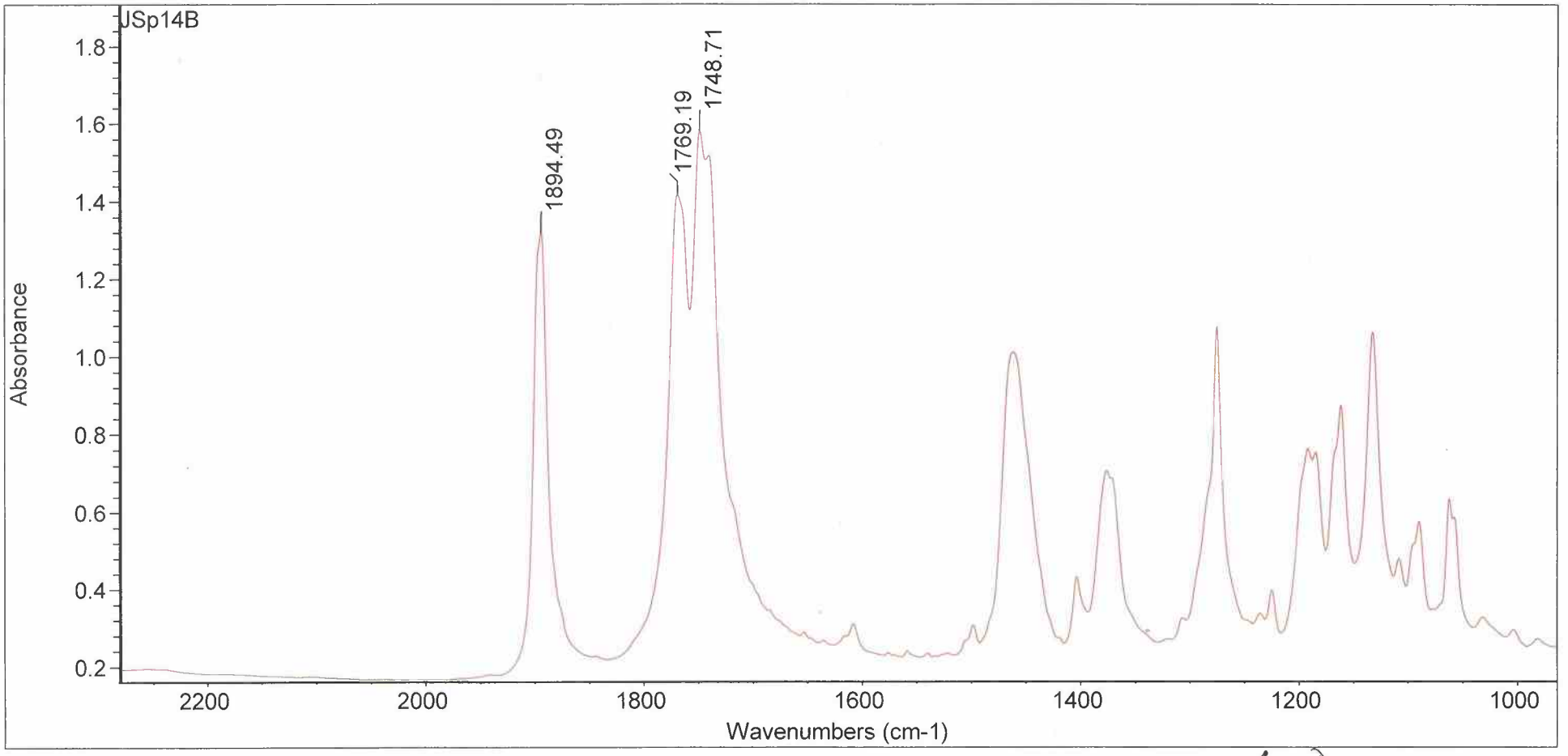
Spectrum:	CRp16			
Region:	2112.93	1609.50		
Absolute threshold:	0.551			
Sensitivity:	74			
Peak list:				
Position:	1760.14	Intensity:	1.314	
Position:	1894.14	Intensity:	1.055	

IR (CH_3CN) (7)

$[Et_4N^+]^{\oplus}$



CH_3CN



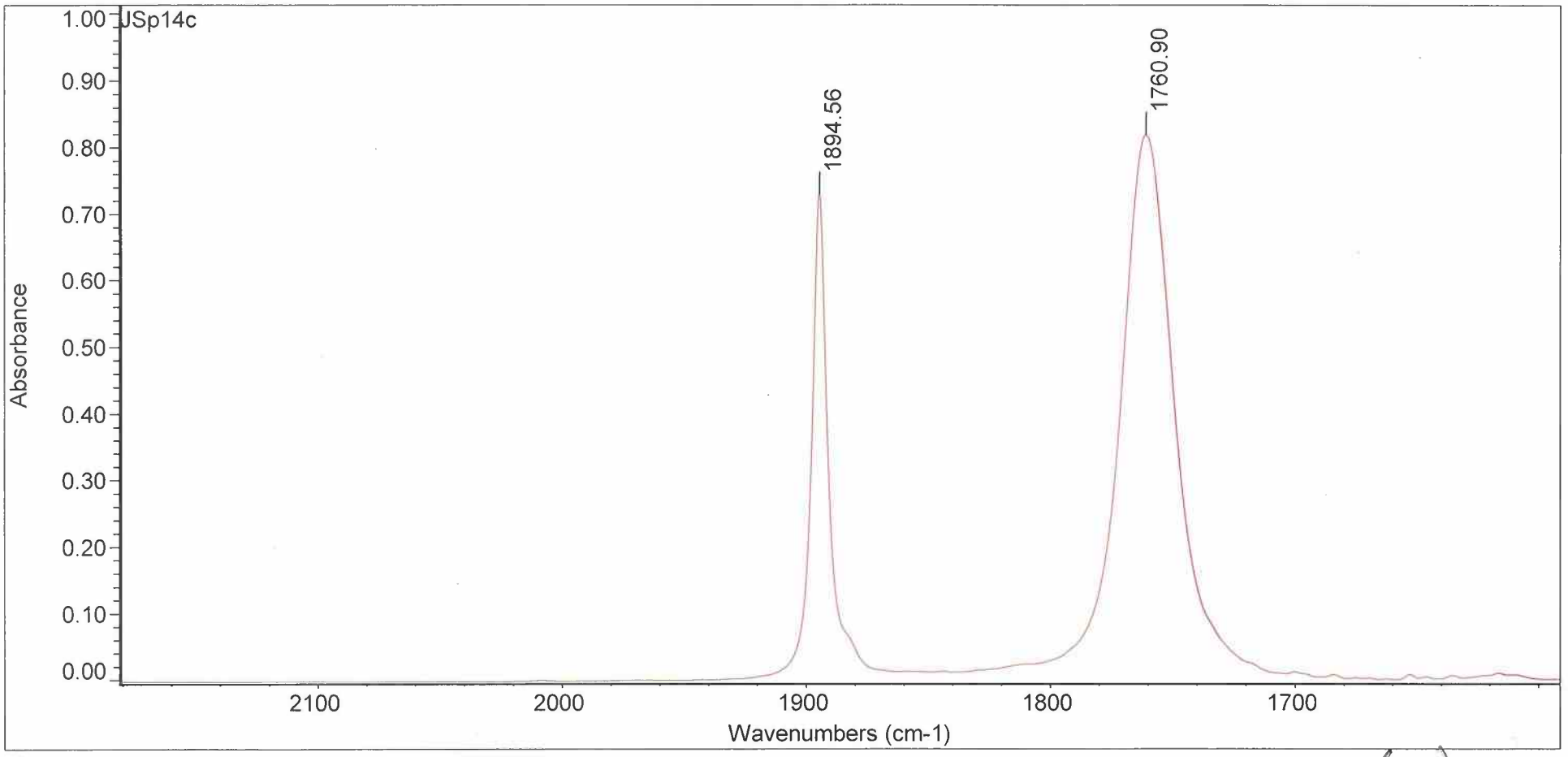
Fri Jul 15 15:12:18 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	JSp14B			
Region:	2281.63	964.24		
Absolute threshold:	1.146			
Sensitivity:	74			
Peak list:				
	Position:	1748.71	Intensity:	1.580
	Position:	1769.19	Intensity:	1.416
	Position:	1894.49	Intensity:	1.319

nujol mull IR (8)

$[Et_4N]^{\oplus}$

mull

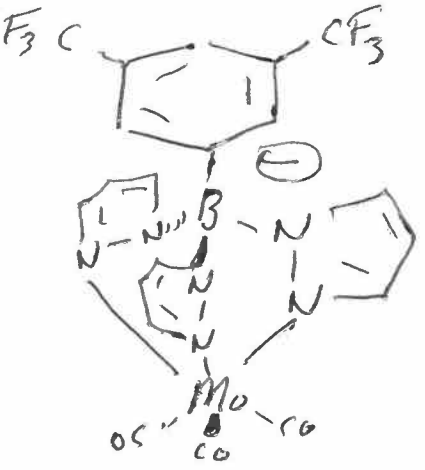


Fri Jul 15 15:10:49 2022 (GMT-05:00)
FIND PEAKS:

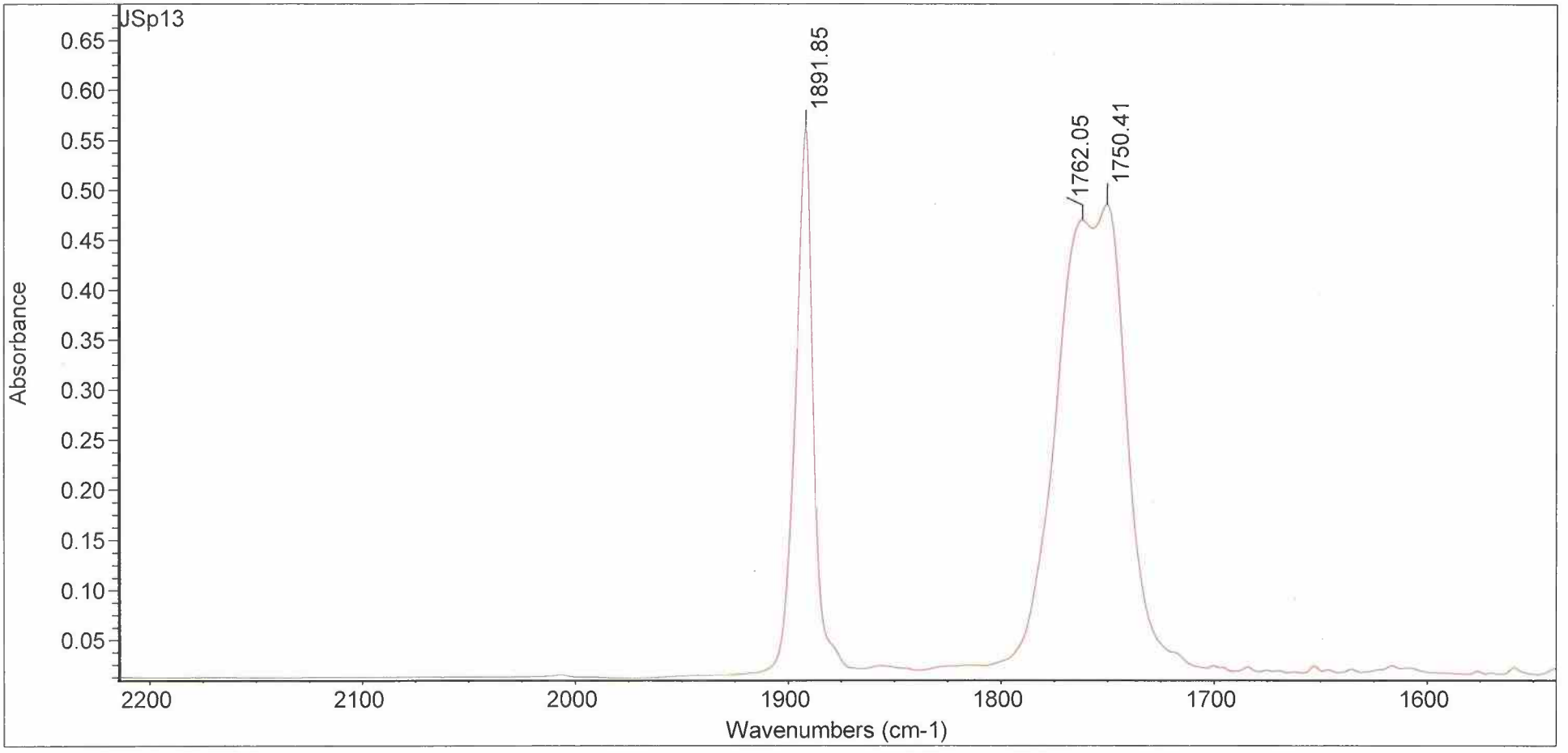
Spectrum:	JSp14c			
Region:	2181.44	1591.39		
Absolute threshold:	0.407			
Sensitivity:	74			
Peak list:				
Position:	1760.90	Intensity:	0.819	
Position:	1894.56	Intensity:	0.732	

(CH_3CN) ~~nujol mull~~ IR (8)

$[Et_4N]^+$



CH_3CN

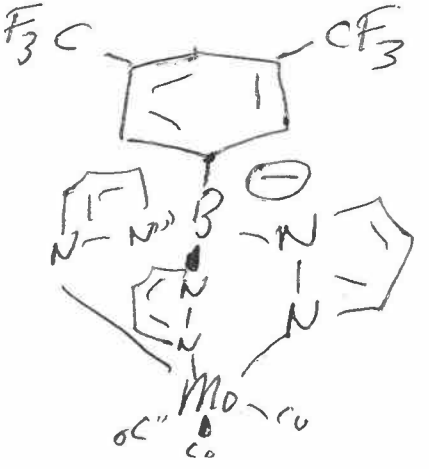


Fri Jul 15 15:20:38 2022 (GMT-05:00)
FIND PEAKS:

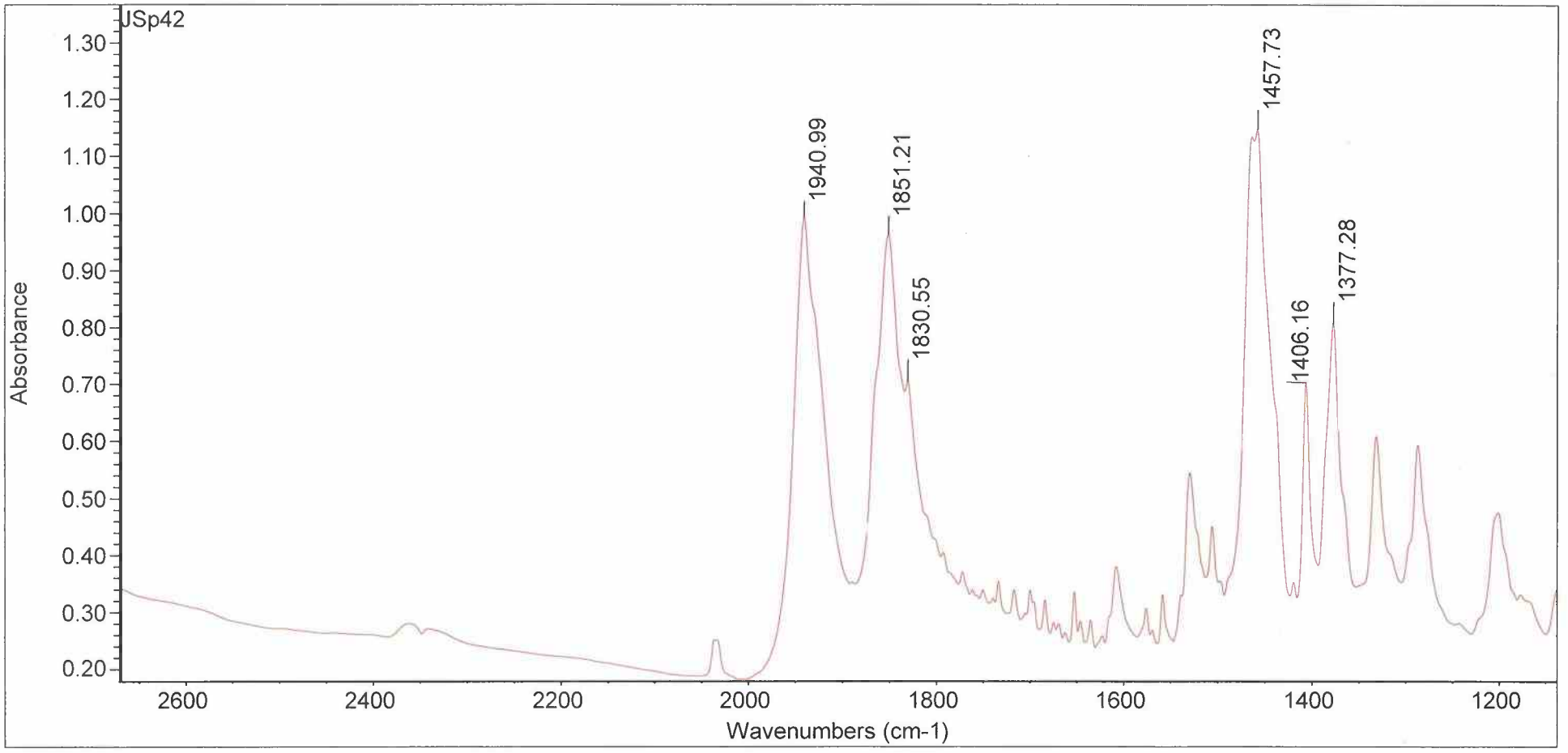
Spectrum:	JSp13			
Region:	2214.83	1539.44		
Absolute threshold:	0.286			
Sensitivity:	74			
Peak list:				
	Position:	1750.41	Intensity:	0.485
	Position:	1762.05	Intensity:	0.470
	Position:	1891.85	Intensity:	0.563

IR (THF) (8)

$[Et_4N]^+$



THF/[Et4N]

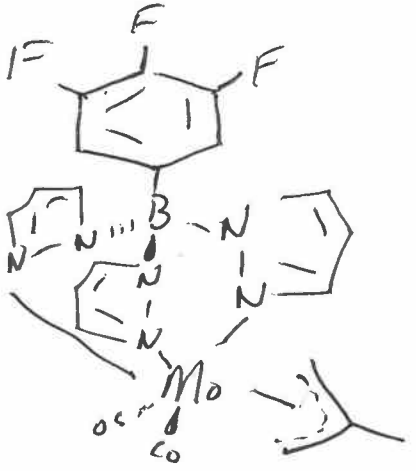


Fri Jul 15 14:08:43 2022 (GMT-05:00)
FIND PEAKS:

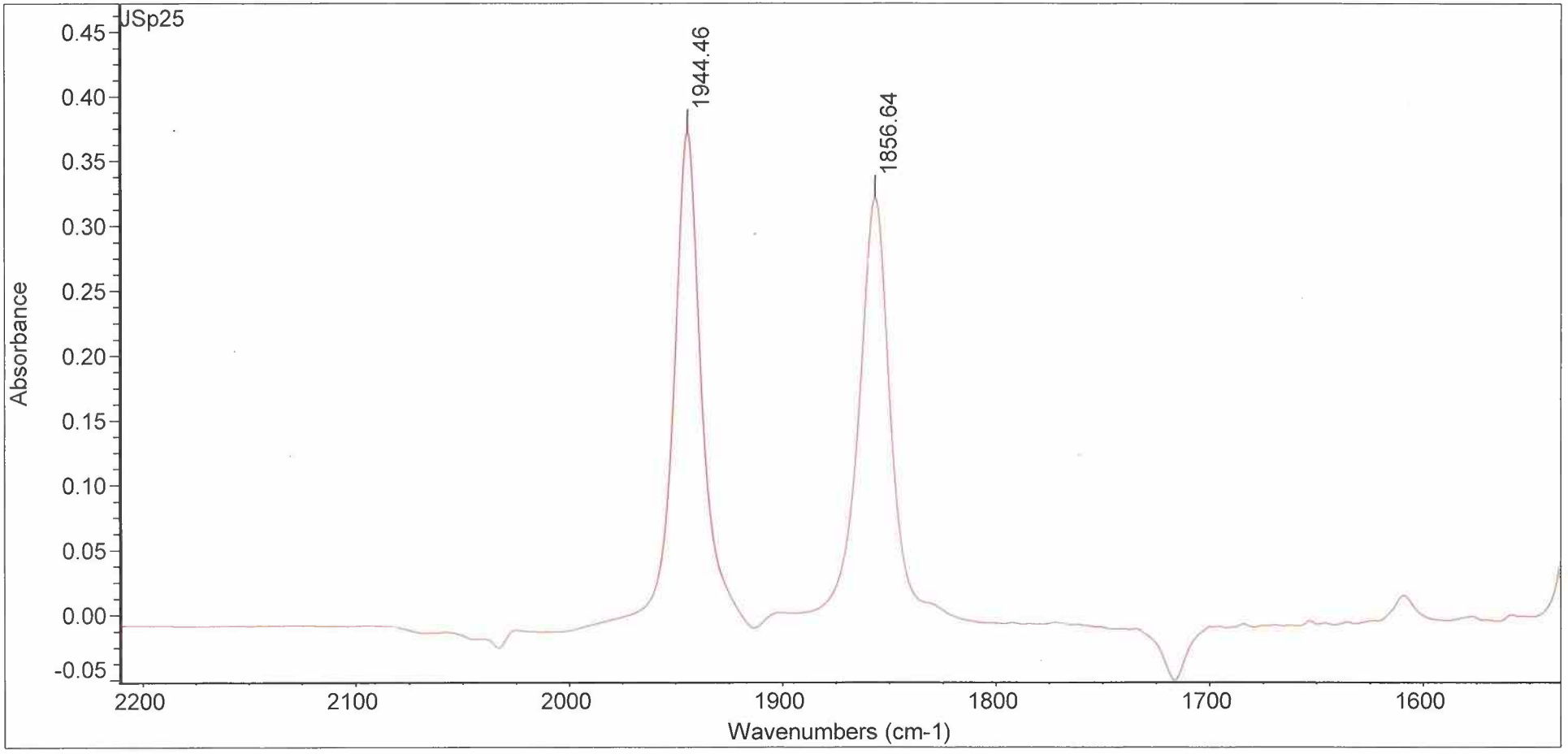
Spectrum: JSp42
Region: 2671.28 1138.66
Absolute threshold: 0.663
Sensitivity: 74
Peak list:

Position:	1377.28	Intensity:	0.806
Position:	1406.16	Intensity:	0.703
Position:	1457.73	Intensity:	1.146
Position:	1830.55	Intensity:	0.703
Position:	1851.21	Intensity:	0.961
Position:	1940.99	Intensity:	0.992

IR nujol mull (9)



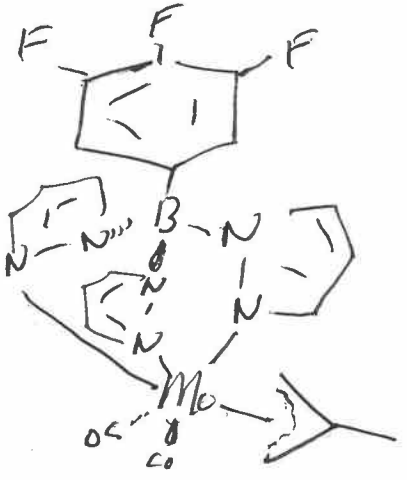
mull



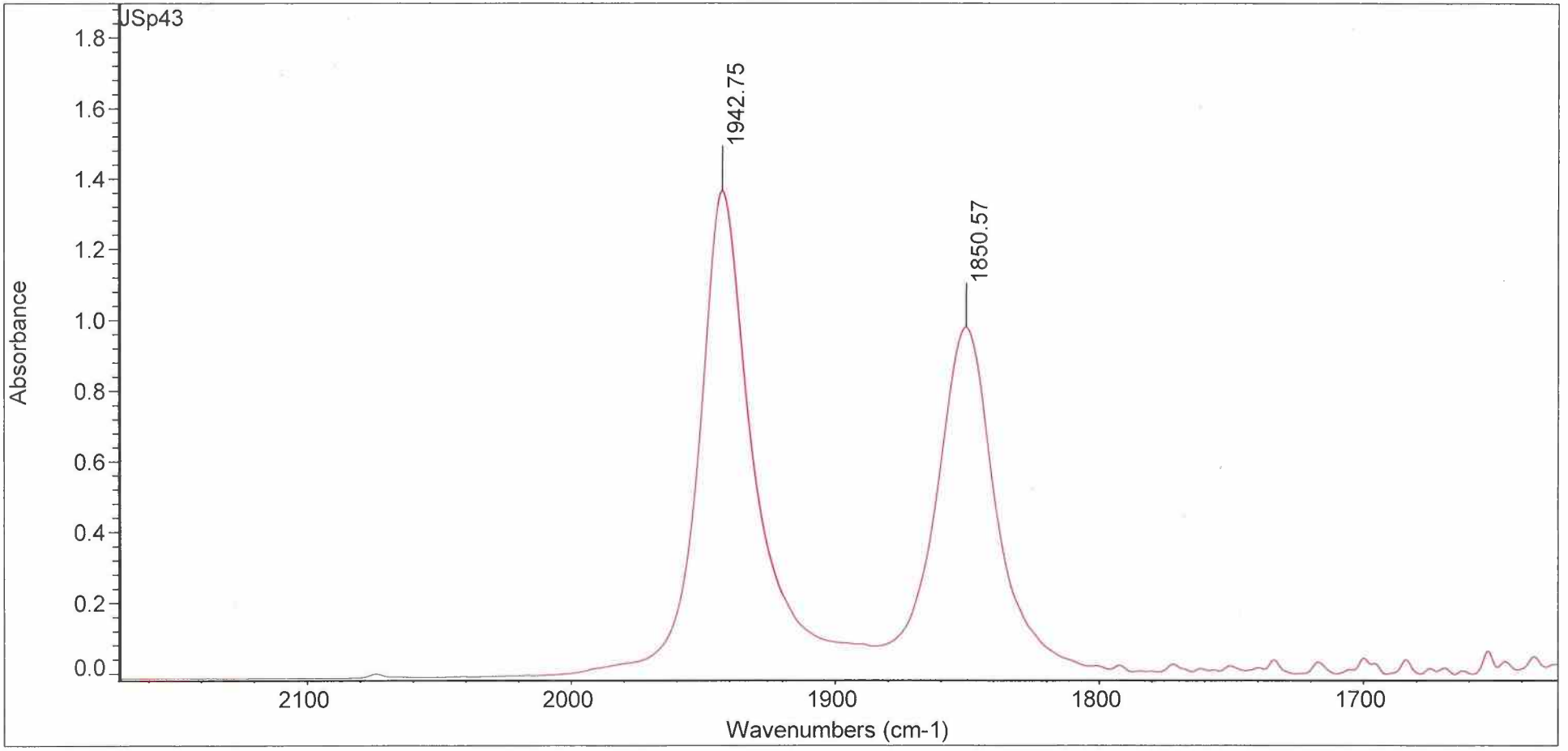
Fri Jul 15 15:49:36 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	JSp25			
Region:	2211.12	1535.73		
Absolute threshold:	0.160			
Sensitivity:	50			
Peak list:				
	Position:	1856.64	Intensity:	0.322
	Position:	1944.46	Intensity:	0.372

IR (THF) (9)



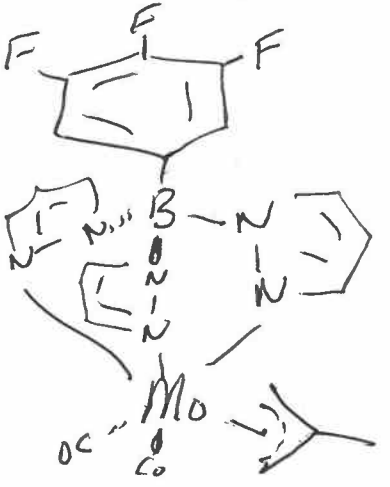
THF



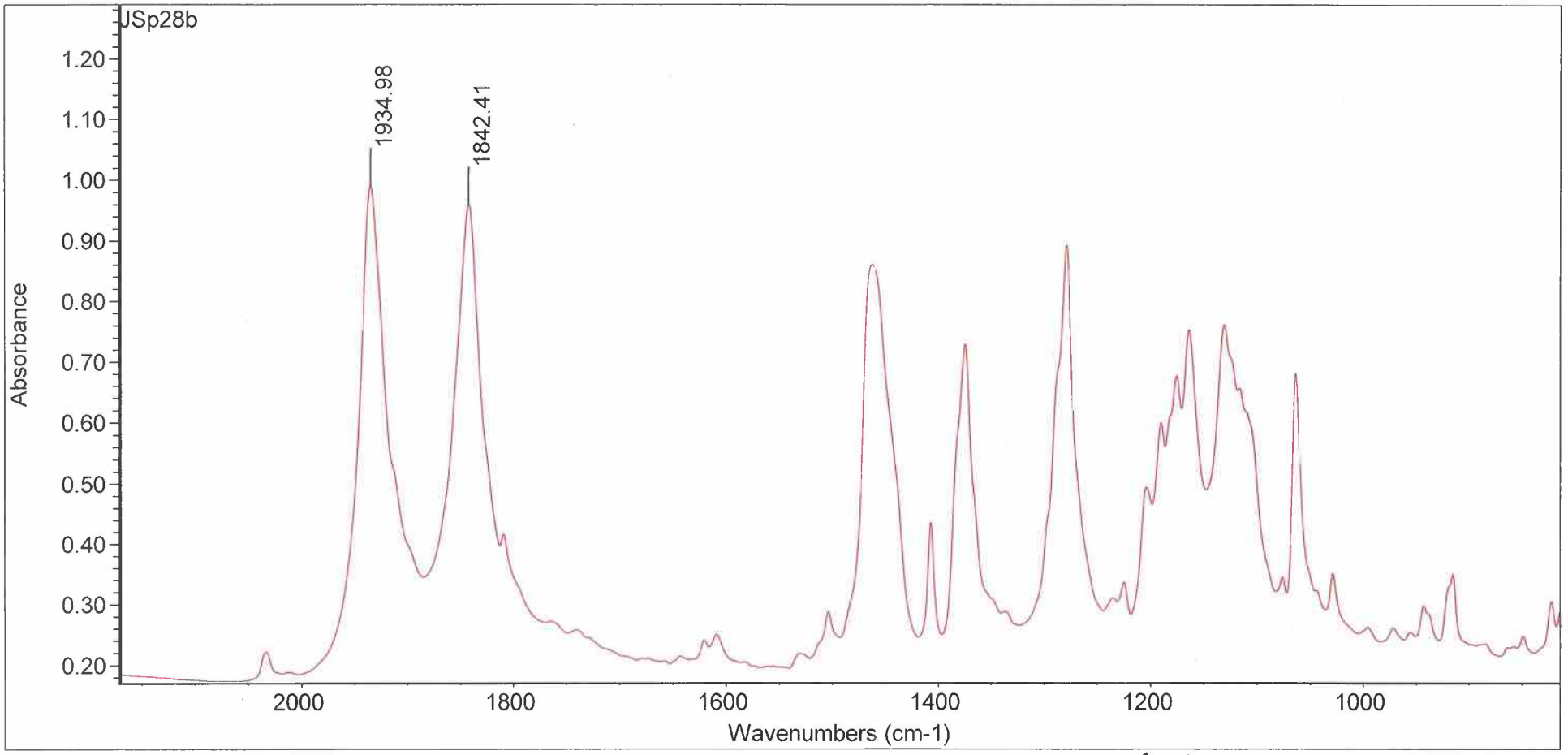
Fri Jul 15 09:42:00 2022 (GMT-05:00)
FIND PEAKS:
Spectrum: JSp43
Region: 2171.60 1626.55
Absolute threshold: 0.674
Sensitivity: 100
Peak list:

Position:	1850.57	Intensity:	0.978
Position:	1942.75	Intensity:	1.365

IR (CH_2Cl_2) (9)



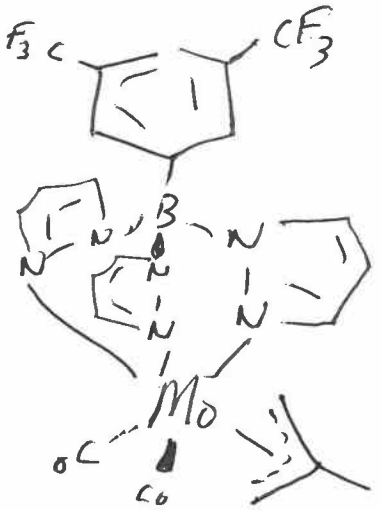
CH_2Cl_2



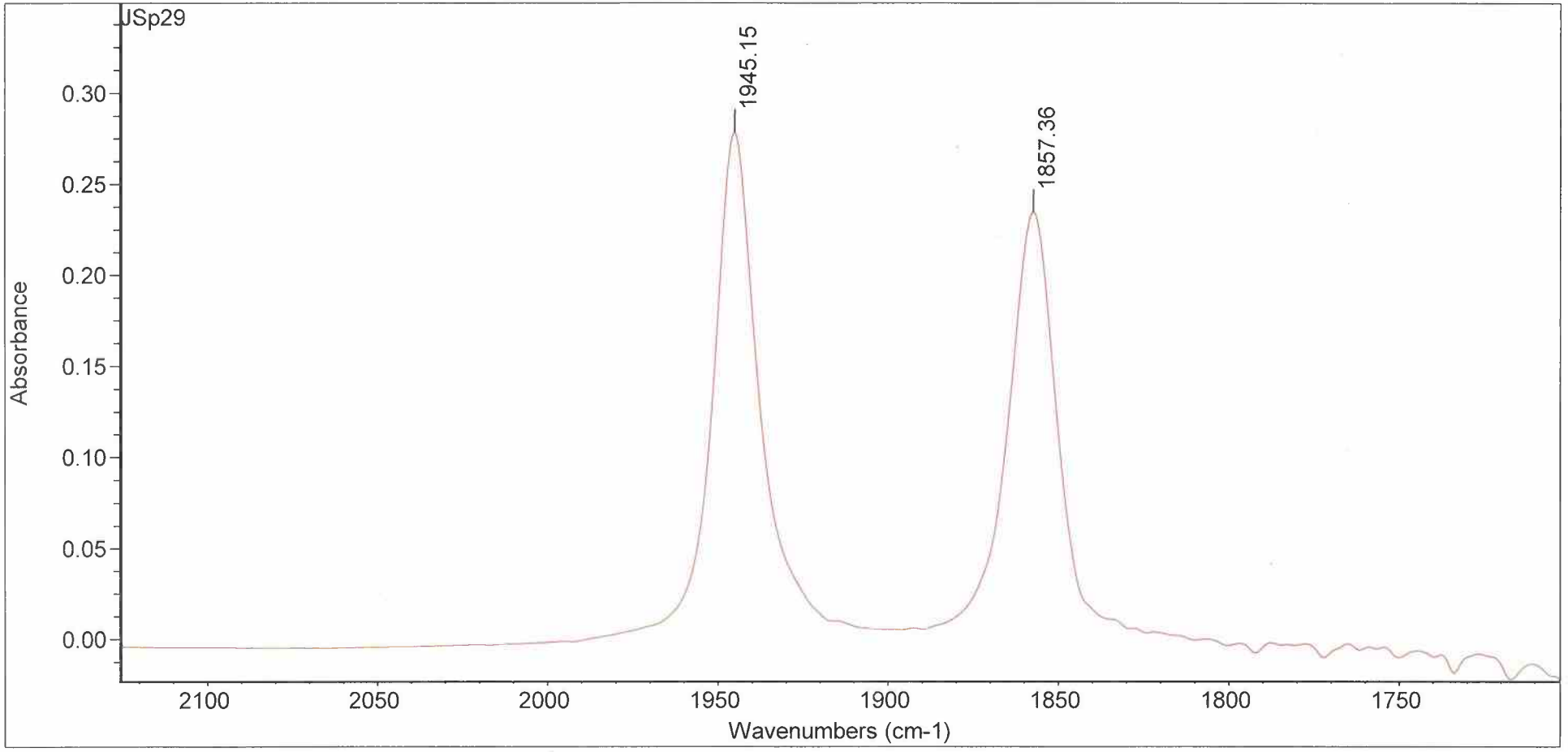
IR nujol mull (10)

Fri Jul 15 09:44:01 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	JSp28b			
Region:	2171.60	814.64		
Absolute threshold:	0.925			
Sensitivity:	100			
Peak list:				
	Position:	1842.41	Intensity:	0.960
	Position:	1934.98	Intensity:	0.991



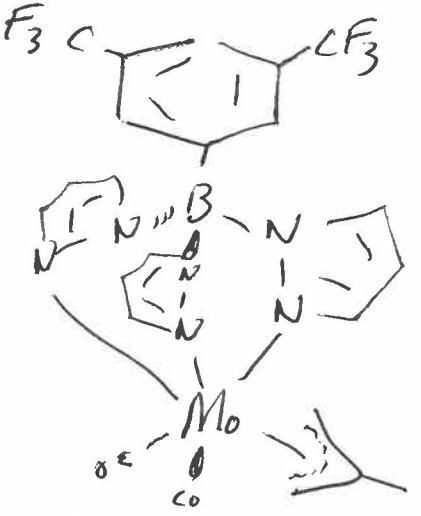
Nujol



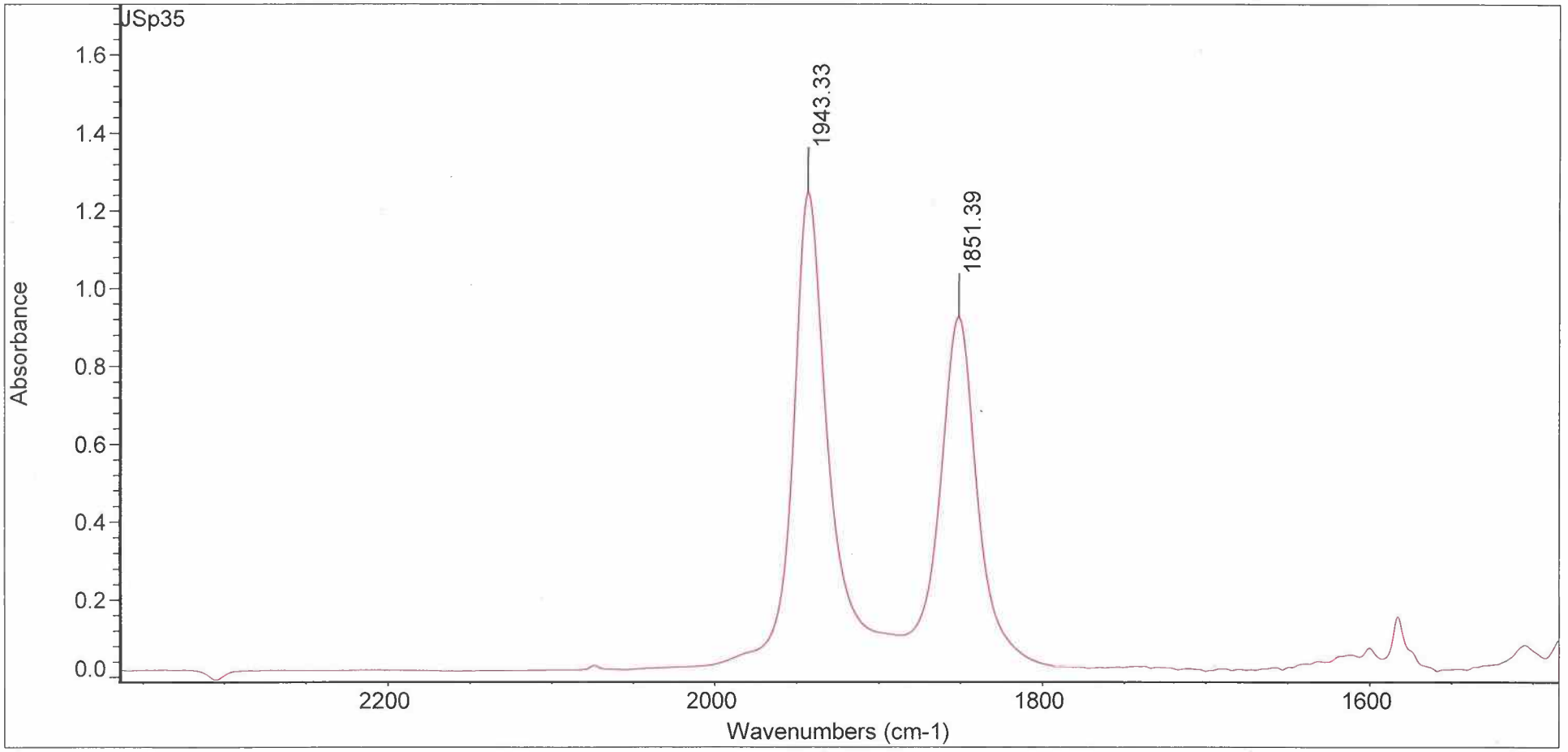
Fri Jul 15 15:56:39 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	JSp29			
Region:	2125.77	1702.72		
Absolute threshold:	0.128			
Sensitivity:	50			
Peak list:				
	Position:	1857.36	Intensity:	0.234
	Position:	1945.15	Intensity:	0.278

IR (THF) (10)



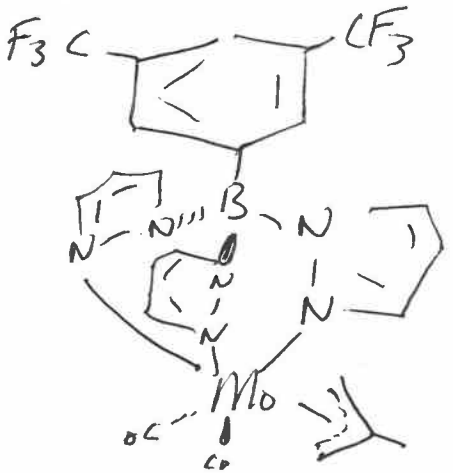
In THF



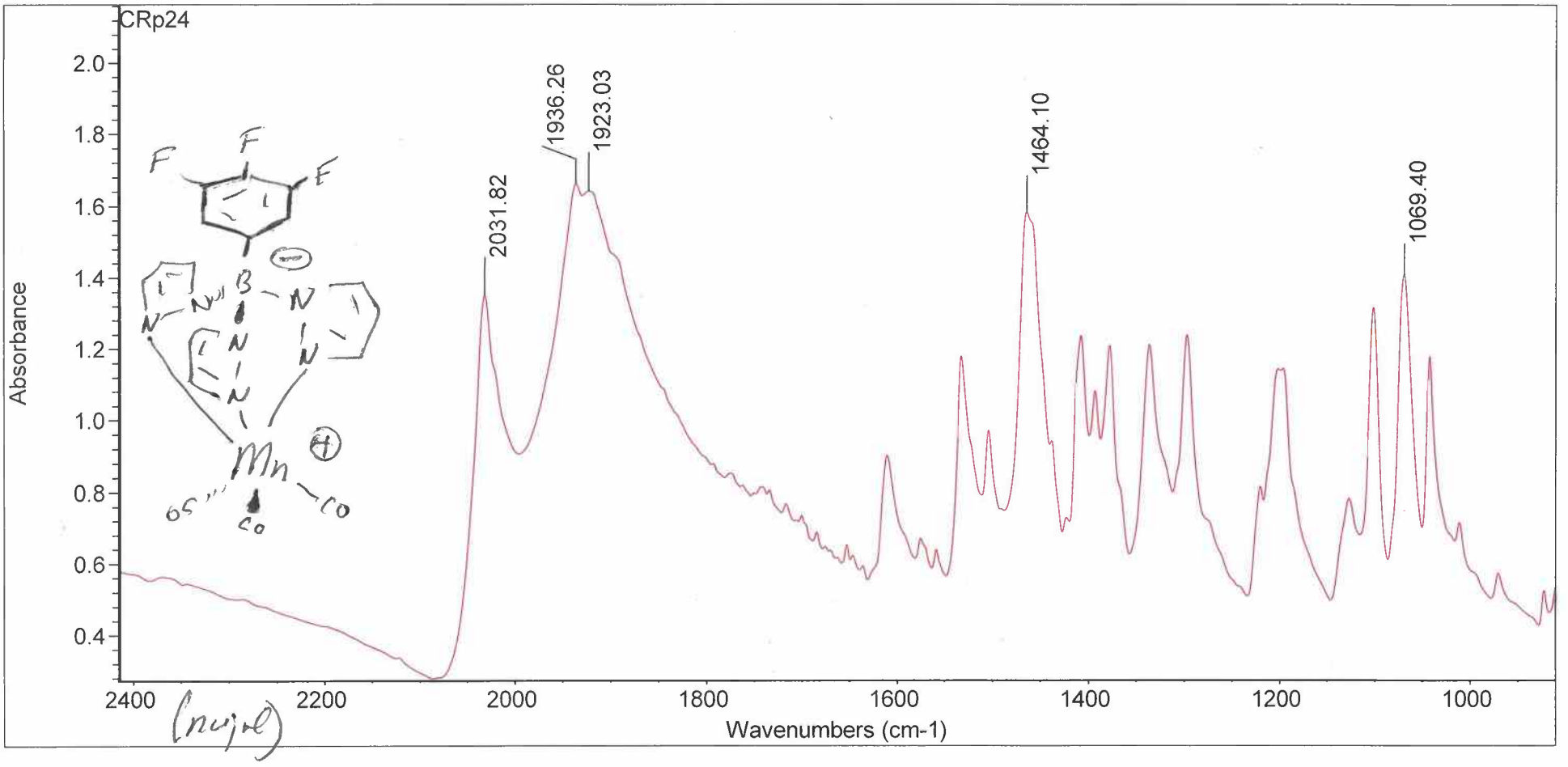
Fri Jul 15 09:45:31 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	JSp35			
Region:	2364.64	1484.61		
Absolute threshold:	0.618			
Sensitivity:	100			
Peak list:				
	Position:	1851.39	Intensity:	0.925
	Position:	1943.33	Intensity:	1.246

IR (CH_2Cl_2) (10)



CH_2Cl_2



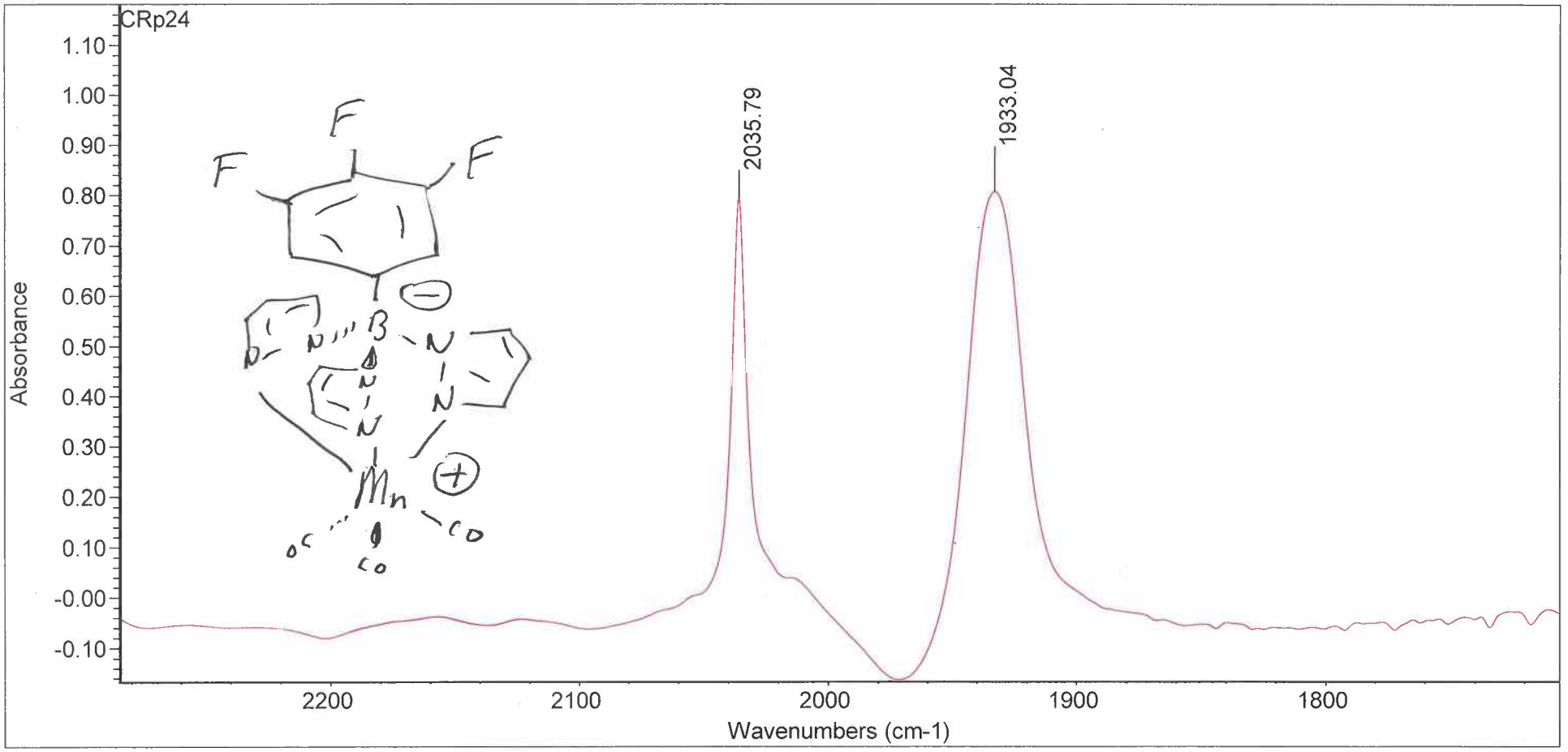
Fri Jul 15 09:51:23 2022 (GMT-05:00)
FIND PEAKS:

Spectrum: CRp24
Region: 2415.74 911.16
Absolute threshold: 1.340
Sensitivity: 90
Peak list:

Position:	1069.40	Intensity:	1.407
Position:	1464.10	Intensity:	1.582
Position:	1923.03	Intensity:	1.641
Position:	1936.26	Intensity:	1.661
Position:	2031.82	Intensity:	1.350

IR (nujol) (11)

Mull

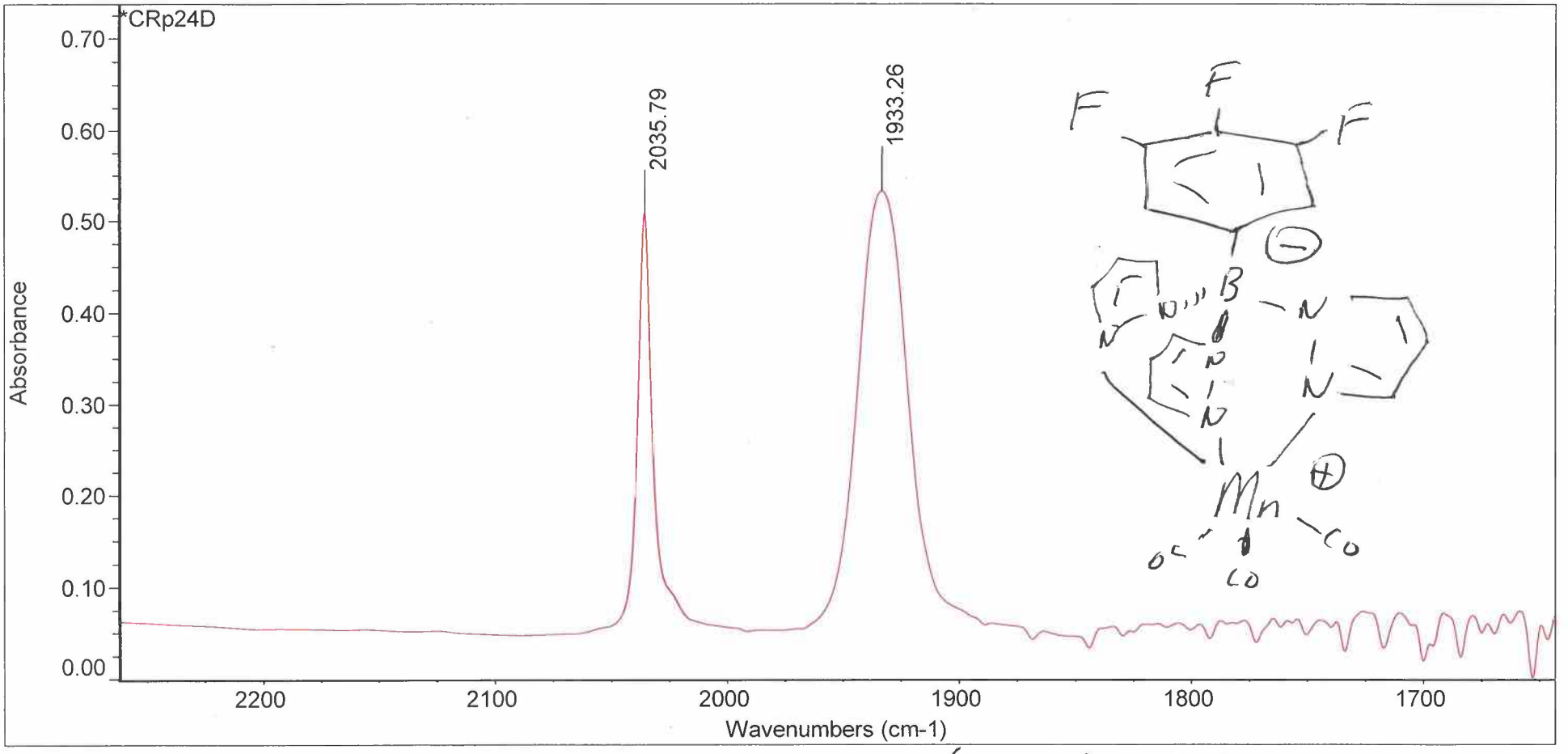


Fri Jul 15 09:47:39 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	CRp24			
Region:	2285.16	1706.04		
Absolute threshold:	0.321			
Sensitivity:	100			
Peak list:				
	Position:	1933.04	Intensity:	0.806
	Position:	2035.79	Intensity:	0.797

IR (THF) (11)

THF



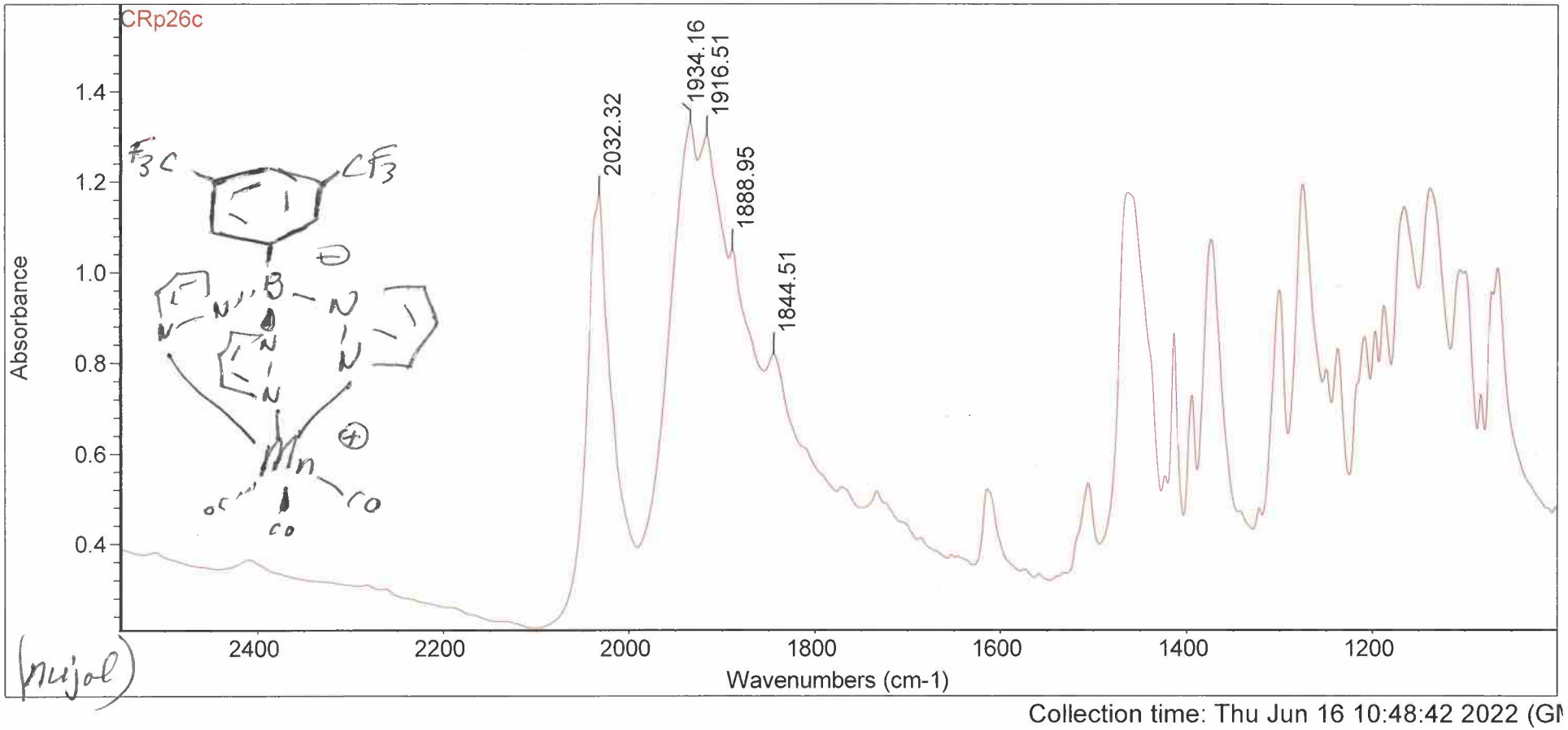
IR (CH_2Cl_2) (11)

Fri Jul 15 09:53:19 2022 (GMT-05:00)
FIND PEAKS:

Spectrum:	*CRp24D			
Region:	2262.45	1643.58		
Absolute threshold:	0.266			
Sensitivity:	90			
Peak list:				
	Position:	1933.26	Intensity:	0.533
	Position:	2035.79	Intensity:	0.508

CH_2Cl_2

Widget Corp. Fri Jul 15 15:28:54 2022 (GM

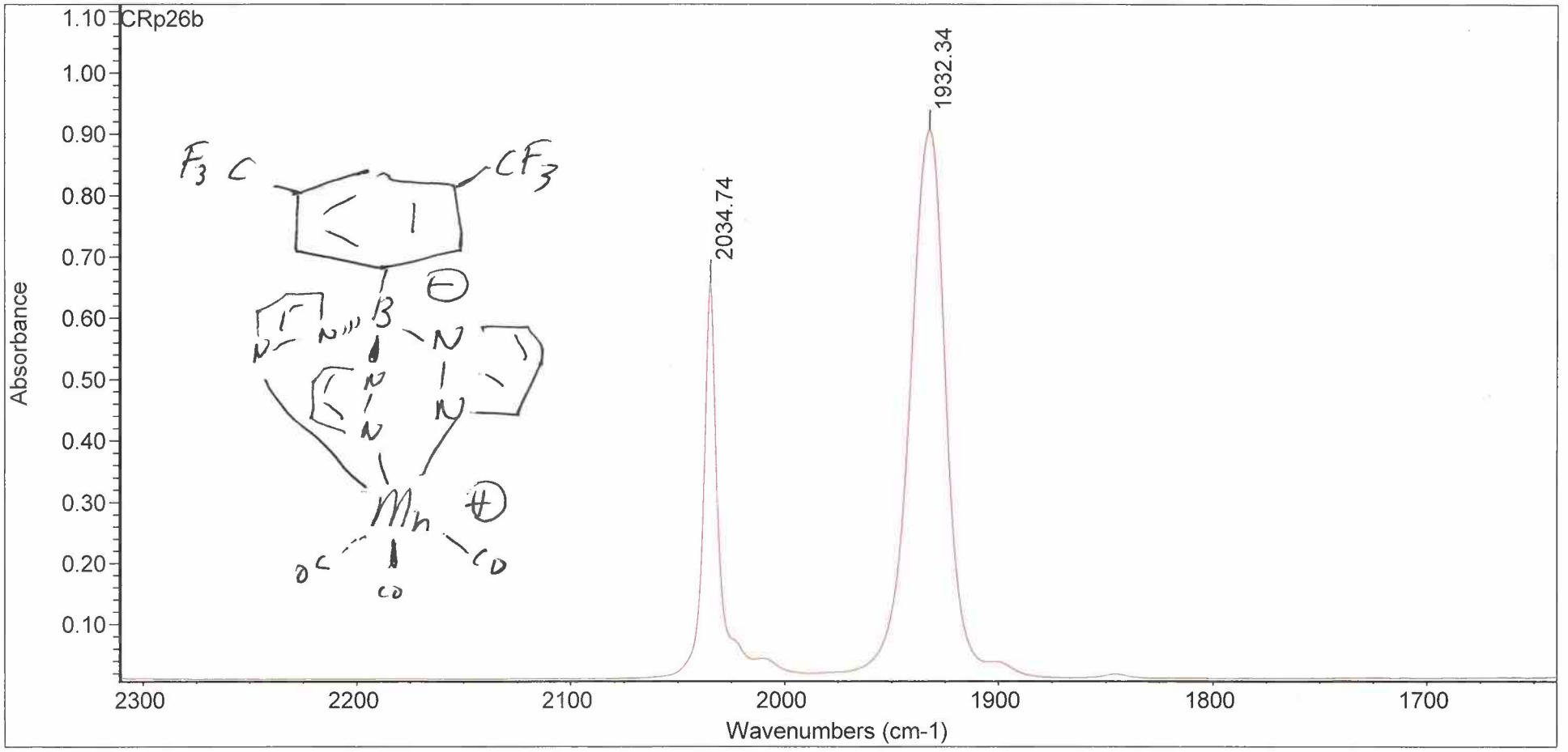


Collection time: Thu Jun 16 10:48:42 2022 (GM

No search results for the selected spectrum!

IR (nujol) (12)

mull



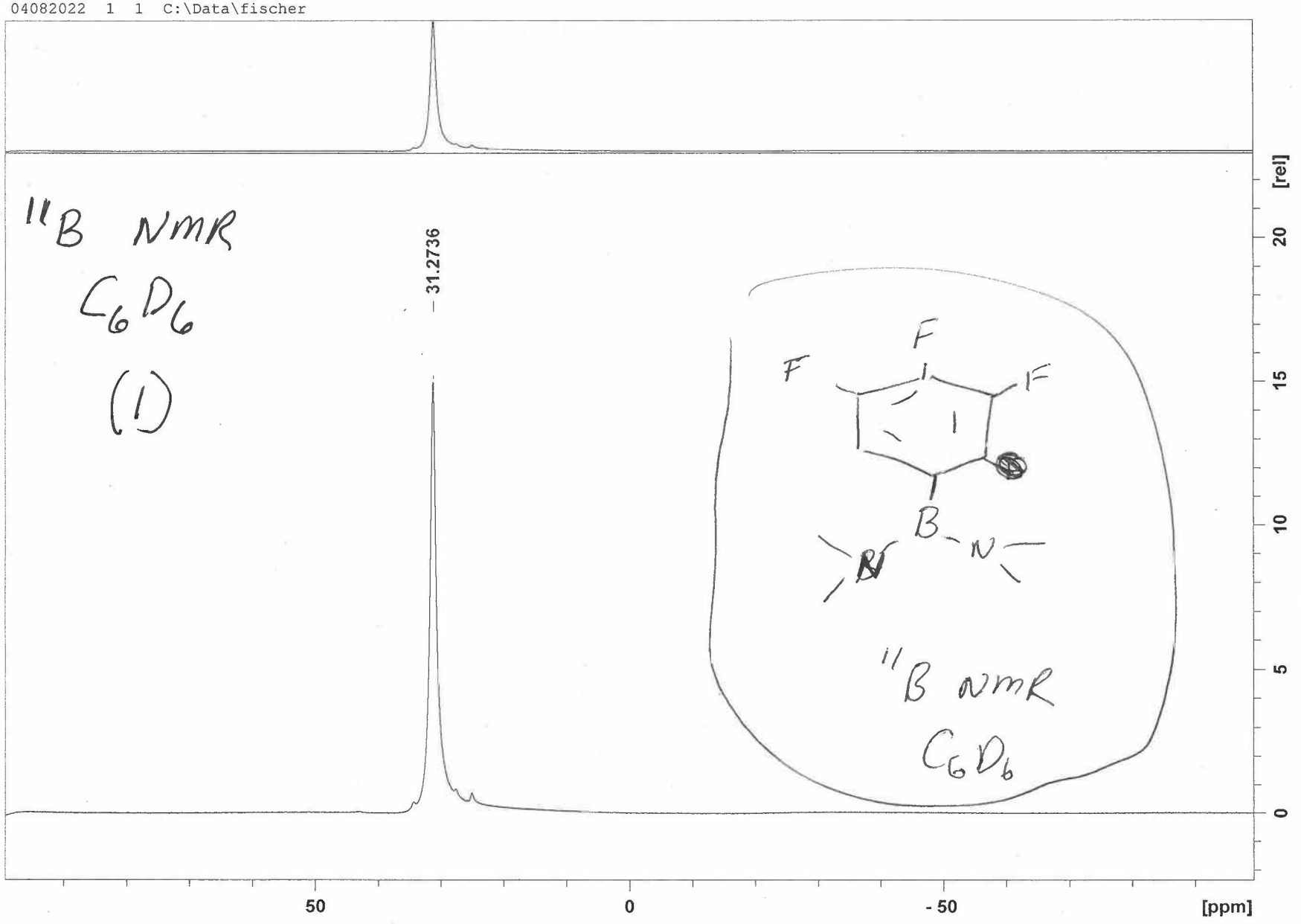
Fri Jul 15 15:38:08 2022 (GMT-05:00)
FIND PEAKS:

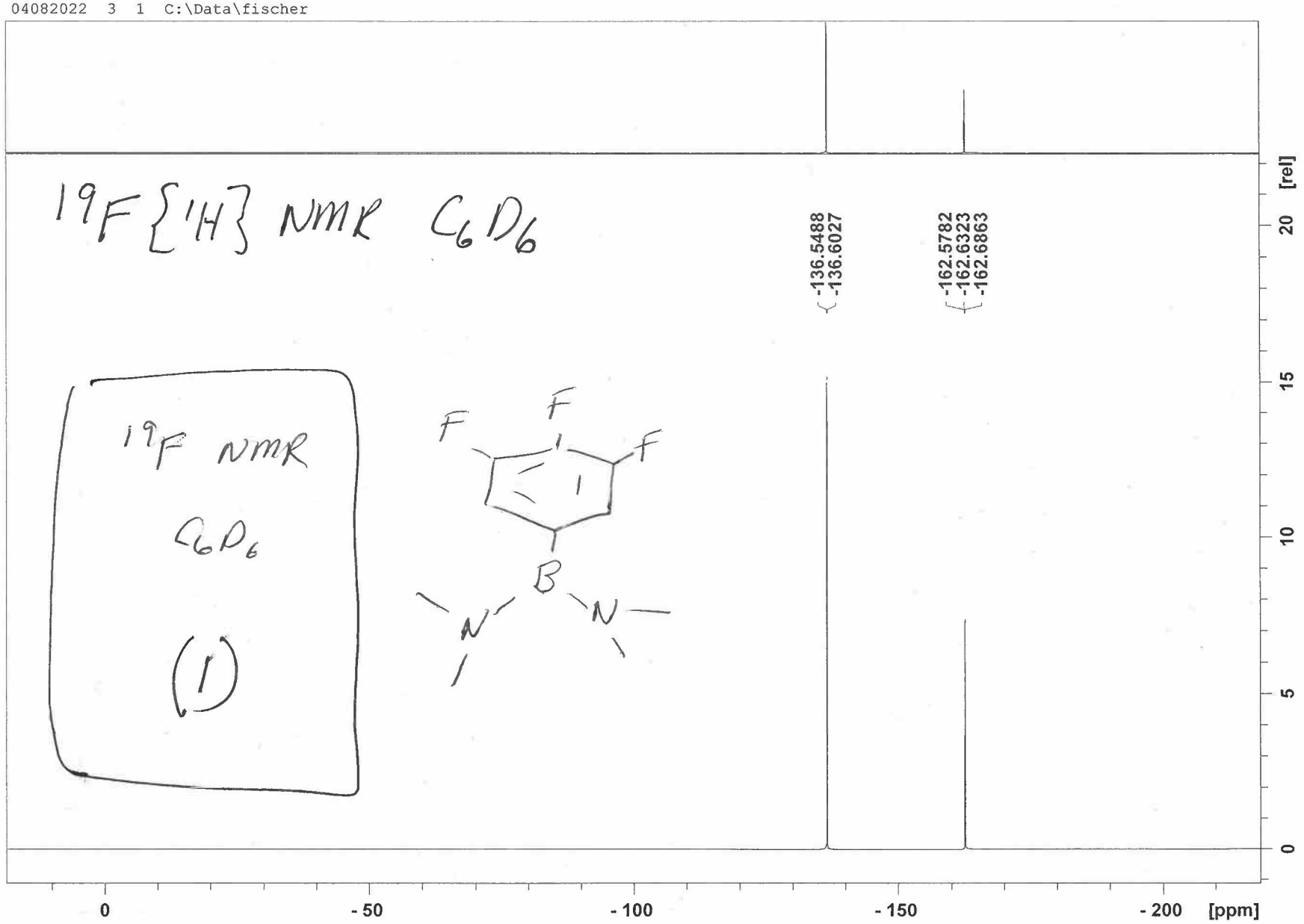
Spectrum:	CRp26b			
Region:	2311.32	1639.64		
Absolute threshold:	0.457			
Sensitivity:	74			
Peak list:				
	Position:	1932.34	Intensity:	0.906
	Position:	2034.74	Intensity:	0.657

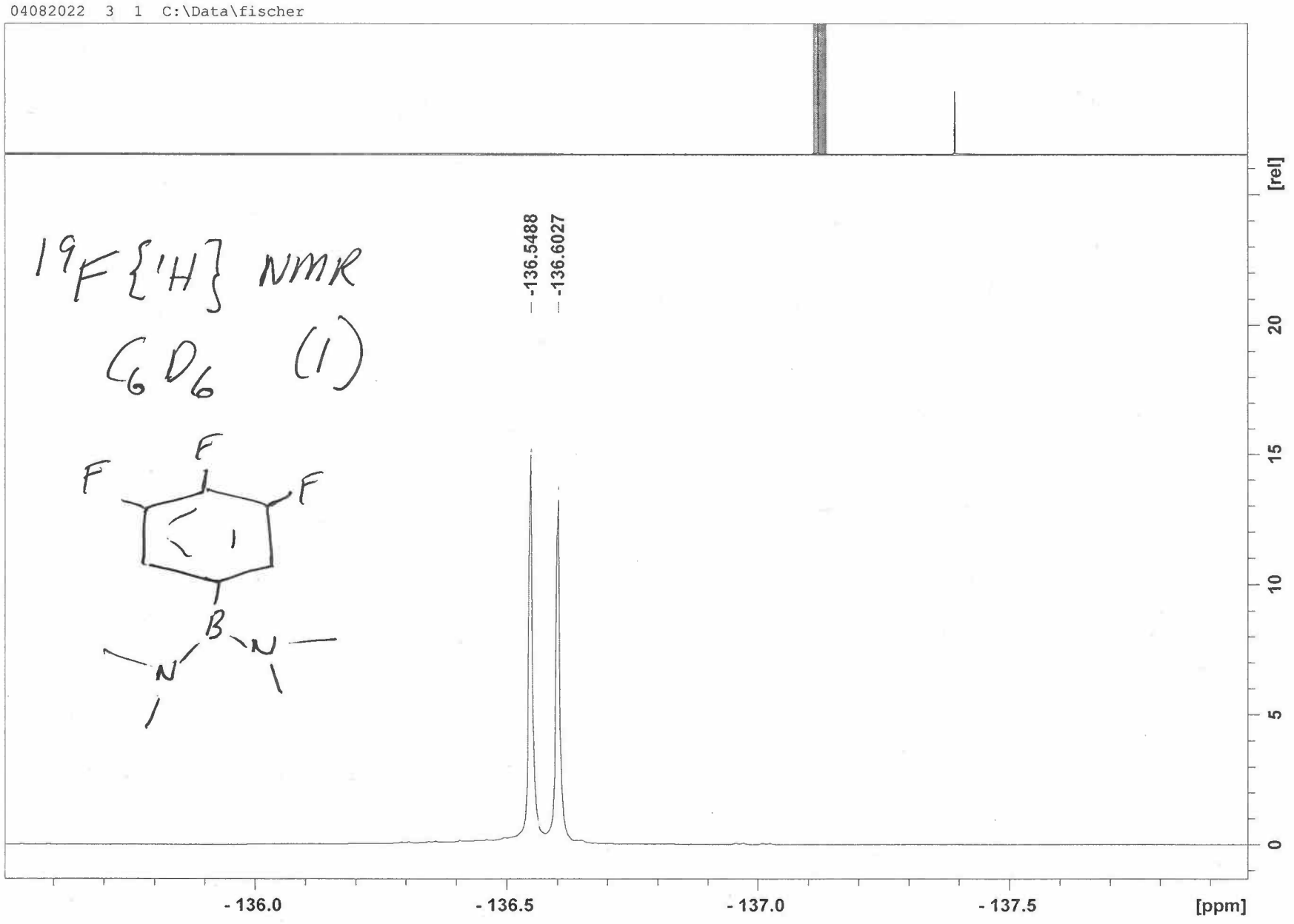
IR (THF) (12)

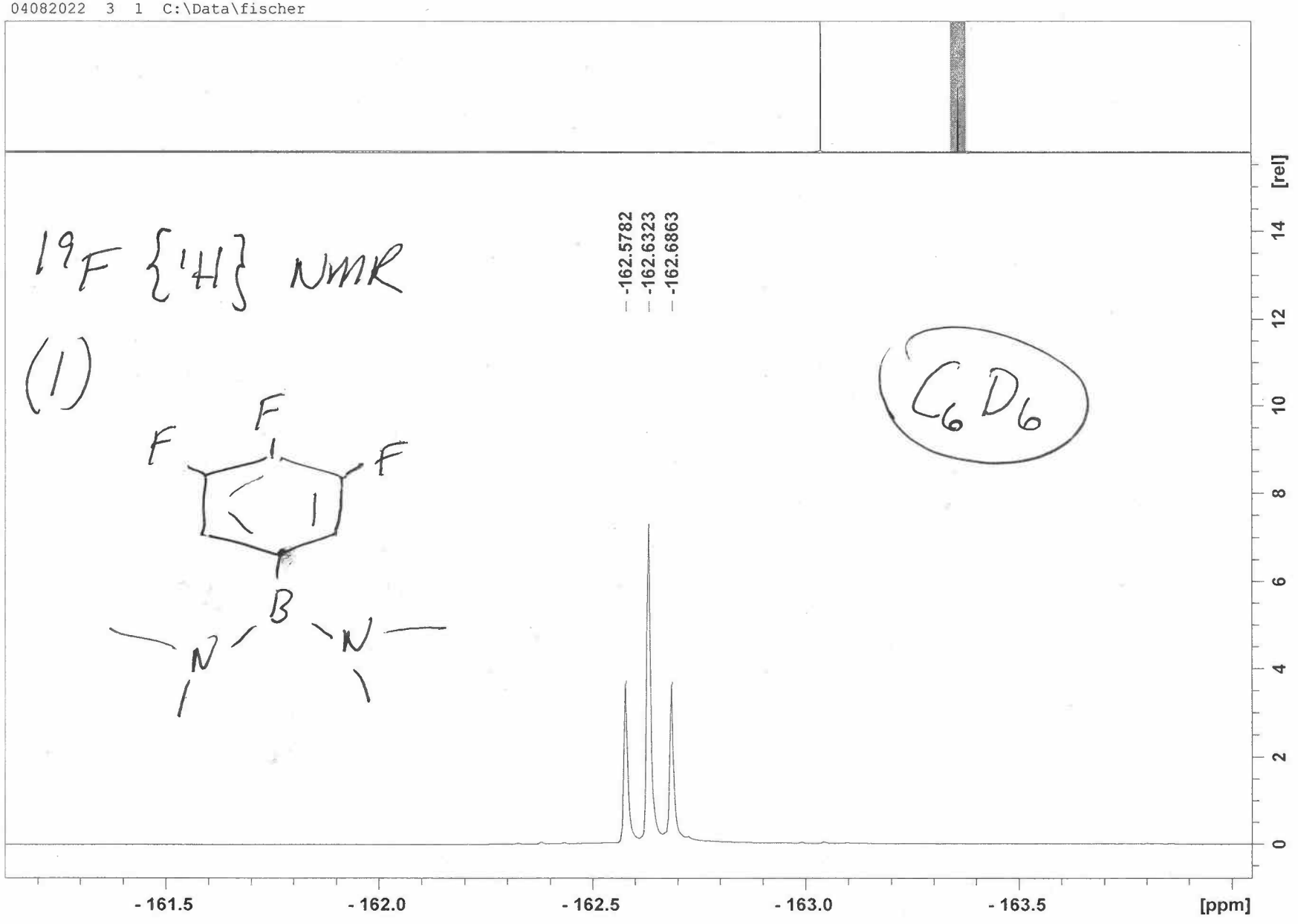
THF After Alumina

VI. NMR Spectra

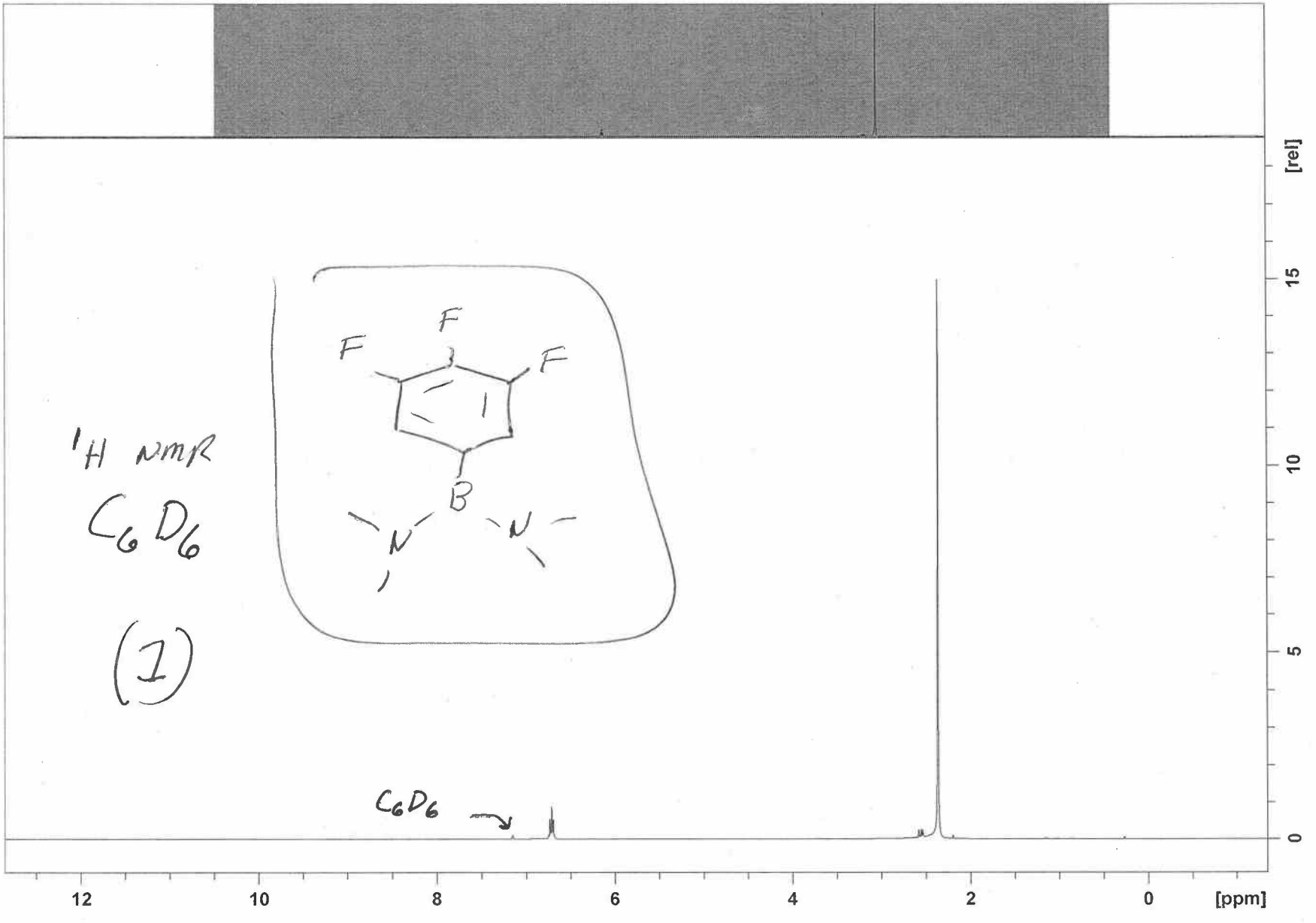

04082022 1 1 C:\Data\fischer
11B NMR
C6D6
(1)
31.2736
F
F
F
B
N
11B NMR
C6D6
[rel]
20
15
10
5
0
50
0
-50
[ppm]

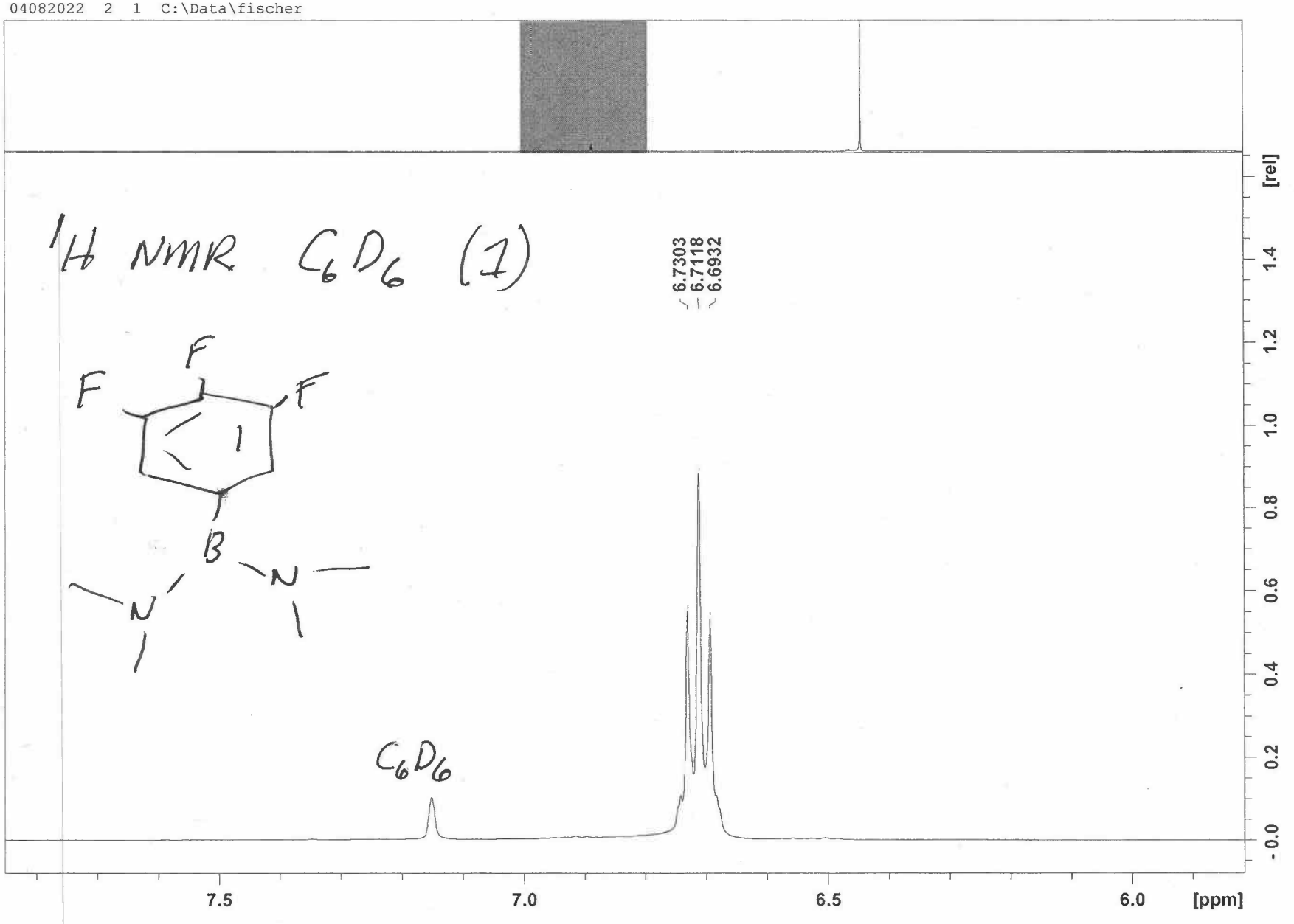

04082022 3 1 C:\Data\fischer
19F{1H} NMR C6D6
-136.5488
-136.6027
-162.5782
-162.6323
-162.6863
19F NMR
C6D6
(1)
F
F
F
B
N
N
0
5
10
15
20
[rel]
0
- 50
- 100
- 150
- 200
[ppm]

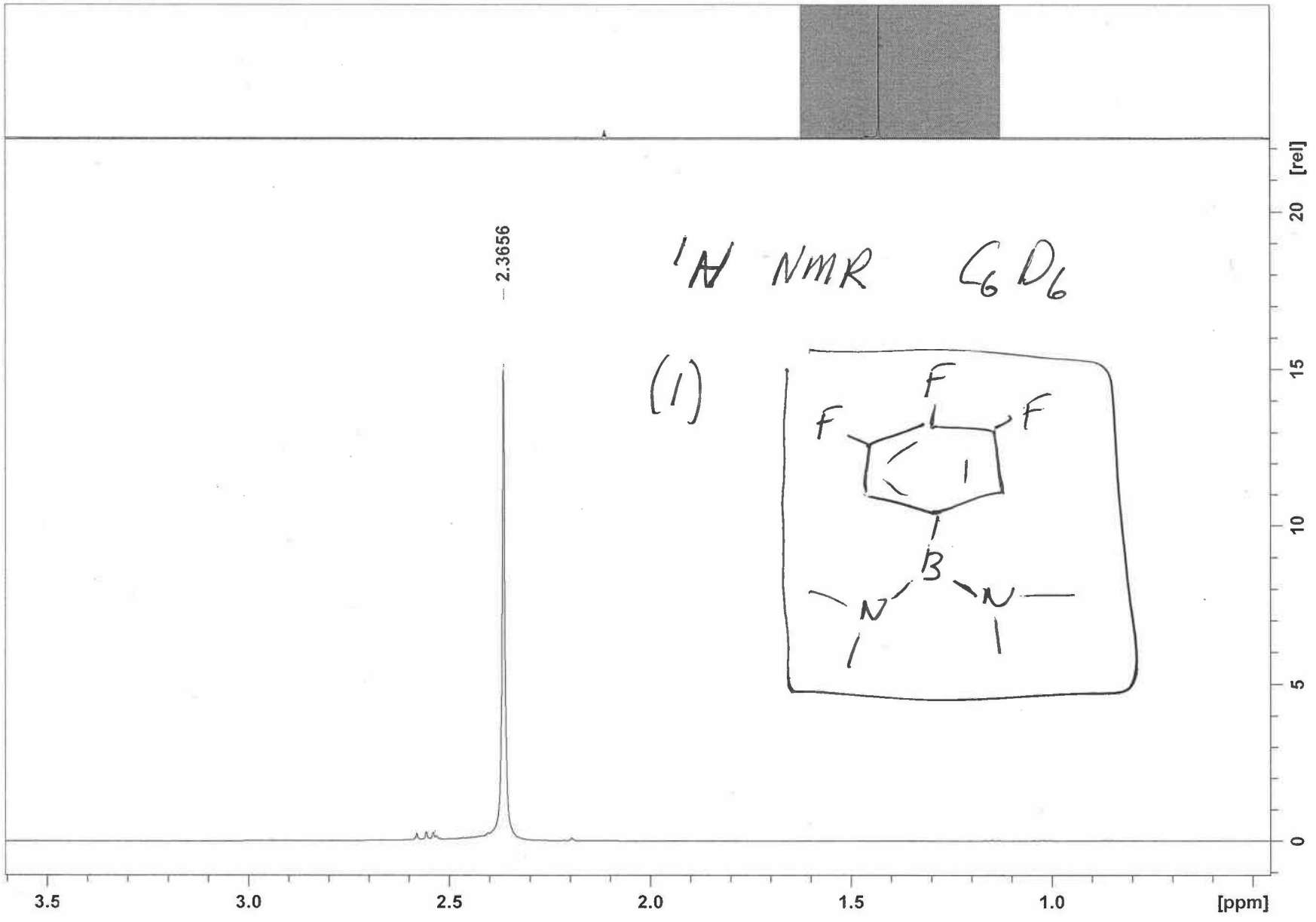

04082022 3 1 C:\Data\fischer
19F{1H} NMR
C6D6 (1)
F
F
F
B
N
N
-136.5488
-136.6027
[rel]
0
5
10
15
20
- 136.0
- 136.5
- 137.0
- 137.5
[ppm]

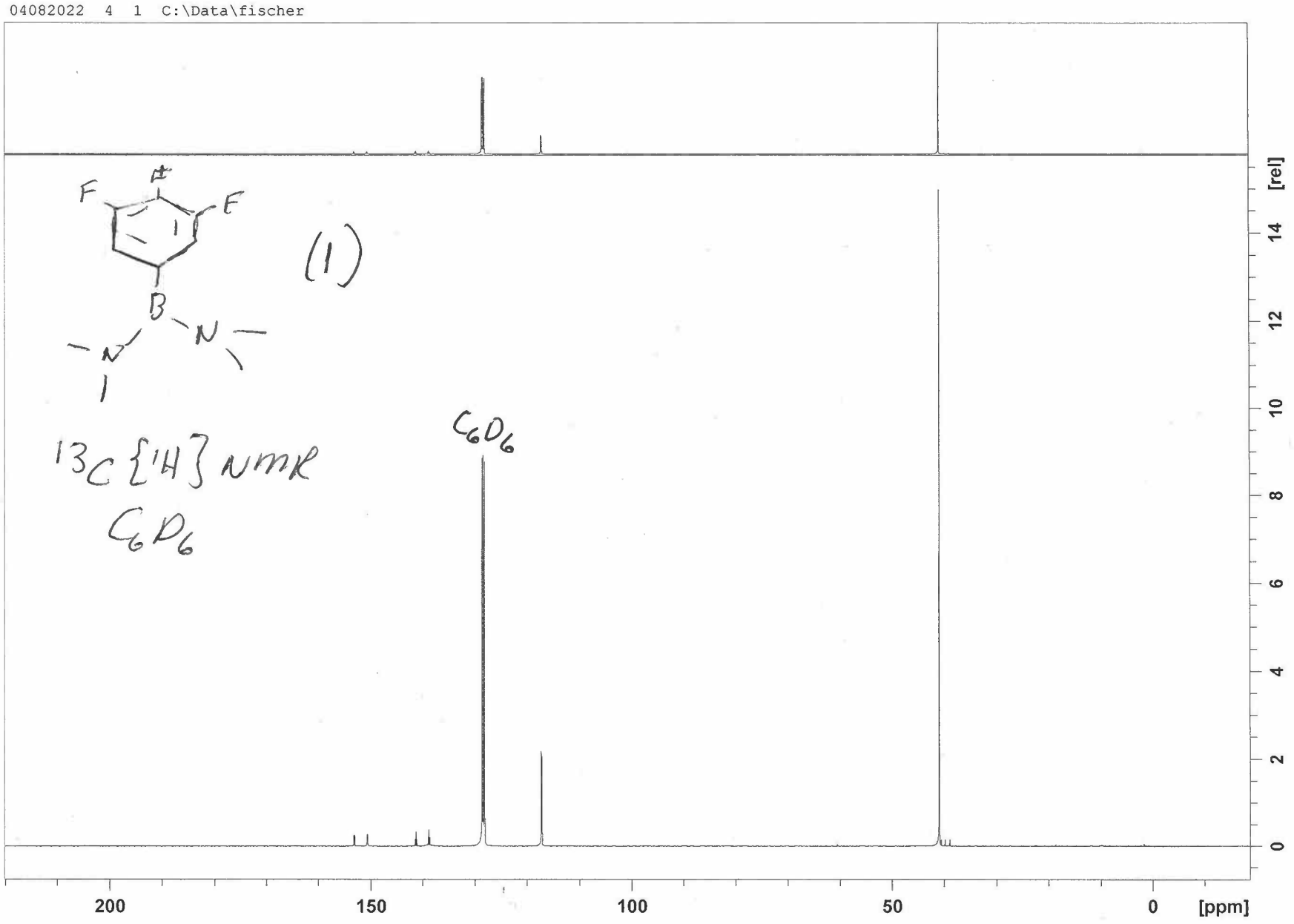

04082022 3 1 C:\Data\fischer
$^{19}F\{^{1}H\}$ NMR
(1)
F
F
F
B
N
N
-162.5782
-162.6323
-162.6863
C_6D_6
- 161.5
- 162.0
- 162.5
- 163.0
- 163.5
[ppm]
0
2
4
6
8
10
12
14
[rel]

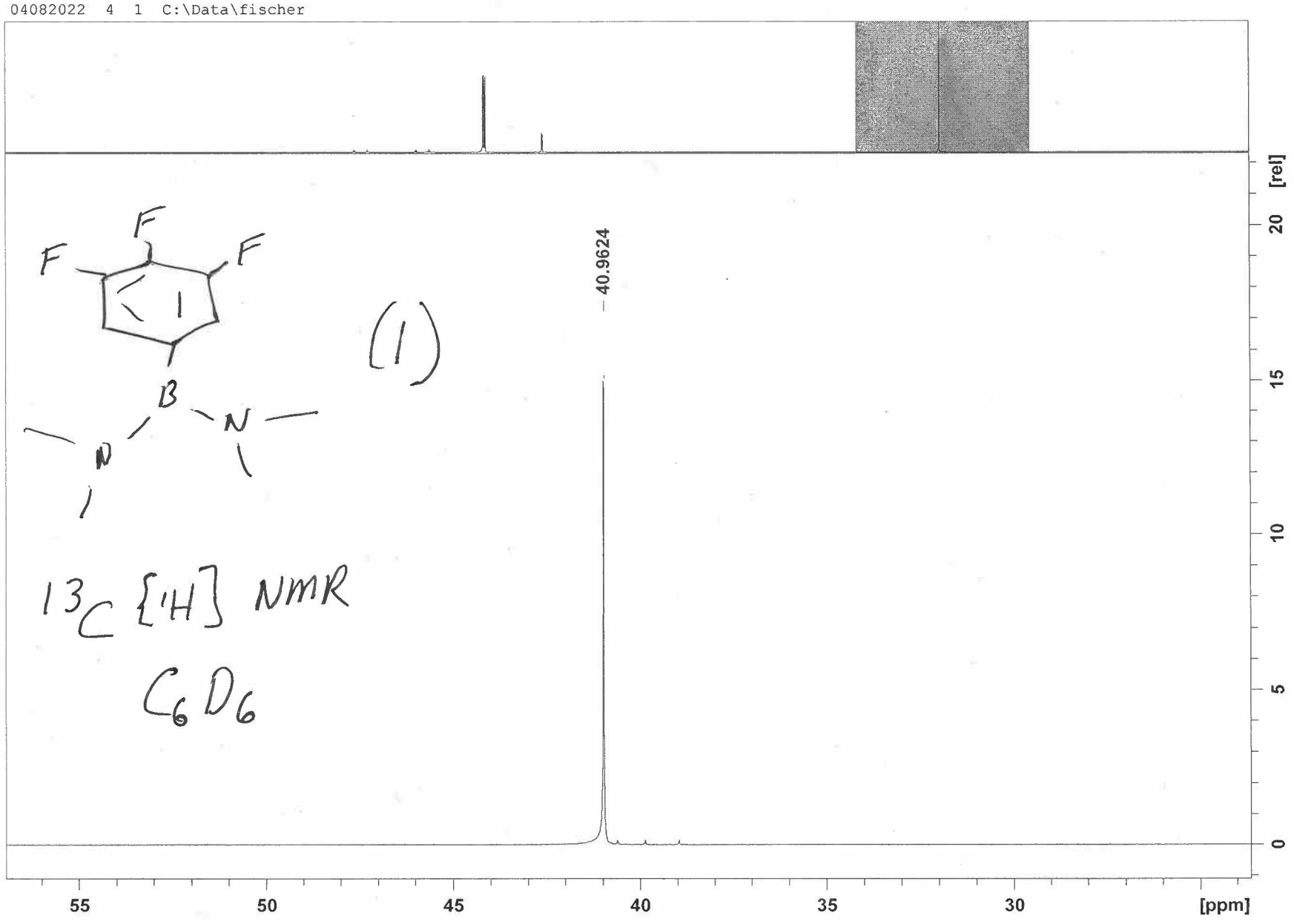
04082022 2 1 C:\Data\fischer

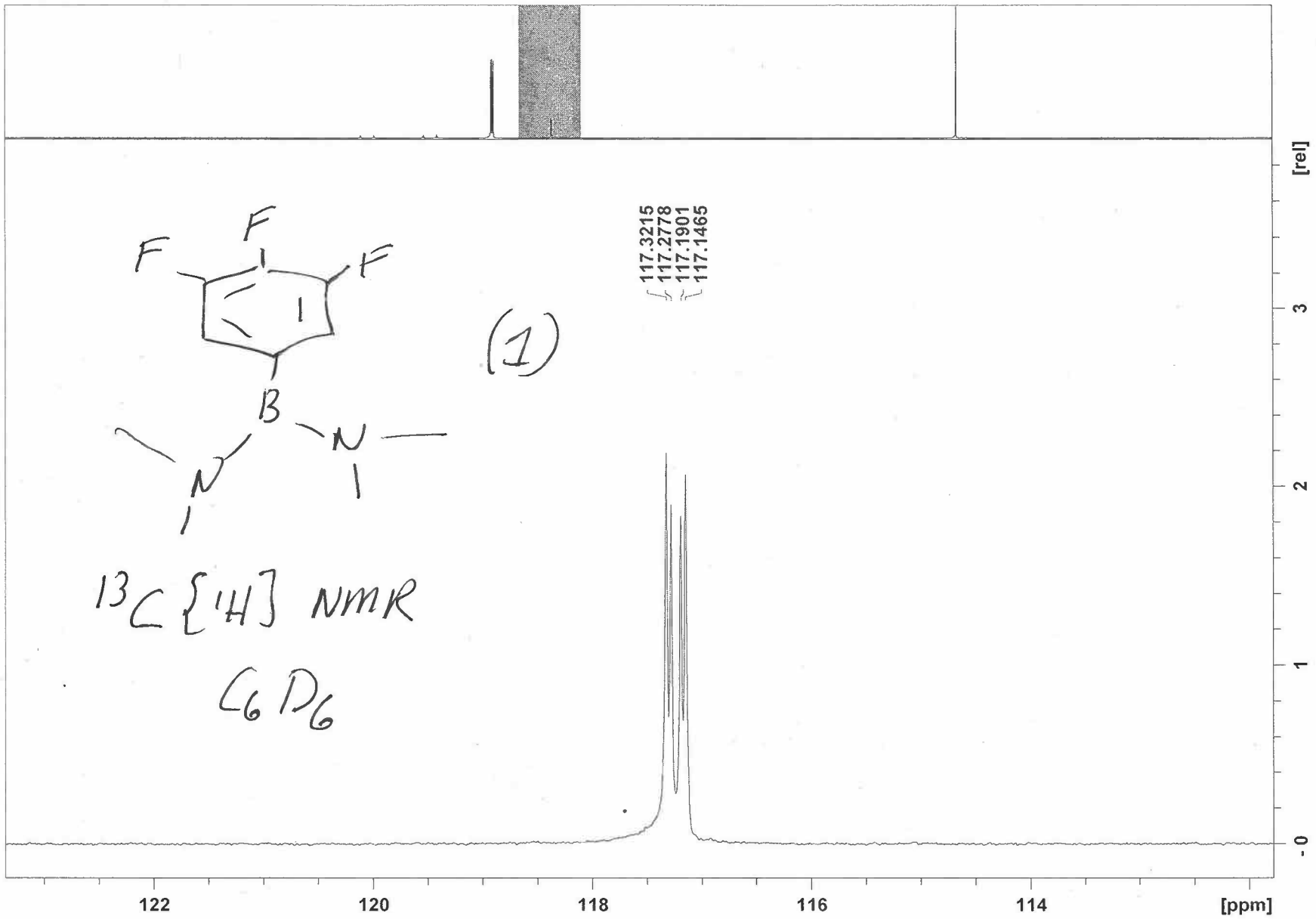


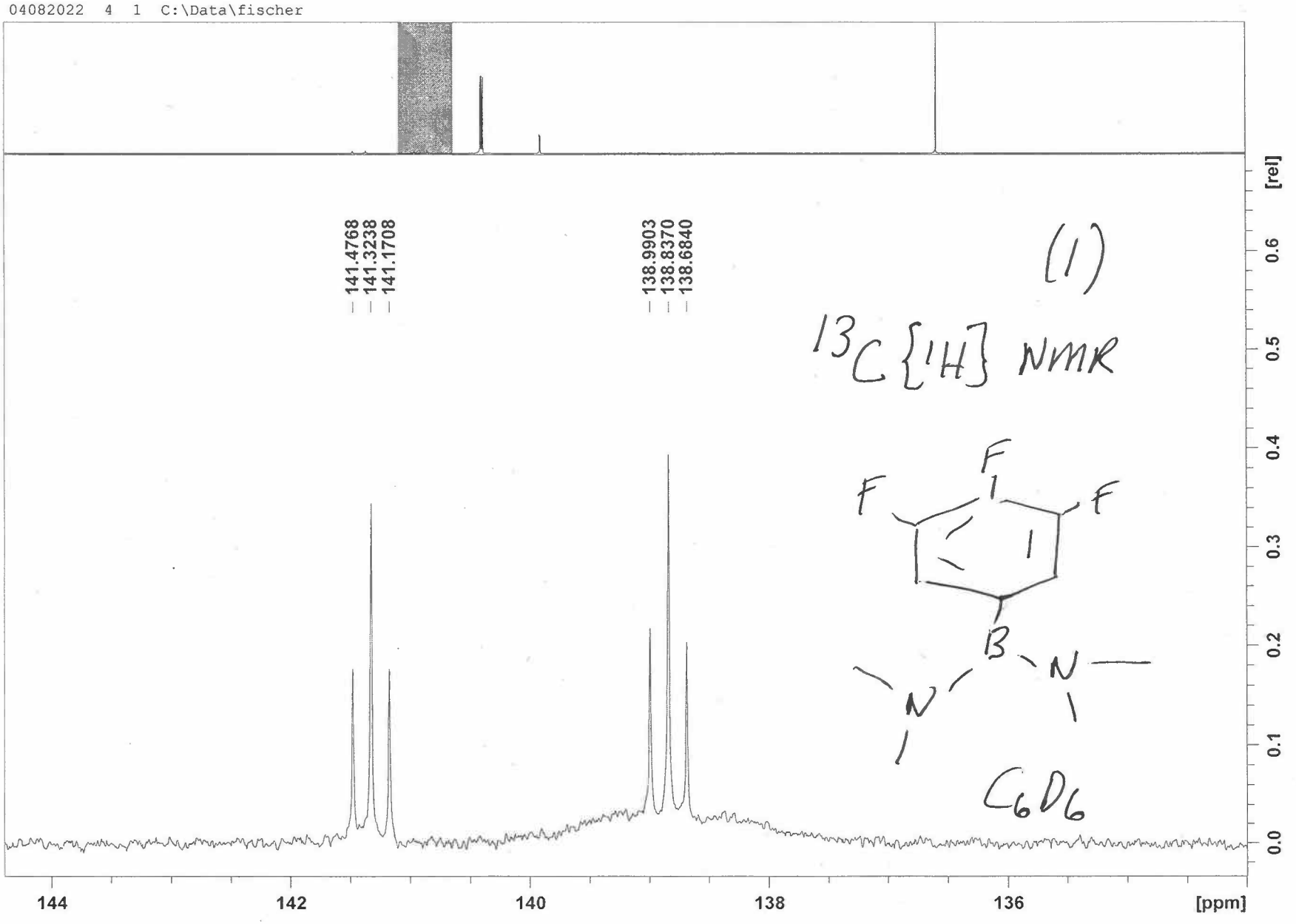

04082022 2 1 C:\Data\fischer
^1H NMR C_6D_6 (1)
6.7303
6.7118
6.6932
F
F
F
1
B
N
N
C_6D_6
7.5
7.0
6.5
6.0
[ppm]
[rel]
1.4
1.2
1.0
0.8
0.6
0.4
0.2
-0.0

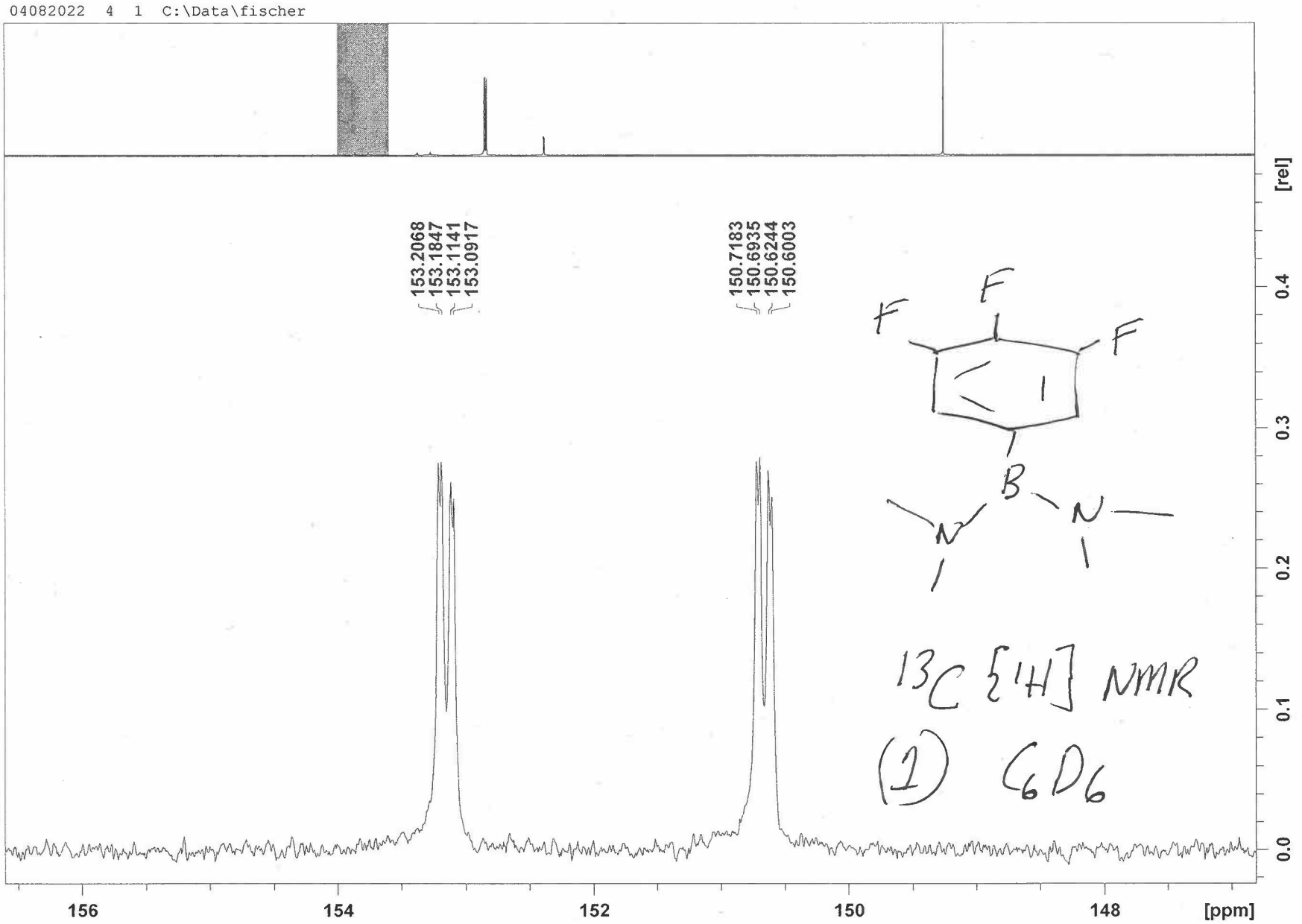

04082022 2 1 C:\Data\fischer
2.3656
^{1}H NMR C$_6$D$_6$
(1)
F
F
F
1
B
N
N
[rel]
20
15
10
5
0
3.5
3.0
2.5
2.0
1.5
1.0
[ppm]

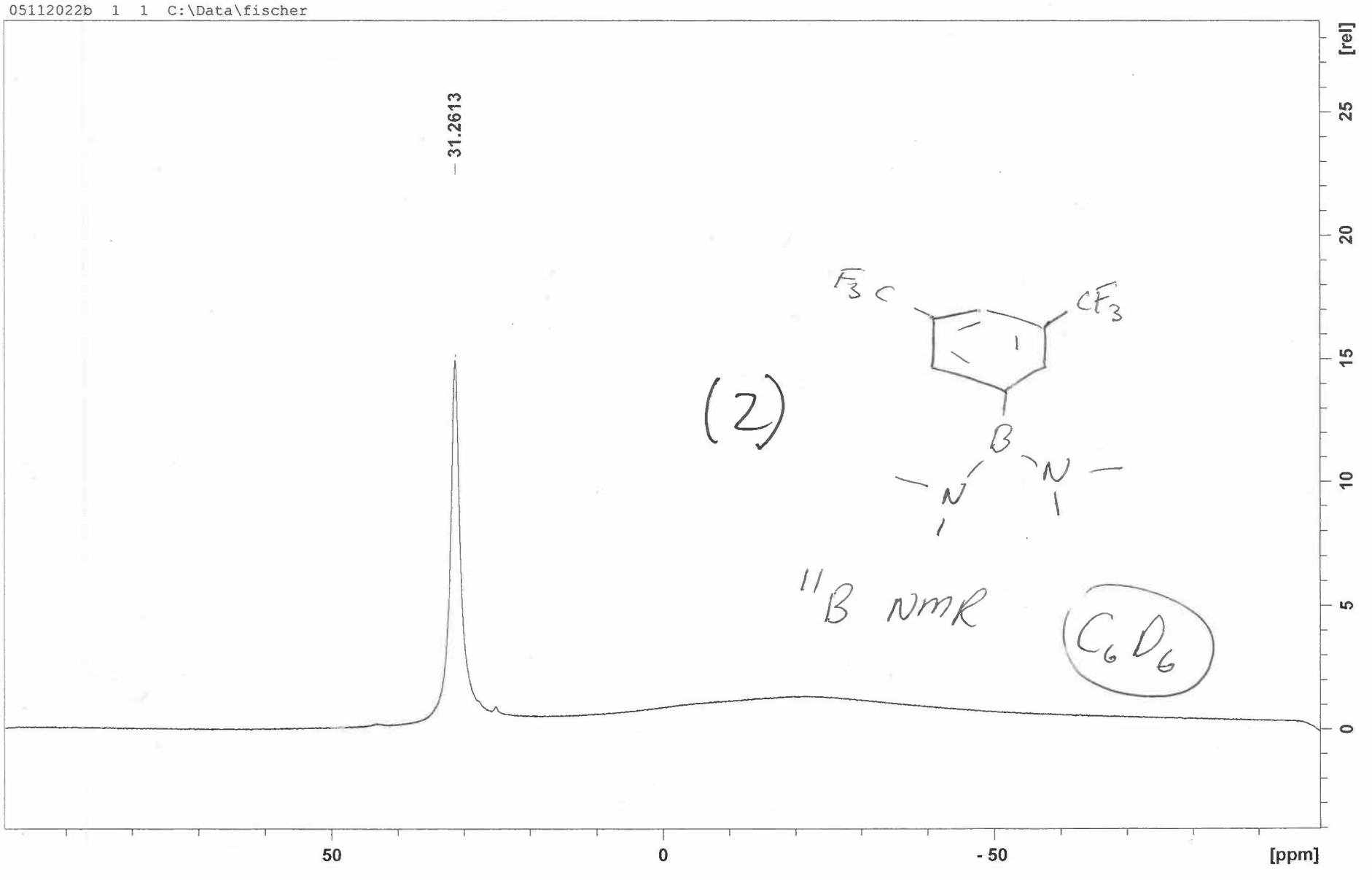

04082022 4 1 C:\Data\fischer
F
F
B
N
N
N
(1)
13C {1H} NMR
C6D6
C6D6
0
2
4
6
8
10
12
14
[rel]
200
150
100
50
0
[ppm]

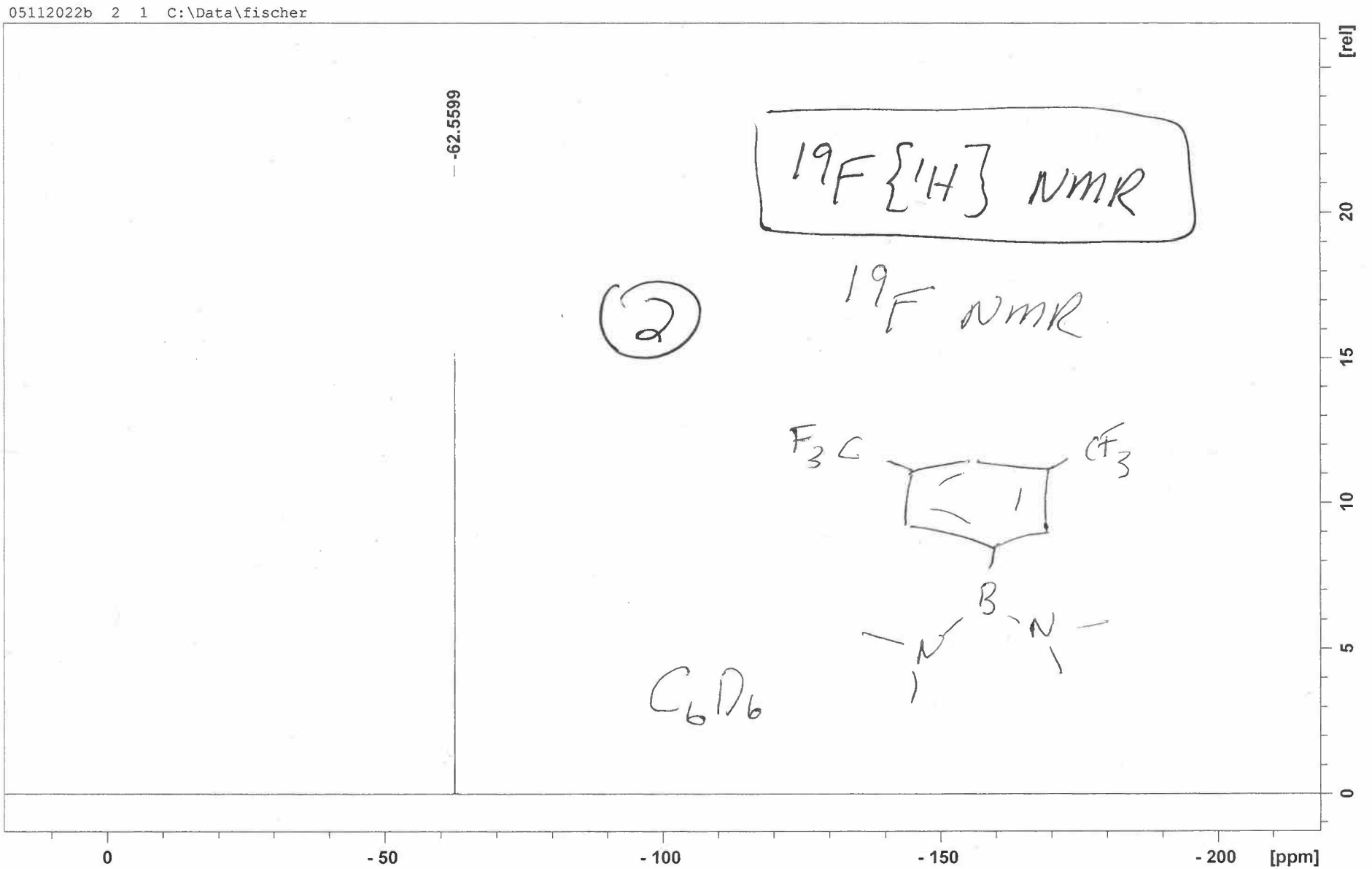

04082022 4 1 C:\Data\fischer
F
F
F
B
N
N
(1)
40.9624
13C {1H} NMR
C6D6
[rel]
0
5
10
15
20
55
50
45
40
35
30
[ppm]

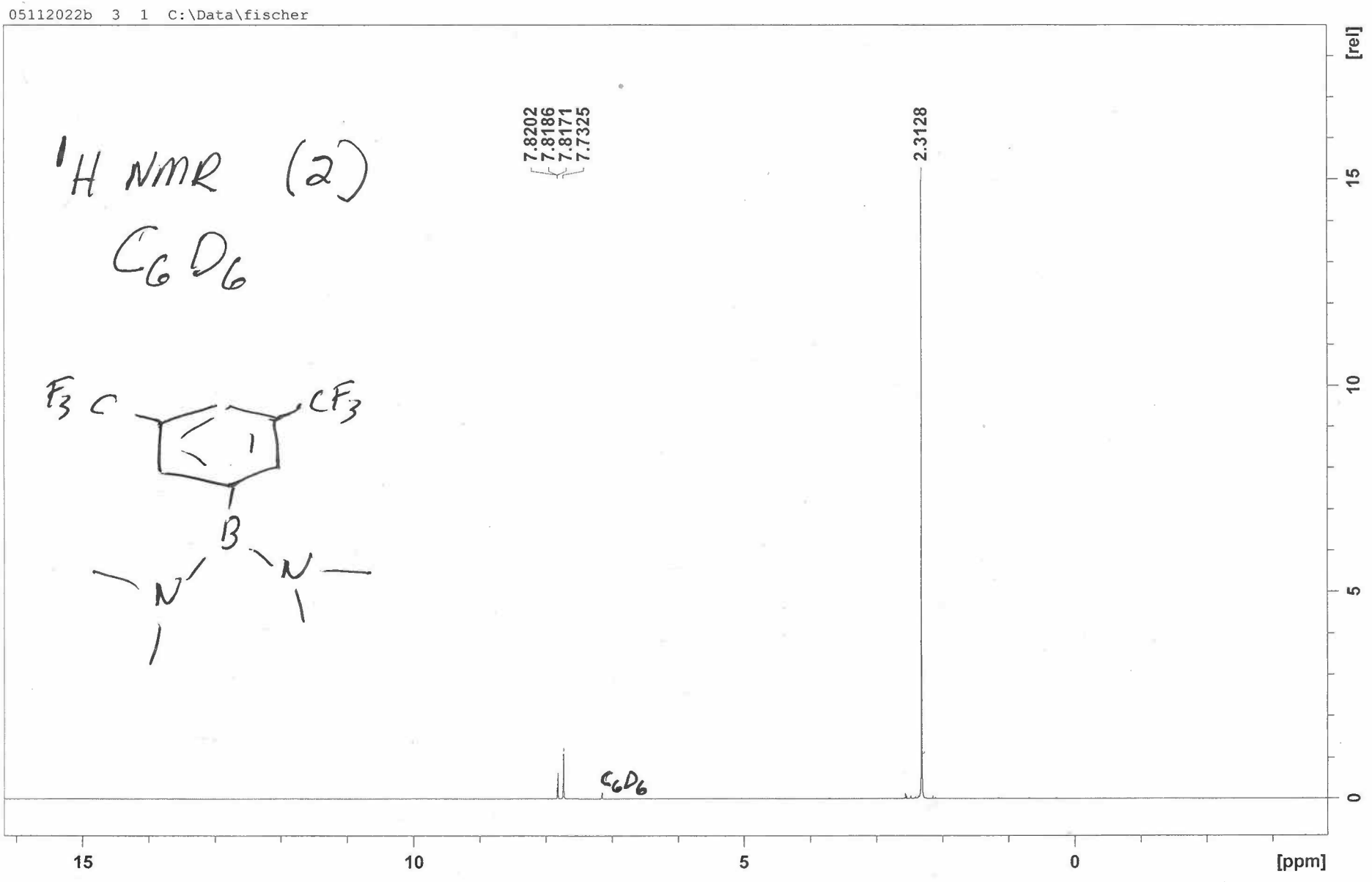

04082022 4 1 C:\Data\fischer
F
F
F
B
N
N
(1)
117.3215
117.2778
117.1901
117.1465
$^{13}C\{^{1}H\}$ NMR
C_6D_6
[rel]
3
2
1
-0
122
120
118
116
114
[ppm]

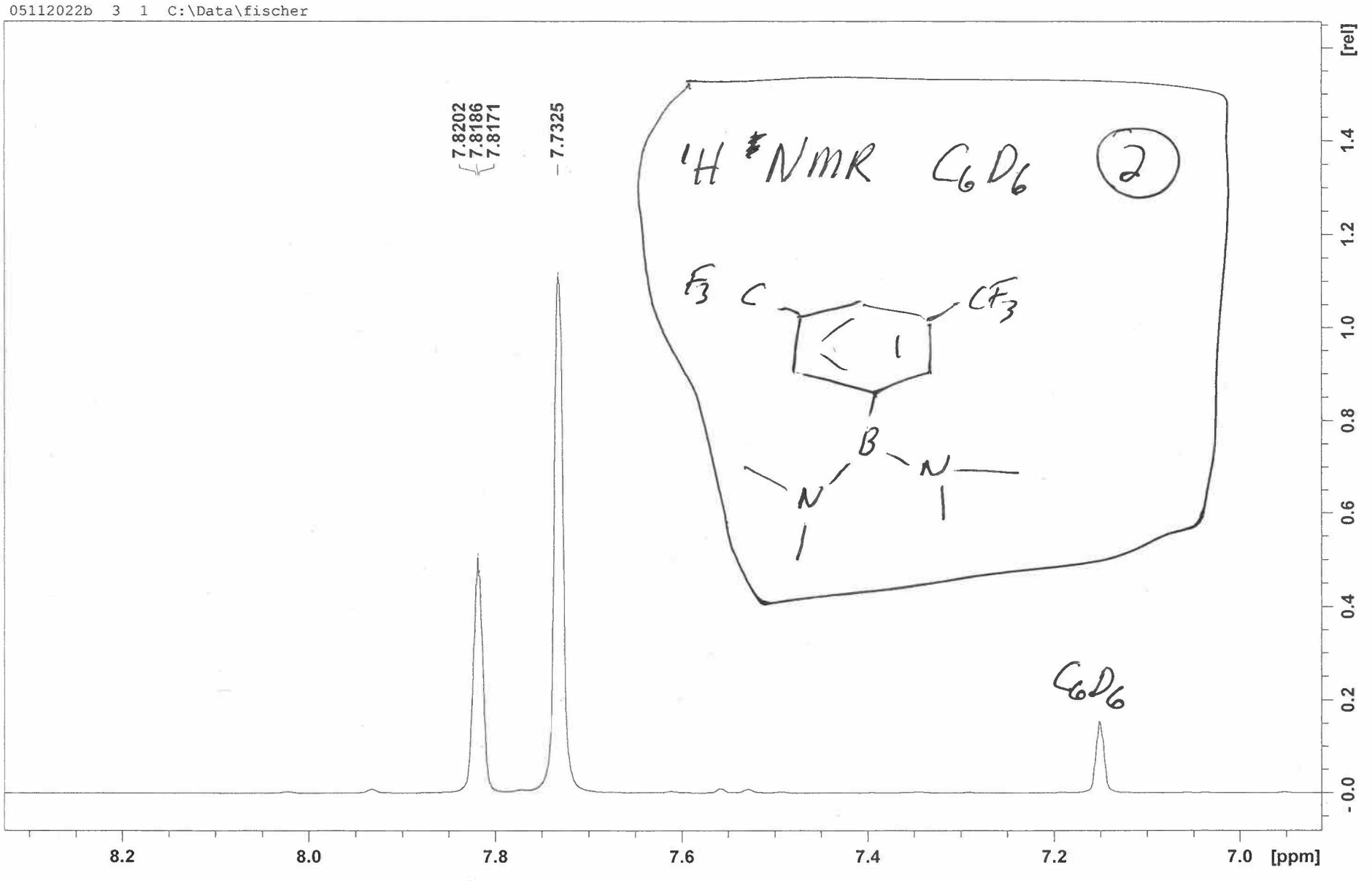

04082022 4 1 C:\Data\fischer
141.4768
141.3238
141.1708
138.9903
138.8370
138.6840
(1)
13C{1H} NMR
F
F
F
B
N
N
C6D6
144
142
140
138
136
[ppm]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[rel]

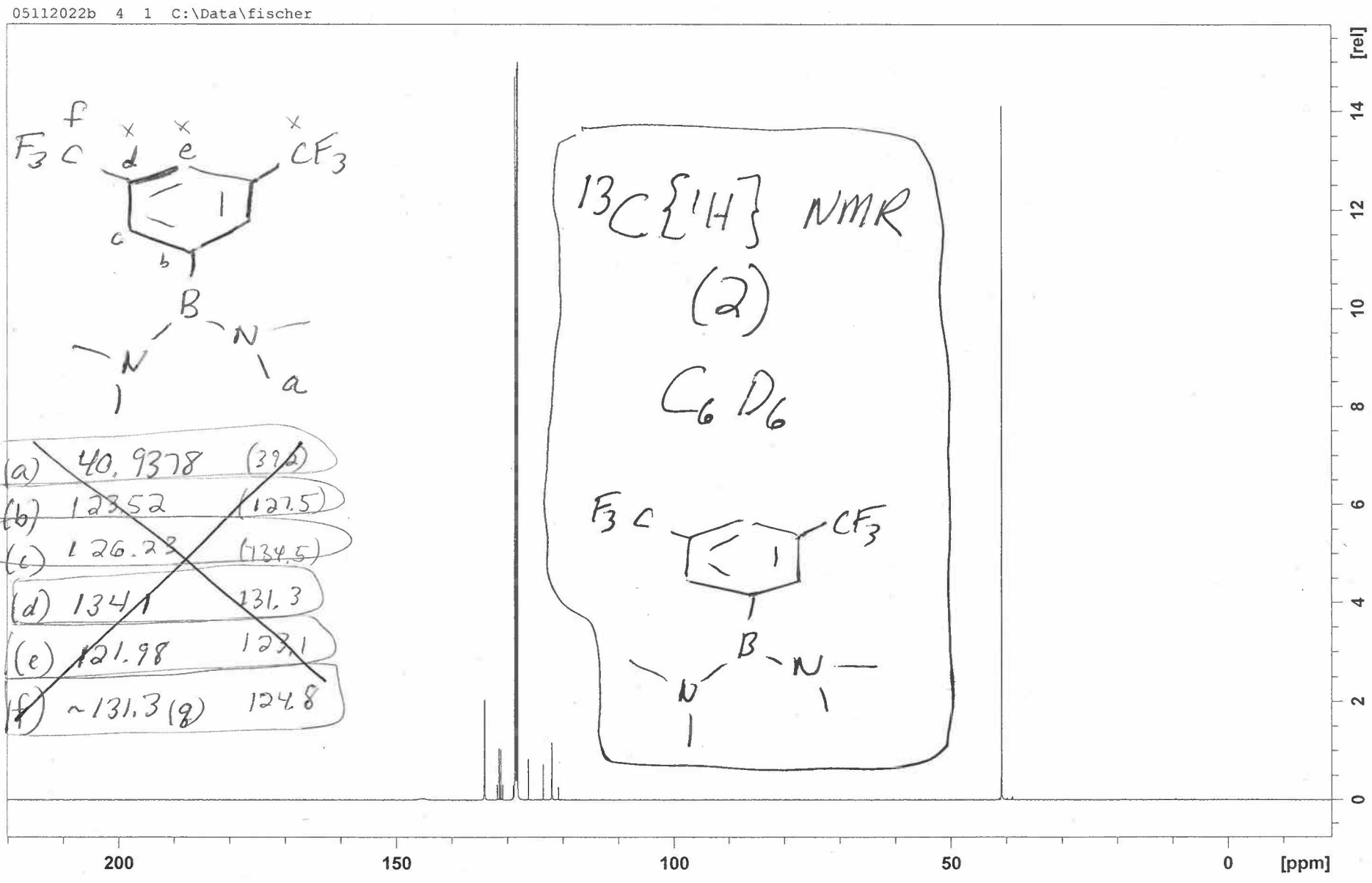

04082022 4 1 C:\Data\fischer
153.2068
153.1847
153.1141
153.0917
150.7183
150.6935
150.6244
150.6003
F
F
F
B
N
N
13C {1H} NMR
(1) C6D6
[rel]
0.0
0.1
0.2
0.3
0.4
156
154
152
150
148
[ppm]

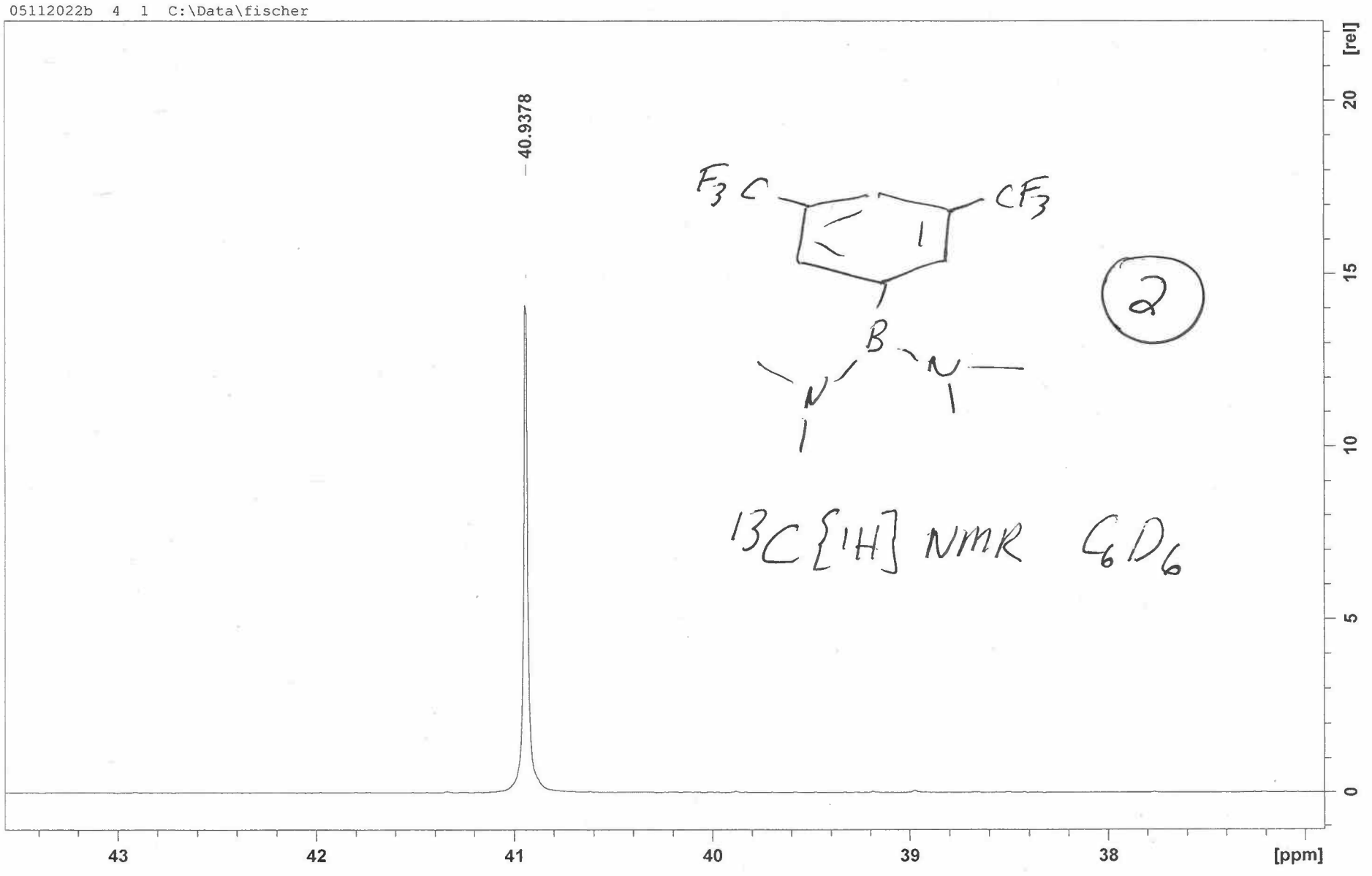

05112022b 1 1 C:\Data\fischer
31.2613
(2)
F_3C
CF_3
B
N
N
^{11}B NMR
C_6D_6
[rel]
25
20
15
10
5
0
50
0
- 50
[ppm]

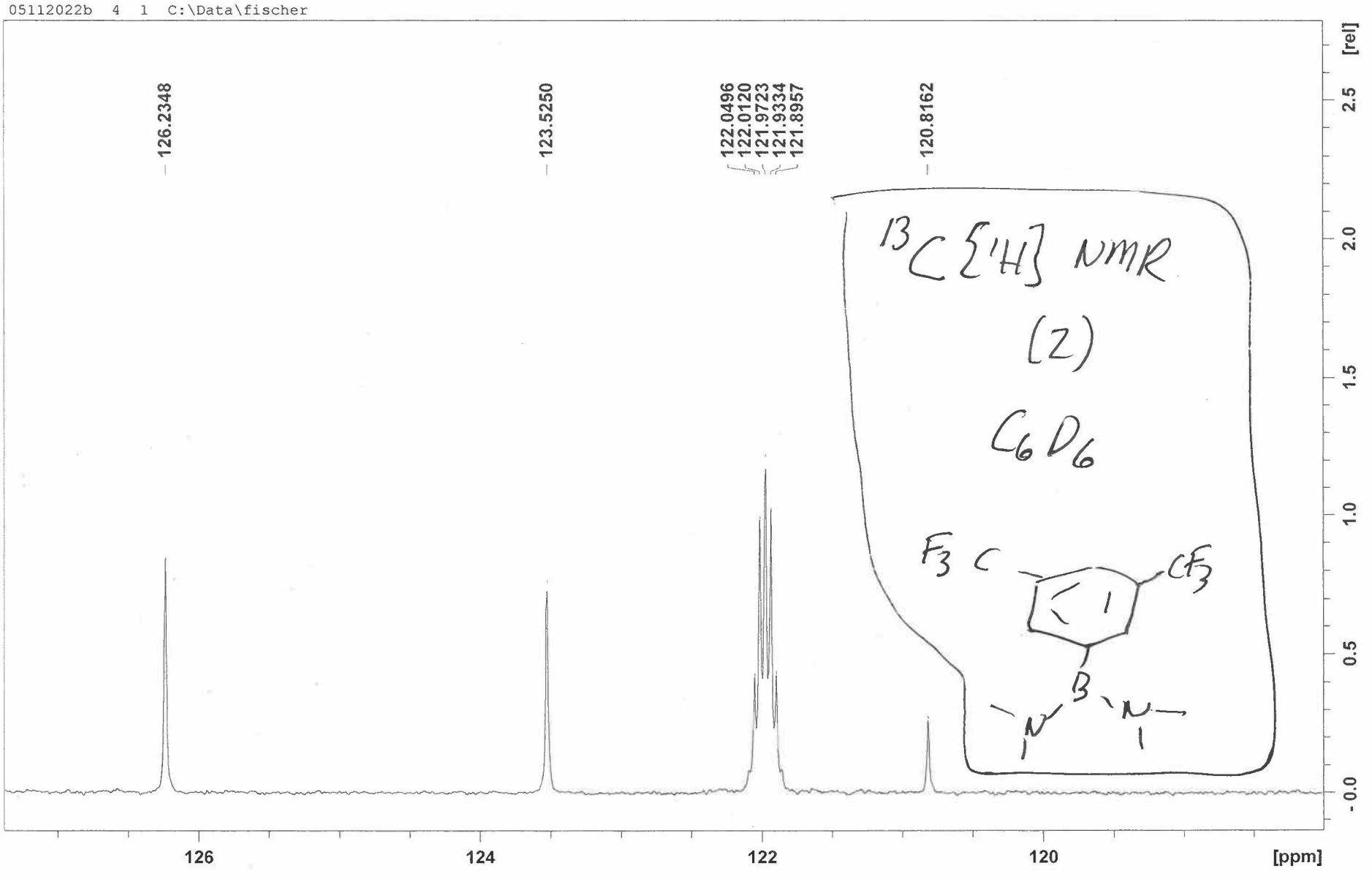

05112022b 2 1 C:\Data\fischer
-62.5599
19F{1H} NMR
(2)
19F NMR
F3C
CF3
B
N
N
C6D6
[rel]
0
5
10
15
20
0
- 50
- 100
- 150
- 200
[ppm]

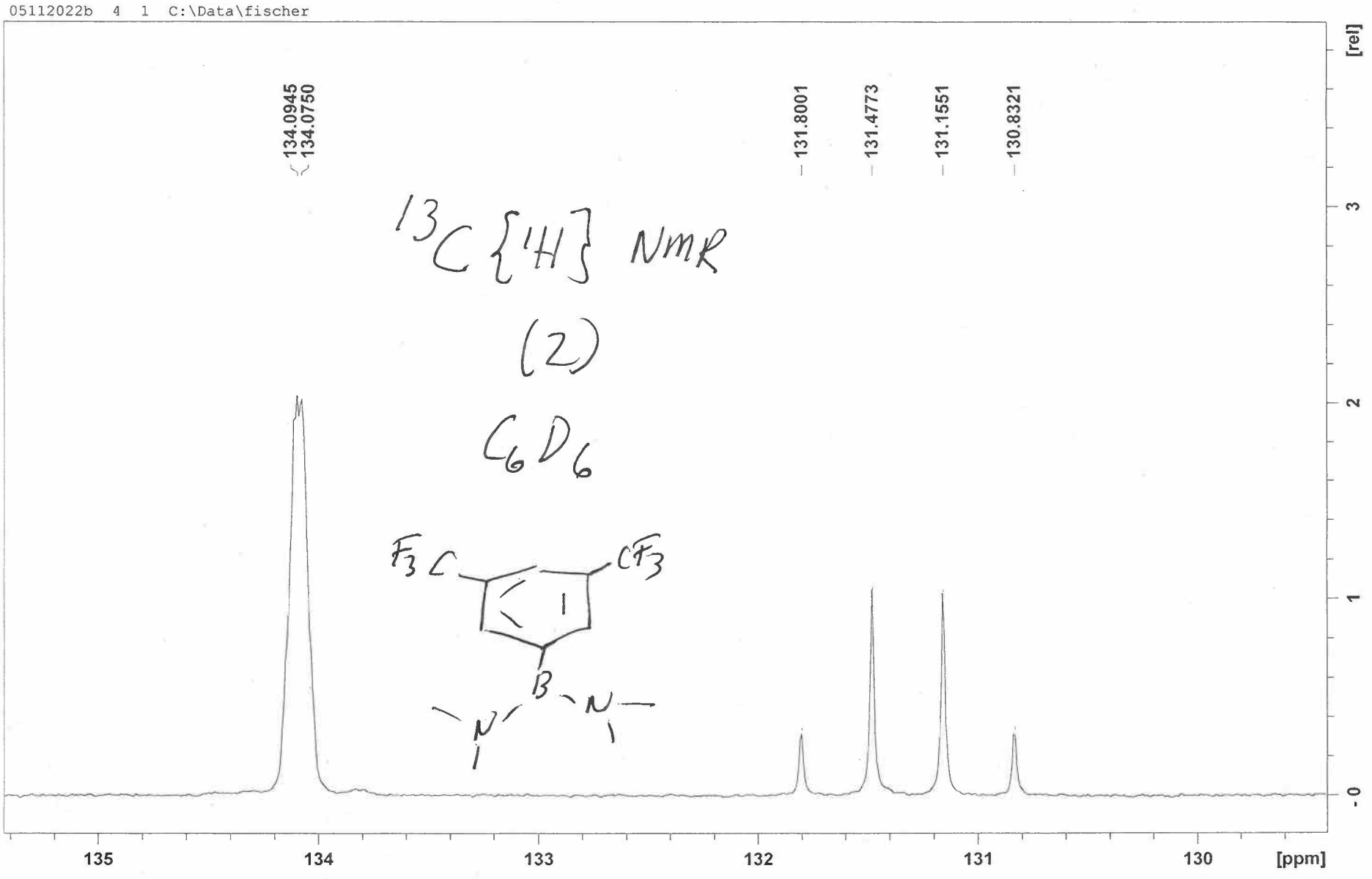

05112022b 3 1 C:\Data\fischer
^1H NMR (2)
C_6D_6
F_3C
CF_3
B
N
N
7.8202
7.8186
7.8171
7.7325
2.3128
C_6D_6
[rel]
15
10
5
0
[ppm]

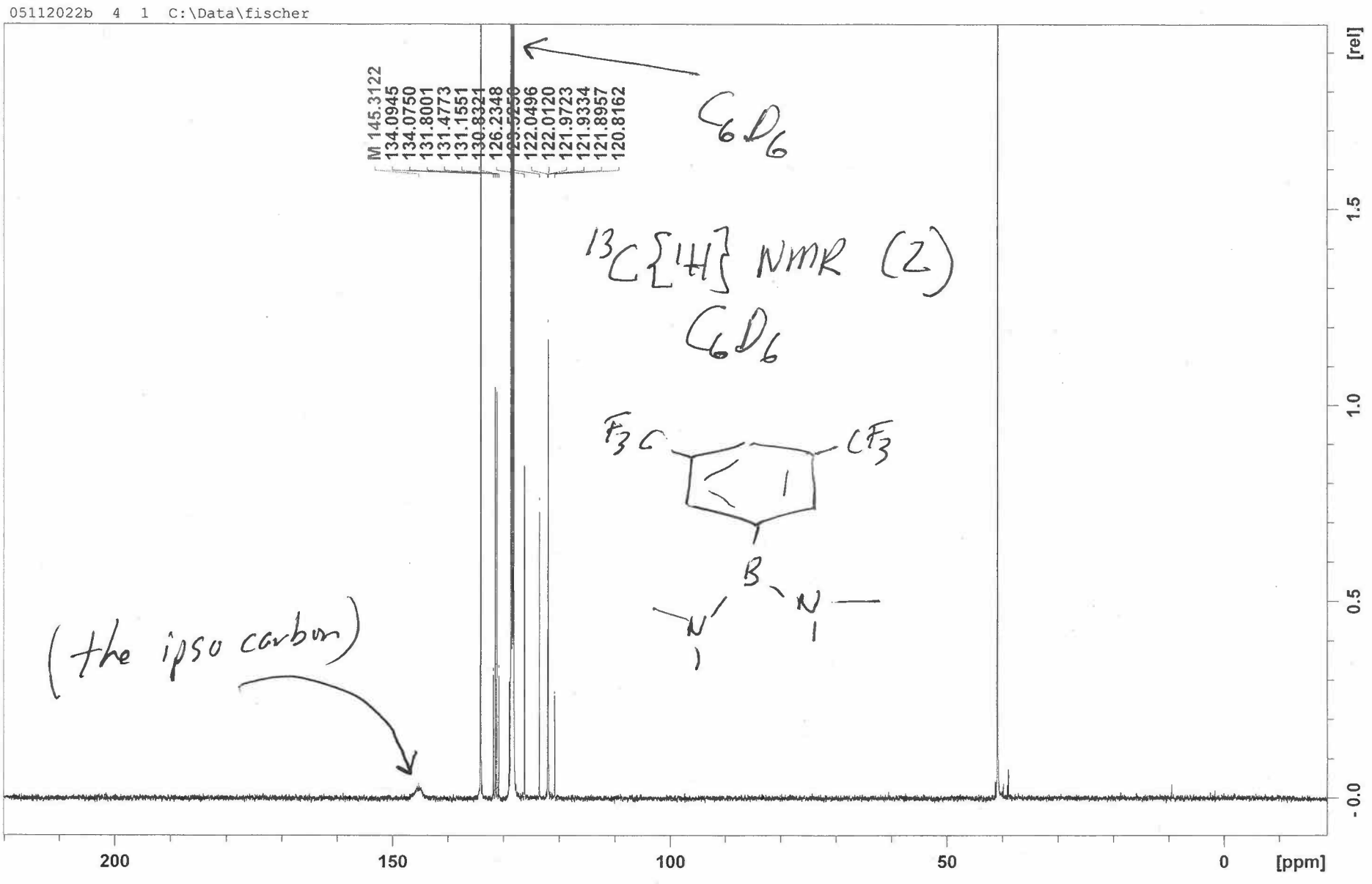

05112022b 3 1 C:\Data\fischer
7.8202
7.8186
7.8171
7.7325
^1H NMR C_6D_6
2
F_3C
CF_3
B
N
N
C_6D_6
[rel]
1.4
1.2
1.0
0.8
0.6
0.4
0.2
-0.0
8.2
8.0
7.8
7.6
7.4
7.2
7.0
[ppm]

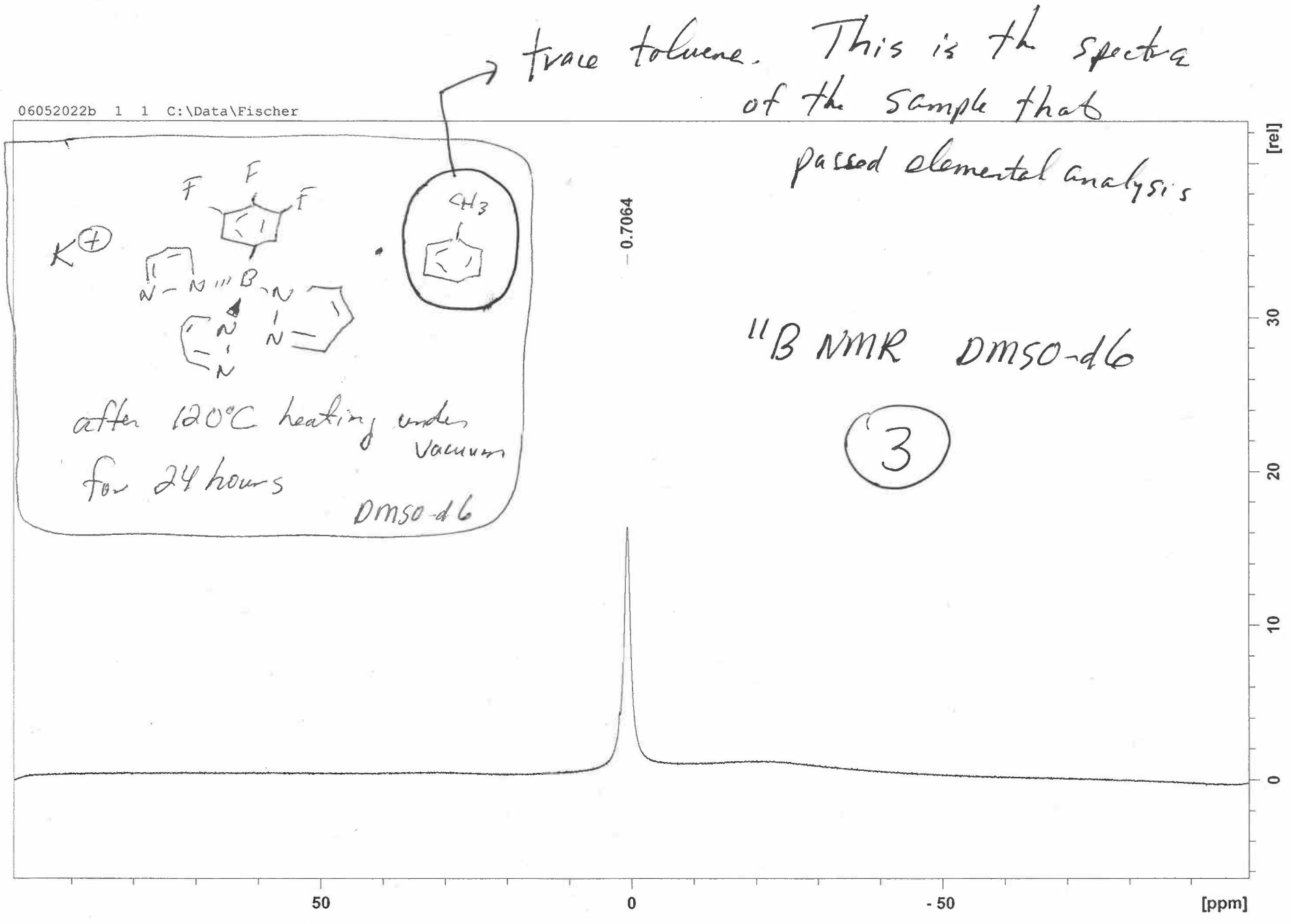

05112022b 4 1 C:\Data\fischer
f
x x x
F3C d e CF3
1
c
b
B
N
N
a
(a) 40.9378 (39.2)
(b) 123.52 (127.5)
(c) 126.22 (134.5)
(d) 134.1 131.3
(e) 121.98 127.1
(f) ~131.3 (q) 124.8
13C{1H} NMR
(2)
C6D6
F3C
CF3
1
B
N
N
200
150
100
50
0
[ppm]
0
2
4
6
8
10
12
14
[rel]

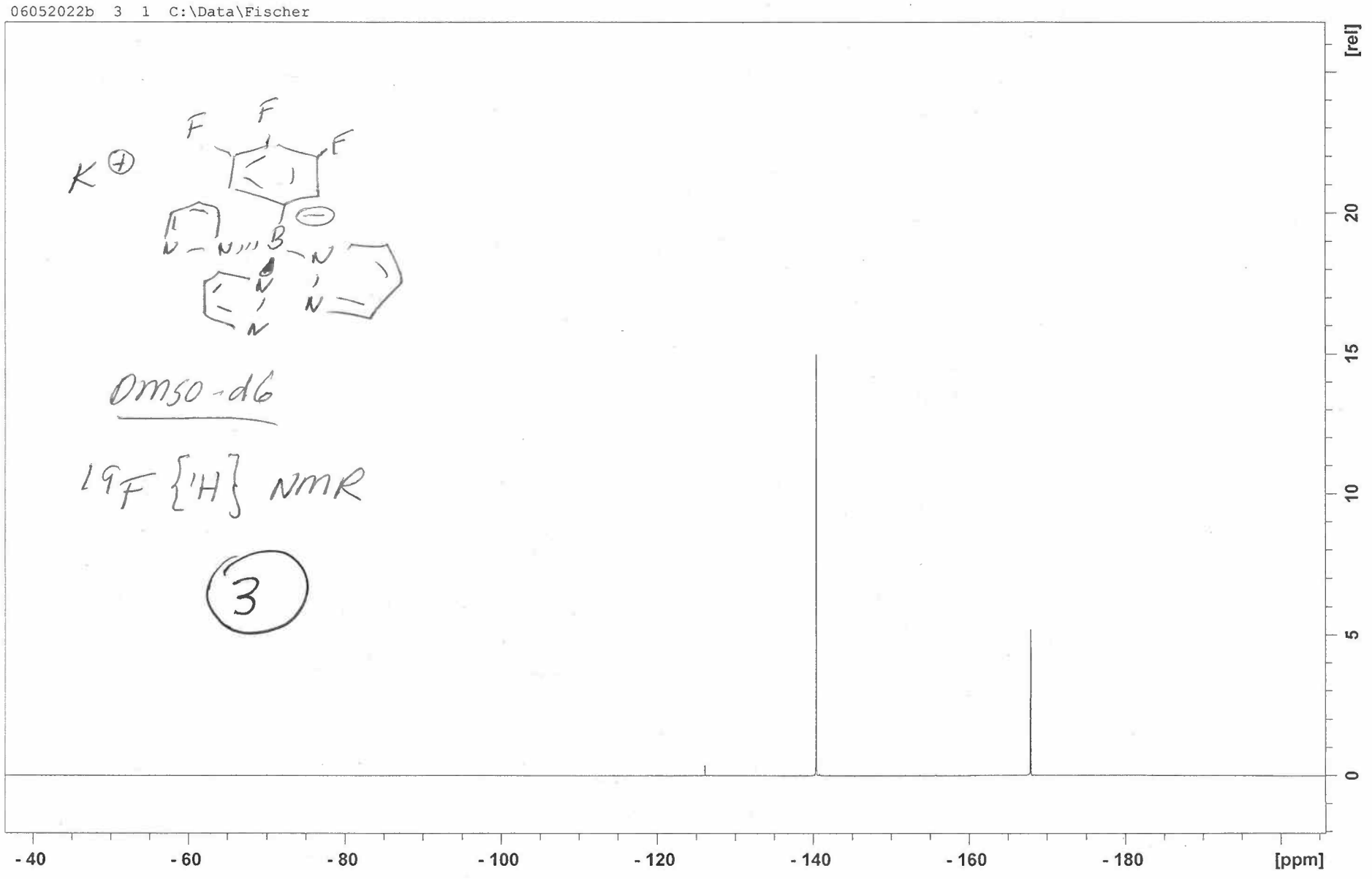

05112022b 4 1 C:\Data\fischer
40.9378
F3C
CF3
B
N
N
2
13C{1H} NMR C6D6
[rel]
20
15
10
5
0
43
42
41
40
39
38
[ppm]

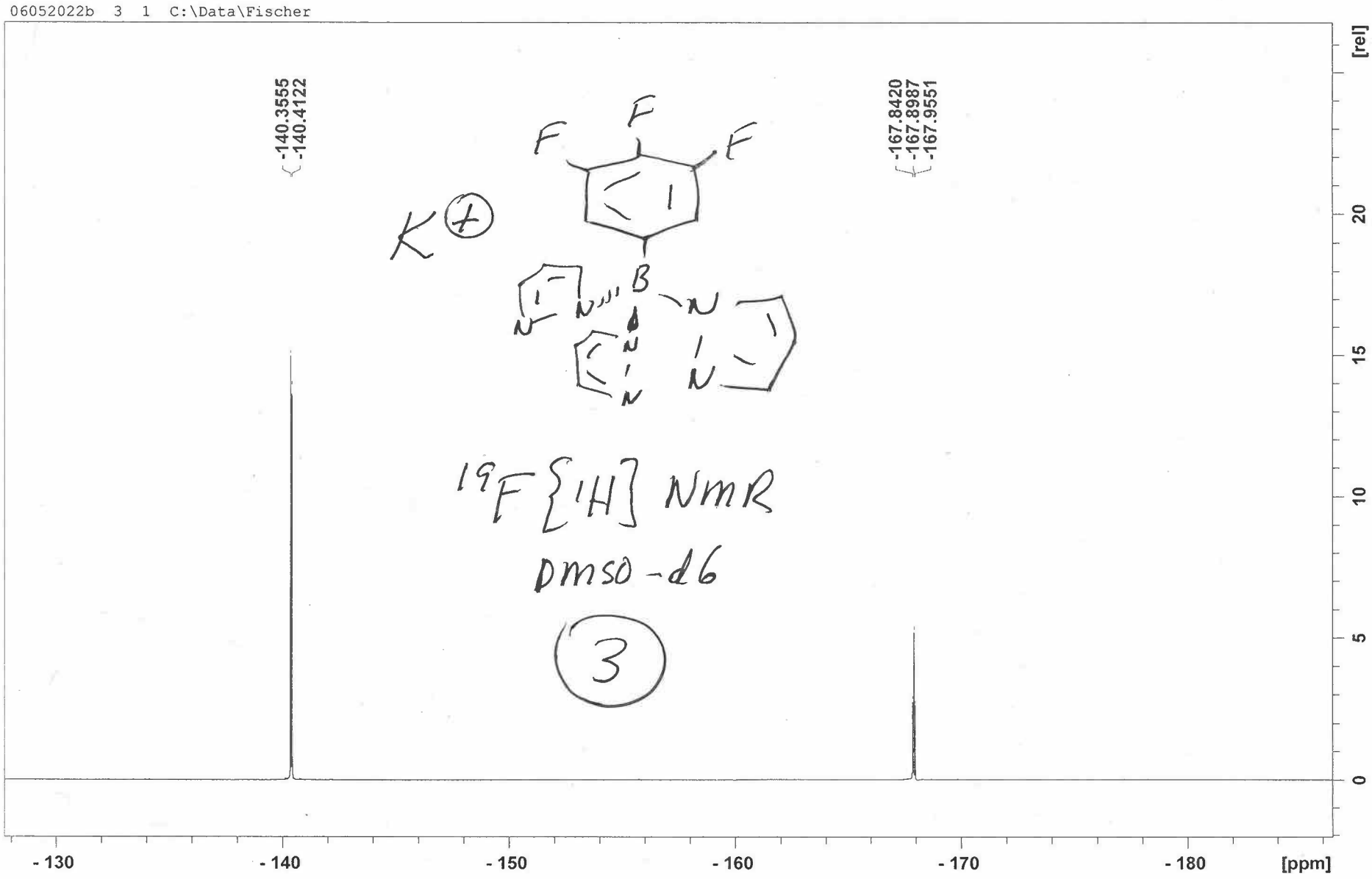

05112022b 4 1 C:\Data\fischer
126.2348
123.5250
122.0496
122.0120
121.9723
121.9334
121.8957
120.8162
13C{1H} NMR
(2)
C6D6
F3C
CF3
B
N
N
126
124
122
120
[ppm]
2.5
2.0
1.5
1.0
0.5
-0.0
[rel]

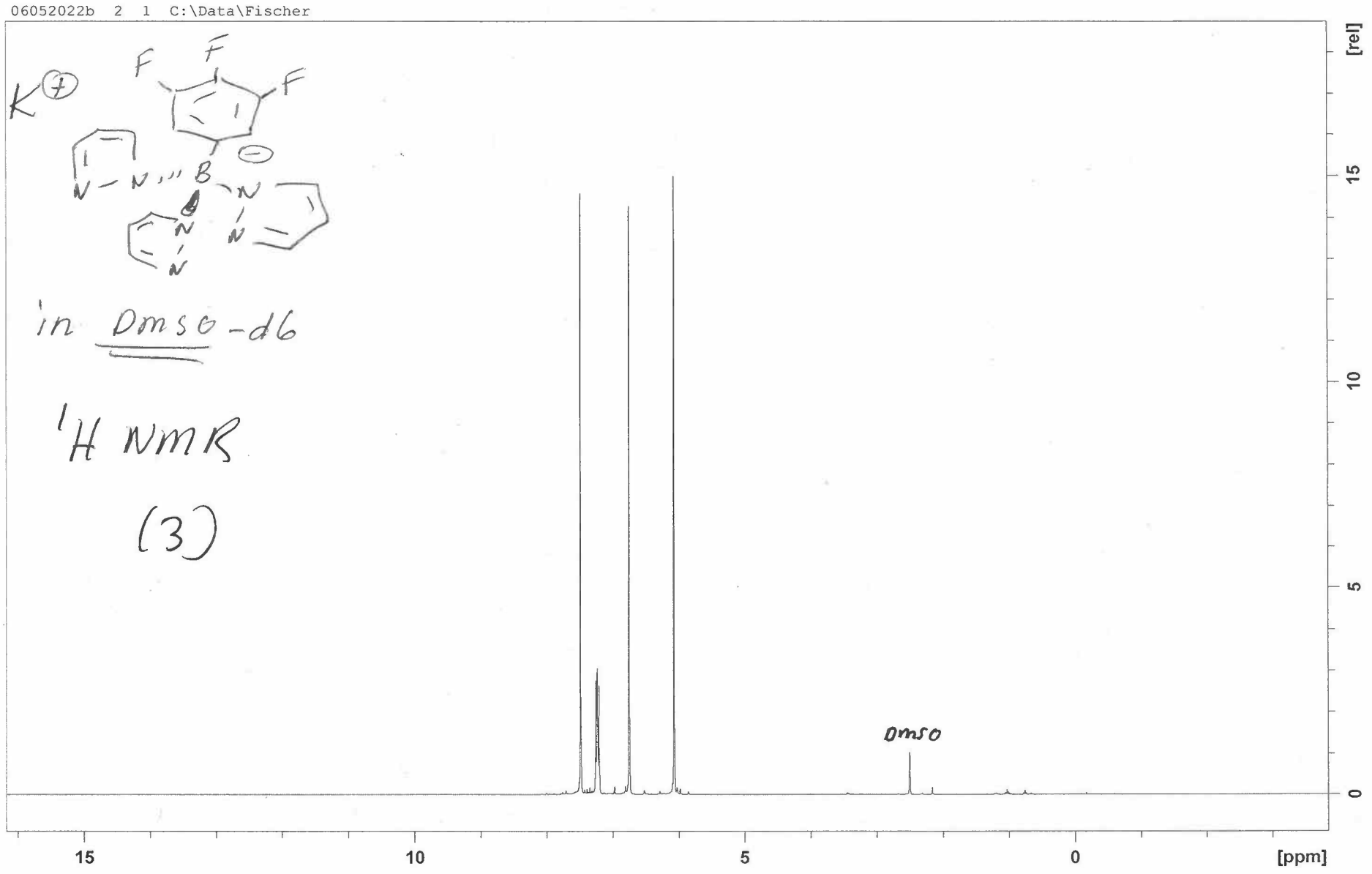

05112022b 4 1 C:\Data\fischer
134.0945
134.0750
131.8001
131.4773
131.1551
130.8321
$^{13}C\{^{1}H\}$ NMR
(2)
C_6D_6
F_3C
CF_3
B
N
N
[rel]
3
2
1
-0
135
134
133
132
131
130
[ppm]

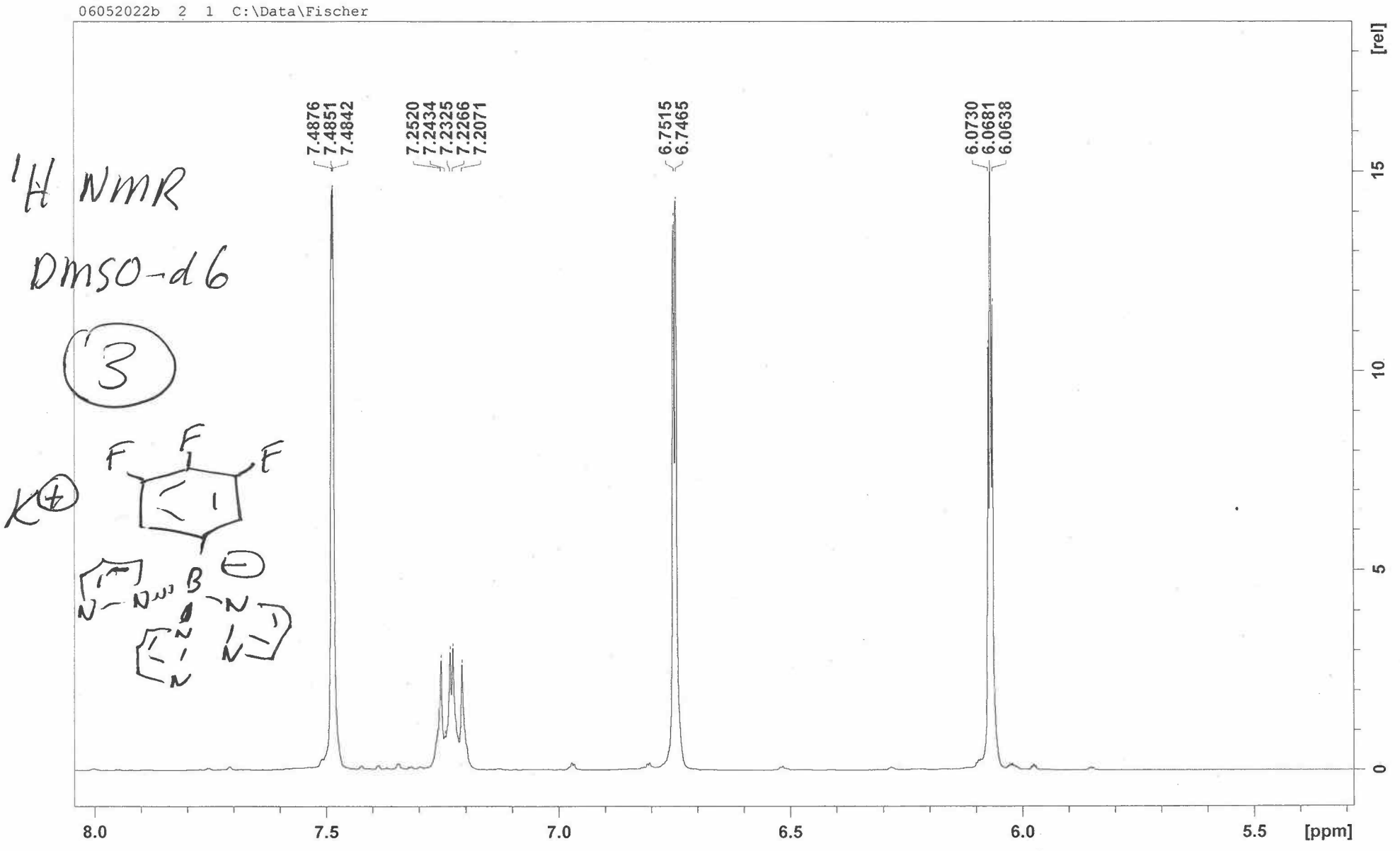

05112022b 4 1 C:\Data\fischer
M 145.3122
134.0945
134.0750
131.8001
131.4773
131.1551
130.8321
126.2348
122.0496
122.0120
121.9723
121.9334
121.8957
120.8162
C6D6
13C{1H} NMR (2)
C6D6
F3C
CF3
B
N
N
(the ipso carbon)
200
150
100
50
0
[ppm]
1.5
1.0
0.5
-0.0
[rel]


trace toluene. This is the spectra of the sample that passed elemental analysis
06052022b 1 1 C:\Data\Fischer
F
F
F
K⊕
CH3
after 120°C heating under vacuum for 24 hours
DMSO-d6
0.7064
11B NMR DMSO-d6
3
[rel]
30
20
10
0
50
0
- 50
[ppm]


06052022b 3 1 C:\Data\Fischer
F
F
F
K⊕
B
N
DMSO-d6
19F {1H} NMR
3
[rel]
20
15
10
5
0
-40
-60
-80
-100
-120
-140
-160
-180
[ppm]


06052022b 3 1 C:\Data\Fischer
-140.3555
-140.4122
-167.8420
-167.8987
-167.9551
F
F
F
K+
B
N
N
N
N
N
N
$^{19}F\{^{1}H\}$ NMR
DMSO-d6
3
[rel]
0
5
10
15
20
- 130
- 140
- 150
- 160
- 170
- 180
[ppm]


06052022b 2 1 C:\Data\Fischer
K⊕
F
F
F
⊖
B
N
N
N
N
N
N
in Dmso-d6
^{1}H NMR
(3)
Dmso
[rel]
15
10
5
0
15
10
5
0
[ppm]

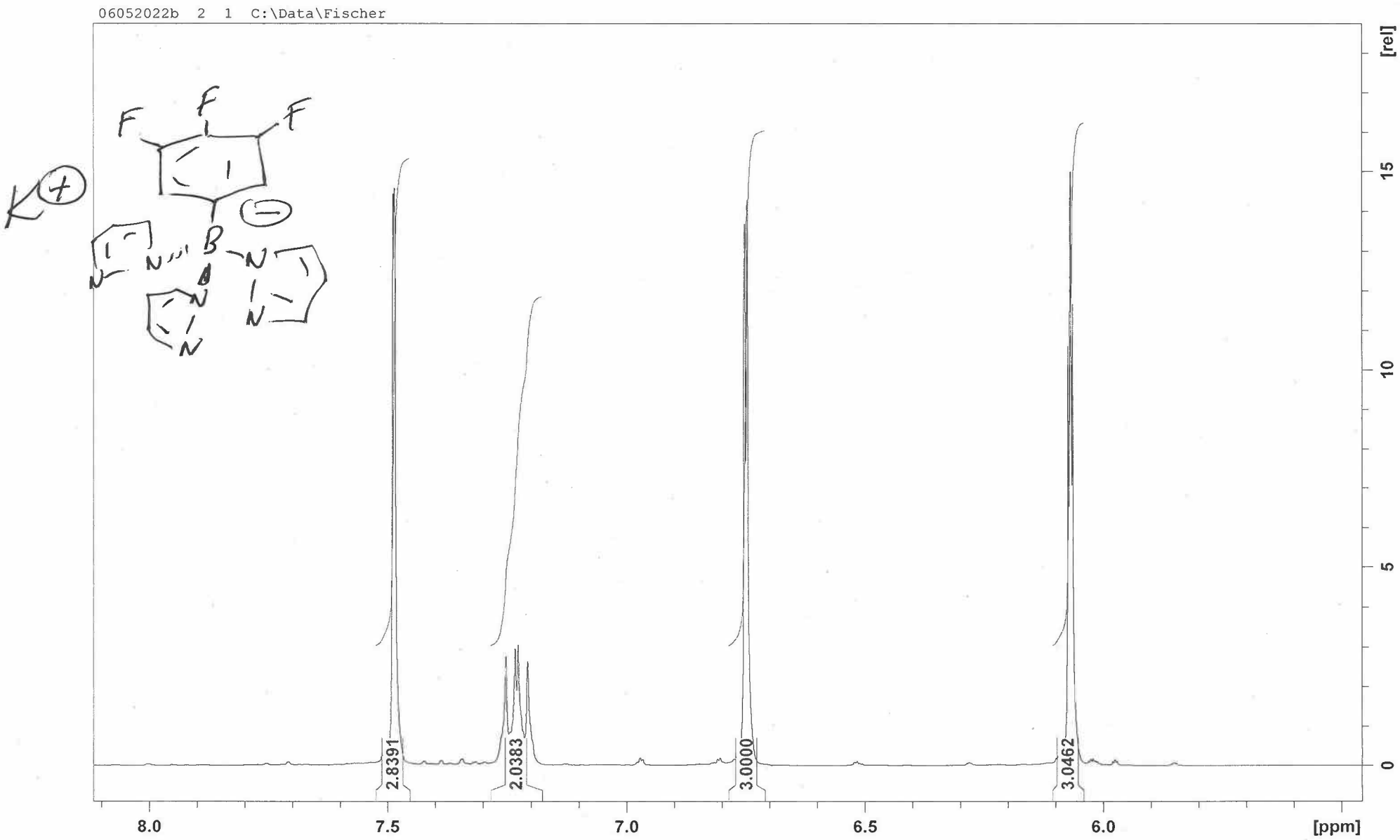


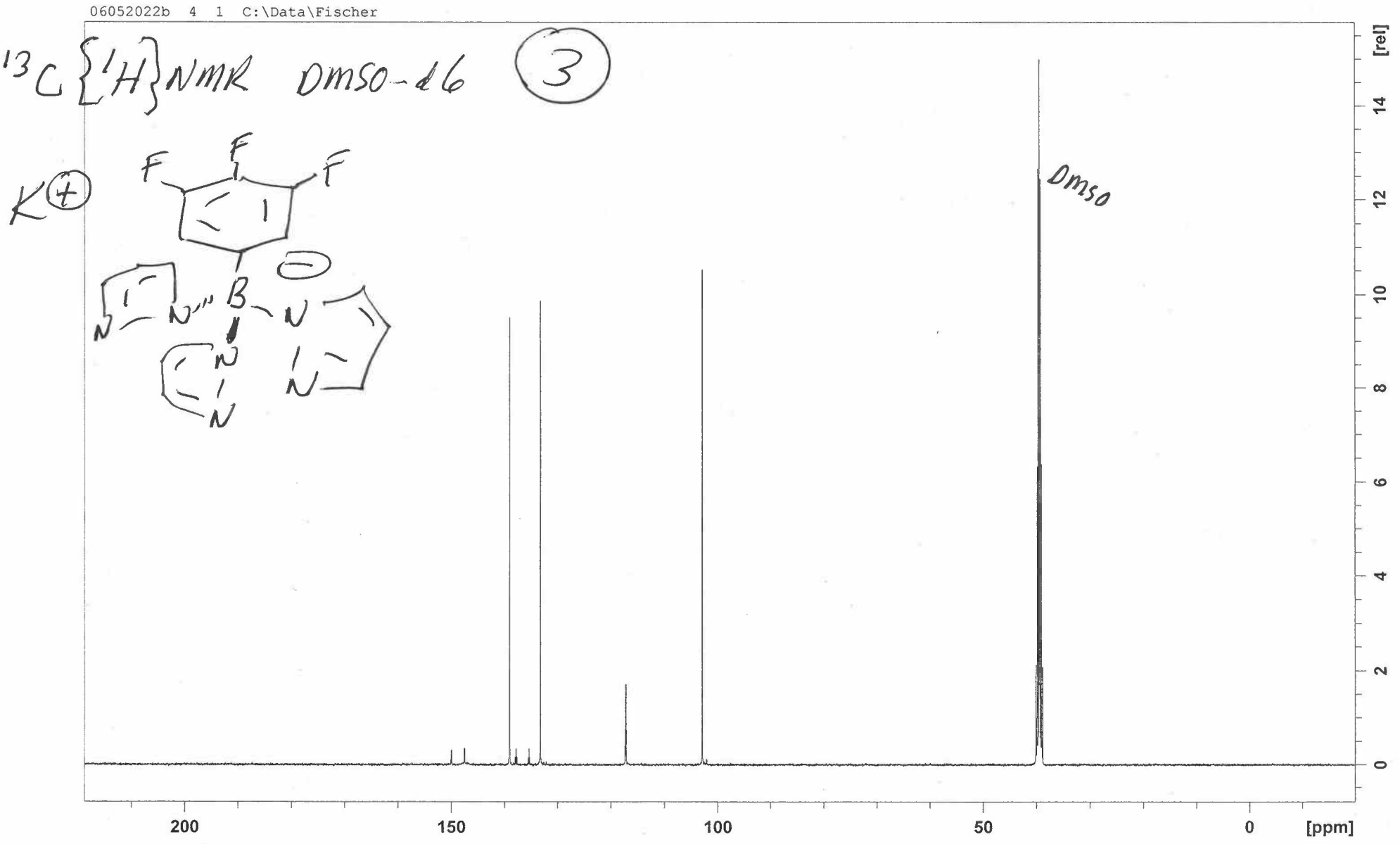
^1H NMR

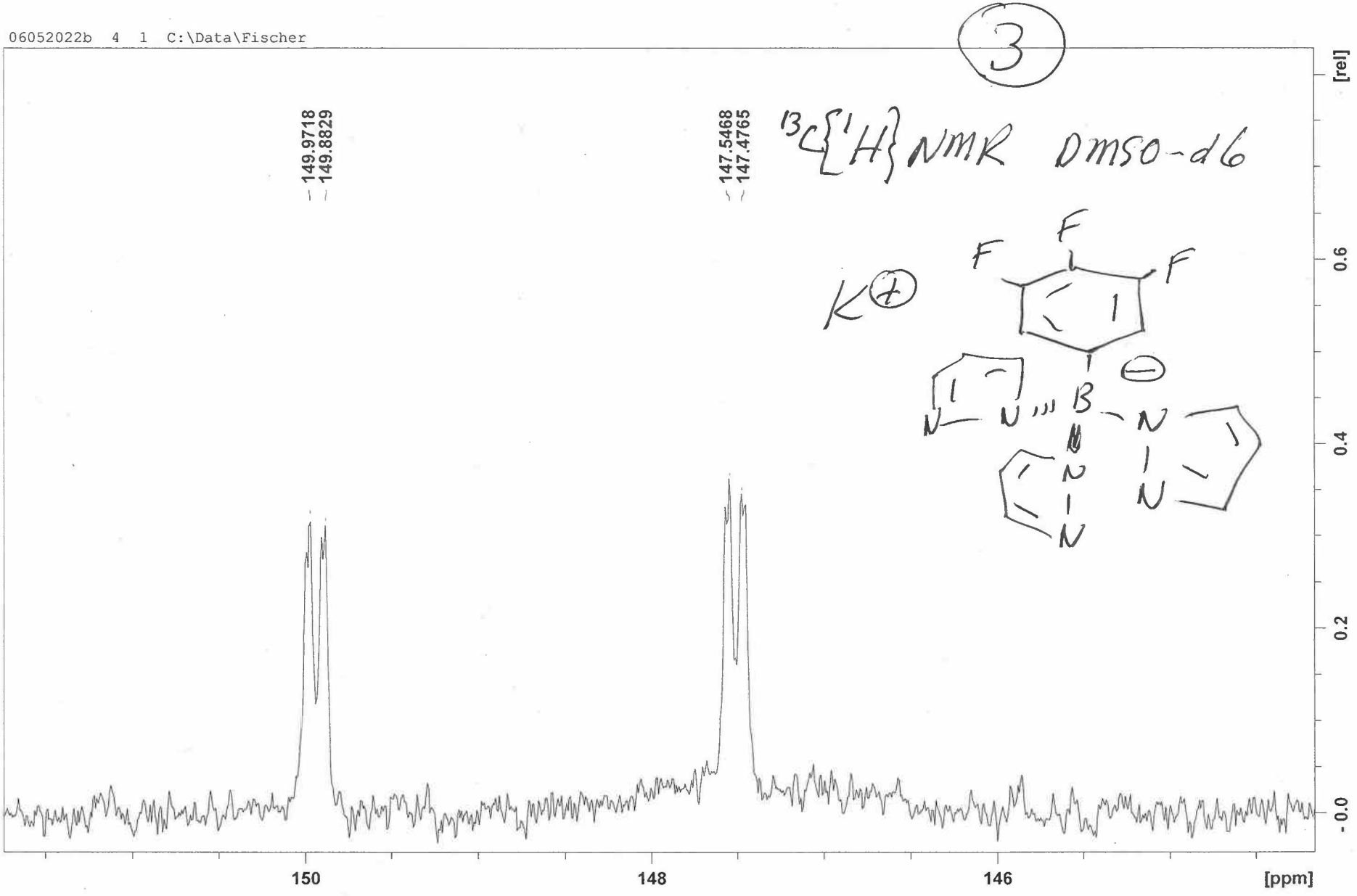
DMSO-d6

3

^1H ^{19}F NMR DMSO-d6 (3)



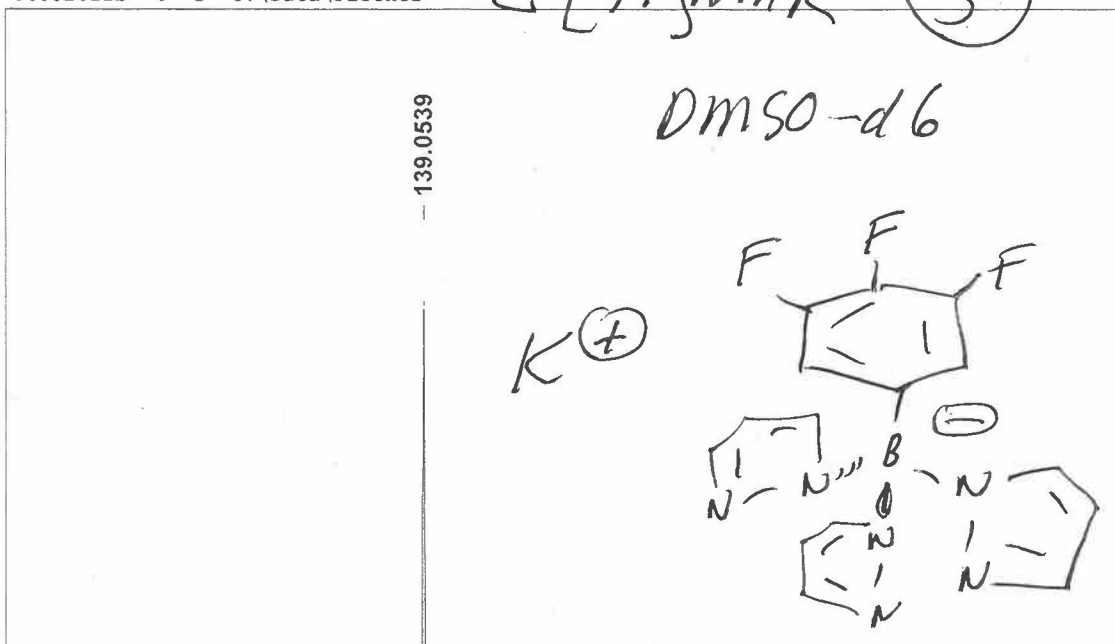

06052022b 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR DMSO-d6
3
K+
DMSO
200
150
100
50
0
[ppm]
[rel]

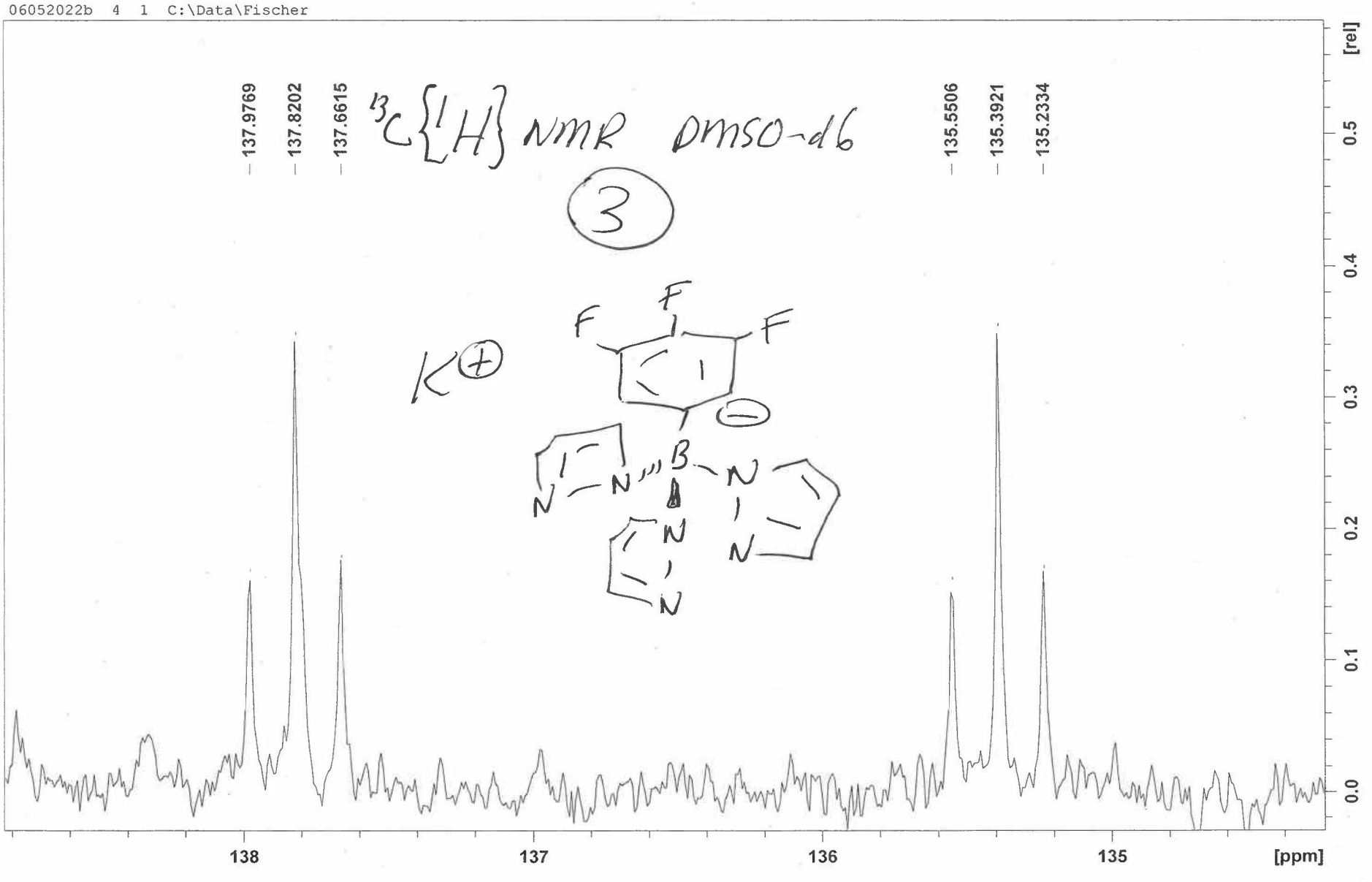

06052022b 4 1 C:\Data\Fischer
3
149.9718
149.8829
147.5468
147.4765
$^{13}C\{^{1}H\}$ NMR DMSO-d6
K⊕
F
F
F
⊖
B
N
N
N
N
N
N
N
[rel]
0.6
0.4
0.2
-0.0
150
148
146
[ppm]

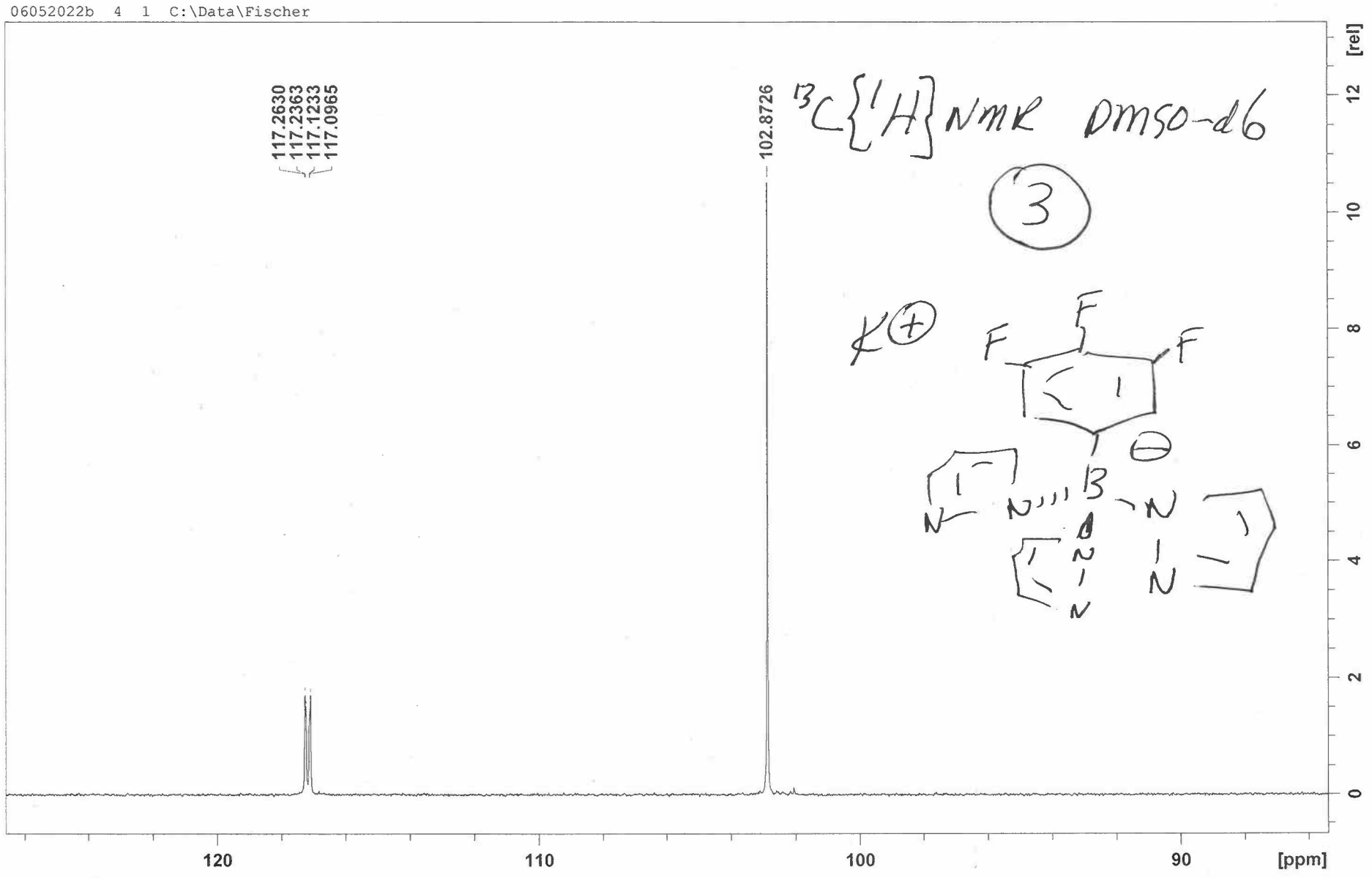
06052022b 4 1 C:\Data\Fischer

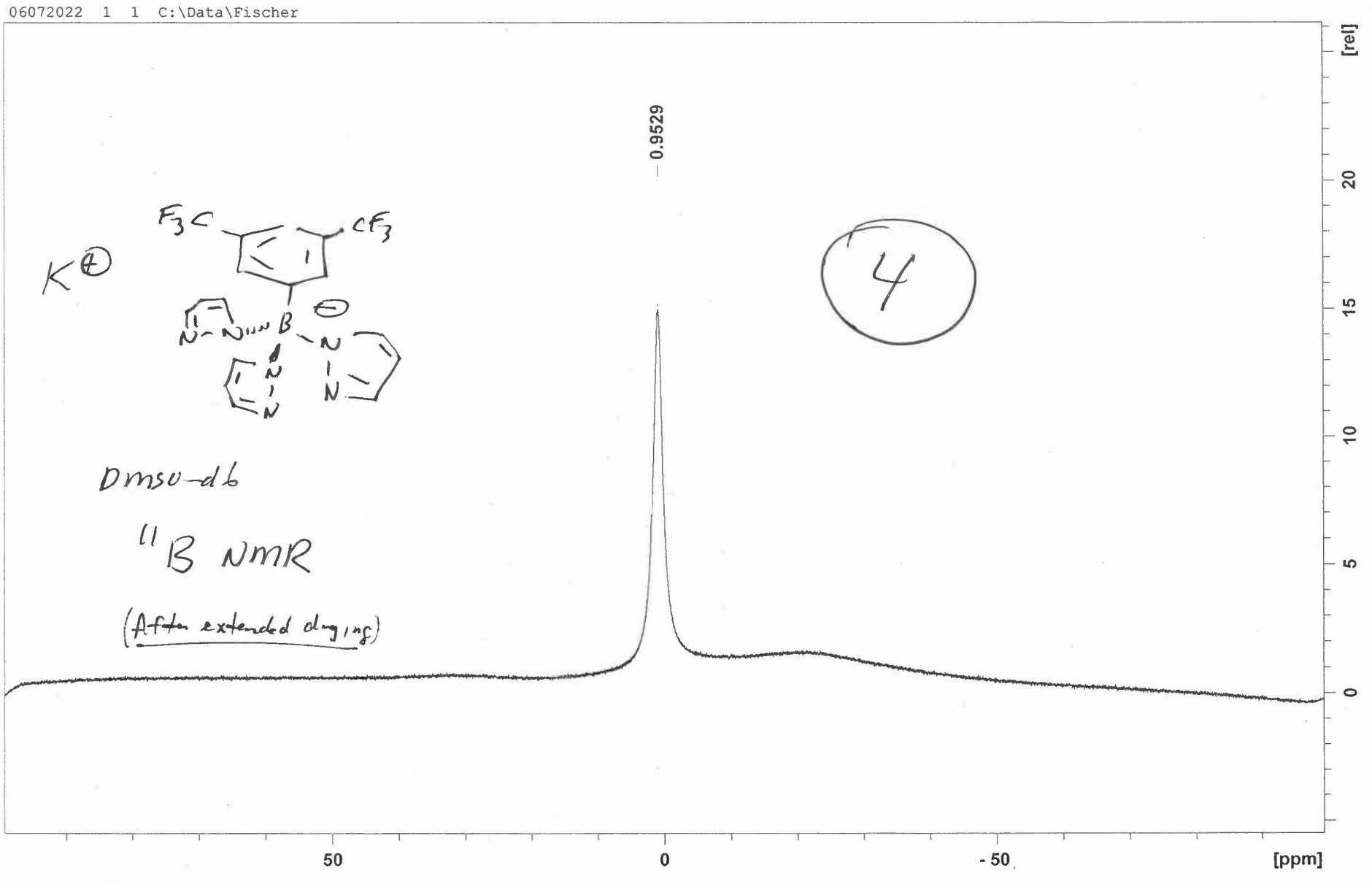
$^{13}C\{^1H\}$ NMR (3)

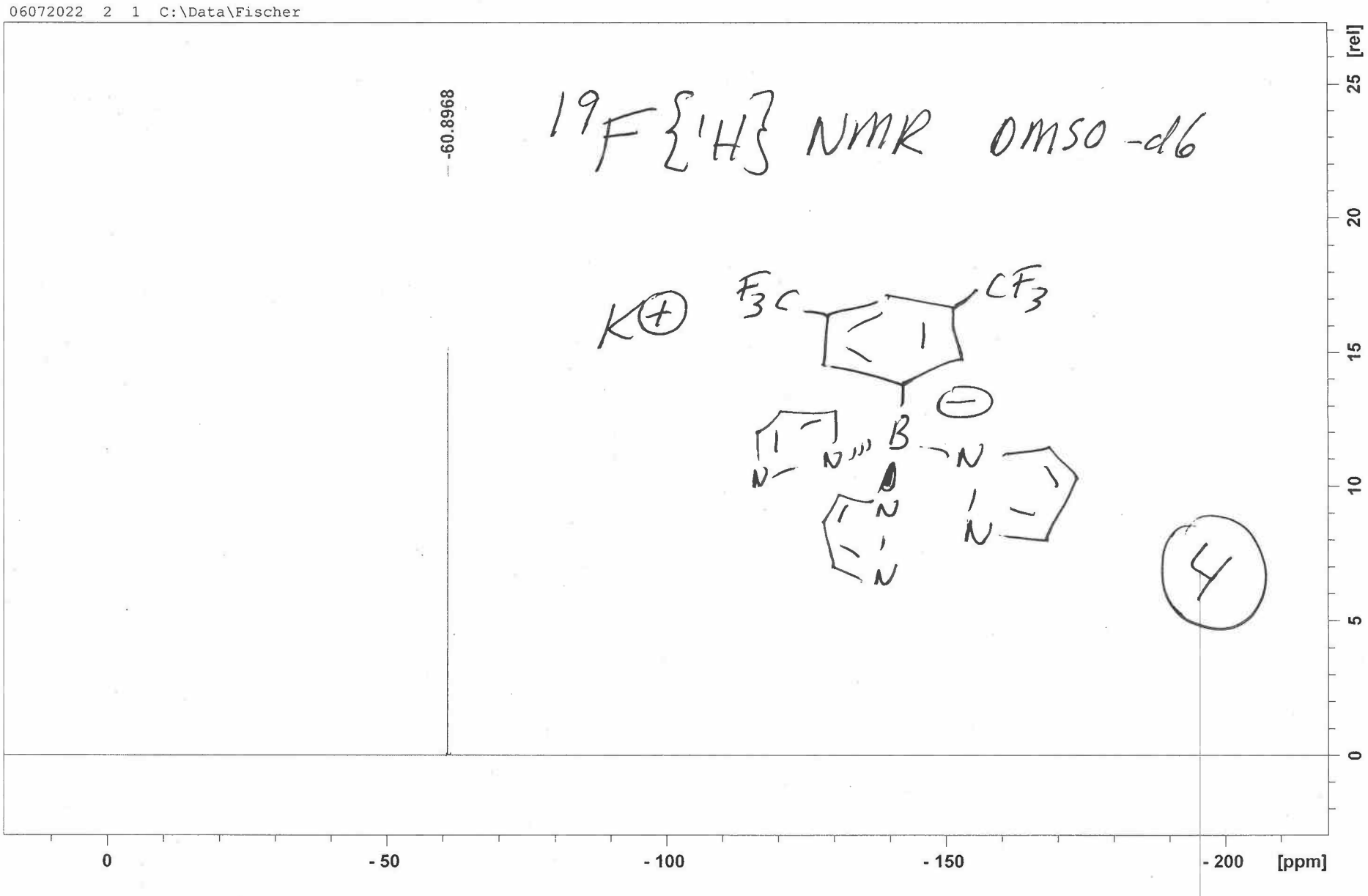
DMSO-d6

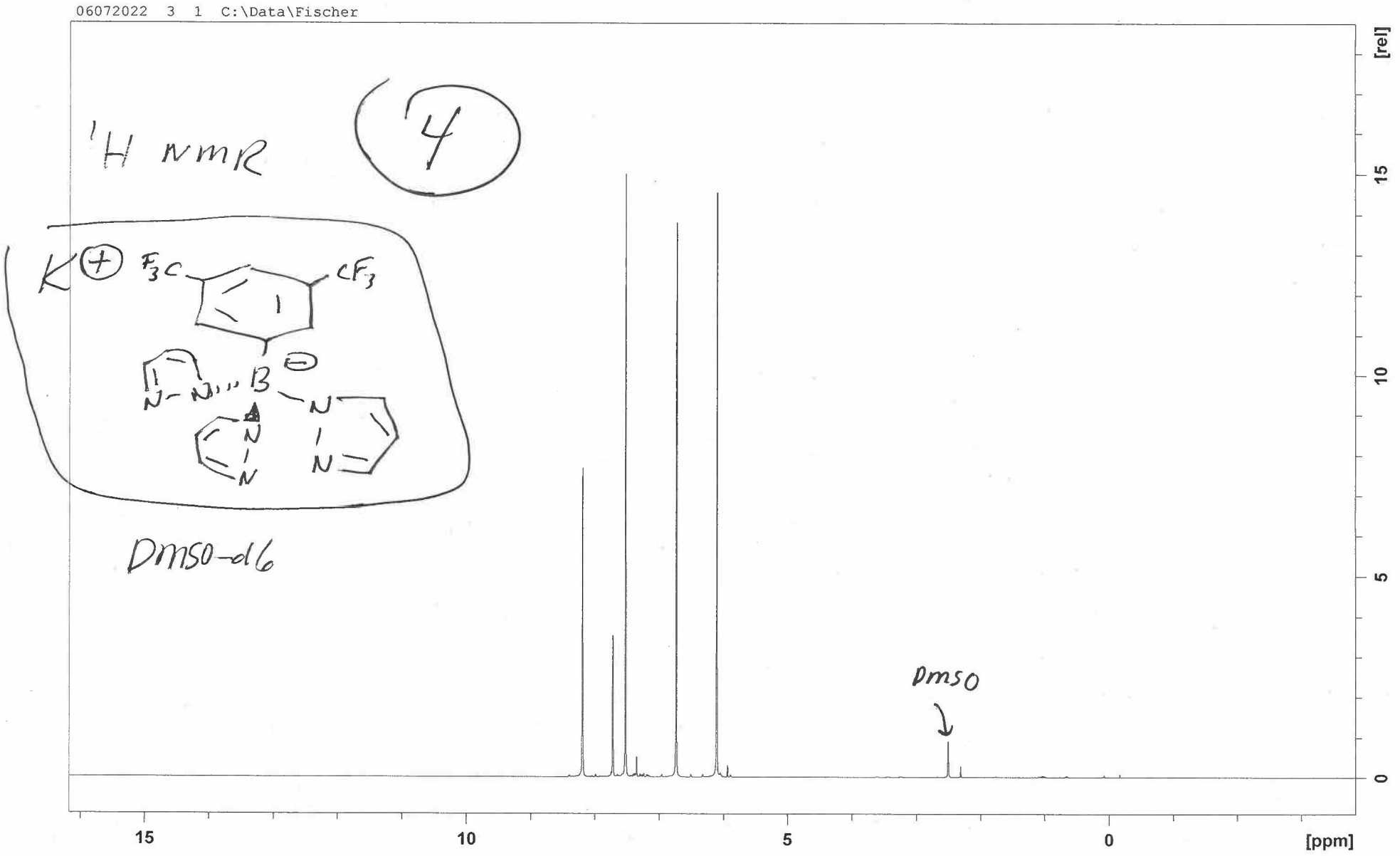


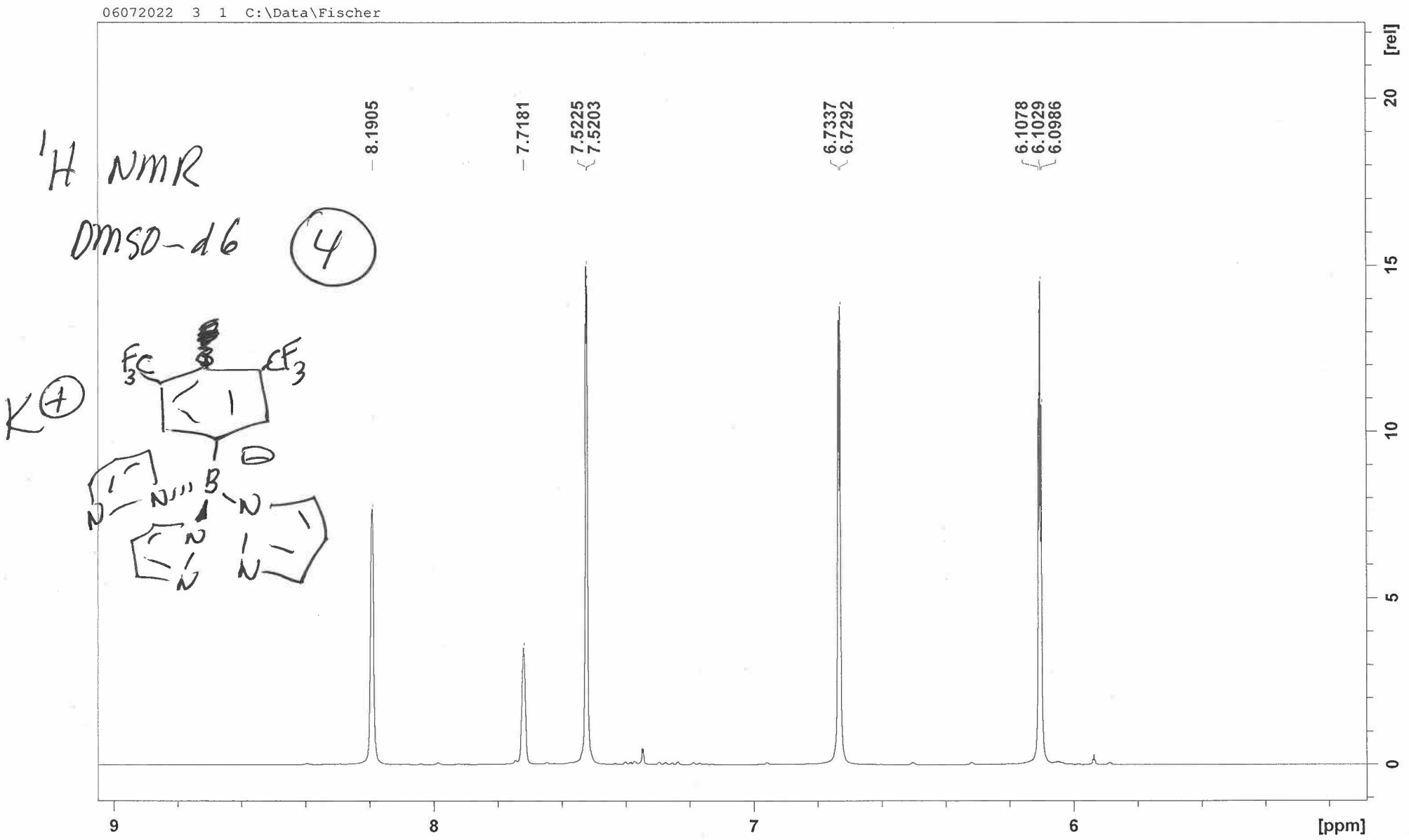

06052022b 4 1 C:\Data\Fischer
137.9769
137.8202
137.6615
135.5506
135.3921
135.2334
$^{13}C\{^{1}H\}$ NMR DMSO-d6
3
K⊕
F
F
F
1
⊖
B
N
N
N
N
N
N
N
0.5
0.4
0.3
0.2
0.1
0.0
[rel]
138
137
136
135
[ppm]

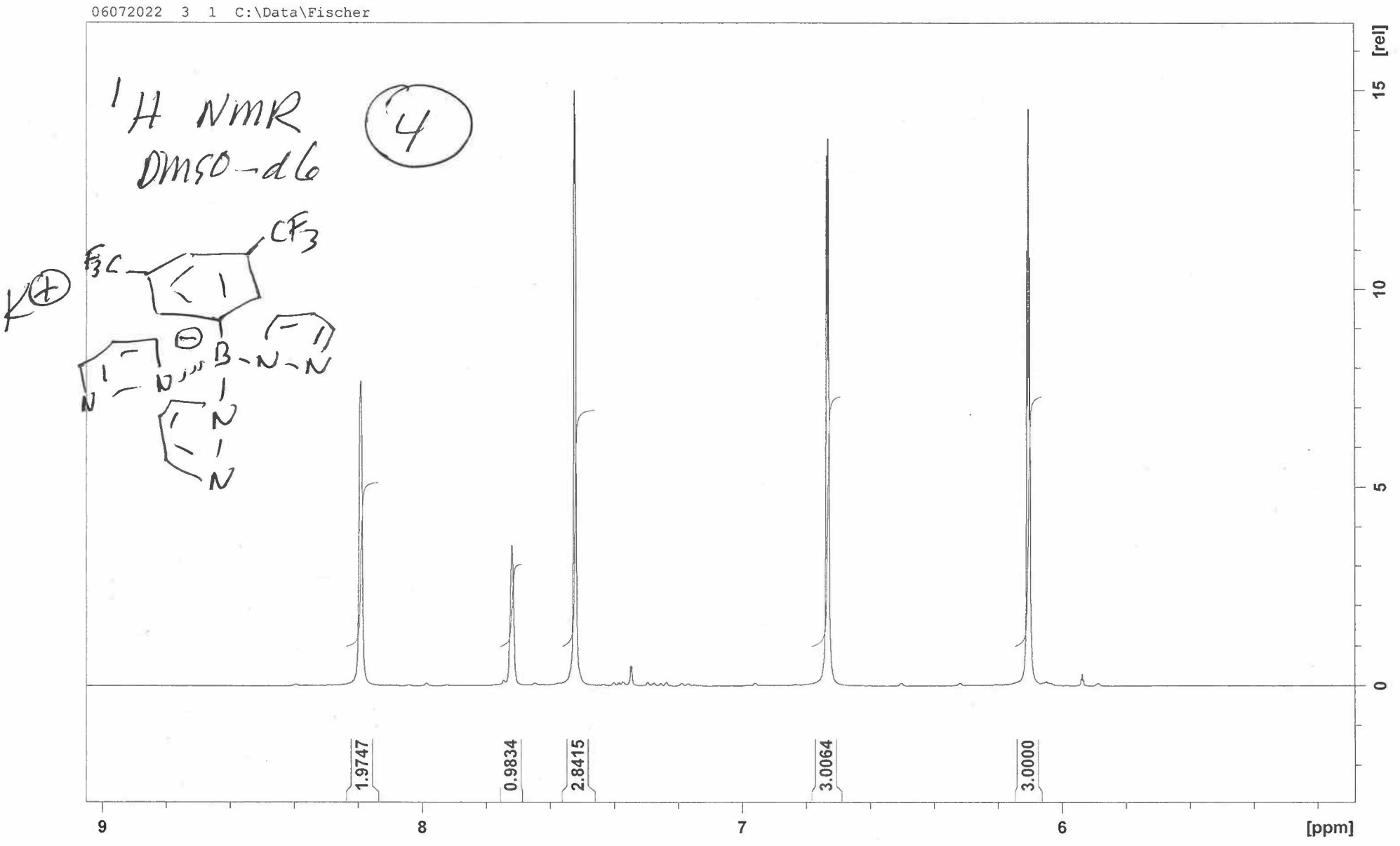

06052022b 4 1 C:\Data\Fischer
117.2630
117.2363
117.1233
117.0965
102.8726
$^{13}C\{^{1}H\}$ NMR DMSO-d6
3
K⊕
F
F
F
⊖
B
N
N
N
N
N
N
120
110
100
90
[ppm]
0
2
4
6
8
10
12
[rel]

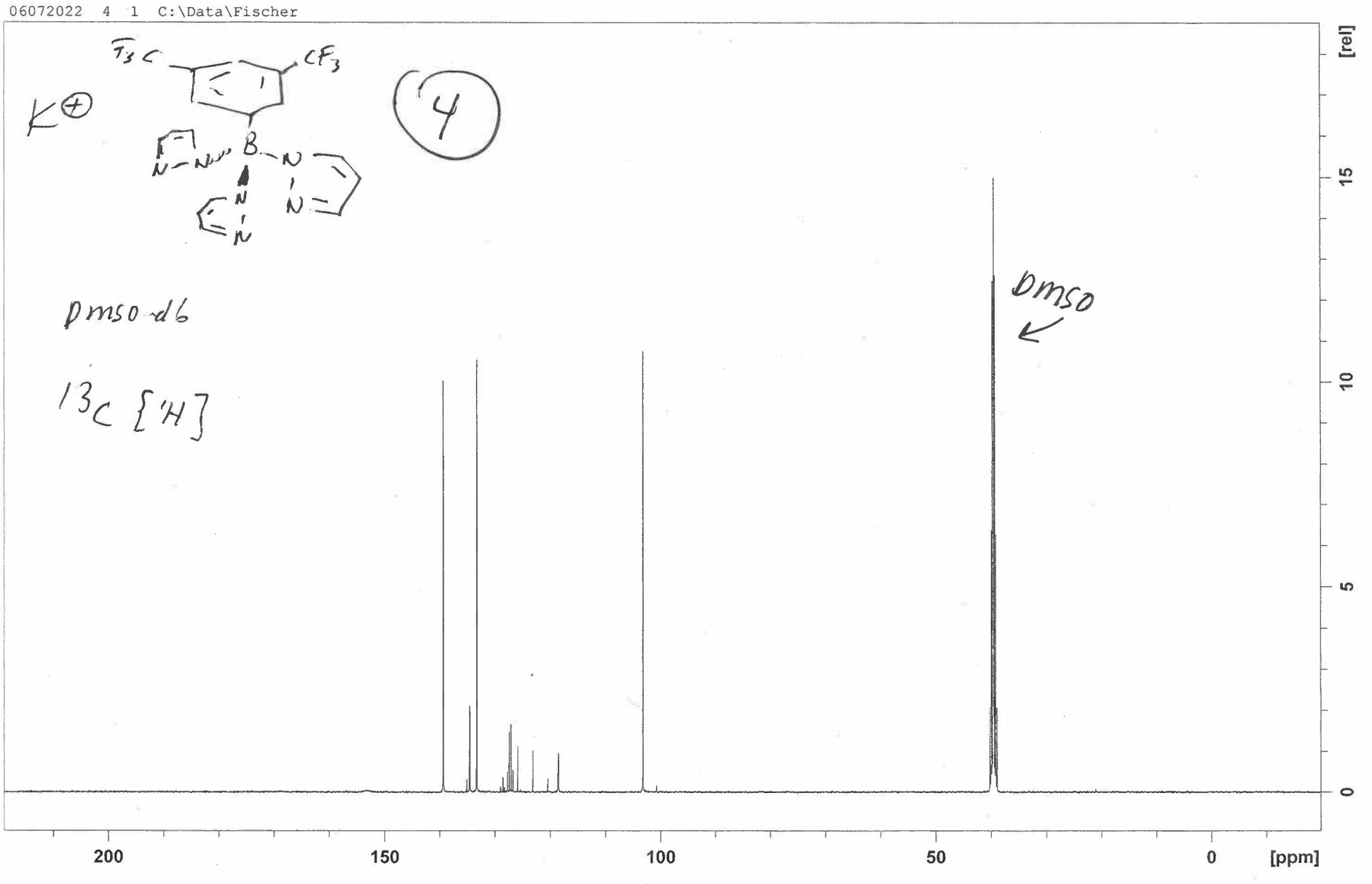

06072022 1 1 C:\Data\Fischer
0.9529
[rel]
20
15
10
5
0
50
0
- 50
[ppm]
F_3C
CF_3
$K^{\oplus}$
4
Dmso-d6
^{11}B NMR
(After extended dwelling)

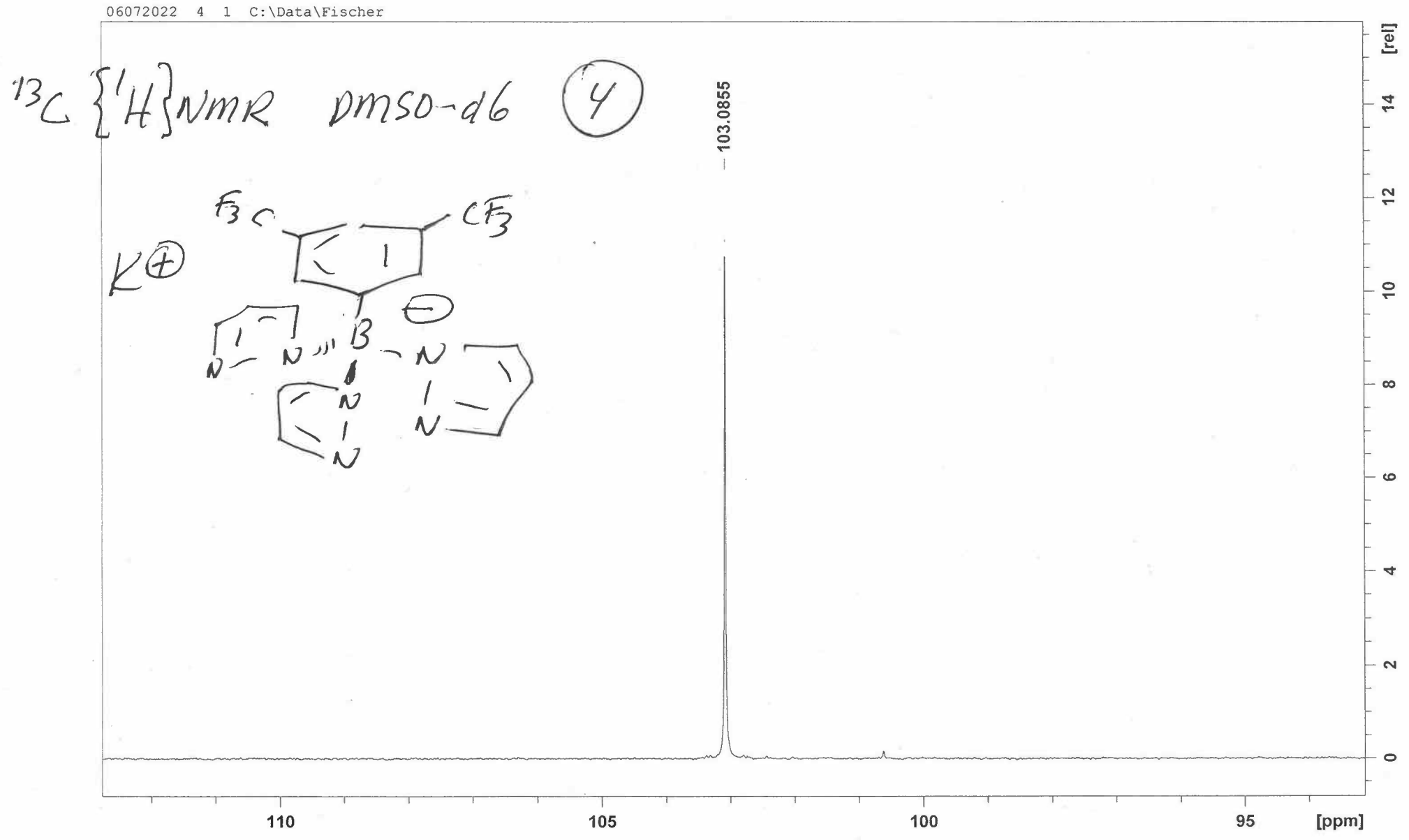

06072022 2 1 C:\Data\Fischer
-60.8968
19F{1H} NMR DMSO-d6
K+
F3C
CF3
B
N
4
25 [rel]
20
15
10
5
0
0
- 50
- 100
- 150
- 200
[ppm]

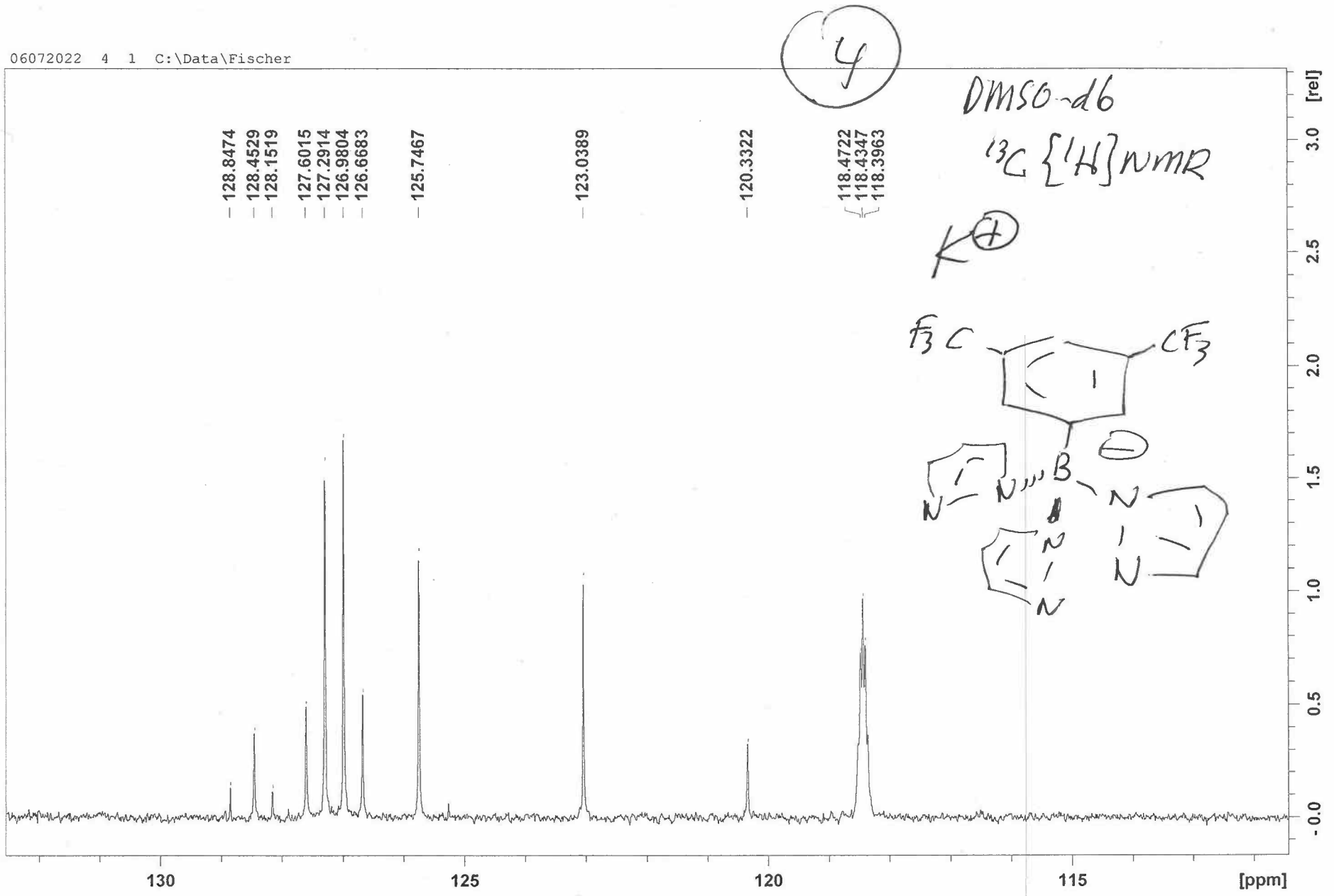

06072022 3 1 C:\Data\Fischer
^{1}H NMR
4
K
F3C
CF3
B
N
DMSO-d6
DMSO
[rel]
0
5
10
15
[ppm]
15
10
5
0

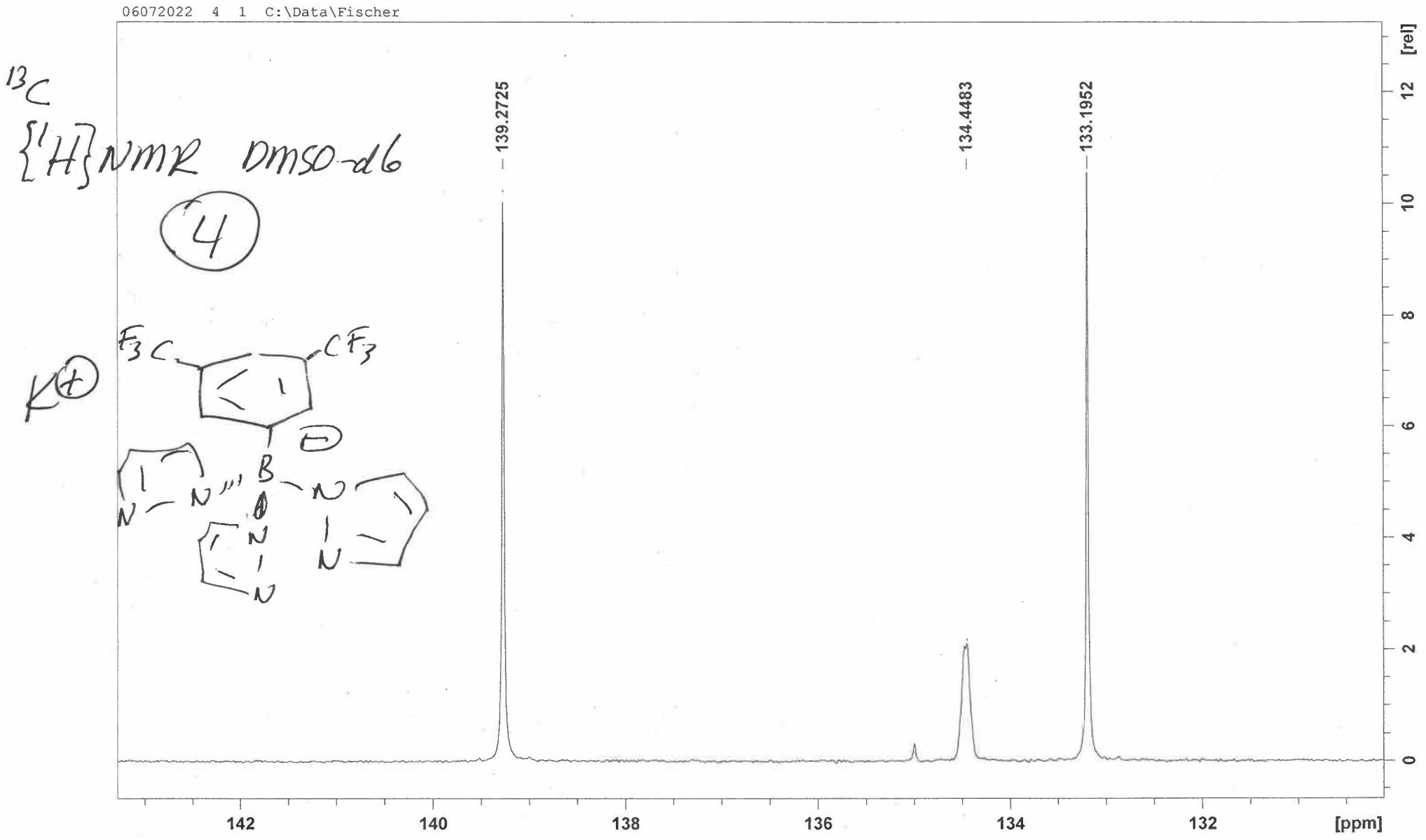

06072022 3 1 C:\Data\Fischer
8.1905
7.7181
7.5225
7.5203
6.7337
6.7292
6.1078
6.1029
6.0986
[rel]
[ppm]
9
8
7
6
0
5
10
15
20
^1H NMR
DMSO-d6
(4)
K(+)
F3C
CF3
B
N


06072022 3 1 C:\Data\Fischer
^1H NMR
DMSO-d6
4
K
CF3
F3C
B
N
1.9747
0.9834
2.8415
3.0064
3.0000
9
8
7
6
[ppm]
15
10
5
0
[rel]


06072022 4 1 C:\Data\Fischer
F3C
CF3
K⊕
4
dmso-d6
13C {1H}
dmso
[rel]
15
10
5
0
200
150
100
50
0
[ppm]

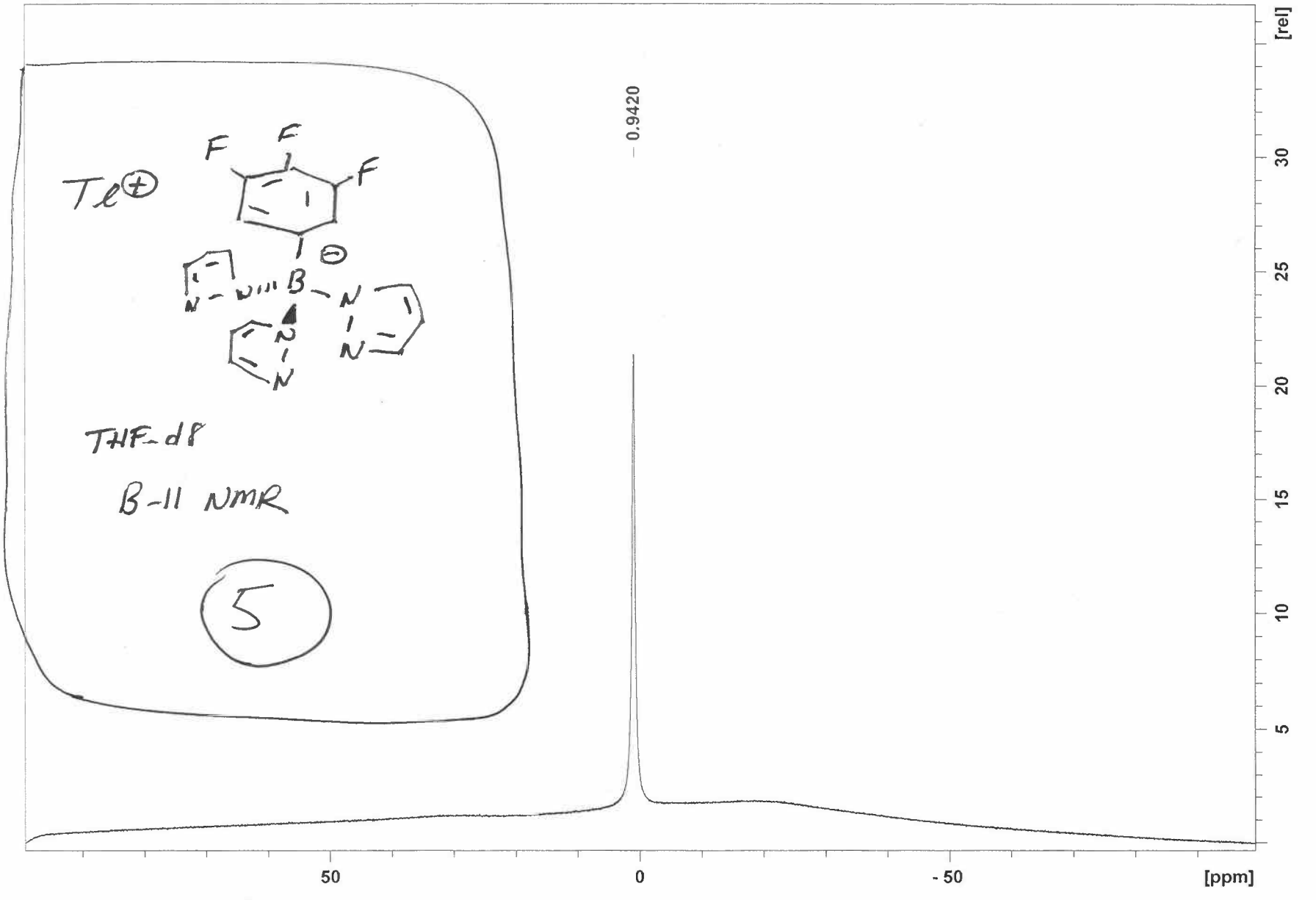

06072022 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$NMR DMSO-d6
4
103.0855
[rel]
[ppm]
110
105
100
95
0
2
4
6
8
10
12
14


06072022 4 1 C:\Data\Fischer
4
DMSO-d6
$^{13}C\{^{1}H\}$ NMR
128.8474
128.4529
128.1519
127.6015
127.2914
126.9804
126.6683
125.7467
123.0389
120.3322
118.4722
118.4347
118.3963
F_3C
CF_3
B
N
[rel]
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
130
125
120
115
[ppm]

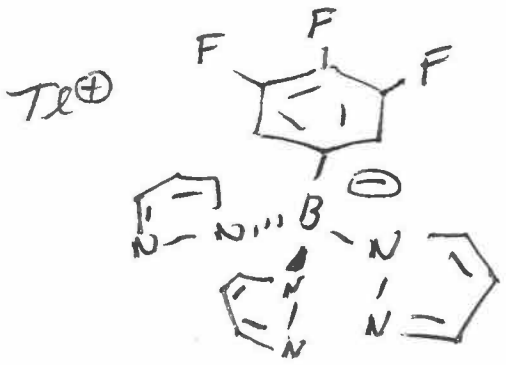

06072022 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR DMSO-d6
4
K⊕
F3C
CF3
⊖
B
N
139.2725
134.4483
133.1952
142
140
138
136
134
132
[ppm]
0
2
4
6
8
10
12
[rel]

Charly's

07152022a 1 1 C:\Data\Fischer



07152022a 3 1 C:\Data\Fischer



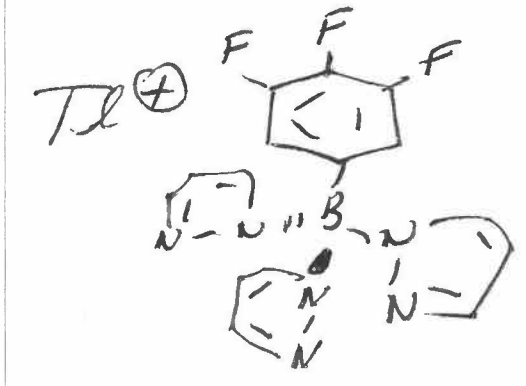
^{19}F NMR

THF-d8

$^{19}F\{^{1}H\}$

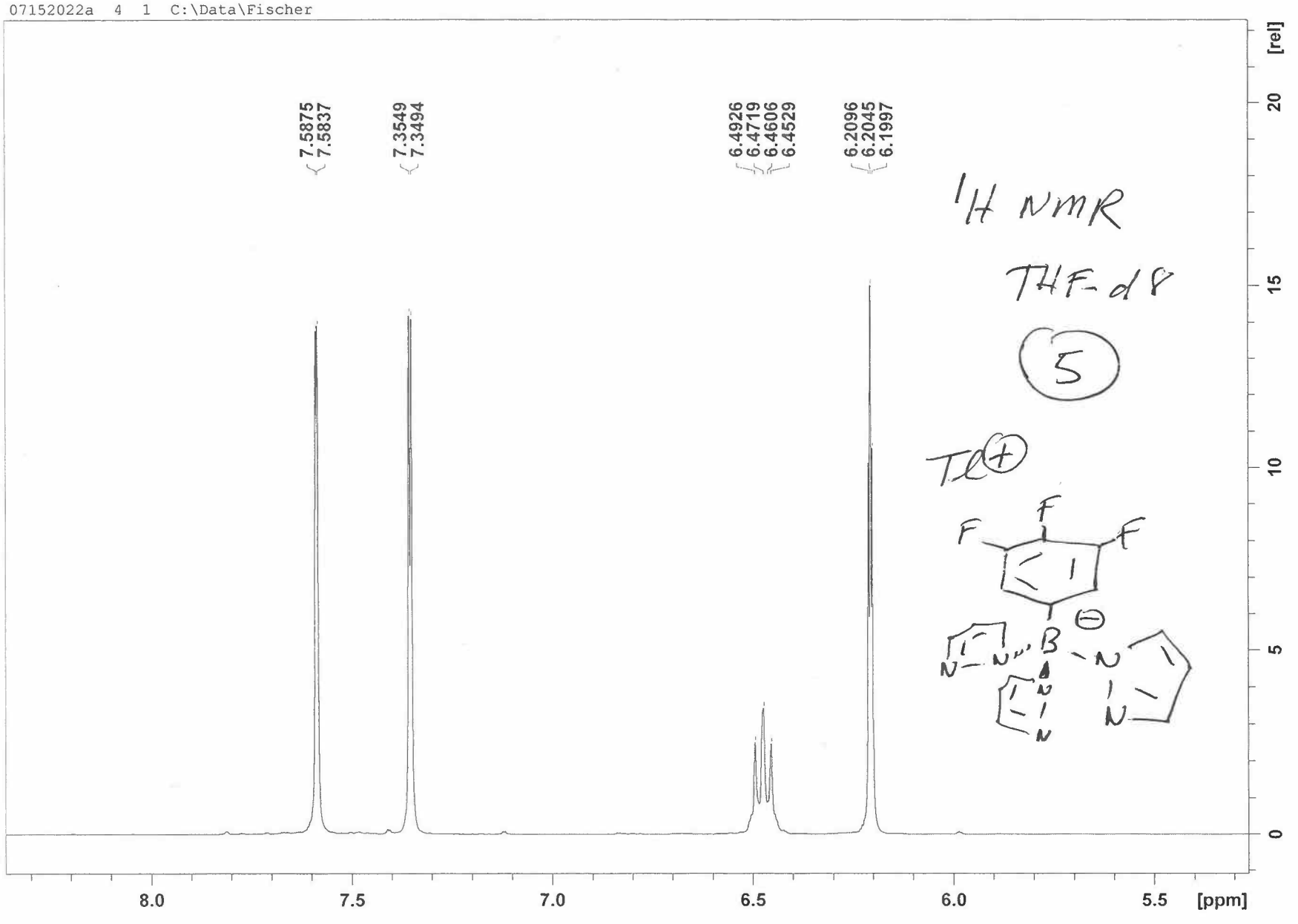
5

07152022a 4 1 C:\Data\Fischer

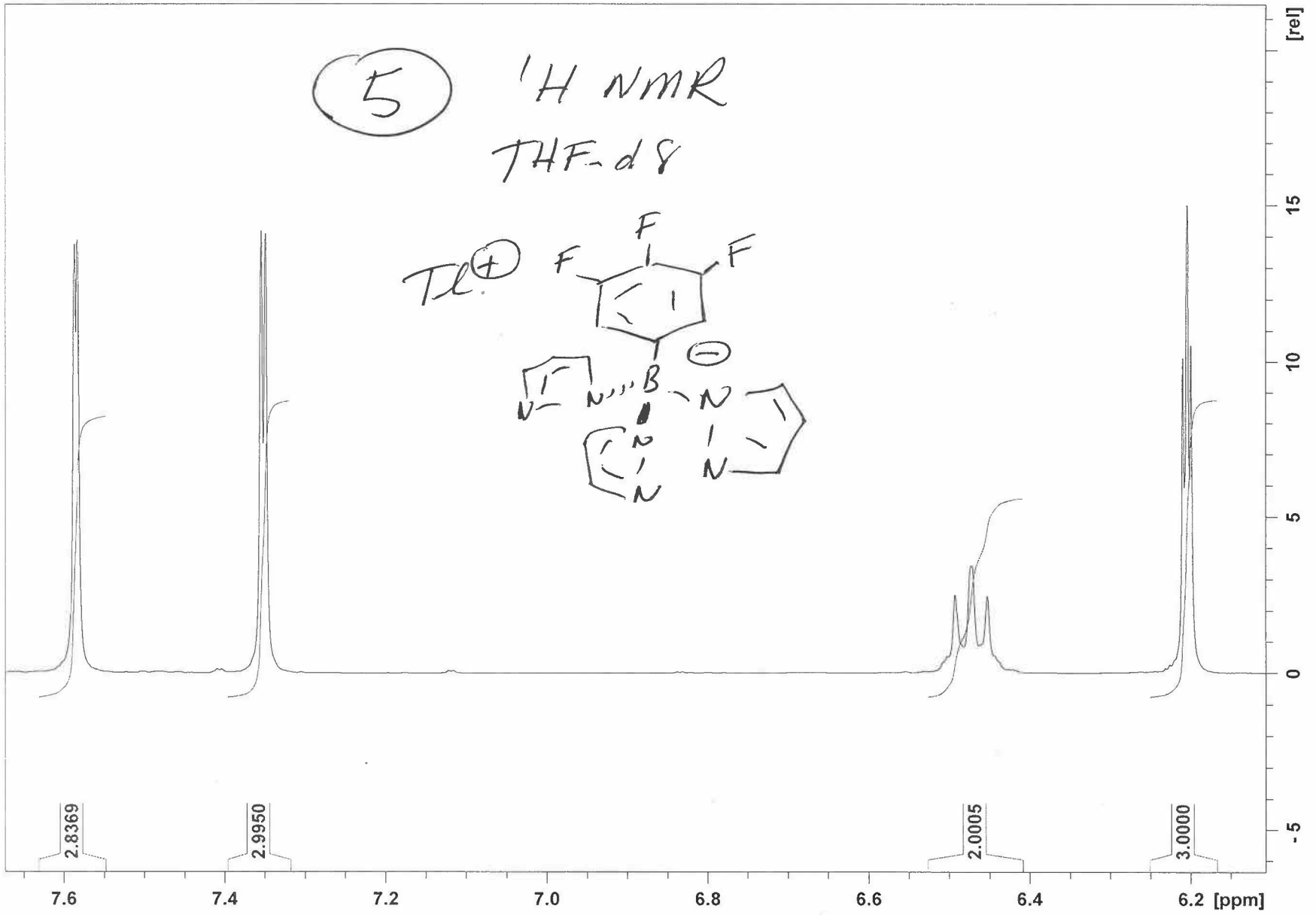


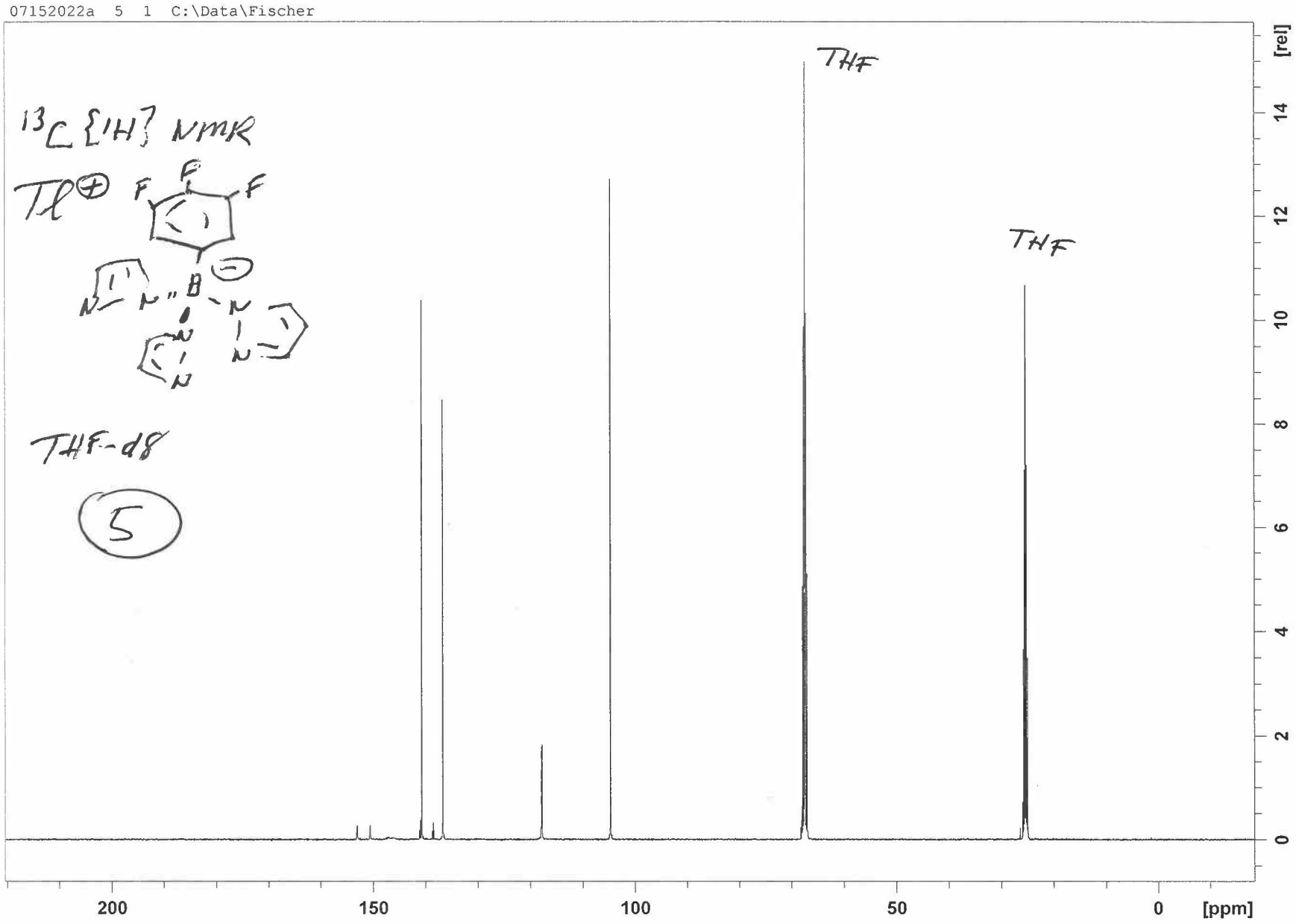
^1H NMR
THF

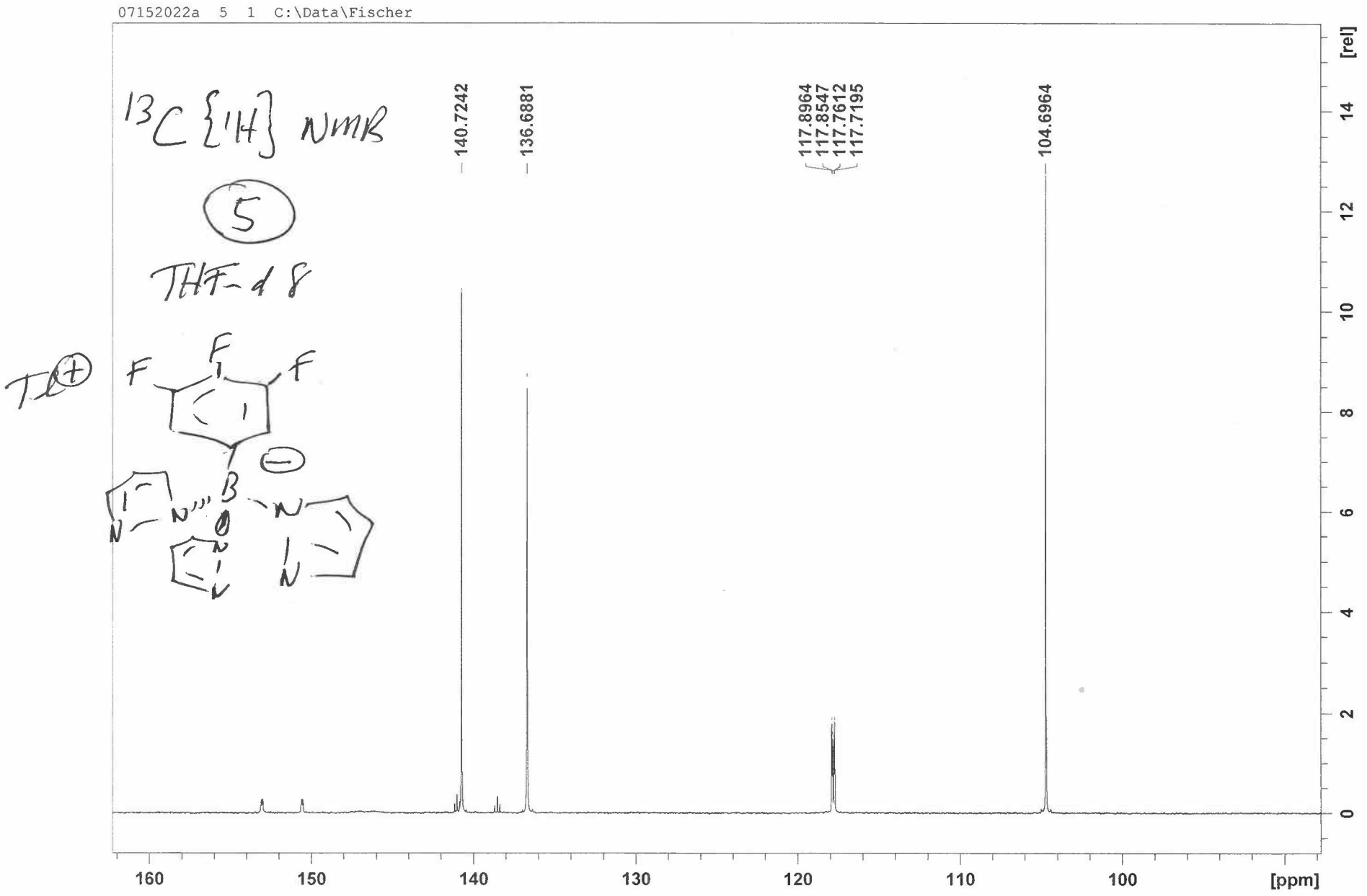
(5)


07152022a 4 1 C:\Data\Fischer
7.5875
7.5837
7.3549
7.3494
6.4926
6.4719
6.4606
6.4529
6.2096
6.2045
6.1997
1H NMR
THF-d8
5
Tl⊕
F
F
F
B
⊖
N
N
N
N
N
N
8.0
7.5
7.0
6.5
6.0
5.5
[ppm]
0
5
10
15
20
[rel]

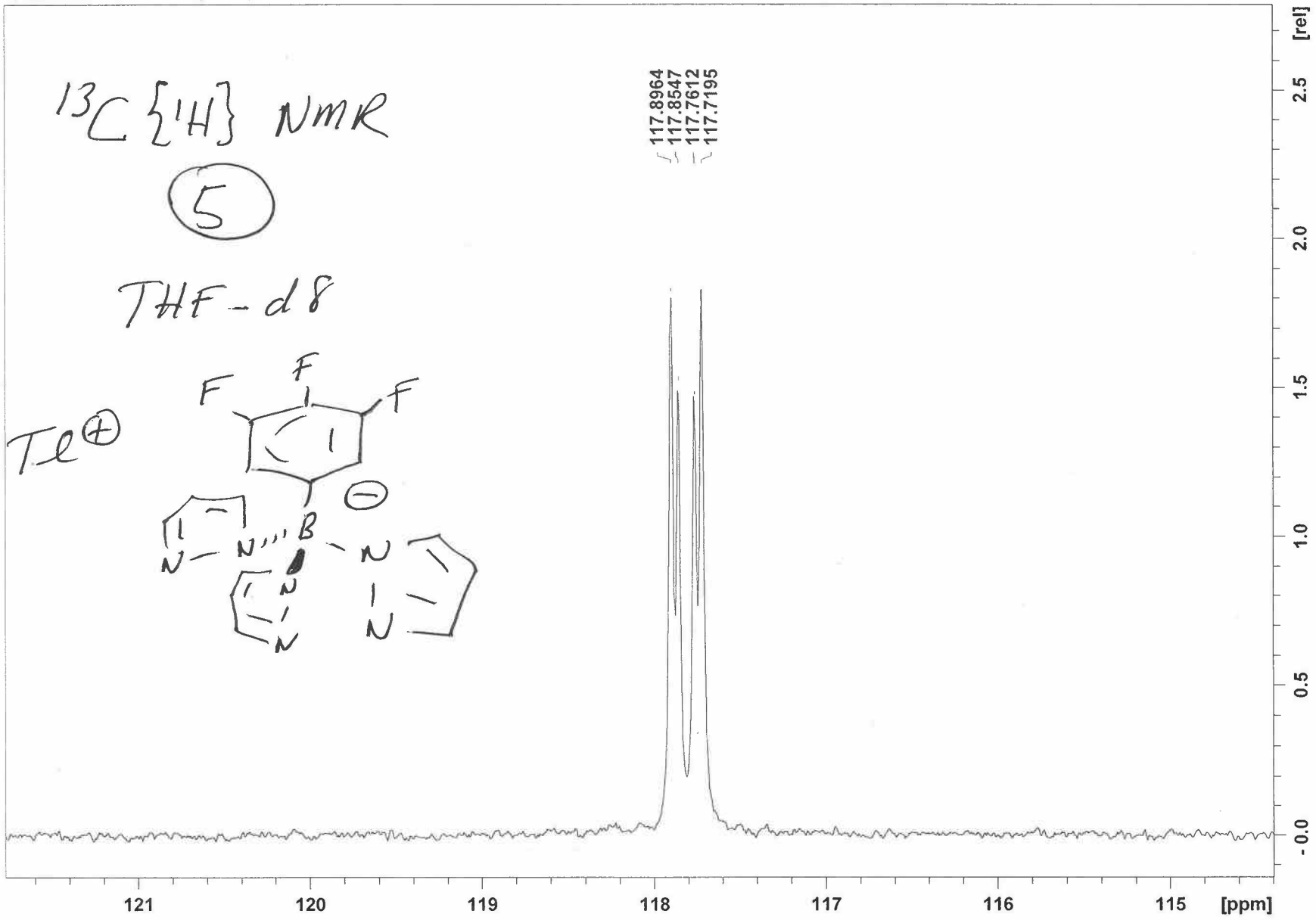
07152022a 4 1 C:\Data\Fischer

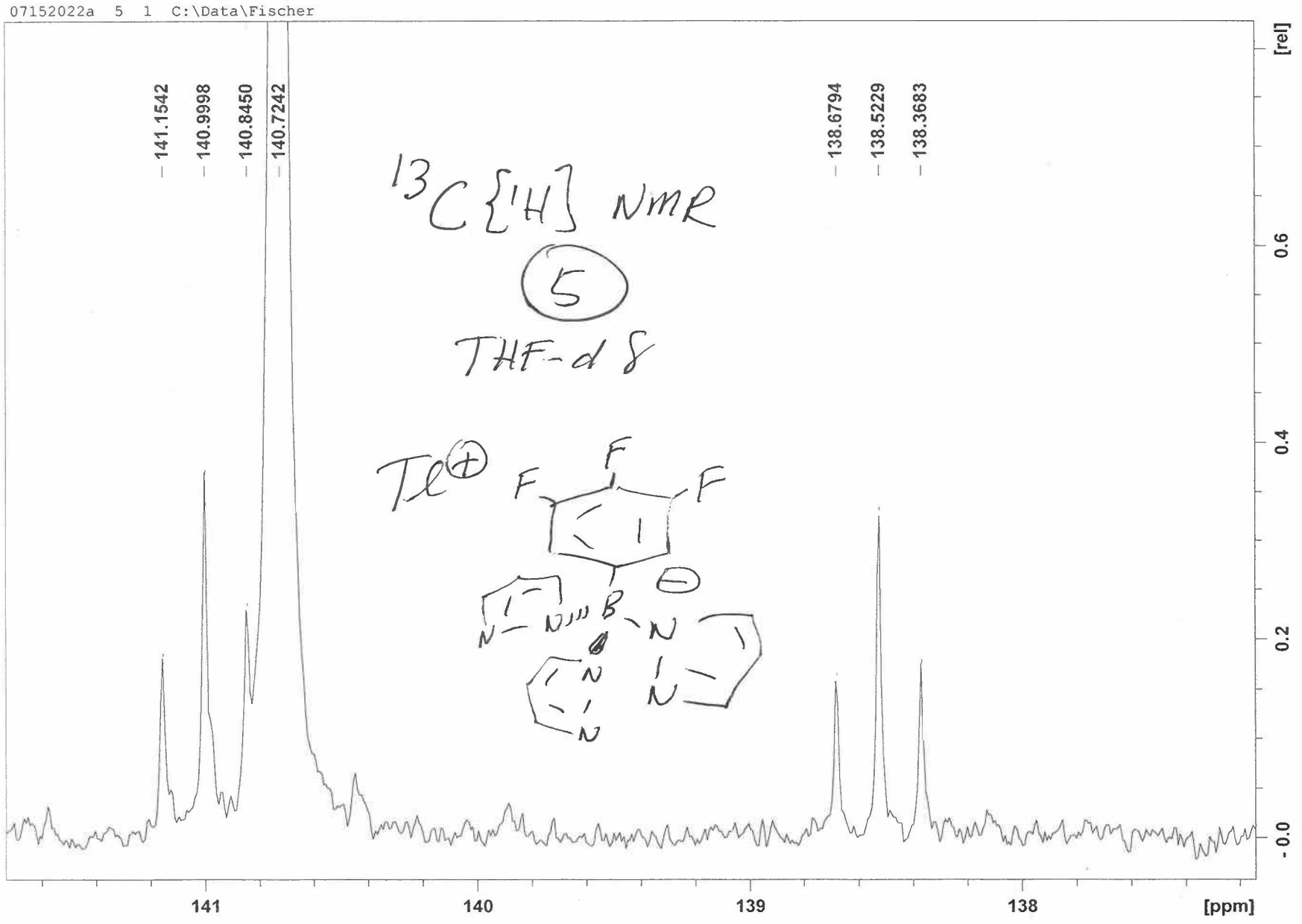


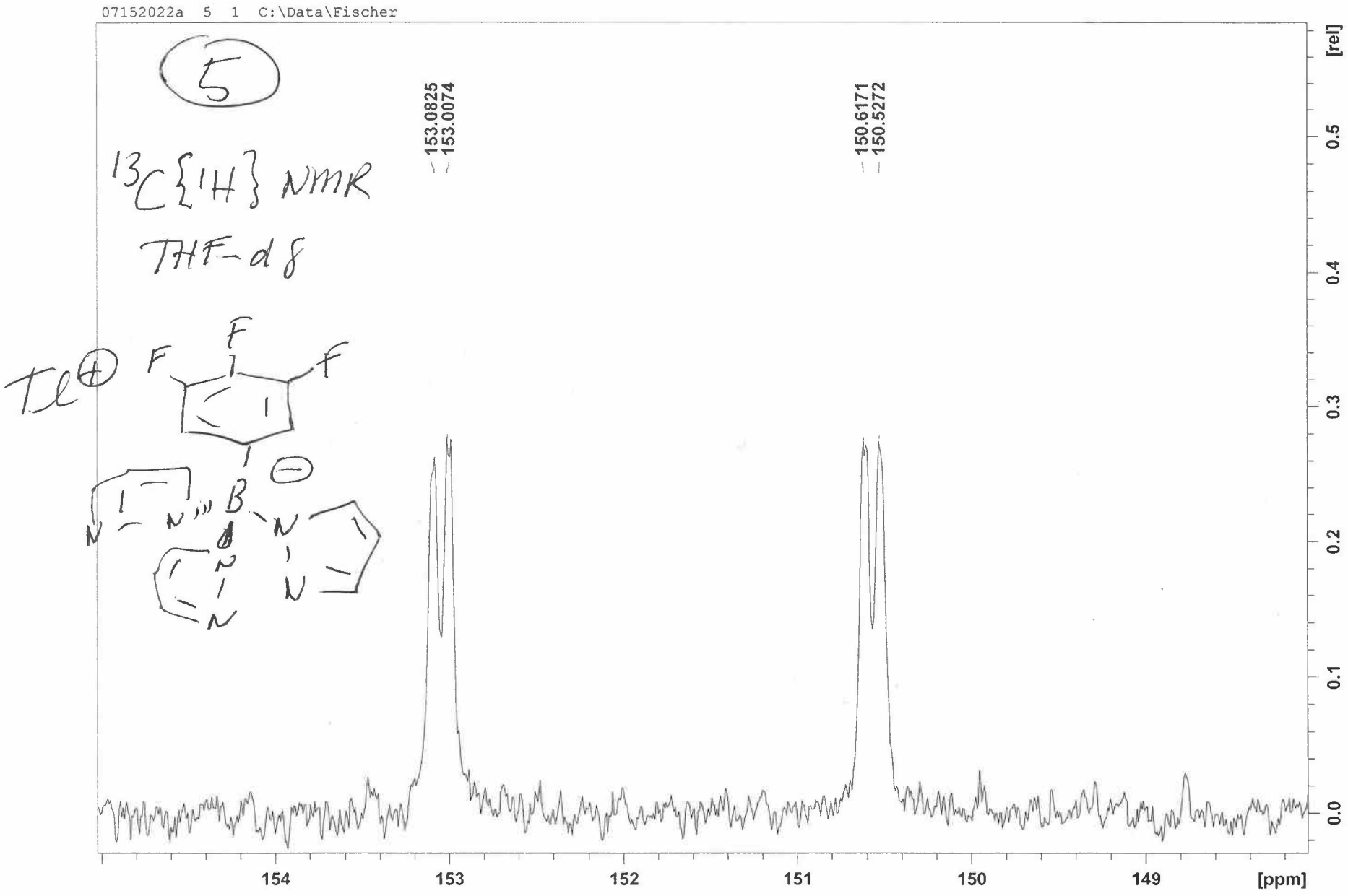

07152022a 5 1 C:\Data\Fischer
13C {1H} NMR
Tl⊕
THF-d8
5
THF
THF
[rel]
0
2
4
6
8
10
12
14
200
150
100
50
0
[ppm]

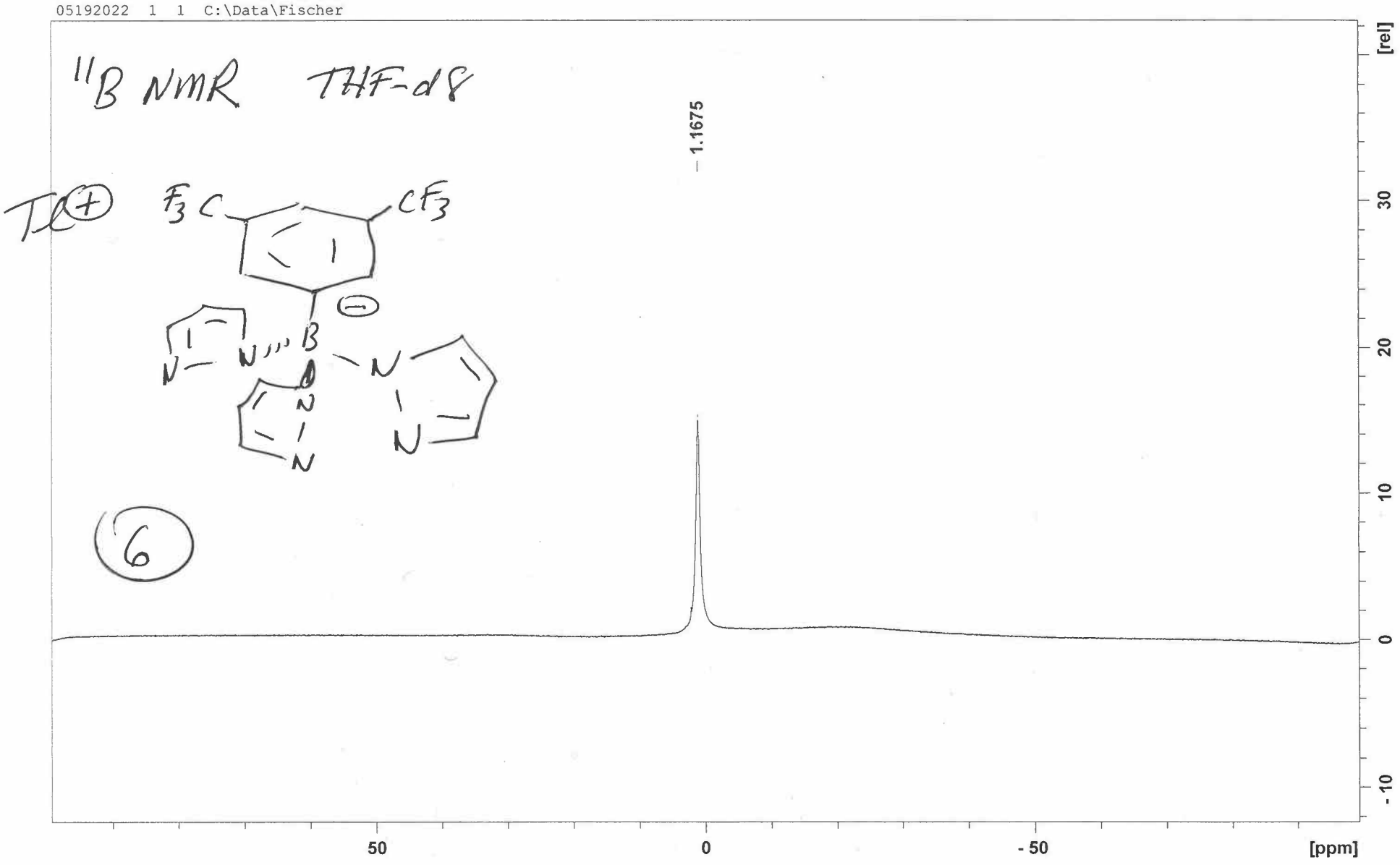

07152022a 5 1 C:\Data\Fischer
13C {1H} NMR
5
THF-d8
Tl+
F
F
F
B
N
N
N
N
N
140.7242
136.6881
117.8964
117.8547
117.7612
117.7195
104.6964
160
150
140
130
120
110
100
[ppm]
0
2
4
6
8
10
12
14
[rel]

07152022a 5 1 C:\Data\Fischer




07152022a 5 1 C:\Data\Fischer
141.1542
140.9998
140.8450
140.7242
138.6794
138.5229
138.3683
13C{1H} NMR
5
THF-d 8
Tl⊕
F
F
F
⊖
B
N
141
140
139
138
[ppm]
[rel]
0.6
0.4
0.2
-0.0


07152022a 5 1 C:\Data\Fischer
5
$^{13}C\{^{1}H\}$ NMR
THF-d8
Tl⊕
153.0825
153.0074
150.6171
150.5272
[rel]
0.5
0.4
0.3
0.2
0.1
0.0
154
153
152
151
150
149
[ppm]

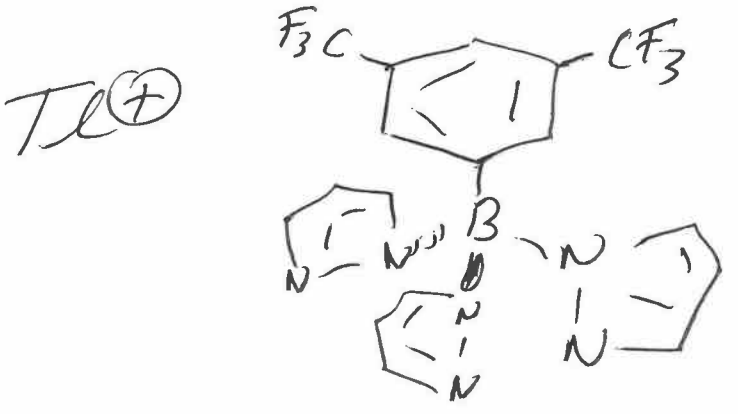

05192022 1 1 C:\Data\Fischer
^{11}B NMR THF-d8
Tl⊕
F_3C
CF_3
⊖
B
N
6
1.1675
[rel]
30
20
10
0
-10
50
0
- 50
[ppm]

07122022 2 1 C:\Data\Fischer

6

$^{19}F\{^{1}H\}$ NMR THF-d8

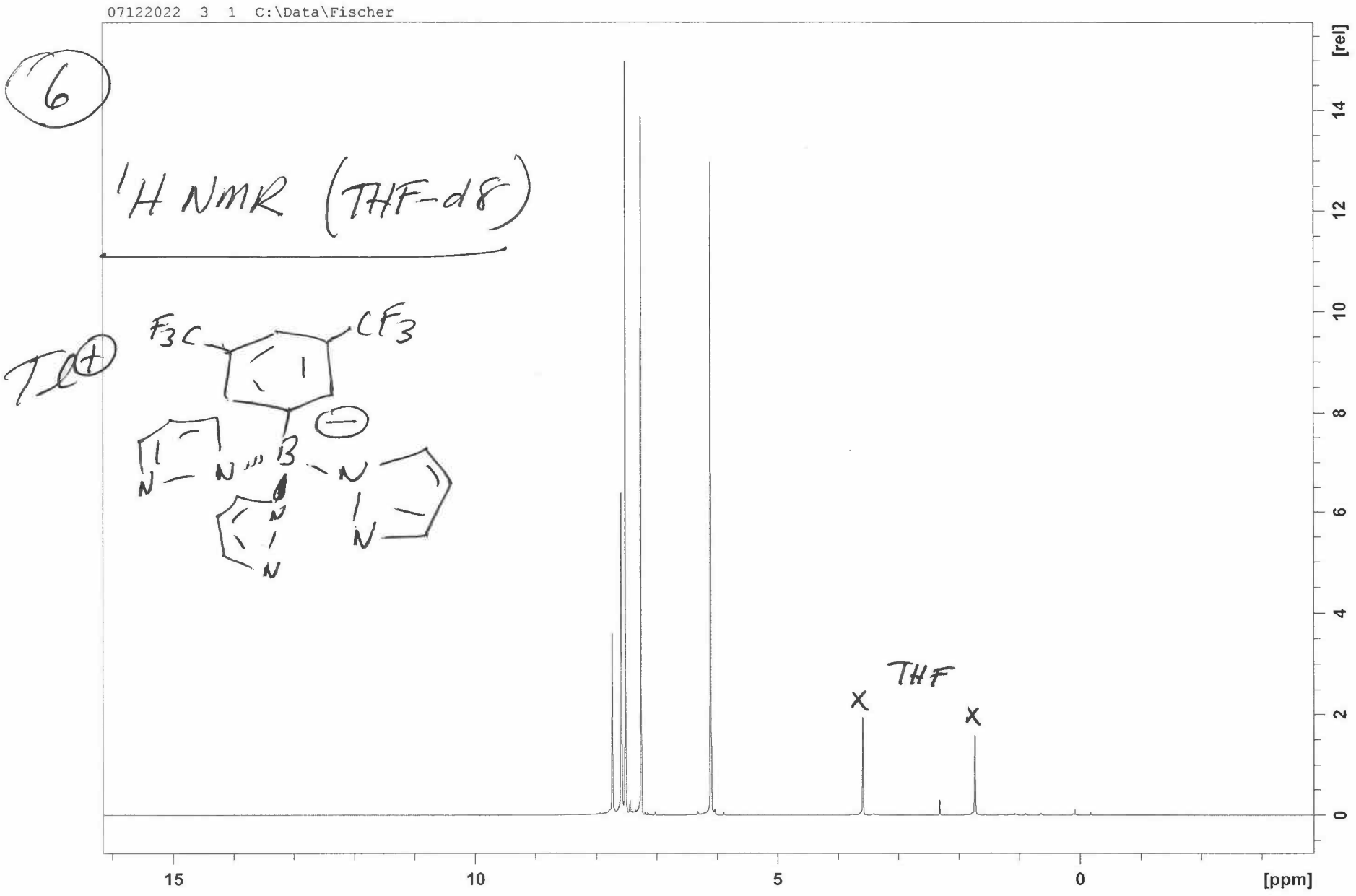
-63.2059



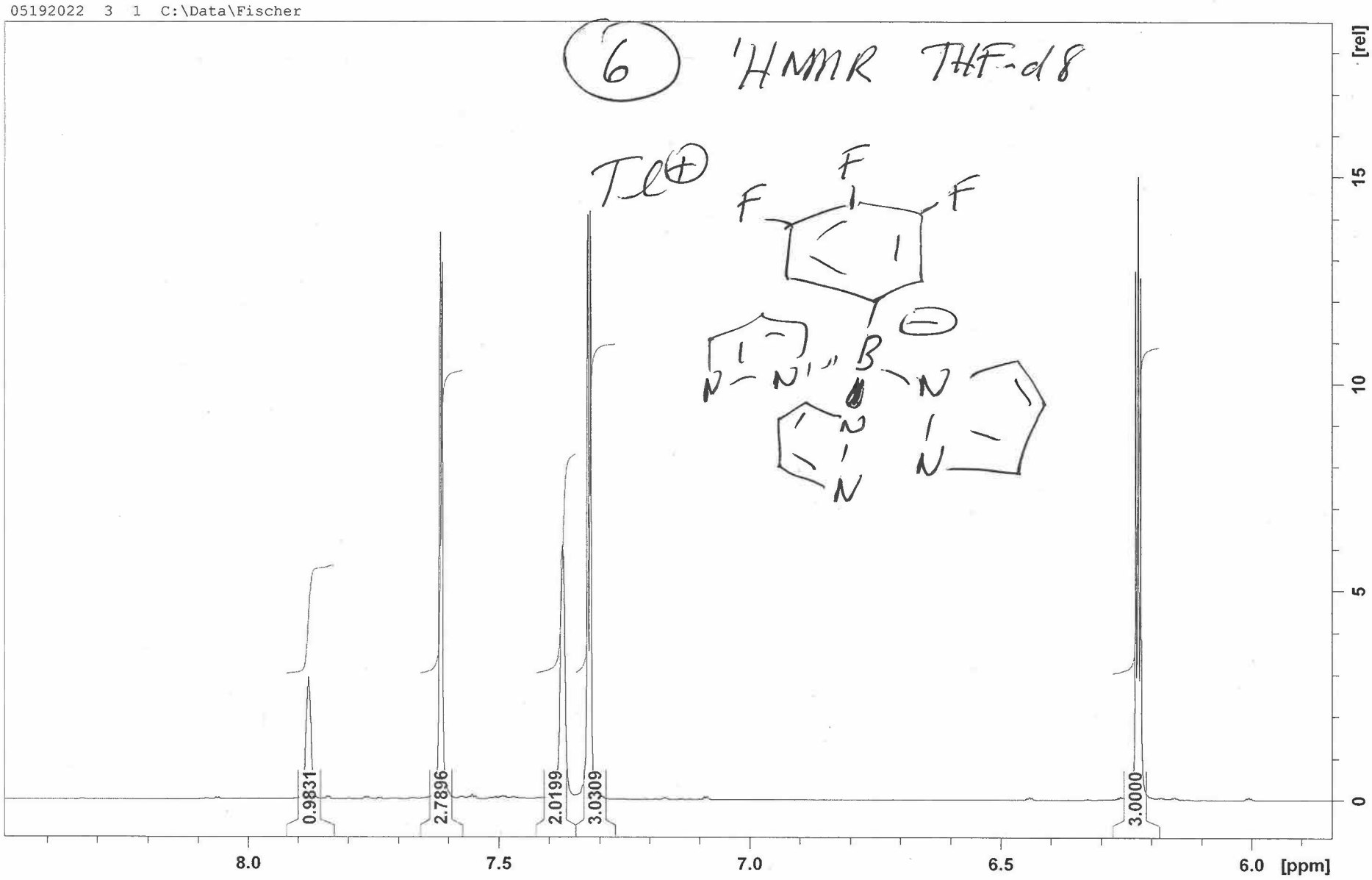
Tl⊕

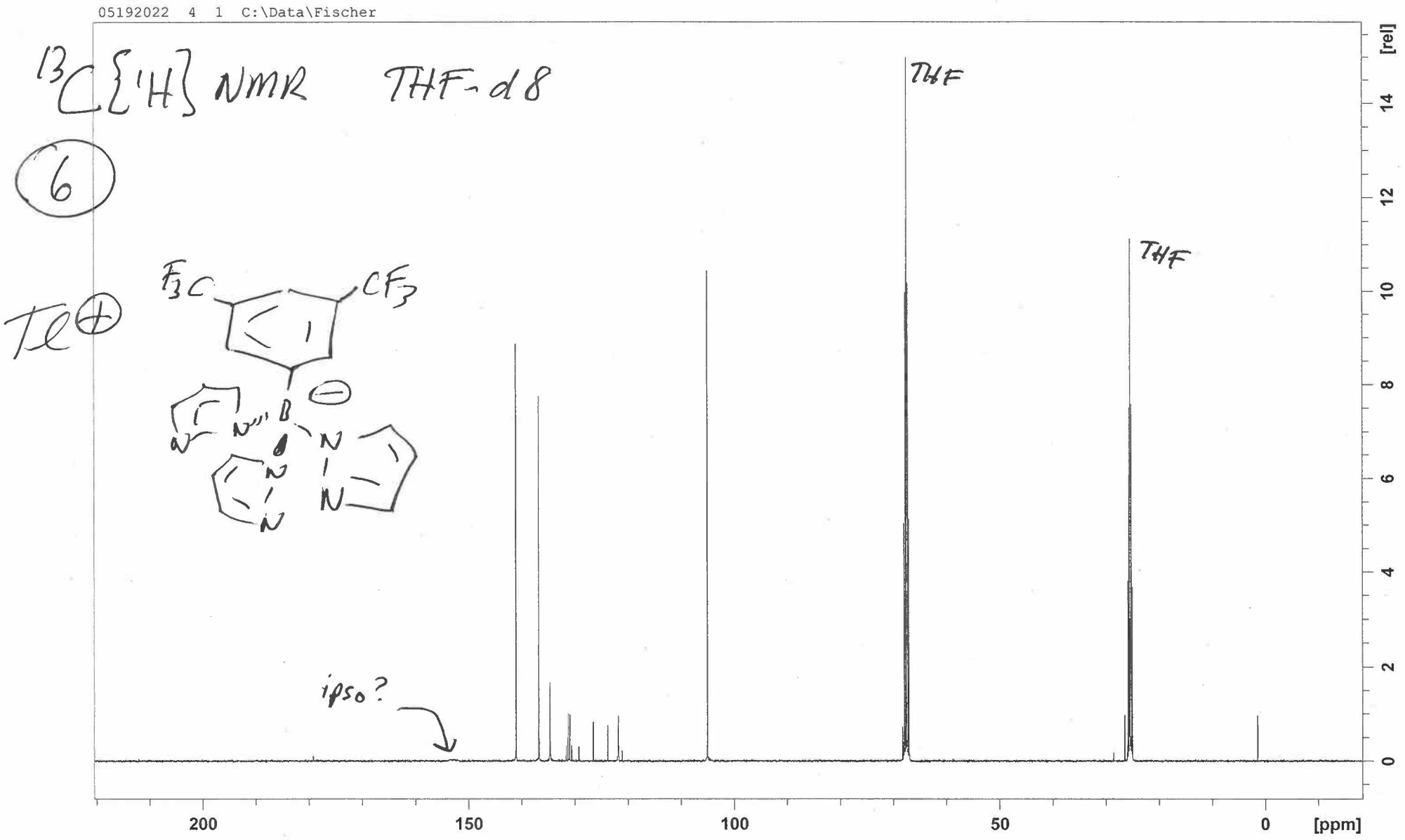
[rel] 20 15 10 5 0

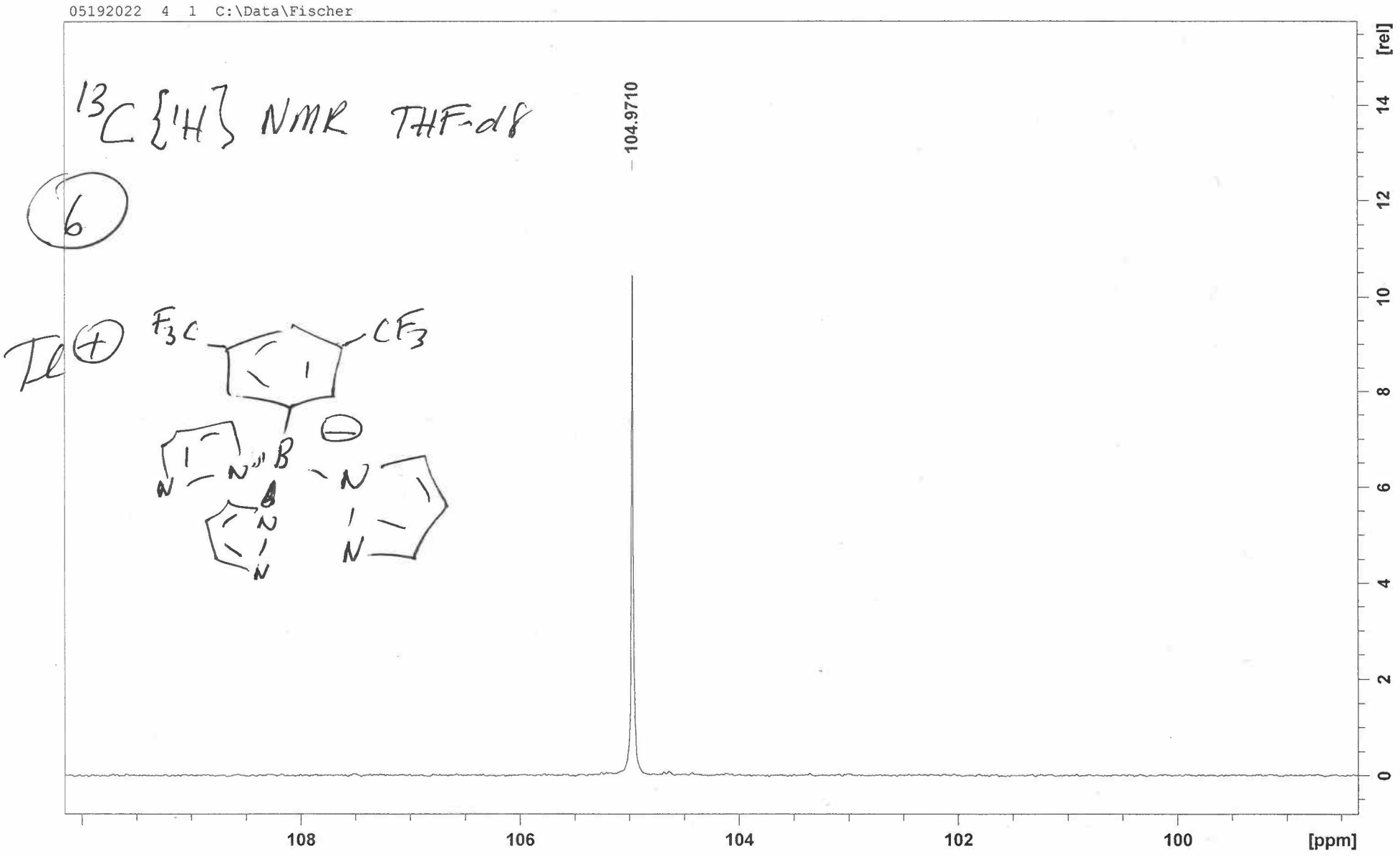
0 - 50 - 100 - 150 - 200 [ppm]

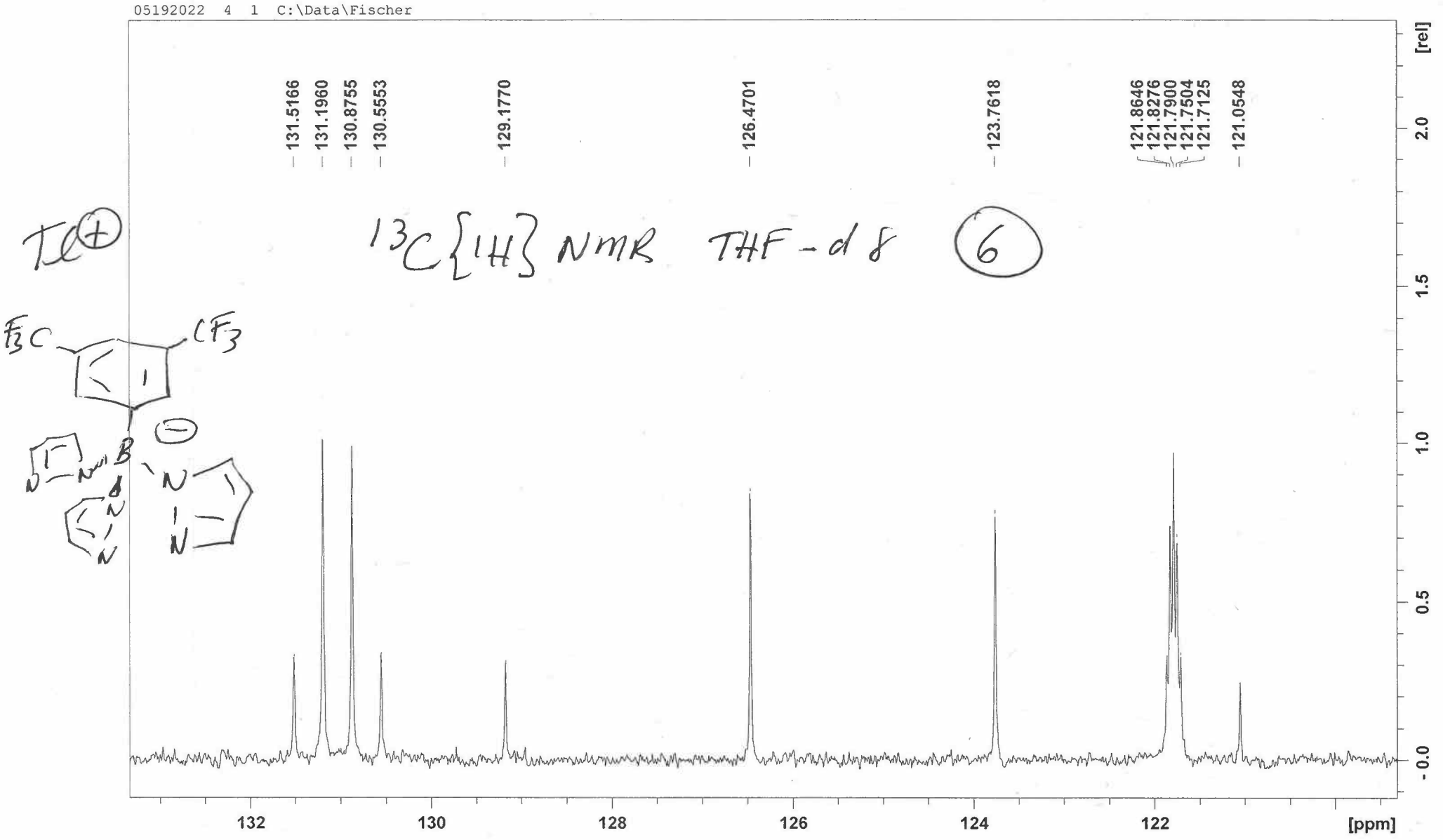

07122022 3 1 C:\Data\Fischer
6
^{1}H NMR (THF-d8)
Tl(+)
F3C
CF3
B
N
THF
X
X
[rel]
[ppm]
15
10
5
0
14
12
10
8
6
4
2
0

05192022 3 1 C:\Data\Fischer
7.8786
7.6166
7.6156
7.6126
7.6113
7.3727
7.3233
7.3222
7.3177
7.3163
6.2301
6.2257
6.2246
6.2202
8.0
7.5
7.0
6.5
6.0
[ppm]
0
5
10
15
20
[rel]
1H NMR
THF-d8
TQ
6


05192022 3 1 C:\Data\Fischer
6
1HNMR THF-d8
Tl⊕
F
F
F
B
⊖
N
N
N
N
N
N
0.9831
2.7896
2.0199
3.0309
3.0000
8.0
7.5
7.0
6.5
6.0
[ppm]
[rel]
0
5
10
15

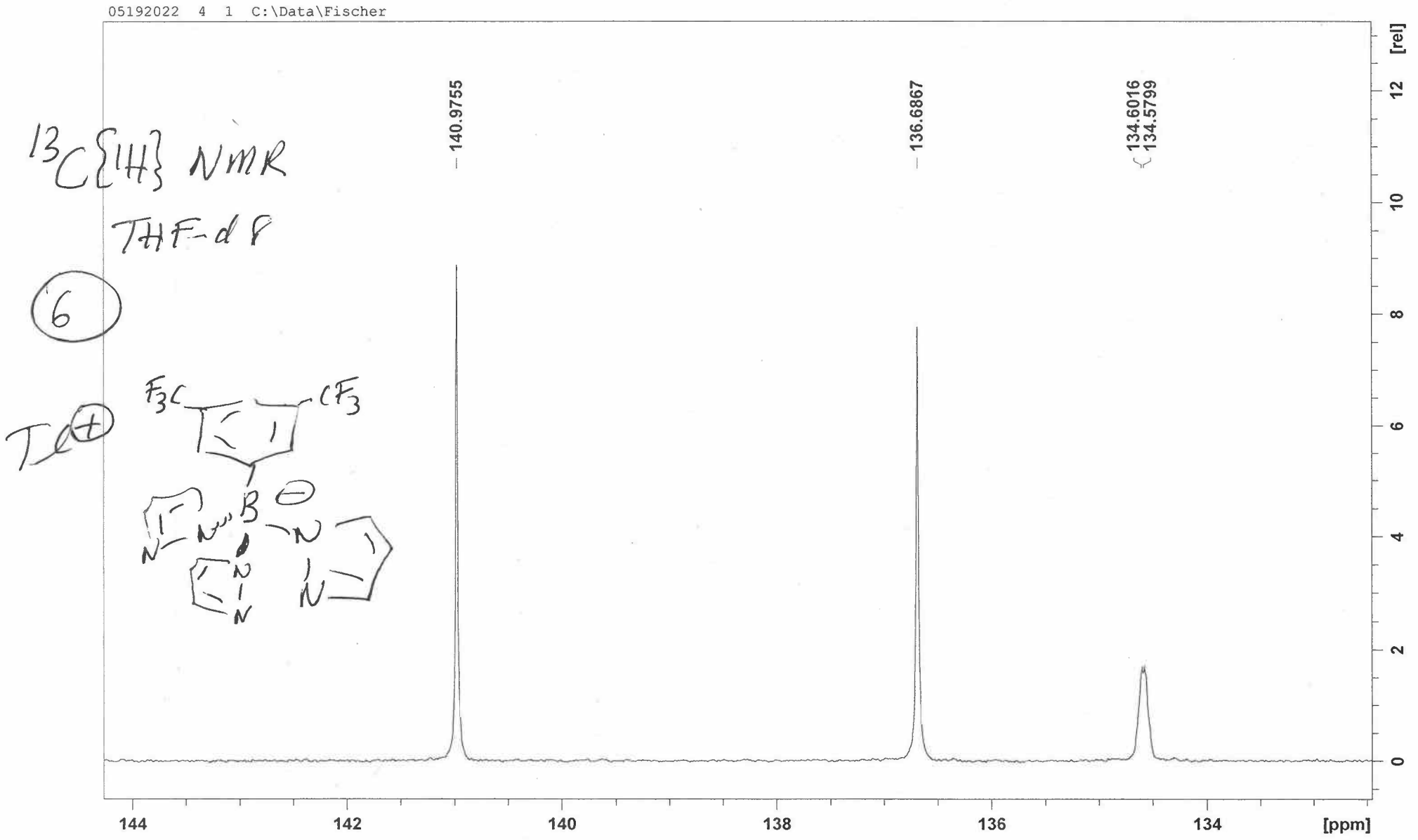

05192022 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR THF-d8
6
Tl⊕
F_3C
CF_3
⊖
B
N
THF
THF
ipso?
200
150
100
50
0
[ppm]
0
2
4
6
8
10
12
14
[rel]


05192022 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR THF-d8
6
Tl⊕
104.9710
108
106
104
102
100
[ppm]
0
2
4
6
8
10
12
14
[rel]

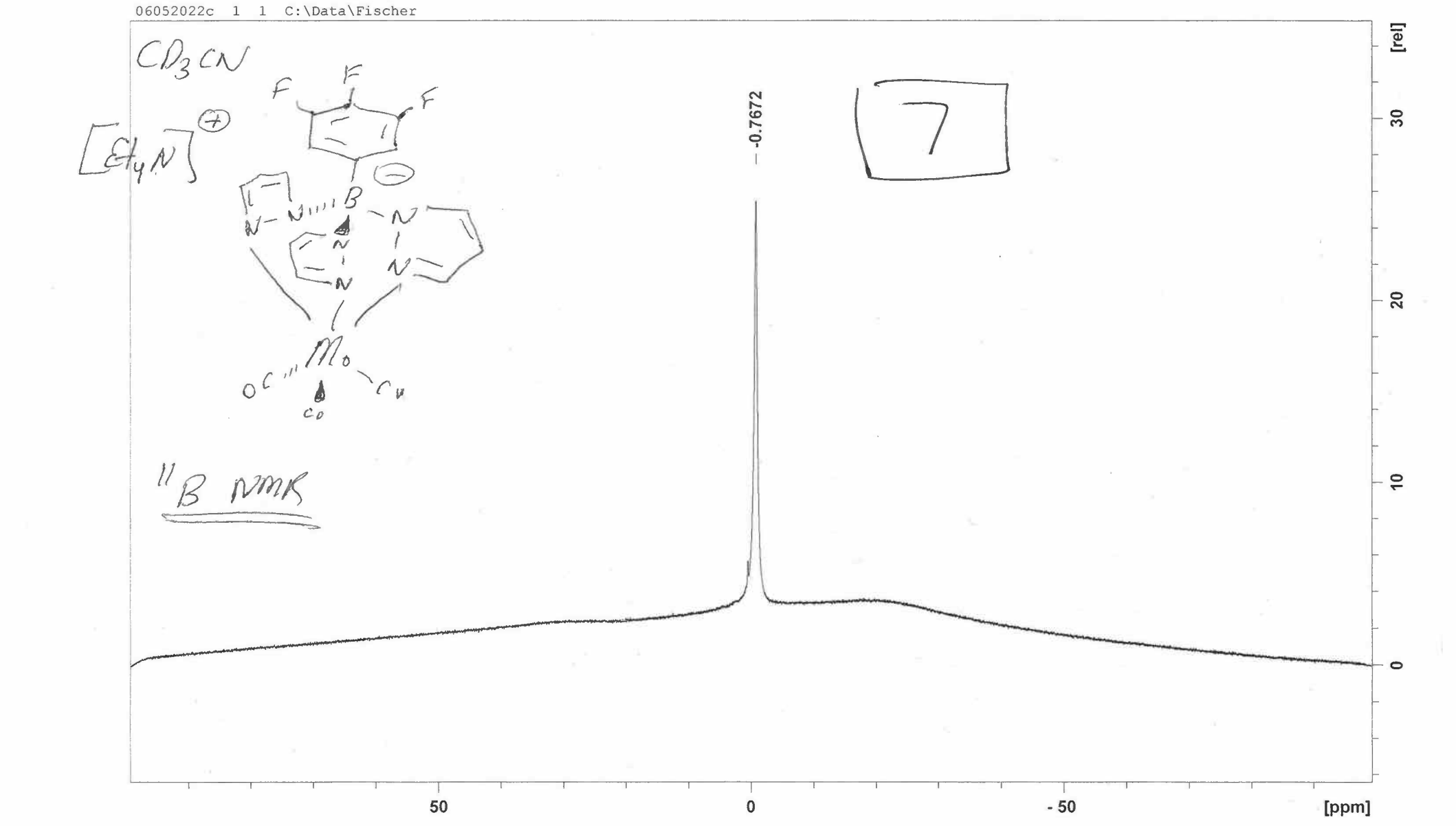


Tl⊕

$^{13}C\{^{1}H\}$ NMR THF-d8 (6)


05192022 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR
THF-d8
6
T⊕
F_3C
CF_3
B⊖
140.9755
136.6867
134.6016
134.5799
[rel]
144
142
140
138
136
134
[ppm]

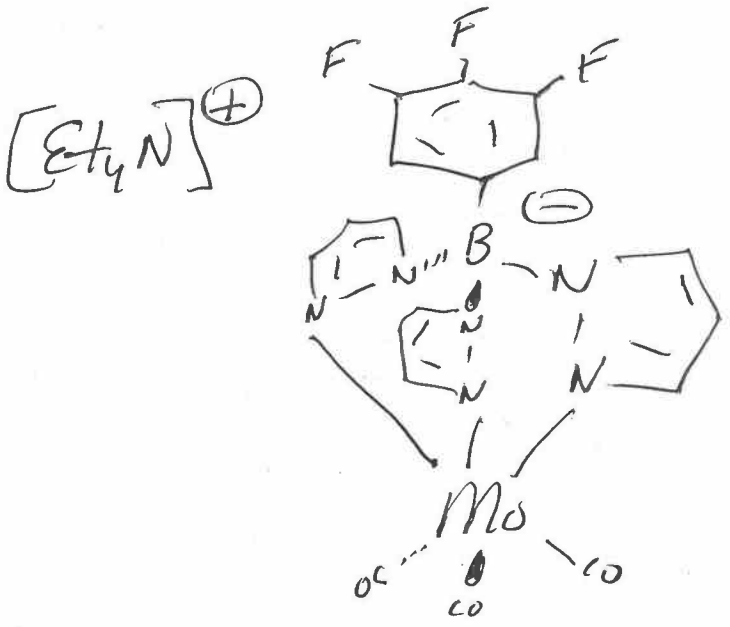
CKp14

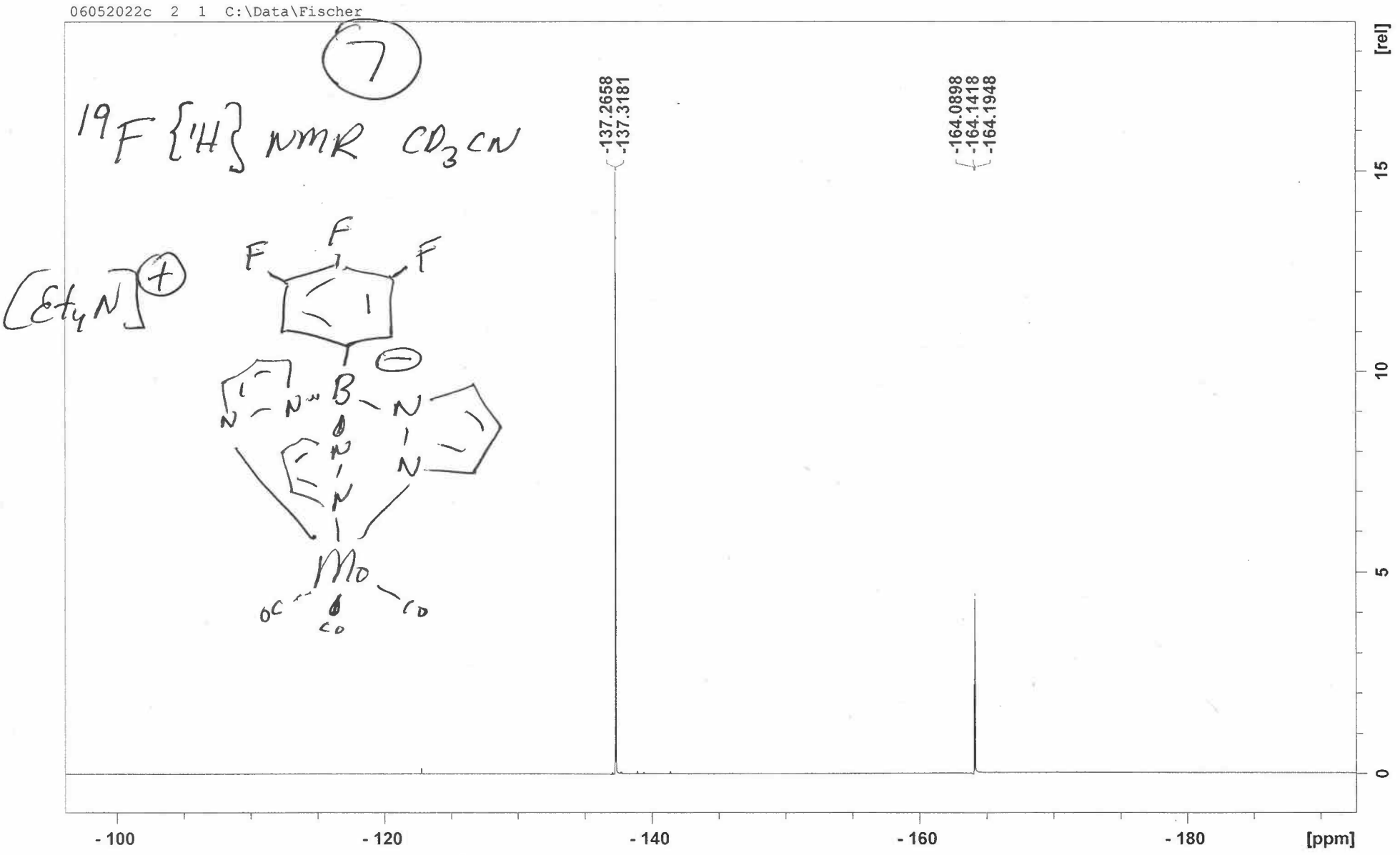

06052022c 1 1 C:\Data\Fischer
CD3CN
[Et4N]
-0.7672
7
11B NMR
50
0
- 50
[ppm]
[rel]
30
20
10
0

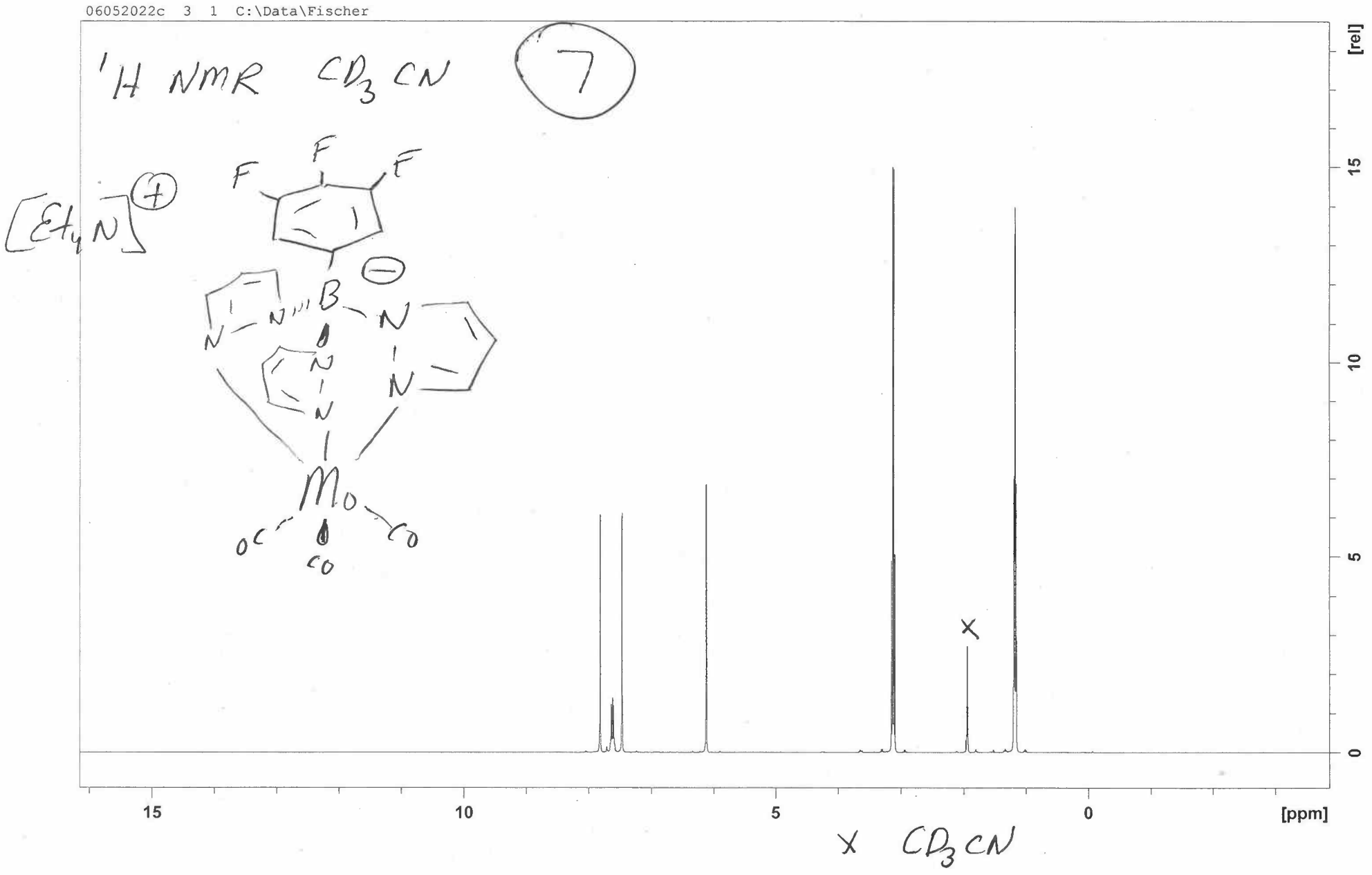
06052022c 2 1 C:\Data\Fischer

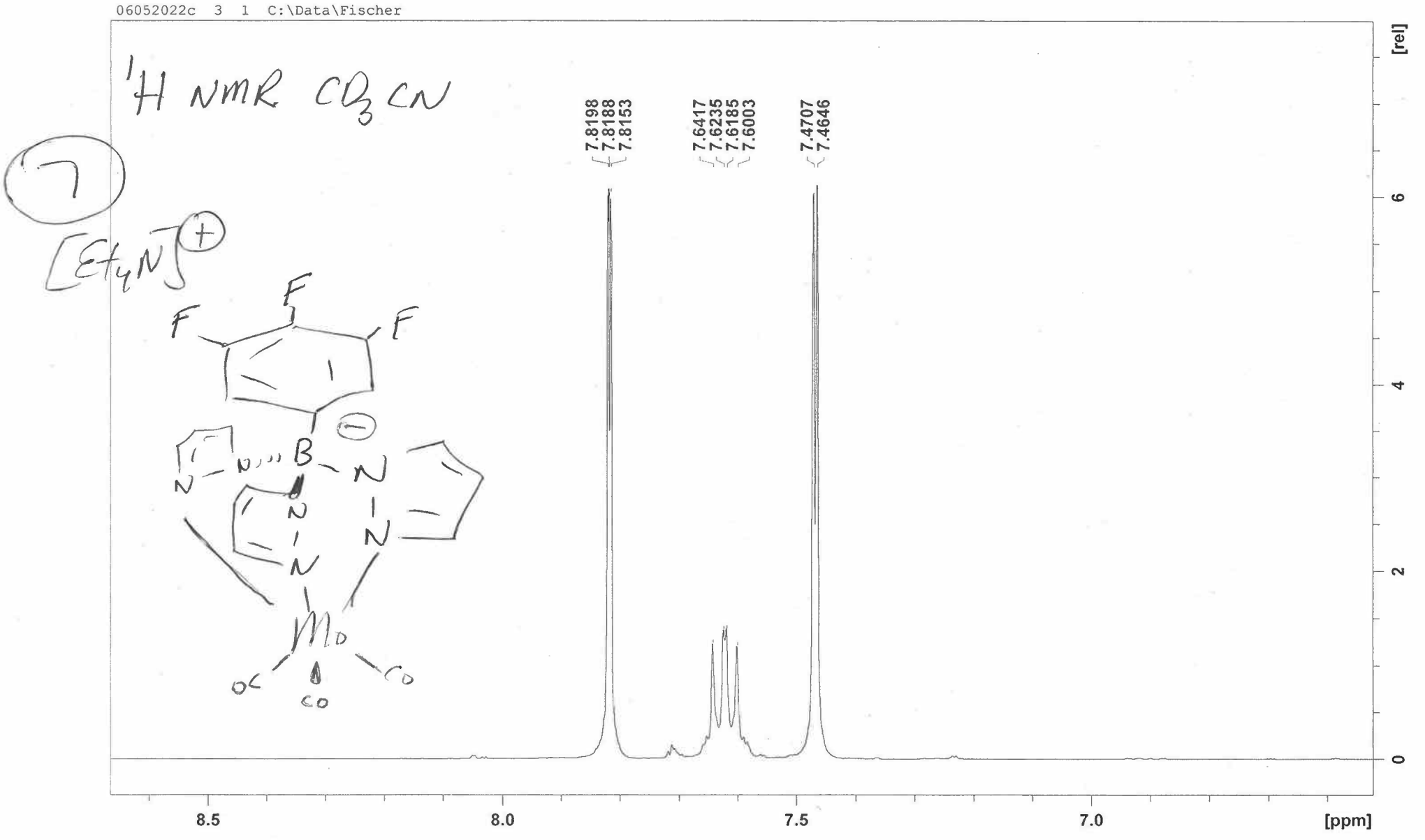
$^{19}F\{^{1}H\}$ NMR CD_3CN

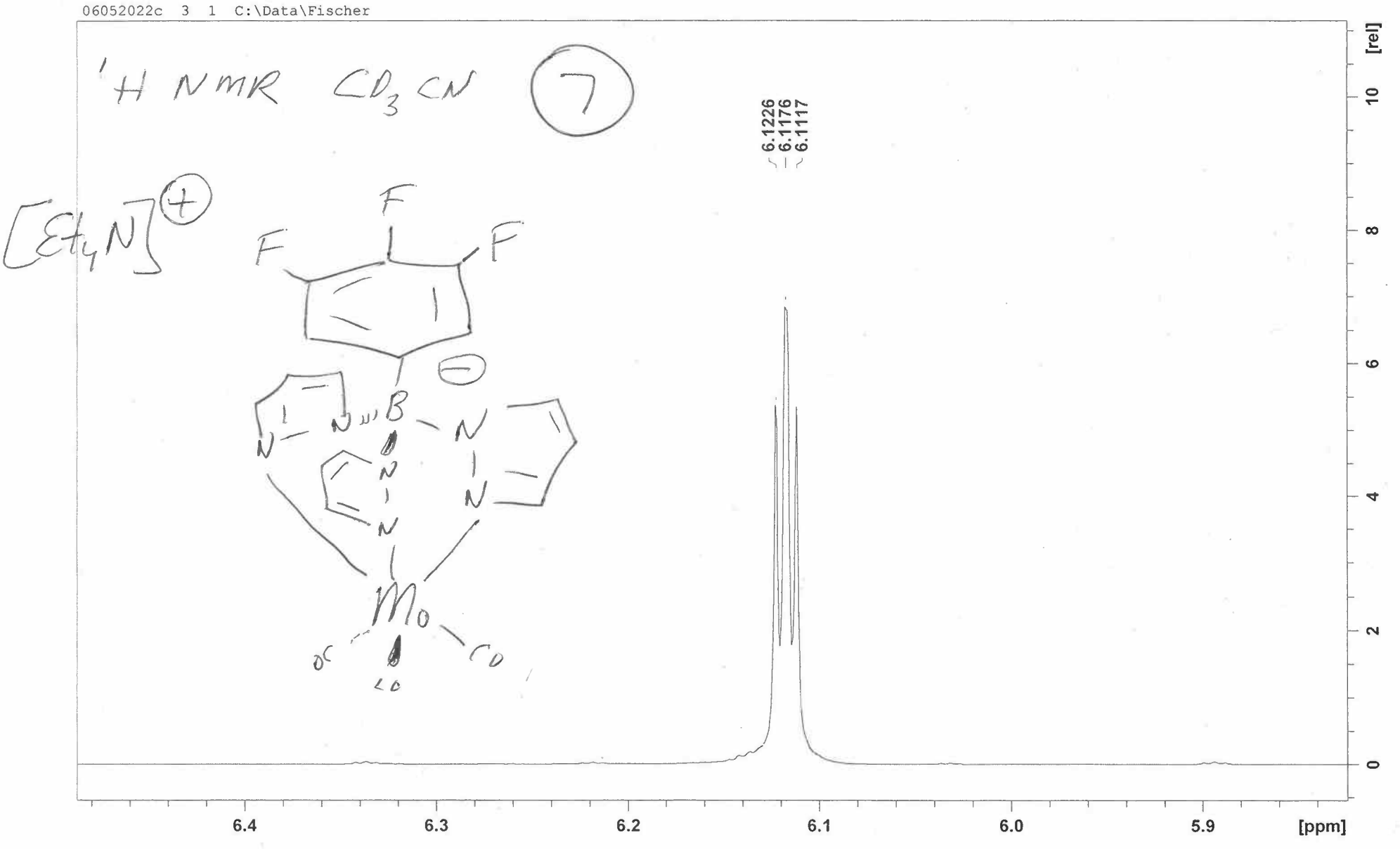
7

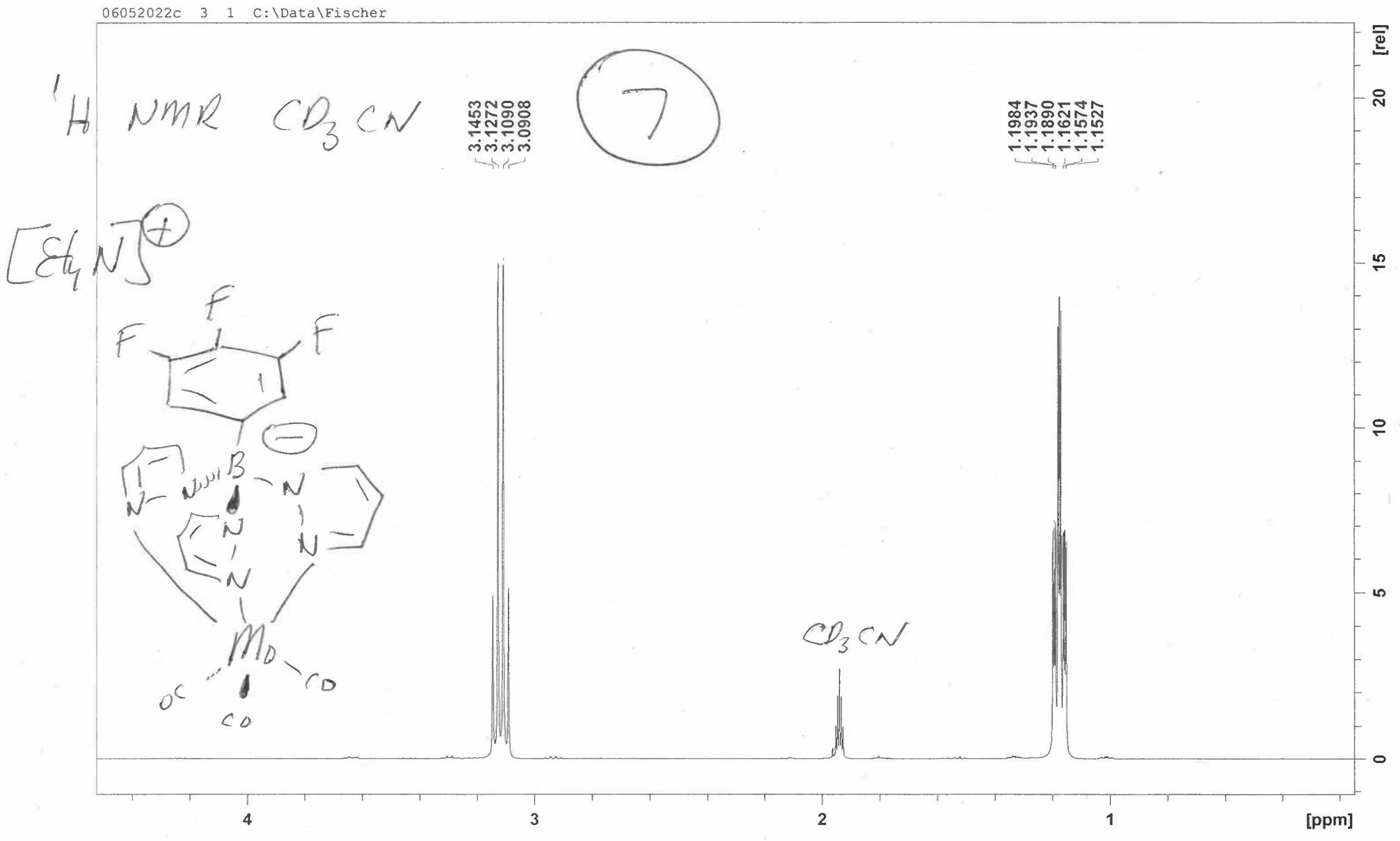


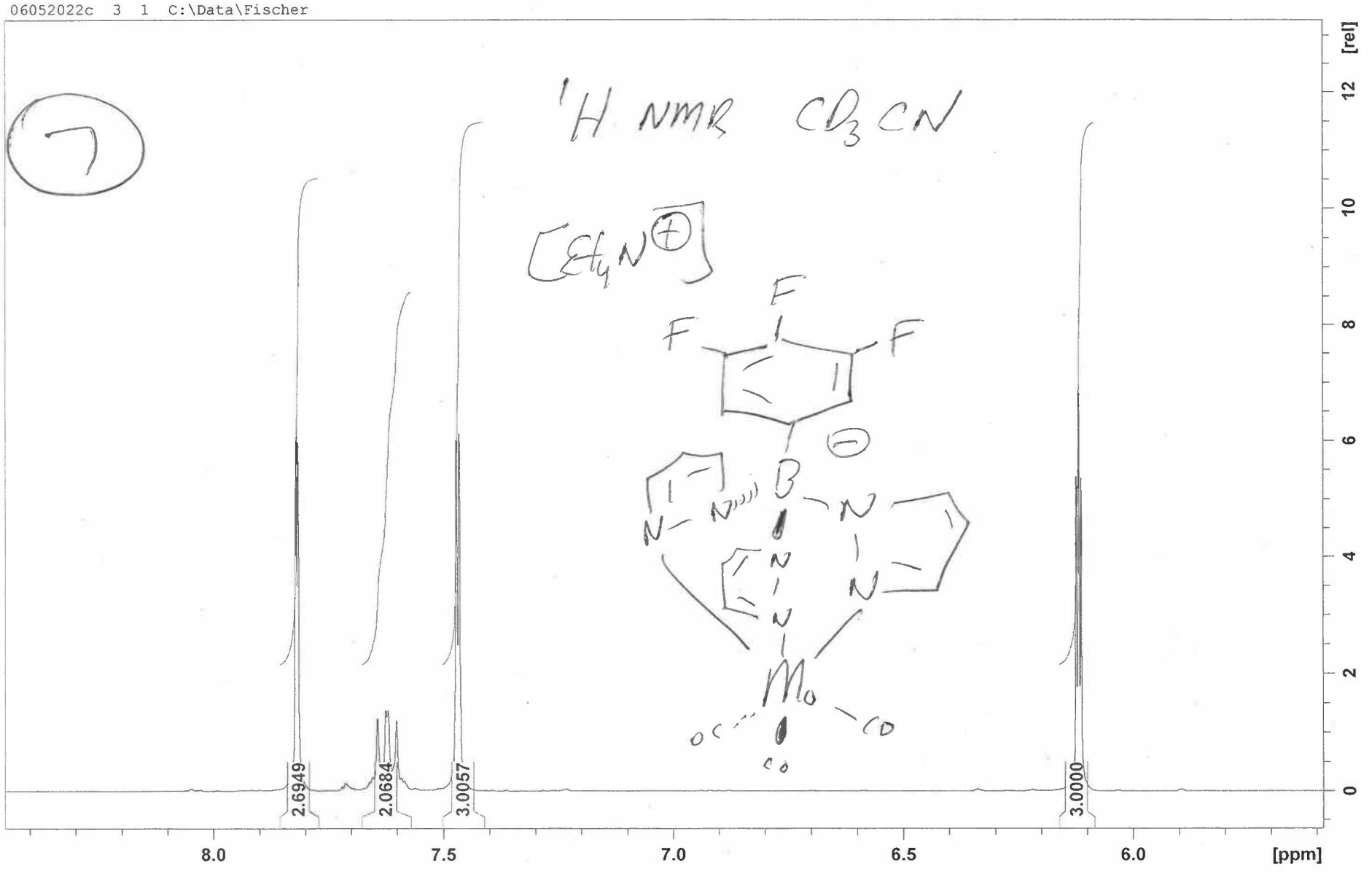

06052022c 2 1 C:\Data\Fischer
7
19F {1H} NMR CD3CN
[Et4N]+
F
F
F
B
N
Mo
OC
CO
CO
-137.2658
-137.3181
-164.0898
-164.1418
-164.1948
[rel]
15
10
5
0
- 100
- 120
- 140
- 160
- 180
[ppm]

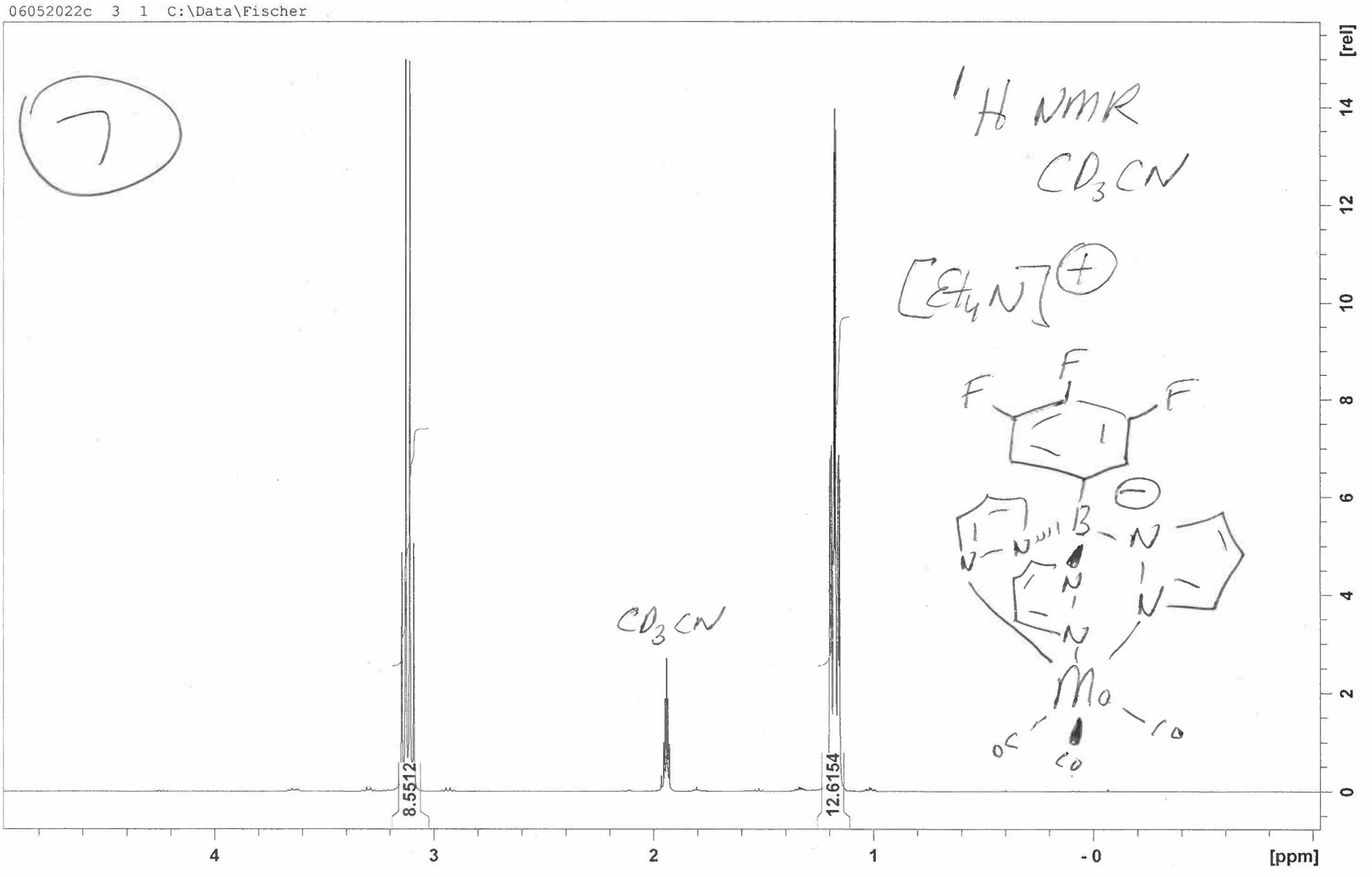

06052022c 3 1 C:\Data\Fischer
^1H NMR CD_3CN
7
$[Et_4N]^+$
F
F
F
B
N
Mo
OC
CO
CO
X
X CD_3CN
15
10
5
0
[ppm]
[rel]

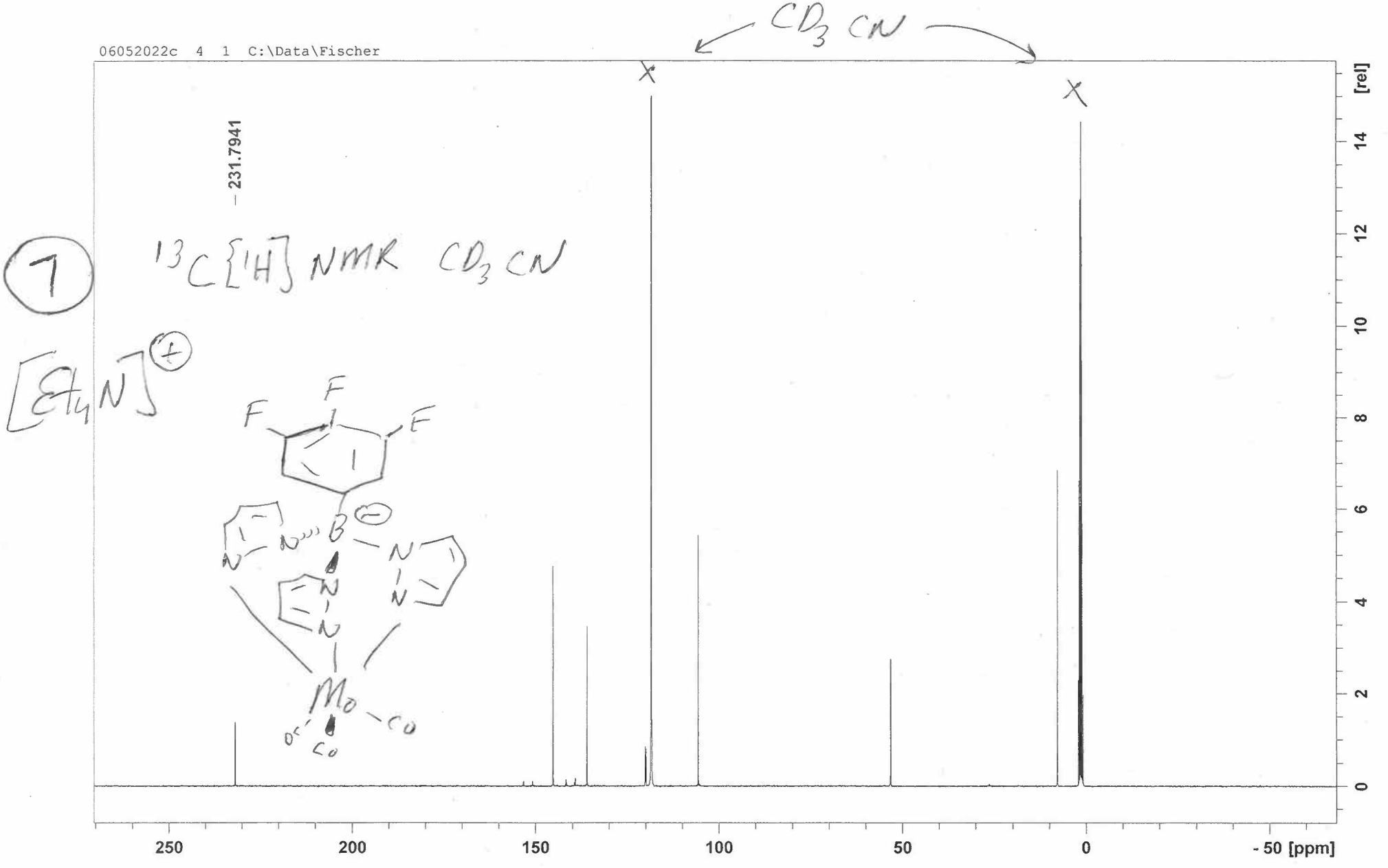

06052022c 3 1 C:\Data\Fischer
^1H NMR CD_3CN
7
$[Et_4N]^+$
F
F
F
B
N
N
N
N
N
N
Mo
OC
CO
CO
7.8198
7.8188
7.8153
7.6417
7.6235
7.6185
7.6003
7.4707
7.4646
[rel]
0
2
4
6
8.5
8.0
7.5
7.0
[ppm]

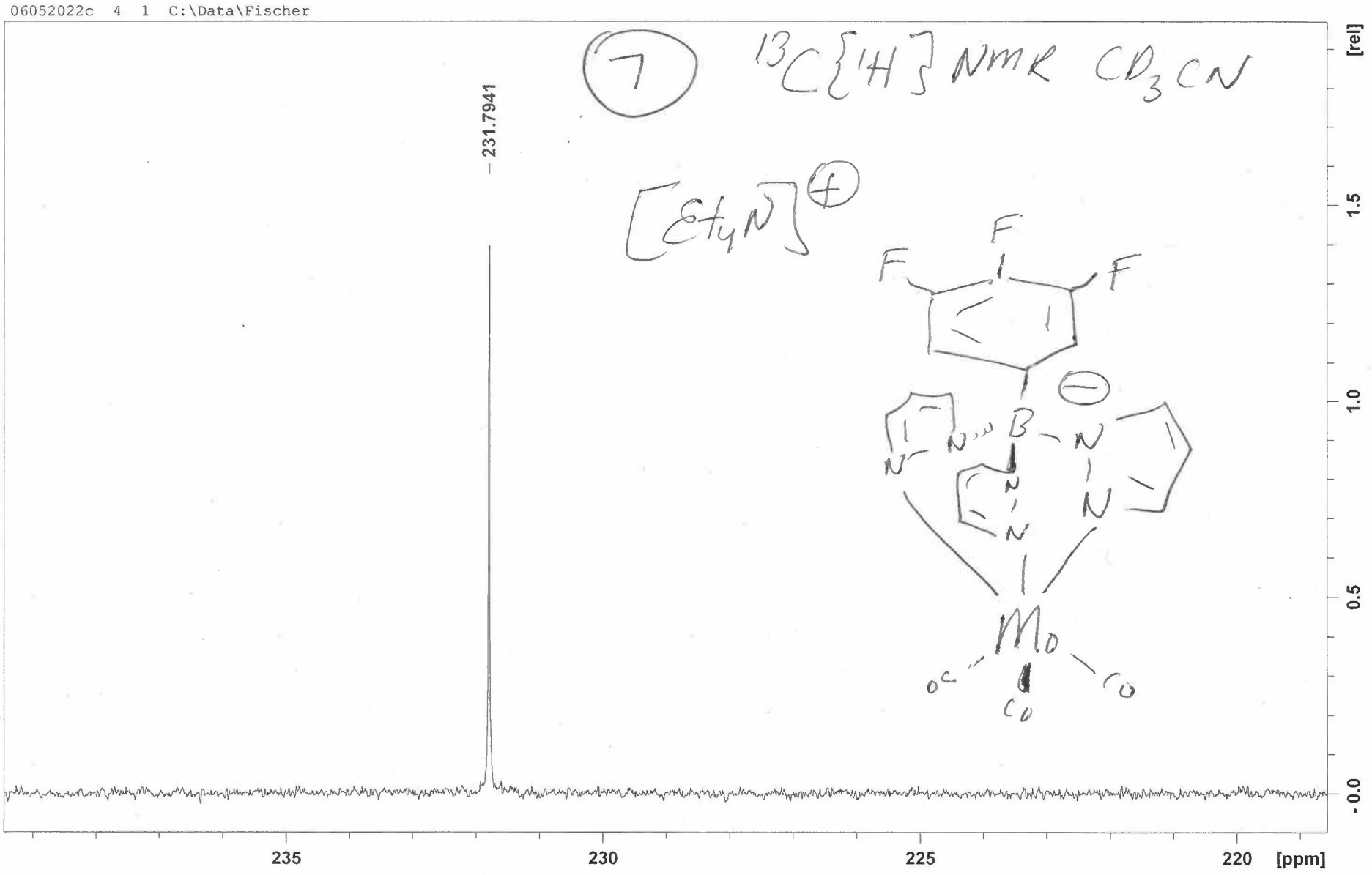

06052022c 3 1 C:\Data\Fischer
^1H NMR CD_3CN
7
$[Et_4N]^+$
6.1226
6.1176
6.1117
F
F
F
B
N
Mo
OC
CO
CO
0
2
4
6
8
10
[rel]
6.4
6.3
6.2
6.1
6.0
5.9
[ppm]

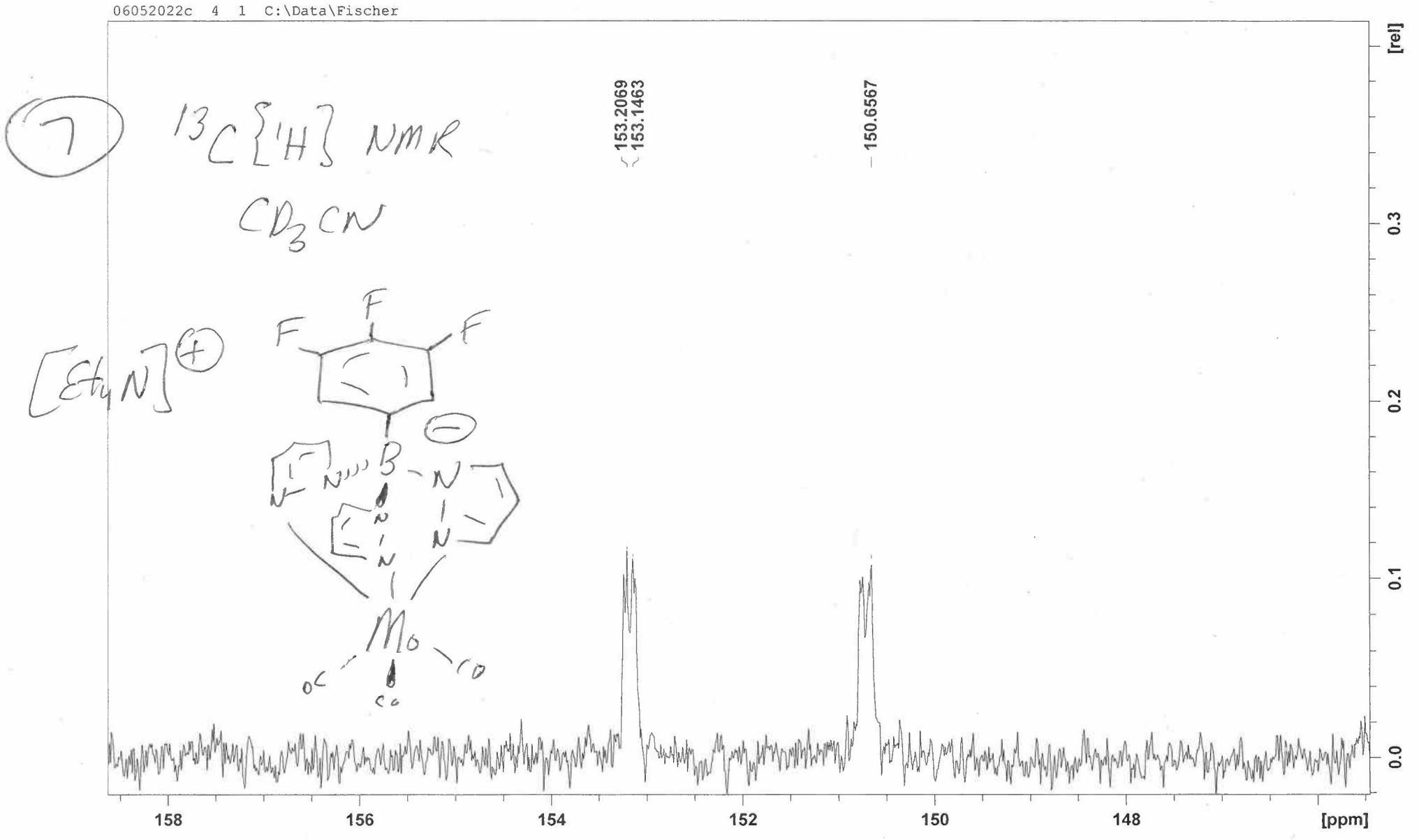

06052022c 3 1 C:\Data\Fischer
^{1}H NMR CD_3CN
7
$[Et_4N]^+$
3.1453
3.1272
3.1090
3.0908
1.1984
1.1937
1.1890
1.1621
1.1574
1.1527
CD_3CN
[rel]
[ppm]
0
5
10
15
20
1
2
3
4

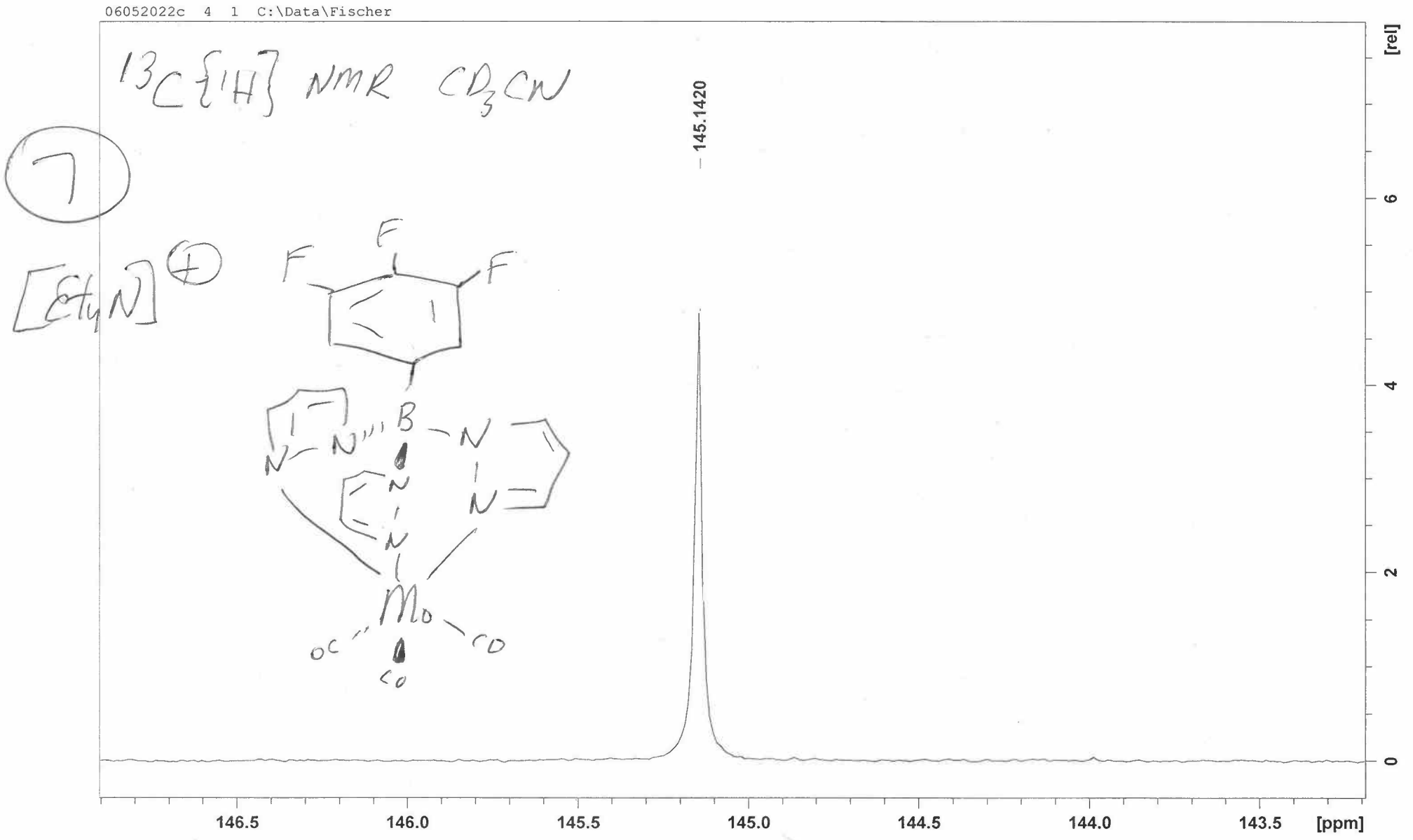

06052022c 3 1 C:\Data\Fischer
7
^1H NMR CD_3CN
$[Et_4N^+]$
F
F
F
B
N
N
N
N
N
N
Mo
OC
CO
CO
2.6949
2.0684
3.0057
3.0000
8.0
7.5
7.0
6.5
6.0
[ppm]
[rel]
0
2
4
6
8
10
12

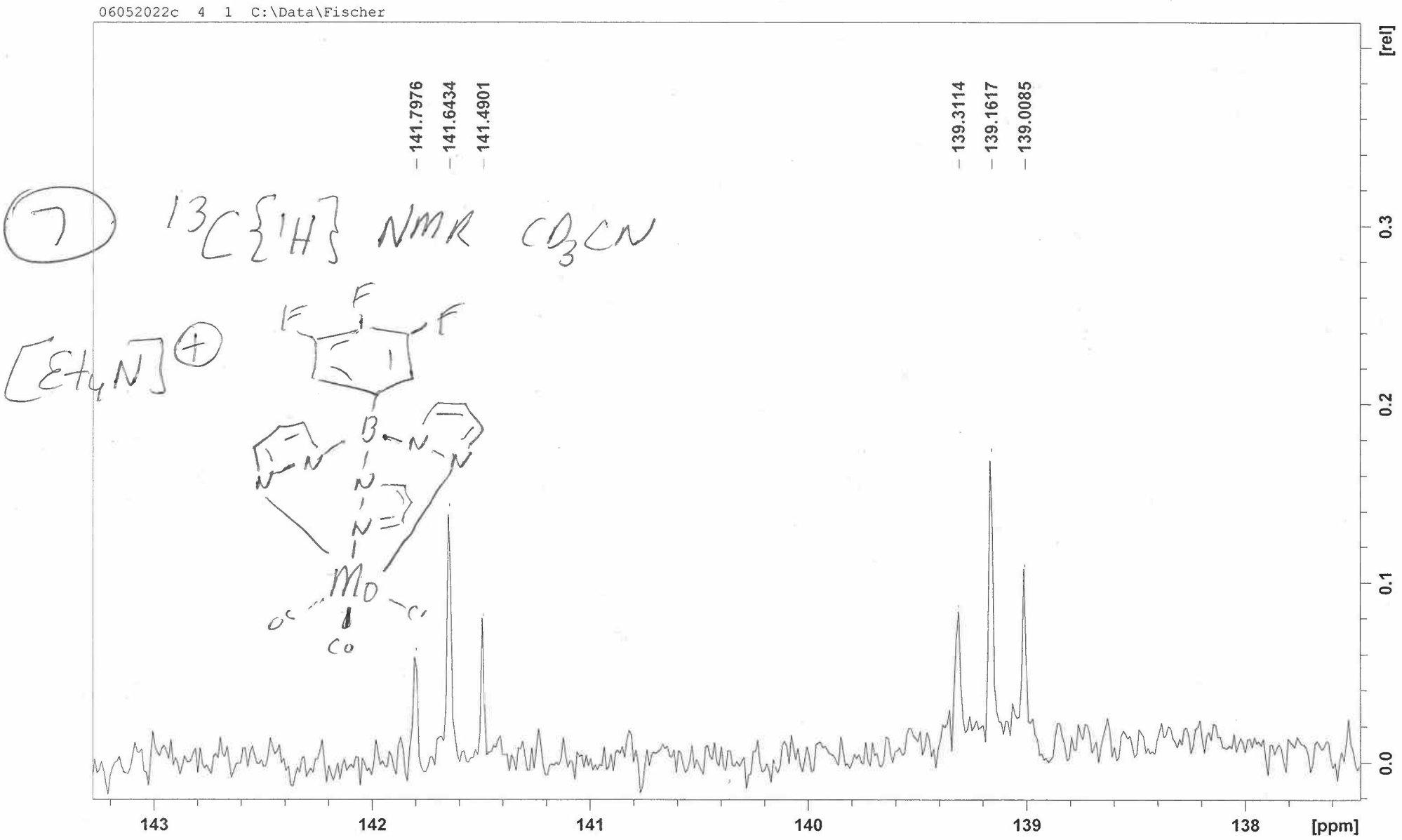

06052022c 3 1 C:\Data\Fischer
7
^{1}H NMR
CD_3CN
$[Et_4N]^+$
CD_3CN
8.5512
12.6154
[rel]
[ppm]
4
3
2
1
- 0
0
2
4
6
8
10
12
14


06052022c 4 1 C:\Data\Fischer
CD_3CN
231.7941
7
$^{13}C\{^1H\}$ NMR CD_3CN
$[Et_4N]^+$
F
F
F
B
N
Mo
CO
CO
CO
[rel]
14
12
10
8
6
4
2
0
250
200
150
100
50
0
- 50 [ppm]


06052022c 4 1 C:\Data\Fischer
7
$^{13}C\{^1H\}$ NMR CD_3CN
$[Et_4N]^+$
231.7941
F
F
F
B
N
Mo
OC
CO
CO
[rel]
1.5
1.0
0.5
-0.0
235
230
225
220
[ppm]


06052022c 4 1 C:\Data\Fischer
7
$^{13}C\{^{1}H\}$ NMR
CD_3CN
$[Et_4N]^{+}$
153.2069
153.1463
150.6567
[rel]
0.3
0.2
0.1
0.0
158
156
154
152
150
148
[ppm]

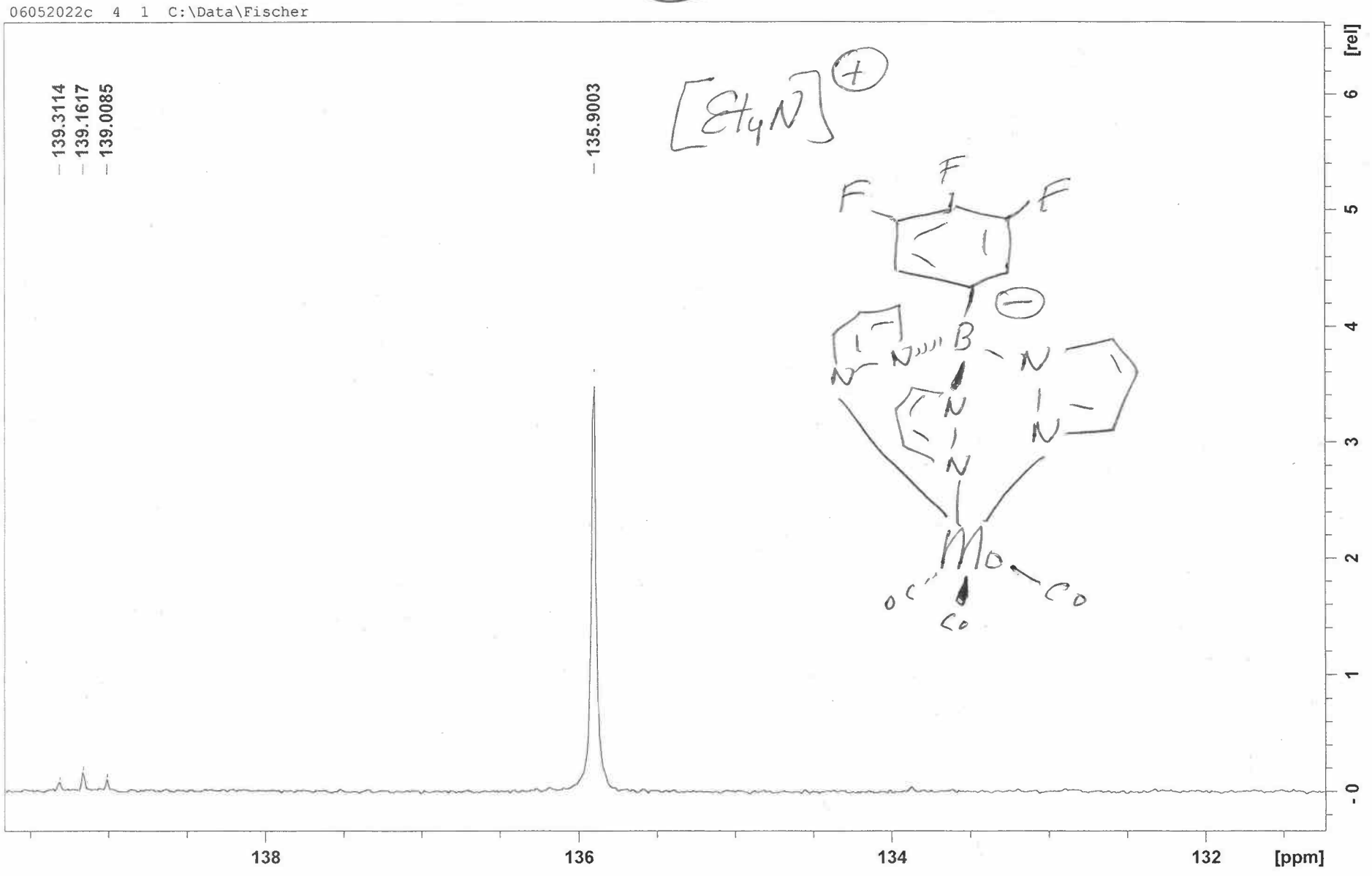

06052022c 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR CD_3CN
7
$[Et_4N]^{\oplus}$
F
F
F
B
N
Mo
OC
CO
CO
145.1420
[rel]
0
2
4
6
146.5
146.0
145.5
145.0
144.5
144.0
143.5
[ppm]

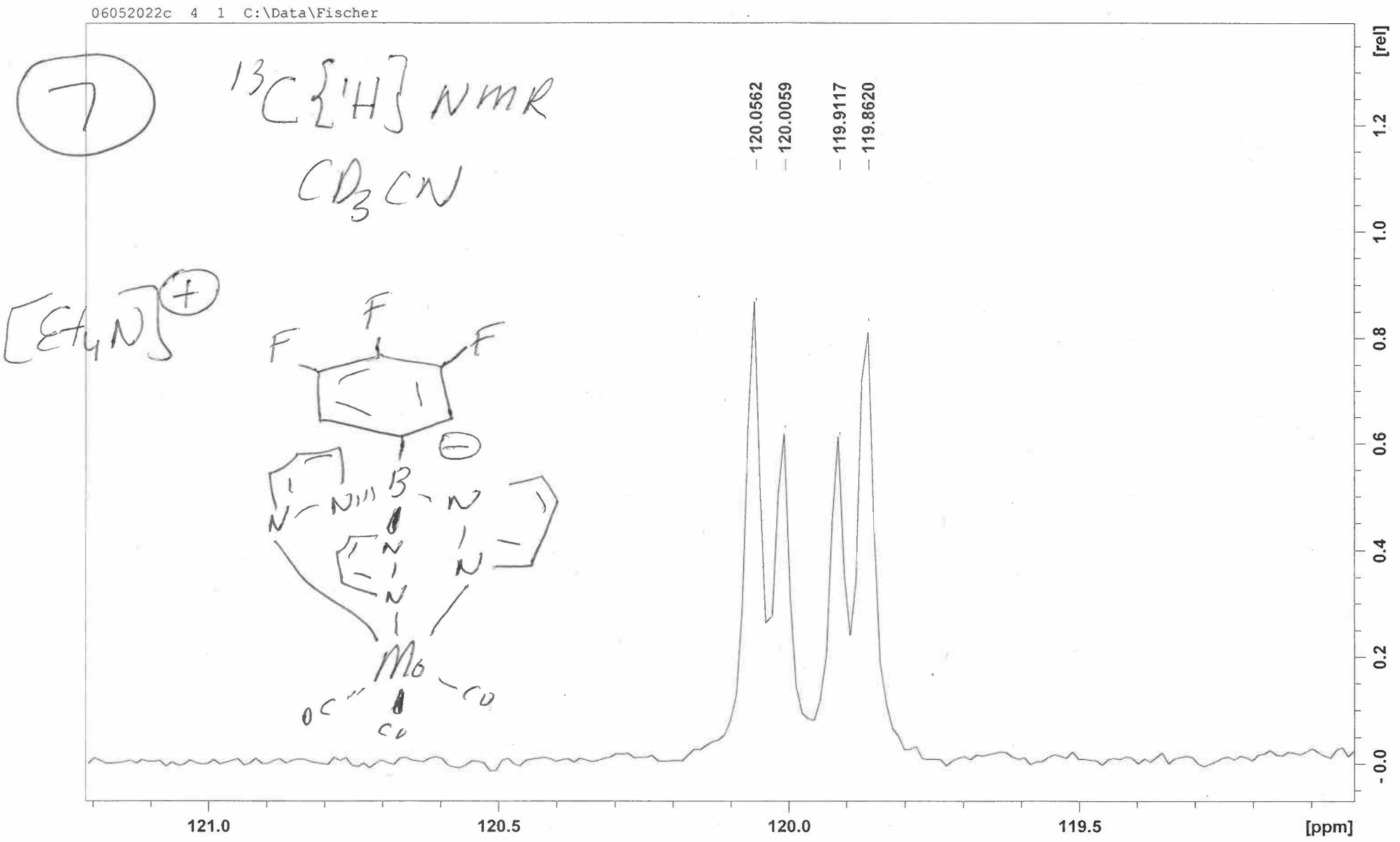


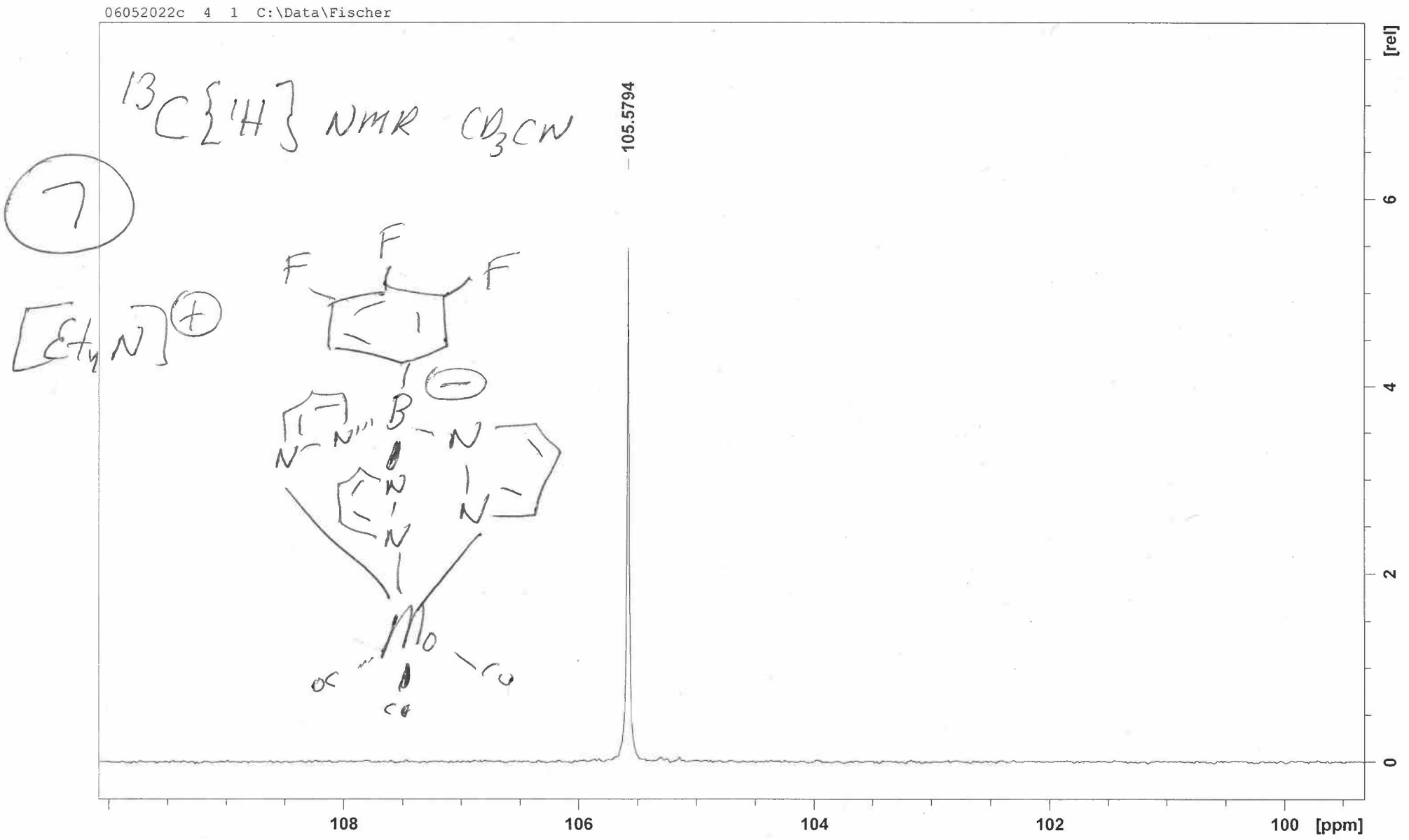
(7) $^{13}C\{^1H\}$ NMR CD_3CN

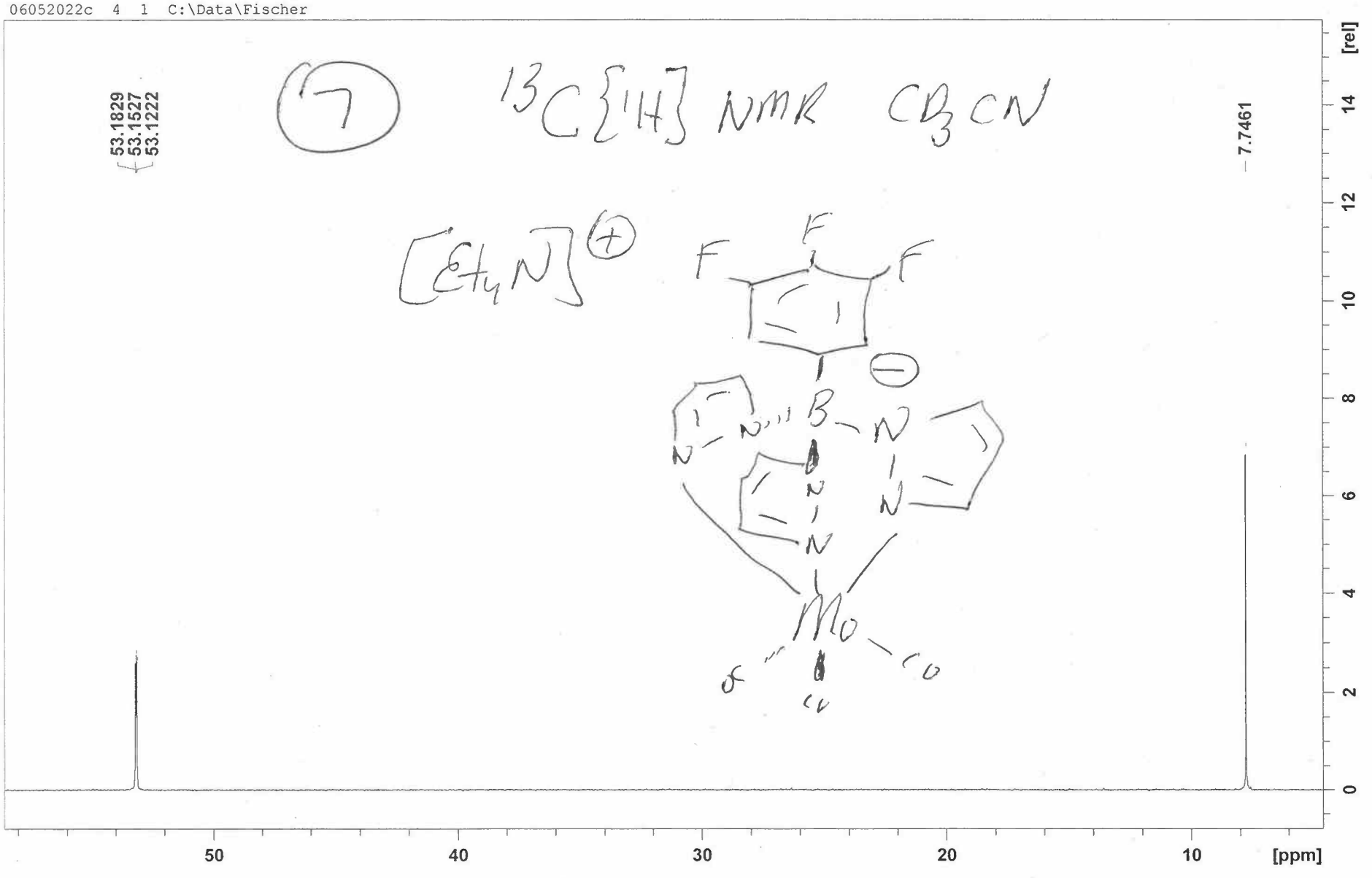
$[Et_4N]^+$

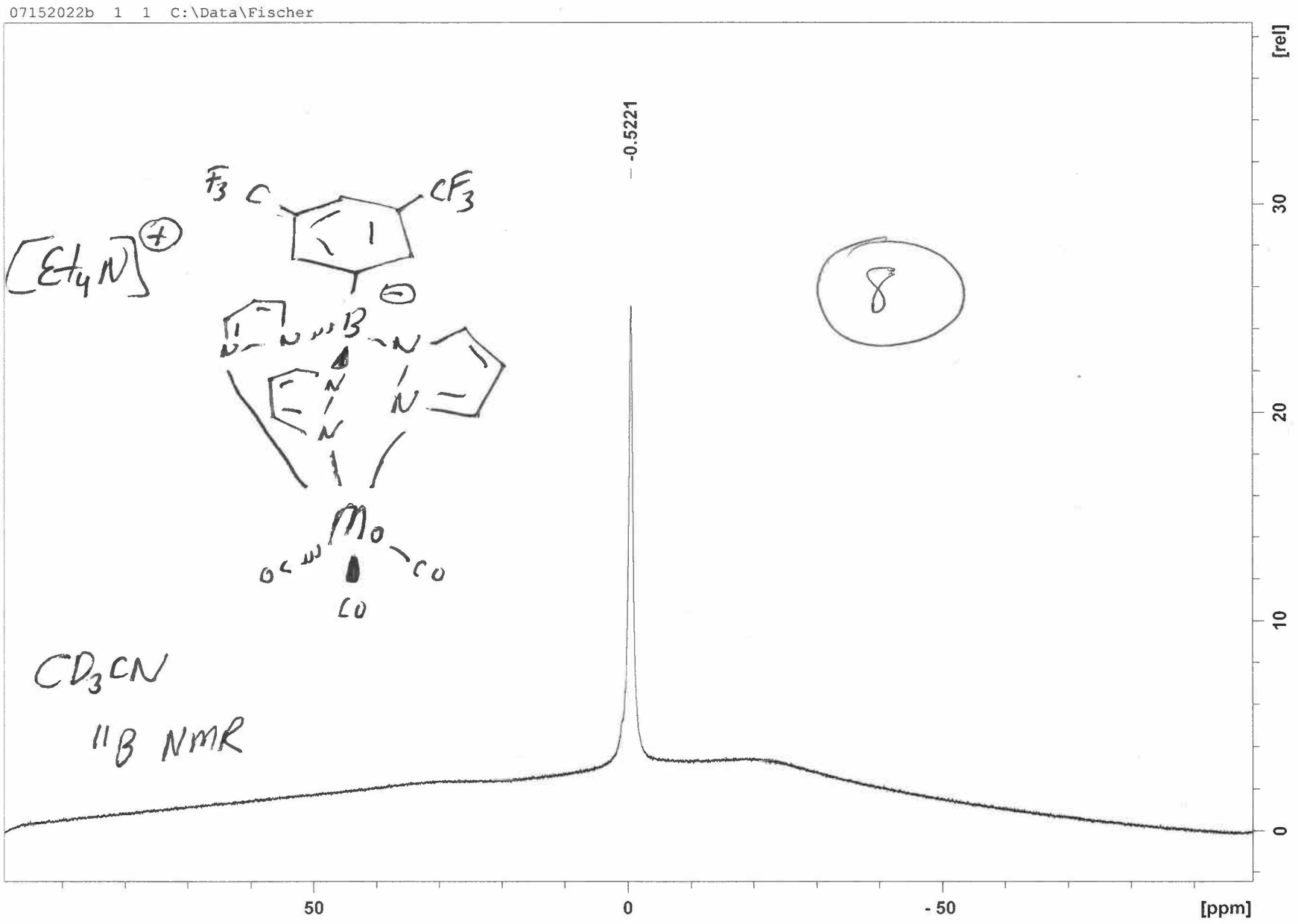
(7) $^{13}C\{^1H\}$ NMR CD_3CN




06052022c 4 1 C:\Data\Fischer
7
$^{13}C\{^{1}H\}$ NMR
CD_3CN
$[Et_4N]^+$
F
F
F
B
N
Mo
CO
OC
CO
120.0562
120.0059
119.9117
119.8620
121.0
120.5
120.0
119.5
[ppm]
[rel]
1.2
1.0
0.8
0.6
0.4
0.2
-0.0


06052022c 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR CD_3CN
7
$[Et_4N]^+$
105.5794
[rel]
0
2
4
6
108
106
104
102
100
[ppm]


06052022c 4 1 C:\Data\Fischer
53.1829
53.1527
53.1222
7.7461
(7)
$^{13}C\{^{1}H\}$ NMR CD_3CN
$[Et_4N]^{\oplus}$
F
F
F
B
N
Mo
CO
CO
CO
[rel]
[ppm]
50
40
30
20
10
0
2
4
6
8
10
12
14


07152022b 1 1 C:\Data\Fischer
-0.5221
[rel]
30
20
10
0
50
0
- 50
[ppm]
[Et4N]+
8
CD3CN
11B NMR

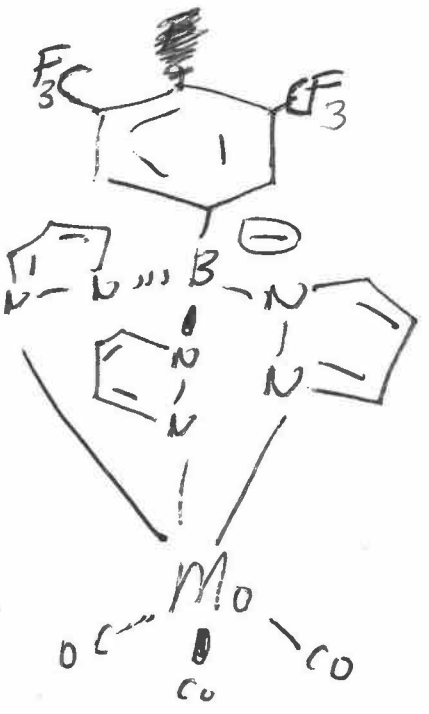
07152022b 2 1 C:\Data\Fischer

$^{19}F\{^{1}H\}$ NMR

^{19}F NMR 376 MHz

8

$[Et_4N]^{+}$



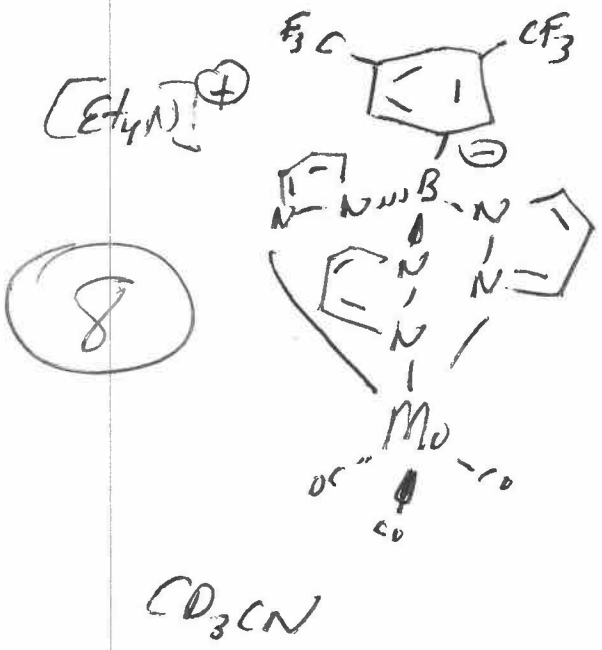
-63.1206

0 -50 -100 -150 -200 [ppm]

0 5 10 15 [rel]

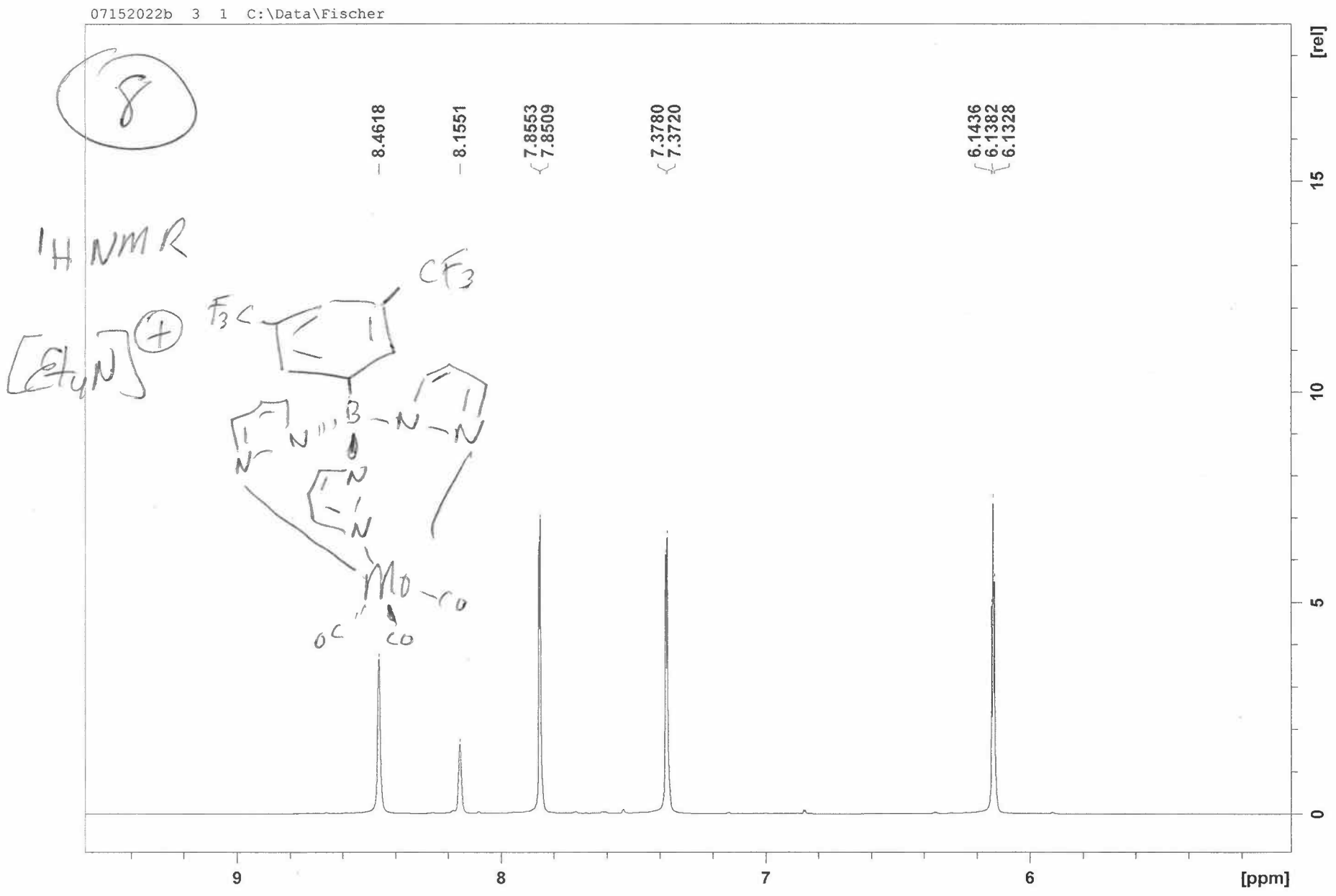
07152022b 3 1 C:\Data\Fischer

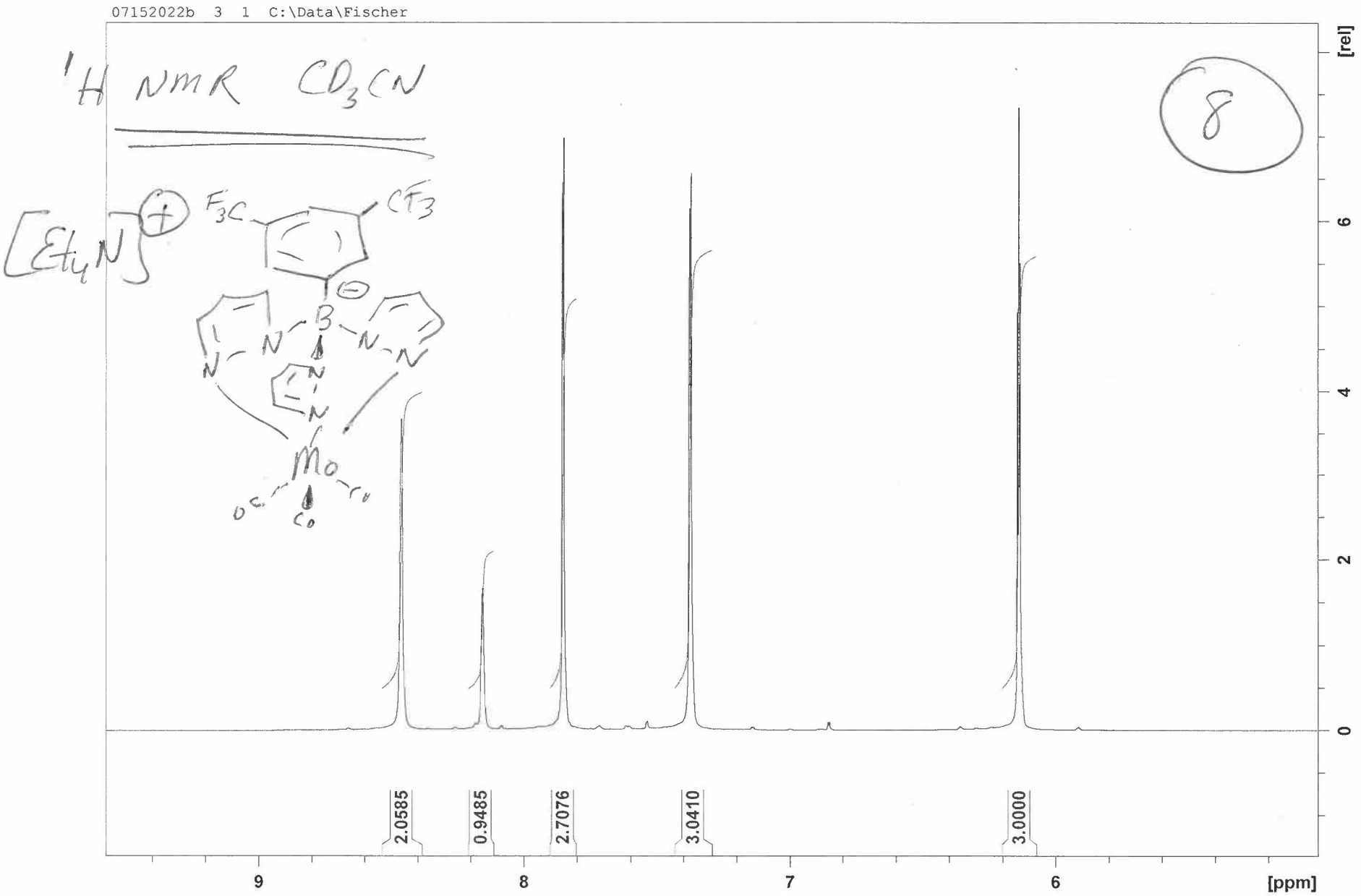
^1H NMR



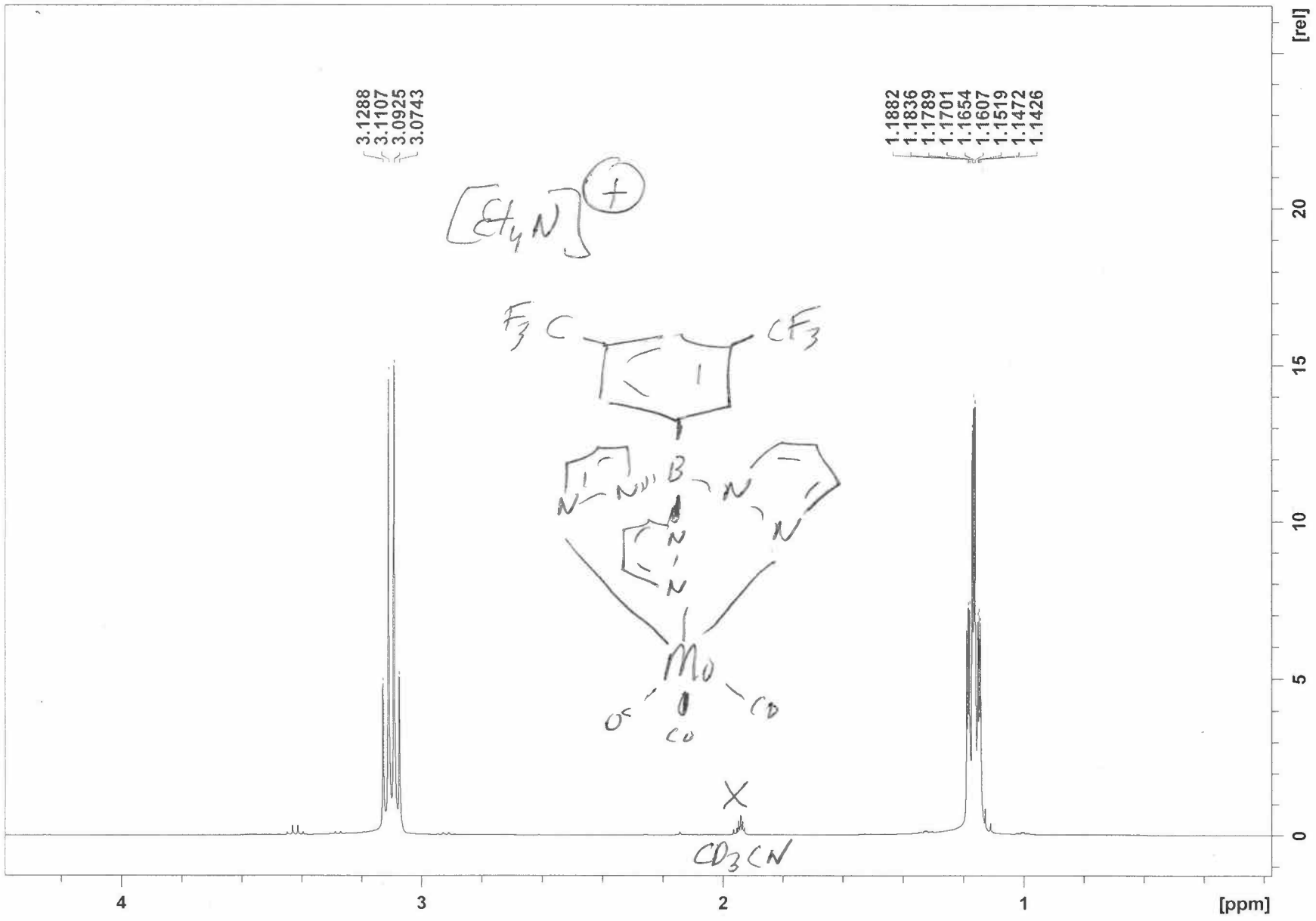
8

CD_3CN

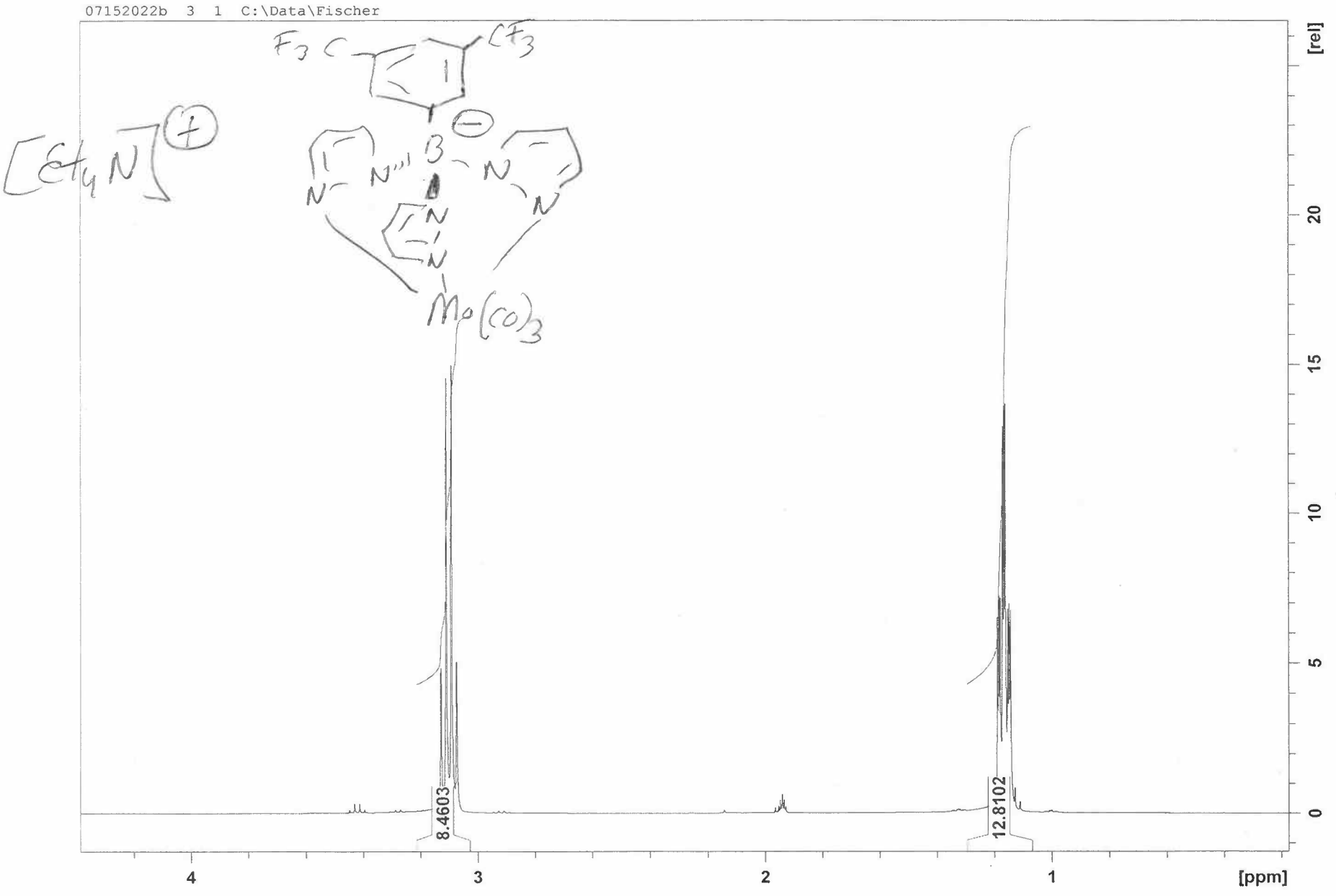

07152022b 3 1 C:\Data\Fischer
8
8.4618
8.1551
7.8553
7.8509
7.3780
7.3720
6.1436
6.1382
6.1328
[rel]
15
10
5
0
9
8
7
6
[ppm]
^1H NMR
$[Et_4N]^+$
CF_3
F_3C
B
N
Mo
OC
CO


07152022b 3 1 C:\Data\Fischer
^1H NMR CD_3CN
8
$[Et_4N]^+$
F_3C
CF_3
B
N
Mo
CO
2.0585
0.9485
2.7076
3.0410
3.0000
9
8
7
6
[ppm]
[rel]
0
2
4
6

^1H NMR CD_3CN (8)

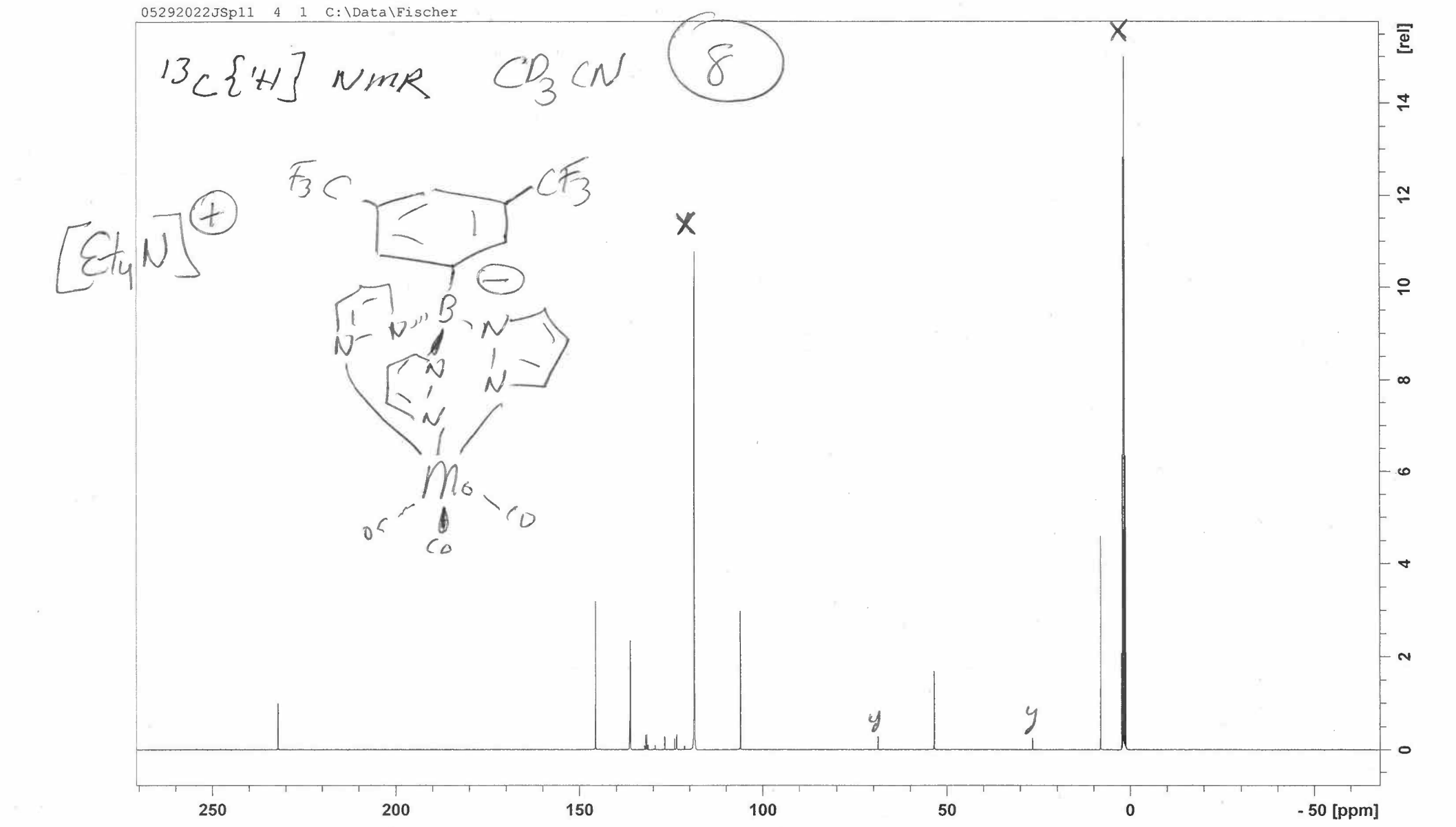


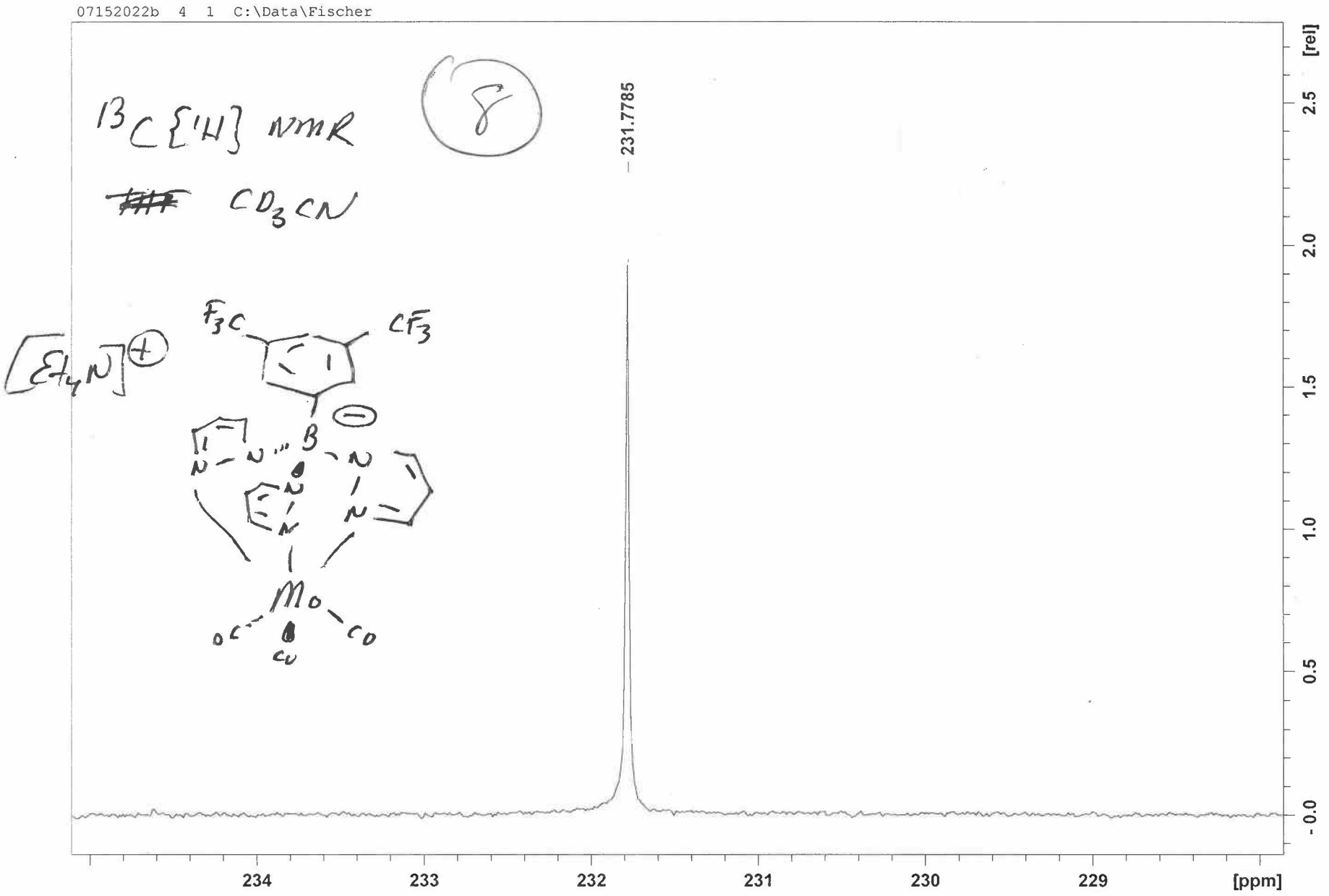
^1H NMR CD_3CN (8)



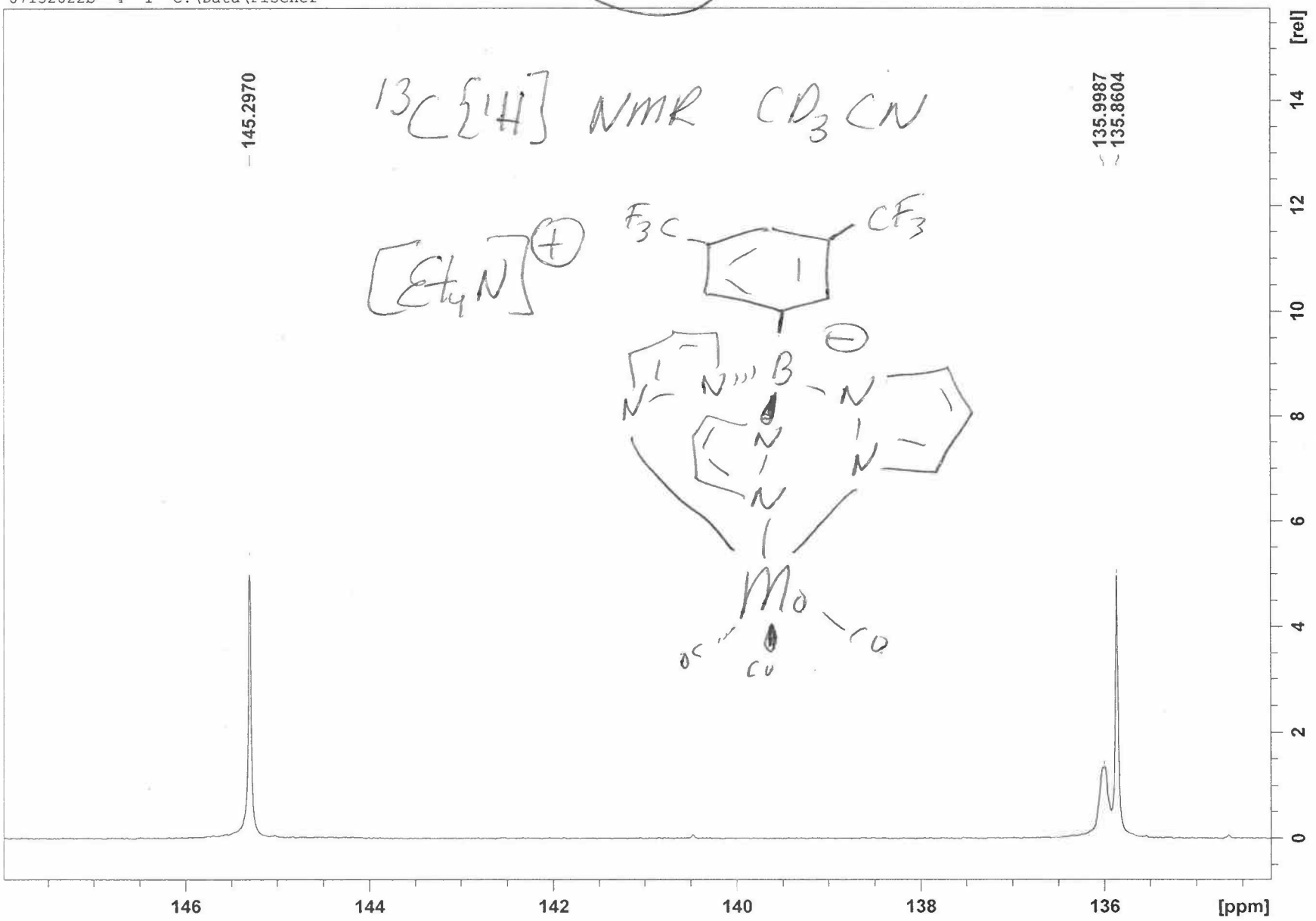
x CD_3CN

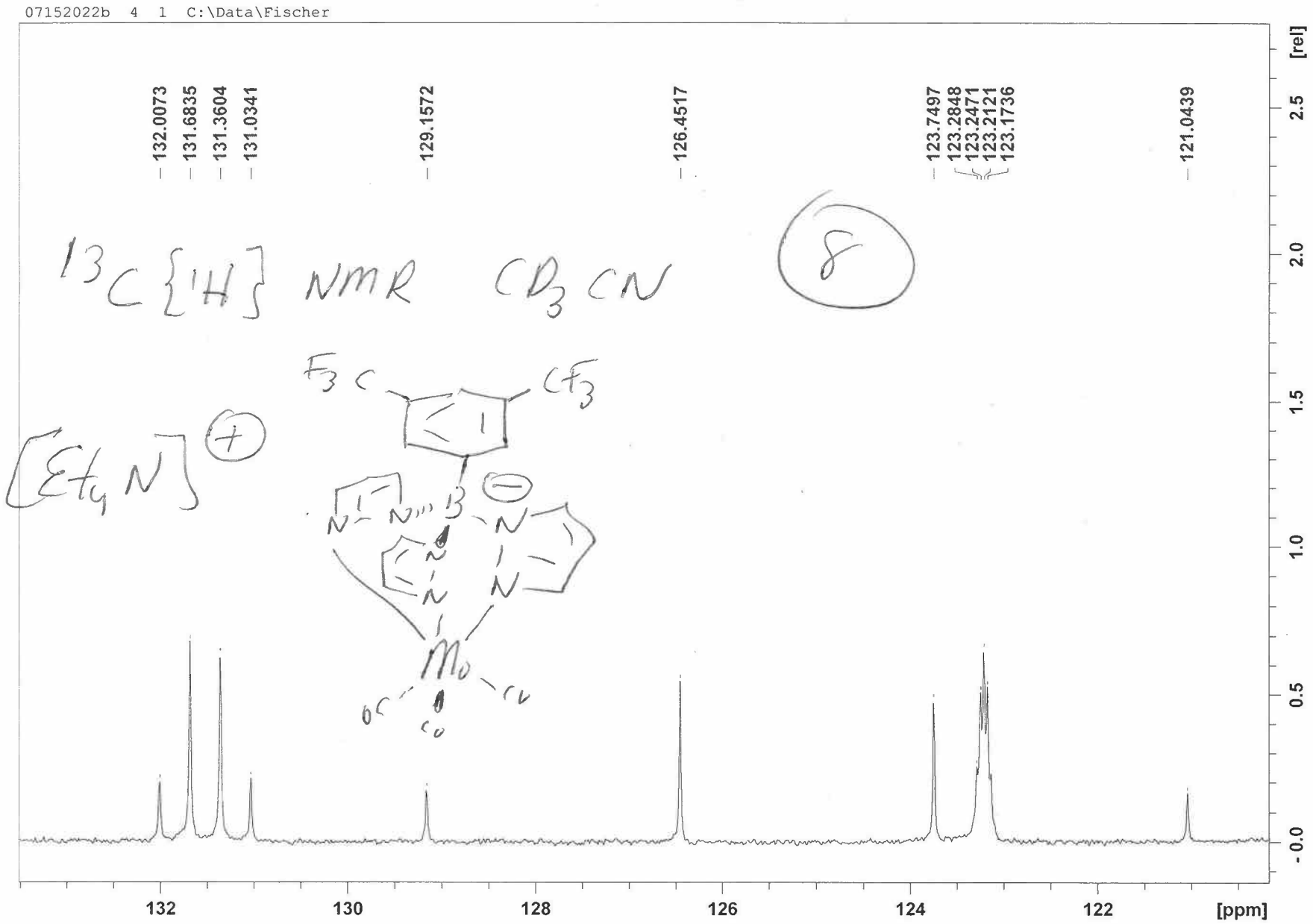
y THF

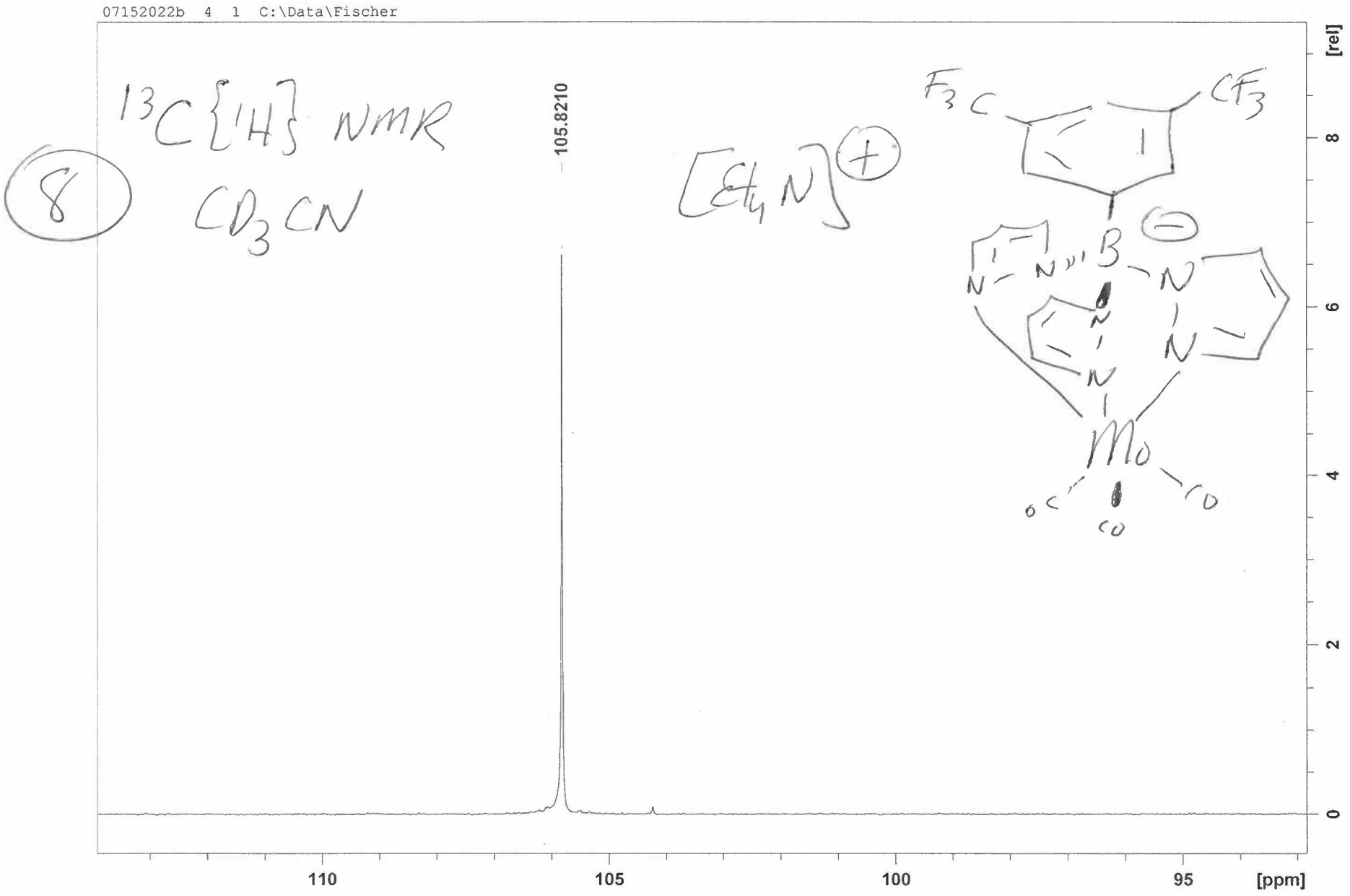

05292022JSp11 4 1 C:\Data\Fischer
$^{13}C\{^1H\}$ NMR CD_3CN
8
$[Et_4N]^+$
F_3C
CF_3
B
Mo
OC
CO
CO
x
x
y
y
0
2
4
6
8
10
12
14
[rel]
250
200
150
100
50
0
- 50 [ppm]


07152022b 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR
8
~~###~~ CD_3CN
$[Et_4N]^{\oplus}$
F_3C
CF_3
Mo
OC
CO
CO
231.7785
[rel]
2.5
2.0
1.5
1.0
0.5
- 0.0
234
233
232
231
230
229
[ppm]

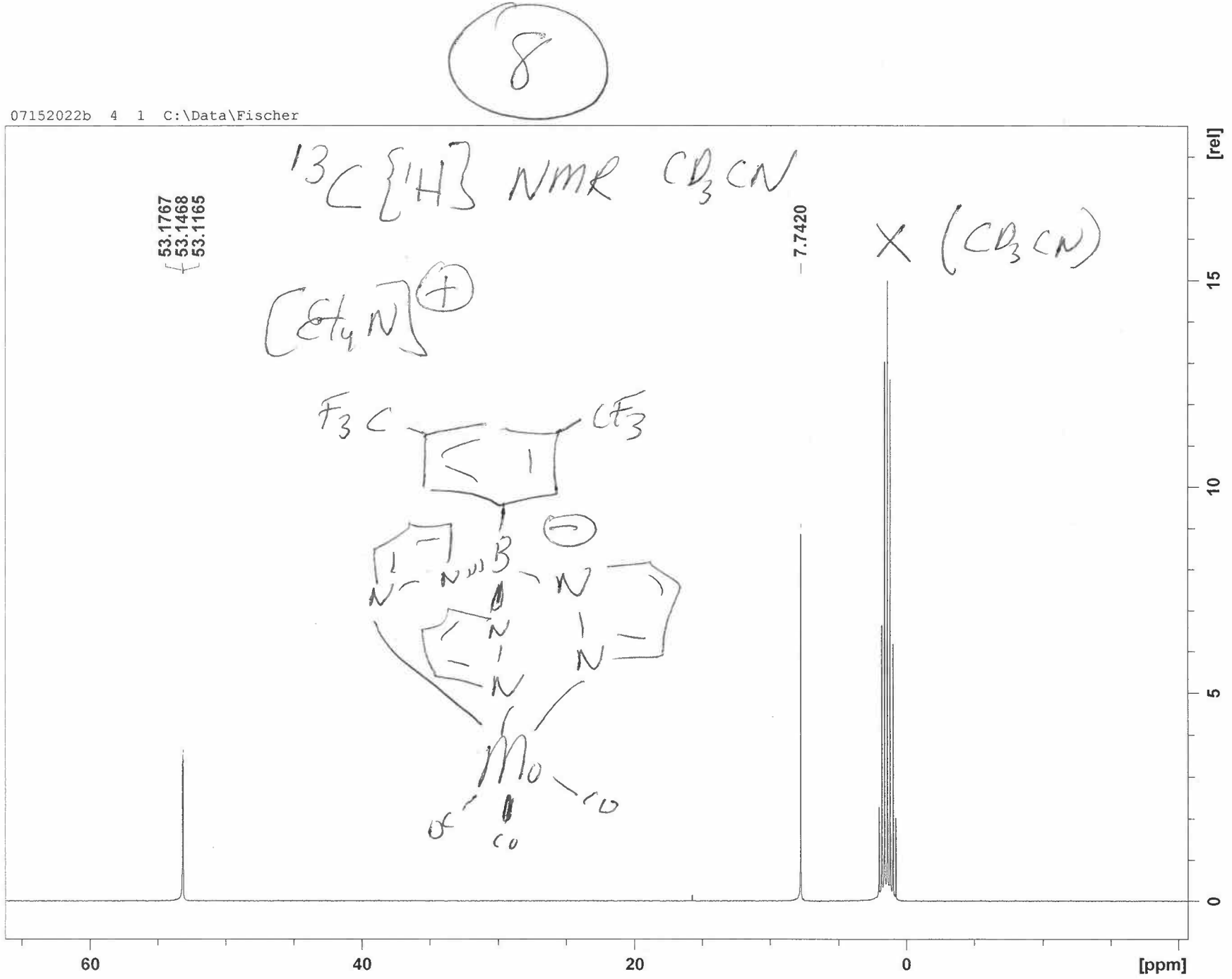
8


07152022b 4 1 C:\Data\Fischer
145.2970
135.9987
135.8604
$^{13}C\{^{1}H\}$ NMR CD_3CN
$[Et_4N]^{+}$
F_3C
CF_3
B
N
Mo
CO
[rel]
0
2
4
6
8
10
12
14
146
144
142
140
138
136
[ppm]

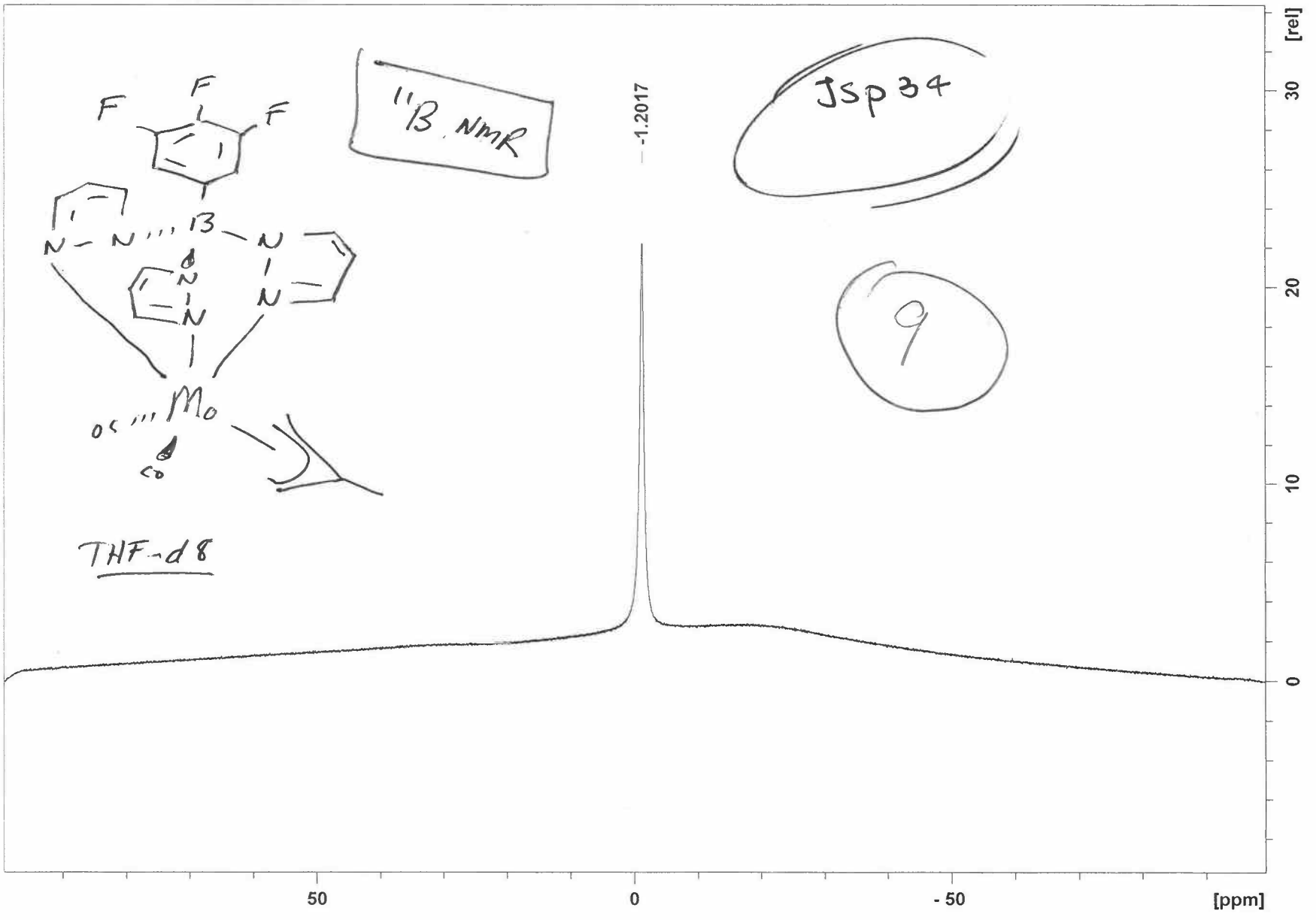

07152022b 4 1 C:\Data\Fischer
132.0073
131.6835
131.3604
131.0341
129.1572
126.4517
123.7497
123.2848
123.2471
123.2121
123.1736
121.0439
[rel]
2.5
2.0
1.5
1.0
0.5
- 0.0
132
130
128
126
124
122
[ppm]
13C{1H} NMR CD3CN
8
[Et4N]+
F3C
CF3
B
Mo
OC
CO
CO

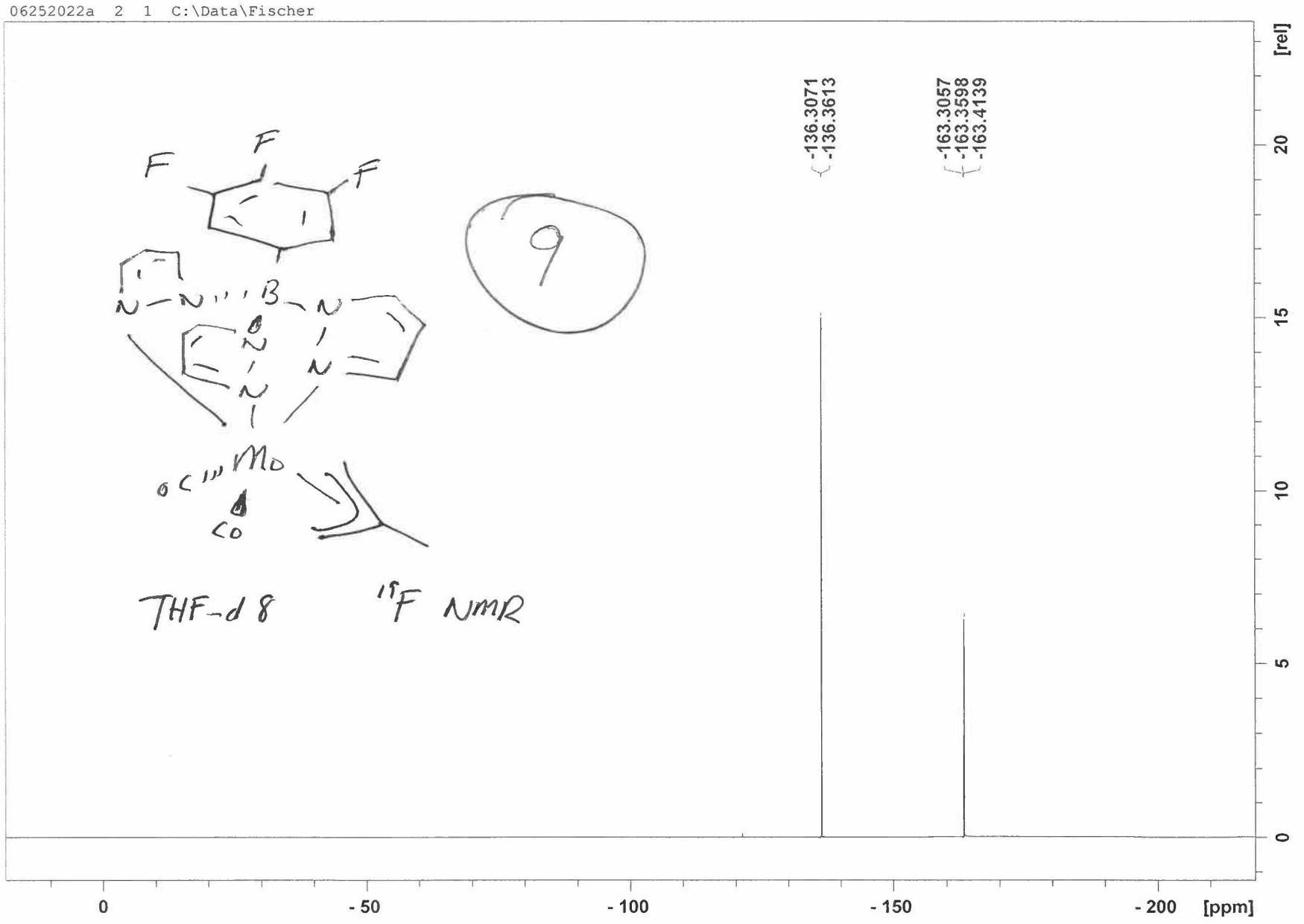

07152022b 4 1 C:\Data\Fischer
8
$^{13}C\{^{1}H\}$ NMR
CD_3CN
105.8210
$[Et_4N]^{+}$
F_3C
CF_3
B
N
Mo
OC
CO
[rel]
0
2
4
6
8
110
105
100
95
[ppm]

8

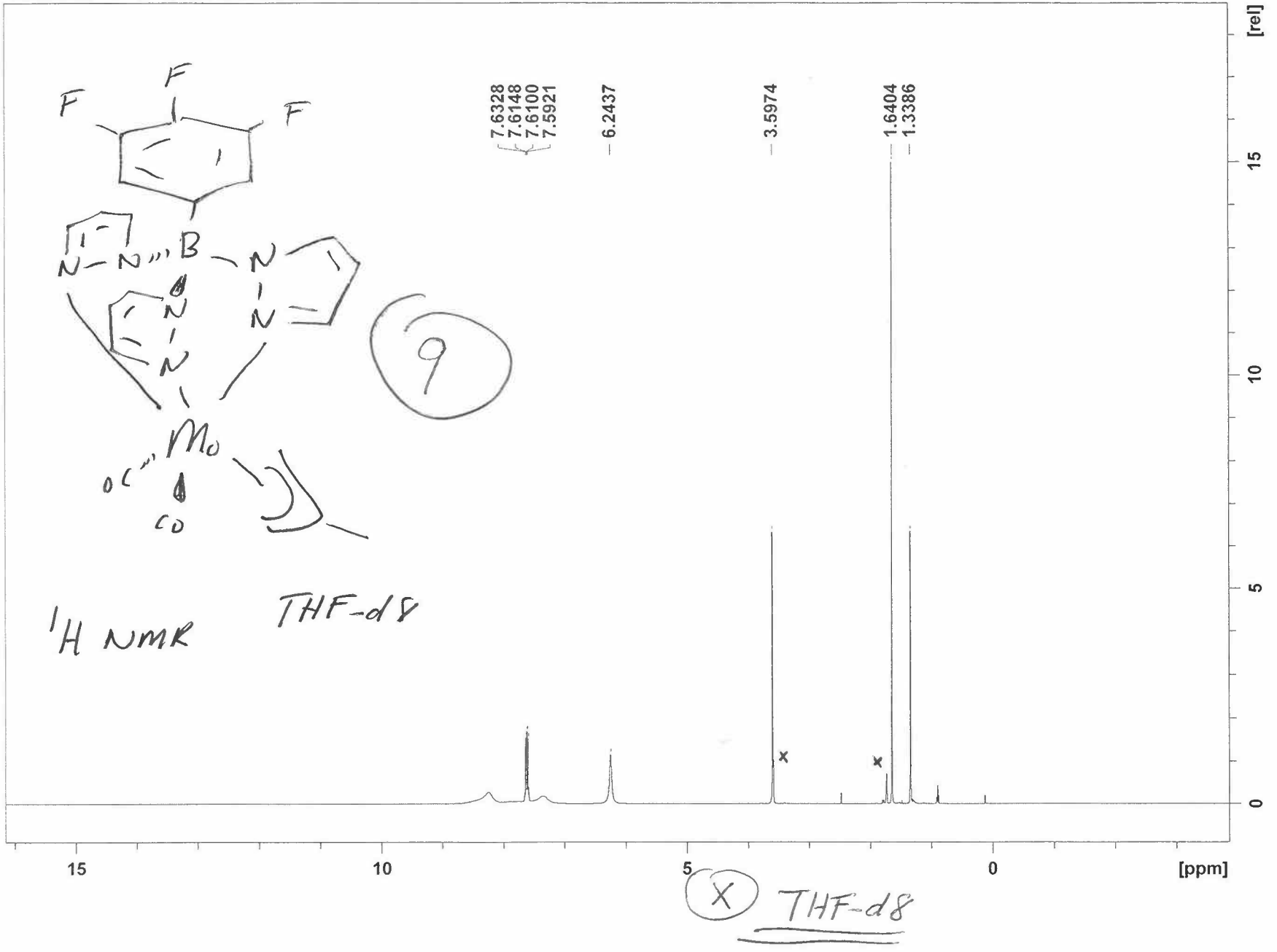

07152022b 4 1 C:\Data\Fischer
13C{1H} NMR CD3CN
53.1767
53.1468
53.1165
7.7420
X (CD3CN)
[Et4N]+
F3C
CF3
B
N
Mo
CO
[rel]
15
10
5
0
60
40
20
0
[ppm]

06252022a 1 1 C:\Data\Fischer



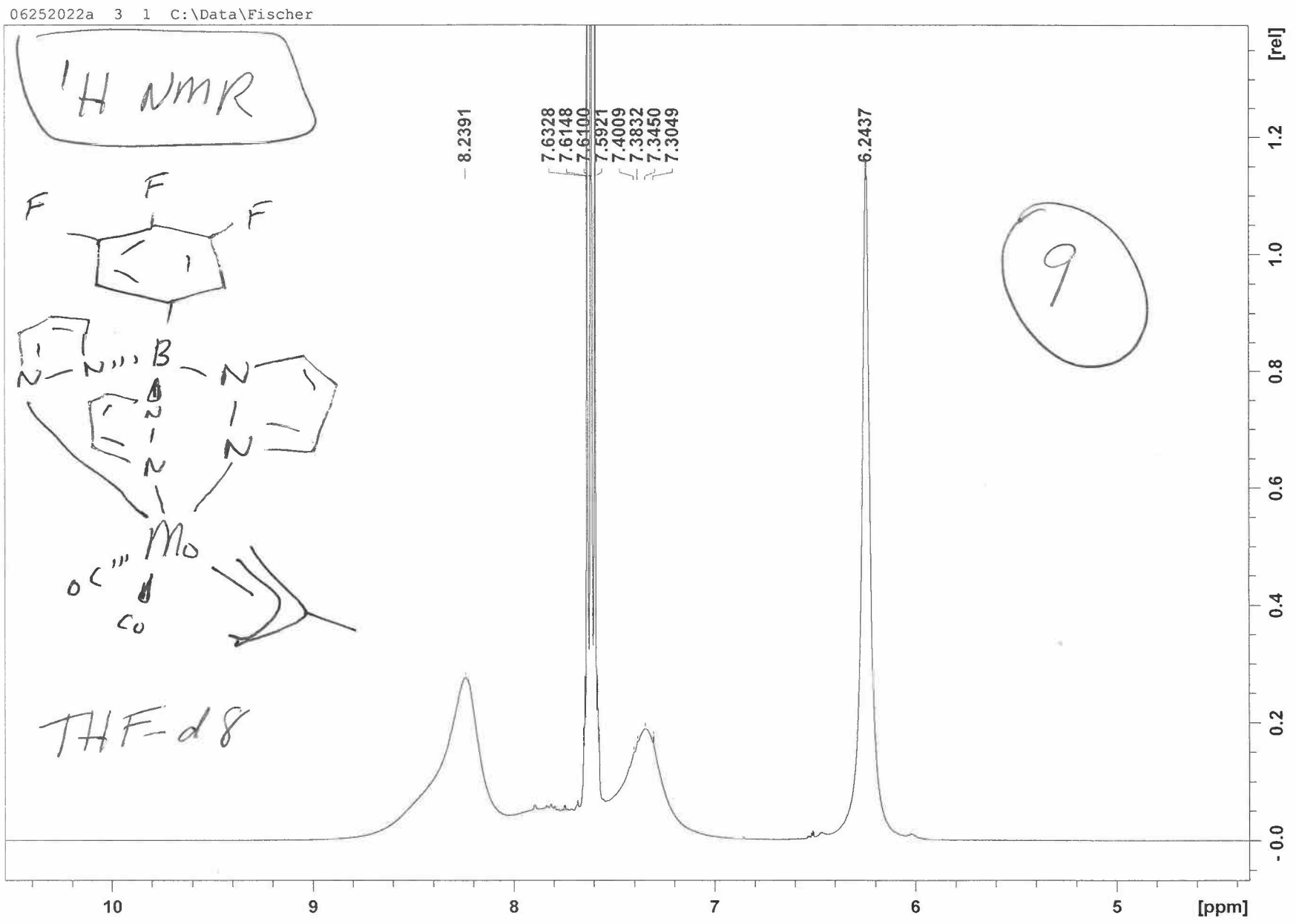

06252022a 2 1 C:\Data\Fischer
-136.3071
-136.3613
-163.3057
-163.3598
-163.4139
[rel]
0
5
10
15
20
0
- 50
- 100
- 150
- 200
[ppm]
F
F
F
9
THF-d 8
19F NMR

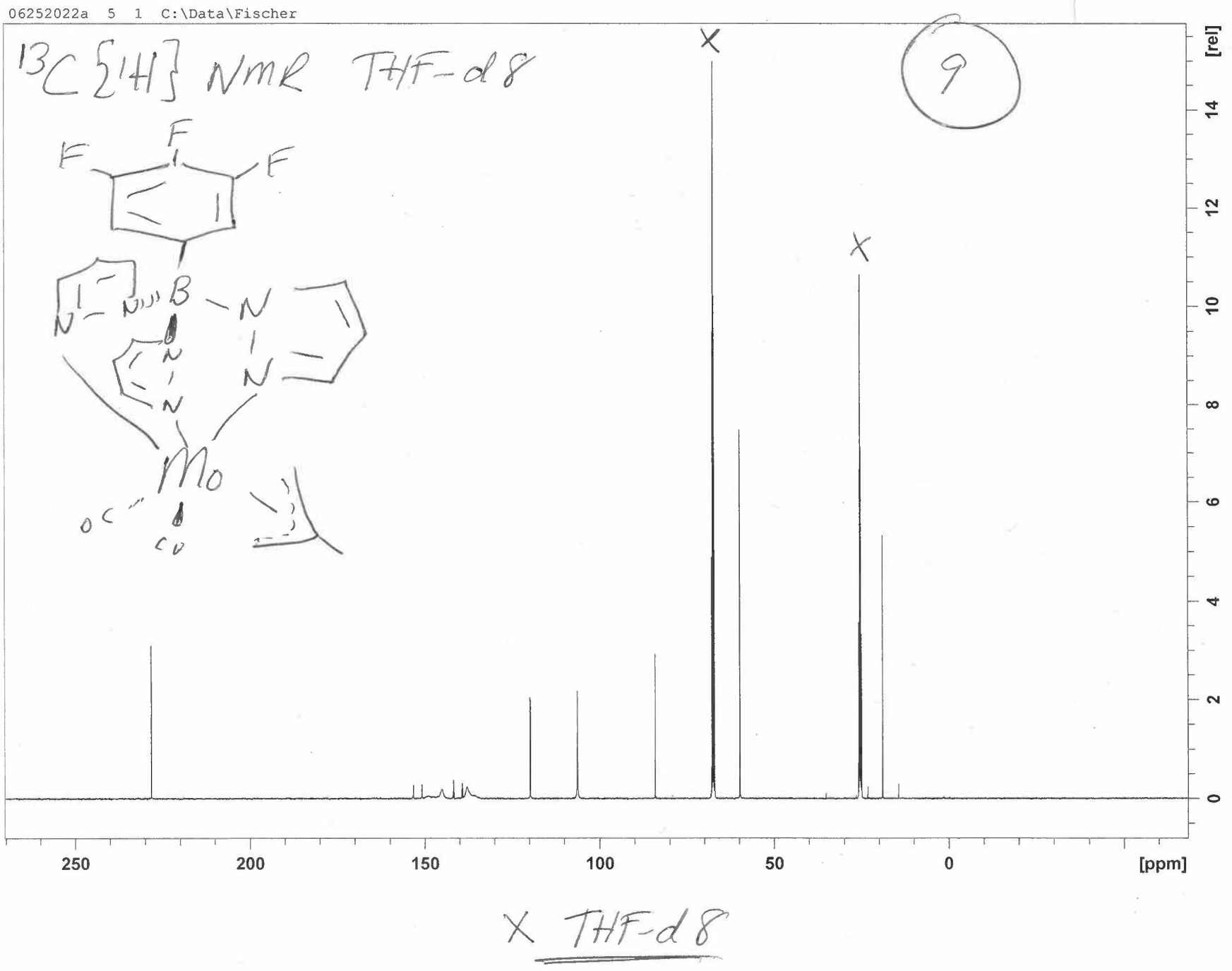
06252022a 3 1 C:\Data\Fischer



9

^1H NMR THF-d8


06252022a 3 1 C:\Data\Fischer
^{1}H NMR
8.2391
7.6328
7.6148
7.6100
7.5921
7.4009
7.3832
7.3450
7.3049
6.2437
9
THF-d8
[rel]
1.2
1.0
0.8
0.6
0.4
0.2
-0.0
10
9
8
7
6
5
[ppm]

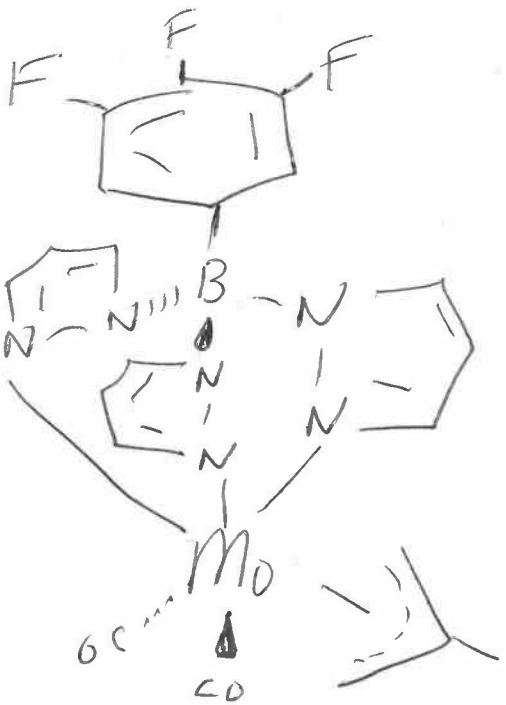

06252022a 5 1 C:\Data\Fischer
$^{13}C\{^1H\}$ NMR THF-d8
9
X
X
F
F
F
B
N
Mo
OC
CO
[rel]
0
2
4
6
8
10
12
14
250
200
150
100
50
0
[ppm]

X THF-d8

06252022a 5 1 C:\Data\Fischer

$^{13}C\{^{1}H\}$ NMR

THF-d 8



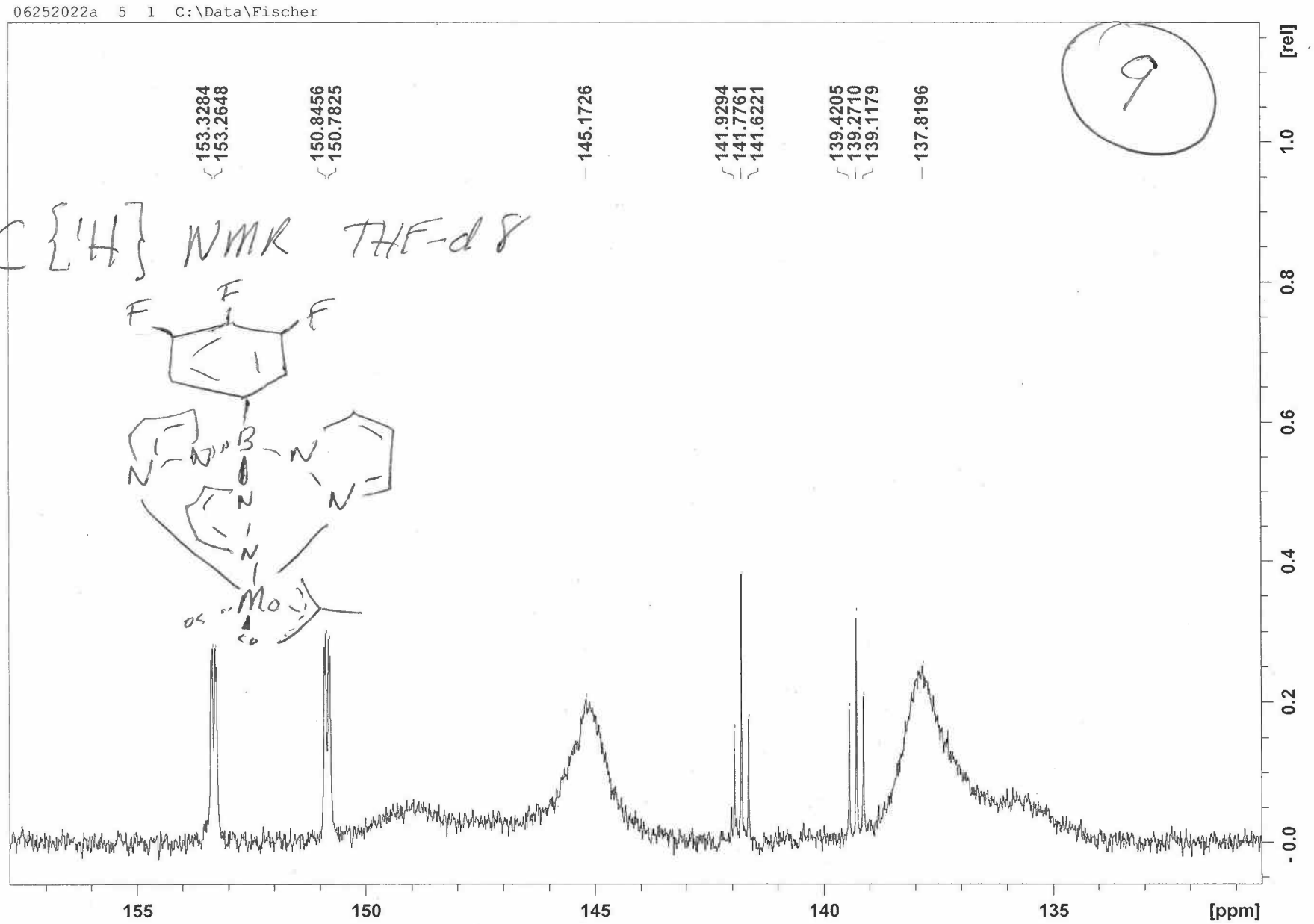
9

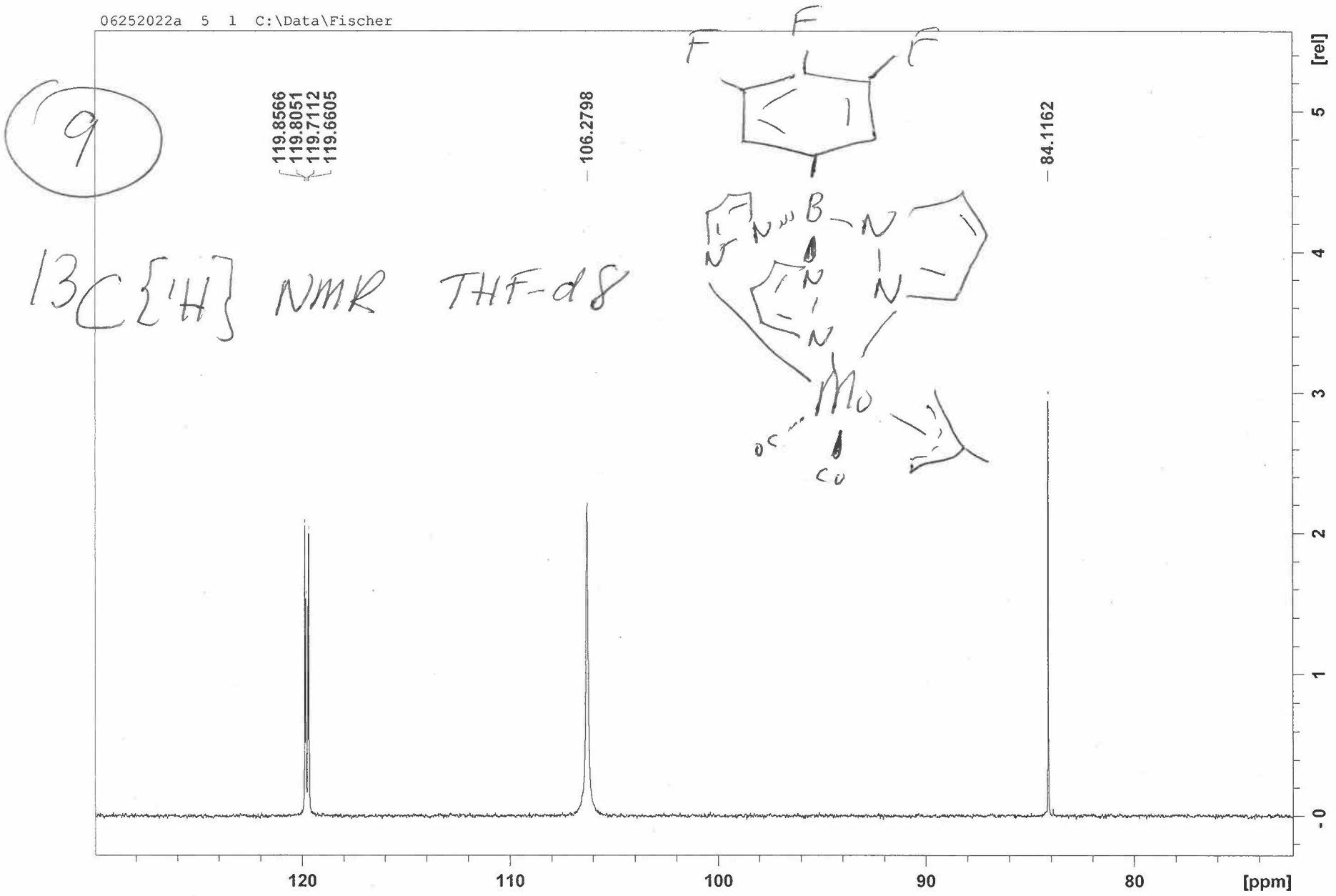
228.2124

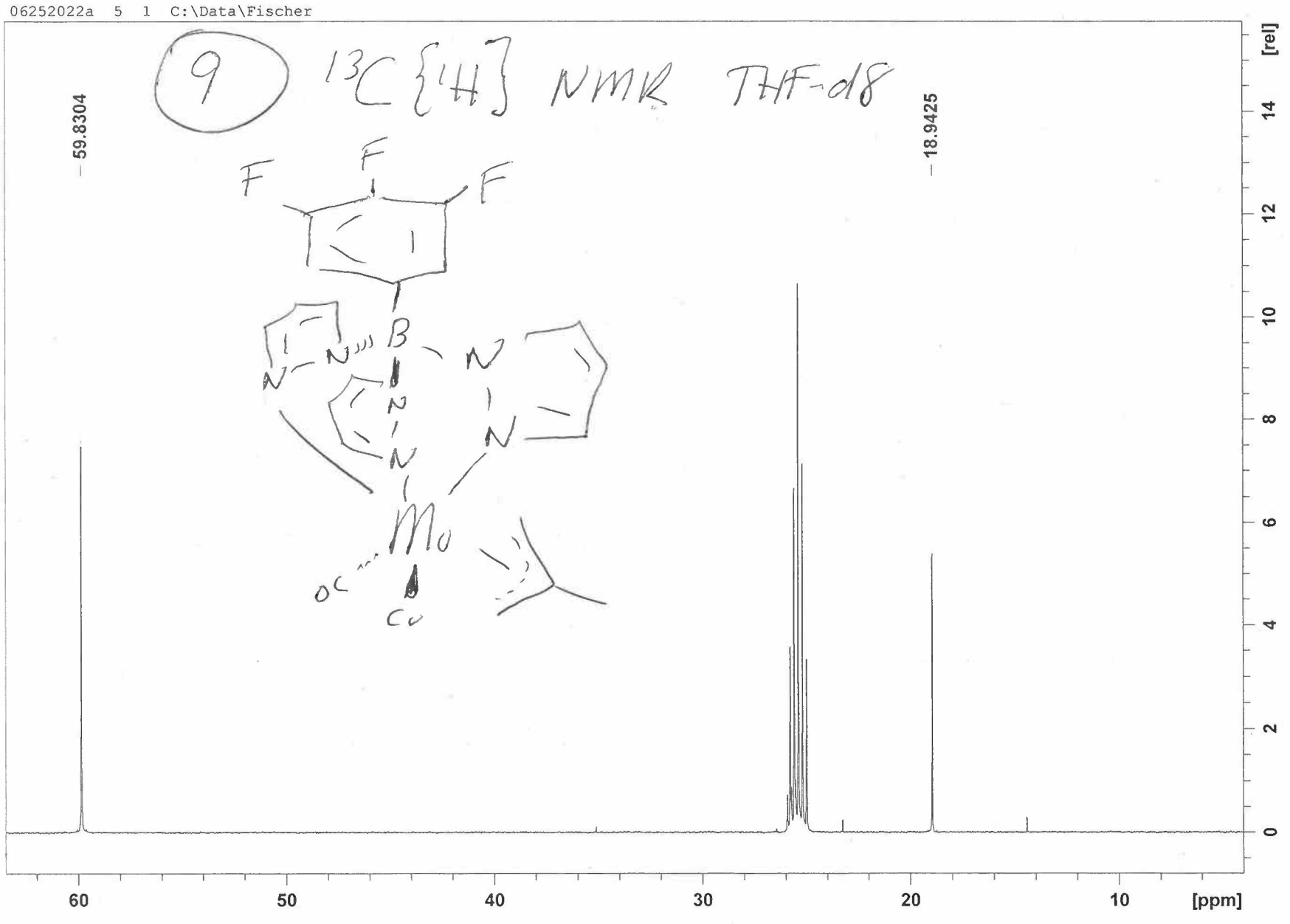
[rel]

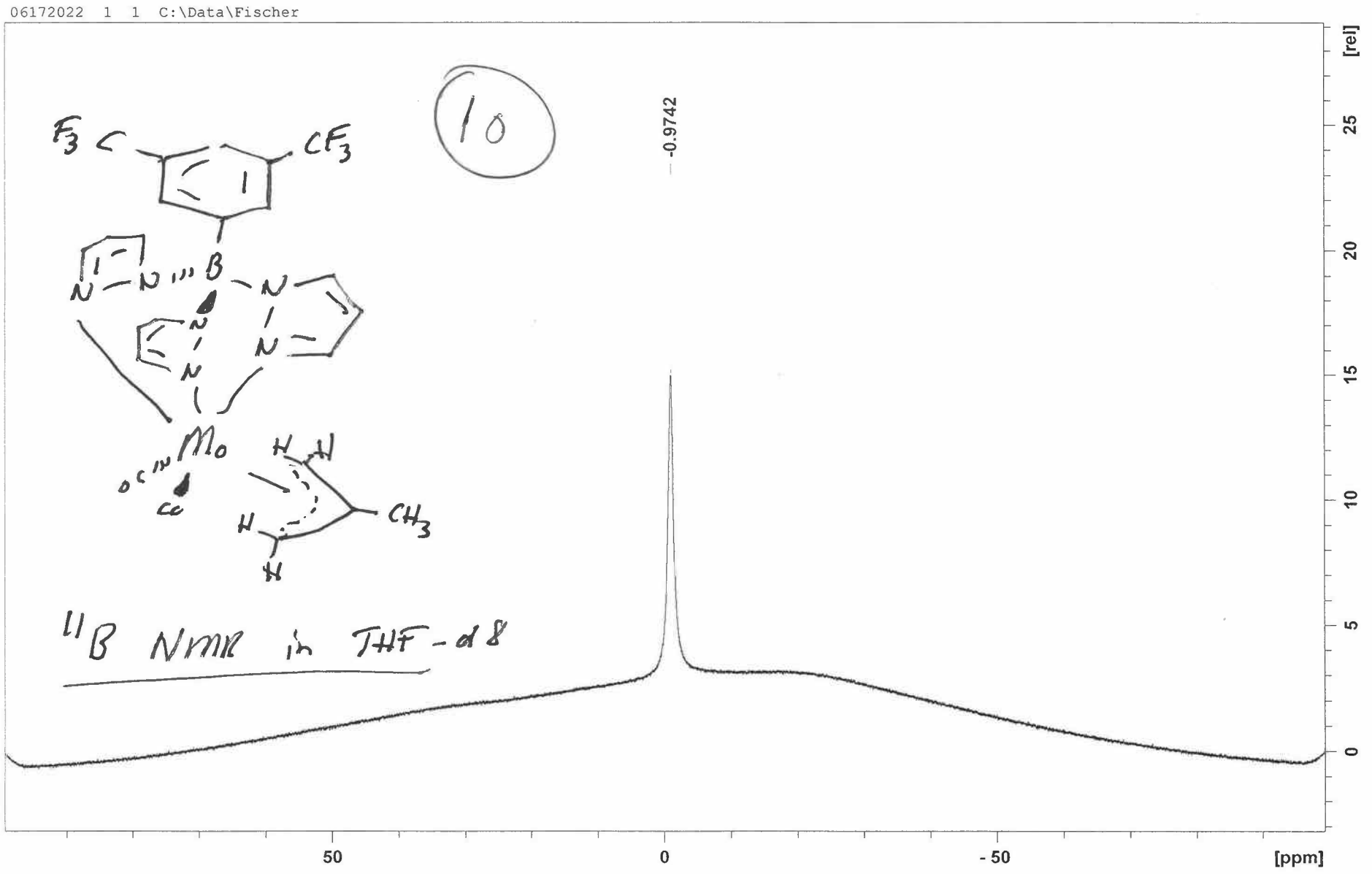
6 5 4 3 2 1 0

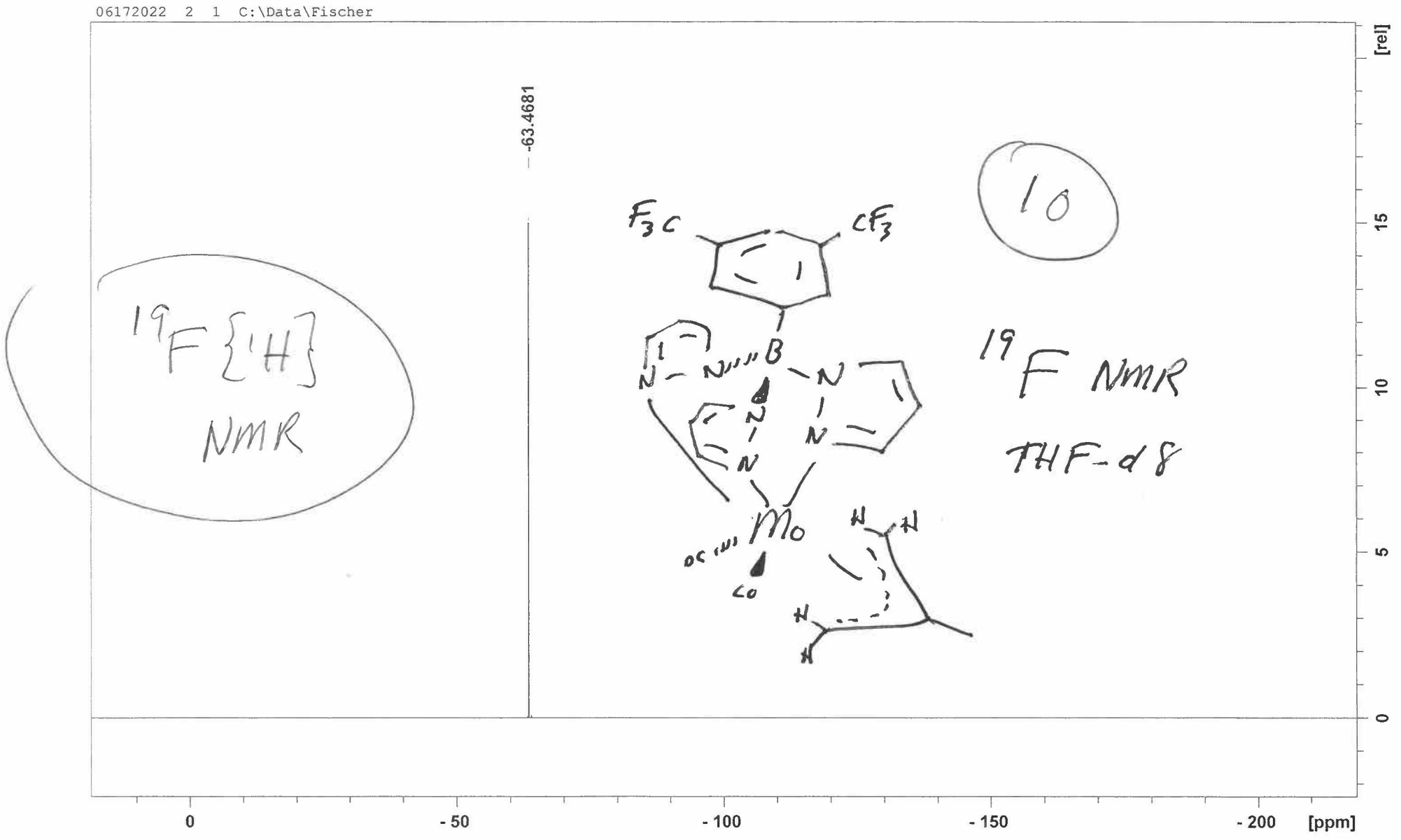
231 230 229 228 227 226 225 [ppm]

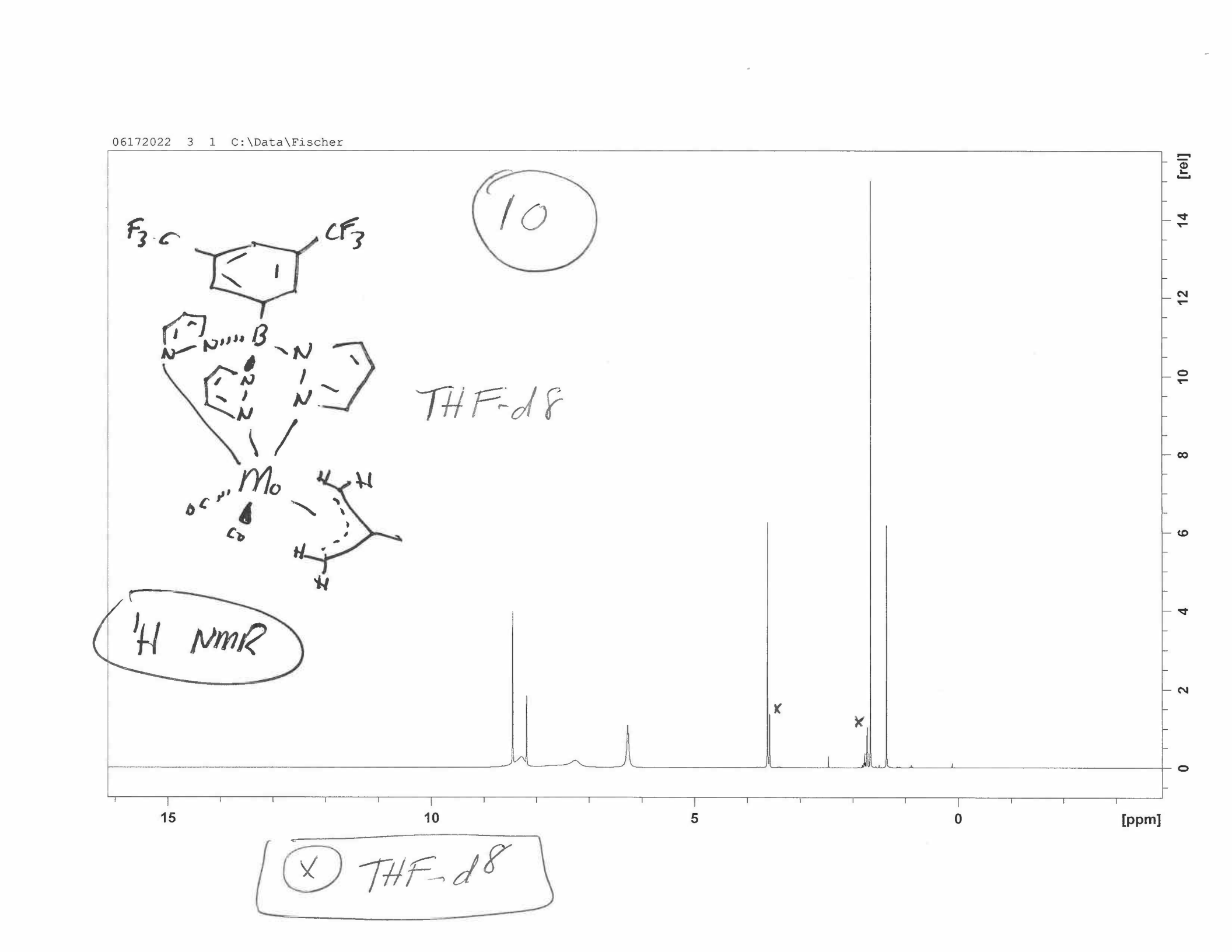

06252022a 5 1 C:\Data\Fischer
153.3284
153.2648
150.8456
150.7825
145.1726
141.9294
141.7761
141.6221
139.4205
139.2710
139.1179
137.8196
9
13C {1H} NMR THF-d8
F
F
F
B
N
N
N
N
N
N
Mo
OC
CO
[rel]
1.0
0.8
0.6
0.4
0.2
-0.0
155
150
145
140
135
[ppm]

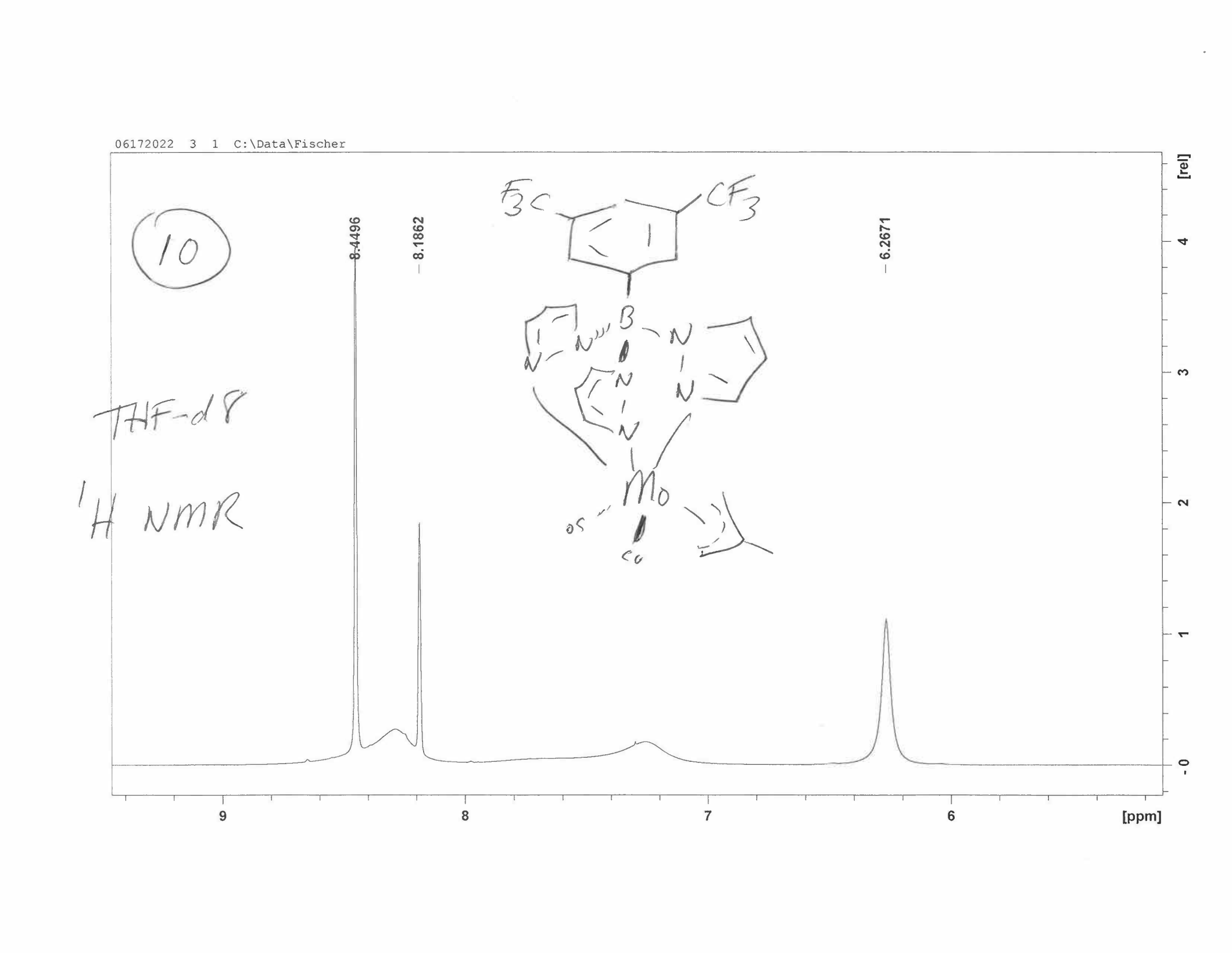

06252022a 5 1 C:\Data\Fischer
9
119.8566
119.8051
119.7112
119.6605
106.2798
84.1162
13C{1H} NMR THF-d8
F
F
F
B
N
Mo
OC
CO
[rel]
5
4
3
2
1
-0
120
110
100
90
80
[ppm]

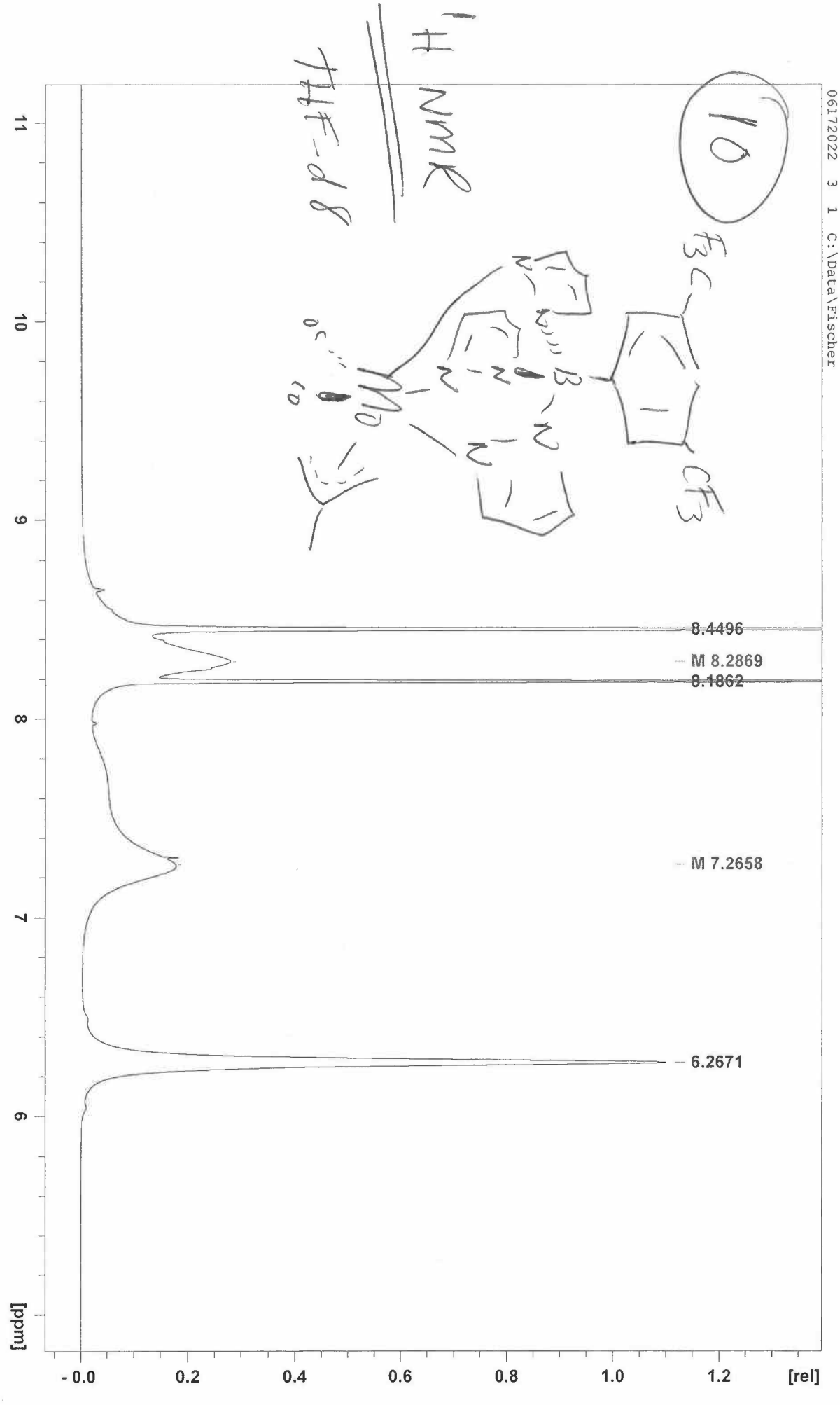

06252022a 5 1 C:\Data\Fischer
9
13C{1H} NMR THF-d8
59.8304
18.9425
F
F
F
B
N
Mo
OC
CO
[rel]
14
12
10
8
6
4
2
0
60
50
40
30
20
10
[ppm]


06172022 1 1 C:\Data\Fischer
10
-0.9742
[rel]
25
20
15
10
5
0
50
0
- 50
[ppm]
^{11}B NMR in THF-d8

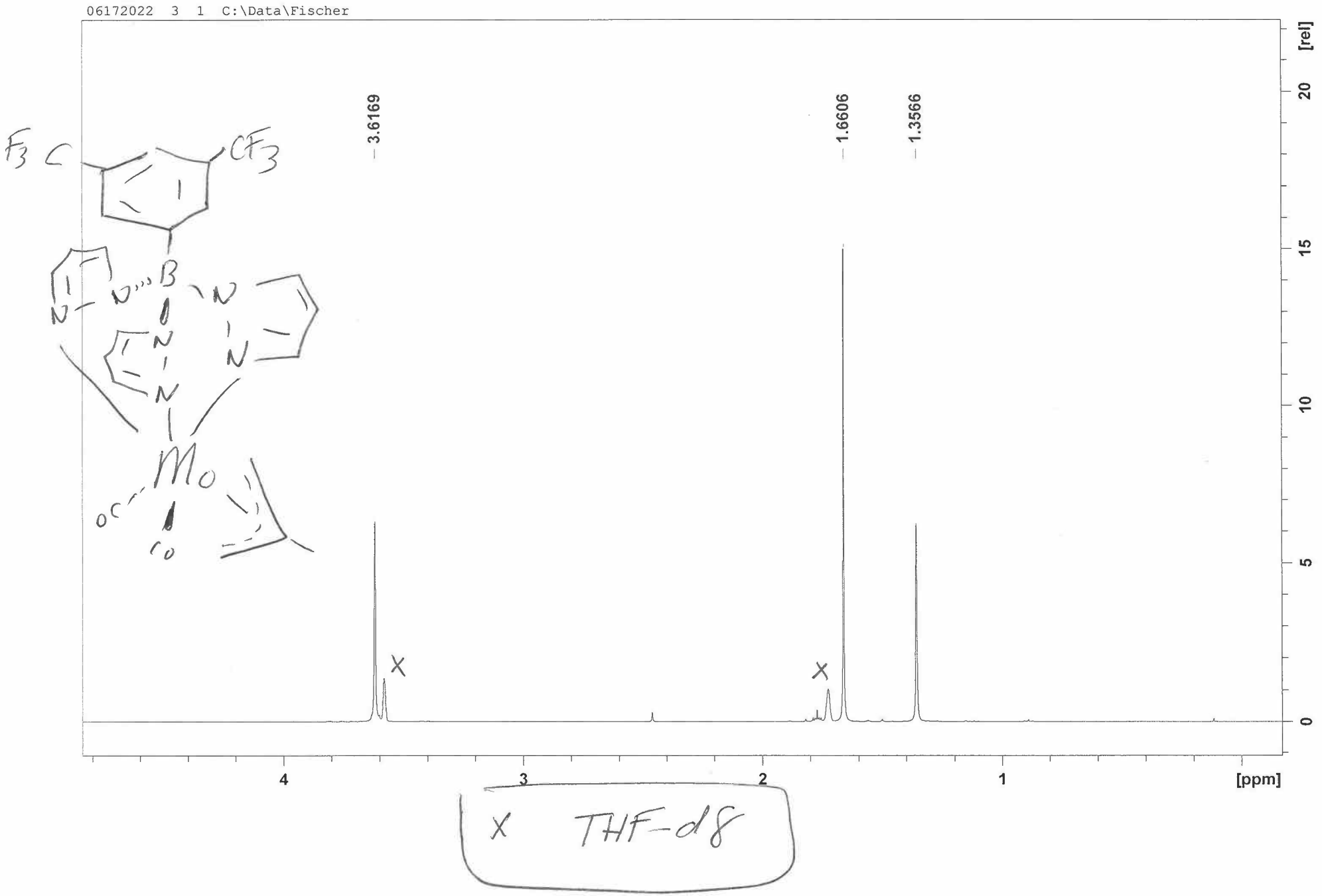

06172022 2 1 C:\Data\Fischer
-63.4681
[rel]
0
5
10
15
0
- 50
- 100
- 150
- 200
[ppm]
$^{19}F\{^{1}H\}$ NMR
10
^{19}F NMR
THF-d8


06172022 3 1 C:\Data\Fischer
10
THF-d8
1H NMR
X THF-d8
X
X
15
10
5
0
[ppm]
[rel]
0
2
4
6
8
10
12
14

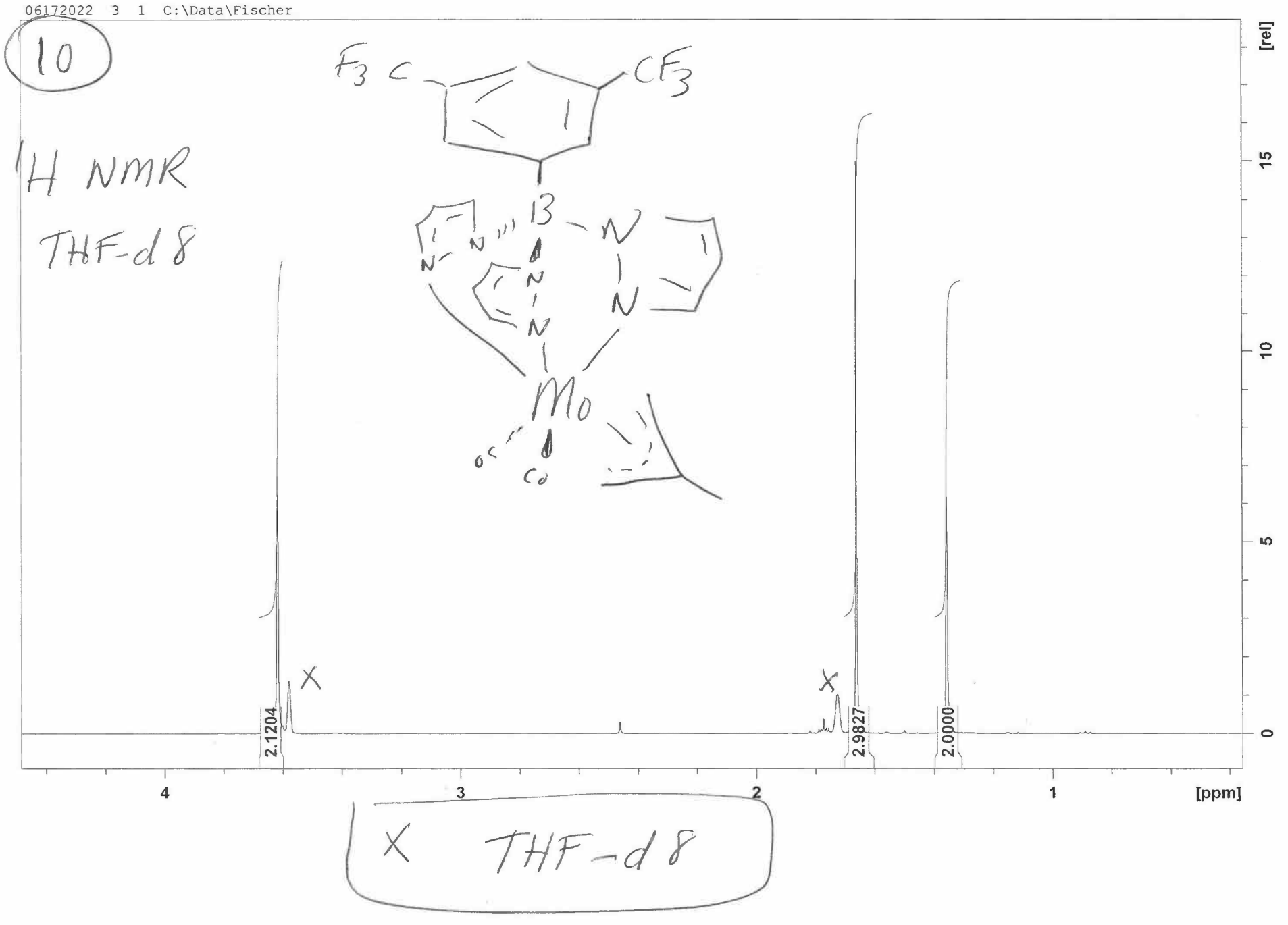

06172022 3 1 C:\Data\Fischer
10
8.4496
8.1862
6.2671
THF-d8
^{1}H NMR
F3C
CF3
B
N
Mo
OC
CO
[rel]
4
3
2
1
-0
9
8
7
6
[ppm]

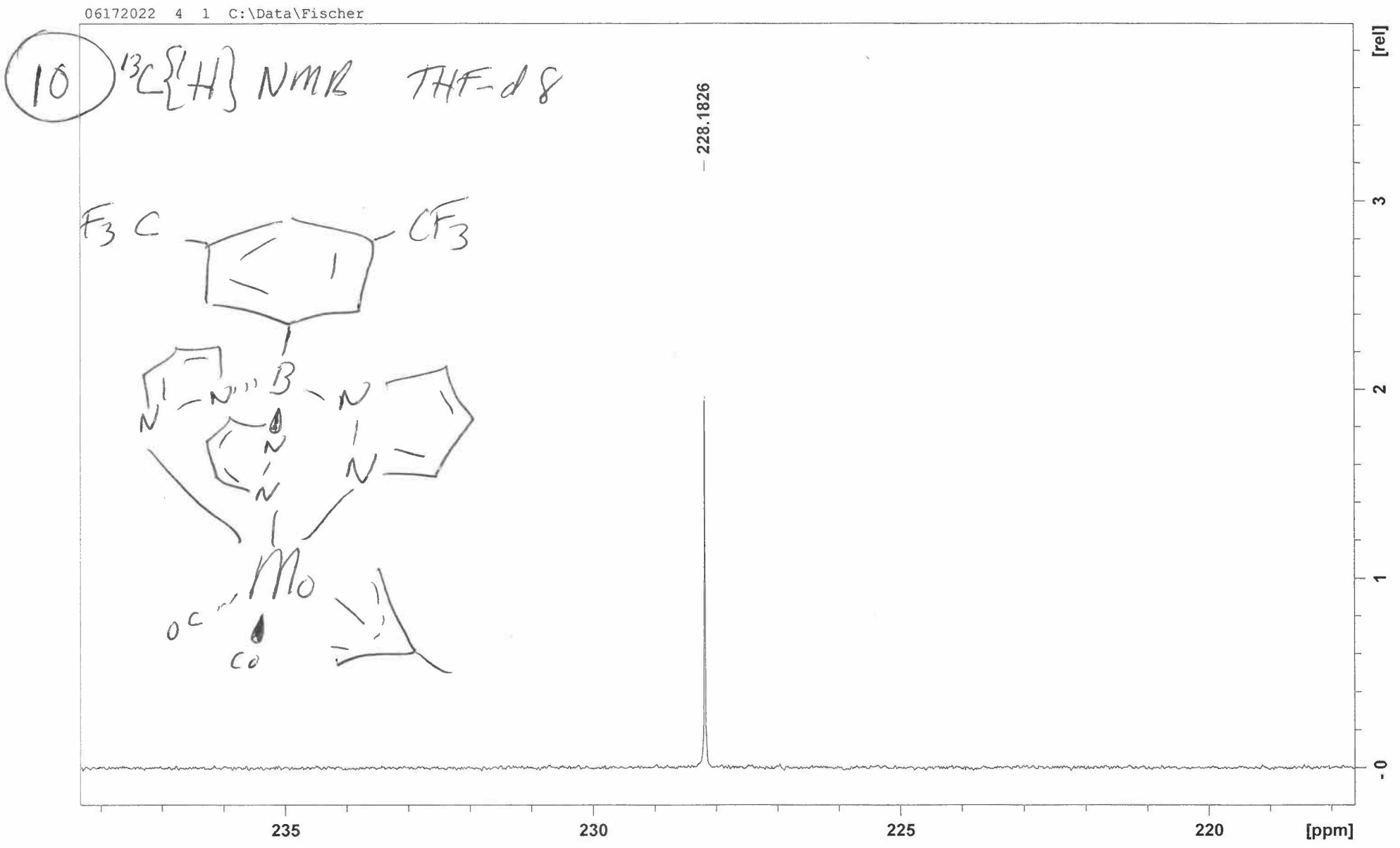

10
^{1}H NMR
THF-d8
F3C
CF3
B
N
O
O
8.4496
M 8.2869
8.1862
M 7.2658
6.2671
06172022 3 1 C:\Data\Fischer
11
10
9
8
7
6
[ppm]
- 0.0
0.2
0.4
0.6
0.8
1.0
1.2
[rel]

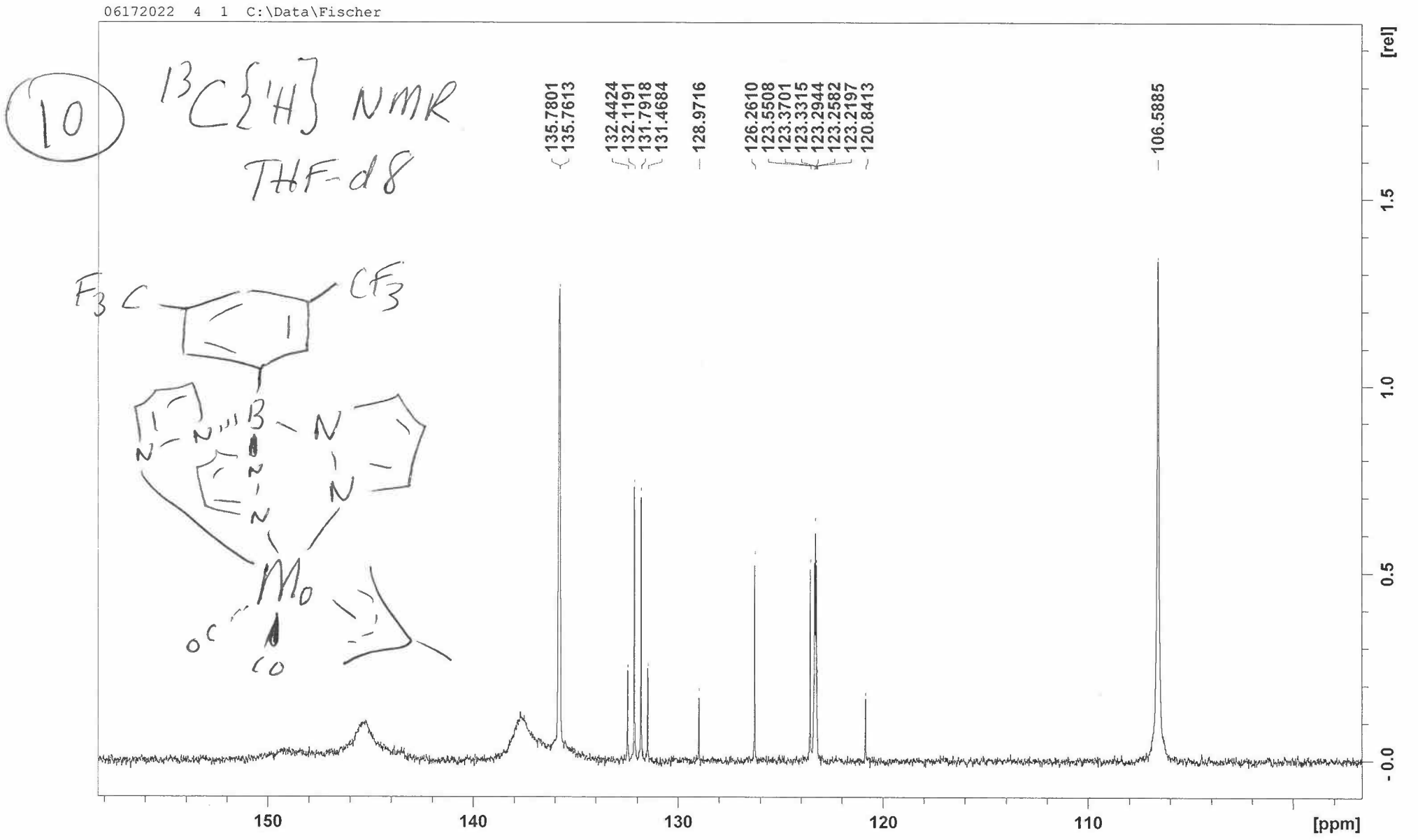
10 ^1H NMR THF-d8



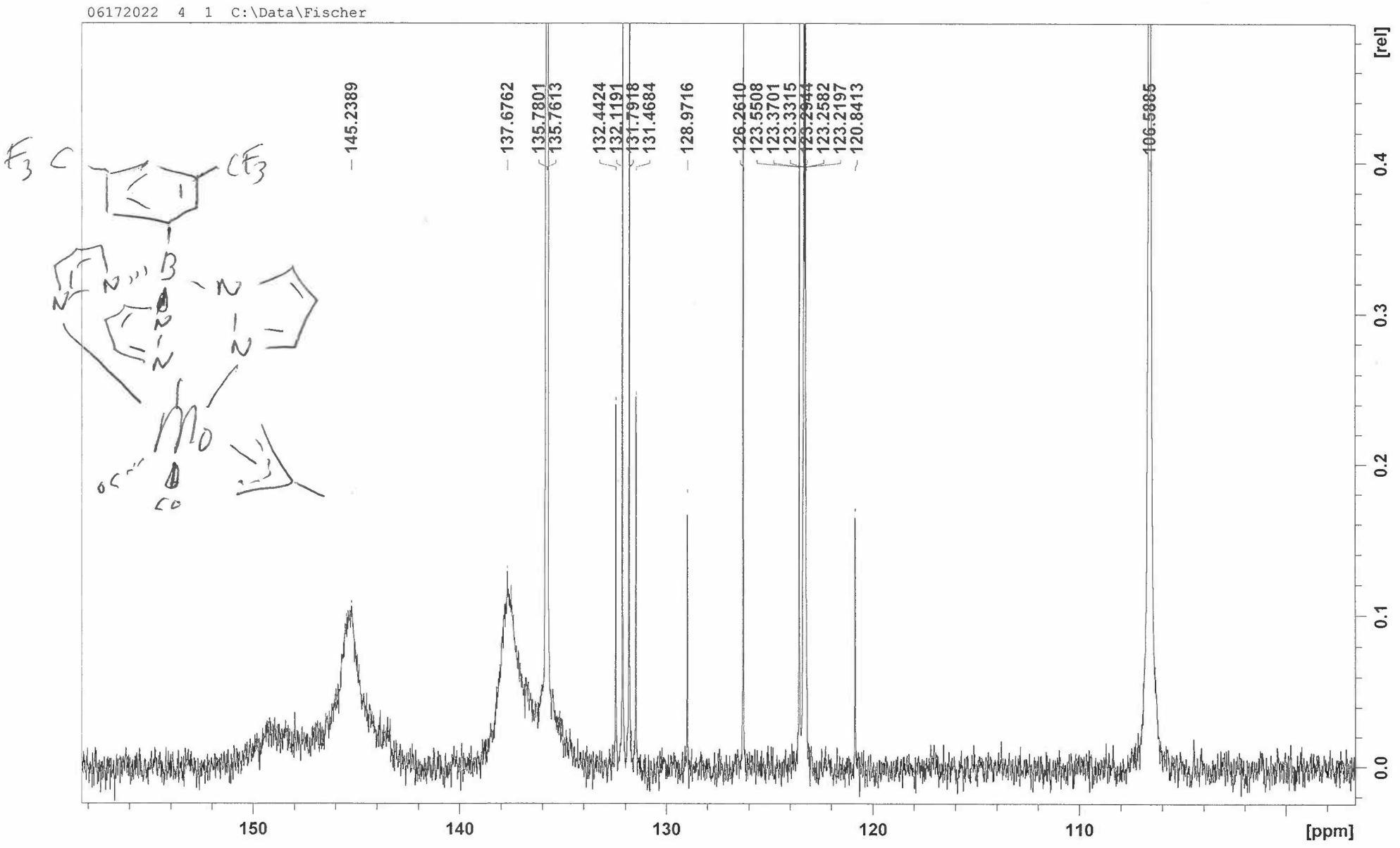
X THF-d8


06172022 3 1 C:\Data\Fischer
10
^{1}H NMR
THF-d 8
F3C
CF3
B
N
Mo
OC
CO
X
X
2.1204
2.9827
2.0000
4
3
2
1
[ppm]
[rel]
0
5
10
15
X THF-d 8

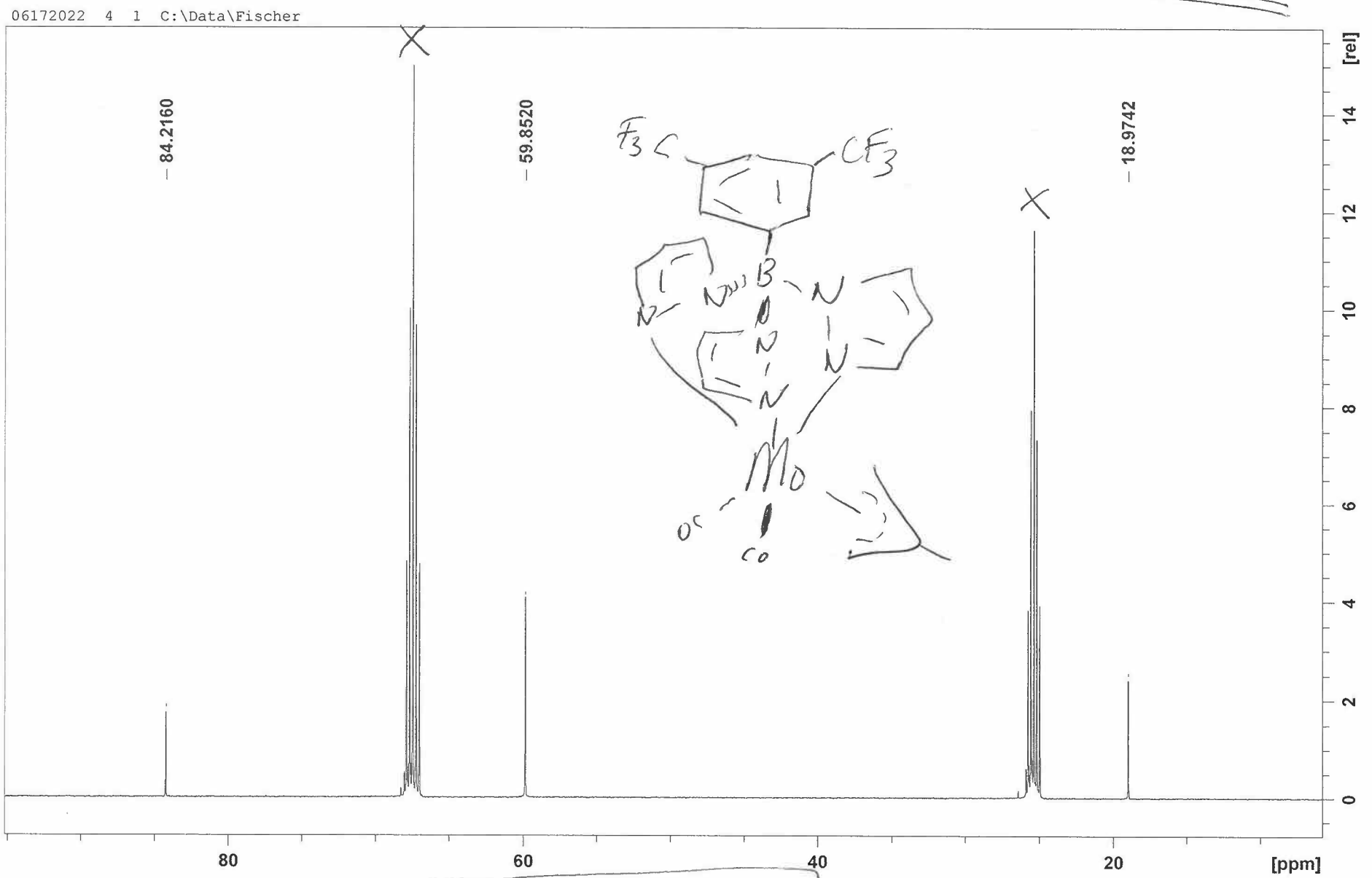

06172022 4 1 C:\Data\Fischer
10 $^{13}C\{^1H\}$ NMR THF-d 8
228.1826
F_3C
CF_3
B
N
Mo
OC
Co
[rel]
3
2
1
-0
235
230
225
220
[ppm]


06172022 4 1 C:\Data\Fischer
10
$^{13}C\{^{1}H\}$ NMR
THF-d8
135.7801
135.7613
132.4424
132.1191
131.7918
131.4684
128.9716
126.2610
123.5508
123.3701
123.3315
123.2944
123.2582
123.2197
120.8413
106.5885
[rel]
1.5
1.0
0.5
-0.0
150
140
130
120
110
[ppm]

10 $^{13}C\{^1H\}$ NMR THF-d8

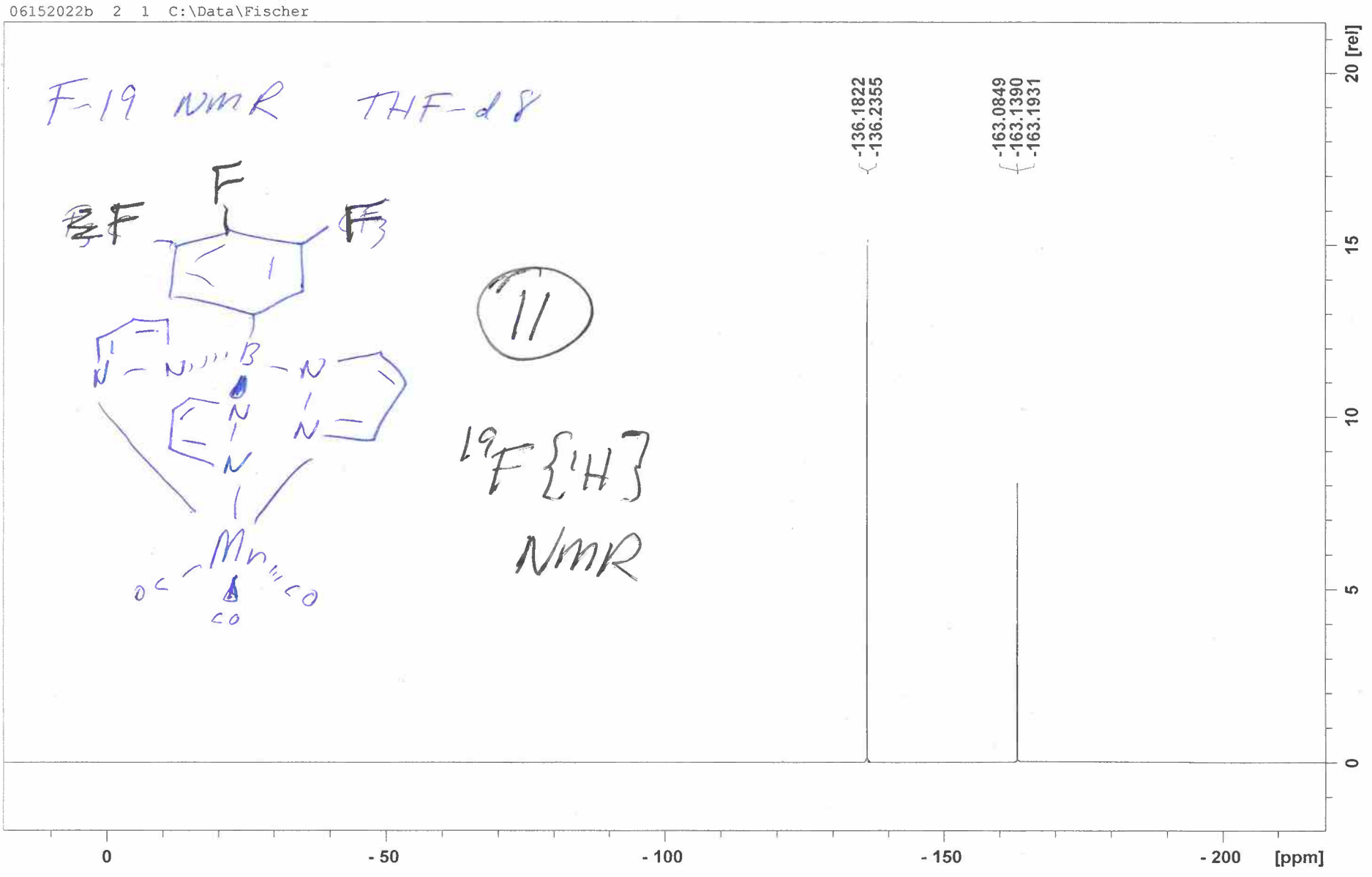


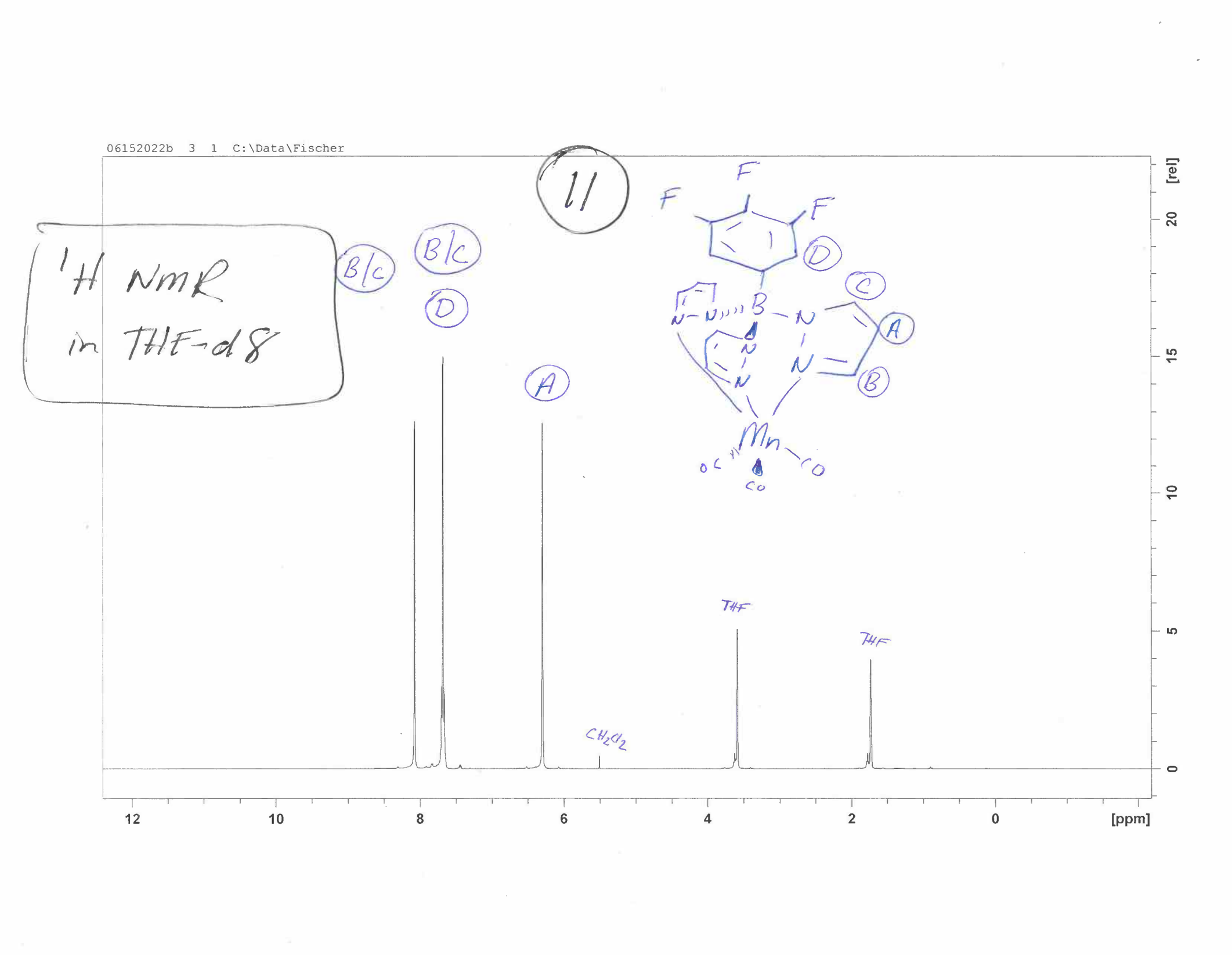
(10) $^{13}C\{^1H\}$ NMR CD_3CN

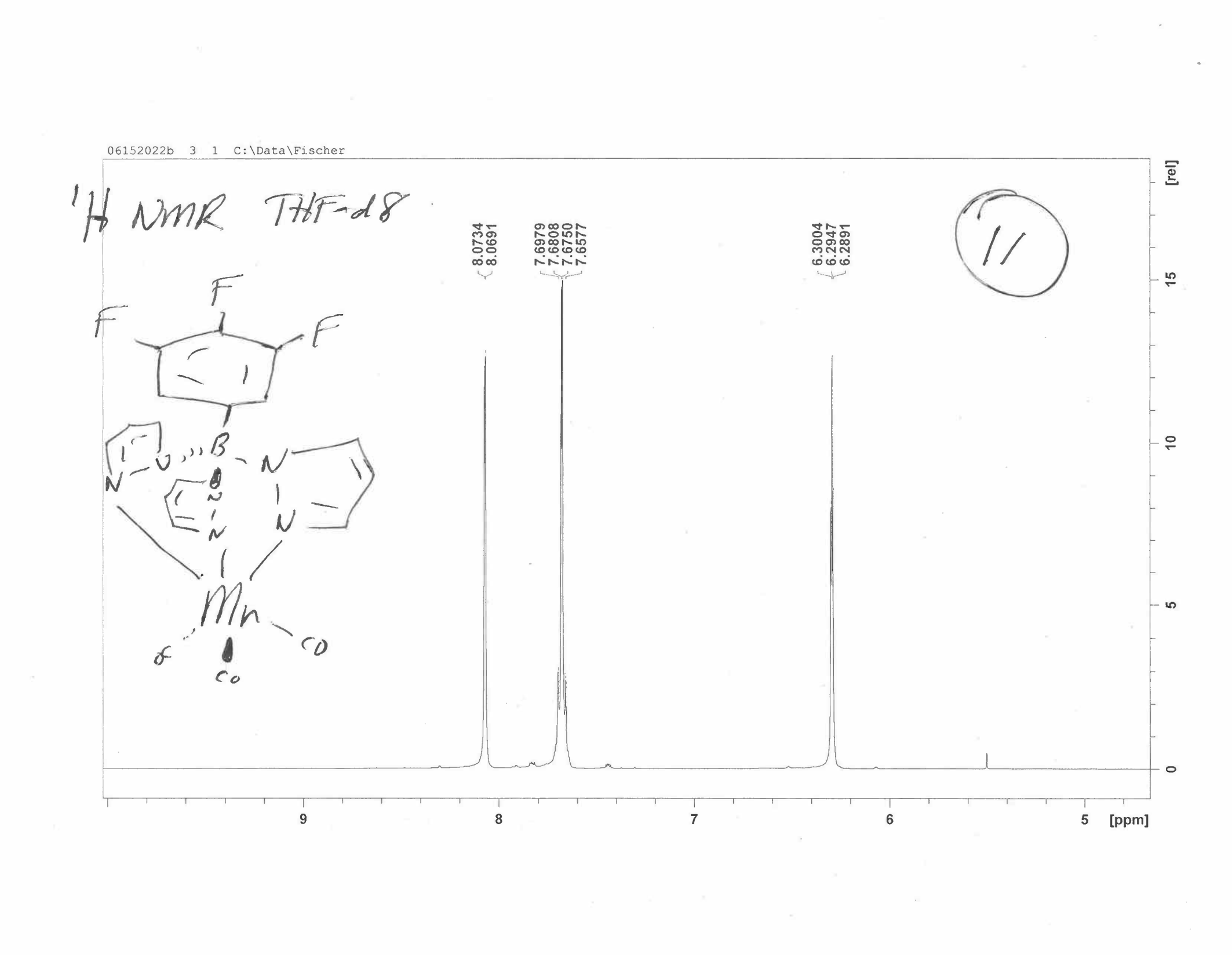


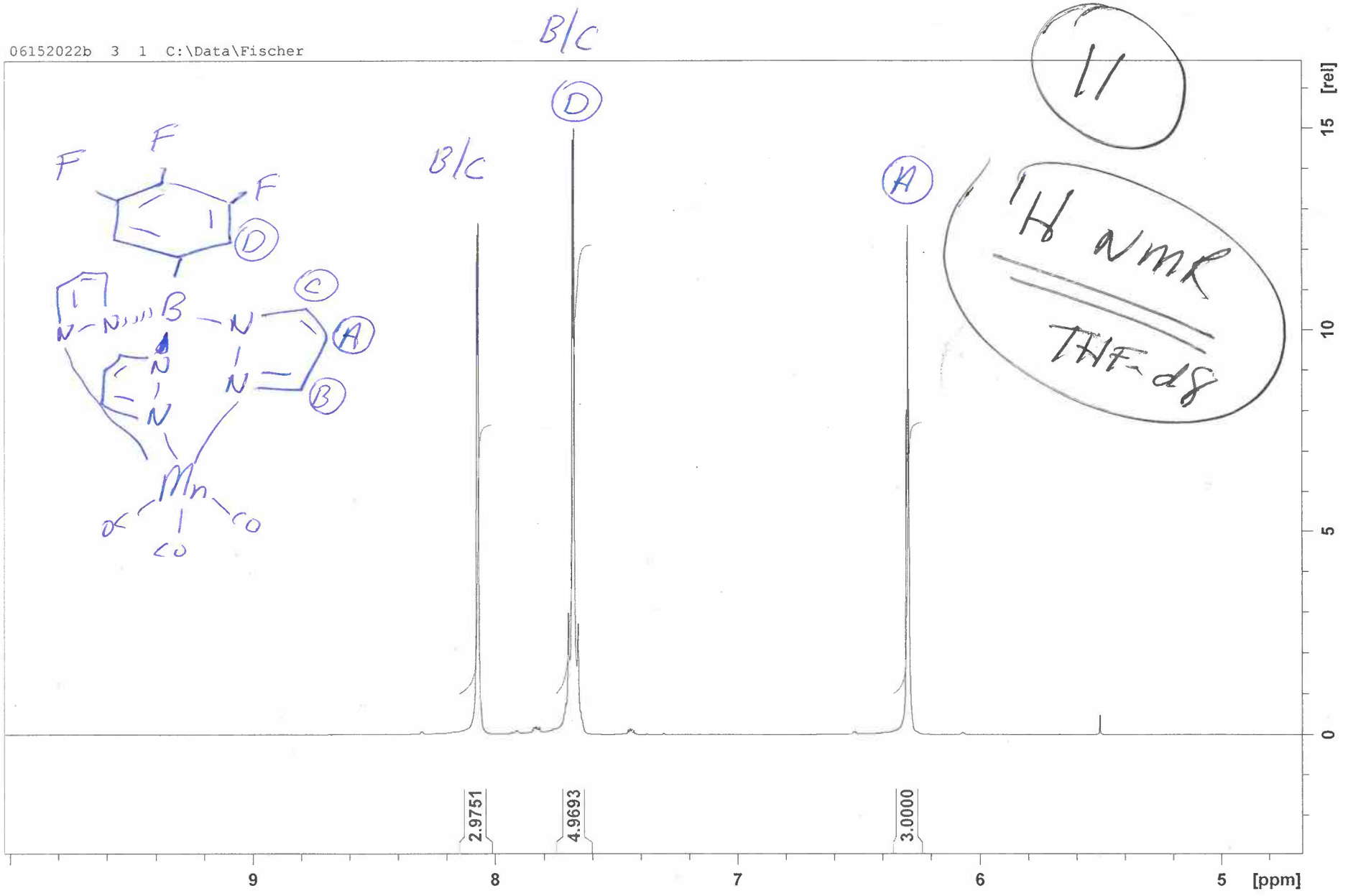
X THF-d8

06152022b 1 1 C:\Data\Fischer
50
0
- 50
[ppm]
10
20
30
40
[rel]
-1.4631
11


06152022b 2 1 C:\Data\Fischer
F-19 NMR THF-d8
11
$^{19}F\{^{1}H\}$ NMR
-136.1822
-136.2355
-163.0849
-163.1390
-163.1931
20 [rel]
15
10
5
0
0
- 50
- 100
- 150
- 200
[ppm]


06152022b 3 1 C:\Data\Fischer
11
^{1}H NMR
in THF-d8
B/C
B/C
D
A
F
F
F
D
C
A
B
Mn
OC
CO
CO
THF
THF
CH_2Cl_2
12
10
8
6
4
2
0
[ppm]
0
5
10
15
20
[rel]


06152022b 3 1 C:\Data\Fischer
1H NMR THF-d8
11
8.0734
8.0691
7.6979
7.6808
7.6750
7.6577
6.3004
6.2947
6.2891
F
F
F
B
N
N
N
N
N
Mn
CO
CO
CO
[rel]
15
10
5
0
9
8
7
6
5
[ppm]

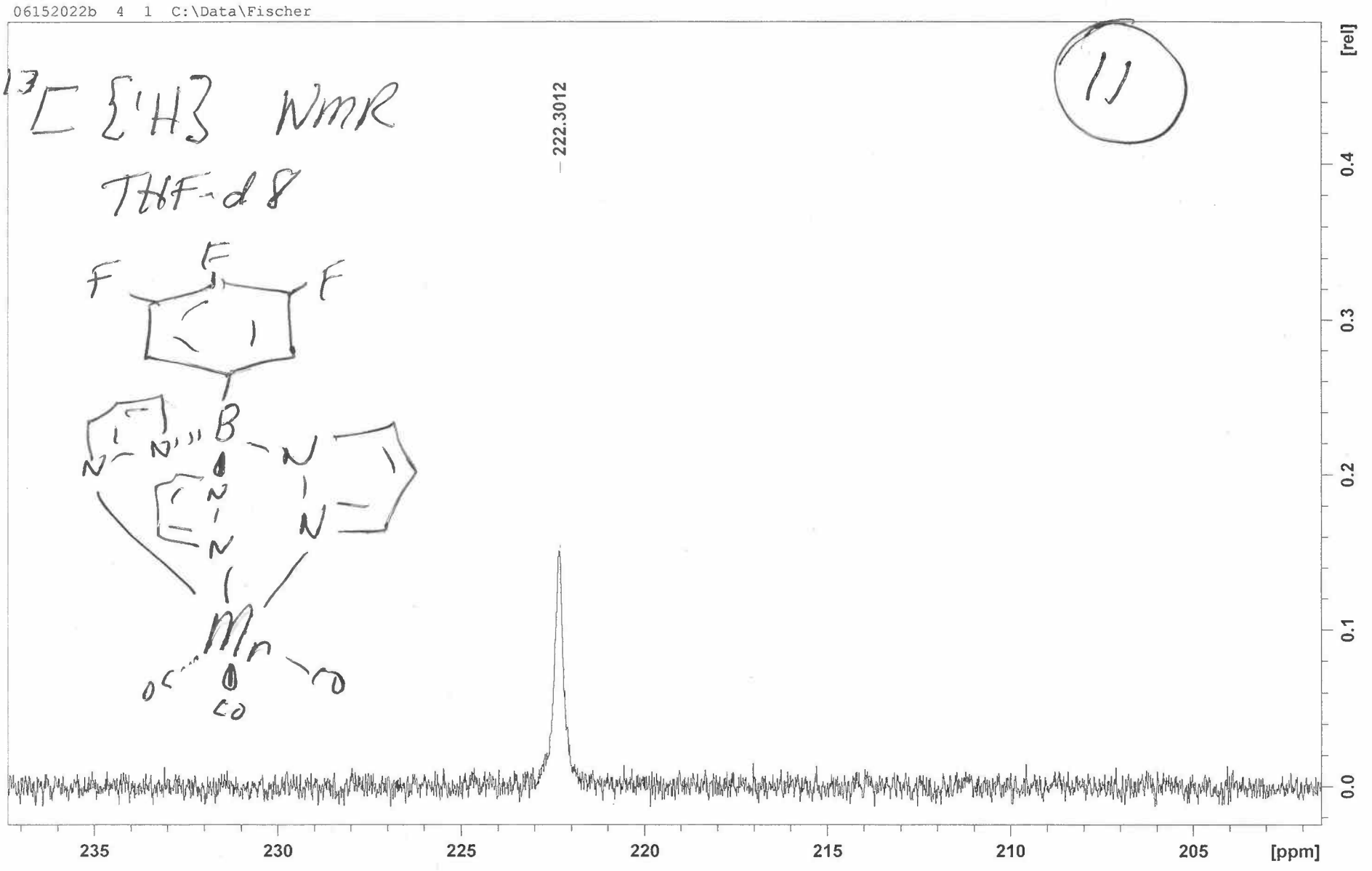

06152022b 3 1 C:\Data\Fischer
B/C
D
B/C
A
11
^{1}H NMR
THF-d8
F
F
F
D
C
A
B
N
N
N
N
N
B
Mn
CO
CO
CO
2.9751
4.9693
3.0000
9
8
7
6
5
[ppm]
15
10
5
0
[rel]

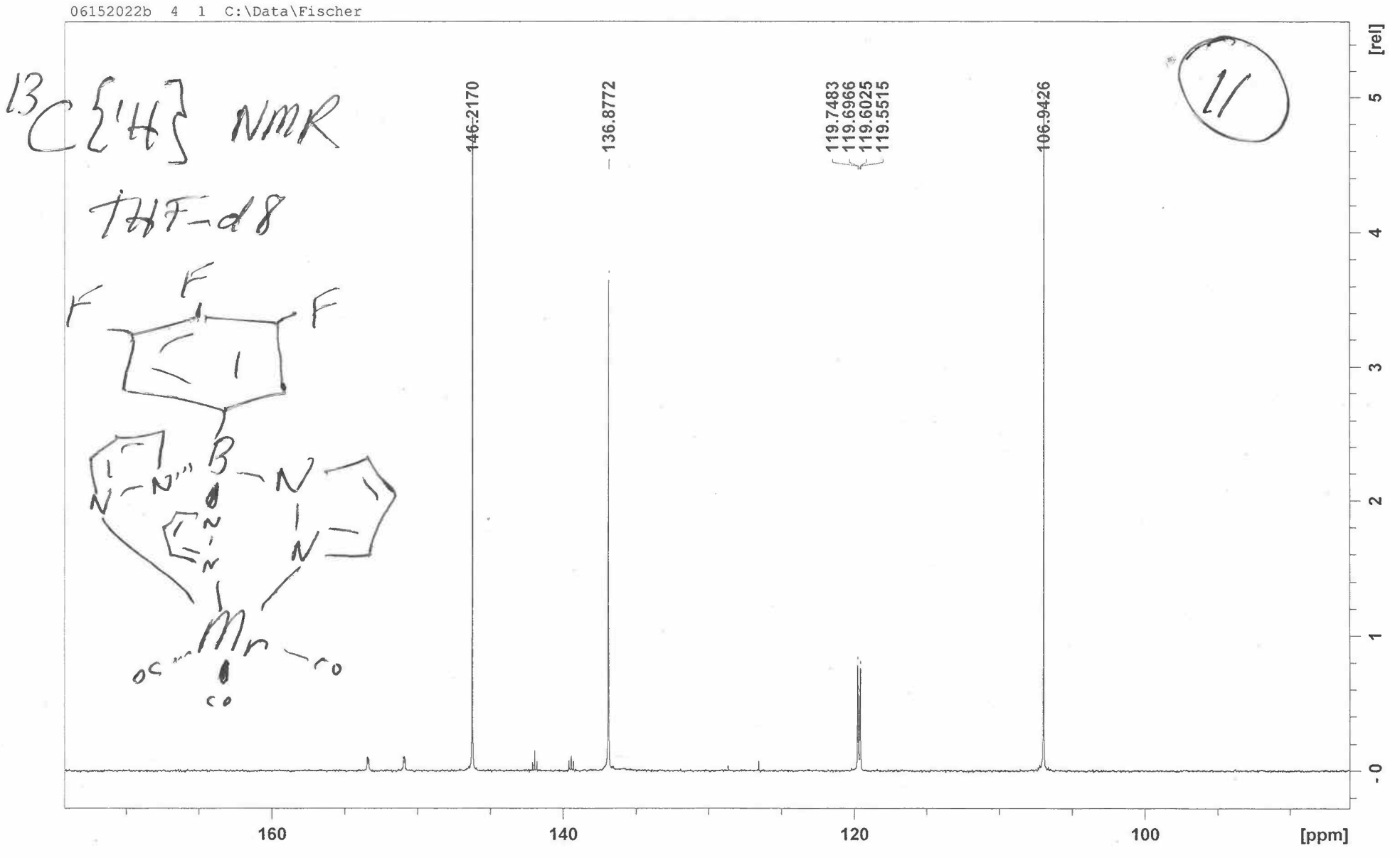
× THF-d8

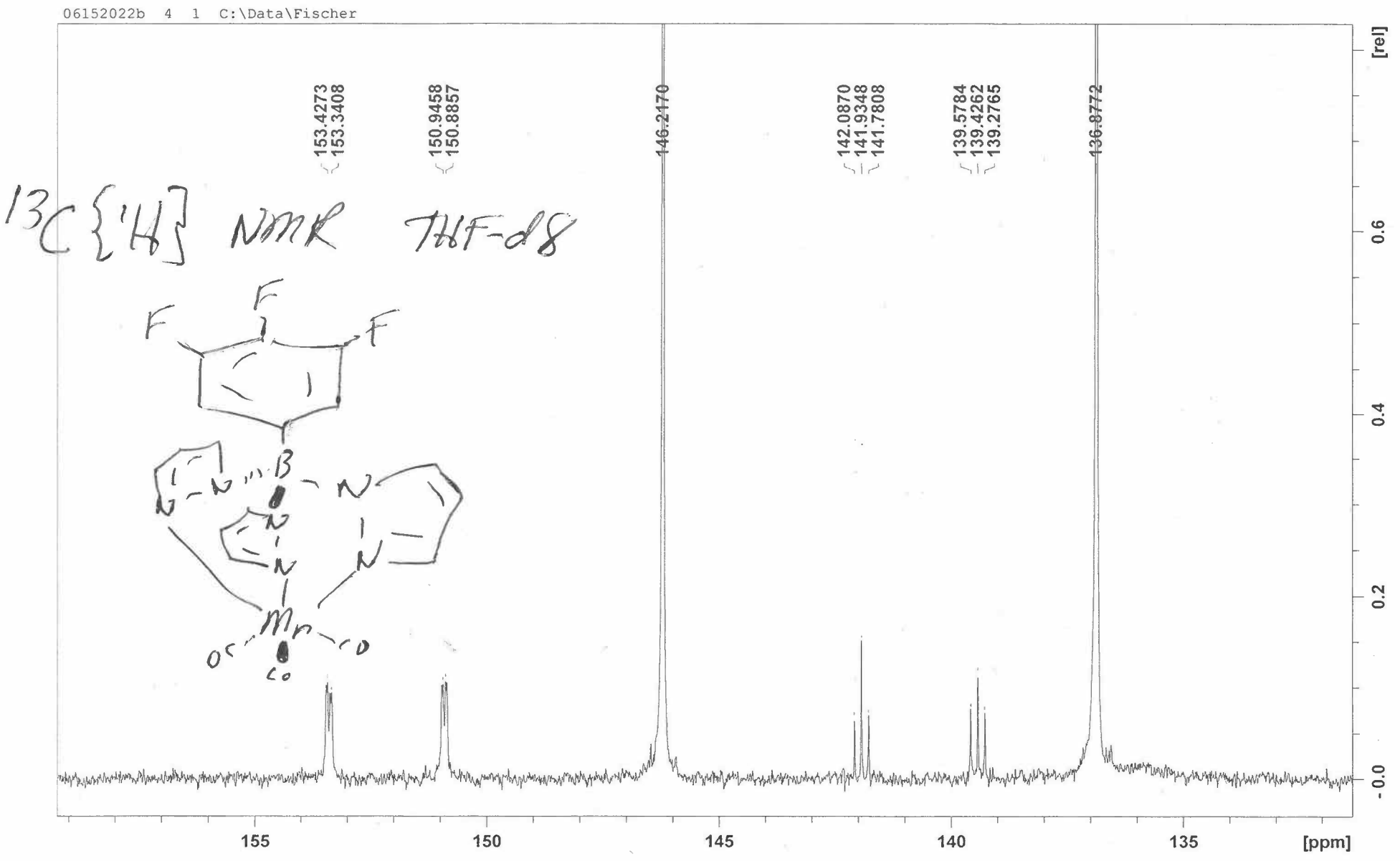
06152022b 4 1 C:\Data\Fischer

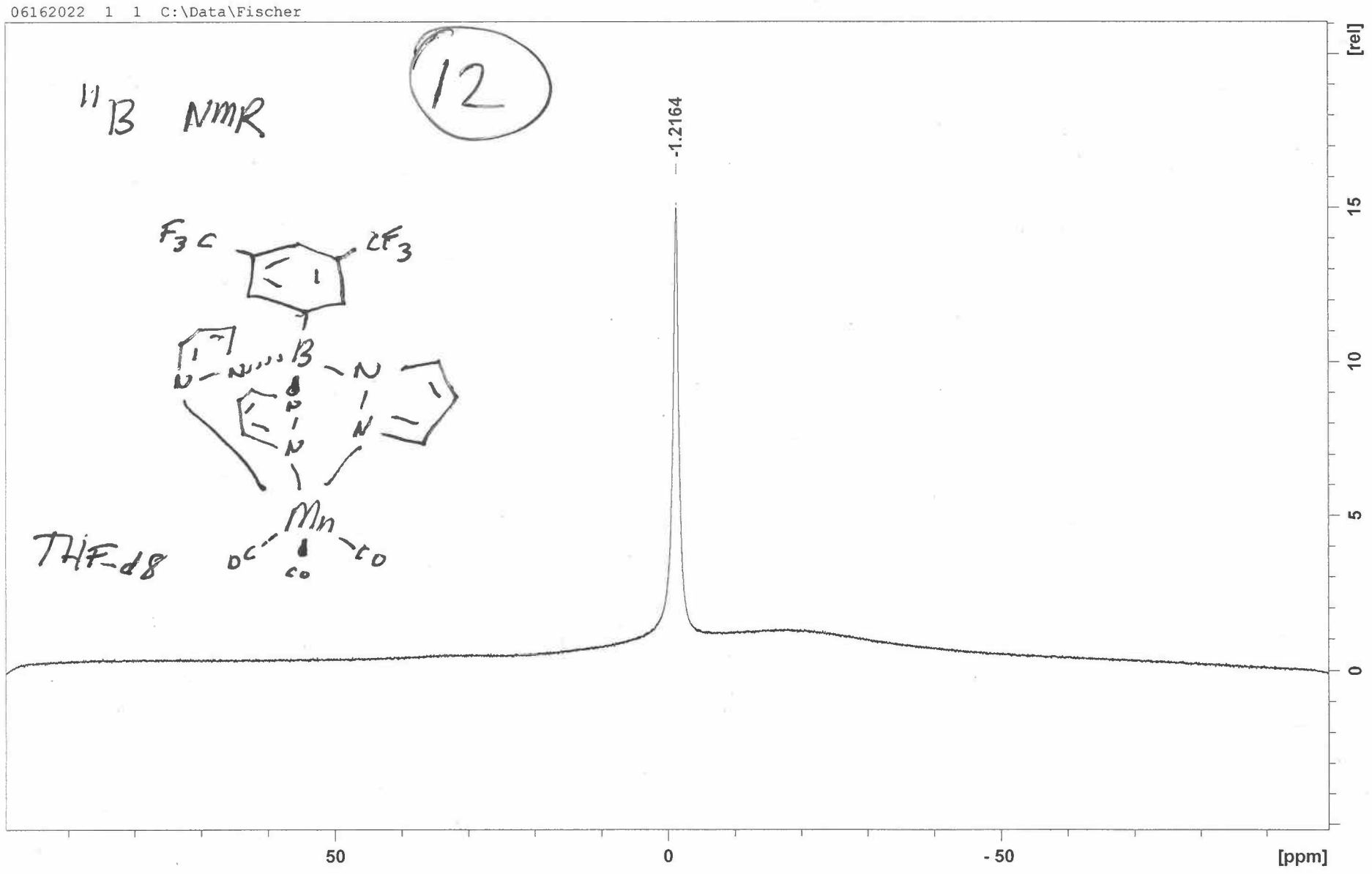
$^{13}C\{^{1}H\}$ NMR THF-d8

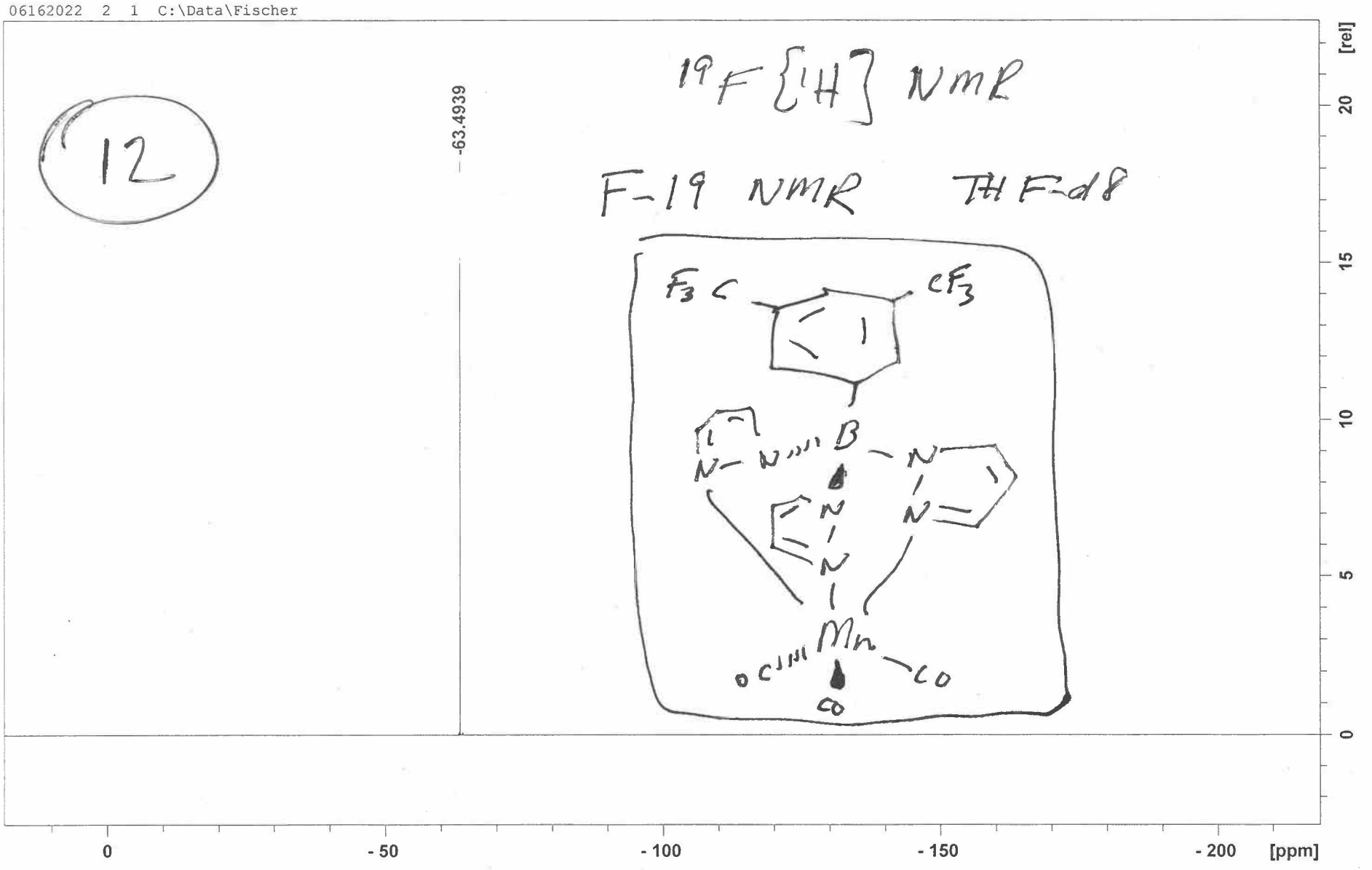
11

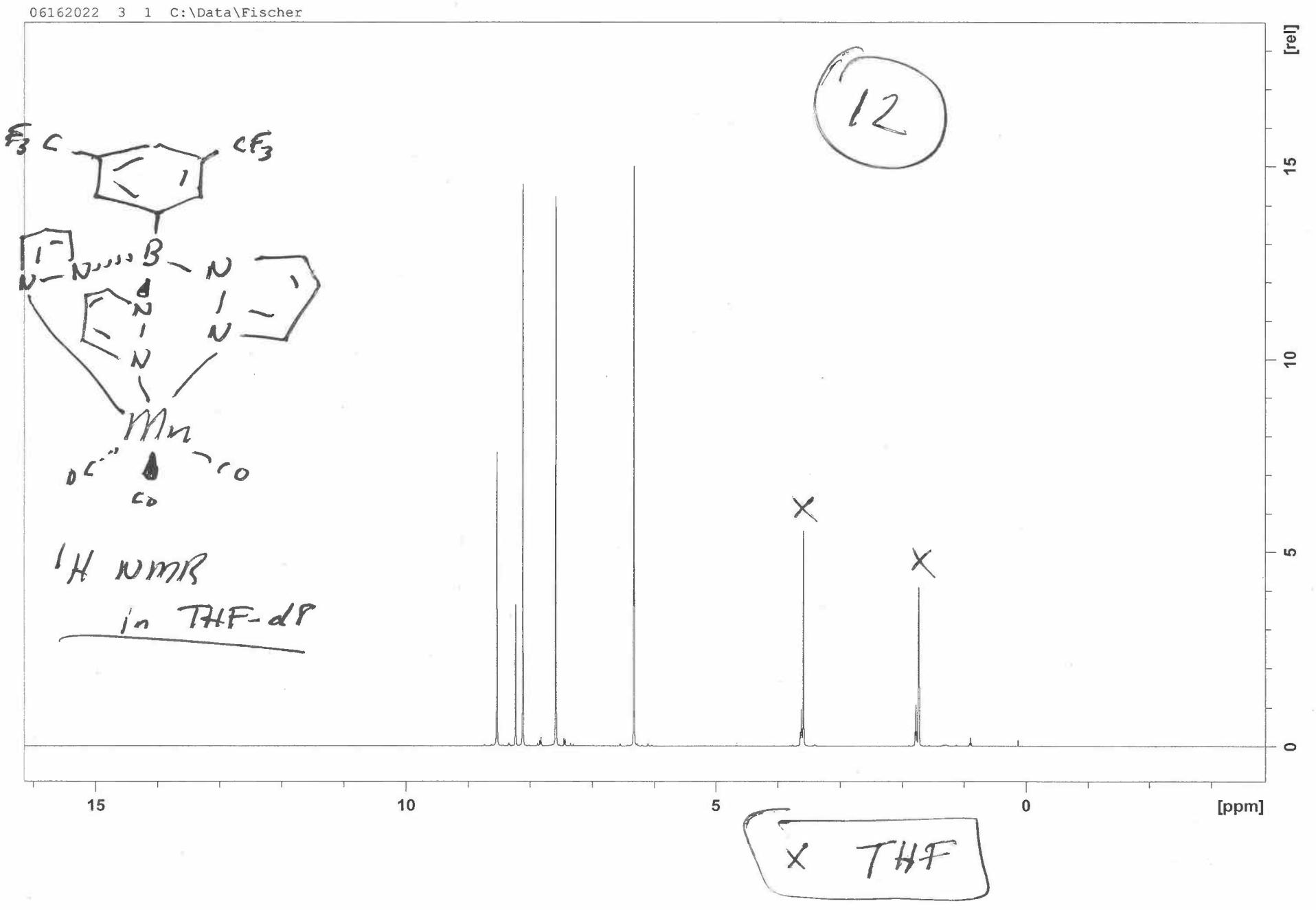

06152022b 4 1 C:\Data\Fischer
$^{13}C\{^1H\}$ NMR
THF-d8
11
222.3012
F
F
F
B
N
Mn
OC
CO
CO
0.0
0.1
0.2
0.3
0.4
[rel]
235
230
225
220
215
210
205
[ppm]

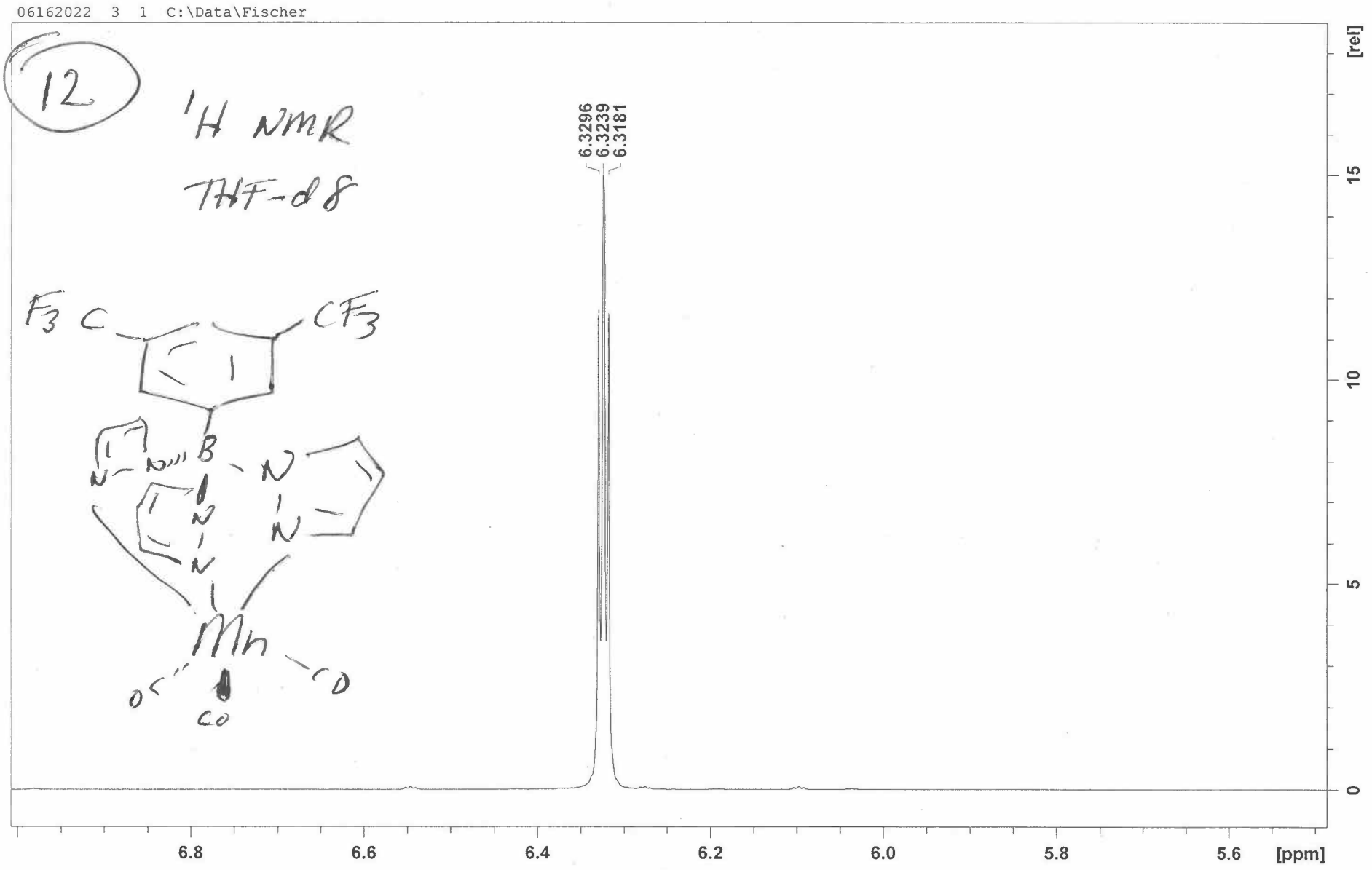

06152022b 4 1 C:\Data\Fischer
$^{13}C\{^{1}H\}$ NMR
THF-d8
11
146.2170
136.8772
119.7483
119.6966
119.6025
119.5515
106.9426
160
140
120
100
[ppm]
[rel]

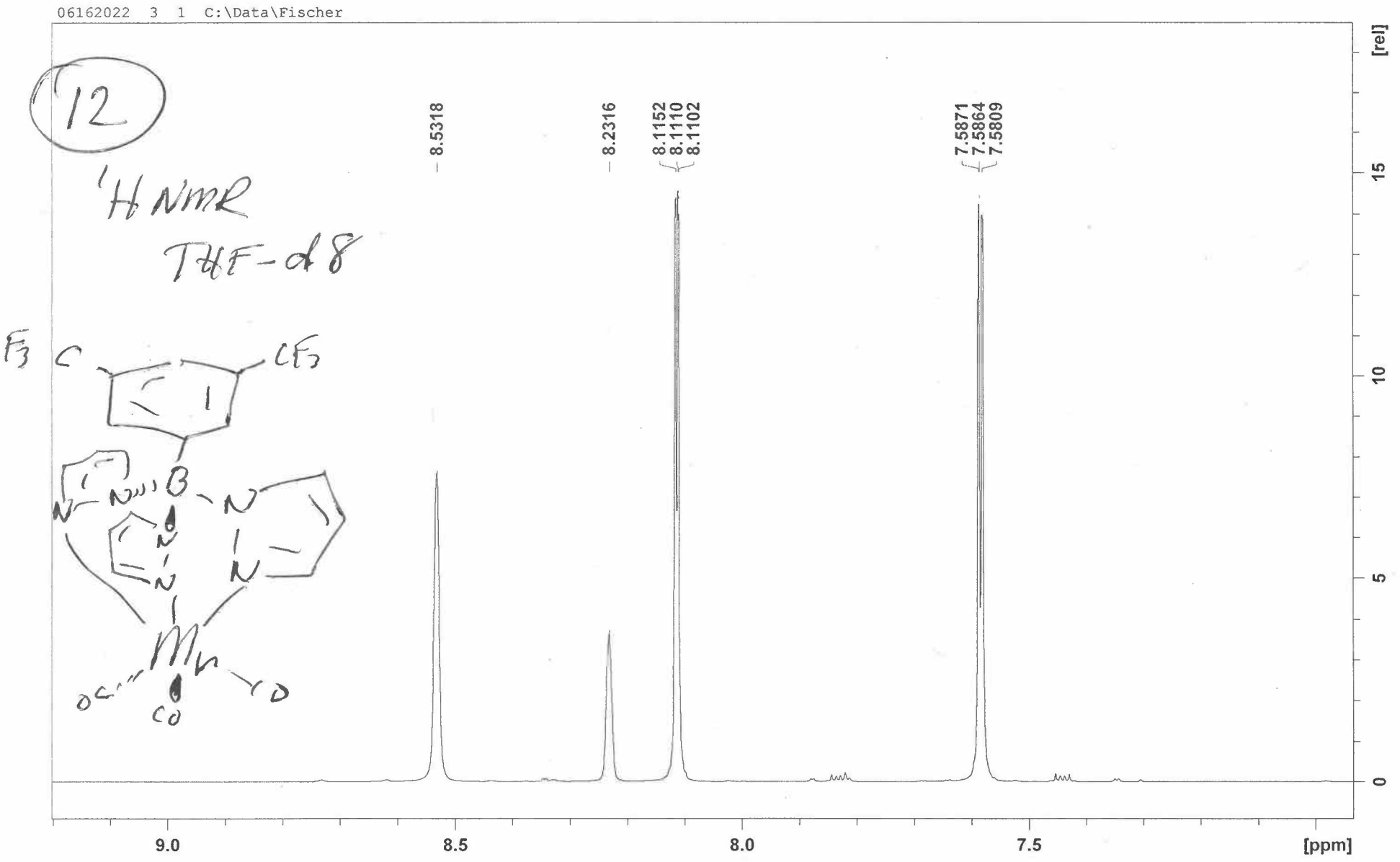

06152022b 4 1 C:\Data\Fischer
153.4273
153.3408
150.9458
150.8857
146.2170
142.0870
141.9348
141.7808
139.5784
139.4262
139.2765
136.8772
13C{1H} NMR THF-d8
F
F
F
B
N
N
N
N
N
N
Mn
OC
CO
CO
[rel]
0.6
0.4
0.2
-0.0
155
150
145
140
135
[ppm]

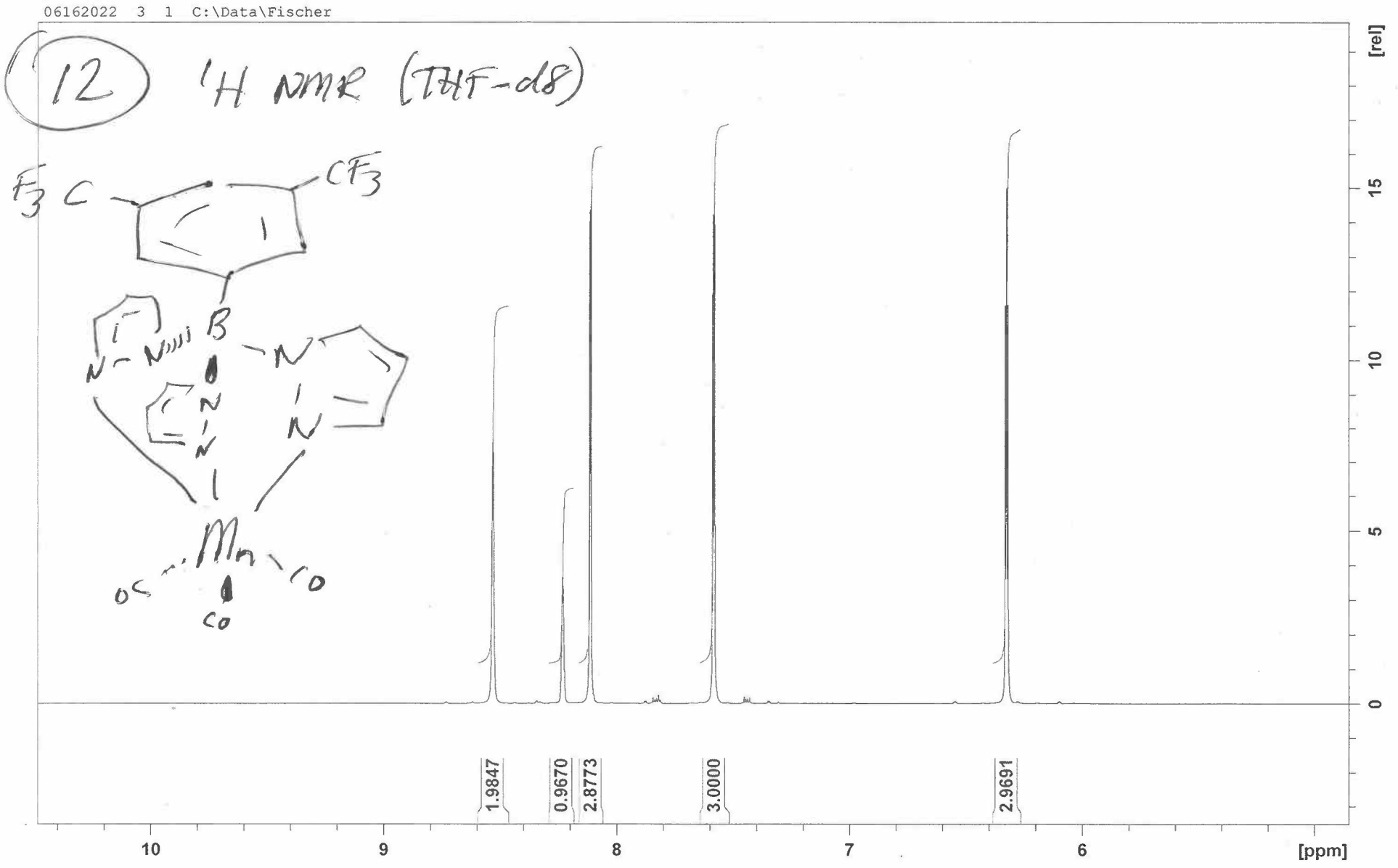

06162022 1 1 C:\Data\Fischer
11B NMR
12
-1.2164
F3C
CF3
THF-d8
Mn
OC
CO
CO
[rel]
15
10
5
0
50
0
- 50
[ppm]


06162022 2 1 C:\Data\Fischer
12
-63.4939
$^{19}F\{^{1}H\}$ NMR
F-19 NMR THF-d8
F_3C
CF_3
B
N
Mn
OC
CO
0
- 50
- 100
- 150
- 200
[ppm]
[rel]
20
15
10
5
0


06162022 3 1 C:\Data\Fischer
12
F_3C
CF_3
B
N
Mn
OC
CO
CO
^1H NMR
in THF-d8
X
X
X THF
15
10
5
0
[ppm]
[rel]
0
5
10
15


06162022 3 1 C:\Data\Fischer
12
^{1}H NMR
THF-d8
6.3296
6.3239
6.3181
[rel]
15
10
5
0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
[ppm]

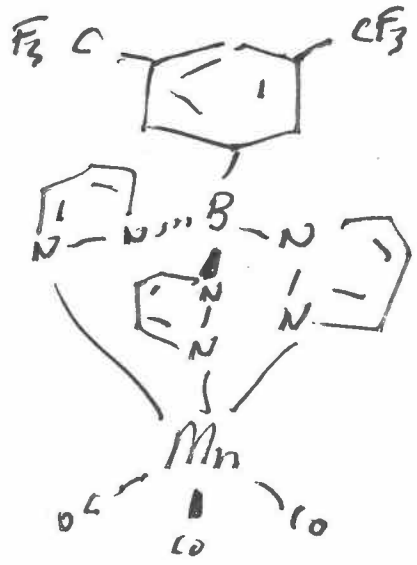

06162022 3 1 C:\Data\Fischer
12
^{1}H NMR
THF-d8
8.5318
8.2316
8.1152
8.1110
8.1102
7.5871
7.5864
7.5809
[rel]
15
10
5
0
9.0
8.5
8.0
7.5
[ppm]


06162022 3 1 C:\Data\Fischer
12
^1H NMR (THF-d8)
F_3C
CF_3
B
N
Mn
OC
CO
[rel]
15
10
5
0
1.9847
0.9670
2.8773
3.0000
2.9691
10
9
8
7
6
[ppm]

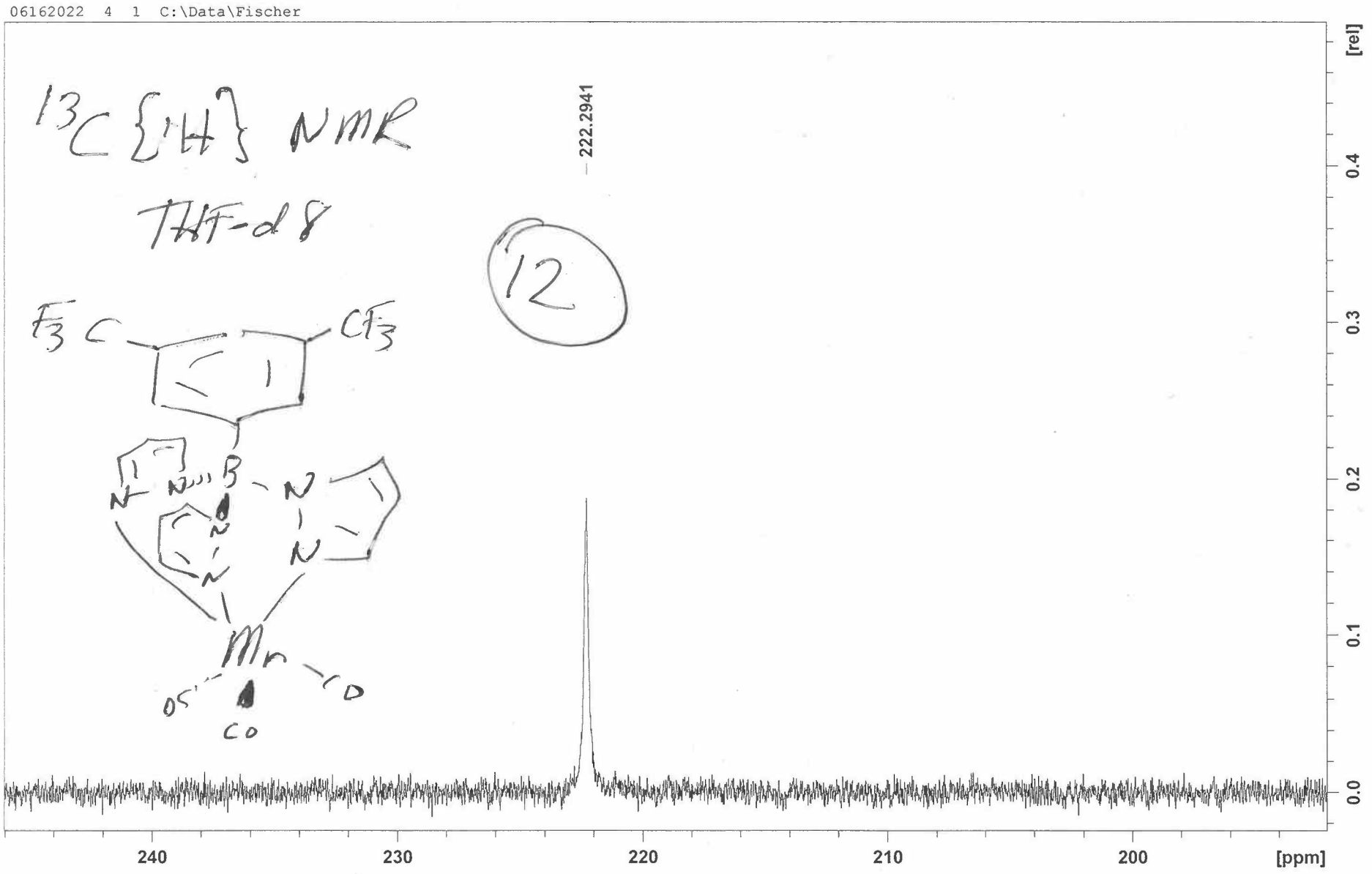
× (THF-d8)

06162022 4 1 C:\Data\Fischer

THF-d8, $^{13}C\{^1H\}$ NMR



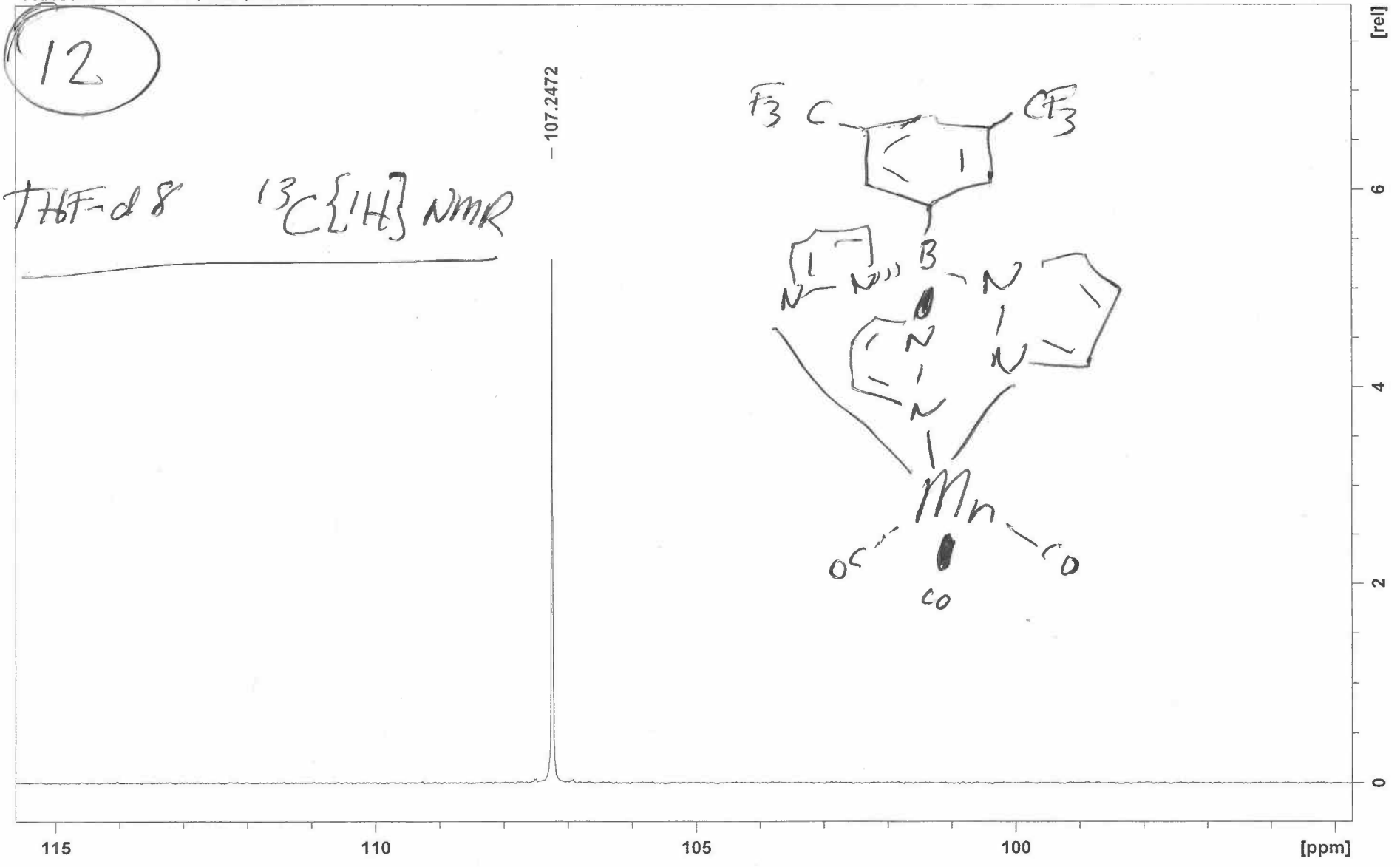
12

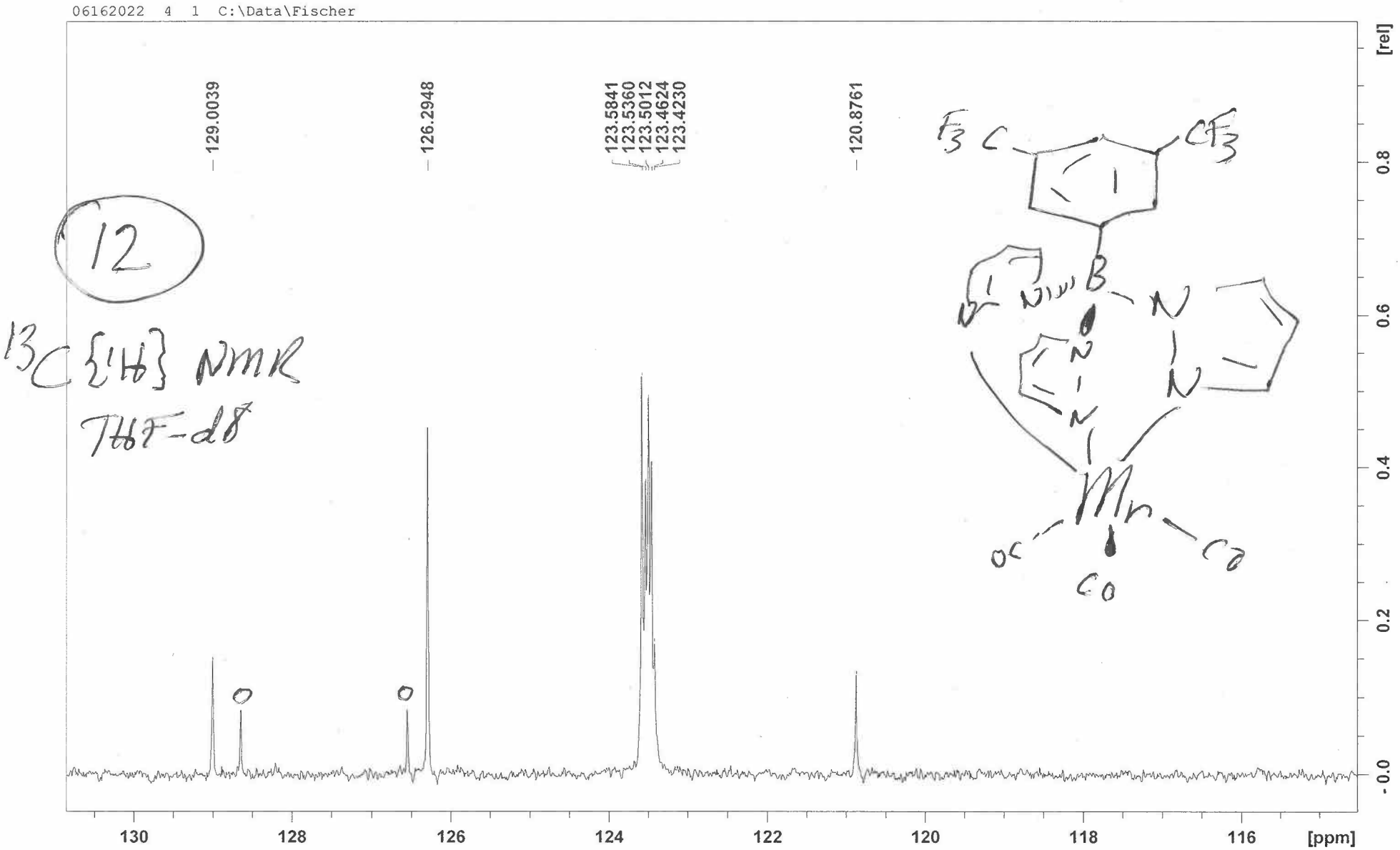

06162022 4 1 C:\Data\Fischer
13C {1H} NMR
THF-d8
12
222.2941
240
230
220
210
200
[ppm]
0.0
0.1
0.2
0.3
0.4
[rel]

06162022 4 1 C:\Data\Fischer

12

THF-d 8 $^{13}C\{^{1}H\}$ NMR



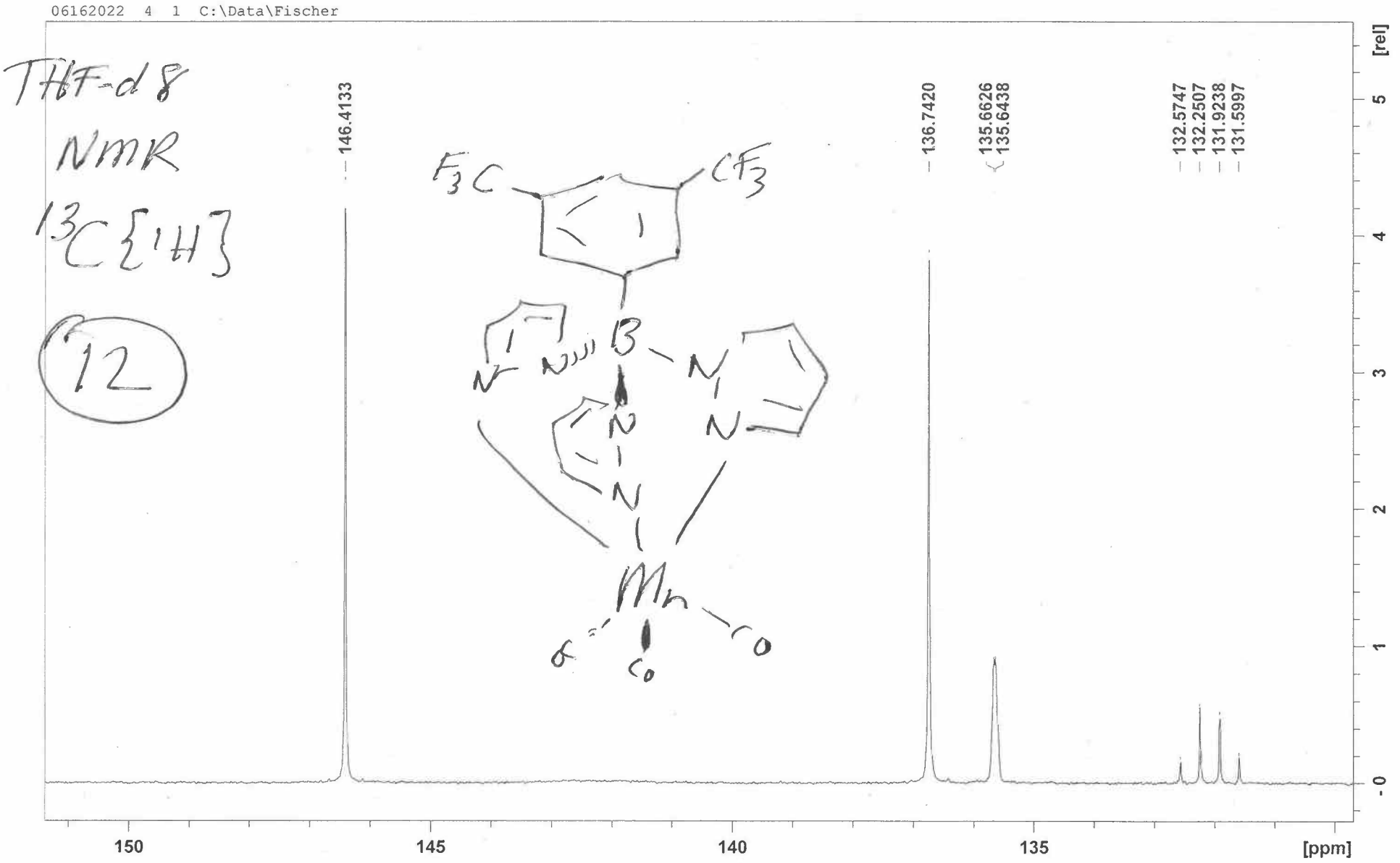


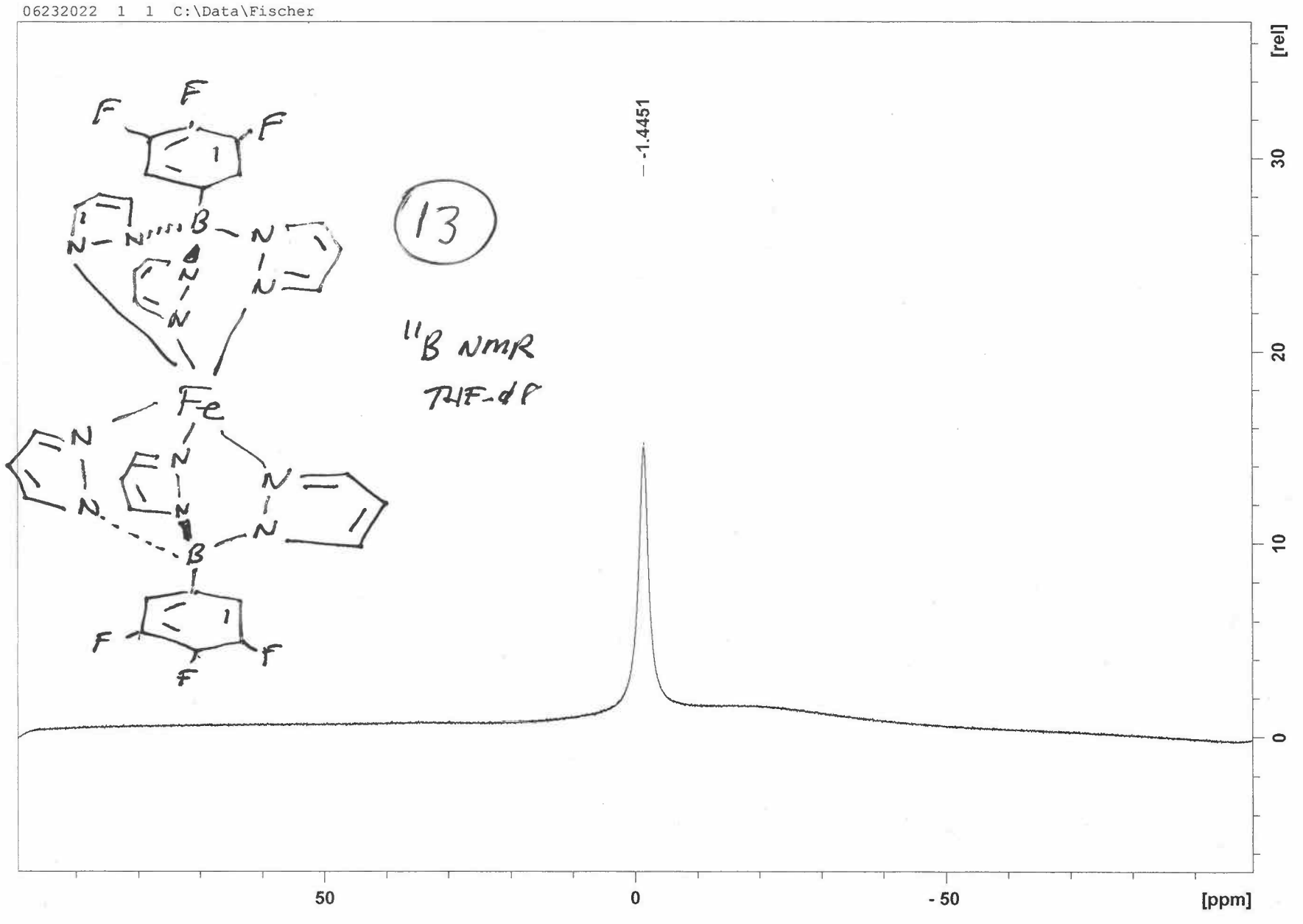
12

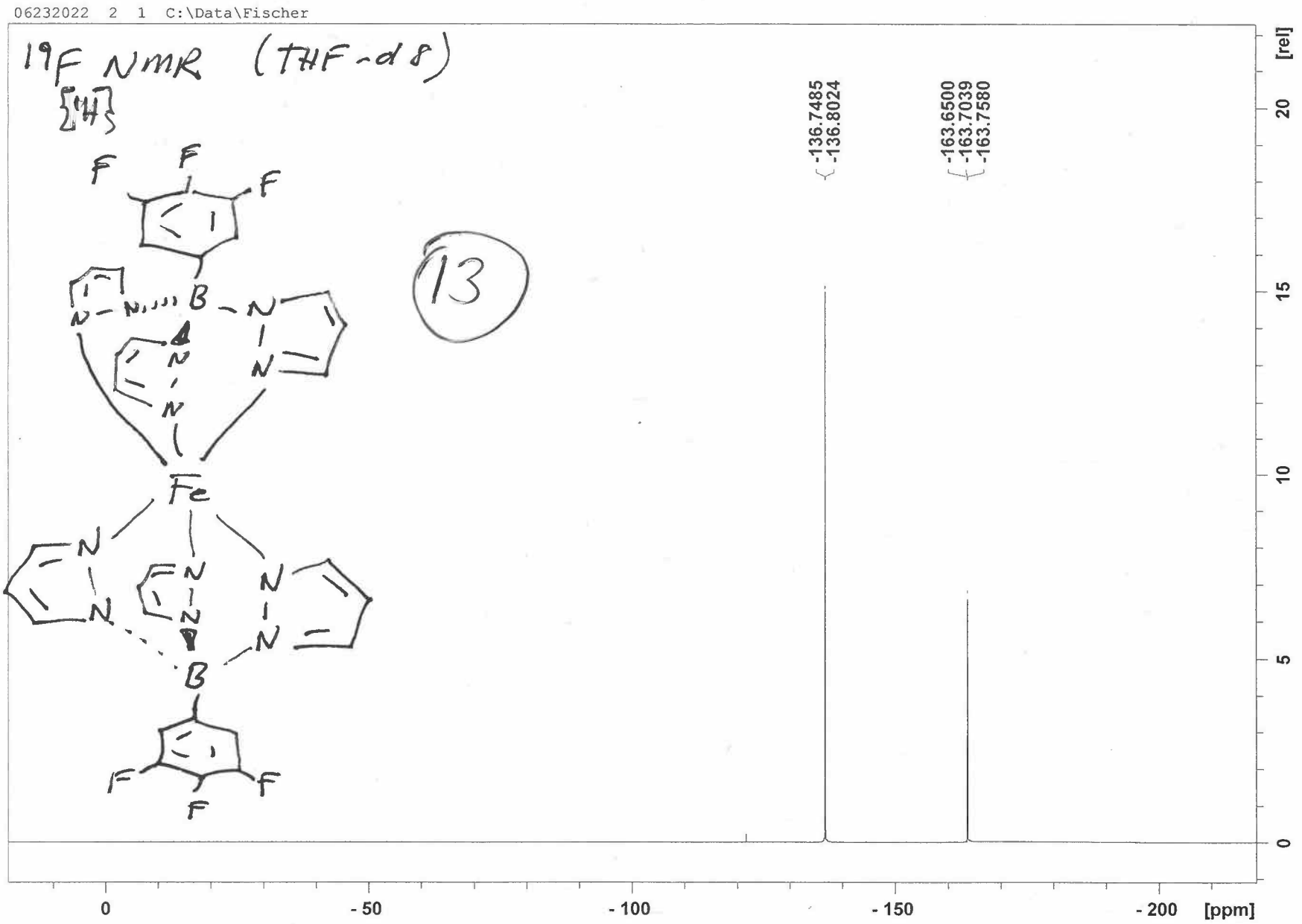
$^{13}C\{^1H\}$ NMR

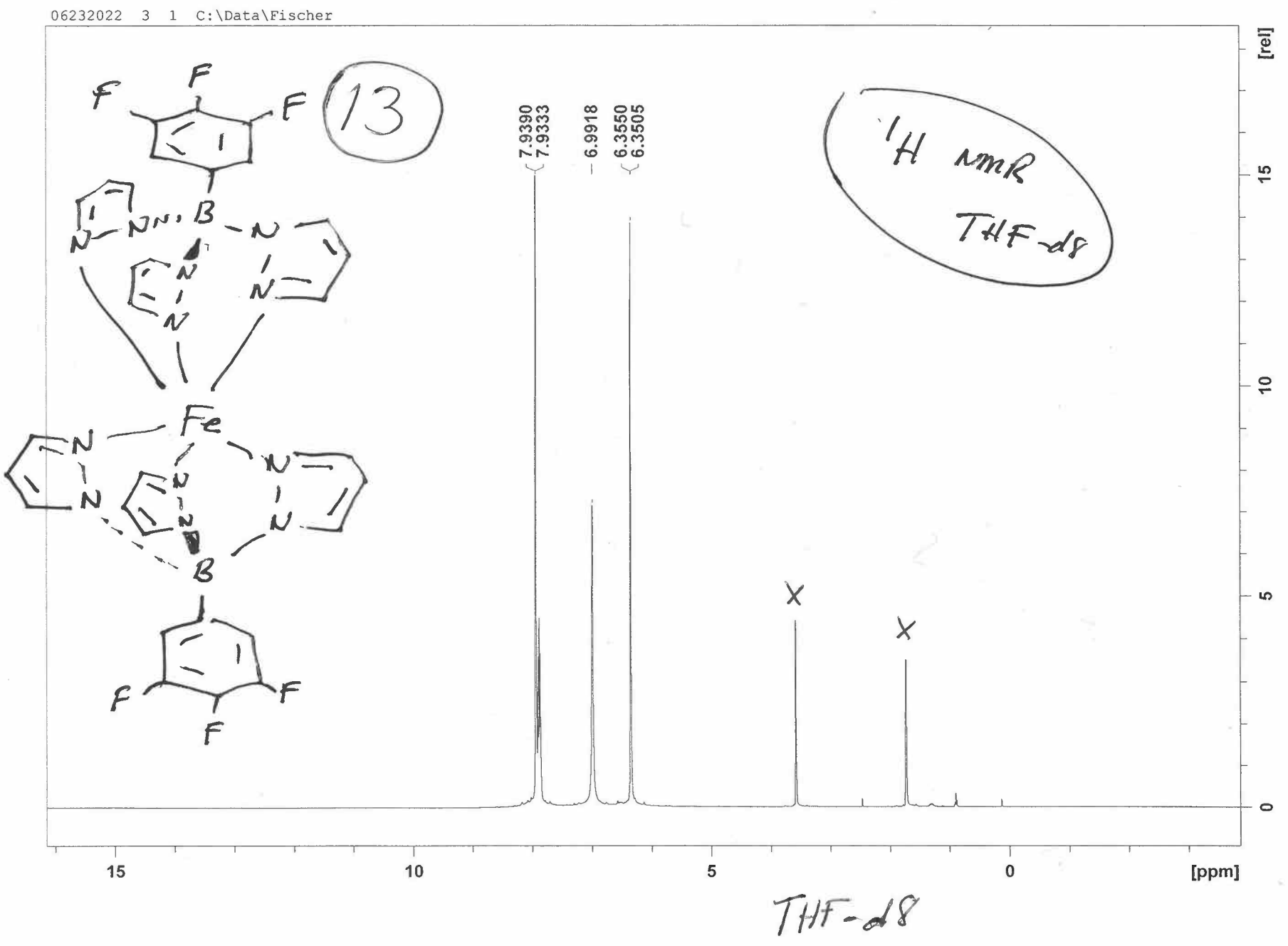
THF-d8

o trace $C_{10}H_8$


06162022 4 1 C:\Data\Fischer
THF-d8
NMR
13C{1H}
12
146.4133
136.7420
135.6626
135.6438
132.5747
132.2507
131.9238
131.5997
F3C
CF3
B
N
Mn
CO
CO
150
145
140
135
[ppm]
[rel]
5
4
3
2
1
0

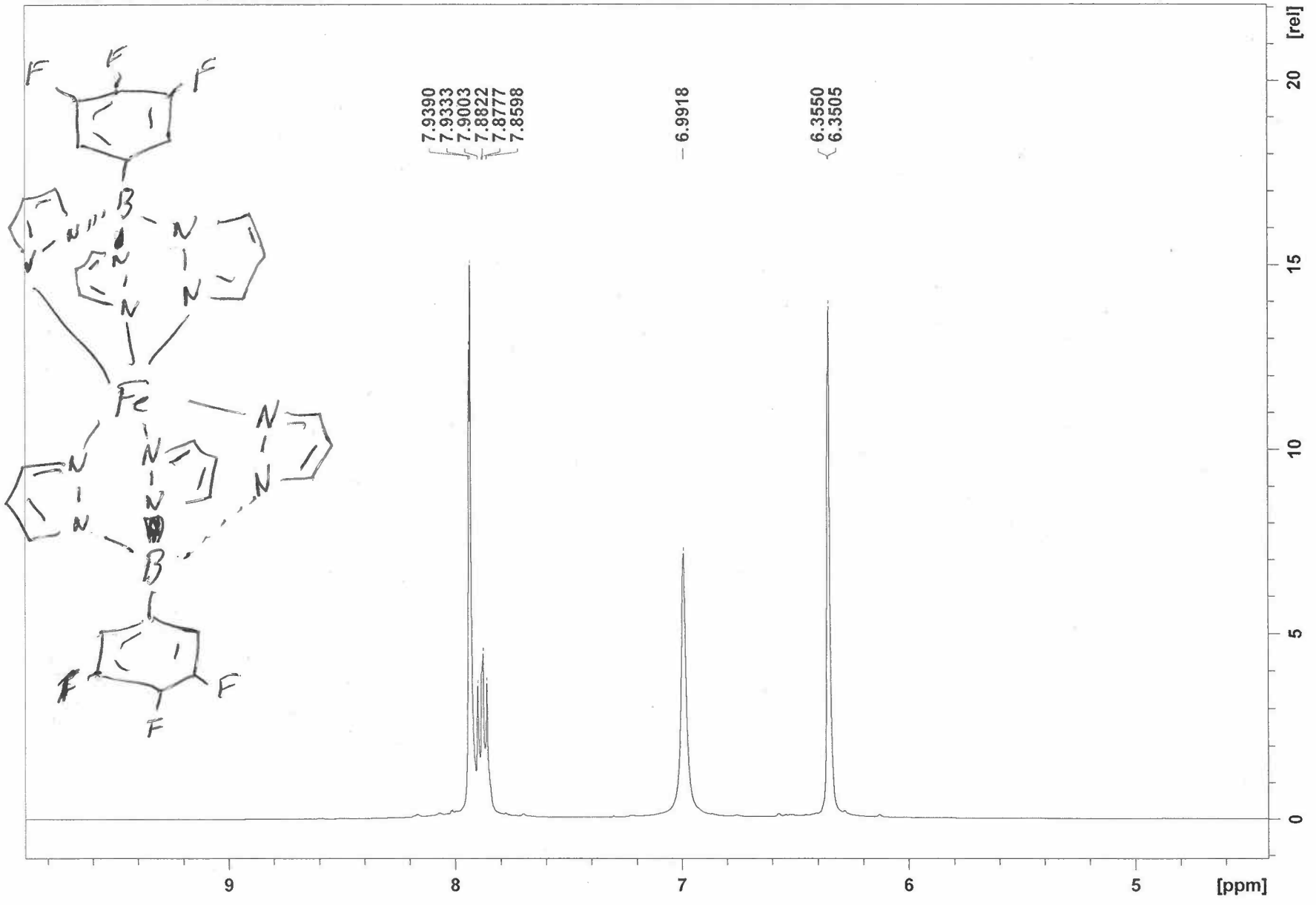

06232022 1 1 C:\Data\Fischer
13
^{11}B NMR
THF-d8
-1.4451
[rel]
30
20
10
0
50
0
- 50
[ppm]


06232022 2 1 C:\Data\Fischer
19F NMR (THF-d8)
{1H}
13
-136.7485
-136.8024
-163.6500
-163.7039
-163.7580
[rel]
0
5
10
15
20
0
- 50
- 100
- 150
- 200
[ppm]


06232022 3 1 C:\Data\Fischer
13
7.9390
7.9333
6.9918
6.3550
6.3505
X
X
[rel]
[ppm]
15
10
5
0
THF-d8

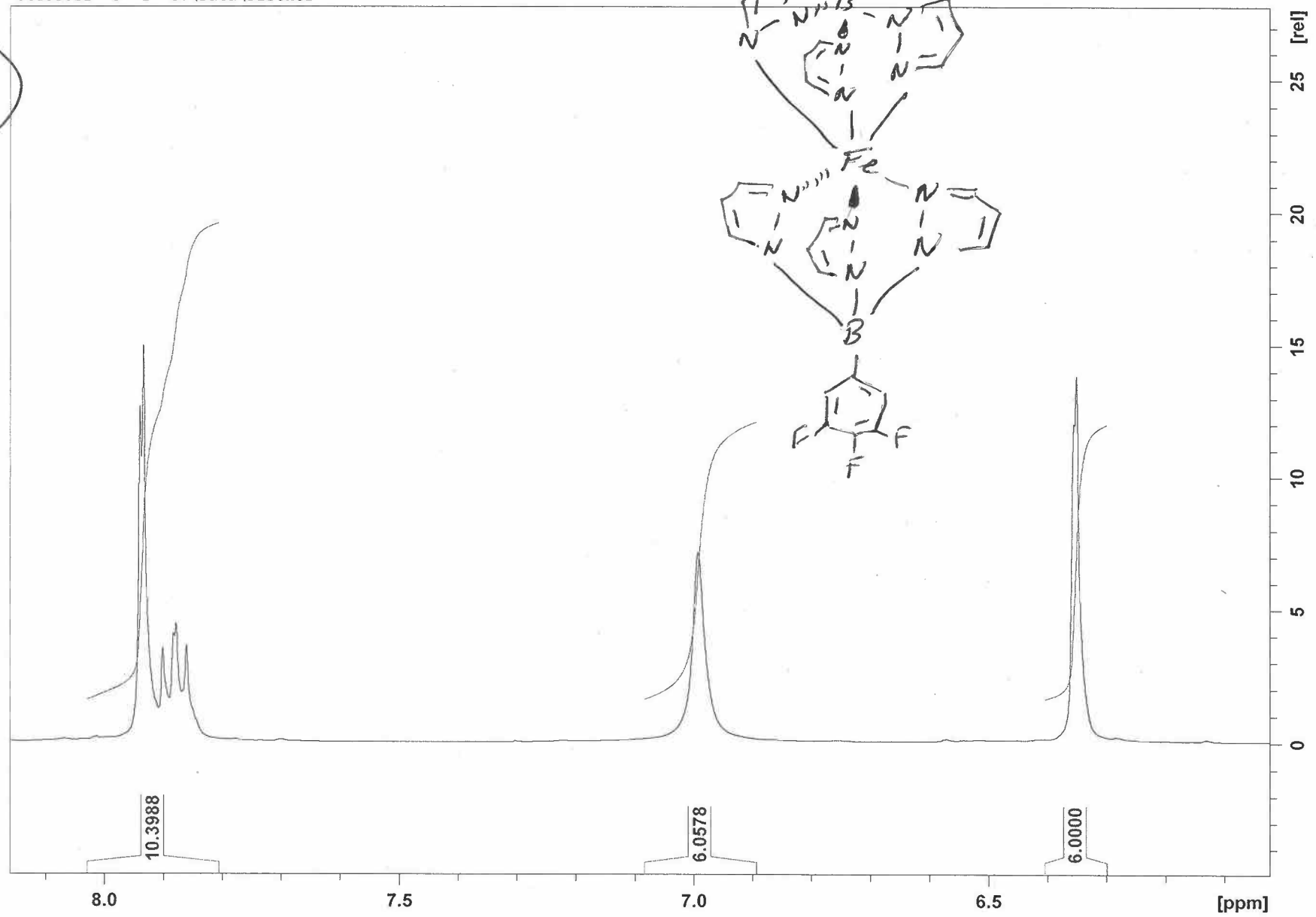
^1H NMR (THF-d8)

13

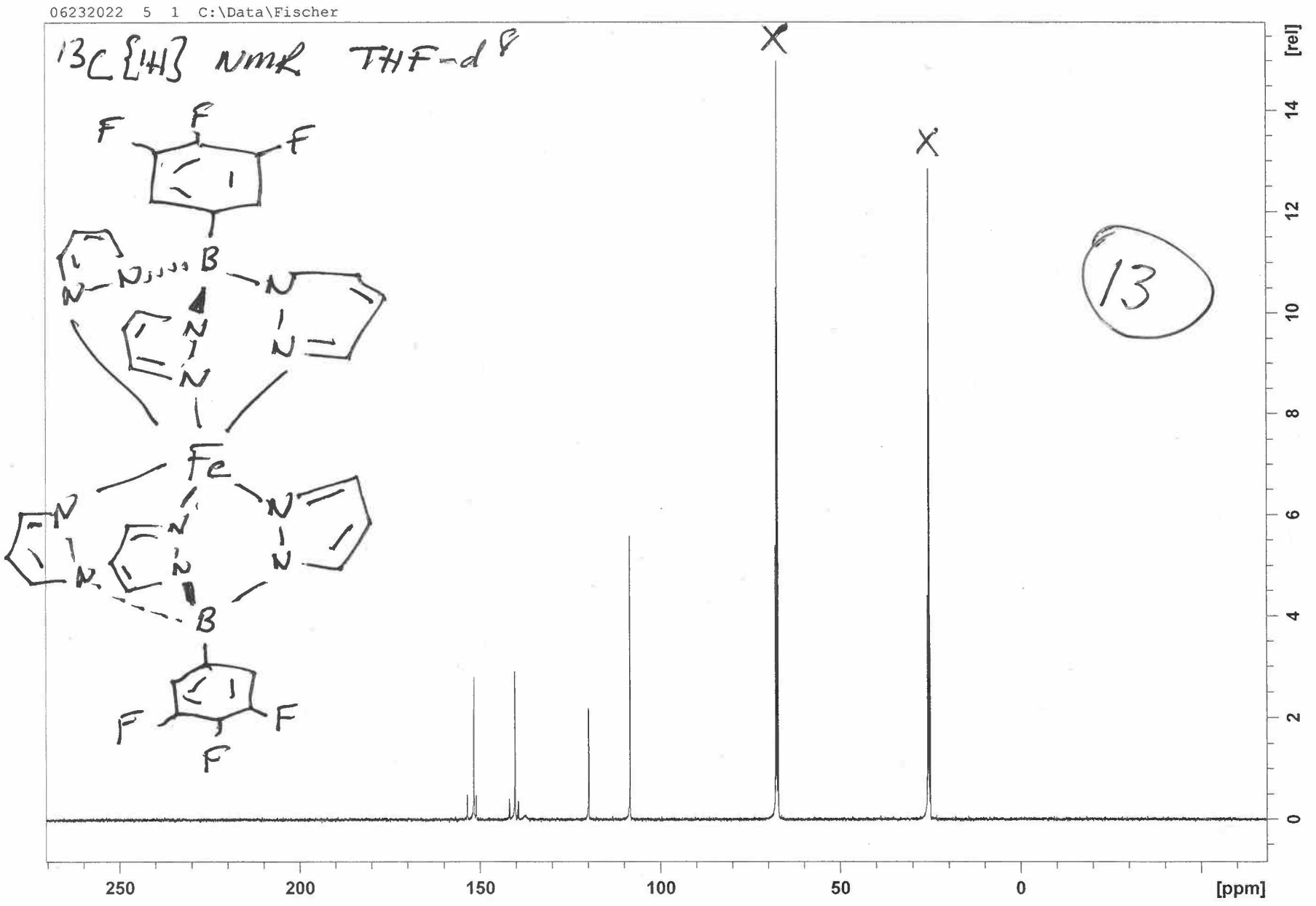


^1H NMR (THF-d8)

13

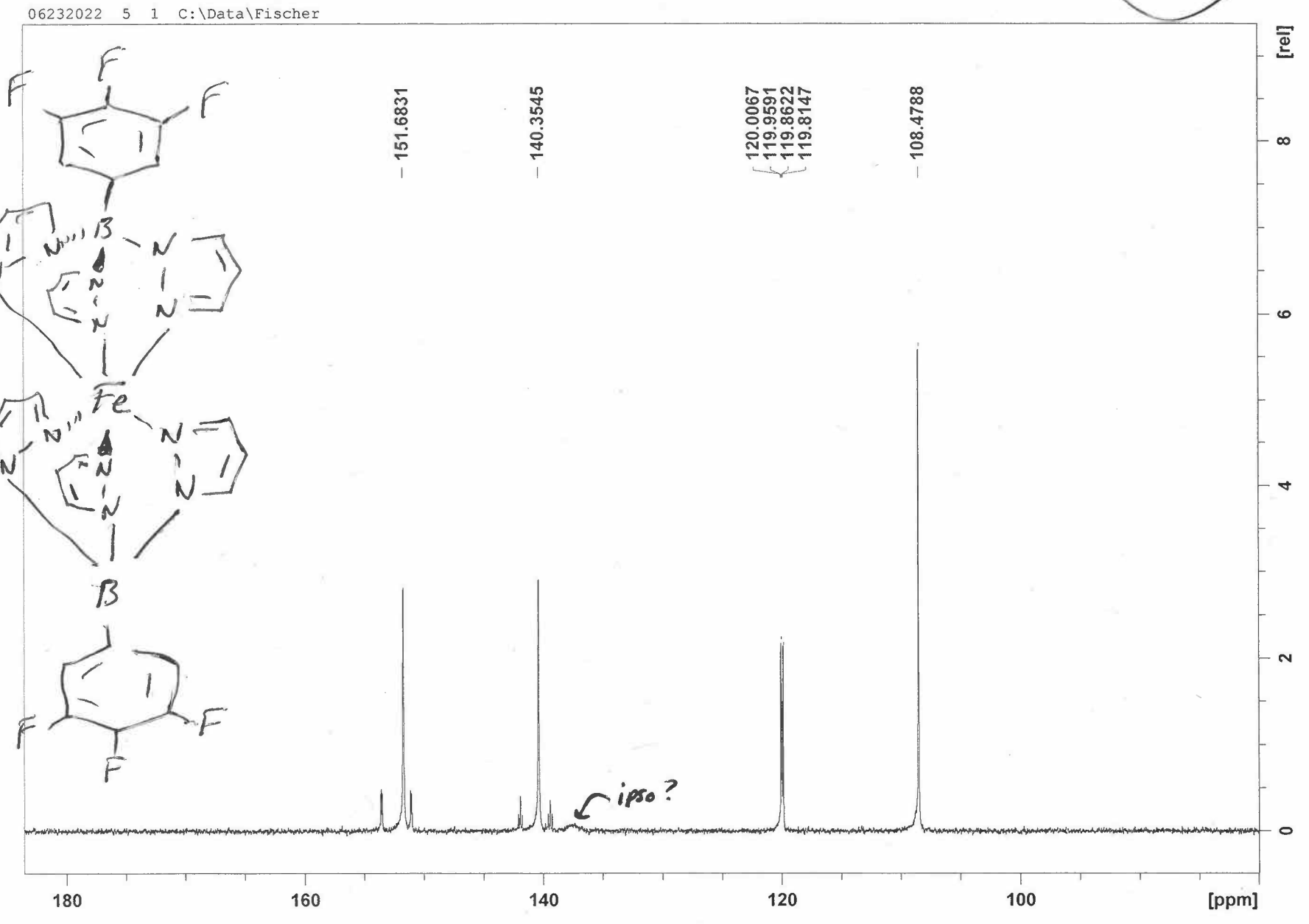


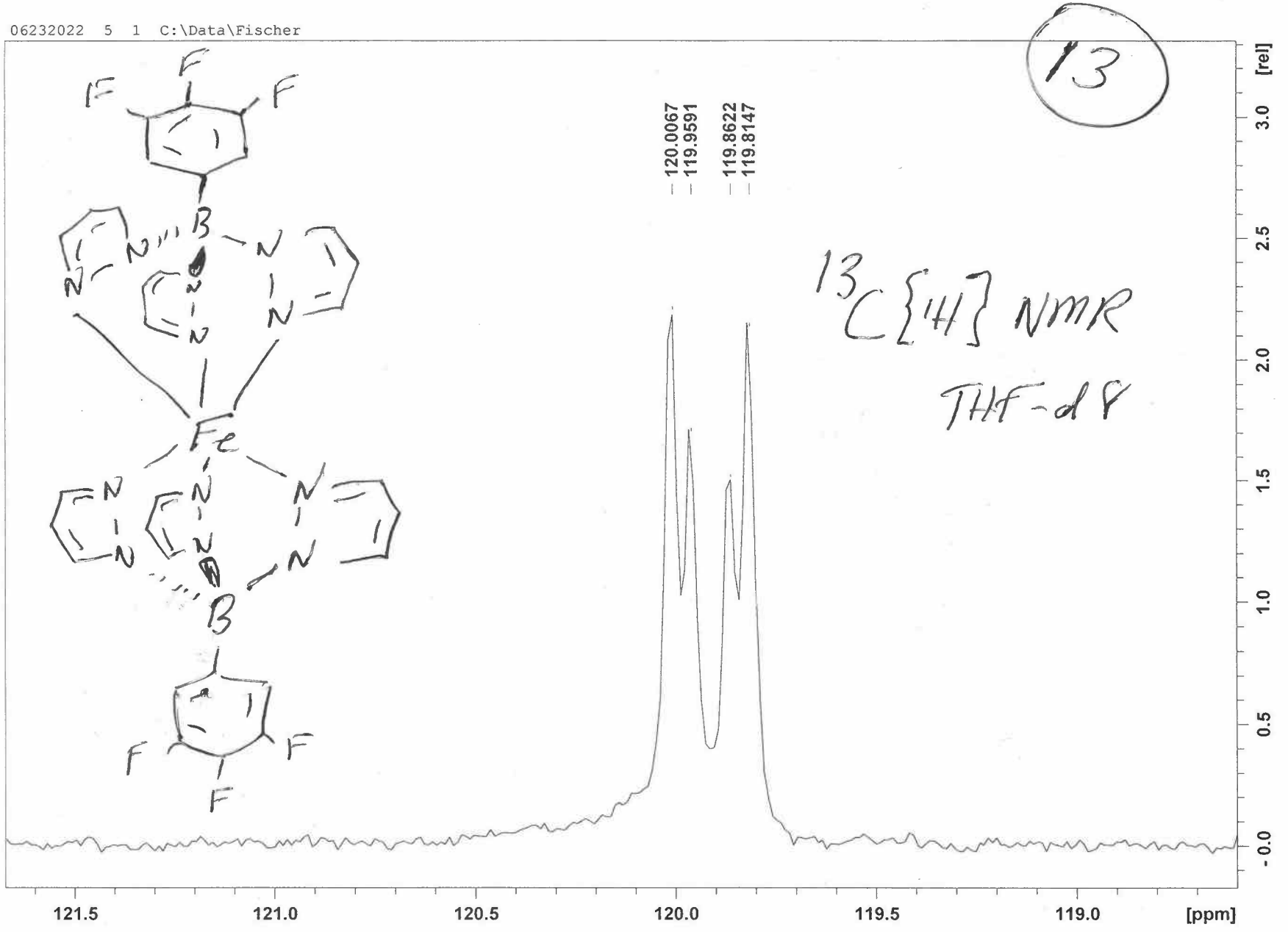
X THF-d8


06232022 5 1 C:\Data\Fischer
13C{1H} NMR THF-d8
X
X
13
[rel]
14
12
10
8
6
4
2
0
250
200
150
100
50
0
[ppm]

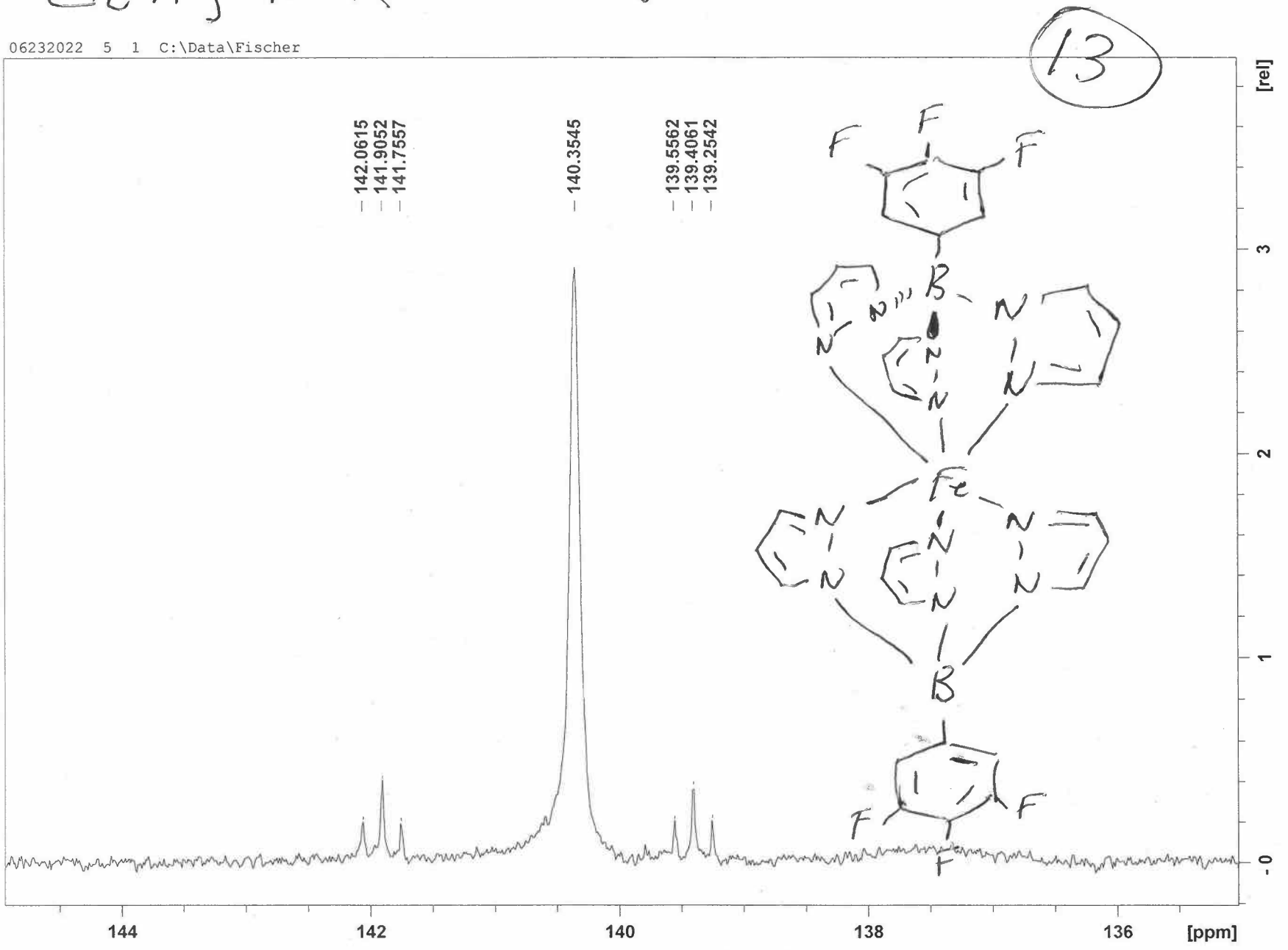
$^{13}C\{^{1}H\}$ NMR THF-d_8

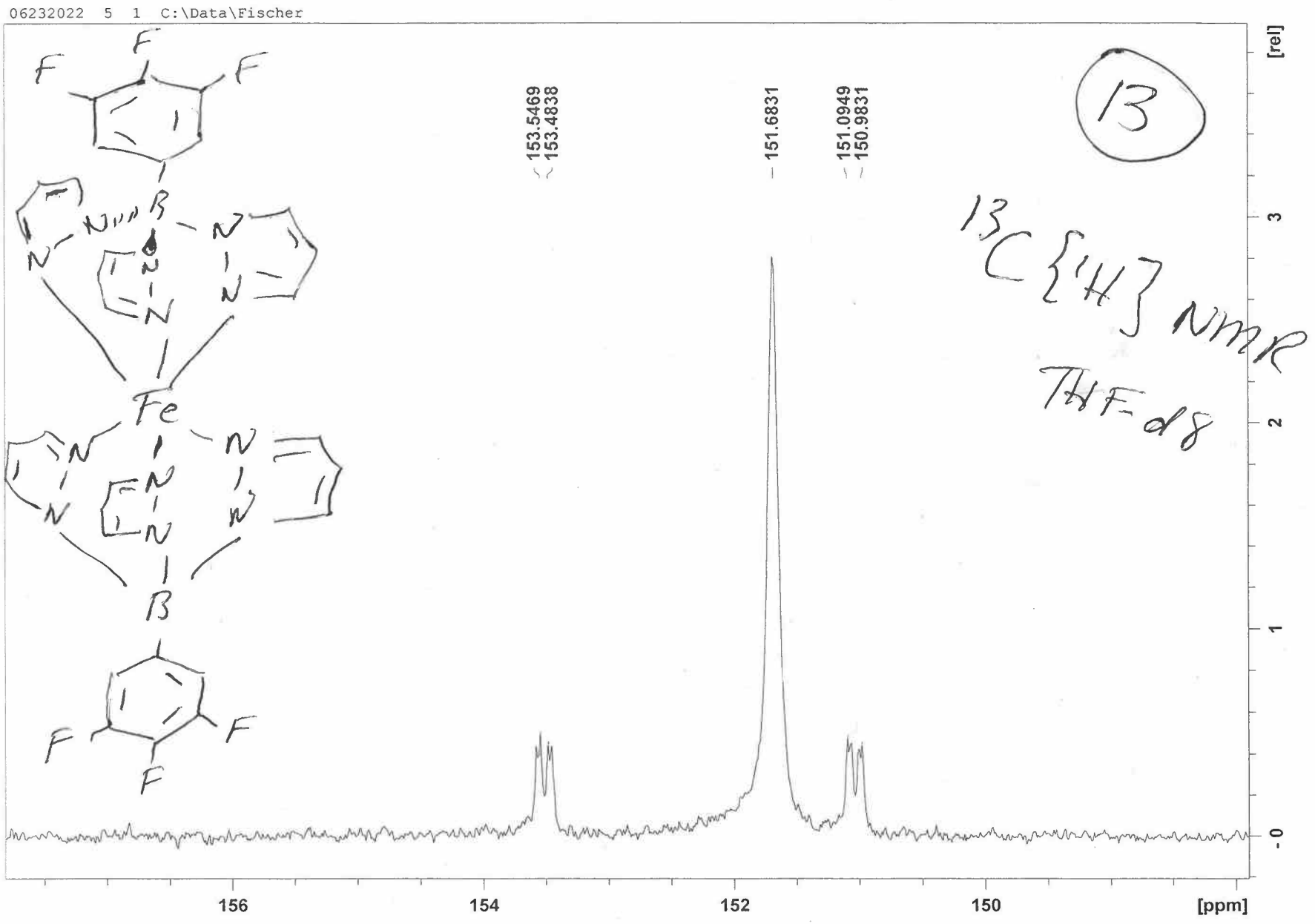
13



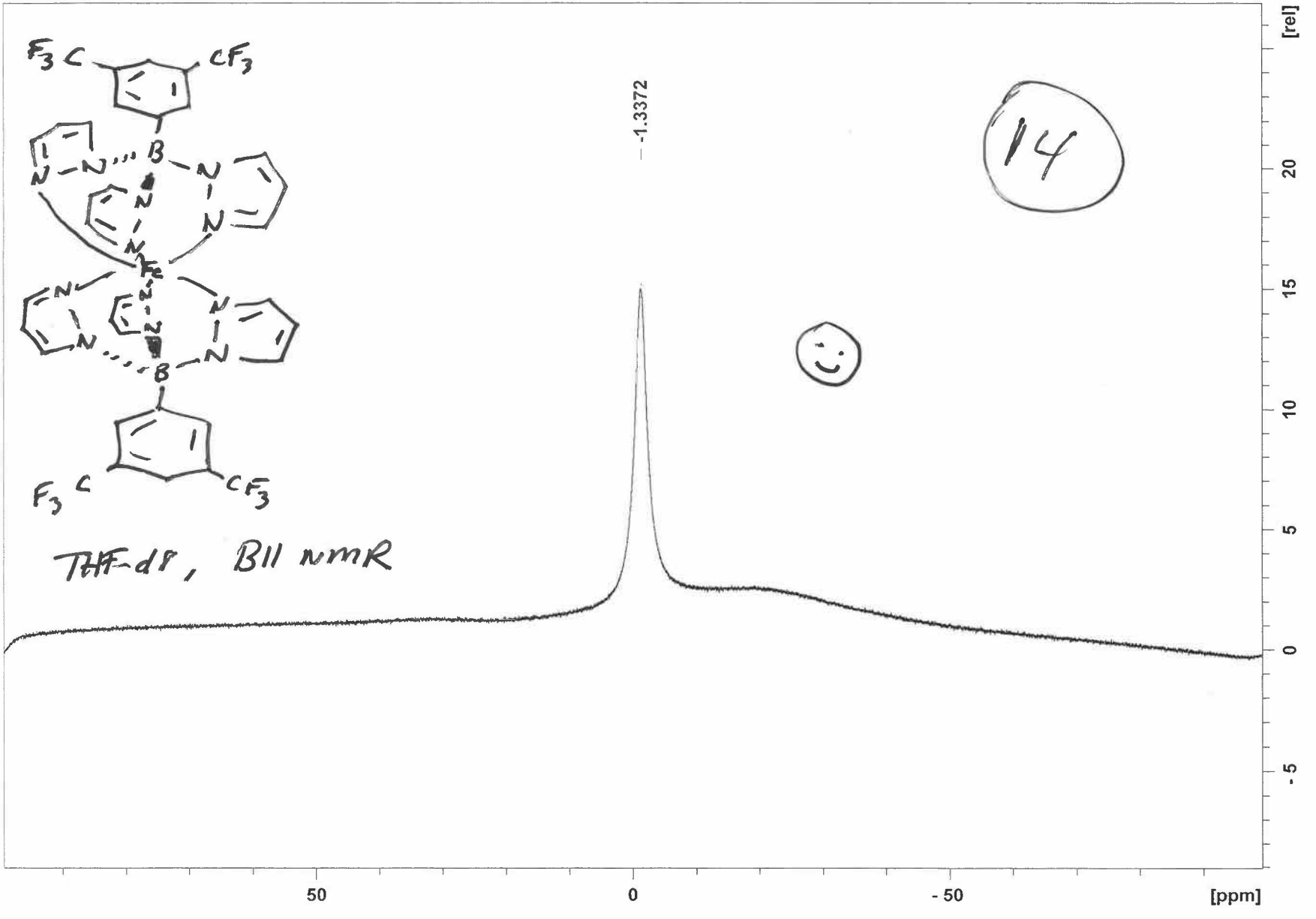

06232022 5 1 C:\Data\Fischer
13
120.0067
119.9591
119.8622
119.8147
13C{1H} NMR
THF-d8
[rel]
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
121.5
121.0
120.5
120.0
119.5
119.0
[ppm]

$^{13}C\{^{1}H\}$ NMR THF-d8



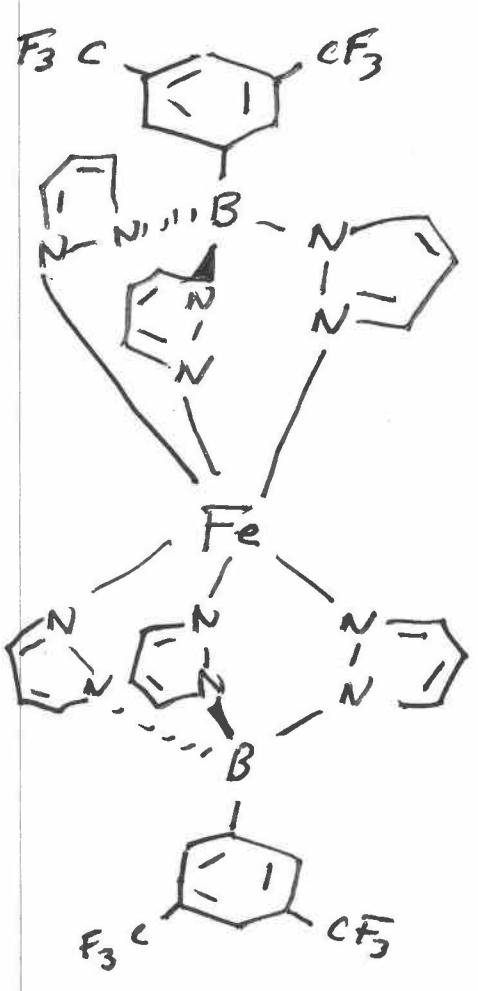

06232022 5 1 C:\Data\Fischer
153.5469
153.4838
151.6831
151.0949
150.9831
13
13C{1H} NMR
THF-d8
[rel]
3
2
1
-0
156
154
152
150
[ppm]

07072022 1 1 C:\Data\Fischer



14

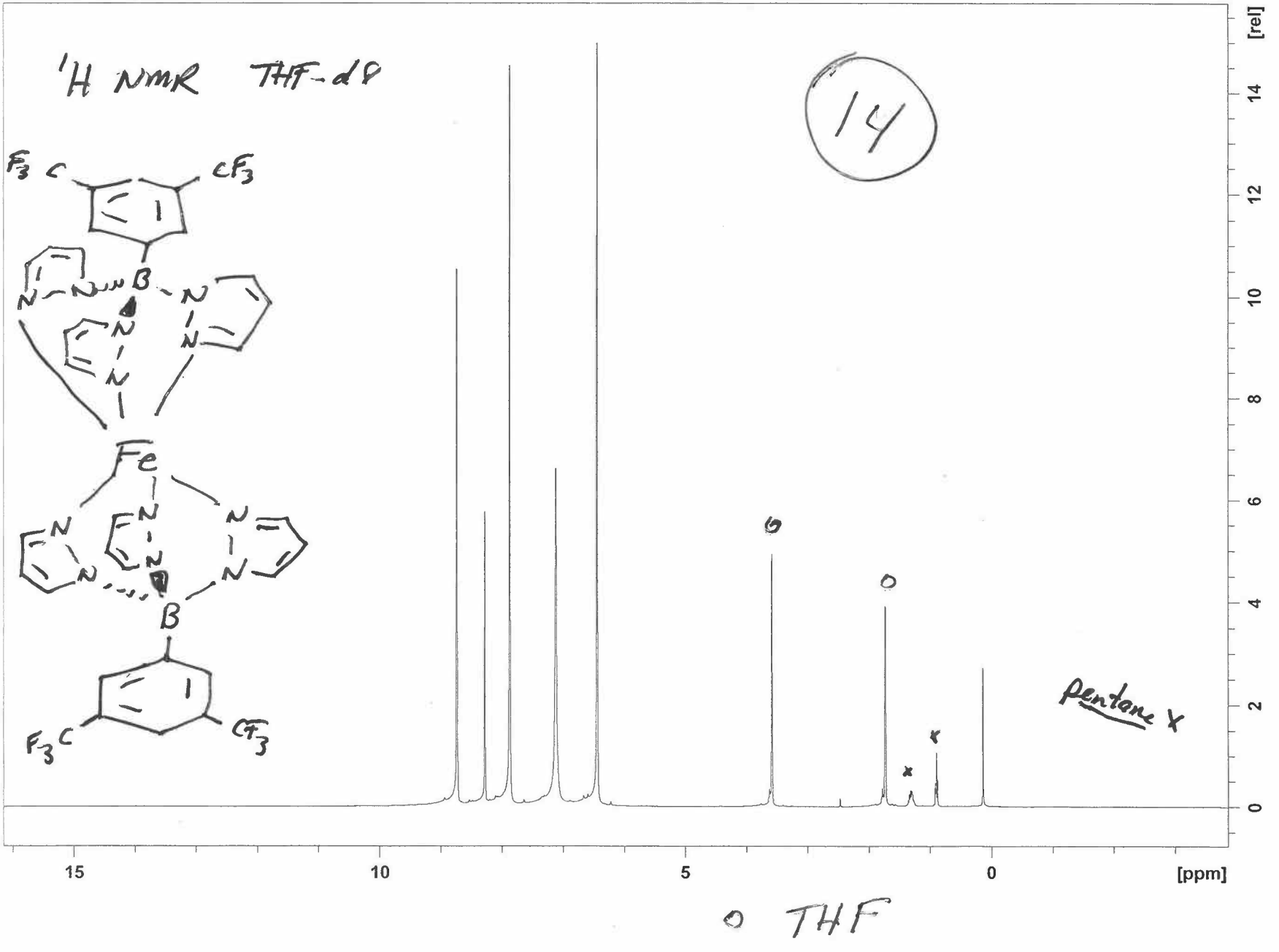
07072022 2 1 C:\Data\Fischer



-63.3248

THF-d8 NMR
F19

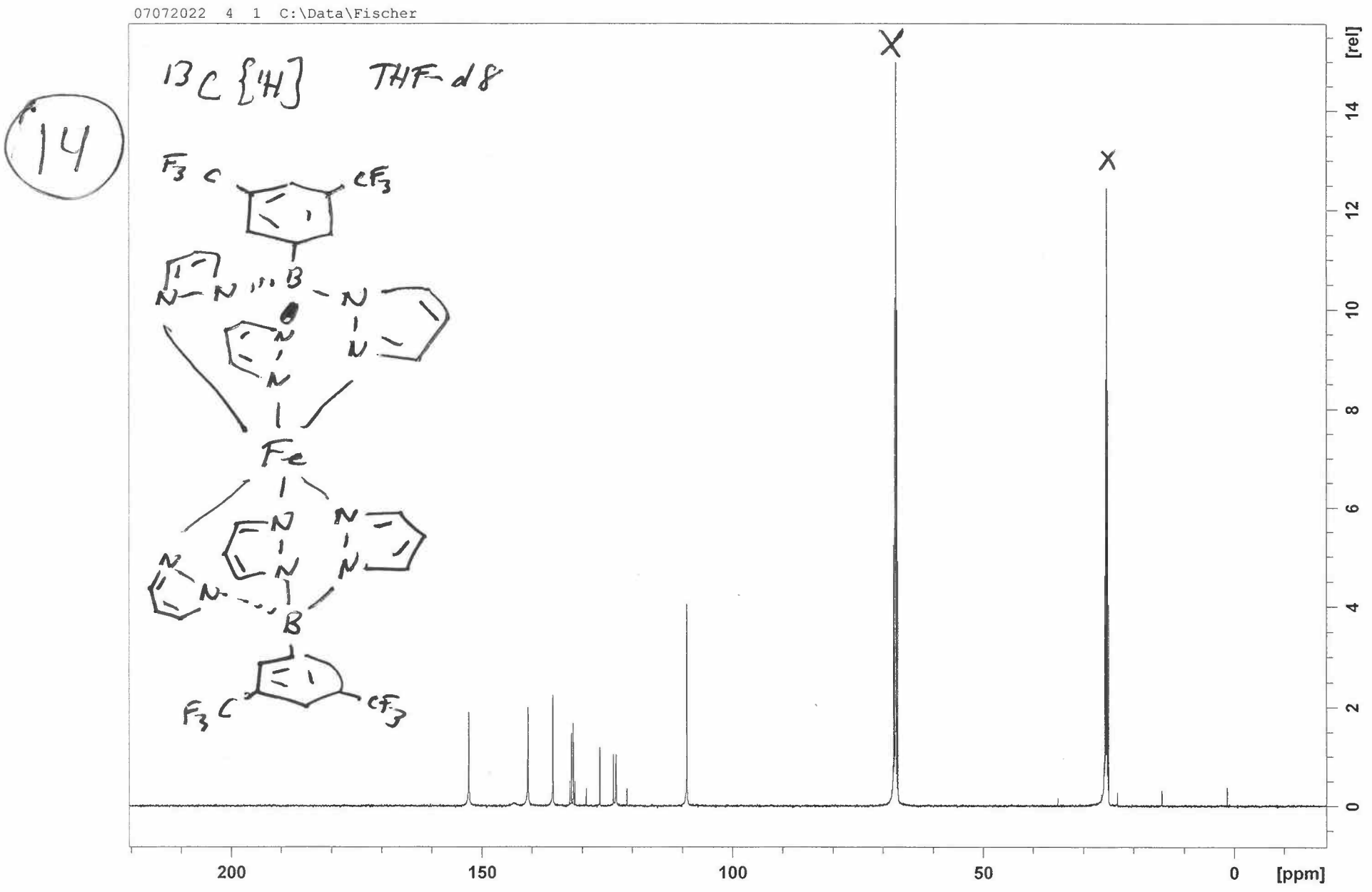
$^{19}F\{^{1}H\}$

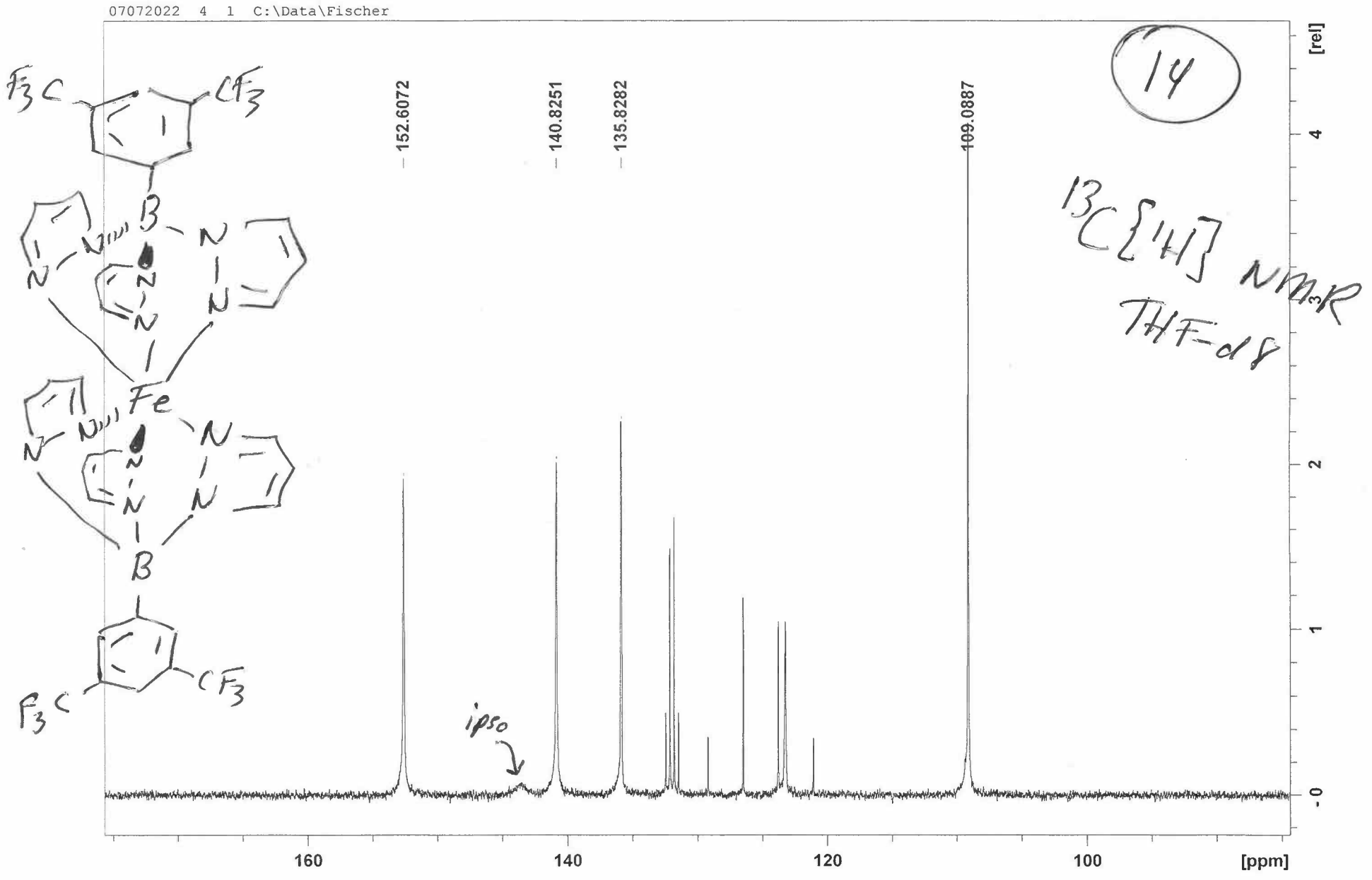

07072022 3 1 C:\Data\Fischer
^{1}H NMR THF-d8
14
G
O
x
x
Pentane x
O THF
15
10
5
0
[ppm]
[rel]
0
2
4
6
8
10
12
14

^{1}H NMR
THF-d_8

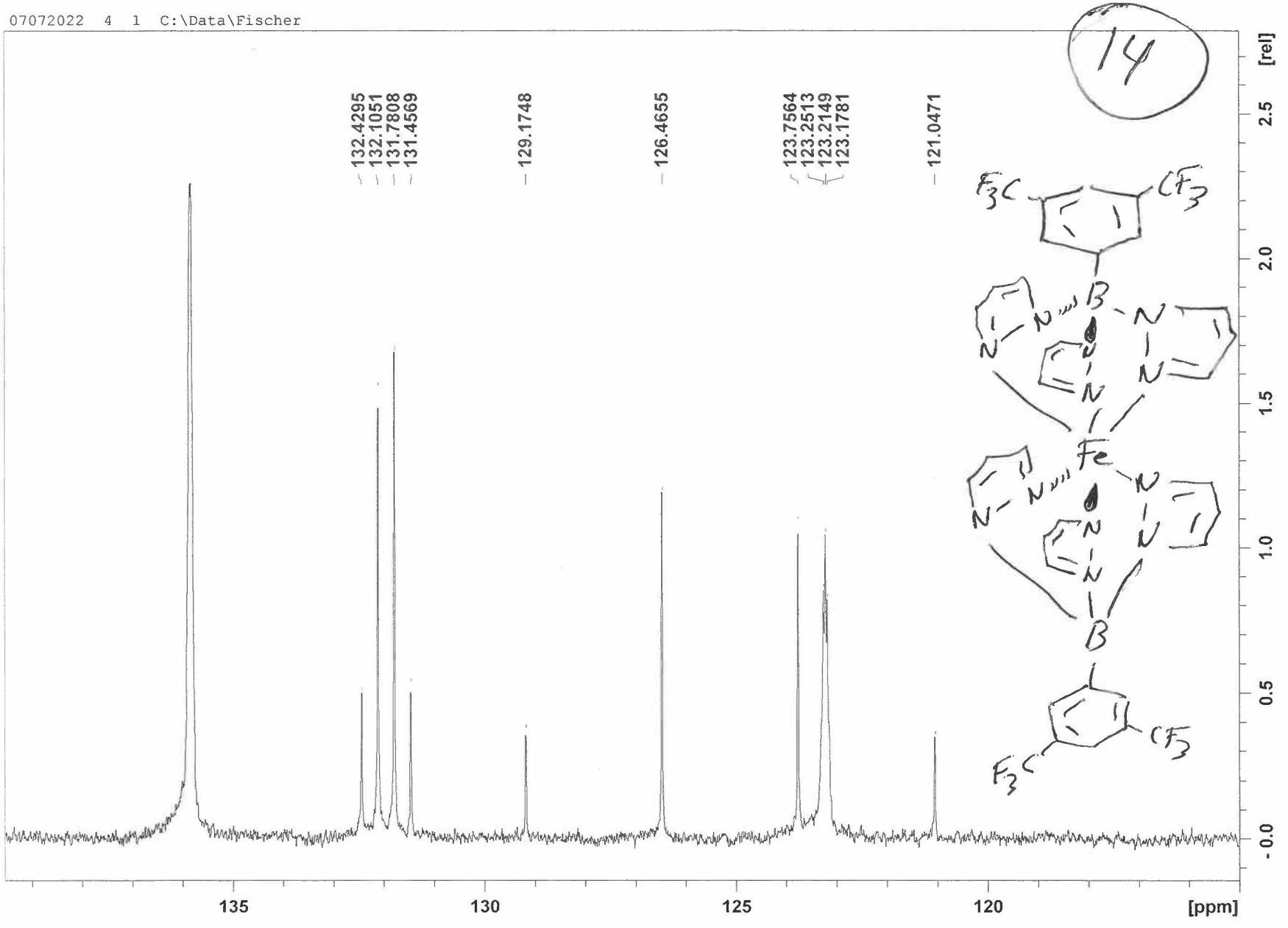
(1y)

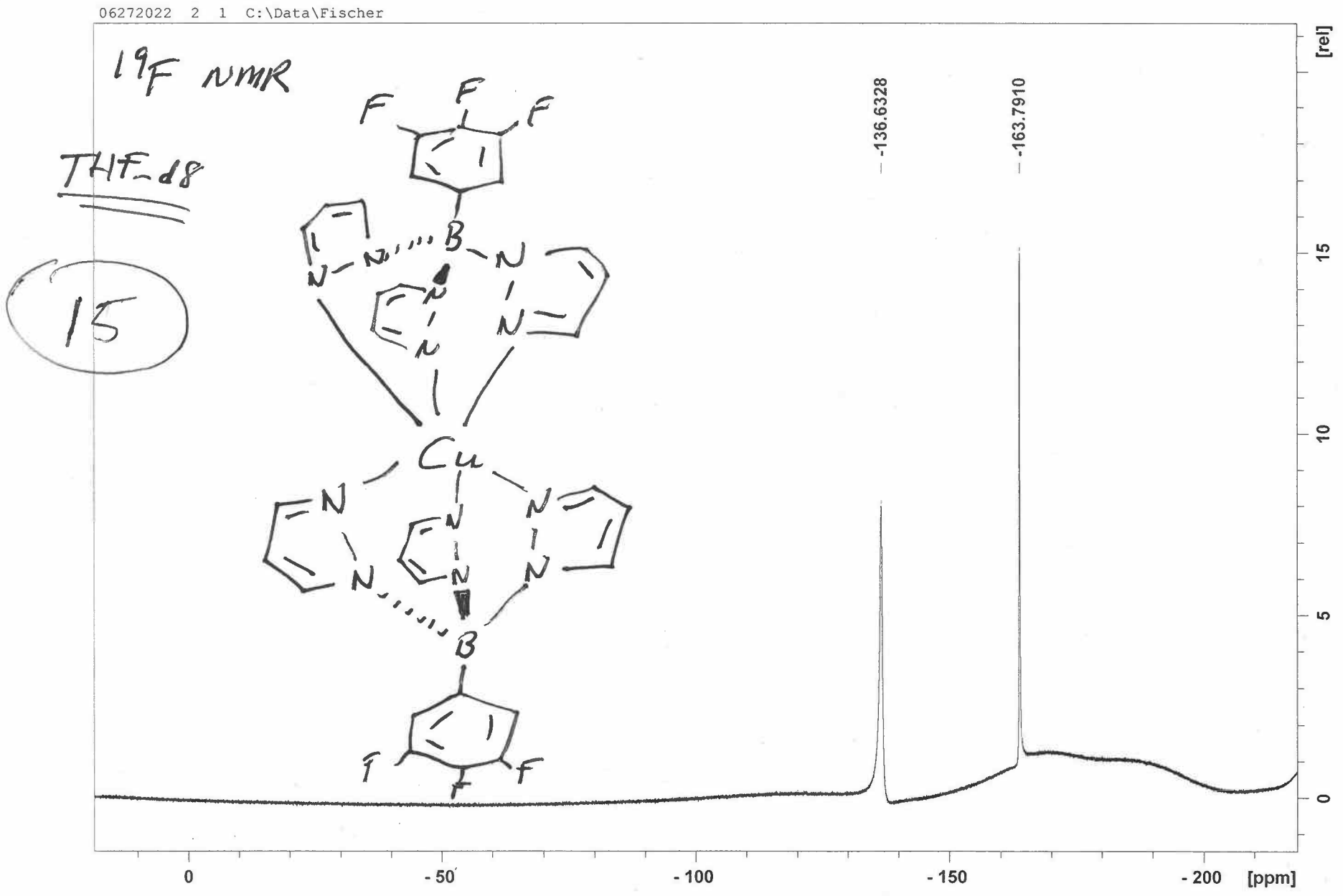
X THF-d8

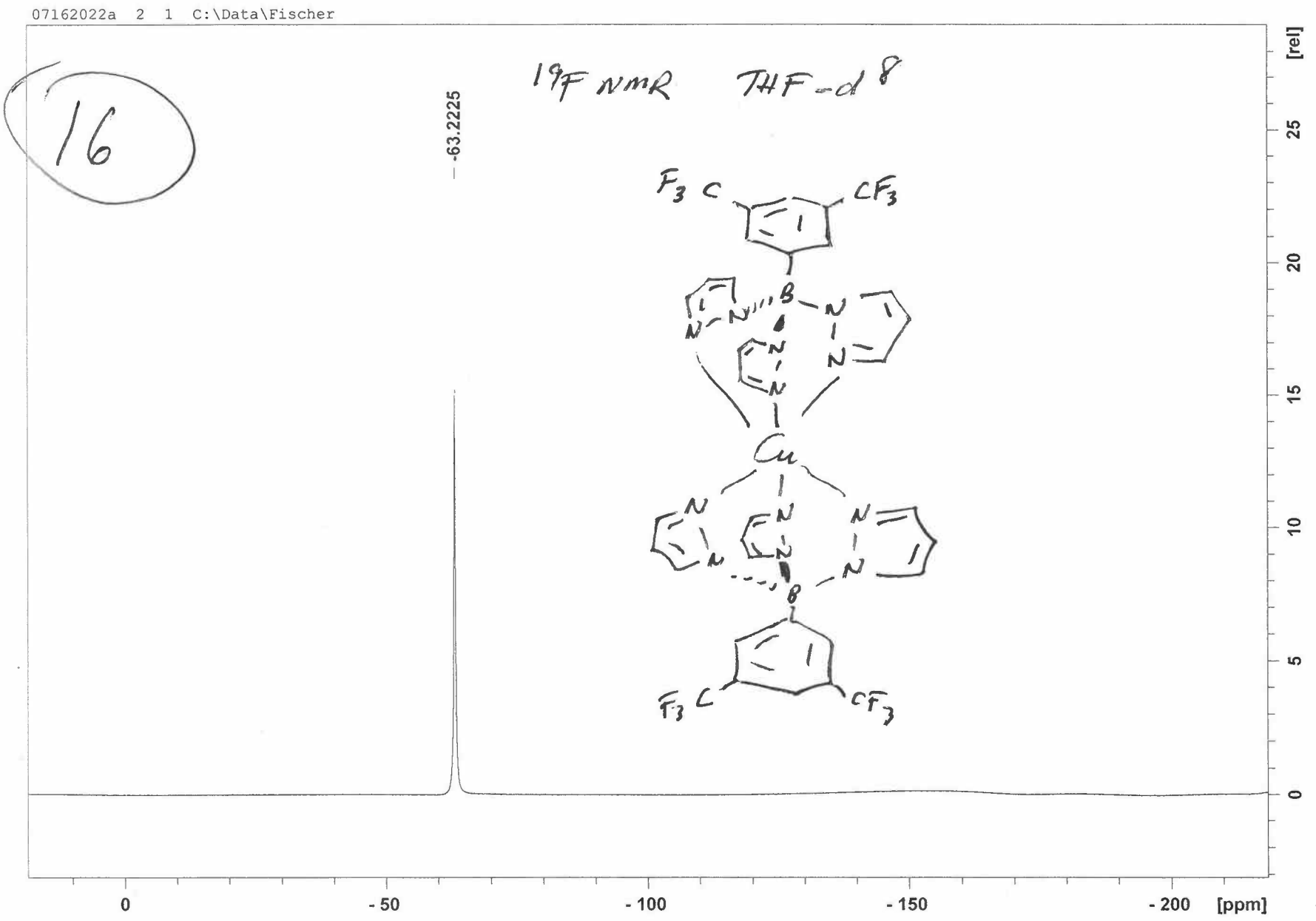

07072022 4 1 C:\Data\Fischer
13C {1H} THF-d8
14
X
X
F3C
CF3
Fe
B
F3C
CF3
[rel]
14
12
10
8
6
4
2
0
200
150
100
50
0
[ppm]


07072022 4 1 C:\Data\Fischer
14
$^{13}C\{^1H\}$ NMR
THF-d8
152.6072
140.8251
135.8282
109.0887
ipso
[rel]
[ppm]
160
140
120
100

$^{13}C\{^{1}H\}$ NMR THF-d8

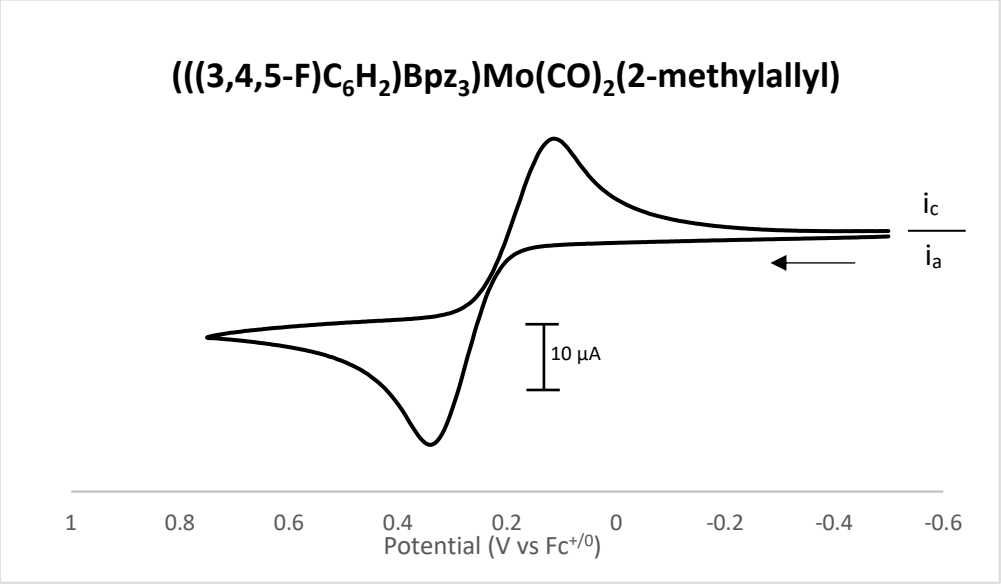



06272022 2 1 C:\Data\Fischer
19F NMR
THF-d8
15
-136.6328
-163.7910
[rel]
0
5
10
15
0
- 50
- 100
- 150
- 200
[ppm]


07162022a 2 1 C:\Data\Fischer
16
19F NMR THF-d8
-63.2225
F3C
CF3
Cu
B
F3C
CF3
[rel]
25
20
15
10
5
0
0
-50
-100
-150
-200
[ppm]

VII. Cyclic Voltammetry Data and Voltammograms

Fig. S12. Cyclic Voltammogram of (((3,4,5-F)C_6H_2)Bpz_3)$Mo(CO)_2$(2-methallyl) (9)



Solvent = Dichloromethane (deoxygenated via sparging with nitrogen and dried via passage through an activated alumina column of a Pure Process Technology solvent purification system; the CH_2Cl_2 was stored over activated 4 Å molecular sieves until use)

Analyte Concentration = 3.4 mM

Supporting Electrolyte = $[NBu_4][B\{3,5\text{-}(CF_3)C_6H_3\}_4]$ (0.10 M)

Atmosphere = Nitrogen

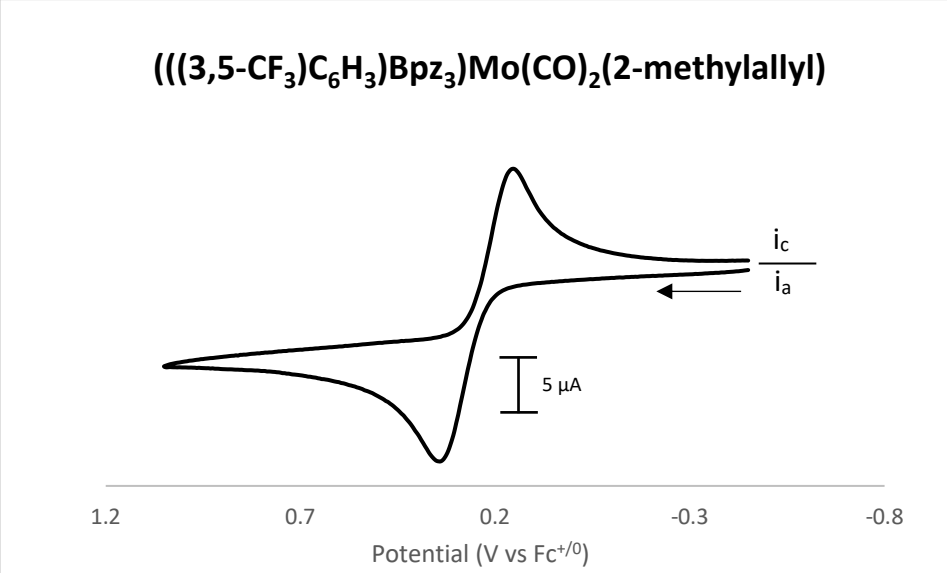
Scan Rate = 0.1 V s^{-1}

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **9** with a 0.10 M $[NBu_4][B\{3,5\text{-}(CF_3)C_6H_3\}_4]$ solution.

Half-Cell Potential = 0.23 V

Fig. S13: Cyclic Voltammogram of (((3,5-CF_3)C_6H_3)Bpz_3)$Mo(CO)_2$(2-methallyl) (10)



Solvent = Dichloromethane (deoxygenated via sparging with nitrogen and dried via passage through an activated alumina column of a Pure Process Technology solvent purification system; the CH_2Cl_2 was stored over activated 4 Å molecular sieves until use)

Analyte Concentration = 1.9 mM

Supporting Electrolyte = [NBu_4][B{3,5-(CF_3)C_6H_3}$_4$] (0.10 M)

Atmosphere = Nitrogen

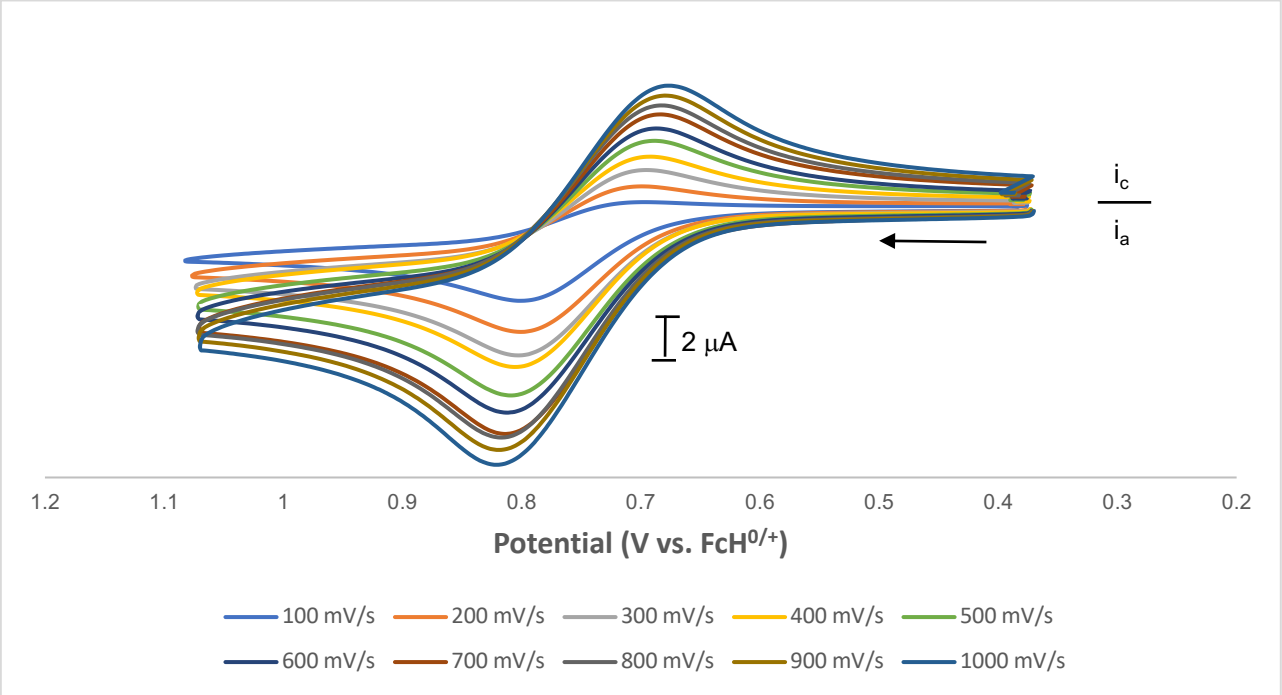
Scan Rate = 0.1 V s^{-1}

Reference = $FeCp_2$/[$FeCp_2$]$^+$

Background scans were obtained prior to the addition of **10** with a 0.10 M [NBu_4][B{3,5-(CF_3)C_6H_3}$_4$] solution.

Half-Cell Potential = 0.25 V

Fig. S14 : Cyclic Voltammograms of $(((3,4,5\text{-}F)C_6H_2)Bpz_3)Mn(CO)_3$ (11)



Solvent = Dichloromethane (Purified by passage through a Solv-Tek solvent system (A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics*, 1996, **15**, 1518.))

Analyte Concentration = 1 mM

Temperature = 21 ± 1 °C

Supporting Electrolyte = $[NBu_4][B(C_6F_5)_4]$ (0.05 M)

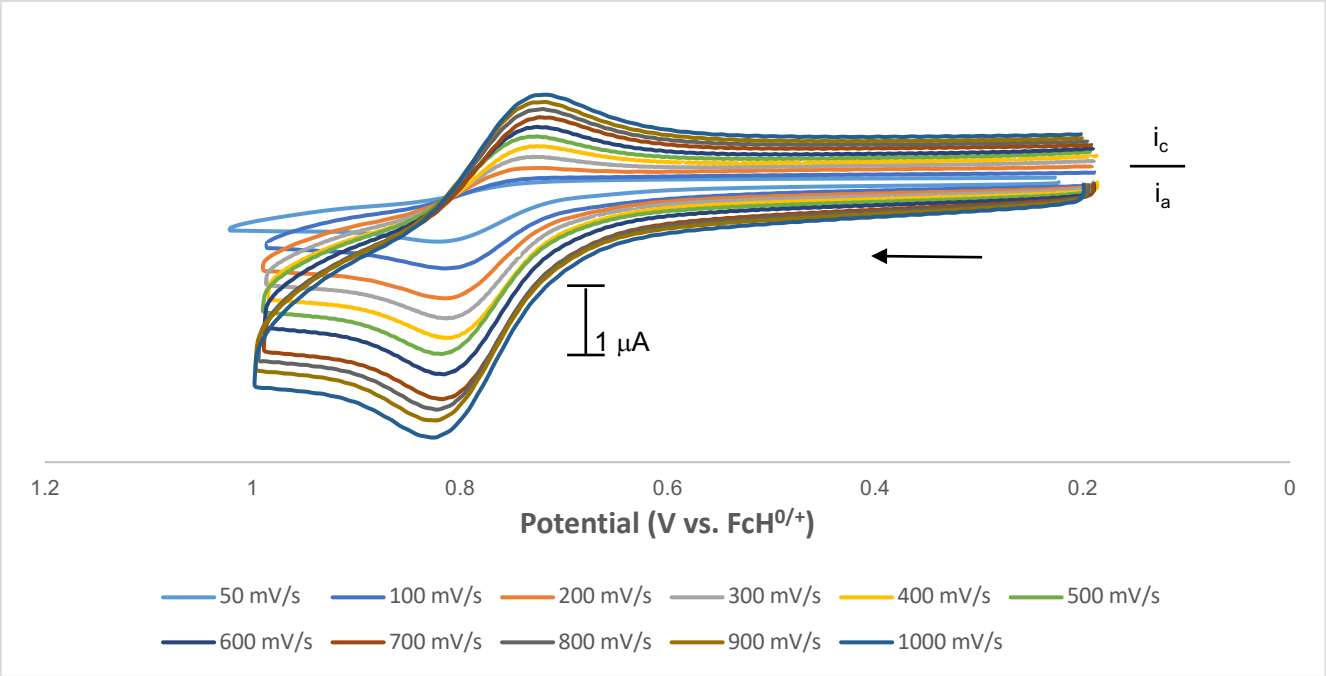
Atmosphere = Argon

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **11** with a 0.05 M $[NBu_4][B(C_6F_5)_4]$ solution.

Half-Cell Potential = 0.75 V

Fig. S15 : Cyclic Voltammograms of $(((3,5\text{-}CF_3)C_6H_3)Bpz_3)Mn(CO)_3$ (12)



Solvent = Dichloromethane (Purified by passage through a Solv-Tek solvent system (A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics*, 1996, **15**, 1518.))

Analyte Concentration = 1 mM

Temperature = 21 ± 1 °C

Supporting Electrolyte = $[NBu_4][B(C_6F_5)_4]$ (0.05 M)

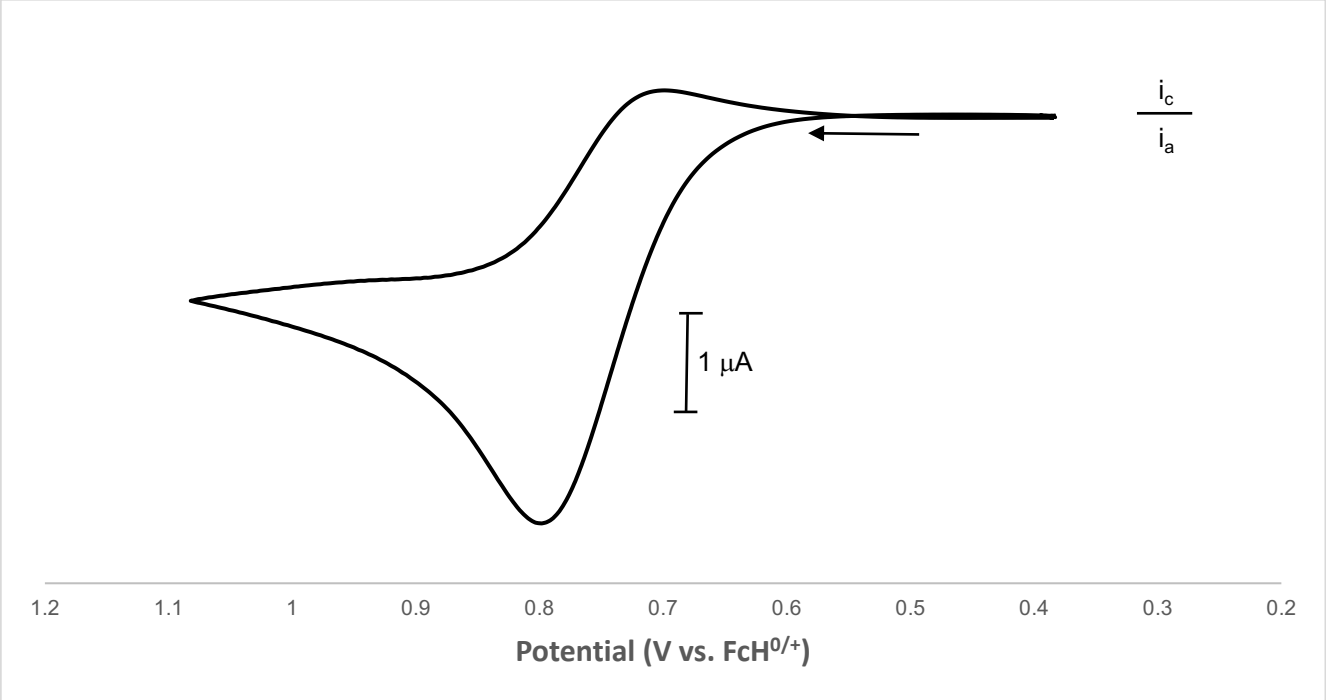
Atmosphere = Argon

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **12** with a 0.05 M $[NBu_4][B(C_6F_5)_4]$ solution.

Half-Cell Potential = 0.77 V

Fig. S16 : Cyclic Voltammogram of $(((3,4,5\text{-}F)C_6H_2)Bpz_3)Mn(CO)_3$ (11) at 0.1 V s^{-1} (i_r/i_f = 0.45)



Solvent = Dichloromethane (Purified by passage through a Solv-Tek solvent system (A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics*, 1996, **15**, 1518.))

Analyte Concentration = 1 mM

Temperature = 21 ± 1 °C

Supporting Electrolyte = $[NBu_4][B(C_6F_5)_4]$ (0.05 M)

Atmosphere = Argon

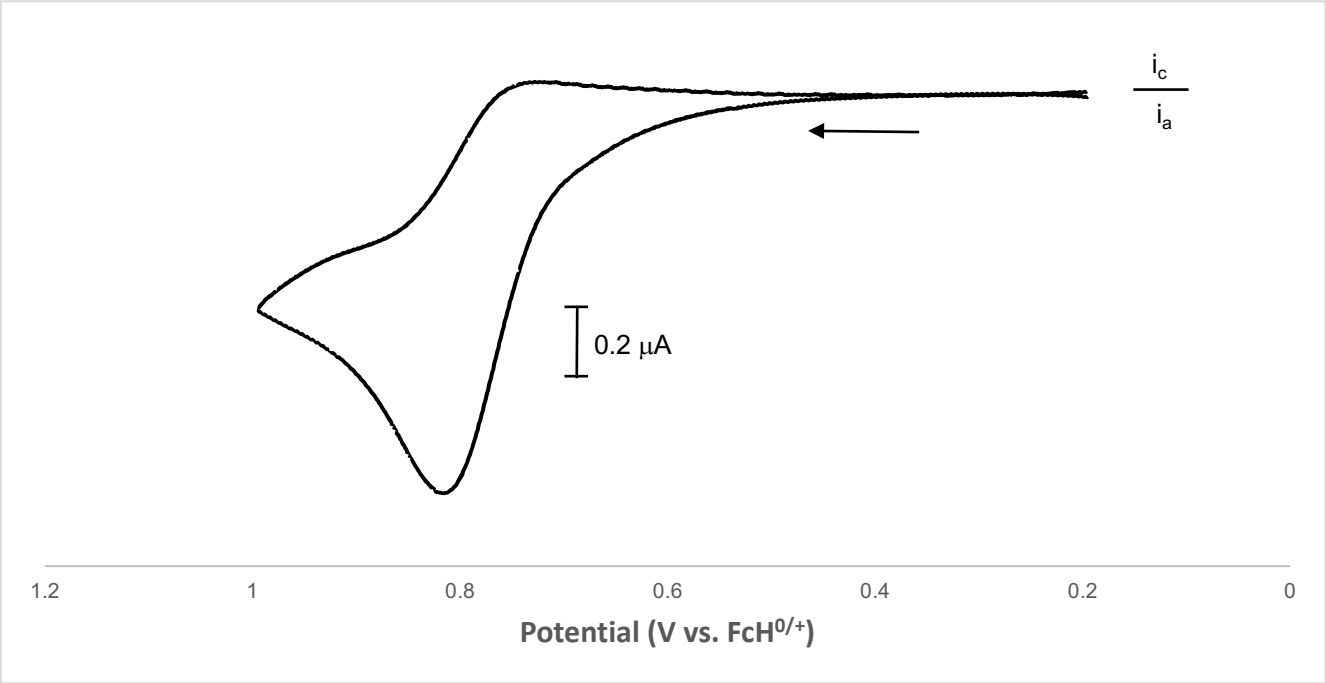
Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **11** with a 0.05 M $[NBu_4][B(C_6F_5)_4]$ solution.

Half-Cell Potential = 0.75 V

Fig. S17 : Cyclic Voltammogram of $(((3,5\text{-}CF_3)C_6H_3)Bpz_3)Mn(CO)_3$ (12) at 0.1 V s^{-1}

(i_r/i_f = 0.33)



Solvent = Dichloromethane (Purified by passage through a Solv-Tek solvent system (A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics*, 1996, **15**, 1518.))

Analyte Concentration = 1 mM

Temperature = 21 ± 1 °C

Supporting Electrolyte = $[NBu_4][B(C_6F_5)_4]$ (0.05 M)

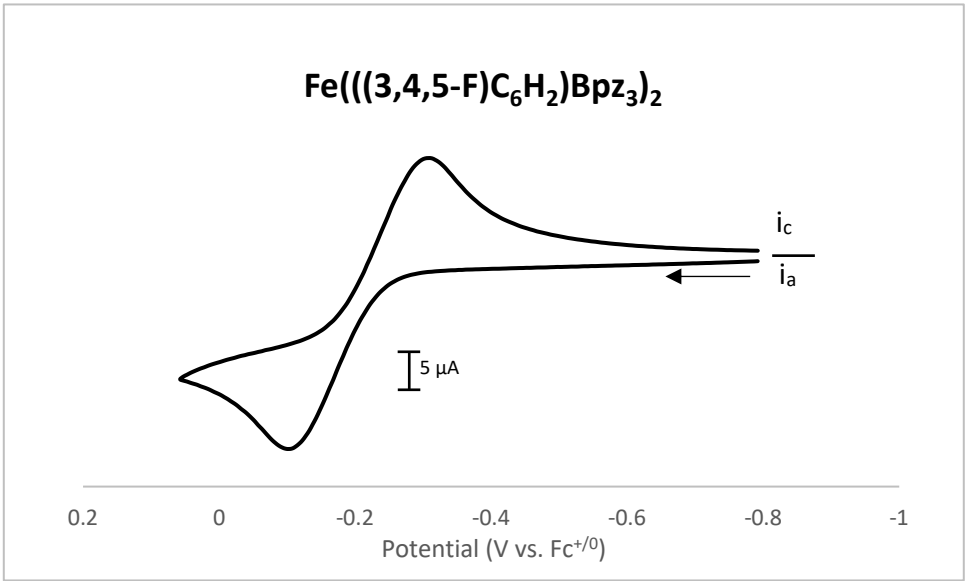
Atmosphere = Argon

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **12** with a 0.05 M $[NBu_4][B(C_6F_5)_4]$ solution.

Half-Cell Potential = 0.77 V

Fig. S18: Cyclic Voltammogram of $Fe(((3,4,5\text{-}F)C_6H_2)Bpz_3)_2$ (13)



Solvent = Dichloromethane (deoxygenated via sparging with nitrogen and dried via passage through an activated alumina column of a Pure Process Technology solvent purification system; the CH_2Cl_2 was stored over activated 4 Å molecular sieves until use)

Analyte Concentration = 2.8 mM

Supporting Electrolyte = $[NBu_4][BPh_4]$ (0.10 M)

Atmosphere = Nitrogen

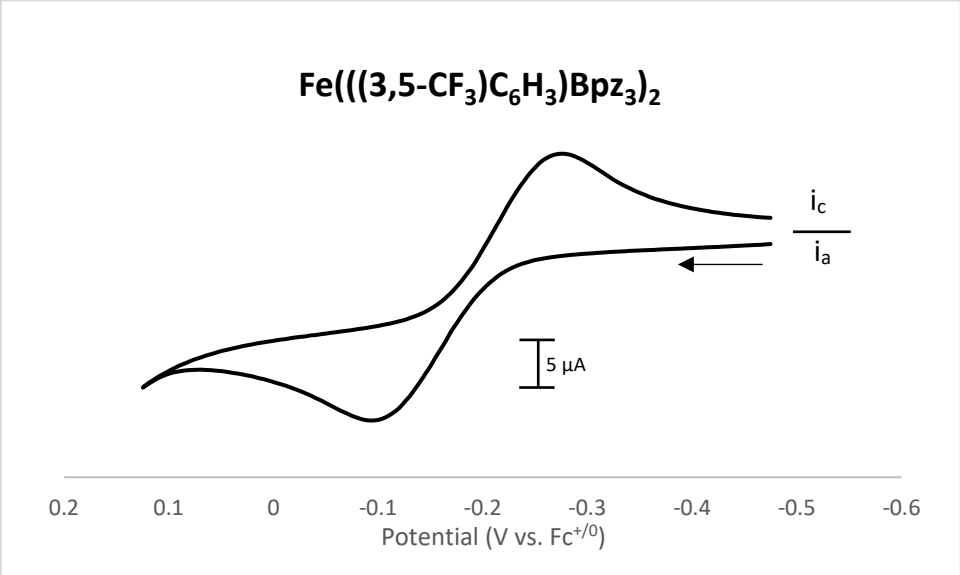
Scan Rate = 0.1 V s^{-1}

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **13** with a 0.10 M $[NBu_4][BPh_4]$ solution.

Half-Cell Potential = -0.21 V

Fig. S19: Cyclic Voltammogram of $Fe(((3,5\text{-}CF_3)C_6H_3)Bpz_3)_2$ (14)



Solvent = Dichloromethane (deoxygenated via sparging with nitrogen and dried via passage through an activated alumina column of a Pure Process Technology solvent purification system; the CH_2Cl_2 was stored over activated 4 Å molecular sieves until use)

Analyte Concentration = 2.3 mM

Supporting Electrolyte = $[NBu_4][BPh_4]$ (0.10 M)

Atmosphere = Nitrogen

Scan Rate = 0.1 V s^{-1}

Reference = $FeCp_2/[FeCp_2]^+$

Background scans were obtained prior to the addition of **14** with a 0.10 M $[NBu_4][BPh_4]$ solution.

Half-Cell Potential = -0.19 V