Electronic Supplementary Information

Non-catalytic oxidative depolymerization of lignin in perfluorodecalin to produce phenolic monomers

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Physical properties of the evaluated solvents

Table. S1 Physical properties of evaluated solvents.[1]

	Perfluorodecalin	Acetonitrile	Ethyl acetate	Butanol	Methanol
Molecular weight (g/mol)	463	41.05	88.11	74.12	32.04
Density (g/ml)	1.93	0.786	0.9	0.810	0.79
Boiling point(°C)	140	81.6	77	117.6	64.7
Vapor pressure (bar @ 20 °C)	0.008	0.12	0.126	0.0067	0.169

Hansen solubility parameters

Table. S2 Hansen solubility parameters of oxygen[2], perfluorodecalin[3] and organic solvents[4] and the solubility distance (R_a) of oxygen and solvents[4].

	Oxygen	Perfluorodecalin	Ethyl acetate	Benzene	Butanol	Acetonitrile	Methanol	Water
δ_D	11.7	13.15	15.8	18.4	16	15.3	15.1	15.5
δ_P	0	0	5.3	0	5.7	18	12.3	16
δ_H	0	0	7.2	2	15.8	6.1	22.3	42
δ_t	11.7	13.15	18.15	18.5	23.2	24.4	29.6	47.86
R_a	-	2.9	12.1	13.5	18.87	20.3	26.35	45.86

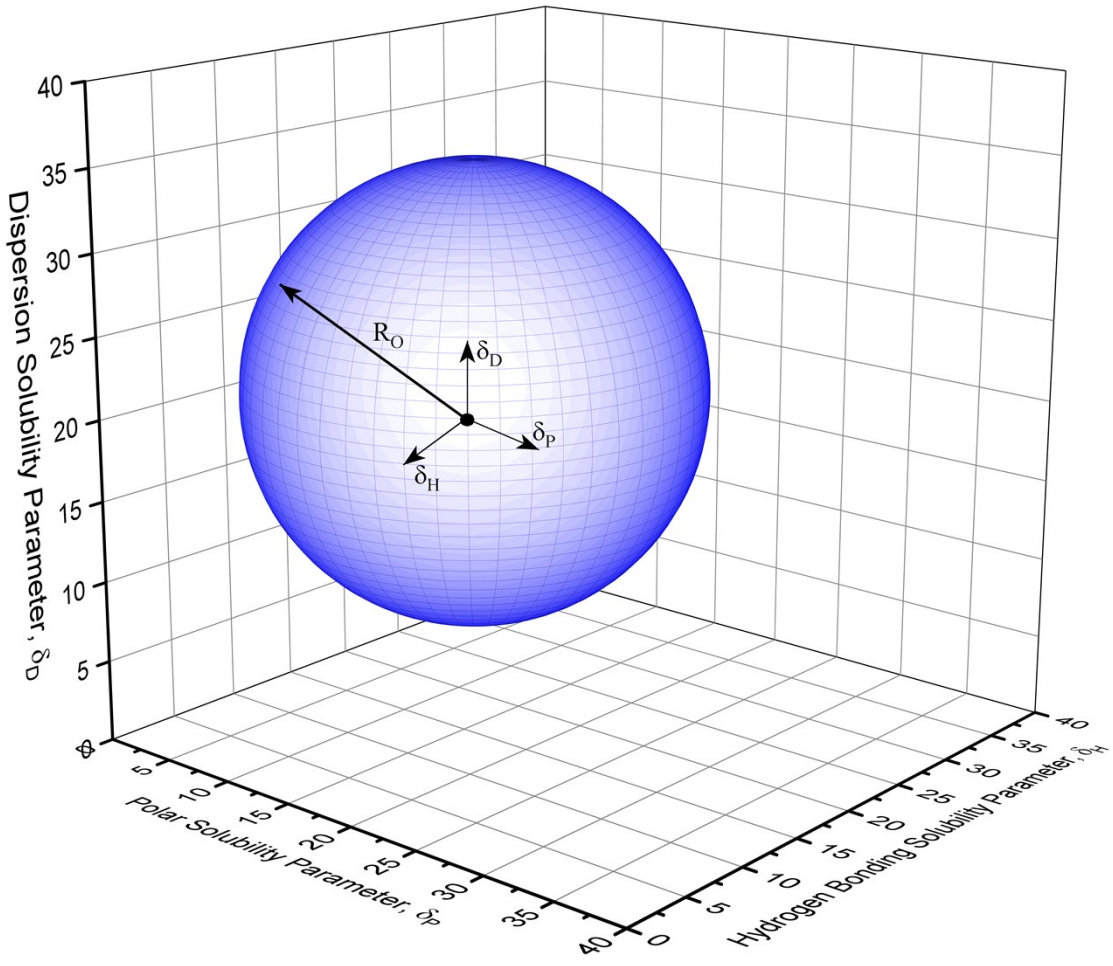

Fig. S1 Hansen solubility sphere of lignin [4] (δ_D = 21.9 MPa$^{0.5}$. δ_P =14.1 MPa$^{0.5}$, δ_H =16.9 MPa$^{0.5}$, R_o=13.7 MPa$^{0.5}$)

Gas chromatograms of lignin oils produced from oxidation in various solvents

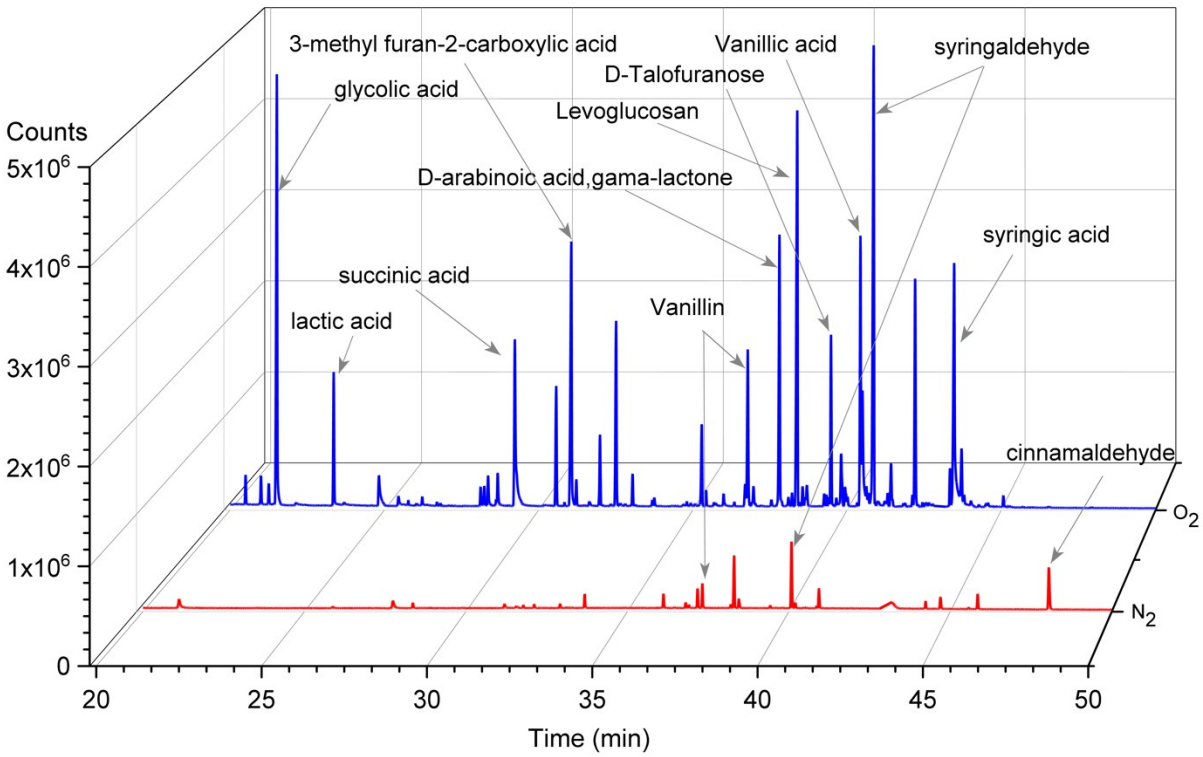

Fig. S2 Gas chromatograms of acetone-extracted lignin oil from reaction in perfluorodecalin under O_2 and N_2 at 250 °C and, 300 psi pressure for 10 min. Deep oxidation of lignin and carbohydrates produced acids like lactic acid, glycolic acid, and succinic acid.

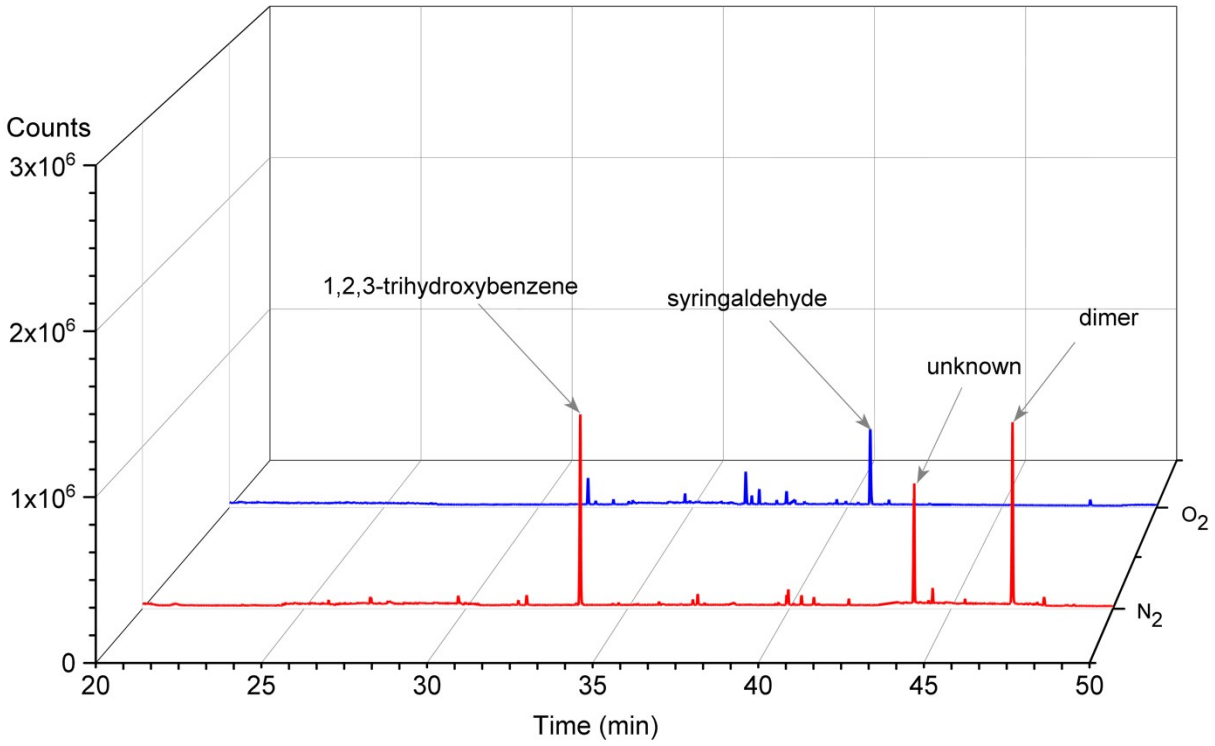

Fig. S3 Gas chromatograms of acetone-extracted lignin oil from reaction in acetonitrile under O_2 and N_2 at 250 °C and 300 psi pressure for 10 min.

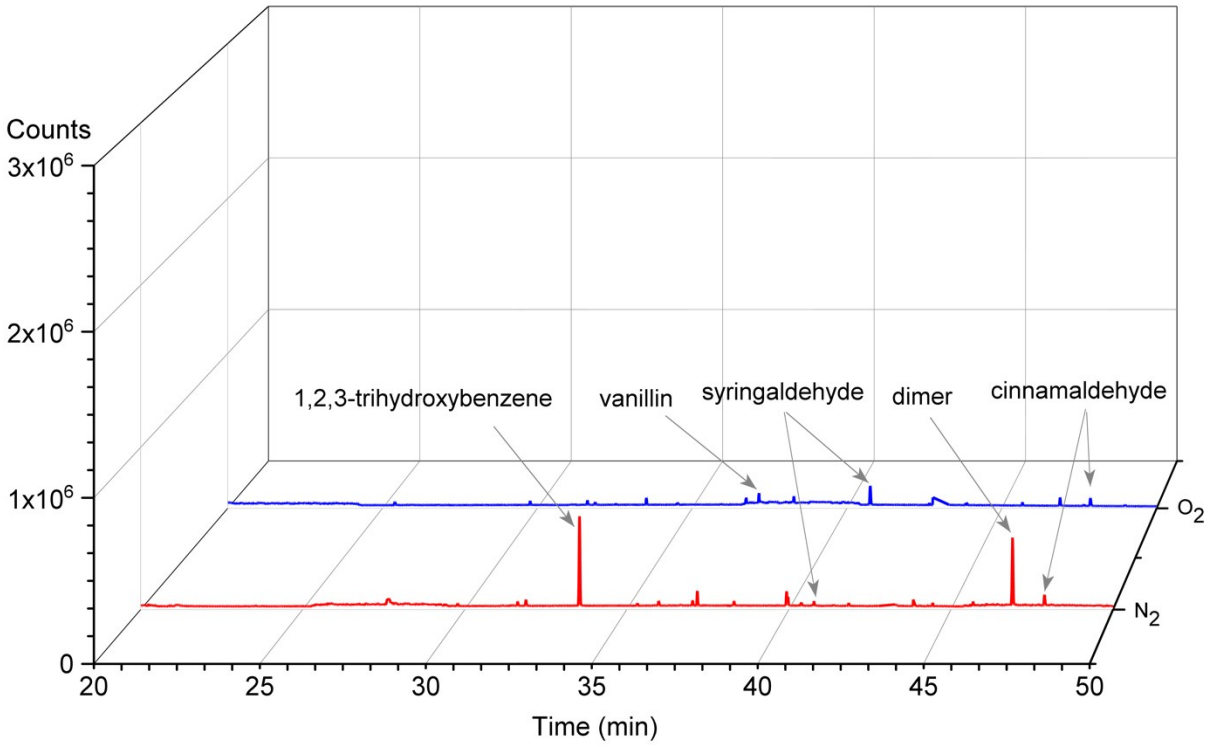

Fig. S4 Gas chromatograms of acetone-extracted lignin oil from reaction in ethyl acetate under O_2 and N_2 at 250 °C and, 300 psi pressure for 10 min.

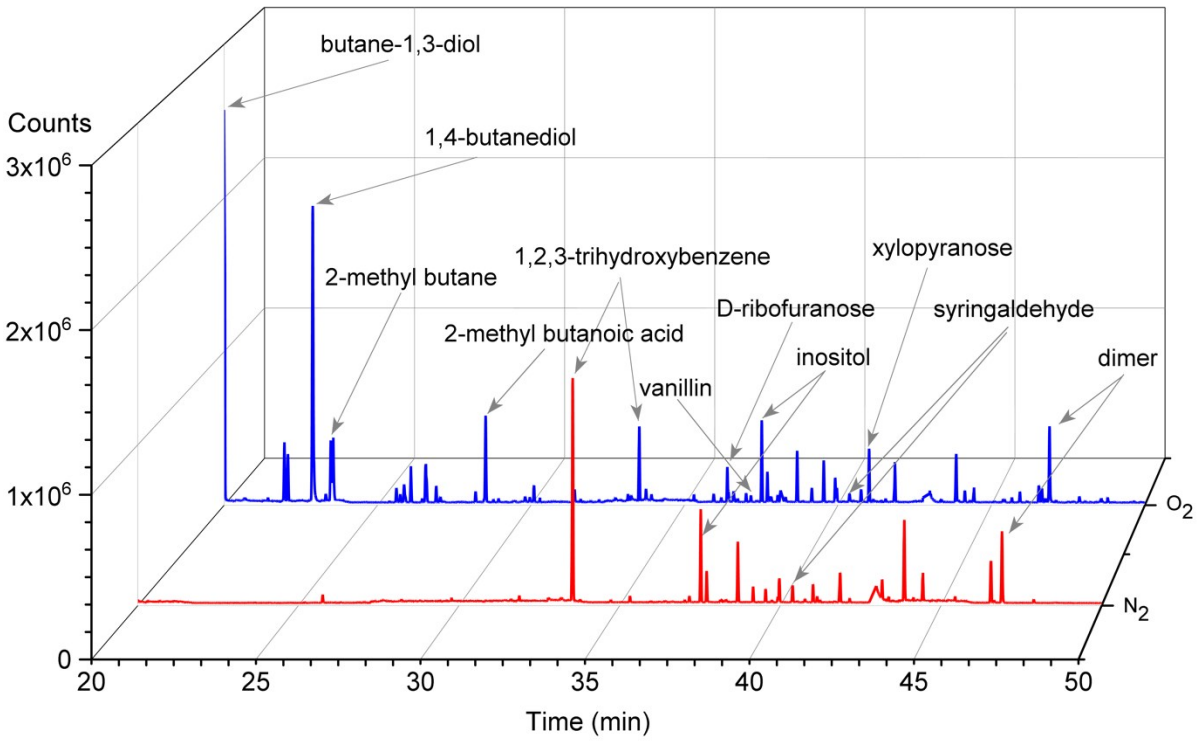

Fig. S5 Gas chromatograms of acetone-extracted lignin oil from reaction in butanol under O_2 and N_2 at 250 °C and, 300 psi pressure for 10 min.

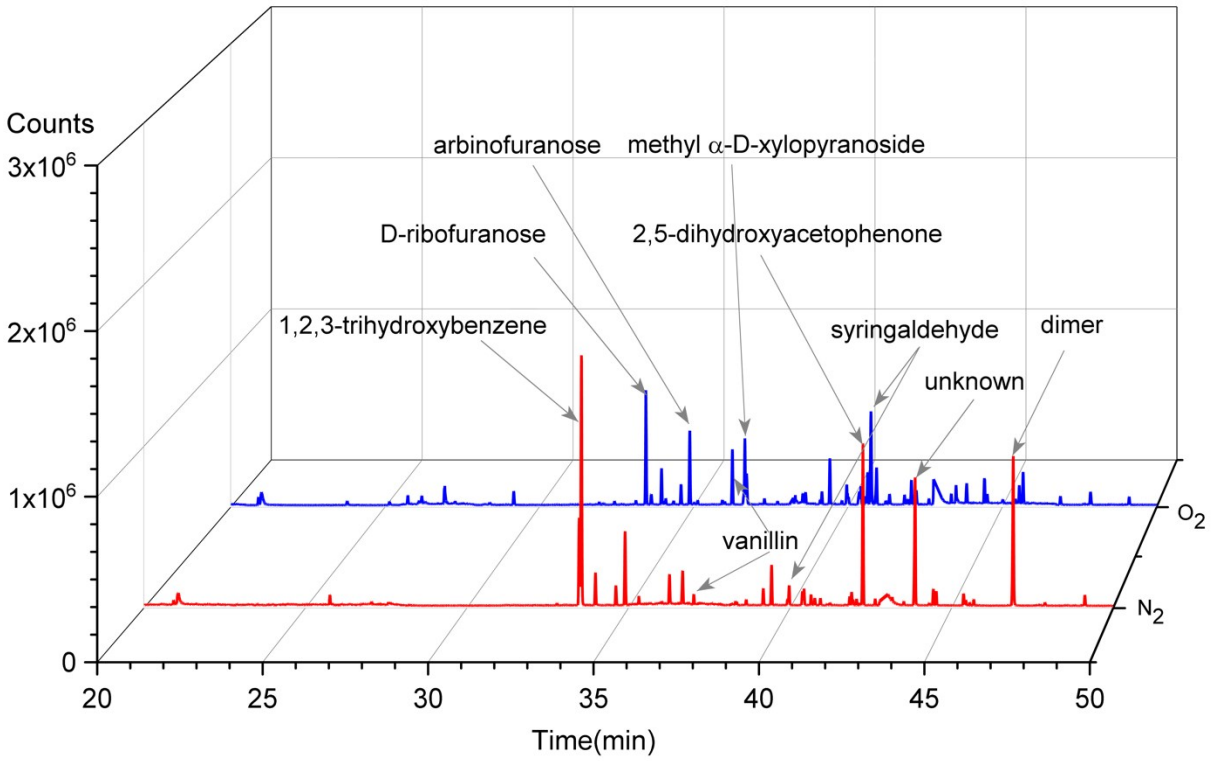

Fig. S6 Gas chromatograms of acetone-extracted lignin oil from reaction in methanol under O_2 and N_2 at 250 °C and 300 psi pressure for 10 min.

GPC results

Table. S3 Number averaged molecular weight (M_n), weight averaged molecular weight (M_w) and polydispersity (PD) of reaction under O_2 or N_2. Reaction conditions: 100 mg red oak, 5 ml solvent, 250 °C, 300 psi pressure for 10 min.

solvent	Gas	M_n	M_w	PD
Acetonitrile	O_2	440	599	1.36
	N_2	497	783	1.58
Ethyl acetate	O_2	460	600	1.3
	N_2	456	583	1.28
Butanol	O_2	597	1385	2.32
	N_2	624	1434	2.3
Methanol	O_2	565	1356	2.4
	N_2	668	1746	2.61

Proximate and ultimate analysis

Table. S4 Proximate and ultimate analysis of red oak

Proximate analysis (% wt)				Ultimate analysis (% wt)				
Volatile	Fixed carbon	Ash	Moisture	C	H	N	S	O
80.1535	15.8484	0.5757	3.4255	46.39	4.988	0.25	.052	48.32

Liquid-liquid separation from perfluorodecalin

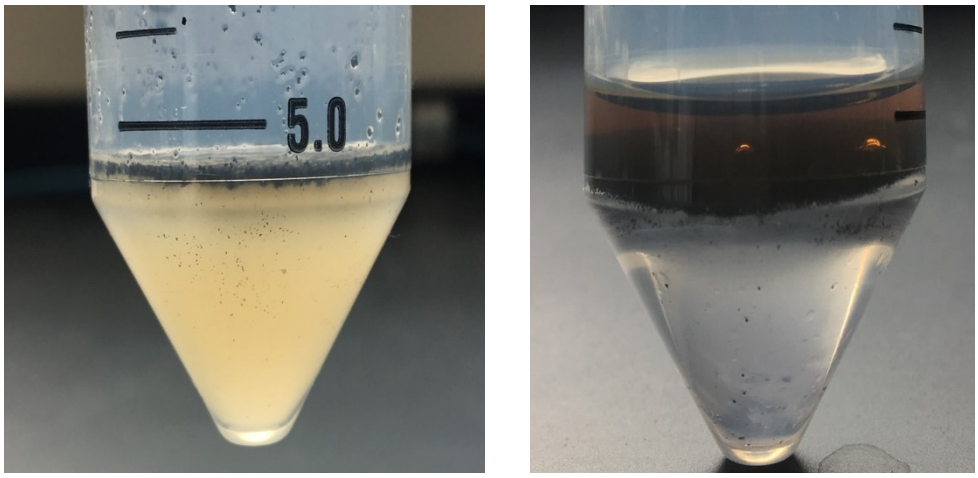

Fig. S7 Phase separation of oxidation products and residual solid biomass from perfluorodecalin before (left) and after (right) addition of acetone.

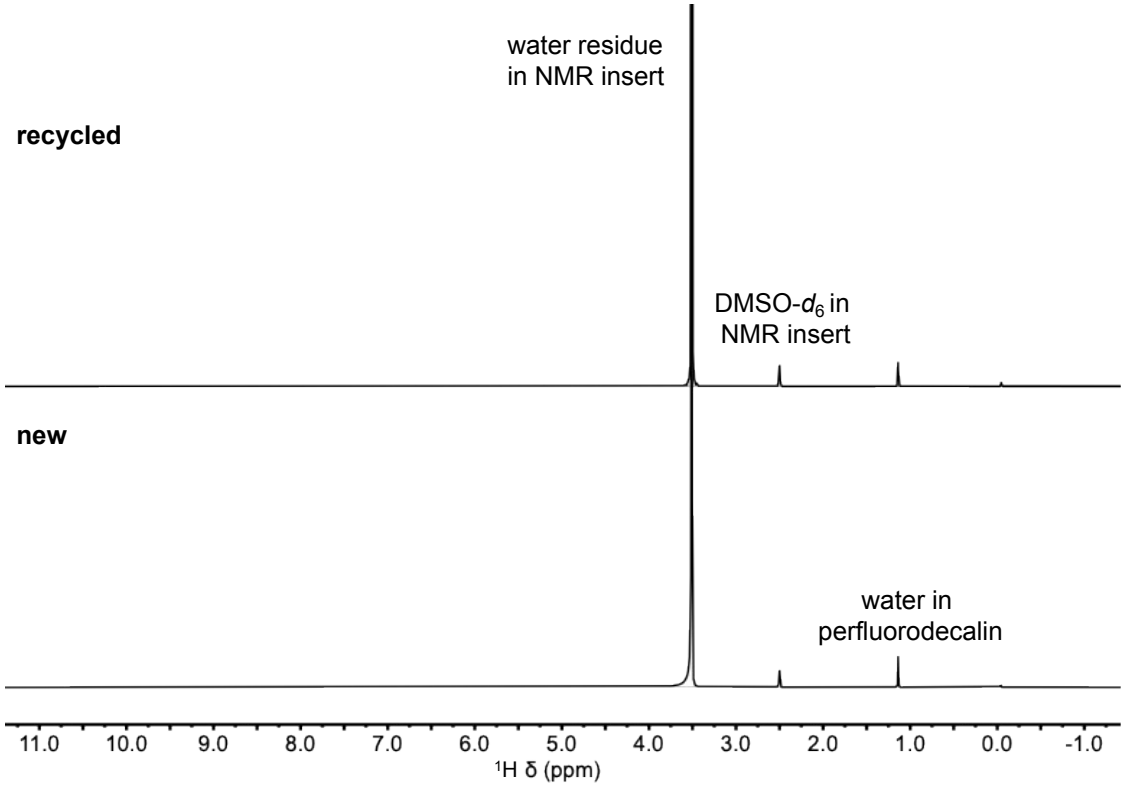

Fig. S8 ^{1}H NMR spectra of new and recycled perfluorodecalin. The spectra were collected with 4 scans and 1 s as the relaxation delay.

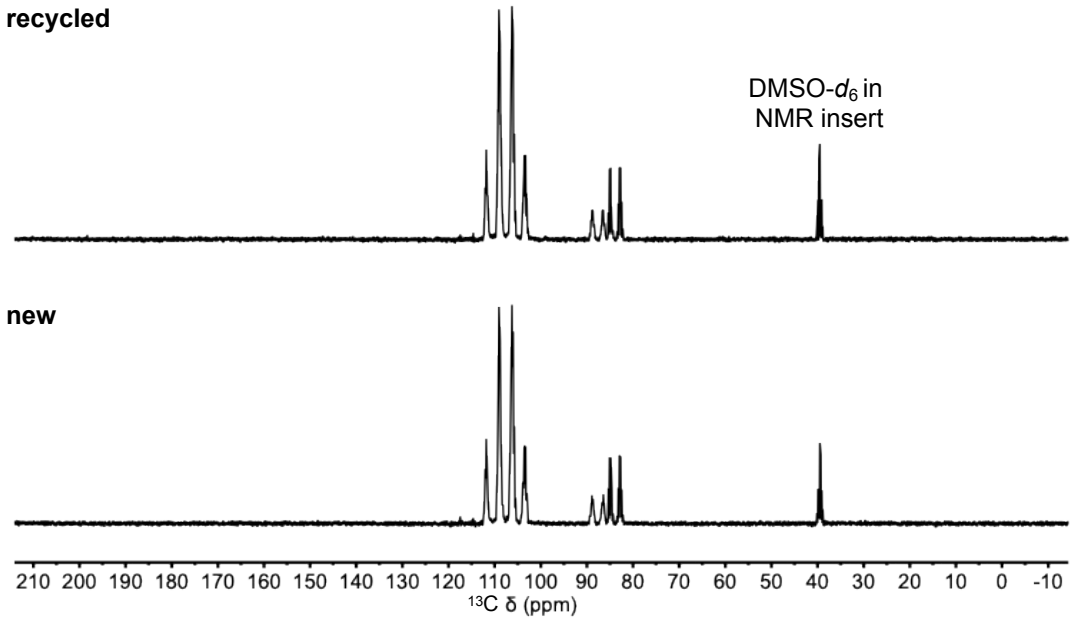

Fig. S9 ^{13}C NMR spectra of new and recycled perfluorodecalin. The spectra were collected with 256 scans and 2 s as the relaxation delay.

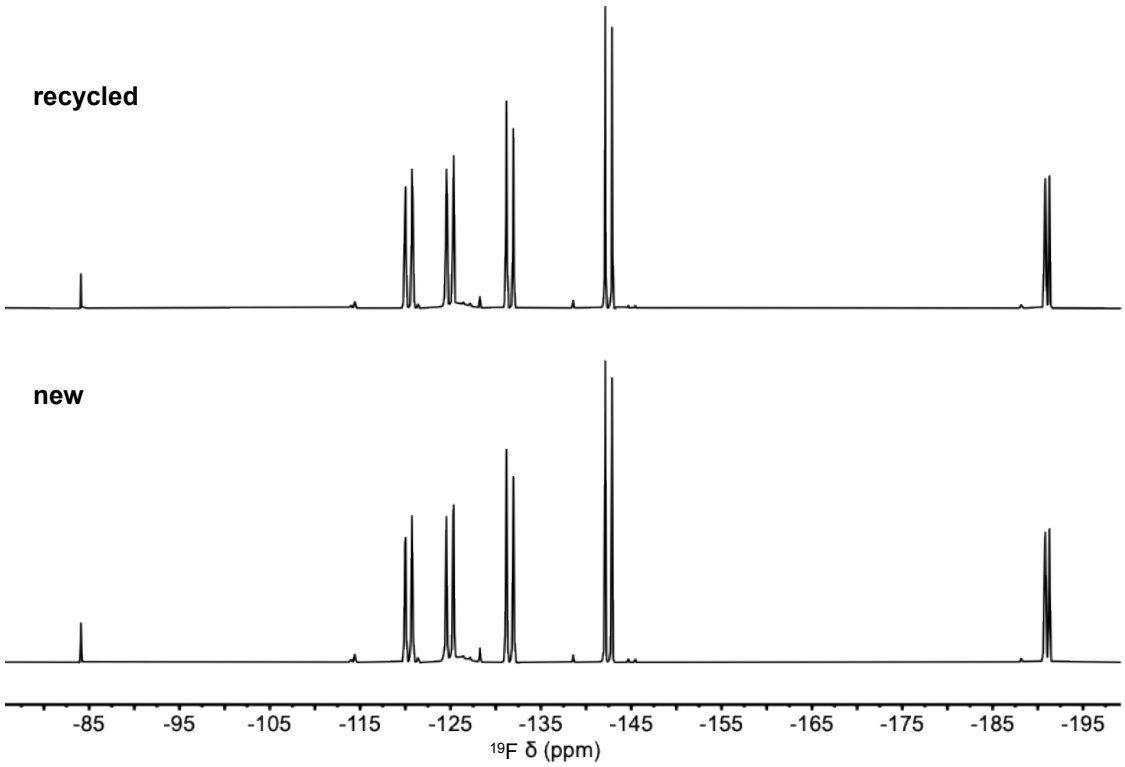

Fig. S10 ^{19}F NMR spectra of new and recycled perfluorodecalin. The spectra were collected with 4 scans and 10 s as the relaxation delay.

The ^{19}F NMR spectra before and after recycling are identical to the literature results[5,6], indicating the decomposition does not occur under our reaction conditions.

Supplementary References

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