Supporting information

Synthesis of high-density aviation fuels with methyl benzaldehyde and cyclohexanone

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Method for the preparation and purification of 1A and 2A

The preparation of **1A** was carried out in a glass batch reactor by the solvent-free aldol condensation of methyl benzaldehydes and cyclohexanone. The temperature of the reactor was controlled by a water bath. Typically, 10 mmol 2-methyl benzaldehyde, 30 mmol cyclohexanone and 2 mmol EAOAc ionic liquid were added into a 35 mL glass batch reactor. The reaction system was stirred at 353 K for 6 h, then cooled down to room temperature. Subsequently, 20 mL CH_2Cl_2 was added into the reactor. The EAOAc ionic liquid catalyst was separated from the mixture by extraction with water (30 mL) for three times. After the removal of CH_2Cl_2 and unreacted cyclohexanone in CH_2Cl_2 phase by vacuum distillation, a mixture of **1A** and **1B** (exists as a yellow solid) was obtained. The yellow solid was added into 400 mL methanol solution (methanol/water volumetric ratio = 5:3). After being stirred for 10 min, the **1A** in the mixture was dissolved. On the contrary, the **1B** in the mixture stayed as solid and could be easily separated by filtration. The filtrate was collected and the solvent was removed by vacuum distillation. After that, some light yellow power was obtained. From the results of GC and NMR, we confirmed that the light yellow power was **1A** which has high purity (about 98%), while the residue yellow solid was determined to be **1B**. By the same method, we also prepared **2A** with 4-methyl benzaldehyde and cyclohexanone.

Table S1. Density and freezing points of the currently used additives in kerosene-type jet fuels, the recently reported biomass derived jet fuel additives and the tricyclic alkanes obtained in this work.

	Density (g mL^{-1})	Freezing point (K)
Cyclohexane	0.78	279.5
1,2,4-Trimethylbenzene	0.88	229.2
Ethyl benzene	0.87	178
Benzene	0.88	267.5
Naphthalene	1.03[a] (or 0.96[b])	353.3
Toluene	0.87	178
Hydrogenated pinene dimers[1]	0.94	< 243
1,1-Dipentylcyclopentane[2]	0.82	-
1,3-Dipentylcyclopentane[3]	0.82	248.4
Mixture of butylcyclopentane and 1,3-dibutylcyclopentane[4]	0.82	179
Di(cyclopentane)[5]	0.87	237.7
Di(cyclohexane)[6]	0.88	277
Spiro[5,6]dodecane[7]	0.89	222
Spiro[4,5]decane[7]	0.87	196
Tri(cyclopentane)[8]	0.91	-
Decalin[9]	0.896	242.6-230.1
Branched decalins[10]	0.88	163
Perhydrofluorene[11]	0.96	330
1-Methyldodecahydro-1*H*-fluorene[c]	0.99	251
3-Methyldodecahydro-1*H*-fluorene[d]	0.96	273

[a] Measured at 293 K in solid state. [b] Measured at 373 K in liquid state. [c] Obtained in this work with small amount of 1-(cyclohexylmethyl)-2-methylcyclohexane impurity. [d] Obtained in this work with small amount of 1-(cyclohexylmethyl)-4-methylcyclohexane impurity.
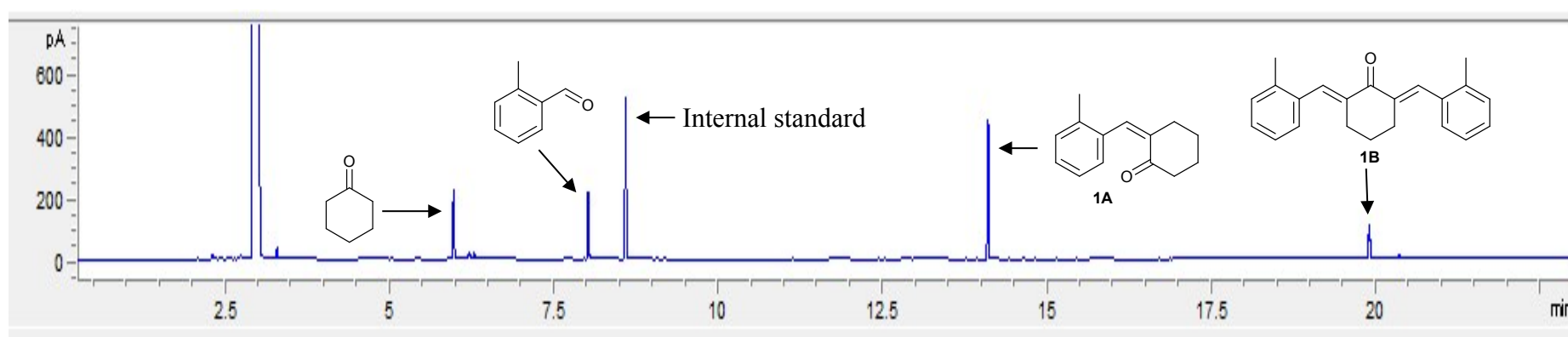
Figure S1. Gas chromatogram of the products from the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone over

EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 10 mmol cyclohexanone, 1 mmol ionic liquids; 333 K, 4 h.
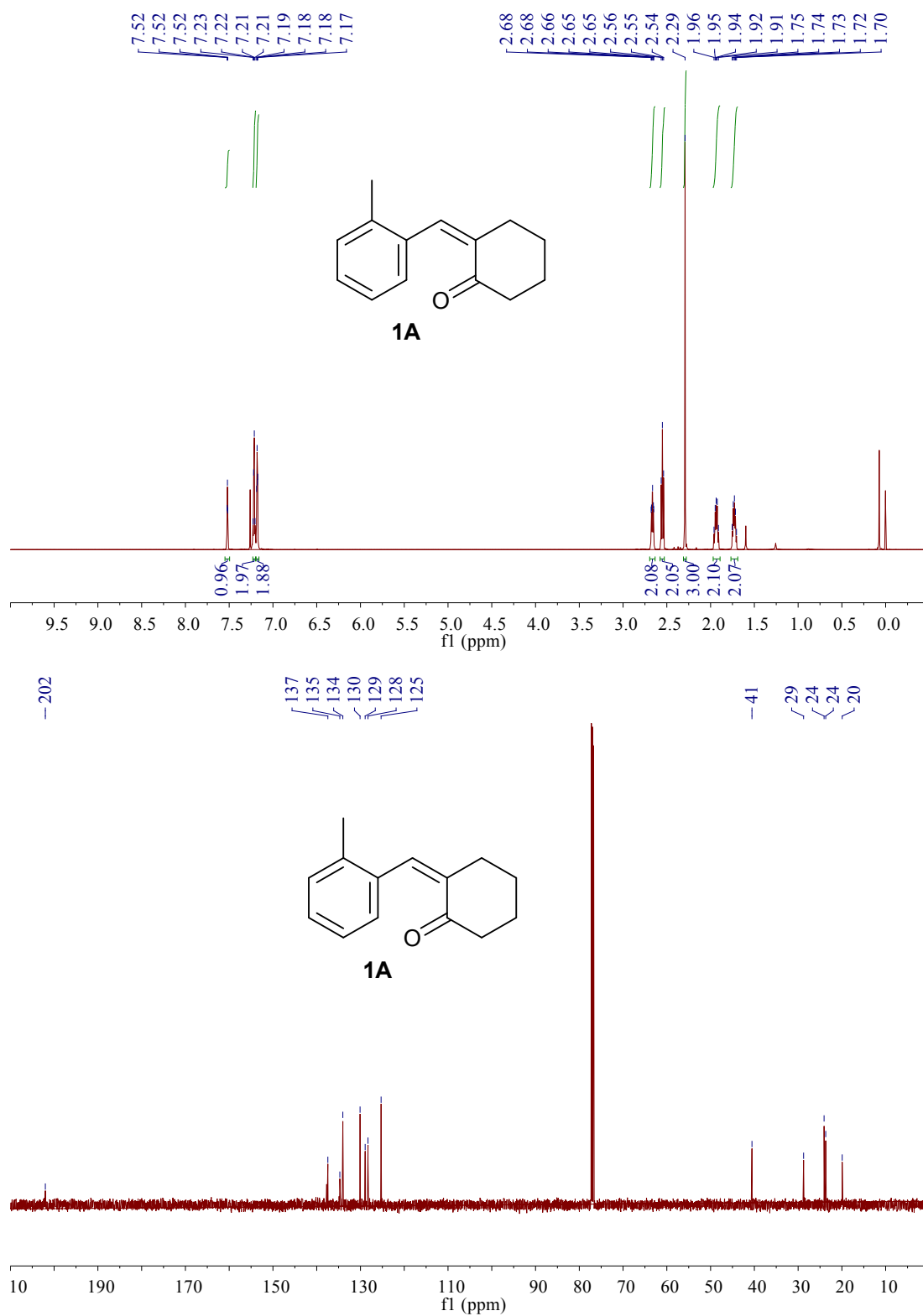
Figure S2. ^{1}H-NMR and ^{13}C-NMR spectra of **1A** from the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone. CDCl$_3$ was used as solvent.
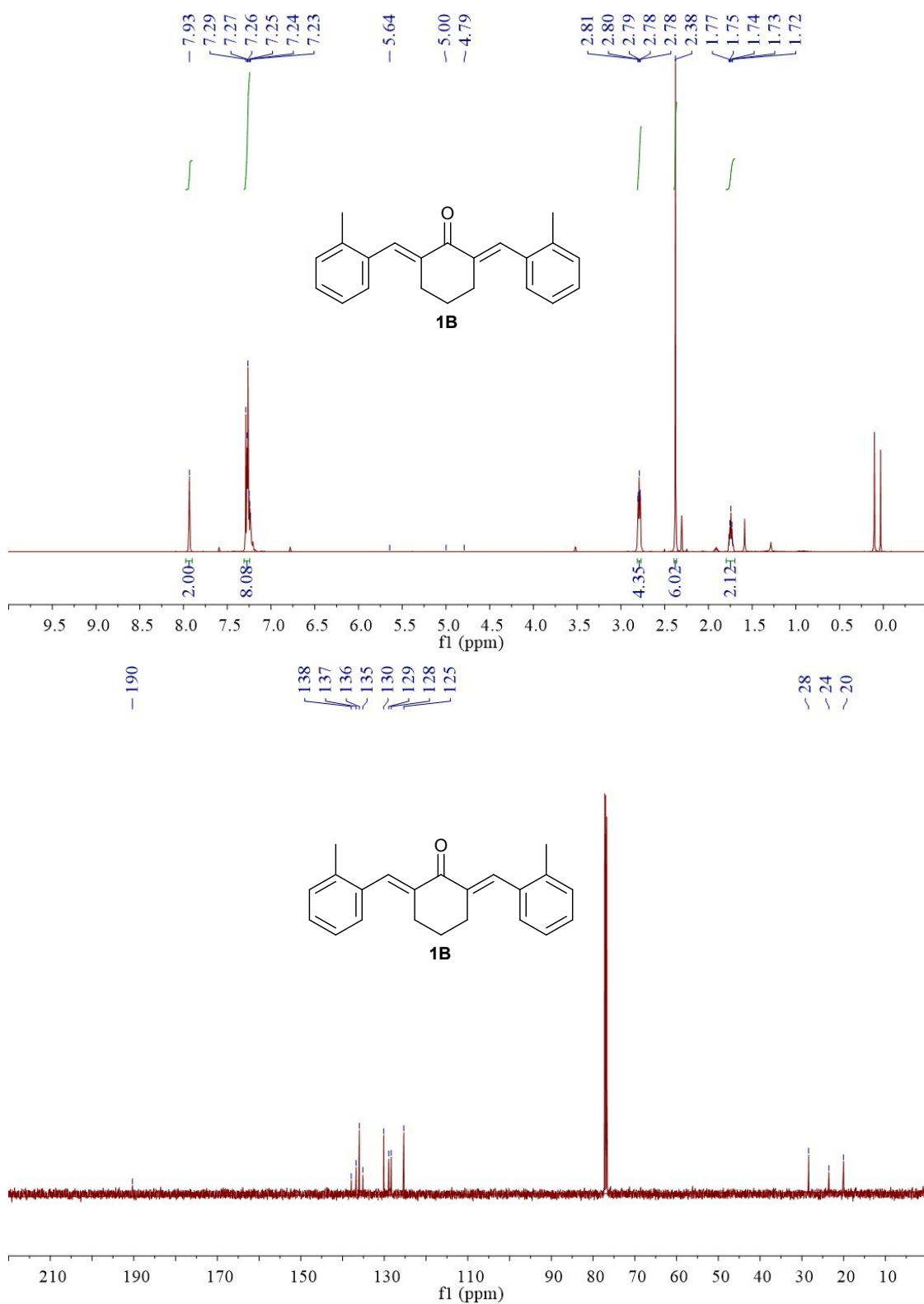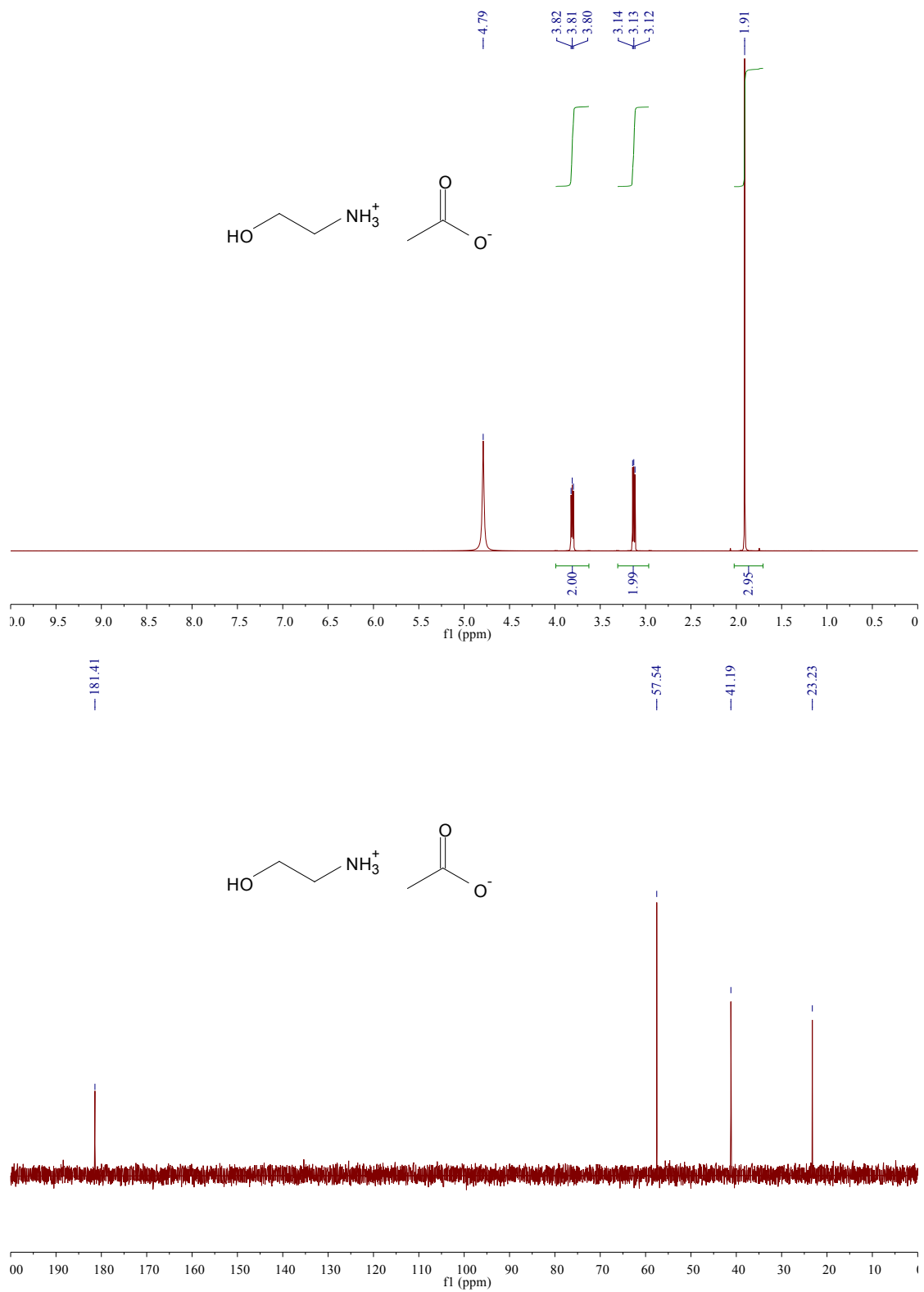
Figure S3. ^{1}H-NMR and ^{13}C-NMR spectra of **1B** from the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone. CDCl$_3$ was used as solvent.

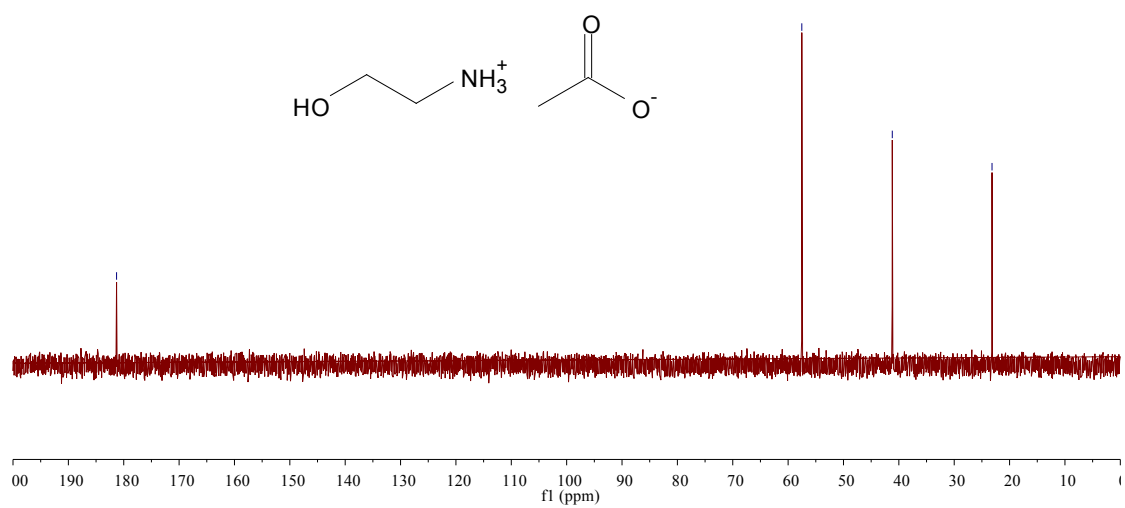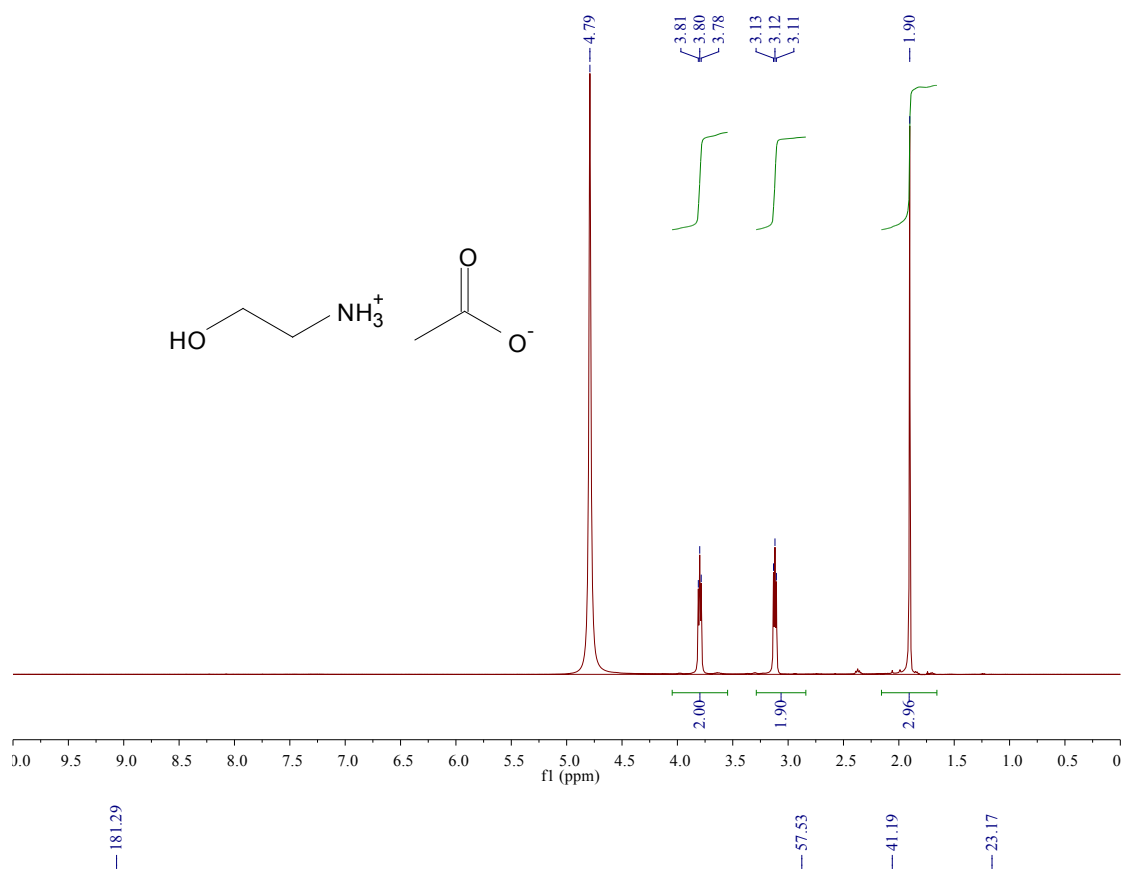**Figure S4**. ^{1}H-NMR and ^{13}C-NMR spectra of the fresh EAOAc ionic liquid catalyst.

Figure S5. ^{1}H-NMR and ^{13}C-NMR spectra of the used EAOAc ionic liquid catalyst.
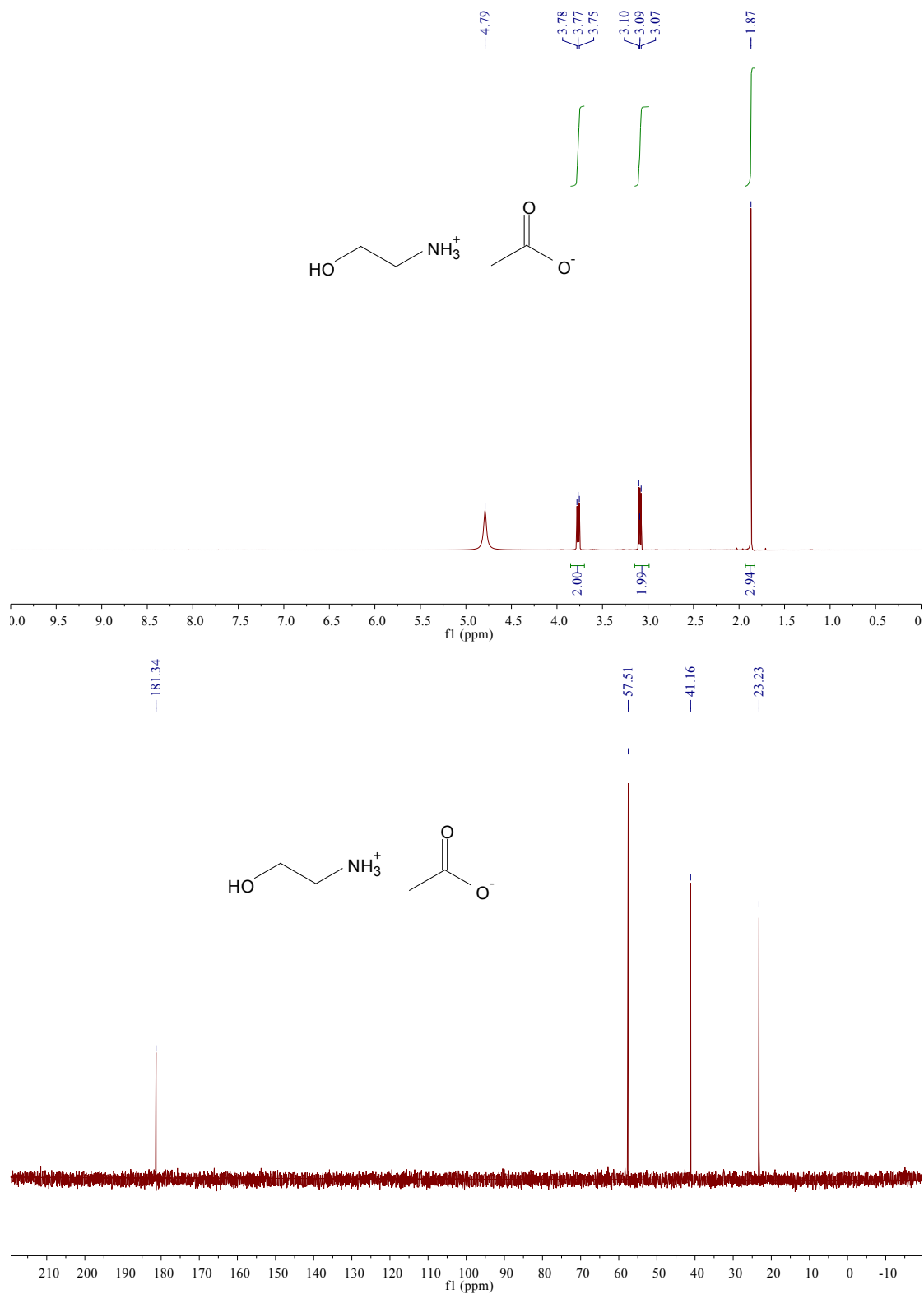
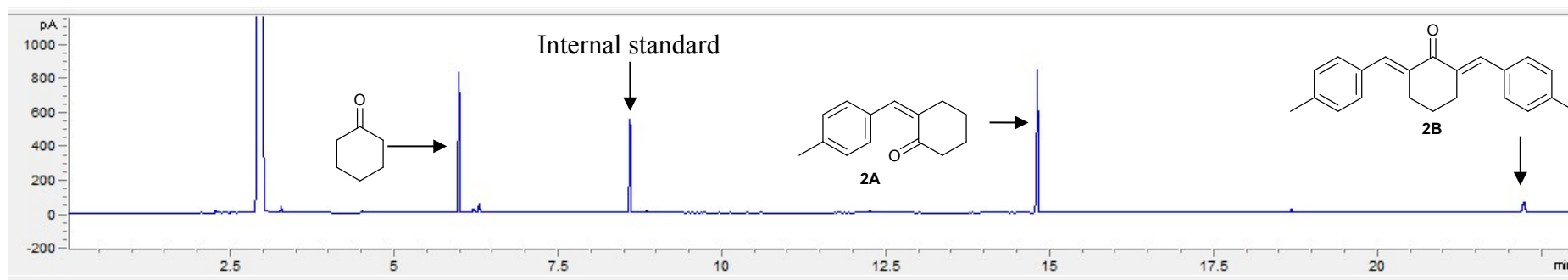**Figure S6**. ^{1}H-NMR and ^{13}C-NMR spectra of the regenerated EAOAc ionic liquid catalyst.

Figure S7. Gas chromatogram of the products from the solvent-free aldol condensation of 4-methyl benzaldehyde and cyclohexanone over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 4-methyl benzaldehyde, 30 mmol cyclohexanone, 2 mmol EAOAc ionic liquids; 353 K, 6 h.
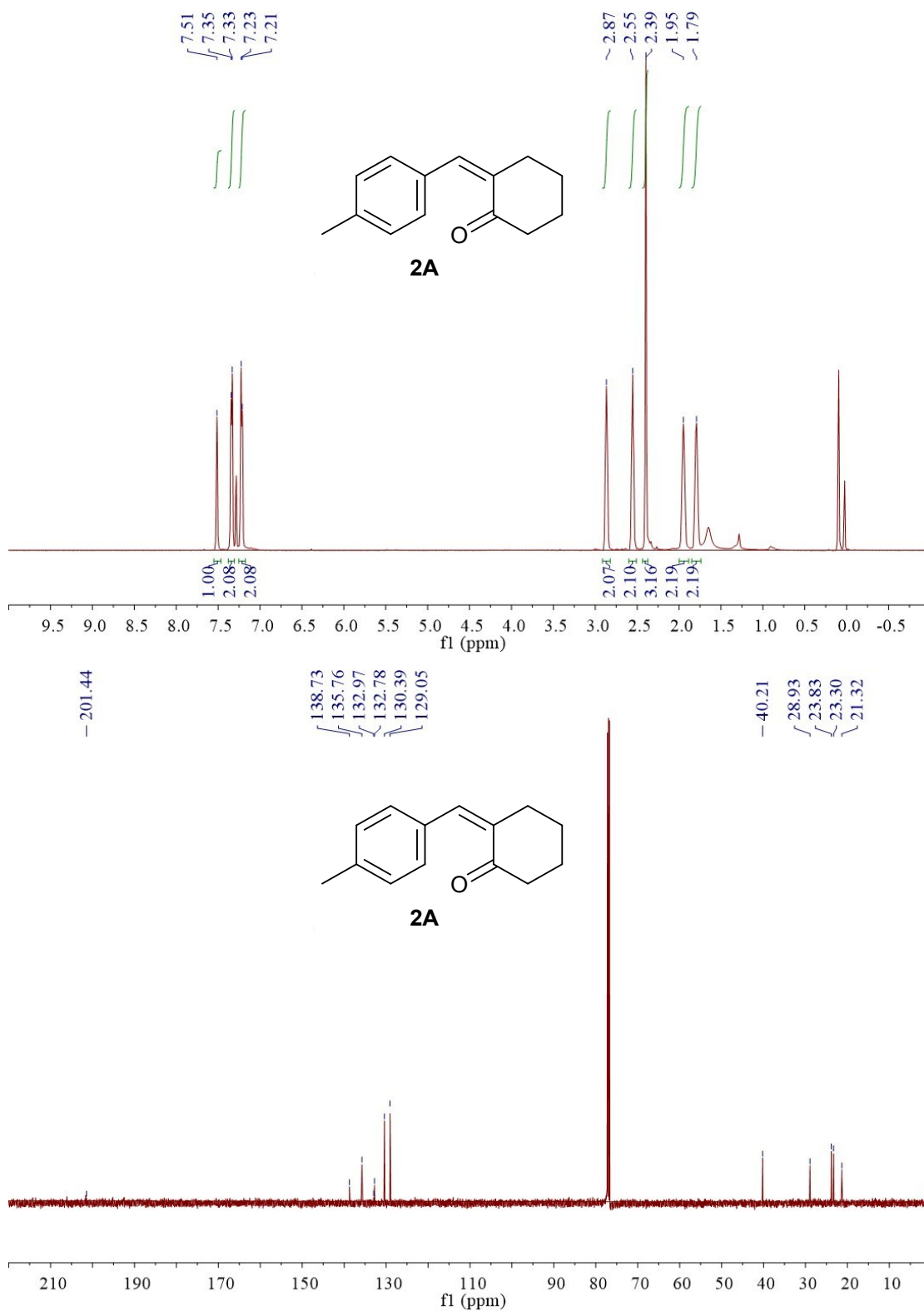
Figure S8. ^{1}H-NMR and ^{13}C-NMR spectra of **2A** from the solvent-free aldol condensation of 4-methyl benzaldehyde and cyclohexanone. CDCl$_3$ was used as solvent.
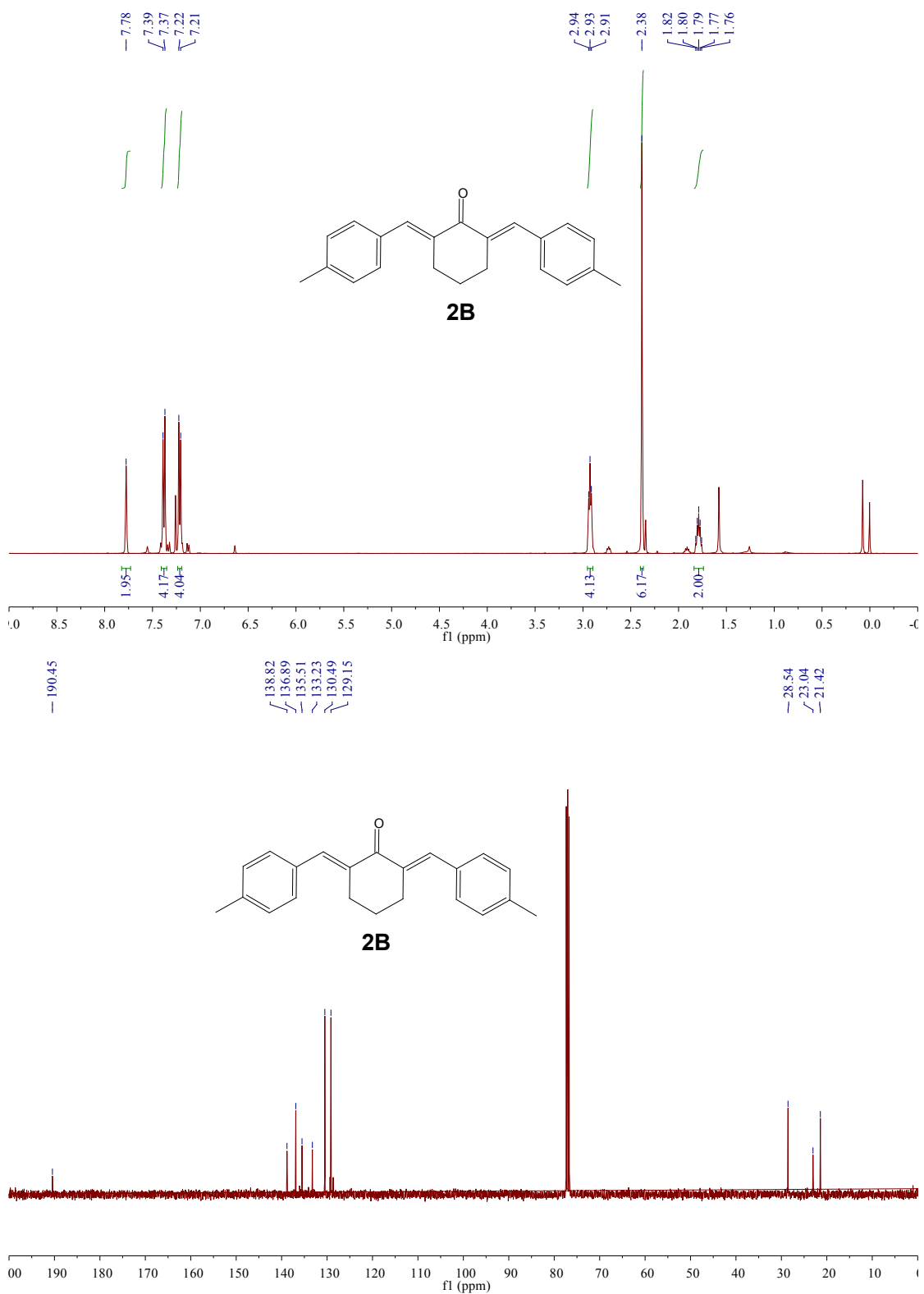
Figure S9. ^{1}H-NMR and ^{13}C-NMR spectra of **2B** from the solvent-free aldol condensation of 4-methyl benzaldehyde and cyclohexanone. CDCl$_3$ was used as solvent.
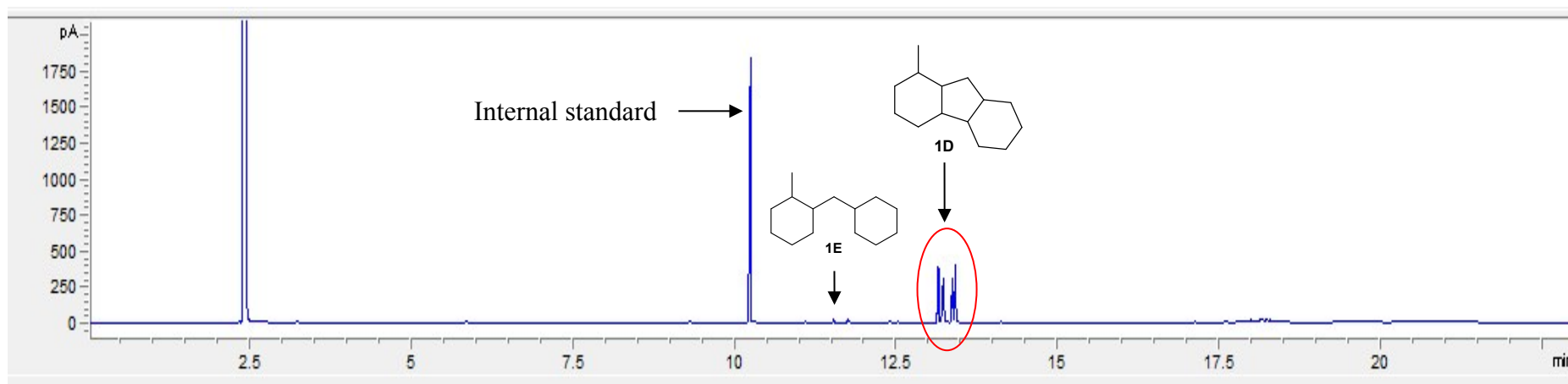
Figure S10. Gas chromatogram of the products from the aqueous phase hydrodeoxygenation of **1A** over the Pd/C catalyst. Reaction conditions:

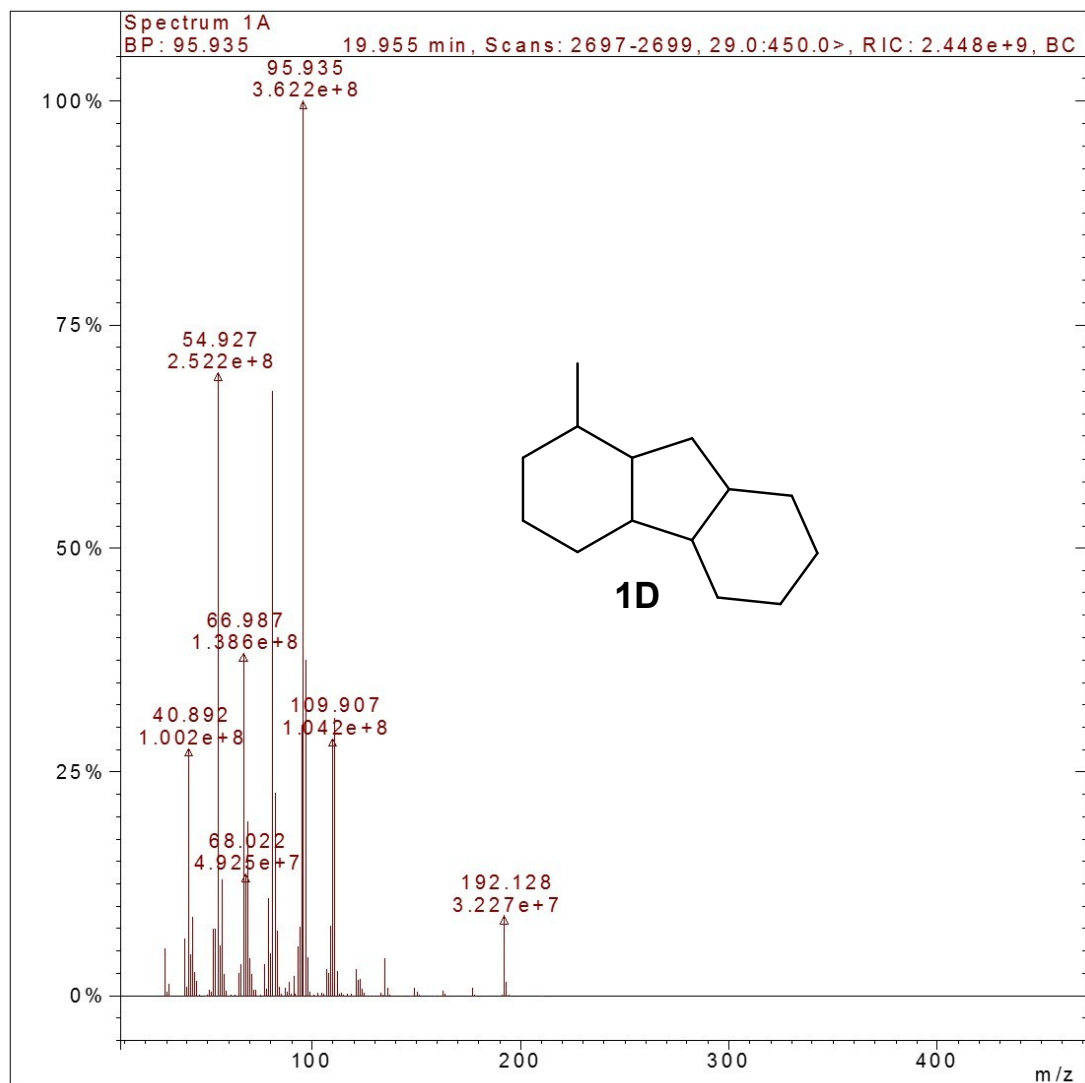453 K, 6 MPa H_2; 1.0 g **1A**, 0.1 g Pd/C catalyst, 35 mL water, 4 h.

Figure S11. Mass spectrogram of **1D** from the aqueous phase hydrodeoxygenation of
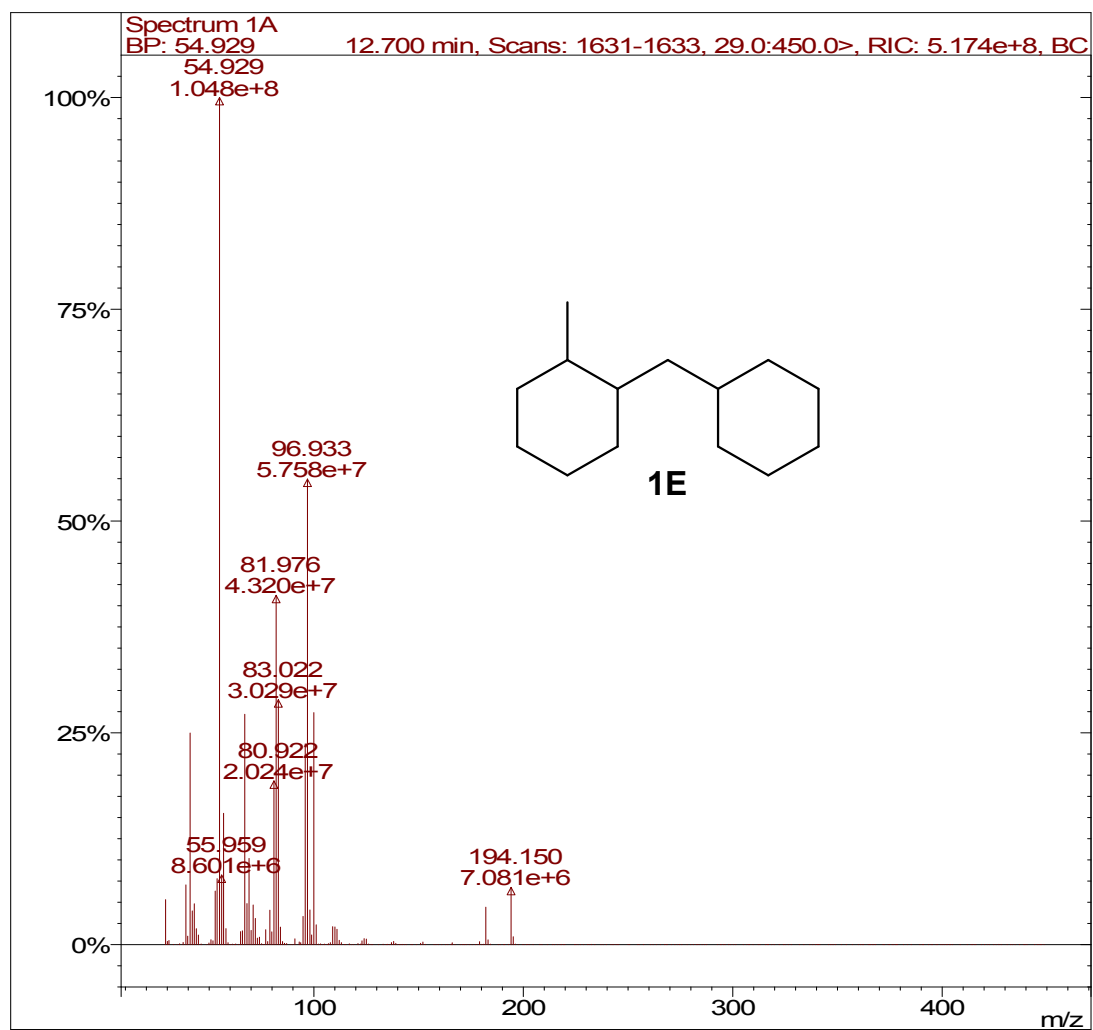
1A over the Pd/C catalyst.

Figure S12. Mass spectrograms of **1E** from the aqueous phase hydrodeoxygenation of
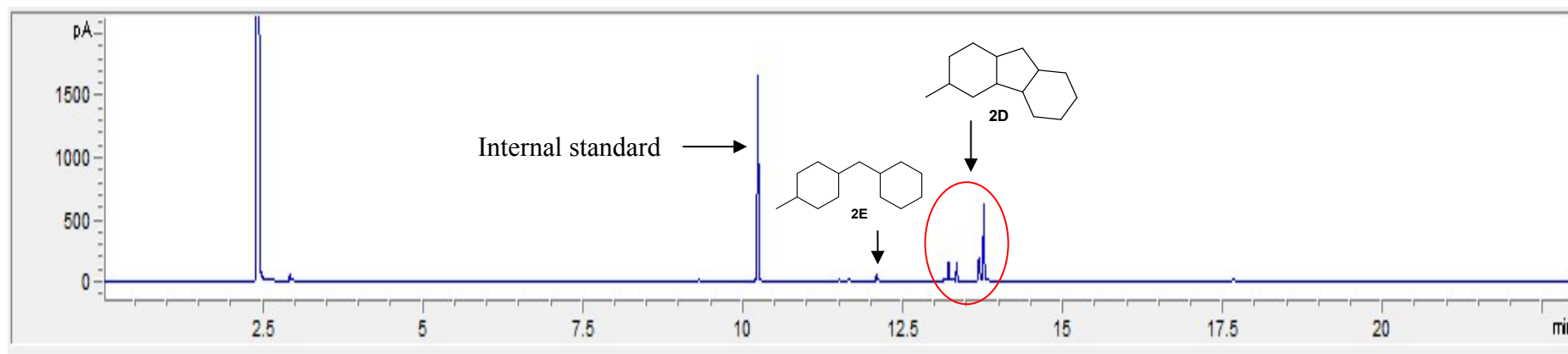
1A over the Pd/C catalyst.

Figure S13. Gas chromatogram of the products from the aqueous phase hydrodeoxygenation of **2A** over the Pd/C catalyst. Reaction conditions:

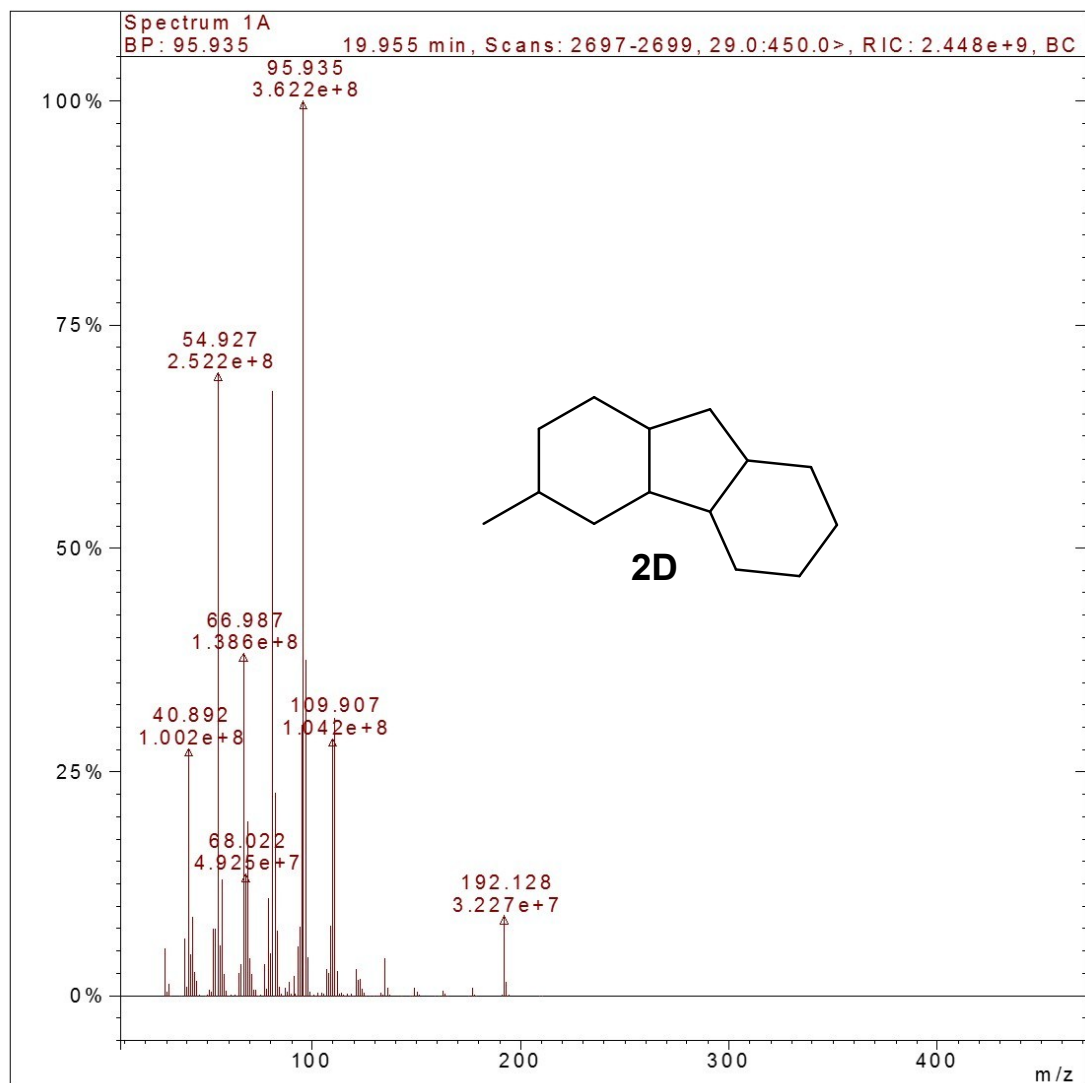453 K, 6 MPa H$_2$; 1.0 g **2A**, 0.1 g Pd/C catalyst, 35 mL water, 4 h.

Figure S14. Mass spectrogram of **2D** from the aqueous phase hydrodeoxygenation of
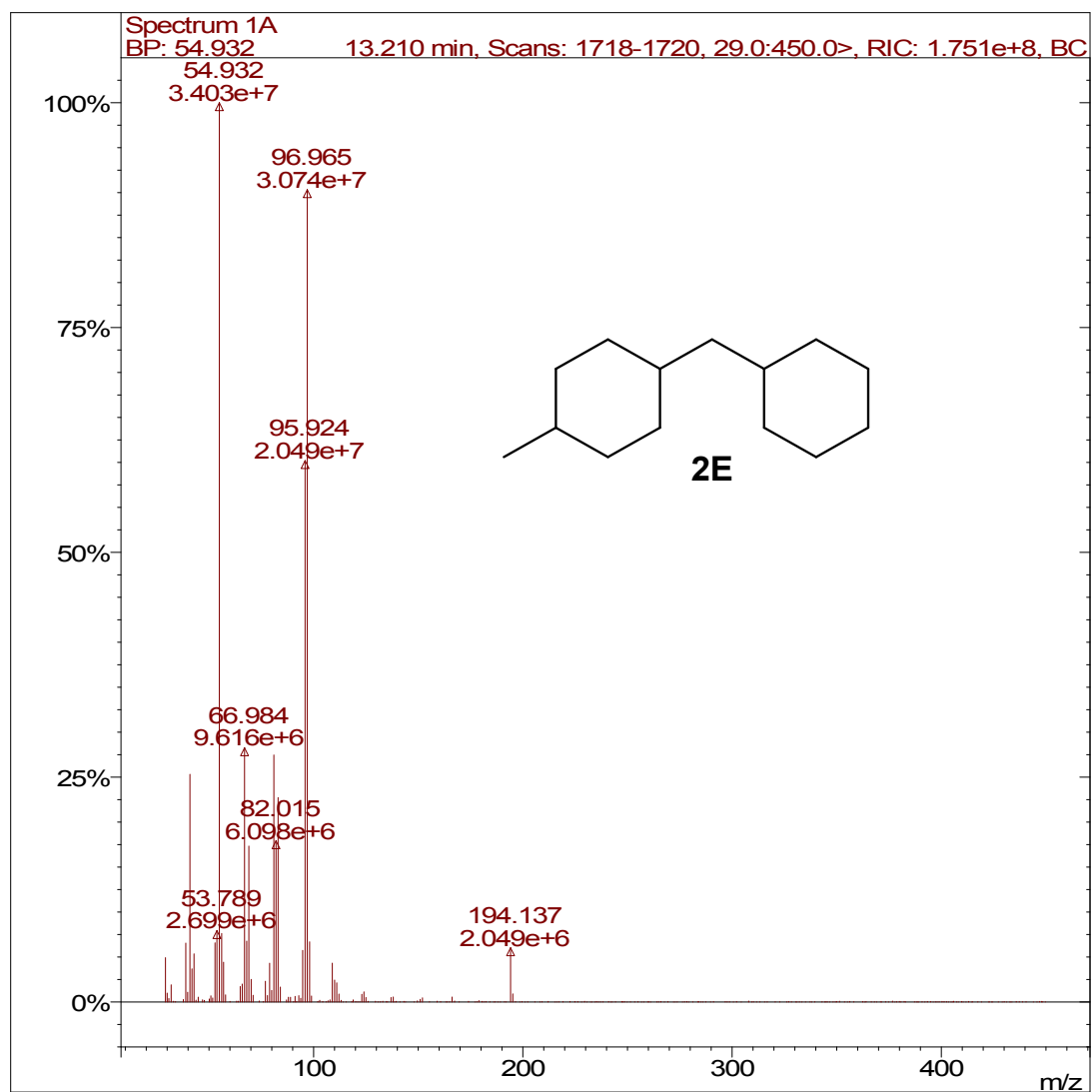
2A over the Pd/C catalyst.

Figure S15. Mass spectrogram of **2E** from the aqueous phase hydrodeoxygenation of

2A over the Pd/C catalyst.

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