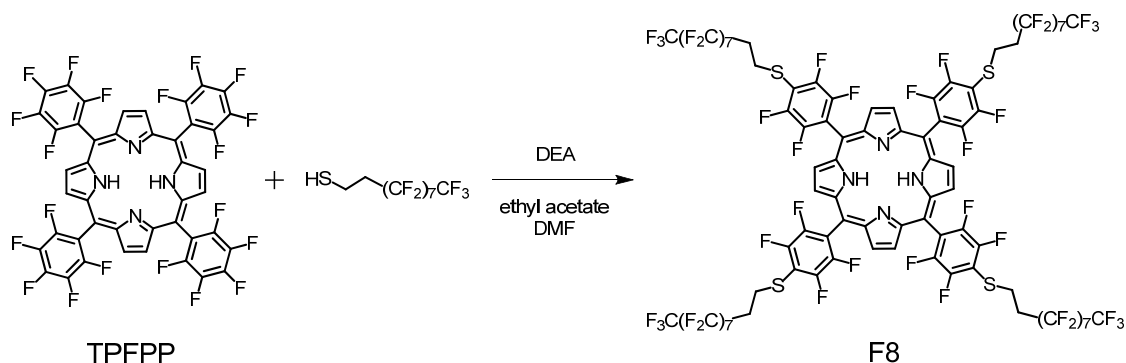


## Electronic Supporting Information

### 1. Synthesis of the photocatalyst F8

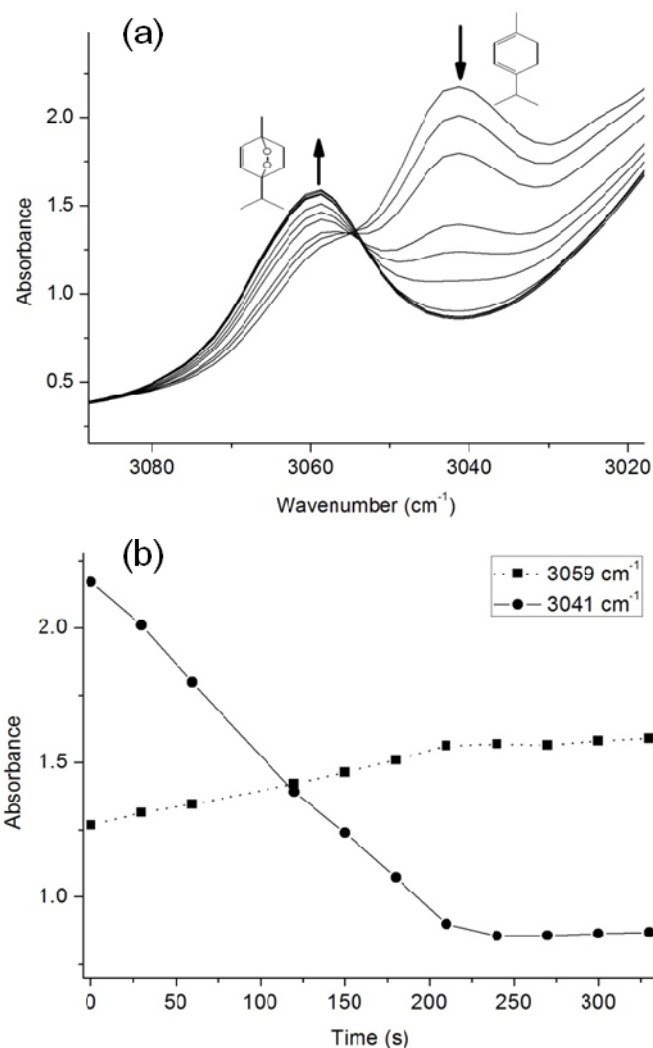


**Scheme S1.** Synthesis of F8

Highly fluorinated photocatalyst F8 was synthesised following a modified reported method (Scheme 1).<sup>1</sup> 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane-1-thiol (325 mg, 0.68 mmol) was dissolved in 15 mL ethyl acetate / DMF (2:1 v/v) with diethylamine (DEA) (0.1 mL, 0.97 mmol) under nitrogen. 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPFPP) (57.5 mg, 0.06 mmol) dissolved in 5 mL DMF was added to this solution. After stirring under nitrogen at room temperature for 8 hours, the product was extracted with HFE-7500 and purified by silica gel chromatography using hexane / acetone (10:1 v/v) to afford purified F8 (112 mg, 67%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): -2.84 (broad s, 2H, pyrrole NH), 2.64 to 2.81 (m, 8H, 2'H), 3.51 (t, *J* = 9.0, 8H, 1'H), 8.93 (s, 8H, pyrrole βH). <sup>19</sup>F-NMR: (CDCl<sub>3</sub>) δ (ppm): -136.04 (dd, *J* = 27.0 Hz, 15.0 Hz, 8F, Ar-o-F), -133.61 (dd, *J* = 27.0 Hz, 15.0 Hz, 8F, Ar-m-F), -126.17 to -126.07 (m, 8F, 3'F), -123.12 (m, 8F, 4'F), -122.70 (m, 8F, 5'F), -121.85 to -121.57 (m, 24F, 6'-8'F), -113.90 to -113.68 (m, 8F, 9'F), -80.78 (t, *J* = 9.0 Hz, 12F, 10'F).

### 2. Batch reaction

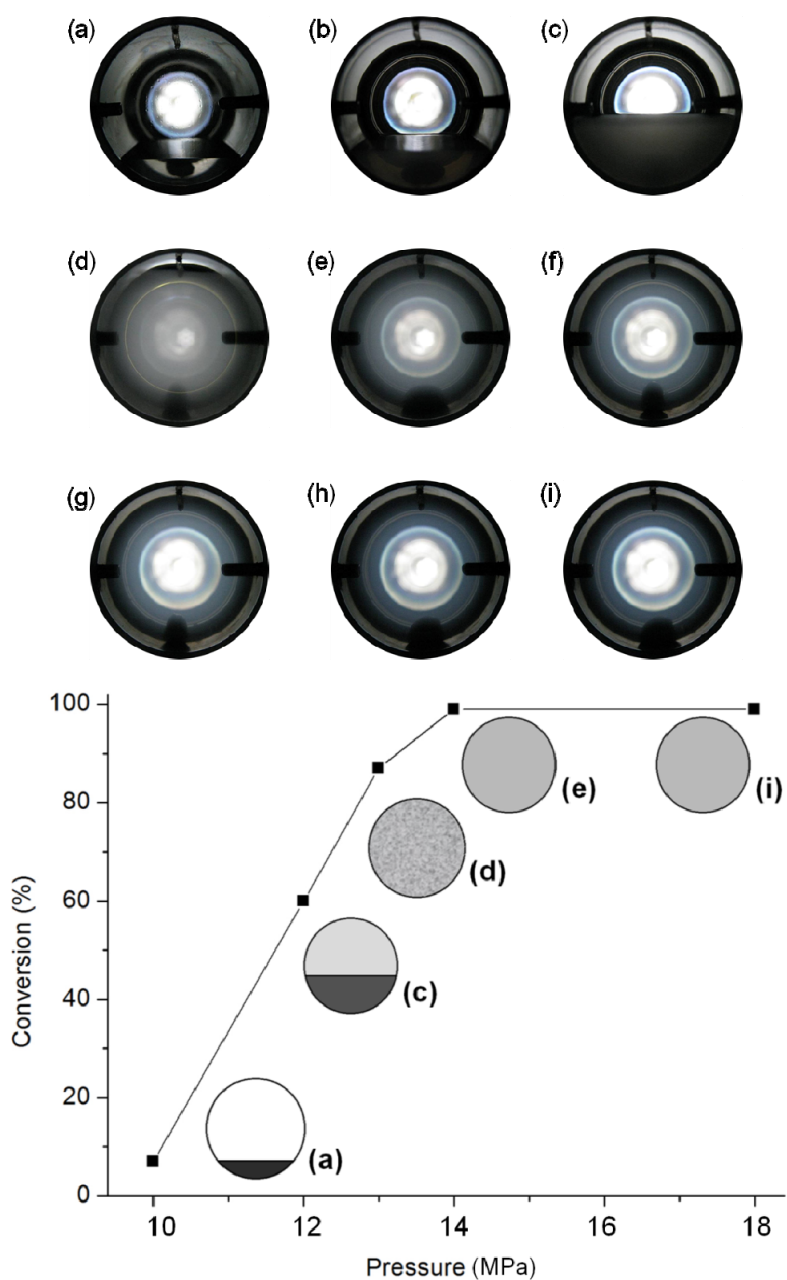
Photo-oxidation of α-terpinene using HFE/F8 in scCO<sub>2</sub> was performed in a high pressure batch cell (0.78 mL, 2 mm pathlength). 30 μL of α-terpinene and 30 μL of F8/HFE solution (5.7 mgmL<sup>-1</sup>) were injected into the cell, which was then filled with CO<sub>2</sub>/O<sub>2</sub> (O<sub>2</sub>: α-terpinene molar ratio = 2:1) mixture to 18 MPa. The batch cell was irradiated with a white LED, and FTIR spectra were taken to monitor the reaction.



**Fig. S1** (a) FTIR monitoring of the photo-oxidation of  $\alpha$ -terpinene using F8/HFE in  $\text{scCO}_2$ . Spectra were recorded at 30 s intervals showing formation of ascaridole ( $3059\text{ cm}^{-1}$ ) and loss of starting material ( $3041\text{ cm}^{-1}$ ); (b) kinetic traces obtained by plotting the band maxima.

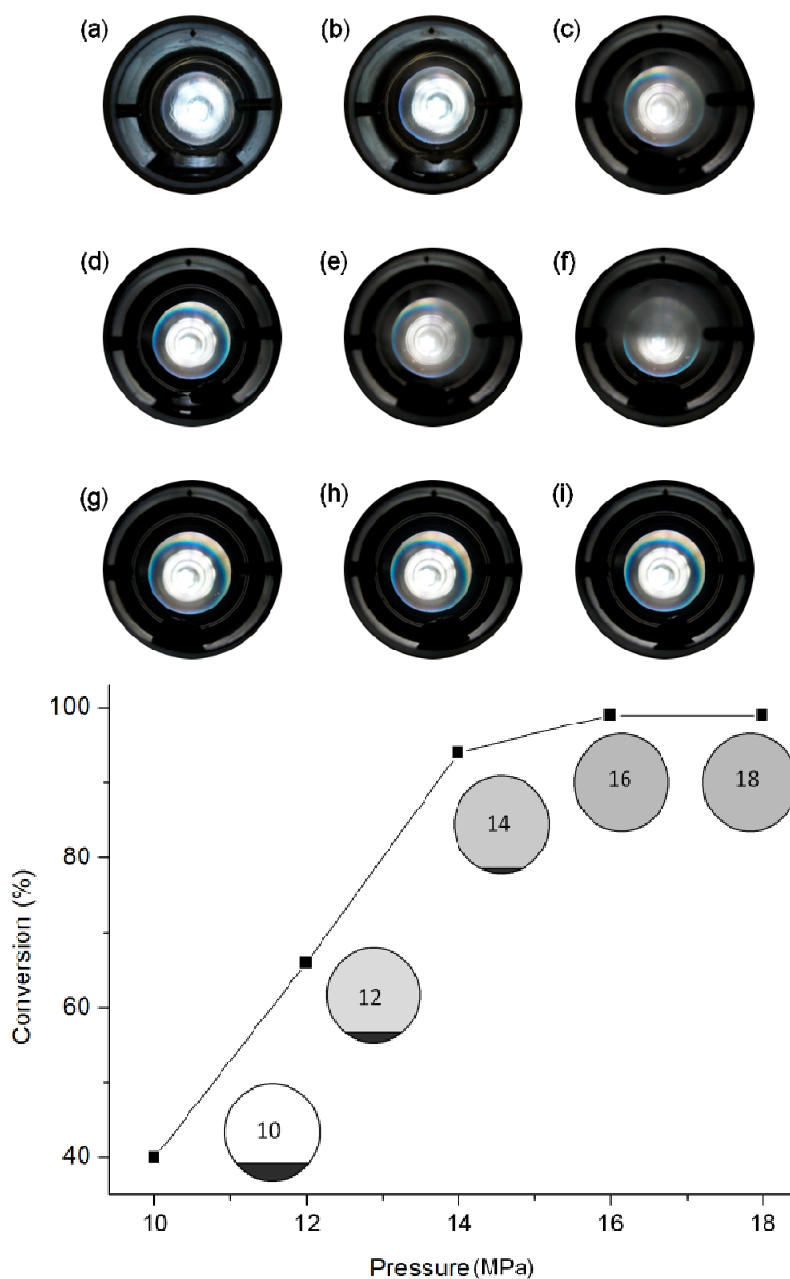
### 3. Phase behaviour

Phase behaviour of the  $\alpha$ -terpinene (6.4 mmol) + HFE (4.0 mmol) +  $\text{CO}_2$  (0.24 mol) +  $\text{N}_2$  (12.5 mmol) system was studied using a variable volume view cell.<sup>2</sup> Molar ratios of all the components were chosen to mimic the continuous flow experiment. For this measurement, we have substituted  $\text{N}_2$  for  $\text{O}_2$  to avoid any potential safety hazard because  $\text{N}_2$  has very similar properties to  $\text{O}_2$  in terms of phase behaviour under this condition. Photographs show the phase behaviour at  $55\text{ }^\circ\text{C}$  under different pressure. The corresponding schematics in the conversion vs. pressure Figure were also labelled for comparison (Fig. S2).



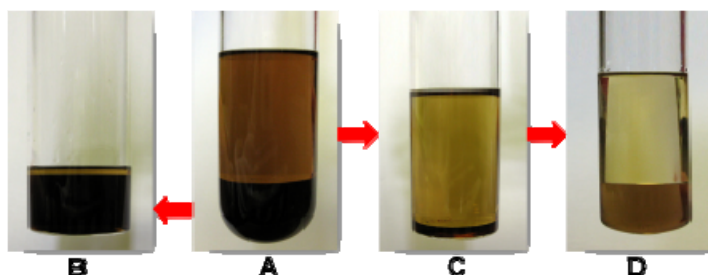
**Fig. S2** (a) 10 Mpa, multi-phase, (b) 11 MPa, multi-phase (c) 12 MPa, multi-phase, (d) 13 MPa, cloudy single phase, (e) 14 MPa, cloudy single phase, (f) 15 MPa, cloudy single phase, (g) 16 MPa, clear single phase, (h) 17 MPa, clear single phase, (i) 18 MPa, clear single phase.

The phase behaviour of the citronellol (5.5 mmol) + HFE (3.9 mmol) + CO<sub>2</sub> (0.24 mol) + N<sub>2</sub> (12.5 mmol) system at 55 °C under different pressure, and the corresponding schematics in the conversion vs. pressure are shown in Fig.S3.



**Fig. S3** (a) 10 MPa, multi-phase, (b) 11 MPa, multi-phase (c) 12 MPa, multi-phase, (d) 13 MPa, multi-phase, (e) 14 MPa, cloudy single phase, (f) 15 MPa, cloudy single phase, (g) 16 MPa, clear single phase, (h) 17 MPa, clear single phase, (i) 18 MPa, clear single phase.

#### 4. Phase separation of HFE and ascaridole



**Fig. S4** The separation of HFE and ascaridole, following the photo-oxidation of  $\alpha$ -terpinene with  $^1\text{O}_2$ . A: mixture collected immediately after reaction; B: fluorous phase (from A) after 48 h showing further separation of ascaridole; C: organic phase after 48 h showing further separation of F8/HFE; D: organic phase after washing with additional HFE.

1. A. Varotto, L. Todaro, M. Vinodu, J. Koehne, G. Liu and C. Drain, *Chem. Commun.*, 2008, **40**, 4921
2. P. Licence, M. P. Dellar, R. G. M. Wilson, P. A. Fields, D. Litchfield, H. M. Woods, M. Poliakov and S. M. Howdle, *Rev. Sci. Instrum.*, 2004, **75**, 3233-3236.