Photo-promoted one-pot coupling isomerization-codimerization of norbornadiene for efficient synthesis of liquid fuel with density higher than 1 g/mL

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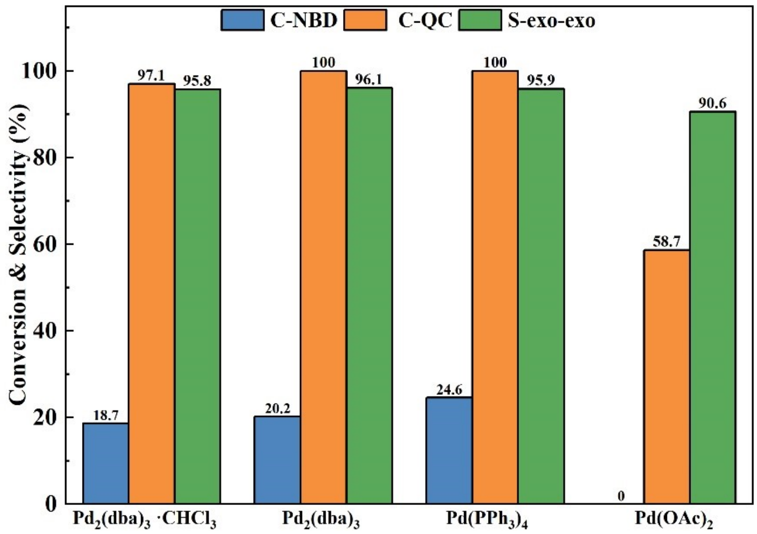

Figure S1. Effect of metal precursor on codimerization. Reaction conditions: 10 mmol of QC, 40 mmol of NBD, n-hexane as solvent. $n_{QC}/n_{metal\ catalyst}$= 300/1, n_{Pd}/n_{TPP} =1/2, 1h.

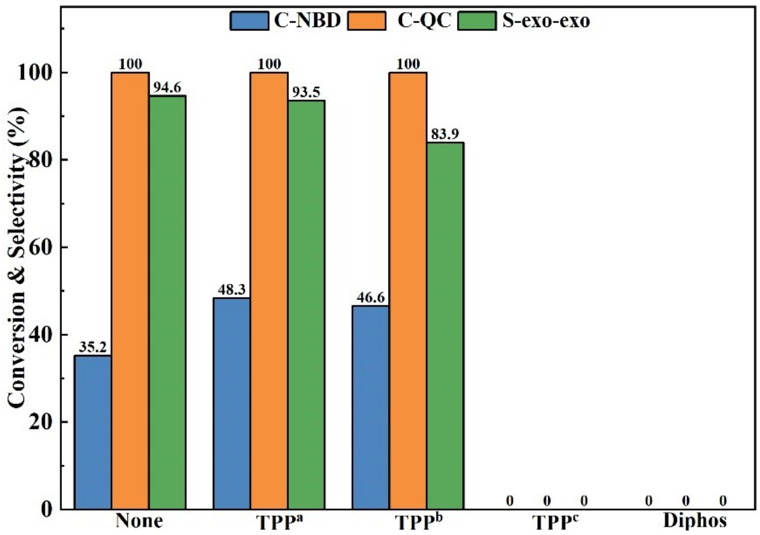

Figure S2. Effect of phosphine ligand type and phosphine complex concentration on codimerization of NBD and QC. Reaction conditions: 10 mmol of QC, 20 mmol of NBD, $n_{QC}/n_{Pd2(dba)3\cdot CHCl3}$= 300/1, n-hexane as solvent. The molar ratios of $Pd_2(dba)_3\cdot CHCl_3$ and TPP were (a) 1/2, (b) 1/4 and (c)1/8.

Figure S3. UV-vis absorption spectra of EMK in different solvents. 1 is cyclohexanone, 2 is benzyl alcohol, 3 is n-butanol, 1+2 is the mixture of cyclohexanone and benzyl alcohol with a volume ratio of 1:1. The ratio of the other binary mixtures is also 1:1. 1+2+3 is the mixture of cyclohexanone, benzyl alcohol and n-butanol with a ratio of 1:1:1.

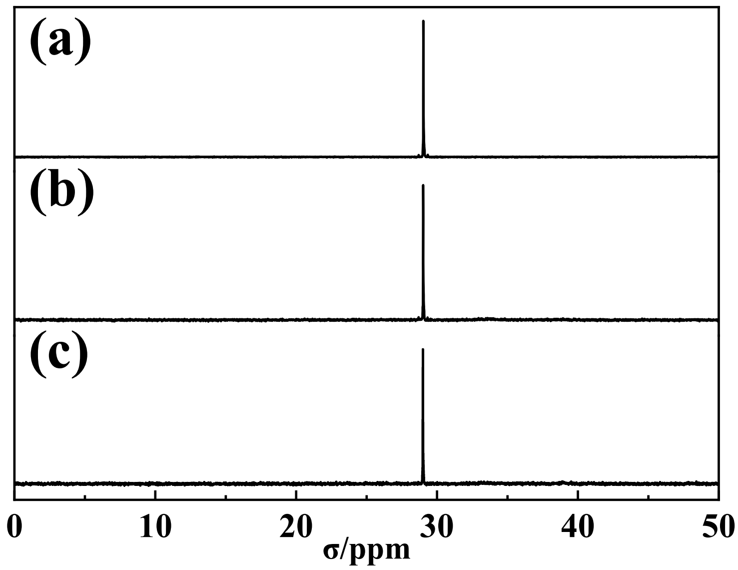

Figure S4. ^{31}P NMR spectra (400 MHz) of TPP in the reaction mixture (a) before reaction and (b-c) after reaction. (b) 60°C, 2 h. (c) 60°C, 2 h, 64 mW/cm^2. Reaction conditions:15 mmol QC, 30 mmol NBD, C_{TPP}=2$C_{Pd2(dba)3 \cdot CHCl3}$=15mmol/L, n-hexane as solvent.

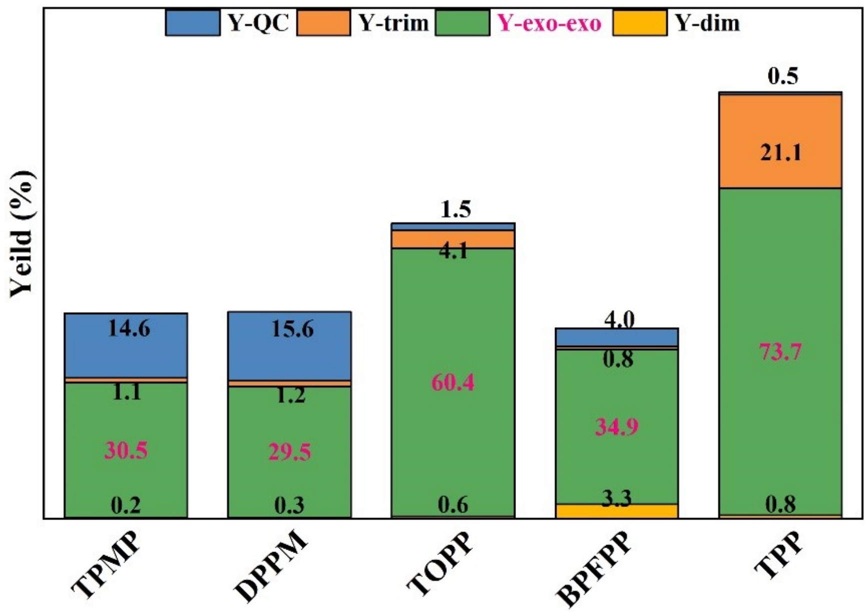

Figure S5. Effect of different monodentate phosphine ligands on coupling reactions. Reaction conditions: 17mmol of NBD, $n_{NBD}/n_{Pd2(dba)3 \cdot CHCl3}/n_P$ = 800/1/2, 253mg of EMK, 25ml of the solvent (the volume ratio of cyclohexanone/benzyl alcohol/n-butanol = 0.36 / 0.29 / 0.35), light intensity of 64mW/cm^2.

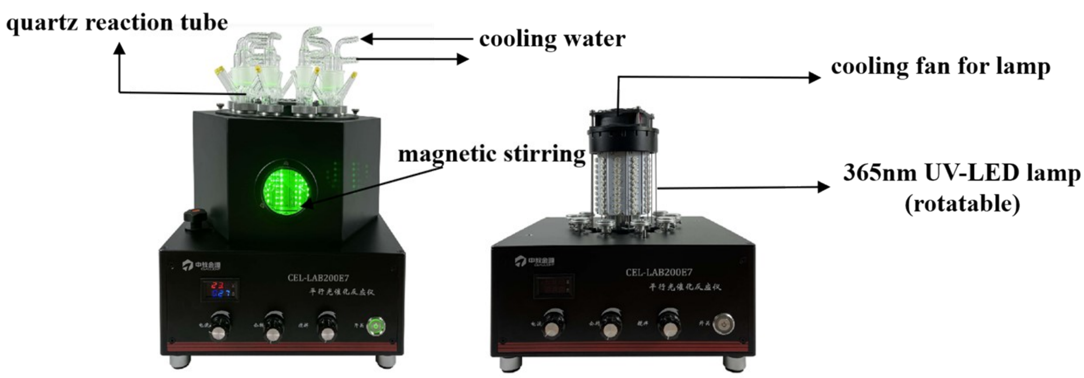

Figure S6. Diagram of the parallel photochemical reactor.

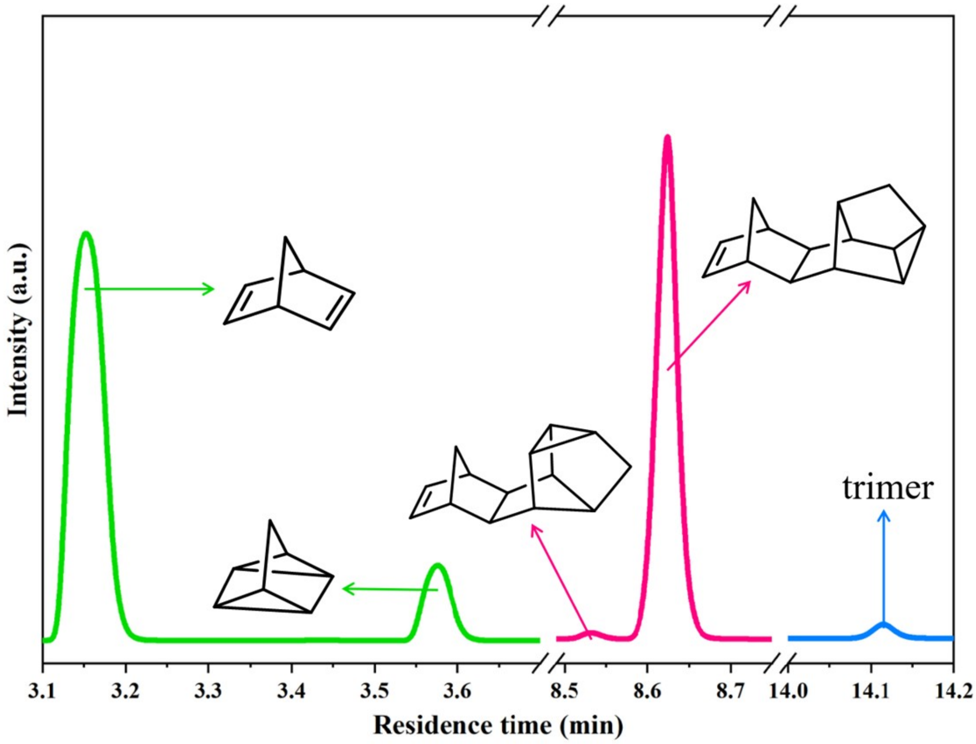

Figure S7. GC spectrum of the product mixture in one-pot coupling isomerization-codimerization reactions.

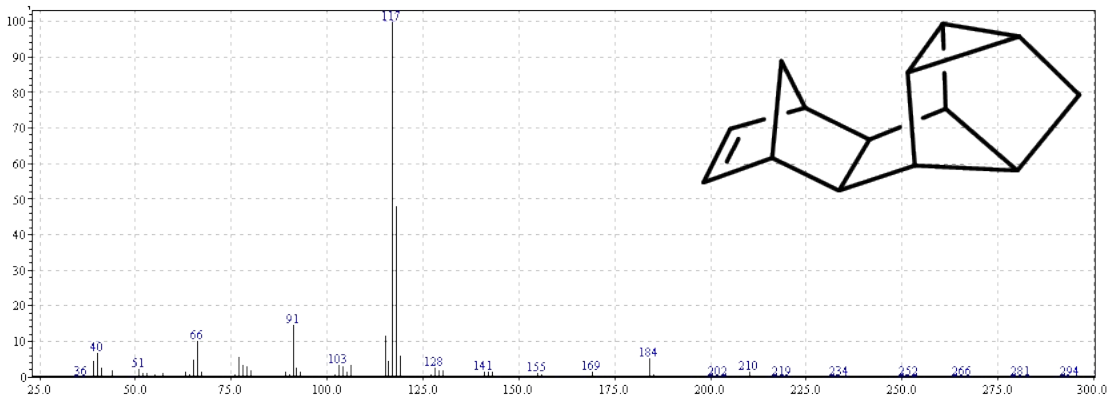

Figure S8. Mass spectrum of exo-endo (exo-endo-hexacyclo[9.2.1.02,10.03,7.04,9.06,8]tetradec-12-ene).

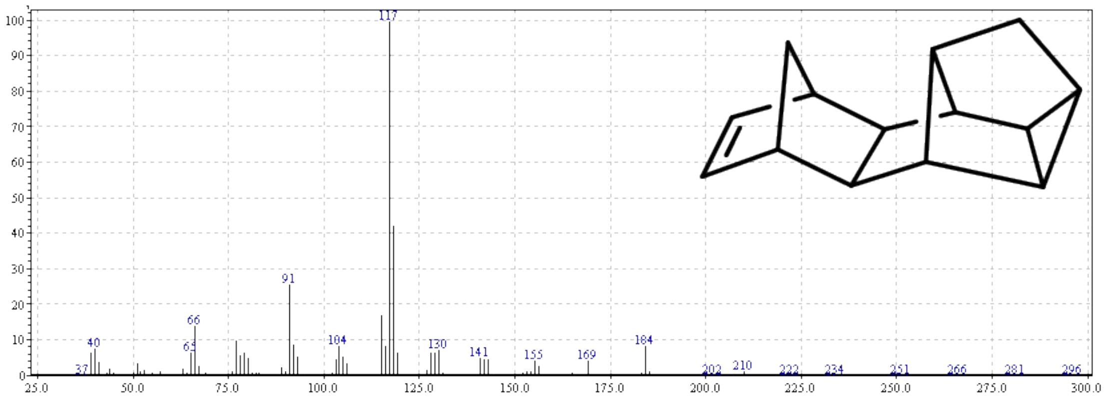

Figure S9. Mass spectrum of exo-exo (exo-exo-

hexacyclo[9.2.1.02,10.03,7.04,9.06,8]tetradec-12-ene).

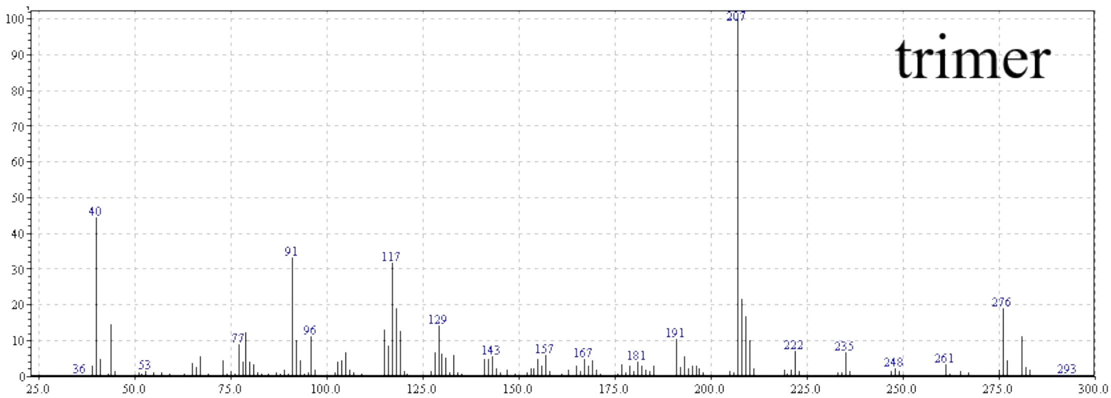

Figure S10. Mass spectrum of NBD trimer.

Table S1. Variables of the NBD coupling reactions.

	$m_{Pd2(dba)3 \cdot CHCl3}$/mg	m_{TPP}/mg	$m_{photosensitizer}$/mg	Time/min	VRsolvent[a]
Minimum	17	8.8	100	60	0
Maximum	26	17.6	300	120	1

[a] VR: Volumetric ratio.

Table S2. Effects of the amounts of photosensitizer and solvent on the coupling reactions.

Entry	m_{EMK}/mg	$V_{acetone}$/ml	Conversion（%）	Selectivity（%）				exo-exo yield（%）
			NBD	QC	exo-endo	exo-exo	trim	
1	100	15	11.4	13.4	0.5	86.1	0	9.8
2	200	15	15.7	18.3	0.2	81.4	0	12.8
3	300	15	15.2	17.9	0.3	81.7	0	12.4
4	200	25	20.6	4.1	0.5	95.4	0	19.6

Reaction conditions: 16mmol of NBD, $n_{NBD}/n_{Pd2(dba)3\cdot CHCl3}/n_{TPP}$ =1000/1/2; acetone as solvent, light intensity of 6mW/cm^2.

Table S3. Summary of the reaction rate equations

Reaction type	Reaction rate equations
Photoisomerization reaction	$r_{NBD} = \frac{dc_{NBD}}{dt} = -k_1 c_{NBD}$
Thermal codimerization reaction	$r_{NBD} = \frac{dc_{NBD}}{dt} = k_{-1} c_{QC} - k_2 c_{NBD} c_{QC}$ $r_{QC} = \frac{dc_{QC}}{dt} = -k_{-1} c_{NBD} - k_2 c_{NBD} c_{QC}$ $r_{exo} = \frac{dc_{exo}}{dt} = k_2 c_{NBD} c_{QC}$
Coupling reactions	$r_{NBD} = \frac{dc_{NBD}}{dt} = -k_1 c_{NBD} + k_{-1} c_{QC} - k_2 c_{NBD} c_{QC}$ $r_{QC} = \frac{dc_{QC}}{dt} = k_1 c_{NBD} - k_{-1} c_{QC} - k_2 c_{NBD} c_{QC}$ $r_{exo} = \frac{dc_{exo}}{dt} = k_2 c_{NBD} c_{QC} - k_3 c_{QC} c_{exo}$