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Article

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Iron(III)-based metalloradical catalysis for asymmetric cyclopropanation via a stepwise radical mechanism

In the format provided by the authors and unedited

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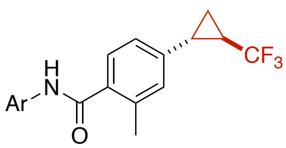
1. General Information

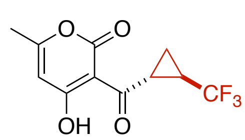
All catalytic reactions were performed in anhydrous solvents under a N_2 atmosphere in an oven-dried glassware following standard Schlenk techniques. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 µm). NMR spectra were acquired using Varian Inova 400 MHz, Bruker 500 MHz and Varian 600 MHz spectrometer. Spectra were processed using MNova software (Mestrelab). Chemical shifts are reported in parts per million (ppm), coupling constants (*J*) in Hz and are calibrated to residual protonated solvent. Infrared spectra of neat samples were acquired using a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® IV digital polarimeter. HPLC measurements were carried out on a Shimadzu HPLC system with Chiralcel OJ-H, OD-H, IA, IB, IC, IF and (*R*,*R*)-Whelk-O1 columns. High-resolution mass spectrometry (DART and ESI) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA. The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer. Activated 4Å molecular sieves were purchased from Sigma-Aldrich. All reagents were purchased either from Aldrich, Alfa Aesar, Acros, Ak Sci, Oakwood Chemicals, Strem Chemicals or TCI and were used without further purification.

2. Selected Examples of Important Compounds Containing CF_3-Substituted Cyclopropane

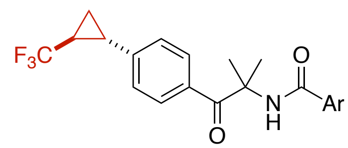
2.1. Figure S1: Bioactive Natural Products and Pharmaceuticals



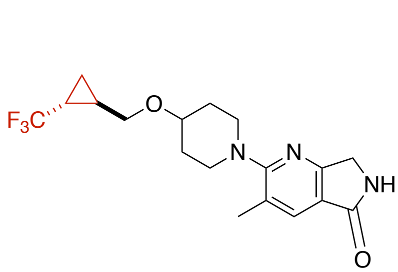
Analgesic



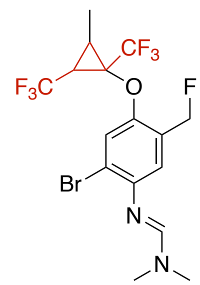
Insecticide



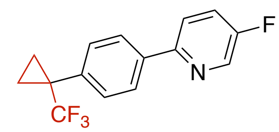
Nematicide



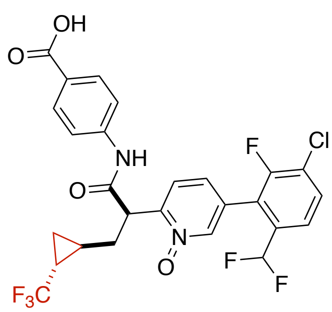
Allosteric Modulator



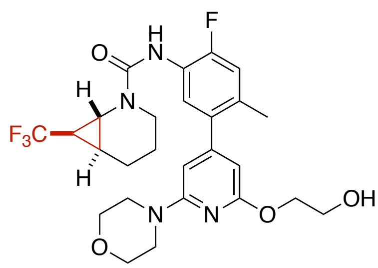
Pesticide



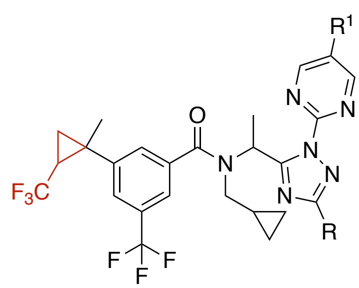
antiproliferative agent



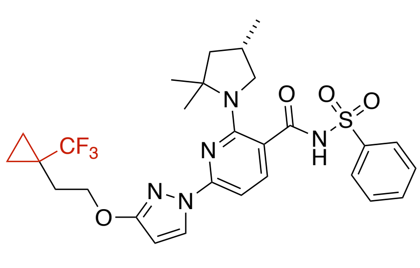
XIa inhibitor



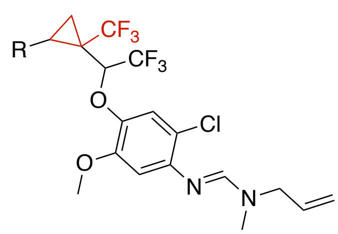
Raf kinases inhibitor



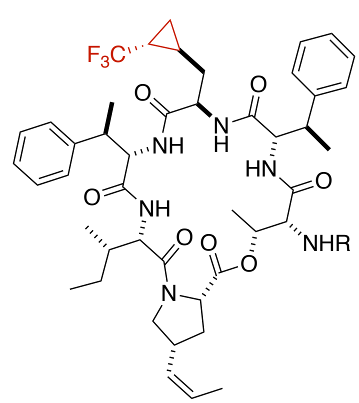
Insecticide



Cystic Fibrosis Transmembrane
Conductance Regulator
Modulator



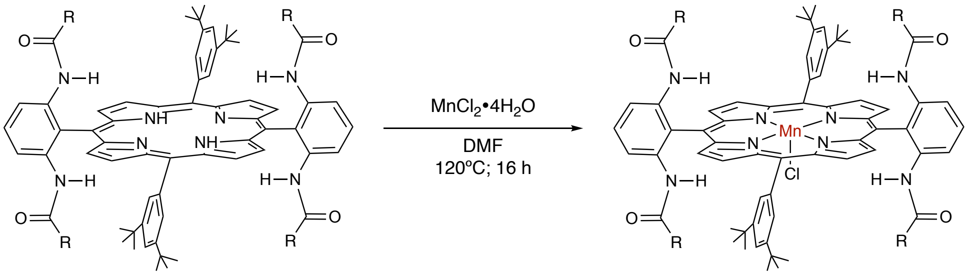
Pesticide



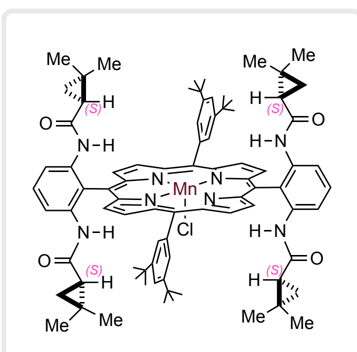
Antibiotic

3. Synthesis of Catalyst

3.1. General Procedure for Preparation of [Mn(Por)Cl]

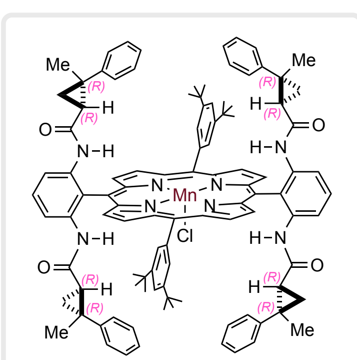


An oven-dried Schlenk tube was charged with 1.0 equivalent of porphyrin and 16.0 equivalents of $MnCl_2$•$4H_2O$. The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and DMF was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at 120 ºC. After 16 h, the reaction mixture was extracted with ethyl acetate and 1N HCl for two times, then the organic layer was washed by brine. The combined ethyl acetate layer was dried with Na_2SO_4, filtered and the solvent was concentrated *in vacuo*. The residue was purified via a flash chromatography to afford the compound.



[Mn(3,5-Di^{t}Bu-ChenPhyrin)Cl] ([Mn(P2)Cl])

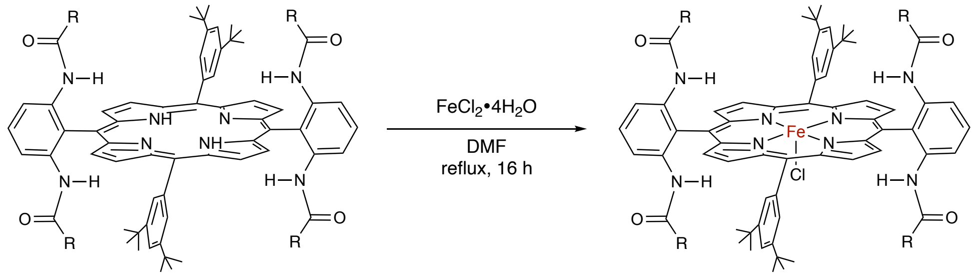
IR (neat, cm^{-1}): 2962, 2870, 1695, 1585, 1465, 1276, 1163, 1009. HRMS-(ESI) calculated for $C_{84}H_{96}ClMnN_8O_4Na$ $[M+Na]^+$: 1393.6521, found 1393.6500. UV–Vis (CH_2Cl_2), λ_{max} nm (log ε): 376(4.84), 401(4.78), 481(5.22), 586(4.13), 621(4.06).



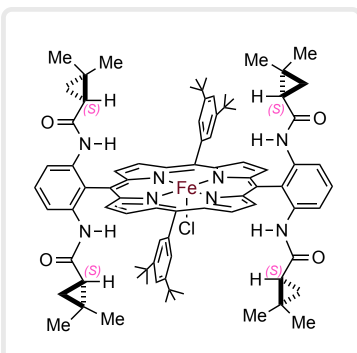
[Mn(3,5-Di^{t}Bu-QingPhyrin)Cl] ([Mn(P3)Cl])

IR (neat, cm^{-1}): 2961, 2870, 1692, 1585, 1466, 1275, 1163, 1009. HRMS-(ESI) calculated for $C_{104}H_{104}ClMnN_8O_4Na$ $[M+Na]^+$: 1641.7147, found 1641.7117. UV–Vis (CH_2Cl_2), λ_{max} nm (log ε): 377(4.75), 401(4.69), 483(5.12), 589(4.04), 623(3.97).

3.2. General Procedure for Preparation of [Fe(Por)Cl]

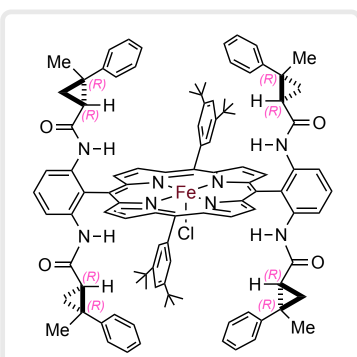


A round bottom flask was charged with 1.0 equivalent of porphyrin, 16.0 equivalents of $FeCl_2$•$4H_2O$ and DMF as the solvent. The mixture was stirred under reflux for 16 h. After the reaction completed, the reaction mixture was extracted with ethyl acetate and 1N HCl for two times, then the organic layer was washed by brine. The combined ethyl acetate layer was dried with Na_2SO_4, filtered and the solvent was concentrated *in vacuo*. The residue was purified by filtering through a plug of silica and then concentrated *in vacuo*.



[Fe(3,5-Di^{t}Bu-ChenPhyrin)Cl] ([Fe(P2)Cl])

IR (neat, cm^{-1}): 3412, 2961, 2869, 1698, 1588, 1465, 1282, 999. HRMS-(ESI) calculated for $C_{84}H_{96}ClFeN_8O_4Na$ $[M+Na]^+$: 1394.6490, found 1394.6467. UV–Vis (CH_2Cl_2), λ_{max} nm (log ε): 377(4.74), 421(5.06), 512(4.15), 666(3.58). The structure was characterized by X-ray crystallography.



[Fe(3,5-Di^{t}Bu-QingPhyrin)Cl] ([Fe(P3)Cl])

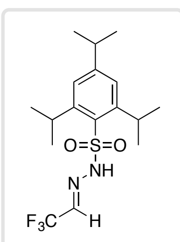
IR (neat, cm^{-1}): 3416, 2961, 2870, 1697, 1587, 1466, 1261, 999. HRMS-(ESI) calculated for $C_{104}H_{104}ClFeN_8O_4Na$ $[M+Na]^+$: 1642.7116, found 1642.7087. UV–Vis (CH_2Cl_2), λ_{max} nm (log ε): 373(4.68), 423(5.03), 511(4.13), 665(3.61). Magnetic susceptibility μ_{eff} = 5.68 μB (SQUID, solid, 6–300K); 5.62 μB (Evans, $CDCl_3$, 500 MHz, 298K).

4. Synthesis of Substrates

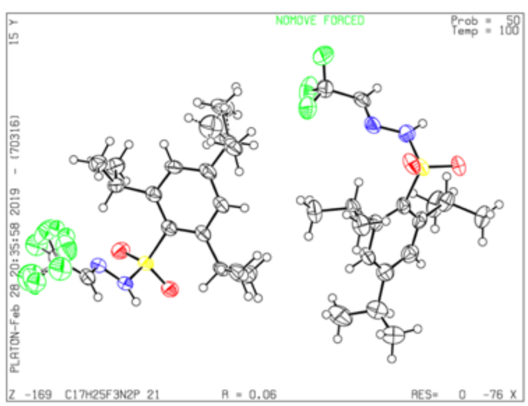
4.1. General Procedure for Preparation of Trifluoroacetaldehyde *N*-Trisylhydrazone

A 100 mL round-bottom flask was charged with 2,4,6-triisopropylbenzenesulfonyl hydrazide (2.0 g, 6.7 mmol) followed by addition of 50 mL of DCE. Once the solid was dissolved, trifluoroacetaldehyde hydrate (1.5 equiv, 10.1 mmol) and acetic acid (10 drops) were added dropwise at 0 degrees Celsius. After the reaction was stirred for 3 h, BF_3•OEt_2 (0.5 equiv, 3.4 mmol) was added dropwise and the reaction was stirred overnight at room temperature. When the reaction was completed, the solvent was removed directly under reduced pressure, and the residue as a solid was triturated with hexanes to give the desired product.

2,2,2-Trifluoroacetaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (1)



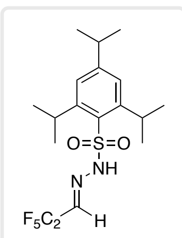
Yield: 88%. White solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.73 (s, 1H), 7.44 (q, J = 4.0 Hz, 1H), 7.25 (d, J = 1.5 Hz, 2H), 4.07 ((hept, J = 6.6 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.18 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.8 Hz, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.3, 150.5, 131.3, 130.5 (q, J = 37.9, 37.5 Hz), 123.7, 119.9 (q, J = 270.9 Hz), 33.3, 29.1, 24.4, 23.2. ^{19}F NMR (470 MHz, DMSO-d_6) δ -66.20 (d, J = 4.0 Hz). IR (neat, cm^{-1}): 3169, 2971, 1601, 1376, 1179, 1136, 1088, 950. HRMS-(DART+) calculated for $C_{17}H_{26}F_3N_2O_2S$ [M+H]$^+$: 379.1662, found: 379.1658. The structure was characterized by X-ray crystallography.



4.2. General Procedure for Preparation of Pentafluoropropionaldehyde *N*-Trisylhydrazone

A 100 mL round-bottom flask was charged with 2,4,6-triisopropylbenzenesulfonyl hydrazide (2.0 g, 6.7 mmol) followed by addition of 50 mL of DCE. Once the solid was dissolved, pentafluoropropionaldehyde hydrate (1.5 equiv, 10.1 mmol) and acetic acid (10 drops) were added dropwise at 0 degrees Celsius. After the reaction was stirred for 3 h, $BF_3•OEt_2$ (0.5 equiv, 3.4 mmol) was added dropwise and the reaction was stirred overnight at room temperature. When the reaction was completed, the solvent was removed directly under reduced pressure, and the residue as a solid was triturated with hexanes to give the desired product.

2,2,3,3,3-Pentafluoropropionaldehyde 2,4,6-triisopropylbenzenesulfonyl hydrazone (4a)



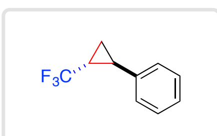
Yield: 82%. White solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.88 (s, 1H), 7.41 (t, J = 6.1 Hz, 1H), 7.26 (s, 2H), 4.05 (hept, J = 6.8 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 1.19 (d, J = 6.9 Hz, 6H), 1.17 (d, J = 6.7 Hz, 12H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.5, 150.6, 131.1, 129.4 (t, J = 28.8 Hz), 123.7, 118.0 (qt, J = 286.7, 37.7 Hz), 109.7 (tq, J = 250.7, 37.7 Hz), 33.4, 29.2, 24.4, 23.3. ^{19}F NMR (471 MHz, DMSO-d_6) δ -83.01, -115.35 (d, J = 7.0 Hz). IR (neat, cm^{-1}): 3164, 2964, 1600, 1319, 1264, 1205, 1171, 1095. HRMS-(DART+) calculated for $C_{18}H_{29}F_5N_3O_2S$ [M+NH_4]$^+$: 446.1895, found: 446.1889.

5. Synthesis of Products

5.1. General Procedure for [Fe(Por)Cl]-Catalyzed Cyclopropanation

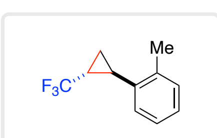
An oven-dried Schlenk tube was charged with 1.0 equivalent of olefin (0.1 mmol), 1.2 equivalents of hydrazone (0.12 mmol), [Fe(Por)Cl] (2 mol %) and 2.4 equivalents of Cs_2CO_3 (0.24 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and hexanes (1 mL) was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at 4 ºC. After 20 h, the reaction mixture was filtered through a plug of silica and then concentrated *in vacuo*. The residue was purified via a flash chromatography to afford the compound as a mixture of *trans*/*cis* diastereomers. (*The modification of reaction conditions is substrate-dependent, the details mentioned in the main text Table 3.*)

((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzene (3a)



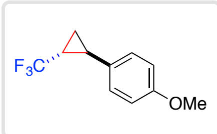
Yield: 92%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 98/2. $[\alpha]_D^{20}$ = (–)-37.99 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.1 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.12 (d, *J* = 7.3 Hz, 2H), 2.36 (dt, *J* = 10.0, 5.5 Hz, 1H), 1.80 (dt, *J* = 14.4, 6.3 Hz, 1H), 1.36 (dt, *J* = 11.1, 5.6 Hz, 1H), 1.17 (q, *J* = 7.0 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.7, 131.2, 129.4, 129.1, 127.6 (q, *J* = 270.9 Hz) 25.6 (q, *J* = 36.9 Hz), 22.2 (q, *J* = 2.7 Hz), 13.4 (q, *J* = 2.5 Hz). ^{19}F NMR (564 MHz, Chloroform-*d*) δ -66.80 (d, *J* = 6.8 Hz). IR (neat, cm^{-1}): 2981, 2888, 1421, 1269, 1144, 906, 731. HPLC analysis *trans*-isomer: *e.e.* = 91%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 7.6 min, t_{minor} = 8.4 min. HRMS-(DART+) calculated for $C_{10}H_{10}F_3$ $[M+H]^+$: 187.0729, found: 187.0726.

1-Methyl-2-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3b)



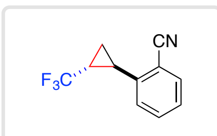
Yield: 95%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-78.97 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 – 7.16 (m, 2H), 7.15 (dd, *J* = 6.5, 3.9 Hz, 1H), 7.02 (d, *J* = 6.9 Hz, 1H), 2.42 (s, 3H), 2.38 – 2.33 (m, 1H), 1.78 – 1.64 (m, 1H), 1.35 (dt, *J* = 10.1, 5.4 Hz, 1H), 1.22 – 1.16 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.2, 136.8, 130.2, 127.2, 126.4 (q, *J* = 271.0 Hz), 126.3, 126.1, 21.9 (q, *J* = 36.6 Hz), 19.6, 18.3 (q, *J* = 2.8 Hz), 9.2 (q, *J* = 2.7 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.45 (d, *J* = 6.7 Hz). IR (neat, cm^{-1}): 3027, 2953, 1418, 1268, 1147, 906, 731. HPLC analysis *trans*-isomer: *e.e.* = 95%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 8.7 min, t_{major} = 9.3 min. HRMS-(DART+) calculated for $C_{11}H_{11}F_3$ $[M]^+$: 200.0807, found: 200.0802.

1-Methoxy-4-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3c)



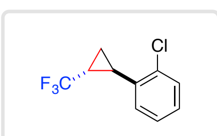
Yield: 81%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 95/5. $[\alpha]_D^{20}$ = (–)-74.98 (c = 0.4, $CHCl_3$). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.06 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 7.5 Hz, 2H), 3.79 (s, 3H), 2.32 (dt, J = 10.3, 5.5 Hz, 1H), 1.72 (dq, J = 13.4, 6.8 Hz, 1H), 1.32 (dt, J = 10.4, 5.5 Hz, 1H), 1.11 (dt, J = 8.6, 6.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.6, 131.1, 127.9, 126.2 (q, J = 271.0 Hz), 114.2, 55.5, 22.8 (q, J = 36.6 Hz), 19.1 (q, J = 2.8 Hz), 10.6 (q, J = 2.7 Hz). ^{19}F NMR (564 MHz, Chloroform-*d*) δ -66.74 (d, J = 6.8 Hz). IR (neat, cm^{-1}): 2959, 2924, 1518, 1420, 1250, 1139, 737. HPLC analysis *trans*-isomer: *e.e.* = 86%. IB (1% isopropanol: 99% hexane, 0.8 ml/min): t_{minor} = 7.9 min, t_{major} = 9.4 min. HRMS-(DART+) calculated for $C_{11}H_{12}F_3O$ $[M+H]^+$: 217.0835, found: 217.0826.

2-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzonitrile (3d)



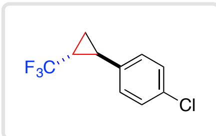
Yield: 96%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 98/2. $[\alpha]_D^{20}$ = (–)-50.98 (c = 0.4, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.69 (dt, J = 10.3, 5.5 Hz, 1H), 1.95 (dq, J = 12.1, 6.1 Hz, 1H), 1.60 – 1.55 (m, 1H), 1.28 – 1.22 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.6, 133.3, 133.2, 127.5, 126.3, 125.5 (q, J = 271.4 Hz), 117.5, 113.8, 22.9 (q, J = 37.5 Hz), 18.4 (q, J = 3.1 Hz), 11.3 (q, J = 2.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.90 (d, J = 6.2 Hz). IR (neat, cm^{-1}): 3066, 2226, 1421, 1268, 1146, 909, 762. HPLC analysis *trans*-isomer: *e.e.* = 92%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 20.1 min, t_{minor} = 22.7 min. HRMS-(DART+) calculated for $C_{11}H_9F_3N$ $[M+H]^+$: 212.0682, found: 212.0677.

1-Chloro-2-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3e)



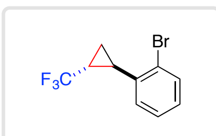
Yield: 99%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-76.97 (c = 0.2, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 1H), 7.12 (dd, J = 6.2, 2.1 Hz, 2H), 6.99 – 6.93 (m, 1H), 2.51 (dt, J = 10.2, 5.7 Hz, 1H), 1.72 (dq, J = 13.4, 6.4, 5.8 Hz, 1H), 1.34 (dt, J = 10.2, 5.6 Hz, 1H), 1.11 (q, J = 6.3 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.5, 135.7, 129.7, 128.3, 127.5, 127.0, 126.0 (q, J = 271.2 Hz), 22.3 (q, J = 37.2 Hz), 18.2 (q, J = 2.9 Hz), 9.9 (q, J = 2.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.71 (d, J = 6.5 Hz). IR (neat, cm^{-1}): 3063, 2964, 1419, 1267, 1139, 995, 751. HPLC analysis *trans*-isomer: *e.e.* = 94%. OJ-H (100% hexane, 0.4 ml/min): t_{major} = 12.6 min, t_{minor} = 13.1 min. HRMS-(DART+) calculated for $C_{10}H_8F_3Cl$ $[M]^+$: 220.0261, found: 220.0260.

1-Chloro-4-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3f)



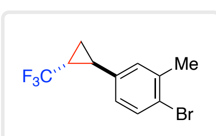
Yield: 83%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 97/3. $[\alpha]_D^{20}$ = (–)-66.98 (*c* = 0.2, CHCl3). [1]H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 2.0 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 2.34 (dt, *J* = 10.3, 5.4 Hz, 1H), 1.77 (dq, *J* = 13.3, 6.6, 6.1 Hz, 1H), 1.39 (dt, *J* = 10.7, 5.6 Hz, 1H), 1.18 – 1.13 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.6, 132.7, 128.9, 128.1, 125.9 (q, *J* = 271.0 Hz), 23.1 (q, *J* = 37.0 Hz), 19.2 (q, *J* = 2.9 Hz), 11.0 (q, *J* = 2.7 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.87 (d, *J* = 6.6 Hz). IR (neat, cm^{-1}): 2998, 2948, 1444, 1236, 1149, 907, 732. HPLC analysis *trans*-isomer: *e.e.* = 86%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 8.1 min, t_{major} = 9.2 min. HRMS-(DART+) calculated for $C_{10}H_9F_3Cl$ [M+H]$^+$: 221.0339, found: 211.0337.

1-Bromo-2-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3g)



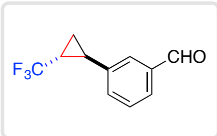
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 98/2. $[\alpha]_D^{20}$ = (–)-45.98 (*c* = 0.2, CHCl3). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 2.57 (dt, *J* = 10.5, 5.7 Hz, 1H), 1.80 (dt, *J* = 13.7, 6.4 Hz, 1H), 1.42 (dd, *J* = 9.8, 5.3 Hz, 1H), 1.19 – 1.14 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.2, 133.1, 128.7, 127.8, 127.7, 126.2, 126.1 (q, *J* = 271.2 Hz), 22.7 (q, *J* = 37.0 Hz), 20.9 (q, *J* = 3.1 Hz), 10.4 (q, *J* = 2.2 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.54 (d, *J* = 6.5 Hz). IR (neat, cm^{-1}): 3064, 2926, 1419, 1267, 1147, 906, 732. HPLC analysis *trans*-isomer: *e.e.* = 92%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 6.8 min, t_{minor} = 7.1 min. HRMS-(DART+) calculated for $C_{10}H_8BrF_3$ [M]$^+$: 263.9756, found: 263.9751.

1-Bromo-2-methyl-4-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)benzene (3h)



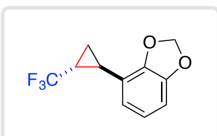
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 97/3. $[\alpha]_D^{20}$ = (–)-73.58 (*c* = 0.5, CHCl3). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.2 Hz, 1H), 6.99 (s, 1H), 6.79 (dd, *J* = 8.2, 1.9 Hz, 1H), 2.37 (s, 3H), 2.29 (dt, *J* = 10.1, 5.3 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.36 (dt, *J* = 9.5, 5.6 Hz, 1H), 1.16 – 1.11 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 138.2, 132.6, 129.2, 125.9 (q, *J* = 271.0 Hz), 125.5, 123.1, 23.1 (q, *J* = 37.0 Hz), 23.0, 19.2 (q, *J* = 2.4 Hz), 10.9 (d, *J* = 2.7 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.85 (d, *J* = 6.5 Hz). IR (neat, cm^{-1}): 2961, 2927, 1467, 1267, 1138, 1029, 816. HPLC analysis *trans*-isomer: *e.e.* = 84%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 10.5 min, t_{major} = 11.1 min. HRMS-(DART+) calculated for $C_{11}H_{10}F_3Br$ [M]$^+$: 277.9912, found: 277.9913.

3-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzaldehyde (3i)



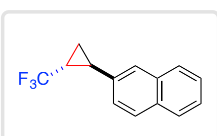
Yield: 94%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 97/3. $[\alpha]_D^{20}$ = (–)-83.97 (*c* = 0.2, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 10.00 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.63 (s, 1H), 7.54 – 7.37 (m, 2H), 2.44 (dt, *J* = 10.4, 5.4 Hz, 1H), 1.87 (hept, *J* = 7.2, 6.6 Hz, 1H), 1.45 (dt, *J* = 11.4, 5.8 Hz, 1H), 1.25 (q, *J* = 7.6, 6.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.1 (d, *J* = 3.0 Hz), 140.4, 136.9, 133.0, 129.5, 128.9, 126.9, 125.8 (q, *J* = 271.1 Hz), 23.3 (q, *J* = 37.1 Hz), 19.4 (q, *J* = 2.9 Hz), 11.1 (q, *J* = 2.7 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.91 (d, *J* = 6.6 Hz). IR (neat, cm^{-1}): 2963, 2824, 1700, 1422, 1270, 1137, 800. HPLC analysis *trans*-isomer: *e.e.* = 83%. IB (5% isopropanol: 95% hexane, 0.8 ml/min): t_{major} = 8.3 min, t_{minor} = 8.8 min. HRMS-(DART+) calculated for $C_{11}H_{10}F_3O$ $[M+H]^+$: 215.0678, found: 215.0675.

4-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzo[d][1,3]dioxole (3j)



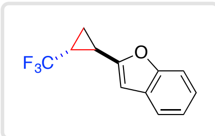
Yield: 62%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 97/3. $[\alpha]_D^{20}$ = (–)-29.32 (*c* = 0.3, $CHCl_3$). ^1H NMR (600 MHz, Chloroform-*d*) δ 6.76 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 5.94 (s, 2H), 2.30 (dt, *J* = 10.1, 5.6 Hz, 1H), 2.01 (dq, *J* = 12.7, 6.3 Hz, 1H), 1.31 (ddd, *J* = 21.1, 9.8, 5.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 145.4, 126.0 (q, *J* = 270.9 Hz), 121.7, 120.7, 120.0, 107.1, 100.8, 21.3 (q, *J* = 37.0 Hz), 14.9 (q, *J* = 2.9 Hz), 9.7 (q, *J* = 2.6 Hz). ^{19}F NMR (564 MHz, Chloroform-*d*) δ -67.01 (d, *J* = 6.5 Hz). IR (neat, cm^{-1}): 2964, 2895, 1454, 1269, 1144, 1065, 932, 767. HPLC analysis *trans*-isomer: *e.e.* = 84%. OD-H (1% isopropanol: 99% hexane, 0.8 ml/min): t_{minor} = 13.9 min, t_{major} = 14.6 min. HRMS-(DART+) calculated for $C_{11}H_9F_3O_2$ $[M]^+$: 230.0549, found: 230.0560.

2-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)naphthalene (3k)



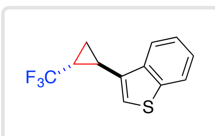
Yield: 91%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 98/2. $[\alpha]_D^{20}$ = (–)-31.99 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.79 (q, *J* = 7.9, 7.0 Hz, 3H), 7.60 – 7.56 (m, 1H), 7.46 (dddd, *J* = 14.5, 8.3, 6.9, 1.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 2.53 (dt, *J* = 10.2, 5.5 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.44 (dt, *J* = 9.5, 5.6 Hz, 1H), 1.32 – 1.27 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.5, 133.5, 132.5, 128.5, 127.8, 127.6, 126.5, 126.1 (q, *J* = 271.1 Hz), 125.8, 125.2, 125.0, 23.1 (q, *J* = 37.0 Hz), 20.0 (q, *J* = 2.7 Hz), 10.9 (q, *J* = 2.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.72 (d, *J* = 6.6 Hz). IR (neat, cm^{-1}): 2920, 1422, 1369, 1269, 1140, 848, 770. HPLC analysis *trans*-isomer: *e.e.* = 91%. IF (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 8.2 min, t_{minor} = 8.5 min. HRMS-(DART+) calculated for $C_{14}H_{11}F_3$ $[M]^+$: 236.0807, found: 236.0808.

2-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzofuran (3l)



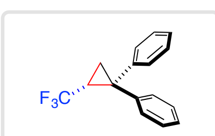
Yield: 99%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-80.47 (*c* = 0.5, $CHCl_3$). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.51 (s, 1H), 2.49 (dt, *J* = 9.8, 5.4 Hz, 1H), 2.16 (hept, *J* = 6.6 Hz, 1H), 1.42 (dq, *J* = 11.3, 5.8, 5.0 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.2, 154.5, 128.7, 125.6 (q, *J* = 271.2 Hz), 123.9, 123.0, 120.5, 111.0, 102.8 (d, *J* = 2.6 Hz), 21.7 (q, *J* = 37.4 Hz), 13.8 (q, *J* = 3.0 Hz), 9.9 (q, *J* = 2.9 Hz). ^{19}F NMR (564 MHz, Chloroform-*d*) δ -67.21 (d, *J* = 6.6 Hz). IR (neat, cm^{-1}): 3058, 2963, 1609, 1453, 1266, 1142, 964, 750. HPLC analysis *trans*-isomer: *e.e.* = 90%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 12.7 min, t_{major} = 13.8 min. HRMS-(DART+) calculated for $C_{12}H_{10}F_3O$ $[M+H]^+$: 227.0678, found: 227.0689.

3-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)benzo[b]thiophene (3m)



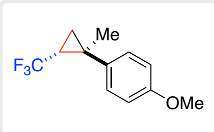
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 96/4. $[\alpha]_D^{20}$ = (+)-73.48 (*c* = 0.4, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 2.50 (dt, *J* = 10.1, 5.4 Hz, 1H), 1.79 (dh, *J* = 12.3, 5.8 Hz, 1H), 1.45 (dt, *J* = 10.0, 5.4 Hz, 1H), 1.32 – 1.23 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.6, 139.2, 134.2, 125.3 (q, *J* = 270.9 Hz), 124.9, 124.5, 123.0, 122.2 (d, *J* = 2.8 Hz), 121.9, 21.4 (q, *J* = 36.7 Hz), 13.8 (q, *J* = 2.9 Hz), 9.0 (q, *J* = 2.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.55 (d, *J* = 6.7 Hz). IR (neat, cm^{-1}): 3058, 2962, 1419, 1362, 1267, 1144, 764. HPLC analysis *trans*-isomer: *e.e.* = 91%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 11.3 min, t_{minor} = 12.7 min. HRMS-(DART+) calculated for $C_{12}H_9F_3S$ $[M]^+$: 242.0372, found: 242.0377.

(*R*)-(2-(Trifluoromethyl)cyclopropane-1,1-diyl)dibenzene (3n)



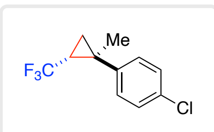
Yield: 88%. White solid. $[\alpha]_D^{20}$ = (–)-85.18 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.11 (m, 6H), 2.35 – 2.25 (m, 1H), 1.85 (t, *J* = 5.6 Hz, 1H), 1.48 (q, *J* = 5.5, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 139.2, 129.8, 128.8, 128.5, 128.0, 127.3, 127.0, 126.0 (q, *J* = 272.0 Hz), 36.1, 26.9 (q, *J* = 35.8 Hz), 15.7 (q, *J* = 2.6 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -61.45 (d, *J* = 7.5 Hz). IR (neat, cm^{-1}): 3060, 2964, 1495, 1409, 1276, 1123, 703. HPLC analysis: *e.e.* = 85%. IF (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 6.5 min, t_{major} = 7.1 min. HRMS-(DART+) calculated for $C_{16}H_{14}F_3$ $[M+H]^+$: 263.1042, found: 263.1034. The structure was characterized by X-ray crystallography.

1-Methoxy-4-((1*R*,2*R*)-1-methyl-2-(trifluoromethyl)cyclopropyl)benzene (3o)



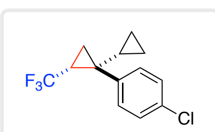
Yield: 95%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-49.32 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 3.79 (s, 3H), 1.72 (dt, *J* = 15.3, 8.5 Hz, 1H), 1.49 (s, 3H), 1.33 – 1.29 (m, 1H), 1.18 (t, *J* = 5.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.4, 137.9, 128.8, 126.9 (q, *J* = 272.0 Hz), 114.1, 55.5, 26.3 (q, *J* = 36.0 Hz), 25.7, 21.2 (q, *J* = 1.9 Hz), 16.8 (q, *J* = 2.4 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.81 (d, *J* = 8.4 Hz). IR (neat, cm^{-1}): 2964, 2931, 1413, 1273, 1140, 830, 738. HPLC analysis *trans*-isomer: *e.e.* = 94%. IB (1% isopropanol: 99% hexane, 0.8 ml/min): t_{minor} = 7.6 min, t_{major} = 8.3 min. HRMS-(DART+) calculated for $C_{12}H_{14}F_3O$ $[M+H]^+$: 231.0991, found: 231.1002.

1-Chloro-4-((1*R*,2*R*)-1-methyl-2-(trifluoromethyl)cyclopropyl)benzene (3p)



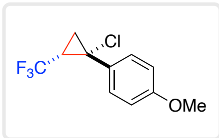
Yield: 97%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-41.13 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 1.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 1.70 (dt, *J* = 15.5, 7.2 Hz, 1H), 1.49 (s, 3H), 1.34 – 1.29 (m, 1H), 1.21 (t, *J* = 5.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.1, 132.7, 129.1, 128.9, 126.6 (q, *J* = 272.3 Hz), 26.3 (q, *J* = 36.0 Hz), 25.8, 20.8 (q, *J* = 1.9 Hz), 16.8 (q, *J* = 2.5 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -59.94 (d, *J* = 8.2 Hz). IR (neat, cm^{-1}): 2964, 2931, 1413, 1273, 1140, 830, 738. HPLC analysis *trans*-isomer: *e.e.* = 98%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 6.1 min, t_{major} = 6.5 min. HRMS-(DART+) calculated for $C_{11}H_{11}ClF_3$ $[M+H]^+$: 235.0495, found: 235.0569.

1-Chloro-4-((1*S*,2*R*)-2-(trifluoromethyl)-[1,1'-bi(cyclopropan)]-1-yl)benzene (3q)



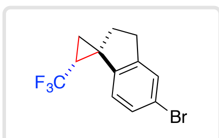
Yield: 51%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-45.32 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 2.2 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 1.76 (dt, *J* = 15.2, 8.3 Hz, 1H), 1.23 (d, *J* = 7.0 Hz, 2H), 1.15 (td, *J* = 8.1, 4.1 Hz, 1H), 0.57 – 0.45 (m, 2H), 0.20 (dq, *J* = 9.7, 5.0 Hz, 1H), 0.12 (dt, *J* = 10.1, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 132.9, 130.5, 128.6, 126.7 (q, *J* = 272.4 Hz), 31.5, 26.9 (q, *J* = 36.6 Hz), 14.3 (q, *J* = 2.3 Hz), 13.5, 5.2 (q, *J* = 2.2 Hz), 3.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -59.63 (d, *J* = 8.3 Hz). IR (neat, cm^{-1}): 3086, 3011, 1493, 1412, 1275, 1127, 1089, 826. HPLC analysis *trans*-isomer: *e.e.* = 98%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 6.2 min, t_{major} = 6.9 min. HRMS-(DART+) calculated for $C_{13}H_{13}ClF_3$ $[M+H]^+$: 261.0652, found: 261.0663.

1-((1*S*,2*S*)-1-Chloro-2-(trifluoromethyl)cyclopropyl)-4-methoxybenzene (3r)



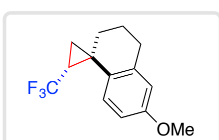
Yield: 60%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 96/4. $[\alpha]_D^{20}$ = (–)-40.58 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.05 (dp, *J* = 10.1, 7.2 Hz, 1H), 1.84 (t, *J* = 6.9 Hz, 1H), 1.75 (dd, *J* = 10.1, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9, 133.2, 129.5, 124.9 (q, *J* = 272.4 Hz), 114.3, 55.5 (q, *J* = 3.4 Hz), 43.9 (q, *J* = 2.3 Hz), 27.9 (q, *J* = 36.9 Hz), 19.2 (q, *J* = 2.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.38 (d, *J* = 7.5 Hz). IR (neat, cm^{-1}): 2960, 2916, 1611, 1516, 1406, 1250, 1129, 831. HPLC analysis *trans*-isomer: *e.e.* = 87%. OD-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{minor} = 5.8 min, t_{major} = 7.1 min. HRMS-(DART+) calculated for $C_{11}H_{11}ClF_3O$ [M+H]$^+$: 251.0445, found: 251.0453.

(1*R*,2*R*)-5'-Bromo-2-(trifluoromethyl)-2',3'-dihydrospiro[cyclopropane-1,1'-indene] (3s)



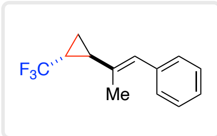
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 93/7. $[\alpha]_D^{20}$ = (–)-74.23 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 (s, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 3.12 – 3.00 (m, 2H), 2.44 (dt, *J* = 15.9, 8.2 Hz, 1H), 2.16 (dt, *J* = 13.5, 7.0 Hz, 1H), 1.89 (dq, *J* = 15.3, 7.6 Hz, 1H), 1.41 (t, *J* = 5.8 Hz, 1H), 1.21 (dd, *J* = 9.1, 5.7 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.2, 144.3, 129.9, 127.9, 126.1 (q, *J* = 272.2 Hz), 120.7, 120.1, 30.8 (q, *J* = 1.9 Hz), 30.7, 29.8 (q, *J* = 1.6 Hz), 26.7 (q, *J* = 36.0 Hz), 18.7 (q, *J* = 2.9 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.54 (d, *J* = 7.6 Hz). IR (neat, cm^{-1}): 2958, 2851, 1598, 1412, 1271, 1134, 1054, 816. HPLC analysis *trans*-isomer: *e.e.* = 95%. OD-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 10.8 min, t_{major} = 12.0 min. HRMS-(DART+) calculated for $C_{12}H_{11}F_3Br$ [M+H]$^+$: 290.9991, found: 290.9985.

(1*R*,2*R*)-6'-Methoxy-2-(trifluoromethyl)-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (3t)



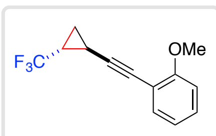
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 96/4. $[\alpha]_D^{20}$ = (–)-28.39 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.69 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 3.77 (s, 3H), 2.86 (t, *J* = 5.7 Hz, 2H), 1.99 – 1.86 (m, 4H), 1.85 – 1.76 (m, 1H), 1.39 (dd, *J* = 8.9, 6.5 Hz, 1H), 1.26 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.8, 139.3, 131.1, 126.4 (q, *J* = 272.8 Hz), 122.9, 113.8, 112.8, 55.4, 30.9, 29.8 (q, *J* = 35.9 Hz), 28.4 (q, *J* = 1.8 Hz), 23.5 (q, *J* = 1.5 Hz), 22.2, 19.8 (q, *J* = 2.8 Hz). ^{19}F NMR (564 MHz, Chloroform-*d*) δ -59.17 (d, *J* = 8.3 Hz). IR (neat, cm^{-1}): 2934, 2836, 1610, 1505, 1413, 1265, 1134, 818. HPLC analysis *trans*-isomer: *e.e.* = 98%. OJ-H (2% isopropanol: 98% hexane, 0.8 ml/min): t_{major} = 11.2 min, t_{minor} = 13.1 min. HRMS-(DART+) calculated for $C_{14}H_{16}F_3O$ [M+H]$^+$: 257.1148, found: 257.1153.

((*E*)-2-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)prop-1-en-1-yl)benzene (3u)



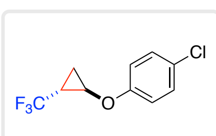
Yield: 95%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 96/4. $[\alpha]_D^{20}$ = (–)-42.49 (*c* = 0.4, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.19 (m, 3H), 6.38 (s, 1H), 2.02 – 1.97 (m, 1H), 1.83 (s, 3H), 1.69 (p, *J* = 6.8 Hz, 1H), 1.15 (dt, *J* = 10.4, 5.9 Hz, 1H), 1.12 – 1.07 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 135.1, 128.9, 128.3, 126.5, 126.2 (q, *J* = 270.9 Hz), 126.1, 24.0 (q, *J* = 2.6 Hz), 20.2 (q, *J* = 36.7 Hz), 16.3, 8.2 (q, *J* = 2.5 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.48 (d, *J* = 6.7 Hz). IR (neat, cm^{-1}): 3024, 2927, 1419, 1325, 1268, 1139, 742. HPLC analysis *trans*-isomer: *e.e.* = 76%. OD-H (1% isopropanol: 99% hexane, 0.8 ml/min): t_{major} = 10.6 min, t_{minor} = 11.7 min. HRMS-(DART+) calculated for $C_{13}H_{14}F_3$ $[M+H]^+$: 227.1042, found: 227.1039.

1-Methoxy-2-(((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)ethynyl)benzene (3v)



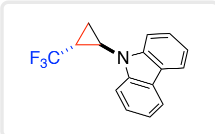
Yield: 98%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-71.44 (*c* = 1.1, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.90 – 6.83 (m, 2H), 3.86 (s, 3H), 1.98 (q, *J* = 9.3, 8.3 Hz, 2H), 1.32 – 1.26 (m, 1H), 1.25 – 1.21 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.3, 133.9, 129.7, 125.3 (q, *J* = 271.1 Hz), 120.6, 112.1, 110.7, 92.4, 74.3, 55.9, 23.1 (q, *J* = 37.0 Hz), 11.7 (q, *J* = 2.6 Hz), 5.6 (q, *J* = 3.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.32 (d, *J* = 5.8 Hz). IR (neat, cm^{-1}): 2940, 2839, 1597, 1418, 1263, 1144, 751. HPLC analysis *trans*-isomer: *e.e.* = 86%. OD-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{major} = 8.2 min, t_{minor} = 9.0 min. HRMS-(DART+) calculated for $C_{13}H_{12}F_3O$ $[M+H]^+$: 241.0835, found: 241.0836.

1-Chloro-4-((1R,2R)-2-(trifluoromethyl)cyclopropoxy)benzene (3w)



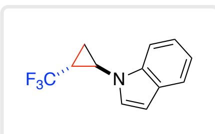
Yield: 64%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (+)-49.98 (*c* = 0.2, $CHCl_3$). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 1H), 7.26 (s, 1H), 6.96 – 6.92 (m, 2H), 3.96 (ddd, *J* = 6.5, 4.0, 2.4 Hz, 1H), 1.87 (dtd, *J* = 9.8, 7.0, 2.6 Hz, 1H), 1.34 – 1.29 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.4, 129.7, 127.1, 125.1 (q, *J* = 270.8 Hz), 116.2, 52.2 (q, *J* = 3.8 Hz), 21.3 (q, *J* = 37.0 Hz), 10.4 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.51 (d, *J* = 6.8 Hz). IR (neat, cm^{-1}): 2925, 2851, 1490, 1409, 1241, 1136, 1084, 824. HPLC analysis *trans*-isomer: *e.e.* = 52%. OD-H (1% isopropanol: 99% hexane, 0.8 ml/min): t_{major} = 9.4 min, t_{minor} = 11.9 min. HRMS-(DART+) calculated for $C_{10}H_9ClF_3O$ $[M+H]^+$: 237.0288, found: 237.0297.

9-((2*R*)-2-(Trifluoromethyl)cyclopropyl)-9H-carbazole (3x)



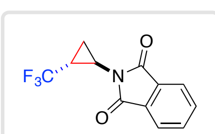
Yield: 76%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-53.79 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.30 – 7.25 (m, 2H), 3.67 (ddd, *J* = 7.6, 4.6, 3.2 Hz, 1H), 2.24 (ddq, *J* = 9.7, 6.5, 3.3 Hz, 1H), 1.78 (q, *J* = 6.9 Hz, 1H), 1.64 (p, *J* = 5.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.8, 126.2, 125.4 (q, *J* = 271.4 Hz), 123.4, 120.6, 120.0, 109.7, 27.4 (q, *J* = 3.9 Hz), 22.1 (q, *J* = 36.6 Hz), 11.2 (q, *J* = 2.2 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -65.75 (d, *J* = 6.6 Hz). IR (neat, cm^{-1}): 3054, 3025, 1597, 1453, 1317, 1263, 1135, 1071. HPLC analysis *trans*-isomer: *e.e.* = 89%. OD-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{major} = 7.9 min, t_{minor} = 10.2 min. HRMS-(DART+) calculated for $C_{16}H_{13}F_3N$ [M+H]$^+$: 276.0995, found: 276.0992.

1-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)-1H-indole (3y)



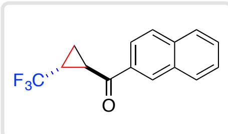
Yield: 83%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (+)-22.99 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 3.3 Hz, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 3.72 (td, *J* = 5.8, 3.2 Hz, 1H), 2.18 – 2.06 (m, 1H), 1.60 (dd, *J* = 8.6, 5.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.2, 129.0, 127.2, 125.3 (q, *J* = 271.2 Hz), 122.5, 121.3, 120.5, 109.9, 102.6 (d, *J* = 2.7 Hz), 30.3 – 30.0 (m), 22.1 (q, *J* = 37.0 Hz), 10.2 (q, *J* = 2.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.01 (d, *J* = 6.8 Hz). IR (neat, cm^{-1}): 3057, 2922, 1466, 1416, 1266, 1143, 1002, 745. HPLC analysis *trans*-isomer: *e.e.* = 92%. OD-H (2% isopropanol: 98% hexane, 0.8 ml/min): t_{minor} = 32.3 min, t_{major} = 35.3 min. HRMS-(DART+) calculated for $C_{12}H_{11}F_3N$ [M+H]$^+$: 226.0838, found: 226.0842.

2-((1*R*,2*R*)-2-(Trifluoromethyl)cyclopropyl)isoindoline-1,3-dione (3z)



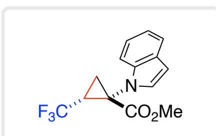
Yield: 50%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-40.98 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 3.0 Hz, 2H), 7.74 (d, *J* = 3.3 Hz, 2H), 3.24 (dt, *J* = 8.3, 4.3 Hz, 1H), 2.36 (dtd, *J* = 12.9, 9.8, 9.1, 5.9 Hz, 1H), 1.62 (dt, *J* = 10.9, 5.8 Hz, 1H), 1.48 (q, *J* = 7.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.0, 134.5, 131.6, 125.3 (q, *J* = 271.1 Hz), 123.6, 24.8 (q, *J* = 4.0 Hz), 19.7 (q, *J* = 37.6 Hz), 8.7 (q, *J* = 2.7 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -66.91 (d, *J* = 6.7 Hz). IR (neat, cm^{-1}): 2962, 2924, 1707, 1422, 1270, 1121, 873, 716. HPLC analysis *trans*-isomer: *e.e.* = 66%. OJ-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{major} = 17.6 min, t_{minor} = 22.1 min. HRMS-(DART+) calculated for $C_{12}H_9F_3NO_2$ [M+H]$^+$: 256.0580, found: 256.0583.

Naphthalen-2-yl((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)methanone (3aa)



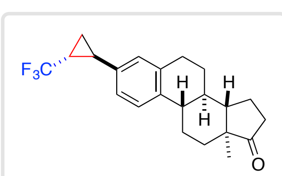
Yield: 43%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-25.99 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.06 – 8.00 (m, 2H), 7.92 (dd, J = 12.6, 8.3 Hz, 2H), 7.62 (dt, J = 20.0, 7.2 Hz, 2H), 3.19 (dd, J = 9.0, 4.7 Hz, 1H), 2.43 (dp, J = 12.7, 6.3 Hz, 1H), 1.60 (dd, J = 9.5, 4.2 Hz, 1H), 1.49 (dt, J = 10.6, 5.2 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.4, 136.0, 134.2, 132.6, 130.4, 129.8, 129.0, 128.9, 128.0, 127.2, 125.4 (q, J = 271.1 Hz), 123.9, 24.0 (q, J = 37.8 Hz), 20.3 (q, J = 2.2 Hz), 12.8 (q, J = 2.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.67 (d, J = 6.6 Hz). IR (neat, cm^{-1}): 3058, 2964, 1672, 1356, 1264, 1148, 757. HPLC analysis *trans*-isomer: *e.e.* = 51%. OJ-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{minor} = 10.8 min, t_{major} = 15.8 min. HRMS-(DART+) calculated for $C_{15}H_{12}F_3O$ $[M+H]^+$: 265.0835, found: 265.0832.

Methyl 1-(1H-indol-1-yl)-2-(trifluoromethyl)cyclopropane-1-carboxylate (3ab)

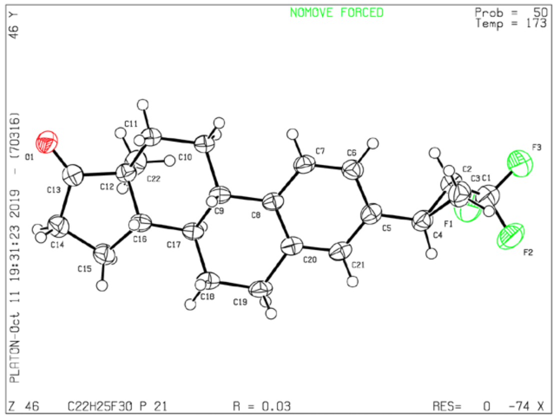


Yield: 74%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 38/62. $[\alpha]_D^{20}$ = (+)-31.99 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 4.6 Hz, 2H), 6.57 (d, J = 3.5 Hz, 1H), 3.64 (s, 3H), 2.81 (dq, J = 10.0, 6.9 Hz, 1H), 2.37 (dd, J = 10.2, 5.5 Hz, 1H), 2.22 – 2.20 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 137.6, 129.6, 127.5, 124.1 (q, J = 272.2 Hz), 122.5, 121.6, 120.6, 109.8, 103.9, 53.7, 41.2, 28.5 (q, J = 37.9 Hz), 18.6. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.12 (d, J = 7.0 Hz). IR (neat, cm^{-1}): 3055, 2956, 1732, 1463, 1263, 1130, 1085, 741. HPLC analysis *cis*-isomer: *e.e.* = 50%. OD-H (5% isopropanol: 95% hexane, 0.8 ml/min): t_{minor} = 8.7 min, t_{major} = 10.6 min. HRMS-(DART+) calculated for $C_{14}H_{13}F_3NO_2$ $[M+H]^+$: 284.0893, found: 284.0887.

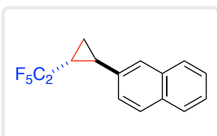
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((1*R*,2*R*)-2-(trifluoromethyl)cyclopropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3ac)



Yield: 80%. White solid. Isolated as a mixture of diastereomers *trans*/*cis*: 96/4. $[\alpha]_D^{20}$ = (+)-43.99 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, J = 8.0 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.88 (s, 1H), 2.90 (dd, J = 8.8, 4.1 Hz, 2H), 2.51 (dd, J = 18.7, 8.8 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.30 (dd, J = 9.8, 4.6 Hz, 1H), 2.20 – 2.11 (m, 1H), 2.11 – 2.01 (m, 2H), 1.97 (dd, J = 9.1, 2.5 Hz, 1H), 1.84 – 1.71 (m, 1H), 1.68 – 1.58 (m, 2H), 1.55 – 1.40 (m, 5H), 1.37 – 1.31 (m, 1H), 1.17 – 1.11 (m, 1H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.9, 138.5, 136.9, 136.7, 127.4, 125.9 (q, J = 229.5 Hz), 125.8, 123.9, 50.6, 48.1, 44.4, 38.3, 36.0, 31.7, 29.5, 26.6, 25.9, 23.0 (q, J = 36.9 Hz), 21.7, 19.3 (d, J = 3.2 Hz), 14.0, 10.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -66.76 (d, J = 6.7 Hz). IR (neat, cm^{-1}): 2930, 2862, 1736, 1421, 1265, 1311, 734. HRMS-(DART+) calculated for $C_{22}H_{26}F_3O$ $[M+H]^+$: 363.1930, found: 363.1927. The structure was characterized by X-ray crystallography.

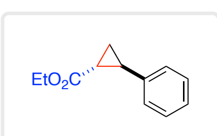


2-((1*R*,2*R*)-2-(Perfluoroethyl)cyclopropyl)naphthalene (5a)



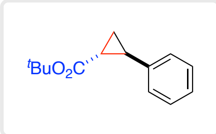
Yield: 80%. Pale yellow solid. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-34.99 (c = 0.8, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.80 (q, J = 7.6 Hz, 3H), 7.59 (s, 1H), 7.47 (p, J = 6.9 Hz, 2H), 7.25 (s, 1H), 2.57 (dt, J = 10.1, 5.6 Hz, 1H), 1.76 (ddt, J = 17.6, 13.3, 6.0 Hz, 1H), 1.48 (dt, J = 10.3, 5.7 Hz, 1H), 1.37 (q, J = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.4, 133.5, 132.6, 128.6, 127.8, 127.6, 126.6, 125.9, 125.3, 125.1, 119.5 (qt, J = 285.8, 38.5 Hz), 114.3 (tq, J = 250.4, 37.5 Hz), 20.4 (t, J = 25.7 Hz), 19.4 (dd, J = 5.0, 2.4 Hz), 9.9 (dd, J = 4.9, 2.4 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -84.88, -119.29 (d, J = 12.7 Hz), -119.85 (d, J = 12.7 Hz), -120.14 (d, J = 13.4 Hz), -120.70 (d, J = 13.3 Hz). IR (neat, cm^{-1}): 3020, 2926, 1346, 1205, 1080, 1037, 758. HPLC analysis *trans*-isomer: *e.e.* = 80%. OD-H (1% isopropanol: 99% hexane, 0.8 ml/min): t_{minor} = 31.6 min, t_{major} = 35.1 min. HRMS-(DART+) calculated for $C_{15}H_{12}F_5$ $[M+H]^+$: 287.0853, found: 287.0850.

Ethyl (1*R*,2*R*)-2-phenylcyclopropane-1-carboxylate (5b)



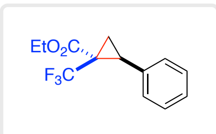
Yield: 88%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-187.38 (c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.56 – 2.48 (m, 1H), 1.94 – 1.87 (m, 1H), 1.60 (dt, J = 9.4, 4.9 Hz, 1H), 1.34 – 1.30 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.6, 140.3, 128.6, 126.6, 126.3, 60.8, 26.3, 24.3, 17.2, 14.4. IR (neat, cm^{-1}): 3024, 2982, 1723, 1438, 1337, 1217, 1186, 754. HPLC analysis *trans*-isomer: *e.e.* = 80%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 14.2 min, t_{minor} = 27.4 min. HRMS-(DART+) calculated for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1066, found: 191.1074.

tert-Butyl (1*R*,2*R*)-2-phenylcyclopropane-1-carboxylate (5c)



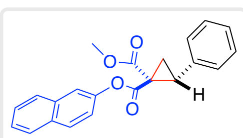
Yield: 82%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-118.98 (c = 0.8, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.28 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.3 Hz, 2H), 2.44 (ddd, J = 9.7, 6.3, 4.2 Hz, 1H), 1.84 (dt, J = 8.8, 4.7 Hz, 1H), 1.53 (dt, J = 9.5, 4.9 Hz, 1H), 1.47 (s, 9H), 1.26 – 1.22 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.7, 140.7, 128.6, 126.5, 126.2, 80.7, 28.3, 25.9, 25.4, 17.2. IR (neat, cm^{-1}): 2978, 1718, 1402, 1367, 1342, 1220, 1151, 756. HPLC analysis *trans*-isomer: *e.e.* = 48%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 7.8 min, t_{minor} = 9.2 min. HRMS-(DART+) calculated for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1379, found: 219.1384.

Ethyl 2-phenyl-1-(trifluoromethyl)cyclopropane-1-carboxylate (5d)



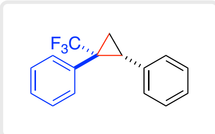
Yield: 43%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 6/94. $[\alpha]_D^{20}$ = (+)-33.99 (c = 0.4, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.30 (d, J = 7.0 Hz, 5H), 4.30 (p, J = 6.3 Hz, 2H), 3.09 (t, J = 9.0 Hz, 1H), 1.93 (dq, J = 8.8, 5.5 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.5, 133.6, 129.6, 128.4, 127.8, 124.2 (q, J = 274.3 Hz), 62.2, 33.1 (q, J = 32.8 Hz), 32.4, 16.3, 14.2. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -61.14. IR (neat, cm^{-1}): 2983, 2926, 1731, 1381, 1286, 1146, 1097, 767. HPLC analysis *cis*-isomer: *e.e.* = 35%. (*R*,*R*)-Whelk-O1 (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 9.5 min, t_{minor} = 10.2 min. HRMS-(DART+) calculated for $C_{13}H_{14}O_2F_3$ $[M+H]^+$: 259.0940, found: 259.0950.

1-Methyl 1-(naphthalen-2-yl) (1*S*,2*R*)-2-phenylcyclopropane-1,1-dicarboxylate (5e)



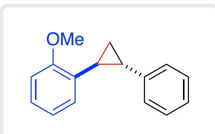
Yield: 74%. White solid. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (+)-109.59 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, J = 10.4, 8.0 Hz, 2H), 7.82 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.34 – 7.27 (m, 6H), 3.46 (s, 3H), 3.42 (t, J = 8.7 Hz, 1H), 2.39 (dd, J = 8.2, 5.3 Hz, 1H), 1.96 (dd, J = 9.2, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 166.9, 148.4, 134.4, 133.8, 131.7, 129.6, 128.7, 128.4, 127.9, 127.8, 127.7, 126.8, 126.0, 121.0, 118.6, 52.6, 37.6, 33.3, 19.9. IR (neat, cm^{-1}): 2919, 1735, 1511, 1333, 1240, 1175, 962, 758. HPLC analysis *trans*-isomer: *e.e.* = 76%. IC (2% isopropanol: 98% hexane, 0.8 ml/min): t_{major} = 19.8 min, t_{minor} = 23.4 min. HRMS-(DART+) calculated for $C_{22}H_{19}O_4$ $[M+H]^+$: 347.1277, found: 347.1268.

1-(Trifluoromethyl)cyclopropane-1,2-diyl)dibenzene (5f)



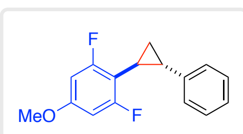
Yield: 75%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 46/54. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.59 (m, 2H), 7.46 – 7.28 (m, 8H), 2.74 (t, *J* = 8.4 Hz, 1H), 1.96 (dd, *J* = 7.4, 5.6 Hz, 1H), 1.61 (ddt, *J* = 9.3, 5.5, 1.9 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.4, 135.5, 131.3, 129.5, 128.7, 128.4, 128.0, 127.2, 126.0 (q, *J* = 274.9 Hz), 35.2 (q, *J* = 31.5 Hz), 29.5, 14.0 (q, *J* = 2.5 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.67. IR (neat, cm^{-1}): 3028, 1602, 1495, 1449, 1356, 1280, 1132, 966. HPLC analysis *cis*-isomer: *e.e.* = 3%. OJ-H (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 23.3 min, t_{minor} = 26.3 min. HRMS-(DART+) calculated for $C_{16}H_{14}F_3$ $[M+H]^+$: 263.1042, found: 263.1040.

1-Methoxy-2-((1*S*,2*S*)-2-phenylcyclopropyl)benzene (5g)



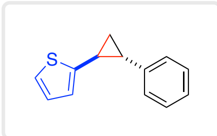
Yield: 98%. White solid. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (+)-238.78 (*c* = 1.5, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.19 (m, 4H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 2.57 – 2.49 (m, 1H), 2.23 – 2.14 (m, 1H), 1.45 (d, *J* = 6.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.3, 143.1, 131.0, 128.4, 126.8, 126.3, 125.7, 125.2, 120.6, 110.4, 55.6, 26.7, 21.8, 17.2. IR (neat, cm^{-1}): 3027, 2834, 1602, 1494, 1458, 1246, 1029, 749. HPLC analysis *trans*-isomer: *e.e.* = 95%. IA (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 6.7 min, t_{major} = 7.0 min. HRMS-(DART+) calculated for $C_{16}H_{17}O$ $[M+H]^+$: 225.1273, found: 225.1275.

1,3-Difluoro-5-methoxy-2-((1*S*,2*S*)-2-phenylcyclopropyl)benzene (5h)



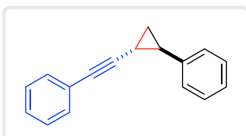
Yield: 97%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 95/5. $[\alpha]_D^{20}$ = (+)-180.46 (*c* = 1.7, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 3H), 6.42 (d, *J* = 9.6 Hz, 2H), 3.77 (s, 3H), 2.41 – 2.33 (m, 1H), 2.03 – 1.95 (m, 1H), 1.54 (d, *J* = 8.7 Hz, 1H), 1.40 (dt, *J* = 10.4, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.0 Hz), 162.7 (d, *J* = 246.0 Hz), 159.0, 142.5, 128.5, 126.3, 126.0, 109.8 (t, *J* = 17.7 Hz), 98.2, 97.9, 55.8, 24.0 (t, *J* = 2.5 Hz), 16.7 (t, *J* = 2.6 Hz), 15.5 (t, *J* = 3.1 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -113.43 (d, *J* = 9.6 Hz). IR (neat, cm^{-1}): 3015, 2938, 1638, 1580, 1440, 1344, 1142, 1043. HPLC analysis *trans*-isomer: *e.e.* = 90%. IA (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 7.0 min, t_{minor} = 8.0 min. HRMS-(DART+) calculated for $C_{16}H_{15}OF_2$ $[M+H]^+$: 261.1085, found: 261.1084.

2-((1*S*,2*S*)-2-Phenylcyclopropyl)thiophene (5i)



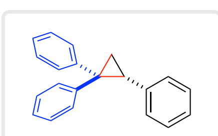
Yield: 63%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 70/30. $[\alpha]_D^{20}$ = (+)-22.49 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.30 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 5.1 Hz, 1H), 6.93 (q, J = 5.4 Hz, 1H), 6.83 (d, J = 3.5 Hz, 1H), 2.37 (dt, J = 9.4, 5.3 Hz, 1H), 2.22 (dt, J = 9.9, 5.2 Hz, 1H), 1.47 (ddt, J = 13.5, 8.8, 5.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.1, 142.0, 128.6, 127.0, 126.1, 126.0, 122.9, 122.4, 28.8, 23.3, 19.3. IR (neat, cm^{-1}): 3026, 2922, 1604, 1499, 1458, 1040, 763. HPLC analysis *trans*-isomer: *e.e.* = 20%. OJ-H (2% isopropanol: 98% hexane, 0.8 ml/min): t_{minor} = 12.1 min, t_{major} = 17.6 min. HRMS-(DART+) calculated for $C_{13}H_{13}S$ $[M+H]^+$: 201.0732, found: 201.0736.

(((1*R*,2*R*)-2-phenylcyclopropyl)ethynyl)benzene (5j)



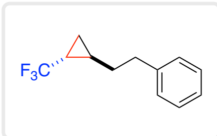
Yield: 24%. Colorless oil. Isolated as a mixture of diastereomers *trans*/*cis*: 99/1. $[\alpha]_D^{20}$ = (–)-60.99 (c = 0.4, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.27 (m, 5H), 7.20 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 2.37 (dt, J = 9.8, 5.5 Hz, 1H), 1.71 (dt, J = 9.5, 5.1 Hz, 1H), 1.43 (dt, J = 9.4, 5.3 Hz, 1H), 1.35 (dt, J = 8.8, 5.6 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.9, 131.8, 128.6, 128.4, 127.8, 126.4, 126.1, 123.8, 92.0, 77.4, 26.7, 18.2, 12.2. IR (neat, cm^{-1}): 3029, 2919, 2226, 1598, 1491, 1216, 1070, 753. HPLC analysis *trans*-isomer: *e.e.* = 89%. IB (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{major} = 10.1 min, t_{minor} = 10.6 min. HRMS-(DART+) calculated for $C_{17}H_{15}$ $[M+H]^+$: 219.1168, found: 219.1176.

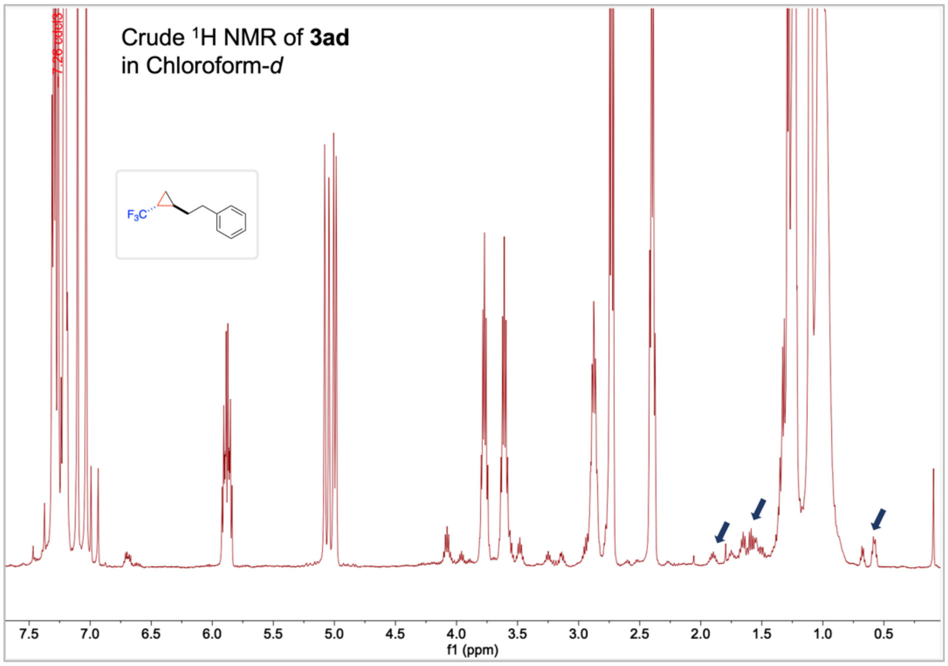
Cyclopropane-1,1,2-triyltribenzene (5k)



Yield: 98%. Colorless oil. ^1H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 4H), 7.22 – 7.02 (m, 9H), 6.91 – 6.85 (m, 2H), 2.87 (dd, J = 9.0, 6.6 Hz, 1H), 2.00 (dd, J = 6.6, 5.4 Hz, 1H), 1.82 (dd, J = 9.0, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.2, 140.3, 138.8, 131.3, 128.5, 128.07, 128.05, 127.8, 127.6, 126.4, 126.0, 125.7, 39.5, 32.5, 21.0. IR (neat, cm^{-1}): 3057, 3024, 1599, 1496, 1445, 1074, 1030, 735. HPLC analysis: *e.e.* = 1%. IB (0.1% isopropanol: 99.9% hexane, 0.8 ml/min): t_{minor} = 7.3 min, t_{major} = 7.5 min. HRMS-(DART+) calculated for $C_{21}H_{19}$ $[M+H]^+$: 271.1481, found: 271.1487.

(2-(-2-(trifluoromethyl)cyclopropyl)ethyl)benzene (3ad)





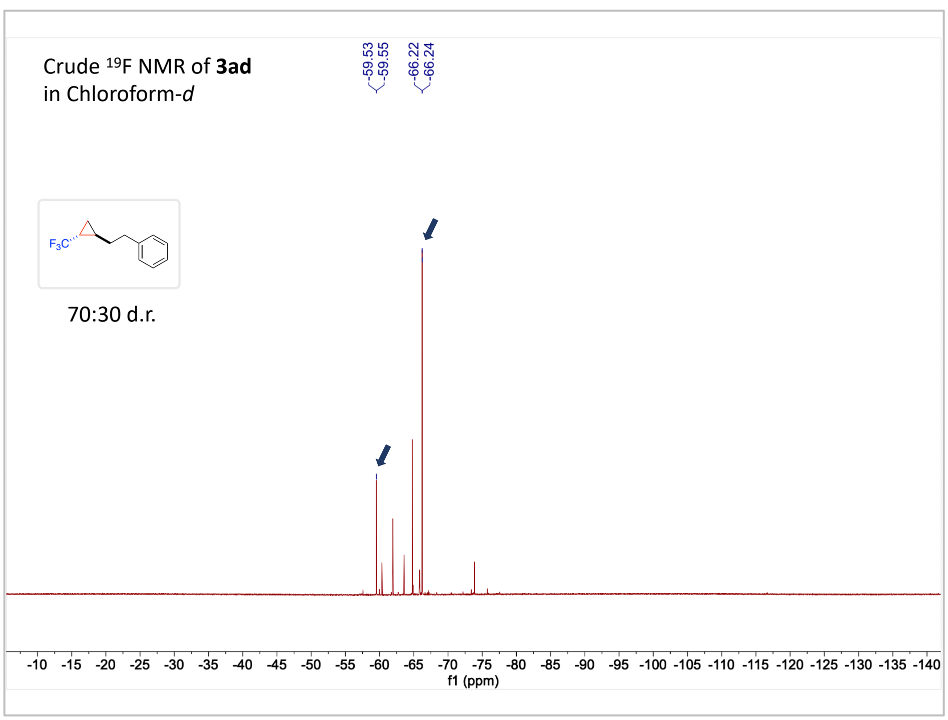
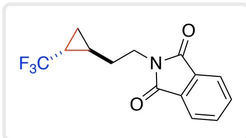
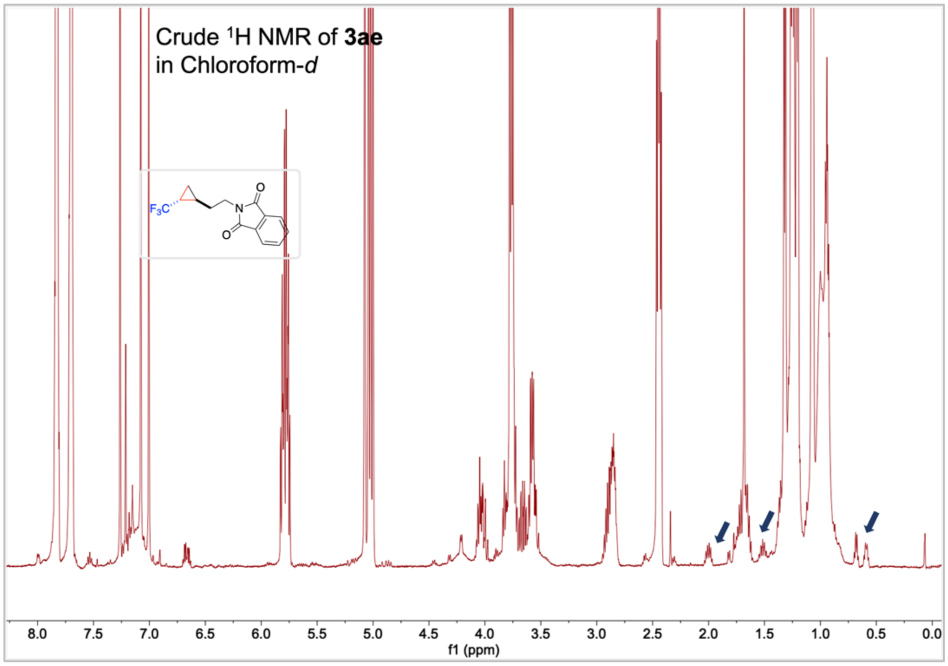


Figure S2: Crude NMR Analysis of **3ad**

2-(2-(-2-(trifluoromethyl)cyclopropyl)ethyl)isoindoline-1,3-dione (3ae)





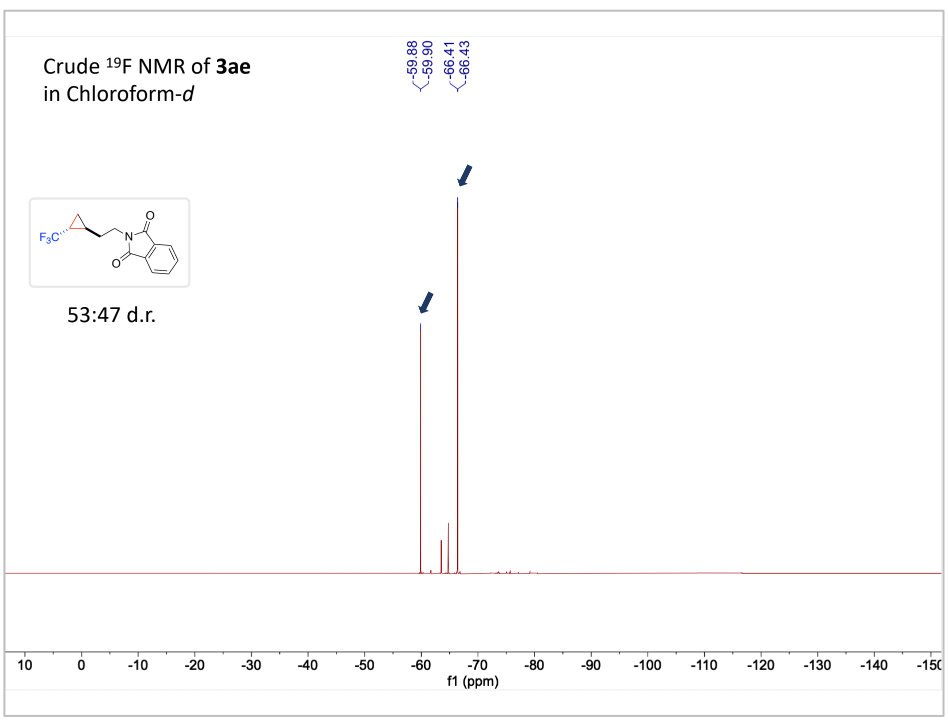
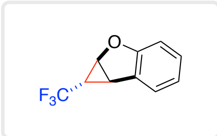


Figure S3: Crude NMR Analysis of **3ae**

1-(Trifluoromethyl)-1a,6b-dihydro-1*H*-cyclopropa[*b*]benzofuran (3af)



97/3 d.r. determined by ^{19}F NMR analysis of reaction mixture. Isolated as a mixture of diastereomers: 99/1 d.r.. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.18 (td, *J* = 7.8, 1.4 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.98 (dd, *J* = 6.0, 1.4 Hz, 1H), 3.11 (dd, *J* = 6.0, 3.5 Hz, 1H), 1.57 (m, 1H). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -64.26 (d, *J* = 7.2 Hz).

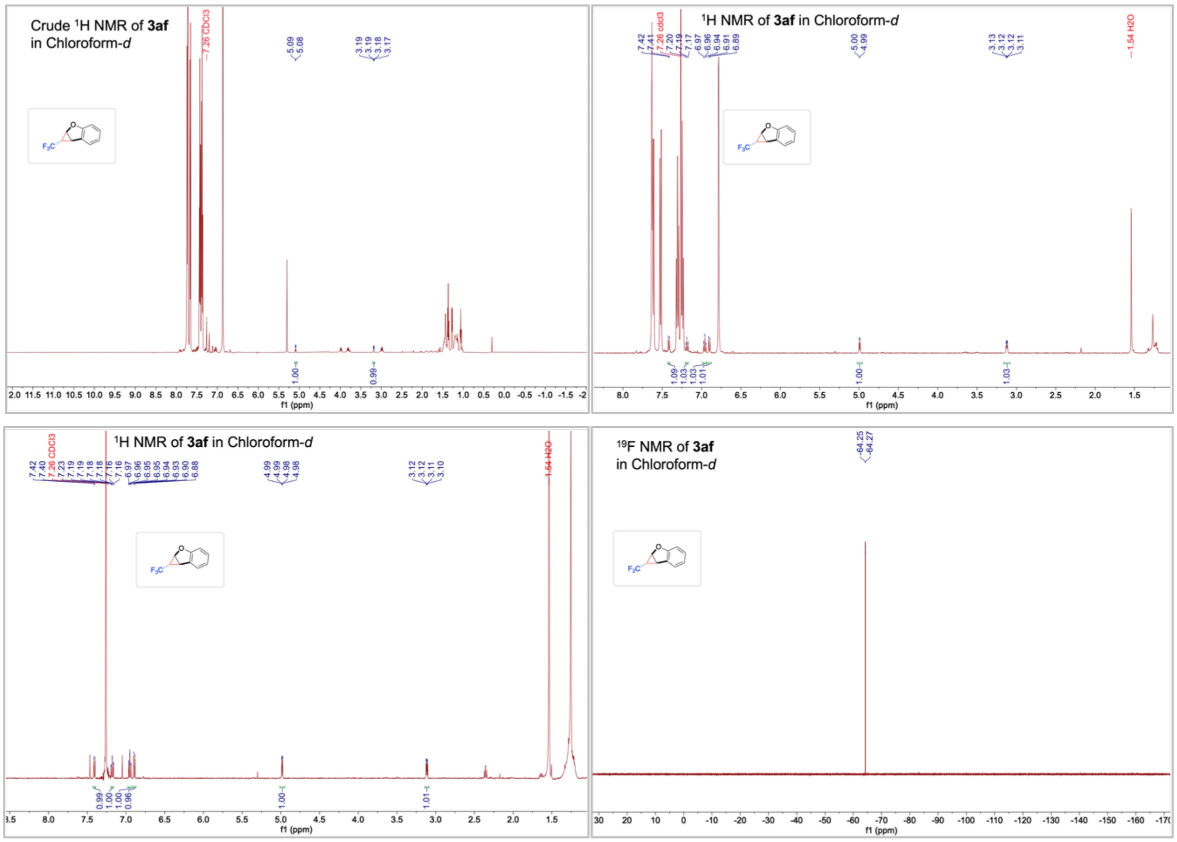
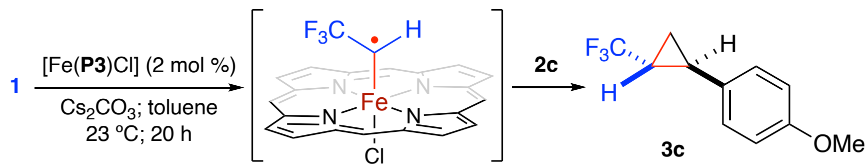


Figure S4: Crude NMR Analysis of **3af**

6. Mechanistic Studies

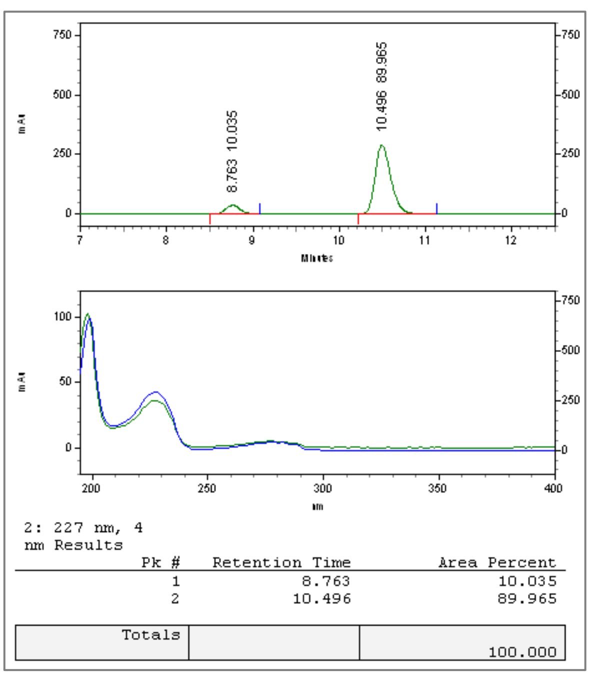
6.1. Comparative Studies on Catalytic Reactions under Inert and Air Atmospheres



An oven-dried Schlenk tube was charged with 1.0 equivalent of olefin (0.1 mmol), 1.2 equivalents of hydrazone **1** (0.12 mmol), [Fe(**P3**)Cl] (2 mol %) and 2.4 equivalents of Cs_2CO_3 (0.24 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times (*skip this step if conducting the reaction under air*). The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The mixture was stirred at rt. After 20 h, the reaction mixture was filtered through a plug of silica and then concentrated *in vacuo*. The residue was purified via a flash chromatography to afford the compound as a mixture of *trans*/*cis* diastereomers.

entry	atmosphere	yield (%)	d.r. (*trans*:*cis*)	e.e. (%)
1	N_2	95	93:7	80
2	Air	93	93:7	80

Entry 1



Entry 2

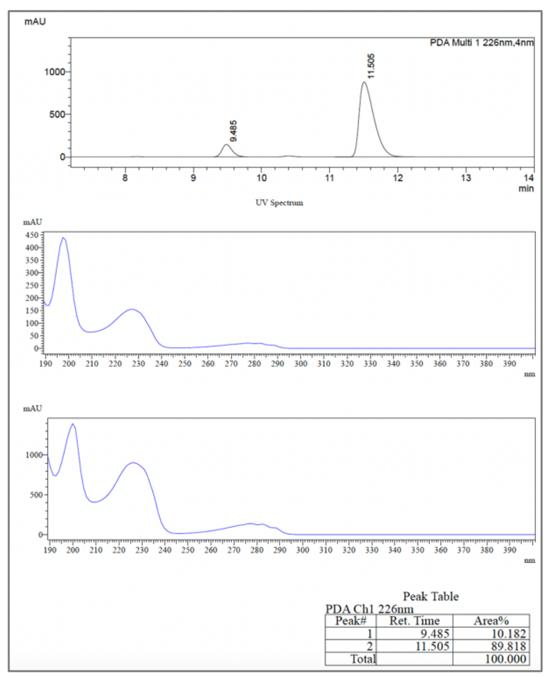
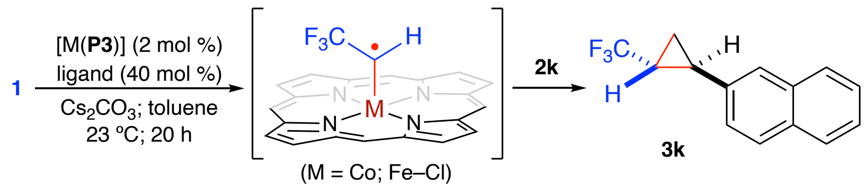


Figure S5: HPLC Analysis of **3c**

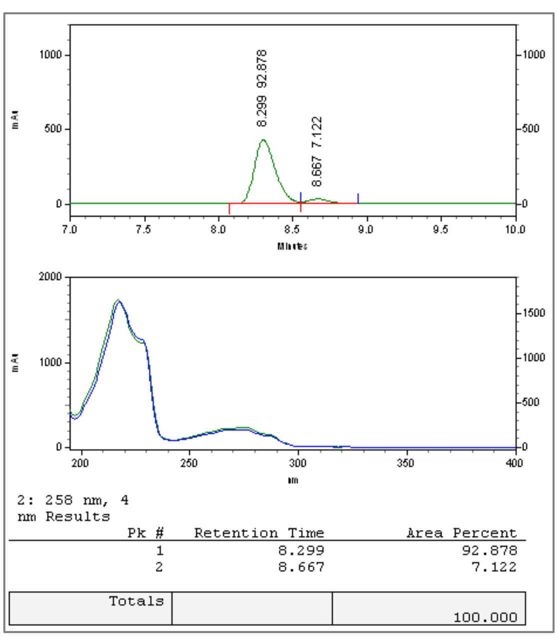
6.2. Comparative Studies on Catalytic Reactions with Ligand



An oven-dried Schlenk tube was charged with 1.0 equivalent of olefin (0.1 mmol), 1.2 equivalents of hydrazone **1** (0.12 mmol), catalyst ([Fe(**P3**)Cl] or [Co(**P3**)]) (2 mol %), DMAP (40 mol %) (*skip adding this additive if conducting the comparison experiments*) and 2.4 equivalents of Cs_2CO_3 (0.24 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at rt. After 20 h, the reaction mixture was filtered through a plug of silica and then concentrated *in vacuo*. The residue was purified via a flash chromatography to afford the compound as a mixture of *trans*/*cis* diastereomers.

entry	catalyst	ligand	yield (%)	d.r. (*trans*:*cis*)	e.e. (%)
1	[Fe(**P3**)Cl]	–	99	98:2	86
2	[Fe(**P3**)Cl]	DMAP	82	98:2	86
3	[Co(**P3**)]	–	99	99:1	75
4	[Co(**P3**)]	DMAP	93	98:2	64

Entry 1



Entry 2

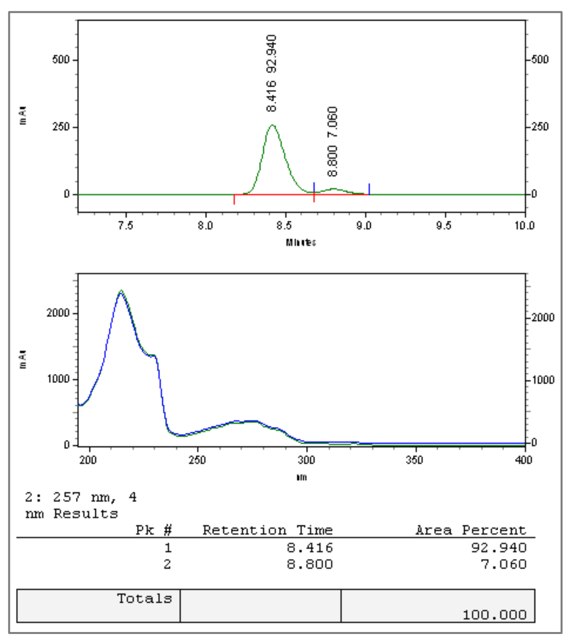
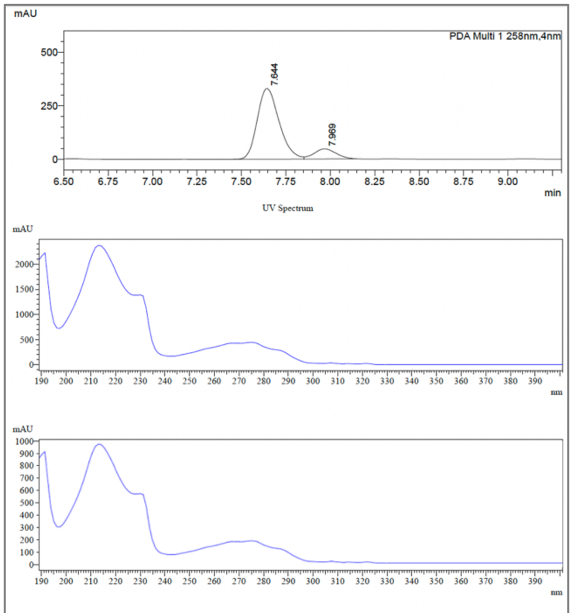


Figure S6: HPLC Analysis of **3**

entry	catalyst	ligand	yield (%)	d.r. (*trans*:*cis*)	e.e. (%)
1	[Fe(**P3**)Cl]	–	99	98:2	86
2	[Fe(**P3**)Cl]	DMAP	82	98:2	86
3	[Co(**P3**)]	–	99	99:1	75
4	[Co(**P3**)]	DMAP	93	98:2	64

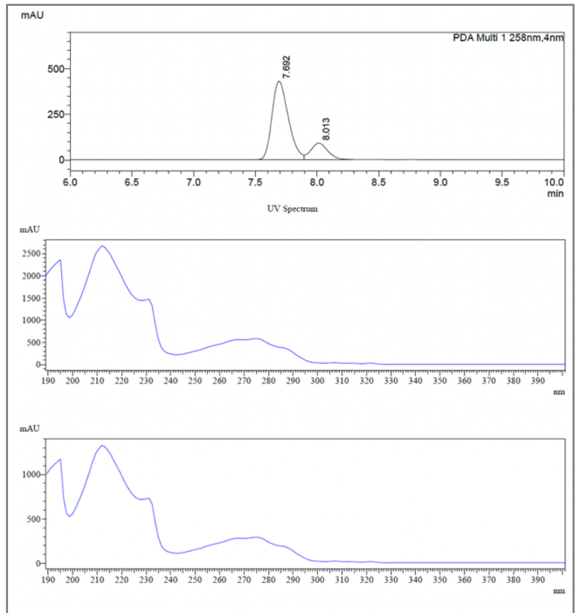
Entry 3



Peak Table
PDA Ch1 258nm

Peak#	Ret. Time	Area%
1	7.644	87.459
2	7.969	12.541
Total		100.000

Entry 4



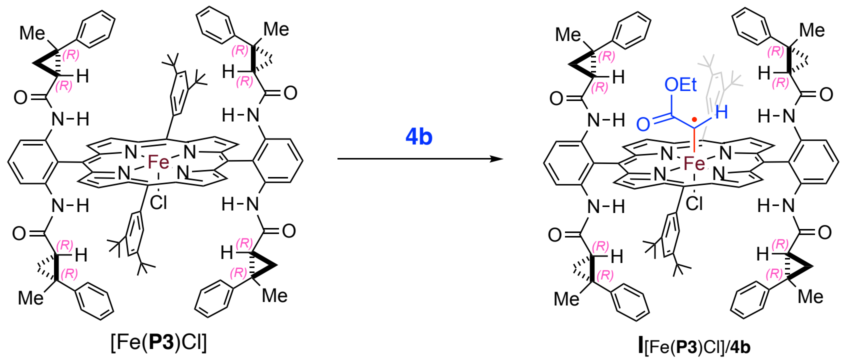
Peak Table
PDA Ch1 258nm

Peak#	Ret. Time	Area%
1	7.692	82.115
2	8.013	17.885
Total		100.000

Figure S7: HPLC Analysis of **3k**

6.3. Detection of Radical Intermediates by HRMS

(HRMS = High-Resolution Mass Spectrometry)



An oven-dried Schlenk tube was charged with 1.0 equivalent of diazo **4b** (0.1 mmol) and [Fe(**P3**)Cl] (2 mol %). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The mixture was stirred at 40 ºC for 1 h, then the resulting solution was collected in a HPLC vial (degassed and backfilled with nitrogen). The sample was further diluted with CH_3CN and immediately injected into HRMS instrument for the detection of the molecular ion signals.

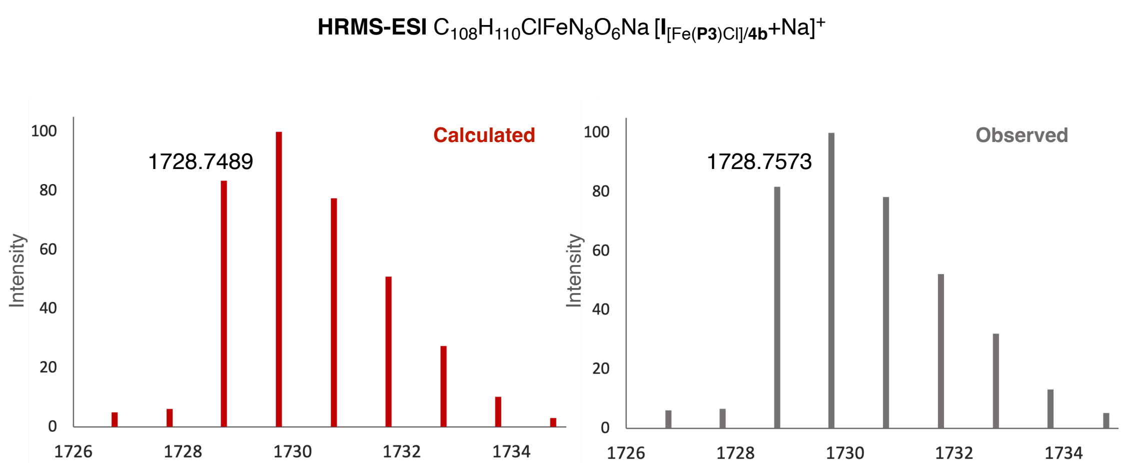
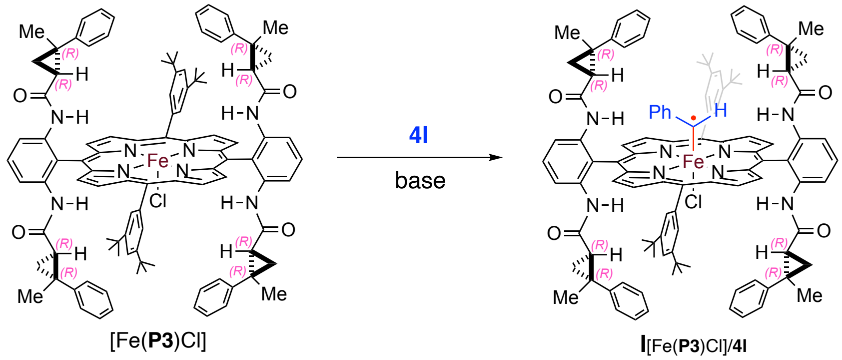


Figure S8: HRMS Analysis of [$\mathbf{I}_{[Fe(\mathbf{P3})Cl]/\mathbf{4b}}$+Na]$^+$



An oven-dried Schlenk tube was charged with 1.0 equivalent of trisylhydrazone **4l** (0.1 mmol), [Fe(**P3**)Cl] (2 mol %) and 2.0 equivalents of Cs_2CO_3 (0.2 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The mixture was stirred at 40 ºC for 1 h, then the resulting solution was collected in a HPLC vial (degassed and backfilled with nitrogen). The sample was further diluted with CH_3CN and immediately injected into HRMS instrument for the detection of the molecular ion signals.

HRMS-ESI $C_{111}H_{110}ClFeN_8O_4K$ $[\mathbf{I}_{[Fe(\mathbf{P3})Cl]/\mathbf{4l}}+K]^+$

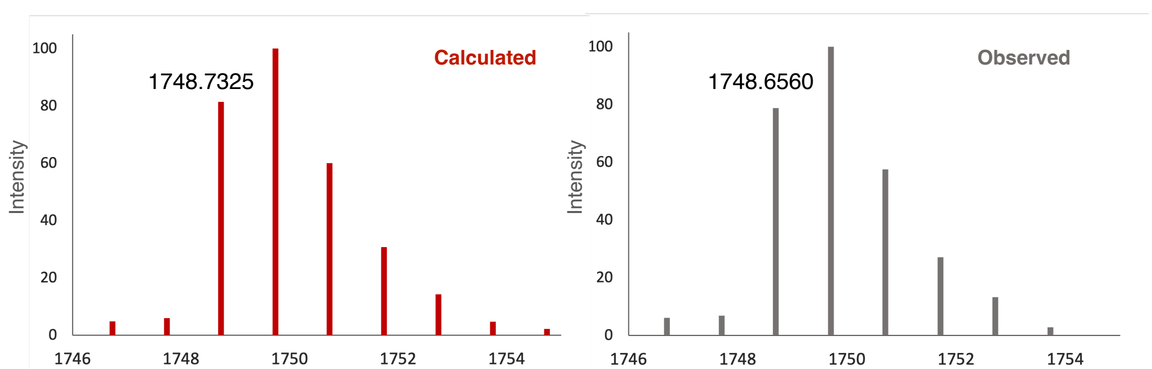
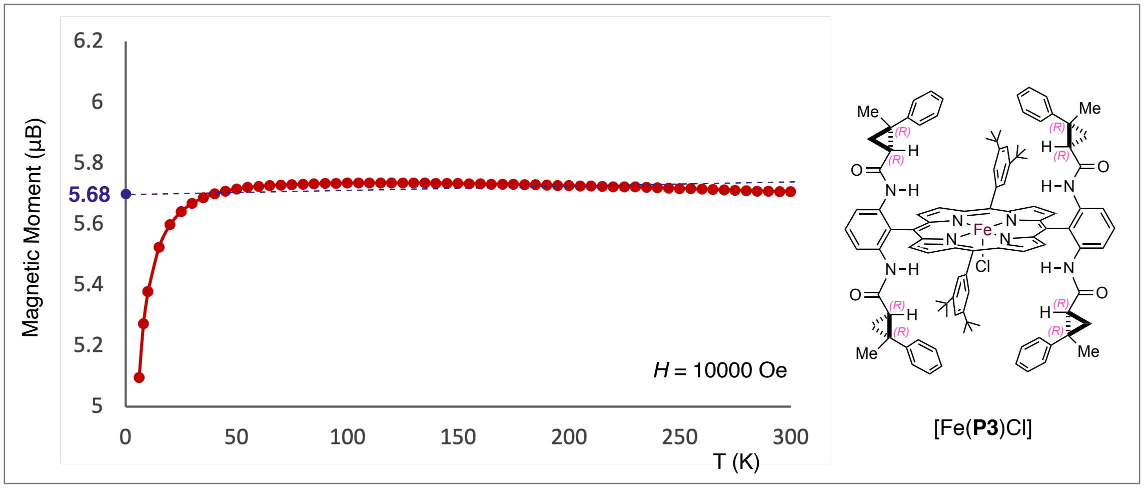


Figure S9: HRMS Analysis of $[\mathbf{I}_{[Fe(\mathbf{P3})Cl]/\mathbf{4l}}+K]^+$

6.4. Determination of Magnetic Susceptibility in [Fe(Por)Cl]

Magnetic susceptibility data of [Fe(Por)Cl] in the solid phase were collected using Quantum Design MPMS SQUID magnetometer over the temperature range from 6 to 300K. (SQUID = superconducting quantum interference device)

Figure S10: Variable Temperature SQUID Measurements of [Fe(**P3**)Cl]



Temp (K)	Mag(uB)
6.00155	5.09555
8.00213	5.27258
10.00178	5.37878
10.00186	5.37885
15.00077	5.52322
20.00042	5.59730
25.00009	5.64055
30.00021	5.66811
35.00000	5.68630
39.99949	5.69886
44.99803	5.70861
49.99618	5.71536
54.99284	5.72015
59.98915	5.72371
64.98427	5.72637
69.97984	5.72808
74.97398	5.72946

79.96930	5.73057
84.96201	5.73153
89.95946	5.73371
94.95320	5.73425
99.94865	5.73446
104.94364	5.73473
109.94061	5.73478
114.93759	5.73484
119.93421	5.73485
124.93184	5.73473
129.92999	5.73463
134.92754	5.73444
139.92593	5.73409
144.92191	5.73367
149.92252	5.73301
154.92107	5.73255
159.91959	5.73207
164.91884	5.73136
169.91755	5.73102
174.91468	5.73047
179.91461	5.72964
184.91448	5.72861
189.91376	5.72764
194.91304	5.72690
199.91243	5.72653
204.91103	5.72531
209.90857	5.72465
214.91053	5.72358
219.91212	5.72280
224.91045	5.72198
229.90924	5.72150
234.90908	5.72040
239.91125	5.71922
244.90933	5.71816
249.90703	5.71713
254.90788	5.71579

259.90919	5.71497
264.90790	5.71338
269.90866	5.71248
274.90843	5.71125
279.90991	5.70988
284.91069	5.70861
289.90897	5.70837
294.90724	5.70717
299.90717	5.70607

Evans Method: The NMR sample was prepared by mixing solvent ($CDCl_3$:$CHCl_3$ = 50:1 v/v) and 4.8 mg of [Fe(**P3**)Cl]. An amount of the stock solution ($CDCl_3$:$CHCl_3$ = 50:1 v/v) was transferred to a capillary tube and the capillary tube was sealed by flame then inserted into the NMR tube. Magnetic susceptibility was measured based on the chemical shift difference ($\Delta\delta$ = 0.307 ppm) of the $CHCl_3$ signal between the inner and the outer tube, which caused by one of the $CHCl_3$ peak has been paramagnetically shifted by the paramagnetic sample in the outer tube. Effective magnetic moment (μ_{eff}) was calculated by Evans method analysis according to literature.[1] Magnetic susceptibility of [Fe(**P3**)Cl]: μ_{eff} = 5.62 μB ($CDCl_3$, 500 MHz, 298K).

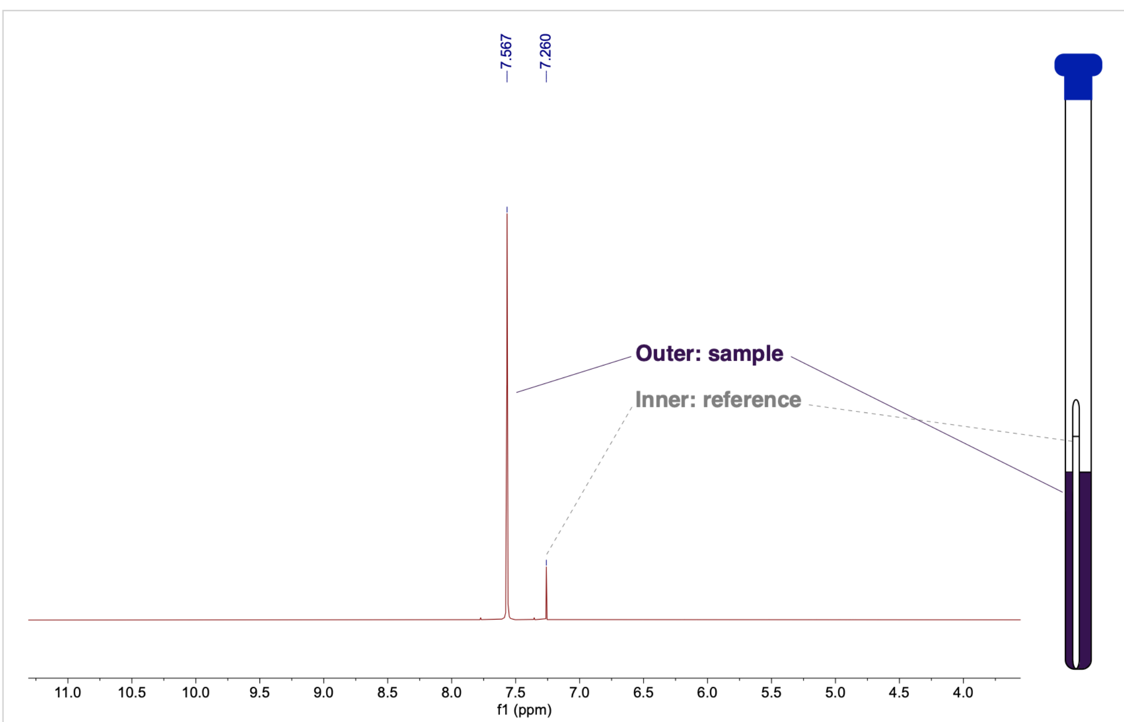
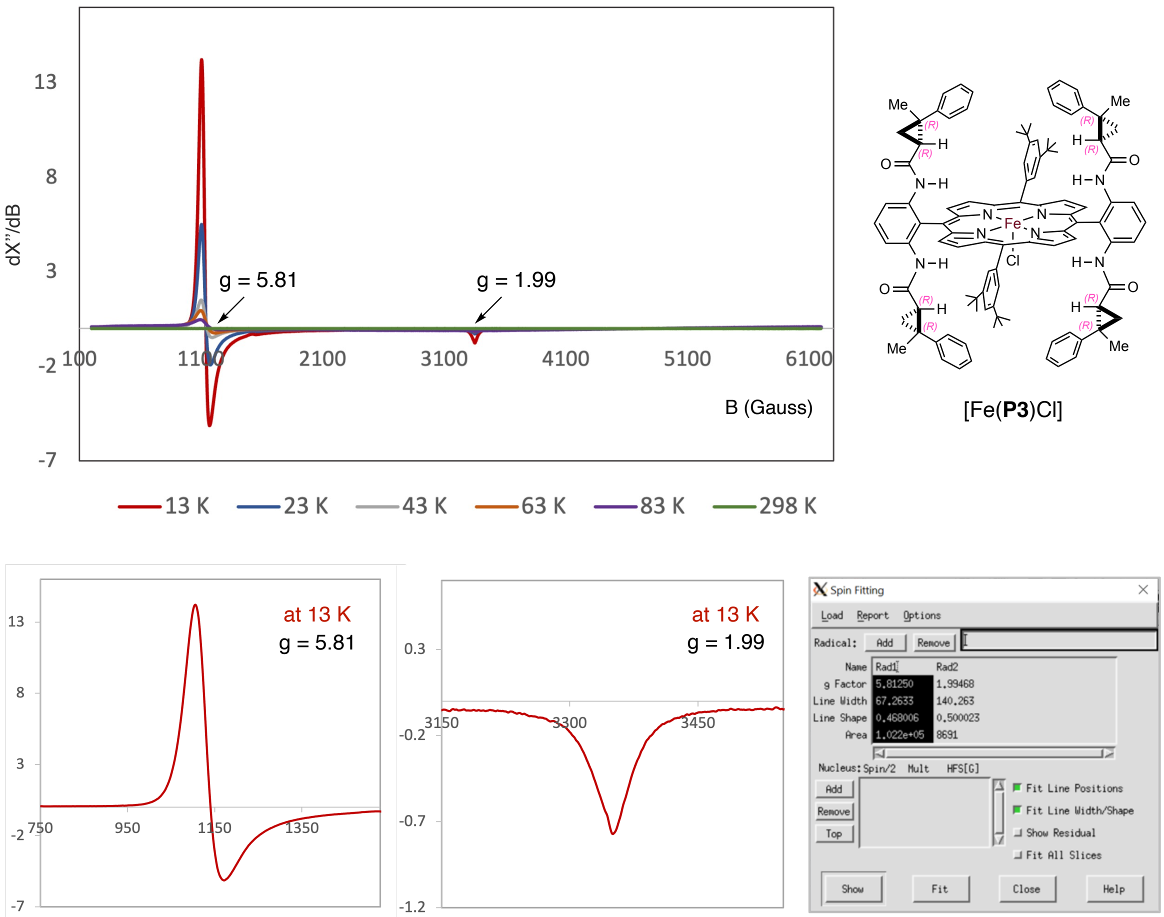


Figure S11: ^{1}H NMR Spectrum of Evans Method on [Fe(**P3**)Cl] and Schematic Diagram of NMR Tube

6.5. Determination of Iron Spin States in [Fe(Por)Cl] by EPR

The EPR spectrum of [Fe(**P3**)Cl] in dichloromethane were recorded on a Bruker EMX-Plus spectrometer over the temperature range from 13 to 298K. *[The simulation of the EPR spectrum was performed by iteration of the isotropic g-values and line widths using the EPR simulation program SpinFit Xenon]*

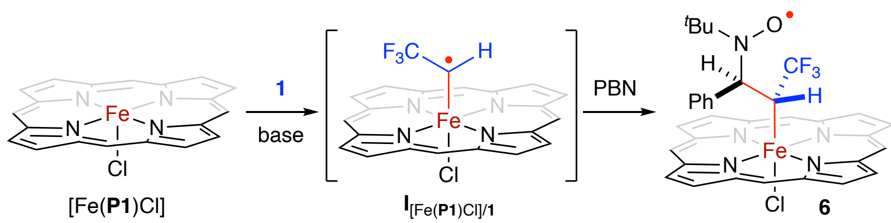
Figure S12: EPR Spectra and Simulation of [Fe(**P3**)Cl] at Variable Temperature



6.6. Radical Trapping by EPR

(EPR = Electron Paramagnetic Resonance Spectroscopy)

Supplemental Experimental Procedure for EPR Experiment: To an oven-dried Schlenk tube, sulfonylhydrazone (or diazo) (0.1 mmol), [Fe(TPP)Cl] (2 mol %) and 1.2 equivalents of PBN (or DMPO) (0.12 mmol) were added. The Schlenk tube was then evacuated and backfilled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and 2.0 equivalents of Et_3N (0.2 mmol) (*skip adding a base if conducting the reaction using diazo as substrate*) and benzene (1.0 mL) were added via a syringe. The mixture was then stirred at 60 ºC for 20 min. The reaction mixture was transferred into a degassed EPR tube (filled with argon) through a syringe. The sample was then carried out for EPR experiment at room temperature.



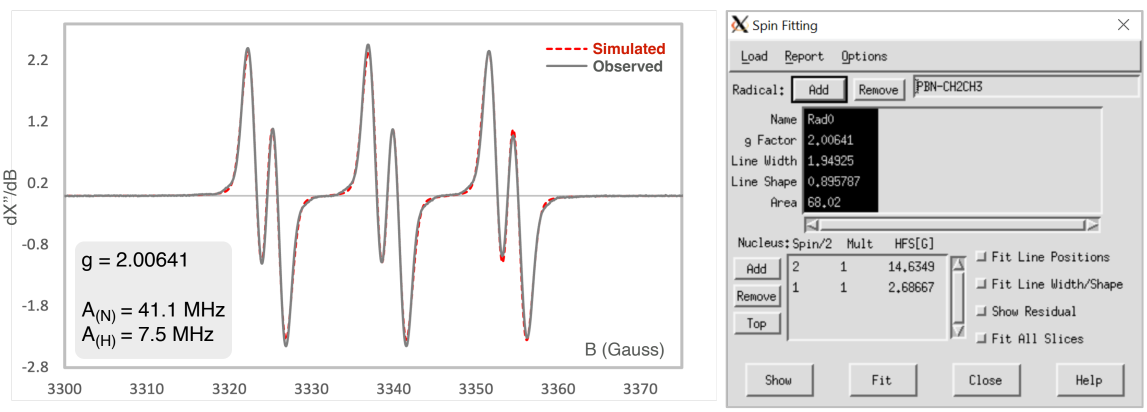


Figure S13: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with PBN

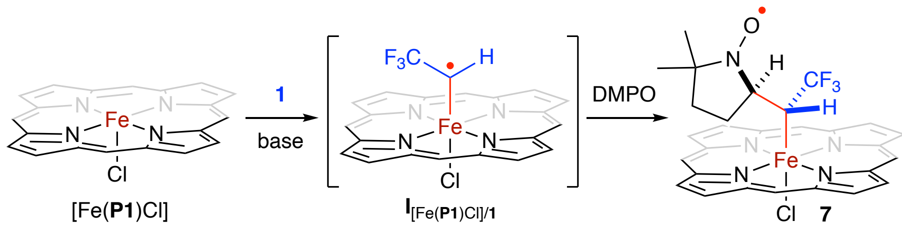
The resulting notable EPR signal (in grey) has been simulated (in red) with g = 2.00641, $A_{(N)}$ = 41.1 MHz, $A_{(H)}$ = 7.5 MHz, which is assigned to PBN (*N*-*tert*-butyl-α-phenylnitrone) adduct of α-Fe(IV)-alkyl radical intermediate.

EPR Simulation Details:

g = 2.00641

$\mathbf{A_{(N)}}$ = 14.6349 x 2.00641 x 1.399611451 = 41.1 MHz

$\mathbf{A_{(H)}}$ = 2.68667 x 2.00641 x 1.399611451 = 7.5 MHz



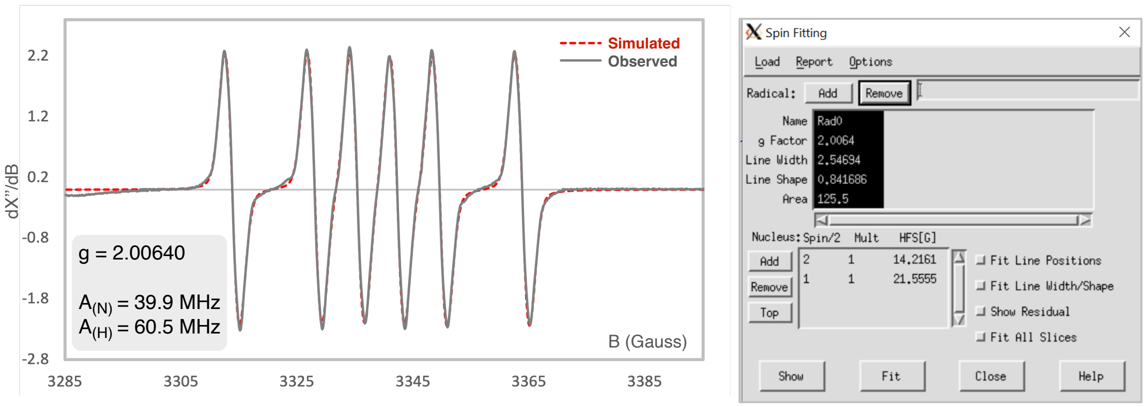


Figure S14: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with DMPO

The resulting notable EPR signal (in grey) has been simulated (in red) with g = 2.00640, $A_{(N)}$ = 39.9 MHz, $A_{(H)}$ = 60.5 MHz, which is assigned to DMPO (5,5-Dimethyl-1-pyrroline *N*-oxide) adduct of α-Fe(IV)-alkyl radical intermediate.

EPR Simulation Details:

g = 2.00640

$\mathbf{A_{(N)}}$ = 14.2161 x 2.00640 x 1.399611451 = 39.9 MHz

$\mathbf{A_{(H)}}$ = 21.5555 x 2.00640 x 1.399611451 = 60.5 MHz

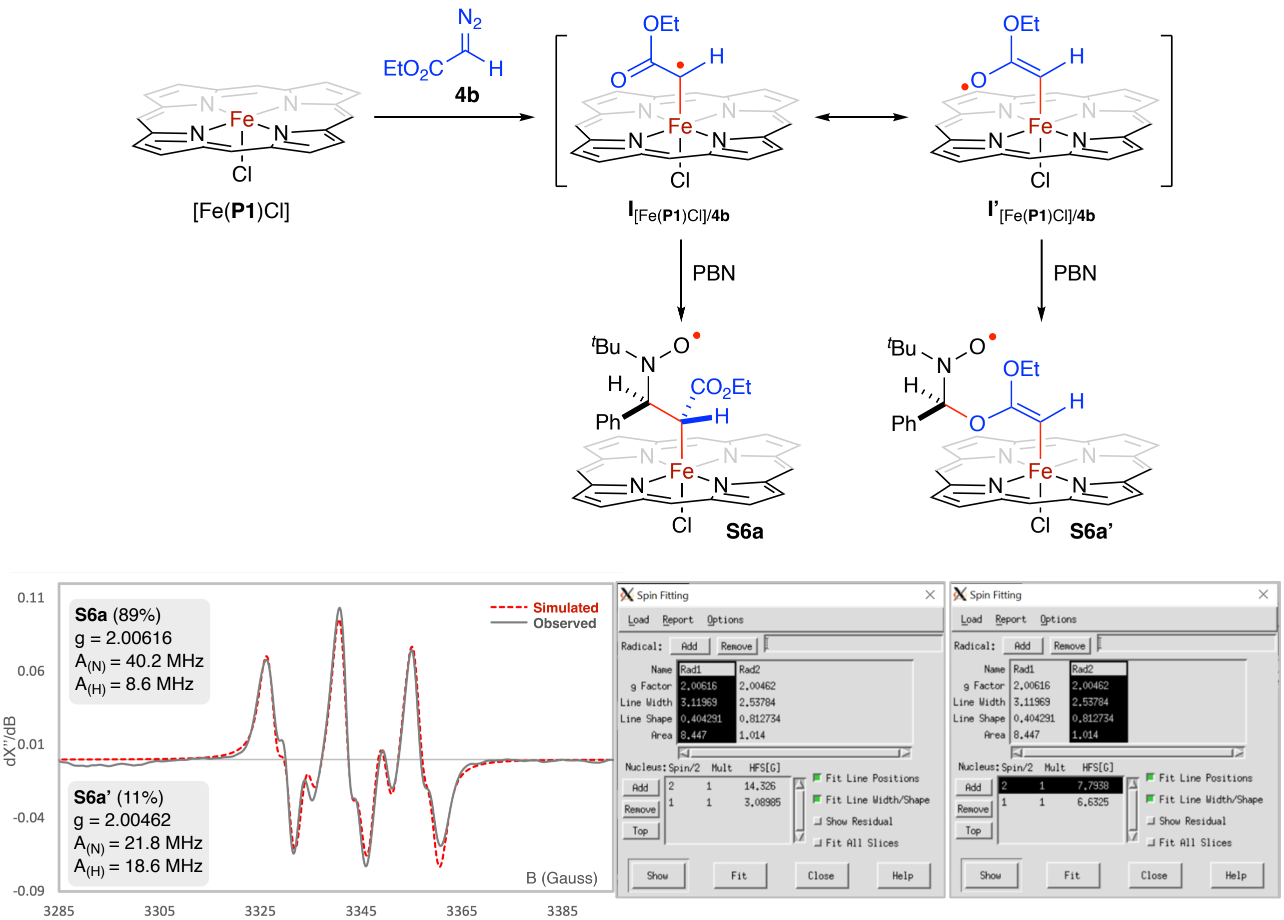


Figure S15: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with PBN

EPR Simulation Details:

S6a (89%)

g = 2.00616

$\mathbf{A_{(N)}}$ = 14.3260 x 2.00616 x 1.399611451 = 40.2 MHz

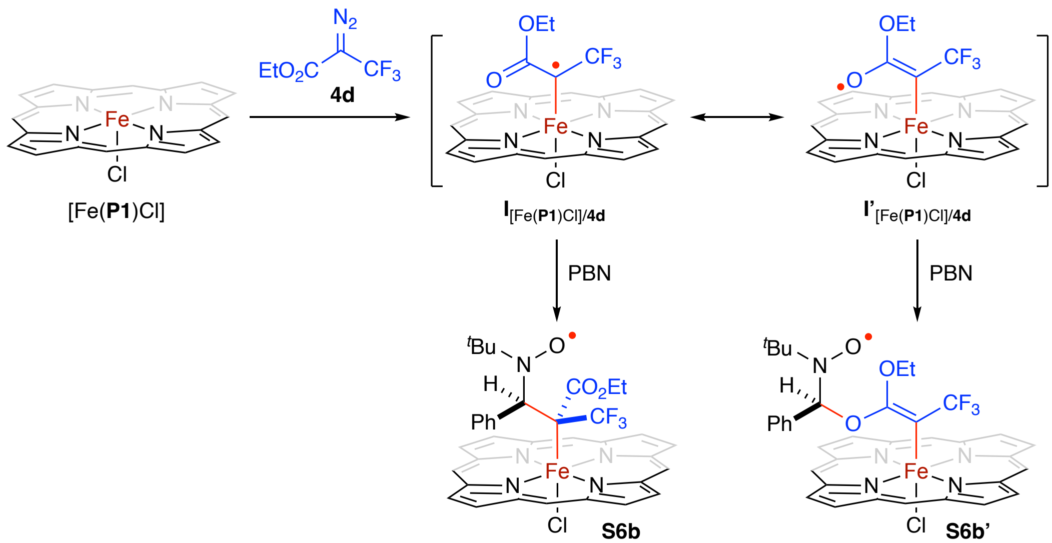
$\mathbf{A_{(H)}}$ = 3.08985 x 2.00616 x 1.399611451 = 8.6 MHz

S6a' (11%)

g = 2.00462

$\mathbf{A_{(N)}}$ = 7.7938 x 2.00462 x 1.399611451 = 21.8 MHz

$\mathbf{A_{(H)}}$ = 6.6325 x 2.00462 x 1.399611451 = 18.6 MHz



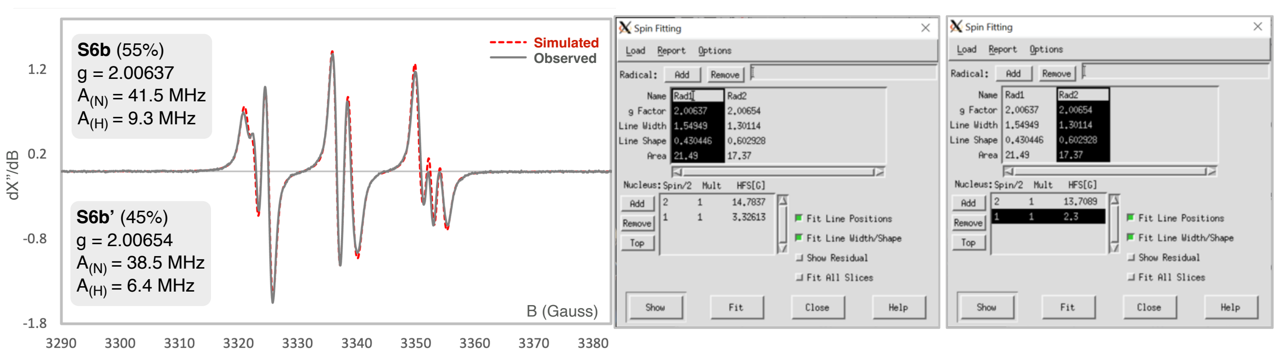


Figure S16: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with PBN

EPR Simulation Details:

S6b (55%)

g = 2.00637

$\mathbf{A_{(N)}}$ = 14.7837 x 2.00637 x 1.399611451 = 41.5 MHz

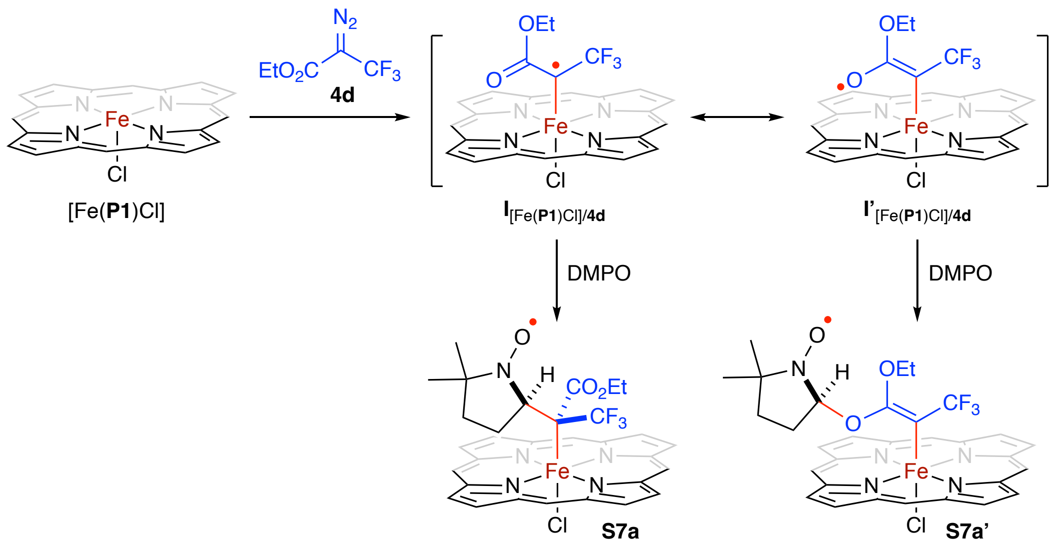
$\mathbf{A_{(H)}}$ = 3.32613 x 2.00637 x 1.399611451 = 9.3 MHz

S6b' (45%)

g = 2.00654

$\mathbf{A_{(N)}}$ = 13.7089 x 2.00654 x 1.399611451 = 38.5 MHz

$\mathbf{A_{(H)}}$ = 2.30000 x 2.00654 x 1.399611451 = 6.4 MHz



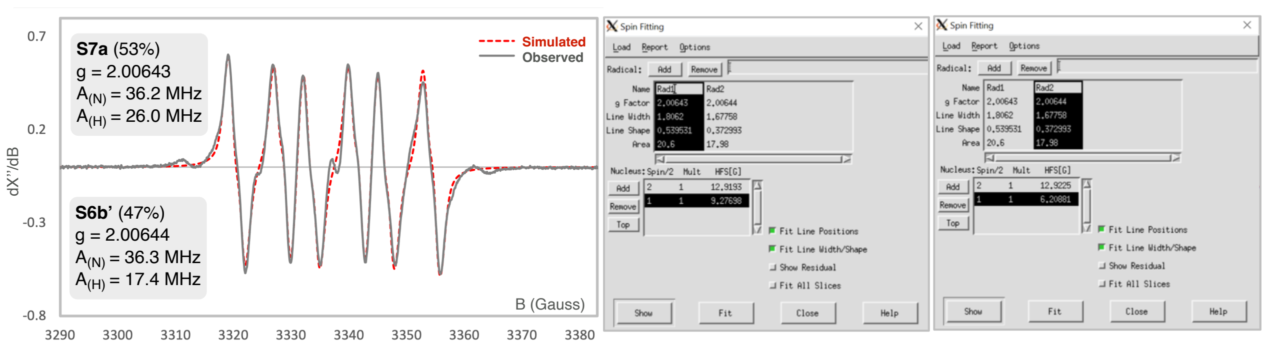


Figure S17: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with DMPO

EPR Simulation Details:

S7a (53%)

g = 2.00643

$\mathbf{A_{(N)}}$ = 12.9193 x 2.00643 x 1.399611451 = 36.2 MHz

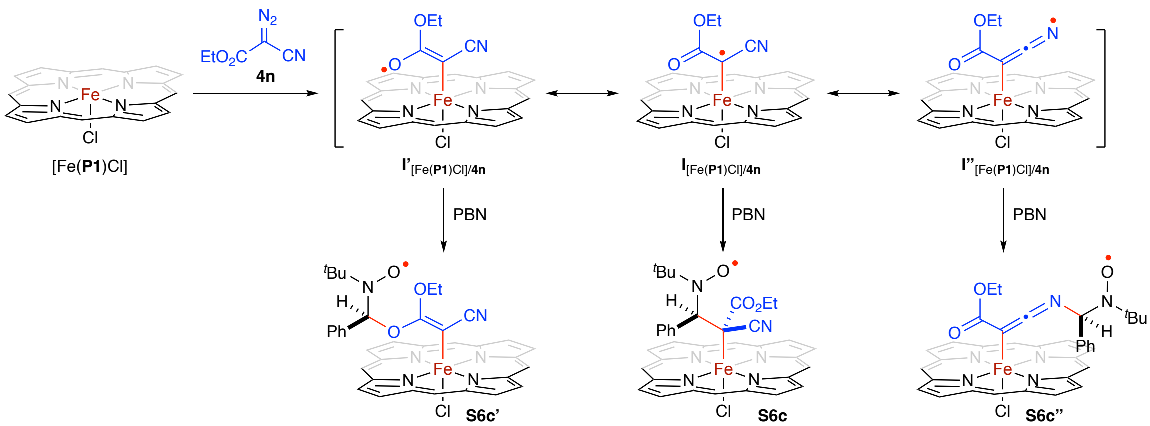
$\mathbf{A_{(H)}}$ = 9.27698 x 2.00643 x 1.399611451 = 26.0 MHz

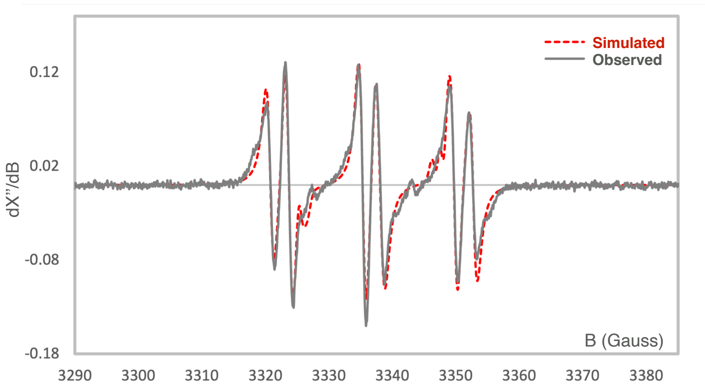
S7a' (47%)

g = 2.00644

$\mathbf{A_{(N)}}$ = 12.9225 x 2.00644 x 1.399611451 = 36.3 MHz

$\mathbf{A_{(H)}}$ = 6.20881 x 2.00644 x 1.399611451 = 17.4 MHz





S6c (93%)
g = 2.00651
$A_{(N)}$ = 40.5 MHz
$A_{(H)}$ = 8.7 MHz

S6c' (4%)
g = 2.00657
$A_{(N)}$ = 34.3 MHz
$A_{(H)}$ = 6.1 MHz

S6c'' (3%)
g = 2.00669
$A_{(N)}$ = 32.1 MHz
$A_{(H)}$ = 6.8 MHz

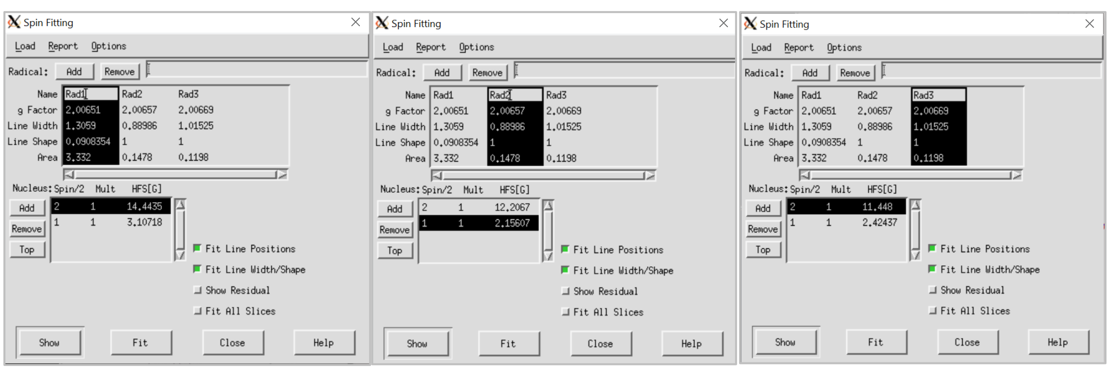


Figure S18: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with PBN

EPR Simulation Details:

S6c (93%)

g = 2.00651

$\mathbf{A_{(N)}}$ = 14.4435 x 2.00651 x 1.399611451 = 40.5 MHz

$\mathbf{A_{(H)}}$ = 3.10718 x 2.00651 x 1.399611451 = 8.7 MHz

S6c’ (4%)

g = 2.00657

$\mathbf{A_{(N)}}$ = 12.2067 x 2.00657 x 1.399611451 = 34.3 MHz

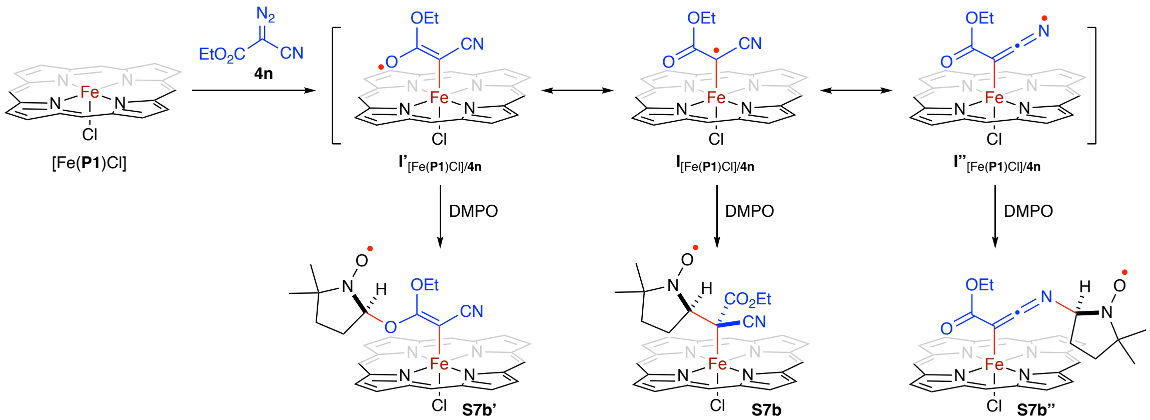
$\mathbf{A_{(H)}}$ = 2.15607 x 2.00657 x 1.399611451 = 6.1 MHz

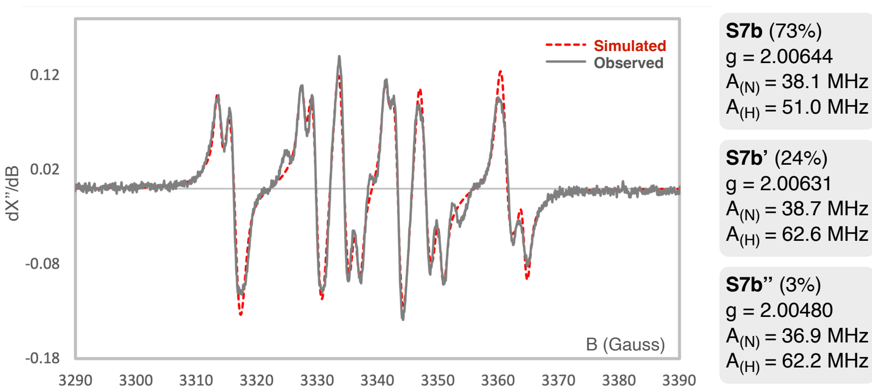
S6c’’ (3%)

g = 2.00669

$\mathbf{A_{(N)}}$ = 11.4480 x 2.00669 x 1.399611451 = 32.1 MHz

$\mathbf{A_{(H)}}$ = 2.42437 x 2.00669 x 1.399611451 = 6.8 MHz





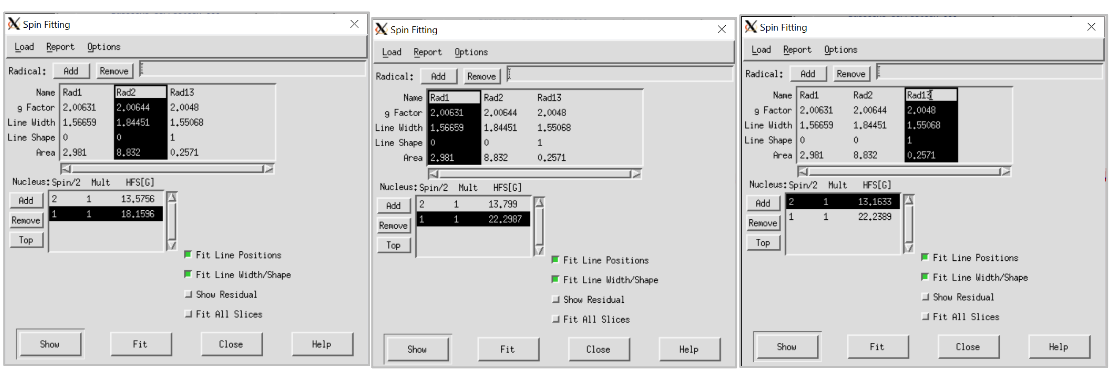


Figure S19: EPR Spectrum and Simulation of α-Fe(IV)-Alkyl Radical with DMPO

EPR Simulation Details:

S7b (73%)

g = 2.00644

$\mathbf{A_{(N)}}$ = 13.5756 x 2.00644 x 1.399611451 = 38.1 MHz

$\mathbf{A_{(H)}}$ = 18.1596 x 2.00644 x 1.399611451 = 51.0 MHz

S7b' (24%)

g = 2.00631

$\mathbf{A_{(N)}}$ = 13.7990 x 2.00631 x 1.399611451 = 38.7 MHz

$\mathbf{A_{(H)}}$ = 22.2987 x 2.00631 x 1.399611451 = 62.6 MHz

S7b'' (3%)

g = 2.00480

$\mathbf{A_{(N)}}$ = 13.1633 x 2.00480 x 1.399611451 = 36.9 MHz

$\mathbf{A_{(H)}}$ = 22.2389 x 2.00480 x 1.399611451 = 62.2 MHz

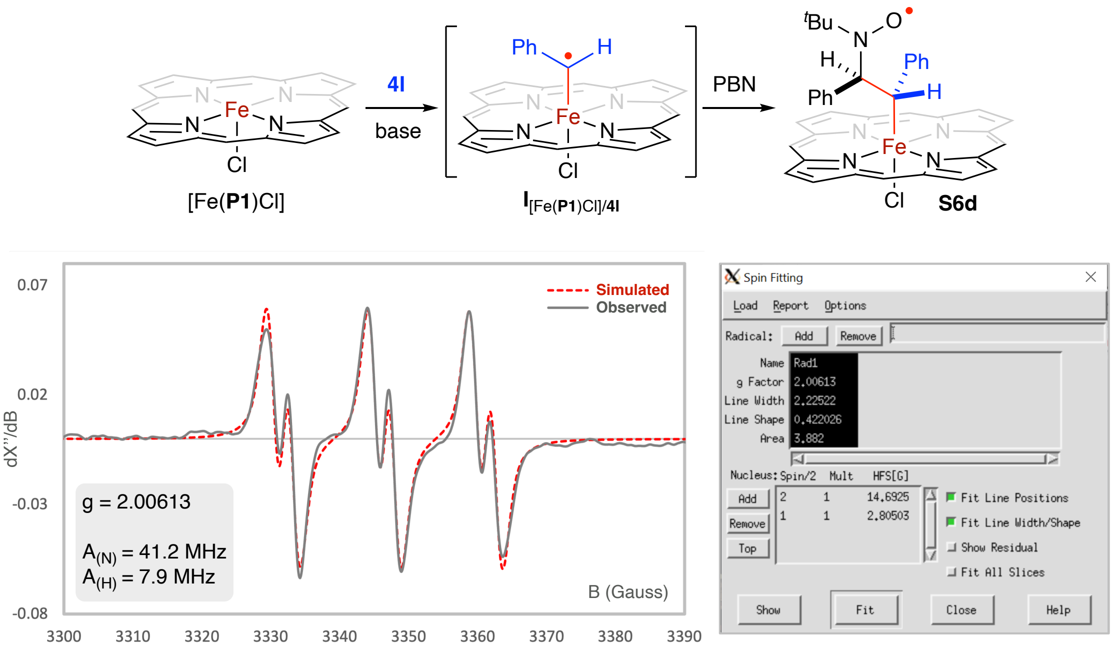


Figure S20: EPR Spectrum and Simulation of α-Fe(IV)-Benzyl Radical with PBN

The resulting notable EPR signal (in grey) has been simulated (in red) with g = 2.00613, $A_{(N)}$ = 41.2 MHz, $A_{(H)}$ = 7.9 MHz, which is assigned to PBN (*N-tert*-butyl-α-phenylnitrone) adduct of α-Fe(IV)-benzyl radical intermediate.

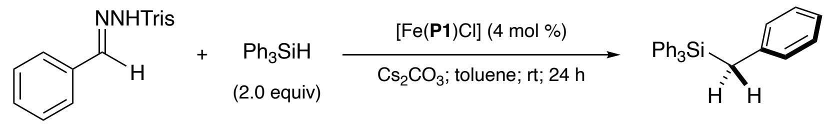
EPR Simulation Details:

g = 2.00613

$\mathbf{A_{(N)}}$ = 14.6925 x 2.00613 x 1.399611451 = 41.2 MHz

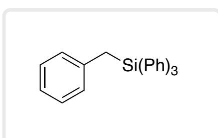
$\mathbf{A_{(H)}}$ = 2.80503 x 2.00613 x 1.399611451 = 7.9 MHz

6.7. Radical Trapping by H-Atom Sources



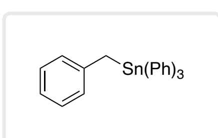
An oven-dried Schlenk tube was charged with 1.0 equivalent of hydrazone (0.1 mmol), 2.0 equivalents of silane/stannane (0.2 mmol), [Fe(**P1**)Cl] (4 mol %) and 2.0 equivalents of Cs_2CO_3 (0.2 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at rt. After 24 h, the reaction mixture was filtered through a plug of silica and concentrated *in vacuo,* then purified via a flash chromatography to afford the desired compound.

Benzyltriphenylsilane (8)

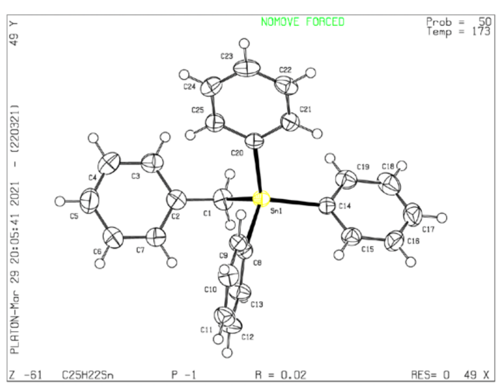


Yield: 31%. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 9H), 7.33 (t, J = 7.6 Hz, 6H), 7.06 (q, J = 6.9 Hz, 3H), 6.85 (d, J = 6.6 Hz, 2H), 2.93 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 136.1, 134.4, 129.7, 129.3, 128.1, 127.9, 124.6, 23.6. IR (neat, cm^{-1}): 3068, 3024, 1598, 1494, 1427, 1208, 1109, 768. HRMS-(DART+) calculated for $C_{25}H_{26}SiN$ $[M+NH_4]^+$: 368.1829, found: 368.1842.

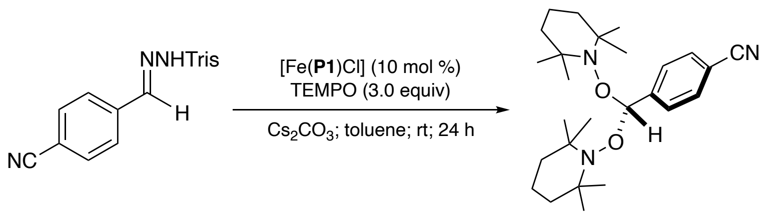
Benzyltriphenylstannane (8')



Yield: 85%. White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 6H), 7.38 – 7.34 (m, 9H), 7.14 (t, J = 7.5 Hz, 2H), 7.08 – 7.01 (m, 3H), 2.99 (t, $J_{Sn\text{-}H}$ = 32.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.8, 138.4, 137.2, 129.1, 128.6, 128.5, 128.0, 124.1, 20.2. IR (neat, cm^{-1}): 3062, 3018, 1598, 1491, 1428, 1207, 1074, 997. The structure was characterized by X-ray crystallography.

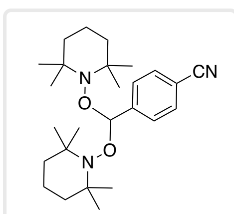


6.8. Radical Trapping by TEMPO

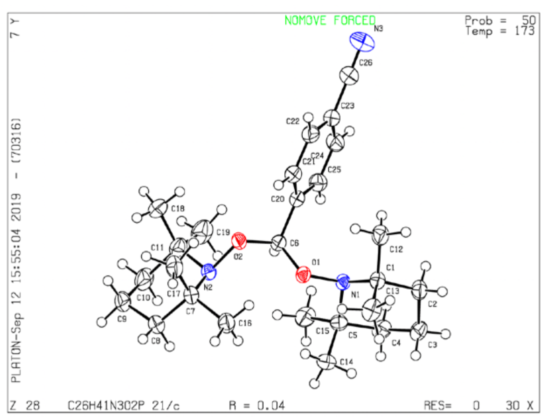


An oven-dried Schlenk tube was charged with 1.0 equivalent of hydrazone (0.1 mmol), 3.0 equivalents of TEMPO (0.3 mmol), [Fe(**P1**)Cl] (10 mol %) and 2.0 equivalents of Cs_2CO_3 (0.2 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene (1 mL) was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at rt. After 24 h, the reaction mixture was filtered through a plug of silica and concentrated *in vacuo*, then purified via a flash chromatography to afford the desired compound.

4-(Bis((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)benzonitrile (9)



Yield: 70%. White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 1.7 Hz, 4H), 6.06 (s, 1H), 1.49 (s, 12H), 1.31 (s, 8H), 1.23 (s, 6H), 0.97 (s, 6H), 0.45 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.6, 131.1, 129.6, 119.3, 111.6, 108.2, 40.8, 40.1, 34.5, 33.1, 21.4, 20.9, 17.3. IR (neat, cm^{-1}): 2974, 2931, 2228, 1466, 1363, 1132, 947, 834. HRMS-(DART+) calculated for $C_{26}H_{42}N_3O_2$ [M+H]$^+$: 428.3272, found: 428.3276. The structure was characterized by X-ray crystallography.



6.9. Probing of Radical Intermediates by Reactions of β-Deuterostyrenes

An oven-dried Schlenk tube was charged with 1.0 equivalent of olefin (0.1 mmol), 1.2 equivalents of hydrazone (0.12 mmol), [Fe(Por)Cl] (2 mol %) and 2.4 equivalents of Cs_2CO_3 (0.24 mmol). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and solvent (1 mL) was added. The Schlenk tube was then purged with nitrogen for 30 sec and the rubber septum was replaced with a Teflon screw cap. The mixture was stirred at 40 ºC. After 20 h, the reaction mixture was filtered through a plug of silica and then concentrated *in vacuo*. The residue was purified via a flash chromatography to afford the compound. (*The modification of reaction conditions is substrate-dependent, the details mentioned in the main text Table 3.*)

Figure S21. The Rationale of both Isotopomers (*trans*;*cis*)-**3c**$_\mathbf{D}$ and (*trans*;*trans*)-**3c**$_\mathbf{D}$ Formation from [Fe(Por)Cl]-Catalyzed Asymmetric Cyclopropanation of (*Z*)-**2c**$_\mathbf{D}$

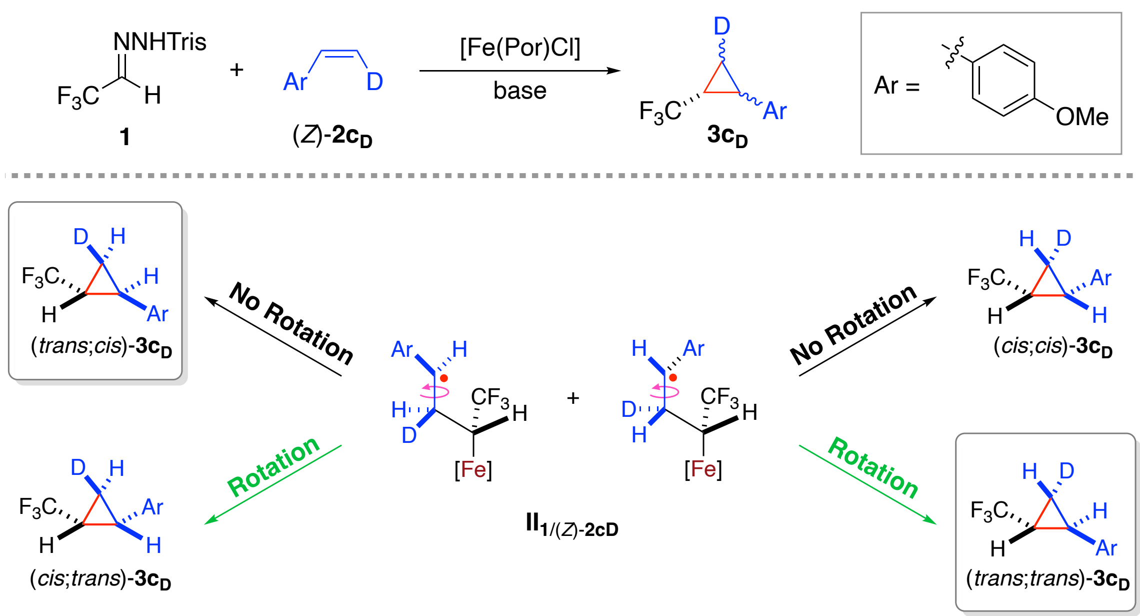


Figure S22. The Rationale of both Isotopomers (*trans*;*cis*)-**3c**$_{\mathbf{D}}$ and (*trans*;*trans*)-**3c**$_{\mathbf{D}}$ Formation from [Fe(Por)Cl]-Catalyzed Asymmetric Cyclopropanation of (*E*)-**2c**$_{\mathbf{D}}$

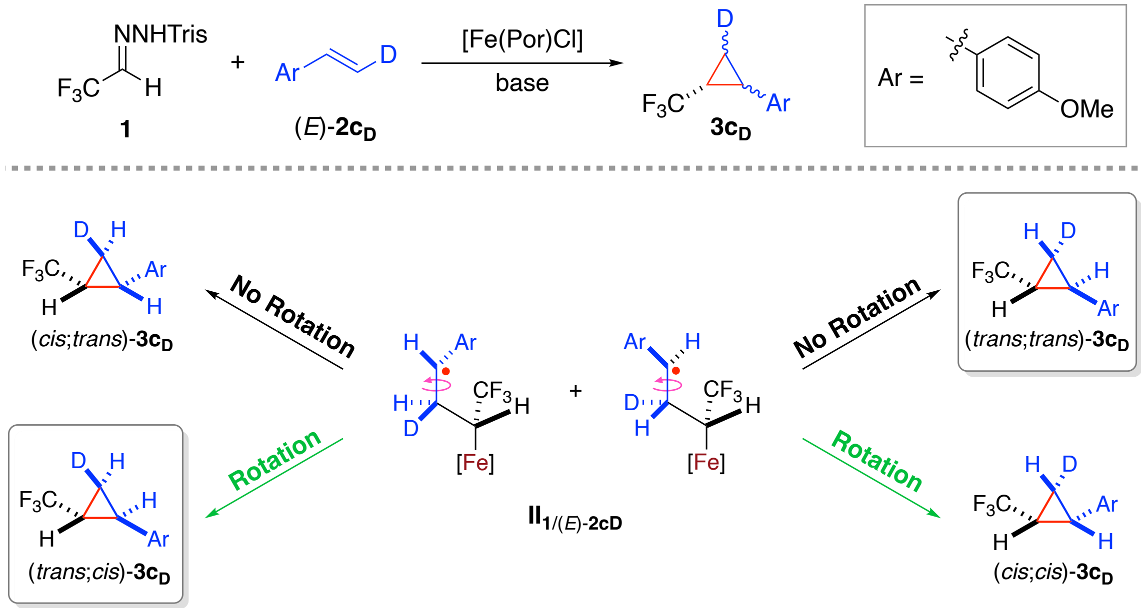


Figure S23. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **3c$_D$** from [Fe(**P1**)Cl]-Catalyzed Cyclopropanation between: **(a)** hydrazone (**1**) and olefin (*Z*)-**2c$_D$** **(b)** hydrazone (**1**) and olefin (*E*)-**2c$_D$**

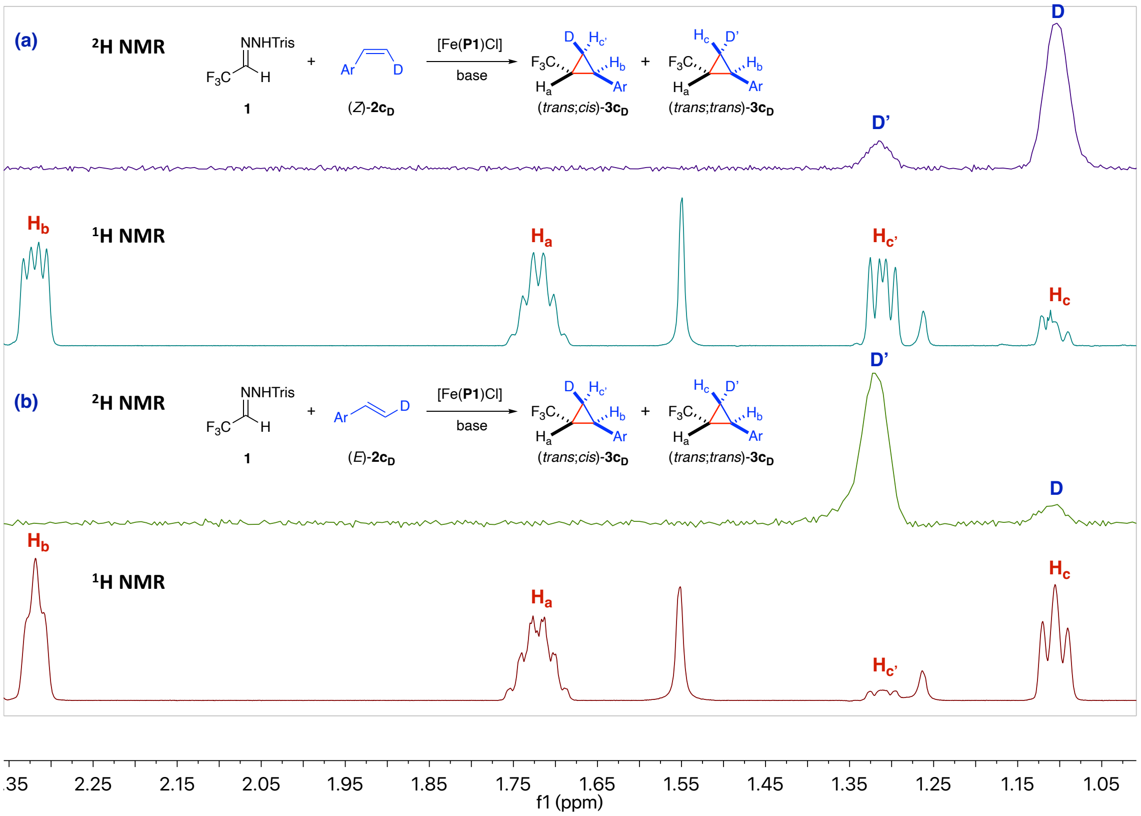


Figure S24. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **3c$_D$** from [Fe(**P2**)Cl]-Catalyzed Cyclopropanation between: **(a)** hydrazone (**1**) and olefin (*Z*)-**2c$_D$** **(b)** hydrazone (**1**) and olefin (*E*)-**2c$_D$**

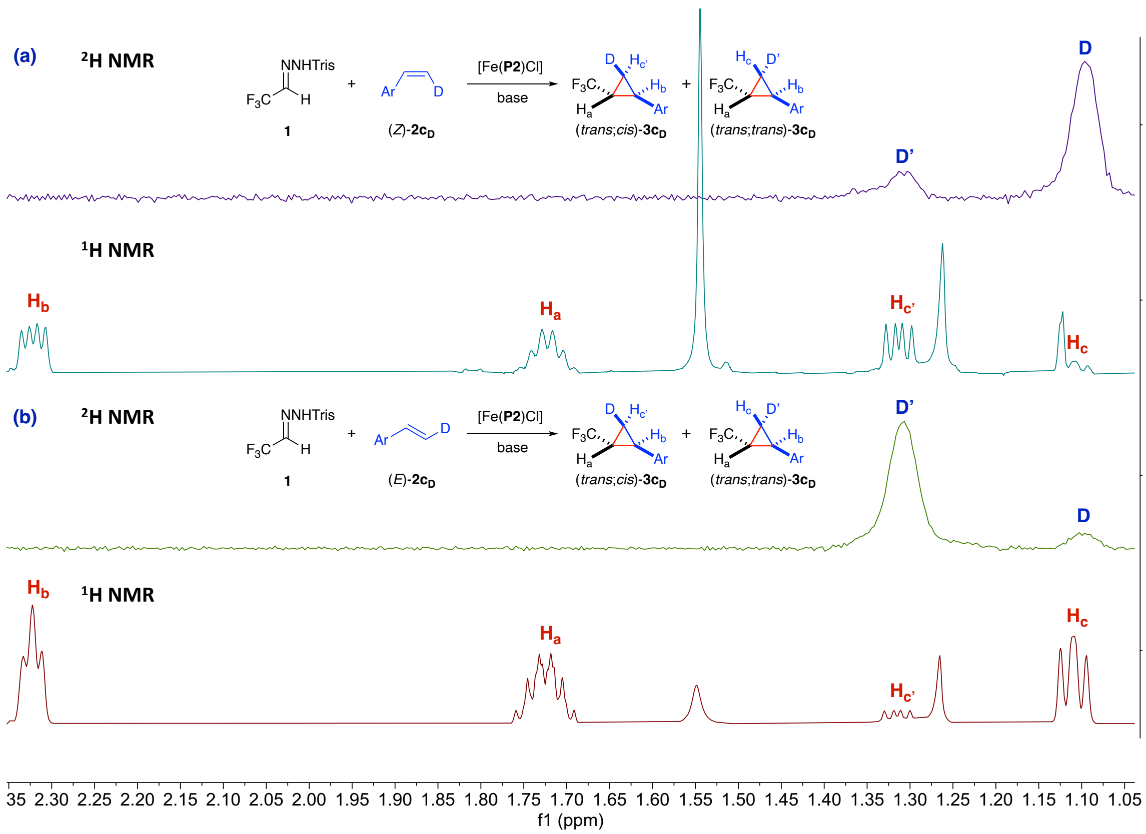


Figure S25. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **3c$_D$** from [Fe(**P3**)Cl]-Catalyzed Cyclopropanation between: **(a)** hydrazone (**1**) and olefin (*Z*)-**2c$_D$** **(b)** hydrazone (**1**) and olefin (*E*)-**2c$_D$**

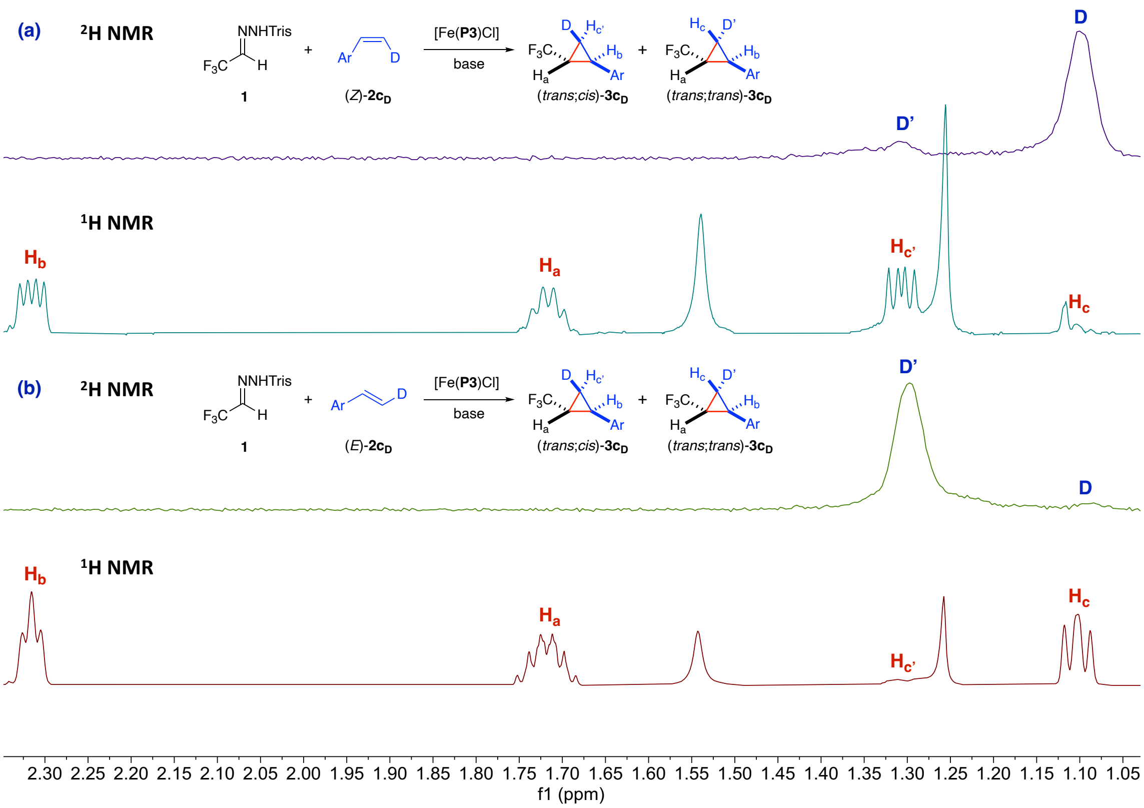


Figure S26. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **5b$_D$** from [Fe(**P2**)Cl]-Catalyzed Cyclopropanation between: **(a)** Diazo (**4b**) and olefin (*Z*)-**2a$_D$** **(b)** Diazo (**4b**) and olefin (*E*)-**2a$_D$**

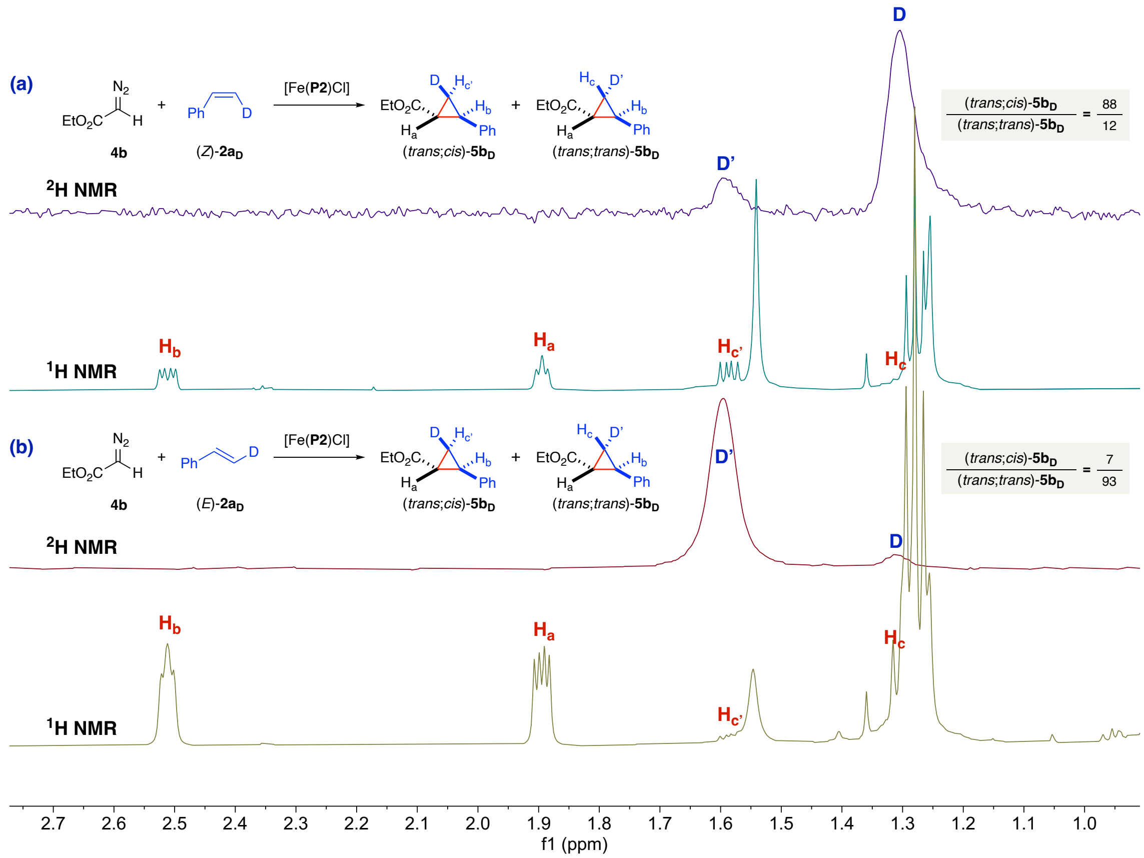
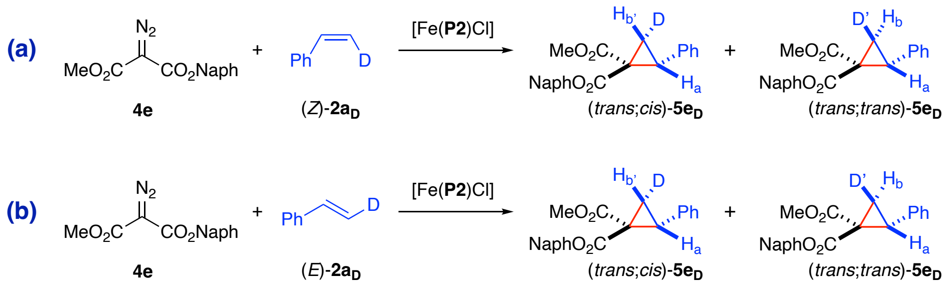


Figure S27. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **5e$_D$** from [Fe(**P2**)Cl]-Catalyzed Cyclopropanation between: **(a)** Diazo (**4e**) and olefin (*Z*)-**2a$_D$** **(b)** Diazo (**4e**) and olefin (*E*)-**2a$_D$**



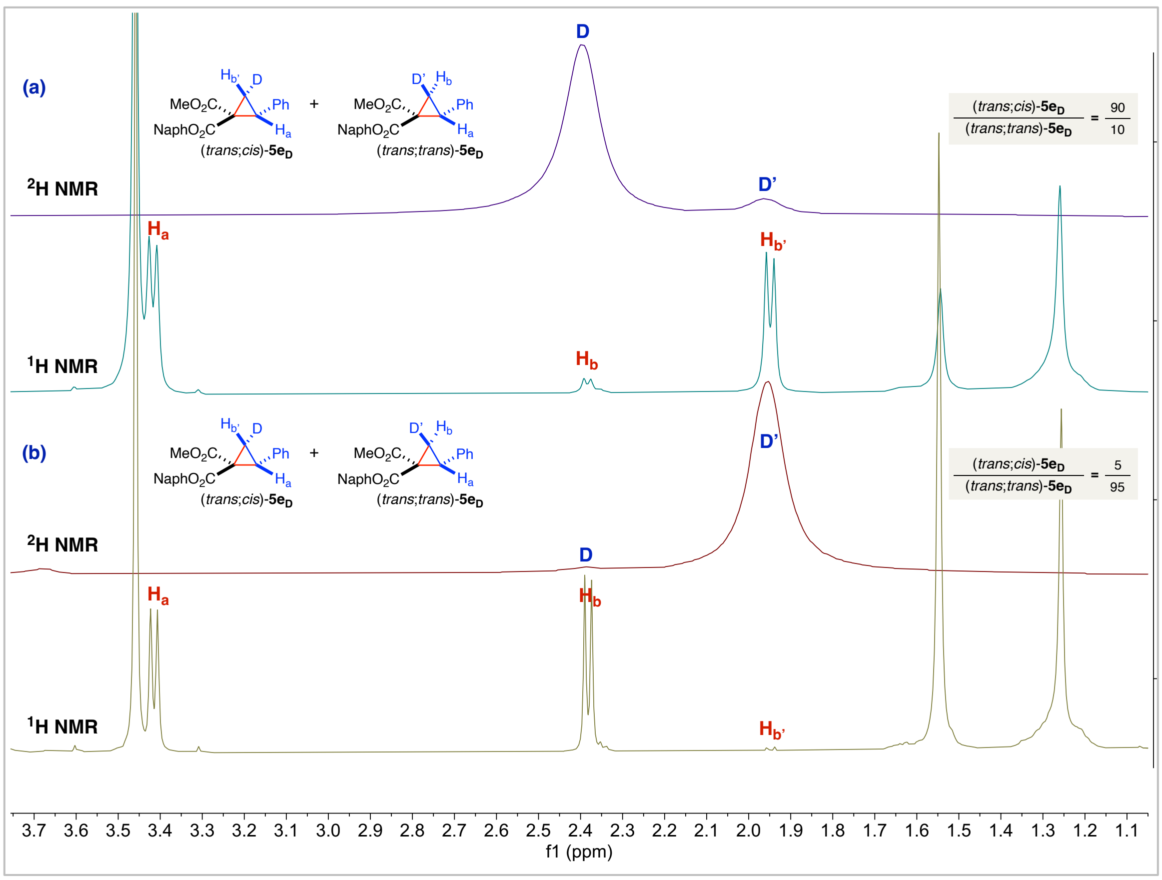
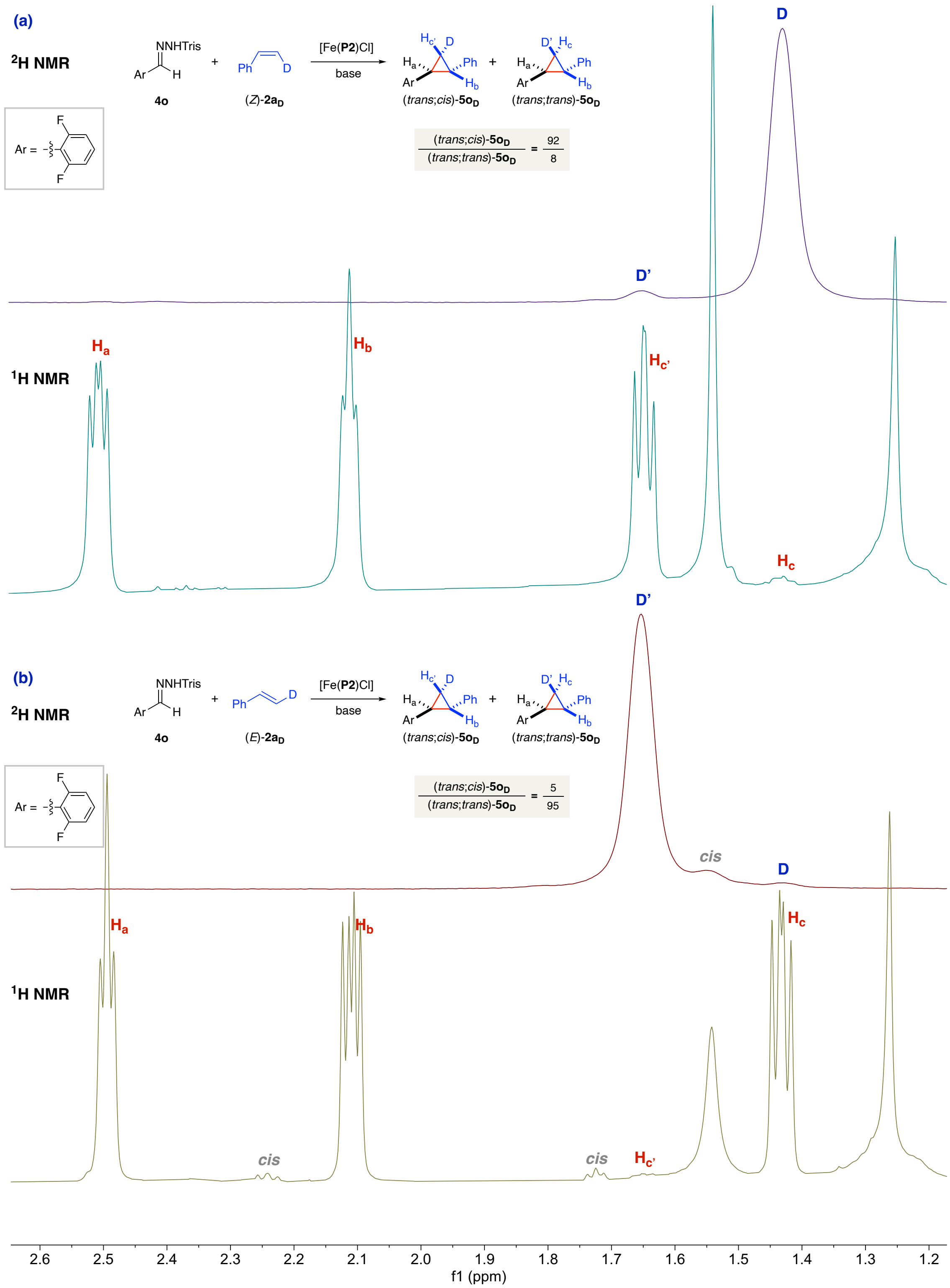


Figure S28. Upfield ^{2}H NMR and ^{1}H NMR for Cyclopropane Isomers **5o$_{D}$** from [Fe(**P2**)Cl]-Catalyzed Cyclopropanation between: **(a)** hydrazone (**4o**) and olefin (*Z*)-**2a$_{D}$** **(b)** hydrazone (**4o**) and olefin (*E*)-**2a$_{D}$**



6.10. Reaction Progress Monitored by NMR Spectroscopy

An oven-dried Schlenk tube was charged with 1.0 equivalent of olefin **2a** (0.05 mmol), 1.2 equivalents of hydrazone **1** (0.06 mmol) and [Fe(**P3**)Cl] (2 mol %). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene-d_8 (0.5 mL) was added. The mixture was stirred at rt. After 10 sec, the reaction mixture was added to the J. Young NMR tube containing 2.4 equivalents of Cs_2CO_3 (0.12 mmol). The NMR spectra were acquired using Varian Inova 400 MHz or Bruke 500 MHz.

Figure S29. ^{1}H NMR Spectrum of the Catalytic Reaction in Toluene-d_8 (t = 0 min)

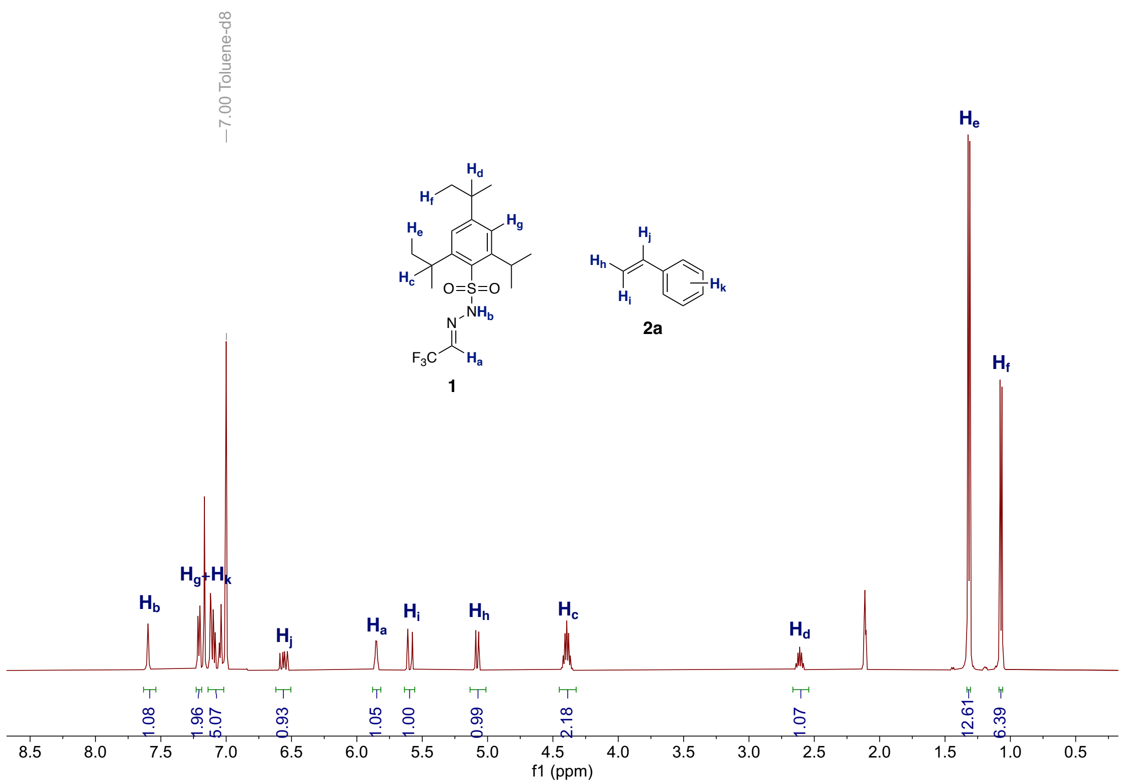


Figure S30. Time-Stacked ^{1}H NMR Spectra of the Catalytic Reaction in Toluene-d_8

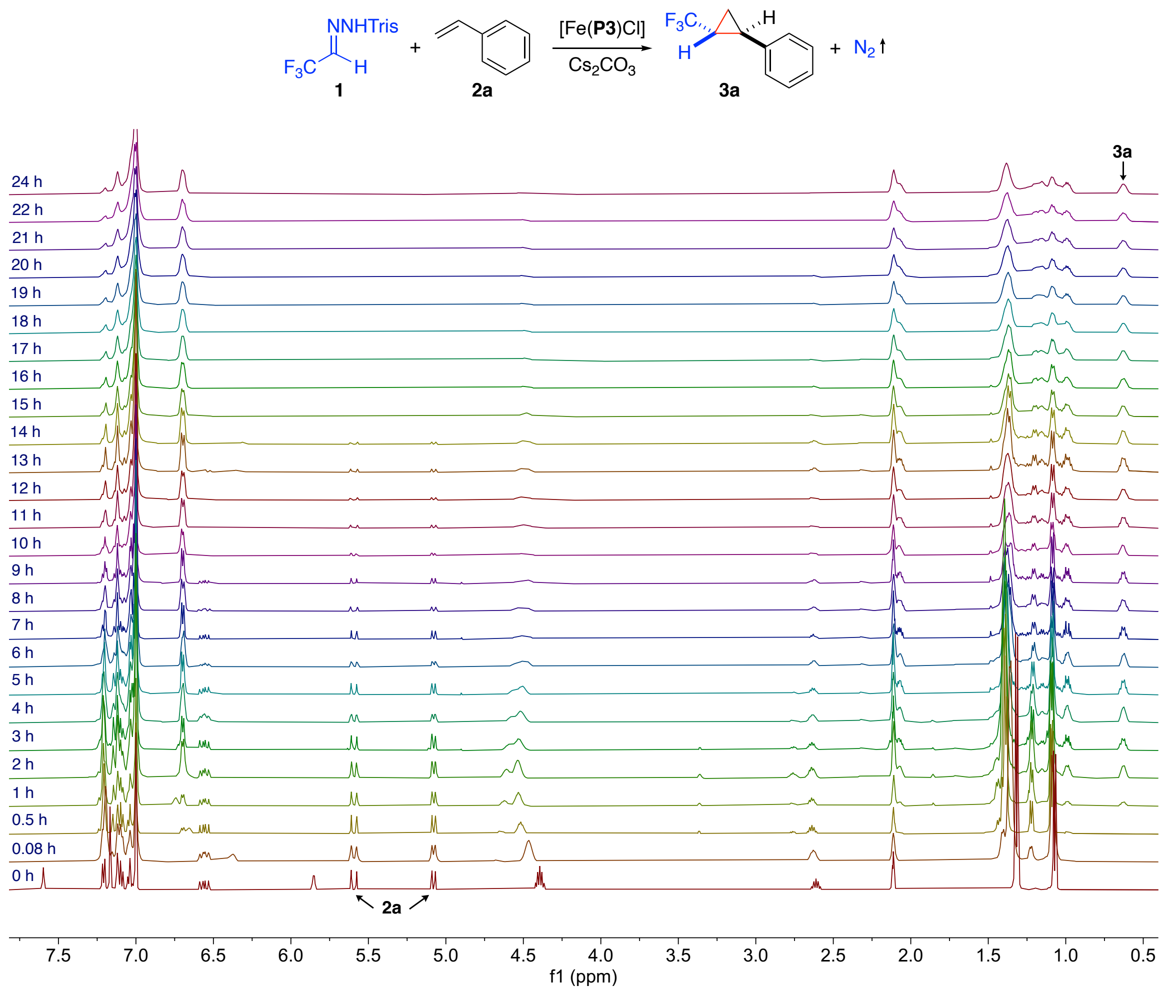
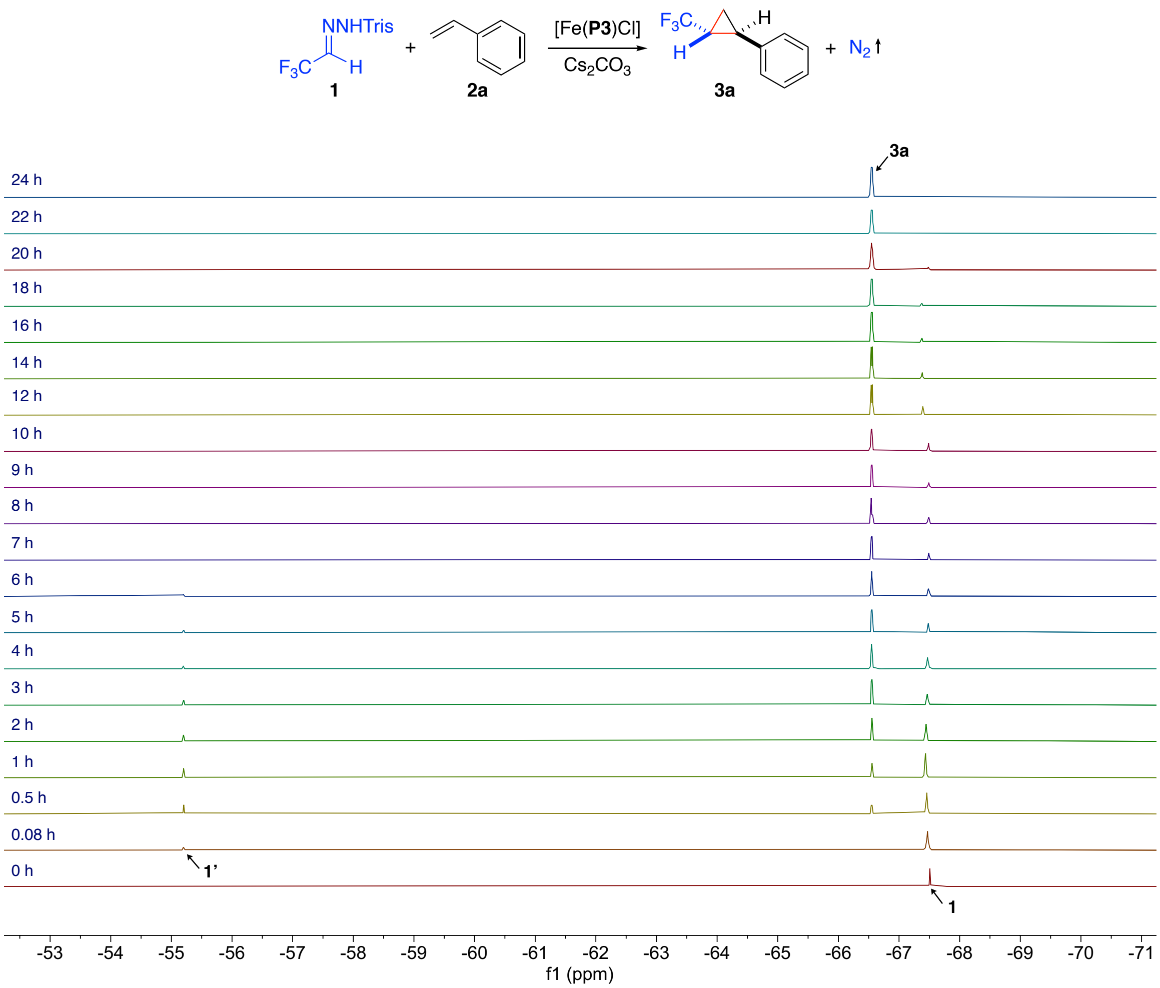


Figure S31. Time-Stacked ^{19}F NMR Spectra of the Catalytic Reaction in Toluene-d_8



6.11. Determination of Kinetic Orders in the Catalytic Reaction

Standard conditions: An oven-dried Schlenk tube was charged with olefin **2a** (0.05 mmol), 1.2 equivalents of hydrazone **1** (0.06 mmol) and [Fe(**P3**)Cl] (2 mol %). The Schlenk tube was then evacuated and back filled with nitrogen three times. The Teflon screw cap was replaced with a rubber septum, and toluene-d_8 (0.5 mL) was added. The mixture was stirred at rt. After 10 sec, the reaction mixture was added to the J. Young NMR tube containing 2.4 equivalents of Cs_2CO_3 (0.12 mmol). The NMR spectra were acquired using Varian Inova 400 MHz or Bruke 500 MHz.

Figure S32. Representative Plot for the Conversion of **1**/**2a** to **3a** versus Time

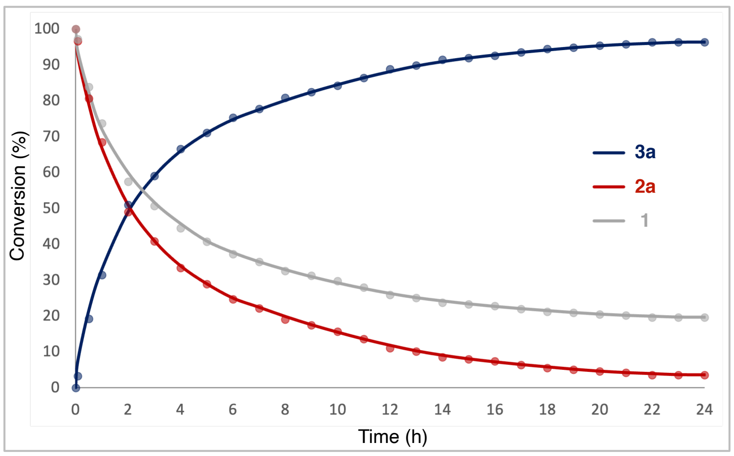
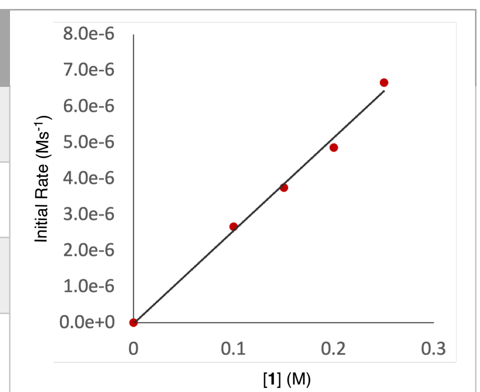


Figure S33. Initial Rate for **3a** Formation versus Variable Concentration of **1**

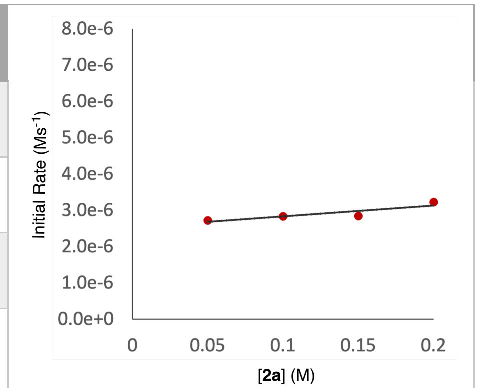
Initial Rate	[1] (M)
2.66667e-06	0.10
3.75000e-06	0.15
4.86111e-06	0.20
6.66667e-06	0.25



*The reaction is first-order in hydrazone **1**.*

Figure S34. Initial Rate for **3a** Formation versus Variable Concentration of **2a**

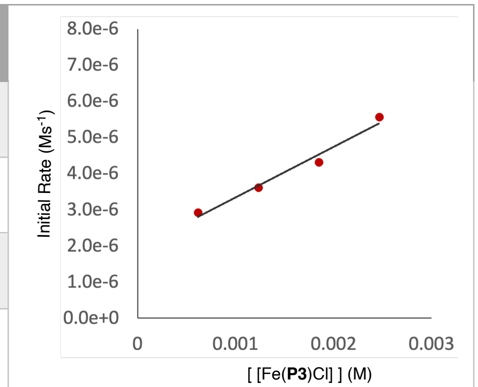
Initial Rate	[2a] (M)
2.72222e-06	0.05
2.83333e-06	0.10
2.84722e-06	0.15
3.22222e-06	0.20



*The reaction is zero-order in olefin **2a**.*

Figure S35. Initial Rate for **3a** Formation versus Variable Concentration of [Fe(**P3**)Cl]

Initial Rate	[[Fe(P3)Cl]] (M)
2.91667e-06	6.167810e-04
3.61111e-06	1.233563e-03
4.30556e-06	1.850344e-03
5.55556e-06	2.467126e-03

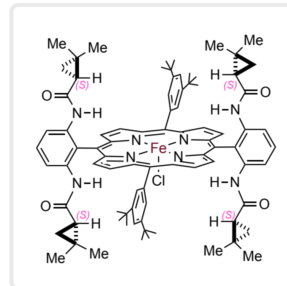


*The reaction is fractional-order (0.5 order) in catalyst [Fe(**P3**)Cl].*

7. X-ray Crystallography

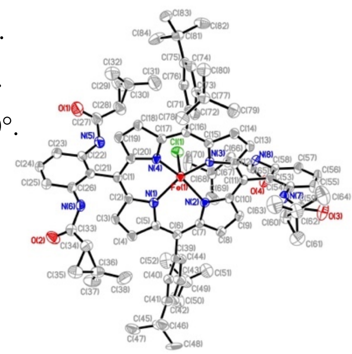
The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2*[2] (Difference Vectors method). Data integration and reduction were performed using SaintPlus.[3] Absorption correction was performed by multi-scan method implemented in SADABS.[4] Space groups were determined using XPREP implemented in APEX2.[2] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 contained in WinGX v1.70.01[5,6,7] program.

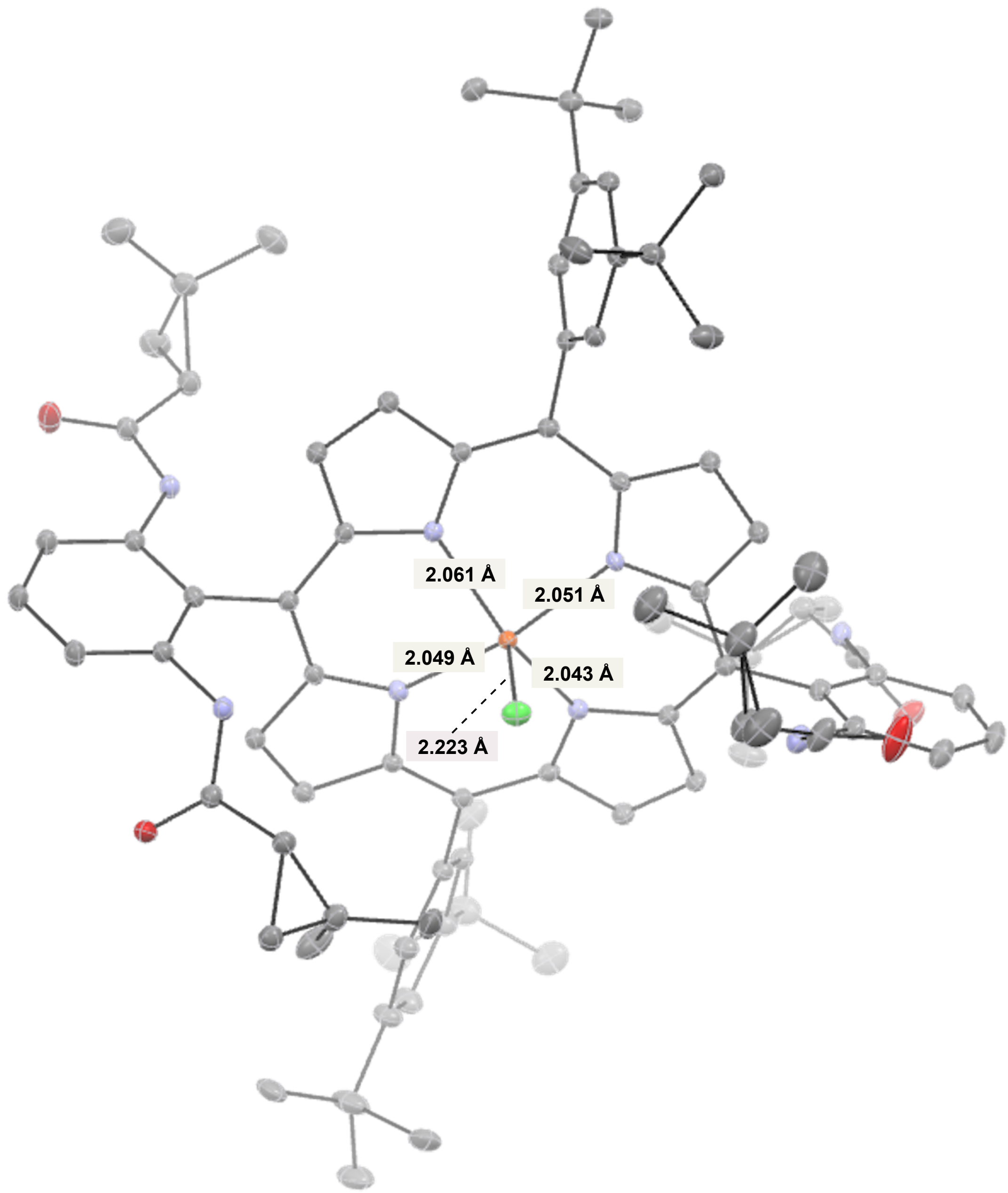
Table S1. Crystal data and structure refinement for C84H96ClFeN8O4 ([Fe(P2)Cl])



CCDC: 2128685

Identification code	C84H96ClFeN8O4	
Empirical formula	C168.25 H192.25 Cl2.75 Fe2 N16 O8	
Formula weight	2775.81	
Temperature	123(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_5$	
Unit cell dimensions	a = 29.9867(13) Å	α= 90°.
	b = 29.9867(13) Å	β= 90°.
	c = 30.2624(14) Å	γ = 120°.
Volume	23566(2) $Å^3$	
Z	6	
Density (calculated)	1.174 Mg/m^3	
Absorption coefficient	2.383 mm^{-1}	
F(000)	8859	
Crystal size	0.460 x 0.240 x 0.170 mm^3	
Theta range for data collection	1.701 to 66.837°.	
Index ranges	-33<=h<=35, -35<=k<=35, -35<=l<=35	
Reflections collected	159992	
Independent reflections	27672 [R(int) = 0.0497]	
Completeness to theta = 66.837°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5524	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27672 / 1929 / 1888	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1185	
R indices (all data)	R1 = 0.0626, wR2 = 0.1275	
Absolute structure parameter	-0.0057(14)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.574 and -0.352 e.$Å^{-3}$	





[Fe(P2)Cl]

Fe–N_p: 2.051(4) Å

Fe–C_{tp}: 0.490 Å

Fe–C_{tN}: 0.477 Å

C_{tN}–N_p: 1.994 Å

Fe–Cl: 2.2234(15) Å

N_p: porphinato nitrogen. C_{tp}: center of the plane of the 24-atom porphinato core. C_{tN}: center of the plane of the four N_p.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for C84H96ClFeN8O4 ([Fe(P2)Cl])

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	6962(1)	190(1)	5350(1)	30(1)
Cl(1)	6731(1)	410(1)	5975(1)	50(1)
O(1)	4534(4)	-1206(7)	6366(4)	94(4)
O(1X)	4630(30)	-1331(17)	6300(20)	87(10)
O(2)	4684(2)	-1247(2)	3788(1)	64(1)
O(3)	9974(2)	1393(2)	4897(2)	68(1)
O(4)	8557(1)	2513(1)	6116(1)	49(1)
N(1)	6466(1)	162(1)	4874(1)	32(1)
N(2)	7491(1)	885(1)	5084(1)	32(1)
N(3)	7575(1)	98(1)	5526(1)	30(1)
N(4)	6513(1)	-595(1)	5393(1)	32(1)
N(5)	5117(2)	-743(2)	5831(2)	50(1)
N(6)	5181(2)	-1282(2)	4337(1)	40(1)
N(7)	9157(2)	1117(2)	5126(1)	39(1)
N(8)	8358(2)	1690(2)	6203(1)	37(1)
C(1)	5717(2)	-673(2)	5089(2)	35(1)
C(2)	5953(2)	-217(2)	4845(2)	34(1)
C(3)	5695(2)	-72(2)	4526(2)	38(1)
C(4)	6048(2)	384(2)	4351(2)	39(1)
C(5)	6524(2)	546(2)	4579(2)	33(1)
C(6)	6959(2)	1034(2)	4552(2)	32(1)
C(7)	7402(2)	1198(2)	4810(2)	32(1)
C(8)	7839(2)	1708(2)	4815(2)	38(1)
C(9)	8193(2)	1707(2)	5092(2)	37(1)
C(10)	7981(2)	1190(2)	5252(2)	33(1)
C(11)	8248(2)	1012(2)	5507(2)	32(1)
C(12)	8060(2)	495(2)	5616(2)	32(1)
C(13)	8356(2)	301(2)	5828(2)	36(1)
C(14)	8053(2)	-213(2)	5862(2)	36(1)
C(15)	7561(2)	-338(2)	5682(2)	32(1)

C(16)	7120(2)	-824(2)	5719(2)	33(1)
C(17)	6625(2)	-930(2)	5605(2)	32(1)
C(18)	6158(2)	-1411(2)	5692(2)	37(1)
C(19)	5761(2)	-1351(2)	5545(2)	39(1)
C(20)	5986(2)	-851(2)	5340(2)	34(1)
C(21)	5143(2)	-999(2)	5079(2)	38(1)
C(22)	4856(2)	-1017(2)	5449(2)	42(1)
C(23)	4317(2)	-1308(2)	5441(2)	53(2)
C(24)	4078(2)	-1592(2)	5070(2)	55(2)
C(25)	4352(2)	-1593(2)	4702(2)	48(1)
C(26)	4883(2)	-1293(2)	4706(2)	40(1)
C(27)	4971(2)	-878(3)	6260(2)	65(2)
C(28)	5386(3)	-592(3)	6574(2)	69(2)
C(29)	5263(3)	-673(4)	7062(2)	90(3)
C(30)	5567(3)	-909(3)	6870(2)	71(2)
C(31)	6131(3)	-645(4)	6947(3)	89(2)
C(32)	5311(3)	-1477(4)	6824(3)	91(2)
C(33)	5075(2)	-1245(2)	3903(2)	43(1)
C(34)	5492(2)	-1181(2)	3601(2)	48(1)
C(35)	5394(3)	-1260(2)	3111(2)	59(2)
C(36)	5733(3)	-732(2)	3276(2)	55(1)
C(37)	5539(3)	-357(3)	3253(2)	70(2)
C(38)	6305(3)	-494(3)	3217(3)	82(2)
C(39)	6948(2)	1409(2)	4231(2)	35(1)
C(40)	6896(2)	1300(2)	3783(2)	38(1)
C(41)	6888(2)	1640(2)	3473(2)	46(1)
C(42)	6931(2)	2093(2)	3637(2)	56(2)
C(43)	6983(2)	2220(2)	4080(2)	52(1)
C(44)	6993(2)	1866(2)	4378(2)	42(1)
C(45)	6833(3)	1519(3)	2978(2)	63(2)
C(46)	6987(9)	1125(8)	2856(6)	60(5)
C(47)	6269(7)	1325(10)	2854(6)	70(5)
C(48)	7169(9)	2013(6)	2706(5)	75(5)
C(46X)	6777(8)	983(6)	2868(7)	42(5)
C(47X)	6427(10)	1554(13)	2747(10)	86(9)
C(48X)	7395(8)	1896(10)	2758(9)	84(7)

C(46Y)	7306(14)	1590(17)	2812(14)	98(11)
C(47Y)	6376(16)	961(14)	2942(16)	121(14)
C(48Y)	6676(14)	1869(13)	2739(11)	80(9)
C(49)	7013(3)	2717(3)	4237(3)	79(2)
C(50)	6861(10)	2995(9)	3938(8)	90(7)
C(51)	7458(7)	3011(6)	4524(7)	70(5)
C(52)	6503(6)	2517(6)	4616(6)	76(5)
C(50X)	6604(8)	2768(9)	4096(9)	110(8)
C(51X)	7536(7)	3182(4)	3950(5)	93(6)
C(52X)	7225(7)	2869(6)	4708(5)	67(4)
C(53)	8773(2)	1411(2)	5665(2)	34(1)
C(54)	9224(2)	1468(2)	5465(2)	36(1)
C(55)	9702(2)	1859(2)	5602(2)	44(1)
C(56)	9733(2)	2188(2)	5938(2)	47(1)
C(57)	9297(2)	2141(2)	6141(2)	43(1)
C(58)	8815(2)	1747(2)	6000(2)	36(1)
C(59)	9521(2)	1092(2)	4867(2)	43(1)
C(60)	9287(2)	651(2)	4554(2)	48(1)
C(61)	9578(3)	667(3)	4143(2)	62(2)
C(62)	9506(2)	296(2)	4490(2)	54(1)
C(63)	9111(3)	-263(2)	4409(3)	77(2)
C(64)	9961(3)	376(3)	4759(3)	81(2)
C(65)	8252(2)	2079(2)	6239(2)	40(1)
C(66)	7742(2)	1928(2)	6444(2)	44(1)
C(67)	7626(2)	2349(2)	6567(2)	48(1)
C(68)	7333(2)	2000(2)	6197(2)	55(1)
C(69)	7428(3)	2203(4)	5738(2)	80(2)
C(70)	6780(2)	1591(3)	6299(3)	80(2)
C(71)	7177(2)	-1248(2)	5918(2)	32(1)
C(72)	7382(2)	-1496(2)	5676(2)	35(1)
C(73)	7410(2)	-1909(2)	5860(2)	34(1)
C(74)	7227(2)	-2062(2)	6284(2)	35(1)
C(75)	7015(2)	-1821(2)	6534(2)	34(1)
C(76)	7000(2)	-1406(2)	6343(2)	35(1)
C(77)	7639(2)	-2176(2)	5582(2)	40(1)
C(78)	7325(2)	-2383(2)	5157(2)	48(1)

C(79)	8205(2)	-1787(2)	5468(2)	52(1)
C(80)	7627(2)	-2628(2)	5830(2)	47(1)
C(81)	6797(2)	-2004(2)	6995(2)	42(1)
C(82)	7206(3)	-1692(2)	7343(2)	59(2)
C(83)	6612(2)	-2577(2)	7056(2)	47(1)
C(84)	6328(3)	-1930(3)	7073(2)	66(2)
Fe(2)	3092(1)	9451(1)	5312(1)	32(1)
Cl(2)	3282(1)	9175(1)	5928(1)	51(1)
O(5)	5368(6)	10733(8)	6414(7)	89(6)
O(6)	5490(6)	10979(9)	3846(8)	62(4)
O(5X)	5438(7)	10569(13)	6385(11)	74(6)
O(6X)	5363(10)	10785(12)	3825(12)	55(5)
O(7)	165(2)	8641(2)	5196(2)	62(1)
O(8)	1390(2)	7098(1)	6165(2)	66(1)
N(9)	3595(2)	9468(2)	4849(1)	35(1)
N(10)	2557(2)	8762(2)	5037(1)	35(1)
N(11)	2493(1)	9561(1)	5484(1)	32(1)
N(12)	3554(1)	10240(1)	5360(1)	32(1)
N(13)	4867(2)	10253(2)	5832(2)	50(1)
N(14)	4958(2)	10962(2)	4378(2)	42(1)
N(15)	897(2)	8599(2)	5116(2)	41(1)
N(16)	1682(2)	7947(2)	6129(2)	43(1)
C(85)	4347(2)	10294(2)	5078(2)	38(1)
C(86)	4108(2)	9837(2)	4836(2)	38(1)
C(87)	4377(2)	9685(2)	4526(2)	43(1)
C(88)	4020(2)	9233(2)	4344(2)	44(1)
C(89)	3536(2)	9080(2)	4559(2)	37(1)
C(90)	3096(2)	8598(2)	4522(2)	38(1)
C(91)	2643(2)	8443(2)	4767(2)	37(1)
C(92)	2193(2)	7941(2)	4764(2)	41(1)
C(93)	1840(2)	7952(2)	5030(2)	41(1)
C(94)	2067(2)	8474(2)	5197(2)	36(1)
C(95)	1806(2)	8652(2)	5454(2)	35(1)
C(96)	2000(2)	9170(2)	5571(2)	35(1)
C(97)	1711(2)	9374(2)	5782(2)	38(1)
C(98)	2022(2)	9884(2)	5819(2)	38(1)

C(99)	2515(2)	10004(2)	5645(2)	35(1)
C(100)	2959(2)	10485(2)	5680(2)	36(1)
C(101)	3448(2)	10584(2)	5566(2)	35(1)
C(102)	3918(2)	11063(2)	5649(2)	43(1)
C(103)	4313(2)	10995(2)	5504(2)	46(1)
C(104)	4079(2)	10488(2)	5312(2)	38(1)
C(105)	4922(2)	10596(2)	5097(2)	40(1)
C(106)	5171(2)	10560(2)	5477(2)	46(1)
C(107)	5705(2)	10823(3)	5499(2)	56(2)
C(108)	5984(2)	11132(3)	5151(2)	60(2)
C(109)	5746(2)	11189(2)	4777(2)	52(1)
C(110)	5218(2)	10916(2)	4749(2)	43(1)
C(111)	4978(2)	10336(3)	6269(2)	60(2)
C(112)	4540(3)	10017(3)	6559(2)	71(2)
C(113)	4623(3)	10047(4)	7057(2)	95(3)
C(114)	4342(3)	10288(4)	6867(2)	86(2)
C(115)	3769(4)	10095(10)	6895(4)	81(6)
C(116)	4639(9)	10915(8)	6856(5)	103(5)
C(615)	3746(8)	9825(14)	6946(10)	78(9)
C(616)	4446(16)	10743(15)	6899(14)	89(11)
C(117)	5077(2)	10948(2)	3949(2)	51(1)
C(118)	4702(2)	10955(2)	3633(2)	51(1)
C(119)	4825(3)	11050(3)	3156(2)	65(2)
C(120)	4435(3)	10527(3)	3296(2)	61(2)
C(121)	4577(5)	10117(3)	3271(3)	101(3)
C(122)	3877(3)	10354(4)	3213(3)	96(3)
C(123)	3104(2)	8222(2)	4198(2)	38(1)
C(124)	3192(2)	8354(2)	3756(2)	45(1)
C(125)	3197(2)	8016(2)	3438(2)	50(1)
C(126)	3111(2)	7545(2)	3588(2)	56(2)
C(127)	3017(2)	7393(2)	4027(2)	52(1)
C(128)	3020(2)	7744(2)	4330(2)	42(1)
C(129)	3307(3)	8184(3)	2955(2)	62(2)
C(130)	3037(6)	8462(5)	2782(4)	55(1)
C(131)	3883(5)	8477(5)	2904(4)	68(2)
C(132)	3129(5)	7681(5)	2663(4)	58(1)

C(630)	2827(5)	8222(6)	2792(5)	55(1)
C(631)	3792(5)	8717(5)	2906(4)	58(1)
C(632)	3369(8)	7849(6)	2640(5)	68(2)
C(133)	2934(3)	6874(3)	4185(3)	70(2)
C(134)	2844(6)	6501(4)	3821(4)	87(4)
C(135)	3367(5)	6949(4)	4500(5)	95(5)
C(136)	2429(5)	6605(4)	4477(4)	78(4)
C(634)	2576(15)	6473(15)	3864(12)	118(16)
C(635)	3498(10)	6958(14)	4073(13)	106(12)
C(636)	2852(12)	6778(11)	4651(7)	77(9)
C(137)	1282(2)	8267(2)	5621(2)	37(1)
C(138)	1234(2)	7924(2)	5953(2)	39(1)
C(139)	754(2)	7569(2)	6121(2)	49(1)
C(140)	321(2)	7561(2)	5950(2)	54(1)
C(141)	356(2)	7892(2)	5616(2)	48(1)
C(142)	838(2)	8248(2)	5454(2)	42(1)
C(143)	1737(2)	7536(2)	6227(2)	47(1)
C(144)	2250(2)	7669(2)	6400(2)	53(1)
C(145)	2329(3)	7235(3)	6571(2)	62(2)
C(146)	2594(2)	7505(2)	6160(2)	58(2)
C(147)	3161(3)	7886(3)	6187(4)	102(3)
C(148)	2414(3)	7227(3)	5733(2)	82(2)
C(149)	588(2)	8805(2)	5031(2)	44(1)
C(150)	824(2)	9250(2)	4726(2)	47(1)
C(151)	500(3)	9457(2)	4532(2)	56(2)
C(152)	898(2)	9772(2)	4874(2)	47(1)
C(153)	729(3)	9826(2)	5329(2)	59(2)
C(154)	1388(2)	10240(2)	4717(2)	62(2)
C(155)	2911(2)	10915(2)	5885(2)	34(1)
C(156)	2963(2)	10988(2)	6336(2)	36(1)
C(157)	2939(2)	11392(2)	6540(2)	38(1)
C(158)	2858(2)	11721(2)	6268(2)	38(1)
C(159)	2806(2)	11661(2)	5812(2)	37(1)
C(160)	2836(2)	11253(2)	5621(2)	37(1)
C(161)	2987(2)	11448(2)	7037(2)	50(1)
C(162)	3406(10)	11362(12)	7217(9)	73(5)

C(163)	2453(9)	11038(8)	7218(9)	83(6)
C(164)	3072(11)	11968(7)	7193(16)	45(3)
C(662)	3531(12)	11530(20)	7139(18)	73(5)
C(663)	2599(19)	10986(16)	7308(15)	83(6)
C(664)	3000(30)	11933(16)	7210(30)	45(3)
C(165)	2702(2)	12014(2)	5514(2)	43(1)
C(166)	2150(2)	11692(3)	5337(2)	58(1)
C(167)	2747(3)	12475(3)	5777(2)	68(2)
C(168)	3083(2)	12218(2)	5135(2)	55(1)
C(1S)	5640(13)	11913(14)	6211(11)	85(9)
Cl(1S)	5836(4)	12066(4)	5735(4)	109(3)
Cl(2S)	5130(5)	11994(5)	6347(4)	130(4)
Cl(3S)	6117(6)	12168(6)	6632(5)	144(4)

Table S3. Bond lengths [Å] and angles [º] for C84H96ClFeN8O4 ([Fe(P2)Cl])

Fe(1)-N(1)	2.043(4)
Fe(1)-N(2)	2.049(4)
Fe(1)-N(4)	2.051(4)
Fe(1)-N(3)	2.061(4)
Fe(1)-Cl(1)	2.2234(15)
O(1)-C(27)	1.225(10)
O(2)-C(33)	1.218(6)
O(3)-C(59)	1.201(6)
O(4)-C(65)	1.216(6)
N(1)-C(2)	1.386(6)
N(1)-C(5)	1.395(6)
N(2)-C(7)	1.377(6)
N(2)-C(10)	1.382(6)
N(3)-C(12)	1.371(6)
N(3)-C(15)	1.372(6)
N(4)-C(17)	1.368(6)
N(4)-C(20)	1.377(6)
N(5)-C(27)	1.364(8)
N(5)-C(22)	1.408(7)
N(5)-H(5N)	0.8800
N(6)-C(33)	1.368(7)
N(6)-C(26)	1.419(7)
N(6)-H(6N)	0.8800
N(7)-C(59)	1.374(6)
N(7)-C(54)	1.413(6)
N(7)-H(7N)	0.8800
N(8)-C(65)	1.358(7)
N(8)-C(58)	1.431(6)
N(8)-H(8N)	0.8800
C(1)-C(20)	1.395(7)
C(1)-C(2)	1.396(7)
C(1)-C(21)	1.495(7)
C(2)-C(3)	1.432(7)
C(3)-C(4)	1.353(7)

C(3)-H(3)	0.9500
C(4)-C(5)	1.437(7)
C(4)-H(4)	0.9500
C(5)-C(6)	1.393(7)
C(6)-C(7)	1.400(7)
C(6)-C(39)	1.500(6)
C(7)-C(8)	1.434(7)
C(8)-C(9)	1.354(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.432(7)
C(9)-H(9)	0.9500
C(10)-C(11)	1.399(7)
C(11)-C(12)	1.396(6)
C(11)-C(53)	1.503(6)
C(12)-C(13)	1.432(7)
C(13)-C(14)	1.348(7)
C(13)-H(13)	0.9500
C(14)-C(15)	1.434(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.400(7)
C(16)-C(17)	1.398(7)
C(16)-C(71)	1.491(6)
C(17)-C(18)	1.445(6)
C(18)-C(19)	1.365(7)
C(18)-H(18)	0.9500
C(19)-C(20)	1.441(7)
C(19)-H(19)	0.9500
C(21)-C(22)	1.393(7)
C(21)-C(26)	1.406(7)
C(22)-C(23)	1.401(7)
C(23)-C(24)	1.375(9)
C(23)-H(23)	0.9500
C(24)-C(25)	1.385(8)
C(24)-H(24)	0.9500
C(25)-C(26)	1.383(7)
C(25)-H(25)	0.9500

C(27)-C(28)	1.458(9)
C(28)-C(29)	1.512(10)
C(28)-C(30)	1.584(10)
C(28)-H(28)	1.0000
C(29)-C(30)	1.521(11)
C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(30)-C(31)	1.484(10)
C(30)-C(32)	1.485(12)
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(34)	1.482(8)
C(34)-C(35)	1.507(9)
C(34)-C(36)	1.528(8)
C(34)-H(34)	1.0000
C(35)-C(36)	1.477(9)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-C(38)	1.501(9)
C(36)-C(37)	1.504(8)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-C(44)	1.382(7)
C(39)-C(40)	1.384(7)
C(40)-C(41)	1.395(7)
C(40)-H(40)	0.9500
C(41)-C(42)	1.390(8)
C(41)-C(45)	1.531(8)

C(42)-C(43)	1.382(9)
C(42)-H(42)	0.9500
C(43)-C(44)	1.404(7)
C(43)-C(49)	1.522(8)
C(44)-H(44)	0.9500
C(45)-C(46)	1.513(15)
C(45)-C(47)	1.535(16)
C(45)-C(48)	1.547(15)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-C(50)	1.451(16)
C(49)-C(51)	1.462(17)
C(49)-C(52)	1.760(17)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-C(58)	1.389(7)
C(53)-C(54)	1.410(7)
C(54)-C(55)	1.386(7)
C(55)-C(56)	1.385(7)
C(55)-H(55)	0.9500
C(56)-C(57)	1.386(7)
C(56)-H(56)	0.9500

C(57)-C(58)	1.401(7)
C(57)-H(57)	0.9500
C(59)-C(60)	1.485(7)
C(60)-C(61)	1.508(8)
C(60)-C(62)	1.521(8)
C(60)-H(60)	1.0000
C(61)-C(62)	1.464(9)
C(61)-H(61A)	0.9900
C(61)-H(61B)	0.9900
C(62)-C(64)	1.501(9)
C(62)-C(63)	1.511(8)
C(63)-H(63A)	0.9800
C(63)-H(63B)	0.9800
C(63)-H(63C)	0.9800
C(64)-H(64A)	0.9800
C(64)-H(64B)	0.9800
C(64)-H(64C)	0.9800
C(65)-C(66)	1.495(7)
C(66)-C(67)	1.515(7)
C(66)-C(68)	1.544(8)
C(66)-H(66)	1.0000
C(67)-C(68)	1.486(8)
C(67)-H(67A)	0.9900
C(67)-H(67B)	0.9900
C(68)-C(69)	1.486(10)
C(68)-C(70)	1.520(9)
C(69)-H(69A)	0.9800
C(69)-H(69B)	0.9800
C(69)-H(69C)	0.9800
C(70)-H(70A)	0.9800
C(70)-H(70B)	0.9800
C(70)-H(70C)	0.9800
C(71)-C(76)	1.382(7)
C(71)-C(72)	1.386(7)
C(72)-C(73)	1.402(7)
C(72)-H(72)	0.9500

C(73)-C(74)	1.381(7)
C(73)-C(77)	1.537(7)
C(74)-C(75)	1.396(7)
C(74)-H(74)	0.9500
C(75)-C(76)	1.395(7)
C(75)-C(81)	1.524(7)
C(76)-H(76)	0.9500
C(77)-C(78)	1.531(7)
C(77)-C(80)	1.534(7)
C(77)-C(79)	1.542(7)
C(78)-H(78A)	0.9800
C(78)-H(78B)	0.9800
C(78)-H(78C)	0.9800
C(79)-H(79A)	0.9800
C(79)-H(79B)	0.9800
C(79)-H(79C)	0.9800
C(80)-H(80A)	0.9800
C(80)-H(80B)	0.9800
C(80)-H(80C)	0.9800
C(81)-C(82)	1.530(8)
C(81)-C(83)	1.530(7)
C(81)-C(84)	1.547(8)
C(82)-H(82A)	0.9800
C(82)-H(82B)	0.9800
C(82)-H(82C)	0.9800
C(83)-H(83A)	0.9800
C(83)-H(83B)	0.9800
C(83)-H(83C)	0.9800
C(84)-H(84A)	0.9800
C(84)-H(84B)	0.9800
C(84)-H(84C)	0.9800
Fe(2)-N(9)	2.039(4)
Fe(2)-N(11)	2.050(4)
Fe(2)-N(10)	2.056(4)
Fe(2)-N(12)	2.063(4)
Fe(2)-Cl(2)	2.2254(15)

O(5)-C(111)	1.259(13)
O(6)-C(117)	1.234(12)
O(7)-C(149)	1.214(7)
O(8)-C(143)	1.215(7)
N(9)-C(86)	1.373(6)
N(9)-C(89)	1.398(6)
N(10)-C(94)	1.366(6)
N(10)-C(91)	1.377(6)
N(11)-C(96)	1.379(6)
N(11)-C(99)	1.385(6)
N(12)-C(104)	1.371(6)
N(12)-C(101)	1.373(6)
N(13)-C(111)	1.355(8)
N(13)-C(106)	1.413(7)
N(13)-H(13N)	0.8800
N(14)-C(117)	1.353(7)
N(14)-C(110)	1.413(7)
N(14)-H(14N)	0.8800
N(15)-C(149)	1.372(7)
N(15)-C(142)	1.416(7)
N(15)-H(15N)	0.8800
N(16)-C(143)	1.357(7)
N(16)-C(138)	1.414(7)
N(16)-H(16N)	0.8800
C(85)-C(86)	1.395(7)
C(85)-C(104)	1.398(7)
C(85)-C(105)	1.495(7)
C(86)-C(87)	1.450(7)
C(87)-C(88)	1.355(8)
C(87)-H(87)	0.9500
C(88)-C(89)	1.441(7)
C(88)-H(88)	0.9500
C(89)-C(90)	1.392(7)
C(90)-C(91)	1.406(7)
C(90)-C(123)	1.502(7)
C(91)-C(92)	1.434(7)

C(92)-C(93)	1.345(7)
C(92)-H(92)	0.9500
C(93)-C(94)	1.449(7)
C(93)-H(93)	0.9500
C(94)-C(95)	1.388(7)
C(95)-C(96)	1.402(7)
C(95)-C(137)	1.499(7)
C(96)-C(97)	1.437(7)
C(97)-C(98)	1.341(7)
C(97)-H(97)	0.9500
C(98)-C(99)	1.434(7)
C(98)-H(98)	0.9500
C(99)-C(100)	1.395(7)
C(100)-C(101)	1.386(7)
C(100)-C(155)	1.502(6)
C(101)-C(102)	1.443(7)
C(102)-C(103)	1.369(7)
C(102)-H(102)	0.9500
C(103)-C(104)	1.442(7)
C(103)-H(103)	0.9500
C(105)-C(110)	1.403(8)
C(105)-C(106)	1.403(8)
C(106)-C(107)	1.388(8)
C(107)-C(108)	1.376(9)
C(107)-H(107)	0.9500
C(108)-C(109)	1.392(9)
C(108)-H(108)	0.9500
C(109)-C(110)	1.374(8)
C(109)-H(109)	0.9500
C(111)-C(112)	1.469(9)
C(112)-C(113)	1.523(10)
C(112)-C(114)	1.538(11)
C(112)-H(112)	1.0000
C(113)-C(114)	1.474(12)
C(113)-H(11A)	0.9900
C(113)-H(11B)	0.9900

C(114)-C(115)	1.516(13)
C(114)-C(116)	1.63(2)
C(115)-H(11C)	0.9800
C(115)-H(11D)	0.9800
C(115)-H(11E)	0.9800
C(116)-H(11F)	0.9800
C(116)-H(11G)	0.9800
C(116)-H(11H)	0.9800
C(117)-C(118)	1.483(8)
C(118)-C(119)	1.484(9)
C(118)-C(120)	1.519(9)
C(118)-H(118)	1.0000
C(119)-C(120)	1.475(9)
C(119)-H(11I)	0.9900
C(119)-H(11J)	0.9900
C(120)-C(121)	1.490(10)
C(120)-C(122)	1.505(11)
C(121)-H(12A)	0.9800
C(121)-H(12B)	0.9800
C(121)-H(12C)	0.9800
C(122)-H(12D)	0.9800
C(122)-H(12E)	0.9800
C(122)-H(12F)	0.9800
C(123)-C(124)	1.381(8)
C(123)-C(128)	1.384(7)
C(124)-C(125)	1.403(7)
C(124)-H(124)	0.9500
C(125)-C(126)	1.380(9)
C(125)-C(129)	1.528(9)
C(126)-C(127)	1.386(9)
C(126)-H(126)	0.9500
C(127)-C(128)	1.395(7)
C(127)-C(133)	1.524(9)
C(128)-H(128)	0.9500
C(129)-C(131)	1.503(14)
C(129)-C(130)	1.514(12)

C(129)-C(132)	1.592(13)
C(130)-H(13A)	0.9800
C(130)-H(13B)	0.9800
C(130)-H(13C)	0.9800
C(131)-H(13D)	0.9800
C(131)-H(13E)	0.9800
C(131)-H(13F)	0.9800
C(132)-H(13G)	0.9800
C(132)-H(13H)	0.9800
C(132)-H(13I)	0.9800
C(133)-C(134)	1.494(10)
C(133)-C(135)	1.533(13)
C(133)-C(136)	1.581(12)
C(134)-H(13J)	0.9800
C(134)-H(13K)	0.9800
C(134)-H(13L)	0.9800
C(135)-H(13M)	0.9800
C(135)-H(13O)	0.9800
C(135)-H(13P)	0.9800
C(136)-H(13Q)	0.9800
C(136)-H(13R)	0.9800
C(136)-H(13S)	0.9800
C(137)-C(138)	1.393(7)
C(137)-C(142)	1.397(7)
C(138)-C(139)	1.390(7)
C(139)-C(140)	1.386(8)
C(139)-H(139)	0.9500
C(140)-C(141)	1.382(8)
C(140)-H(140)	0.9500
C(141)-C(142)	1.388(7)
C(141)-H(141)	0.9500
C(143)-C(144)	1.477(8)
C(144)-C(145)	1.527(8)
C(144)-C(146)	1.529(9)
C(144)-H(144)	1.0000
C(145)-C(146)	1.480(9)

C(145)-H(14A)	0.9900
C(145)-H(14B)	0.9900
C(146)-C(148)	1.485(10)
C(146)-C(147)	1.504(10)
C(147)-H(14C)	0.9800
C(147)-H(14D)	0.9800
C(147)-H(14E)	0.9800
C(148)-H(14F)	0.9800
C(148)-H(14G)	0.9800
C(148)-H(14H)	0.9800
C(149)-C(150)	1.479(8)
C(150)-C(151)	1.510(8)
C(150)-C(152)	1.534(7)
C(150)-H(150)	1.0000
C(151)-C(152)	1.504(8)
C(151)-H(15A)	0.9900
C(151)-H(15B)	0.9900
C(152)-C(153)	1.503(8)
C(152)-C(154)	1.515(8)
C(153)-H(15C)	0.9800
C(153)-H(15D)	0.9800
C(153)-H(15E)	0.9800
C(154)-H(15F)	0.9800
C(154)-H(15G)	0.9800
C(154)-H(15H)	0.9800
C(155)-C(156)	1.378(7)
C(155)-C(160)	1.393(7)
C(156)-C(157)	1.395(6)
C(156)-H(156)	0.9500
C(157)-C(158)	1.395(7)
C(157)-C(161)	1.514(8)
C(158)-C(159)	1.390(7)
C(158)-H(158)	0.9500
C(159)-C(160)	1.395(7)
C(159)-C(165)	1.537(7)
C(160)-H(160)	0.9500

C(161)-C(162)	1.503(13)
C(161)-C(164)	1.524(12)
C(161)-C(163)	1.552(13)
C(162)-H(16A)	0.9800
C(162)-H(16B)	0.9800
C(162)-H(16C)	0.9800
C(163)-H(16D)	0.9800
C(163)-H(16E)	0.9800
C(163)-H(16F)	0.9800
C(164)-H(16G)	0.9800
C(164)-H(16H)	0.9800
C(164)-H(16I)	0.9800
C(165)-C(168)	1.516(8)
C(165)-C(166)	1.535(8)
C(165)-C(167)	1.541(8)
C(166)-H(16J)	0.9800
C(166)-H(16K)	0.9800
C(166)-H(16L)	0.9800
C(167)-H(16M)	0.9800
C(167)-H(16O)	0.9800
C(167)-H(16P)	0.9800
C(168)-H(16Q)	0.9800
C(168)-H(16R)	0.9800
C(168)-H(16S)	0.9800
C(1S)-Cl(1S)	1.54(4)
C(1S)-Cl(2S)	1.71(4)
C(1S)-Cl(3S)	1.78(4)
C(1S)-H(1S)	1.0000

N(1)-Fe(1)-N(2)	86.67(15)
N(1)-Fe(1)-N(4)	87.17(15)
N(2)-Fe(1)-N(4)	157.20(16)
N(1)-Fe(1)-N(3)	148.95(15)
N(2)-Fe(1)-N(3)	87.08(15)
N(4)-Fe(1)-N(3)	86.94(15)
N(1)-Fe(1)-Cl(1)	106.48(12)

N(2)-Fe(1)-Cl(1)	103.34(12)
N(4)-Fe(1)-Cl(1)	99.46(12)
N(3)-Fe(1)-Cl(1)	104.56(11)
C(2)-N(1)-C(5)	105.4(4)
C(2)-N(1)-Fe(1)	124.4(3)
C(5)-N(1)-Fe(1)	128.9(3)
C(7)-N(2)-C(10)	105.9(4)
C(7)-N(2)-Fe(1)	128.0(3)
C(10)-N(2)-Fe(1)	123.7(3)
C(12)-N(3)-C(15)	105.8(4)
C(12)-N(3)-Fe(1)	124.4(3)
C(15)-N(3)-Fe(1)	127.9(3)
C(17)-N(4)-C(20)	106.2(4)
C(17)-N(4)-Fe(1)	127.8(3)
C(20)-N(4)-Fe(1)	122.9(3)
C(27)-N(5)-C(22)	127.4(5)
C(27)-N(5)-H(5N)	116.3
C(22)-N(5)-H(5N)	116.3
C(33)-N(6)-C(26)	126.1(4)
C(33)-N(6)-H(6N)	117.0
C(26)-N(6)-H(6N)	117.0
C(59)-N(7)-C(54)	129.4(4)
C(59)-N(7)-H(7N)	115.3
C(54)-N(7)-H(7N)	115.3
C(65)-N(8)-C(58)	123.5(4)
C(65)-N(8)-H(8N)	118.2
C(58)-N(8)-H(8N)	118.2
C(20)-C(1)-C(2)	123.8(4)
C(20)-C(1)-C(21)	117.3(4)
C(2)-C(1)-C(21)	118.9(4)
N(1)-C(2)-C(1)	125.6(4)
N(1)-C(2)-C(3)	109.9(4)
C(1)-C(2)-C(3)	124.5(4)
C(4)-C(3)-C(2)	107.7(4)
C(4)-C(3)-H(3)	126.2
C(2)-C(3)-H(3)	126.2

C(3)-C(4)-C(5)	107.1(4)
C(3)-C(4)-H(4)	126.4
C(5)-C(4)-H(4)	126.4
C(6)-C(5)-N(1)	124.7(4)
C(6)-C(5)-C(4)	125.2(4)
N(1)-C(5)-C(4)	109.7(4)
C(5)-C(6)-C(7)	124.2(4)
C(5)-C(6)-C(39)	117.8(4)
C(7)-C(6)-C(39)	118.0(4)
N(2)-C(7)-C(6)	124.7(4)
N(2)-C(7)-C(8)	109.6(4)
C(6)-C(7)-C(8)	125.7(4)
C(9)-C(8)-C(7)	107.7(4)
C(9)-C(8)-H(8)	126.2
C(7)-C(8)-H(8)	126.2
C(8)-C(9)-C(10)	106.7(4)
C(8)-C(9)-H(9)	126.6
C(10)-C(9)-H(9)	126.6
N(2)-C(10)-C(11)	125.0(4)
N(2)-C(10)-C(9)	110.1(4)
C(11)-C(10)-C(9)	124.7(4)
C(12)-C(11)-C(10)	124.3(4)
C(12)-C(11)-C(53)	119.3(4)
C(10)-C(11)-C(53)	116.4(4)
N(3)-C(12)-C(11)	125.5(4)
N(3)-C(12)-C(13)	109.9(4)
C(11)-C(12)-C(13)	124.5(4)
C(14)-C(13)-C(12)	107.4(4)
C(14)-C(13)-H(13)	126.3
C(12)-C(13)-H(13)	126.3
C(13)-C(14)-C(15)	106.7(4)
C(13)-C(14)-H(14)	126.7
C(15)-C(14)-H(14)	126.7
N(3)-C(15)-C(16)	125.6(4)
N(3)-C(15)-C(14)	110.2(4)
C(16)-C(15)-C(14)	123.7(4)

C(17)-C(16)-C(15)	124.1(4)
C(17)-C(16)-C(71)	117.9(4)
C(15)-C(16)-C(71)	117.9(4)
N(4)-C(17)-C(16)	124.9(4)
N(4)-C(17)-C(18)	110.3(4)
C(16)-C(17)-C(18)	124.8(4)
C(19)-C(18)-C(17)	106.4(4)
C(19)-C(18)-H(18)	126.8
C(17)-C(18)-H(18)	126.8
C(18)-C(19)-C(20)	106.9(4)
C(18)-C(19)-H(19)	126.5
C(20)-C(19)-H(19)	126.5
N(4)-C(20)-C(1)	124.9(4)
N(4)-C(20)-C(19)	109.9(4)
C(1)-C(20)-C(19)	124.9(4)
C(22)-C(21)-C(26)	118.9(5)
C(22)-C(21)-C(1)	119.7(5)
C(26)-C(21)-C(1)	121.5(5)
C(21)-C(22)-C(23)	120.5(5)
C(21)-C(22)-N(5)	119.0(5)
C(23)-C(22)-N(5)	120.5(5)
C(24)-C(23)-C(22)	118.8(5)
C(24)-C(23)-H(23)	120.6
C(22)-C(23)-H(23)	120.6
C(23)-C(24)-C(25)	122.0(5)
C(23)-C(24)-H(24)	119.0
C(25)-C(24)-H(24)	119.0
C(26)-C(25)-C(24)	119.0(5)
C(26)-C(25)-H(25)	120.5
C(24)-C(25)-H(25)	120.5
C(25)-C(26)-C(21)	120.7(5)
C(25)-C(26)-N(6)	121.0(5)
C(21)-C(26)-N(6)	118.2(4)
O(1)-C(27)-N(5)	123.0(8)
O(1)-C(27)-C(28)	123.8(8)
N(5)-C(27)-C(28)	113.2(6)

C(27)-C(28)-C(29)	118.4(7)
C(27)-C(28)-C(30)	117.6(7)
C(29)-C(28)-C(30)	58.8(5)
C(27)-C(28)-H(28)	116.5
C(29)-C(28)-H(28)	116.5
C(30)-C(28)-H(28)	116.5
C(28)-C(29)-C(30)	63.0(5)
C(28)-C(29)-H(29A)	117.5
C(30)-C(29)-H(29A)	117.5
C(28)-C(29)-H(29B)	117.5
C(30)-C(29)-H(29B)	117.5
H(29A)-C(29)-H(29B)	114.5
C(31)-C(30)-C(32)	115.1(7)
C(31)-C(30)-C(29)	118.6(7)
C(32)-C(30)-C(29)	119.0(7)
C(31)-C(30)-C(28)	114.1(7)
C(32)-C(30)-C(28)	120.1(6)
C(29)-C(30)-C(28)	58.2(5)
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
O(2)-C(33)-N(6)	122.3(5)
O(2)-C(33)-C(34)	124.8(5)
N(6)-C(33)-C(34)	112.8(5)
C(33)-C(34)-C(35)	120.1(5)
C(33)-C(34)-C(36)	120.6(5)
C(35)-C(34)-C(36)	58.2(4)

C(33)-C(34)-H(34)	115.3
C(35)-C(34)-H(34)	115.3
C(36)-C(34)-H(34)	115.3
C(36)-C(35)-C(34)	61.6(4)
C(36)-C(35)-H(35A)	117.6
C(34)-C(35)-H(35A)	117.6
C(36)-C(35)-H(35B)	117.6
C(34)-C(35)-H(35B)	117.6
H(35A)-C(35)-H(35B)	114.7
C(35)-C(36)-C(38)	118.6(6)
C(35)-C(36)-C(37)	118.0(6)
C(38)-C(36)-C(37)	114.6(6)
C(35)-C(36)-C(34)	60.2(4)
C(38)-C(36)-C(34)	114.9(5)
C(37)-C(36)-C(34)	119.9(5)
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(44)-C(39)-C(40)	119.6(5)
C(44)-C(39)-C(6)	120.5(5)
C(40)-C(39)-C(6)	119.9(4)
C(39)-C(40)-C(41)	121.7(5)
C(39)-C(40)-H(40)	119.1
C(41)-C(40)-H(40)	119.1
C(42)-C(41)-C(40)	116.6(5)
C(42)-C(41)-C(45)	121.8(5)
C(40)-C(41)-C(45)	121.6(5)

C(43)-C(42)-C(41)	123.9(5)
C(43)-C(42)-H(42)	118.0
C(41)-C(42)-H(42)	118.0
C(42)-C(43)-C(44)	117.1(5)
C(42)-C(43)-C(49)	121.1(5)
C(44)-C(43)-C(49)	121.8(5)
C(39)-C(44)-C(43)	121.0(5)
C(39)-C(44)-H(44)	119.5
C(43)-C(44)-H(44)	119.5
C(46)-C(45)-C(41)	112.6(8)
C(46)-C(45)-C(47)	110.7(12)
C(41)-C(45)-C(47)	107.2(8)
C(46)-C(45)-C(48)	108.1(12)
C(41)-C(45)-C(48)	110.6(8)
C(47)-C(45)-C(48)	107.5(13)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(45)-C(47)-H(47A)	109.5
C(45)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(45)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(45)-C(48)-H(48A)	109.5
C(45)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(45)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(50)-C(49)-C(51)	118.6(13)
C(50)-C(49)-C(43)	119.1(12)
C(51)-C(49)-C(43)	111.5(9)

C(50)-C(49)-C(52)	97.6(13)
C(51)-C(49)-C(52)	101.1(11)
C(43)-C(49)-C(52)	104.7(7)
C(49)-C(50)-H(50A)	109.5
C(49)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(49)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(49)-C(51)-H(51A)	109.5
C(49)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(49)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(49)-C(52)-H(52A)	109.5
C(49)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(49)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(58)-C(53)-C(54)	119.4(4)
C(58)-C(53)-C(11)	119.2(4)
C(54)-C(53)-C(11)	121.3(4)
C(55)-C(54)-C(53)	119.8(5)
C(55)-C(54)-N(7)	123.3(4)
C(53)-C(54)-N(7)	116.8(4)
C(56)-C(55)-C(54)	119.5(5)
C(56)-C(55)-H(55)	120.2
C(54)-C(55)-H(55)	120.2
C(55)-C(56)-C(57)	122.0(5)
C(55)-C(56)-H(56)	119.0
C(57)-C(56)-H(56)	119.0
C(56)-C(57)-C(58)	118.2(5)
C(56)-C(57)-H(57)	120.9
C(58)-C(57)-H(57)	120.9

C(53)-C(58)-C(57)	120.9(4)
C(53)-C(58)-N(8)	119.6(4)
C(57)-C(58)-N(8)	119.5(4)
O(3)-C(59)-N(7)	123.1(5)
O(3)-C(59)-C(60)	124.8(5)
N(7)-C(59)-C(60)	112.1(4)
C(59)-C(60)-C(61)	119.3(5)
C(59)-C(60)-C(62)	121.8(5)
C(61)-C(60)-C(62)	57.8(4)
C(59)-C(60)-H(60)	115.3
C(61)-C(60)-H(60)	115.3
C(62)-C(60)-H(60)	115.3
C(62)-C(61)-C(60)	61.5(4)
C(62)-C(61)-H(61A)	117.6
C(60)-C(61)-H(61A)	117.6
C(62)-C(61)-H(61B)	117.6
C(60)-C(61)-H(61B)	117.6
H(61A)-C(61)-H(61B)	114.7
C(61)-C(62)-C(64)	119.3(6)
C(61)-C(62)-C(63)	117.6(6)
C(64)-C(62)-C(63)	114.3(6)
C(61)-C(62)-C(60)	60.6(4)
C(64)-C(62)-C(60)	119.7(5)
C(63)-C(62)-C(60)	115.0(5)
C(62)-C(63)-H(63A)	109.5
C(62)-C(63)-H(63B)	109.5
H(63A)-C(63)-H(63B)	109.5
C(62)-C(63)-H(63C)	109.5
H(63A)-C(63)-H(63C)	109.5
H(63B)-C(63)-H(63C)	109.5
C(62)-C(64)-H(64A)	109.5
C(62)-C(64)-H(64B)	109.5
H(64A)-C(64)-H(64B)	109.5
C(62)-C(64)-H(64C)	109.5
H(64A)-C(64)-H(64C)	109.5
H(64B)-C(64)-H(64C)	109.5

O(4)-C(65)-N(8)	121.4(5)
O(4)-C(65)-C(66)	123.9(5)
N(8)-C(65)-C(66)	114.6(4)
C(65)-C(66)-C(67)	118.5(5)
C(65)-C(66)-C(68)	121.4(5)
C(67)-C(66)-C(68)	58.1(4)
C(65)-C(66)-H(66)	115.6
C(67)-C(66)-H(66)	115.6
C(68)-C(66)-H(66)	115.6
C(68)-C(67)-C(66)	61.9(4)
C(68)-C(67)-H(67A)	117.6
C(66)-C(67)-H(67A)	117.6
C(68)-C(67)-H(67B)	117.6
C(66)-C(67)-H(67B)	117.6
H(67A)-C(67)-H(67B)	114.7
C(67)-C(68)-C(69)	119.5(6)
C(67)-C(68)-C(70)	115.8(6)
C(69)-C(68)-C(70)	115.5(6)
C(67)-C(68)-C(66)	60.0(4)
C(69)-C(68)-C(66)	120.6(5)
C(70)-C(68)-C(66)	114.2(6)
C(68)-C(69)-H(69A)	109.5
C(68)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(68)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5
C(68)-C(70)-H(70A)	109.5
C(68)-C(70)-H(70B)	109.5
H(70A)-C(70)-H(70B)	109.5
C(68)-C(70)-H(70C)	109.5
H(70A)-C(70)-H(70C)	109.5
H(70B)-C(70)-H(70C)	109.5
C(76)-C(71)-C(72)	120.4(4)
C(76)-C(71)-C(16)	118.5(4)
C(72)-C(71)-C(16)	121.0(4)

C(71)-C(72)-C(73)	120.2(5)
C(71)-C(72)-H(72)	119.9
C(73)-C(72)-H(72)	119.9
C(74)-C(73)-C(72)	118.2(4)
C(74)-C(73)-C(77)	123.0(4)
C(72)-C(73)-C(77)	118.8(4)
C(73)-C(74)-C(75)	122.7(4)
C(73)-C(74)-H(74)	118.6
C(75)-C(74)-H(74)	118.6
C(76)-C(75)-C(74)	117.6(4)
C(76)-C(75)-C(81)	120.1(4)
C(74)-C(75)-C(81)	122.2(4)
C(71)-C(76)-C(75)	120.8(4)
C(71)-C(76)-H(76)	119.6
C(75)-C(76)-H(76)	119.6
C(78)-C(77)-C(80)	108.3(4)
C(78)-C(77)-C(73)	109.2(4)
C(80)-C(77)-C(73)	111.8(4)
C(78)-C(77)-C(79)	109.8(5)
C(80)-C(77)-C(79)	108.0(4)
C(73)-C(77)-C(79)	109.6(4)
C(77)-C(78)-H(78A)	109.5
C(77)-C(78)-H(78B)	109.5
H(78A)-C(78)-H(78B)	109.5
C(77)-C(78)-H(78C)	109.5
H(78A)-C(78)-H(78C)	109.5
H(78B)-C(78)-H(78C)	109.5
C(77)-C(79)-H(79A)	109.5
C(77)-C(79)-H(79B)	109.5
H(79A)-C(79)-H(79B)	109.5
C(77)-C(79)-H(79C)	109.5
H(79A)-C(79)-H(79C)	109.5
H(79B)-C(79)-H(79C)	109.5
C(77)-C(80)-H(80A)	109.5
C(77)-C(80)-H(80B)	109.5
H(80A)-C(80)-H(80B)	109.5

C(77)-C(80)-H(80C)	109.5
H(80A)-C(80)-H(80C)	109.5
H(80B)-C(80)-H(80C)	109.5
C(75)-C(81)-C(82)	110.0(5)
C(75)-C(81)-C(83)	111.3(4)
C(82)-C(81)-C(83)	109.6(5)
C(75)-C(81)-C(84)	110.2(4)
C(82)-C(81)-C(84)	108.5(5)
C(83)-C(81)-C(84)	107.3(4)
C(81)-C(82)-H(82A)	109.5
C(81)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5
C(81)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5
C(81)-C(83)-H(83A)	109.5
C(81)-C(83)-H(83B)	109.5
H(83A)-C(83)-H(83B)	109.5
C(81)-C(83)-H(83C)	109.5
H(83A)-C(83)-H(83C)	109.5
H(83B)-C(83)-H(83C)	109.5
C(81)-C(84)-H(84A)	109.5
C(81)-C(84)-H(84B)	109.5
H(84A)-C(84)-H(84B)	109.5
C(81)-C(84)-H(84C)	109.5
H(84A)-C(84)-H(84C)	109.5
H(84B)-C(84)-H(84C)	109.5
N(9)-Fe(2)-N(11)	150.07(16)
N(9)-Fe(2)-N(10)	86.78(16)
N(11)-Fe(2)-N(10)	87.57(15)
N(9)-Fe(2)-N(12)	87.41(15)
N(11)-Fe(2)-N(12)	86.40(15)
N(10)-Fe(2)-N(12)	156.94(16)
N(9)-Fe(2)-Cl(2)	105.19(12)
N(11)-Fe(2)-Cl(2)	104.73(12)
N(10)-Fe(2)-Cl(2)	100.46(12)

N(12)-Fe(2)-Cl(2)	102.60(12)
C(86)-N(9)-C(89)	105.9(4)
C(86)-N(9)-Fe(2)	123.9(3)
C(89)-N(9)-Fe(2)	128.8(3)
C(94)-N(10)-C(91)	106.7(4)
C(94)-N(10)-Fe(2)	123.0(3)
C(91)-N(10)-Fe(2)	127.9(3)
C(96)-N(11)-C(99)	105.4(4)
C(96)-N(11)-Fe(2)	124.4(3)
C(99)-N(11)-Fe(2)	128.3(3)
C(104)-N(12)-C(101)	105.9(4)
C(104)-N(12)-Fe(2)	123.0(3)
C(101)-N(12)-Fe(2)	128.3(3)
C(111)-N(13)-C(106)	127.1(5)
C(111)-N(13)-H(13N)	116.5
C(106)-N(13)-H(13N)	116.5
C(117)-N(14)-C(110)	126.2(4)
C(117)-N(14)-H(14N)	116.9
C(110)-N(14)-H(14N)	116.9
C(149)-N(15)-C(142)	127.5(5)
C(149)-N(15)-H(15N)	116.3
C(142)-N(15)-H(15N)	116.3
C(143)-N(16)-C(138)	125.6(4)
C(143)-N(16)-H(16N)	117.2
C(138)-N(16)-H(16N)	117.2
C(86)-C(85)-C(104)	123.7(5)
C(86)-C(85)-C(105)	119.1(4)
C(104)-C(85)-C(105)	117.2(4)
N(9)-C(86)-C(85)	126.3(4)
N(9)-C(86)-C(87)	110.0(4)
C(85)-C(86)-C(87)	123.6(5)
C(88)-C(87)-C(86)	107.0(5)
C(88)-C(87)-H(87)	126.5
C(86)-C(87)-H(87)	126.5
C(87)-C(88)-C(89)	107.4(5)
C(87)-C(88)-H(88)	126.3

C(89)-C(88)-H(88)	126.3
C(90)-C(89)-N(9)	125.1(4)
C(90)-C(89)-C(88)	125.1(4)
N(9)-C(89)-C(88)	109.4(4)
C(89)-C(90)-C(91)	124.0(4)
C(89)-C(90)-C(123)	117.9(4)
C(91)-C(90)-C(123)	118.1(4)
N(10)-C(91)-C(90)	124.7(4)
N(10)-C(91)-C(92)	109.1(4)
C(90)-C(91)-C(92)	126.1(4)
C(93)-C(92)-C(91)	108.0(4)
C(93)-C(92)-H(92)	126.0
C(91)-C(92)-H(92)	126.0
C(92)-C(93)-C(94)	106.6(5)
C(92)-C(93)-H(93)	126.7
C(94)-C(93)-H(93)	126.7
N(10)-C(94)-C(95)	126.1(4)
N(10)-C(94)-C(93)	109.6(4)
C(95)-C(94)-C(93)	124.1(5)
C(94)-C(95)-C(96)	124.5(5)
C(94)-C(95)-C(137)	117.9(4)
C(96)-C(95)-C(137)	117.5(4)
N(11)-C(96)-C(95)	124.7(4)
N(11)-C(96)-C(97)	109.9(4)
C(95)-C(96)-C(97)	125.4(4)
C(98)-C(97)-C(96)	107.4(4)
C(98)-C(97)-H(97)	126.3
C(96)-C(97)-H(97)	126.3
C(97)-C(98)-C(99)	107.3(4)
C(97)-C(98)-H(98)	126.3
C(99)-C(98)-H(98)	126.3
N(11)-C(99)-C(100)	125.5(4)
N(11)-C(99)-C(98)	109.9(4)
C(100)-C(99)-C(98)	124.2(4)
C(101)-C(100)-C(99)	124.3(4)
C(101)-C(100)-C(155)	117.6(4)

C(99)-C(100)-C(155)	117.9(4)
N(12)-C(101)-C(100)	124.7(4)
N(12)-C(101)-C(102)	110.4(4)
C(100)-C(101)-C(102)	124.9(4)
C(103)-C(102)-C(101)	106.5(4)
C(103)-C(102)-H(102)	126.7
C(101)-C(102)-H(102)	126.7
C(102)-C(103)-C(104)	106.5(5)
C(102)-C(103)-H(103)	126.7
C(104)-C(103)-H(103)	126.7
N(12)-C(104)-C(85)	124.8(4)
N(12)-C(104)-C(103)	110.5(4)
C(85)-C(104)-C(103)	124.5(5)
C(110)-C(105)-C(106)	119.2(5)
C(110)-C(105)-C(85)	122.0(5)
C(106)-C(105)-C(85)	118.8(5)
C(107)-C(106)-C(105)	120.2(5)
C(107)-C(106)-N(13)	121.2(5)
C(105)-C(106)-N(13)	118.6(5)
C(108)-C(107)-C(106)	119.1(6)
C(108)-C(107)-H(107)	120.5
C(106)-C(107)-H(107)	120.5
C(107)-C(108)-C(109)	121.9(5)
C(107)-C(108)-H(108)	119.1
C(109)-C(108)-H(108)	119.1
C(110)-C(109)-C(108)	119.1(6)
C(110)-C(109)-H(109)	120.4
C(108)-C(109)-H(109)	120.4
C(109)-C(110)-C(105)	120.5(5)
C(109)-C(110)-N(14)	121.4(5)
C(105)-C(110)-N(14)	118.1(5)
O(5)-C(111)-N(13)	122.8(12)
O(5)-C(111)-C(112)	120.8(12)
N(13)-C(111)-C(112)	113.9(6)
C(111)-C(112)-C(113)	119.2(6)
C(111)-C(112)-C(114)	118.4(7)

C(113)-C(112)-C(114)	57.6(5)
C(111)-C(112)-H(112)	116.3
C(113)-C(112)-H(112)	116.3
C(114)-C(112)-H(112)	116.3
C(114)-C(113)-C(112)	61.7(5)
C(114)-C(113)-H(11A)	117.6
C(112)-C(113)-H(11A)	117.6
C(114)-C(113)-H(11B)	117.6
C(112)-C(113)-H(11B)	117.6
H(11A)-C(113)-H(11B)	114.7
C(113)-C(114)-C(115)	127.4(13)
C(113)-C(114)-C(112)	60.7(5)
C(115)-C(114)-C(112)	119.8(10)
C(113)-C(114)-C(116)	117.1(10)
C(115)-C(114)-C(116)	107.7(13)
C(112)-C(114)-C(116)	117.6(9)
C(114)-C(115)-H(11C)	109.5
C(114)-C(115)-H(11D)	109.5
H(11C)-C(115)-H(11D)	109.5
C(114)-C(115)-H(11E)	109.5
H(11C)-C(115)-H(11E)	109.5
H(11D)-C(115)-H(11E)	109.5
C(114)-C(116)-H(11F)	109.5
C(114)-C(116)-H(11G)	109.5
H(11F)-C(116)-H(11G)	109.5
C(114)-C(116)-H(11H)	109.5
H(11F)-C(116)-H(11H)	109.5
H(11G)-C(116)-H(11H)	109.5
O(6)-C(117)-N(14)	120.7(12)
O(6)-C(117)-C(118)	125.1(12)
N(14)-C(117)-C(118)	113.8(5)
C(117)-C(118)-C(119)	120.9(5)
C(117)-C(118)-C(120)	120.2(5)
C(119)-C(118)-C(120)	58.8(4)
C(117)-C(118)-H(118)	115.1
C(119)-C(118)-H(118)	115.1

C(120)-C(118)-H(118)	115.1
C(120)-C(119)-C(118)	61.8(4)
C(120)-C(119)-H(11I)	117.6
C(118)-C(119)-H(11I)	117.6
C(120)-C(119)-H(11J)	117.6
C(118)-C(119)-H(11J)	117.6
H(11I)-C(119)-H(11J)	114.7
C(119)-C(120)-C(121)	117.6(7)
C(119)-C(120)-C(122)	118.2(6)
C(121)-C(120)-C(122)	115.8(7)
C(119)-C(120)-C(118)	59.4(4)
C(121)-C(120)-C(118)	119.0(6)
C(122)-C(120)-C(118)	115.3(6)
C(120)-C(121)-H(12A)	109.5
C(120)-C(121)-H(12B)	109.5
H(12A)-C(121)-H(12B)	109.5
C(120)-C(121)-H(12C)	109.5
H(12A)-C(121)-H(12C)	109.5
H(12B)-C(121)-H(12C)	109.5
C(120)-C(122)-H(12D)	109.5
C(120)-C(122)-H(12E)	109.5
H(12D)-C(122)-H(12E)	109.5
C(120)-C(122)-H(12F)	109.5
H(12D)-C(122)-H(12F)	109.5
H(12E)-C(122)-H(12F)	109.5
C(124)-C(123)-C(128)	118.9(5)
C(124)-C(123)-C(90)	119.3(5)
C(128)-C(123)-C(90)	121.7(5)
C(123)-C(124)-C(125)	122.0(5)
C(123)-C(124)-H(124)	119.0
C(125)-C(124)-H(124)	119.0
C(126)-C(125)-C(124)	116.6(5)
C(126)-C(125)-C(129)	123.4(5)
C(124)-C(125)-C(129)	119.9(6)
C(125)-C(126)-C(127)	123.7(5)
C(125)-C(126)-H(126)	118.2

C(127)-C(126)-H(126)	118.2
C(126)-C(127)-C(128)	117.3(5)
C(126)-C(127)-C(133)	122.6(5)
C(128)-C(127)-C(133)	120.0(6)
C(123)-C(128)-C(127)	121.5(5)
C(123)-C(128)-H(128)	119.3
C(127)-C(128)-H(128)	119.3
C(131)-C(129)-C(130)	114.7(9)
C(131)-C(129)-C(125)	106.6(7)
C(130)-C(129)-C(125)	115.1(7)
C(131)-C(129)-C(132)	103.9(8)
C(130)-C(129)-C(132)	108.1(8)
C(125)-C(129)-C(132)	107.6(7)
C(129)-C(130)-H(13A)	109.5
C(129)-C(130)-H(13B)	109.5
H(13A)-C(130)-H(13B)	109.5
C(129)-C(130)-H(13C)	109.5
H(13A)-C(130)-H(13C)	109.5
H(13B)-C(130)-H(13C)	109.5
C(129)-C(131)-H(13D)	109.5
C(129)-C(131)-H(13E)	109.5
H(13D)-C(131)-H(13E)	109.5
C(129)-C(131)-H(13F)	109.5
H(13D)-C(131)-H(13F)	109.5
H(13E)-C(131)-H(13F)	109.5
C(129)-C(132)-H(13G)	109.5
C(129)-C(132)-H(13H)	109.5
H(13G)-C(132)-H(13H)	109.5
C(129)-C(132)-H(13I)	109.5
H(13G)-C(132)-H(13I)	109.5
H(13H)-C(132)-H(13I)	109.5
C(134)-C(133)-C(127)	114.2(7)
C(134)-C(133)-C(135)	113.0(9)
C(127)-C(133)-C(135)	110.5(6)
C(134)-C(133)-C(136)	105.1(8)
C(127)-C(133)-C(136)	108.8(6)

C(135)-C(133)-C(136)	104.5(8)
C(133)-C(134)-H(13J)	109.5
C(133)-C(134)-H(13K)	109.5
H(13J)-C(134)-H(13K)	109.5
C(133)-C(134)-H(13L)	109.5
H(13J)-C(134)-H(13L)	109.5
H(13K)-C(134)-H(13L)	109.5
C(133)-C(135)-H(13M)	109.5
C(133)-C(135)-H(13O)	109.5
H(13M)-C(135)-H(13O)	109.5
C(133)-C(135)-H(13P)	109.5
H(13M)-C(135)-H(13P)	109.5
H(13O)-C(135)-H(13P)	109.5
C(133)-C(136)-H(13Q)	109.5
C(133)-C(136)-H(13R)	109.5
H(13Q)-C(136)-H(13R)	109.5
C(133)-C(136)-H(13S)	109.5
H(13Q)-C(136)-H(13S)	109.5
H(13R)-C(136)-H(13S)	109.5
C(138)-C(137)-C(142)	119.1(5)
C(138)-C(137)-C(95)	119.5(5)
C(142)-C(137)-C(95)	121.4(5)
C(139)-C(138)-C(137)	120.9(5)
C(139)-C(138)-N(16)	119.6(5)
C(137)-C(138)-N(16)	119.5(4)
C(140)-C(139)-C(138)	118.6(5)
C(140)-C(139)-H(139)	120.7
C(138)-C(139)-H(139)	120.7
C(141)-C(140)-C(139)	121.8(5)
C(141)-C(140)-H(140)	119.1
C(139)-C(140)-H(140)	119.1
C(140)-C(141)-C(142)	119.0(5)
C(140)-C(141)-H(141)	120.5
C(142)-C(141)-H(141)	120.5
C(141)-C(142)-C(137)	120.6(5)
C(141)-C(142)-N(15)	121.5(5)

C(137)-C(142)-N(15)	117.9(5)
O(8)-C(143)-N(16)	121.4(6)
O(8)-C(143)-C(144)	124.1(5)
N(16)-C(143)-C(144)	114.5(5)
C(143)-C(144)-C(145)	118.3(5)
C(143)-C(144)-C(146)	121.5(5)
C(145)-C(144)-C(146)	57.9(4)
C(143)-C(144)-H(144)	115.6
C(145)-C(144)-H(144)	115.6
C(146)-C(144)-H(144)	115.6
C(146)-C(145)-C(144)	61.1(4)
C(146)-C(145)-H(14A)	117.7
C(144)-C(145)-H(14A)	117.7
C(146)-C(145)-H(14B)	117.7
C(144)-C(145)-H(14B)	117.7
H(14A)-C(145)-H(14B)	114.8
C(145)-C(146)-C(148)	118.5(6)
C(145)-C(146)-C(147)	117.6(7)
C(148)-C(146)-C(147)	115.4(7)
C(145)-C(146)-C(144)	61.0(4)
C(148)-C(146)-C(144)	118.6(6)
C(147)-C(146)-C(144)	114.8(6)
C(146)-C(147)-H(14C)	109.5
C(146)-C(147)-H(14D)	109.5
H(14C)-C(147)-H(14D)	109.5
C(146)-C(147)-H(14E)	109.5
H(14C)-C(147)-H(14E)	109.5
H(14D)-C(147)-H(14E)	109.5
C(146)-C(148)-H(14F)	109.5
C(146)-C(148)-H(14G)	109.5
H(14F)-C(148)-H(14G)	109.5
C(146)-C(148)-H(14H)	109.5
H(14F)-C(148)-H(14H)	109.5
H(14G)-C(148)-H(14H)	109.5
O(7)-C(149)-N(15)	123.1(5)
O(7)-C(149)-C(150)	123.6(5)

N(15)-C(149)-C(150)	113.3(5)
C(149)-C(150)-C(151)	119.8(5)
C(149)-C(150)-C(152)	119.9(5)
C(151)-C(150)-C(152)	59.2(4)
C(149)-C(150)-H(150)	115.5
C(151)-C(150)-H(150)	115.5
C(152)-C(150)-H(150)	115.5
C(152)-C(151)-C(150)	61.2(4)
C(152)-C(151)-H(15A)	117.6
C(150)-C(151)-H(15A)	117.6
C(152)-C(151)-H(15B)	117.6
C(150)-C(151)-H(15B)	117.6
H(15A)-C(151)-H(15B)	114.8
C(153)-C(152)-C(151)	119.6(5)
C(153)-C(152)-C(154)	114.2(5)
C(151)-C(152)-C(154)	117.6(5)
C(153)-C(152)-C(150)	119.5(5)
C(151)-C(152)-C(150)	59.6(4)
C(154)-C(152)-C(150)	115.6(5)
C(152)-C(153)-H(15C)	109.5
C(152)-C(153)-H(15D)	109.5
H(15C)-C(153)-H(15D)	109.5
C(152)-C(153)-H(15E)	109.5
H(15C)-C(153)-H(15E)	109.5
H(15D)-C(153)-H(15E)	109.5
C(152)-C(154)-H(15F)	109.5
C(152)-C(154)-H(15G)	109.5
H(15F)-C(154)-H(15G)	109.5
C(152)-C(154)-H(15H)	109.5
H(15F)-C(154)-H(15H)	109.5
H(15G)-C(154)-H(15H)	109.5
C(156)-C(155)-C(160)	120.0(4)
C(156)-C(155)-C(100)	119.5(4)
C(160)-C(155)-C(100)	120.5(4)
C(155)-C(156)-C(157)	121.7(5)
C(155)-C(156)-H(156)	119.2

C(157)-C(156)-H(156)	119.2
C(158)-C(157)-C(156)	117.1(5)
C(158)-C(157)-C(161)	123.4(4)
C(156)-C(157)-C(161)	119.5(5)
C(159)-C(158)-C(157)	122.9(4)
C(159)-C(158)-H(158)	118.6
C(157)-C(158)-H(158)	118.6
C(158)-C(159)-C(160)	118.2(5)
C(158)-C(159)-C(165)	122.7(4)
C(160)-C(159)-C(165)	119.1(4)
C(155)-C(160)-C(159)	120.3(5)
C(155)-C(160)-H(160)	119.9
C(159)-C(160)-H(160)	119.9
C(162)-C(161)-C(157)	112.5(11)
C(162)-C(161)-C(164)	109.6(15)
C(157)-C(161)-C(164)	112(2)
C(162)-C(161)-C(163)	111.0(9)
C(157)-C(161)-C(163)	105.0(12)
C(164)-C(161)-C(163)	106.3(12)
C(161)-C(162)-H(16A)	109.5
C(161)-C(162)-H(16B)	109.5
H(16A)-C(162)-H(16B)	109.5
C(161)-C(162)-H(16C)	109.5
H(16A)-C(162)-H(16C)	109.5
H(16B)-C(162)-H(16C)	109.5
C(161)-C(163)-H(16D)	109.5
C(161)-C(163)-H(16E)	109.5
H(16D)-C(163)-H(16E)	109.5
C(161)-C(163)-H(16F)	109.5
H(16D)-C(163)-H(16F)	109.5
H(16E)-C(163)-H(16F)	109.5
C(161)-C(164)-H(16G)	109.5
C(161)-C(164)-H(16H)	109.5
H(16G)-C(164)-H(16H)	109.5
C(161)-C(164)-H(16I)	109.5
H(16G)-C(164)-H(16I)	109.5

H(16H)-C(164)-H(16I)	109.5
C(168)-C(165)-C(166)	110.4(5)
C(168)-C(165)-C(159)	110.5(4)
C(166)-C(165)-C(159)	107.4(5)
C(168)-C(165)-C(167)	108.5(5)
C(166)-C(165)-C(167)	109.1(5)
C(159)-C(165)-C(167)	111.0(5)
C(165)-C(166)-H(16J)	109.5
C(165)-C(166)-H(16K)	109.5
H(16J)-C(166)-H(16K)	109.5
C(165)-C(166)-H(16L)	109.5
H(16J)-C(166)-H(16L)	109.5
H(16K)-C(166)-H(16L)	109.5
C(165)-C(167)-H(16M)	109.5
C(165)-C(167)-H(16O)	109.5
H(16M)-C(167)-H(16O)	109.5
C(165)-C(167)-H(16P)	109.5
H(16M)-C(167)-H(16P)	109.5
H(16O)-C(167)-H(16P)	109.5
C(165)-C(168)-H(16Q)	109.5
C(165)-C(168)-H(16R)	109.5
H(16Q)-C(168)-H(16R)	109.5
C(165)-C(168)-H(16S)	109.5
H(16Q)-C(168)-H(16S)	109.5
H(16R)-C(168)-H(16S)	109.5
Cl(1S)-C(1S)-Cl(2S)	115(2)
Cl(1S)-C(1S)-Cl(3S)	116(2)
Cl(2S)-C(1S)-Cl(3S)	111(2)
Cl(1S)-C(1S)-H(1S)	104.8
Cl(2S)-C(1S)-H(1S)	104.8
Cl(3S)-C(1S)-H(1S)	104.8

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3) for C84H96ClFeN8O4 ([Fe(P2)Cl])

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	26(1)	25(1)	37(1)	1(1)	-2(1)	12(1)
Cl(1)	60(1)	58(1)	40(1)	-3(1)	5(1)	35(1)
O(1)	46(4)	163(7)	47(4)	-2(5)	9(3)	32(5)
O(1X)	40(13)	141(9)	40(20)	13(11)	23(14)	18(9)
O(2)	59(3)	102(4)	48(2)	-2(2)	-6(2)	52(3)
O(3)	40(2)	55(2)	95(4)	-30(2)	11(2)	13(2)
O(4)	42(2)	37(2)	71(3)	5(2)	10(2)	21(2)
N(1)	29(2)	28(2)	39(2)	1(2)	0(2)	14(2)
N(2)	31(2)	28(2)	35(2)	2(2)	1(2)	13(2)
N(3)	26(2)	29(2)	34(2)	-1(2)	0(2)	13(2)
N(4)	26(2)	21(2)	43(2)	2(2)	-1(2)	9(2)
N(5)	38(2)	59(3)	49(3)	0(2)	-3(2)	23(2)
N(6)	28(2)	38(2)	49(3)	4(2)	-4(2)	13(2)
N(7)	30(2)	33(2)	49(3)	-8(2)	-1(2)	11(2)
N(8)	31(2)	33(2)	42(2)	1(2)	6(2)	12(2)
C(1)	32(2)	32(2)	42(3)	-2(2)	-2(2)	16(2)
C(2)	29(2)	33(2)	42(3)	0(2)	-2(2)	17(2)
C(3)	29(2)	33(2)	49(3)	2(2)	-9(2)	15(2)
C(4)	37(3)	37(3)	44(3)	1(2)	-5(2)	19(2)
C(5)	32(2)	35(2)	37(3)	0(2)	0(2)	22(2)
C(6)	33(2)	32(2)	35(3)	0(2)	2(2)	18(2)
C(7)	33(2)	28(2)	37(3)	2(2)	3(2)	17(2)
C(8)	39(3)	31(2)	44(3)	2(2)	4(2)	18(2)
C(9)	30(2)	30(2)	47(3)	-1(2)	2(2)	13(2)
C(10)	31(2)	27(2)	38(3)	-2(2)	2(2)	13(2)
C(11)	29(2)	30(2)	37(3)	-2(2)	2(2)	14(2)
C(12)	26(2)	34(2)	36(3)	-4(2)	0(2)	15(2)
C(13)	29(2)	34(2)	44(3)	-1(2)	-2(2)	15(2)
C(14)	33(2)	35(2)	40(3)	2(2)	1(2)	18(2)
C(15)	31(2)	32(2)	35(3)	0(2)	2(2)	19(2)
C(16)	35(2)	31(2)	37(3)	0(2)	1(2)	18(2)

C(17)	36(2)	27(2)	36(3)	2(2)	0(2)	16(2)
C(18)	32(2)	32(2)	43(3)	1(2)	-4(2)	14(2)
C(19)	33(2)	30(2)	49(3)	1(2)	-4(2)	12(2)
C(20)	31(2)	28(2)	37(3)	-2(2)	-2(2)	11(2)
C(21)	32(2)	37(3)	43(3)	8(2)	-2(2)	17(2)
C(22)	34(3)	49(3)	44(3)	7(2)	-3(2)	21(2)
C(23)	35(3)	72(4)	48(3)	14(3)	4(2)	24(3)
C(24)	26(3)	68(4)	54(3)	17(3)	-3(2)	11(3)
C(25)	36(3)	45(3)	52(3)	9(2)	-6(2)	12(2)
C(26)	34(2)	36(3)	49(3)	8(2)	-3(2)	17(2)
C(27)	44(3)	105(5)	47(3)	-8(3)	-1(3)	39(3)
C(28)	62(4)	97(5)	51(4)	-16(3)	-8(3)	43(4)
C(29)	89(5)	150(8)	46(4)	-17(4)	-5(4)	70(6)
C(30)	63(4)	108(5)	45(4)	-5(3)	-2(3)	45(4)
C(31)	70(5)	125(7)	76(5)	-7(5)	-10(4)	51(5)
C(32)	84(5)	110(6)	67(5)	12(4)	4(4)	40(5)
C(33)	41(3)	41(3)	50(3)	-1(2)	-1(2)	23(2)
C(34)	48(3)	49(3)	53(3)	6(2)	4(2)	30(3)
C(35)	74(4)	64(4)	51(3)	-3(3)	3(3)	44(3)
C(36)	67(4)	53(3)	50(3)	6(3)	3(3)	34(3)
C(37)	110(6)	64(4)	57(4)	7(3)	4(4)	59(4)
C(38)	70(4)	87(5)	80(5)	37(4)	23(4)	33(4)
C(39)	34(2)	32(2)	40(3)	4(2)	2(2)	17(2)
C(40)	39(3)	38(3)	40(3)	2(2)	1(2)	21(2)
C(41)	51(3)	47(3)	42(3)	8(2)	1(2)	25(3)
C(42)	70(4)	46(3)	54(3)	13(3)	-6(3)	30(3)
C(43)	68(4)	42(3)	53(3)	4(2)	-7(3)	33(3)
C(44)	47(3)	40(3)	43(3)	1(2)	-2(2)	24(2)
C(45)	84(5)	69(4)	42(3)	9(3)	-2(3)	42(4)
C(46)	59(12)	98(13)	33(8)	-3(8)	-1(9)	47(12)
C(47)	85(10)	104(17)	35(9)	-5(10)	-2(8)	57(11)
C(48)	112(14)	83(11)	25(8)	22(7)	22(8)	44(11)
C(49)	117(6)	54(4)	87(5)	-9(3)	-27(4)	59(4)
C(50)	108(16)	65(13)	121(17)	-4(10)	-33(12)	61(13)
C(51)	83(11)	33(8)	99(15)	-3(8)	-21(9)	32(8)
C(52)	81(10)	54(9)	113(13)	-20(8)	-11(8)	48(8)

C(50X)	144(16)	113(19)	133(19)	-27(14)	-27(14)	110(16)
C(51X)	142(13)	28(6)	93(10)	0(6)	10(9)	29(7)
C(52X)	88(11)	44(9)	74(8)	-6(6)	6(7)	38(8)
C(53)	33(2)	28(2)	38(3)	1(2)	0(2)	13(2)
C(54)	32(2)	29(2)	45(3)	-1(2)	2(2)	13(2)
C(55)	32(3)	39(3)	54(3)	-9(2)	3(2)	13(2)
C(56)	28(2)	41(3)	62(3)	-13(3)	-3(2)	10(2)
C(57)	34(3)	38(3)	46(3)	-9(2)	-1(2)	11(2)
C(58)	33(2)	31(2)	41(3)	2(2)	4(2)	15(2)
C(59)	36(3)	34(3)	54(3)	-7(2)	3(2)	15(2)
C(60)	41(3)	45(3)	57(3)	-13(3)	-1(2)	19(2)
C(61)	72(4)	60(4)	57(4)	-10(3)	9(3)	36(3)
C(62)	57(3)	45(3)	65(4)	-15(3)	-7(3)	31(3)
C(63)	85(5)	48(4)	96(6)	-22(4)	-11(4)	33(4)
C(64)	76(5)	85(5)	103(6)	-30(4)	-22(4)	55(4)
C(65)	35(3)	41(3)	44(3)	1(2)	0(2)	17(2)
C(66)	40(3)	41(3)	52(3)	-2(2)	4(2)	20(2)
C(67)	42(3)	50(3)	50(3)	-5(2)	2(2)	22(3)
C(68)	44(3)	63(4)	59(4)	-14(3)	-4(3)	29(3)
C(69)	74(5)	139(7)	51(4)	-10(4)	-7(3)	72(5)
C(70)	34(3)	71(4)	130(7)	-35(4)	-4(4)	23(3)
C(71)	26(2)	28(2)	38(3)	0(2)	-2(2)	11(2)
C(72)	31(2)	35(2)	38(3)	1(2)	1(2)	15(2)
C(73)	31(2)	34(2)	38(3)	-2(2)	-4(2)	16(2)
C(74)	35(3)	31(2)	41(3)	3(2)	-2(2)	18(2)
C(75)	31(2)	29(2)	42(3)	3(2)	0(2)	14(2)
C(76)	33(2)	31(2)	39(3)	-4(2)	-1(2)	15(2)
C(77)	43(3)	39(3)	42(3)	-1(2)	1(2)	24(2)
C(78)	57(3)	48(3)	47(3)	-6(2)	-3(3)	32(3)
C(79)	44(3)	55(3)	64(4)	-1(3)	7(3)	30(3)
C(80)	54(3)	46(3)	55(3)	-1(2)	1(3)	34(3)
C(81)	50(3)	40(3)	43(3)	7(2)	6(2)	26(2)
C(82)	94(5)	50(3)	38(3)	-3(2)	-7(3)	40(3)
C(83)	46(3)	45(3)	50(3)	14(2)	11(2)	24(3)
C(84)	77(4)	62(4)	76(5)	32(3)	40(4)	48(4)
Fe(2)	33(1)	28(1)	38(1)	-3(1)	1(1)	18(1)

Cl(2)	66(1)	50(1)	44(1)	2(1)	-7(1)	35(1)
O(5)	67(6)	118(11)	58(6)	-18(7)	0(5)	28(6)
O(6)	51(7)	97(12)	52(6)	4(9)	5(6)	47(8)
O(5X)	47(7)	105(13)	39(9)	-7(8)	4(6)	15(7)
O(6X)	50(8)	99(13)	35(8)	6(9)	5(7)	50(9)
O(7)	41(2)	59(3)	90(3)	9(2)	3(2)	27(2)
O(8)	63(3)	29(2)	101(4)	-2(2)	1(2)	20(2)
N(9)	35(2)	32(2)	42(2)	-4(2)	-2(2)	19(2)
N(10)	40(2)	32(2)	36(2)	-4(2)	-3(2)	21(2)
N(11)	33(2)	29(2)	35(2)	-5(2)	-1(2)	17(2)
N(12)	32(2)	28(2)	40(2)	-5(2)	0(2)	17(2)
N(13)	41(2)	60(3)	49(3)	-6(2)	-2(2)	25(2)
N(14)	37(2)	44(2)	50(3)	-4(2)	3(2)	25(2)
N(15)	40(2)	40(2)	46(3)	-2(2)	2(2)	21(2)
N(16)	49(2)	28(2)	46(3)	-4(2)	-2(2)	14(2)
C(85)	38(3)	39(3)	45(3)	-1(2)	0(2)	24(2)
C(86)	35(2)	39(3)	46(3)	-2(2)	0(2)	24(2)
C(87)	36(3)	48(3)	49(3)	-6(2)	5(2)	24(2)
C(88)	41(3)	46(3)	52(3)	-3(2)	3(2)	26(2)
C(89)	41(3)	40(3)	38(3)	-5(2)	-1(2)	27(2)
C(90)	45(3)	41(3)	36(3)	-3(2)	-4(2)	28(2)
C(91)	45(3)	35(2)	38(3)	-5(2)	-4(2)	26(2)
C(92)	45(3)	38(3)	44(3)	-8(2)	-6(2)	25(2)
C(93)	41(3)	34(3)	47(3)	-6(2)	-4(2)	18(2)
C(94)	38(3)	29(2)	41(3)	-2(2)	-3(2)	17(2)
C(95)	39(3)	33(2)	35(3)	-1(2)	-1(2)	19(2)
C(96)	33(2)	32(2)	39(3)	1(2)	0(2)	17(2)
C(97)	31(2)	37(3)	46(3)	-4(2)	1(2)	17(2)
C(98)	39(3)	35(2)	44(3)	-4(2)	-3(2)	23(2)
C(99)	40(3)	33(2)	37(3)	-2(2)	-1(2)	22(2)
C(100)	43(3)	34(2)	37(3)	-3(2)	2(2)	24(2)
C(101)	39(2)	34(2)	37(3)	-2(2)	1(2)	22(2)
C(102)	41(3)	37(3)	52(3)	-6(2)	4(2)	21(2)
C(103)	38(3)	37(3)	56(3)	-5(2)	7(2)	15(2)
C(104)	41(3)	31(2)	43(3)	1(2)	3(2)	20(2)
C(105)	39(3)	42(3)	47(3)	-9(2)	3(2)	26(2)

C(106)	43(3)	54(3)	46(3)	-12(2)	-1(2)	28(3)
C(107)	47(3)	79(4)	46(3)	-16(3)	-4(2)	35(3)
C(108)	34(3)	77(4)	58(4)	-22(3)	-1(2)	21(3)
C(109)	39(3)	56(3)	57(3)	-16(3)	4(2)	20(3)
C(110)	38(3)	48(3)	50(3)	-9(2)	1(2)	26(2)
C(111)	48(3)	80(4)	53(3)	6(3)	-1(3)	32(3)
C(112)	52(4)	99(5)	54(4)	0(3)	-3(3)	32(4)
C(113)	78(5)	140(8)	54(4)	26(5)	2(4)	45(5)
C(114)	78(5)	130(7)	51(4)	-12(4)	0(4)	53(5)
C(115)	71(7)	98(14)	66(8)	-2(7)	18(6)	37(7)
C(116)	103(12)	102(9)	55(8)	-21(7)	20(8)	14(10)
C(117)	49(3)	61(4)	53(3)	2(3)	-1(2)	35(3)
C(118)	47(3)	51(3)	62(3)	-1(3)	-5(3)	29(3)
C(119)	60(4)	76(4)	63(4)	14(3)	-5(3)	37(3)
C(120)	76(4)	59(4)	50(4)	2(3)	1(3)	34(3)
C(121)	194(10)	81(5)	56(5)	-4(4)	-6(5)	89(6)
C(122)	67(5)	111(7)	74(5)	-10(5)	-10(4)	17(5)
C(123)	37(3)	43(3)	41(3)	-12(2)	-8(2)	25(2)
C(124)	52(3)	55(3)	43(3)	-9(2)	-8(2)	37(3)
C(125)	50(3)	70(4)	43(3)	-17(3)	-9(2)	39(3)
C(126)	67(4)	67(4)	49(3)	-25(3)	-12(3)	46(3)
C(127)	58(3)	47(3)	57(3)	-17(3)	-8(3)	31(3)
C(128)	43(3)	44(3)	43(3)	-12(2)	-8(2)	25(2)
C(129)	71(4)	89(4)	43(3)	-15(3)	-9(3)	52(4)
C(130)	65(3)	53(3)	54(3)	5(3)	5(2)	34(3)
C(131)	94(4)	68(3)	58(3)	-9(3)	-6(3)	54(3)
C(132)	56(3)	75(3)	52(3)	-6(2)	-6(2)	38(3)
C(630)	65(3)	53(3)	54(3)	5(3)	5(2)	34(3)
C(631)	56(3)	75(3)	52(3)	-6(2)	-6(2)	38(3)
C(632)	94(4)	68(3)	58(3)	-9(3)	-6(3)	54(3)
C(133)	88(5)	52(4)	81(5)	-14(3)	-6(4)	42(4)
C(134)	134(11)	40(5)	88(8)	-12(5)	35(7)	44(6)
C(135)	106(9)	60(6)	137(12)	12(6)	-18(8)	55(6)
C(136)	108(8)	52(5)	76(7)	6(5)	25(6)	41(6)
C(137)	38(3)	29(2)	40(3)	-5(2)	1(2)	14(2)
C(138)	43(3)	26(2)	42(3)	-7(2)	-1(2)	12(2)

C(139)	50(3)	35(3)	50(3)	0(2)	6(2)	13(2)
C(140)	47(3)	41(3)	60(4)	1(3)	8(3)	13(3)
C(141)	38(3)	38(3)	60(4)	-5(2)	0(2)	13(2)
C(142)	44(3)	35(3)	45(3)	-6(2)	-1(2)	19(2)
C(143)	59(3)	34(3)	45(3)	3(2)	5(2)	21(3)
C(144)	68(4)	37(3)	57(4)	-4(2)	-8(3)	28(3)
C(145)	82(4)	62(4)	57(4)	10(3)	0(3)	47(4)
C(146)	57(3)	51(3)	70(4)	16(3)	4(3)	31(3)
C(147)	63(4)	69(5)	181(10)	41(5)	13(5)	39(4)
C(148)	114(6)	115(6)	58(4)	7(4)	12(4)	89(6)
C(149)	42(3)	42(3)	50(3)	-8(2)	-4(2)	21(2)
C(150)	52(3)	50(3)	46(3)	-1(2)	0(2)	31(3)
C(151)	65(4)	56(4)	55(4)	-4(3)	-10(3)	38(3)
C(152)	48(3)	47(3)	50(3)	-3(2)	-2(2)	28(3)
C(153)	72(4)	60(4)	58(4)	-6(3)	1(3)	44(3)
C(154)	60(4)	56(4)	71(4)	6(3)	4(3)	31(3)
C(155)	28(2)	28(2)	44(3)	-4(2)	3(2)	11(2)
C(156)	38(3)	28(2)	45(3)	-4(2)	2(2)	18(2)
C(157)	33(2)	30(2)	45(3)	-7(2)	1(2)	12(2)
C(158)	31(2)	30(2)	52(3)	-9(2)	-1(2)	15(2)
C(159)	31(2)	32(2)	48(3)	-5(2)	-1(2)	16(2)
C(160)	34(3)	36(3)	42(3)	-7(2)	-2(2)	20(2)
C(161)	68(4)	40(3)	45(3)	-5(2)	3(3)	30(3)
C(162)	126(9)	87(14)	46(9)	-14(9)	-19(8)	84(10)
C(163)	122(10)	53(6)	36(9)	-2(4)	16(8)	15(7)
C(164)	44(8)	49(4)	49(4)	-13(4)	-3(7)	27(5)
C(662)	126(9)	87(14)	46(9)	-14(9)	-19(8)	84(10)
C(663)	122(10)	53(6)	36(9)	-2(4)	16(8)	15(7)
C(664)	44(8)	49(4)	49(4)	-13(4)	-3(7)	27(5)
C(165)	52(3)	40(3)	48(3)	-7(2)	-5(2)	31(3)
C(166)	56(3)	75(3)	52(3)	-6(2)	-6(2)	38(3)
C(167)	94(4)	68(3)	58(3)	-9(3)	-6(3)	54(3)
C(168)	65(3)	53(3)	54(3)	5(3)	5(2)	34(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for C84H96ClFeN8O4 ([Fe(P2)Cl])

	x	y	z	U(eq)
H(5N)	5407	-453	5788	59
H(6N)	5459	-1300	4392	48
H(7N)	8836	880	5071	47
H(8N)	8134	1386	6311	44
H(3)	5340	-263	4452	45
H(4)	5991	565	4120	47
H(8)	7875	1996	4654	45
H(9)	8519	1992	5167	44
H(13)	8703	499	5926	43
H(14)	8146	-448	5983	43
H(18)	6133	-1710	5825	44
H(19)	5404	-1592	5573	47
H(23)	4121	-1309	5688	64
H(24)	3712	-1794	5066	66
H(25)	4178	-1796	4451	57
H(28)	5659	-239	6483	82
H(29A)	4901	-911	7147	108
H(29B)	5449	-372	7260	108
H(31A)	6266	-273	6973	134
H(31B)	6201	-774	7220	134
H(31C)	6298	-712	6698	134
H(32A)	4942	-1619	6774	136
H(32B)	5460	-1563	6573	136
H(32C)	5363	-1625	7095	136
H(34)	5731	-1291	3724	57
H(35A)	5557	-1428	2948	71
H(35B)	5049	-1347	3002	71
H(37A)	5800	-24	3372	106
H(37B)	5467	-315	2945	106
H(37C)	5222	-489	3427	106

H(38A)	6479	-146	3341	123
H(38B)	6423	-704	3369	123
H(38C)	6385	-477	2901	123
H(40)	6864	984	3684	45
H(42)	6923	2328	3432	68
H(44)	7030	1941	4685	50
H(46A)	6945	1061	2537	90
H(46B)	7348	1256	2937	90
H(46C)	6768	803	3015	90
H(47A)	6176	1584	2936	106
H(47B)	6223	1262	2535	106
H(47C)	6046	1004	3013	106
H(48A)	7076	2274	2780	113
H(48B)	7533	2145	2776	113
H(48C)	7111	1932	2390	113
H(46D)	7047	951	3021	63
H(46E)	6438	709	2966	63
H(46F)	6809	955	2548	63
H(47D)	6428	1469	2434	129
H(47E)	6093	1312	2878	129
H(47F)	6486	1905	2772	129
H(48D)	7660	1863	2921	127
H(48E)	7393	1797	2448	127
H(48F)	7471	2253	2771	127
H(46G)	7398	1363	2969	146
H(46H)	7270	1508	2496	146
H(46I)	7576	1949	2855	146
H(47G)	6065	944	3063	182
H(47H)	6318	856	2630	182
H(47I)	6455	729	3108	182
H(48G)	6348	1812	2860	120
H(48H)	6942	2229	2783	120
H(48I)	6636	1788	2423	120
H(50A)	6559	2749	3767	134
H(50B)	6775	3220	4108	134
H(50C)	7145	3204	3735	134

H(51A)	7515	2774	4707	105
H(51B)	7764	3221	4343	105
H(51C)	7393	3236	4716	105
H(52A)	6542	2315	4852	114
H(52B)	6508	2820	4743	114
H(52C)	6175	2304	4463	114
H(50D)	6644	3093	4207	165
H(50E)	6595	2767	3772	165
H(50F)	6283	2480	4209	165
H(51D)	7845	3170	4034	140
H(51E)	7475	3119	3632	140
H(51F)	7584	3522	4021	140
H(52D)	7514	2807	4748	100
H(52E)	7345	3235	4755	100
H(52F)	6953	2663	4921	100
H(55)	10007	1901	5468	53
H(56)	10062	2453	6031	56
H(57)	9325	2371	6370	51
H(60)	8905	486	4518	58
H(61A)	9379	531	3867	74
H(61B)	9928	966	4103	74
H(63A)	9101	-470	4664	115
H(63B)	8771	-296	4368	115
H(63C)	9205	-385	4144	115
H(64A)	9851	97	4975	122
H(64B)	10222	376	4563	122
H(64C)	10108	706	4913	122
H(66)	7605	1629	6652	53
H(67A)	7439	2309	6848	57
H(67B)	7887	2708	6493	57
H(69A)	7206	1927	5533	119
H(69B)	7350	2484	5717	119
H(69C)	7789	2333	5660	119
H(70A)	6622	1382	6035	120
H(70B)	6778	1370	6539	120
H(70C)	6585	1758	6391	120

H(72)	7503	-1385	5384	42
H(74)	7246	-2341	6412	42
H(76)	6866	-1228	6507	42
H(78A)	7329	-2099	4993	72
H(78B)	7477	-2543	4974	72
H(78C)	6970	-2641	5231	72
H(79A)	8403	-1655	5742	78
H(79B)	8349	-1957	5291	78
H(79C)	8221	-1500	5300	78
H(80A)	7826	-2502	6104	71
H(80B)	7270	-2884	5901	71
H(80C)	7777	-2786	5644	71
H(82A)	7063	-1812	7639	89
H(82B)	7505	-1737	7300	89
H(82C)	7313	-1327	7313	89
H(83A)	6474	-2684	7355	70
H(83B)	6342	-2778	6839	70
H(83C)	6901	-2638	7012	70
H(84A)	6191	-2049	7370	99
H(84B)	6435	-1565	7043	99
H(84C)	6061	-2130	6854	99
H(13N)	4573	9979	5762	60
H(14N)	4692	11004	4431	50
H(15N)	1164	8697	4939	49
H(16N)	1948	8255	6180	52
H(87)	4735	9868	4463	51
H(88)	4079	9050	4116	53
H(92)	2152	7651	4603	49
H(93)	1506	7673	5096	49
H(97)	1363	9182	5879	45
H(98)	1933	10123	5938	45
H(102)	3947	11365	5778	51
H(103)	4671	11236	5526	55
H(107)	5875	10789	5750	67
H(108)	6349	11313	5167	71
H(109)	5946	11413	4545	63

H(112)	4275	9675	6439	85
H(11A)	4422	9726	7230	114
H(11B)	4975	10278	7169	114
H(11C)	3691	10334	6738	121
H(11D)	3578	9753	6760	121
H(11E)	3668	10074	7206	121
H(11F)	4415	11028	6723	155
H(11G)	4728	11048	7158	155
H(11H)	4955	11044	6680	155
H(61C)	3726	9490	6910	117
H(61D)	3637	9851	7246	117
H(61E)	3520	9857	6731	117
H(61F)	4189	10790	6737	133
H(61G)	4443	10829	7211	133
H(61H)	4788	10970	6774	133
H(118)	4487	11096	3754	62
H(11I)	4703	11257	2996	78
H(11J)	5163	11104	3056	78
H(12A)	4287	9790	3373	151
H(12B)	4661	10080	2965	151
H(12C)	4877	10211	3460	151
H(12D)	3662	10001	3322	145
H(12E)	3785	10583	3368	145
H(12F)	3820	10364	2895	145
H(124)	3252	8682	3666	54
H(126)	3116	7312	3378	67
H(128)	2962	7654	4634	50
H(13A)	2665	8246	2827	83
H(13B)	3163	8788	2941	83
H(13C)	3109	8531	2466	83
H(13D)	4027	8272	3024	101
H(13E)	3972	8546	2590	101
H(13F)	4026	8803	3065	101
H(13G)	2753	7465	2678	88
H(13H)	3235	7780	2356	88
H(13I)	3288	7488	2777	88

H(63D)	2769	8445	2993	83
H(63E)	2892	8368	2493	83
H(63F)	2521	7878	2789	83
H(63G)	3772	8960	3110	88
H(63H)	4098	8692	2974	88
H(63I)	3815	8840	2602	88
H(63J)	3437	8004	2345	101
H(63K)	3658	7804	2732	101
H(63L)	3052	7512	2632	101
H(13J)	2794	6178	3948	131
H(13K)	2536	6433	3654	131
H(13L)	3142	6646	3623	131
H(13M)	3409	7197	4730	142
H(13O)	3279	6619	4636	142
H(13P)	3689	7080	4334	142
H(13Q)	2462	6831	4724	117
H(13R)	2132	6539	4296	117
H(13S)	2381	6279	4592	117
H(63M)	2684	6596	3562	177
H(63N)	2587	6154	3910	177
H(63O)	2225	6406	3912	177
H(63P)	3566	7025	3756	159
H(63Q)	3759	7253	4241	159
H(63R)	3510	6648	4153	159
H(63S)	3116	7076	4814	115
H(63T)	2511	6723	4730	115
H(63U)	2872	6472	4727	115
H(139)	723	7336	6347	58
H(140)	-8	7321	6064	65
H(141)	54	7877	5500	57
H(144)	2434	8001	6567	64
H(14A)	2542	7302	6840	74
H(14B)	2038	6878	6544	74
H(14C)	3288	8037	5895	152
H(14D)	3220	8159	6397	152
H(14E)	3344	7710	6287	152

H(14F)	2623	7452	5492	123
H(14G)	2447	6918	5740	123
H(14H)	2052	7126	5687	123
H(150)	1099	9266	4528	56
H(15A)	569	9580	4222	67
H(15B)	133	9288	4620	67
H(15C)	1032	10042	5510	88
H(15D)	514	9987	5308	88
H(15E)	530	9485	5464	88
H(15F)	1473	10176	4419	92
H(15G)	1338	10539	4710	92
H(15H)	1670	10309	4919	92
H(156)	3016	10756	6512	44
H(158)	2838	11997	6400	45
H(160)	2805	11205	5310	44
H(16A)	3422	11402	7539	109
H(16B)	3332	11014	7141	109
H(16C)	3737	11615	7087	109
H(16D)	2186	11101	7096	124
H(16E)	2382	10694	7129	124
H(16F)	2452	11059	7541	124
H(16G)	2799	12023	7076	68
H(16H)	3066	11974	7517	68
H(16I)	3407	12242	7087	68
H(66A)	3592	11573	7459	109
H(66B)	3555	11237	7035	109
H(66C)	3791	11845	6988	109
H(66D)	2666	11065	7624	124
H(66E)	2249	10912	7238	124
H(66F)	2632	10686	7237	124
H(66G)	3029	11947	7530	68
H(66H)	3292	12237	7078	68
H(66I)	2678	11924	7122	68
H(16J)	1908	11563	5585	88
H(16K)	2070	11907	5147	88
H(16L)	2120	11401	5166	88

H(16M)	2503	12348	6023	101
H(16O)	3098	12680	5892	101
H(16P)	2669	12688	5582	101
H(16Q)	3433	12422	5252	83
H(16R)	3057	11929	4963	83
H(16S)	3006	12435	4944	83
H(1S)	5499	11533	6223	102

Table S6. Torsion angles [º] for C84H96ClFeN8O4 ([Fe(P2)Cl])

C(5)-N(1)-C(2)-C(1)	-178.8(5)
Fe(1)-N(1)-C(2)-C(1)	-10.2(7)
C(5)-N(1)-C(2)-C(3)	0.9(5)
Fe(1)-N(1)-C(2)-C(3)	169.5(3)
C(20)-C(1)-C(2)-N(1)	-11.9(8)
C(21)-C(1)-C(2)-N(1)	169.3(5)
C(20)-C(1)-C(2)-C(3)	168.4(5)
C(21)-C(1)-C(2)-C(3)	-10.4(8)
N(1)-C(2)-C(3)-C(4)	1.7(6)
C(1)-C(2)-C(3)-C(4)	-178.6(5)
C(2)-C(3)-C(4)-C(5)	-3.5(6)
C(2)-N(1)-C(5)-C(6)	169.4(5)
Fe(1)-N(1)-C(5)-C(6)	1.5(7)
C(2)-N(1)-C(5)-C(4)	-3.1(5)
Fe(1)-N(1)-C(5)-C(4)	-171.0(3)
C(3)-C(4)-C(5)-C(6)	-168.3(5)
C(3)-C(4)-C(5)-N(1)	4.2(6)
N(1)-C(5)-C(6)-C(7)	2.1(7)
C(4)-C(5)-C(6)-C(7)	173.5(5)
N(1)-C(5)-C(6)-C(39)	-177.0(4)
C(4)-C(5)-C(6)-C(39)	-5.6(7)
C(10)-N(2)-C(7)-C(6)	176.3(4)
Fe(1)-N(2)-C(7)-C(6)	-21.0(7)
C(10)-N(2)-C(7)-C(8)	-1.3(5)
Fe(1)-N(2)-C(7)-C(8)	161.4(3)
C(5)-C(6)-C(7)-N(2)	7.9(7)
C(39)-C(6)-C(7)-N(2)	-172.9(4)
C(5)-C(6)-C(7)-C(8)	-174.9(5)
C(39)-C(6)-C(7)-C(8)	4.2(7)
N(2)-C(7)-C(8)-C(9)	-0.1(6)
C(6)-C(7)-C(8)-C(9)	-177.6(5)
C(7)-C(8)-C(9)-C(10)	1.4(6)
C(7)-N(2)-C(10)-C(11)	-172.5(5)
Fe(1)-N(2)-C(10)-C(11)	23.8(6)

C(7)-N(2)-C(10)-C(9)	2.2(5)
Fe(1)-N(2)-C(10)-C(9)	-161.5(3)
C(8)-C(9)-C(10)-N(2)	-2.3(6)
C(8)-C(9)-C(10)-C(11)	172.4(5)
N(2)-C(10)-C(11)-C(12)	2.1(8)
C(9)-C(10)-C(11)-C(12)	-171.8(5)
N(2)-C(10)-C(11)-C(53)	-178.7(4)
C(9)-C(10)-C(11)-C(53)	7.4(7)
C(15)-N(3)-C(12)-C(11)	178.9(5)
Fe(1)-N(3)-C(12)-C(11)	-15.6(6)
C(15)-N(3)-C(12)-C(13)	0.6(5)
Fe(1)-N(3)-C(12)-C(13)	166.1(3)
C(10)-C(11)-C(12)-N(3)	-6.6(8)
C(53)-C(11)-C(12)-N(3)	174.3(4)
C(10)-C(11)-C(12)-C(13)	171.5(5)
C(53)-C(11)-C(12)-C(13)	-7.6(7)
N(3)-C(12)-C(13)-C(14)	0.6(6)
C(11)-C(12)-C(13)-C(14)	-177.7(5)
C(12)-C(13)-C(14)-C(15)	-1.5(5)
C(12)-N(3)-C(15)-C(16)	170.1(5)
Fe(1)-N(3)-C(15)-C(16)	5.3(7)
C(12)-N(3)-C(15)-C(14)	-1.5(5)
Fe(1)-N(3)-C(15)-C(14)	-166.4(3)
C(13)-C(14)-C(15)-N(3)	2.0(6)
C(13)-C(14)-C(15)-C(16)	-169.9(5)
N(3)-C(15)-C(16)-C(17)	-0.6(8)
C(14)-C(15)-C(16)-C(17)	170.0(5)
N(3)-C(15)-C(16)-C(71)	-177.0(4)
C(14)-C(15)-C(16)-C(71)	-6.4(7)
C(20)-N(4)-C(17)-C(16)	179.4(5)
Fe(1)-N(4)-C(17)-C(16)	-20.3(7)
C(20)-N(4)-C(17)-C(18)	-0.4(5)
Fe(1)-N(4)-C(17)-C(18)	159.9(3)
C(15)-C(16)-C(17)-N(4)	8.3(8)
C(71)-C(16)-C(17)-N(4)	-175.3(4)
C(15)-C(16)-C(17)-C(18)	-171.9(5)

C(71)-C(16)-C(17)-C(18)	4.5(7)
N(4)-C(17)-C(18)-C(19)	-2.6(6)
C(16)-C(17)-C(18)-C(19)	177.6(5)
C(17)-C(18)-C(19)-C(20)	4.2(6)
C(17)-N(4)-C(20)-C(1)	-171.4(5)
Fe(1)-N(4)-C(20)-C(1)	27.2(7)
C(17)-N(4)-C(20)-C(19)	3.1(5)
Fe(1)-N(4)-C(20)-C(19)	-158.4(3)
C(2)-C(1)-C(20)-N(4)	2.6(8)
C(21)-C(1)-C(20)-N(4)	-178.6(5)
C(2)-C(1)-C(20)-C(19)	-171.0(5)
C(21)-C(1)-C(20)-C(19)	7.8(7)
C(18)-C(19)-C(20)-N(4)	-4.7(6)
C(18)-C(19)-C(20)-C(1)	169.7(5)
C(20)-C(1)-C(21)-C(22)	73.9(6)
C(2)-C(1)-C(21)-C(22)	-107.2(6)
C(20)-C(1)-C(21)-C(26)	-105.5(6)
C(2)-C(1)-C(21)-C(26)	73.4(6)
C(26)-C(21)-C(22)-C(23)	-2.5(8)
C(1)-C(21)-C(22)-C(23)	178.0(5)
C(26)-C(21)-C(22)-N(5)	176.9(5)
C(1)-C(21)-C(22)-N(5)	-2.5(7)
C(27)-N(5)-C(22)-C(21)	-146.7(6)
C(27)-N(5)-C(22)-C(23)	32.8(9)
C(21)-C(22)-C(23)-C(24)	2.8(8)
N(5)-C(22)-C(23)-C(24)	-176.6(5)
C(22)-C(23)-C(24)-C(25)	-1.0(9)
C(23)-C(24)-C(25)-C(26)	-0.9(9)
C(24)-C(25)-C(26)-C(21)	1.1(8)
C(24)-C(25)-C(26)-N(6)	179.9(5)
C(22)-C(21)-C(26)-C(25)	0.6(7)
C(1)-C(21)-C(26)-C(25)	180.0(5)
C(22)-C(21)-C(26)-N(6)	-178.2(4)
C(1)-C(21)-C(26)-N(6)	1.2(7)
C(33)-N(6)-C(26)-C(25)	44.2(7)
C(33)-N(6)-C(26)-C(21)	-137.0(5)

C(22)-N(5)-C(27)-O(1)	-15.9(18)
C(22)-N(5)-C(27)-C(28)	164.1(6)
O(1)-C(27)-C(28)-C(29)	-5.1(19)
N(5)-C(27)-C(28)-C(29)	175.0(7)
O(1)-C(27)-C(28)-C(30)	62.5(18)
N(5)-C(27)-C(28)-C(30)	-117.5(7)
C(27)-C(28)-C(29)-C(30)	106.8(8)
C(28)-C(29)-C(30)-C(31)	102.1(8)
C(28)-C(29)-C(30)-C(32)	-109.3(8)
C(27)-C(28)-C(30)-C(31)	142.0(7)
C(29)-C(28)-C(30)-C(31)	-109.9(8)
C(27)-C(28)-C(30)-C(32)	-0.6(9)
C(29)-C(28)-C(30)-C(32)	107.4(8)
C(27)-C(28)-C(30)-C(29)	-108.1(8)
C(26)-N(6)-C(33)-O(2)	-4.2(8)
C(26)-N(6)-C(33)-C(34)	173.3(5)
O(2)-C(33)-C(34)-C(35)	-17.0(9)
N(6)-C(33)-C(34)-C(35)	165.5(5)
O(2)-C(33)-C(34)-C(36)	51.6(8)
N(6)-C(33)-C(34)-C(36)	-125.9(6)
C(33)-C(34)-C(35)-C(36)	109.4(6)
C(34)-C(35)-C(36)-C(38)	103.9(6)
C(34)-C(35)-C(36)-C(37)	-110.2(6)
C(33)-C(34)-C(36)-C(35)	-108.6(6)
C(33)-C(34)-C(36)-C(38)	141.3(6)
C(35)-C(34)-C(36)-C(38)	-110.0(7)
C(33)-C(34)-C(36)-C(37)	-1.5(9)
C(35)-C(34)-C(36)-C(37)	107.1(7)
C(5)-C(6)-C(39)-C(44)	118.4(5)
C(7)-C(6)-C(39)-C(44)	-60.8(6)
C(5)-C(6)-C(39)-C(40)	-62.0(6)
C(7)-C(6)-C(39)-C(40)	118.8(5)
C(44)-C(39)-C(40)-C(41)	0.2(8)
C(6)-C(39)-C(40)-C(41)	-179.5(5)
C(39)-C(40)-C(41)-C(42)	-0.6(8)
C(39)-C(40)-C(41)-C(45)	179.7(5)

C(40)-C(41)-C(42)-C(43)	0.6(9)
C(45)-C(41)-C(42)-C(43)	-179.7(6)
C(41)-C(42)-C(43)-C(44)	-0.1(10)
C(41)-C(42)-C(43)-C(49)	-178.3(6)
C(40)-C(39)-C(44)-C(43)	0.3(8)
C(6)-C(39)-C(44)-C(43)	179.9(5)
C(42)-C(43)-C(44)-C(39)	-0.3(9)
C(49)-C(43)-C(44)-C(39)	177.8(6)
C(42)-C(41)-C(45)-C(46)	158.9(11)
C(40)-C(41)-C(45)-C(46)	-21.4(13)
C(42)-C(41)-C(45)-C(47)	-79.1(12)
C(40)-C(41)-C(45)-C(47)	100.6(12)
C(42)-C(41)-C(45)-C(48)	37.8(13)
C(40)-C(41)-C(45)-C(48)	-142.5(11)
C(42)-C(43)-C(49)-C(50)	15.1(16)
C(44)-C(43)-C(49)-C(50)	-163.0(13)
C(42)-C(43)-C(49)-C(51)	-128.8(11)
C(44)-C(43)-C(49)-C(51)	53.1(13)
C(42)-C(43)-C(49)-C(52)	122.7(8)
C(44)-C(43)-C(49)-C(52)	-55.4(9)
C(12)-C(11)-C(53)-C(58)	-108.0(5)
C(10)-C(11)-C(53)-C(58)	72.8(6)
C(12)-C(11)-C(53)-C(54)	75.4(6)
C(10)-C(11)-C(53)-C(54)	-103.8(5)
C(58)-C(53)-C(54)-C(55)	-0.2(7)
C(11)-C(53)-C(54)-C(55)	176.4(5)
C(58)-C(53)-C(54)-N(7)	-179.6(4)
C(11)-C(53)-C(54)-N(7)	-3.0(7)
C(59)-N(7)-C(54)-C(55)	-1.6(8)
C(59)-N(7)-C(54)-C(53)	177.8(5)
C(53)-C(54)-C(55)-C(56)	0.4(8)
N(7)-C(54)-C(55)-C(56)	179.8(5)
C(54)-C(55)-C(56)-C(57)	-0.4(9)
C(55)-C(56)-C(57)-C(58)	0.1(9)
C(54)-C(53)-C(58)-C(57)	0.0(7)
C(11)-C(53)-C(58)-C(57)	-176.7(5)

C(54)-C(53)-C(58)-N(8)	180.0(4)
C(11)-C(53)-C(58)-N(8)	3.3(7)
C(56)-C(57)-C(58)-C(53)	0.1(8)
C(56)-C(57)-C(58)-N(8)	-179.9(5)
C(65)-N(8)-C(58)-C(53)	-126.8(5)
C(65)-N(8)-C(58)-C(57)	53.2(7)
C(54)-N(7)-C(59)-O(3)	-1.2(9)
C(54)-N(7)-C(59)-C(60)	178.5(5)
O(3)-C(59)-C(60)-C(61)	-22.6(9)
N(7)-C(59)-C(60)-C(61)	157.7(5)
O(3)-C(59)-C(60)-C(62)	45.7(9)
N(7)-C(59)-C(60)-C(62)	-134.1(6)
C(59)-C(60)-C(61)-C(62)	111.2(6)
C(60)-C(61)-C(62)-C(64)	-109.6(6)
C(60)-C(61)-C(62)-C(63)	104.7(6)
C(59)-C(60)-C(62)-C(61)	-106.9(6)
C(59)-C(60)-C(62)-C(64)	2.2(9)
C(61)-C(60)-C(62)-C(64)	109.0(7)
C(59)-C(60)-C(62)-C(63)	144.3(6)
C(61)-C(60)-C(62)-C(63)	-108.9(7)
C(58)-N(8)-C(65)-O(4)	-3.5(8)
C(58)-N(8)-C(65)-C(66)	177.3(5)
O(4)-C(65)-C(66)-C(67)	-9.0(8)
N(8)-C(65)-C(66)-C(67)	170.2(5)
O(4)-C(65)-C(66)-C(68)	59.1(8)
N(8)-C(65)-C(66)-C(68)	-121.7(5)
C(65)-C(66)-C(67)-C(68)	111.1(6)
C(66)-C(67)-C(68)-C(69)	-110.4(6)
C(66)-C(67)-C(68)-C(70)	104.3(6)
C(65)-C(66)-C(68)-C(67)	-106.2(6)
C(65)-C(66)-C(68)-C(69)	2.3(9)
C(67)-C(66)-C(68)-C(69)	108.6(7)
C(65)-C(66)-C(68)-C(70)	146.8(5)
C(67)-C(66)-C(68)-C(70)	-106.9(6)
C(17)-C(16)-C(71)-C(76)	-71.0(6)
C(15)-C(16)-C(71)-C(76)	105.7(5)

C(17)-C(16)-C(71)-C(72)	106.1(5)
C(15)-C(16)-C(71)-C(72)	-77.2(6)
C(76)-C(71)-C(72)-C(73)	0.1(7)
C(16)-C(71)-C(72)-C(73)	-177.0(4)
C(71)-C(72)-C(73)-C(74)	0.4(7)
C(71)-C(72)-C(73)-C(77)	179.9(4)
C(72)-C(73)-C(74)-C(75)	0.1(7)
C(77)-C(73)-C(74)-C(75)	-179.3(4)
C(73)-C(74)-C(75)-C(76)	-1.1(7)
C(73)-C(74)-C(75)-C(81)	177.9(5)
C(72)-C(71)-C(76)-C(75)	-1.2(7)
C(16)-C(71)-C(76)-C(75)	176.0(4)
C(74)-C(75)-C(76)-C(71)	1.6(7)
C(81)-C(75)-C(76)-C(71)	-177.4(4)
C(74)-C(73)-C(77)-C(78)	120.8(5)
C(72)-C(73)-C(77)-C(78)	-58.6(6)
C(74)-C(73)-C(77)-C(80)	1.0(7)
C(72)-C(73)-C(77)-C(80)	-178.5(4)
C(74)-C(73)-C(77)-C(79)	-118.8(5)
C(72)-C(73)-C(77)-C(79)	61.8(6)
C(76)-C(75)-C(81)-C(82)	-85.8(6)
C(74)-C(75)-C(81)-C(82)	95.2(6)
C(76)-C(75)-C(81)-C(83)	152.6(5)
C(74)-C(75)-C(81)-C(83)	-26.4(7)
C(76)-C(75)-C(81)-C(84)	33.7(7)
C(74)-C(75)-C(81)-C(84)	-145.3(5)
C(89)-N(9)-C(86)-C(85)	-179.1(5)
Fe(2)-N(9)-C(86)-C(85)	-11.4(7)
C(89)-N(9)-C(86)-C(87)	1.2(5)
Fe(2)-N(9)-C(86)-C(87)	168.8(3)
C(104)-C(85)-C(86)-N(9)	-12.2(8)
C(105)-C(85)-C(86)-N(9)	167.1(5)
C(104)-C(85)-C(86)-C(87)	167.6(5)
C(105)-C(85)-C(86)-C(87)	-13.2(8)
N(9)-C(86)-C(87)-C(88)	1.9(6)
C(85)-C(86)-C(87)-C(88)	-177.9(5)

C(86)-C(87)-C(88)-C(89)	-4.0(6)
C(86)-N(9)-C(89)-C(90)	169.6(5)
Fe(2)-N(9)-C(89)-C(90)	2.8(7)
C(86)-N(9)-C(89)-C(88)	-3.7(5)
Fe(2)-N(9)-C(89)-C(88)	-170.5(3)
C(87)-C(88)-C(89)-C(90)	-168.4(5)
C(87)-C(88)-C(89)-N(9)	4.9(6)
N(9)-C(89)-C(90)-C(91)	1.7(8)
C(88)-C(89)-C(90)-C(91)	173.9(5)
N(9)-C(89)-C(90)-C(123)	-178.7(4)
C(88)-C(89)-C(90)-C(123)	-6.5(8)
C(94)-N(10)-C(91)-C(90)	177.2(5)
Fe(2)-N(10)-C(91)-C(90)	-20.2(7)
C(94)-N(10)-C(91)-C(92)	-0.6(5)
Fe(2)-N(10)-C(91)-C(92)	162.0(3)
C(89)-C(90)-C(91)-N(10)	7.3(8)
C(123)-C(90)-C(91)-N(10)	-172.3(4)
C(89)-C(90)-C(91)-C(92)	-175.3(5)
C(123)-C(90)-C(91)-C(92)	5.1(8)
N(10)-C(91)-C(92)-C(93)	-0.3(6)
C(90)-C(91)-C(92)-C(93)	-178.1(5)
C(91)-C(92)-C(93)-C(94)	1.1(6)
C(91)-N(10)-C(94)-C(95)	-174.5(5)
Fe(2)-N(10)-C(94)-C(95)	21.9(7)
C(91)-N(10)-C(94)-C(93)	1.2(5)
Fe(2)-N(10)-C(94)-C(93)	-162.4(3)
C(92)-C(93)-C(94)-N(10)	-1.4(6)
C(92)-C(93)-C(94)-C(95)	174.3(5)
N(10)-C(94)-C(95)-C(96)	3.5(8)
C(93)-C(94)-C(95)-C(96)	-171.6(5)
N(10)-C(94)-C(95)-C(137)	-176.2(5)
C(93)-C(94)-C(95)-C(137)	8.7(7)
C(99)-N(11)-C(96)-C(95)	178.6(5)
Fe(2)-N(11)-C(96)-C(95)	-16.1(7)
C(99)-N(11)-C(96)-C(97)	0.8(5)
Fe(2)-N(11)-C(96)-C(97)	166.0(3)

C(94)-C(95)-C(96)-N(11)	-6.8(8)
C(137)-C(95)-C(96)-N(11)	172.9(4)
C(94)-C(95)-C(96)-C(97)	170.7(5)
C(137)-C(95)-C(96)-C(97)	-9.5(7)
N(11)-C(96)-C(97)-C(98)	0.8(6)
C(95)-C(96)-C(97)-C(98)	-177.0(5)
C(96)-C(97)-C(98)-C(99)	-2.0(6)
C(96)-N(11)-C(99)-C(100)	171.3(5)
Fe(2)-N(11)-C(99)-C(100)	6.8(7)
C(96)-N(11)-C(99)-C(98)	-2.0(5)
Fe(2)-N(11)-C(99)-C(98)	-166.5(3)
C(97)-C(98)-C(99)-N(11)	2.5(6)
C(97)-C(98)-C(99)-C(100)	-170.8(5)
N(11)-C(99)-C(100)-C(101)	-1.5(8)
C(98)-C(99)-C(100)-C(101)	170.9(5)
N(11)-C(99)-C(100)-C(155)	-176.9(4)
C(98)-C(99)-C(100)-C(155)	-4.5(7)
C(104)-N(12)-C(101)-C(100)	-179.6(5)
Fe(2)-N(12)-C(101)-C(100)	-18.4(7)
C(104)-N(12)-C(101)-C(102)	0.3(6)
Fe(2)-N(12)-C(101)-C(102)	161.4(4)
C(99)-C(100)-C(101)-N(12)	7.5(8)
C(155)-C(100)-C(101)-N(12)	-177.1(4)
C(99)-C(100)-C(101)-C(102)	-172.3(5)
C(155)-C(100)-C(101)-C(102)	3.1(8)
N(12)-C(101)-C(102)-C(103)	-2.3(6)
C(100)-C(101)-C(102)-C(103)	177.5(5)
C(101)-C(102)-C(103)-C(104)	3.2(6)
C(101)-N(12)-C(104)-C(85)	-173.3(5)
Fe(2)-N(12)-C(104)-C(85)	24.3(7)
C(101)-N(12)-C(104)-C(103)	1.8(6)
Fe(2)-N(12)-C(104)-C(103)	-160.6(4)
C(86)-C(85)-C(104)-N(12)	4.9(8)
C(105)-C(85)-C(104)-N(12)	-174.4(5)
C(86)-C(85)-C(104)-C(103)	-169.6(5)
C(105)-C(85)-C(104)-C(103)	11.2(8)

C(102)-C(103)-C(104)-N(12)	-3.2(6)
C(102)-C(103)-C(104)-C(85)	171.9(5)
C(86)-C(85)-C(105)-C(110)	79.2(6)
C(104)-C(85)-C(105)-C(110)	-101.5(6)
C(86)-C(85)-C(105)-C(106)	-101.6(6)
C(104)-C(85)-C(105)-C(106)	77.7(6)
C(110)-C(105)-C(106)-C(107)	-2.9(8)
C(85)-C(105)-C(106)-C(107)	177.9(5)
C(110)-C(105)-C(106)-N(13)	177.3(5)
C(85)-C(105)-C(106)-N(13)	-2.0(7)
C(111)-N(13)-C(106)-C(107)	32.9(9)
C(111)-N(13)-C(106)-C(105)	-147.2(6)
C(105)-C(106)-C(107)-C(108)	2.6(9)
N(13)-C(106)-C(107)-C(108)	-177.5(5)
C(106)-C(107)-C(108)-C(109)	-0.2(9)
C(107)-C(108)-C(109)-C(110)	-1.9(9)
C(108)-C(109)-C(110)-C(105)	1.6(8)
C(108)-C(109)-C(110)-N(14)	179.6(5)
C(106)-C(105)-C(110)-C(109)	0.7(8)
C(85)-C(105)-C(110)-C(109)	180.0(5)
C(106)-C(105)-C(110)-N(14)	-177.3(4)
C(85)-C(105)-C(110)-N(14)	1.9(7)
C(117)-N(14)-C(110)-C(109)	46.6(8)
C(117)-N(14)-C(110)-C(105)	-135.3(6)
C(106)-N(13)-C(111)-O(5)	5.1(18)
C(106)-N(13)-C(111)-C(112)	167.2(6)
O(5)-C(111)-C(112)-C(113)	-21.5(19)
N(13)-C(111)-C(112)-C(113)	176.0(7)
O(5)-C(111)-C(112)-C(114)	45.1(18)
N(13)-C(111)-C(112)-C(114)	-117.3(7)
C(111)-C(112)-C(113)-C(114)	106.9(9)
C(112)-C(113)-C(114)-C(115)	106.7(11)
C(112)-C(113)-C(114)-C(116)	-108.0(9)
C(111)-C(112)-C(114)-C(113)	-108.3(8)
C(111)-C(112)-C(114)-C(115)	132.9(12)
C(113)-C(112)-C(114)-C(115)	-118.8(14)

C(111)-C(112)-C(114)-C(116)	-1.0(12)
C(113)-C(112)-C(114)-C(116)	107.3(11)
C(110)-N(14)-C(117)-O(6)	-12.6(16)
C(110)-N(14)-C(117)-C(118)	174.4(5)
O(6)-C(117)-C(118)-C(119)	-5.5(17)
N(14)-C(117)-C(118)-C(119)	167.2(6)
O(6)-C(117)-C(118)-C(120)	64.0(16)
N(14)-C(117)-C(118)-C(120)	-123.3(6)
C(117)-C(118)-C(119)-C(120)	108.8(6)
C(118)-C(119)-C(120)-C(121)	-109.0(7)
C(118)-C(119)-C(120)-C(122)	104.3(7)
C(117)-C(118)-C(120)-C(119)	-110.0(6)
C(117)-C(118)-C(120)-C(121)	-3.3(10)
C(119)-C(118)-C(120)-C(121)	106.7(8)
C(117)-C(118)-C(120)-C(122)	140.9(7)
C(119)-C(118)-C(120)-C(122)	-109.1(7)
C(89)-C(90)-C(123)-C(124)	-59.3(6)
C(91)-C(90)-C(123)-C(124)	120.4(5)
C(89)-C(90)-C(123)-C(128)	121.5(5)
C(91)-C(90)-C(123)-C(128)	-58.8(7)
C(128)-C(123)-C(124)-C(125)	0.3(8)
C(90)-C(123)-C(124)-C(125)	-179.0(5)
C(123)-C(124)-C(125)-C(126)	-0.3(8)
C(123)-C(124)-C(125)-C(129)	-178.7(5)
C(124)-C(125)-C(126)-C(127)	0.7(9)
C(129)-C(125)-C(126)-C(127)	179.1(6)
C(125)-C(126)-C(127)-C(128)	-1.1(9)
C(125)-C(126)-C(127)-C(133)	-178.8(6)
C(124)-C(123)-C(128)-C(127)	-0.6(8)
C(90)-C(123)-C(128)-C(127)	178.6(5)
C(126)-C(127)-C(128)-C(123)	1.0(8)
C(133)-C(127)-C(128)-C(123)	178.8(5)
C(126)-C(125)-C(129)-C(131)	-93.2(9)
C(124)-C(125)-C(129)-C(131)	85.1(8)
C(126)-C(125)-C(129)-C(130)	138.4(9)
C(124)-C(125)-C(129)-C(130)	-43.4(10)

C(126)-C(125)-C(129)-C(132)	17.8(9)
C(124)-C(125)-C(129)-C(132)	-163.9(7)
C(126)-C(127)-C(133)-C(134)	-13.0(12)
C(128)-C(127)-C(133)-C(134)	169.3(9)
C(126)-C(127)-C(133)-C(135)	115.6(9)
C(128)-C(127)-C(133)-C(135)	-62.0(10)
C(126)-C(127)-C(133)-C(136)	-130.1(8)
C(128)-C(127)-C(133)-C(136)	52.2(9)
C(94)-C(95)-C(137)-C(138)	71.6(6)
C(96)-C(95)-C(137)-C(138)	-108.1(5)
C(94)-C(95)-C(137)-C(142)	-109.1(6)
C(96)-C(95)-C(137)-C(142)	71.1(6)
C(142)-C(137)-C(138)-C(139)	-0.5(7)
C(95)-C(137)-C(138)-C(139)	178.8(5)
C(142)-C(137)-C(138)-N(16)	-178.9(4)
C(95)-C(137)-C(138)-N(16)	0.4(7)
C(143)-N(16)-C(138)-C(139)	43.4(8)
C(143)-N(16)-C(138)-C(137)	-138.2(5)
C(137)-C(138)-C(139)-C(140)	0.1(8)
N(16)-C(138)-C(139)-C(140)	178.6(5)
C(138)-C(139)-C(140)-C(141)	0.6(9)
C(139)-C(140)-C(141)-C(142)	-1.1(9)
C(140)-C(141)-C(142)-C(137)	0.8(8)
C(140)-C(141)-C(142)-N(15)	-179.5(5)
C(138)-C(137)-C(142)-C(141)	0.0(7)
C(95)-C(137)-C(142)-C(141)	-179.3(5)
C(138)-C(137)-C(142)-N(15)	-179.7(4)
C(95)-C(137)-C(142)-N(15)	1.0(7)
C(149)-N(15)-C(142)-C(141)	30.0(8)
C(149)-N(15)-C(142)-C(137)	-150.3(5)
C(138)-N(16)-C(143)-O(8)	0.4(9)
C(138)-N(16)-C(143)-C(144)	178.9(5)
O(8)-C(143)-C(144)-C(145)	-8.8(9)
N(16)-C(143)-C(144)-C(145)	172.8(5)
O(8)-C(143)-C(144)-C(146)	59.1(8)
N(16)-C(143)-C(144)-C(146)	-119.4(6)

C(143)-C(144)-C(145)-C(146)	111.3(6)
C(144)-C(145)-C(146)-C(148)	-108.8(6)
C(144)-C(145)-C(146)-C(147)	104.5(7)
C(143)-C(144)-C(146)-C(145)	-105.8(6)
C(143)-C(144)-C(146)-C(148)	2.8(9)
C(145)-C(144)-C(146)-C(148)	108.6(7)
C(143)-C(144)-C(146)-C(147)	145.0(6)
C(145)-C(144)-C(146)-C(147)	-109.1(7)
C(142)-N(15)-C(149)-O(7)	-13.0(9)
C(142)-N(15)-C(149)-C(150)	166.1(5)
O(7)-C(149)-C(150)-C(151)	-12.5(8)
N(15)-C(149)-C(150)-C(151)	168.5(5)
O(7)-C(149)-C(150)-C(152)	57.0(8)
N(15)-C(149)-C(150)-C(152)	-122.1(5)
C(149)-C(150)-C(151)-C(152)	109.1(6)
C(150)-C(151)-C(152)-C(153)	-108.9(6)
C(150)-C(151)-C(152)-C(154)	105.0(6)
C(149)-C(150)-C(152)-C(153)	0.0(8)
C(151)-C(150)-C(152)-C(153)	109.0(6)
C(149)-C(150)-C(152)-C(151)	-109.0(6)
C(149)-C(150)-C(152)-C(154)	142.7(5)
C(151)-C(150)-C(152)-C(154)	-108.4(6)
C(101)-C(100)-C(155)-C(156)	-87.0(6)
C(99)-C(100)-C(155)-C(156)	88.7(6)
C(101)-C(100)-C(155)-C(160)	90.4(6)
C(99)-C(100)-C(155)-C(160)	-93.9(6)
C(160)-C(155)-C(156)-C(157)	0.3(7)
C(100)-C(155)-C(156)-C(157)	177.7(4)
C(155)-C(156)-C(157)-C(158)	0.3(7)
C(155)-C(156)-C(157)-C(161)	178.7(5)
C(156)-C(157)-C(158)-C(159)	-0.6(7)
C(161)-C(157)-C(158)-C(159)	-178.9(5)
C(157)-C(158)-C(159)-C(160)	0.2(7)
C(157)-C(158)-C(159)-C(165)	178.2(5)
C(156)-C(155)-C(160)-C(159)	-0.8(7)
C(100)-C(155)-C(160)-C(159)	-178.2(4)

C(158)-C(159)-C(160)-C(155)	0.5(7)
C(165)-C(159)-C(160)-C(155)	-177.6(4)
C(158)-C(157)-C(161)-C(162)	-138.6(15)
C(156)-C(157)-C(161)-C(162)	43.2(15)
C(158)-C(157)-C(161)-C(164)	-14.4(14)
C(156)-C(157)-C(161)-C(164)	167.3(13)
C(158)-C(157)-C(161)-C(163)	100.6(14)
C(156)-C(157)-C(161)-C(163)	-77.6(15)
C(158)-C(159)-C(165)-C(168)	129.1(5)
C(160)-C(159)-C(165)-C(168)	-52.9(6)
C(158)-C(159)-C(165)-C(166)	-110.5(5)
C(160)-C(159)-C(165)-C(166)	67.5(6)
C(158)-C(159)-C(165)-C(167)	8.7(7)
C(160)-C(159)-C(165)-C(167)	-173.3(5)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for C84H96ClFeN8O4 ([Fe(P2)Cl]) [Å and º]

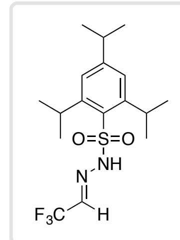
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6N)...O(4)#1	0.88	2.01	2.882(5)	170.3
N(14)-H(14N)...O(8)#2	0.88	2.05	2.884(6)	157.5

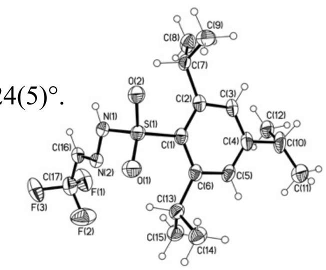
Symmetry transformations used to generate equivalent atoms:

#1 x-y,x-1,z-1/6   #2 x-y+1,x+1,z-1/6

Table S8. Crystal data and structure refinement for C17H25F3N2O2S (1)

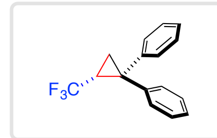
CCDC: 2128686



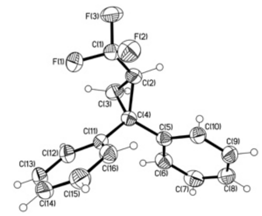


Identification code	C17H25F3N2O2S	
Empirical formula	C17 H25 F3 N2 O2 S	
Formula weight	378.45	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 16.6602(10) Å	α= 90°.
	b = 5.9607(5) Å	β= 92.424(5)°.
	c = 19.8051(12) Å	γ = 90°.
Volume	1965.0(2) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	1.824 mm^{-1}	
F(000)	800	
Crystal size	0.520 x 0.140 x 0.100 mm^3	
Theta range for data collection	2.233 to 66.883°.	
Index ranges	-19<=h<=19, -6<=k<=7, -23<=l<=17	
Reflections collected	9844	
Independent reflections	5941 [R(int) = 0.0562]	
Completeness to theta = 66.883°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5512	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5941 / 394 / 493	
Goodness-of-fit on F^2	0.976	
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1398	
R indices (all data)	R1 = 0.0692, wR2 = 0.1480	
Absolute structure parameter	0.04(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.326 and -0.336 e.$Å^{-3}$	

Table S9. Crystal data and structure refinement for C16H13F3 (3n)

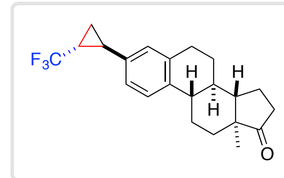


CCDC: 2128688

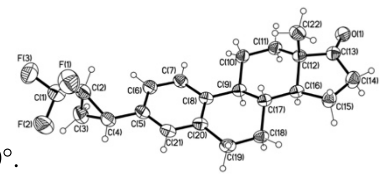


Identification code	C16H13F3	
Empirical formula	C16 H13 F3	
Formula weight	262.26	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.5726(4) Å	α= 90°.
	b = 6.4407(3) Å	β= 104.8920(10)°.
	c = 12.4882(5) Å	γ = 90°.
Volume	666.36(5) Å^3	
Z	2	
Density (calculated)	1.307 Mg/m^3	
Absorption coefficient	0.883 mm^{-1}	
F(000)	272	
Crystal size	0.420 x 0.160 x 0.120 mm^3	
Theta range for data collection	3.662 to 66.716°.	
Index ranges	-10<=h<=10, -7<=k<=7, -14<=l<=14	
Reflections collected	21888	
Independent reflections	2333 [R(int) = 0.0276]	
Completeness to theta = 66.716°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6551	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2333 / 1 / 172	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0718	
R indices (all data)	R1 = 0.0280, wR2 = 0.0722	
Absolute structure parameter	0.06(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.092 and -0.174 e.Å^{-3}	

Table S10. Crystal data and structure refinement for C22H25F3O (3ac)

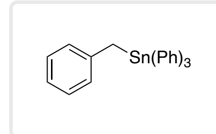


CCDC: 2128687

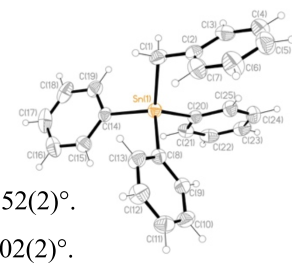


Identification code	C22H25F3O	
Empirical formula	C22 H25 F3 O	
Formula weight	362.42	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.3887(8) Å	α= 90°.
	b = 6.2200(5) Å	β= 94.562(5)°.
	c = 12.9743(10) Å	γ = 90°.
Volume	916.16(12) Å^3	
Z	2	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.828 mm^{-1}	
F(000)	384	
Crystal size	0.460 x 0.340 x 0.120 mm^3	
Theta range for data collection	3.417 to 66.679°.	
Index ranges	-13<=h<=12, -7<=k<=7, -15<=l<=15	
Reflections collected	22920	
Independent reflections	3198 [R(int) = 0.0385]	
Completeness to theta = 66.679°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3198 / 1 / 235	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0841	
R indices (all data)	R1 = 0.0341, wR2 = 0.0875	
Absolute structure parameter	-0.06(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.139 and -0.154 e.Å^{-3}	

Table S11. Crystal data and structure refinement for C25H22Sn (8')

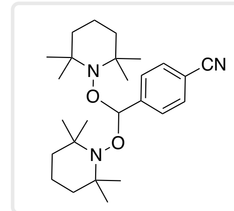


CCDC: 2128689



Identification code	C25H22Sn	
Empirical formula	C25 H22 Sn	
Formula weight	441.11	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8972(5) Å	α= 102.852(2)°.
	b = 10.6653(6) Å	β= 103.602(2)°.
	c = 11.2929(6) Å	γ = 111.8350(10)°.
Volume	1010.05(9) Å^3	
Z	2	
Density (calculated)	1.450 Mg/m^3	
Absorption coefficient	10.071 mm^{-1}	
F(000)	444	
Crystal size	0.380 x 0.140 x 0.050 mm^3	
Theta range for data collection	4.289 to 66.672°.	
Index ranges	-11<=h<=11, -12<=k<=12, -13<=l<=12	
Reflections collected	16699	
Independent reflections	3538 [R(int) = 0.0382]	
Completeness to theta = 66.672°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.3038	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3538 / 0 / 235	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0610	
R indices (all data)	R1 = 0.0243, wR2 = 0.0619	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.496 and -0.423 e.Å^{-3}	

Table S12. Crystal data and structure refinement for C26H41N3O2 (9)



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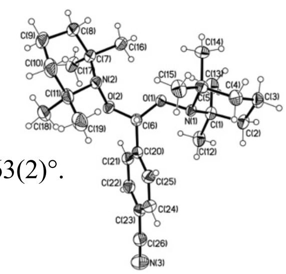


Identification code	C26H41N3O2	
Empirical formula	C26 H41 N3 O2	
Formula weight	427.62	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.2817(8) Å	α= 90°.
	b = 12.4152(7) Å	β= 102.863(2)°.
	c = 13.8340(7) Å	γ = 90°.
Volume	2558.8(2) $Å^3$	
Z	4	
Density (calculated)	1.110 Mg/m^3	
Absorption coefficient	0.546 mm^{-1}	
F(000)	936	
Crystal size	0.440 x 0.360 x 0.180 mm^3	
Theta range for data collection	2.966 to 66.395°.	
Index ranges	-18<=h<=17, -14<=k<=14, -16<=l<=16	
Reflections collected	24383	
Independent reflections	4416 [R(int) = 0.0252]	
Completeness to theta = 66.395°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6841	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4416 / 0 / 288	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0921	
R indices (all data)	R1 = 0.0400, wR2 = 0.0957	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.168 and -0.175 e.$Å^{-3}$	

8. DFT Calculations

Considering the cost of time and computing resources for the large system with [Fe(**P3**)Cl], the geometry optimizations were performed with the Gaussian 16[8] at the BP86[9,10]/def2-SVP[11,12] level of theory in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency).

Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy and thermal corrections (entropy and enthalpy, 298.15 K, 1 atm) were obtained from these calculations. Intrinsic reaction coordinate (IRC) calculations were performed with local quadratic approximation (LQA)[13,14] method to ensure the transition states found connected the reactant and the product. To further improve the accuracy of energies, single point energies were carried out at the TPSSh[15]/def2-tzvp[13,14] level of theory along with Grimme's dispersion correction[16] (D3BJ) and SMD[17] solvation model (in *n*-hexane).

Independent Gradient Model (IGM)[18] analysis was performed with Multiwfn[19] software package using high quality grid option to generate files for further plotting. The visualization of IGM analysis results were presented with VMD[20] visualization software. As shown in Scheme SX, the 3D diagrams of optimized structures were generated with CYLview software[21], and the NCI (noncovalent interaction) visual representations and spin density isosurface map of optimized structures were generated with VMD.

Figure S36: Calculated Energy Diagram for Radical Cyclopropanation of Styrene (**2a**) with Diazo (**1'**) by [Fe(**P3**)Cl]

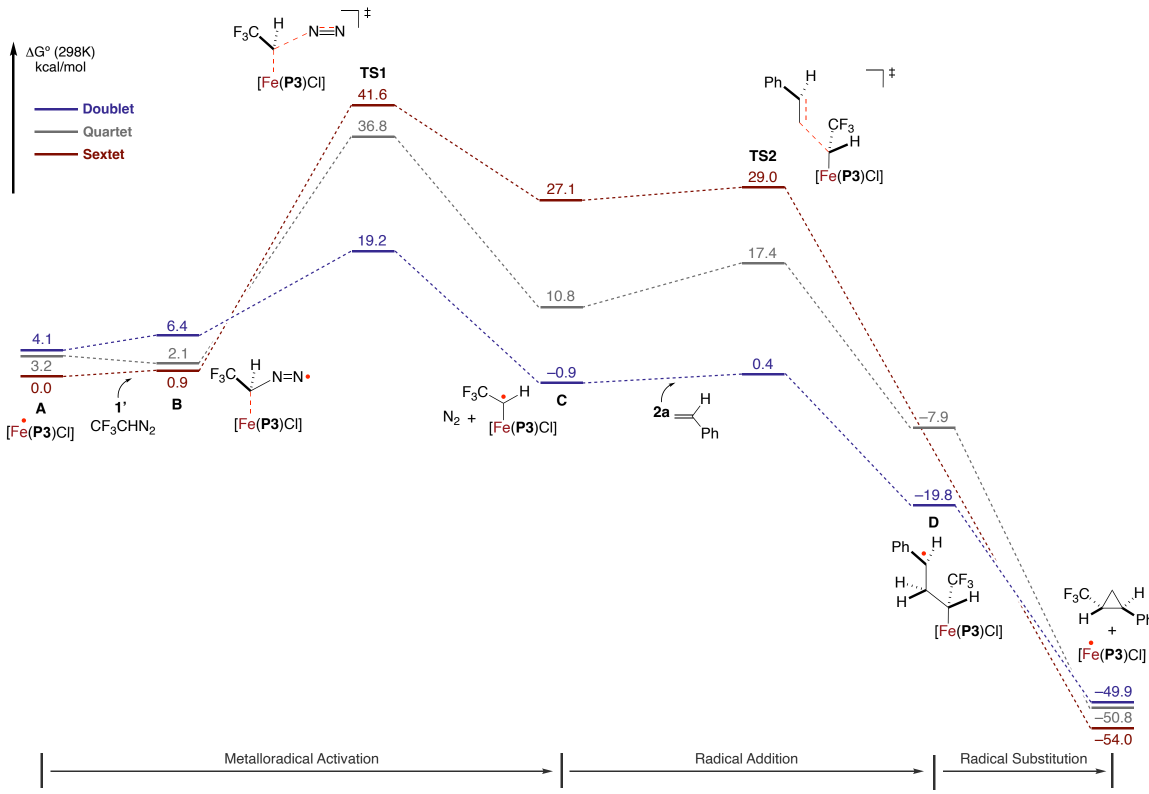
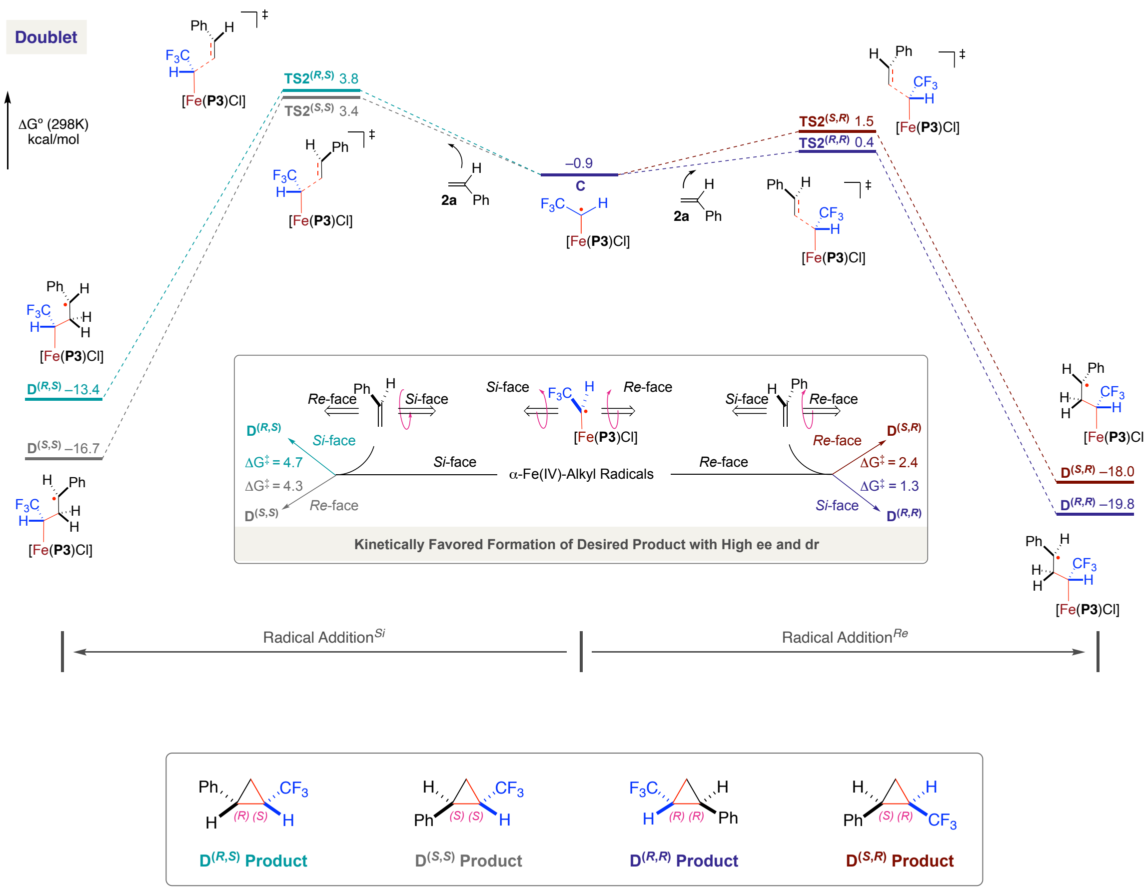


Figure S37: Calculated Energy Diagram for Enantioselectivity and Diastereoselectivity on Radical Cyclopropanation of Styrene (**2a**) with Diazo (**1’**) by [Fe(**P3**)Cl]



D$^{(R,R)}$: *Re*-face of intermediate **C** undergoes radical addition to *Si*-face of **2a**

D$^{(S,S)}$: *Si*-face of intermediate **C** undergoes radical addition to *Re*-face of **2a**

D$^{(S,R)}$: *Re*-face of intermediate **C** undergoes radical addition to *Re*-face of **2a**

D$^{(R,S)}$: *Si*-face of intermediate **C** undergoes radical addition to *Si*-face of **2a**

The following radical substitution steps of four intermediates (**D)** are all barrierless.

Figure S38: Calculated Energy Diagram for Cyclopropanation of Styrene (**2a**) with Diazo (**1’**) by [Fe(**P3**)Cl] through Radical Stepwise and Concerted Pathway

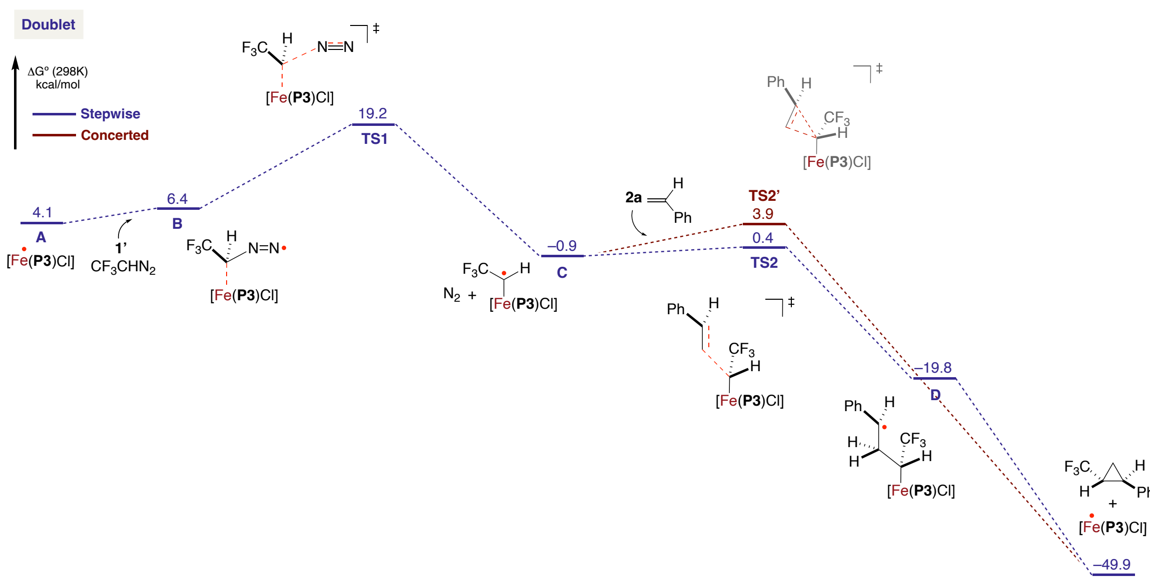
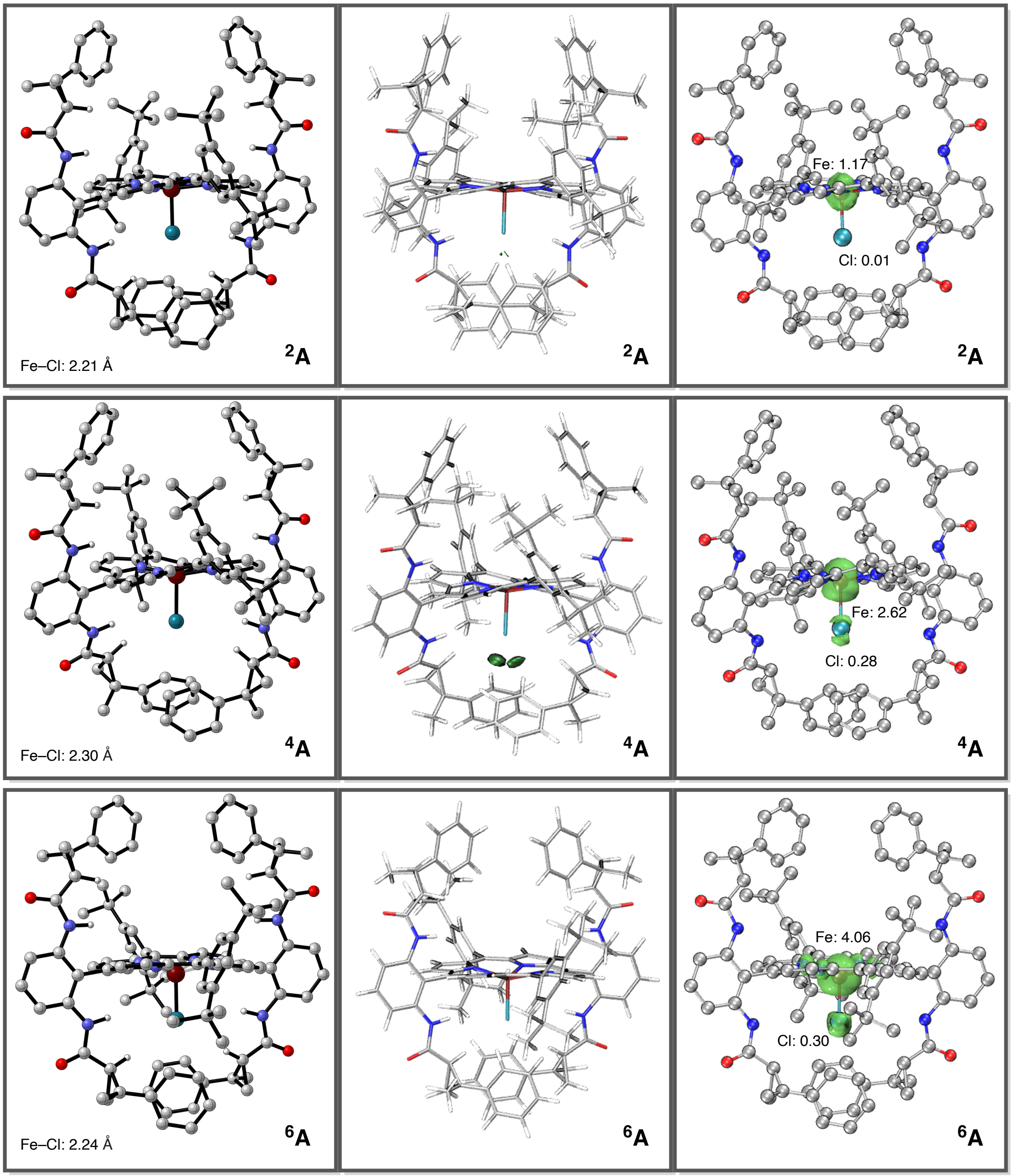
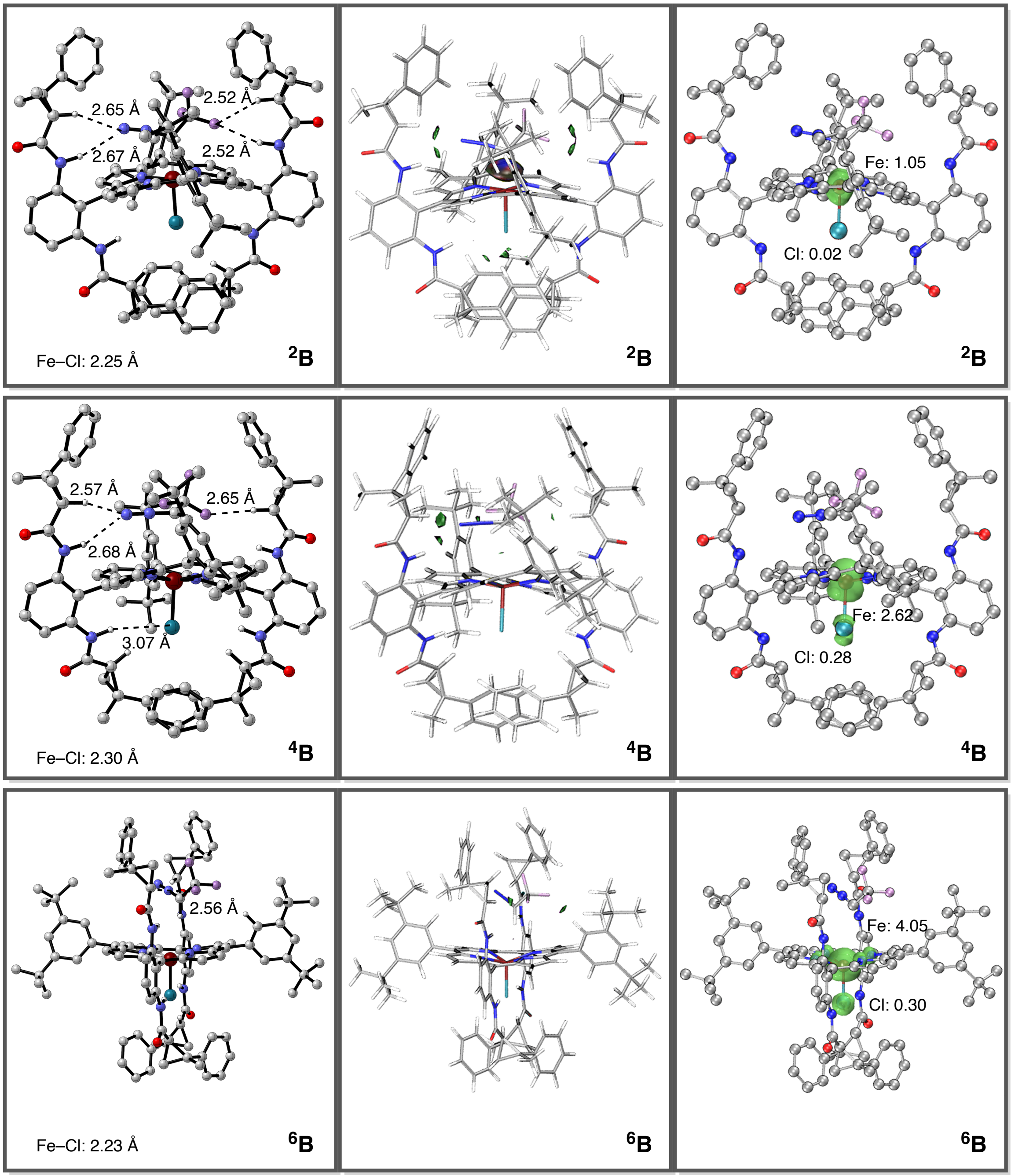


Figure S39: Optimized Structure Models, NCI Visual Representation and Spin Density Representation of Intermediates and Transition States (with **1’**)

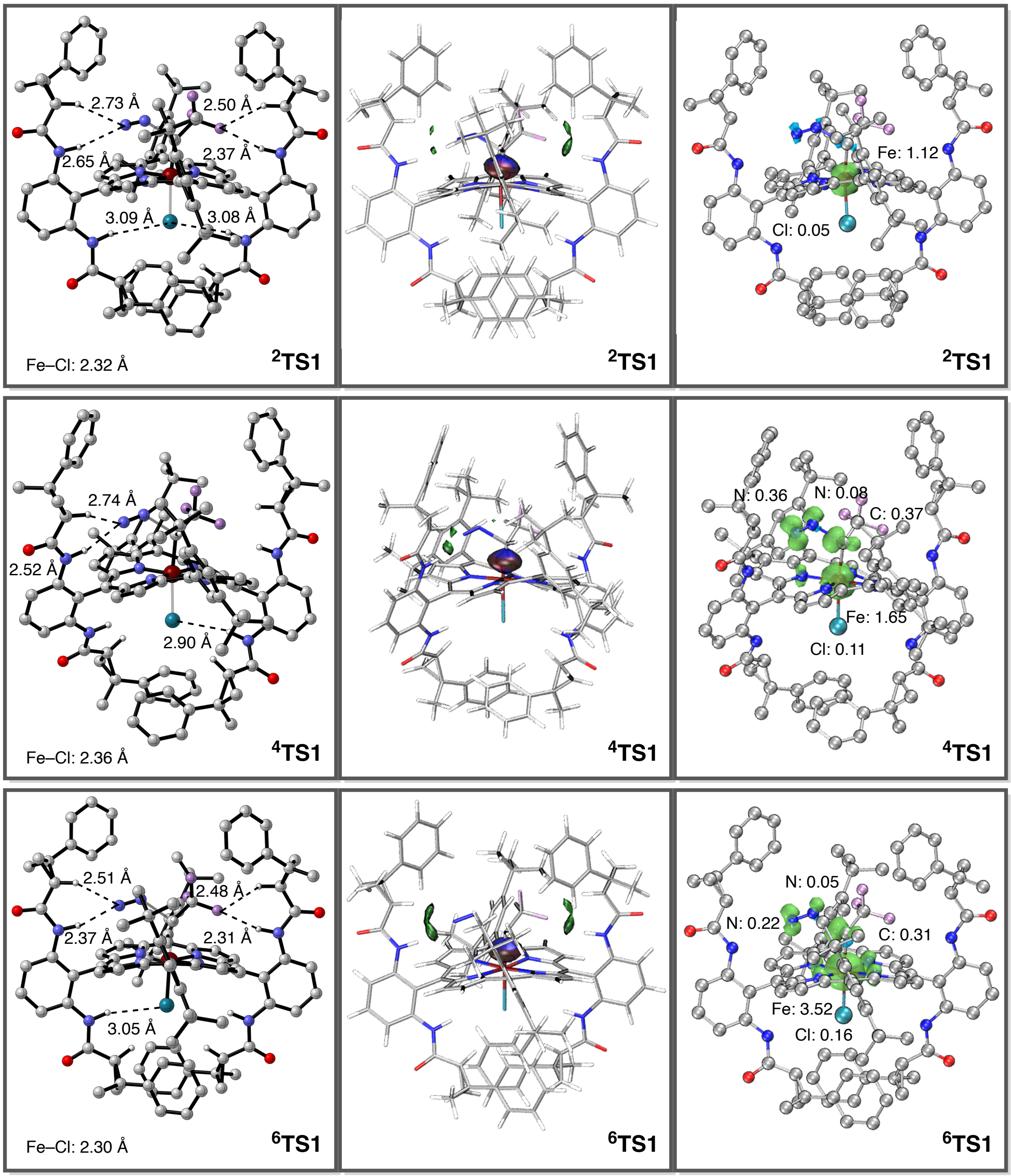
Catalyst [Fe(P3)Cl]



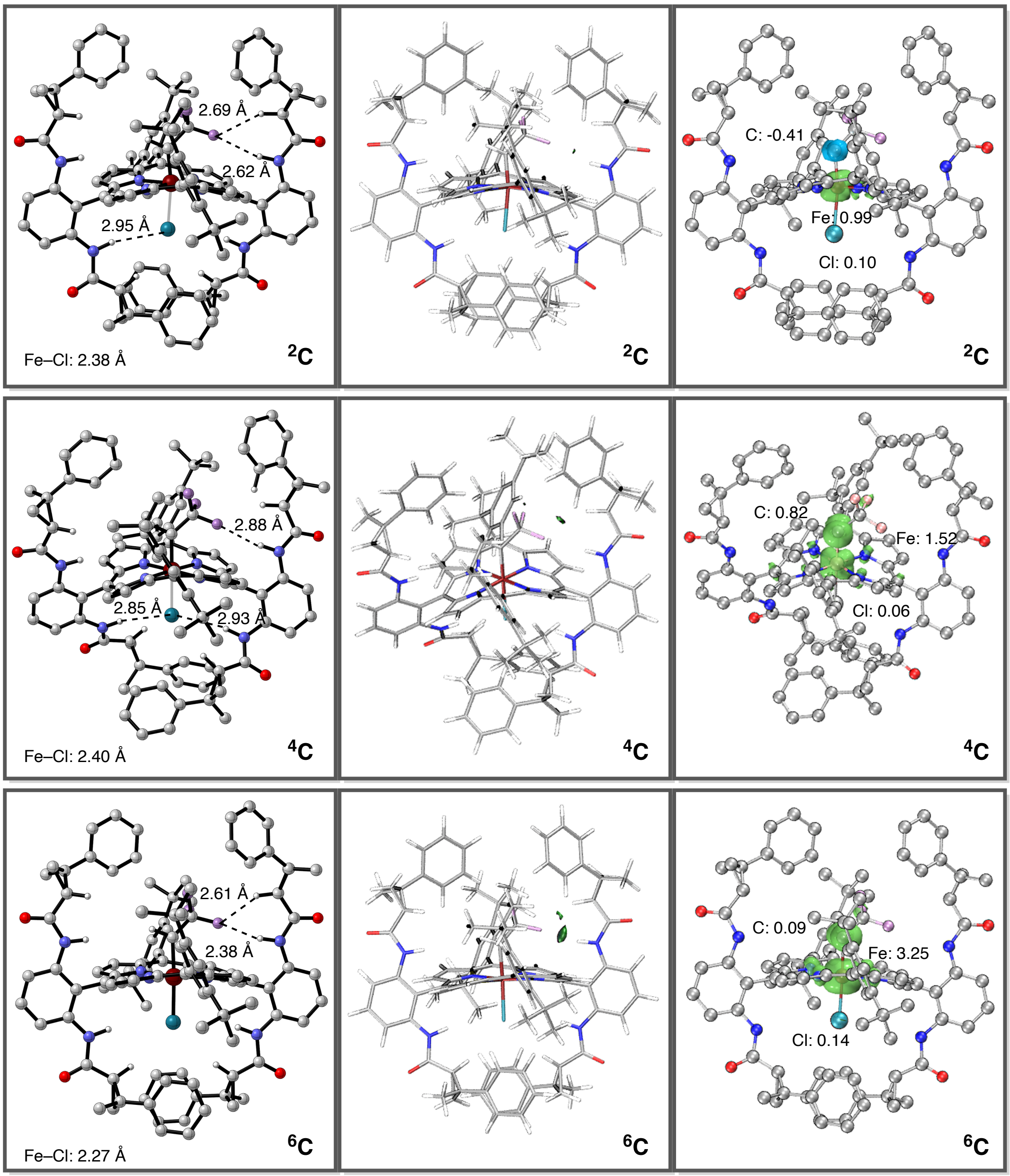
Intermediate B



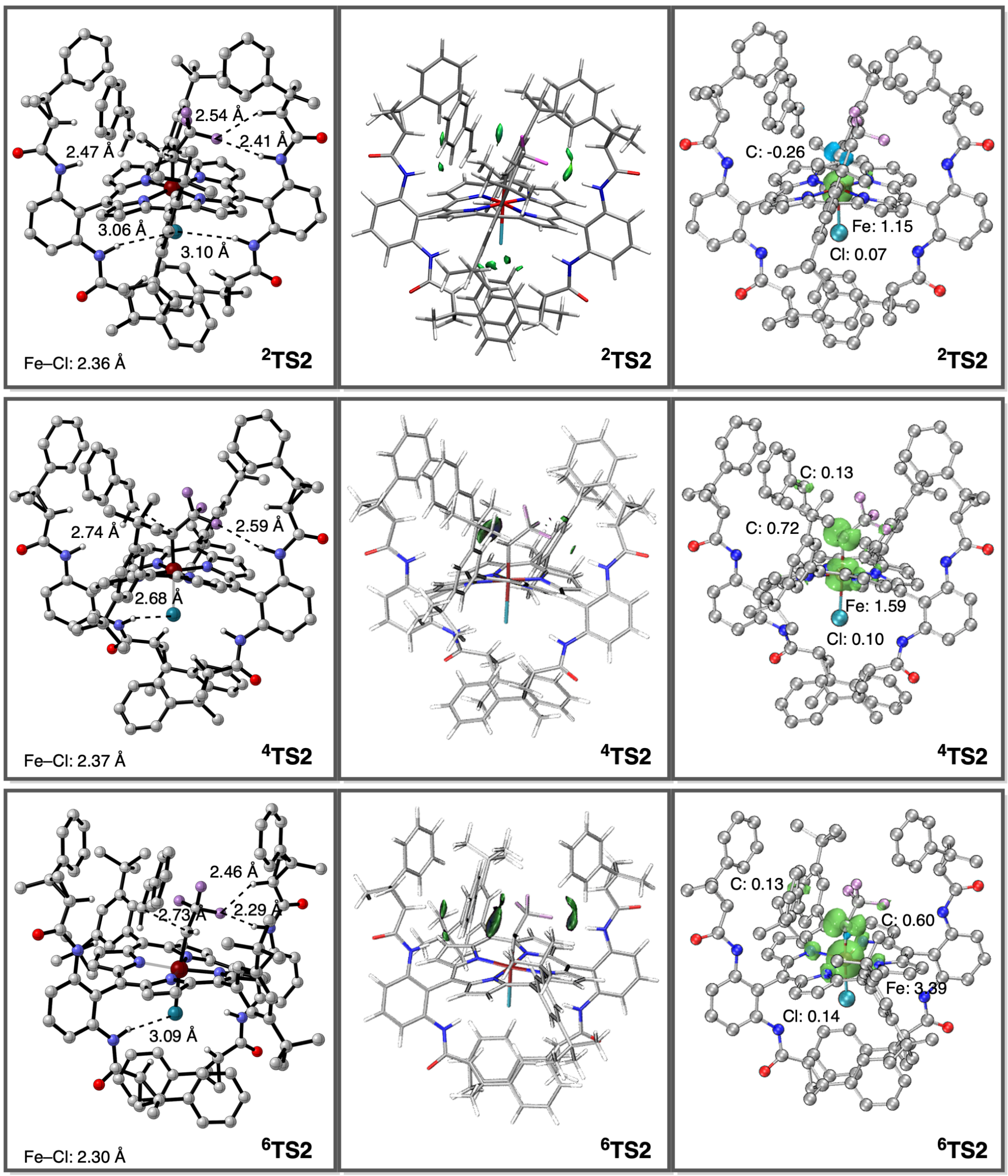
Transition State 1



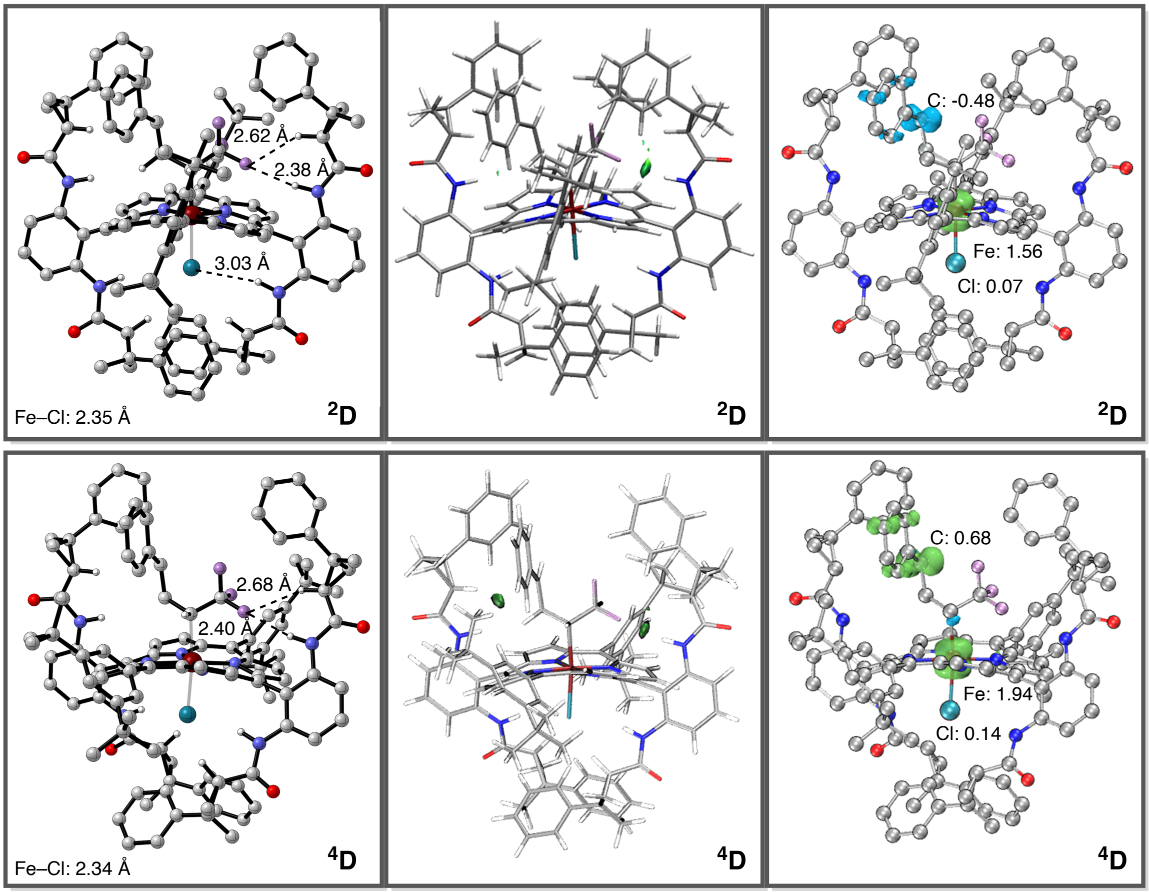
Intermediate C



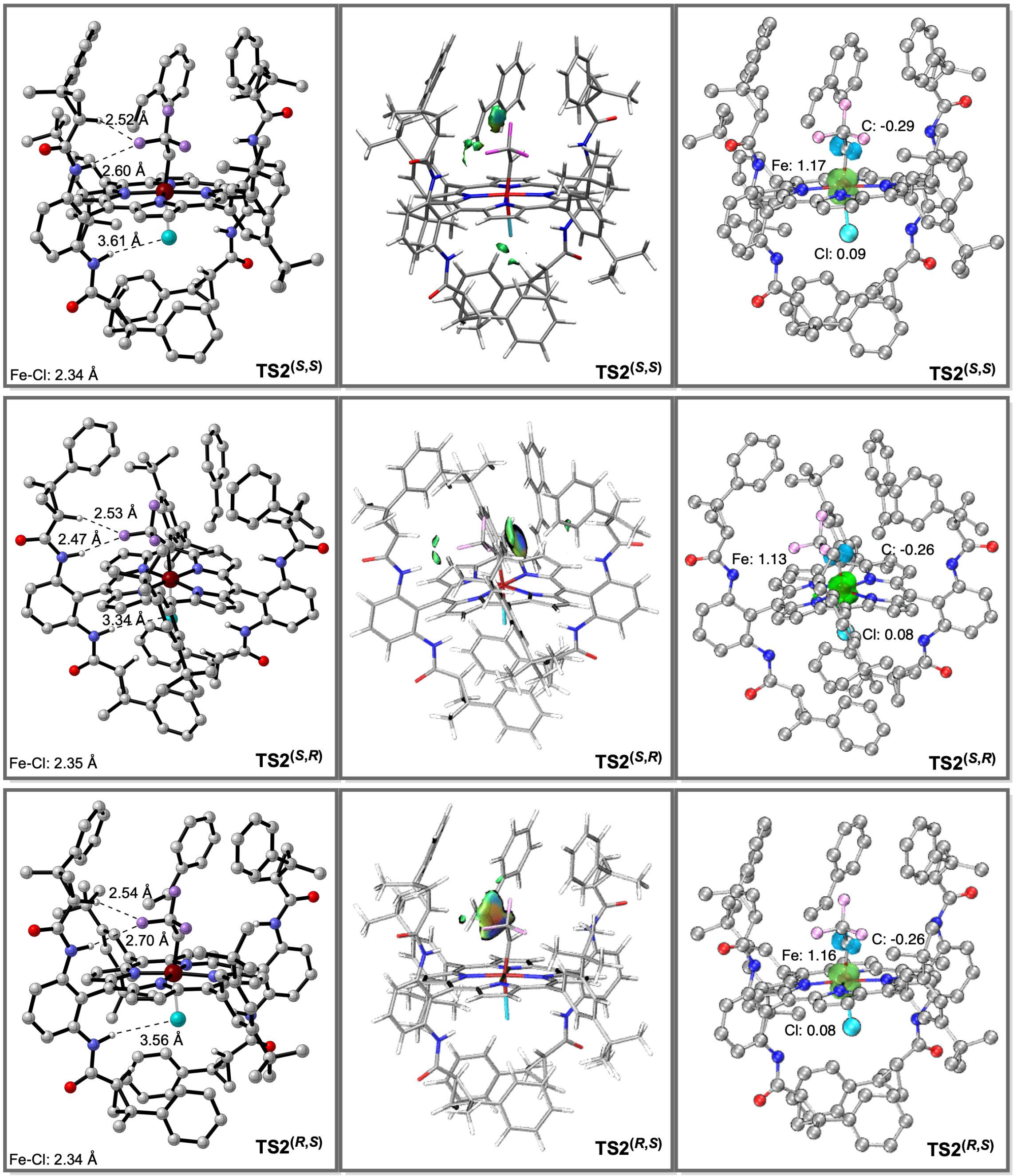
Transition State 2



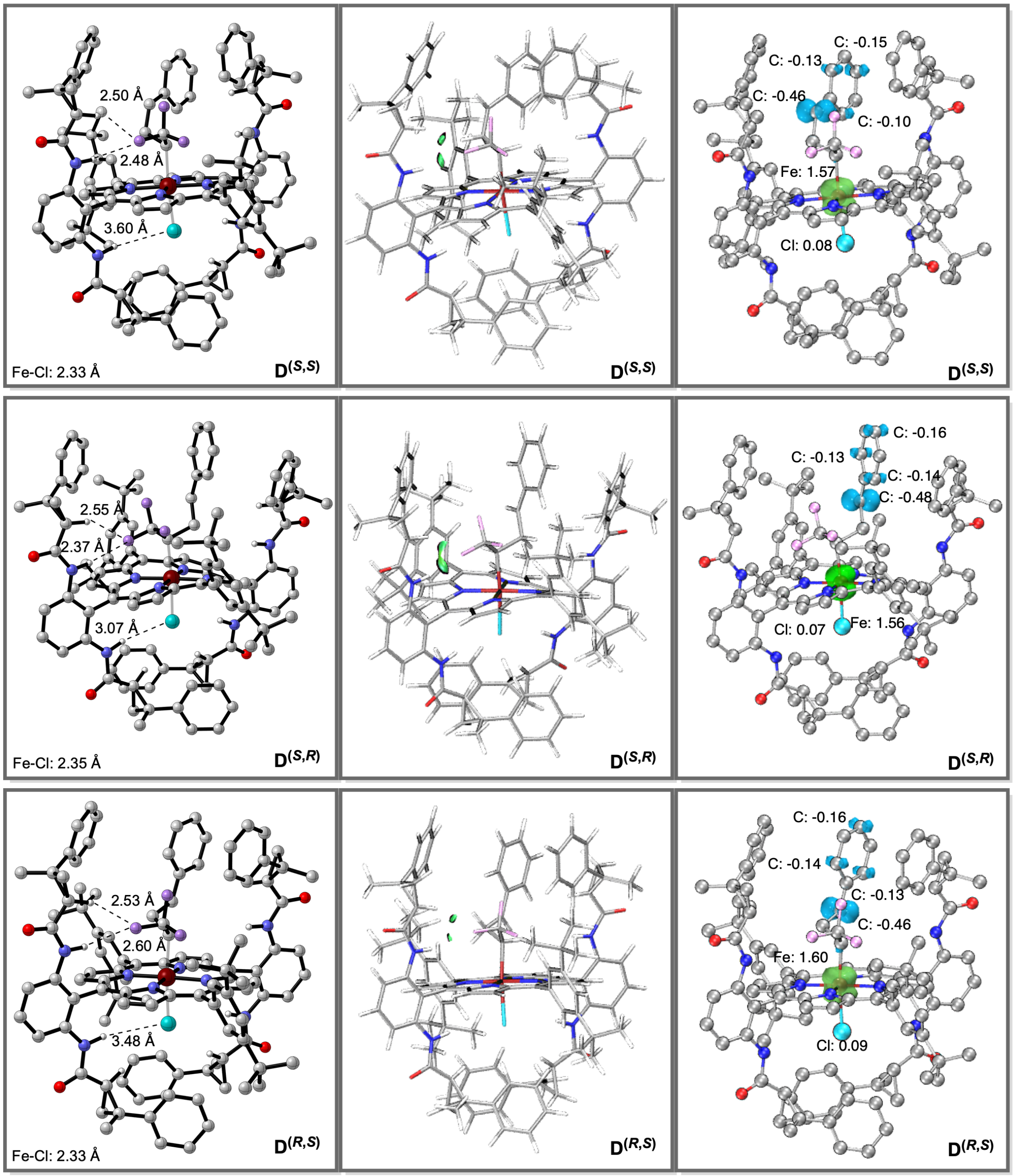
Intermediate D



Transition State 2



Intermediate D



Transition State 2’

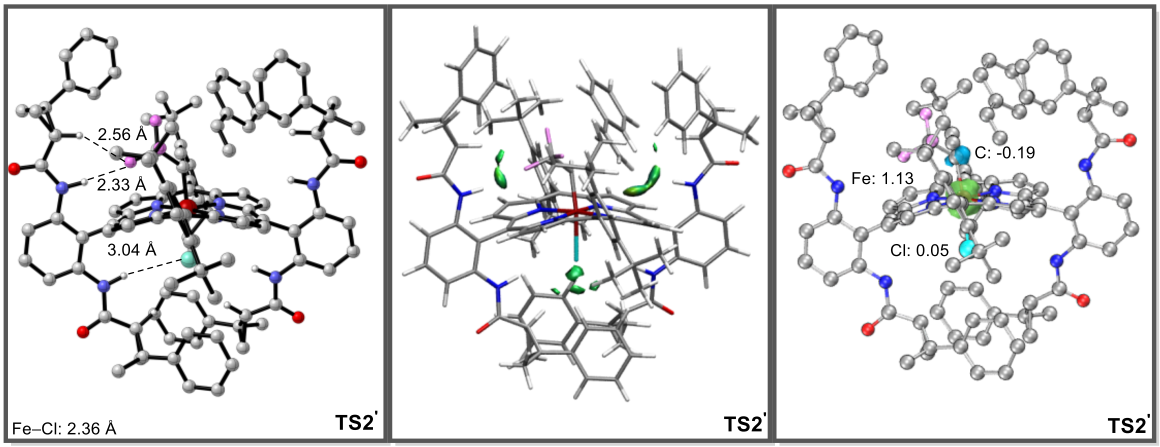


Figure S40: Calculated Energy Diagram for Cyclopropanation of Styrene (**2a**) with Diazo (**4b**) by [Fe(**P3**)Cl] through Radical Stepwise and Concerted Pathway

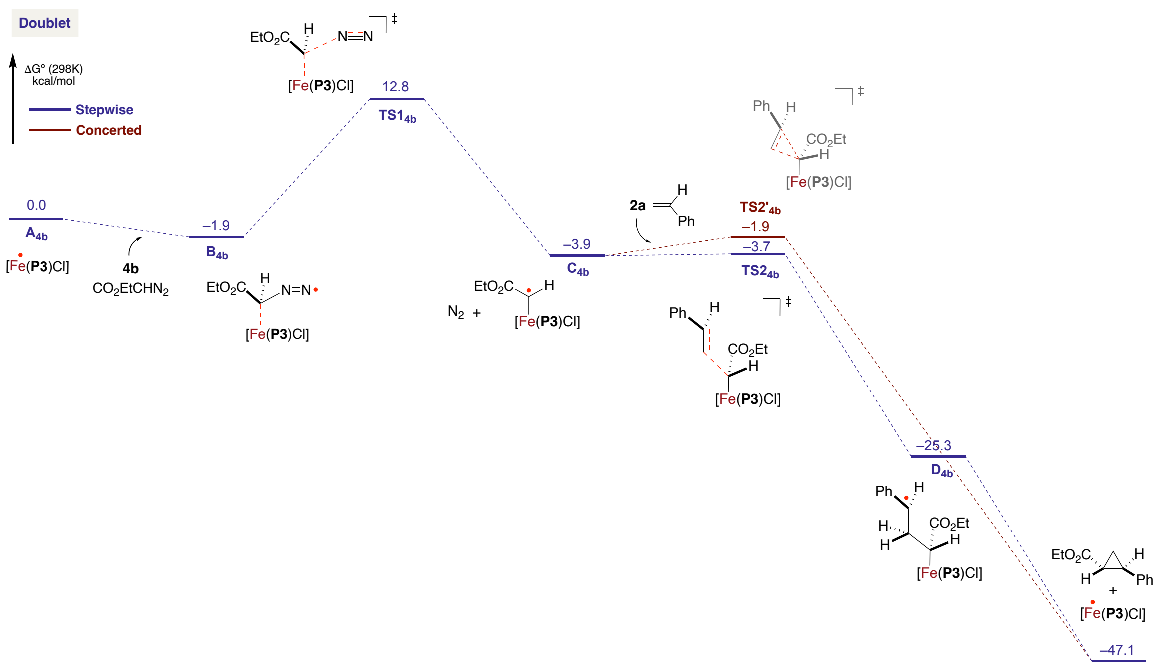
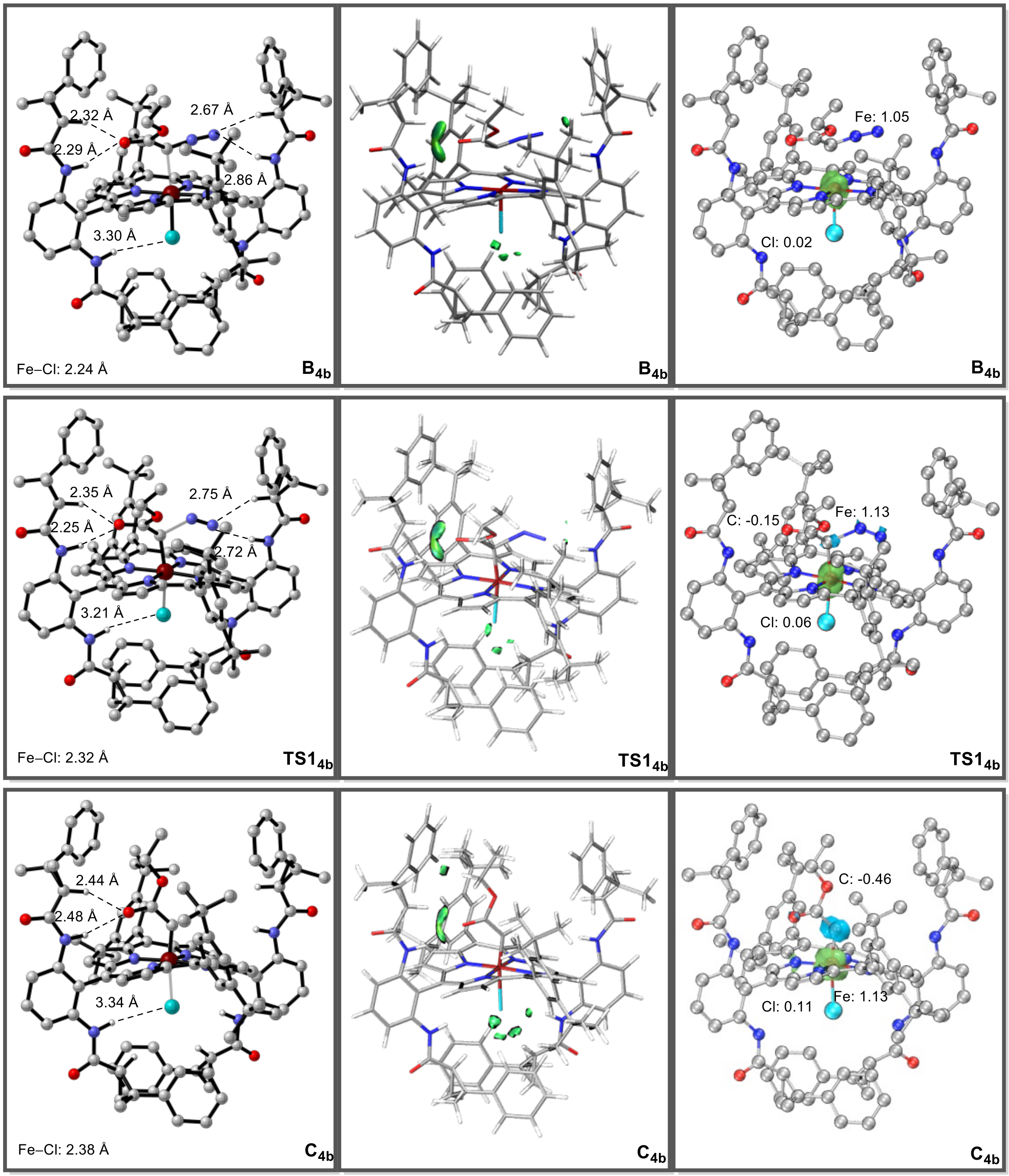
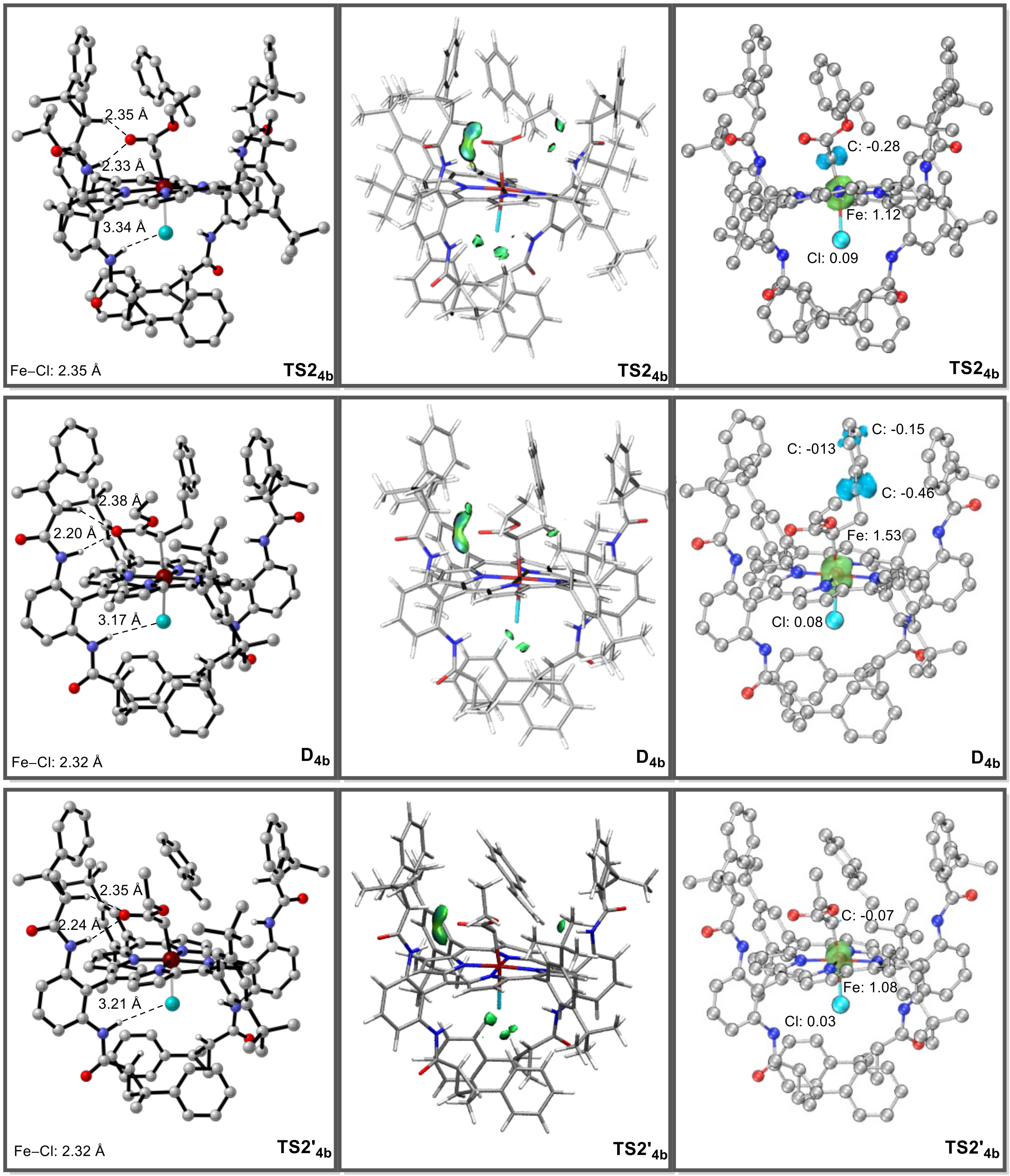


Figure S41: Optimized Structure Models, NCI Visual Representation and Spin Density Representation of Intermediates and Transition States (with **4b**)





2.35 Å
2.33 Å
3.34 Å
Fe–Cl: 2.35 Å
TS2$_{4b}$
TS2$_{4b}$
C: -0.28
Fe: 1.12
Cl: 0.09
TS2$_{4b}$
2.38 Å
2.20 Å
3.17 Å
Fe–Cl: 2.32 Å
D$_{4b}$
D$_{4b}$
C: -0.15
C: -013
C: -0.46
Fe: 1.53
Cl: 0.08
D$_{4b}$
2.35 Å
2.24 Å
3.21 Å
Fe–Cl: 2.32 Å
TS2'$_{4b}$
TS2'$_{4b}$
C: -0.07
Fe: 1.08
Cl: 0.03
TS2'$_{4b}$

Figure S42: Calculated Energy Diagram for Cyclopropanation of Styrene (**2a**) with Diazo (**4l'**) by [Fe(**P3**)Cl] through Radical Stepwise and Concerted Pathway

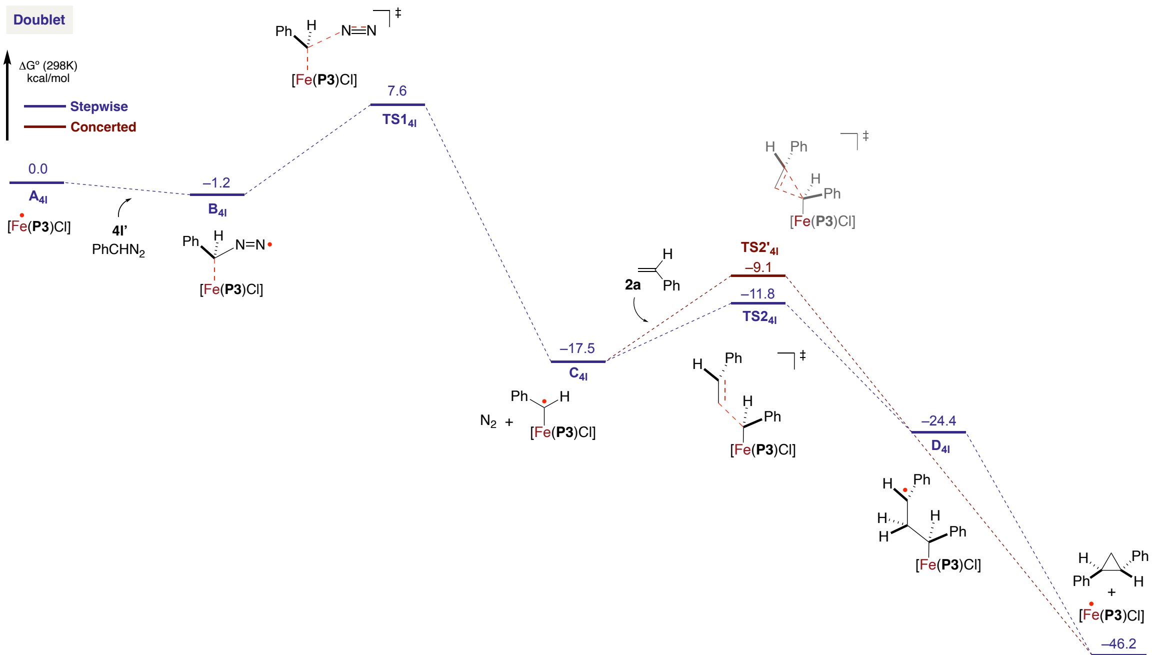
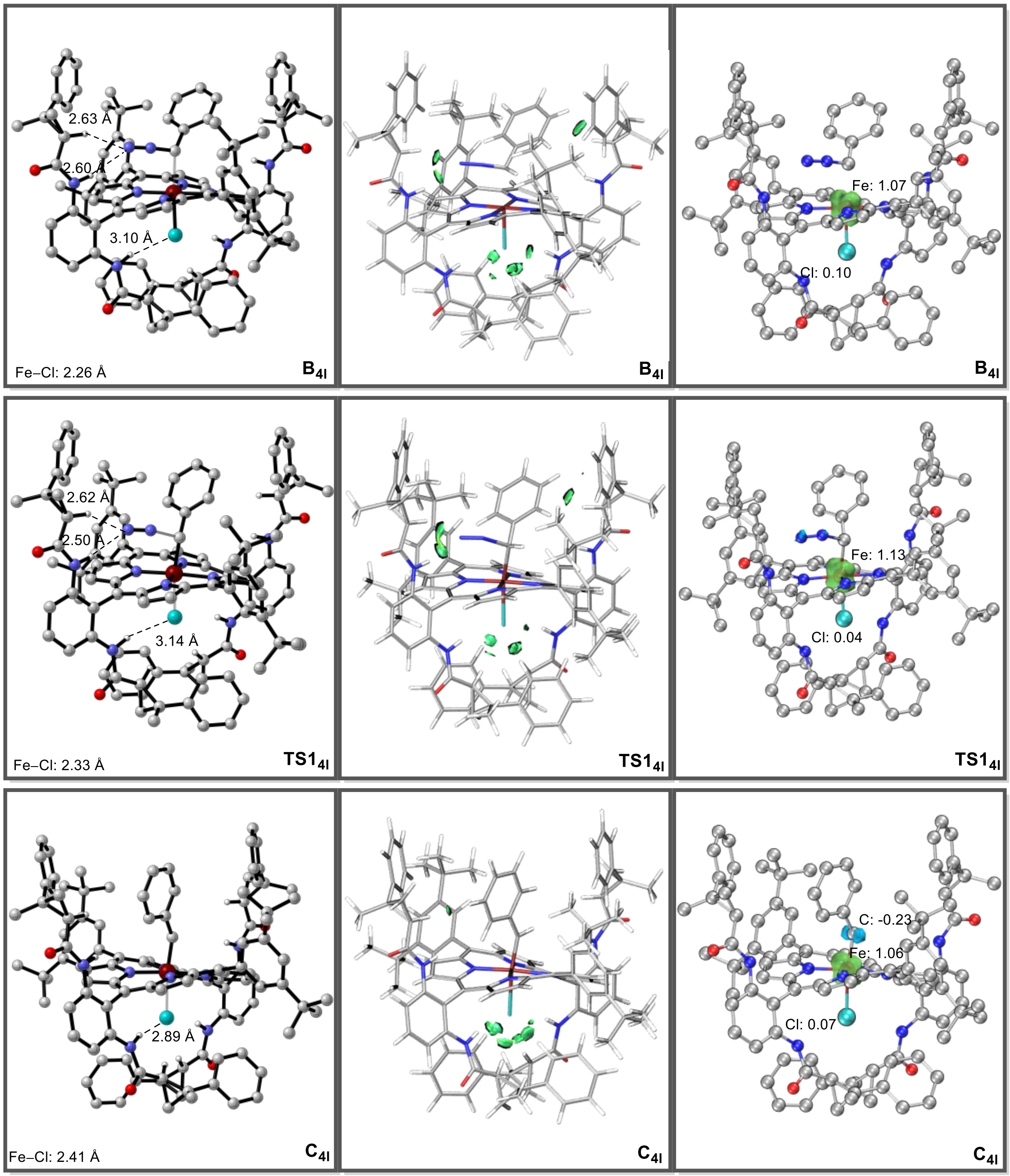
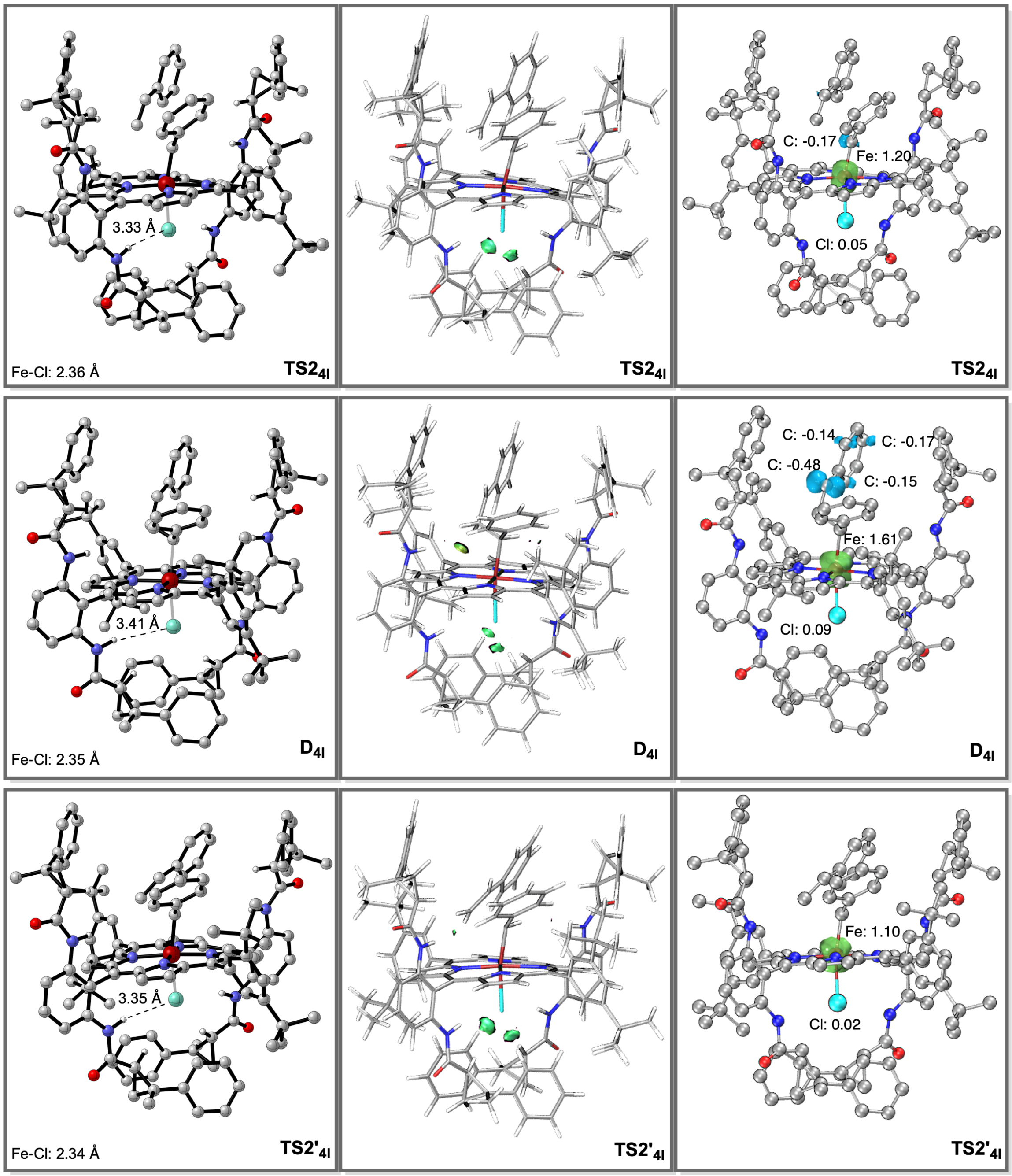


Figure S43: Optimized Structure Models, NCI Visual Representation and Spin Density Representation of Intermediates and Transition States (with **4l'**)




3.33 Å
Fe-Cl: 2.36 Å
TS2$_{4l}$
TS2$_{4l}$
C: -0.17
Fe: 1.20
Cl: 0.05
TS2$_{4l}$
3.41 Å
Fe-Cl: 2.35 Å
D$_{4l}$
D$_{4l}$
C: -0.14
C: -0.17
C: -0.48
C: -0.15
Fe: 1.61
Cl: 0.09
D$_{4l}$
3.35 Å
Fe-Cl: 2.34 Å
TS2'$_{4l}$
TS2'$_{4l}$
Fe: 1.10
Cl: 0.02
TS2'$_{4l}$

9. References

(1) (a) Shirakawa, Y.; Yano, Y.; Niwa, Y.; Inabe, K.; Umezawa, N.; Kato, N.; Hisamatsu, Y.; Higuchi, T. *Inorg. Chem.* **2019**, *58*, 4268–4274. (b) Leeladee, P.; Baglia, R. A.; Prokop, K. A.; Latifi, R.; de Visser, S. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2012**, *134*, 10397–10400. (c) Gutzeit, F.; Dommaschk, M.; Levin, N.; Buchholz, A.; Schaub, E.; Plass, W.; Näther, C.; Herges, R. *Inorg. Chem.* **2019**, *58*, 12542–12546.

(2) Bruker (2012). *APEX2* . Bruker AXS Inc., Madison, Wisconsin, USA.

(3) Bruker (2012). SAINT. Data Reduction Software.

(4) Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.

(5) Farrugia L.J. Appl. Cryst. (1999). 32, 837-838

(6) Sheldrick, G.M. (2012 Beta) SHELXL-97. Program for the Refinement of Crystal

(7) Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473

(8) Frisch, M. J. *et al.*, *Gaussian 16*, *Revision C01*, Gaussian, Inc., Wallingford CT, **2016**.

(9) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.

(10) (a) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. *J. Am. Chem. Soc.* **2010**, *132*, 10891. (b) Lee, W.-C. C.; Wang, D.-S.; Zhang, C.; Xie, J.; Li, B.; Zhang, X. P. *Chem* **2021**, *7,* 1588.

(11) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

(12) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(13) Page, M.; McIver, J. W. *J. Chem. Phys.* **1988**, *88*, 922.

(14) Page, M.; Doubleday, C.; McIver, J. W. *J. Chem. Phys.* **1990**, *93*, 5634.

(15) (a) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401. (b) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003,** *119*, 12129-12137. (c) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2004,** *121*, 11507-11507.

(16) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. **2010**, *132*, 154104.

(17) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

(18) Lefebvre, C.; Rubez, G.; Khartabil, H.; Boisson, J.-C.; Contreras-Garcia, J.; Henon, E. *Phys. Chem. Chem. Phys.* **2017**, *19*, 17928.

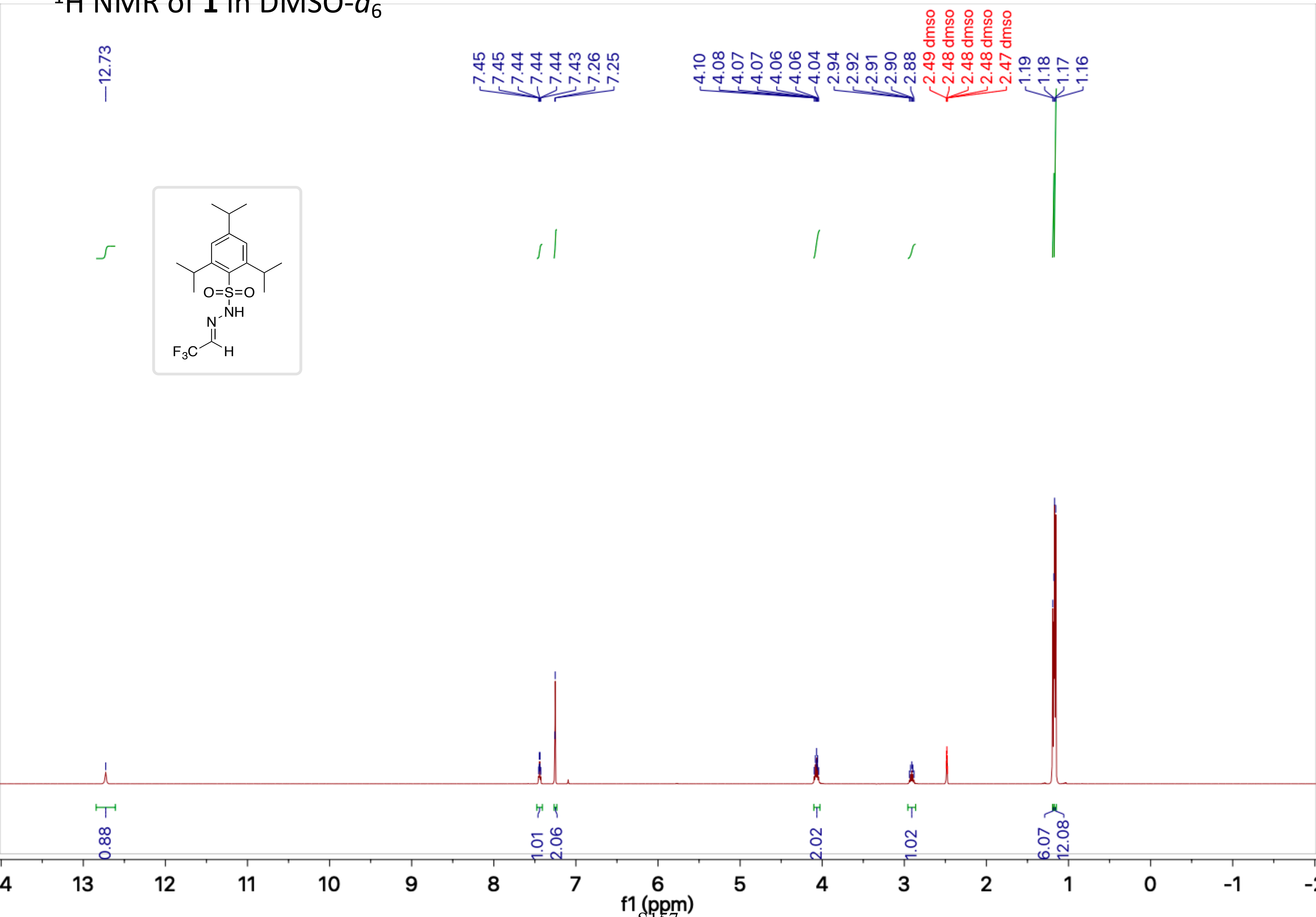
(19) Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580.

(20) Humphrey, W.; Dalke, A.; Schulten, K. *J. Mol. Graph.* **1996**, *14*, 33.

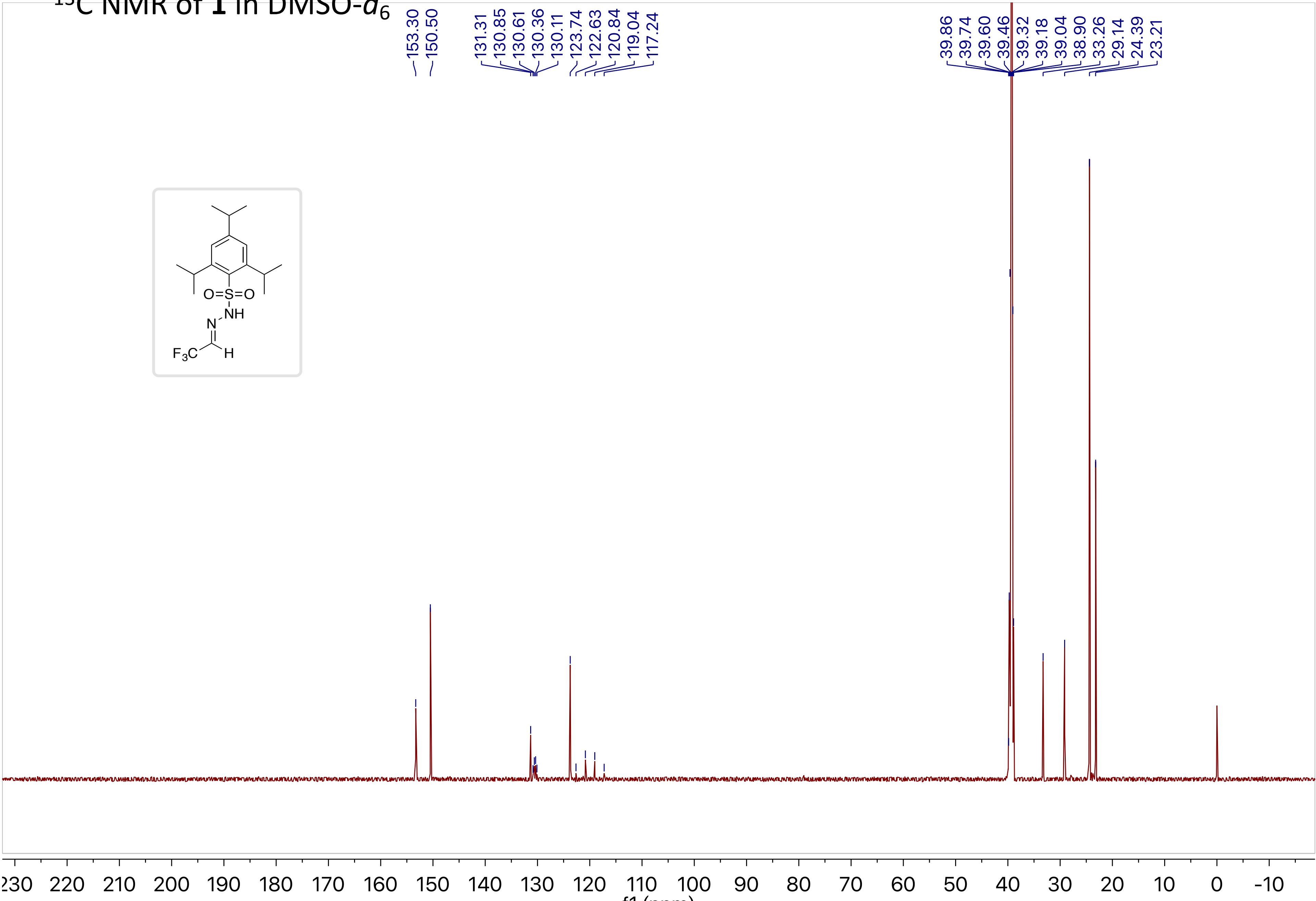
(21) Legault, C. Y. CYLview, 1.0b (Universite de Sherbrooke, Quebec, Montreal, Canada, 2009)

10. NMR/HPLC Spectra

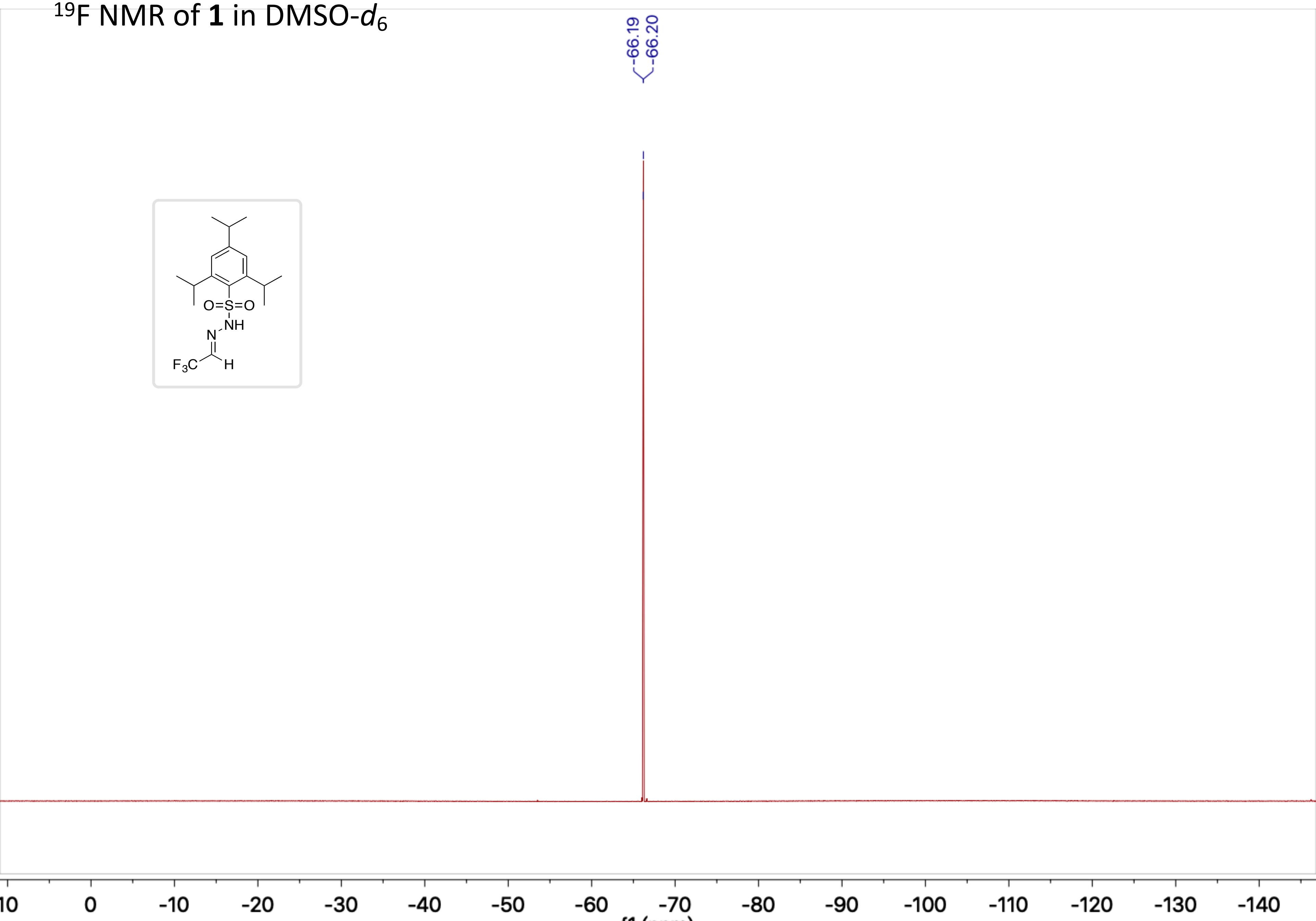
^{1}H NMR of **1** in DMSO-d_6



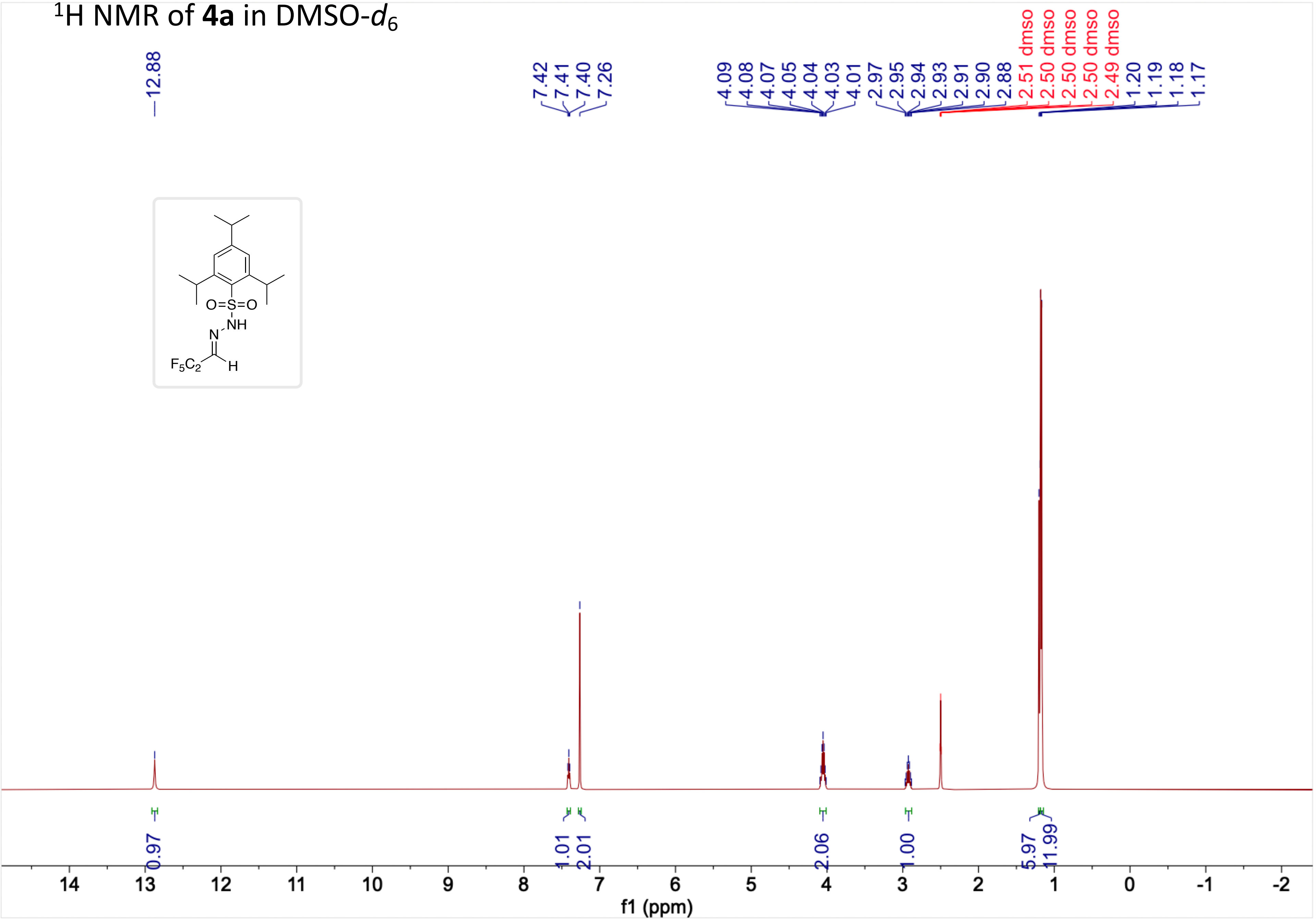
^{13}C NMR of **1** in DMSO-d_6



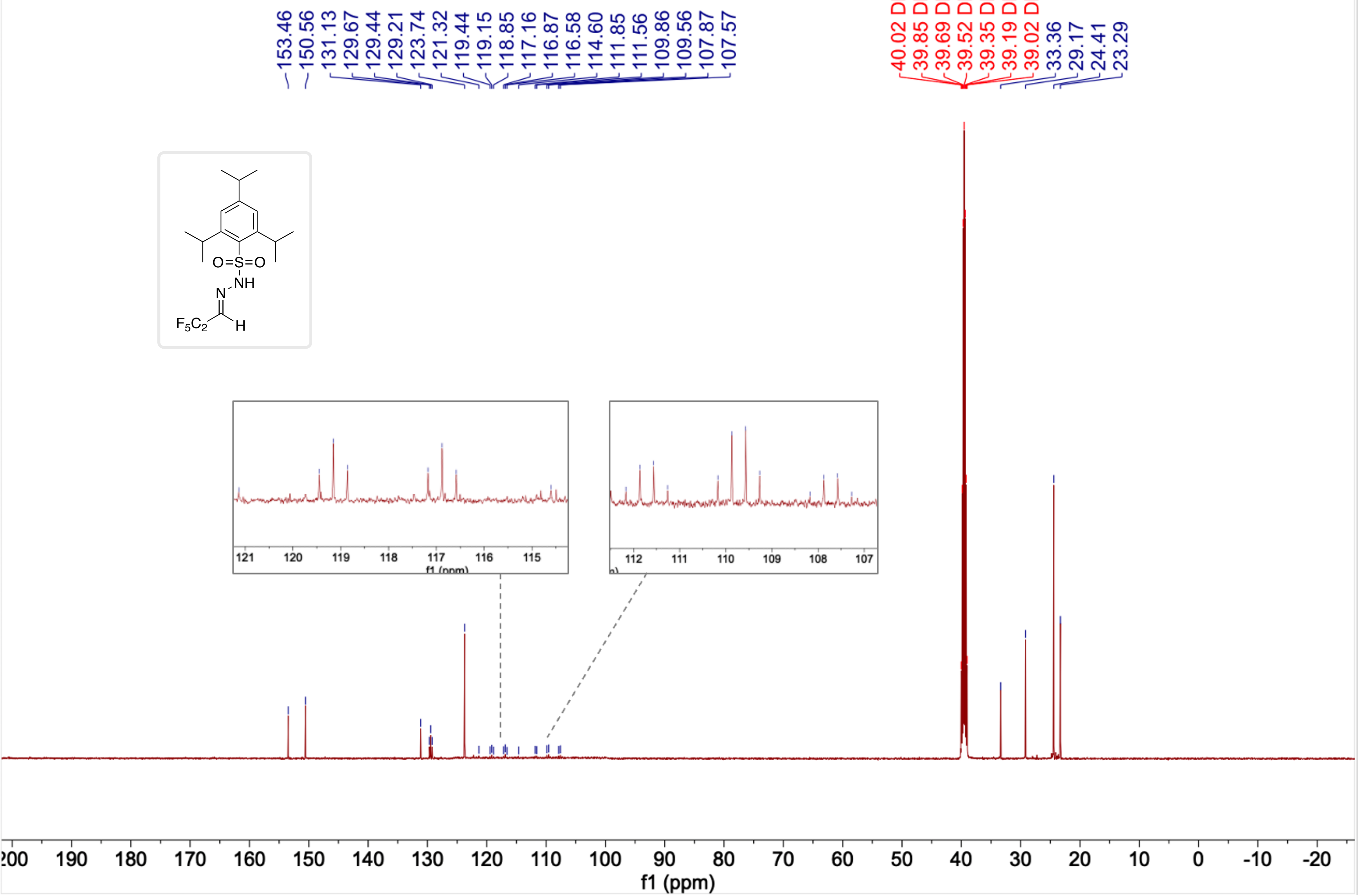
^{19}F NMR of **1** in DMSO-d_6



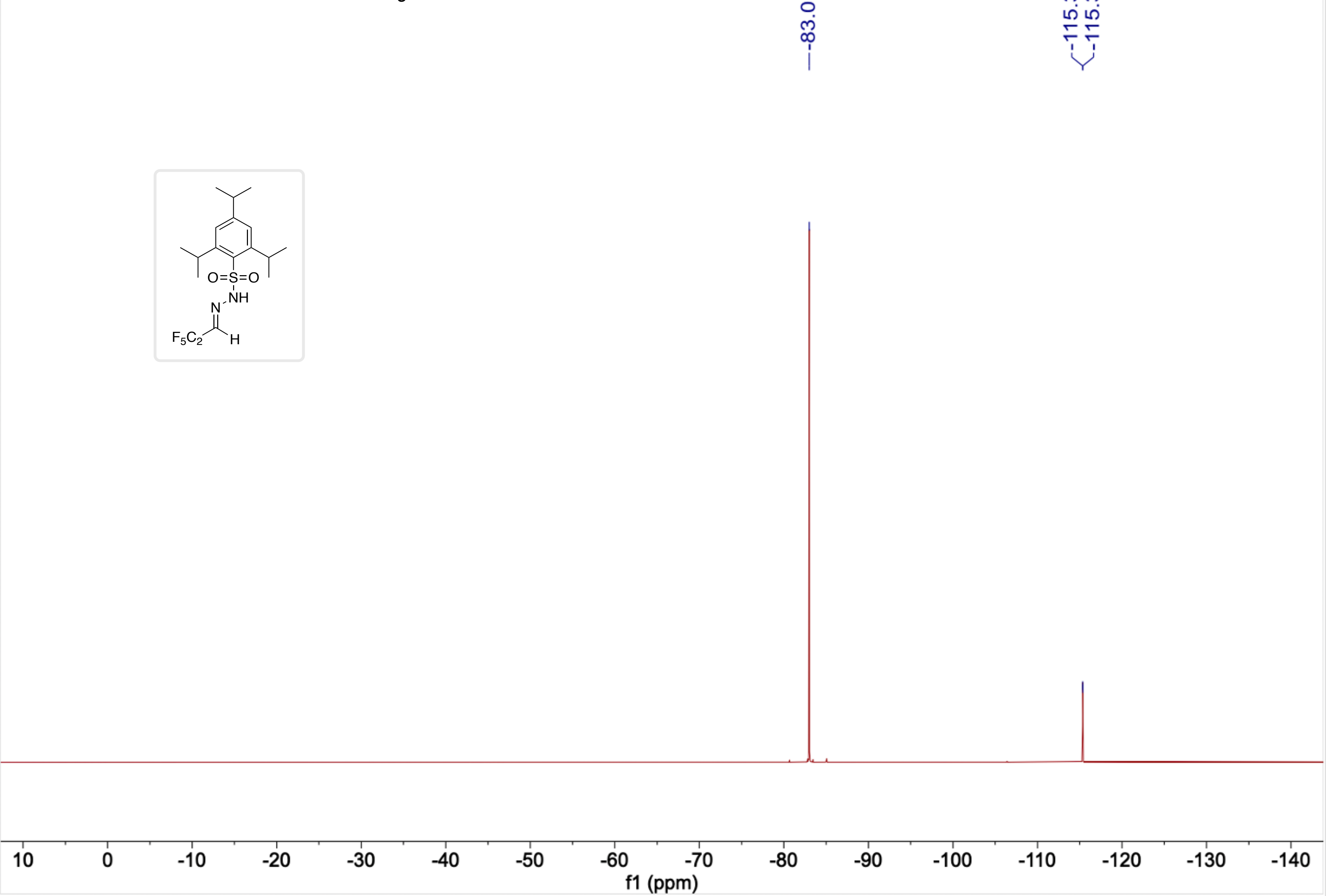
^1H NMR of **4a** in DMSO-d_6



^{13}C NMR of **4a** in DMSO-d_6

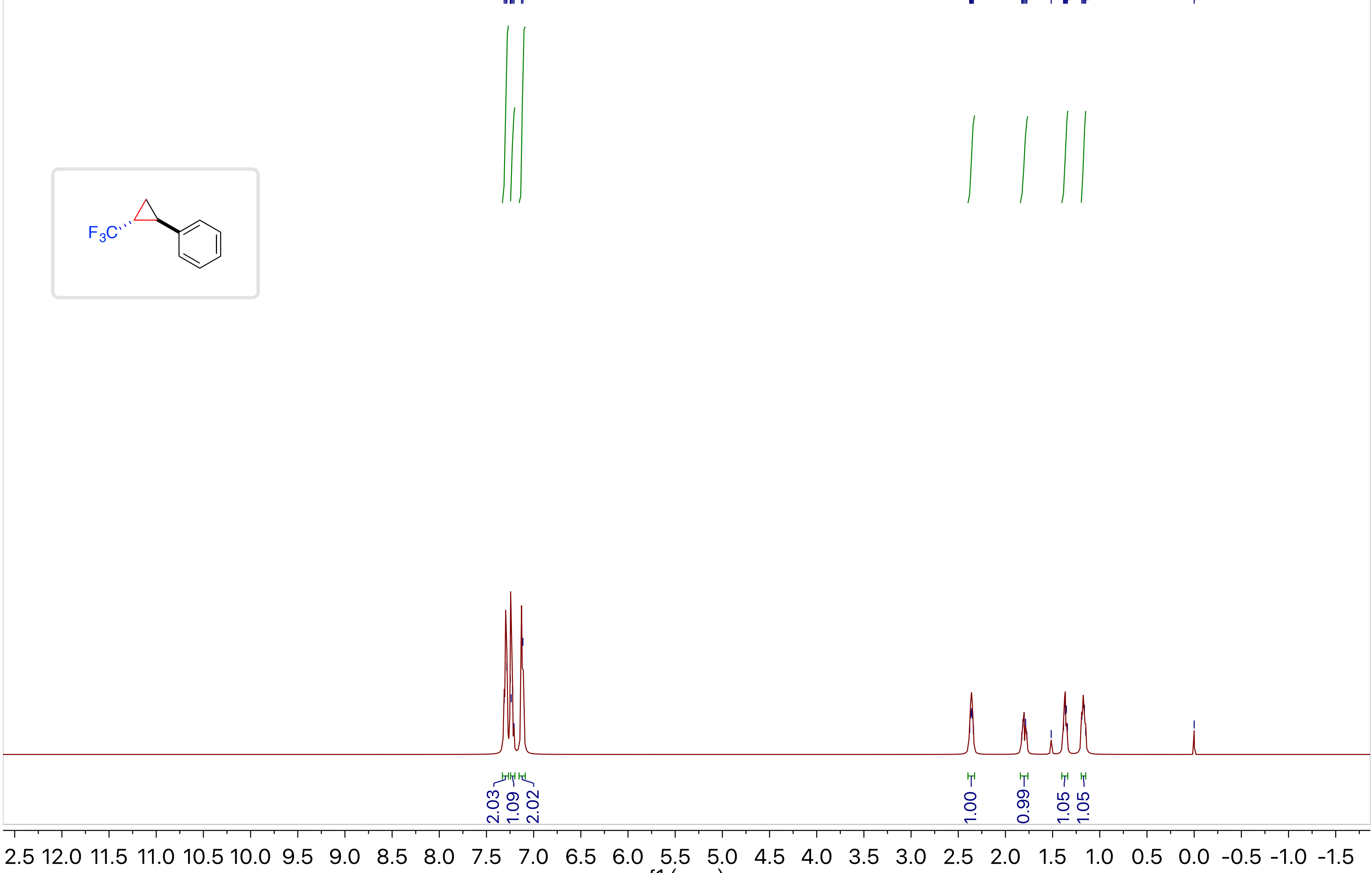


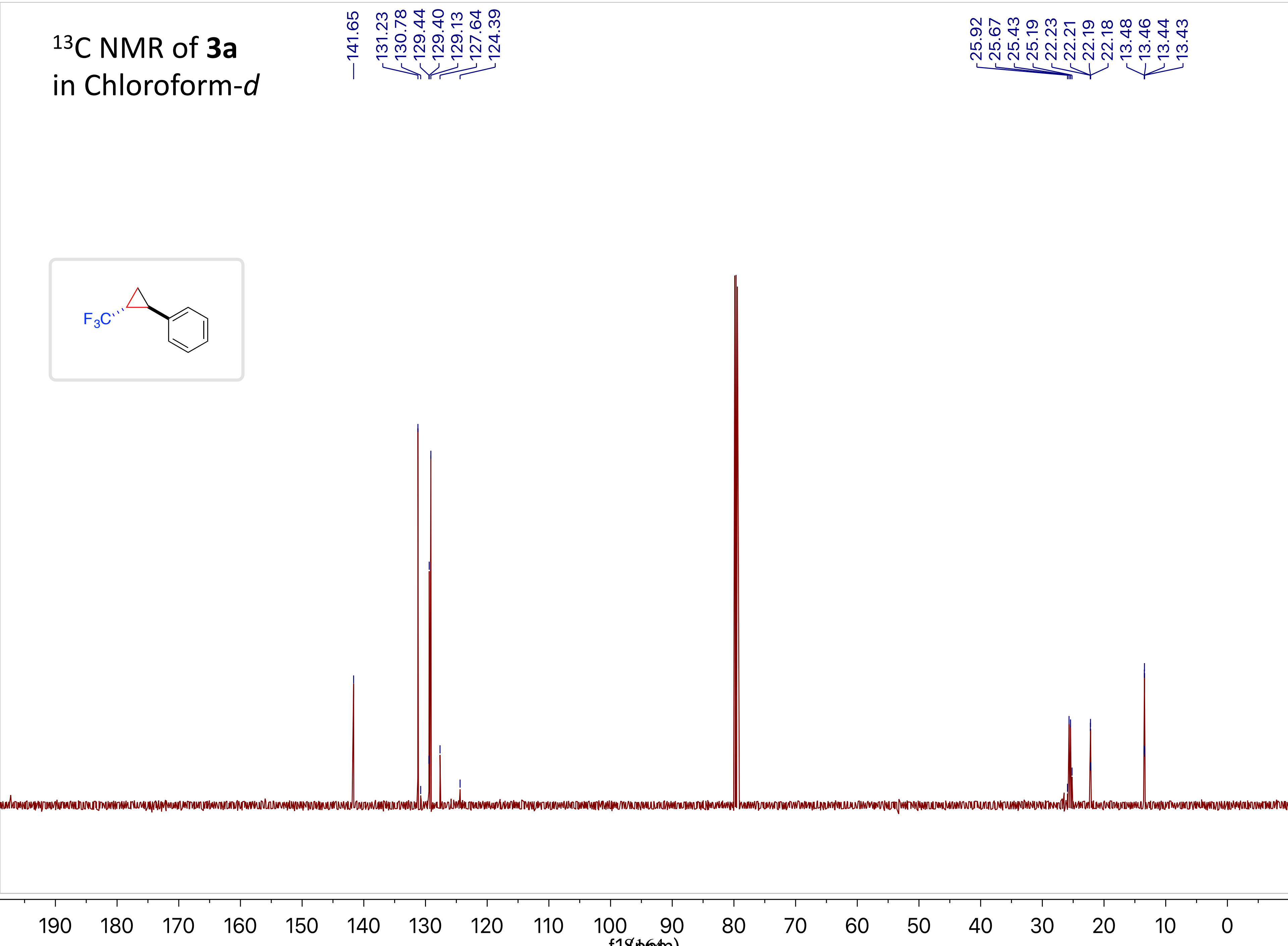
^{19}F NMR of **4a** in DMSO-d_6



^1H NMR of **3a**

in Chloroform-*d*

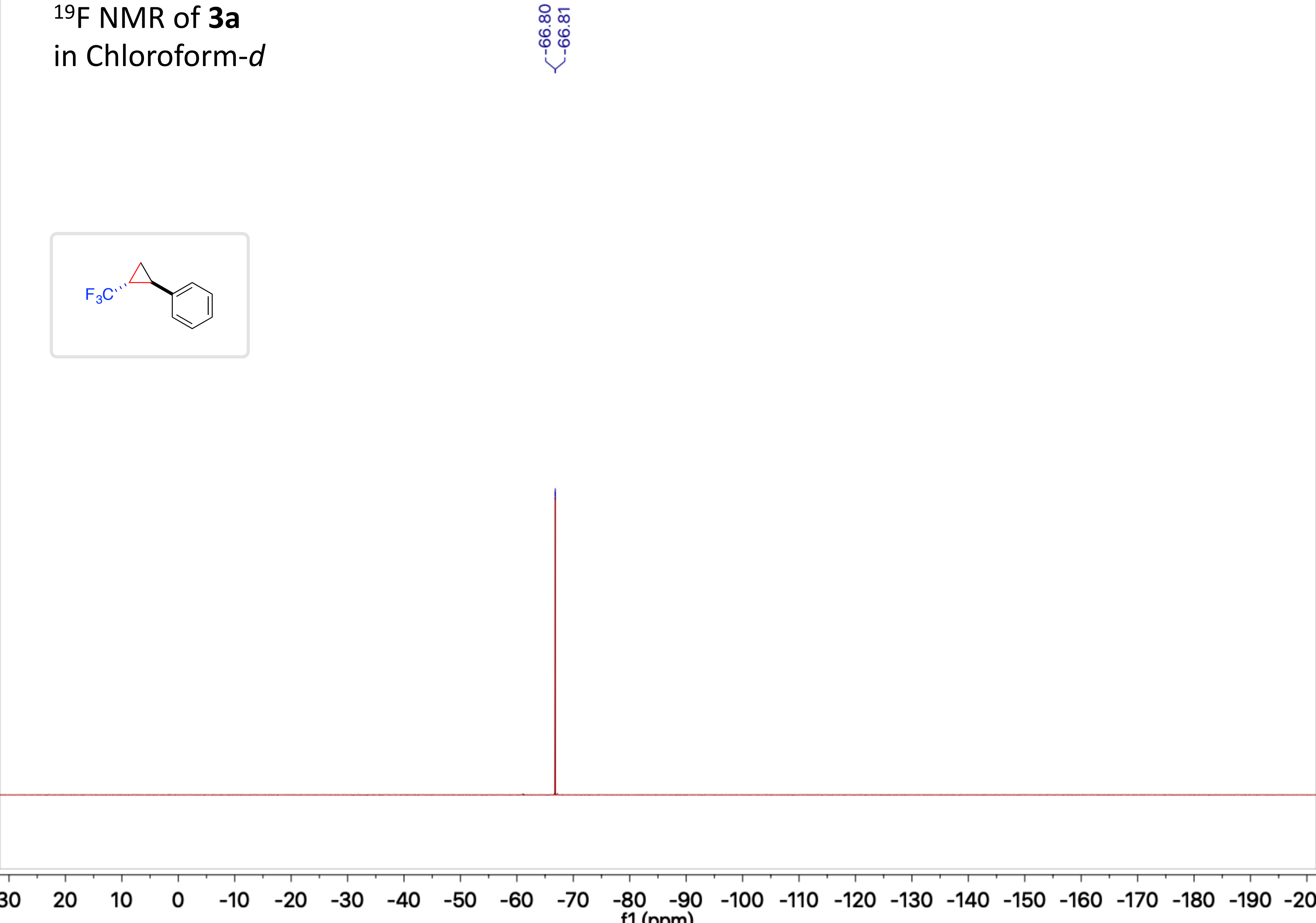


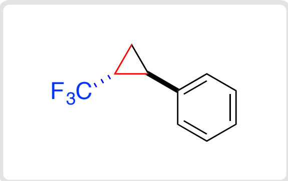


13C NMR of 3a
in Chloroform-d
141.65
131.23
130.78
129.44
129.40
129.13
127.64
124.39
25.92
25.67
25.43
25.19
22.23
22.21
22.19
22.18
13.48
13.46
13.44
13.43
F3C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

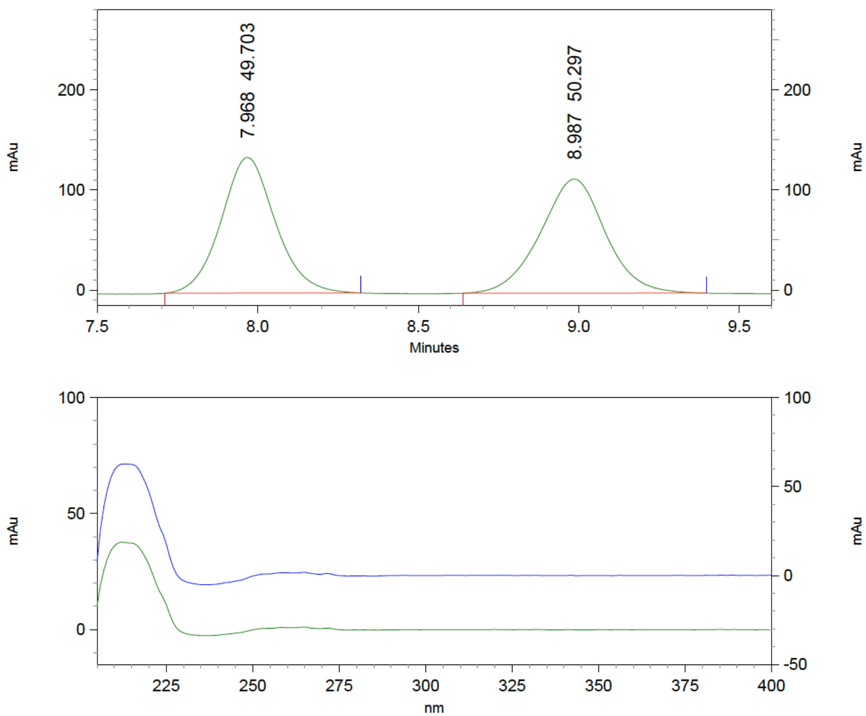
S164

[19]F NMR of **3a**
in Chloroform-*d*



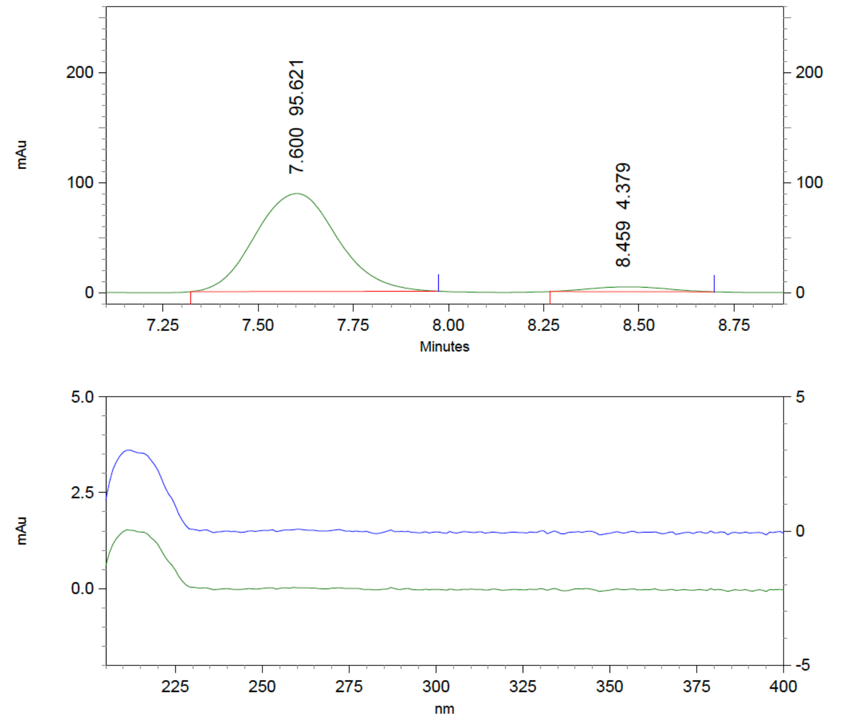


HPLC of **3a**



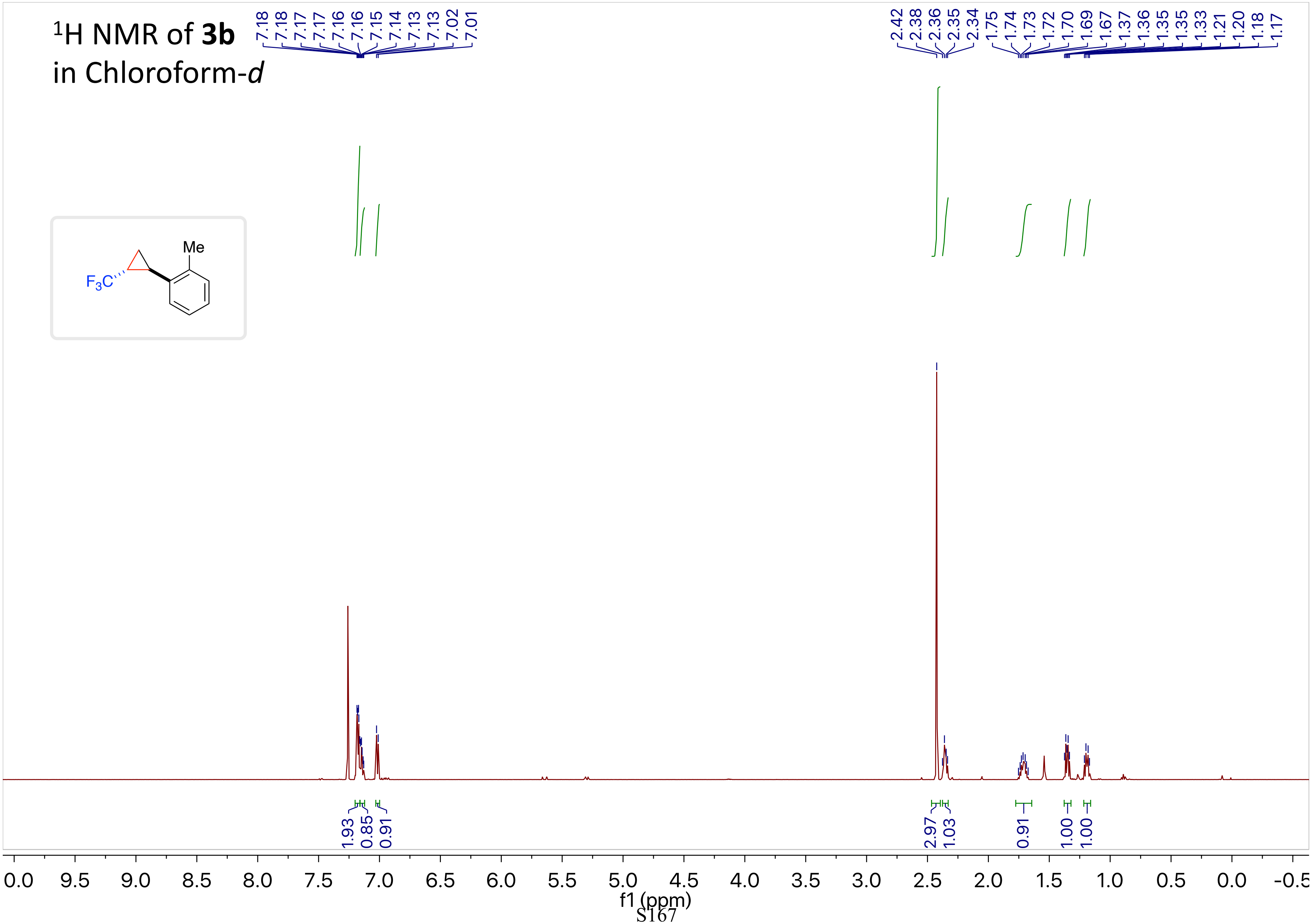
4: 218 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	7.968	49.703
2	8.987	50.297
Totals		100.000



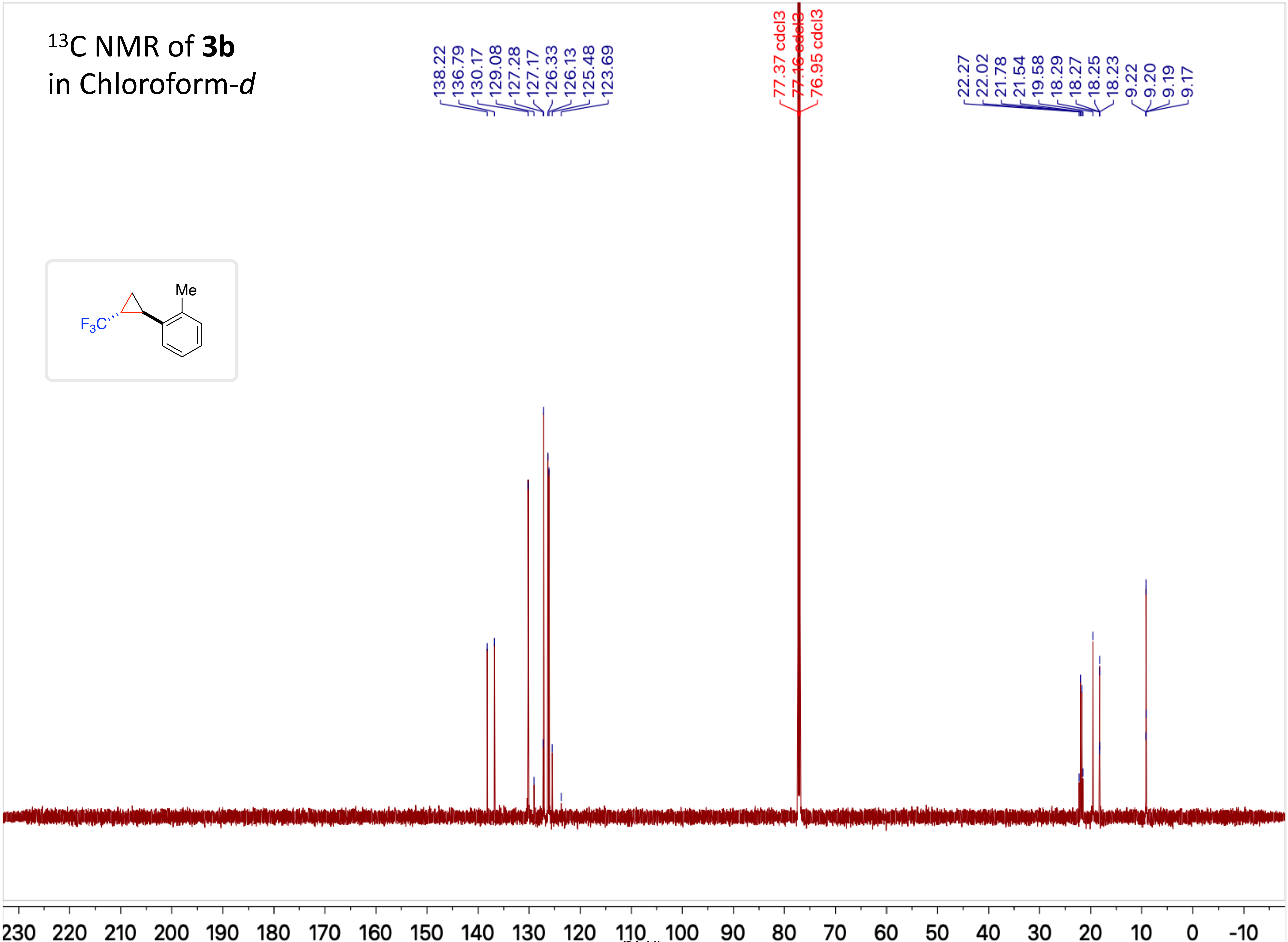
4: 218 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	7.600	95.621
2	8.459	4.379
Totals		100.000

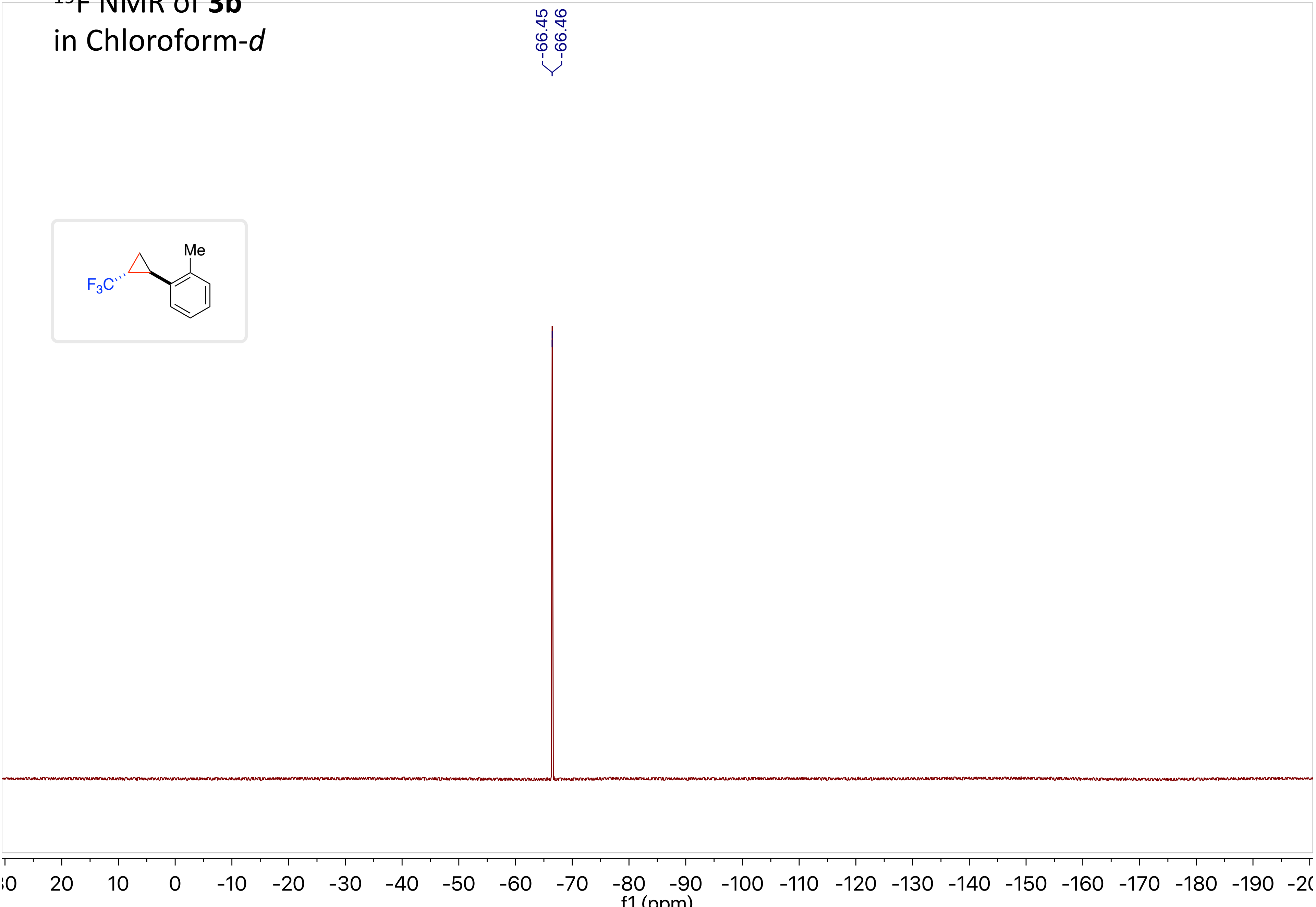


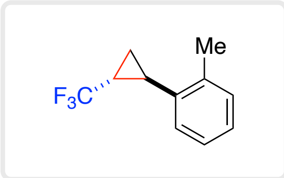
1H NMR of 3b
in Chloroform-d
Me
F3C
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.13
7.02
7.01
2.42
2.38
2.36
2.35
2.34
1.75
1.74
1.73
1.72
1.70
1.69
1.67
1.37
1.36
1.35
1.35
1.33
1.21
1.20
1.18
1.17
1.93
0.85
0.91
2.97
1.03
0.91
1.00
1.00
f1 (ppm)

^{13}C NMR of **3b** in Chloroform-*d*

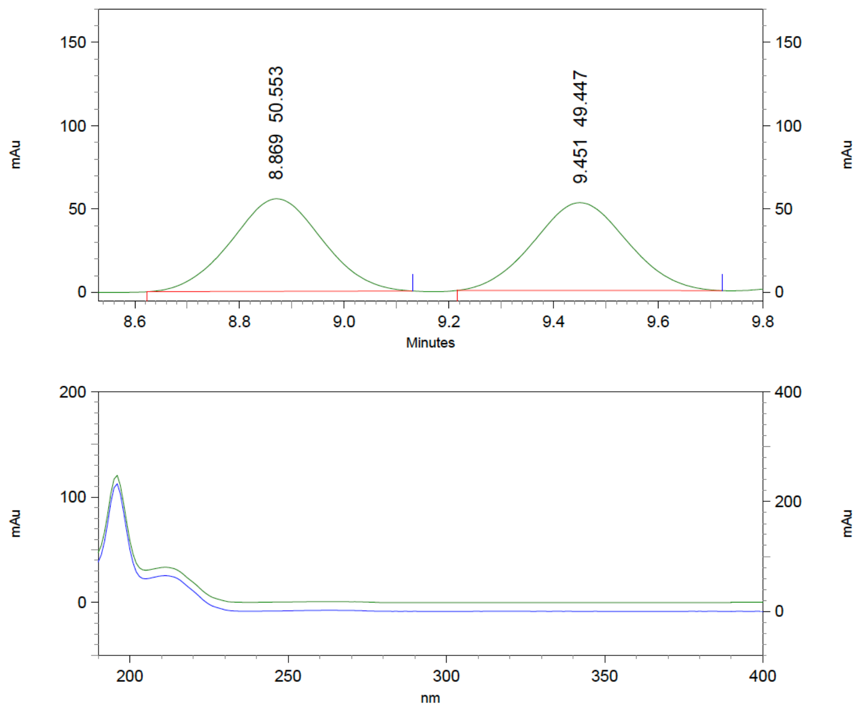


[19]F NMR of **3b**
in Chloroform-*d*



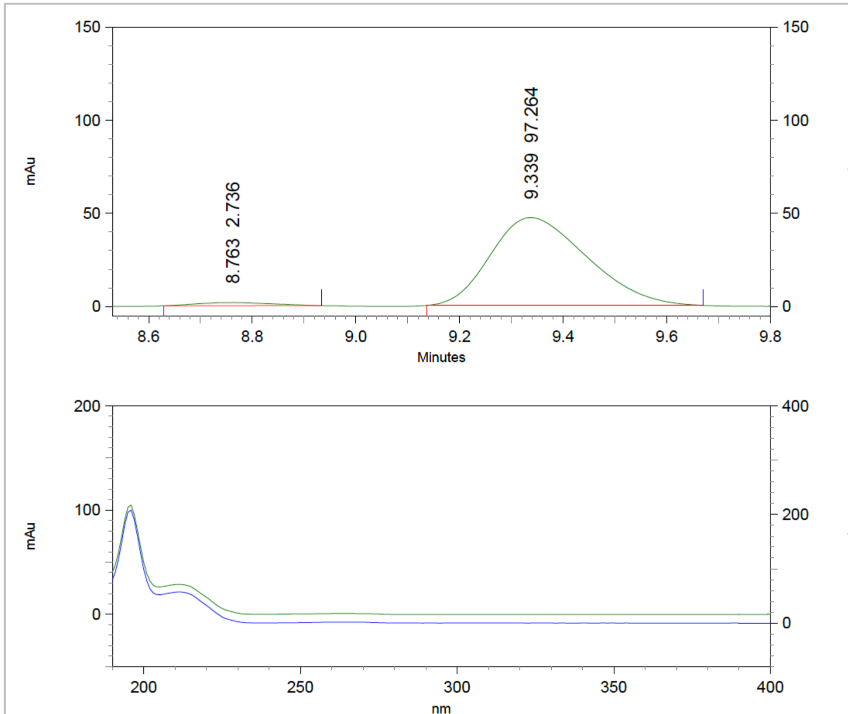


HPLC of **3b**



4: 222 nm, 4
nm Results

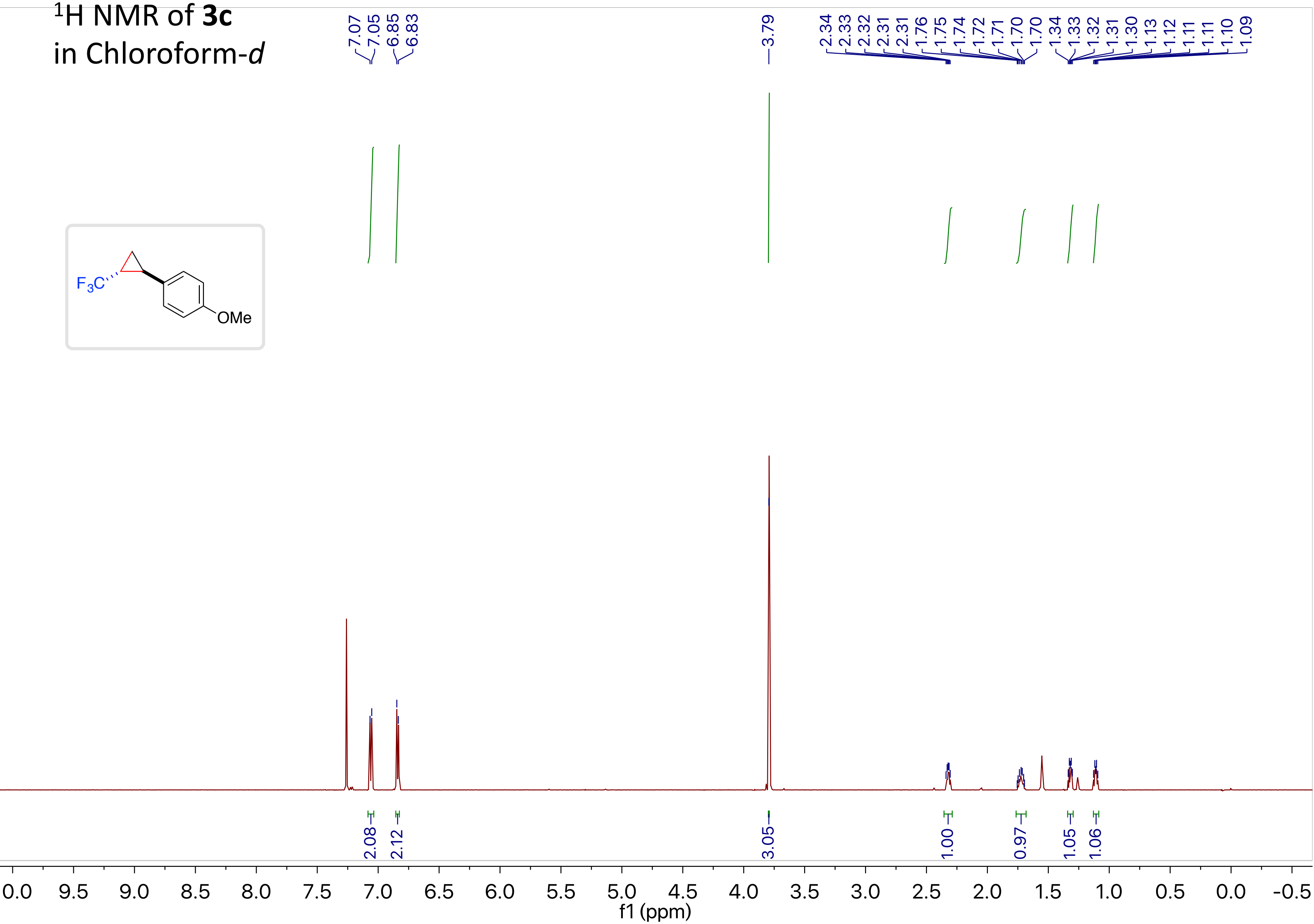
Pk #	Retention Time	Area Percent
1	8.869	50.553
2	9.451	49.447
Totals		100.000



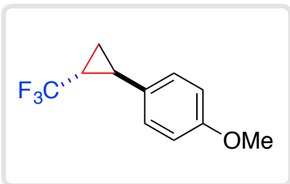
4: 222 nm, 4
nm Results

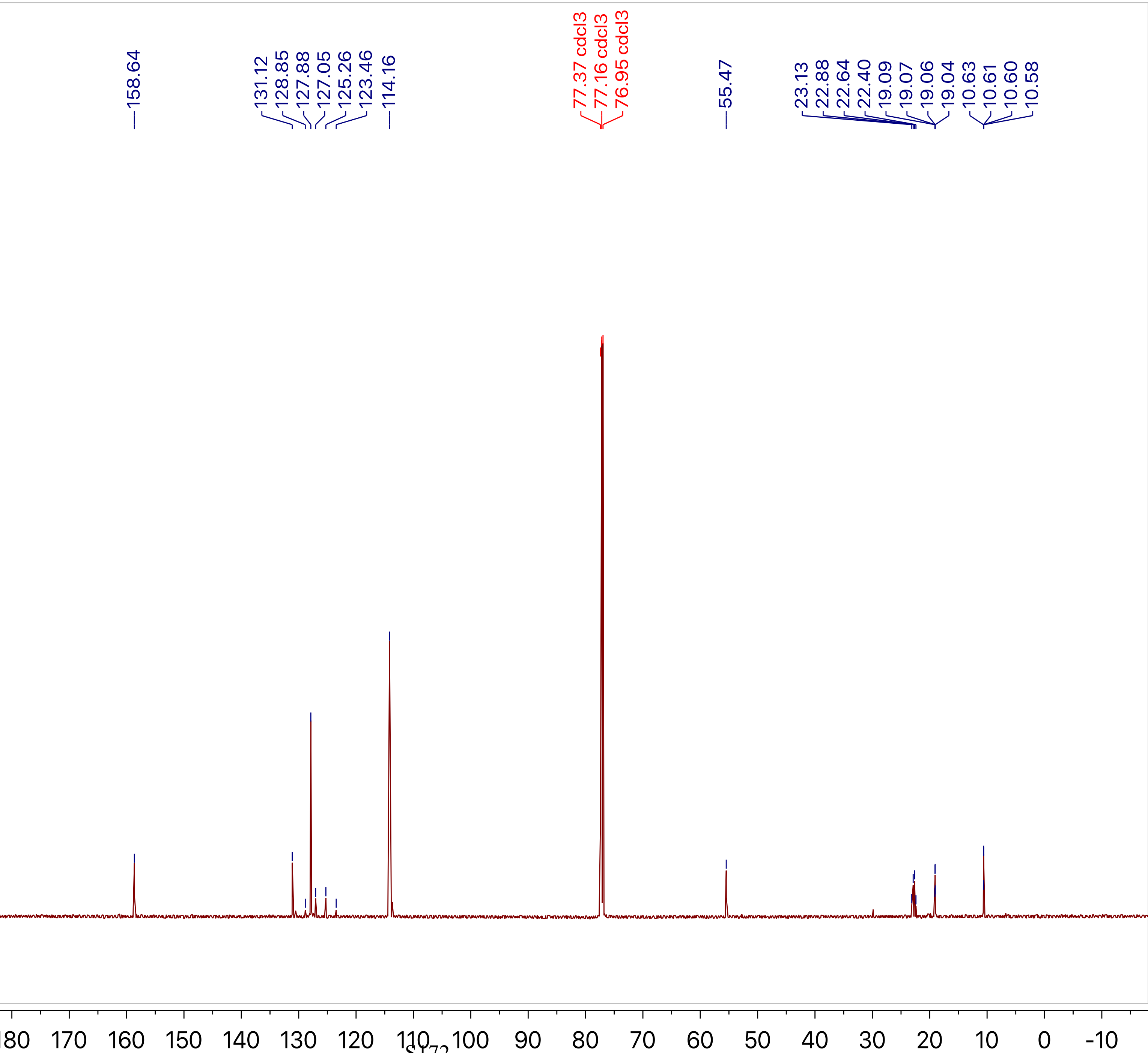
Pk #	Retention Time	Area Percent
1	8.763	2.736
2	9.339	97.264
Totals		100.000

^{1}H NMR of **3c** in Chloroform-*d*

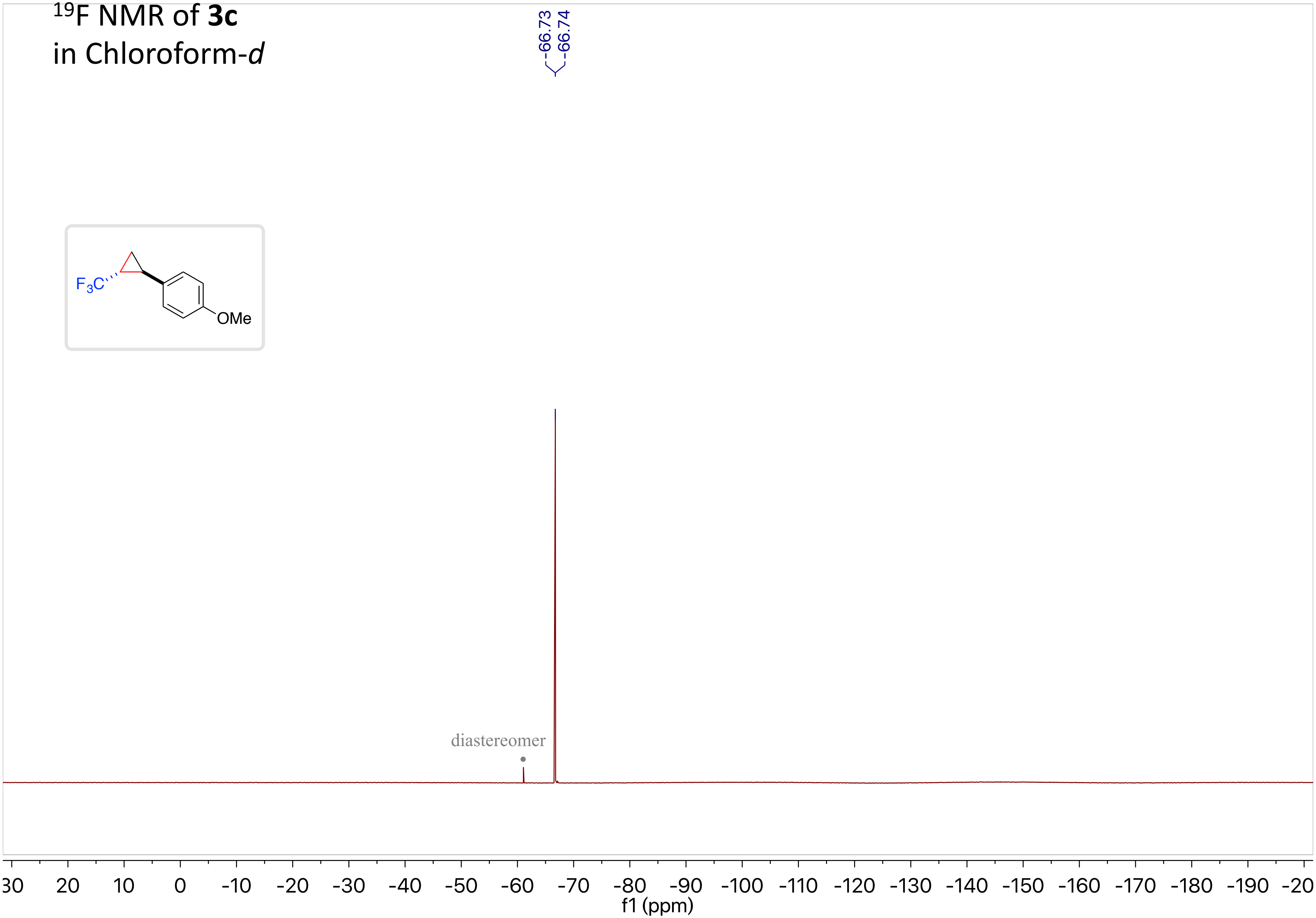


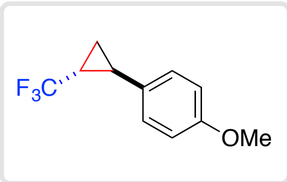
^{13}C NMR of **3c**
in Chloroform-*d*



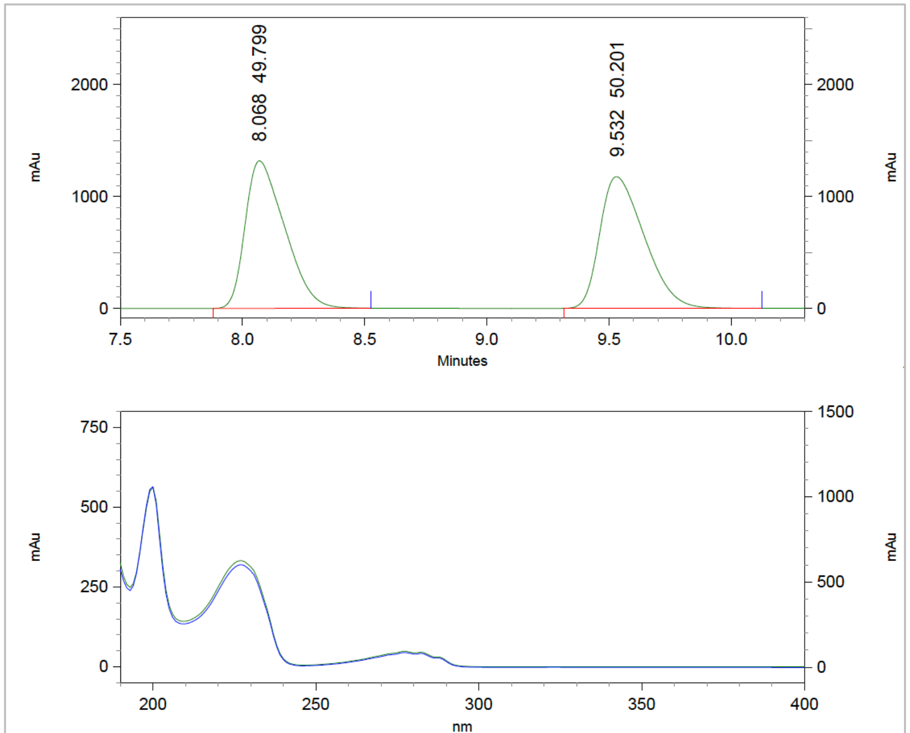


^{19}F NMR of **3c**
in Chloroform-*d*



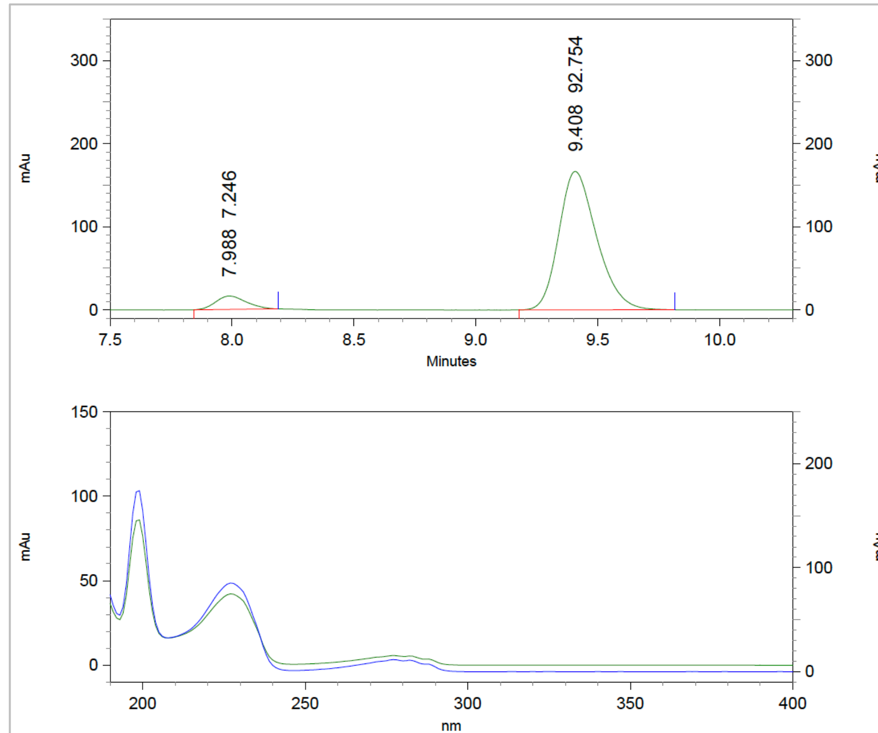


HPLC of **3c**



4: 226 nm, 4
nm Results

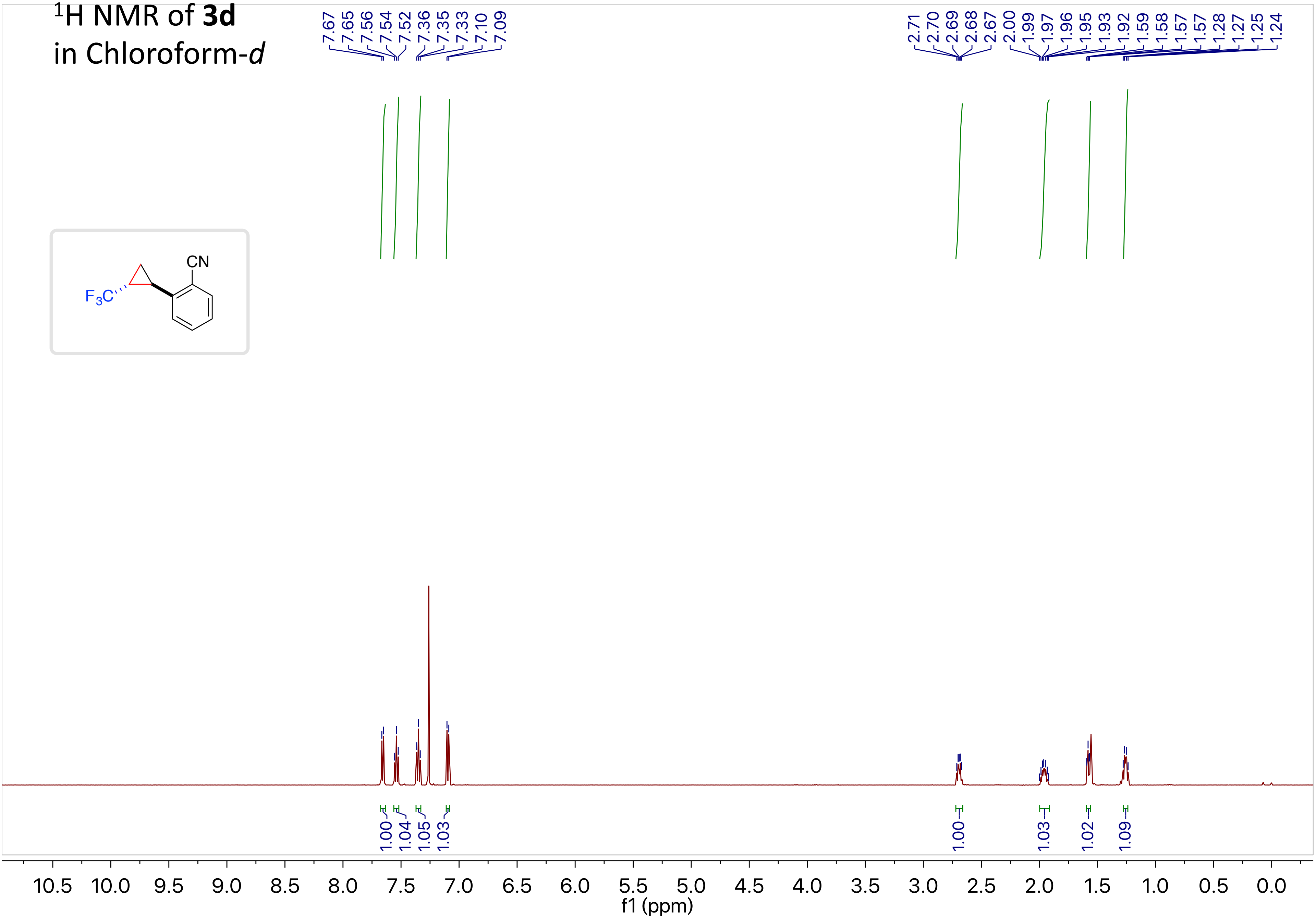
Pk #	Retention Time	Area Percent
1	8.068	49.799
2	9.532	50.201
Totals		100.000



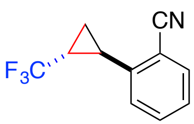
4: 226 nm, 4
nm Results

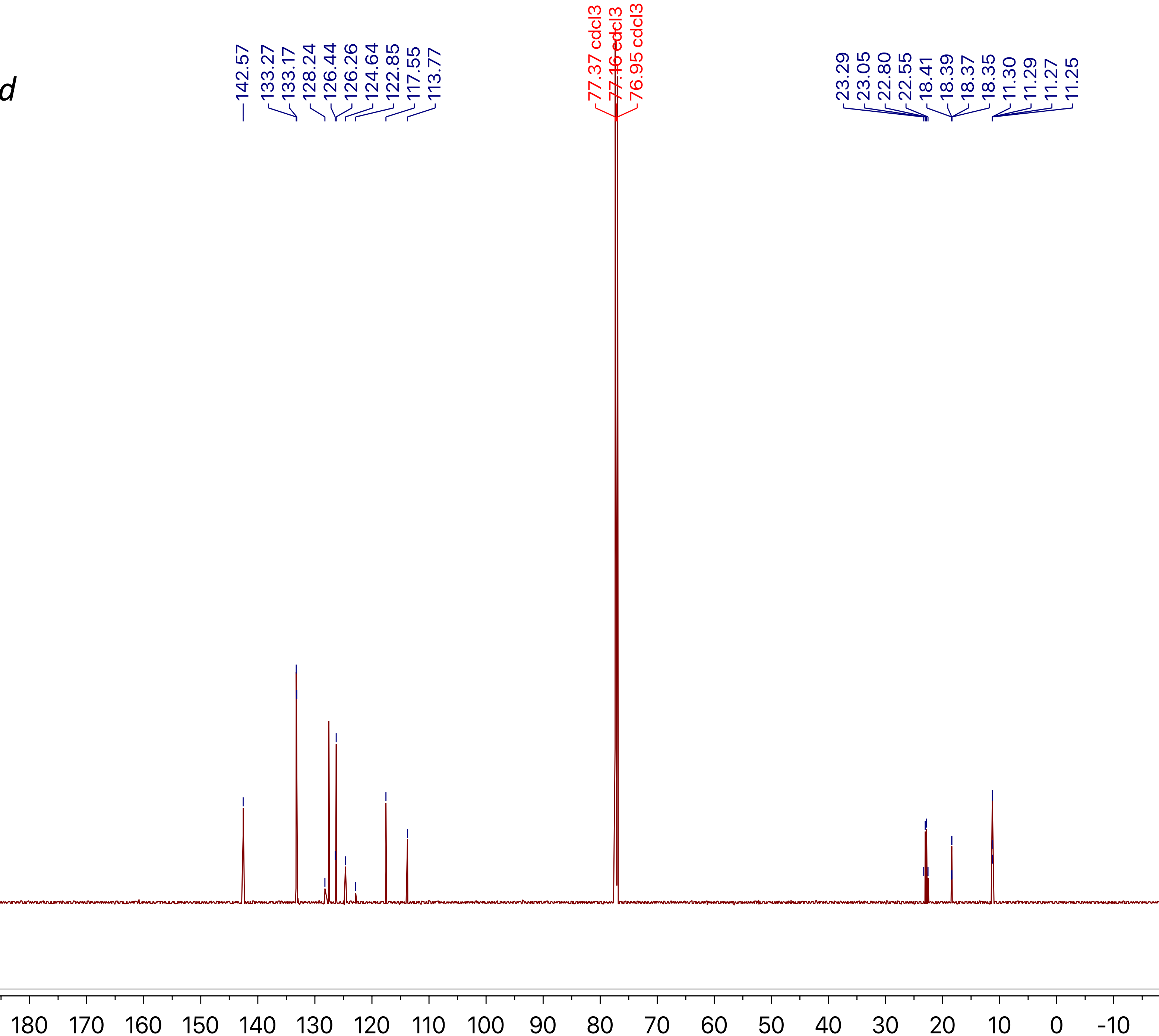
Pk #	Retention Time	Area Percent
1	7.988	7.246
2	9.408	92.754
Totals		100.000

^{1}H NMR of **3d**
in Chloroform-*d*

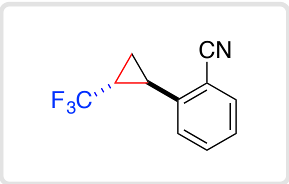


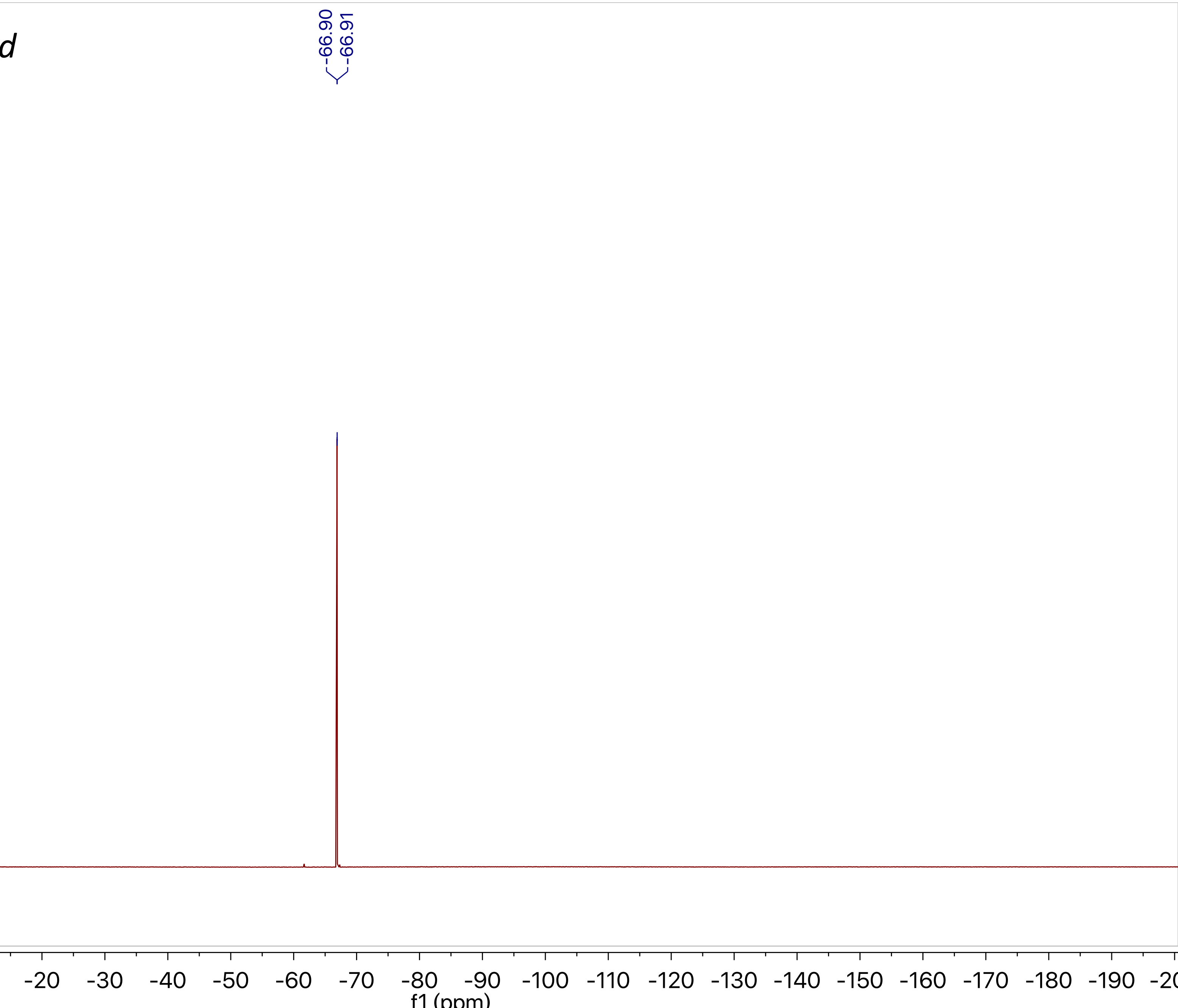
^{13}C NMR of **3d**
in Chloroform-*d*

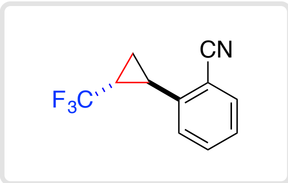




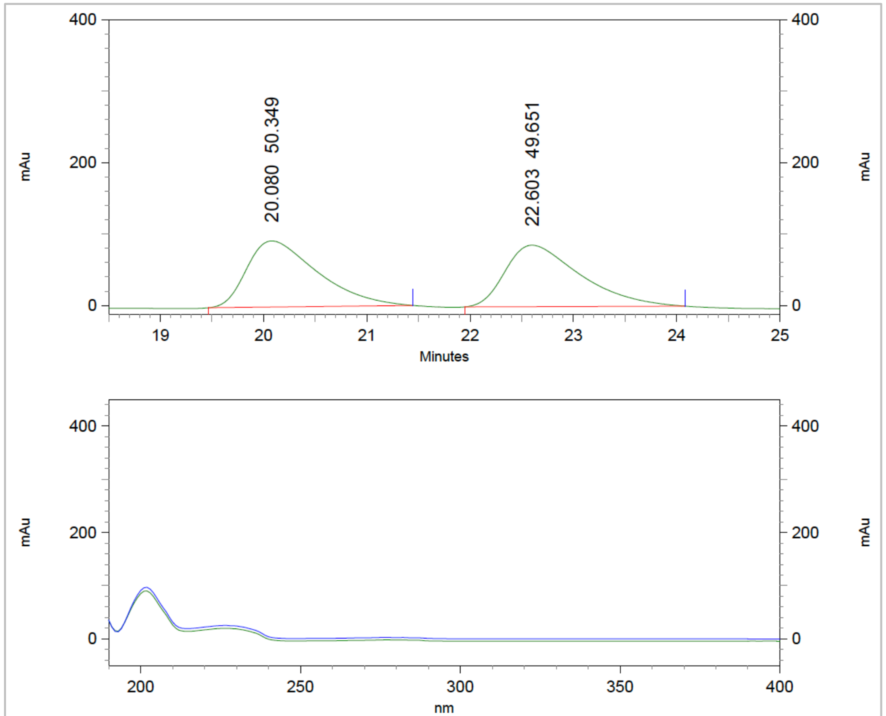
^{19}F NMR of **3d**
in Chloroform-*d*





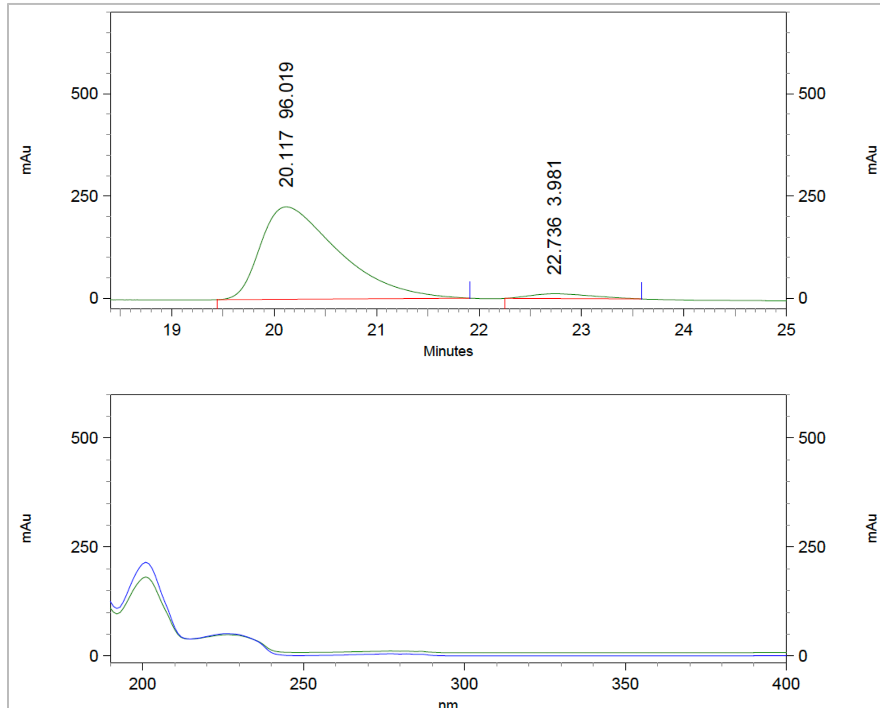


HPLC of **3d**



4: 204 nm, 4 nm Results

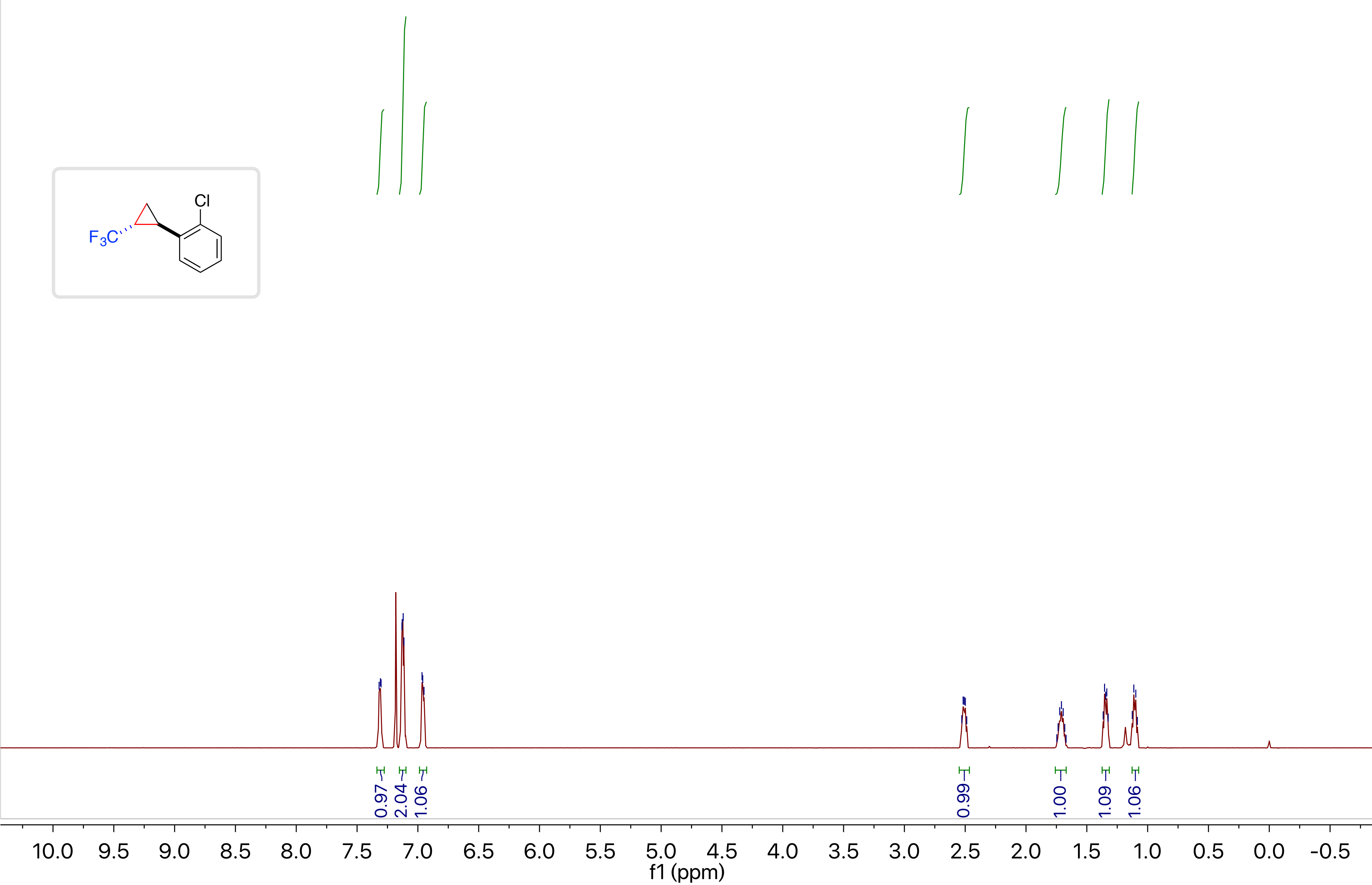
Pk #	Retention Time	Area Percent
1	20.080	50.349
2	22.603	49.651
Totals		100.000



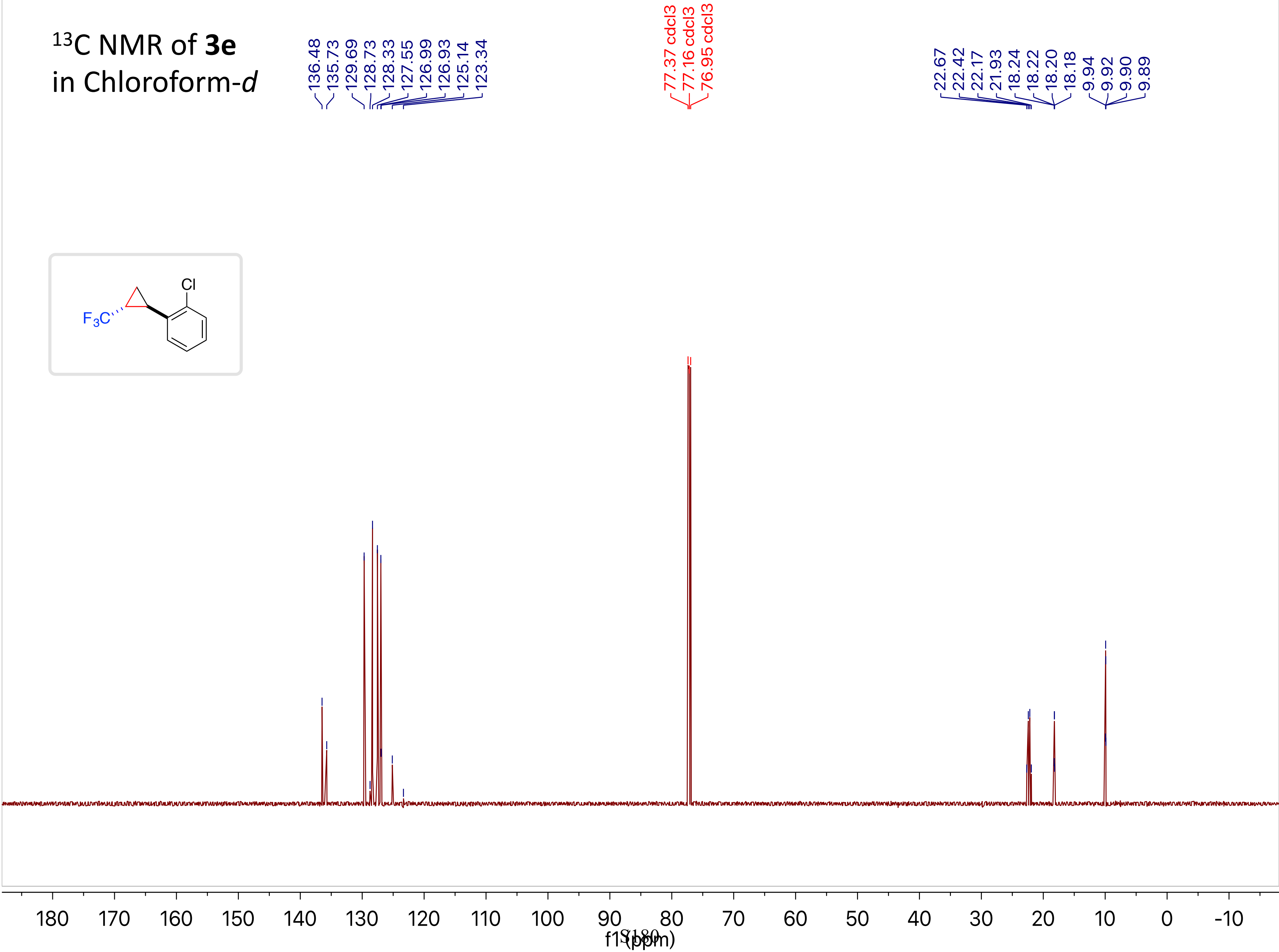
2: 202 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	20.117	96.019
2	22.736	3.981
Totals		100.000

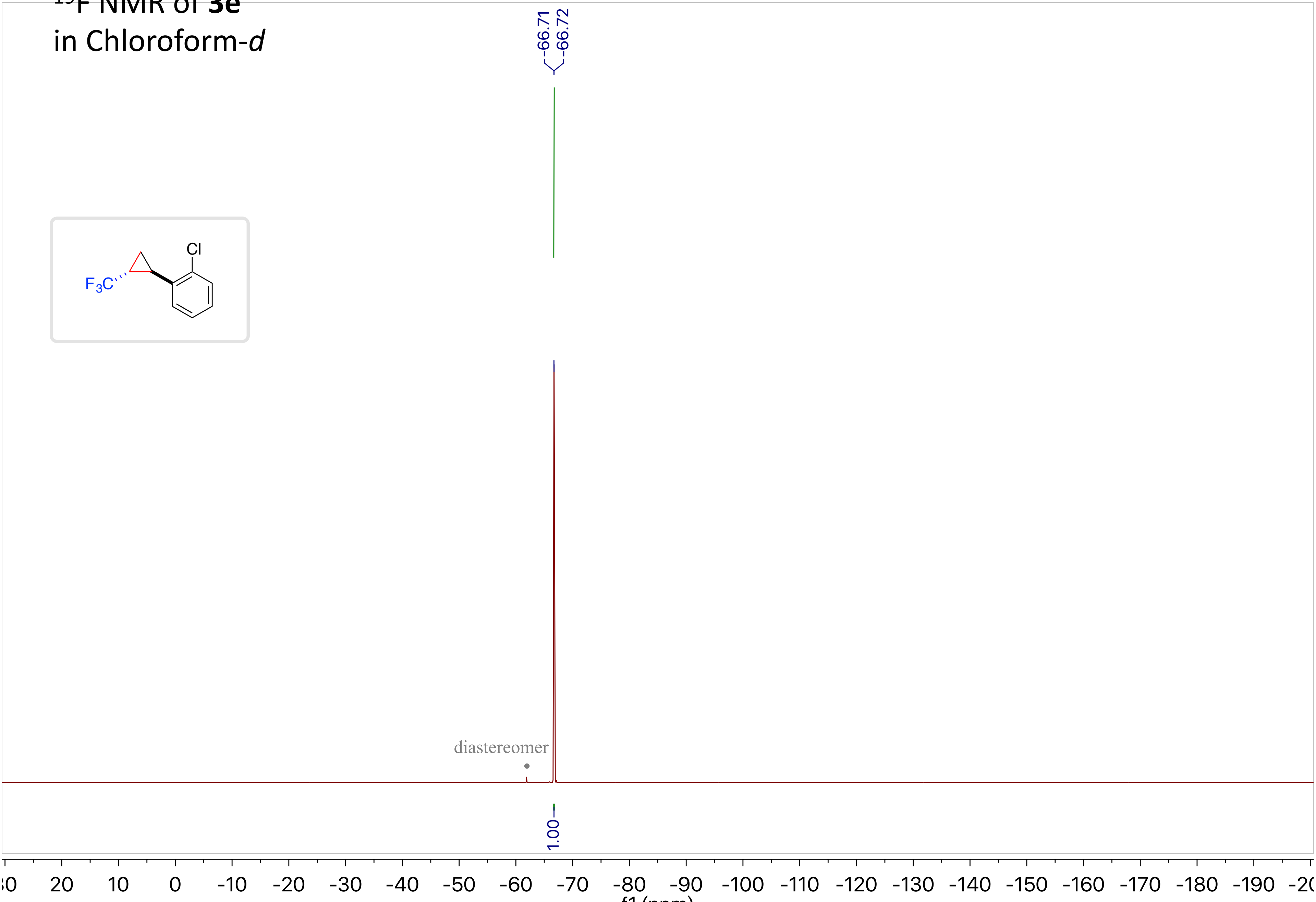
^{1}H NMR of **3e** in Chloroform-*d*

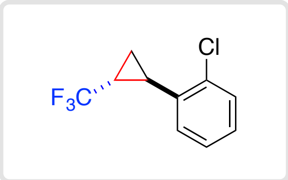


^{13}C NMR of **3e**
in Chloroform-*d*

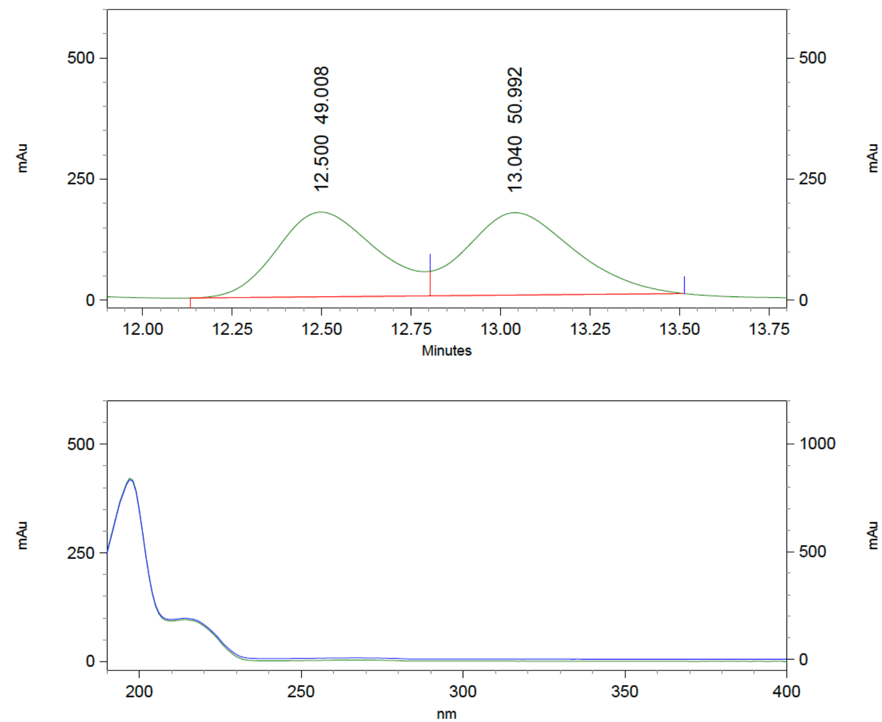


^{19}F NMR of **3e** in Chloroform-*d*



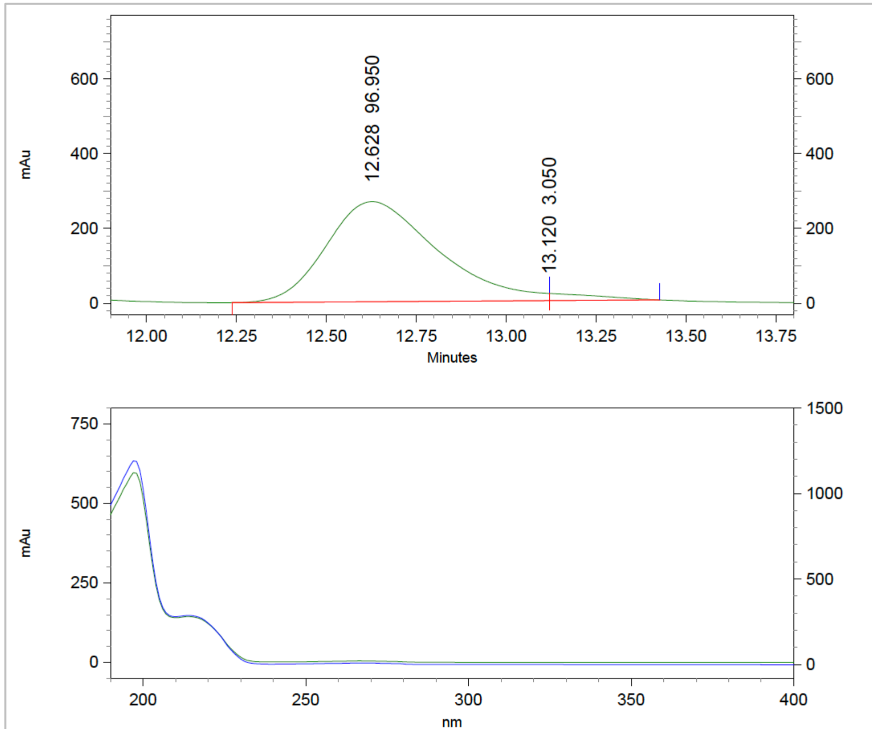


HPLC of **3e**



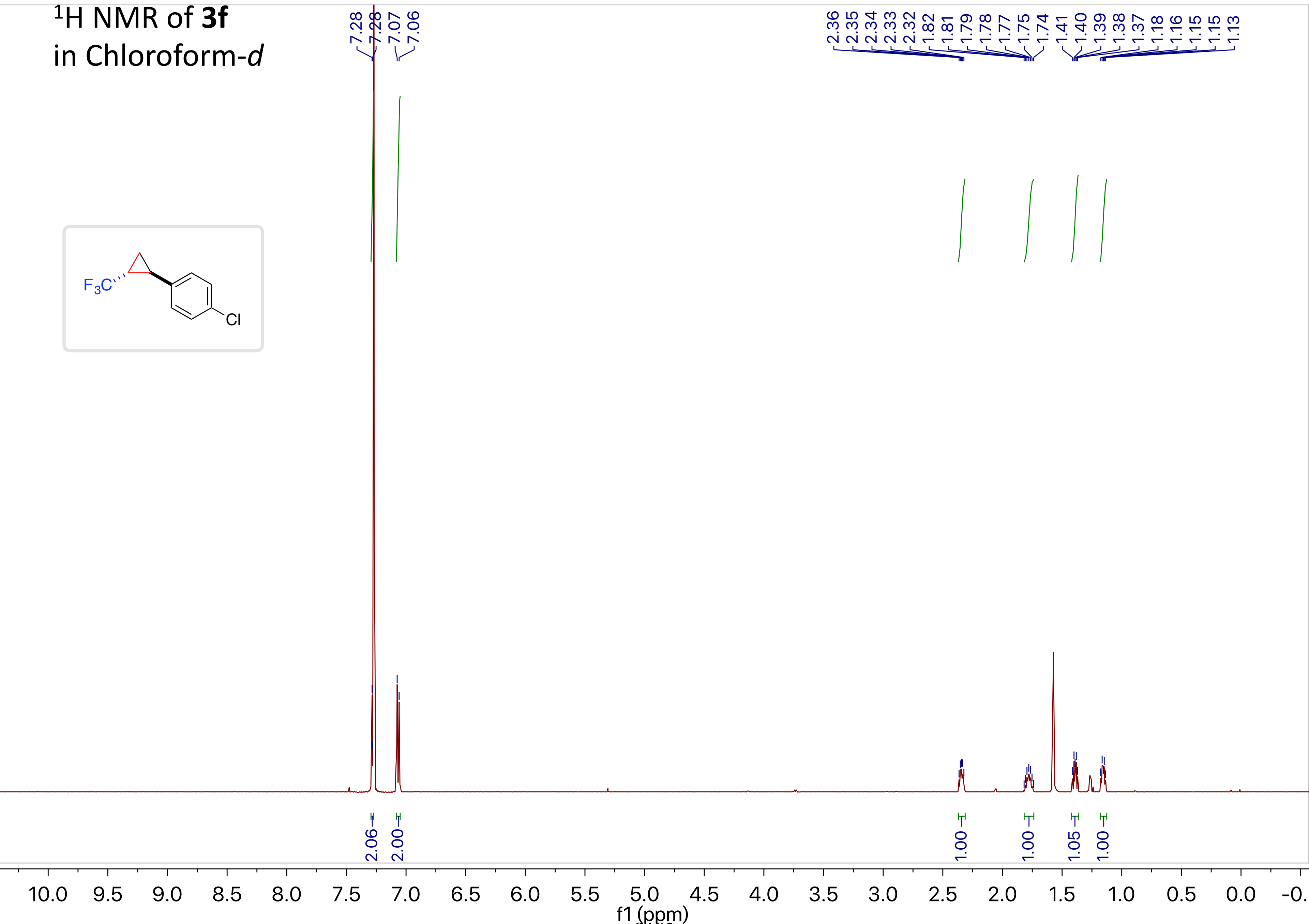
4: 225 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.500	49.008
2	13.040	50.992
Totals		100.000

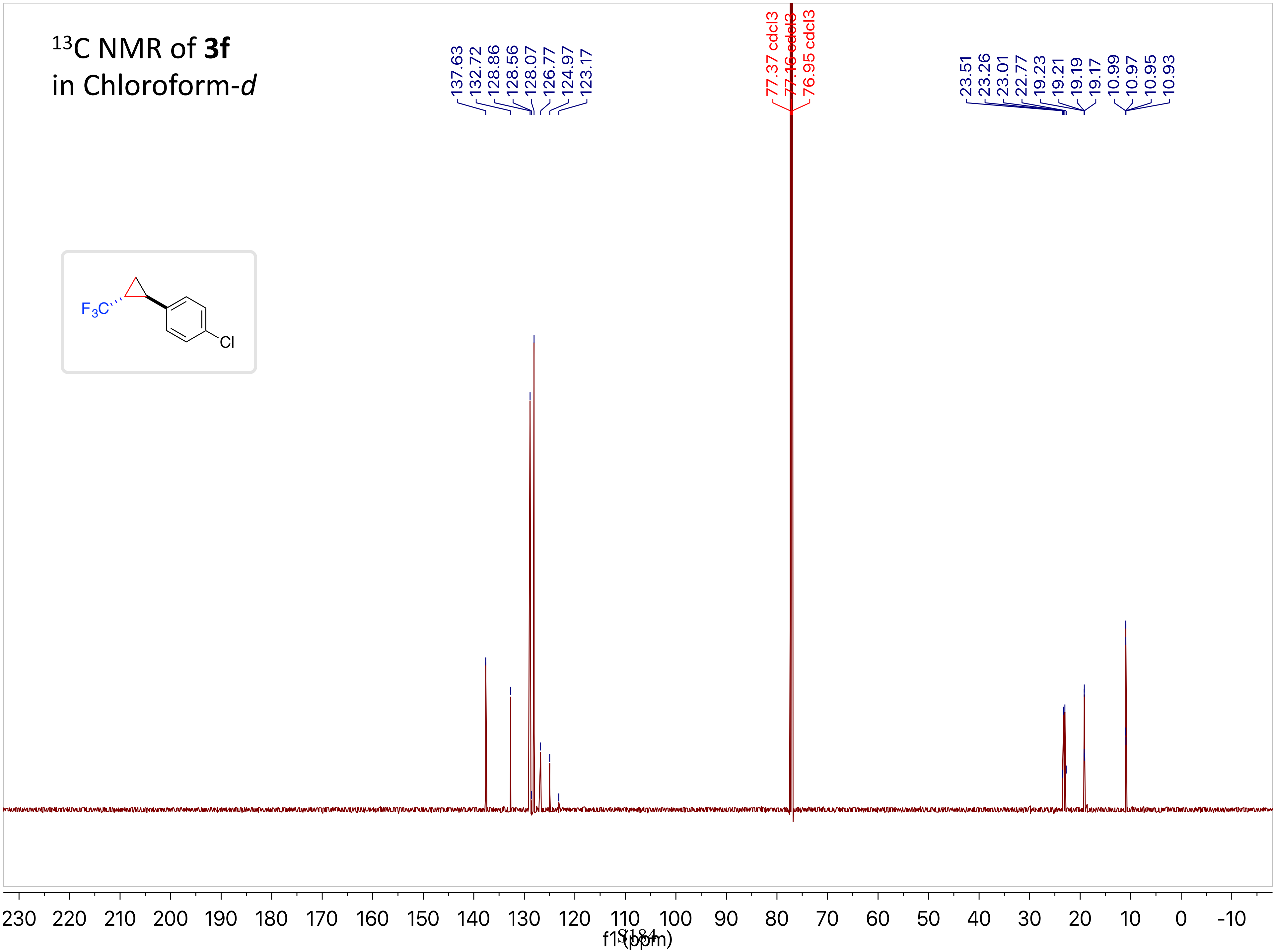


4: 225 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	12.628	96.950
2	13.120	3.050
Totals		100.000

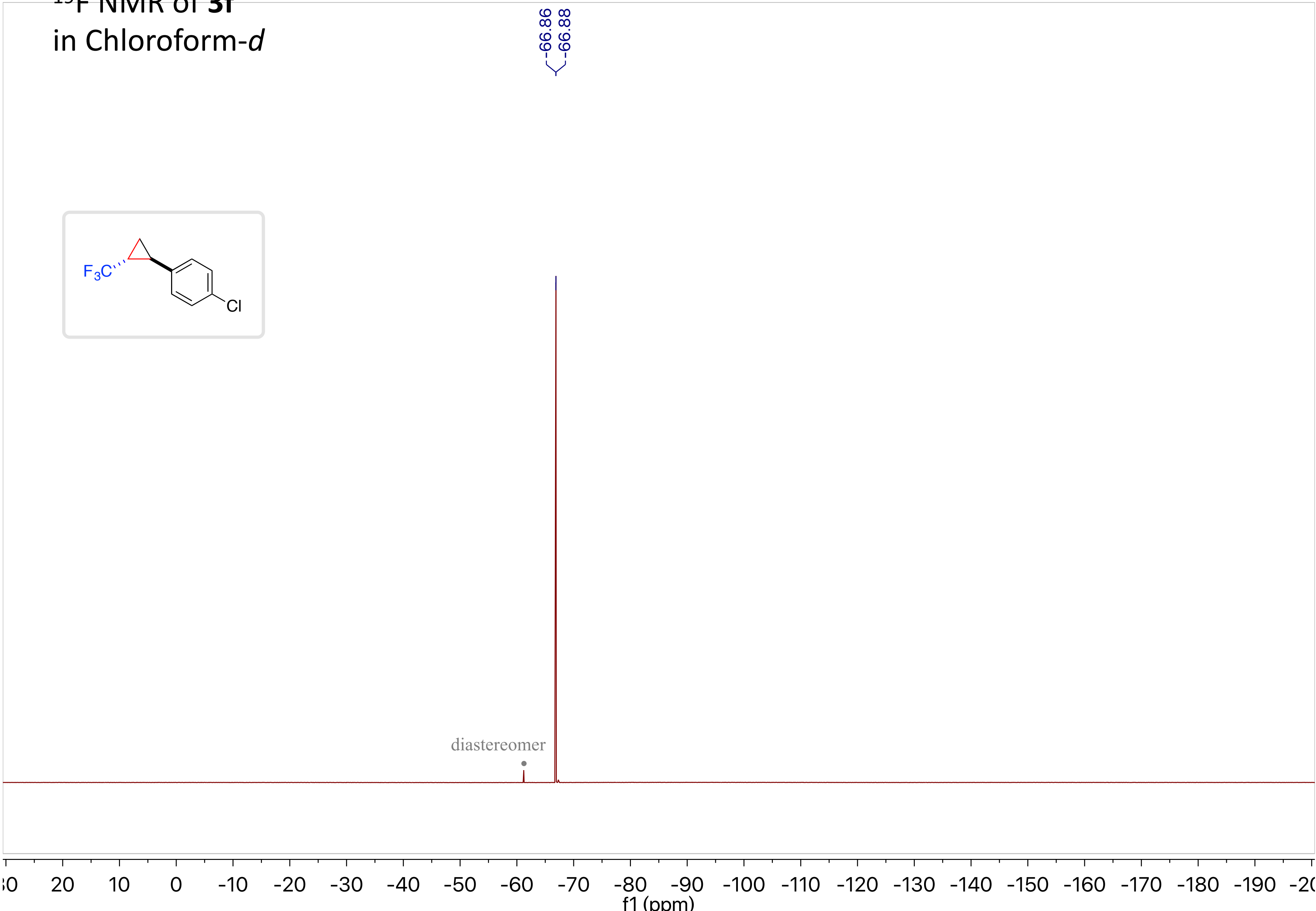


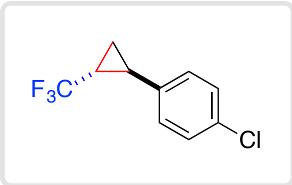
1H NMR of 3f
in Chloroform-d
F3C
Cl
7.28
7.28
7.07
7.06
2.36
2.35
2.34
2.33
2.32
1.82
1.81
1.79
1.78
1.77
1.75
1.74
1.41
1.40
1.39
1.38
1.37
1.18
1.16
1.15
1.15
1.13
2.06
2.00
1.00
1.00
1.05
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



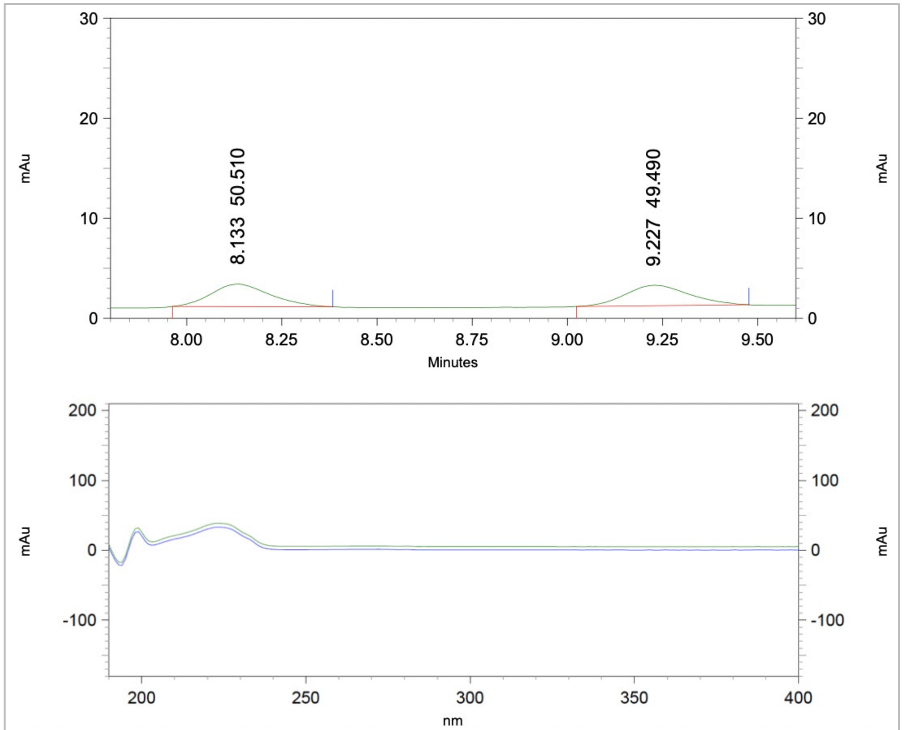
^{13}C NMR of **3f**
in Chloroform-*d*
137.63
132.72
128.86
128.56
128.07
126.77
124.97
123.17
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
23.51
23.26
23.01
22.77
19.23
19.21
19.19
19.17
10.99
10.97
10.95
10.93
F_3C
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR of **3f**
in Chloroform-*d*



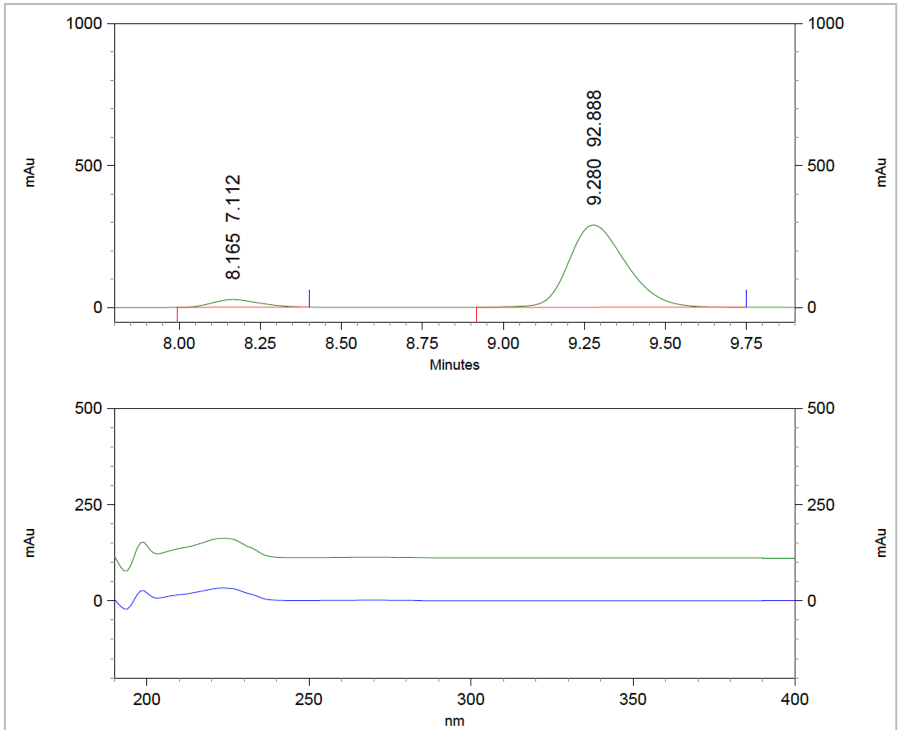


HPLC of **3f**



2: 229 nm, 4
nm Results

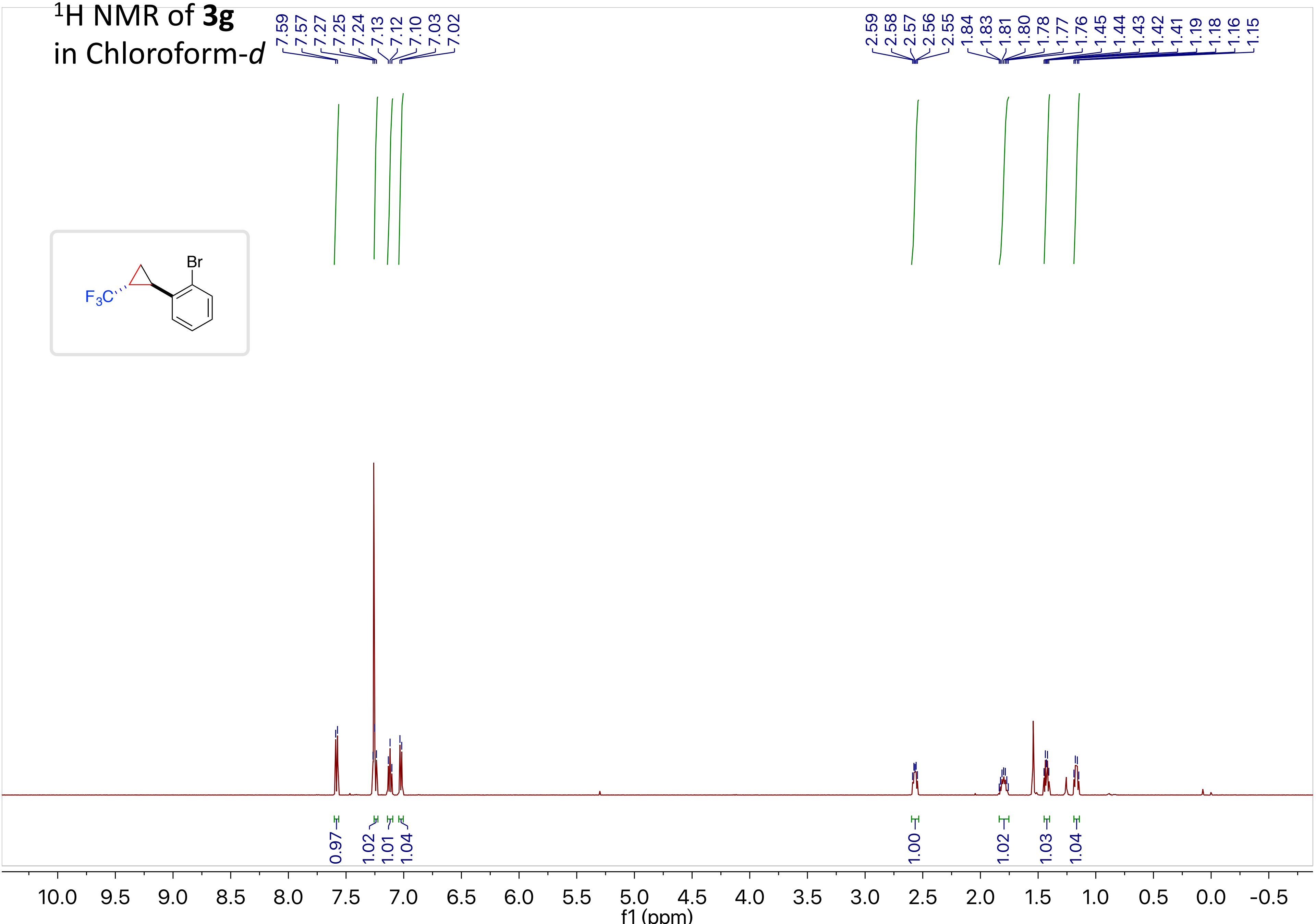
Pk #	Retention Time	Area Percent
1	8.133	50.510
2	9.227	49.490
Totals		100.000



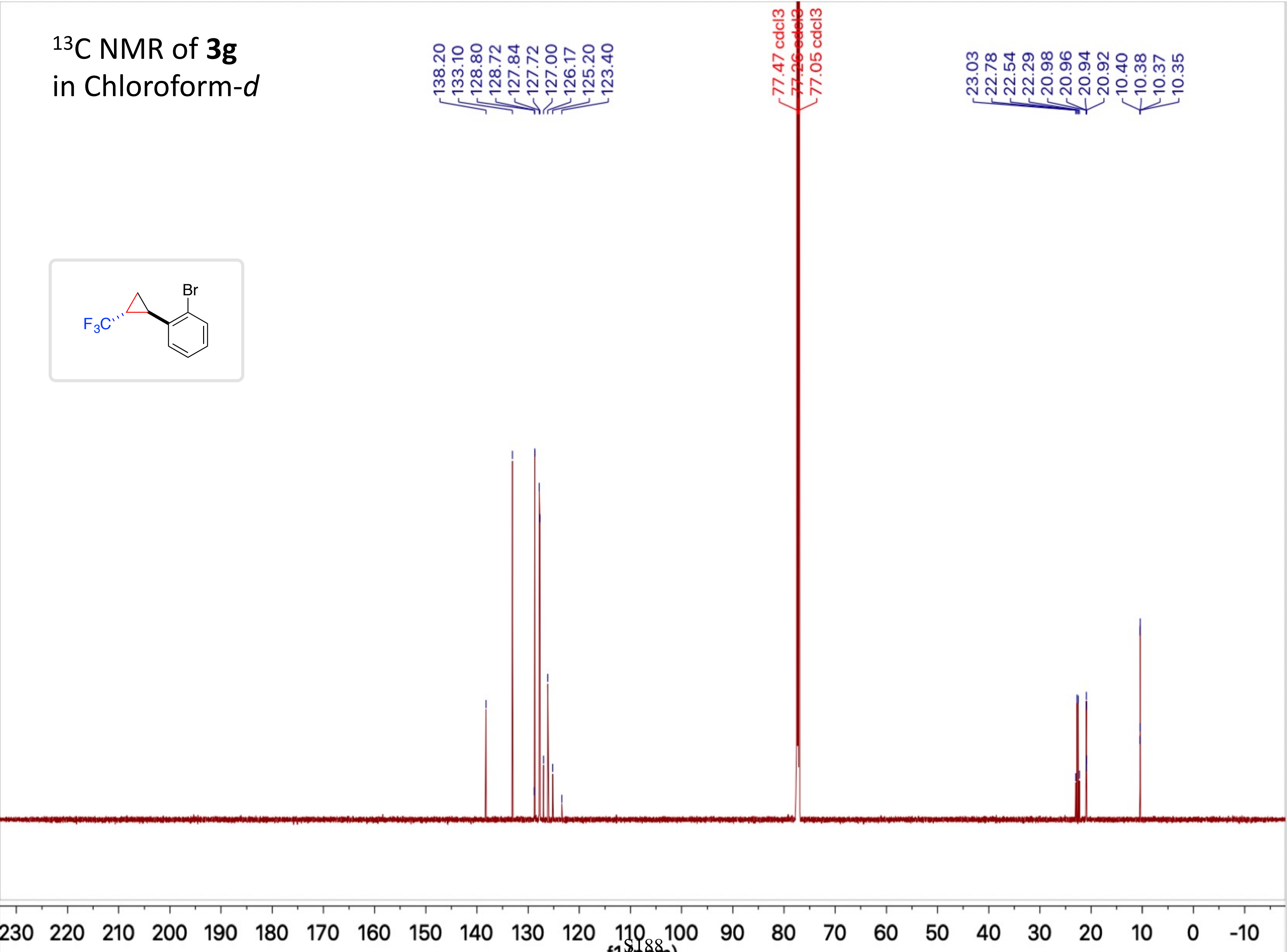
2: 228 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	8.165	7.112
2	9.280	92.888
Totals		100.000

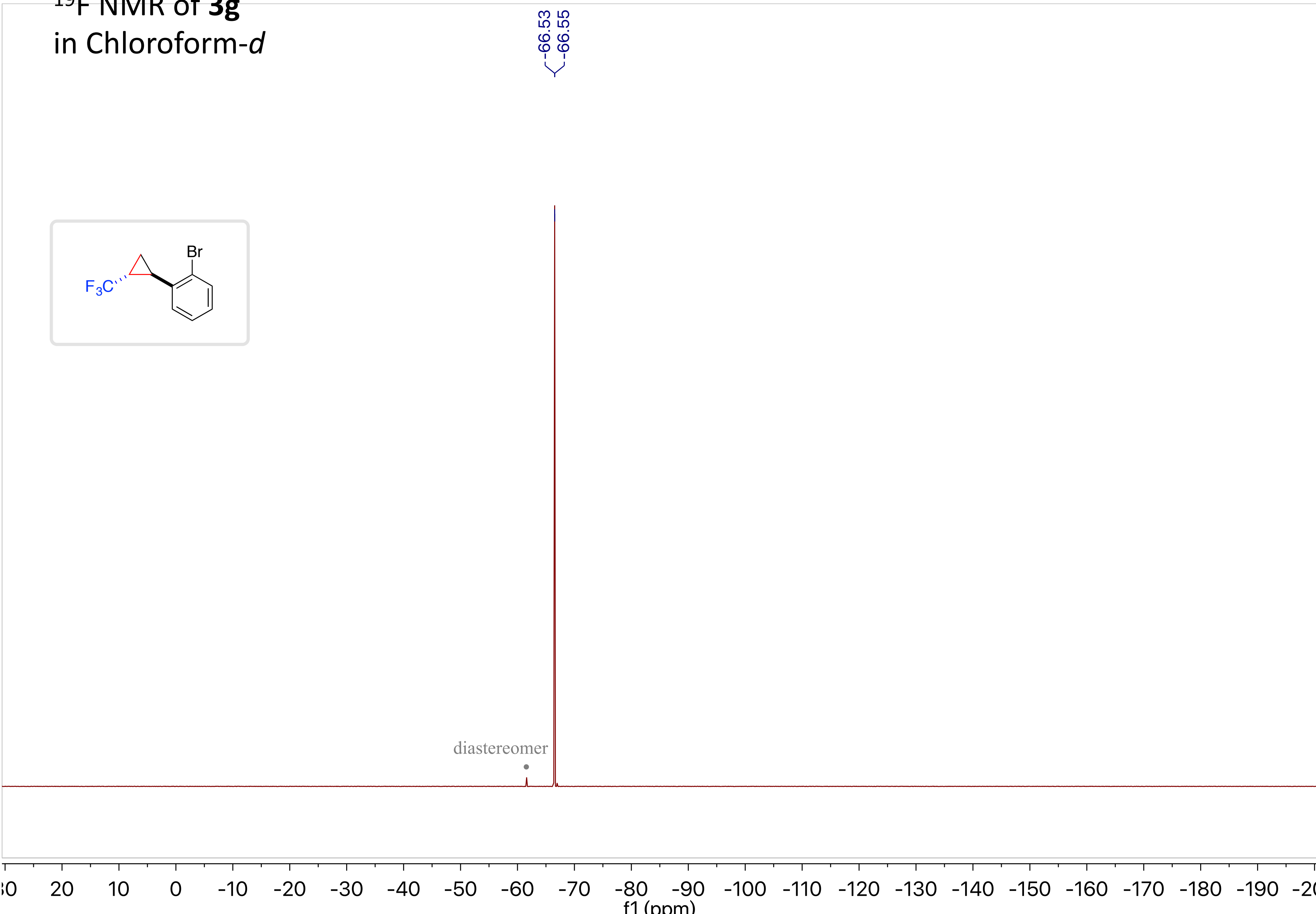
^{1}H NMR of **3g** in Chloroform-*d*

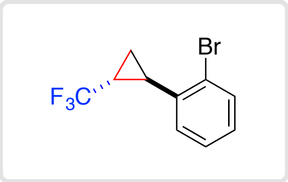


^{13}C NMR of **3g**
in Chloroform-*d*

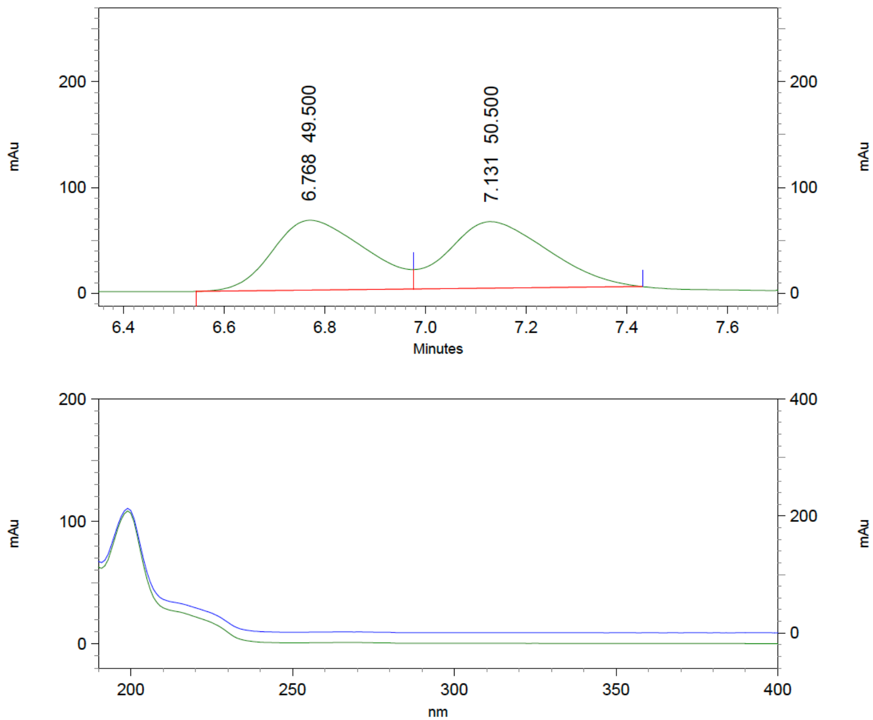


[19]F NMR of **3g**
in Chloroform-*d*



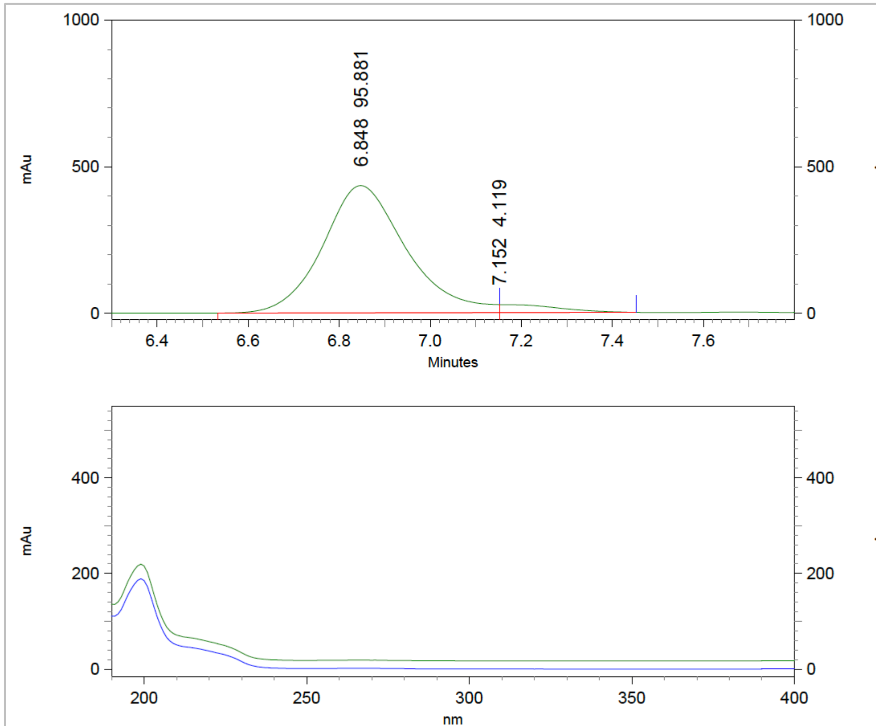


HPLC of **3g**



4: 225 nm, 4 nm Results

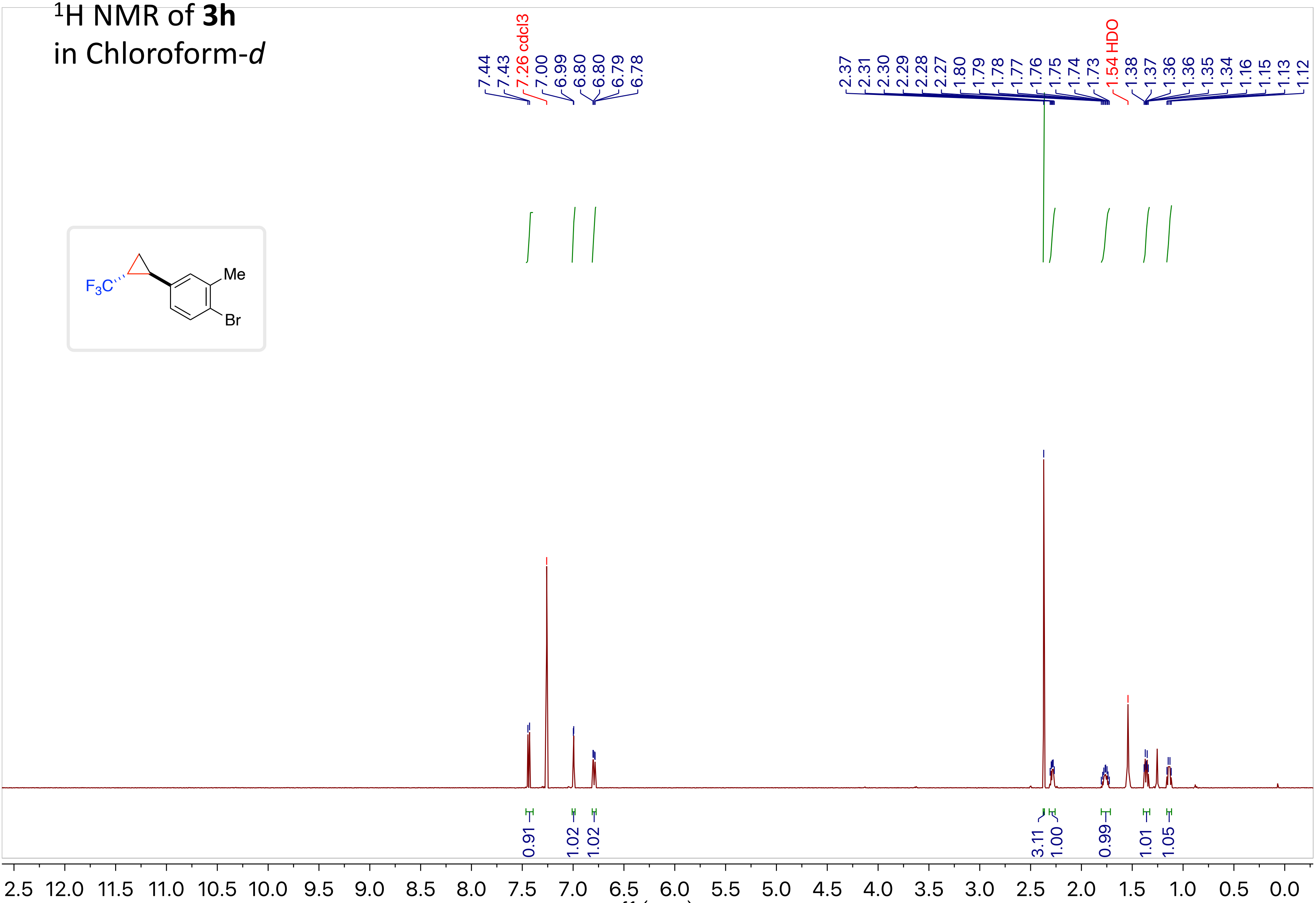
Pk #	Retention Time	Area Percent
1	6.768	49.500
2	7.131	50.500
Totals		100.000



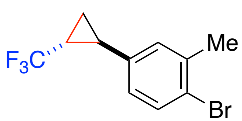
2: 225 nm, 4 nm Results

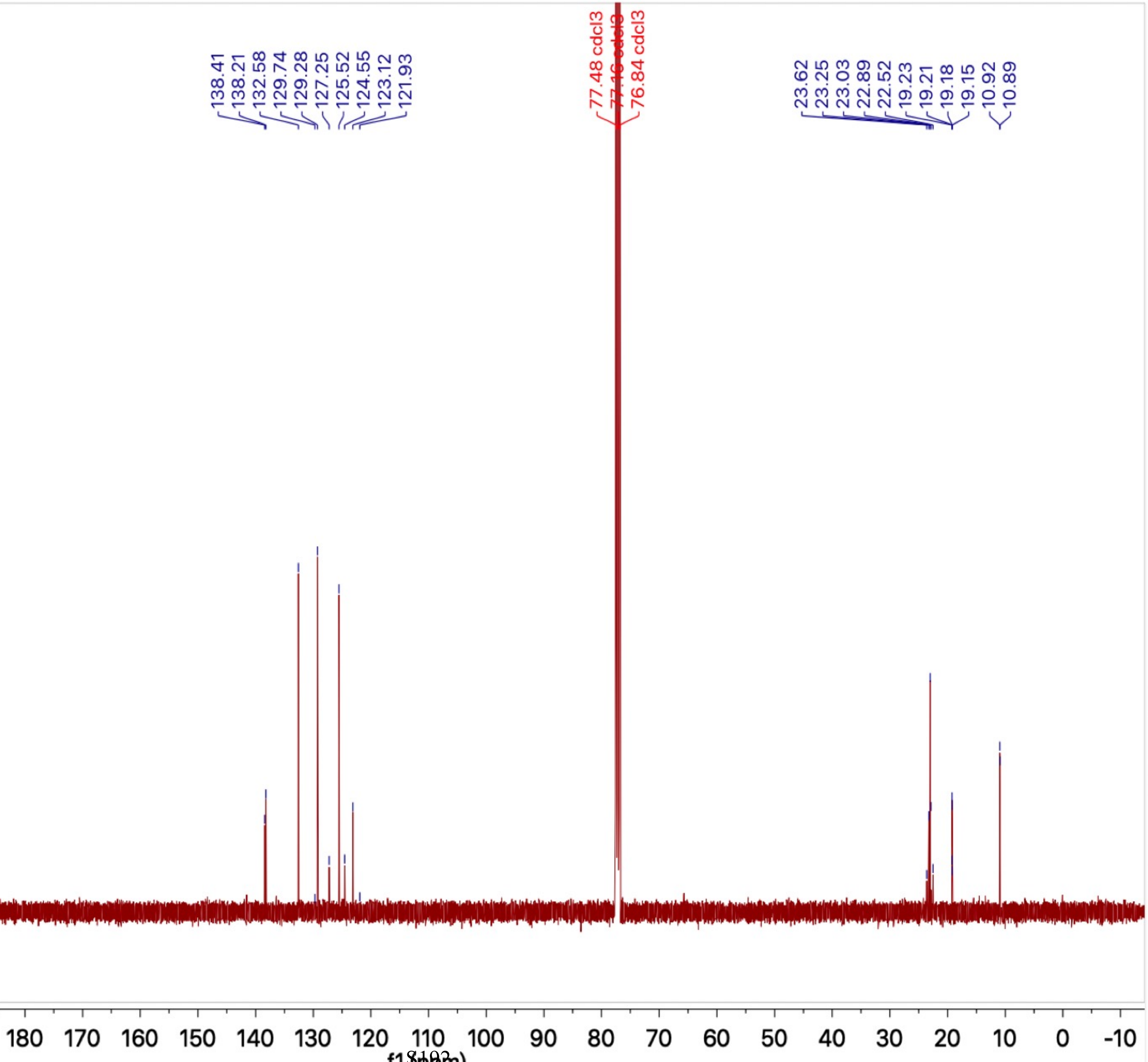
Pk #	Retention Time	Area Percent
1	6.848	95.881
2	7.152	4.119
Totals		100.000

[1]H NMR of **3h**
in Chloroform-*d*

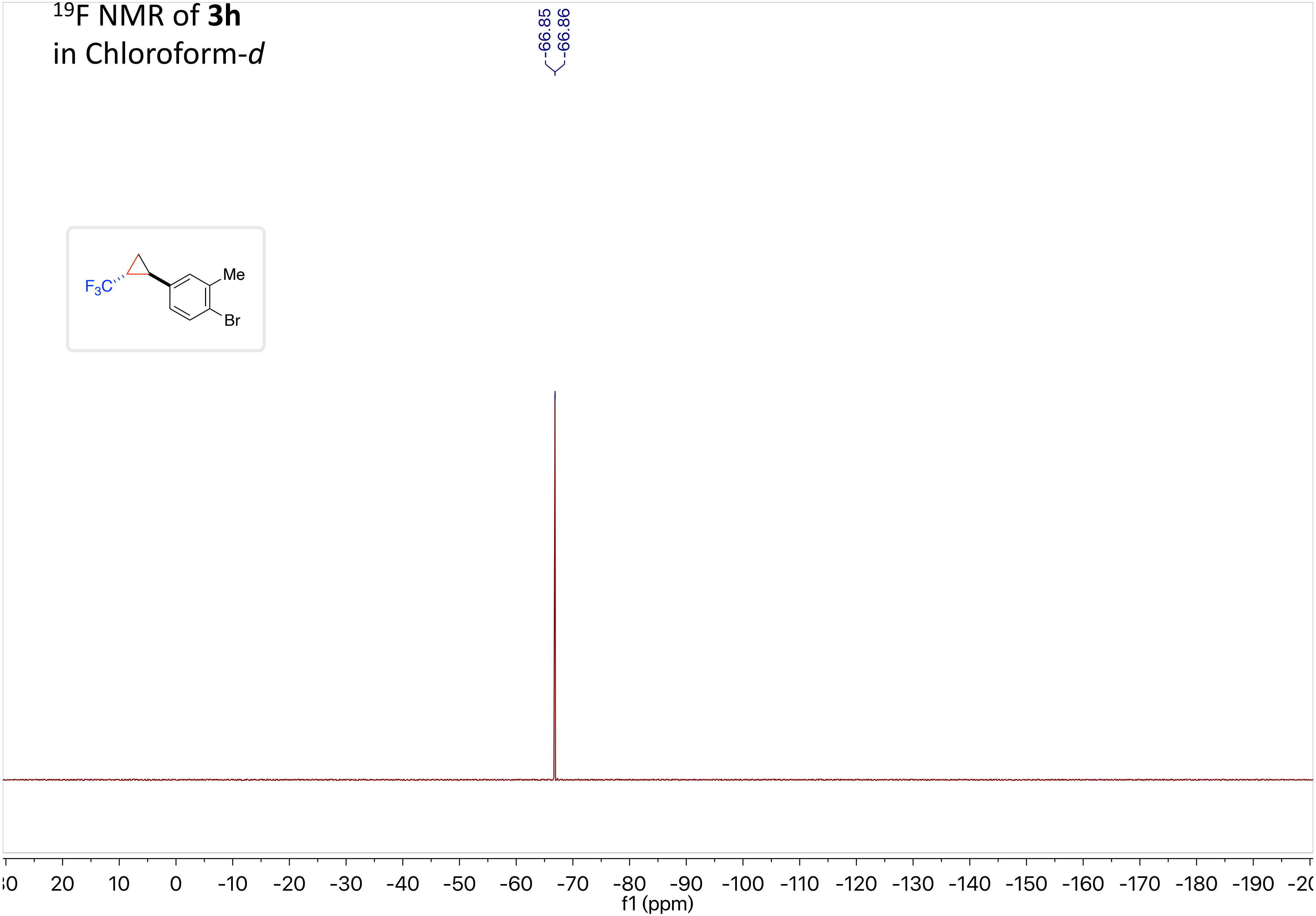


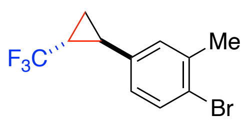
[13]C NMR of **3h** in Chloroform-*d*



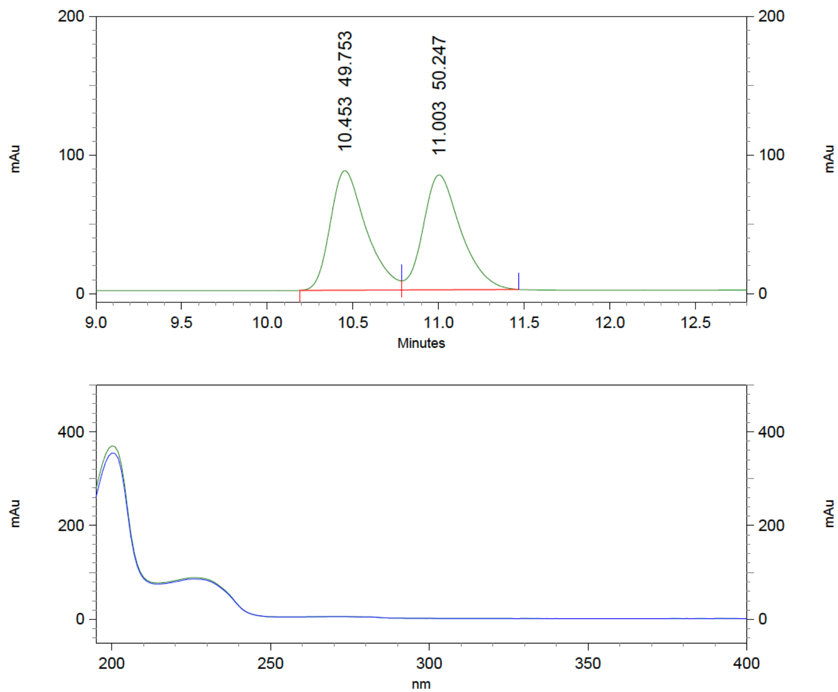


[19]F NMR of **3h**
in Chloroform-*d*



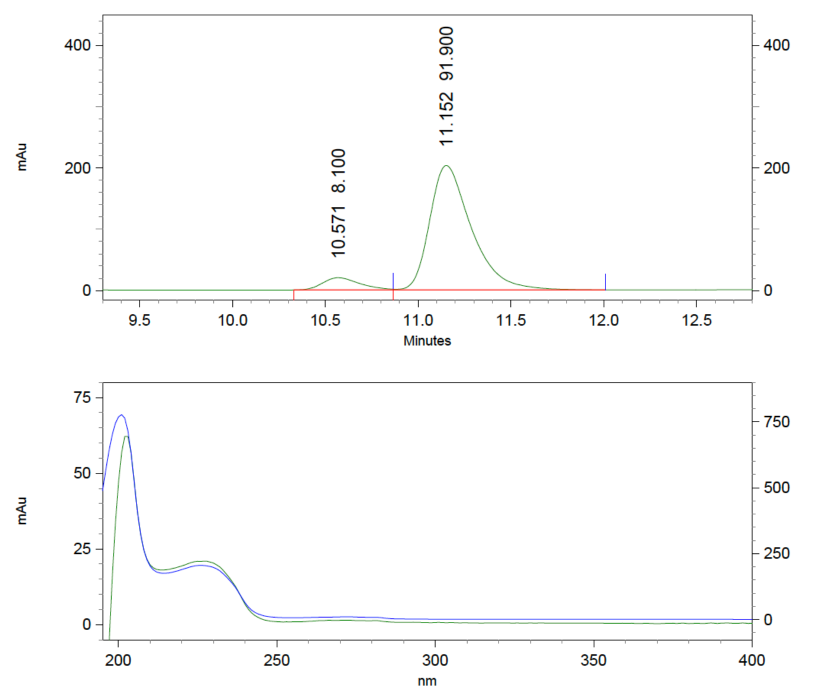


HPLC of **3h**



4: 226 nm, 4
nm Results

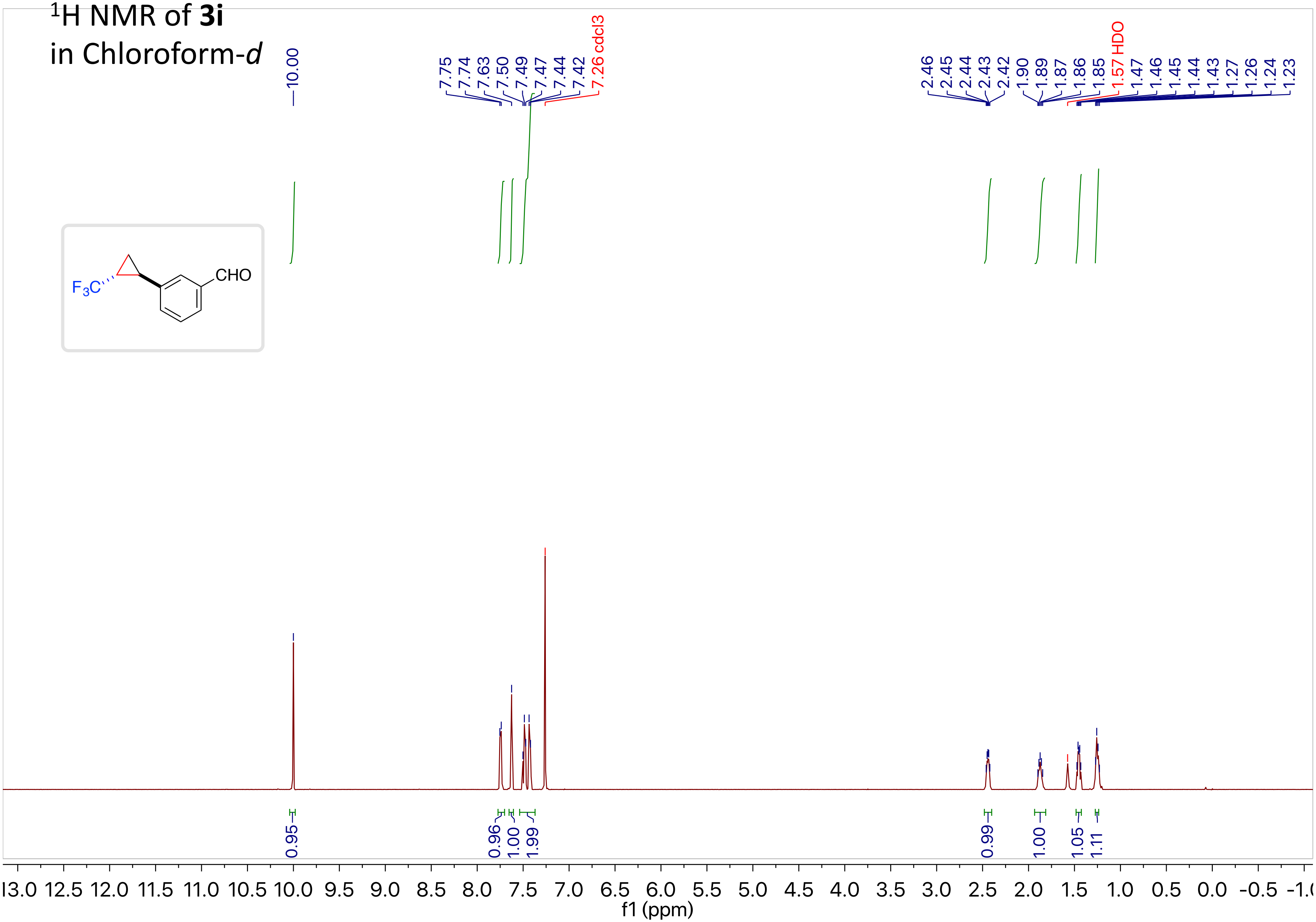
Pk #	Retention Time	Area Percent
1	10.453	49.753
2	11.003	50.247
Totals		100.000

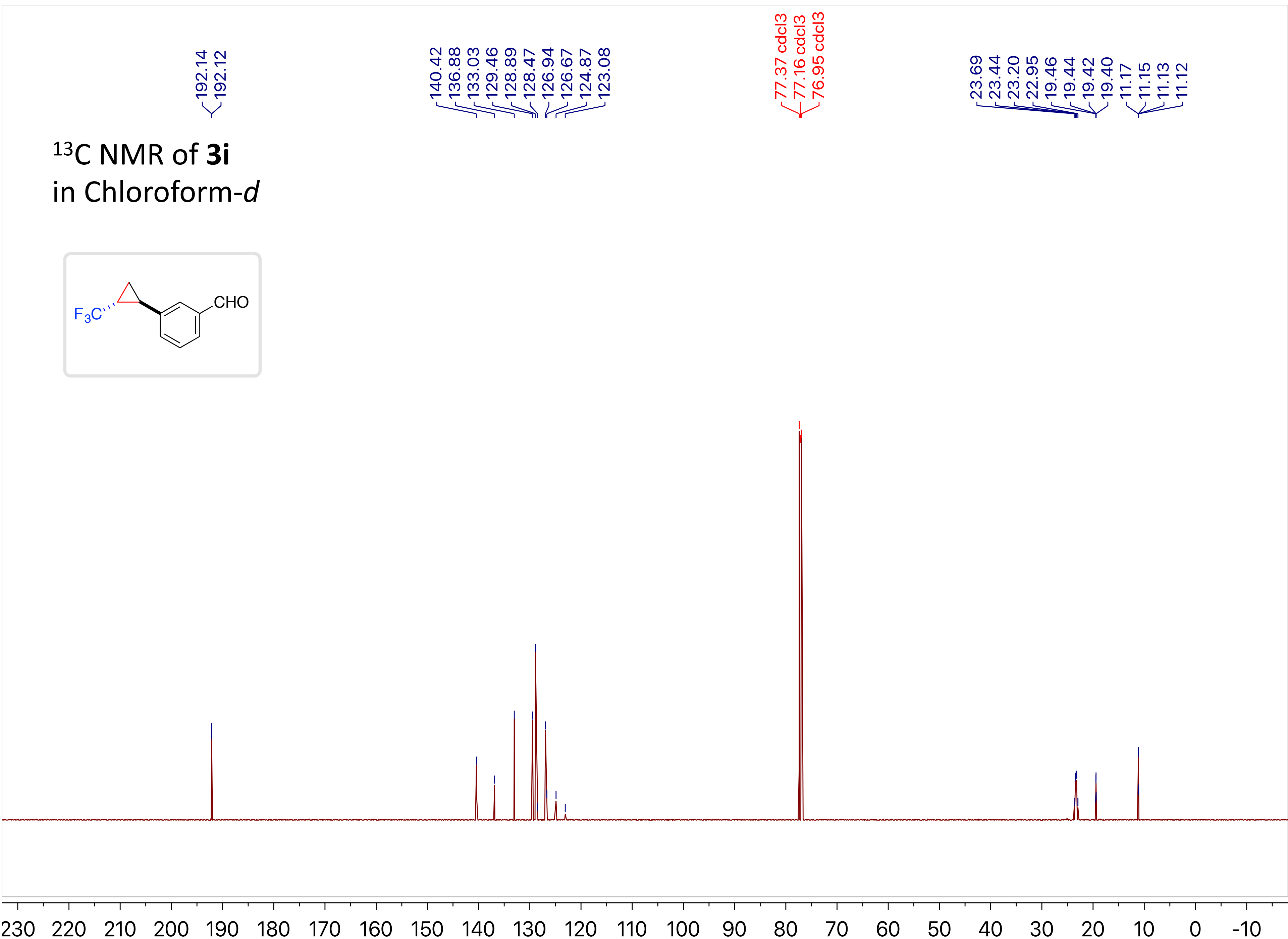


4: 226 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	10.571	8.100
2	11.152	91.900
Totals		100.000

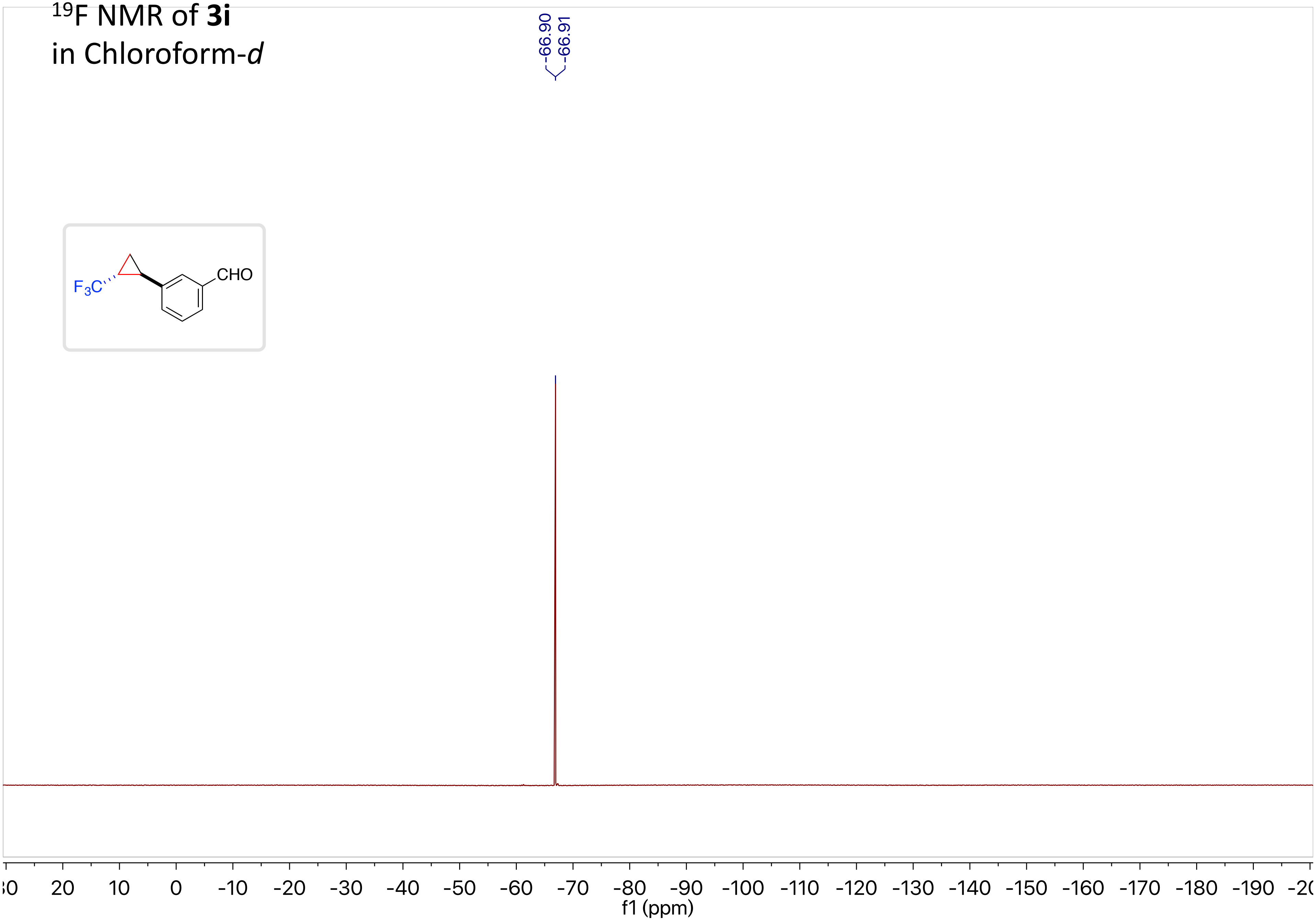
[1]H NMR of **3i**
in Chloroform-*d*

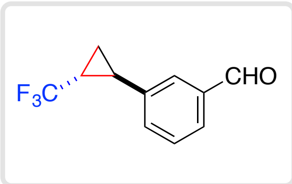




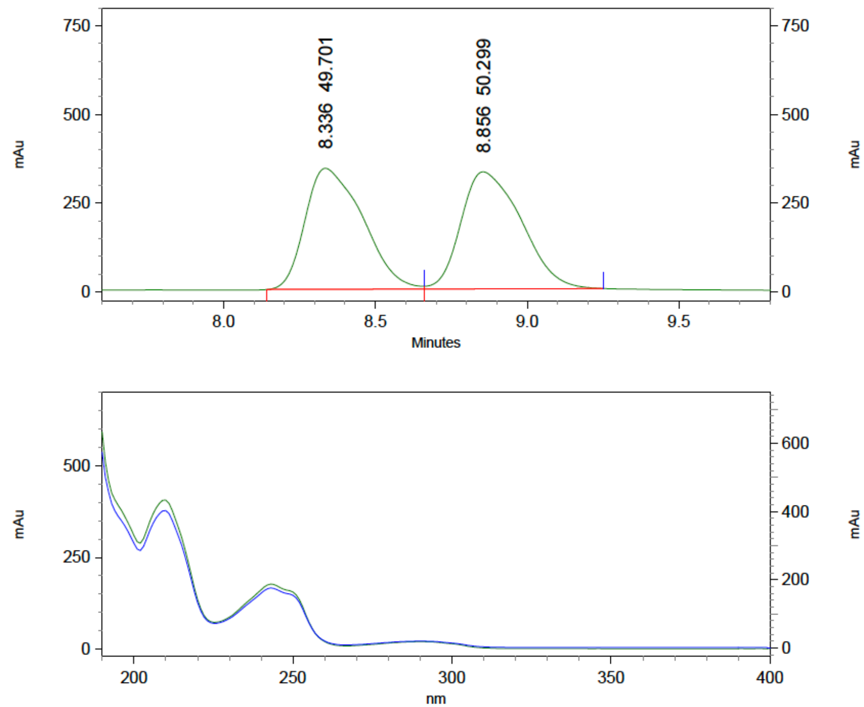
192.14
192.12
140.42
136.88
133.03
129.46
128.89
128.47
126.94
126.67
124.87
123.08
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
23.69
23.44
23.20
22.95
19.46
19.44
19.42
19.40
11.17
11.15
11.13
11.12
13C NMR of 3i
in Chloroform-d
F3C
CHO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR of **3i**
in Chloroform-*d*



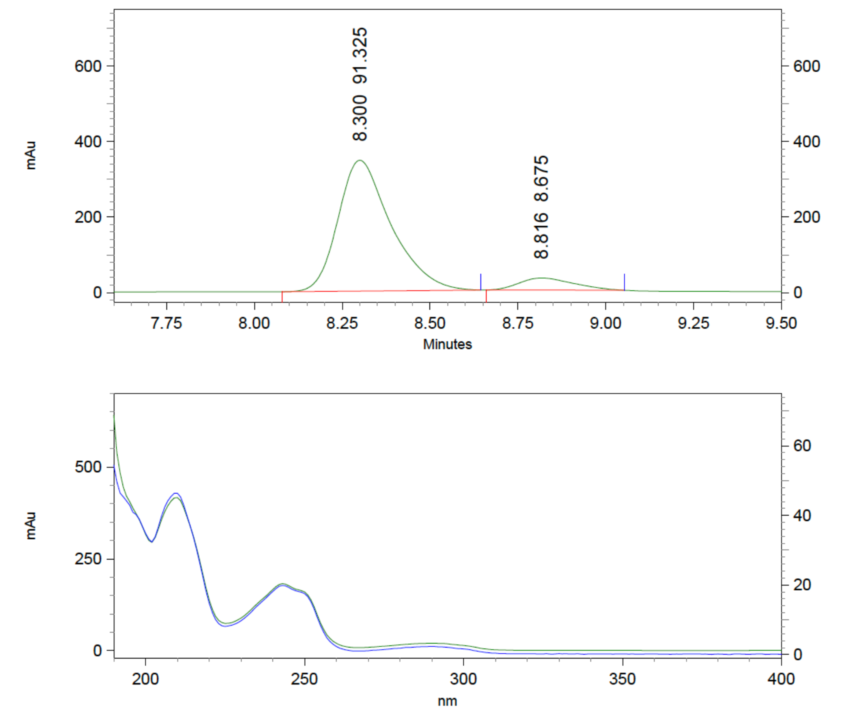


HPLC of **3i**



3: 219 nm, 4
nm Results

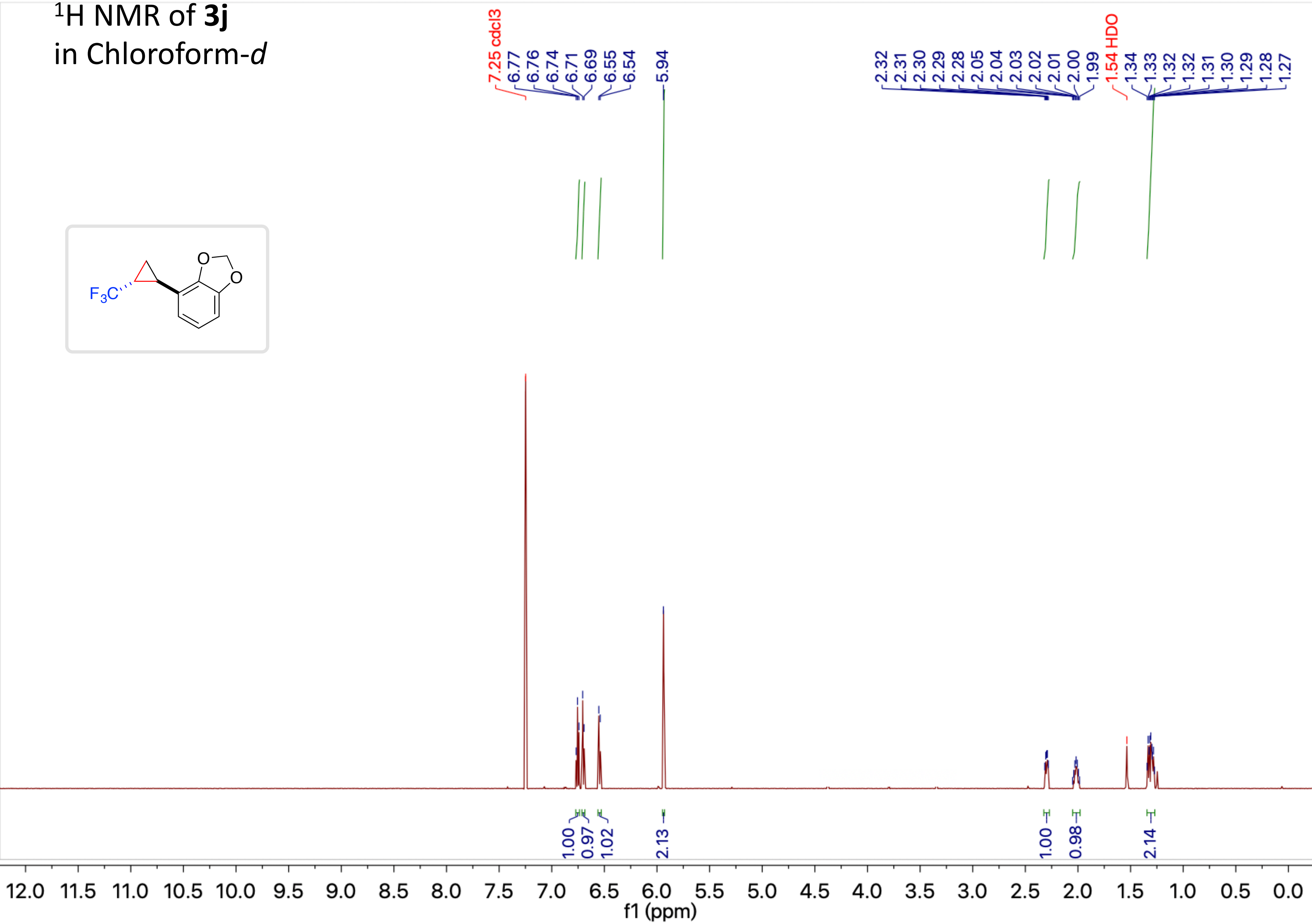
Pk #	Retention Time	Area Percent
1	8.336	49.701
2	8.856	50.299
Totals		100.000



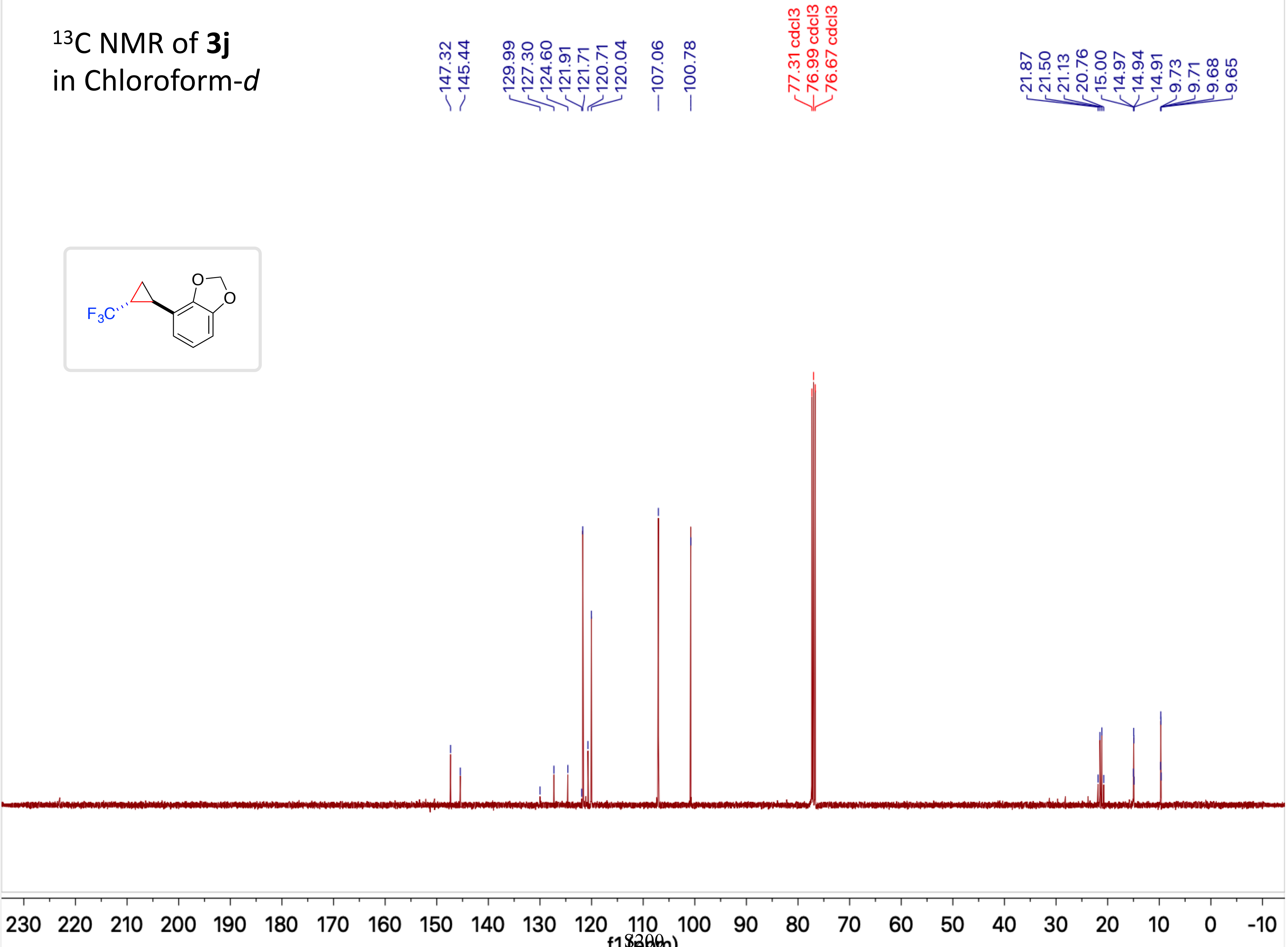
3: 219 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	8.300	91.325
2	8.816	8.675
Totals		100.000

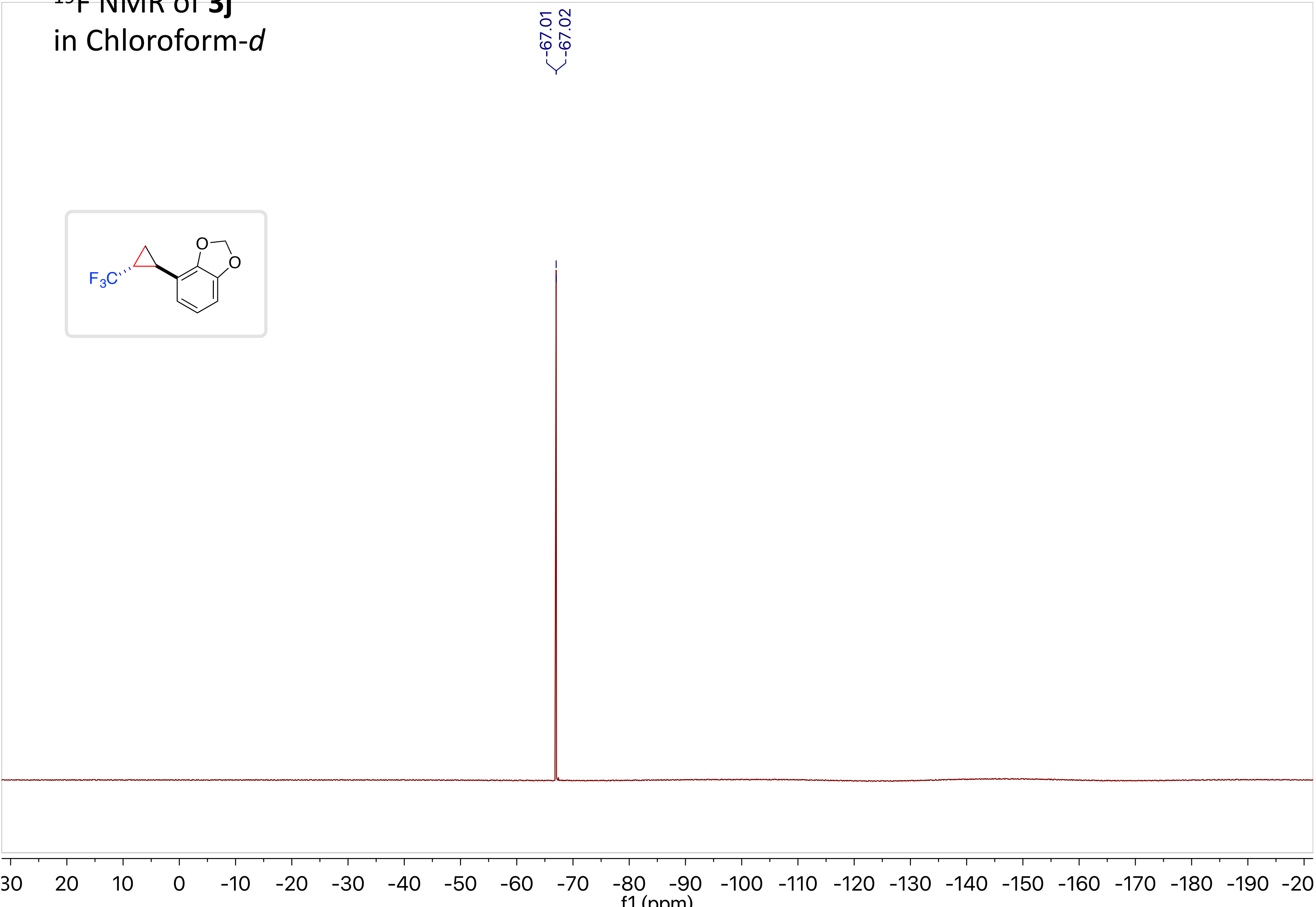
[1]H NMR of **3j**
in Chloroform-*d*

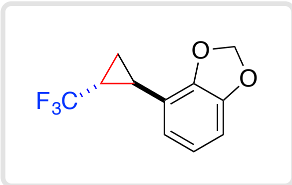


^{13}C NMR of **3j**
in Chloroform-*d*

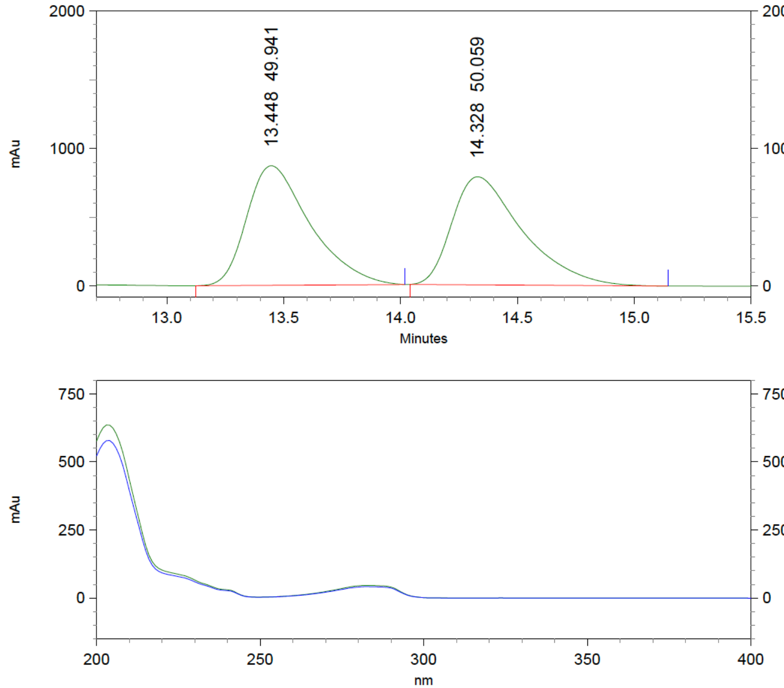


[19]F NMR of **3j**
in Chloroform-*d*



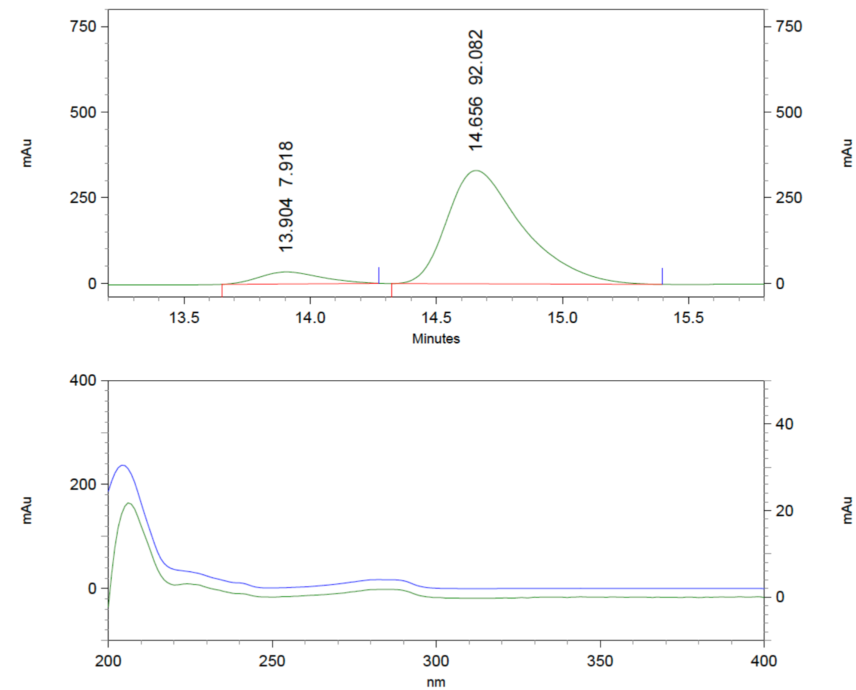


HPLC of **3j**



4: 210 nm, 4 nm Results

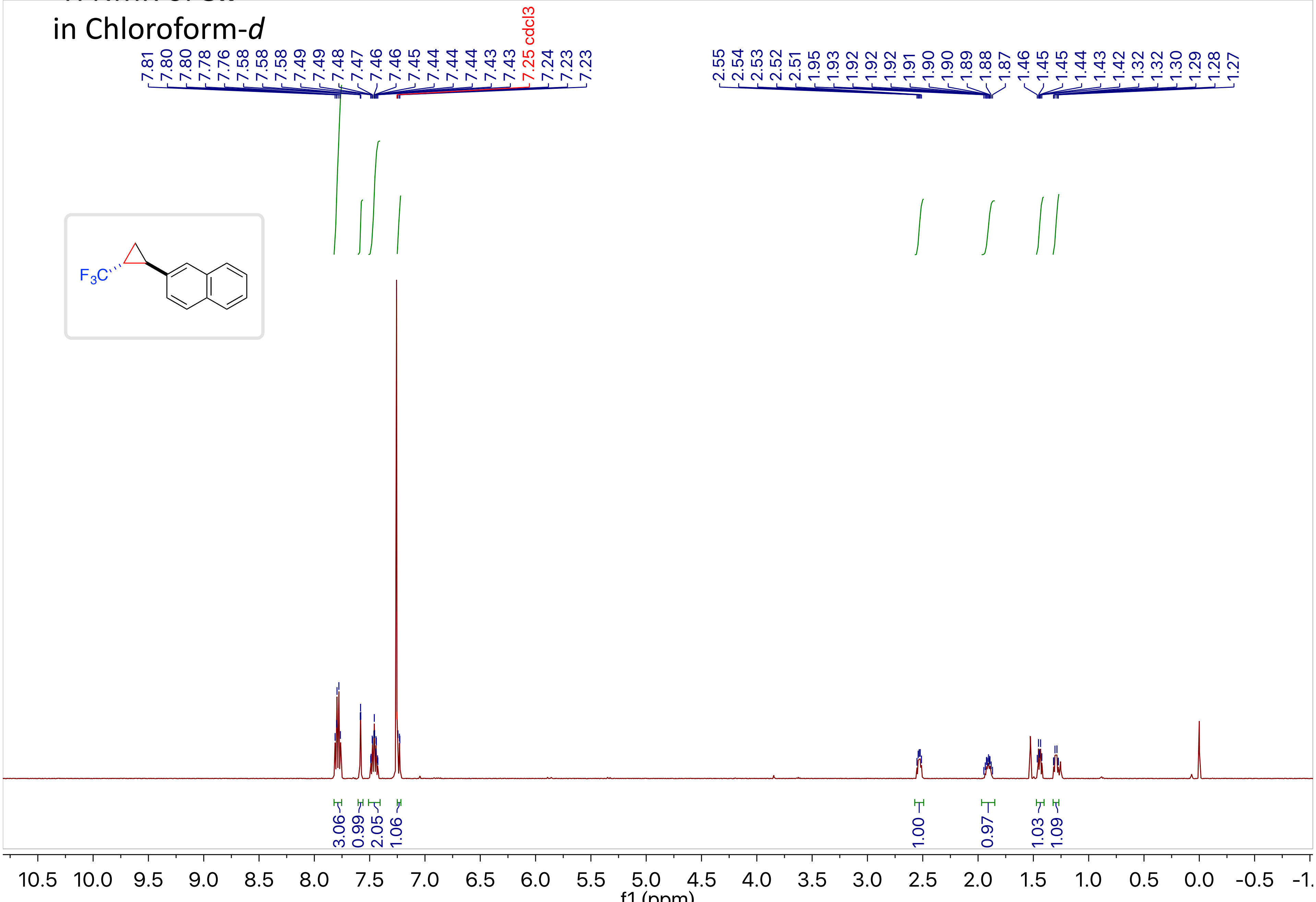
Pk #	Retention Time	Area Percent
1	13.448	49.941
2	14.328	50.059
Totals		100.000



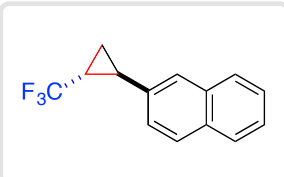
4: 210 nm, 4 nm Results

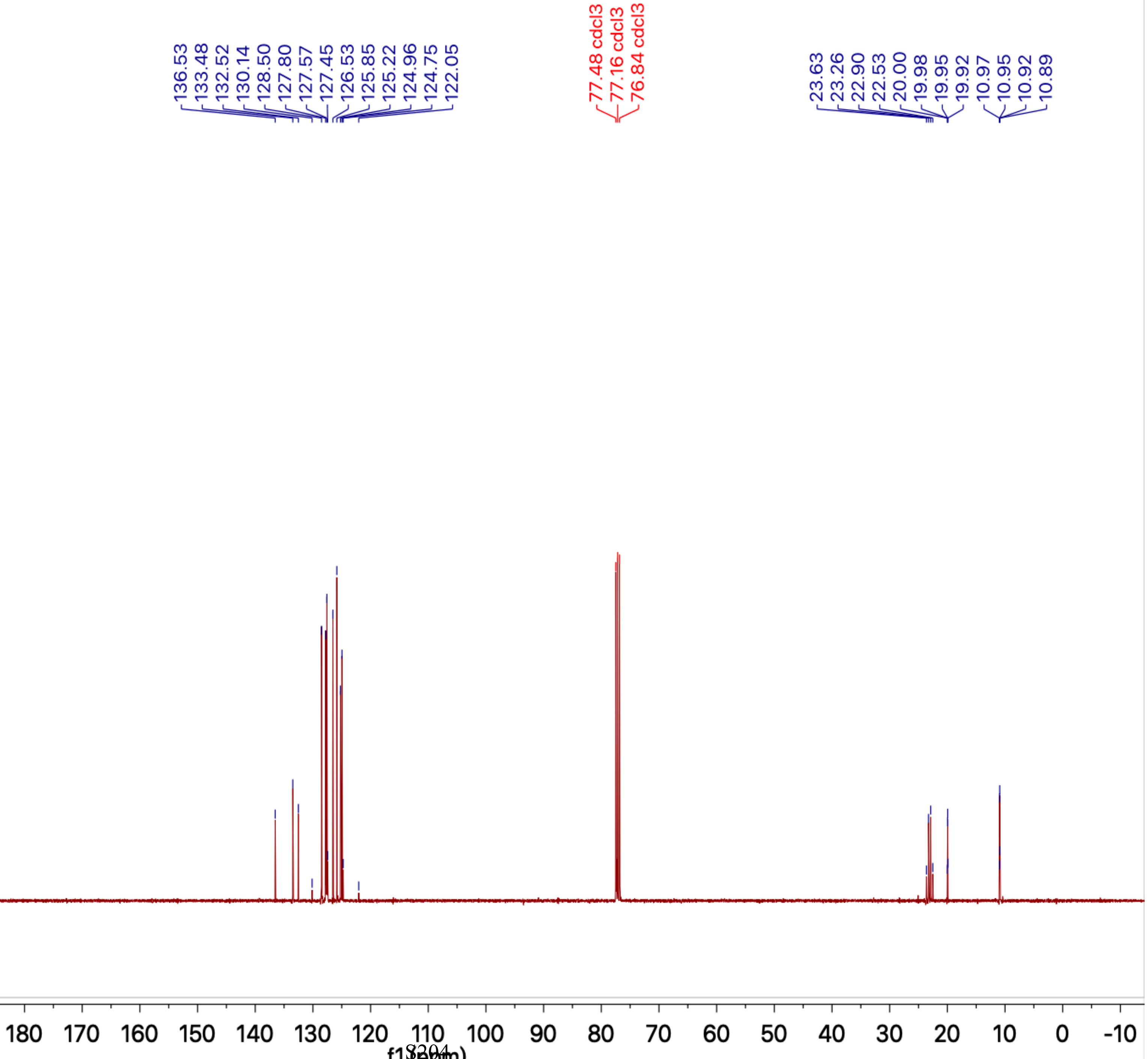
Pk #	Retention Time	Area Percent
1	13.904	7.918
2	14.656	92.082
Totals		100.000

^{1}H NMR of **3k**
in Chloroform-*d*

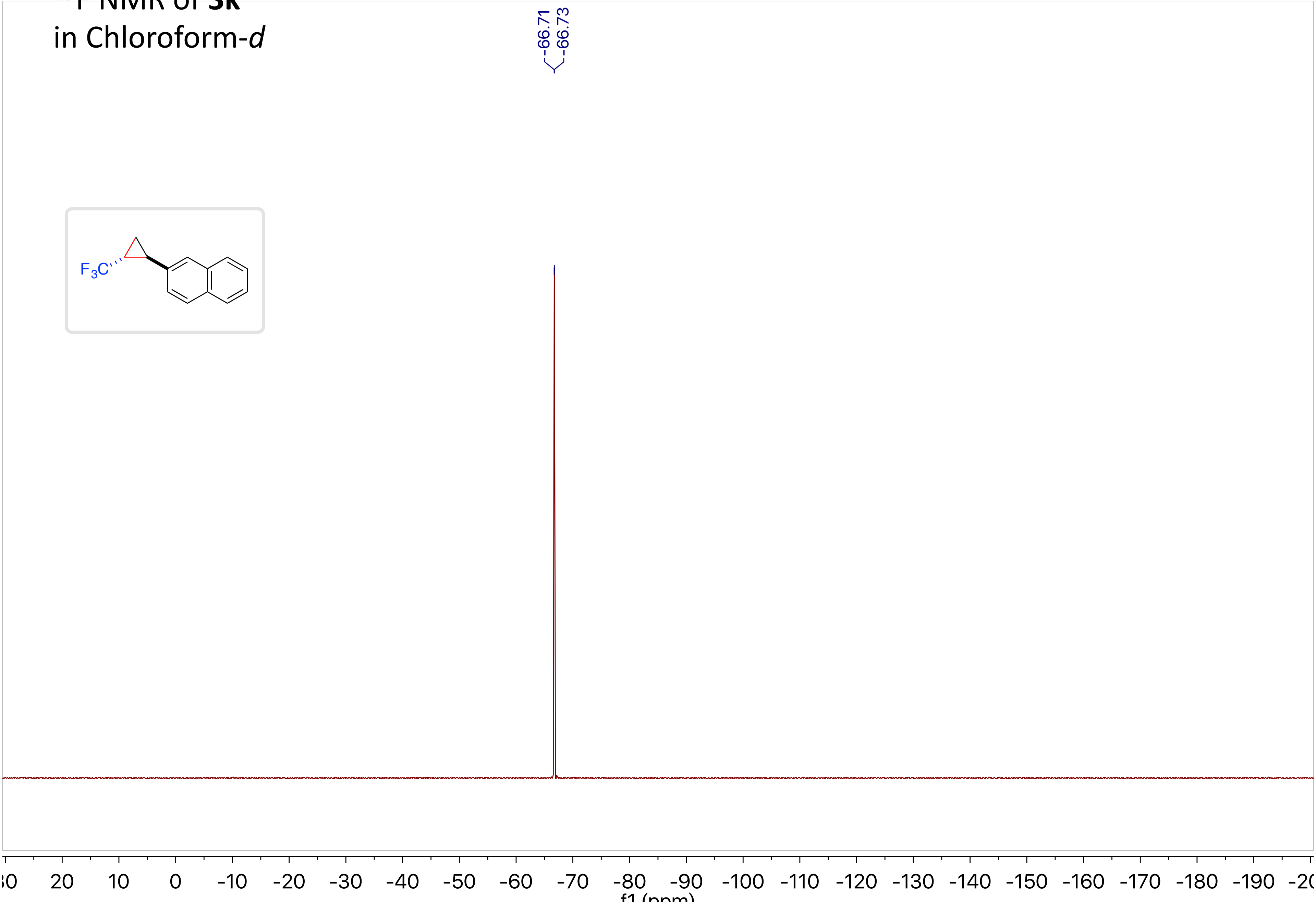


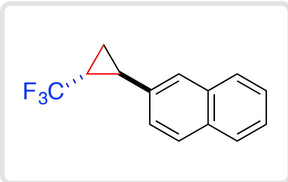
^{13}C NMR of **3k** in Chloroform-*d*



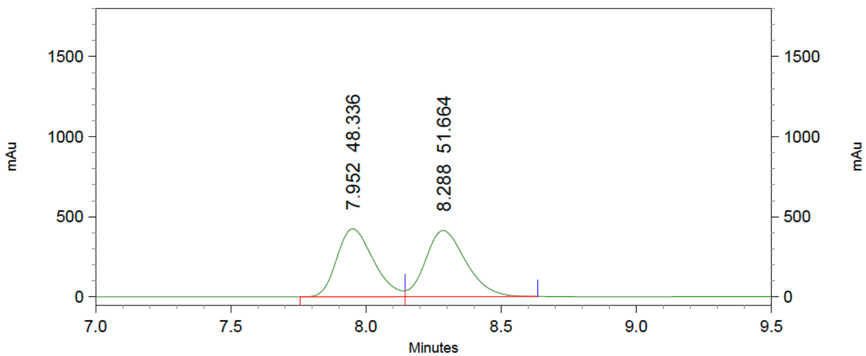


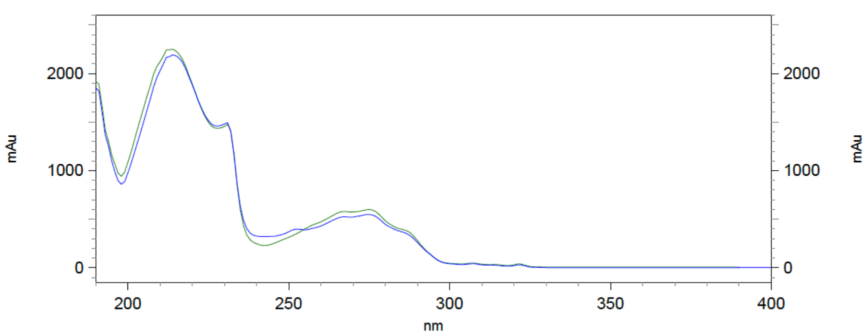
[19]F NMR of **3k**
in Chloroform-*d*





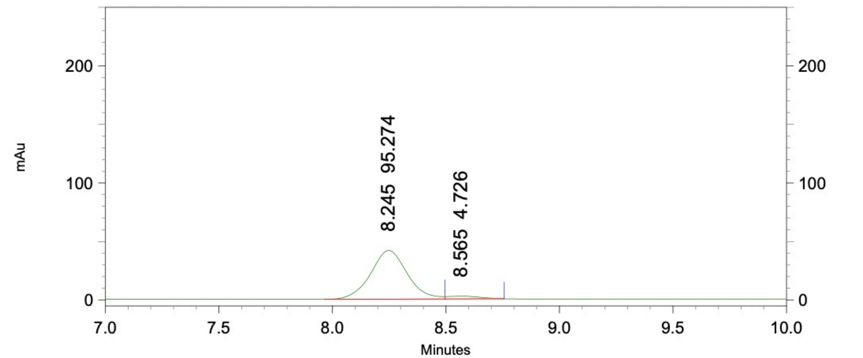
HPLC of **3k**

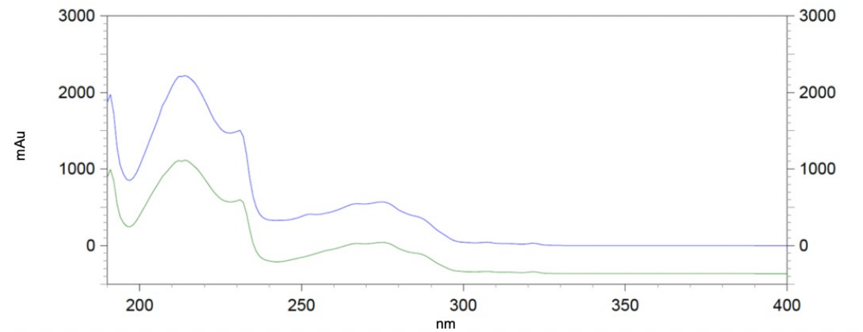




4: 258 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	7.952	48.336
2	8.288	51.664
Totals		100.000

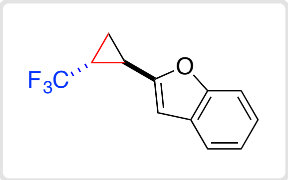


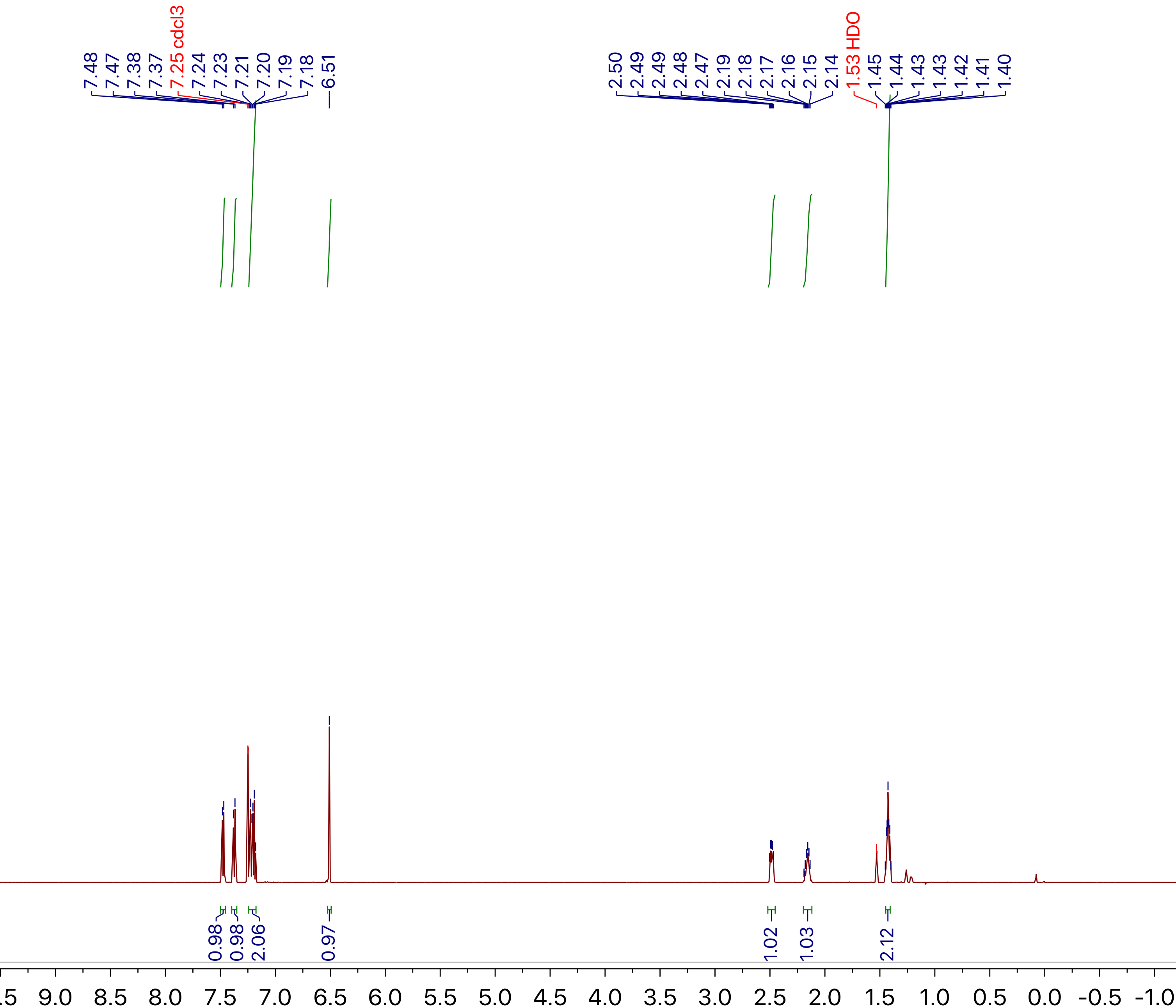


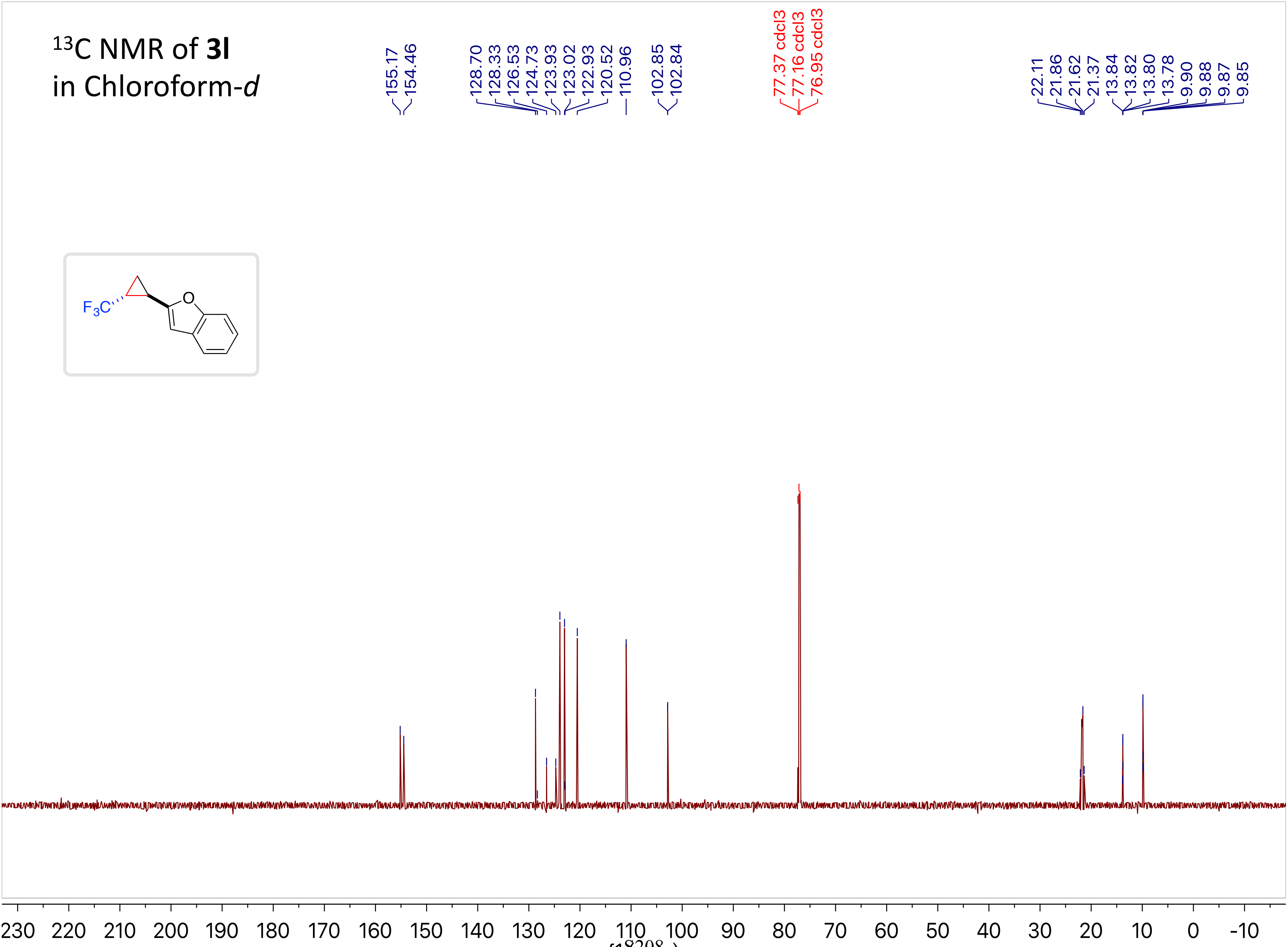
4: 257 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	8.245	95.274
2	8.565	4.726
Totals		100.000

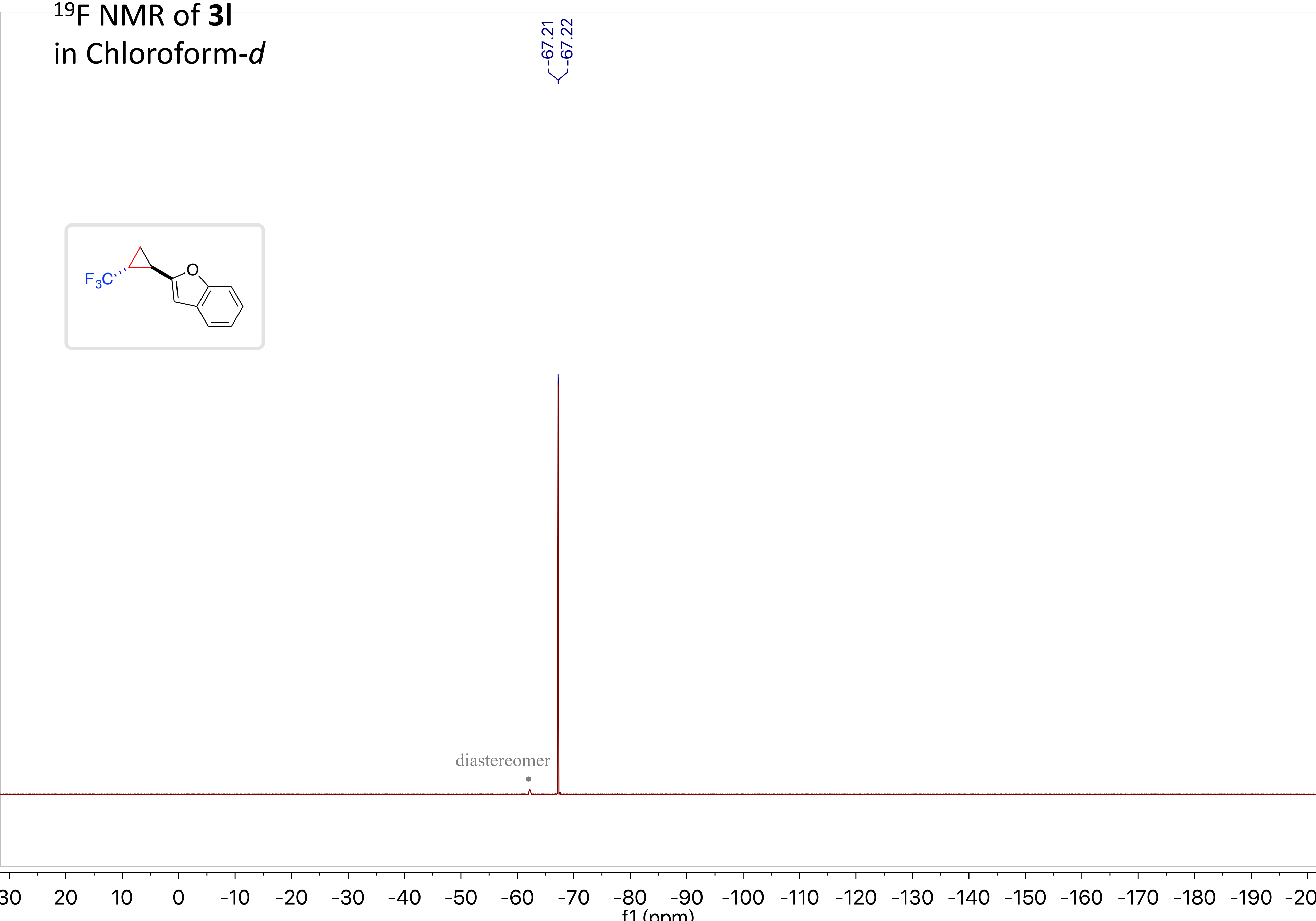
^{1}H NMR of **3l**
in Chloroform-*d*

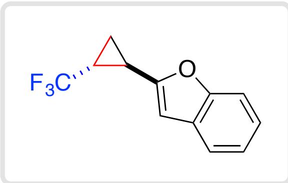




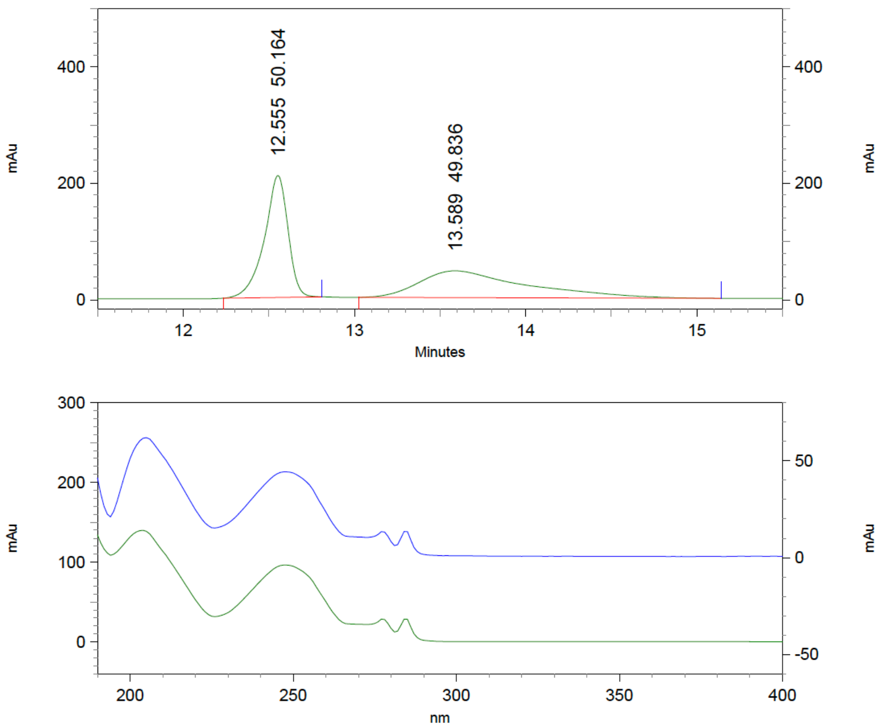

13C NMR of 3l
in Chloroform-d
155.17
154.46
128.70
128.33
126.53
124.73
123.93
123.02
122.93
120.52
110.96
102.85
102.84
77.37 cdcl3
77.16 cdcl3
76.95 cdcl3
22.11
21.86
21.62
21.37
13.84
13.82
13.80
13.78
9.90
9.88
9.87
9.85
F3C
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR of **3l**
in Chloroform-*d*



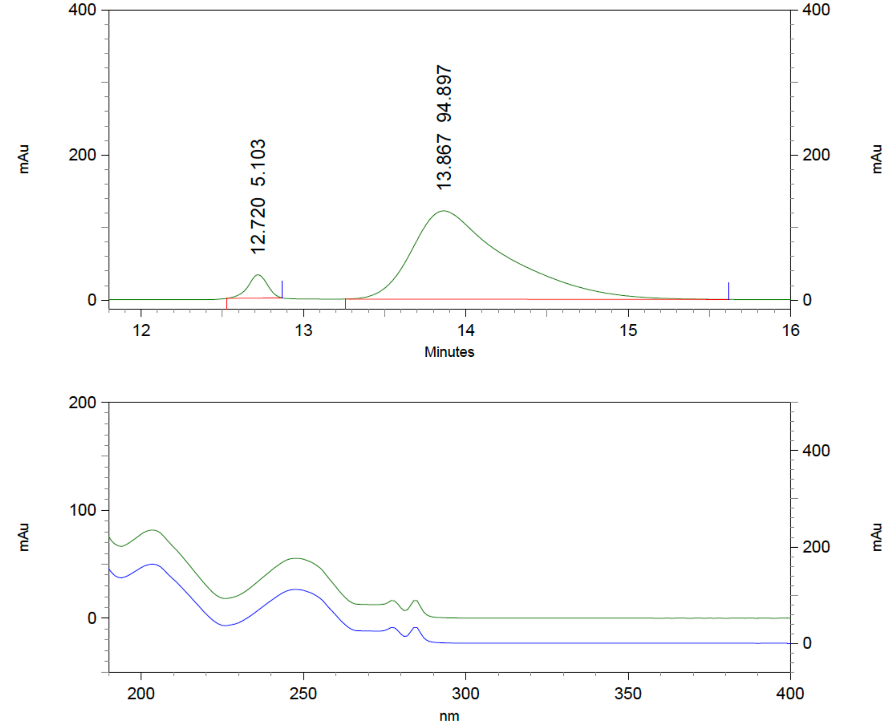


HPLC of **3l**



4: 220 nm, 4 nm Results

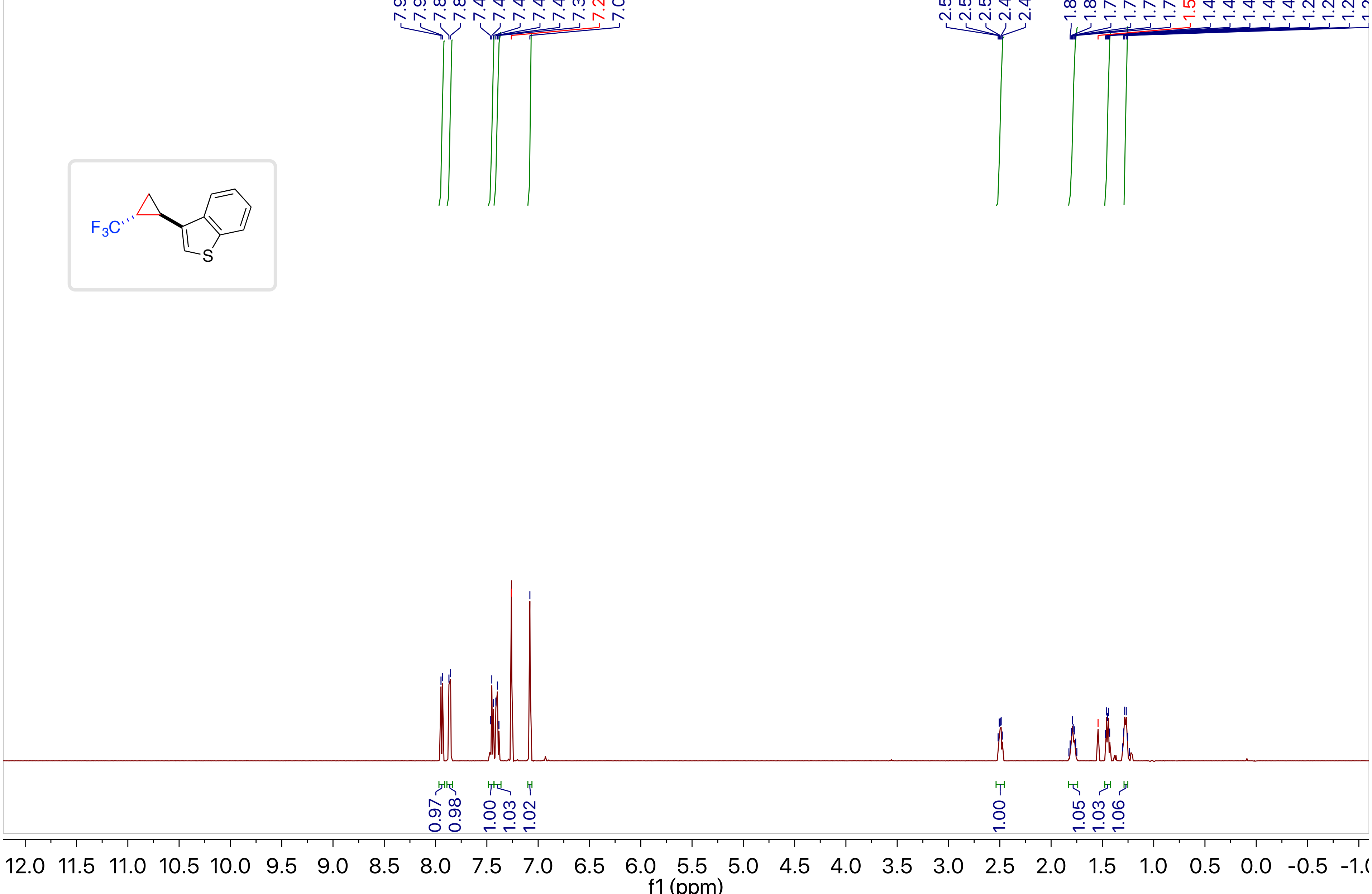
Pk #	Retention Time	Area Percent
1	12.555	50.164
2	13.589	49.836
Totals		100.000



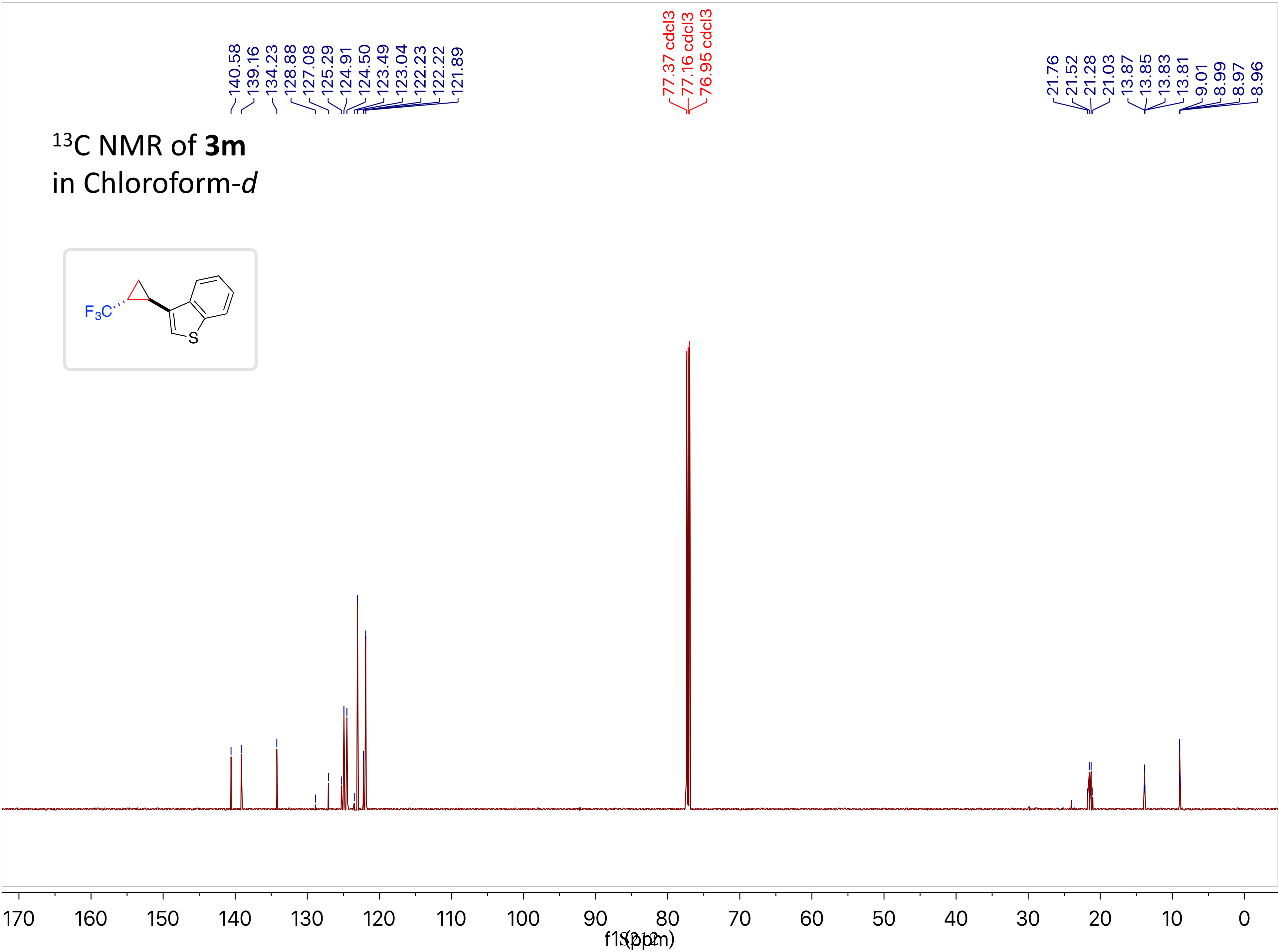
4: 220 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	12.720	5.103
2	13.867	94.897
Totals		100.000

^{1}H NMR of **3m** in Chloroform-*d*

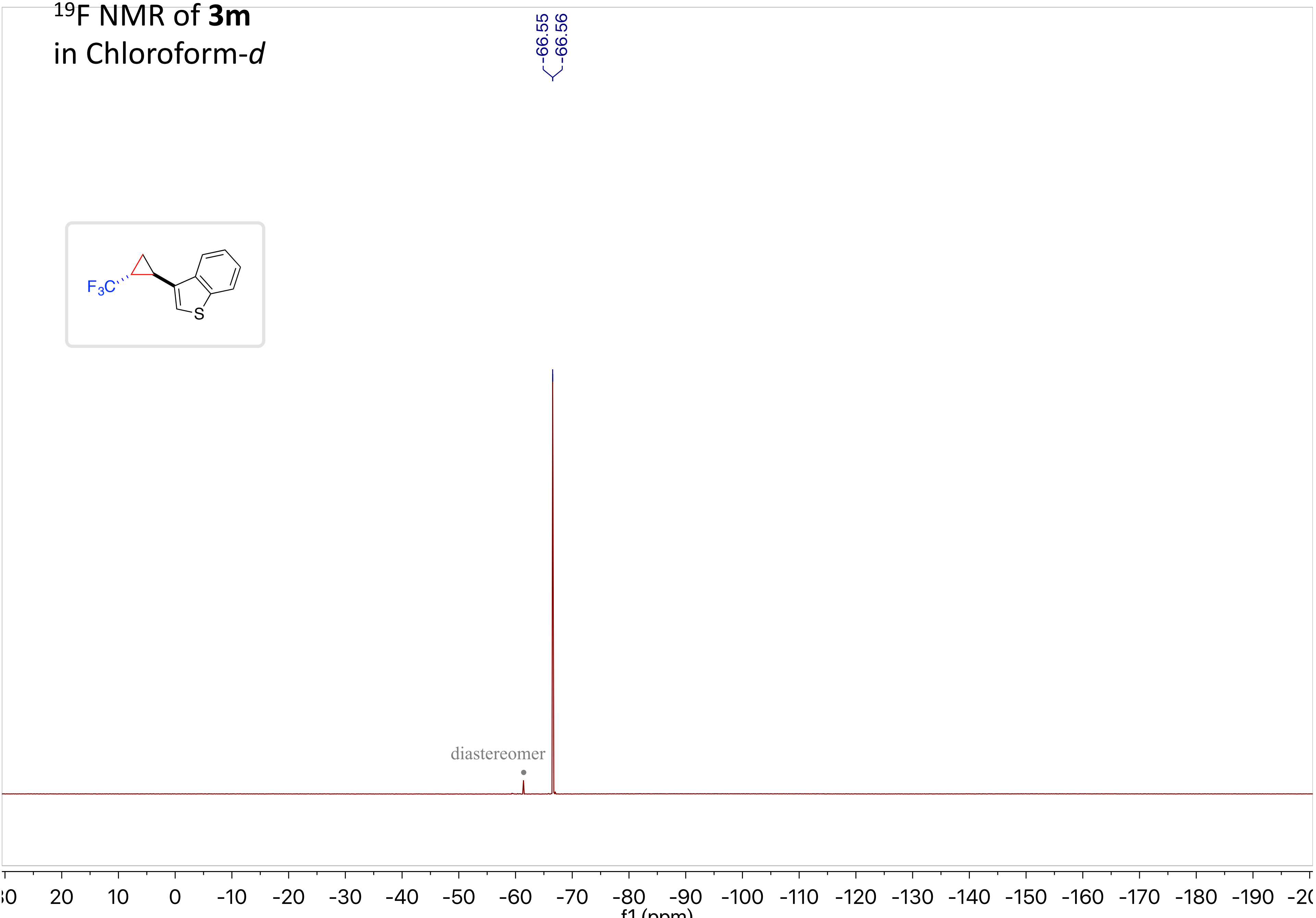


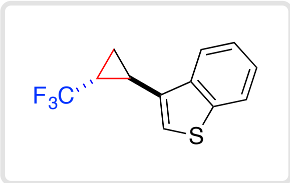
^{13}C NMR of **3m**
in Chloroform-*d*



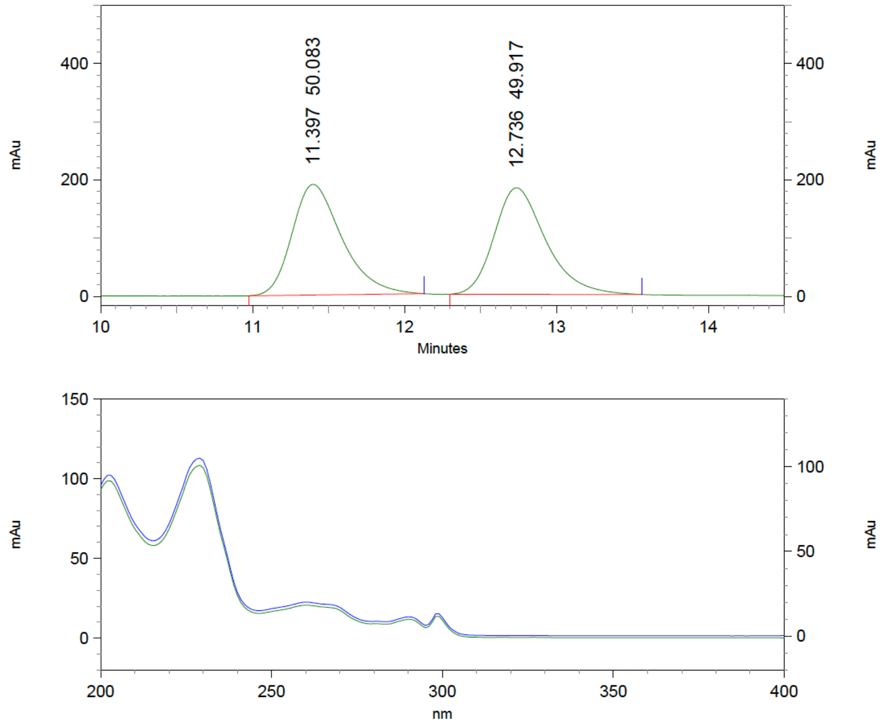
S212

[19]F NMR of **3m**
in Chloroform-*d*



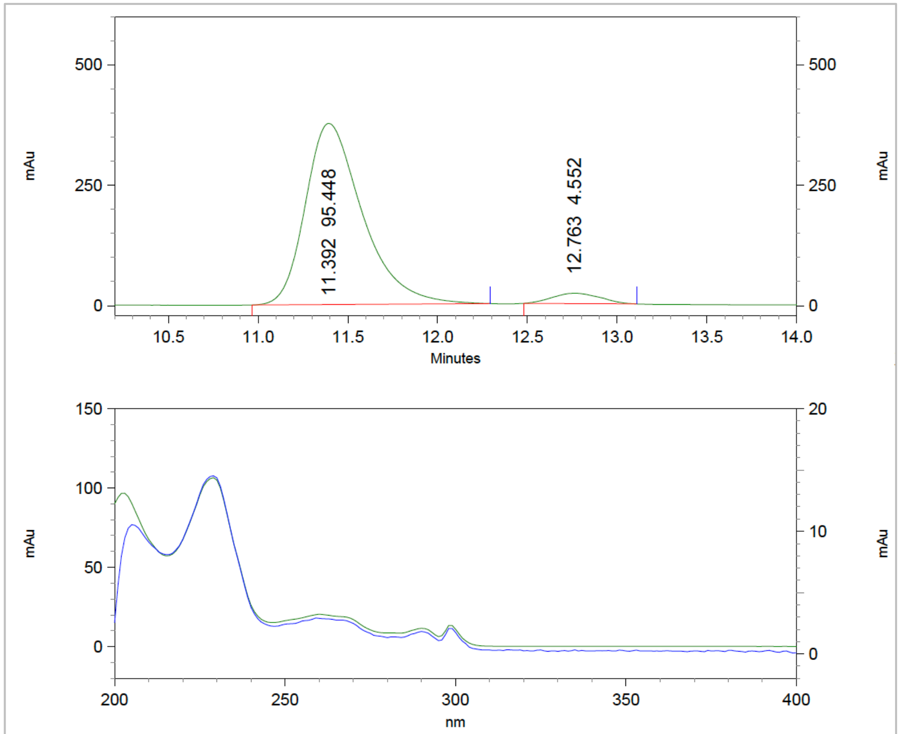


HPLC of **3m**



3: 225 nm, 4 nm Results

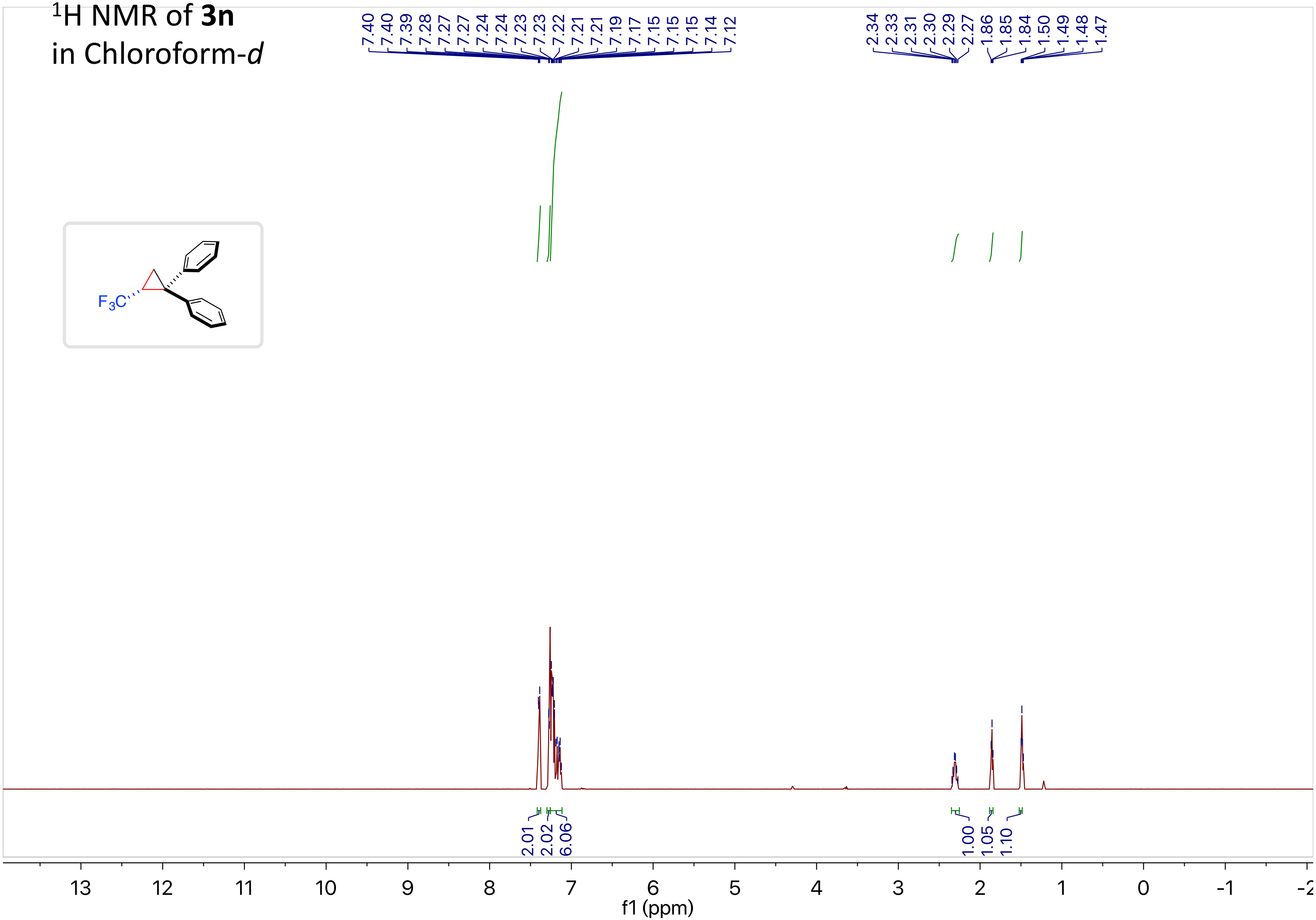
Pk #	Retention Time	Area Percent
1	11.397	50.083
2	12.736	49.917
Totals		100.000

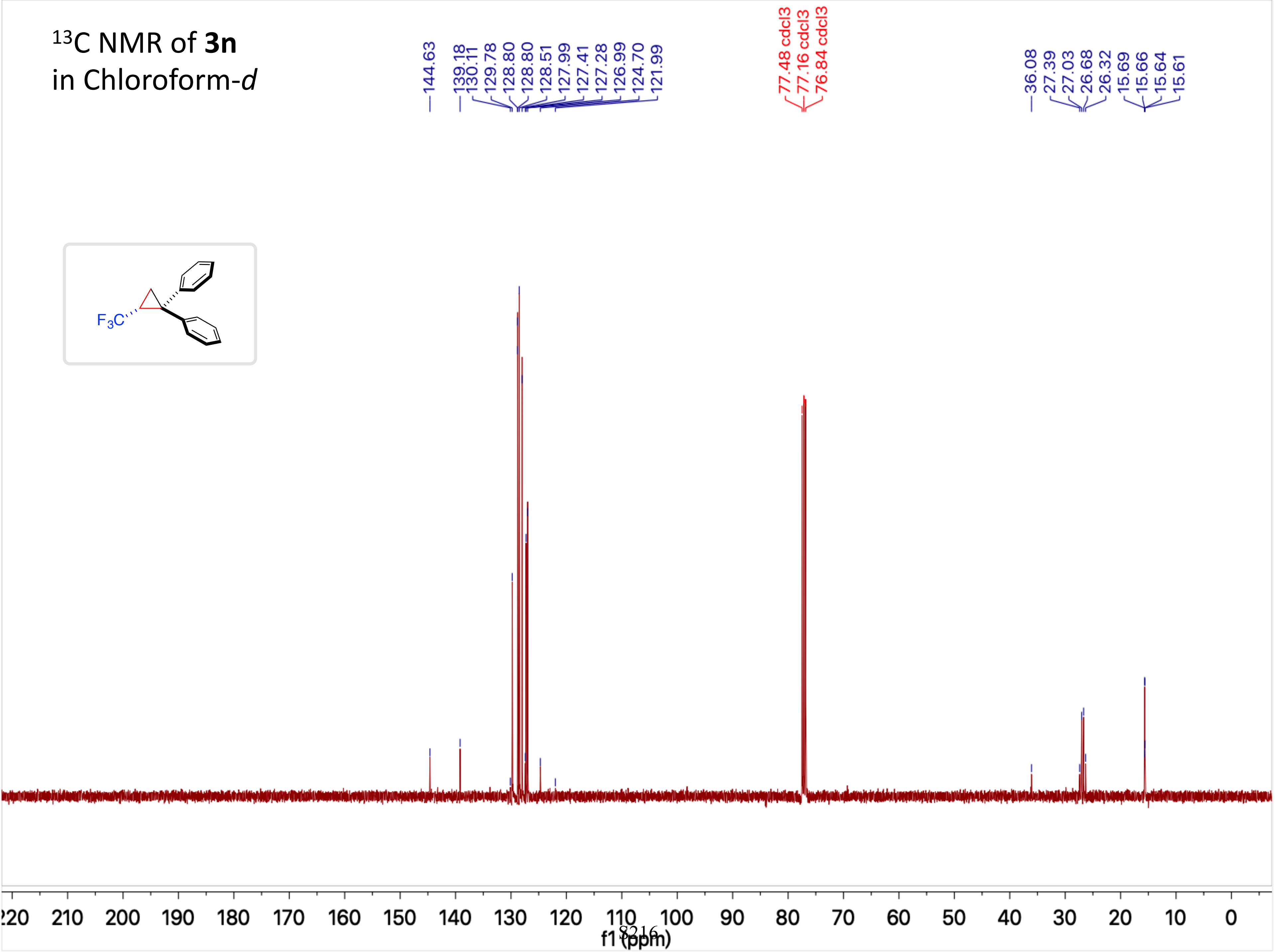


4: 225 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	11.392	95.448
2	12.763	4.552
Totals		100.000

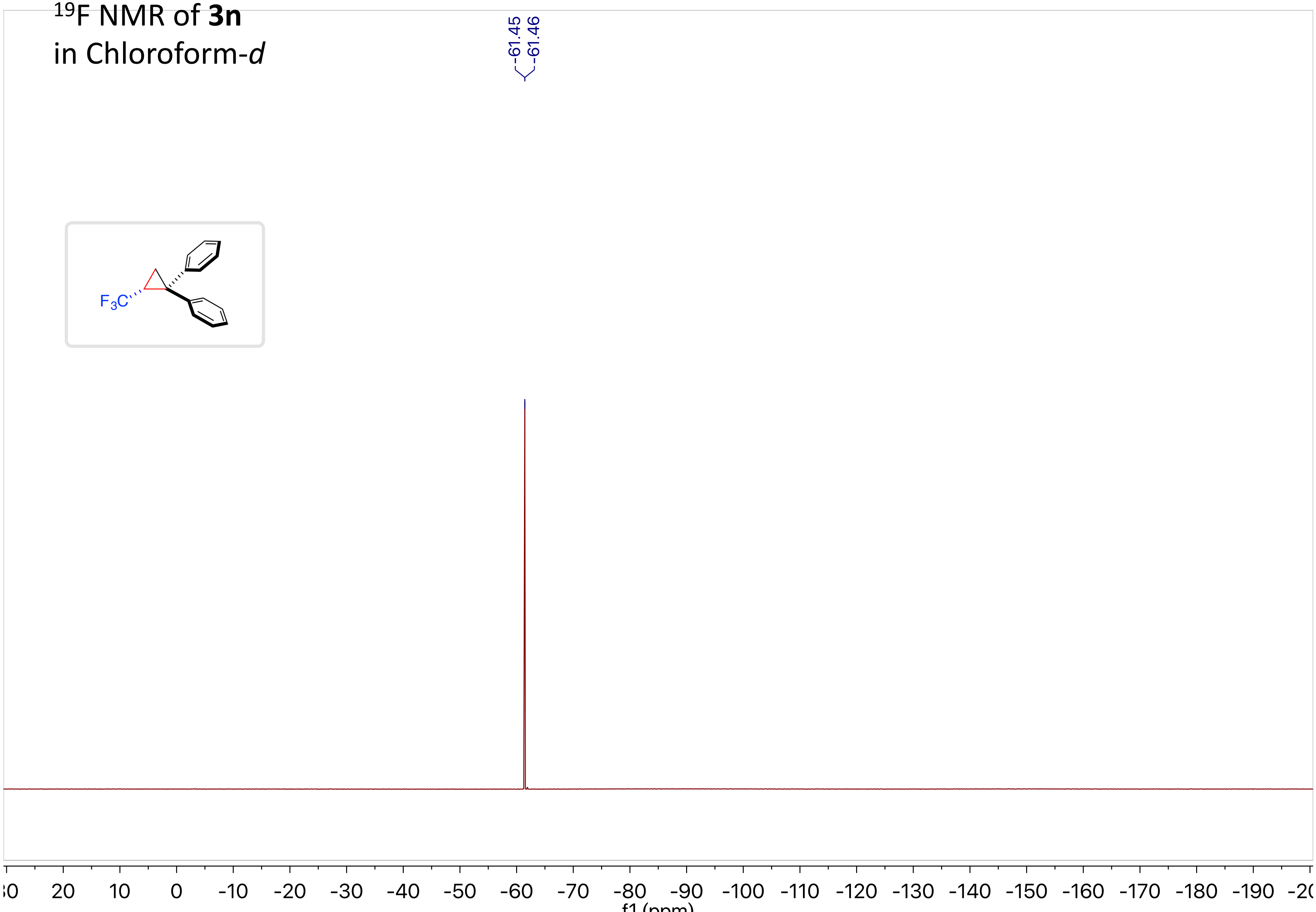
^{1}H NMR of **3n**
in Chloroform-*d*

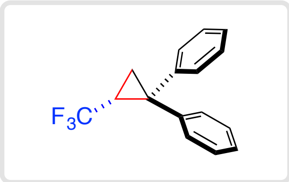




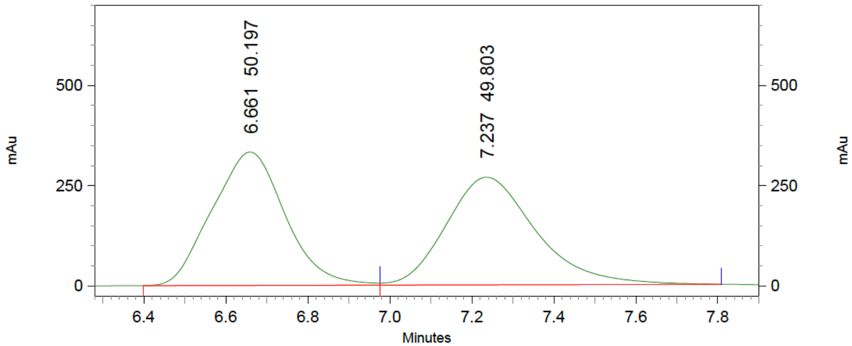
^{13}C NMR of **3n**
in Chloroform-*d*
144.63
139.18
130.11
129.78
128.80
128.80
128.51
127.99
127.41
127.28
126.99
124.70
121.99
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
36.08
27.39
27.03
26.68
26.32
15.69
15.66
15.64
15.61
F_3C
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

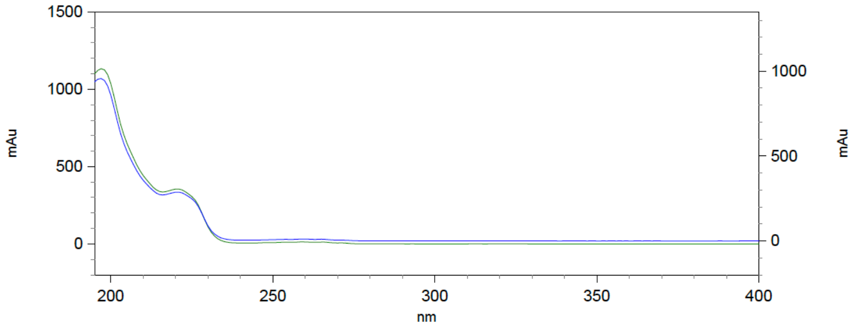
^{19}F NMR of **3n**
in Chloroform-*d*





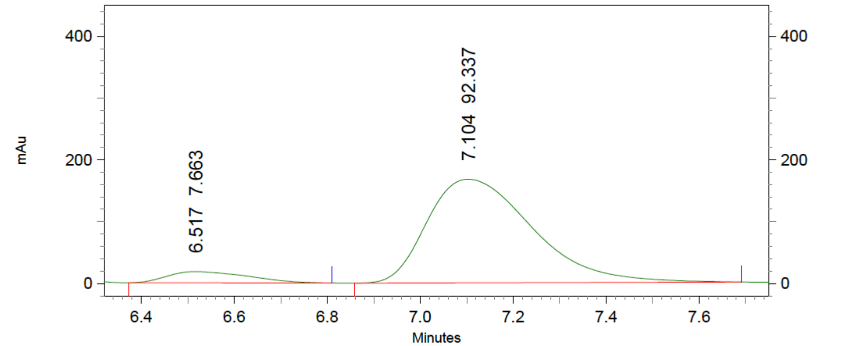
HPLC of **3n**

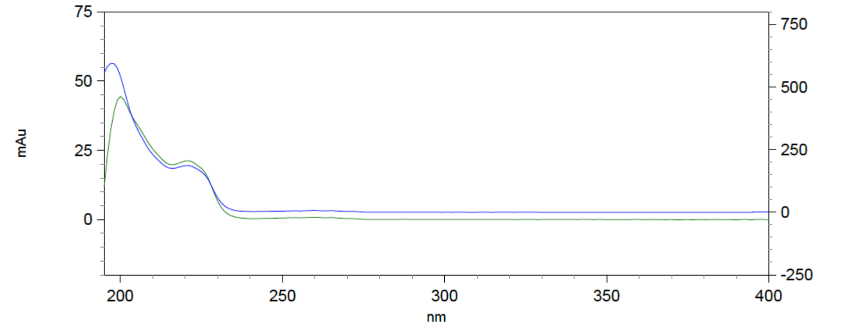




4: 223 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	6.661	50.197
2	7.237	49.803
Totals		100.000

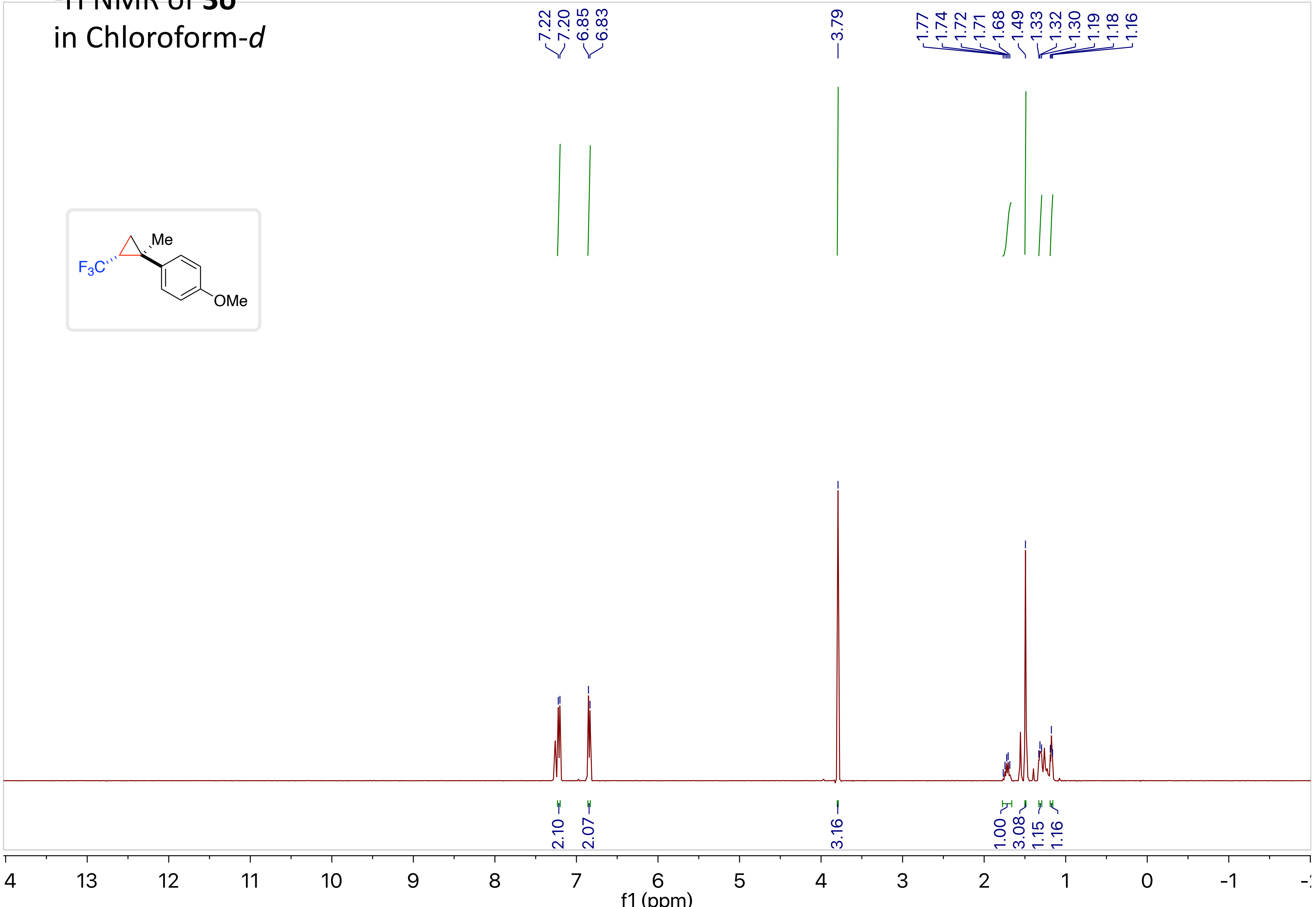




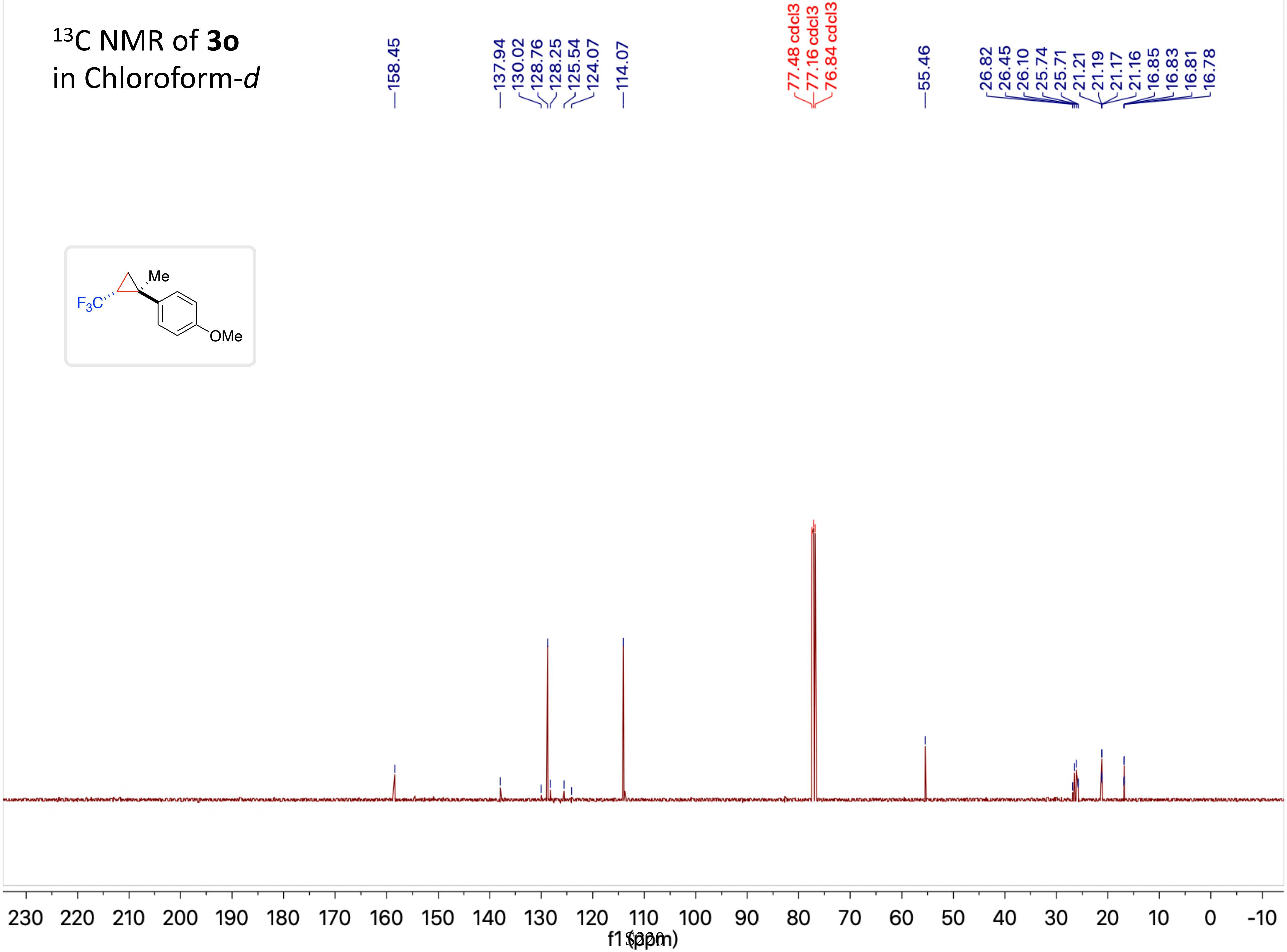
4: 224 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	6.517	7.663
2	7.104	92.337
Totals		100.000

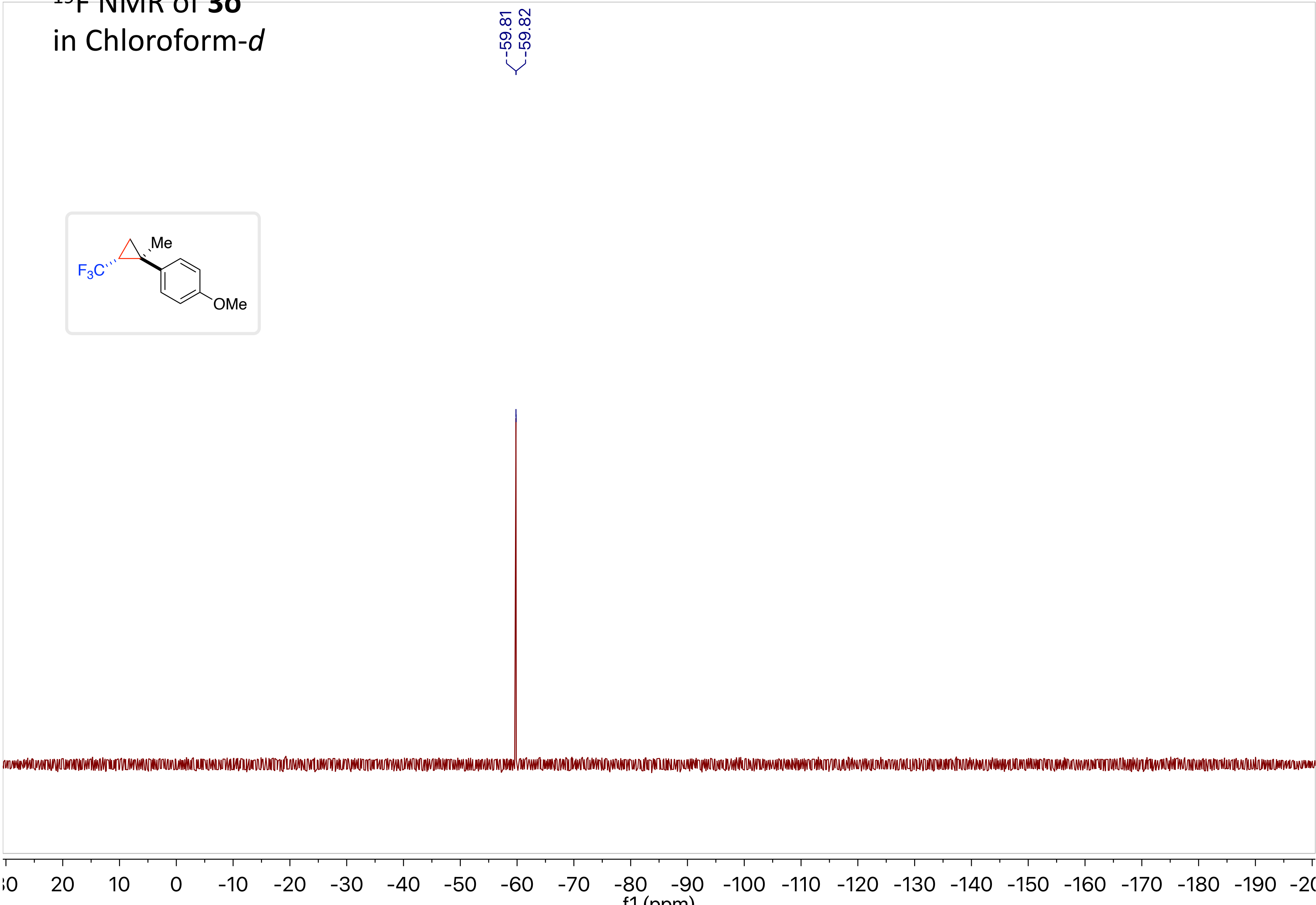
^{1}H NMR of **3o**
in Chloroform-*d*



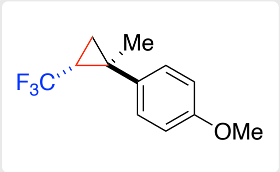
^{13}C NMR of **3o**
in Chloroform-*d*

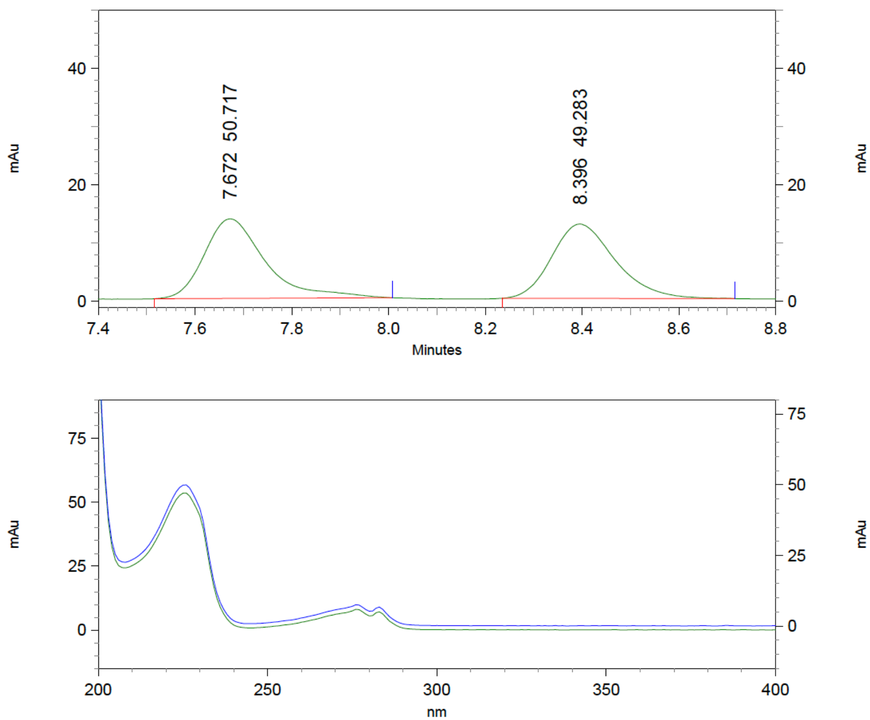


^{19}F NMR of **3o**
in Chloroform-*d*



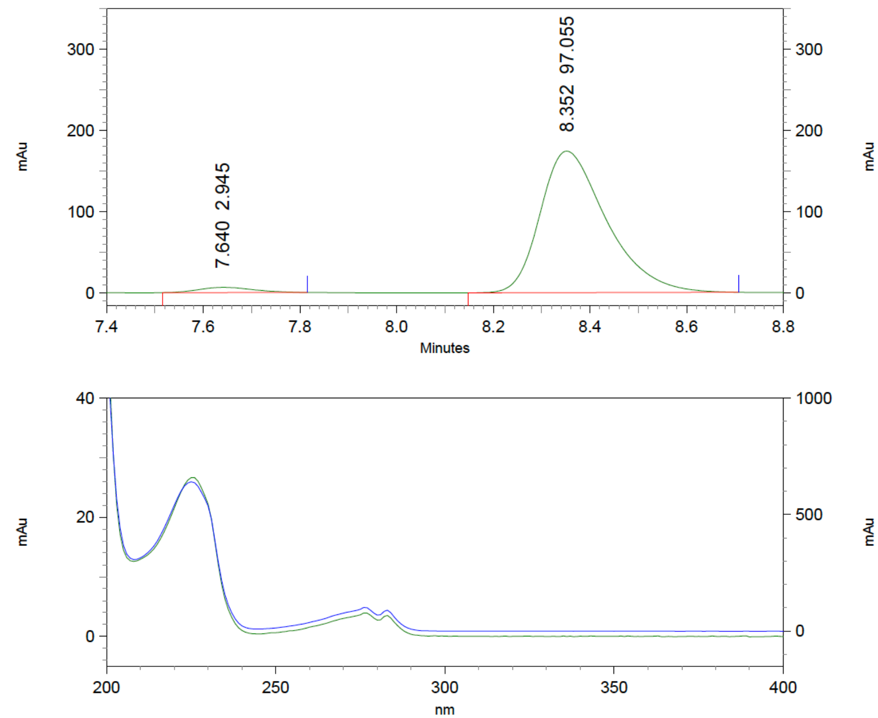
HPLC of **3o**





3: 237 nm, 4 nm Results

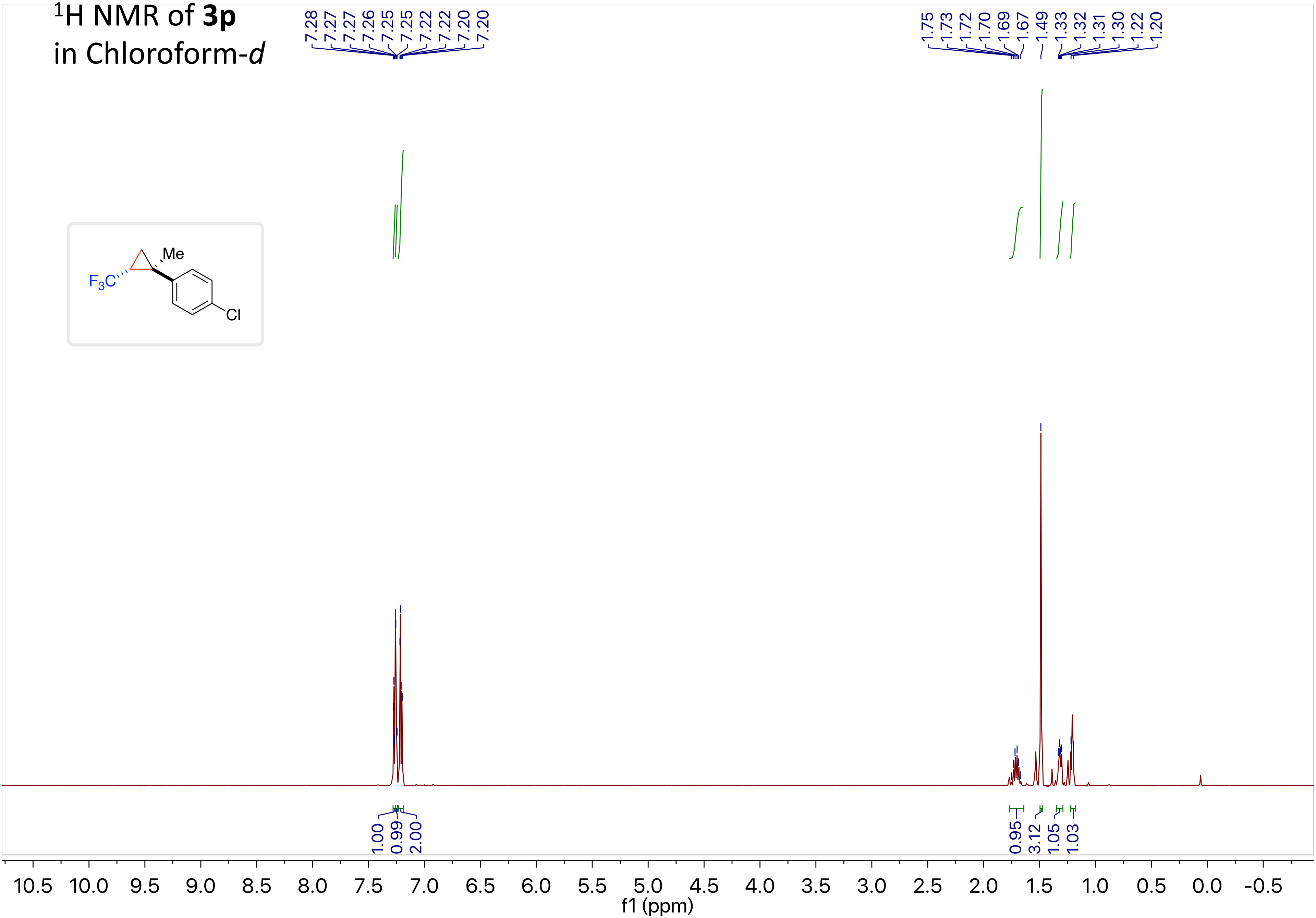
Pk #	Retention Time	Area Percent
1	7.672	50.717
2	8.396	49.283
Totals		100.000



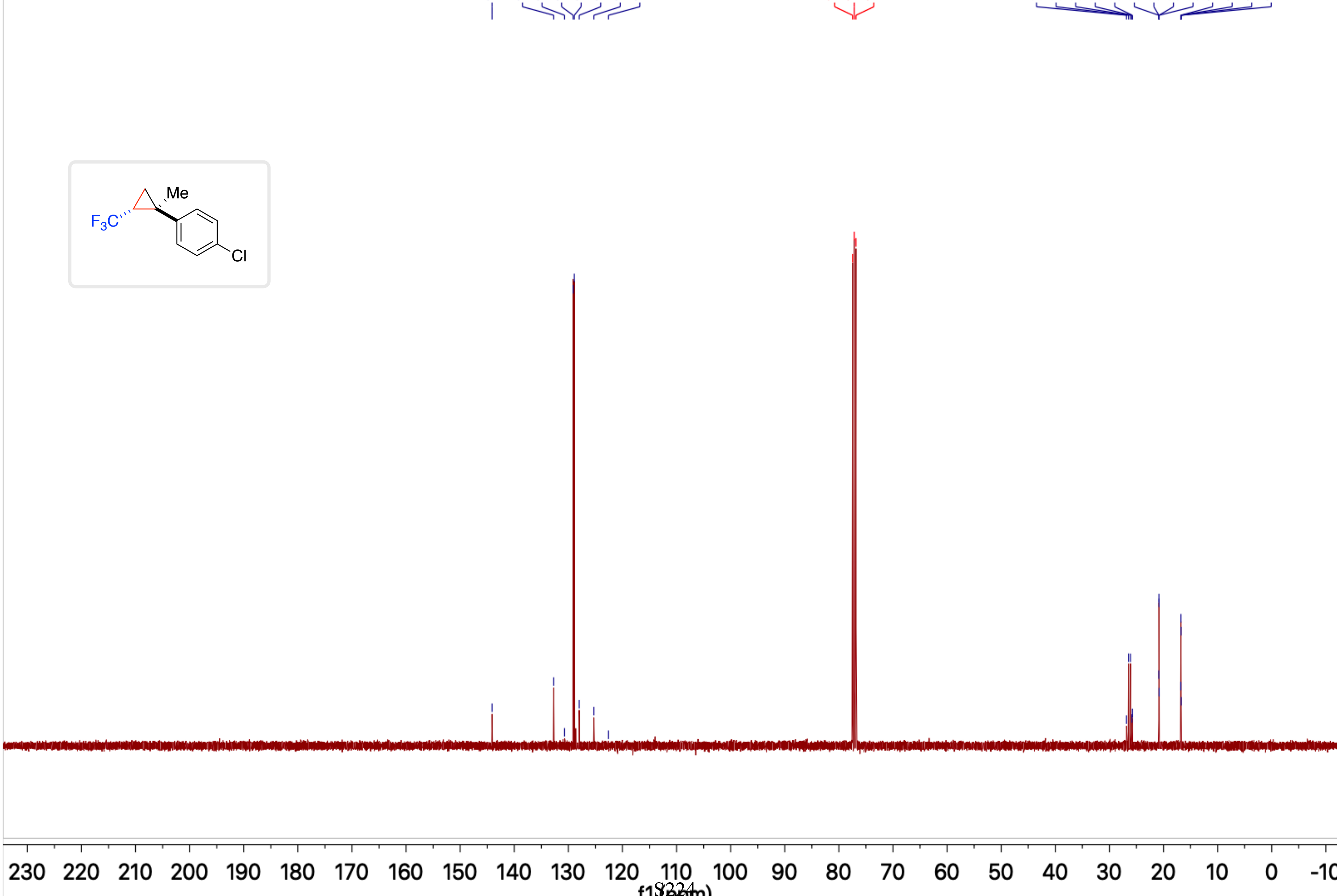
3: 237 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	7.640	2.945
2	8.352	97.055
Totals		100.000

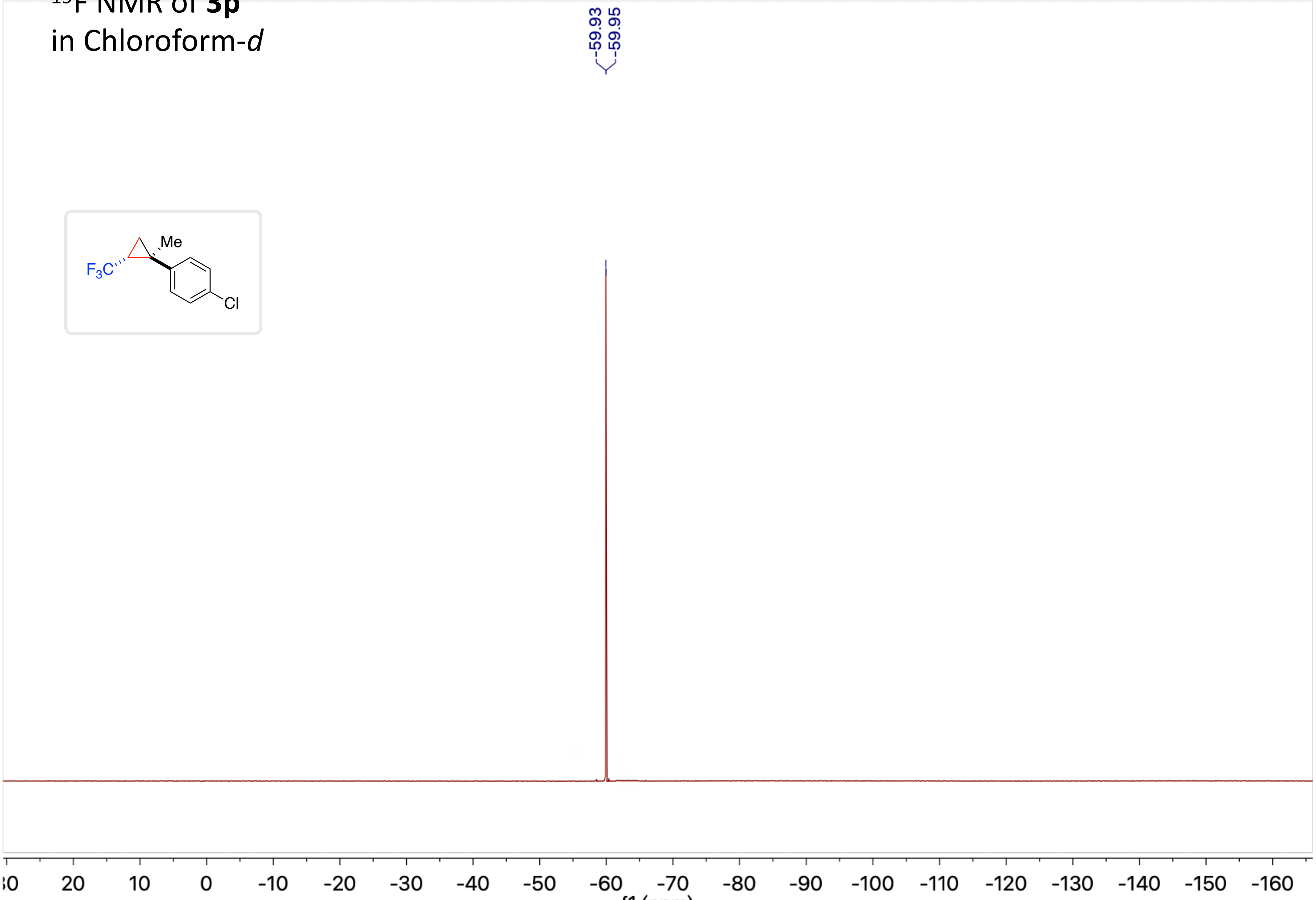
^{1}H NMR of **3p**
in Chloroform-*d*

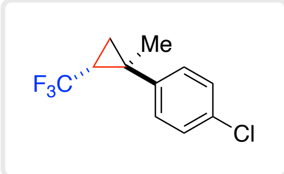


^{13}C NMR of **3p**
in Chloroform-*d*

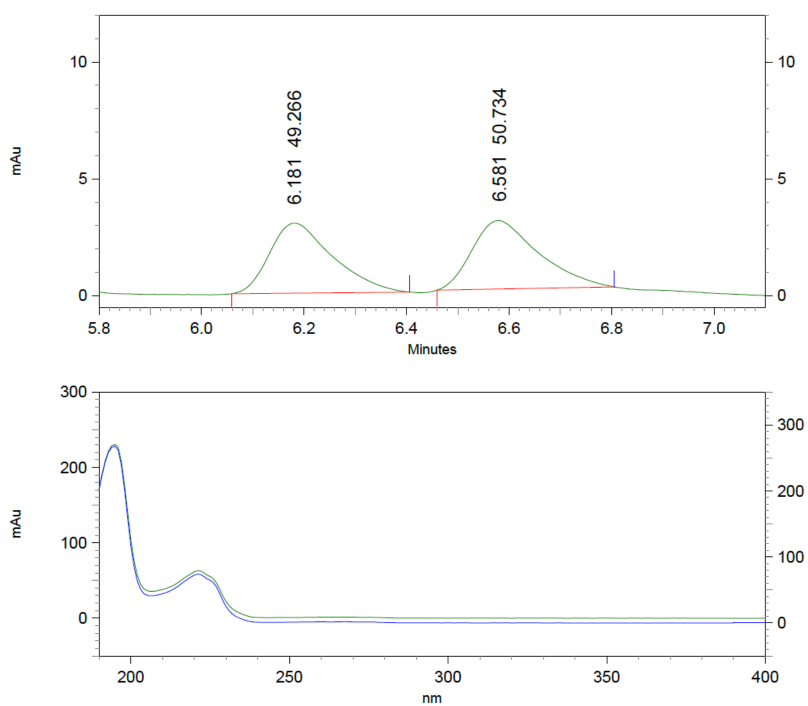


^{19}F NMR of **3p**
in Chloroform-*d*



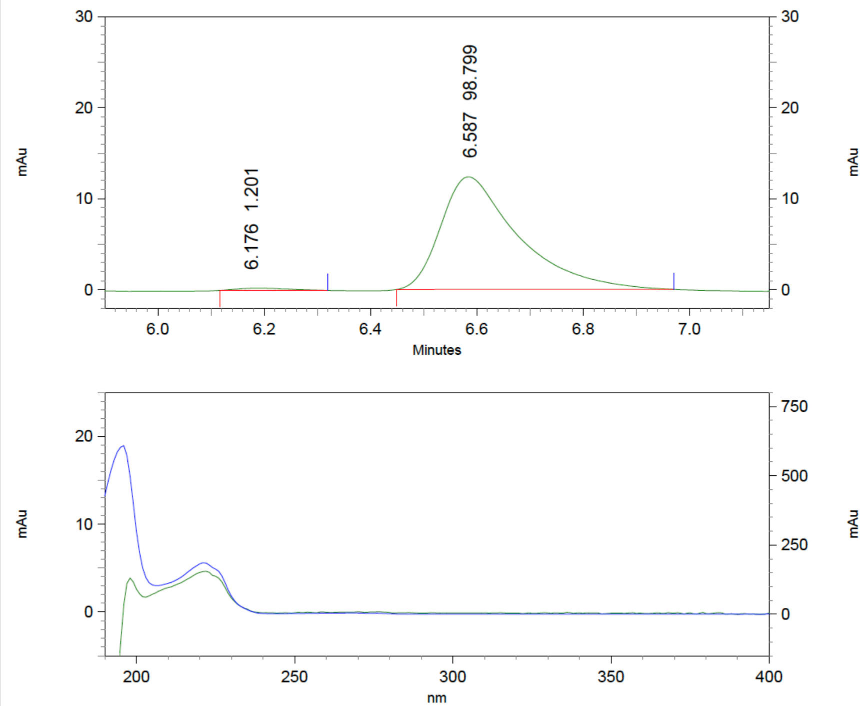


HPLC of **3p**



4: 237 nm, 4
nm Results

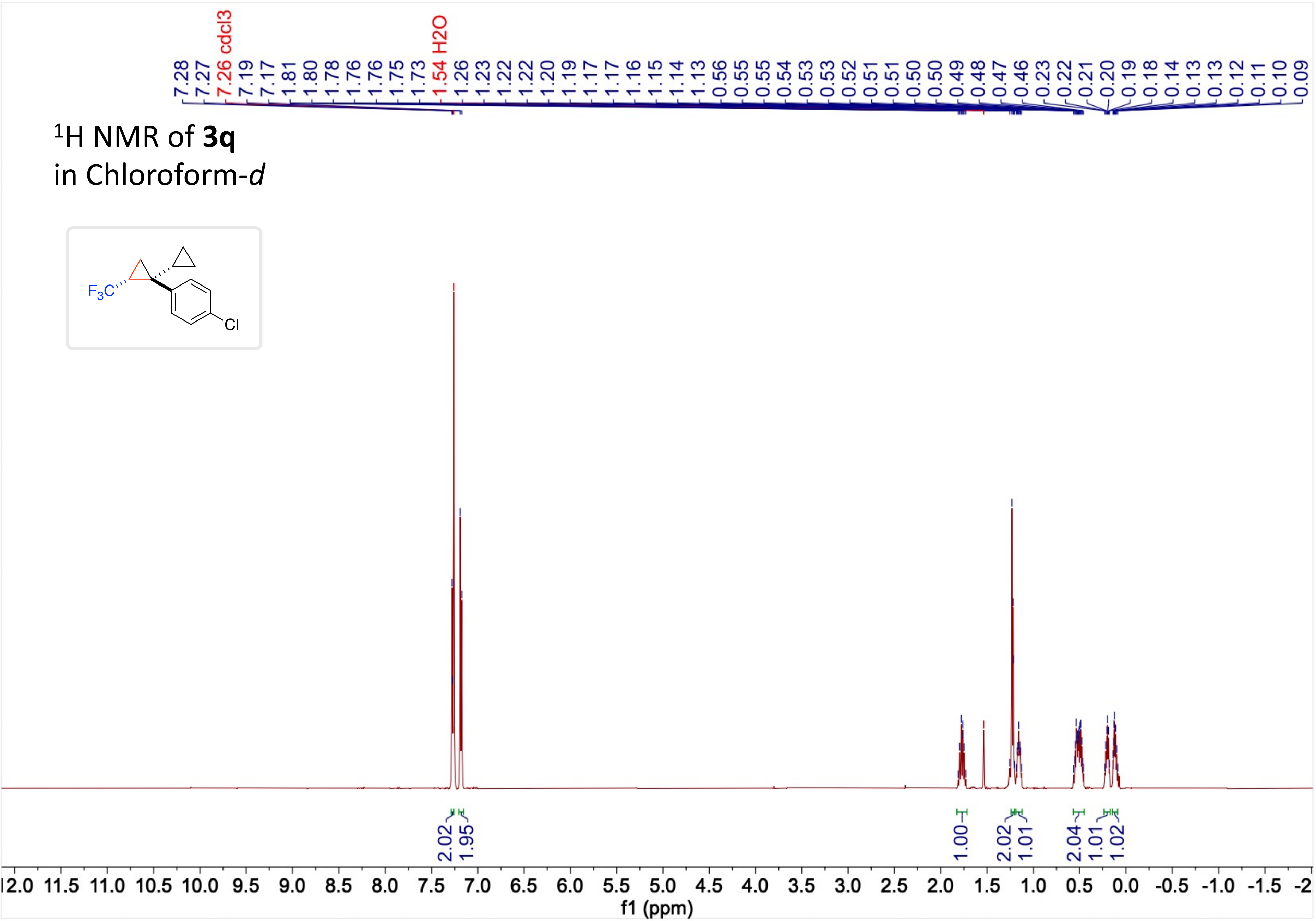
Pk #	Retention Time	Area Percent
1	6.181	49.266
2	6.581	50.734
Totals		100.000



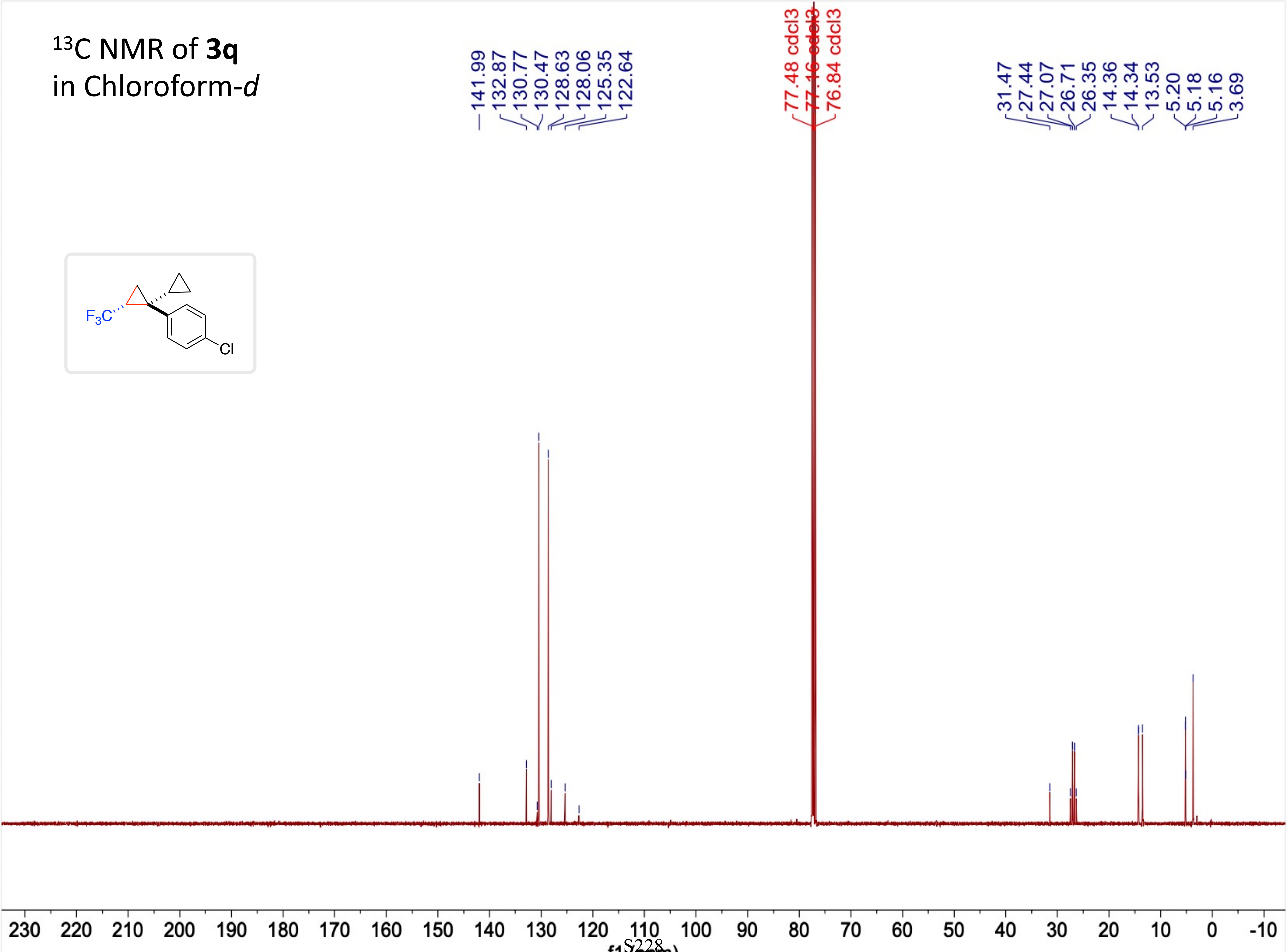
4: 236 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	6.176	1.201
2	6.587	98.799
Totals		100.000

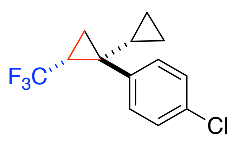
^{1}H NMR of **3q** in Chloroform-*d*

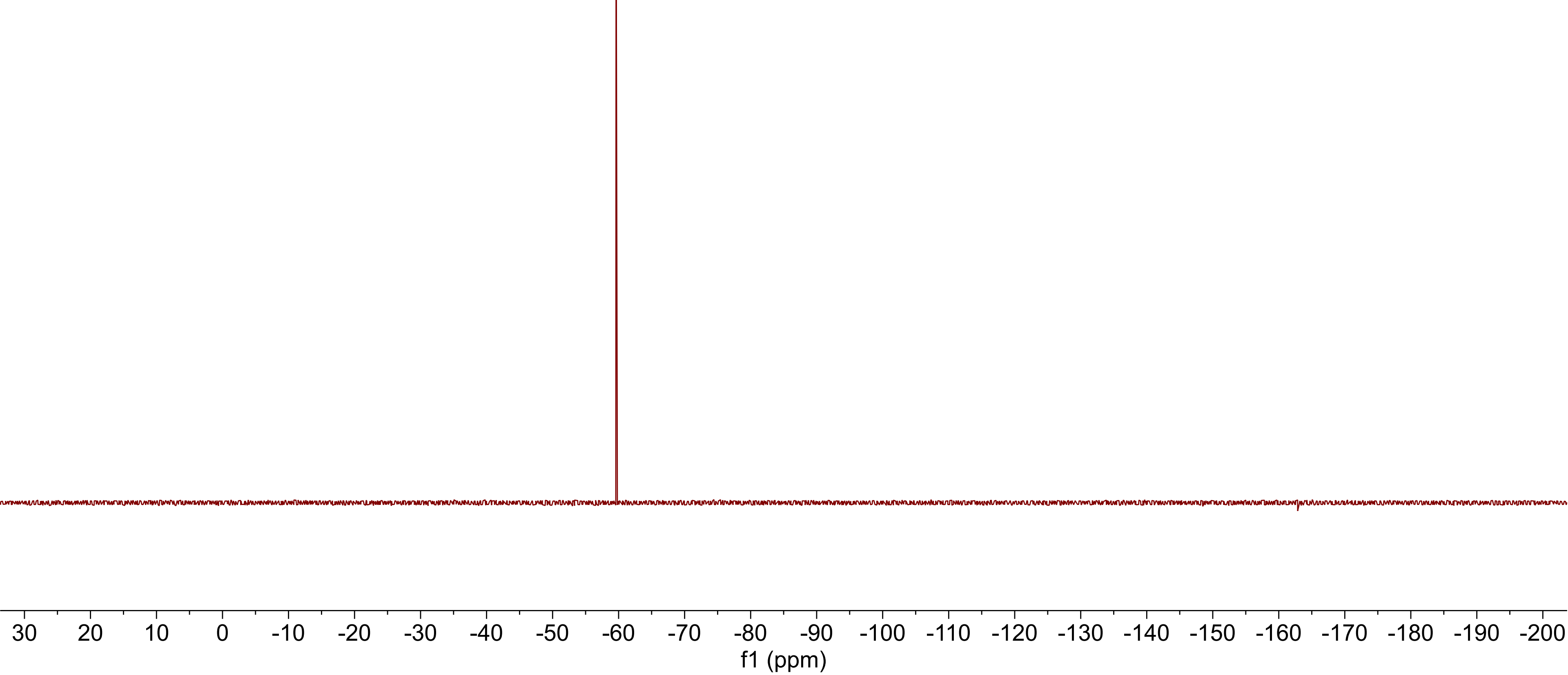


^{13}C NMR of **3q**
in Chloroform-*d*

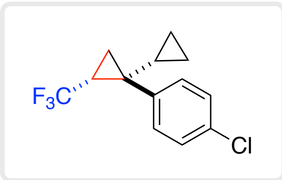


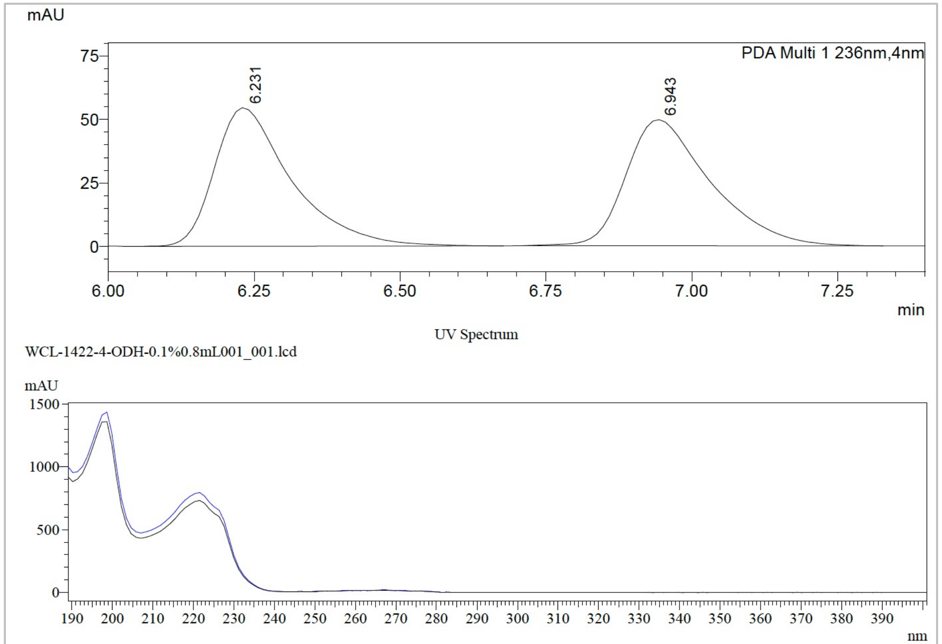
^{19}F NMR of **3q**
in Chloroform-*d*





HPLC of **3q**

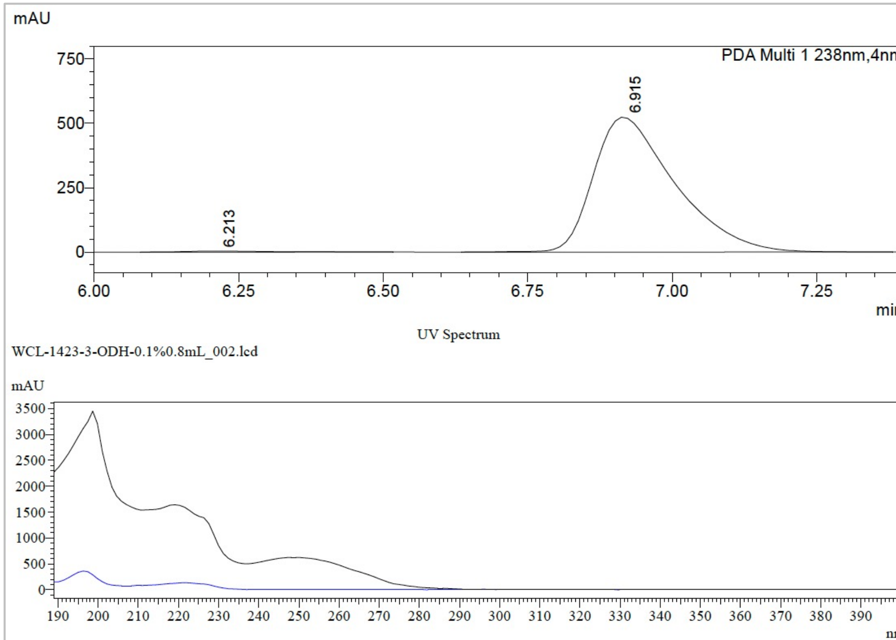




Peak Table

PDA Ch1 236nm

Peak#	Ret. Time	Area%
1	6.231	49.831
2	6.943	50.169
Total		100.000

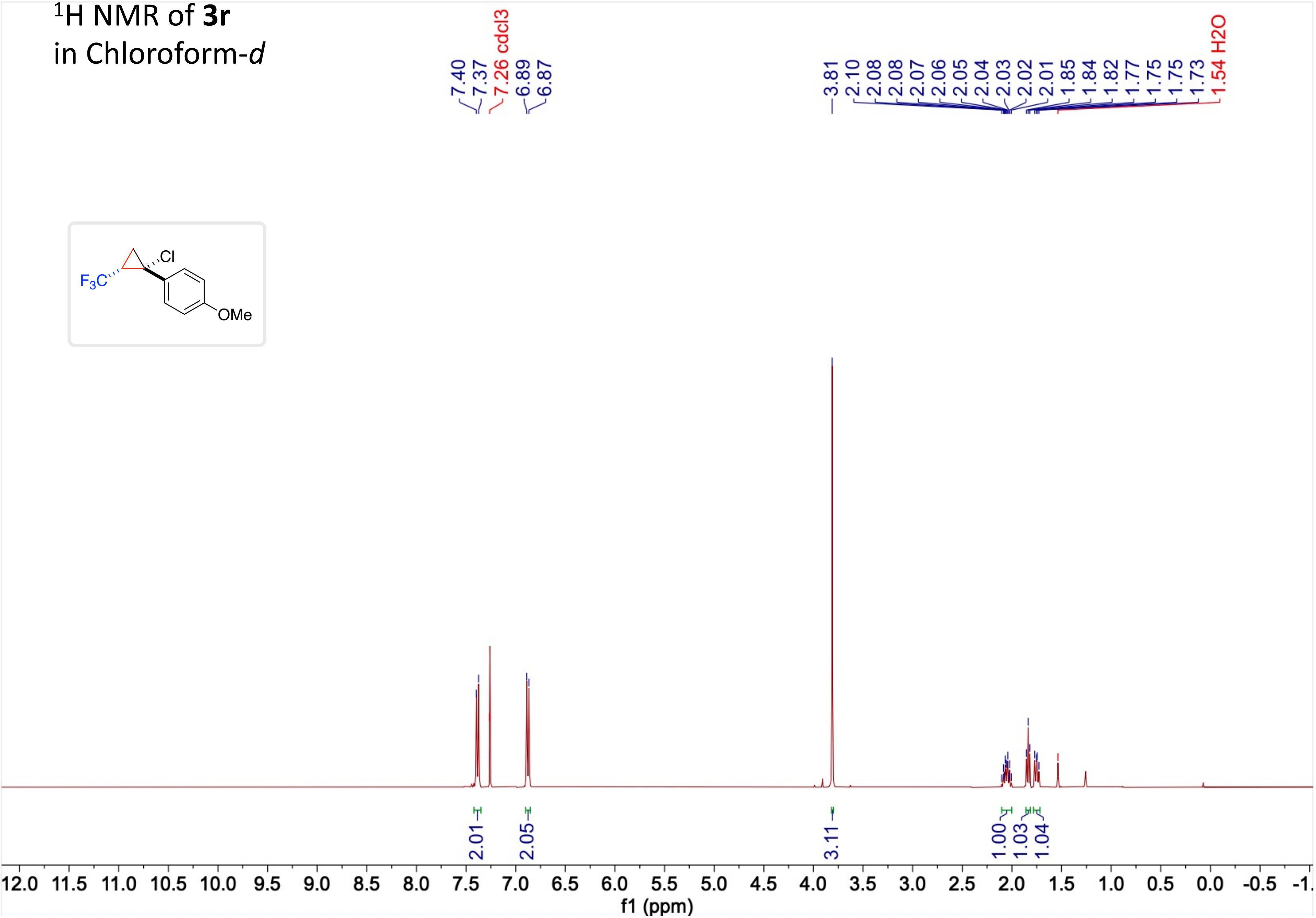


Peak Table

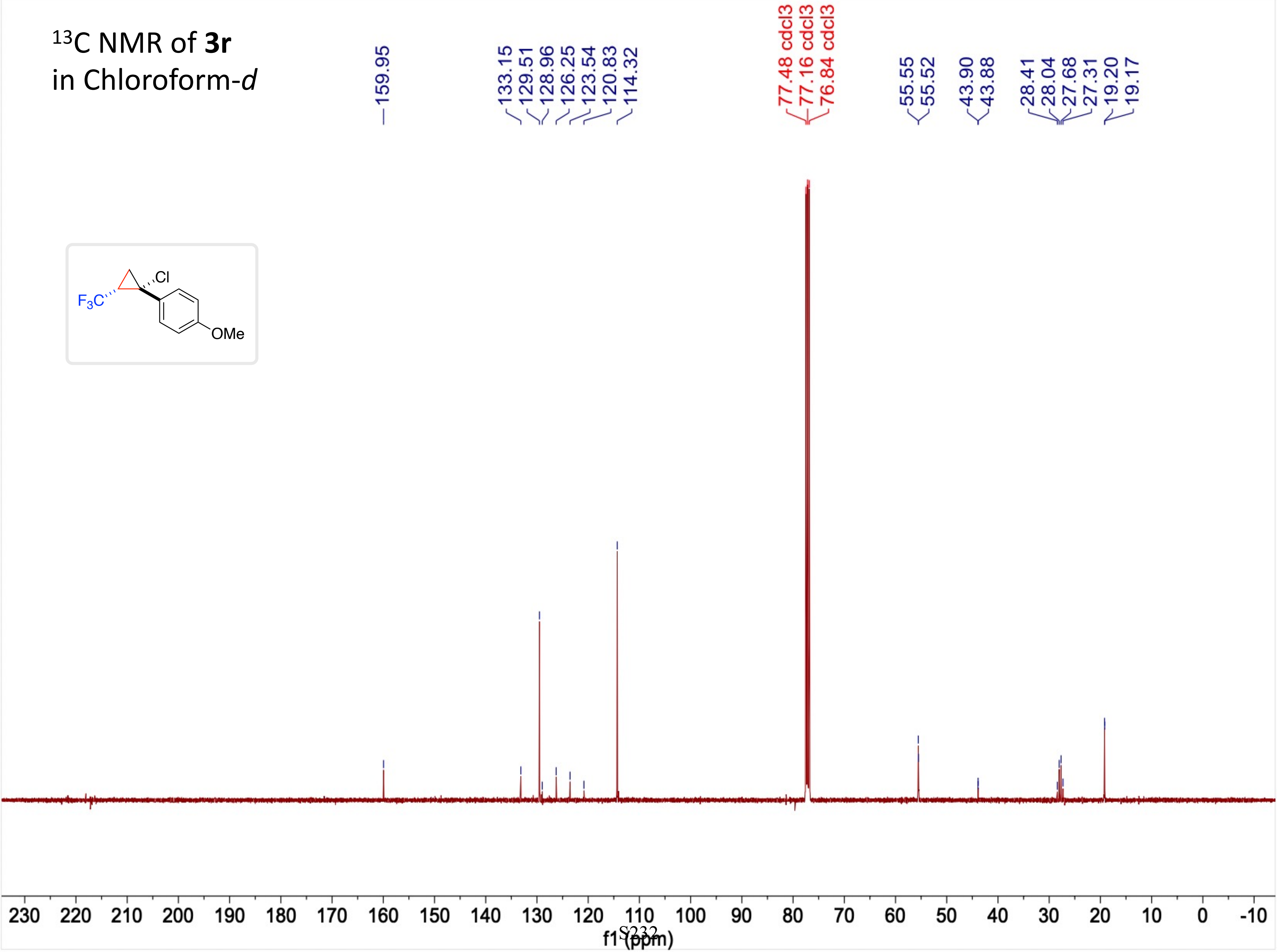
PDA Ch1 238nm

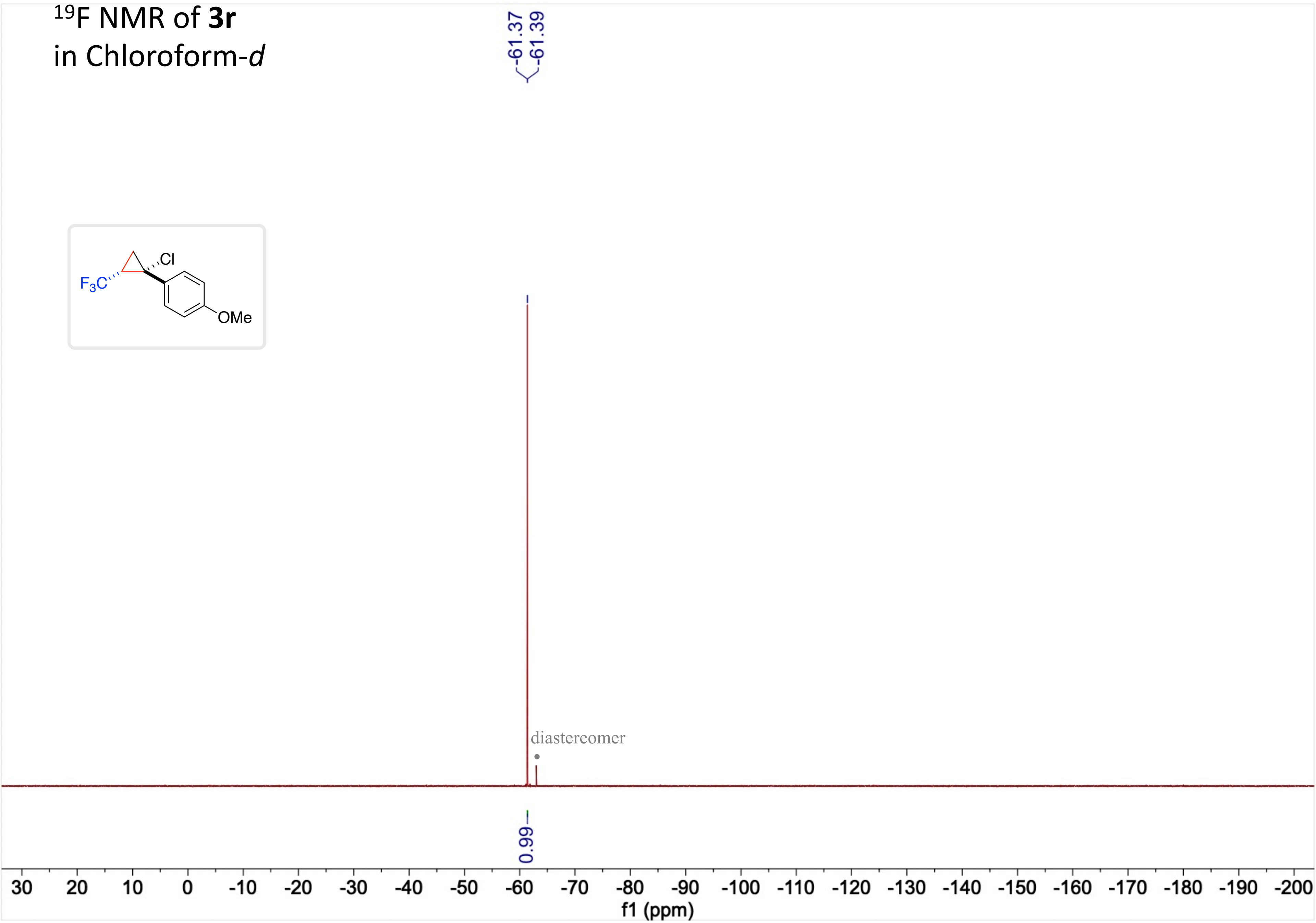
Peak#	Ret. Time	Area%
1	6.213	0.839
2	6.915	99.161
Total		100.000

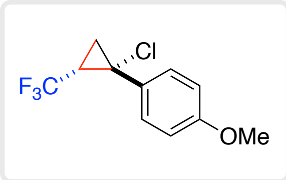
^{1}H NMR of **3r**
in Chloroform-*d*



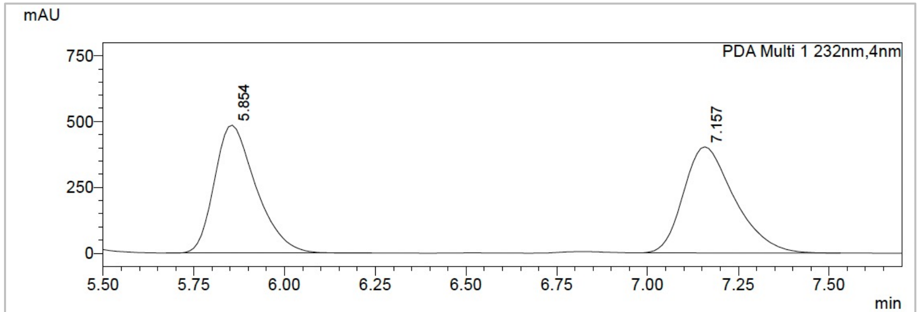
[13]C NMR of **3r**
in Chloroform-*d*




19F NMR of 3r
in Chloroform-d
-61.37
-61.39
Cl
F3C
OMe
diastereomer
0.99
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

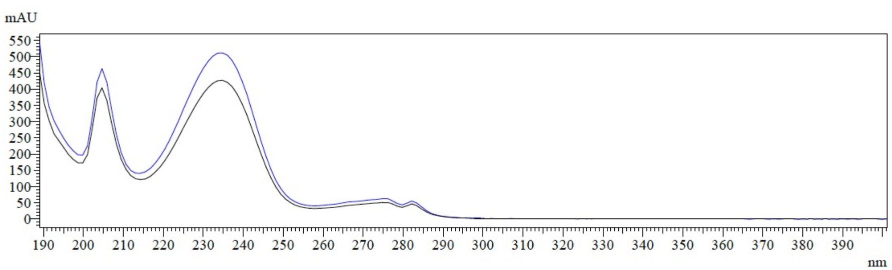


HPLC of **3r**



UV Spectrum

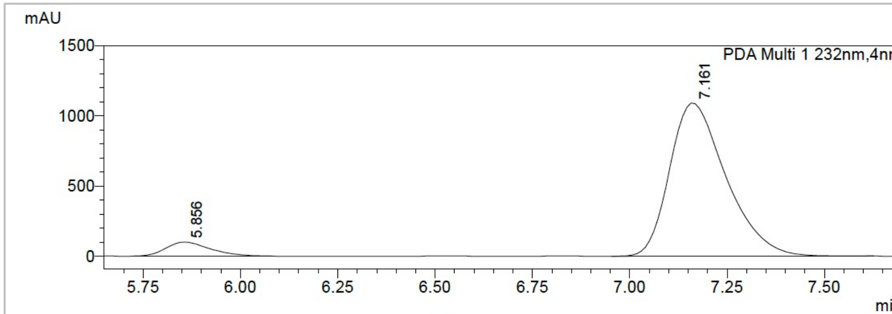
WCL-1441-3-ODH-5%0.8mL_001.lcd



Peak Table

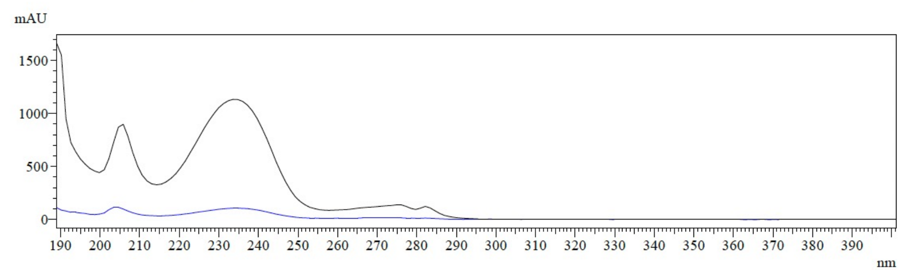
PDA Ch1 232nm

Peak#	Ret. Time	Area%
1	5.854	49.637
2	7.157	50.363
Total		100.000



UV Spectrum

WCL-1442-3-ODH-5%0.8mL_002.lcd

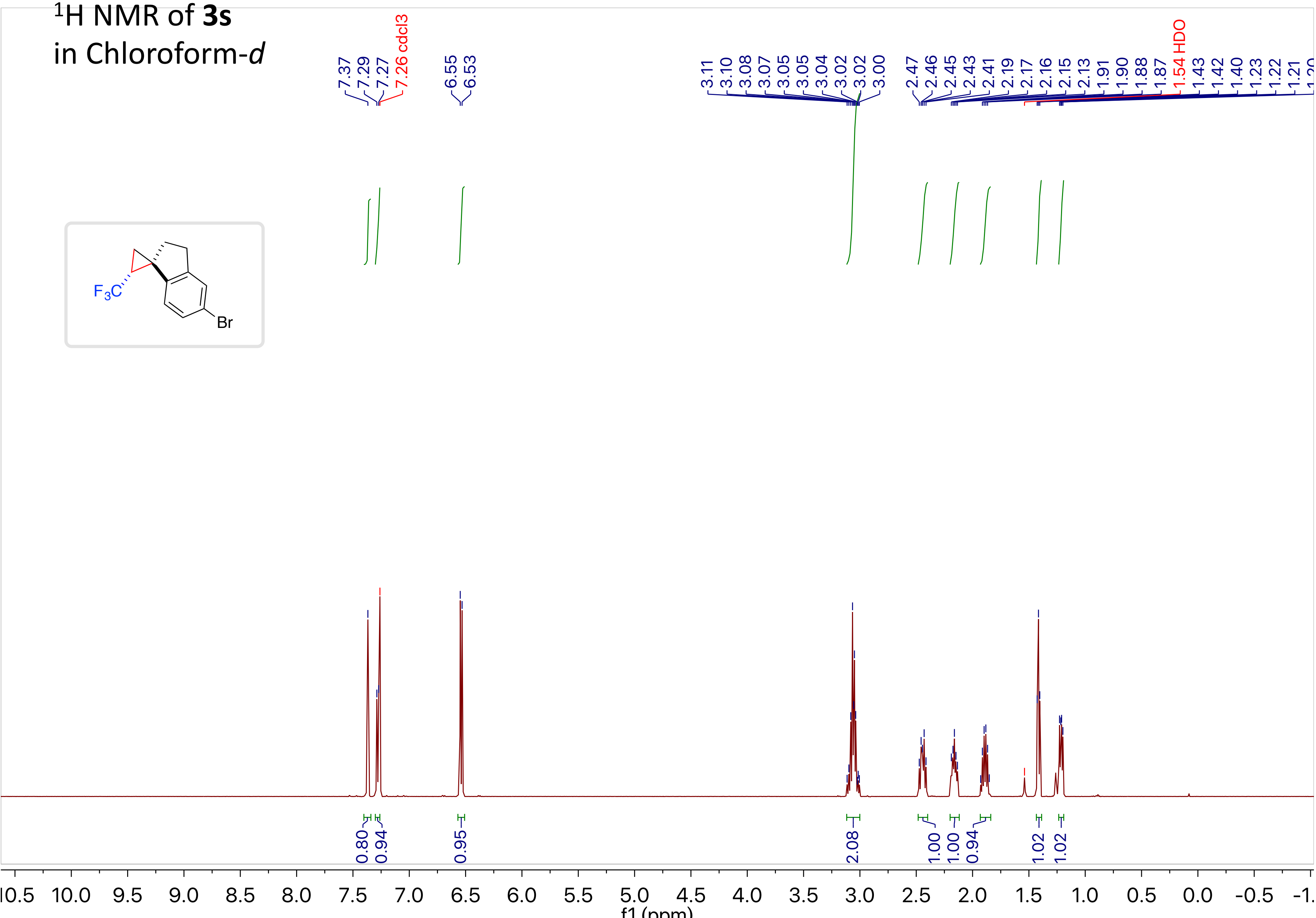


Peak Table

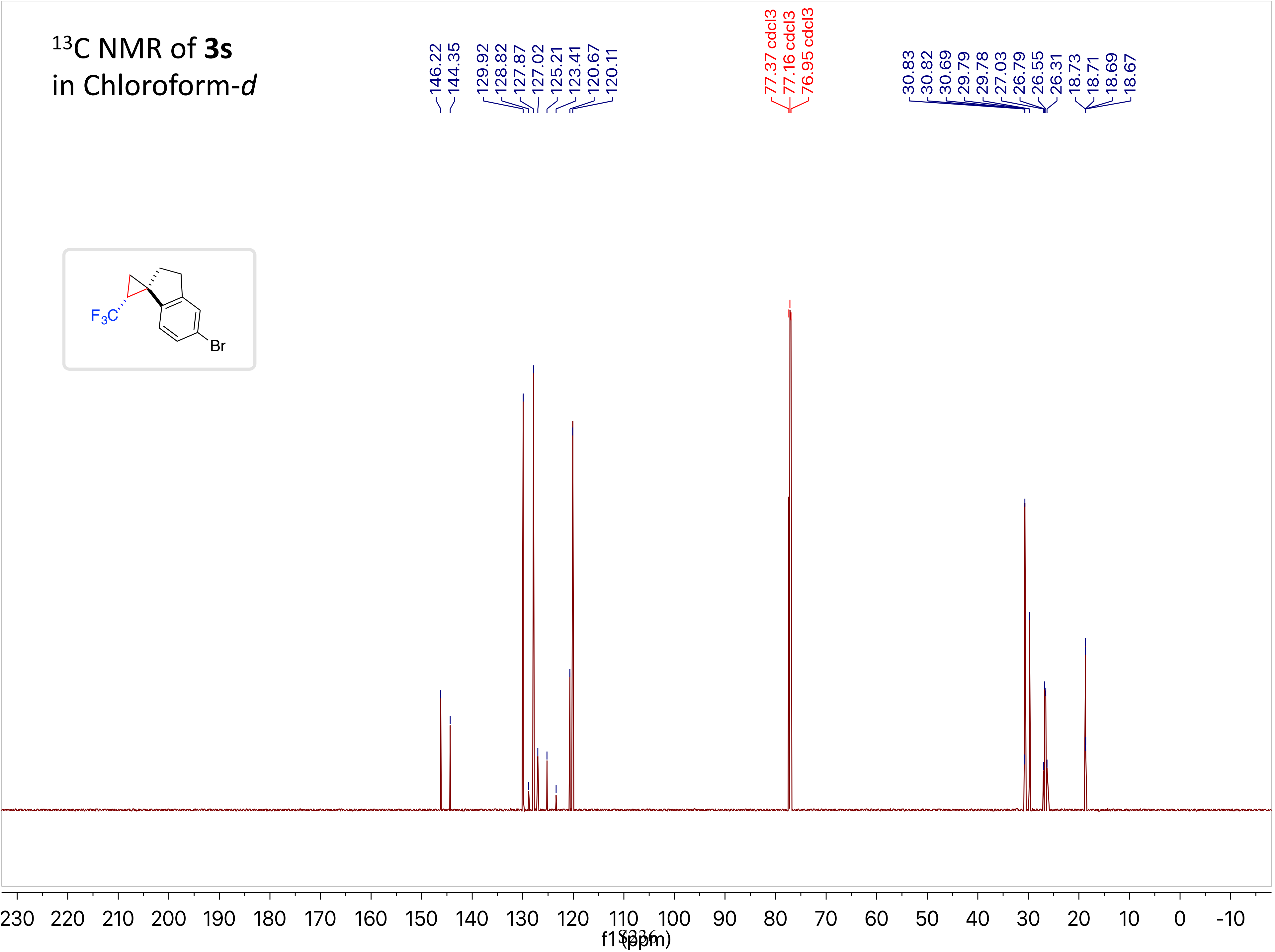
PDA Ch1 232nm

Peak#	Ret. Time	Area%
1	5.856	6.695
2	7.161	93.305
Total		100.000

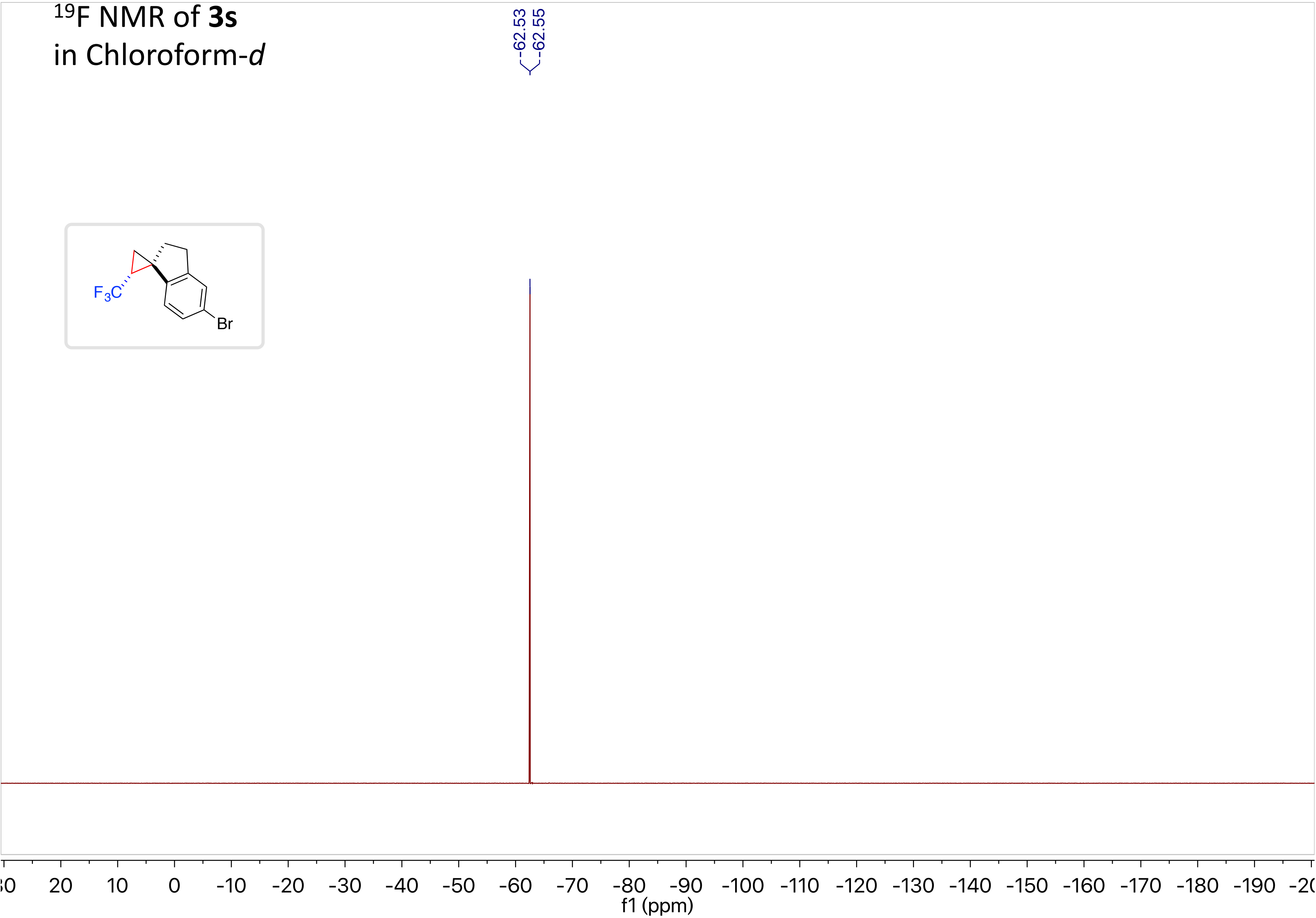
^{1}H NMR of **3s**
in Chloroform-*d*

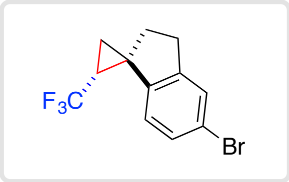


^{13}C NMR of **3s** in Chloroform-*d*

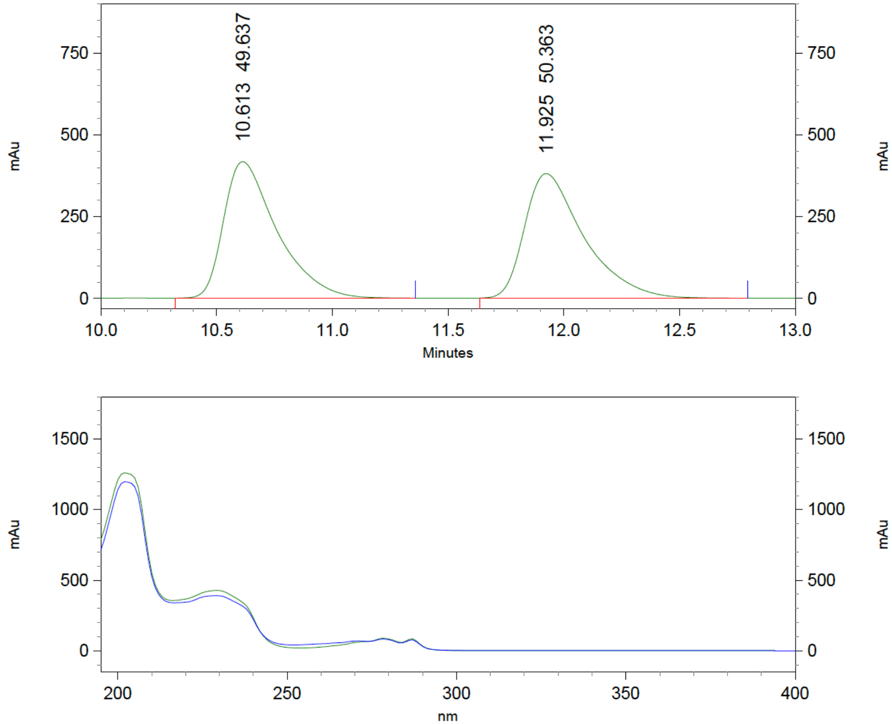


^{19}F NMR of **3s**
in Chloroform-*d*



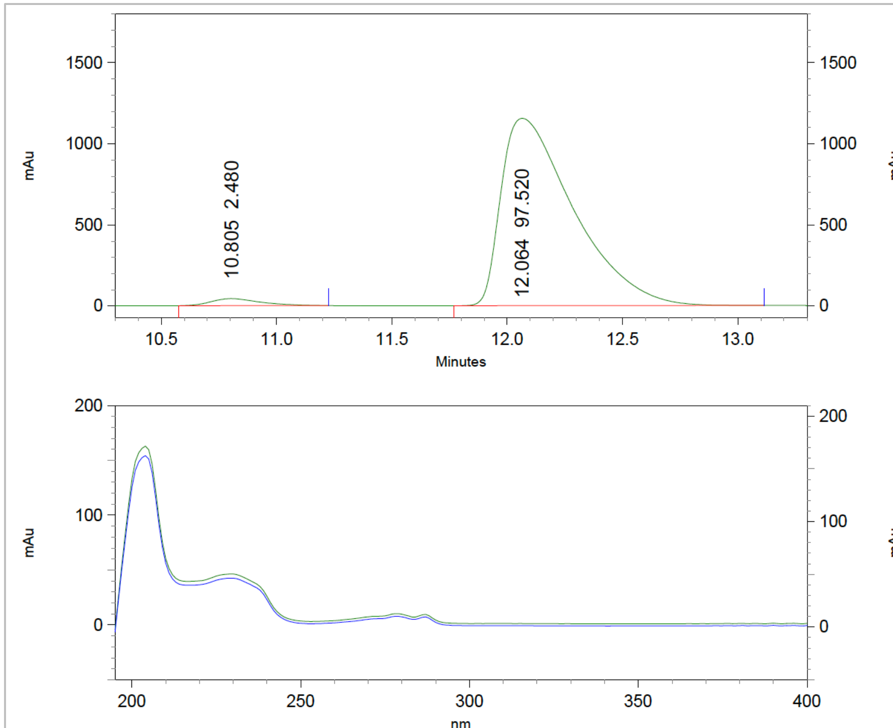


HPLC of **3s**



2: 231 nm, 4 nm Results

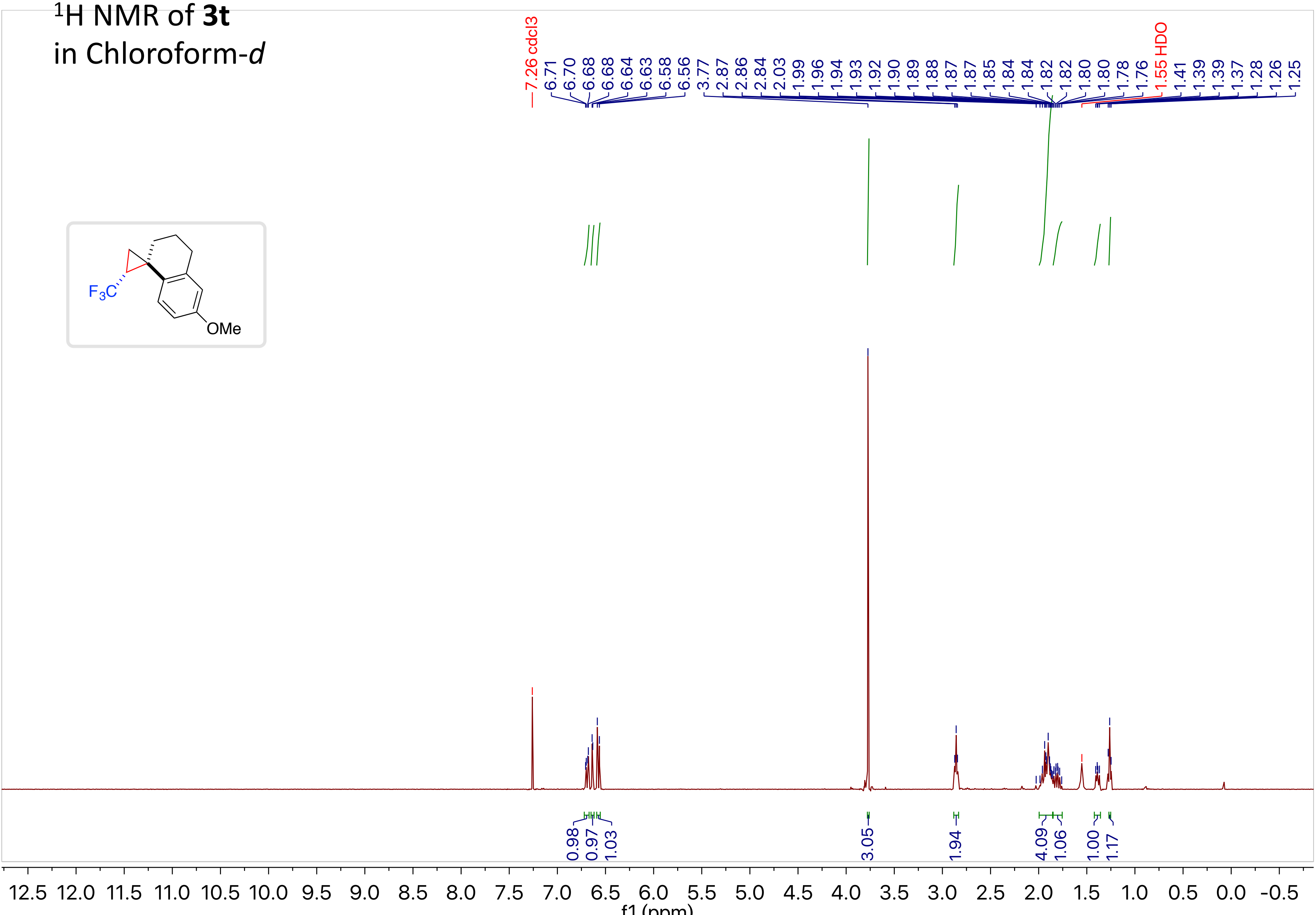
Pk #	Retention Time	Area Percent
1	10.613	49.637
2	11.925	50.363
Totals		100.000



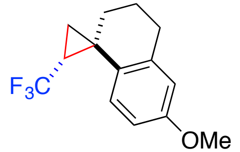
2: 231 nm, 4 nm Results

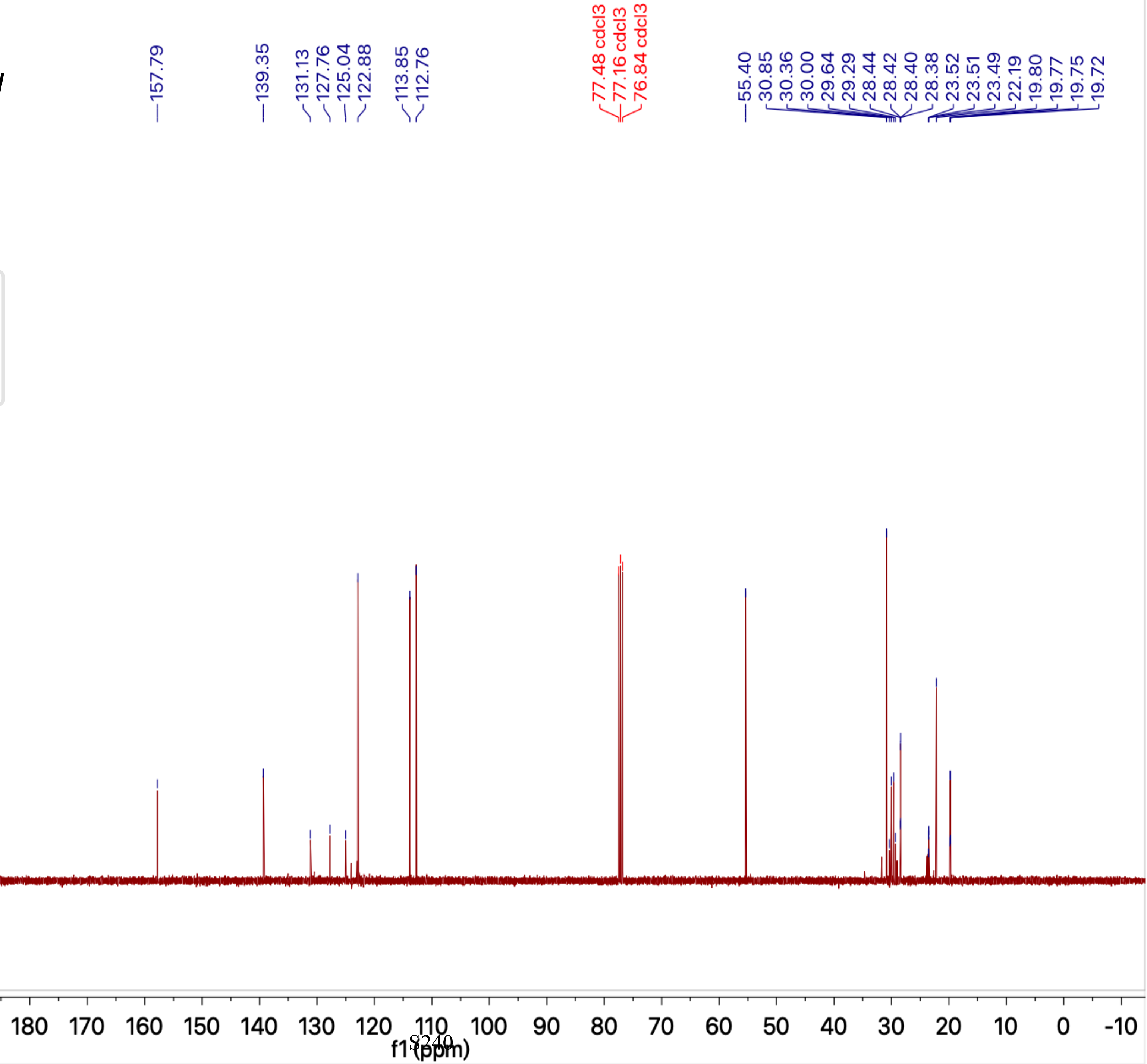
Pk #	Retention Time	Area Percent
1	10.805	2.480
2	12.064	97.520
Totals		100.000

^{1}H NMR of **3t** in Chloroform-*d*

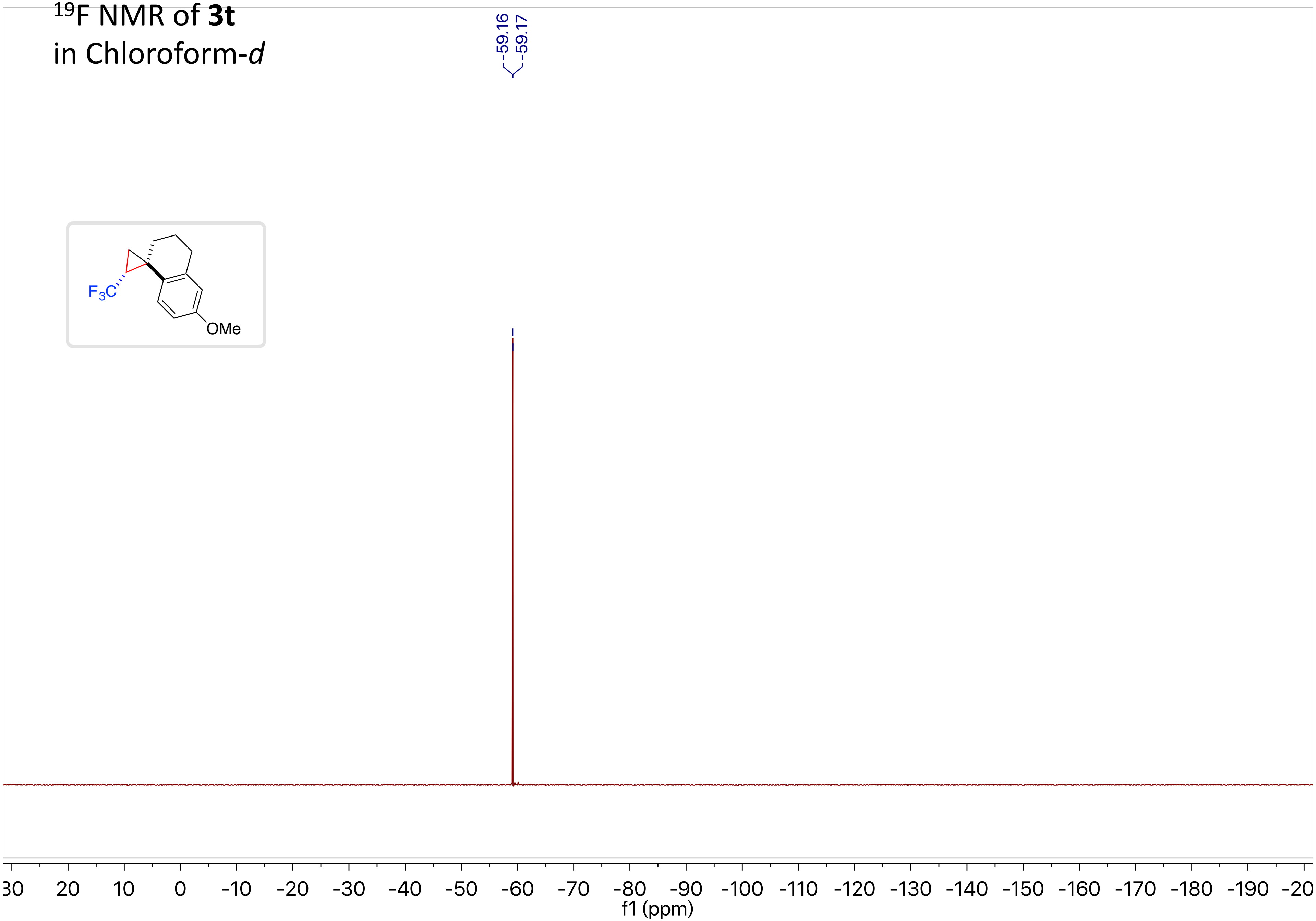


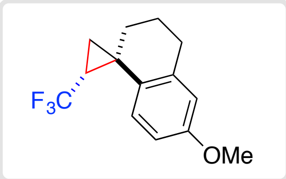
^{13}C NMR of **3t**
in Chloroform-*d*



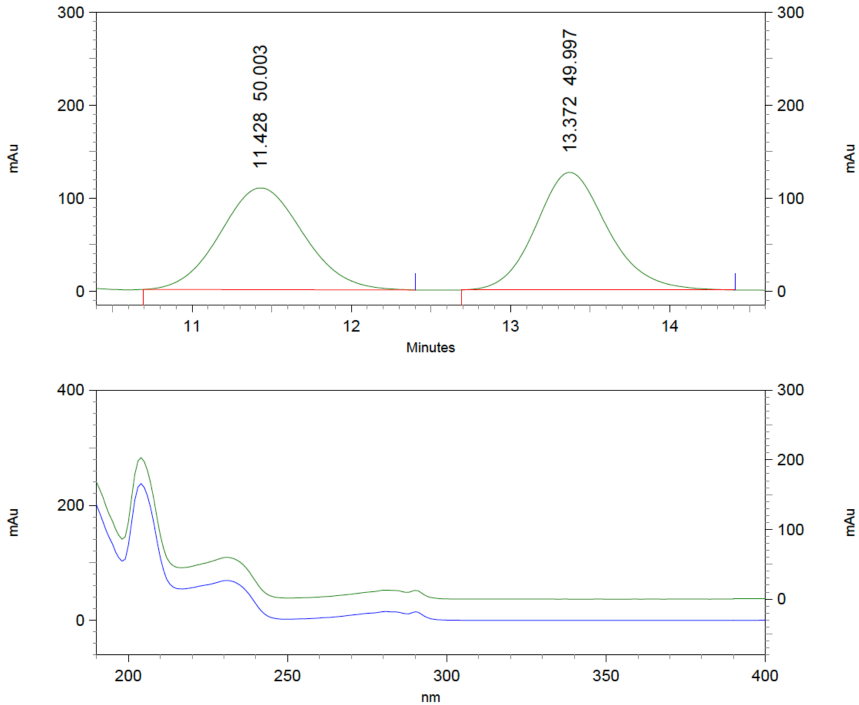


^{19}F NMR of **3t**
in Chloroform-*d*



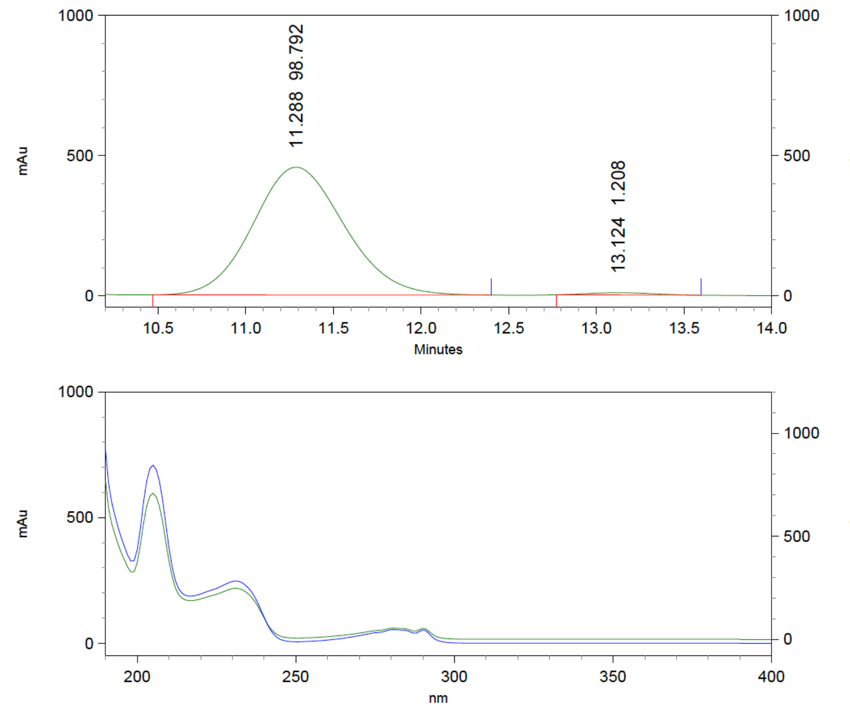


HPLC of **3t**



4: 234 nm, 4 nm Results

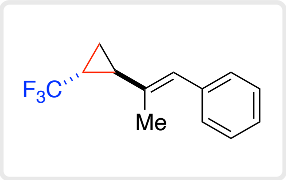
Pk #	Retention Time	Area Percent
1	11.428	50.003
2	13.372	49.997
Totals		100.000

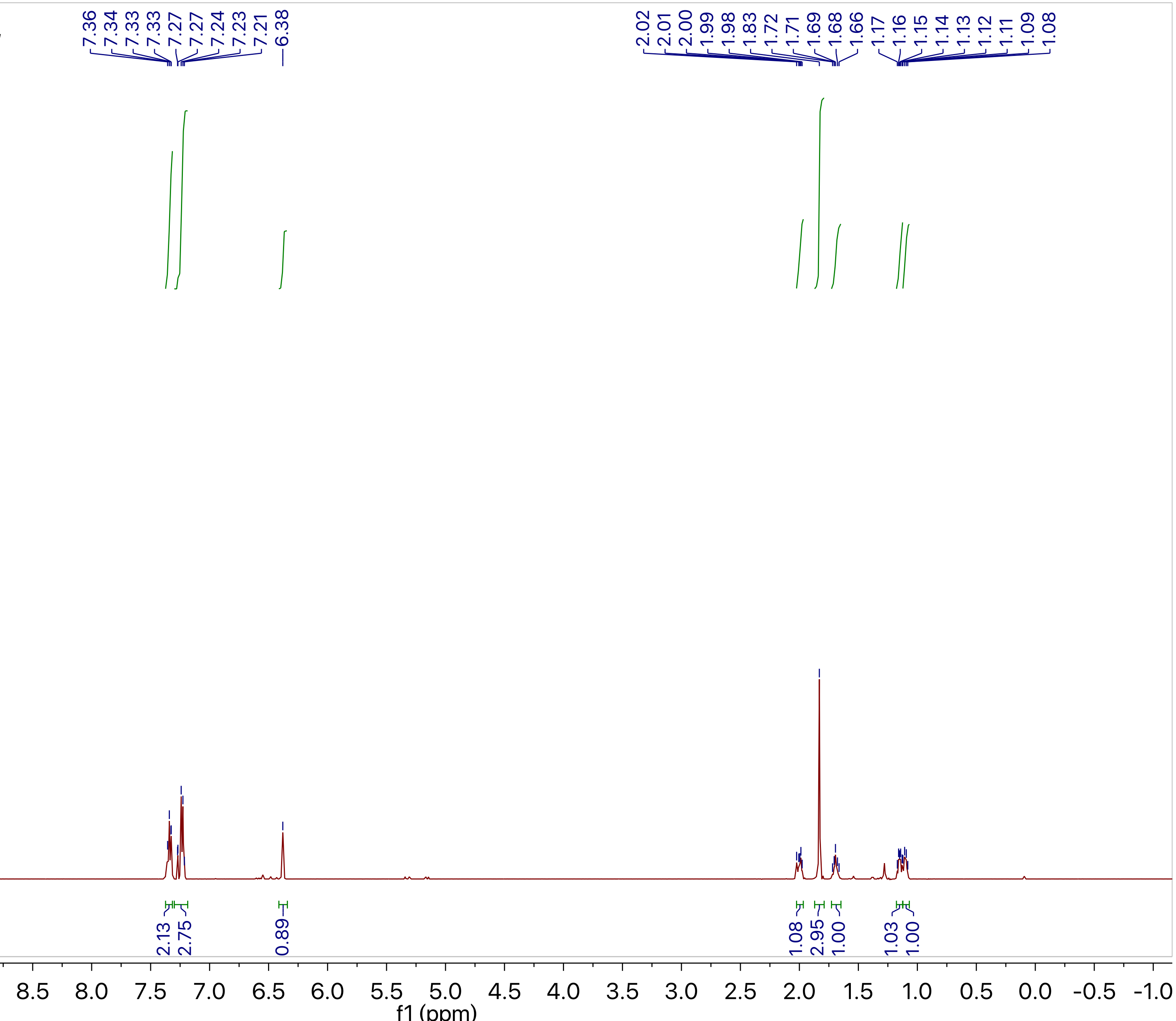


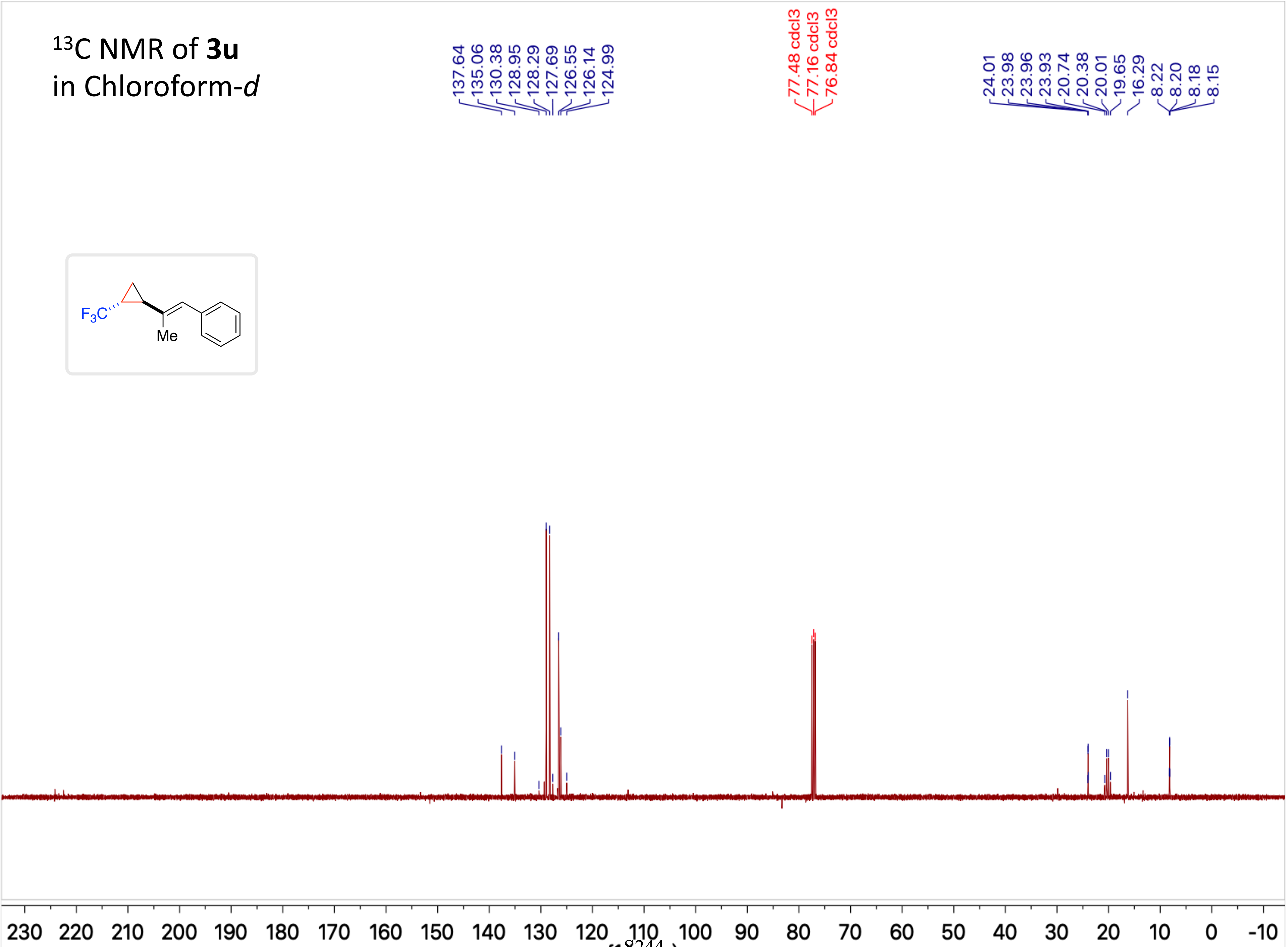
4: 234 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	11.288	98.792
2	13.124	1.208
Totals		100.000

^{1}H NMR of **3u**
in Chloroform-*d*

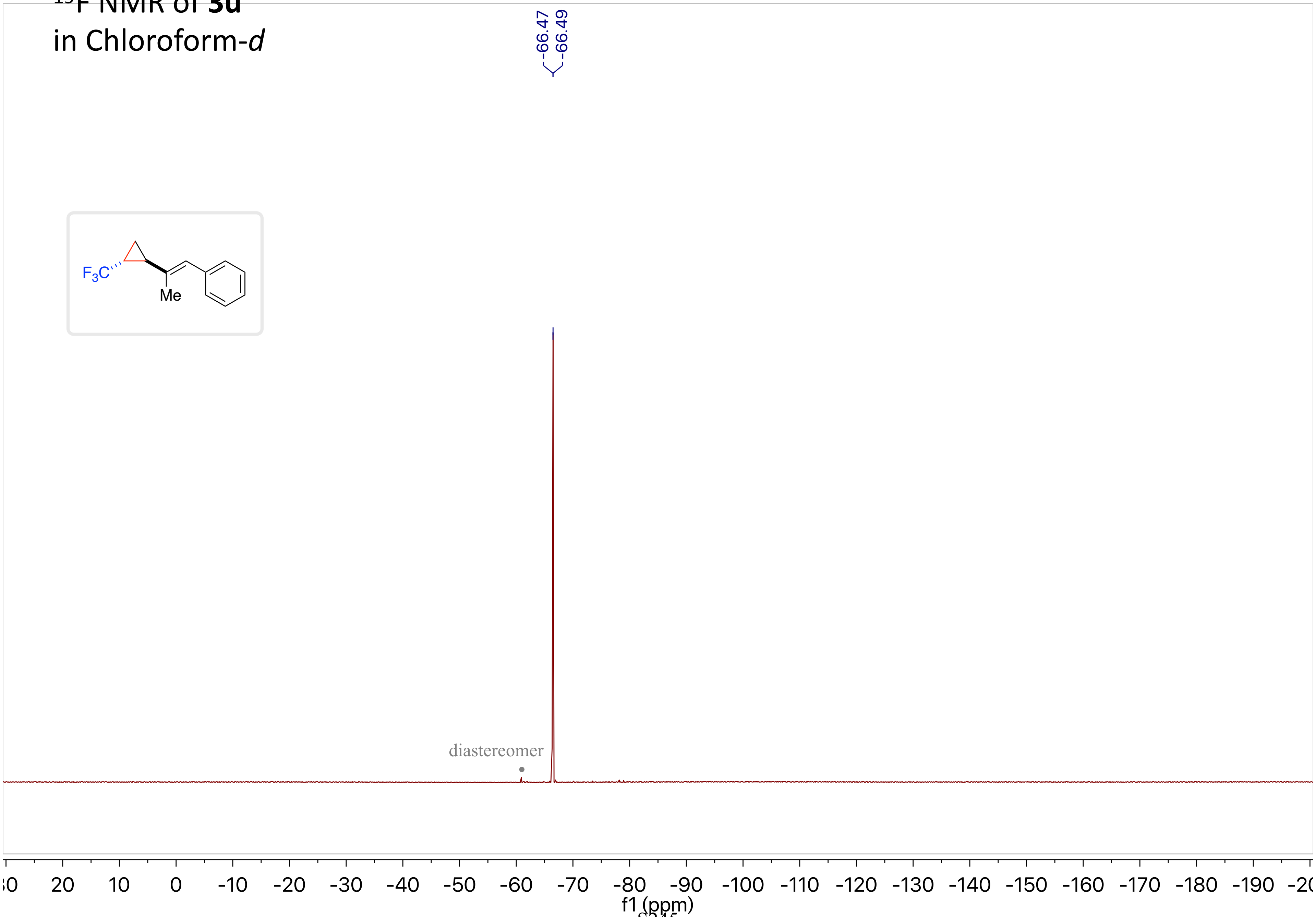




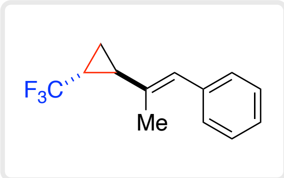


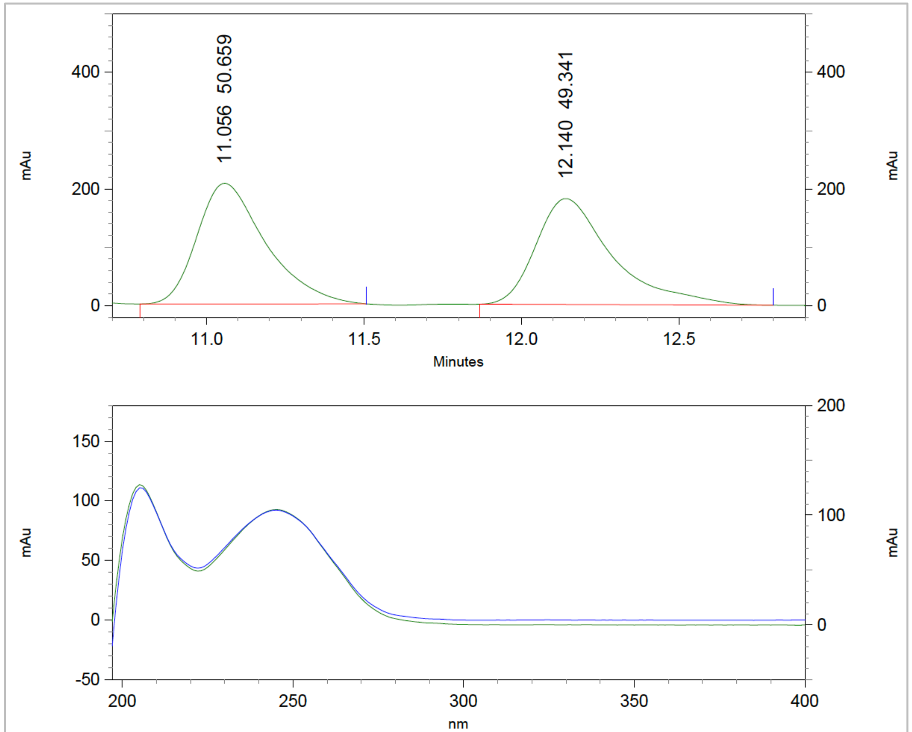
13C NMR of 3u
in Chloroform-d
137.64
135.06
130.38
128.95
128.29
127.69
126.55
126.14
124.99
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
24.01
23.98
23.96
23.93
20.74
20.38
20.01
19.65
16.29
8.22
8.20
8.18
8.15
F3C
Me
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

[19]F NMR of **3u**
in Chloroform-*d*



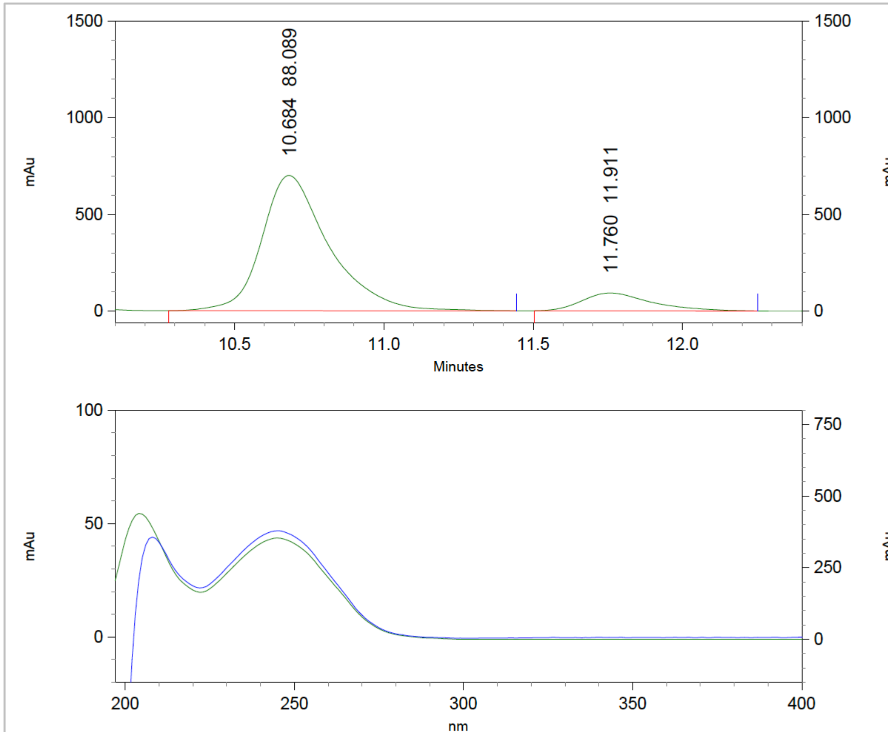
HPLC of **3u**





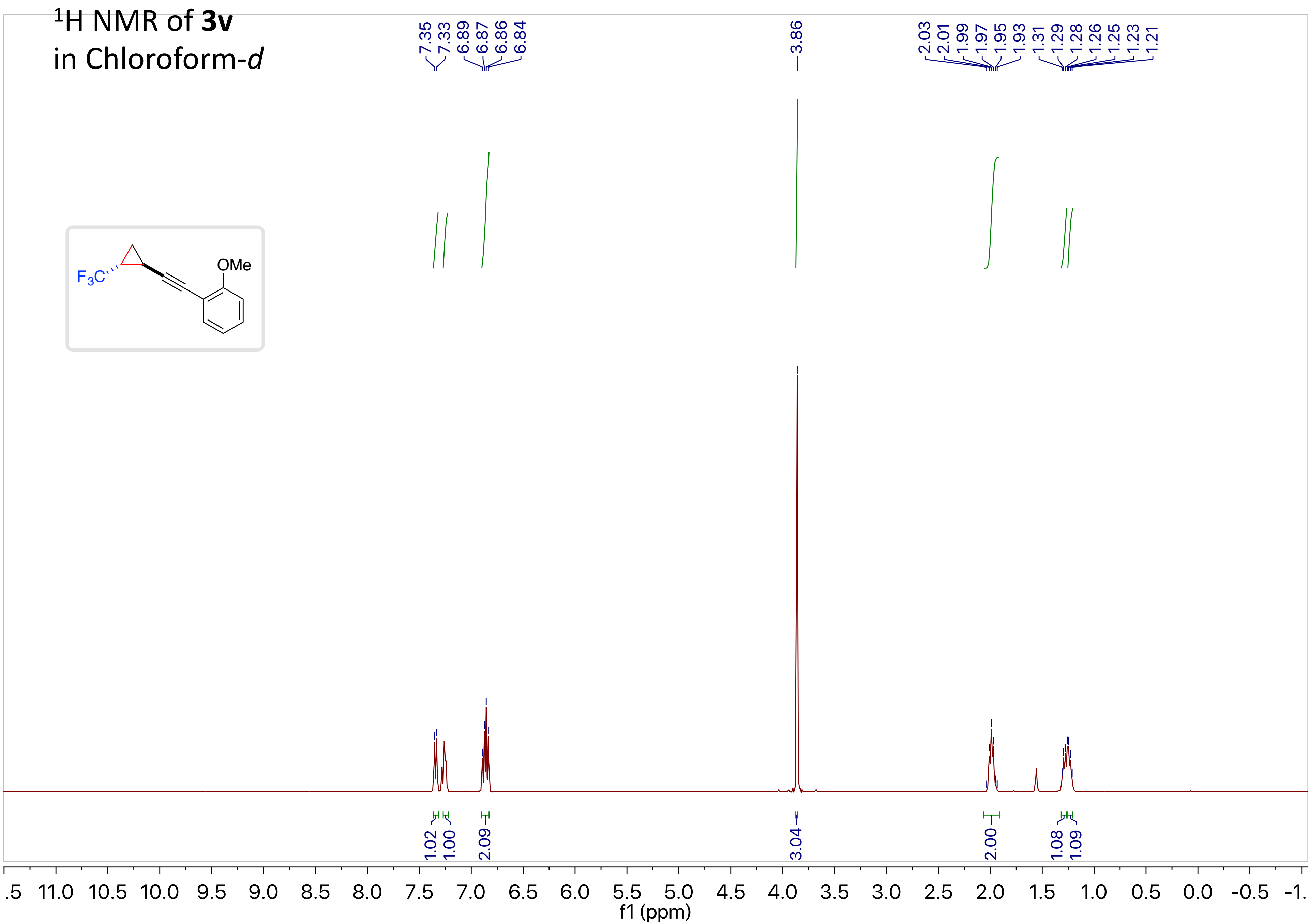
3: 245 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	11.056	50.659
2	12.140	49.341
Totals		100.000



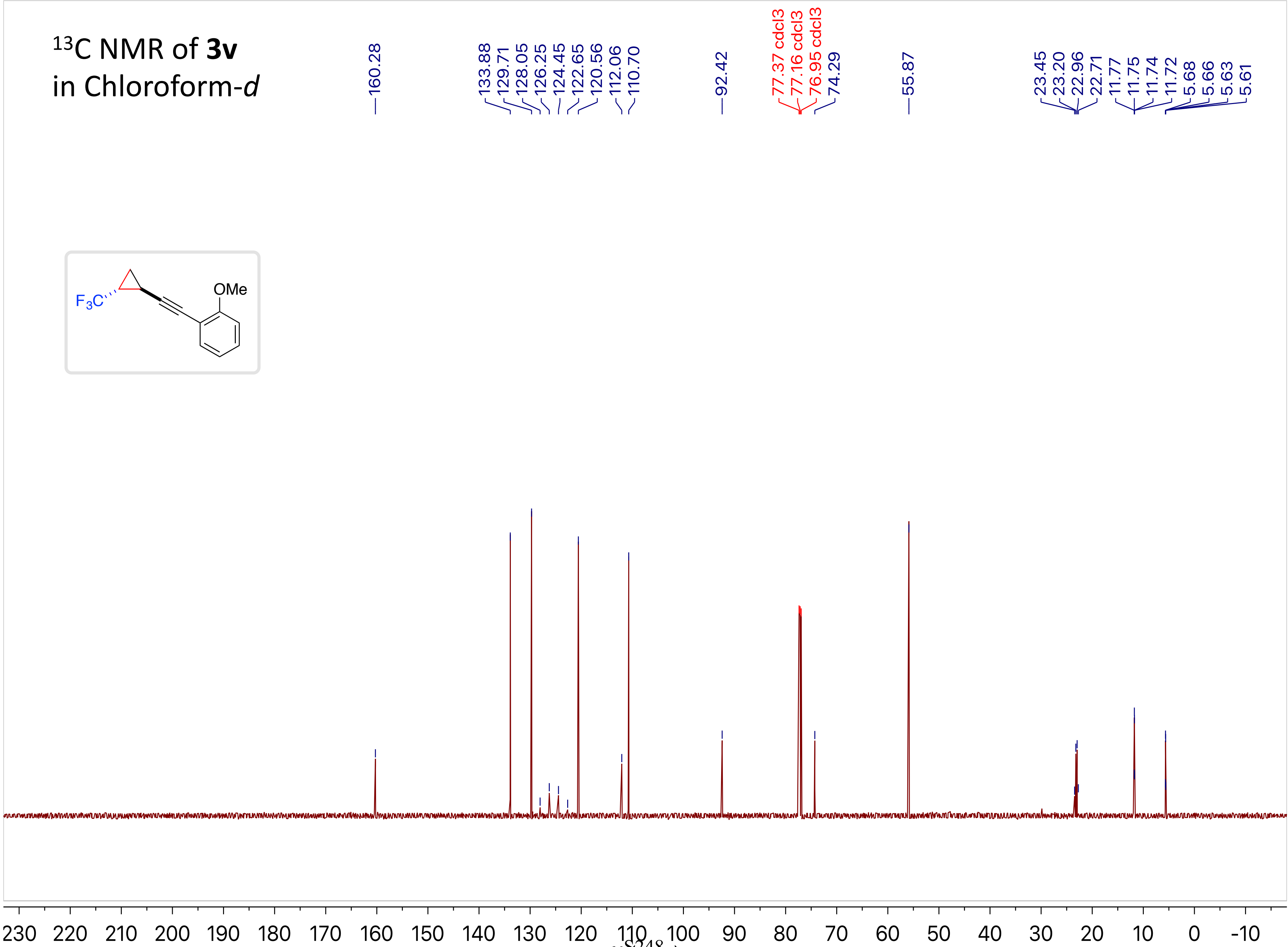
3: 246 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	10.684	88.089
2	11.760	11.911
Totals		100.000

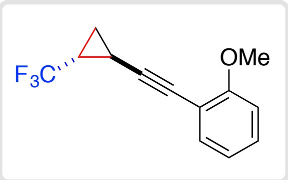


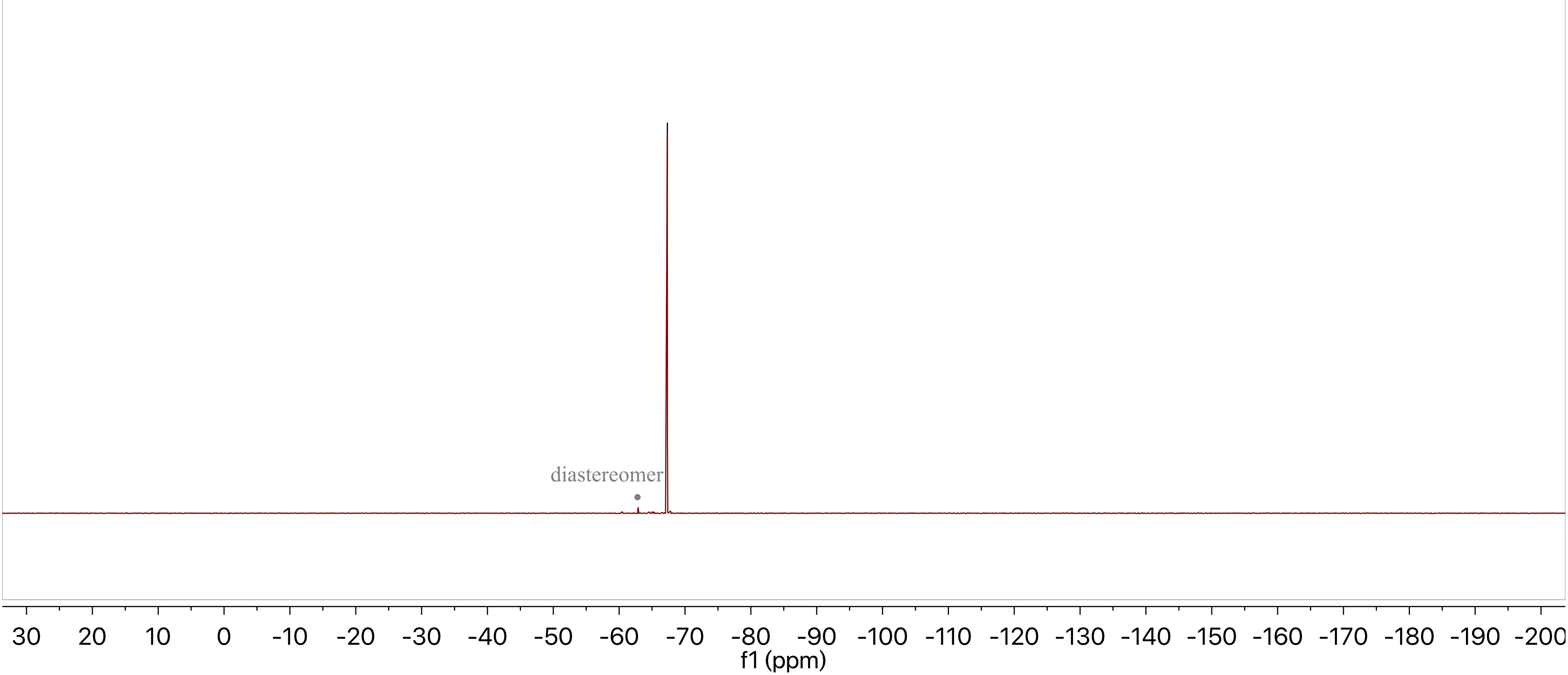
1H NMR of 3v
in Chloroform-d
7.35
7.33
6.89
6.87
6.86
6.84
3.86
2.03
2.01
1.99
1.97
1.95
1.93
1.31
1.29
1.28
1.26
1.25
1.23
1.21
F3C
OMe
1.02
1.00
2.09
3.04
2.00
1.08
1.09
f1 (ppm)

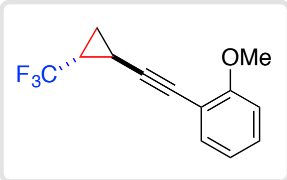
^{13}C NMR of **3v**
in Chloroform-*d*



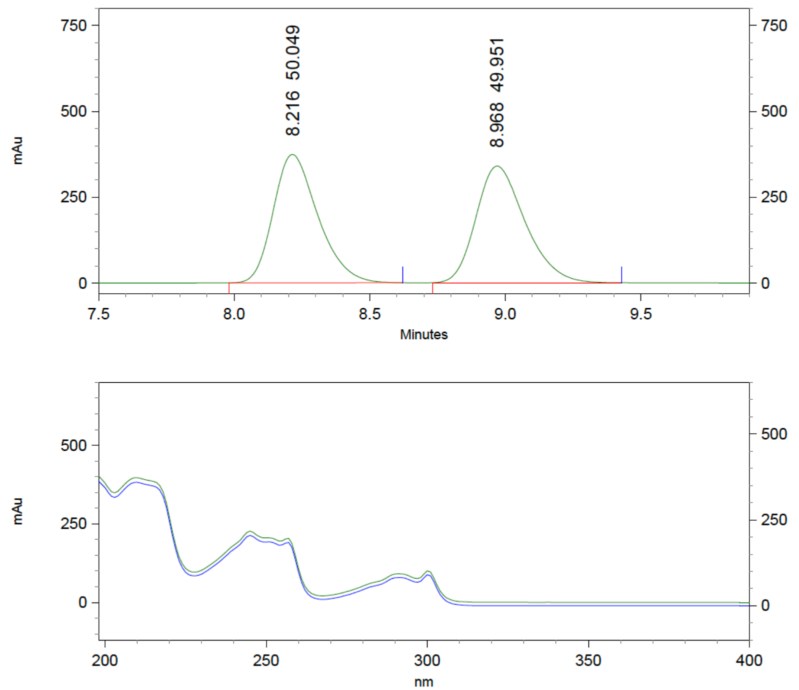
^{19}F NMR of **3v**
in Chloroform-*d*





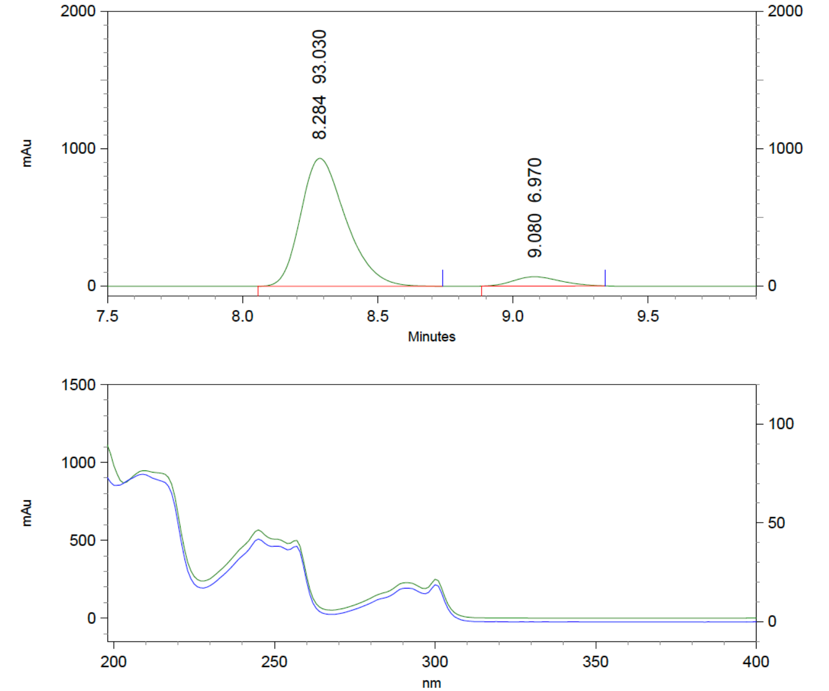


HPLC of **3v**



4: 222 nm, 4
nm Results

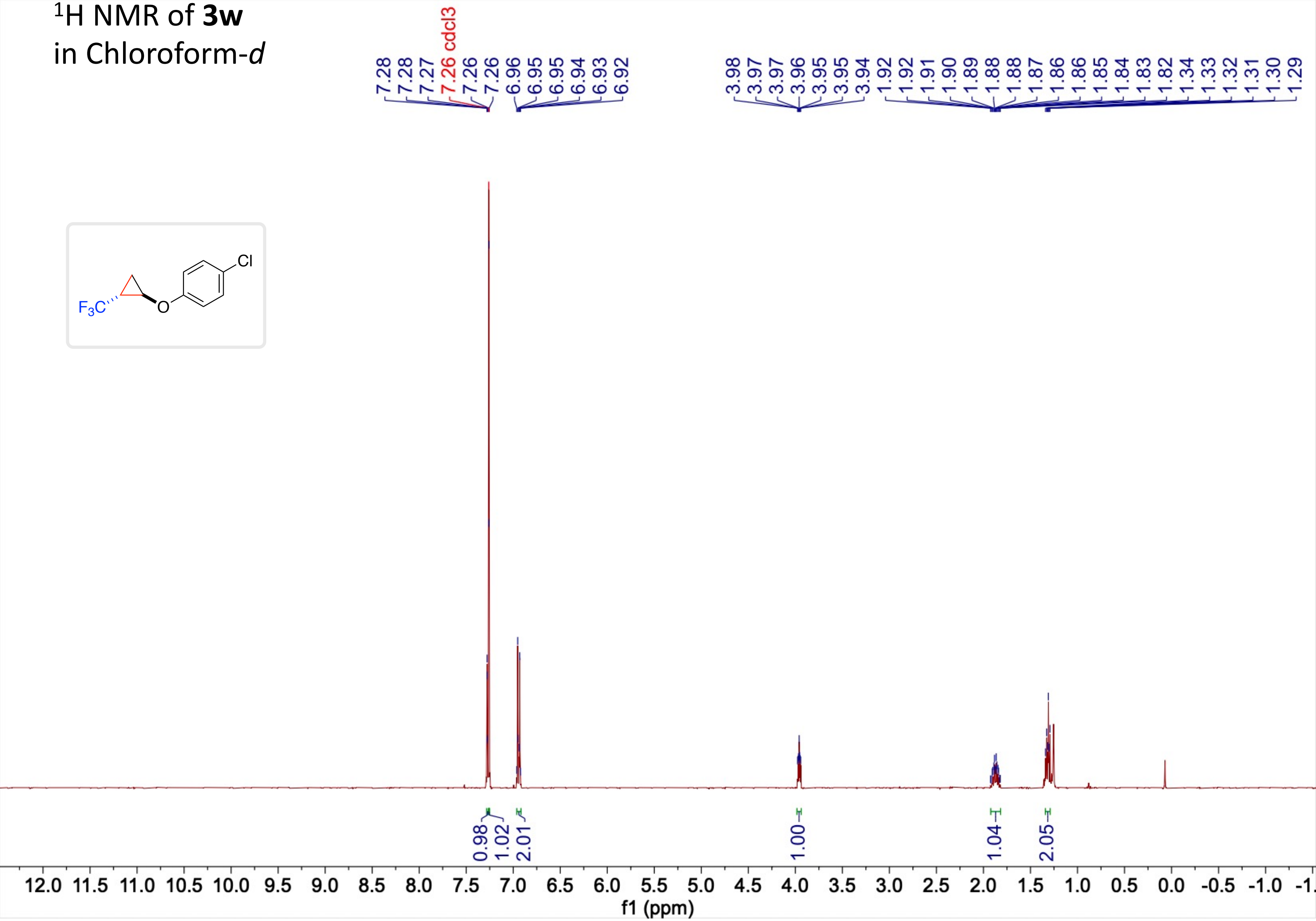
Pk #	Retention Time	Area Percent
1	8.216	50.049
2	8.968	49.951
Totals		100.000



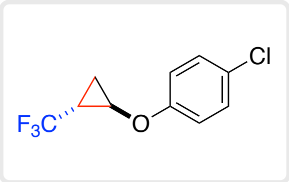
4: 222 nm, 4
nm Results

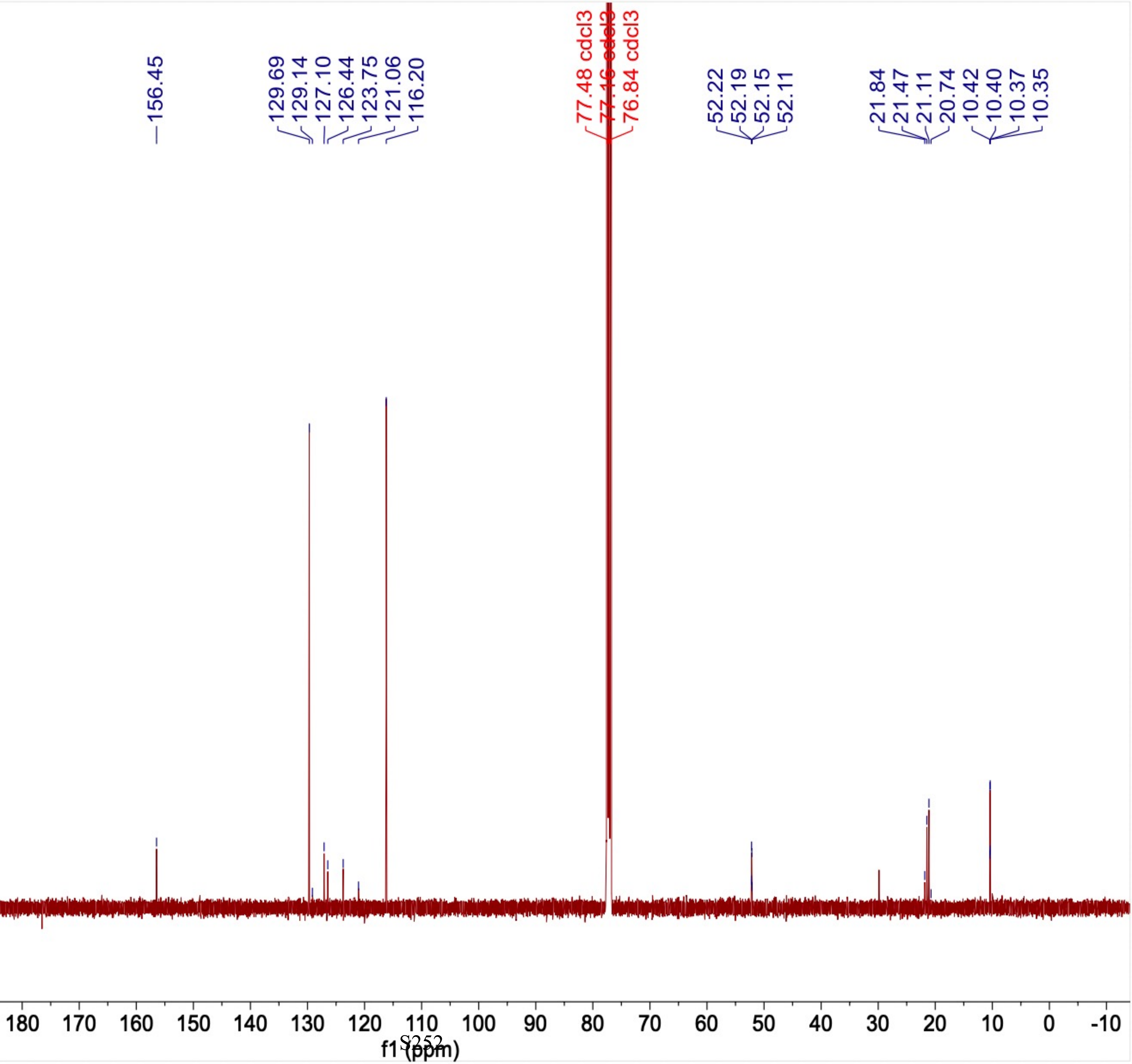
Pk #	Retention Time	Area Percent
1	8.284	93.030
2	9.080	6.970
Totals		100.000

^{1}H NMR of **3w**
in Chloroform-*d*

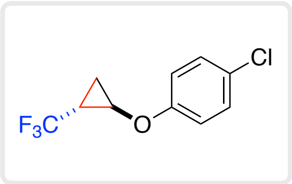


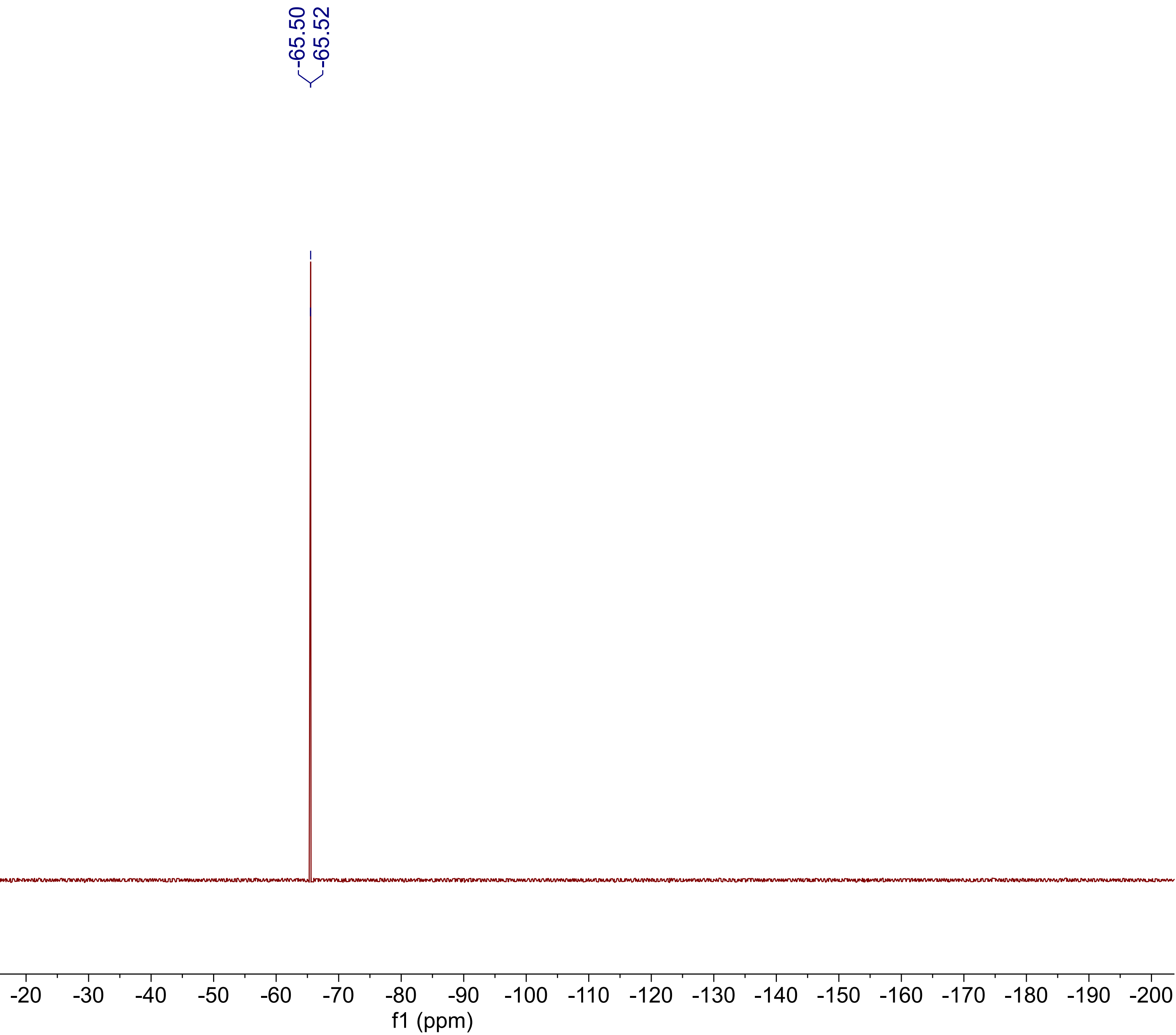
^{13}C NMR of **3w**
in Chloroform-*d*



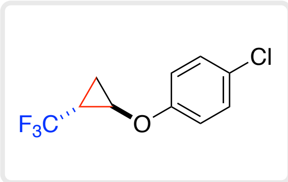


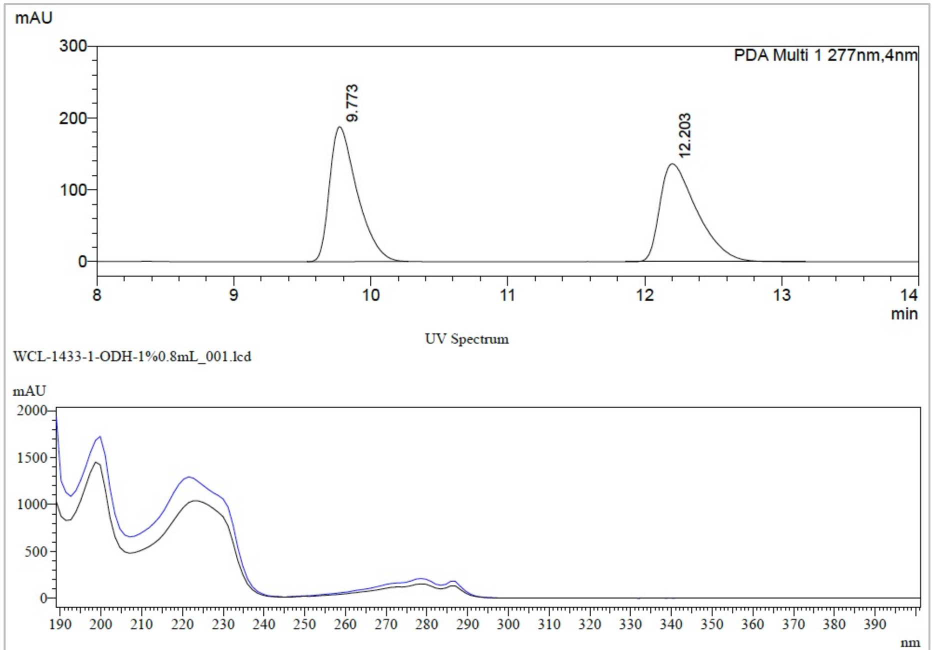
^{19}F NMR of **3w**
in Chloroform-*d*





HPLC of **3w**

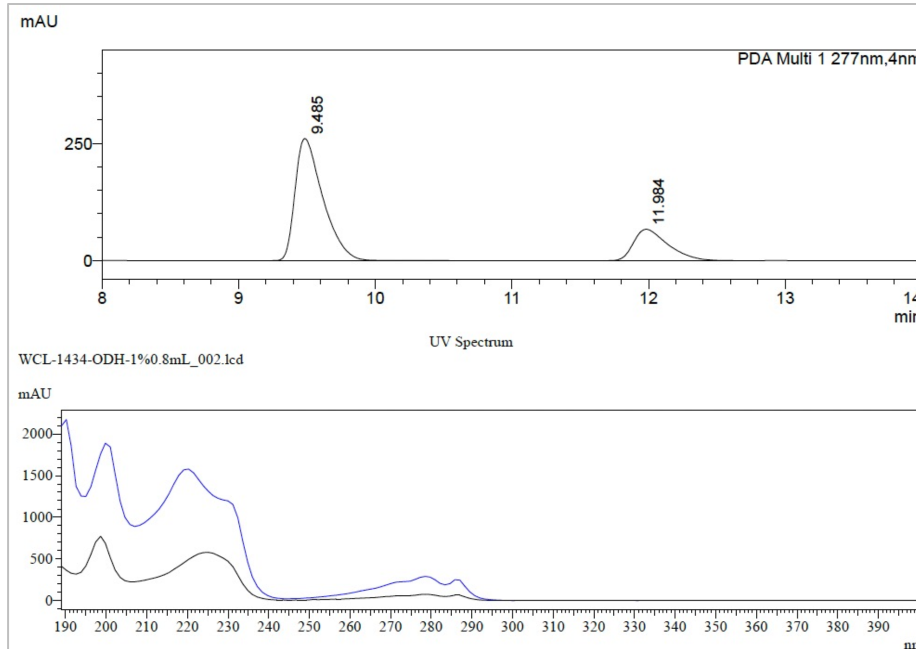




Peak Table

PDA Ch1 277nm

Peak#	Ret. Time	Area%
1	9.773	50.574
2	12.203	49.426
Total		100.000

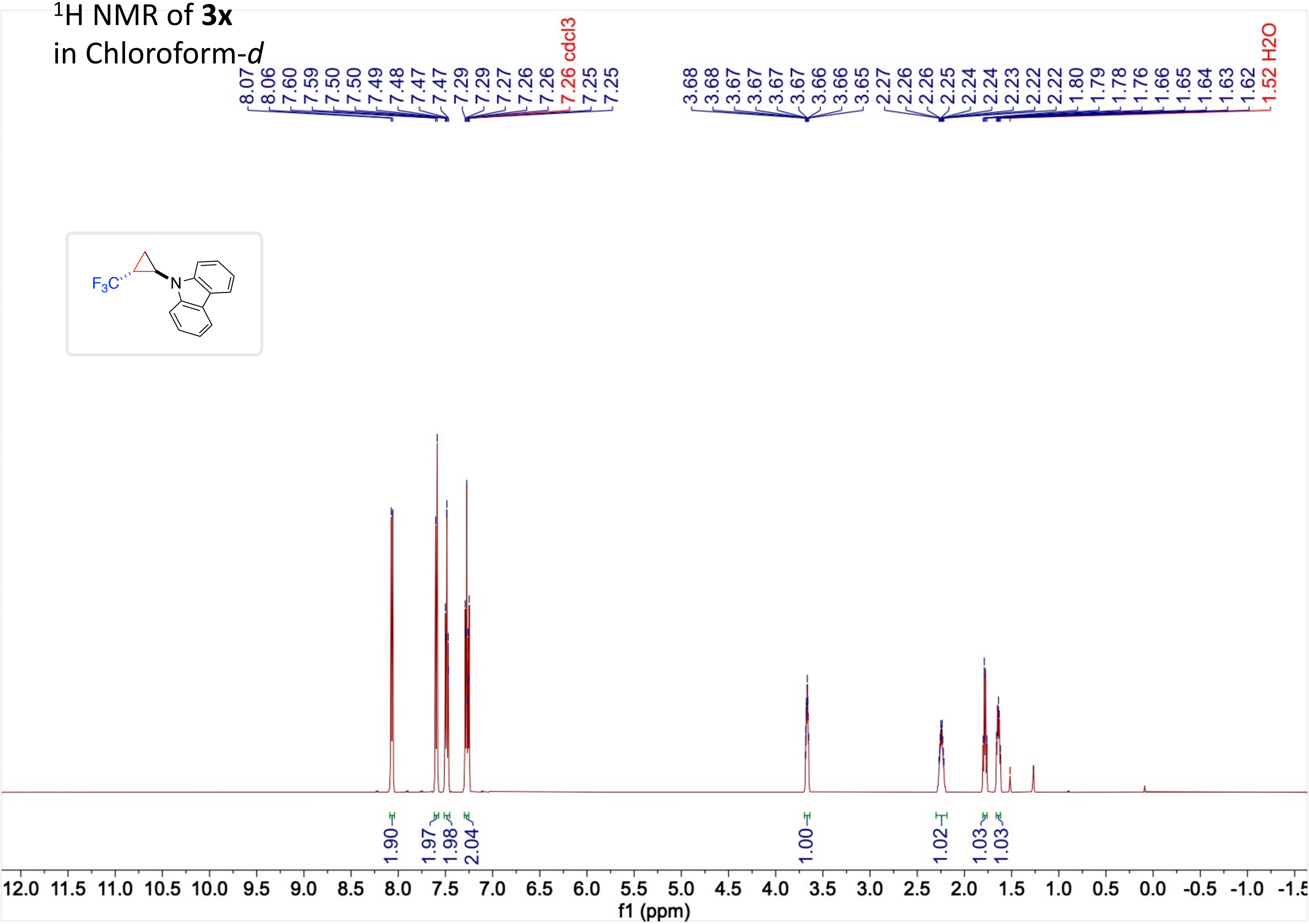


Peak Table

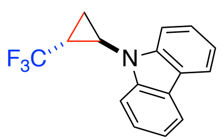
PDA Ch1 277nm

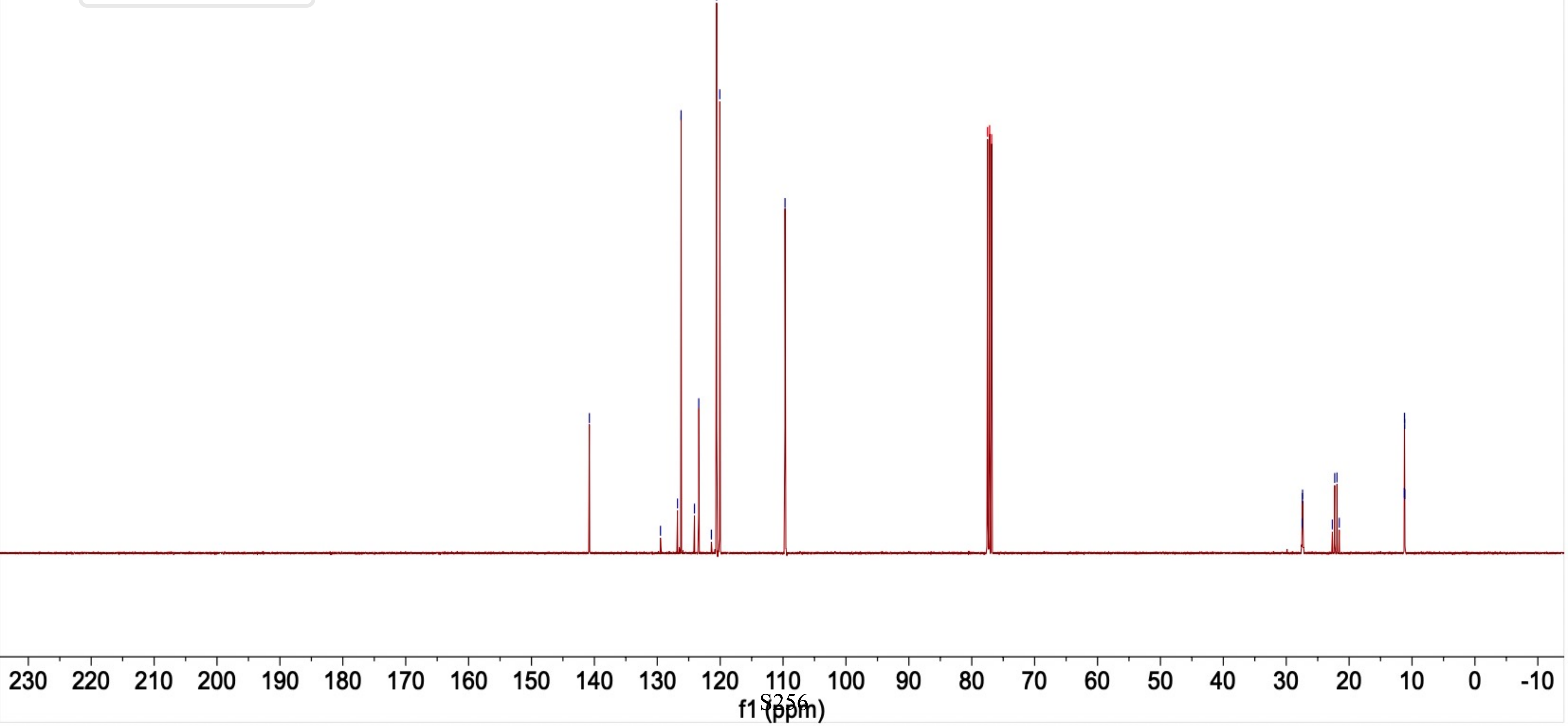
Peak#	Ret. Time	Area%
1	9.485	75.784
2	11.984	24.216
Total		100.000

^{1}H NMR of **3x**
in Chloroform-*d*

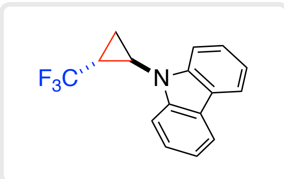


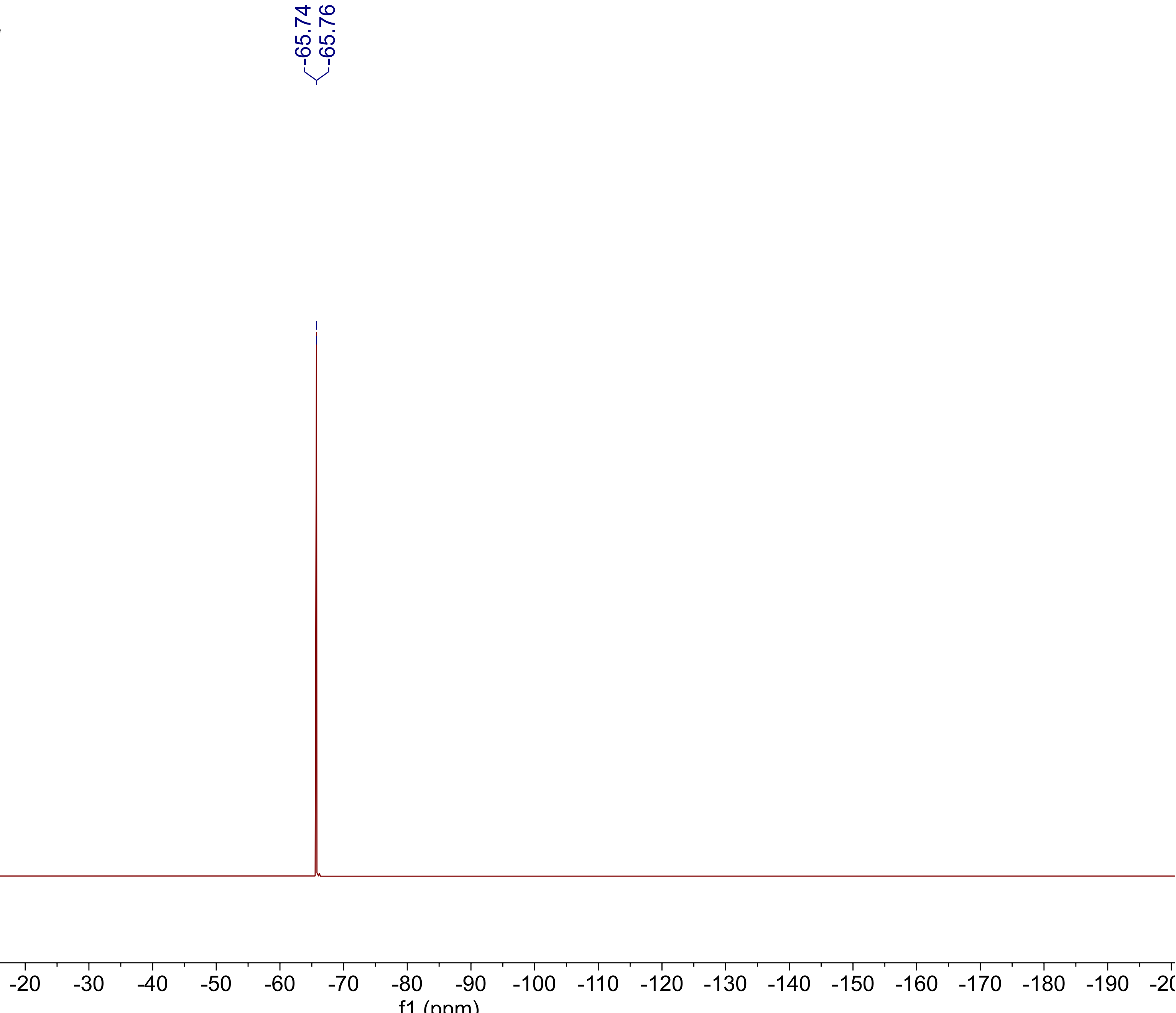
^{13}C NMR of **3x**
in Chloroform-*d*



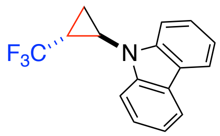


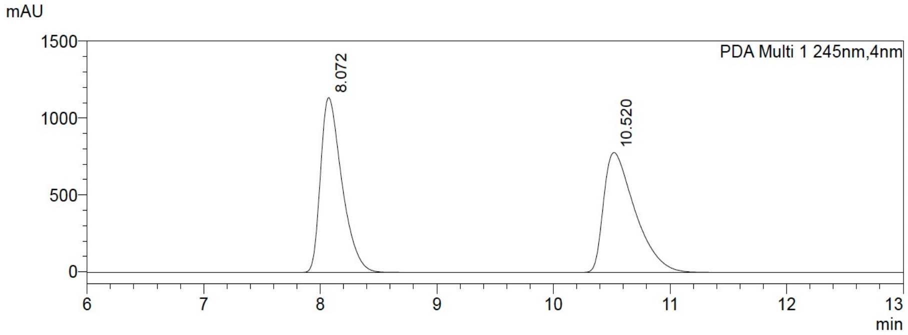
[19]F NMR of **3x**
in Chloroform-*d*





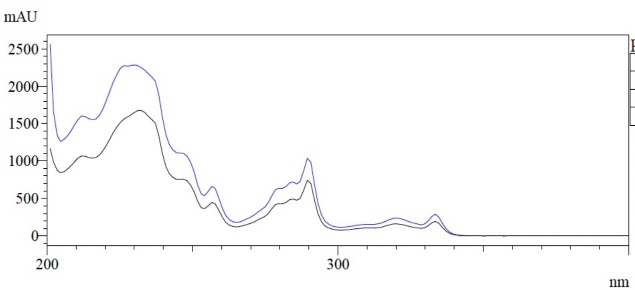
HPLC of **3x**





UV Spectrum

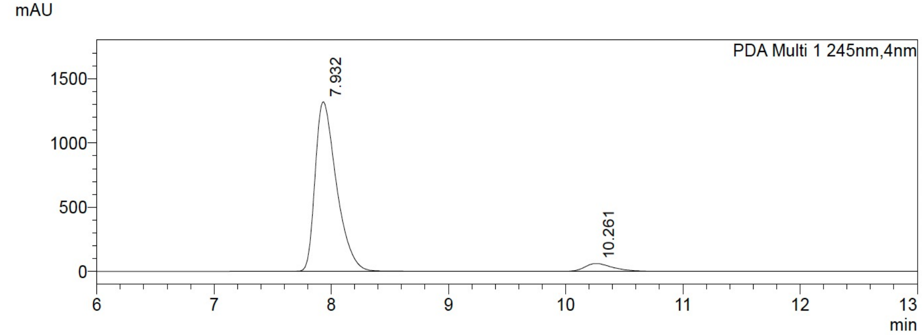
WCL-1413-ODH-5%0.8mL_001.lcd



Peak Table

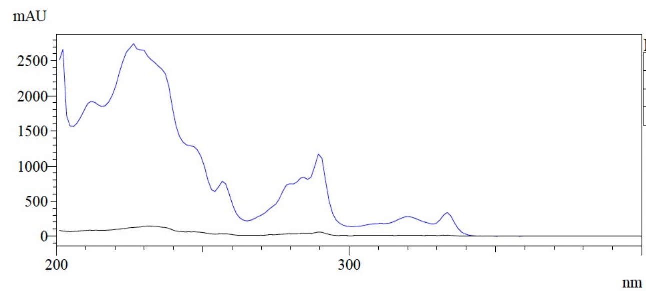
PDA Ch1 245nm

Peak#	Ret. Time	Area%
1	8.072	49.860
2	10.520	50.140
Total		100.000



UV Spectrum

WCL-1414-ODH-5%0.8mL_002.lcd

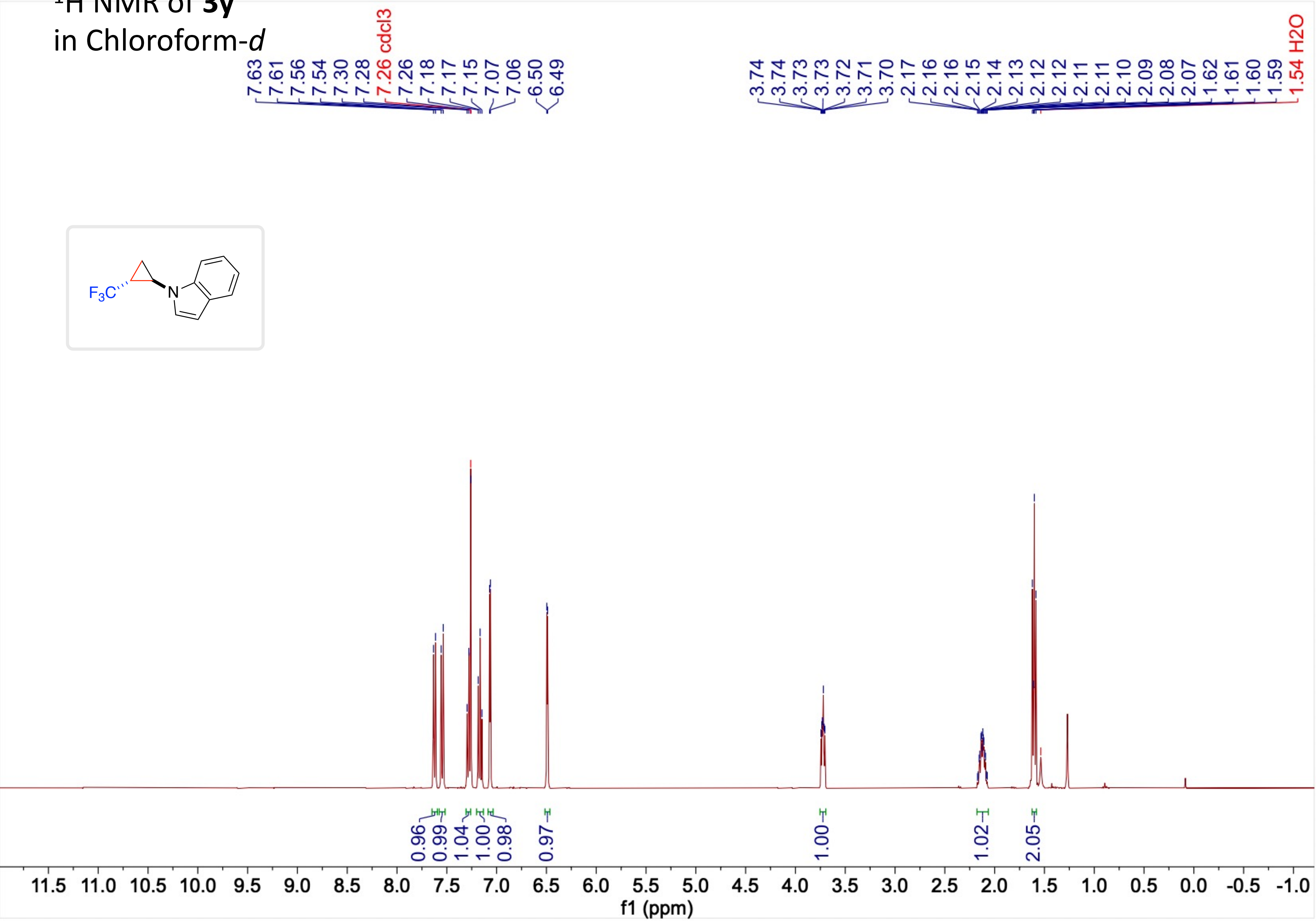


Peak Table

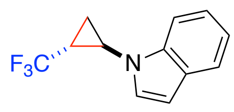
PDA Ch1 245nm

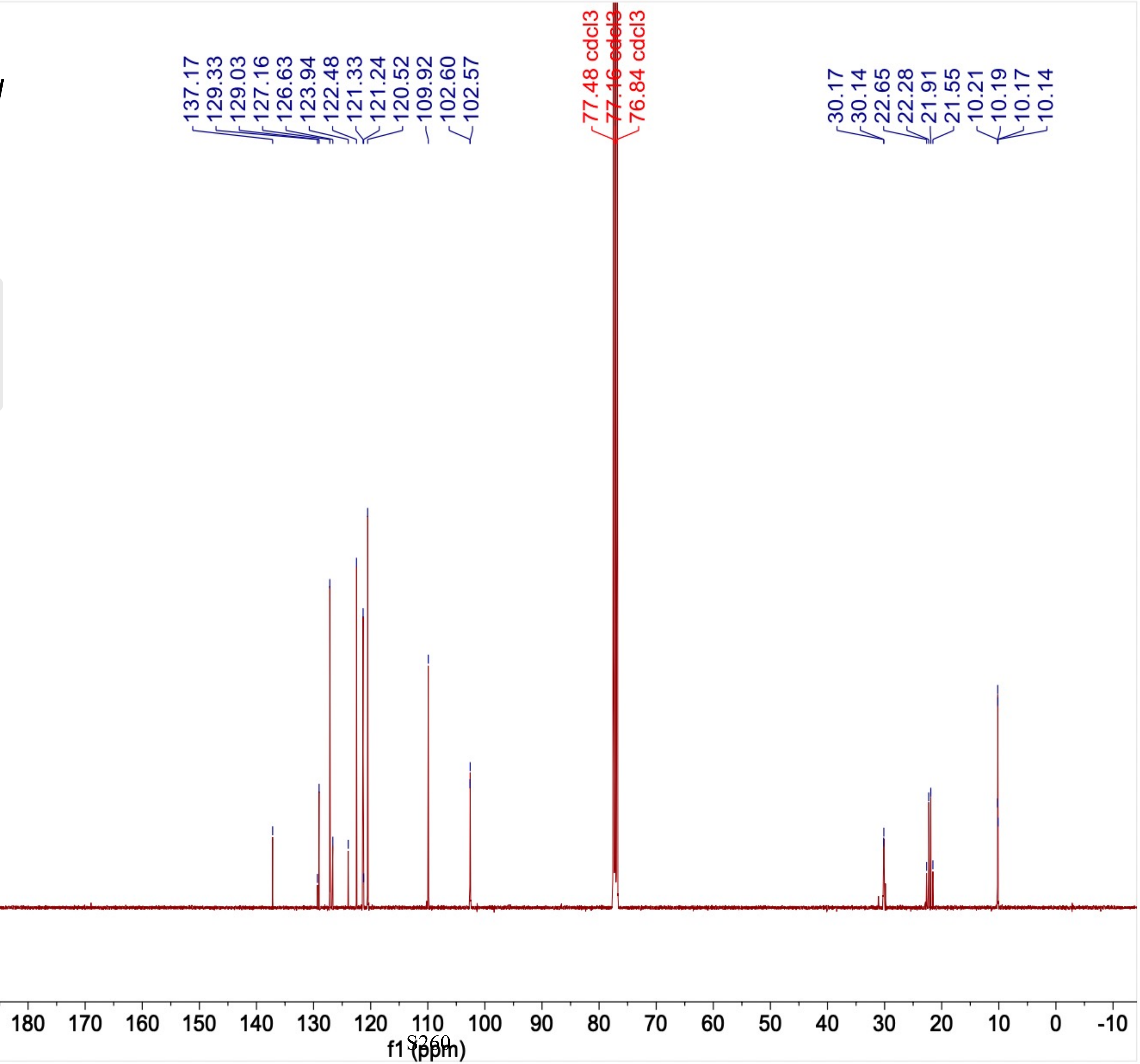
Peak#	Ret. Time	Area%
1	7.932	94.446
2	10.261	5.554
Total		100.000

^1H NMR of **3y**
in Chloroform-*d*

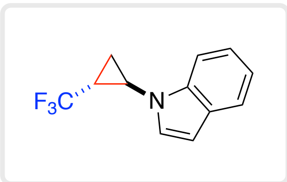


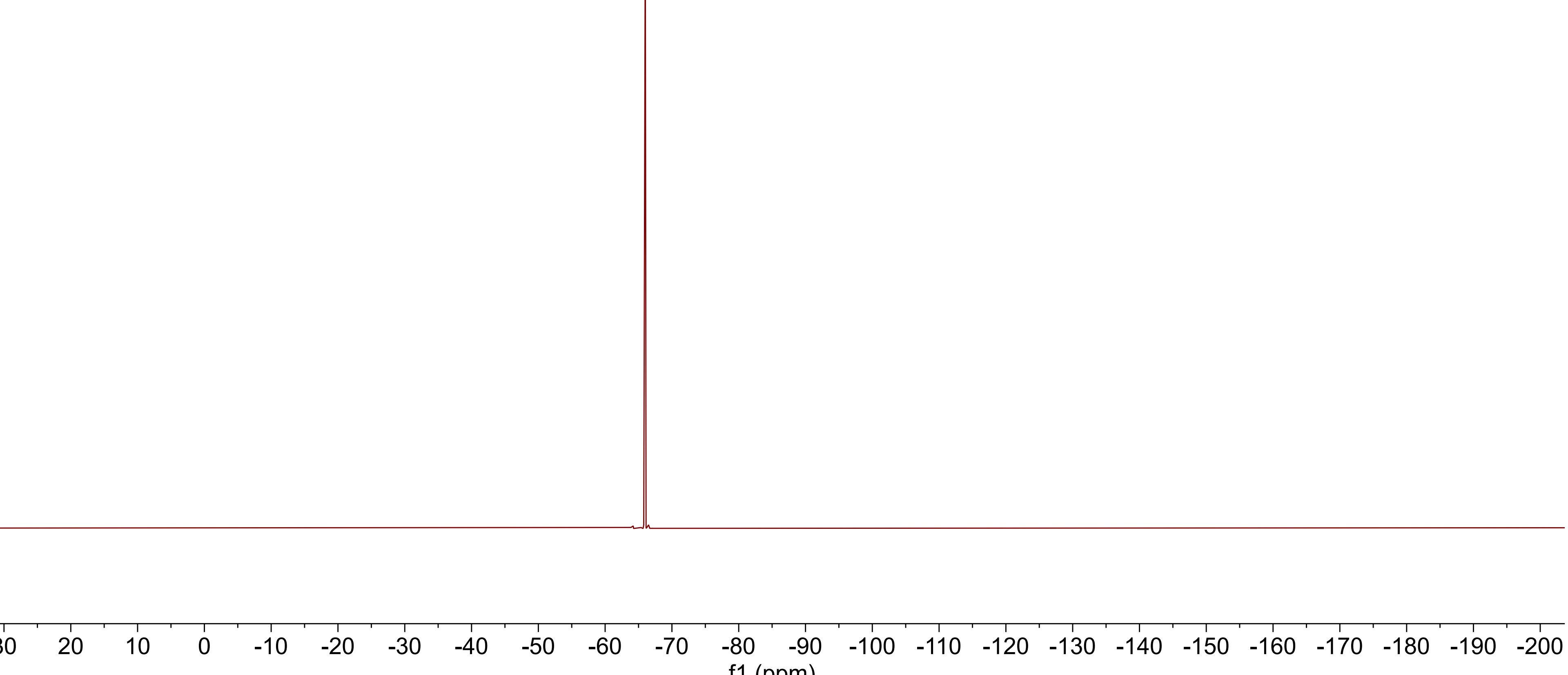
^{13}C NMR of **3y**
in Chloroform-*d*

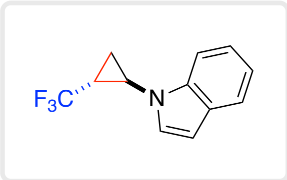




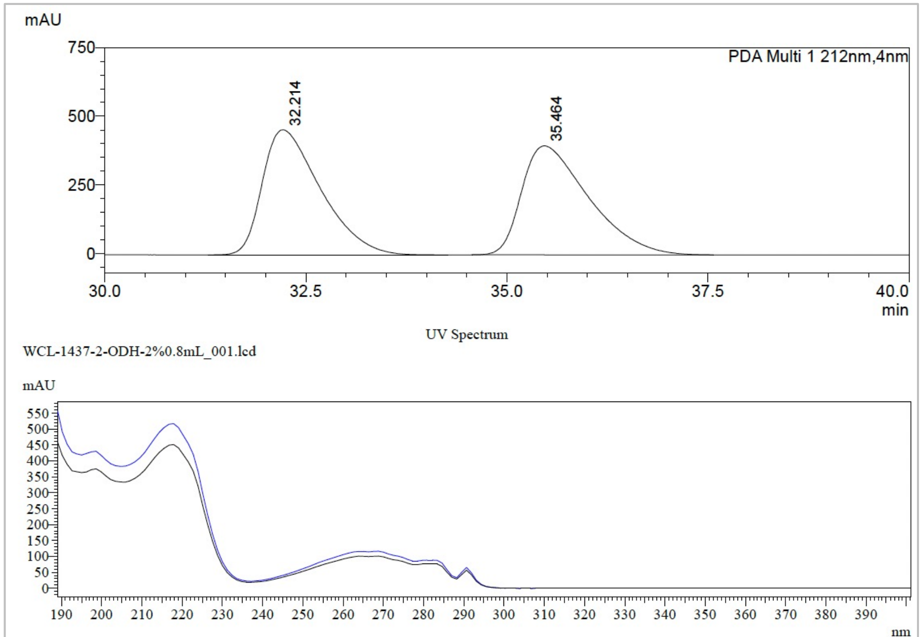
[19]F NMR of **3y**
in Chloroform-*d*







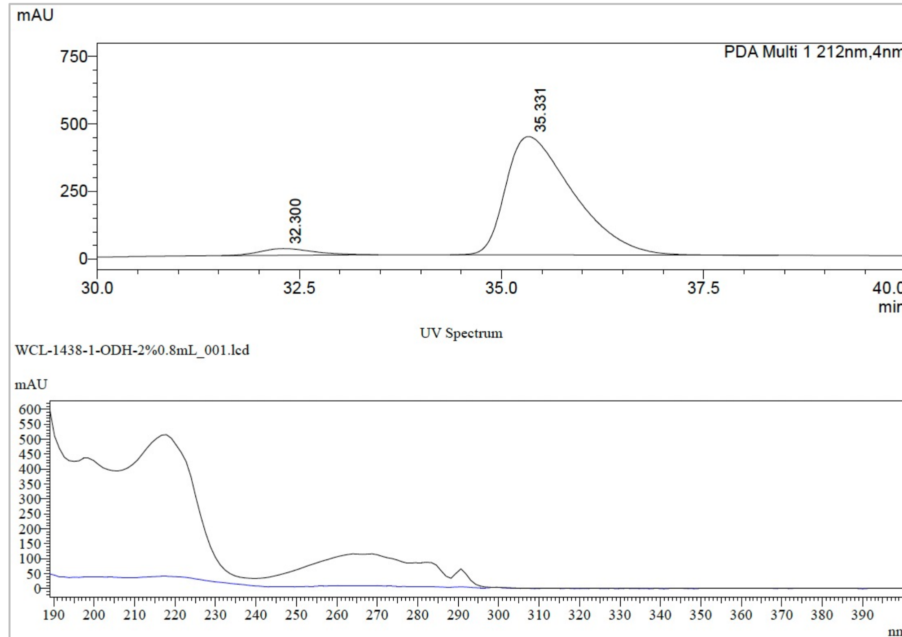
HPLC of **3y**



Peak Table

PDA Ch1 212nm

Peak#	Ret. Time	Area%
1	32.214	49.903
2	35.464	50.097
Total		100.000

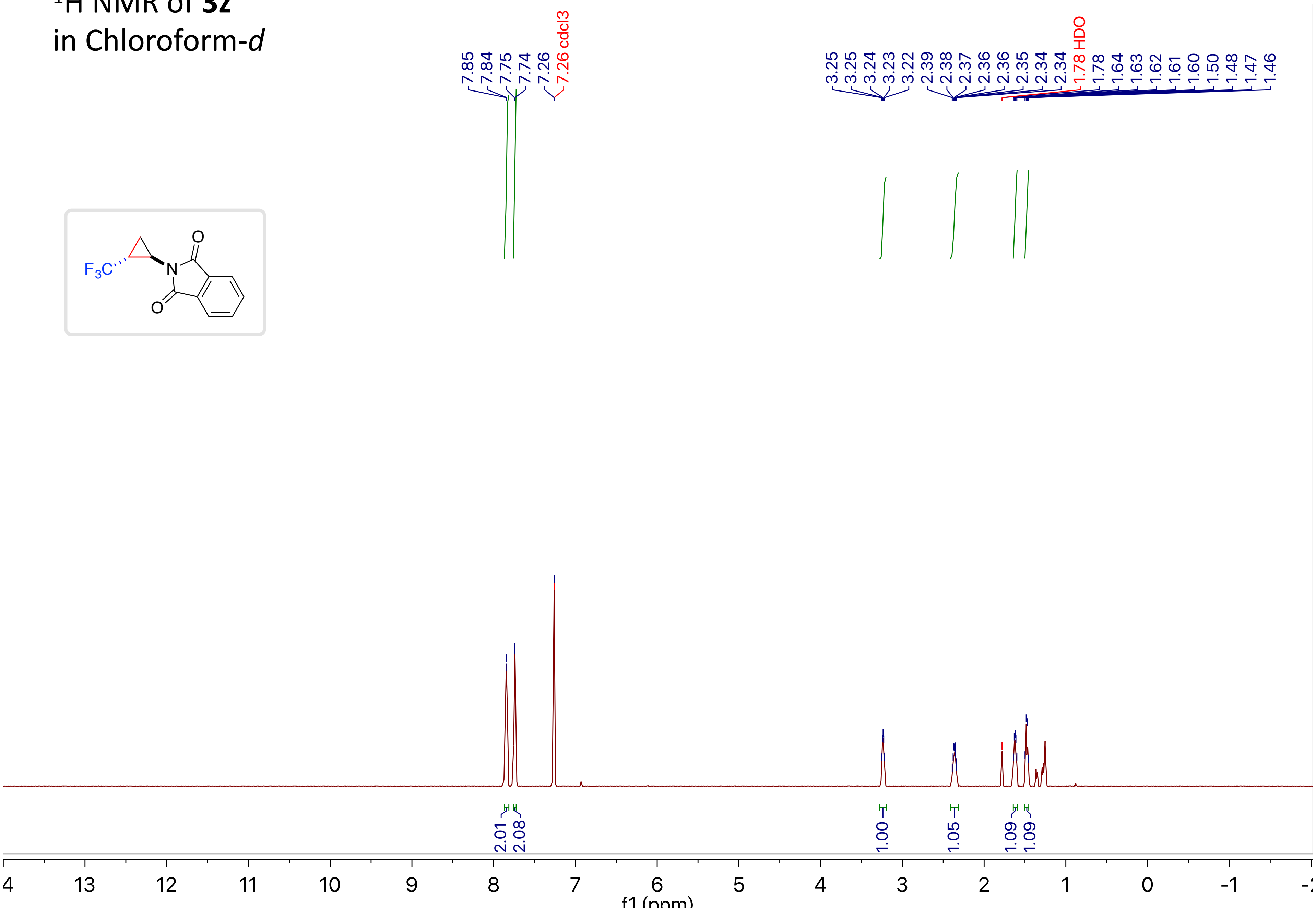


Peak Table

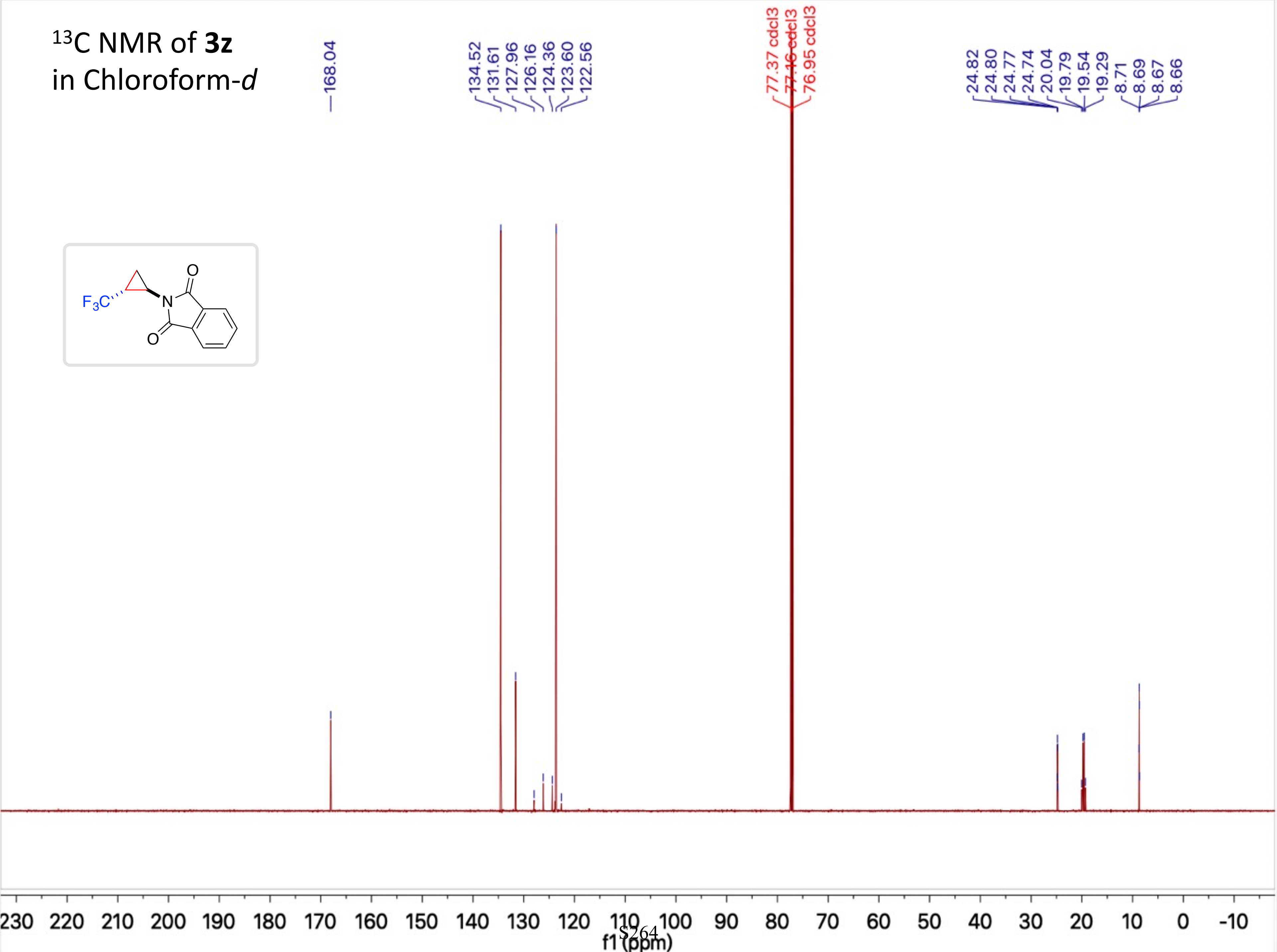
PDA Ch1 212nm

Peak#	Ret. Time	Area%
1	32.300	4.185
2	35.331	95.815
Total		100.000

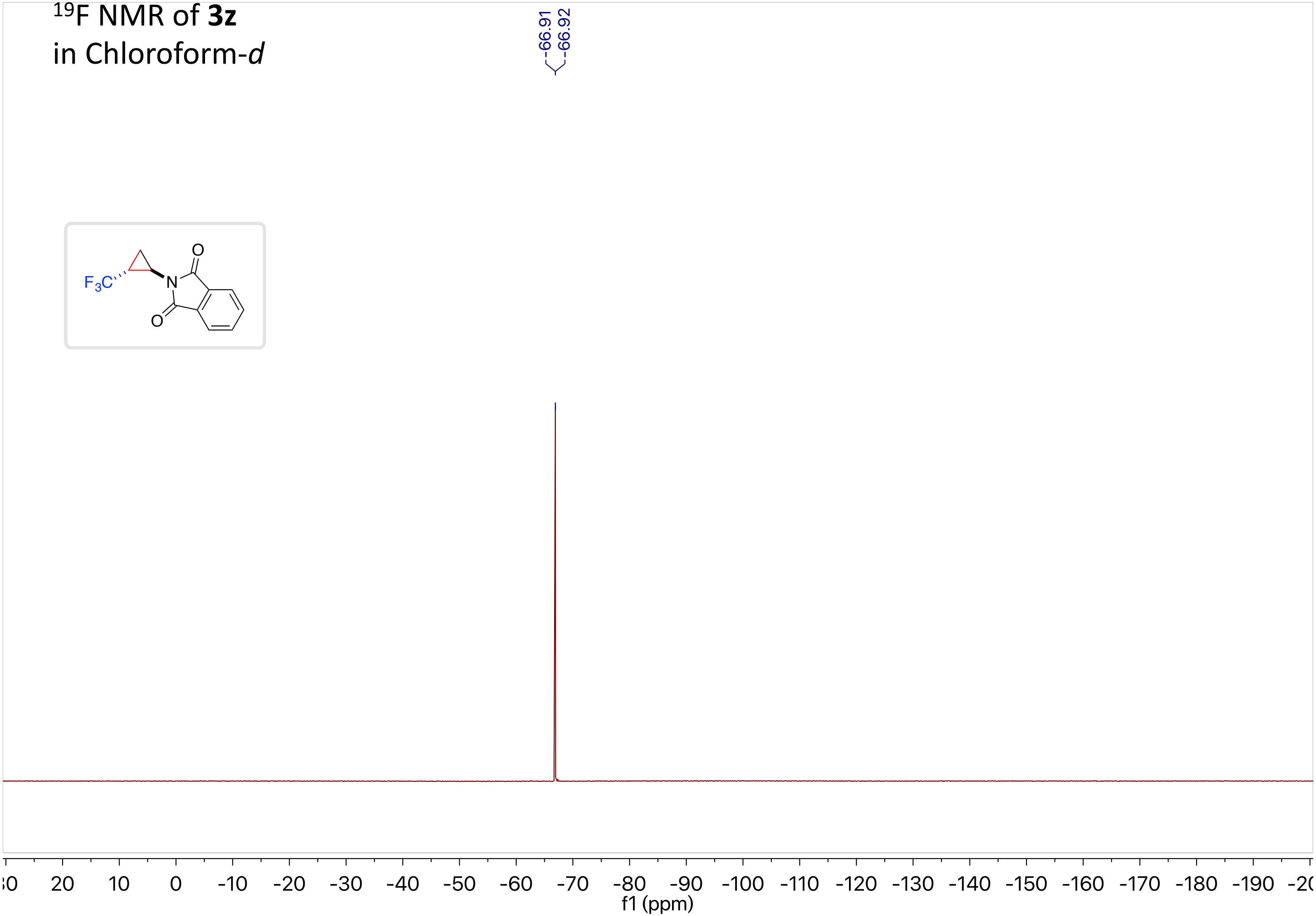
^{1}H NMR of **3z**
in Chloroform-*d*

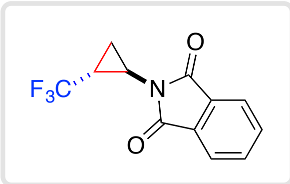


^{13}C NMR of **3z** in Chloroform-*d*

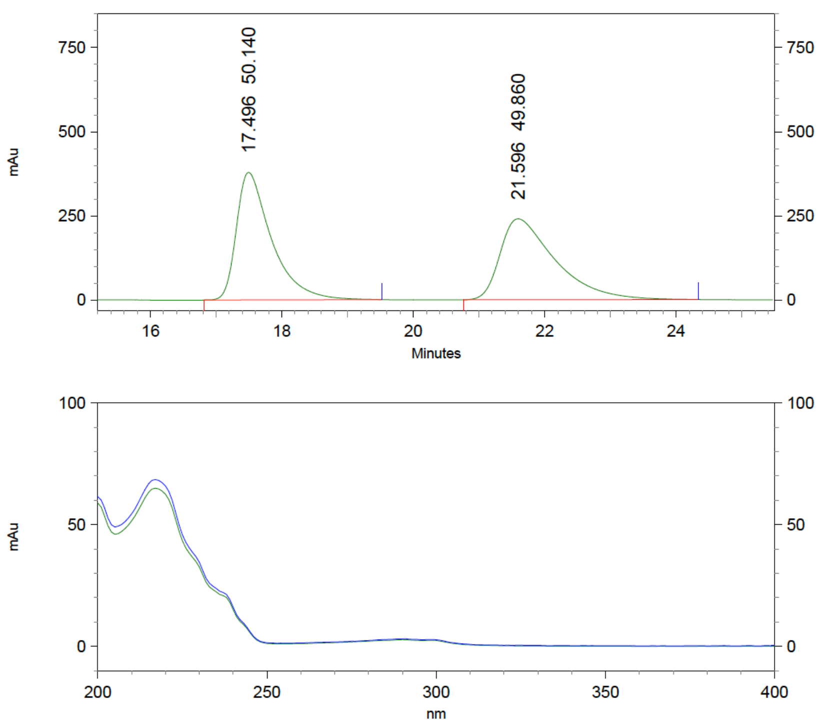


^{19}F NMR of **3z**
in Chloroform-*d*



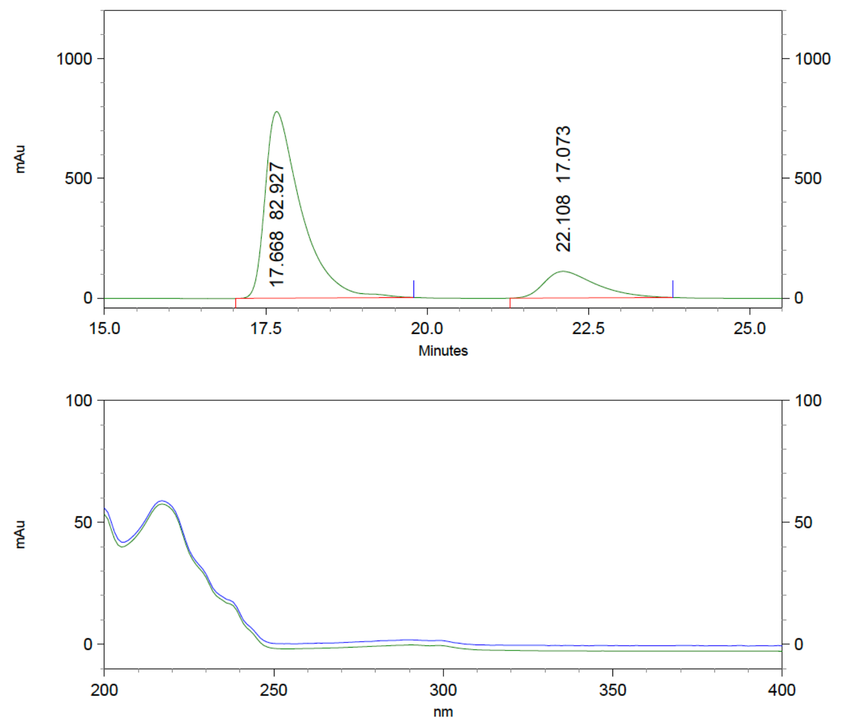


HPLC of **3z**



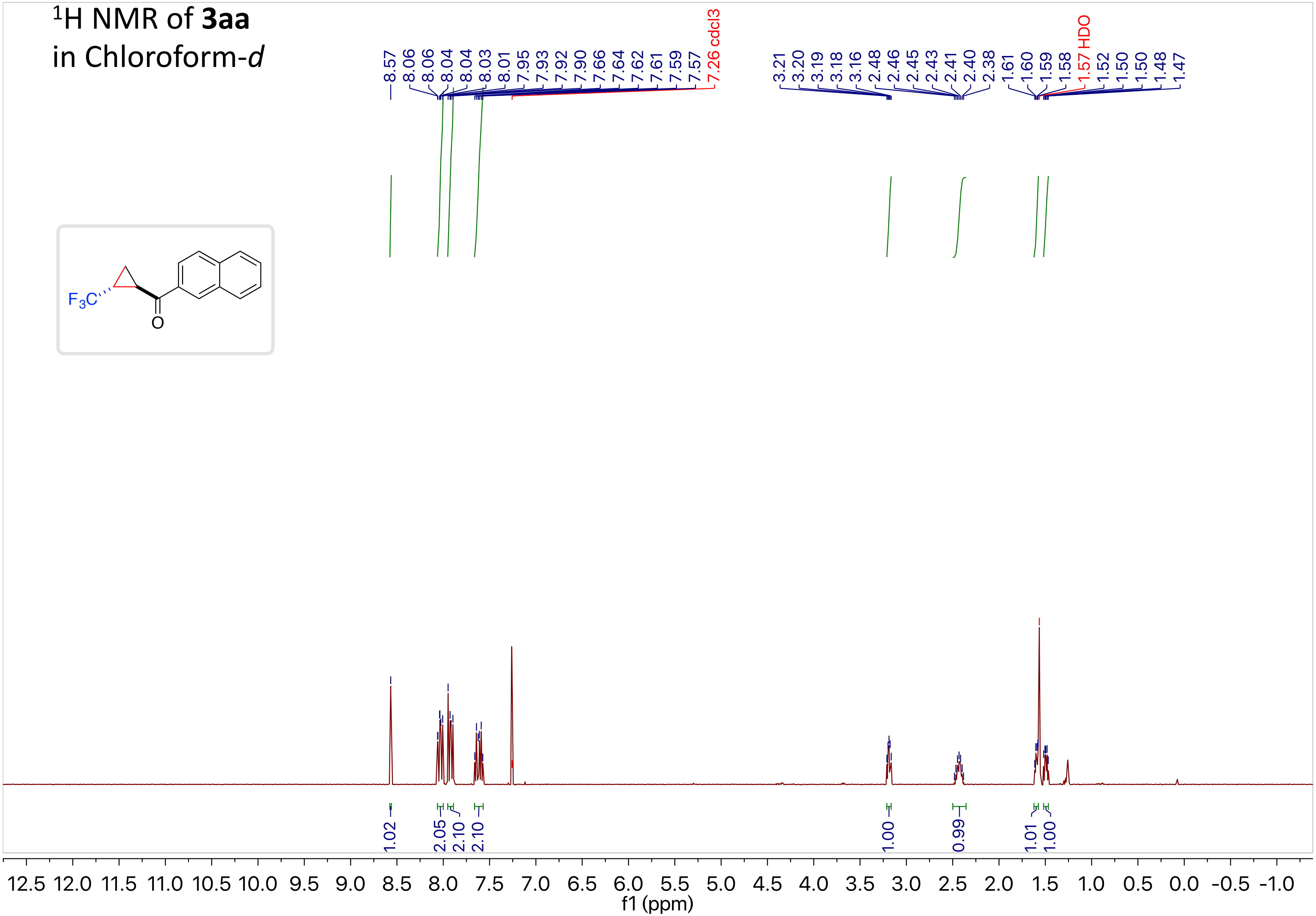
4: 219 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	17.496	50.140
2	21.596	49.860
Totals		100.000



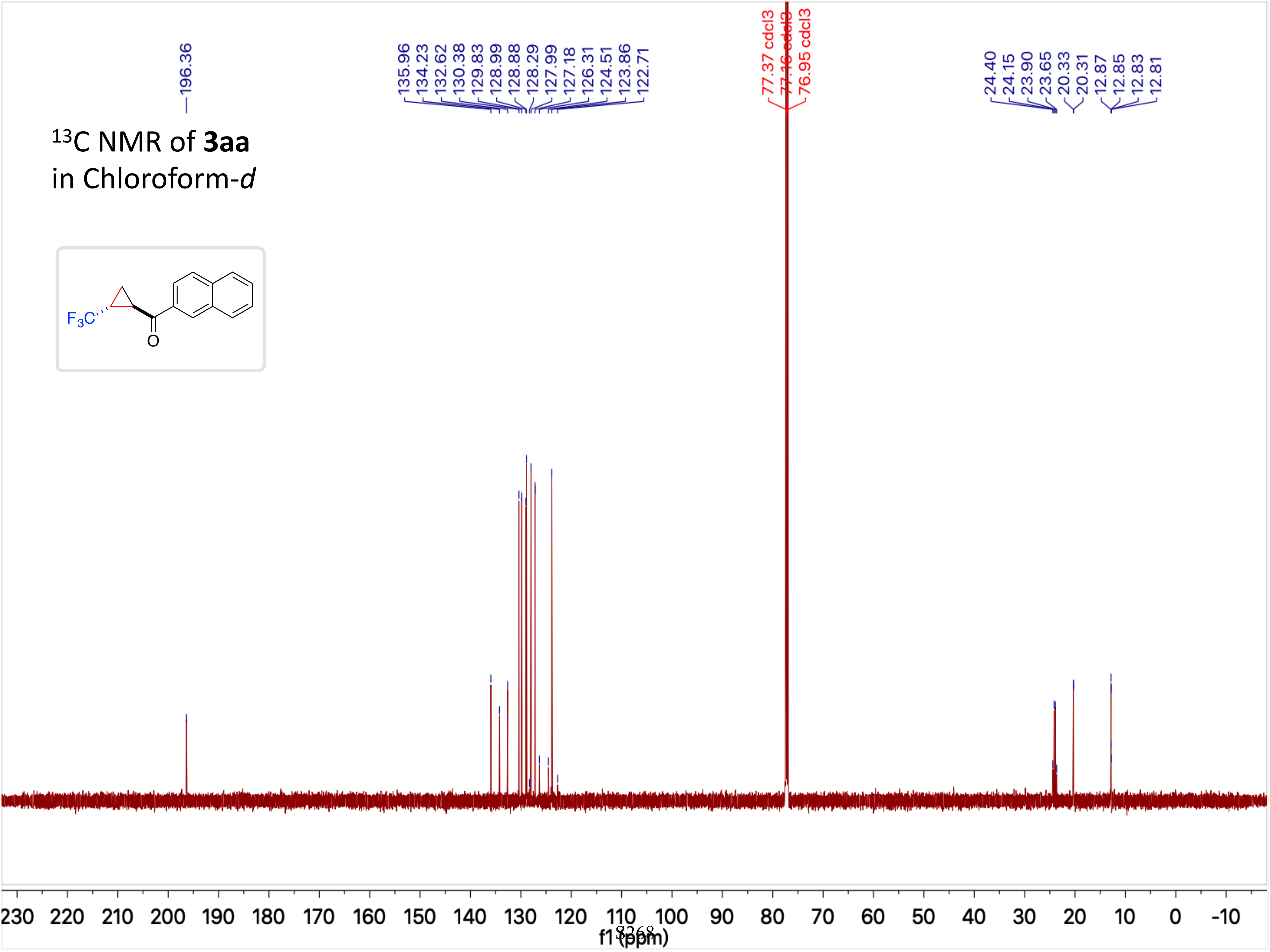
4: 220 nm, 4
nm Results

Pk #	Retention Time	Area Percent
1	17.668	82.927
2	22.108	17.073
Totals		100.000

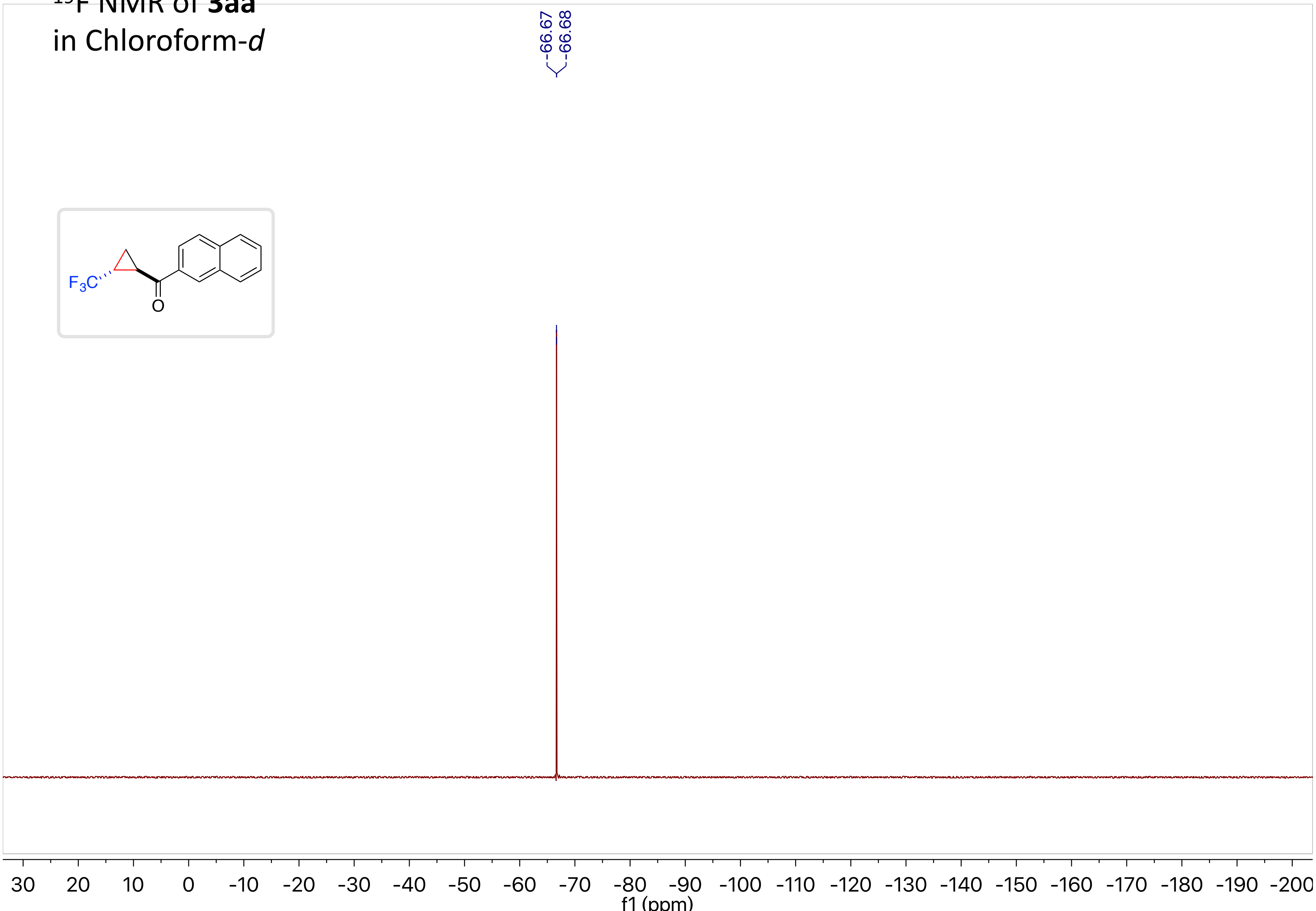


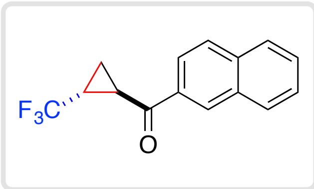
1H NMR of 3aa
in Chloroform-d
F3C
O
8.57 8.06 8.06 8.04 8.04 8.03 8.01 7.95 7.93 7.92 7.90 7.66 7.64 7.62 7.61 7.59 7.57 7.26 cdcl3
3.21 3.20 3.19 3.18 3.16 2.48 2.46 2.45 2.43 2.41 2.40 2.38 1.61 1.60 1.59 1.58 1.57 HDO 1.52 1.50 1.50 1.48 1.47
1.02 2.05 2.10 2.10 1.00 0.99 1.01 1.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

^{13}C NMR of **3aa** in Chloroform-*d*

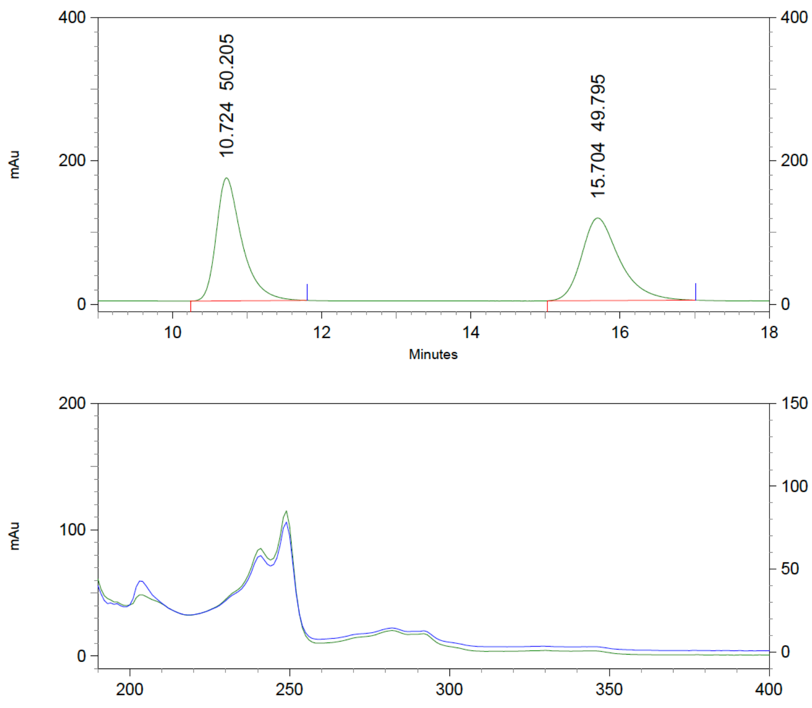


[19]F NMR of **3aa**
in Chloroform-*d*





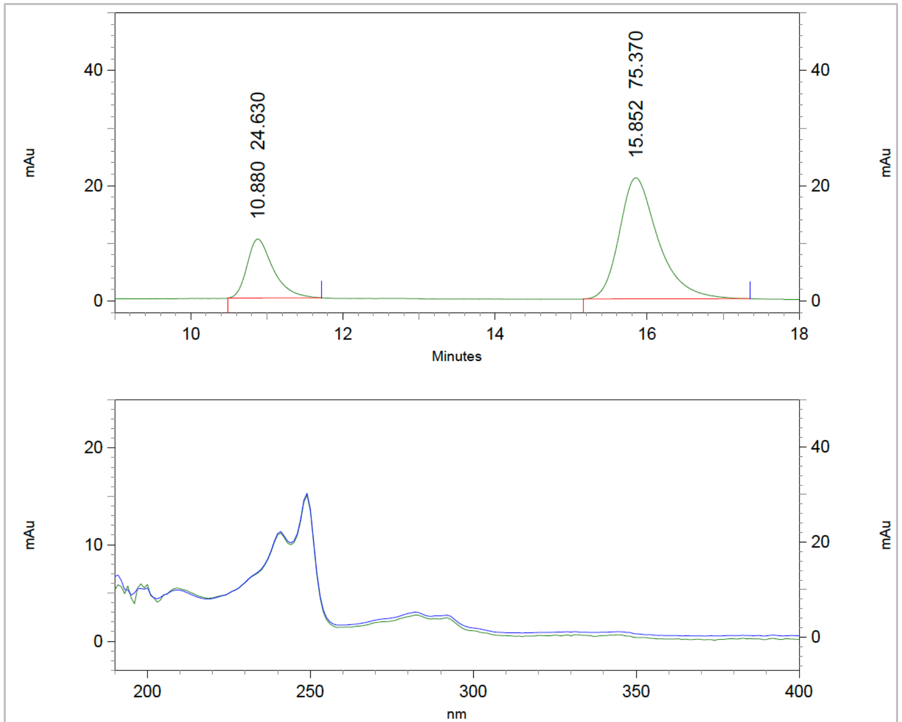
HPLC of **3aa**



4: 246 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	10.724	50.205
2	15.704	49.795
Totals		100.000

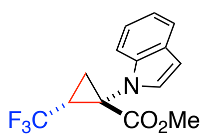
3



2: 245 nm, 4 nm Results

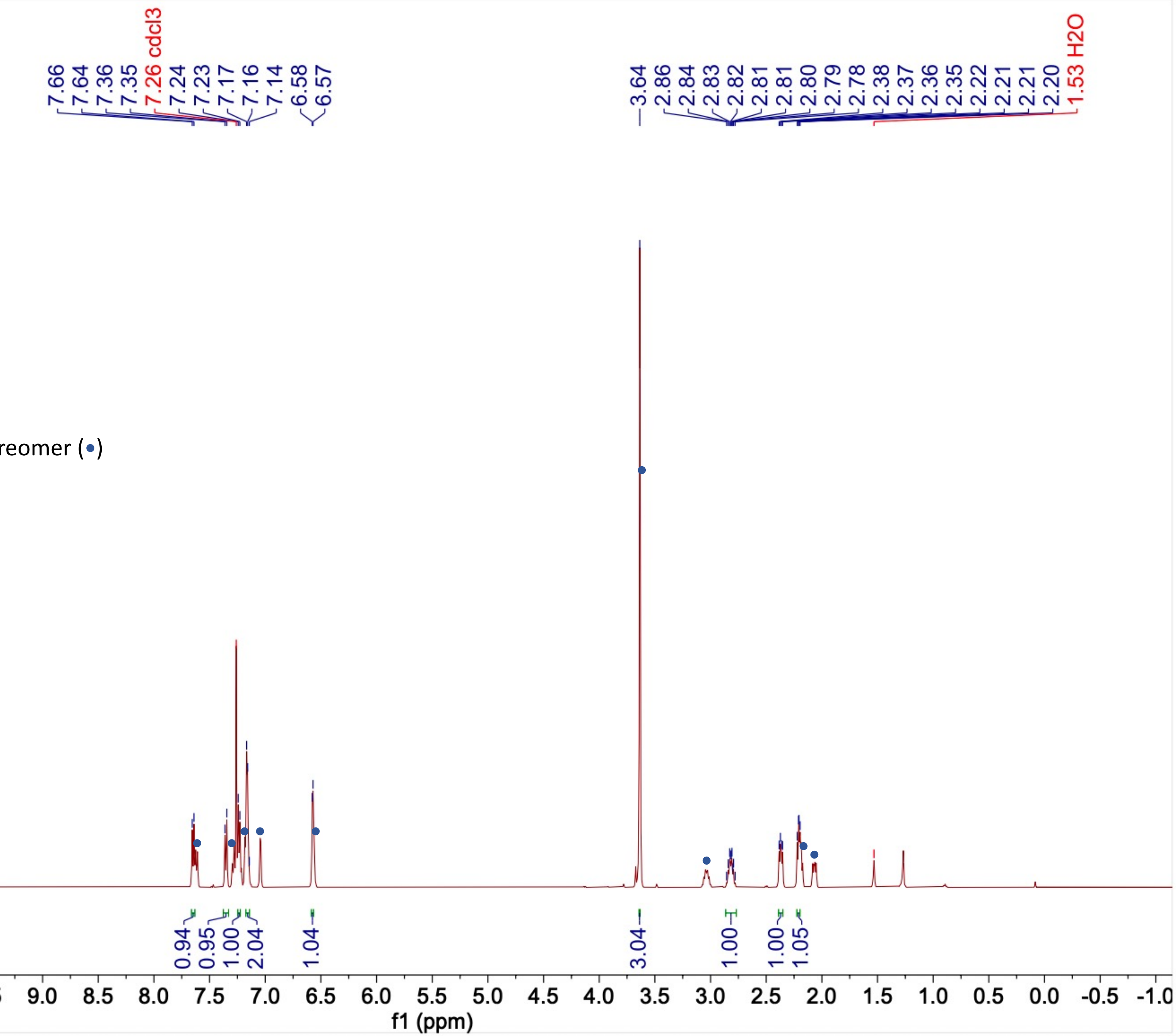
Pk #	Retention Time	Area Percent
1	10.880	24.630
2	15.852	75.370
Totals		100.000

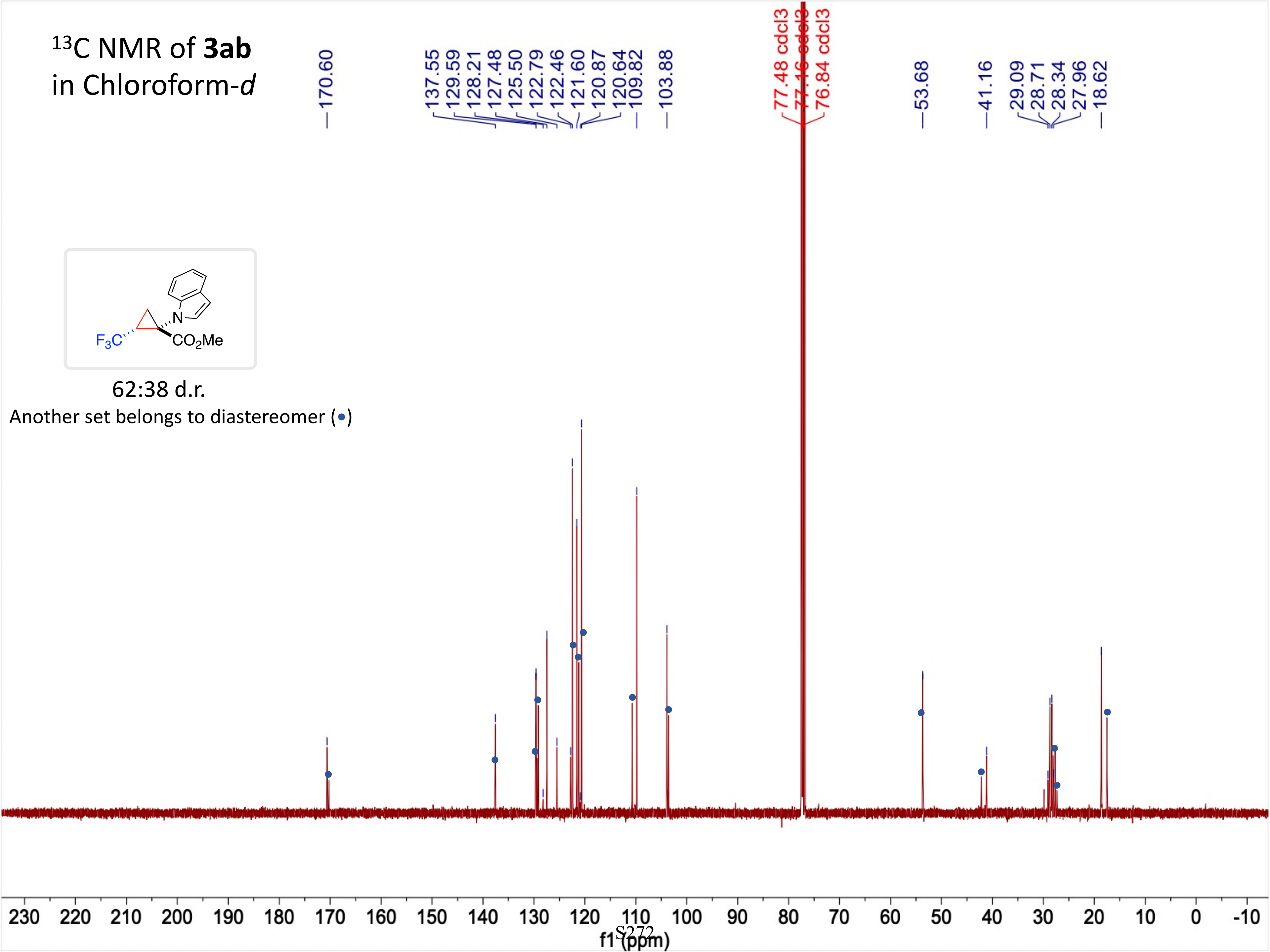
^{1}H NMR of **3ab** in Chloroform-*d*



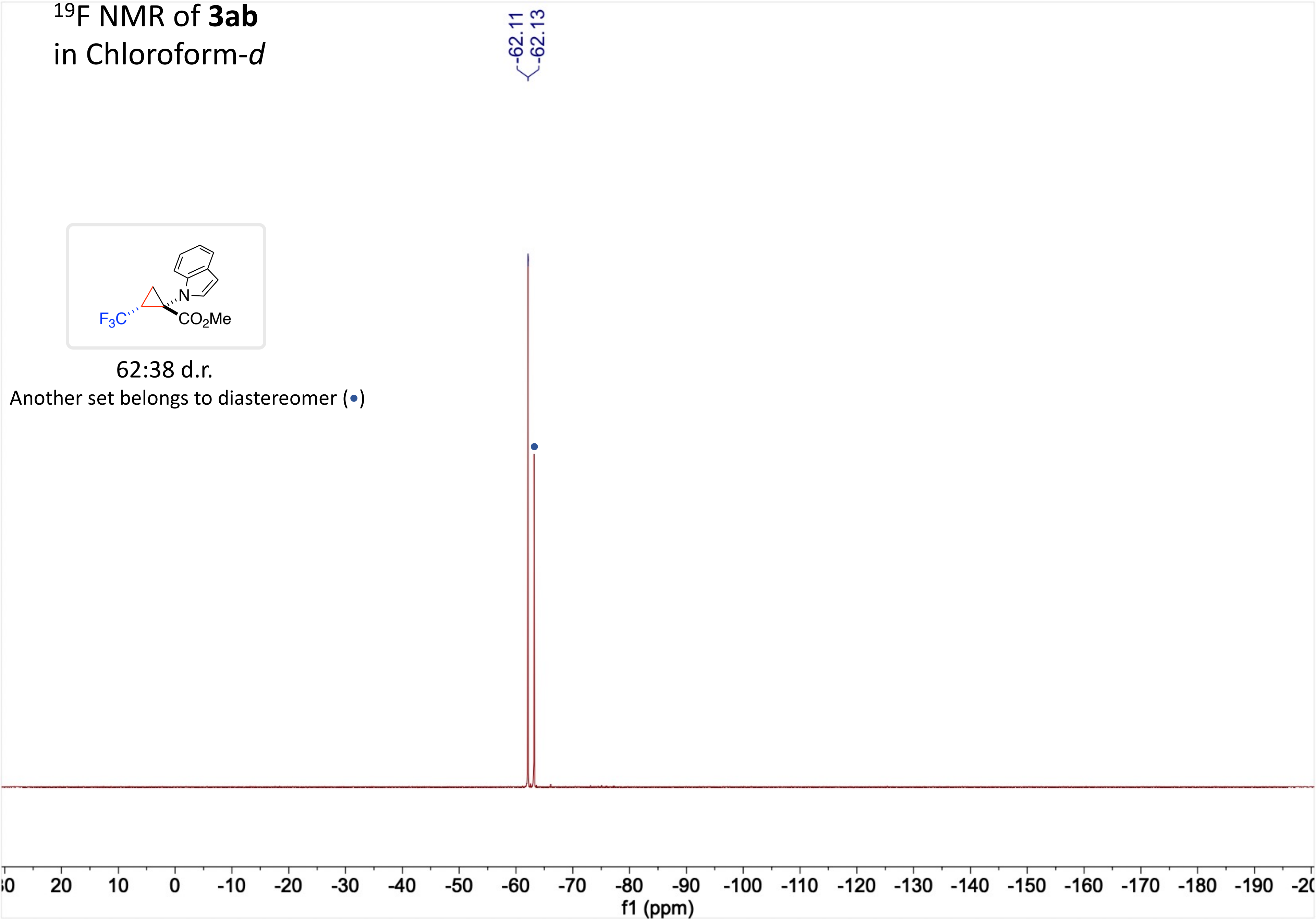
62:38 d.r.

Another set belongs to diastereomer (•)



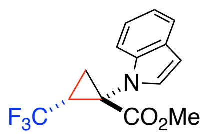


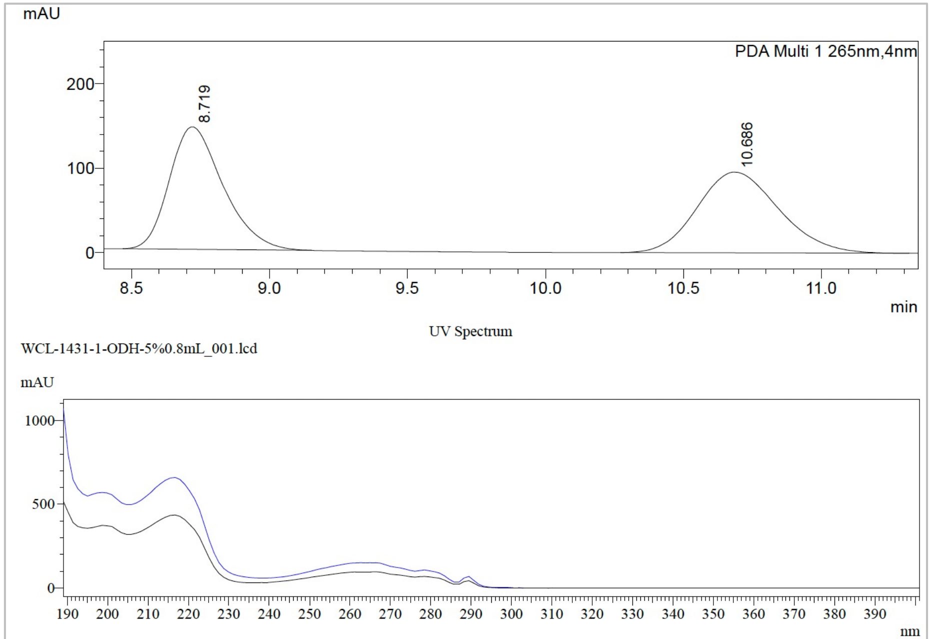
^{13}C NMR of **3ab**
in Chloroform-*d*
170.60
137.55
129.59
128.21
127.48
125.50
122.79
122.46
121.60
120.87
120.64
109.82
103.88
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
53.68
41.16
29.09
28.71
28.34
27.96
18.62
N
F3C
CO2Me
62:38 d.r.
Another set belongs to diastereomer (•)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



19F NMR of 3ab
in Chloroform-d
-62.11
-62.13
F3C
N
CO2Me
62:38 d.r.
Another set belongs to diastereomer (•)
f1 (ppm)

HPLC of **3ab**

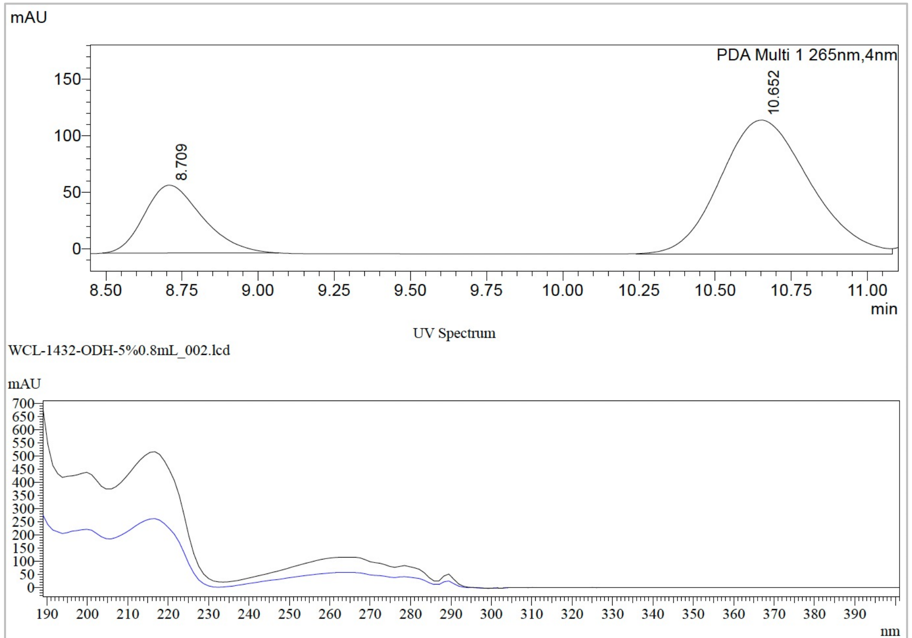




Peak Table

PDA Ch1 265nm

Peak#	Ret. Time	Area%
1	8.719	49.964
2	10.686	50.036
Total		100.000

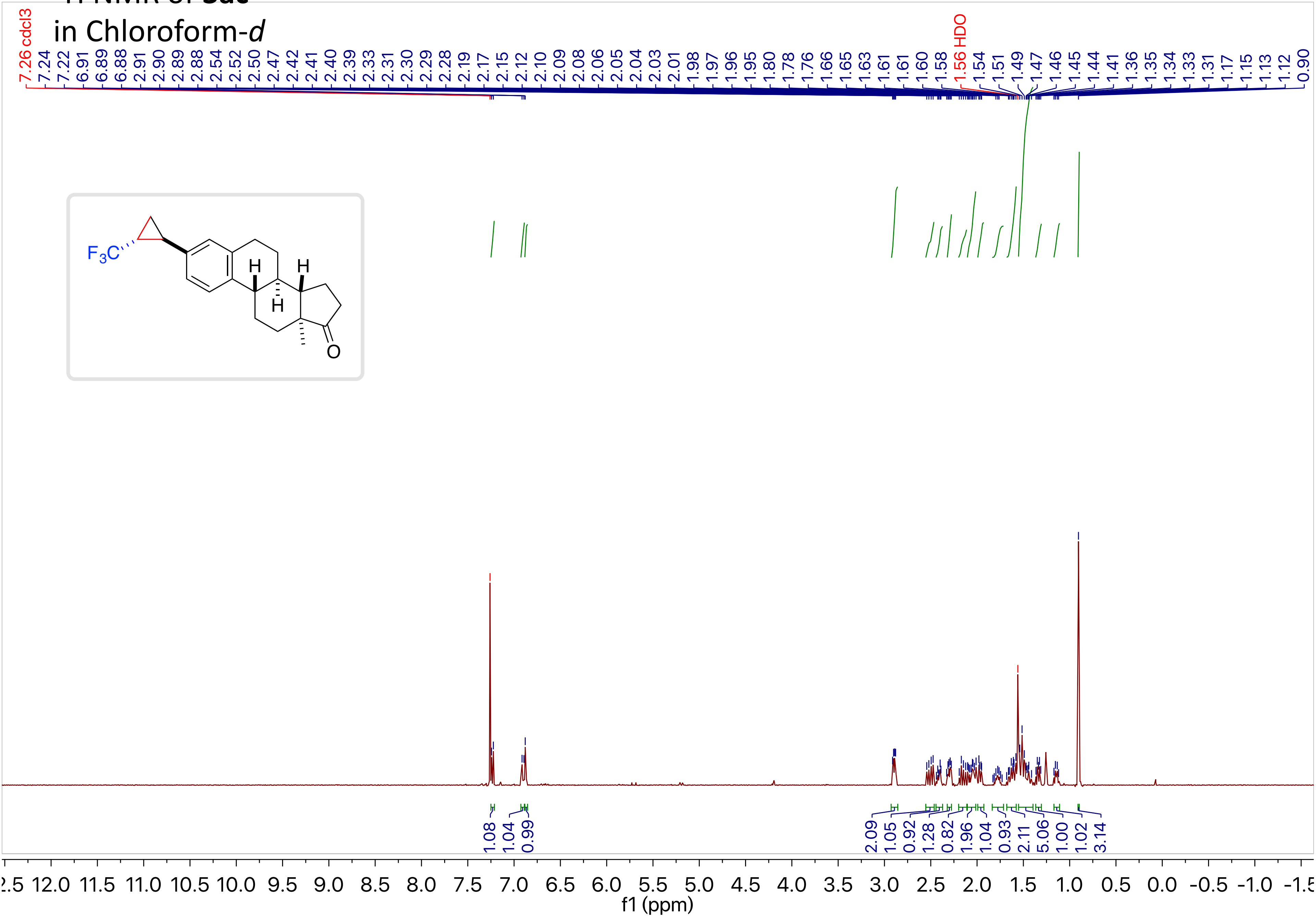


Peak Table

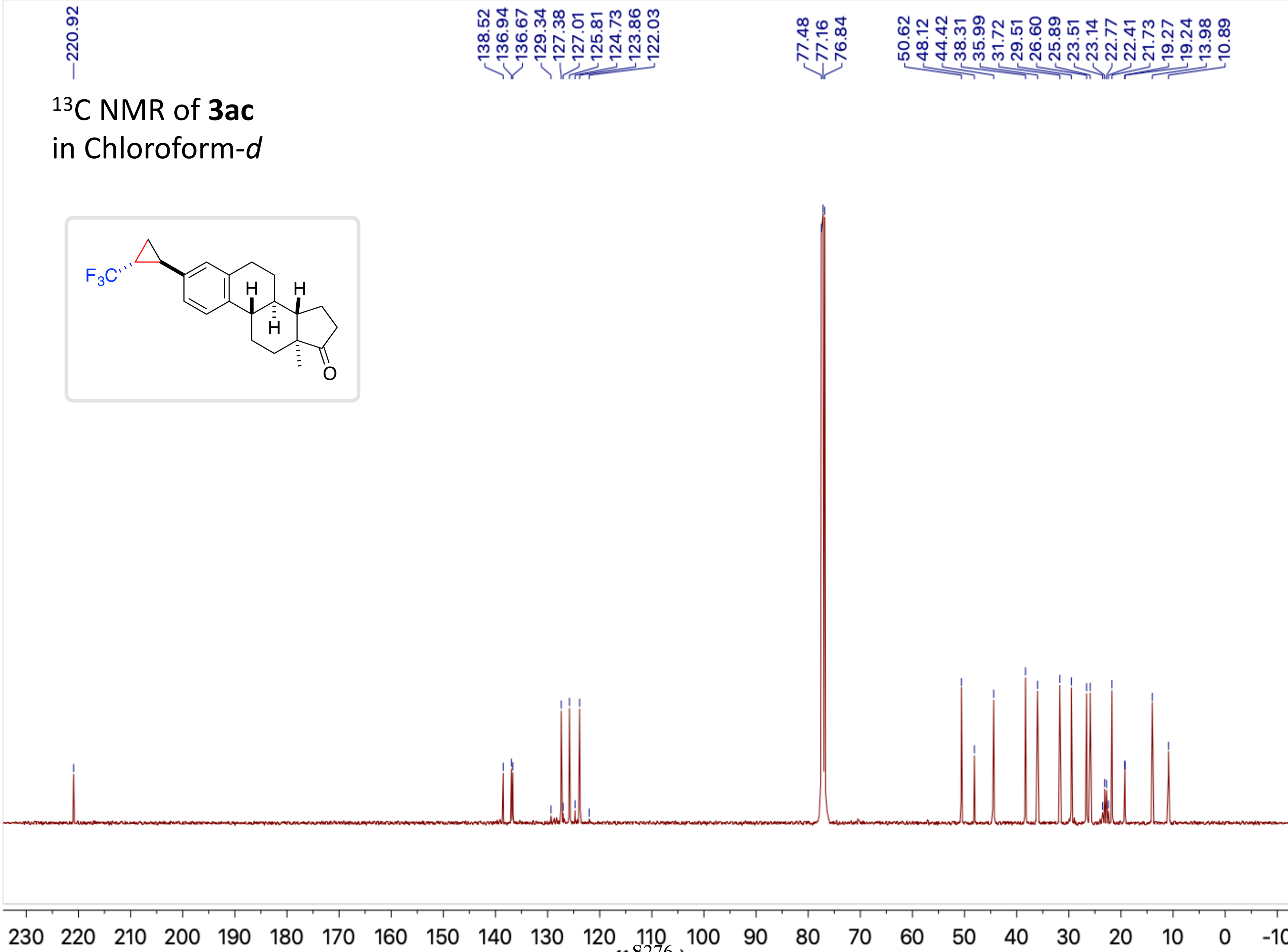
PDA Ch1 265nm

Peak#	Ret. Time	Area%
1	8.709	24.850
2	10.652	75.150
Total		100.000

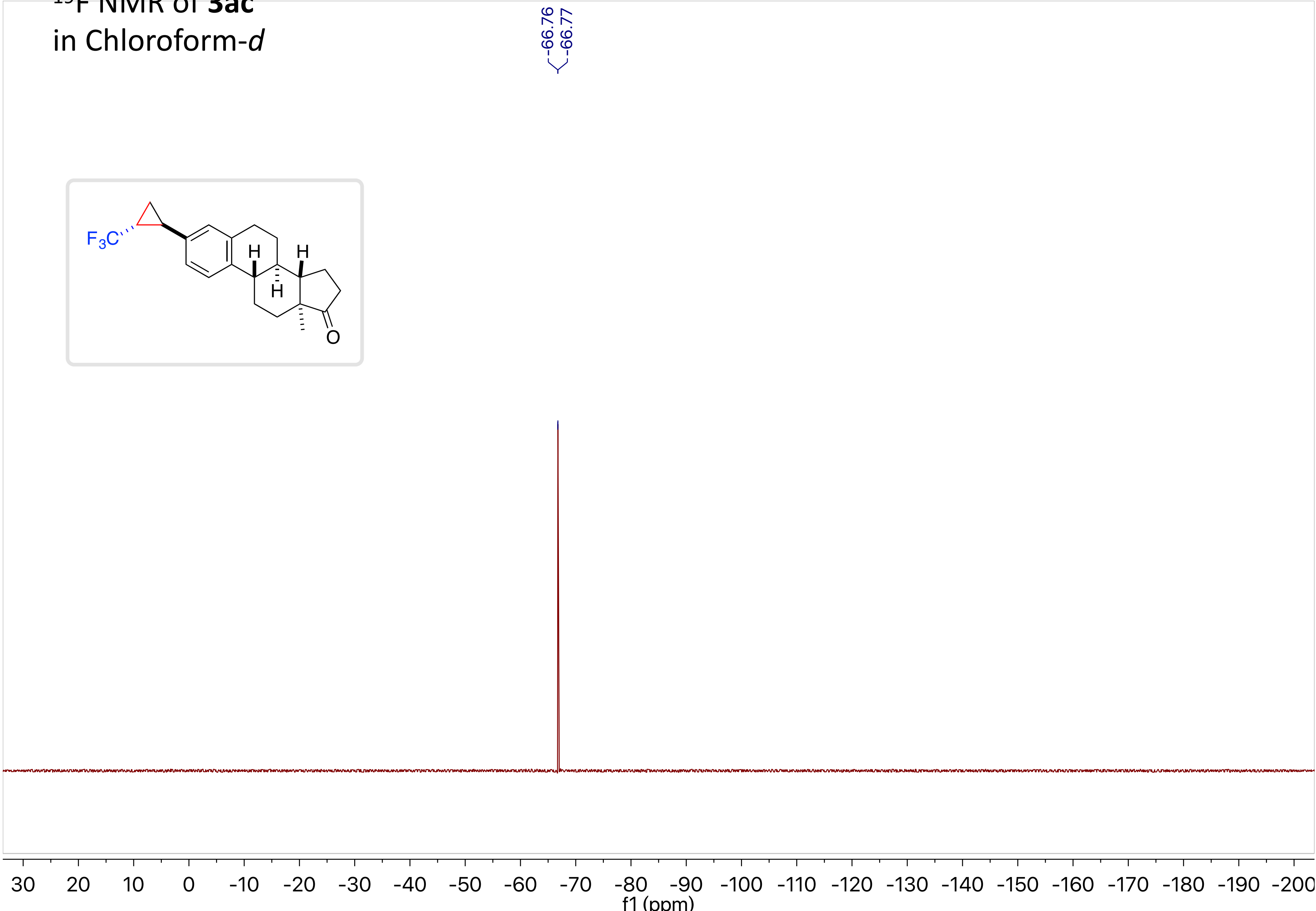
[1]H NMR of **3ac**
in Chloroform-*d*



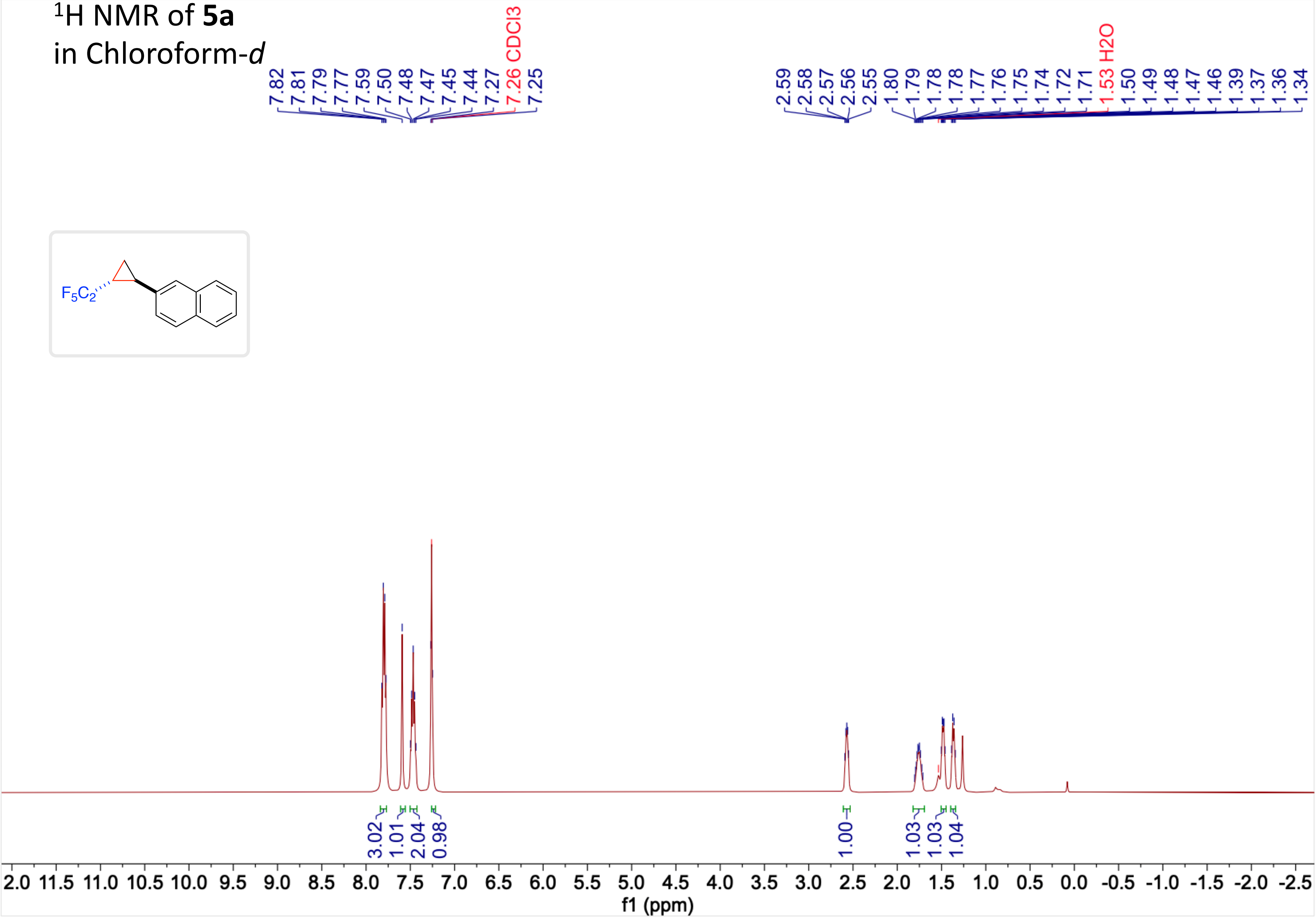
^{13}C NMR of **3ac**
in Chloroform-*d*

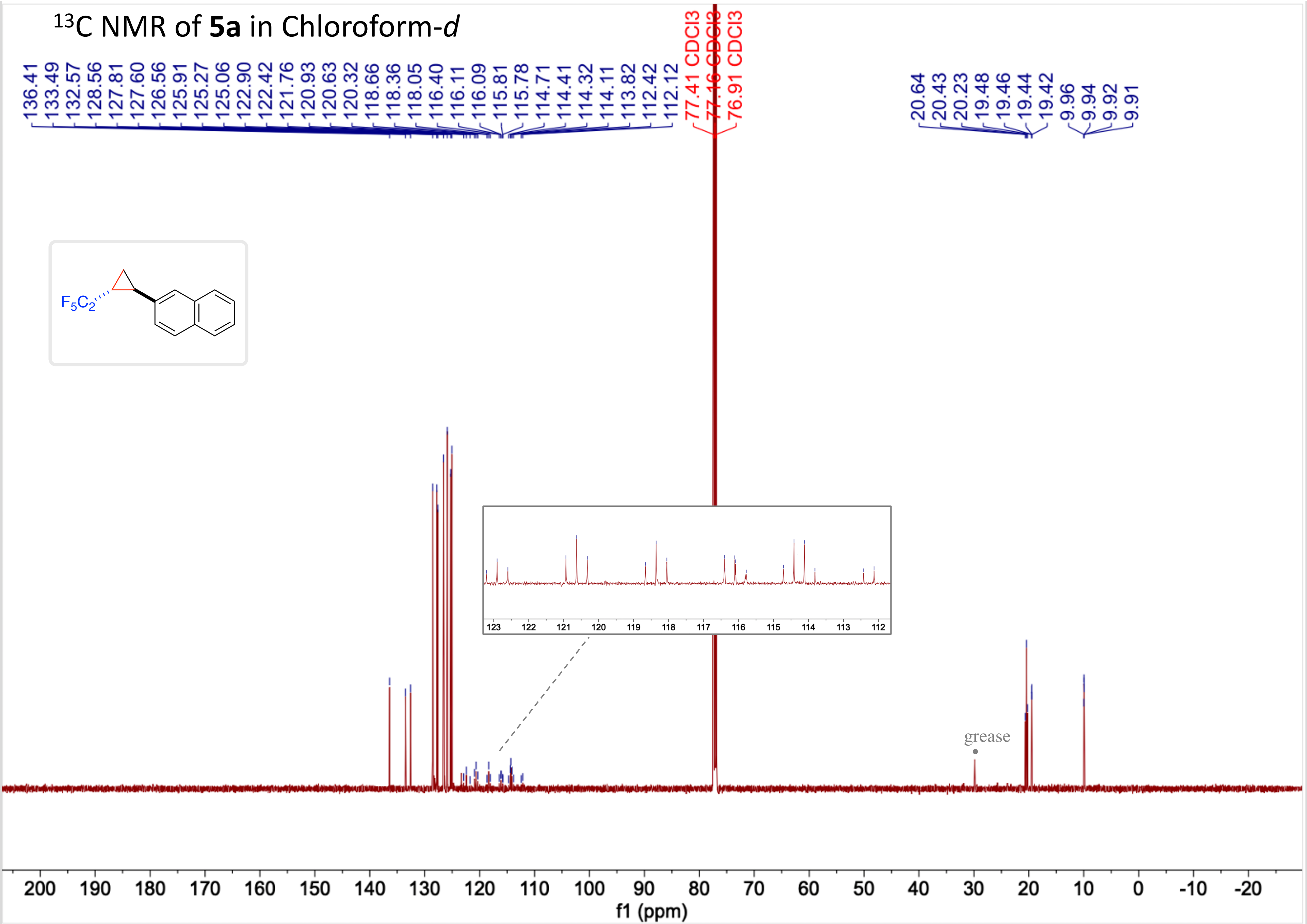


^{19}F NMR of **3ac**
in Chloroform-*d*



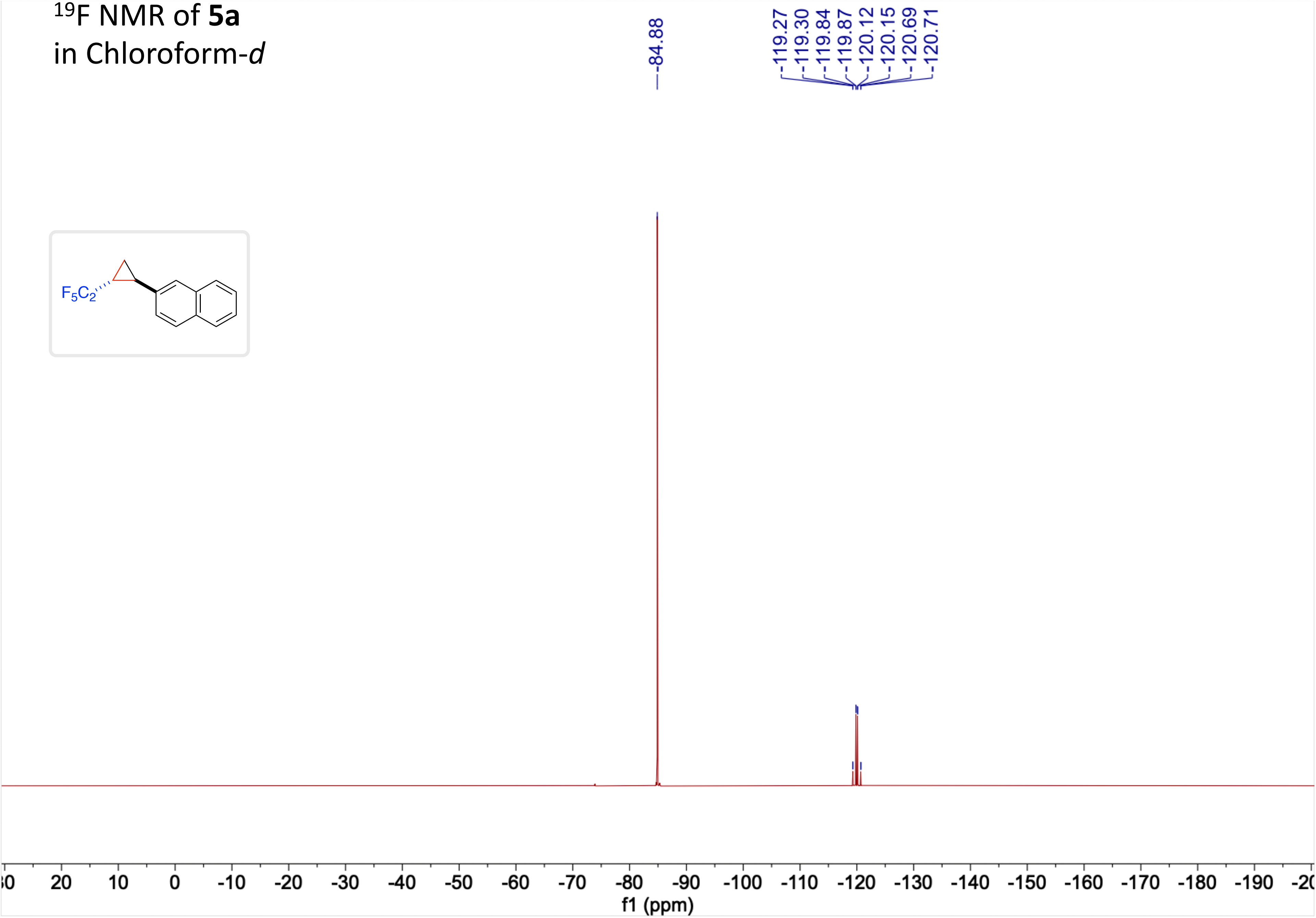
[1]H NMR of **5a** in Chloroform-*d*

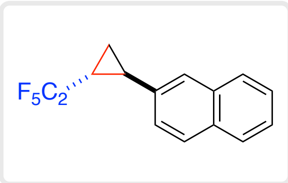




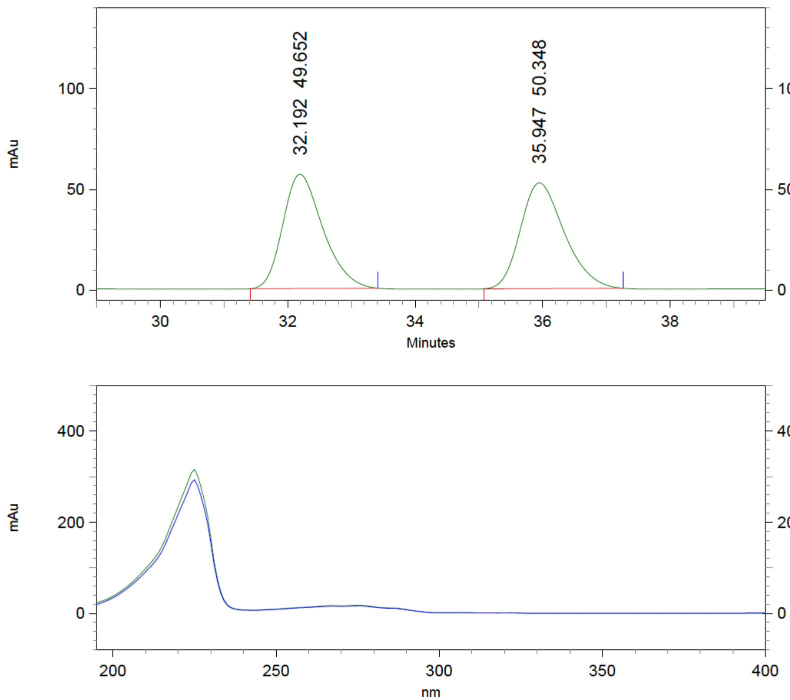
13C NMR of 5a in Chloroform-d
136.41
133.49
132.57
128.56
127.81
127.60
126.56
125.91
125.27
125.06
122.90
122.42
121.76
120.93
120.63
120.32
118.66
118.36
118.05
116.40
116.11
116.09
115.81
115.78
114.71
114.41
114.32
114.11
113.82
112.42
112.12
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
20.64
20.43
20.23
19.48
19.46
19.44
19.42
9.96
9.94
9.92
9.91
F5C2
grease
f1 (ppm)

^{19}F NMR of **5a**
in Chloroform-*d*



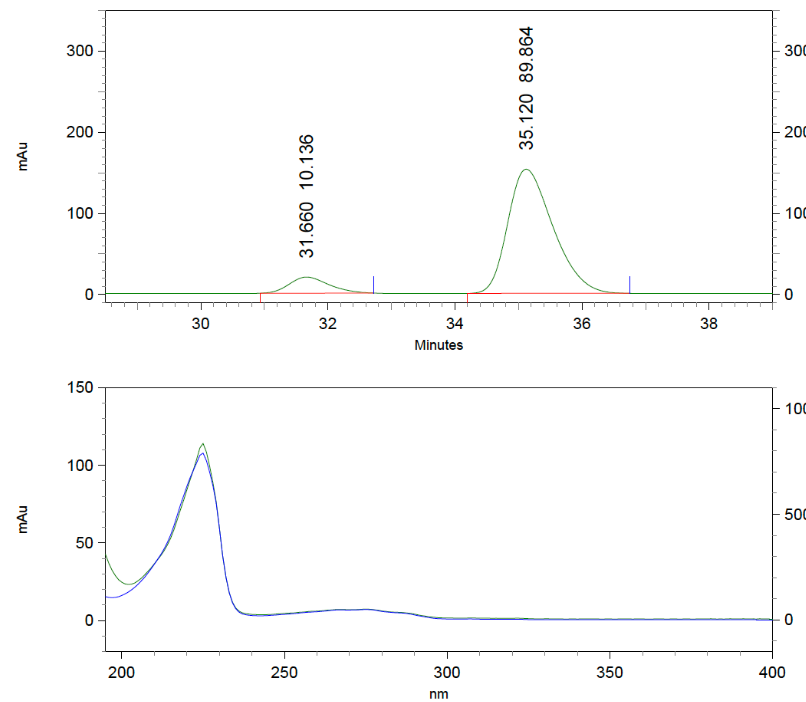


HPLC of **5a**



4: 233 nm, 4
nm Results

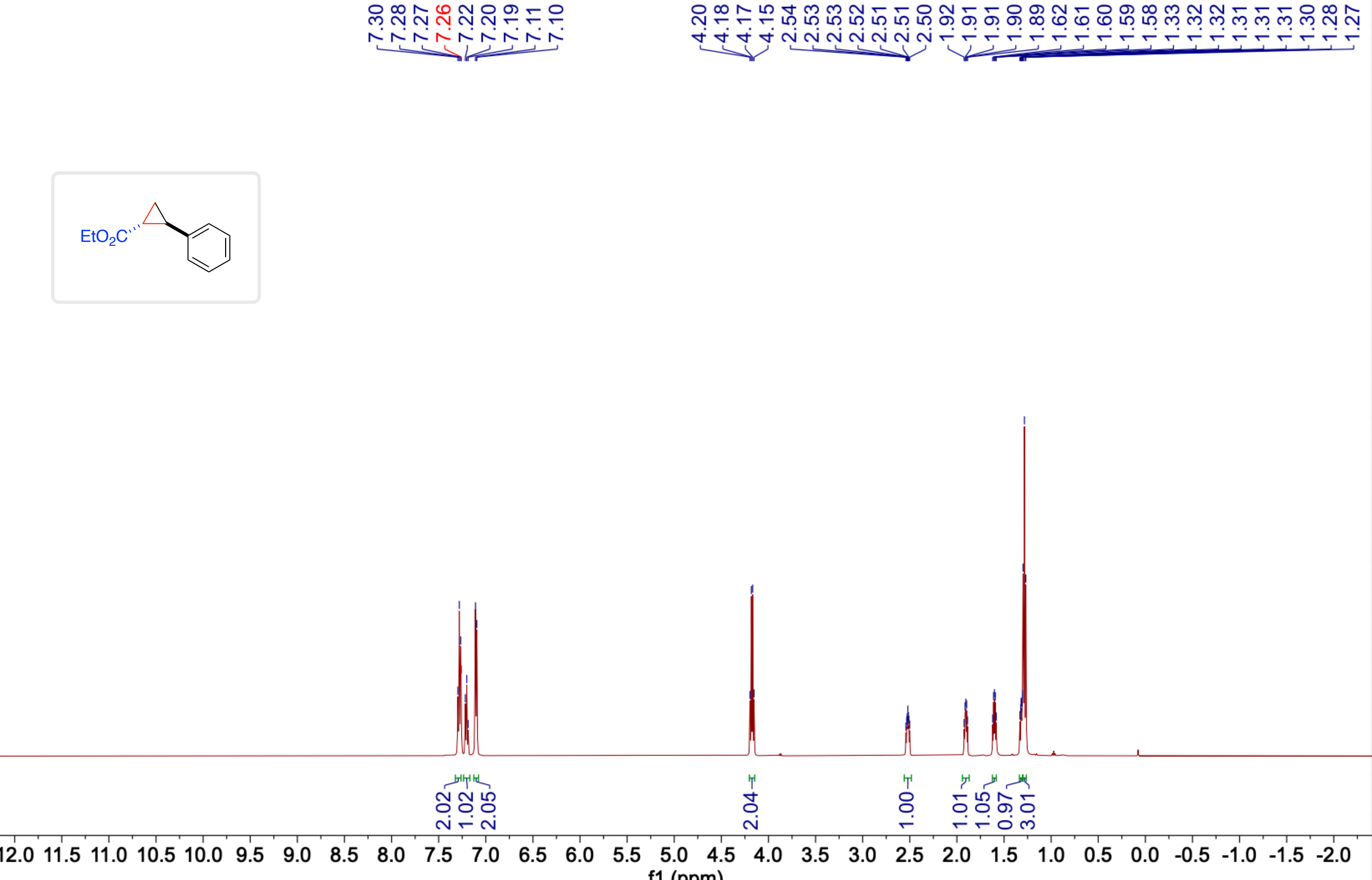
Pk #	Retention Time	Area Percent
1	32.192	49.652
2	35.947	50.348
Totals		100.000



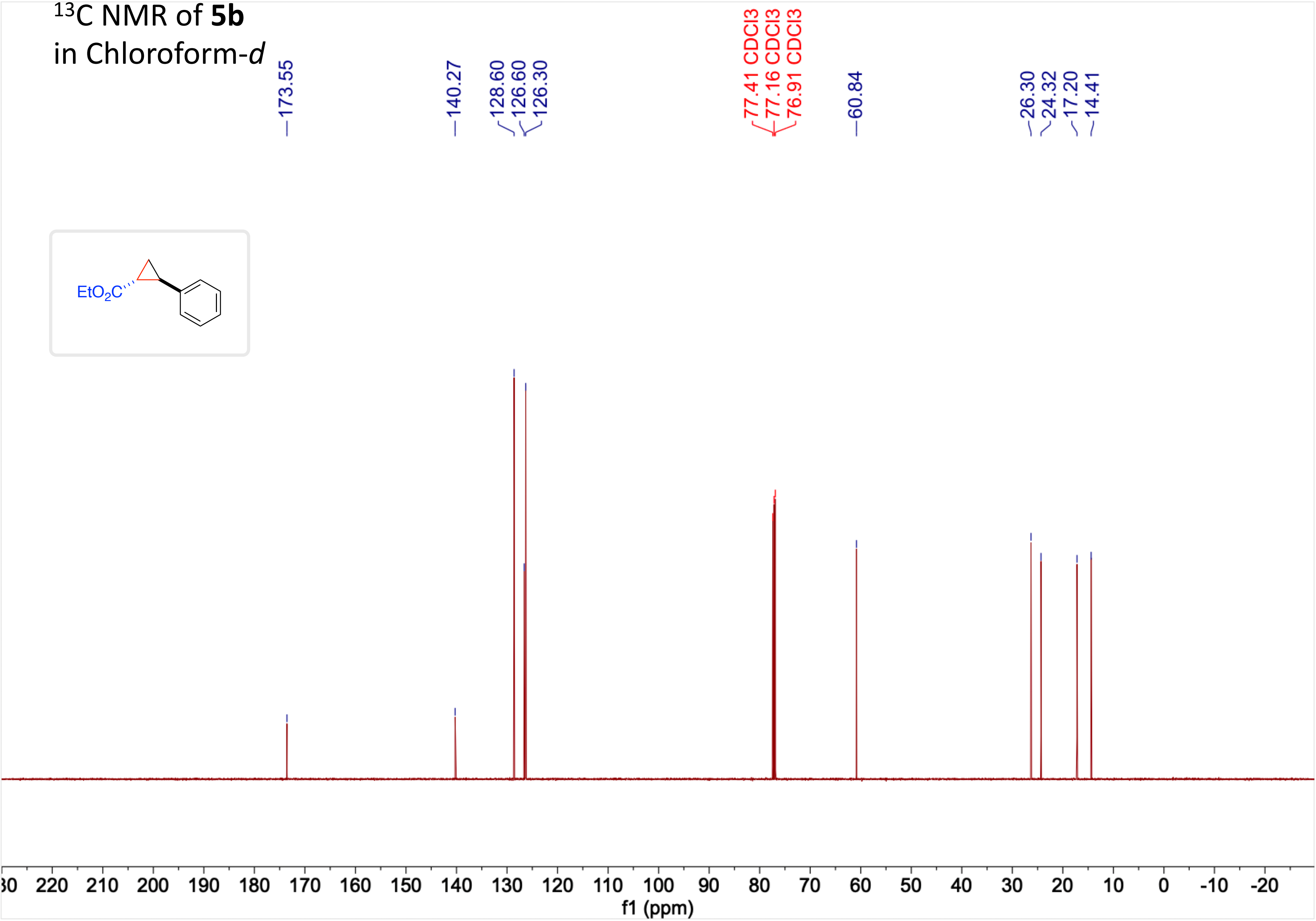
4: 233 nm, 4
nm Results

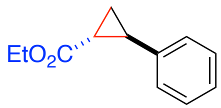
Pk #	Retention Time	Area Percent
1	31.660	10.136
2	35.120	89.864
Totals		100.000

^{1}H NMR of **5b** in Chloroform-*d*

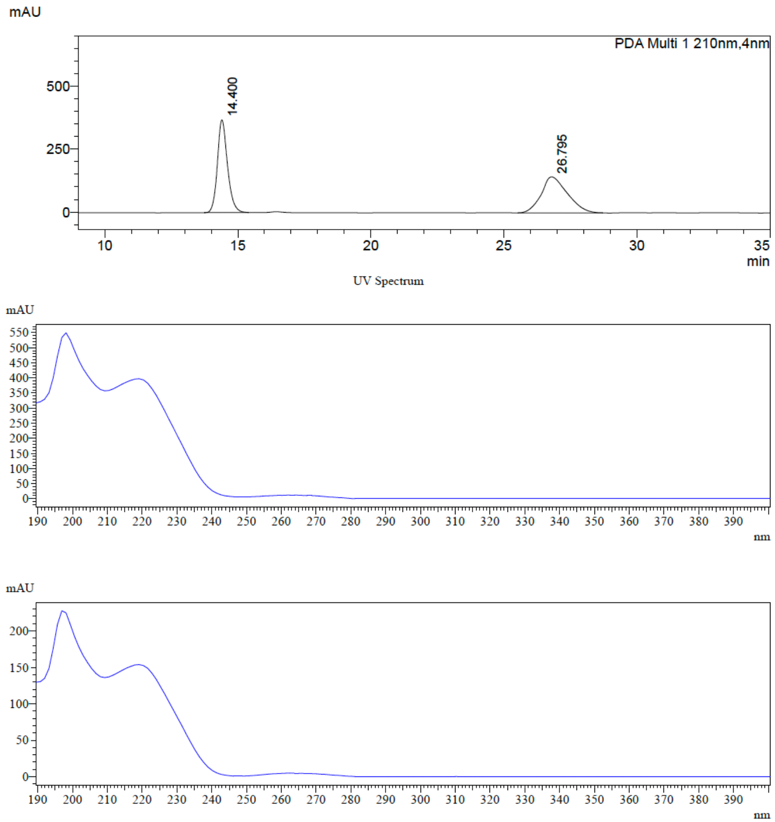


^{13}C NMR of **5b**
in Chloroform-*d*





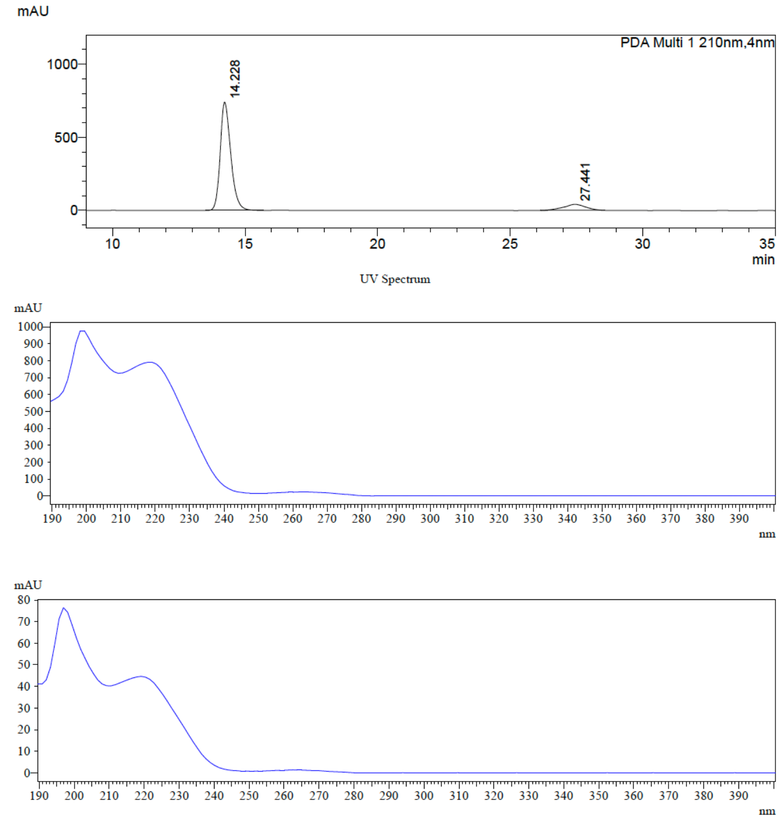
HPLC of **5b**



Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area%
1	14.400	49.685
2	26.795	50.315
Total		100.000

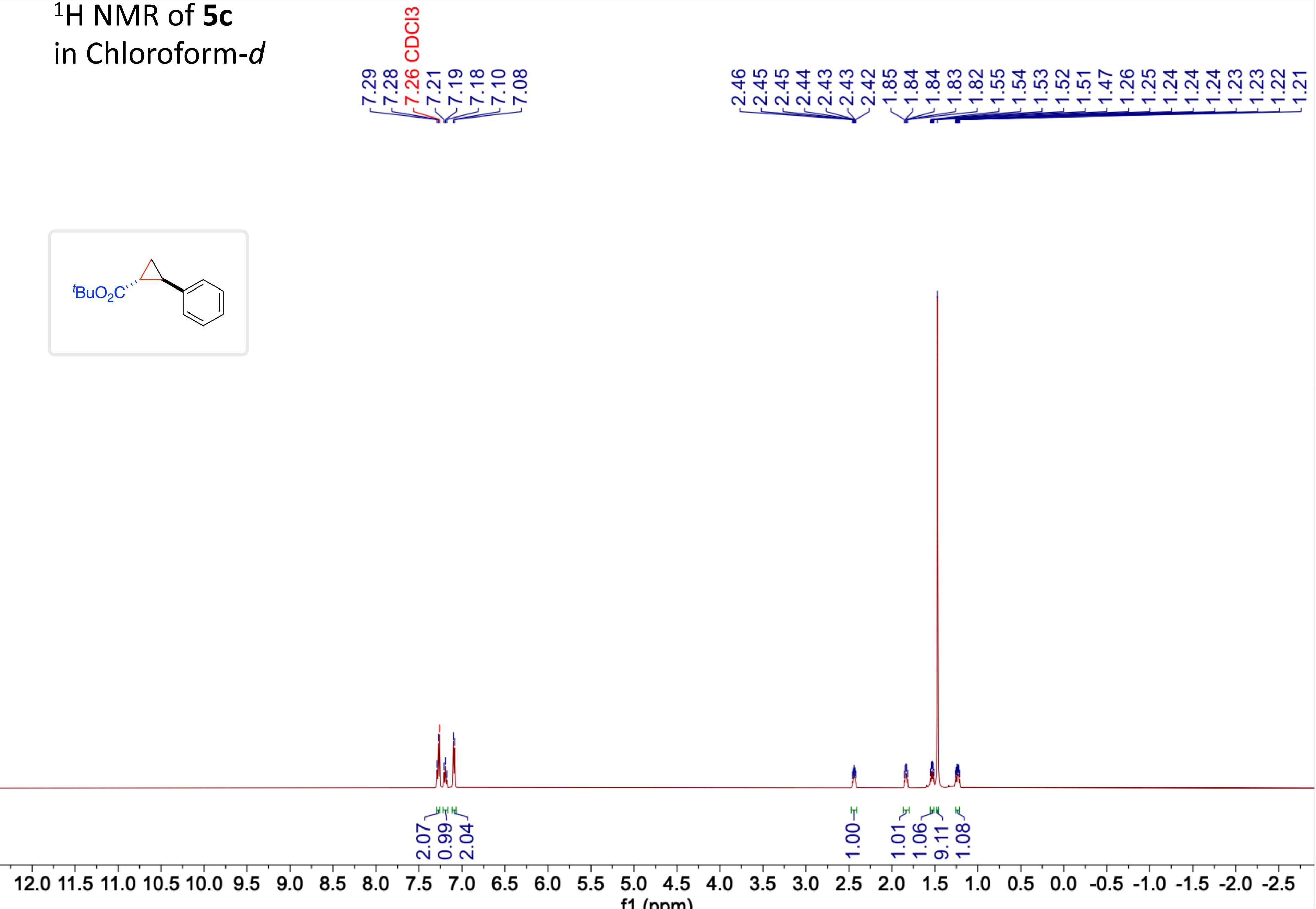


Peak Table

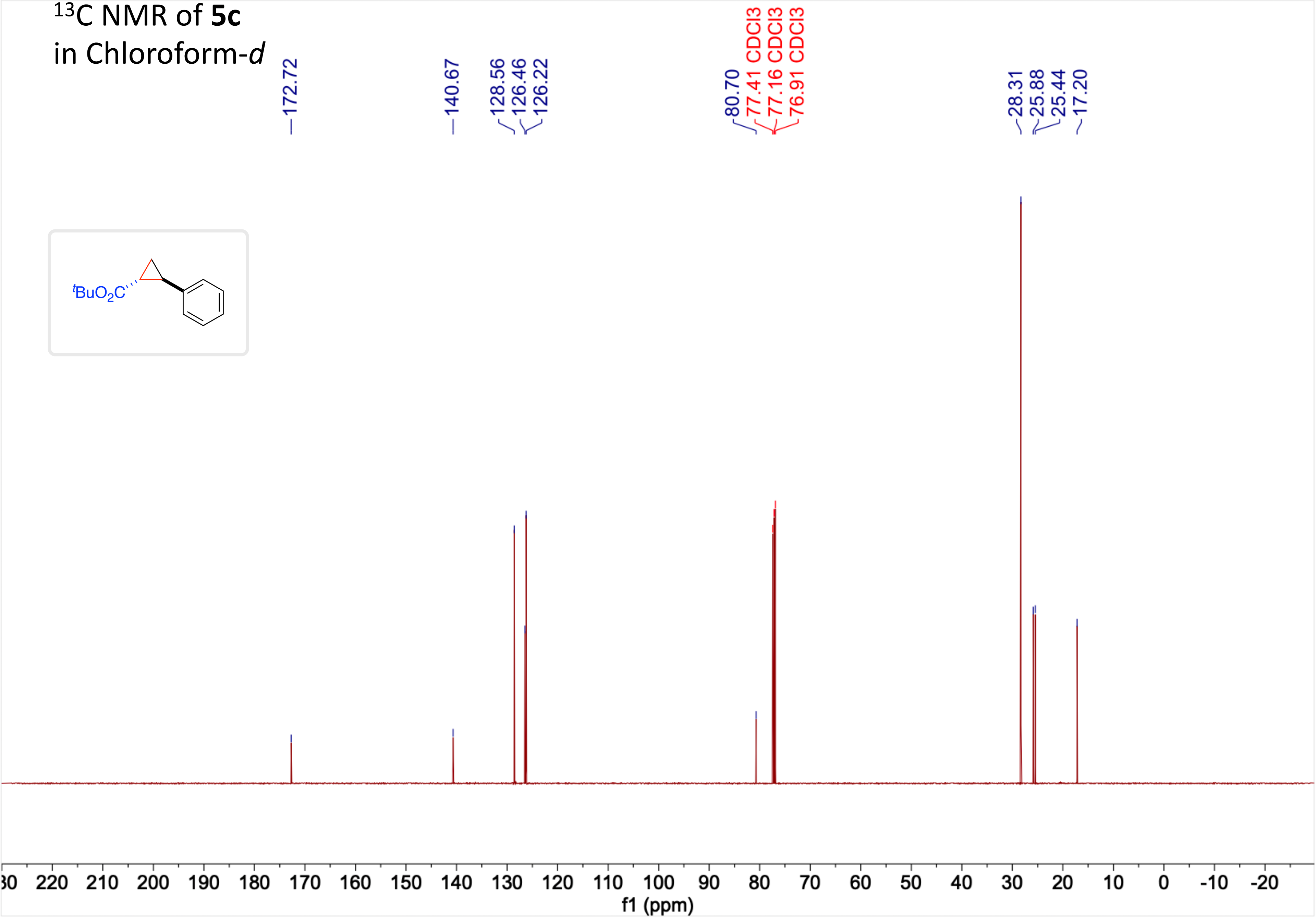
PDA Ch1 210nm

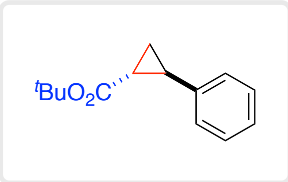
Peak#	Ret. Time	Area%
1	14.228	89.820
2	27.441	10.180
Total		100.000

^{1}H NMR of **5c**
in Chloroform-*d*

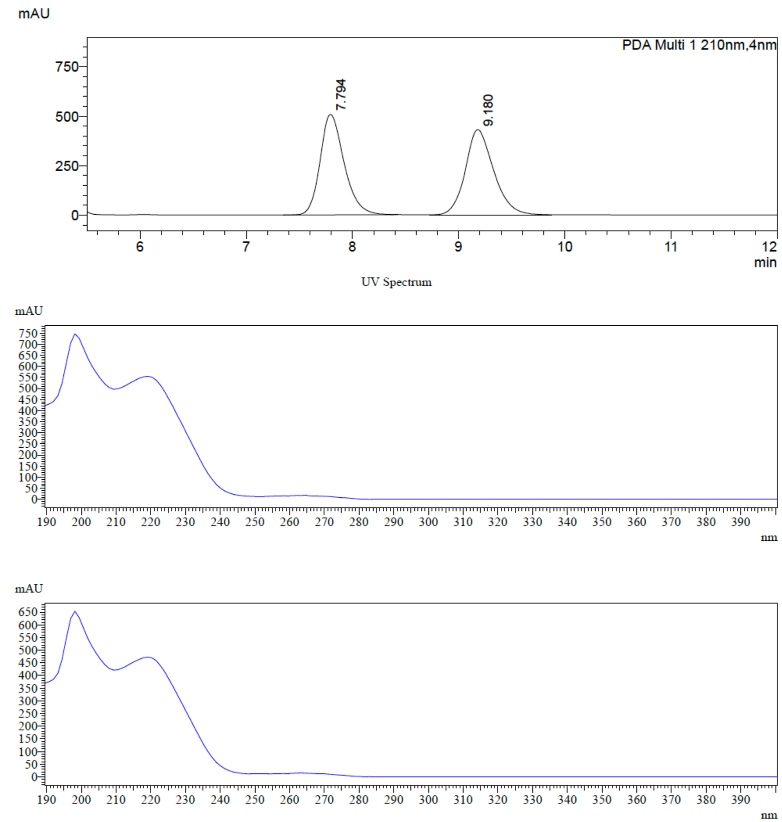


^{13}C NMR of **5c** in Chloroform-*d*





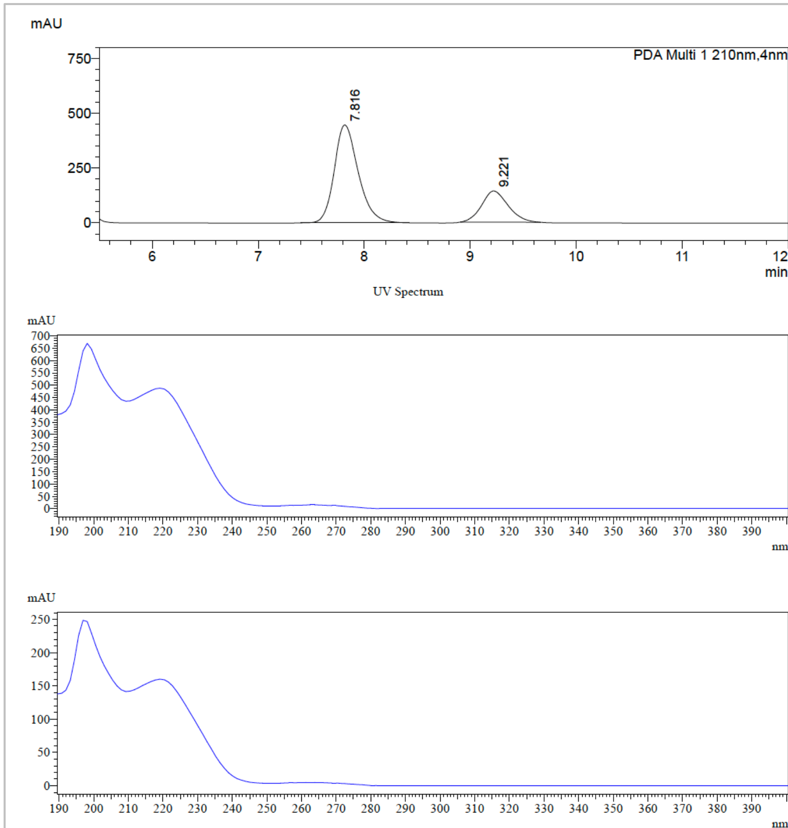
HPLC of **5c**



Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area%
1	7.794	50.043
2	9.180	49.957
Total		100.000

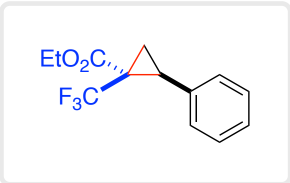


Peak Table

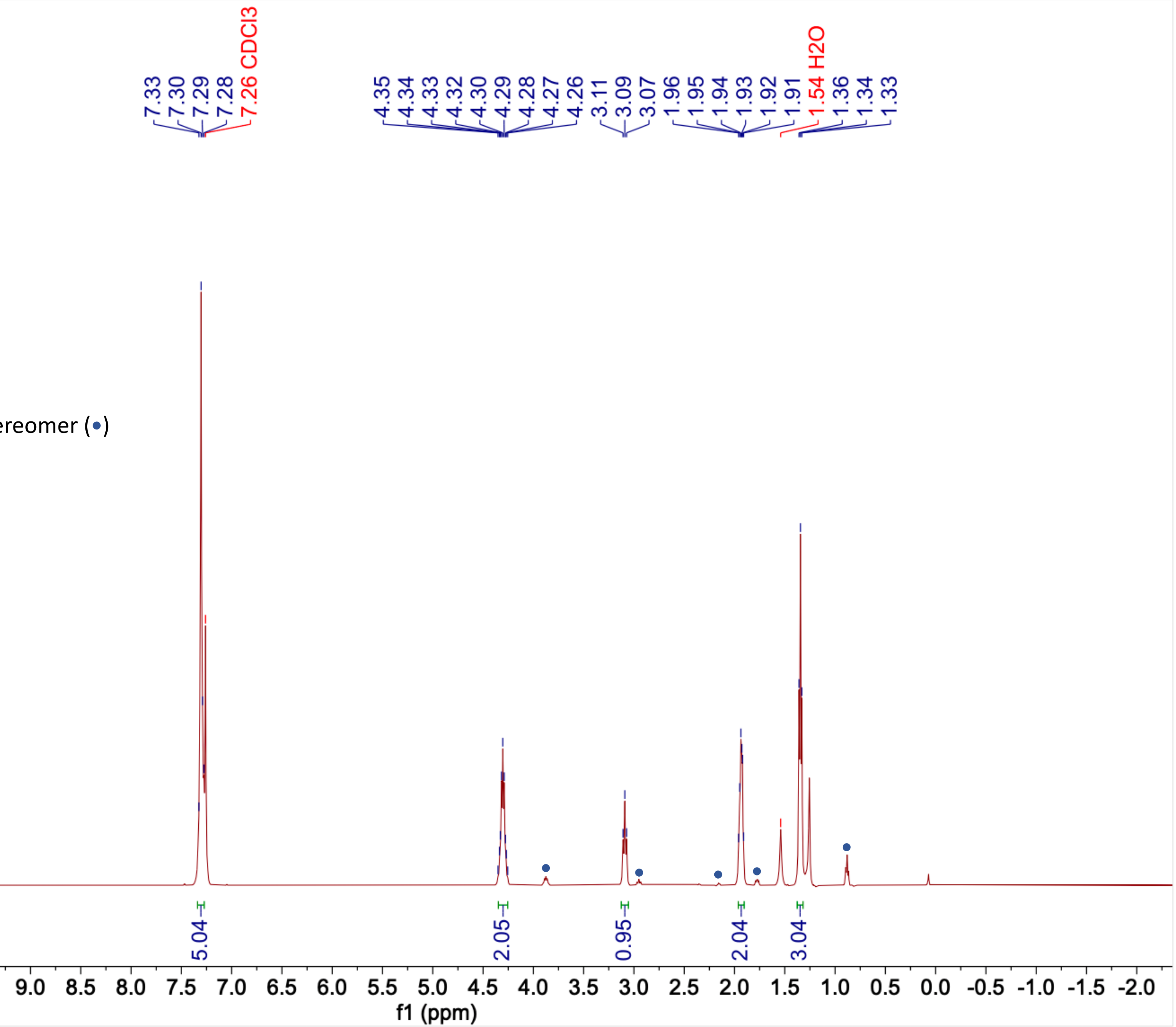
PDA Ch1 210nm

Peak#	Ret. Time	Area%
1	7.816	73.899
2	9.221	26.101
Total		100.000

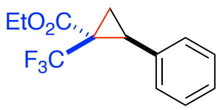
^{1}H NMR of **5d** in Chloroform-*d*

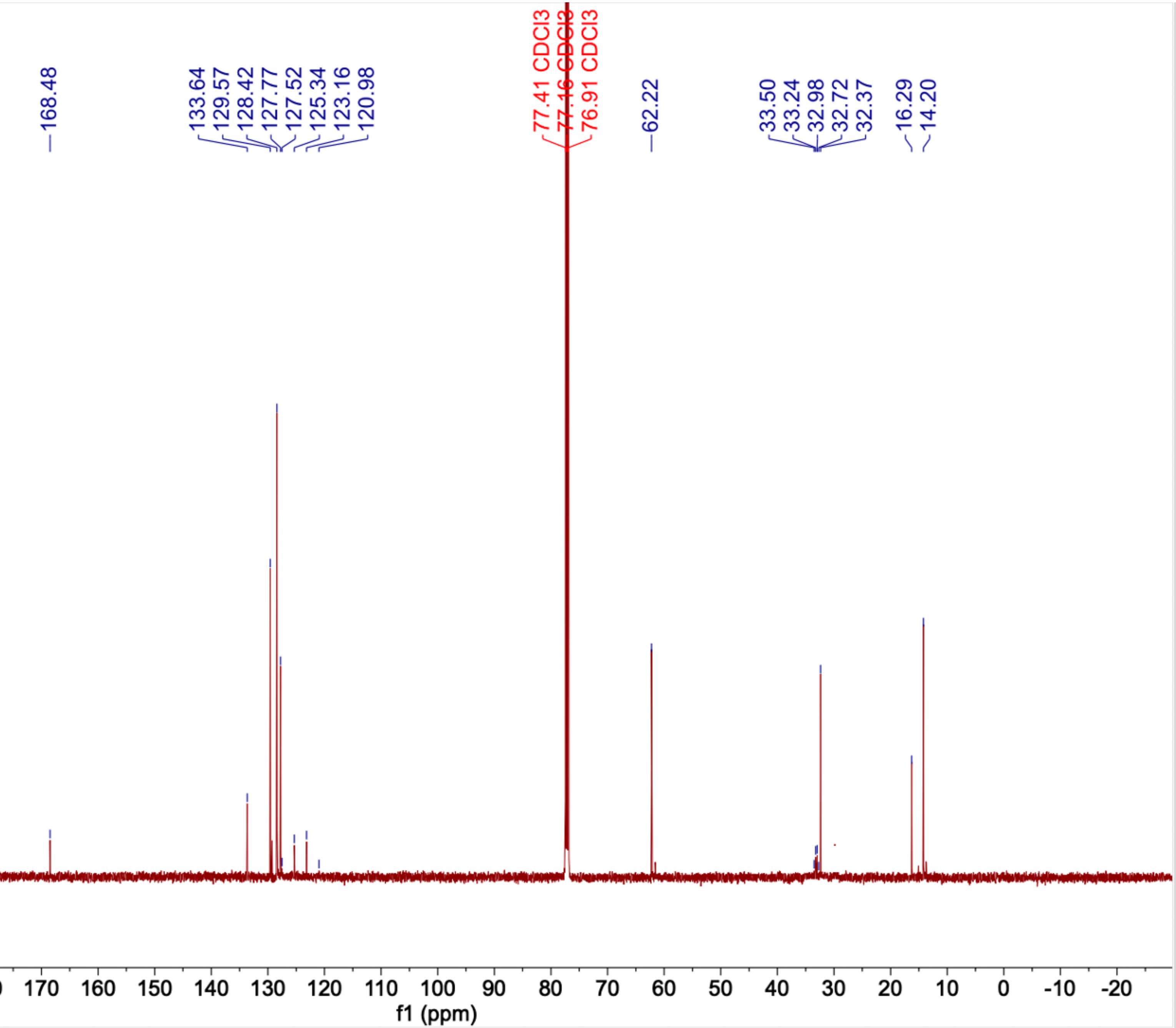


Another set belongs to diastereomer (•)

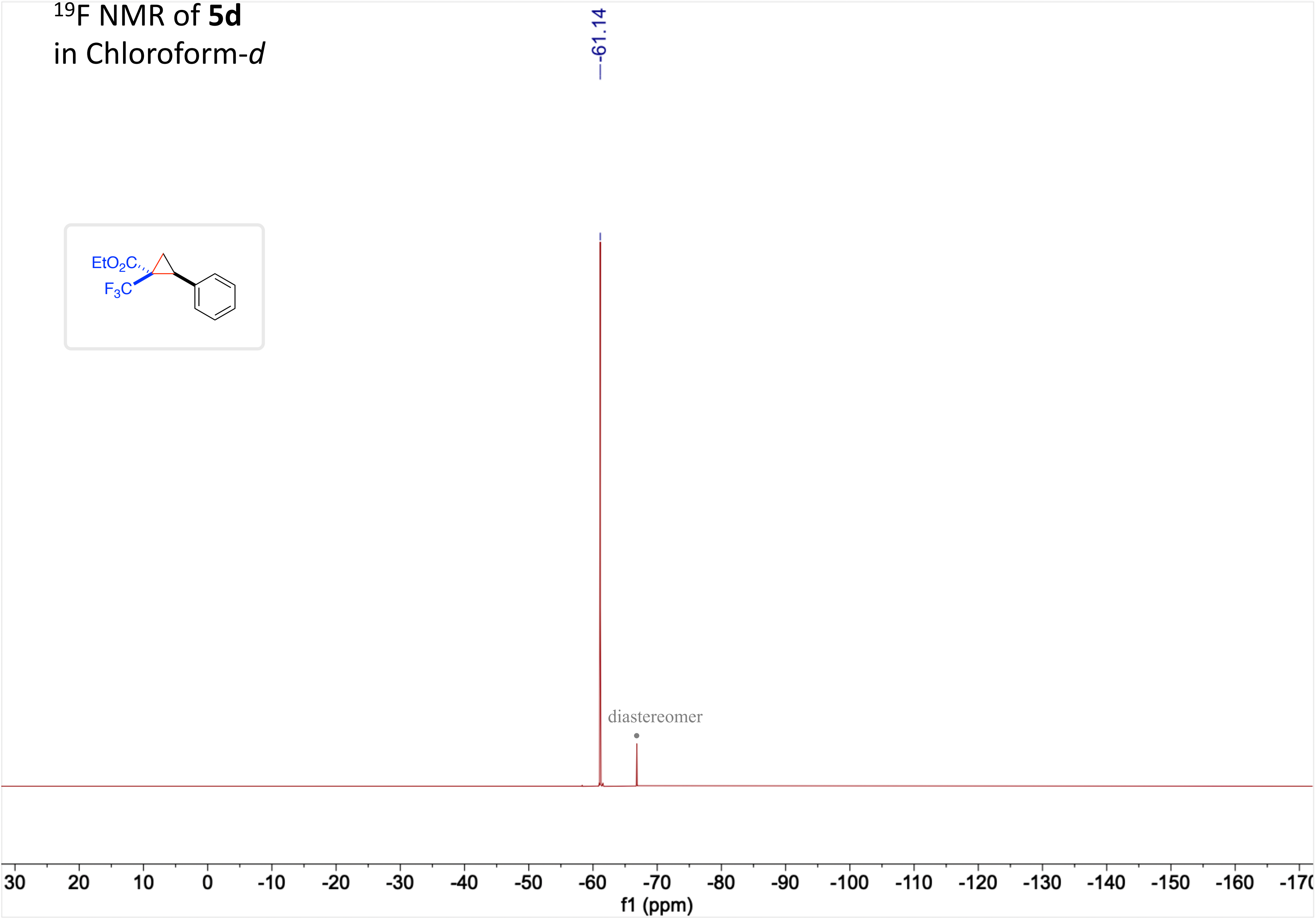


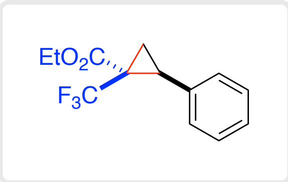
^{13}C NMR of **5d**
in Chloroform-*d*



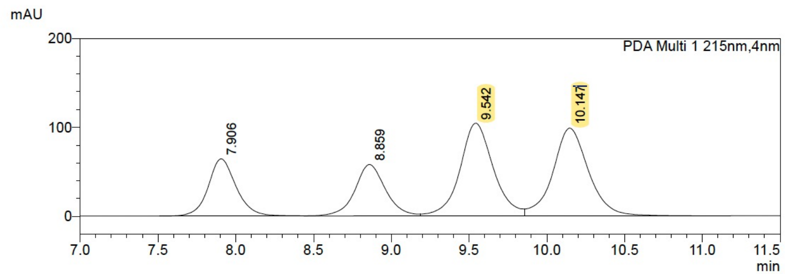


^{19}F NMR of **5d**
in Chloroform-*d*



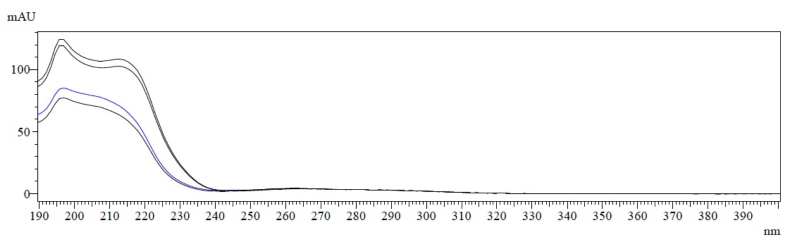


HPLC of **5d**



UV Spectrum

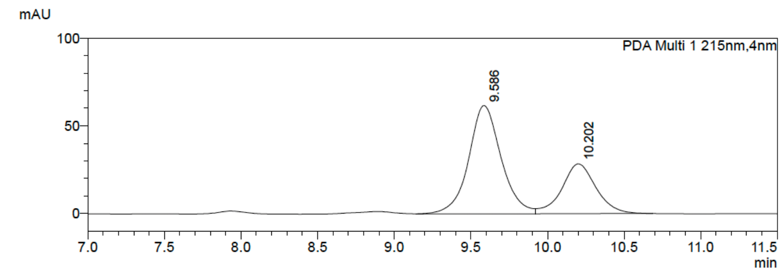
WCL-2387-W-0.1%0.8mL001_002.lcd



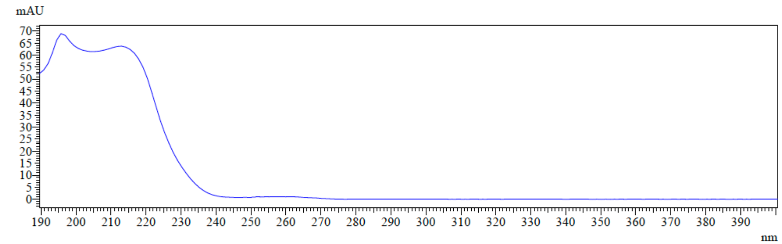
Peak Table

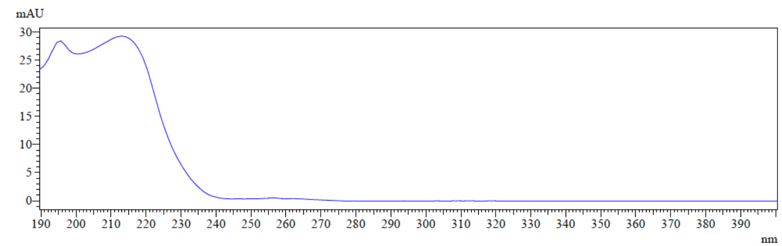
PDA Ch1 215nm

Peak#	Ret. Time	Area%
1	7.906	17.069
2	8.859	16.787
3	9.542	32.958
4	10.147	33.186
Total		100.000



UV Spectrum



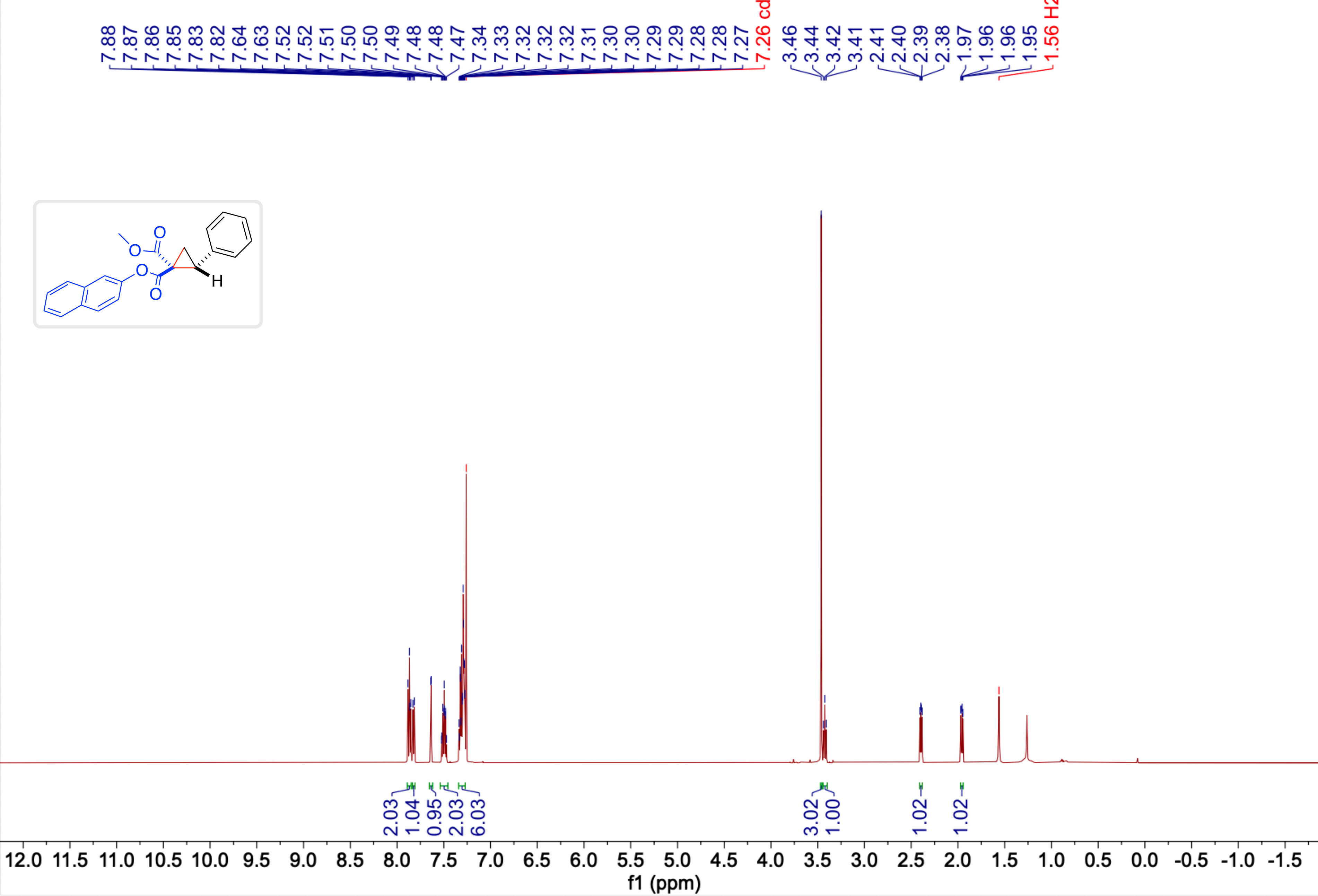


Peak Table

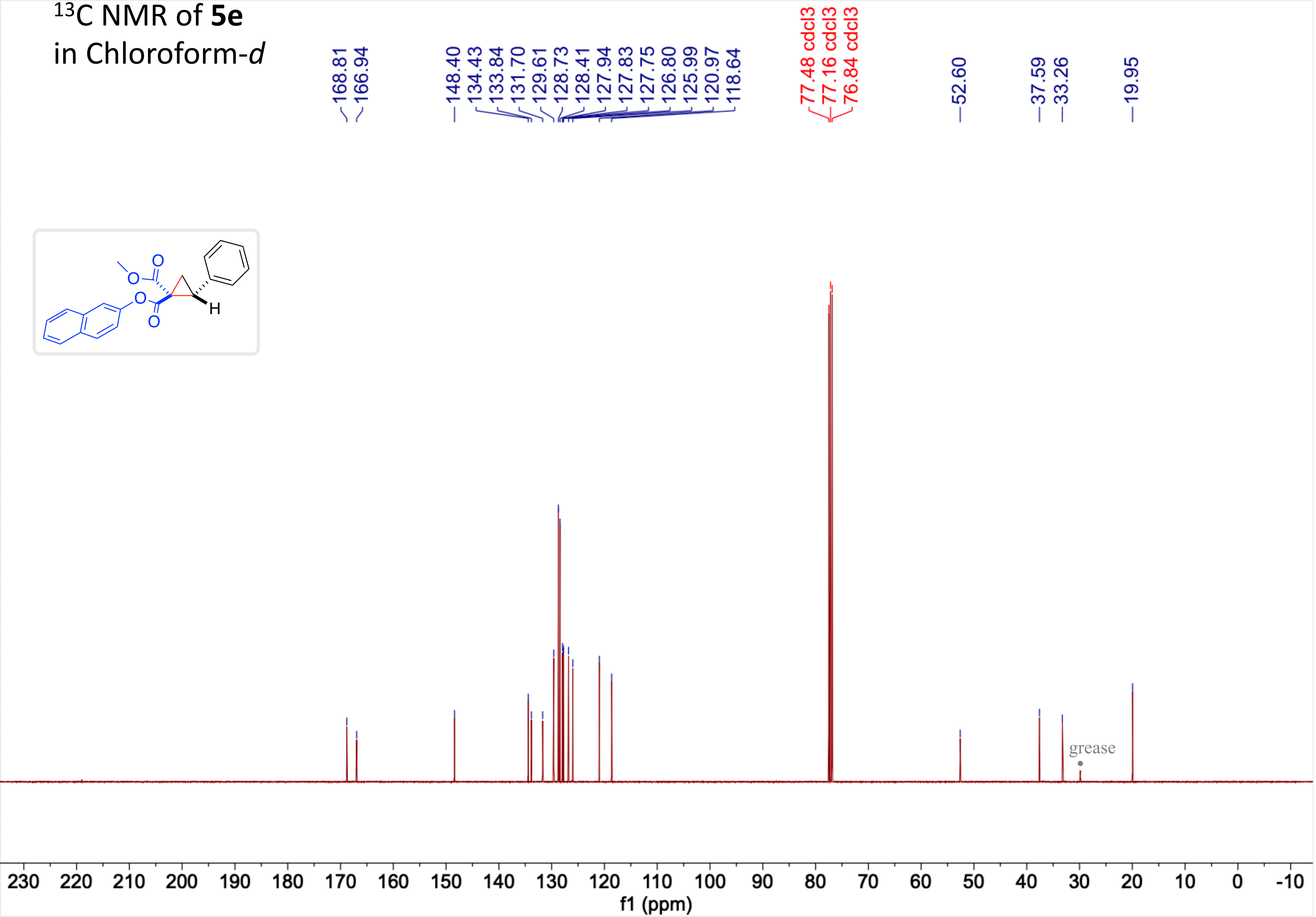
PDA Ch1 215nm

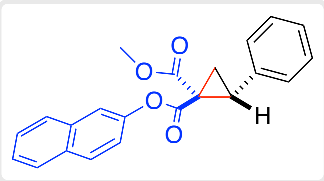
Peak#	Ret. Time	Area%
1	9.586	67.451
2	10.202	32.549
Total		100.000

[1]H NMR of **5e** in Chloroform-*d*

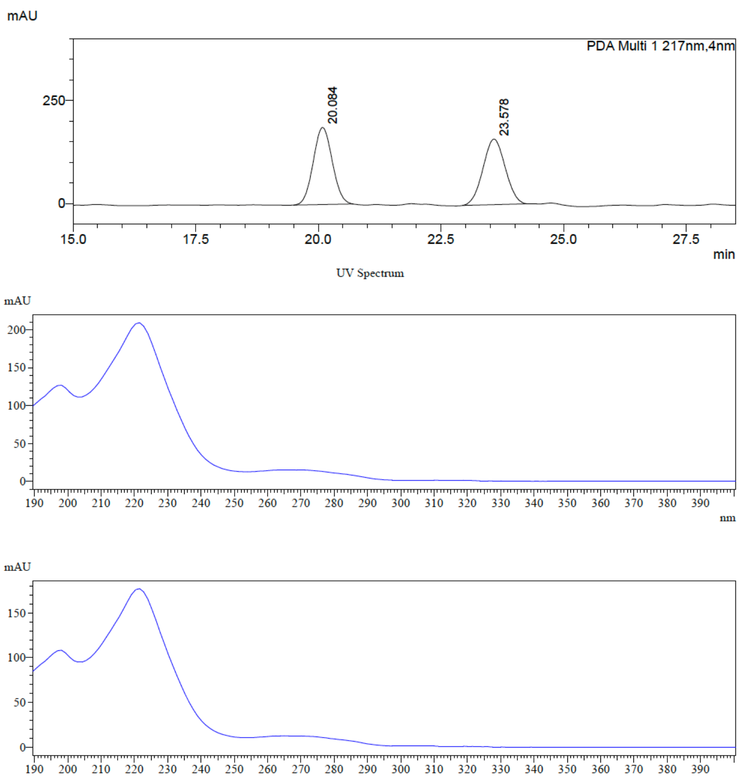


^{13}C NMR of **5e** in Chloroform-*d*





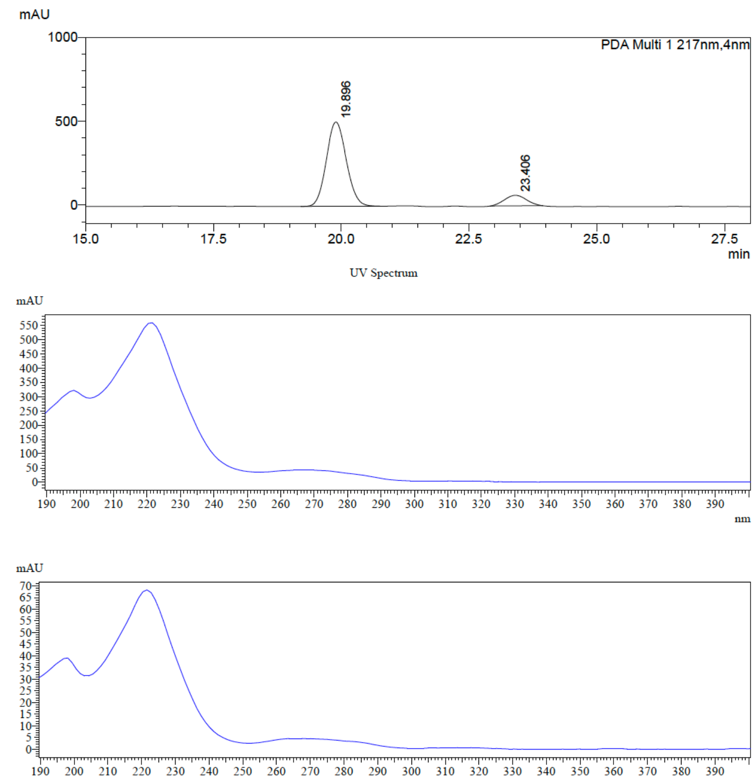
HPLC of **5e**



Peak Table

PDA Ch1 217nm

Peak#	Ret. Time	Area%
1	20.084	50.219
2	23.578	49.781
Total		100.000

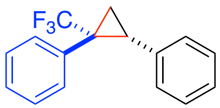


Peak Table

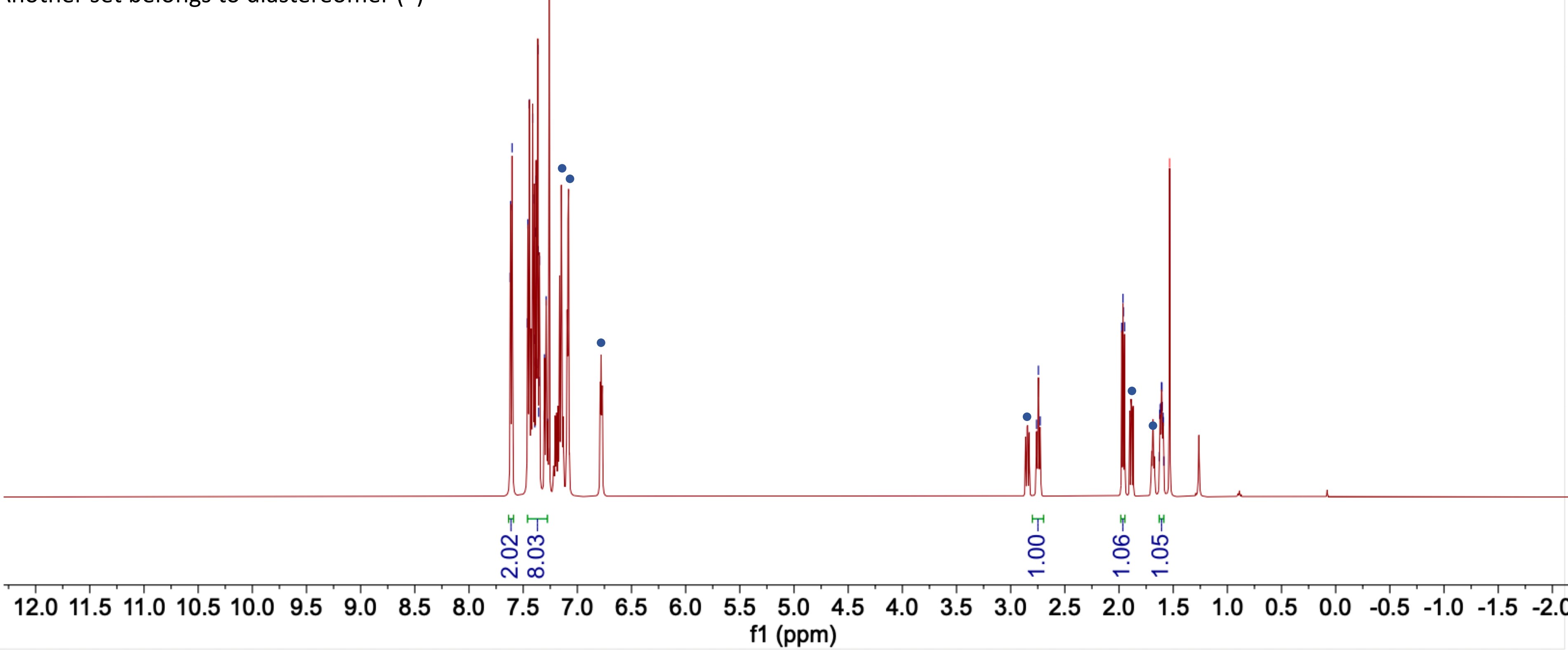
PDA Ch1 217nm

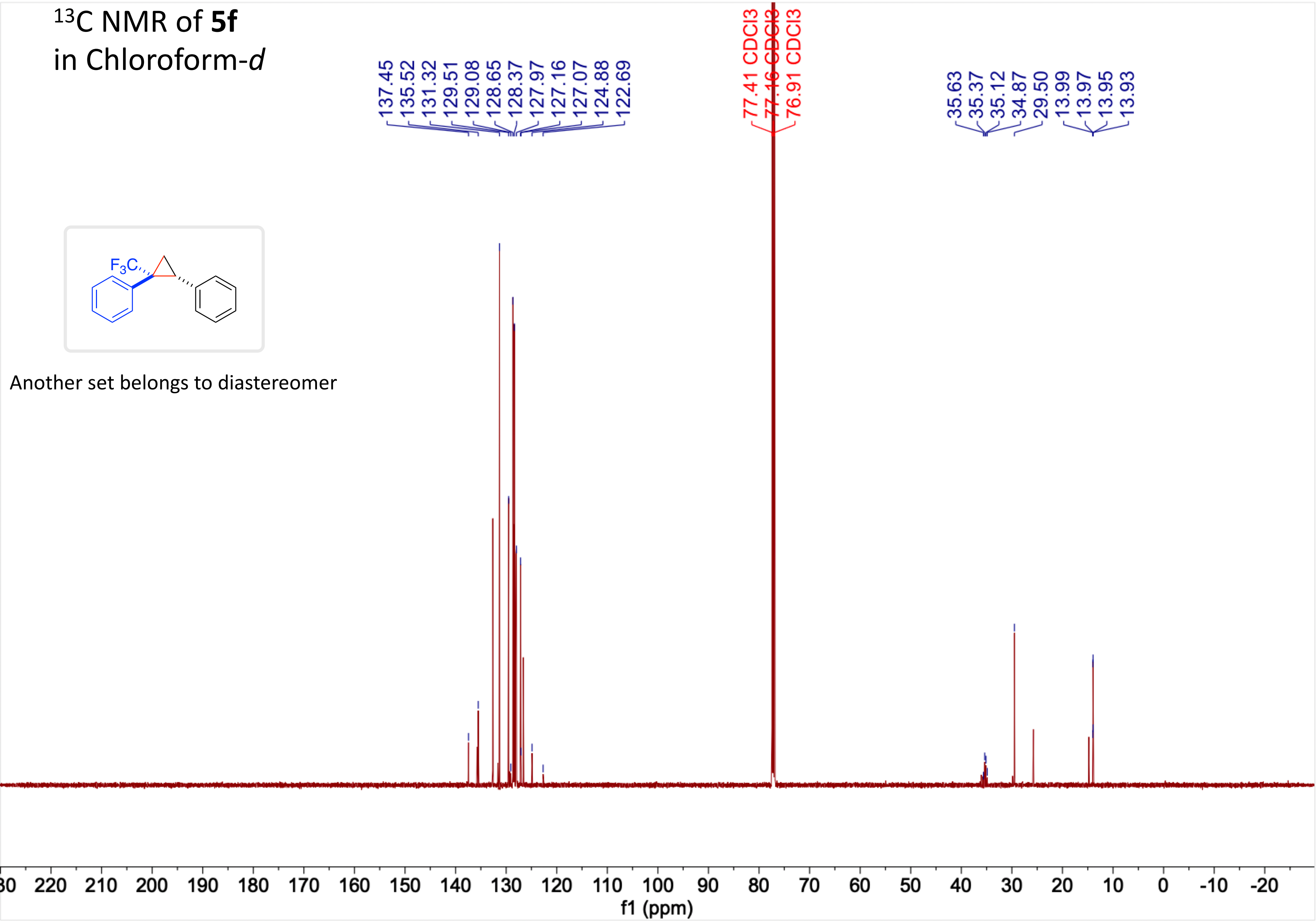
Peak#	Ret. Time	Area%
1	19.896	87.856
2	23.406	12.144
Total		100.000

^{1}H NMR of **5f**
in Chloroform-*d*

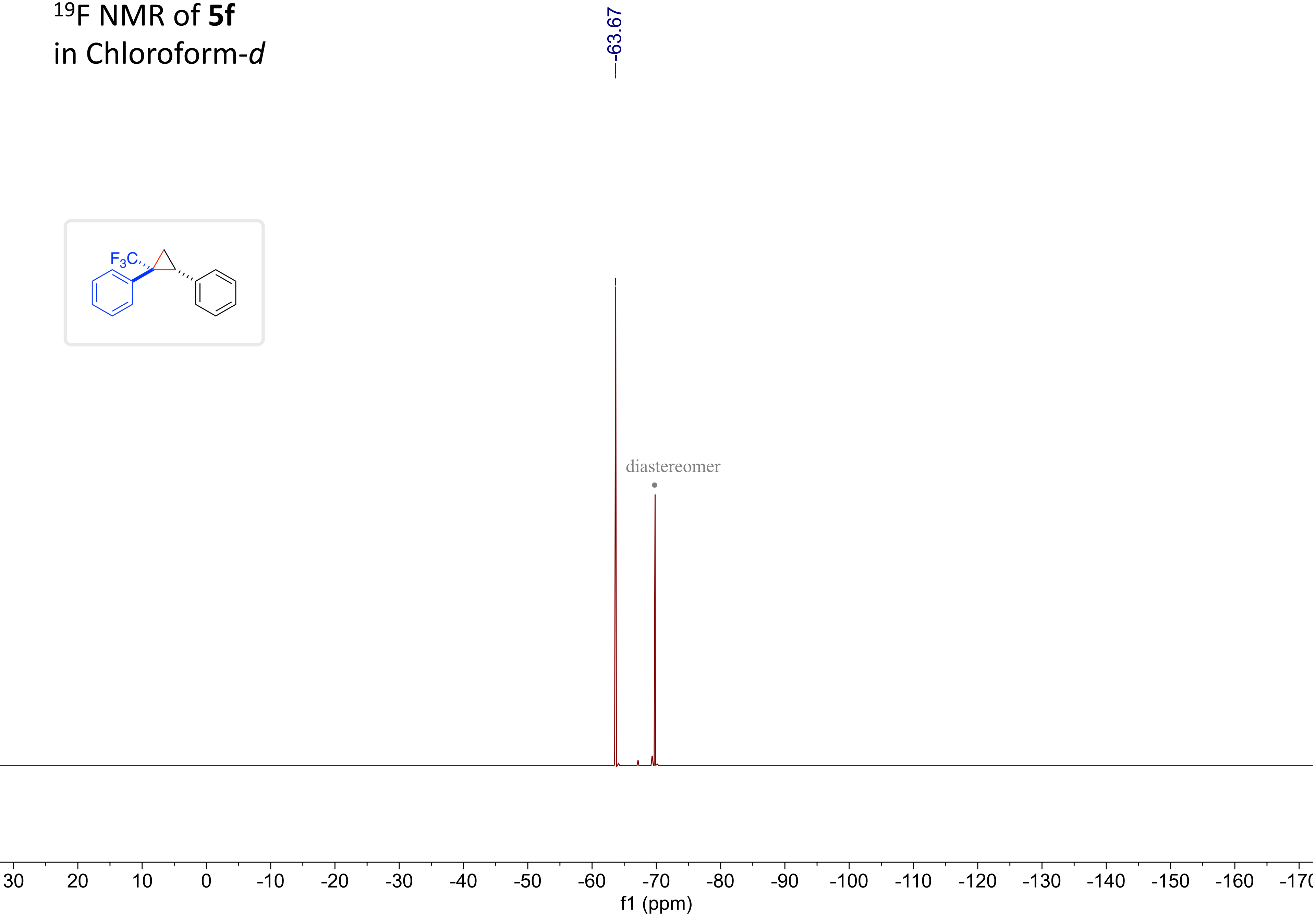


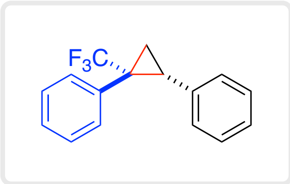
Another set belongs to diastereomer (•)



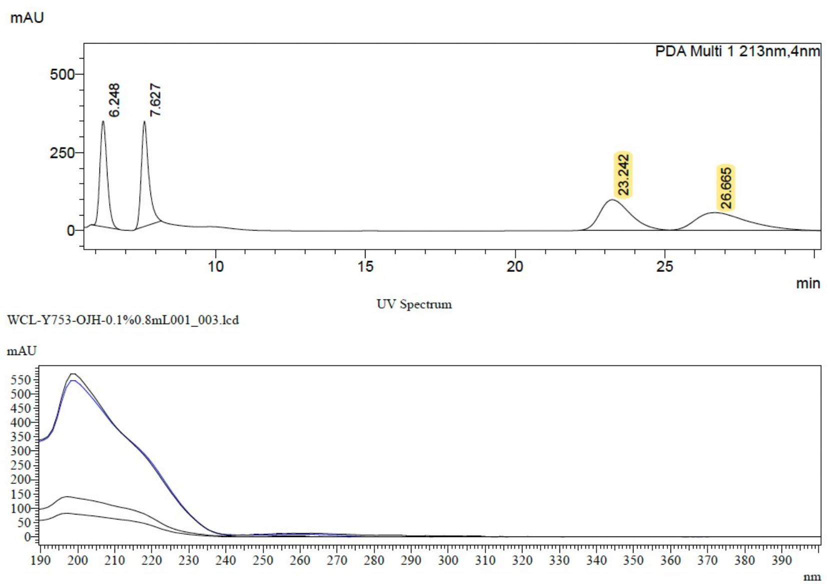

^{13}C NMR of **5f**
in Chloroform-*d*
Another set belongs to diastereomer
F3C
137.45
135.52
131.32
129.51
129.08
128.65
128.37
127.97
127.16
127.07
124.88
122.69
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
35.63
35.37
35.12
34.87
29.50
13.99
13.97
13.95
13.93
f1 (ppm)

[19]F NMR of **5f**
in Chloroform-*d*





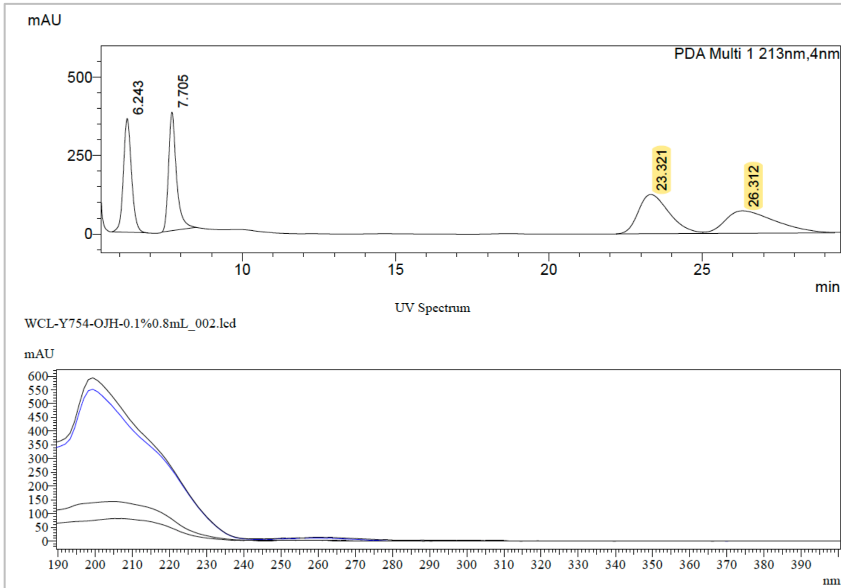
HPLC of **5f**



Peak Table

PDA Ch1 213nm

Peak#	Ret. Time	Area%
1	6.248	22.376
2	7.627	23.185
3	23.242	27.282
4	26.665	27.157
Total		100.000

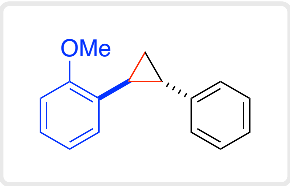


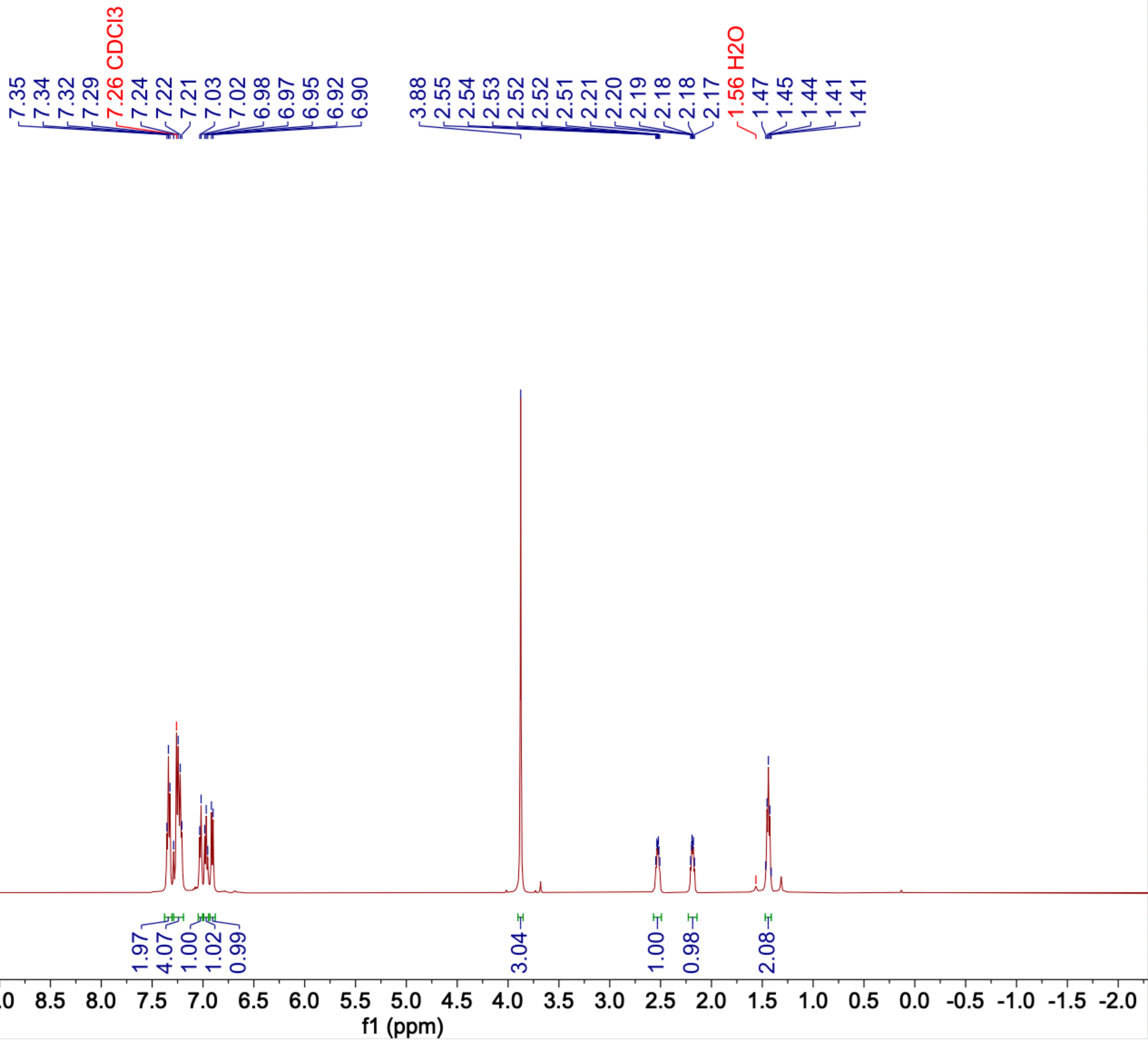
Peak Table

PDA Ch1 213nm

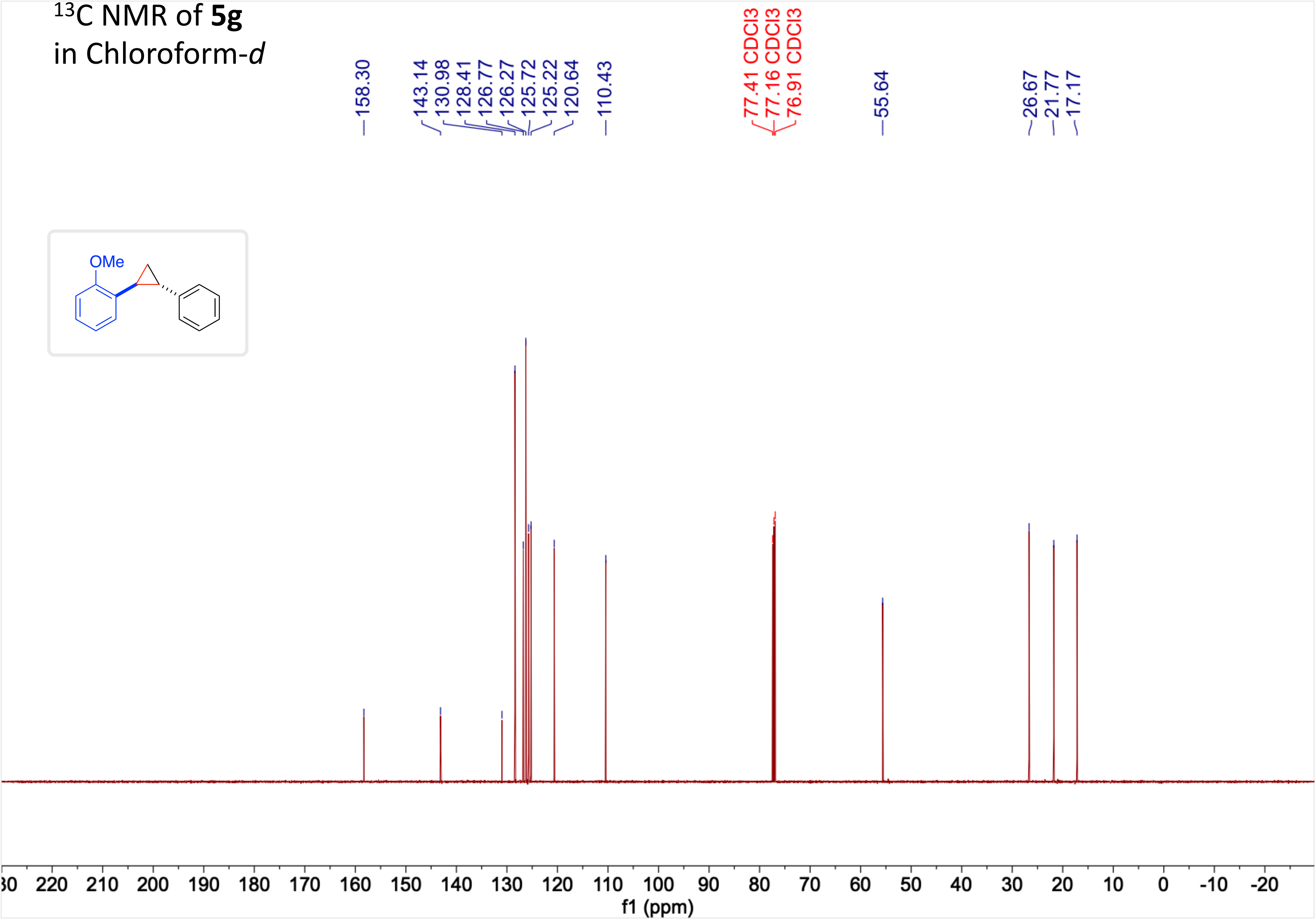
Peak#	Ret. Time	Area%
1	6.243	21.927
2	7.705	22.340
3	23.321	28.762
4	26.312	26.971
Total		100.000

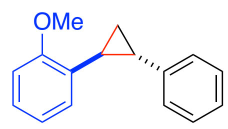
^{1}H NMR of **5g**
in Chloroform-*d*



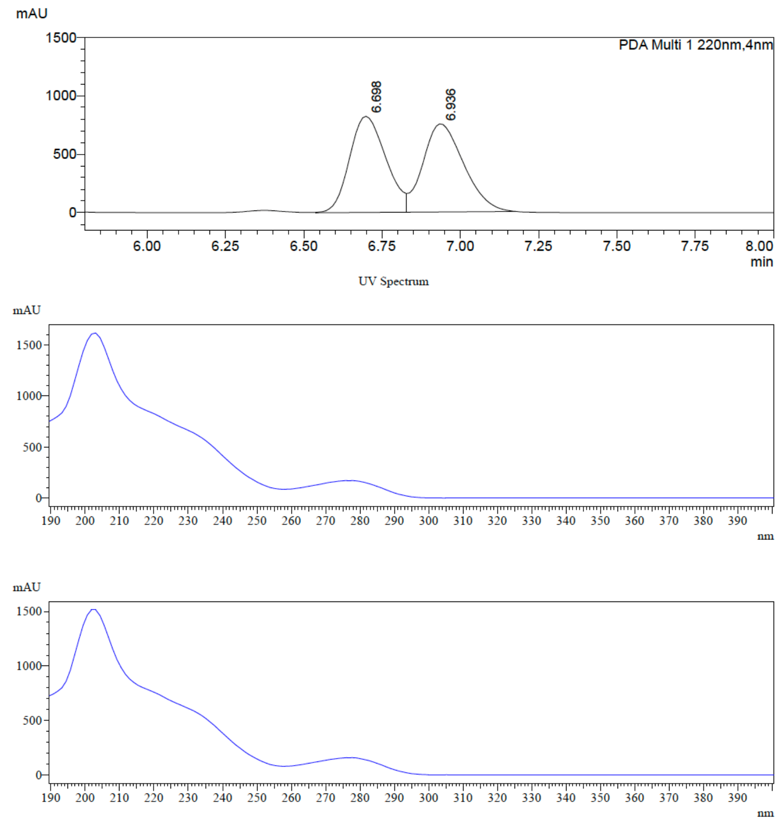


^{13}C NMR of **5g**
in Chloroform-*d*





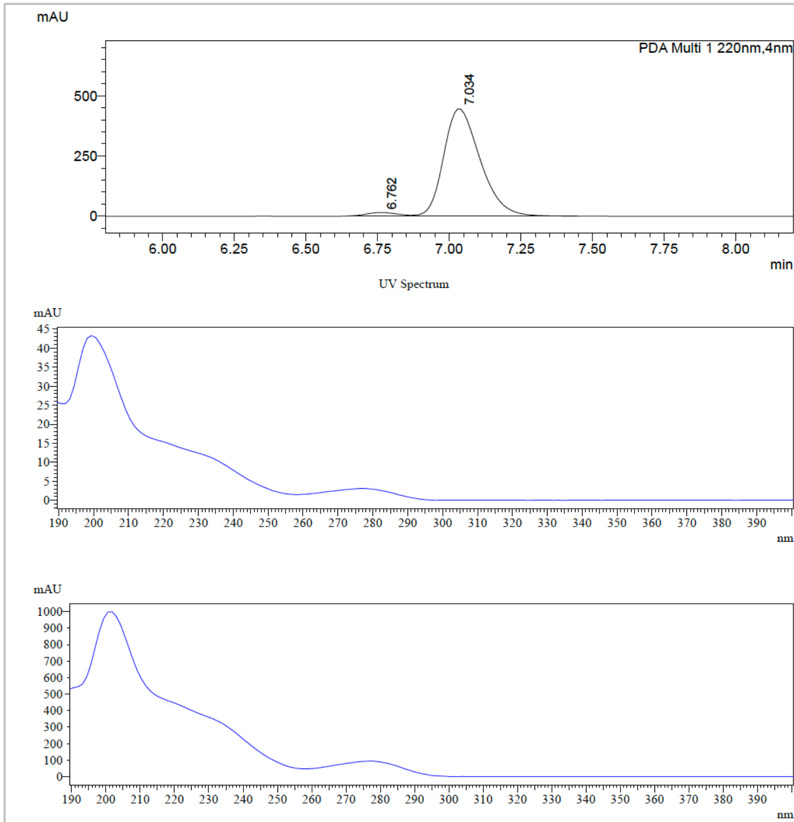
HPLC of **5g**



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area%
1	6.698	49.502
2	6.936	50.498
Total		100.000

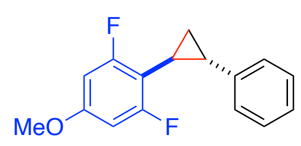


Peak Table

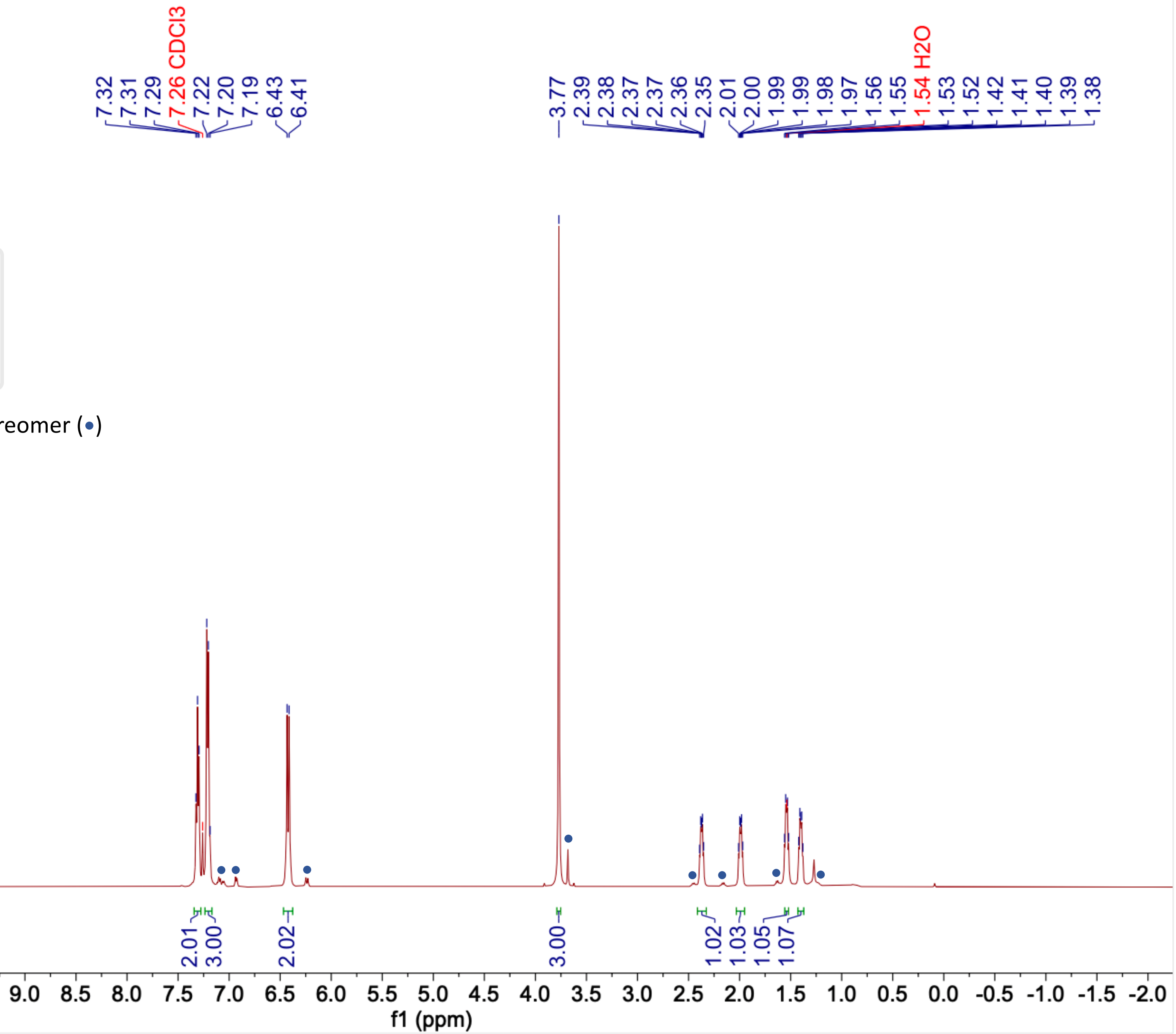
PDA Ch1 220nm

Peak#	Ret. Time	Area%
1	6.762	2.592
2	7.034	97.408
Total		100.000

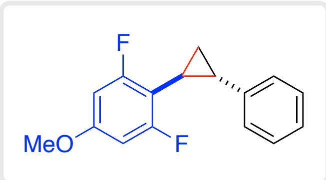
[1]H NMR of **5h**
in Chloroform-*d*



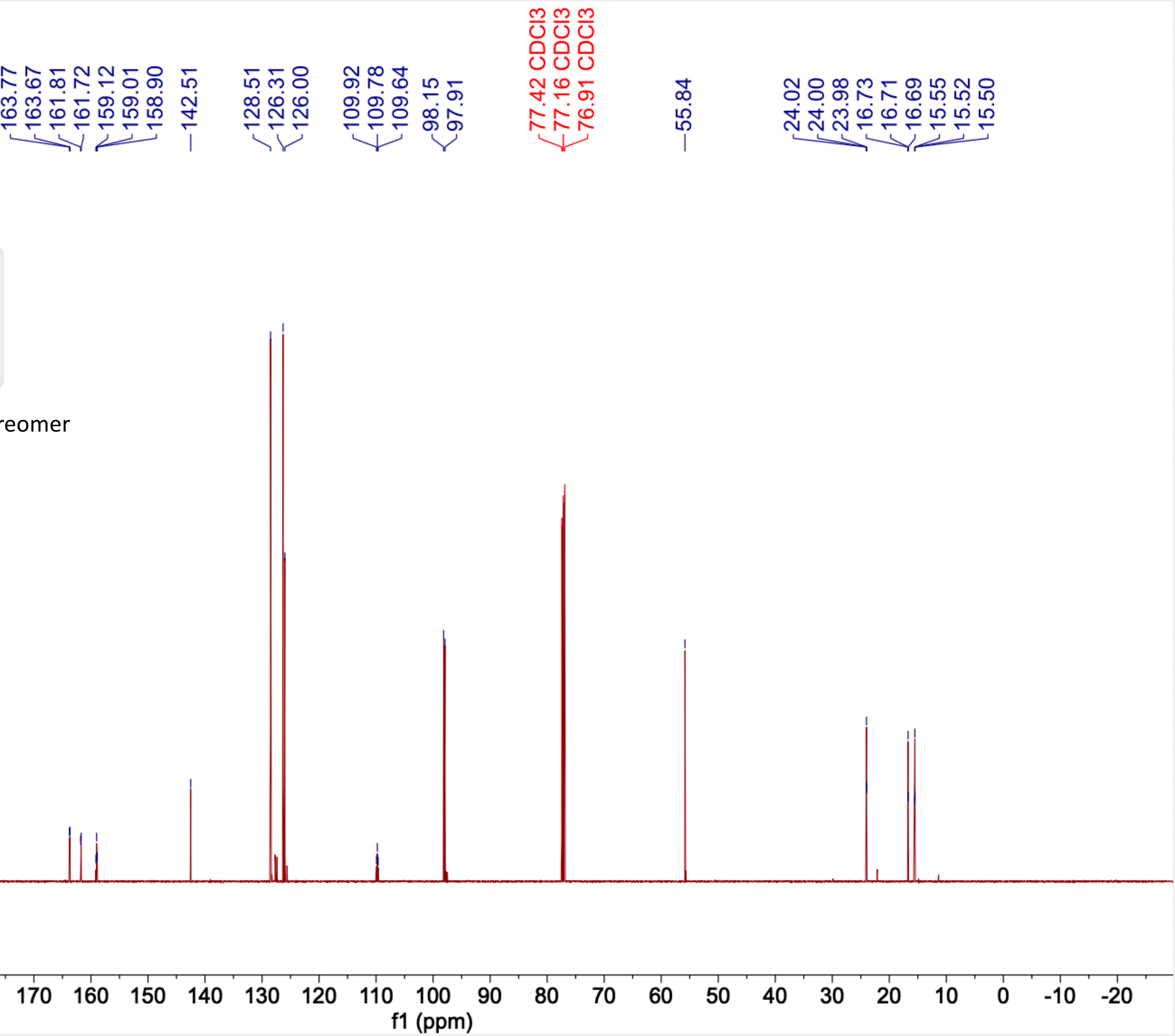
Another set belongs to diastereomer (•)



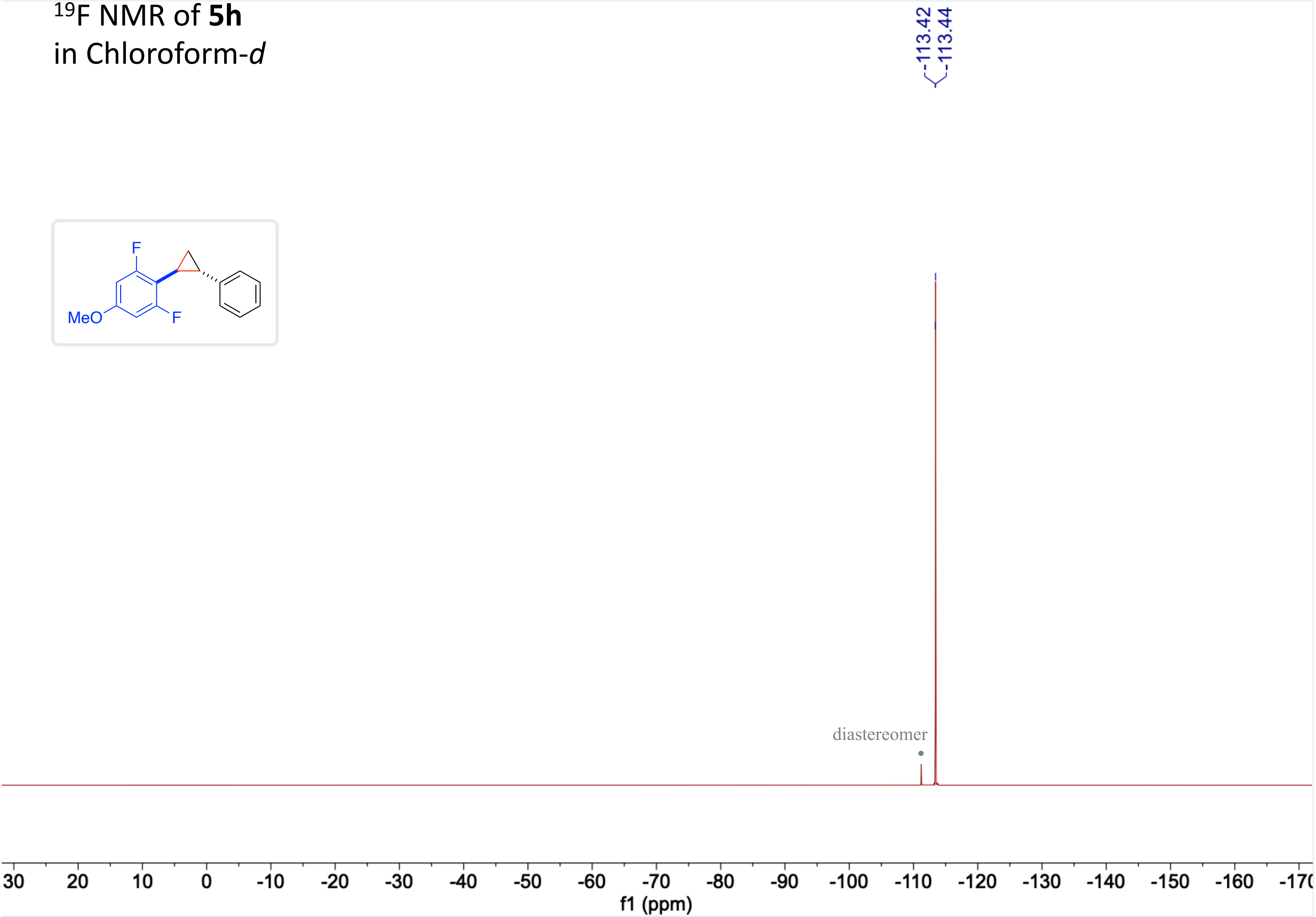
^{13}C NMR of **5h**
in Chloroform-*d*

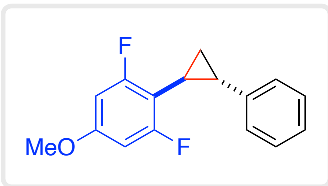


Another set belongs to diastereomer

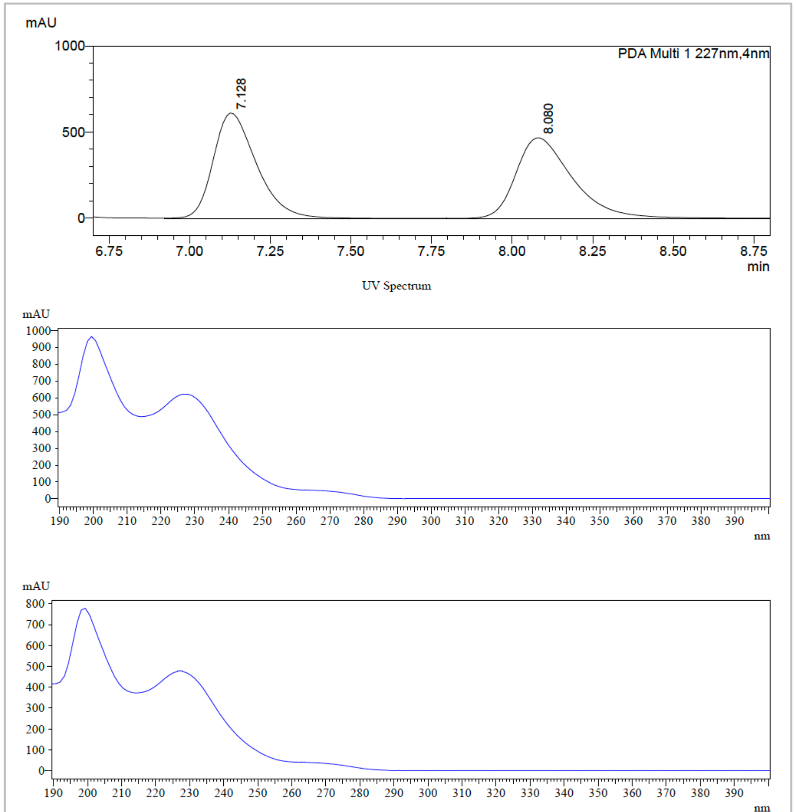


^{19}F NMR of **5h**
in Chloroform-*d*





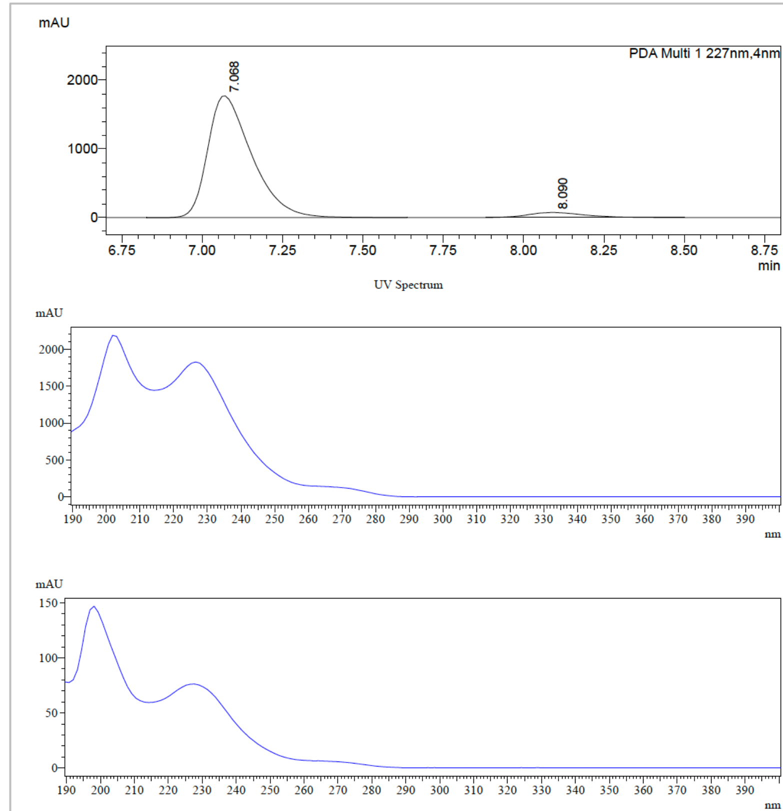
HPLC of **5h**



Peak Table

PDA Ch1 227nm

Peak#	Ret. Time	Area%
1	7.128	49.920
2	8.080	50.080
Total		100.000

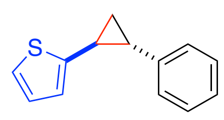


Peak Table

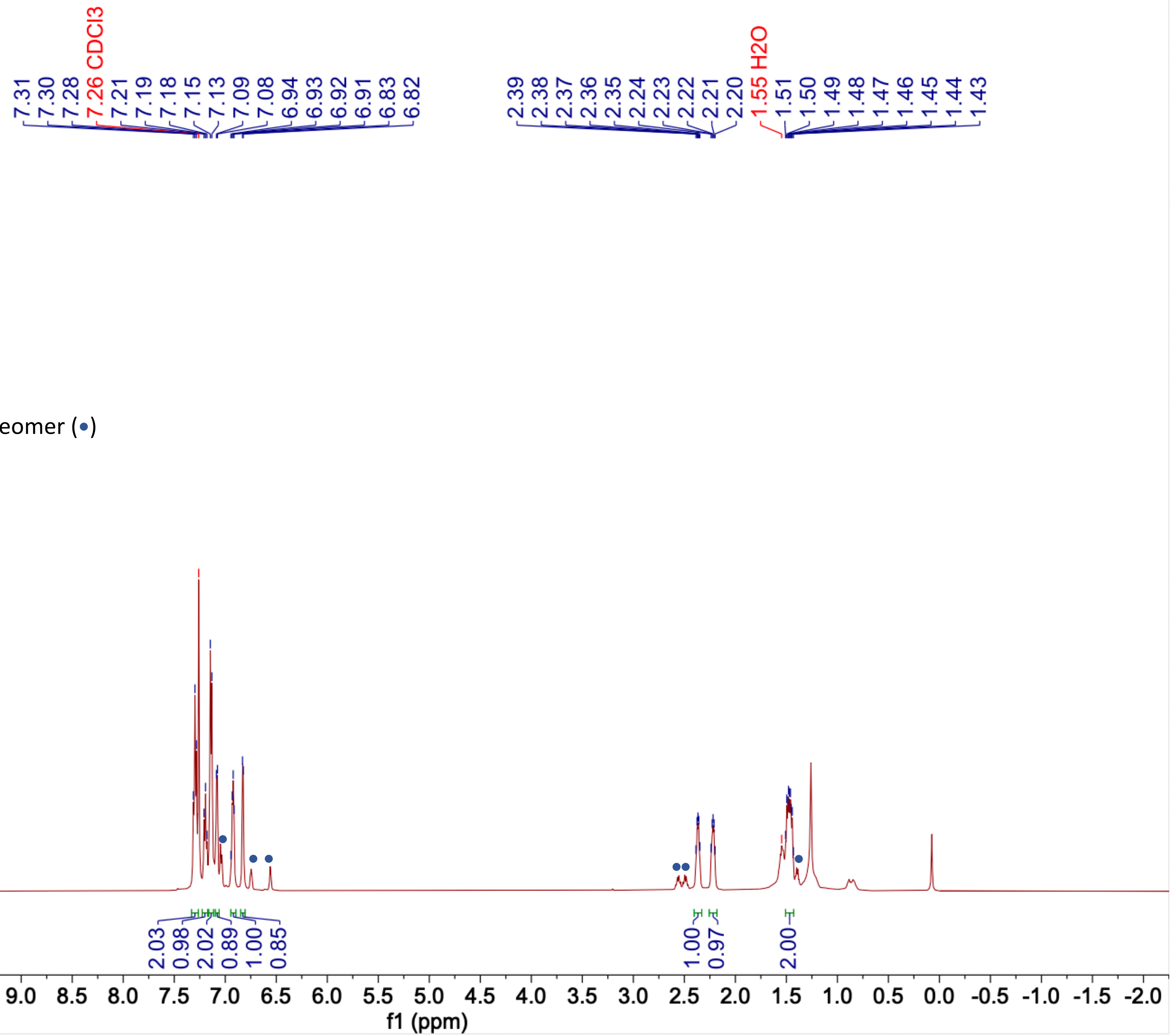
PDA Ch1 227nm

Peak#	Ret. Time	Area%
1	7.068	95.006
2	8.090	4.994
Total		100.000

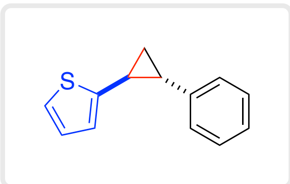
^{1}H NMR of **5i**
in Chloroform-*d*



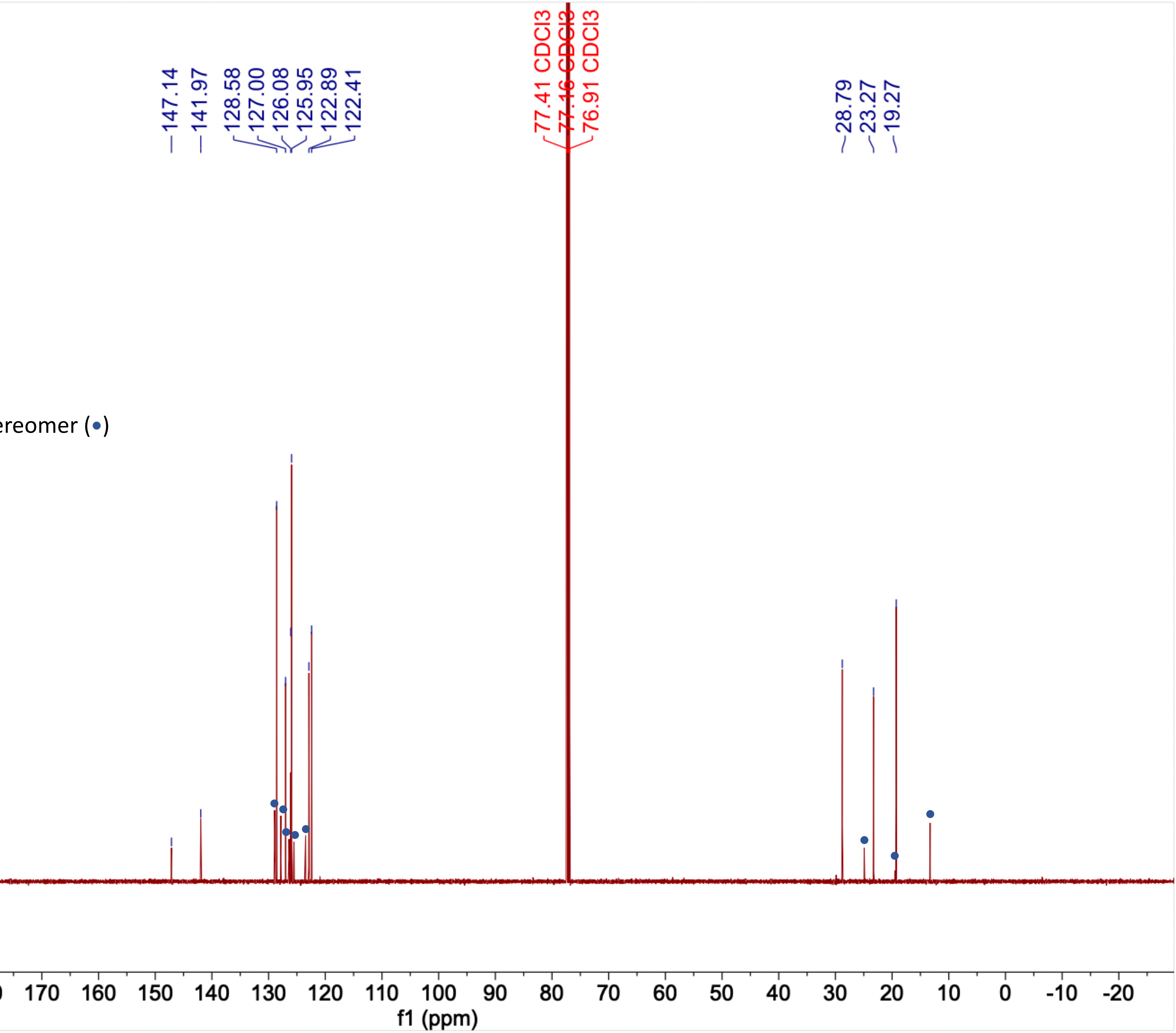
Another set belongs to diastereomer (•)

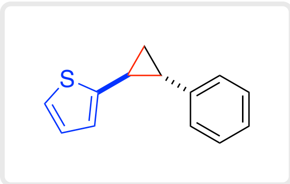


^{13}C NMR of **5i**
in Chloroform-*d*

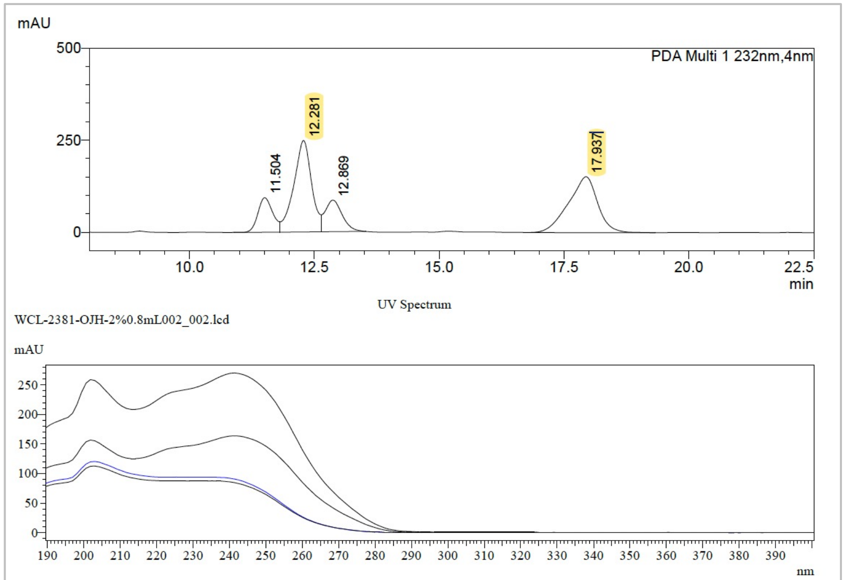


Another set belongs to diastereomer (•)





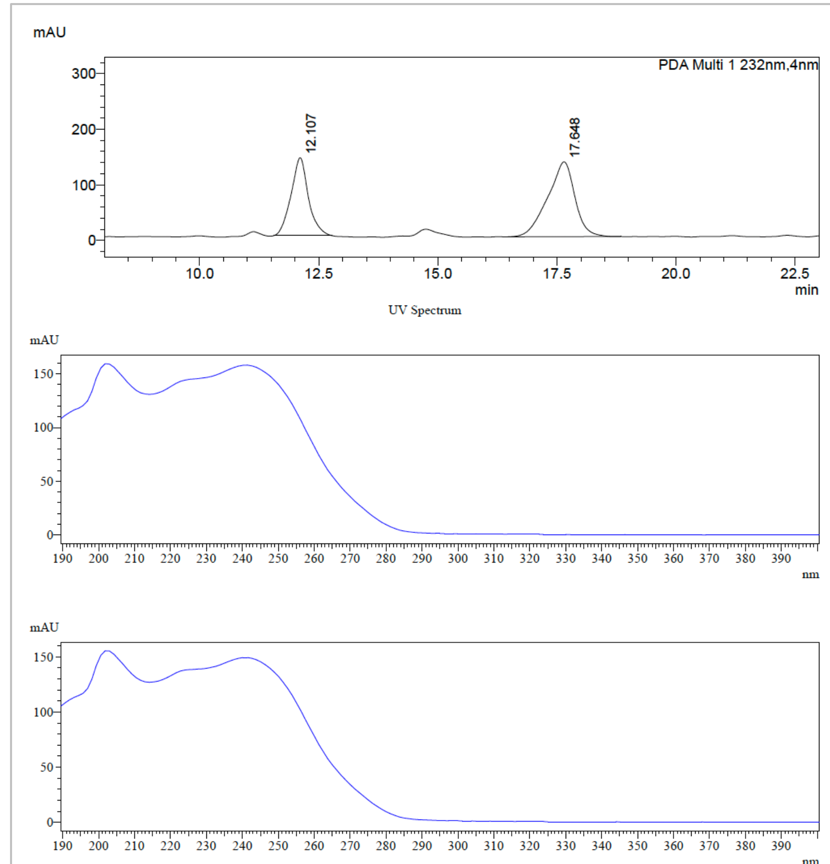
HPLC of **5i**



Peak Table

PDA Ch1 232nm

Peak#	Ret. Time	Area%
1	11.504	11.933
2	12.281	37.837
3	12.869	12.427
4	17.937	37.803
Total		100.000

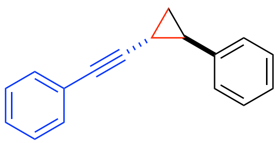


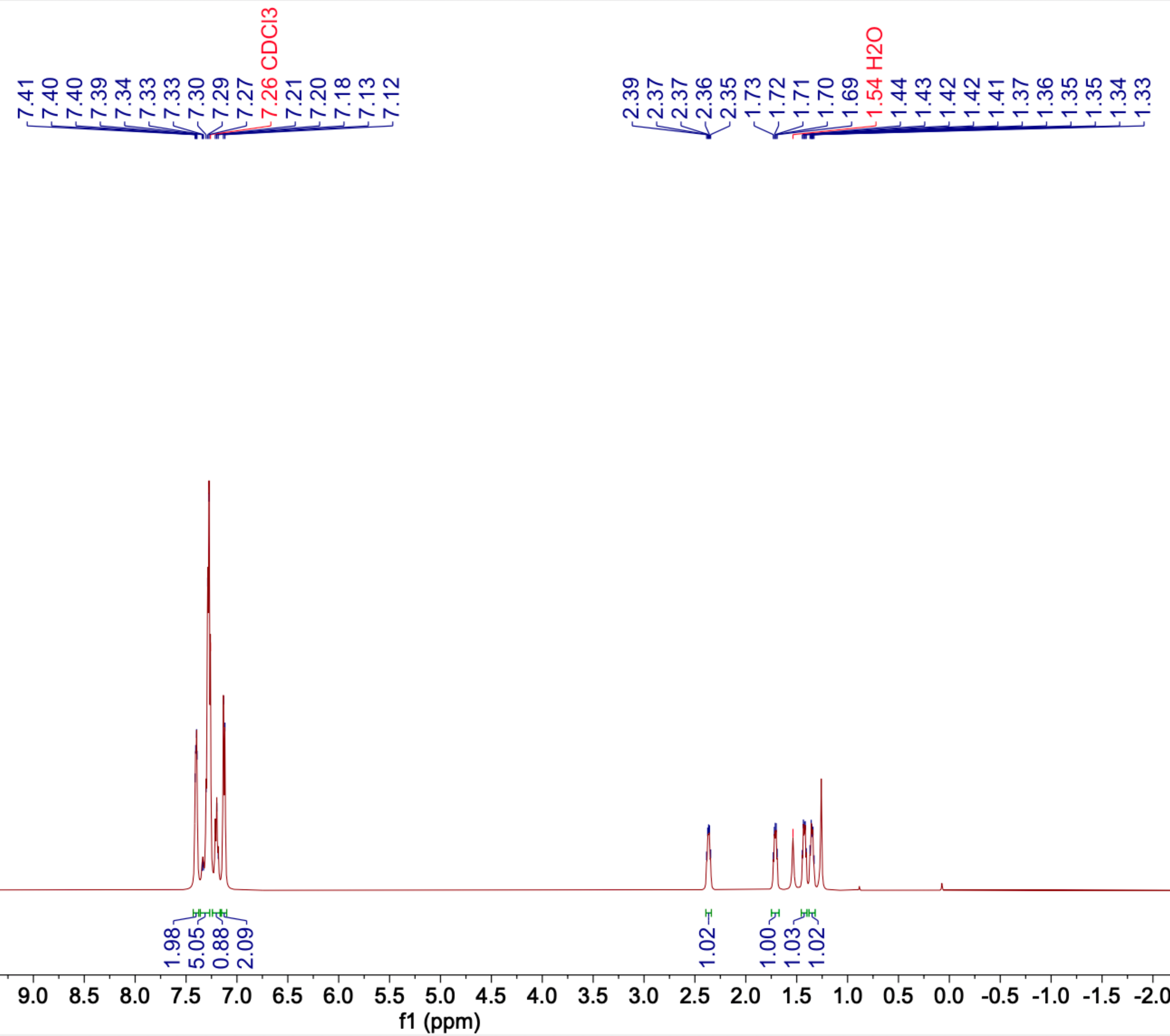
Peak Table

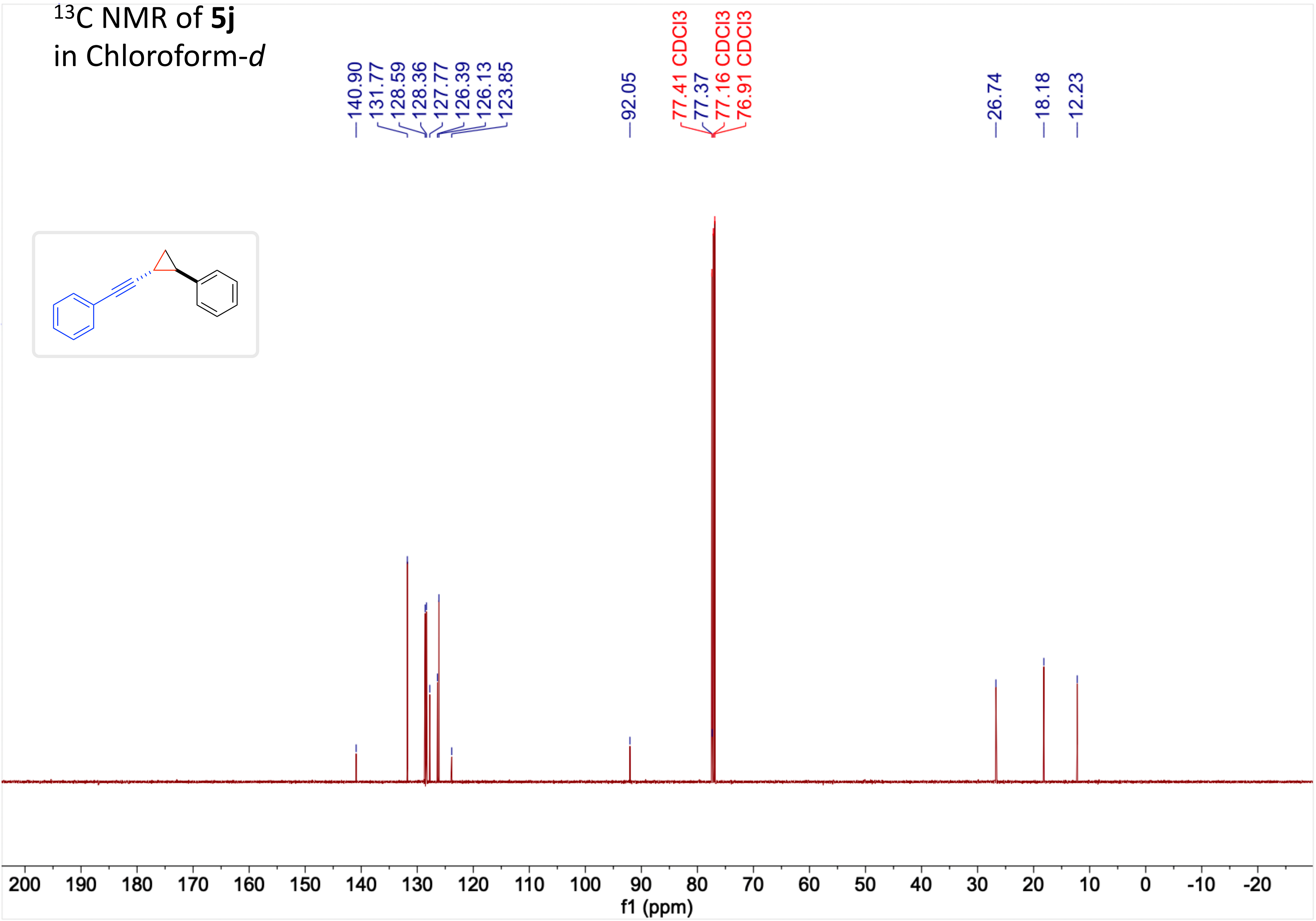
PDA Ch1 232nm

Peak#	Ret. Time	Area%
1	12.107	39.821
2	17.648	60.179
Total		100.000

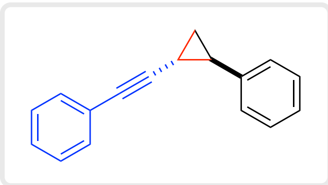
[1]H NMR of **5j**
in Chloroform-*d*



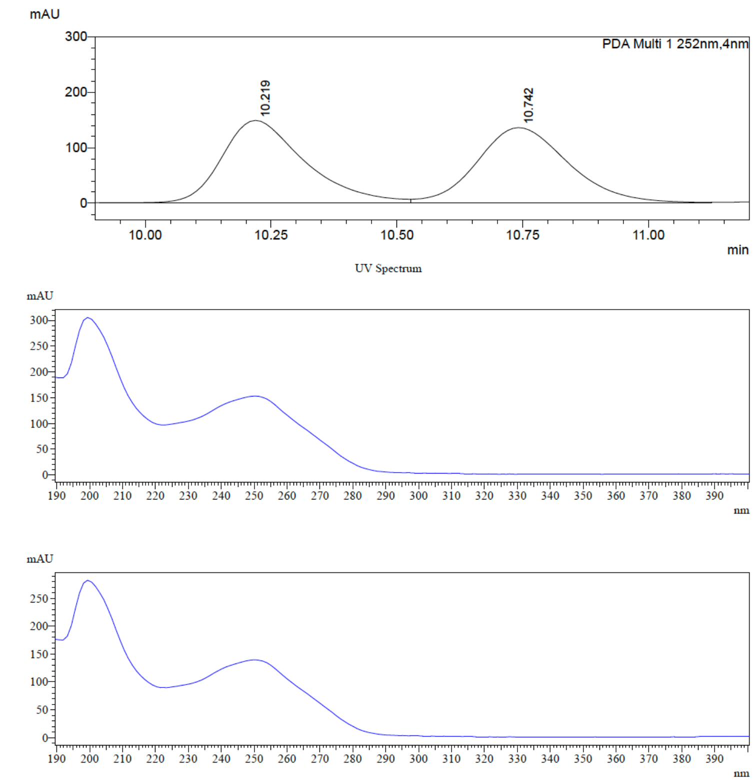




13C NMR of 5j
in Chloroform-d
140.90
131.77
128.59
128.36
127.77
126.39
126.13
123.85
92.05
77.41 CDCl3
77.37
77.16 CDCl3
76.91 CDCl3
26.74
18.18
12.23
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



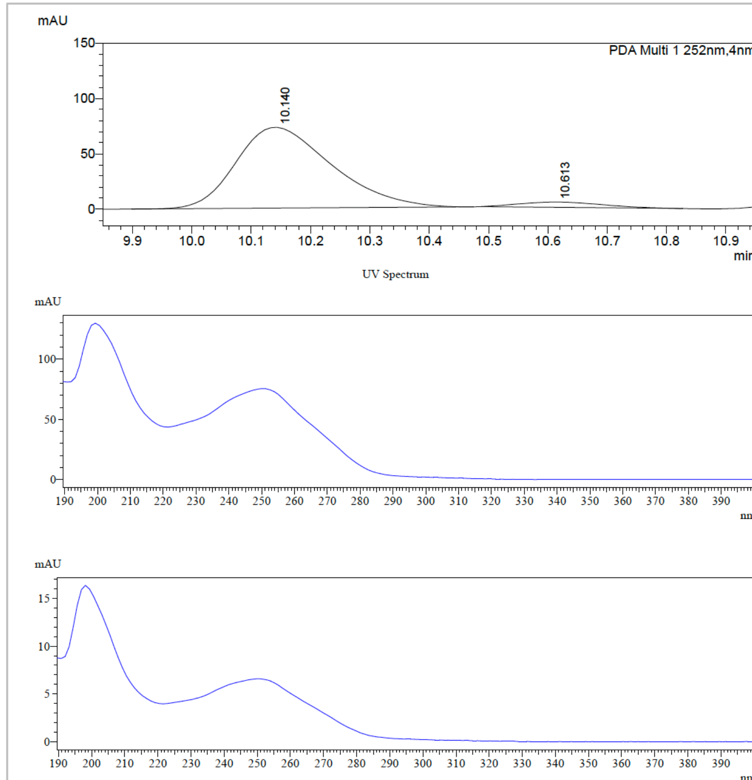
HPLC of **5j**



Peak Table

PDA Ch1 252nm

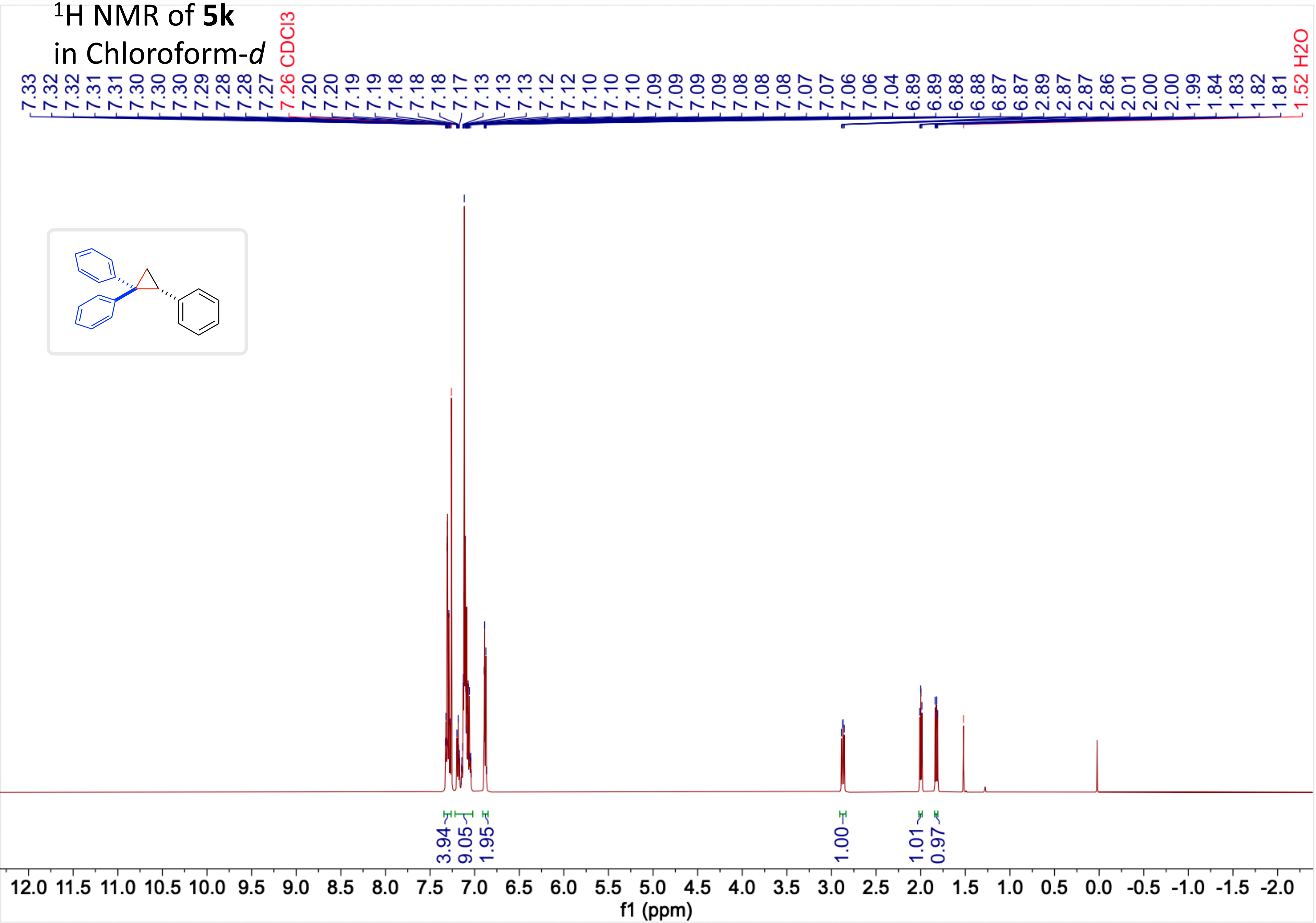
Peak#	Ret. Time	Area%
1	10.219	49.925
2	10.742	50.075
Total		100.000



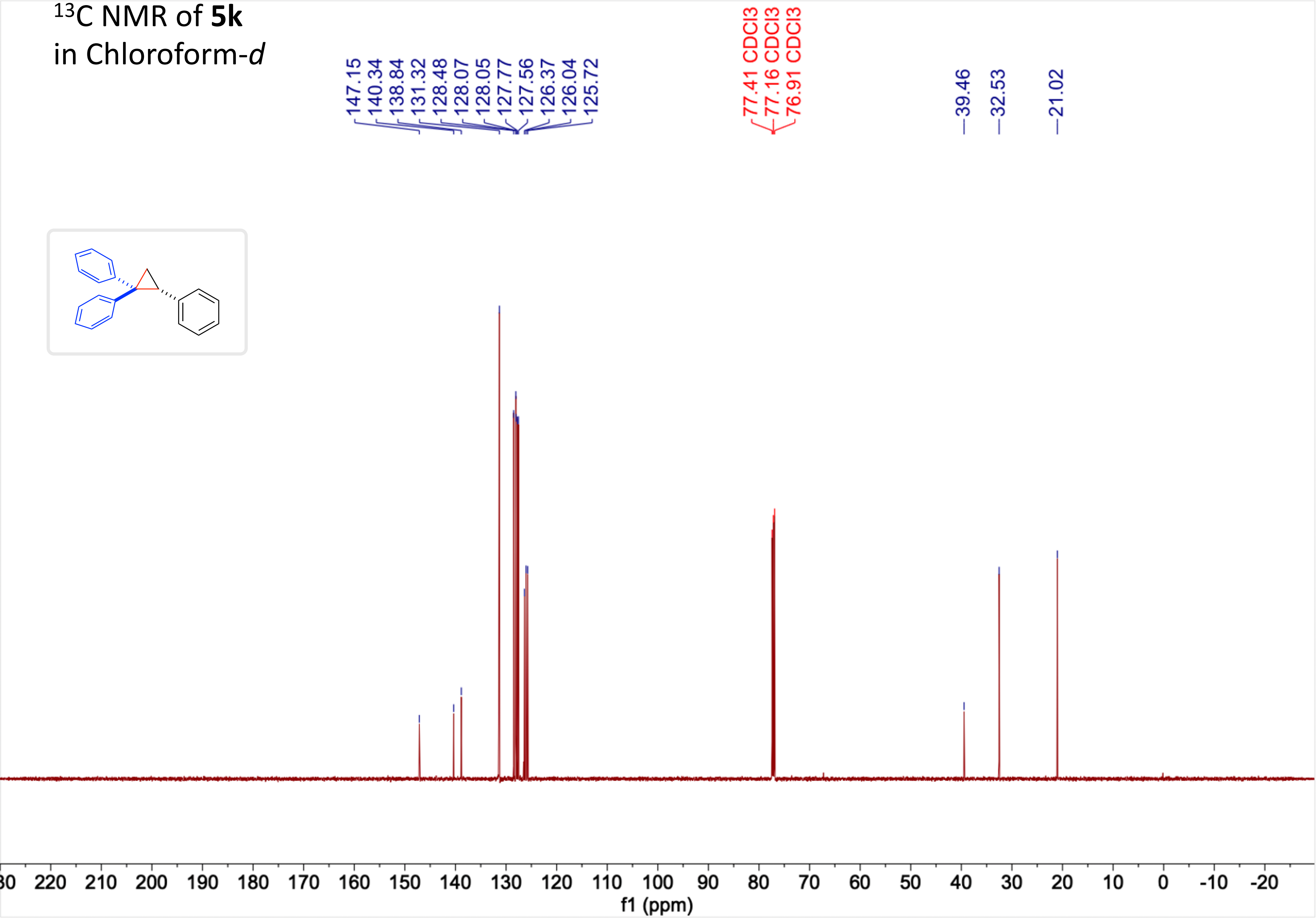
Peak Table

PDA Ch1 252nm

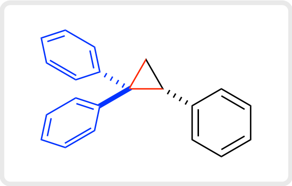
Peak#	Ret. Time	Area%
1	10.140	94.667
2	10.613	5.333
Total		100.000

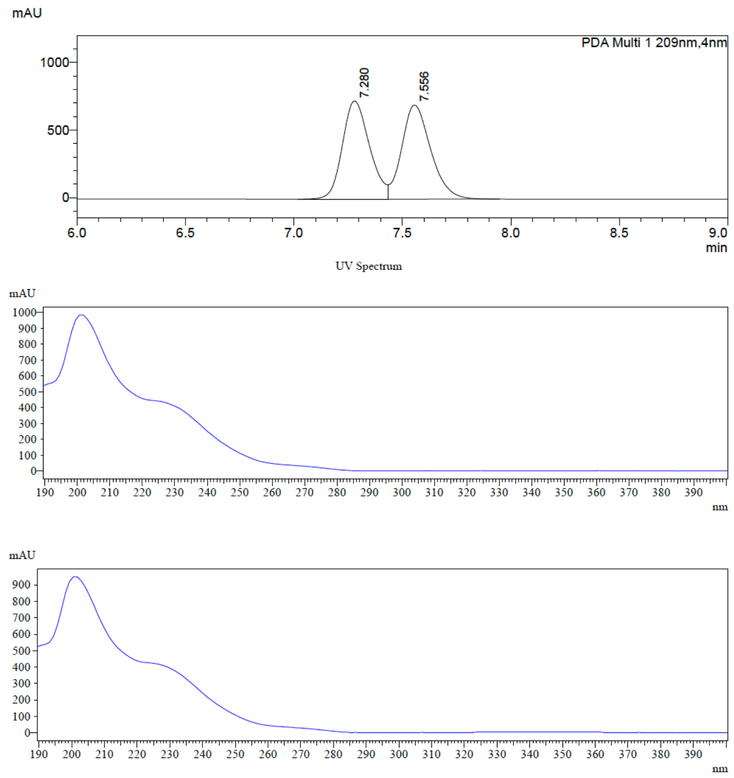

1H NMR of 5k
in Chloroform-d
7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.27
7.26 CDCl3
7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.13 7.13 7.13 7.12 7.12 7.10 7.10 7.10 7.09 7.09 7.09 7.09 7.08 7.08 7.08 7.07 7.07 7.06 7.06 7.04 6.89 6.89 6.88 6.88 6.87 6.87 2.89 2.87 2.87 2.86 2.01 2.00 2.00 1.99 1.84 1.83 1.82 1.81
1.52 H2O
3.94
9.05
1.95
1.00
1.01
0.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

^{13}C NMR of **5k**
in Chloroform-*d*



HPLC of **5k**

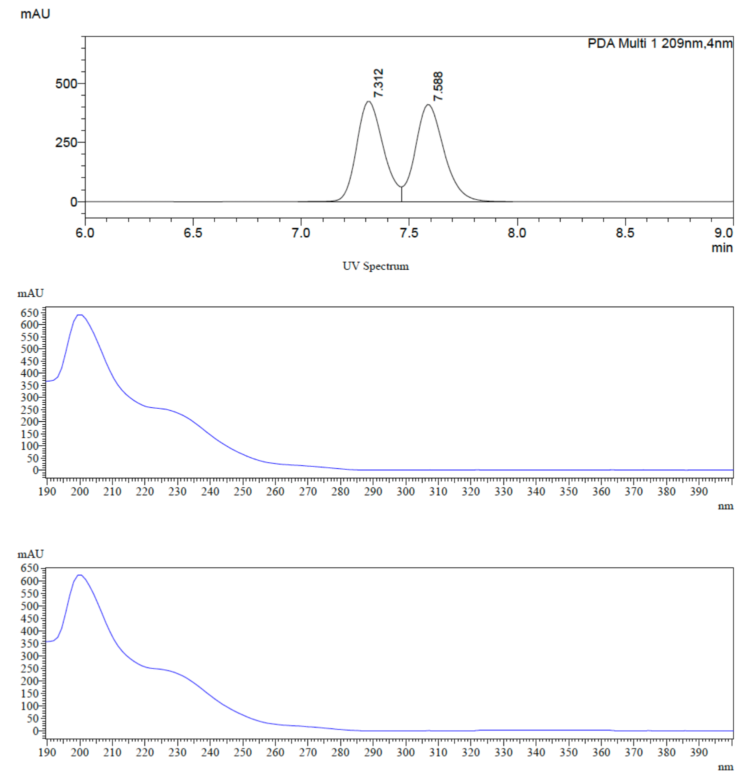




Peak Table

PDA Ch1 209nm

Peak#	Ret. Time	Area%
1	7.280	49.650
2	7.556	50.350
Total		100.000

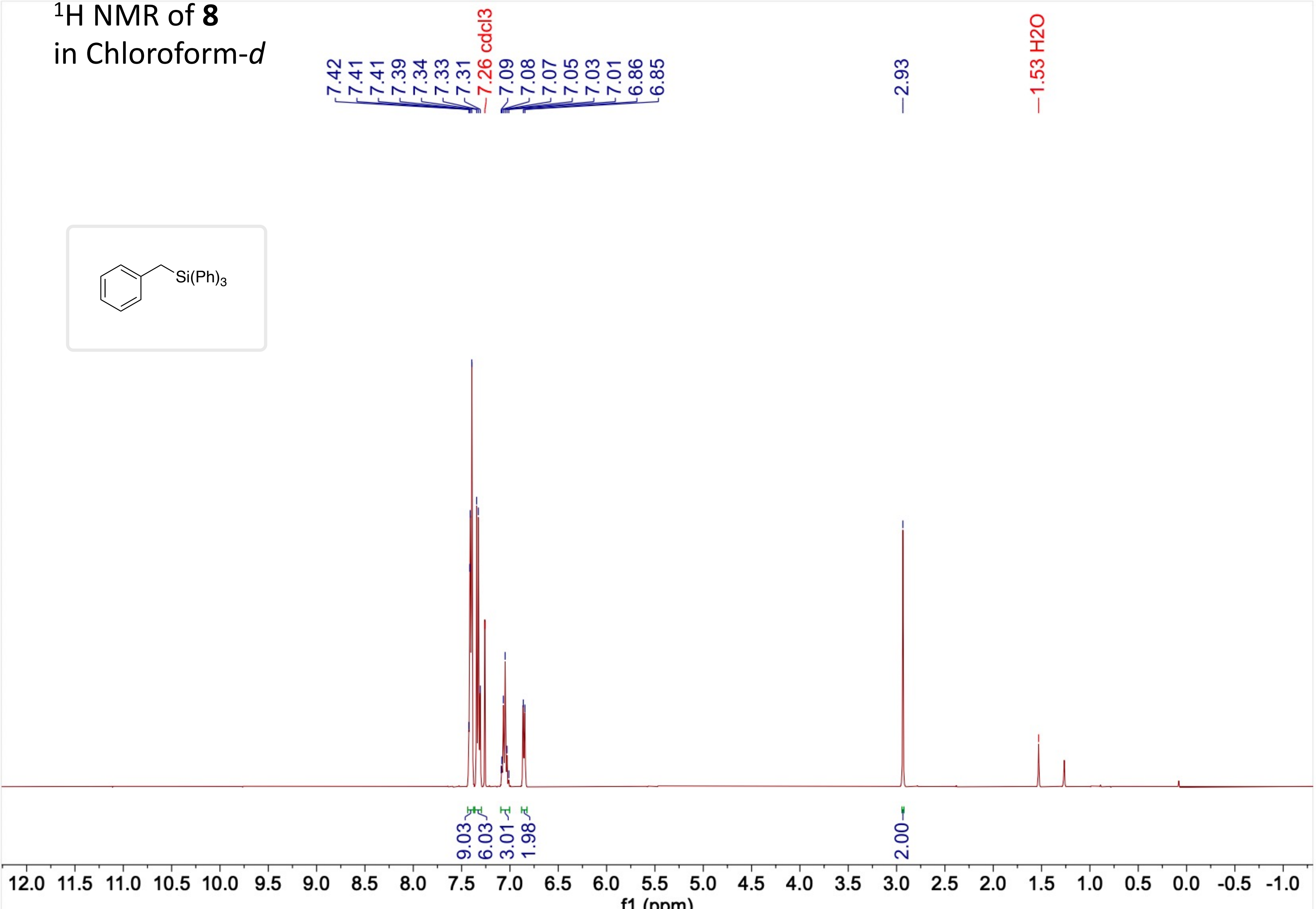


Peak Table

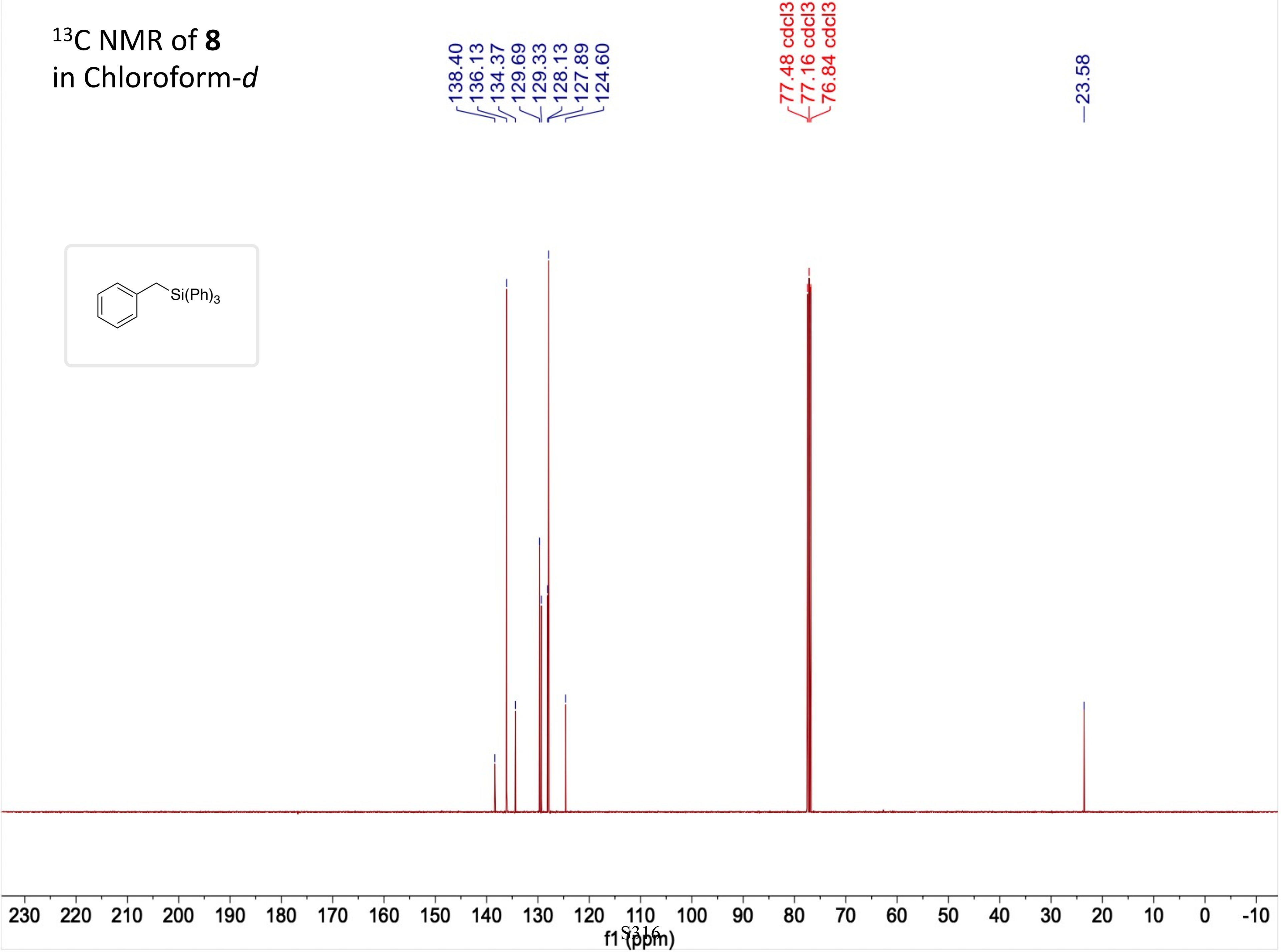
PDA Ch1 209nm

Peak#	Ret. Time	Area%
1	7.312	49.467
2	7.588	50.533
Total		100.000

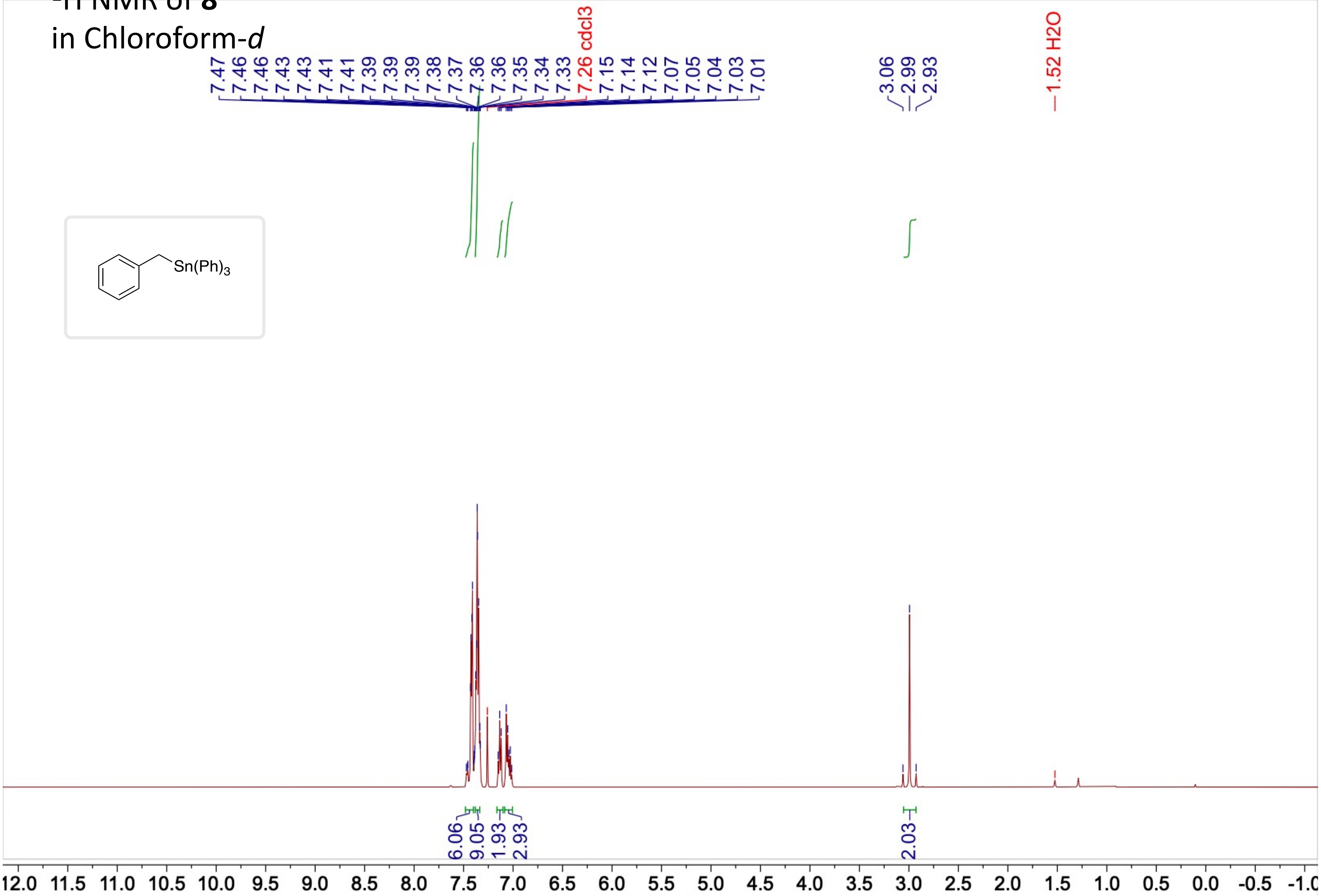
^{1}H NMR of **8**
in Chloroform-*d*



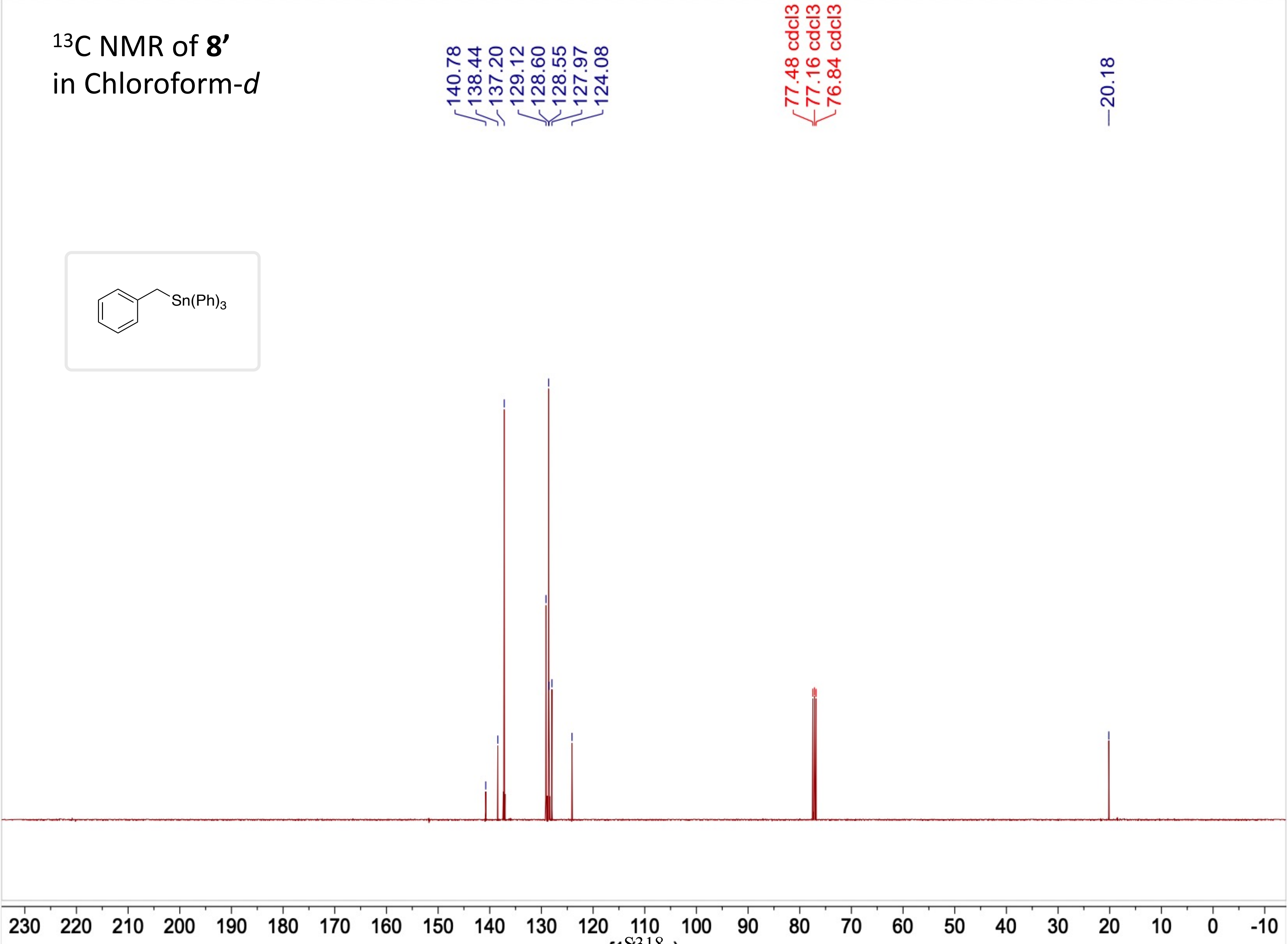
^{13}C NMR of **8**
in Chloroform-*d*



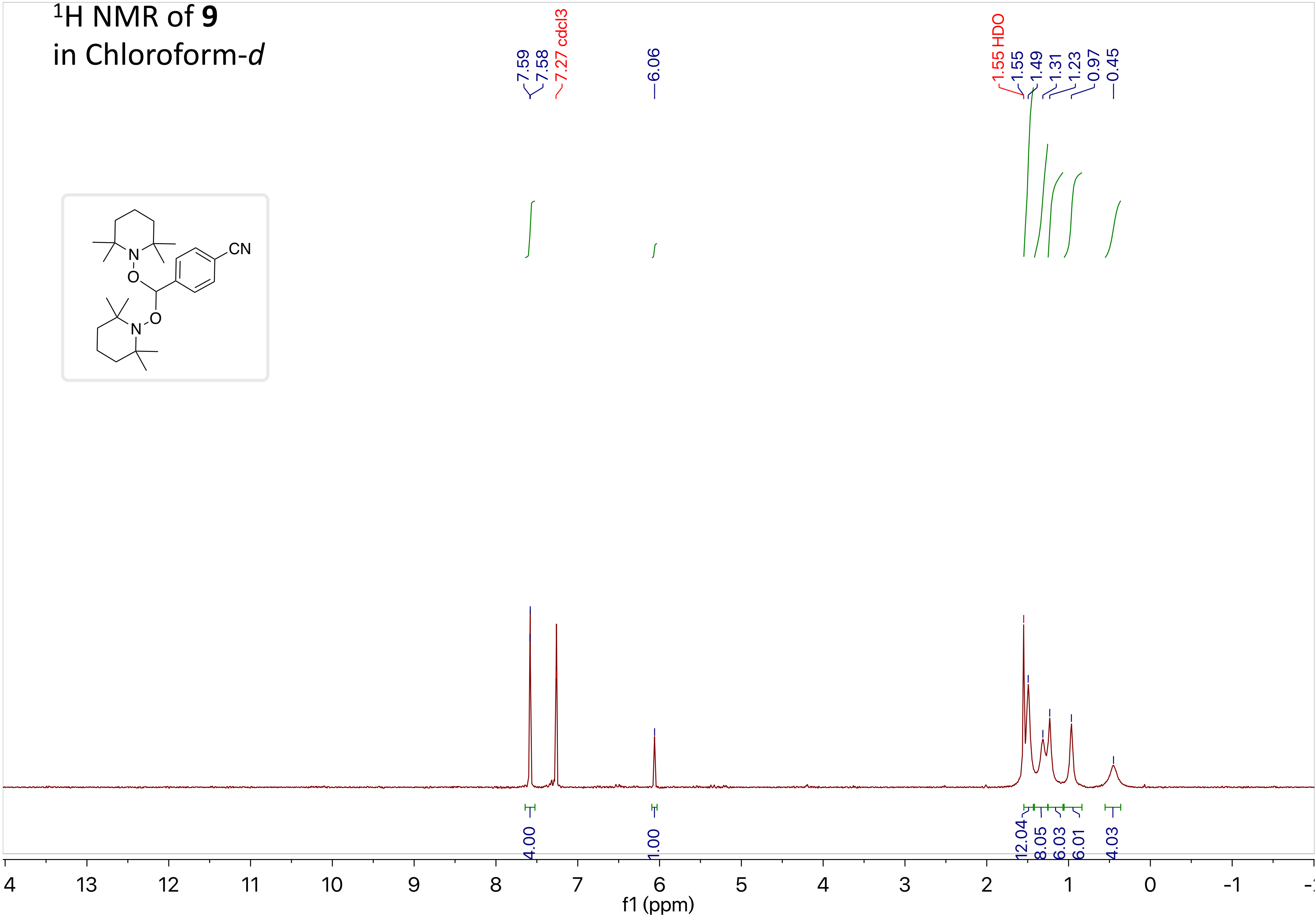
[1]H NMR of **8'**
in Chloroform-*d*



^{13}C NMR of **8'** in Chloroform-*d*



^{1}H NMR of **9** in Chloroform-*d*



^{13}C NMR of **9**
in Chloroform-*d*