

Supporting Information for
Discovery and Elucidation of Counteranion Dependence in Photoredox Catalysis

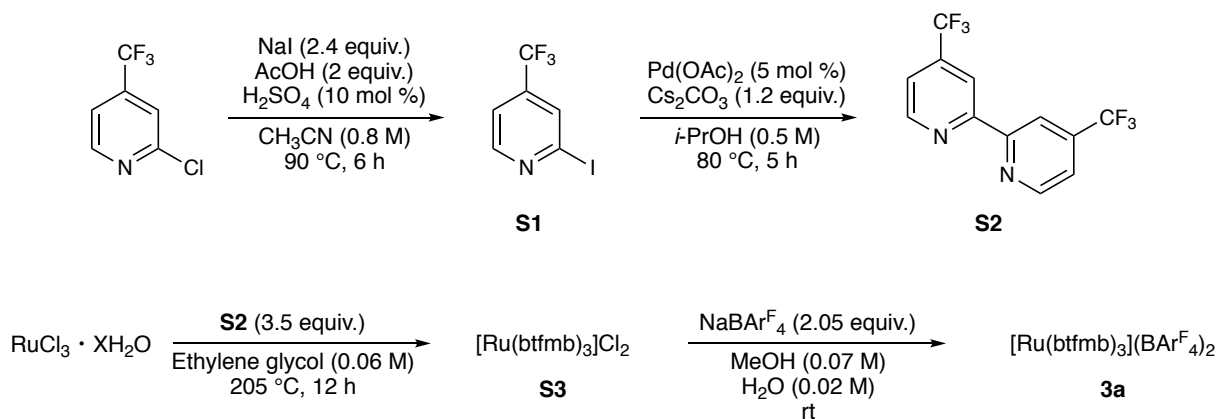
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I. General Experimental Information for Synthetic Studies

Dichloromethane (CH₂Cl₂), tetrahydrofuran, diethyl ether (Et₂O), toluene, and acetonitrile (CH₃CN) were dried by passage through columns of activated alumina. Ethylene glycol was used as received. Water was purified by a Milli-Q system (Millipore Corporation) to achieve a resistivity of 18.2 MΩ cm⁻¹ at 25 °C. Reagents were purchased from commercial sources unless otherwise noted. Chromatography was performed with Purasil 60 Å silica gel (230–400 mesh) or with neutral alumina (Aldrich product # 11028). High vacuum refers to a reduced pressure that was measured to be 60 mTorr or lower using a McLeod gauge. Anethole was purified by chromatography on silica gel (hexanes: EtOAc = 20:1) and was subsequently submitted to fractional distillation under high vacuum at 95 °C. Purified anethole was stored at room temperature in a vial wrapped in aluminum foil. Isoprene was fractionally distilled from CaH₂ under N₂ at 45 °C and stored at 5 °C. ¹H, ¹³C, ¹⁹F, ¹¹B, and ³¹P NMR data for all previously uncharacterized compounds were obtained using Bruker Avance III 400 MHz and Bruker Avance III 500 MHz spectrometers and are referenced to TMS (0.00 ppm) or residual protio solvent signal. The NMR and mass spectroscopy facilities are supported by the NSF (CHE-1048642), the NIH (S10OD020022-1), the University of Wisconsin, and a generous gift from Paul J. and Margaret M. Bender.

II. Synthesis of Polypyridyl Ru(II) Complexes



2-Iodo-4-(trifluoromethyl)pyridine (S1). A 250 mL round-bottom flask with a magnetic stirrer was charged with 2-chloro-4-(trifluoromethyl)pyridine (8.00 g, 44.1 mmol, 5.67 mL, 1 equiv.), NaI (15.8 g, 106 mmol, 2.4 equiv.), glacial AcOH (5.04 mL, 88.1 mmol, 2 equiv.), and CH₃CN (55 mL, 0.8 M). To the resulting faint yellow solution was added conc. H₂SO₄ (239 μL, 4.41 mmol, 0.1 equiv.) in a single portion, and the reaction turned bright red. The

reaction vessel was fitted with a water-cooled condenser before being placed in a 90 °C oil bath for 6 h. The resulting brown reaction was allowed to cool to rt, and the solvent was removed *in vacuo*. To the remaining residue was added H₂O (75 mL) and, with rapid stirring, solid NaHCO₃ until the reaction mixture reached pH = 7. The aqueous mixture was transferred to a separatory funnel and extracted with CH₂Cl₂ (3 x 100 mL). Residual iodine was removed by washing the combined organic phases with a saturated solution of sodium bisulfite (2 x 75 mL). The organic layer was washed with brine (1 x 50 mL), dried over Na₂SO₄, filtered, and concentrated *in vacuo* to afford a yellow oil that was purified via flash column chromatography on silica (hexanes:EtOAc = 20:1) to afford 8.25 g (30.2 mmol, 69% yield) of **S1** as a clear oil. ¹H NMR (500.0 MHz, CDCl₃) δ 8.57 (d, *J* = 5.1 Hz, 1H), 7.96 (s, 1H), 7.49 (d, *J* = 5.1 Hz, 2H); ¹³C NMR (125.7 MHz, CDCl₃) δ 151.6, 139.5 (q, *J*_{C-F} = 34.3 Hz), 130.7 (q, *J*_{C-F} = 3.6 Hz), 121.6 (q, *J*_{C-F} = 273.3 Hz), 118.5 (q, *J*_{C-F} = 3.6 Hz), 118.0. These data are consistent with previously reported values.¹ Note: the iodopyridine is unstable towards long-term storage and should be used immediately or stored in a cool, dark place.

4,4'-Bis(trifluoromethyl)-2,2'-bipyridine (S2). A 250 mL round-bottom flask with a magnetic stirrer was charged with Pd(OAc)₂ (339 mg, 1.51 mmol, 0.05 equiv.) and Cs₂CO₃ (11.8 g, 36.3 mmol, 1.2 equiv.). The flask was equipped with a water-cooled condenser and was purged with N₂. Subsequently, a solution of **S1** (8.25 g, 30.2 mmol, 1 equiv.) in *i*-PrOH (60 mL, 0.5 M) was added. The reaction was heated to an oil bath temperature of 80 °C under N₂ for 5 h. The reaction was allowed to cool to room temperature and was filtered through a pad of Celite. The filter cake was washed with CH₂Cl₂ (3 x 50 mL), and the volatiles were removed *in vacuo* to afford a brown solid. Insoluble impurities were removed by washing the brown solid with CH₂Cl₂ and filtering. The solvent was removed *in vacuo*, and the crude product was purified via flash column chromatography on silica (hexanes:EtOAc = 10:1) to afford 2.46 g (8.41 mmol, 56% yield) of **S2** as a bright yellow solid. ¹H NMR (500.0 MHz, CDCl₃) δ 8.89 (d, *J* = 5.0 Hz, 2H), 8.73 (s, 2H), 7.59 (d, *J* = 5.0 Hz, 2H); ¹³C NMR (125.7 MHz, CDCl₃) δ 156.1, 150.3, 139.6 (q, *J*_{C-F} = 34.3 Hz), 122.8 (q, *J*_{C-F} = 273.3 Hz), 119.9 (q, *J*_{C-F} = 3.6 Hz), 117.2 (q, *J*_{C-F} = 3.6 Hz). These data are consistent with previously reported values.²

[Ru(btmb)₃]Cl₂ (S3). A 100 mL round-bottom flask with a magnetic stirrer was charged with RuCl₃•XH₂O (Strem Chemicals) (379 mg, 1.83 mmol, 1 equiv.) and **S2** (1.87 g, 6.40 mmol, 3.5 equiv.). The flask was equipped with a water-cooled condenser and was purged with N₂. Subsequently, ethylene glycol (30 mL, 0.06 M) was added, and the reaction was heated to an oil bath temperature of 205 °C under N₂ for 12 h. The resulting dark red/black mixture was allowed to cool to rt. The crude reaction was added dropwise to a rapidly stirred mixture of Et₂O/acetone (1:1, 250 mL) over 15 min. The resulting homogeneous mixture was transferred to a dropping funnel and added slowly to a rapidly stirred solution of Et₂O (1.4 L) over 1 h. A red solid crashed out of solution during the addition and was isolated via slow filtration on a medium-porosity fritted funnel. The solid was washed with Et₂O (2 x 30 mL), then passed through the fritted funnel with CH₃CN. The volatiles were removed and the solid was dried under high vacuum. Thereafter, the dry solid was dissolved in CH₃OH (100 mL) and added dropwise to a rapidly stirred solution of Et₂O (350 mL) over 45 min. A red solid precipitated throughout the addition and was isolated on a fritted funnel and washed with Et₂O (2 x 30 mL). The purified solid was dried under high vacuum at 70 °C for 2 h to afford 1.40 g (1.38 mmol, 76% yield) of **S3** as a red solid. ¹H NMR (500.0 MHz, CD₃OD) δ 9.40 (s, 6H), 8.15 (d, *J* = 5.9 Hz, 6H), 7.87 (dd, *J* = 5.9, 1.6 Hz, 6H); ¹³C NMR (125.7 MHz, CD₃OD) δ 159.1, 155.0, 141.1 (q, *J*_{C-F} = 35.8 Hz), 125.6 (q, *J*_{C-F} = 3.3 Hz), 123.5 (q, *J*_{C-F} = 274.6 Hz), 123.3 (q, *J*_{C-F} = 3.3 Hz); ¹⁹F NMR (376.5 MHz, CD₃OD) δ -66.1. HRMS (+ p): calculated for C₃₆H₁₈ClF₁₈N₆Ru²⁺ [*M*²⁺ + A⁻]⁺ = 1013.0032. Found = 1013.0039. Calculated for C₃₆H₁₈F₁₈N₆Ru²⁺ [*M*]²⁺ = 489.0169. Found = 489.0166.

[Ru(btmb)₃](BAR^F₄)₂ (3a). A 25 mL round-bottom flask with a magnetic stirrer was charged with **S3** (100 mg, 0.0987 mmol, 1 equiv.) and H₂O (4.2 mL, 0.02 M). To this solution was added a solution of NaBAR^F₄ (Alfa Aesar) (179 mg, 0.202 mmol, 2.05 equiv.) in CH₃OH (1.4 mL, 0.07 M). An orange precipitate immediately formed, and the solution became difficult to stir. Additional H₂O (2 mL) was added, stirring was continued for 10 min, and the orange solid was isolated on a fritted funnel, washed with H₂O (2 x 3 mL), and dried. The dried solid was dissolved in acetone/CH₂Cl₂ (1:1, ~5 mL) and purified via gravity elution through a column of neutral Al₂O₃ using CH₂Cl₂ as the eluent. The first band that eluted was determined to be the desired product, so these fractions were combined, the

volatiles were removed *in vacuo*, and the resulting solid was dried under high vacuum. This residue was dissolved in a minimum volume of CH₂Cl₂ (5 mL) and passed through a 0.2 μm Whatman PTFE filter to remove residual NaBAr^F₄. To the filtrate was slowly added hexanes (30 mL) and an orange solid precipitated. The solid was isolated on a fritted funnel and dried under high vacuum to afford 220 mg (0.0819 mmol, 83% yield) of **3a** as a reddish/orange solid. ¹H NMR (500.0 MHz, CD₃OD) δ 9.41 (s, 6H), 8.14 (d, *J* = 5.9 Hz, 6H), 7.86 (dd, *J* = 5.9, 1.6 Hz, 6H), 7.60 (m, 24H); ¹³C NMR (125.7 MHz, CD₃OD) δ 162.9 (q, *J*_{C-B} = 49.7 Hz), 159.2, 154.8, 141.4 (q, *J*_{C-F} = 35.9 Hz), 135.8, 130.4 (qq, *J*_{C-F} = 31.6, 3.1 Hz), 125.7 (q, *J*_{C-F} = 271.6 Hz), 125.5 (q, *J*_{C-F} = 3.5 Hz), 124.1 (q, *J*_{C-F} = 273.8 Hz), 123.3 (q, *J*_{C-F} = 3.2 Hz), 118.5 (m); ¹⁹F NMR (376.5 MHz, CD₃OD) δ -64.3, -66.2; ¹¹B NMR (128.3 MHz, CD₃OD) δ -6.77. HRMS (+ p): calculated for C₃₆H₁₈F₁₈N₆Ru²⁺ [M]²⁺ = 489.0169. Found = 489.0167. (- p): calculated C₃₂H₁₂BF₂₄ [A⁻] = 863.0654. Found = 863.0653.

[Ru(btffmb)₃](OTf)₂ (3b). A 20 mL scintillation vial with a magnetic stirrer was charged with **S3** (250 mg, 0.25 mmol, 1 equiv.) and H₂O (10 mL, 0.025 M). To this solution was added a solution of sodium triflate (NaOTf, 370 mg, 1.7 mmol, 6.9 equiv.) in H₂O (3 mL, 0.57 M). An orange precipitate immediately formed, and the solution became difficult to stir. Additional H₂O (4 mL) was added and stirring was continued for 10 min, and the orange solid was isolated on a fritted funnel, washed with H₂O (2 x 5 mL), and dried. The dried product was sonicated in H₂O (5 mL) for 2 min and isolated on a fritted funnel. The solid was collected and dried under high vacuum to afford 200 mg (0.157 mmol, 67% yield) of **3b** as a reddish/orange solid. ¹H NMR (500.0 MHz, CD₃OD) δ 9.34 (s, 6H), 8.14 (d, *J* = 5.9 Hz, 6H), 7.84 (dd, *J* = 5.9, 1.2 Hz, 6H); ¹³C NMR (125.7 MHz, CD₃OD) δ 159.1, 154.9, 141.2 (q, *J*_{C-F} = 35.7 Hz), 125.5 (q, *J*_{C-F} = 3.4 Hz), 123.5 (q, *J*_{C-F} = 273.4 Hz), 123.3 (m), 121.6 (q, *J*_{C-F} = 318.4 Hz); ¹⁹F NMR (376.5 MHz, CD₃OD) δ -66.13, -80.11. HRMS (+ p): calculated for C₃₇H₁₈F₂₁N₆O₃SRu⁺ [M²⁺ + A⁻]⁺ = 11263.9864. Found = 1126.9866. Calculated for C₃₆H₁₈F₁₈N₆Ru²⁺ [M]²⁺ = 489.0169. Found = 489.0164. (- p): calculated CF₃O₃S⁻ [A⁻] = 148.9526. Found = 148.9526.

Note: the mass spectrum of **3b** included a signal corresponding to the mass of the monoanionic ruthenium tris(trifluoromethanesulfonate), [[Ru(btffmb)₃](OTf)₃]⁻ complex. This indicates a strong interaction between the ruthenium catalyst and triflate anions, consistent with the conclusions of this paper. Calculated for C₃₉H₁₈F₂₇N₆O₉S₃Ru⁻ [M + 3A⁻]⁻ = 1424.8915. Found = 1424.8924.

Sodium 3,5-bis(trifluoromethyl)benzenesulfonate (Ar^FSO₃Na) (S4). A 25 mL round-bottom flask with a magnetic stirrer was charged with 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (3.35 g, 10.70 mmol) and millipore H₂O (12 mL, 0.9 M). A reflux condenser was attached, and the heterogeneous reaction was heated to an oil bath temperature of 107 °C and stirred for 3 h. Thereafter, the reaction was briefly cooled, and a distillation head was attached. The residual H₂O and dissolved HCl (g) were distilled away, and the resulting pale-yellow solid remaining in the distillation flask was dried *in vacuo*. This solid was dissolved in H₂O (10 mL), and 4 M NaOH was added to the resulting homogeneous solution to achieve pH = 7. Throughout this process, a white solid precipitated from solution and was isolated. Two successive recrystallizations from boiling H₂O (~10 mL) followed by drying under high vacuum in a desiccator over P₂O₅ for 12 h provided 2.47 g (7.81 mmol, 73% yield) of **S4** as colorless needles. ¹H NMR (500.0 MHz, CD₃OD) δ 8.34 (s, 2H), 8.06 (s, 1H), ¹³C NMR (125.7 MHz, CD₃OD) δ 149.6, 133.0 (q, *J*_{C-F} = 33.8 Hz), 127.7 (q, *J*_{C-F} = 3.5 Hz), 124.8 (septet, *J*_{C-F} = 3.8 Hz), 124.6 (q, *J*_{C-F} = 272.4 Hz); ¹⁹F NMR (376.5 MHz, CD₃OD) δ -64.5.

[Ru(btffmb)₃](Ar^FSO₃)₂ (3d). A 50 mL round-bottom flask with a magnetic stirrer was charged with **S3** (450 mg, 0.444 mmol, 1 equiv.), **S4** (393 mg, 1.24 mmol, 2.8 equiv.) and MeOH (22 mL, 0.02 M). The flask was fitted with a reflux condenser, and the reaction was heated to an oil bath temperature of 75 °C for 90 min. After cooling to room temperature, MeOH was removed *in vacuo* to afford a red residue that was dissolved in acetone/CH₂Cl₂ (1:1, ~8 mL) and subsequently purified via gravity elution through a column of neutral Al₂O₃ using acetone/CH₂Cl₂ (1:1) as the eluent. The first band that eluted was determined to be the desired product, so these fractions were combined, and the volatiles were removed *in vacuo*. The product was dissolved in a minimum volume

of EtOAc and passed through a 0.2 μm Whatman PTFE filter to remove residual **S4**. The filtrate was layered hexanes and left to crystallize at 5 $^{\circ}\text{C}$. The red needles that formed were isolated, washed with hexanes, and dried under high vacuum at 100 $^{\circ}\text{C}$ for 3 h to obtain 593 mg (0.379 mmol, 85% yield) of **3d** as a reddish/orange solid. ^1H NMR (500.0 MHz, CD_3OD) δ 9.36 (s, 6H), 8.23 (s, 4H), 8.15 (d, $J = 5.9$ Hz, 6H), 8.05 (s, 2H), 7.85 (d, $J = 5.9$ Hz, 6H); ^{13}C NMR (125.7 MHz, CD_3OD) δ 159.3, 155.1, 149.7, 141.5 (q, $J_{\text{C-F}} = 35.5$ Hz), 133.0 (q, $J_{\text{C-F}} = 33.6$ Hz), 127.6 (q, $J_{\text{C-F}} = 3.6$ Hz), 125.7 (m), 124.8 (m), 124.7 (q, $J = 277.7$ Hz), 123.9 (q, $J_{\text{C-F}} = 273.2$ Hz), 123.4 (q, $J = 3.6$ Hz); ^{19}F NMR (376.5 MHz, CD_3OD) δ -64.5, -66.1. HRMS (+ p): calculated for $\text{C}_{44}\text{H}_{21}\text{F}_{18}\text{N}_6\text{O}_3\text{SRu}^+ [\text{M}^{2+} + \text{A}^-]^+$ = 1271.0051. Found = 1271.0053. Calculated for $\text{C}_{36}\text{H}_{18}\text{F}_{18}\text{N}_6\text{Ru}^{2+} [\text{M}]^{2+}$ = 489.0169. Found = 489.0167. (- p): calculated $\text{C}_8\text{H}_3\text{F}_6\text{O}_3\text{S}^- [\text{A}^-]$ = 292.9713. Found = 292.9714.

[Ru(btmb)₃](OTs)₂ (3e). Prepared according to the procedure outlined for **3d** using **S3** (80.5 mg, 0.0795 mmol, 1 equiv.), sodium *p*-toluenesulfonate (61.2 mg, 0.315 mmol, 2.2 equiv.) and MeOH (8.0 mL, 0.01 M). Obtained 90 mg (0.0729 mmol, 51% yield) of **3e** as a reddish/orange solid. ^1H NMR (500.0 MHz, CD_3OD) δ 9.36 (s, 6H), 8.15 (d, $J = 5.9$ Hz, 6H), 7.83 (d, $J = 5.9$ Hz, 6H), 7.64 (d, $J = 8.1$ Hz, 4H), 7.21 (d, $J = 8.1$ Hz, 4H), 2.37 (s, 6H); ^{13}C NMR (125.7 MHz, CD_3OD) δ 159.3, 155.1, 143.8, 141.8, 141.5 (q, $J_{\text{C-F}} = 35.4$ Hz), 129.9, 127.0, 125.7 (q, $J_{\text{C-F}} = 3.4$ Hz), 123.9 (q, $J_{\text{C-F}} = 272.7$ Hz), 123.4 (q, $J_{\text{C-F}} = 3.4$ Hz), 21.4; ^{19}F NMR (376.5 MHz, CD_3OD) δ -66.1. HRMS (+ p): calculated for $\text{C}_{43}\text{H}_{23}\text{F}_{18}\text{N}_6\text{O}_3\text{SRu}^+ [\text{M}^{2+} + \text{A}^-]^+$ = 1149.0465. Found = 1149.0475. Calculated for $\text{C}_{36}\text{H}_{18}\text{F}_{18}\text{N}_6\text{Ru}^{2+} [\text{M}]^{2+}$ = 489.0169. Found = 489.0169. (- p): calculated $\text{C}_7\text{H}_7\text{O}_3\text{S}^- [\text{A}^-]$ = 171.0121. Found = 171.0122.

Sodium 3,5-bis(trifluoromethyl)benzenecarboxylate (Ar^FCO₂Na) (S5). To a 250 mL round-bottom flask was added 3,5-bis(trifluoromethyl)benzenecarboxylic acid (1g, 3.90 mmol, 1 equiv.), NaOH (138 mg, 3.45 mmol, 0.95 equiv.), and CH_3CN (50 mL, 0.08 M). The reaction was stirred for 90 min and the solvent was removed under vacuum. To remove leftover carboxylic acid, the product was suspended in diethyl ether and filtered. The diethyl ether was removed, and 711 mg (2.54 mmol, 74%) of **S5** was isolated as a white power. ^1H NMR (500.0 MHz, CD_3OD) δ 8.52 (s, 2H), 8.00 (s, 1H); ^{13}C NMR (125.7 MHz, CD_3OD) δ 169.7, 140.68, 130.1 (q, $J_{\text{C-F}} = 33.3$ Hz), 129.1 (q, $J_{\text{C-F}} = 3.2$ Hz), 123.5 (q, $J_{\text{C-F}} = 272.4$ Hz), 122.9 (sept, $J_{\text{C-F}} = 3.9$ Hz); ^{19}F NMR (376.5 MHz, CD_3OD) δ -64.3.

[Ru(btmb)₃](Ar^FCO₂)₂ (3f). Prepared according to the procedure outlined for **3d** using **S3** (150 mg, 0.143 mmol, 1 equiv.), **S5** (43.2 mg, 0.222 mmol, 2.8 equiv.), and MeOH (4.0 mL, 0.02 M). Obtained 77.1 mg (0.0584 mmol, 73% yield) of **3f** as a reddish/orange solid. ^1H NMR (500.0 MHz, CD_3OD) δ 9.31 (s, 6H), 8.36 (s, 4H), 8.07 (d, $J = 5.9$ Hz, 6H), 7.89 (s, 2H), 7.76 (dd, $J_{\text{C-F}} = 5.9, 1.6$ Hz, 6H); ^{13}C NMR (125.7 MHz, CD_3OD) δ 169.3, 157.1, 153.4, 140.7, 139.9 (q, $J_{\text{C-F}} = 35.8$ Hz), 130.8 (q, $J_{\text{C-F}} = 33.1$ Hz), 129.1 (q, $J_{\text{C-F}} = 3.6$ Hz), 124.1 (q, $J_{\text{C-F}} = 3.5$ Hz), 123.5 (q, $J_{\text{C-F}} = 271.9$ Hz), 122.9 (sept, $J_{\text{C-F}} = 123.4$ Hz), 122.1 (q, $J_{\text{C-F}} = 273.3$ Hz), 121.9 (q, $J_{\text{C-F}} = 3.6$ Hz); ^{19}F NMR (376.5 MHz, CD_3OD) δ -64.3, -66.1. HRMS (+ p): calculated for $\text{C}_{45}\text{H}_{21}\text{F}_{24}\text{N}_6\text{O}_2\text{Ru}^+ [\text{M}^{2+} + \text{A}^-]^+$ = 1271.0051. Found = 1271.0053. Calculated for $\text{C}_{36}\text{H}_{18}\text{F}_{18}\text{N}_6\text{Ru}^{2+} [\text{M}]^{2+}$ = 489.0169. Found = 489.0167. (- p): calculated $\text{C}_9\text{H}_3\text{F}_6\text{O}_2^- [\text{A}^-]$ = 257.0043. Found = 257.0044.

[Ru(btmb)₃](PF₆)₂ (3c). To a 25 mL round-bottom flask with a magnetic stirrer was charged **S3** (261 mg, 0.258 mmol, 1 equiv.) and millipore H_2O (13 mL, 0.02 M). To the resulting dark red solution was added ammonium hexafluorophosphate (88.2 mg, 0.541 mmol, 2.1 equiv.). A reddish/orange solid immediately precipitated and stirring was continued for 10 min before the solid was isolated on a fritted funnel, washed with H_2O (2 x 3 mL), and dried. Recrystallization from an acetone/ Et_2O bilayer provided 252 mg (0.199 mmol, 77% yield) of **3c** as a reddish/orange solid. ^1H NMR (500.0 MHz, $(\text{CD}_3)_2\text{SO}$) δ 9.57 (s, 6H), 8.03 (d, $J = 6.0$ Hz, 6H), 7.88 (dd, $J = 6.0, 1.4$ Hz, 6H); ^{13}C NMR (125.7 MHz, $(\text{CD}_3)_2\text{SO}$) δ 157.4, 153.8, 137.9 (q, $J_{\text{C-F}} = 34.7$ Hz), 124.0 (q, $J_{\text{C-F}} = 3.4$ Hz), 122.5 (q, $J_{\text{C-F}} = 273.4$ Hz), 121.9 (q, $J_{\text{C-F}} = 3.4$ Hz); ^{19}F NMR (376.5 MHz, $(\text{CD}_3)_2\text{SO}$) δ -63.0, -70.1 (d, $J_{\text{F-P}} = 711.2$ Hz); ^{31}P NMR (162.0 MHz, $(\text{CD}_3)_2\text{SO}$) δ -144.2 (septet, $J_{\text{P-F}} = 711.5$ Hz). These data are consistent with previously reported values.³ $\text{C}_{36}\text{H}_{18}\text{F}_{24}\text{N}_6\text{PRu}^+ [\text{M}^{2+} + \text{A}^-]^+$ = 1122.9990. Found = 1123.0004. Calculated for $\text{C}_{36}\text{H}_{18}\text{F}_{18}\text{N}_6\text{Ru}^{2+} [\text{M}]^{2+}$ = 489.0169. Found = 489.0171. (- p): calculated $\text{PF}_6^- [\text{A}^-]$ = 144.9647. Found = 144.9648.

III. Visible Light Photocatalysis of Radical Cation [4+2] Diels–Alder Cycloadditions

General procedure for experiments in Table 1: A stock solution of anethole (54.6 mg, 55.3 μL , 0.368 mmol), isoprene (75.3 mg, 111 μL , 1.11 mmol), and trimethyl(phenyl)silane internal standard (55.4 mg, 63.4 μL , 0.368 mmol) in dry CH_2Cl_2 (4.38 mL) was prepared. 810 μL aliquots of this stock solution were added to oven-dried 25 mL Schlenk tubes containing the appropriate ruthenium photocatalyst (6.14×10^{-4} mmol, 1 mol%). This afforded reaction mixtures containing anethole (9.1 mg, 0.0614 mmol, 1 equiv.), isoprene (12.5 mg, 0.184 mmol, 3 equiv.), and trimethyl(phenyl)silane internal standard (9.2 mg, 0.0614 mmol, 1 equiv.) in CH_2Cl_2 (0.77 mL, 0.08 M). A stir bar was added to each reaction. The solutions were submitted to three freeze-pump-thaw cycles, purged with N_2 , and irradiated at room temperature using a 23 W compact fluorescent light (CFL) bulb. The yields and amount of remaining anethole in Table 1 were determined by ^1H NMR analysis of the unpurified reaction mixtures. ^1H NMR analysis of the cycloadduct was consistent with previously reported values.⁴

General procedure for experiments with anion binder 7 in Table 4: A stock solution of anethole, isoprene, and trimethyl(phenyl)silane internal standard in dry CH_2Cl_2 was added to oven-dried 25 mL Schlenk tubes containing the appropriate ruthenium photocatalyst (6.14×10^{-4} mmol, 1 mol%) and thiophosphotriamide **7** (9.2 mg, 0.0123 mmol, 20 mol%).⁵ A stir bar was added to each reaction. The solutions were submitted to three freeze-pump-thaw cycles, purged with N_2 , and irradiated at room temperature using a 23 W compact fluorescent light (CFL) bulb. The yields in Table 4 were determined by ^1H NMR analysis of the unpurified reaction mixtures.

IV. UV-Vis Spectra, Photoluminescence Spectra, and Chain Length Measurements

UV-Vis spectroscopy: Solution spectra were measured in CH_2Cl_2 or acetonitrile at a ruthenium photocatalyst concentration of 3.9×10^{-5} M. UV-vis absorption spectra were recorded at room temperature using a Cary 50 spectrophotometer over a scan range of 600 nm \rightarrow 200 nm at a scan rate of 300 nm/min and resolution of 0.5 nm.

Steady-state photoluminescence spectroscopy: Steady-state photoluminescence spectra were obtained at room temperature using a Hitachi F4500 fluorescence spectrophotometer with a scan range of 478 nm \rightarrow 678 nm at a scan rate of 240 nm/min and resolution of 0.5 nm. The excitation wavelength was the peak of the MLCT absorbance spectra. Emission and excitation slit widths were maintained at 5 nm.

Solution spectra were measured in CH_2Cl_2 or acetonitrile at a ruthenium photocatalyst [Ru] concentration of 3.9×10^{-5} M. The following sample preparation procedure was carried out in the dark. Samples were degassed by three freeze-pump-thaw cycles and subsequently transferred to fluorescence cuvettes that had been purged with N_2 for 30 min. All photoluminescence spectra were acquired normal to the incident beam.

Excited-state photoluminescence quenching experiments were carried out as follows: the luminescence intensity of a 3.9×10^{-5} M solution of [Ru] in CH_2Cl_2 was measured. Subsequently, aliquots of a 1.6×10^{-2} M stock solution of anethole quencher in CH_2Cl_2 were added to 2.0 mL of 7.8×10^{-5} M solutions of [Ru] in CH_2Cl_2 . The final solution volume was adjusted to 4.0 mL via dilution with CH_2Cl_2 . Samples were degassed as described above, and the luminescence intensities were determined. The ratio of unquenched (F_0) to quenched (F) photoluminescence intensity was plotted against [anethole]. The data were linear and followed Stern–Volmer kinetics. A linear regression yielded the Stern–Volmer constants (K_{SV}) and division by the unquenched excited-state lifetime provided the bimolecular quenching rate constants (k_q).

The effect of thiophosphotriamide **7** on the photoluminescence of the $[\text{Ru}(\text{btfmb})_3](\text{Ar}^{\text{F}}\text{SO}_3)_2$ photocatalyst was investigated as follows: $[\text{Ru}(\text{btfmb})_3](\text{Ar}^{\text{F}}\text{SO}_3)_2$ (**3d**, 15.3 mg, 9.8 μmol) was dissolved in CH_2Cl_2 (25 mL) to produce a 3.9×10^{-4} M stock solution. A 10 mL aliquot of the stock solution was diluted to 50 mL with CH_2Cl_2 to produce a final concentration of 7.8×10^{-5} M. Thiophosphotriamide **7** (81.5 mg, 0.109 mmol) was dissolved in CH_2Cl_2 to produce a 0.0109 M solution. Both solutions were transferred to a respective 25 mL Schlenk tubes (8 mL of solution **7**, 14 mL of solution **3d**). To another Schlenk tube was added 8 mL CH_2Cl_2 . The three Schlenk tubes were then subjected to 3 freeze-pump-thaw cycles. Aliquots of each solution were transferred under N_2 to a N_2 sparged cuvette. The ruthenium concentration was maintained at 4.0×10^{-5} M, while the concentration of **7** was varied through different

addition volumes of the stock solution. The neat CH₂Cl₂ was used to maintain an overall total volume of 3 mL in the cuvette.

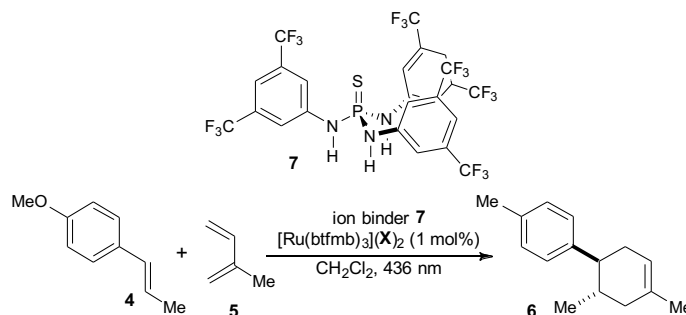
Sample preparation for excited-state lifetime measurements was as follows: a 3.9×10^{-5} M solution of the respective ruthenium photosensitizer in CH₂Cl₂ was degassed by 3 freeze-pump-thaw cycles and transferred to a N₂-purged cuvette using standard Schlenk technique. Lifetime measurements were collected by the frequency-domain method with an ISS K2 multifrequency cross-correlation phase and modulation fluorometer. The excitation source was intensity modulated through varying MHz frequencies at the sample's absorption maximum, producing shifts in the intensity and phase of fluorescence emission. Comparison to a standard (in this case fluorescein and glycogen) allows lifetime determination. Data was analyzed in Vinci (ISS).

Chain Length: Chain lengths of radical cation Diels–Alder cycloadditions were determined as follows. The quantum yields (Φ) for the respective reactions were determined by the method outlined by Cismesia and Yoon.⁶ To ascertain chain length, the following formula was employed:

$$\text{chain length} = \frac{\Phi(\tau^{-1} + k_{q,\text{anethole}}[\text{anethole}] + k_{q,\text{isoprene}}[\text{isoprene}] + k_{q,[2+2]}[2 + 2])}{k_{q,\text{anethole}}[\text{anethole}]}$$

where τ is the excited-state lifetime of the respective photocatalyst ($\tau^{-1} = k_r + k_{nr}$), $k_{q,\text{anethole}}$, $k_{q,\text{isoprene}}$, and $k_{q,[2+2]}$ are the rates of excited-state quenching by the designated species, and [anethole], [isoprene], and [2+2] are the concentrations of the designated species. The [2+2] product results from homodimerization of anethole and forms in very small amounts (~2%) at low conversions of anethole. Furthermore, the rate of excited-state quenching by isoprene was very small. Therefore, the final two terms in the numerator were determined to be negligible, and thus were ignored. Using this formula, chain lengths were determined for radical cation Diels–Alder cycloadditions catalyzed by [Ru(btfmtb)₃](BAr^F₄)₂ (quantum yield = 26, chain length = 26) and [Ru(btfmtb)₃](Ar^FSO₃)₂ (quantum yield = 0.35, chain length = 0.40). Subsequently, a radical cation cycloaddition catalyzed by [Ru(btfmtb)₃](Ar^FSO₃)₂ was performed in the presence of thiophosphotriamide **7** (20 mol%) (quantum yield = 7, chain length = 8). Therefore, thiophosphotriamide **7** exerts its greatest effect on chain length. See Table S11.

Table S11. Quantum Yield and Chain Length of Diels–Alder Reaction



entry	counteranion (X)	H-bond cat 7	quantum yield	chain length
1	BAr ^F ₄ ⁻ (3a)	0 mol%	26	26
2	Ar ^F SO ₃ ⁻ (3d)	0 mol%	0.35	0.4
3	Ar ^F SO ₃ ⁻ (3d)	20 mol%	7	8

V. Cyclic Voltammetry Experiments

Cyclic voltammetry was performed on a BASi EC Epsilon potentiostat connected to a BASi C3 cell stand and analyzed on a PC using Epsilon software. A three-electrode setup was employed: Pt wire counter electrode, glassy carbon working electrode, and a Ag/AgNO₃ (0.01 M AgNO₃, 0.1 M *n*-Bu₄N⁺ PF₆⁻ in CH₃CN) quasi-reference electrode containing a polished silver wire immersed in the electrolyte solution. The entire assembly of this electrode was contained in a glass body, the tip of which consisted of a Vycor plug. The electrolyte solution in the electrode was replaced daily to ensure the Vycor plug was free of contaminants. With this setup, Fc/Fc⁺ (0.1 M *n*-Bu₄N⁺ PF₆⁻ in CH₃CN) was measured to be 0.093 V vs. Ag/AgNO₃. A typical experiment was performed as follows: dry solvent and *n*-Bu₄N⁺ X⁻ electrolyte (0.1 M) (for example, *n*-Bu₄N⁺ BAR^F₄⁻ was used in the analysis of [Ru(btmb)₃](BAR^F₄)₂) were introduced to the cell, the solution was sparged with dry N₂ with stirring for 5 min, and subsequently a voltammogram was recorded to establish background. Thereafter, the appropriate ruthenium catalyst complex (0.001 M) was introduced under N₂ and a second spectrum was collected. Finally, ferrocene internal standard (~0.001 M) was added, and a final voltammogram was collected. After referencing to ferrocene, voltammograms were referenced to SCE by adding 0.30 V to all potentials. Stirring was performed prior to each run to ensure exposure of electrodes to fresh analyte. The scan rate was typically 100 mV/s. Between each catalyst complex analyzed, the glassy carbon working electrode was polished on Al₂O₃, sonicated in ultrapure H₂O, and washed in the organic solvent used for analysis.

For experiments performed in CH₂Cl₂, the working and reference electrodes were placed as close as possible without touching to minimize Ohmic drop in the poorly conductive, highly resistive CH₂Cl₂ solvent. IR compensation experiments were performed in CH₂Cl₂ in the presence of an appropriate *n*-Bu₄N⁺ X⁻ electrolyte.⁷ The uncompensated resistance was found to vary slightly with *n*-Bu₄N⁺ X⁻ electrolyte and was typically between 550–850 Ohm. However, when IR compensation was applied, the half-wave potentials of both ferrocene and the catalyst redox couple of interest showed minimal (< 30 mV) shifts, and due to distortions sometimes introduced into the data by using IR compensation, compensation was not employed. It should be noted that all redox couples in CH₂Cl₂ exhibited quasi-reversible behavior, with 90 mV < ΔE_p < 180 mV (peak separation increased with increasing Lewis basicity of X⁻ in supporting electrolyte and catalyst complex) and 1.1 < i_p/i_{pa} < 1.4. Redox couples in CH₃CN exhibited reversible, Nernstian behavior.

Preparation of supporting electrolytes

Tetrabutylammonium tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate (*n*-Bu₄N⁺ BAR^F₄⁻) (S6). To a 25 mL round-bottom flask with a stir bar was added NaBAR^F₄ (1.33 g, 1.53 mmol, 1 equiv.) and distilled acetone (5.0 mL, 0.3 M). The solution was stirred until homogeneous, and subsequently, a solution of tetrabutylammonium chloride (426 mg, 1.53 mmol, 1 equiv.) in acetone (1.2 mL) was added. NaCl immediately precipitated from solution. The reaction was stirred for an additional 15 min before being filtered through a 0.2 μM Whatman filter. Acetone was removed *in vacuo*, and the resulting viscous oil was dried under high vacuum for 1 h. Thereafter, the oil was dissolved in CH₂Cl₂ (10 mL), filtered, and CH₂Cl₂ was removed *in vacuo*. The oil was again dried on high vacuum and crystallization was induced by cooling to -78 °C and allowing slow warming to room temperature under high vacuum. The resulting white solid was dried to constant mass to obtain 1.68 g (1.52 mmol, 99% yield) of S6 as a white, hygroscopic solid. ¹H NMR (500.0 MHz, CDCl₃) δ 7.69 (s, 8H), 7.53 (s, 4H), 2.99 (m, 8H), 1.53 (m, 8H), 1.33 (dq, *J* = 14.8, 7.2 Hz, 8H), 0.93 (t, *J* = 7.2 Hz, 12H); ¹³C NMR (125.7 MHz, CDCl₃) δ 161.7 (q, *J*_{C-B} = 49.6 Hz), 134.8, 128.8 (qq, *J*_{C-F} = 31.6, 3.1 Hz), 124.5 (q, *J*_{C-F} = 271.6 Hz), 117.4 (m), 58.9, 23.6, 19.5, 13.1; ¹⁹F NMR (376.5 MHz, CDCl₃) δ -62.4; ¹¹B NMR (128.3 MHz, CDCl₃) δ -6.63.

Tetrabutylammonium 3,5-bis(trifluoromethyl)benzenesulfonate (*n*-Bu₄N⁺ Ar^FSO₃⁻) (S7). A 100 mL round-bottom flask with a magnetic stirrer was charged with 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (Matrix Scientific) (1.99 g, 6.35 mmol) and H₂O (15 mL, 0.4 M). A reflux condenser was attached, and the heterogeneous reaction was heated to an oil bath temperature of 107 °C and stirred for 3 h. Thereafter, the reaction was briefly

cooled, and a distillation head was attached. The residual H₂O and dissolved HCl (g) were distilled off and the resulting pale-yellow solid remaining in the distillation flask was dried *in vacuo*. This solid was dissolved in H₂O (4 mL, 1.6 M) and a 1.0 M solution of tetrabutylammonium hydroxide in MeOH was added to achieve pH = 7. Subsequently, H₂O and MeOH were removed *in vacuo*, the residue obtained was dried on high vacuum and thereafter was dissolved in CH₂Cl₂ and filtered to remove insoluble solids. Recrystallization from H₂O followed by drying under high vacuum provided 2.06 g (3.85 mmol, 61% yield) of **S7** as colorless needles. ¹H NMR (500.0 MHz, CDCl₃) δ 8.40 (s, 2H), 7.81 (s, 1H), 3.30 (m, 8H), 1.65 (m, 8H), 1.42 (dq, *J* = 14.8, 7.2 Hz, 8H), 0.99 (t, *J* = 7.2 Hz, 12H); ¹³C NMR (125.7 MHz, CDCl₃) δ 149.4, 131.2 (q, *J*_{C-F} = 33.4 Hz), 126.8 (q, *J*_{C-F} = 3.5 Hz), 123.0 (q, *J*_{C-F} = 272.4 Hz), 122.5 (septet, *J*_{C-F} = 3.8 Hz), 58.8, 23.9, 19.7, 13.5; ¹⁹F NMR (376.5 MHz, CDCl₃) δ -62.8.

Tetrabutylammonium *p*-toluenesulfonate (*n*-Bu₄N⁺ OTs⁻) (S8**).** A 25 mL round-bottom flask with a magnetic stirrer was charged with *p*-toluenesulfonic acid monohydrate (1.00 g, 5.26 mmol) and H₂O (3 mL, 1.8 M). A 1.0 M solution of tetrabutylammonium hydroxide in MeOH was added over 5 min to achieve pH = 7 (5.2 mL added). The exothermic reaction was allowed to stir for 15 min, and subsequently, H₂O and MeOH were removed *in vacuo*. The residue obtained was dissolved in CH₂Cl₂, transferred to a separatory funnel, separated from residual H₂O, and filtered to remove insoluble solids. Removal of CH₂Cl₂ *in vacuo* followed by recrystallization from H₂O and drying under high vacuum provided 1.38 g (3.85 mmol, 63% yield) of **S8** as colorless needles. Spectral data were consistent with previously reported values.⁸

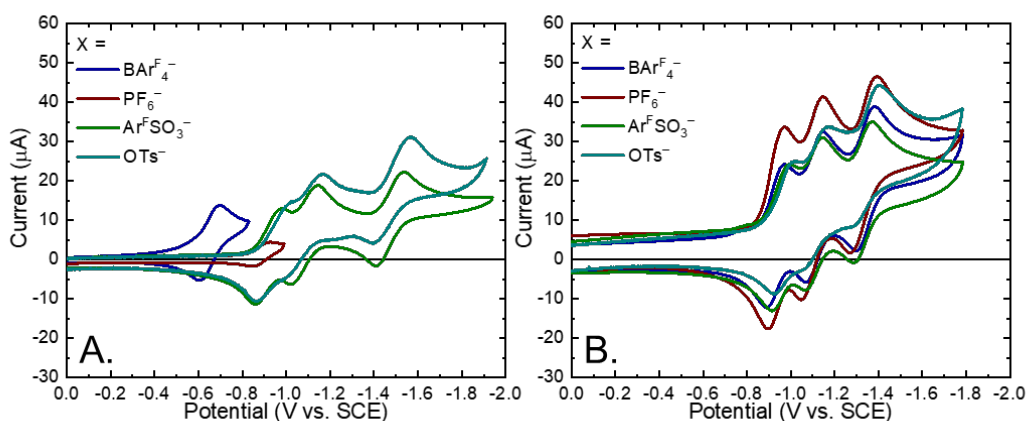


Figure S11. Cyclic voltammograms of the [Ru(btmb)₃](X)₂ catalysts in A. CH₂Cl₂ and B. CH₃CN at a scan rate of 100 mV/sec and 0.1 M electrolyte solution composed of the *n*-Bu₄N⁺ salt of the indicated counterion.

Table S12. Electrochemical potentials of [Ru(btmb)₃](X)₂ in CH₃CN.

entry	catalyst	ΔG _{ES} (eV)	Ru ^{2+/+} (V)	Ru ^{2+*/+} (V)	Ru ^{+/0} (V)	Ru ^{0/-} (V)
1	3a	2.04	-0.93	+1.11	-1.11	-1.35
2	3c	2.04	-0.93	+1.11	-1.10	-1.33
3	3d	2.04	-0.95	+1.09	-1.11	-1.34
4	3e	2.04	-0.98	+1.06	-1.11	-1.35

VI. ^1H NMR Experiments

Hydrogen-Bond Donor Co-Catalyst Titration:

The equilibrium constant for the binding of $\text{Ar}^{\text{F}}\text{SO}_3^-$ to thiophosphotriamide **7** was determined through NMR titration studies. A solution of thiophosphotriamide **7** (0.16 mg, 0.21 μmol , 1.0 equiv.) in CD_2Cl_2 (500 μL) was transferred to an NMR tube. Separately, a stock solution containing both $n\text{-Bu}_4\text{N}^+ \text{Ar}^{\text{F}}\text{SO}_3^-$ (5.6 mg, 10.5 μmol) and thiophosphotriamide **7** (1.3 mg, 1.74 μmol) in CD_2Cl_2 (4.0 mL) was prepared. Increasing amounts of this solution were titrated into the NMR tube in 10 μL aliquots. The titration was quantified by monitoring the chemical shift of the aromatic C–H resonances of **7**, which moved downfield with increasing concentration of $n\text{-Bu}_4\text{N}^+ \text{Ar}^{\text{F}}\text{SO}_3^-$.

The changes in chemical shift (Δppm) were fit to a 1:1 binding model. Microsoft Excel was used to alter K_a to minimize the error between the calculated and experimental chemical shifts. The resulting binding isotherm is shown below. $K_a = 1.3 \times 10^6$.

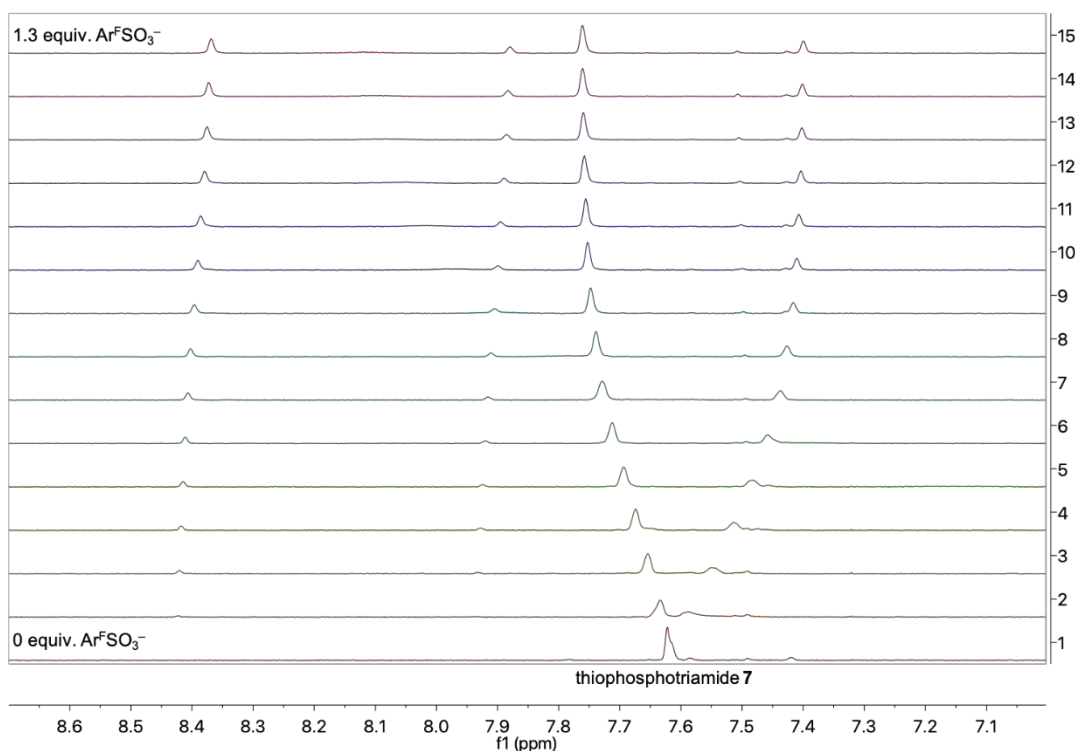


Figure S12. Aromatic region of the ^1H NMR titration of thiophosphotriamide **7** with $n\text{-Bu}_4\text{N}^+ \text{Ar}^{\text{F}}\text{SO}_3^-$ in CD_2Cl_2 . The C–H chemical shift of **7** is noted in the figure.

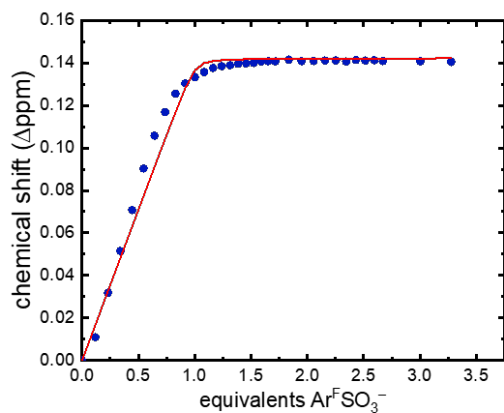
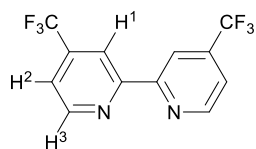


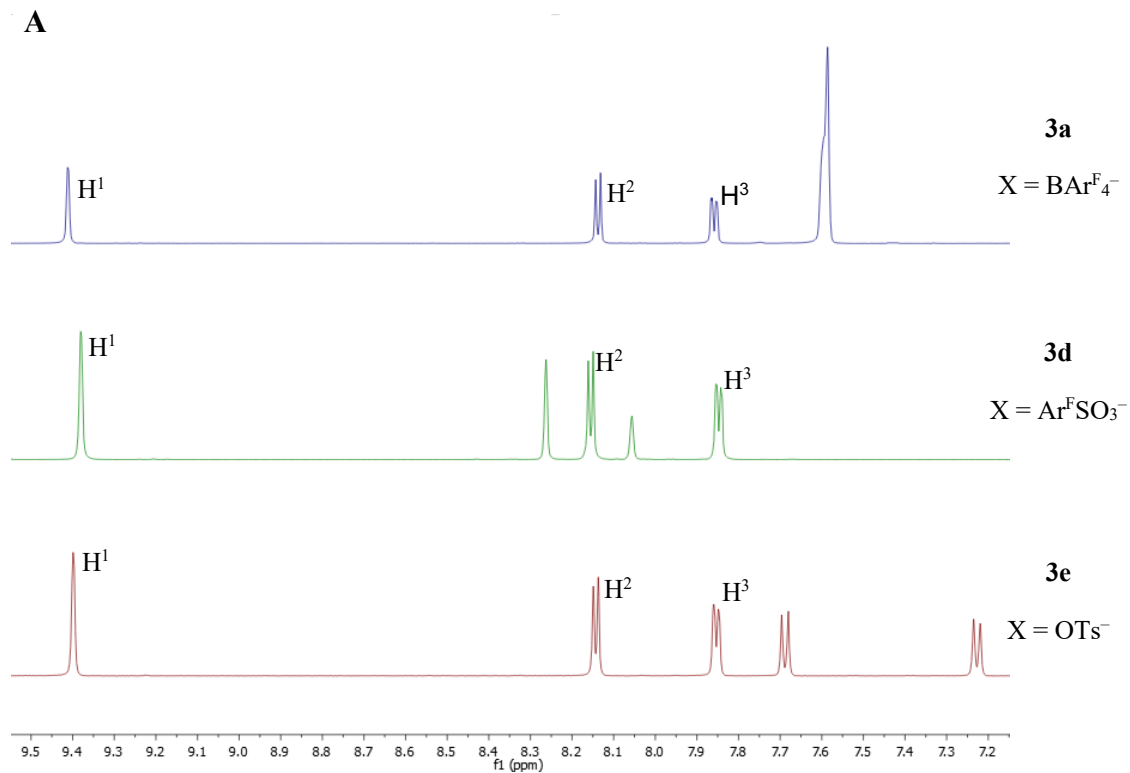
Figure S13. Change in chemical shift of the thiophosphotriamide **7** C–H resonance, blue circles. Overlaid is the best fit to a 1:1 binding model, solid line.

Chemical Shift Dependence on Counteranion Identity:

^1H NMR Spectra of $[\text{Ru}(\text{btfmb})_3](\text{X})_2$ (expansions of aromatic regions shown)



^1H NMR Spectra in CD_3OD



^1H NMR Spectra in CD_2Cl_2

B

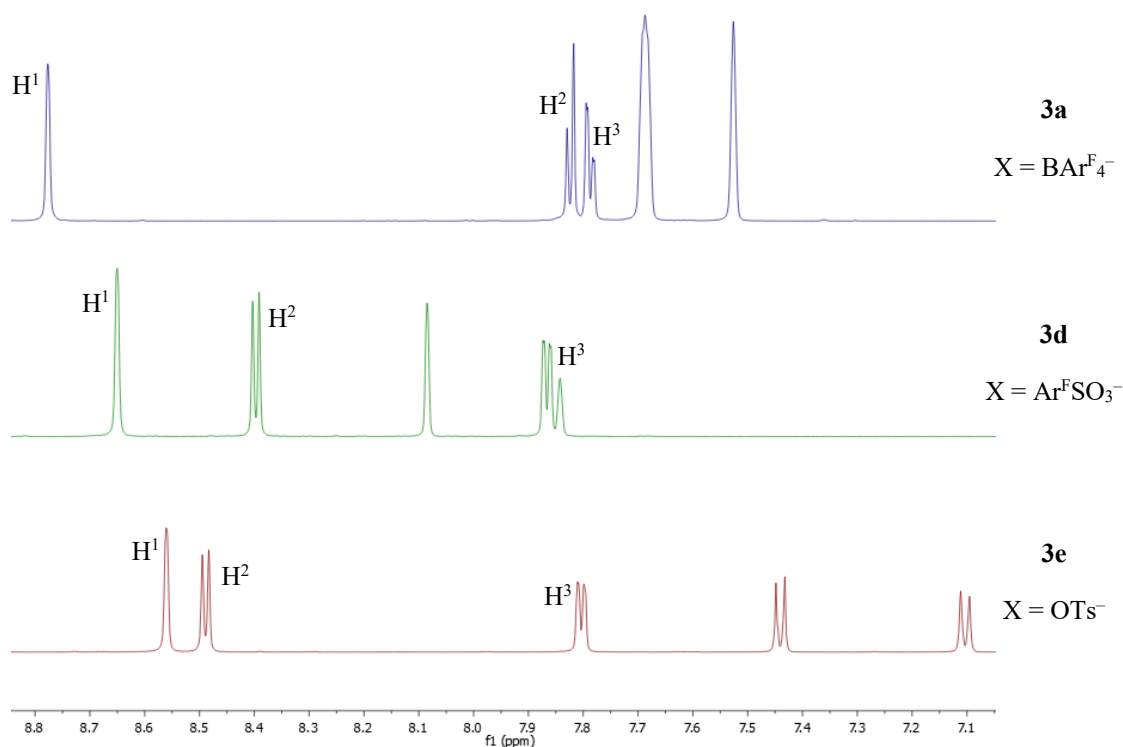
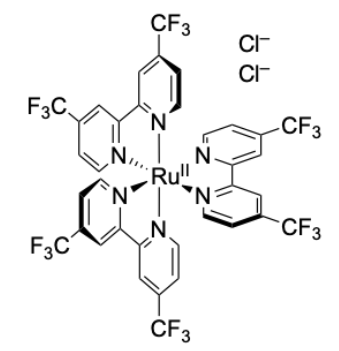
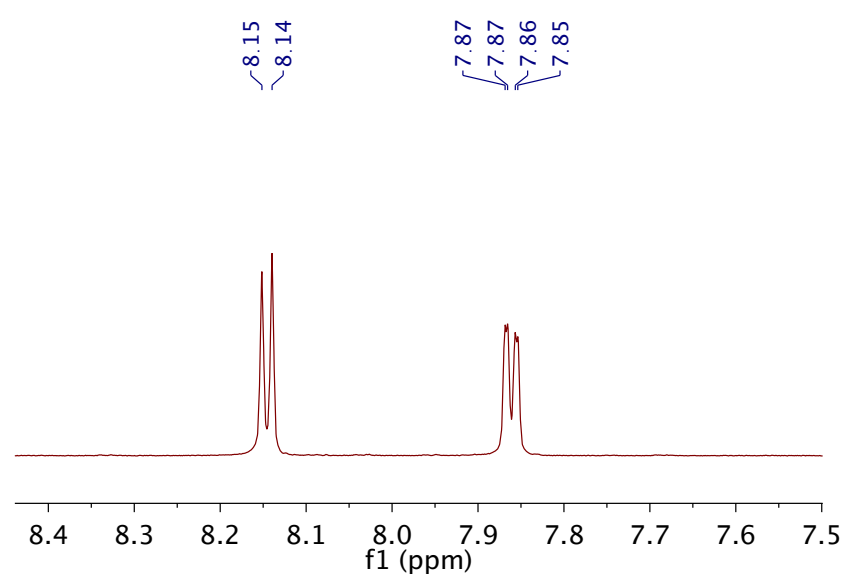


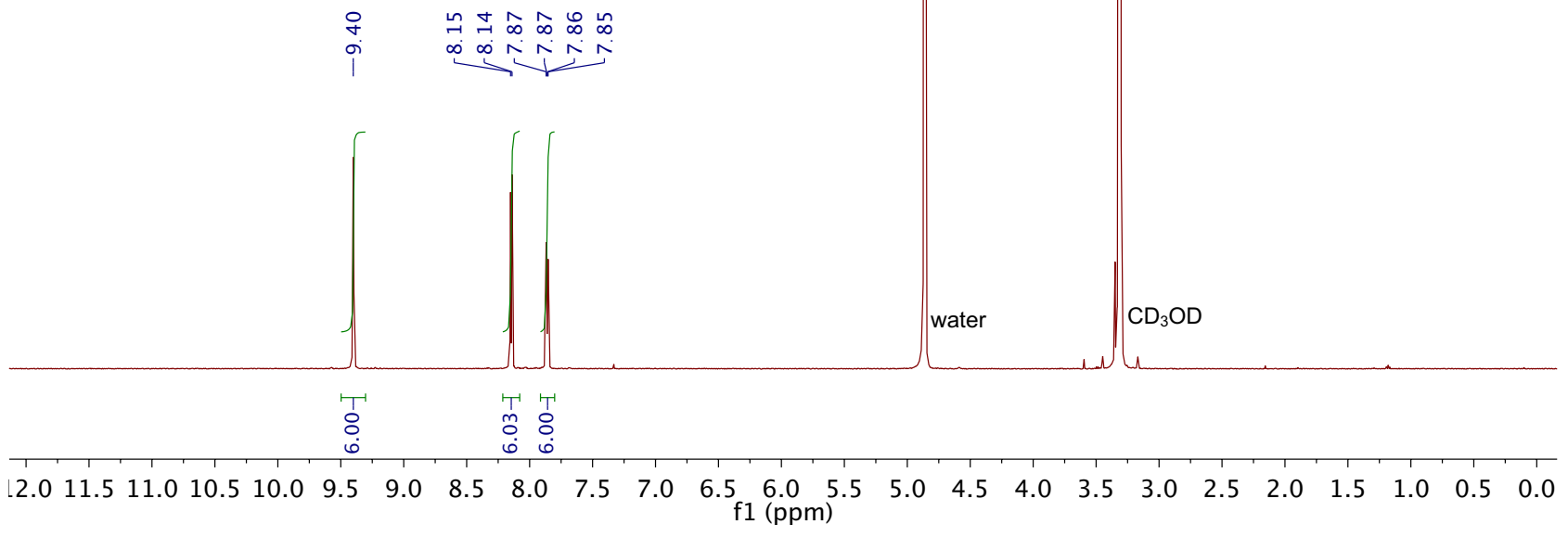
Figure SI4. The ^1H NMR chemical shifts for catalysts **3a**, **3d**, and **3e** in CD_3OD (A) and CD_2Cl_2 (B). In CD_2Cl_2 significant changes in the proton spectra of the btmb ligands were measured between the photocatalysts. These changes tracked the coordinating ability of the counteranion in good agreement with the hypothesis of Meyer and coworkers of specific interactions between the counteranion and specific positions on the ligands.⁹

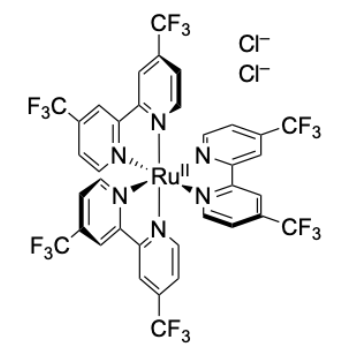
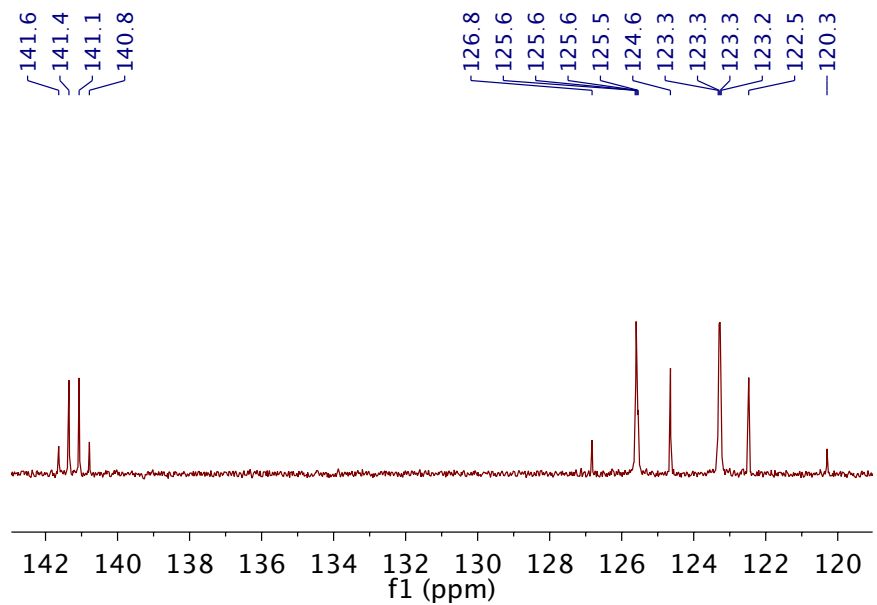
VII. References

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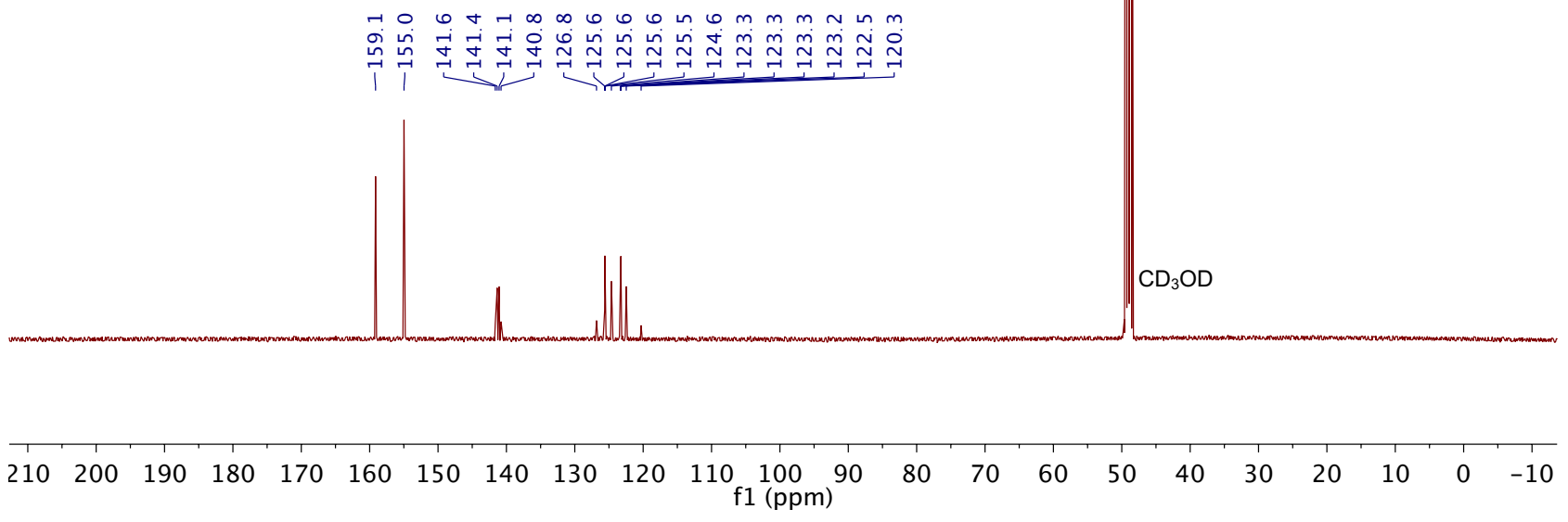


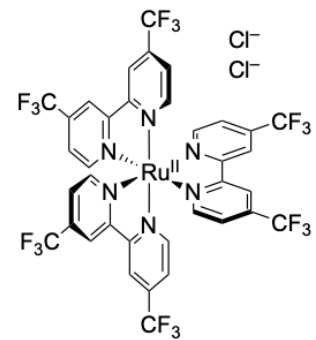
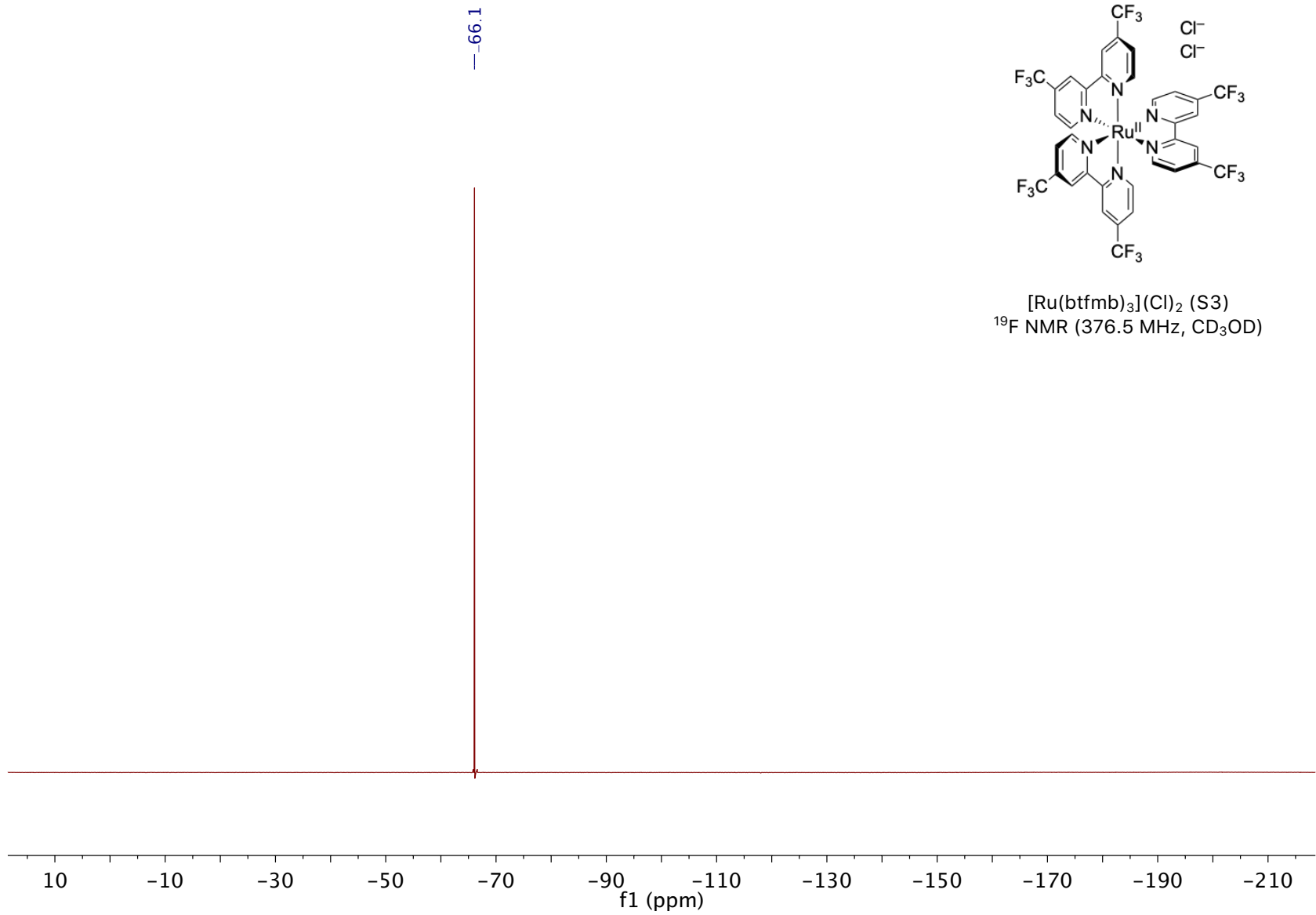
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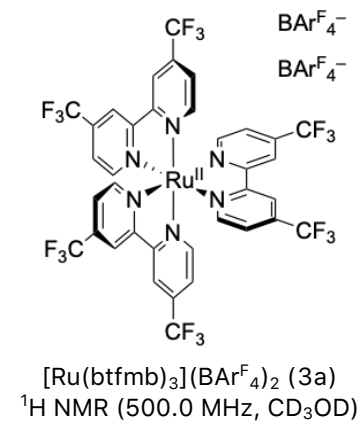
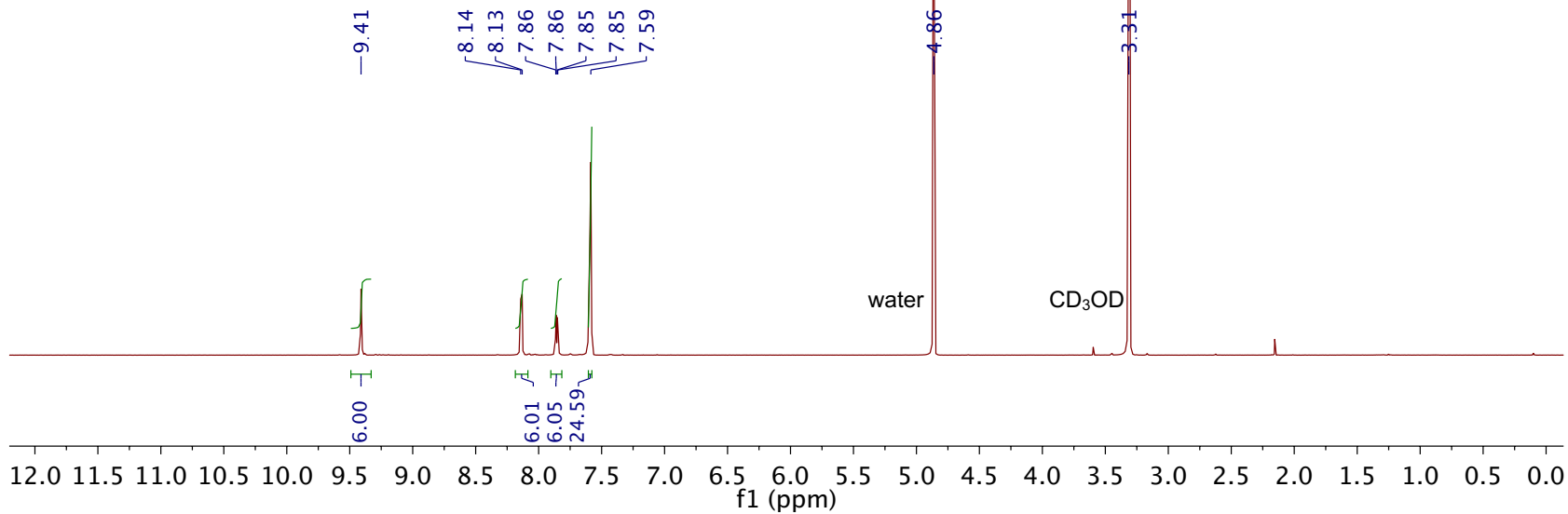
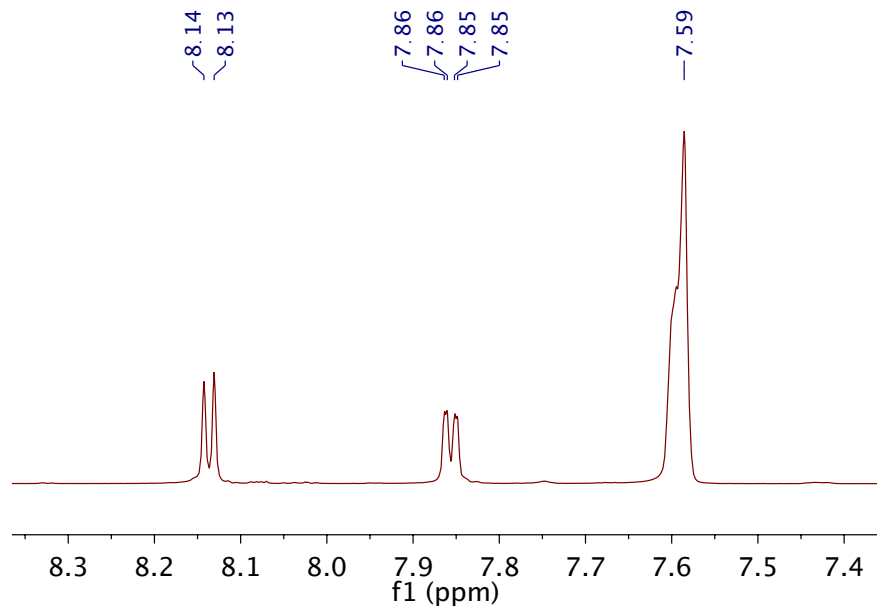


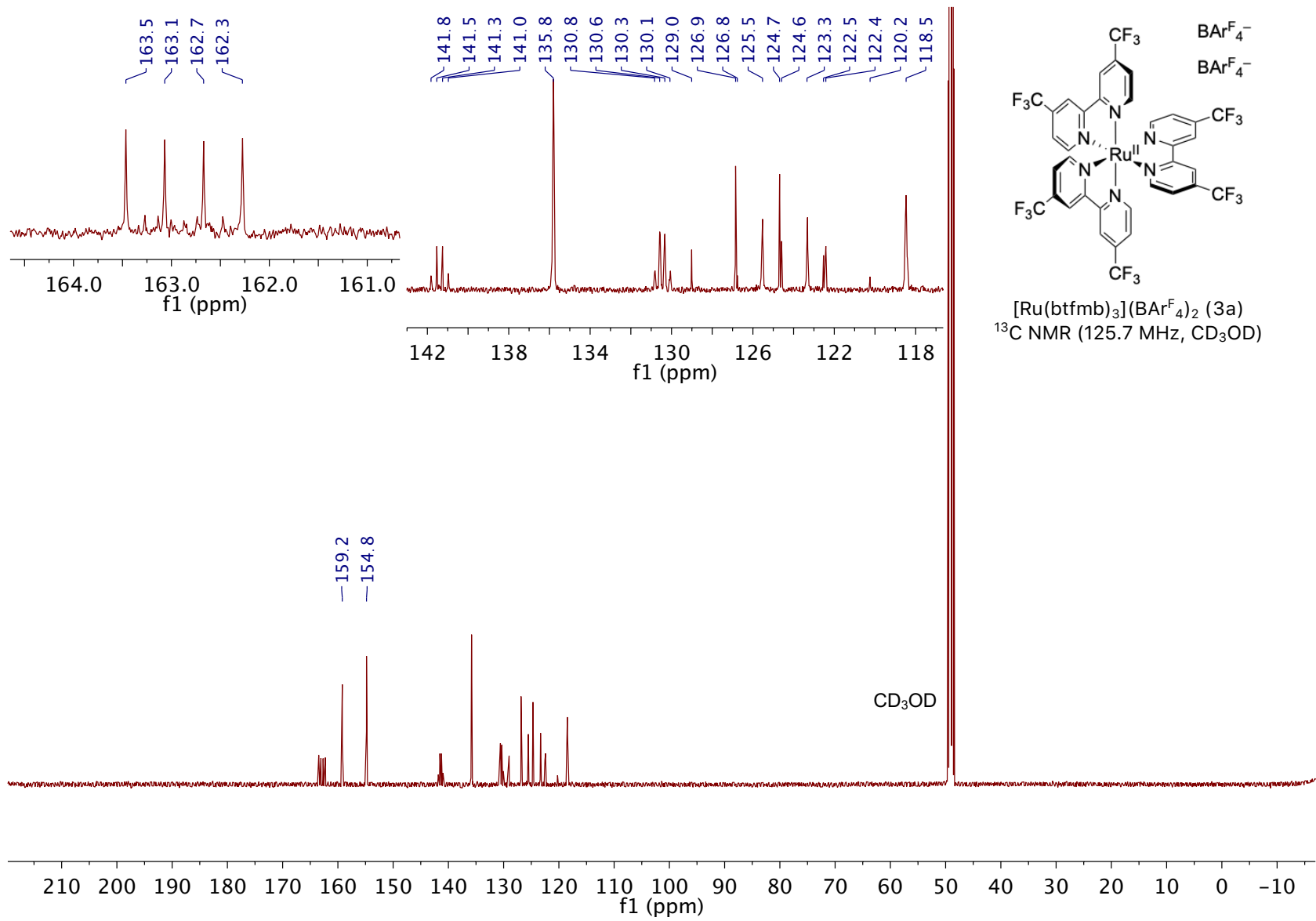
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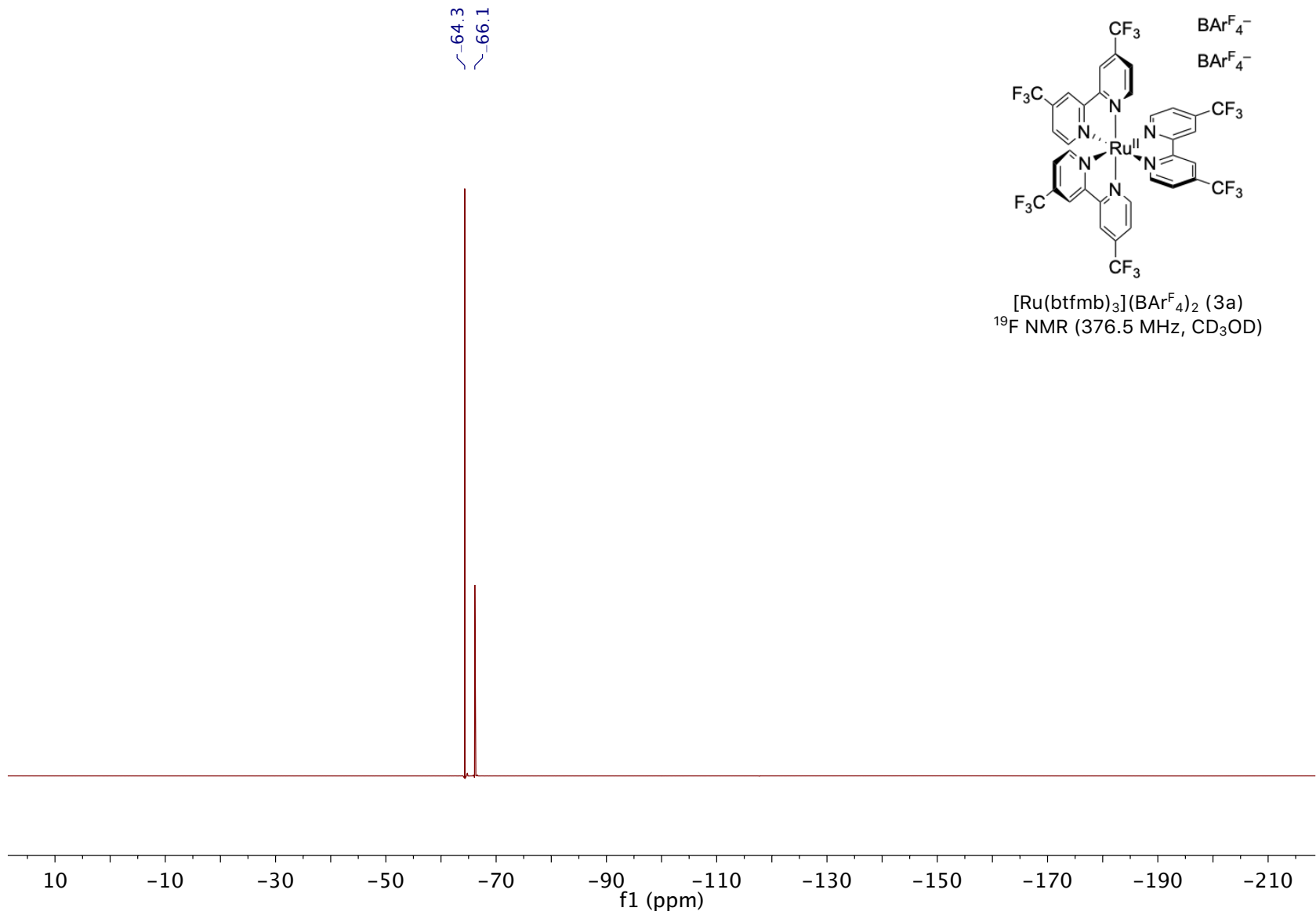


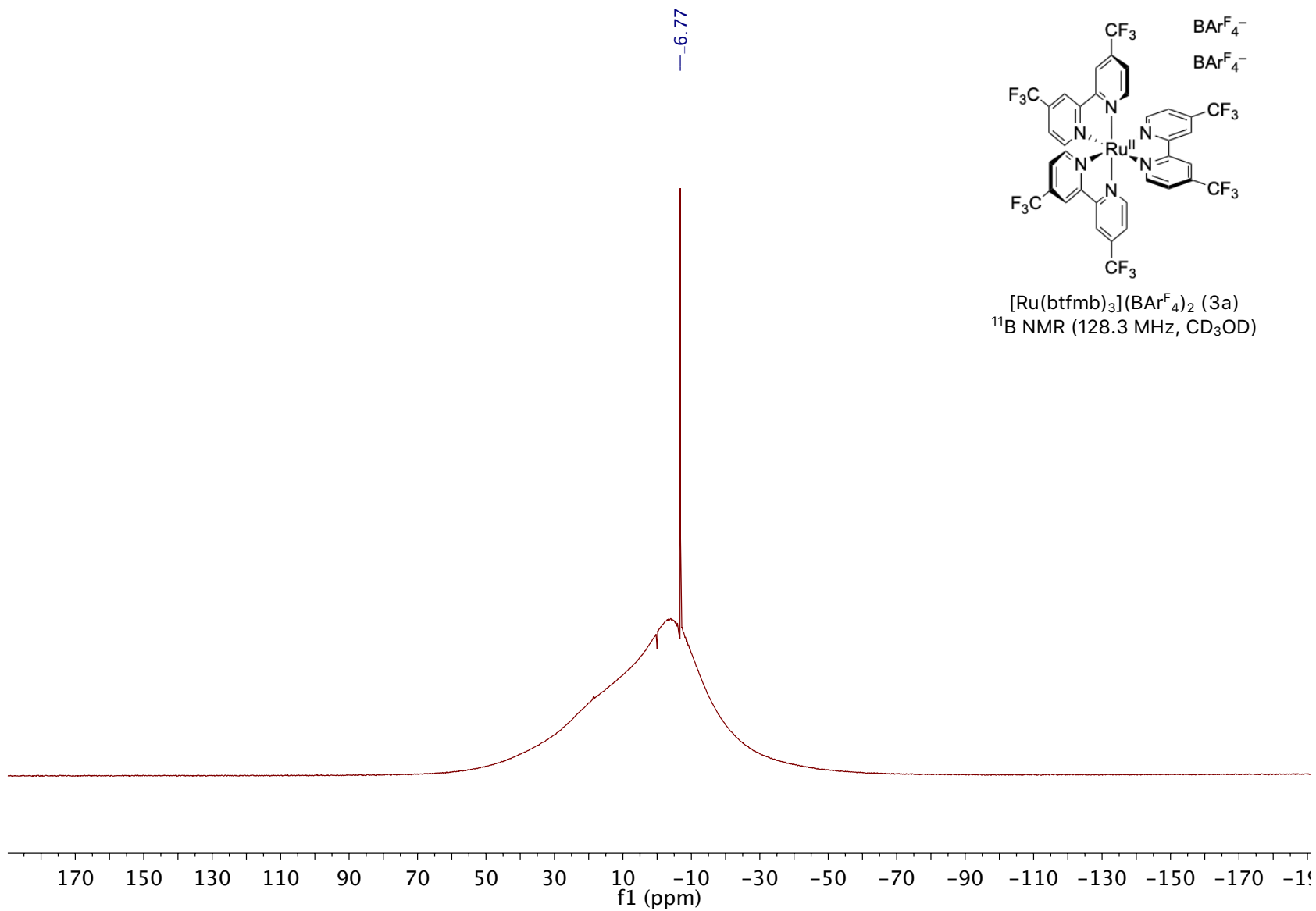


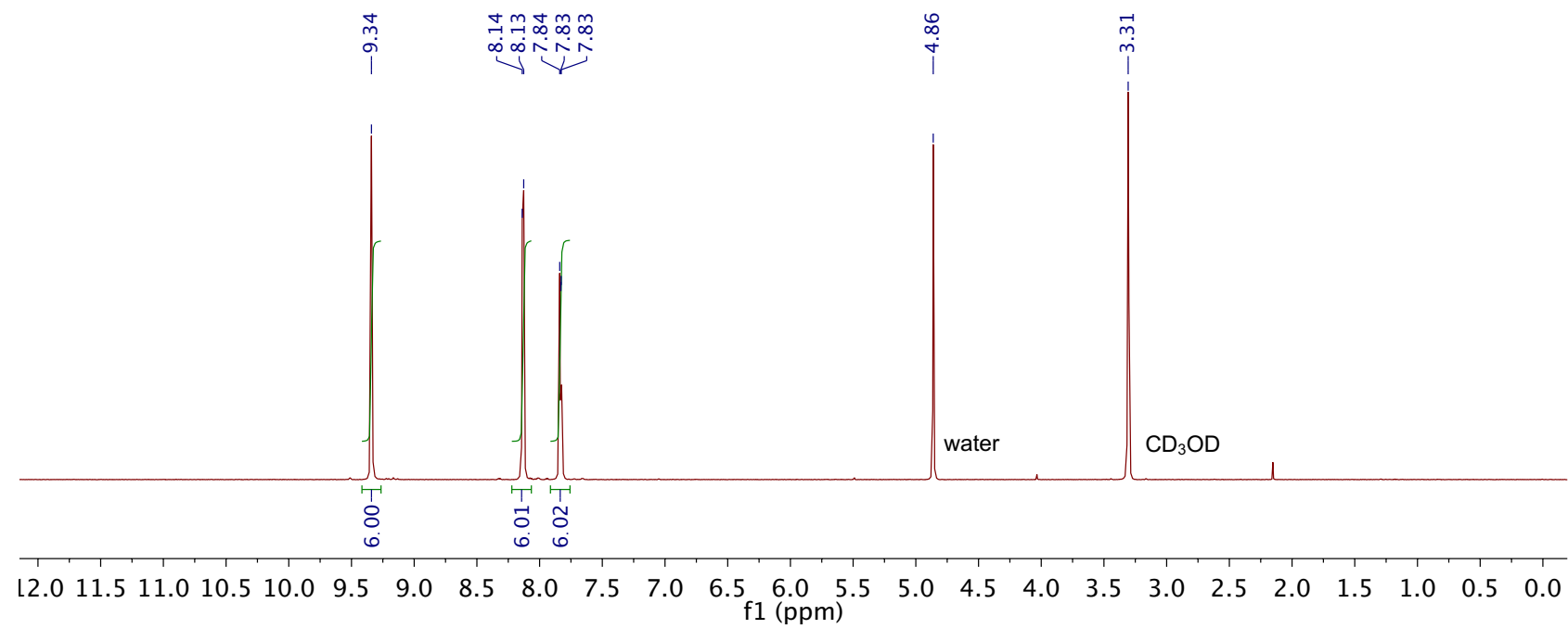
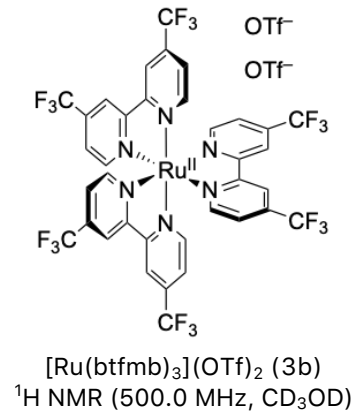
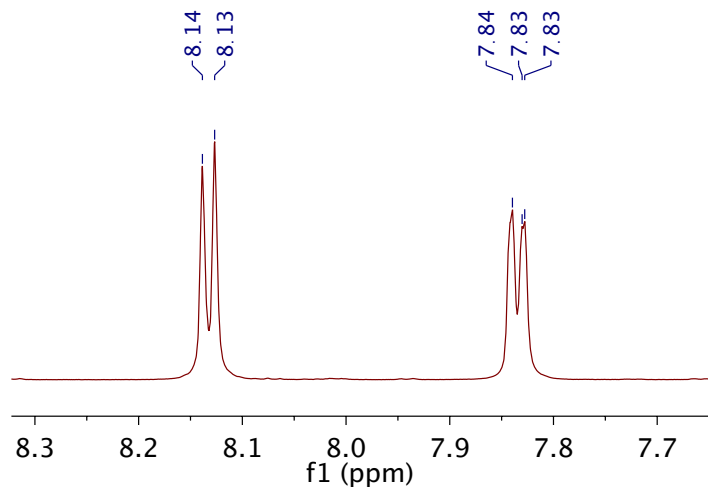
[Ru(btmb)₃](Cl)₂ (S3)
¹⁹F NMR (376.5 MHz, CD₃OD)

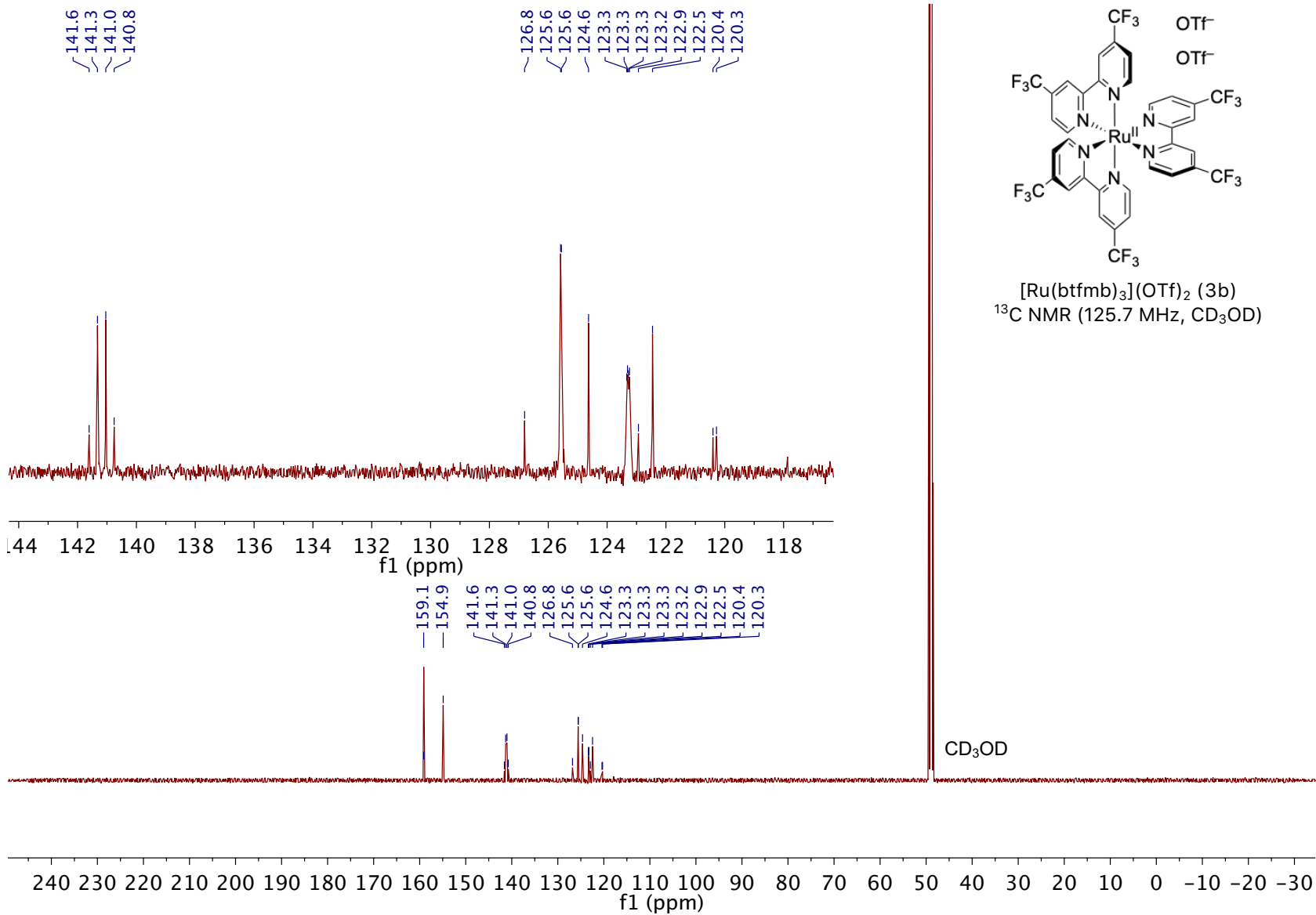


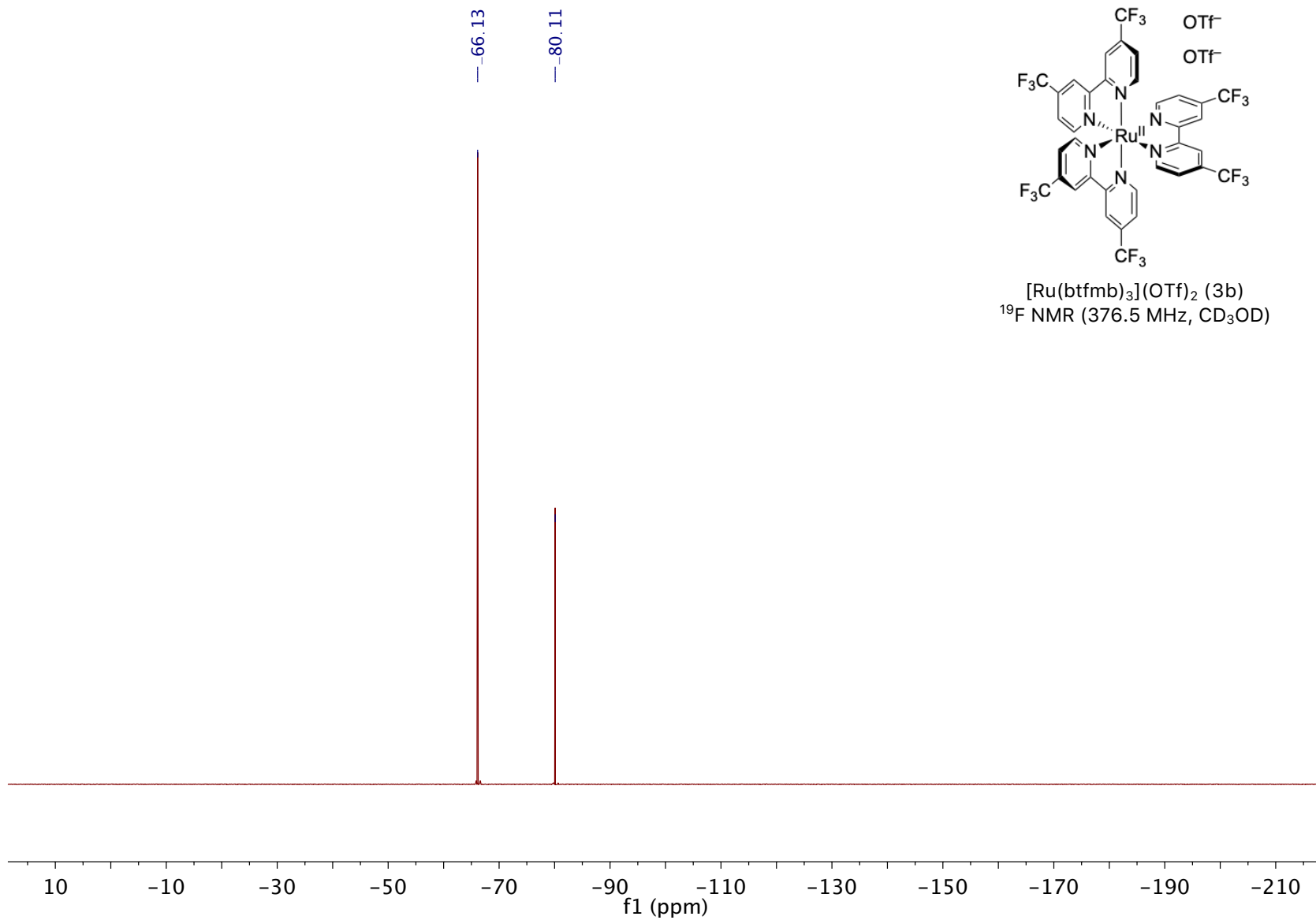


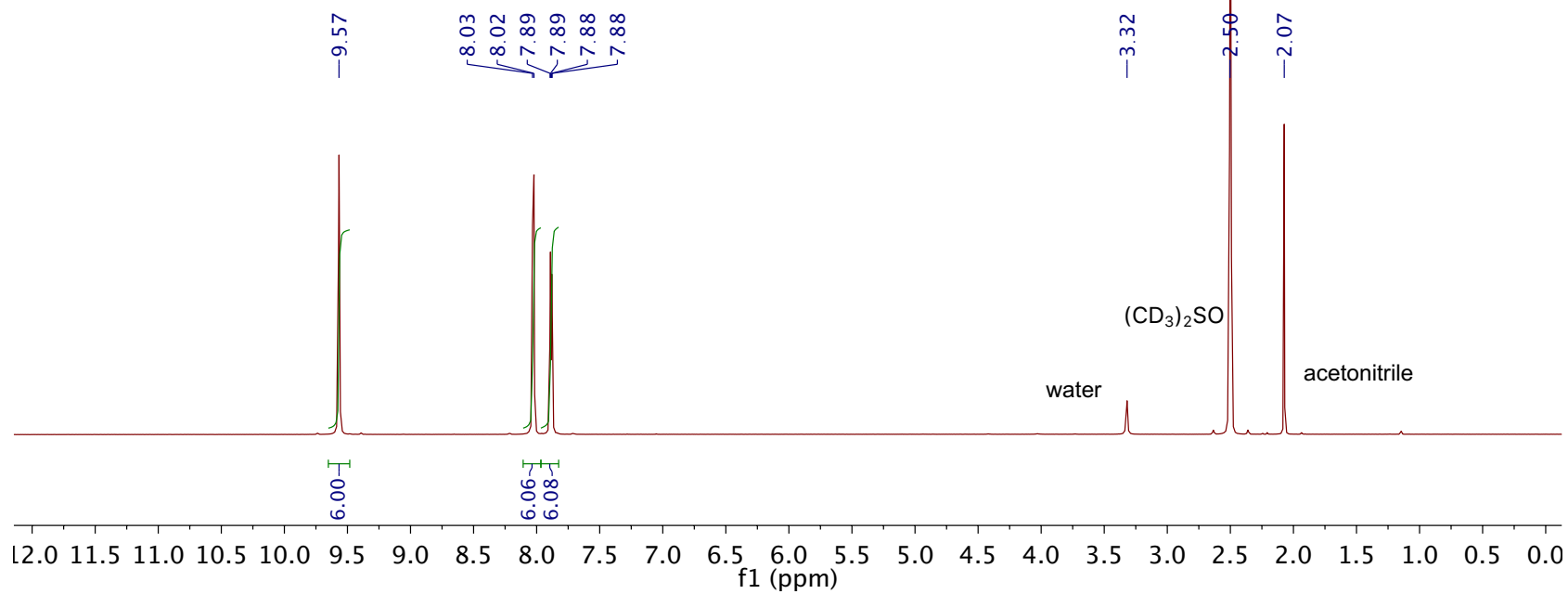
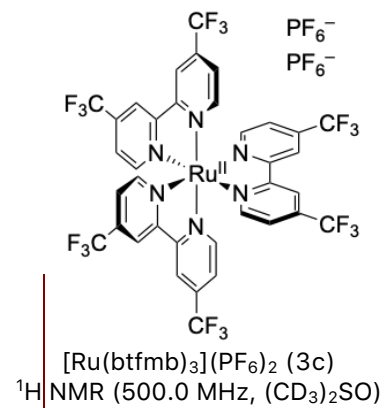
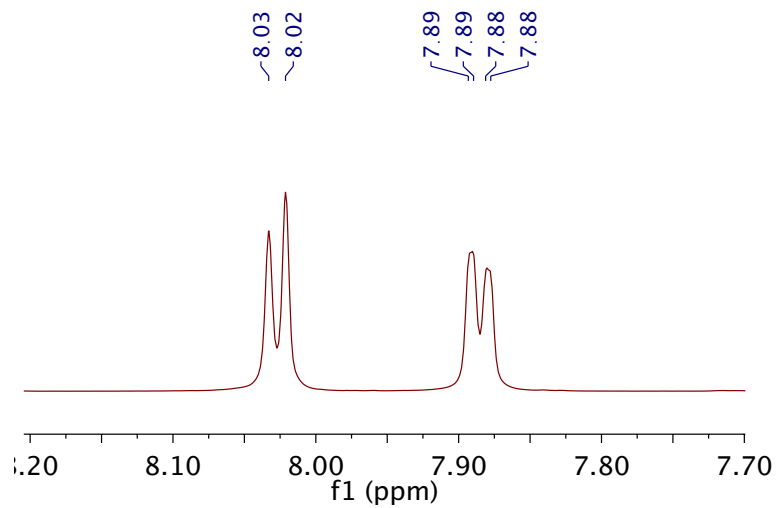


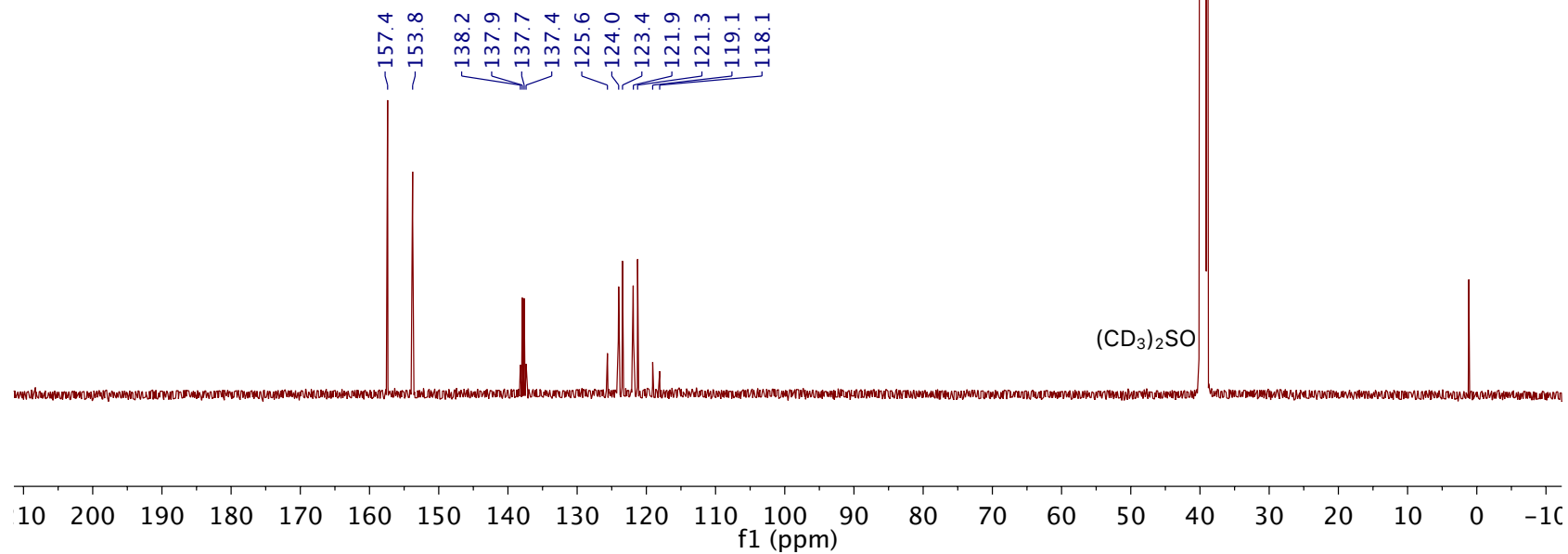
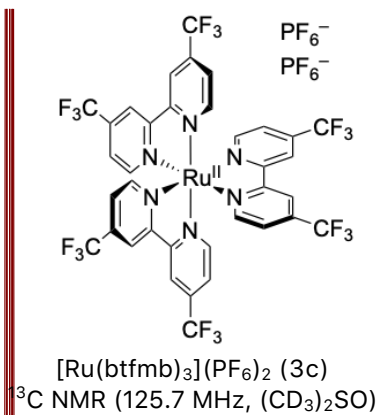
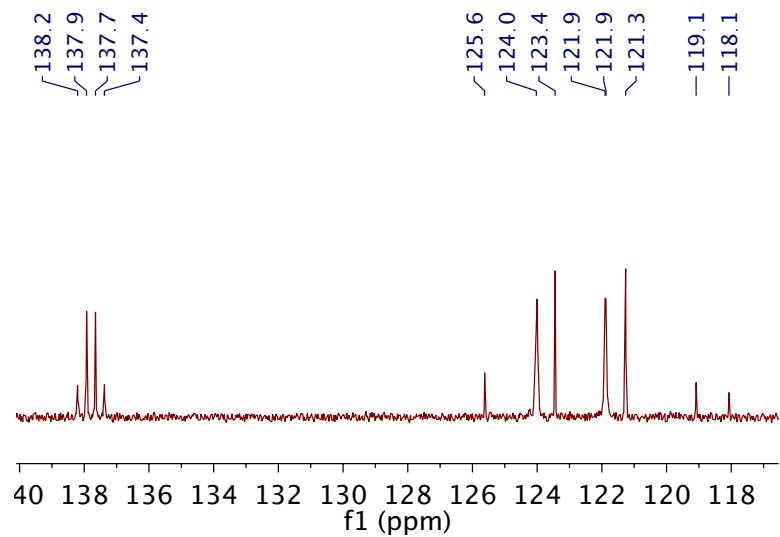


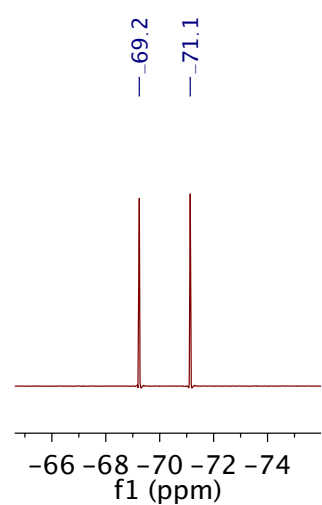




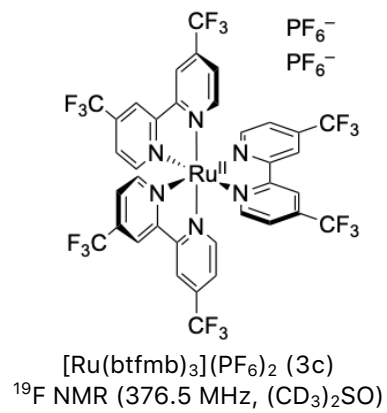
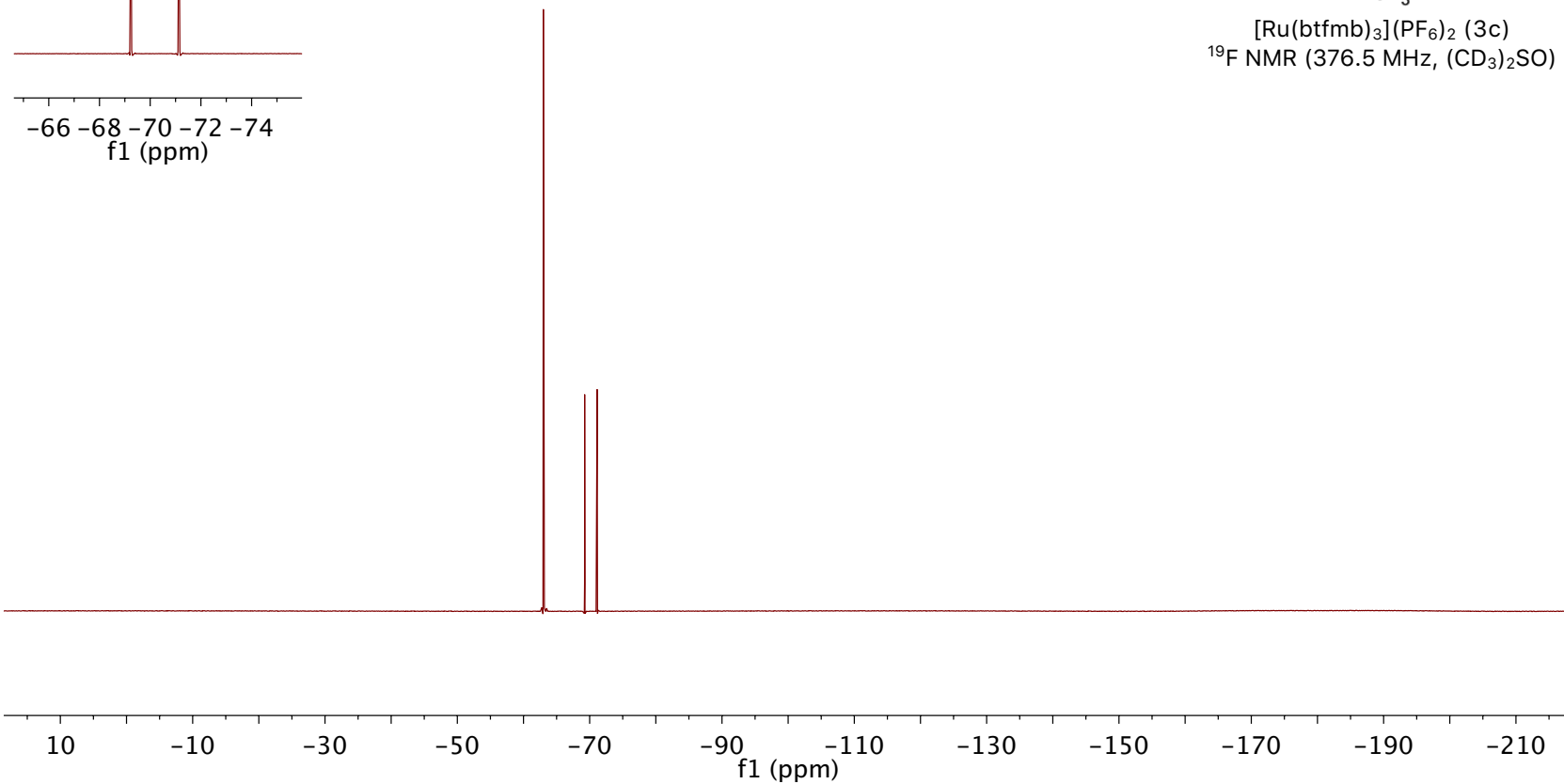


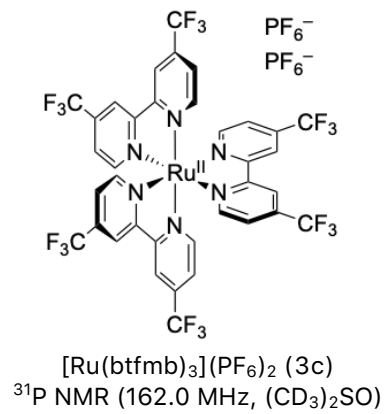




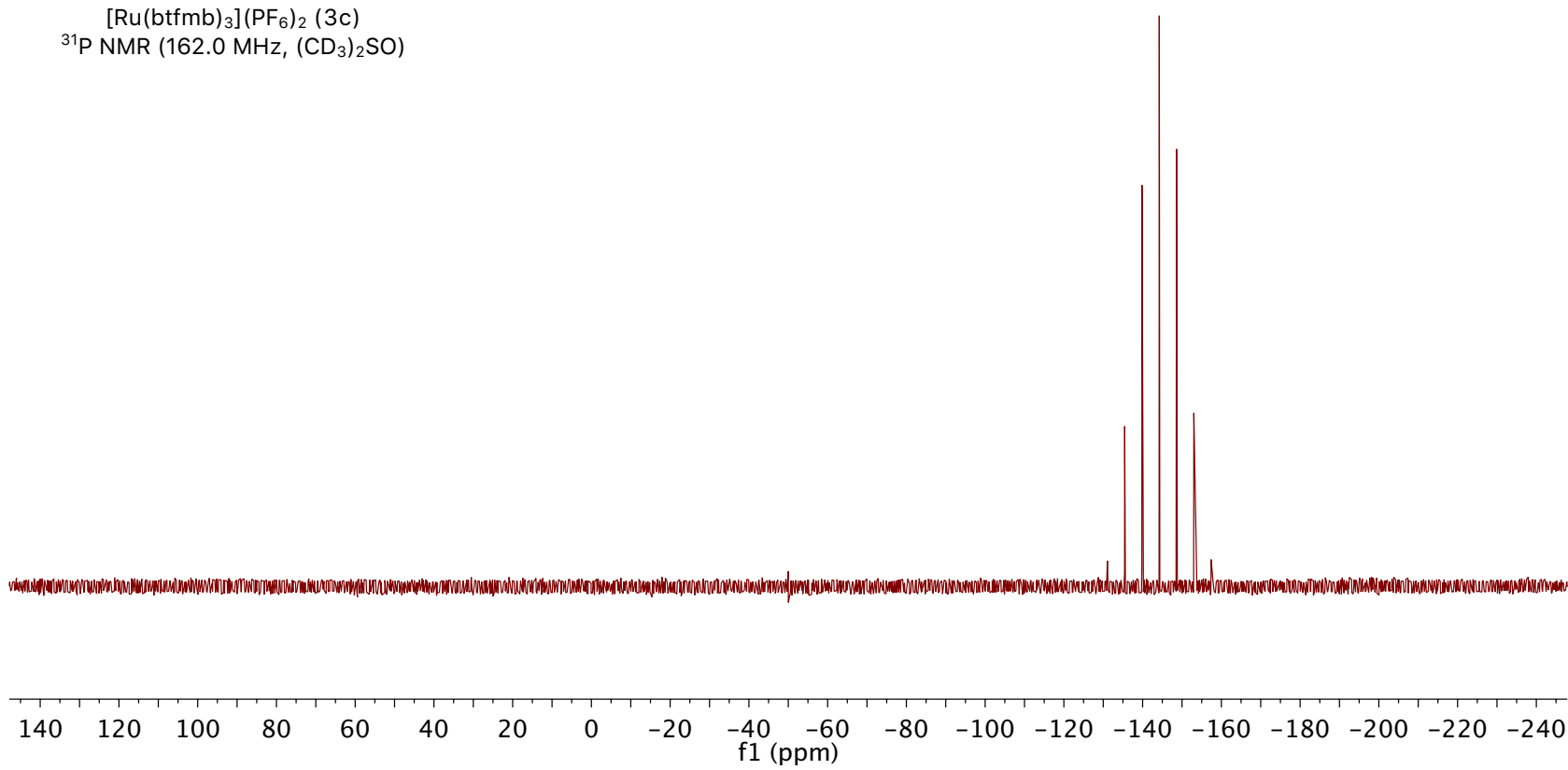


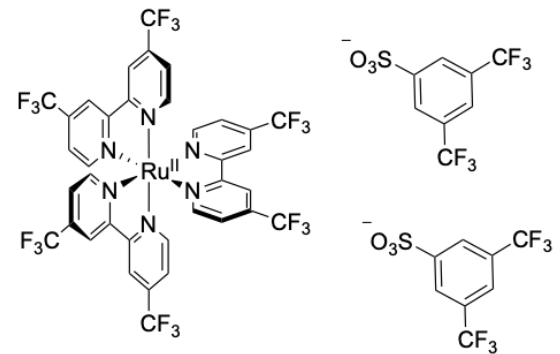
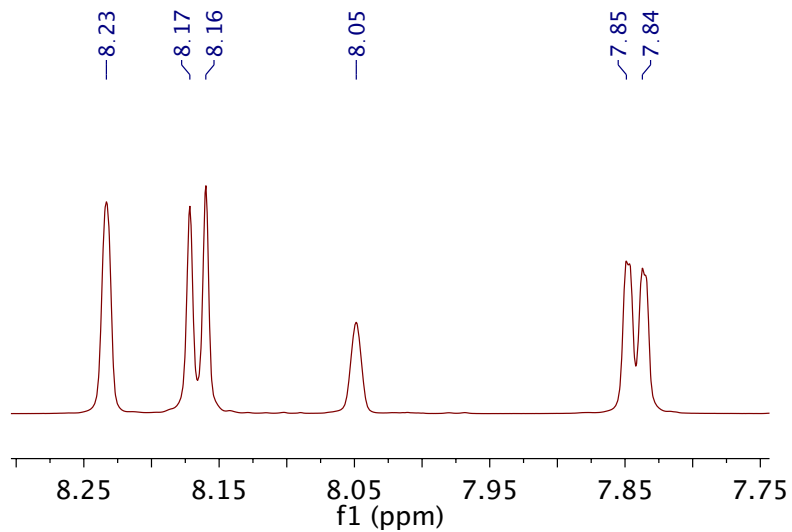
-63.0
-69.2
-71.1



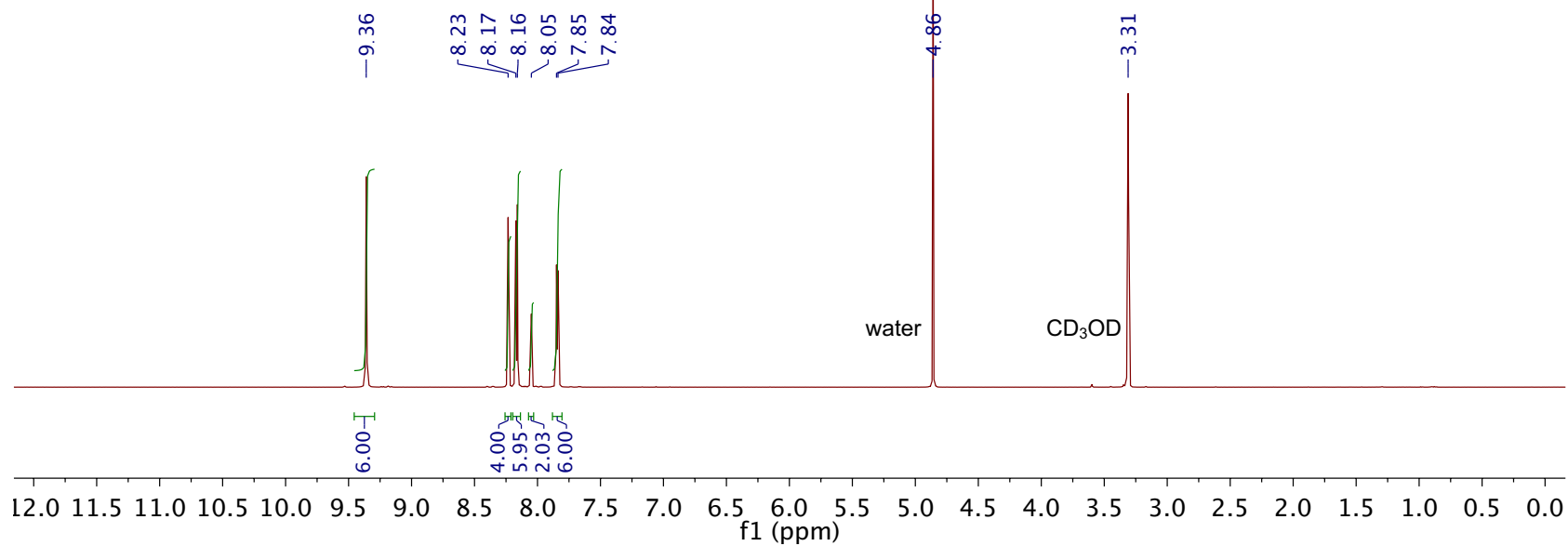


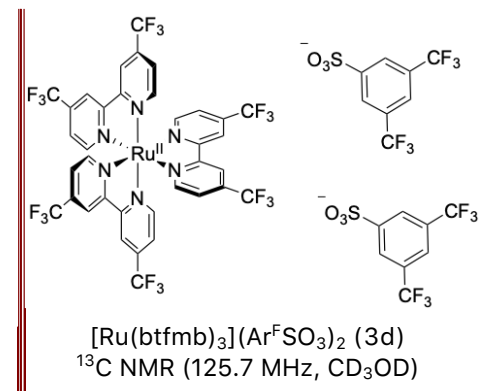
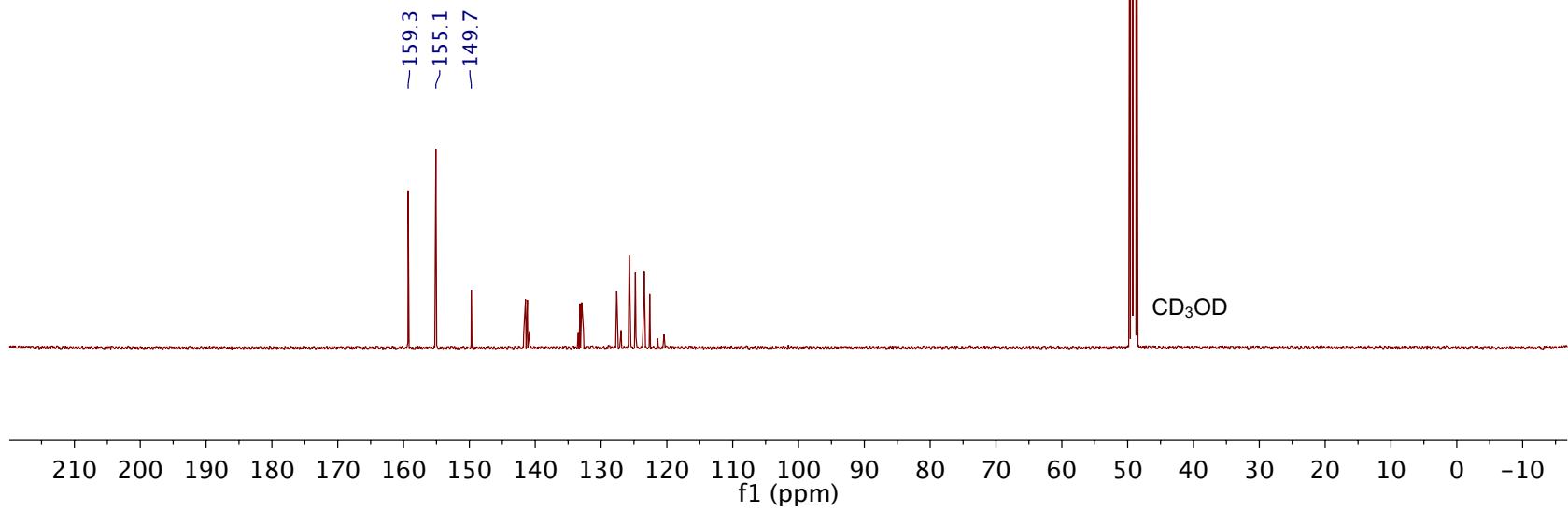
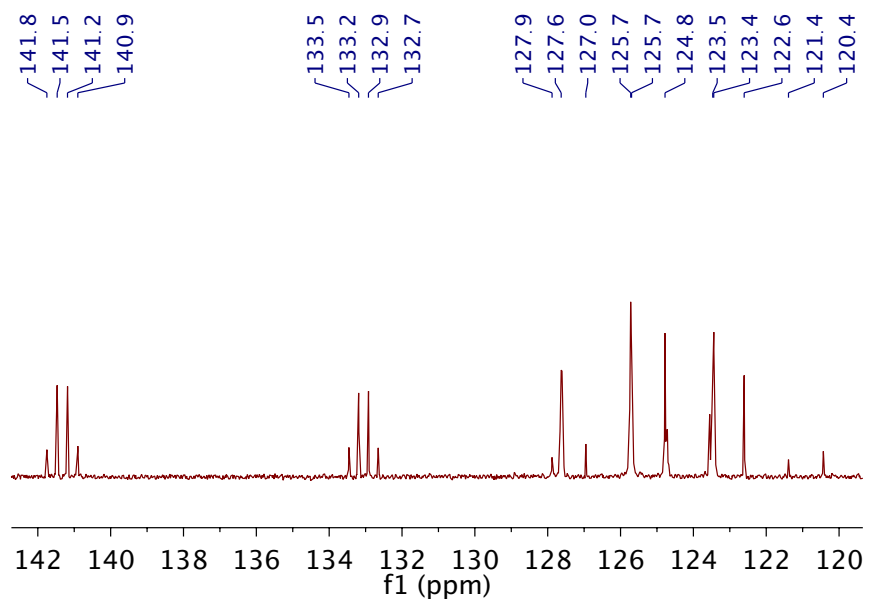
131.1
135.4
139.8
144.2
148.6
153.0
157.4

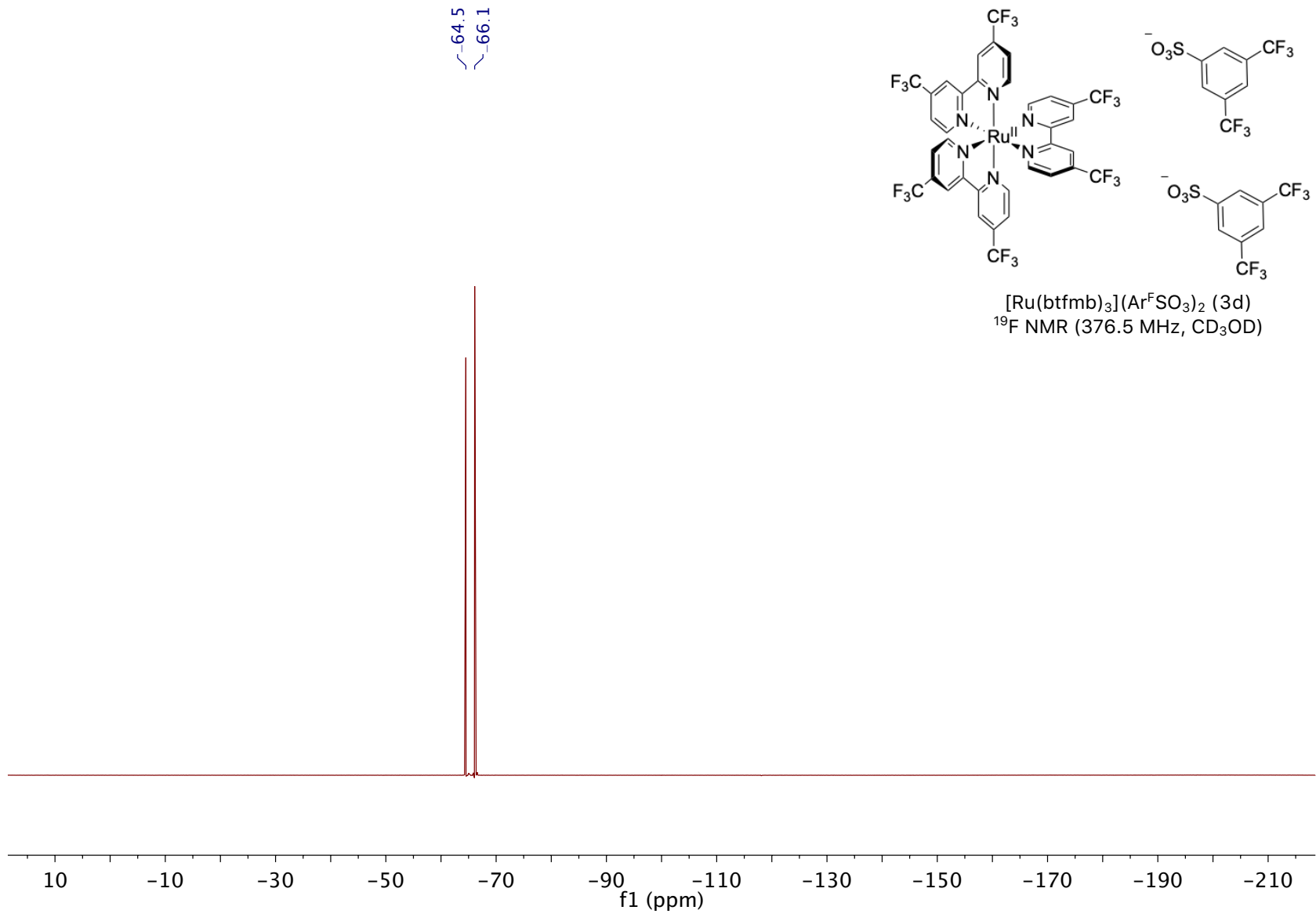


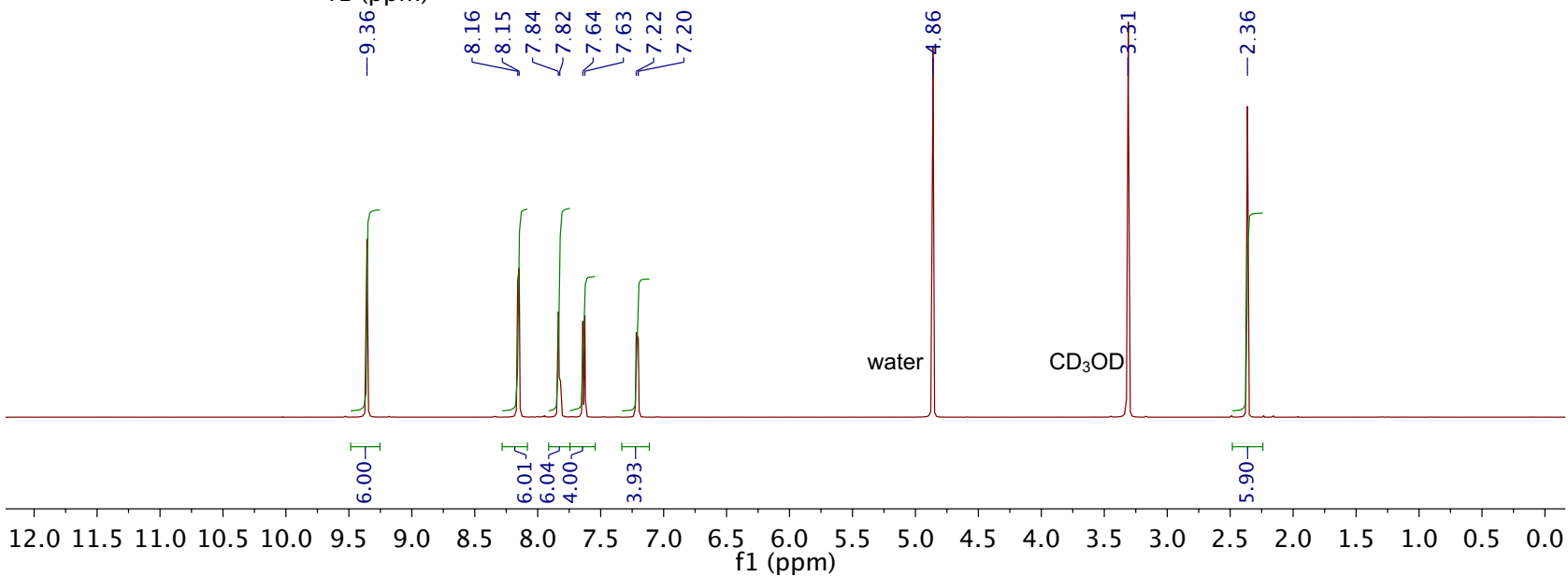
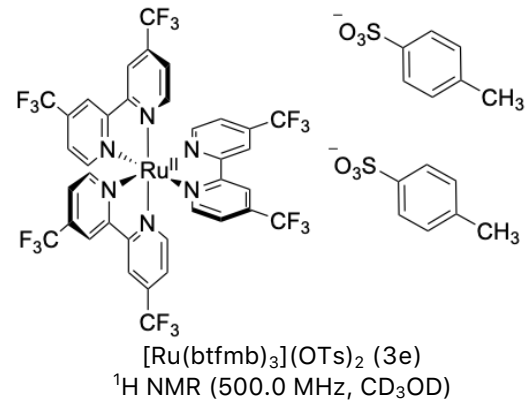
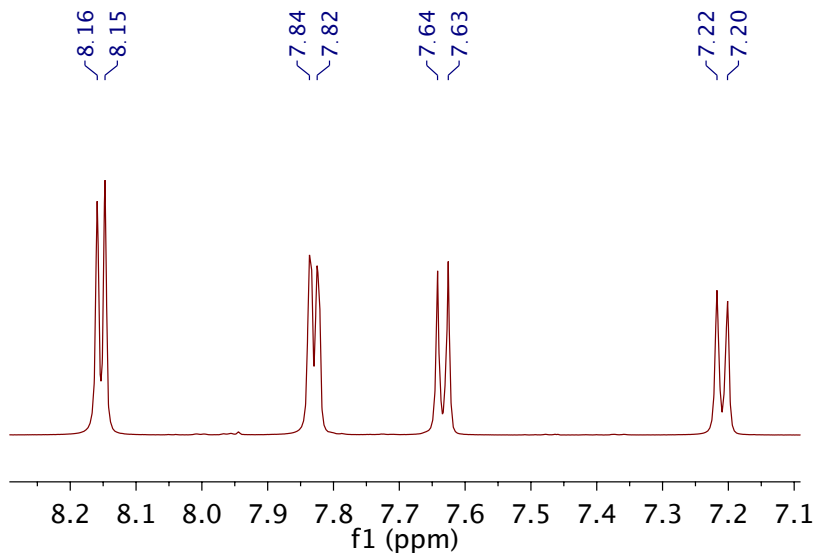


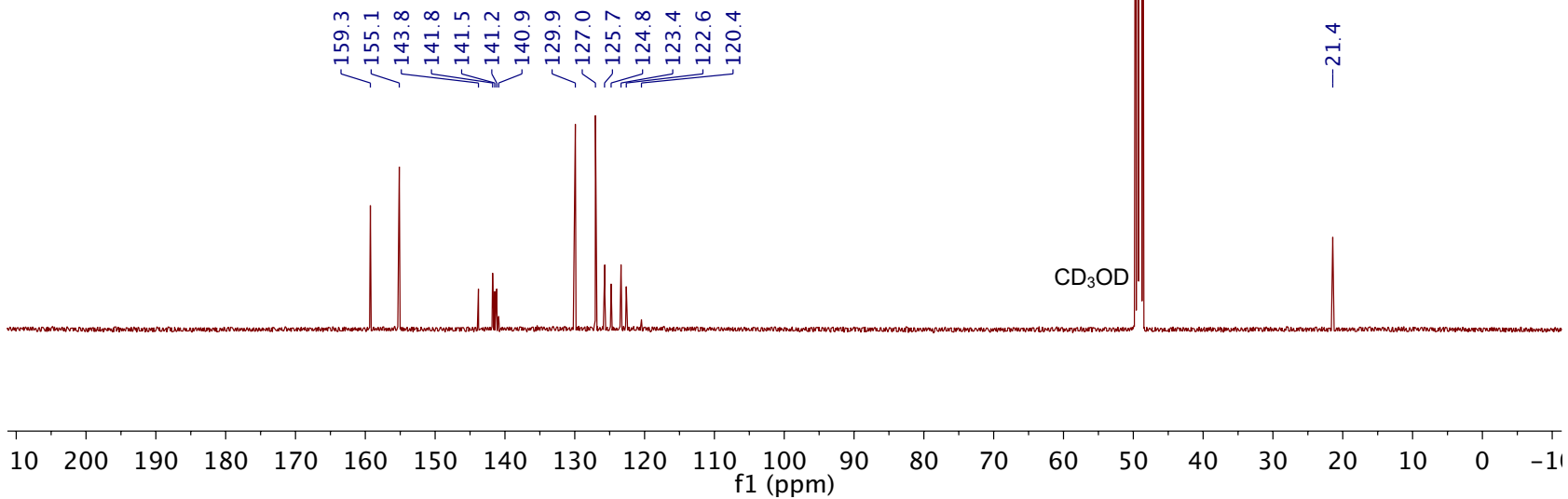
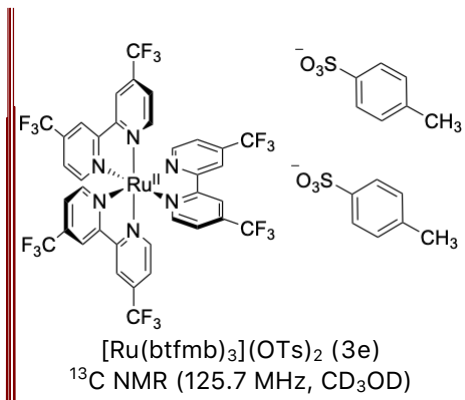
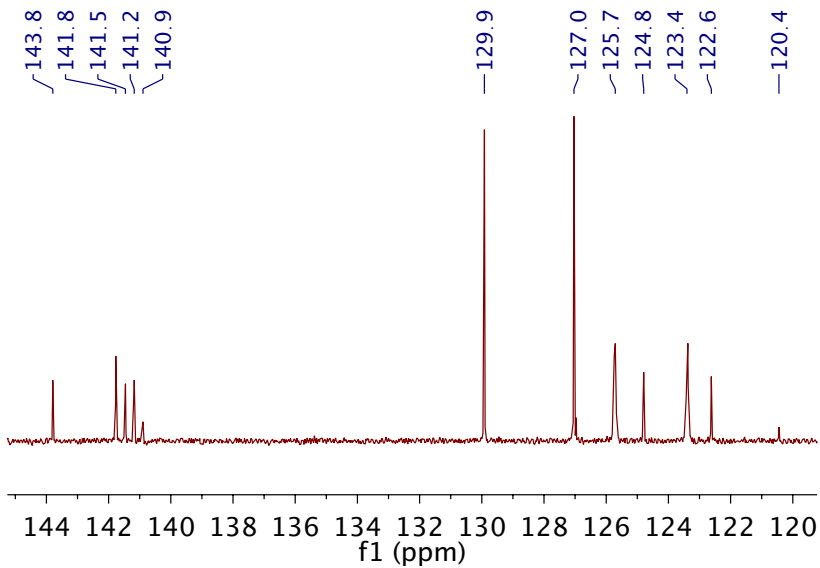
[Ru(btmb)₃](Ar^FSO₃)₂ (3d)
¹H NMR (500.0 MHz, CD₃OD)

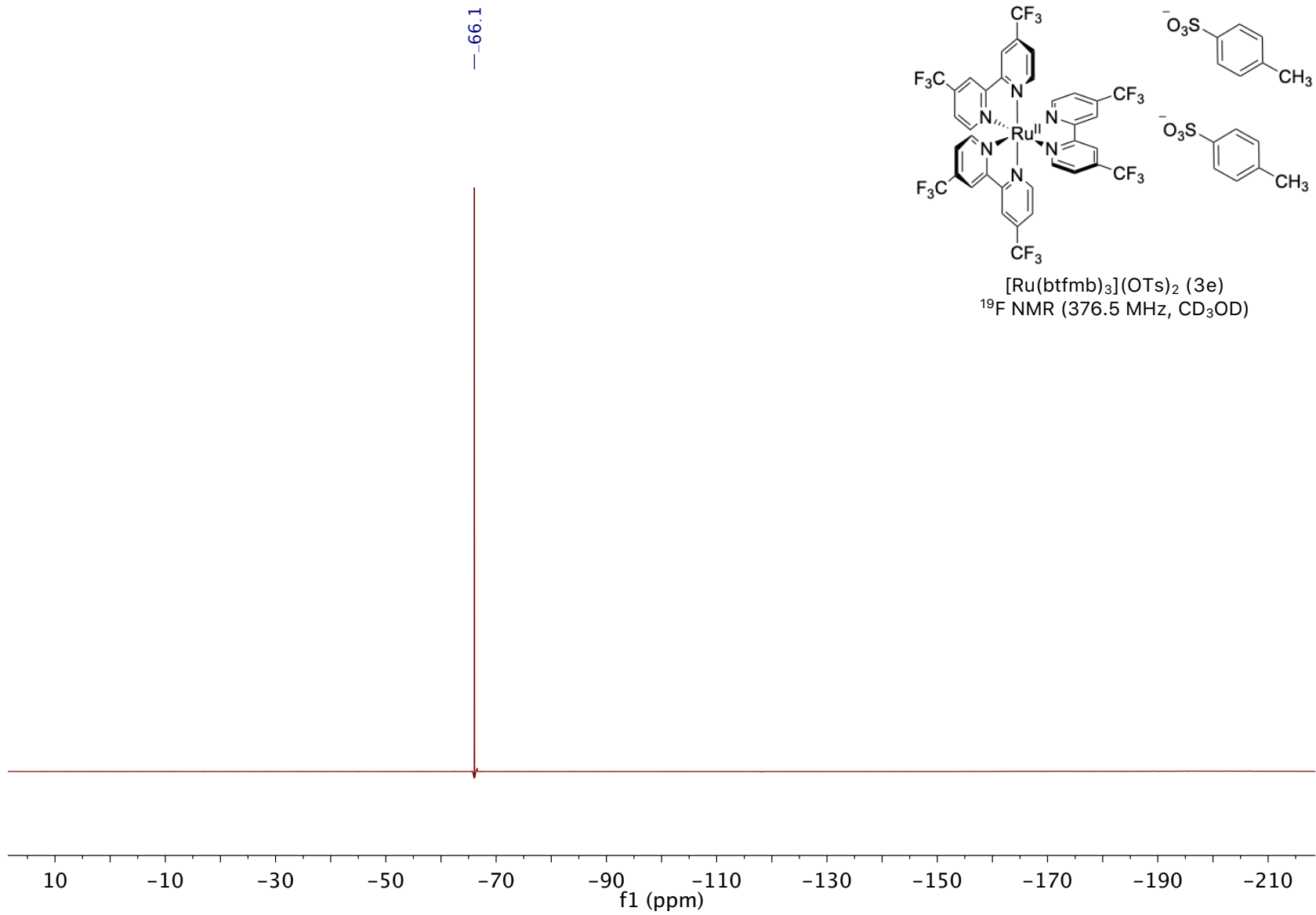


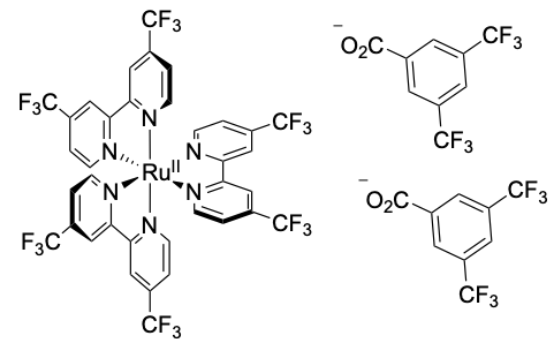
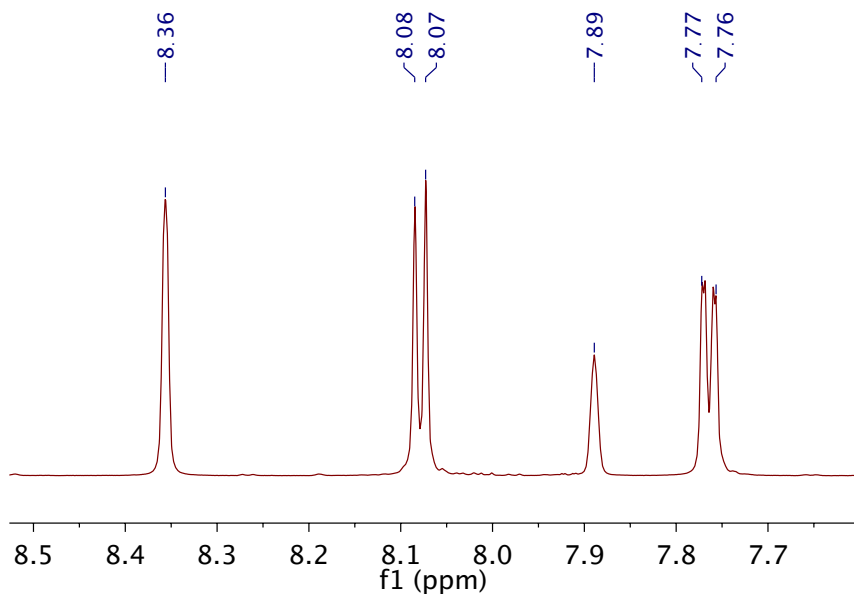




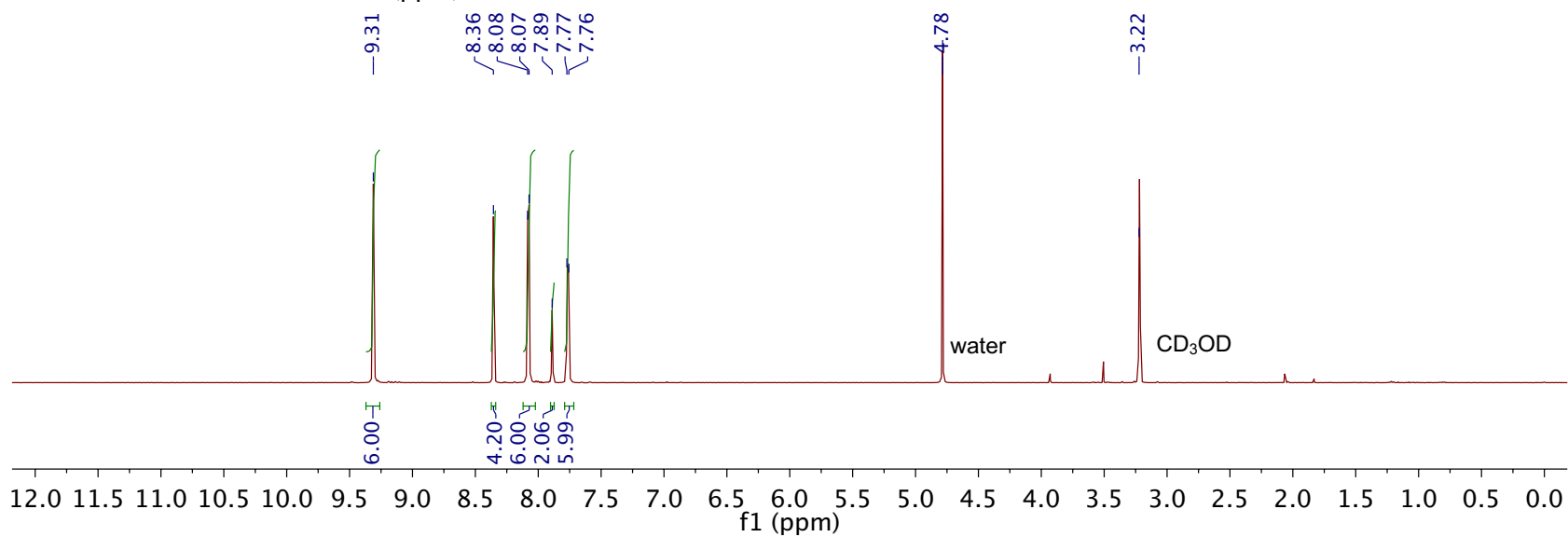


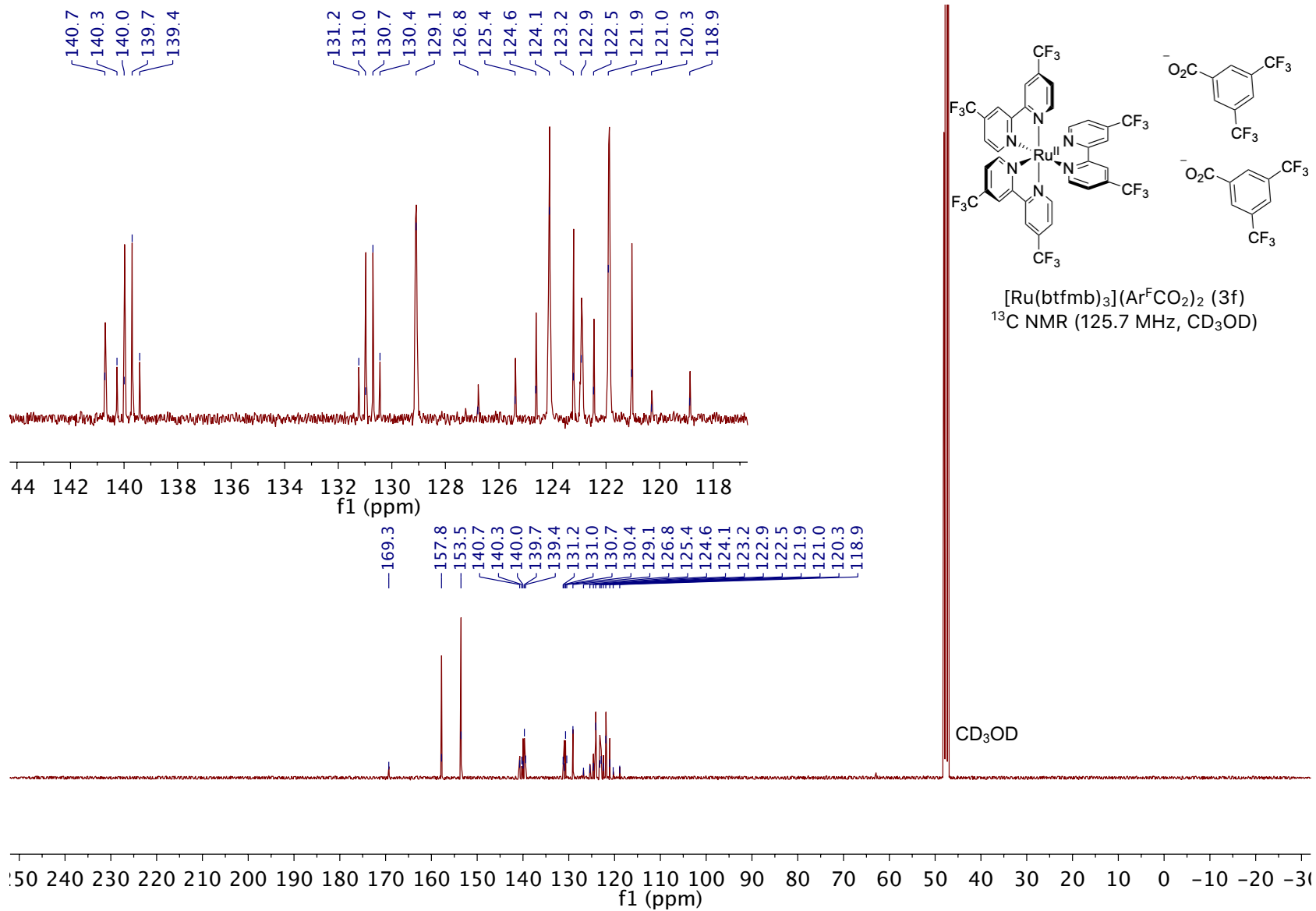


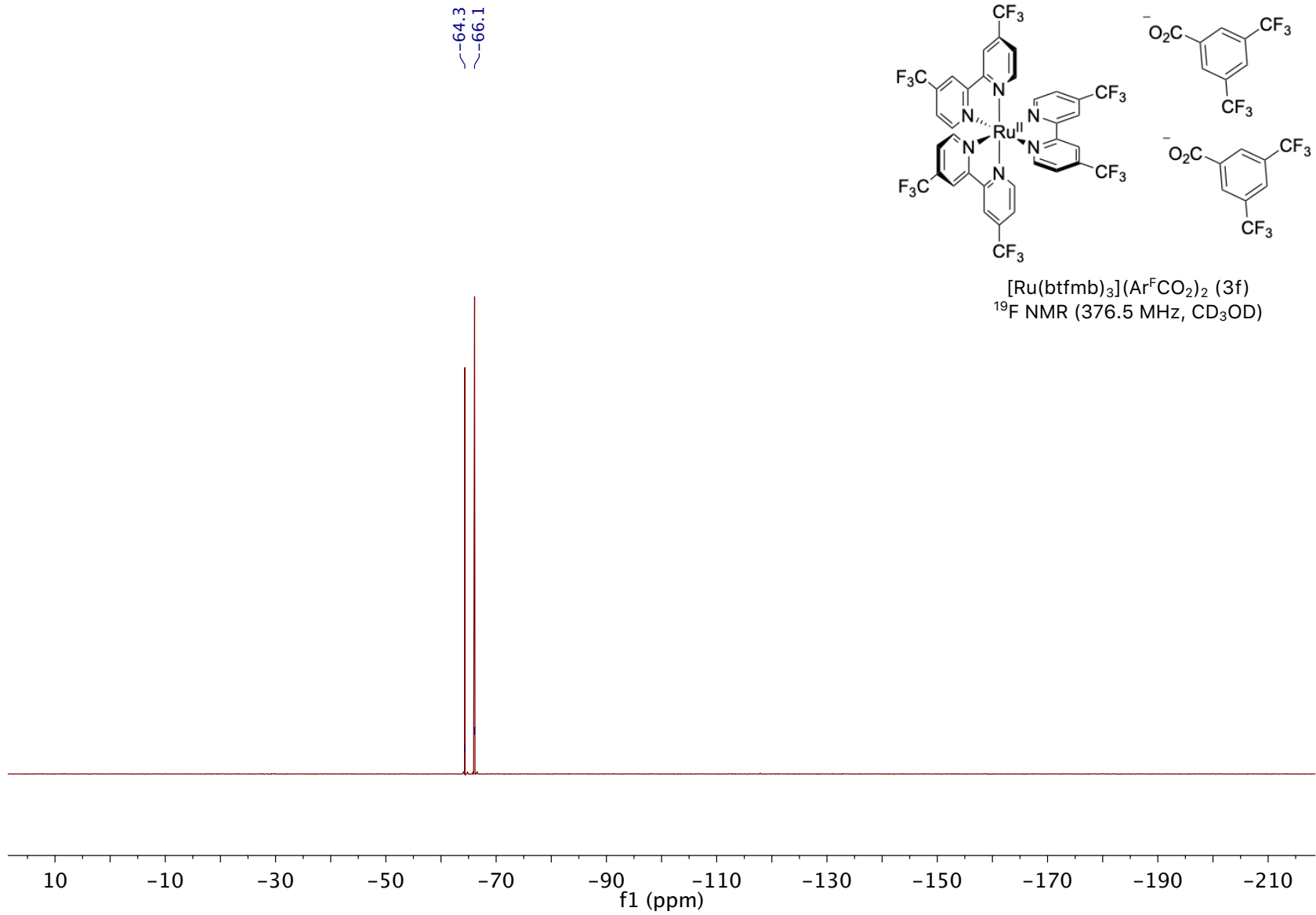


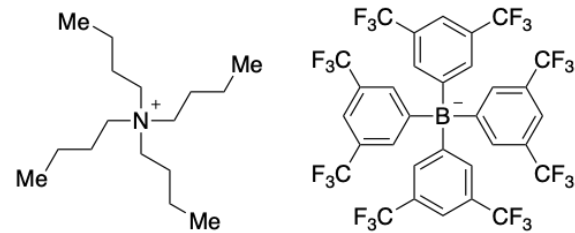
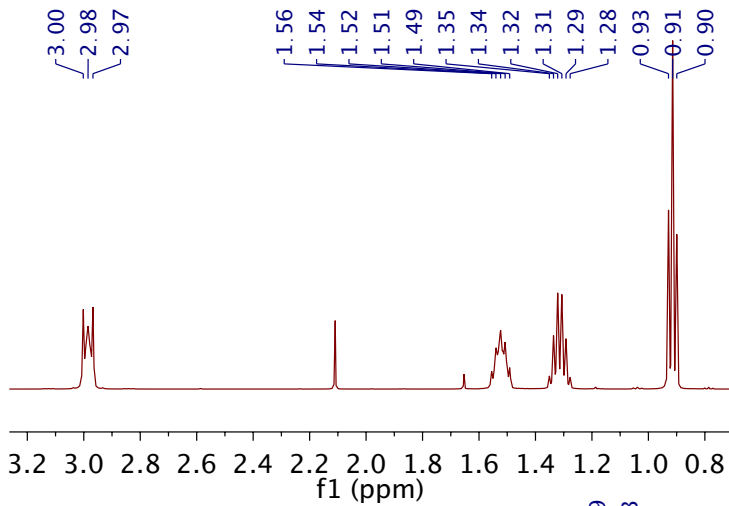


[Ru(btmb)₃](Ar^FCO₂)₂ (3f)
¹H NMR (500.0 MHz, CD₃OD)

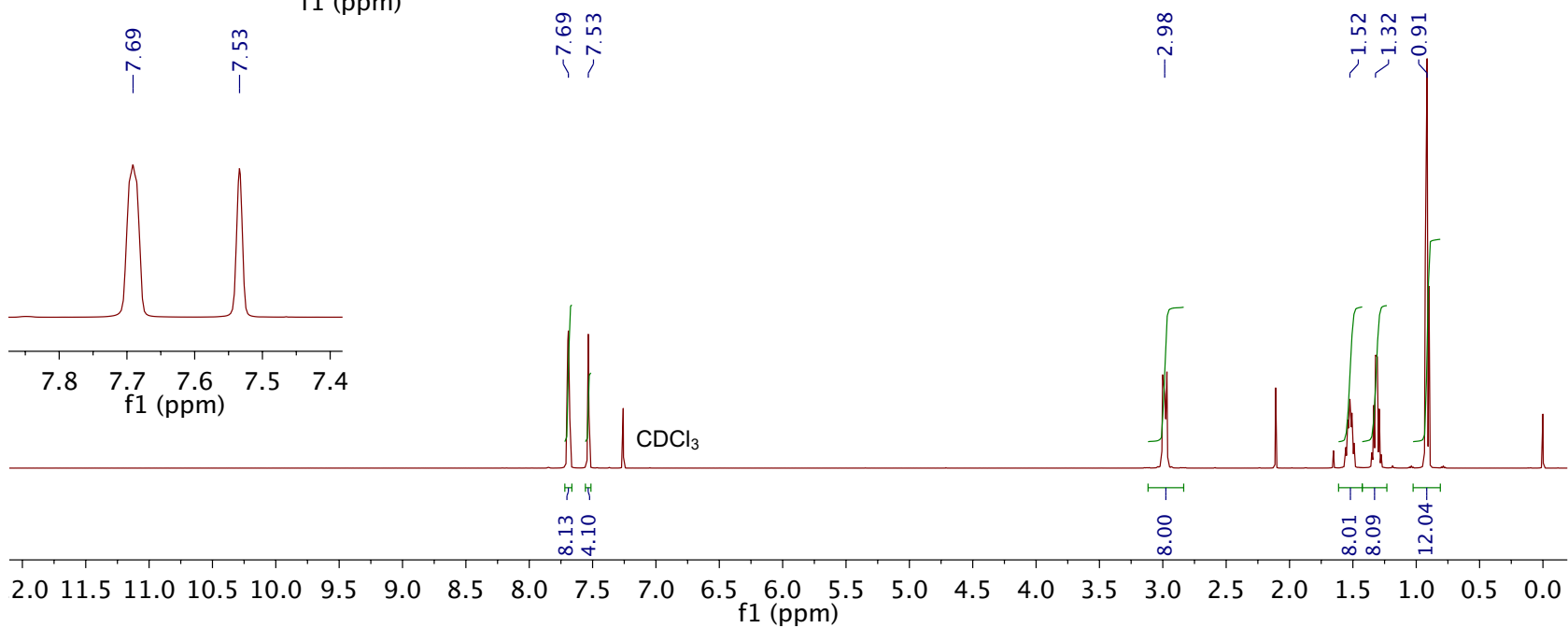


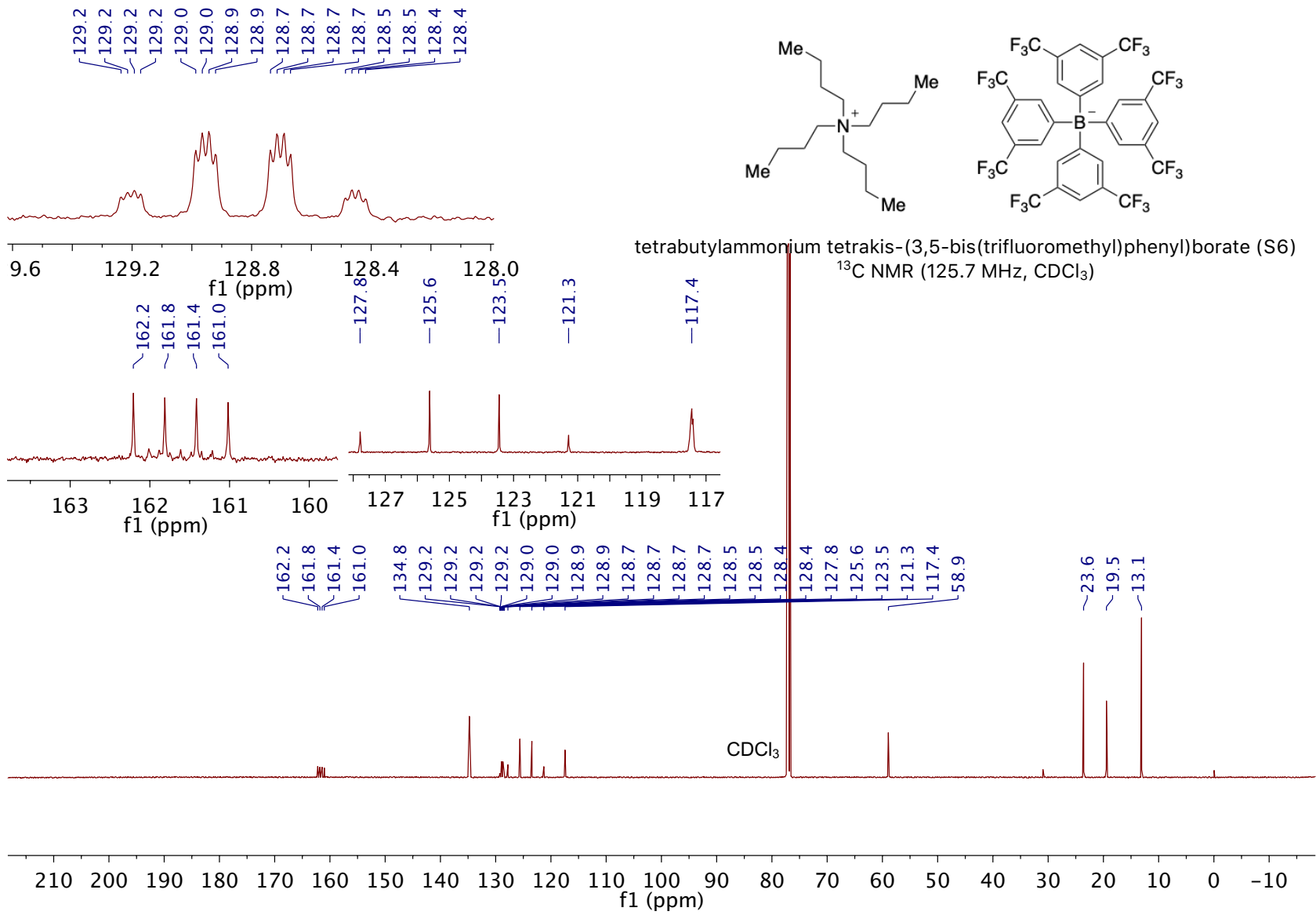


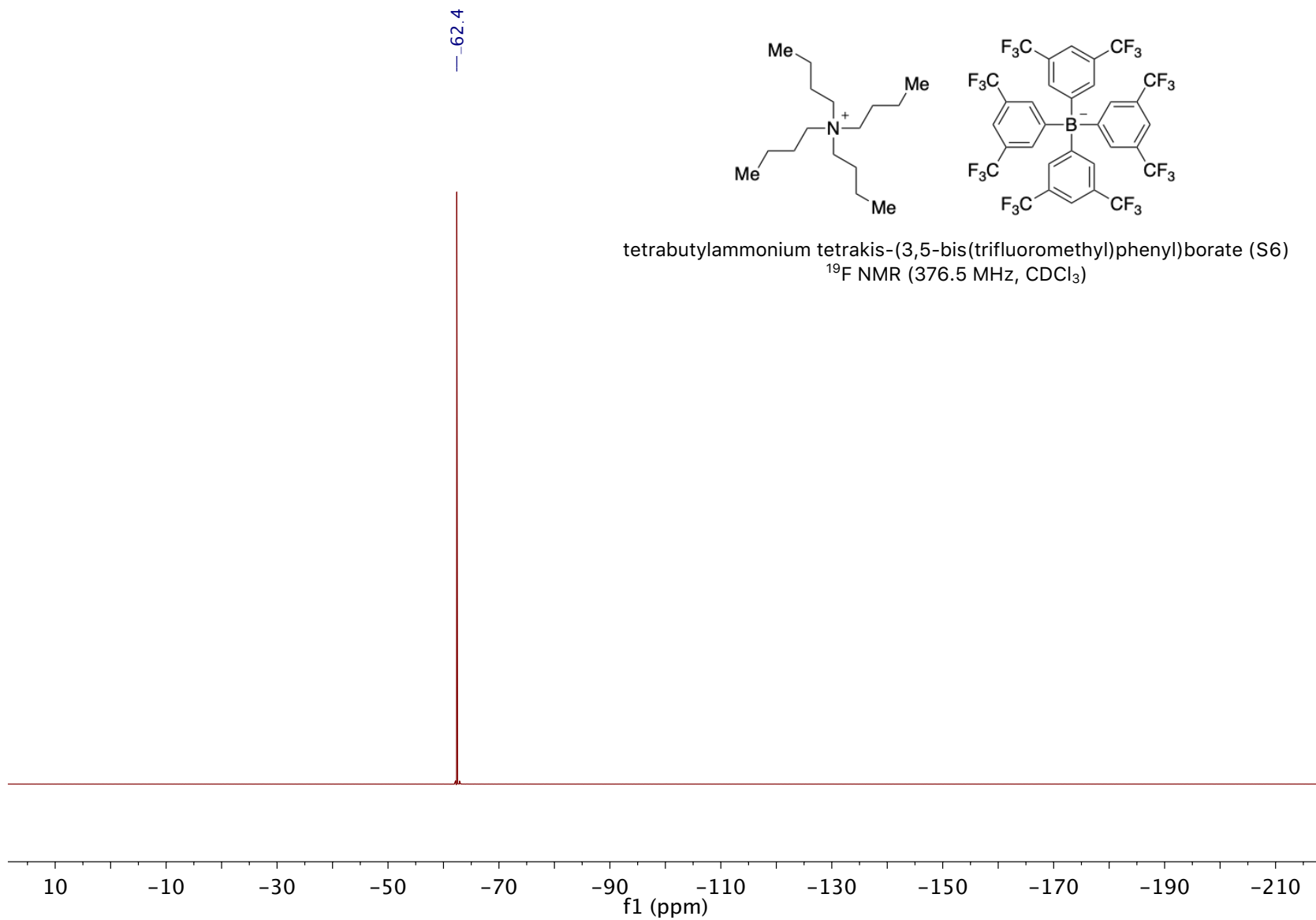


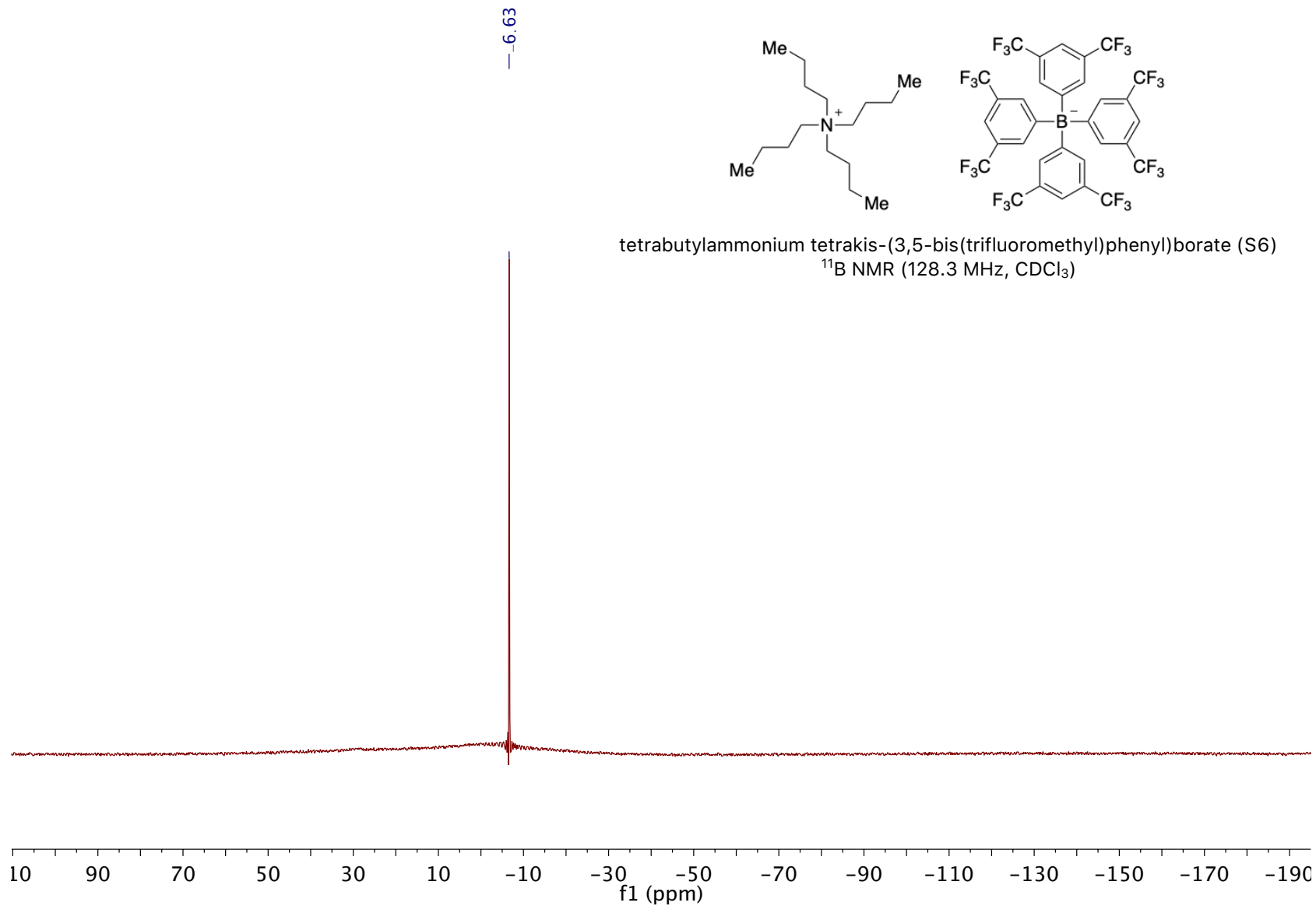


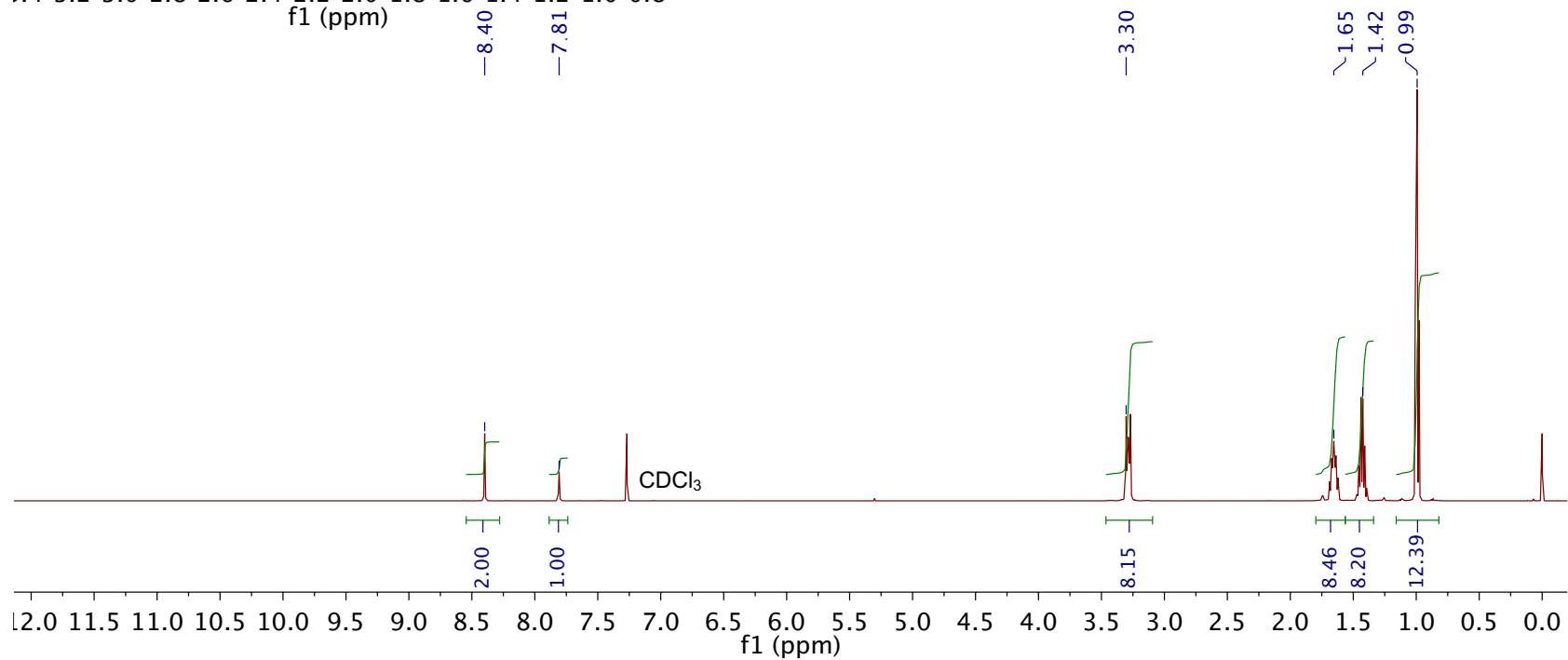
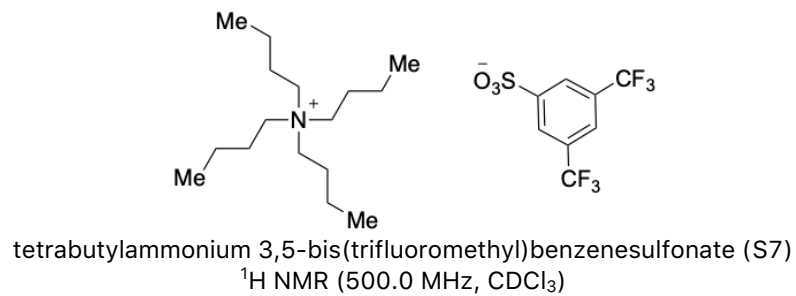
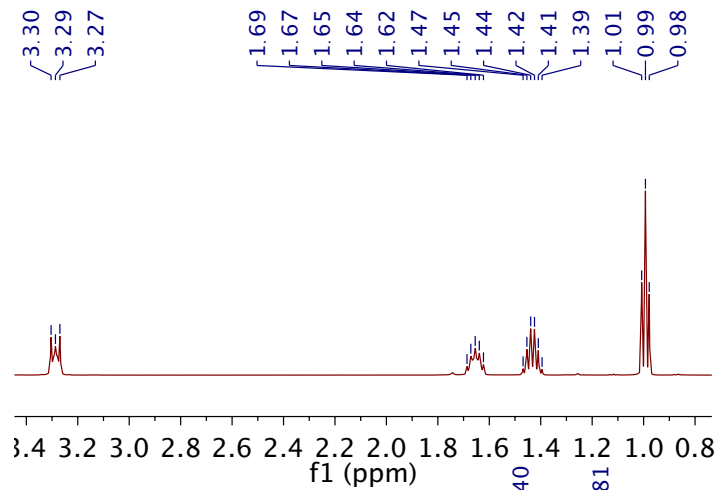
tetrabutylammonium tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate (S6)
 ^1H NMR (500.0 MHz, CDCl_3)

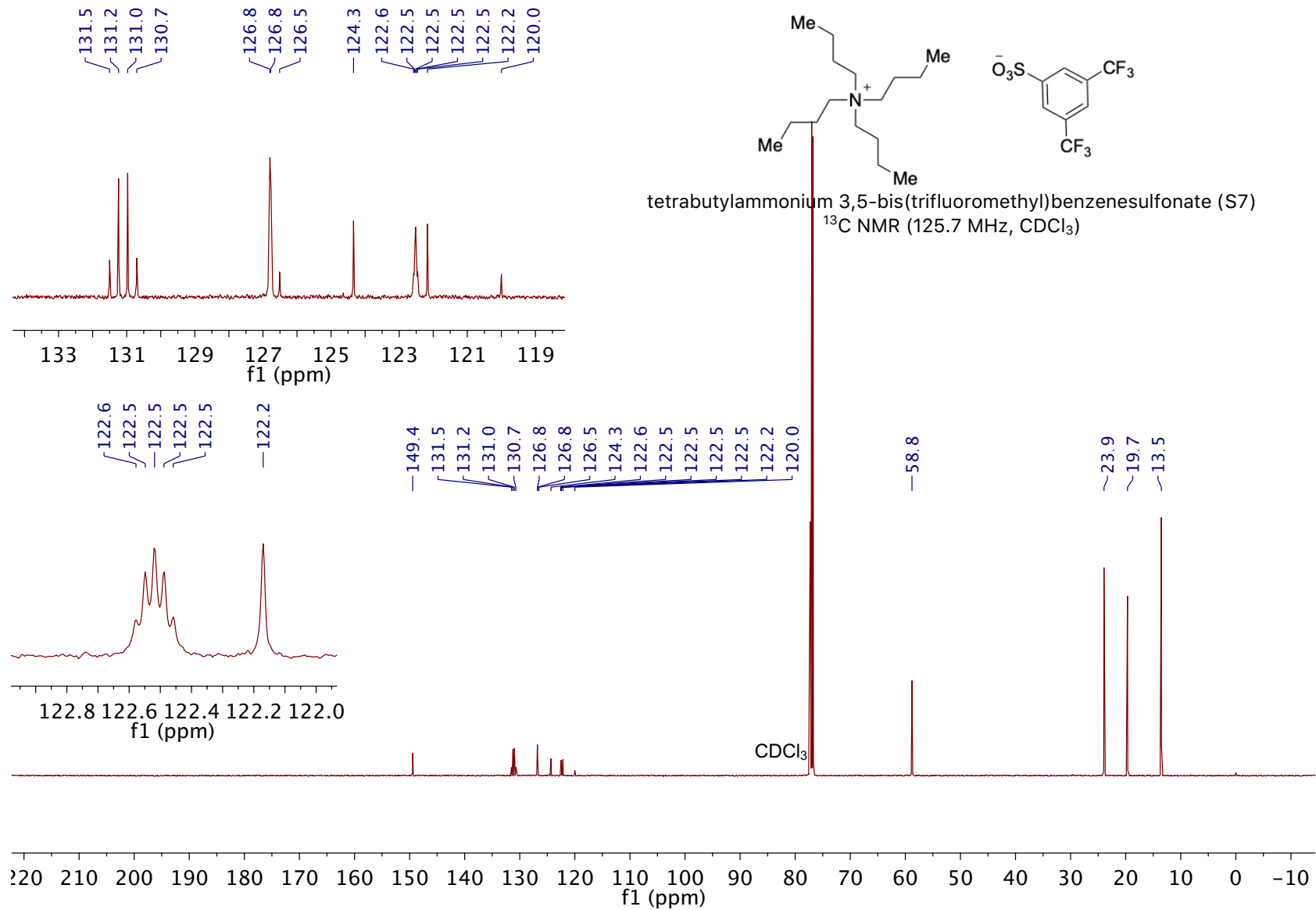




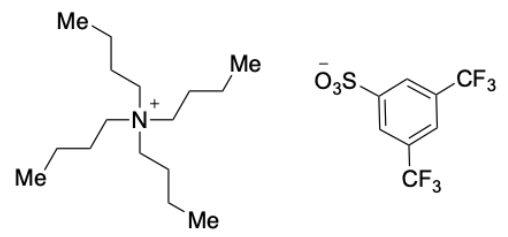




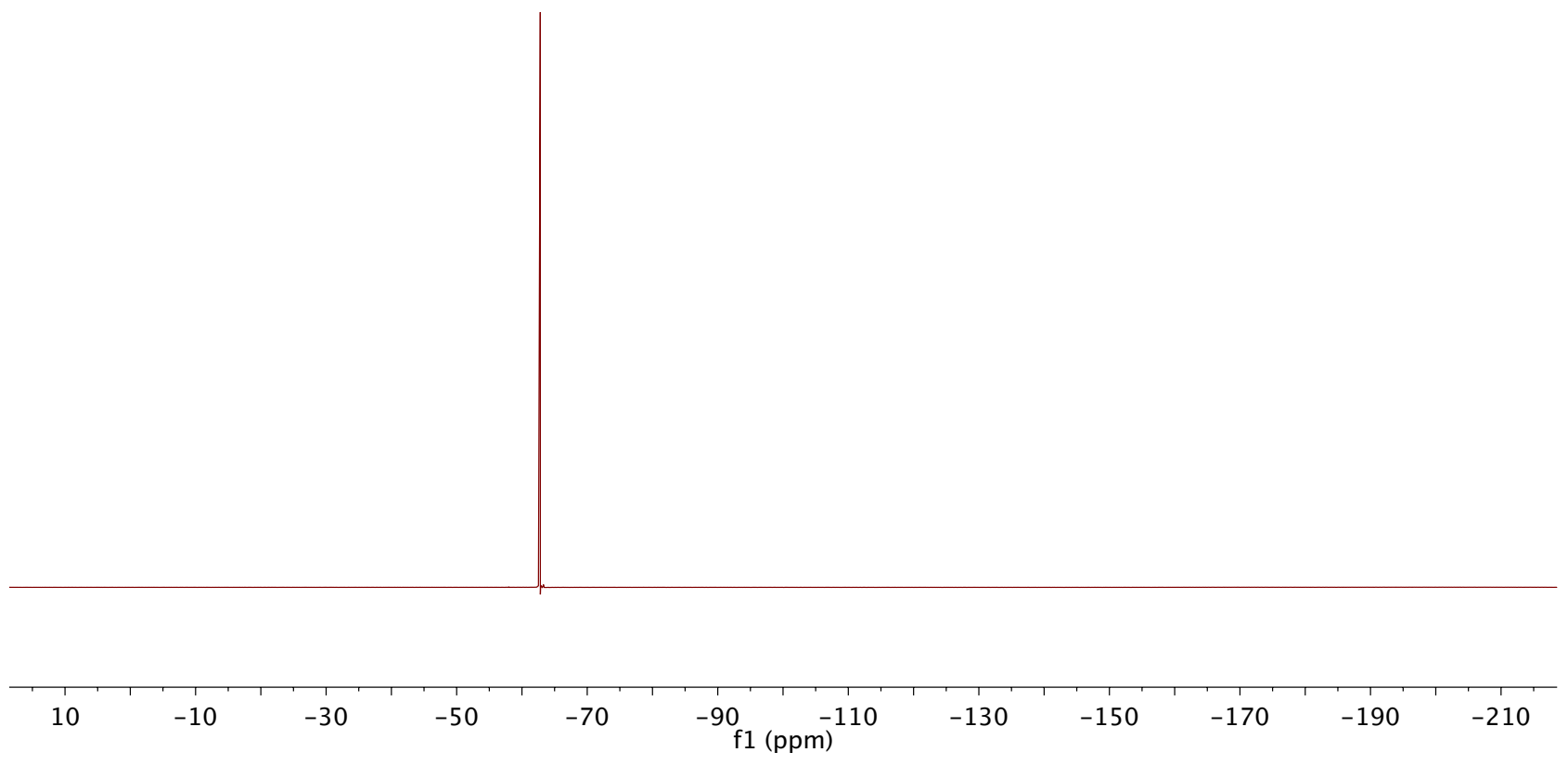




-62.8



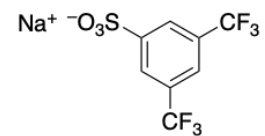
tetrabutylammonium 3,5-bis(trifluoromethyl)benzenesulfonate (S7)
¹⁹F NMR (376.5 MHz, CDCl₃)



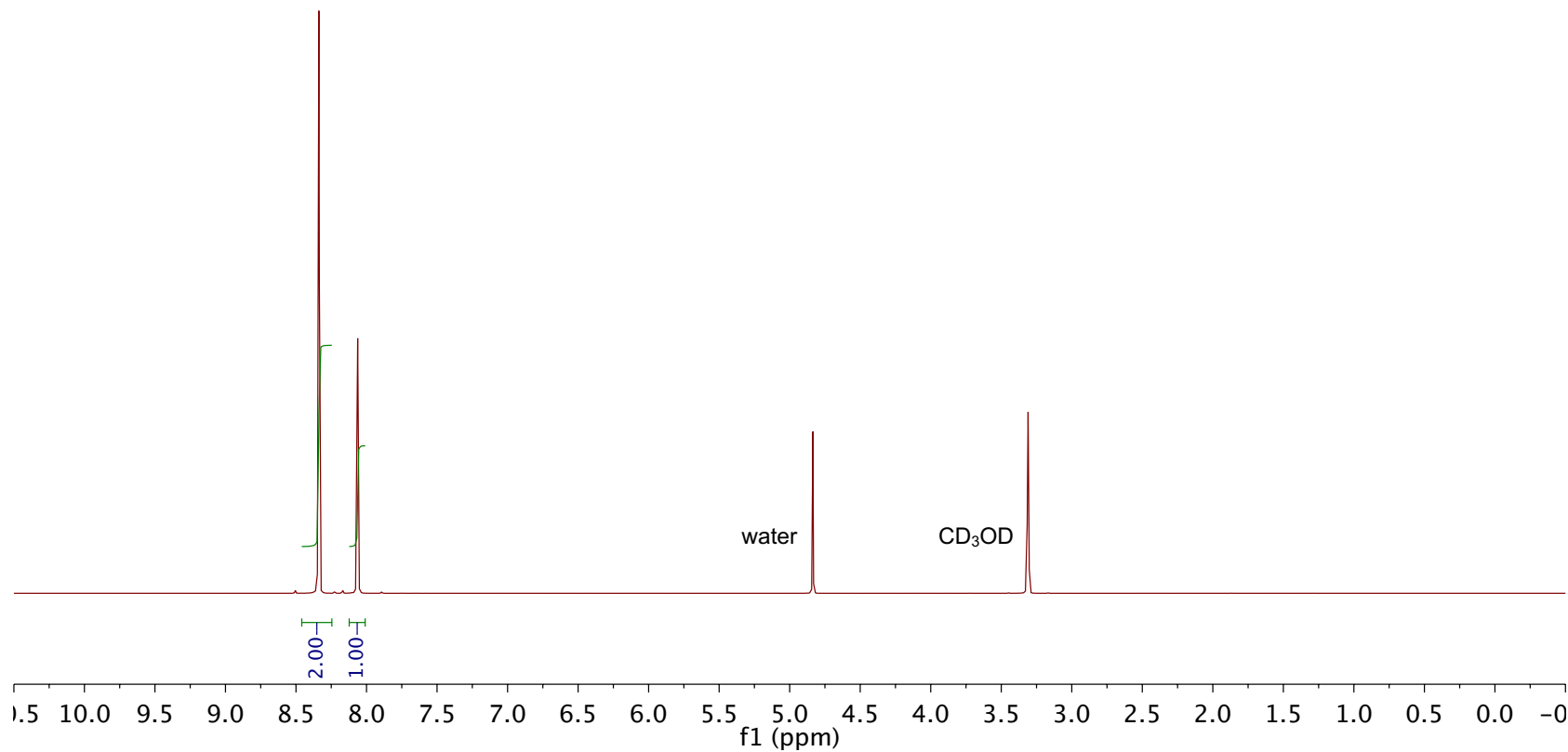
— 8.34
— 8.06

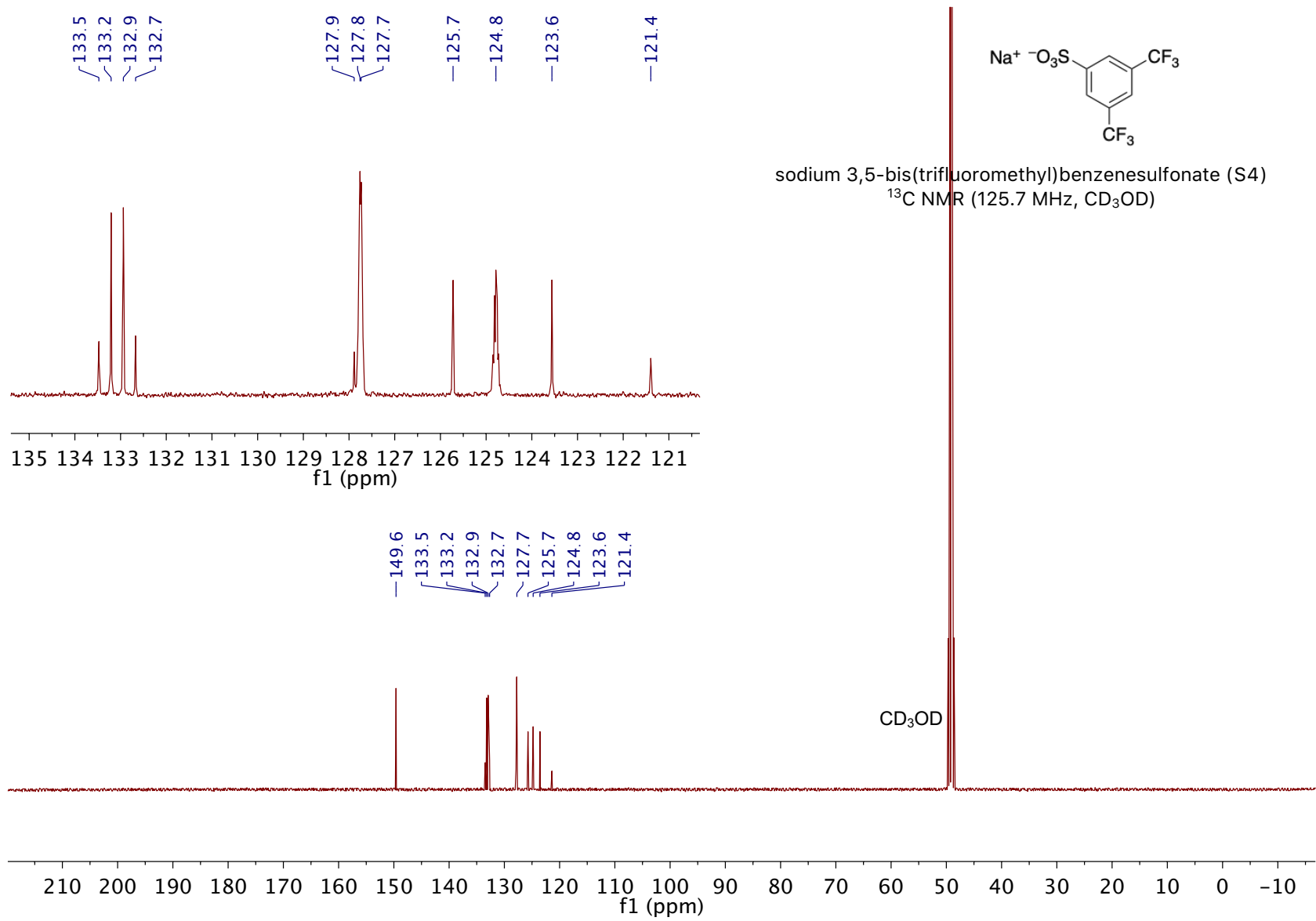
— 4.84

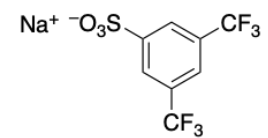
— 3.31



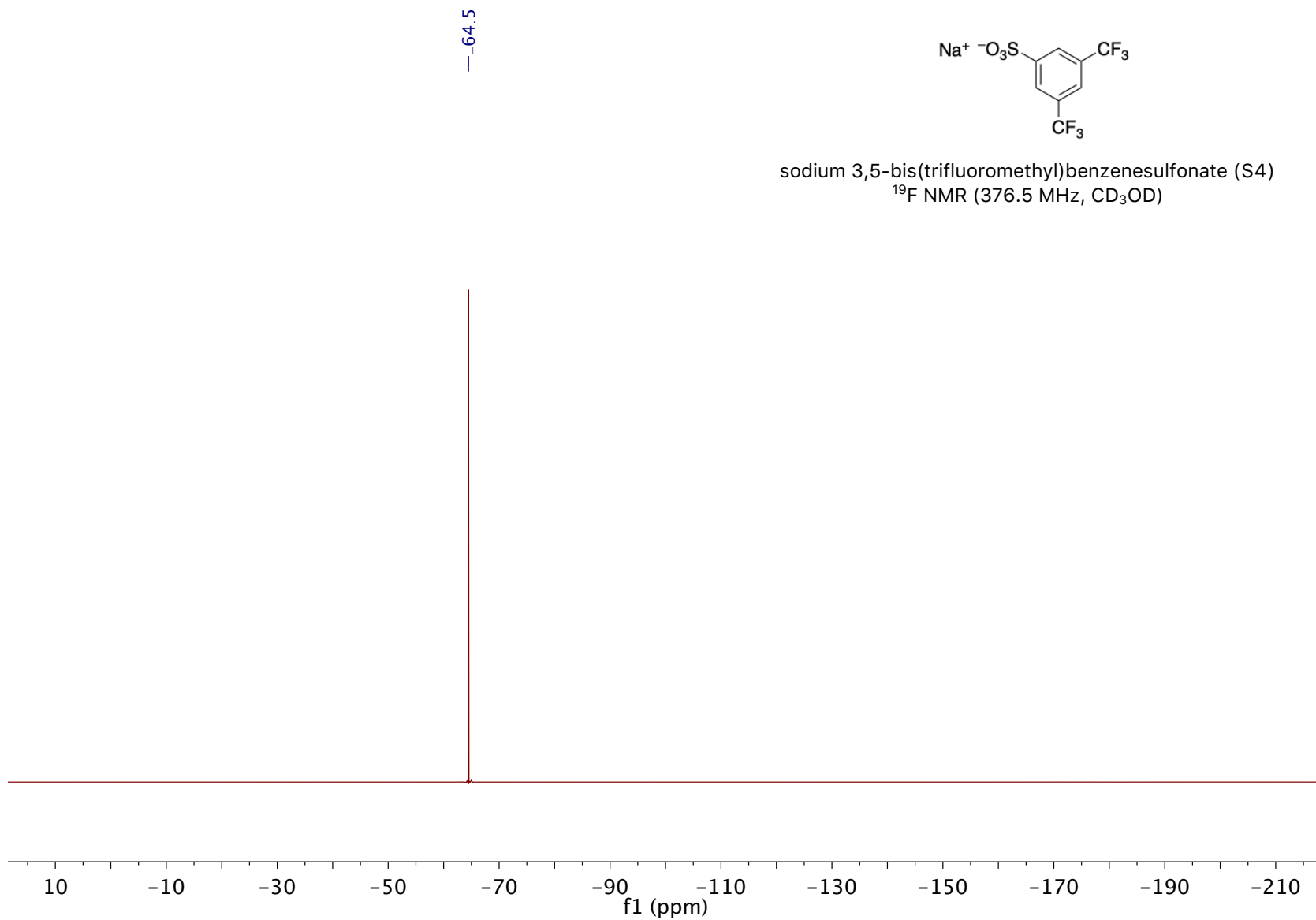
sodium 3,5-bis(trifluoromethyl)benzenesulfonate (S4)
¹H NMR (500.0 MHz, CD₃OD)

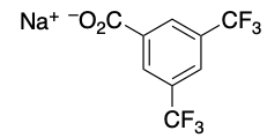




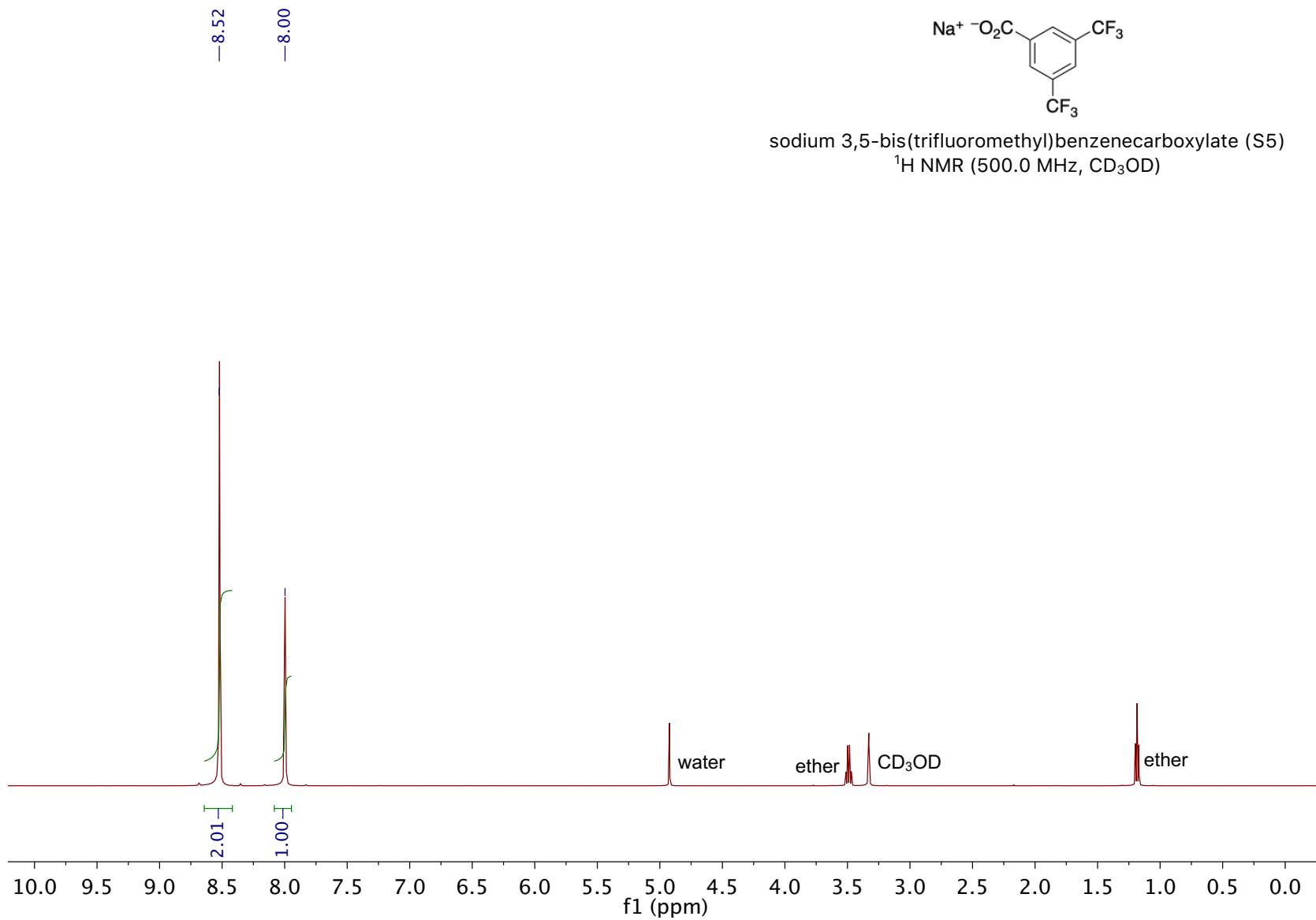


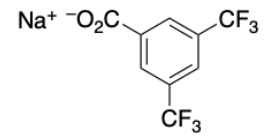
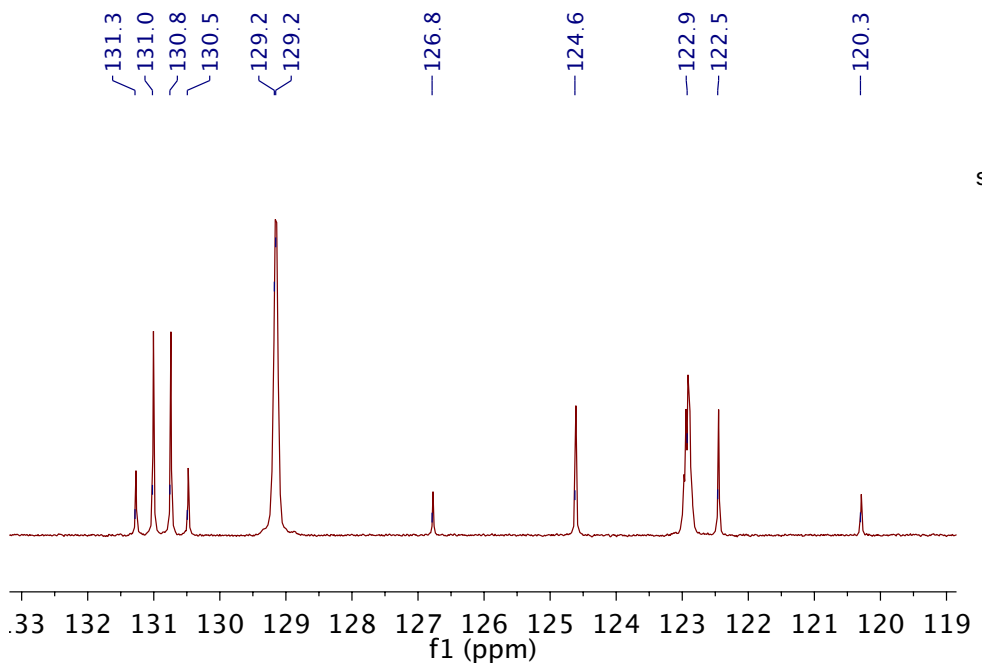
sodium 3,5-bis(trifluoromethyl)benzenesulfonate (S4)
¹⁹F NMR (376.5 MHz, CD₃OD)



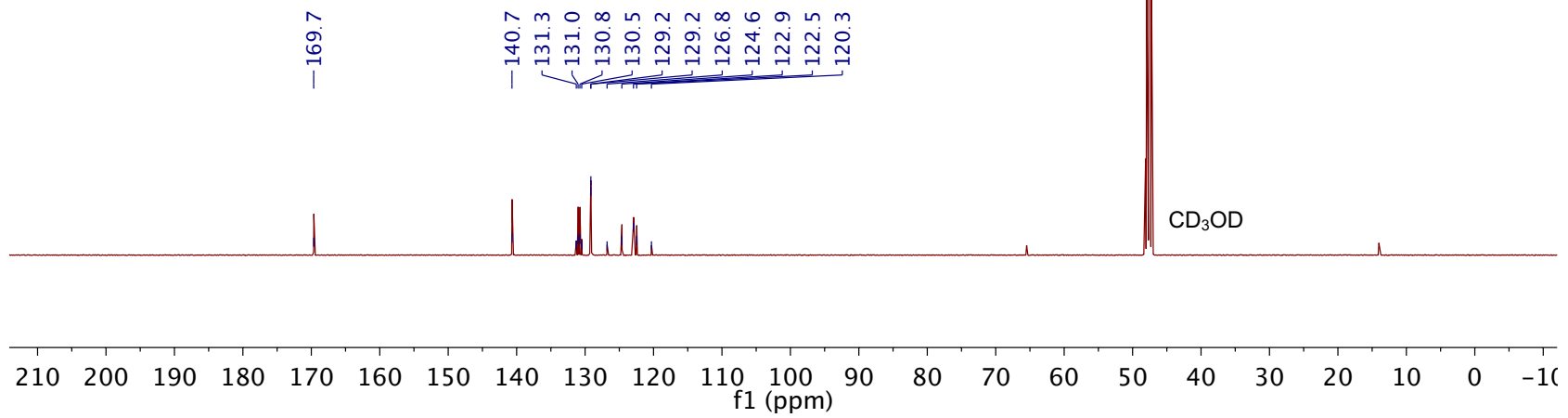


sodium 3,5-bis(trifluoromethyl)benzenecarboxylate (S5)
¹H NMR (500.0 MHz, CD₃OD)

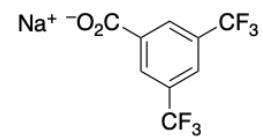




sodium 3,5-bis(trifluoromethyl)benzenecarboxylate (S5)
¹³C NMR (125.7 MHz, CD₃OD)



--64.3



sodium 3,5-bis(trifluoromethyl)benzenecarboxylate (S5)
¹⁹F NMR (376.5 MHz, CD₃OD)

