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Radical-Cation Vinylcyclopropane Rearrangements by TiO_2 Photocatalysis

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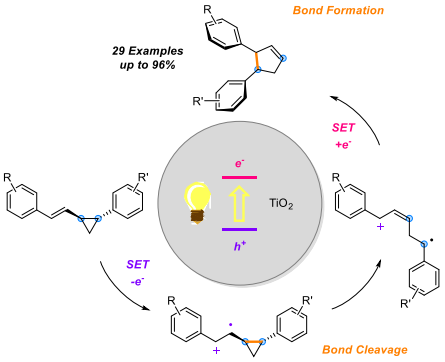


ABSTRACT

Radical cation vinylcyclopropane rearrangements by TiO_2 photocatalysis in lithium perchlorate/nitromethane solution are described. The reactions are triggered by oxidative single electron transfer, which is followed by immediate ring-opening of the cyclopropanes to generate distonic radical cations as unique reactive intermediates. This approach can also be applied to vinylcyclobutane, leading to the construction of six-membered rings. A stepwise mechanism via

distonic radical cations is proposed based on preliminary mechanistic studies, which is supported by DFT calculations.

INTRODUCTION

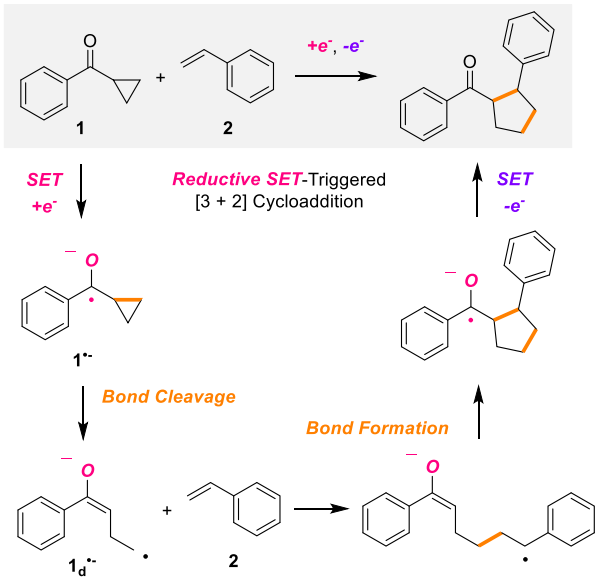
Synthetic organic chemistry has developed in tandem with the advancement of catalysis, where non- or less-reactive small molecules are activated to undergo chemical transformations. Catalytic activation of small molecules can be carried out by enzymes, transition metals, Lewis acids/bases, and organocatalysts. Among the simplest approaches is the use of a proton and/or electron as a catalyst.[1] While the addition or removal of a proton is well-documented in textbooks as acid/base catalysis, the corresponding mode of small molecule activation using an electron, referred to as redox catalysis, is somewhat less widespread. However, explosive growth in the use of photochemical[2] and electrochemical[3] reactions in this field has recently established the concept of redox catalysis, where reductive and/or oxidative single electron transfer (SET) is involved. SET primarily produces radical ions from neutral closed shell small molecules, offering distinctive reactivities that are difficult to achieve by neutral radicals or ions. Understanding radical ion reactivities should lead to the design of novel chemical transformations.

Distonic radical ions are transient species with formally separated radical and charge sites. They potentially exhibit independent radical and ion reactivities, which may differ from typical radical ions. However, distonic radical ions are not commonly used as reactive intermediates in the field of synthetic organic chemistry, likely due to the lack of simple generation methods. In this context, Yoon recently reported reductive SET-triggered formal [3 + 2] cycloadditions between

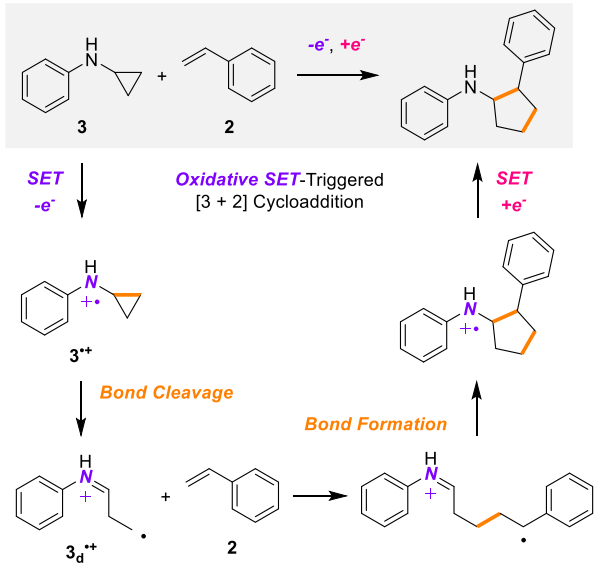
cyclopropyl phenyl ketone (**1**) and styrene (**2**) by photocatalysis (Scheme 1).[4] The distonic radical ion ($\mathbf{1_d}^{\bullet-}$) is proposed as a reactive intermediate, which is generated from the radical anion ($\mathbf{1}^{\bullet-}$) via immediate ring-opening, known as a radical clock reaction. In addition, Zheng reported oxidative SET-triggered formal [3 + 2] cycloadditions between *N*-cyclopropylaniline (**3**) and styrene (**2**) by photocatalysis, where the distonic radical cation ($\mathbf{3_d}^{\bullet+}$) is likely to be involved as a reactive intermediate (Scheme 2).[5] SET in combination with cyclopropyl ring-opening would be a versatile approach to generate distonic radical ions.[6]

We have been developing oxidative SET-triggered cycloadditions by photocatalysis[7] and electrocatalysis.[8] The use of lithium perchlorate ($LiClO_4$)/nitromethane (CH_3NO_2) solution has facilitated the generation of radical cations from electron-rich alkenes and styrenes, providing unique reactive intermediates for carbon−carbon bond formations.[9] We questioned whether the distonic radical cation ($\mathbf{4_d}^{\bullet+}$) could be generated to realize formal [5 + 2] cycloadditions with styrene (**2**) (Scheme 3). Described herein is our serendipitous finding that vinylcyclopropane rearrangements can be triggered by oxidative SET, in which distonic radical cations are likely to be involved as reactive intermediates.

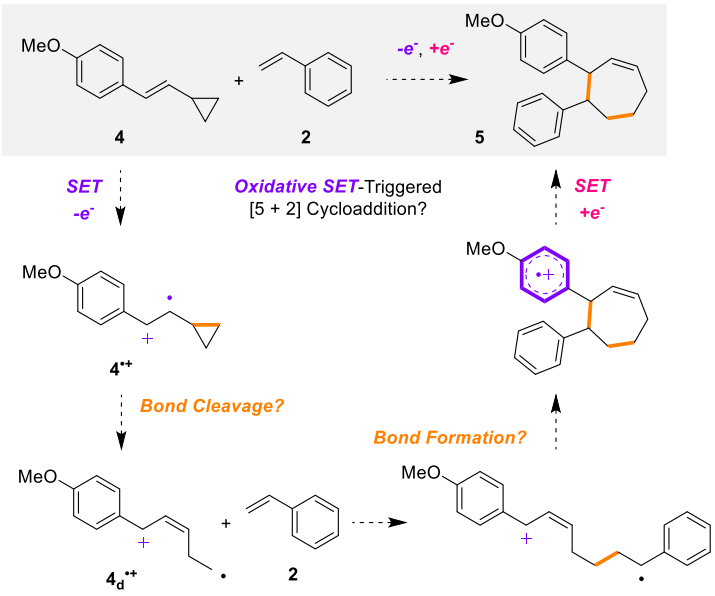
Scheme 1. Reductive SET-Triggered [3 + 2] Cycloaddition.



Scheme 2. Oxidative SET-Triggered [3 + 2] Cycloaddition.



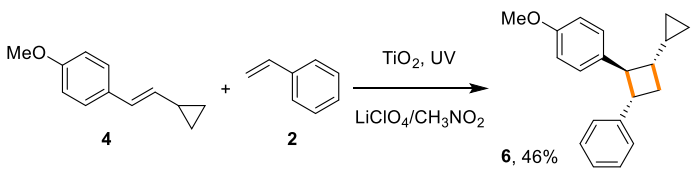
Scheme 3. Working Hypothesis.



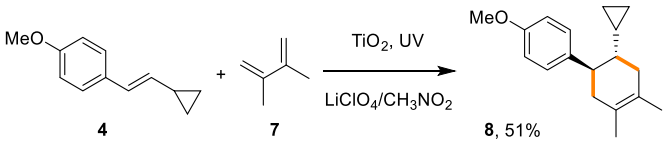
RESULTS AND DISCUSSION

The present work began with the reaction of the vinylcyclopropane (**4**) with styrene (**2**) under TiO_2 photocatalysis conditions. Unfortunately, the reaction gave the corresponding [2 + 2] cycloadduct (**6**) instead of [5 + 2] cycloadduct (**5**) (Scheme 4).[10] This outcome clearly suggests that while the radical cation (**4**$^{\bullet+}$) was indeed generated by the oxidative SET, it was not followed by immediate ring-opening. This hypothesis was further confirmed by the fact that the reaction with 2,3-dimethyl-1,3-butadiene (**7**) gave [4 + 2] cycloadduct (**8**) (Scheme 5).[11]

Scheme 4. [2 + 2] Cycloaddition of the Vinylcyclopropane (**4**).

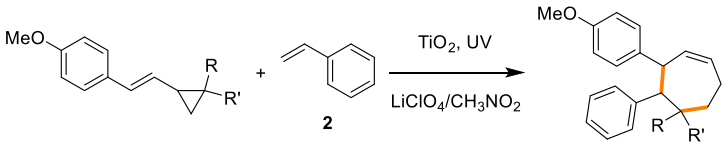


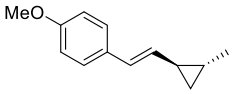
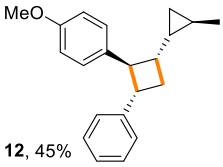
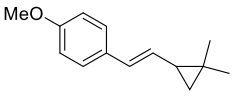
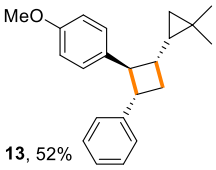
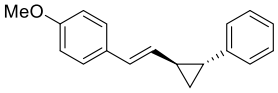
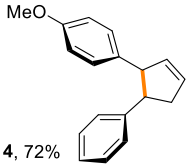
Scheme 5. [4 + 2] Cycloaddition of the Vinylcyclopropane (**4**).



In order to facilitate the ring-opening, vinylcyclopropanes (**9**–**11**) with additional substituents were synthesized and used for the reaction with styrene (**2**) (Table 1). The radical cations of the vinylcyclopropanes (**9**–**11**) were expected to generate secondary, tertiary, or benzyl radicals via ring-opening, respectively, which are more stable than primary radicals. Unfortunately, the reactions of the vinylcyclopropanes (**9**, **10**) gave the corresponding [2 + 2] cycloadducts (**12**, **13**), suggesting that ring-opening did not take place, despite the generation of radical cations (**9**$^{\bullet+}$, **10**$^{\bullet+}$) by oxidative SET. The reaction of vinylcyclopropane (**11**) also failed to give the [5 + 2] cycloadduct, however, cyclopentene (**14**) was obtained in 72% yield.

Table 1. Reactions of Vinylcyclopropanes (**9**–**11**).

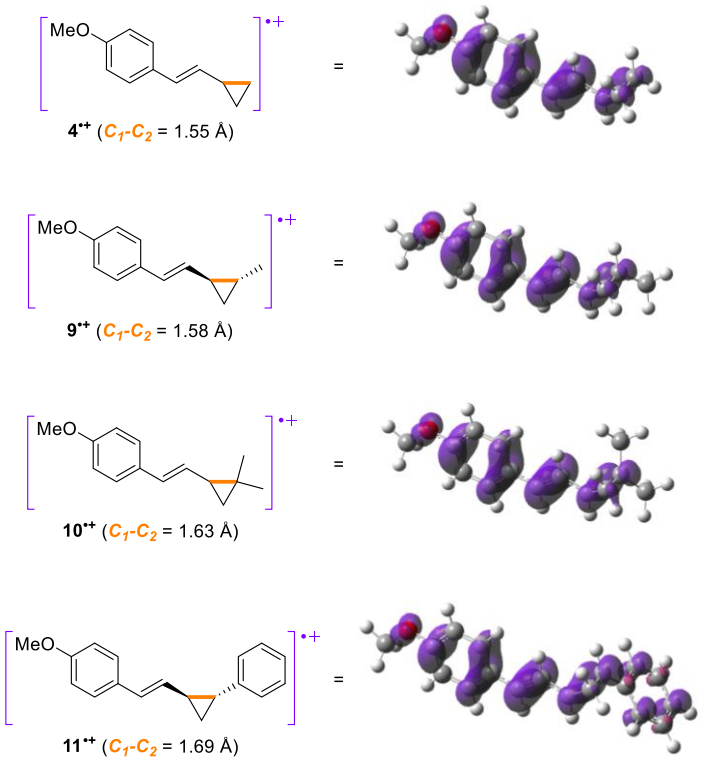


Substrate	Product
 **9**	 **12**, 45%
 **10**	 **13**, 52%
 **11**	 **14**, 72%

All reactions were carried out on a 0.20 mmol scale of the vinylcyclopropane (**9**-**11**) with 2 equiv of styrene (**2**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 1 h. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard.

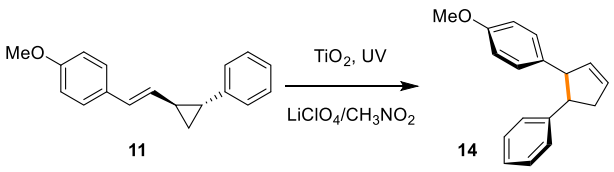
These observations were supported by DFT calculations (Figure 1). In the optimized structures of the radical cations (**4**$^{\bullet+}$, **9**$^{\bullet+}$, **10**$^{\bullet+}$, **11**$^{\bullet+}$), the bond length between C_1 and C_2 in the cyclopropyl framework was found to vary from 1.55 Å to 1.69 Å in response to the substituents. This trend indicates that the ring-opening was most favored in the radical cation (**11**$^{\bullet+}$), which was in good accordance with the experimental results.

Figure 1. Optimized Structures and Spin Density Distributions of the Radical Cations ($\mathbf{4}^{\bullet+}$, $\mathbf{9}^{\bullet+}$, $\mathbf{10}^{\bullet+}$, $\mathbf{11}^{\bullet+}$).



When the reaction of the vinylcyclopropane (**11**) was carried out in the absence of styrene (**2**), the yield of the cyclopentene (**14**) was significantly improved to 94% (Table 2, Entry 1). Control studies showed that both TiO_2 and light were necessary for efficient conversion to the cyclopentene (**14**) (Entries 2−4) and the use of $LiClO_4/CH_3NO_2$ solution was essential for the reaction (Entries 5−7). The vinylcyclopropane rearrangement remained high-yielding even on a 1 mmol scale (Entry 8).

Table 2. Optimization of the Conditions for the Vinylcyclopropane Rearrangement.



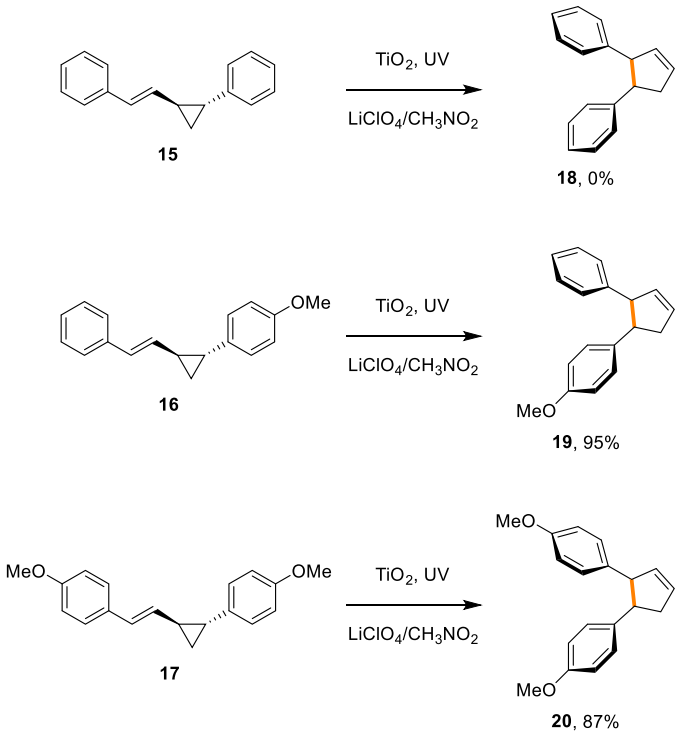
11 **14**

Entry	Conditions[a]	Yield (%)[b]
1		94 (0)
2	No TiO_2	11 (45)
3	No Light	9 (56)
4	No TiO_2, No Light	0 (100)
5	No $LiClO_4$	0 (100)
6	$LiClO_4/CH_3CN$	0 (72)
7	$LiClO_4/CH_3OH$	0 (100)
8	1.0 mmol Scale	81 (0)

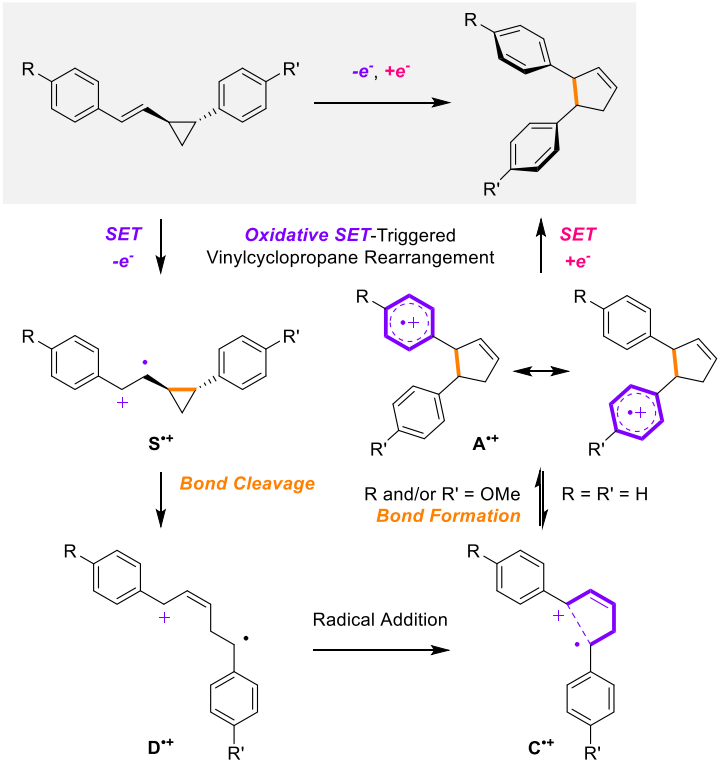
[a]Unless otherwise stated, reactions were carried out on a 0.20 mmol scale of the vinylcyclopropane (**11**) and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 1 h. [b]Determined by ^1H NMR analysis using benzaldehyde as an internal standard. Recovered starting material is reported in parentheses.

To gain further mechanistic insights, the vinylcyclopropanes (**15**–**17**) were synthesized and used for the reaction (Scheme 6). The reaction of the vinylcyclopropane (**15**), which has a nonsubstituted phenyl ring, did not give the cyclopentene (**18**) under TiO_2 photocatalysis conditions. On the other hand, the vinylcyclopropanes (**16**, **17**) were efficiently converted into the cyclopentenes (**19**, **20**), suggesting that either or both aryl rings must be electron-rich. On the basis of these results, a stepwise mechanism via distonic radical cations can be proposed (Scheme 7). The reaction is triggered by oxidative SET, which is followed by immediate ring-opening to generate a distonic radical cation ($\mathbf{D}^{\bullet+}$). Intramolecular radical addition then gives a transient cyclopentenyl radical cation ($\mathbf{C}^{\bullet+}$). When either or both aryl rings are electron-rich, the cyclopentenyl radical cation ($\mathbf{C}^{\bullet+}$) is efficiently converted into the aryl radical cation ($\mathbf{A}^{\bullet+}$), which affords the corresponding cyclopentenes by reductive SET.

Scheme 6. Preliminary Mechanistic Studies.

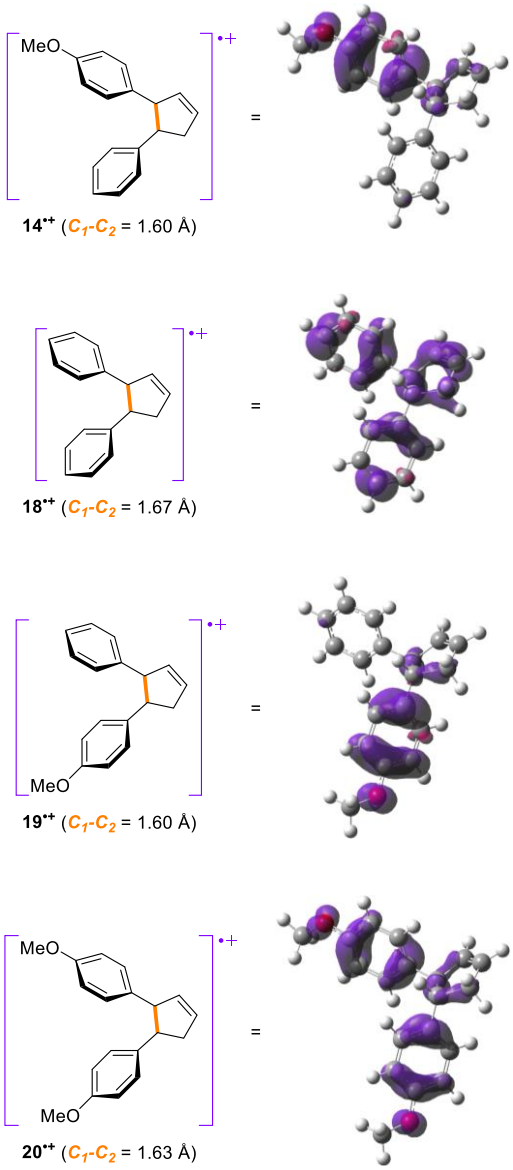


Scheme 7. Plausible Reaction Mechanism.



DFT calculations supported a formal expression of the reaction mechanism (Figure 2). In the optimized structures of the radical cations (**14**$^{\bullet+}$, **19**$^{\bullet+}$, **20**$^{\bullet+}$), spin densities were mainly localized in the aryl rings, suggesting that the aryl radical cations were more stable than the cyclopentenyl radical cations in these cases. On the other hand, the spin density in the optimized structure of the radical cation (**18**$^{\bullet+}$) was distributed over the entire molecule, including the cyclopentenyl moiety. Furthermore, the bond length between C_1 and C_2 in the cyclopentenyl framework was found to be 1.67 Å, which was in good accordance with the formal mechanistic understanding.

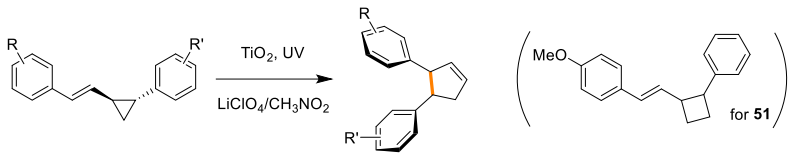
Figure 2. Optimized Structures and Spin Density Distributions of the Radical Cations (**14**$^{\bullet+}$, **18**$^{\bullet+}$, **19**$^{\bullet+}$, **20**$^{\bullet+}$).

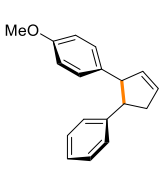


The scope of the aryl rings in the reaction was investigated using variously substituted vinylcyclopropanes (Scheme 8). The positioning effect of the methoxy group in either aryl ring was found to be similar, namely, *ortho*-substitutions (**21**, **23**) were less effective than *para*-variants (**14**, **19**) and *meta*-substitutions (**22**, **24**) were not productive. Installation of additional methoxy groups (**25**, **26**) had a negligible impact on the reaction, while the yields were finely

tuned by using weak electron-donating methyl groups (**27**−**32**). When both aryl rings were electron-rich, the corresponding cyclopentenes (**20**, **33**−**37**) were obtained in high yields. Several heteroarenes, except pyridine (**41**), and aryl halides were also found to be compatible with the reaction to give the corresponding cyclopentenes (**38**−**40**, **42**−**45**) in moderate to excellent yields. Strong electron-withdrawing cyano and trifluoromethyl groups had a negative effect on the reaction (**46**, **47**), likely because the nucleophilicity of the benzyl radical was decreased, inhibiting the intramolecular radical additions (from $\mathbf{D}^{\bullet+}$ to $\mathbf{C}^{\bullet+}$ in Scheme 7). Indeed, when the positions of the methoxy and trifluoromethyl groups were switched, the corresponding cyclopentene (**48**) was obtained in high yield. It should be noted that the rearrangement of donor-acceptor cyclopropanes (**49**, **50**) did not take place, suggesting that the method described herein would be complementary to previously reported Lewis acid-triggered versions.[12] Furthermore, vinylcyclobutane (**51**) was found to be productive under TiO_2 photocatalysis conditions, offering a unique approach to access six-membered rings.

Scheme 8. Scope of the Vinylcyclopropane Rearrangements.





14, 94%
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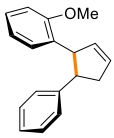

21, 61%
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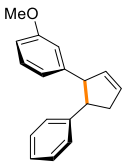
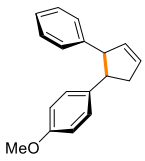


22, 0%



19, 95%
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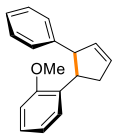

23, 49%
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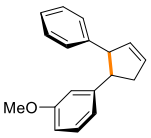
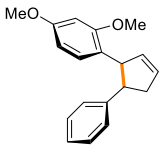


24, 0%



25, 91%
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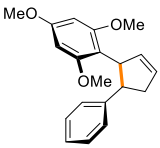

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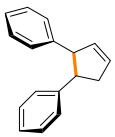
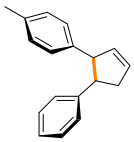


18, 0%



27, 13%
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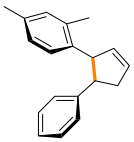

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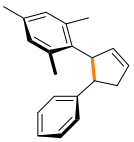

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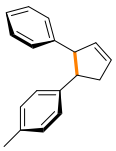

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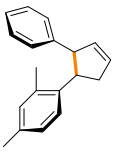
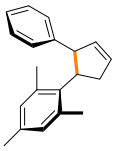


31, 65%
cis : *trans* = 1 : 8



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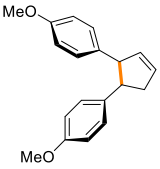

20, 87%
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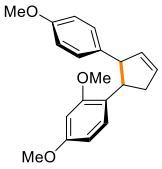

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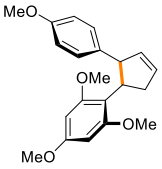
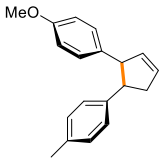
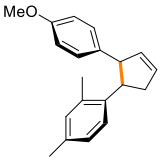


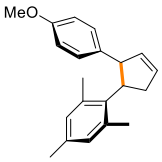
34, 92%
cis : *trans* = 1 : 2



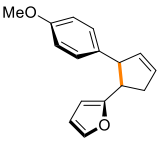
35, 68%
cis : *trans* = 1 : 2



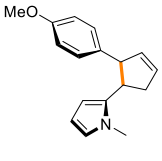
36, 78%
cis : *trans* = 1 : 2



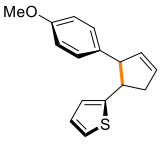
37, 79%
cis : *trans* = 1 : 7



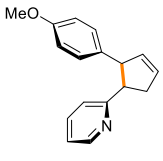
38, 46%
cis : *trans* = 1 : 2



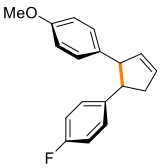
39, 65%
cis : *trans* = 1 : 3



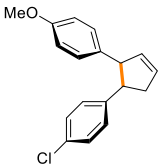
40, 96%
cis : *trans* = 1 : 2



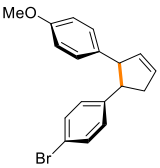
41, 0%



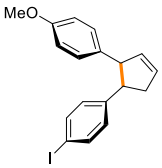
42, 91%
cis : *trans* = 2 : 3



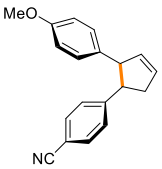
43, 87%
cis : *trans* = 3 : 5



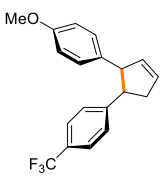
44, 81%
cis : *trans* = 2 : 3



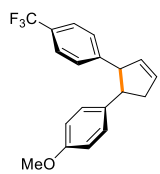
45, 56%
cis : *trans* = 2 : 3



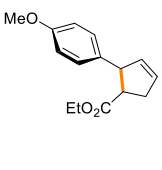
46, 75%
cis : *trans* = 1 : 4



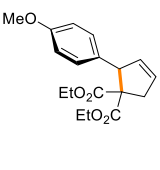
47, 46%
cis : *trans* = 1 : 1



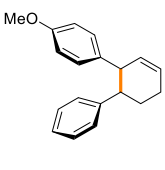
48, 86%
cis : *trans* = 1 : 3



49, 0%



50, 0%



51, 94%
cis : *trans* = 2 : 3

All reactions were carried out on a 0.20 mmol scale of the vinylcyclopropane and 100 mg of TiO_2 in 4 mL of CH_3NO_2 using a 15 W UV lamp at rt for 1 h. Yields were determined by ^1H NMR analysis using benzaldehyde as an internal standard.

CONCLUSION

In conclusion, we have demonstrated that radical cation vinylcyclopropane rearrangements are enabled by TiO_2 photocatalysis in $LiClO_4/CH_3NO_2$ solution. The reactions are triggered by oxidative single electron transfer, followed by immediate ring-opening to generate distonic radical cations. SET in combination with cyclopropyl ring-opening would be a versatile approach to generate distonic radical ions, which can be used as unique reactive intermediates in the field of synthetic organic chemistry. Furthermore, we found that this method can be applied to vinylcyclobutane for accessing six-membered rings. A stepwise mechanism via distonic radical cations can be proposed based on preliminary mechanistic studies, which are supported by DFT calculations. Further experimental and theoretical studies of reactions involving SET in combination with cycloalkyl ring-opening are under investigation in our laboratory.

EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were purchased from commercial sources and used without further purification. Reactions were monitored using thin-layer chromatography (TLC) with silica gel plates, and detection by UV absorption (254 nm) and by heating the plates after dipping them in a solution of 12 M molybdo(VI) phosphoric acid n-hydrate in 95% ethanol. Silica gel (particle size 40−50 μm) was used for column chromatography. ^{1}H nuclear magnetic resonance (NMR) spectra were collected on a 500 MHz NMR spectrometer using the deuterated solvent as an internal deuterium reference. Chemical shift data are given in δ units calibrated

with residual protic solvent. The multiplicity of a signal is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. $^{13}C\{^{1}H\}$ NMR spectra were collected at 125 MHz with proton decoupling using the deuterated solvent as an internal carbon reference. High-resolution mass spectra (HRMS) were collected using electrospray ionization (ESI) or direct analysis in real-time (DART) time-of-flight (TOF) spectrometers.

1-(2-Cyclopropylvinyl)-4-methoxybenzene (4, *cis* : *trans* = 1 : 4). White solid. To a solution of (4-methoxyphenylmethyl)triphenylphosphonium chloride (**S1**, 8.38 g, 20.0 mmol) in tetrahydrofuran (60 mL) stirred at 0 °C was added potassium *tert*-butoxide (2.24 g, 20.0 mmol). After the color turned red, the cyclopropanecarboxaldehyde (**S2**, 753 μL ,10.0 mmol) was added, stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the titled compound (**4**, 1.31 g, 7.60 mmol) in 76% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (2H, d, *J* = 8.6 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.41 (1H, d, *J* = 16.0 Hz), 5.59 (1H, dd, *J* = 16.0, 9.2 Hz), 3.78 (3H, s), 1.57-1.49 (1H, m), 0.84-0.77 (2H, m), 0.49-0.44 (2H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 158.4, 132.5, 130.6, 126.8, 126.6, 113.9, 55.1, 14.5, 7.1; HRMS m/z: $[M + H]^+$ calcd for $C_{12}H_{15}O$ 175.1123; found 175.1110.

2-Cyclopropyl-4'-methoxy-4,5-dimethyl-1,2,3,6-tetrahydro-1,1'-biphenyl (8, *cis* : *trans* = 1 : 12). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 51% (determined by NMR), isolated in 46% (51 mg, 0.18 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.09 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 3.80 (3H, s), 2.65-2.59 (1H, m), 2.29-2.13 (2H, m), 2.07-1.99 (1H, m), 1.93-1.85 (1H, m), 1.64 (3H, s), 1.63 (3H, s), 1.10-1.01 (1H, m), 0.45-0.37 (1H, m), 0.24-0.18 (1H, m), 0.07-0.01 (1H, m), -0.03- -0.09 (1H,

m), -0.27- -0.32 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl3) δ 157.7, 138.2, 128.8, 125.2, 125.2, 113.4, 55.3, 46.6, 44.4, 40.2, 37.9, 19.0, 18.8, 15.8, 5.0, 1.8 ; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{29}O_2$ 277.2168; found 277.2177.

1-Methoxy-4-(2-(2-methylcyclopropyl)vinyl)benzene (9, *cis* : *trans* = 1 : 30). White solid. To a solution of crotonic acid (**S3**, 2.58 g, 30 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (4.39 g, 45.0 mmol) in dichloromethane (80 mL) stirred at room temperature were added *N*,*N'*-diisopropylcarbodiimide (6.97 mL, 45.0 mmol), 4-dimethylaminopyridine (36.7 mg, 0.30 mmol), and *N*,*N*-diisopropylethylamine (10.3 mL, 60.0 mmol). The resulting reaction mixture was stirred at room temperature overnight, diluted with water, and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 1/1) gave the Weinreb amide (**S4**) in 60% yield (2.32 g, 18.0 mmol). To a solution of trimethylsulfoxonium iodide (7.92 g, 36.0 mmol) in dimethyl sulfoxide (80 mL) stirred with a water bath was added NaH (1.44 g, 36.0 mmol). The resulting reaction mixture was stirred with a water bath for 30 min, the Weinreb amides (**S4**, 2.32 g, 18.0 mmol) was added. The resulting reaction mixture was stirred with a water bath for 4 h, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 1/1) gave the cyclopropane (**S5**) in 78% yield (2.01 g, 14.0 mmol). To a solution of the cyclopropane (**S5**, 1.72 g, 12.0 mmol) in tetrahydrofuran (50 mL) stirred at 0 °C was added lithium aluminum hydride (683 mg, 18.0 mmol). The resulting reaction mixture was stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with pentane. The combined organic layers were dried over sodium sulfate, filtered, and used without further purification. To a

solution of (4-methoxyphenylmethyl)triphenylphosphonium chloride (**S1**, 10.0 g, 24.0 mmol) in tetrahydrofuran (60 mL) stirred at 0 °C was added potassium *tert*-butoxide (2.69 g, 24.0 mmol). After the color turned red, the aldehyde (**S6**) was added, stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the titled compounds in 24% yield (542 mg, 2.90 mmol) over 2 steps. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.22 (2H, d, *J* = 8.6 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.36 (1H, d, *J* = 16.0 Hz), 5.62 (1H, dd, *J* = 15.5, 8.6 Hz), 3.78 (3H, s), 1.25-1.19 (1H, m), 1.10 (3H, d, *J* = 5.7 Hz), 0.89-0.82 (1H, m), 0.68-0.63 (1H, m), 0.57-0.52 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.4, 132.4, 130.7, 126.6, 126.3, 113.9, 55.2, 23.4, 18.6, 15.6, 15.6; HRMS m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O$ 189.1279; found 189.1258.

1-Methoxy-4-(2-(2-methylcyclopropyl)vinyl)benzene (10, *cis* : *trans* = 1 : 7). White solid. To a solution of the 2,2-dimethylcyclopropanecarboxylic acid (**S7**, 5.00 g, 43.8 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (5.85 g, 60.0 mmol) in dichloromethane (100 mL) stirred at room temperature were added *N*,*N'*-diisopropylcarbodiimide (9.29 mL, 60.0 mmol), 4-dimethylaminopyridine (48.9 mg, 0.40 mmol), and *N*,*N*-diisopropylethylamine (13.6 mL, 80 mmol). The resulting reaction mixture was stirred at room temperature overnight, diluted with water, and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 1/1) gave the Weinreb amide in 54 % yield (**S8**, 3.73 g, 23.7 mmol). To a solution of the Weinreb amide (**S8**, 3.14 g, 20.0 mmol) in tetrahydrofuran (50 mL) stirred at 0 °C was added lithium aluminum hydride (949 mg, 25.0 mmol). The resulting reaction mixture was stirred at

0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with pentane. The combined organic layers were dried over sodium sulfate, filtered, and used without further purification. To a solution of (4-methoxyphenylmethyl)triphenylphosphonium chloride (**S1**, 12.6 g, 30.0 mmol) in tetrahydrofuran (80 mL) stirred at 0 °C was added potassium *tert*-butoxide (3.36 g, 30.0 mmol). After the color turned red, the aldehyde (**S9**) was added, stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the titled compound (**10**) in 12% yield (485 mg, 2.40 mmol) over 2 steps. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 6.40 (1H, d, *J* = 16.0 Hz), 5.84 (1H, dd, *J* = 16.0, 9.2 Hz), 3.79 (3H, s), 1.42-1.36 (1H, m), 1.12 (3H, s), 1.11 (3H, s), 0.74 (1H, dd, *J* = 8.6, 4.6 Hz), 0.46 (1H, t, *J* = 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.5, 130.9, 129.4, 128.6, 126.7, 113.9, 55.3, 28.5, 27.2, 22.1, 20.8, 19.4; HRMS m/z: $[M + H]^+$ calcd for $C_{14}H_{19}O$ 203.1436; found 203.1428.

General Procedure for the Synthesis of the Vinylcyclopropanes (11, 15−17, S17−S44). To a solution of malonic acid (**S10**, 6.25 g, 60.0 mmol) and the respective benzaldehyde (**S11**, 30.0 mmol) in pyridine (80 mL) stirred at 130 °C was added piperidine (3 mL). The resulting reaction mixture was stirred at 130 °C for 5 h, acidified with 1 M HCl aq., diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, concentrated in vacuo, and used without further purification. To a solution of the respective substituted cinnamic acids (**S12**) and *N*,*O*-dimethylhydroxylamine hydrochloride (4.39 g, 45.0 mmol) in dichloromethane (80 mL) stirred at room temperature were added *N*,*N'*-

diisopropylcarbodiimide (6.97 mL, 45.0 mmol), 4-dimethylaminopyridine (36.7 mg, 0.30 mmol), and *N*,*N*-diisopropylethylamine (10.3 mL, 60.0 mmol). The resulting reaction mixture was stirred at room temperature overnight, diluted with water, and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 2/1−1/2) gave the respective Weinreb amides (**S13**) in 38−66% yield over 2 steps. To a solution of trimethylsulfoxonium iodide (4.84 g, 22.0 mmol) in dimethyl sulfoxide (60 mL) stirred with a water bath was added NaH (880 mg, 22.0 mmol). The resulting reaction mixture was stirred with a water bath for 30 min, the respective Weinreb amides (**S13**, 11.0 mmol) was added. The resulting reaction mixture was stirred with a water bath for 4 h, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 2/1−1/2) gave the respective cyclopropanes (**S14**) in 76−84% yield. To a solution of the respective cyclopropanes (**S14**, 8.00 mmol) in tetrahydrofuran (50 mL) stirred at 0 °C was added lithium aluminum hydride (380 mg, 10.0 mmol). The resulting reaction mixture was stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and used without further purification. To a solution of the respective (arylmethyl)triphenylphosphonium halides (**S16**, 16.0 mmol) in tetrahydrofuran (60 mL) stirred at 0 °C was added potassium *tert*-butoxide (1.80 g, 16.0 mmol). After the color turned red, the respective aldehydes (**S15**) was added, stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography

(hexane/ethyl acetate = 50/1−10/1) gave the titled compounds (**11**, **15**−**17**, **S17**−**S44**) in 24−65% yield over 2 steps.

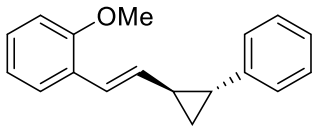
1-Methoxy-4-(2-(2-phenylcyclopropyl)vinyl)benzene (11, *cis* : *trans* = 1 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.23 (4H, m), 7.16 (1H, t, *J* = 7.5 Hz), 7.09 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.43 (1H, d, *J* = 16.0 Hz), 5.78 (1H, dd, *J* = 16.0, 8.6 Hz), 3.80 (3H, s), 2.04-1.99 (1H, m), 1.84-1.78 (1H, m), 1.32-1.26 (1H, m), 1.23-1.18 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 142.3, 130.6, 130.3, 128.4, 127.7, 126.8, 125.6, 125.6, 113.9, 55.2, 27.5, 25.6, 17.1; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1441.

2-(2-Phenylcyclopropyl)vinylbenzene (15, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.22 (6H, m), 7.21-7.13 (2H, m), 7.12-7.04 (2H, m), 6.47 (1H, d, *J* = 15.5 Hz), 5.90 (1H, dd, *J* = 15.5, 8.6 Hz), 2.06-2.00 (1H, m), 1.86-1.79 (1H, m), 1.34-1.26 (1H, m), 1.25-1.18 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.1, 137.5, 132.8, 128.5, 128.4, 128.3, 128.3, 126.8, 125.7, 125.6, 27.5, 25.7, 17.2; HRMS m/z: $[M + H]^+$ calcd for $C_{17}H_{17}$ 221.1330; found 221.1341.

1-Methoxy-4-(2-styrylcyclopropyl)benzene (16, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.25 (4H, m), 7.21-7.16 (1H, m), 7.03 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.47 (1H, d, *J* = 16.0 Hz), 5.90 (1H, dd, *J* = 15.5, 8.6 Hz), 3.78 (3H, s), 2.03-1.97 (1H, m), 1.79-1.72 (1H, m), 1.28-1.21 (1H, m), 1.19-1.14 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.8, 137.6, 134.0, 133.1, 128.5, 128.0, 126.8, 126.7, 125.6, 113.8, 55.2, 27.0, 25.0, 16.7; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1435.

1-Methoxy-4-(2-(2-(4-methoxyphenyl)cyclopropyl)vinyl)benzene (17, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 20/1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (2H, d, *J* = 8.6 Hz), 7.03 (2H, d, *J* = 8.6 Hz), 6.83 (4H, d, *J* = 8.6 Hz), 6.42 (1H, d, *J* = 15.5 Hz), 5.76 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 3.78 (3H, s), 2.00-1.95 (1H, m), 1.76-1.69 (1H, m), 1.25-1.19 (1H, m), 1.17-1.12 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 157.8, 134.3, 130.9, 130.5, 129.9, 128.8, 126.8, 114.0, 113.9, 55.4, 55.3, 27.0, 24.9, 16.6; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O_2$ 281.1542; found 281.1541.

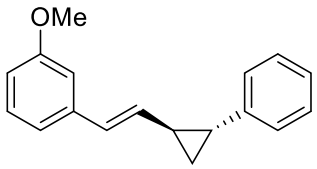
1-Methoxy-2-(2-(2-phenylcyclopropyl)vinyl)benzene (S17, *cis* : *trans* = 1 : 15). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S17

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (1H, dd, *J* = 7.5, 1.2 Hz), 7.27 (2H, t, *J* = 7.5 Hz), 7.20-7.14 (2H, m), 7.10 (2H, dd, *J* = 8.6, 1.7 Hz), 6.90 (1H, t, *J* = 7.5 Hz), 6.85 (1H, d, *J* = 8.0 Hz), 6.80 (1H, d, *J* = 15.5 Hz), 5.91 (1H, dd, *J* = 16.0, 8.6 Hz), 3.84 (3H, s), 2.06-2.01 (1H, m), 1.90-1.84 (1H, m), 1.33-1.29 (1H, m), 1.25-1.20 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.1, 142.3, 133.6, 128.4, 127.8, 126.5, 126.2, 125.7, 125.6, 123.0, 120.6, 110.7, 55.4, 28.1, 25.8, 17.4; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1432.

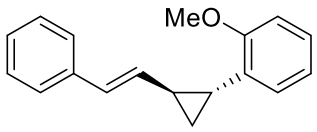
1-Methoxy-3-(2-(2-phenylcyclopropyl)vinyl)benzene (S18, *cis* : *trans* = 1 : 10). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S18

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (2H, t, *J* = 7.5 Hz), 7.20 (1H, t, *J* = 8.0 Hz), 7.17 (1H, t, *J* = 7.5 Hz), 7.10 (2H, d, *J* = 7.5 Hz), 6.92 (1H, d, *J* = 8.0 Hz), 6.85 (1H, m), 6.75 (1H, dd, *J* = 8.0, 2.3 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 5.90 (1H, dd, *J* = 16.0, 8.6 Hz), 3.81 (3H, s), 2.05 (1H, m), 1.83 (1H, m), 1.33 (1H, m), 1.23 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.8, 142.0, 138.9, 133.2, 129.5, 128.3, 128.1, 125.6, 125.6, 118.3, 112.3, 111.0, 55.0, 27.5, 25.7, 17.1; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1424.

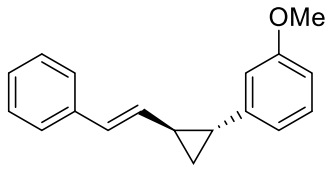
1-Methoxy-2-(2-styrylcyclopropyl)benzene (S19, *cis* : *trans* = 1 : 10). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S19

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (2H, d, *J* = 6.9 Hz), 7.29 (2H, t, *J* = 7.5 Hz), 7.20-7.13 (2H, m), 6.92-6.83 (3H, m), 6.49 (1H, d, *J* = 16.0 Hz), 5.96 (1H, dd, *J* = 15.5, 8.6 Hz), 3.85 (3H, s), 2.39-2.34 (1H, m), 1.83-1.77 (1H, m), 1.31-1.24 (1H, m), 1.21-1.15 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.4, 138.1, 133.9, 130.7, 129.0 128.4, 127.1, 127.0, 126.2, 125.1, 121.0, 110.7, 55.8, 26.7, 20.2, 16.5; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1450.

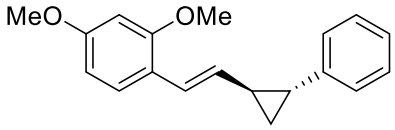
1-Methoxy-3-(2-styrylcyclopropyl)benzene (S20, *cis* : *trans* = 1 : 5). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S20

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.26 (4H, m), 7.22-7.16 (2H, m), 6.74-6.68 (2H, m), 6.65-6.64 (1H, m), 6.48 (1H, d, *J* = 16.0 Hz), 5.90 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 2.05-1.99 (1H, m), 1.97-1.80 (1H, m), 1.35-1.29 (1H, m), 1.24-1.19 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.6, 143.7, 137.3, 132.5, 129.2, 128.4, 128.2, 126.6, 125.6, 117.8, 111.6, 110.7, 54.7, 27.4, 25.6, 17.0; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1442.

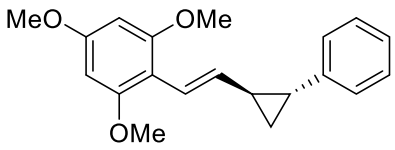
2,4-Dimethoxy-1-(2-(2-phenylcyclopropyl)vinyl)benzene (S21, *cis* : *trans* = 1 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 20/1).



S21

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30-7.26 (2H, m), 7.26-7.22 (1H, m), 7.15 (1H, t, *J* = 7.5 Hz), 7.09 (2H, dd, *J* = 8.0, 1.2 Hz), 6.70 (1H, d, *J* = 15.5 Hz), 6.47-6.42 (2H, m), 5.81 (1H, dd, *J* = 16.0, 8.6 Hz), 3.82 (3H, s), 3.80 (3H, s), 2.04-1.98 (1H, m), 1.87-1.80 (1H, m), 1.28 (1H, dt, *J* = 8.6, 5.2 Hz), 1.21 (1H, dt, *J* = 8.6, 5.2); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.0, 157.4, 142.7, 131.6, 128.5, 127.0, 125.8, 125.6, 122.9, 119.8, 104.9, 98.6, 55.6, 55.5, 28.2, 25.9, 17.4; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{20}O_2$ 281.1542; found 281.1512.

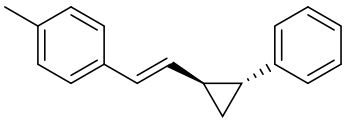
1,3,5-Trimethoxy-2-(2-(2-phenylcyclopropyl)vinyl)benzene (S22, *cis* : *trans* = 1 : 10). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1).



S22

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.22 (2H, m), 7.14 (1H, t, *J* = 7.5 Hz), 7.09 (2H, dd, *J* = 8.6, 1.7 Hz), 6.71 (1H, d, *J* = 16.0 Hz), 6.20 (1H, dd, *J* = 16.0, 8.6 Hz), 6.13 (2H, s), 3.82 (6H, s), 3.81 (3H, s), 2.04-1.98 (1H, m), 1.85-1.78 (1H, m), 1.27 (1H, dt, *J* = 8.0, 5.2 Hz), 1.20 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.2, 158.5, 142.5, 134.0, 128.0, 125.3, 125.1, 118.4, 107.6, 90.4, 55.3, 54.8, 29.2, 25.5, 17.2; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{22}O_3$ 310.1569; found 310.1572.

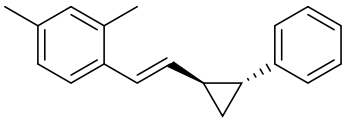
1-Methyl-4-(2-(2-phenylcyclopropyl)vinyl)benzene (S23, *cis* : *trans* = 1 : 8). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S23

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (2H, t, *J* = 7.7 Hz), 7.21 (2H, d, *J* = 8.0 Hz), 7.16 (1H, t, *J* = 6.9 Hz), 7.11-7.07 (4H, m), 6.45 (1H, d, *J* = 16.0 Hz), 5.86 (1H, dd, *J* = 15.5, 8.6 Hz), 2.32 (3H, s), 2.05-2.00 (1H, m),1.85-1.79 (1H, m), 1.33-1.28 (1H, m), 1.23-1.19 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 136.4, 134.7, 131.7, 129.2, 128.4, 128.2, 125.7, 125.6, 27.6, 25.7, 21.2, 17.2; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}$ 235.1487; found 235.1496.

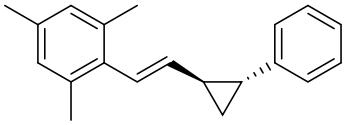
2,4-Dimethyl-1-(2-(2-phenylcyclopropyl)vinyl)benzene (S24, *cis* : *trans* = 1 : 6). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S24

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.26 (3H, m), 7.17 (1H, t, *J* = 8.6 Hz), 7.10 (2H, dd, *J* = 8.0, 1.2 Hz), 6.99-6.92 (2H, m), 6.65 (1H, d, *J* = 16.0 Hz), 5.72 (1H, dd, *J* = 15.5, 8.6 Hz), 2.30 (3H, s), 2.29 (3H, s), 2.05-1.99 (1H, m), 1.89-1.83 (1H, m), 1.34-1.29 (1H, m), 1.24-1.19 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 136.2, 134.5, 133.6, 133.0, 131.0, 128.3, 126.8, 125.9, 125.6, 125.5, 124.9, 27.9, 25.7, 21.0, 19.8, 17.3; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}$ 249.1643; found 249.1647.

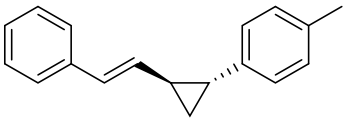
1,3,5-Trimethyl-2-(2-(2-phenylcyclopropyl)vinyl)benzene (S25, *cis* : *trans* = 1 : 9). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S25

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (2H, t, *J* = 7.5 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 7.11 (2H, d, *J* = 7.5 Hz), 6.85 (2H, s), 6.40 (1H, d, *J* = 16.0 Hz), 5.36 (1H, dd, *J* = 16.6, 8.6 Hz), 2.27 (6H, s), 2.26 (3H, s), 2.01-1.95 (1H, m), 1.91-1.84 (1H, m), 1.27 (1H, dt, *J* = 8.6, 5.2 Hz), 1.18 (1H, dt, *J* = 9.2, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.5, 137.2, 135.8, 135.8, 135.6, 134.1, 128.6, 128.4, 125.6, 125.6, 27.5, 25.3, 21.1, 21.0, 17.1; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}$ 263.1800; found 263.1784.

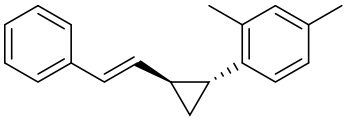
1-Methyl-4-(2-styrylcyclopropyl)benzene (S26, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S26

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.26 (4H, m), 7.18 (1H, t, *J* = 6.8 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 7.00 (2H, d, *J* = 8.0 Hz), 6.47 (1H, d, *J* = 16.0 Hz), 5.90 (1H, dd, *J* = 16.0, 8.6 Hz), 2.32 (3H, s), 2.04-1.98 (1H, m), 1.82-1.76 (1H, m), 1.29 (1H, dt, *J* = 8.6, 5.2 Hz), 1.19 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.1, 137.6, 135.3, 133.1, 129.1, 128.6, 128.1, 126.8, 125.7, 125.7, 27.3, 25.5, 21.0, 17.0; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}$ 235.1487; found 235.1506.

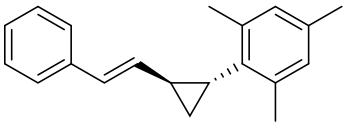
2,4-Dimethyl-1-(2-styrylcyclopropyl)benzene (S27, *cis* : *trans* = 1 : 8). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S27

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (2H, m), 7.29 (2H, t, *J* = 7.5 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 6.99-6.98 (1H, m), 6.96-6.90 (1H, d, *J* = 15.5 Hz), 5.98 (1H, dd, *J* = 15.5, 8.6 Hz), 2.36 (3H, s), 2.29 (3H, s), 2.04-1.98 (1H, m), 1.69-1.61 (1H, m), 1.34-1.29 (1H, m), 1.14 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.8, 137.6, 136.8, 135.5, 133.6, 130.6, 128.6, 128.0, 126.7, 126.4, 125.8, 125.7, 25.3, 23.7, 21.0, 19.8, 14.9; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}$ 249.1643; found 249.1664.

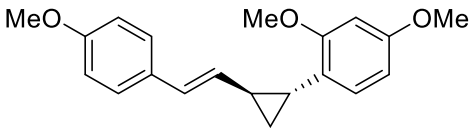
1,3,5-Trimethyl-2-(2-styrylcyclopropyl)benzene (S28, *cis* : *trans* = 1 : 6). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S28

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (2H, m), 7.30 (2H, t, *J* = 7.5 Hz), 7.19 (1H, t, *J* = 7.5 Hz), 6.84 (2H, s), 6.56 (1H, d, *J* = 16.0 Hz), 5.98 (1H, dd, *J* = 16.0, 9.2 Hz), 2.37 (6H, s), 2.26 (3H, s), 1.87-1.81 (1H, m), 1.69-1.61 (1H, m), 1.27-1.22 (1H, m), 1.12-1.06 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.8, 137.7, 135.9, 135.0, 133.8, 128.8, 128.6, 128.3, 126.8, 125.8, 25.4, 22.4, 20.9, 20.9, 17.5; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}$ 263.1800; found 263.1790.

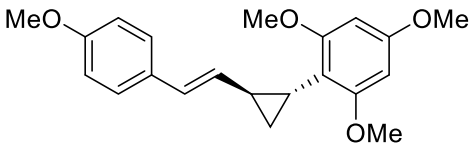
2,4-Dimethoxy-1-(2-(4-methoxystyryl)cyclopropyl)benzene (S29, *cis* : *trans* = 1 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1).



S29

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.81-6.77 (1H, m), 6.47-6.42 (2H, m), 6.42 (1H, d, *J* = 16.0 Hz), 5.82 (1H, dd, *J* = 15.5, 8.6 Hz), 3.81 (3H, s), 3.79 (3H, s), 3.78 (3H, s), 2.23-2.15 (1H, m), 1.73-1.66 (1H, m), 1.19 (1H, dt, *J* = 8.6, 5.2 Hz), 1.09 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.0, 158.8, 158.5, 131.5, 129.9, 127.2, 126.7, 125.5, 122.9, 113.9, 104.0, 98.5, 55.5, 55.3, 55.2, 25.5, 19.4, 15.5; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}O_3$ 311.1647; found 311.1667.

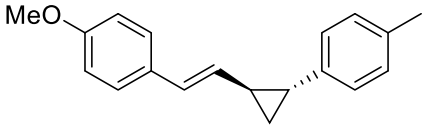
1,3,5-Trimethoxy-2-(2-(4-methoxystyryl)cyclopropyl)benzene (S30, *cis* : *trans* = 1 : 6). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1).



S30

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 6.12 (2H, s), 5.84 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (12H, s), 2.02-1.95 (1H, m), 1.90-1.84 (1H, m), 1.43-1.38 (1H, m), 1.05-1.00 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.0, 159.2, 158.4, 132.8, 131.0, 129.8, 126.7, 113.9, 109.9, 91.0, 55.8, 55.3, 55.3, 23.4, 16.6, 15.2; HRMS m/z: $[M + H]^+$ calcd for $C_{21}H_{25}O_4$ 341.1753; found 341.1743.

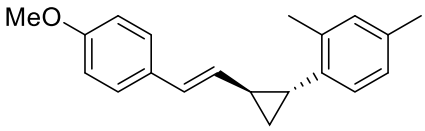
1-Methoxy-4-(2-(2-(p-tolyl)cyclopropyl)vinyl)benzene (S31, *cis* : *trans* = 1 : 5). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S31

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 7.08 (2H, d, *J* = 8.0 Hz), 6.98 (2H, d, *J* = 8.0 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 6.41 (1H, d, *J* = 16.0 Hz), 5.76 (1H, dd, *J* = 15.5, 8.6 Hz), 3.78 (3H, s), 2.01-1.95 (1H, m), 1.79-1.72 (1H, m), 1.28-1.22 (1H, m), 1.18-1.13 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 139.2, 135.0, 130.7, 130.4, 129.0, 127.5, 126.8, 125.6, 113.9, 55.1, 27.3, 25.3, 21.0, 16.8; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O$ 265.1592; found 265.1591.

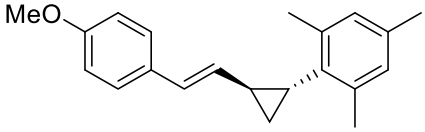
1-(2-(4-Methoxystyryl)cyclopropyl)-2,4-dimethylbenzene (S32, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S32

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (2H, d, *J* = 8.6 Hz), 7.00-6.86 (3H, m), 6.84 (2H, d, *J* = 8.6 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 5.84 (1H, dd, *J* = 15.5, 8.6 Hz), 3.81 (3H, s), 2.35 (3H, s), 2.29 (3H, s), 2.03-1.94 (1H, m), 1.66-1.59 (1H, m), 1.33-1.24 (1H, m), 1.11 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.5, 137.6, 136.8, 135.3, 131.1, 130.5, 130.4, 127.4, 126.7, 126.4, 125.6, 113.9, 55.0, 25.2, 23.5, 20.9, 19.8, 14.8; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}O$ 279.1749; found 279.1731.

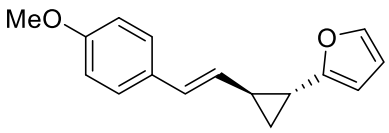
2-(2-(4-Methoxystyryl)cyclopropyl)-1,3,5-trimethylbenzene (S33, *cis* : *trans* = 1 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S33

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.6 Hz), 6.84 (2H, m), 6.50 (1H, d, *J* = 16.0 Hz), 5.84 (1H, dd, *J* = 15.5, 9.2 Hz), 3.81 (3H, s), 2.37 (6H, s), 2.25 (3H, s), 1.83-1.78 (1H, m), 1.66-1.59 (1H, m), 1.24-1.15 (1H, m), 1.09-1.04 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 138.8, 135.8, 135.1, 131.5, 128.8, 127.7, 126.8, 114.0, 55.4, 25.3, 22.3, 21.9, 20.6, 17.3; HRMS m/z: $[M + H]^+$ calcd for $C_{21}H_{25}O$ 293.1905; found 293.1932.

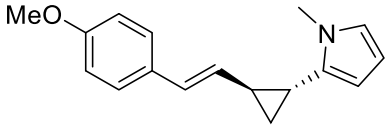
2-(2-(4-Methoxystyryl)cyclopropyl)furan (S34, *cis* : *trans* = 1 : 10). Pale yellow solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S34

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26-7.25(1H, m), 7.25 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.44 (1H, d, *J* = 16.0 Hz), 6.29-6.27 (1H, m), 5.99 (1H, d, *J* = 2.9 Hz), 5.72 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 2.06-1.99 (1H, m), 1.95-1.89 (1H, m), 1.37-1.31 (1H, m), 1.14-1.09 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 155.6, 140.4, 130.2, 129.5, 128.2, 126.8, 113.9, 110.4, 103.7, 55.0, 24.6, 18.7, 14.6; HRMS m/z: $[M + H]^+$ calcd for $C_{16}H_{17}O_2$ 241.1229; found 241.1203.

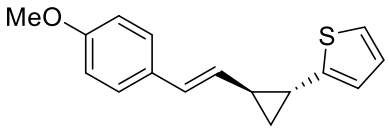
2-(2-(4-Methoxystyryl)cyclopropyl)-1-methyl-1H-pyrrole (S35, *cis* : *trans* = 1 : 5). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S35

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 6.56-6.55 (1H, m), 6.45 (1H, d, *J* = 16.0 Hz), 6.03-6.00 (1H, m), 5.82-5.80 (1H, m), 5.78 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 3.62 (3H, s), 1.83-1.78 (1H, m), 1.70-1.63 (1H, m), 1.26-1.20 (1H, m), 1.11-1.07 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 133.9, 132.9, 130.4, 129.8, 126.7, 121.3, 114.0, 106.4, 104.7, 55.2, 33.8, 24.5, 17.0, 14.3; HRMS m/z: $[M + H]^+$ calcd for $C_{17}H_{20}ON$ 254.1545; found 254.1535.

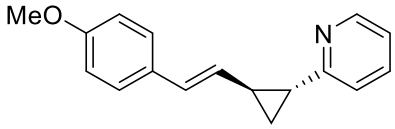
2-(2-(4-Methoxystyryl)cyclopropyl)thiophene (S36, *cis* : *trans* = 1 : 15). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S36

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (2H, d, *J* = 8.6 Hz), 7.06 (1H, dd, *J* = 5.2, 1.2 Hz), 6.90 (1H, dd, *J* = 4.6, 3.4 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.79 (1H, d, *J* = 3.4 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 5.75 (1H, dd, *J* = 16.0, 8.6 Hz), 3.80 (3H, s), 2.24-2.19 (1H, m), 1.88-1.82 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.7, 146.7, 130.2, 129.6, 128.1, 126.8, 126.8, 122.6, 122.0, 113.9, 55.1, 28.0, 21.0, 18.0; HRMS m/z: $[M + H]^+$ calcd for $C_{16}H_{17}OS$ 257.1000; found 257.0971.

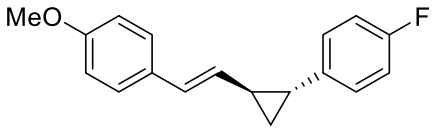
2-(2-(4-Methoxystyryl)cyclopropyl)pyridine (S37, *cis* : *trans* = 2 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1).



S37

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.47-8.45 (1H, m), 7.55-7.52 (1H, m), 7.25 (2H, d, *J* = 8.6 Hz), 7.17 (1H, d, *J* = 8.6 Hz), 7.06-7.02 (1H, m), 6.83 (2H, d, *J* = 8.6 Hz), 6.46 (1H, d, *J* = 15.5 Hz), 5.80 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 2.19-2.09 (2H, m), 1.67-1.59 (1H, m), 1.25-1.20 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.9, 158.6, 149.2, 135.7, 130.1, 129.8, 128.1, 126.7, 121.8, 120.4, 113.9, 55.1, 27.6, 27.0, 17.6; HRMS m/z: $[M + H]^+$ calcd for $C_{17}H_{18}ON$ 252.1388; found 252.1369.

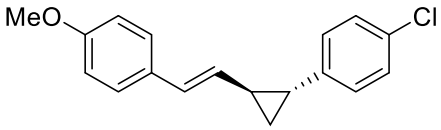
1-Fluoro-4-(2-(4-methoxystyryl)cyclopropyl)benzene (S38, *cis* : *trans* = 1 : 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S38

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 8.6 Hz), 7.07-7.03 (2H, m), 6.98-6.93 (2H, m), 6.83 (2H, d, *J* = 8.6 Hz), 6.43 (1H, d, *J* = 16.0 Hz), 5.76 (1H, dd, *J* = 16.0, 8.6 Hz), 3.80 (3H, s), 2.02-1.97 (1H, m), 1.78-1.71 (1H, m), 1.24 (1H, dt, *J* = 8.6, 5.2 Hz), 1.19 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.2 (d, J = 243.5 Hz), 158.7, 137.9 (d, J = 2.4 Hz), 130.5, 130.3, 127.8, 127.2 (d, J = 7.2 Hz), 126.8, 115.2 (d, J = 21.6 Hz), 114.0, 55.3, 27.3, 24.9, 16.9; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OF$ 269.1342; found 269.1312.

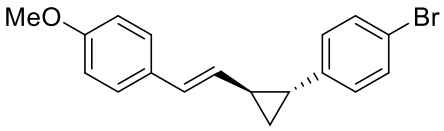
1-Chloro-4-(2-(4-methoxystyryl)cyclopropyl)benzene (S39, *cis* : *trans* = 4 : 1). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S39

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (2H, d, *J* = 8.6 Hz), 7.23 (2H, d, *J* = 8.6 Hz), 7.00 (2H, d, *J* = 8.6 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.37 (1H, d, *J* = 11.5 Hz), 5.17 (1H, dd, *J* = 11.5, 9.2 Hz), 3.79 (3H, s), 2.09-2.03 (1H, m), 2.00-1.95 (1H, m), 1.25 (1H, dt, *J* = 8.0, 5.2 Hz), 1.15 (1H, dt, *J* = 9.2, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.3, 140.6, 132.6, 130.1, 130.0, 129.8, 128.5, 127.0, 127.0, 113.7, 55.2, 25.6, 24.2, 18.4; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OCl$ 285.1046; found 285.1033.

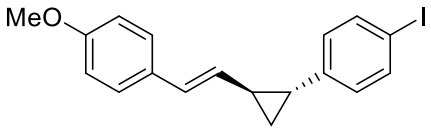
1-Bromo-4-(2-(4-methoxystyryl)cyclopropyl)benzene (S40, *cis* : *trans* = 2 : 3). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S40

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (2H, d, *J* = 8.0 Hz), 7.25 (2H, d, *J* = 9.2 Hz), 6.96 (2H, d, *J* = 8.0 Hz), 6.83 (2H, d, *J* = 9.2 Hz), 6.43 (2H, d, *J* = 16.0 Hz), 5.75 (1H, dd, *J* = 15.5, 8.6 Hz), 3.80 (3H, s), 1.99-1.94 (1H, m), 1.80-1.74 (1H, m), 1.28-1.19 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.7, 141.4, 132.5, 131.3, 130.2, 129.8, 128.0, 127.4, 119.1, 114.0, 55.2, 27.6, 25.1, 17.2; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OBr$ 329.0541; found 329.0544.

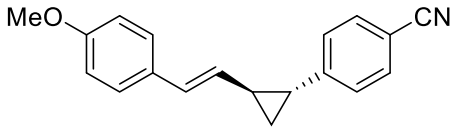
1-Iodo-4-(2-(4-methoxystyryl)cyclopropyl)benzene (S41, *cis* : *trans* = 1 : 6). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S41

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (2H, d, *J* = 8.6 Hz), 7.25 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.42 (1H, d, *J* = 16.0 Hz), 5.75 (1H, dd, *J* = 16.0, 8.6 Hz), 3.80 (3H, s), 1.98-1.92 (1H, m), 1.80-1.73 (1H, m), 1.25 (1H, dt, *J* = 8.6, 5.2 Hz), 1.20 (1H, dt, *J* = 8.6, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.7, 142.2, 137.3, 130.3, 130.1, 128.1, 127.8, 126.8, 114.0, 90.2, 55.3, 27.7, 25.3, 17.2; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OI$ 377.0402; found 377.0404.

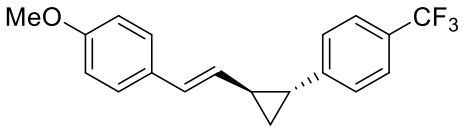
4-(2-(4-Methoxystyryl)cyclopropyl)benzonitrile (S42, *cis* : *trans* = 1 : 3). Pale yellow solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S42

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (2H, d, *J* = 8.6 Hz), 7.26 (2H, d, *J* = 8.6 Hz), 7.15 (2H, d, *J* = 8.6 Hz), 6.85 (2H, d, *J* = 8.6 Hz), 6.45 (1H, d, *J* = 15.5 Hz), 5.75 (1H, dd, *J* = 16.0, 8.6 Hz), 3.80 (3H, s), 2.07-2.01 (1H, m), 1.89-1.83 (1H, m), 1.38-1.30 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.6, 148.2, 131.9, 131.9, 129.7, 129.6, 126.7, 125.9, 119.4, 113.8, 108.7, 55.0, 28.7, 25.6, 17.9; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}ON$ 276.1388; found 276.1402.

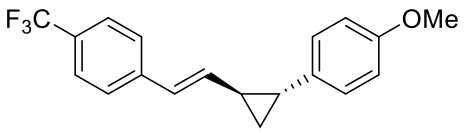
1-Methoxy-4-(2-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)vinyl)benzene (S43, *cis* : *trans* = 1: 4). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S43

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (2H, d, *J* = 8.0 Hz), 7.25 (2H, d, *J* = 8.6 Hz), 7.16 (2H, d, *J* = 8.0 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 6.44 (1H, d, *J* = 15.5 Hz), 5.76 (1H, dd, *J* = 15.5, 8.6 Hz), 3.79 (3H, s), 2.08-2.02 (1H, m), 1.86-1.80 (1H, m), 1.33 (1H, dt, *J* = 8.6, 5.7 Hz), 1.27 (1H, dt, *J* = 8.6, 5.7 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.8, 146.7, 130.1, 129.7, 128.4, 127.8 (q, *J* = 32.4 Hz), 126.9, 125.8, 125.3 (q, *J* = 3.6 Hz), 124.5 (q, *J* = 272.3 Hz), 114.0, 55.2, 28.2, 25.5, 17.6; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}OF_3$ 319.1310; found 319.1323.

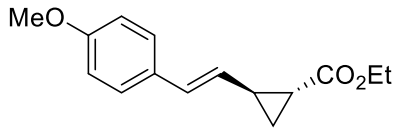
1-Methoxy-4-(2-(4-(trifluoromethyl)styryl)cyclopropyl)benzene (S44, *cis* : *trans* = 1 : 7). White solid (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1).



S44

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (2H, d, *J* = 8.0 Hz), 7.39 (2H, d, *J* = 8.0 Hz), 7.04 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 6.49 (1H, d, *J* = 15.5 Hz), 5.99 (1H, dd, *J* = 15.5, 8.6 Hz), 3.79 (3H, s), 2.08-2.02 (1H, m), 1.81-1.74 (1H, m), 1.30 (1H, dt, *J* = 8.6, 5.2 Hz), 1.20 (1H, dt, *J* = 9.2, 5.2 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.0, 141.1, 136.1, 133.7, 128.4 (q, *J* = 32.4 Hz), 126.9, 126.7, 125.8, 125.5 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 272.3 Hz), 113.9, 55.2, 27.1, 25.3, 16.9; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}OF_3$ 319.1310; found 319.1281.

Ethyl-2-(4-methoxystyryl)cyclopropane-1-carboxylate (S48, *trans*). Colorless oil.

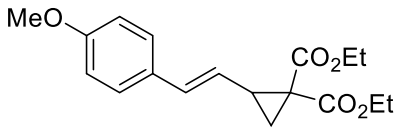


S48

To a solution of triethyl phosphonoacetate (**S46**, 4.48 g, 20.0 mmol) in tetrahydrofuran (60 mL) stirred at room temperature was added NaH (800 mg, 20.0 mmol). The resulting reaction mixture was stirred at room temperature for 15 min and 4-methoxycinnamaldehyde (**S45**, 1.62 g, 10.0 mmol) was added. The resulting reaction mixture was stirred at room temperature overnight, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) gave the ester (**S47**) in 78% yield (1.81 g, 7.80 mmol). To a solution of trimethylsulfoxonium iodide (3.30 g, 15.0 mmol) in dimethyl sulfoxide (60 mL) stirred with a water bath was added NaH (600 mg, 15.0 mmol). The resulting reaction mixture

was stirred with a water bath for 30 min, the ester (**S47**, 1.74 g, 7.50 mmol) was added. The resulting reaction mixture was stirred with a water bath for 4 h, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) gave the vinylcyclopropane (**S48**) in 82% yield (1.51 g, 6.15 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.48 (1H, d, *J* = 15.5 Hz), 5.61 (1H, dd, *J* = 16.0, 8.6 Hz), 4.15 (2H, q, *J* = 7.5 Hz), 3.80 (3H, s), 2.18-2.11 (1H, m), 1.74-1.70 (1H, m), 1.48-1.43 (1H, m), 1.28 (3H, t, *J* = 6.9 Hz) ,1.09-1.04 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.5, 158.9, 129.8, 129.7, 127.8, 127.0, 114.0, 60.6, 55.2, 25.6, 22.2, 15.9, 14.3; HRMS m/z: $[M + H]^+$ calcd for $C_{15}H_{19}O_3$ 247.1334; found 247.1340.

Diethyl-2-(4-methoxystyryl)cyclopropane-1,1-dicarboxylate (S51, *trans*). Colorless oil.

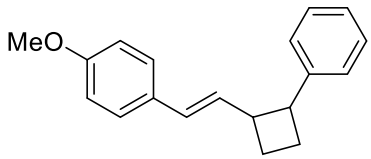


S51

To a solution of 4-methoxycinnamaldehyde (**S45**, 1.63 g, 12.0 mmol) and diethylmalonate (**S49**, 1.74 g, 13.2 mmol) in toluene (70 mL) stirred at room temperature were added piperidine (0.23 mL, 2.40 mmol) and acetic acid (0.14 mL, 2.40 mmol). The resulting reaction mixture was refluxed overnight, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) gave the ester (**S50**) in 93% yield (2.79 g, 11.2 mmol). To a solution of trimethylsulfoxonium iodide (4.40 g, 20.0 mmol) in dimethyl sulfoxide (60 mL) stirred with a water bath was added NaH (800 mg, 20.0 mmol). The resulting reaction

mixture was stirred with a water bath for 30 min, the ester (**S50**, 3.04 g, 10.0 mmol) was added. The resulting reaction mixture was stirred with a water bath for 4 h, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 10/1) gave the vinylcyclopropane (**S51**) in 86% yield (2.74 g, 8.60 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.23 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 6.58 (1H, d, *J* = 15.5 Hz), 5.68 (1H, dd, *J* = 15.5, 8.6 Hz), 4.28-4.14 (4H, m), 3.80 (3H, s), 2.75-2.69 (1H, m), 1.80 (1H, dd, *J* = 8.0, 5.2 Hz), 1.65 (1H, dd, *J* = 8.0, 5.2 Hz), 1.28 (3H, t, *J* = 7.5 Hz) ,1.22 (3H, t, *J* = 7.5 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.2, 167.2, 158.9, 132.7, 129.2, 126.9, 122.0, 113.6, 61.2, 61.0, 54.7, 35.9, 31.0, 20.5, 13.9, 13.8; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{23}O_5$ 319.1545; found 319.1530.

1-Methoxy-4-(2-(2-phenylcyclobutyl)vinyl)benzene (S59, *dr* = 11 : 5 : 1 : 1). White solid.



S59

To a solution of (3-bromopropyl)triphenylphosphonium bromide (**S52**, 13.9 g, 30.0 mmol) in tetrahydrofuran (80 mL) stirred at room temperature was added potassium *tert*-butoxide (6.74 g, 30.0 mmol). The resulting reaction mixture was stirred at 70 °C for 1 h, benzaldehyde (**S53**, 2.04 mL, 20.0 mmol) was added, refluxed for 3 h, diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the cyclopropane (**S54**, 2.47 g, 19.0 mmol) in 95% yield. To a solution of the cyclopropane (**S54**, 2.47 g, 19.0 mmol) in

dichloromethane (80 mL) stirred at 0 °C was added *m*-CPBA (4.37 g, 19.0 mmol). The resulting reaction mixture was stirred at 0 °C for 1 h, diluted with Na_2SO_3 aq., and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the cyclobutanone (**S55**, 2.47 g, 16.9 mmol) in 89% yield. To a solution of (methoxymethyl)triphenylphosphonium chloride (**S56**, 11.0 g, 32.0 mmol) in tetrahydrofuran (80 mL) stirred at 0 °C was added potassium *tert*-butoxide (3.59 g, 32.0 mmol). After the color turned red, the cyclobutanone (**S55**, 2.34 g, 16.0 mmol) was added, and the reaction was stirred at 50 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 20/1) gave the enol ether (**S57**, 1.73 g, 9.92 mmol) in 62% yield. To a solution of the enol ether (**S57**, 1.57 g, 9.00 mmol) in acetone (50 mL) stirred at room temperature was added a catalytic amount of concentrated sulfuric acid. The resulting reaction mixture was stirred at room temperature until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 5/1) gave the aldehyde (**S58**, 937 mg, 5.85 mmol) in 65% yield. To a solution of (4-methoxyphenylmethyl)triphenylphosphonium chloride (**S1**, 4.90 g, 11.7 mmol) in tetrahydrofuran (80 mL) stirred at 0 °C was added potassium *tert*-butoxide (1.31 g, 11.7 mmol). After the color turned red, the aldehyde (**S58**, 937 mg, 5.85 mmol) was added, stirred at 0 °C until the starting material was consumed (checked by thin layer chromatography), diluted with water, and extracted with ethyl acetate. The combined organic

layers were dried over sodium sulfate, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 50/1) gave the titled compound (**S59**, 529 mg, 2.00 mmol) in 34% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31-7.16 (5H, m), 7.29 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.32 (1H, d, *J* = 16.0 Hz), 6.23 (1H, dd, *J* = 16.0, 6.9 Hz), 3.79 (3H, s), 3.42-3.30 (2H, m), 2.30-2.20 (1H, m), 2.20-2.04 (2H, m), 2.02-1.85 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.8, 144.6, 131.4, 129.7, 128.2, 127.2, 126.6, 126.5, 126.0, 113.9, 55.2, 46.9, 46.9, 25.6, 25.3; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O$ 265.1592; found 265.1621.

General Procedure for the TiO_2 Photocatalytic Reactions (14, 19−21, 23, 25−40, 42−48). To a solution of $LiClO_4$ (1.0 M) in CH_3NO_2 (4 mL) stirred at room temperature were added the respective vinylcyclopropanes (0.20 mmol). The resulting reaction mixture was stirred at room temperature in front (5 cm) of a 15 W UV lamp (365 nm, Analytik Jena AG, XX-15L) until the starting material was consumed (checked by TLC), diluted with water, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. Yields reported in the manuscript were determined by ^{1}H NMR analysis. Silica gel column chromatography was carried out on 0.40 mmol scale (2 batches of the reactions) using hexane/ethyl acetate = 50/1−10/1.

1-Methoxy-4-(5-phenylcyclopent-2-en-1-yl)benzene (14, *cis* : *trans* = 2 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield (0.40 mmol); 94% (determined by NMR), isolated in 90% (90 mg, 0.36 mmol). Product yield (1.00 mmol); 81% (determined by NMR), isolated in 78% (194 mg, 0.78 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.24 (2H, m), 7.21-7.16 (3H, m), 7.00 (2H, d, *J* = 8.6 Hz), 6.79 (2H, d, *J* = 8.6 Hz), 5.97-5.94 (1H, m), 5.80-5.76 (1H, m), 3.91-3.87 (1H, m), 3.76 (3H, s), 3.23-3.18 (1H, m), 2.96-2.89 (1H, m), 2.63-2.55 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.1, 145.9,

137.3, 133.8, 129.7, 128.5, 128.3, 127.4, 126.1, 113.8, 59.7, 55.3, 54.8, 41.7; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_2$ 251.1436; found 251.1410.

1-Methoxy-4-(2-phenylcyclopent-3-en-1-yl)benzene (19, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 95% (determined by NMR), isolated in 92% (92 mg, 0.37 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28-7.24 (2H, m), 7.21-7.17 (1H, t, *J* = 7.5 Hz), 7.11 (2H, d, *J* = 8.6 Hz), 7.10-7.07 (2H, m), 6.82 (2H, d, *J* = 8.6 Hz), 6.00-5.97 (1H, m), 5.82-5.79 (1H, m), 3.91-3.87 (1H, m), 3.79 (3H, s), 3.24-3.18 (1H, m), 2.96-2.89 (1H, m), 2.60-2.54 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.0, 145.2, 137.8, 133.5, 130.9, 128.4, 128.3, 127.4, 126.3, 113.8, 60.6, 55.3, 54.0, 41.8; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1435.

4,4'-(Cyclopent-3-ene-1,2-diyl)bis(methoxybenzene) (20, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 20/1). Product yield; 87% (determined by NMR), isolated in 80% (90 mg, 0.32 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.09 (2H, d, *J* = 8.6 Hz), 6.99 (2H, d, *J* = 8.6 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.79 (2H, d, *J* = 8.6 Hz), 5.96-5.93 (1H, m), 5.79-5.75 (1H, m), 3.86-3.81 (1H, m), 3.77 (3H, s), 3.75 (3H, s), 3.15 (1H, dt, *J* = 8.6, 7.5 Hz), 2.93-2.85 (1H, m), 2.58-2.51 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.2, 158.0, 137.9, 137.4, 133.9, 130.7, 128.4, 113.9, 59.8, 55.4, 54.2, 41.8; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O_2$ 281.1542; found 281.1519.

1-Methoxy-2-(5-phenylcyclopnt-2-en-1-yl)benzene (21, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 61% (determined by NMR), isolated in 59% (59 mg, 0.24 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.23 (3H, m), 7.20-7.15 (2H, m), 7.01-6.89 (2H, m), 6.84-6.79 (2H, m), 6.02-5.99 (1H, m),

5.79-5.76 (1H, m), 4.39-4.35 (1H, m), 3.57 (3H, s), 3.28-3.22 (1H, m), 2.96-2.89 (1H, m), 2.58-2.51 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.2, 147.1, 133.4, 130.9, 128.5, 128.2, 127.5, 127.2, 127.2, 125.8, 120.6, 110.6, 55.2, 52.9, 52.8, 41.4; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1420.

1-Methoxy-2-(2-phenylcyclopent-3-en-1-yl)benzene (23, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 49% (determined by NMR), isolated in 35% (35 mg, 0.14 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27-7.20 (2H, m), 7.20-7.11 (3H, m), 7.01-6.95 (1H, m), 6.90 (1H, t, *J* = 7.5 Hz), 6.84 (1H, d, *J* = 8.0 Hz), 6.80 (1H, dt, *J* = 8.0, 1.7 Hz), 6.00-5.96 (1H, m), 5.84-5.80 (1H, m), 4.08-4.03 (1H, m), 3.69 (3H, s), 3.63-3.58 (1H, m), 2.88 (1H, ddq, *J* = 16.6, 7.5, 2.3 Hz), 2.60-2.53 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 157.4, 145.6, 133.7, 133.6, 131.2, 128.3, 128.0, 127.5, 127.1, 126.1, 120.6, 110.8, 58.2, 55.4, 48.2, 40.0; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O$ 251.1436; found 251.1409.

2,4-Dimethoxy-1-(5-phenylcyclopent-2-en-1-yl)benzene (25, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 20/1). Product yield; 91% (determined by NMR), isolated in 89% (100 mg, 0.36 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28-7.22 (3H, m), 7.07 (1H, d, *J* = 8.0 Hz), 7.00-6.92 (1H, m), 6.83 (1H, t, *J* 8.6 Hz), 6.44 (1H, dd, *J* = 8.6, 2.3 Hz), 6.40 (1H, d, *J* = 2.3 Hz), 6.00-5.96 (1H, m), 5.77-5.74 (1H, m), 4.29-4.25 (1H, m), 3.79 (3H, s), 3.55 (3H, s), 3.21 (1H, dt, *J* = 8.6, 6.3 Hz), 2.95-2.87 (1H, m), 2.56-2.50 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.2, 158.1, 147.1, 133.6, 130.6, 128.1, 127.8, 127.2, 126.9, 125.8, 104.0, 98.6, 55.4, 55.1, 53.0, 52.5, 41.2; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{20}O_2$ 281.1542; found 281.1558.

1,3,5-Trimethoxy-2-(5-phenylcyclopent-2-en-1-yl)benzene (26, *cis* : *trans* = 1 : 6). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1). Product yield; 85% (determined by NMR), isolated in 60% (74 mg, 0.24 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25-7.17 (4H, m), 7.14-7.08 (1H, m), 6.08 (2H, s), 5.77-5.73 (1H, m), 5.68-5.65 (1H, m), 4.56-4.51 (1H, m), 3.76 (3H, s), 3.60 (6H, s), 3.02-2.94 (1H, m), 2.58-2.51 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 159.6, 159.4, 147.3, 134.5, 128.0, 127.3, 126.9, 125.5, 112.7, 91.5, 56.0, 55.2, 50.2, 49.1, 42.0; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{22}O_3$ 310.1569; found 310.1571.

1-Methyl-4-(5-phenylcyclopent-2-en-1-yl)benzene (27, *cis* : *trans* = 1 : 4). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 13% (determined by NMR), isolated in 11% (10 mg, 0.04 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.24 (2H, m), 7.21-7.16 (3H, m), 7.07 (2H, d, *J* = 8.0 Hz), 6.99 (2H, d, *J* = 8.0 Hz), 5.99-5.95 (1H, m), 5.81-5.77 (1H, m), 3.93-3.89 (1H, m), 3.24 (1H, dt, *J* = 8.6, 7.5 Hz), 2.99-2.91 (1H, m), 2.63-2.56 (1H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 146.1, 142.2, 135.9, 133.9, 130.8, 129.3, 128.6, 127.5, 127.4, 126.2, 60.2, 54.6, 41.9, 21.2; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}$ 235.1487; found 235.1511.

2,4-Dimethyl-1-(5-phenylcyclopent-2-en-1-yl)benzene (28, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 44% (determined by NMR), isolated in 36% (36 mg, 0.14 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29-7.15 (4H, m), 7.02-6.94 (2H, m), 6.90-6.87 (1H, m), 6.85-6.78 (1H, m), 6.02-5.98 (1H, m), 5.77-5.72 (1H, m), 4.19-4.13 (1H, m), 3.23-3.16 (1H, m), 3.00-2.91 (1H, m), 2.62-2.54 (1H, m), 2.28 (3H, s), 1.88 (3H, s); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 146.7, 140.4, 135.9, 135.5, 134.0, 131.0, 130.8, 128.5, 127.1, 126.9, 126.7, 126.1, 56.3, 54.3, 41.7, 21.0, 19.7; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}$ 249.1643; found 249.1647.

1,3,5-Trimethyl-2-(5-phenylcyclopent-2-en-1-yl)benzene (29, *cis* : *trans* = 1 : 4). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 71% (determined by NMR), isolated in 60% (63 mg, 0.24 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25-7.20 (2H, m), 7.19-7.13 (2H, m), 7.02-6.94 (1H, m), 6.80-6.66 (2H, br), 5.85-5.81 (1H, m), 5.80-5.76 (1H, m), 4.42-4.36 (1H, m), 3.51 (1H, dt, *J* = 9.2, 8.6 Hz), 3.07-2.99 (1H, m), 2.81-2.73 (1H, m), 2.800-2.30 (3H, br), 2.28 (3H, s), 2.10-1.63 (3H, br); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.3, 137.4, 136.2, 135.4, 134.7, 134.7, 128.4,128.4, 127.5, 126.1, 57.0, 51.2, 41.7, 21.0, 20.8; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}$ 263.1800; found 263.1784.

1-Methyl-4-(2-phenylcyclopent-3-en-1-yl)benzene (30, *cis* : *trans* = 1 : 9). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 26% (determined by NMR), isolated in 21% (20 mg, 0.08 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (2H, t, *J* = 7.5 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 7.11-7.07 (6H, m), 5.99-5.96 (1H, m), 5.82-5.78 (1H, m), 3.94-3.90 (1H, m), 3.25-3.19 (1H, m), 2.96-2.89 (1H, m), 2.61-2.54 (1H, m), 2.32 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.3, 142.8, 135.6, 133.6, 130.9, 129.2, 128.4, 127.4, 127.3, 126.3, 60.5, 54.2, 41.9, 21.1; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{19}$ 235.1487; found 235.1482.

2,4-Dimethyl-1-(2-phenylcyclopent-3-en-1-yl)benzene (31, *cis* : *trans* = 1 : 8). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 65% (determined by NMR), isolated in 56% (56 mg, 0.22 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (1H, d, *J* = 8.0 Hz), 7.23 (2H, t, *J* = 7.5 Hz), 7.17 (1H, t, *J* = 7.5 Hz), 7.09 (2H, d, *J* = 6.9 Hz), 7.01 (1H, d, *J* = 11.5 Hz), 6.90 (1H, s), 6.00-5.97 (1H, m), 5.84-5.80 (1H, m), 3.97-3.92 (1H, m), 3.52-3.46 (1H, m), 2.99-2.90 (1H, m), 2.54-2.46 (1H, m), 2.28 (3H, s), 1.97 (3H, s); ^{13}C{^{1}H}

NMR (125 MHz, $CDCl_3$) δ 145.5, 141.2, 135.7, 135.2, 133.6, 131.0, 128.4, 127.2, 126.9, 126.2, 60.4, 49.5, 41.5, 21.0, 19.8; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}$ 249.1643; found 249.1641.

1,3,5-Trimethyl-2-(2-phenylcyclopent-3-en-1-yl)benzene (32, *cis* : *trans* = 1 : 14). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 85% (determined by NMR), isolated in 77% (81 mg, 0.31 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.23 (2H, t, *J* = 7.5 Hz), 7.16 (1H, t, *J* = 6.9 Hz), 7.08-7.04 (2H, m), 6.95-6.64 (2H, br), 6.03-5.99 (1H, m), 5.87-5.82 (1H, m), 4.11-4.05 (1H, m), 3.72-3.65 (1H, m), 2.91-2.83 (1H, m), 2.70-2.62 (1H, m), 2.50-2.25 (3H, br), 2.24 (3H, s), 1.90-1.66 (3H, br); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 146.5, 138.0, 136.8, 135.1, 133.4, 131.6, 131.1-130.5 (br), 129.0-128.5 (br), 128.4, 127.2, 126.2, 58.7, 48.3, 39.8, 21.5-21.0 (br), 20.8, 20.3-19.9 (br); HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}$ 263.1800; found 263.1775.

2,4-Dimethoxy-1-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (33, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 10/1). Product yield; 89% (determined by NMR), isolated in 71% (88 mg, 0.28 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.09 (1H, d, *J* = 8.0 Hz), 7.04 (2H, d, *J* = 8.6 Hz), 6.78 (2H, d, *J* = 8.6 Hz), 6.43 (1H, d, *J* = 2.3 Hz), 6.41 (1H, dd, *J* = 8.0, 2.3 Hz), 5.97-5.93 (1H, m), 5.80-5.77 (1H, m), 3.99-3.95 (1H, m), 3.78 (3H, s), 3.75 (3H, s), 3.69 (3H, s), 3.49-3.43 (1H, m), 2.86-2.79 (1H, m), 2.56-2.48 (1H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.0, 158.4, 157.9, 137.8, 133.9, 130.9, 129.3, 128.3, 126.0, 113.6, 103.9, 98.8, 57.2, 55.4, 55.3, 55.3, 48.2, 39.9; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}O_3$ 311.1647; found 311.1622.

1,3,5-Trimethoxy-2-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (34, *cis* : *trans* = 1 : 2). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate =

10/1). Product yield; 92% (determined by NMR), isolated in 85% (116 mg, 0.34 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99 (2H, d, *J* = 8.6 Hz), 6.75 (2H, d, *J* = 8.6 Hz), 6.12 (2H, s), 5.94-5.91 (1H, m), 5.80-5.77 (1H, m), 4.20-4.15 (1H, m), 3.79 (3H, s), 3.79-3.72 (1H, m), 3.76 (3H, s), 3.63 (6H, s), 2.82-2.74 (1H, m), 2.60-2.53 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.5, 159.2, 157.7, 138.8, 134.2, 131.3, 128.2, 113.3, 112.1, 91.6, 56.0, 55.2, 55.2, 55.2, 43.4, 38.3; HRMS m/z: $[M + H]^+$ calcd for $C_{21}H_{25}O_4$ 341.1753; found 341.1740.

1-Methoxy-4-(5-(p-tolyl)cyclopent-2-en-1-yl)benzene (35, *cis* : *trans* = 1 : 2). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 68% (determined by NMR), isolated in 66% (70 mg, 0.26 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.08 (4H, s), 7.00 (2H, d, *J* = 8.6 Hz), 6.79 (2H, d, *J* = 8.6 Hz), 5.97-5.93 (1H, m), 5.79-5.75 (1H, m), 3.89-3.85 (1H, m), 3.76 (3H, s), 3.20-3.14 (1H, m), 2.95-2.87 (1H, m), 2.59-2.52 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.1, 142.8, 137.3, 135.5, 133.8, 129.7, 129.1, 128.2, 127.3, 113.8, 59.7, 55.3, 54.4, 41.7, 21.1; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O$ 265.1592; found 265.1593.

1-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)-2,4-dimethylbenzene (36, *cis* : *trans* = 1 : 2). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 78% (determined by NMR), isolated in 75% (83 mg, 0.30 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (1H, d, *J* = 8.0 Hz), 7.01 (2H, d, *J* = 8.6 Hz), 7.00-6.98 (1H, m), 6.90 (1H, m), 6.78 (2H, d, *J* = 8.6 Hz), 5.98-5.93 (1H, m), 5.82-5.77 (1H, m), 3.92-3.87 (1H, m), 3.76 (3H, s), 3.48-3.41 (1H, m), 2.97-2.89 (1H, m), 2.52-2.45 (1H, m), 2.28 (3H, s), 1.98 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.1, 141.2, 137.6, 135.8, 133.9, 133.7, 130.9, 130.7, 128.1, 126.9, 126.2, 113.8, 59.6, 55.3, 49.6, 41.4, 21.0, 19.8 ; HRMS m/z: $[M + H]^+$ calcd for $C_{20}H_{23}O$ 279.1749; found 279.1738.

2-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)-1,3,5-trimethylbenzene (37, *cis* : *trans* = 1 : 7). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 79% (determined by NMR), isolated in 76% (89 mg, 0.30 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.97 (2H, d, *J* = 8.6 Hz), 6.93-6.67 (2H, br), 6.77 (2H, d, *J* = 8.6 Hz), 4.05-4.00 (1H, m), 3.75 (3H, s), 3.68-3.62 (1H, m), 2.89-2.80 (1H, m), 2.68-2.60 (1H, m), 2.50-2.22 (3H, br), 2.24 (3H, s), 1.95-1.72 (3H, br); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.0, 138.7, 138.1, 136.8, 135.0, 133.7, 131.3, 128.0, 113.7, 57.9, 55.3, 48.4, 39.7, 20.8; HRMS m/z: $[M + H]^+$ calcd for $C_{21}H_{25}O$ 293.1905; found 293.1921.

2-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)furan (38, *cis* : *trans* = 1 : 2). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 46% (determined by NMR), isolated in 40% (38 mg, 0.16 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.33 (1H, m), 7.09 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.29-6.27 (1H, m), 6.09-6.05 (1H, m), 5.99 (1H, d, *J* = 2.9 Hz), 5.77-5.74 (1H, m), 4.02-3.97 (2H, m), 3.78 (3H, s), 3.31-3.25 (1H, m), 2.88-2.81 (1H, m), 2.70-2.62 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.3, 158.0, 141.2, 133.9, 133.6, 130.4, 128.4, 113.9, 110.1, 104.6, 56.2, 55.3, 47.8, 38.5; HRMS m/z: $[M + H]^+$ calcd for $C_{16}H_{17}O_2$ 241.1229; found 241.1213.

2-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)-1-methyl-1H-pyrrole (39, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 65% (determined by NMR), isolated in 56% (57 mg, 0.22 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.09 (2H, d, *J* = 8.6 Hz), 6.81 (2H, d, *J* = 8.6 Hz), 6.49-6.47 (1H, m), 6.09-6.05 (2H, m), 5.94-5.90 (1H, m), 5.77-5.73 (1H, m), 3.93-3.88 (1H, m), 3.78 (3H, s), 3.27-3.21 (1H, m), 3.21 (3H, s), 2.94-2.87 (1H, m), 2.58-2.50 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ

158.3, 137.2, 136.6, 130.2, 128.4, 121.6, 113.9, 106.5, 104.3, 58.3, 55.3, 46.3, 40.4, 33.9; HRMS m/z: $[M + H]^+$ calcd for $C_{17}H_{20}ON$ 254.1545; found 254.1531.

2-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)thiophene (40, *cis* : *trans* = 1 : 2). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 96% (determined by NMR), isolated in 85% (87 mg, 0.34 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.12 (1H, dd, *J* = 5.2, 1.2 Hz), 7.08 (2H, d, *J* = 8.6 Hz), 6.91 (1H, t, *J* = 5.2 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.75-6.73 (1H, m), 5.97-5.93 (1H, m), 5.79-5.76 (1H, m), 3.93-3.88 (1H, m), 3.79 (3H, s), 3.53-3.47 (1H, m), 3.02-2.94 (1H, m), 2.68-2.61 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.4, 148.8, 134.2, 134.0, 130.3, 128.5, 126.7, 123.6, 122.8, 113.8, 59.9, 55.2, 50.3, 42.1; HRMS m/z: $[M + H]^+$ calcd for $C_{16}H_{17}OS$ 257.1000; found 257.0985.

1-Fluoro-4-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (42, *cis* : *trans* = 2 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 91% (determined by NMR), isolated in 75% (80 mg, 0.30 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.15-7.10 (2H, m), 6.99 (2H, d, *J* = 8.6 Hz), 6.97-6.92 (2H, m), 6.80 (2H, d, *J* = 8.6 Hz), 6.73-6.69 (2H, m), 5.97-5.93 (1H, m), 5.79-5.76 (1H, m), 3.85-3.80 (1H, m), 3.77 (3H, s), 3.22-3.16 (1H, m), 2.96-2.88 (1H, m), 2.58-2.50 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.5 Hz), 158.2, 141.4 (d, *J* = 2.4 Hz), 137.0, 133.8, 130.6, 128.7 (d, *J* = 7.2 Hz), 128.3, 115.1 (d, *J* = 20.4 Hz), 113.9, 59.9, 55.3, 54.2, 41.6; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OF$ 269.1342; found 269.1315.

1-Chloro-4-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (43, *cis* : *trans* = 3 : 5). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 87% (determined by NMR), isolated in 68% (77 mg, 0.27 mmol). ^{1}H NMR

($CDCl_3$, 500 MHz) δ 7.22 (2H, d, *J* = 8.6 Hz), 7.10 (2H, d, *J* = 8.0 Hz), 6.98 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 5.96-5.93 (1H, m), 5.78-5.75 (1H, m), 3.84-3.80 (1H, m), 3.76 (1H, m), 3.20 (1H, m), 2.95-2.88 (1H, m), 2.57-2.50 (1H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.3, 144.2, 136.8, 133.8, 132.5, 131.7, 130.5, 128.8, 128.5, 128.2, 113.9, 59.8, 55.3, 54.3, 41.5; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OCl$ 285.1046; found 285.1032.

1-Bromo-4-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (44, *cis* : *trans* = 2 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 81% (determined by NMR), isolated in 74% (97 mg, 0.30 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38 (2H, d, *J* = 8.6 Hz), 7.05 (2H, d, *J* = 8.6 Hz), 6.98 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 5.97-5.93 (1H, m), 5.79-5.75 (1H, m), 3.84-3.80 (1H, m), 3.78 (3H, s), 3.18-3.13 (1H, m), 2.96-2.88 (1H, m), 2.58-2.50 (1H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2, 144.8, 136.8, 133.8, 131.5, 130.5, 129.2, 128.3, 119.8, 113.9, 59.8, 55.3, 54.3, 41.5; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OBr$ 329.0541; found 329.0565.

1-Iodo-4-(2-(4-methoxyphenyl)cyclopent-3-en-1-yl)benzene (45, *cis* : *trans* = 2 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 56% (determined by NMR), isolated in 45% (68 mg, 0.18 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58 (2H, d, *J* = 8.6 Hz), 6.98 (2H, d, *J* = 8.6 Hz), 6.92 (2H, d, *J* = 8.6 Hz), 6.80 (2H, d, *J* = 8.6 Hz), 5.97-5.93 (1H, m), 5.79-5.75 (1H, m), 3.84-3.80 (1H, m), 3.77 (3H, s), 3.17-3.11 (1H, m), 2.95-2.88 (1H, m), 2.57-2.50 (1H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2, 145.5, 137.5, 133.8, 131.7, 130.7, 129.5, 128.2, 113.9, 91.2, 59.7, 55.3, 54.4, 41.5; HRMS m/z: $[M + H]^+$ calcd for $C_{18}H_{18}OI$ 377.0402; found 377.0381.

4-(2-(4-Methoxyphenyl)cyclopent-3-en-1-yl)benzonitrile (46, *cis* : *trans* = 1 : 4). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 75% (determined by NMR), isolated in 66% (73 mg, 0.26 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (2H, d, *J* = 6.9 Hz), 7.28 (2H, d, *J* = 6.9 Hz), 6.98 (2H, d, *J* = 6.9 Hz), 6.81 (2H, d, *J* = 6.9 Hz), 5.99-5.96 (1H, m), 5.81-5.76 (1H, m), 3.88-3.83 (1H, m), 3.78 (3H, s), 3.29-3.22 (1H, m), 3.01-2.92 (1H, m), 2.61-2.53 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.4, 151.5, 136.3, 133.7, 132.4, 130.4, 128.2, 128.1, 119.2, 114.0, 109.9, 59.8, 55.3, 54.8, 41.2; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}ON$ 276.1388; found 276.1394.

1-Methoxy-4-(5-(4-(trifluoromethyl)phenyl)cyclopent-2-en-1-yl)benzene (47, *cis* : *trans* = 1 : 1). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 46% (determined by NMR), isolated in 40% (51 mg, 0.16 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (2H, d, *J* = 8.0 Hz), 7.29 (2H, d, *J* = 8.6 Hz), 6.99 (2H, d, *J* = 8.6 Hz), 6.82 (2H, d, *J* = 8.6 Hz), 5.99-5.96 (1H, m), 5.81-5.77 (1H, m), 3.90-3.86 (1H, m), 3.78 (3H, s), 3.29-3.23 (1H, m), 3.00-2.93 (1H, m), 2.62-2.54 (1H, m); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.3, 150.0, 136.7, 133.8, 130.5, 128.2, 127.9 (q, *J* = 32.4 Hz), 127.7, 125.4 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 271.1 Hz), 113.9, 59.8, 55.3, 54.6, 41.5; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}OF_3$ 319.1310; found 319.1293.

1-Methoxy-4-(2-(4-(trifluoromethyl)phenyl)cyclopent-3-en-1-yl)benzene (48, *cis* : *trans* = 1 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 86% (determined by NMR), isolated in 80% (102 mg, 0.32 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ7.50 (2H, d, *J* = 8.0 Hz), 7.18 (2H, d, *J* = 8.0 Hz), 7.09 (2H, d, *J* = 8.6 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.05-6..01 (1H, m), 5.80-5.76 (1H, m), 3.97-3.92 (1H, m), 3.80 (3H, s), 3.20-3.14 (1H, m), 2.97-2.90 (1H, m), 2.64-2.56 (1H, m); ^{13}C{^{1}H} NMR (125 MHz,

$CDCl_3$) δ 158.2, 149.3, 136.9, 131.9, 128.6 (q, *J* = 32.4 Hz), 128.3, 127.7, 125.4 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 272.3 Hz), 113.9, 60.4, 55.3, 54.2, 41.8; HRMS m/z: $[M + H]^+$ calcd for $C_{19}H_{18}OF_3$ 319.1310; found 319.1309.

4-Methoxy-1',2',3',4'-tetrahydro-1,1':2',1"-terphenyl (51, *cis* : *trans* = 2 : 3). Colorless oil (purified by silica gel column chromatography using hexane/ethyl acetate = 50/1). Product yield; 94% (determined by NMR), isolated in 89% (94 mg, 0.36 mmol). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.17 (2H, t, *J* = 6.9 Hz), 7.13-7.08 (1H, m), 6.97 (2H, d, *J* = 6.9 Hz), 6.83 (2H, d, *J* = 8.6 Hz), 6.67 (2H, d, *J* = 8.6 Hz), 5.95-5.89 (1H, m), 5.75-5.70 (1H, m), 3.71 (3H, s), 3.46-3.40 (1H, m), 3.21 (3H, s), 2.71-2.64 (1H, m), 2.40-2.15 (2H, m), 2.02-1.89 (2H, m); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.8, 145.6, 136.9, 131.4, 129.2, 128.1, 127.7, 127.5, 126.0, 113.3, 55.2, 49.5, 45.1, 30.0, 25.7; HRMS m/z: $[M + H]^+$ calcd for $C_{17}H_{20}ON$ 265.1592; found 265.1598.

Theoretical Calculations. Structure optimizations of all stationary points and frequency analyses were carried out at the B3LYP level of density functional theory (DFT) with the 6-311G++(2d,2p) basis set in nitromethane (PCM model). No imaginary frequency was observed for all compounds.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Copies of ^1H and $^{13}C\{^1H\}$ NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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