Supplementary information for "Selective deuteration as a tool for resolving autoxidation mechanisms in α-pinene ozonolysis"

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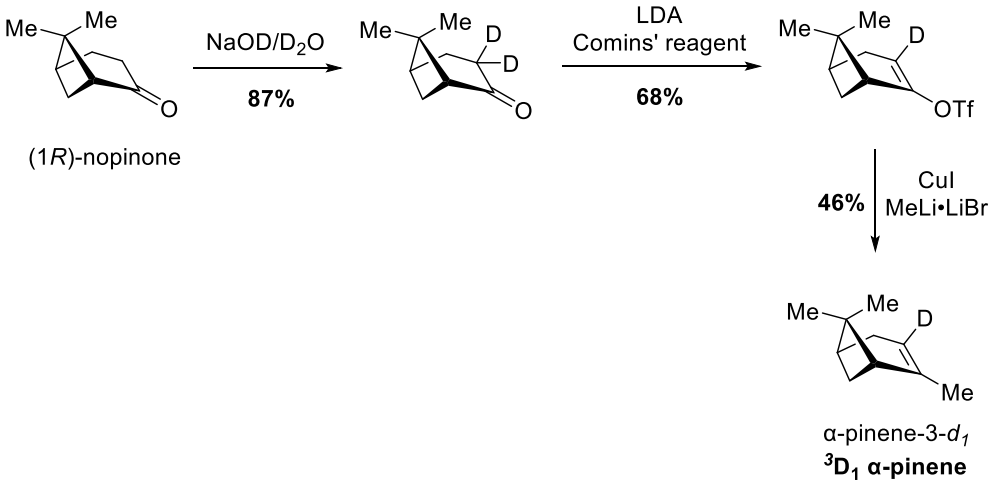
The contents of this supplementary information describe the experimental methods used when synthesising the $^3D_1$ selectively deuterated a-pinene sample.

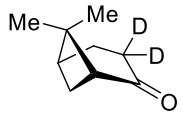
1. General Experimental

All experiments were conducted under a nitrogen atmosphere in flame-dried glassware. All reagents were used as purchased. Reaction solvents were purchased as anhydrous or purified by either a solvent purification column or distillation. Starting materials and reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. Diisopropylamine was distilled over CaH_2 prior to use. Purifications of products were performed by flash column chromatography using silica gel (230 – 400 mesh) as a stationary phase. Analytical thin-layer chromatography technique was performed on silica gel pre-coated glass-backed plates, and the reactions were examined by staining with potassium permanganate stain or *p*-anisaldehyde stain. A Bruker Avance III 500 MHz instrument was used to record 1 H and 13C NMR spectra of all compounds. NMR data are reported as brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signals are detailed in ppm and coupling constants in Hz. High-resolution mass spectra were recorded with a time of flight (TOF) mass analyzer Bruker Impact-II Mass Spectrometer. A Bruker Tensor 37 FTIR spectrometer was used to obtain infrared spectra of compounds and data were reported in cm^{-1}.

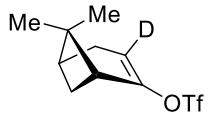
2. Experimental Procedures for the Synthesis of α-Pinene-3-*d*$_1$ (^{3}D$_1$ α-pinene)

Scheme S1 Synthesis route to α-Pinene-3-*d*$_1$ **(^{3}D$_1$ α-pinene)**

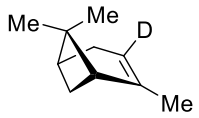




(1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-*d*$_2$: To a solution of (1*R*)-nopinone (2.10 g, 15 mmol, 1 equiv) in 40 mL DMSO-*d*$_6$ was added 7 mL 40 wt% NaOD in D_2O. Reaction was heated to 90 °C for 3 hours, then cooled to room temperature and diluted with D_2O (40 mL) and Et_2O (40 mL). The organic phase was collected and the aqueous layer extracted with Et_2O (3 x 40 mL). Combined organics were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography on silica gel using 15% - 20% Et_2O in pentane as the eluent afforded the title compound (1.83 g, 87%) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 – 2.47 (m, 2H), 2.26 – 2.19 (m, 1H), 2.07 – 1.98 (m, 1H), 1.96 – 1.89 (m, 1H), 1.57 (d, J = 10.3 Hz, 1H), 1.32 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 215.07, 57.96, 41.22, 40.37, 32.01 (m, 1C), 25.89, 25.25, 22.10, 21.20. FT-IR (neat): 2930, 2874, 1715, 1459. 1370, 1268, 1159, 1053 cm^{-1}. HRMS (APCI): Exact mass calcd for $C_9H_{12}D_2O$ $[M+H]^+$, 141.1243. Found 141.1242.

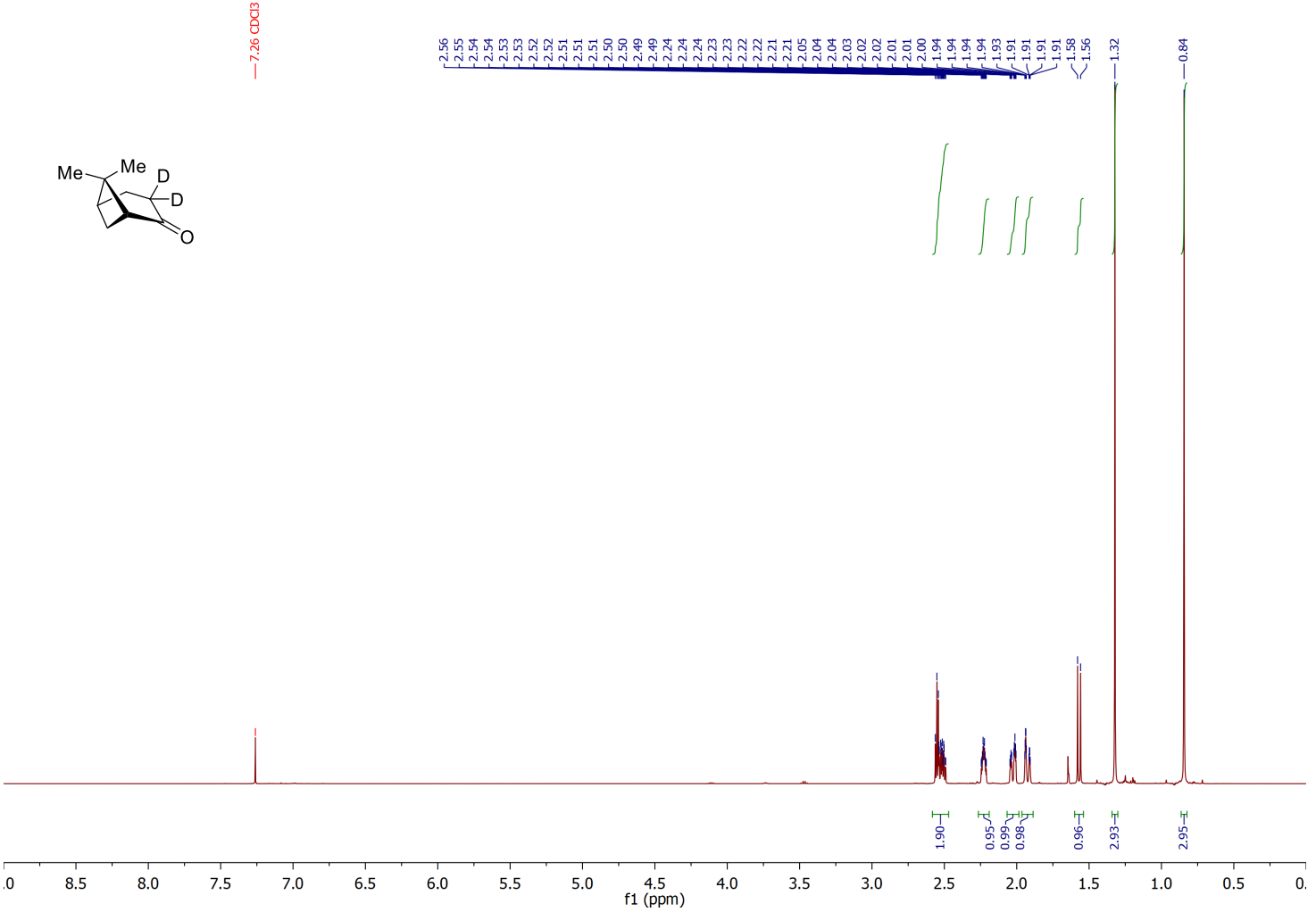


(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate: To a solution of diisopropylamine (0.9 mL, 6.42 mmol, 1.5 equiv) in THF (12 mL) at -78 ºC was added *n*-butyllithium (2.5 mL, 6.42 mmol, 2.5 M in hexanes, 1 equiv). After 15 minutes, (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-*d*$_2$ (**S1**) (600 mg, 4.28 mmol, 1 equiv) in THF (10 mL) was added dropwise into the solution of LDA and stirred for 40 minutes. At this time, a solution of Comins' reagent (3.36 g, 8.56 mmol, 2 equiv) in THF (8 mL) was added over a period of 15 minutes. The resulting mixture was warmed to 0 ºC and stirred for 2 hours. Reaction was diluted with D_2O (50 mL) and Et_2O (25 mL) and transferred to a separatory funnel. The organic phase was collected and the aqueous layer extracted with Et_2O (3 x 30 mL).
The combined organics were dried with $MgSO_4$. Concentration under reduced pressure and flash column chromatography on silica gel in 0% - 3% Et_2O in pentane as the eluent afforded the title compound (790 mg, 68% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): 2.56 (dt, J = 9.1, 5.7 Hz, 1H), 2.41 – 2.25 (m, 3H), 2.17 – 2.12 (m, 1H), 1.38 (d, J = 9.2 Hz, 1H), 1.35 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 154.98, 118.54 (q, 1C, J = 321 Hz), 111.23 (m, 1C), 46.27, 40.11, 39.72, 31.71, 28.07, 25.48, 25.47, 20.81, 20.80. FT-IR (neat): 2940, 2841, 1653, 1418, 1202, 1138, 1058. HRMS (APCI): APCI, Exact mass calcd for $C_{10}H_{12}F_3O_3S$ $[M-D]^-$, 269.0645. Found 269.0640.

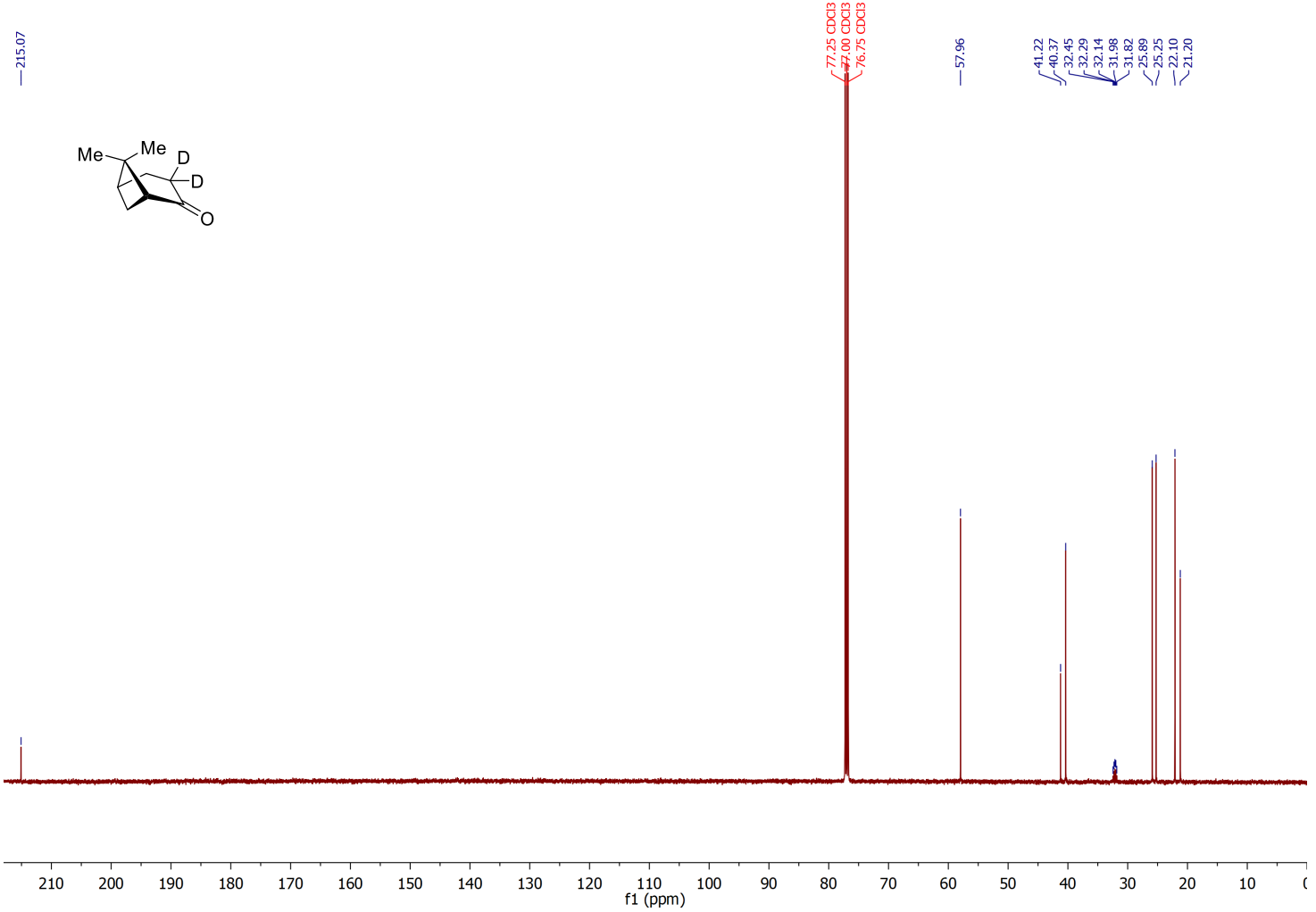


(1*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene-3-*d* ($^3D_1$-α-pinene): Methyllithium lithium bromide complex (3.9 mL, 5.86 mmol, 1.5 M in Et_2O, 3.5 equiv) was added to a slurry of CuI (0.80g, 4.18 mmol, 2.5 equiv) in THF (8 mL) at -5 ºC. After stirring for 15 minutes, a room temperature solution of (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate (0.45 g, 1.67 mmol, 1 equiv) in THF (7 mL) was added dropwise. Reaction mixture turned dark red. Reaction warmed to room temperature overnight. Reaction mixture was recooled to 0 ºC, then quenched with dropwise addition of H_2O until bubbling subsided. Reaction mixture was diluted with H_2O (50 mL) and extracted with pentane (3 x 30 mL). Combined organics were dried with Na_2SO_4 and filtered. Concentration under reduced pressure and flash column chromatography on silica gel in 100% pentane as the eluent afforded the title compound (105 mg, 46% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (dt, J = 8.5, 5.6 Hz, 1H), 2.28 – 2.11 (m, 2H), 2.11 – 2.03 (m, 1H), 1.93 (t, J = 5.6 Hz, 1H), 1.66 (t, J = 2.2 Hz, 3H), 1.27 (s, 3H), 1.15 (d, J = 8.5 Hz, 1H), 0.84 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) 144.41, 115.68 (m, 1C), 47.01, 47.00, 40.71, 37.97, 31.47, 31.14, 26.37, 22.93, 20.79. FT-IR (neat): 2986, 2917, 2834, 1469, 1436, 1380, 1365, 1207, 1099, 1061 cm^{-1}. HRMS (APCI): Exact mass calcd for $C_{10}H_{15}D$ $[M+H]^+$, 138.1388. Found 138.1388.

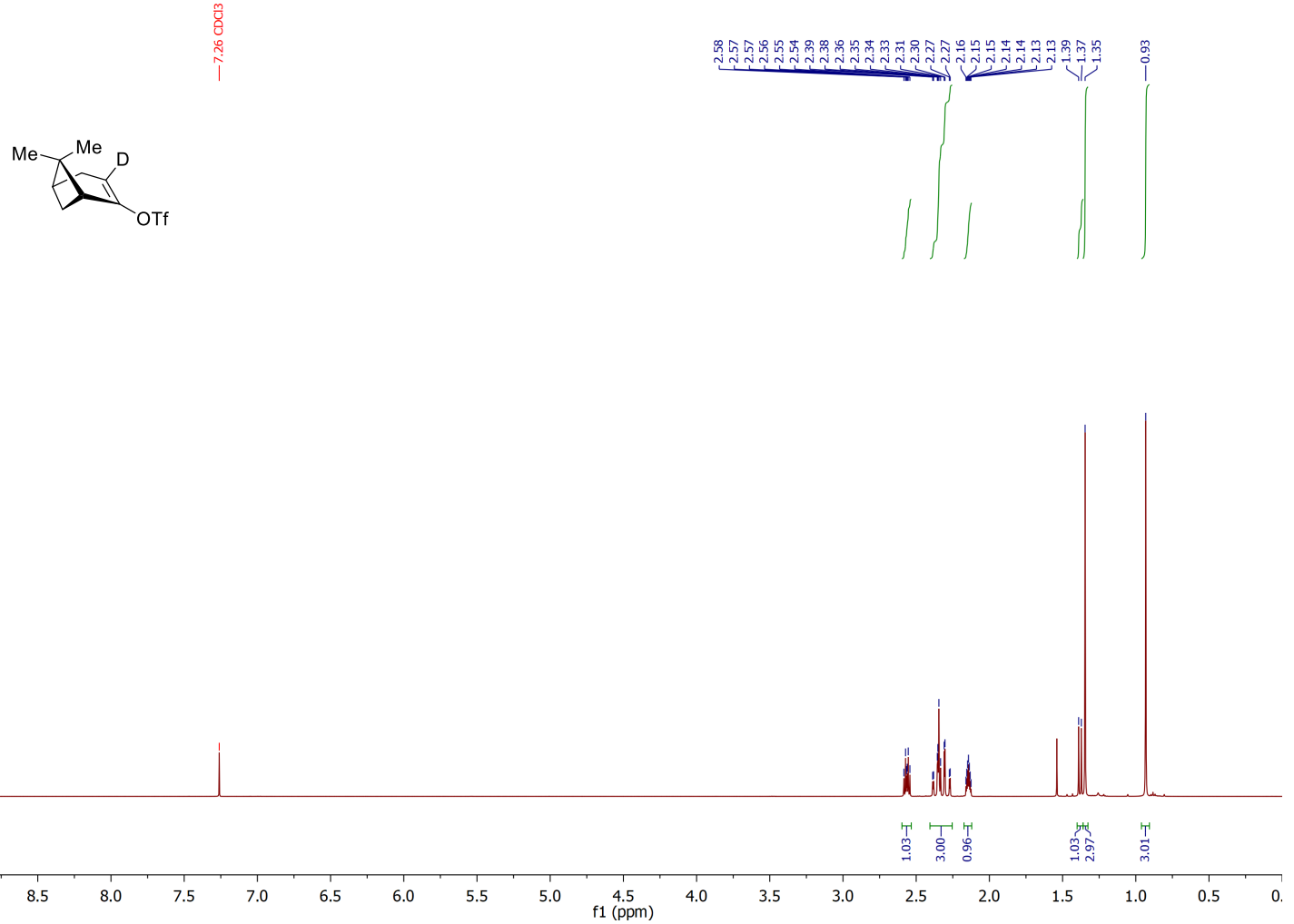
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-d_2.



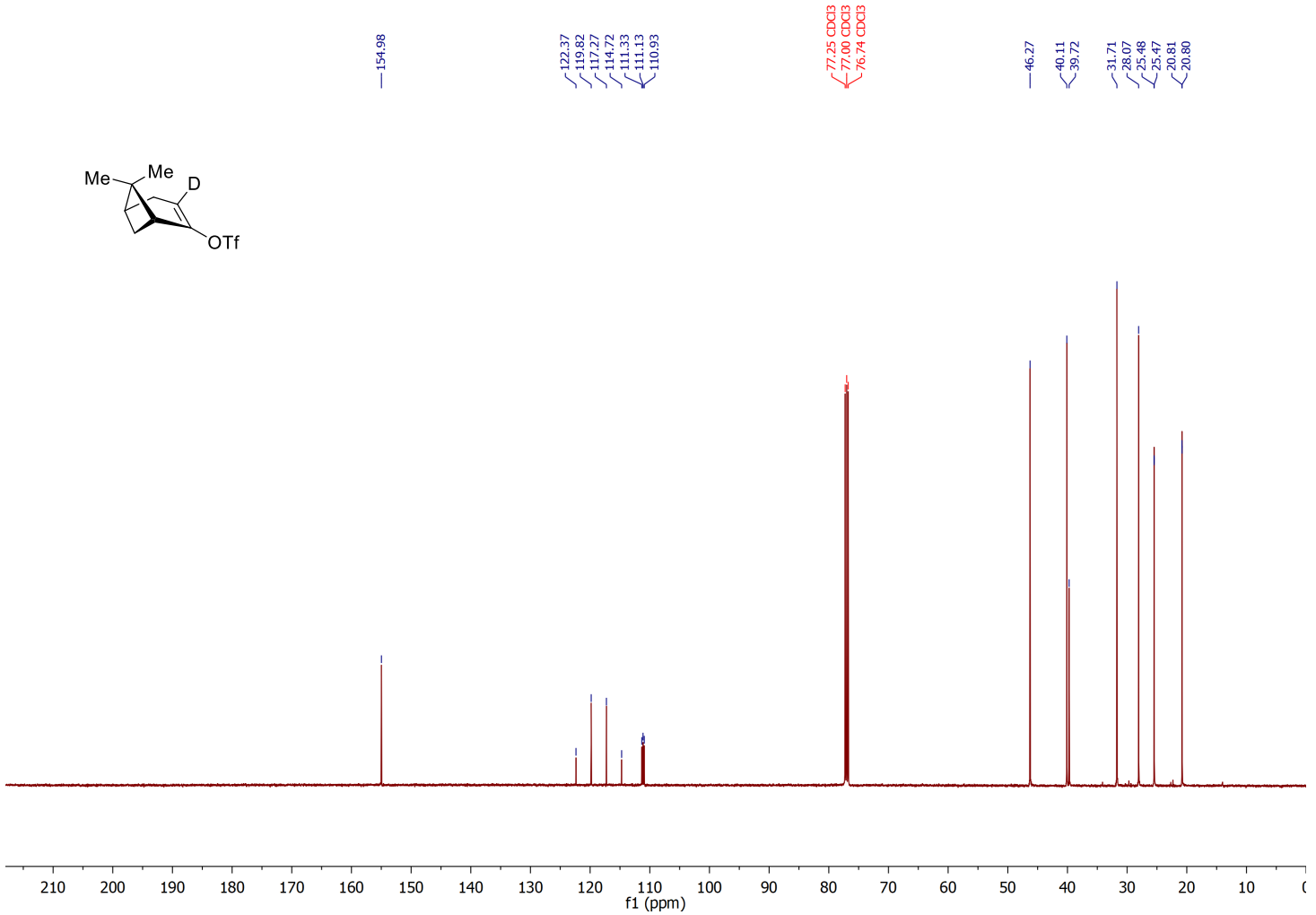
^{13}C NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-d_2.



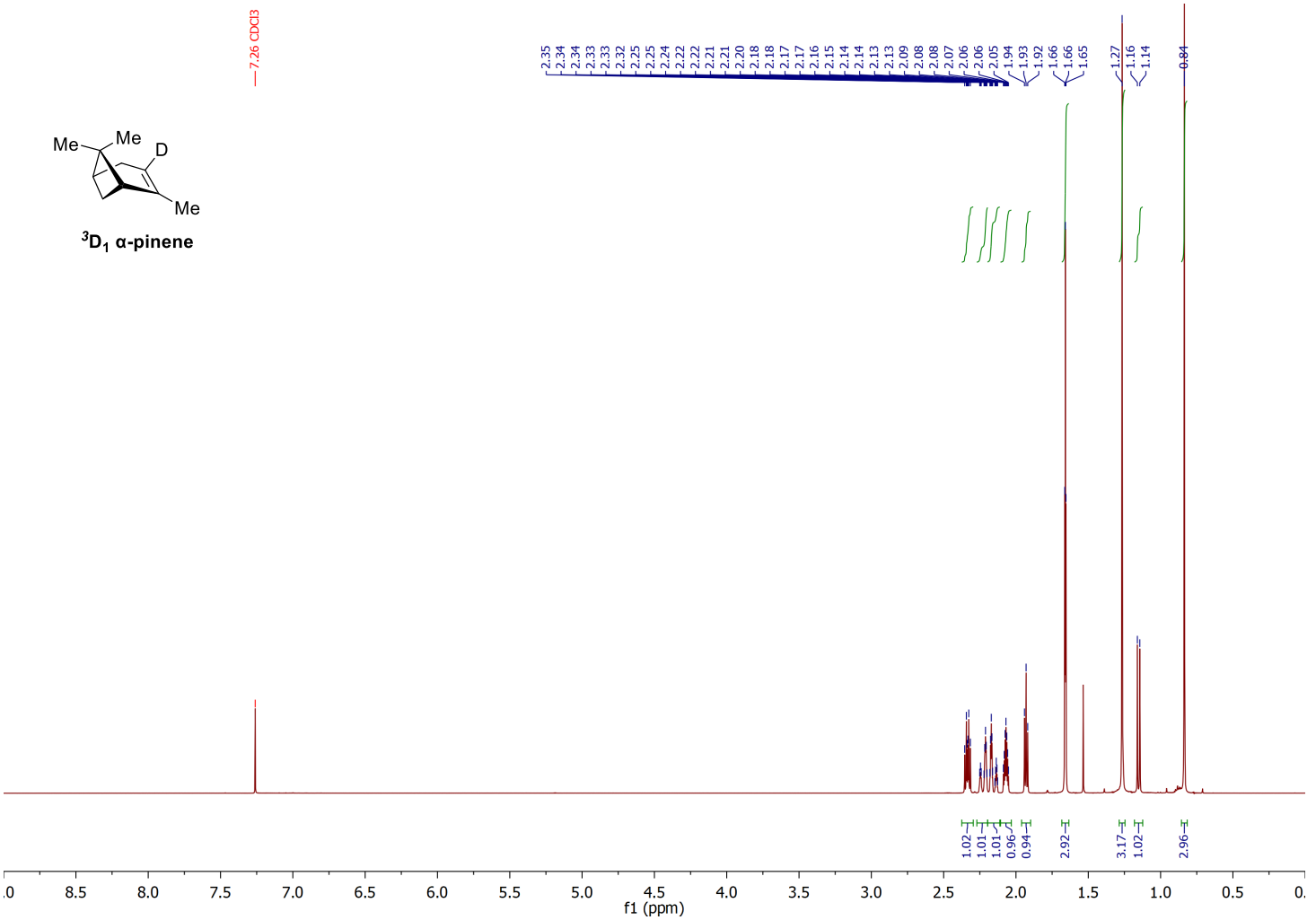
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate



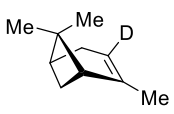
^{13}C NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of (1*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene-3-*d*.



^{13}C NMR (500 MHz, $CDCl_3$) spectrum of (1*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene-3-*d*.



$^3D_1$ α-pinene