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# Ene di- and trimerization of 1-methyl-2-phenylcyclopropene

Hung-Chun Lin, Ru-Ting Tsai, Hsiao-Pin Wu, Hsin-Yi Lee, Gon-Ann Lee *

*Department of Chemistry, Fu Jen Catholic University Xinzhuang, New Taipei 24205, Taiwan, ROC*

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ABSTRACT

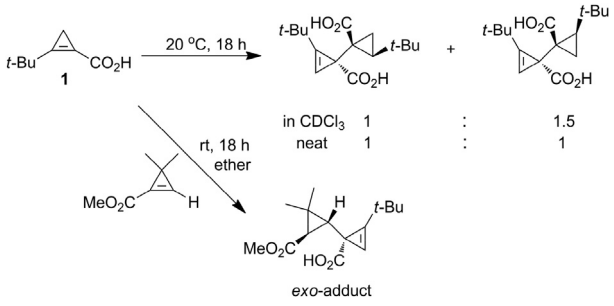
1,2-Disubstituted cyclopropene, 1-methyl-2-phenylcyclopropene (**18**), was generated by bromo-lithium exchange of 1-bromo-2-phenylcyclopropene followed by treatment with methyl iodide. Compound **18** was oxidized by oxygen to give the α,β-unsaturated carbonyl product **25** and diketone **27** and the tautomeric, β-hydroxyl-α,β-unsaturated ketone **28**. However, compound **28** reacted further with the cyclopropene **18** in a retro-Claisen-like reaction to generate adduct **26**. Furthermore, compound **18** underwent ene dimerization in neat condition to form the *endo*-dimer **40** and *exo*-dimer **41** followed by oxidization with oxygen to give aldehyde **39**. It is noteworthy that the *endo*-dimer **40** and *exo*-dimer **41** could be trapped with thiophenol to give adduct **42** and **43**. In addition, the ene reaction of *exo*-dimer **41** with monomer **18** gave an *exo-exo* ene trimer **46** through an *exo*-transition state which was also trapped by thiophenol to give adducts **44** and **45**.



## 1. Introduction

Small-ring cycloalkenes have been a subject of considerable interest because the energy content of these compounds relative to their acyclic counterparts often confers unique properties. Cyclopropenes can spontaneously undergo unique reactions at room temperature via ene reactions,[1] [2+2] cycloadditions,[2] or ring opening-ring closure reactions[3] to release the high degree of olefinic strain. Consequently, the chemistry of cyclopropenes is very rich, and attract both theoretical and experimental chemists on it.[4]

Cyclopropenes normally undergo the most favored type of isomerizations or dimerizations.[5] Due to their high strain energy, cyclopropenes bearing a 3-hydrogen usually undergo ene dimerizations and polymerizations via ene reaction to release the high olefinic strain energy. 1,2-Disubstituted cyclopropenes generally undergo ene reactions to form several regio- and stereodimers. For that reason, to understand the regio- and stereochemistry of ene reactions of cyclopropenes is an important aspect in the synthesis of functionalized cyclopropenes. Baird reported that a 1,2-substituted cyclopropene, 2-*tert*-butylcyclopropenecarboxylic acid (**1**), underwent ene reactions to form two stereodimers that were proposed to be formed from *endo*- and *exo*-transition structures which were further studied by theoretical calculations (Scheme 1).[1d] Baird also reported that compound **1** and 3,3-dimethylcyclopropenecarboxylic acid only underwent a crossed ene reaction via an *exo* approach of the dimethylcyclopropene and the ene dimer of **1** was not observed. This crossed ene reaction resulted from two different cyclopropenes but only one contained 3-hydrogens.




**Scheme 1.** Ene and crossed ene reactions of **1** and 3,3-dimethylcyclopropenecarboxylic acid.[1d]

Literature reports concerning, the chemistry of 1-phenylcyclopropenes are extensive (Scheme 2). DeBoer's group claimed that 1,2-diphenylcyclopropene (**2**), when irradiated in the presence of a sensitizer in an NMR tube, was converted into the [2+2] cycloaddition product **3** followed by a thermal rearrangement to 1,4-cyclohexadiene **4**.[6] Weyerstahl reported that, when 1-chloro-2-phenylcyclopropene (**5**) was allowed to stand in benzene at rt for 2 days, it was converted into the [2+2] dimer **6** in 4% yield, which isomerized to 1,2-dichloro-4,5-diphenylcyclohexa-1,4-diene (**7**) and followed by oxidation to form 4′,5′-dichloro-*o*-terphenyl

* Corresponding author. Tel.: +886 2 29053582; e-mail address: 016850@mail.fju.edu.tw (G.-A. Lee).

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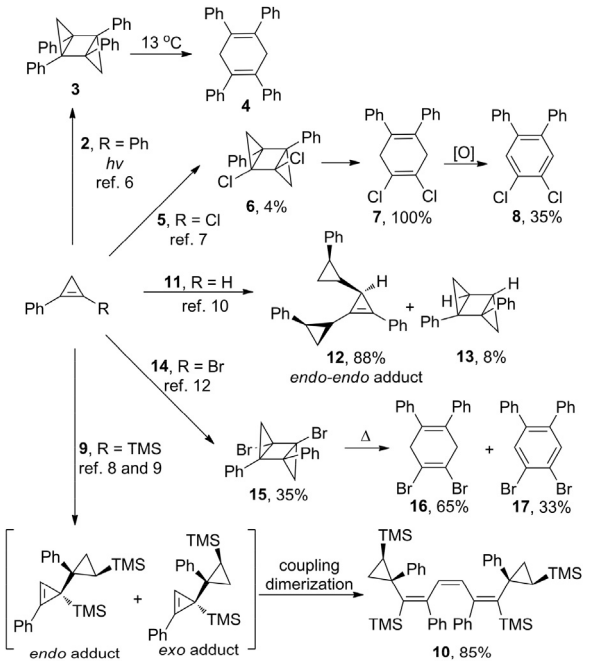
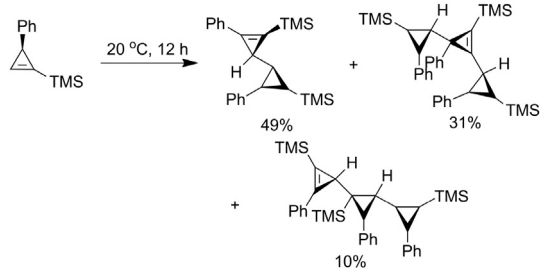
(**8**).[7] We recently reported that the ene dimerizations of 1-trimethylsilyl-2-phenylcyclopropene (**9**) afforded *endo*- and *exo*-dimers, which subsequently underwent a crossed coupling reaction to yield the tetramer **10** as the sole product.[8,9] 1-Phenylcyclopropene (**11**) undergoes ene dimerization and ene trimerization through an *endo*-transition state.[10] In the meantime, the [2+2] adduct, *trans*-1,2-diphenylbicyclo[3.1.0.0$^{2,4}$]hexane (**13**), was also formed. In the literature, ene dimerizations of cyclopropenes are very common, whereas polymerization reactions of cyclopropenes are rare. Schlatter's group generated cyclopropene, which underwent ene polymerization, to yield an isolable polymer.[1a] The bicyclo[5.1.0]hept-1(8)-ene underwent ene trimerization to give an ene trimer.[2f] However, this ene trimer was isolated in the form of a crude mixture and was characterized only by $^1$H NMR and mass




**Scheme 2.** The chemistry of 1-phenylcyclopropenes.

spectrometry. Baird and co-workers also reported that the highly stereocontrolled ene reaction of 1-trimethylsilyl-3-phenylcyclopropene resulted in the formation of a single dimer and the stereochemistry of the two trimers was distinguished on the basis of $^1$H NMR spectrum only (Scheme 3).[11] In our previous publication, 1-bromo-2-phenylcyclopropene (**14**) was synthesized and underwent [2+2] dimerization to generate 1,2-dibromo-4,5-diphenyltricyclo[3.1.0.0$^{2,4}$]hexane (**15**), which, on heating, was converted to 1,2-dibromo-4,5-diphenylcyclohexa-1,4-diene (**16**) followed by oxidation to yield 4′,5′-dibromo-*o*-terphenyl (**17**) (Scheme 2).[12] We also applied theoretical and experimental



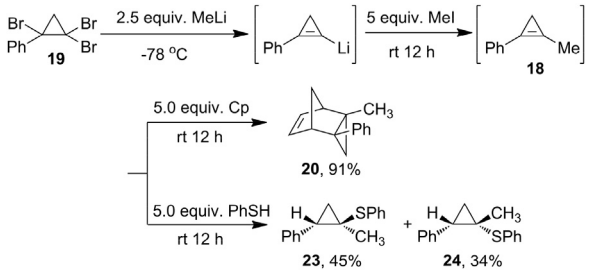

**Scheme 3.** Ene dimerization and trimerizations of 1-trimethylsilyl-3-phenylcyclopropene.[11]

approaches to develop a method for the synthesis of a crossed [2+2] cycloadduct which, on heating and oxidation, was converted into a 4′-bromo-*o*-terphenyl derivative.

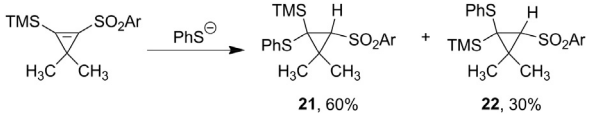
1,1,2-Trihalocyclopropanes are very useful precursors for preparing a series of 1-substituted cyclopropenes via 1-lithiocyclopropenes with suitable electrophiles in reasonable to good yields.[5j] Baird reported that 1,1,2-tribromocyclopropanes, when reacted with 2.1 equiv of butyl lithium followed by treatment with alkyl iodide, gave 1-alkyl cyclopropenes. We also found that 1,8,8-tribromobicyclo[5.1.0]octane, when reacted with 2.5 equiv of methyl lithium followed by methylation with methyl iodide, formed 8-methylbicyclo[5.1.0]oct-1(8)-ene.[13] Although 1-methyl-2-phenylcyclopropene (**18**) has been synthesized through substituted 1,1-difluorocyclopropanes via reacting with methyllithium,[6b] the chemistry of **18** has not been investigated yet. In this study, we utilized this synthetic route to the preparation and study of the chemistry of **18**.

## 2. Results and discussion

We previously reported on a straightforward synthesis of 1,2-disubstituted cyclopropenes, using 1,1,2-tribromo-2-phenylcyclopropane (**19**),[8,9,12,14] which was generated by the addition of dibromocarbene to α–bromostyrene. Treatment of **19** with 2.5 equiv of methyl lithium in diethyl ether at −78 °C generated the anionic 1-lithio-2-phenylcyclopropene, and further reaction with methyl iodide, produced 1-methyl-2-phenylcyclopropene **18**. The cyclopropene **18** was trapped with cyclopentadiene to give the corresponding [4+2] cycloadduct **20** in 91% yield (Scheme 4). The addition of cyclopropene with thiophenol was reported by Padwa, treating trimethylsilyl sulfonyl cyclopropene with thiophenol and an equivalent amount of base resulted in the formation of the silyl-substituted cyclopropanes **21** and **22** in the ratio 2:1 (Scheme 5).[15] Herein, when **18** was treated




**Scheme 4.** The trapping of cyclopropene **18**.




**Scheme 5.** The trapping of cyclopropene with thiophenol.[15]

with thiophenol, cyclopropane **23** and **24** were produced. The structure of **24** was confirmed by single-crystal X-ray analysis (Fig. 1). Based on the results of this experiment, the *cis* addition as the major adduct, which was previously noted by Padwa's group, is an interconversion of the carbanion lone pair. The favored cyclopropyl carbanion will be the one that stabilized by the adjacent thiophenyl moiety, leading to a 4:3 mixture of isomers **23** and **24**.

To clarify the chemistry of cyclopropene **18**, a $CH_2Cl_2$ solution of cyclopropene **18** was exposed to air for 10 days, the oxidized products **25**, **26**, **27**, and **28** were produced (Scheme 6). The oxidation of most of cyclopropenes by oxygen to produce α,β-unsaturated carbonyl compounds via vinylcarbene intermediates is

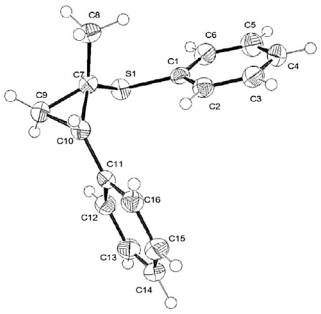
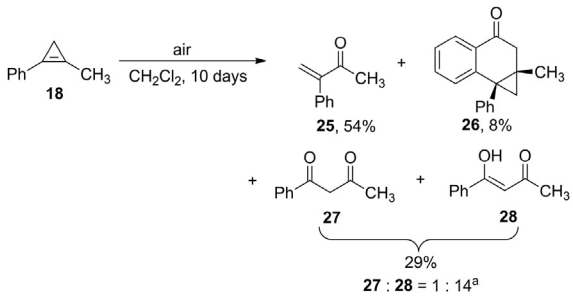
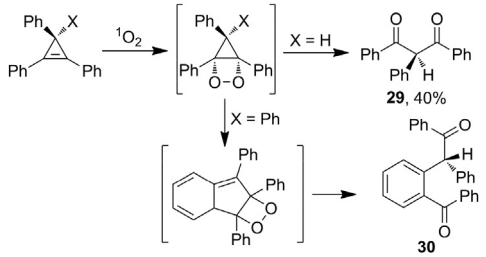


**Fig. 1.** The X-ray crystal structure **24**.

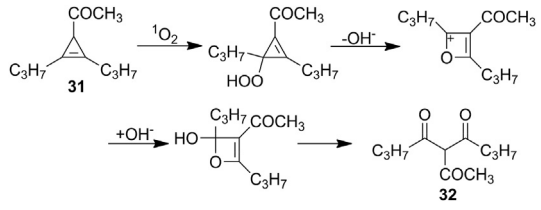
well known. However, there are only three reports about the oxidation of cyclopropenes by singlet oxygen ($^1O_2$) to generate diketones. Griffin reported that 1,2,3-triphenylcyclopropene and tetraphenylcyclopropene are oxidized by dye-sensitized photooxidation reactions via a [2+2] intermediate to yield diketones **29** and **30**, respectively (Scheme 7).[16] Frimer reported that the cyclopropene **31** reacted with photogenerated singlet oxygen via an ene reaction to give the diketone **32** (Scheme 8).[17]




**Scheme 6.** The treatment of cyclopropene **18** in air.[a] The ratio was determined by $^1H$ NMR.

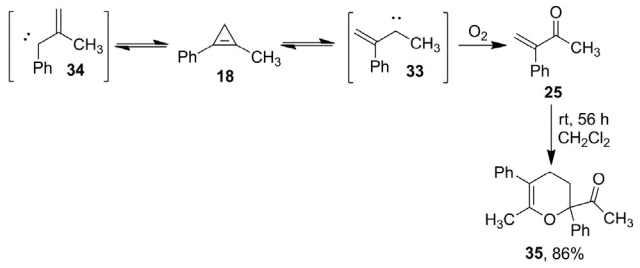



**Scheme 7.** Photooxidations of strained cyclopropenes.[16]




**Scheme 8.** Proposed mechanism for the reaction of cyclopropene **31** with singlet oxygen.[17]

As a result, an equilibrium mixture of cyclopropene **18** and vinylcarbenes, **33** and/or **34**, underwent a ring opening-ring closure reaction at room temperature. Due to the resonance effect of the phenyl group, carbene **34** is more stable than **33**. Therefore, oxygen would insert into the more reactive vinylcarbene **33** to form an α,β-unsaturated ketone **25** in 54% yield,[18] while cyclopropene **18** also simultaneously reacted with oxygen to give a 1:13 mixture of diketone **27** and tautomer **28** via a rare [2+2] cycloaddition. The isolated enone **25** spontaneously undergoes a single regioselective [4+2] cyclization at room temperature to generate a six-membered heterocycle **35** that was identical to that reported by Wilson (Scheme 9).[19]




**Scheme 9.** The [4+2] cyclization of enone **25**.

The structure of **26** was determined by single-crystal X-ray analysis (Fig. 2). A possible reaction mechanism is depicted in Scheme 10. In the mechanism for the formation of **26**, **28** might react with **18** via intermolecular Diels–Alder reaction to form **36**, which can be transformed to **37** by isomerization and oxidation. The intermediate **37** would undergo a retro-Claisen-like reaction in solution to form **38**, which isomerizes to **26**.

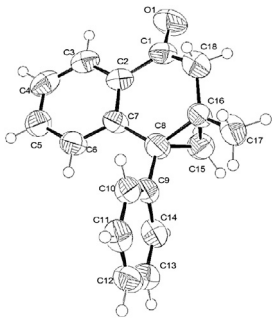
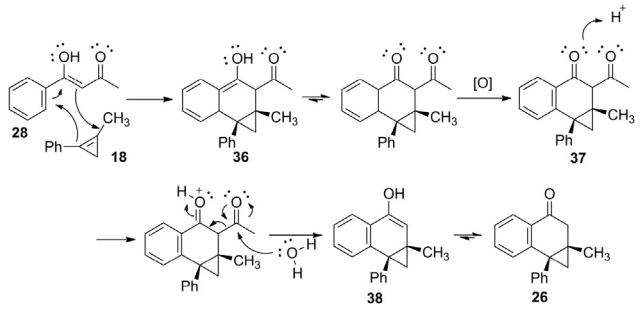


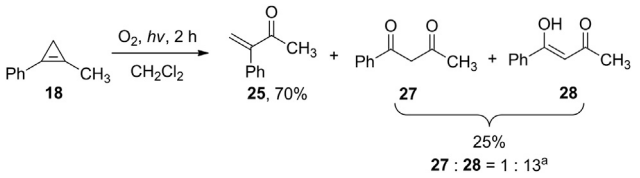
**Fig. 2.** The X-ray crystal structure **26**.




**Scheme 10.** Proposed mechanism for the formation of **26**.

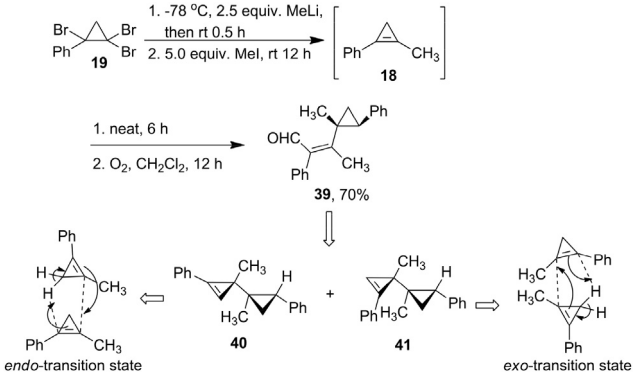
To increase the yield and shorten the reaction time, the UV irradiation of cyclopropene **18** in the presence of oxygen was carried out, which resulted in a higher yield of **25** than the previous reaction we mentioned. The overall reaction required only 2 h to reach completion (Scheme 11).

Furthermore, cyclopropene **18** was allowed to stand under vacuum at room temperature for 6 h after which time the ene dimers **40** and **41** likely were generated as detected by analysis of the



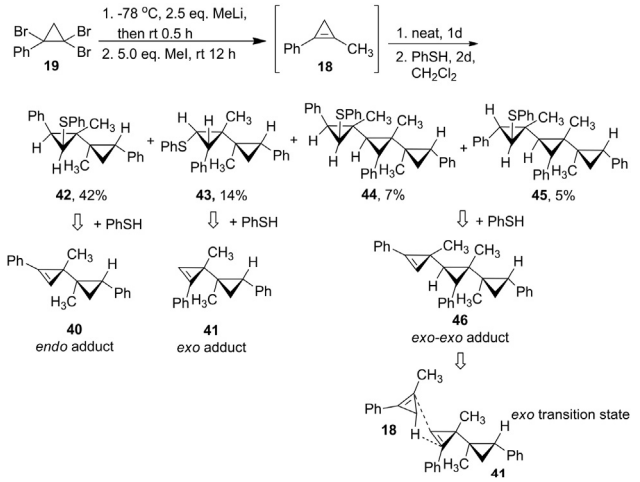

**Scheme 11.** The photosensitized oxidation of **18**.[a] The ratio was determined by $^1$H NMR.

crude mixture by GC-Mass and $^1$H NMR spectra. The ene dimers were unstable in the presence of oxygen but inactive with respect to cyclopentadiene, furan, or diphenylisobenzofuran. When the dimers were treated with oxygen, *a,ß*-unsaturated carbonyl compound **39** was obtained, and its structure was established by Mass, IR and NMR spectra (Scheme 12). Compound **39** may well be formed from **40** and/or **41**, which are produced via a cyclopropene-vinylcarbene rearrangement followed by oxidization with oxygen. The ene dimer **40** appears to be formed via an *endo*-transition state and the ene dimer **41** via an *exo*-transition.




**Scheme 12.** Oxidation of the ene dimers **40** and **41**.

In order to understand the stereochemistry of ene dimerization of **18**, cyclopropene **18** held neat for one day. After this time the solution was treated with thiophenol and adducts **42**–**45** were obtained (Scheme 13). The structures of these compounds were confirmed by single-crystal X-ray analysis (Figs. 3–6). Product **42** was formed from the *trans*-trapped thiophenol of *endo*-dimer **40**, and **43** was formed from *exo*-dimer **41**. It is interesting to note that




**Scheme 13.** Ene reactions of **18** with thiophenol as trapping reagent.

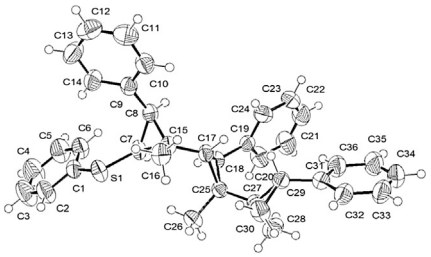


**Fig. 3.** The X-ray crystal structure **42**.

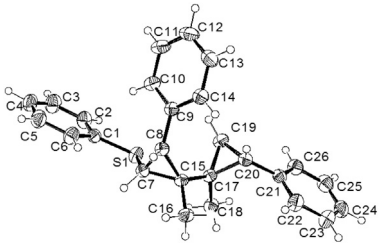


**Fig. 4.** The X-ray crystal structure **43**.

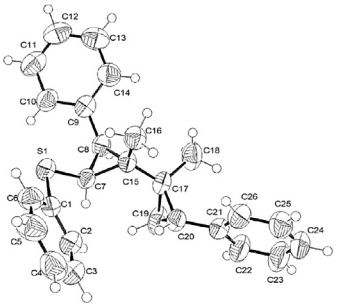


**Fig. 5.** The X-ray crystal structure **44**.

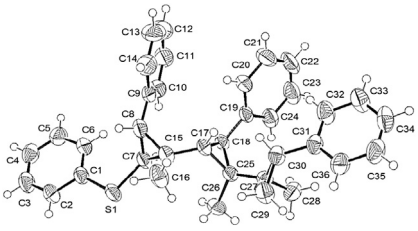


**Fig. 6.** The X-ray crystal structure **45**.

compounds **44** and **45** were generated by the reaction of the *exo-exo* ene trimer **46** with thiophenol via a *cis*- or *trans*-addition. The ene trimer **46** was generated from the ene reaction of the enolphile, *exo*-dimer **41**, and the 3-hydrogen donator **18** via an *exo*-transition state. Based on the results of this experiment, steric repulsion between methyl and methyl groups must be less than that between methyl and phenyl groups or phenyl and phenyl groups as expected. As a result, *endo* **40** and *exo* **41** are preferentially formed in these reactions.

The theoretical calculations were carried out for the ene dimers using B3LYP/6-31G(d,p), and the heat of formation were determined. The result indicated that the heats for ene trimerization of *endo-exo* and *endo-endo* dimers were less than *exo-exo* trimer **46**,[20] besides, the *endo* transition state of *endo*-ene dimer with monomer **18** shows the apparent steric hindrance between

cyclopropene **18** and methyl group of dimer. As the reason, only *exo-exo* trimer **46** could be obtained. We also provide the theoretical calculations to the possible ene tetramers via *endo* or *exo* transition state between ene trimer **46** and monomer **18**. However the heat of ene reaction were less than that of ene trimer **46**, indicating why there is no observation of ene tetramerization.

## 3. Conclusion

In summary, we report on an easier route to the synthesis of 1-methyl-2-phenylcyclopropene (**18**). Compound **18** was oxidized by oxygen to give the α,β-unsaturated carbonyl product **25**, diketone **27** and tautomer **28**. However, compound **28** reacted with cyclopropene **18** in a retro-Claisen-like reaction to generate 1a,2-dihydro-1*H*-cyclopropa[*a*]naphthalen-3(7b*H*)-one **26**. Furthermore, compound **18** underwent ene dimerization in the neat condition to form the *endo*-dimer **40** and *exo*-dimer **41** that was followed by aerial oxidization to give aldehyde **39**. It is noteworthy that the *endo*-dimer **40** and the *exo*-dimer **41** could be trapped with thiophenol to give adduct **42** and **43**, and that the ene reaction of *exo*-dimer **41** with monomer **18** led to an *exo-exo* ene trimer **46** through an *exo*-transition state which was also trapped by thiophenol to give adducts **44** and **45**.

## 4. Experimental section

### 4.1. General

All solvents were dried using standard methods. Melting points are uncorrected. Proton NMR spectra were measured in $CDCl_3$ solution on a 300 MHz NMR spectrometer, with $CHCl_3$ (7.26 ppm) as the internal standard. Carbon-13 NMR were measured in $CDCl_3$ solution on a 75 MHz NMR spectrometer and referenced to $CDCl_3$ (77.1 ppm). Chemical shifts ($\delta$) are expressed in parts per million (ppm) downfield from tetramethylsilane. Coupling constants ($J$) are expressed in hertz (Hz). Infrared spectra were obtained with a Perkin-Elmer 1600 instrument. X-ray data for compounds were recorded with a Kappa CCD diffractometer. Column chromatography was performed on silica gel (70–230 mesh). Solvents are of reagent grade.

### 4.2. Trapping of 1-methyl-2-phenylcyclopropene (18) with cyclopentadiene

Methyllithium (1.5 M in ether, 23.5 mL, 35 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (5.0 g, 14 mmol) in 30 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (4.4 mL, 71 mmol) was added and stirred for 12 h, and then cyclopentadiene (5.7 mL, 68 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the ether and Cp dimer were removed under reduced pressure and the residue was purified by flash column chromatography (hexanes) to give colorless liquid **20** (2.5 g, 91%).

*4.2.1. 2-Methyl-4-phenyltricyclo[3.2.1.0$^{2,4}$]oct-6-ene (**20**).* IR (neat): $\tilde{\nu}$=3059, 2960, 2932, 2922, 2863, 1600, 1495, 1451, 1379, 1327, 1304, 1247, 1230, 1194, 1131, 1097, 1058, 1028, 1013, 943, 914, 900, 890, 860, 847, 803 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.26–7.35 (m, 4H), 7.13–7.24 (m, 1H), 6.05–6.12 (m, 1H), 5.97–6.05 (m, 1H), 2.92–3.03 (m, 1H), 2.66 (ddd, $J$=5.4, 3, 1.2 Hz, 1H), 2.32 (dt, $J$=7, 1.7 Hz, 1H), 1.79 (d, $J$=7 Hz, 1H), 1.02–1.13 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=142.45 (C), 135.02 (CH), 133.65 (CH), 128.21 (CH), 128.14 (CH), 125.37 (CH), 60.86 ($CH_2$), 52.00 (CH), 49.74 (CH), 31.55 (C), 28.60 (C), 27.40 ($CH_2$), 17.68 ($CH_3$). MS: $m/z$ (%)=196 (89) $[M]^+$, 181 (100), 167 (49), 165 (70), 155 (44), 115 (43), 104 (35), 91 (55), 77 (42). HRMS: calcd for $C_{15}H_{16}$ 196.1252; found 196.1253.

### 4.3. Trapping of 1-methyl-2-phenylcyclopropene (18) with thiophenol

Methyllithium (1.5 M in ether, 14 mL, 21 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (3.0 g, 8.4 mmol) in 12 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (2.7 mL, 43 mmol) was added and stirred for 12 h, and then thiophenol (4.3 mL, 42 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 50 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (hexanes) to give colorless liquid **23** (0.91 g, 45%) and white solid **24** (0.69 g, 34%).

*4.3.1. trans-1-Methyl-2-phenyl-2-phenylsulfenyl cyclopropane (**23**).* IR (neat): $\tilde{\nu}$=3063, 3028, 3002, 2963, 2926, 2858, 1603, 1583, 1497, 1478, 1450, 1438, 1380, 1265, 1175, 1083, 1024, 776, 737, 699 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.46–7.53 (m, 2H), 7.30–7.40 (m, 4H), 7.18–7.29 (m, 4H), 2.65 (dd, $J$=9.1, 6.6 Hz, 1H), 1.52 (dd, $J$=9.1, 5.6 Hz, 1H), 1.37 (dd, $J$=6.6, 5.6 Hz, 1H), 1.22 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=137.58 (C), 136.52 (C), 129.63 (CH), 129.01 (CH), 128.96 (CH), 128.33 (CH), 126.53 (CH), 126.23 (CH), 32.10 (CH), 28.06 (C), 20.55 ($CH_2$), 20.49 ($CH_3$). MS: $m/z$ (%)=242 (3.09) $[M+2]^+$, 241 (7.77) $[M+1]^+$, 240 (42.97) $[M]^+$, 131 (100), 115 (44), 91 (58), 77 (21), 59 (24). HRMS: calcd for $C_{16}H_{16}S$ 240.0973; found 240.0977. $C_{16}H_{16}S$ (240.36): calcd. C 79.95, H 6.71, S 13.34; found C 79.67, H 6.90, S 13.40.

*4.3.2. cis-1-Methyl-2-phenyl-2-phenylsulfenyl cyclopropane (**24**).* Mp 66–68 °C. IR (neat): $\tilde{\nu}$=3059, 3044, 3018, 3001, 2988, 2974, 2960, 2923, 1598, 1580, 1495, 1478, 1459, 1437, 1381, 1249, 1086, 1063, 1023, 765, 734, 695, 685 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.27–7.35 (m, 4H), 7.16–7.26 (m, 5H), 7.01–7.16 (m, 1H), 2.35 (dd, $J$=8.7, 6.7 Hz, 1H), 1.64 (s, 3H), 1.56 (dd, $J$=6.7, 5.6 Hz, 1H), 1.39 (dd, $J$=8.7, 5.6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=138.04 (C), 135.80 (C), 129.50 (CH), 128.88 (CH), 128.59 (CH), 127.83 (CH), 126.45 (CH), 125.77 (CH), 31.87 (CH), 30.30 (C), 27.28 ($CH_3$), 21.69 ($CH_2$). MS: $m/z$ (%)=242 (0.52) $[M+2]^+$, 241 (1.63) $[M+1]^+$, 240 (8.9) $[M]^+$, 131 (100), 129 (23), 115 (21), 91 (37), 77 (11). HRMS: calcd for $C_{16}H_{16}S$ 240.0973; found 240.0963. $C_{16}H_{16}S$ (240.36): calcd. C 79.95, H 6.71, S 13.34; found C 79.80, H 6.55, S 13.21.

### 4.4. The treatment of cyclopropene 18 in air

Methyllithium (1.5 M in ether, 47 mL, 71 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (10.0 g, 28 mmol) in 60 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (8.8 mL, 0.14 mol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent changed from ether to $CH_2Cl_2$ (30 mL) and stirred for 10 days on air. The residue was purified by column chromatography (1% EA/hexanes) to give yellow liquid **25** (2.2 g, 54%), white solid **26** (0.28 g, 8%), white solid **27** and **28** (1.31 g, **27**: **28**=1: 13, 29%).

*4.4.1. 3-Phenylbut-3-en-2-one (**25**).* $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.30–7.42 (m, 5H), 6.18 (s, 1H), 5.98 (s, 1H), 2.45 ppm (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=199.28 (C), 149.36 (C), 136.96 (C), 128.40 (CH), 128.09 (CH), 128.04 (CH), 125.86 ($CH_2$), 27.32 ($CH_3$).

*4.4.2. 1a-Methyl-7b-phenyl-1a,2-dihydro-1H-cyclopropa[a]-naphthalen-3(7bH)-one (**26**).* Mp 100–101 °C. IR (neat): $\tilde{\nu}$=3061, 2972, 2870, 1678, 1595, 1494, 1476, 1452, 1410, 1380, 1351, 1287, 1252, 1194, 1159, 1113, 1079, 1080, 1016, 964, 951, 923, 887, 860, 840 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.93 (dd, $J$=7.7, 1.4 Hz, 1H), 7.32–7.50 (m, 4H), 7.16–7.31 (m, 3H), 6.79 (dd, $J$=7.7, 0.7 Hz, 1H), 3.11 (d, $J$=17.8 Hz, 1H), 2.88 (d, $J$=17.8 Hz, 1H), 1.70 (d, $J$=4.9 Hz, 1H), 1.02 (s, 3H), 0.76 (d, $J$=4.9 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=197.03 (C), 150.09 (C), 140.07 (C), 133.18 (CH), 131.97 (CH), 130.75 (CH), 130.14 (C), 128.97 (CH), 128.70 (CH), 127.15 (CH), 126.99 (CH), 125.45 (CH), 43.88 ($CH_2$), 35.11 (C), 32.28 ($CH_2$), 23.10 ($CH_3$), 22.01 (C). MS: $m/z$ (%)=248 (100) [M]$^+$, 233 (40), 215 (38), 207 (37), 193 (29), 178 (33), 165 (26), 128(8), 115(8), 91 (9), 77 (7). HRMS: calcd for $C_{18}H_{16}O$ 248.1201; found 248.1210. $C_{18}H_{16}O$ (248.32): calcd. C 87.06, H 6.49, found C 86.99, H 6.79.

*4.4.3. (Z)-4-Hydroxy-4-phenylbut-3-en-2-one (**27**) and tautomer **28**.* $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.84–7.92 (m, 2H), 7.41–7.54 (m, 3H), 6.19 (s, 1H), 2.21 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=193.82 (C), 183.45 (C), 135.02 (C), 132.35 (CH), 128.69 (CH), 127.09 (CH), 96.78 (CH), 25.91 ($CH_3$).

### 4.5. The [4+2] cyclization of enone 25

Methyllithium (1.5 M in ether, 23.5 mL, 35 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (5.0 g, 14 mmol) in 30 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (4.4 mL, 71 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent changed from ether to $CH_2Cl_2$ (30 mL) and stirred with oxygen for 19 h. The residue was purified by column chromatography (3% EA/hexanes) to give yellow liquid **25**. And a solution of **25** in $CH_2Cl_2$ (30 mL) at room temperature was stirred for 56 h. The mixture was purified by readily by flash column chromatography to give white solid **35** (1.76 g, 86%).

*4.5.1. 1-(6-Methyl-2,5-diphenyl-3,4-dihydro-2H-pyran-2-yl)-ethanone (**35**).* $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.53 (d, $J$=7.4 Hz, 2H), 7.39 (t, $J$=7.3 Hz, 2H), 7.26–7.35 (m, 3H), 7.20 (t, $J$=7.3 Hz, 1H), 7.12 (d, $J$=7 Hz, 2H), 2.55–2.70 (m, 1H), 2.25–2.40 (m, 1H), 2.18 (s, 3H), 2.06–2.16 (m, 2H), 1.98 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=209.16 (C), 145.94 (C), 141.46 (C), 139.35 (C), 128.83 (CH), 128.63 (CH), 128.17 (CH), 127.93 (CH), 126.27 (CH), 125.16 (CH), 111.51 (C), 85.88 (C), 30.08 ($CH_2$), 24.89 ($CH_2$), 24.53 ($CH_3$), 18.21 ($CH_3$).

### 4.6. The photosensitized oxidation of 18

Methyllithium (1.5 M in ether, 10 mL, 15 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (2.0 g, 5.6 mmol) in 8 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (1.8 mL, 29 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 50 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. After filtration, a solution of **18** in 12 mL of $CH_2Cl_2$ was purged with oxygen and irradiated with UV–vis light, equipped with a water-cooled 450W 5 inch arc IMMER UV–vis lamp (Mode #7825-34, Ace Glass, Inc.), while stirring for a total of 2 h. The residue was purified by column chromatography (1% EA/hexanes) to give yellow liquid **25** (0.57 g, 70%), white solid **27** and **28** (0.23 g, **27**: **28**=1: 13, 25%).

### 4.7. The oxidation of the ene dimers 40 and 41

Methyllithium (1.5 M in ether, 10 mL, 15 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (2 g, 5.6 mmol) in 8 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (1.8 mL, 29 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 50 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. Ether was removed under reduced pressure and the residue was stirred at room temperature for 6 h. About 10 mL of $CH_2Cl_2$ was added, and stirred with oxygen for 12 h, and the mixture was concentrated, and chromatographed (3% EA/hexanes) to give white solid **39** (0.54 g, 70%).

*4.7.1. (Z)-3-(trans-1-Methyl-2-phenylcyclopropyl)-2-phenylbut-2-enal (**39**).* Mp 95–96 °C. IR (neat): $\tilde{\nu}$=3029, 2932, 2922, 1671, 1601, 1494, 1450, 1372, 1214, 1144, 1085, 1056, 1024, 1101, 970, 934, 846 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=10.65 (s, 1H), 7.31–7.44 (m, 5H), 7.22–7.31 (m, 3H), 7.03–7.10 (m, 2H), 2.38 (t, $J$=7.8 Hz, 1H), 2.02 (s, 3H), 1.38–1.50 (m, 2H), 1.17 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=191.90 (CH), 164.41 (C), 140.28 (C), 137.45 (C), 135.48 (C), 129.82 (CH), 128.80 (CH), 128.40 (CH), 128.27 (CH), 127.50 (CH), 126.53 (CH), 28.94 (CH), 27.56 (C), 21.22 ($CH_3$), 20.39 ($CH_3$), 20.23 ($CH_2$). MS: $m/z$ (%)=276 (3) [M]$^+$, 247 (29), 172 (100), 122 (22), 105 (15), 70 (31), 61 (58). HRMS: calcd for $C_{20}H_{20}O$ 276.1514; found 276.1513.

### 4.8. Ene reactions trapped with thiophenol

Methyllithium (1.5 M in ether, 23.5 mL, 35 mmol) was added dropwise from a syringe to stirred solution of 1,1,2-tribromo-2-phenylcyclopropane (**19**) (5.0 g, 14 mmol) in 30 mL of dry ether at −78 °C. The mixture was allowed to warm to rt and stirred for 0.5 h. Methyl iodide (4.4 mL, 71 mmol) was added and stirred for 12 h. The mixture was poured into a 250-mL beaker with 100 g of crushed ice. The organic layer was separated and washed with water and brine, and then dried over anhydrous magnesium sulfate. Ether was removed under reduced pressure and the residue was stirred at room temperature for 1d. A solution of thiophenol (7 mL, 68 mmol) and $CH_2Cl_2$ was added and stirred for 2 days, and the mixture was concentrated, and chromatographed (hexanes) to give white solid **42** (0.96 g, 42%), white solid **43** (0.33 g, 14%), white solid **44** (0.16 g, 7%), white solid **45** (0.12 g, 5%).

*4.8.1. (1R*,1′R*,2S*,2′S*,3S*)-1,1′-Dimethyl-2′,3-diphenyl-2-phenylsulfenyl bicyclopropane (**42**).* Mp 98–99 °C. IR (neat): $\tilde{\nu}$=3080, 3067, 3023, 2988, 2976, 2952, 2927, 1600, 1579, 1495, 1476, 1449, 1438, 1376, 1150, 1084, 1069, 1025, 776, 759, 739, 688 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$=7.36–7.45 (m, 2H), 7.25–7.35 (m, 9H), 7.12–7.25 (m, 4H), 2.63 (d, $J$=8.8 Hz, 1H), 2.48 (d, $J$=8.8 Hz, 1H), 2.06 (dd, $J$=8.8, 6.6 Hz, 1H), 1.26 (s, 3H), 0.93–1.06 (m, 4H), 0.83 (t, $J$=6 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$=139.28 (C), 138.14 (C), 136.21 (C), 130.47 (CH), 129.05 (CH), 128.94 (CH), 128.24 (CH), 128.13 (CH), 128.08 (CH), 126.56 (CH), 125.95 (CH), 125.65 (CH), 32.30 (C), 30.90 (CH), 30.55 (CH), 29.20 (C), 27.64 (CH), 18.36 ($CH_3$), 15.81 ($CH_2$), 15.10 ($CH_3$). MS: $m/z$ (%)=370 (4) [M]$^+$, 261 (21), 212 (16), 170 (87), 169 (49), 167 (29), 149 (26), 105 (21), 91 (100), 70 (34),

57 (53). HRMS: calcd for $C_{26}H_{26}S$ 370.1755; found 370.1756. $C_{26}H_{26}S$ (370.55): calcd. C 84.27, H 7.07, S 8.65 found C 84.03, H 7.32, S 8.34.

*4.8.2. (1S*,1′R*,2S*,2′S*,3S*)-1,1′-Dimethyl-2′,3-diphenyl-2-phenylsulfenyl bicyclopropane (**43**).* Mp 123–124 °C. IR (neat): $\tilde{\nu}$=3082, 3056, 3021, 3009, 2993, 2970, 2958, 2924, 2868, 1954, 1937, 1869, 1847, 1803, 1784, 1599, 1579, 1497, 1480, 1440, 1372, 1289, 1177, 1152, 1091, 1026, 776, 736, 696 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.59–7.48 (m, 2H), 7.43 (d, 2H, $J$=7.5 Hz), 7.32 (t, 2H, $J$=7.7 Hz), 7.29–7.22 (m, 2H), 7.22–7.15 (m, 5H), 7.11 (d, 2H, $J$=7.2 Hz), 2.61 (d, 1H, $J$=8.1 Hz), 2.46 (d, 1H, $J$=8.1 Hz), 2.37 (dd, 1H, $J$=8.7, 6.2 Hz), 1.65 (s, 3H), 0.91 (s, 3H), 0.68 (dd, 1H, $J$=8.7, 6.2 Hz), 0.56 (t, 1H, $J$=6.2 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=139.69 (C), 139.27 (C), 136.49 (C), 129.52 (CH), 129.12 (CH), 128.93 (CH), 128.07 (CH), 127.93 (CH), 126.41 (CH), 126.22 (CH), 125.74 (CH), 124.76 (CH), 35.13 (CH), 32.93 (CH), 31.48 (C), 28.34 ($CH_3$), 27.26 (CH), 25.96 (C), 19.91 ($CH_3$), 17.63 ($CH_2$). MS: $m/z$ (%)=370 (0.31) $[M]^+$, 261 (26), 247 (83), 170 (26), 167 (23), 105 (20), 91 (100). HRMS calcd for $C_{26}H_{26}S$ $m/z$ 370.1755, found 370.1751. $C_{26}H_{26}S$ (370.55): calcd. C 84.27, H 7.07, S 8.65; found C 83.98, H 7.24, S 8.51.

*4.8.3. (1R*,1′R*,1″R*,2S*,2′R*,2″S*,3S*,3′R*)-2-Phenylsulfenyl-1,1″,2′-trimethyl-2″,3,3′-triphenyl-1,1′:2′,1″-tercyclopropane (**44**).* Mp 130–133 °C. IR (neat): $\tilde{\nu}$=3058, 3024, 2986, 2958, 2928, 1674, 1600, 1584, 1497, 1479, 1439, 1374, 1209, 1155, 1091, 748, 733, 696 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.41–7.49 (m, 2H), 7.32–7.40 (m, 6H), 7.27–7.32 (m, 4H), 7.13–7.26 (m, 3H), 6.96–7.09 (m, 3H), 6.28–6.39 (m, 2H), 2.67 (d, $J$=8.1 Hz, 1H), 2.49 (d, $J$=8.1 Hz, 1H), 1.96–2.08 (m, 3H), 1.42 (s, 3H), 1.21 (s, 3H), 0.71 (s, 3H), 0.59–0.69 (m, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=139.40 (C), 138.87 (C), 137.99 (C), 136.23 (C), 130.31 (CH), 129.88 (CH), 129.38 (CH), 128.98 (CH), 128.47 (CH), 128.24 (CH), 127.87 (CH), 127.57 (CH), 126.51 (CH), 126.16 (CH), 125.59 (CH), 125.48 (CH), 35.48 (C), 34.58 (CH), 33.50 (CH), 31.82 (CH), 31.21 (CH), 27.60 (CH), 25.21 (C), 24.73 (C), 19.72 ($CH_3$), 17.40 ($CH_3$), 17.38 ($CH_3$), 16.30 ($CH_2$). MS: $m/z$ (%)=500 (0.17) $[M]^+$, 391 (16), 247 (52), 233 (64), 131 (83), 129 (43), 115 (21), 105 (36), 91 (100). HRMS: calcd for $C_{36}H_{36}S$ 500.2538; found 500.2547. $C_{36}H_{36}S$ (500.74): calcd. C 86.35, H 7.25, S 6.40 found C 86.16, H 6.90, S 6.15.

*4.8.4. (1R*,1′R*,1″R*,2S*,2′R*,2″S*,3R*,3′R*)-2-Phenylsulfenyl-1,1″,2′-trimethyl-2″,3,3′-triphenyl-1,1′:2′,1″-tercyclopropane (**45**).* Mp 164–167 °C. IR (neat): $\tilde{\nu}$=3081, 3055, 3026, 2996, 2980, 2950, 2929, 1601, 1583, 1496, 1478, 1445, 1376, 1155, 1092, 1081, 1025, 736, 697, 689 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=7.42–7.54 (m, 2H), 7.18–7.30 (m, 4H), 7.09–7.18 (m, 4H), 7.04–7.09 (m, 1H), 6.92–7.04 (m, 5H), 6.46 (d, $J$=7.1 Hz, 2H), 6.13–6.30 (m, 2H), 2.97 (d, $J$=5.5 Hz, 1H), 2.27 (d, $J$=5.5 Hz, 1H), 1.75–1.89 (m, 2H), 1.57 (s, 3H), 1.41 (s, 3H), 1.35 (d, $J$=6.3 Hz, 1H), 0.57–0.70 (m, 4H), 0.53 (t, $J$=5.0 Hz, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$=139.45 (C), 137.83 (C), 137.64 (C), 137.25 (C), 129.57 (CH), 129.43 (CH), 128.99 (CH), 128.68 (CH), 128.64 (CH), 128.48 (CH), 127.60 (CH), 127.44 (CH), 126.16 (CH), 125.81 (CH), 125.48 (CH), 125.33 (CH), 39.57 (CH), 35.66 (CH), 33.74 (C), 30.42 (C), 29.99 (CH), 29.04 (CH), 27.51 (CH), 24.82 (C), 23.08 ($CH_3$), 20.38 ($CH_3$), 17.39 ($CH_3$), 16.07 ($CH_2$). MS: $m/z$ (%)=500 (0.1) $[M]^+$, 392 (50), 391 (97), 299 (30), 287 (69), 259 (35), 248 (65), 247 (100), 233 (97), 171 (54), 131 (98), 105 (37), 91 (46). HRMS: calcd for $C_{36}H_{36}S$ 500.2538; found 500.2541. $C_{36}H_{36}S$ (500.74): calcd. C 86.35, H 7.25, S 6.40 found C 85.96, H 7.59, S 6.00.

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## Supplementary data

Supplementary data (Spectral data and X-ray data for all new compounds, as well as the computational details. CCDC 892221 (**24**), 892222 (**26**), 892223 (**42**), 1421398 (**43**), 892224 (**44**), 892225 (**45**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.11.024.

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20. There is one ene trimer, *endo-endo* I, more stable than *exo-exo* 46. However, the apparent steric hindrance between cyclopropene 18 and methyl group of dimer of *endo* transition state would make the *endo* ene reaction forbidden.