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# Selective deuteration as a tool for resolving autoxidation mechanisms in $\alpha$-pinene ozonolysis

**Melissa Meder et al.**

*Correspondence to:* Melissa Meder (melissa.meder@helsinki.fi) and Mikael Ehn (mikael.ehn@helsinki.fi)

## S1. 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 $cm^{-1}$.

## S2. Experimental Procedures

### S2.1. Synthesis of α-Pinene-10-*d*$_3$ ($^{10}$D$_3$ α-pinene) and α-Pinene-7-*d*$_3$ ($^{7}$D$_2$ α-pinene)

Synthesis of the $^{10}D_3$ and $^{7}D_2$ α-pinene species was carried out according to the published literature procedures from our laboratory (see, Upshur, M. A., Chase, H. M., Strick, B. F., Ebben, C. J., Fu, L., Wang, H., Thomson, R. J., and Geiger, F. M.: Vibrational Mode Assignment of α-Pinene by Isotope Editing: One Down, Seventy-One To Go, The Journal of Physical Chemistry A, 120, 2684–2690, https://doi.org/10.1021/acs.jpca.6b01995, pMID: 27063197, 2016 and Upshur, M. A., Vega, M. M., Bé, A. G., Chase, H. M., Zhang, Y., Tuladhar, A., Chase, Z. A., Fu, L., Ebben, C. J., Wang, Z., Martin, S. T., Geiger, F. M., and Thomson, R. J.: Synthesis and surface spectroscopy of α-pinene isotopologues and their corresponding secondary organic material, Chem. Sci., 10, 8390–8398, https://doi.org/10.1039/C9SC02399B, 2019). Spectral data were in accordance with the published data. Copies of clean 1H NMR spectra of both $^{10}D_3$ and $^{7}D_2$ α-pinene species are provided as evidence of purity and deuterium incorporation.

### S2.2. Synthesis of α-Pinene-3-*d*$_1$ ($^{3}$D$_1$ α-pinene)

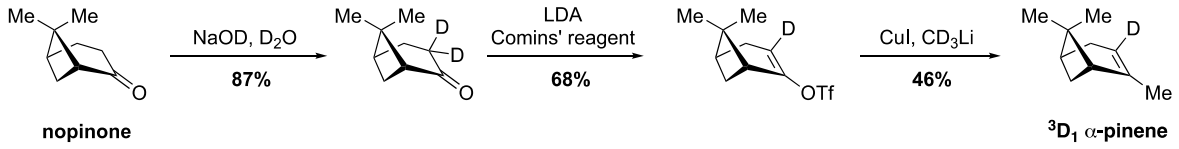


**Figure S1. Scheme S1** Synthesis route to α-Pinene-3-*d*$_1$ **($^{3}$D$_1$ α-pinene)**

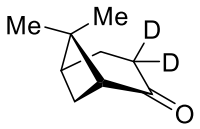


**Figure S2. (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-*d*$_2$**

**(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.

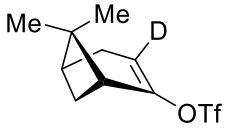


**Figure S3. (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate**

**(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.

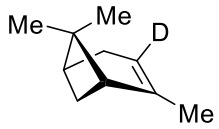


**Figure S4. (1*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene-3-*d* ($^3D_1$-α-pinene)**

**(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.

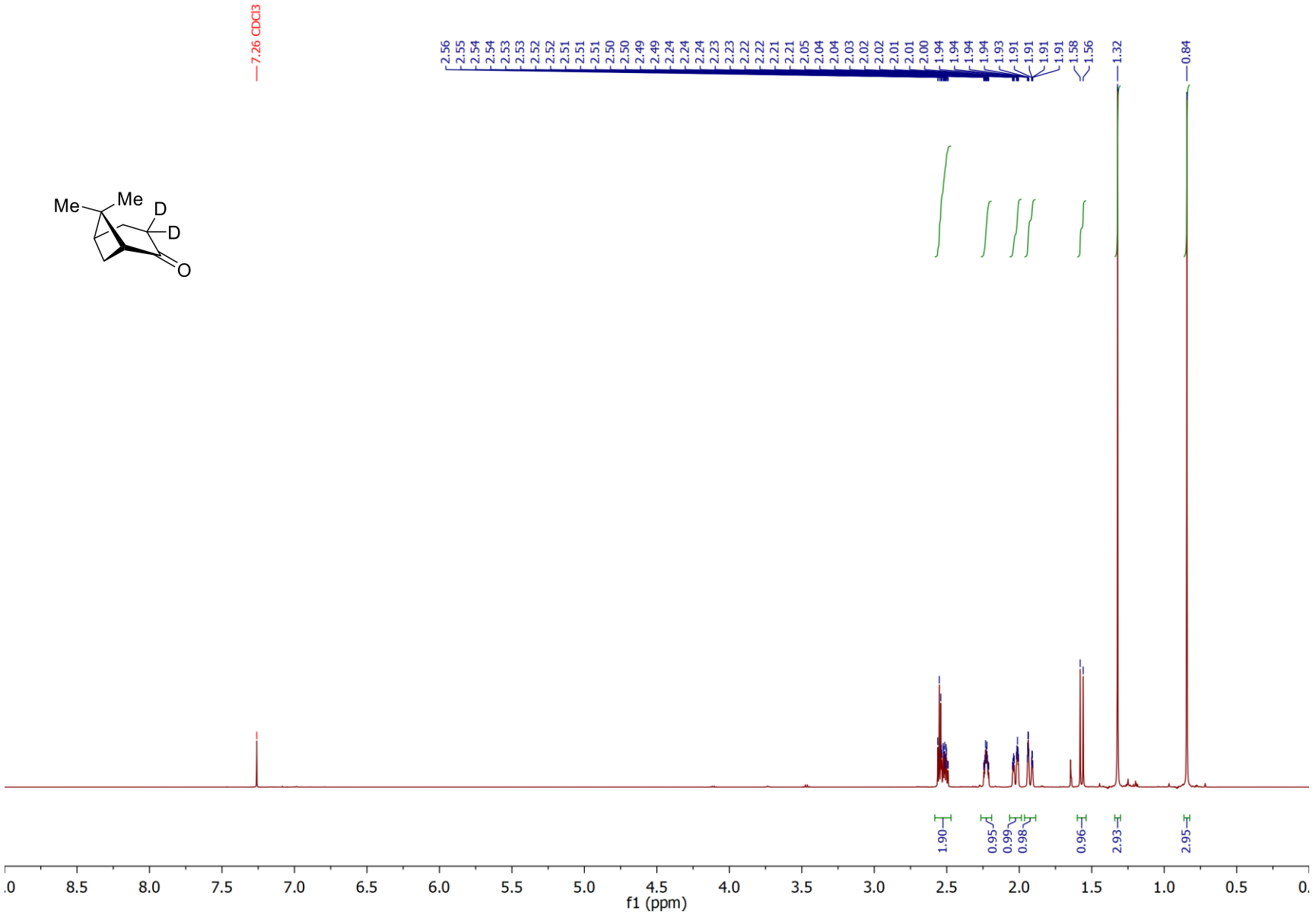


**Figure S5. $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-$d_2$.**

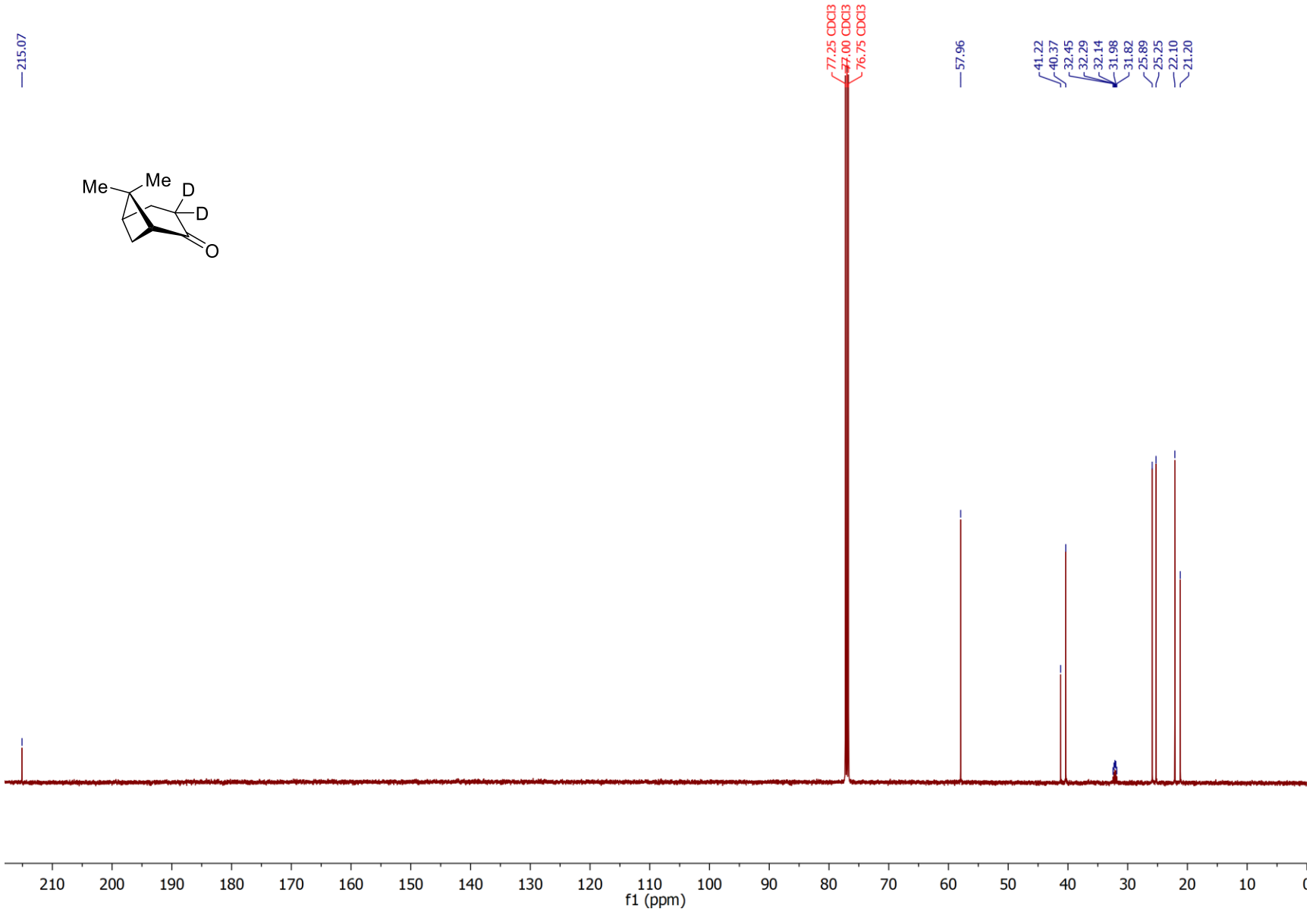


**Figure S6. $^{13}$C NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]heptan-2-one-3,3-$d_2$.**

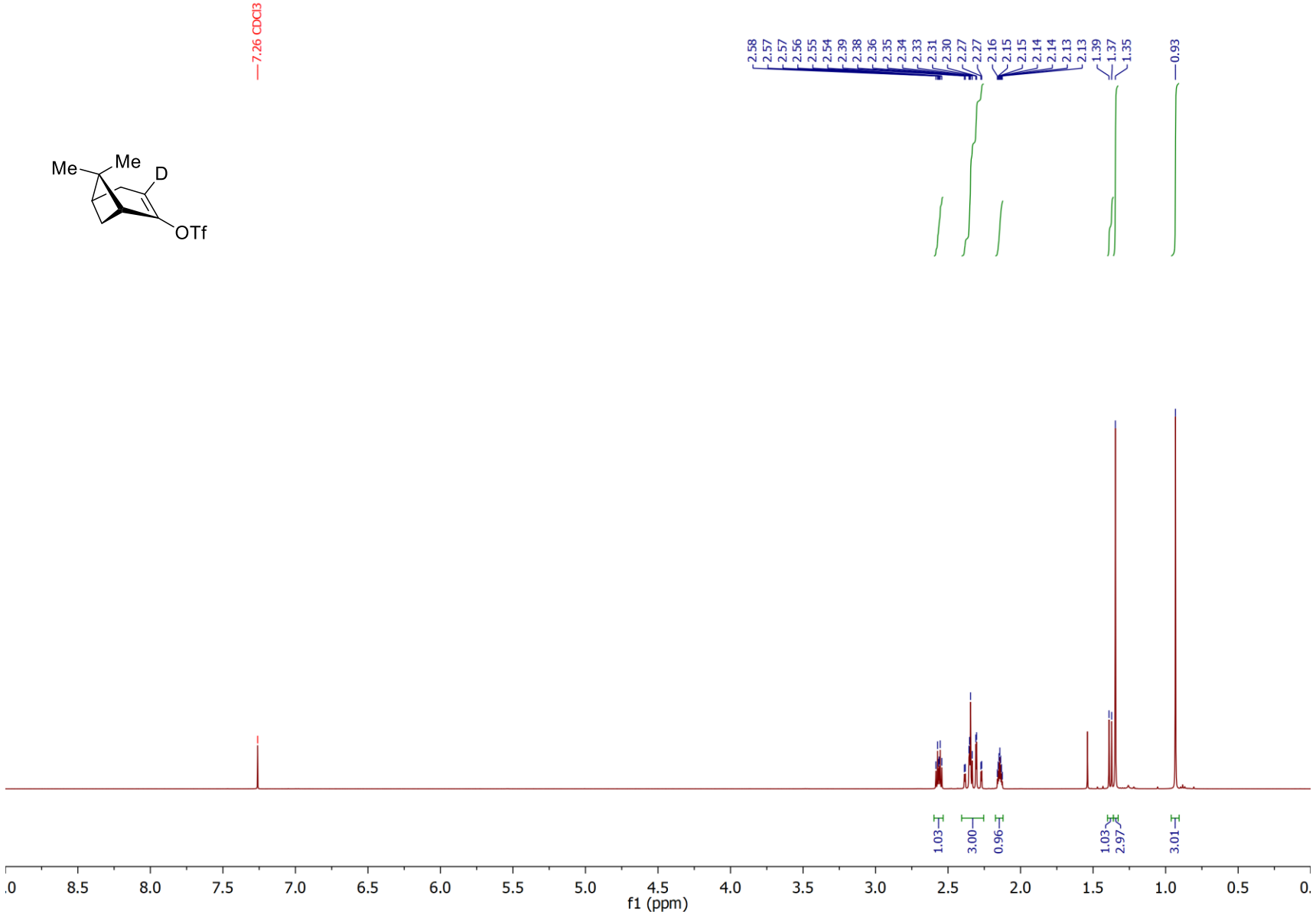


**Figure S7. $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate**

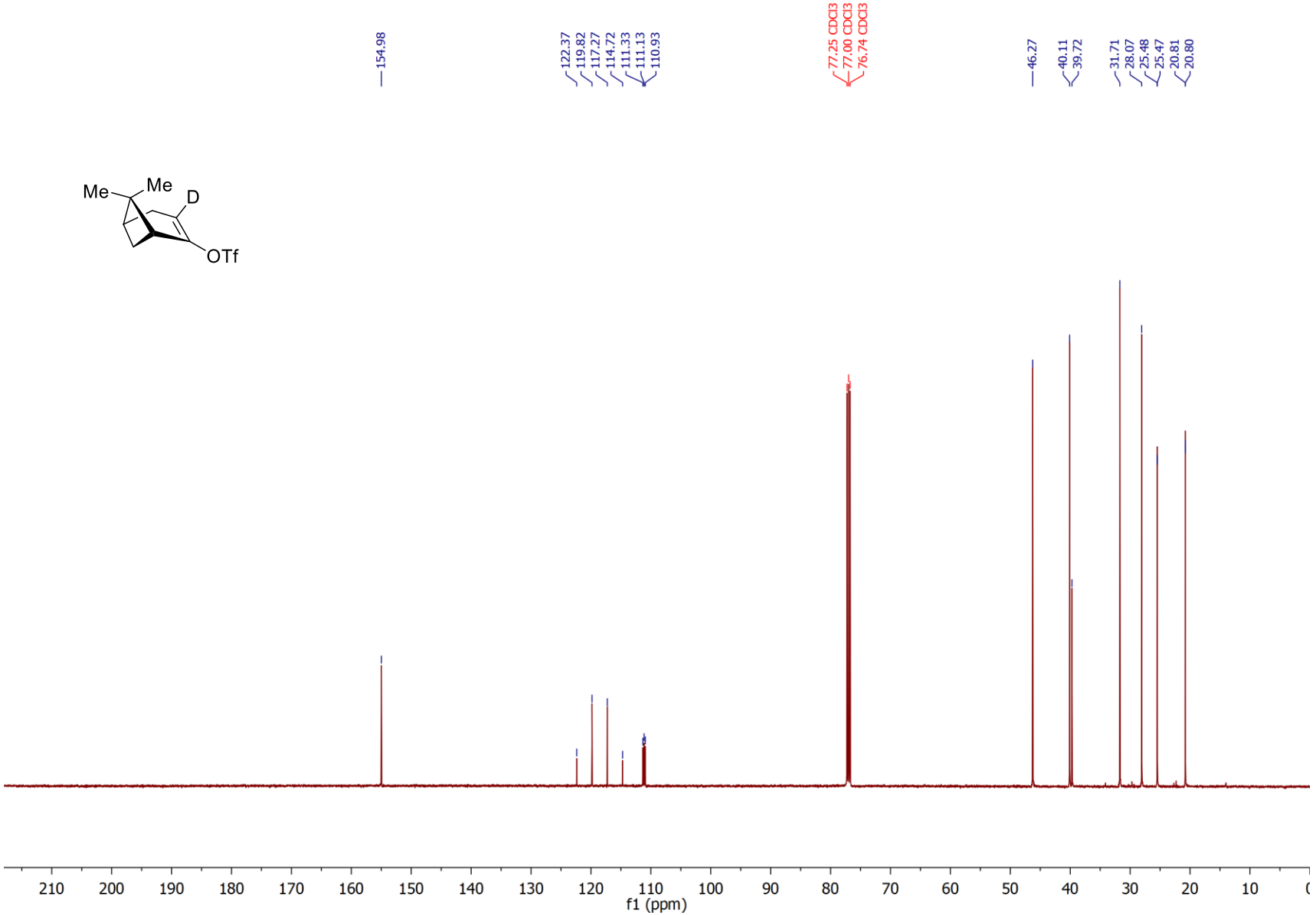


**Figure S8. $^{13}$C NMR (500 MHz, $CDCl_3$) spectrum of (1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl-3-*d* trifluoromethanesulfonate**

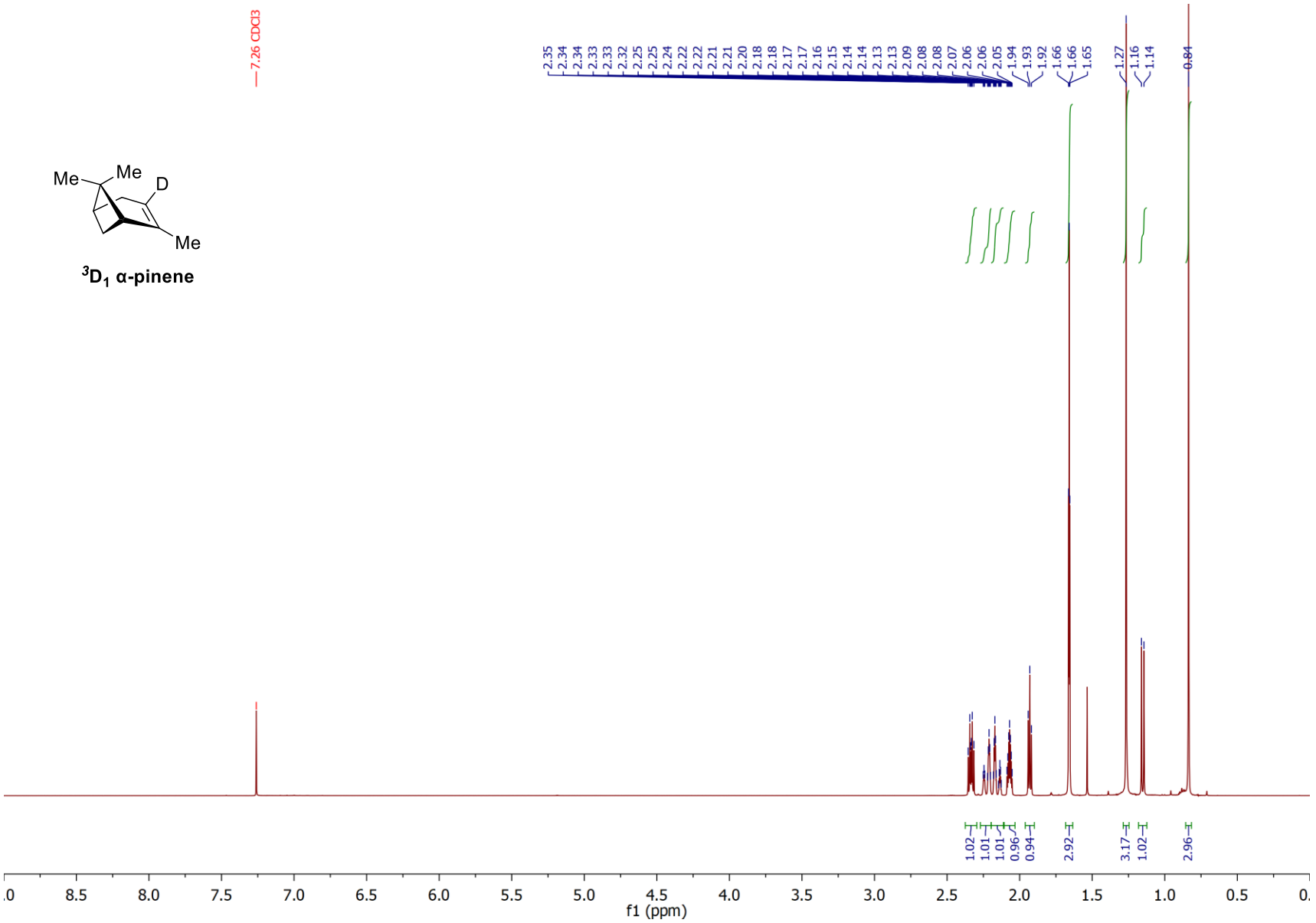


**Figure S9. $^1$H NMR (500 MHz, $CDCl_3$) spectrum of $^3D_1$ α-pinene.**

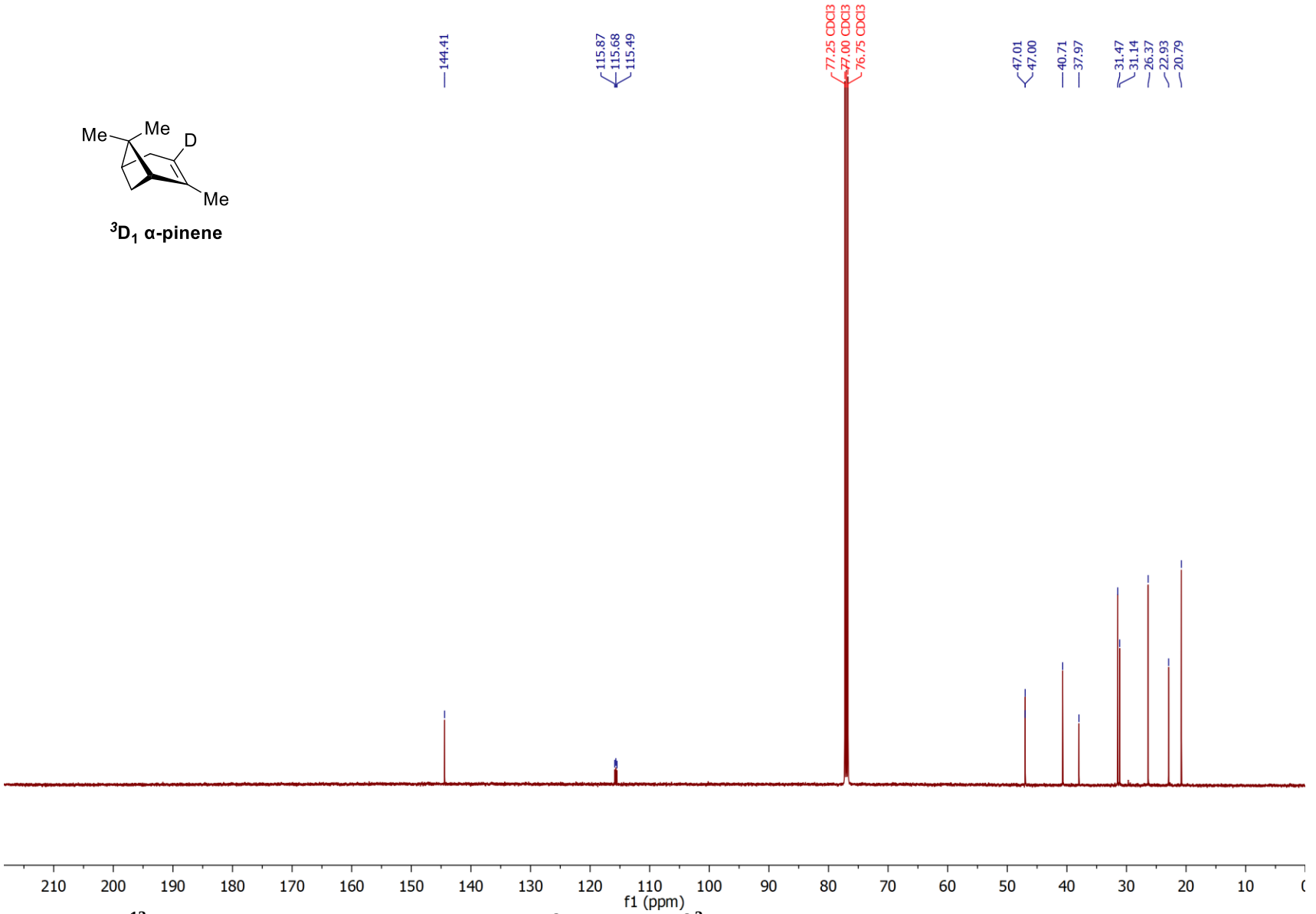


**Figure S10. $^{13}C$ NMR (500 MHz, $CDCl_3$) spectrum of spectrum of $^3D_1$ α-pinene.**

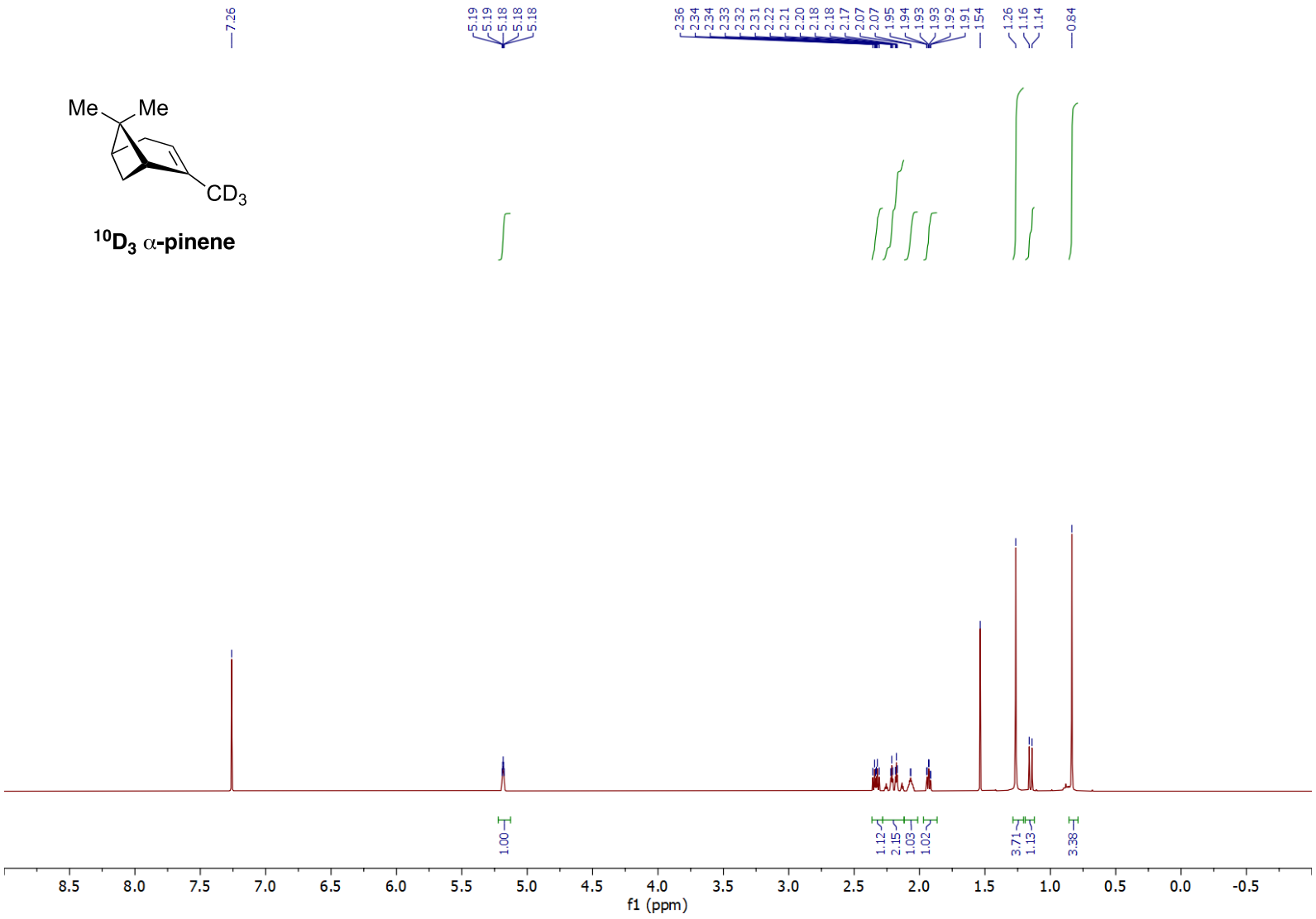


**Figure S11. $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of $^{10}D_3$ α-pinene.**

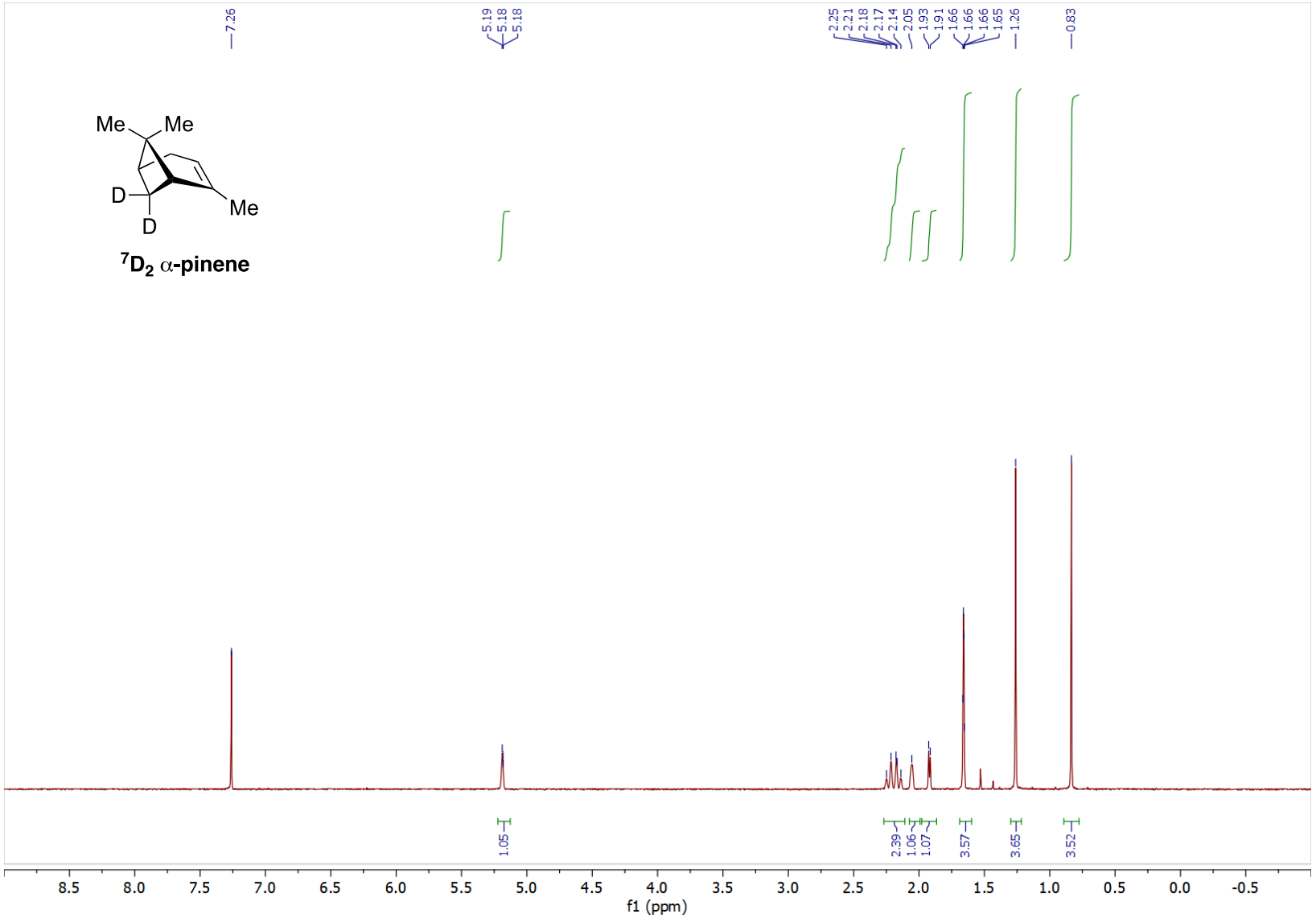


**Figure S12. $^{1}$H NMR (500 MHz, $CDCl_3$) spectrum of $^{7}D_2$ α-pinene.**