Supporting Information

Iron-free mechanochemical limonene inverse vulcanization

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Materials and Methods

All the chemicals were used as received. (*R*)-Limonene (97%) was purchased from Aldrich. Elemental sulphur for industrial use (98.5%) was purchased from A.M.C. Cunha Lda. All solvents were analysis grade. The ATR spectra were acquired in a Perkin Elmer 1000. The NMR spectra were obtained in a Bruker-400 equipment (400 MHz). The mass spectra were acquired using a LCQ Fleet Mass Spectrometer with an ESI source (Thermo Scientific) interfaced with an HPLC-DAD (Varian) (mass range: 50–2000 Da).

Mechanosynthesis

The inverse vulcanization was carried out in a PM100 planetary ball mill (Retsch). For the mechanosynthesis we used a zirconium oxide milling jar of 50 mL and 200 zirconium oxide balls of 5 mm diameter. The synthesis was optimized regarding the reaction time and the operating frequency of the equipment.

(*R*)-Limonene inverse vulcanization

(*R*)-Limonene (1 mL, 1.5 equiv.) and sulphur (1 g, 0.47 mmol, 1.0 equiv.) were added to the zirconium oxide reactor containing 200 zirconium oxide balls. The optimized parameters for the inverse vulcanization were 2 hours of reaction at 500 rpm, with rotation inversion cycles of 15 min (5 secs pause between inversion cycles). After this period, the viscous solid (light yellow paste) that was formed was removed from the reactor (and balls) with dichloromethane washings (3✕15 mL). The collected mixture was filtered, and the dichloromethane fraction evaporated to dryness, which after drying under vacuum, led to a yellow solid (477 mg, 32.3 wt% yield based on recovered sulphur). The dichloromethane insoluble fraction was obtained as a light yellow solid (362 mg, conversion yield 63.8%) and was found to be only sulphur (no signals detected by ^{1}H-NMR, $CDCl_3/CS_2$ 1:1). The ratio between the soluble and the insoluble fraction is 57:43. FTIR-ATR δ (cm^{-1}): 2919, 2851, 1447, 1370, 748. ^{1}H-NMR (400 MHz, $CDCl_3/CS_2$ 9:1) δ (ppm): 5.30 (m), 4.73 (m), 4.70 (m), 2.18-1.54 (m), 1.26 (s), 0.87 (t, *J*= 9 Hz).

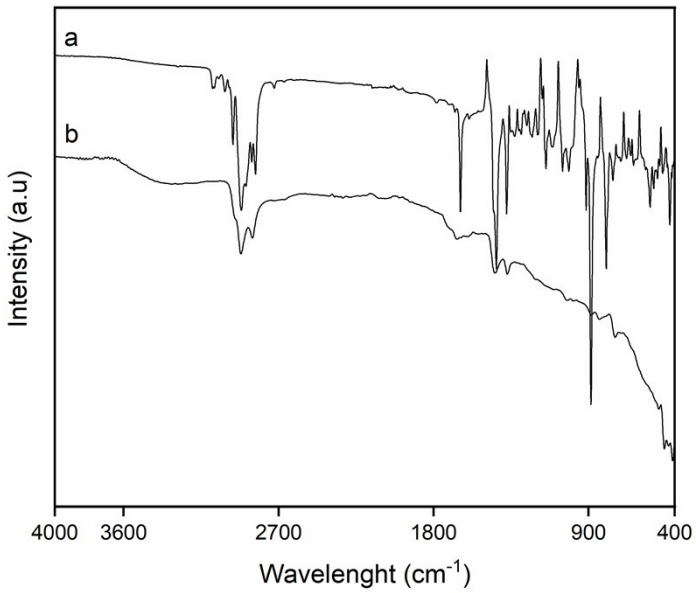

Figure S1. ATR spectrum of (*R*)-limonene (**a**) and (*R*)-limonene thiiranes and oligosulfides (**b**).

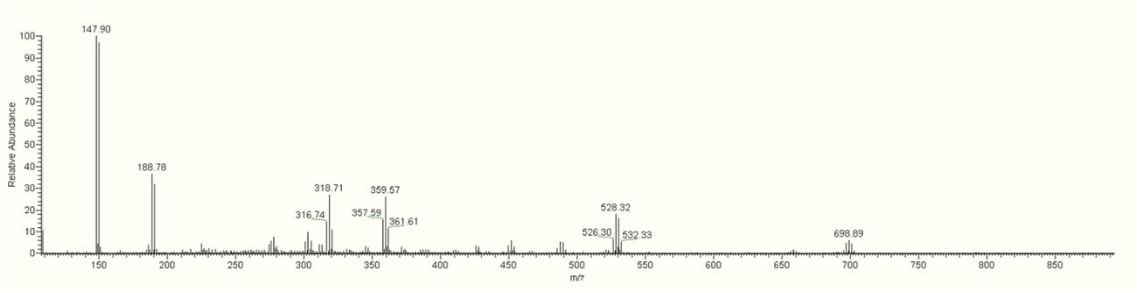

Figure S2. Mass spectrum of the injection of solvents mixture (water, methanol and acetonitrile) and silver nitrate using the positive mode (control).

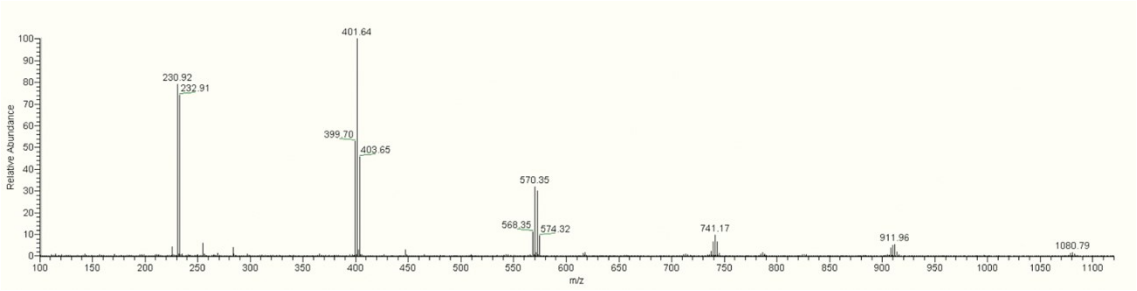

Figure S3. Mass spectrum of the injection of solvents mixture (water, methanol and acetonitrile) and silver nitrate using the negative mode (control).

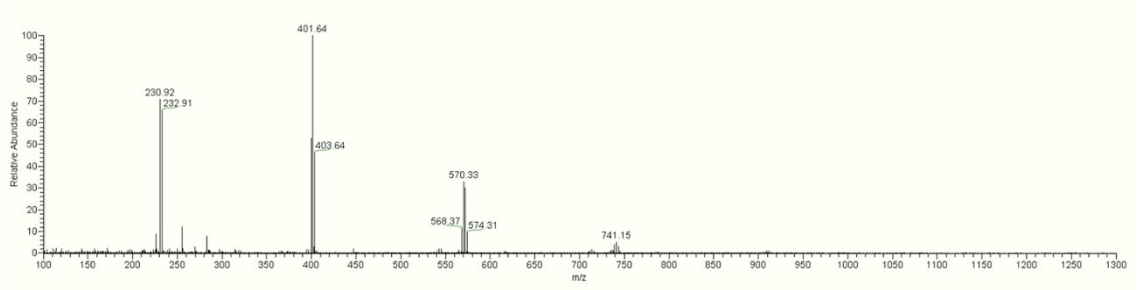

Figure S4. Mass spectrum of (*R*)-limonene thiiranes and polysulfides using the negative mode.