Title
Ruthenium-Catalyzed Cyclization/Cycloaromatization of Conjugated Trienes

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Ruthenium-Catalyzed Cyclization/Cycloaromatization of Conjugated Trienes

A Thesis submitted in partial satisfaction of the
requirements for the degree
Master of Science

in

Chemistry

by

Li-An Wang

Committee in charge:

Professor Joseph O'Connor, Chair
Professor Charles Perrin
Professor Jeffrey Rinehart

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The Thesis of Li-An Wang is approved, and is acceptable in quality and form for publication on microfilm and electronically:

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ABSTRACT OF THE THESIS

Ruthenium-Catalyzed Cyclization/Cycloaromatization of Conjugated Trienes

by

Li-An Wang

Master of Science in Chemistry

University of California San Diego, 2019

Professor Joseph M. O'Connor, Chair

The work describes mechanistic studies on ruthenium-accelerated cyclization/cycloaromatization of trienes. In the beginning, thermal and photochemical reactions of trienes were conducted in order to compare the temperatures and reaction times to those for

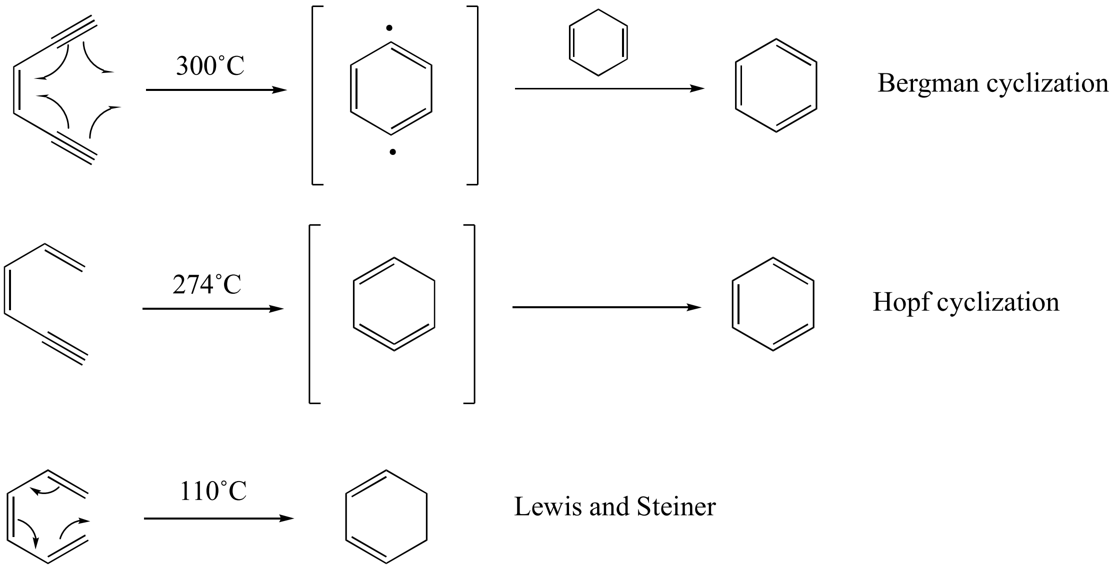
ruthenium-accelerated analogues. According to the Woodward-Hoffmann rules, cyclization of trienes to cyclohexadienes should proceed in a disrotatory fashion. In the literature, Chaudret and co-workers published that $[Cp^*Ru(OMe)]_2$/HOTf could lead to cycloaromatization of (*E*)-1,3,5-hexatriene, while the mechanism for this reaction was not discussed. And based on previous work from the O'Connor lab, the authors demonstrated that $[Cp^*Ru(NCMe)_3]PF_6$ mediated the cyclization of conjugated enediynes and dienynes at room temperature, possibly via the formation of hexahapto intermediates, η^6-enediyne and η^6-dienyne, respectively. Consequently, we proposed that $[CpRu(NCMe)_3]PF_6$ would trigger the cycloaromatization of trienes at room temperature via η^6-(acyclic triene) metal intermediates, followed by elimination of two hydrogen atoms to generate an arene product.

In the reactions of trienes with $[CpRu(NCMe)_3]PF_6$, η^4- and η^6-acyclic metal complexes were clearly identified by ^1H NMR spectroscopy and X-ray crystallography. Subsequently, the isolated η^6-acyclic metal complex was heated at 50 ˚C to give 6,7-dimethyl-1,2,3,4-tetrahydronaphthalene. Thus, the hexahapto metal complex was implicated in acceleration of the cyclization. Moreover, the reaction of 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene with $[CpRu(NCMe)_3]PF_6$ sufficiently illustrated that 6π electrocyclization of trienes proceeds in a disrotatory fashion. An agostic interaction was also observed by ^1H NMR spectroscopy in a η^4-cyclohexadiene ruthenium intermediate, followed by a [1,5]-hydride shift. Most surprisingly, a truly catalytic reaction was found in the reactions of (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene and (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene with $[CpRu(NCMe)_3]PF_6$ since the appearance of a free cyclohexadiene derivative was observed and excess triene was consumed. Based on the results of these experiments, several reasonable mechanisms for ruthenium-mediated cyclization of trienes were proposed.

Ruthenium-Catalyzed Cyclization/Cycloaromatizations of Conjugated Trienes

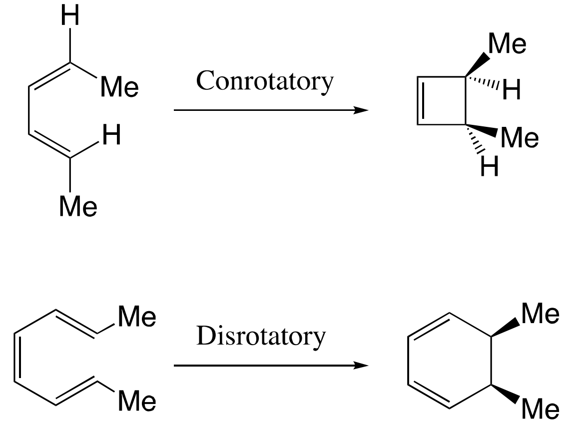
A. Introduction

Thermal cycloaromatization reactions of polyunsaturated molecules play an important role in the modern history of synthetic organic chemistry. Bergman cyclization and Hopf cyclization are the well-known examples of electrocyclizations of enediynes and dienynes, respectively.[1,2] The thermal cyclization of trienes to cyclohexadiene was also studied by Lewis and Steiner.[3] High temperatures are required for cycloaromatization to occur, thereby limiting the scope and usefulness of these reactions (Scheme 1). Our major goal for this work is to activate 6π electrocyclizations at room temperature by treating conjugated trienes with transition metal complexes. The synthesis of organometallic complexes and their subsequent reactions with conjugated trienes are described in this dissertation.



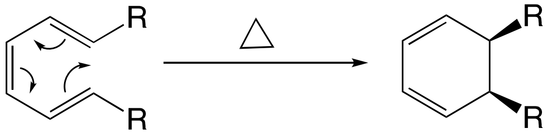
Scheme 1. Bergman cyclization, Hopf cyclization, and 6π electrocyclization of *cis*-1,3,5-hexatriene to cyclohexadiene.

Thermal electrocyclizations of trienes are concerted and stereospecific. The Woodward-Hoffman theory on the conservation of orbital symmetry[4] predicts the stereochemical outcome for 6π electrocyclizations. The authors predicted that conjugated molecules with [4n] π-electrons would undergo a thermal conrotatory process. In the conversion of *cis*-3,4-dimethylcyclobutene to *cis,trans*-2-hexadiene, the reacting carbons rotate in the same direction, either clockwise or counterclockwise. On the contrary, under thermal conditions, trienes with [4n+2] π-electrons proceeds via a disrotatory ring closure, wherein the reacting carbons rotate in opposite directions (Scheme 2).



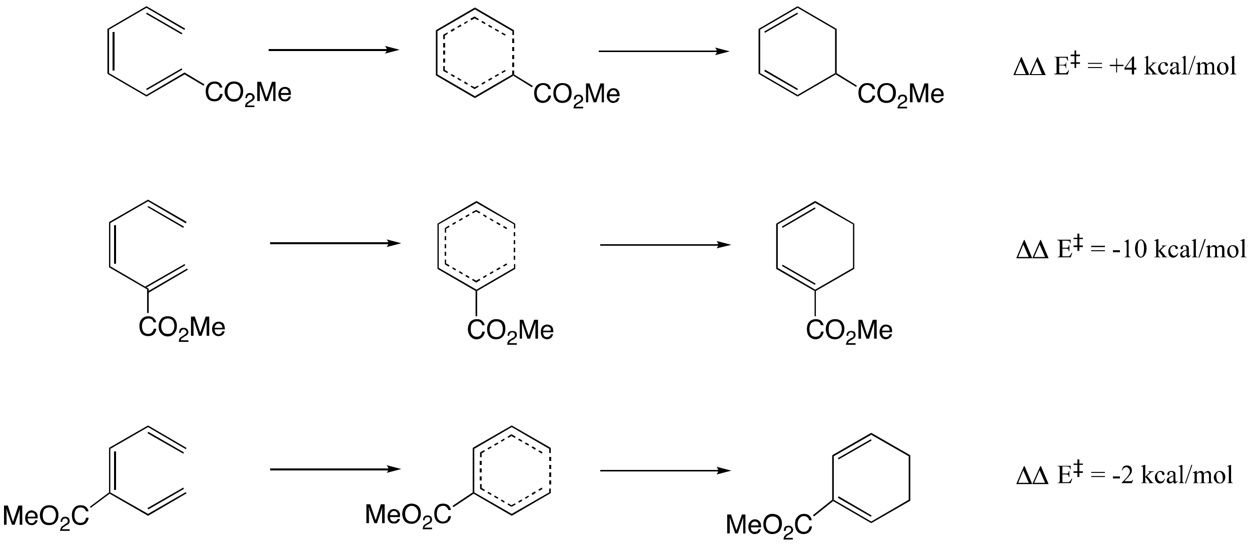
Scheme 2. Stereochemical outcomes for thermolysis of *cis,trans*-1,3-butadiene and *tans,trans*-1,3,5-hexatriene.

Under the Woodward-Hoffmann rules, the stereochemical outcomes of thermal cyclization of trienes proceed in a disrotatory fashion (Scheme 3).



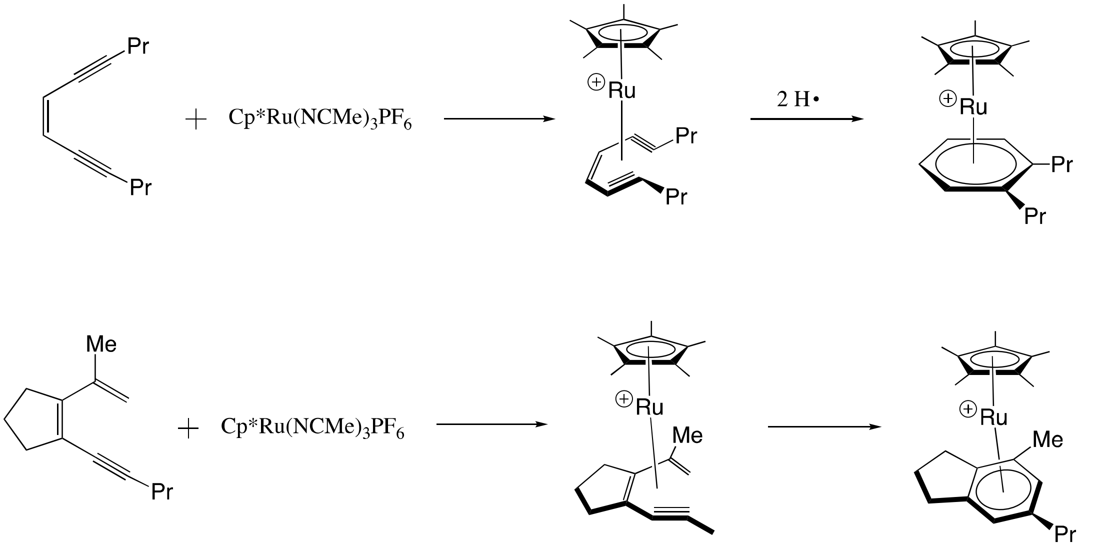
Scheme 3. Thermal electrocyclization of trienes.

Even though electrocyclizations of trienes occur under milder conditions (≥110 ˚C) than in the case of enediynes and dienynes, heat is required to overcome the activation barrier. The first catalyzed electrocyclization of trienes was reported by Bergman and Trauner, in a paper entitled ‘‘Catalysis of 6π Electrocyclizations’’.[5] It was previously known that electron-withdrawing groups located at the 2-position of hexatrienes would decrease the electrocyclization energy barriers (Scheme 4). Based on this theory, Bergman and Trauner hypothesized that coordination of a Lewis acid to a Lewis basic electron-withdrawing group at the 2-position of hexatriene would increase the electron-withdrawing group effect, thus lower the electrocyclization energy barriers.



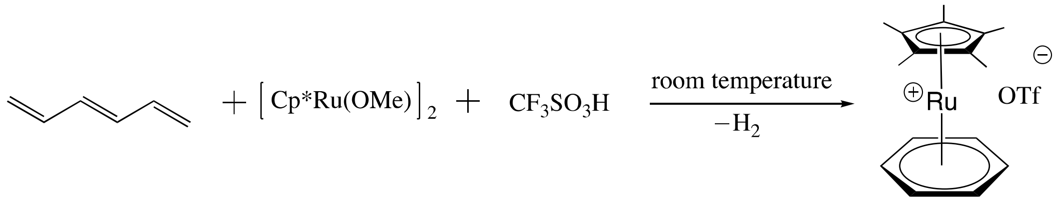
Scheme 4. Thermal electrocyclization of trienes.

Next, according to publications from the O’Connor lab, the authors demonstrated that [Cp*Ru(NCMe)$_3$]PF$_6$ accelerates the Bergman and Hopf cyclizations at ambient temperature, possibly via the formation of hexahapto, η^6-enediyne and η^6-dienyne intermediates, respectively (Scheme 5).[6,7]



Scheme 5. [Cp*Ru(NCMe)$_3$]PF$_6$ triggers the cycloaromatization of enediynes and dienynes at room temperature.

Furthermore, in 1993 Chaudret and co-workers published that when (*E*)-1,3,5-hexatriene was treated with [Cp*Ru(OMe)]$_2$ and CF$_3$SO$_3$H, a benzene derivative was formed, [Cp*Ru(η^6-C$_6$H$_6$)](CF$_3$SO$_3$) (Scheme 6).[8]



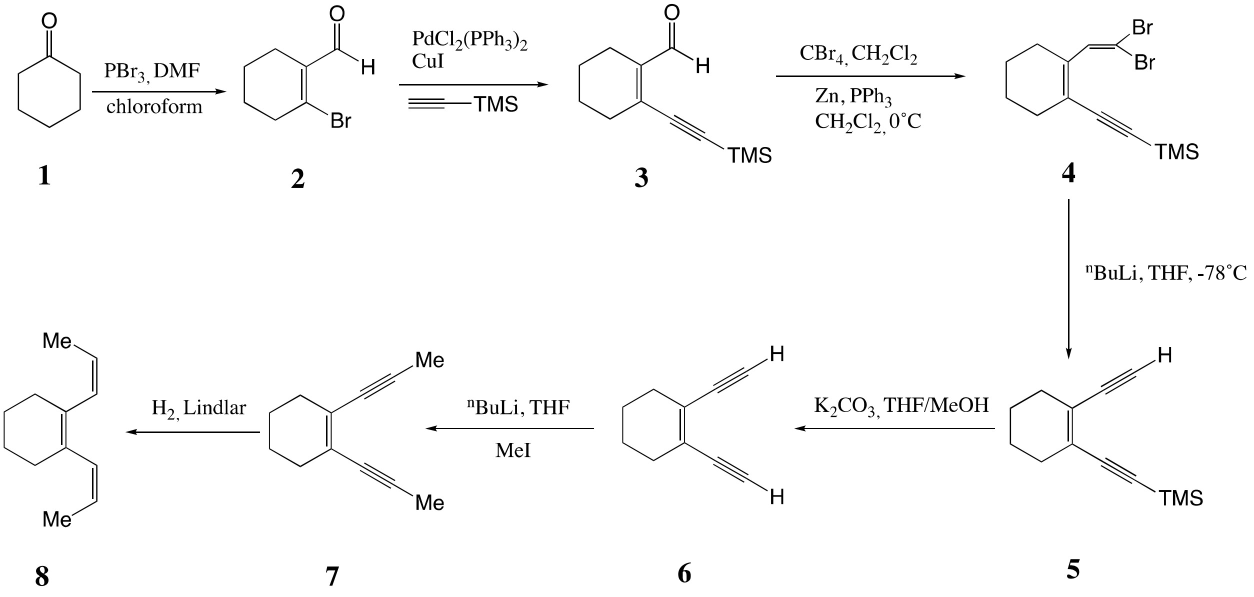
Scheme 6. [Cp*Ru(OMe)]$_2$/HOTf triggers the cycloaromatization of (*E*)-1,3,5-hexatriene at room temperature.

As stated in Woodward-Hoffmann rules, the cyclization of trienes should proceed in a disrotatory fashion. And drawing inspiration from work in the O'Connor lab and Chaudret lab, we proposed that ruthenium would trigger the cycloaromatizations of trienes at low temperature via fascinated mechanisms, with two hydrogen atoms ultimately being lost to generate aromatic products.

B. Results and Discussion

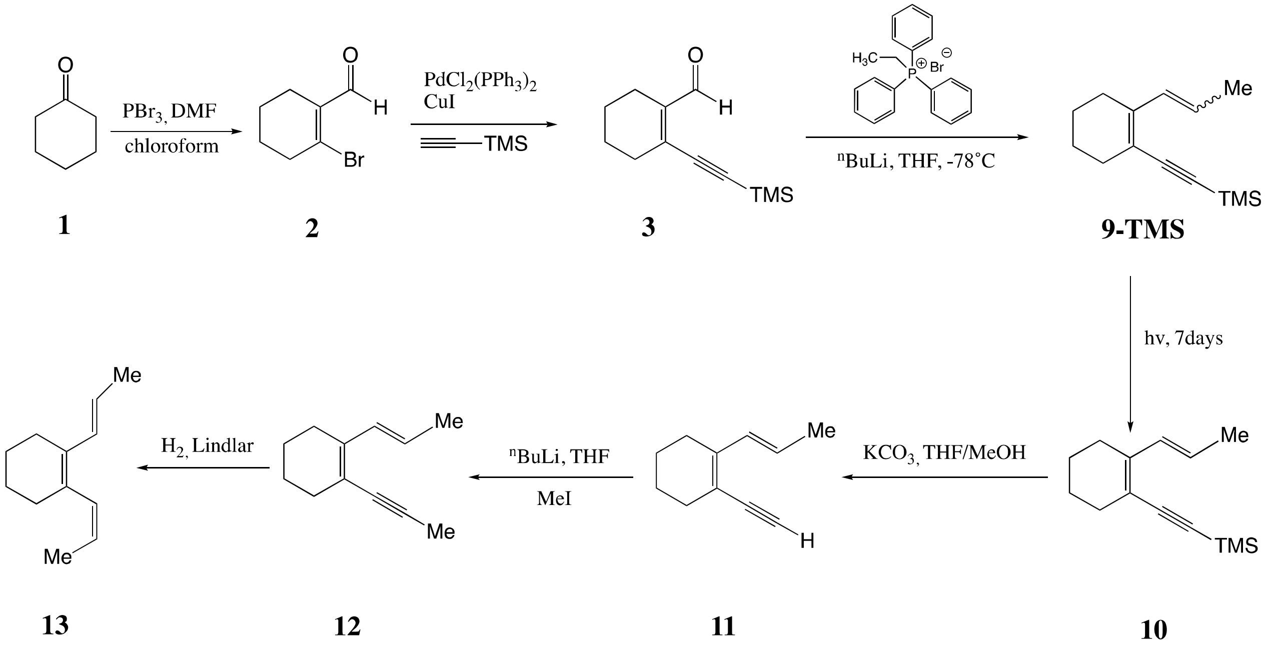
1. Synthesis of Trienes

The first aim was the synthesis of trienes. To make **8**, we started with compound **2** which could be prepared in one step from cyclohexanone (**1**). Sonogoshira coupling of **2** with trimethylsilylacetylene afforded aldehyde **3**. Enediyne (**7**) was obtained in good to excellent yields by following the Corey-Fuchs reaction on **3** followed by desilylation to the acetylide and methylation. Then **7** was treated with Lindlar catalyst in the presence of quinoline and H_2 gas in hexanes for 12 h. The reaction mixture was filtered through Celite, concentrated, and purified by flash column chromatography to give ZZZ-triene **8** in 44% yield (Scheme 7).



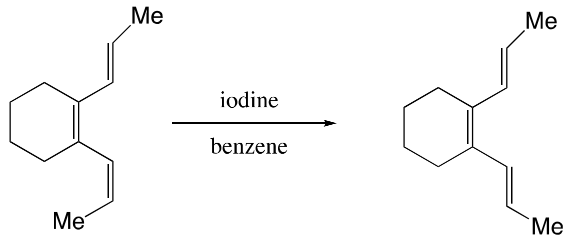
Scheme 7. Synthetic route to *ZZZ*-triene **8**.

The *EZZ*-triene **13**, a diastereomer of **8**, was also desired. Thus, we started with cyclohexanone (**1**). By following the preparation in Dr. Hitt's thesis, an *E*/*Z* mixture of **9-TMS** can be obtained in 3 steps in good yield. Compound **9-TMS** was photolyzed for 7 days in acetone to give **10** in 57% yield after purification. Desilylation of **10** with K_2CO_3 in MeOH gave **11** which was deprotonated and methylated with iodomethane to generate **12**. Subsequently, a Lindlar reduction was utilized to reduce the alkyne in **12** thereby affording *EZZ*-triene **13** in 94% yield (Scheme 8).



Scheme 8. Synthetic route to *EZZ*-triene **13**.

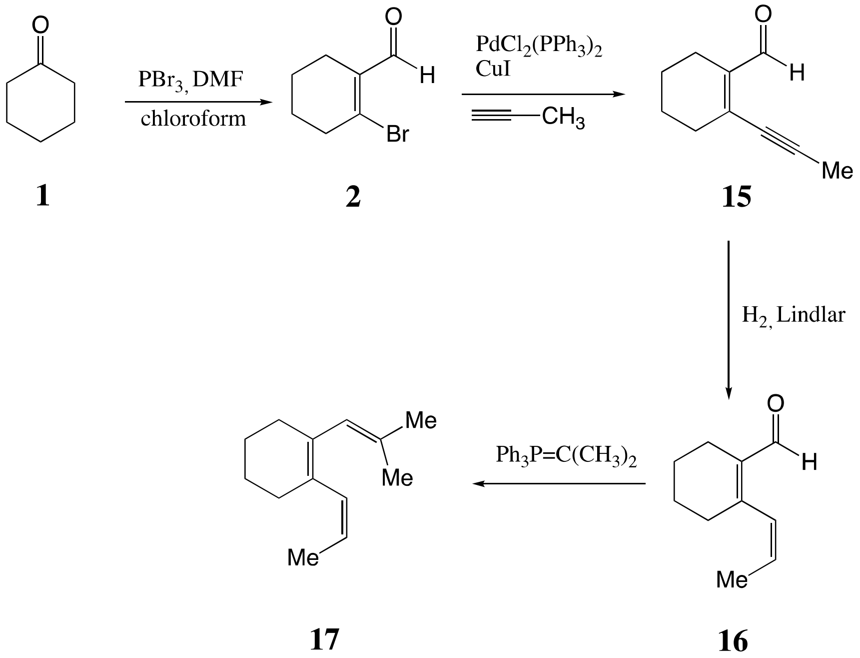
For the synthesis of *EZE*-triene **14**, iodine was mixed with **13** in benzene and the solution was stirred for 30 h to afford **14** as a colorless oil in 46.2% yield after silica gel chromatography (Scheme 9).



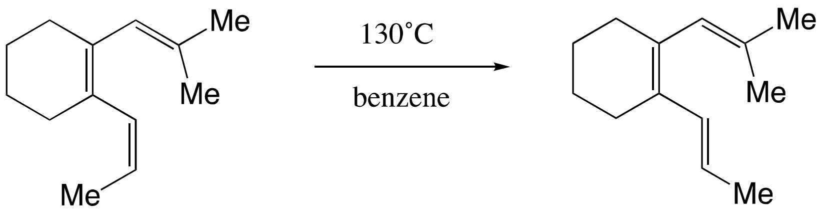
13 **14**

Scheme 9. Synthetic route to *EZE*-triene **14**.

In order to synthesize trimethyl substituted triene **17**, we also started with cyclohexanone (**1**). Compound **16** can be made in 3 steps in good yield by following the experimental procedure in Dr. Hitt's thesis. A Wittig olefination of **16** with isopropyltriphenyl phosphonium bromide provided **17** in 87% yield (Scheme 10). Homologation of **17**, followed by heating at 130 °C for 6 h, generated **18** in 87.5% yield (Scheme 11).



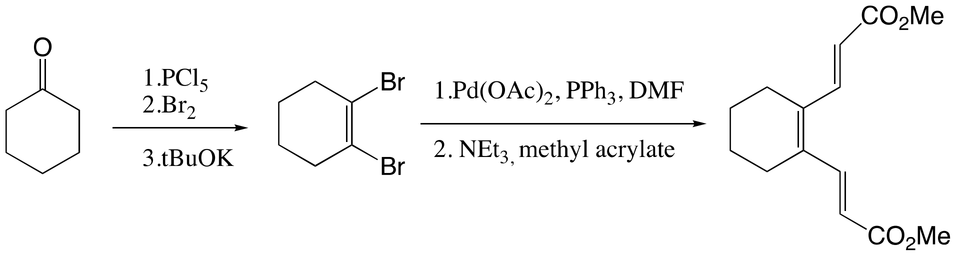
Scheme 10. Synthetic route to trimethyl triene **17**.



17 **18**

Scheme 11. Synthetic route to trimethyl triene **18**.

Finally, the diester triene **20** was prepared in order to obtain more information on the scope and mechanism of the desired ruthenium-accelerated cyclization. In the literature, the Heck reaction generally yields alkenes with a *trans* configuration. Starting from cyclohexanone (**1**), 1,2-dibromocyclohexene (**19**) was obtained in 3 steps in 30% yield. The Heck reaction of **19** with methyl acrylate in DMF at 100 °C for 72 h, gave product **20** in 25% to 40% yield (Scheme 12).[9]

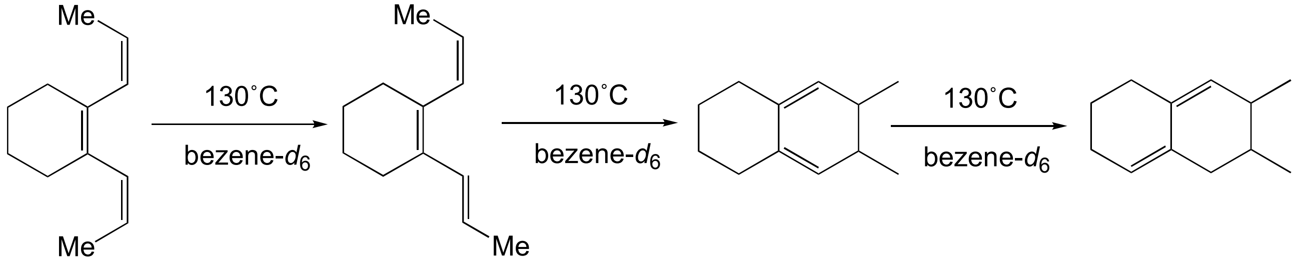


1 **19** **20**

Scheme 12. Synthetic route to diester triene **20**.

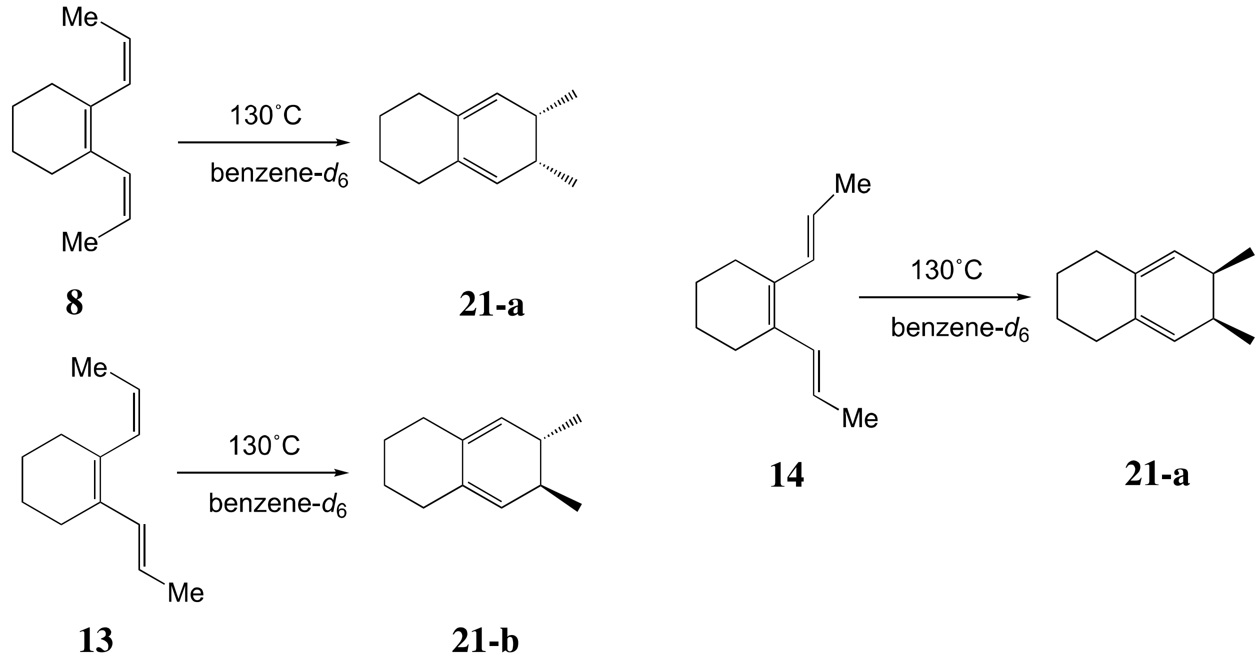
2. Thermal and Photochemical Reactions of Trienes

The thermal reactivity of trienes was next examined. Heating a benzene-d_6 solution of **8** at 130 ˚C in a propane flame-sealed NMR tube for 60 min led to **13** in 96.5% yield. The reaction was continuously heated at 130 ˚C, and slow consumption of **8** was observed over the reaction period. After 9 days, a 22% yield of **21** was observed, with characteristic ^{1}H NMR resonances for **21** observed at δ 5.31 (bs, 2H, vinyl-*H*) and 1.01 (d, 6H, J = 6.0 Hz, Me). After 29 days, 88% of **13** was converted and compound **22** was observed in 51.8% yield (Scheme 13). The formation of **21** might come from three different triene isomers, which would lead to two possible stereochemical outcomes after proceeding in a disrotatory fashion (Scheme 14).



8 **13** **21** **22**

Scheme 13. Thermal reaction of *ZZZ*-triene **8**.



Scheme 14. Two possible stereochemical outcomes for electrocyclization of cyclohexadiene **21**.

The thermal reaction of **8** can be further understood by comparison of calculated energies for the three dimethyl triene isomers (**8**, **13**, **14**) done by Prof. Kim Baldridge at Tianjin University (Figure 1). The *ZZZ*-isomer **8** is less stable than the *EZZ*-isomer **13**, which is less stable than *EZE*-isomer **14**. This is consistent with our observation that heating the *ZZZ*-isomer **8** at 130 ˚C led to the formation of the *EZZ*-isomer **13** which is more stable. Unexpectedly, there was no formation of *EZE*-**14** upon heating for longer times. The *EZZ*-isomer **13** may have decomposed (oligomerized or cyclized thermally) instead of forming *EZE*-isomer **14**.

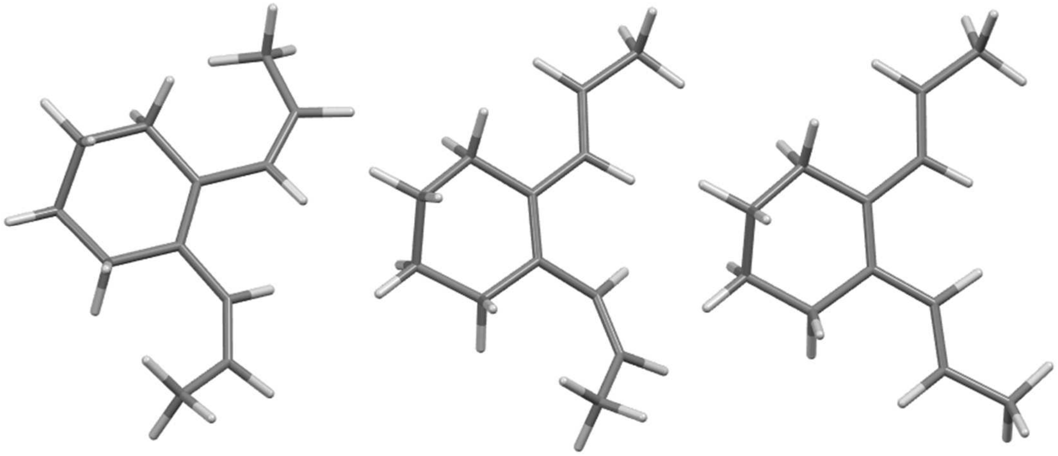
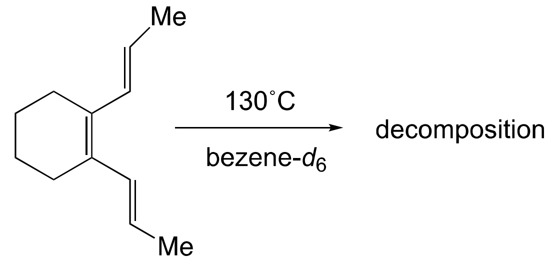


Figure 1. Calculated structure for **8**, **13** and **14** were carried out using the BP86 density functional, with an ultrafine grid, together with the Def2-TZVPP basis set.

Table 1. Calculated ΔG values for **8**, **13** and **14**.

Compound	**ΔG (kcal/mol)**
ZZZ-**8**	9.81
EZZ-**13**	4.97
EZE-**14**	0.0

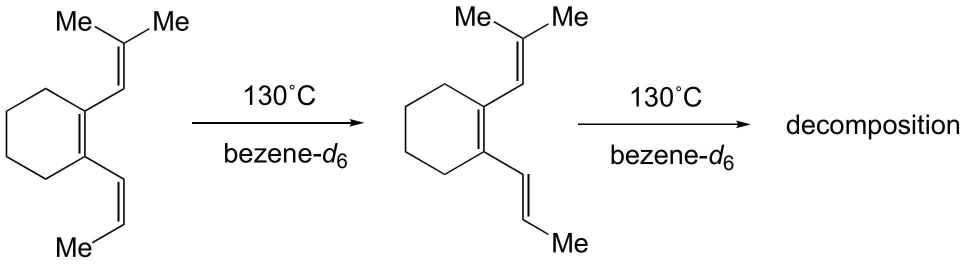
The thermal reaction of **14** was carried out in benzene-d_6 at 130 ˚C in a flame-sealed NMR tube. After 5 days, all the starting material was consumed, as determined by disappearance of the vinyl hydrogen at resonances δ 5.64 (d, 2H) and 6.94 (d, 2H, J = 14 Hz), and multiple products were observed to form. However, there was no clear evidence for formation of cyclohexadiene **21** (Scheme 15).



14

Scheme 15. Thermal reaction of *EZE*-triene **14**.

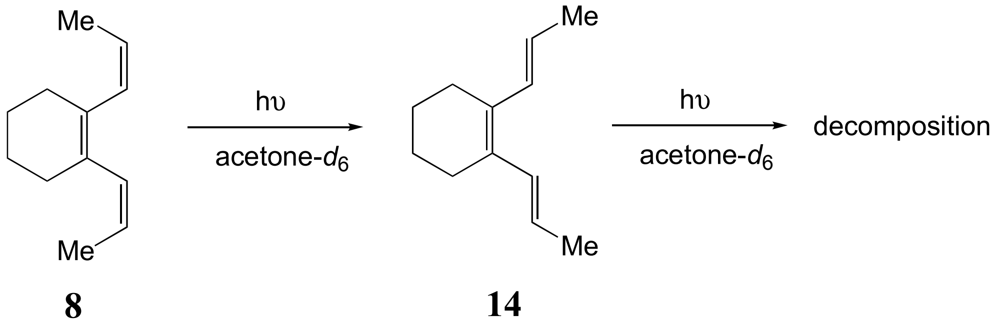
The thermal reaction of **17** in benzene-d_6 was carried out in a flame-sealed NMR tube heated at 130 ˚C. After 6 h, all of **17** was consumed and new resonances for **18** were observed (88.8% yield). Continued heating at 130 ˚C, led to slow consumption of compound **18**. After 15 days, 91.2% of **18** was converted based on the integration of vinyl hydrogen resonance at δ 6.60 (d, 1H, J =15.6 Hz) relative to resonances for the internal standard. There was no evidence for formation of 6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (**23**; Scheme 16).



17 **18**

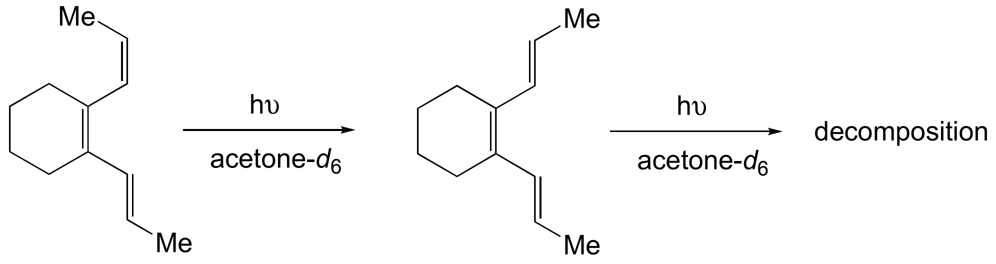
Scheme 16. Thermal reaction of trimethyl triene **17**.

The photolysis of the trienes was also examined. Photolysis of an acetone-d_6 solution of **8** in a J. Young NMR tube was carried out in a Rayonette photoreactor equipped with UV broadband lamps with λ centered at 254 nm. After 200 min, compound **14** was observed, based on a characteristic vinyl hydrogen resonance at δ 6.78 (d, 2H, J = 15.2 Hz). NMR spectroscopy revealed that 60.7% of **8** was consumed based on the integration of the vinyl hydrogen resonance at δ 5.83 (d, 2H, J = 10.8 Hz) relative to internal standard, and a 23.3% yield of **14** was observed. It was found that at longer irradiation times, both starting material **8** and **14** slowly decomposed. After 6.5 h, compounds **8** and **14** were absent and numerous resonances were observed, indicating the formation of multiple products of unknown structure (Scheme 17).



Scheme 17. Photochemical reaction of *ZZZ*-triene **8**.

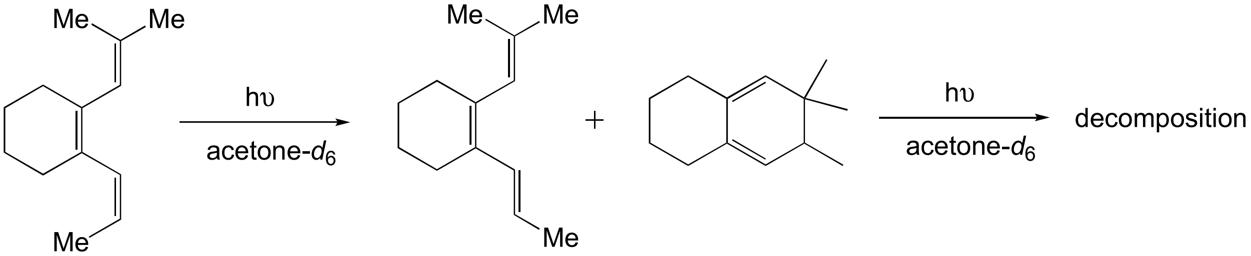
An NMR-tube-scale reaction in which an acetone-d_6 solution of **13** was photolyzed for two days led to the formation of compound **14**, based on the appearance of a ^{1}H NMR vinyl hydrogen resonance at δ 6.78 (d, 2H, J = 15.6 Hz). The yield of **14** (96.4%) was calculated based on 83.5% conversion of **13**. It was found that at longer irradiation times, both starting material **13** and product **14** slowly decomposed in the solution. After 35 days, compound **13** was absent and ~ 90% of **14** had decomposed. However, there was no clear evidence for formation of cyclohexadiene **21** (Scheme 18).



13 **14**

Scheme 18. Photochemical reaction of *EZZ*-triene **13**.

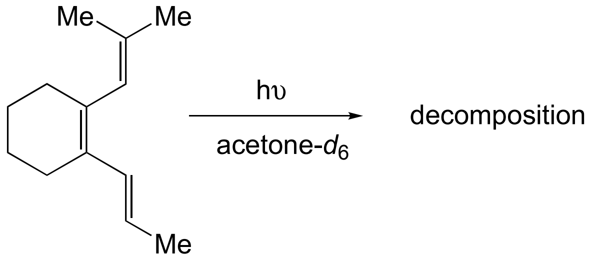
A small-scaled photolysis of **17** in acetone-d_6 solvent was conducted and monitored by ^{1}H NMR spectroscopy. After 2 h, compound **23** was observed, based on the presence of characteristic vinyl hydrogen resonances at δ 5.15 (d, 1H, J = 10.8 Hz) and 5.13 (s, 1H). Compound **18** was also observed, based on the observation of characteristic vinyl hydrogen resonances at δ 6.27 (d, 1H, J = 15.6 Hz), 5.59 (s, 1H), and 5.57 (s, 1H). The conversion of **17** was calculated to be 54%, and the yields for **23** and **18** were determined to be 6.6% and 46.8%, respectively. It was found that at longer irradiation times, both starting material **17** and products (**18** and **23**) slowly decomposed. After 6 days, compounds **17**, **18** and **23** were absent and resonances attributed to uncharacterized products were observed (Scheme 19).



17 **18** **23**

Scheme 19. Photochemical reaction of trimethyl triene **17**.

A solution of **18** in acetone-d_6 solvent was also photolyzed in a pyrex J. Young tube for 7 days, during which time all of the starting material disappeared, with no evidence for any formation of **23** (Scheme 20).



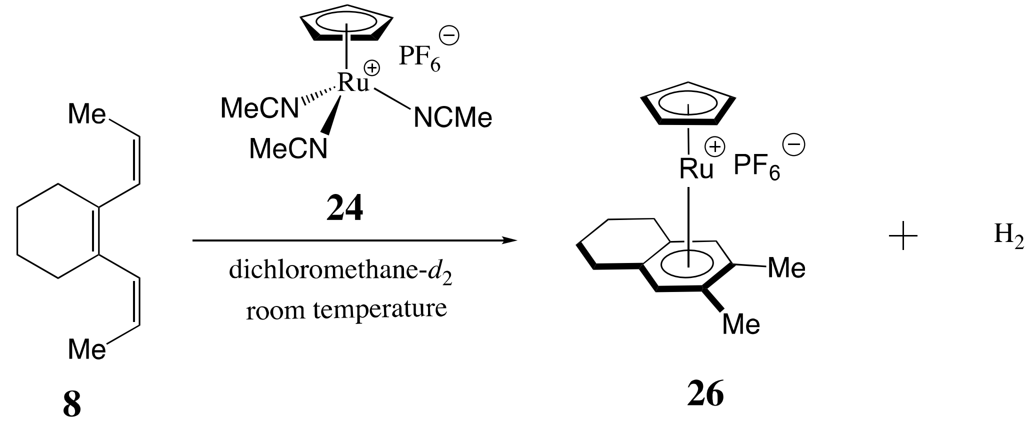
18

Scheme 20. Photochemical reaction of trimethyl triene **18**.

Based on the above results, we concluded that cyclization of trienes to cyclohexadiene derivatives directly by thermal or photochemical reactions can often be problematic. Although some cyclized products were observed, it took long reaction times and gave cyclohexadiene products in very low yield. Consequently, the development of other methodologies to overcome these challenges is desired.

3. Ruthenium-Catalyzed Cyclization/Cycloaromatizations of Trienes

ZZZ-Triene **8** (4.8 mg, 0.03 mmol) and ruthenium complex **24** (12.8 mg, 0.03 mmol) were added into an oven-dried J. Young NMR tube, with 1,3,5-tri-tert-butylbenzene added as an internal standard. The tube was cooled in a dry ice-acetone bath and then placed under vacuum. After 1.1 mL of dry dichloromethane-d_2 was distilled into the tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. The NMR tube was kept at – 78 °C, and an initial ^{1}H NMR spectrum was recorded immediately. The reaction was subsequently warmed up to room temperature and then monitored by ^{1}H NMR spectroscopy. After 100 min, all of the *ZZZ*-triene **8** was consumed, and the resonances of **26** were observed. A 92.6% yield for **26** was calculated by the integration of the Cp resonance at δ 5.37 (s, 5H) relative to resonances of the internal standard (Scheme 21).



Scheme 21. Reaction of **8** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

To crystalize product **26**, 56 mg of **8** (0.35 mmol) and **21** (100 mg, 0.23 mmol) were added into an oven-dried 100 mL Schlenk flask. The flask was cooled in a dry ice-acetone bath and placed under vacuum. After 20 mL of dry dichloromethane was distilled into the flask under vacuum, the flask was degassed via 3 cycles of freeze/pump/thaw/degas. Then the reaction mixture was allowed to stir at room temperature for 2 h, followed by addition of Et$_2$O (80 mL) to afford **26** (Figure 2) as a colorless flake crystal (90.5 mg, 83.5% yield).

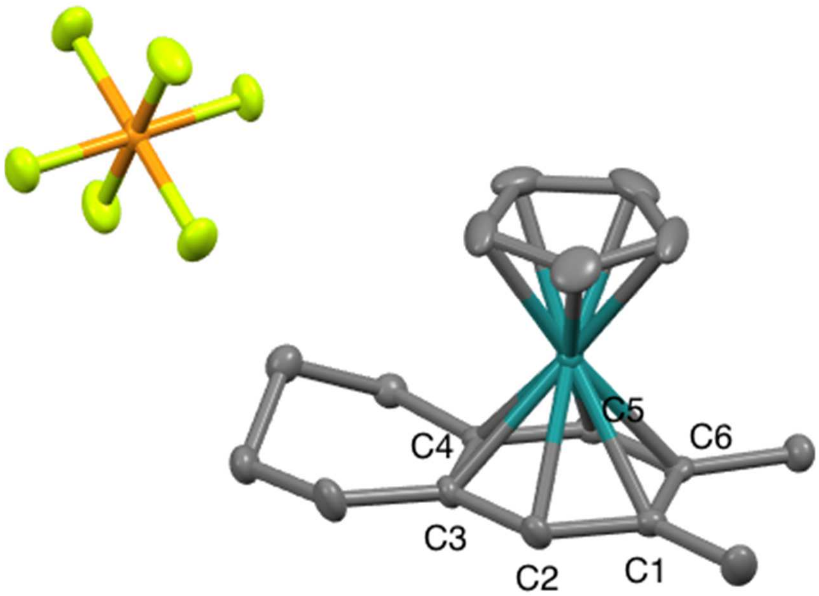


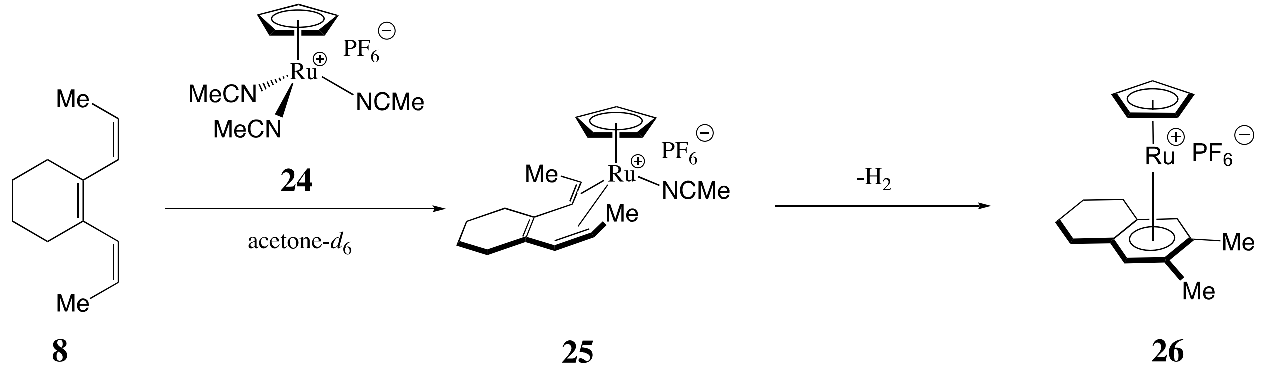
Figure 2. X-ray structure for arene product **26**. All hydrogens have been omitted for clarity.

Table 2. Selected Bond Distances (Å) for arene product **26**.

Bond (A-B)	**Length (Å)**	**Bond (A-B)**	**Length (Å)**
Ru-C1	2.229(2)	C1-C2	1.423(4)
Ru-C2	2.196(2)	C2-C3	1.419(4)
Ru-C3	2.227(2)	C3-C4	1.424(3)
Ru-C4	2.224(2)	C4-C5	1.416(4)
Ru-C5	2.194(2)	C5-C6	1.420(4)
Ru-C6	2.232(2)	C1-C6	1.428(3)

From this crystal structure, π-electron delocalization is obvious due to the similar C-C bond lengths in arene ring. Moreover, the bond lengths are in the range of 1.416 Å and 1.428 Å which are a bit of longer than the C-C bond lengths in benzene, which is attributed to π-back bonding which lengthens C=C bond.

The reaction was repeated and monitored by ^{1}H NMR spectroscopy at – 45 °C. After 45 min, a ^{1}H NMR spectrum indicated that 73% of **24** was consumed, based on the Cp resonance at δ 4.34 (s, 5H), and resonances for complex **25** were observed at δ 1.48 (d, 3H, J = 6.5 Hz, Me), 1.73 (m, 2H, methylene-*H*), 1.77 (d, 3H, *J* = 5.5 Hz, Me), 2.55 (s, 3H, NCMe), 4.02 (d, 1H, *J* = 9.0 Hz, vinyl-*H*), 4.51 (d, 1H, *J* = 9.5 Hz, vinyl-*H*), 4.75 (m, 1H, vinyl-*H*), 5.13 (m, 1H, vinyl-*H*), 5.26 (s, 5H, Cp). A 97.7% yield for **25** was calculated based on the integration of Cp resonance at δ 5.26 (s, 5H) relative to the resonances for converted **24** (Scheme 22).



Scheme 22. Reaction of **8** with [CpRu(NCMe)$_3$]PF$_6$ (**24**) leading to η^4-triene **25**.

To crystalize η^4-triene **25**, dry hexanes (2 mL) were distilled into the NMR tube, and the tube was kept at – 40 °C for several days to obtain crystals of **25**, which were suitable for X-ray crystallography analysis (Figure 3).

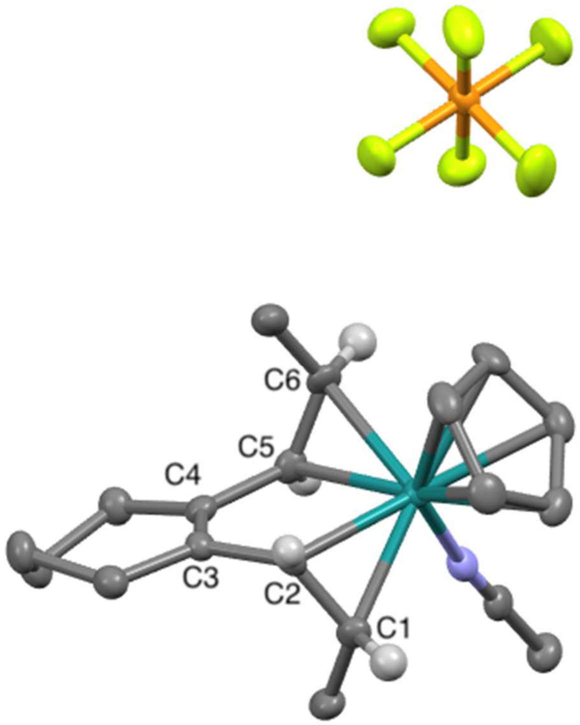


Figure 3. X-ray structure for η^4-triene **25**. Most hydrogens have been omitted for clarity.

Table 3. Selected Bond Distances (Å) for η^4-triene **25**.

Bond (A-B)	Length (Å)	Bond (A-B)	Length (Å)
Ru-C1	2.217(5)	C1-C2	1.410(7)
Ru-C2	2.240(5)	C2-C3	1.481(7)
Ru-C3	3.151(5)	C3-C4	1.317(6)
Ru-C4	3.182(5)	C4-C5	1.487(7)
Ru-C5	2.308(5)	C5-C6	1.382(6)
Ru-C6	2.273(5)	C1-C6	3.885(6)

The X-ray structure of η^4-triene **25** clearly indicates that ruthenium is coordinated to C1=C2 and C5=C6, as indicated by their longer bond distances compared to that for C3=C4. This is because π-back donation from the metal to the alkene π^* orbital increases the bond length. In addition, the calculated structures for the η^4-complex **25** and the alternative symmetric isomer **46**, carried by Kim Baldridge at Tianjin University, found that the symmetric isomer **27** was less stable

($\Delta H = 4.49$ kcal/mol and $\Delta G = 3.40$ kcal/mol) - consistent with the fact that we don't observe its formation (Figure 4). The non-bonded C1····C6 distance for **25** is 3.885 Å, whereas the less stable isomer has a 3.782 Å C1····C6 distance. Both distances may make it difficult for cyclization to occur without conversion to an additional intermediate.

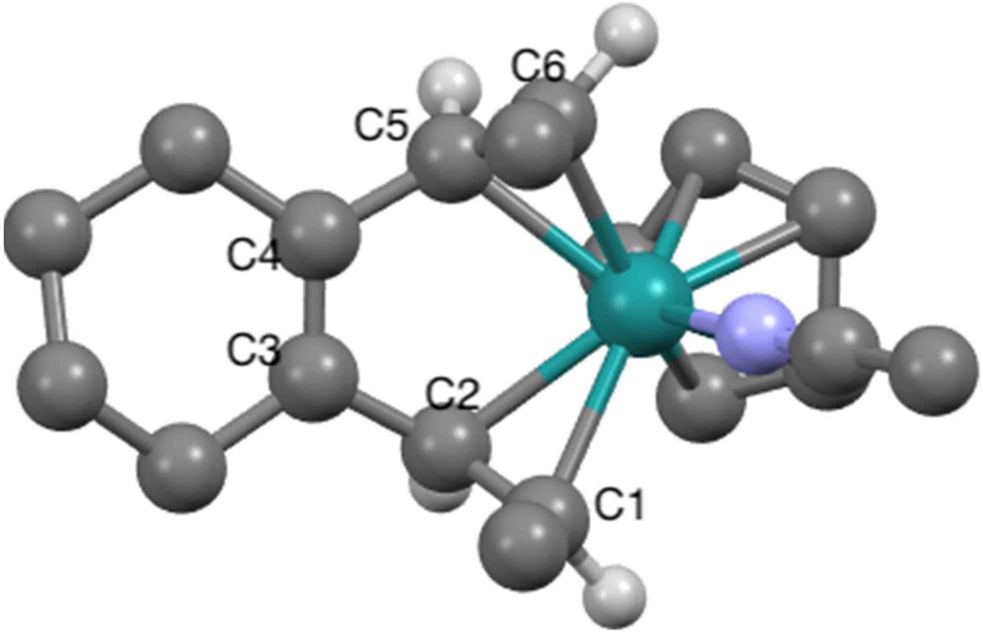
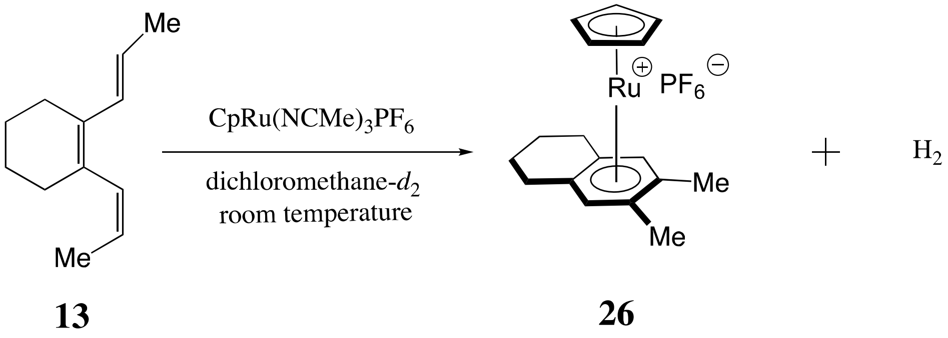


Figure 4. Calculated structure for symmetric isomer **27**.

Table 4. Selected Bond Distances (Å) for symmetric isomer **27**.

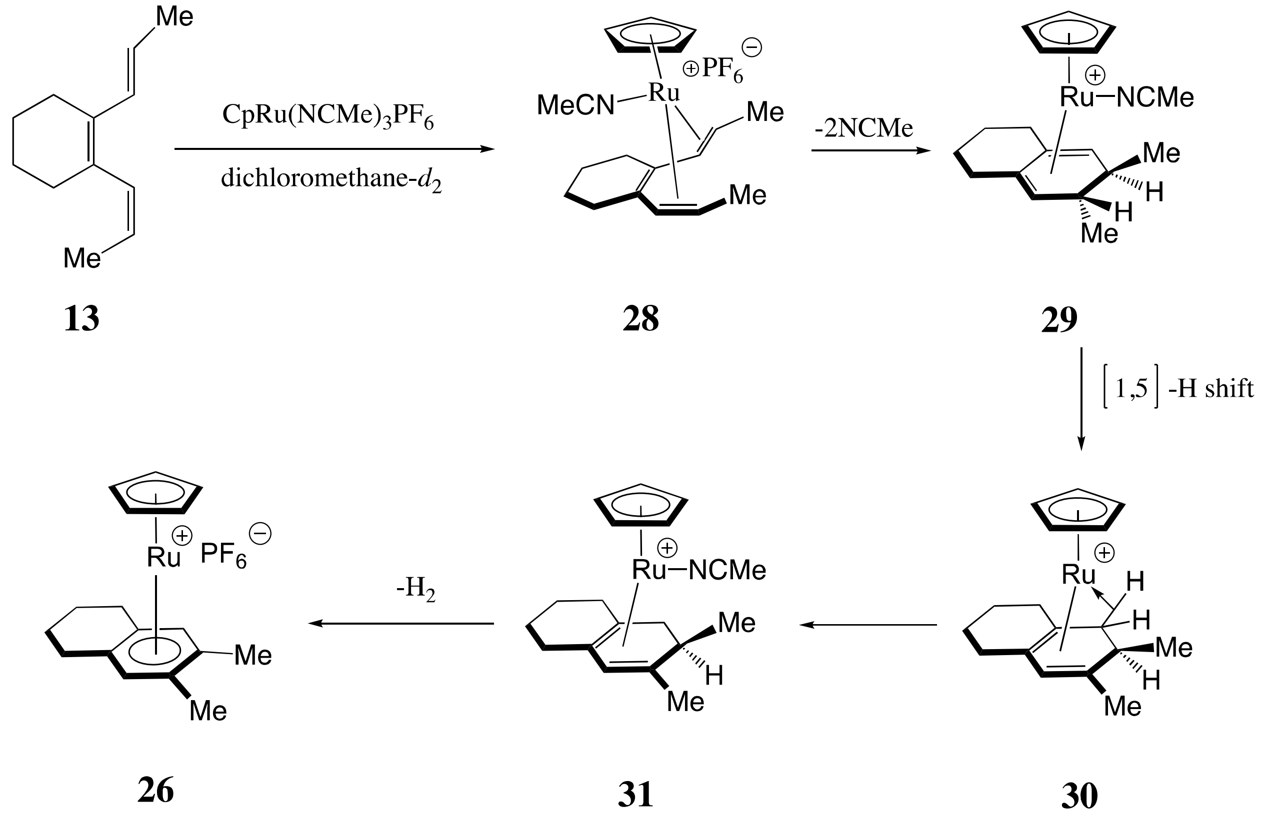
Bond (A-B)	Length (Å)	Bond (A-B)	Length (Å)
Ru-C1	2.334	C1-C2	1.403
Ru-C2	2.259	C2-C3	1.492
Ru-C3	3.166	C3-C4	1.343
Ru-C4	3.169	C4-C5	1.490
Ru-C5	2.264	C5-C6	1.405
Ru-C6	2.328	C1-C6	3.782

EZZ-Triene **13** (2 mg, 0.012 mmol) and **24** (5 mg, 0.012 mmol) were added into an oven-dried J. Young NMR tube and 1,3,5-tri-tert-butylbenzene was added as internal standard. After dry dichloromethane-d_2 was distilled into the tube under vacuum, the reaction was warmed to room temperature and then the reaction progress was monitored by ^{1}H NMR spectroscopy. After 30 min, all of **13** was consumed, based on the absence of a vinyl hydrogen resonance at δ 6.30 (d, 1H, J = 15.6 Hz), and resonances for **26** were observed (95% NMR yield; Scheme 23).



Scheme 23. Reaction of **13** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

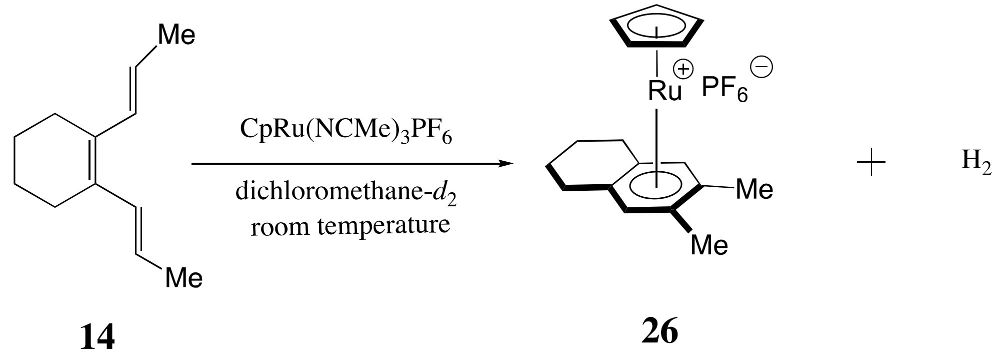
To explore cycloaromatization mechanism, the reaction of **13** and **24** was carried out again, but at − 60 ˚C in the probe of an ECA500 NMR spectrometer, and an initial ^{1}H NMR spectrum was recorded immediately. Then the reaction was monitored by ^{1}H NMR spectroscopy while slowly increasing the temperature. After 30 min at − 20 ˚C, new resonances attributed to intermediate **28** were observed, and integration of the Cp resonance at δ 4.97 (s, 5H) relative to those for the internal standard indicated a 20.2% yield of **28**. Upon slowly increasing the temperature, a new set of resonances attributed to intermediate **29** was observed following a slow increase of the temperature to − 10 ˚C. A 24.0% yield of **29** was calculated at this point, based on the integration of the Cp resonance at δ 5.00 (s, 5H). After slowly increasing the temperature to 0 ˚C for 20 min, **30** was observed to form in 37.8% yield, based on the integration of Cp resonance at δ 5.18 (s, 5H). Then the reaction mixture temperature was allowed to increase to 10 ˚C for 20 min, and intermediate **31** was observed to form in 22.0% yield, based on the integration of a Cp resonance at δ 4.95 (s, 5H). Finally, the reaction mixture was warmed to 23 ˚C. After 30 min, all the intermediate resonances disappeared, and final product **26** was observed in 94.3% yield (Scheme 24).



Scheme 24. Reaction of **13** with [CpRu(NCMe)$_3$]PF$_6$ (**24**) at low temperature leading to observation of **28**, **29**, **30**, **31**.

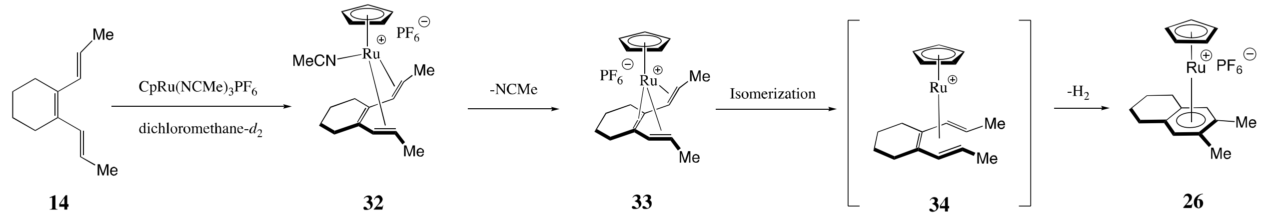
For this reaction, due to the formation of multiple intermediates at the same time, isolation of any one of the intermediates was a difficult task. However, the appearance of complex **29** is strong evidence that a ruthenium-accelerated disrotatory 6π electrocyclization had occurred. Two different methyl resonances were observed by ^{1}H NMR spectroscopy. On the other hand, the formation of **30**, following formation of cyclohexadiene **29**, suggests that rearrangement to **30** involves a [1,5]-hydride shift that is facilitated by an agostic interaction, consistent with the work of Stryker.[10]

EZE-Triene **14** (1.87 mg, 0.012 mmol) and **21** (5 mg, 0.012 mmol) were added into an oven-dried J. Young NMR tube with 1,3,5-tri-tert-butylbenzene as internal standard. After dry dichloromethane-d_2 was distilled into the tube under vacuum, the reaction was warmed to room temperature and monitored by ^{1}H NMR spectroscopy. After 70 min, all of **14** was consumed, based on the absence of a vinyl hydrogen resonance at δ 6.74 (d, 2H, J = 15.6 Hz), and resonances for **23** indicated its formation in 87.3% NMR yield (Scheme 25).



Scheme 25. Reaction of **14** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

Surprisingly, when the reaction of **14** and **24** was repeated and monitored by ^{1}H NMR spectroscopy at – 30 ˚C for 10 min, a ^{1}H NMR spectrum of the sample indicated the simultaneous appearance of **32** and **33** followed by slow disappearance of **32** and slow increment of **33**. After 2.5 h at – 20 ˚C, a ^{1}H NMR spectrum indicated that 85% of **24** was consumed, based on the Cp resonance at δ 4.25 (s, 5H), and resonances for **33** that were observed at δ 1.66 (d, 3H, J = 6.0 Hz, Me), 1.73 (m, 2H, methylene-*H*), 2.07 (d, 3H, J = 6.0 Hz, Me), 2.98 (d, 1H, J = 17.0 Hz, methylene-H), 3.61 (m, 1H, vinyl-*H*), 5.10 (1H, vinyl-*H*), 5.13 (s, 5H, Cp), 6.07 (m, 1H, vinyl-*H*). The yield of **33** (92%) was calculated based on the integration of the Cp resonance at δ 5.13 (s, 5H) relative to converted **24** (Scheme 26).



Scheme 26. Reaction of **14** with [CpRu(NCMe)$_3$]PF$_6$ (**24**) was monitored by ^{1}H NMR spectroscopy at low temperature to observe intermediate **32** and **33**.

For the crystallization of intermediate **33**, dry hexanes (2 mL) was distilled into the NMR tube and the tube was kept at – 20 ˚C for several days to induce crystallization of **33** in a form suitable for X-ray crystallography analysis (Figure 5).

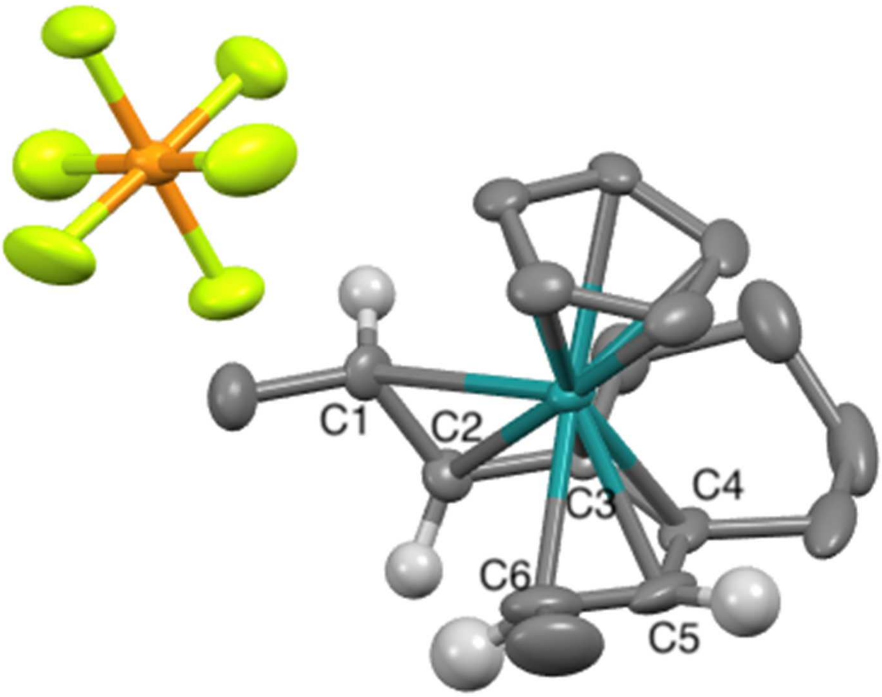


Figure 5. X-ray structure for η^6-triene **33**. Most hydrogens have been omitted for clarity.

Table 5. Selected Bond Distances (Å) for η^6-triene **33**.

Bond (A-B)	Length (Å)	Bond (A-B)	Length (Å)
Ru-C1	2.362(5)	C1-C2	1.369(8)
Ru-C2	2.195(6)	C2-C3	1.447(6)
Ru-C3	2.174(6)	C3-C4	1.432(7)
Ru-C4	2.253(6)	C4-C5	1.428(7)
Ru-C5	2.176(7)	C5-C6	1.425(8)
Ru-C6	2.227(6)	C1-C6	3.430(8)

The similarity of the bond lengths in the **33** triene π-system reveals significant delocalization, which is supported by comparison to the calculated bond distances in metal-free triene **14** (Figure 6).

It should be noted that the metal complexation shortens the non-bonded C1····C6 distance by 2.224 Å, which might accelerate the cyclization by bringing C1 and C6 closer together. Nevertheless, non-bonded C1····C6 distance of 3.430 Å for **33** seems too long to cyclize directly.

Instead, complex **33** may isomerize to symmetric intermediate **34** which has a shorter non-bonded C1····C6 distance, thereby triggering carbon-carbon bond formation to ultimately give the arene product.

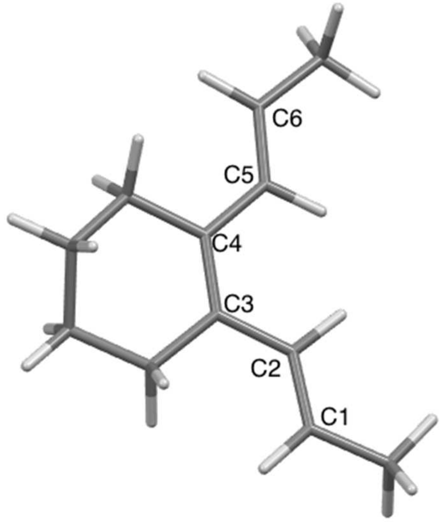


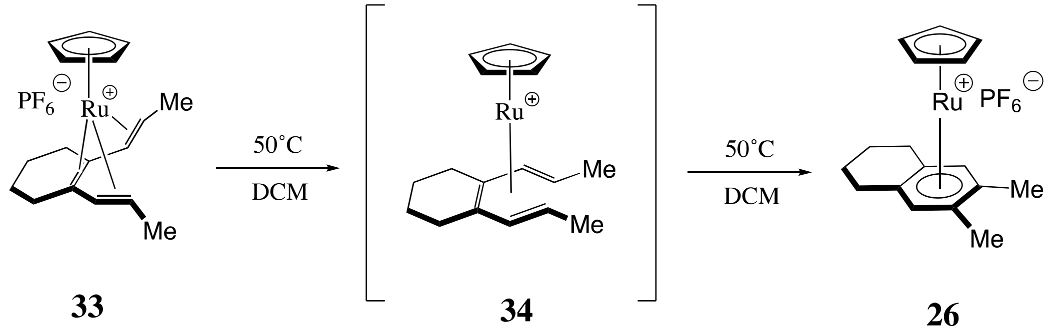
Figure 6. Calculated structure for *EZE*-triene **14**.

Table 6. Selected Bond Distances (Å) for *EZE*-triene **14**.

Bond (A-B)	Length (Å)
C1-C2	1.354
C2-C3	1.460
C3-C4	1.380
C4-C5	1.461
C5-C6	1.354
C1-C6	5.654

For the isolation of **33**, a similar larger scale reaction was carried out at – 20 ˚C for 7 h. After solvent was evaporated, dry diethyl ether was distilled into the tube at – 20 ˚C to crash out **33** as yellow powder, which was filtered and washed with cold hexanes under nitrogen to give 11.9 mg of **33** (87% yield). Subsequently, isolated **33** was heated to give aromatic product **26** which is consistent with our proposal that η^6-metal complexation accelerates 6π electrocyclizations

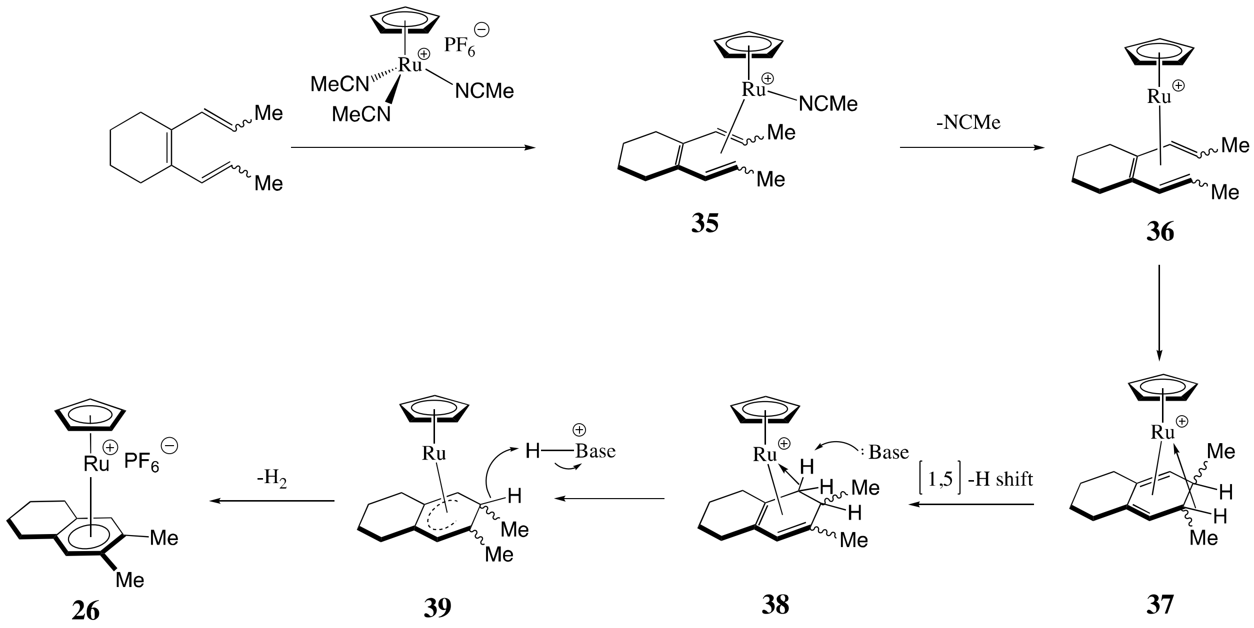
(Scheme 27). Even though **34** was not observed, the isomerization of **33** is proposed to give symmetric **34** which may more readily cycloaromatize due to the non-bonded C1····C6 distance.



33 **34** **26**

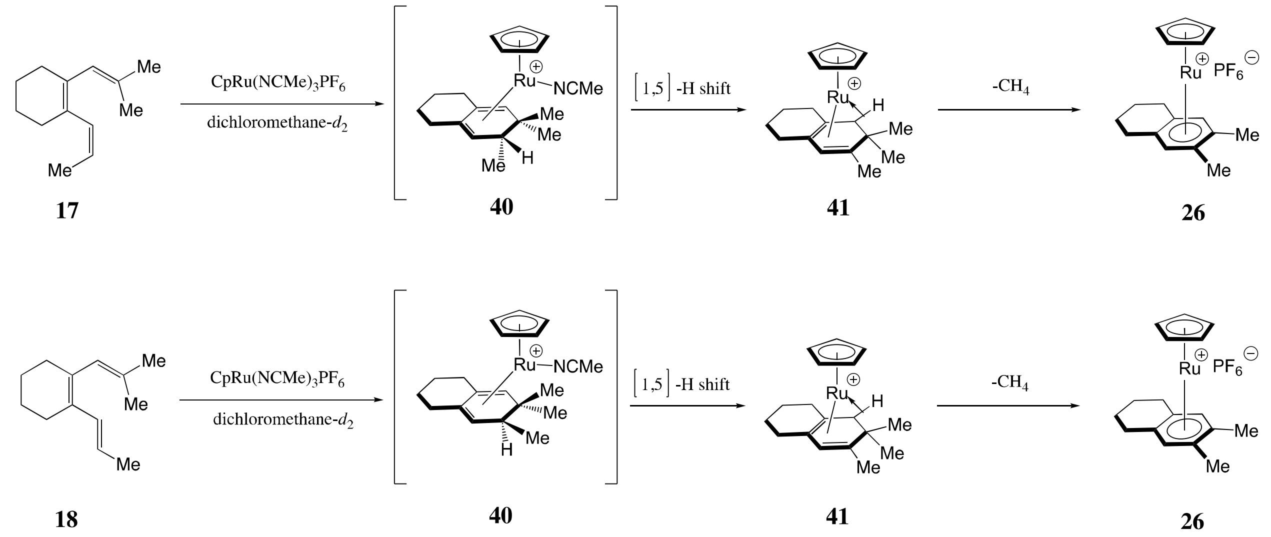
Scheme 27. Thermolysis of η^6-triene **33** at 50 ˚C to afford aromatic product **26**.

Based on the above results, we proposed a mechanism for the reaction of dimethyl trienes with $[CpRu(NCMe)_3]PF_6$ (**24**), as shown in Scheme 28. When the two compounds are mixed in dichloromethane-d_2, a ligand exchange reaction could happen to form tetrahapto ruthenium complex **35** in which the ruthenium is bonded to two double bonds. Then an open coordination site on ruthenium would result from loss of acetonitrile, so that ruthenium can bind to all three double bonds to form hexahapto intermediate **36**. The hexahapto-coordination would then induce cyclization to η^4-cyclohexadiene **37** with the methyl groups at the *E*-position of the trienes brought toward ruthenium via a disrotatory 6π electrocyclization. After a rapid [1,5]-hydride shift, the η^4-cyclohexadiene complex with an agostic interaction (**38)** is obtained. Then the deprotonation of **38** by base would lead to formation of cyclohexadienyl intermediate **39**. Finally, cleavage of the *exo* C-H bond would generate aromatic product **26** at ambient temperature.



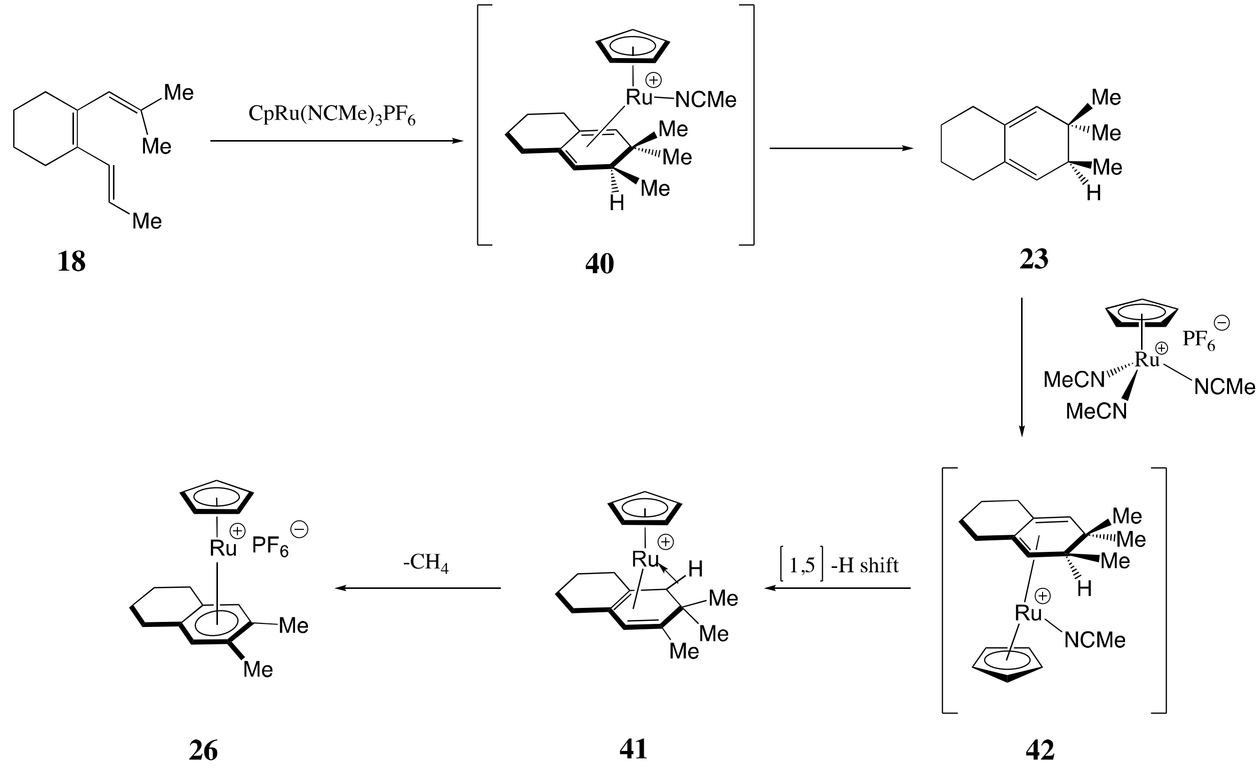
Scheme 28. Mechanism for the formation of **26** from dimethyl trienes (three isomers) and $[CpRu(NCMe)_3]PF_6$ (**24**).

The mechanisms of ruthenium-triggered cycloaromatization are fascinating and at first glance mysterious. More extensive studies are needed to further explore potential intermediates during the ruthenium-mediated 6π electrocyclizations. Therefore, trimethyl trienes **17** and **18** were synthesized. Compound **17** and **18** were treated with **24** in dichloromethane-d_2, intermediate **41** started to form after 30 min, the resonances of **41** were observed at δ – 8.03 (d, 1H, , J = 18 Hz, agostic-*H*), 0.50 (s, 3H, Me), 1.30 (s, 3H, Me), 1.61 (s, 3H, Me), 1.85 (m, 1H, methylene-*H*), 2.56 (m, 1H, methylene-*H*), 2.89 (m, 1H, methylene-*H*), 3.23 (m, 1H, methylene-*H*), and 5.19 (s, 5H, Cp). After 90 min, the yield of **41** was 76%. After three days, 30% of **41** had been transformed into complex **26 (**Scheme 29).



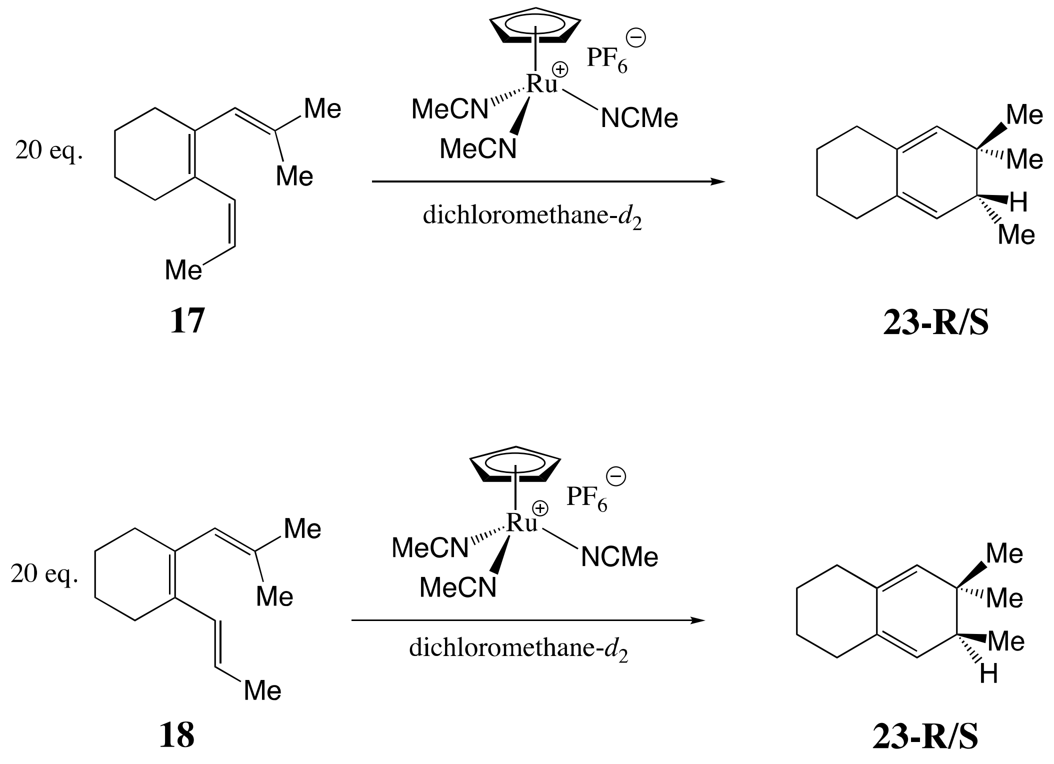
Scheme 29. Reactions of **17** and **18** with [CpRu(NCMe)$_3$]PF$_6$ (**24**) at room temperature to give observable intermediate **41** and aromatized product **26**.

However, the η^4-cyclohexadiene with agostic interaction (**41)** was not supposed to be observed since the agostic hydrogen was *exo* to the metal.[9] Nonetheless, it is a remarkable fact that the reaction of trimethyl trienes (*E*/*Z* isomers) with [CpRu(NCMe)$_3$]PF$_6$ (**24**) is a catalytic reaction which indicated that ruthenium could dissociated cyclohexadiene **23**. Then ruthenium was hypothesized to attach to cyclohexadiene **23** again from the other face, to place the agostic hydrogen *endo* to the metal. A subsequent [1,5]-hydride shift would form intermediate **41** with an agostic interaction (Scheme 30).



Scheme 30. Reaction of **18** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

The catalytic reaction is a tremendous breakthrough. Upon increasing the loading of ruthenium catalyst to 20 mol%, all the triene **17** and **18** can be consumed in 30 min to give a quantitative yield of **23-R/S** (Scheme 31). Free cyclohexadiene **23-R/S** can also be isolated and characterized.

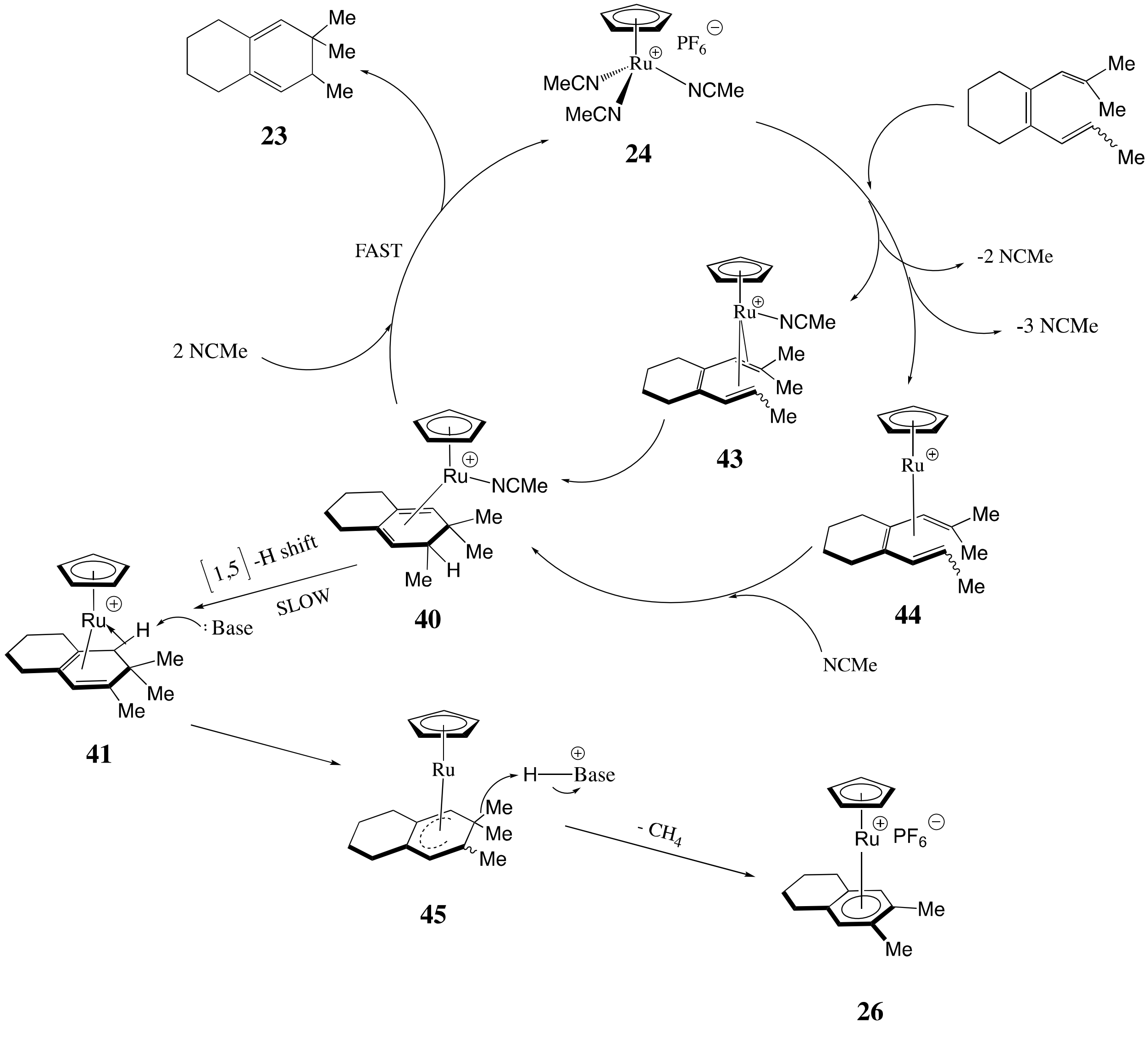


17 **23-R/S**

18 **23-R/S**

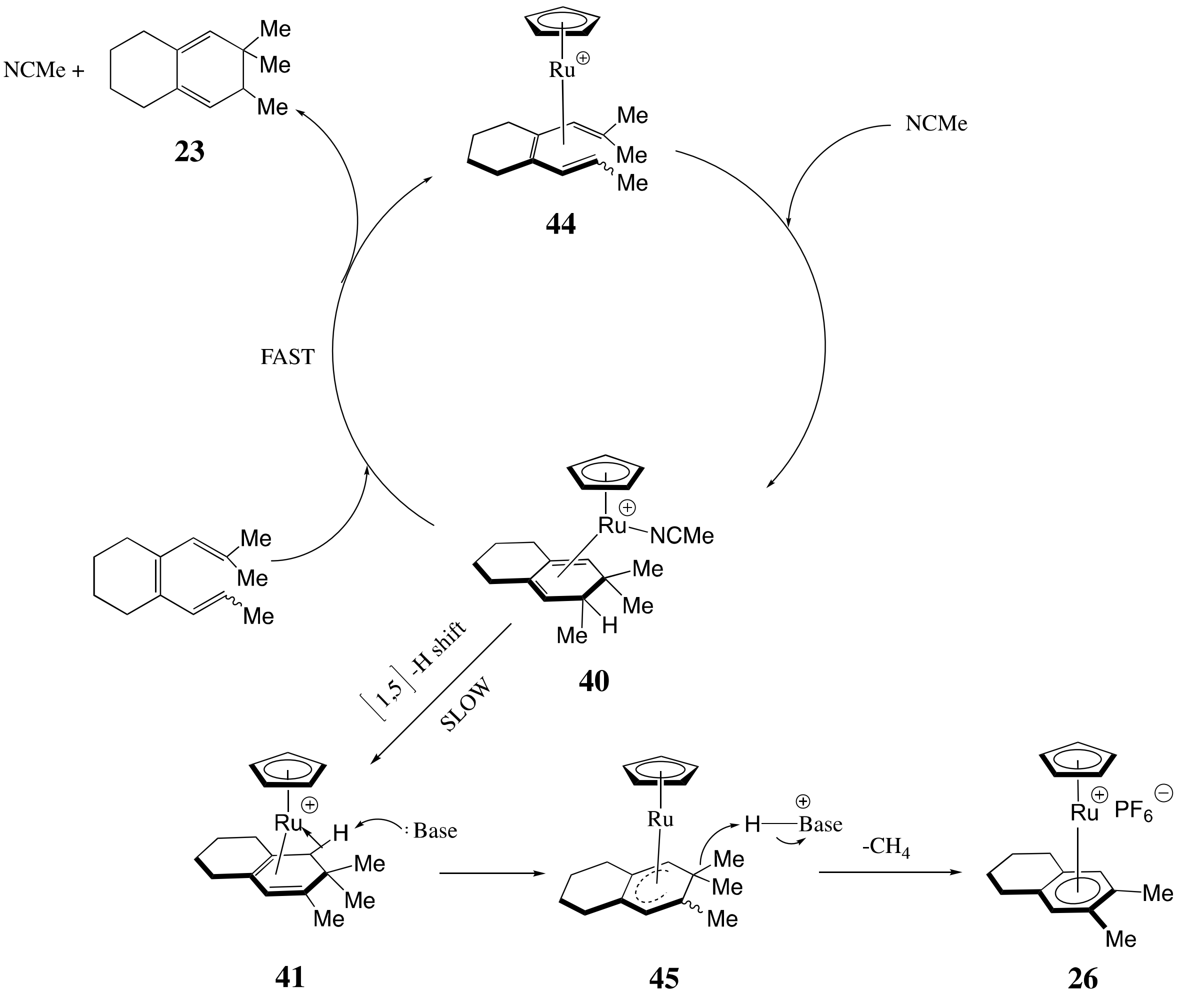
Scheme 31. Catalytic reaction of **17** and **18** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

For the reaction of trimethyl trienes (*E*/*Z* isomers) with [CpRu(NCMe)$_3$]PF$_6$ (**24**), two mechanisms came up. When the dimethyl trienes are treated with [CpRu(NCMe)$_3$]PF$_6$ (**24**) in dichloromethane-*d*$_2$, a ligand exchange reaction could happen to form either tetrahapto ruthenium complex **43,** in which the ruthenium is bonded to two double bonds, or hexahapto ruthenium complex **44** for which ruthenium is coordinated to all three double bonds. Then tetrahapto-coordination and hexahapto-coordination would both cyclize to form η^4-cyclohexadiene **40** and the groups at *E*-position of trienes would be *endo* to ruthenium via a disrotatory 6π electrocyclization. Through the dissociation of the metal with alkenes, shown as fast step, free cyclohexadiene **23** could be obtained. Moreover, [CpRu(NCMe)$_3$]PF$_6$ (**24**) was utilized as a catalyst to trigger the cyclization of trienes in a catalytic cycle. When trienes disappeared, the reaction would rapidly go through a [1,5]-hydride shift, which is the slow step, to afford a η^4-cyclohexadiene with an agostic interaction, **41.** Subsequently, the deprotonation of **41** leads to formation of cyclohexadienyl intermediate **45**, followed by cleavage of the *exo* C-C bond to generate aromatic product (Scheme 32).



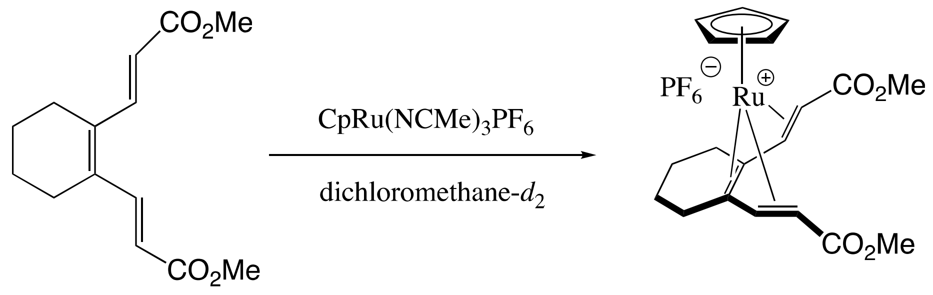
Scheme 32. Mechanism for the reaction of **17** and **18** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

Here's the other mechanism. Depending on previous results, we proposed all three double bonds of the triene need to be bind to ruthenium at the same time in order to realize the cyclization, as shown for complex **44**. The hexahapto intermediate would cyclize to form η^4-cyclohexadiene **40** via a disrotatory 6π electrocyclization. With an excess of trienes, ruthenium would liberate free cyclohexadiene **23**. Next, ruthenium could coordinate a new molecule of triene and repeat the cycle until all of the triene is consumed. The reaction would then to form an η^6-cyclohexadiene with an agostic interaction (**41**), followed by deprotonation by base to give cyclohexadienyl intermediate **45**. Finally, a ruthenium-assisted cleavage of the *exo* C-C bond would generate the aromatic product (Scheme 33).



Scheme 33. Mechanism for the reaction of **17** and **18** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

To investigate the electronic effect on cyclization of trienes, the reaction of *EZE* diester triene **20** with **24** in acetone was monitored by ^{1}H NMR spectroscopy. After 3 h, a ^{1}H NMR spectrum was obtained, showing the diagnostic resonances of **46** at δ 5.99 (d, 1H, J = 9.2 Hz, vinyl-*H*), 5.67 (s, 5H, Cp), 3.85 (s, 3H, Me), 3.72 (s, 3H, Me), 3.28 (m, 1H, methylene-*H*), 3.23 (m, 1H, methylene-*H*), 2.89 (m, 2H, methylene-*H*), 2.60 (m, 2H, methylene-*H*), and 1.89 (m, 2H, methylene-*H*) (Scheme 34). In order to isolate **46**, a larger scale was conducted in a similar fashion. After stirring at room temperature for 5 min, Et_2O was added to afford **46** as a yellow solid (71.2% yield). The structure of **46** was confirmed by X-ray crystallographic analysis (Figure 7).



20 **46**

Scheme 34. Reaction of **20** with $[CpRu(NCMe)_3]PF_6$ (**24**).

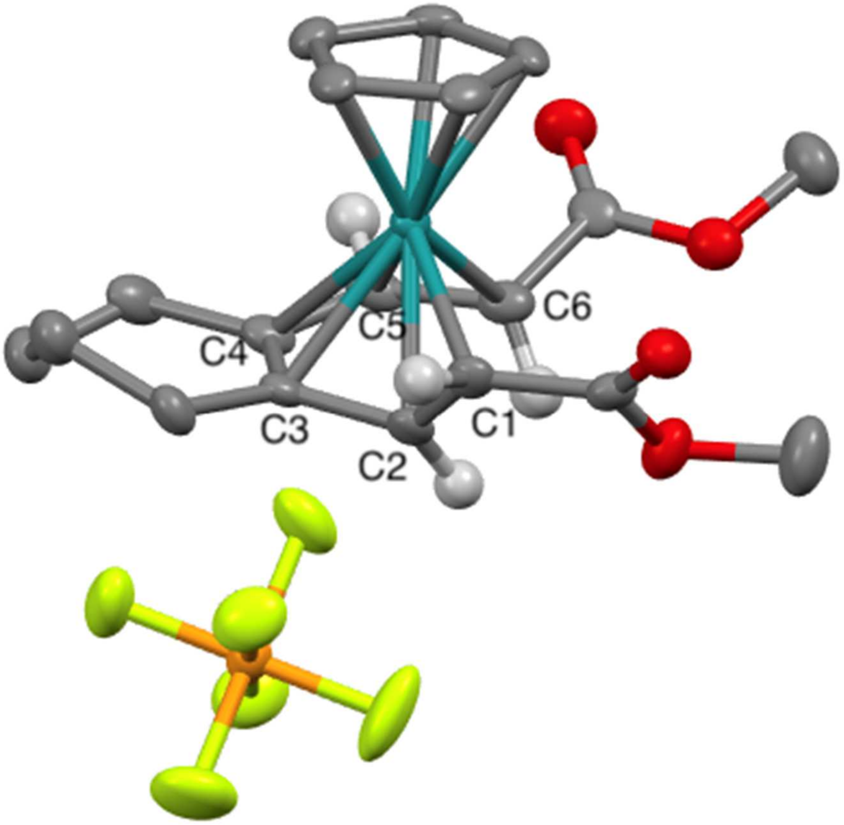
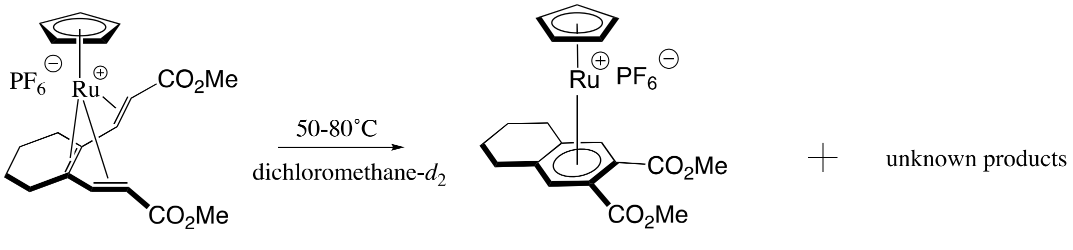


Figure 7. X-ray structure for η^6-triene **46**. Most hydrogens have been omitted for clarity.

Table 7. Selected Bond Distances (Å) for η^6-triene **46**.

Bond (A-B)	Length (Å)	Bond (A-B)	Length (Å)
Ru-C1	2.288(3)	C1-C2	1.370(4)
Ru-C2	2.179(3)	C2-C3	1.436(5)
Ru-C3	2.205(3)	C3-C4	1.422(4)
Ru-C4	2.280(3)	C4-C5	1.438(4)
Ru-C5	2.162(3)	C5-C6	1.409(5)
Ru-C6	2.189(3)	C1-C6	3.356(4)

When **46** was heated at 50 - 80 ˚C for 60 h, it didn't aromatize quickly. Based on the spectrum, it looks like it did cyclize with a 40% yield based on the appearance of methyl, Cp, and aromatic hydrogen resonances at δ 3.94, 5.41, and 6.51, with an integration of 6:5:2 (Scheme 35). Complex **46** might be too stable to generate arene product.



46 **47**

Scheme 35. Reaction of η^6-triene **46** with [CpRu(NCMe)$_3$]PF$_6$ (**24**).

C. Conclusions

In summary, the thermal and photochemical reactions of trienes are not an efficient way to carry out 6π electrocyclizations with the triene substrates described herein. On the contrary, we demonstrated that [CpRu(NCMe)$_3$]PF$_6$ (**24**) accelerates the cyclization and cycloaromatization of trienes at ambient temperatures. A series of fascinating mechanisms and novel intermediates have been deciphered. We synthesized some essential and unknown substrates and identified several significant intermediate structures via ^{1}H NMR spectroscopy and X-ray crystallography. According to the results from the reaction of trienes with [CpRu(NCMe)$_3$]PF$_6$ (**24**), the intermediate hexahapto complex may facilitate acceleration of 6π electrocyclizations. Additionally, the formation of η^4-cyclohexadiene **29** is an important intermediate that proves ruthenium-mediated 6π electrocyclization of trienes proceeds through a disrotatory ring closure process. Ruthenium also assists the migration of a hydride to generate an isomerized cyclohexadiene complex that exhibits an agostic bond. This intermediate undergoes deprotonation by weak (possibly adventitious) base to form a cyclohexadienyl intermediate. In the final step, the cleavage of an *exo* C-H bond (in the case of the dimethyl triene) and cleavage of the an *exo* C-C bond (in the case of the trimethyl triene) leads to the aromatic product **26** at ambient temperature. To our surprise, an incredible catalytic reaction of trimethyl trienes (*E*/*Z* isomer) with $[CpRu(NCMe)_3]PF_6$ (**24**) has been observed.

In the future, additional substrates will be examined in reactions with the ruthenium complex in order to obtain more comprehensive evidence that may support our theory. We are also optimistic to utilize other transition metals will be found to catalyze the cyclization/cycloaromatization of trienes.

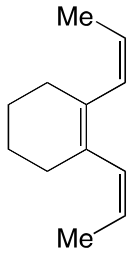
D. Experimental Section

1. General Information:

All organometallic reagents were manipulated under an inert gas atmosphere, using standard Schlenk techniques or a nitrogen-filled glove box. Solvents were dried by passage through an alumina column. Chloroform-*d* was refluxed over CaH_2 for two days and then freeze-pump-thaw-degassed prior to use. Benzene-d_6 was dried over sodium/benzophenone ketyl and distilled prior to use. Acetone-d_6 was dried over activated molecular sieves for 2 h before distillation into a dry Schlenk flask. Dichloromethane-d_2 was dried over activated molecular sieves for 12 h prior to use. NMR-tube-scale reactions were performed in J. Young NMR tubes equipped with a Teflon needle-valve adapter. Flash column chromatographic purifications were conducted using silica gel. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Mercury 300 (^1H, 300 MHz; ^{13}C, 75.5 MHz), Varian Mercury 400 (^1H, 400 MHz; ^{13}C, 100.7 MHz), Varian VX500 (^1H, 500 MHz; ^{13}C, 126 MHz) or JEOL ECA500 (^1H, 500 MHz; ^{13}C, 126 MHz) spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported relative to residual proton or carbon chemical shifts for the solvent. Mass spectral analyses were performed by Chemistry and Biochemistry Molecular Spectrometry Facility at UC San Diego. IR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Crystallography data were collected by Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54178 Å) at the UC San Diego Crystallography laboratory. Melting points were measured by an electrothermal EZ-Melt instrument. Elemental analyses were performed by NuMega laboratories.

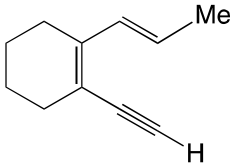
2. Synthesis and Characterization Data

1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (8): Hydrogen gas (1 atm) was bubbled through a stirring mixture of quinoline (0.114 mL, 0.97 mmol) and Lindlar Pd (1.097 g, 0.51 mmol) in hexanes (110 mL) at 23 ˚C for 10 min before addition of 1,2-di(prop-1-yn-1-yl)cyclohex-1-ene (**7**; 0.77 g, 4.86 mmol). After stirring at 23 ˚C under a hydrogen atmosphere (1 atm) for 12 h, the reaction mixture was filtered through Celite, concentrated, and purified by flash column chromatography (silica gel, hexanes) to afford **8** as a colorless oil (0.35 g, 2.16 mmol, 44% yield). IR (film, cm^{-1}) 3000, 2930, 2858, 1641, 1437, 1365, 1034. ^{1}H NMR (400 MHz, C_6D_6): δ 6.03 (d, 2H, $^3J_{HH}$ = 10.8 Hz vinyl-*H*), 5.43 (m, 2H, vinyl-*H*), 2.18 (m, 4H, methylene-*H*), 1.63 (d, 6H, $^3J_{HH}$ = 6 Hz, Me), 1.52 (m, 4H, methylene-*H*). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 132.0 (vinyl-*C*), 131.4 (vinyl-*C*), 124.3 (vinyl-*C*), 30.1 (methylene-*C*), 23.1 (methylene-*C*), 15.3 (Me). HRMS for $[C_{12}H_{19}]^+$: 163.1481 (Theo. Mass), 163.1480 (Mass Measured), Delta (– 0.6 ppm).



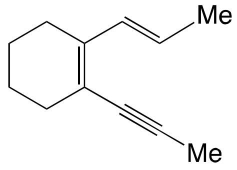
8

(*E*)-1-ethynyl-2-(prop-1-en-1-yl)cyclohex-1-ene (11): Anhydrous K_2CO_3 (2.9 g, 21 mmol) was added to a 23 ˚C solution of (*E*)-trimethyl((2-(prop-1-en-1-yl)cyclohex-1-en-1-yl)ethynyl)silane (**10**; 1.47 g, 6.7 mmol) in THF/MeOH (1:1, 70 mL). After stirring at 23 ˚C for 1.5 h, 100 mL of water was added, and the reaction mixture was extracted with pentane (3 x 70 mL). The organic extracts were dried over anhydrous $MgSO_4$, concentrated, and purified by flash silica column chromatography (silica gel, pentane) to afford **11** as a colorless oil (0.86 g, 5.8 mmol, 86.5% yield). IR (film, cm^{-1}) 3032, 2931, 2085, 1638, 1585, 1446, 1374. ^1H NMR (400 MHz, $CDCl_3$): δ 6.81 (d, 1H, $^3J_{HH}$ = 16 Hz, vinyl-*H*), 5.81 (m, 1H, vinyl-*H*), 3.23 (s, 1H, C≡C-*H*), 2.24 (m, 4H, methylene-*H*), 1.83 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me), 1.63 (m, 4H, methylene-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 142.3 (vinyl-*C*), 131.5 (vinyl-*C*), 126.0 (vinyl-*C*), 115.9 (vinyl-*C*), 84.4 (*C*≡C-H), 81.5 (C≡*C*-H), 30.6 (methylene-*C*), 25.3 (methylene-*C*), 22.5 (methylene-*C*), 22.2 (methylene-*C*), 18.8 (Me). HRMS for $[C_{11}H_{15}]^+$: 147.1168 (Theo. Mass), 147.1169 (Mass Measured), Delta (0.7 ppm).



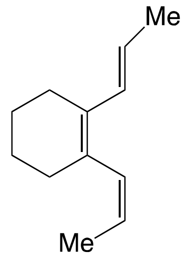
11

(*E*)-1-(prop-1-en-1-yl)-2-(prop-1-yn-1-yl)cyclohex-1-ene (12): *n*-Butyllithium (3.48 mL, 8.7 mmol; 2.5 M in hexanes) was added dropwise by syringe to a – 78 ˚C solution of (*E*)-1-ethynyl-2-(prop-1-en-1-yl)cyclohex-1-ene (**11**; 0.86 g, 5.8 mmol) in THF (110 mL). After stirring at – 78 ˚C for 2 h, iodomethane (0.722 mL, 11.6 mmol) was introduced by syringe. The reaction mixture was allowed to stir for 4.5 h while slowly warming to 23 ˚C. The mixture was poured over sat. aq. NH_4Cl (60 mL) and extracted with hexanes (3 x 60 mL). The organics extracts were successively washed with water (50 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, hexanes) to afford **12** as a colorless oil (0.87 g, 5.425 mmol, 92% yield). IR (film, cm^{-1}) 3031, 2927, 2858, 2222, 1639, 1589, 1446, 1434, 1373. ^1H NMR (400 MHz, $CDCl_3$): δ 6.79 (d, 1H, $^3J_{HH}$ = 15.6 Hz, vinyl-*H*), 5.73 (m, 1H, vinyl-*H*), 2.20 (m, 4H, methylene-*H*), 2.04 (s, 3H, Me), 1.82 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me), 1.61 (m, 4H, methylene-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1 (vinyl-*C*), 131.8 (vinyl-*C*), 124.6 (vinyl-*C*), 117.6 (vinyl-*C*), 90.1 (*C*≡C-Me), 80.2 (C≡*C*-Me), 31.1 (methylene-*C*), 25.2 (methylene-*C*), 22.7 (methylene-*C*), 22.4 (methylene-*C*), 18.8 (C=C-*Me*), 4.8 (C≡C-*Me*). HRMS for $[C_{12}H_{17}]^+$: 161.1325 (Theo. Mass), 161.1326 (Mass Measured), Delta (0.6 ppm).



12

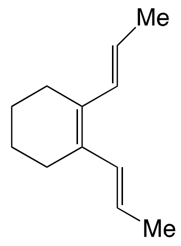
1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (13): Hydrogen gas (1 atm) was bubbled through a 23 ˚C mixture of quinoline (0.0638 mL, 0.54 mmol) and Lindlar Pd (0.612 g, 0.29 mmol) in hexanes (100 mL) for 10 min, followed by the addition of (*E*)-1-(prop-1-en-1-yl)-2-(prop-1-yn-1-yl)cyclohex-1-ene (**12**; 0.87 g, 5.43 mmol). After stirring at 23 ˚C under a hydrogen atmosphere (1 atm) for 8 h, the reaction mixture was filtered through Celite, concentrated, and purified by flash column chromatography (silica gel, hexanes) to afford **13** as a colorless oil (0.575 g, 3.55 mmol, 94% yield). IR (film, cm^{-1}) 3032, 2923, 2858, 1994, 1639, 1608, 1446, 1373, 972. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.31 (d, 1H, $^{3}J_{HH}$ = 15.6 Hz, vinyl-*H*), 5.87 (d, 1H, $^{3}J_{HH}$ =11.2 Hz, vinyl-*H*), 5.62 (m, 1H, vinyl-*H*), 5.55 (m, 1H, vinyl-*H*), 2.18 (m, 2H, methylene-*H*), 2.05 (m, 2H, methylene-*H*), 1.76 (d, 3H, $^{3}J_{HH}$ = 6.4 Hz, Me) , 1.64 (m, 4H, methylene-*H*), 1.53 (d, 3H, $^{3}J_{HH}$ = 7.2 Hz, Me). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 132.1 (vinyl-*C*), 131.8 (vinyl-*C*), 130.9 (vinyl-*C*), 129.8(vinyl-*C*), 125.9 (vinyl-*C*), 121.9 (vinyl-*C*), 30.7 (methylene-*C*), 25.4 (methylene-*C*), 22.99 (methylene-*C*), 22.97 (methylene-*C*), 18.8 (Me), 14.9 (Me). HRMS for [$C_{12}H_{19}$]+: 163.1481 (Theo. Mass), 163.1482 (Mass Measured), Delta (0.6 ppm).



13

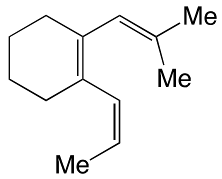
1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene (14): A benzene-d_6 solution (10 mL) of iodine (5 mg, 0.02 mmol) and 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**; 0.2 g, 1.2 mmol) was stirred at 23 ˚C, during which time the reaction progress was monitored by ^{1}H NMR spectroscopy. After 30 h, the reaction mixture was concentrated, and iodine was sublimed from the flask under high vacuum. The crude product was purified by flash column chromatography (silica gel with hexanes) to afford **14** as a colorless oil (0.09 g, 0.55 mmol, 45.8% yield). IR (film, cm^{-1}) 3042, 1666, 1455, 1256. ^{1}H NMR (400 MHz, C_6D_6): δ 6.94 (d, 2H, $^{3}J_{HH}$ = 15.2 Hz, vinyl-*H*), 5.64 (m, 2H, vinyl-*H*), 2.22 (m, 4H, methylene-*H*), 1.72 (d, 6H, $^{3}J_{HH}$ = 6.4 Hz, Me), 1.52 (m, 4H, methylene-*H*). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 130.7 (vinyl-*C*), 129.9

(vinyl-*C*), 123.3 (vinyl-*C*), 26.9 (methylene-*C*), 23.1 (methylene-*C*), 19.0 (Me). HRMS for $[C_{12}H_{19}]^+$: 163.1481 (Theo. Mass), 163.1481 (Mass Measured), Delta (0 ppm).



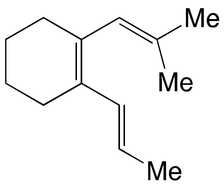
14

(*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (17): *n*-Butylithium (5.19 mL, 12.98 mmol; 2.5 M in hexanes) was added dropwise to a THF solution of isopropyltriphenyl phosphonium iodide (6.47 g, 14.9 mmol) maintained at – 78 ˚C under a nitrogen atmosphere. The reaction mixture was warmed to 0 ˚C and (*Z*)-2-(prop-1-en-1-yl)cyclohex-1-ene-1-carbaldehyde (**16**; 1.49 g, 9.9 mmol) was added dropwise. The mixture was stirred at 0 ˚C for 30 min, warmed to 23 ˚C. After 3 h at 23 ˚C the reaction was quenched with saturated aqueous NH_4Cl (50 mL) and extracted with hexanes (3 x 100 mL). The organic extracts were washed with brine (100 mL), dried with anhydrous $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, hexanes) to afford **17** as a clear oil (1.52 g, 8.62 mmol, 87% yield). IR (film, cm^{-1}) 2999, 2918, 2852, 2727, 2663, 1992, 1665, 1640, 1446, 1375, 1275, 1206, 1127, 1036. ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (d, 1H, $^3J_{HH}$ = 11.6 Hz, vinyl-*H*), 5.58 (s, 1H, vinyl-*H*), 5.33 (m, 1H, vinyl-*H*), 2.20 (m, 2H, methylene-*H*), 2.07 (m, 2H, methylene-*H*), 1.72 (s, 3H, Me), 1.63 (d, 3H, $^3J_{HH}$ = 7.2 Hz, Me), 1.62 (m, 4H, methylene-*H*), 1.54 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (126 MHz, CDCl3): δ 133.2 (vinyl-*C*), 132.8 (vinyl-*C*), 131.7 (vinyl-*C*), 130.9 (vinyl-*C*), 126.6 (vinyl-*C*), 123.3 (vinyl-*C*), 30.5 (methylene-*C*), 30.0 (methylene-*C*), 26.1 (Me), 23.3 (methylene-*C*), 23.1 (methylene-*C*), 19.9 (Me), 15.3 (Me). HRMS for $[C_{13}H_{21}]^+$: 177.1638 (Theo. Mass), 177.1639 (Mass Measured), Delta (0.6 ppm).



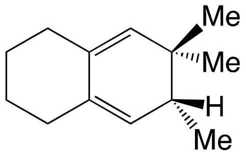
17

(*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (18): A benzene-d_6 solution (15 mL) of (*Z*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 800 mg, 4.54 mmol) was heated at 130 ˚C for 6 h. The solution was then concentrated under vacuum and subjected to flash column chromatography (silica gel, hexanes) to afford **18** as a clear oil (0.7 g, 4.0 mmol, 87.5% yield). IR (film, cm^{-1}) 3027, 2909, 2850, 1580, 1533, 1439. ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 6.27 (d, 1H, $^3J_{HH}$ = 16.0 Hz, vinyl-*H*), 5.60 (s, 1H, vinyl-*H*), 5.57 (m, 1H, vinyl-*H*), 2.16 (m, 2H, methylene-*H*), 2.00 (m, 2H, methylene-*H*), 1.79 (s, 3H, Me), 1.76 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me), 1.61 (m, 4H, methylene-*H*), 1.51 (s, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): *δ* 133.9 (vinyl-*C*), 133.3 (vinyl-*C*), 132.7 (vinyl-*C*), 130.0 (vinyl-*C*), 126.7 (vinyl-*C*), 121.4 (vinyl-*C*), 31.3 (methylene-*C*), 25.7 (methylene-*C*), 25.6 (Me), 23.33 (methylene-*C*), 23.32 (methylene-*C*), 19.7 (Me), 18.9 (Me). HRMS for [$C_{13}H_{21}$]+: 177.1638 (Theo. Mass), 177.1641 (Mass Measured), Delta (1.7 ppm).



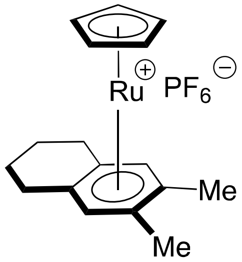
18

(R)-6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (23-R): A dichloromethane solution (8 mL) of (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 0.14 g, 0.79 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 68 mg, 0.16 mmol) was stirred at 23 ˚C for 40 min. The solution was poured into hexanes (100 mL), and the resulting solution was passed through a short plug of Celite followed by a short plug of silica gel with hexanes / EtOAc (1 : 1, 100 mL) as eluant. Then the solution was concentrated, and purified by flash column chromatography (silica gel, hexanes) to afford **23-R** as a colorless oil (0.13 g, 0.74 mmol, 92% yield). IR (film, cm^{-1}) 2958, 2925, 2854, 1737, 1459, 1435, 1369, 1369, 1244, 818. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14 (bs, 1H, vinyl-*H*), 5.13 (s, 1H, vinyl-*H*), 2.22 (m, 4H, methylene-*H*), 2.10 (m, 1H, C*H*Me), 1.62 (m, 2H, methylene-*H*), 1.46 (m, 2H, methylene-*H*), 0.98 (s, 3H, Me), 0.91 (d, 3H, $^3J_{HH}$ = 7.2 Hz, Me), 0.77 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 133.3 (vinyl-*C*), 132.9 (vinyl-*C*), 132.5 (vinyl-*C*), 126.7 (vinyl-*C*), 39.3, 34.2, 31.0, 30.8, 28.3, 25.02, 24.99, 20.5 (Me), 14.3 (Me). HRMS for $[C_{13}H_{21}]^+$: 177.1638 (Theo. Mass), 177.1640 (Mass Measured), Delta (1.1 ppm).



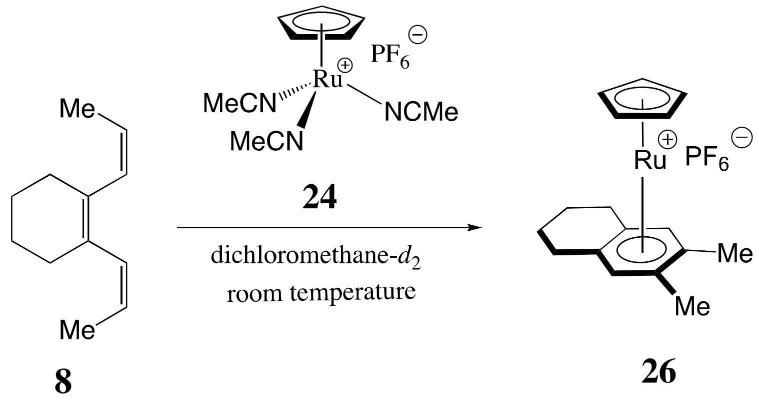
23-R

(η^5-cyclopentadienyl)(η^6-6,7-dimethyl-1,2,3,4-tetrahydronaphthalene)Ru hexafluorophosphate (26): A dichloromethane solution (20 mL) of 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**8**; 56 mg, 0.35 mmol) and $[CpRu(NCMe)_3]PF_6$ (**24**; 100 mg, 0.23 mmol) was stirred at ambient temperature for 2 h, and then layered with Et_2O (80 mL) to afford **26** as colorless flake crystals (90.5 mg, 83.5% yield). Mp: 266.7 ˚C; IR (film, cm^{-1}) 3113, 3082, 2939, 1473, 1454, 1433, 1416, 1391, 1038, 1005. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.01 (s, 2H, aromatic-*H*), 5.11 (s, 5H, Cp), 2.78 (m, 2H, methylene-*H*), 2.62 (m, 2H, methylene-*H*), 2.30 (s, 6H, Me), 1.83 (m, 2H, methylene-*H*), 1.73 (m, 2H, methylene-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 102.5 (Ar), 100.7 (Ar), 87.5 (Ar), 81.3 (Cp), 28.1 (methylene-*C*), 22.5 (methylene-*C*) 18.7 (Me). HRMS for $[C_{17}H_{21}Ru]^+$: 327.0686 (Theo. Mass), 327.0682 (Mass Measured), Delta (– 1.2 ppm).

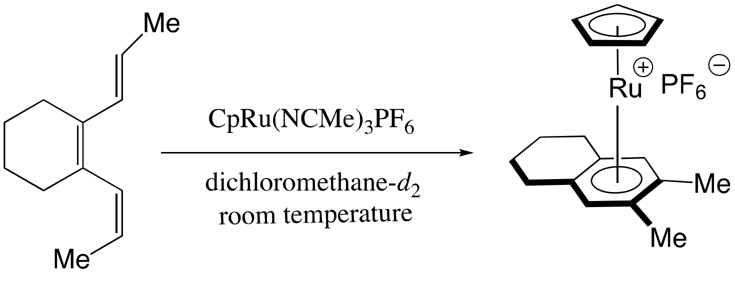


26

NMR-tube-scale reaction of 8 with [CpRu(NCMe)$_3$]PF$_6$ (24) to generate 26 in dichloromethane-*d*$_2$: Triene **8** (4.8 mg, 0.03 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 12.8 mg, 0.03 mmol) were added into an oven-dried J. Young NMR tube, with 1,3,5-tri-tert-butylbenzene added as an internal standard. Dry dichloromethane-*d*$_2$ (1.1 mL) was distilled into the tube under vacuum, and the solution was degassed via 3 cycles of freeze/pump/thaw/degas. The sample was kept at – 78 ˚C, and an initial ^{1}H NMR spectrum was recorded immediately at – 78 ˚C? in the cold probe. The reaction was subsequently warmed up to ambient temperature and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 100 min, **8** was completely consumed, based on the disappearance of a resonance of vinyl hydrogen at δ 5.85 (d, 2H, $^3J_{HH}$ = 11.6 Hz), and resonances for **26** were observed at δ 6.01 (s, 2H, aromatic-*H*), 5.11 (s, 5H, Cp), 2.78 (m, 2H, methylene-*H*), 2.62 (m, 2H, methylene-*H*), 2.30 (s, 6H, Me), 1.83 (m, 2H, methylene-*H*), and 1.73 (m, 2H, methylene-*H*). An 92.6% NMR yield of **26** was determined by comparing the integration of the Cp resonance at δ 5.11 (s, 5H), to that for the internal standard at δ 7.24 (s, 3H).

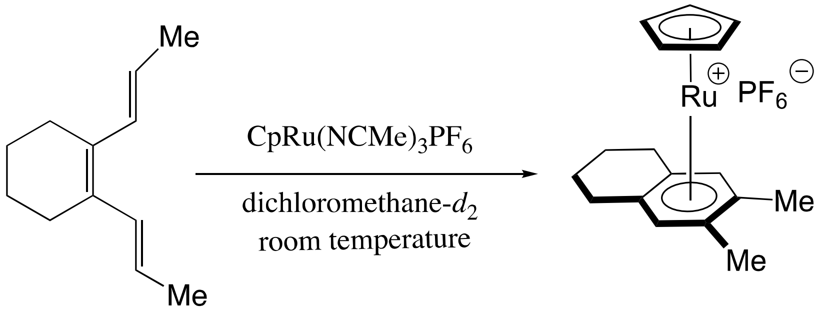


NMR-tube-scale reaction of 13 with [CpRu(NCMe)$_3$]PF$_6$ (24) to generate 26 in dichloromethane-*d*$_2$: Triene **13** (2 mg, 0.012 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 5 mg, 0.012 mmol) were added into an oven-dried J. Young NMR tube, with added 1,3,5-tri-tert-butylbenzene as internal standard. The tube was maintained at – 78 ˚C and dry dichloromethane-*d*$_2$ (0.45 mL) was distilled into the tube under vacuum. The tube was degassed via 3 cycles of freeze/pump/thaw/degas. The NMR tube was kept at – 78 ˚C, and an initial ^{1}H NMR spectrum was recorded immediately in the cold NMR probe. The reaction was subsequently warmed up to ambient temperature and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 30 min, all **13** was consumed based on disappearance of a vinyl hydrogen resonance at δ 6.30 (d, 1H, $^3J_{HH}$ = 15.6 Hz), and the resonances for **26** were observed at δ 6.01 (s, 2H, aromatic-*H*), 5.11 (s, 5H, Cp), 2.78 (m, 2H, methylene-*H*), 2.62 (m, 2H, methylene-*H*), 2.30 (s, 6H, Me), 1.83 (m, 2H, methylene-*H*), and 1.73 (m, 2H, methylene-*H*). A 95% yield of **26** was determined by comparing the integration of the Cp resonance at δ 5.11 (s, 5H) to that for the internal standard at δ 7.24 (s, 3H).



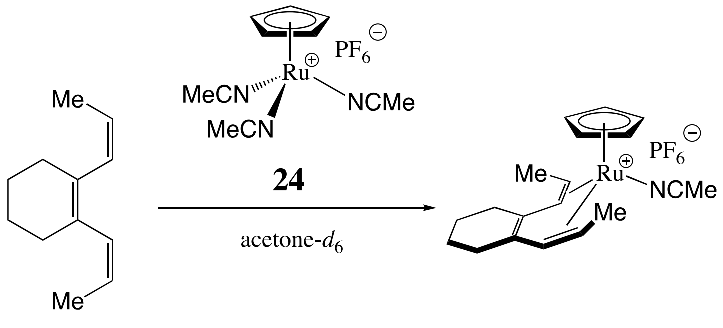
13 **26**

NMR-tube-scale reaction of 14 with [CpRu(NCMe)$_3$]PF$_6$ (24) to generate 26 in dichloromethane-*d*$_2$: Triene **14** (1.87 mg, 0.012 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 5 mg, 0.012 mmol) were added into an oven-dried J. Young NMR tube, with added 1,3,5-tri-tert-butylbenzene as internal standard. The tube was cooled to – 78 ˚C and placed under vacuum. After 0.45 mL of dry dichloromethane-d_2 was distilled into the tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. The sample was maintained at – 78 °C, and an initial ^{1}H NMR spectrum was recorded immediately in the cold probe. The reaction was subsequently warmed to ambient temperature and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 70 min, all of **14** was consumed, based on disappearance of the vinyl hydrogen resonance at δ 6.74 (d, 2H, $^3J_{HH}$ = 15.6 Hz), and resonances for **26** were observed at δ 6.01 (s, 2H, aromatic-*H*), 5.11 (s, 5H, Cp), 2.78 (m, 2H, methylene-*H*), 2.62 (m, 2H, methylene-*H*), 2.30 (s, 6H, Me), 1.83 (m, 2H, methylene-*H*), and 1.73 (m, 2H, methylene-*H*). An 87.3% yield of **26** was determined by comparing the integration of the Cp resonance at δ 5.11 (s, 5H) to that for the internal standard at δ 7.24 (s, 3H).



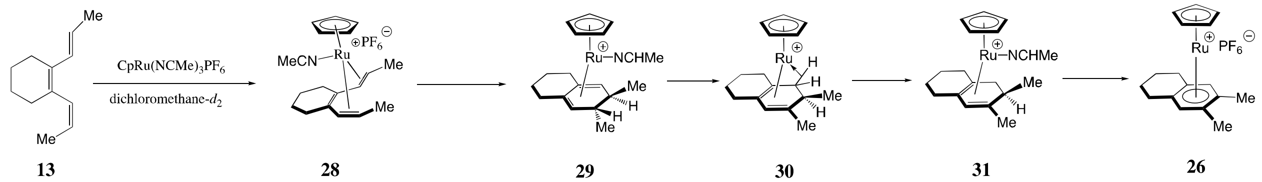
14 **26**

NMR-tube-scale reaction to generate (η^5-cyclopentadienyl)(η^4-1,2-di((Z)-prop-1-en-1-yl)cyclohex-1-ene)Ru(acetonitrile) hexafluorophosphate intermediate (25) in acetone-d_6: 1,2-Di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**8**) (4.8 mg, 0.03 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 12.84 mg, 0.03 mmol) were added into an oven-dried J. Young NMR tube, with added 1,3,5-tri-tert-butylbenzene as internal standard. The tube was frozen by cooling in a liquid nitrogen bath and then placed under vacuum. After 0.7 mL of dry acetone-d_6 was distilled into the tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. The sample was placed in the – 60 °C probe of a JEOL ECA500 NMR instrument, and an initial ^{1}H NMR spectrum was recorded immediately. Then the reaction mixture was monitored by ^{1}H NMR spectroscopy at – 45 ˚C. After 45 min, a ^{1}H NMR spectrum indicated that 73% of [CpRu(NCMe)$_3$]PF$_6$ (**24**) was consumed, based on a decrease in the intensity of the Cp resonance at δ 4.34 (s, 5H), and resonances for complex **25** were observed at δ 1.48 (d, 3H, $^3J_{HH}$ = 6.5 Hz, Me), 1.73 (m, 2H, methylene-*H*), 1.77 (d, 3H, $^3J_{HH}$ = 5.5 Hz, Me), 2.55 (s, 3H, NCMe), 4.02 (d, 1H, $^3J_{HH}$ = 9.0 Hz, vinyl-*H*), 4.51 (d, 1H, $^3J_{HH}$ = 9.5 Hz, vinyl-*H*), 4.75 (m, 1H, vinyl-*H*), 5.13 (m, 1H, vinyl-*H*), and 5.26 (s, 5H, Cp). A 97.7% yield of **25** was calculated based on the integration of the Cp resonance at δ 5.26 (s, 5H) relative to that for converted **24**, based on the internal standard at δ 7.24 (s, 3H). Dry hexanes (2 mL) were then distilled into the NMR tube, and the tube maintained at – 40 ˚C for several days to induce crystallization of **25**, in a form suitable for X-ray crystallography analysis.

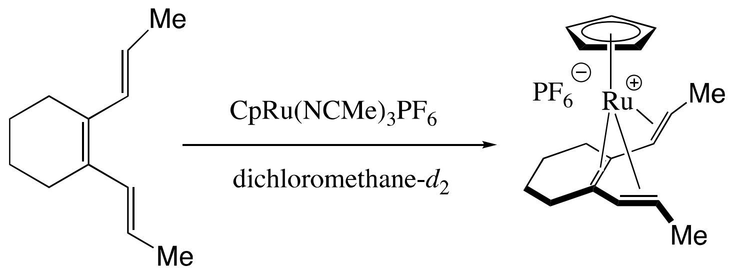


8 **25**

NMR-tube-scale reaction of [CpRu(NCMe)$_3$]PF$_6$ (24) with 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (13) at low temperature in dichloromethane-d_2: 1-((*E*)-Prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**; 5 mg, 0.031 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 10 mg, 0.023 mmol) were added into an oven-dried J. Young NMR tube. The tube was frozen by liquid nitrogen immediately and then placed under vacuum. After 0.75 mL of dry CD$_2$Cl$_2$ was distilled into the tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. The NMR tube was placed in the – 60 ˚C in the probe of a JEOL ECA500 NMR instrument, and an initial ^{1}H NMR spectrum was recorded immediately. Then the sample was monitored by ^{1}H NMR spectroscopy while slowly increasing temperature. After 30 min at – 20 ˚C, a new set of resonances for intermediate **28** were observed at δ 1.45 (d, 3H, $^3J_{HH}$ = 6 Hz, Me), 1.82 (d, 3H, $^3J_{HH}$ = 6 Hz, Me), 2.44 (s, 3H, NCMe), 3.75 (d, 1H, $^3J_{HH}$ = 13 Hz, vinyl-*H*), 4.38 (d, 1H, $^3J_{HH}$ = 10 Hz, vinyl-*H*), 4.62 (m, 2H, vinyl-*H*), and 4.97 (s, 5H, Cp). A 20.2% yield of **28** was calculated based on the integration of the Cp resonance at δ 4.97 (s, 5H) relative to that for the internal standard at δ 7.22 (s, 3H). Then the sample was maintained at – 20 ˚C for 300 min before warming to – 10 ˚C for 50 min. A new set of resonances attributed to intermediate **29** was observed at δ 0.92 (d, 3H, $^3J_{HH}$ = 6.5 Hz, Me), 1.24 (d, 3H, $^3J_{HH}$ = 6.5 Hz, Me), 2.57 (s, 3H, NCMe), 5.00 (s, 5H, Cp), and 5.37 (bs, 2H, vinyl-*H*). A 24.0% yield of **29** was calculated based on the integration of Cp resonance at δ 5.00 (s, 5H) relative to the internal standard resonance at δ 7.22 (s, 3H). The sample was then maintained at – 5 ˚C for 20 min, and at 0 ˚C for 20 min, resulting the observation of a new set of resonances attributed to **30** at δ – 7.90 (t, 1H, $^3J_{HH}$ = 16.0 Hz, agostic-*H*), 0.90 (d, 3H, $^3J_{HH}$ = 7.0 Hz, Me), 1.81 (s, 3H, Me), 5.18 (s, 5H, Cp), and 5.25 (s, 1H, vinyl-*H*). A 37.8% yield of **30** was calculated based on the integration of the Cp resonance at δ 5.18 (s, 5H) relative to that for the internal standard at δ 7.23 (s, 3H). The sample was maintained at 5 ˚C for 20 min, and 10 ˚C for another 20 min, leading to the observation of a new set of resonances attributed to **31** at δ 0.92 (d, 3H, $^3J_{HH}$ = 7.0 Hz, Me), 1.75 (s, 3H, Me), 2.63 (s, 3H, NCMe), 4.60 (s, 1H, vinyl-*H*), and 4.95 (s, 5H, Cp). A 22.0% yield of **31** was calculated based on the integration of the Cp resonance at δ 4.95 (s, 5H) relative to that for the internal standard at δ 7.23 (s, 3H). Then the sample was then warmed to 23 ˚C and after 30 min at that temperature, all the intermediate resonances disappeared, and resonances for **26** were observed at δ 1.73 (m, 2H, methylene-H), 1.83 (m, 2H, methylene-*H*), 2.30 (s, 3H, Me), 2.62 (m, 2H, methylene-*H*), 2.78 (m, 2H, methylene-*H*), 5.11 (s, 5H, Cp), and 6.01 (s, 2H, arene-*H*). A 94.3% yield of **26** was calculated by integration of the Cp resonance at δ 5.11 (s, 5H) relative to that for the internal standard at δ 7.24 (s, 3H).



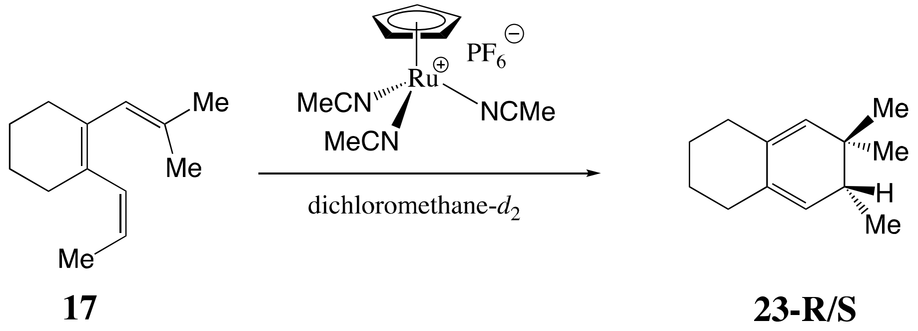
NMR-tube-scale reaction to generate (η^5-cyclopentadienyl)(η^6-1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene)Ru hexafluorophosphate intermediate (33) in dichloromethane-d_2: 1,2-di((*E*)-Prop-1-en-1-yl)cyclohex-1-ene (**14**; 1.9 mg, 0.0117 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 5 mg, 0.0115 mmol) were added into an oven-dried J. Young NMR tube, with added 1,3,5-tri-tert-butylbenzene as internal standard. The tube was frozen by liquid nitrogen and then placed under vacuum. After dry dichloromethane-d_2 **(**0.65 mL) was distilled into the tube under vacuum, the sample was degassed via 3 cycles of freeze/pump/thaw/degas. The sample was maintained at – 60 ˚C in the JEOL ECA500 NMR instrument probe, and an initial ^{1}H NMR spectrum was recorded immediately. The probe was then warmed to – 20 ˚C (2.5 h), and then – 10 ˚C (20 min), while monitoring the reaction progress by ^{1}H NMR spectroscopy, after which time, a ^{1}H NMR spectrum indicated that 85% of **24** was consumed, based on a decrease in the intensity of the Cp resonance at δ 4.25 (s, 5H), and resonances attributed to complex **33** were observed at δ 1.66 (d, 3H, $^3J_{HH}$ = 6.0 Hz, Me), 1.73 (m, 2H, methylene-*H*), 2.07 (d, 3H, $^3J_{HH}$ = 6.0 Hz, Me), 2.98 (d, 1H, $^3J_{HH}$ = 17.0 Hz, vinyl-*H*), 3.61 (m, 1H, vinyl-*H*), 5.10 (1H, vinyl-*H*), 5.13 (s, 5H, Cp), and 6.07 (m, 1H, vinyl-*H*). A 92% yield of **33** was calculated based on the integration of Cp resonance at δ 5.13 (s, 5H) relative to the Cp resonance at δ 4.25 (s, 5H) for converted **24**, based on the internal standard at at δ 7.22 (s, 3H). To crystallize **33**, a similar reaction was conducted using 1,2-di((E)-prop-1-en-1-yl)cyclohex-1-ene (**14**; 2.0 mg, 0.012 mmol) and **24** (5.0 mg, 0.012 mmol) in 0.7 mL of the dry dichloromethane at an initial temperature of – 78 ˚C, and then at – 20 ˚C for 7 h. Dry hexanes (2 mL) were then distilled into the NMR tube at – 78 ˚C, and the tube was kept at – 20 ˚C for several days to induce crystallization of **33** in a form suitable for X-ray crystallography analysis. For the isolation of **33** as a powder, a larger scale reaction was conducted in a similar fashion using 1,2-di((E)-prop-1-en-1-yl)cyclohex-1-ene (**14**) (6.0 mg, 0.037 mmol) and **24** (12.0 mg, 0.029 mmol) in dry dichloromethane (1.4 mL), initially at a temperature of – 78 ˚C, and subsequently at – 20 ˚C for 7 h. The reaction solution was concentrated under vacuum and dry diethyl ether (4 mL) was distilled into the tube at – 20 ˚C to crash out **33** as yellow powder, which was filtered and washed with cold hexanes under nitrogen to give 11.9 mg of **33** (87% yield). A ^{1}H NMR analysis of the isolated powder indicated the presence of a trace amount of **26** (less than 5%). For **33**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.33 (m, 1H, methylene-*H*), 1.68 (d, 3H, $^3J_{HH}$ = 5.6 Hz, Me), 1.75 (m, 1H, methylene-*H*), 1.79 (m, 1H, methylene-*H*), 1.93 (m, 2H, methylene-*H*), 2.09 (d, 3H, $^3J_{HH}$ = 5.6 Hz, Me), 2.22 (d, 1H, $^3J_{HH}$ = 13.2 Hz, vinyl-*H*), 2.30-2.48 (m, 2H, methylene-*H*), 3.00 (m, 1H, methylene-*H*), 3.65 (m, 1H, vinyl-*H*), 5.12 (1H, vinyl-*H*), 5.14 (s, 5H, Cp), 6.13 (m, 1H, vinyl-*H*). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 20.4 (Me), 21.8 (methylene-*C*), 22.5 (methylene-*C*), 23.9 (Me), 28.2 (methylene-*C*), 30.9 (methylene-*C*), 65.0 ($CHCH_3$), 86.9 (Cp), 91.1 (*C*HCH_3), 91.2 (*C*CCH_3), 100.5 (ring vinyl-*C*), 105.5 (C*C*CH_3), 113.0 (ring vinyl-*C*). HRMS for $[C_{17}H_{23}Ru]^+$: 323.0870 (Theo. Mass), 323.0854 (Mass Measured), Delta (-4.9 ppm).



14 **33**

NMR-tube-scale reaction of [CpRu(NCMe)$_3$]PF$_6$ (24) - catalyzed 6πcyclization of (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (17) in dichloromethane-*d*$_2$: (*Z*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 40 mg, 0.227 mmol) and [CpRu(NCMe)$_3$]PF$_6$ (**24**; 5 mg, 0.0115 mmol) were added into an oven-dried J. Young NMR tube with added 1,3,5-tri-tert-butylbenzene as internal standard. The sample was immediately cooled in a dry ice-acetone bath and dry dichloromethane-*d*$_2$ (0.8 mL) was distilled into the tube under vacuum. The cold sample tube was vortexed to dissolve all the solids. After the tube was degassed via 3 cycles of freeze/pump/thaw/degas, an initial ^{1}H NMR spectrum was recorded immediately, and then the reaction progress was monitored by ^{1}H NMR spectroscopy at ambient temperature. After 100 min, 83% of **17** was consumed based on integration of the vinyl hydrogen resonance at δ 5.84 (d, 1H, $^3J_{HH}$ = 11.6 Hz) relative to the internal standard at δ 7.24 (s, 3H), and resonances of **23-R/S** were observed at δ 0.77 (s, 3H, Me), 0.90 (d, 3H, $^3J_{HH}$ = 7.2 Hz, Me), 0.97 (s, 3H, Me), 1.45 (m, 2H, methylene-*H*), 1.61 (m, 2H, methylene-*H*), 2.0-2.3 (m, 5H, methylene-*H* and C*H*Me), 5.13 (s, 1H, vinyl-*H*), and 5.14 (bs, 1H, vinyl-*H*). A70.5% yield of **23-R/S** was calculated by integration of a methyl resonance at δ 0.77 (s, 3H) relative to the internal standard resonance at δ 7.24 (s, 3H).

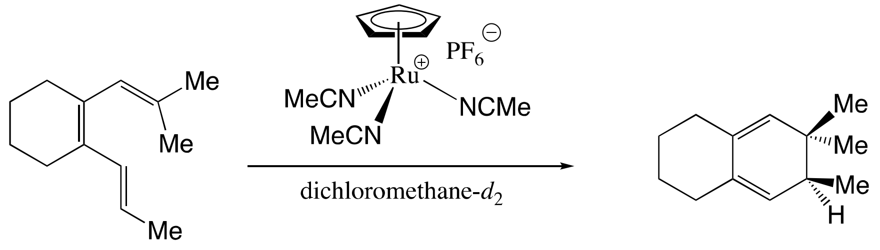
NOTE: Longer reaction time can cause some decomposition of the desired product (**23-R/S**). In addition, when the loading of the ruthenium catalyst was increased to 20 mol%, all of triene **17** was consumed in 30 min, with a quantitative yield of **23-R/S**.



17 **23-R/S**

NMR-tube-scale reaction of [CpRu(NCMe)$_3$]PF$_6$ (24) - catalyzed 6*π* cyclization of (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (18) in dichloromethane-*d*$_2$: A nearly identical reaction of **18** and [CpRu(NCMe)$_3$]PF$_6$ (**24**) to that described above led to 79% consumption of **18** after 100 min, based on the integration of the vinyl hydrogen resonance at δ 6.26 (d, 1H, $^3J_{HH}$ = 15.2 Hz) based on the internal standard at δ 7.24 (s, 3H). A 67% yield of **23-R/S** was calculated by the integration of methyl resonance at δ 0.77 (s, 3H) relative to the internal standard resonance at δ 7.24 (s, 3H).

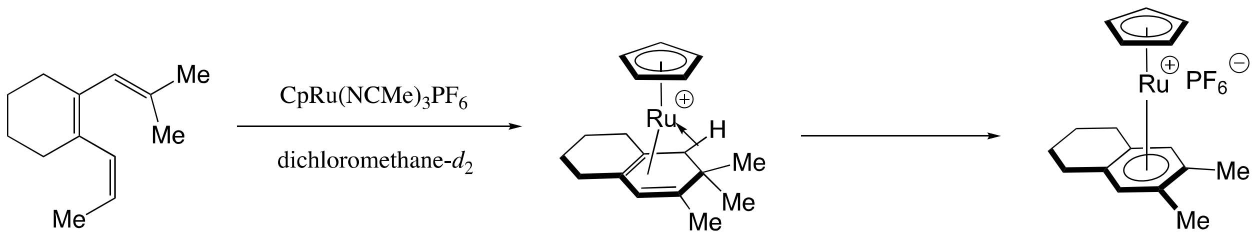
NOTE: Longer reaction time can also cause some decomposition of the desired product (**23-R/S**). In addition, an increased loading of ruthenium catalyst (20 mol%) led to complete consumption of triene **18** within 30 min and quantitative formation of **23-R/S**.



18 **23-R/S**

NMR-tube-scale reaction of [CpRu(NCMe)$_3$]PF$_6$ and (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (17) via (η^5-cyclopentadienyl)(η^6-6,6,7-trimethyl-1,2,3,4,5,6-hexahydronaphthalene) Ru(II) hexafluorophosphate (41) in dichloromethane-*d*$_2$:

(*Z*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 4 mg, 0.0227 mmol) and $[CpRu(NCMe)_3]PF_6$ (**24**; 5.0 mg, 0.0115 mmol) were added to an oven-dried J. Young NMR tube, with added 1,3,5-tri-tert-butylbenzene as internal standard. The sample was immediately cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry dichloromethane-d_2 was distilled into the NMR tube, the tube was degassed via 3 cycles of freeze/pump/thaw/degas, and an initial ^{1}H NMR spectrum was recorded immediately, and then the reaction mixture was monitored by ^{1}H NMR spectroscopy at ambient temperature. After 30 min, all of triene **17** was consumed, and the formation of cyclohexadiene **23-R/S** was observed in quantitively yield. Intermediate **41** started to form at this point, with resonances for **41** observed at δ – 8.03 (d, 1H, , $^2J_{HH}$ = 18 Hz, agostic-*H*), 0.50 (s, 3H, Me), 1.30 (s, 3H, Me), 1.61 (s, 3H, Me), 1.85 (m, 1H, methylene-*H*), 2.56 (m, 1H, methylene-*H*), 2.89 (m, 1H, methylene-*H*), 3.23 (m, 1H, methylene-*H*), and 5.19 (s, 5H, Cp). After 90 min, a 76% yield of **41** was calculated by integration of the methyl resonance at δ 0.50 (s, 3H) relative to the internal standard resonance at δ 7.24 (s, 3H). After a longer time, complex **23** was observed to form, with characteristic resonances at δ 2.30 (s, 6H, Me), 2.78 (m, 2H, methylene-*H*), 5.12 (s, 5H, Cp), and 6.01 (s, 2H, Ar). After three days, 30% of **41** had been transformed to complex **26** based on the integration of Cp resonance at δ 5.12 (s, 5H) relative to the internal standard resonance at δ 7.24 (s, 3H).

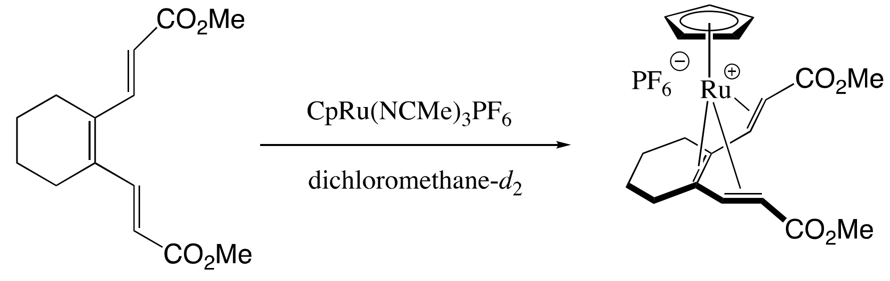


17 **41** **26**

NMR-tube-scale reaction to generate 46 in acetone-d_6: Dimethyl 3,3'-(cyclohex-1-ene-1,2-diyl)(2*E*,2'*E*)-diacrylate (**20**; 17.3 mg, 0.07 mmol) and **24** (20 mg, 0.05 mmol) were added into a J. Young NMR tube, with 1,3,5-tri-*tert*-butylbenzene added as internal standard. After 0.45 mL of dry acetone-d_6 was distilled into the tube under vacuum, the sample was degassed via 3 cycles of freeze/pump/thaw/degas. An initial ^{1}H NMR spectrum was recorded immediately at room temperature, and the reaction was monitored by ^{1}H NMR spectroscopy at ambient temperature. After 3 h, a second ^{1}H NMR spectrum was collected, which showed the diagnostic resonances of **46** at δ 5.99 (d, 1H, $^3J_{HH}$ = 9.2 Hz, vinyl-*H*), 5.67 (s, 5H, Cp), 3.85 (s, 3H, Me), 3.72 (s, 3H, Me), 3.28 (m, 1H, methylene-*H*), 3.23 (m, 1H, methylene-*H*), 2.89 (m, 2H, methylene-*H*), 2.60 (m, 2H, methylene-*H*), and 1.89 (m, 2H, methylene-*H*).

Preparation of 46 in dichloromethane: Dimethyl 3,3'-(cyclohex-1-ene-1,2-diyl)(2*E*,2'*E*)-diacrylate (**20**; 87 mg, 0.35 mmol) and **24** (100 mg, 0.23 mmol) were added into a 100 mL Schlenk flask. The flask was cooled in a dry ice-acetone bath and then placed under vacuum. After 20 mL of dry acetone was distilled into the flask under vacuum, the flask was degassed via 3 cycles of freeze/pump/thaw/degas. After stirring at ambient temperature for 5 min, the solvent was evaporated under vacuum and 20 mL of dry dichloromethane was distilled into the flask. Then the reaction mixture was allowed to stir for 5 min at ambient temperature followed by pouring the mixture over Et_2O (80 mL) to afford **46** as a yellow solid (92 mg, 71.2% yield). Decomposition point : 98.7 °C; IR (CH_2Cl_2, cm^{-1}) 3116, 3016, 2946, 2873, 1716, 1438, 1326, 1276, 1203, 1041. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 5.88 (d, 1H, $^3J_{HH}$ = 9.6 Hz, vinyl-*H*), 5.70 (d, 1H, $^3J_{HH}$ = 12.4 Hz, vinyl-*H*), 5.40 (s, 5H, *Cp*), 3.90 (s, 3H, Me), 3.75 (s, 3H, Me), 3.64 (d, 1H, $^3J_{HH}$ = 9.6 Hz, vinyl-*H*), 3.36 (d, 1H, $^3J_{HH}$ = 12 Hz, vinyl-*H*), 3.22 (m, 1H, methylene-*H*), 3.18 (m, 1H, methylene-*H*), 2.55 (m, 2H, methylene-*H*), 1.95 (m, 2H, methylene-*H*), 1.33 (m, 2H, methylene-*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 500 MHz): δ 173.0 (*C*O_2Me), 167.9 (*C*O_2Me), 118.2 (vinyl-*C*), 110.4 (vinyl-*C*), 105.5 (vinyl-*C*), 90.5 (*Cp*) 89.8 (vinyl-*C*), 89.8 (vinyl-*C*), 66.8 (vinyl-

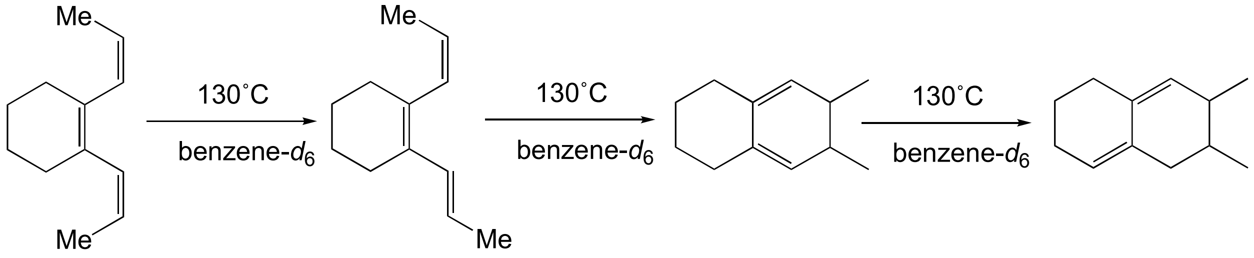
C), 30.8 (*C*H_2), 27.8 (*C*H_2), 22.0 (*C*H_2), 21.2 (*C*H_2), $^{13}C\{^1H\}$ NMR (acetone, 500 MHz): *δ* 173.6 (*C*O_2Me), 168.7 (*C*O_2Me), 118.7 (vinyl-*C*), 111.0 (vinyl-*C*), 105.8 (vinyl-*C*), 91.2 (*Cp*) 90.2 (vinyl-*C*), 90.2 (vinyl-*C*), 67.4 (vinyl-*C*), 53.6 (*Me*), 52.9(*Me*), 28.0 (*C*H_2), 22.4 (*C*H_2), 21.5 (*C*H_2). HRMS for $[C_{19}H_{23}O_4Ru]^+$: 417.0640 (Theo. Mass), 417.0636 (Mass Measured), Delta (– 1.0 ppm).



20 **46**

NMR-tube-scale reaction of heating 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (8) in benzene-*d*$_6$: 1,2-Di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**8**; 3 mg, 0.018 mmol) was added into a 5 mm medium-wall NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry benzene-*d*$_6$ was distilled into the NMR tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. Then the NMR tube was flame-sealed, and an initial ^{1}H NMR spectrum was recorded immediately. The tube was than placed into an oil bath at 130 ˚C, and the reaction was monitored by ^{1}H NMR spectroscopy. After 60 min, all of **8** was consumed, based on the absence of vinyl hydrogen resonances at *δ* 5.42 (m, 2H) and 6.02 (d, 2H, $^3J_{HH}$ = 11.2 Hz), and new resonances for 1-((E)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene were observed at *δ* 1.51 (m, 4H, methylene-*H*), 1.58 (d, 3H, $^3J_{HH}$ = 5.2 Hz, Me), 1.72 (d, 3H, $^3J_{HH}$ = 6.0 Hz, Me), 2.06 (m, 2H, methylene-*H*), 2.19 (m, 2H, methylene-*H*), 5.61 (m, 1H, vinyl-*H*), 5.44 (m, 1H, vinyl-*H*), 5.96 (d, 1H, $^3J_{HH}$ =10.8 Hz vinyl-*H*), and 6.59 (d, 1H, $^3J_{HH}$ =15.6 Hz, vinyl-*H*). A 96.5% yield of

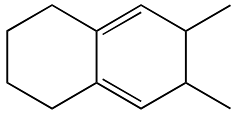
13 was calculated by integration of the vinyl hydrogen resonance at δ 6.59 (d, 1H, $^3J_{HH}$ =15.6 Hz) relative to the internal standard resonance at δ 7.42 (s, 3H). Upon heating the sample at 130 ˚C, compound **13** was slowly consumed, and after 9 days the maximum yield (22%) of **21** was observed, based on characteristic resonances at δ 5.31 (bs, 2H, vinyl-*H*) and 1.01 (d, 6H, $^3J_{HH}$ = 6.0 Hz, Me). After 29 days, 88% of **13** was consumed, based on the integration of the vinyl hydrogen resonance at δ 6.59 (d, 1H, $^3J_{HH}$ =15.6 Hz) relative to that of the internal standard at δ 7.42 (s, 3H). Resonances for compound **22** were observed at δ 0.92 (d, 3H, $^3J_{HH}$ = 6.4 Hz, Me), 0.99 (d, 3H, $^3J_{HH}$ = 7.2 Hz, Me), 5.22 (bs, 1H, vinyl-*H*), and 5.44 (bs, 1H, vinyl-*H*). A 51.8% yield of **22** was calculated based on the integration of the vinyl hydrogen at δ 5.22 (bs, 1H) relative to the internal standard resonance at δ 7.42 (s, 3H).



8 **13** **21** **22**

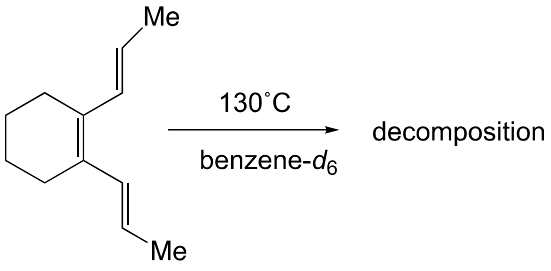
Preparation of 6,7-dimethyl-1,2,3,4,6,7-hexahydronaphthalene (21): 1-((*E*)-Prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**; 100 mg, 0.616 mmol) was added into a side-armed Schlenk flask. After 20 mL of dry benzene was distilled into the NMR tube under vacuum, the flask was degassed via 3 cycles of freeze/pump/thaw/degas. Then the flask was submerged in an oil bath at 180 ˚C, and the reaction mixture was heated for 30 h. After concentration and chromatography on silica gel with hexanes, 73.5 mg (73% yield) of **21** was obtained as clear oil. IR (film, cm^{-1}) 2989, 2927, 2873, 2835, 1658, 1588, 1450, 1434, 1369, 1245. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 5.25 (bs, 2H, vinyl-*H*), 2.22 (m, 4H, methylene-*H* and CH_3CH), 1.92 (bs, 2H, methylene-*H*), 1.65 (m, 2H, methylene-*H*), 1.45 (m, 2H, methylene-*H*), 0.99 (d, 6H, $^3J_{HH}$ = 6.8 Hz, Me). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 134.1 (vinyl-*C*), 127.2 (vinyl-*C*), 36.1 (CH_3CH), 31.2 (methylene-*C*), 25.0 (methylene-*C*), 19.5 (Me). HRMS for $[C_{12}H_{19}]+$: 163.1481 (Theo. Mass), 163.1482 (Mass Measured), Delta (0.6 ppm).



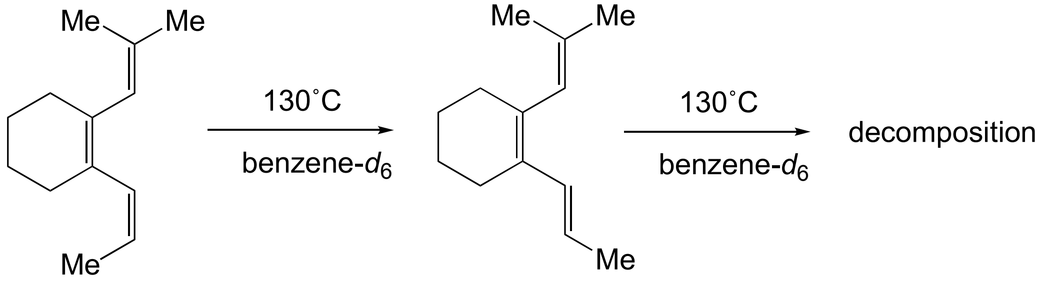
21

NMR-tube-scale thermolysis of 1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene (14) in benzene-*d*$_6$: 1,2-di((*E*)-Prop-1-en-1-yl)cyclohex-1-ene (**14**; 3 mg, 0.018 mmol) was added into a 5-mm medium-wall NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry benzene-*d*$_6$ was distilled into the NMR tube under vacuum, the sample was degassed via 3 cycles of freeze/pump/thaw/degas. Then the NMR tube was flame-sealed and an initial ^{1}H NMR spectrum was recorded immediately. The tube was then placed into an oil bath at 130 ˚C, and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 5 days, all of the starting material was consumed, based on the absence of vinyl hydrogen resonances at δ 5.64 (d, 2H) and 6.94 (d, 2H, $^3J_{HH}$ = 14 Hz). In addition, multiple new unassigned resonances were observed. There was no evidence for formation of 6,7-dimethyl-1,2,3,4,6,7-hexahydronaphthalene (**21**).



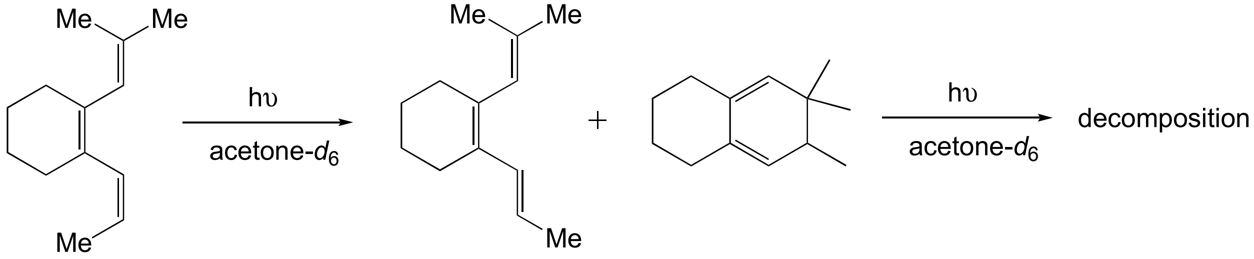
14

NMR-tube-scale thermolysis of (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (17) in benzene-d_6: (*Z*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 4 mg, 0.023 mmol) was added into a 5-mm medium-wall NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.5 mL of dry benzene-d_6 was distilled into the NMR tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. Then the NMR tube was flame-sealed and an initial ^{1}H NMR spectrum was recorded immediately. The tube was then placed into an oil bath at 130 ˚C, and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 6 h, all of **17** was consumed, based on the absence of vinyl hydrogen resonances at δ 5.41 (m, 1H) and 5.75 (s, 1H) and 6.09 (d, 1H, $^3J_{HH}$ = 11.6 Hz); and new resonances for (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**18**) were observed at δ 1.57 (m, 4H, methylene-*H*), 1.59 (s, 3H, Me), 1.71 (s, 3H, Me), 1.73 (d, 3H, $^3J_{HH}$ = 6.8 Hz, Me), 2.08 (m, 2H, methylene-*H*), 2.21 (m, 2H, methylene-*H*), 5.62 (m, 1H, vinyl-*H*), 5.74 (s, 1H, vinyl-*H*), and 6.60 (d, 1H, $^3J_{HH}$ =15.6 Hz, vinyl-*H*). An 88.8% yield of **18** was calculated by integration of the vinyl hydrogen resonance at δ 6.60 (d, 1H, $^3J_{HH}$ =15.6 Hz) relative to that of the internal standard at δ 7.42 (s, 3H). The reaction was heated at 130 ˚C, and slow consumption of compound **18** was observed. After 15 days, 91.2% of **18** was consumed, based on the integration of a vinyl hydrogen resoanance at δ 6.60 (d, 1H, $^3J_{HH}$ =15.6 Hz) relative to the internal standard resonance at δ 7.42 (s, 3H). There was no evidence for formation of 6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (**23**).



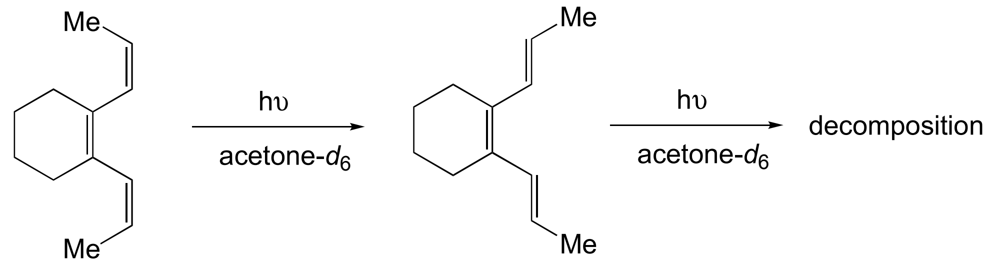
17 **18**

NMR-tube-scale photolysis reaction of (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (17) in acetone-*d*$_6$: (*Z*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**; 4.0 mg, 0.023 mmol) was added into a J. Young NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry acetone-*d*$_6$ was distilled into the NMR tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. An initial ^{1}H NMR spectrum was recorded immediately. The tube was then placed in a Rayonette photoreactor equipped with UV broadband lamps centered at 254 nm, and the reaction was monitored by ^{1}H NMR spectroscopy. After 2 h, compound **23** was observed based on the presence of characteristic vinyl hydrogen resonances at δ 5.15 (d, 1H, $^3J_{HH}$ = 10.8 Hz) and 5.13 (s, 1H). Compound **18** was also observed based on characteristic vinyl hydrogen resonances at δ 6.27 (d, 1H, $^3J_{HH}$ = 15.6 Hz), 5.59 (s, 1H), and 5.57 (s, 1H). The conversion of **17** was calculated to be 54% based on the integration of vinyl hydrogen resonance at δ 5.83 (d, 1H, $^3J_{HH}$ = 11.6 Hz) relative to the internal standard resonance at δ 7.28 (s, 3H). The yields for **23** and **18** were 6.6% and 46.8%, respectively. It was found that at longer irradiation times, both starting material **17** and products, **18** and **23**, underwent slow decomposition. After 4 days, compounds **17** and **23** were absent, and after 6 days, compound **18** was no longer present. The decomposition products were not characterized.



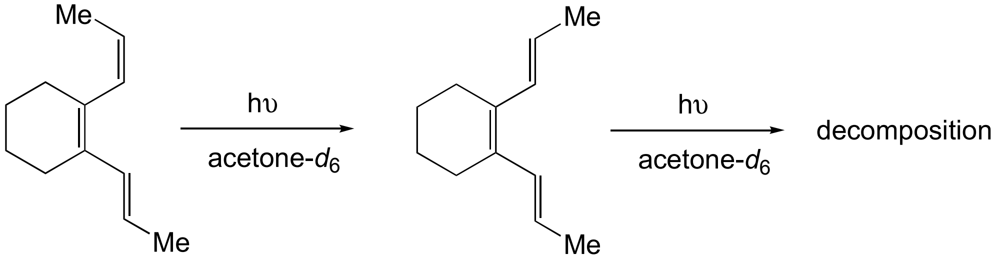
17 **18** **23**

NMR-tube-scale photolysis reaction of 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (8) in acetone-*d*₆: 1,2-di((Z)-Prop-1-en-1-yl)cyclohex-1-ene (**8**; 3 mg, 0.018 mmol) was added into a J. Young NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry acetone-d_6 was distilled into the NMR tube, the sample was degassed via 3 cycles of freeze/pump/thaw/degas. An initial ^{1}H NMR spectrum was recorded immediately. Then the tube was placed in a Rayonette photoreactor equipped with UV broadband lamps with wavelengths centered at 254 nm, and the reaction was monitored by ^{1}H NMR spectroscopy. After 200 min, compound **14** was observed, based on a characteristic vinyl hydrogen resonance at δ 6.78 (d, 2H, $^3J_{HH}$ = 15.2 Hz). The conversion of **8** was calculated as 60.7% based on the integration of a vinyl hydrogen resonance at δ 5.83 (d, 2H, $^3J_{HH}$ = 10.8 Hz), relative to the internal standard resonance at δ 7.28 (s, 3H). The yield of **14** was 23.3%. It was found that at longer irradiation times, both starting material **8**, and product **14**, slowly decomposed. After 6.5 h, resonances for compounds **8** and **14** were absent. No attempt was made to characterize the decomposition products.



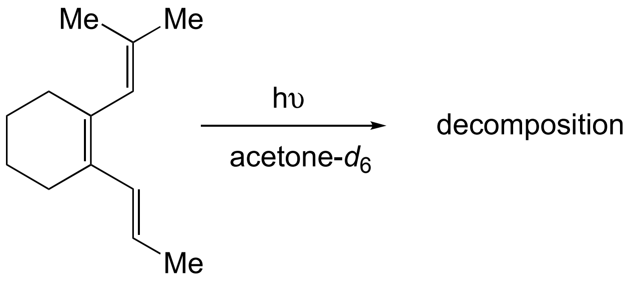
8 **14**

NMR-tube-scale photolysis reaction of 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (13) in acetone-*d*₆: 1-((*E*)-Prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**; 3 mg, 0.018 mmol) was added into a J. Young NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was coolerd in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry acetone-d_6 was distilled into the NMR tube, the sample was degassed via 3 cycles of freeze/pump/thaw/degas. An initial ^{1}H NMR spectrum was recorded immediately. Then the tube was placed in a Rayonette photoreactor equipped with UV broadband lamps centered at 254 nm, and the reaction was monitored by ^{1}H NMR spectroscopy. After 2 days, compound **14** was observed, based on a characteristic vinyl hydrogen resonance at δ 6.78 (d, 2H, $^3J_{HH}$ = 15.6 Hz). The conversion of **13** was calculated as 83.5%, based on integration of vinyl hydrogen at δ 6.30 (d, 1H, $^3J_{HH}$ = 15.6 Hz) relative to that for the internal standard at δ 7.28 (s, 3H). A 96.4% yield of **14** was obtained based on 83.5% of conversion of **13**. It was found that at longer irradiation times, both starting material **13**, and product **14**, underwent slow decomposition. After 35 days, compound **13** was absent and ~ 90% of **14** had decomposed.



13 **14**

NMR-tube-scale photolysis reaction of (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (18) in acetone-*d_6*: (*E*)-1-(2-Methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (4 mg, 0.023 mmol) was added into a J. Young NMR tube, with added 1,3,5-tri-*tert*-butylbenzene as internal standard. The tube was cooled in a dry ice-acetone bath and placed under vacuum. After 0.45 mL of dry acetone-d_6 was distilled into the NMR tube under vacuum, the tube was degassed via 3 cycles of freeze/pump/thaw/degas. An initial ^{1}H NMR spectrum was recorded immediately. The tube was then placed in a Rayonette photoreactor equipped with UV broadband lamps centered at 254 nm, and the reaction progress was monitored by ^{1}H NMR spectroscopy. After 7 days, all of the starting material had disappeared, and there was no evidence for formation of 6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (**23**).



18

3. ^{1}H and ^{13}C NMR Spectra:

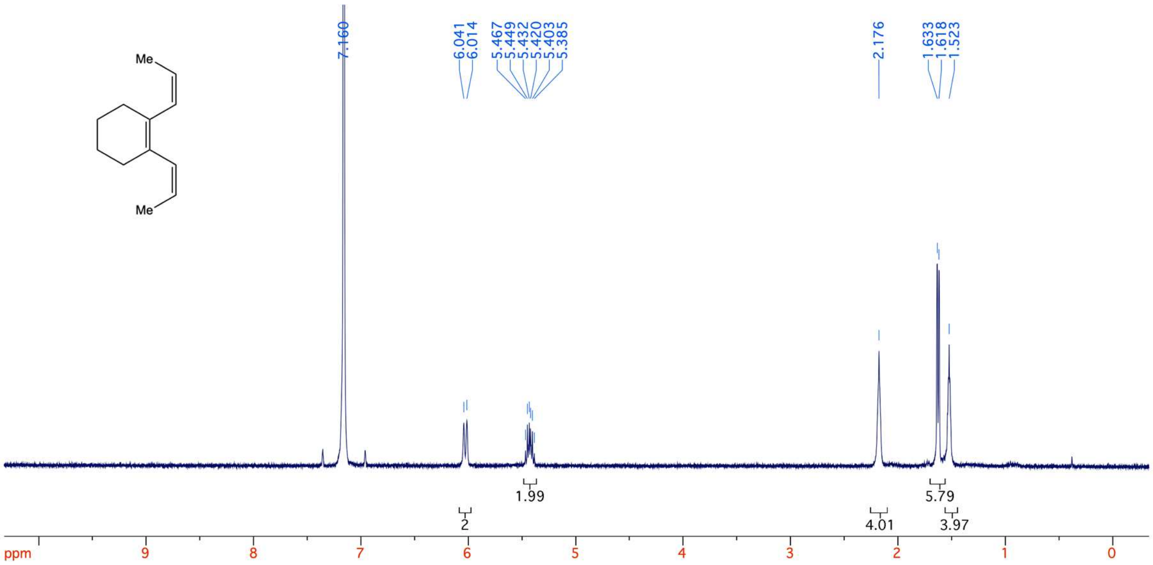


Figure 8. 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**8**), ^{1}H NMR spectrum (400 MHz, C_6D_6).

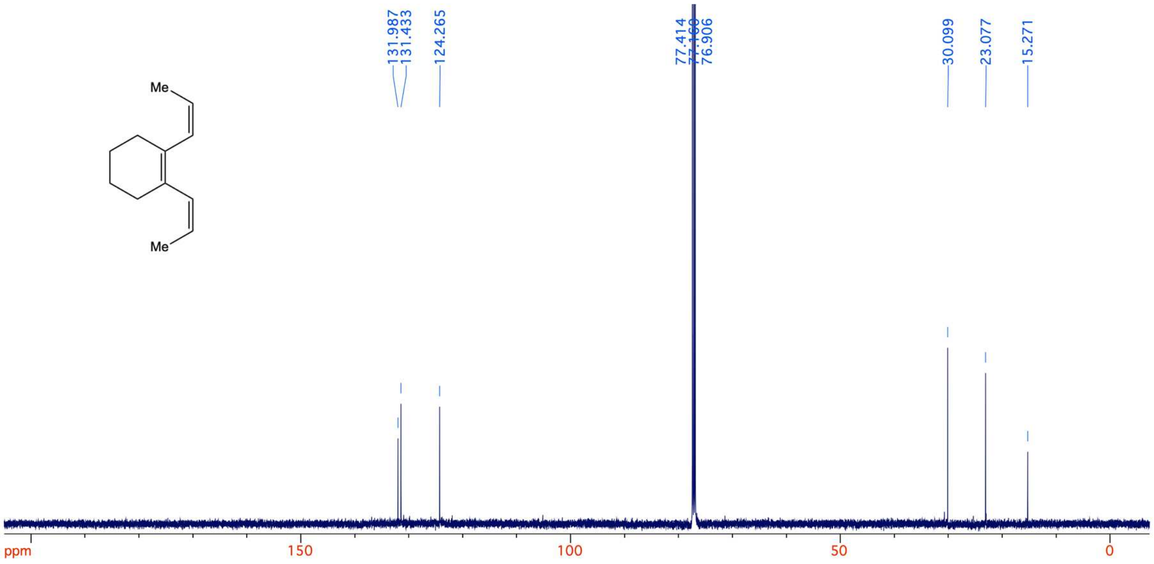


Figure 9. 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**8**), $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$).

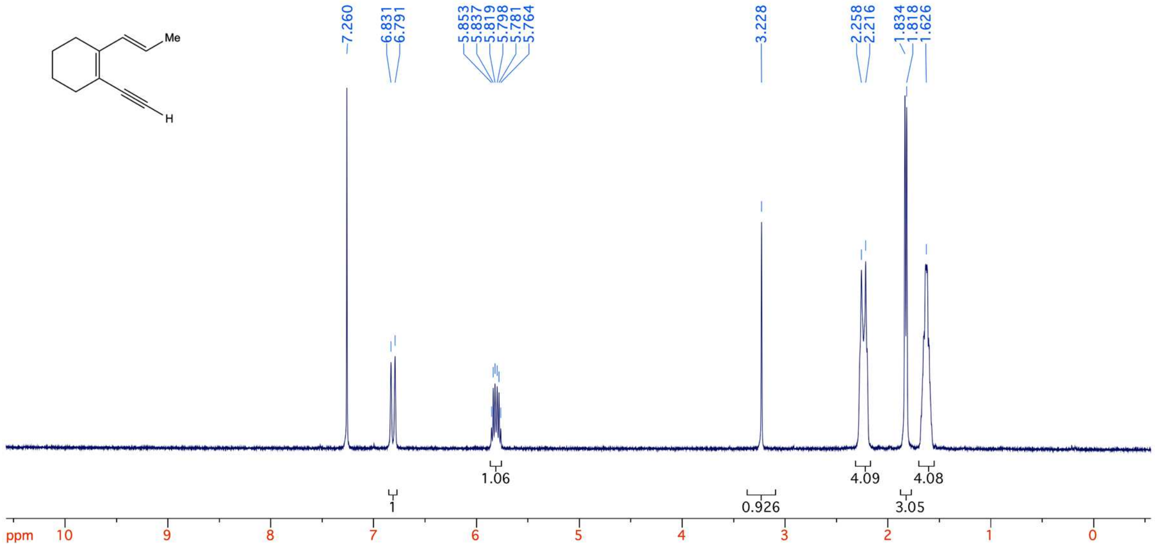


Figure 10. (*E*)-1-ethynyl-2-(prop-1-en-1-yl)cyclohex-1-ene (**11**), ^{1}H NMR spectrum (400 MHz, CDCl$_3$).

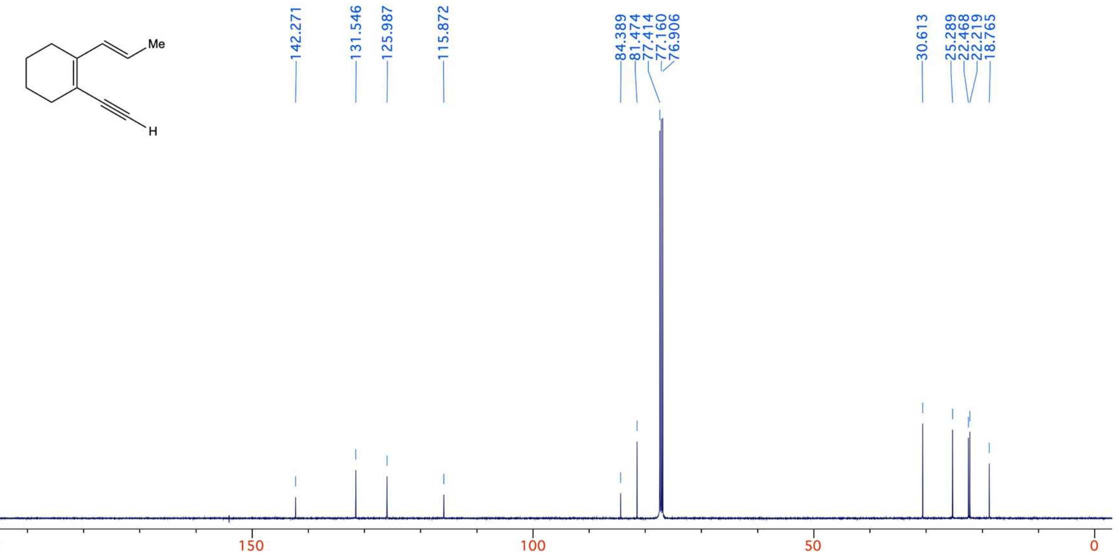


Figure 11. (*E*)-1-ethynyl-2-(prop-1-en-1-yl)cyclohex-1-ene (**11**), $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$).

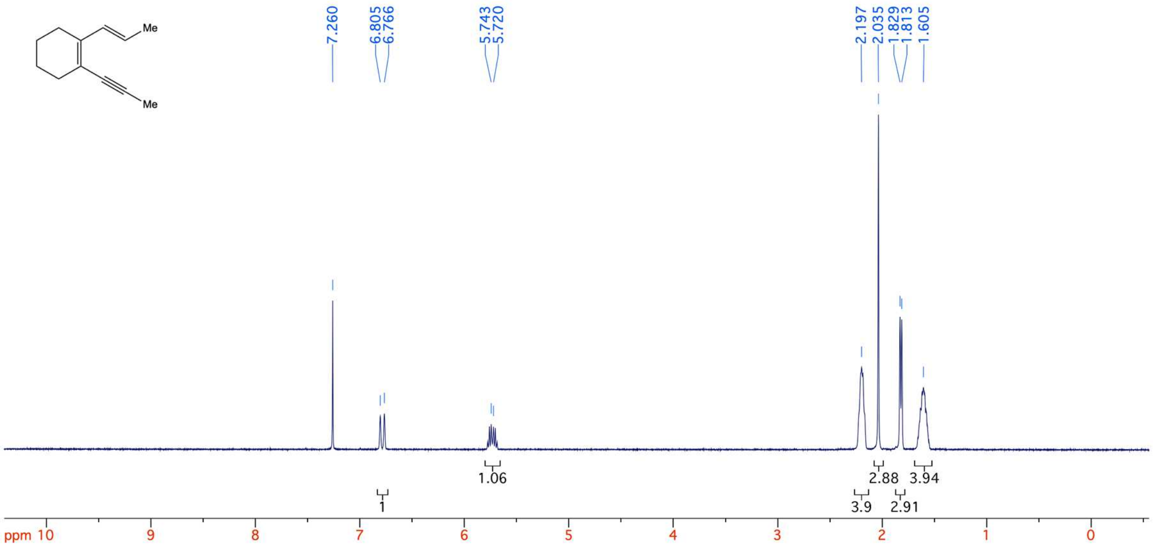


Figure 12. (*E*)-1-(prop-1-en-1-yl)-2-(prop-1-yn-1-yl)cyclohex-1-ene (**12**), ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

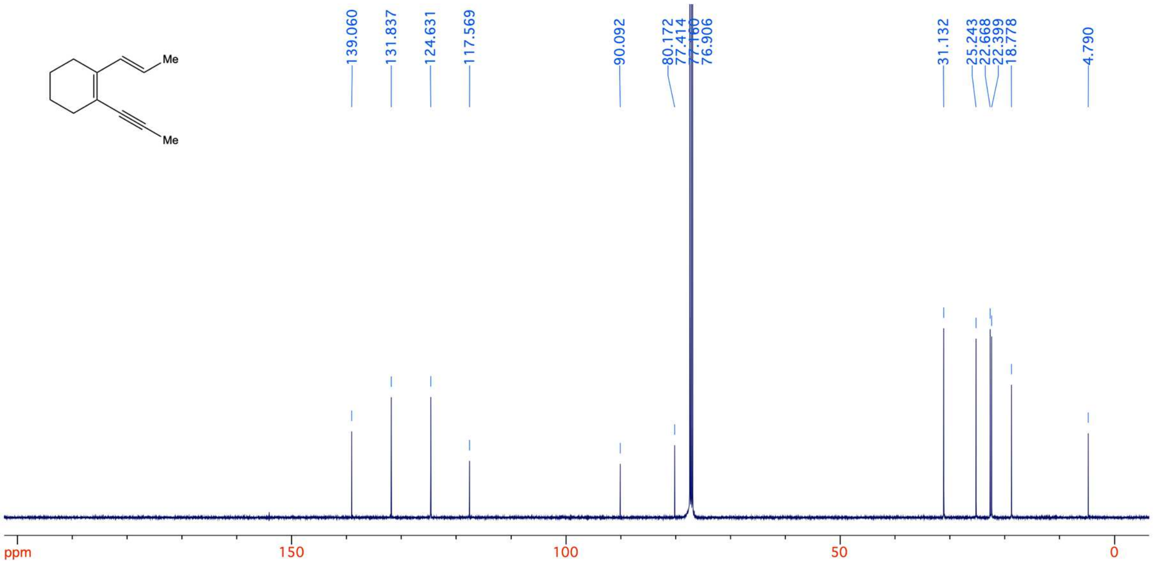


Figure 13. (*E*)-1-(prop-1-en-1-yl)-2-(prop-1-yn-1-yl)cyclohex-1-ene (**12**), $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$).

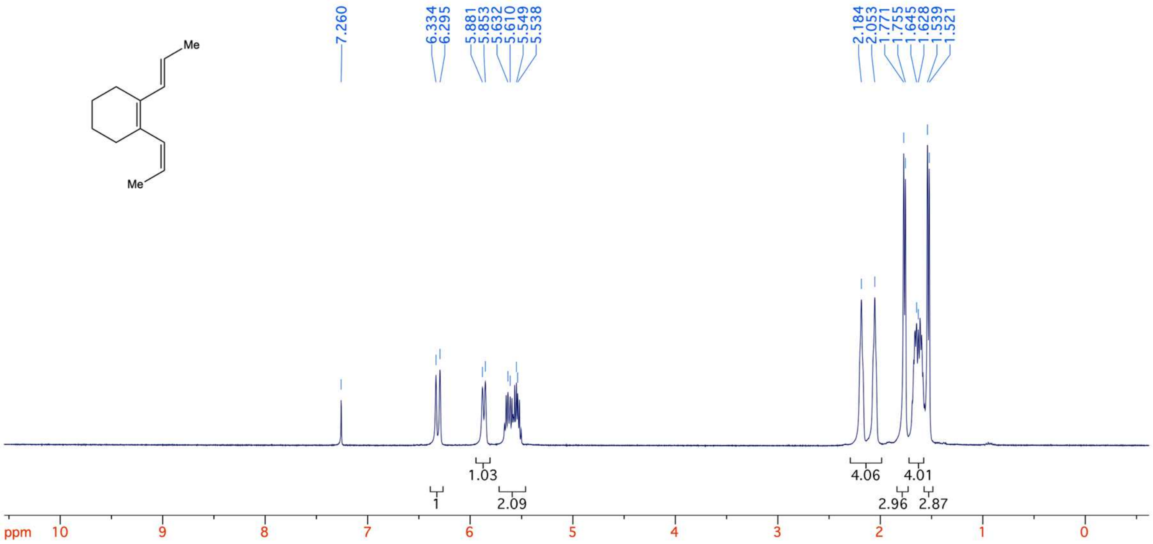


Figure 14. 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**), ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

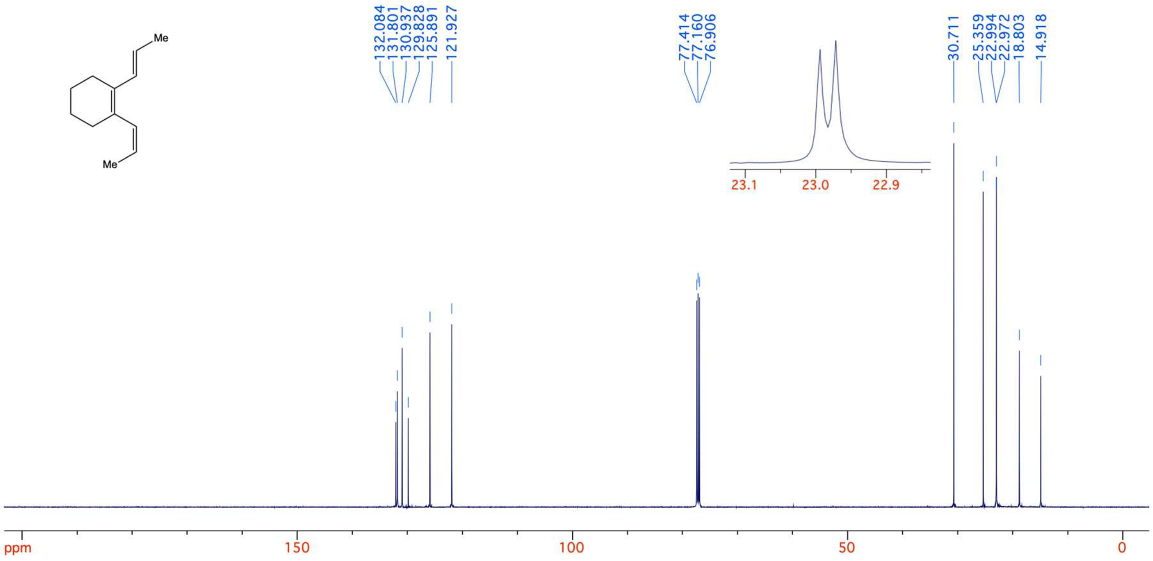


Figure 15. 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene (**13**), $^{13}C\{^1H\}$ NMR spectrum (500 MHz, $CDCl_3$).

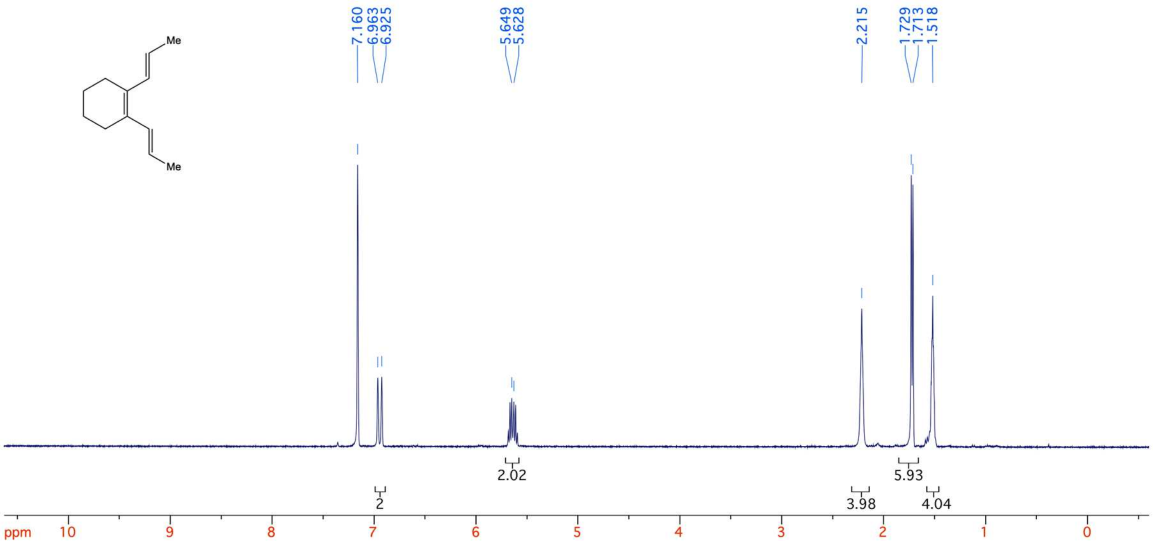


Figure 16. 1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene (**14**), ^{1}H NMR spectrum (400 MHz, C_6D_6).

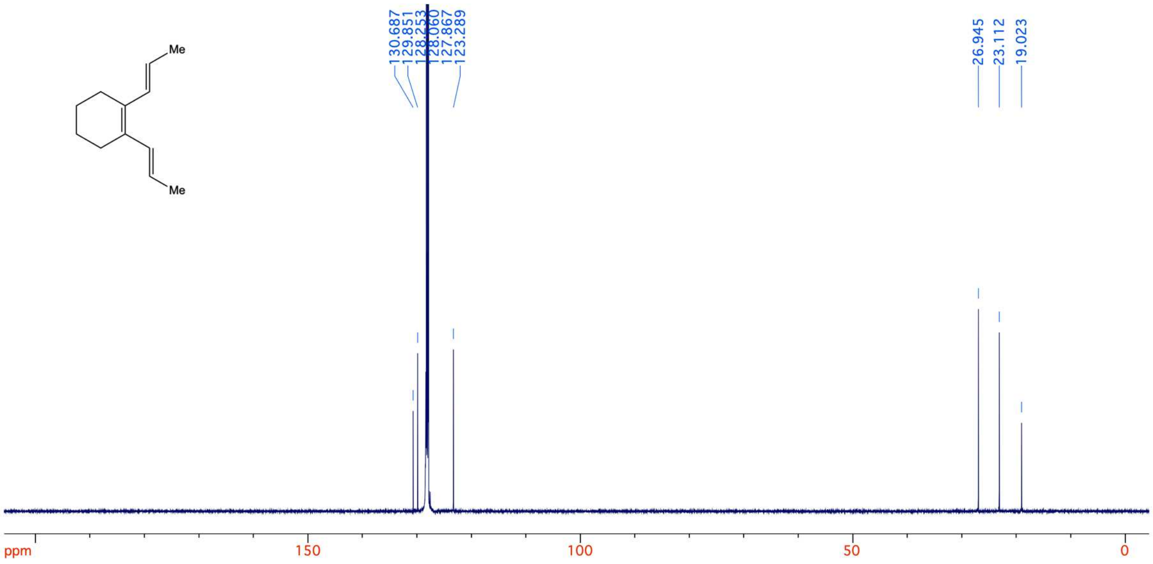


Figure 17. 1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene (**14**), $^{13}C\{^1H\}$ NMR spectrum (500 MHz, C_6D_6).

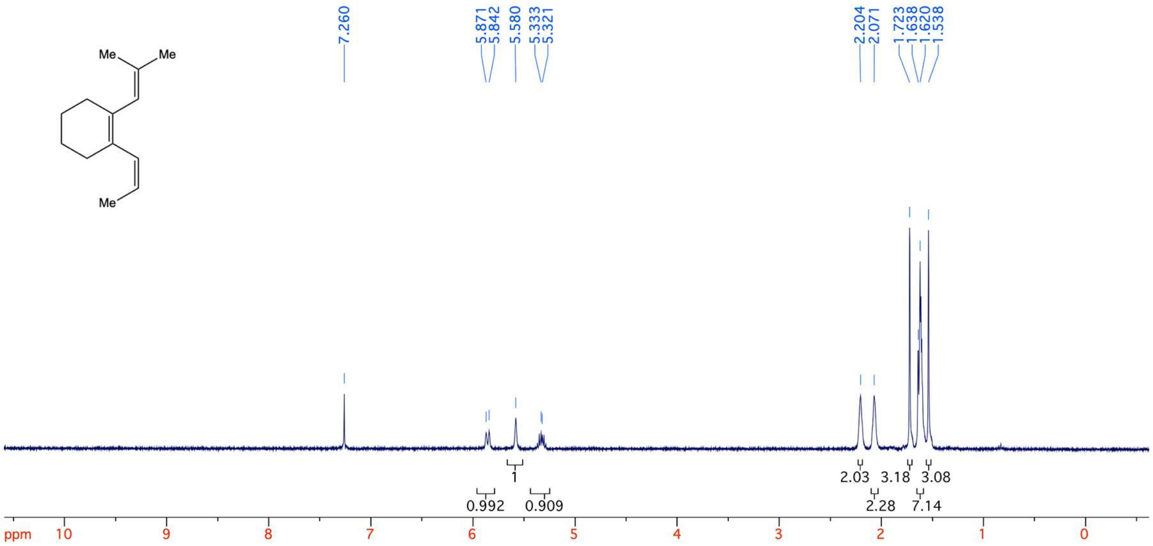


Figure 18. (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**), ^{1}H NMR spectrum (400 MHz, CDCl$_3$).

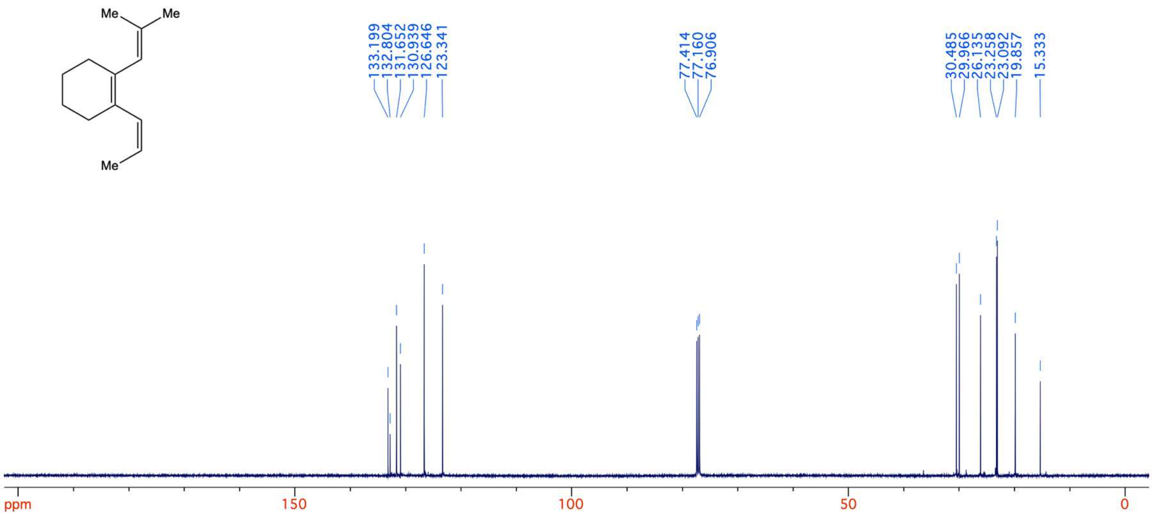


Figure 19. (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**17**), $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, $CDCl_3$).

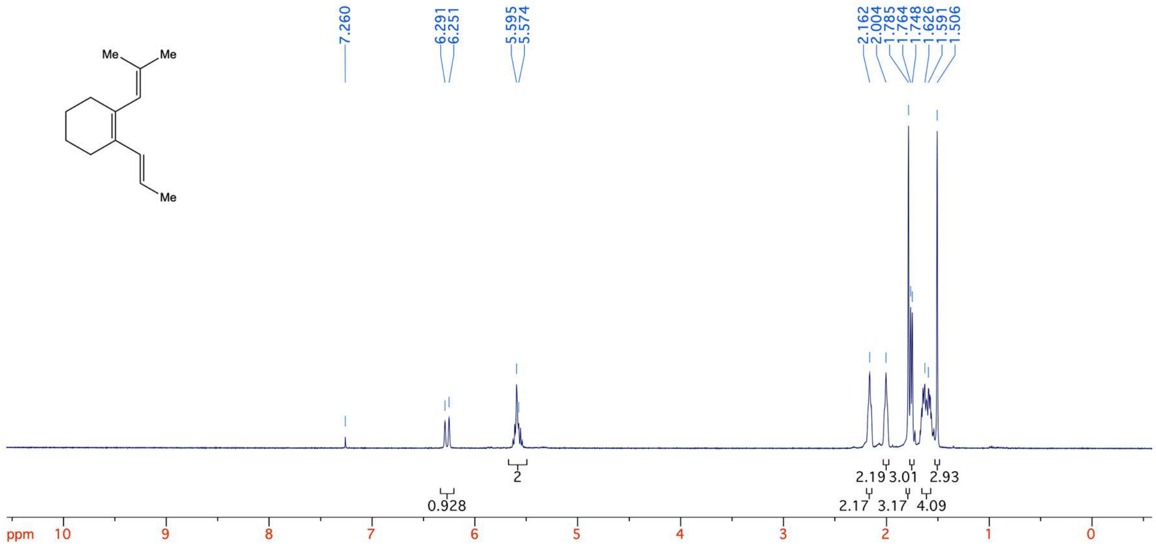


Figure 20. (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**18**), ^{1}H NMR spectrum (400 MHz, $CDCl_3$).

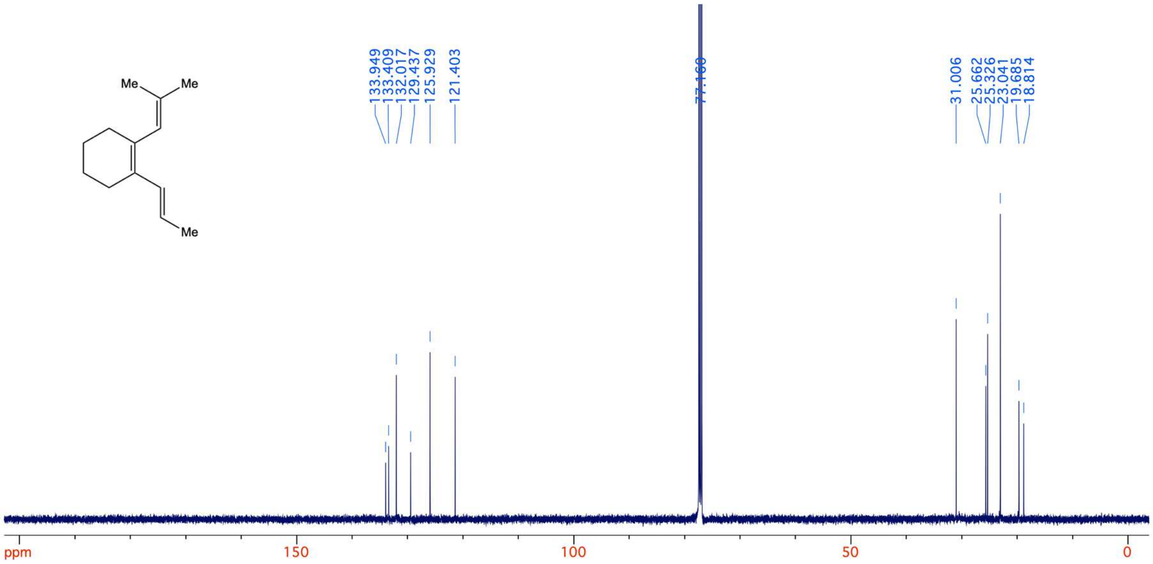


Figure 21. (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene (**18**), ^{13}C{^{1}H} NMR spectrum (500 MHz, CDCl$_3$).

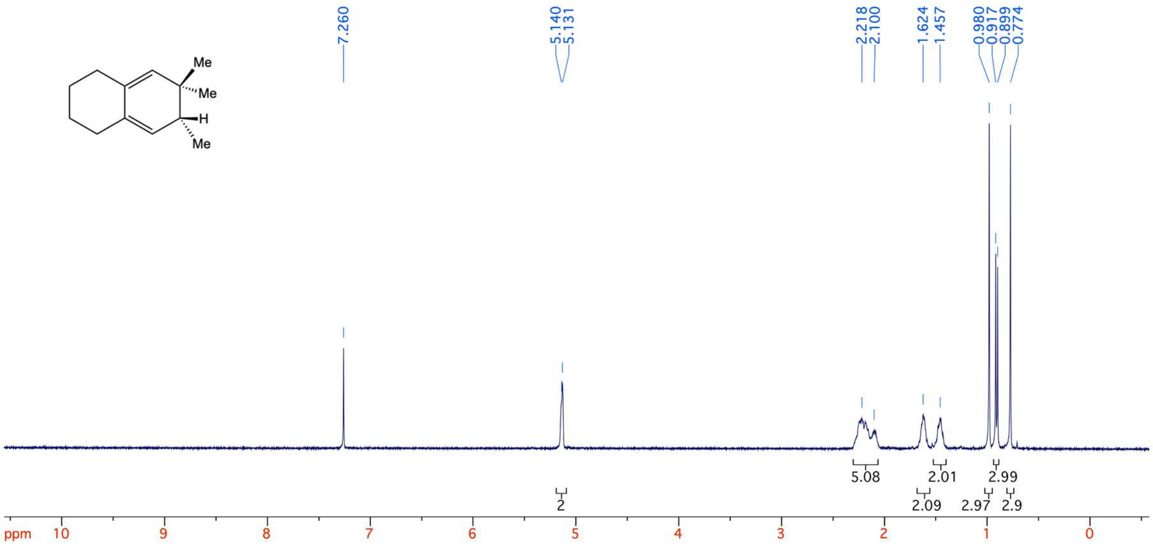


Figure 22. (R)-6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (**23-R/S**), ^{1}H NMR spectrum (400 MHz, CDCl$_3$).

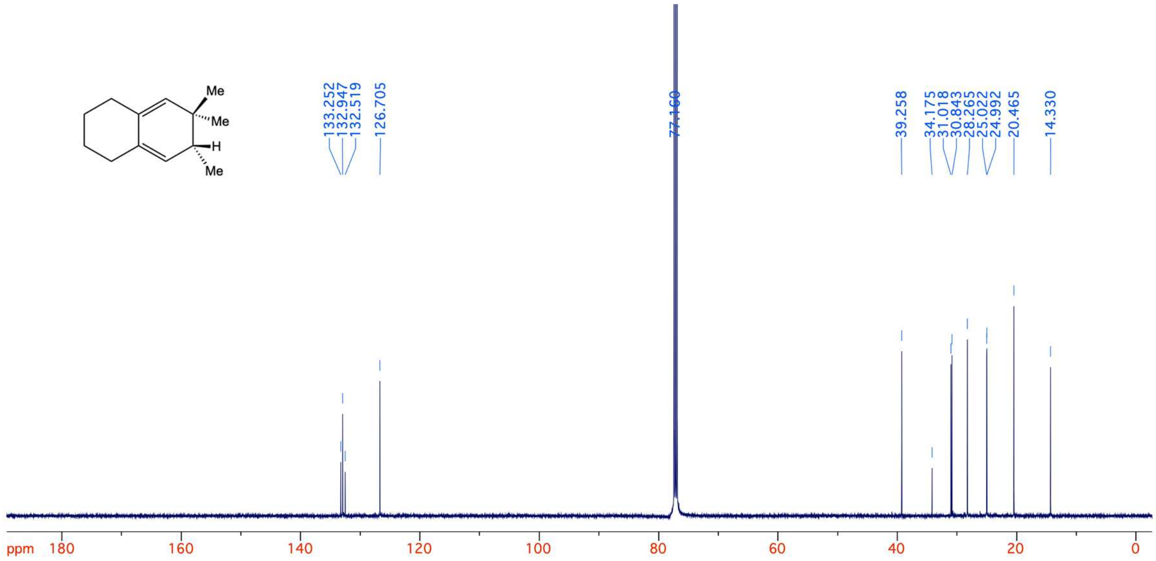


Figure 23. (R)-6,6,7-trimethyl-1,2,3,4,6,7-hexahydronaphthalene (**23-R/S**), $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, CDCl$_3$).

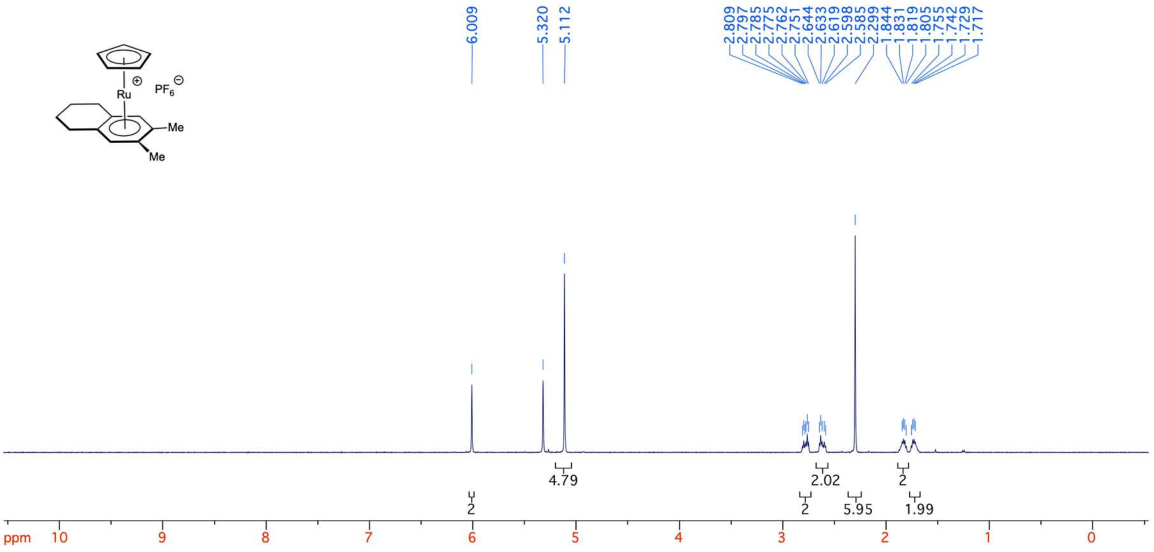


Figure 24. (η^5-cyclopentadienyl)(η^6-6,7-dimethyl-1,2,3,4-tetrahydronaphthalene)Ru hexafluorophosphate (**26**), ^{1}H NMR spectrum (400 MHz, CD_2Cl_2).

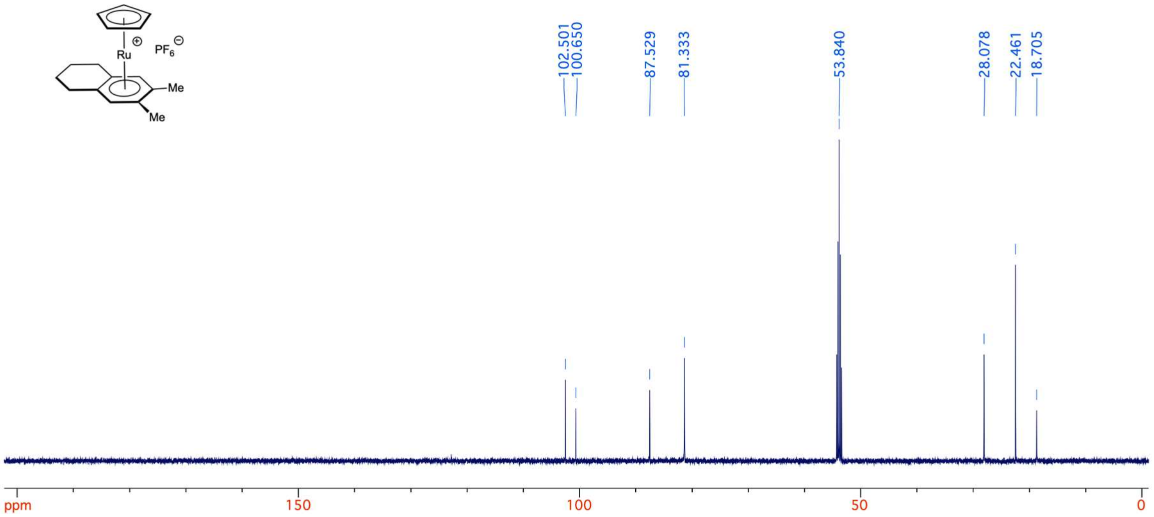


Figure 25. (η^5-cyclopentadienyl)(η^6-6,7-dimethyl-1,2,3,4-tetrahydronaphthalene)Ru hexafluorophosphate (**26**), $^{13}C\{^1H\}$ NMR spectrum (500 MHz, CD_2Cl_2).

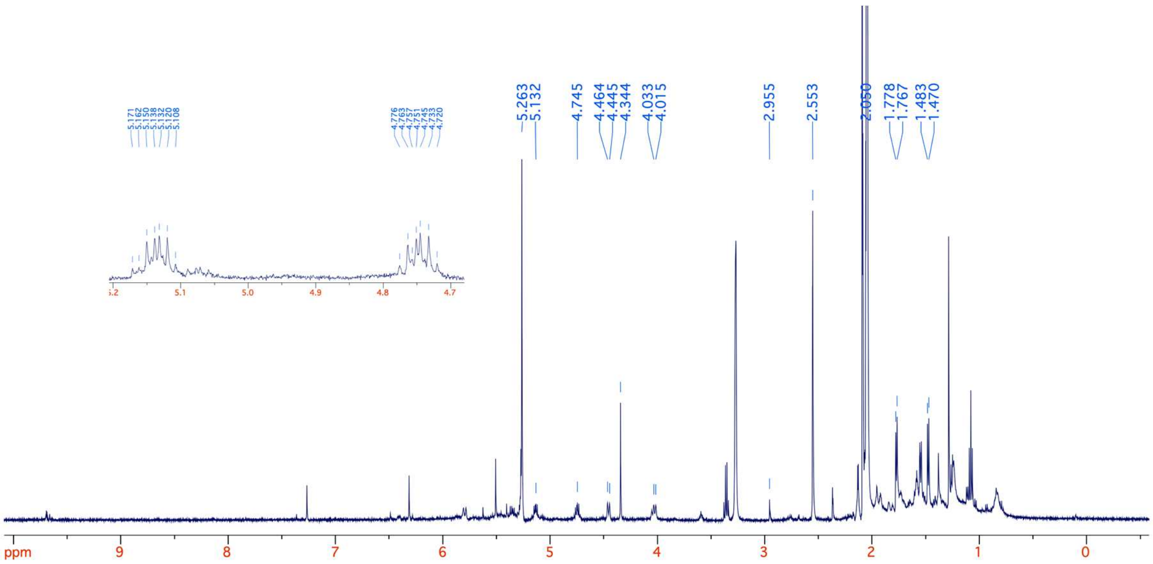


Figure 26. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of crude reaction mixture of **8** with [CpRu(NCMe)$_3$]PF$_6$ to generate (η^5-cyclopentadienyl)(η^4-1,2-di((Z)-prop-1-en-1-yl)cyclohex-1-ene)Ru acetonitrile hexafluorophosphate intermediate (**25**) in acetone-d_6.

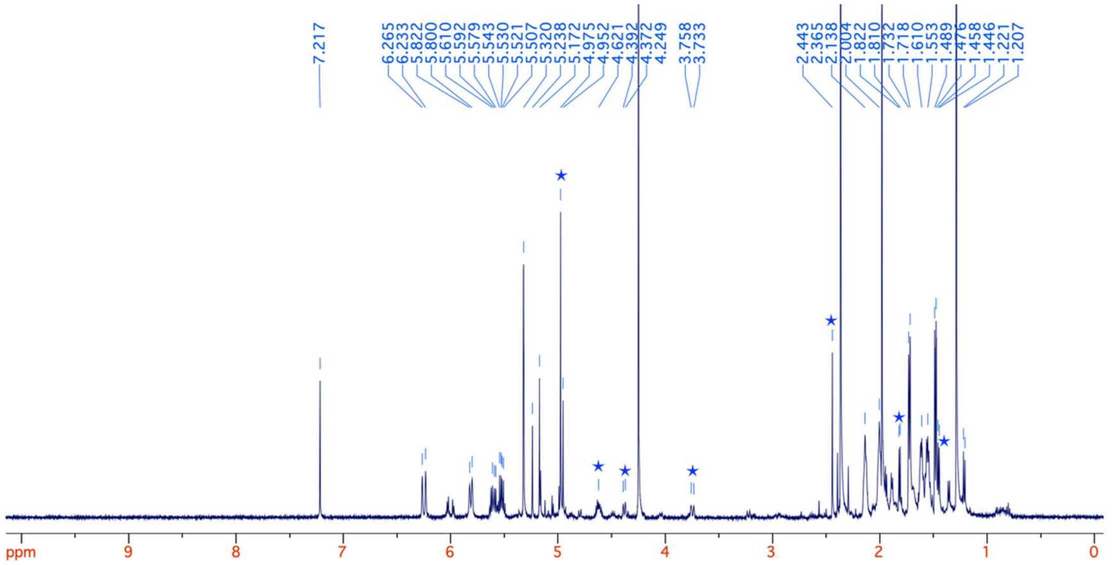


Figure 27. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **13** with $[CpRu(NCMe)_3]PF_6$ to generate complex **28** (labeled with blue star) at – 20 ˚C in dichloromethane-d_2.

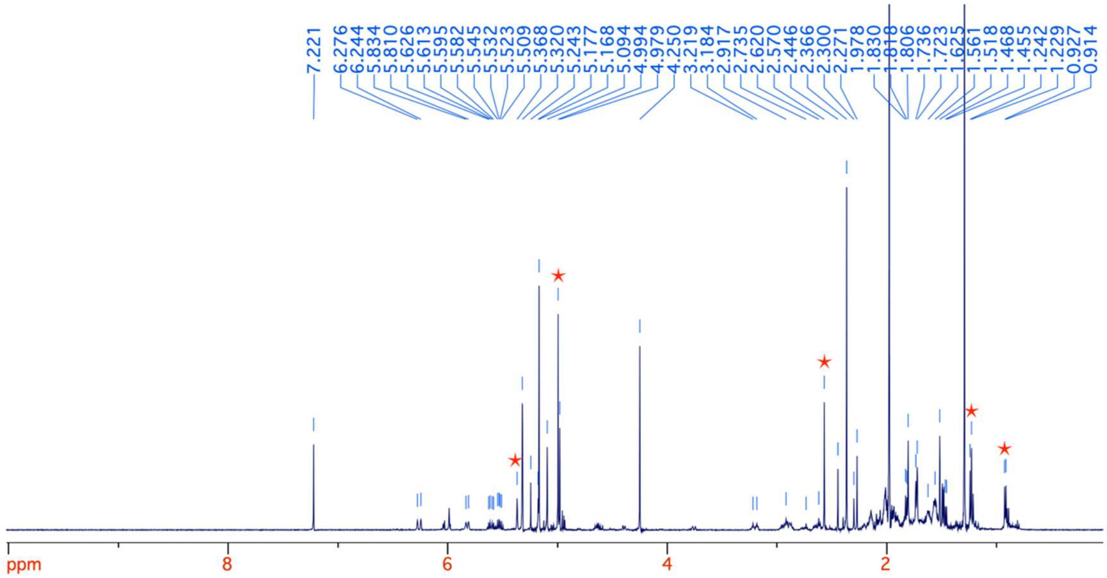


Figure 28. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **13** with $[CpRu(NCMe)_3]PF_6$ to generate complex **29** (labeled with red star) at – 10 ˚C in dichloromethane-d_2.

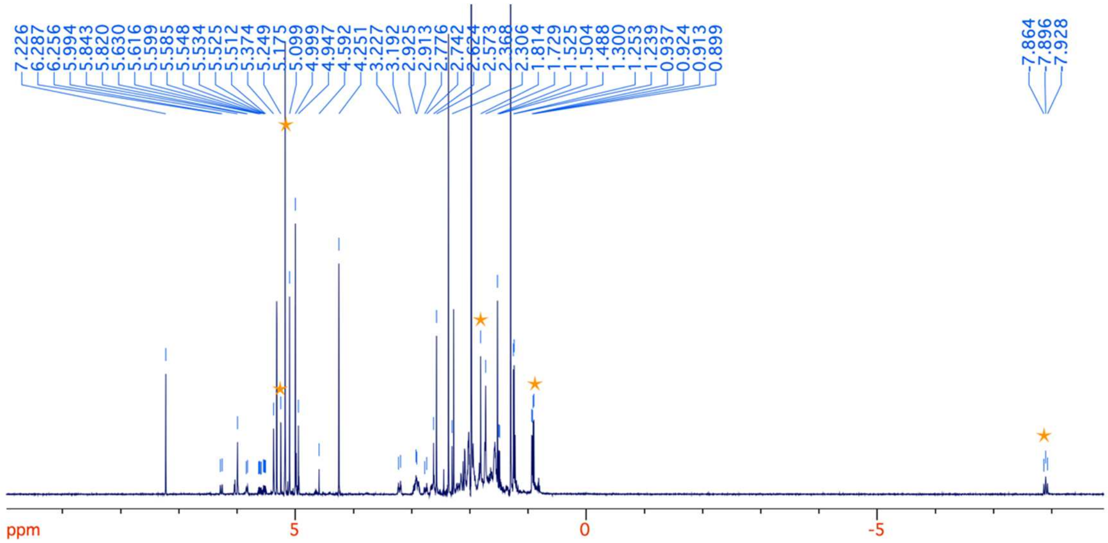


Figure 29. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **13** with $[CpRu(NCMe)_3]PF_6$ to generate complex **30** (labeled with orange star) at 0 ˚C in dichloromethane-d_2.

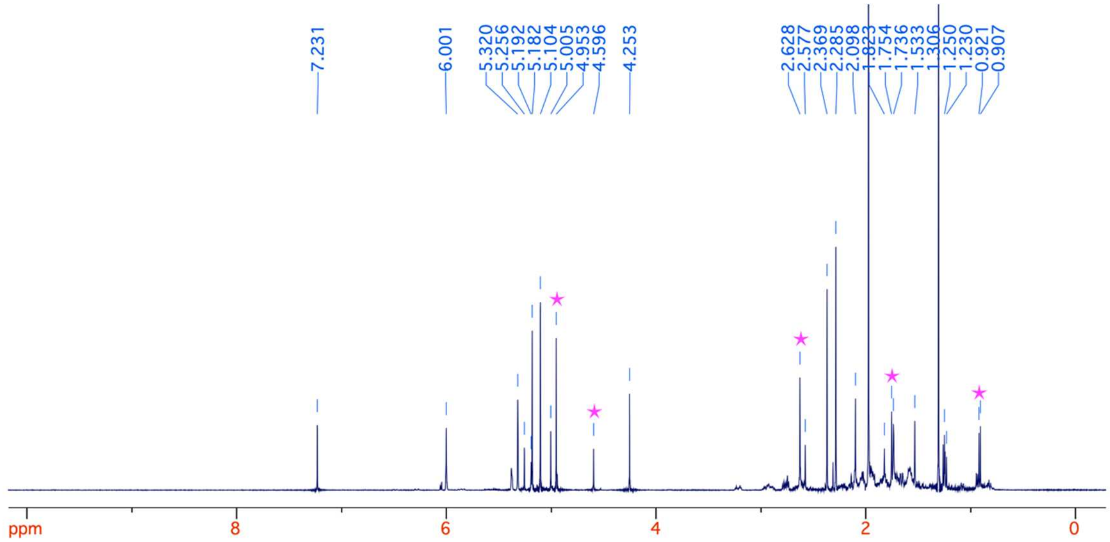


Figure 30. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **13** with $[CpRu(NCMe)_3]PF_6$ to generate complex **31** (labeled with pink star) at 10 ˚C in dichloromethane-d_2.

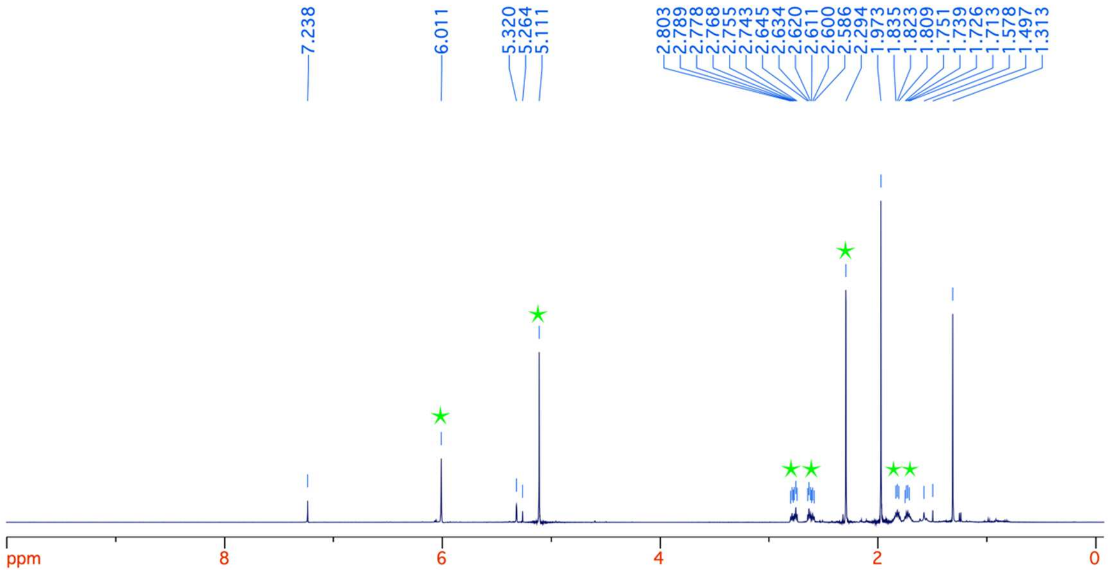


Figure 31. 1H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **13** with $[CpRu(NCMe)_3]PF_6$ to generate complex **26** (labeled with green star) at 23 ˚C in dichloromethane-d_2.

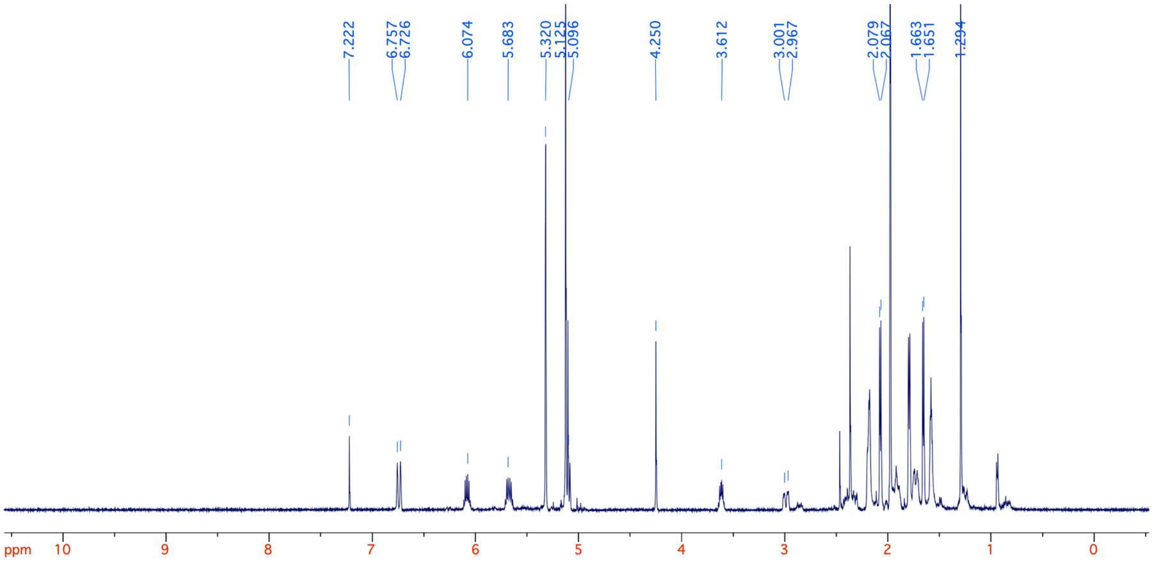


Figure 32. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of crude reaction mixture of **14** with $[CpRu(NCMe)_3]PF_6$ to generate (η^5-cyclopentadienyl)(η^6-1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene)Ru hexafluorophosphate intermediate (**33**) in dichloromethane-d_2.

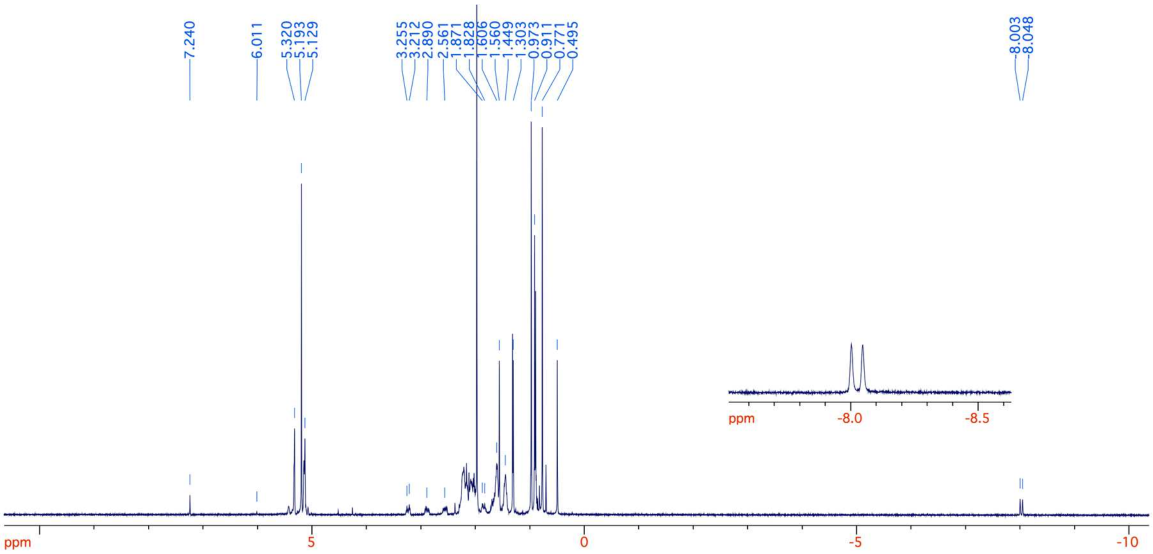


Figure 33. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of crude reaction mixture of **17** with $[CpRu(NCMe)_3]PF_6$ to generate (η^5-cyclopentadienyl)(η^6-6,6,7-trimethyl-1,2,3,4,5,6-hexahydronaphthalene) Ru(II) hexafluorophosphate (**41**) intermediate in dichloromethane-d_2.

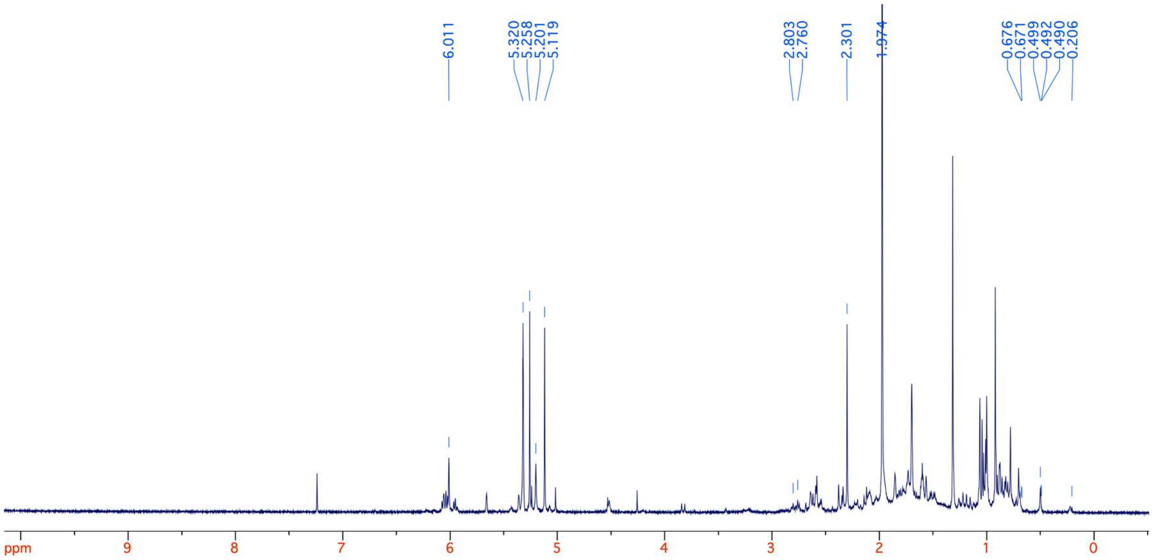


Figure 34. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of crude reaction mixture of **17** with $[CpRu(NCMe)_3]PF_6$ to generate (η^5-cyclopentadienyl)(η^6-6,7-dimethyl-1,2,3,4-tetrahydronaphthalene)Ru hexafluorophosphate (**26**) in dichloromethane-*d*$_2$.

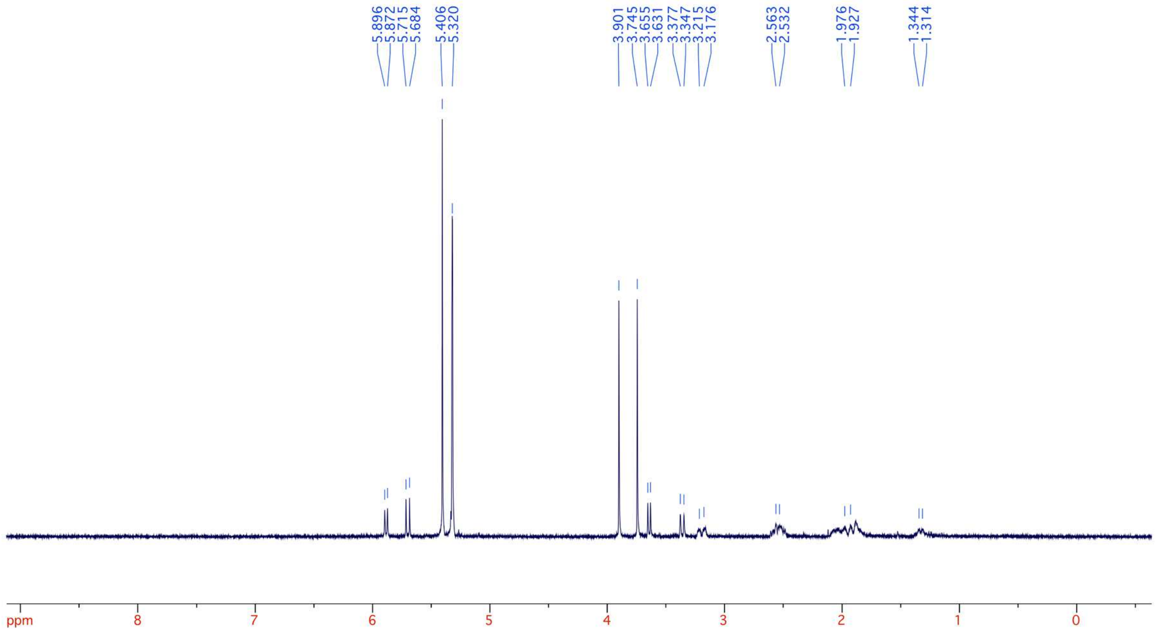


Figure 35. ^{1}H NMR spectrum (DCM, 400 MHz) of **46**.

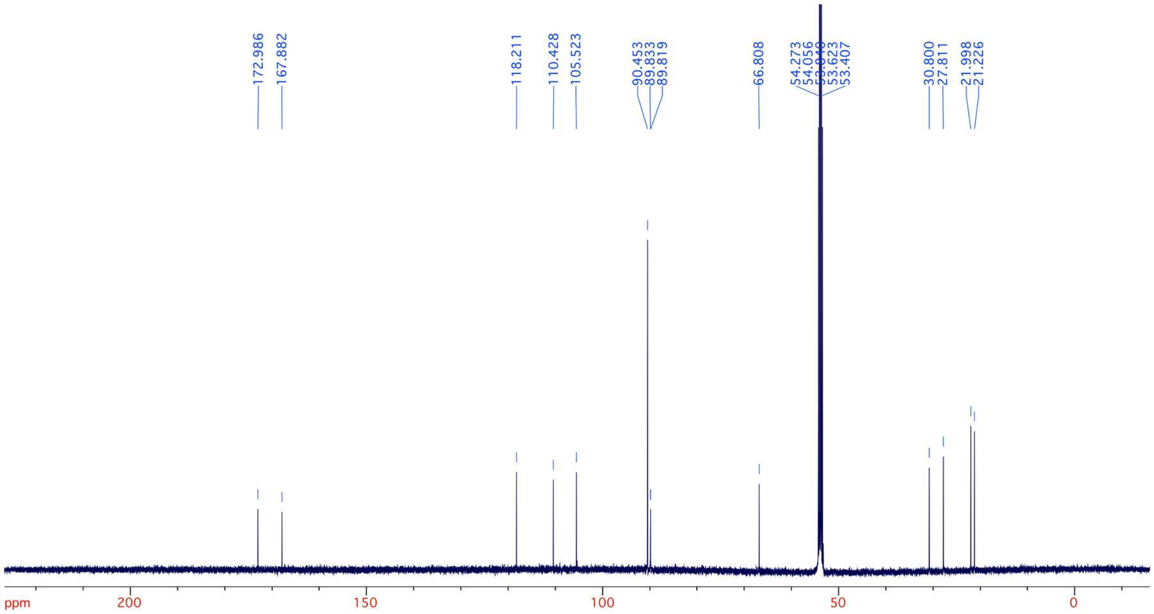


Figure 36. $^{13}C\{^1H\}$ NMR spectrum (DCM, 500 MHz) of **46**.

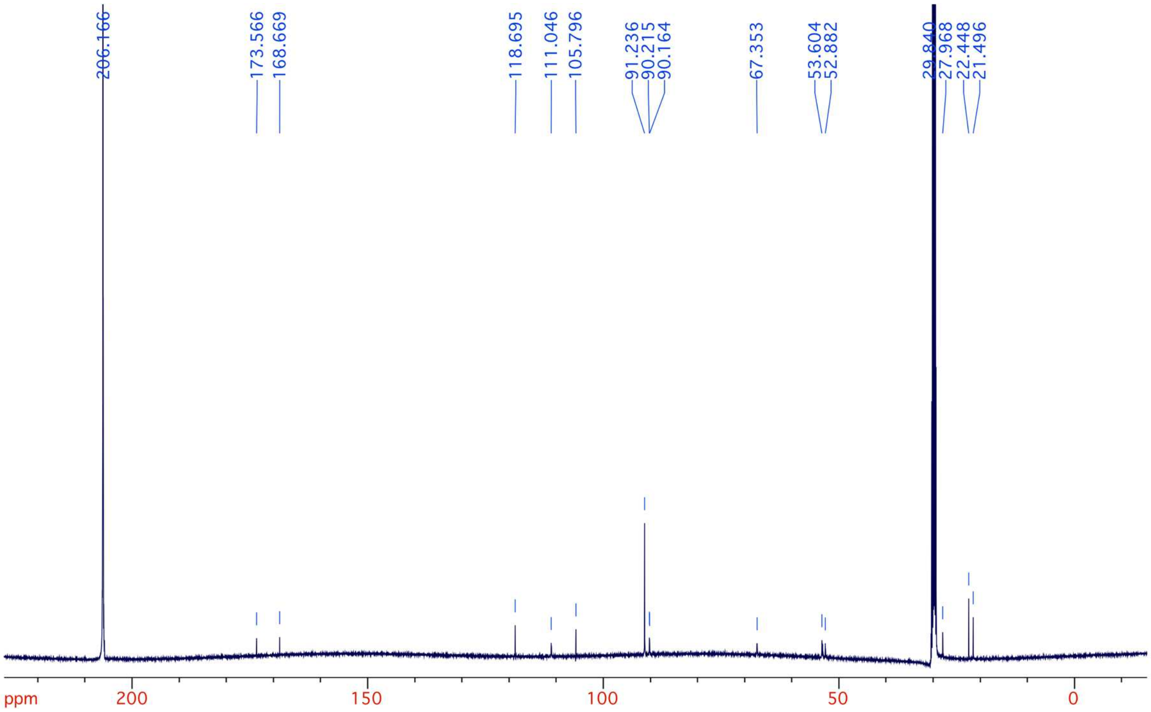


Figure 37. $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6, 500 MHz) of **46**.

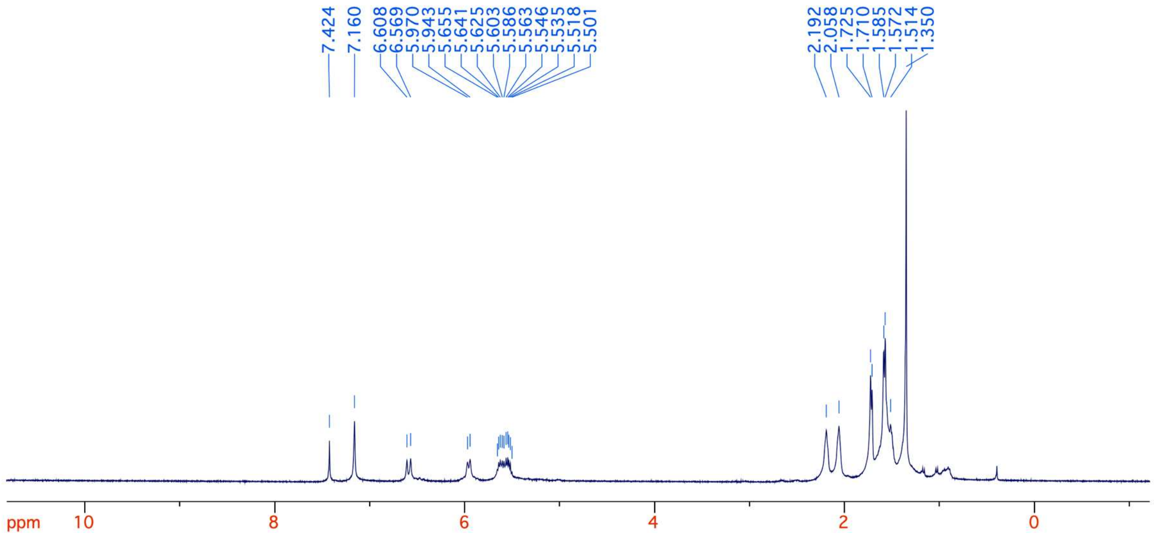


Figure 38. ^{1}H NMR (benzene-d_6, 400 MHz) spectrum of crude reaction mixture of heating 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 1 h.

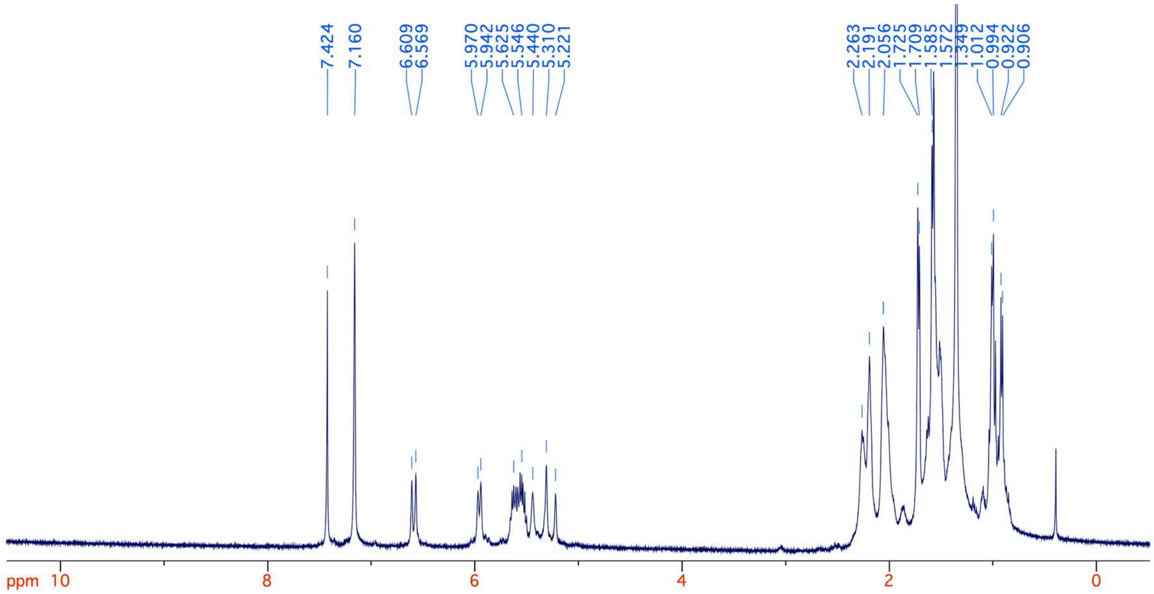


Figure 39. ^{1}H NMR (benzene-d_6, 400 MHz) spectrum of crude reaction mixture of heating 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 9 days.

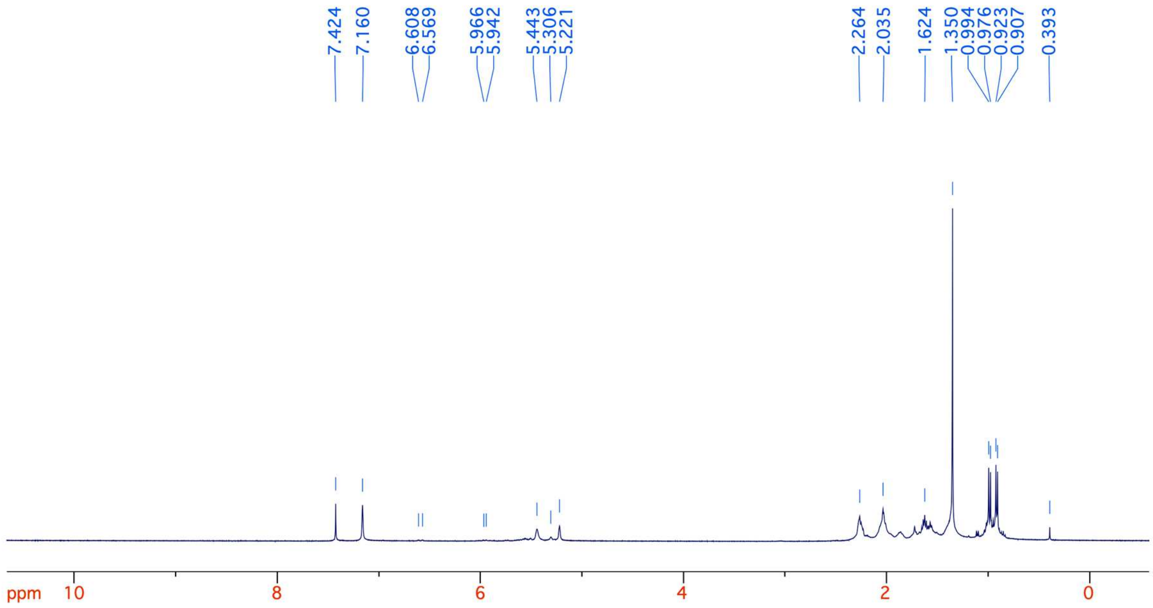


Figure 40. ^{1}H NMR (benzene-d_6, 400 MHz) spectrum of crude reaction mixture of heating 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 29 days.

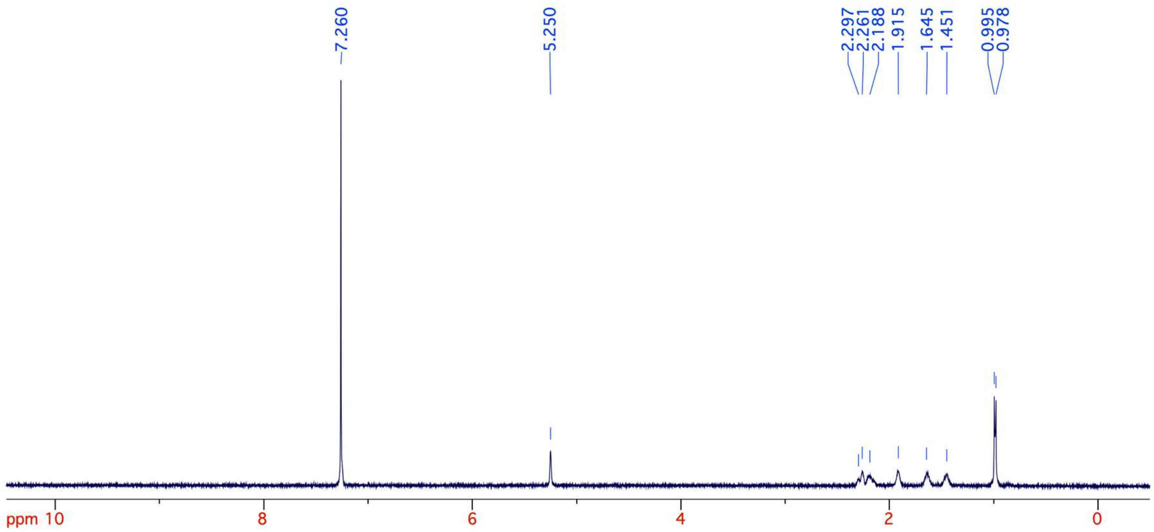


Figure 41. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 6,7-dimethyl-1,2,3,4,6,7-hexahydronaphthalene.

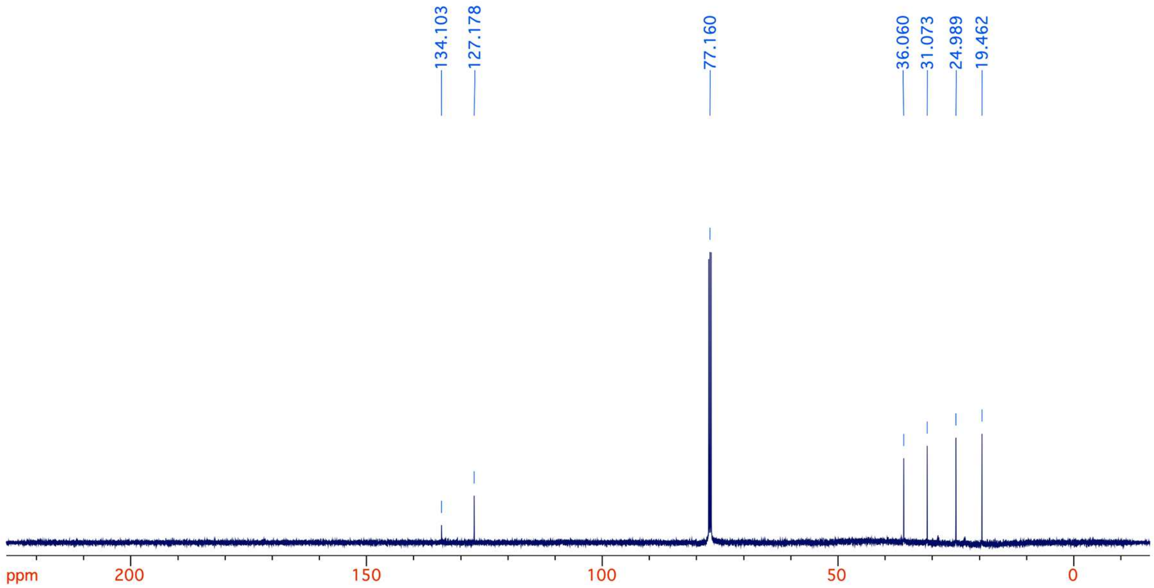


Figure 42. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) spectrum of 6,7-dimethyl-1,2,3,4,6,7-hexahydronaphthalene.

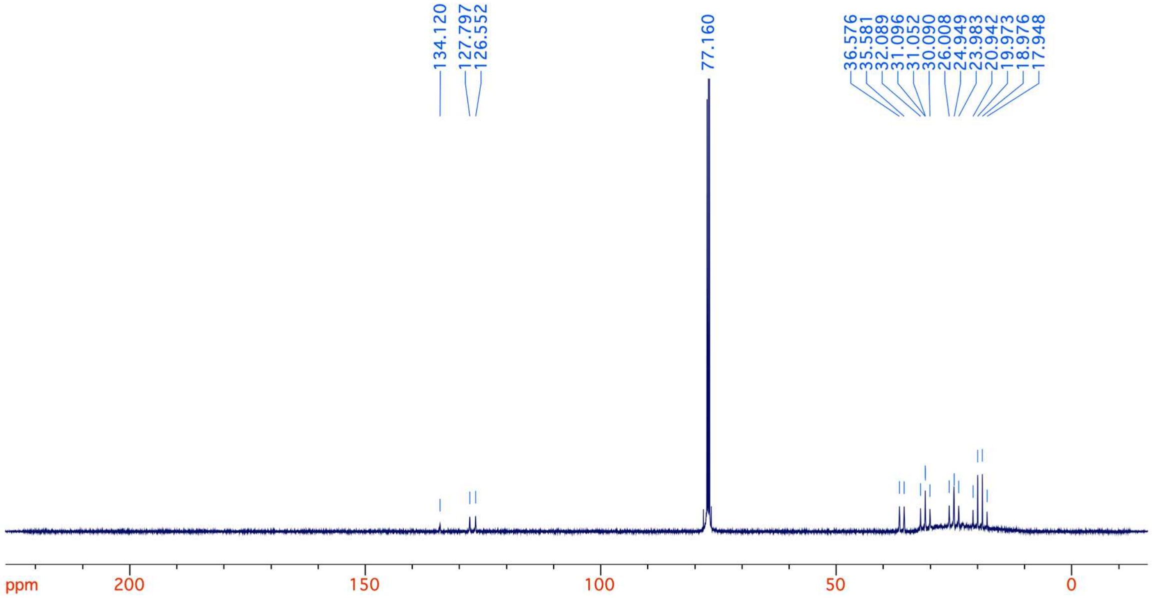


Figure 43. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of 6,7-dimethyl-1,2,3,4,6,7-hexahydronaphthalene.

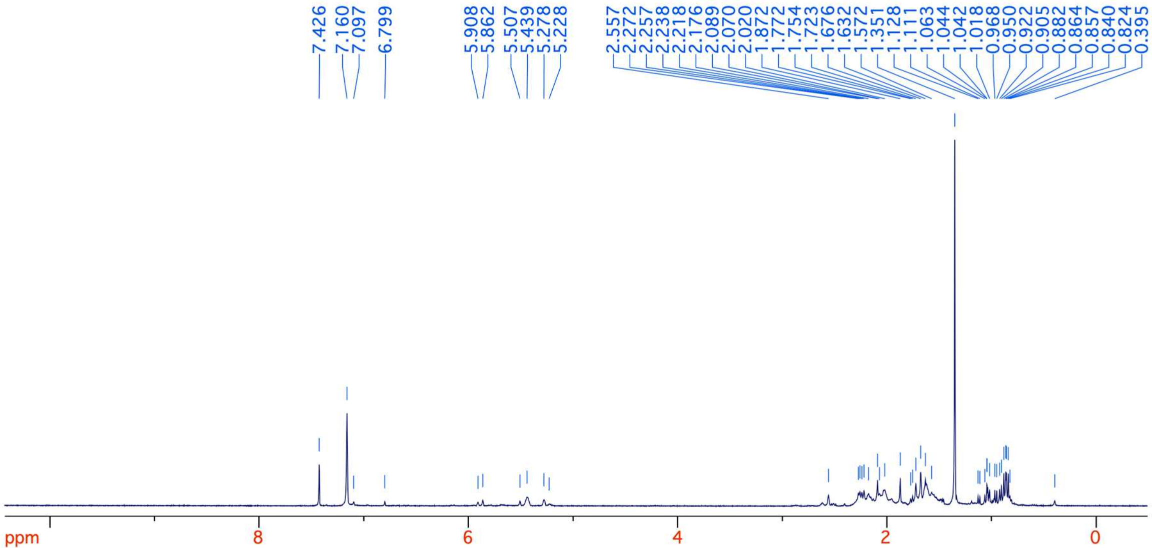


Figure 44. ^{1}H NMR (benzene-d_6, 400 MHz) spectrum of crude reaction mixture of heating 1,2-di((*E*)-prop-1-en-1-yl)cyclohex-1-ene for 5 days.

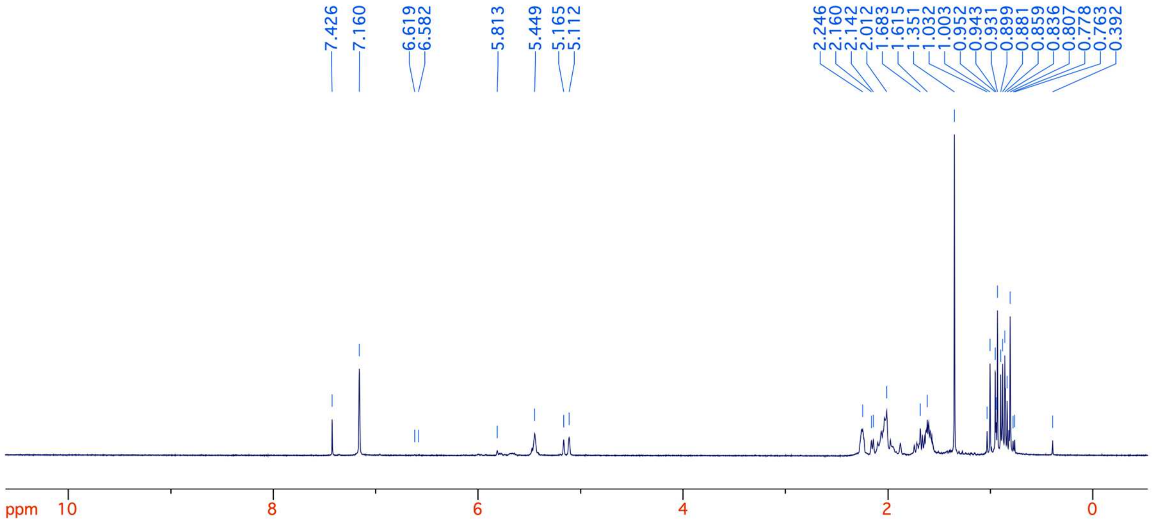


Figure 45. ^{1}H NMR (benzene-d_6, 400 MHz) spectrum of crude reaction mixture of heating (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene for 15 days.

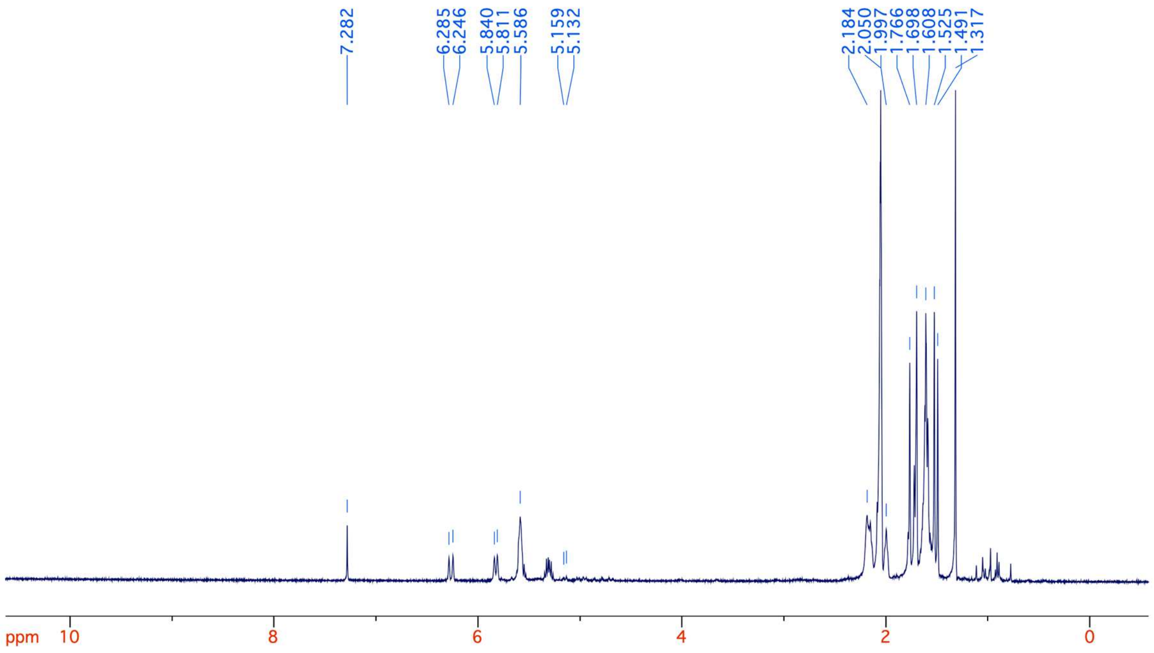


Figure 46. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene for 2 h.

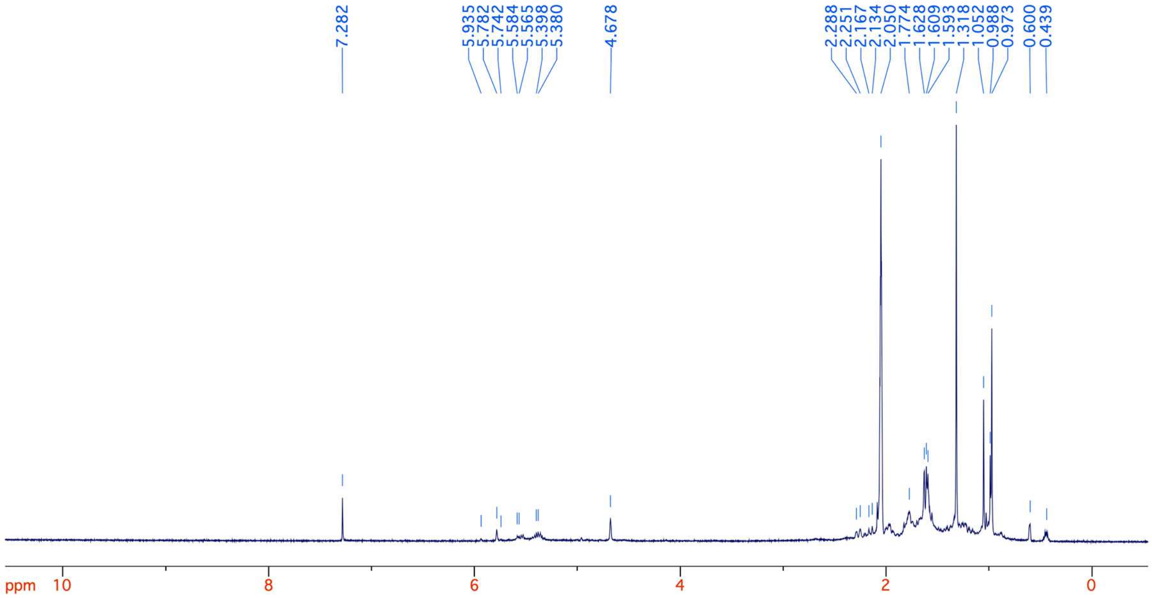


Figure 47. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing (*Z*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene for 4 days.

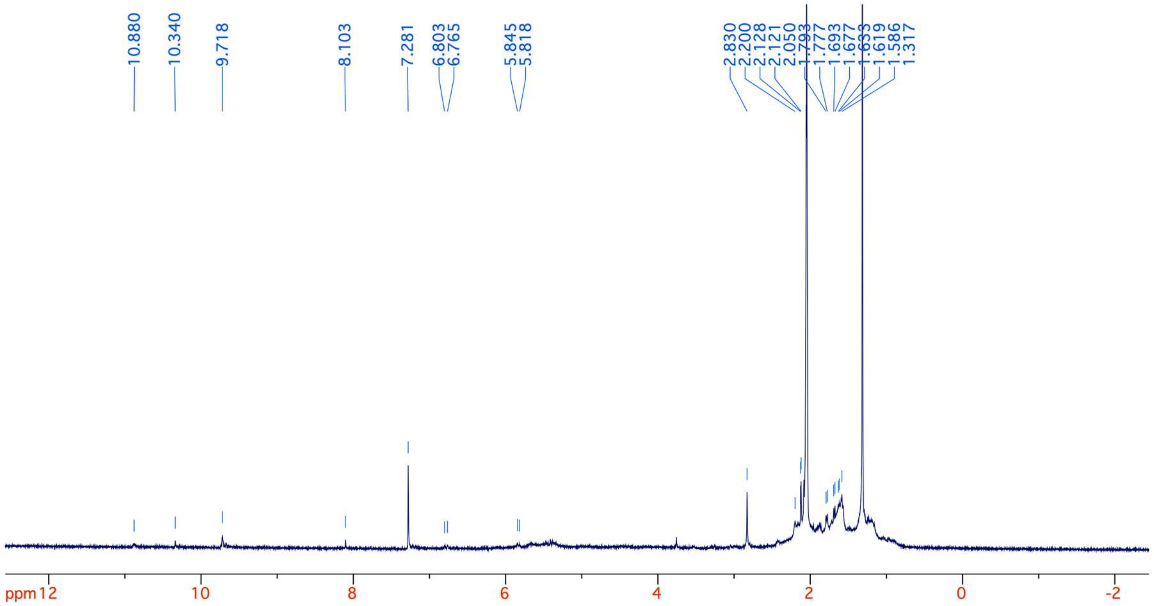


Figure 48. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 200 min.

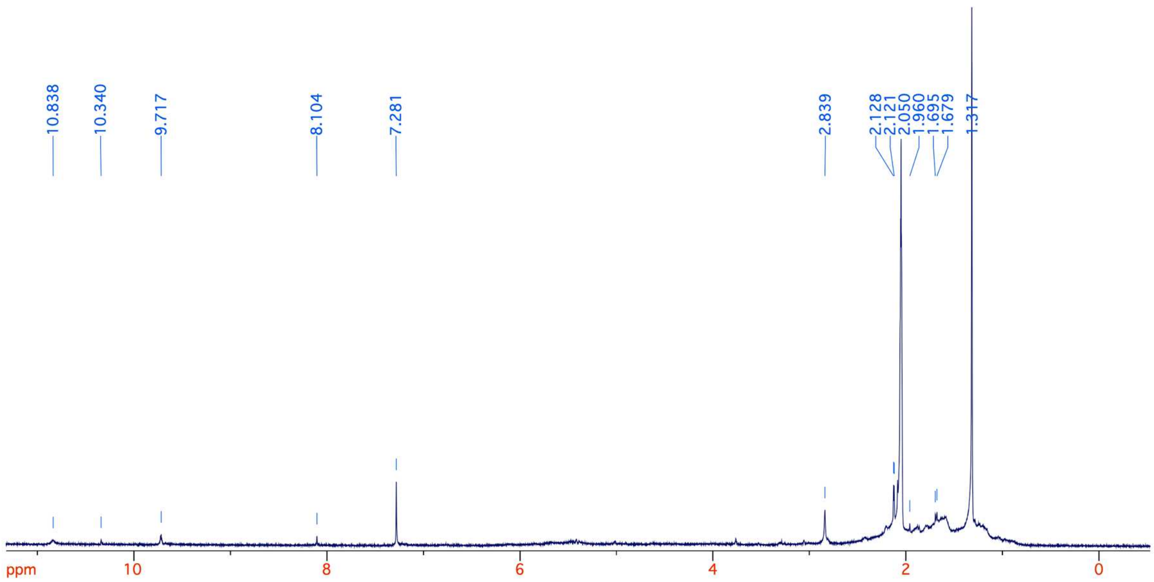


Figure 49. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing 1,2-di((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 6.5 h.

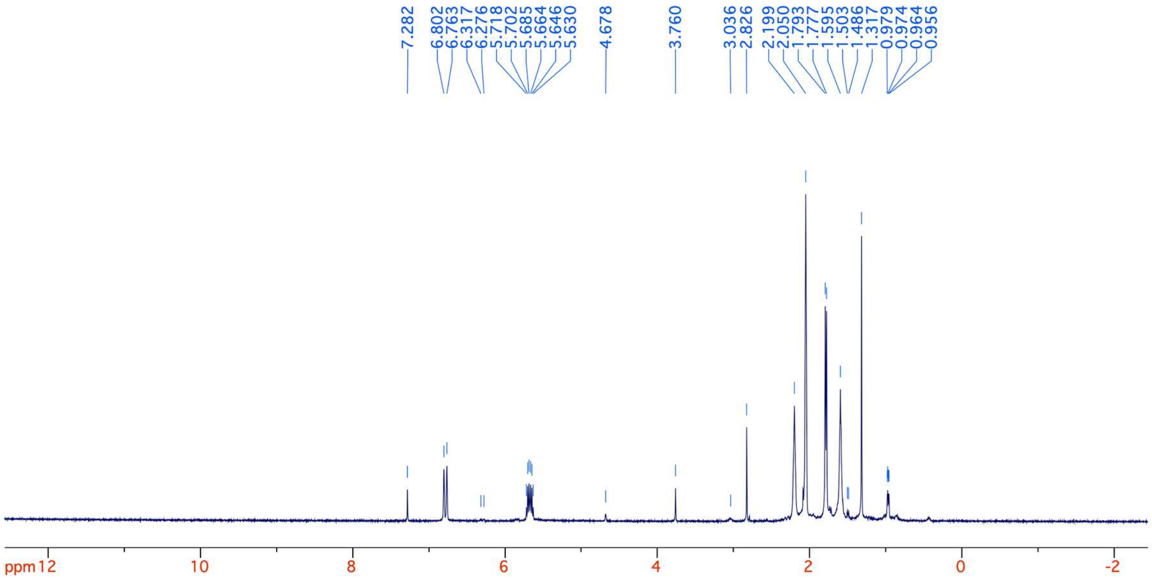


Figure 50. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 2 days.

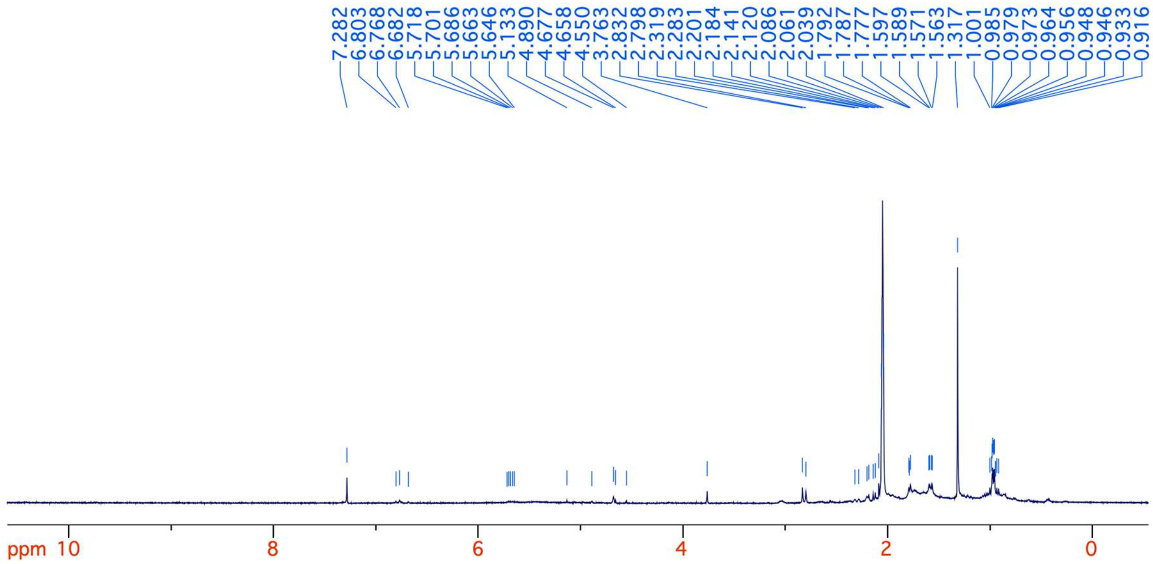


Figure 51. ^{1}H NMR (acetone -d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing 1-((*E*)-prop-1-en-1-yl)-2-((*Z*)-prop-1-en-1-yl)cyclohex-1-ene for 35 days.

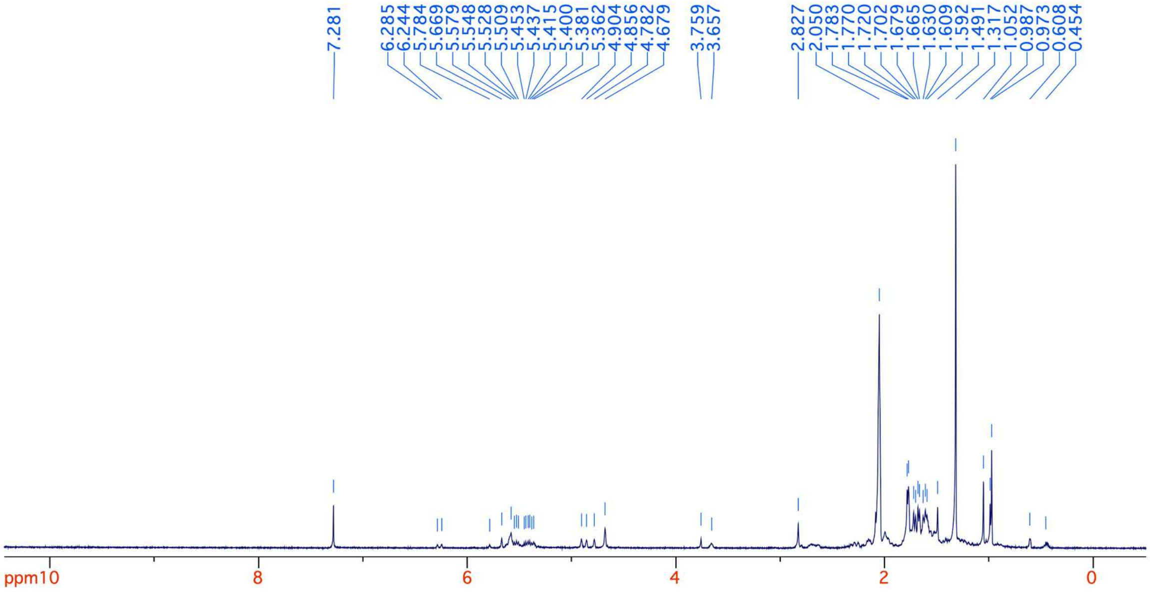


Figure 52. ^{1}H NMR (acetone-d_6, 400 MHz) spectrum of crude reaction mixture of photolyzing (*E*)-1-(2-methylprop-1-en-1-yl)-2-(prop-1-en-1-yl)cyclohex-1-ene for 7 days.

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