Electronic Supplementary Information

Micro-flow nanocatalysis: Synergic effect of TfOH@SPIONs and micro-flow technology as an efficient and robust catalytic system for the synthesis of plasticizers

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METHODS:

All chemicals were purchased from Merck Company. Silica-coated magnetite nanoparticles (SPIONs) were synthesized according to the literature. All known organic products were identified by the comparison of their physical and spectral data with those of authentic samples.

The catalyst was analyzed by FT-IR (Fourier transform infrared spectroscopy, Nicolet-Impact 400D spectrophotometer in KBr pellets and reported in cm\(^{-1}\)), XRD (Powder X-ray diffraction, D8 Advance DVANCE with Davinci, Bruker), TEM (Philips CM30 unit operated at 150 kV) and VSM (Vibrating sample magnetometer at Meghnatis Daghigh Kavir Co.).

Thin layer chromatography (TLC) was performed on UV-active aluminum-backed plates of silica gel (TLC Silica gel 60 F254). \(^1\)HNMR spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl\(_3\) with chemical shift (\(\delta\)) given in ppm and coupling constants given in Hz. The sonication was performed in a UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe.

Catalyst Synthesis

To a mixture of SPIONs (1.0 g) in diethyl ether (50 ml), TfOH (1.5 mmol) was added dropwise, and the resulting suspension was sonicated in the ultrasonic bath for 60
min at room temperature. The solvent was removed and the residue was heated under vacuum at 70 °C for 24 h to obtain TfOH@SPION.

**Microreactor Designing**

The microreactor system used in this study includes an in-house-made tubing glass reactor which can be implemented in any chemistry laboratory. The microtube reactor was fabricated in a glass column (internal diameter, 0.5 mm; internal volume, 0.6 mL; length, 200 cm), which was placed in an oil bath. The dispersed mixture of substrates and the catalyst was delivered to the microreactor by a peristaltic pump. A temperature controller (TC) was used for balancing and setting up heating and a back-pressure regulator (BPR) for pressure control.

**General procedure for synthesis of plasticizers**

A sonicated mixture of 1 mL dicarboxylic acid:alcohol (1:3 molar ratio) or tricarboxylic acid:alcohol (1:4 molar ratio), and the catalyst (40 mg, 0.13 mol% based on TfOH) at ambient temperature and pressure was fed to the microreactor by a peristaltic pump. Afterwards, the flow rate of the mixture was adjusted to the desired value (0.4 mL/h). The reactor was then heated at 90 °C. After the residence time was reached (15–95 min), the discharge was collected out of the BP in a glass vessel equipped with an external permanent magnet (Scheme 1). The collected catalyst by the magnet, was washed two times with absolute ethanol (2×1 mL), air-dried, and
used directly for the next round. After separation of the catalyst from the resulting crude product, the volatiles were removed in vacuum. The organic residue was extracted with ethyl acetate/water (3×5 mL), and the combined organic phase was dried over anhydrous Na$_2$SO$_4$. Pure products were obtained in 75–96% yields after removal of solvent under reduced pressure.

**Figure S1:** Comparison of FT-IR spectrums of (a) Fe$_3$O$_4$, (b) SPIONs and (c) TfOH@SPIONs
**Figure S2:** Comparison of XRD spectra of (a) SPIONs and (b) TfOH@SPIONs

**Figure S3:** (a) TEM image of TfOH@SPIONs and (b) TfOH@SPIONs particle size distribution histogram
Figure S4: The dc magnetic characterization of the nanoparticles
NMR spectra of the products

Figure S5. $^1$H NMR spectrum of bis(2-ethylhexyl) adipate.
Figure S6. $^1$H NMR spectrum of dibutyl phthalate.
Figure S7. $^1$H NMR spectrum of tributyl citrate.
Figure S8. $^1$H NMR spectrum of tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate.
Figure S9. $^1$H NMR spectrum of bis(2-ethylhexyl) decanedioate.
Figure S10. $^1$H NMR spectrum of tributyl benzene-1,2,4-tricarboxylate.
Figure S11. $^1$H NMR spectrum of diisobutyl phthalate.
Figure S12. $^1$H NMR spectrum of bis(2-ethylhexyl) phthalate.
Figure S13. $^1$H NMR spectrum of dibutyl decanedioate.