Supplementary Information for

Upgrading biomass-derived glycerol into terminal olefin via molybdenum-catalyzed carbon-chain extension

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1. Experimental section.

1.1 Materials and reagents.

All chemicals were of analytical grade and used as received without further purification unless otherwise indicated. Glycerol (CAS: 56-81-5) and sodium sulfite (CAS: 7757-83-7) were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group. Triphenylphosphine (CAS: 603-35-0) was purchased from J&K Scientific Ltd.. 2-Methyl-8-quinolinol (CAS: 826-81-3) and 1,2,4,5-tetramethylbenzene (CAS: 95-93-2) were purchased from Adamas-beta Reagent. Molybdenyl acetylacetonate (CAS: 17524-05-9), 8-hydroxyquinoline (CAS: 148-24-3), 1,10-phenanthroline monohydrate (CAS: 5144-89-8), 8-hydroxy-5-nitroquinoline (CAS: 4008-48-4) and ammonium phosphomolybdate hydrate (CAS: 54723-94-3) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.. Molybdenum trioxide (CAS: 1313-27-5), Ammonium molybdate tetrahydrate (CAS: 12054-85-2), 1,4-dioxane and 1-butanol was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd.. Molybdenum chloride oxide (CAS: 13637-68-8) was purchased from Macklin Reagent Co. Ltd.. Ammonium perrhenate (CAS: 13598-65-7) was purchased from Alfa Aesar Fine Chemicals & Metals of Thermo Fisher Scientific.

1.2 Analysis and characterization.

The quantitative analysis was performed by Agilent Technologie 7890A equipped with an Agilent 19095J-323 HP-5 capillary column (30 m × 0.530 mm × 1.5 μm), with an FID detector. The qualitative analysis was performed by Agilent 7890B GC/5975 C equipped with an HP-5 MS column (30 m × 250 μm × 0.25 μm), and with an FID detector, and EI (70 eV) was applied for MS-based analyses. High-resolution mass spectrometry (HRMS) measurements were performed by Agilent Q-TOF 6540, using electrospray ionization (ESI) technique. Fourier transform infrared (FTIR) spectra were recorded by Thermofisher Scientific Nicolet iS50 IR spectrometer (KBr, 4000-400 cm-1). Powder X-ray diffraction (XRD) spectra were recorded by PANalytical X'pert Pro-1 diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermofisher ESCALAB 250Xi equipped with monochromated Al Kα (1486.6 eV) X-ray source and the working pressure in the analyzing chamber was less than 7.1×10-5 Pa. The field-emission scanning electron microscopy (SEM) images and element distribution maps were performed on a JSM-7800F (Japan) instrument. Selected-area electron diffraction (SAED) pattern was obtained on an instrument of JEM-2100 (Japan). Nuclear magnetic resonance

(NMR) spectra were recorded by Bruker AVANCE III 400 MHz and AVANCE III HD 700 MHz at 298 K in $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

2. Catalyst preparation

Mo-8-HQ was prepared according to the known procedure[1]: Molybdenyl acetylacetonate ($MoO_2(acac)_2$, 1 mmol) and 8-hydroxyquinoline (8-HQ, 2 mmol) were respectively dissolved in 10 mL methanol, then $MoO_2(acac)_2$ methanolic solution was added into the 8-HQ methanolic solution under vigorously stirring. The mixture was continuously stirred for 24 h at room temperature. The solvent was then removed by filtration and the resulting residue was washed with methanol several times. The resulting light-yellow solid was dried in vacuum condition overnight and labeled as Mo-8-HQ.

Mo-Phen was prepared according to the known procedure[2]: Molybdenum chloride oxide (MoO_2Cl_2, 1 mmol) and 1,10-phenanthroline monohydrate (Phen, 1.0 mmol) were respectively dissolved in 5 mL ethanol, then MoO_2Cl_2 ethanolic solution was added into the Phen ethanolic solution drop by drop under vigorous stirring. The mixture was continuously stirred for 24 h at room temperature. Then, the solvent was removed by filtration and the resulting residue was washed with ethanol for several times. The resulting beige powder was dried in vacuum condition overnight and labeled as Mo-Phen.

Mo-(5N)8-HQ and Mo-8-HQD were synthesized following the procedure: $MoO_2(acac)_2$ (1 mmol) and 8-hydroxy-5-nitroquinoline ((5N)8-HQ, 2 mmol) or 2-methyl-8-quinolinol (8-hydroxyquinaldine, 8-HQD, 2 mmol) were respectively dissolved in 10 mL methanol, then $MoO_2(acac)_2$ methanolic solution was added into the ligand methanolic solution under vigorously stirring. The mixture was continuously stirred for 24 h at room temperature. The solvent was then removed by filtrating and the resulting residue was washed with methanol several times. The resulting solid was dried in vacuum condition overnight and labeled as Mo-(5N)8-HQ or Mo-8-HQD respectively. FTIR analysis indicated that peak at 2919 cm^{-1} disappeared in both spectra of two samples (Fig. S1, a and c), while signals which did not present in $MoO_2(acac)_2$ or ligands appeared at fingerprint area (480 ~ 520 cm^{-1}). XRD spectra further proved the complexes had probably formed (Fig. S1, b and d).

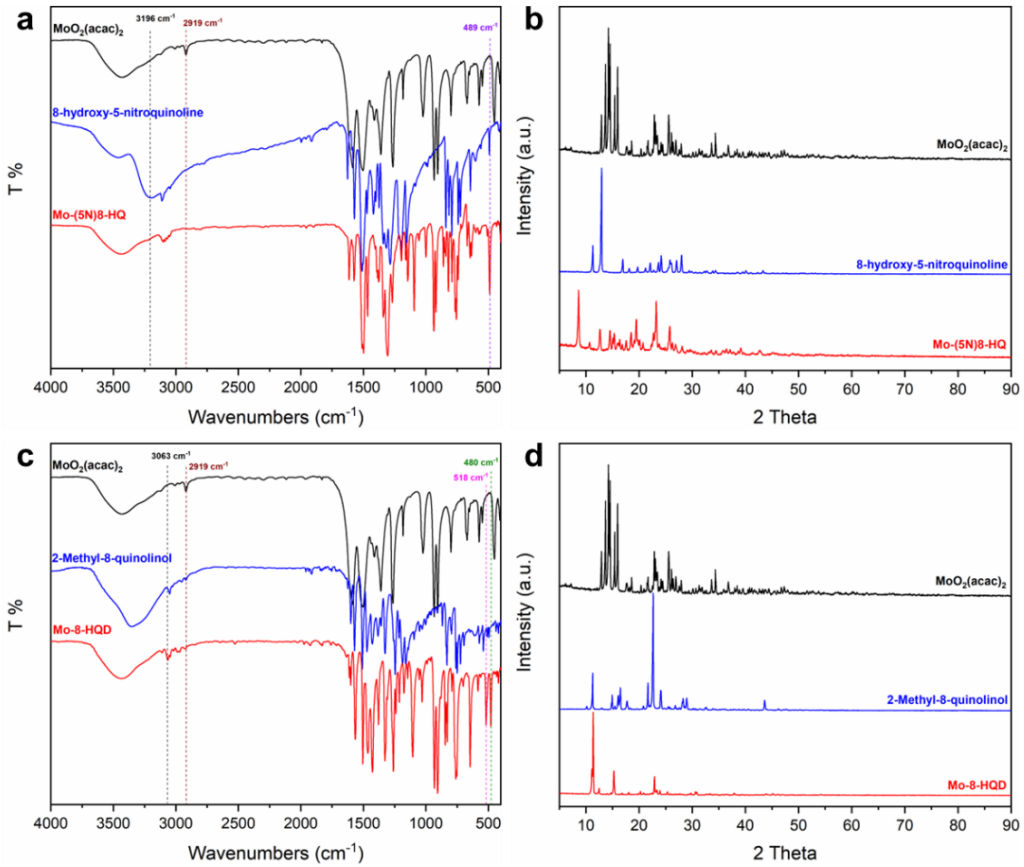


Fig. S1. Characterization of Mo-(5N)8-HQ and Mo-8-HQD. (a) FTIR spectroscopy of $MoO_2(acac)_2$, 8-hydroxy-5-nitroquinoline and Mo-(5N)8-HQ. (b) XRD of $MoO_2(acac)_2$, 8-hydroxy-5-nitroquinoline and Mo-(5N)8-HQ. (c) FTIR spectroscopy of $MoO_2(acac)_2$, 2-methyl-8-quinolinol and Mo-8-HQD. (d) XRD of $MoO_2(acac)_2$, 2-methyl-8-quinolinol and Mo-8-HQD.

3. General procedure.

In a typical experiment, glycerol (1.0 mmol) dissolved in solvent (1,4-dioxane, 10 mL) was loaded in a 50 mL batch reactor (Parr Instrument Company) together with reductant (triphenylphosphine, 1.5 mmol) and catalyst (0.1 mmol) under nitrogen atmosphere and magnetic stirring. The temperature was controlled with a band heater from 20 °C to the target temperature at a rate of 4 °C/min and then maintained for a certain time. After the reaction, the reactor was cooled down to room temperature. The solution was added a certain amount of internal standard (1,2,4,5-tetramethylbenzene) and analyzed by gas chromatography. Reaction products were quantified using multi-point calibration curve.

The conversion of starting material (glycerol or allyl alcohol in the corresponding cases) was calculated using the equation below:

$$\text{Conversion} = \left(1 - \frac{\text{moles of starting material remained}}{\text{moles of starting material initially added}}\right) \times 100\%$$

The carbon yield was calculated using the equation below:

$$\text{Yield}=\left(\frac{\text{moles of C in product i}}{\text{moles of C in starting material initially added}}\right)\times 100\%$$

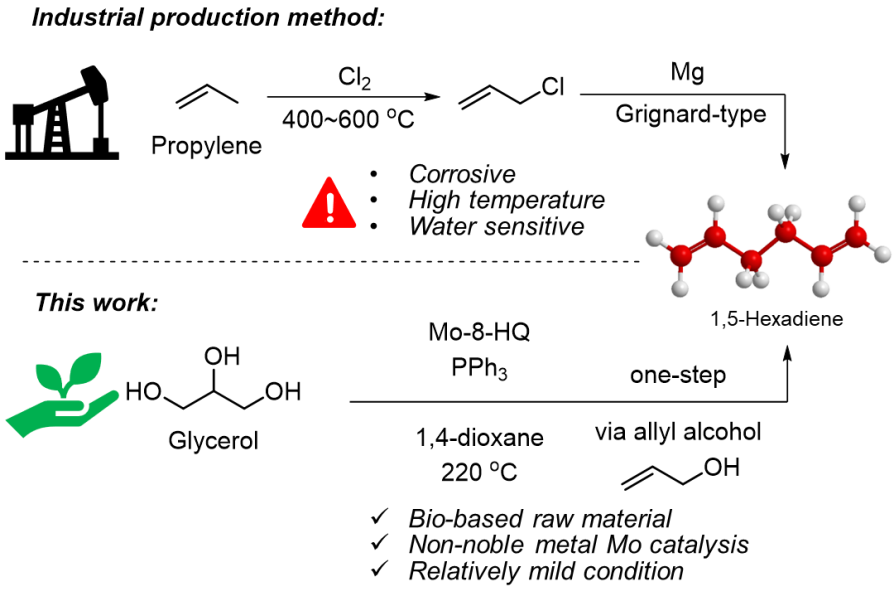
The distribution was calculated based on GC detection using the equation below:

$$\text{Distribution}=\left(\frac{\text{GC signal area of product i}}{\text{GC signal area of all detected products}}\right)\times 100\%$$

4. Computation method of density functional theory (DFT).

All the geometrical structures were optimized at the PBE0 level with D3 version of Grimme's dispersion correction with Becke-Johnson damping by the ORCA package.[3-5] The def2-SVP basis set was used for all atoms.[6] Frequency analyses were performed at the same level. All positive frequencies that are less than 100 cm^{-1} are set to 100 cm^{-1} for thermodynamics calculations.[7] The single point energies were revised at the PBE0-D3(BJ)/def2-TZVP level by using the SMD solvation model.[8] Relative Gibbs free energies include singlet point energies at the higher level and thermal corrections to Gibbs free energies at the experimental temperature.

5. Industrial production route of 1,5-hexadiene.



Scheme S1. Comparison of 1,5-hexadiene industrial production method with glycerol-origin production method.

6. Quantitative and qualitative analysis of reaction solution.

6.1 Gas chromatography analysis.

Temperature program for quantitative: Initially maintain at 80 °C for 4 min, then ramp up to 100 °C at a rate of 15 °C/min, hold up for 0.5 min, ramp up to 240 °C at a rate of 40 °C, and hold up for additional 5 min.

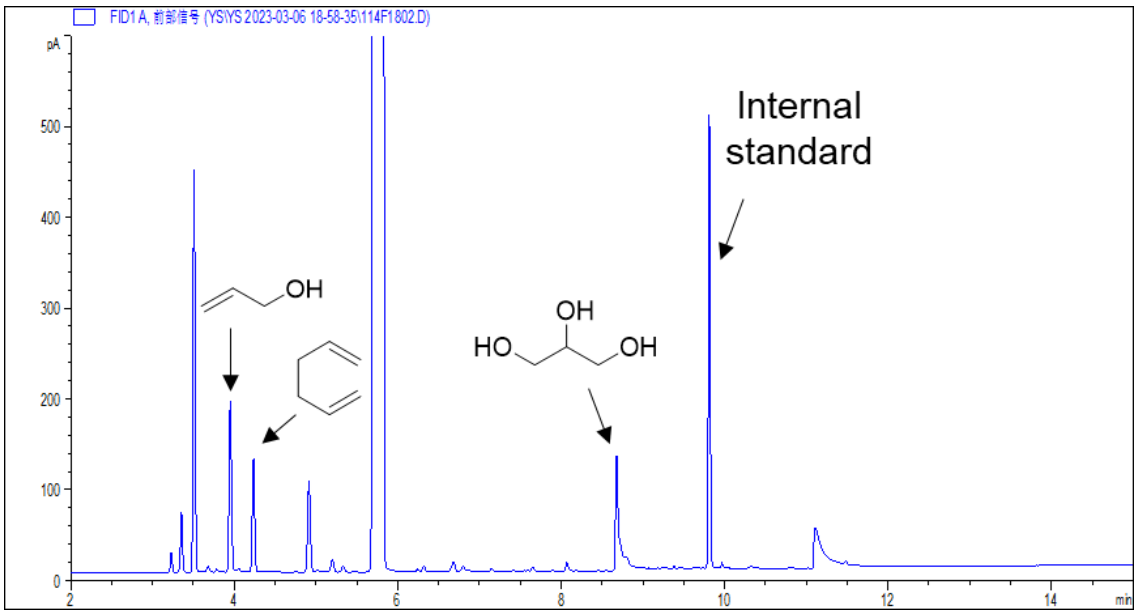


Fig. S2. A typical GC chromatogram of glycerol conversion to 1,5-hexadiene and allyl alcohol.

Blank experiments: 3 blank experiments only added glycerol and (1) triphenylphosphine (PPh_3), (2) 8-hydroxyquinoline (8-HQ), (3) PPh_3 and 8-HQ were conducted, and the liquid phase was analyzed by GC (Table S1).

Table S1. Blank experiments without Mo catalysts.

Entry	Addition	Conversion of glycerol (%)	Yield of 1,5-hexadiene (%)	Yield of allyl alcohol (%)
1	PPh_3	0	0	0
2	8-HQ	0	0	0
3[b]	PPh_3+8-HQ	15	2	1

Reaction conditions: glycerol (1.0 mmol), additions (triphenylphosphine (1.5 equiv.), 8-hydroxyquinoline (20 mol%)), 1,4-dioxane (10 mL), 180 °C, 120 min, nitrogen atmosphere.

6.2 GC-MS analysis of mechanism verification experiments.

Gas-phase analysis: After a standard reaction, 10 bar of N_2 was filled into the ice-bathed autoclave, and gas was collected using a gas bag and analyzed by GC-MS (Fig. S3, S4).

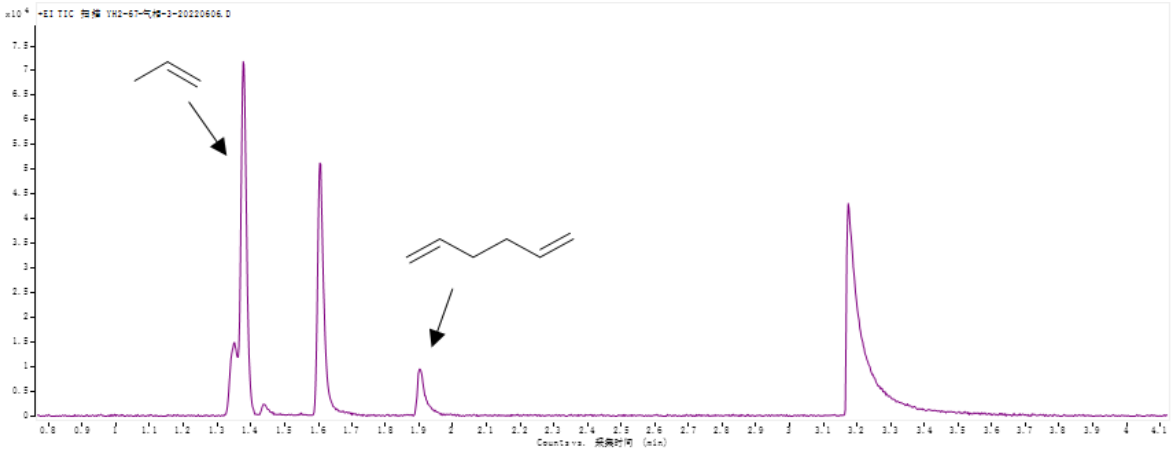


Fig. S3. Total ion chromatogram (TIC) for the gas-phase of glycerol conversion. Reaction condition: glycerol (1.0 mmol), Mo-8-HQ (10 mol%), triphenylphosphine (1.5 equiv.), 1,4-dioxane (10 mL), 220 °C, 120 min, nitrogen atmosphere.

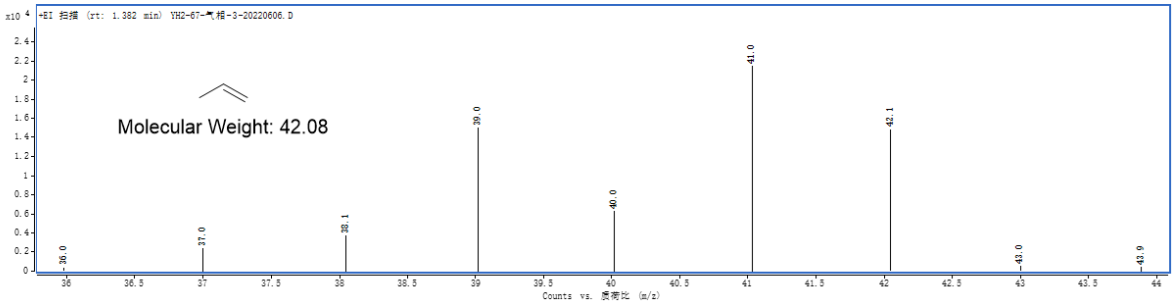


Fig. S4. Mass spectrum of propylene. MS (70 eV): m/z (%) 42.1 (69) [M+], 41.0 (100), 40.0(29), 39.0 (70), 38.1 (17), 37.0(11), 36.0 (2).

Free radical capture experiment: 2 equiv. of 9,10-dihydroanthracene (a high-temp tolerance radical scavenger) was added along with the standard condition. The liquid phase was analyzed by GC-MS (Fig. S5, S6) and GC as same as other reactions.

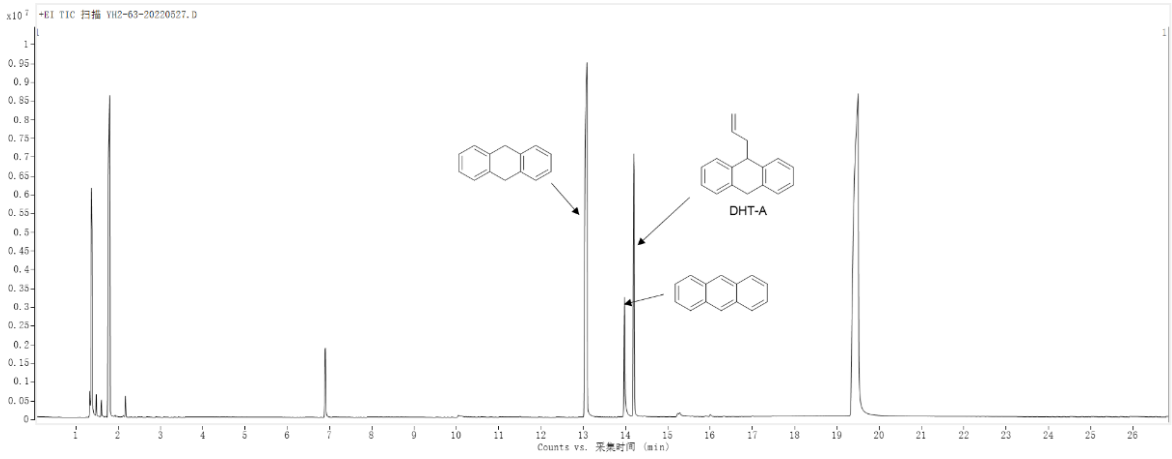


Fig. S5. Total ion chromatogram (TIC) for the allyl radical capture experiment. Reaction condition: glycerol (1.0 mmol), Mo-8-HQ (10 mol%), triphenylphosphine (1.5 equiv.), 9,10-dihydroanthracene (2 equiv.), 1,4-dioxane (10 mL), 220 °C, 120 min, nitrogen atmosphere.

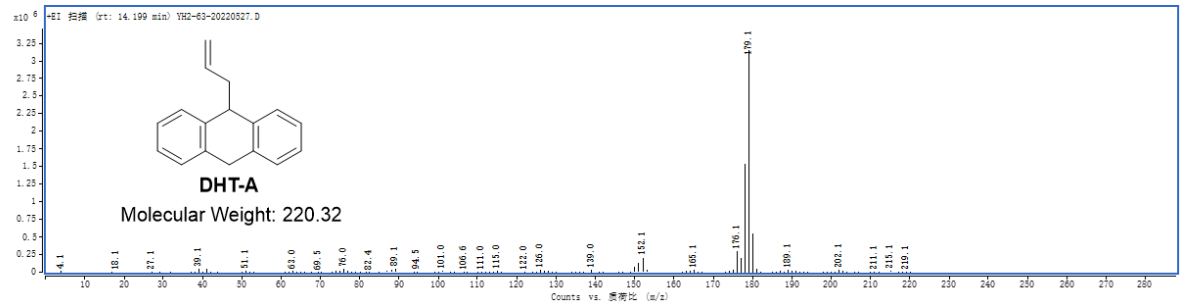


Fig. S6. Mass spectrum of the radical captured product. MS (70 eV): m/z (%) 220.1 (0.1) [M+], 189.1 (1), 179.1(100), 152.1 (6).

Moreover, while the starting material was changed into allyl alcohol instead of glycerol, the allyl radical-captured product (DHT-A) was also detected, indicating that the radical was probably generated in the deoxygenation coupling step (Fig. S7).

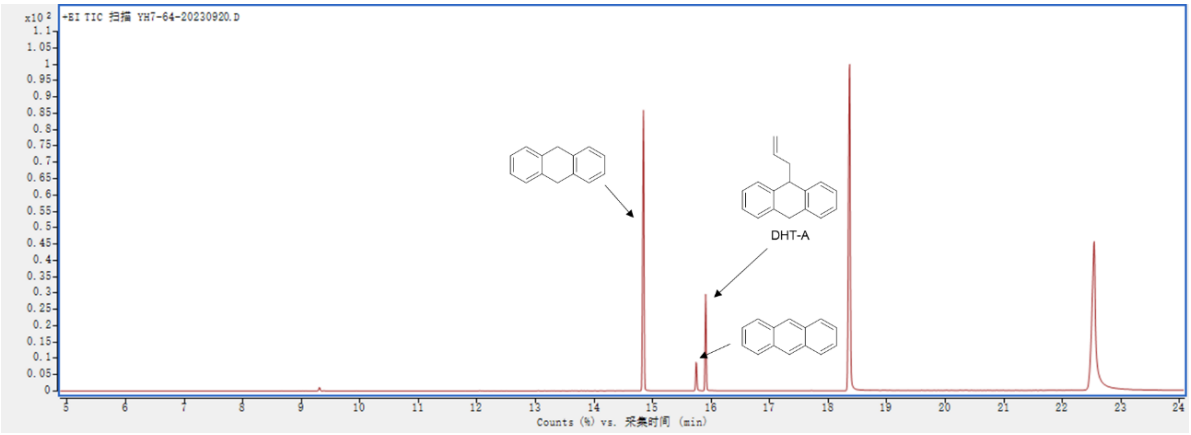


Fig. S7. Total ion chromatogram (TIC) for the allyl radical capture experiment. Reaction condition: allyl alcohol (1.0 mmol), Mo-8-HQ (10 mol%), triphenylphosphine (1.5 equiv.), 9,10-dihydroanthracene (2 equiv.), 1,4-dioxane (10 mL), 220 °C, 120 min, nitrogen atmosphere.

Blank experiment: 4 blank experiments without additional reductant were conducted and the liquid phase was analyzed by GC-MS (Fig. S8).

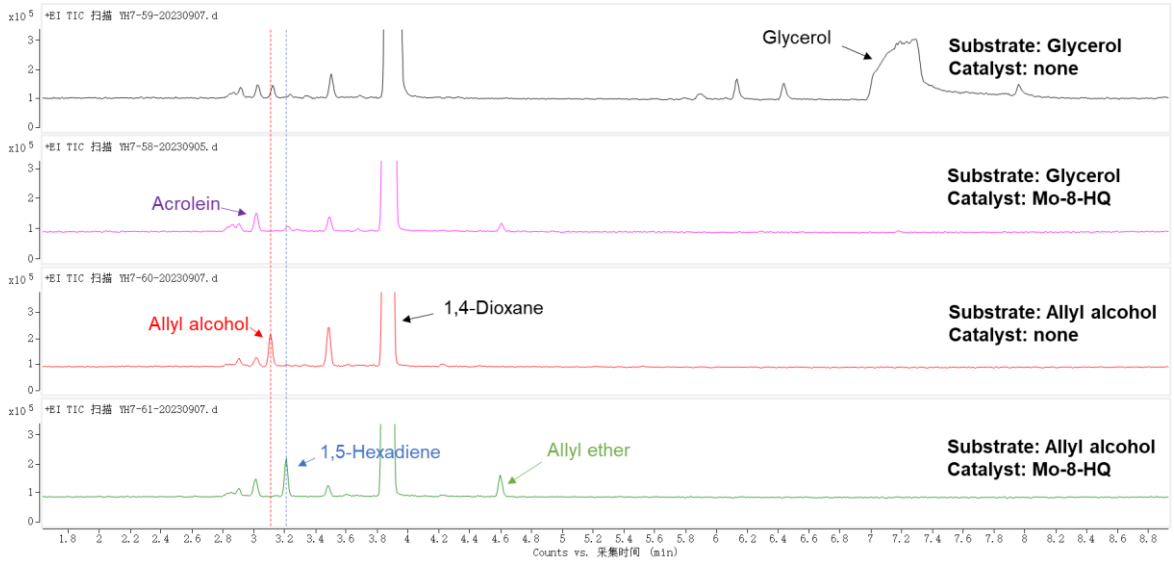


Fig. S8. Total ion chromatograms (TIC) and (by-)product verification for blank experiments. Reaction condition: substrate (1.0 mmol), catalyst (10 mol% or blank), 1,4-dioxane (10 mL), 220 ^{o}C, 120 min, nitrogen atmosphere.

6.3 HRMS analysis of by-products.

Reaction solution analysis: After a standard reaction, the color of the reaction solution was observed to change from clear colorless to dark wine-red (Fig. S9). The solution was filtered and the red jelly-like substance stuck to the filter membrane was collected and analyzed by HRMS (Fig. S10 and Table S2).

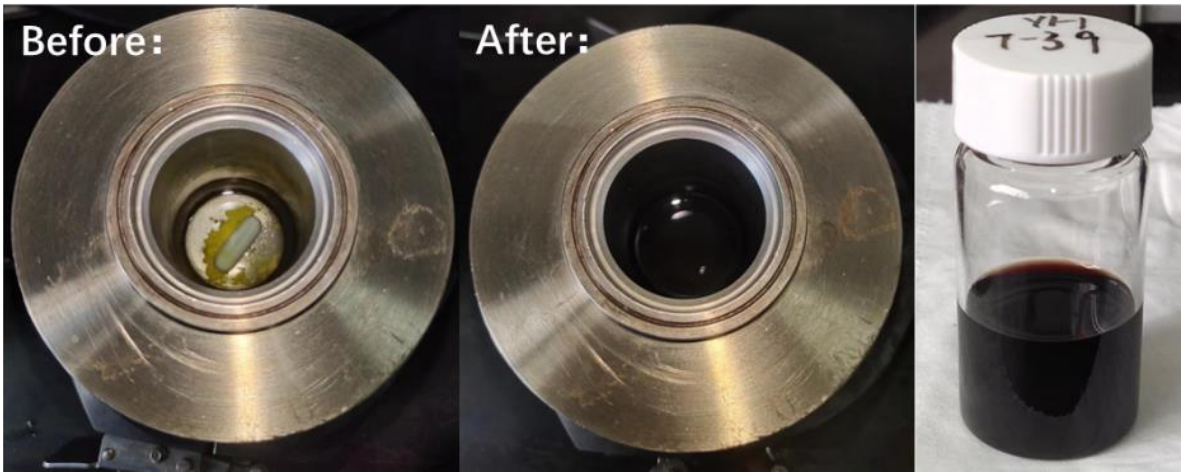


Fig. S9. Comparison of the reaction solution form before and after the reaction.

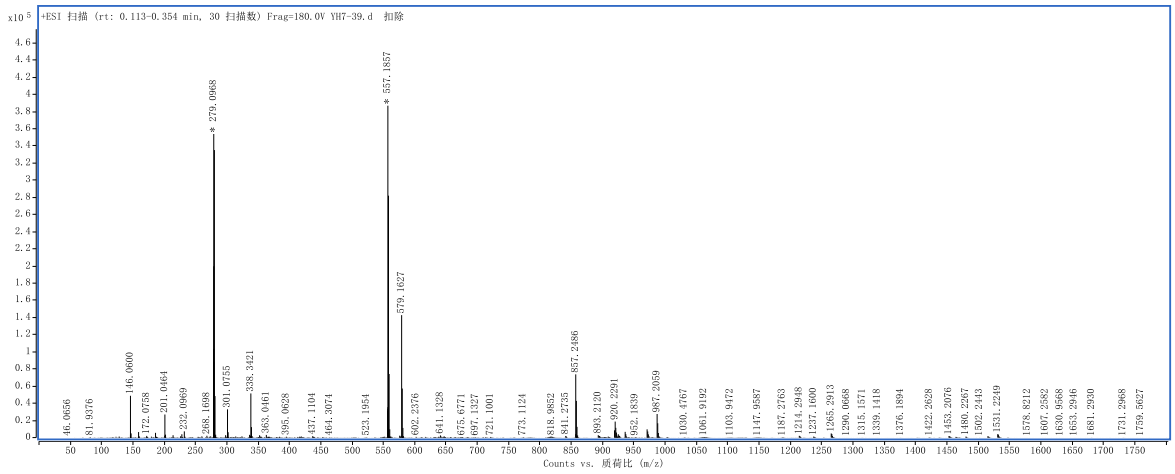


Fig. S10. Total mass spectrum of the filtrate after a typical reaction.

Table S2. Identification of possible sources of partial molecular ion peaks.

m/z	Possible source of generation
146.0600	8-Hydroxyquinoline +H
201.0464	**8-Hydroxyquinoline +acrolein**
232.0969	**4 Allyl alcohol**
279.0968	$OPPh_3$+H
301.0755	$OPPh_3$+Na
338.3421	**$OPPh_3$+ Allyl alcohol +2H**
557.1857	2$OPPh_3$+H
579.1627	2$OPPh_3$+Na
857.2486	3$OPPh_3$+Na
920.2291	**17 Allyl alcohol -5H_2O+Na**
987.2059	**17 Allyl alcohol +H**

7. Catalyst Recyclability

After a standard reaction, the solvent was removed by rotatory evaporation, and the residue was sufficiently dispersed in ethyl acetate and then filtered to remove organic components, mainly triphenylphosphine oxide. The dried recycled catalyst is reddish brown (Fig. S11), and the morphology changed compared to the fresh Mo-8-HQ according to the XRD pattern (Fig. S12).

Fig. S11. Morphology of fresh and used Mo-8-HQ.

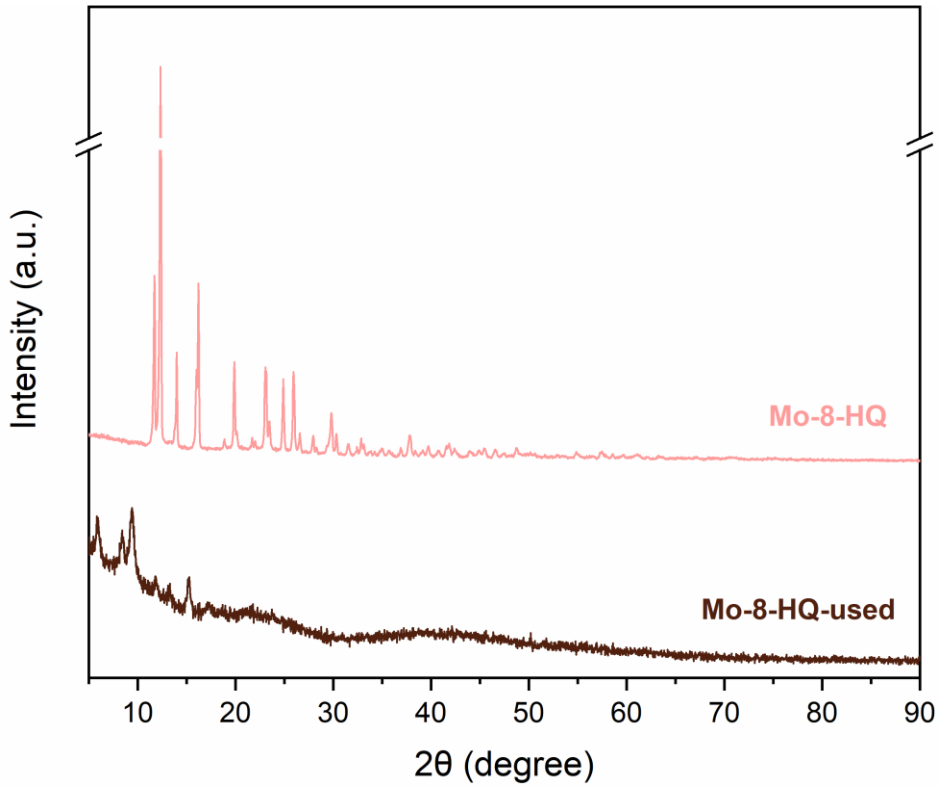


Fig. S12. XRD patterns of fresh and used Mo-8-HQ.

8. Study of Mo catalysts in different valent

Catalyst treatment: In the first sample, Mo-8-HQ (0.25 mmol) along with 5 mL 1,4-dioxane was loaded in a sealed tube. The mixture was continuously stirred for 1 h at 150 °C. There was no obvious color change in the reaction mixture. The solvent was then removed by filtrating and the resulting residue was washed with 1,4-dioxane several times. The resulting light-yellow solid was dried in vacuum condition overnight and labeled as Mo-8-HQ-o for subsequent analysis and experiments.

In the second sample, Mo-8-HQ (0.25 mmol), triphenylphosphine (0.5 mmol) along with 5 mL 1,4-dioxane loaded in a sealed tube. The mixture was continuously stirred for 1 h at 180 °C.The solvent was then removed by filtrating and the resulting residue was washed with 1,4-dioxane several times. The resulting black powder was dried in vacuum condition overnight and labeled as Mo-8-HQ-r for subsequent analysis and experiments (Fig. S11).

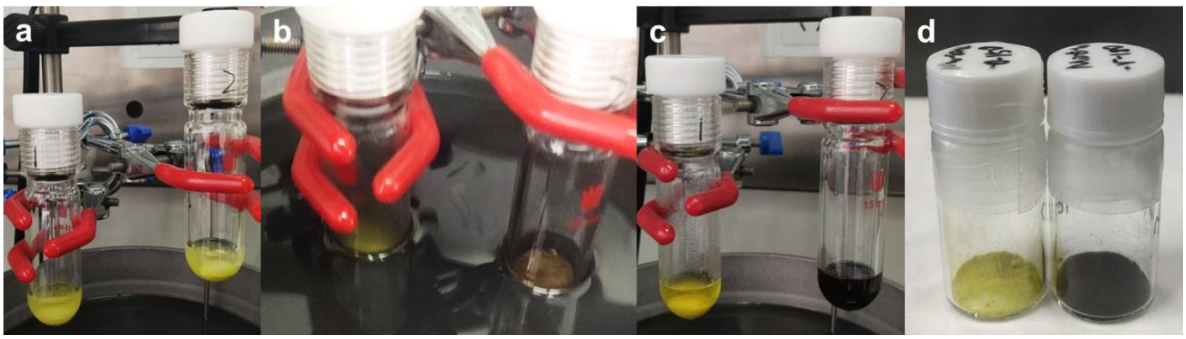


Fig. S13. Treatment of Mo-8-HQ for different valent of Mo catalysts. (a) Before the reaction. (b) Heated at ~100 °C. (c) Reaction mixtures after heating. Left: 150 °C; right: 180 °C. (d) Filter residue of proceeded catalysts. Left: Mo-8-HQ-o; right: Mo-8-HQ-r.

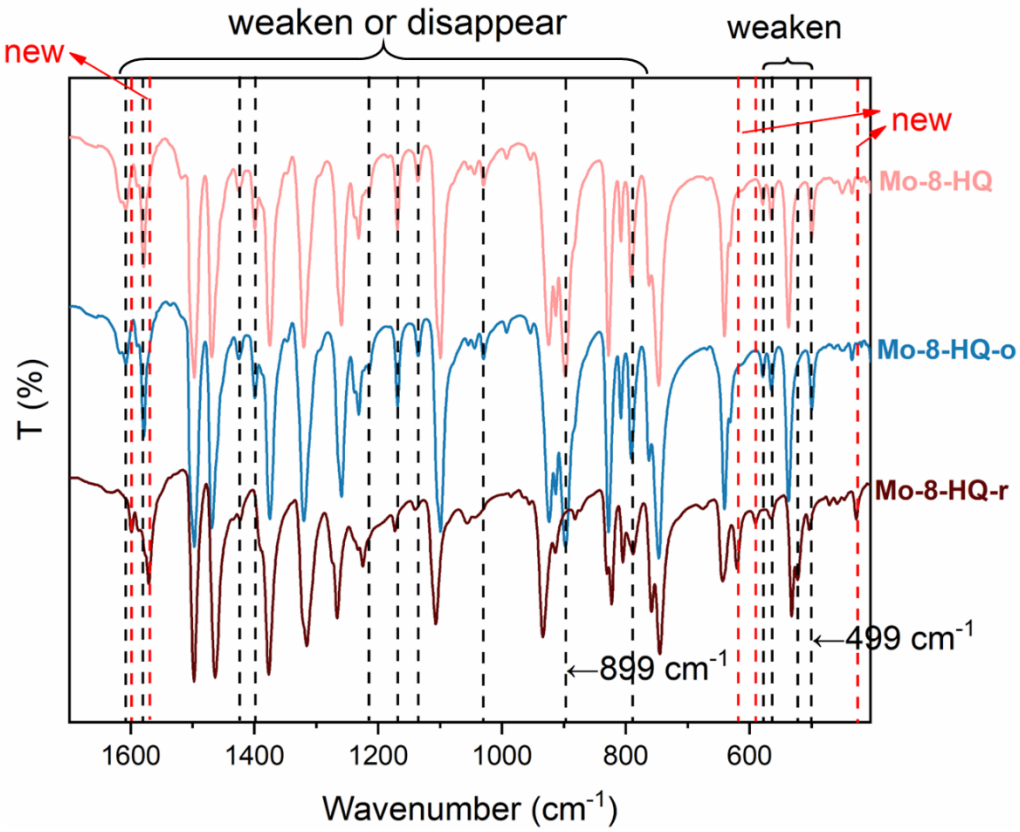


Fig. S14. Detailed FTIR spectra of Mo-8-HQ, Mo-8-HQ-o and Mo-8-HQ-r at 400~1700 cm^{-1}. Black dashline: signals weaken or disappear in Mo-8-HQ-r compared with Mo-8-HQ. Red dashline: signals newly emerged in Mo-8-HQ-r compared with Mo-8-HQ.

9. Substrate scope of allyl alcohol-type biomass in deoxygenation coupling.

Generally, substrate (1 mmol) dissolved in 1,4-dioxane (20 mL) was loaded in a 50 mL batch reactor (Parr Instrument Company) together with triphenylphosphine (1.5 mmol) and Mo-8-HQ (0.1 mmol) under nitrogen atmosphere and magnetic stirring. The temperature was controlled by a band heater at 180 °C for 840 minutes in the cases of furfuryl alcohol, 5-methylfurfuryl alcohol, and 5-hydroxymethylfurfural, or 200 °C for 360 minutes in the case of cinnamyl alcohol. After the reaction, the reactor was cooled down to room temperature. The solution was added a certain amount of internal standard (1,2,4,5-tetramethylbenzene) and analyzed by gas chromatography and GC-MS. Reaction products were quantified using multi-point calibration curve. Coupling products (including isomers) was separated by column chromatography and analyzed by ^{1}H and ^{13}C NMR.

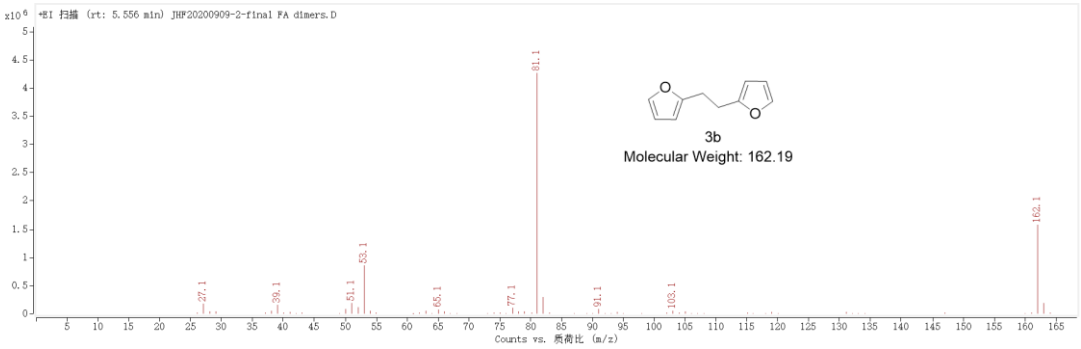


Fig. S15. Mass spectrum of the coupling products by furfuryl alcohol. **3b**: MS (70 eV): m/z (%) 162 (37) [M^+], 81 (100), 53 (20), 39 (4), 27 (4).

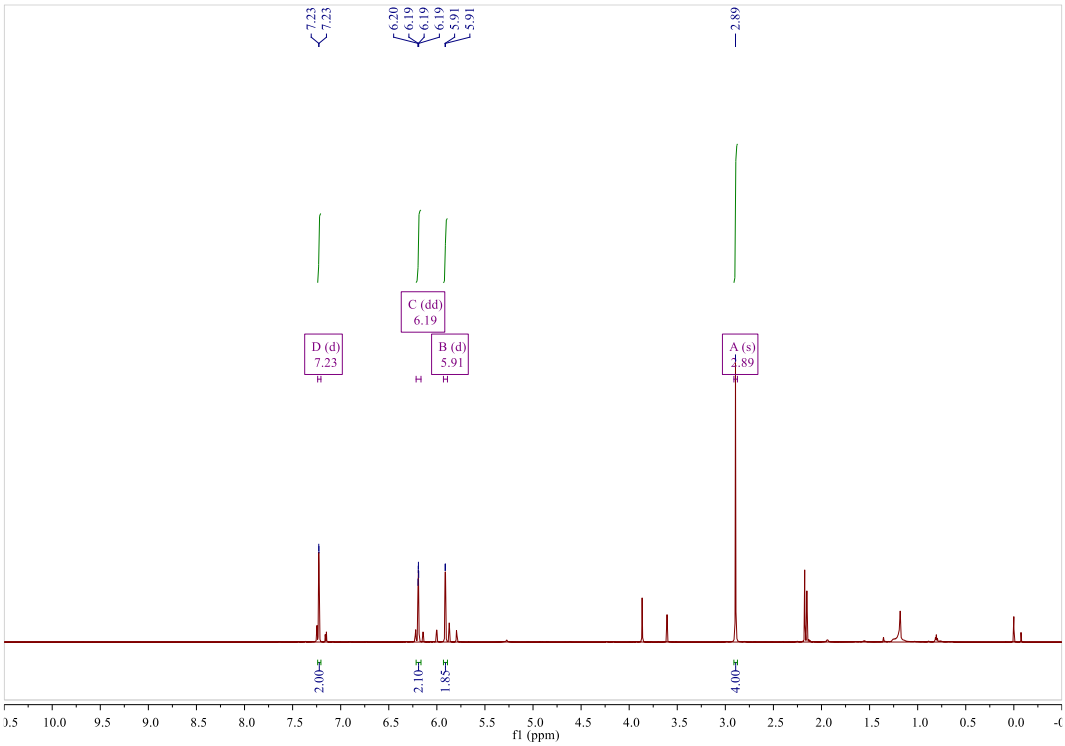


Fig. S16. ^{1}H NMR spectrum of the coupling products by furfuryl alcohol. 1,2-di(furan-2-yl)ethane (**3b**): ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.23 (d, *J* = 1.1 Hz, 2H), 6.19 (dd, *J* = 3.0, 1.9 Hz, 2H), 5.91 (d, *J* = 3.1 Hz, 2H), 2.89 (s, 4H).

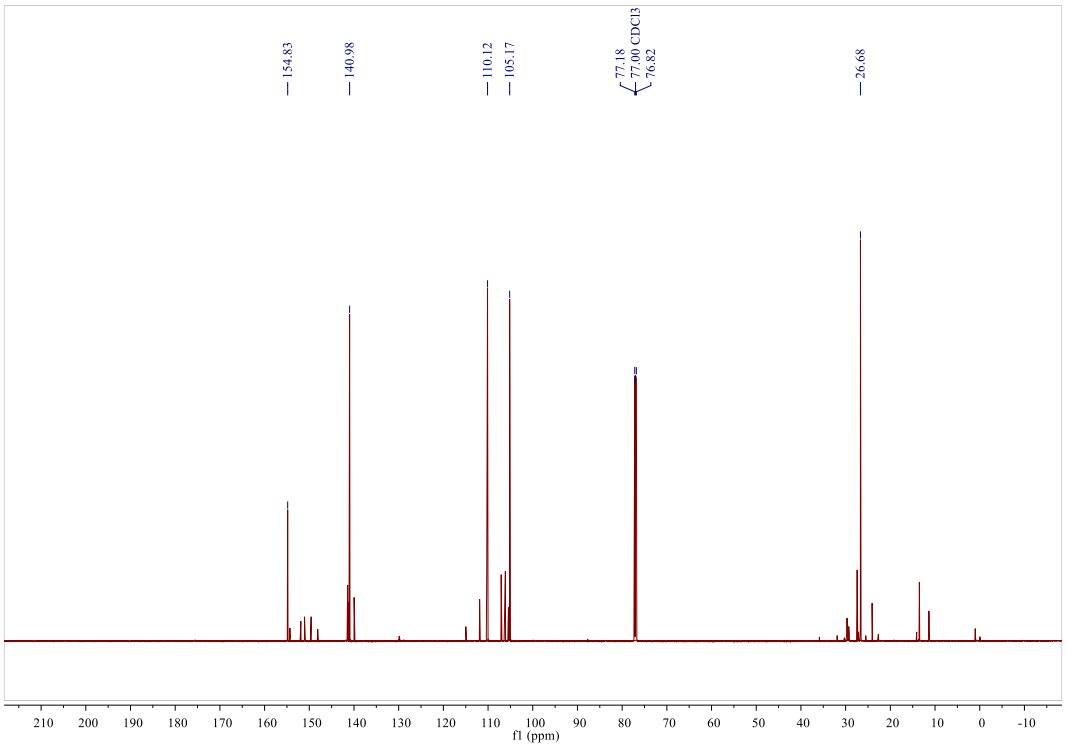


Fig. S17. ^{13}C NMR spectrum of the coupling products by furfuryl alcohol. 1,2-di(furan-2-yl)ethane (**3b**): ^{13}C NMR (176 MHz, $CDCl_3$) δ 154.83, 140.98, 110.12, 105.17, 26.68.

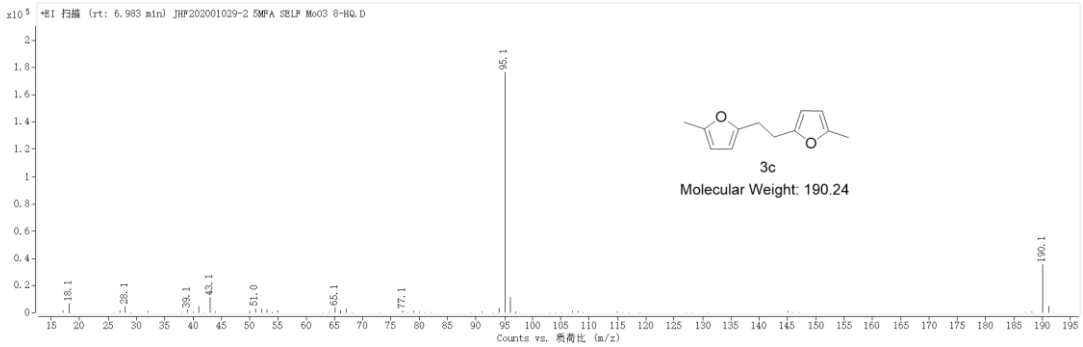


Fig. S18. Mass spectrum of the coupling products by 5-methylfurfuryl alcohol. **3c**: MS (70 eV): m/z (%) 190 (20) [M^+], 95 (100), 43 (6), 28 (3), 18 (4).

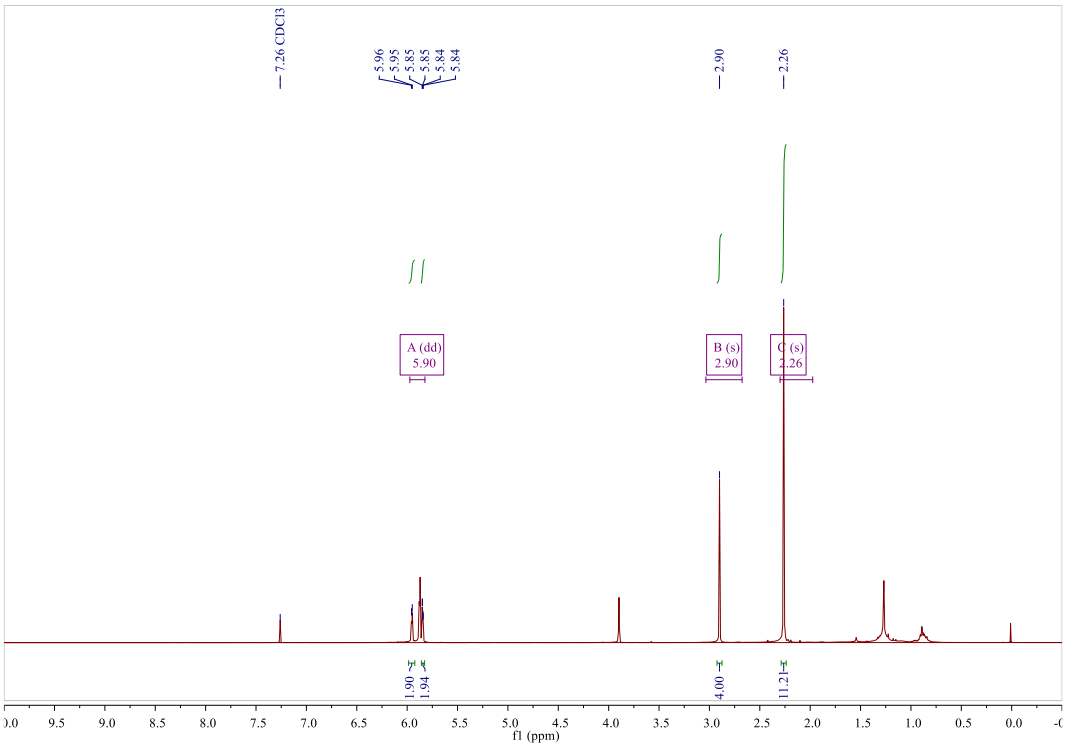


Fig. S19. ^{1}H NMR spectrum of the coupling products by 5-methylfurfuryl alcohol. 1,2-bis(5-methylfuran-2-yl)ethane (**3c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, *J* = 42.5, 2.9 Hz, 4H), 2.90 (s, 4H), 2.26 (s, 6H).

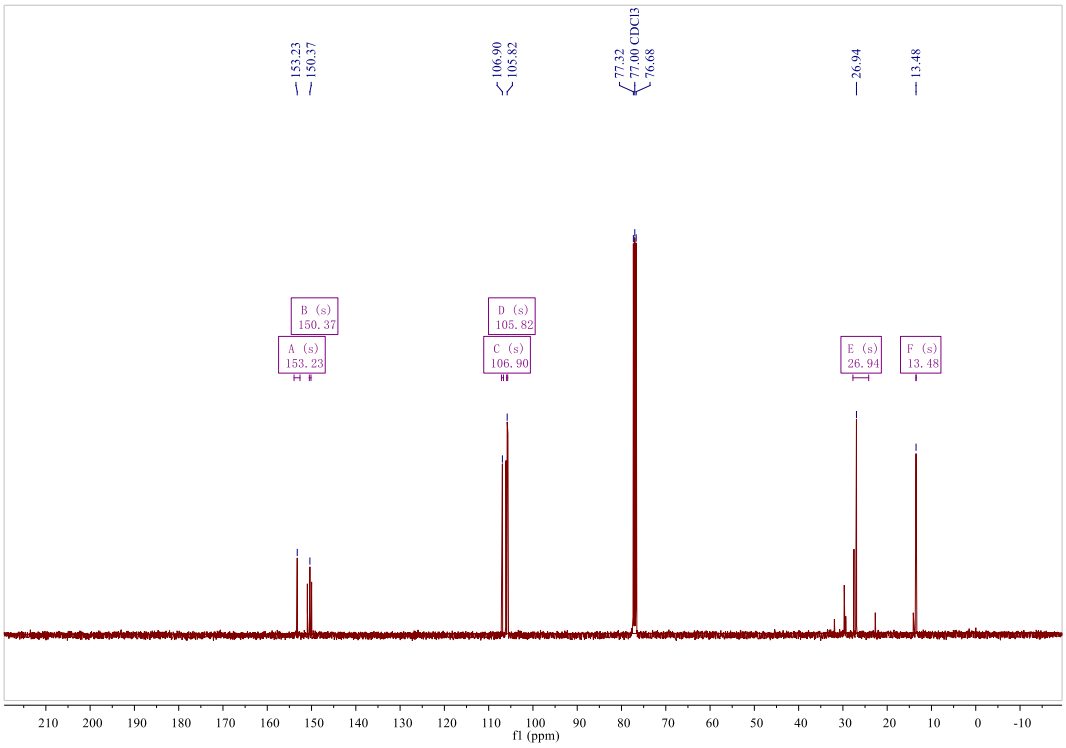


Fig. S20. ^{13}C NMR spectrum of the coupling products by 5-methylfurfuryl alcohol. 1,2-bis(5-methylfuran-2-yl)ethane (**3c**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.23, 150.37, 106.90, 105.82, 26.94, 13.48.

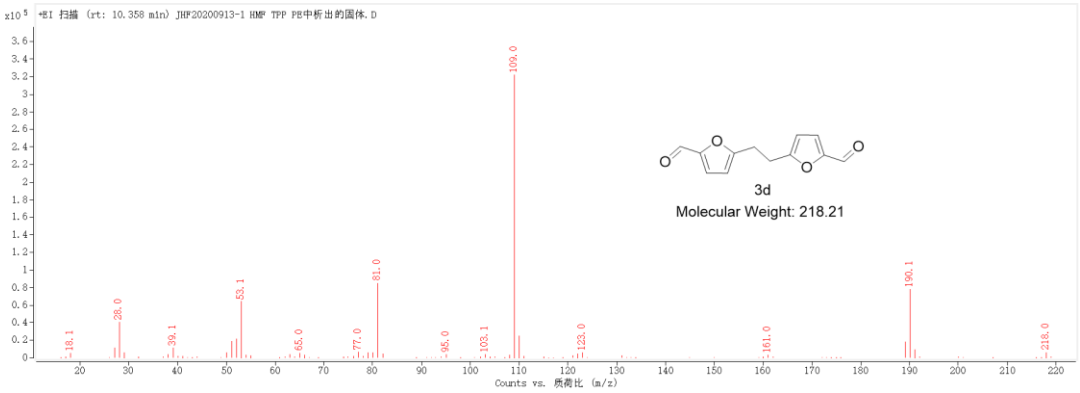


Fig. S21. Mass spectrum of the coupling products by 5-hydroxymethylfurfural. **3d**: MS (70 eV): m/z (%) 218 (2) [M^+], 190 (24), 109 (100), 81 (26), 53 (20), 28 (13).

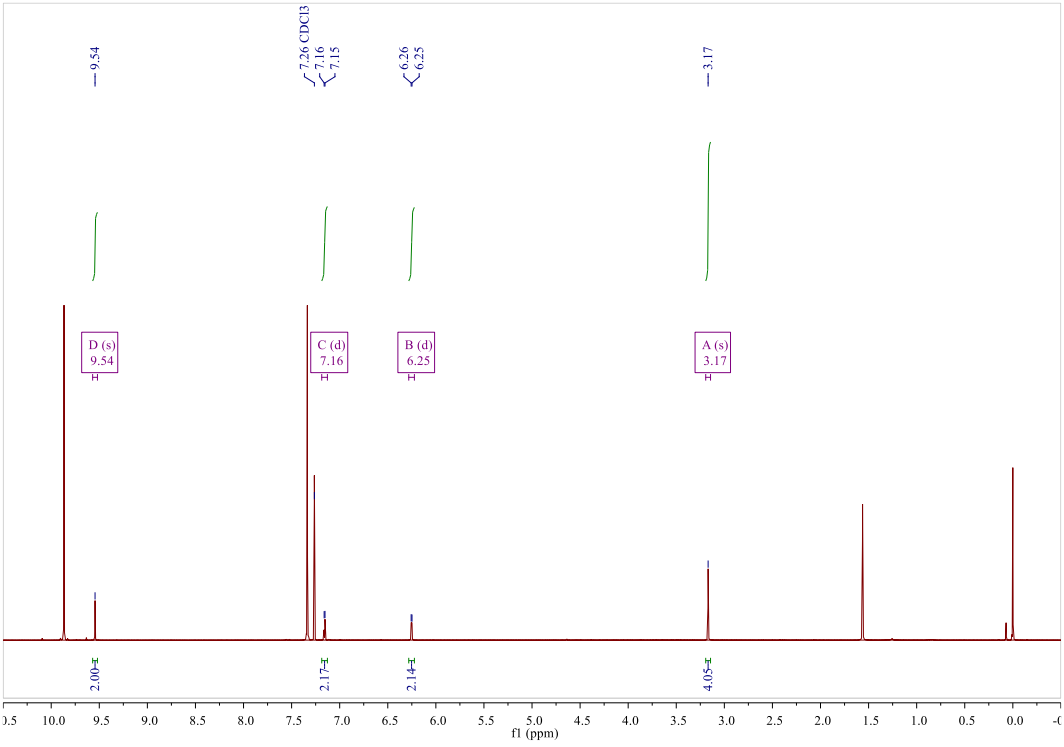


Fig. S22. ^{1}H NMR spectrum of the coupling products by 5-hydroxymethylfurfural. 5,5'-(ethane-1,2-diyl)bis(furan-2-carbaldehyde) (**3d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 2H), 7.16 (d, *J* = 3.5 Hz, 2H), 6.25 (d, *J* = 3.5 Hz, 2H), 3.17 (s, 4H).

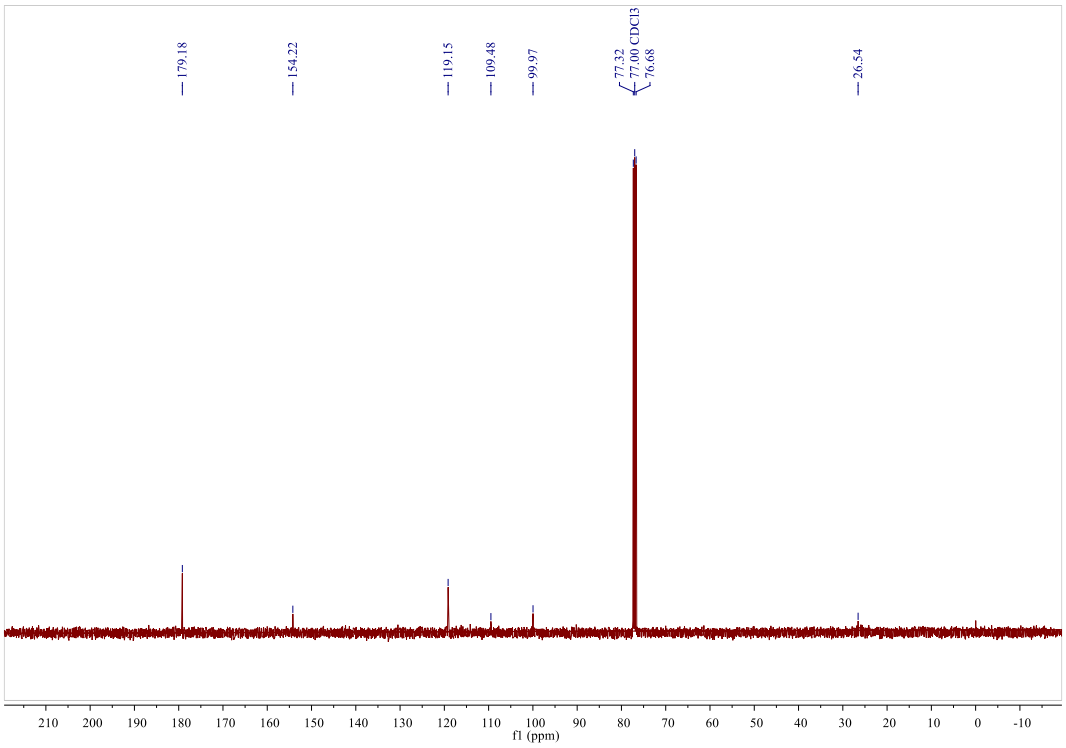


Fig. S23. ^{13}C NMR spectrum of the coupling products by 5-hydroxymethylfurfural. 5,5'-(ethane-1,2-diyl)bis(furan-2-carbaldehyde) (**3d**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.18, 154.22, 119.15, 109.48, 99.97, 26.54.

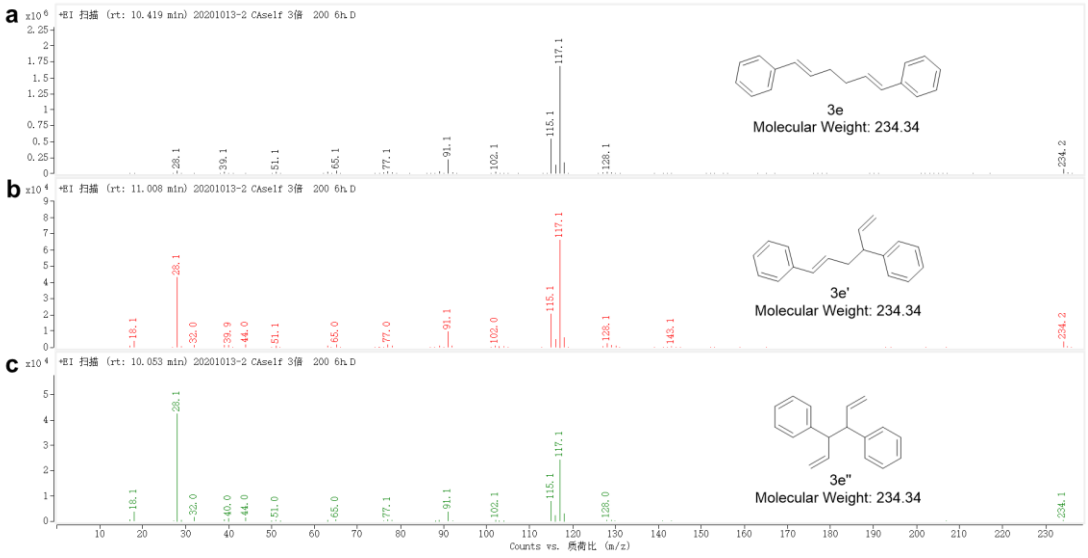


Fig. S24. Mass spectrum of the coupling products by cinnamyl alcohol. a (**3e**): MS (70 eV): m/z (%) 234 (4) [M^+], 117 (100), 115 (32), 91 (13), 28 (2). b (**3e'**): MS (70 eV): m/z (%) 234 (6) [M^+], 117 (100), 115 (31), 91 (15), 28 (65), 18 (6). c (**3e"**): MS (70 eV): m/z (%) 234 (1) [M^+], 117 (57), 115 (19), 91 (9), 28 (100), 18 (9). **3e"** was detected in trace amount.

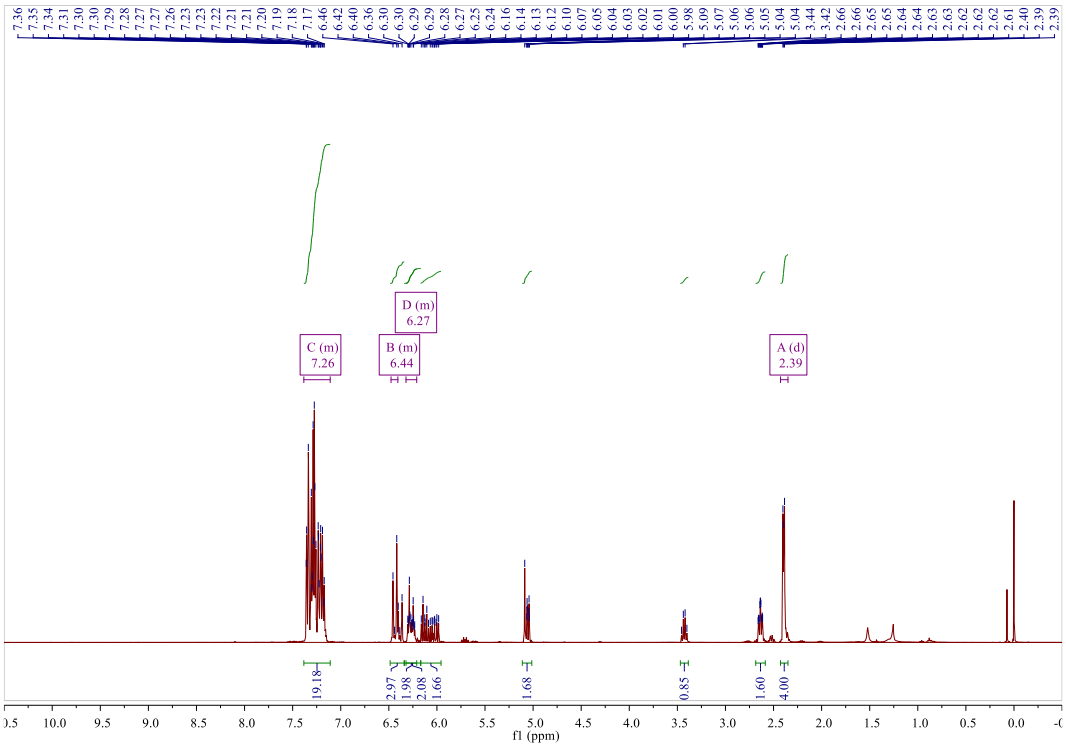


Fig. S25. ^{1}H NMR spectrum of the coupling products by cinnamyl alcohol. 1,6-diphenylhexa-1,5-diene (**3e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.11 (m, 10H), 6.48–6.41 (m, 2H), 6.32–6.21 (m, 2H), 2.39 (d, *J* = 6.7 Hz, 4H). Hexa-1,5-diene-1,4-diyldibenzene (**3e'**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.11 (m, 10H), 6.49–6.34 (m, 2H), 6.17–5.96 (m, 1H), 5.11–5.01 (m, 2H), 3.43 (q, *J* = 7.4 Hz, 1H), 2.64 (tdd, *J* = 7.2, 2.8, 1.3 Hz, 2H). The ratio of **3e** and **3e'** is 1:0.85.

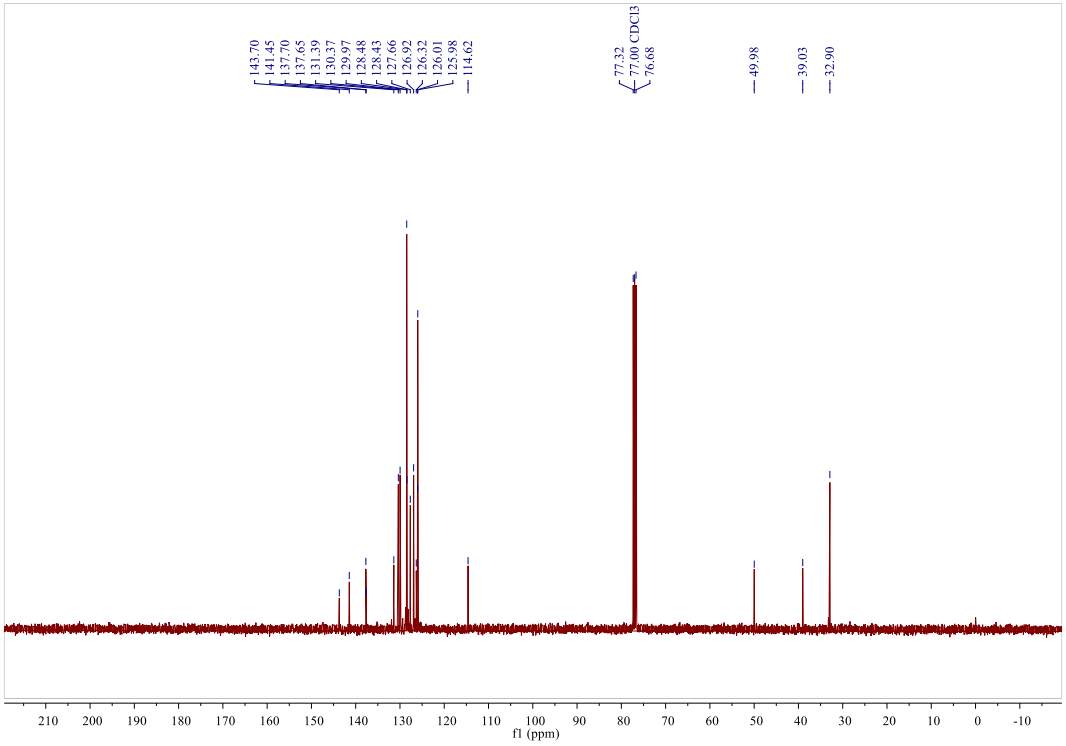


Fig. S26. ^{13}C NMR spectrum of the coupling products by cinnamyl alcohol. 1,6-diphenylhexa-1,5-diene (**3e**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.70, 130.37, 129.97, 128.48, 126.92, 125.98, 32.90. Hexa-1,5-diene-1,4-diyldibenzene (**3e'**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 141.45, 137.65, 131.39, 128.48, 128.43, 127.66, 126.32, 126.01, 125.98, 114.62, 49.98 , 39.03.

10. References

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