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Josiphos-Catalyzed Asymmetric Homodimerization of Ketoketenes

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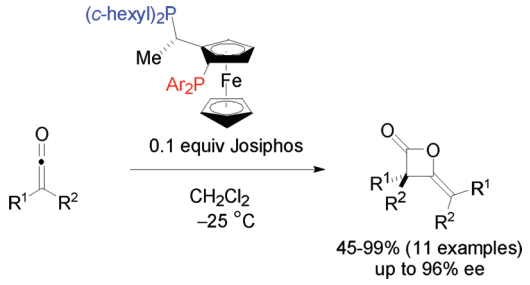
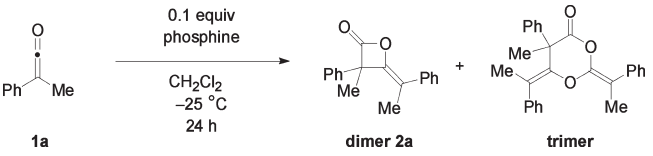


In this paper the development of a chiral phosphine-catalyzed homodimerization of ketoketenes that provides access to a variety of highly substituted ketoketene dimer β-lactones (11 examples) is reported. The Josiphos catalytic system displays good to excellent enantioselectivity (up to 96% ee). Ring-opening reactions of the enantioenriched ketoketene dimers were also carried out to access 1,3-diketones, enol esters, and β-hydroxyketones with good diastereoselectivity.

β-Lactones are important molecules which have been used by many groups as intermediates for the synthesis of complex molecules, and indeed often function as integral structural features of biologically active molecules.[1,2] An important route to β-lactones can be achieved via dimerization of ketenes.[3−5] Some time ago, Elam and, shortly after, Bentrude showed that dimethylketene could be homodimerized using trialkylphosphites as nucleophilic catalysts.[4c,d] More recently, Calter showed that a nucleophilic catalyst (TMS-quinine or TMS-quinidine) could catalyze the homodimerization of alkyl-substituted aldoketenes with high enantioselectivity.[6] While aldoketene dimer β-lactones have been used extensively in the synthesis of polyketides (polypropionates) by Calter and co-workers, ketoketene dimers have received less attention due to the paucity of general methods for their preparation.[5,7−9] In 2008 our group reported a versatile trialkylphosphine catalytic system that provided a general method for ketoketene (disubstituted ketene) homodimerization.[5] Around the same time Ye's group also published their work on the asymmetric N-heterocyclic carbene-catalyzed homodimerization reaction.[8] However, the latter method was found to be unsuitable for the dimerization of ortho-substituted arylketoketenes and dialkylketenes.[8] In this communication we report that Josiphos, a chiral diphosphine possessing

TABLE 1. Catalyst Screening for Catalytic Asymmetric Homodimerization of Ketoketenes



entry	phosphine	concn (M)	dimer:trimer[a]	convn (% yield)[b,c]	% ee[d]
1[e]	**3**	0.5	nd	(78)	33
2	**4a**	0.5	69:31	>99	80
3	**4b**	0.5	70:30	>99	78
4	**4c**	0.5	64:36	>99	2
5	**4d**	0.5		0	
6	**4e**	0.5	70:30	>99	82
7	**4e**	0.125	97:3	>99	80
8[f]	**4e**	0.125	97:3	>99 (74)	90

[a]Dimer:trimer ratio determined by ^{1}H NMR or GC-MS analysis of crude product. [b]Percent yield is isolated yield for **2a**. [c]Z:E > 97:3 as determined by GC-MS analysis, and a comparison of spectroscopic data with that of ref 8. [d]Percent ee of dimer determined by chiral HPLC analysis. [e]Reaction conducted at −78 °C for 48 h. [f]Catalyst solution was cooled to −25 °C.

(1) (a) Taunton, J.; Collins, J. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10412–10422. (b) Wan, Z.; Nelson, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 10470–10471. (c) Nelson, S. G.; Cheung, W. S.; Kassick, A. J.; Hilfiker, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 13654–13655. (d) Shen, X.; Wasmuth, A. S.; Zhao, J.; Zhu, C.; Nelson, S. G. *J. Am. Chem. Soc.* **2006**, *128*, 7438–7439. (e) Wang, Y.; Tennyson, R.; Romo, D. *Heterocycles* **2004**, *64*, 605–658.

(2) (a) Pommier, A.; Pons, J.-M. *Synthesis* **1995**, 729–744. (b) Yang, H. W.; Romo, D. *J. Org. Chem.* **1997**, *62*, 4–5. (c) Dymock, B. W.; Kocienski, P. J.; Pons, J.-M. *Synthesis* **1998**, 1655–1661. (d) Reddy, L. R.; Saravanan, P.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 6230–6231.

(3) (a) Paull, D. H.; Weatherwax, A.; Lectka, T. *Tetrahedron* **2009**, *65*, 6771–6803. (b) Orr, R. K.; Calter, M. A. *Tetrahedron* **2003**, *59*, 3545–3565. (c) Schneider, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 744–746. (d) Yang, H. W.; Romo, D. *Tetrahedron* **1999**, *55*, 6403–6434.

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(5) (a) Kerrigan, N. J.; Ibrahim, A. A.; Harzmann, G. D. *Abstracts of Papers*, 236th National Meeting of the American Chemical Society, Philadelphia, PA; American Chemical Society: Washington, DC, 2008; ORGN 531. (b) Ibrahim, A. A.; Harzmann, G. D.; Kerrigan, N. J. *J. Org. Chem.* **2009**, *74*, 1777–1780. (c) Ibrahim, A. A.; Smith, S. M.; Henson, S.; Kerrigan, N. J. *Tetrahedron Lett.* **2009**, *50*, 6919–6922.

(6) (a) Calter, M. A. *J. Org. Chem.* **1996**, *61*, 8006–8007. (b) Calter, M. A.; Orr, R. K. *Org. Lett.* **2003**, *5*, 4745–4748. (c) Purohit, V. C.; Richardson, R. D.; Smith, J. W.; Romo, D. *J. Org. Chem.* **2006**, *71*, 4549–4558.

(7) (a) Calter, M. A.; Song, W.; Zhou, J. *J. Org. Chem.* **2004**, *69*, 1270–1275. (b) Calter, M. A.; Liao, W. *J. Am. Chem. Soc.* **2002**, *124*, 13127–13129.

(8) Lv, H.; Zhang, Y.- R.; Huang, X.-L.; Ye, S. *Adv. Synth. Catal.* **2008**, *350*, 2715–2718.

(9) Lewis base-catalyzed enantioselective approaches to β-lactones from ketoketenes and aldehydes: (a) Wilson, J. E.; Fu, G. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6358–6360. (b) He, L.; Lv, H.; Zhang, Y.-R.; Ye, S. *J. Org. Chem.* **2008**, *73*, 8101–8103. (c) Mondal, M.; Ibrahim, A. A.; Wheeler, K. A.; Kerrigan, N. J. *Org. Lett.* **2010**, *12*, 1664–1667.

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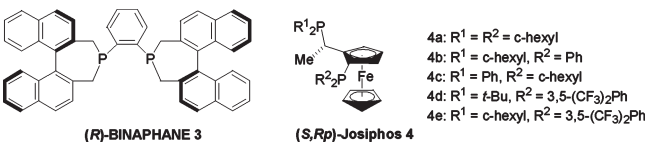
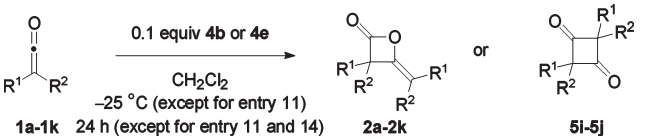
planar chirality, acts as an excellent nucleophilic catalyst for the asymmetric homodimerization of alkylarylketenes, including ortho-substituted examples, and for the homodimerization of dialkylketenes. To the best of our knowledge, this is the first report of Josiphos being used as a nucleophilic catalyst, having previously been more commonly employed as a ligand in transition metal-catalyzed asymmetric reactions.[10]

We began our studies on the development of the asymmetric ketoketene homodimerization reaction with (*R*)-BINAPHANE as the nucleophilic catalyst (Table 1, entry 1). Although we had previously found (*R*)-BINAPHANE **3** to be a good catalyst for the dimerization of ethylphenylketene, it proved to be less successful with methylphenylketene as a substrate (entry 1).[5a,b] As many complex molecule targets of interest (e.g., LY426965) possess a methyl group at a quaternary stereocenter, we were motivated to develop a more general method for the asymmetric homodimerization of ketoketenes.[11] After an investigation of other axially chiral phosphines proved fruitless, we turned out attention to chiral phosphines possessing planar chirality.[12,13] Commercially available Josiphos derivatives **4a**−**e** were examined for reactivity and enantioselectivity in the dimerization of methylphenylketene (entries 2−8).[14]



Josiphos **4e** was determined to be the optimal catalyst with very good enantioselectivity being obtained (Table 1, entry 8). Excellent selectivity for dimer over trimer was achieved after the reaction was diluted to 0.125 M concentration (of ketene in CH_2Cl_2) (entries 7 and 8). Interestingly, the introduction of a more electron donating and sterically bulky *t*-Bu group at R^1 on Josiphos (**4d**) inhibited the reaction completely (entry 5). Introduction of electron withdrawing and/or sterically bulky substituents at R^2 on the cyclopentadienyl phosphino group led to a minor improvement in enantioselectivity (entry 6 vs entry 3). Cooling of the catalyst solution to −25 °C prior to addition to the cooled methylphenylketene solution led to a significant improvement in enantioselectivity (entry 8). Both lower and higher temperatures (−78 and 0 °C) than −25 °C had a deleterious effect on enantioselectivity. The use of LiI as an additive was found to lead to a less clean, sluggish reaction (46% conversion after 24 h), in contrast to our earlier findings with the PBu_3 catalytic system.[5b]

TABLE 2. Scope of Josiphos-Catalyzed Asymmetric Homodimerization of Ketoketenes



entry	R^1	R^2	product	% yield[a]	% ee[b]	config
1[c]	Ph	Me	(−)-**2a**	65	94	*S*
2[d]	Ph	Me	(+)-**2a**	74	90	*R*
3[e]	Ph	Et	(−)-**2b**	93	86	*S*
4[f]	Ph	Et	(+)-**2b**	86	90	*R*
5[f]	Ph	*n*-Bu	**2c**	90	89	*R*
6[e]	4-tolyl	Et	**2d**	99	85	*S*
7[e]	4-ClPh	Et	**2e**	81	94	*S*
8[d]	2-tolyl	Me	**2f**	80	94	*R*
9[c]	2-ClPh	Me	**2g**	45	96	*S*
10[e]	3-thienyl	Et	**2h**	68	46	*S*
11[g]	3-thienyl	Et	**2h**	61	78	*S*
12[d]	*c*-hexyl	Me	**5i**	97[h]	na	
13[e]	*c*-hexyl	Et	**5j**	77[h]	na	
14[d]	Me	Me	**2k**	75	na	

[a]Isolated yield (%). Dimer:trimer ≥ 97:3 in all cases. *Z*:*E* > 97:3 as determined by GC-MS analysis, and a comparison of spectroscopic data with that of ref 8. [b]Percent ee determined by chiral HPLC analysis. [c](*S*,R_p)-**4e** was used as catalyst (method A). [d](*R*,S_p)-**4e** was used as catalyst (method A). [e](*S*,R_p)-**4b** was used as catalyst (method B). [f](*R*,S_p)-**4b** was used as catalyst (method B). [g](*R*)-BINAPHANE was used as catalyst and reaction conducted at −78 °C for 48 h (method C). [h]Obtained as a mixture of cis- and trans-isomers.

We then proceeded to evaluate the substrate scope of the Josiphos-catalyzed methodology (Table 2). Variation of the alkyl substituent proved successful (entry 2 vs entry 4 and entry 5) using Josiphos **4b** or **4e**. Those substrates with R^2 = CH_3 were dimerized with optimal conversion and enantioselectivity (90−96% ee) using **4e** (method A in the Supporting Information). Less reactive substrates, that possess more sterically demanding alkyl substituents (Et or *n*-Bu), were dimerized more efficiently through the use of the less sterically hindered **4b** (method B in the Supporting Information) at a slightly higher concentration (0.25 M), without any increase in trimer formation (dimer:trimer ≥ 97:3). The methodology proved to be highly tolerant of variation in the aryl group (tolyl, chlorophenyl, and 3-thienyl). Significantly, sterically demanding substrates (2-tolyl or 2-chlorophenyl as R^1) were dimerized efficiently and with excellent enantioselectivity (94−96% ee), whereas the N-heterocyclic carbene-catalyzed method of Ye's group does not tolerate ortho-substituted substrates.[8] In addition, the present methodology's tolerance of ortho-substituted substrates nicely complements our recently reported BINAPHANE-catalyzed formal [2 + 2]-cycloaddition of ketoketenes and aldehydes which gave modest enantioselectivity (up to 54% ee) for β-lactones derived from ortho-substituted arylketoketenes.[9c] Ready access to both enantiomers of a given ketoketene dimer through use of commercially available antipodes of Josiphos is another clear advantage of the phosphine-catalyzed methodology (Table 2, entry 1 vs entry 2, entry 3 vs entry 4).[14] The major olefin isomer in each case (**2a**−**h**) was determined to be the *Z*-isomer through a comparison of spectroscopic data with that reported by Ye and co-workers.[8]

Furthermore, the methodology could be extended to the more reactive dialkylketenes. Dialkylketenes gave the

(10) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066.

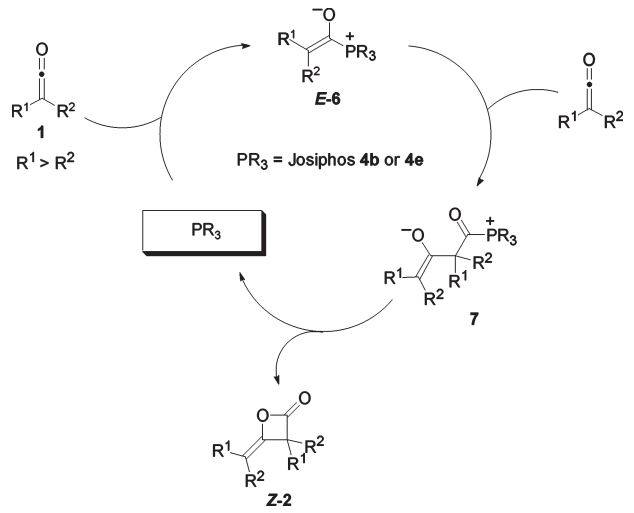
(11) (a) Rasmussen, K.; Calligaro, D. O.; Czachura, J. F.; Dreshfield-Ahmad, L. J.; Evans, D. C.; Hemrick-Luecke, S. K.; Kallman, M. J.; Kendrick, W. T.; Leander, J. D.; Nelson, D. L.; Overshiner, C. D.; Wainscott, D. B.; Wolff, M. C.; Wong, D. T.; Branchek, T. A.; Zgombick, J. M.; Xu, Y.- C. *J. Pharmacol. Exp. Ther.* **2000**, *294*, 688–700. (b) Huang, A.; Kodanko, J. J.; Overman, L. E. *J. Am. Chem. Soc.* **2004**, *126*, 14043–14053.

(12) Ferrocenylamines possessing planar chirality have been extensively used to catalyze asymmetric reactions of ketoketenes, see: (a) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578–1579. (b) Lee, E. C.; Hodous, B. L.; Bergin, E.; Shih, C.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 11586–11587. (c) Reference 9a.

(13) MOP, BINAP, and various phosphepines gave low enantioselectivity (< 30% ee) for the dimerization of methylphenylketene **1a**.

(14) Josiphos derivatives **4a**−**e** are available from Aldrich and from Strem.

SCHEME 1. Mechanism of Josiphos-Catalyzed Ketoketene Homodimerization



β-lactone or 1,3-cyclobutanedione regioisomer when exposed to Josiphos catalysis, depending upon the alkyl substituents present. Dimethylketene was efficiently dimerized to give the β-lactone regioisomer (Table 2, entry 14). On the other hand, cyclohexylethylketene and cyclohexylmethylketene were dimerized to give achiral 1,3-cyclobutanediones, rather than the β-lactone regioisomer (Table 2, entries 12 and 13).[15] The switch in regioselectivity may be due to the higher reactivity of cyclohexylalkylketene-derived enolate **7i/7j** at the carbon atom C, compared to the lower reactivity of dimethylketene- or alkylarylketene-derived enolates **7** at the carbon atom C (see Scheme 1). Alkylarylketene-derived enolates **7** would be expected to be more stabilized at the carbon atom C than dialkylketene-derived enolates, and hence should favor cyclization through the oxygen atom O of the enolate (Table 2, entries 1−11).

One possible mechanism for the formation of dimer **2** is presented in Scheme 1. Nucleophilic attack of Josiphos, through the P(*c*-hexyl)$_2$ group, on the less sterically hindered side of the ketoketene **1** (where R^2 = less sterically demanding substitutent) would result in the stereoselective formation of phosphonium enolate *E*-**6**. Nucleophilic addition of *E*-**6** to a second molecule of **1** would give rise to a second enolate intermediate **7**. 4-*Exo-trig* cyclization of **7** and elimination of the phosphine would result in generation of the ketene dimer product *Z*-**2**. ^{31}P NMR monitoring at −30 °C of the **4b**-catalyzed dimerization of ethylphenylketene revealed new signals at 40.4 ppm (d) (along with free diphenylphosphino group at −27.9 ppm (d)) and at 40.1 ppm (d) (along with free diphenylphosphino group at −28.1 ppm (d)). The signals between 40 and 41 ppm are consistent with

SCHEME 2. Enantioselection Model

tetravalent phosphonium species.[16,17] Both signals appeared approximately equal by integration throughout the time of reaction monitoring at −30 °C, but the most intense signals were due to the free Josiphos catalyst **4b** (^{31}P NMR δ 15.5 (d), and −25.5 (d) ppm). This suggests that free Josiphos **4b** is the resting state of the catalyst (at least for the formation of ethylphenylketene dimer **2b**).

An alternative mechanism would involve attack of the O atom (rather than the C atom) of phosphonium enolate **6** on a second molecule of ketoketene **1**. This mechanism was proposed by Bentrude and co-workers in the P(OMe)$_3$-mediated dimerization of dimethylketene. They isolated and characterized a pentacovalent phosphorane intermediate species, which only decomposed to ketene dimer upon heating to > 60 °C.[4d] However, due to the absence of any observed ^{31}P NMR signals in the region −50 to −80 ppm in the Josiphos-catalyzed reaction, the involvement of pentacovalent phosphorus intermediates appears unlikely.[17] Indeed the electron-donating *c*-hexyl groups of Josiphos would be expected to stabilize the positively charged phosphorus in a phosphonium intermediate to a greater extent than when P(OMe)$_3$ is used as a promoter. Hence, cyclization to a pentacovalent intermediate would be disfavored.[16b] However, a mechanism where **6** is reacting through O (rather than C), and catalyzing the homodimerization without the intermediacy of a pentacovalent phosphorus species, cannot be ruled out.

We propose that asymmetric induction is obtained through (S,R_p)-Josiphos **4b**/**4e** sterically blocking the *si*-face of the phosphonium enolate **6a** (R^1 = Ph, R^2 = Me), while the *re*-face is left relatively open, leading to the formation of the (*S*)-enantiomer of methylphenylketene dimer **2a** (Scheme 2). Formation of the (*S*)-enantiomer of the methylphenylketene dimer **2a** was confirmed by a comparison of its specific rotation value with a literature value.[8]

To demonstrate the synthetic utility of the enantioenriched ketoketene dimers, a number of ring-opening reactions were performed (Scheme 3). Methylphenylketene dimer **2a** (94% ee) was efficiently converted to 1,3-diketone **8a** with good diastereoselectivity (dr = 88:12), through reaction with *n*-BuLi (2 equiv) followed by quenching with water.[5c] **2a** was also converted to enol ester **9a** with excellent diastereoselectivity (dr > 99:1), through reaction with *n*-BuLi (1 equiv) followed by addition of propionyl chloride. Finally, ethylphenylketene dimer **2b** (90% ee) was elaborated to β-hydroxyketone **10b** (91% ee) with high diastereoselectivity (dr > 99:1).[18] The aldol and Claisen condensation-type products

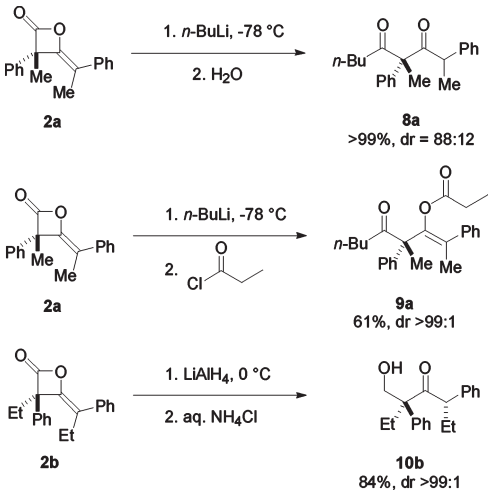
(15) Josiphos-catalyzed homodimerization of isopropylmethylketene also gave the 1,3-cyclobutanedione regioisomer, with only trace β-lactone being formed.

(16) (a) Vedejs, E.; Diver, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 3358–3359. (b) Zhu, X.-F.; Henry, C. E.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 6722–6723.

(17) (a) Hudson, H. R.; Dillon, K. B.; Walker, B. J. ^{31}P NMR Data of Four Coordinate Phosphonium Salts and Betaines. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; pp 181−226. (b) Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230–235. (c) Chestnut, D. B.; Quin, L. D. *Tetrahedron* **2005**, *61*, 12343–12349.

(18) The relative stereochemistry of **10b** was confirmed to be *syn* by a comparison with the spectroscopic data presented in ref 8. The relative stereochemistry of **8a** has not been determined. Both **8a** and **9a** were determined to be optically active (see the Supporting Information) but the ee values of **8a** and **9a** were not determined unambiguously by HPLC analysis. However, as no bonds at the quaternary stereocenter are cleaved in the formation of **8a** or **9a**, retention of chirality is assumed.

SCHEME 3. Ring-Opening Reactions of Enantioenriched Ketoketene Dimers



obtained in this way point toward the potential of ketoketene dimers for synthesis.

In summary, we have developed a versatile chiral phosphine-catalyzed enantioselective homodimerization of ketoketenes that provides access to highly substituted ketoketene dimer β-lactones with good to excellent enantioselectivity (85−96% ee for nine examples). Future studies will focus on gaining a more detailed understanding of the mode of enantioselectivity of this reaction, and on the application of the methodology to complex molecule synthesis.

Experimental Section

Method A for Dimerization of Methyl-Substituted Ketoketenes. Ketoketene[19] (0.34 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2.2 mL) and cooled to −25 °C. (*S*)-1-{(R_p)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]phosphino]ferrocenyl}ethyldicyclohexylphosphine or (*R*)-1-{(S_p)-2-[bis[3,5-bis(trifluoromethyl)-phenyl]phosphino]ferrocenyl}ethyldicyclohexylphosphine (0.03 mmol, 0.1 equiv) was dissolved in CH_2Cl_2 (0.5 mL), and was then transferred via syringe to the flask containing the ketoketene solution. The resulting solution (0.125 M of ketoketene in solvent) was stirred for 24 h at −25 °C before being briefly warmed to room temperature. The reaction was then quenched by the addition of aqueous H_2O_2 solution (50%, 2 drops) at room temperature. After 10 min of stirring at room temperature, the solvent was removed under reduced pressure. The crude product was dissolved in 10% EtOAc/hexane (5 mL) and dichloromethane (1 mL). The resulting solution was passed through a plug column of neutral silica (2 × 2 cm, 4 g) [50 × weight of reaction mixture]. The plug column was eluted with 10% EtOAc/hexane (100 mL), and the solvent was removed under reduced pressure to furnish the desired ketoketene dimer with ≥95% purity in most cases (as determined by GC-MS and ^{1}H NMR analysis). Further purification was carried out in some cases as specified in the Supporting Information.

***β*-Lactone (−)-2a (Table 2, entry 1):** Methylphenylketene (510 mg, 3.85 mmol) and (*S*)-1-{(R_p)-2-[bis[3,5-bis(trifluoromethyl)-phenyl]phosphino]ferrocenyl}ethyldicyclohexylphosphine (333 mg, 0.39 mmol) were stirred for 24 h at −25 °C, then (−)-**2a** was isolated as a colorless oil (331 mg, 65%). The *Z*:*E* olefin ratio was determined to be > 97:3 by GCMS analysis of the crude β-lactone; HPLC analysis: 94% ee [Daicel Chiralpak AD column; 1 mL/min; solvent system: 2% isopropanol in hexane; retention times: 5.0 min (minor), 6.6 min (major)]; $[\alpha]^{23}_D$ −68.3 (*c* 0.41, $CHCl_3$); IR (thin film) 1881, 1844, 1699, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50−7.10 (m, 10H), 1.90 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 146.9, 136.2, 135.2, 129.3, 128.6, 128.6, 127.6, 127.4, 126.2, 108.6, 64.4, 19.6, 15.5; MS (EI 70 eV) *m*/*z* 264, 132, 104, 78; (M^+ + Na) HRMS *m*/*z* calcd for $C_{18}H_{16}O_2Na$ 287.1043, found 287.1039.

Acknowledgment. Support has been provided by the National Science Foundation (Grant CHE-0911483 to N.J.K. and CHE-0821487 for NMR facilities at Oakland University) and by Oakland University (N.J.K.). We thank Eric C. Salo for performing an additional experiment.

Supporting Information Available: Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

(19) For preparation of ketoketenes see: (a) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 10006–10007. (b) Wiskur, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 6176–6177. (c) Allen, A. D.; Baigrie, L. M.; Gong, L.; Tidwell, T. T. *Can. J. Chem.* **1991**, *69*, 138–145. (d) Wilson, J. E.; Fu, G. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6358–6360.