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[3+2] Photooxygenation of aryl cyclopropanes via visible light photocatalysis

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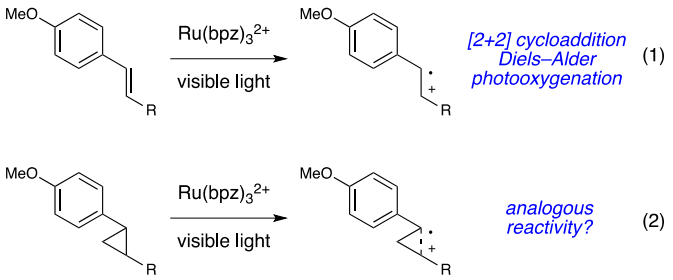
ABSTRACT

We report that $Ru(bpz)_3^{2+}$ is an excellent sensitizer for the photooxygenation of aryl cyclopropanes upon irradiation with visible light. The effectiveness of this photocatalyst enables the synthesis of a range of five-membered endoperoxides in excellent yield with quite low (0.5 mol %) catalyst loadings even when standard household light sources are utilized.

1. Introduction

Cyclic peroxides are the characteristic pharmacophores of a class of biologically active compounds that exhibit a range of potent antibacterial, anticancer, and antimalarial activities.[1] Five-membered endoperoxides, in particular, have also been valued as synthetic intermediates because of the ease with which their O–O bonds can be reductively cleaved to afford 1,3-diols.[2] Many methods for the preparation of five-membered endoperoxides involve sequences that require pre-installation of the reactive peroxide moiety,[3] which often limits the scope and yield of the reaction. An attractive alternative strategy involves the ring-expanding reaction of cyclopropanes with molecular oxygen. Vinylcyclopropanes can be induced to undergo this transformation upon reaction with phenylthiyl or phenylselenyl radicals,[4] although the requirement for a vinyl substituent represents a significant limitation on the generality of this process. An arguably more general method is the photooxygenation of aryl cyclopropanes, originally developed by Mizuno and Otsuji,[5] which is commonly catalyzed by organic PET sensitizers such as 9,10-dicyanoanthracene (DCA, **2**).

For the past several years, our research group has been developing methods that exploit the remarkable photoredox properties of transition metal polypyridyl complexes to perform a variety of synthetically useful radical ion processes.[6,7] We have found that electron-deficient bipyrazyl and bipyrimidyl complex of Ru(II) in particular are excellent catalysts for the photochemical one-electron oxidation of electron-rich styrenes (Eq. 1), which has enabled us to develop a suite of synthetically useful reactions of the resulting radical cations.[8,9] Recognizing that the chemistry of cyclopropanes can often offer homologous reactivity to that of olefins, we have become interested in exploring radical cation reactions of electron-rich cyclopropanes (Eq. 2). Zheng recently demonstrated that $Ru(bpz)_3^{2+}$ (**1**) is an effective visible light photocatalyst for the [3+2] cycloaddition of amine-substituted cyclopropanes with a variety of alkenes.[10] In this manuscript, we demonstrate that $Ru(bpz)_3^{2+}$ also catalyzes aerobic photo-oxygenation of electron-rich aryl cyclopropanes upon irradiation with visible light and is a markedly more effective catalyst for this transformation than DCA (Scheme 1).



Scheme 1.

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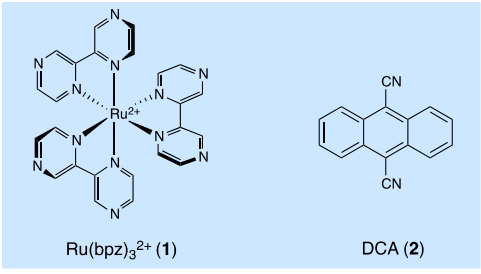
2. Results and discussion

We began our initial investigations by examining the reaction of 1-(*p*-methoxyphenyl)-2-phenylcyclopropane (**3a**) under conditions based upon those we had developed for the synthesis of six-membered endoperoxides by aerobic [2+2+2] cycloaddition.[11] Thus, irradiation of a solution of **3a** in $MeNO_2$ with a 23 W compact fluorescent light bulb (CFL) in the presence of 0.5 mol % $Ru(bpz)_3(PF_6)_2$ under an atmosphere of O_2 afforded 16% yield of the expected endoperoxide **4a** (Table 1, entry 1); this compound was isolated as a 3:1 mixture of *syn* to *anti* diastereomers. While the reaction was much less efficient under an atmosphere of air in place of oxygen (entry 2), the yield could be easily improved to synthetically useful levels by conducting the reaction under 2 atm of oxygen (entry 3). We attempted the same reaction using 10 mol % of DCA as a sensitizer and observed no formation of **4a** (entry 4), indicating that $Ru(bpz)_3^{2+}$ is indeed a more effective visible light photocatalyst for this transformation. Nitromethane proved to be essential in this reaction; other solvents resulted in dramatically diminished reactivity (entries 5–8). However, a 1:1 mixture of $MeNO_2$ and toluene allowed us to conduct the reaction at −30 °C, which resulted in a modest improvement of both the *syn*/*anti* ratio and the yield of the reaction (entry 9). Control experiments under these conditions showed that no reaction occurred in the absence of light or of $Ru(bpz)_3^{2+}$, confirming the necessity of photoexcited Ru(II) in order for this transformation to occur.

Experiments probing the scope of this reaction are summarized in Table 2. Mizuno and Otsuji's proposal for the mechanism of the DCA-sensitized photooxygenation of cyclopropanes[5] suggests that this reaction is initiated by one-electron oxidation of the substrate to afford the corresponding radical cation. In line with this expectation, no endoperoxide is formed from unsubstituted 1,2-diphenylcyclopropane (entry 2), even after long reaction times. We similarly observed no reaction using a cyclopropane substrate bearing one 3-methoxyphenyl substituent (entry 3). The analogous 2-methoxy-substituted substrate underwent photooxygenation, but at a significantly slower rate than the

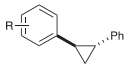
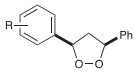
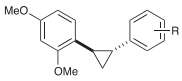
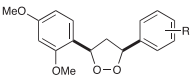
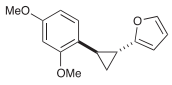
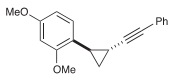
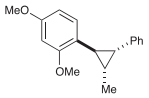
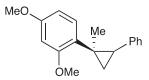
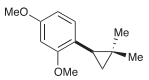
Table 1
Optimization of photooxygenation of **1**



Entry	O_2	Solvent	T (°C)	Yield[a] (%)	*syn*/*anti*[b]
1	15 psi	$MeNO_2$	23	16	3:1
2	Air	$MeNO_2$	23	3	3:1
3	30 psi	$MeNO_2$	23	90	4:1
4[c]	30 psi	$MeNO_2$	23	0	—
5	30 psi	MeCN	23	36	4:1
6	30 psi	Acetone	23	2	—
7	30 psi	Toluene	23	0	—
8	30 psi	DMSO	23	0	—
9[d]	30 psi	1:1 $MeNO_2$/toluene	−30	99	5:1
10[d,e]	30 psi	1:1 $MeNO_2$/toluene	−30	0	—
11[d,f]	30 psi	1:1 $MeNO_2$/toluene	−30	0	—

[a] Yields determined by ^1H NMR spectroscopy using an internal standard unless otherwise noted.
[b] Diastereomer ratios determined by ^1H NMR analysis of the unpurified reaction mixture.
[c] Using 10 mol % of 9,10-dicyanoanthracene (DCA) as photosensitizer in place of $Ru(bpz)_3(PF_6)_2$.
[d] Reaction time: 3 h.
[e] Reaction conducted in the dark.
[f] Reaction conducted without $Ru(bpz)_3^{2+}$.

Table 2
Scope of the photooxygenation reaction[a]

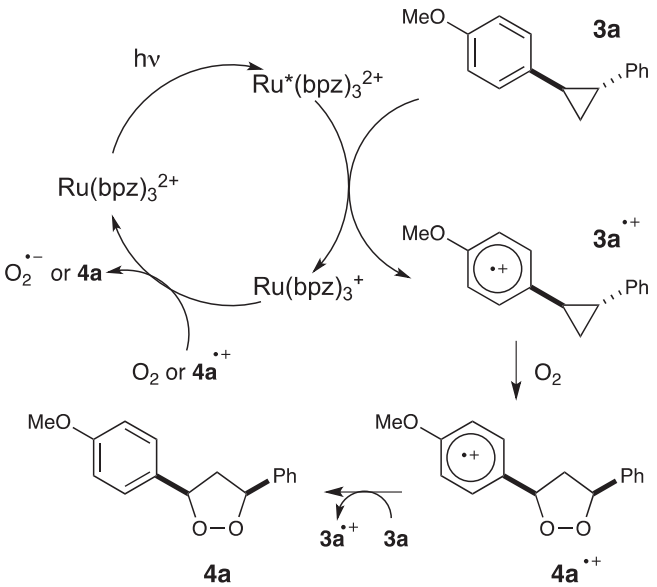
Entry	substrate	Product	Time (h)	Yield[b] (%)	*syn*/*anti*[c]
					
1	**3a** R=4-OMe	**4a**	3	99	5:1
2	**3b** R=H	**4b**	48	0	—
3	**3c** R=3-OMe	**4c**	48	0	—
4[d]	**3d** R=2-OMe	**4d**	48	47	5:1
5	**3e** R=4-OH	**4e**	1	78	>10:1
6	**3f** R=4-OTIPS	**4f**	3	95	4:1
7	**3g** R=4-NH_2	**4g**	1	70	>10:1
8	**3h** R=4-NHBoc	**4h**	3	93	5:1
9	**3i** R=2,4-OMe	**4i**	1	99	10:1
10[d]	**3j** R=3,4-OMe	**4j**	24	77	5:1
					
11	**3k** R=2,4-OMe	**4k**	1	98	6:1
12	**3l** R=4-OMe	**4l**	1	99	9:1
13	**3m** R=4-Me	**4m**	1	98	10:1
14	**3n** R=4-Br	**4n**	1	99	9:1
15	**3o** R=4-Cl	**4o**	1	98	10:1
16	**3p** R=3-Cl	**4p**	1	97	>10:1
17	**3q** R=2-Cl	**4q**	1	99	10:1
18	**3r** R=4-CF_3	**4r**	1	98	10:1
19	**3s** R=2-CF_3	**4s**	1	94	>10:1
20	 **3t**	**4t**	1	75	6:1
21	 **3u**	**4u**	24	98	1:1
22	 **3v**	**4v**	1	96	10:1
23	 **3w**	**4w**	1	99	6:1
24	 **3x**	**4x**	12	94	—

[a] Unless otherwise noted, reactions were conducted in 1:1 $MeNO_2$/toluene using 0.5 mol % $Ru(bpz)_3^{2+}$, 30 psi O_2, and a 23 W CFL bulb.
[b] Values represent the averaged isolated yields from two reproducible experiments.
[c] Diastereomer ratios determined by ^1H NMR analysis of the unpurified reaction mixture.
[d] Reaction conducted using 5 mol % $Ru(bpz)_3(PF_6)_2$.

4-substituted isomer; only modest yields were obtained using a higher loading (5 mol %) of the photocatalyst (entry 4). However, a variety of aryl cyclopropanes bearing electron-donating 4-substituents react smoothly and provide the corresponding endoperoxides in good yield (entries 5–8). Aryl cyclopropanes bearing multiple electron-donating substituents are also easily converted in high yields (entries 9 and 10).

Provided that one of the aryl groups on the cyclopropane substrate bears an electron-donating 2- or 4-substituent, we found the scope of cyclopropanes that successfully undergo photooxygenation to be quite broad. Substrates bearing a second phenyl group with either electron-donating (entries 11–13) or electron-withdrawing (entries 14–19) substitution patterns are easily tolerated. The cyclopropane could also be substituted with a heteroaryl group (entry 20) or an alkyne (entry 21), although the latter reaction required much longer reaction times to proceed to completion. We also examined photooxygenations of 1,2-diarylcyclopropanes bearing additional alkyl substituents on the central ring (entries 22 and 23), and in all cases, the bond linking the two benzylic carbons exclusively undergoes photooxygenation, consistent with the expectation that the weakest bond in the cyclopropane be the most likely to fragment and undergo the reaction. Finally, while we were able to obtain good yields of endoperoxide from a substrate bearing geminal methyl substituents on the cyclopropane (entry 24), other less-substituted monoaryl cyclopropanes failed to give appreciable yields of the photooxygenation product.

Our working model for the mechanism of this process is summarized in Scheme 2. Photoexcitation of the $Ru(bpz)_3^{2+}$ chromophore affords a strongly oxidizing (+1.4 V vs SCE) excited state that we propose can be reductively quenched by the aryl cyclopropane substrate. The resulting aryl cyclopropane radical cation undergoes stepwise reaction with ground-state triplet oxygen to afford endoperoxide radical cation **4a**$^{\bullet+}$, which would lose an electron to produce the final product, presumably by chain-propagating oxidation of another equivalent of substrate cylcopropane **3a**. Regeneration of the Ru(II) photocatalyst requires a one-electron oxidation, which could be accomplished either by chain-terminating reaction with radical cation **4a**$^{\bullet+}$ or by reaction with molecular oxygen.



Scheme 2.

3. Conclusion

In summary, a wide range of electron-rich aryl cyclopropanes participate in aerobic [3+2] photooxygenation reactions upon irradiation with visible light in the presence of $Ru(bpz)_3^{2+}$. In line with our previous investigations involving photogenerated alkene radical cations, we find that this photooxygenation reaction is markedly more efficient using this Ru(II) chromophore in place of DCA and enables the use of readily accessible household lighting sources in place of conventional photochemical instrumentation. The 1,2-dioxolane products are formed cleanly in high yield and can be easily isolated by filtration through silica gel. We anticipate that this method could be applied to the synthesis and discovery of novel endoperoxide compounds with potent bioactivity profiles.

4. Experimental section

4.1. General information

THF and CH_2Cl_2 were purified by elution through alumina as described by Grubbs.[12] $MeNO_2$ was purified by distillation from $MgSO_4$ prior to use. A 23 W compact fluorescent light bulb was used for all photochemical reactions depicted in Tables 1 and 2. Flash column chromatography was performed with Silicycle 40–63 Å silica (230–400 mesh). $Ru(bpz)_3(PF_6)_2$[13] was prepared as previously described. Diastereomer ratios for all compounds were determined by ^1H NMR analysis of the unpurified reaction mixture. ^1H and ^{13}C NMR data for all previously uncharacterized compounds were obtained using Varian Inova-500 and Varian Unity-500 spectrometers and are referenced to TMS (0.0 ppm) and $CDCl_3$ (77.0 ppm), respectively. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. Mass spectrometry was performed with a Waters (Micromass) AutoSpec (electrospray ionization, time-of-flight analyzer).

4.2. Synthesis of cyclopropane substrates

Cyclopropane substrates **3a**,[14] **3b**,[14] **3c**,[15] **3g**,[16] **3i**[17] were prepared as previously reported.

4.2.1. General procedure for synthesis of cyclopropane substrates. Cyclopropane substrates were prepared using the method of Beech et al.,[18] as follows. A 100 mL round-bottomed flask was charged with the appropriate benzaldehyde (1 equiv) and acetophenone (1 equiv) in 12.5 mL EtOH. Added 12.5 mL of 6 M NaOH and stirred the reaction mixture at room temperature for 12–24 h. The reaction mixture was cooled to 0 °C and neutralized with 6 M HCl. The solids were isolated by filtration, washed with water, and placed in a second 100 mL round-bottomed flask along with 25 mL EtOH. Hydrazine monohydrate (3.0 mL, 62 mmol) was added slowly to the resulting solution. The flask was fitted with a reflux condenser, and the solution was heated to reflux for 2 h. The reaction mixture was then treated with 500 mg KOH (8.9 mmol). Upon consumption of the starting material, the flask was cooled to ambient temperature, and the residue was loaded directly onto a silica gel column and eluted with a gradient of 16:1 to 3:1 hexanes/EtOAc to obtain the desired cyclopropane.

The diastereomeric purity of the product could be upgraded photocatalytically. A solution of the cyclopropane (1.0 g, 1 equiv) in $MeNO_2$ was placed in a 20 mL vial. The solution was sparged with N_2 gas before adding $Ru(bpz)_3(PF_6)_2$ (0.1 mol %) and sealing the vial with a Teflon cap. The reaction mixture was irradiated in front of a 23 W CFL light bulb for 1–3 h, and the pure product was isolated

by passing the solution through a pad of silica gel and removing the solvent by rotary evaporation to afford pure *trans* cyclopropane.

*4.2.2. trans-1-(2′-Methoxyphenyl)-2-phenylcyclopropane(**3d**).* Prepared from 13.6 g (100 mmol) of benzaldehyde and 12.0 g (100 mmol) of 2′-methoxyacetophenone using the general procedure to afford 15.7 g (70% yield) of cyclopropane. The cyclopropane was isomerized using 3.9 mg (0.004 mmol) of $Ru(bpz)_3(PF_6)_2$ in 7.4 mL of $MeNO_2$ to obtain 999 mg (100% yield) of the pure trans diastereomer. All analytical data were consistent with previously reported values.[19]

*4.2.3. trans-1-(4′-Hydroxyphenyl)-2-phenylcyclopropane (**3e**).* Prepared from 2.5 mL (25 mmol) of benzaldehyde and 3.4 g (25 mmol) of 2′-hydroxyacetophenone using the general procedure to afford 2.6 g (49% yield) of diastereomerically pure cyclopropane as a crystalline solid. Mp: 72–73 °C (hexane/EtOAc). IR (neat) 3396, 3029, 1615, 1600, 1516, 1449, 1225 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.28 (t, J=7.8 Hz, 2H), 7.17 (t, J=7.4 Hz, 1H), 7.14–7.11 (m, 2H), 7.02 (d, J=8.6 Hz, 2H), 6.76 (d, J=8.6 Hz, 2H), 5.22 (br s, 1H), 2.14–2.05 (m, 2H), 1.41–1.34 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 153.4, 142.6, 134.7, 128.3, 127.1, 125.7, 125.6, 115.3, 27.4, 27.2, 17.8. HRMS (EI) calculated for $[C_{15}H_{14}O]^+$ (M^+) requires m/z 210.1040, found m/z 210.1033.

*4.2.4. trans-1-Phenyl-2-(4′-triisopropylsilyloxyphenyl)cyclopropane (**3f**).* A 25 mL round-bottomed flask was charged with 500 mg (2.38 mmol) **3e** and 5.9 mL DMF. To this solution were added 324 mg (4.76 mmol) imidazole and 0.76 mL (3.57 mmol) TIPSCl. After 24 h the flask was placed in a water bath, and the reaction was quenched by slow addition of water. The mixture was extracted three times with hexanes, and the combined organic phases were dried over $MgSO_4$ and concentrated by rotary evaporation. Purification on SiO_2 afforded 377 mg (43% yield) of a clear oil. IR (neat) 2945, 2867, 1607, 1513, 1463, 1265 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.27 (t, J=7.5 Hz, 2H), 7.16 (t, J=7.5 Hz, 1H), 7.14–7.10 (m, 2H), 6.98 (d, J=8.6 Hz, 2H), 6.80 (d, J=8.6 Hz, 2H), 2.13–2.05 (m, 2H), 1.36 (ddd, J=7.9, 6.6, 0.9 Hz, 2H), 1.28–1.20 (m, 3H), 1.10 (d, J=7.2 Hz, 18H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 154.2, 142.8, 134.7, 128.3, 126.7, 125.7, 125.6, 119.7, 27.5, 27.4, 18.0, 17.9, 12.7. HRMS (EI) calculated for $[C_{24}H_{34}OSi]^+$ (M^+) requires m/z 366.2374, found m/z 366.2387.

*4.2.5. trans-tert-Butyl 4-(2-phenylcyclopropyl)phenylcarbamate (**3h**).* A 100 mL round-bottomed flask was charged with 1.05 g (5 mmol) **3g** and 30 mL 1,4-dioxane. To this solution were added 0.84 mL (6 mmol) of Et_3N and 1.31 g (6 mmol) Boc_2O. After 24 h, the solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography (gradient, 8:1 to 3:1 hexanes/EtOAc) to afford 1.41 g (91% yield) of a yellow oil. IR (neat) 3394, 2981, 2934, 1808, 1727, 1593, 1525, 1162, 1110, 1072 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.30–7.25 (m, 4H), 7.14–7.11 (m, 2H), 7.09–7.05 (m, 3H), 6.41 (br s, 1H), 2.15–2.07 (m, 2H), 1.51 (s, 9H), 1.42–1.38 (m, 2H). HRMS (EI) calculated for $[C_{20}H_{23}NO_2]^+$ (M^+) requires m/z 309.1724, found m/z 309.1716.

*4.2.6. trans-1-(3′,4′-Dimethoxyphenyl)-2-phenylcyclopropane (**3j**).* Prepared from 8.3 g (50 mmol) of benzaldehyde and 6.0 g (50 mmol) of 2′-methoxyacetophenone using the general procedure to afford 10.0 g (79% yield) of cyclopropane. The cyclopropane was isomerized using 3.4 mg (0.004 mmol) of $Ru(bpz)_3(PF_6)_2$ in 6.6 mL of $MeNO_2$ to obtain 987 mg (99% yield) of the pure trans diastereomer. IR (neat) 3000, 2934, 2834, 1604, 1589, 1518, 1254, 1236, 1140, 1028 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.28 (t, J=7.27 Hz, 2H), 7.17 (t, J=7.4 Hz, 1H), 7.15–7.11 (m, 2H), 6.80 (d, J=7.9 Hz, 1H), 6.71–6.67 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.13 (ddd, J=8.4, 6.5, 4.6 Hz, 1H), 2.09 (ddd, J=8.4, 6.2, 4.6 Hz, 1H), 1.43–1.37 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 148.9, 147.3, 142.6, 135.0, 128.3, 125.6, 117.5, 111.3, 109.8, 55.9, 55.8, 27.7, 27.5, 17.7. HRMS (EI) calculated for $[C_{17}H_{18}O_2]^+$ (M^+) requires m/z 254.1302, found m/z 254.1309.

*4.2.7. trans-1,2-Bis(2′,4′-dimethoxyphenyl)cyclopropane (**3k**).* Prepared from 4.15 g (25 mmol) of 2,4-dimethoxybenzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 7.3 g (93% yield) of cyclopropane. The cyclopropane was isomerized using 2.8 mg (0.0032 mmol) of $Ru(bpz)_3(PF_6)_2$ in 5.3 mL of $MeNO_2$ to obtain 842 mg (84% yield) of the pure trans diastereomer as a crystalline solid. Mp: 78–80 °C (hexane/EtOAc). IR (neat) 2999, 2937, 2835, 1615, 1585, 1506, 1290, 1208, 1037 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 6.96 (d, J=8.2 Hz, 2H), 6.45–6.41 (m, 4H), 3.79 (s, 6H), 3.77 (s, 6H), 2.26 (t, J=7.3 Hz, 2H), 1.19 (t, J=7.3 Hz, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.1, 158.7, 126.0, 123.7, 103.9, 98.4, 55.4, 55.2, 19.2, 15.5. HRMS (ESI) calculated for $[C_{19}H_{22}O_4]^+$ (M^+) requires m/z 314.1513, found m/z 314.1505.

*4.2.8. trans-1-(2′,4′-Dimethoxyphenyl)-2-(4′-methoxyphenyl)cyclopropane (**3l**).* Prepared from 4.15 g (25 mmol) 2,4-dimethoxybenzaldehyde and 3.75 g (25 mmol) of 4′-methoxyacetophenone using the general procedure to afford 4.79 g (67% yield) of cyclopropane. The cyclopropane was isomerized using 3 mg (0.0035 mmol) of $Ru(bpz)_3(PF_6)_2$ in 8.9 mL of $MeNO_2$ to obtain 954 mg (95% yield) of the pure trans diastereomer as a crystalline solid. Mp: 103–106 °C (hexane/ethyl acetate). IR (neat) 2988, 2926, 2835, 1613, 1586, 1508, 1157, 1034 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.13 (d, J=8.3 Hz, 2H), 6.88 (d, J=7.9 Hz, 1H), 6.83 (d, J=8.3 Hz, 2H), 6.46–6.41 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 2.25 (dt, J=8.7, 5.5 Hz, 1H), 2.00 (dt, J=8.7, 5.5 Hz, 1H), 1.29–1.22 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.1, 158.9, 157.7, 135.2, 127.3, 125.9, 123.4, 113.7, 103.9, 98.4, 55.5, 55.4, 55.3, 25.2, 20.8, 15.9. HRMS (ESI) calculated for $[C_{18}H_{20}O_3]^+$ (M^+) requires m/z 284.1407, found m/z 284.1408.

*4.2.9. trans-1-(2′,4′-Dimethoxyphenyl)-2-(4′-methylphenyl)cyclopropane (**3m**).* Prepared from 2.95 g (25 mmol) 4-methylbenzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 5.57 g (83% yield) of cyclopropane. The cyclopropane was isomerized using 3.2 mg (0.0037 mmol) of $Ru(bpz)_3(PF_6)_2$ in 9.2 mL of $MeNO_2$ to obtain 993 mg (99% yield) of the pure trans diastereomer as a crystalline solid. Mp: 67–68 °C (hexane/ethyl acetate). IR (neat) 3001, 2957, 2939, 2835, 1613, 1586, 1507, 1464, 1207, 1157 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.08 (s, 4H), 6.87 (d, J=8.2 Hz, 1H), 6.45–6.40 (m, 2H), 3.772 (s, 3H), 3.767 (s, 3H), 2.32–2.27 (m, 4H), 2.01 (ddd, J=8.1, 6.2, 4.8 Hz, 1H), 1.31–1.25 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.1, 158.9, 140.1, 134.9, 128.9, 126.0, 125.9, 123.3, 103.9, 98.4, 55.4, 55.3, 25.6, 21.2, 20.9, 16.3. HRMS (EI) calculated for $[C_{18}H_{20}O_2]^+$ (M^+) requires m/z 268.1458, found m/z 268.1470.

*4.2.10. trans-1-(4′-Bromophenyl)-2-(2′,4′-dimethoxyphenyl)cyclopropane (**3n**).* Prepared from 4.6 g (25 mmol) 4-bromobenzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 5.06 g (61% yield) of cyclopropane. The cyclopropane was isomerized using 2.6 mg (0.003 mmol) of $Ru(bpz)_3(PF_6)_2$ in 5 mL of $MeNO_2$ to obtain 961 mg (96% yield) of the pure trans diastereomer as a crystalline solid. Mp: 84–85 °C (hexane/ethyl acetate). IR (neat) 3003, 2958, 2936, 2836, 1612, 1586, 1507, 1489, 1207 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.39 (d, J=8.4 Hz, 2H), 7.05 (d, J=8.4 Hz, 2H), 6.88 (d, J=8.3 Hz, 1H), 6.45 (d, J=2.5 Hz, 1H), 6.43 (dd, J=8.3, 2.5 Hz,

1H), 3.80 (s, 3H), 3.80 (s, 3H), 2.27 (ddd, *J*=8.9, 6.2, 5.1 Hz, 1H), 1.98 (dt, *J*=8.7, 5.1 Hz, 1H), 1.35 (ddd, *J*=8.7, 6.2, 5.1 Hz, 1H), 1.27 (dd, *J*=8.9, 5.1 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.2, 159.1, 142.3, 131.2, 127.9, 126.0, 122.8, 119.0, 103.9, 98.5, 55.5, 55.4, 25.5, 21.8, 16.2. HRMS (EI) calculated for $[C_{17}H_{17}BrO_2]^+$ (M^+) requires *m*/*z* 332.0407, found *m*/*z* 332.0417.

*4.2.11. trans-1-(4′-Chlorophenyl)-2-(2′,4′-dimethoxyphenyl)cyclopropane (**3o**).* Prepared from 4.15 g (25 mmol) 2′,4′-dimethoxybenzaldehyde and 3.24 g (25 mmol) of 4′-chloroacetophenone using the general procedure to afford 6.31 g (87% yield) of cyclopropane. The cyclopropane was isomerized using 3 mg (0.0035 mmol) of $Ru(bpz)_3(PF_6)_2$ in 8.8 mL of $MeNO_2$ to obtain 995 mg (99% yield) of the pure trans diastereomer as a crystalline solid. Mp: 76–78 °C (hexane/ethyl acetate). IR (neat) 3001, 2956, 2835, 1614, 1586, 1509, 1208, 1037 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.23 (d, *J*=8.2 Hz, 2H), 7.10 (d, *J*=8.2 Hz, 2H), 6.88 (d, *J*=8.2 Hz, 1H), 6.46–6.41 (m, 2H), 3.788 (s, 3H), 3.786 (s, 3H), 2.27 (dt, *J*=8.9, 5.5 Hz, 1H), 1.98 (dt, *J*=8.9, 5.3 Hz, 1H), 1.34 (dt, *J*=8.8, 5.5 Hz, 1H), 1.27 (dt, *J*=8.8, 5.5 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.15, 159.09, 141.7, 131.0, 128.3, 127.4, 126.0, 122.8, 103.9, 98.4, 55.4, 55.3, 25.4, 21.7, 16.2. HRMS (EI) calculated for $[C_{17}H_{17}ClO_2]^+$ (M^+) requires *m*/*z* 288.0912, found *m*/*z* 288.0907.

*4.2.12. trans-1-(3′-Chlorophenyl)-2-(2′,4′-dimethoxyphenyl)cyclopropane (**3p**).* Prepared from 2.83 g (25 mmol) 3-chlorobenzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 5.38 g (75% yield) of cyclopropane. The cyclopropane was isomerized using 3 mg (0.0035 mmol) of $Ru(bpz)_3(PF_6)_2$ in 5.8 mL of $MeNO_2$ to obtain 999 mg (100% yield) of the pure trans diastereomer as a crystalline solid. Mp: 55–56 °C (hexane/ethyl acetate). IR (neat) 3001, 2956, 2835, 1615, 1598, 1509, 1290, 1208, 1037 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.19–7.15 (m, 2H), 7.13–7.10 (m, 1H), 7.06–7.02 (dt, 1H), 6.86 (d, *J*=8.3 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 2.29 (ddd, *J*=8.9, 6.2, 4.9 Hz, 1H), 1.98 (dt, *J*=8.9, 5.3 Hz, 1H), 1.34 (ddd, *J*=8.7, 6.3, 5.2 Hz, 1H), 1.28 (dt, *J*=8.8, 5.3 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.1, 145.4, 134.1, 129.4, 126.2, 126.1, 125.5, 124.3, 122.6, 103.8, 98.4, 55.4, 55.3, 25.6, 21.8, 16.3. HRMS (EI) calculated for $[C_{17}H_{17}ClO_2]^+$ (M^+) requires *m*/*z* 288.0912, found *m*/*z* 288.0917.

*4.2.13. trans-1-(2′-Chlorophenyl)-2-(2′,4′-dimethoxyphenyl)cyclopropane (**3q**).* Prepared from 2.82 g (25 mmol) 2-chlorobenzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 6.22 g (86% yield) of cyclopropane. The cyclopropane was isomerized using 3 mg (0.0035 mmol) of $Ru(bpz)_3(PF_6)_2$ in 5.8 mL of $MeNO_2$ to obtain 977 mg (98% yield) of the pure trans diastereomer as a colorless oil. IR (neat) 3001, 2956, 2835, 1615, 1598, 1509, 1290, 1208, 1037 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.34 (dd, *J*=8.1, 1.2 Hz, 1H), 7.20–7.16 (m, 1H), 7.12 (dd, *J*=7.8, 1.7 Hz, 1H), 7.09 (td, *J*=7.6, 1.7 Hz, 1H), 6.99 (d, *J*=8.1 Hz, 1H), 6.47–6.42 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.39 (dt, *J*=8.8, 5.4 Hz, 1H), 2.32 (dt, *J*=8.8, 5.4 Hz, 1H), 1.33 (ddd, *J*=8.6, 6.2, 4.9 Hz, 1H), 1.28 (ddd, *J*=8.8, 5.8, 4.9 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.2, 159.1, 140.3, 135.1, 129.0, 126.7, 126.5, 126.2, 122.7, 103.8, 98.4, 55.4, 55.3, 22.9, 20.6, 15.8. HRMS (EI) calculated for $[C_{17}H_{17}ClO_2]^+$ (M^+) requires *m*/*z* 288.0912, found *m*/*z* 288.0917.

*4.2.14. trans-1-(2′,4′-Dimethoxyphenyl)-2-(4′-trifluoromethylphenyl)cyclopropane (**3r**).* Prepared from 2.41 mL (25 mmol) of 4-(trifluoromethyl)benzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 3.7 g (65% yield) of cyclopropane. The cyclopropane was isomerized using 2.7 mg (0.0031 mmol) of $Ru(bpz)_3(PF_6)_2$ in 8.2 mL of $MeNO_2$ to obtain 997 mg (100% yield) of the pure trans diastereomer as a crystalline solid. Mp: 93–95 °C (hexane/ethyl acetate). IR (neat) 2998, 2967, 1616, 1584, 1508, 1324, 1120 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.52 (d, *J*=8.1 Hz, 2H), 7.25 (d, *J*=8.1 Hz, 2H), 6.89 (d, *J*=8.1 Hz, 1H), 6.47–6.42 (m, 2H), 3.792 (s, 3H), 3.789 (s, 3H), 2.34 (ddd, *J*=8.9, 6.2, 5.0 Hz, 1H), 2.06 (dt, *J*=8.7, 5.2 Hz, 1H), 1.42 (ddd, *J*=8.7, 6.2, 5.2 Hz, 1H), 1.35 (dt, *J*=8.9, 5.5 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.2, 159.2, 147.6, 126.1, 126.1, 125.2 (q, *J*=3.8 Hz), 122.4, 103.9, 98.5, 55.4, 55.4, 25.9, 22.4, 16.7. HRMS (EI) calculated for $[C_{18}H_{17}F_3O_2]^+$ (M^+) requires *m*/*z* 322.1176, found *m*/*z* 322.1171.

*4.2.15. trans-1-(2′,4′-Dimethoxyphenyl)-2-(2′-trifluoromethylphenyl)cyclopropane (**3s**).* Prepared from 3.3 mL (25 mmol) 2-(trifluoromethyl)benzaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 67.3 g (91% yield) of cyclopropane. The cyclopropane was isomerized using 2.7 mg (0.0031 mmol) of $Ru(bpz)_3(PF_6)_2$ in 5.2 mL of $MeNO_2$ to obtain 980 mg (98% yield) of the pure trans diastereomer as a colorless oil. IR (neat) 3004, 3939, 2837, 1614, 1587, 1510, 1316, 1209, 1158, 1125, 1036 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.60 (d, *J*=7.7 Hz, 1H), 7.45 (t, *J*=7.7 Hz, 1H), 7.28–7.20 (m, 2H), 6.94 (d, *J*=8.1 Hz, 1H), 6.47–6.42 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 2.44 (dt, *J*=8.9, 5.5 Hz, 1H), 2.41–2.35 (m, 1H), 1.38 (ddd, *J*=8.9, 6.1, 5.1 Hz, 1H), 1.33 (dt, *J*=8.9, 5.5 Hz, 1H); ^{13}C NMR: (125.7 MHz, CDCl3) δ 159.2, 159.2, 141.6, 131.8, 126.3, 126.2, 125.7 (q, *J*=5.8 Hz), 125.4, 122.4, 103.9, 98.4, 55.4, 55.3, 21.9, 21.9, 21.2, 16.8. HRMS (EI) calculated for $[C_{18}H_{17}F_3O_2]^+$ (M^+) requires *m*/*z* 322.1176, found *m*/*z* 322.1187.

*4.2.16. trans-1-(2′,4′-Dimethoxyphenyl)-2-(2′-furyl)cyclopropane (**3t**).* Prepared from 2.07 mL (25 mmol) of 2-furaldehyde and 4.5 g (25 mmol) of 2′,4′-dimethoxyacetophenone using the general procedure to afford 5.04 g (83% yield) of cyclopropane. The cyclopropane was isomerized using 3.5 mg (0.004 mmol) of $Ru(bpz)_3(PF_6)_2$ in 6.8 mL of $MeNO_2$ to obtain 918 mg (92% yield) of the pure trans diastereomer as a colorless oil. IR (neat) 2938, 2836, 1611, 1507, 1208, 1120, 1036 cm^{-1}. ^{1}H NMR: (500.2 MHz, $CDCl_3$) δ 7.27 (dd, *J*=2.0, 1.0 Hz, 1H), 6.87 (d, *J*=8.4 Hz, 1H), 6.45 (d, *J*=2.4 Hz, 1H), 6.42 (dd, *J*=8.4, 2.4 Hz, 1H), 6.29 (dd, *J*=3.2, 1.8 Hz, 1H), 6.03 (d, *J*=3.2 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.44–2.39 (m, 1H), 2.07 (dt, *J*=8.8, 5.2 Hz, 1H), 1.36 (ddd, *J*=8.8, 5.6, 4.6 Hz, 1H), 1.24 (ddd, *J*=8.8, 6.2, 4.6 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 159.2, 159.1, 156.7, 140.4, 126.1, 122.3, 110.3, 103.9, 103.6, 98.5, 55.5, 55.4, 19.3, 18.7, 14.5. HRMS (EI) calculated for $[C_{15}H_{16}O_3]^+$ (M^+) requires *m*/*z* 244.1094, found *m*/*z* 244.1104.

*4.2.17. trans-2,4-Dimethoxy-1-(2-(phenylethynyl)cyclopropyl)benzene (**3u**).* Ethyl diethylphosphonoacetate (6.72 g, 30 mmol) was added to a suspension of 60% NaH (1.20 g, 30 mmol) in 80 mL THF at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The flask was again cooled to 0 °C, and 2,4-dimethoxybenzaldehyde (4.98 g, 30 mmol) was added. The reaction mixture was warmed to 40 °C for 4 h and quenched with saturated NH_4Cl (aq). The mixture was extracted twice with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was placed in a 250 mL round-bottomed flask and dissolved in 100 mL CH_2Cl_2. The flask was cooled to −78 °C, and a 1.0 M solution of DIBAL-H in hexanes (90 mL, 90 mmol) was added dropwise by syringe. After 30 min at −78 °C and 1 h at 0 °C, the reaction was quenched by adding a saturated aqueous solution of Rochelle's salt and stirred at room temperature for an additional 1 h. The mixture was extracted twice with Et_2O, and the combined organic layers were washed with brine and dried over $MgSO_4$. After concentration

by rotary evaporation, the residue was used to next step without further purification.

The resulting cinnamyl alcohol was dissolved in CH_2Cl_2 (300 mL). A solution of $ZnEt_2$ (35 mL, 35 mmol, 1.17 equiv, 1 M in hexane) was added dropwise at 0 °C. The suspension was stirred for 30 min. In a second flask, $ZnEt_2$ (35 mL, 35 mmol, 1.17 equiv, 1 M in hexane) was added to diiodomethane (4.8 mL, 60 mmol, 2 equiv) in dry CH_2Cl_2 (90 mL) and stirred for 30 min at 0 °C. The solution in the first flask was transferred into the second flask at 0 °C and the mixture was stirred at room temperature for 1.5 h. A saturated solution of NH_4Cl (50 mL) was added, followed by aq 10% HCl (100 mL). The mixture was extracted with DCM (300 mL), then the organic layer was washed with saturated solutions of Na_2SO_3, $NaHCO_3$, and brine. After drying over $MgSO_4$ and concentrating by rotary evaporation, the residue was purified with column chromatography (hexane/EtOAc=5:1) to afford the cyclopropylmethanol (5.2 g, 83% in three steps).

To a stirred solution of above cyclopropyl alcohol (2.08 g, 10 mmol) in CH_2Cl_2 (20 mL) was added PCC (4.48 g, 20 mmol, 2.0 equiv) at room temperature. After 4 h, the mixture was filtered though a plug of Celite and concentrated. The residue was purified with column chromatography (hexane/EtOAc=10:1) to afford the aldehyde (1.62 g, 79%). To a stirred solution of PPh_3 (1.60 g, 6 mmol) in CH_2Cl_2 (10 mL) was added CBr_4 (2.0 g, 6 mmol) at 0 °C. After 1 h, the aldehyde (1.03 g, 5 mmol) was added into the reaction mixture. After 2 h, the reaction mixture was filtered through a plug of Celite and concentrated. The residue was purified with column chromatography (hexane/EtOAc=10:1) to afford the dibromoalkene (1.54 g, 86%). This material was dissolved in THF (10 mL) and treated with *n*-BuLi (2 mL, 2.5 M in hexane) at −78 °C. The reaction mixture was warmed to room temperature slowly over 3 h and then quenched with saturated NH_4Cl (10 mL). The mixture was extracted with ether (3×20 mL), then the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was placed in a 25 mL round-bottomed with PhI (1.22 g, 6 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 2 mol %), CuI (38 mg, 4 mol %), CH_3CN (5 mL), and Et_3N (1 mL). After stirring 9 h, the reaction mixture was treated with 10 mL of water and extracted with ether (3×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude product were purified by column chromatography (hexane/EtOAc=10:1) to afford the desired product (0.83 g, 60% in two steps) as a crystalline solid. Mp: 46–48 °C (hexane/ethyl acetate). IR (neat) 3003, 2956, 2936, 2835, 2226, 1615, 1586, 1509, 1209 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.42–7.38 (m, 2H), 7.30–7.24 (m, 3H), 6.81 (d, *J*=8.3 Hz, 1H), 6.45 (d, *J*=2.4 Hz, 1H), 6.40 (dd, *J*=8.3, 2.4 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.48 (ddd, *J*=8.9, 6.4, 4.8 Hz, 1H), 1.62 (dt, *J*=8.6, 4.8 Hz, 1H), 1.32 (dt, *J*=8.9, 4.6 Hz, 1H), 1.24 (ddd, *J*=8.6, 6.4, 4.6 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.3, 159.3, 131.6, 128.1, 127.4, 126.3, 124.0, 121.4, 103.8, 98.5, 92.7, 55.5, 55.4, 21.0, 16.6, 10.0. HRMS (EI) calculated for $[C_{19}H_{18}O_2]^+$ (M^+) requires *m*/*z* 278.1302, found *m*/*z* 278.1308.

*4.2.18. 2,4-Dimethoxy-1-(2-methyl-3-phenylcyclopropyl)benzene (**3v**).* Prepared from 4.15 g (25 mmol) 2,4-dimethyloxybenzaldehyde and 3.35 g (25 mmol) ethyl phenyl ketone using the general procedure to afford 0.74 g (11% yield) of diastereomerically pure cyclopropane as a colorless oil. IR (neat) 3000, 2953, 2835, 1614, 1507, 1465, 1208 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.05–7.00 (m, 2H), 6.99–6.95 (m, 1H), 6.85–6.81 (m, 2H), 6.27 (dd, *J*=8.4, 2.4 Hz, 1H), 6.23 (d, *J*=2.4 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 3H), 2.15–2.11 (m, 2H), 1.67–1.60 (m, 1H), 1.37 (d, *J*=5.9 Hz, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.6, 159.0, 139.7, 130.0, 127.8, 127.2, 124.9, 119.2, 103.4, 98.2, 55.3, 55.2, 31.9, 28.6, 19.0, 18.9. HRMS (EI) calculated for $[C_{18}H_{20}O_2]^+$ (M^+) requires *m*/*z* 268.1458, found *m*/*z* 268.1455.

*4.2.19. 2,4-Dimethoxy-1-(1-methyl-2-phenylcyclopropyl)benzene (**3w**).* Sodium methoxide was freshly prepared by adding 660 mg of Na to 20 mL of methanol in a flame-dried 50 mL round-bottomed flask. Dimethyl 2-oxo-2-phenylethylphosphonate (2.75 g, 12 mmol) was added to the solution. After 20 min, 1.8 g (10 mmol) 2′,4′-dimethoxyacetophenone was added, and the flask was fitted with a reflux condenser and heated to reflux for 24 h. After cooling to room temperature, the reaction was quenched with water and extracted five times with CH_2Cl_2. The organic phases were dried over $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by flash column chromatography to obtain 950 mg (3.37 mmol, 34% yield) of 3-(2,4-dimethoxyphenyl)-1-phenylprop-2-en-1-one as a yellow oil. This material was immediately placed in a 100 mL round-bottomed flask and dissolved in 10 mL EtOH. Hydrazine monohydrate (0.5 mL, 10.3 mmol) was added, the flask was fitted with a reflux condenser, and the reaction mixture was heated to reflux for 2 h. Potassium hydroxide (0.1 g, 1.78 mmol) was added, and after 15 min the reaction mixture was cooled to room temperature. The reaction mixture was loaded directly onto a silica gel column with dichloromethane. After flash column chromatography (gradient, 8:1 to 4:1 hexanes/EtOAc), 232.2 mg (0.87 mmol, 26% yield, 1:1 dr) of the title compound was obtained as a yellow oil. IR (neat) 2999, 2955, 2835, 1615, 1583, 1506, 1208 cm^{-1}. ^1H NMR: (499.9 MHz, CDCl3) δ 7.38 (d, *J*=7.4 Hz, 1H), 7.31 (t, *J*=7.7 Hz, 1H), 7.23 (d, *J*=8.3 Hz, 0.5H), 7.20 (t, *J*=7.4 Hz, 0.5H), 7.09 (d, *J*=8.3 Hz, 0.5H), 6.99 (t, *J*=7.4 Hz, 1H), 6.93 (t, *J*=7.4 Hz, 0.5H), 6.72–6.69 (m, 1H), 6.47 (d, *J*=2.4 Hz, 0.5H), 6.43 (dd, *J*=8.4, 2.6 Hz, 0.5H), 6.34 (dd, *J*=8.4, 2.6 Hz, 0.5H), 6.12 (d, *J*=2.4 Hz, 0.5H), 3.89 (s, 1.5H), 3.78 (s, 1.5H), 3.70 (s, 1.5H), 3.28 (s, 1.5H), 2.23 (dd, *J*=8.6, 6.5 Hz, 0.5H), 2.13 (dd, *J*=8.5, 6.0 Hz, 0.5H), 1.44 (s, 1.5H), 1.32 (t, *J*=5.6 Hz, 0.5H), 1.25 (dd, *J*=8.6, 4.9 Hz, 0.5H), 1.17 (dd, *J*=8.6, 5.2 Hz, 0.5H), 1.09 (dd, *J*=6.1, 4.9 Hz, 0.5H), 0.98 (s, 1.5H). HRMS (EI) calculated for $[C_{18}H_{20}O_2]^+$ (M^+) requires *m*/*z* 268.1458, found *m*/*z* 268.1458.

*4.2.20. 1-(2,2-Dimethylcyclopropyl)-2,4-dimethoxybenzene (**3x**).* A solution of isopropyltriphenylphosphonium iodide (6.48 g, 15 mmol) in THF (25 mL) at 0 °C was treated with *n*-BuLi (2 mL, 2.5 M in hexane). After 1 h, 2,4-dimethoxybenzaldehyde (1.98 g, 12 mmol) was added, and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was then filtered through a plug of Celite with ether/hexane (1:1) and concentrated by rotary evaporation. The residue was purified with column chromatography (hexane/EtOAc=20:1) to afford 1.94 g (84%) of pure Wittig adduct. The styrene thus obtained was dissolved in $CHCl_3$ (15 mL) and treated with NaOH (50% aq) and 0.1 mL of $BnMe_3NCl$ (40% in MeOH). After 16 h, the reaction mixture was partitioned between DCM (50 mL) and water (10 mL), and the aqueous layer was extracted with DCM (2×10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified with column chromatography (hexane/EtOAc=50:1) to afford the corresponding dichlorocyclopropane (2.24 g, 82% yield). A stirred solution of the dichlorocyclopropane (0.825 g, 3 mmol) in EtOH (10 mL) was warmed to 80 °C and treated with five portions of solid sodium metal over 6 h. After 10 h more, the reaction mixture was cooled to room temperature and quenched by slow addition of 10 mL water. The reaction mixture was concentrated and extracted with ether (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and purified by column chromatography (hexane/DCM=4:1) to afford the desired product (0.329 g, 53%) as an oil. IR (neat) 2996, 2941, 2866, 1616, 1585, 1508, 1208 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 6.89 (d, *J*=8.0 Hz, 1H), 6.44 (d, *J*=2.3 Hz, 1H), 6.38 (dd, *J*=8.0, 2.3 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 1.72 (dd, *J*=8.0,

6.1 Hz, 1H), 1.22 (s, 3H), 0.72–0.63 (m, 5H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.4, 157.6, 126.9, 120.4, 104.2, 98.4, 83.7, 77.8, 55.4, 55.3, 53.7, 26.3, 26.0. HRMS (EI) calculated for $[C_{13}H_{18}O_2]^+$ (M^+) requires m/z 206.1302, found m/z 206.1306.

4.3. Synthesis of endoperoxides

4.3.1. General procedure for photooxygenation of aryl cyclopropanes. A 0.05 M solution of the cyclopropane substrate (1 equiv) in 1:1 toluene/$MeNO_2$ was placed in a 35 mL pressure vessel along with $Ru(bpz)_3(PF_6)_2$ (0.005 or 0.05 equiv). A pressure regulator gauge was attached, and the solution was pressurized to 30 psi with O_2. The vessel was placed cooled to −30 °C and irradiated with a 23 W CFL bulb. Following irradiation, the vessel was depressurized and the solution was filtered through a pad of silica with CH_2Cl_2. The solvent was then removed by rotary evaporation to obtain analytically pure endoperoxide.

*4.3.2. cis-3-(4′-Methoxyphenyl)-5-phenyl-1,2-dioxolane (**4a**).* Prepared according to the general procedure using 112.2 mg (0.5 mmol) of **3a**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 3 h to afford a colorless oil; 126.5 mg (99% yield) in experiment 1 and 126.3 mg (99% yield) in experiment 2 with a 5:1 dr. All analytical data were consistent with previously reported values.[5b]

*4.3.3. cis-3-(2′-Methoxyphenyl)-5-phenyl-1,2-dioxolane (**4d**).* Prepared according to the general procedure using 112.2 mg (0.5 mmol) of **3d**, 21.6 mg (0.025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 48 h to afford a colorless oil; 61.5 mg (48% yield) in experiment 1 and 57.6 mg (45% yield) in experiment 2 with a 5:1 dr. IR (neat) 2960, 2903, 2838, 1687, 1602, 1495, 1244, 1028 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.59 (d, J=7.3 Hz, 1H), 7.47–7.22 (m, 6H), 7.02–6.96 (m, 1H), 6.90–6.84 (m, 1H), 5.73 (t, J=7.3 Hz, 1H), 5.37 (t, J=7.8 Hz, 1H), 3.79 (s, 3H), 3.52 (dt, J=12.5, 7.6 Hz, 1H), 2.55 (ddd, J=12.4, 8.1, 6.6 Hz, 1H); 13C NMR: (125.7 MHz, CDCl3) δ 156.2, 138.0, 128.6, 128.5, 128.2, 126.9, 126.6, 125.8, 120.6, 110.2, 83.4, 78.4, 55.2, 50.7. HRMS (EI) calculated for $[C_{16}H_{15}O]^+$([M−OOH]$^+$) requires m/z 223.1118, found m/z 223.1113.

*4.3.4. cis-3-(4′-Hydroxyphenyl)-5-phenyl-1,2-dioxolane (**4e**).* Prepared according to the general procedure using 105.1 mg (0.5 mmol) of **3e**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 92.1 mg (76% yield) experiment 1 and 97.1 mg (80% yield) in experiment 2 with a >10:1 dr. IR (neat) 3385, 3064, 3031, 2903, 1654, 1600, 1517, 1449, 1219 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.38–7.34 (m, 2H), 7.33–7.28 (m, 1H), 7.23 (d, J=8.5 Hz, 2H), 6.79 (d, J=8.5 Hz, 2H), 5.60 (br s, 1H), 5.44 (t, J=7.3 Hz, 1H), 5.36 (t, J=7.6 Hz, 1H), 3.39 (dt, J=12.5, 7.3 Hz, 1H), 7.0 (dt, J=12.5, 7.6 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 155.9, 139.0, 129.4, 128.7, 128.5, 128.2, 126.4, 115.6, 83.4, 83.4, 51.2. HRMS (EI) calculated for $[C_{15}H_{14}O_3]^+$ (M^+) requires m/z 242.0938, found m/z 242.0932.

*4.3.5. cis-Triisopropyl(4-(5-phenyl-1,2-dioxolan-3-yl)phenoxy)silane (**4f**).* Prepared according to the general procedure using 183.3 mg (0.5 mmol) of **3f**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 3 h to afford a colorless oil; 189.7 mg (95% yield) in experiment 1 and 187.4 mg (94% yield) in experiment 2 with a 4:1 dr. IR (neat) 2945, 2867, 1608, 1512, 1463, 1268 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 7.24 (d, J=8.6 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 5.44 (t, J=7.5 Hz, 1H), 5.37 (t, J=7.5 Hz, 1H), 3.41 (dt, J=12.3, 7.4 Hz, 1H), 2.70 (dt, J=12.3, 7.6 Hz, 1H), 1.30–1.20 (m, 3H), 1.09 (d, J=7.3 Hz, 18H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 155.9, 139.0, 129.4, 128.7, 128.5, 128.2, 126.4, 115.6, 83.4, 83.4, 51.2. HRMS (EI) calculated for $[C_{24}H_{34}O_3Si]^+$ (M^+) requires m/z 398.2272, found m/z 398.2278.

*4.3.6. cis-4-(5-Phenyl-1,2-dioxolan-3-yl)benzenamine (**4g**).* Prepared according to the general procedure using 104.3 mg (0.5 mmol) of **3g**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 85.1 mg (71% yield) in experiment 1 and 82.5 mg (68% yield) in experiment 2 with a >10:1 dr. IR (neat) 3463, 3375, 3222, 3032, 2916, 1623, 1520, 1286 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.43 (d, J=7.3 Hz, 2H), 7.37 (t, J=7.3 Hz, 2H), 7.31 (t, J=7.3 Hz, 1H), 7.17 (d, J=8.2 Hz, 2H), 6.64 (d, J=8.2 Hz, 2H), 5.44 (t, J=7.3 Hz, 1H), 5.32 (dd, J=8.2, 7.2 Hz, 1H), 3.70 (br s, 2H), 3.37 (dt, J=12.4, 7.3 Hz, 1H), 2.70 (ddd, J=12.4, 8.2, 7.3 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 146.8, 139.8, 128.6, 128.4, 128.0, 126.6, 126.3, 115.0, 83.6, 83.2, 51.1. HRMS (EI) calculated for $[C_{15}H_{15}NO_2]^+$ (M^+) requires m/z 241.1098, found m/z 241.1100.

*4.3.7. cis-tert-Butyl 4-(5-phenyl-1,2-dioxolan-3-yl)phenylcarbamate (**4h**).* Prepared according to the general procedure using 150.2 mg (0.5 mmol) of **3h**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 3 h to afford a colorless oil; 156.2 mg (94% yield) as an oil in experiment 1 and 151.4 mg (91% yield) in experiment 2 with a 5:1 dr. IR (neat) 3347, 3033, 2980, 2932, 1807, 1729, 1616, 1597, 1525, 1159 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.41–7.33 (m, 6H), 7.32–7.28 (m, 3H), 6.59 (br s, 1H), 5.43 (t, J=7.4 Hz, 1H), 5.38 (t, J=7.4 Hz, 1H), 3.42 (dt, J=12.5, 7.4 Hz, 1H), 2.67 (dt, J=12.5, 7.4 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 152.6, 138.9, 138.4, 132.6, 128.6, 128.2, 127.4, 126.5, 118.6, 83.3, 83.0, 51.4, 28.3, 27.3. HRMS (EI) calculated for $[C_{20}H_{23}NO_4]^+$ (M^+) requires m/z 341.1622, found m/z 341.1612.

*4.3.8. cis-3-(2′,4′-Dimethoxyphenyl)-5-phenyl-1,2-dioxolane (**4i**).* Prepared according to the general procedure using 127.2 mg (0.5 mmol) of **3i**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 140.0 mg (99% yield) in experiment 1 and 139.2 mg (98% yield) in experiment 2 with a 10:1 dr. IR (neat) 2960, 2939, 2837, 1613, 1589, 1507, 1287, 1209, 1035 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.43 (d, J=8.4 Hz, 1H), 7.37–7.25 (m, 5H), 6.49 (dd, J=8.4, 2.3 Hz, 1H), 6.44 (d, J=2.3 Hz, 1H), 5.68 (t, J=7.2 Hz, 1H), 5.38 (t, J=7.7 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.44 (dt, J=12.4, 7.7 Hz, 1H), 2.58 (ddd, J=12.4, 7.7, 7.2 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.5, 157.6, 138.6, 128.5, 128.1, 127.0, 126.7, 120.0, 104.2, 98.4, 83.3, 78.3, 55.3, 55.2, 50.4. HRMS (EI) calculated for $[C_{17}H_{18}O_4]^+$ (M^+) requires m/z 286.1200, found m/z 286.1187.

*4.3.9. cis-3-(3′,4′-Dimethoxyphenyl)-5-(4′-methoxyphenyl)-1,2-dioxolane (**4j**).* Prepared according to the general procedure using 127.2 mg (0.5 mmol) of **3i**, 21.6 mg (0.025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 24 h to afford a colorless oil; 107.4 mg (75% yield) in experiment 1 and 112.3 mg (78% yield) in experiment 2 with a 5:1 dr. IR (neat) 2958, 2936, 2836, 1606, 1594, 1518, 1464, 1263, 1140 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.42 (d, J=7.7 Hz, 2H), 7.36 (dd, J=7.7, 7.6 Hz, 2H), 7.30 (t, J=7.6 Hz, 1H), 6.90 (dd, J=8.3, 1.8 Hz, 1H), 6.84 (d, J=1.8 Hz, 1H), 6.81 (d, J=8.3 Hz, 1H), 5.46 (t, J=7.1 Hz, 1H), 5.37 (t, J=7.4 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.45 (dt, J=12.3, 7.4 Hz, 1H), 2.72 (dt, J=12.3, 7.1 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 149.0, 139.3, 130.5, 128.6, 128.0, 126.6, 126.3, 119.4, 110.9, 109.6, 83.1, 83.0, 55.8, 55.6, 51.3. HRMS (EI) calculated for $[C_{17}H_{18}O_4]^+$ (M^+) requires m/z 286.1200, found m/z 286.1209.

*4.3.10. cis-3,5-Bis(2′,4′-dimethoxyphenyl)-1,2-dioxolane (**4k**).* Prepared according to the general procedure using 157.1 mg

(0.5 mmol) of **3k**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 168.4 mg (97% yield) as an oil in experiment 1 and 171.2 mg (99% yield) in experiment 2 with a 6:1 dr. IR (neat) 3001, 2940, 2838, 1613, 1507, 1210 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.37 (d, J=8.6 Hz, 2H), 6.46 (dd, J=8.6, 2.3 Hz, 2H), 6.42 (d, J=2.3 Hz, 2H), 5.66 (t, J=7.4 Hz, 2H), 3.77 (s, 6H), 3.76 (s, 6H), 3.40 (dt, J=12.3, 7.6 Hz, 1H), 2.45 (dt, J=12.3, 7.3 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.4, 157.7, 127.1, 119.9, 104.2, 98.2, 77.9, 55.2, 49.0. HRMS (EI) calculated for $[C_{19}H_{22}O_6]^+$ (M^+) requires m/z 346.1411, found m/z 346.1400.

*4.3.11. cis-3-(2′,4′-Dimethoxyphenyl)-5-(4′-methoxyphenyl)-1,2-dioxolane (**4l**).* Prepared according to the general procedure using 142.2 mg (0.5 mmol) of **3l**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 156.6 mg (99% yield) as an oil in experiment 1 and 155.1 mg (98% yield) in experiment 2 with a 9:1 dr. IR (neat) 3001, 2959, 2937, 1676, 1613, 1515, 1251, 1034 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.47 (d, J=8.4 Hz, 1H), 7.26 (d, J=8.7 Hz, 2H), 6.84 (d, J=8.7 Hz, 2H), 6.50 (dd, J=8.4, 2.5 Hz, 1H), 6.44 (d, J=2.5 Hz, 1H), 5.67 (t, J=7.1 Hz, 1H), 5.32 (t, J=7.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.39 (dt, J=12.5, 7.6 Hz, 1H), 2.58–2.52 (m, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.4, 159.6, 157.5, 129.7, 128.4, 126.8, 120.6, 113.9, 104.2, 98.3, 83.2, 78.3, 55.3, 55.2, 55.1, 50.2. HRMS (EI) calculated for $[C_{18}H_{20}O_5]^+$ (M^+) requires m/z 316.1306, found m/z 316.1292.

*4.3.12. cis-3-(2′,4′-Dimethoxyphenyl)-5-(4′-methylphenyl)-1,2-dioxolane (**4m**).* Prepared according to the general procedure using 134.2 mg (0.5 mmol) of **3m**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 147.2 mg (98% yield) in experiment 1 and 146.5 mg (98% yield) in experiment 2 with a 9:1 dr. IR (neat) 3000, 2958, 2837, 1614, 1589, 1507, 1209, 1035 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.46 (d, J=8.6 Hz, 1H), 7.23 (d, J=7.9 Hz, 2H), 7.12 (d, J=7.9 Hz, 2H), 6.50 (dd, J=8.6, 2.4 Hz, 1H), 6.44 (d, J=2.4 Hz, 1H), 5.67 (t, J=7.1 Hz, 1H), 5.34 (t, J=7.7 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.41 (dt, J=12.4, 7.5 Hz, 1H), 2.56 (ddd, J=12.4, 7.7, 7.1 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.4, 157.6, 137.9, 135.2, 129.2, 126.9, 126.9, 120.3, 104.2, 98.3, 83.3, 78.2, 55.3, 55.3, 50.4, 21.1. HRMS (EI) calculated for $[C_{18}H_{20}O_4]^+$ (M^+) requires m/z 300.1357, found m/z 300.1351.

*4.3.13. cis-3-(4′-Bromophenyl)-5-(2′,4′-dimethoxyphenyl)-1,2-dioxolane (**4n**).* Prepared according to the general procedure using 166.6 mg (0.5 mmol) of **3n**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h as a colorless oil; 180.7 mg (99% yield) in experiment 1 and 180.2 mg (99% yield) in experiment 2 with a 9:1 dr. IR (neat) 3000, 2960, 2937, 1616, 1589, 1507, 1209 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.43 (d, J=8.2 Hz, 2H), 7.36 (d, J=8.4 Hz, 1H), 7.22 (d, J=8.2 Hz, 2H), 6.47 (dd, J=8.4, 2.4 Hz, 1H), 6.43 (d, J=2.4 Hz, 1H), 5.64 (t, J=7.4 Hz, 1H), 5.33 (t, J=7.5 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.43 (dt, J=12.2, 7.5 Hz, 1H), 2.52 (dt, J=12.2, 7.4 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.6, 157.7, 138.3, 131.6, 128.3, 127.0, 121.8, 119.1, 104.2, 98.4, 82.5, 78.3, 55.3, 55.2, 50.2. HRMS (EI) calculated for $[C_{17}H_{17}BrO_4]^+$ (M^+) requires m/z 364.0305, found m/z 364.0321.

*4.3.14. cis-3-(4′-Chlorophenyl)-5-(2′,4′-dimethoxyphenyl)-1,2-dioxolane (**4o**).* Prepared according to the general procedure using 144.4 mg (0.5 mmol) of **3o**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 158.8 mg (99% yield) in experiment 1 and 153.5 mg (96% yield) in experiment 2 with a 10:1 dr. IR (neat) 3001, 2960, 2837, 1615, 1589, 1507, 1209 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.36 (d, J=8.4 Hz, 1H), 7.27 (s, 4H), 6.47 (dd, J=8.6, 2.5 Hz, 1H), 6.43 (d, J=2.5 Hz, 1H), 5.65 (t, J=7.4 Hz, 1H), 5.34 (t, J=7.6 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.43 (dt, J=12.3, 7.6 Hz, 1H), 2.52 (dt, J=12.3, 7.4 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.6, 157.7, 137.7, 133.7, 128.6, 128.0, 127.0, 119.2, 104.2, 98.4, 82.4, 78.3, 55.2, 55.2, 50.2. HRMS (EI) calculated for $[C_{17}H_{17}ClO_4]^+$ (M^+) requires m/z 320.0810, found m/z 320.0822.

*4.3.15. cis-3-(3′-Chlorophenyl)-5-(2′,4′-dimethoxyphenyl)-1,2-dioxolane (**4p**).* Prepared according to the general procedure using 144.4 mg (0.5 mmol) of **3p**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 157.2 mg (98% yield) as an oil in experiment 1 and 154.3 mg (96% yield) in experiment 2 with a >10:1 dr. IR (neat) 3001, 2960, 2837, 1614, 1589, 1507, 1209 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.35 (d, J=8.0 Hz, 1H), 7.25–7.21 (m, 3H), 6.48 (dd, J=8.5, 2.4 Hz, 1H), 6.43 (d, J=2.4 Hz, 1H), 5.64 (t, J=7.4 Hz, 1H), 5.35 (t, J=7.4 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.43 (dt, J=12.4, 7.4 Hz, 1H), 2.56 (dt, J=12.4, 7.4 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.7, 157.8, 141.7, 134.3, 129.8, 128.0, 127.2, 126.6, 124.6, 118.7, 104.2, 98.5, 82.4, 78.5, 55.3, 55.2, 50.0. HRMS (EI) calculated for $[C_{17}H_{17}ClO_4]^+$ (M^+) requires m/z 320.0810, found m/z 320.0819.

*4.3.16. cis-3-(2′-Chlorophenyl)-5-(2′,4′-dimethoxyphenyl)-1,2-dioxolane (**4q**).* Prepared according to the general procedure using 144.4 mg (0.5 mmol) of **3q**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 158.9 mg (99% yield) in experiment 1 and 159.2 mg (99% yield) in experiment 2 with a 10:1 dr. IR (neat) 3000, 2960, 2837, 1615, 1589, 1508, 1288, 1209, 1035 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.70 (dd, J=8.0, 1.5 Hz, 1H), 7.31 (dd, J=8.0, 0.9 Hz, 1H), 7.27 (td, J=7.3, 0.9 Hz, 1H), 7.22 (d, J=8.2 Hz, 1H), 7.18 (td, J=7.7, 1.5 Hz, 1H), 6.44–6.39 (m, 2H), 5.73 (dd, J=8.0, 6.0 Hz, 1H), 5.65 (t, J=7.7 Hz, 1H), 3.75 (s, 1H), 3.71 (s, 1H), 3.60 (dt, J=12.4, 8.0 Hz, 1H), 2.46 (ddd, J=12.4, 8.0, 6.0 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.8, 158.2, 139.2, 131.5, 129.2, 128.4, 127.6, 126.9, 126.5, 117.5, 104.3, 98.4, 80.0, 78.3, 55.2, 55.2, 49.1. HRMS (EI) calculated for $[C_{17}H_{17}ClO_4]^+$ (M^+) requires m/z 320.0810, found m/z 320.0809.

*4.3.17. cis-3-(2′,4′-Dimethoxyphenyl)-5-(4′-trifluoromethylphenyl)-1,2-dioxolane (**4r**).* Prepared according to the general procedure using 161.2 mg (0.5 mmol) of **3r**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 171.7 mg (97% yield) as an oil in experiment 1 and 174.4 mg (98% yield) in experiment 2 with a 10:1 dr. IR (neat) 2962, 2942, 2840, 1616, 1589, 1508, 1326, 1124 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.59 (d, J=7.8 Hz, 2H), 7.48 (d, J=8.2 Hz, 2H), 7.33 (d, J=8.2 Hz, 1H), 6.48 (dd, J=8.4, 2.5 Hz, 1H), 6.44 (d, J=2.5 Hz, 1H), 5.66 (t, J=7.4 Hz, 1H), 5.45 (t, J=7.4 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.49 (dt, J=12.2, 7.6 Hz, 1H), 2.57 (dt, J=12.2, 7.2 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.8, 157.9, 144.0, 127.2, 126.7, 125.5 (q, J=3.9 Hz), 118.6, 104.3, 98.5, 82.3, 78.5, 55.3, 55.2, 50.2. HRMS (EI) calculated for $[C_{18}H_{17}F_3O_4]^+$ (M^+) requires m/z 354.1074, found m/z 354.1086.

*4.3.18. cis-3-(2′,4′-Dimethoxyphenyl)-5-(2′-trifluoromethylphenyl)-1,2-dioxolane (**4s**).* Prepared according to the general procedure using 161.2 mg (0.5 mmol) of **3s**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 163.4 mg (92% yield) as an oil in experiment 1 and 169.5 mg (96% yield) in experiment 2 with a >10:1 dr. IR (neat) 3003, 2962, 2941, 2839, 1616, 1589, 1507, 1314, 1121 cm^{-1}. ^1H NMR: (499.9 MHz, $CDCl_3$) δ 7.90 (d, J=8.0 Hz,

1H), 7.60 (d, *J*=8.0 Hz, 1H), 7.56 (t, *J*=7.7 Hz, 1H), 7.38–7.32 (m, 2H), 6.48 (dd, *J*=8.5, 2.3 Hz, 1H), 6.43 (d, *J*=2.3 Hz, 1H), 5.81 (t, *J*=7.6 Hz, 1H), 5.66 (t, *J*=7.6 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.52 (dt, *J*=12.7, 7.6 Hz, 1H), 2.49 (dt, *J*=12.7, 7.6 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.9, 158.1, 140.0, 132.4, 127.5, 127.3, 127.1, 125.6 (q, *J*=5.6 Hz), 117.7, 104.3, 98.5, 79.2 (q, *J*=2.0 Hz), 78.6, 55.3, 55.3, 51.1. HRMS (EI) calculated for $[C_{18}H_{17}F_3O_4]^+$ (M^+) requires *m*/*z* 354.1074, found *m*/*z* 354.1079.

*4.3.19. cis-3-(2′,4′-Dimethoxyphenyl)-5-(2′-furyl)-1,2-dioxolane (**4t**).* Prepared according to the general procedure using 122.2 mg (0.5 mmol) of **3t**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 101.9 mg (74% yield) as an oil in experiment 1 and 105.6 mg (76% yield) in experiment 2 with a 6:1 dr. IR (neat) 3001, 2940, 2838, 1613, 1507, 1209, 1034 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.46 (d, *J*=8.7 Hz, 1H), 7.41 (s, 1H), 6.50 (dd, *J*=8.2, 2.2 Hz, 1H), 6.45 (d, *J*=2.2 Hz, 1H), 6.37 (d, *J*=3.1 Hz, 1H), 6.34 (dd, *J*=3.1, 1.8 Hz, 1H), 5.66 (t, *J*=7.5 Hz, 1H), 5.41 (t, *J*=7.5 Hz, 1H), 3.29 (dt, *J*=12.2, 7.7 Hz, 1H), 2.81 (dt, *J*=12.2, 7.2 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.6, 157.8, 151.0, 143.1, 127.1, 119.2, 110.4, 109.5, 104.3, 98.4, 77.7, 76.2, 55.4, 55.3, 45.5. HRMS (EI) calculated for $[C_{15}H_{16}O_5]^+$ (M^+) requires *m*/*z* 276.0993, found *m*/*z* 276.0984.

*4.3.20. 3-(2,4-Dimethoxyphenyl)-5-(phenylethynyl)-1,2-dioxolane (**4u**).* Prepared according to the general procedure using 139.2 mg (0.5 mmol) of **3u**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 24 h as a colorless oil; 151.9 mg (98% yield) in experiment 1 and 152.7 mg (98% yield) in experiment 2 with approx. 1:1 dr. IR (neat) 3001, 2962, 2938, 2837, 2232, 1615, 1507, 1209, 1034 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.54 (d, *J*=8.5 Hz, cis, 1H), 7.48–7.45 (m, *J*=trans Hz, 2H), 7.44–7.41 (m, *J*=cis Hz, 2H), 7.36 (d, *J*=8.5 Hz, trans, 1H), 7.33–7.27 (m, *J*=cis and trans Hz, 6H), 6.52–6.43 (m, *J*=cis and trans Hz, 4H), 5.70 (dd, *J*=7.7, 6.1 Hz, trans, 1H), 5.60 (t, *J*=7.4 Hz, cis, 1H), 3.81–3.77 (m, *J*=cis and trans Hz, 12H), 3.34 (dt, *J*=12.2, 8.3 Hz, cis, 1H), 3.17 (ddd, *J*=12.3, 8.0, 5.2 Hz, trans, 1H), 2.91 (ddd, *J*=12.3, 8.0, 6.1 Hz, trans, 1H), 2.73 (ddd, *J*=12.2, 6.8, 5.5 Hz, cis, 1H). HRMS (EI) calculated for $[C_{19}H_{18}O_4]^+$ (M^+) requires *m*/*z* 310.1200, found *m*/*z* 310.1197.

*4.3.21. 3-(2,4-Dimethoxyphenyl)-4-methyl-5-phenyl-1,2-dioxolane (**4v**).* Prepared according to the general procedure using 134.2 mg (0.5 mmol) of **3v**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 3 h to afford a colorless oil; 142.6 mg (95% yield) as an oil in experiment 1 and 145.7 mg (97% yield) in experiment 2 with a 10:1 dr. IR (neat) 2966, 2936, 2838, 1676, 1612, 1507, 1456, 1209 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.47 (d, *J*=8.5 Hz, 1H), 7.38–7.26 (m, 5H), 6.53 (dd, *J*=8.5, 2.3 Hz, 1H), 6.47 (d, *J*=2.3 Hz, 1H), 5.47 (d, *J*=7.6 Hz, 1H), 5.28 (d, *J*=6.2 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.22–3.13 (m, 1H), 0.80 (d, *J*=6.9 Hz, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.8, 158.4, 136.7, 128.1, 128.0, 127.6, 126.8, 118.1, 104.4, 98.5, 85.4, 83.7, 55.4, 55.3, 53.8, 13.9. HRMS (EI) calculated for $[C_{18}H_{20}O_4]^+$ (M^+) requires *m*/*z* 300.1358, found *m*/*z* 300.1363.

*4.3.22. 3-(2,4-Dimethoxyphenyl)-3-methyl-5-phenyl-1,2-dioxolane (**4w**).* Prepared according to the general procedure using 134.2 mg (0.5 mmol) of **3w**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 1 h to afford a colorless oil; 148.5 mg (99% yield) as a solid in experiment 1 and 146.9 mg (98% yield) in experiment 2 with a 9:1 dr. Mp: 99–100 °C (hexane/EtOAc). IR (neat) 2960, 2934, 2837, 1615, 1586, 1505, 1208 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.62 (d, *J*=8.5 Hz, 1H), 7.24–7.20 (m, 3H), 7.15–7.11 (m, 2H), 6.52 (dd, *J*=8.5, 2.5 Hz, 1H), 6.48 (d, *J*=2.5 Hz, 1H), 5.36 (t, *J*=8.1 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.16 (dd, *J*=12.8, 8.1 Hz, 1H), 2.87 (dd, *J*=12.8, 8.1 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 159.9, 156.5, 137.7, 128.4, 128.2, 127.2, 126.5, 126.1, 103.6, 99.0, 86.5, 84.2, 55.6, 55.3, 55.1, 24.9. HRMS (EI) calculated for $[C_{18}H_{20}O_4]^+$ (M^+) requires *m*/*z* 300.1357, found *m*/*z* 300.1346.

*4.3.23. 5-(2,4-Dimethoxyphenyl)-3,3-dimethyl-1,2-dioxolane (**4x**).* Prepared according to the general procedure using 103 mg (0.5 mmol) of **3x**, 2.2 mg (0.0025 mmol) of $Ru(bpz)_3(PF_6)_2$, 5 mL of toluene, 5 mL of nitromethane, and an irradiation time of 12 h to afford a colorless oil; 110.4 mg (93% yield) as an oil in experiment 1 and 112.1 mg (94% yield) in experiment 2. IR (neat) 2974, 2934, 2838, 1615, 1589, 1507, 1209 cm^{-1}. ^{1}H NMR: (499.9 MHz, $CDCl_3$) δ 7.41 (d, *J*=8.6 Hz, 1H), 6.49 (dd, *J*=8.6, 2.4 Hz, 1H), 6.43 (d, *J*=2.4 Hz, 1H), 5.54 (t, *J*=7.6 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.80 (dd, *J*=11.9, 8.0 Hz, 1H), 2.29 (dd, *J*=11.9, 7.2 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 160.4, 157.6, 126.9, 120.4, 104.2, 98.4, 83.7, 77.8, 55.4, 55.3, 53.7, 26.3, 26.0. HRMS (EI) calculated for $[C_{13}H_{18}O_4]^+$ (M^+) requires *m*/*z* 238.1200, found *m*/*z* 238.1208.

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