

## Supplementary Information

### **Electric Production of High-quality Fuels via Electron Beam Irradiation at Ambient Conditions**

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**This SI has 26 pages and includes 17 figures, four schemes, and one table:**

1. Materials and methods
2. Figures S1 (Experimental setup)
3. Figures S2-S17 (Sample Characterization)
4. Scheme S1-S4 (Illustration of radical creation and reaction pathways)
5. Table S1 (Physiochemical properties of irradiated hydrocarbon compounds)

## Material and Methods

### Materials

Unless stated otherwise, all gas and liquids used in this paper are high-purity (>99%). Lab solvents DCM, mineral spirits and acetone were used when required. Pentane (MilliporeSigma; product number: 236705-2L), Cyclohexane (MilliporeSigma; product number: 227048-1L), Methylcyclohexane (MilliporeSigma; product number: 300306-100ML), Ethylbenzene (MilliporeSigma; product number: 296848-100ML), Tetralin (MilliporeSigma; product number: 522651-1L), Toluene (MilliporeSigma; product number: 244511-100ML), Benzene (MilliporeSigma; product number: 401765-100ML), and Methylanthalene (MilliporeSigma; product number: W319309-100G-K) are irradiated.

### Preparation of reactor

Commercially available aluminum tube (multipurpose 6061, 12.5 mm OD, 9mm ID, and 50 cm length), stainless tube fittings and brass ball valve used to house liquid in the reactor. Reactors were cleaned by acetone before loading samples. One pressure relief valve and pressure gage were used to monitor pressure in the system. System was leaking checked at 60 psi before loading liquid samples. Liquid samples were loaded into system and sealed with helium at 5 psi. System pressure was checked before irradiation test to make sure no system leaking.

About 5 kg ice was mixed with water in the cooling water bath. Temperature of the cooling water was monitored during each experiment. Temperature was maintained in 5-10 °C range with a circulation pump. Reactor was partially submerged in water and fixed in the water bath. Reactor temperature was in equilibrium with cooling water.

### Preparation of test

Reactors were carefully aligned with the beam to make sure samples absorb radiation uniformly. Solid alanine dosimeters were used to measure dose rate (kJ/kg-s) absorbed by the sample. Exposure time was calculated based on the desired specific energy input (kJ/kg) and measured dose rate. When reactor with sample was ready, beam was turned on. Temperature and system pressure were monitored in real-time when beam was on to make sure pressure was below the pressure relief setting pressure and sample temperature below the boiling point of each sample. Beam was turned off when specific energy input reached desired values. Reactors with treated samples were closed and stored at lab conditions before samples were collected into a glass jar.

### Sample characterization

Treated liquid samples were first poured into a glass jar (ULINE; product number: S-15846M-W), then stored in a refrigerator. Liquid products were analyzed by Thermo Scientific DSQ II GC-MS (gas chromatography-mass spectrometry) and Agilent 6890N series gas chromatograph with flame ionization detector (GC-FID). The liquid samples for the GC-MS and GC-FID analysis were prepared by mixing 8 mg of the treated sample with 2.4 g of Dichloromethane (Sigma-Aldrich; product number: 270997). Diluted sample (1 $\mu$ L) was injected into a space on the top of the GC column. Liquid product was first identified using C<sub>8</sub>-C<sub>40</sub> alkanes calibration standard (Sigma-Aldrich; product number: 40147-U). The concentration of the liquid products was quantified calculating the normalized peak areas in GC-MS. Mass spectrum of each new peaks was analyzed

by the GC-MS system and compared to the mass spectrum library to identify the chemical structure of them. Results from both GCs help verify each other.

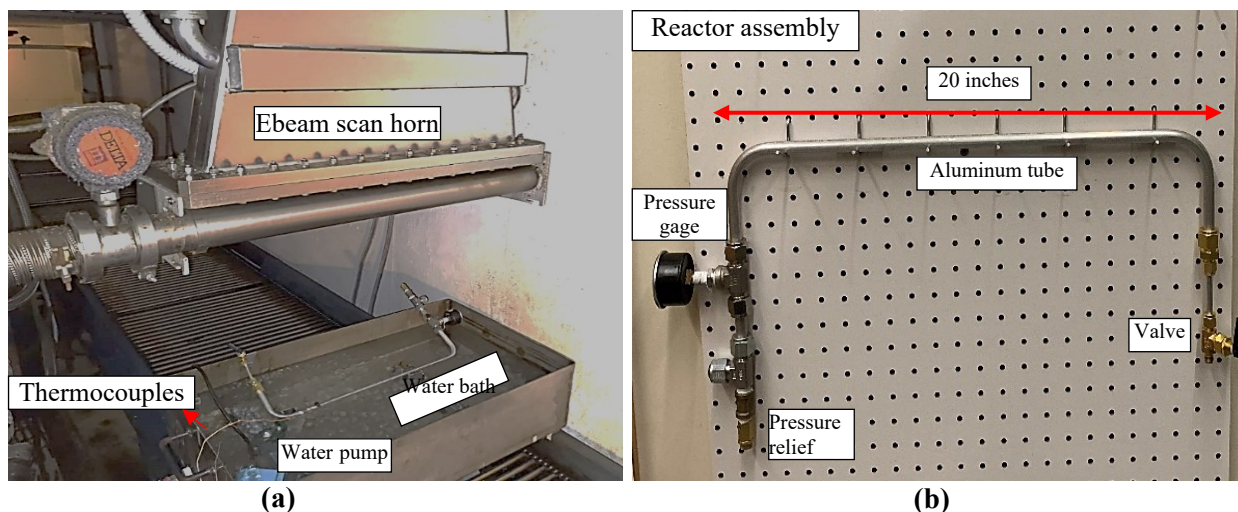
#### Conversion in treated sample

Conversion of each compound to each hydrocarbon compound in different ranges was calculated based on both GC-FID and GC-MS peak area. Peak area corresponding to each compound within one sample was first calculated. Peak area was then normalized by the total peak areas. Normalized peak area corresponding to each compound is proportional to its mass concentration in the sample. The proportionality constant was determined by calibrant (Sigma Aldrich; part number: 49452-U). Normalized peak areas in treated sample subtract the same peaks in control sample and the difference represents conversion to each compound.

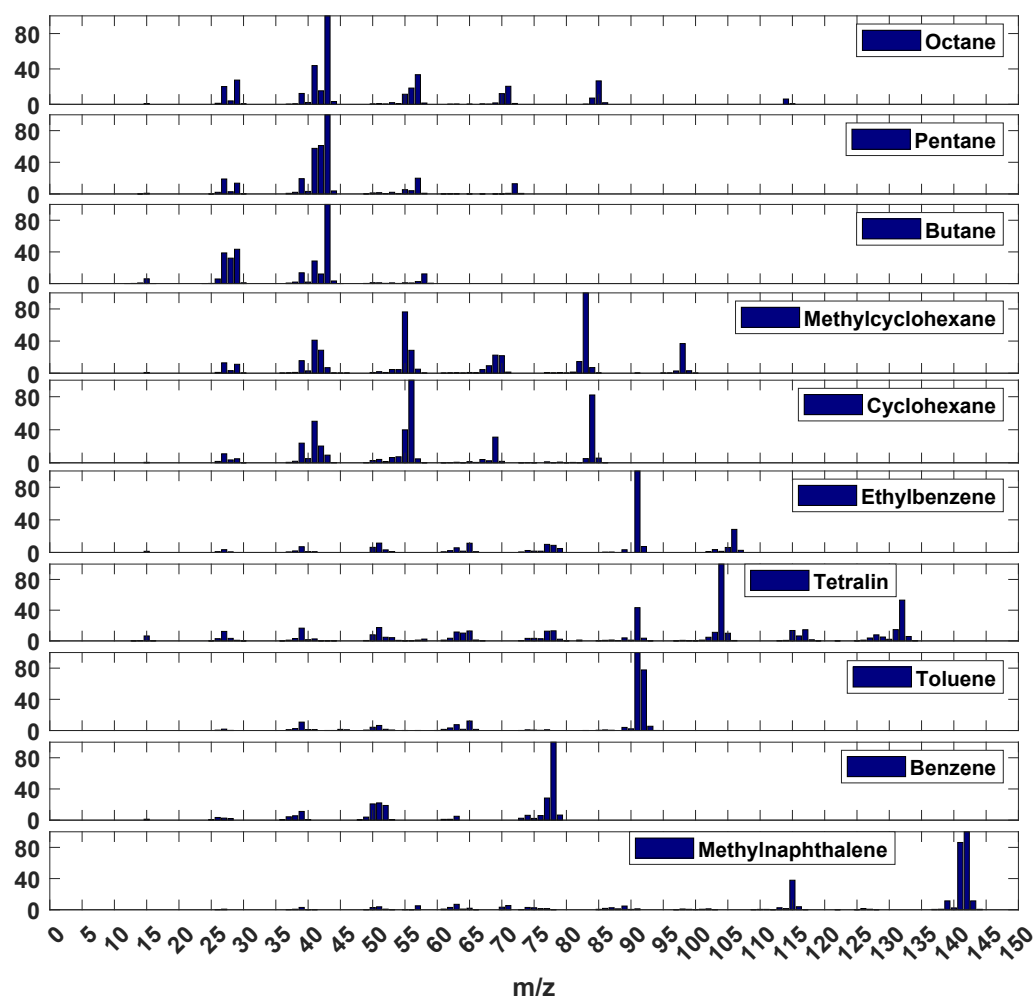
$$C_i (\%) = A_{i-treated} - A_{i-control}$$

$$C_{total} (\%) = \sum_{i=6}^{i=15} (A_{i-treated} - A_{i-control})$$

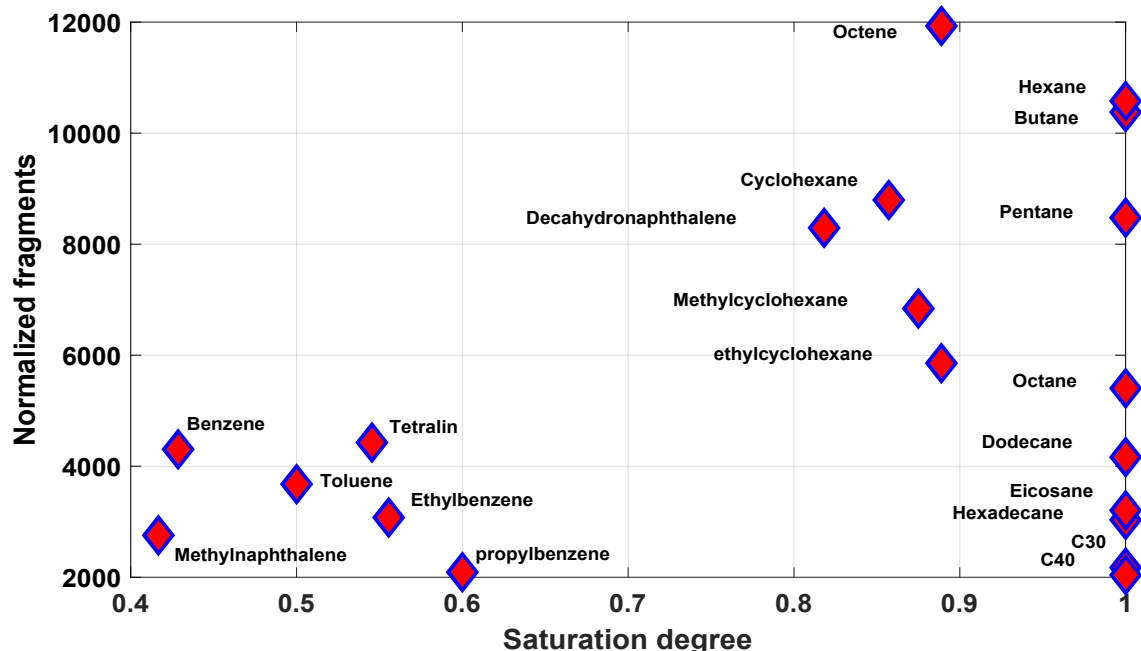
Where  $C_i$  is conversion to each compound including multiple hydrocarbon products.  $C_{total}$  is the conversion of pentane and its equal to the sum of all products.  $A_{i-treated}$  and  $A_{i-control}$  are normalized area of new hydrocarbon compound in treated sample and control sample, respectively. Conversion to gaseous hydrocarbon products smaller than  $C_5$  was not studied at each individual carbon number. But mass loss due to those gaseous hydrocarbons is estimated.



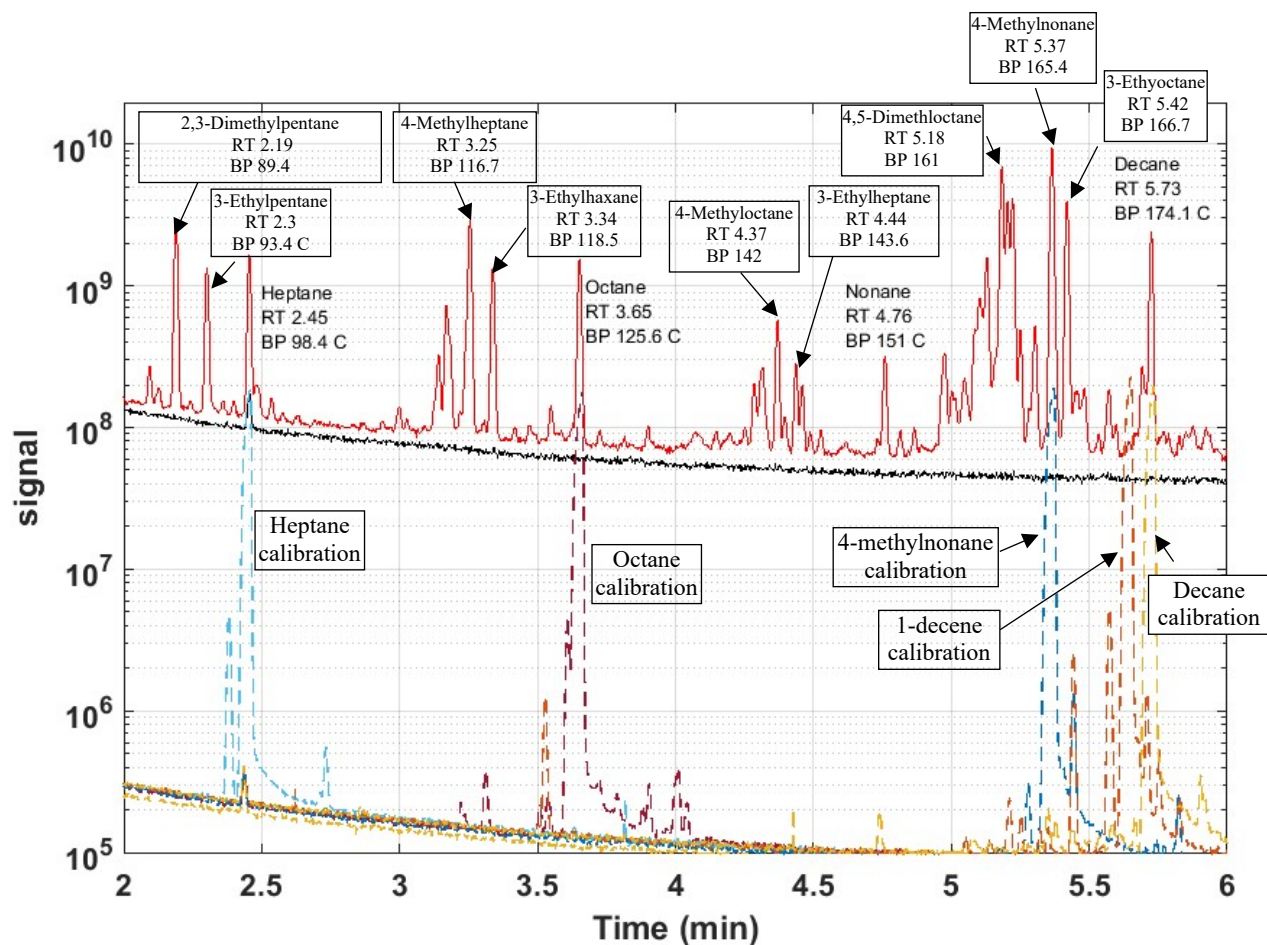
**Figure S1. Experimental setup used to irradiate liquid samples at ambient conditions. (a),** electron beam scan horn and water bath. Beam coming from the scan horn is about 22-inch long, slightly longer than the tube length to make sure sample was irradiated uniformly. Ice water bath was used to keep the sample cold during the irradiation test. Reactor was submerged into the ice water bath. Ice water bath was inside a stainless-steel container and a water pump was used to circulate cold water near the reactor wall. Two thermocouples monitor the real-time reactor temperature. **(b),** the reactor was made of  $\frac{1}{2}$  inch OD aluminum tubes with thin wall. The length of the tube is 20 inches. Tube was sealed with a ball valve on one side and a pressure relief valve on the other side. One pressure gage was used to allow for real time monitor of the system pressure. Reactor was first washed with pentane to remove potential contaminates. Then pentane sample was loaded into the reactor. System was purged with inert gas for about two minutes at 0.5 SLPM to remove air, then sealed at 5 psig. Pressure relief valve values setting point was 50 psig.



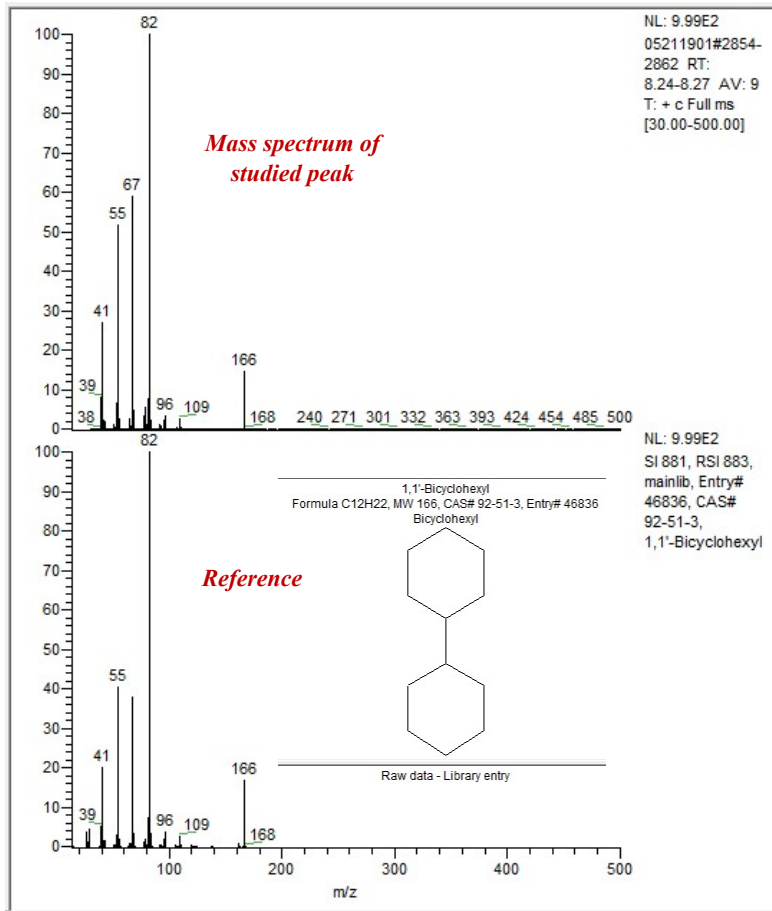
**Figure S2. Mass spectrum of multiple compounds studied in this paper.** Mass spectrum data is an important indicator of the crackability of a molecule when colliding with a high energy electron under very low pressure.



**Figure S3. Normalized fragments of each compound vary with its saturation degree by electronic ionization. Data was derived based on the mass spectrum from NIST Standard Reference Database 69: NIST Chemistry WebBook owned by NIST Mass Spectrometry Data Center.** Fragments were normalized by its total carbon bond number for each compound. Normalized fragments are used to characterize the crackability of a molecule. Aromatics, cyclic alkanes, and straight alkanes have very different crackability indicated by different number of fragments. Order of crackability: straight alkanes > cyclic alkanes > aromatics. Crackability generally increases with increasing the saturation degree.

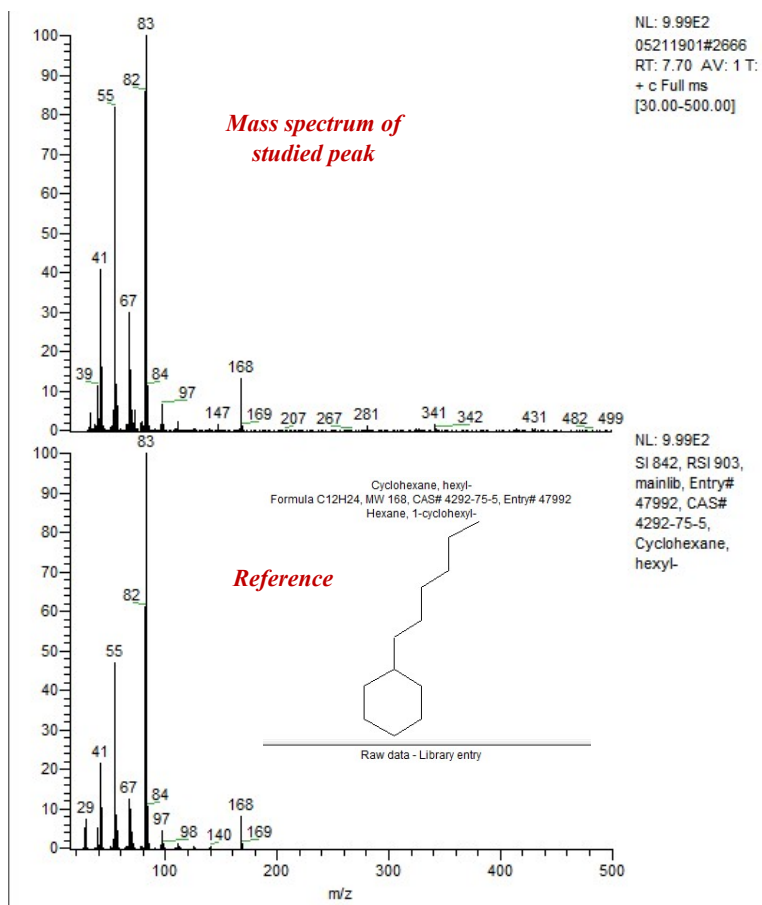


**Figure S4.** GC-MS signals of raw pentane (black line) and irradiated pentane (red line). Signal was focused in 2-6 minutes to study compounds in  $C_7$ - $C_{10}$  group. System was calibrated with pure hydrocarbon compounds including heptane, octane, 4-methylnonane, 1-decene and decane. Calibration signals were used to identify peaks in irradiated pentane. Peaks corresponding to heptane, octane, nonane and decane were identified on signal of irradiated pentane. Branched compounds appeared on the left of alkanes at each carbon group owing to their lower boiling points. Based on the retention time of each peak and known calibration signals, boiling point of each peak was derived. The derived boiling point was compared with data from the National Institute of Standards and Technology (NIST) Database to identify the name and possible chemical structure of each compound. Mass spectrum of those identified compounds were also compared with the NIST mass spectra library. Some of the identified compounds were labeled on the top of corresponding peaks.

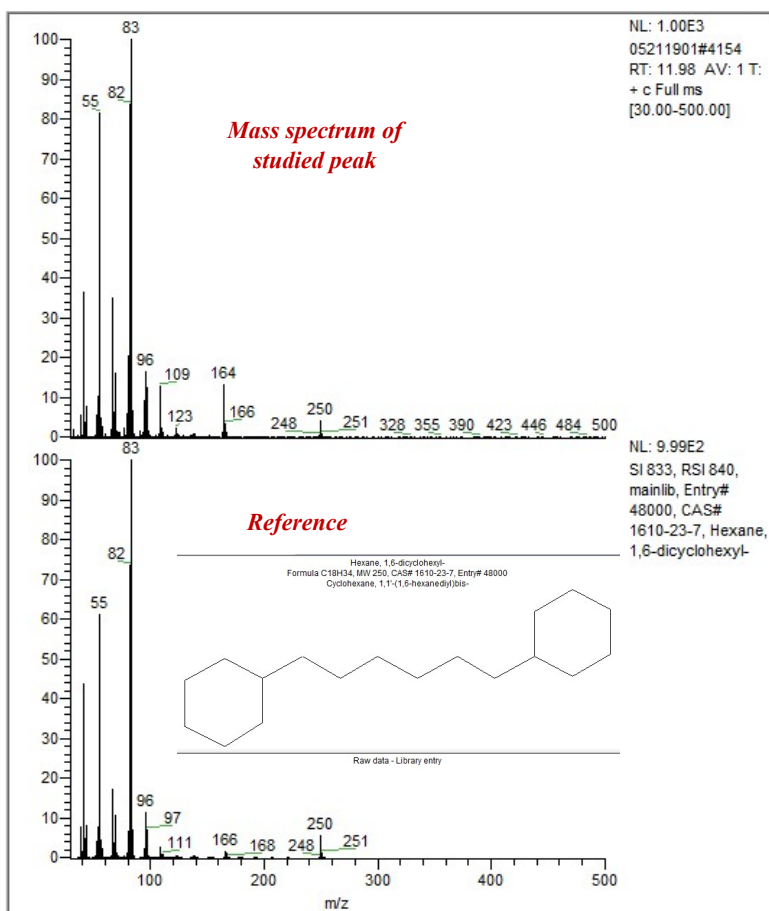


**Figure S5. Mass spectrum of Bicyclohexyl (C<sub>12</sub>H<sub>22</sub>) peak at 8.25 minutes in irradiated cyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**

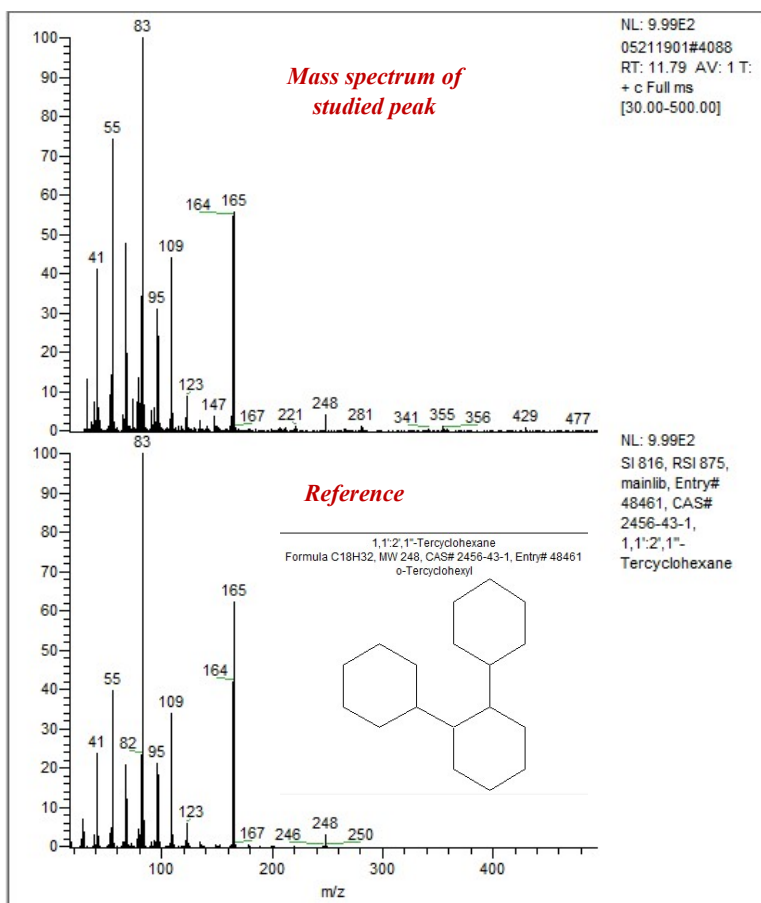




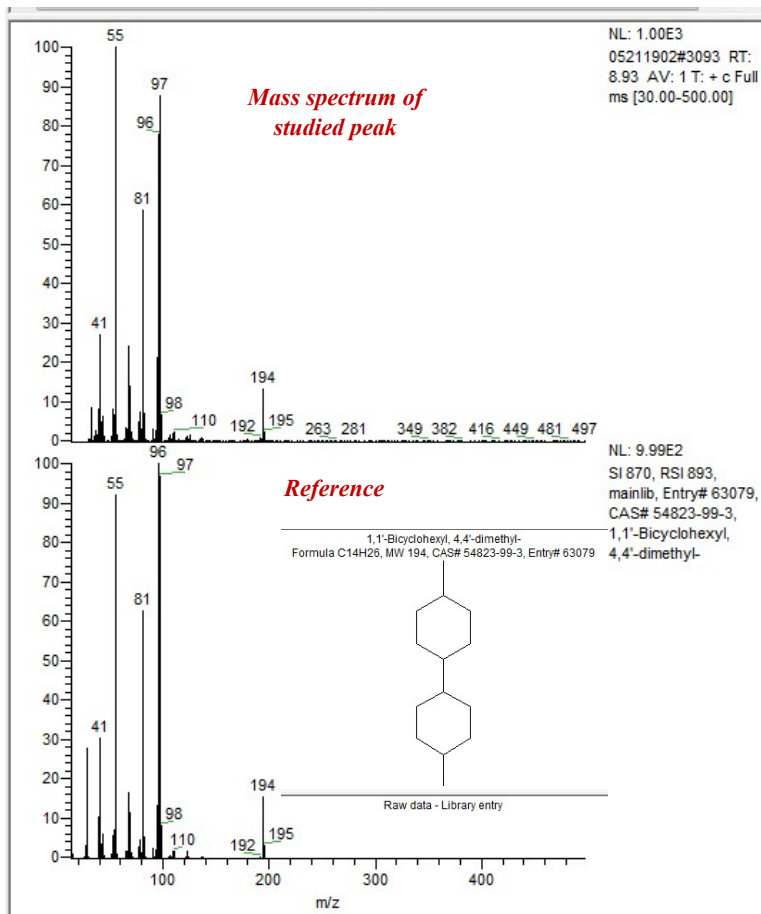
**Figure S6. Mass spectrum of Hexyl-cyclohexane (C<sub>12</sub>H<sub>24</sub>) peak at 7.7 minutes in irradiated cyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



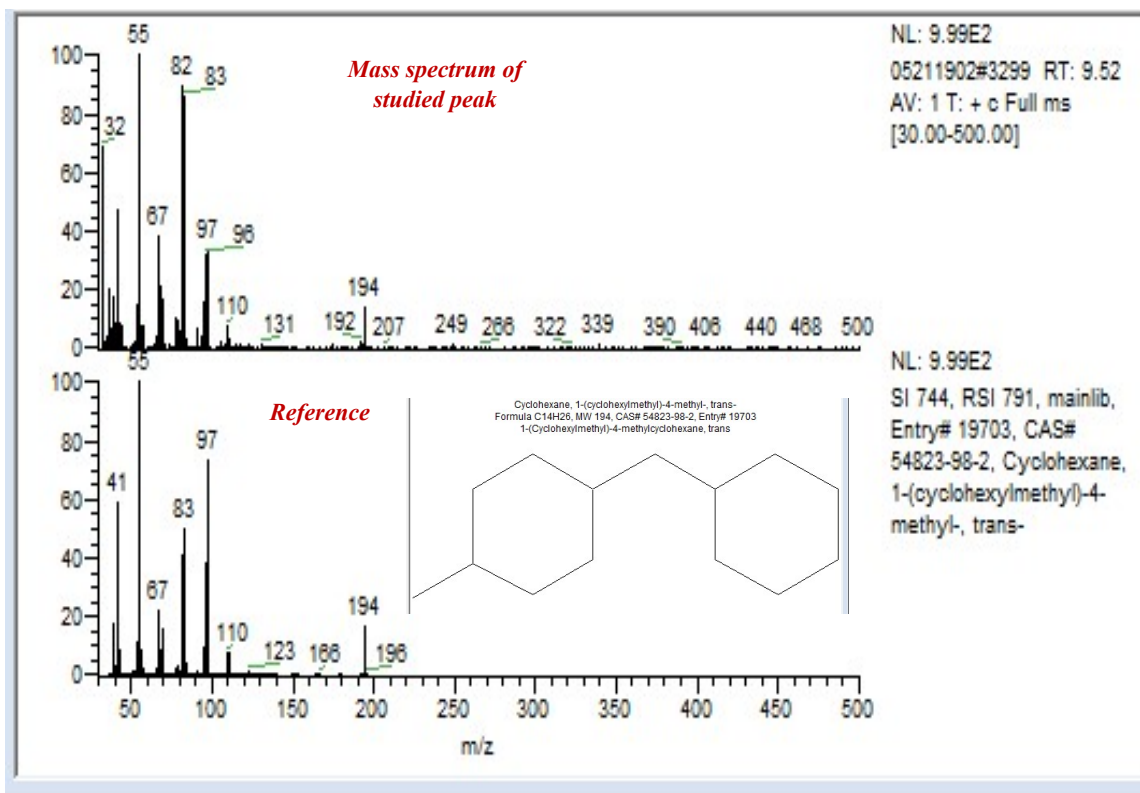
**Figure S7. Mass spectrum of Hexane, 1,6-dicyclohexyl (C<sub>18</sub>H<sub>34</sub>) peak at 11.98 minutes in irradiated cyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



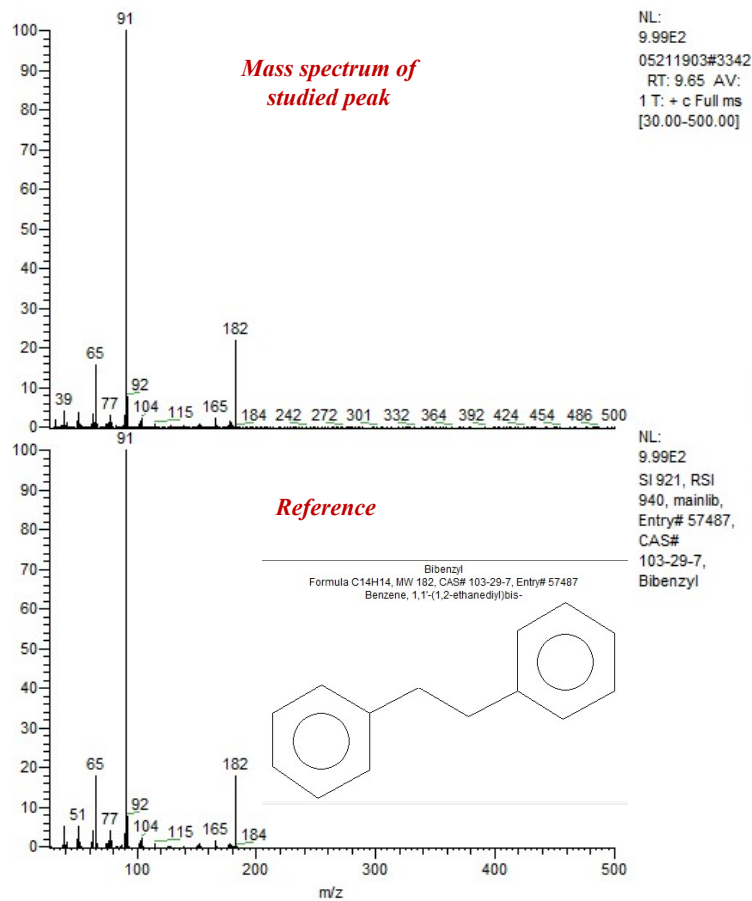
**Figure S8. Mass spectrum of 1,1':2',1''-Tercyclohexane (C<sub>18</sub>H<sub>32</sub>) peak at 11.79 minutes in irradiated cyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



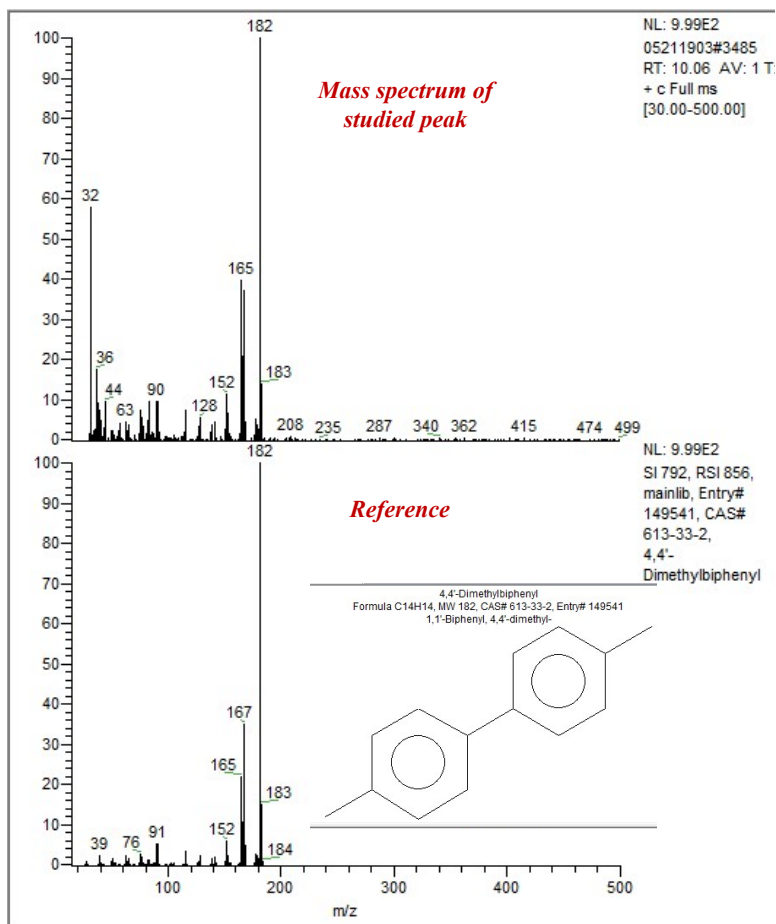
**Figure S9. Mass spectrum of 1,1-bicyclohexyl,4,4-dimethyl- ( $C_{14}H_{26}$ ) peak at 11.79 minutes in irradiated methylcyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



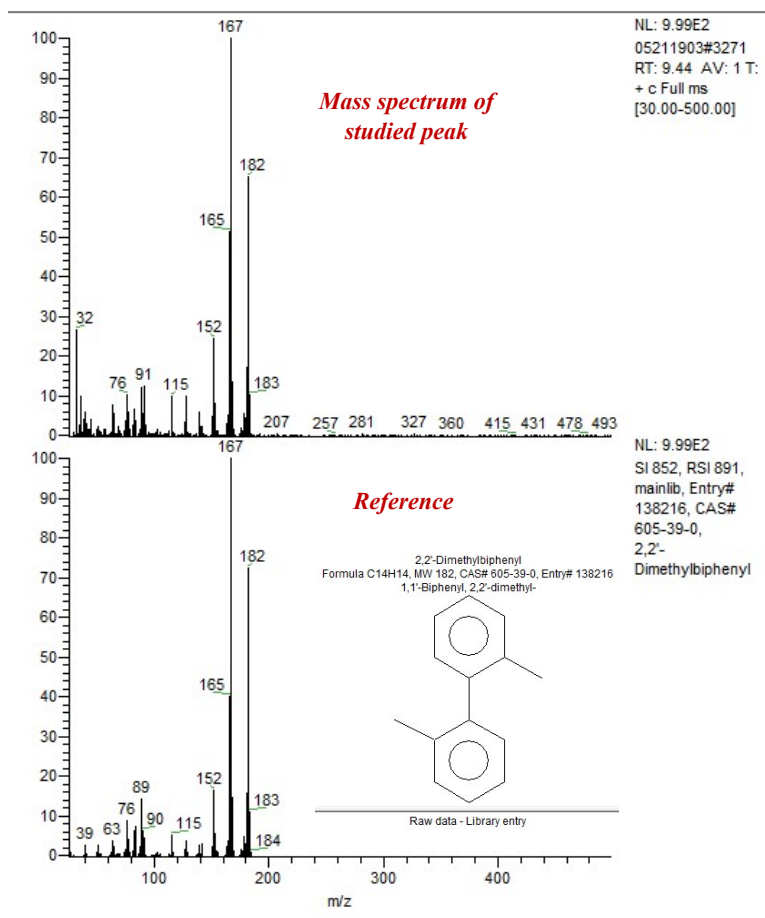
**Figure S10. Mass spectrum of 1-cyclohexylmethyl-4-methyl,trans- (C<sub>14</sub>H<sub>26</sub>) peak at 9.52 minutes in irradiated methylcyclohexane compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



**Figure S11. Mass spectrum of Bibenzyll (C<sub>14</sub>H<sub>14</sub>) peak at 9.65 minutes in irradiated Toluene compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**

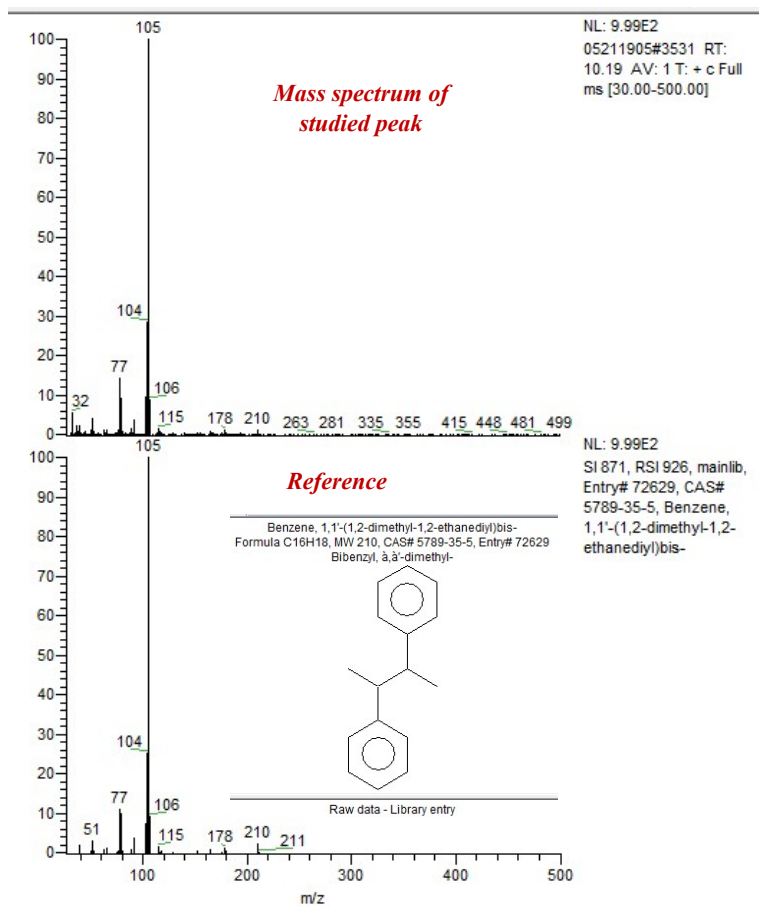


**Figure S12. Mass spectrum of 4,4'-Dimethylbiphenyl (C<sub>14</sub>H<sub>14</sub>) peak at 10.06 minutes in irradiated Toluene compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**

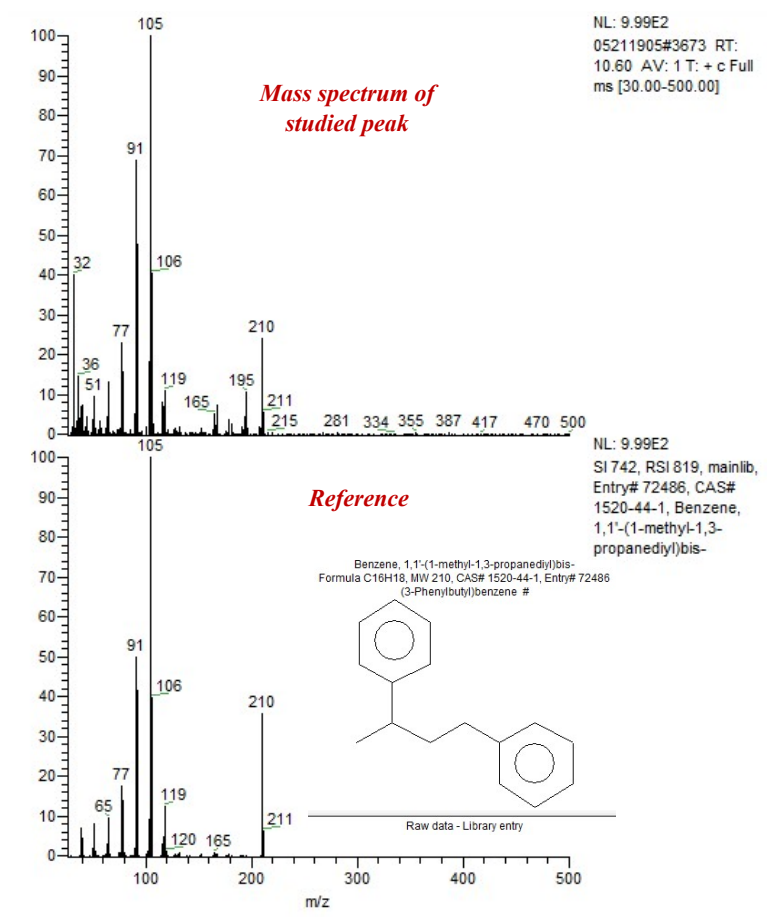


**Figure S13. Mass spectrum of 2,2'-Dimethylbiphenyl (C<sub>14</sub>H<sub>14</sub>) peak at 9.44 minutes in irradiated Toluene compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**

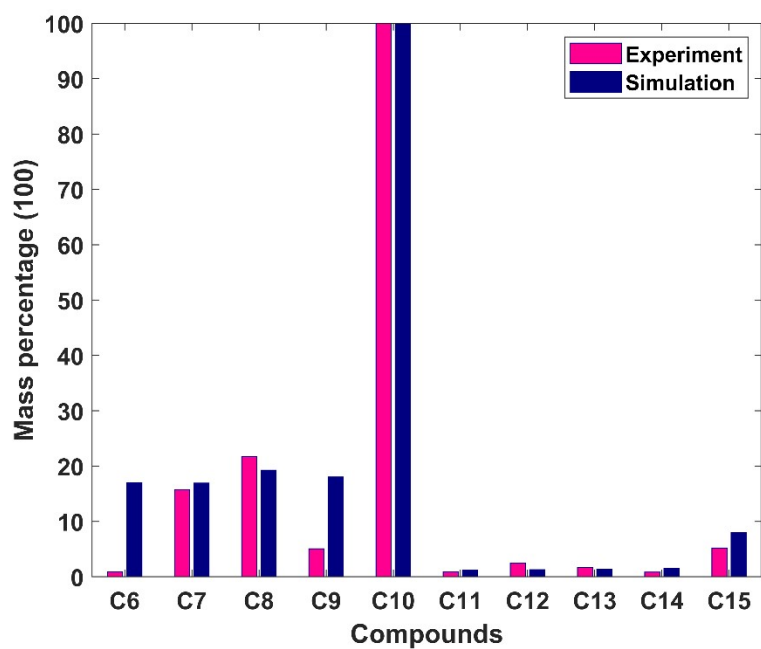




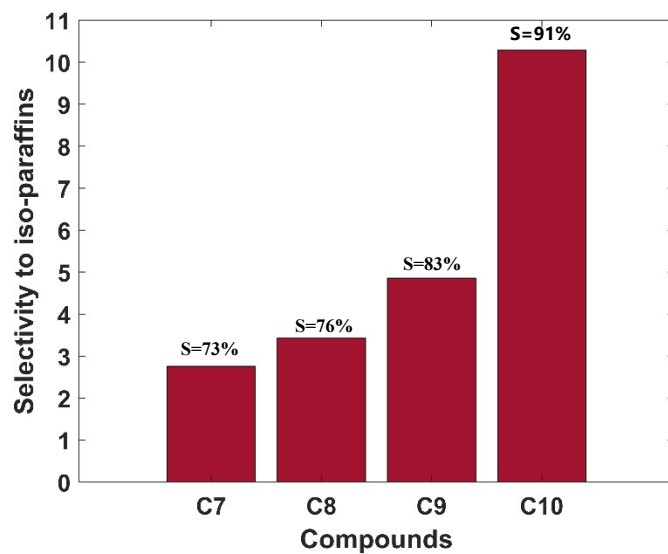
**Figure S14. Mass spectrum of Benzene, 1,1'-(1,2-dimethyl-1,2-ethanediyl) bis- (C<sub>16</sub>H<sub>18</sub>) peak at 10.19 minutes in irradiated Ethylbenzene compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



**Figure S15. Mass spectrum of Benzene, 1,1'-(1-methyl-1,3-propanediyl) bis- (C<sub>16</sub>H<sub>18</sub>) peak at 10.6 minutes in irradiated Ethylbenzene compared to the reference in MS library. Structure of the compound is identified and match the reference shown on the plot.**



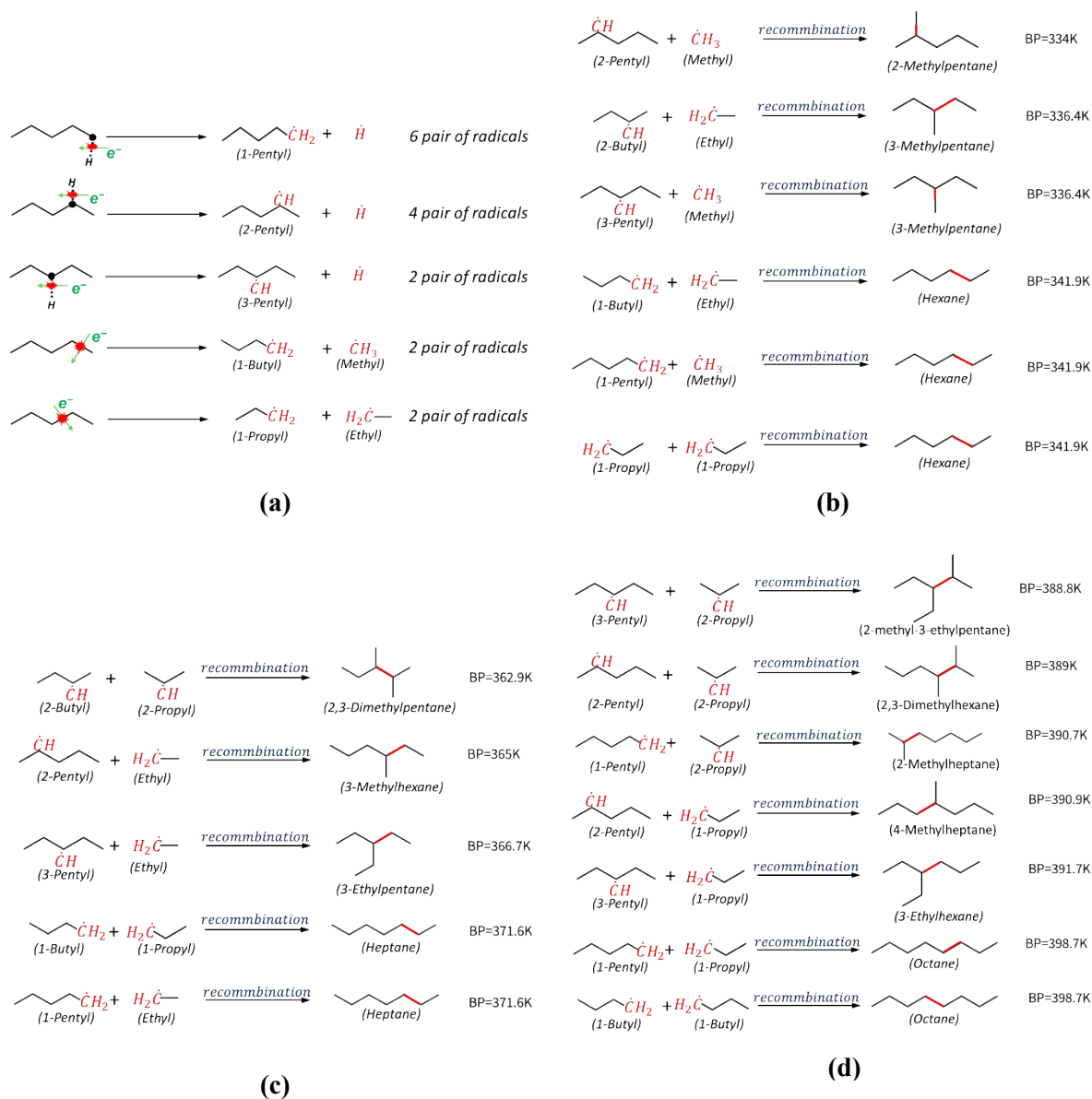
**Figure S16. Mass distribution of each group in irradiated pentane normalized by decane.** Results are compared to simulation based on a random cracking and free pairing model. Experimental results and modeled results match well in most of the carbon groups studied here.

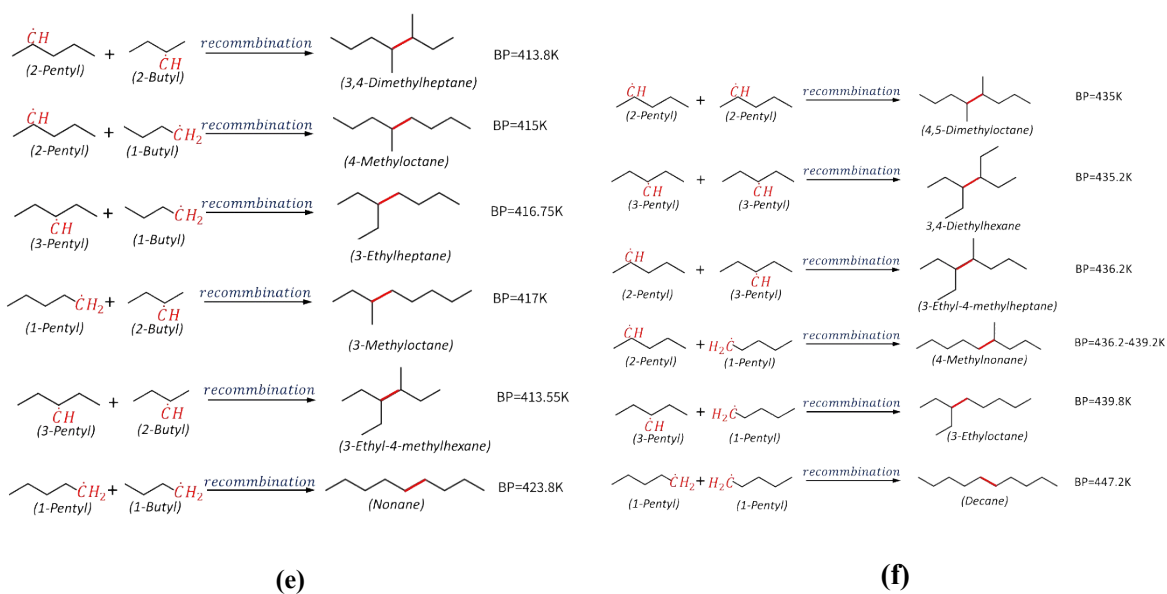


**Figure S17.** Product mass distribution in irradiated pentane among C<sub>7</sub>-C<sub>10</sub> groups which are branched alkanes and straight alkane quantified by the peak area corresponding to each product.

**Scheme S1:** Radicals creation by irradiation of pentane (C<sub>5</sub>H<sub>12</sub>) and their recombination reaction

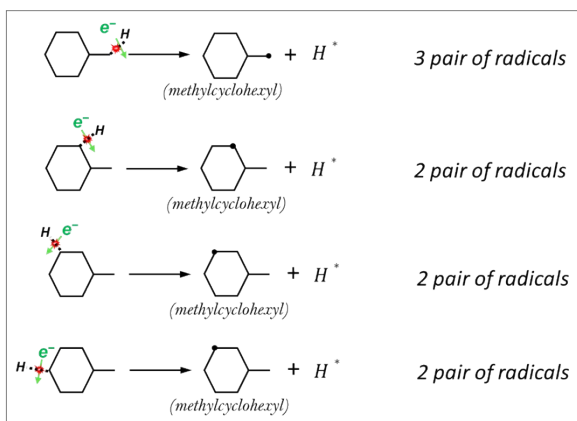
pathways to produce larger molecules in the range of C<sub>6</sub>-C<sub>10</sub>. **a**, pathways to create radicals by irradiating pentane. Pentyl and hydrogen radicals are created in reactions 1-3 due to carbon-hydrogen bond rupture. Butyl and methyl radicals are created in reaction 4 due to carbon-carbon bond rupture between the first and second carbon atom. Ethyl and propyl radicals are created in reaction 5 due to carbon-carbon bond rupture between the second and third carbon atom; **b**, C<sub>6</sub> group; **c**, C<sub>7</sub> group with 8 isomers identified and; **d**, C<sub>8</sub> group with 16 isomers identified; **e**, C<sub>9</sub> group with 17 isomers identified; **f**, C<sub>10</sub> group with 22 isomers identified by GCMS and 5 recombination reaction pathways.



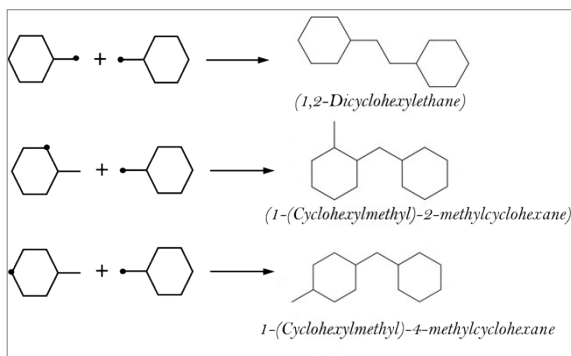


**Scheme S2: Radicals creation by irradiation of methylcyclohexane, toluene and benzene and their free pairing reaction pathways to produce larger molecules (dimers). a, pathways to create radicals by irradiating**

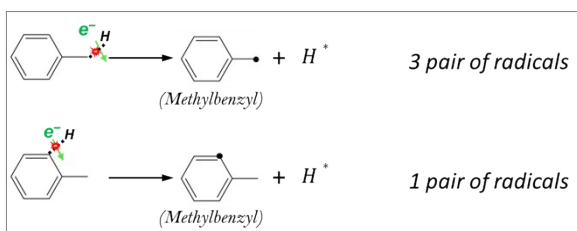
methylcyclohexane. **b**, larger hydrocarbon molecules are created via free pairing reactions of methylcyclohexyl radicals. **c**, pathways to create radicals by irradiating toluene. **d**, larger hydrocarbon molecules are created via free pairing reactions of methylbenzyl radicals. **e**, pathways to create radicals by irradiating benzene. **f**, larger hydrocarbon molecules are created via free pairing reactions of benzyl radicals.



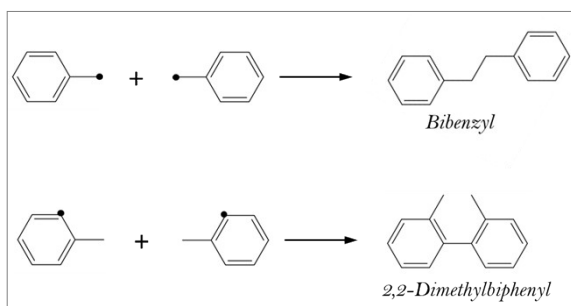
**(a)**



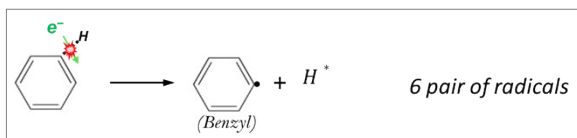
**(b)**



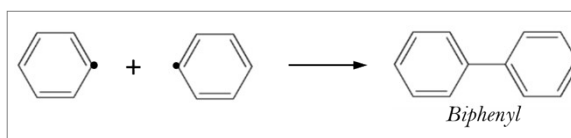
**(c)**



**(d)**



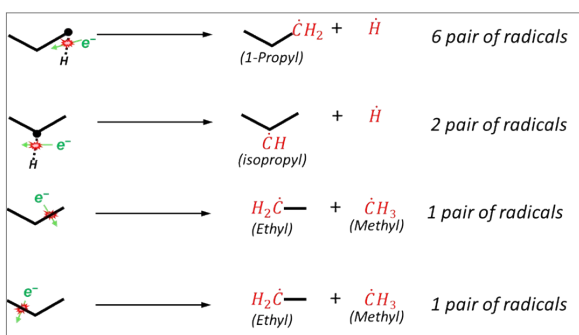
**(e)**



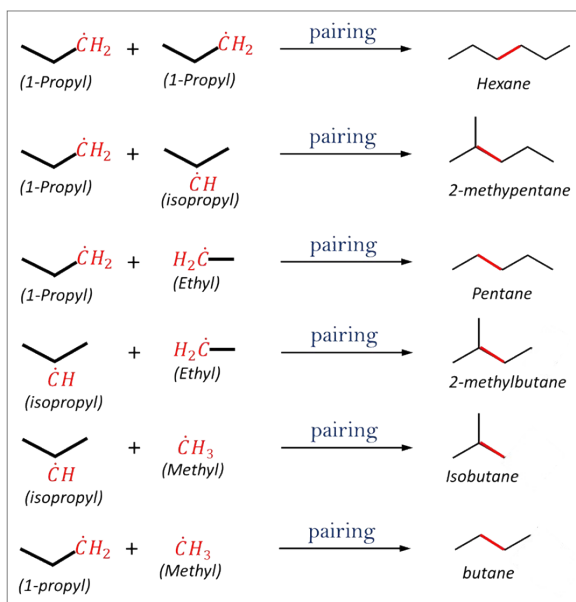
**(f)**

**Scheme S3: Radicals creation by irradiation of propane C<sub>3</sub>H<sub>8</sub> and their free pairing reaction pathways to**

**produce larger molecules in the range of C<sub>4</sub>-C<sub>6</sub>.** **a**, pathways to create radicals by irradiating propane. Six pairs of 1-propyl and hydrogen radicals, two pair of isopropyl and hydrogen radicals, two pair of methyl and ethyl radicals are created due to carbon-carbon and carbon-hydrogen bond rupture. **b**, larger hydrocarbon molecules are created via free pairing reactions of radicals. Production mechanism of molecules in the range of C<sub>4</sub>-C<sub>6</sub> are illustrated here including hexane, 2-methylpentane, pentane, 2-methylbutane, isobutane and butane.



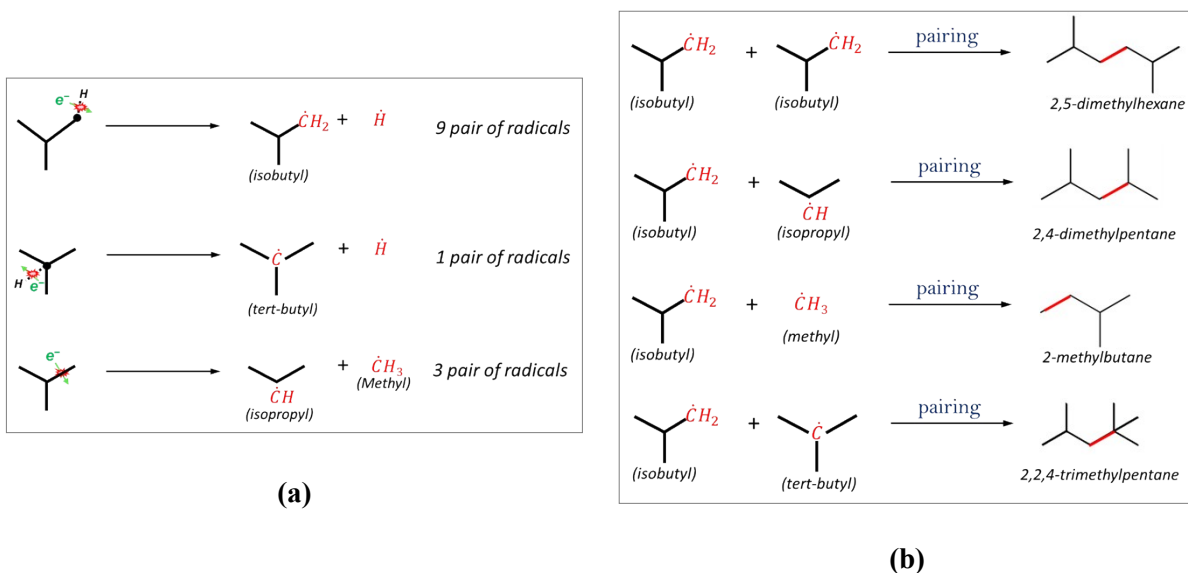
**(a)**



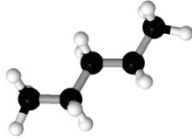
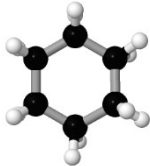
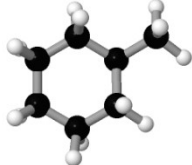
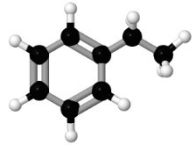
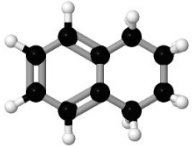
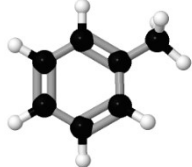
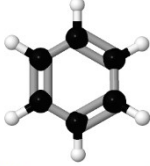
**(b)**



**Scheme S4: Radicals creation by irradiation of isobutane  $C_4H_{10}$  and their free pairing reaction pathways to produce larger molecules in the range of  $C_5-C_8$ .** **a**, pathways to create radicals by irradiating isobutane. Nine pairs of isobutyl and hydrogen radicals, one pair of tert-butyl and hydrogen radicals, three pair of isopropyl and methyl radicals are created due to carbon-carbon and carbon-hydrogen bond rupture. **b**, hydrocarbon isomers are created via free pairing reactions of radicals. Reaction pathways for production of isomers in the range of  $C_5-C_8$  are illustrated here including 2,5-dimethylhexane, 2,4-dimethylpentane, 2-methylbutane and 2,2,4-trimethylpentane. All those compounds are highly desired gasoline range fuel components.



**Table S1: Physiochemical properties of irradiated hydrocarbon compounds: chemical formula, boiling point, and saturation degree (SD).**

Samples	Formula	BP (°C)	SD	Structure
Pentane	C <sub>5</sub> H <sub>12</sub>	36	1	
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	81	0.875	
Methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	101	0.857	
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	136	0.5556	
Tetralin	C <sub>10</sub> H <sub>12</sub>	207	0.5455	
Toluene	C <sub>7</sub> H <sub>8</sub>	111	0.5	
Benzene	C <sub>6</sub> H <sub>6</sub>	80	0.4286	
Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	242	0.4167	