Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information (SI)

Diverse Continuous Photooxygenation Reactions of (+) and (-)-α-Pinenes to the Corresponding Pinocarvones or trans-Pinocarveols

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1. Complementary General Information

The CG-MS yields were determined in a SHIMADZU equipment: GCMS-QP5000 and GC17A using argon as gas (column 30 m, NA-5 MS XIL – 0.25 mm, 0.25 µm – Bonded T max: 330-350 °C): samples were prepared in ethyl acetate; injection temperature 250°C, injection split ratio 19, carrier gas He, pressure 100 KPa, and column flow rate 1.3 mL/min; oven temperature setting was 100°C for 5 min, heated at 15 $°C.min^{-1}$ to 150°C, then heated at 7.5 $°C.min^{-1}$ to 220 °C, and finally heated at 10 $°C.min^{-1}$ to 280 °C and held for 7 min. Conversion percentages were analysed on the basis of chromatogram areas, with mass ion source temperature 250°C, interface temperature 280°C, and solvent cut time 5 min. The standard curve was constructed for the measured product, and quantifications were performed using dodecane as an internal standard.

Continuous-flow experiments were performed using Syrris equipment (Asia modules): two channels of a syringe pump (500 and 1000 µL), a KNAUER HPLC pump (AZURA P 4.1S), and a microchip reactor (250 µL). Two back-pressure regulators (BPR with pressures as specified). For pumping the Ph_3P solution, a Peristaltic Pump (New Era, model NE-9004C) was used.

a. Batch photoreactor construction

Details on the construction of this photoreactor can be obtained in our previous publication,[1,2] and pictures of the steps and materials are presented in Figures S1-S2.

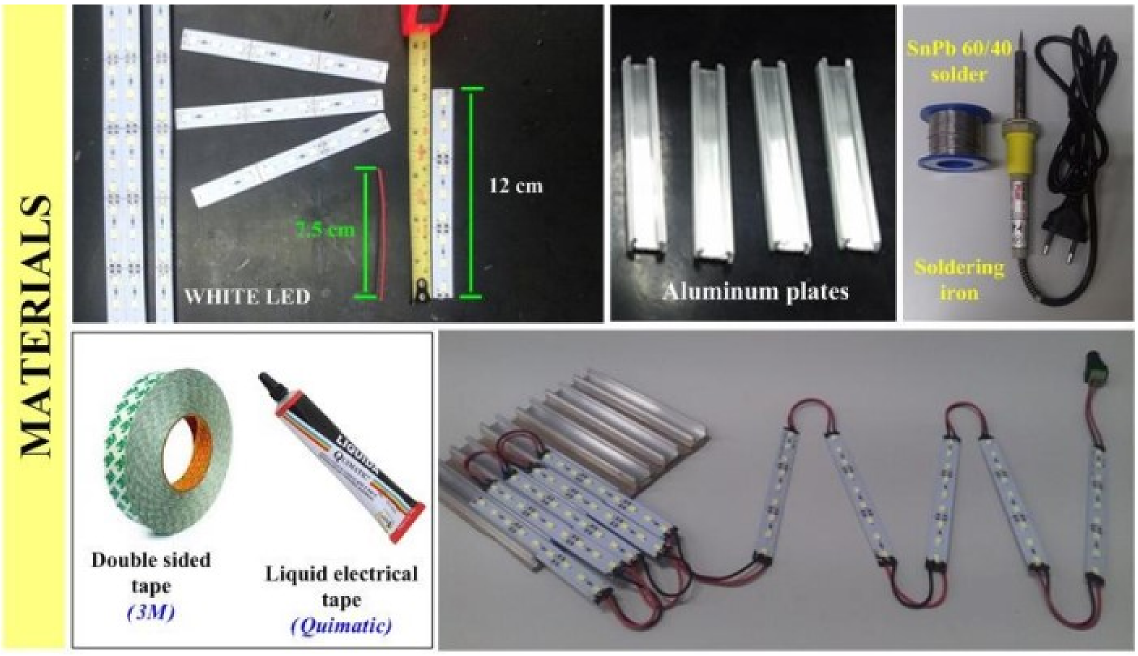


Figure S1. Materials used in the batch photoreactor.

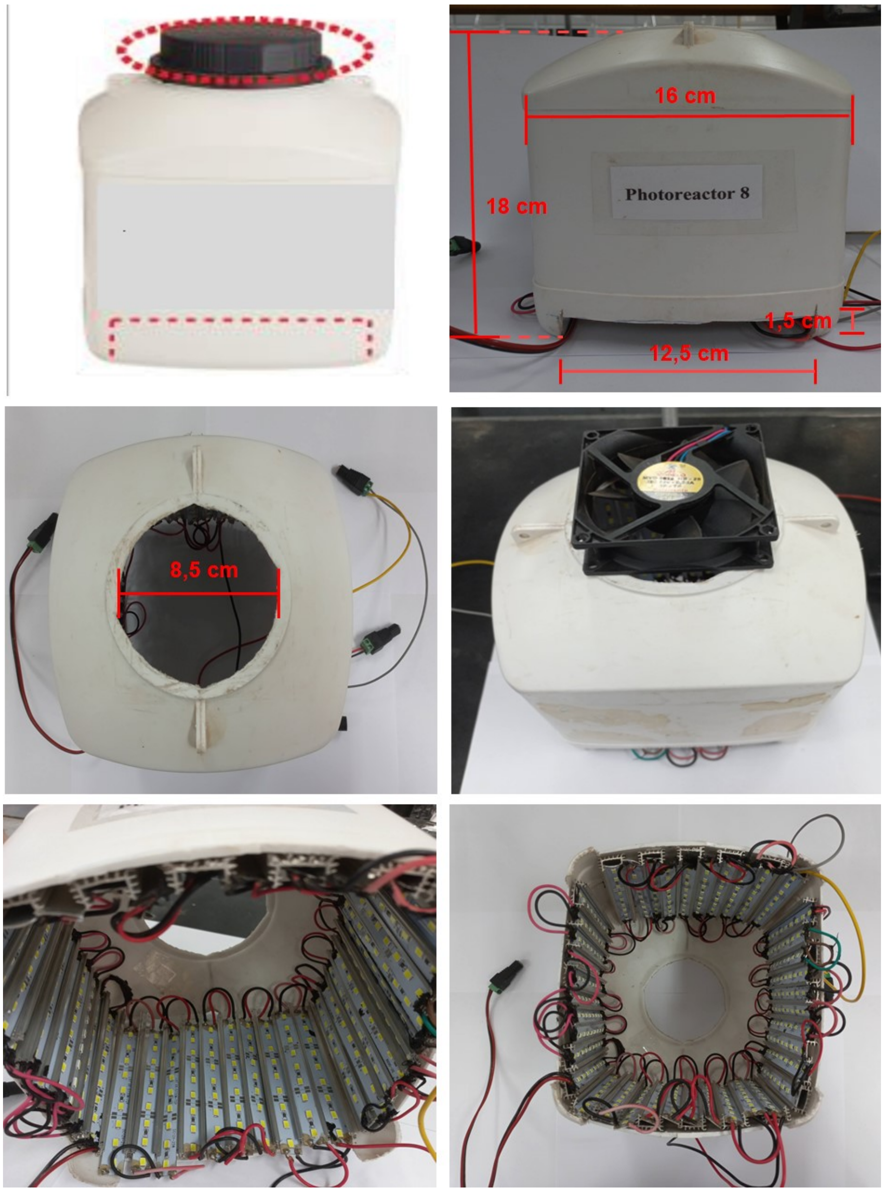


Figure S2. Step-by-Step of Batch photoreactor assembly.

b. Continuous Flow photoreactor construction

Details on the construction of this photoreactor can be obtained in our previous publication,[1,2] and pictures of the steps and materials are presented in Figures S3.

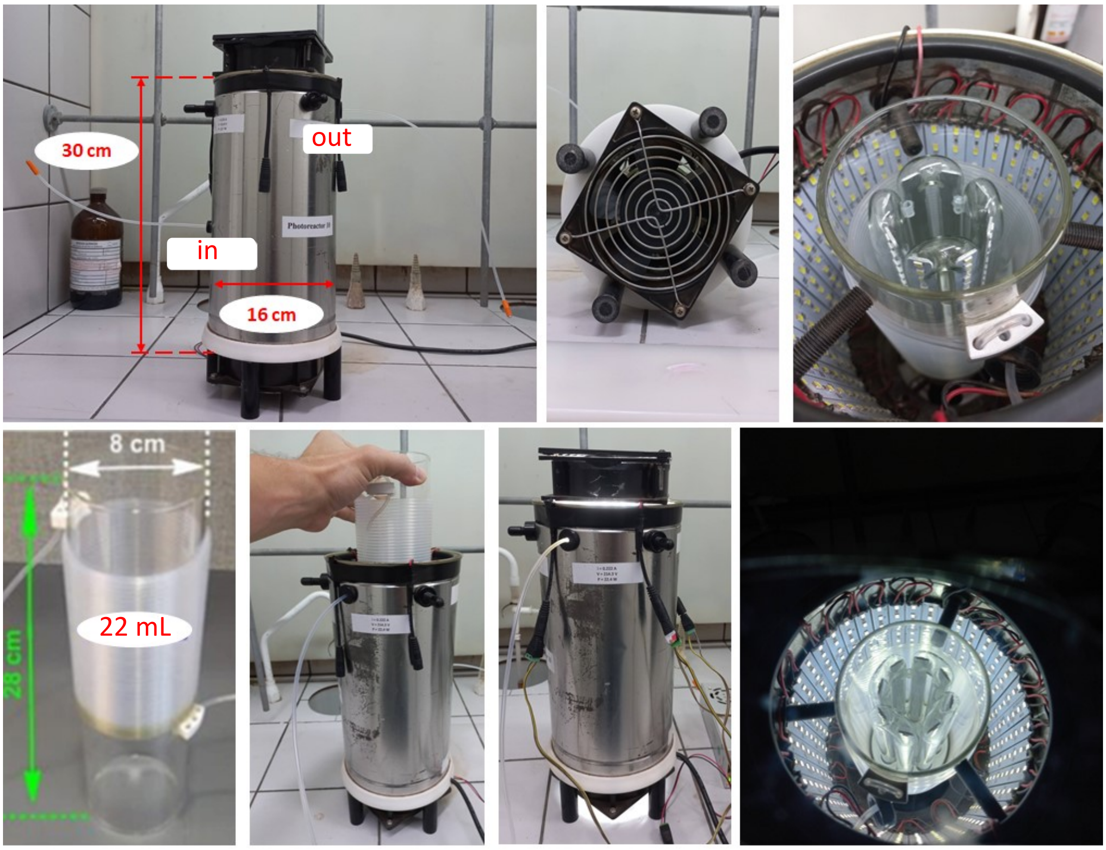


Figure S3. Final assembly of the photoreactor and PFA tubular reactor for continuous flow synthesis.

c. Tube-in-tube reactor

The tube-in-tube (TIT) reactor used to oxygenate the solutions was constructed in our lab, based on the model by the Ley group[3]. Details of the construction of this reactor can be obtained in our previous work,[1,2] and pictures of the steps and materials are presented in Figures S4.

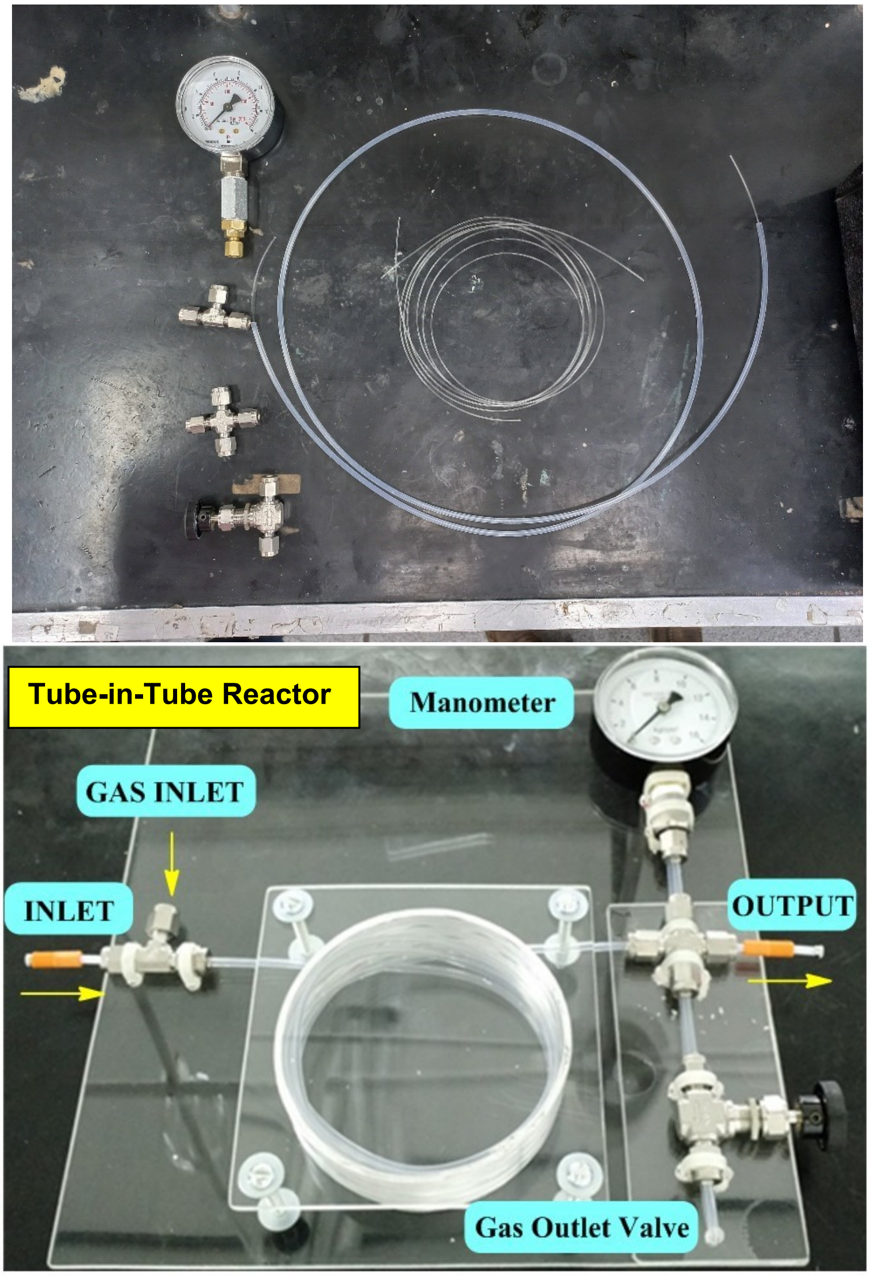
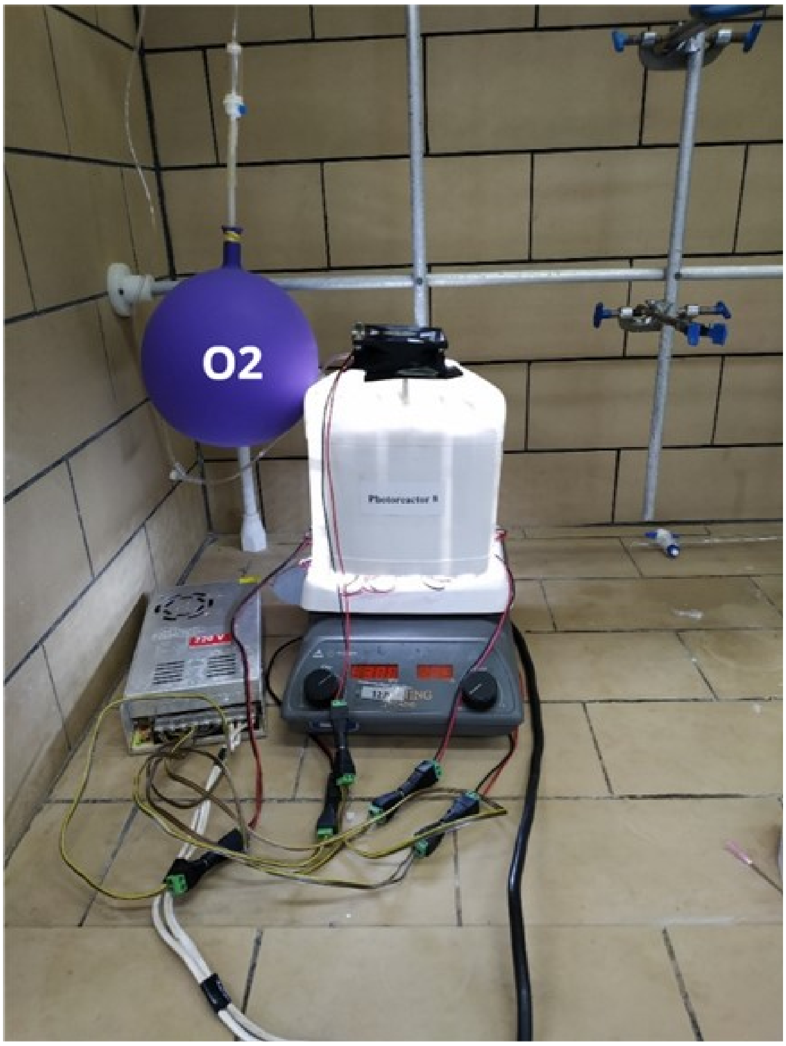


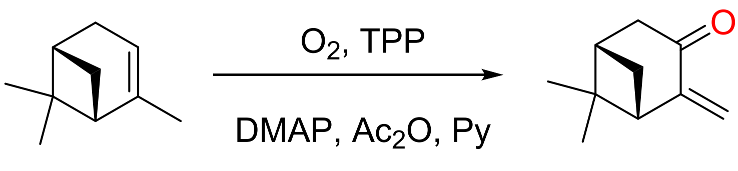
Figure S4. Our home-made tube-in-tube reactor.

2. Batch results - setup S1

a)



b)



1a **2a**

Figure S5 – a) Batch setup reactor for the synthesis of (-)-pinocarvone. b) Conversion of (+)-α-pinene into (-)-pinocarvone.

3. Flow setup S1

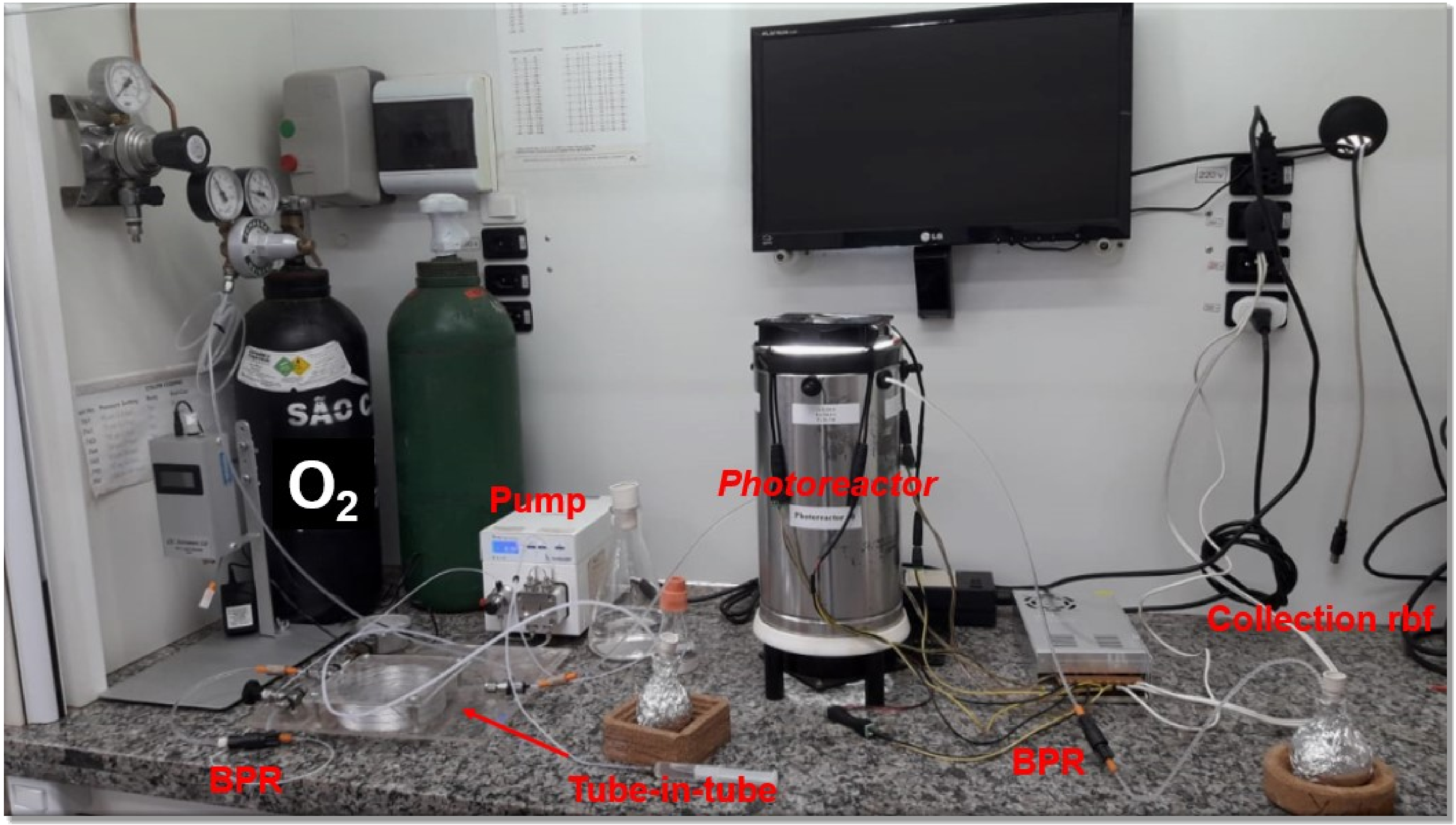


Figure S6 - Flow setup 1 for the synthesis of (-)-pinocarvone (**2a**).

4. Flow Setup S2

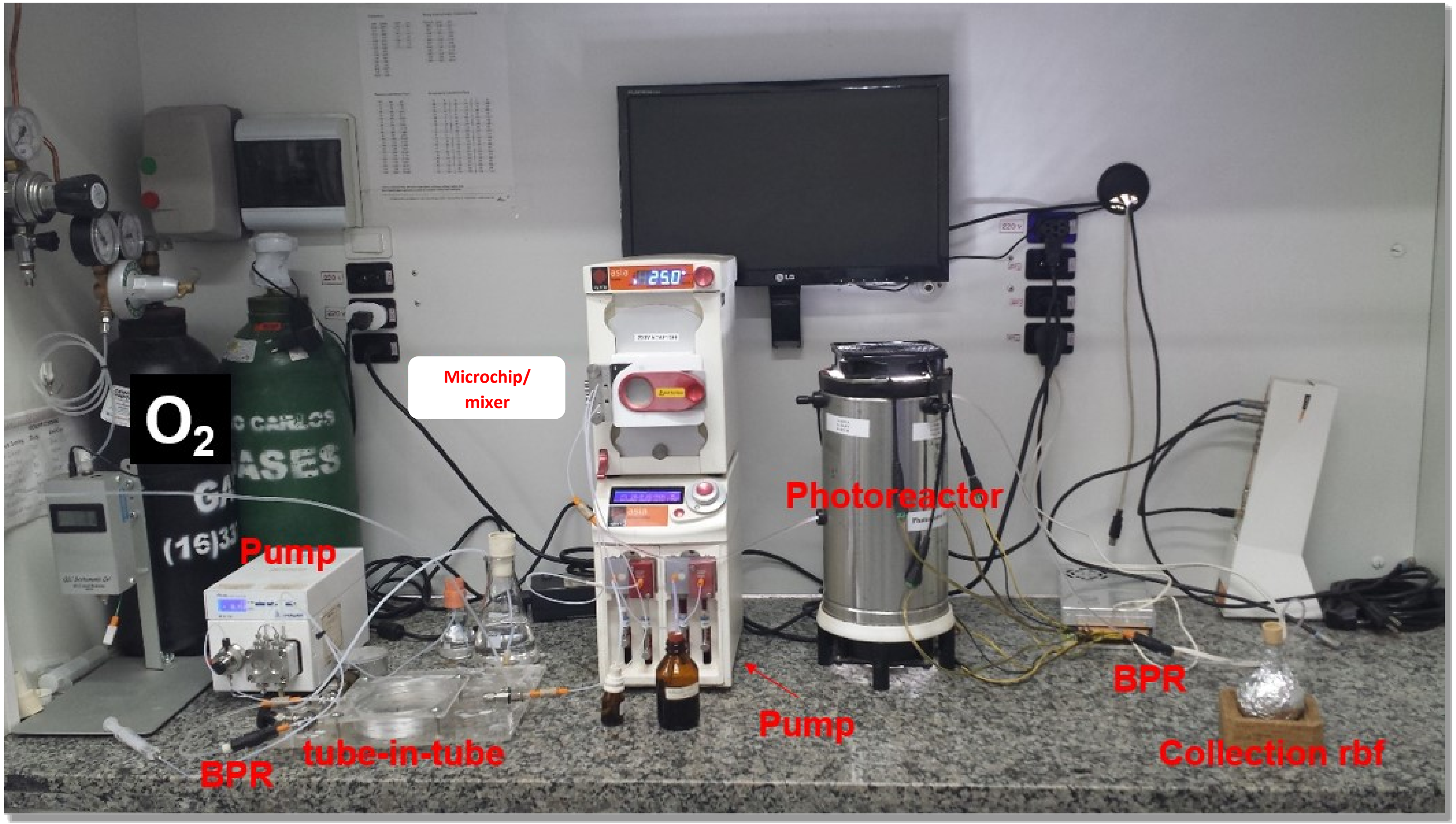


Figure S7 – Flow setup 2 for the synthesis of pinocarvones (**2a-b**)

Flow setup S3

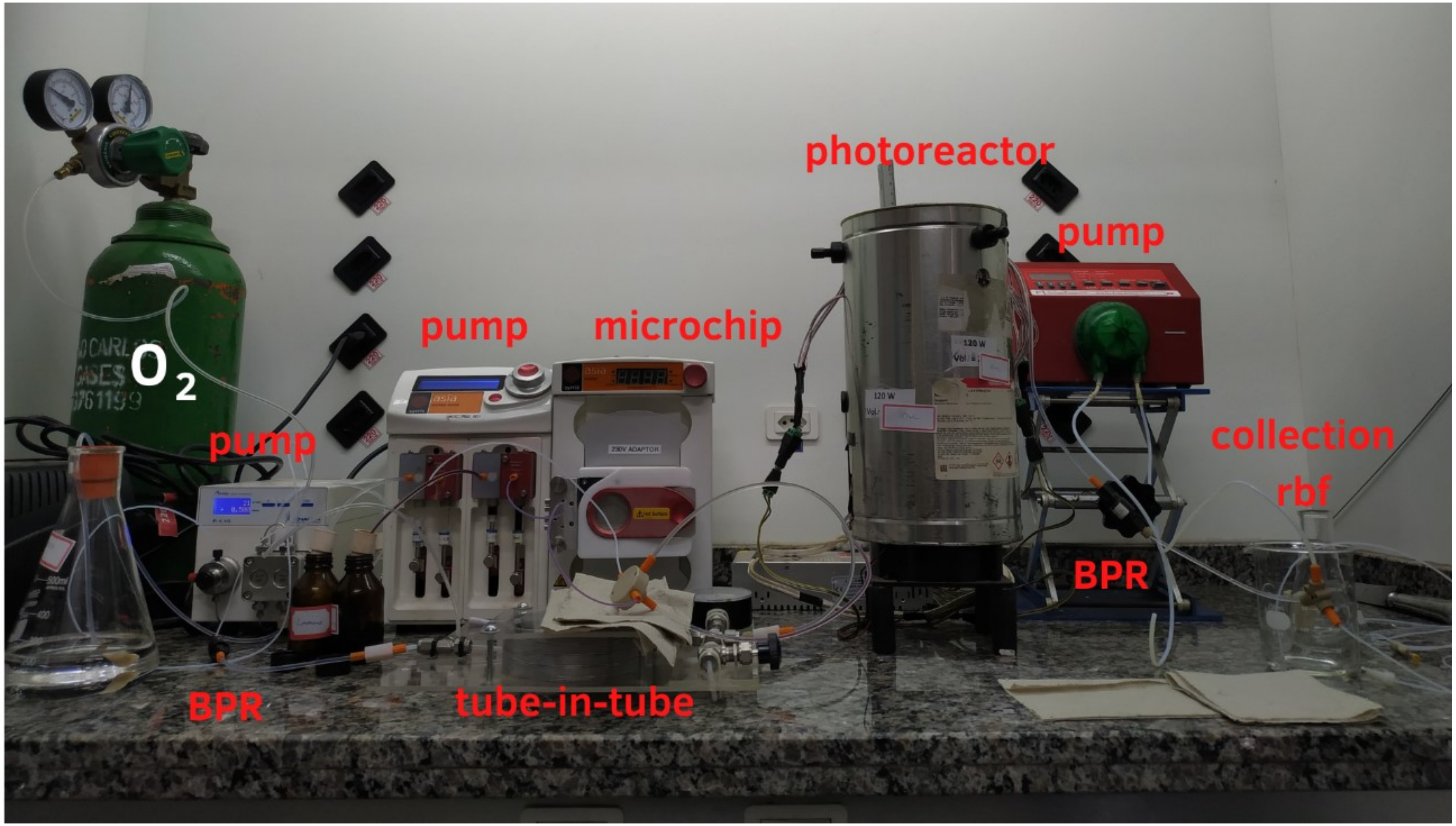
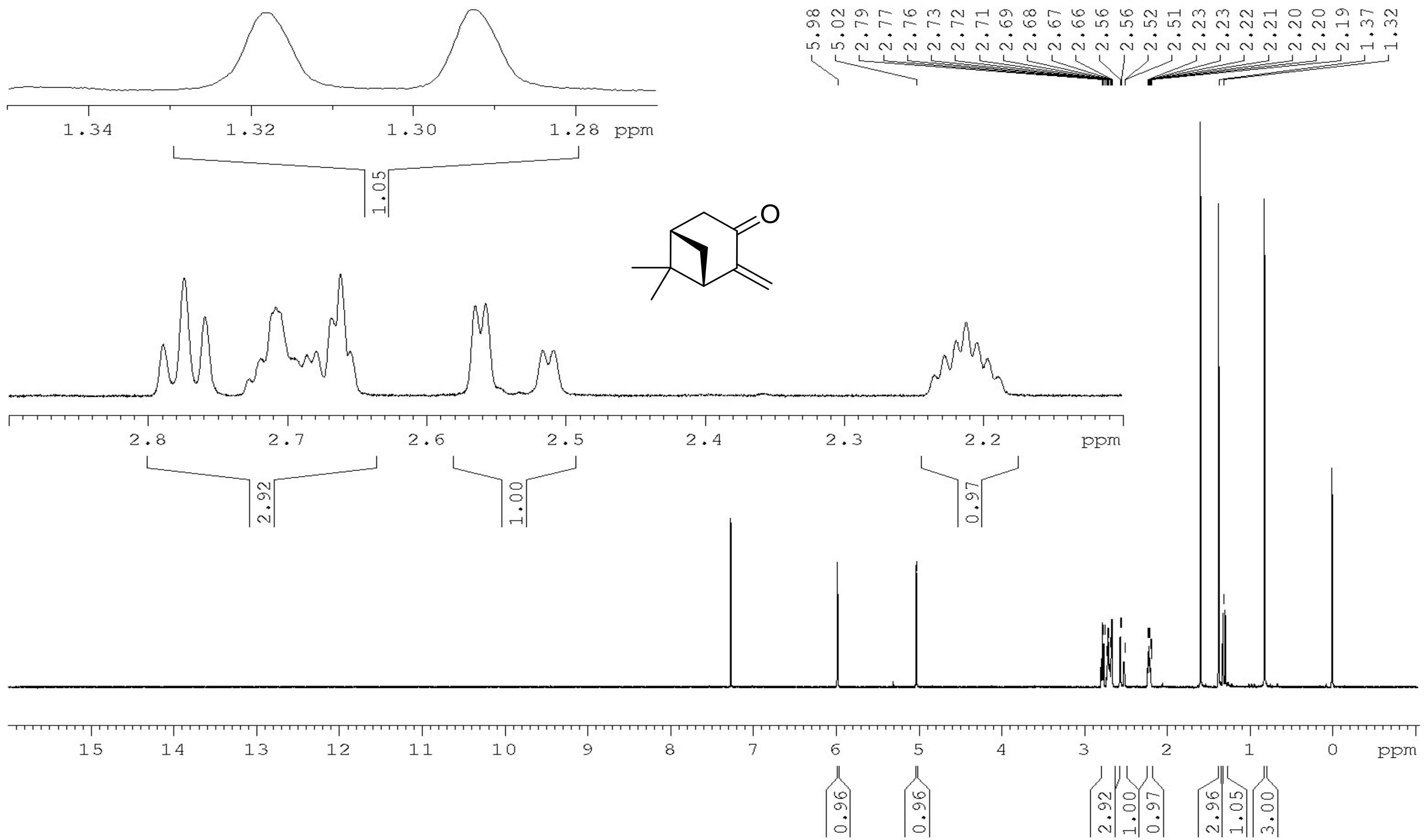
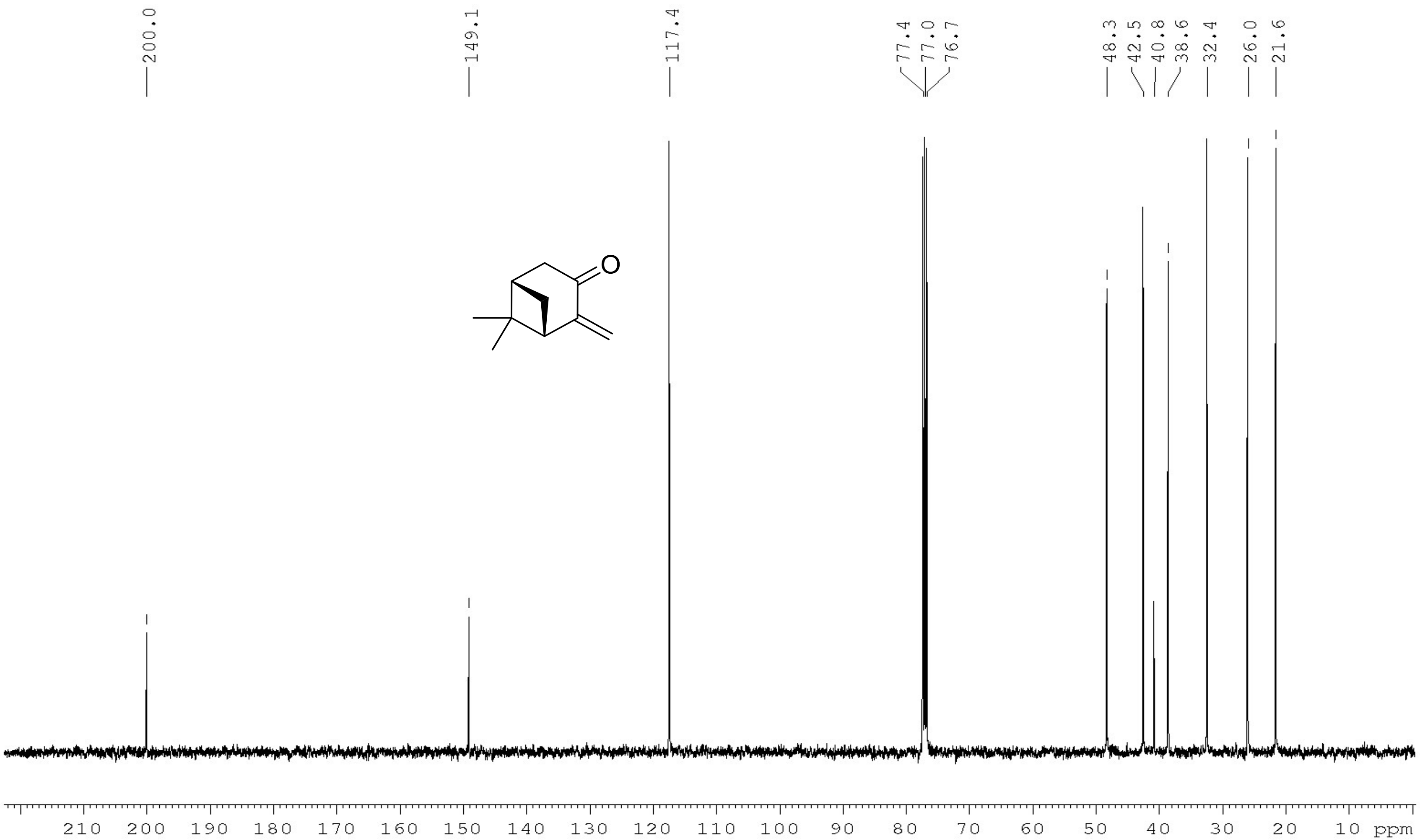


Figure S8 - Flow setup 3 for the synthesis of the trans-pinocarveols (**3a-b**)..

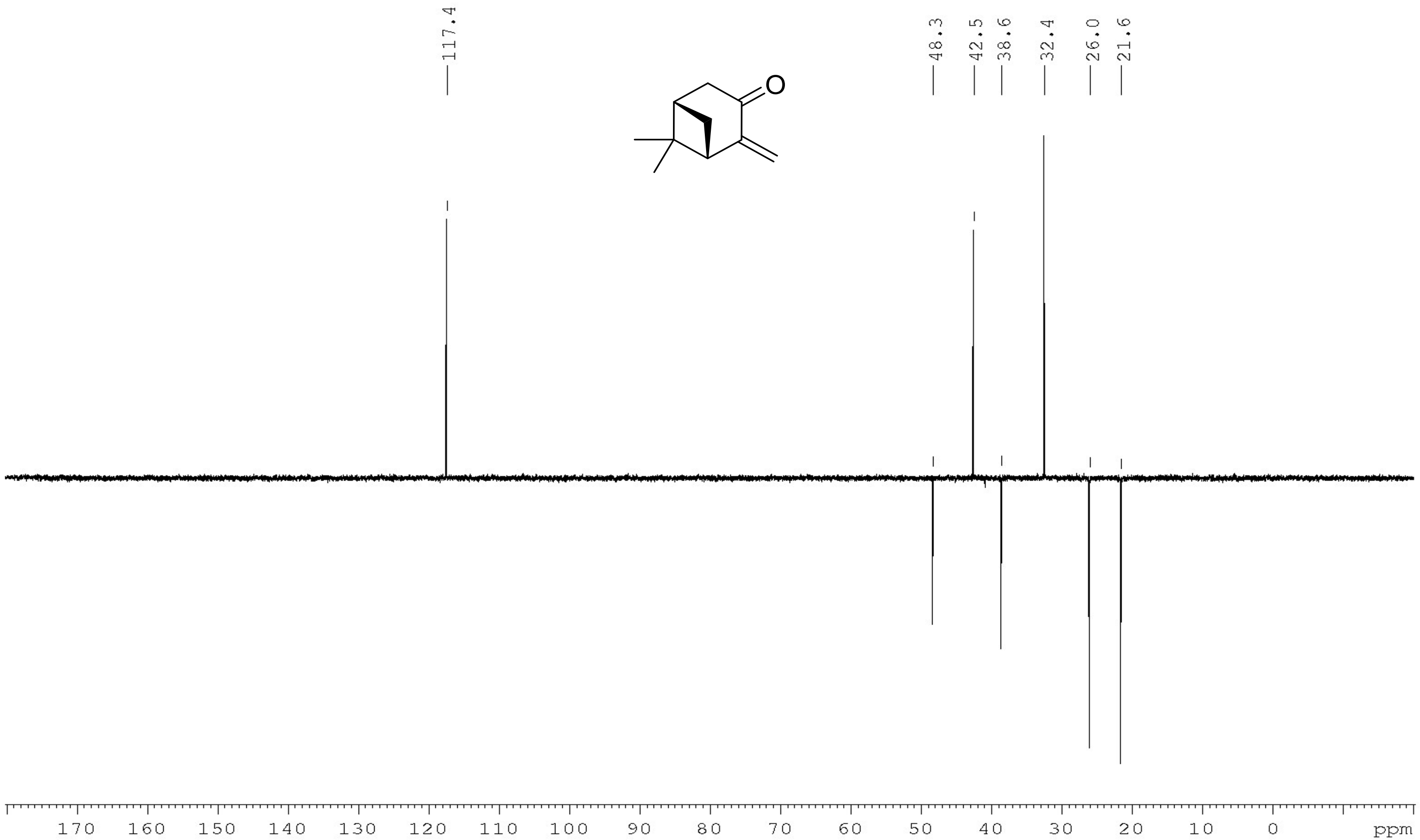
5. NMR Spectra



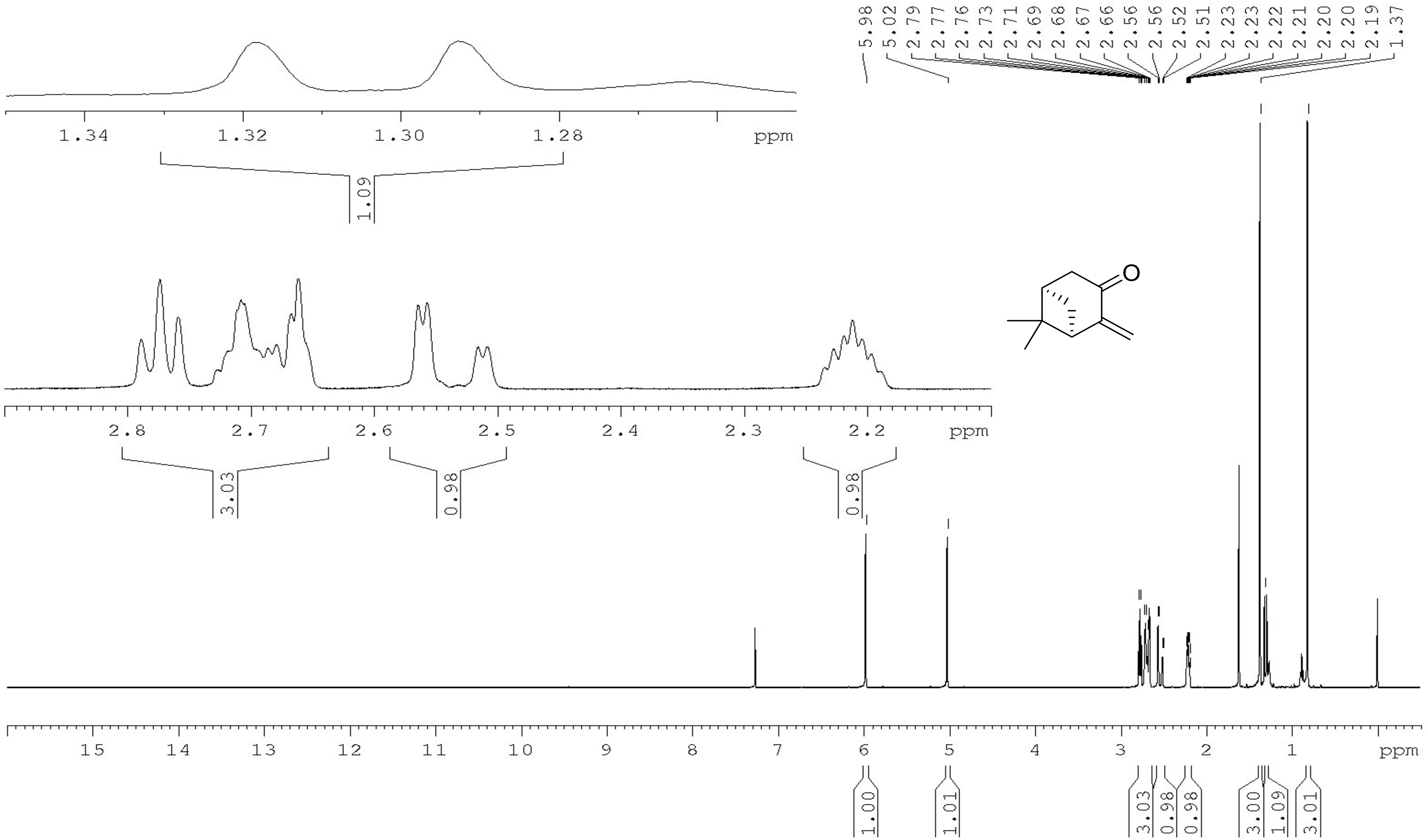
^{1}H NMR ($CDCl_3$) – 400 MHz



$^{13}C\{^1H\}$ NMR ($CDCl_3$) – 100 MHz



DEPT-135 ^{13}C NMR ($CDCl_3$) – 100 MHz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0.98
3.00
1.09
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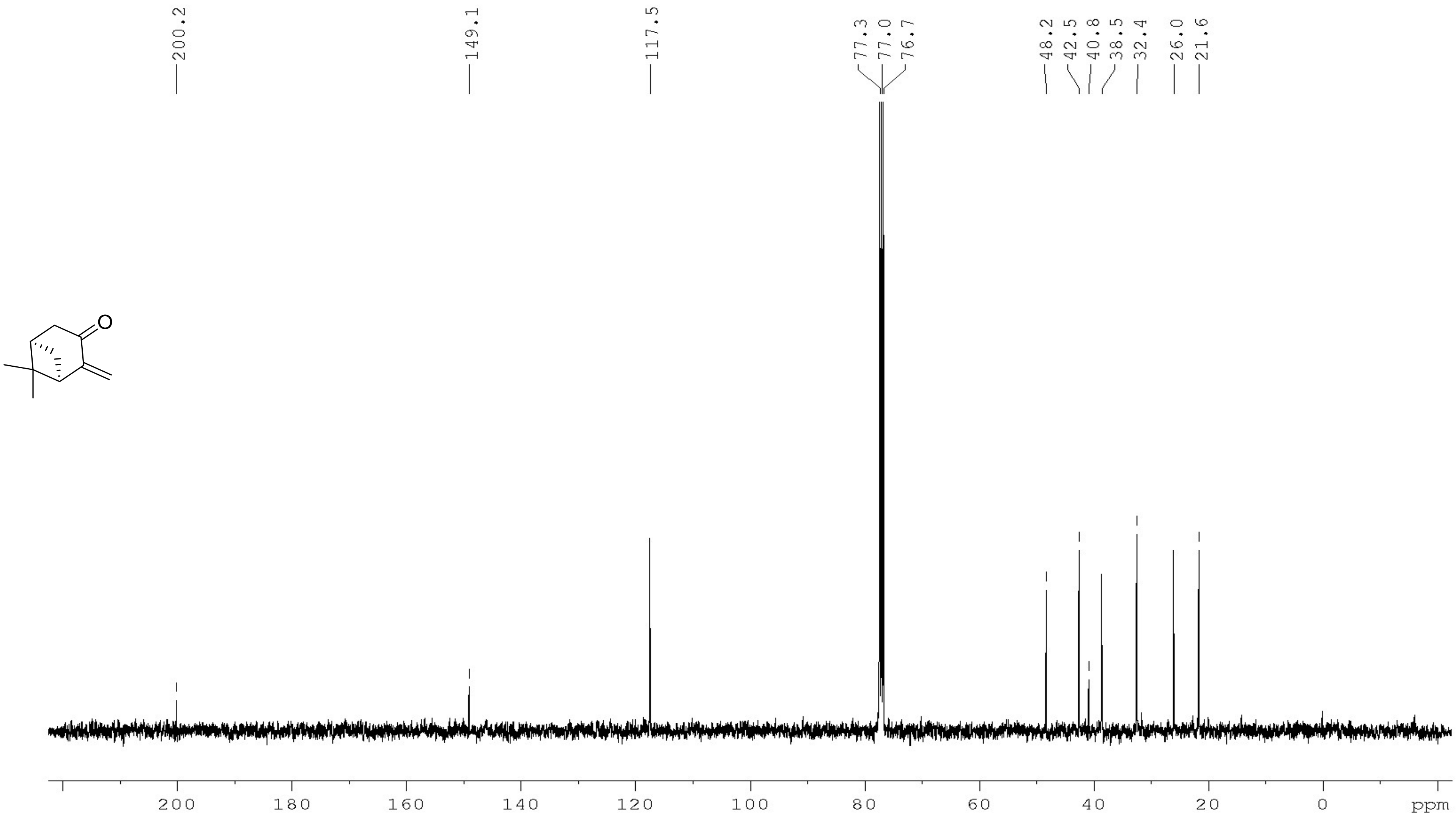
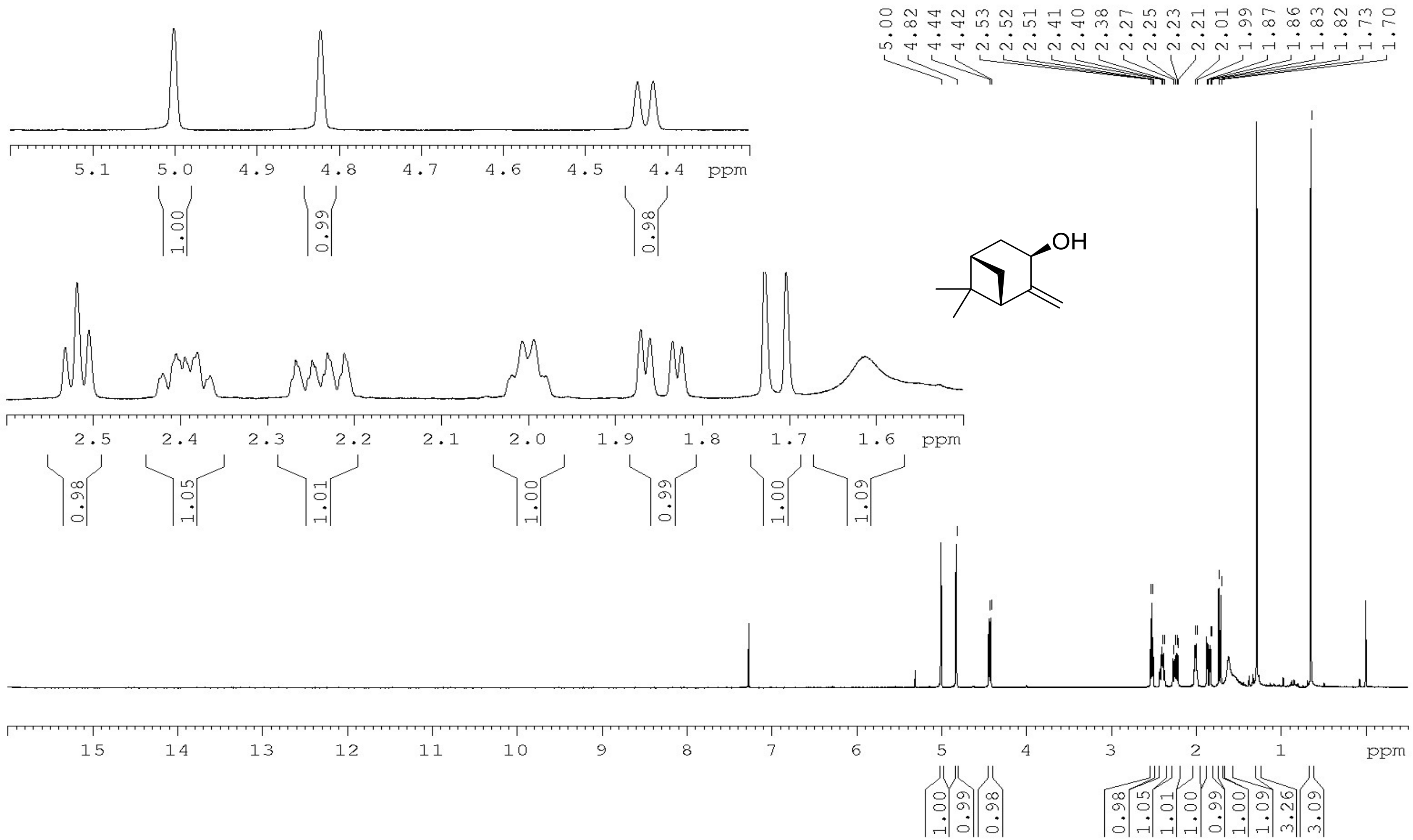
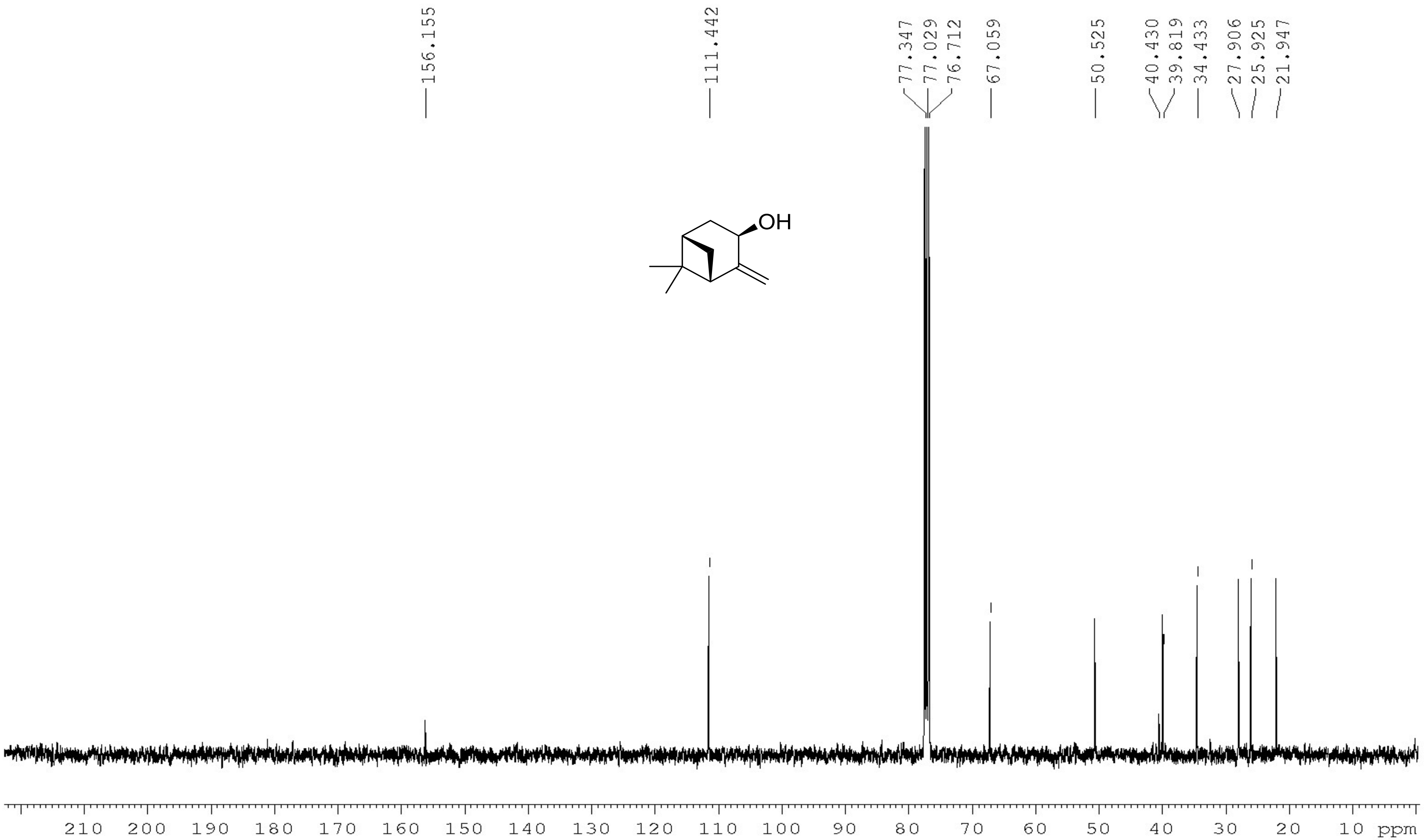
^{1}H NMR ($CDCl_3$) – 400 MHz



$^{13}C\{1H\}$ NMR ($CDCl_3$) – 100 MHz

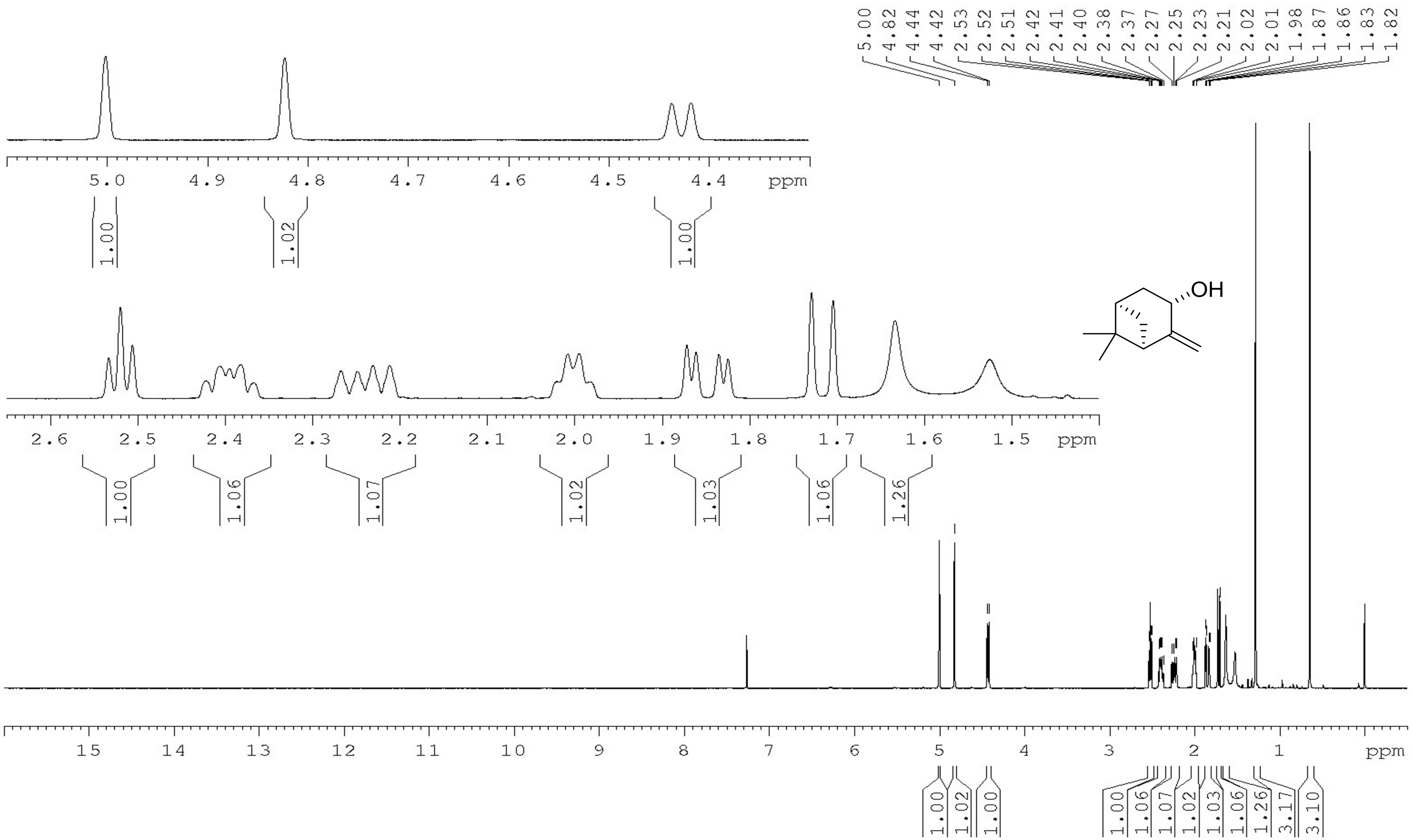


^{1}H NMR ($CDCl_3$) – 400 MHz

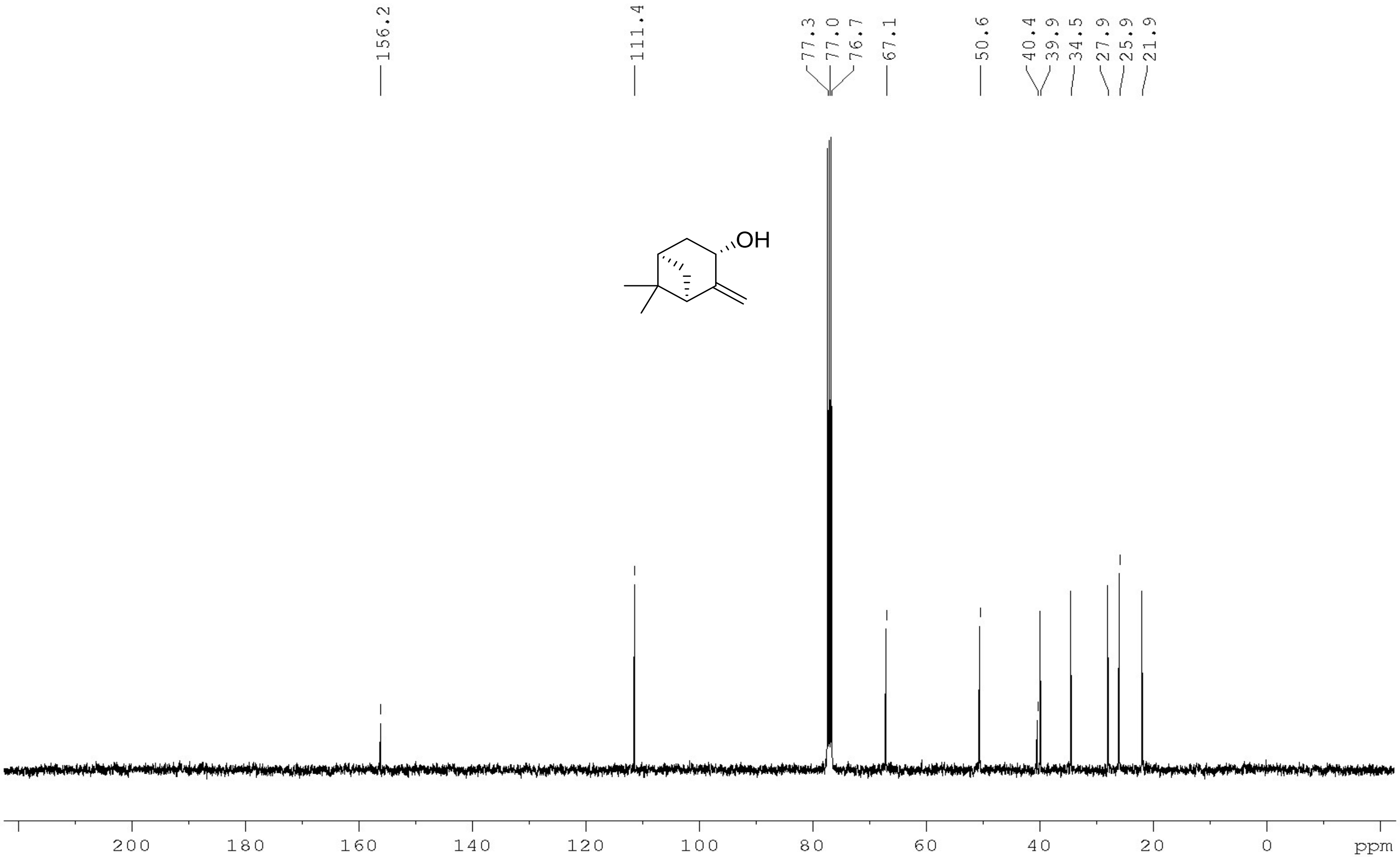


1

^{3}C{1H} NMR ($CDCl_3$) – 100 MHz



^{1}H NMR ($CDCl_3$) – 400 MHz



$^{13}C\{1H\}$ NMR ($CDCl_3$) – 100 MHz

6. References

1 J. M. De Souza, T. J. Brocksom, D. T. McQuade and K. T. De Oliveira, *J. Org. Chem.*, 2018, **83**, 7574–7585.

2 A. A. N. De Souza, N. S. Silva, A. V Müller, A. S. Polo, T. J. Brocksom and K. T. De Oliveira, 2018, **83**, 15077–15086.

3 P. B. Cranwell, M. O'Brien, D. L. Browne, P. Koos, A. Polyzos, M. Peña-López and S. V. Ley, *Org. Biomol. Chem.*, 2012, **10**, 5774–5779.