*Supporting Information*

# Synthesis of Carboxylic Acid and Dimer Ester Surrogates to Constrain the Abundance and Distribution of Molecular Products in α-Pinene and β-Pinene Secondary Organic Aerosol

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## S1. Adjustment of Mass Fractions in Published LC/(–)ESI-MS Studies of SOA from α-Pinene Ozonolysis

*Zhang et al. (2015)*.[1] For the mass fractions of identified monomers and dimers reported in Zhang et al.,[1] Fig. 3 ($MF_{\text{reported}}$), calculated using compound-specific, computationally derived (–)ESI efficiencies normalized to that of *cis*-pinonic acid (*RIE*; Zhang et al.,[1] *SI Appendix*, Table S2),[a] adjusted mass fractions ($MF_{\text{adjusted}}$) were obtained as follows:

$$MF_{\text{adjusted}} = MF_{\text{reported}} \cdot \frac{RIE}{\left(\frac{(-)ESI_{\text{surrogate}}}{(-)ESI_{cis-\text{pinonic}}}\right)} \quad \text{(S1)}$$

where the bracketed term is the measured (–)ESI efficiency of the most representative surrogate (carboxylic acid **1–3** or dimer ester **4–6**) normalized to that of *cis*-pinonic acid (Figure 2). The calculation for *cis*-pinic acid ($C_9H_{14}O_4$) is shown as an example: $5.3\% = 21\% \cdot \frac{0.73}{2.91}$.

*Kristensen et al. (2017)*.[2] Mass fractions of identified monomers reported in Kristensen et al.,[2] Table 3S were quantified using representative surrogates [i.e., *cis*-pinonic acid, *cis*-pinic acid, pimelic acid, terpenylic acid, diaterpenylic acid acetate (DTAA), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)] and, therefore, were not adjusted. For the mass fractions of identified dimers reported in Kristensen et al.,[2] Table 4S ($MF_{\text{reported}}$), calculated using "an average standard calibration curve of *cis*-pinic acid and DTAA" given that "most of the suggested molecular structures for the identified dimer esters have moieties resembling *cis*-pinic acid and DTAA,"[3] adjusted mass fractions ($MF_{\text{adjusted}}$) were obtained as follows:

$$MF_{\text{adjusted}} = MF_{\text{reported}} \cdot \frac{(-)ESI_{cis-\text{pinic}}}{(-)ESI_{\text{dimer}}} \quad \text{(S2)}$$

where $(-)ESI_{cis\text{-pinic}}$ is the measured (–)ESI efficiency of *cis*-pinic acid (Table S2; assumes *cis*-pinic acid and DTAA have similar (–)ESI efficiencies as both are pinene-derived dicarboxylic acids) and $(-)ESI_{\text{dimer}}$ is the measured (–)ESI efficiency of the most representative surrogate dimer (dimer ester **4–6**; Table S2). The calculation for pinonyl-pinyl ester ($C_{19}H_{28}O_7$) is shown as an example: $0.08\% = 0.94\% \cdot \frac{2076\ \mu M^{-1}}{25418\ \mu M^{-1}}$.

[a]For *RIE* estimates, "molecules that have two or more equivalent sites for deprotonation (e.g., dicarboxylic acids) were not taken into account" (Zhang et al.,[1] *SI Appendix*, S3.2.2), leading to systematic underprediction of *RIE* for polycarboxylic monomers and dimers, given the dependence of (–)ESI efficiency on the number of ionizable carboxyl groups.

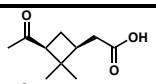
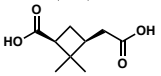
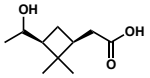
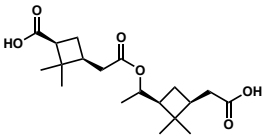
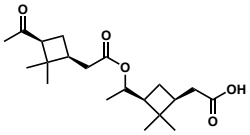
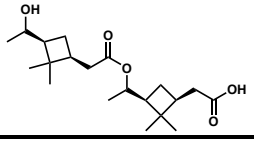
## S2. Tables S1–S4

**Table S1.** Initial conditions and SOA properties for α-pinene and β-pinene ozonolysis experiments in the CTEC.[a]

| VOC | Exp. | $[VOC]_0$ (ppb) | $[O_3]_0$ (ppb) | $[(NH_4)_2SO_4]_0$ ($\mu m^3$ $cm^{-3}$) | [SOA] ($\mu g$ $m^{-3}$)[b] | Bulk O:C[b] | Bulk $\overline{OS}_C$[b,c] | SOA Mass Fraction (%)[b,d] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Monomer | Dimer | Total |
| α-Pinene | 1 | 97 | 150 | 86 | 264 | 0.41 | –0.88 | 20.4 | 1.2 | 21.6 |
| | 2 | 105 | 150 | 213 | 207 | 0.42 | –0.86 | 22.0 | 1.3 | 23.3 |
| | 3 | 110 | 150 | 203 | 215 | 0.42 | –0.86 | 21.9 | 1.3 | 23.2 |
| | 4 | 106 | 150 | 223 | 243 | 0.40 | –0.89 | 17.7 | 1.1 | 18.8 |
| β-Pinene | 5 | 96 | 150 | 137 | 93 | 0.38 | –0.90 | 14.2 | 2.6 | 16.8 |
| | 6 | 95 | 150 | 192 | 75 | 0.38 | –0.90 | 18.0 | 3.5 | 21.5 |
| | 7 | 93 | 150 | 243 | 57 | 0.35 | –0.92 | 18.4 | 4.1 | 22.4 |
| | 8 | 95 | 150 | 283 | 77 | 0.36 | –0.93 | 15.3 | 3.4 | 18.8 |
| | 9 | 95 | 150 | 211 | 87 | 0.35 | –0.94 | 12.0 | 2.7 | 14.8 |

[a] ~5-h duration; $T_0 = 295 \pm 2$ K; P = 1 atm; RH < 5%; $[NO_x]_0 < 0.5$ ppb; no OH scavenger.
[b] Calculated for suspended SOA after ~5 h of ozonolysis (see Figure 1).
[c] Average carbon oxidation state ($\overline{OS}_C = 2$ O:C − H:C).
[d] Method uncertainty is estimated to be ±23% (relative). See Experimental for details.

**Table S2.** UPLC/(–)ESI-Q-TOF-MS analytical figures of merit for carboxylic acids **1–3** and dimer esters **4–6**.[a]

| Compound | Observed *m/z* (–) | Molecular Formula | $t_R$ (min) | Molecular Structure | (–)ESI Efficiency ($\mu M^{-1}$) | Concentration Range ($\mu$M) | LOD (nM)[b] | LOQ (nM)[c] |
|---|---|---|---|---|---|---|---|---|
| **1** | 183.1024 | $C_{10}H_{16}O_3$ | 5.09 |  | 713 ± 7 | 0.200–5.00 | 7.2 | 24 |
| **2** | 185.0815 | $C_9H_{14}O_4$ | 4.45 |  | 2076 ± 17 | 0.200–5.00 | 2.4 | 8.1 |
| **3** | 185.1179 | $C_{10}H_{18}O_3$ | 4.72 |  | 328 ± 4 | 0.200–3.00 | 12 | 39 |
| **4** | 353.1967 | $C_{19}H_{30}O_6$ | 6.71 |  | 25418 ± 237 | 0.200–1.00 | 0.53 | 1.8 |
| **5** | 351.2178 | $C_{20}H_{32}O_5$ | 7.46 |  | 13235 ± 209 | 0.200–2.00 | 0.80 | 2.7 |
| **6** | 353.2332 | $C_{20}H_{34}O_5$ | 7.05 |  | 15079 ± 172 | 0.200–2.00 | 0.60 | 2.0 |

[a]Weighted (1/X), linear ($R^2 > 0.998$) calibration curves were generated from triplicate measurements of equimolar aqueous solutions of carboxylic acids **1–3** and dimer esters **4–6**. Intercepts of calibration curves were not statistically different from zero.
[b]Limit of detection (LOD); calculated as three times the standard deviation of the blank ($3\sigma_{blank}$).
[c]Limit of quantitation (LOQ); calculated as ten times the standard deviation of the blank ($10\sigma_{blank}$).

**Table S3.** Molecular products identified in SOA produced from ozonolysis of α-pinene and β-pinene.

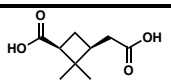
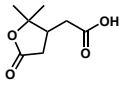
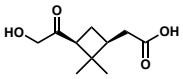
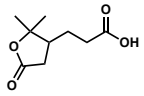
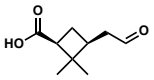
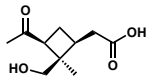
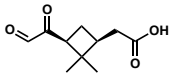
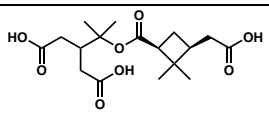
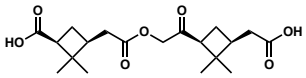
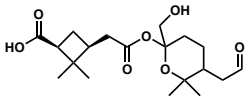
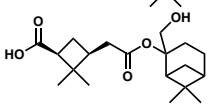
| Carbon Number | Observed *m/z* (–) | Molecular Formula | Error (ppm) | O:C | $\overline{OS}_C$ [a] | logC* ($\mu$g m$^{-3}$)[b] | $t_R$ (min) | (–)ESI Surrogate[c] | SOA Mass Fraction (%)[d,e] α-Pinene | SOA Mass Fraction (%)[d,e] β-Pinene |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_7$ | 173.0456 | $C_7H_{10}O_5$ | 3.5 | 0.71 | 0.00 | –0.5 | 2.21 | 2 | 0.07 ± 0.01 | 0.03 ± 0.01 |
| | 175.0616 | $C_7H_{12}O_5$ | 5.7 | 0.71 | –0.29 | –0.5 | 2.46 | 2 | 0.05 ± 0.04 | 0.05 ± 0.005 |
| $C_8$ | 185.0451 | $C_8H_{10}O_5$ | 0.5 | 0.63 | 0.00 | –0.7 | 3.84 | 2 | 0.07 ± 0.01 | 0.04 ± 0.01 |
| | 171.0669 | $C_8H_{12}O_4$ | 7.0 | 0.50 | –0.50 | 1.2 | 4.07 | 1†,‡,§,¶ | 3.36 ± 0.59 | 3.27 ± 0.63 |
| | | | | | | | 4.20 | 2†,‡,¶ | 0.17 ± 0.02 | 0.15 ± 0.03 |
| | 187.0615 | $C_8H_{12}O_5$ | 4.8 | 0.63 | –0.25 | –0.7 | 3.48 | 1 | 0.20 ± 0.03 | 0.36 ± 0.07 |
| | | | | | | | 3.91 | 1 | 0.35 ± 0.02 | 0.34 ± 0.06 |
| | | | | | | | 2.86 | 1 | 0.40 ± 0.09 | 0.34 ± 0.06 |
| | 203.0554 | $C_8H_{12}O_6$ | –1.0 | 0.75 | 0.00 | –2.7 | 3.86 | 2‡ | 0.11 ± 0.01 | 0.07 ± 0.02 |
| | | | | | | | 3.59 | 2‡ | 0.03 ± 0.002 | 0.04 ± 0.01 |
| | 173.0826 | $C_8H_{14}O_4$ | 6.9 | 0.50 | –0.75 | 1.2 | 3.67 | 1 | 0.40 ± 0.07 | 0.37 ± 0.06 |
| | 189.0770 | $C_8H_{14}O_5$ | 3.7 | 0.63 | –0.50 | –0.7 | 3.49 | 2‡,§,¶ | 0.06 ± 0.04 | 0.18 ± 0.04 |
| | | | | | | | 5.31 | 1 | 0.23 ± 0.02 | 0.16 ± 0.04 |
| | 205.0722 | $C_8H_{14}O_6$ | 4.9 | 0.75 | –0.25 | –2.7 | 3.83 | 2 | 0.22 ± 0.03 | 0.97 ± 0.12 |
| $C_9$ | 183.0668 | $C_9H_{12}O_4$ | 6.0 | 0.44 | –0.44 | 0.9 | 4.10 | 1 | 0.04 ± 0.02 | 0.12 ± 0.02 |
| | 215.0564 | $C_9H_{12}O_6$ | 3.7 | 0.67 | 0.00 | –3.0 | 3.86 | 2 | 0.10 ± 0.01 | 0.38 ± 0.07 |
| | | | | | | | 3.59 | 2 | 0.06 ± 0.01 | 0.10 ± 0.02 |
| | 169.0872 | $C_9H_{14}O_3$ | 4.1 | 0.33 | –0.89 | 2.8 | 4.71 | 1§ | 1.10 ± 0.13 | 1.06 ± 0.21 |
| | 185.0825 | $C_9H_{14}O_4$ | 5.9 | 0.44 | –0.67 | 0.9 | 4.45 | 2†,‡,§,¶,⋆ | 3.86 ± 0.59 | 3.30 ± 0.56 |
| | | | | | | | 4.39 | 1†,¶ | – | 1.45 ± 0.25 |
| | 201.0762 | $C_9H_{14}O_5$ | –0.5 | 0.56 | –0.44 | –1.0 | 3.65 | 1 | 0.52 ± 0.05 | 1.21 ± 0.20 |
| | | | | | | | 4.20 | 1 | – | 0.29 ± 0.05 |
| | | | | | | | 4.31 | 1 | 0.15 ± 0.02 | – |
| | 187.0972 | $C_9H_{16}O_4$ | 1.1 | 0.44 | –0.89 | 0.9 | 5.16 | 2 | 0.04 ± 0.004 | 0.16 ± 0.02 |
| | | | | | | | 4.00 | 2 | – | 0.08 ± 0.01 |
| | 219.0879 | $C_9H_{16}O_6$ | 4.6 | 0.67 | –0.44 | –3.0 | 4.14 | 2 | – | 0.04 ± 0.01 |
| $C_{10}$ | 197.0801 | $C_{10}H_{14}O_4$ | –6.6 | 0.40 | –0.60 | 0.6 | 3.93 | 1 | 0.52 ± 0.24 | – |
| | | | | | | | 4.49 | 1§ | 0.66 ± 0.29 | – |
| | 213.0767 | $C_{10}H_{14}O_5$ | 1.9 | 0.50 | –0.40 | –1.3 | 3.89 | 1 | 0.19 ± 0.12 | – |
| | | | | | | | 4.13 | 1 | 0.49 ± 0.05 | – |
| | 229.0720 | $C_{10}H_{14}O_6$ | 3.5 | 0.60 | –0.20 | –3.2 | 4.35 | 2 | 0.14 ± 0.02 | – |
| | 183.1030 | $C_{10}H_{16}O_3$ | 4.9 | 0.30 | –1.00 | 2.4 | 5.09 | 1‡,§,⋆ | 0.32 ± 0.05 | – |
| | 199.0979 | $C_{10}H_{16}O_4$ | 4.5 | 0.40 | –0.80 | 0.6 | 4.16 | 1‡,§ | 3.66 ± 0.69 | 0.75 ± 0.13 |
| | | | | | | | 4.30 | 1‡ | 0.91 ± 0.16 | 0.08 ± 0.03 |
| | 215.0917 | $C_{10}H_{16}O_5$ | –0.9 | 0.50 | –0.60 | –1.3 | 4.43 | 1 | 0.45 ± 0.03 | – |
| | | | | | | | 5.03 | 1 | 1.19 ± 0.17 | – |
| | 231.0872 | $C_{10}H_{16}O_6$ | 1.3 | 0.60 | –0.40 | –3.2 | 4.61 | 2†,‡,§ | 0.10 ± 0.01 | – |
| | | | | | | | 4.23 | 2†,‡ | 0.13 ± 0.01 | – |
| | | | | | | | 5.29 | 2†,‡ | 0.13 ± 0.01 | – |
| | 201.1127 | $C_{10}H_{18}O_4$ | 0.0 | 0.40 | –1.00 | 0.6 | 5.63 | 1 | 0.05 ± 0.01 | 0.20 ± 0.08 |
| $C_{15}$ | 315.1448 | $C_{15}H_{24}O_7$ | 1.3 | 0.47 | –0.67 | –6.6 | 5.34 | 6 | 0.01 ± 0.002 | 0.02 ± 0.01 |
| | | | | | | | 5.95 | 6 | – | 0.01 ± 0.002 |
| | 331.1404 | $C_{15}H_{24}O_8$ | 3.3 | 0.53 | –0.53 | –8.5 | 5.67 | 6 | <0.01 | 0.03 ± 0.005 |
| | | | | | | | 5.52 | 6 | <0.01 | 0.01 ± 0.002 |
| | 347.1346 | $C_{15}H_{24}O_9$ | 1.2 | 0.60 | –0.40 | –10.5 | 5.32 | 6 | – | 0.02 ± 0.003 |
| | 333.1551 | $C_{15}H_{26}O_8$ | 0.6 | 0.53 | –0.67 | –8.5 | 5.98 | 6 | <0.01 | 0.03 ± 0.003 |
| | 311.1503 | $C_{16}H_{24}O_6$ | 2.6 | 0.38 | –0.75 | –5.1 | 5.93 | 6 | 0.06 ± 0.01 | 0.09 ± 0.02 |
| | 343.1386 | $C_{16}H_{24}O_8$ | –2.0 | 0.50 | –0.50 | –8.8 | 5.42 | 4†,§ | 0.01 ± 0.001 | 0.02 ± 0.003 |
| | | | | | | | 5.33 | 4†,§ | <0.01 | 0.02 ± 0.003 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 5.16 | 4[†] | 0.01 ± 0.002 | 0.02 ± 0.005 |
| | 313.1661 | $C_{16}H_{26}O_6$ | 3.2 | 0.38 | −0.88 | −5.1 | 6.23 | 6[§] | 0.02 ± 0.002 | 0.06 ± 0.01 |
| | 329.1607 | $C_{16}H_{26}O_7$ | 2.1 | 0.44 | −0.75 | −6.9 | 5.59 | 6 | 0.04 ± 0.004 | 0.14 ± 0.03 |
| $C_{16}$ | | | | | | | 5.27 | 6 | 0.01 ± 0.001 | 0.02 ± 0.005 |
| | | | | | | | 5.10 | 6 | <0.01 | 0.01 ± 0.003 |
| | 345.1549 | $C_{16}H_{26}O_8$ | 0.0 | 0.50 | −0.63 | −8.8 | 5.48 | 6 | – | 0.03 ± 0.01 |
| | | | | | | | 4.89 | 6 | 0.01 ± 0.001 | 0.02 ± 0.004 |
| | | | | | | | 5.68 | 6 | 0.01 ± 0.001 | – |
| | 361.1512 | $C_{16}H_{26}O_9$ | 3.6 | 0.56 | −0.50 | −10.7 | 5.17 | 6 | – | 0.01 ± 0.003 |
| | | | | | | | 4.94 | 6 | 0.01 ± 0.001 | 0.02 ± 0.005 |
| | | | | | | | 5.60 | 6 | 0.01 ± 0.002 | – |
| | 377.1455 | $C_{16}H_{26}O_{10}$ | 1.9 | 0.63 | −0.38 | −12.7 | 5.27 | 6 | 0.02 ± 0.003 | 0.15 ± 0.02 |
| | 363.1640 | $C_{16}H_{28}O_9$ | −4.1 | 0.56 | −0.63 | −10.7 | 5.01 | 6 | – | 0.01 ± 0.002 |
| | 323.1509 | $C_{17}H_{24}O_6$ | 4.3 | 0.35 | −0.71 | −5.4 | 6.05 | 6 | 0.01 ± 0.001 | – |
| | | | | | | | 6.29 | 6 | <0.01 | – |
| | 309.1699 | $C_{17}H_{26}O_5$ | −1.0 | 0.29 | −0.94 | −3.6 | 5.90 | 6[§] | 0.02 ± 0.002 | – |
| | 325.1672 | $C_{17}H_{26}O_6$ | 6.5 | 0.35 | −0.82 | −5.4 | 5.87 | 4[§] | – | 0.02 ± 0.005 |
| | | | | | | | 5.76 | 4[§] | 0.01 ± 0.002 | – |
| | | | | | | | 6.14 | 4[§] | 0.01 ± 0.001 | – |
| | 341.1607 | $C_{17}H_{26}O_7$ | 2.1 | 0.41 | −0.71 | −7.2 | 5.80 | 6 | 0.06 ± 0.005 | 0.11 ± 0.02 |
| | | | | | | | 6.46 | 6 | – | 0.02 ± 0.004 |
| | 357.1555 | $C_{17}H_{26}O_8$ | 1.7 | 0.47 | −0.59 | −9.1 | 5.43 | 4[†,‡,§] | 0.22 ± 0.02 | 0.59 ± 0.12 |
| | | | | | | | 5.24 | 4[†] | – | 0.06 ± 0.01 |
| $C_{17}$ | 373.1485 | $C_{17}H_{26}O_9$ | −3.8 | 0.53 | −0.47 | −11.0 | 4.90 | 6 | – | 0.03 ± 0.004 |
| | | | | | | | 5.36 | 6 | 0.01 ± 0.001 | 0.01 ± 0.002 |
| | 311.1859 | $C_{17}H_{28}O_5$ | 0.3 | 0.29 | −1.06 | −3.6 | 7.13 | 6 | – | 0.01 ± 0.01 |
| | 327.1808 | $C_{17}H_{28}O_6$ | 0.0 | 0.35 | −0.94 | −5.4 | 6.05 | 6 | 0.01 ± 0.001 | – |
| | 343.1761 | $C_{17}H_{28}O_7$ | 1.2 | 0.41 | −0.82 | −7.2 | 5.76 | 6 | – | 0.03 ± 0.005 |
| | | | | | | | 5.90 | 6 | – | 0.02 ± 0.004 |
| | | | | | | | 6.09 | 6 | – | 0.01 ± 0.001 |
| | 359.1714 | $C_{17}H_{28}O_8$ | 2.2 | 0.47 | −0.71 | −9.1 | 6.02 | 6 | – | 0.05 ± 0.01 |
| | 375.1653 | $C_{17}H_{28}O_9$ | −0.5 | 0.53 | −0.59 | −11.0 | 4.78 | 6 | – | 0.03 ± 0.01 |
| | | | | | | | 6.34 | 6 | – | 0.01 ± 0.003 |
| | 391.1599 | $C_{17}H_{28}O_{10}$ | −1.3 | 0.59 | −0.47 | −13.0 | 5.40 | 6 | – | 0.03 ± 0.005 |
| | 337.1634 | $C_{18}H_{26}O_6$ | −5.0 | 0.33 | −0.78 | −5.7 | 6.32 | 6 | 0.07 ± 0.01 | 0.02 ± 0.005 |
| | 353.1604 | $C_{18}H_{26}O_7$ | 1.1 | 0.39 | −0.67 | −7.6 | 5.88 | 6 | 0.02 ± 0.002 | – |
| | 369.1554 | $C_{18}H_{26}O_8$ | 1.4 | 0.44 | −0.56 | −9.4 | 5.16 | 6 | 0.01 ± 0.001 | 0.02 ± 0.004 |
| | | | | | | | 5.36 | 6 | – | 0.02 ± 0.002 |
| | 307.1893 | $C_{18}H_{28}O_4$ | −5.2 | 0.22 | −1.11 | −2.2 | 6.65 | 6 | 0.01 ± 0.002 | – |
| | 323.1860 | $C_{18}H_{28}O_5$ | 0.6 | 0.28 | −1.00 | −3.9 | 6.22 | 6 | – | 0.04 ± 0.01 |
| | | | | | | | 6.99 | 6[¶] | – | 0.01 ± 0.004 |
| | | | | | | | 6.83 | 6 | 0.01 ± 0.001 | – |
| | 339.1822 | $C_{18}H_{28}O_6$ | 4.1 | 0.33 | −0.89 | −5.7 | 6.72 | 6 | – | 0.13 ± 0.02 |
| | | | | | | | 6.45 | 6 | – | 0.06 ± 0.01 |
| | | | | | | | 5.86 | 6 | 0.03 ± 0.002 | – |
| | 355.1754 | $C_{18}H_{28}O_7$ | −0.8 | 0.39 | −0.78 | −7.6 | 5.38 | 6 | – | 0.08 ± 0.02 |
| | | | | | | | 6.37 | 6[¶] | – | 0.01 ± 0.004 |
| $C_{18}$ | 371.1707 | $C_{18}H_{28}O_8$ | 0.3 | 0.44 | −0.67 | −9.4 | 5.58 | 6 | – | 0.06 ± 0.01 |
| | 387.1651 | $C_{18}H_{28}O_9$ | −1.0 | 0.50 | −0.56 | −11.3 | 5.55 | 6 | 0.06 ± 0.003 | – |
| | 403.1601 | $C_{18}H_{28}O_{10}$ | −0.7 | 0.56 | −0.44 | −13.2 | 6.09 | 6 | 0.01 ± 0.001 | – |
| | 419.1525 | $C_{18}H_{28}O_{11}$ | −6.7 | 0.61 | −0.33 | −15.2 | 4.80 | 6 | – | 0.01 ± 0.003 |
| | 341.1960 | $C_{18}H_{30}O_6$ | −1.2 | 0.33 | −1.00 | −5.7 | 7.01 | 6 | – | 0.02 ± 0.004 |
| | 357.1919 | $C_{18}H_{30}O_7$ | 1.7 | 0.39 | −0.89 | −7.6 | 7.04 | 6 | – | 0.07 ± 0.02 |
| | | | | | | | 6.79 | 6 | – | 0.02 ± 0.003 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 373.1851 | $C_{18}H_{30}O_8$ | −2.9 | 0.44 | −0.78 | −9.4 | 5.82 | 6 | – | 0.03 ± 0.005 |
| | | | | | | | 5.00 | 6 | – | 0.03 ± 0.01 |
| | | | | | | | 6.09 | 6 | – | 0.01 ± 0.002 |
| | 389.1814 | $C_{18}H_{30}O_9$ | 0.5 | 0.50 | −0.67 | −11.3 | 6.29 | 6 | – | 0.40 ± 0.08 |
| | | | | | | | 6.13 | 6 | 0.02 ± 0.002 | – |
| | 405.1764 | $C_{18}H_{30}O_{10}$ | 0.7 | 0.56 | −0.56 | −13.2 | 4.61 | 4¶ | – | 0.03 ± 0.005 |
| | 335.1862 | $C_{19}H_{28}O_5$ | 1.2 | 0.26 | −0.95 | −4.3 | 7.12 | 6 | 0.02 ± 0.002 | – |
| | 351.1828 | $C_{19}H_{28}O_6$ | 5.7 | 0.32 | −0.84 | −6.1 | 5.87 | 6 | – | 0.02 ± 0.004 |
| | 367.1766 | $C_{19}H_{28}O_7$ | 2.5 | 0.37 | −0.74 | −7.9 | 6.10 | 4‡,§ | 0.12 ± 0.01 | – |
| | | | | | | | 6.00 | 4‡ | 0.04 ± 0.004 | – |
| | 399.1663 | $C_{19}H_{28}O_9$ | 2.0 | 0.47 | −0.53 | −11.6 | 5.86 | 6 | 0.07 ± 0.005 | – |
| | | | | | | | 5.99 | 6 | 0.06 ± 0.01 | – |
| | 337.2027 | $C_{19}H_{30}O_5$ | 3.6 | 0.26 | −1.05 | −4.3 | 7.31 | 6¶ | – | 0.11 ± 0.02 |
| | | | | | | | 7.54 | 6 | – | 0.01 ± 0.001 |
| | | | | | | | 6.07 | 6 | 0.05 ± 0.005 | – |
| $C_{19}$ | | | | | | | 7.48 | 6 | 0.01 ± 0.001 | – |
| | 353.1961 | $C_{19}H_{30}O_6$ | −0.8 | 0.32 | −0.95 | −6.1 | 6.28 | 6 | – | 0.02 ± 0.005 |
| | 369.1916 | $C_{19}H_{30}O_7$ | 0.8 | 0.37 | −0.84 | −7.9 | 6.62 | 6¶ | 0.02 ± 0.005 | 0.12 ± 0.02 |
| | | | | | | | 6.72 | 6 | – | 0.07 ± 0.02 |
| | | | | | | | 5.96 | 6 | 0.02 ± 0.003 | – |
| | 385.1873 | $C_{19}H_{30}O_8$ | 2.9 | 0.42 | −0.74 | −9.7 | 6.14 | 6 | 0.01 ± 0.001 | – |
| | | | | | | | 5.48 | 6 | 0.01 ± 0.003 | – |
| | 417.1769 | $C_{19}H_{30}O_{10}$ | 1.9 | 0.53 | −0.53 | −13.5 | 6.88 | 6 | – | 0.04 ± 0.01 |
| | 403.1963 | $C_{19}H_{32}O_9$ | −1.2 | 0.47 | −0.74 | −11.6 | 6.40 | 6 | – | 0.01 ± 0.003 |
| | | | | | | | | **TOTAL MONOMER** | 20.51 ± 2.45 | 15.60 ± 2.65 |
| | | | | | | | | **TOTAL DIMER** | 1.27 ± 0.11 | 3.26 ± 0.60 |
| | | | | | | | | **TOTAL** | 21.78 ± 2.55 | 18.86 ± 3.19 |

[a]Average carbon oxidation state ($\overline{OS}_C$ = 2 O:C − H:C).
[b]Saturation mass concentration (C*). Estimated using the empirical model of Donahue et al.[4]
[c]Assigned based on comparison with *authentic standards and/or LC/(−)ESI-MS data from †Yasmeen et al. (2010),[5] ‡Yasmeen et al. (2012),[6] §Zhang et al. (2015),[1] and ¶Kenseth et al. (2018).[7] Structures containing (hydro)peroxide functionalities were not considered.[7,8] Absent structural information, carboxylic acid **1** and dimer ester **6** were used, unless O:C > 0.65 or $\overline{OS}_C$ > −0.25.
[d]Calculated for suspended SOA after ~5 h of ozonolysis (see Figure 1) and reported as averages of replicate experiments for α-pinene ($n$ = 4) and β-pinene ($n$ = 5) together with standard deviations (1σ).
[e]Method uncertainty is estimated to be ±23% (relative). See Experimental for details.

**Table S4.** Major monomers and dimers identified in SOA produced from ozonolysis of α-pinene and β-pinene.[a]

| Observed *m/z* (–) | Molecular Formula | $t_R$ (min) | Compound Assignment[b] | Proposed Molecular Structure[b] | SOA Mass Fraction[c,d] (%) α-Pinene | SOA Mass Fraction[c,d] (%) β-Pinene |
|---|---|---|---|---|---|---|
| 185.0825 | $C_9H_{14}O_4$ | 4.45 | *cis*-Pinic acid[†,‡,§,¶,⋆] |  | 3.86 ± 0.59 | 3.30 ± 0.56 |
| 171.0669 | $C_8H_{12}O_4$ | 4.07 | Terpenylic acid[†,‡,§] |  | 3.36 ± 0.59 | 3.27 ± 0.63 |
| 199.0979 | $C_{10}H_{16}O_4$ | 4.16 | 10-hydroxypinonic acid[‡,§] |  | 3.66 ± 0.69 | 0.75 ± 0.13 |
| 185.0825 | $C_9H_{14}O_4$ | 4.39 | Homoterpenylic acid[†] |  | – | 1.45 ± 0.25 |
| 215.0917 | $C_{10}H_{16}O_5$ | 5.03 | – | – | 1.19 ± 0.17 | – |
| 169.0872 | $C_9H_{14}O_3$ | 4.71 | *cis*-Pinalic acid[§] |  | 1.10 ± 0.13 | 1.06 ± 0.21 |
| 199.0979 | $C_{10}H_{16}O_4$ | 4.30 | 8-hydroxypinonic acid[‡] |  | 0.91 ± 0.16 | N/A |
| 197.0801 | $C_{10}H_{14}O_4$ | 4.49 | Oxopinonic acid[§] |  | 0.66 ± 0.29 | – |
| 201.0762 | $C_9H_{14}O_5$ | 3.65 | – | – | N/A | 1.21 ± 0.20 |
| 205.0722 | $C_8H_{14}O_6$ | 3.83 | – | – | N/A | 0.97 ± 0.12 |
| 357.1555 | $C_{17}H_{26}O_8$ | 5.43 | Pinyl-diaterpenyl ester[†,‡,§] |  | 0.22 ± 0.02 | 0.59 ± 0.12 |
| 367.1766 | $C_{19}H_{28}O_7$ | 6.10 | Pinonyl-pinyl ester[‡,§] |  | 0.12 ± 0.01 | – |
| 337.1634 | $C_{18}H_{26}O_6$ | 6.32 | – | – | 0.07 ± 0.01 | N/A |
| 399.1663 | $C_{19}H_{28}O_9$ | 5.86 | – | – | 0.07 ± 0.005 | – |
| 387.1651 | $C_{18}H_{28}O_9$ | 5.55 | – | – | 0.06 ± 0.003 | – |
| 399.1663 | $C_{19}H_{28}O_9$ | 5.99 | – | – | 0.06 ± 0.01 | – |
| 337.2027 | $C_{19}H_{30}O_5$ | 6.07 | – | – | 0.05 ± 0.005 | – |
| 389.1814 | $C_{18}H_{30}O_9$ | 6.29 | – | – | – | 0.40 ± 0.08 |
| 377.1455 | $C_{16}H_{26}O_{10}$ | 5.27 | – | – | N/A | 0.15 ± 0.02 |
| 329.1607 | $C_{16}H_{26}O_7$ | 5.59 | – | – | N/A | 0.14 ± 0.03 |
| 339.1822 | $C_{18}H_{28}O_6$ | 6.72 | – | – | – | 0.13 ± 0.02 |
| 369.1916 | $C_{19}H_{30}O_7$ | 6.62 | –[¶] |  | N/A | 0.12 ± 0.02 |
| 337.2027 | $C_{19}H_{30}O_5$ | 7.31 | –[¶] |  | – | 0.11 ± 0.02 |
| 311.1503 | $C_{16}H_{24}O_6$ | 5.93 | – | – | 0.06 ± 0.01 | 0.09 ± 0.02 |
| | | | | **TOTAL MONOMER** | 14.73 ± 2.02 | 12.01 ± 2.05 |
| | | | | **TOTAL DIMER** | 0.72 ± 0.07 | 1.74 ± 0.31 |
| | | | | **TOTAL** | 15.45 ± 2.08 | 13.75 ± 2.33 |

[a]Monomer mass fraction >0.65%. Dimer mass fraction >0.05% for α-pinene and >0.09% for β-pinene. N/A denotes below threshold.
[b]Based on comparison with *authentic standards and/or LC/(–)ESI-MS data from [†]Yasmeen et al. (2010),[5] [‡]Yasmeen et al. (2012),[6] [§]Zhang et al. (2015),[1] and [¶]Kenseth et al. (2018).[7]
[c]Calculated for suspended SOA after ~5 h of ozonolysis (see Figure 1) and reported as averages of replicate experiments for α-pinene ($n$ = 4) and β-pinene ($n$ = 5) together with standard deviations (1σ).
[d]Method uncertainty is estimated to be ±23% (relative). See Experimental for details.

## S3. Figures S1–S3

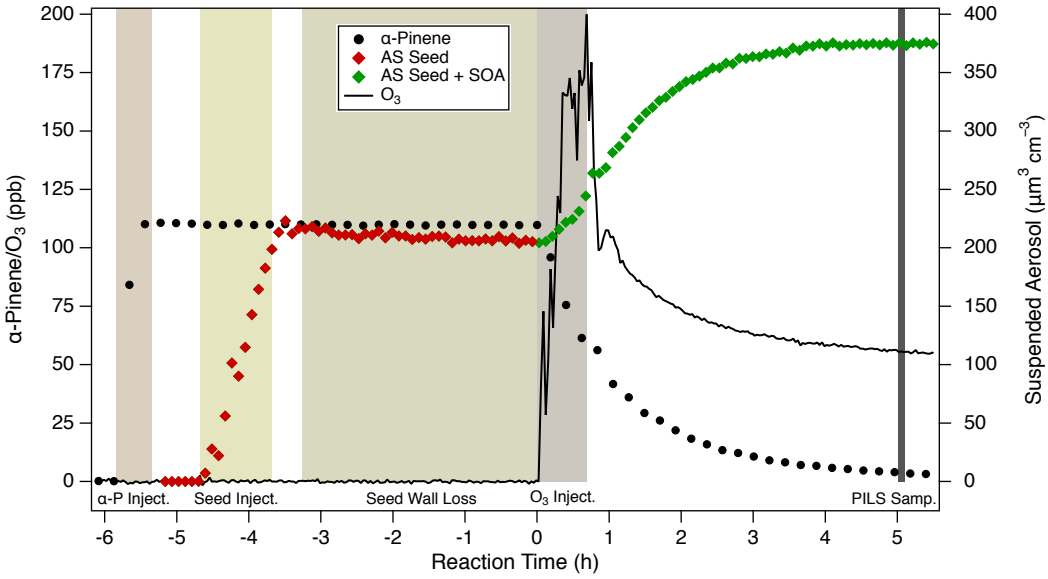



**Figure S1.** Time series of GC/FID-derived α-pinene mixing ratios, $O_3$ mixing ratios, and SMPS-derived suspended aerosol volume concentrations for a representative α-pinene ozonolysis experiment in the CTEC (Table S1, Exp. 3). Shading denotes sequential periods of α-pinene injection (30 min), $(NH_4)_2SO_4$ (AS) seed injection (1 h), AS seed wall loss (3.25 h), $O_3$ injection (42 min), and PILS sample collection (5 min).

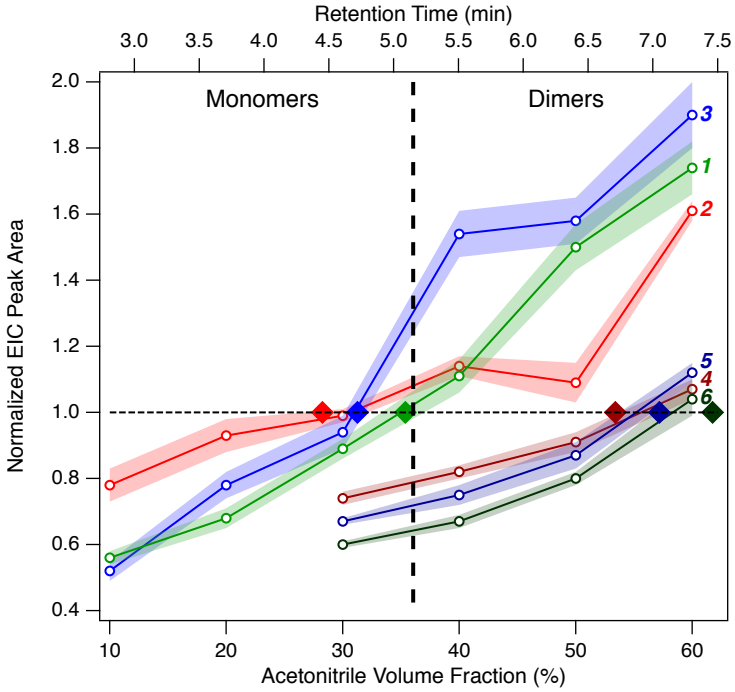



**Figure S2.** Influence of eluent composition on the (–)ESI efficiencies of carboxylic acids **1–3** and dimer esters **4–6**, evaluated for an equimolar (1.00 $\mu$M) aqueous solution via isocratic UPLC/(–)ESI-Q-TOF-MS; all other acquisition parameters [e.g., total flow rate, injection volume, and (–)ESI conditions] were unchanged. Profiles for each compound are plotted as the average (1σ) EIC peak area of triplicate measurements, normalized to the EIC peak area from the gradient method, as a function of isocratic acetonitrile volume fraction. Vertical dashed line separates ranges of acetonitrile content within which monomers (10–38%) and dimers (34–63%) in α-pinene and β-pinene SOA elute during gradient UPLC, while diamonds denote acetonitrile volume fractions at which carboxylic acids **1–3** and dimer esters **4–6** elute during gradient UPLC. Retention times in the gradient method ($t_R$ 2.81–7.30 min) corresponding to the given acetonitrile volume fractions (10–60%) are also shown.

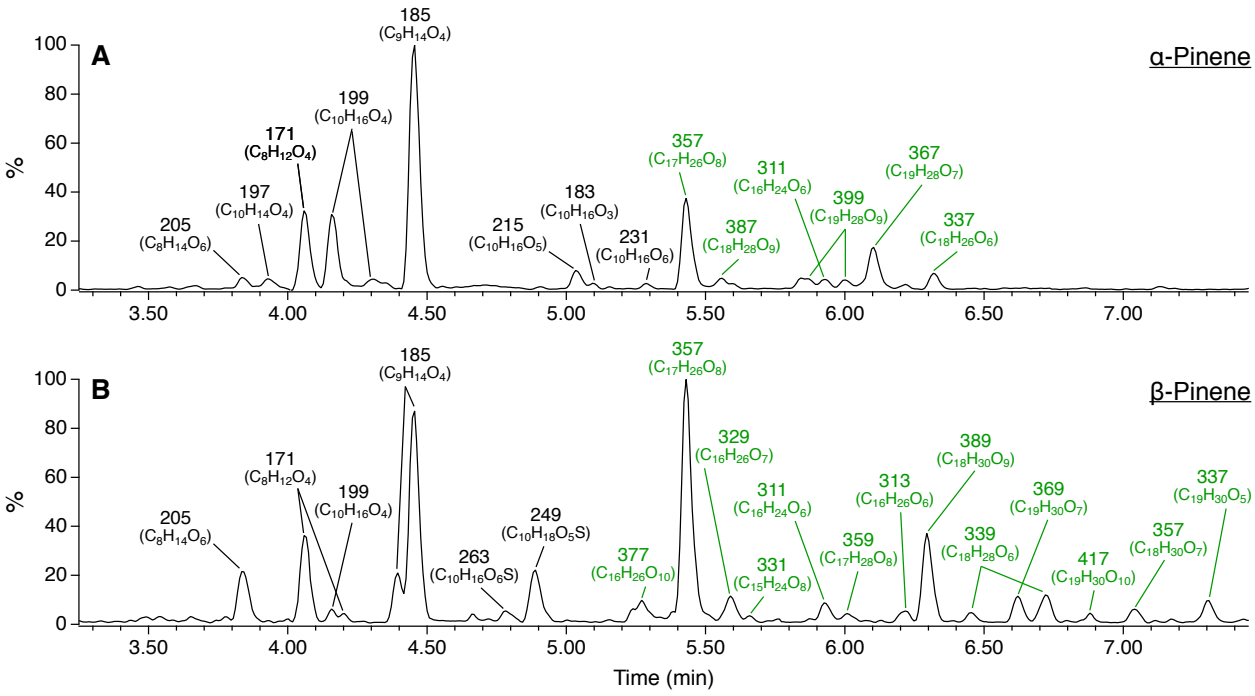
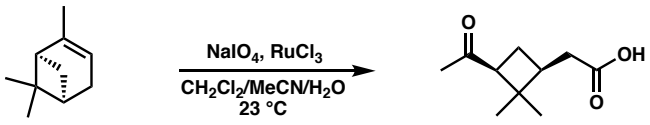



**Figure S3.** Representative UPLC/(–)ESI-Q-TOF-MS BPI chromatograms of SOA produced from ozonolysis of (A) α-pinene and (B) β-pinene after ~5 h of reaction in the CTEC (see Figure 1). Numbers correspond to nominal *m/z* values of $[M–H]^-$ ions. Molecular formulas ($C_xH_yO_z$) were assigned with mass tolerances of <7 ppm and supported by associated $^{13}C$ isotope distributions. Chromatograms consist of monomeric (black) and dimeric (green) regions.

## S4. Synthetic Procedures and Characterization Data

### General Information

Unless otherwise stated, reactions were performed in flame-dried glassware under ambient conditions using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reagents were purchased from commercial sources and used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (250 μm) and visualized by UV fluorescence quenching, potassium permanganate staining, or *p*-anisaldehyde staining. Silicycle Silia*Flash* P60 Academic Silica gel (particle size 40–63 μm) was used for flash chromatography. Preparative HPLC was performed using an Agilent 1200 HPLC system equipped with an ACE $C_{18}$ column (5 μm, 21.2 mm × 250 mm). $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian Inova 500 (500 and 125 MHz, respectively) spectrometer and are reported in terms of chemical shift relative to $CHCl_3$ (δ 7.26 and 77.16 ppm, respectively). Data for $^{1}H$ NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant, integration). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were obtained from thin films deposited on NaCl plates using a Perkin Elmer Spectrum BXII spectrometer and are reported in frequency of absorption ($cm^{-1}$). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm) using a 100 mm path-length cell. High resolution mass spectra (HRMS) were acquired using a Waters ACQUITY UPLC I-Class system coupled to a Xevo G2-S ESI-Q-TOF-MS (see Experimental).

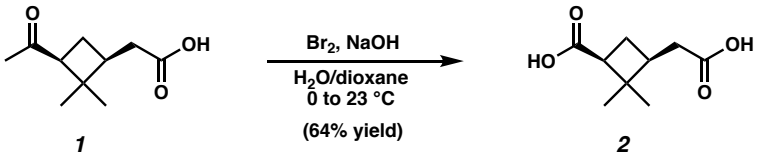



*(+)-α-pinene* *1*

**2-((1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl)acetic acid ((+)-*cis*-pinonic acid, 1)**

(+)-*cis*-Pinonic acid (**1**) was prepared according to a modified literature procedure[1] from commercial (+)-α-pinene (98%, 89% ee, Sigma-Aldrich). To a stirred solution of (+)-α-pinene (5.00 mL, 31.5 mmol, 1.0 equiv) in $CH_2Cl_2$/MeCN/$H_2O$ (2:2:3, 260 mL) at 23 °C was added $NaIO_4$ (26.8 g, 125.3 mmol, 4.0 equiv) followed by catalytic $RuCl_3$ hydrate (240 mg). After 24 h, TLC

indicated complete conversion of the starting material and the mixture was diluted with $Et_2O$ (200 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 150 mL). The combined organic phases were filtered through celite and concentrated. The crude residue was dissolved in $Et_2O$ (100 mL) and extracted with 10% aqueous $Na_2CO_3$ (3 × 150 mL). The aqueous phases were combined, acidified to pH 1 with concentrated $H_2SO_4$, and extracted with $Et_2O$ (3 × 150 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (40% EtOAc/hexanes) to afford the title compound as a white solid (5.13 g, 27.8 mmol, 88% yield). $[\alpha]_D^{25} = +81.4°$ (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.89 (dd, *J* = 10.2, 7.6 Hz, 1H), 2.42 – 2.26 (m, 3H), 2.05 (s, 3H), 2.03 – 1.91 (m, 2H), 1.33 (s, 3H), 0.88 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 207.8, 179.1, 54.3, 43.4, 37.8, 35.0, 30.3, 30.3, 23.1, 17.5; IR (thin film, NaCl) 2959, 1731, 1708, 1184, 956 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_{10}H_{15}O_3$ = 183.1021, found 183.1024. All physical and spectral data were in good accordance with previously reported values.[9–11]

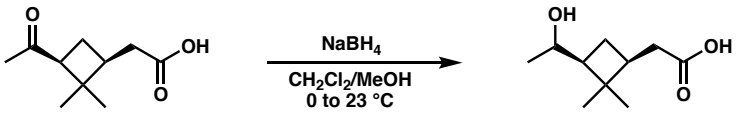



1 2

**(1*S*,3*S*)-3-(carboxymethyl)-2,2-dimethylcyclobutane-1-carboxylic acid ((+)-*cis*-pinic acid, 2)**

(+)-*cis*-Pinic acid (**2**) was prepared according to a modified literature procedure.[1] To a stirred solution of (+)-*cis*-pinonic acid (**1**) (2.50 g, 13.6 mmol, 1.0 equiv) in $H_2O$/dioxane (1:5, 200 mL) at 0 °C was added dropwise an aqueous solution of NaOBr, prepared via addition of $Br_2$ (2.30 mL, 44.9 mmol, 3.3 equiv) to a solution of NaOH (7.05 g, 176.3 mmol, 13.0 equiv) in $H_2O$ (68 mL) at 0 °C. The mixture was stirred for 16 h and gradually allowed to warm to 23 °C, at which point TLC indicated complete consumption of **1**. The mixture was washed with $CH_2Cl_2$ (3 × 100 mL) and 40% aqueous $NaHSO_3$ (63 mL) was added. The aqueous phase was acidified to pH 1 with concentrated HCl and extracted with $Et_2O$ (3 × 150 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (40% EtOAc/hexanes) followed by preparative HPLC [$H_2O$/MeCN; 40.0 mL $min^{-1}$; λ = 220 nm; (0–8.0 min) 82% $H_2O$, (8.0–10.0 min) 100% MeCN; 450 μL injection; $t_R$ =

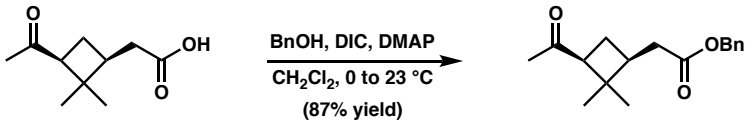
3.02 min] to afford the title compound as a white solid (1.61 g, 8.65 mmol, 64% yield). $[\alpha]_D^{25}$ = +4.6° (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.78 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.44 – 2.30 (m, 3H), 2.16 – 2.09 (m, 1H), 1.97 – 1.89 (m, 1H), 1.24 (s, 3H), 1.01 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 179.4, 179.1, 46.2, 43.1, 38.1, 35.3, 30.0, 24.4, 17.7; IR (thin film, NaCl) 2959, 1703, 1422, 1248, 937 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_9H_{13}O_4$ = 185.0814, found 185.0815. All physical and spectral data were in good accordance with previously reported values.[9,11]




*1* *3*

**2-((1*S*,3*S*)-3-(1-hydroxyethyl)-2,2-dimethylcyclobutyl)acetic acid ((+)-*cis*-pinolic acid, 3)**

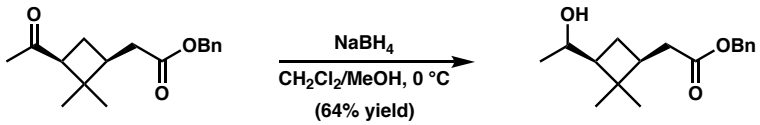
To a stirred solution of (+)-*cis*-pinonic acid (**1**) (2.00 g, 10.9 mmol, 1.0 equiv) in $CH_2Cl_2$/MeOH (4:1, 109 mL) at 0 °C was added $NaBH_4$ (2.46 g, 65.0 mmol, 6.0 equiv) in one portion. The resulting suspension was stirred for 10 h and gradually allowed to warm to 23 °C, at which point TLC indicated complete consumption of **1**. The reaction mixture was cooled to 0 °C, quenched by slow addition of saturated aqueous $NH_4Cl$, and diluted with $Et_2O$ (100 mL) and $H_2O$ (100 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated to provide the crude product in quantitative yield as a mixture of epimers ($^1$H NMR shows epimers form in 2:1 ratio). The crude product was purified by flash chromatography (40% EtOAc/hexanes) to afford the major epimer as a white solid (1.32 g, 7.09 mmol, 65% yield). $[\alpha]_D^{25}$ = –28.7° (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 3.73 (dq, *J* = 10.0, 6.2 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.27 – 2.16 (m, 2H), 2.07 – 1.98 (m, 1H), 1.78 (dt, *J* = 8.0, 10.2 Hz, 1H), 1.24 – 1.17 (m, 1H), 1.15 (s, 3H), 1.06 (d, *J* = 6.2 Hz, 3H), 1.03 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 179.0, 69.4, 50.4, 40.0, 37.8, 35.0, 31.0, 26.6, 21.3, 16.9; IR (thin film, NaCl) 3304, 2962, 1684, 1255, 1169, 668 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_{10}H_{17}O_3$ = 185.1178, found 185.1179. All physical and spectral data were in good accordance with previously reported values.[12]




*1* *1a*

**benzyl 2-((1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl)acetate (1a)**

To a stirred solution of (+)-*cis*-pinonic acid (**1**) (3.00 g, 16.3 mmol, 1.0 equiv), benzyl alcohol (5.08 mL, 48.9 mmol, 3.0 equiv), and DMAP (199 mg, 1.63 mmol, 0.10 equiv) in $CH_2Cl_2$ (33 mL) at 0 °C was added DIC (2.55 mL, 16.3 mmol, 1.0 equiv) dropwise. The mixture was stirred for 24 h and gradually allowed to warm to 23 °C, at which point TLC indicated complete consumption of **1**. The solution was diluted with $Et_2O$ (100 mL) and $H_2O$ (100 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (30% $Et_2O$/hexanes) to afford the title compound as a colorless oil (3.89 g, 14.2 mmol, 87% yield). $[\alpha]_D^{25}$ +44.8° (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.08 (s, 2H), 2.85 (dd, *J* = 10.2, 7.5 Hz, 1H), 2.42 – 2.26 (m, 3H), 2.02 (s, 3H), 2.00 – 1.94 (m, 1H), 1.93 – 1.86 (m, 1H), 1.28 (s, 3H), 0.84 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 207.5, 172.6, 135.9, 128.6, 128.3, 128.3, 66.2, 54.2 43.3, 38.0, 35.2, 30.2, 30.2, 23.0, 17.3; IR (thin film, NaCl) 2954, 1733, 1704, 1164, 977, 751, 699 cm$^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M+Na]^+$ $C_{17}H_{22}O_3Na$ = 297.1467, found 297.1476.



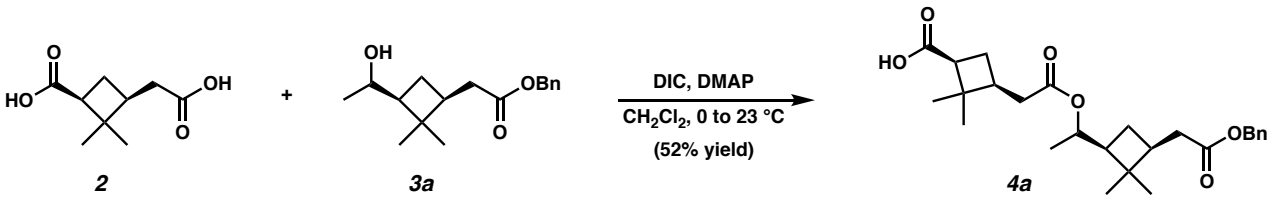

*1a* *3a*

**benzyl 2-((1*S*,3*S*)-3-(1-hydroxyethyl)-2,2-dimethylcyclobutyl)acetate (3a)**

To a stirred solution of benzyl ester **1a** (2.00 g, 7.29 mmol, 1.0 equiv) in $CH_2Cl_2$/MeOH (4:1, 73 mL) at 0 °C was added $NaBH_4$ (827 mg, 21.9 mmol, 3.0 equiv) in one portion. The resulting suspension was stirred at 0 °C for 10 min, at which time TLC indicated complete consumption of **1a**. The mixture was quenched by slow addition of saturated aqueous $NH_4Cl$, then diluted with $Et_2O$ (100 mL) and $H_2O$ (100 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated to provide the crude product as a mixture of epimers. The crude product was

purified by flash chromatography (40% $Et_2O$/hexanes) to afford the major epimer as a colorless oil (1.28 g, 4.63 mmol, 64% yield). $[\alpha]_D^{25}$ –23.8° (*c* 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 5.09 (s, 2H), 3.69 (dq, *J* = 10.0, 6.2 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.28 – 2.17 (m, 2H), 2.00 – 1.93 (m, 1H), 1.75 (dt, *J* = 8.0, 10.2 Hz, 1H), 1.16 (m, 1H), 1.11 (s, 3H), 1.04 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 173.0, 136.0, 128.6, 128.3, 128.2, 69.2, 66.2, 50.3, 39.9, 37.9, 35.3, 30.9, 26.6, 21.3, 16.8; IR (thin film, NaCl) 3425, 2960, 1734, 1456, 1164, 750, 698 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M+Na]^+$ $C_{17}H_{24}O_3Na$ = 299.1623, found 299.1616.

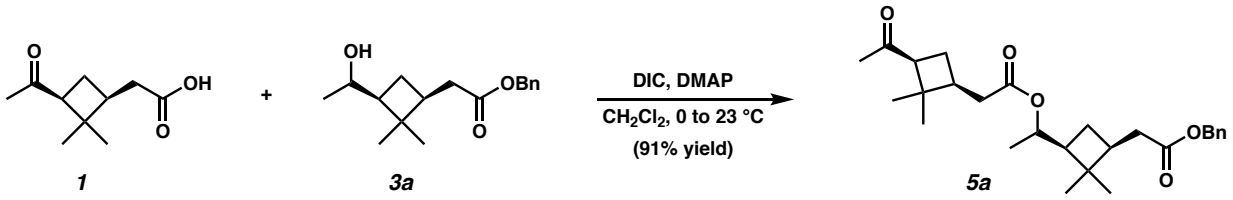
*Note: Deviation from the procedure described above by allowing the reaction to warm to room temperature and stir for prolonged periods of time (i.e., 10 h) was found to result in formation of significant quantities of the methyl ester of **3a**, which is extremely difficult to separate from **3a**.*




**(1*S*,3*S*)-3-(2-(1-((1*S*,3*S*)-3-(2-(benzyloxy)-2-oxoethyl)-2,2-dimethylcyclobutyl)ethoxy)-2-oxoethyl)-2,2-dimethylcyclobutane-1-carboxylic acid (4a)**

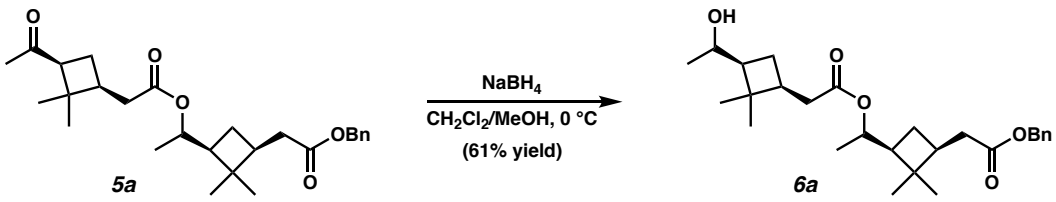
To a stirred solution of alcohol **3a** (100 mg, 0.362 mmol, 1.00 equiv), (+)-*cis*-pinic acid (**2**) (101 mg, 0.543 mmol, 1.5 equiv), and DMAP (4.4 mg, 0.0362 mmol, 0.10 equiv) in $CH_2Cl_2$ (3.6 mL) at 0 °C was added DIC (85 μL, 0.543 mmol, 1.5 equiv) dropwise. The mixture was stirred for 24 h and gradually allowed to warm to 23 °C, at which point TLC indicated complete consumption of **3a**. The solution was diluted with $Et_2O$ (20 mL) and $H_2O$ (20 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (30–40% $Et_2O$/hexanes) to afford the title compound as a colorless oil (83 mg, 0.187 mmol, 52% yield). $[\alpha]_D^{25}$ = –11.3° (*c* 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.08 (s, 2H), 4.76 (dq, *J* = 10.2, 6.1 Hz, 1H), 2.78 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.41 – 2.29 (m, 3H), 2.28 – 2.18 (m, 3H), 2.14–2.08 (m, 1H), 2.06 – 1.95 (m, 2H), 1.89 (dt, *J* = 11.2, 10.3 Hz, 1H), 1.25 (s, 3H), 1.22 (m, 1H), 1.06 (s, 3H), 1.04 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 3H), 0.86 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 178.8, 172.9, 172.2, 136.0, 128.6, 128.4, 128.3, 71.8, 66.3,

47.0, 46.1, 43.0, 39.9, 38.4, 38.1, 35.9, 35.2, 30.5, 30.1, 26.5, 24.5, 17.7, 17.7, 16.9; IR (thin film, NaCl) 2958, 1731, 1456, 1170, 1067, 750, 697 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_{26}H_{35}O_6$ = 443.2434, found 443.2442.




**benzyl 2-((1*S*,3*S*)-3-(1-(2-((1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl)acetoxy)ethyl)-2,2-dimethylcyclobutyl)acetate (5a)**

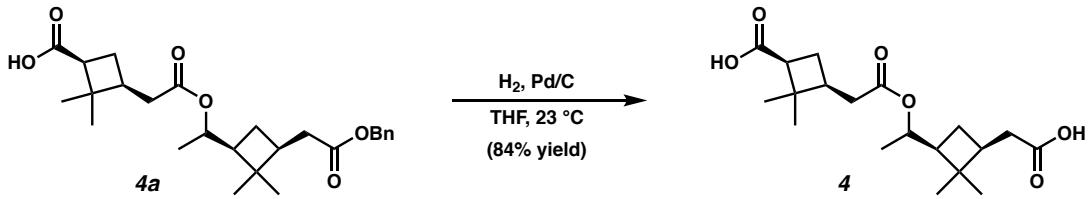
To a stirred solution of alcohol **3a** (1.00 g, 3.62 mmol, 1.0 equiv), (+)-*cis*-pinonic acid (**1**) (1.33 g, 7.24 mmol, 2.0 equiv), and DMAP (44 mg, 0.362 mmol, 0.10 equiv) in $CH_2Cl_2$ (36 mL) at 0 °C was added DIC (1.14 mL, 7.24 mmol, 2.0 equiv) dropwise. The mixture was stirred for 24 h and gradually allowed to warm to 23 °C, at which point TLC indicated complete consumption of **3a**. The solution was diluted with $Et_2O$ (100 mL) and $H_2O$ (100 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography (30% $Et_2O$/hexanes) to afford the title compound as a colorless oil (1.46 g, 3.31 mmol, 91% yield). $[\alpha]_D^{25}$ +22.4° (*c* 1.0, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.06 (s, 2H), 4.74 (dq, *J* = 10.2, 6.1 Hz, 1H), 2.85 (dd, *J* = 10.0, 7.7 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.28 – 2.19 (m, 3H), 2.16 (dd, *J* = 15.4, 7.7 Hz, 1H), 2.02 (s, 3H), 2.00 – 1.87 (m, 4H), 1.30 (s, 3H), 1.22 (m, 1H), 1.04 (s, 3H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.84 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 207.5, 172.8, 172.2, 136.0, 128.6, 128.3, 128.3, 71.7, 66.2, 54.2, 47.0, 43.3, 39.8, 38.1, 38.0, 35.6, 35.2, 30.4, 30.3, 30.2, 26.4, 23.1, 17.6, 17.4, 16.8; IR (thin film, NaCl) 2956, 1731, 1706, 1455, 1369, 1167, 698 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M+Na]^+$ $C_{27}H_{38}O_5Na$ = 465.2617, found 465.2611.




5a 6a

**benzyl 2-((1*S*,3*S*)-3-(1-(2-((1*S*,3*S*)-3-(1-hydroxyethyl)-2,2-dimethylcyclobutyl) acetoxy)ethyl)-2,2-dimethylcyclobutyl)acetate (6a)**

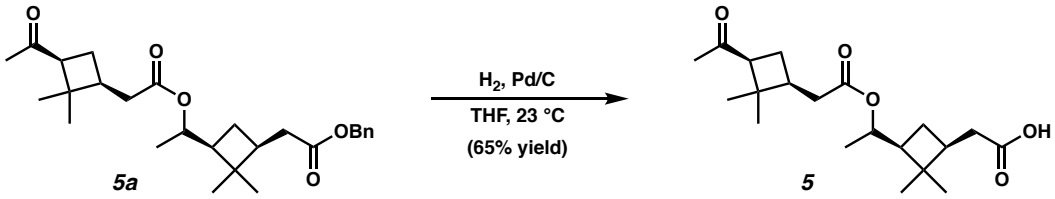
To a stirred solution of benzyl ester **5a** (400 mg, 0.904 mmol, 1.0 equiv) in $CH_2Cl_2$/MeOH (4:1, 9.0 mL) at 0 °C was added $NaBH_4$ (103 mg, 2.72 mmol, 3.0 equiv) in one portion. The resulting suspension was stirred at 0 °C for 10 min, at which time TLC indicated complete consumption of **5a**. The mixture was quenched by slow addition of saturated aqueous $NH_4Cl$, then diluted with $Et_2O$ (100 mL) and $H_2O$ (100 mL). The layers were separated and the aqueous layer was extracted with $Et_2O$ (3 × 100 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated to provide the crude product as a mixture of epimers. The crude product was purified by flash chromatography (40% $Et_2O$/hexanes) to afford the major epimer as a colorless oil (245 mg, 0.551 mmol, 61% yield). $[\alpha]_D^{25}$ –22.1° (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 5.07 (s, 2H), 4.74 (dq, *J* = 10.2, 6.1 Hz, 1H), 3.68 (dq, *J* = 10.0, 6.2 Hz, 1H), 2.41 – 2.05 (m, 6H), 2.04 – 1.91 (m, 3H), 1.73 (dt, *J* = 8.0, 10.2 Hz, 1H), 1.21 (m, 1H), 1.13 (s, 3H), 1.12 (m, *J* = 10.4 Hz, 1H), 1.05 (s, 3H), 1.03 (d, *J* = 6.1 Hz, 3H), 1.02 (d, *J* = 6.2 Hz, 3H), 1.00 (s, 3H), 0.85 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 172.9, 172.6, 136.0, 128.6, 128.3, 128.3, 71.5, 69.2, 66.2, 50.3, 47.0, 39.9, 39.9, 38.1, 38.1, 35.8, 35.2, 31.1, 30.4, 26.7, 26.5, 21.3, 17.7, 16.9, 16.8; IR (thin film, NaCl) 3504, 2958, 1732, 1456, 1367, 1187, 1166, 750, 698 cm$^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M+Na]^+$ $C_{27}H_{40}O_5Na$ = 467.2773, found 467.2773.




4a 4

**(1*S*,3*S*)-3-(2-(1-((1*S*,3*S*)-3-(carboxymethyl)-2,2-dimethylcyclobutyl)ethoxy)-2-oxoethyl)-2,2-dimethylcyclobutane-1-carboxylic acid (4)**

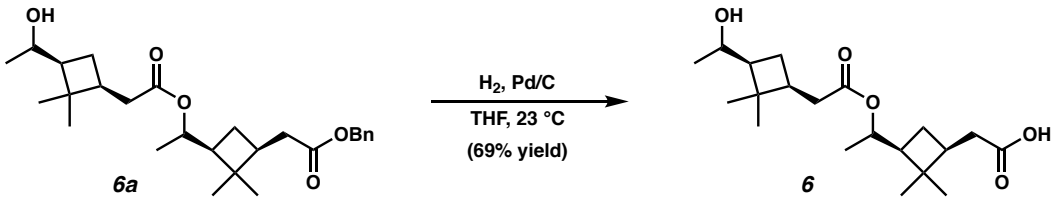
In a 2-necked round bottom flask equipped with a 3-way valve at 23 °C, benzyl ester **4a** (100 mg, 0.225 mmol, 1.0 equiv) was dissolved in THF (2.3 mL) and to this solution was added Pd/C (10% w/w, 25 mg). The flask was evacuated and backfilled with $N_2$ (3×), then purged and backfilled with $H_2$ (3×). The suspension was stirred for 2 h under $H_2$ (1 atm, balloon), at which point TLC indicated complete consumption of **4a**. The flask was evacuated and backfilled with $N_2$ (3×), then the suspension was diluted with EtOAc (20 mL), filtered through celite, and concentrated. The crude product was purified by flash chromatography (50% EtOAc/hexanes) to afford the title compound as a white solid (67 mg, 0.189 mmol, 84% yield). $[\alpha]_D^{25} = -11.4°$ (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 4.76 (dq, *J* = 10.2, 6.1 Hz, 1H), 2.77 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.41 – 2.29 (m, 3H), 2.28 – 2.18 (m, 3H), 2.15 – 1.94 (m, 3H), 1.88 (dt, *J* = 11.0, 10.3 Hz, 1H), 1.24 (s, 3H), 1.22 (m, 1H), 1.09 (s, 3H), 1.04 (d, *J* = 6.1 Hz, 3H), 0.99 (s, 3H), 0.87 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 179.8, 179.2, 172.3, 71.8, 47.1, 46.2, 43.1, 39.9, 38.5, 37.8, 35.9, 35.0, 30.5, 30.1, 26.5, 24.5, 17.7, 17.7, 16.9 ; IR (thin film, NaCl) 2957, 1704, 1247, 1211, 958, 739 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M-H]^-$ $C_{19}H_{29}O_6$ = 353.1964, found 353.1967.




**2-((1*S*,3*S*)-3-(1-(2-((1*S*,3*S*)-3-acetyl-2,2-dimethylcyclobutyl)acetoxy)ethyl)-2,2-dimethylcyclobutyl)acetic acid (5)**

In a 2-necked round bottom flask equipped with a 3-way valve at 23 °C, benzyl ester **5a** (400 mg, 0.904 mmol, 1.0 equiv) was dissolved in THF (9.1 mL) and to this solution was added Pd/C (10%, 100 mg). The flask was evacuated and backfilled with $N_2$ (3×), then purged and backfilled with $H_2$ (3×). The suspension was stirred for 2 h under $H_2$ (1 atm, balloon), at which point TLC indicated complete consumption of **5a**. The flask was evacuated and backfilled with $N_2$ (3×), then the suspension was diluted with EtOAc (50 mL), filtered through celite, and concentrated. The crude product was purified by flash chromatography (40% EtOAc/hexanes) to afford the title compound as a white solid (206 mg, 0.585 mmol, 65% yield). $[\alpha]_D^{25}$ +29.4°(*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 4.74 (dq, *J* = 10.2, 6.1 Hz, 1H), 2.85 (dd, *J* = 10.0, 7.8 Hz, 1H), 2.37 – 2.09 (m,

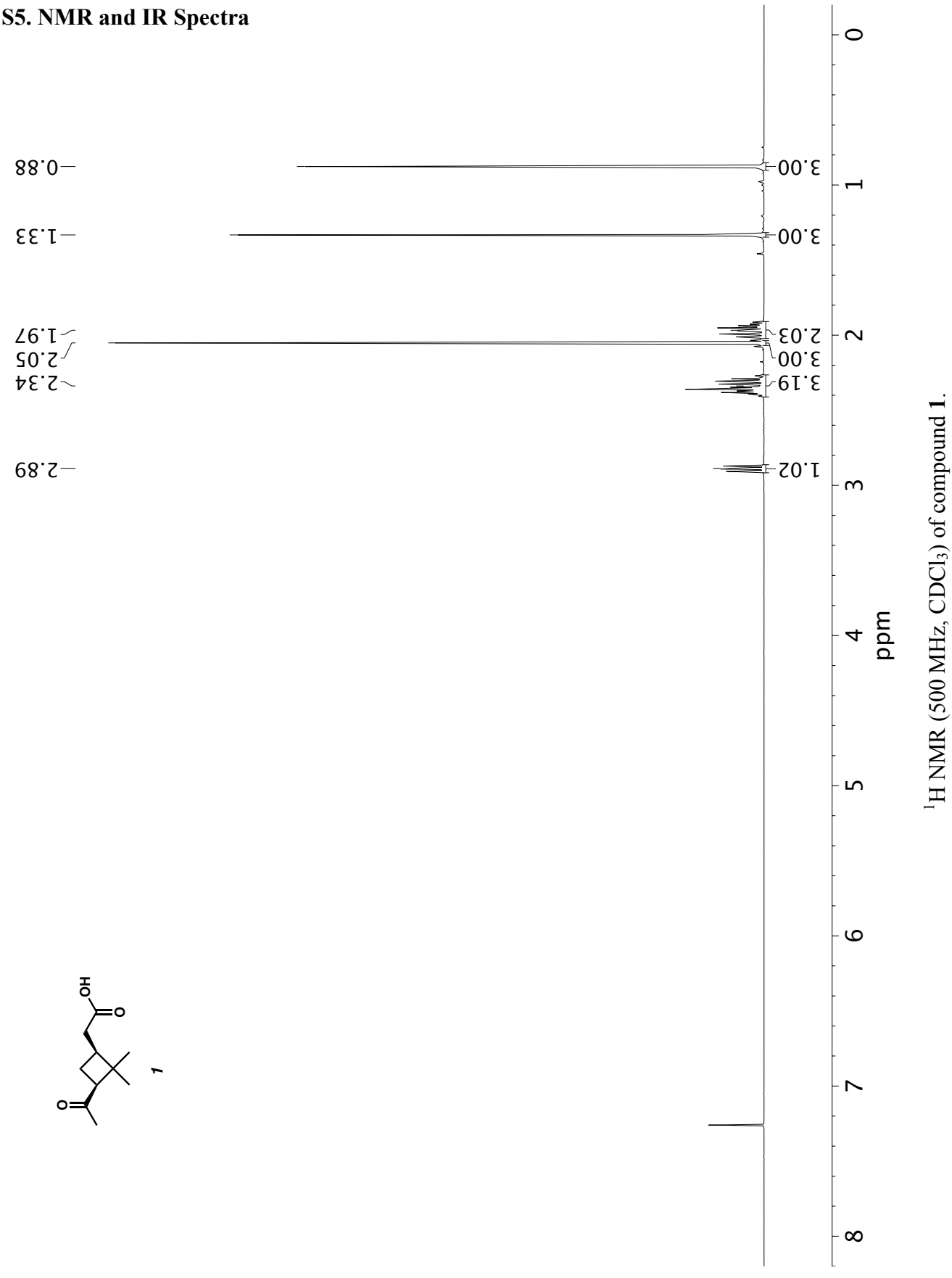
6H), 2.08 – 1.83 (m, 7H), 1.29 (s, 3H), 1.22 (m, 1H), 1.06 (s, 3H), 1.01 (d, $J$ = 6.1 Hz, 3H), 0.84 (s, 3H), 0.82 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 207.9, 179.1, 172.3, 71.7, 54.3, 47.0, 43.4, 39.9, 38.1, 37.8, 35.6, 34.9, 30.5, 30.3, 30.2, 26.4, 23.2, 17.6, 17.4, 16.8; IR (thin film, NaCl) 2956, 1728, 1706, 1369, 1180, 959, 867 cm$^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_{20}H_{31}O_5$ = 351.2171, found 351.2178.



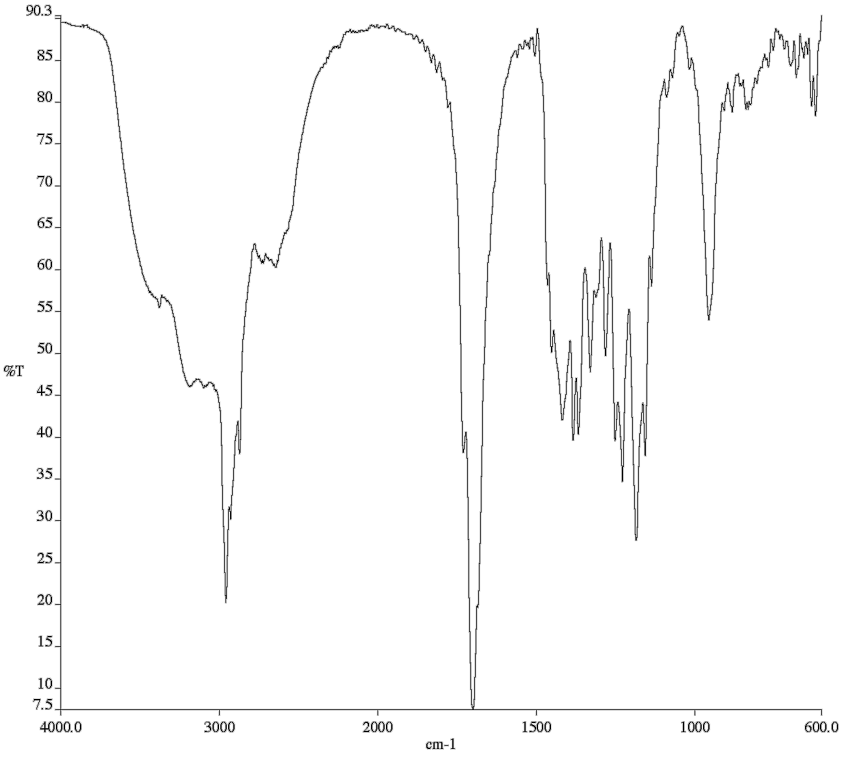

**2-((1*S*,3*S*)-3-(1-(2-((1*S*,3*S*)-3-(1-hydroxyethyl)-2,2-dimethylcyclobutyl)acetoxy) ethyl)-2,2-dimethylcyclobutyl)acetic acid (6)**

In a 2-necked round bottom flask equipped with a 3-way valve, benzyl ester **6a** (100 mg, 0.225 mmol, 1.0 equiv) was dissolved in THF (2.3 mL) and to this solution was added Pd/C (10% w/w, 25 mg). The flask was evacuated and backfilled with $N_2$ (3×), then purged and backfilled with $H_2$ (3×). The suspension was stirred for 2 h under $H_2$ (1 atm, balloon), at which point TLC indicated complete consumption of **6a**. The flask was evacuated and backfilled with $N_2$ (3×), then the suspension was diluted with EtOAc (20 mL), filtered through celite, and concentrated. The crude product was purified by flash chromatography (50% EtOAc/hexanes) to afford the title compound as a white solid (55 mg, 0.156 mmol, 69% yield). $[\alpha]_D^{25}$ –17.8° (*c* 1.0, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 4.74 (dq, $J$ = 10.1, 6.1 Hz, 1H), 3.69 (dq, $J$ = 10.0, 6.2 Hz, 1H), 2.39 – 1.92 (m, 9H), 1.74 (dt, $J$ = 8.0, 10.2 Hz, 1H), 1.21 (m, 1H), 1.14 (m, $J$ = 10.4 Hz, 1H), 1.12 (s, 3H), 1.08 (s, 3H), 1.03 (d, $J$ = 6.1 Hz, 3H), 1.02 (d, $J$ = 6.2 Hz, 3H), 0.99 (s, 3H), 0.86 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 178.6, 172.7, 71.6, 69.4, 50.2, 47.1, 39.9, 39.9, 38.1, 37.9, 35.8, 35.0, 31.0, 30.5, 26.7, 26.5, 21.2, 17.7, 16.9, 16.8; IR (thin film, NaCl) 3441, 2959, 1709, 1451, 1368, 1191, 874, 736, 668 cm$^{-1}$; HRMS (ESI-TOF) *m/z* calc'd for $[M–H]^-$ $C_{20}H_{33}O_5$ = 353.2328, found 353.2332.

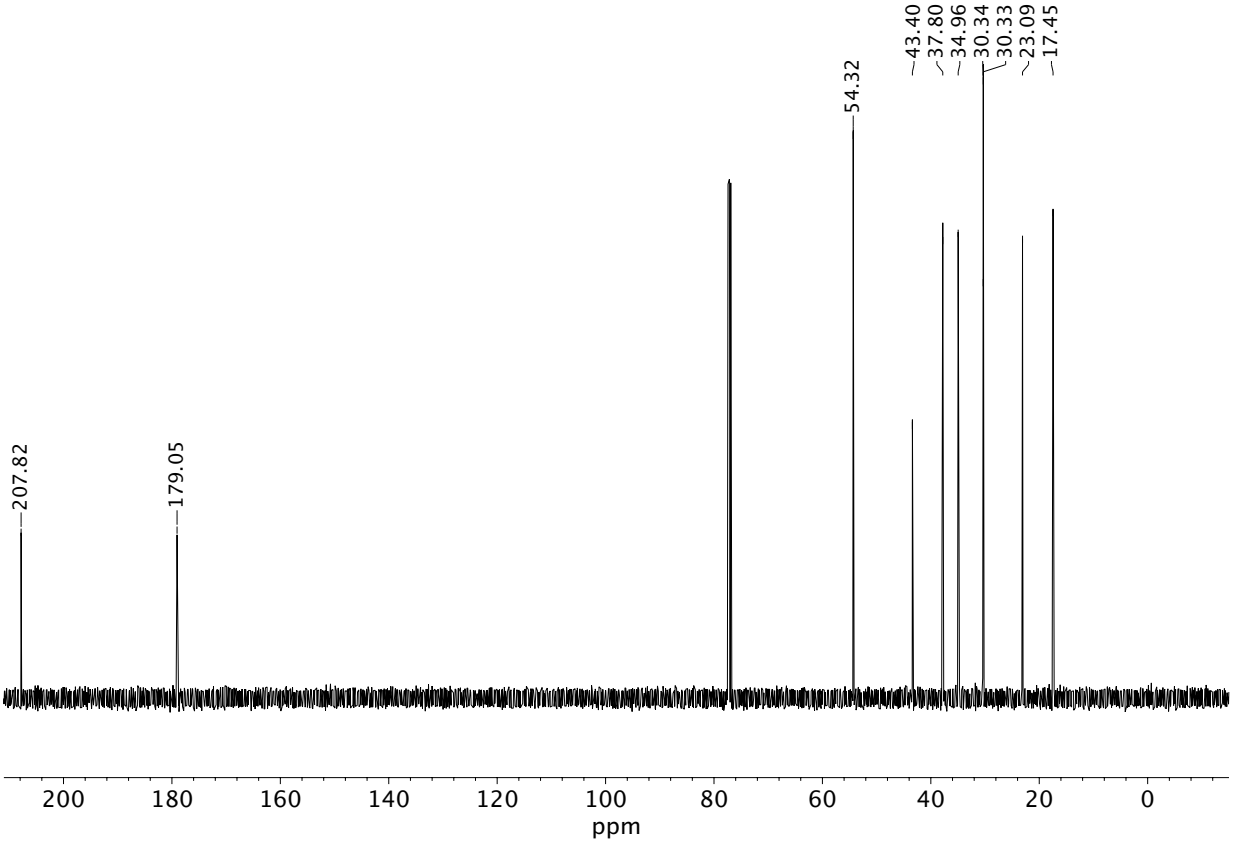
**S5. NMR and IR Spectra**



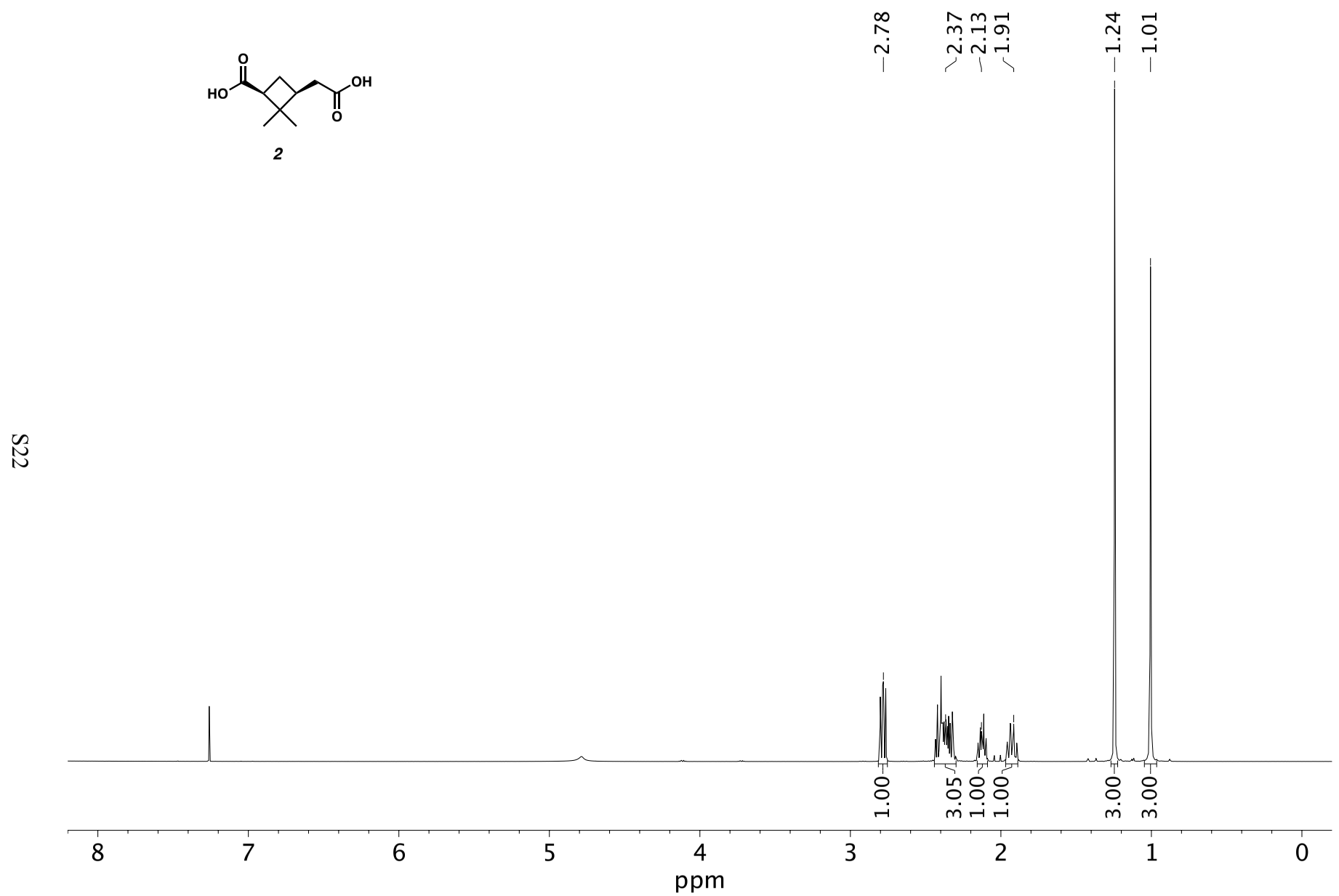

$^1$H NMR (500 MHz, $CDCl_3$) of compound **1**.



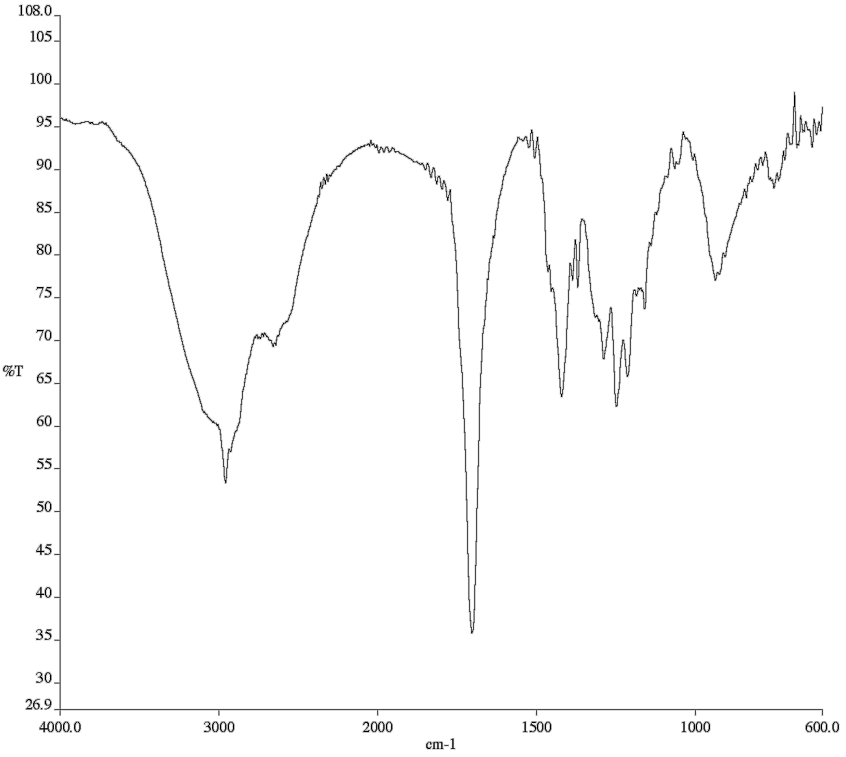

Infrared spectrum (thin film, NaCl) of compound **1**.



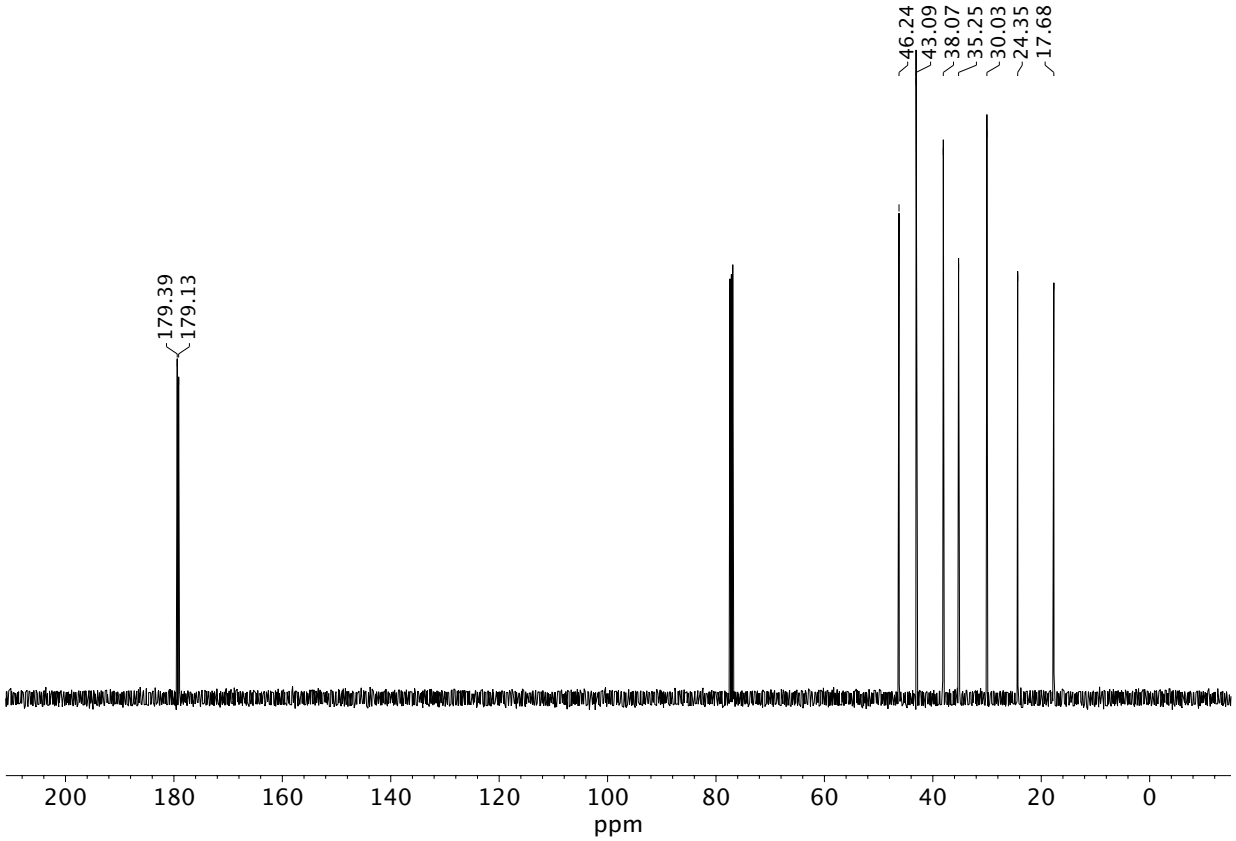

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **1**.



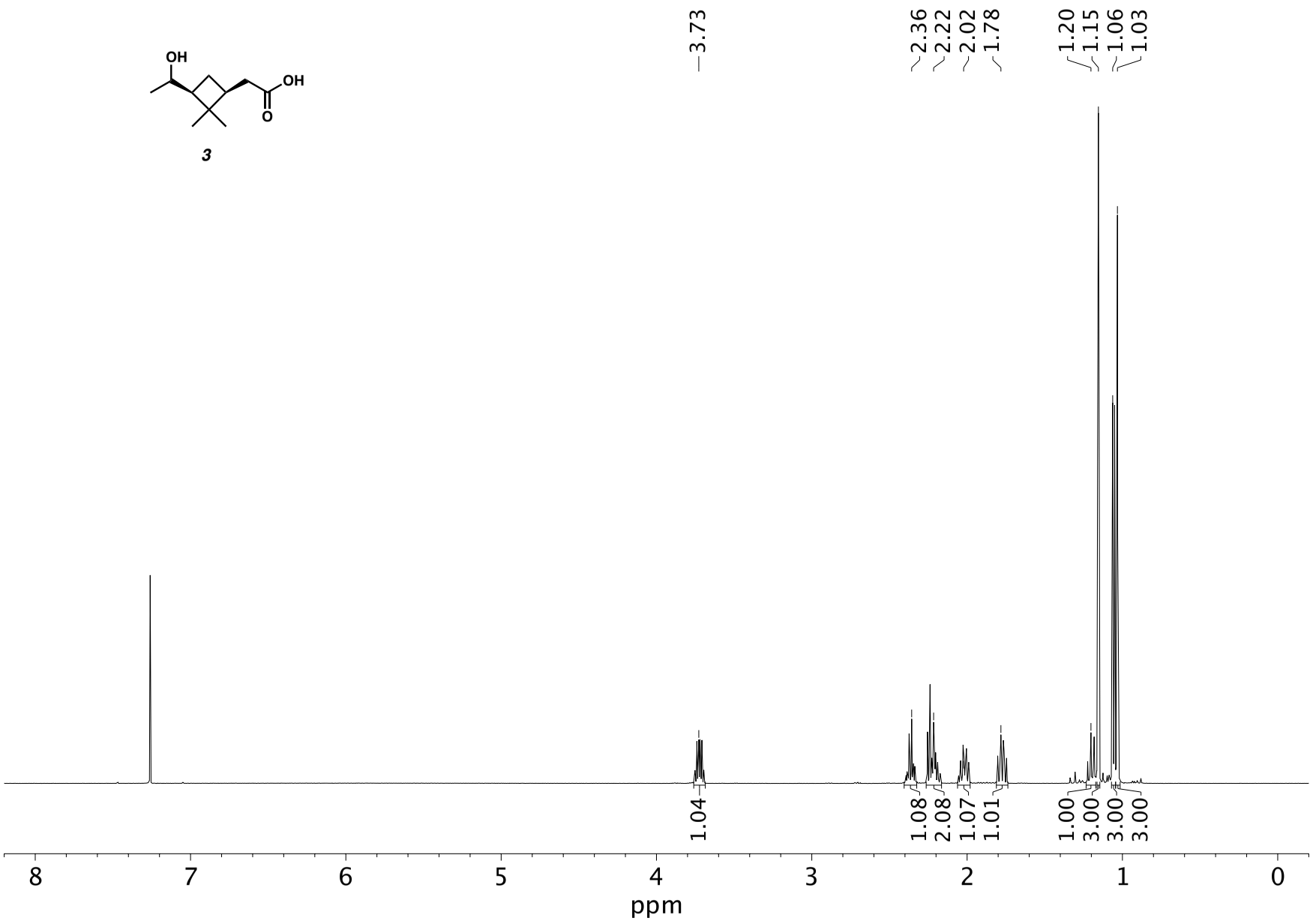

$^1$H NMR (500 MHz, $CDCl_3$) of compound **2**.



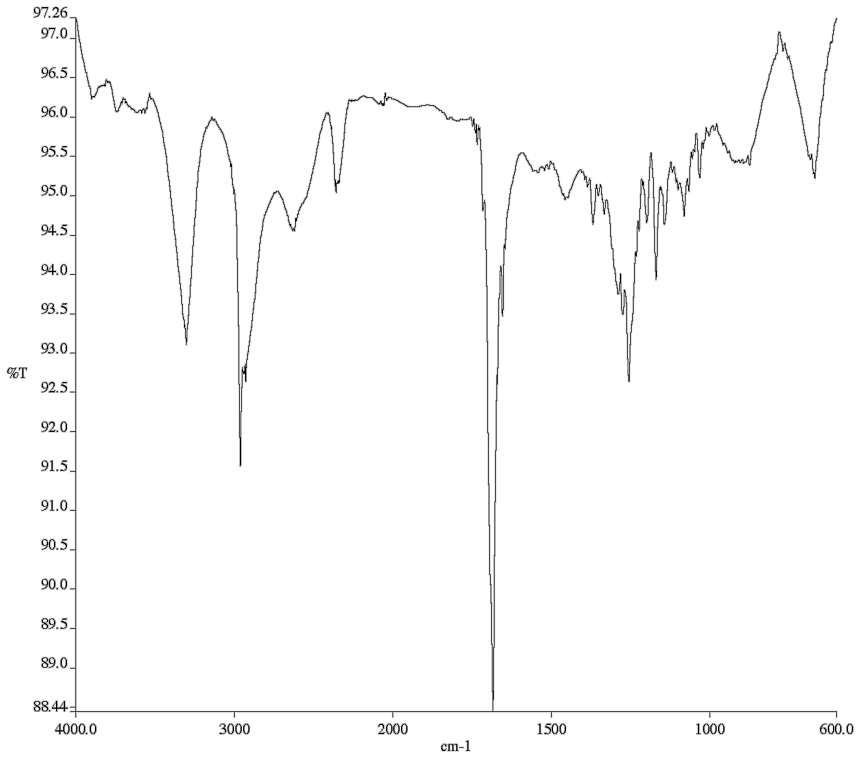

Infrared spectrum (thin film, NaCl) of compound **2**.



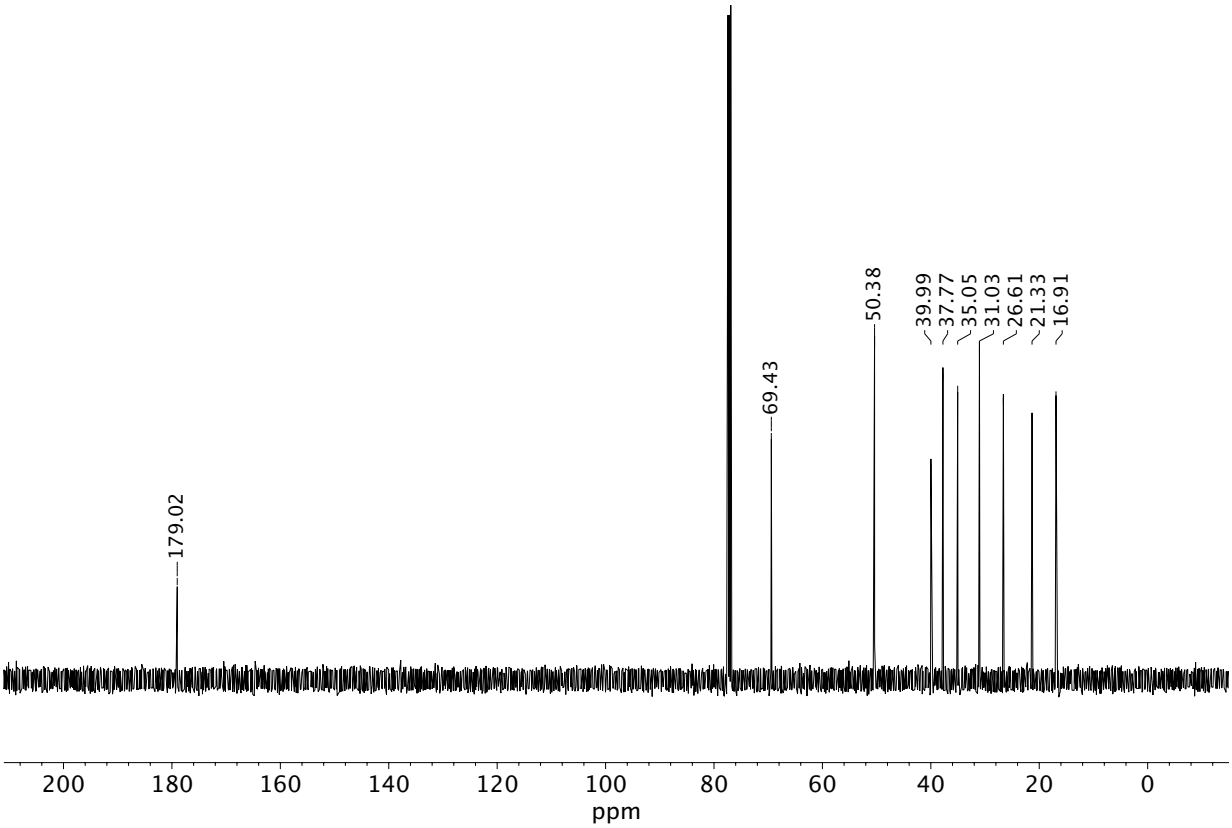

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **2**.



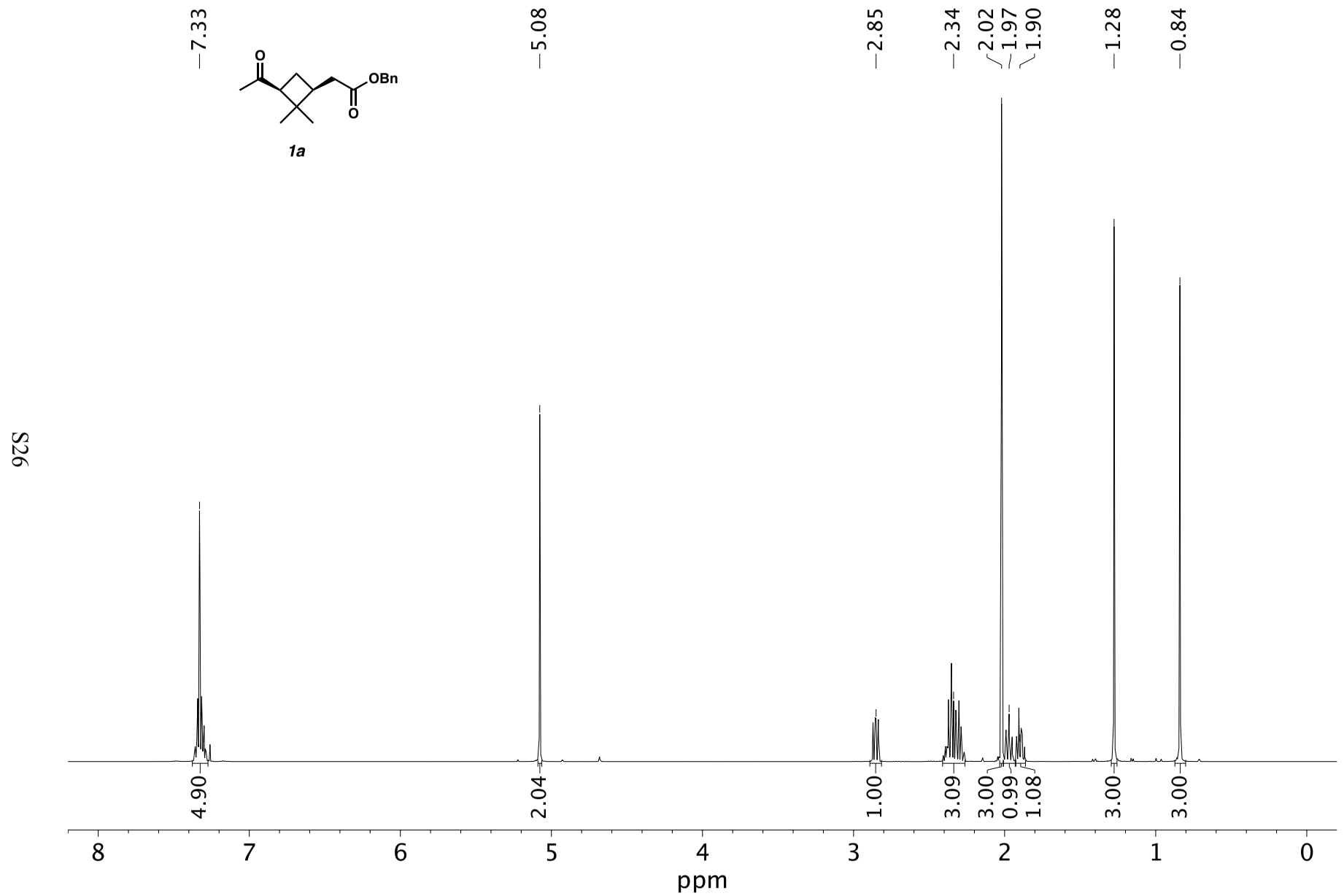

$^1$H NMR (500 MHz, $CDCl_3$) of compound **3**.



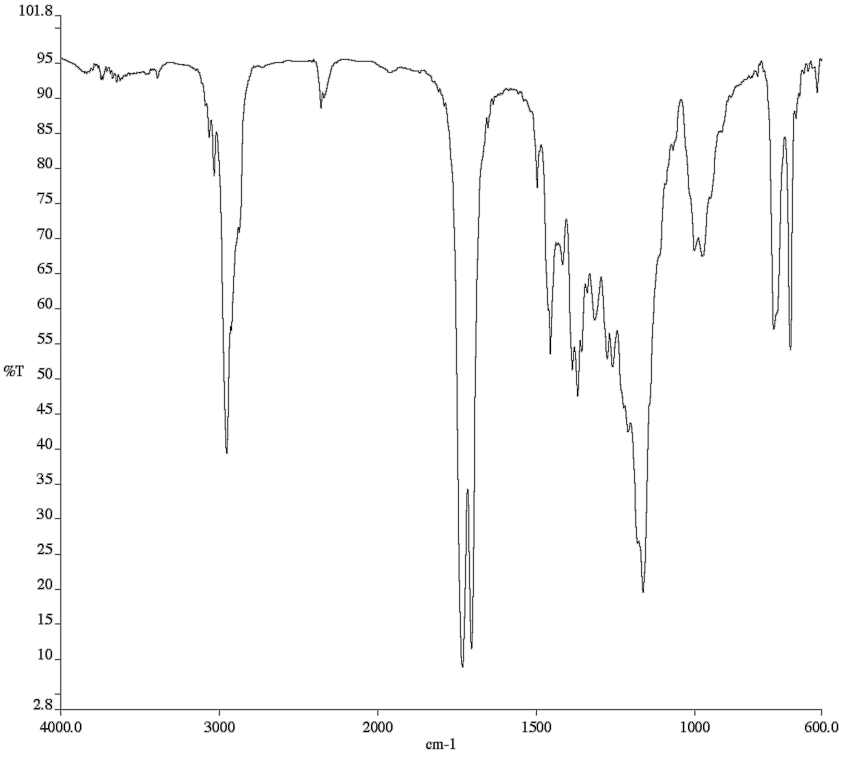

Infrared spectrum (thin film, NaCl) of compound **3**.



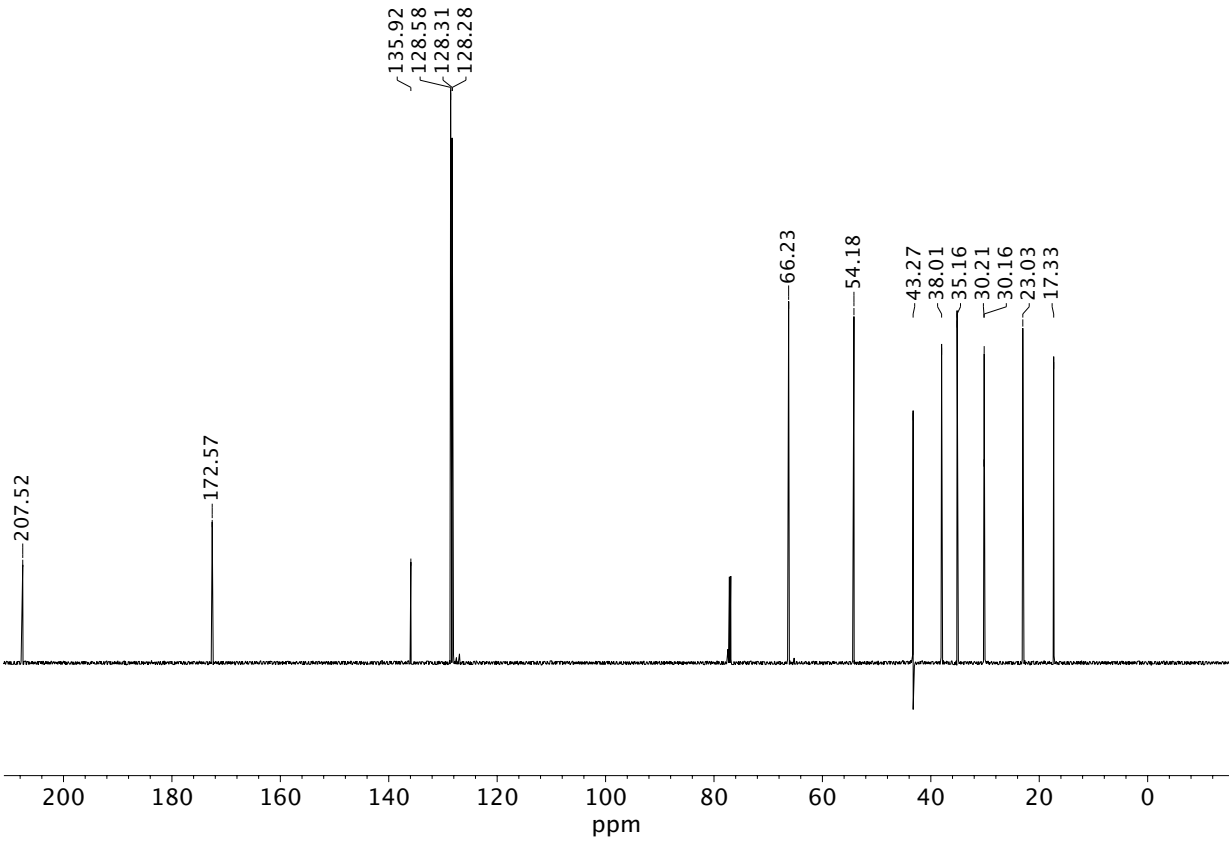

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **3**.



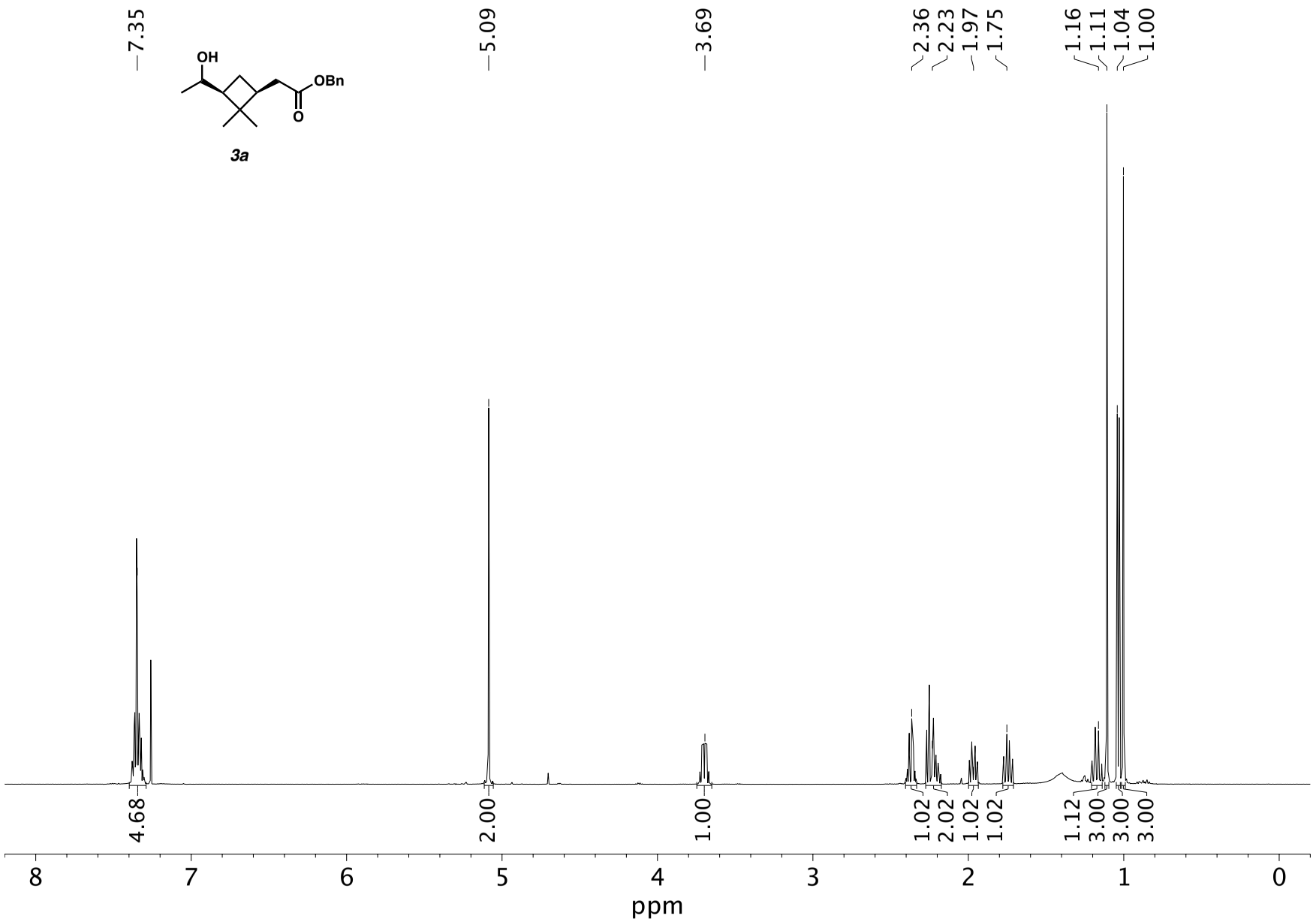

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **1a**.




Infrared spectrum (thin film, NaCl) of compound **1a**.

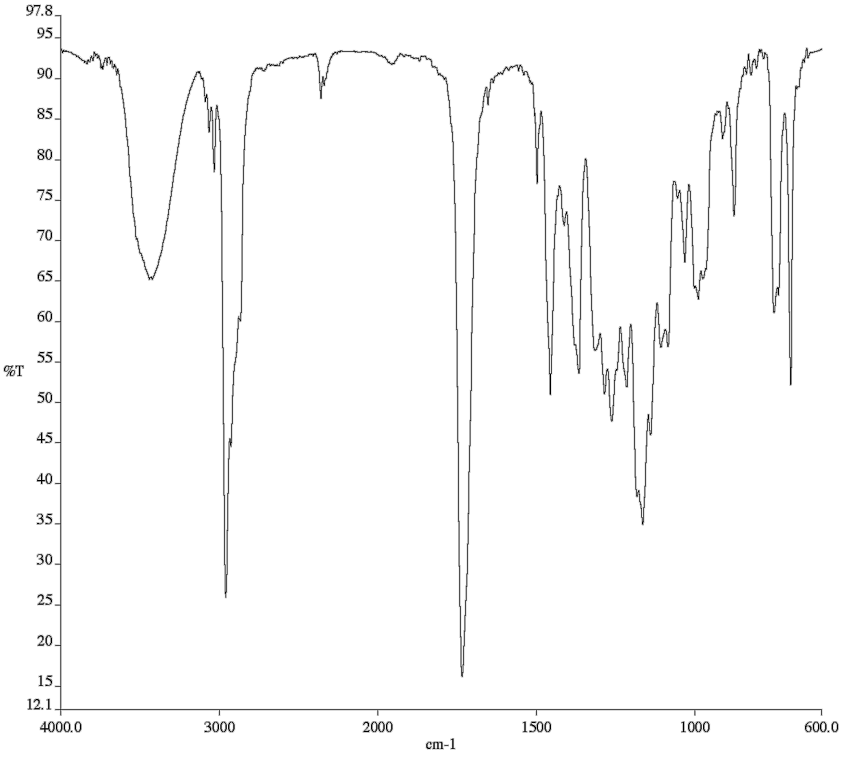



$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **1a**.

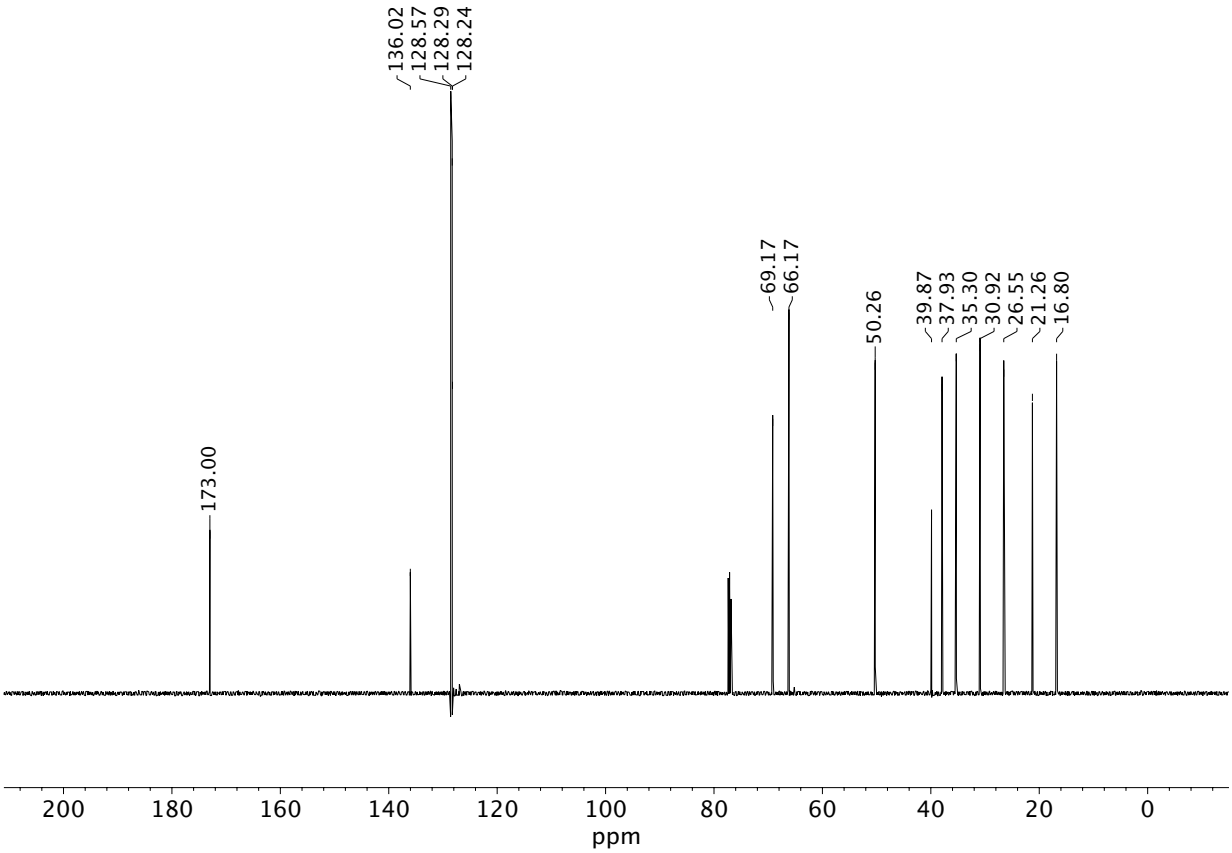




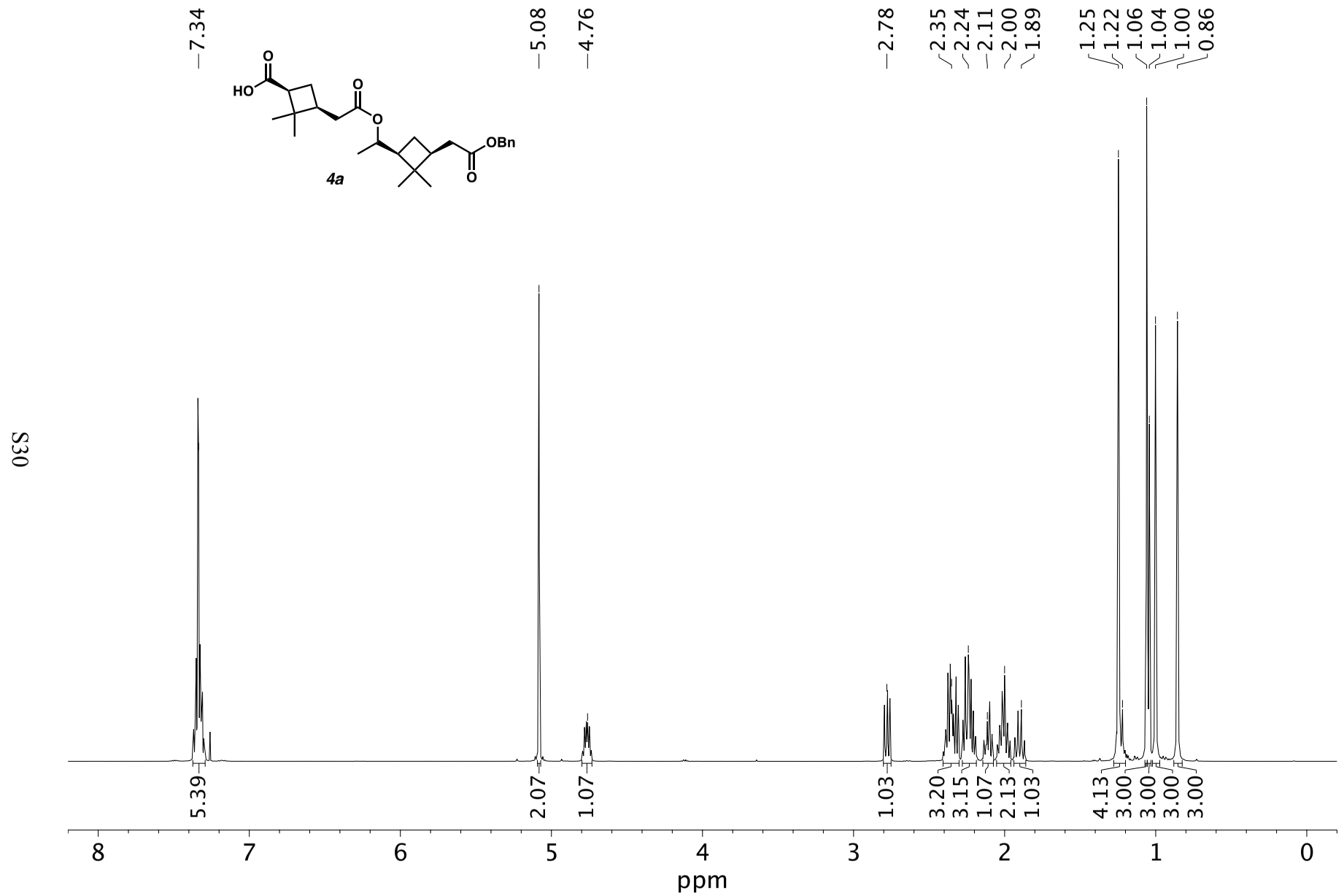

$^1$H NMR (500 MHz, $CDCl_3$) of compound **3a**.




Infrared spectrum (thin film, NaCl) of compound **3a**.

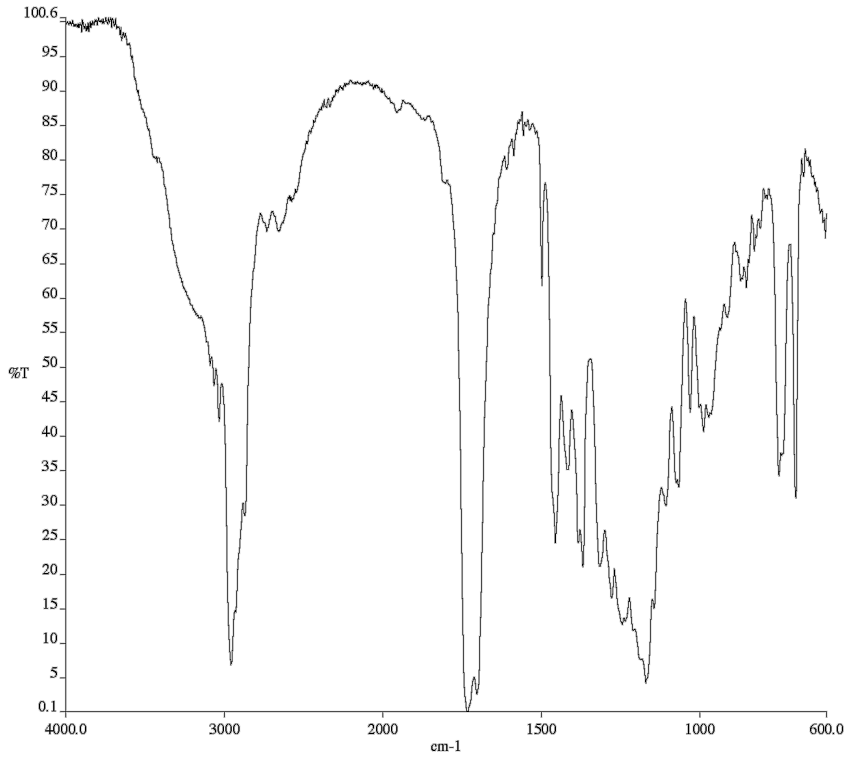



$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **3a**.

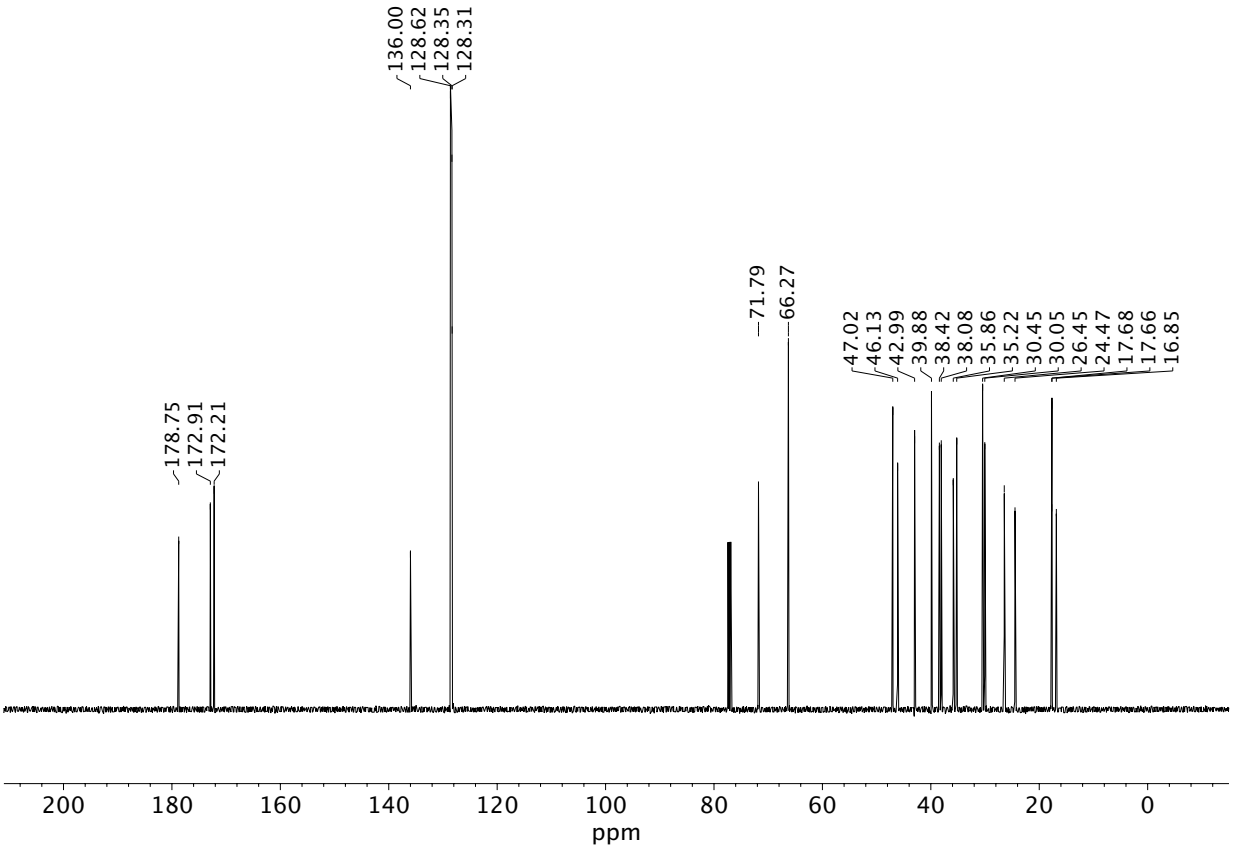




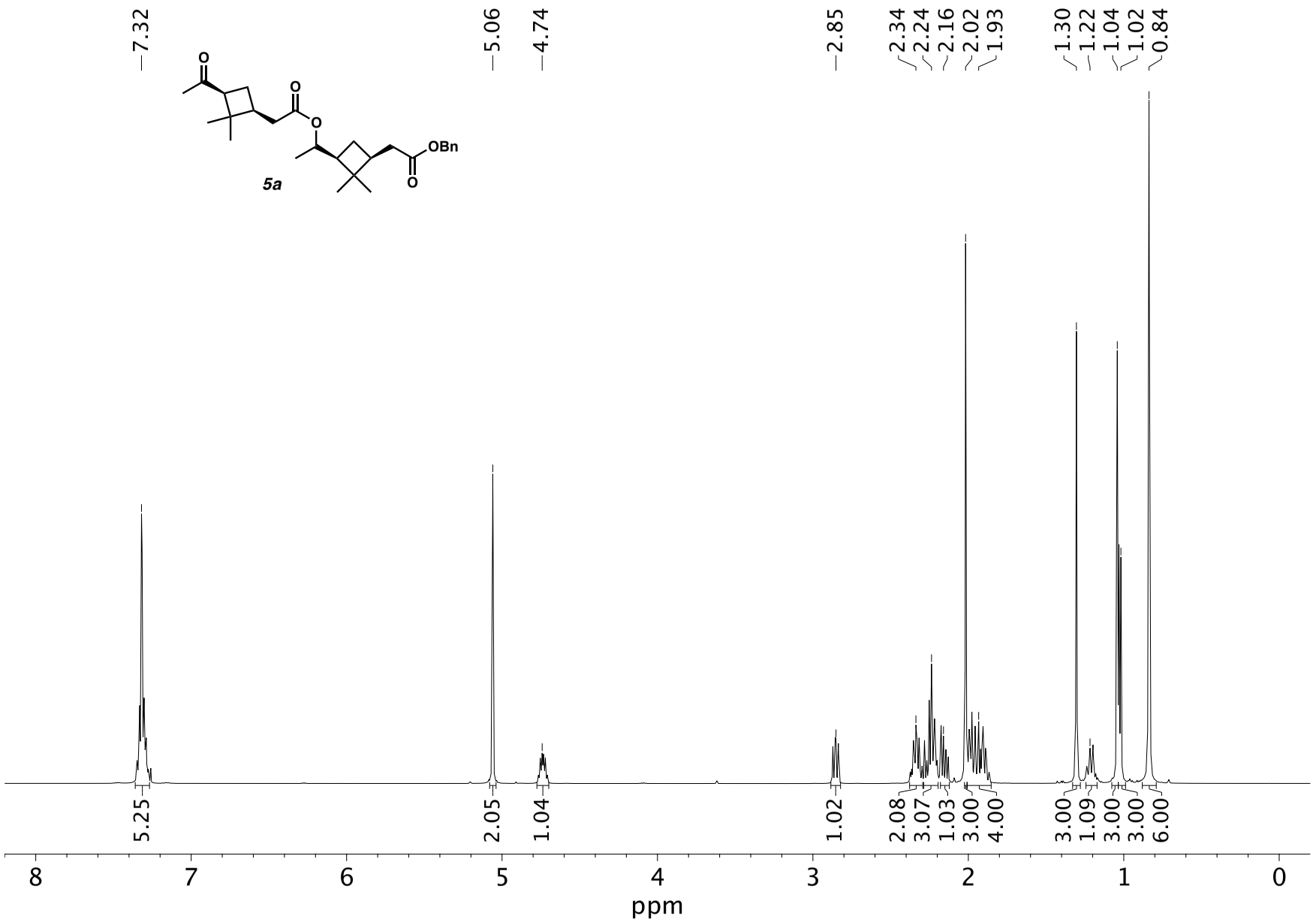

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **4a**.



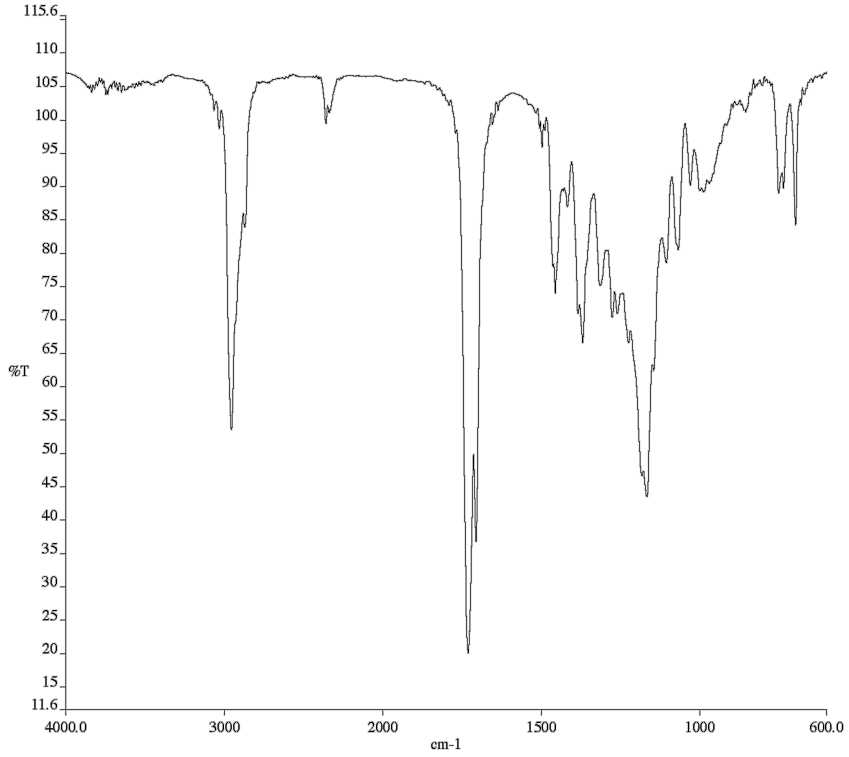

Infrared spectrum (thin film, NaCl) of compound **4a**.



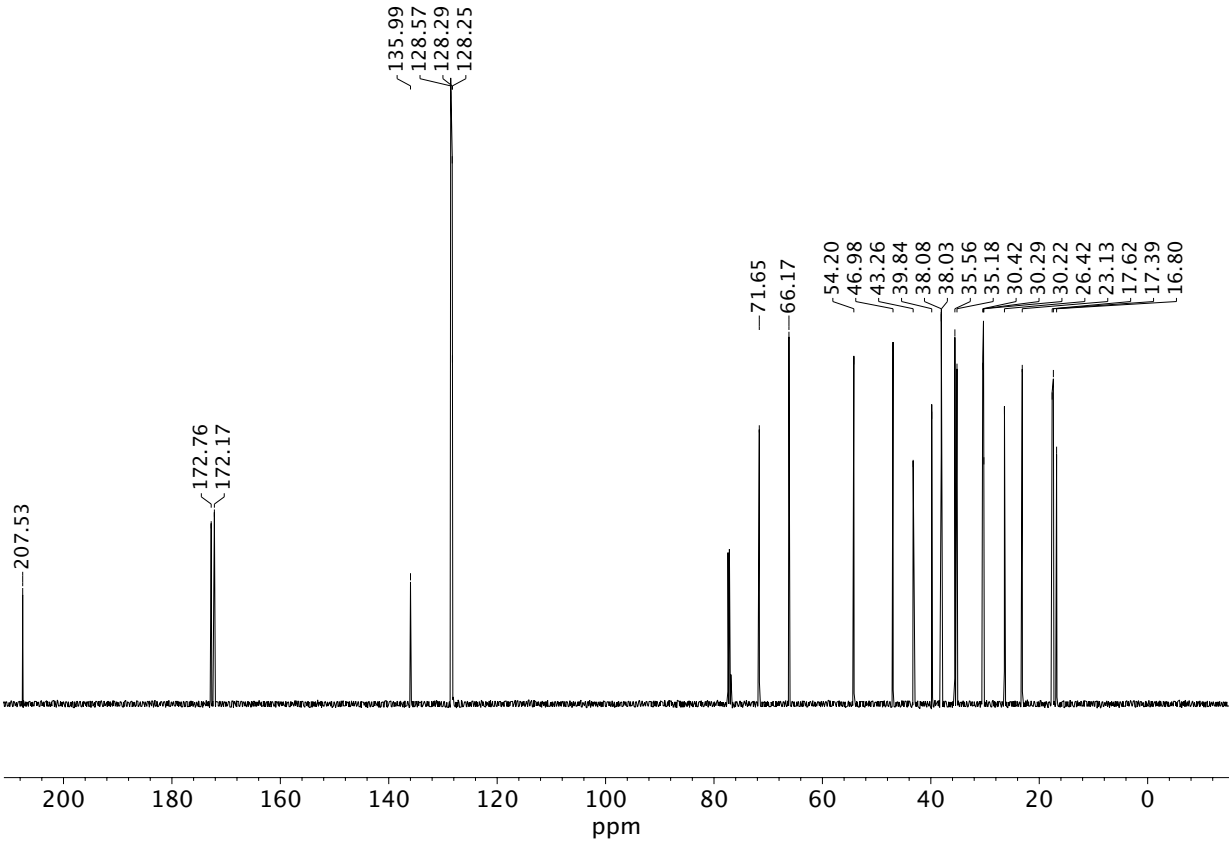

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **4a**.



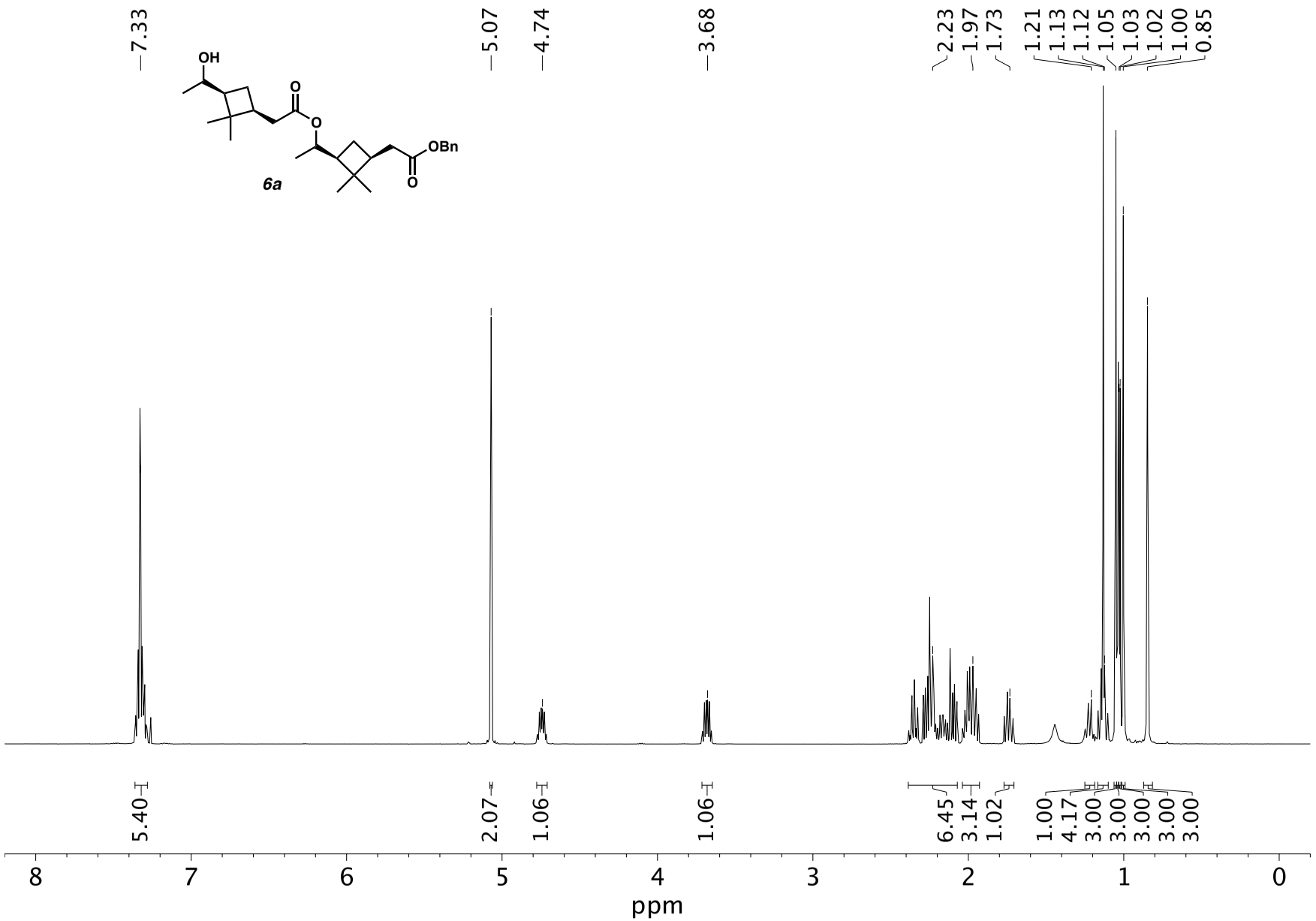

$^1$H NMR (500 MHz, $CDCl_3$) of compound **5a**.



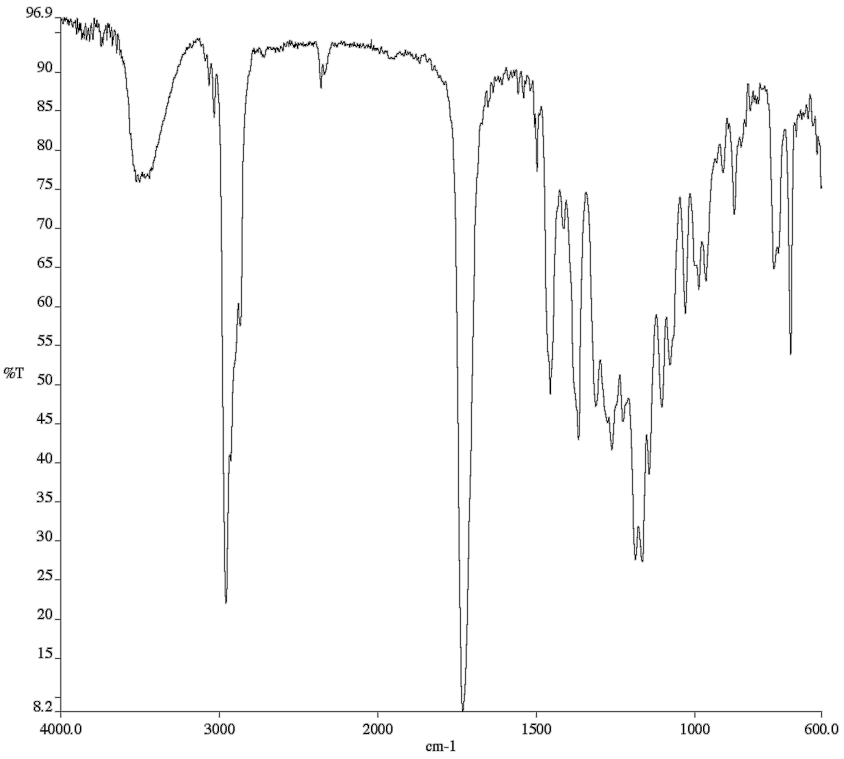

Infrared spectrum (thin film, NaCl) of compound **5a**.



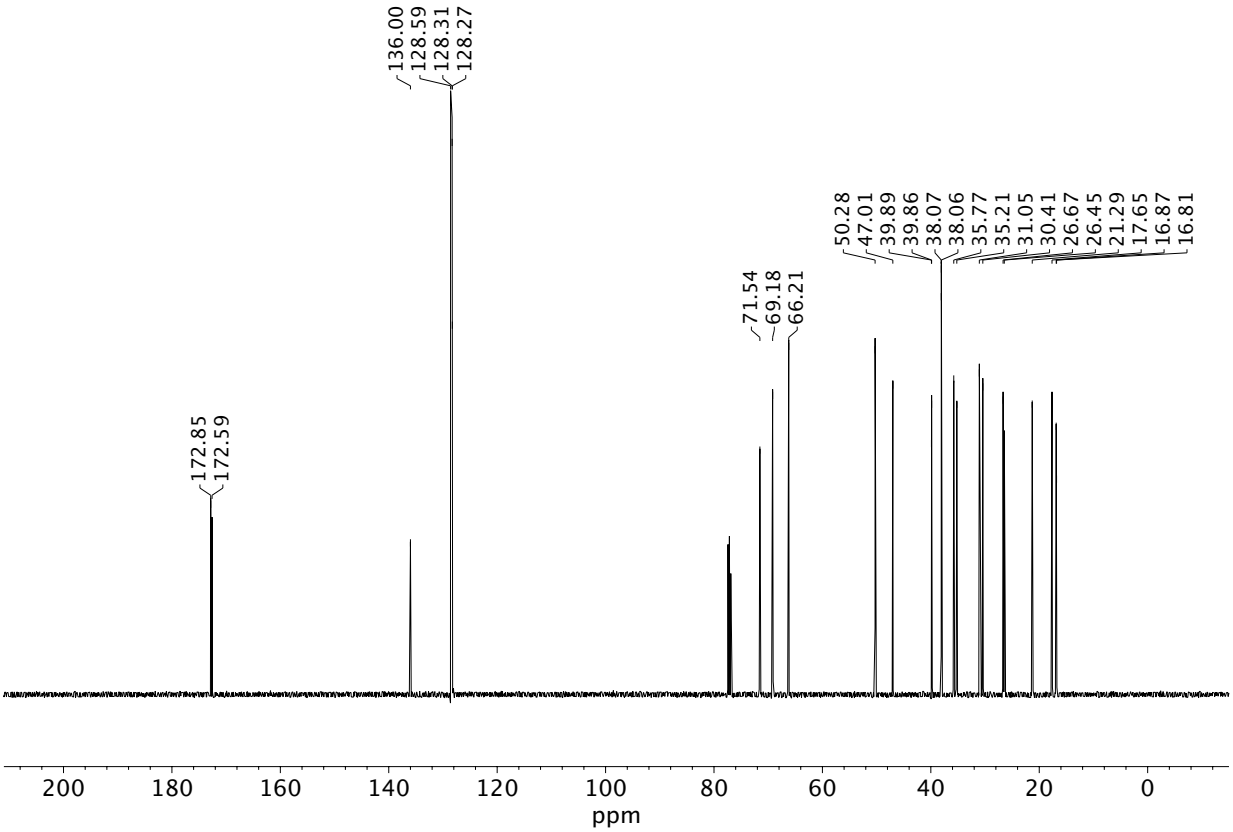

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **5a**.



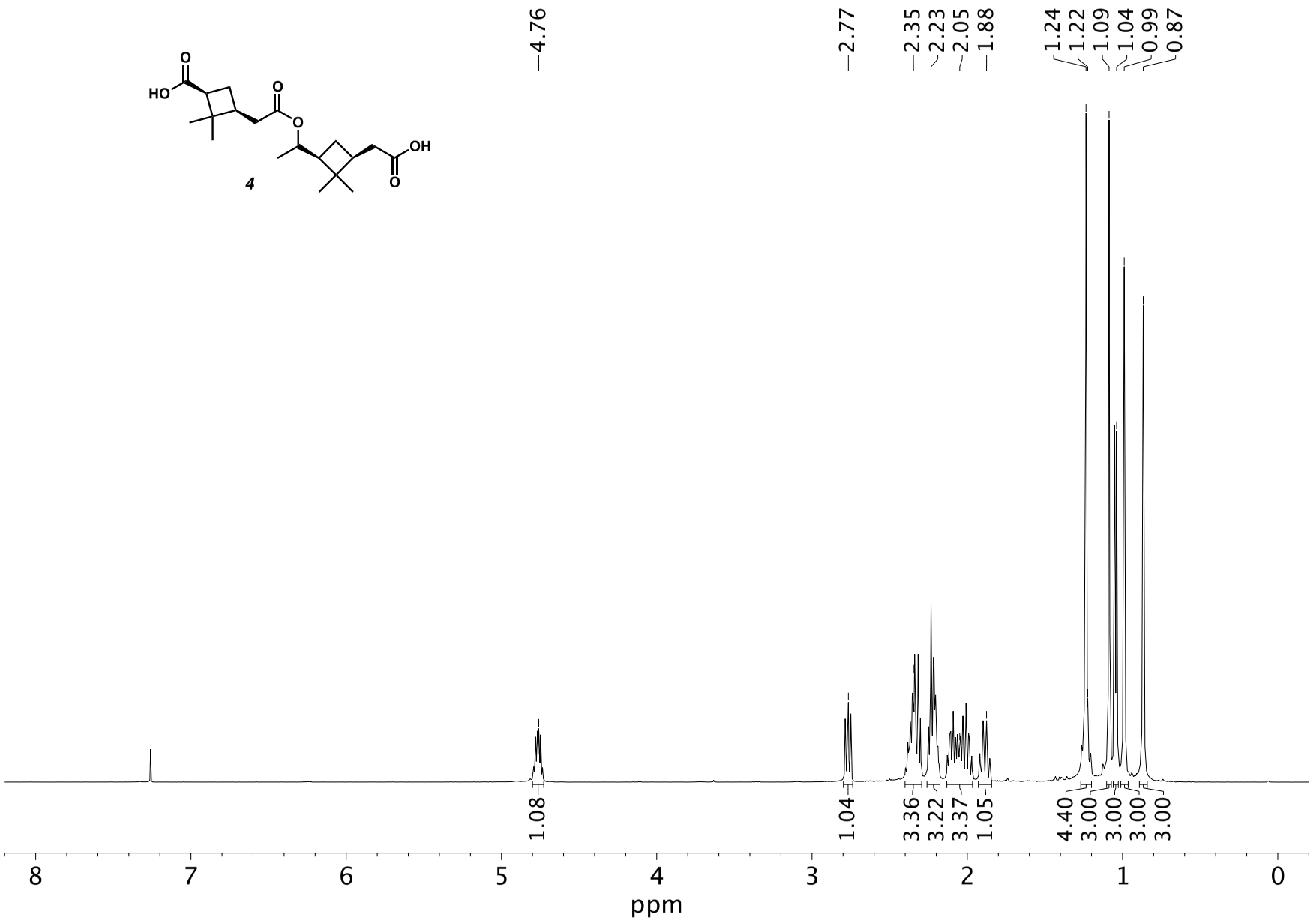

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **6a**.



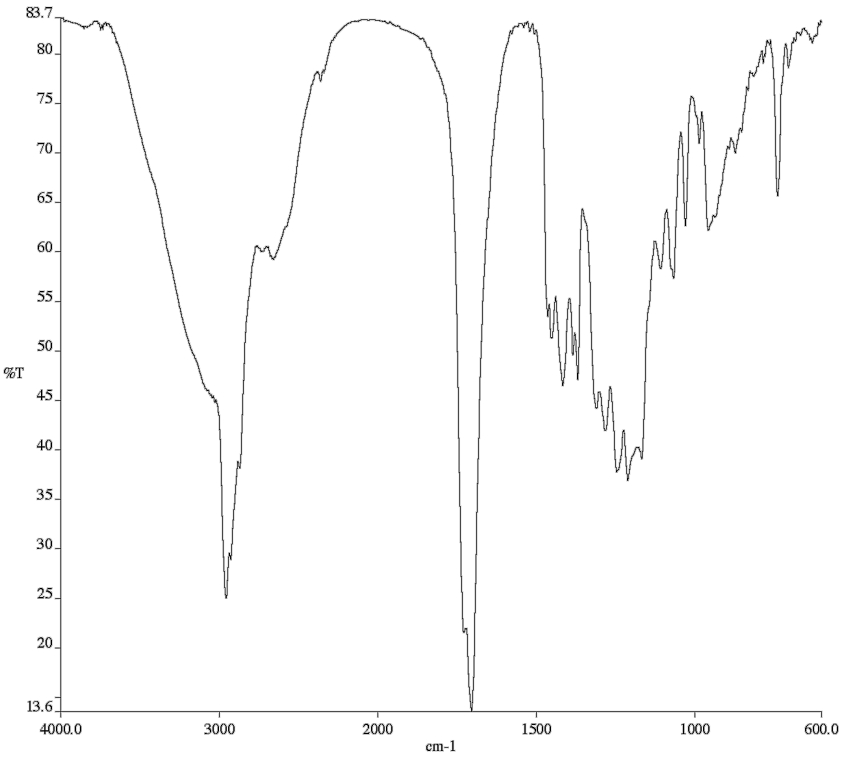

Infrared spectrum (thin film, NaCl) of compound **6a**.



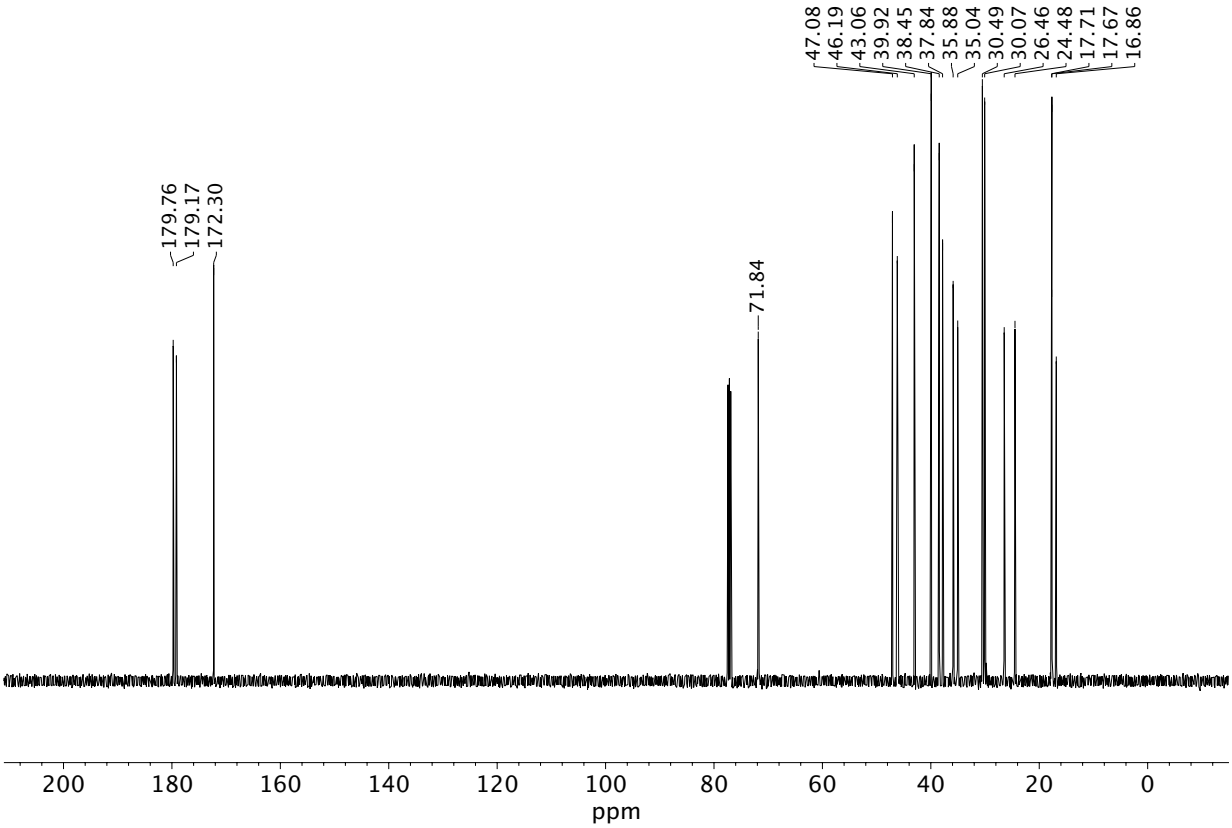

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **6a**.



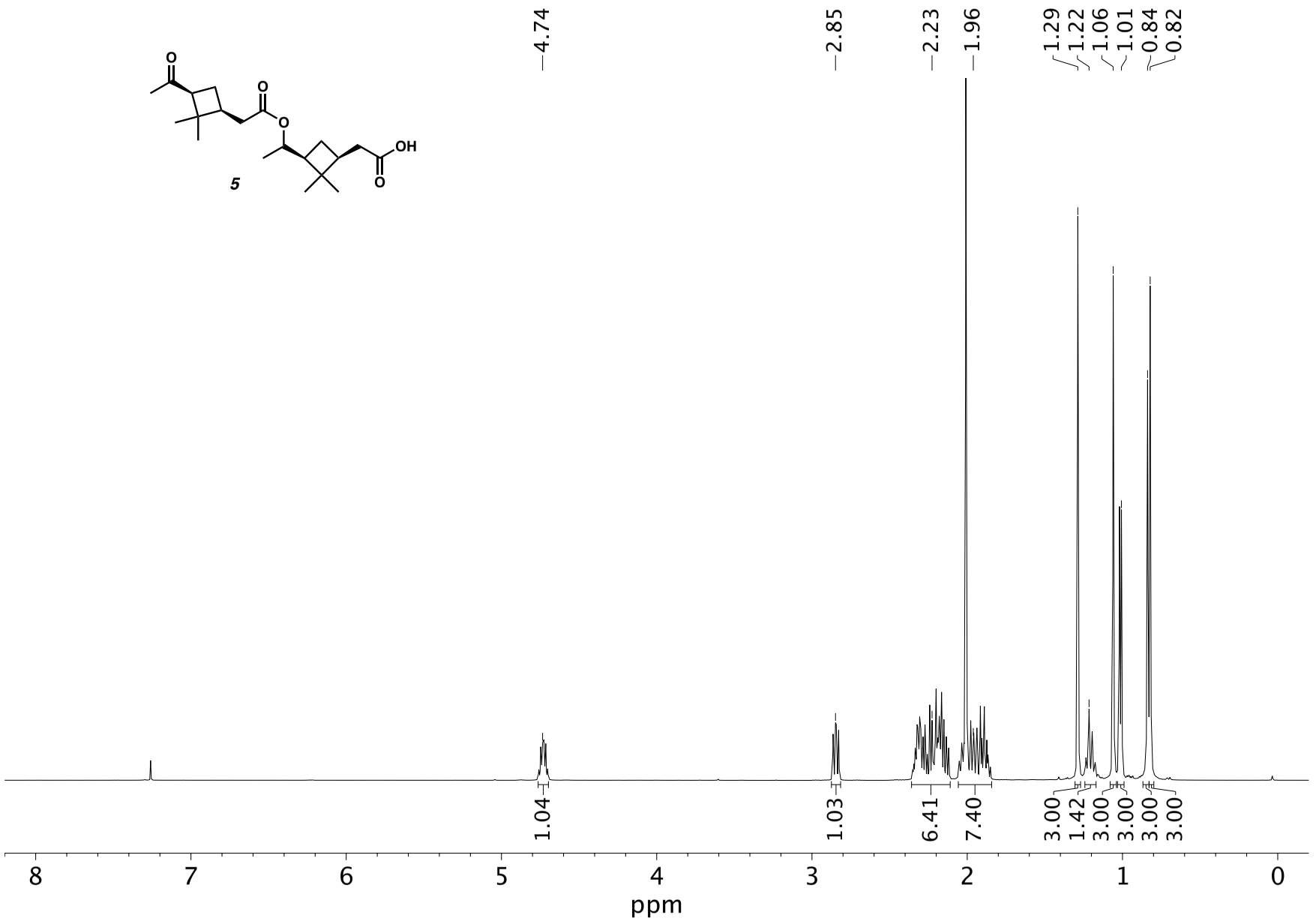

$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **4**.



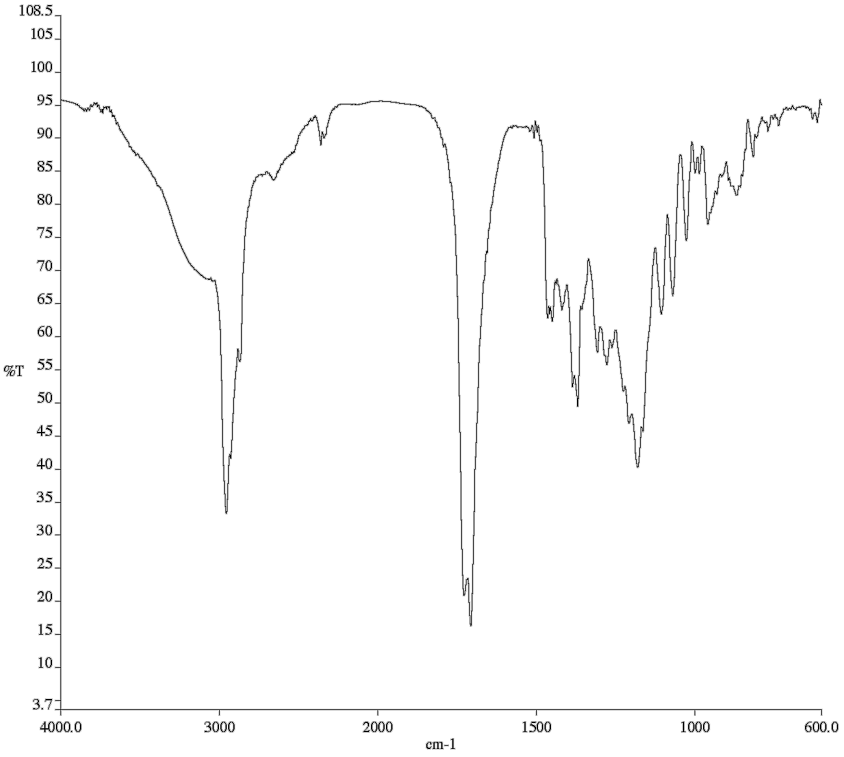

Infrared spectrum (thin film, NaCl) of compound **4**.



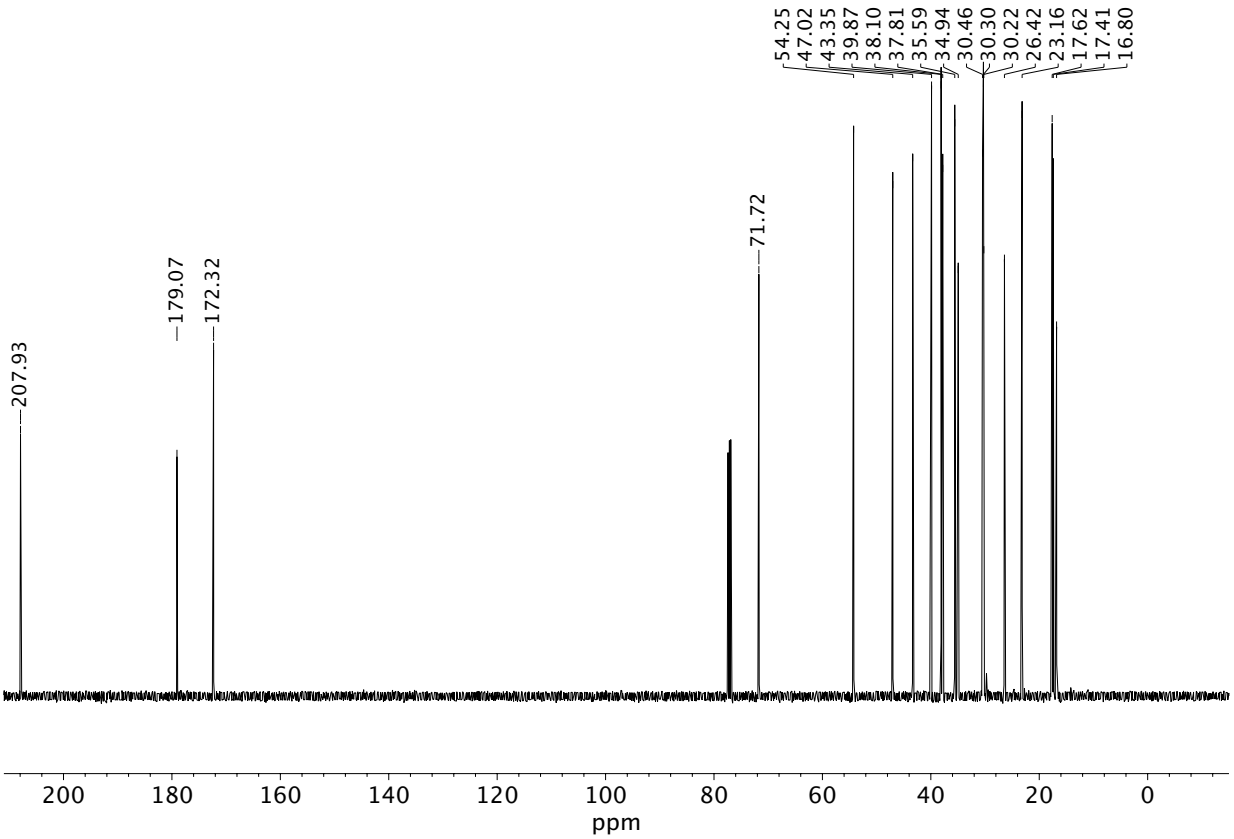

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **4**.



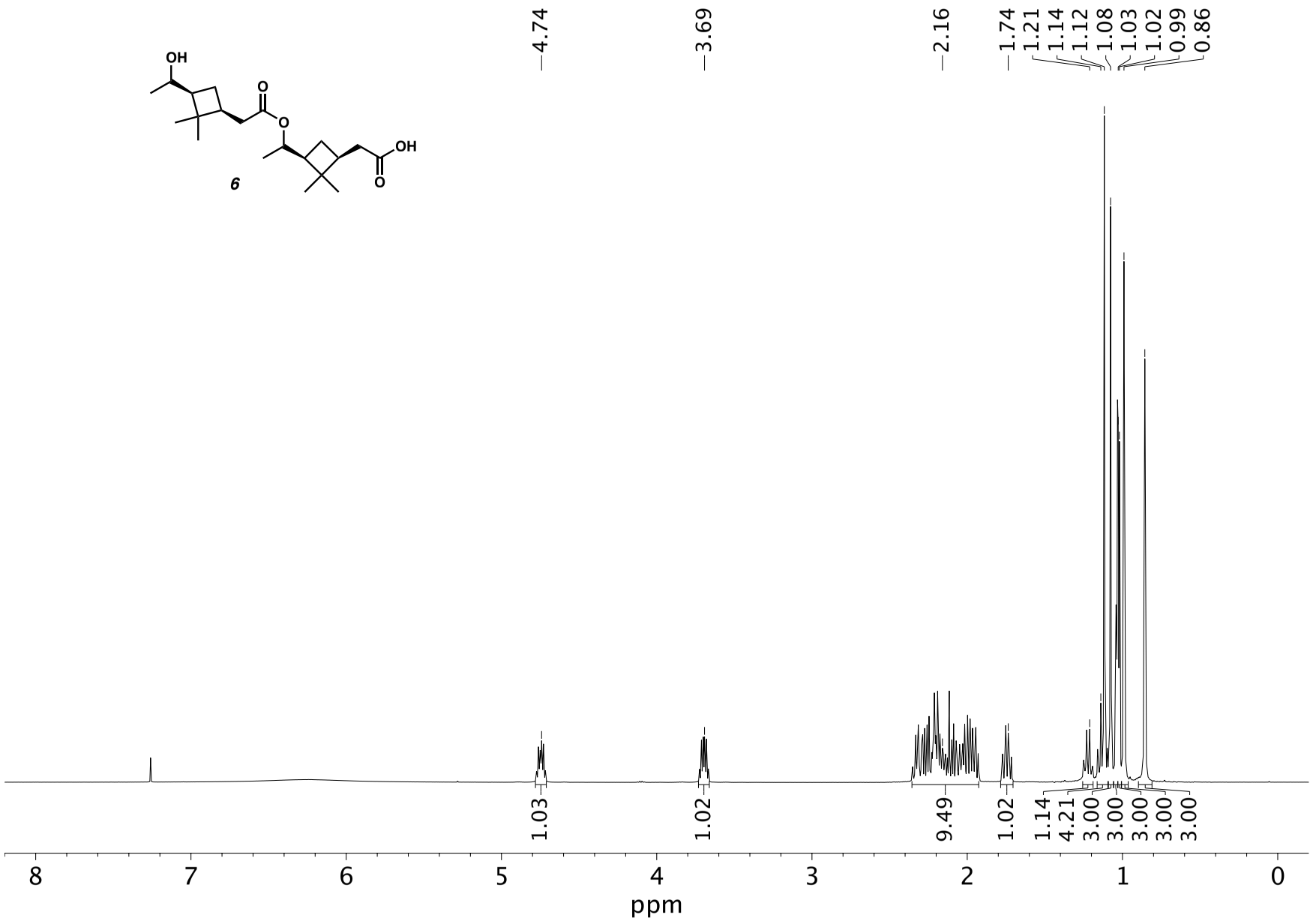

$^1$H NMR (500 MHz, $CDCl_3$) of compound **5**.



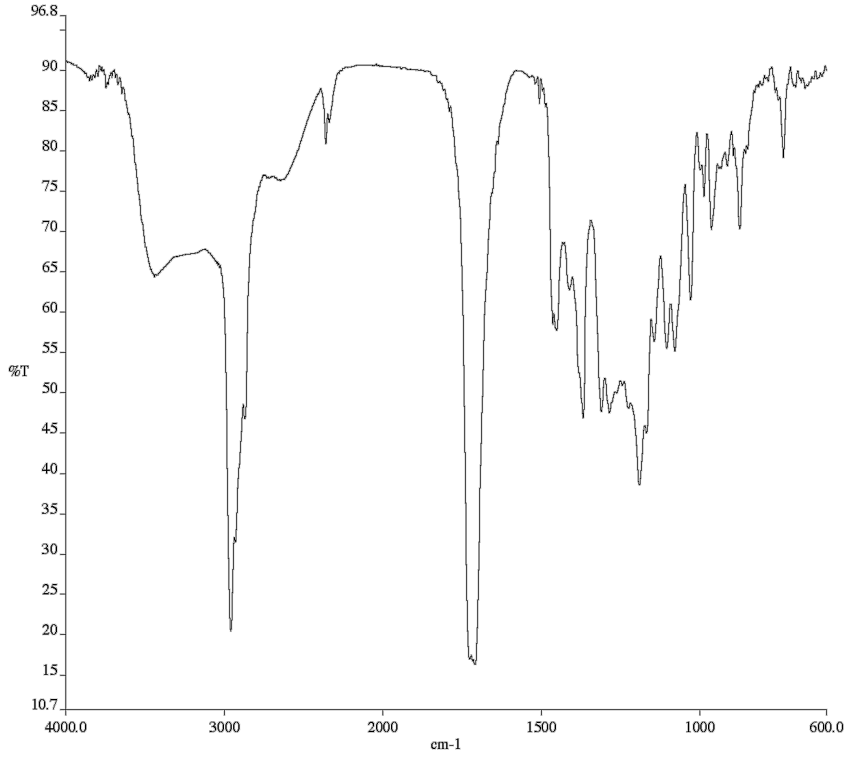

Infrared spectrum (thin film, NaCl) of compound **5**.



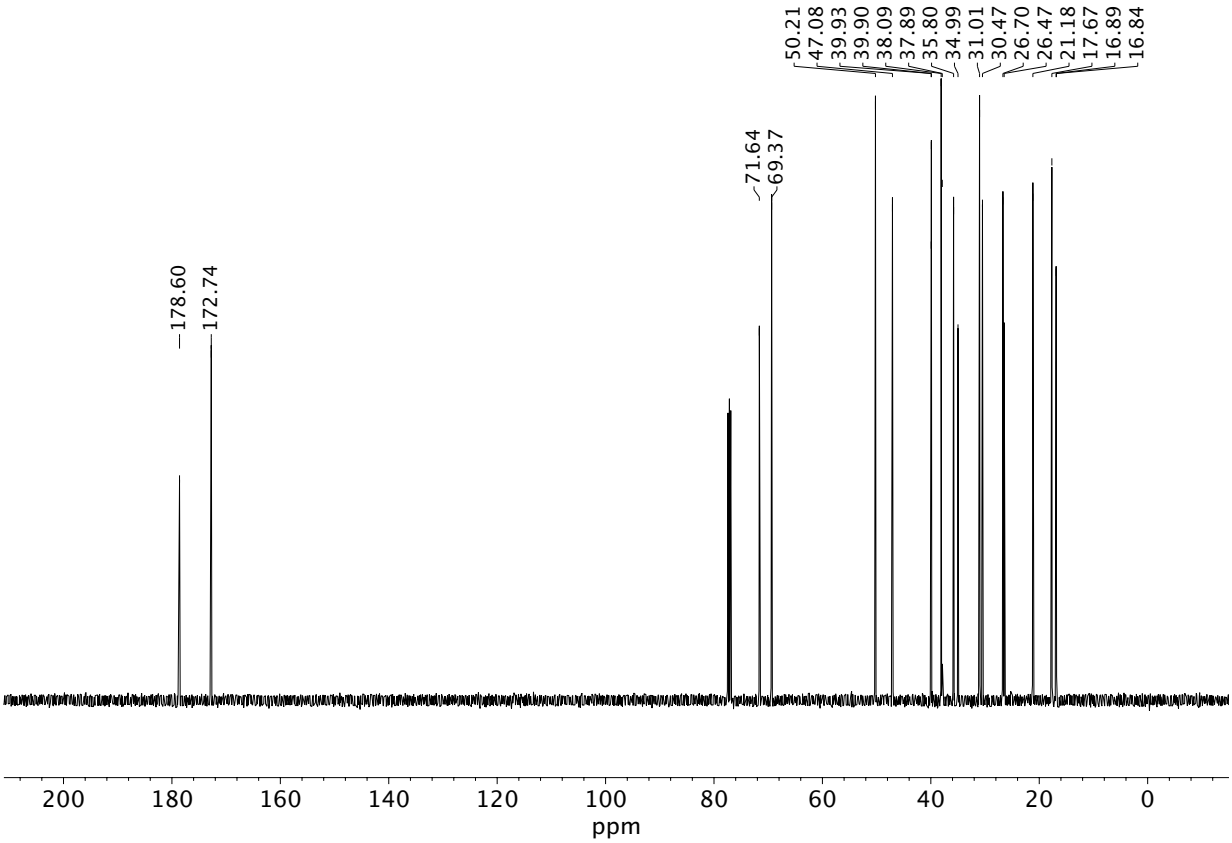

$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **5**.




$^{1}$H NMR (500 MHz, $CDCl_3$) of compound **6**.




Infrared spectrum (thin film, NaCl) of compound **6**.




$^{13}C$ NMR (125 MHz, $CDCl_3$) of compound **6**.

## S6. References


(1) Zhang, X.; McVay, R. C.; Huang, D. D.; Dalleska, N. F.; Aumont, B.; Flagan, R. C.; Seinfeld, J. H. Formation and evolution of molecular products in α-pinene secondary organic aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (46), 14168–14173.

(2) Kristensen, K.; Jensen, L. N.; Glasius, M.; Bilde, M. The effect of sub-zero temperature on the formation and composition of secondary organic aerosol from ozonolysis of alpha-pinene. *Environ. Sci.: Processes Impacts* **2017**, *19* (10), 1220–1234.

(3) Kristensen, K. Department of Chemistry, Aarhus University, Aarhus, Denmark. Personal communication, 2017.

(4) Donahue, N. M.; Epstein, S. A.; Pandis, S. N.; Robinson, A. L. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmos. Chem. Phys.* **2011**, *11* (7), 3303–3318.

(5) Yasmeen, F.; Vermeylen, R.; Szmigielski, R.; Iinuma, Y.; Böge, O.; Herrmann, H.; Maenhaut, W.; Claeys, M. Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of α- and β-pinene. *Atmos. Chem. Phys.* **2010**, *10* (19), 9383–9392.

(6) Yasmeen, F.; Vermeylen, R.; Maurin, N.; Perraudin, E.; Doussin, J.-F.; Claeys, M. Characterisation of tracers for aging of α-pinene secondary organic aerosol using liquid chromatography/negative ion electrospray ionisation mass spectrometry. *Environ. Chem.* **2012**, *9* (3), 236–246.

(7) Kenseth, C. M.; Huang, Y.; Zhao, R.; Dalleska, N. F.; Hethcox, J. C.; Stoltz, B. M.; Seinfeld, J. H. Synergistic $O_3$ + OH oxidation pathway to extremely low-volatility dimers revealed in β-pinene secondary organic aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (33), 8301–8306.

(8) Zhao, R.; Kenseth, C. M.; Huang, Y.; Dalleska, N. F.; Seinfeld, J. H. Iodometry-Assisted Liquid Chromatography Electrospray Ionization Mass Spectrometry for Analysis of Organic Peroxides: An Application to Atmospheric Secondary Organic Aerosol. *Environ. Sci. Technol.* **2018**, *52* (4), 2108–2117.

(9) Moglioni, A. G.; García-Expósito, E.; Aguado, G. P.; Parella, T.; Branchadell, V.; Moltrasio, G. Y.; Ortuño, R. M. Divergent Routes to Chiral Cyclobutane Synthons from

(−)-α-Pinene and Their Use in the Stereoselective Synthesis of Dehydro Amino Acids. *J. Org. Chem.* **2000**, *65* (13), 3934–3940.

(10) Fernández, F.; López, C.; Hergueta, A. R. Synthesis of a Precursor of Cyclobutane Carbocyclic Nucleosides from α-Pinene. *Tetrahedron* **1995**, *51* (37), 10317–10322.

(11) Kołodziejczyk, A.; Pyrcz, P.; Pobudkowska, A.; Błaziak, K.; Szmigielski, R. Physicochemical Properties of Pinic, Pinonic, Norpinic, and Norpinonic Acids as Relevant α-Pinene Oxidation Products. *J. Phys. Chem. B* **2019**, *123* (39), 8261–8267.

(12) Hergueta, A. R.; López, C.; Fernández, F.; Caamaño, O.; Blanco, J. M. Synthesis of two enantiomerically pure precursors of cyclobutane carbocyclic nucleosides. *Tetrahedron: Asymmetry* **2003**, *14* (23), 3773–3778.