

# Chemical Engineering Journal

## MeSesamol, a bio-based and versatile polar aprotic solvent for organic synthesis and depolymerization --Manuscript Draft--

|                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|-----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Manuscript Number:    | CEJ-D-23-09457                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| Article Type:         | Research Paper                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| Section/Category:     | Green and Sustainable Science and Engineering                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
| Keywords:             | green solvent; Michael addition; cross-coupling; depolymerization; BPA-PC; PET                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| Corresponding Author: | Gyorgy Szekely<br>King Abdullah University of Science and Technology<br>SAUDI ARABIA                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| First Author:         | Gyula Dargo                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| Order of Authors:     | Gyula Dargo                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
|                       | David Kis                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|                       | Martin Gede                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
|                       | Sushil Kumar, Dr.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|                       | Jozsef Kupai, Prof.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
|                       | Gyorgy Szekely                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| Abstract:             | <p>Applications of polar aprotic solvents are inevitable in the chemical industry, but few nonhazardous alternatives are available. Herein, we propose methyl sesamol (MeSesamol) as a promising new bio-based alternative for polar aprotic solvents and demonstrate its versatile applications. MeSesamol was derived from natural resources using environmentally friendly and facile procedures, such as methylation using dimethyl carbonate. MeSesamol has a distinctive smell and demonstrates excellent properties as a green solvent: high boiling and open-cup flash points, immiscibility with water but miscibility with common organic solvents, high stability and resistance to several acids and bases. MeSesamol was an effective solvent in nine C–C coupling reactions, including the Suzuki and Sonogashira reactions and asymmetric Michael addition. MeSesamol lies close to dichloromethane (DCM) in Hansen space and achieves a similar or higher yield and enantiomeric excess (up to 97% and 99%, respectively) in the asymmetric Michael reactions compared to DCM. MeSesamol proved to be an excellent recyclable solvent in the depolymerizations of bisphenol-A polycarbonate (BPA–PC) and polyethylene terephthalate (PET). MeSesamol was recycled in five reaction cycles with excellent efficiency (92%–100%) and outstanding cumulative monomer yields (92% bisphenol-A from BPA–PC and 92% terephthalic acid from PET). To properly compare the depolymerization reactions, we propose two green metrics, namely, the corrected energy-economy factor (<math>\epsilon_{\text{corr}}</math>) and the corrected environmental energy impact (<math>\xi_{\text{corr}}</math>).</p> |

# MeSesamol, a bio-based and versatile polar aprotic solvent for organic synthesis and depolymerization

Gyula Dargo<sup>a</sup>, David Kis<sup>a</sup>, Martin Gede<sup>b,c</sup>, Sushil Kumar<sup>b</sup>, Jozsef Kupai<sup>a\*</sup>, and Gyorgy Szekely<sup>b,c\*</sup>

<sup>a</sup> Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Muegyetem rakpart 3., H-1111 Budapest, Hungary

<sup>b</sup> Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology, (KAUST), Thuwal 23955-6900, Saudi Arabia

<sup>c</sup> Chemical Engineering Program, Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology, (KAUST), Thuwal 23955-6900, Saudi Arabia

\*Corresponding authors: kupai.jozsef@vbk.bme.hu, gyorgy.szekely@kaust.edu.sa

## Keywords

green solvent, Michael addition, cross-coupling, depolymerization, BPA-PC, PET

## Abstract

Applications of polar aprotic solvents are inevitable in the chemical industry, but few nonhazardous alternatives are available. Herein, we propose methyl sesamol (MeSesamol) as a promising new bio-based alternative for polar aprotic solvents and demonstrate its versatile applications. MeSesamol was derived from natural resources using environmentally friendly and facile procedures, such as methylation using dimethyl carbonate. MeSesamol has a distinctive smell and demonstrates excellent properties as a green solvent: high boiling and open-cup flash points, immiscibility with water but miscibility with common organic solvents, high stability and resistance to several acids and bases. MeSesamol was an effective solvent in nine C–C coupling reactions, including the Suzuki and Sonogashira reactions and asymmetric Michael addition. MeSesamol lies close to dichloromethane (DCM) in Hansen space and achieves a similar or higher yield and enantiomeric excess (up to 97% and 99%, respectively) in the asymmetric Michael reactions compared to DCM. MeSesamol proved to be an excellent recyclable solvent in the depolymerizations of bisphenol-A polycarbonate (BPA–PC) and polyethylene terephthalate (PET). MeSesamol was recycled in five reaction cycles with excellent efficiency (92%–100%) and outstanding cumulative monomer yields (92% bisphenol-A from BPA–PC and 92% terephthalic acid from PET). To properly compare the depolymerization reactions, we propose two green metrics, namely, the corrected energy-economy factor ( $\epsilon_{\text{corr}}$ ) and the corrected environmental energy impact ( $\xi_{\text{corr}}$ ).

## 1. Introduction

The continued extraction of limited fossil fuels and the resulting environmental problems have driven the search for renewable materials and energy sources. In fact, the search for renewables is among the largest challenges of humankind. The same endeavor is devoted to solvents, which comprise a large proportion of waste from chemical industries [1].

In 2015, the United Nations announced 17 major Sustainable Development Goals, including reduction of environmental impacts by the chemical sector [2]. In the same year, the ACS Green Chemistry Institute Pharmaceutical Roundtable encouraged the replacement of polar aprotic and halogenated solvents with new green solvents [3]. Most of the green solvents are less toxic, contain no halogen atoms, and have a low vapor pressure, thereby reducing occupational exposure and environmental releases to the atmosphere. A green solvent should also be thermally stable and easily available from natural and renewable sources. It is important to highlight that green solvents are not the sole requirements of sustainable chemistry; low energy demand and reduced waste generation are also essential for promoting green chemistry [4].

To meet the increasingly stringent environmental regulations, pharmaceutical companies such as GSK [5], Pfizer [6], AstraZeneca [7], and Sanofi [8] have published their own solvent-sustainability guides to aid comparisons of different solvents [9]. These guidelines and recent reviews stress the need for finding greener solvents. Polar aprotic solvents (PASs) and chlorinated solvents are especially difficult to replace with greener alternatives [10,11].

Among the widely used PASs in organic synthesis are *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP), which are noted for their remarkable solubilization power. PASs are the favored solvents in  $S_N2$  reactions because they effectively solvate the cations while leaving the anions free as nucleophiles. PASs are also commonly employed in cross-coupling reactions [12], solid-phase peptide synthesis [13], and fabrication of polymer membranes [14]. The polymer industry heavily relies on PASs because most polymers are poorly solubilized in non-PASs. Approximately 400 million tons of plastic are produced globally each year, although polymer recycling remains problematic and faces many challenges [15]. For instance, BPA-PC must be collected and recycled because its monomer (bisphenol-A) is a possible xenoestrogen and poses a major health concern. Furthermore, BPA-PC is used in a wide variety of consumer and industrial products, such as electronic components, storage devices (CDs and DVDs), automobiles, and safety equipment. Unless recycled, the resulting BPA-PC waste accumulates rapidly. Although several methods for the chemical recycling of BPA-PC have been developed over the past few decades, most of these methods require elevated temperatures [16]. Similarly, PET has been chemolytically depolymerized using recyclable heterogeneous organocatalysts [68] and KOH in alcohols (e.g., MeOH, EtOH) [17–19]. Thielemans and co-workers simultaneously depolymerized a mixed stream of PET and BPA-PC within 2 minutes via KOH-in-MeOH hydrolysis (KMH) under microwave-assisted heating to 130 °C [20].

PASs are usually derived from fossil-based sources and most of them are hazardous to human health and the environment. Therefore, they should be substituted with greener solvents. Green alternatives are preferably derived from renewable sources and should be safer to handle, less toxic, and exhibit similar to or better solubilization power than fossil-based derivatives. Recently, bio-based solvents derived from biomass resources have promised to halt the depletion of fossil energy [21,22]. Among the promising bio-based solvents are  $\gamma$ -valerolactone (GVL) [23], *p*-cymene [24], dimethyl isosorbide (DMI) [25], dihydrolevoglucosenone (cyrene) [26,27], diformylxylose [28], and methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (sold under the brand name Rhodiasolv PolarClean) [29,30]. Cyrene has been already used in several industrially relevant applications: as a replacement solvent in the production of a revolutionary graphene ink [31], in drug discovery as solvent in amide bond formation [32], as a mediator of carbon–carbon coupling reactions [33], and as the drug-delivery medium in antibacterial susceptibility testing [34].

The 1,3-benzodioxole scaffold of sesamol is ubiquitous in biomasses and natural compounds (such as piperine and bicuculline). Sesamol is a white crystalline solid with a melting point of 62–65 °C. We converted sesamol to its methyl ether, which is a colorless liquid and a green solvent candidate. Moreover, we hypothesized that methylation improves the stability of sesamol by inhibiting its oxidation. Therefore, starting from sesamol, we attempted a green synthesis of MeSesamol and investigated the potential applicability of MeSesamol as a greener alternative for traditional PASs (Fig. 1.).



**Fig. 1.** MeSesamol as a promising alternative for traditional PASs

## 2. Materials and methods

### 2.1. General information

The starting materials and reagents were purchased from commercially available sources (Merck, TCI Europe, and VWR). The depolymerization reactions were performed using Makrolon® 2658 BPA-PC granules and PET flakes from HUKE Ltd. (Hungary). Infrared (IR) spectra were recorded on a Bruker Alpha-T Fourier-transform IR (FTIR) spectrometer. Optical rotations were measured on a PerkinElmer 241 polarimeter calibrated by measuring the optical rotations of both enantiomers of menthol. Thin-layer chromatography

(TLC) was performed using silica gel 60 F<sub>254</sub> (Merck) plates. The reactions were monitored by TLC and high-performance liquid chromatography–mass spectrometry (HPLC–MS). The solvent ratios in the eluents are given in volume units (mL mL<sup>-1</sup>). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX-500 Avance spectrometer (at 500 and 126 MHz for the <sup>1</sup>H and <sup>13</sup>C spectra, respectively) or on a Bruker 300 Avance spectrometer (at 300 and 75.5 MHz for the <sup>1</sup>H and <sup>13</sup>C spectra, respectively) at specified temperatures. High-resolution MS was measured on a Bruker MicroTOF II instrument using positive electrospray ionization. The measured values are reported to four decimal places. HPLC–MS was performed on an HPLC system using a Shimadzu LCMS-2020 (Shimadzu Corp., Japan) device equipped with a Reprospher (Altmann Analytik Corp., Germany) 100 Å C18 (5 µm; 100 × 3 mm) column and a positive/negative double ion source with a quadrupole MS analyzer in the range 50–1000 m/z. The flash point was measured using Marcusson's open-cup method. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out on a TGA 209 F1 analyzer (Netzsch) under an N<sub>2</sub> atmosphere over the temperature range 30–900 °C. Low-temperature DSC measurements were performed on a DSC 250 (TA instruments) over the temperature range –90–170 °C. The Hansen solubility parameters were determined using HSPiP Software (5<sup>th</sup> Edition version 5.4.06). Further details are available in the Supplementary Material.

## 2.2. Experimental

### 2.2.1. MeSesamol synthesis

*Synthesis of MeSesamol using methyl iodide:* Sesamol (10 g, 72.5 mmol) was dissolved in acetone (160 mL), and K<sub>2</sub>CO<sub>3</sub> (35 g, 254 mmol). After adding methyl iodide (9 mL, 20.5 g, 145 mmol), the reaction mixture was stirred overnight at room temperature under argon atmosphere. Once the reaction was complete, the K<sub>2</sub>CO<sub>3</sub> was filtered and washed with acetone (30 mL). The volatile components were removed under reduced pressure. Water (40 mL) was added and the product was extracted with dichloromethane (3 × 40 mL). The combined organic phase was sequentially washed with hydrochloric acid (30 mL, 1 M) and aqueous NaOH (20 mL, 0.5 M), then dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was purified by vacuum distillation (bp 102 °C at 2.2 mmHg). The resulting colorless liquid was characterized as follows: *R*<sub>f</sub>: 0.70 (SiO<sub>2</sub> TLC, heptane:EtOAc = 4:1) HRMS *m/z*: [M + H]<sup>+</sup> calculated for [C<sub>8</sub>H<sub>9</sub>O<sub>3</sub>]<sup>+</sup>: expected 153.0552; found 153.0515. δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>, 27 °C): 3.75 (s, 3H); 5.91 (s, 2H); 6.32 (dd, *J* = 8.5 Hz, 2.5 Hz 1H); 6.49 (d, *J* = 2.5 Hz, 1H); 6.71 (d, *J* = 8.5 Hz, 1H) ppm. δ<sub>C</sub> (126 MHz, CDCl<sub>3</sub>, 27 °C): 56.1; 97.6; 101.2; 104.8; 108.0; 141.7; 148.4; 155.3 ppm.

*Synthesis of MeSesamol using DMC without MeOH removal:* Sesamol (10 g, 72.5 mmol) was dissolved in dimethyl carbonate (DMC) (50 mL, 0.594 mol). After adding K<sub>2</sub>CO<sub>3</sub> (11 g, 79.6 mmol) and an appropriate catalyst—1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.17 mL, 14.5 mmol), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (1.79 mL, 14.5 mmol), or cetyltrimethylammonium bromide (CTAB) (10.6 g, 29.1 mmol)—the reaction mixture was refluxed in an oil bath. Once the reaction was complete (based on TLC with SiO<sub>2</sub>, heptane:EtOAc

127 = 2:1), the solid was filtered and washed with EtOAc. The volatile components were removed *in vacuo* and  
128 the crude product was purified by vacuum distillation, similarly to the above-mentioned process.

129 *Synthesis of MeSesamol using DMC with MeOH removal and DMC replenishment:* Sesamol (10 g,  
130 72.5 mmol) was dissolved in DMC (50 mL, 0.594 mol). After adding DBU (16.2 mL, 0.109 mol), the reaction  
131 mixture was refluxed in an oil bath. The methanol produced during the reaction was removed by distillation  
132 and the DMC was replenished to its original volume at half hour intervals. Based on a TLC analysis (SiO<sub>2</sub>,  
133 heptane:EtOAc = 2:1), the reaction was completed at 2 h. The volatile components were removed *in vacuo*  
134 and EtOAc (30 mL) was added to the remaining mixture. The organic phase was extracted with mixed cc. HCl  
135 (10 mL) and water (20 mL). The HCl addition induced considerable gas evolution. The organic phase was  
136 washed with water (20 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was  
137 purified by vacuum distillation as described above.

138 *Synthesis of MeSesamol using DMC with MeOH removal and no DMC replenishment:* Sesamol (10 g,  
139 72.5 mmol) was dissolved in DMC (30 mL, 0.356 mol). After adding DBU (16.2 mL, 0.109 mol), the reaction  
140 mixture was refluxed in an oil bath. During the reaction, the formed methanol was removed by distillation  
141 using a Vigreux column, avoiding the need for DMC replenishment (see Fig. S1 in the Supplementary  
142 Material). The reflux temperature was maintained steadily between 94 and 98 °C, which marked the  
143 endpoint of the reaction. Based on a TLC analysis (SiO<sub>2</sub>, heptane:EtOAc = 2:1), the reaction was completed at  
144 3 h. The volatile components were removed *in vacuo* and EtOAc (30 mL) was added to the residue. The  
145 organic phase was extracted with a mixture of cc. HCl (10 mL) and water (20 mL). Again, the HCl addition  
146 induced considerable gas evolution. The organic phase was washed with water (20 mL), dried over MgSO<sub>4</sub>,  
147 filtered, and concentrated *in vacuo*. The crude product was purified by vacuum distillation as described  
148 above. This synthesis was up-scaled threefold under the same reaction conditions (see Section 2.3 in the  
149 Supplementary Material).

#### 150 2.2.2. General procedure of thiourea organocatalysts synthesis

151 A solution of an appropriate isothiocyanate (0.1 mmol) in MeSesamol (200 µL) was added to a solution of  
152 cinchona amine (32.3 mg, 0.1 mmol) in MeSesamol (300 µL), and the reaction mixture was stirred for 2.5 h at  
153 room temperature. The crude product was purified by preparative TLC on silica gel (EtOAc:EtOH:NH<sub>3</sub> (aq) =  
154 10:1:0.1) to obtain the corresponding organocatalyst. The spectral data were fully consistent with those  
155 reported in the literature [35,36].

#### 156 2.2.3. General procedure for Michael addition of pentane-2,4-dione to *trans*-β-nitrostyrene

157 *trans*-β-Nitrostyrene (11.7 mg, 0.0785 mmol) and the corresponding organocatalyst were dissolved in  
158 MeSesamol or DCM (500 µL) in a small vial. Subsequently, pentane-2,4-dione (20 µL, 0.196 mmol) was added  
159 to this solution and the resulting reaction mixture was stirred at room temperature for 24 h. The crude  
160 product was purified by preparative TLC on silica gel (heptane:EtOAc = 2:1) to obtain a Michael adduct. The

161 spectroscopic data of the product were consistent with the reported data (the absolute configuration was  
162 determined from optical rotation of the products) [37]. Enantiomeric excess values were determined by  
163 chiral HPLC on a Shimadzu LC-20 instrument (Shimadzu Corp., Japan) using a Phenomenex Lux Cellulose-3  
164 column (3  $\mu$ m, 250  $\times$  4.6 mm) and an acetonitrile–water (40:60) eluent with a flow rate of 0.6 mL min<sup>-1</sup>. The  
165 column temperature was 30 °C and the UV detection wavelength was 222 nm.  $t_{R,(S)}$  = 12.3 min and  $t_{R,(R)}$  =  
166 14.6 min.

#### 167 2.2.4. General procedure of the Suzuki reaction

168 The [1, 1'-bis(diphenylphosphino ferrocene)dichloropalladium(II) (Pd(dppf)Cl<sub>2</sub>) catalyst (8 mg,  
169 0.0109 mmol, 4 mol%), the corresponding boronic acid derivative (0.287 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (178 mg,  
170 0.547 mmol) were placed into a glass vial. The vial was capped and purged with nitrogen gas before adding  
171 a solution of aromatic halides (0.274 mmol) in MeSesamol (500  $\mu$ L). The reaction mixture was stirred at 80 °C  
172 for 5 h. The mixture was diluted with EtOAc (5 mL) and washed with water (5 mL). The organic phase was  
173 separated and the aqueous phase was extracted with EtOAc (3  $\times$  3 mL). The volatile components were  
174 evaporated *in vacuo*. The preparative yields of entries 1 and 2 in Table 4 were determined after precipitation  
175 in heptane. The yields of all other entries were determined by quantitative NMR using ethylene carbonate  
176 as an internal standard.

#### 177 2.2.5. Procedure of the Sonogashira reaction

178 The [1, 1'-bis(diphenylphosphino ferrocene)dichloropalladium(II) (Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) (3.5 mg, 2 mol%) and CuI  
179 (1.9 mg, 4 mol%) catalysts were charged into a glass vial. The vial was capped and purged with nitrogen gas  
180 before adding a solution of iodobenzene (28  $\mu$ L, 51.0 mg, 0.25 mmol), phenylacetylene (29  $\mu$ L, 26.9 mg,  
181 0.263 mmol), and triethylamine (38  $\mu$ L, 27.8 mg, 0.275 mmol) in MeSesamol (500  $\mu$ L). The reaction mixture  
182 was stirred at room temperature for 1 h, and purified by preparative TLC on silica gel (heptane:EtOAc =  
183 100:1). The product was obtained as pale-yellow crystals (36.6 mg, 82%).

#### 184 2.2.6. General procedure of BPA–PC depolymerization

185 The BPA–PC granules (approximately 0.5 g), KOH-in-MeOH solution (1.25 M, 10 mL), and MeSesamol  
186 (10 mL) were charged into a round-bottom flask. The purity of the applied potassium hydroxide flakes was  
187 89.6% (Lach-ner Ltd., Czech Republic). The resulting heterogeneous mixture was stirred magnetically at 500  
188 rpm for 1 h at room temperature. Next, distilled water (10 mL) was added and the mixture was stirred until  
189 the white precipitate had completely dissolved (5 min). The resulting two phases were separated and  
190 MeSesamol was reused in the following reaction cycle. The aqueous phase was adjusted to an acidic pH with  
191 concentrated hydrochloric acid (1.5 mL). The volatile components of the obtained homogeneous solution  
192 were removed *in vacuo*. As the volatile components evaporated, BPA precipitated from the water. The flask  
193 was stored in a refrigerator for 1 h to allow the complete crystallization of BPA. The crystallized BPA was

194 filtered, washed with distilled water (2 × 25 mL), heptane (2 × 25 mL), and dried under vacuum to afford  
195 white crystals of BPA.

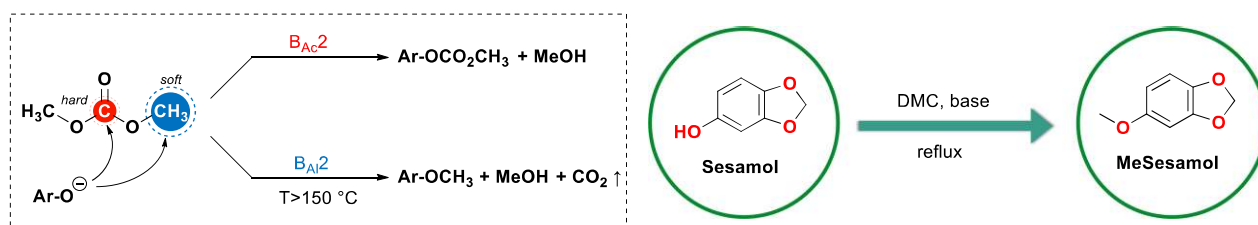
### 196 2.2.7. General procedure of PET depolymerization

197 The PET flakes (approximately 0.5 g), KOH-in-MeOH or KOH-in-EtOH solution (1.25 M, 10 mL), and  
198 MeSesamol (10 mL) were charged into a round-bottom flask. The procedure was identical to that of BPA-PC  
199 depolymerization (subsection 2.2.6) except for the temperature of magnetic stirring (50 °C). The pH of the  
200 resulting aqueous phase was adjusted to 2 with concentrated hydrochloric acid. After pH adjustment, the  
201 white precipitate was filtered, washed with distilled water (2 × 25 mL), MeOH or EtOH (2 × 25 mL), and dried  
202 under a vacuum to obtain white–pale-yellow crystals of TPA.

## 203 3. Results and discussion

### 204 3.1. Synthesis of MeSesamol

205 Sesamol can be synthesized in large quantities using safrole as the precursor (see Scheme S1 in the  
206 Supplementary material). Meanwhile, MeSesamol can be prepared using well-established methylating  
207 agents such as dimethyl sulfate or methyl halides. Methyl iodide with potassium carbonate in acetone  
208 afforded MeSesamol in quantitative yields [38]. As methyl iodide is toxic and expensive, we hypothesized  
209 that MeSesamol synthesis can be made a green process using DMC as the methylating agent. DMC is more  
210 environmentally friendly than methyl iodide and plays the dual role of a solvent and an electrophilic reagent.  
211 DMC can undergo two types of electrophilic reactions, namely, carboxymethylation and methylation  
212 (Scheme 1) [25,39–42]. High temperatures (above 150 °C) promote the methylation reaction (via the  $B_{Al}2$   
213 mechanism), which has a higher activation barrier than carboxymethylation. As the boiling point of DMC is  
214 90 °C, the temperature-dependent methylation reaction is usually performed under pressure. Methylation  
215 at lower temperatures under atmospheric pressure can proceed in the presence of quaternary ammonium  
216 salts [43,44], ionic liquid [45], a strong cyclic amidine base [46,47], such as DBU, and 1,4-  
217 diazabicyclo[2.2.2]octane, or microwave heating [47].



218  
219 **Scheme 1.** Dual reactivity of dimethyl carbonate [25,39–42] and MeSesamol syntheses using dimethyl carbonate as the methylating  
220 agent

221

222 A DBU catalyst with  $K_2CO_3$  base afforded MeSesamol in 74% yield but the reaction time was excessively  
223 long (30 h; see entry 1 of Table 1). After replacing DBU with a DBN or CTAB catalyst, the reaction time was

marginally shortened but the yields were slightly lower (entries 2–3 in Table 1). Replacing the K<sub>2</sub>CO<sub>3</sub> base with DBU allowed a homogeneous reaction with a greatly enhanced reaction rate (entries 4–5 in Table 1). The methanol produced during this reaction lowered the reflux temperature but could be continuously removed to promote methylation. The loss of DMC was successfully prevented by enhancing the plate number of the distillation unit. The use of a Vigreux column (see Fig. S1 in the Supplementary material for the reaction apparatus) removed the need for continuous DMC replenishment (entry 5 of Table 1). Overall, this efficient and green method can methylate sesamol under atmospheric pressure, obtaining MeSesamol with 89%–92% yield in 3 h.

232

**Table 1.** Synthesis of MeSesamol using DMC as the methylating agent

| Entry | Catalyst    | Base                                  | DMC                 | MeOH removal | Reaction time [h] | Yield [%] |
|-------|-------------|---------------------------------------|---------------------|--------------|-------------------|-----------|
| 1     | 0.2 eq DBU  | 1.1 eq K <sub>2</sub> CO <sub>3</sub> | 8.2 eq              | ✗            | 30                | 74        |
| 2     | 0.2 eq DBN  | 1.1 eq K <sub>2</sub> CO <sub>3</sub> | 8.2 eq              | ✗            | 26                | 63        |
| 3     | 0.4 eq CTAB | 1.1 eq K <sub>2</sub> CO <sub>3</sub> | 8.2 eq              | ✗            | 22                | 62        |
| 4     | 1.5 eq DBU  |                                       | 8.2 eq <sup>a</sup> | ✓            | 2                 | 91        |
| 5     | 1.5 eq DBU  |                                       | 4.9 eq <sup>b</sup> | ✓            | 3                 | 89–92     |

<sup>a</sup> DMC was replenished to its initial volume every half hour; <sup>b</sup> DMC loss was prevented using a Vigreux column

### 3.2. Properties of MeSesamol

The physical properties of MeSesamol are summarized in Table 2. MeSesamol is a colorless-to-pale-yellow liquid with a pleasant smell that can potentially assist the detection of solvent spills and leaks during industrial processes. MeSesamol has a relatively high boiling point (229–230 °C) and consequently a low vapor pressure and low exposure risk to humans. However, as the removal of MeSesamol from the product solution by distillation is energy-intensive, it should be replaced by crystallization or extraction from MeSesamol. From DSC measurements, the melting point of MeSesamol was determined as –18 °C (see Figure S23B in the Supplementary Material). MeSesamol showed a higher density at 23 °C (1.21 g mL<sup>–1</sup>) than conventional PASs (DMF: 0.95 g mL<sup>–1</sup>, DMSO: 1.10 g mL<sup>–1</sup>, NMP: 1.03 g mL<sup>–1</sup>) and medium viscosity (4.14 mPas). The flash point can provide valuable information on the potential safety risks of solvents, which are flammable. The higher open-cup flash point of MeSesamol (123 °C) than those of DMSO (95 °C), DMF (58 °C), DMAc (70 °C), and NMP (86 °C) implies that MeSesamol is safer than conventional solvents.

247

**Table 2.** Physical properties of MeSesamol and common bio-based solvents

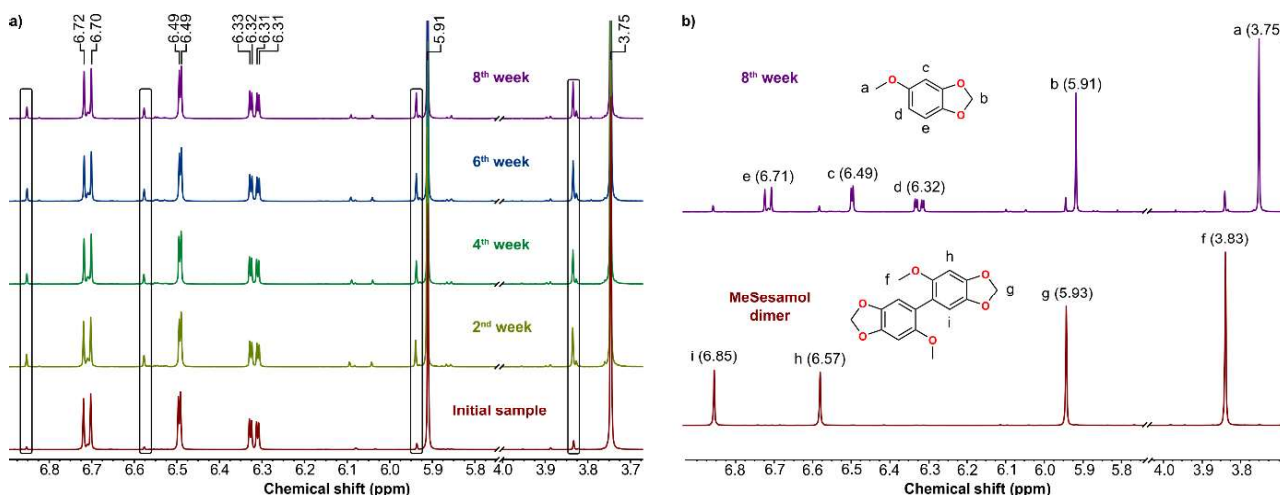
| Green solvent    | Boiling point [°C] | Melting point [°C] | Density [g mL <sup>–1</sup> ] | Viscosity [mPas] | Flash point [°C] |
|------------------|--------------------|--------------------|-------------------------------|------------------|------------------|
| GVL              | 207–208            | –31                | 1.05                          | 1.86             | 96 <sup>a</sup>  |
| <i>p</i> -Cymene | 177                | –68                | 0.86                          | 3.40             | 52 <sup>b</sup>  |

|           |         |     |      |      |                  |
|-----------|---------|-----|------|------|------------------|
| Cyrene    | 226     | -20 | 1.25 | 14.5 | 108 <sup>b</sup> |
| MeSesamol | 229–230 | -18 | 1.21 | 4.14 | 123 <sup>a</sup> |

<sup>a</sup> open-cup flash point; <sup>b</sup> closed-cup flash point

The stability of MeSesamol was tested under different conditions: in a closed transparent vial, under air exposure, under sparging with argon gas, and in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT). BHT is widely used to prevent oxidation of ethereal solvents (e.g., tetrahydrofuran [THF]) and consequent formation of free radical-mediated peroxide. Using peroxide strips, we confirmed that no peroxide formed in MeSesamol after two-months of storage. During the eight-week period, the samples were also investigated weekly by <sup>1</sup>H-NMR. Under all tested conditions, new signals appeared in the <sup>1</sup>H-NMR spectra after one week (Fig. 2a). The new signals close to the NMR signals of MeSesamol were assigned to dimerization of MeSesamol [48,49]. To check this assignment, the dimer was synthesized and its structure was confirmed by two-dimensional NMR (Figs. S19–22). Comparing the NMR spectra obtained during the stability study with that of the synthesized dimer, we concluded that MeSesamol was dimerized during storage (Fig. 2b).

The products of organic syntheses often contain impurities of trace solvents. Therefore, to assist the identification of MeSesamol as a residual solvent, we measured the NMR spectra of MeSesamol in dimethylsulfoxide-*d*<sub>6</sub>, CDCl<sub>3</sub>, CD<sub>3</sub>OD, CD<sub>3</sub>CN, acetone-*d*<sub>6</sub>, THF-*d*<sub>8</sub>, and toluene-*d*<sub>8</sub> (subsection 2.4.1. in the Supporting Material) and submitted them to the recently established and searchable NMR-impurity database [50].



**Fig. 2.** Comparison of <sup>1</sup>H-NMR spectra of MeSesamol obtained weekly (a) and the MeSesamol dimer (b)

The thermal stability of MeSesamol was assessed over five days at 100 °C. Although a yellow discoloration was observed over time, the HPLC and NMR results showed no detectable changes (refer to Section 7 in the Supplementary Material). MeSesamol also remained stable over five days in the presence of common acids

272 and bases. The selected acids [hydrochloric acid (1 M), acetic acid, and trifluoroacetic acid) and bases  
 273 (sodium hydroxide solution (1 M), triethylamine, and pyridine] are commonly used in organic chemical  
 274 reactions. Again, slight discoloration was observed in several cases, but the HPLC and NMR results remained  
 275 unchanged (refer to Fig. S17 in the Supplementary Material).

276 Miscibility tests were performed in 19 organic solvents and water (Section 9 in the Supplementary  
 277 material). All organic solvents were fully miscible with MeSesamol within the tested range of solvent ratios  
 278 (4:1 to 1:4) but no apparent miscibility was observed with water. We thus determined the exact solubility of  
 279 water using HPLC. The water solubility of MeSesamol was 1.15 g L<sup>-1</sup> at room temperature. In comparison,  
 280 cyrene and GVL were fully miscible with water, 2-MeTHF was highly soluble in water (solubility = 140 g L<sup>-1</sup>),  
 281 and *p*-cymene was partially soluble in water (solubility = 20 mg L<sup>-1</sup>). The nonmiscibility of MeSesamol with  
 282 water is advantageous for extractions as it facilitates the reaction work-up.

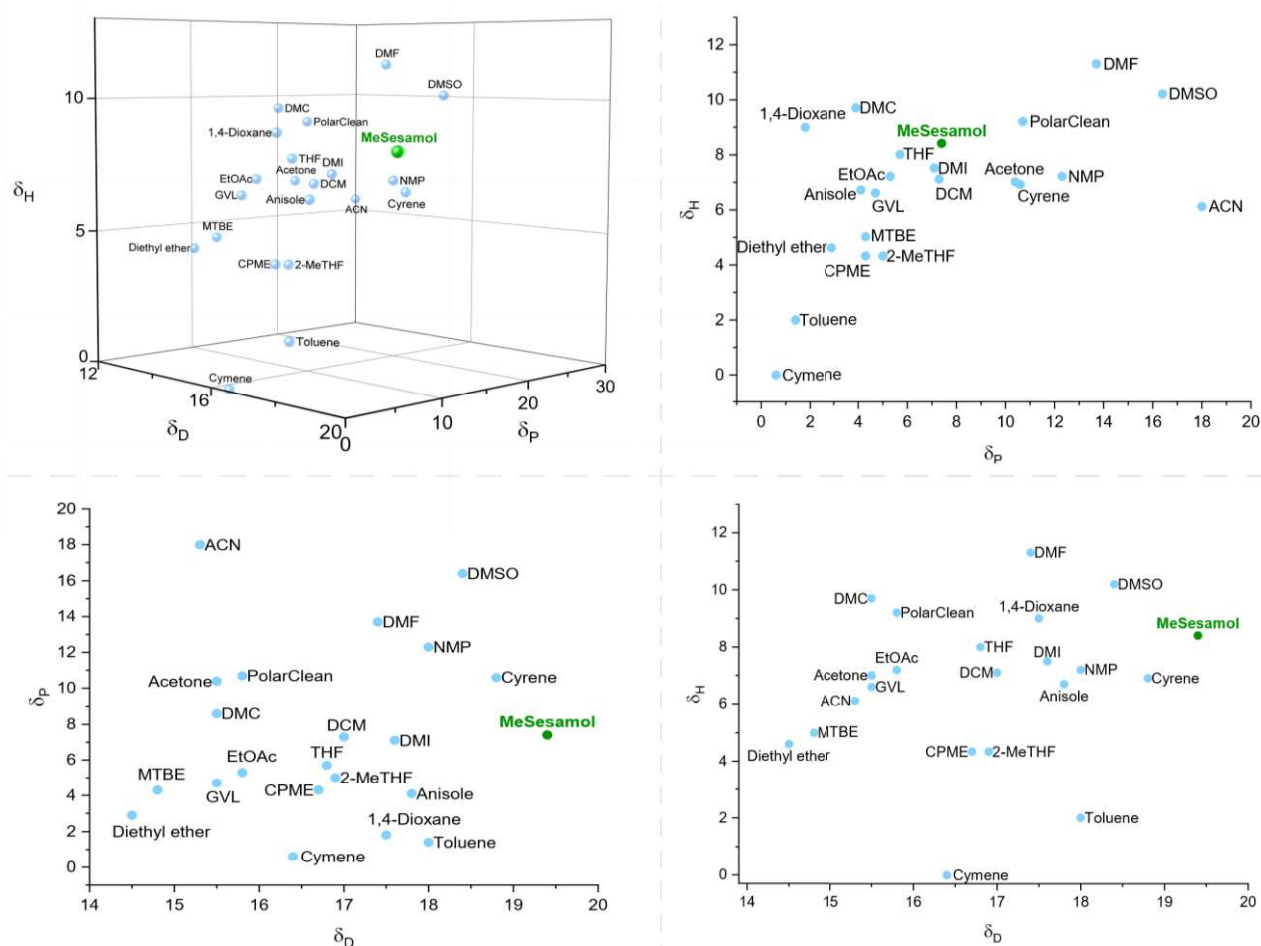
283 The miscibilities of the solvents and compatibilities of MeSesamol with polymers were determined using  
 284 the Hansen solubility parameter (HSP) model. HSPs are useful for evaluating polymer synthesis, polymer  
 285 materials, and polymer degradation. The HSPs of MeSesamol were determined using HSPiP software and  
 286 compared with those of some commonly used organic and bio-based solvents (Fig. 3, Table S1). If two  
 287 solvents locate closely in Hansen space, that is, their Hansen distance ( $R_a$ ) is small, they probably have similar  
 288 solubility characteristics and dissolve the same types of solutes. The  $R_a$  values suggest that MeSesamol is a  
 289 greener alternative to DCM, THF, and NMP (Table 3).

290 **Table 3.** Calculated Hansen solubility parameters of MeSesamol and the solvents closest to MeSesamol in Hansen space, where  $\delta_D$ ,  
 291  $\delta_P$ , and  $\delta_H$  denote the dispersion, polar intermolecular, and hydrogen bonding forces, respectively.

| Class              | Solvent          | $\delta_D$ | $\delta_P$ | $\delta_H$ | Hildebrand values | $R_a$ |
|--------------------|------------------|------------|------------|------------|-------------------|-------|
|                    | MeSesamol        | 19.4       | 7.4        | 8.4        | 22.4              | –     |
| Green solvents     | DMI <sup>a</sup> | 17.6       | 7.1        | 7.5        | 20.4              | 3.72  |
|                    | Cyrene           | 18.8       | 10.6       | 6.9        | 22.7              | 3.73  |
|                    | Anisole          | 17.8       | 4.1        | 6.7        | 19.5              | 4.90  |
|                    | DCM              | 17         | 7.3        | 7.1        | 19.8              | 4.97  |
| Undesired solvents | THF              | 16.8       | 5.7        | 8          | 19.5              | 5.49  |
|                    | NMP              | 18         | 12.3       | 7.2        | 23.0              | 5.77  |

292 <sup>a</sup> dimethyl isosorbide

293

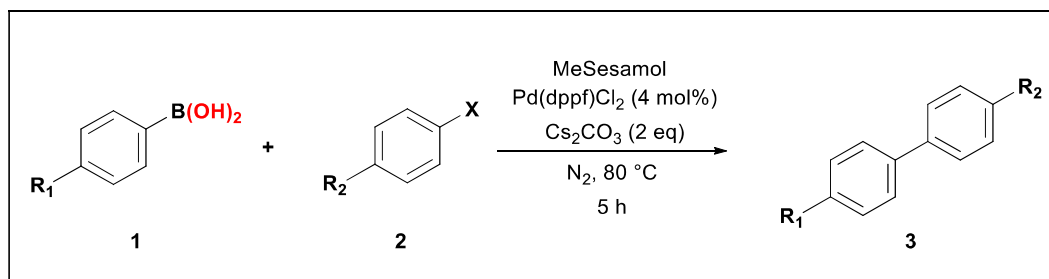


**Fig. 3.** Locations of MeSesamol and common organic solvents visualized in 3D Hansen space (upper left) and in 2D projected planes

### 3.3. Application of MeSesamol as a reaction media

The Suzuki–Miyaura cross-coupling reaction is widely used as a Pd-catalyzed C–C bond-forming reaction in chemical industries. The original Suzuki–Miyaura reaction was performed in THF, EtOH, and benzene solvents [51] but has since been achieved in environmentally friendly media such as water, biomass-derived solvents, deep eutectic solvents, and supercritical carbon dioxide [52]. Here we reacted iodo- (**2a**) or bromophenol (**2b**) and 4-methoxyphenylboronic acid (**1a**) using Pd(dppf)Cl<sub>2</sub> catalyst and MeSesamol solvent (entries 1–2 in Table 4). The scope of the reaction was further expanded to electron-rich and electron-deficient boronic acids and aryl halides (entries 3–11 of Table 4). As substitutes of the boronic acid derivative (**1a–1b**), electron-donating groups gave higher yields (72–87%; see entries 1–8 in Table 4) than the electron-withdrawing methoxycarbonyl groups (**1c**, 48–78%; see entries 9–11 of Table 4).

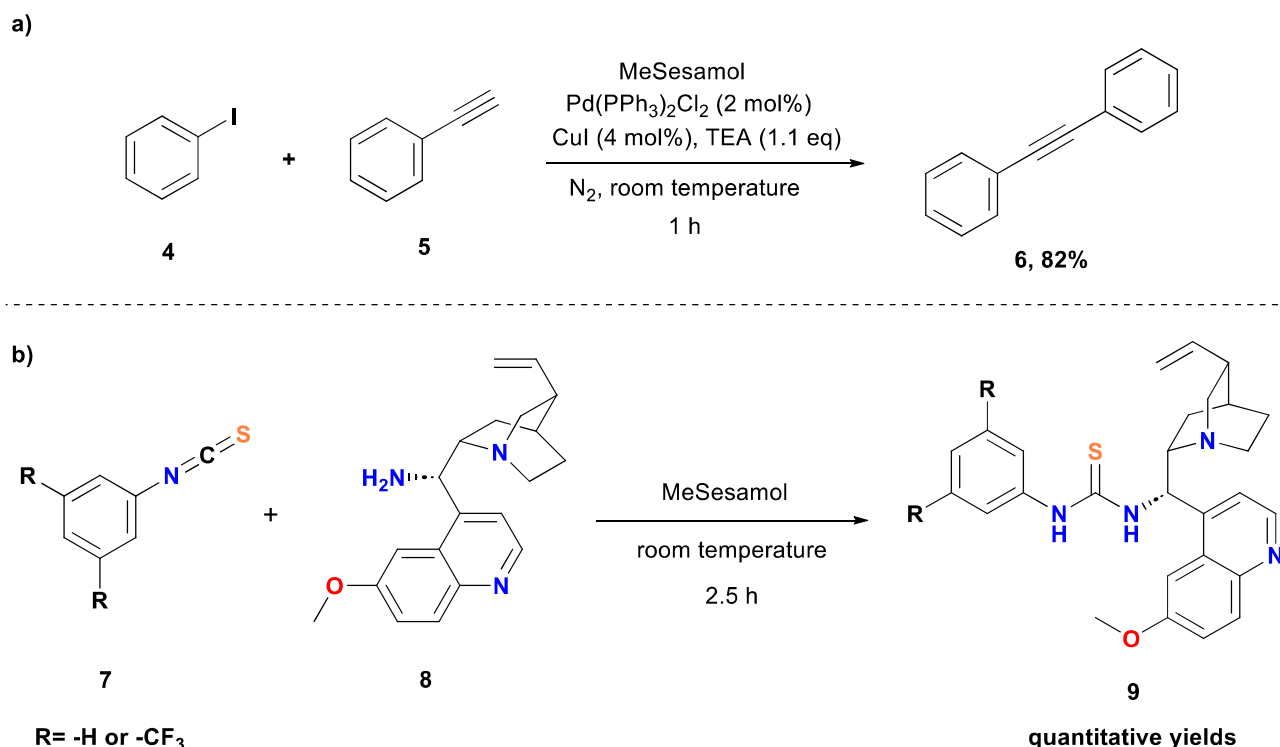
**Table 4.** Use of MeSesamol solvent in Suzuki–Miyaura cross-coupling reactions



| Entry | R <sub>1</sub>       | R <sub>2</sub>     | X   | Yield <sup>a</sup> [%] |
|-------|----------------------|--------------------|-----|------------------------|
| 1     | –OMe ( <b>1a</b> )   | –OH ( <b>2a</b> )  | –I  | 72 (74) <sup>b</sup>   |
| 2     | –OMe ( <b>1a</b> )   | –OH ( <b>2b</b> )  | –Br | 74 (80) <sup>b</sup>   |
| 3     | –Me ( <b>1b</b> )    | –H ( <b>2c</b> )   | –I  | 84                     |
| 4     | –Me ( <b>1b</b> )    | –H ( <b>2d</b> )   | –Br | 80                     |
| 5     | –Me ( <b>1b</b> )    | –OMe ( <b>2e</b> ) | –Br | 79                     |
| 6     | –OMe ( <b>1a</b> )   | –H ( <b>2c</b> )   | –I  | 83                     |
| 7     | –OMe ( <b>1a</b> )   | –H ( <b>2d</b> )   | –Br | 87                     |
| 8     | –OMe ( <b>1a</b> )   | –OMe ( <b>2e</b> ) | –Br | 77                     |
| 9     | –COOMe ( <b>1c</b> ) | –H ( <b>2c</b> )   | –I  | 54                     |
| 10    | –COOMe ( <b>1c</b> ) | –H ( <b>2d</b> )   | –Br | 78                     |
| 11    | –COOMe ( <b>1c</b> ) | –OMe ( <b>2e</b> ) | –Br | 48                     |

<sup>a</sup> NMR yield with ethylene carbonate as the internal standard; <sup>b</sup> isolated yield, dppf: 1,1'-bis(diphenylphosphino)ferrocene

MeSesamol was also applied as the solvent in *sp*<sup>2</sup>–*sp* carbon–carbon bond formation via the Sonogashira reaction. When iodobenzene (**4**) was coupled with phenylacetylene (**5**) using Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, copper iodide co-catalysts and triethylamine base, the product (**6**) was obtained in high isolated yield (82%) at room temperature (Scheme 2a).



**Scheme 2.** MeSesamol as a solvent in (a) the Sonogashira cross-coupling reaction and (b) thiourea synthesis

Recently, interest in organocatalysis has increased since David MacMillan and Benjamin List were awarded the 2021 Nobel Prize for their groundbreaking work in asymmetric organocatalysis [53]. Thioureas—a class of hydrogen-bond organocatalysts—are among the most widely used organocatalysts owing to their excellent catalytic activity in various organic transformations. The thiourea moiety combined with a chiral backbone (such as a cinchona alkaloid) can be used in enantioselective reactions such as asymmetric Michael addition [54]. For example, Hayashi [55] reported a key role for asymmetric Michael addition (a conjugate addition reaction) in the enantioselective formation of carbon–carbon bonds in chiral active pharmaceutical ingredients (e.g., oseltamivir, prostaglandin E1, and baclofen) [55].

Here we synthesized two cinchona alkaloid-derived thiourea organocatalysts (**8**) starting from the corresponding isothiocyanate (**7**) applying MeSesamol as the solvent. The nucleophilic addition of cinchona amine (**8**) to isothiocyanate (**7**) gave the thiourea organocatalyst (**9**) in quantitative yield (Scheme 2b). The synthesized thiourea organocatalysts were applied to the asymmetric Michael addition of acetylacetone (**10**) and *trans*- $\beta$ -nitrostyrene (**11**). To further expand the application possibilities of MeSesamol as solvent, we additionally synthesized four squaramide organocatalysts. Like thioureas, squaramides act as double-hydrogen-bond donors in organocatalytic reactions. To prove the similar solubility characteristics of MeSesamol and DCM (as implied by the HSPs in Table 3), all reactions were also carried out in DCM (Fig. 4). In all cases, the yields and enantiomeric excess values in MeSesamol were similar to or better than those obtained in DCM. Our findings demonstrate that MeSesamol is a greener alternative to DCM with competitive performance.

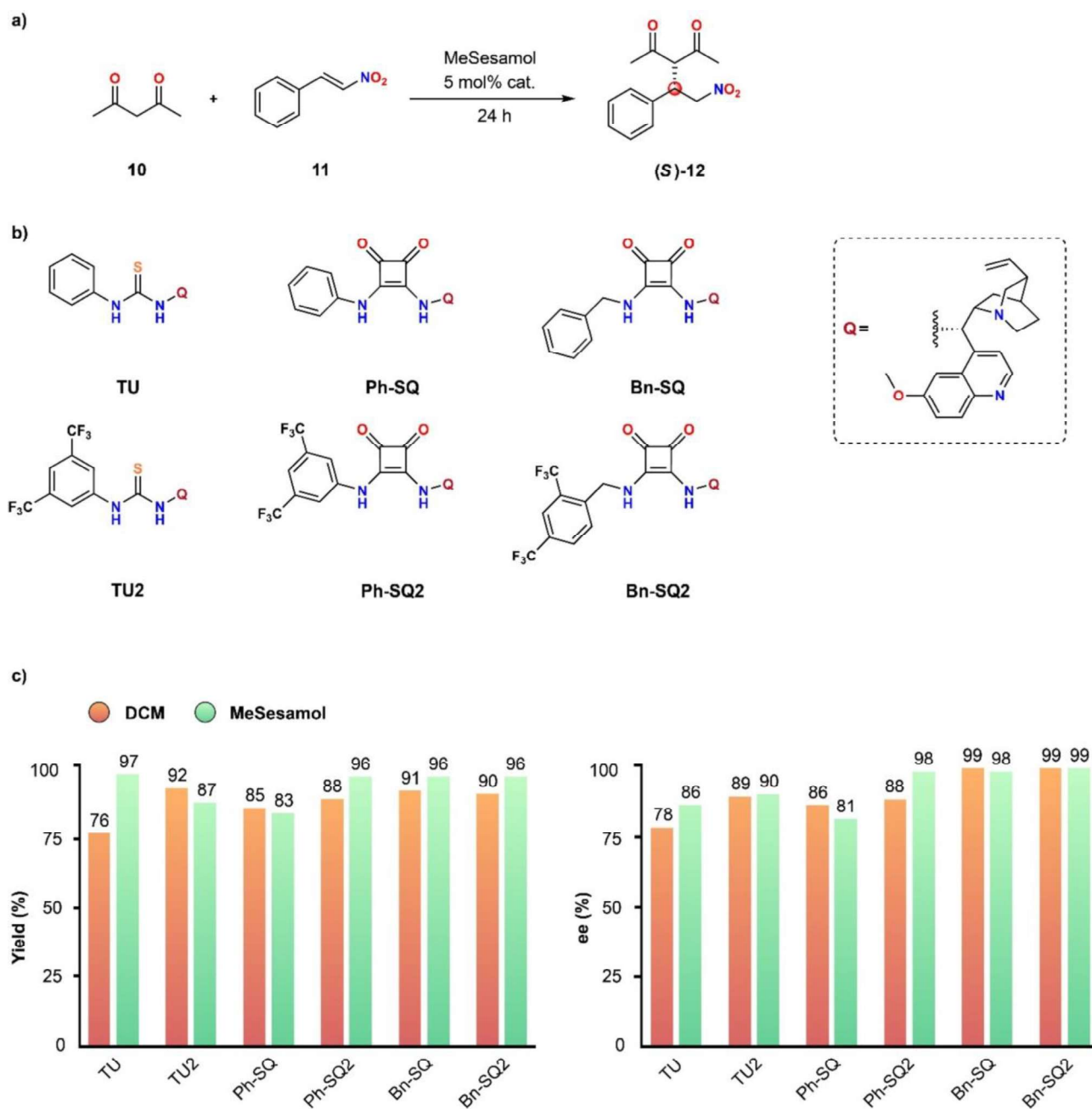
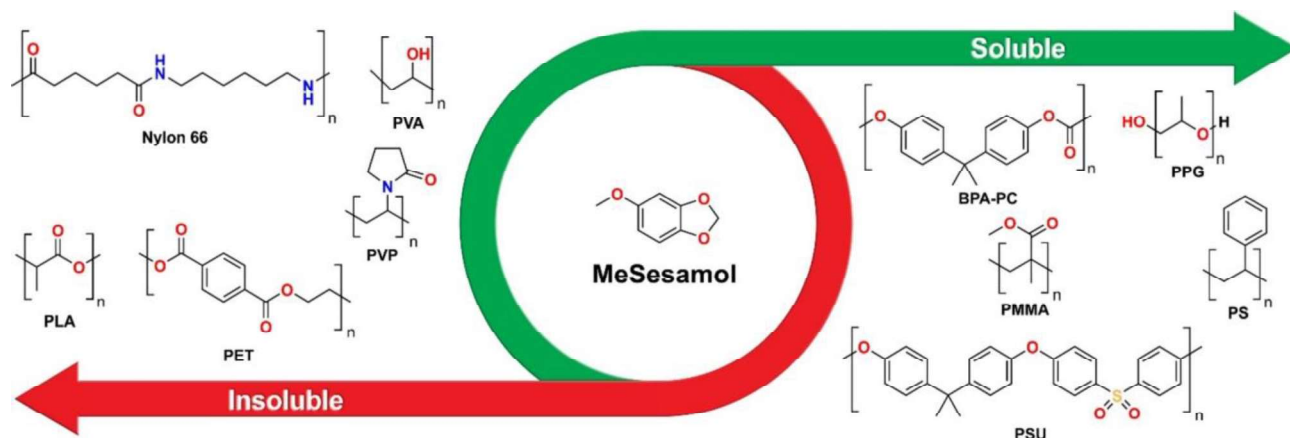


Fig. 4. Application of MeSesamol in an asymmetric Michael addition model reaction (a), the structure of organocatalysts used in this reaction scope (b), reaction yields and enantiomeric excess values using DCM and MeSesamol as solvents in the model reactions (c)

### 3.4. Application of MeSesamol in polymer science

Another essential property of solvents is high solubilization power. To reduce environmental impacts, polymer science is increasingly adopting green solvents in processes ranging from polymer fabrication to polymer degradation [56–60]. From an industrial perspective, expanding the palette of green alternatives that can replace traditional polar aprotic solvents (e.g., NMP, DMF, DMAc) poses a major challenge [59,61]. The HSP values place MeSesamol within the polar aprotic region of Hansen space, suggesting that MeSesamol is a good solvent choice for several polymers. The solubility performance of MeSesamol was evaluated

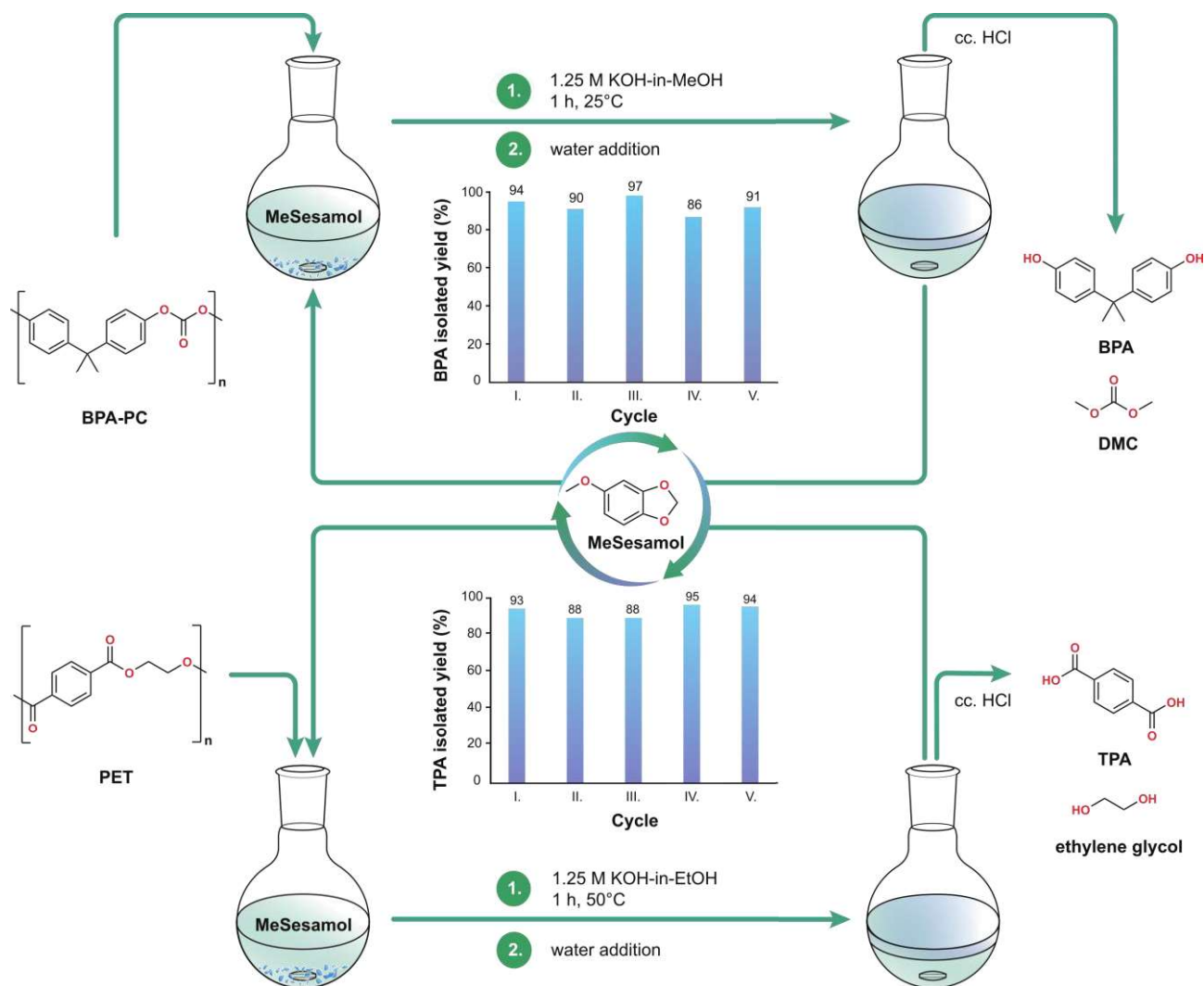
347 through solubility trials on conventional and emerging polymers (see Section 12 in the Supplementary  
 348 Material). The solubility properties of the most common polymers are shown in Fig. 5.



349  
 350 **Fig. 5.** Solubilizability of polymers with MeSesamol (all polymers are listed in Table S3)

351

352 BPA–PC was found to be soluble in MeSesamol at room temperature, opening opportunities for BPA–PC  
 353 depolymerization in the highly efficient KMH system. Depolymerization was completed within a remarkably  
 354 short time (within 1 h) at room temperature. After adding water to the reaction mixture, the reactants were  
 355 facily separated from the valuable monomers. This method also allowed the straightforward recovery and  
 356 reuse of MeSesamol. As shown in Fig. 6, MeSesamol was recycled through four additional reactions with no  
 357 significant change in monomer yields. To isolate BPA, the pH was adjusted with aqueous HCl solution. This  
 358 process induced the formation of potassium chloride, a valuable by-product with wide-ranging applications  
 359 from fertilizers to medicine and food processing. Moreover, the other by-product, namely dimethyl  
 360 carbonate, can be used for the preparation of MeSesamol. Throughout the five reaction cycles, MeSesamol  
 361 was recycled with high efficiency (96–100%) and achieved high BPA yields (up to 97%; see Fig. 6).



**Fig. 6.** MeSesamol as a recyclable solvent in the depolymerization of BPA–PC and PET. Upon completion of the reaction, water was added, the product was isolated from the aqueous phase, while MeSesamol was reused in another reaction cycle.

PET can be chemically recycled under basic conditions. Full conversion during PET hydrolysis usually requires high temperatures (above 100 °C) and takes several hours [62]. Although PET is insoluble in MeSesamol at room temperature (Fig. 5), considerable swelling of the polymer was observed in MeSesamol. Similarly to BPA–PC depolymerization, we thus implemented the depolymerization reaction in the KOH-in-alcohol system at 50 °C (Figs. 6 and S34). To improve the environmental friendliness of the depolymerization process, MeOH was replaced with EtOH, a less toxic, mass-produced green solvent from renewable sources. MeSesamol was also recycled after water addition and reused in additional reaction cycles. Over five reaction cycles in the KOH-in-MeOH system, the MeSesamol recovery was high (92–96%) and the TPA yields were excellent (82–92%) (Fig. S34). The TPA yields (88–95%) in the KOH-in-EtOH system were slightly higher than in KOH-in-MeOH system over the five reaction cycles. Therefore, the KOH-in-EtOH process is favorable in terms of HSE and yield.

MeSesamol played an essential role in the depolymerization reactions. Under the same conditions but without MeSesamol, the depolymerization conversion rates of BPA-PC and PET were only 5% and 28%, respectively. As efficient, low-temperature depolymerization methods for BPA-PC and PET are scarce in the literature, the exploitation of MeSesamol and optimization of its reaction conditions are recommended as future work.

### 3.5. Sustainability assessment

Recently, Thielemans and co-workers proposed a new green metric for comparing PET and BPA-PC depolymerization methods [17,20,62]. This metric, called the environmental energy impact ( $\xi$ , Eq. 2), is calculated as the ratio of the environmental factor ( $E_{factor}$ ) to the energy-economy factor ( $\varepsilon$ ). The latter is a function of the yield  $Y$ , the reaction temperature  $T$ , and the reaction time  $t$  (Eq. 3). The authors also suggested modifying  $E_{factor}$  as Eq. 4, because an estimated 90% of the solvent can be recycled through industrial processes [62]. Although the energy-economy factor can be usefully compared among different techniques at elevated temperatures, it ignores an important fact: reactions at ambient temperatures have no extra energy demand. Therefore, we propose an energy-economy factor that also makes reactions at standard ambient temperature (25 °C) comparable (Eq. 5.1). To avoid division by zero, we let  $\varepsilon_{corr}$  equal the reaction yield at 25 °C (Eq. 5.2). This adjustment allows better comparisons of the energy impacts among reactions, even those conducted at ambient temperatures, because lowering the reaction temperature lowers the energy demand, thus increasing the  $\varepsilon_{corr}$  (Table 6; see Supplementary Material for details). Moreover, the energy demands of ambient temperature reactions decisively depend on the reaction time, as the  $\varepsilon_{corr}$  values of such reactions are almost identical. Eqs. (2)–(5) are given as

$$\xi = \frac{E_{factor}}{\varepsilon} \quad (2)$$

$$\varepsilon = \frac{Y}{T \cdot t} \quad (3)$$

$$E_{factor} = \frac{[0.1 \cdot (\frac{\text{solvent}}{\text{polymer}} \text{ mass ratio}) + \frac{\text{catalyst}}{\text{polymer}} \text{ mass ratio} + \frac{\text{other substances}}{\text{polymer}} \text{ mass ratio}] \cdot m_{polymer}}{Y \cdot \frac{MM_{product}}{MM_{polymer}} \cdot m_{polymer}} \quad (4)$$

$$\varepsilon_{corr} = \frac{Y}{(T - 25 \text{ }^{\circ}\text{C}) \cdot t} \quad (5.1)$$

$$\varepsilon_{corr} = Y \quad \text{if } T = 25 \text{ }^{\circ}\text{C} \quad (5.2)$$

As shown in Table 5, our method has a slightly higher energy-economy factor than some of the most prominent BPA-PC depolymerization methods reported in the literature (see Supplementary Material for details). Comparing the green chemistry metrics between our method and other PET depolymerization processes (Table 6, see Supplementary Material for details), our method is one of the lowest-temperature alkaline-hydrolysis methods for the conversion of waste PET, although the  $\varepsilon_{corr}$  is an order of magnitude larger in microwave-assisted depolymerizations than in the conventional heating used in our method. Microwave heating offers an extremely short reaction time, thus, it has great  $\varepsilon_{corr}$  value; however, microwave-heated

409 methods are potentially difficult to scale-up. Overall, BPA-PC and PET chemolytic depolymerization in  
 410 MeSesamol solvent achieves outstanding performance and MeSesamol can be recycled through several  
 411 reactions, reducing waste generation.

412

413 **Table 5.** Green chemistry metrics of our method and the most prominently reported BPA-PC depolymerization methods, calculated  
 414 using the corrected energy-economy coefficient

| Ref                  | T<br>[°C] | Reaction<br>time<br>[min] | Catalyst | Solvent              | Reaction<br>condition   | $\epsilon$<br>[°C <sup>-1</sup> min <sup>-1</sup> ] | $\xi$<br>[°C min] | $\epsilon_{\text{corr}}$<br>[°C <sup>-1</sup> min <sup>-1</sup> ] | $\xi_{\text{corr}}$<br>[°C min] |
|----------------------|-----------|---------------------------|----------|----------------------|-------------------------|-----------------------------------------------------|-------------------|-------------------------------------------------------------------|---------------------------------|
| [63]                 | 67        | 10                        | NaOH     | THF+H <sub>2</sub> O | MW                      | $1.2 \times 10^{-3}$                                | 495               | $1.9 \times 10^{-3}$                                              | 310                             |
| [63]                 | 67        | 10                        | KOH      | THF+H <sub>2</sub> O | MW                      | $1.2 \times 10^{-3}$                                | 493               | $1.9 \times 10^{-3}$                                              | 309                             |
| [64]                 | 40        | 10                        | NaOH     | NMP+MeOH             | conventional<br>heating | $1.9 \times 10^{-3}$                                | 236               | $4.9 \times 10^{-3}$                                              | 88                              |
| [64]                 | 40        | 35                        | NaOH     | THF+MeOH             | conventional<br>heating | $6.8 \times 10^{-4}$                                | 553               | $1.8 \times 10^{-3}$                                              | 207                             |
| [65]                 | 30        | 15                        | NaOH     | THF+MeOH             | ultrasound              | $2.1 \times 10^{-3}$                                | 225               | $1.3 \times 10^{-3}$                                              | 38                              |
| <b>This<br/>work</b> | 25        | 60                        | KOH      | MeSesamol<br>+ MeOH  | conventional<br>heating | $6.1 \times 10^{-4}$                                | 7973              | $9.2 \times 10^{-1}$                                              | 5                               |

415

416 **Table 6.** Green chemistry metrics of PET depolymerization ordered by decreasing temperature, calculated using the corrected energy-  
 417 economy factor

| Ref                  | T<br>[°C] | Reaction time<br>[min] | Catalyst           | Solvent               | Reaction<br>condition   | $\epsilon_{\text{corr}}$<br>[°C <sup>-1</sup> min <sup>-1</sup> ] | $\xi_{\text{corr}}$<br>[°C min] |
|----------------------|-----------|------------------------|--------------------|-----------------------|-------------------------|-------------------------------------------------------------------|---------------------------------|
| [66]                 | 220       | 2                      | NaOH (aq)          | H <sub>2</sub> O      | MW                      | $2.5 \times 10^{-3}$                                              | 266                             |
| [17]                 | 120       | 1                      | KOH                | MeOH                  | MW                      | $9.9 \times 10^{-3}$                                              | 198                             |
| [67]                 | 110       | 30                     | NaOH (aq)          | EtOH+H <sub>2</sub> O | conventional<br>heating | $3.5 \times 10^{-4}$                                              | 18618                           |
| [68]                 | 90        | 45                     | NaOH (aq),<br>TBAI | H <sub>2</sub> O      | ultrasound              | $3.4 \times 10^{-4}$                                              | 11610                           |
| [19]                 | 80        | 60                     | KOH                | EtOH+H <sub>2</sub> O | conventional<br>heating | $3.0 \times 10^{-4}$                                              | 8049                            |
| <b>This<br/>work</b> | 50        | 60                     | KOH                | MeSesamol<br>+EtOH    | conventional<br>heating | $6.1 \times 10^{-4}$                                              | 8267                            |

## 418 Conclusion

419 We have demonstrated the green synthesis and multiple applications of MeSesamol as a new bio-based  
 420 solvent. Methylation with DMC afforded MeSesamol in excellent yield (up to 91%) after only 3 h. We  
 421 determined the main physical properties and stability of MeSesamol under practically relevant conditions.  
 422 MeSesamol is advantaged by a high boiling point (which reduces environmental emissions and human  
 423 exposure), a high open-cup flash point, water immiscibility, and a pleasant distinctive smell. We  
 424 demonstrated that undesired PASS and DCM can be potentially replaced with MeSesamol in several  
 425 reactions, including the cross-coupling Suzuki and Sonogashira reactions, thiourea syntheses, and  
 426 asymmetric Michael additions. To facilitate the uptake of MeSesamol in polymer science, we measured the  
 427 solubilities of 44 polymers in MeSesamol. BPA-PC and PET were fully depolymerized in MeSesamol with high

monomer yields (up to 97%). As MeSesamol is immiscible with water, it was efficiently recycled after depolymerization via simple phase separation. Meanwhile, owing to the excellent solubilization power of MeSesamol, the proposed method degraded the polymers at much lower temperatures than previously described methods while delivering comparable or superior energy-economy impact. Energy-economy is of paramount importance for solving the modern energy crisis.

## Acknowledgment

The authors are grateful to Zsuzsanna Feher, Johanna Kiss, and Reka Nemeth from the Budapest University of Technology and Economics for their helpful advice on the depolymerization of polymers. This research was funded by the National Research, Development, and Innovation Office (grant number FK138037), the Richter Gedeon Excellence PhD Scholarship of the Richter Gedeon Talentum Foundation, Richter Gedeon Plc. (G. D.) and the King Abdullah University of Science and Technology (KAUST). Further support was provided by the UNKP-22-1-I-BME-144 and UNKP-22-2-II-BME-145 New National Excellence Program of the Ministry for Culture and Innovation sourced from the National Research, Development and Innovation Fund.

## References

- [1] E.A. Aboagye, J.D. Chea, K.M. Yenkie, Systems level roadmap for solvent recovery and re-use in industries, *IScience*. 24 (2021) 103114. <https://doi.org/10.1016/J.ISCI.2021.103114>.
- [2] SDGs-Chemistry, (n.d.). <https://www.acs.org/sustainability/chemistry-sustainable-development-goals.html>.
- [3] M.C. Bryan, P.J. Dunn, D. Entwistle, F. Gallou, S.G. Koenig, J.D. Hayler, M.R. Hickey, S. Hughes, M.E. Kopach, G. Moine, P. Richardson, F. Roschangar, A. Steven, F.J. Weiberth, Key Green Chemistry research areas from a pharmaceutical manufacturers' perspective revisited, *Green Chem.* 20 (2018) 5082–5103. <https://doi.org/10.1039/C8GC01276H>.
- [4] C.J. Clarke, W.C. Tu, O. Levers, A. Bröhl, J.P. Hallett, Green and Sustainable Solvents in Chemical Processes, *Chem. Rev.* 118 (2018) 747–800. <https://doi.org/10.1021/acs.chemrev.7b00571>.
- [5] C.M. Alder, J.D. Hayler, R.K. Henderson, A.M. Redman, L. Shukla, L.E. Shuster, H.F. Sneddon, Updating and further expanding GSK's solvent sustainability guide, *Green Chem.* 18 (2016) 3879–3890. <https://doi.org/10.1039/C6GC00611F>.
- [6] K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy,

- 459 D.A. Perry, M. Stefaniak, Green chemistry tools to influence a medicinal chemistry and research  
460 chemistry based organisation, *Green Chem.* 10 (2008) 31–36. <https://doi.org/10.1039/B711717E>.
- 461 [7] L.J. Diorazio, D.R.J. Hose, N.K. Adlington, Toward a More Holistic Framework for Solvent Selection,  
462 *Org. Process Res. Dev.* 20 (2016) 760–773. <https://doi.org/10.1021/acs.oprd.6b00015>.
- 463 [8] D. Prat, O. Pardigon, H.W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S.  
464 Ruisseau, P. Cruciani, P. Hosek, Sanofi’s Solvent Selection Guide: A Step Toward More Sustainable  
465 Processes, *Org. Process Res. Dev.* 17 (2013) 1517–1525. <https://doi.org/10.1021/op4002565>.
- 466 [9] F.P. Byrne, S. Jin, G. Paggiola, T.H.M. Petchey, J.H. Clark, T.J. Farmer, A.J. Hunt, C. Robert McElroy, J.  
467 Sherwood, Tools and techniques for solvent selection: green solvent selection guides, *Sustain. Chem.*  
468 *Process.* 4 (2016) 1–24. <https://doi.org/10.1186/S40508-016-0051-Z>.
- 469 [10] A. Jordan, P. Stoy, H.F. Sneddon, Chlorinated Solvents: Their Advantages, Disadvantages, and  
470 Alternatives in Organic and Medicinal Chemistry, *Chem. Rev.* 121 (2021) 1582–1622.  
471 [https://doi.org/10.1021/ACS.CHEMREV.0C00709/SUPPL\\_FILE/CROC00709\\_SI\\_001.PDF](https://doi.org/10.1021/ACS.CHEMREV.0C00709/SUPPL_FILE/CROC00709_SI_001.PDF).
- 472 [11] A. Jordan, C.G.J. Hall, L.R. Thorp, H.F. Sneddon, Replacement of Less-Preferred Dipolar Aprotic and  
473 Ethereal Solvents in Synthetic Organic Chemistry with More Sustainable Alternatives, *Chem. Rev.* 122  
474 (2022) 6749–6794.  
475 [https://doi.org/10.1021/ACS.CHEMREV.1C00672/ASSET/IMAGES/LARGE/CR1C00672\\_0046.JPEG](https://doi.org/10.1021/ACS.CHEMREV.1C00672/ASSET/IMAGES/LARGE/CR1C00672_0046.JPEG).
- 476 [12] J. Sherwood, J.H. Clark, I.J.S. Fairlamb, J.M. Slattery, Solvent effects in palladium catalysed cross-  
477 coupling reactions, *Green Chem.* 21 (2019) 2164–2213. <https://doi.org/10.1039/C9GC00617F>.
- 478 [13] K. Wegner, D. Barnes, K. Manzor, A. Jardine, D. Moran, Evaluation of greener solvents for solid-phase  
479 peptide synthesis, *Green Chem. Lett. Rev.* 14 (2021) 152–164.  
480 <https://doi.org/10.1080/17518253.2021.1877363>.
- 481 [14] Y.H. See Toh, F.W. Lim, A.G. Livingston, Polymeric membranes for nanofiltration in polar aprotic  
482 solvents, *J. Membr. Sci.* 301 (2007) 3–10. <https://doi.org/10.1016/J.MEMSCI.2007.06.034>.
- 483 [15] R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, *Sci. Adv.* 3 (2017).  
484 <https://doi.org/10.1126/SCIADV.1700782>.
- 485 [16] J.G. Kim, Chemical recycling of poly(bisphenol A carbonate), *Polym. Chem.* 11 (2020) 4830–4849.  
486 <https://doi.org/10.1039/C9PY01927H>.
- 487 [17] J.J. Rubio Arias, W. Thielemans, Instantaneous hydrolysis of PET bottles: an efficient pathway for the  
488 chemical recycling of condensation polymers, *Green Chem.* 23 (2021) 9945–9956.  
489 <https://doi.org/10.1039/D1GC02896K>.
- 490 [18] L.C. Hu, A. Oku, E. Yamada, K. Tomari, Alkali-Decomposition of Poly(ethylene terephthalate) in Mixed

- Media of Nonaqueous Alcohol and Ether. Study on Recycling of Poly(ethylene terephthalate), *Polym. J.* 29 (1997) 708–712. <https://doi.org/10.1295/polymj.29.708>.
- [19] X.-L. Wang, W.-L. An, R. Du, F. Tian, Y. Yang, X. Zhao, S. Xu, Y.-Z. Wang, Rapid hydrolysis of PET in high-concentration alcohol aqueous solution by pore formation and spontaneous separation of terephthalate, *J. Environ. Chem. Eng.* (2023) 109434. <https://doi.org/10.1016/J.JECE.2023.109434>.
- [20] J.J. Rubio Arias, E. Barnard, W. Thielemans, Ultrafast Simultaneous and Selective Depolymerization of Heterogeneous Streams of Polyethylene Terephthalate and Polycarbonate: Towards Industrially Feasible Chemical Recycling, *ChemSusChem*. 15 (2022) e202200625. <https://doi.org/10.1002/CSSC.202200625>.
- [21] Y. Gu, F. Jérôme, Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry, *Chem. Soc. Rev.* 42 (2013) 9550–9570. <https://doi.org/10.1039/C3CS60241A>.
- [22] J.H. Clark, T.J. Farmer, A.J. Hunt, J. Sherwood, Opportunities for Bio-Based Solvents Created as Petrochemical and Fuel Products Transition towards Renewable Resources, *Int. J. Mol. Sci.* 16 (2015) 17101–17159. <https://doi.org/10.3390/IJMS160817101>.
- [23] I.T. Horváth, H. Mehdi, V. Fábos, L. Boda, L.T. Mika,  $\gamma$ -Valerolactone—a sustainable liquid for energy and carbon-based chemicals, *Green Chem.* 10 (2008) 238–242. <https://doi.org/10.1039/B712863K>.
- [24] J.H. Clark, D.J. Macquarrie, J. Sherwood, A quantitative comparison between conventional and bio-derived solvents from citrus waste in esterification and amidation kinetic studies, *Green Chem.* 14 (2012) 90–93. <https://doi.org/10.1039/C1GC16299C>.
- [25] P. Tundo, F. Aricò, G. Gauthier, L. Rossi, A.E. Rosamilia, H.S. Bevinakatti, R.L. Sievert, C.P. Newman, Green Synthesis of Dimethyl Isosorbide, *ChemSusChem*. 3 (2010) 566–570. <https://doi.org/10.1002/CSSC.201000011>.
- [26] J. Sherwood, M. De bruyn, A. Constantinou, L. Moity, C.R. McElroy, T.J. Farmer, T. Duncan, W. Raverty, A.J. Hunt, J.H. Clark, Dihydrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents, *Chem. Commun.* 50 (2014) 9650–9652. <https://doi.org/10.1039/C4CC04133J>.
- [27] J.E. Camp, Bio-available Solvent Cyrene: Synthesis, Derivatization, and Applications, *ChemSusChem*. 11 (2018) 3048–3055. <https://doi.org/10.1002/CSSC.201801420>.
- [28] A.O. Komarova, G.R. Dick, J.S. Luterbacher, Diformylxylose as a new polar aprotic solvent produced from renewable biomass, *Green Chem.* 23 (2021) 4790–4799. <https://doi.org/10.1039/D1GC00641J>.
- [29] A. Randová, L. Bartovská, P. Morávek, P. Matějka, M. Novotná, S. Matějková, E. Drioli, A. Figoli, M. Lanč, K. Friess, A fundamental study of the physicochemical properties of Rhodiasolv®Polarclean: A

- 523 promising alternative to common and hazardous solvents, *J. Mol. Liq.* 224 (2016) 1163–1171.  
 524 <https://doi.org/10.1016/J.MOLLIQ.2016.10.085>.
- 525 [30] L. Cseri, G. Szekely, Towards cleaner PolarClean: efficient synthesis and extended applications of the  
 526 polar aprotic solvent methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate, *Green Chem.* 21 (2019)  
 527 4178–4188. <https://doi.org/10.1039/C9GC01958H>.
- 528 [31] K. Pan, Y. Fan, T. Leng, J. Li, Z. Xin, J. Zhang, L. Hao, J. Gallop, K.S. Novoselov, Z. Hu, Sustainable  
 529 production of highly conductive multilayer graphene ink for wireless connectivity and IoT applications,  
 530 *Nat. Commun.* 2018 91. 9 (2018) 1–10. <https://doi.org/10.1038/s41467-018-07632-w>.
- 531 [32] K.L. Wilson, J. Murray, C. Jamieson, A.J.B. Watson, Cyrene as a bio-based solvent for HATU mediated  
 532 amide coupling, *Org. Biomol. Chem.* 16 (2018) 2851–2854. <https://doi.org/10.1039/C8OB00653A>.
- 533 [33] K.L. M. Wilson Jane; Jamieson, Craig; Watson, Allan J. B., Cyrene as a Bio-Based Solvent for the Suzuki–  
 534 Miyaura Cross-Coupling, *Synlett.* 29 (2018) 650–654. <https://doi.org/10.1055/s-0036-1589143>.
- 535 [34] J.E. Camp, S.B. Nyamini, F.J. Scott, Cyrene<sup>TM</sup> is a green alternative to DMSO as a solvent for  
 536 antibacterial drug discovery against ESKAPE pathogens, *RSC Med. Chem.* 11 (2020) 111–117.  
 537 <https://doi.org/10.1039/C9MD00341J>.
- 538 [35] B. Vakulya, S. Varga, A. Csámpai, T. Soós, Highly enantioselective conjugate addition of nitromethane  
 539 to chalcones using bifunctional cinchona organocatalysts, *Org. Lett.* 7 (2005) 1967–1969.  
 540 <https://doi.org/10.1021/ol050431s>.
- 541 [36] G. Zhang, C. Zhu, D. Liu, J. Pan, J. Zhang, D. Hu, B. Song, Solvent-free enantioselective conjugate  
 542 addition and bioactivities of nitromethane to Chalcone containing pyridine, *Tetrahedron.* 73 (2017)  
 543 129–136. <https://doi.org/10.1016/J.TET.2016.11.063>.
- 544 [37] C. Didaskalou, J. Kupai, L. Cseri, J. Barabas, E. Vass, T. Holtzl, G. Szekely, Membrane-Grafted  
 545 Asymmetric Organocatalyst for an Integrated Synthesis-Separation Platform, *ACS Catal.* 8 (2018)  
 546 7430–7438. <https://doi.org/10.1021/acscatal.8b01706>.
- 547 [38] P.F. Schuda, W.A. Price, Total Synthesis of Isoflavones: Jamaicin, Calopogonium Isoflavone-B,  
 548 Pseudobaptigenin, and Maxima Substance-B. Friedel-Crafts Acylation Reactions with Acid-Sensitive  
 549 Substrates, *J. Org. Chem.* 52 (1987) 1972–1979. <https://doi.org/10.1021/JO00386A014>.
- 550 [39] G. Fiorani, A. Perosa, M. Selva, Dimethyl carbonate: a versatile reagent for a sustainable valorization  
 551 of renewables, *Green Chem.* 20 (2018) 288–322. <https://doi.org/10.1039/C7GC02118F>.
- 552 [40] Y. Ono, Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign  
 553 building block, *Appl. Catal. A Gen.* 155 (1997) 133–166. [https://doi.org/10.1016/S0926-860X\(96\)00402-4](https://doi.org/10.1016/S0926-860X(96)00402-4).

- 555 [41] P. Tundo, M. Selva, The Chemistry of Dimethyl Carbonate, *Acc. Chem. Res.* 35 (2002) 706–716.  
556 <https://doi.org/10.1021/AR010076F>.
- 557 [42] P.H. Vendramini, L.A. Zeoly, R.A. Cormanich, M. Buehl, M.N. Eberlin, B.R.V. Ferreira, Unveiling the  
558 mechanism of N-methylation of indole with dimethylcarbonate using either DABCO or DBU as  
559 catalyst, *J. Mass Spectrom.* 56 (2021) e4707. <https://doi.org/10.1002/JMS.4707>.
- 560 [43] A. Ben Taleb, G. Jenner, Scope of the N-alkylation of amides and the C-alkylation of malonates by  
561 methyl formate and dimethyl carbonate, *J. Mol. Catal.* 84 (1993) L131–L136.  
562 [https://doi.org/10.1016/0304-5102\(93\)85044-T](https://doi.org/10.1016/0304-5102(93)85044-T).
- 563 [44] S. Ouk, S. Thiebaud, E. Borredon, P. Legars, L. Lecomte, O-Methylation of phenolic compounds with  
564 dimethyl carbonate under solid/liquid phase transfer system, *Tetrahedron Lett.* 43 (2002) 2661–  
565 2663. [https://doi.org/10.1016/S0040-4039\(02\)00201-0](https://doi.org/10.1016/S0040-4039(02)00201-0).
- 566 [45] L.S. Zhen, Z.J. Xuan, M.M. Wei, X.H. Bao, N. Sun, Catalytic O-methylation of phenols with dimethyl  
567 carbonate to aryl methyl ethers using [BMIm]Cl, *Green Chem.* 7 (2005) 97–99.  
568 <https://doi.org/10.1039/B411201F>.
- 569 [46] W.C. Shieh, M. Lozanov, M. Loo, O. Repič, T.J. Blacklock, DABCO- and DBU-accelerated green  
570 chemistry for N-, O-, and S-benylation with dibenzyl carbonate, *Tetrahedron Lett.* 44 (2003) 4563–  
571 4565. [https://doi.org/10.1016/S0040-4039\(03\)00992-4](https://doi.org/10.1016/S0040-4039(03)00992-4).
- 572 [47] W.C. Shieh, S. Dell, O. Repič, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and microwave-accelerated  
573 green chemistry in methylation of phenols, indoles, and benzimidazoles with dimethyl carbonate, *Org.*  
574 *Lett.* 3 (2001) 4279–4281. <https://doi.org/10.1021/OL016949N>.
- 575 [48] Y. Makino, S. Uchiyama, K.I. Ohno, H. Arakawa, Low-cost fluorimetric determination of radicals based  
576 on fluorogenic dimerization of the natural phenol sesamol, *Anal. Chem.* 82 (2010) 1213–1220.  
577 <https://doi.org/10.1021/AC9029778>.
- 578 [49] K. Kikugawa, M. Arai, T. Kurechi, Participation of sesamol in stability of sesame oil, *J. Am. Oil Chem.*  
579 *Soc.* 60 (1983) 1528–1533. <https://doi.org/10.1007/BF02666577>.
- 580 [50] L. Cseri, S. Kumar, P. Palchuber, G. Szekely, NMR Chemical Shifts of Emerging Green Solvents, Acids,  
581 and Bases for Facile Trace Impurity Analysis, *ACS Sustain. Chem. Eng.* 11 (2023) 5696–5725.  
582 <https://doi.org/10.1021/acssuschemeng.3c00244>.
- 583 [51] N. Miyaura, K. Yamada, A. Suzuki, A new stereospecific cross-coupling by the palladium-catalyzed  
584 reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides, *Tetrahedron Lett.* 20 (1979) 3437–  
585 3440. [https://doi.org/10.1016/S0040-4039\(01\)95429-2](https://doi.org/10.1016/S0040-4039(01)95429-2).
- 586 [52] S.E. Hooshmand, B. Heidari, R. Sedghi, R.S. Varma, Recent advances in the Suzuki–Miyaura cross-

587 coupling reaction using efficient catalysts in eco-friendly media, *Green Chem.* 21 (2019) 381–405.  
 588 <https://doi.org/10.1039/C8GC02860E>.

589 [53] D. Castelvechi, E. Stoye, ‘Elegant’ catalysts that tell left from right scoop chemistry Nobel, *Nature*.  
 590 598 (2021) 247–248. <https://doi.org/10.1038/D41586-021-02704-2>.

591 [54] S.J. Connon, Asymmetric catalysis with bifunctional cinchona alkaloid -based urea and thiourea  
 592 organocatalysts, *Chem. Commun.* 0 (2008) 2499–2510. <https://doi.org/10.1039/B719249E>.

593 [55] Y. Hayashi, Pot economy and one-pot synthesis, *Chem. Sci.* 7 (2016) 866–880.  
 594 <https://doi.org/10.1039/c5sc02913a>.

595 [56] T. Erdmenger, C. Guerrero-Sanchez, J. Vitz, R. Hoogenboom, U.S. Schubert, Recent developments in  
 596 the utilization of green solvents in polymer chemistry, *Chem. Soc. Rev.* 39 (2010) 3317–3333.  
 597 <https://doi.org/10.1039/B909964F>.

598 [57] T. Marino, F. Galiano, A. Molino, A. Figoli, New frontiers in sustainable membrane preparation:  
 599 Cyrene™ as green bioderived solvent, *J. Membr. Sci.* 580 (2019) 224–234.  
 600 <https://doi.org/10.1016/J.MEMSCI.2019.03.034>.

601 [58] V.A. Pereira, P. V. Mendonça, J.F.J. Coelho, A.C. Serra, Liquid salts as eco-friendly solvents for atom  
 602 transfer radical polymerization: a review, *Polym. Chem.* 10 (2019) 4904–4913.  
 603 <https://doi.org/10.1039/C9PY00865A>.

604 [59] S. Fadlallah, A.A.M. Peru, L. Longé, F. Allais, Chemo-enzymatic synthesis of a levoglucosenone-derived  
 605 bi-functional monomer and its ring-opening metathesis polymerization in the green solvent Cyrene™,  
 606 *Polym. Chem.* 11 (2020) 7471–7475. <https://doi.org/10.1039/D0PY01471K>.

607 [60] M. Ramírez-Martínez, S.L. Aristizábal, G. Szekely, S.P. Nunes, Bio-based solvents for polyolefin  
 608 dissolution and membrane fabrication: from plastic waste to value-added materials, *Green Chem.*  
 609 (2022) 435–437. <https://doi.org/10.1039/D2GC03181G>.

610 [61] D. Kim, S.P. Nunes, Green solvents for membrane manufacture: Recent trends and perspectives, *Curr.*  
 611 *Opin. Green Sustain. Chem.* 28 (2021) 100427. <https://doi.org/10.1016/J.COGLSC.2020.100427>.

612 [62] E. Barnard, J.J. Rubio Arias, W. Thielemans, Chemolytic depolymerisation of PET: a review, *Green*  
 613 *Chem.* 23 (2021) 3765–3789. <https://doi.org/10.1039/D1GC00887K>.

614 [63] L. Rosi, M. Bartoli, A. Undri, M. Frediani, P. Frediani, Synthesis of dianols or BPA through catalytic  
 615 hydrolysis/glycolysis of waste polycarbonates using a microwave heating, *J. Mol. Catal. Chem.* 408  
 616 (2015) 278–286. <https://doi.org/10.1016/J.MOLCATA.2015.07.027>.

617 [64] F.S. Liu, Z. Li, S.T. Yu, X. Cui, C.X. Xie, X.P. Ge, Methanolysis and hydrolysis of polycarbonate under  
 618 moderate conditions, *J. Polym. Environ.* 17 (2009) 208–211. <https://doi.org/10.1007/s10924-009->

- 619 0140-0.
- 620 [65] C.S. Bhogle, A.B. Pandit, Ultrasound assisted methanolysis of polycarbonate at room temperature,  
621 Ultrason. Sonochem. 58 (2019) 104667. <https://doi.org/10.1016/J.ULTSONCH.2019.104667>.
- 622 [66] A. Căta, M.N. Ștefănuț, I.M.C. Ienașcu, C. Tănasie, M. Miclău, ALKALINE HYDROLYSIS OF  
623 POLYETHYLENE TEREPHTHALATE UNDER MICROWAVE IRRADIATION, Rev. Roum. Chim. 62 (2017)  
624 531–538. <http://web.icf.ro/rrch/> (accessed February 19, 2023).
- 625 [67] M. Yamashita, H. Mukai, Alkaline Hydrolysis of Polyethylene Terephthalate at Lower Reaction  
626 Temperature, Sci. Eng. Rev. Doshisha Univ. 52 (2011) 143–148.
- 627 [68] N.R. Paliwal, A.K. Mungray, Ultrasound assisted alkaline hydrolysis of poly(ethylene terephthalate) in  
628 presence of phase transfer catalyst, Polym. Degrad. Stab. 98 (2013) 2094–2101.  
629 <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2013.06.030>.