Supporting information

Enhanced Mixing of Biphasic Liquid-Liquid Systems for the Synthesis of *gem*-Dihalocyclopropanes using Packed Bed Reactors

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Optimal Continuous Flow Setup for the *gem*-Dichloropropanation of Alkenes (Table 3, entries 9-11 and Figure 5)

The flow experiments were performed using the continuous flow setup shown in Figure S1. The organic solution was pumped by using a Syrris® Asia syringe pump and the alkaline aqueous solution was pumped using a Vapourtec® SF-10 peristaltic pump. Both streams were combined in a Y-mixer before entering two Omnifit® packed-bed reactors connected in series filled with PTFE particles (>40 µm). Both columns were arranged in a vertical orientation and the reaction mixture was passed through them from the bottom upwards. The columns were heated by using a Syrris® column heater. The flow system was pressurized by applying a Swagelok® back-pressure regulator.

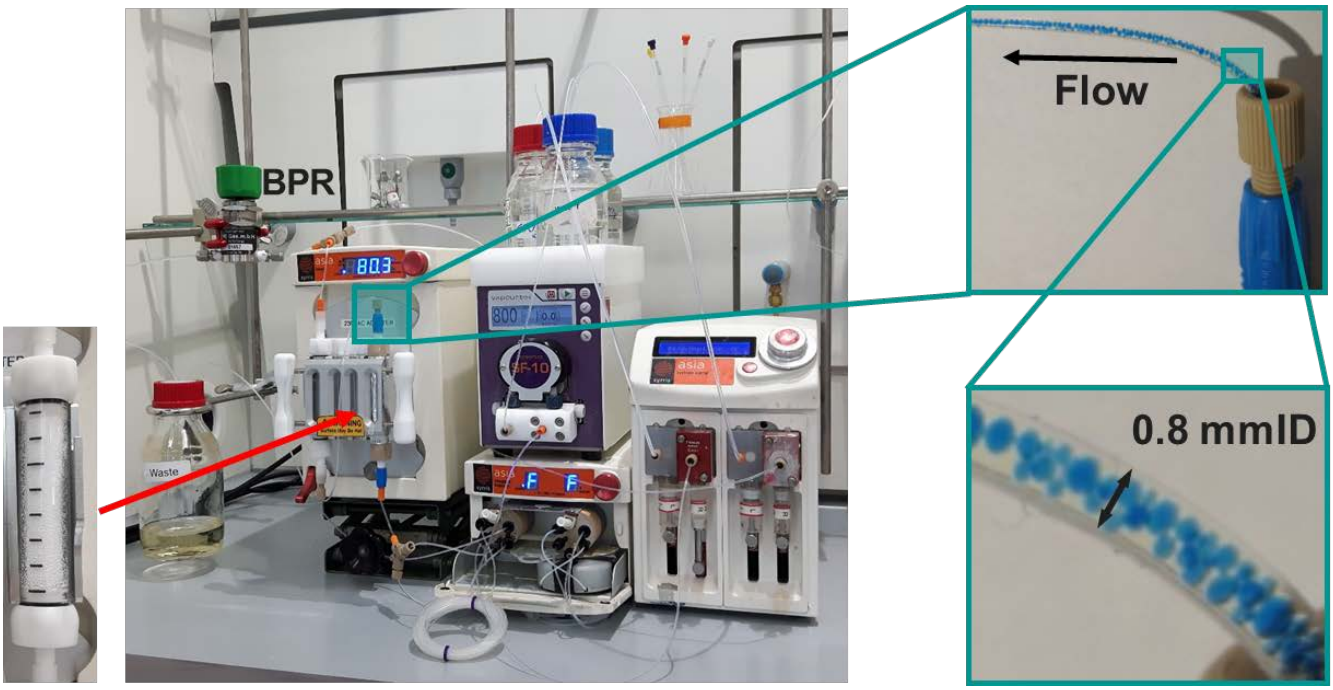

Figure S1: Utilized continuous flow setup.

Synthesis of 4-hydroxystyrene. A solution of methyltriphenylphosphonium bromide (22.0 g, 180 mmol, 1.00 equiv.) in THF (360 mL) was treated with *t*-BuOK (50.5 g, 450 mmol, 2.50 equiv.) at 0 °C. The suspension was stirred at this temperature for 10 min, before being allowed to warm to ambient temperature and stirred for further 20 min. Then, a solution of 4-hydroxybenzaldehyde (70.9 g, 270 mmol, 1.50 equiv.) in THF (180 mL) was added dropwise to the reaction mixture over 45 min and stirred after complete addition for 60 min at ambient temperature. The reaction was quenched with sat. aq. NH_4Cl solution (900 mL) and extracted with DCM (800 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under

reduced pressure. EtOAc (700 mL) was added to the resulting residue and the mixture was put in a freezer to crystallize triphenylphosphine oxide (TPPO) at -18 °C for 24 h. The crystals were filtered off and the solution was concentrated under reduced pressure (at this point around 20 mol% TPPO was still present). The residue was purified by flash column chromatography over silica gel (eluent: EtOAc:40-60 petroleum ether 1:20) to afford 21.2 g of 4-hydroxystyrene (98%) as a pale yellow solid.

Synthesis of methyl 2-methyl-2-(4-vinylphenoxy)propanoate 3. To a solution of 4-hydroxystyrene (21.2 g, 176 mmol) in acetonitrile (100 mL) was added cesium carbonate (29.7 g, 212 mmol, 1.20 equiv.). Methyl 2-bromoisobutyrate (38.3 g, 212 mmol, 1.20 equiv.) was added dropwise and the mixture was stirred at 40 °C for 24 h. After completion of the reaction, the mixture was filtered over diatomaceous earth and the filter cake was washed with acetonitrile (3 × 150 mL). The filtrates were combined and acetonitrile was removed under reduced pressure. The residue was dissolved in EtOAc (300 mL) and washed with brine (500 mL). The organic layer was concentrated under reduced pressure to give 38.3 g (174 mmol, 99%) of the crude product **3** which was used in the next step without further purification.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36-7.29 (2H, m), 6.89-6.77 (2H, m), 6.67 (1H, dd, ^{3}J = 17.6 Hz, ^{3}J = 10.9 Hz), 5.64 (1H, d, ^{3}J = 17.6 Hz), (1H, d, ^{3}J = 10.9 Hz), 3.79 (3H, s), 1.62 (6H, s). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 174.8, 155.1, 136.1, 131.8, 127.6, 127.1, 119.0, 115.4, 112.3, 79.2, 52.5, 25.4.

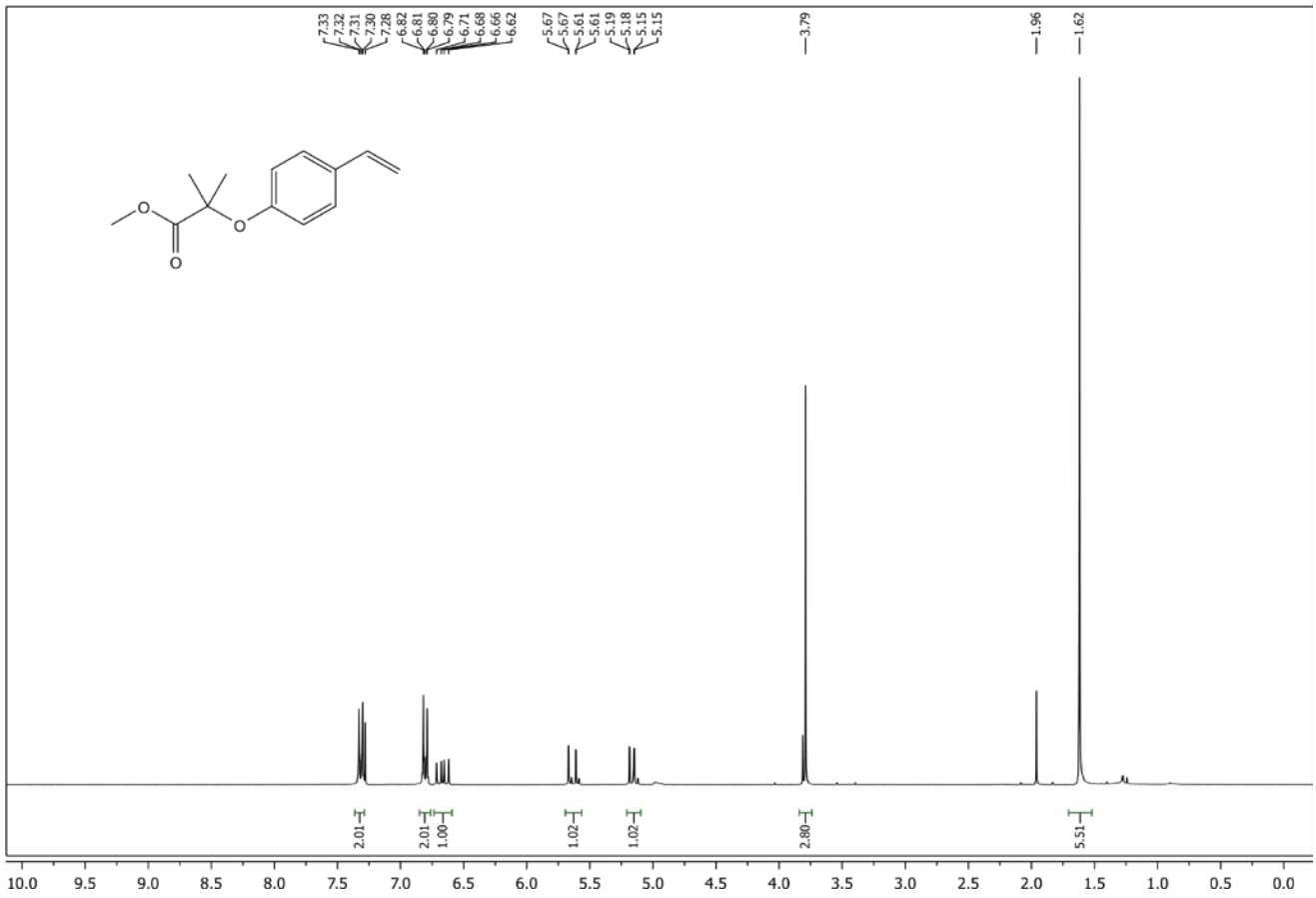

Figure S2. ^{1}H-NMR spectrum of **3** (300 MHz) in $CDCl_3$.

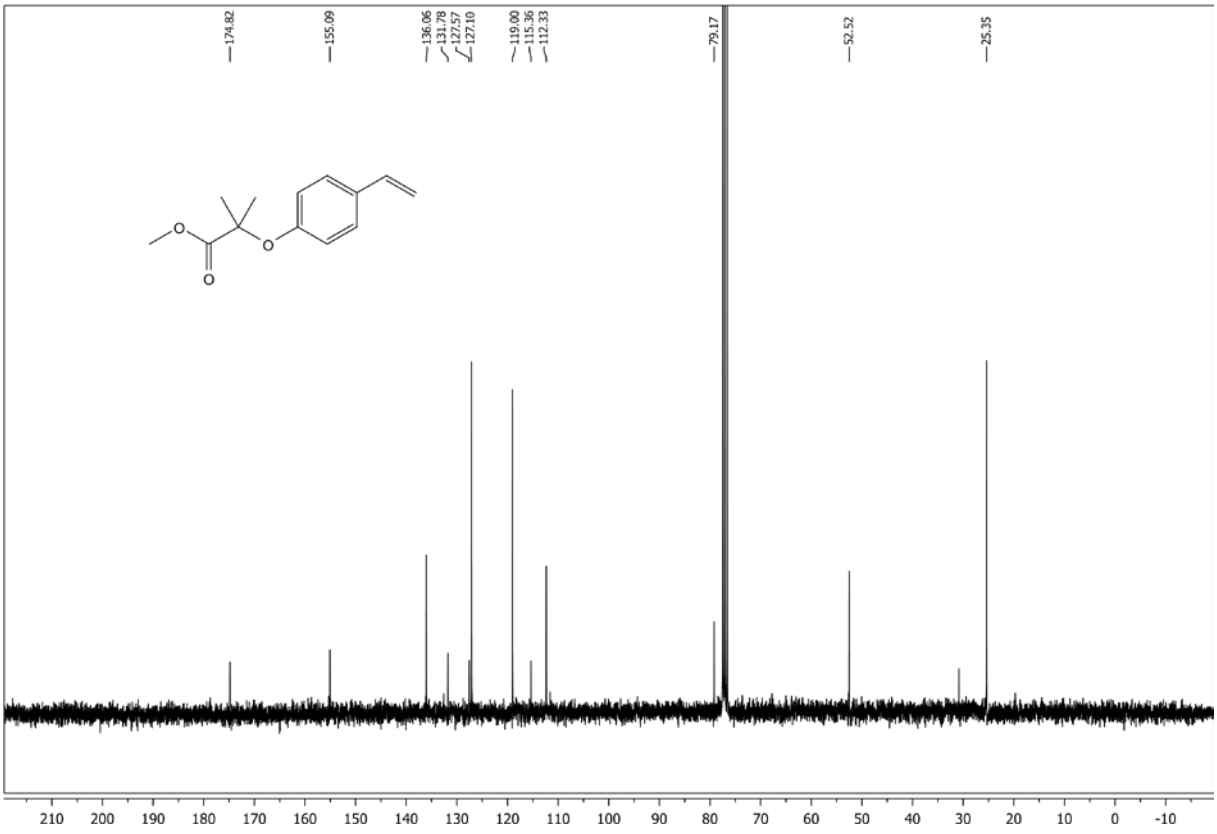

Figure S3: ^{13}C-NMR spectrum of **3** (75 MHz) in $CDCl_3$.

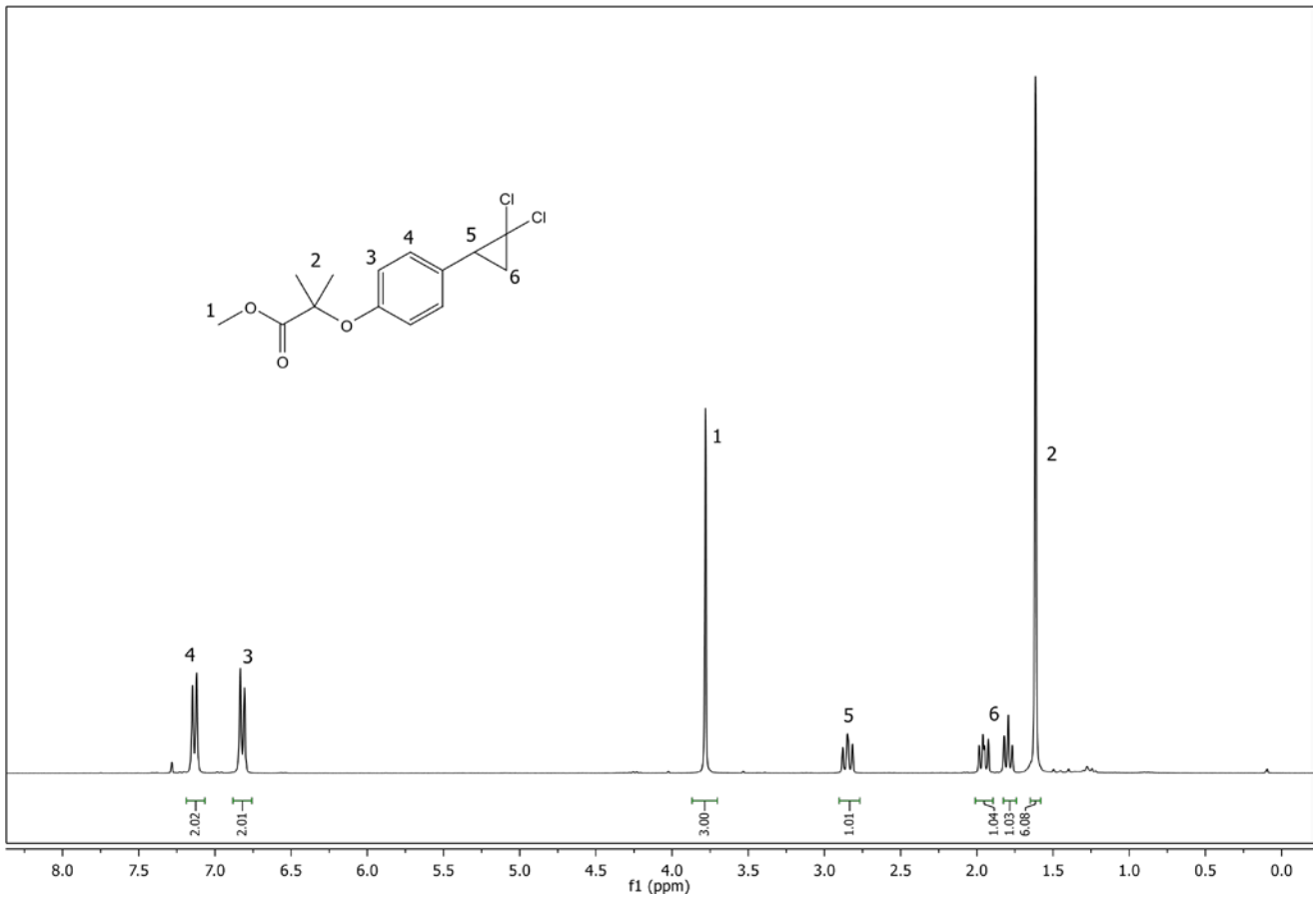

Figure S4. ^{1}H-NMR spectrum of **4** (300 MHz) in $CDCl_3$.

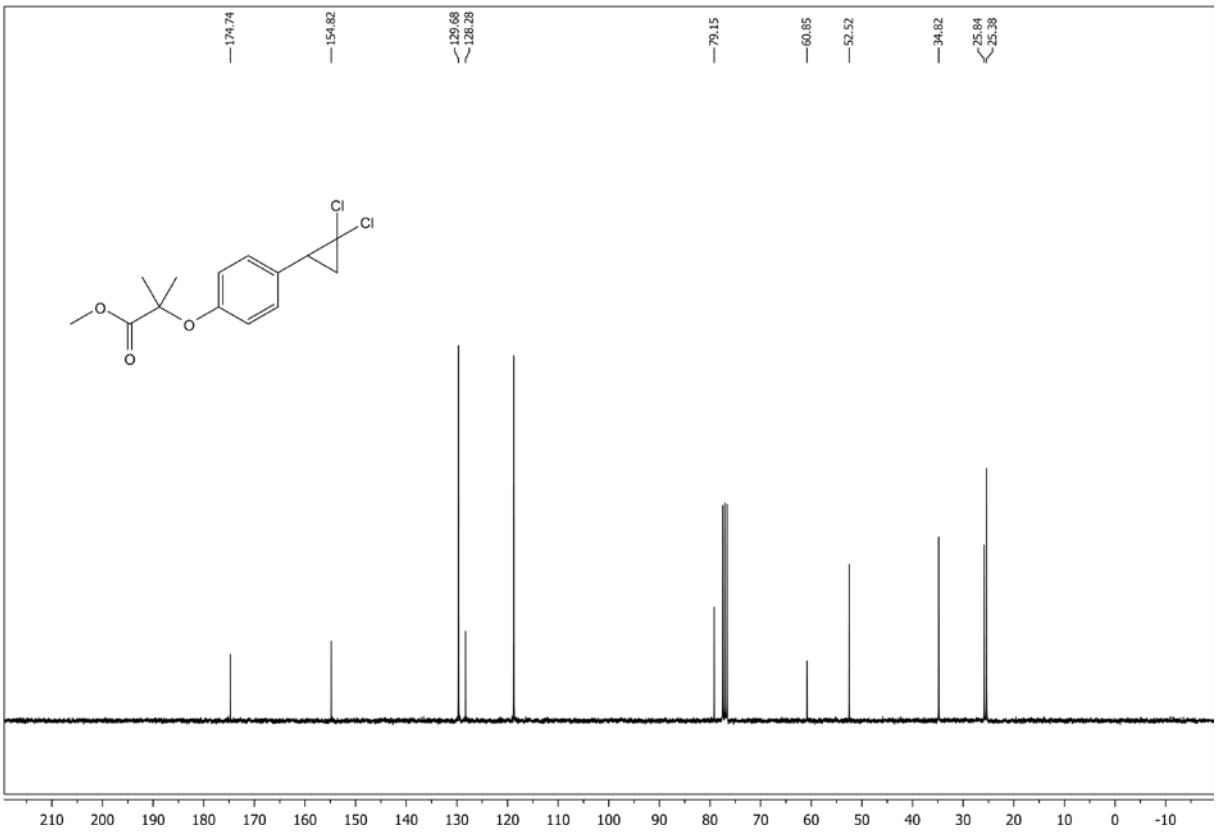

Figure S5.: ^{13}C-NMR spectrum of **4** (75 MHz) in $CDCl_3$.