Electronic supplementary information for

Self-photosensitized [2+2] cycloaddition for synthesis of high-energy-density fuels

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Table S1. Properties of the reactant and products.

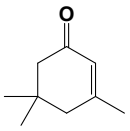
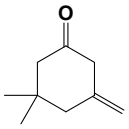
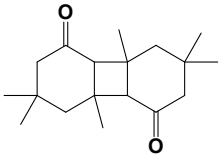
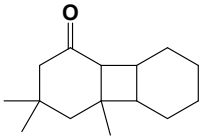
Property	Isophorone	Isomer	Self-adduct	Co-adduct
Structural formula				
Molecular formula	$C_9H_{14}O$	$C_9H_{14}O$	$C_{18}H_{28}O_2$	$C_{15}H_{24}O$
Molecular weight	**138**	**138**	**276**	**220**

Figure S1 GC spectra of isophorone self-cycloaddition reaction solution.

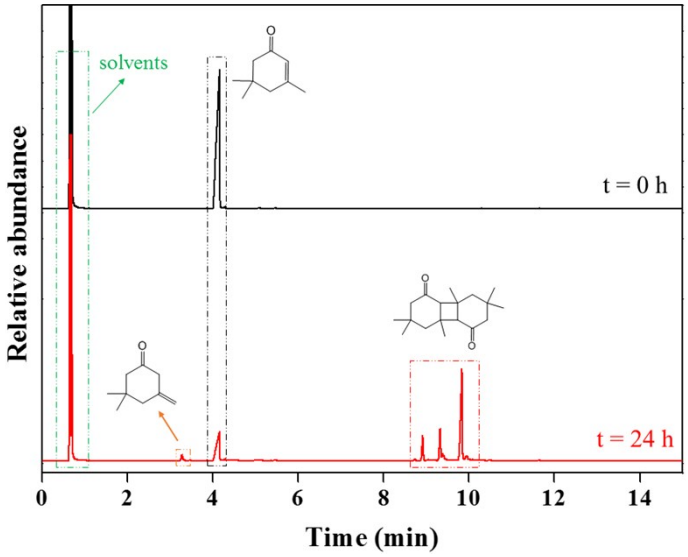


Figure S2 Mass spectra of self-adduct.

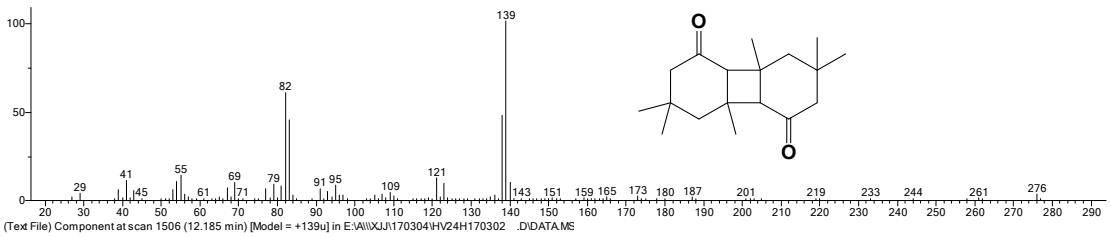
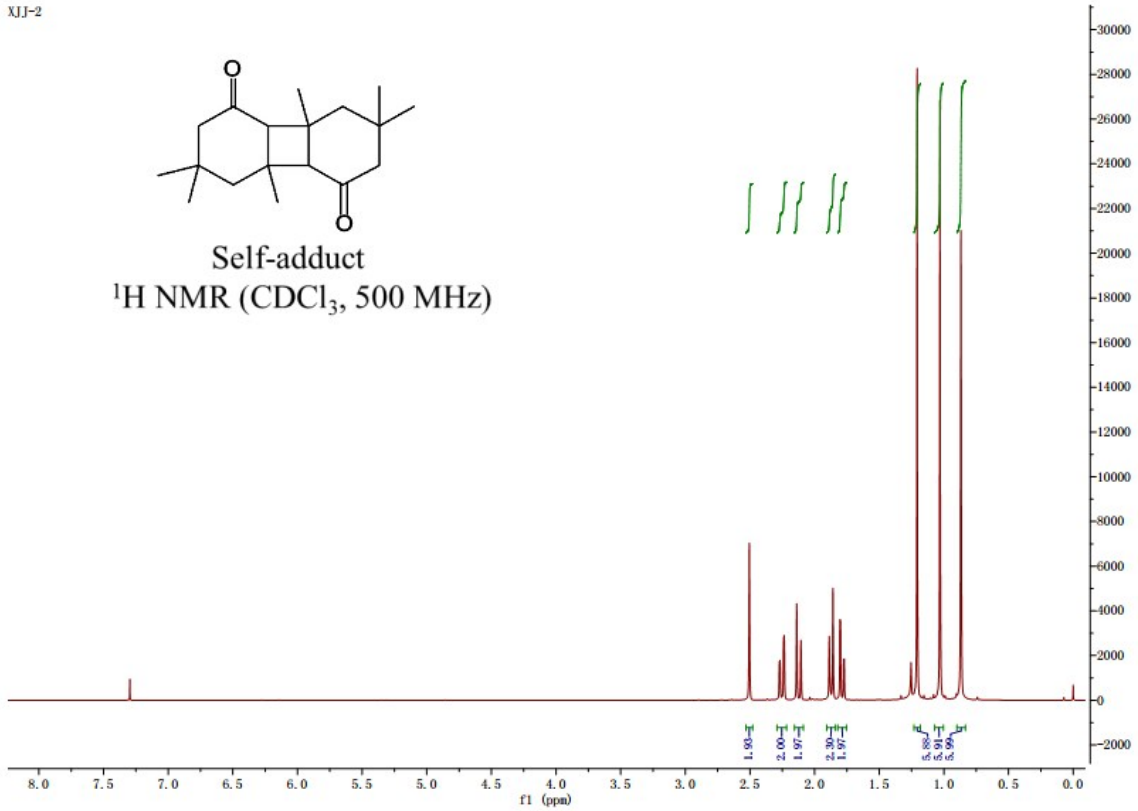


Figure S3 ^{1}H and ^{13}C NMR spectra of self-adduct (One of the isomers obtained by recrystallization).



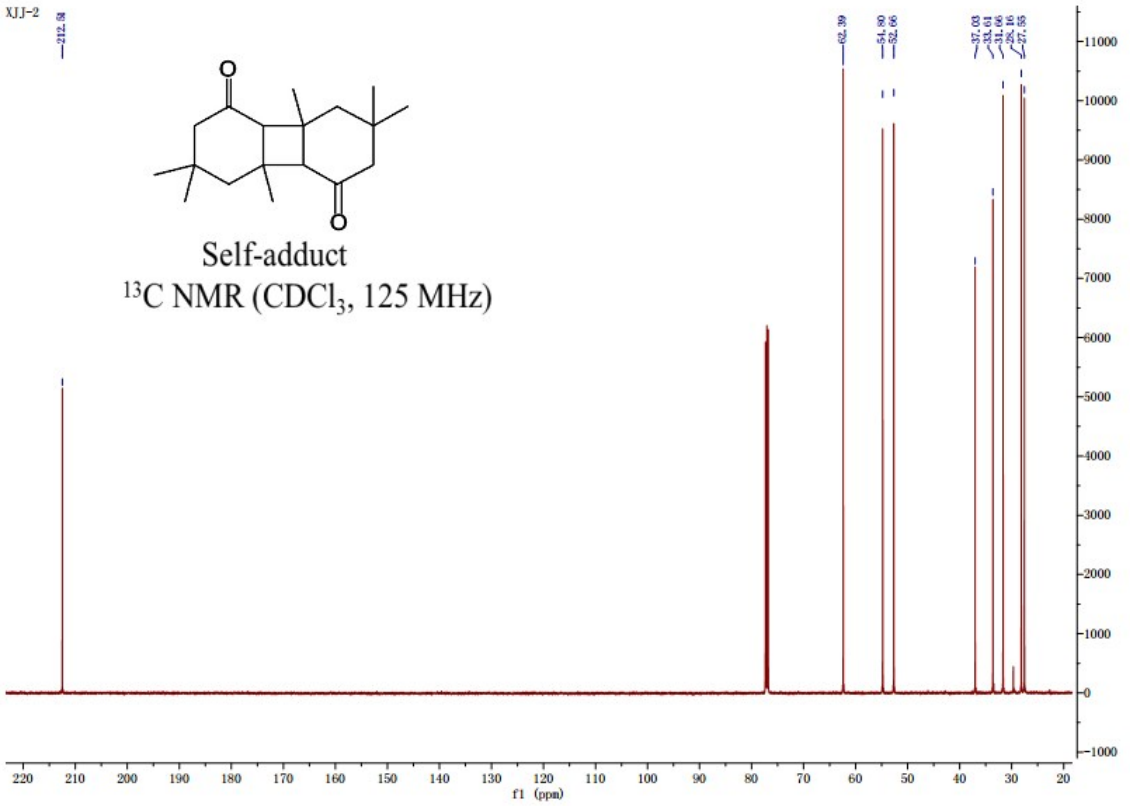


Figure S4 Mass spectra of photoisomerized product 3-methylidene-5,5-dimethylcyclohexanone.

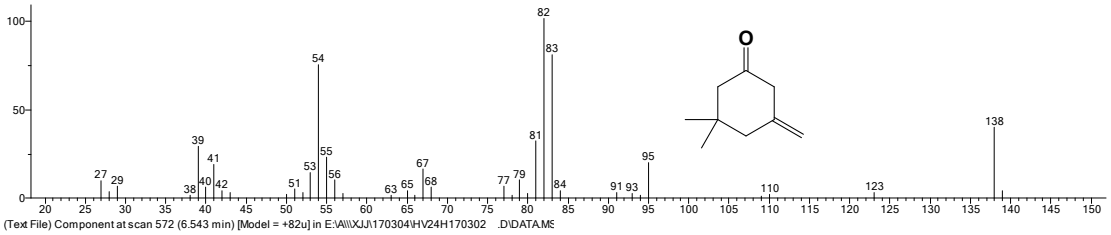
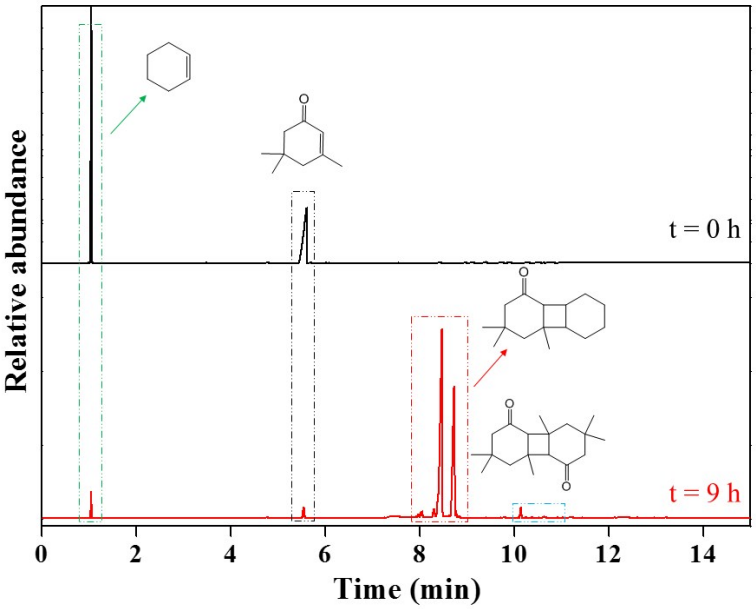


Figure S5 GC spectra of isophorone and cyclohexene co-cycloaddition reaction solution.



The co-adduct of cyclohexene and isophorone has several stereoisomers as follows.

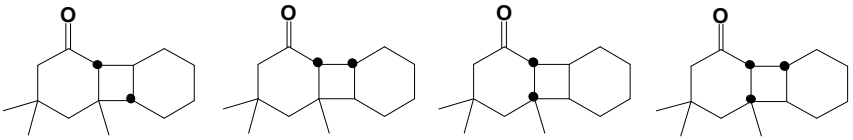


Figure S6 Mass spectra of co-adduct.

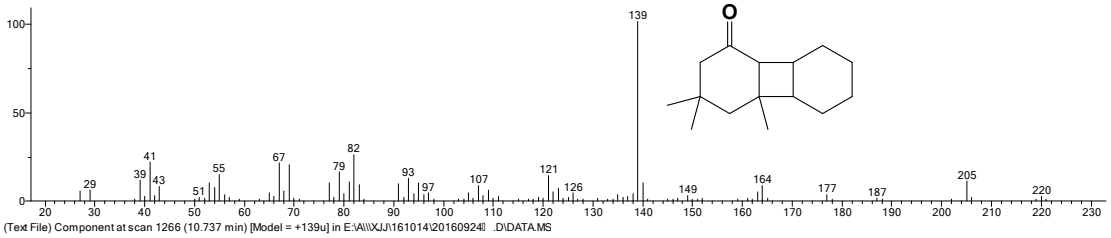
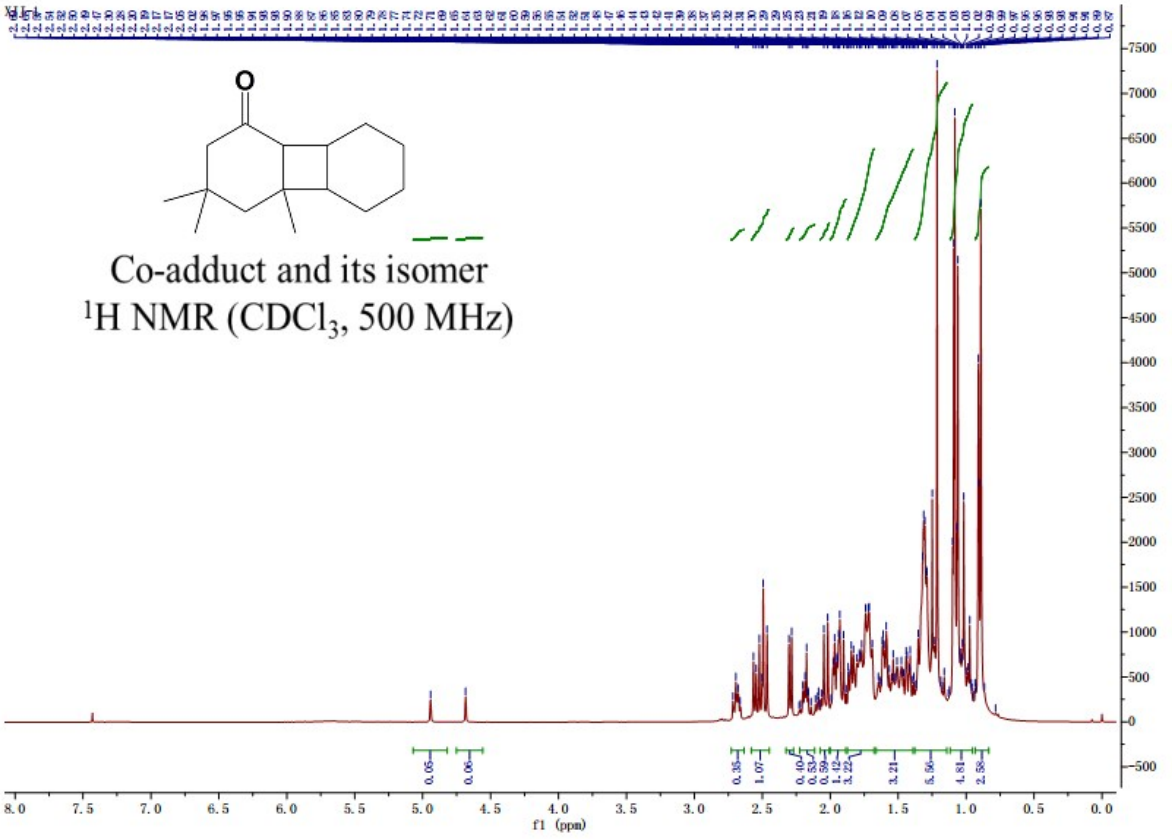


Figure S7 ^{1}H and ^{13}C NMR spectra of co-adduct.



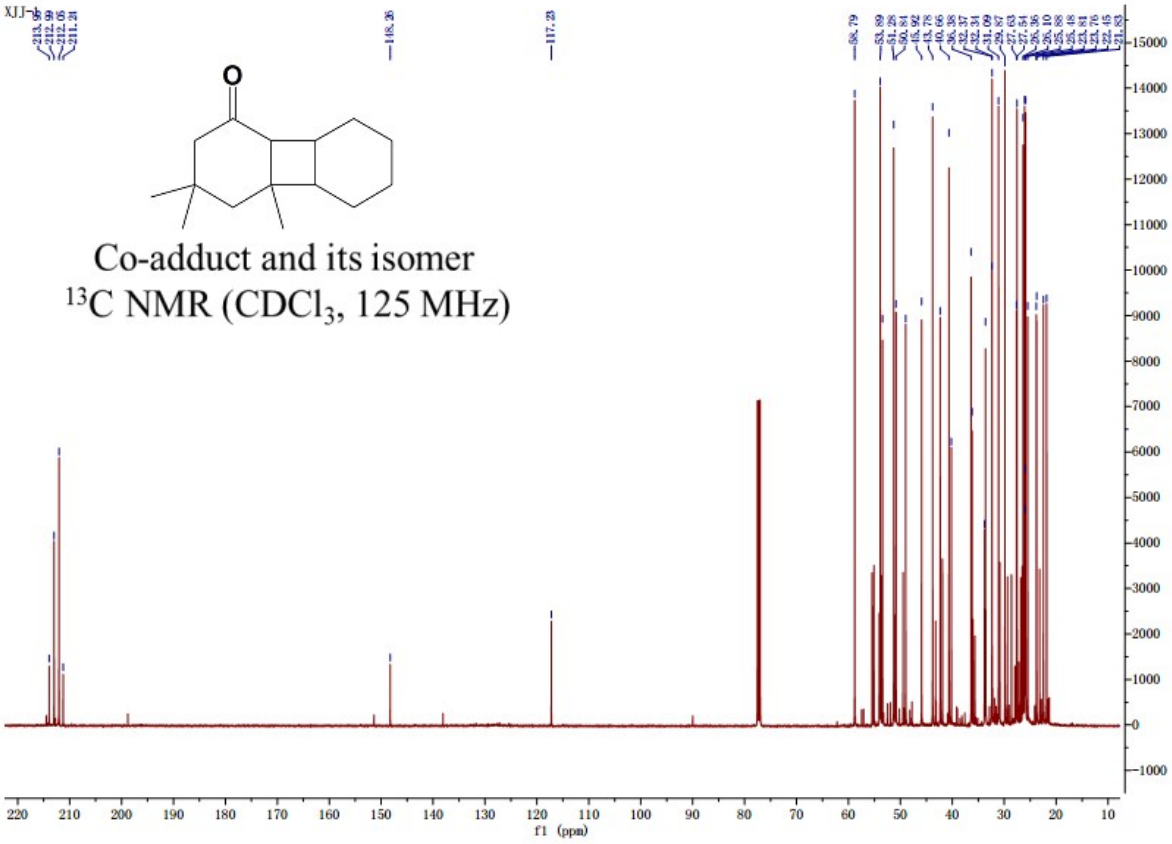
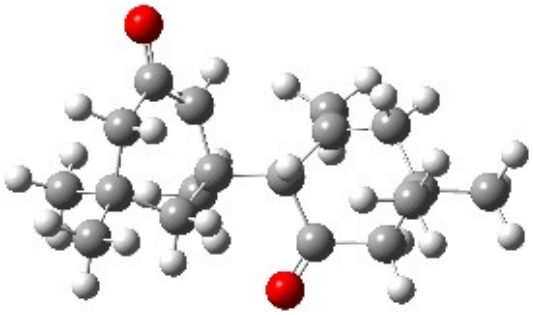
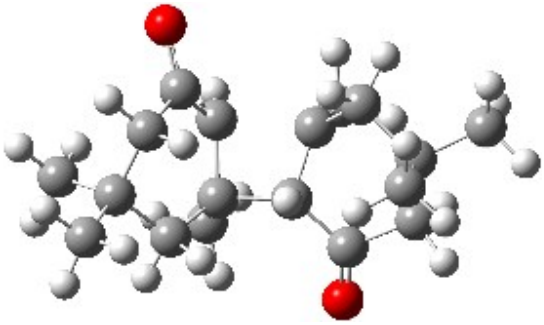


Figure S8 Structures of the stationary species in Figure 4.

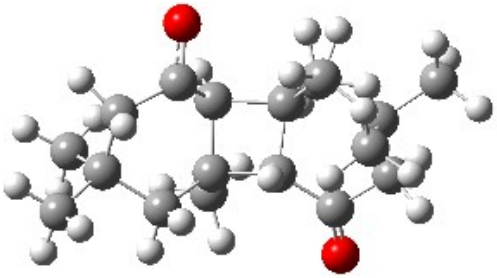
Biradical 1



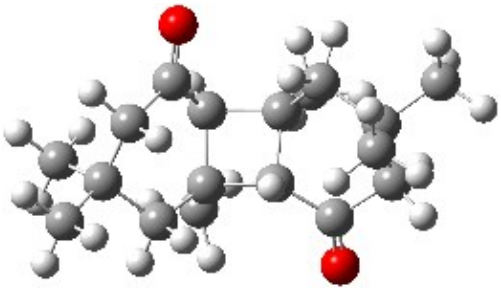
TS1



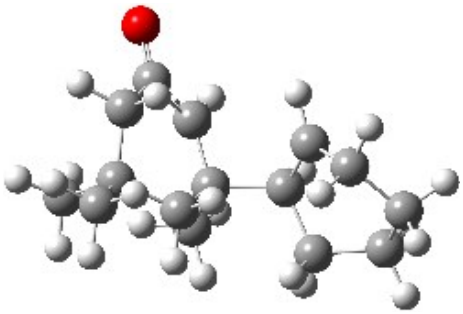
Triplet 1



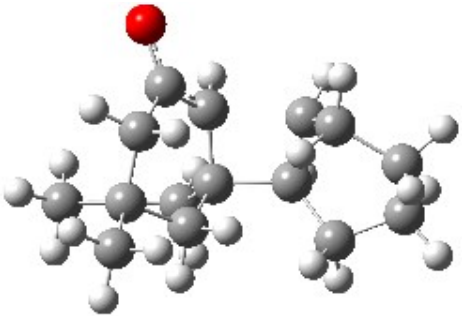
Self-adduct



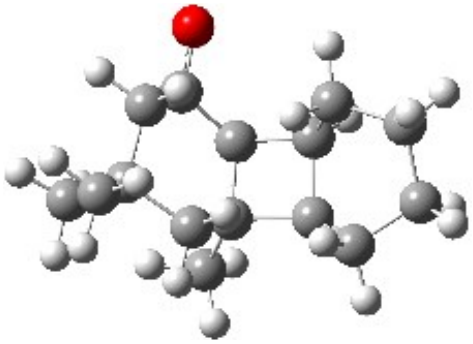
Biradical 2



TS2



Triplet 2



Co-adduct

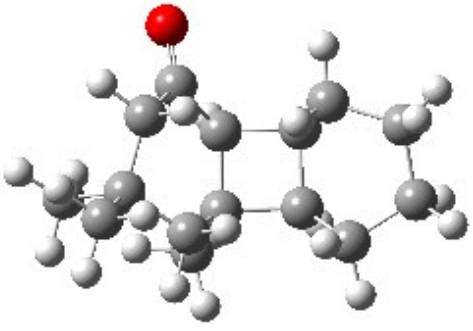


Figure S9 Mass spectra of isophorone and n-hexene co-adduct.

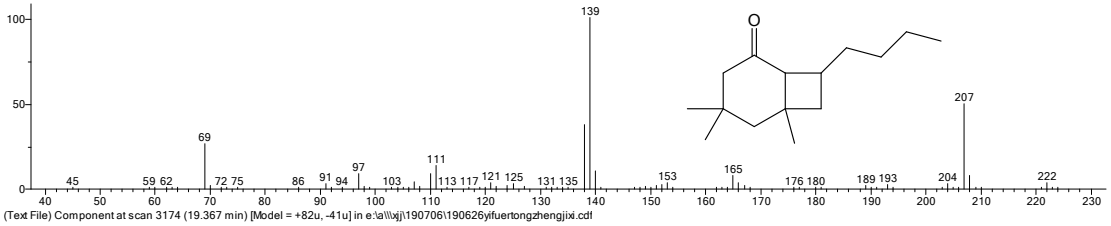


Figure S10 GC spectra of isophorone and n-hexene reaction solution.

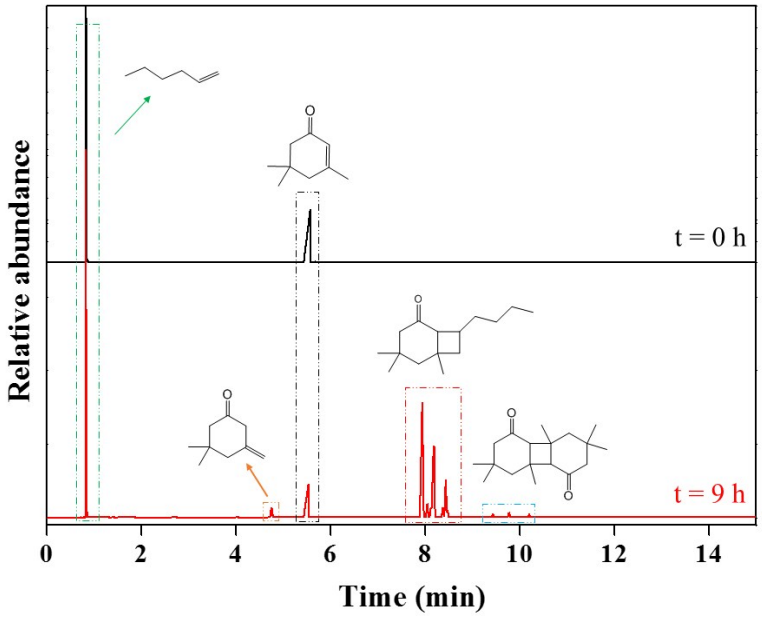


Figure S11 Mass spectra of isophorone and 1-octene co-adduct.

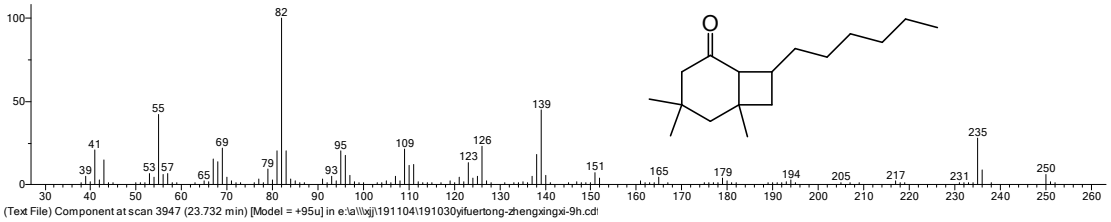


Figure S12 GC spectra of isophorone and 1-octene reaction solution.

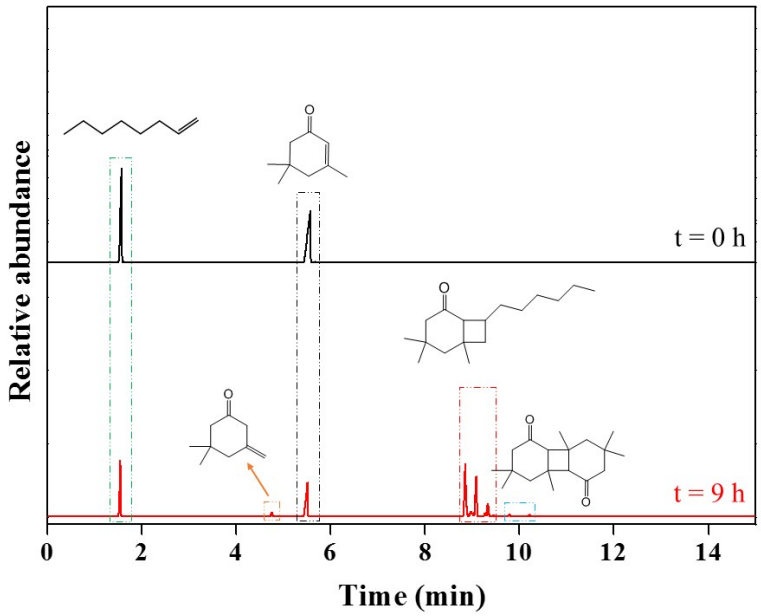


Figure S13 Mass spectra of isophorone and cyclopentene co-adduct.

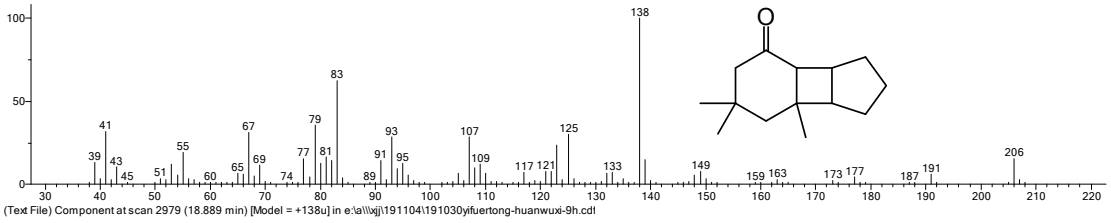


Figure S14 GC spectra of isophorone and cyclopentene reaction solution.

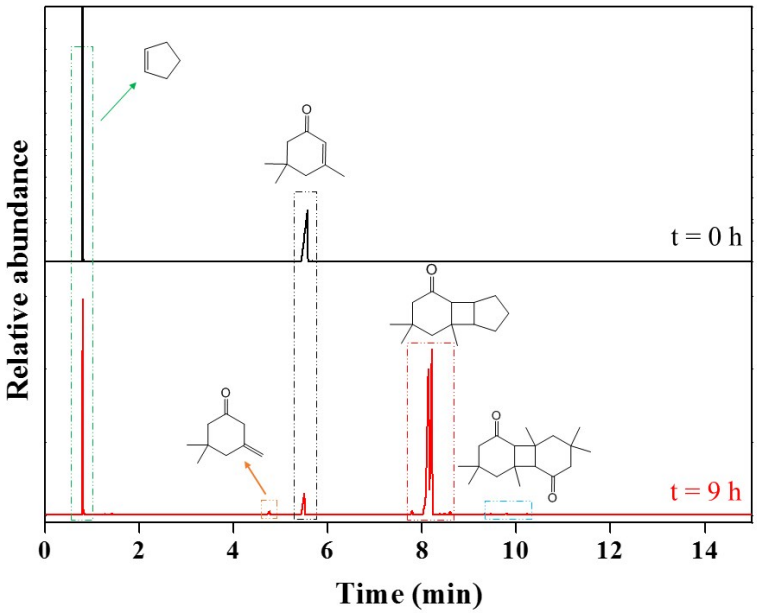


Figure S15 Mass spectra of isophorone and cycloheptene co-adduct.

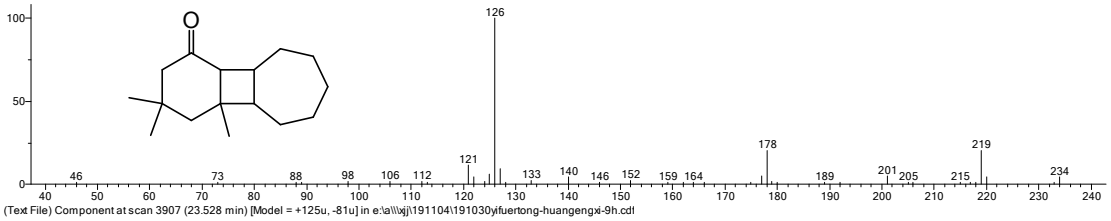


Figure S16 GC spectra of isophorone and cycloheptene reaction solution.

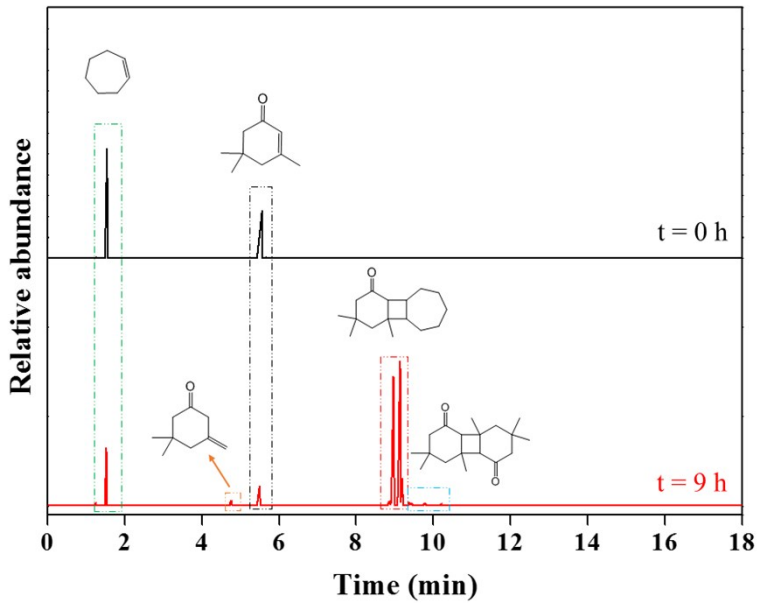


Figure S17 Mass spectra of isophorone and norbornene co-adduct.

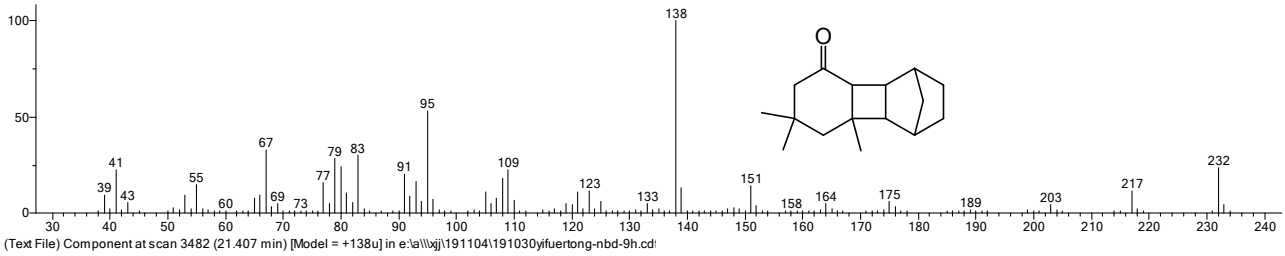


Figure S18 GC spectra of isophorone and norbornene reaction solution.

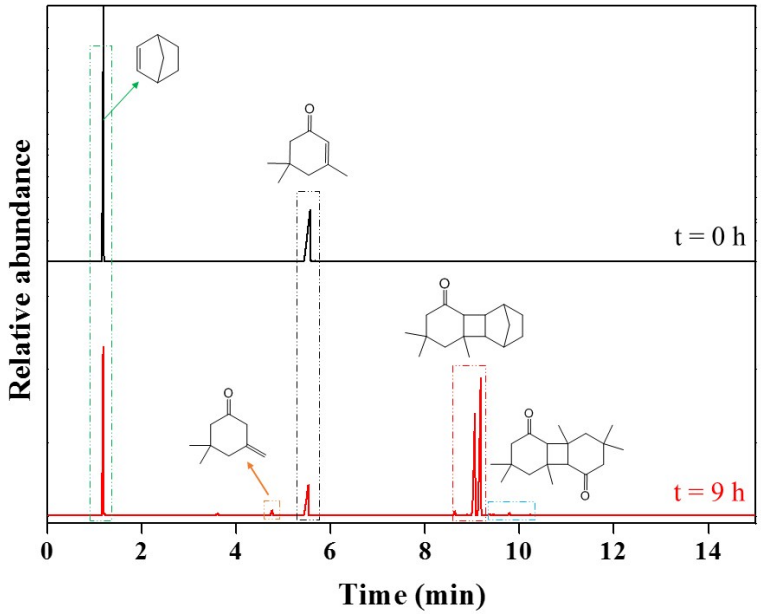


Figure S19 Mass spectra of isophorone and vinyl cyclohexane co-adduct.

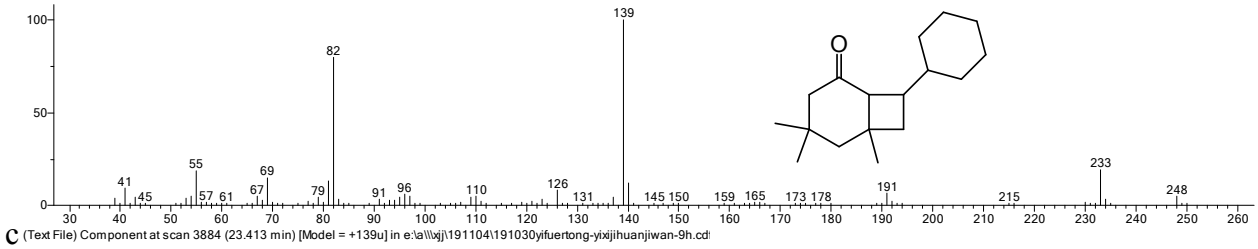


Figure S20 GC spectra of isophorone and vinyl cyclohexane reaction solution.

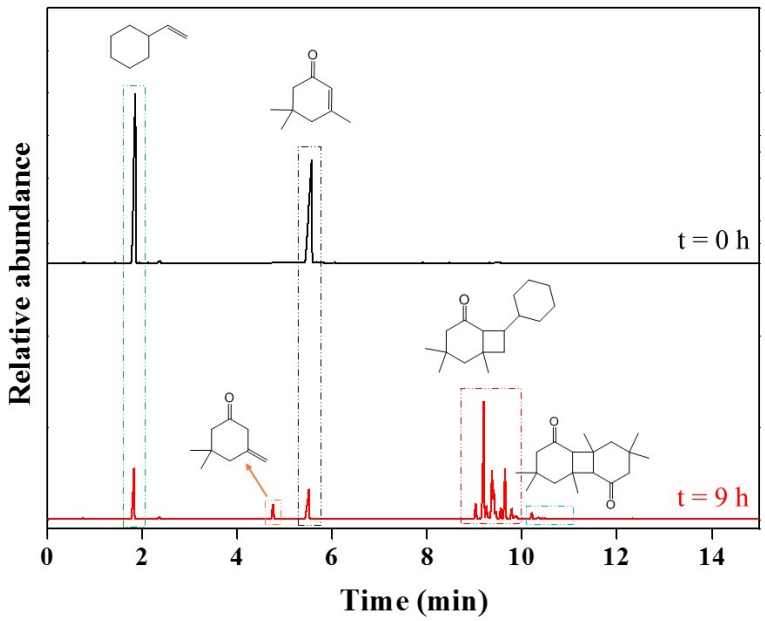
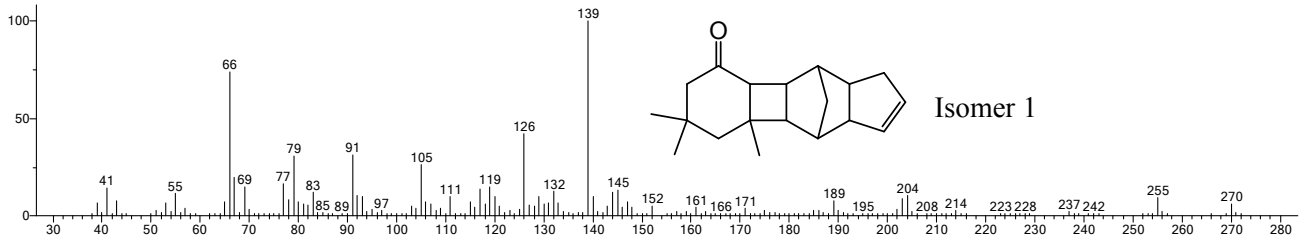


Figure S21 Mass spectra of isophorone and dicyclopentadiene co-adducts.



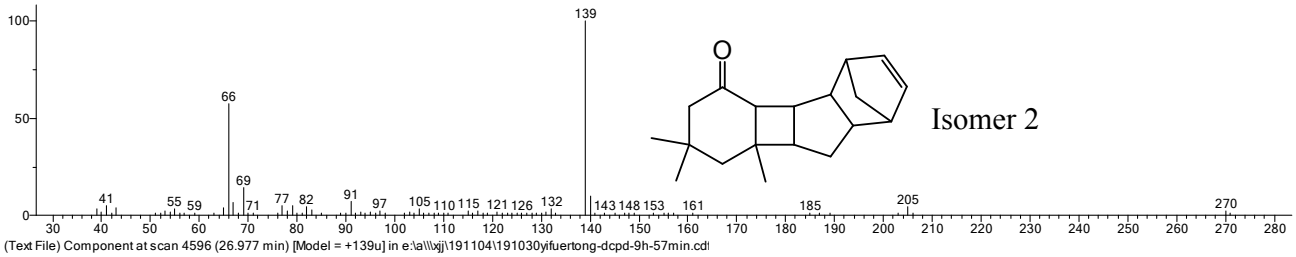


Figure S22 GC spectra of isophorone and dicyclopentadiene reaction solution.

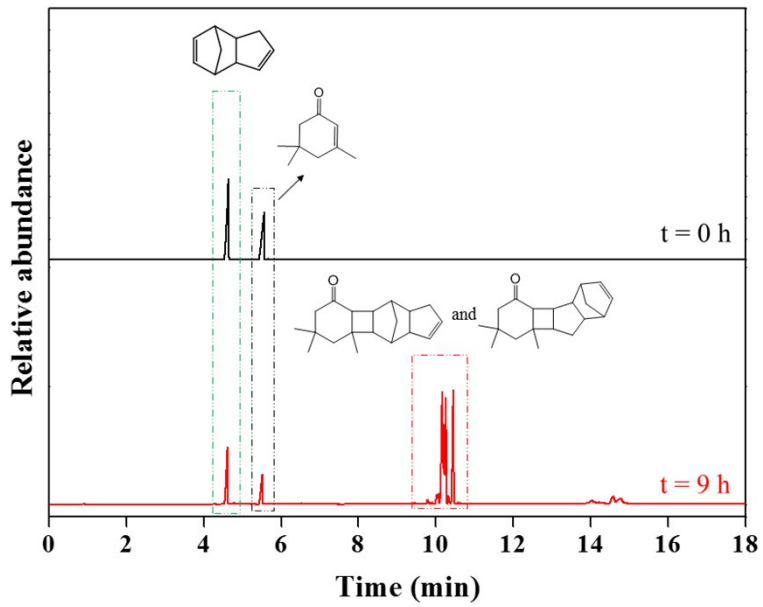


Figure S23 Mass spectra of isophorone and styrene co-adduct.

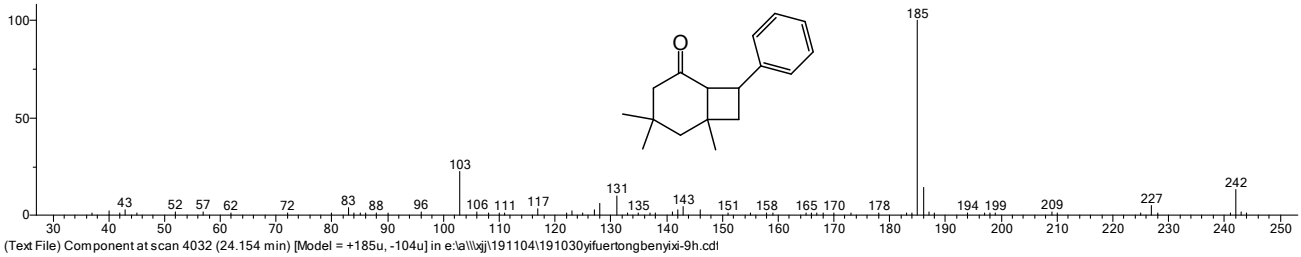


Figure S24 Mass spectra of styrene self-adduct.

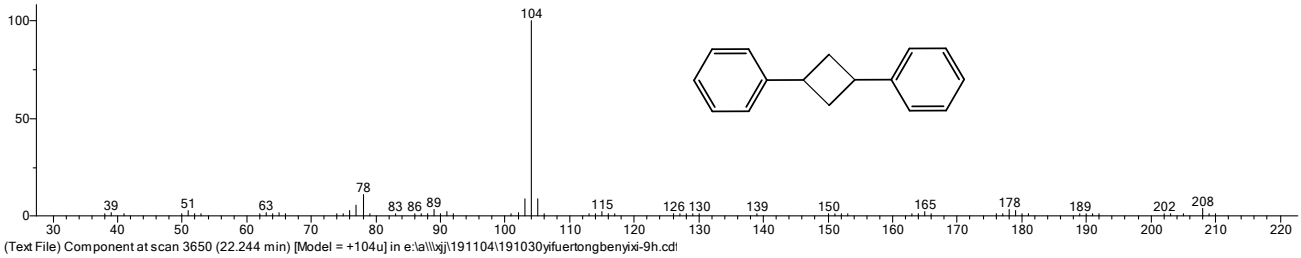


Figure S25 GC spectra of isophorone and styrene reaction solution.

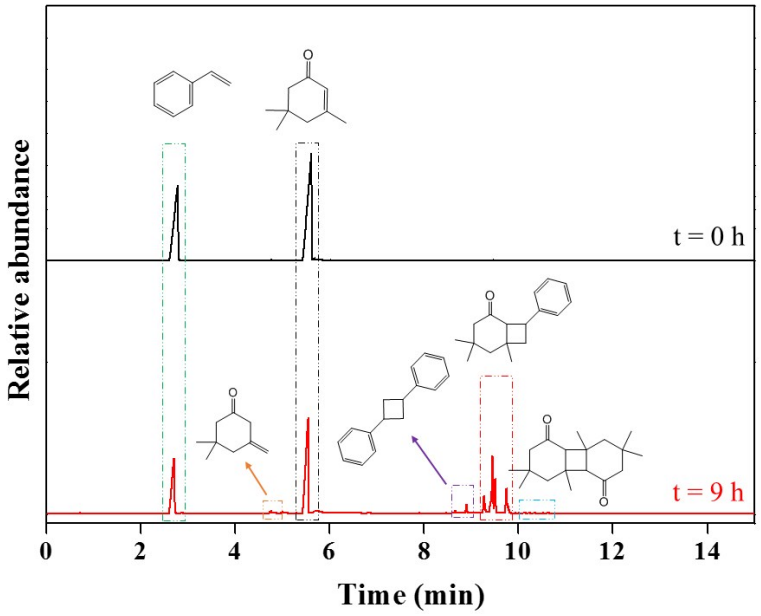


Figure S26 Mass spectra of the fuel derived from isophorone self-cycloaddition.

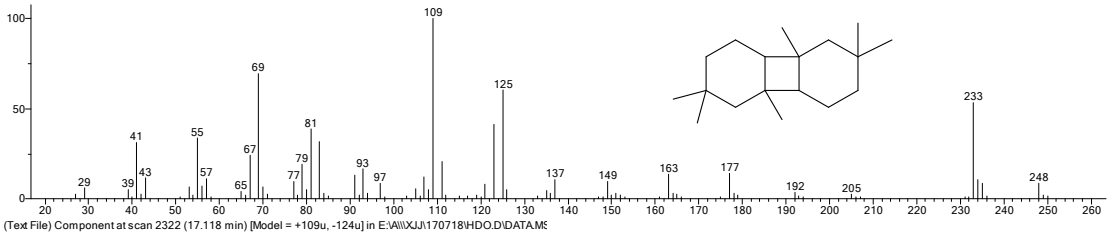
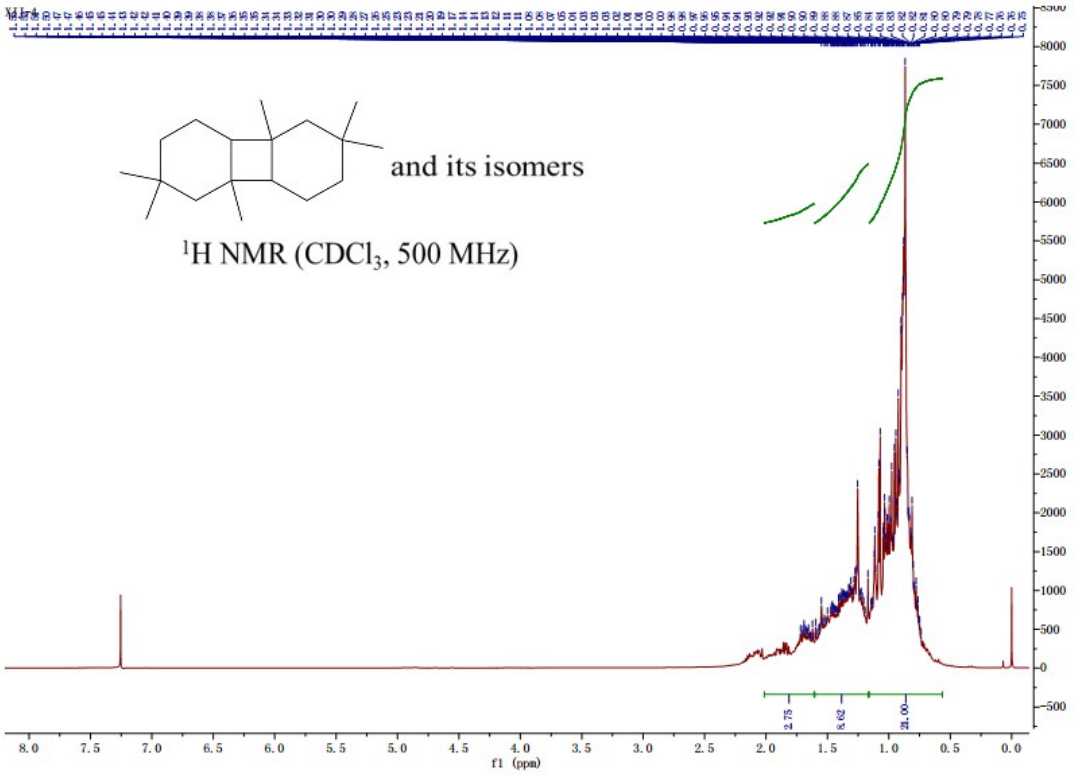


Figure S27. ^{1}H and ^{13}C NMR spectra of the obtained fuel derived from isophorone self-cycloaddition.



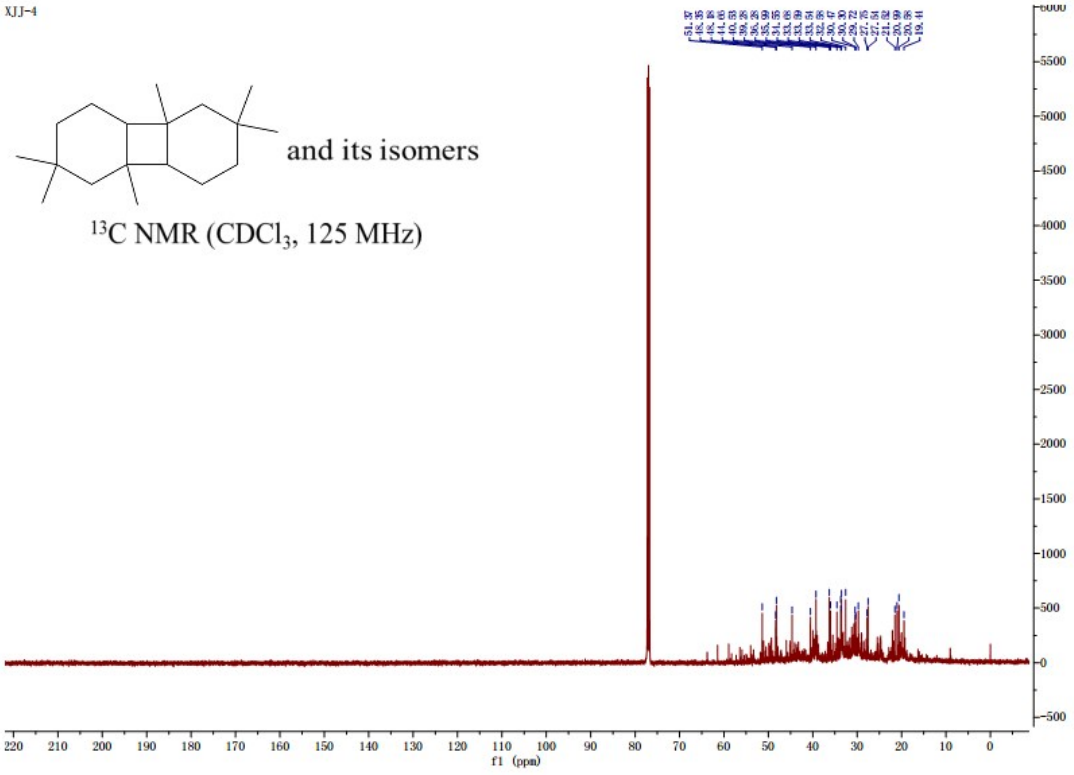


Figure S28 GC spectra of the obtained fuel derived from isophorone self-cycloaddition after vacuum distillation.

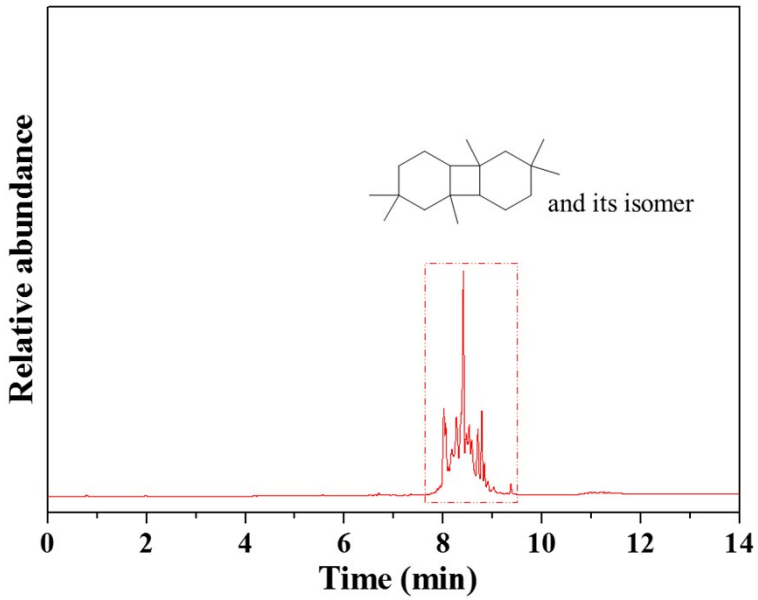
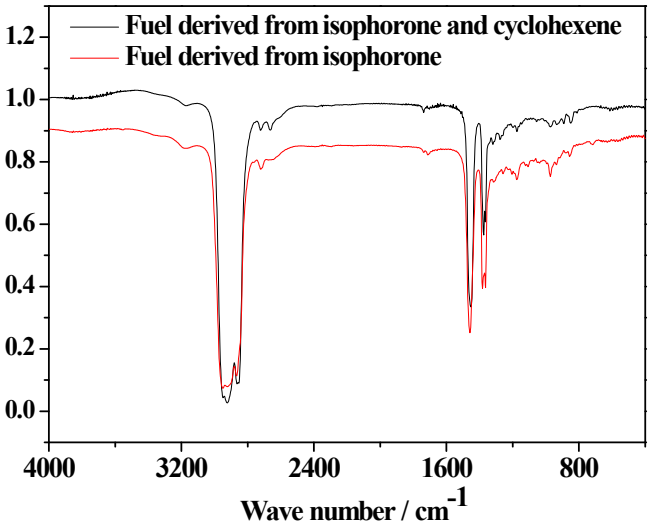


Figure S29. FTIR spectra of the final high-density fuel molecules.



2923 cm^{-1} and 2866 cm^{-1} belong to the stretching vibration of C-H in -CH_2-. 1457 cm^{-1} is the rocking vibration of methyl and methine. 1364 cm^{-1} and 1382cm^{-1} are the characteristic cleavage absorption peak of isopropyl.

Figure S30 Mass spectra of the fuel derived from co-cycloaddition of isophorone and cyclohexene.

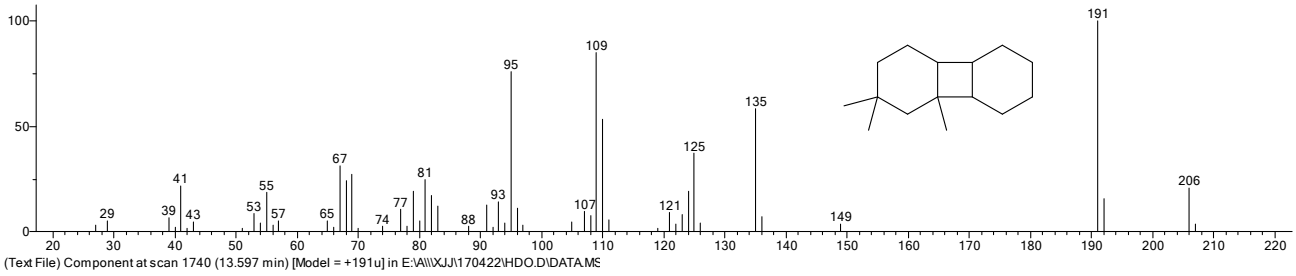
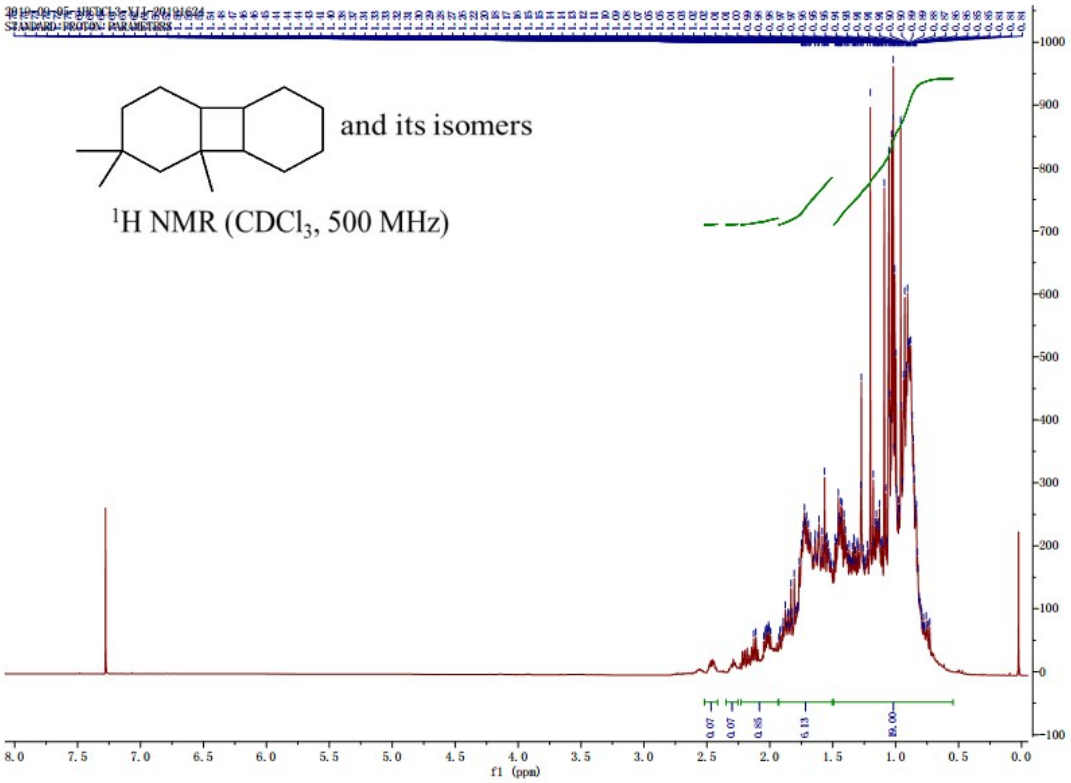


Figure S31. ^{1}H and ^{13}C NMR spectra of the fuel derived from co-cycloaddition of isophorone and cyclohexene.



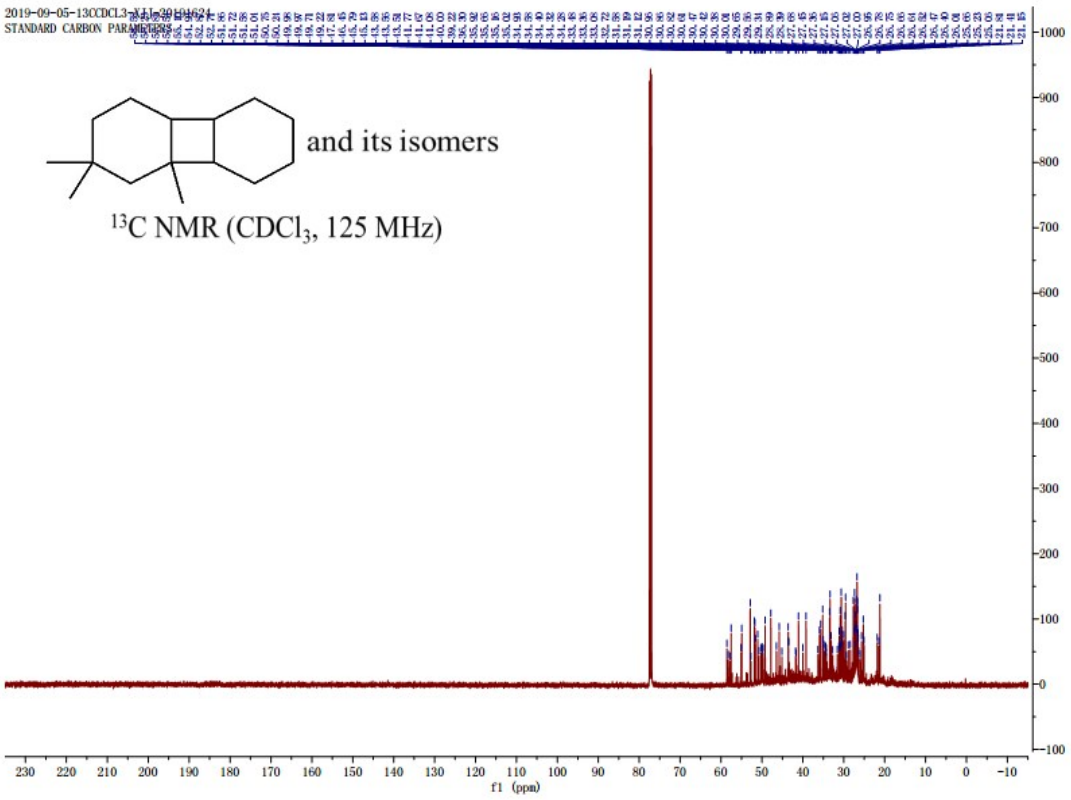


Figure S32 GC spectra of the fuel derived from co-cycloaddition of isophorone and cyclohexene after vacuum distillation.