

B(C₆F₅)₃-catalysed isomerization of terminal olefins

He Wang ^{a,1}, Fanwei Meng ^{a,1} and Xin Tao ^{a,*}

^a *Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education and Faculty of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, PR China*

*Corresponding author: Xin Tao(taox091@nenu.edu.cn)

1. General information

All reactions were carried out under N₂ atmosphere except noted. All experiments were carried out using standard Schlenk techniques under dry nitrogen. Solvents were purified and dried according to conventional methods prior to use. All reagents were purchased from commercial suppliers and need to be purified by adding molecular sieves or were prepared according to literature procedures. Purification of reaction products was carried out by flash column chromatography on silica gel (300-400 mesh). Chemical yields refer to pure isolated substances. NMR tube reactions were performed in resealable NMR tubes (J. Young). ¹H and ¹³C NMR spectra in C₆D₆ were obtained using a Bruker DPX-600 or Bruker DPX-500 spectrometer. All coupling constants (J values) were reported in Hertz (Hz). All chemical shifts were quoted in ppm and 6.72 ppm for mesitylene as an internal standard.

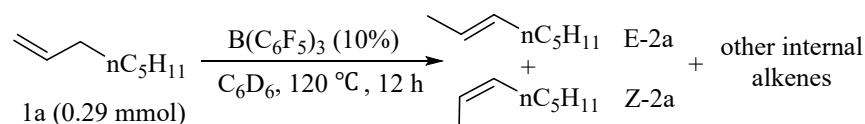
List of abbreviation

Entry	Chemical name	Abbreviation
1	Deuterated benzene	C ₆ D ₆
2	1,2-Dichloroethane	ClCH ₂ CH ₂ Cl
3	Trichloromethane	CHCl ₃
4	Acetonitrile	CH ₃ CN
5	Tetrahydrofuran	THF
6	1,2-Dimethoxyethane	DME
7	Dichloromethane	CH ₂ Cl ₂

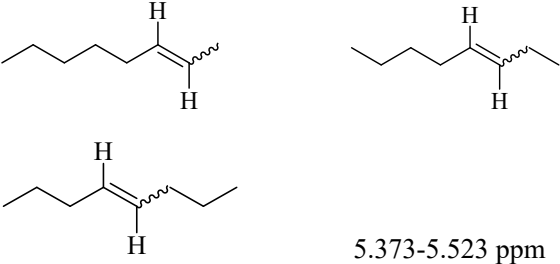
2. ¹HNMR details

We used the Grotjahn method ^[1] to calculate the yield of olefin product and the amount of remaining materials. In each case, the signal integration value of the internal standard mesitylene (6.72 ppm) was set to 1.00 integration units. The ¹H resonance of the H atom in the double bond was used to determine the conversion and yield of the internal olefin (see below).

Table S1. Conversion and yield calculated by Grotjahn method (0.29 mmol 1-octene)



Time	0 h	12 h
 5.745-5.826 ppm	0.63	0.07
 4.975-5.057 ppm	1.33	0.04
Units per proton ^a	0.653	0.036
% starting material remaining ^b	100	5.5

	0	1.26
5.373-5.523 ppm		
Units per proton ^a	0	0.63
% yield of total internal alkenes ^c	0	96.4

^a Calculated by taking the average of integrations of the specified resonances.

^b Calculated by dividing the unit protons of the starting material after 12 hours by the unit protons of 0 hours. For example, in this case, the percentage of starting material remaining after 12 hours: $0.036/0.653 = 5.5\%$. ^c Calculated by dividing the number of unit protons in the olefin double bond after 12 hours by the number of unit protons in the starting material after 0 hours. For example, in this case, the yield percentage of 2-olefin after 12 hours: $0.63/0.653 = 96.4\%$.

The yields of (*E*)-2-alkene, (*Z*)-2-alkene, and other alkenes were determined by assigning the ¹H NMR signal of the CH₃ group (see below for an example of 1-octene isomerization). The triplet characteristic peak of the CH₃ group of (*E*)-3-alkene is sometimes partially overlapped by other signals. For example, as shown by the isomerization of 1-octene in the figure, the left peak of this triplet state overlaps with the impurity signal (the impurity remains intact throughout the isomerization process). In this case, the resolved peak of the triplet state was used to calculate the yield. Note that in most cases, other olefins refer primarily to (*E*)-3-alkenes, as the number of (*Z*)-3-alkenes and higher homologues is too small to allow a definitive determination. Calculation of (*E*)-2-octene, *E/Z* ratio and (*E*)-3-octene:

$$(\textit{E})\text{-2-octene} = 96.4\% \times 0.56 / (0.56 + 0.19 + 0.04) = 68.3\%$$

$$(\textit{E})\text{-2-octene} : (\textit{Z})\text{-2-octene} = 0.56 : 0.19 = 2.95 : 1$$

$$(\textit{E})\text{-3-octene} = 96.4\% \times 0.04 / (0.56 + 0.19 + 0.04) = 4.9\%$$

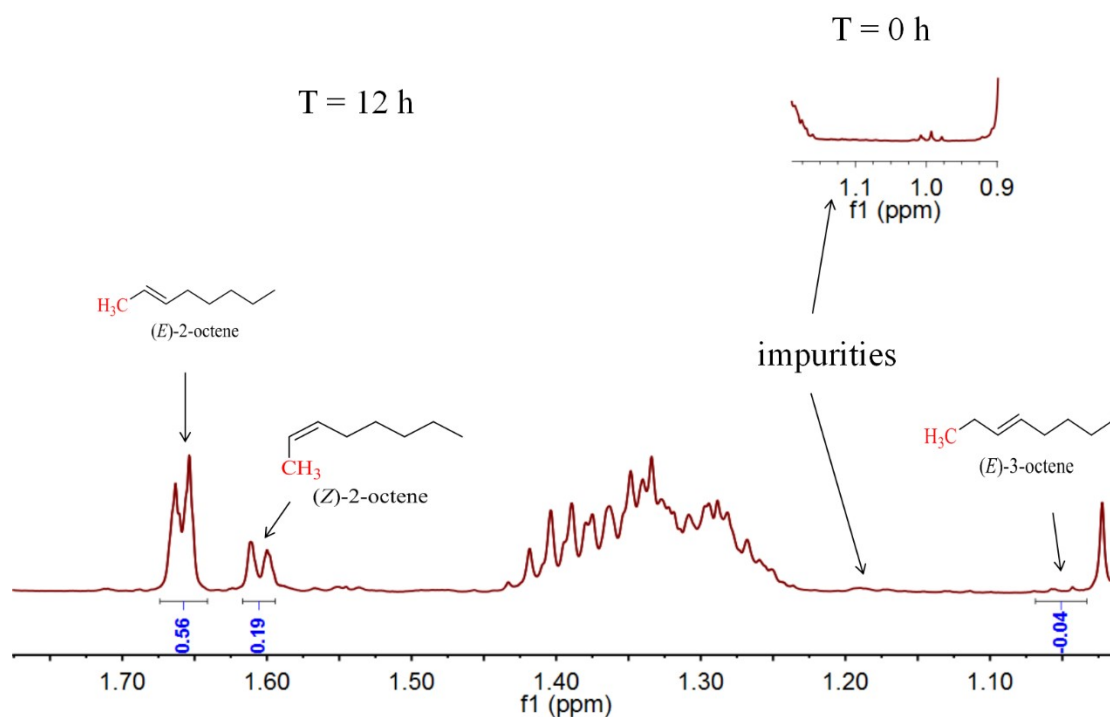


Figure S1: ¹H NMR spectrum of specific CH₃ group for 12 hours

3. General Experimental Procedures and Characterization Data for Starting Materials

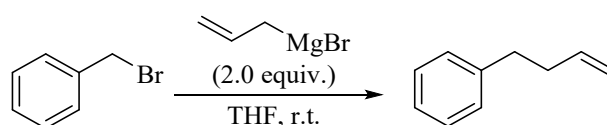
Preparation of catalyst

Bis(pentafluorophenyl)borane [HB(C₆F₅)₂] [2]: To a Schlenk flask of B(C₆F₅)₃ (7.68 g, 15.00 mmol) in toluene (75 mL), Et₃SiH (1.74 g, 15.00 mmol) was added. The flask was sealed, then heated to 80 °C and stirred for 3 days. The flask was cooled to room temperature, resulting in a precipitate, which was vacuum filtered and washed with cold toluene and pentanes to yield the target product as a white crystalline powder (3.11 g, 59.9 %). ¹H NMR (500 MHz, CDCl₃) δ 2.18 (s, B-H). ¹⁹F NMR (471 MHz, CDCl₃) δ -132.27 (d, *J* = 14.4 Hz, 2F), -147.21 (t, *J* = 20.2 Hz, 1F), -158.89 (td, *J* = 7.6, 20.9 Hz, 2F).

(C₆F₅)H₂B·SMe₂ [3]: An excess of H₃B·SMe₂ (2.40 mL, 25.3 mmol) was added to a solution of (C₆F₅)₃B·OEt₂ (4.36 g, 7.4 mmol) in toluene (60 mL). The solution was heated to 80 °C for 2 h before an aliquot was checked by ¹⁹F and ¹¹B NMR to ensure

the reaction had gone to completion. The volatiles were removed under reduced pressure to yield a colorless solid. Colorless crystals were obtained by recrystallization at -25 °C in dichloromethane-light petroleum solution. The product was obtained by filtration (3.95g, 73%). ¹H NMR (500 MHz, C₆D₆): δ 2.84 (2H, m, BH₂), 1.20 (6H, s, CH₃). ¹³C NMR (126 MHz, C₆D₆): δ 22.2 (CH₃). ¹¹B NMR (160 MHz, C₆D₆): δ -17.2 (1B, t, *J*_{BH}=105 Hz). ¹⁹F NMR (471 MHz, C₆D₆): δ -130.4 (2F, d, *J*_{FF}= 17 Hz), -157.6 (1F, t, *J*_{FF} = 20 Hz), -163.8 (2F, m).

General procedure for the synthesis of but-3-en-1-ylbenzene (1m) ^[4]



Under Nitrogen atmosphere, benzylbromide (855 mg, 5.0 mmol) was dissolved in THF (2 mL/mmol) and allylmagnesium bromide (1.0 M in Et₂O, 12.0 mL, 12.0 mmol) was added dropwise. The reaction mixture was stirred at room temperature and refluxing for 4 h. Then the reaction progress was monitored by gas chromatography. Upon full consumption of starting material, the reaction mixture was cooled in an ice bath and NH₄Cl (saturated aqueous solution) was added to quench the reaction. The aqueous phase was then extracted with CH₂Cl₂ (3 × 2 mL/mmol substrate). The combined organic layer was dried over MgSO₄ and concentrated under reduced pressure. The obtained crude was further purified by column chromatography. But-3-en-1-ylbenzene was obtained in 93% yield (617 mg, 4.66 mmol) as a colorless liquid after purification by column chromatography (pentane). ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.16 (m, 3H), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 5.02 (m, 1H), 4.99 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 2.75 – 2.70 (m, 2H), 2.43 – 2.35 (m, 2H).

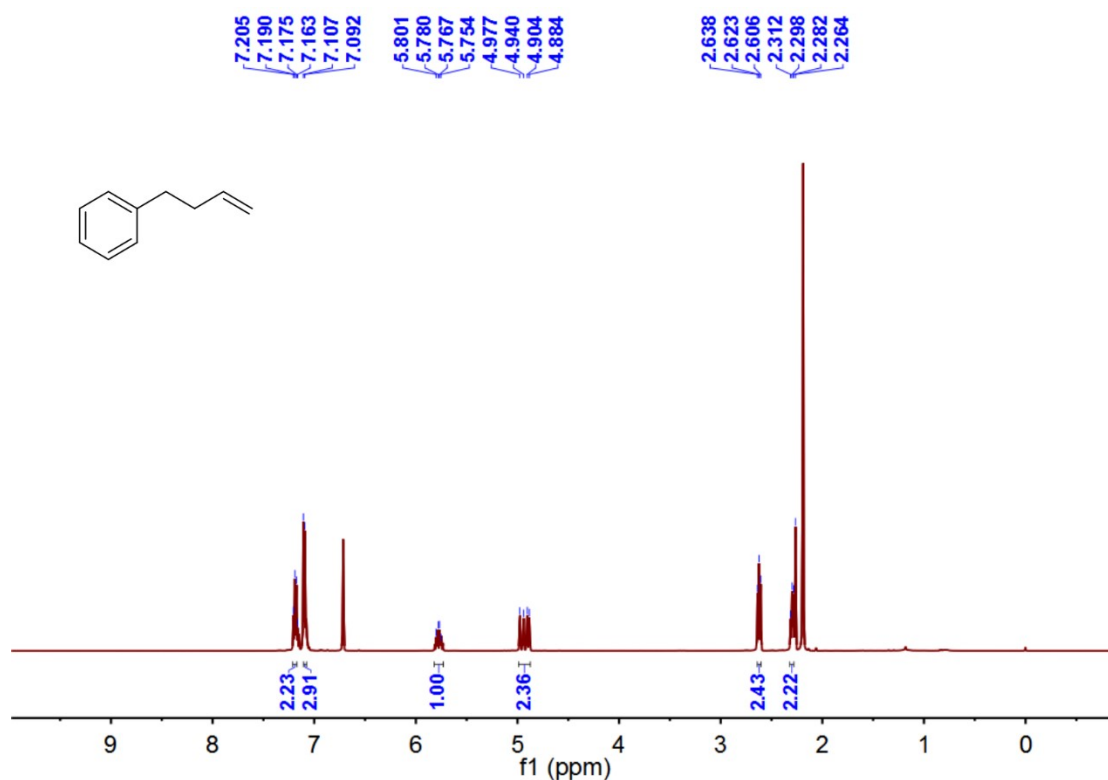
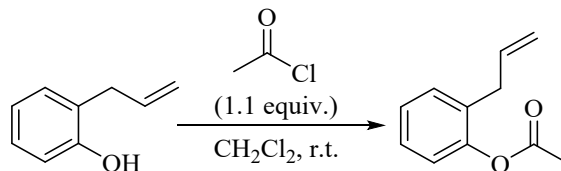


Figure S2. ^1H NMR spectrum of 1m.

General procedure for the synthesis of but-3-en-1-ylbenzene ^[5]



A 25 mL flask was charged with o-allylphenol (5.3 mmol) and dichloromethane (6 mL), cooled to 0 °C, and triethylamine (2.31 mL, 5.0 mmol) was added. After 1 min, acetyl chloride (5.5 mmol) was slowly added, and the reaction stirred at r.t. for 6 h. Then, ethyl acetate (10 mL) was added and the mixture washed with saturated aqueous NH_4Cl (5 mL). The organic layers were dried (MgSO_4), concentrated and subjected to SiO_2 flash column chromatography. ^1H NMR (500 MHz, CDCl_3) δ 7.17 (t, $J = 6.9$ Hz, 2H), 7.11 (t, $J = 7.1$ Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 5.87 – 5.78 (m, 1H), 5.03 – 4.96 (m, 2H), 3.23 (d, $J = 6.6$ Hz, 2H), 2.22 (s, 3H).

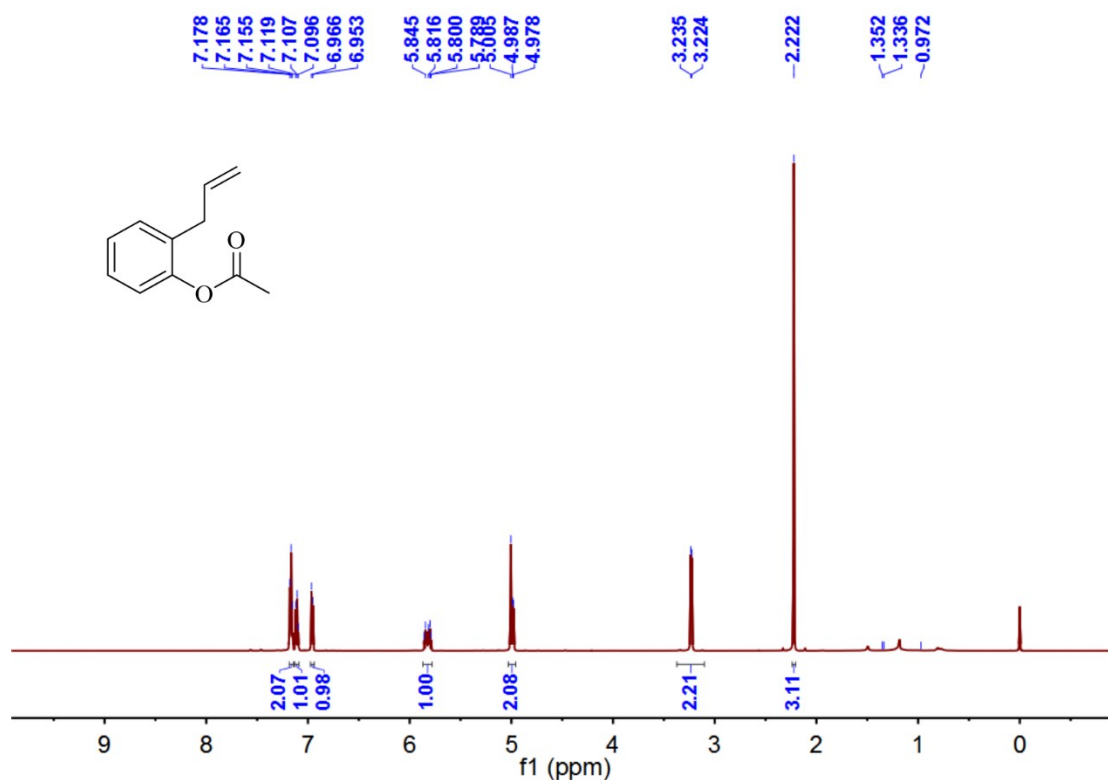
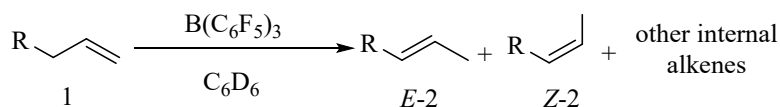


Figure S3. ^1H NMR spectrum of but-3-en-1-ylbenzene.

Experimental procedure:

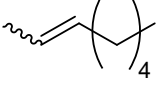


In a nitrogen filled glovebox, 1-alkenes (0.29 mmol), mesitylene (0.145 mmol, 17.4 mg, used as internal standard) and dry deuterated C_6D_6 (0.5 mL) were added to a J-Young NMR tube and an initial NMR spectrum was acquired. Back to the glove box, tris(pentafluorophenyl) (5 or 10 mol%) was added to the mixed liquid. The reaction was allowed to proceed at the setting temperature and monitored by ^1H NMR spectroscopy. The conversion, (*E*)-2-alkene and other internal alkenes, and *E/Z* ratio were determined by integration of suitable ^1H NMR signals. After all the volatiles were removed under reduced pressure, the resulted crude product was further purified by flash column chromatography (hexane or CH_2Cl_2). Finally, the yield was calculated from the residue.

The unreacted starting material was not separated from the product, so the conversion and *E/Z* ratio were determined by integrating the appropriate ^1H NMR signal.

4. NMR Data of the E-Olefins Products

Oct-2-ene (2a):

 ^1H NMR (500 MHz, C_6D_6) δ 5.49 – 5.38 (m, 2H), 2.07 – 1.92 (m, 2H), 1.61 (*E*, d, $J = 4.9$ Hz, 3H), 1.56 (*Z*, d, $J = 5.6$ Hz, 3H), 1.38 – 1.18 (m, 6H), 0.98 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 129.3, 123.4, 30.4, 28.4, 24.7, 21.8, 16.7, 12.9. The spectroscopic data correspond to reported data [6]. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 96% of dec-2-ene, E/Z ratio of 78:22.

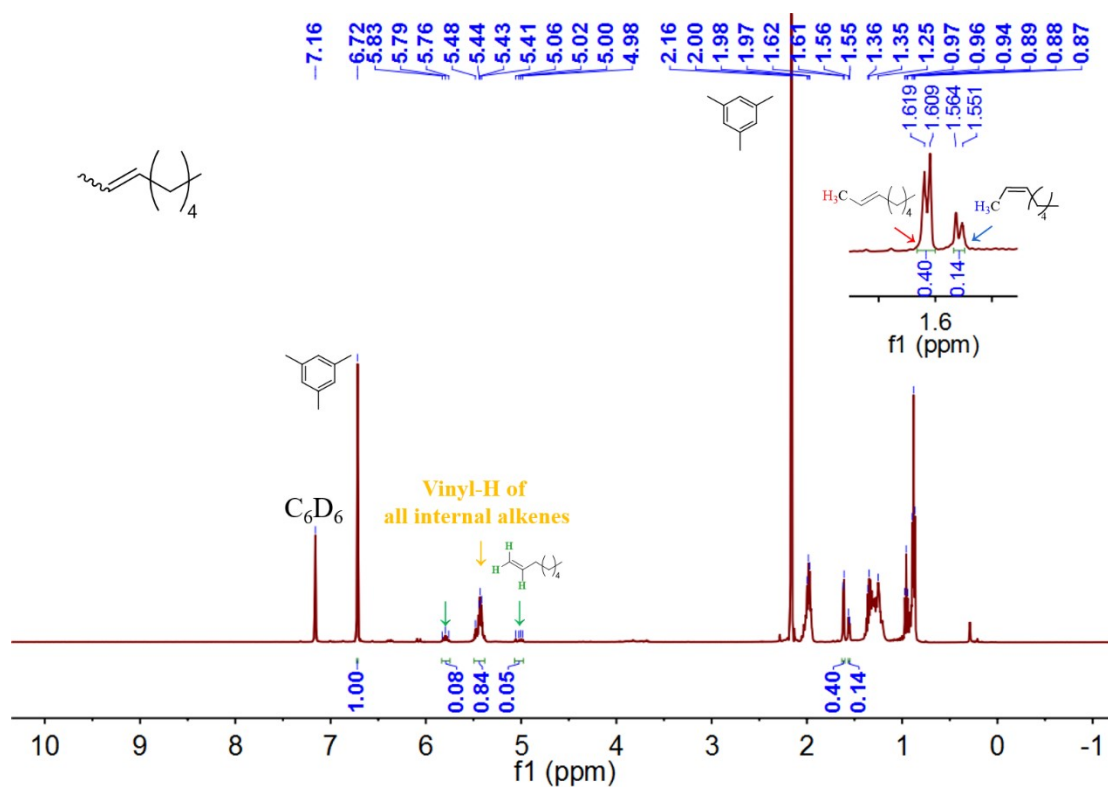


Figure S4. ^1H NMR spectrum of product mixture from isomerization of **1a**.

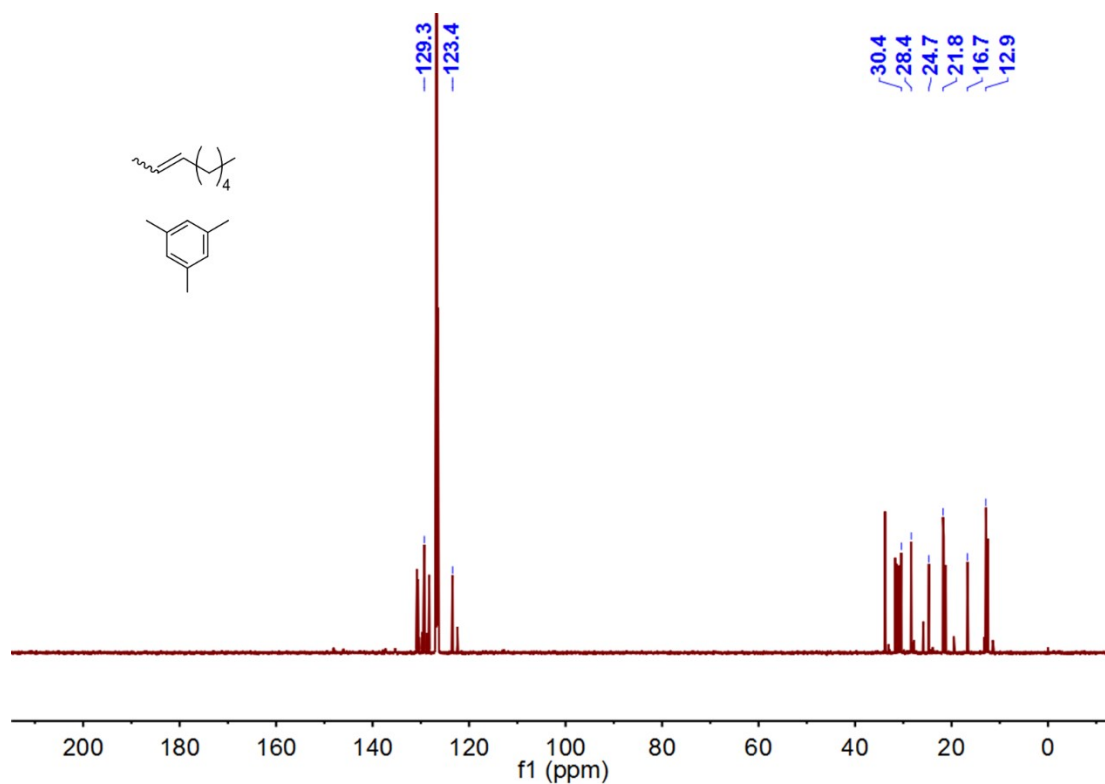
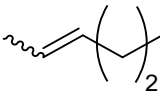


Figure S5. ^{13}C NMR spectrum of product mixture from isomerization of **1a**.

Hex-2-ene (2b):


 ^1H NMR (500 MHz, C_6D_6) δ 5.50 – 5.35 (m, 2H), 2.04 – 1.93 (m, 2H), 1.60 – 1.57 (*E*, m, 3H), 1.55–1.53 (*Z*, m, 3H), 1.44 – 1.33 (m, 2H), 0.91 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 130.3, 123.6, 24.6, 21.7, 16.7, 12.5. The spectroscopic data correspond to reported data [6]. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 95% of hex-2-ene, E/Z ratio of 76:24.

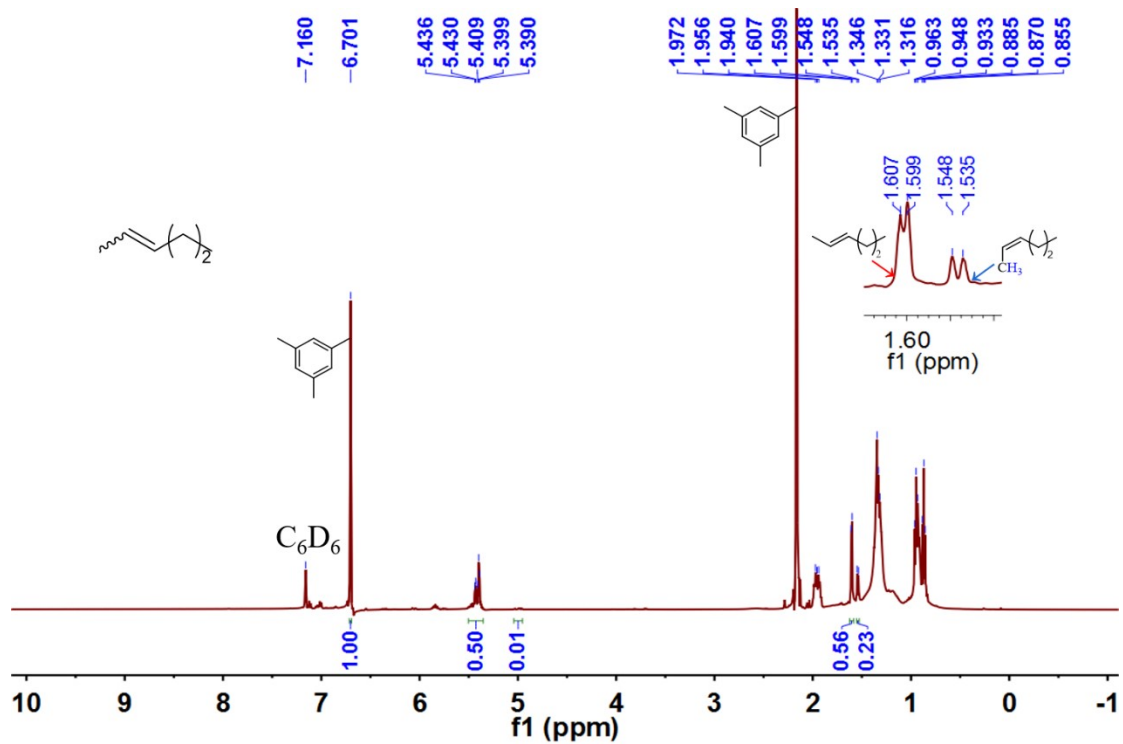


Figure S6. ^1H NMR spectrum of product mixture from isomerization of **1b**.

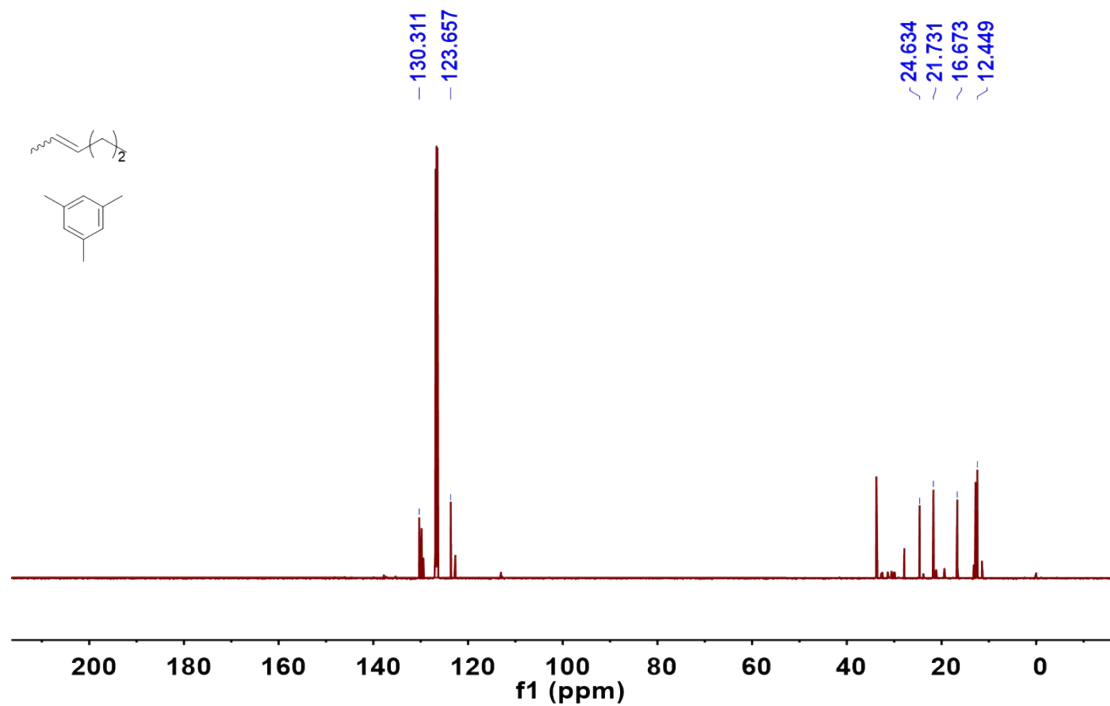
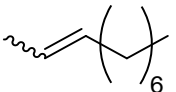
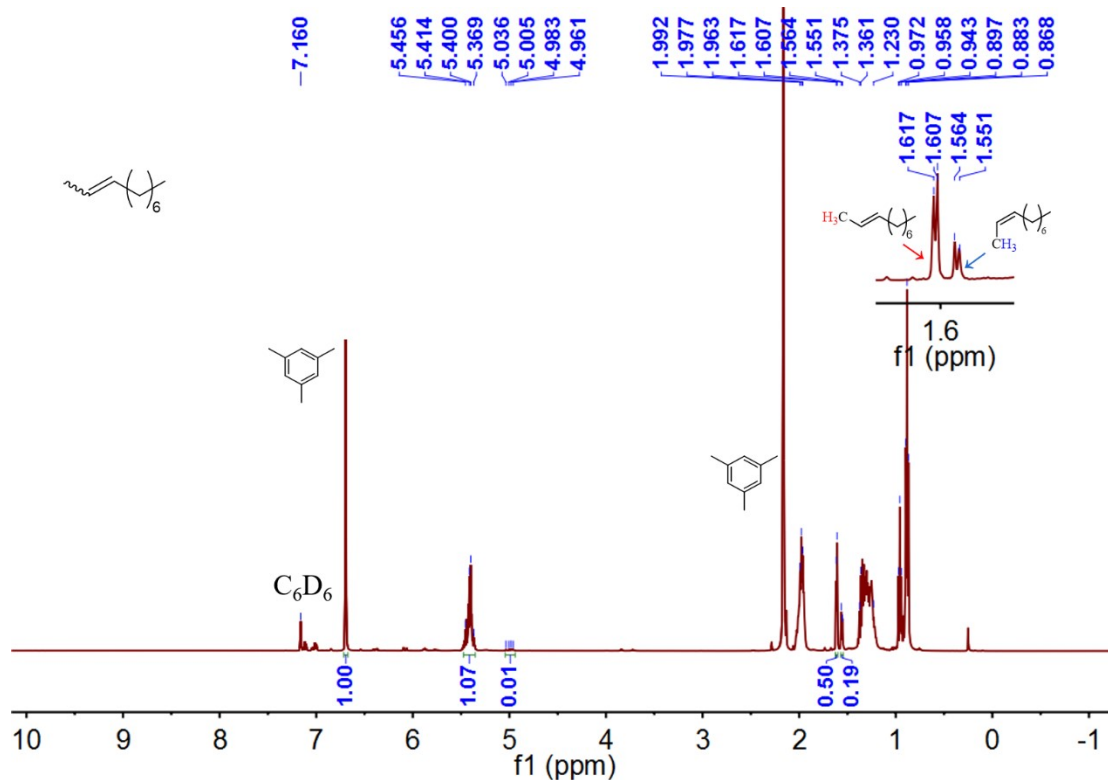


Figure S7. ^{13}C NMR spectrum of product mixture from isomerization of **1b**.

Dec-2-ene (2c):

 $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 5.45 – 5.36 (m, 2H), 1.99 – 1.96 (m, 2H), 1.64 – 1.58 (*E*, m, 3H), 1.57 – 1.53 (*Z*, m, 3H), 1.38 – 1.18 (m, 10H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, C_6D_6) δ 130.0, 124.4, 32.7, 31.4, 29.7, 22.7, 13.9. The spectroscopic data correspond to reported data [6]. $^1\text{H NMR}$ analysis revealed that the mixture contained 5% of unreacted starting material, 90% of dec-2-ene, *E/Z* ratio of 79:21.



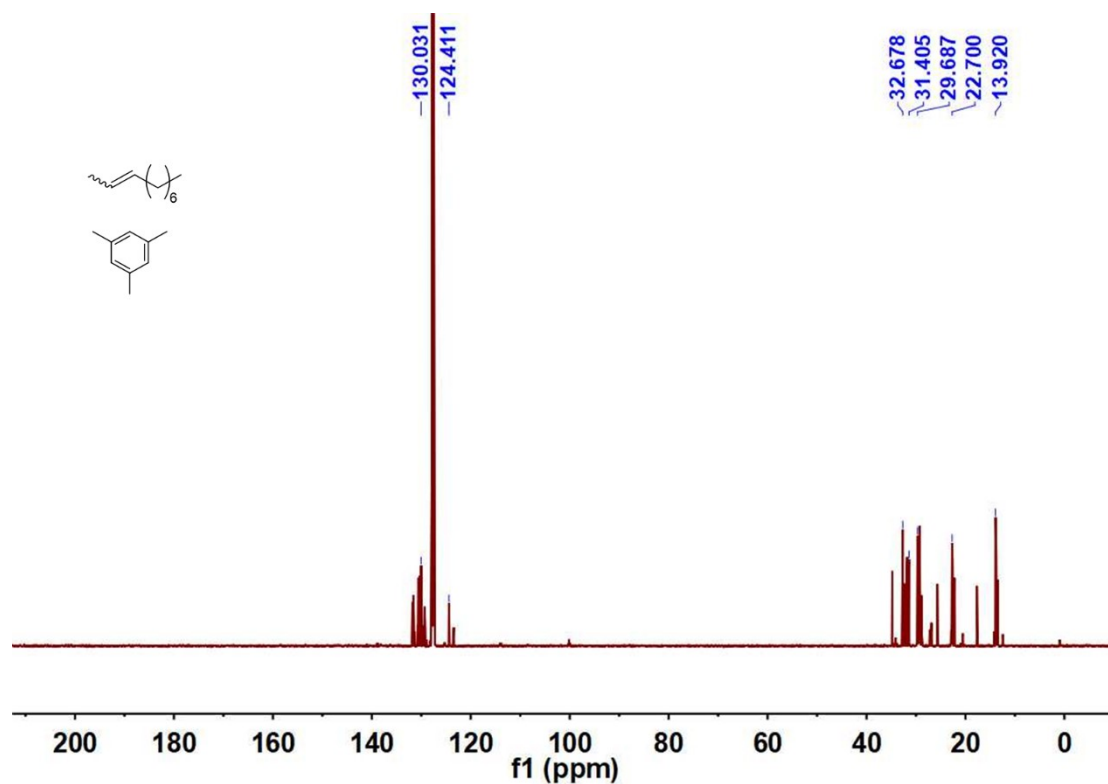
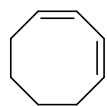


Figure S9. ^{13}C NMR spectrum of product mixture from isomerization of **1c**.

(1Z, 3Z)-cycloocta-1,3-diene (2d):



^1H NMR (500 MHz, C_6D_6) δ 5.84 (d, $J = 10.4$ Hz, 2H), 5.56 (dd, $J = 17.6$, 7.3 Hz, 2H), 2.12 (s, 4H), 1.41 (dd, $J = 5.6$, 2.7 Hz, 4H). ^{13}C NMR (151 MHz, C_6D_6) δ 130.2, 125.3, 27.3, 22.4. The spectroscopic data correspond to reported data [7]. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 90% of (1Z, 3Z)-cycloocta-1,3-diene.

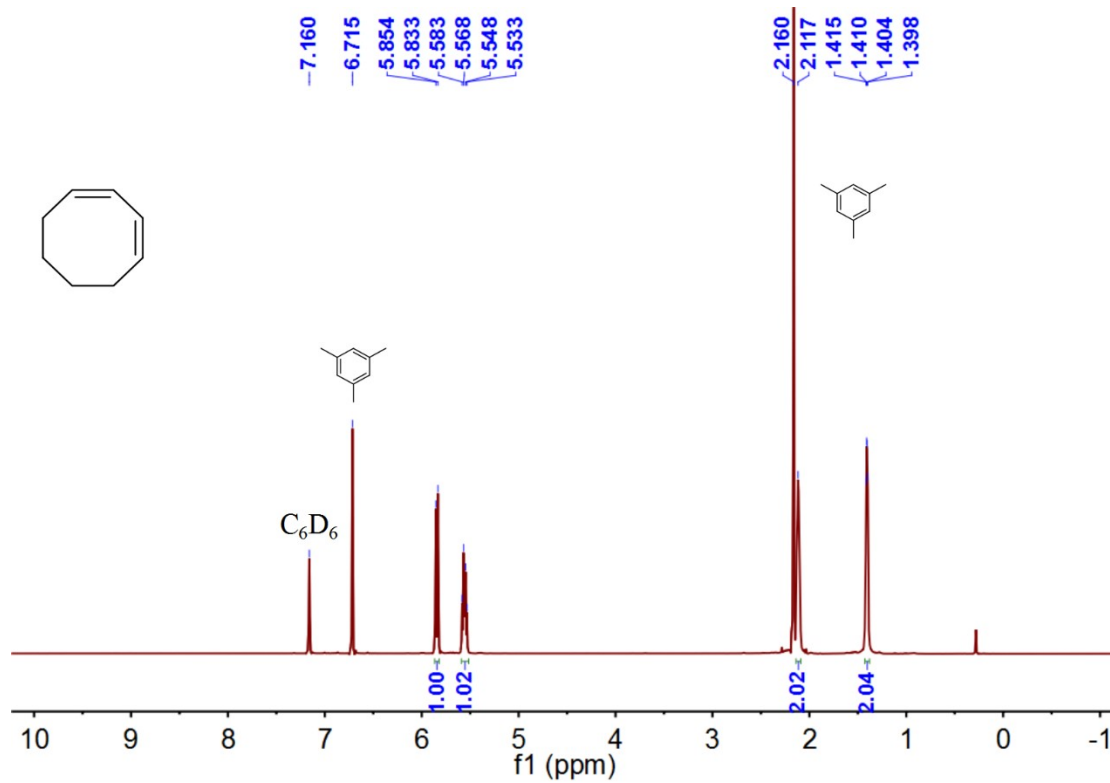


Figure S10. ^1H NMR spectrum of product mixture from isomerization of **1d**.

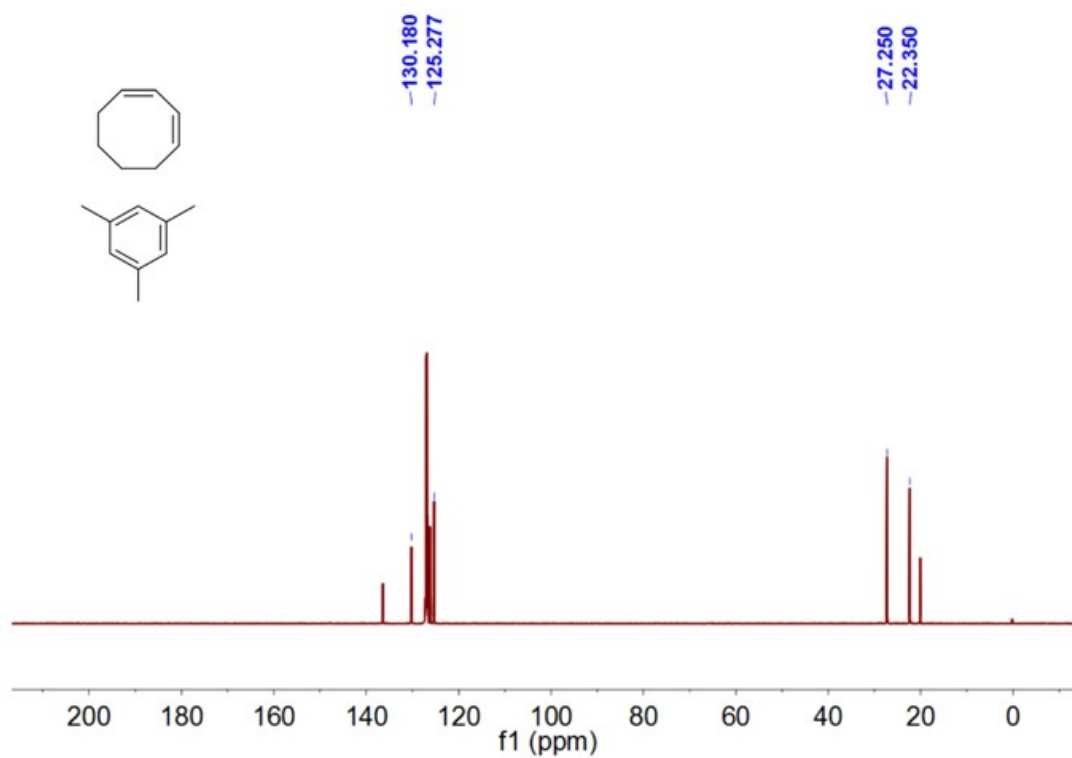
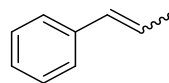


Figure S11. ^{13}C NMR spectrum of product mixture from isomerization of **1d**.

Prop-1-en-1-ylbenzene (2e):



^1H NMR (500 MHz, C_6D_6) δ 7.18-7.03 (m, 5H), 6.29 (dd, $J = 15.7, 1.4$ Hz, 1H), 6.03 (dq, $J = 15.7, 6.6$ Hz, 1H), **1.71 (Z, dd, $J = 6.7, 1.7$ Hz, 3H)**, **1.65 (E, dd, $J = 6.7, 1.7$ Hz, 3H)**. ^{13}C NMR (126 MHz, C_6D_6) δ 137.3, 130.5, 127.6, 125.9, 125.19, 124.3, 13.4. The spectroscopic data correspond to reported data [8]. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 90% of prop-1-en-1-ylbenzene, *E/Z* ratio of 93:7.

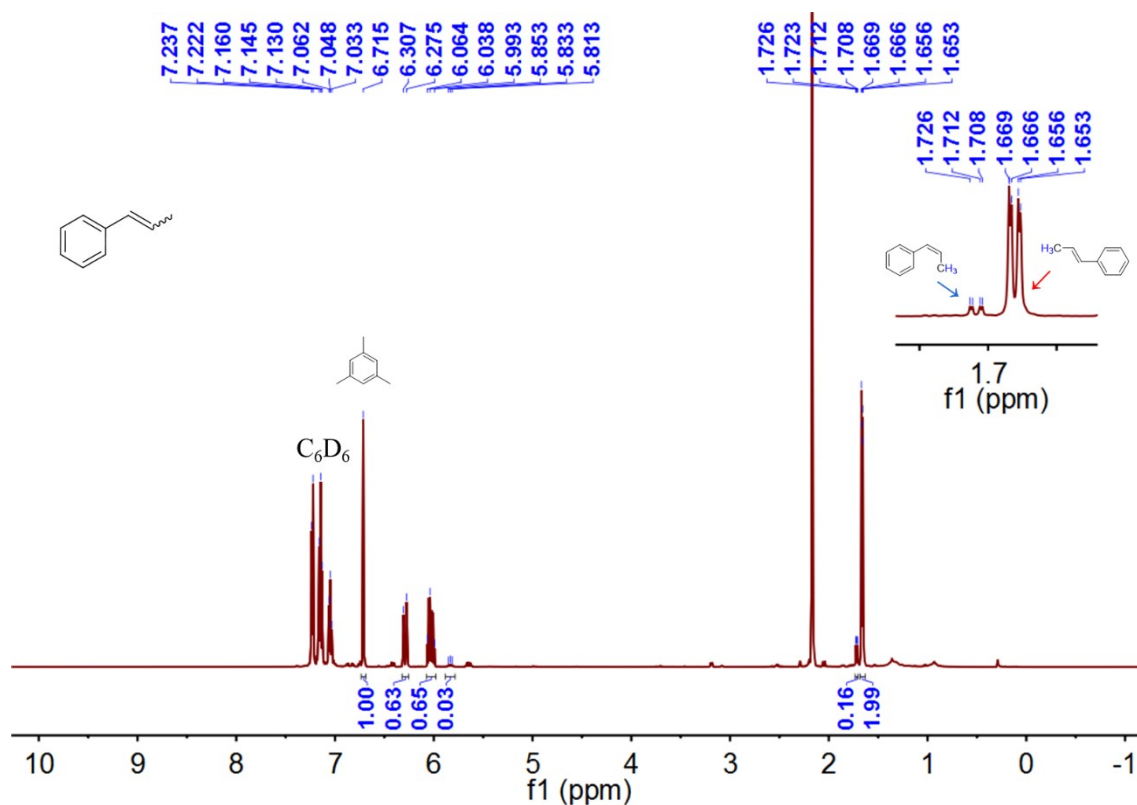


Figure S12. ^1H NMR spectrum of product mixture from isomerization of **1e**.

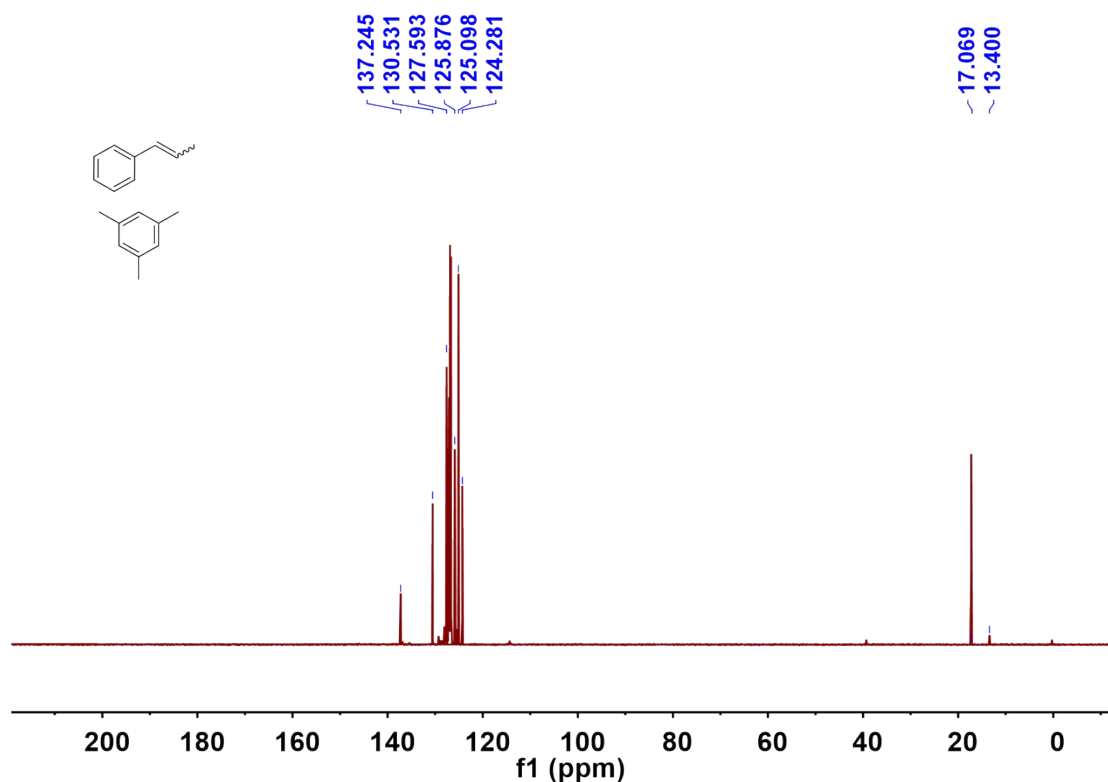
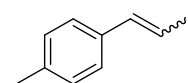


Figure S13. ^{13}C NMR spectrum of product mixture from isomerization of **1e**.

1-methyl-4-(prop-1-en-1-yl)benzene (2f):



^1H NMR (500 MHz, C_6D_6) δ 7.18 (t, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 7.9$ Hz, 2H), 6.33 (d, $J = 16.5$ Hz, 1H), 6.04 (dd, $J = 15.7, 6.6$ Hz, 1H), 2.13 (s, 3H), **1.76 (Z, dd, $J = 6.6$ Hz, 3H), 1.68 (E, dd, $J = 6.6$ Hz, 3H)**. ^{13}C NMR (126 MHz, C_6D_6) δ 136.1, 135.4, 131.3, 129.1, 125.9, 124.0, 20.7, 18.1. The spectroscopic data correspond to reported data ^[9]. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 90% of 1-methyl-4-(prop-1-en-1-yl)benzene, *E/Z* ratio of 92:8.

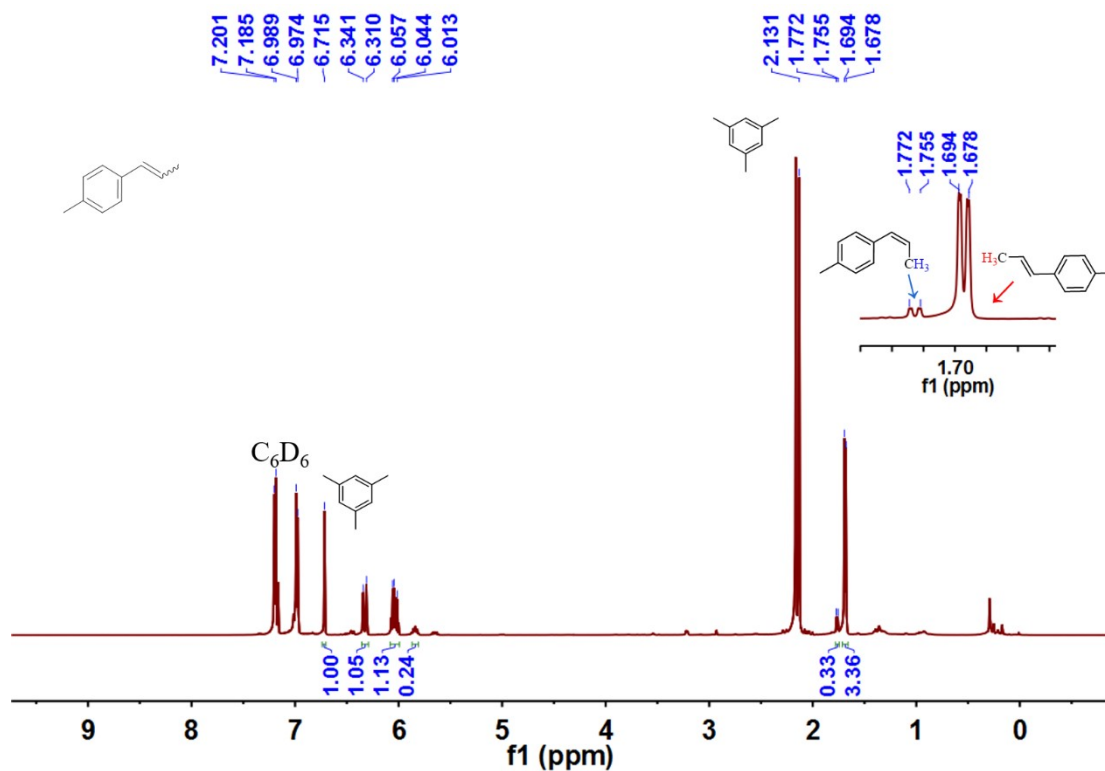


Figure S14. 1H NMR spectrum of product mixture from isomerization of **1f**.

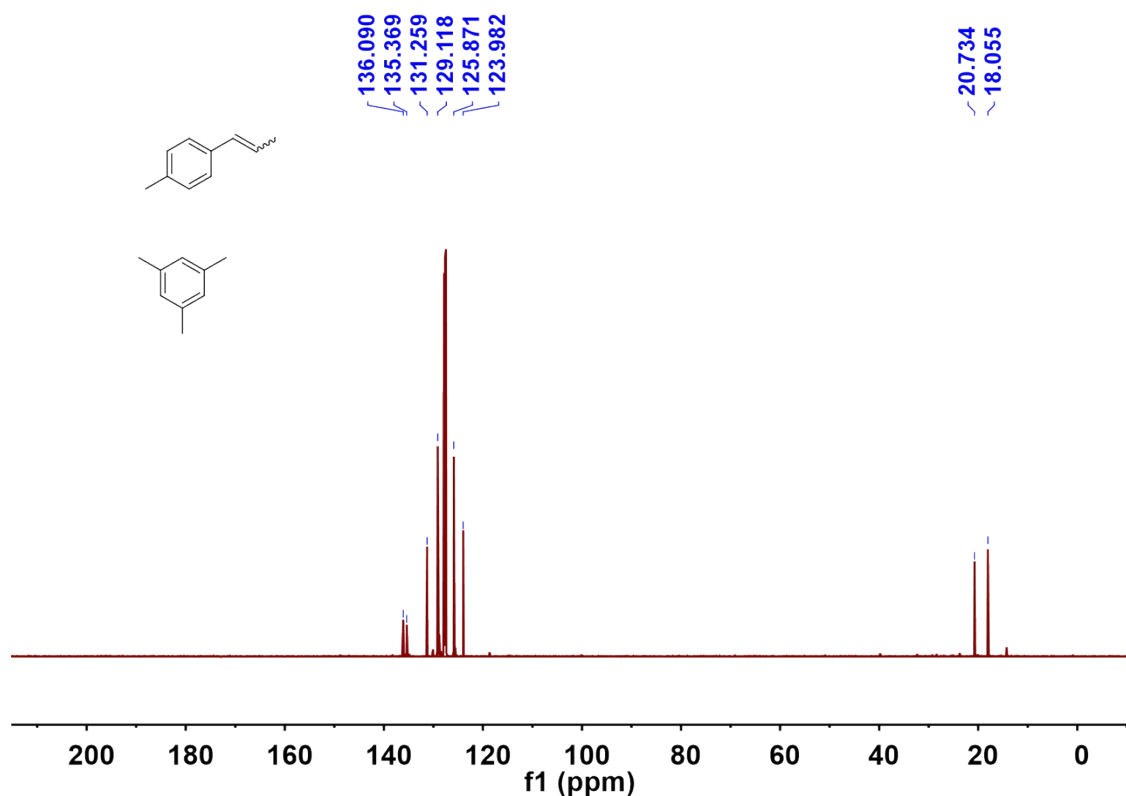
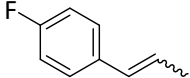


Figure S15. ^{13}C NMR spectrum of product mixture from isomerization of **1f**.

1-fluoro-4-(prop-1-en-1-yl)benzene (2g):

 $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 6.99 – 6.93 (m, 2H), 6.78 (t, $J = 8.7$ Hz, 2H), 6.14 (d, $J = 15.7$ Hz, 1H), 5.83 (dd, $J = 15.7, 6.7$ Hz, 1H), **1.74 (Z, d, $J = 6.6$ Hz, 3H), 1.62 (E, d, $J = 6.6$ Hz, 3H)**. The spectroscopic data correspond to reported data [9]. $^{13}\text{C NMR}$ (126 MHz, C_6D_6) δ 136.1, 128.9 (d, $J = 7.8$ Hz), 128.0, 115.7, 114.5, 114.1, 113.9, 111.7, 38.9, 38.1. $^1\text{H NMR}$ analysis revealed that the mixture contained 1% of unreacted starting material, 78% of 1-fluoro-4-(prop-1-en-1-yl)benzene, *E/Z* ratio of 99:1.

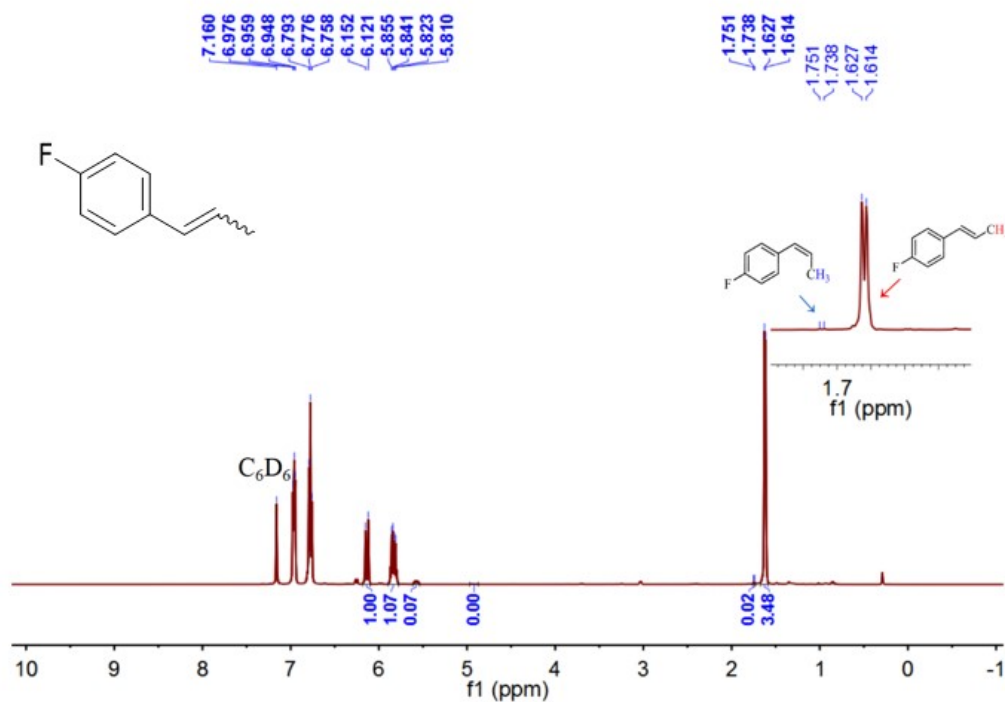


Figure S16. $^1\text{H NMR}$ spectrum of product mixture from isomerization of **1g**.

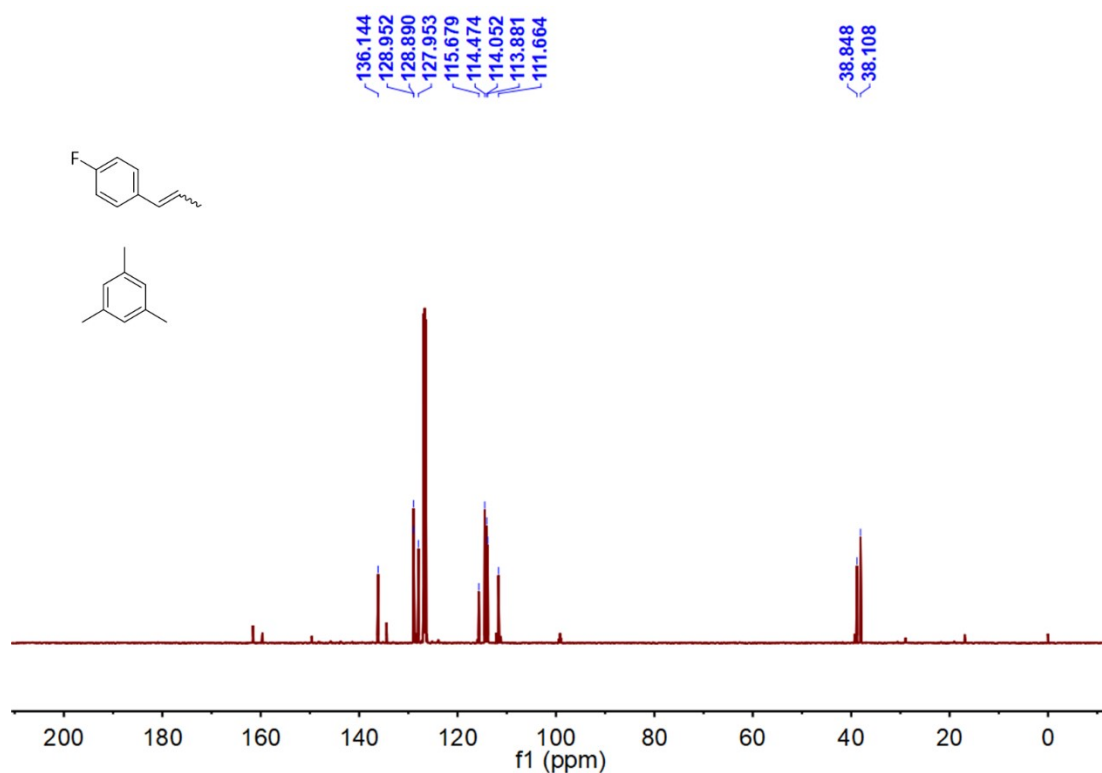
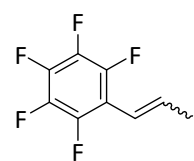


Figure S17. ^{13}C NMR spectrum of product mixture from isomerization of **1g**.

1,2,3,4,5-pentafluoro-6-(prop-1-en-1-yl)benzene (2h):



^1H NMR (500 MHz, C_6D_6) δ 6.33 – 6.21 (m, 1H), 6.04 (dd, $J = 28.9$, 17.1 Hz, 1H), **1.59 (Z, d, $J = 7.5$ Hz, 3H)**, **1.54 (E, d, $J = 6.6$ Hz, 3H)**. ^{13}C NMR (126 MHz, C_6D_6) δ 136.6, 132.6, 128.7, 128.0, 127.2, 124.3, 116.3, 35.9, 20.3. ^1H NMR analysis revealed that the mixture contained 70% of unreacted starting material, 25% of 1,2,3,4,5-pentafluoro-6-(prop-1-en-1-yl)benzene, E/Z ratio of 92:8.

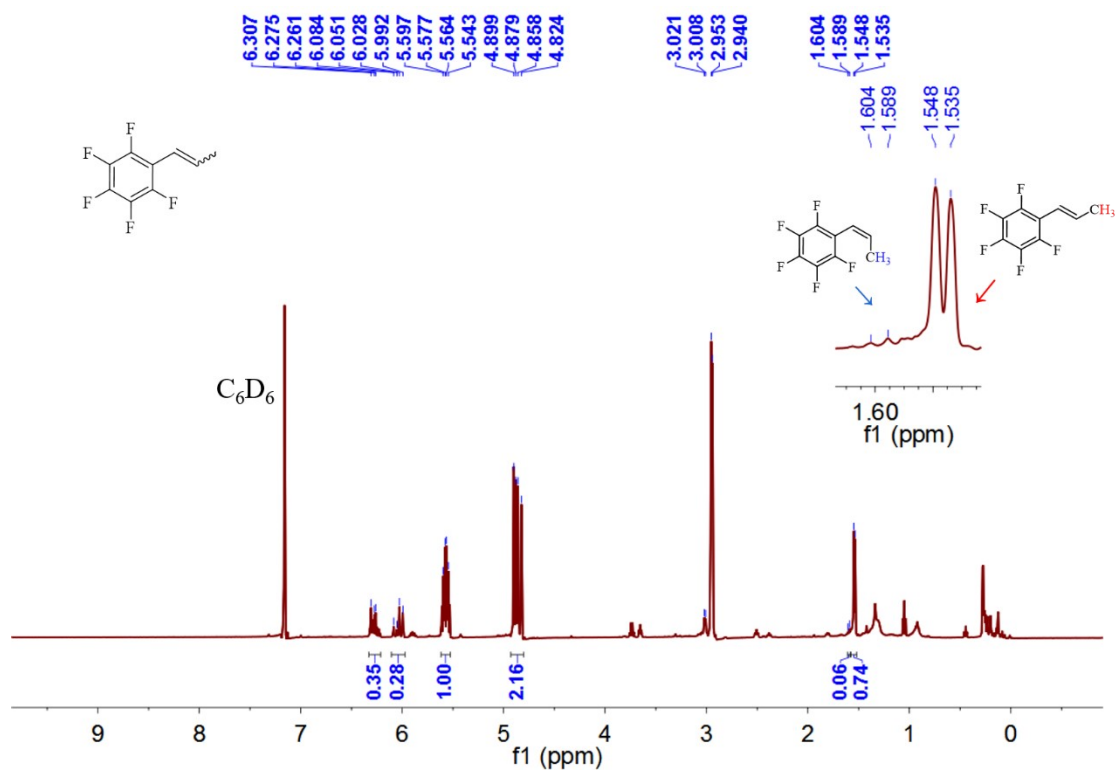


Figure S18. ¹H NMR spectrum of product mixture from isomerization of **1h**.

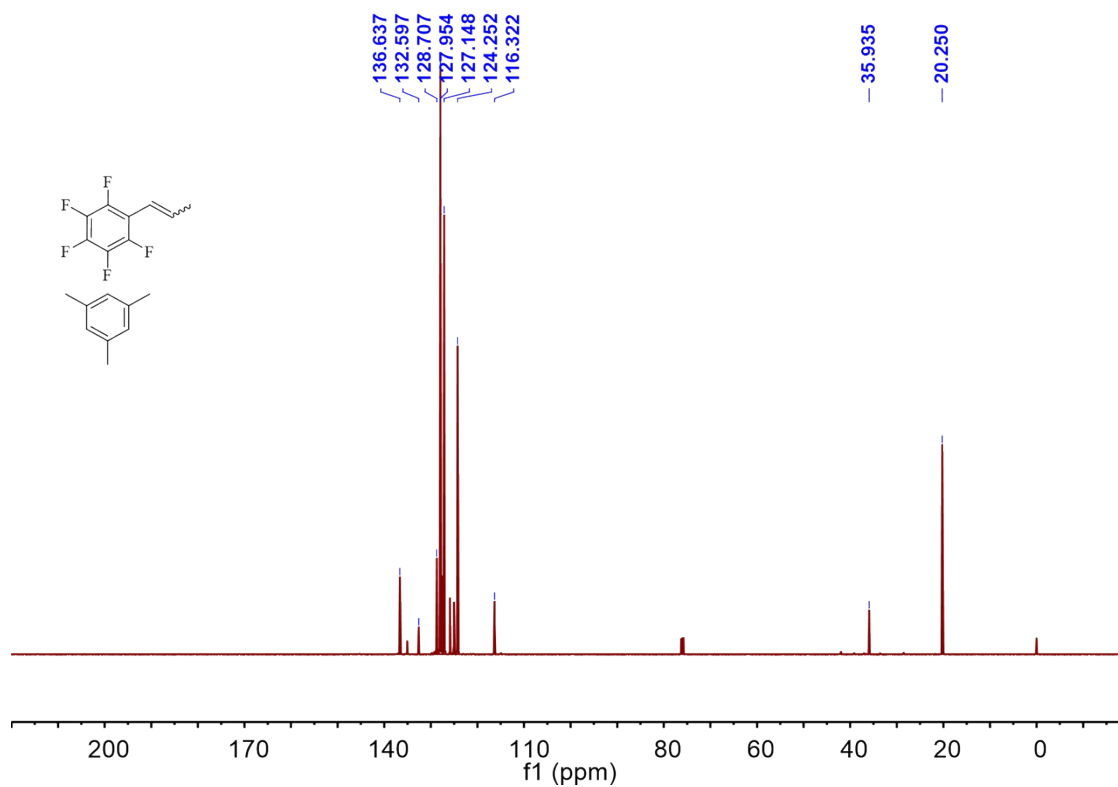
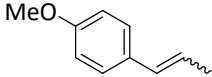


Figure S19. ¹³C NMR spectrum of product mixture from isomerization of **1h**.

1-methoxy-4-(prop-1-en-1-yl)benzene (**2i**):

 $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 6.90 (d, $J = 8.7$ Hz, 2H), 6.47 (d, $J = 8.8$ Hz, 2H), 6.02 (d, $J = 15.7$ Hz, 1H), 5.67 (dd, $J = 15.7, 6.6$ Hz, 1H), 3.05 (s, 3H), **1.48 (Z, dd, $J = 6.7, 1.7$ Hz, 3H)**, **1.42 (E, dd, $J = 6.7, 1.7$ Hz, 3H)**. $^{13}\text{C NMR}$ (126 MHz, C_6D_6) δ 157.6, 137.2, 128.7, 126.2, 122.0, 114.2, 53.6, 38.5, 17.3. The spectroscopic data correspond to reported data [9]. $^1\text{H NMR}$ analysis revealed that the mixture contained 1% of unreacted starting material, 87% of 1-methoxy-4-(prop-1-en-1-yl)benzene, E/Z ratio of 94:6.

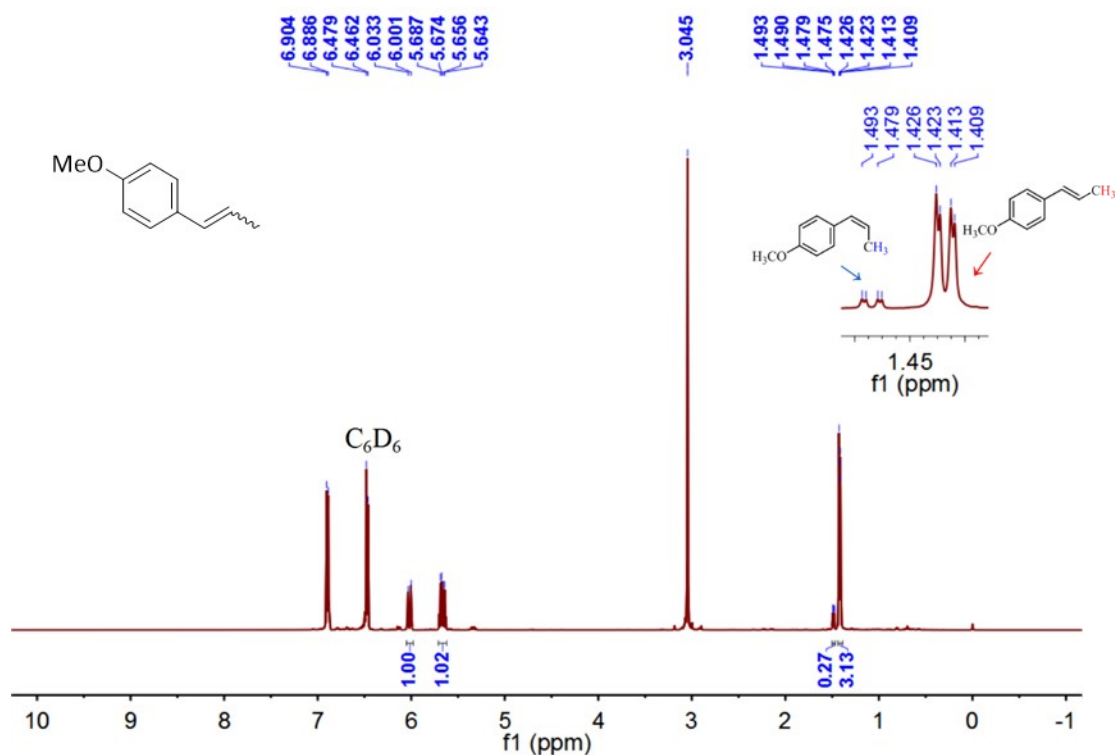


Figure S20. $^1\text{H NMR}$ spectrum of product mixture from isomerization of **1i**.

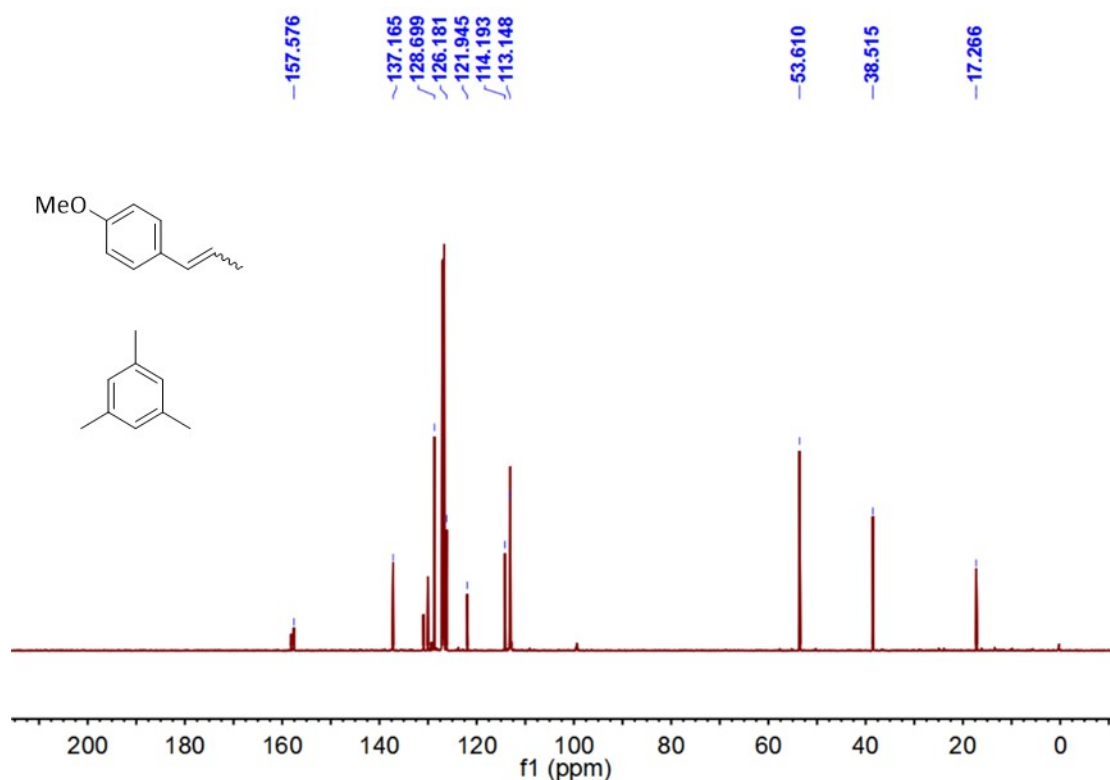


Figure S21. ¹³C NMR spectrum of product mixture from isomerization of **1i**.

1,2-dimethoxy-4-(prop-1-en-1-yl)benzene (2j):

COc1ccc(C=C)cc1OC
¹H NMR (500 MHz, C₆D₆) δ 6.85 (d, *J* = 5.9 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 6.6 Hz, 1H), 3.46 (s, 3H), 3.42 (s, 3H), **1.82 (Z, dd, *J* = 6.6 Hz, 3H)**, **1.73 (E, dd, *J* = 6.6 Hz, 3H)**. The spectroscopic data correspond to reported data [9]. ¹³C NMR (126 MHz, C₆D₆) δ 157.3, 136.9, 130.7, 128.5, 128.2, 114.0, 112.8, 53.4, 38.3, 11.3. ¹H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 96% of 1,2-dimethoxy-4-(prop-1-en-1-yl)benzene, *E/Z* ratio of 93:7.

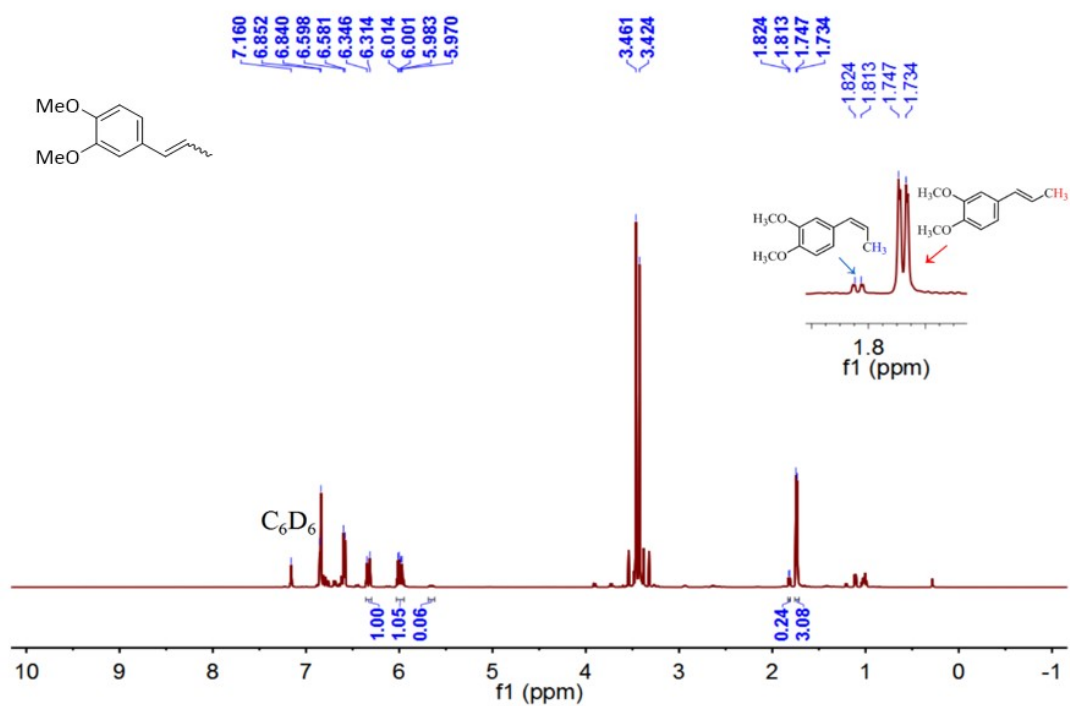


Figure S22. ^1H NMR spectrum of product mixture from isomerization of **1j**.

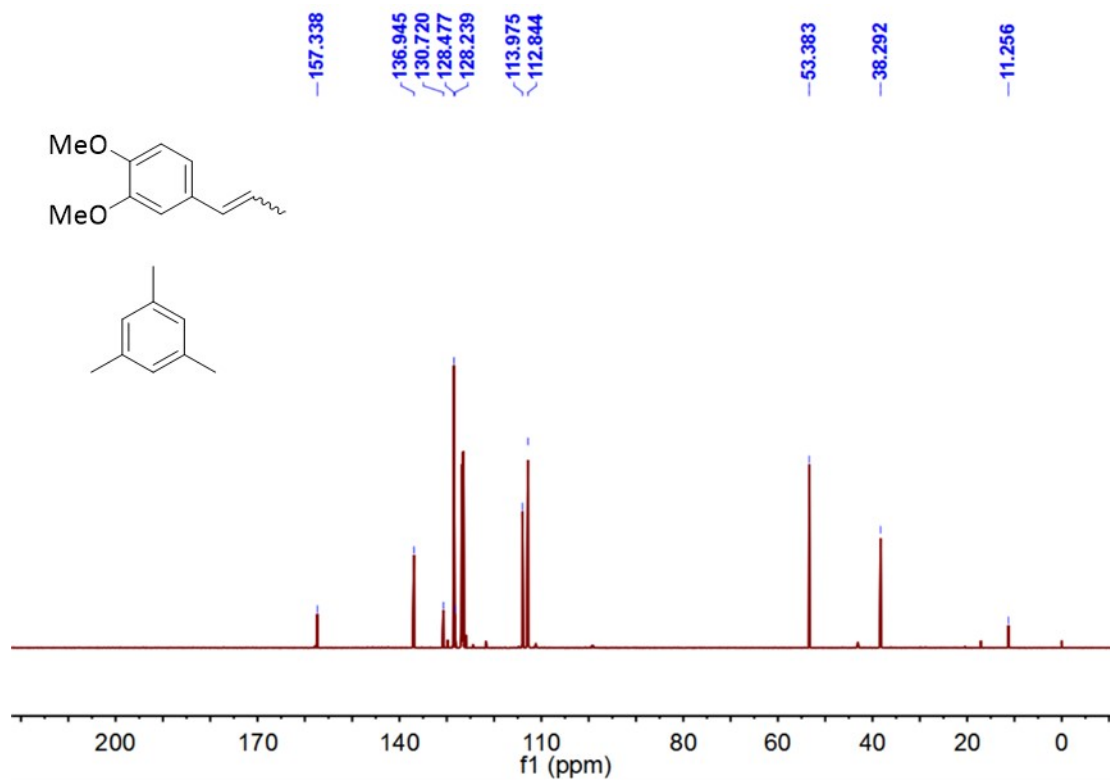
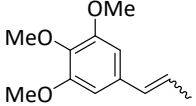


Figure S23. ^{13}C NMR spectrum of product mixture from isomerization of **1j**.

1,2,3-trimethoxy-4-(prop-1-en-1-yl)benzene (2k):

 $^1\text{H NMR}$ (500 MHz, C_6D_6) δ 6.84 (s, 1H), 6.63 – 6.57 (s, 1H), 6.33 (d, $J = 16.7$ Hz, 1H), 5.99 (dd, $J = 15.6, 6.6$ Hz, 1H), 3.50 – 3.40 (m, 9H), **1.81 (Z, dd, $J = 8.0$ Hz, 3H), 1.74 (E, dd, $J = 8.0$ Hz, 3H)**. The spectroscopic data correspond to reported data [9]. $^{13}\text{C NMR}$ (126 MHz, C_6D_6) δ 136.1, 133.5, 129.1, 128.2, 126.0, 125.6, 125.4, 125.0, 124.5, 19.9, 18.4, 17.4. $^1\text{H NMR}$ analysis revealed that the mixture contained 1% of unreacted starting material, 90% of 1,2,3-trimethoxy-4-(prop-1-en-1-yl)benzene, *E/Z* ratio of 94:6.

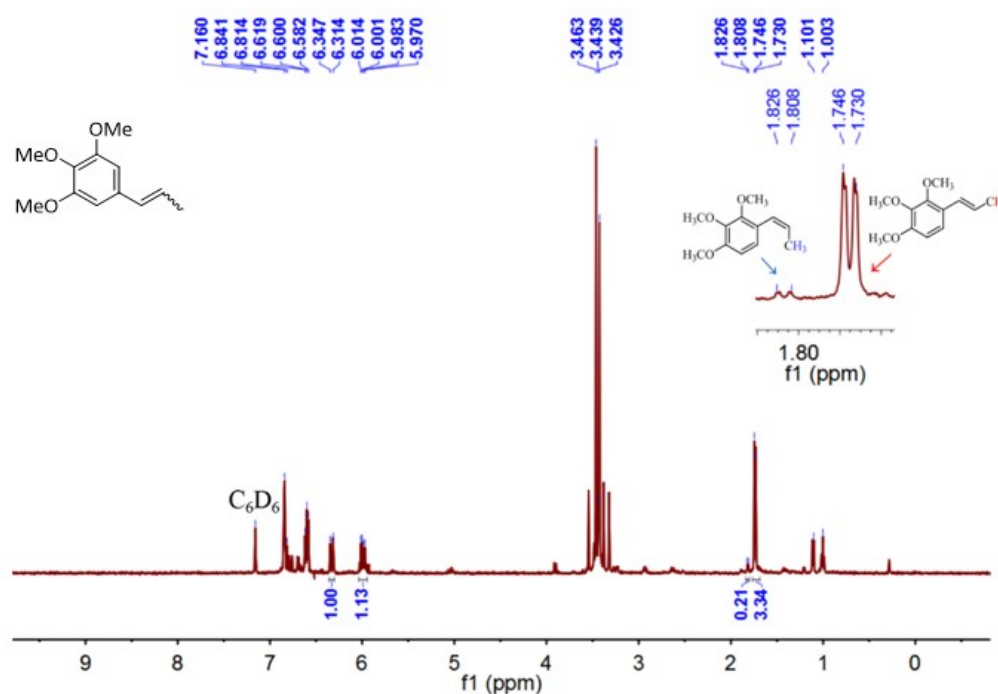


Figure S24. $^1\text{H NMR}$ spectrum of product mixture from isomerization of **1k**.

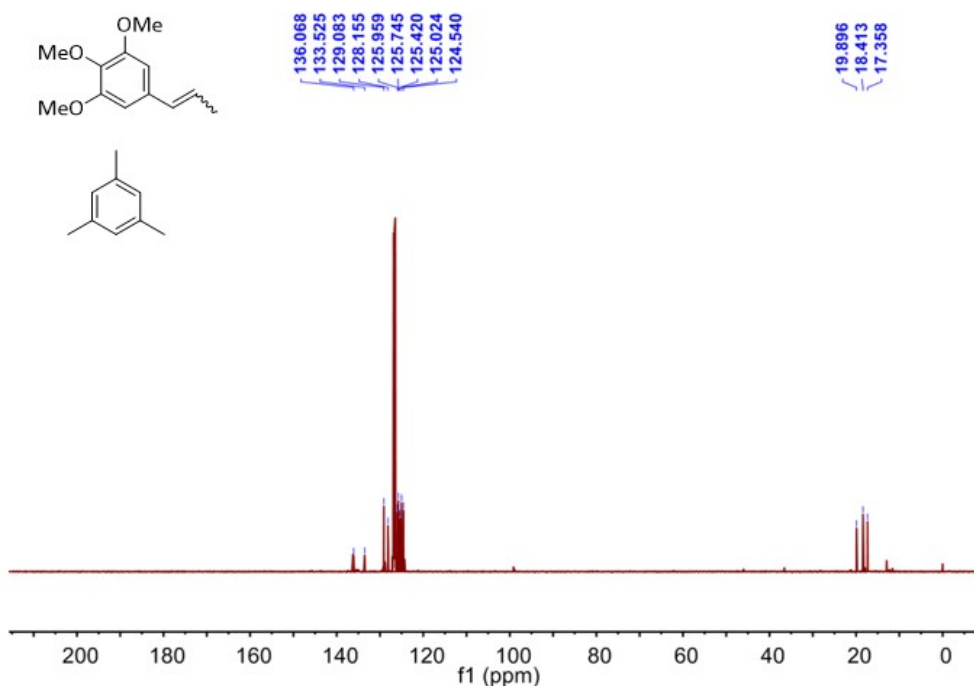
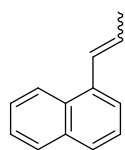


Figure S25. ¹³C NMR spectrum of product mixture from isomerization of **1k**.

1-(prop-1-en-1-yl)naphthalene (2l):



¹H NMR (500 MHz, C₆D₆) δ 8.05-7.66 (m, 3H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.28 (dd, *J* = 13.6, 7.5 Hz, 4H), 6.09 – 6.00 (m, 1H), 5.85 (d, *J* = 11.4 Hz, 1H), **1.73 (E, dd, *J* = 6.6 Hz, 3H)**, **1.58 (Z, dd, *J* = 6.6 Hz, 3H)**. ¹³C NMR (126 MHz, C₆D₆) δ 135.0, 133.1, 130.6, 127.6, 126.5, 124.7, 123.2, 122.7, 17.6, 13.4. The spectroscopic data correspond to reported data ^[9]. ¹H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 72% of 1-(prop-1-en-1-yl)naphthalene, *E/Z* ratio of 83:17.

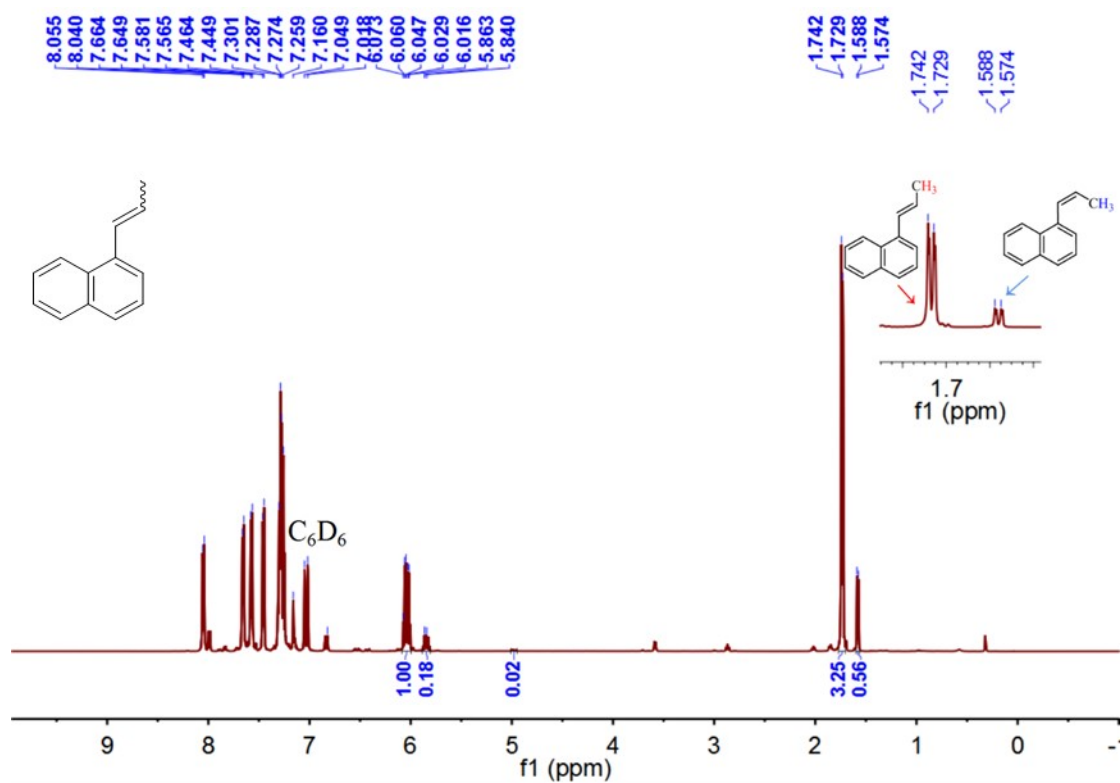


Figure S26. ¹H NMR spectrum of product mixture from isomerization of **11**.

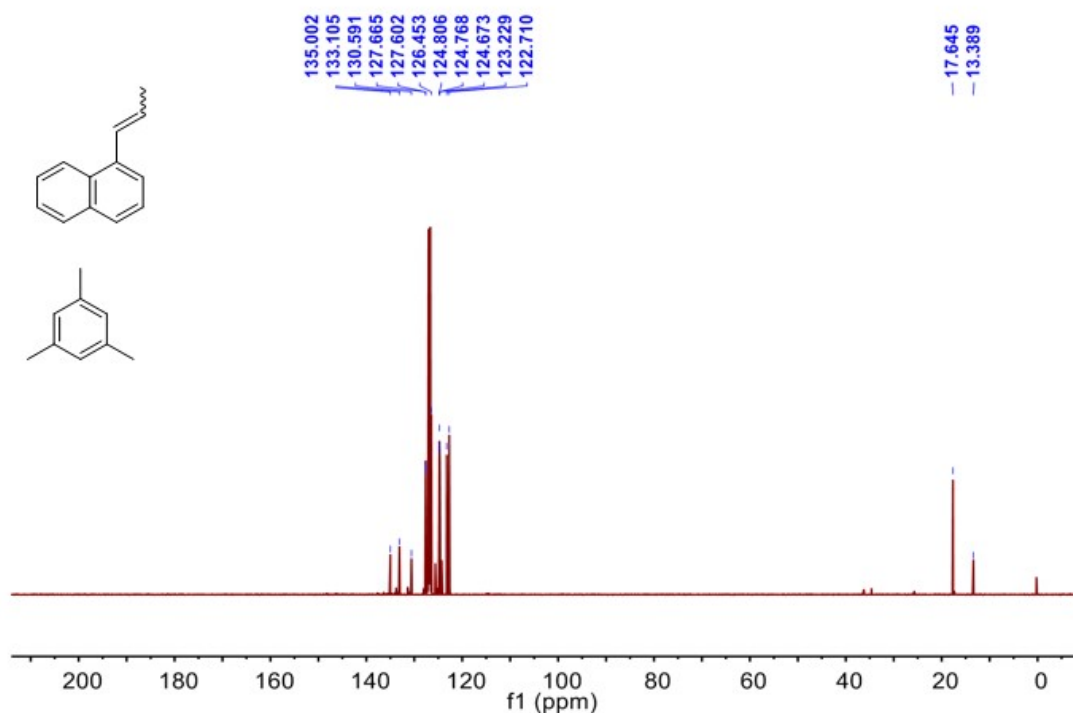
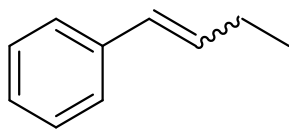


Figure S27. ¹³C NMR spectrum of product mixture from isomerization of **11**.

But-1-en-1-ylbenzene (2m):



^1H NMR (500 MHz, C_6D_6) δ 7.16-7.05 (m, 5H), 6.31 (*E*, d, $J = 15.8$ Hz, 1H), 6.11 (*E*, dd, $J = 22.4, 6.5$ Hz, 1H), 5.57 – 5.48 (*Z*, d, $J = 15.8$ Hz, 1H), 5.41 – 5.34 (*Z*, dd, $J = 22.4, 6.5$ Hz, 1H), 2.08 – 2.02 (m, 2H), 0.96 (t, $J = 7.5$ Hz, 3H). The spectroscopic data correspond to reported data ^[9]. ^{13}C NMR (126 MHz, C_6D_6) δ 137.0, 136.2, 131.0, 128.2, 127.4, 126.0, 125.7, 125.0, 25.0, 12.4. ^1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 94% of but-1-en-1-ylbenzene, *E/Z* ratio of 89:11.

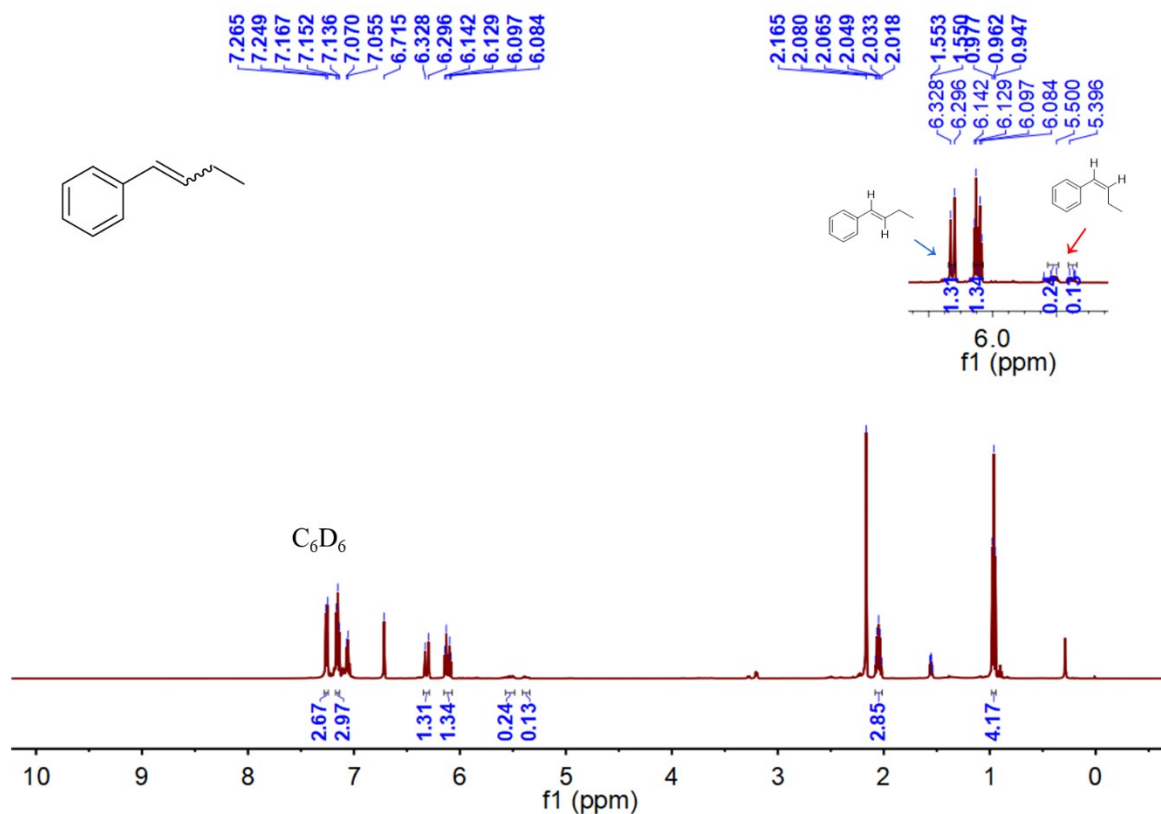


Figure S28. ^1H NMR spectrum of product mixture from isomerization of **1m**.

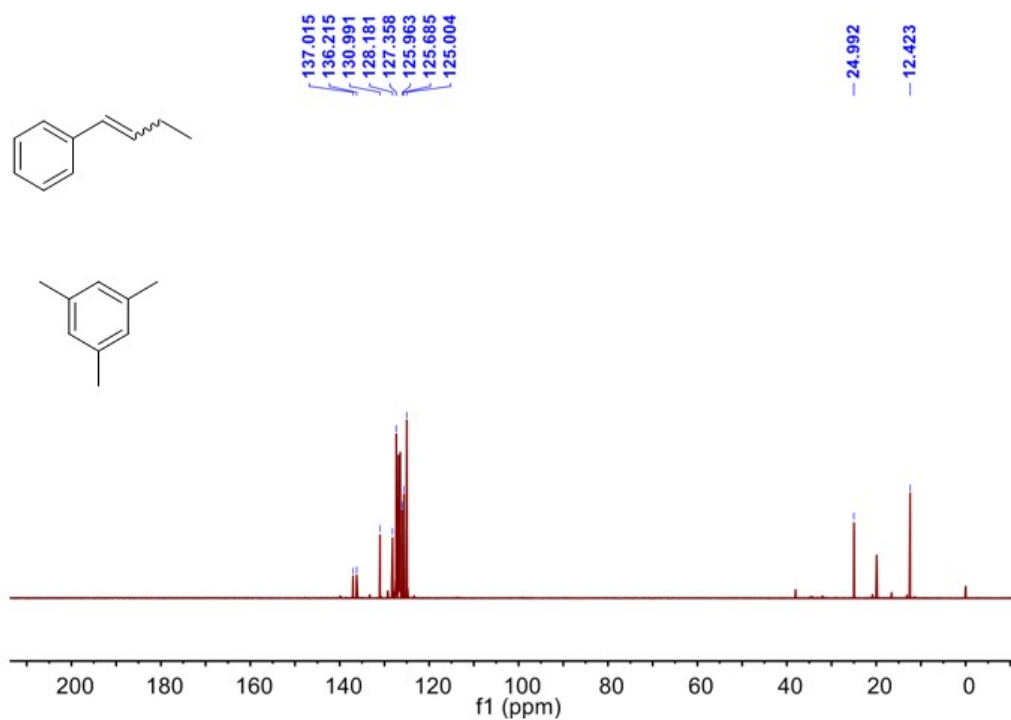


Figure S29. ¹³C NMR spectrum of product mixture from isomerization of **1m**.

Phenyl(prop-1-en-1-yl)sulfane:

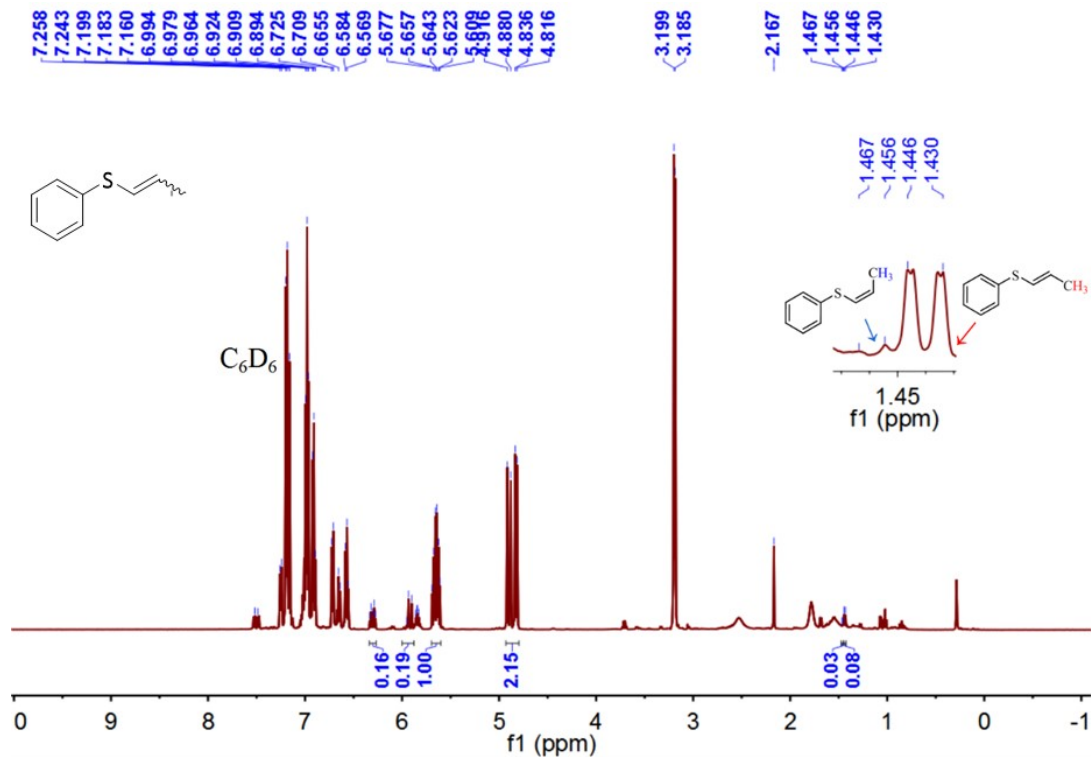


Figure S30. ¹H NMR spectrum of product mixture from isomerization of Phenyl(prop-1-en-1-yl)sulfane.

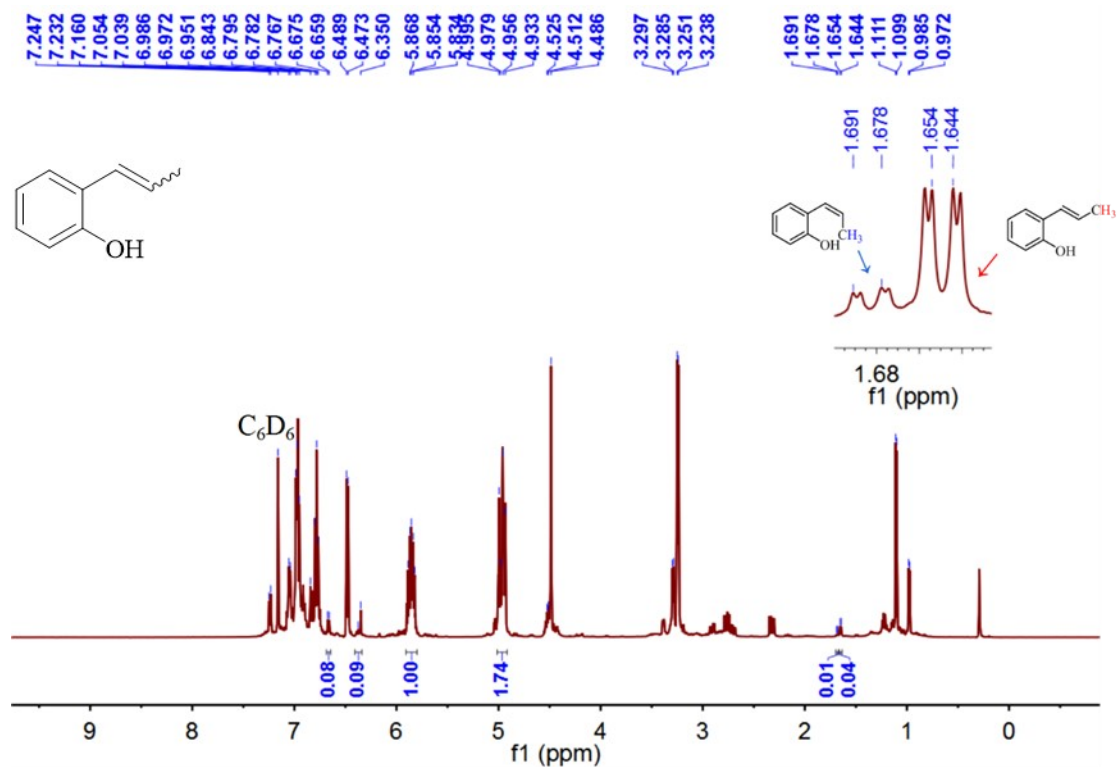


Figure S31. ^1H NMR spectrum of product mixture from isomerization of 2-allylphenol.

2-(prop-1-en-1-yl)phenyl acetate:

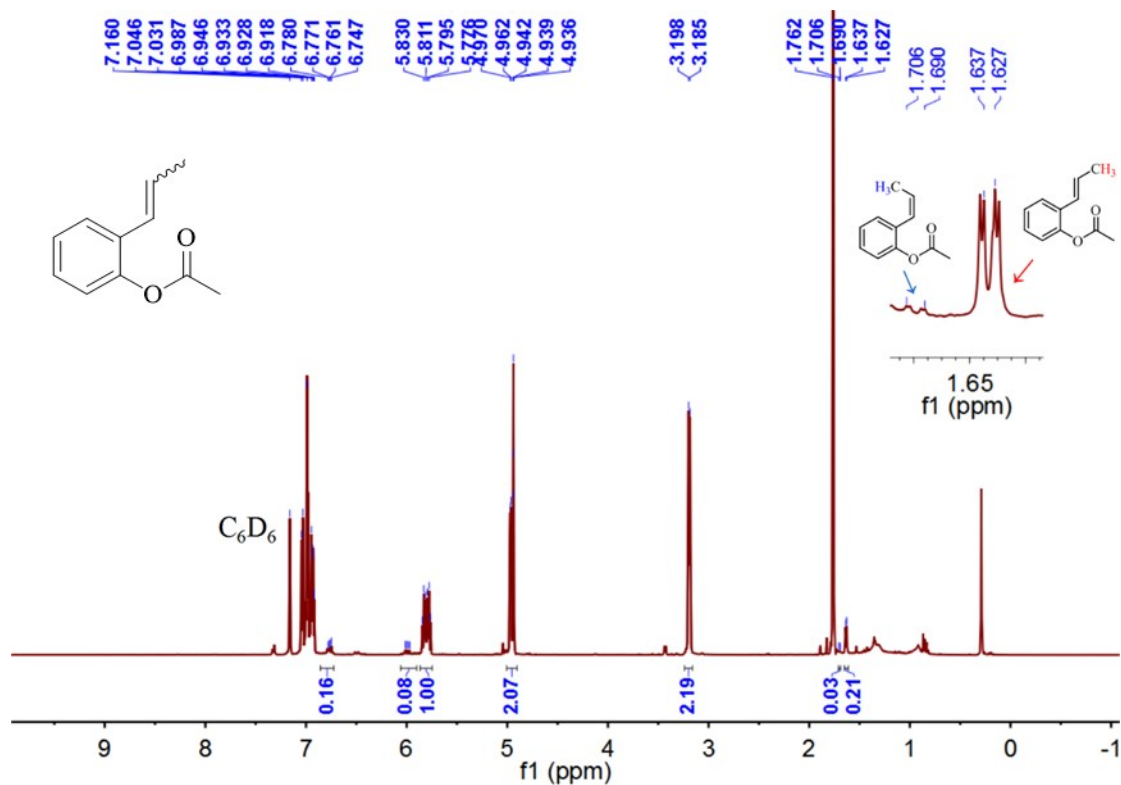


Figure S32. ^1H NMR spectrum of product mixture from isomerization of 2-allylphenyl acetate.

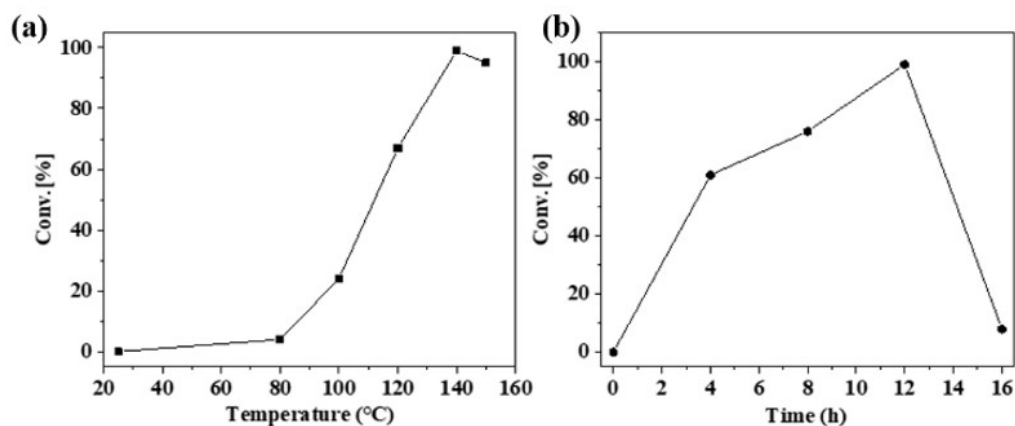


Figure S33. Effect of reaction temperature (a) and reaction time (b) on conversion rate.

5. gram-scale experiment

In a glovebox, allylbenzene (1.0 g, 8.0 mmol), dry deuterated C_6D_6 (3 mL) and $B(C_6F_5)_3$ (10 mol%) were added to a pressure bottle. The mixture was heated to 140 °C for 12 h and cooled to room temperature. After all the volatiles were removed under reduced pressure, the resulted crude product was further purified by flash column chromatography (petroleum) to give prop-1-en-1-ylbenzene (870 mg, 87%). 1H NMR (500 MHz, C_6D_6) δ 7.20-7.00 (m, 5H), 6.25 (dd, $J = 15.8, 1.1$ Hz, 1H), 6.05 – 5.96 (m, 1H), 1.71 (Z, dd, $J = 6.7, 1.7$ Hz, 3H), 1.65 (E, dd, $J = 6.7, 1.7$ Hz, 3H). 1H NMR analysis revealed that the mixture contained 1% of unreacted starting material, 99% of prop-1-en-1-ylbenzene, *E/Z* ratio of 94:6.

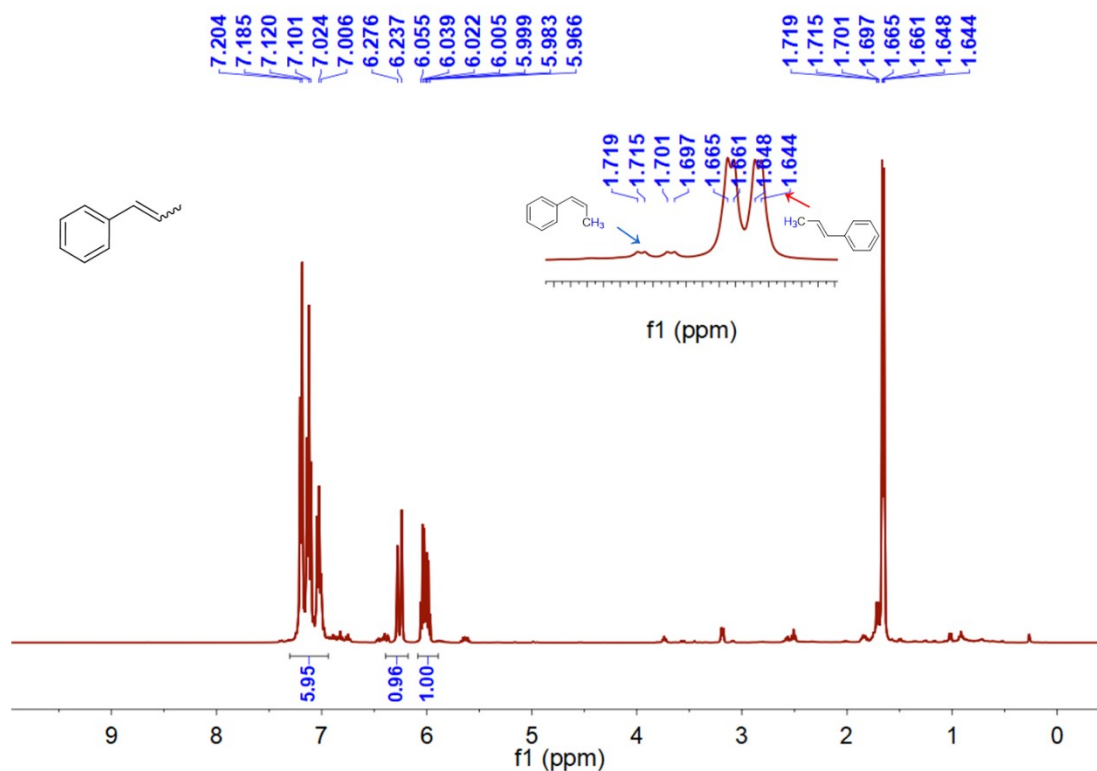


Figure S34. ^1H NMR spectrum of the isolated prop-1-en-1-ylbenzene of gram-scale experiment.

6. References

- [1] C.R. Larsen, G. Erdogan, D.B. Grotjahn, General Catalyst Control of the Monoisomerization of 1-Alkenes to *trans*-2-Alkenes. *J. Am. Chem. Soc.*, 2014, **136**, 1226-1229.
- [2] J.N. Bentley, E. Pradhan, T. Zeng, C.B. Caputo, Bis(pentafluorophenyl)phenothiazylborane – An Intramolecular Frustrated Lewis Pair Catalyst for Stannane Dehydrocoupling. *Dalton Trans.*, 2020, **49**, 16054-16058.
- [3] A.M. Fuller, D.L. Hughes, S.J. Lancaster, C.M. White, Synthesis and Structure of the Dimethyl Sulfide Adducts of Mono- and Bis(pentafluorophenyl)borane. *Organometallics.*, 2010, **29**, 2194–2197
- [4] R. Liu, Z.H. Lu, X.H. Hu, J.L. Li, X.J. Yang, Monocarboxylation and intramolecular coupling of butenylated arenes via palladium-catalyzed C-H activation process. *Org. Lett.*, 2015, **17**, 1489-1492.

- [5] G.G. Condorelli, A. Motta, G. Pellegrino, Site-Specific Anchoring of Tetrairon(III) Single Molecule Magnets on Functionalized Si(100) Surfaces. *Chem. Mater.*, 2008, **20**, 2405–2411.
- [6] Y. Wang, C. Qin, X. Jia, X. Leng, Z. Huang, An Agostic Iridium Pincer Complex as a Highly Efficient and Selective Catalyst for Monoisomerization of 1-Alkenesto trans-2-Alkenes. *Angew. Chem., Int. Ed.* 2017, **56**, 1614–1618.
- [7] A. Koenig, C. Wagner, M. Bette, D. Steinborn, On the isomerization of cyclooctyne into cycloocta-1,3-diene: synthesis, characterization and structure of a dinuclear platinum(II) complex with a μ - η^2 : η^2 -1,3-COD ligand. *Dalton Trans.*, 2012, **41**, 7156–7162.
- [8] A.L. Kocen, M. Brookhart, O. Daugulis, Palladium-catalysed alkene chain-running isomerization. *Chem. Commun.*, 2017, **53**, 10010–10013.
- [9] H. Liu, M. Xu, C. Cai, J. Chen, Y. Gu, Y. Xia, Cobalt-Catalyzed Z to E-Isomerization of Alkenes: An Approach to (E)- β -Substituted Styrenes. *Org. Lett.*, 2020, **22**, 1193–1198.