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Catalytic Enantioselective Allylic Oxidation of Olefins with Copper(I) Catalysts and New Perester Oxidants

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Abstract: Asymmetric allylic oxidation of cyclic olefins using a catalytic amount of copper(I) bisoxazoline complexes and new peresters was investigated to give allylic benzoate esters in high selectivity (~80%ee), yield (70-80%), and at reasonable rates (5-7 d) at -20 °C in acetonitrile. Cyclohexene reacted with *para*-chloro *tert*-butylperbenzoate and 15 mol% diphenylbisoxazoline-copper(I) hexafluorophosphate to give benzoate product in 83% yield and 75% ee. © 1997 Elsevier Science Ltd.

Asymmetric allylic oxidation using peresters and copper catalysis continues to attract considerable attention.[1] The ability to convert simple olefins into allylesters is an important transformations with many potential synthetic applications. The allylic process, unlike other more well known stereogenic olefin oxidations, epoxidation[2] and dihydroxylation,[3] maintains the olefin in the product for subsequent transformations. Kharasch first reported allylic oxidation with *t*-butyl perbenzoate and catalytic copper(I) in refluxing benzene.[4] Yields of allyl ester products were in general high with regioselectivity, for terminal olefins, of 9:1 for the internal secondary ester over the terminal primary isomer. Previous attempts to develop asymmetric versions of this reaction have employed copper camphorate complexes as catalysts with cyclic olefins and copper salts with amino acids.[5] The selectivities were low with cyclohexene being the best at 30% ee determined using optical rotations. We and others have recently reported the use of copper(I) triflate bisoxazoline complexes as catalysts for asymmetric allylic oxidation at lower temperatures.[6] While the

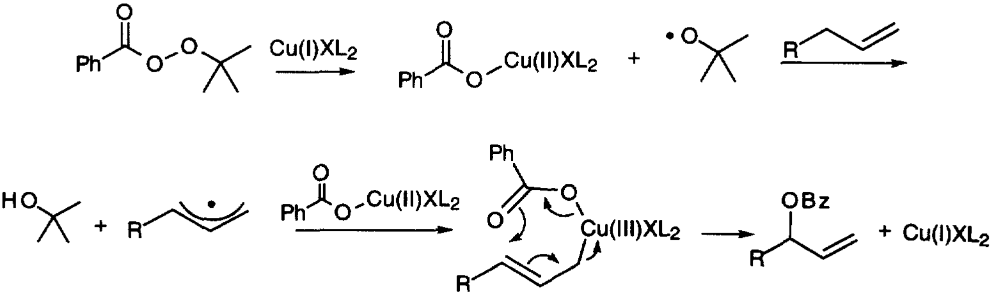


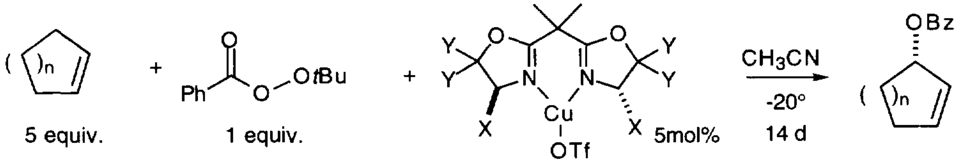
Figure 1. Mechanism of Allylic Olefin Oxidation With Cu(I) and Perester.

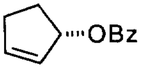
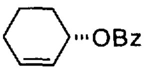
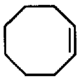
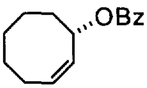
selectivities were greatly improved to the 80% ee range, the reaction rates and yields were very low. We now report the use of new perester oxidants that greatly improve both the rates and the yields of the reaction.

The mechanism has been shown to involve homolysis of the perester oxygen-oxygen bond by copper(I) to give a copper(II) benzoate intermediate and *t*-butoxy radical (fig. 1).[7] The *t*-butoxy radical abstracts an allylic, prochiral hydrogen atom to give *t*-butanol and an allylic radical.[8] Rapid addition of copper(II) to the allyl radical to generate copper(III) benzoate with the bound allyl fragment then occurs.[9] The geometry of the olefin is maintained by the allyl radical as shown using internal olefins due to the high barrier to rotation (~20 kcal/mol).[10] The final step of the chain mechanism is rearrangement of the copper(III) intermediate to give the product and regenerate the copper(I) catalyst.[11]

The asymmetric allylic oxidation depends on the use of a ligand (L) that can coordinate copper(III) as the allyl benzoate product is being formed. Recently the use of bisoxazoline copper catalysts for catalytic asymmetric cyclopropanation[12] and aziridination[13] have been reported with high selectivities. We and others have recently reported the use of copper(I) triflate complexes of this type for the Kharasch reaction.[6] Key results are summarized below in Table 1. Using commercially available *tert*-butyl

Table 1. Asymmetric Allylic Oxidation.



Olefin	Product	Ligand (X,Y)	Yield%	ee%
				
"	"	*t*Bu, Me	41	42
"	"	Ph, Me	49	**81**
				
"	"	*t*Bu, H	43	**80**
"	"	*t*Bu, Me	49	67
"	"	Ph, Me	44	47
		*t*Bu, H	44	13
"	"	*t*Bu, Me	43	0

Isolated yields are based on perester. The freezer used for -20° C. The ee's were determined using the chiral shift reagent Eu(hfc)$_3$.

perbenzoate reacted with excess olefin in acetonitrile at -20 °C for 2 weeks, the cyclopentyl and cyclohexyl benzoate products were obtained in high selectivity, 81 and 80% ee. This is a departure from the conditions of Kharasch where refluxing benzene and copper(I) bromide were used. Another key feature of this study is the use of the the bis-gemdimethylbisoxazoline ligands (Y=Me) that could be recovered after the reaction. Also the selectivity for cyclohexene was low when the inexpensive diphenyl ligand (X=ph), derived from phenylglycine, was used. The selectivity for cyclooctene and acylic olefins was low with both ligands. While the first step of finding a selective catalyst was met by this study, major problems with the rate of the reaction and low yields were clearly evident.

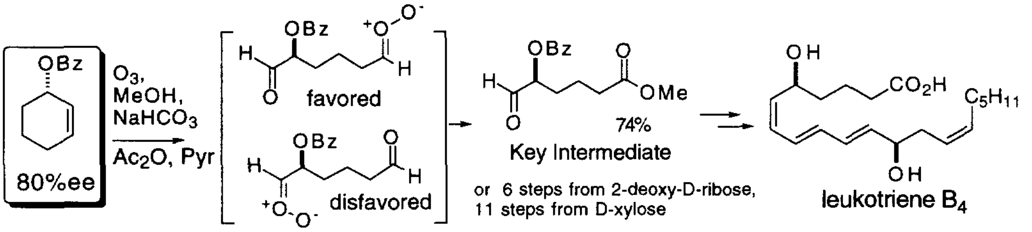


Figure 2. Conversion of cyclohexenyl benzoate to leukotriene B_4 using selectrive ozonolysis.

The potential for synthetic applications for cycloalkenols derived from simple cyclic olefins is great. A particulary clear example is the known conversion of *(S)*-cyclohexenyl benzoate to the key aldehyde-methyl ester intermediate for the synthesis of the important inflammation mediator leukotriene B_4 (figure 2). Using the selective ozonolysis work-up method of Schreiber, Wallace has shown that this compound can be accessed in a single step in high yield where other routes have required multiple steps from sugar based percursors.[14] Twelve routes to leukotriene B_4 have been published using the key aldehyde-methyl ester shown as an intermediate. The most efficient route used 6 steps from 2-deoxy-D-ribose and the least efficeint used 11 steps from D-xylose. Now using an asymmetric allylic oxidation the intermediate can be accessed in only two steps starting with cyclohexene.

All previous asymetric allylic oxidations have suffered from very low yields and low reaction rates.[1, 6] With a goal of increasing the rate of reaction, new electron deficient peresters were synthesized (figure 3). This modification was planed with the idea of weakening the perester bond leading to more rapid bond homolysis. The rate of formation of copper(II) benzoate and *tert*-butoxy radical should then increase. The rates of hydrogen atom abstraction and copper(II) addition to the allyl radical are both known to be very fast, nearly diffusion controlled processes.[9] The acid chlorides were reacted with anhydrous *tert* -butyl hydrogen peroxide and pyridine in pentane to give the indicated peresters **1-4** as stable, chromatographable products in high yields (figure 3). It is important to point out that the peresters, unlike the peracids, MCPBA for example,

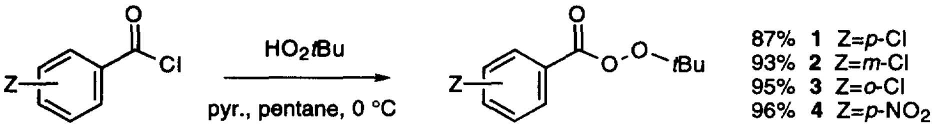
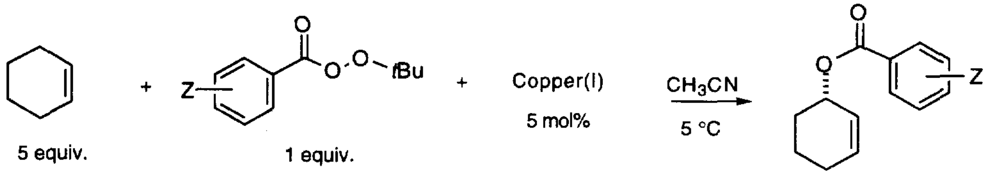


Figure 3. Synthesis of substituted perbenzoate esters from the acid chlorides and *tert*-butyl hydrogen peroxide.

are not shock sensitive with no reported incidences, however the usual percausions were taken to ensure safe handling. The chloroperesters are oils as the parent perbenzoate (Z=H) while the *para*-nitroperester is a solid that is conviently purified by recrystallization.

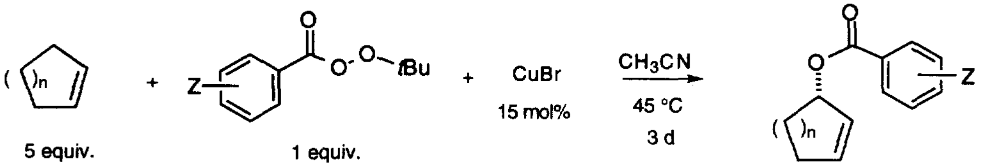
Initially the new peresters were screened for reactivity using 5 mol% of copper(I) without an asymmetric ligand (Table 2). Copper was used in 5 mol% amounts, with excess olefin as before. The temperature was raised to 5 °C and the time was held constant to allow for direct comparison. Copper(I) hexafluorophosphate tetracetonitrile[15] gave a yield of 61% (based on the perester) with the *meta*-chloro perester, while copper(I) bromide was lower at 42%. The trend was reversed with the *ortho*-chloride perester with copper(I) bromide giving the higher yield at 74%. Nitroperester **4** proved gave ester product in poor yield with all copper(I) salts tested. Other forms of copper(I), tetrafluoroborate and hexafluoroantimonate, also gave poor yields with the new peresters.

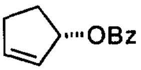
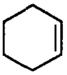
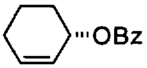
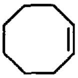
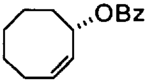
Table 2. Reaction of peresters and cyclohexene with copper(I) salts at 5 mol% without ligand at constant temperature (5 °C).



Perester	Copper(I)	Time (d)	Yield%
2 *m*-Cl	CuBr	5	42
"	$CuPF_6•(CH_3CN)_4$	5	61
3 *o*-Cl	CuBr	5	74
"	$CuPF_6•(CH_3CN)_4$	5	13
4 *p*-NO2	CuBr	5	23
"	$CuPF_6•(CH_3CN)_4$	5	15

Table 3. Reactions of cycloalkenes with copper(I) bromide and peresters at 45 °C.

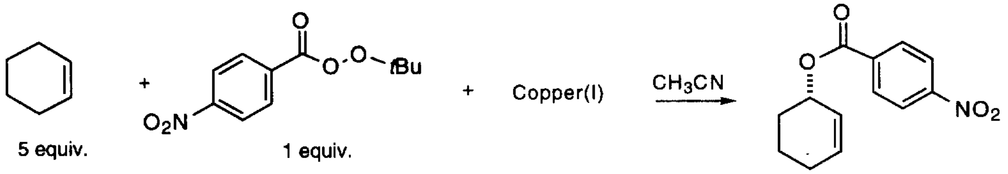


Olefin	Product	Perester	Yield%
		1 *p*-Cl	65
"	"	2 *m*-Cl	81
"	"	3 *o*-Cl	89
"	"	4 *p*-NO2	54
		1 *p*-Cl	59
"	"	2 *m*-Cl	77
"	"	3 *o*-Cl	83
"	"	4 *p*-NO2	57
		4 *p*-NO2	43

To assess the effect of the substrate the various peresters were reacted with cyclopentene, -hexene, and octene and 15 mol% copper(I) bromide at higher temperature, 45 °C for 3 d again without ligand (Table 3). The highest yields were obtained using the *ortho* and *meta*-chloroperesters. Interestingly the *para*-chloro- and nitroperesters were lower indicating that the electron withdrawing effect may not be beneficial for the reaction. In this case, using copper(I) bromide without ligand, a coordination effect with the *ortho*-chloro may be promoting higher yields.[16] A low yield for cyclooctene was again noted as seen before in the initial asymmetric studies. This is probably due to improper alignment of the allyl radical intermediate when contrained in an eight-membered ring.

Next the effect of copper catalyst stoichiometry was explored by reacting copper(I) bromide with cyclohexene with the less reactive nitroperester as stoichiometric oxidant at 5 °C for 5 d (Table 4). The yields clearly show a trend of improvement going from 47 to 72% as the amount of the catalyst was increased from 5 to 20 mol%.

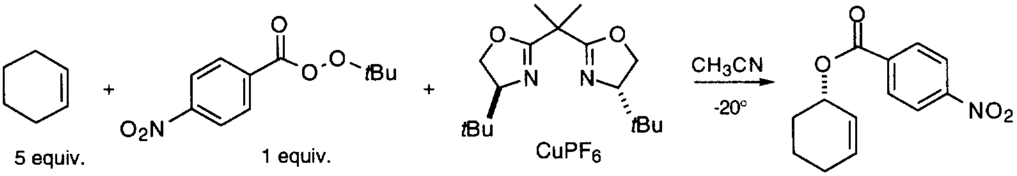
Table 4. Copper(I) bromide catalyst at various amounts with cyclohexene and nitroperester at 5 °C.



Copper(I)	mol %	Time (d)	Yield%
CuBr	5	5	47
"	10	5	63
"	20	5	72

With these preliminary reactivity experiments complete, our attention turned to the asymmetric reaction. As with the yields, the selectivities also improved as the amount of the copper(I)•ligand complex was increased (Table 5). The copper•ligand complexes were formed by reacting the copper(I) hexafluorophosphate tetracetonitrile with the bisoxazoline in acetonitrile at rt for 2 h. This form of copper(I), as opposed to copper(I) triflate, is air stable and not hydroscopic.[15] Cyclohexene was reacted with *p*-nitroperester and copper(I)•*tert*-butylbisoxazoline in acetonitrile at -20 °C for 7 d. At 5 mol% the ee was found to be 63%. At 15 mol% the selectivity was raised to 76% ee. The yield under these conditions was also increased from 34% to 60%. This is a significant improvement compared to the parent perester where a time of 14 d was needed to achieve a yield of only 43%.[6]

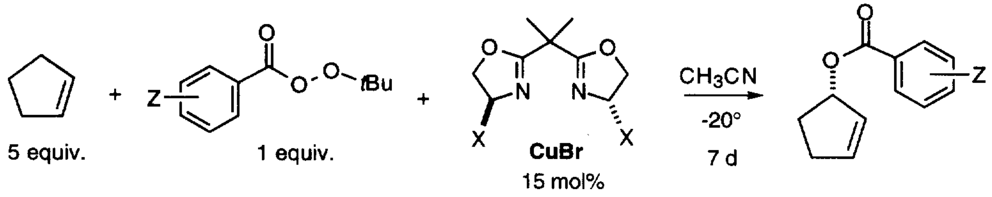
Table 5. Effect of catalyst stoichiometry on enantiomeric excess using *tert*-butylbisoxazoline and copper(I).



Copper(I)•L	mol %	Time (d)	Yield%	ee%
CuPF$_6$	5	7	34	63
"	15	7	60	76

The ee's were determined using the chiral shift reagent Eu(hfc)$_3$

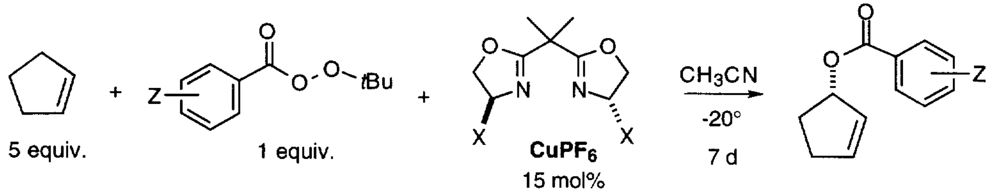
Table 6. Cyclopentene with copper(I) bromide•bisoxazolines.



Perester	Ligand	Yield%	ee%
1 *p*-Cl	X=*t*Bu	75	45
"	X=Ph	63	32
4 *p*-NO_2	X=*t*Bu	52	53
"	X=Ph	37	54

The effect of the ligand was then investigated using copper(I) bromide. The copper complexed diphenyl and the di-*tert*-butyl bisoxazolines were used as catalyst for the oxidation of cyclopentene with the new peresters (Table 6). After reacting at -20 °C for 7 d the yields were found to range from 37 to 63% and the selectivities were unimpressive at only 50% ee. The *mets* and *para* peresters were worse in this case with lower yields and selectivity. Previously is was found that the superior ligand for cyclopentene was the gem-dimethylbisoxazoline.[6]

Table 7. Cyclopentene with copper(I) hexafluorophosphate•bisoxazolines.

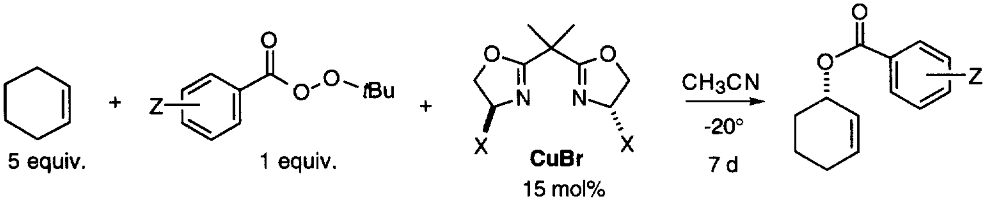


Perester	Ligand	Yield%	ee%
1 *p*-Cl	X=*t*Bu	76	57
"	X=Ph	82	39
2 *m*-Cl	X=*t*Bu	67	51
"	X=Ph	64	29
3 *o*-Cl	X=*t*Bu	76	66
"	X=Ph	70	10
4 *p*-NO_2	X=*t*Bu	49	53
"	X=Ph	48	31

Interestingly, by simply changing to the copper(I) hexafluorophosphate complex, the yields and selectivities both improved (Table 7). The conditions were the same at -20 °C for 7 d using 15 mol% catalyst. The di-*tert*-butylbisoxazoline catalyst consistently gave higher yields and selectivities. The *ortho*-chloroperbenzoate was the best providing product in 76% yield and 66% ee. When the catalyst is changed to the diphenyl ligand in this case the selectivity dramatically drops to 10% ee.

These same trends were found when cyclohexene was used as the substrate (Table 8). With copper(I) bromide, the di-*tert*-butylbisoxazoline catalyst was superior both in yield and selectivity. The nitroperester gave product in 63% ee, while the selectivity with the diphenyl ligand dropped to 7% ee. The other oxidants not shown were found to give product with lower yields and selectivities in this series.

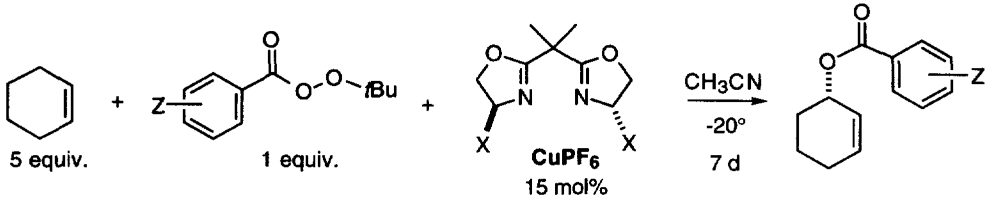
Table 8. Cyclohexene with copper(I) bromide•bisoxazolines.



Perester	Ligand	Yield%	ee%
1 *p*-Cl	X=*t*Bu	72	57
"	X=Ph	67	20
4 *p*-NO_2	X=*t*Bu	53	63
"	X=Ph	47	7

As seen above with cyclopentene, a simple change to copper(I) hexafluorophosphate as the copper source gave dramatically improved results. Importantly, now the diphenylbisoxazoline ligand gave product in high selectivity and yield. The diphenylbisoxazoline is easily made begining with the inexpensive starting material phenylglycine while the di-*tert*-butyl ligand requires the expensive*tert*-leucine.[6] The yields were better with the diphenyl ligand and the selectivities were uniformly high, ranging from 71 to 76 % ee. This results are a significant advance for the rate the reaction at this low temperature where high selectivities can be achieved. Contrasted with previous results for cyclohexene, where the di-*tert*-butyl ligand gave poor yields after 14 d, high selectivity can now be obtained after only 7 d using the more accessable catalyst. Efforts are now underway to dicover new ligands to further increase the selectivity using these new oxidants and widen the scope of the reaction to new substrates.

Table 9. Cyclohexene with copper(I) hexafluorophosphate•bisoxazolines.



Perester	Ligand	Yield%	ee%
1 *p*-Cl	X=*t*Bu	73	75
"	X=Ph	83	75
2 *m*-Cl	X=*t*Bu	46	72
"	X=Ph	69	74
3 *o*-Cl	X=*t*Bu	67	73
"	X=Ph	78	71
4 *p*-NO_2	X=*t*Bu	60	76
"	X=Ph	71	76

Experimental Section

General. Acetonitrile were dried over calcium hydride. All olefins were purified by distillation prior to use. Temperature of 5°C was maintained by a refrigerator. The freezer was used for -20°C. Isolated yields were based on consumed perester. Bisoxazoline A and B were purchased from Aldrich Co., C and D were prepared by Michael G. Pamment. NMR spectra were performed on Varian Gemini 300. Enantiomeric excesses were determined by the integration of ^{1}H NMR signals for phenyl-protons of the benzoate with chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III). Mass spectra were recorded at 70 eV. Melting points are uncorrected.

A. Preparation of peresters. CAUTION! Peroxy compound present a serious detonation hazard. While peresters are not nearly as reactive as peracids, use of a blast shield and a teflon coated spatula, for solid material, are recommended. In an ice-cooled pentane solution of acid chloride (20 mmole in 40ml), was nadded pyridine, followed by the slow addition of t-butyl hydroperoxide. White precipitation of pyridinium chloride was formed. The reaction was stirred for 4 hours, then was washed with ice-cooled 10% H_2SO_4 (H_2O), 50% $NaHCO_3$ (H_2O) and pure water. The organic layer was collected and the solvent was taken off on rotor-vapor. The yield were 87%, 93%, 95% and 96% for perester 1, 2, 3, and 4, respectively.

t-Butyl p-chloroperbenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (t, 1H), 7.88 (t, 1H), 7.45 (t, 1H), 7.43 (t, 1H), 1.41 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.4, 139.9, 130.5, 129.1, 126.1, 84.2, 26.3. MS (CI), M/e 158 ($M+H-C_4H_9O$), 73 (base, C_4H_9O).

t-Butyl m-chloroperbenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (t, 1H), 7.84 (dt,1H), 7.57 (dq, 1H), 7.41 (t, 1H), 1.41 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.0, 134.9, 133.5, 130.0, 129.4, 129.2, 127.3, 84.4, 26.3. MS (CI), M/e 229 (M+H), 73 (base, C_4H_9O).

t-Butyl o-chloroperbenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dt, 1H), 7.46 (m, 2H), 7.34 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.6, 132.9, 131.1, 130.9, 128.6, 126.8, 84.3, 26.4. MS (CI), M/e 229 (M+H), 73 (base, C_4H_9O).

t-Butyl p-nitroperbenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (t, 1H), 8.31 (t, 1H), 8.16 (t, 1H), 8.13 (t, 1H), 1.44 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.3, 150.1, 133.2, 130.4, 123.9, 84.8, 26.3. MS (CI), M/e 240 (M+H), 73 (base, C_4H_9O).

B. Allylic Oxidation. An acetonitrile (1ml) solution of bisoxazoline (1.5 mmole) and copper(I) (1.5 mmole) was stirred at room temperature for 2 hours. Without further separation, olefin (5 mmole), perester (1 mmole) and 2 ml of acetonitrile were added. The solution was degased by nitrogen and stirred at -20 °C for 7 days. The reaction was extracted with ether. The organic layer was concentrated and further purified by chromatron.

2-Cyclopentenyl p-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dt, 2H), 7.44 (dt, 2H). 6.18 (m, 1H), 5.98 (m, 1H), 5.95 (m, 1H), 2.63-2.52 (m, 1H), 2.46-2.32 (m, 2H), 2.07-1.96 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.3, 136.8, 135.6, 128.6, 126.8, 126.7, 126.2, 79.1, 28.8, 27.5. MS (CI), M/e 224 (M+H), 67 (base, C_5H_7).

2-Cyclopentenyl m-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (t, 1H), 7.92 (dt, 1H), 7.52 (dq, 1H), 7.37 (t, 1H), 6.18 (m, 1H), 5.95 (m, 1H), 5.93 (m, 1H), 2.68-2.51 (m, 1H), 2.47-2.63 (m, 2H), 2.05-1.90 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.9, 135.7, 130.5, 130.4, 130.0, 127.2, 126.7, 125.3, 79.2, 28.8, 27.4. MS (CI), M/e 224 (M+H), 67 (base, C_5H_7).

2-Cyclopentenyl o-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (dd, 1H), 7.46-7.36 (m, 2H), 7.30 (dt, 1H), 6.18 (m, 1H), 5.97 (m, 1H), 5.95 (m, 1H), 2.68-2.51 (m, 1H), 2.47-2.62 (m, 2H), 2.08-1.95 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.0, 135.8, 129.9, 128.8, 128.6, 126.6, 124.1, 79.5, 28.8, 27.4. MS (CI), M/e 224 (M+H), 158 (base, M+H-C_5H_6).

2-Cyclopentenyl p-nitrobenzoate. mp 82°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (dt, 2H), 8.19 (dt, 2H), 6.21 (m, 1H), 5.99 (m, 1H), 5.95 (m, 1H), 2.69-2.53 (m, 1H), 2.48-2.35 (m, 2H), 2.07-1.93 (m, 1H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 164.5. 150.2, 138.6, 136.1, 130.7, 128.8, 123.5, 82.4, 31.25, 29.9. MS (CI), M/e 234 (M+H), 67 (base, C_5H_7).

2-Cyclohexenyl p-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dt, 2H), 7.40 (dt, 2H), 6.02 (m, 1H), 5.82 (m, 1H), 5.50 (m,1H), 2.21-1.63 (br, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.0, 136.8, 130.7, 128.6, 126.8, 126.2, 123.1, 66.5, 26.0, 22.5, 16.5. MS (CI), M/e 238 (M+H), 81 (base, C_6H_9).

2-Cyclohexenyl m-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (t, 1H), 7.94 (td, 1H), 7.51 (M, 1H), 7.38 (t, 1H), 6.03 (M, 1H), 5.82 (M, 1H), 5.51 (m, 1H), 2.20-1.63 (br, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.6, 130.8, 130.4, 127.3, 127.2, 125.4, 123.0, 66.7, 25.9, 22.5, 16.5. MS (CI), M/e 238 (M+H), 81 (base, C_6H_9).

2-Cyclohexenyl o-chlorobenzoate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, 1H), 7.42 (m, 2H), 7.31 (td, 1H), 6.03 (m, 1H), 5.86 (m, 1H), 5.53 (m, 1H), 2.20-1.65 (br, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.2, 130.9, 129.9, 128.9, 128.6, 124.1, 122.8, 67.0, 25.9, 22.5, 16.4. MS (CI), M/e 238 (M+H), 158 (base, M+H-C_5H_6).

2-Cyclohexenyl p-nitrobenzoate. mp 76°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (dt, 2H), 8.22 (dt, 2H), 6.05 (m, 1H), 5.83 (M, 1H), 5.53 (m, 1H), 2.25-1.65 (br, 6H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 164.0, 150.1, 136.2, 133.7, 130.8, 125.0, 123.5, 69.9, 28.3, 24.9, 18.9. MS (CI), M/e 248 (M+H), 81 (base, C_6H_9).

2-Cyclooctenyl p-nitrobenzoate. mp 85°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (dt, 2H), 8.24 (dt, 2H), 5.95 (m, 1H), 5.78 (m, 1H), 5.63 (m, 1H), 2.50-1.80 (br, 10H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.7, 149.3, 132.2, 130.7, 130.5, 129.9, 123.5, 74.2, 35.1, 31.0, 25.8, 25.2, 23.4. MS (CI), M/e 276 (M+H), 109 (base, C_8H_{13}).

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