Synthesis of 2-Acylvinyl Ethers by Reaction of Chromium (Fischer) Carbene Complexes and Stabilized Sulfur Ylides[1]

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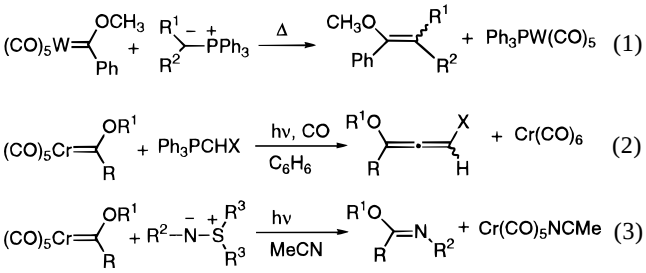
Irradiation (λ > 360 nm) of equimolar amounts of alkoxychromium(0) carbene complexes **1** and stabilized sulfur ylides **2** renders 2-acylvinyl ethers **3** in good to excellent yields as *E*/*Z* mixtures upon visible (sunlight preferred) oxidation to eliminate the metallic moiety. Formation of 2-acylvinyl ethers **3** is compatible with different groups attached to the carbene oxygen, including chiral fragments and unsaturated substituents. Variation of the substituent at the carbene carbon including alkyl, cycloalkyl, aromatic, and heteroaromatic substituents is also viable. The overall process is equivalent to the totally site-selective enolization of a β-keto ester or β-diketone. 2-Acylvinyl ethers **3** are obtained with yields and selectivities ranking among the best of the synthetic approaches to these compounds reported previously. 2-Acylvinyl ethers **3** can be obtained also in the dark at room temperature, but reaction times are considerably longer.

Introduction

The activated ester-like behavior of group 6 metal carbenes makes these compounds interesting surrogates[2] for organic esters.[3] In fact, low yielding or nonviable transformations on esters or amides can be highly efficient on chromium carbene complexes. The electrophilia of the carbene carbon and the ability of the metal to stabilize negative charge set up the differences. Since the metal moiety can be eliminated during the reaction, or after the reaction is completed, the overall transformation is equivalent to effecting the process on the unreactive carbon analog. The Wittig reaction[4] is one example of an unusual transformation[5] on organic esters but that is high yielding with tungsten carbene complexes as reported by Casey more than 20 years ago.[6] Thus, the reaction of pentacarbonyl(methoxyphenylcarbene)tungsten(0) and simple phosphorous ylides yields vinyl ethers (eq 1). The analogous reactions with simple diazoalkanes[7] circumvents the competitive abstraction of the α-proton attached to the carbene carbon,



(1)

(2)

(3)

a problem found when phosphorous ylides are used. An elegant variation of the reactivity of carbene complexes and phosphorous ylides has been reported by Hegedus.[8] In this case the Wittig-like reaction is on a photogenerated ketene[9] to produce captodative allenes (eq 2). Again, competitive deprotonation is not a shortcoming for this process, probably due to the use of stabilized, less basic ylides. In this context, we reported[10] that sulfilimines (N−S ylides) are also capable to produce Wittig-like products, namely imidates, with chromium carbene complexes (eq 3). The use of strongly basic aliphatic sulfilimines was, once again, compatible with alkyl-substituted carbene complexes. A final example of the Wittig-like behavior of chromium carbene complexes can be found in their reaction with dimethyl sulfoxide[11] which is one of the standard procedures to oxidize alkoxychromium carbene complexes and form the organic esters. In this paper we report in full[1] the use of sulfur ylides to prepare differently functionalized 2-acylvinyl ethers.

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(2) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 725. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

(3) For reviews on the chemistry of group 6 metal carbene complexes, see, for example: (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (b) *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

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(7) Casey, C. P.; Bertz, S. H.; Burkhardt, T. *Tetrahedron Lett.* **1973**, 1421.

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(11) See, for example: (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229. (c) Wulff, W. D.; Anderson, B. A.; Toole, A. *J. Am. Chem. Soc.* **1989**, *111*, 5485.

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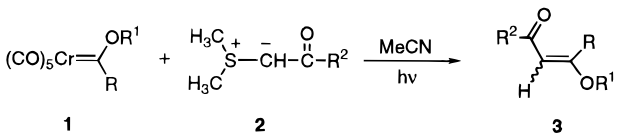
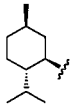
Scheme 1[a]



1 2 3

[a] The reaction was carried out at room temperature.

Table 1. Synthesis of 2-Acylvinyl Ethers 3

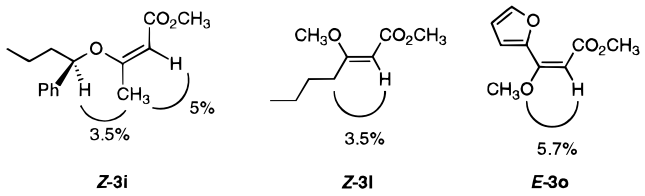
Entry	1	2	R	R^1	R^2	3	*E/Z*[a,b]	Yield (%) *E*	Yield (%) *Z*
1	1a	2a	Me	Me	OMe	3a	2.3:1	65	
2	1a	2b	Me	Me	O*t*-Bu	3b	4:1	73	
3	1a	2c	Me	Me	Ph	3c	100:0	81	
4	1b	2a	Me	CH_2Ph	OMe	3d	5.6:1	60	
5	1c	2a	Ph	Me	OMe	3e	4.:1	70	
6	1c	2c	Ph	Me	Ph	3f	4.6:1	90	
7	1d	2a	Me		OMe	3g	2.3:1	41	29
8	1e	2a	Me		OMe	3h	3.4:1	68	22
9	1f	2a	Me		OMe	3i	4:1	51	15
10	1f	2c	Me		Ph	3j	4:1	48	d
11	1g	2a	Me		OMe	3k	1.6:1	34	23
12	1h	2a	Bu	Me	OMe	3l	3.5:1	52	20
13	1i	2a		Me	OMe	3m	2.4:1	23	30
14	1j	2a		Me	OMe	3n	2.4:1	50	12
15	1k	2a		Me	OMe	3o[c]	1:1	19	41

[a] Determined by integration of well-resolved signals in the ^1H NMR spectra of crude reaction mixtures. [b] Yields are for pure, isolated *E* and *Z* isomers, except for entries 1−6, where the reported yields are for pure mixtures of *E/Z* isomers. [c] The reaction was instantaneous. No irradiation was needed. [d] The *Z* isomer decomposed during purification by flash chromatography.

Results and Discussion

Irradiation of equimolecular amounts of complex **1** and ylide **2** (450-W, medium-pressure Hg lamp, Pyrex filter, and Pyrex well) in degassed MeCN as solvent gave smoothly the corresponding 2-acylvinyl ethers **3**, after oxidation to eliminate the metallic moiety. Compounds **3** were usually obtained as *E/Z* mixtures except in the reaction of complex **1a** and ylide **2c**, which produce the enol ether **3c** as a single *E* isomer (Scheme 1, Table 1). Formation of 2-acylvinyl ethers **3** is compatible with different groups attached to the carbene oxygen, including chiral fragments (Entries 9−11) and unsaturated substituents (entries 7 and 8). Variation of the substituent at the carbene carbon proved to be also successful. Thus, alkyl, cycloalkyl, aromatic, and heteroaromatic substituents can be incorporated to the 2-acylvinyl ether. Data on Table 1 show a clear predominance of the *E* isomer in the reaction mixtures, except for furan derived enol ethers (entry 15). However, nonstabilized sulfur ylides, generated in different conditions and at different temperatures,[12] resulted in the instantaneous consumption of the starting complex to give pale yellow solutions from which we were unable to isolate any identifiable product. These results contrast with the analogous reaction of complexes **1** and nonstabilized phosphorous or nitrogen ylides which forms enol ethers.[6,7]

Reaction of chromium carbene complexes **1** and sulfur ylides **2** at room temperature and in the dark formed also 2-acylvinyl ethers **3**. However, considerably longer reaction times are required to complete the reaction. The crude reaction mixtures obtained in the dark are always contaminated with the ester formed by oxidation of the starting carbene due to the longer reaction times required. The *E/Z* selectivity of the thermal reactions was in most cases essentially analogous to that obtained under irradiation. A selected number of experiments carried out in both reaction conditions are collected in Table 2. It can be seen that the selectivity was inverted (entry 5) or decreased (entry 4) by switching the reaction conditions. The observed selectivities may be due to isomerization by light once the *Z*-enol is formed. To test this point, the crude reaction mixture obtained in the reaction of complex **1c** and ylide **2a** in the dark (1:3 *E/Z*) was irradiated for 16 h prior to oxidation. After this time the crude reaction mixture was oxidized under the standard conditions. The *E/Z* ratio of the final mixture was increased (1:1.3 *E/Z*) although the *Z* isomer is still favored. It may be concluded that in some cases irradiation may promote the partial *E/Z* isomerization favoring the most stable *E* isomer. Nevertheless, this isomerization should not be solely responsible for the observed selectivity in photochemical conditions.[13] The role of solvent in the stereochemical outcome of the reaction was also studied. Complex **1a** and ylide **2a** were reacted in five different solvents both at room temperature in the dark and under irradiation. The observed selectivities are listed in Table 2 (Entries 1−5). Irradiation resulted, again, in shorter reaction times in all cases. Although better selectivities can be obtained with less polar solvents, in terms of solubility of reagents and to obtain cleaner reaction mixtures, MeCN was the solvent of choice.



Z-3i *Z*-3l *E*-3o

Figure 1.

The stereochemistry of 2-acylvinyl ethers **3** was determined by NOE experiments carried out in selected compounds. Thus, irradiation of the Me group (δ = 1.77) in compound *Z*-**3i** resulted in 3.5% and 5% increments of the signal corresponding to the benzyl proton (δ = 5.01) and the vinylic proton (δ = 4.80), respectively. Thus, a *Z* configuration was assigned for this isomer.

(12) The following nonstabilized ylides were tested: Dimethylsulfonium methylide, diphenylsulfonium cyclopropylide, tetrahydrothiophenylethylide, and tetrahydrothiophenylbenzylide. (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353. (b) Trost, B. M.; Bogdanowicz, M. *J. Am. Chem. Soc.* **1971**, *93*, 3773. Phase-transfer modification: (c) Borredon, M. E.; Delmas, M.; Gaset, A. *Tetrahedron* **1987**, *43*, 3945.

(13) On standing an *E/Z* mixture in $CDCl_3$ at room temperature for a few days a similar change in the *E/Z* composition of some samples has been observed.

Table 2. Thermal and Photochemical *E/Z* Selectivity in the Formation of 2-Acylvinyl Ethers 3

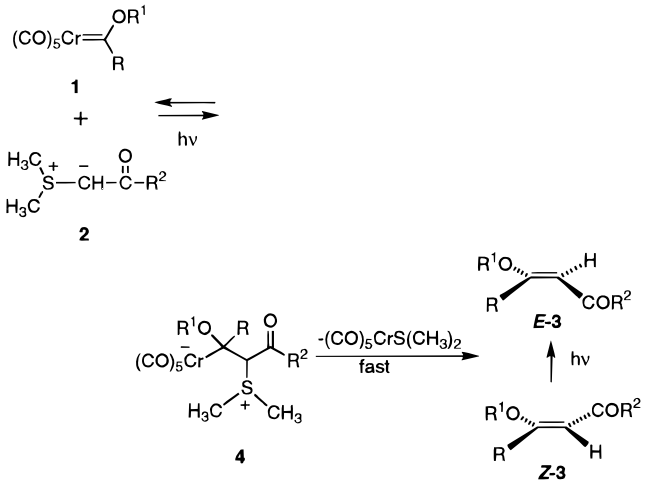
entry	1	2	R	R^1	R^2	solvent	3	E/Z^a (Δ)	E/Z^a (*hν*)
1	**1a**	**2a**	Me	Me	OMe	MeCN	**3a**	2.3:1	2.3:1
2						hexane		4:1	5.6:1
3						DCM		4.5:1	3:1
4						Et_2O		2.3:1	4:1
5						THF		3.3:1	3.5:1
6	**1a**	**2b**	Me	Me	O*t*-Bu	MeCN	**3b**	4:1	4:1
7	**1a**	**2c**	Me	Me	Ph	MeCN	**3c**	100:0	100:0
8	**1b**	**2a**	Me	CH_2Ph	OMe	MeCN	**3d**	1.4:1	5.6:1
9	**1c**	**2a**	Ph	Me	OMe	MeCN	**3e**	1:3.0	4:1
10	**1d**	**2c**	Ph	Me	Ph	MeCN	**3f**	4.6:1	4.6:1

[a] Determined by integration of well-resolved signals in the ^1H NMR spectra of crude reaction mixtures.

Analogous results were obtained for compounds *Z*-**3l** and *E*-**3o** (Figure 1). The stereochemistry of the remaining compounds was assigned by comparison of their NMR data with those from compounds **3i**,**l**,**o** and from reported NMR data for similar compounds.[14]

Two facts have to be considered before proposing a reaction pathway for the reaction of chromiumcarbene complexes and sulfur ylides. First, the *E/Z* selectivity of the reaction does not follow a precise correlation with the steric bulkiness of the groups attached to the carbene carbon of complexes **1** and the carbonyl group on ylides **2**. In fact, although the *E/Z* selectivity, in general, improved when the bulkiness of the groups on the reagents did, this is not the case for example for ylide **2c** having a phenacyl substituent. Its reaction with complex **1a** gave the *E* isomer of enol ether **3c** (entry 3, Table 1), exclusively. However, ylide **2c** reacted with the bulkier complex **1f** (entry 10, Table 1) to yield a 4:1 *E/Z* mixture of enol ethers **3j**. These differences are not easily understood in terms of steric hindrance. The second experimental fact is the acceleration of the reaction rate under photochemical conditions. Thus, while photochemical reactions are completed within hours, the same reaction carried out in the dark requires days to completion in most of the cases tested. A similar acceleration of the reaction rate by irradiation has been observed by us in the reaction of carbene complexes and sulfilimines to form imidates.[10]

Scheme 2



The reaction pathway to 2-acylvinyl ethers (Scheme 2) may begin with the nucleophilic addition of the ylide **2** to the electrophilic carbene carbon of complexes **1** to form the zwitterionic intermediate **4**. Decomposition of this intermediate would yield the *E/Z* mixture of 2-acylvinyl ethers, **3**. The *Z*-enol ether may in turn equilibrate with its *E* isomer by the action of light. Paralleling the widely studied mechanism for the Wittig reaction[4] and the addition of sulfur ylides to carbonyl compounds,[15] the second step of the proposed reaction pathway may be fast, as it is with stabilized phosphorous ylides. It is reasonable to admit that the rate-determining step may be the nucleophilic addition to the carbene carbon. This step has been proposed to be reversible in the addition of sulfur ylides to carbonyl compounds.[16] One of the reviewers proposed that the poor selectivities obtained in some cases, even with bulky substituents, and faster rates with irradiation may suggest a free-radical process. To test this fact, four separate experiments were carried out. Equimolar amounts of chromium carbene complex **1a** and ylide **2a** were irradiated in MeCN in the presence of hydroquinone (0.2, 0.6, and 1 equiv of hydroquinone, respectively) and in the absence of hydroquinone. The *E/Z* selectivity obtained was analogous in all cases (2.3:1). These results are, in our opinion, against participation of radical species in the process leading to 2-acylvinyl ethers. However, to explain the actual role of light in the reaction rate further experimental evidence is needed. Finally, the observed *E* selectivity is not easily explained in terms of an steric model as stated above. This fact, and the observed partial *E/Z* isomerization of the final enol ethers by the light, render any explanation speculative at this moment.

In conclusion, the reaction of chromium carbene complexes and sulfur ylides represents a new stereoselective entry to 2-acylvinyl ethers. Different substituents can be incorporated to the double bond, including chiral moieties. The overall process would be equivalent to the totally site-selective enolization of a β-keto ester or β-diketone. Yields and selectivities rank among the best of the synthetic approaches to these compounds reported previously.[17]

Experimental Section

General Methods. Melting points were taken on a Gallemkamp apparatus and are uncorrected. ^1H NMR and

(14) Brower, H.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 601 and references therein.

(15) *The Chemistry of Sulfonium Group, Parts 1 and 2*; Stirling, C. J. M., Ed.; John Wiley & Sons Ltd.: New York, 1981; Chapters 12 and 16.

(16) Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 8424.

(17) For a review on the synthesis of enol ethers, see: Chan, T. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 2, pp 595−628.

^{13}C NMR spectra were recorded in $CDCl_3$, on Varian XL-300S (300 and 75.43 MHz) and Bruker 250-AM (250 and 62.5 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (^1H, 0.0 ppm) or $CDCl_3$ (^{13}C, 76.9 ppm). IR spectra were taken on a Perkin-Elmer 781 spectrometer in $CHCl_3$ solution. Specific rotation $[\alpha]_D$ is given in deg per dm at the specified temperature, and the concentration (*c*) is expressed in g per 100 mL in $CHCl_3$. Elemental analyses were obtained from the UCM Microanalysis Service (Facultad de Farmacia, UCM, Madrid).

All solvents used in this work were purified by distillation. Tetrahydrofuran (THF) and Et_2O were distilled from Na−benzophenone. Hexane, CH_2Cl_2, and MeCN were distilled from CaH_2. Flame-dried glassware and standard Schlenk techniques were use for moisture-sensitive reactions. For purification of crude reaction mixtures by flash chromatography, Merck silica gel (230−400 Mesh) or Florisil was used as the stationary phase. Identification of products was made by TLC (Kiesegel 60F-254). UV light (λ = 254 nm) and 5% phosphomolybdic acid solution in 95% EtOH were use to develop the plates. A 450-W lamp medium-pressure mercury lamp (Applied Photophysics), with a Pyrex filter and Pyrex well, was used for irradiations.

The following chemicals were prepared according to literature procedures: pentacarbonyl[(methoxy)(methyl)carbene]-chromium(0),[18] pentacarbonyl[(benzyloxy)(methyl)carbene]-chromium(0),[19] pentacarbonyl[(methoxy)(phenyl)carbene]-chromium(0),[18] pentacarbonyl[(3-buten-1-oxy)(methyl)carbene]-chromium(0),[21] pentacarbonyl[(3-butyn-1-oxy)(methyl)carbene]-chromium(0),[20] pentacarbonyl[(methyl)(*R*)-(+)-(1-phenylbutyl-1-oxy)carbene]chromium(0),[10a] pentacarbonyl[*l*-(−)-(menthyl-oxy)(methyl)carbene]chromium(0),[20] pentacarbonyl[(*n*-butyl)-(methoxy)carbene]chromium(0),[18] pentacarbonyl[(cyclopropyl)-(methoxy)carbene]chromium(0),[21] pentacarbonyl[(methoxy)(1-naphthyl)carbene]chromium(0),[22] pentacarbonyl[(2-furyl)-(methoxy)carbene]chromium(0),[23] ((methoxycarbonyl)methylene)dimethylsulfurane,[24] ((*tert*-butoxycarbonyl)methylene)dimethylsulfurane,[24] phenacylidenedimethylsulfurane.[25]

Spectroscopic and analytical data for compounds **3** are for each pure, separated isomer except for compounds **3a**−**f**. In these cases data are listed from the spectra of analytically pure, isomeric mixtures.

General Procedure for the Reactions of Complexes 1 and Ylides 2. Alkoxychromium carbene **1** (1 mmol) was placed in a Pyrex test tube equipped with a stirring bar. The test tube was sealed with a rubber septum, evacuated, and purged with argon (three cycles). Degassed MeCN (5 mL) and ylide **2** (1 mmol) in MeCN (5 mL) were added with a syringe. The resulting solution was irradiated in a water bath until complete disappearance (TLC) of the starting carbene. The solution was stirred during irradiation, and an argon atmosphere was maintained during the process (argon balloon). The solvent was removed under reduced pressure, the brown residue was dissolved in methyl acetate or ethyl acetate, and the resulting solution was filtered through Celite, diluted with one volume of pentane, and air-oxidized in a lightbox (9 × 20 W fluorescent bulbs) or under direct sun-light[26] until a clear colorless solution with a brown precipitate was obtained. Filtration of the brown precipitate (Celite) and removal of the solvent gave almost pure product **3** as mixture of *E*/*Z* stereoisomers. Pure compounds **3** were obtained, and in most cases both isomers were separated by flash chromatography through a short path of deactivated silica gel. Thermal reactions were carried out by following the same procedure but strictly excluding light. Compounds **3** are very sensitive to hydrolysis and should be purified with acid-free solvents.

Methyl 3-Methoxy-2-butenoates, 3a. Following the general procedure, 0.25 g (1.0 mmol) of complex **1a** and 0.13 g (1.0 mmol) of ylide **2a** were irradiated for 3 h (thermal reaction: 4 days). After oxidation, ^1H NMR analysis showed a mixture of isomers *E*/*Z* = 2.3:1. Flash chromatography of the crude mixture gave 0.09 g (65%) of compounds **3a** as colorless oil.

***E* Isomer.** ^1H NMR: δ 2.30 (s, 3H, CH_3), 3.63 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.03 (s, 1H, =CH). ^{13}C NMR: δ 173.1 (C3), 168.2 (C1), 90.4 (C2), 55.3 (OCH_3), 50.6 (OCH_3), 18.8 (C4).

***Z* Isomer.** ^1H NMR: δ 2.03 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.91 (s, 1H, =CH). ^{13}C NMR: δ 168.0 (C3), 165.8 (C1), 95.1 (C2), 56.1 (OCH_3), 50.5 (OCH_3), 19.0 (C4). IR ($CHCl_3$): ν 1735 (C=O), 1630 (C=C). Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.10; H, 7.43.

***tert*-Butyl 3-Methoxy-2-butenoates, 3b.** Following the general procedure, 0.50 g (2 mmol) of complex **1a** and 0.35 g (2 mmol) of ylide **2b** were irradiated for 5 h (thermal reaction: 16 h). After oxidation ^1H NMR analysis of the crude mixture showed a 4.0:1 mixture of *E*/*Z* isomers. Flash chromatography of the crude mixture gave 0.25 g (73%) of compound **3b** as colorless oil.

***E* Isomer.** ^1H NMR: δ 1.48 [s, 9H, $(CH)_3C$], 2.25 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 4.95 (s, 1H, =CH). ^{13}C NMR: δ 171.9 (C3), 167.4 (C1), 92.4 (C2), 79.1 [$OC(CH_3)_3$], 55.2 (OCH_3), 28.0 [$C(CH_3)_3$], 18.7 (C4).

***Z* Isomer.** ^1H NMR: δ 1.46 [s, 9H, $(CH)_3$], 1.99 (s, 3H, CH_3), 3.63 (s, 3H, OCH_3), 4.84 (s, 1H, =CH). ^{13}C NMR: δ 171.6 (C3), 164.4 (C1), 96.9 (C2), 78.5 [$OC(CH_3)_3$], 55.2 (OCH_3), 28.3 [$C(CH_3)_3$], 18.7 (C4). IR ($CHCl_3$): ν 1715 (C=O), 1630 (C=C). Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.60; H, 9.31%.

3-Methyl-3-methoxy-1-phenylpropenone, 3c. Following the general procedure, 0.10 g (0.4 mmol) of complex **1a** and 0.08 g (0.4 mmol) of ylide **2c** were irradiated for 2.5 h (thermal reaction: 18 h). After oxidation, ^1H NMR analysis of the crude mixture showed only the *E* isomer. Flash chromatography of the crude mixture gave 0.06 g (81%) of compound **3c** as pale yellow oil. ^1H NMR: δ 2.41 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 6.15 (s, 1H, =CH), 7.4−7.9 (m, 5H, Ar). ^{13}C NMR: δ 190.3 (C1), 174.8 (C3), 140.4, 131.7, 128.3, 127.6, 96.1 (C2), 55.6 (OCH_3), 20.2 (CH_3). IR ($CHCl_3$): ν 1660 (C=O), 1590 (C=C). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.75; H, 6.97.

Methyl 3-(Benzyloxy)-2-butenoate, 3d. Following the general procedure, 0.33 g (1 mmol) of complex **1b** and 0.14 g (1 mmol) of ylide **2a** were irradiated for 16 h (thermal reaction: 4 days). After oxidation, ^1H NMR analysis of the crude mixture showed a 5.6:1 mixture of *E*/*Z* isomers. Flash chromatography of the crude mixture gave 0.12 g (60%) of compounds **3d** as colorless oil.

***E* Isomer.** ^1H NMR: δ 2.36 (s, 3H, CH_3), 3.68 (s, 3H, OCH_3), 4.82 (s, 2H, CH_2), 5.15 (s, 1H, =CH), 7.3−7.4 (m, 5H, Ar). ^{13}C NMR: δ 172.1 (C3), 168.2 (C1), 91.6 (C2), 70.1 (CH_2), 50.7 (OCH_3), 19.0 (CH_3).

***Z* Isomer.** ^1H NMR: δ 1.99 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 4.68 (s, 2H, CH_2), 4.99 (s, 1H, =CH). ^{13}C NMR: δ 170.7 (C3), 169.7 (C1), 96.5 (C2), 64.9 (CH_2), 50.6 (OCH_3), 19.5 (CH_3). IR ($CHCl_3$): ν 1715 (C=O), 1630 (C=C). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.76; H, 6.69.

Methyl 3-Methoxy-3-phenylpropenoates, 3e. Following the general procedure, 0.16 g (0.5 mmol) of complex **1c** and 0.07 g (0.5 mmol) of ylide **2a** were irradiated for 3 h (thermal reaction: 4 days). After oxidation, ^1H NMR analysis of the crude mixture showed a mixture of *E*/*Z* isomers = 4.0:1. Flash

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chromatography of the crude mixture gave 0.07 g (70%) of compounds **3e** as colorless oil.

***E* Isomer.** ^{1}H NMR: δ 3.58 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.27 (s, 1H, =CH). ^{13}C NMR: δ 171.5 (C3), 167.0 (C1), 91.8 (C2), 56.2 (OCH_3), 50.8 (OCH_3).

***Z* Isomer.** ^{1}H NMR: δ 3.74 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.23 (s, 1H, =CH). ^{13}C NMR: δ 168.8 (C3), 165.5 (C1), 99.4 (C2), 60.3 (OCH_3), 51.0 (OCH_3). IR ($CHCl_3$): ν 1730 (C=O), 1620 (C=C). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.55; H, 5.95.

3-Methoxy-1,3-diphenylpropenones, 3f. Following the general procedure, 0.50 g (1.6 mmol) of complex **1c** and 0.32 g (1.6 mmol) of ylide **2c** were irradiated for 4.5 h (thermal reaction: 24 h). After oxidation, ^{1}H NMR analysis of the crude mixture showed a 4.6:1 mixture of *E*/*Z* isomers. Flash chromatography of the crude mixture gave 0.21 g (90%) of compound **3f** as pale yellow oil.

***E* Isomer.** ^{1}H NMR: δ 3.93 (s, 3H, OCH_3), 6.20 (s, 1H, =CH). ^{13}C NMR: δ 190.6 (C1), 171.4 (C3), 98.2 (C2), 56.4 (OCH_3).

***Z* Isomer.** ^{1}H NMR: δ 3.94 (s, 3H, OCH_3), 6.45 (s, 1H, =CH). ^{13}C NMR: δ 188.4 (C1), 169.0 (C3), 102.6 (C2), 61.5 (OCH_3). IR ($CHCl_3$): ν 1665 (C=O), 1610 (C=C). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.55; H, 5.79.

Methyl 3-(3-Butenyloxy)-2-butenoate, 3g. Reaction time: 18 h. From 0.30 g (1.0 mmol) of complex **1d** and 0.14 g (1.0 mmol) of ylide **2a** was obtained an *E*/*Z* mixture (2.3:1) of vinyl ethers **3g** which were separated by chromatography (20:1 hexanes/EtOAc) to yield 0.05 g (29%) of the *Z* isomer (colorless oil) and 0.07 g (41%) of the *E* isomer (colorless oil).

Methyl *Z*-3-(3-Butenyloxy)-2-butenoate, *Z*-3g. ^{1}H NMR: δ 2.01 (s, 3H, CH_3), 2.49 (qd, 2H, $J_1 = 6.8$ Hz, $J_2 = 1.1$ Hz, CH_2C=), 3.65 (s, 3H, OCH_3), 4.07 (t, 2H, $J = 6.8$ Hz, CH_2O), 4.91 (s, 1H, CH=C), 5.07−5.17 (m, 2H, =CH_2), 5.74−5.90 (m, 1H, *CH*=CH_2). ^{13}C NMR: δ 167.6, 166.0 (CO_2CH_3, C3), 133.9 (*CH*=CH_2), 117.6 (=CH_2), 95.9 (C2), 68.5 (CH_2O), 50.7 (OCH_3), 34.2 (CH_2C=), 19.8 (C4). IR ($CHCl_3$): ν 1710, 1640. Anal. Calcd for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.60; H, 8.39.

Methyl *E*-3-(3-Butenyloxy)-2-butenoate, *E*-3g. ^{1}H NMR: δ 2.30 (s, 3H, CH_3), 2.47 (qd, 2H, $J_1 = 6.6$ Hz, $J_2 = 1.0$ Hz, CH_2C=), 3.67 (s, 3H, OCH_3), 3.80 (t, 2H, $J = 6.6$ Hz, CH_2-O), 5.01 (s, 1H, CH=C), 5.07−5.17 (m, 2H, =CH_2), 5.74−5.90 (m, 1H, *CH*=CH_2). ^{13}C NMR: δ 172.6, 168.5 (CO_2CH_3, C3), 134.0 (*CH*=CH_2), 117.4 (=CH_2), 90.9 (C2), 67.4 (CH_2O), 50.8 (OCH_3), 33.0 (CH_2C=), 19.1 (C4). Anal. Calcd for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.61; H, 8.52.

Methyl 3-(3-Butynyloxy)-2-butenoate, 3h. Reaction time: 18 h. From 0.50 g (1.7 mmol) of complex **1e** and 0.23 g (1.7 mmol) of ylide **2a** was obtained an *E*/*Z* mixture (3.4:1) of vinyl ethers **3h** which were separated by chromatography (15:1 hexanes/EtOAc) to yield 0.05 g (22%) of the *Z* isomer (colorless oil) and 0.15 g (68%) of the *E* isomer (colorless oil).

Methyl *Z*-3-(3-Butynyloxy)-2-butenoate, *Z*-3h. ^{1}H NMR: δ 2.00 (sa, 4H, CH_3, ≡CH), 2.62 (td, 2H, $J_1 = 7.2$ Hz, $J_2 = 2.4$ Hz, CH_2C≡CH), 3.63 (s, 3H, OCH_3), 4.14 (t, 2H, $J = 7.2$ Hz, CH_2-O), 4.94 (s, 1H, =CH). ^{13}C NMR: δ 167.0, 165.7 (CO_2CH_3, C3), 96.7 (C2), 79.9 (C≡), 70.3 (≡CH), 67.1 (CH_2O), 50.7 (OCH_3), 20.1, 20.0 (C4, CH_2C≡). IR ($CHCl_3$): ν 2115, 1715, 1630. Anal. Calcd for $C_9H_{12}O_3$: C, 64.26; H, 7.20. Found: C, 64.40; H, 7.45.

Methyl *E*-3-(3-Butynyloxy)-2-butenoate, *E*-3h. ^{1}H NMR: δ 2.03 (t, 1H, $J = 2.7$ Hz, ≡CH), 2.31 (s, 3H, CH_3), 2.61 (td, 2H, $J_1 = 7.2$ Hz, $J_2 = 2.7$ Hz, CH_2C≡CH), 3.67 (s, 3H, OCH_3), 3.87 (t, 2H, $J = 7.2$ Hz, CH_2O), 5.01 (s, 1H, =CH). ^{13}C NMR: δ 172.0, 168.2 (CO_2CH_3, C3), 91.4 (C2), 79.9 (C≡), 70.2 (≡CH), 65.9 (CH_2O), 50.8 (OCH_3), 19.0, 18.9 (C4, CH_2C≡). IR ($CHCl_3$): ν 2115, 1710, 1630. Anal. Calcd for $C_9H_{12}O_3$: C, 64.26; H, 7.20. Found: C, 64.40; H, 7.26.

Methyl 3-((1-*R*-Phenylbutyl)oxy)-2-butenoate, 3i. Reaction time: 16 h. From 0.37 g (1.0 mmol) of complex **1f** and 0.13 g (1.0 mmol) of ylide **2a** was obtained a *E*/*Z* mixture (4:1) of vinyl ethers **3i** which were separated by chromatography (30:1 to 20:1 hexanes/EtOAc) to yield 0.04 g (15%) of the *Z* isomer (colorless oil) and 0.13 g (51%) of the *E* isomer (yellow oil).

(−)-Methyl *Z*-3-((1-*R*-phenylbutyl)oxy)-2-butenoate, *Z*-3i. $[\alpha]_D^{24}$ −297° ($c = 0.79$, $CHCl_3$). ^{1}H NMR: δ 0.84 (t, 3H, $J =$ 7.5 Hz, CH_3CH_2), 1.22−1.47 (m, 2H, Bu), 1.63−1.76 (m, 1H, Bu), 1.77 (s, 3H, CH_3), 1.81−1.97 (m, 1H, Bu), 3.62 (s, 3H, OCH_3), 4.80 (s, 1H, CH=), 5.01 (dd, 1H, $J_1 = 6.9$ Hz, $J_2 = 6.0$ Hz, CHPh), 7.15−7.27 (m, 5H, arom). ^{13}C NMR: δ 167.2, 165.7 (CO_2CH_3, C3), 141.6, 128.5, 127.6, 125.9 (arom), 97.2 (C2), 80.4 (OCH), 50.5 (OCH_3), 40.4 (CH_2), 20.0 (CH_2), 18.4 (C4), 13.8 (CH_3). IR ($CHCl_3$): ν 1720, 1635 1500, 1460. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.54; H, 8.12. Found: C, 72.68; H, 8.25.

(+)-Methyl *E*-3-((1-*R*-phenylbutyl)oxy)-2-butenoate, *E*-3i. $[\alpha]_D^{24}$ +109° ($c = 1.47$, $CHCl_3$). ^{1}H NMR: δ 0.83 (t, 3H, $J =$ 7.5 Hz, CH_3CH_2), 1.15−1.45 (m, 2H, Bu), 1.54−1.71 (m, 1H, Bu), 1.76−1.88 (m, 1H, Bu), 2.26 (s, 3H, CH_3), 3.47 (s, 3H, OCH_3), 4.82 (s, 1H, CH=), 4.87 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 5.4$ Hz, CHPh), 7.12−7.24 (m, 5H, arom). ^{13}C NMR: δ 171.1, 168.2 (CO_2CH_3, C3), 140.7, 128.5, 127.6, 125.5 (arom), 92.8 (C2), 79.8 (OCH), 50.5 (OCH_3), 40.2 (CH_2), 19.2 (CH_2), 18.7 (C4), 13.7 (CH_3). IR ($CHCl_3$): ν 1720, 1630, 1590, 1500. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.54; H, 8.12. Found: C, 72.50; H, 8.39.

3-((1-*R*-phenylbutyl)oxy)-3-methyl-1-phenylpropenone, 3j. Reaction time: 21 h. From 0.37 g (1.0 mmol) of complex **1f** and 0.20 g (1.0 mmol) of ylide **2c** was obtained, after 21 h, an *E*/*Z* mixture (4:1) of vinyl ethers **3i** which were separated by chromatography (30:1 hexanes/EtOAc) to yield 0.14 g (48%) of the *E* isomer (yellow oil). The *Z* isomer decomposed during purification.

(+)-*E*-3-((1-*R*-phenylbutyl)oxy)-3-methyl-1-phenylpropenone, *E*-3j. $[\alpha]_D^{24}$ +150° ($c = 0.80$, $CHCl_3$). ^{1}H NMR: δ 0.95 (t, 3H, $J = 7.2$ Hz, CH_3CH_2), 1.28−1.56 (m, 2H, Bu), 1.66−1.85 (m, 1H, Bu), 1.91−2.06 (m, 1H, Bu), 2.44 (s, 3H, CH_3), 5.07 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 5.4$ Hz, CHPh), 6.00 (s, 1H, =CH), 7.30−7.53 (m, 10H, arom). ^{13}C NMR: δ 190.3 (CO), 172.2 (C=), 140.9, 140.3, 131.5, 128.7, 128.2, 127.8, 127.5, 125.6 (arom), 99.7 (=CH), 80.5 (CHPh), 40.3 (CH_2CH), 20.2 (CH_2), 18.8 (CH_3C=), 13.8 (CH_3). IR ($CHCl_3$): ν 1655, 1580, 1500, 1400. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.81; H, 7.12.

Methyl 3-(1-(−)-Menthyloxy)-2-butenoate, 3k. Reaction time: 24 h. From 0.50 g (1.5 mmol) of complex **1g** and 0.2 g (1.5 mmol) of ylide **2a** was obtained a *E*/*Z* mixture (1.6:1) of vinyl ethers **3k** which were separated by chromatography (30:1 hexanes/EtOAc) to yield 0.09 g (23%) of the *Z* isomer (colorless oil) and 0.13 g (34%) of the *E* isomer (colorless oil).

(−)-Methyl *Z*-3-(1-(−)-Menthyloxy)-2-butenoate, *Z*-3k. $[\alpha]_D^{24}$ −5° ($c = 1.23$, $CHCl_3$). ^{1}H NMR: δ 0.77 (d, 3H, $J = 7.2$ Hz, CH_3CH), 0.91 (d, 6H, $J = 6.9$ Hz, 2 × CH_3^{i}Pr), 0.87−1.04 (m, 2H), 1.17−1.26 (m, 1H), 1.33−1.46 (m, 1H), 1.50−1.62 (m, 1H), 1.64−1.73 (m, 2H), 1.85−1.93 (m, 1H), 2.00 (s, 3H, CH_3), 2.10−2.21 (m, 1H), 3.63 (s, 3H, OCH_3), 4.00 (dt, 1H, $J_1 = 10.5$ Hz, $J_2 = 4.2$ Hz, OCH), 4.87 (s, 1H, =CH). ^{13}C NMR: δ 167.2, 165.7 (CO_2CH_3, C3), 96.3 (C2), 78.4 (OCH), 50.3 (OCH_3), 47.6, 41.9, 34.1, 31.5, 25.6, 23.3, 22.0, 20.8, 19.6 (C4), 16.3. IR ($CHCl_3$): ν 1705, 1630, 1515, 1450. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.81; H, 10.31. Found: C, 70.75; H, 10.52.

(−)-Methyl *E*-3-(1-(−)-Menthyloxy)-2-butenoate, *E*-3k. $[\alpha]_D^{24}$ −126° ($c = 1.02$, $CHCl_3$). ^{1}H NMR: δ 0.65 (d, 3H, $J =$ 4.8 Hz, CH_3CH), 0.82 (d, 3H, $J = 7.4$ Hz, CH_3^{i}Pr), 0.85 (d, 3H, $J = 7.4$ Hz, CH_3^{i}Pr), 0.76−1.06 (m, 3H), 1.28−1.42 (m, 2H), 1.58−1.68 (m, 2H), 1.85−1.98 (m, 1H), 2.02−2.12 (m, 1H), 2.22 (s, 3H, CH_3C=), 3.61 (s, 3H, OCH_3), 3.85 (dt, 1H, $J_1 = 10.5$ Hz, $J_2 = 4.2$ Hz, OCH), 4.98 (s, 1H, =CH). ^{13}C NMR: δ 171.8, 168.7 (CO_2CH_3, C3), 90.0 (C2), 50.6 (OCH_3), 47.4, 39.0, 34.3, 31.2, 26.3, 23.6, 22.0, 20.5, 19.5 (C4), 16.6. IR ($CHCl_3$): ν 1705, 1615. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.81; H, 10.31. Found: C, 70.86; H, 10.52.

Methyl 3-Methoxy-2-heptenoate, 3l. Reaction time: 16 h. From 0.75 g (2.6 mmol) of complex **1h** and 0.34 g (2.6 mmol)

of ylide **2a** was obtained an *E*/*Z* mixture (3.5:1) of vinyl ethers **3l** which were separated by chromatography (20:1 hexanes/EtOAc) to yield 0.09 g (20%) of the *Z* isomer (colorless oil) and 0.23 g (52%) of the *E* isomer (colorless oil).

Methyl *Z*-3-Methoxy-2-heptenoate, *Z*-3l. ^{1}H NMR: δ 0.93 (t, 3H, J = 7.1 Hz, CH_3), 1.23−1.58 (m, 4H, 2 × CH_2), 2.25 (t, 2H, J = 6.9 Hz, CH_2C=), 3.65 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.93 (s, 1H, =CH). ^{13}C NMR: δ 171.9, 165.9 (CO_2-CH_3, C3), 94.8 (C2), 56.7 (OCH_3), 50.6 (OCH_3), 32.4 (CH_2), 29.2 (CH_2), 22.1 (CH_2), 13.7 (CH_3). IR ($CHCl_3$): ν 1715, 1640. Anal. Calcd for $C_9H_{16}O_3$: C, 62.75; H, 9.37. Found: C, 62.81; H, 9.21.

Methyl *E*-3-Methoxy-2-heptenoate, *E*-3l. ^{1}H NMR: δ 0.91 (t, 3H, J = 7.2 Hz, CH_3CH_2), 1.35 (sex., 2H, J = 6.5 Hz, CH_3CH_2), 1.53 (qt, 2H, J = 7.2 Hz, CH_2), 2.74 (t, 2H, J = 7.4 Hz, CH_2C=), 3.62 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 4.99 (s, 1H, CH=). ^{13}C NMR: δ 177.0, 167.9 (CO_2CH_3, C3), 89.8 (C2), 55.2 (OCH_3), 50.5 (OCH_3), 31.6 (CH_2), 29.5 (CH_2), 22.4 (CH_2), 13.7 (CH_3). IR ($CHCl_3$): ν 1710, 1625, 1460, 1440. Anal. Calcd for $C_9H_{16}O_3$: C, 62.75; H, 9.37. Found: C, 62.66; H, 9.23.

Methyl 3-Cyclopropyl-2-propenoate, 3m. Reaction time: 17 h. From 0.28 g (1.0 mmol) of complex **1i** and 0.14 g (1.0 mmol) of ylide **2a** was obtained an *E*/*Z* mixture (2.4:1) of vinyl ethers **3m** which were separated by chromatography (20:1 hexanes/EtOAc) to yield 0.04 g (23%) of the *Z* isomer (colorless oil) and 0.05 g (30%) of the *E* isomer (colorless oil).

Methyl *Z*-3-Cyclopropyl-2-propenoate, *Z*-3m. ^{1}H NMR: δ 0.71−0.76 (m, 2H, CH_2), 0.84−0.91 (m, 2H, CH_2), 1.48−1.58 (m, 1H, CH), 3.64 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.92 (s, 1H, =CH). ^{13}C NMR: δ 172.8, 166.0 (CO_2CH_3, C3), 92.8 (C2), 57.3 (OCH_3), 50.6 (OCH_3), 13.6 (CH), 6.6 (2 × CH_2). IR ($CHCl_3$): ν 1710, 1630, 1460. Anal. Calcd for $C_8H_{12}O_3$: C, 61.51; H, 7.75. Found: C, 61.28; H, 7.86.

Methyl *E*-3-Cyclopropyl-2-propenoate, *E*-3m. ^{1}H NMR: δ 0.77−0.81 (m, 2H, CH_2), 0.92−0.97 (m, 2H, CH_2), 3.11−3.23 (m, 1H, CH), 3.57 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 5.06 (s, 1H, =CH). ^{13}C NMR: δ 175.5, 168.7 (CO_2CH_3, C3), 89.6 (C2), 55.2 (OCH_3), 50.6 (OCH_3), 11.5 (CH), 7.1 (2 × CH_2). IR ($CHCl_3$): ν 1705, 1605. Anal. Calcd for $C_8H_{12}O_3$: C, 61.51; H, 7.75. Found: C, 61.56; H, 7.91.

Methyl 3-(1-Naphthyl)-2-propenoate, 3n. Reaction time: 16 h. From 0.73 g (2.0 mmol) of complex **1j** and 0.27 g (2.0 mmol) of ylide **2a** was obtained an *E*/*Z* mixture (2.4:1) of vinyl ethers **3n** which were separated by chromatography (10:1 hexanes/EtOAc) to yield 0.06 g (12%) of the *Z* isomer (colorless oil) and 0.24 g (50%) of the *E* isomer (colorless solid, mp 67−9 °C).

Methyl *Z*-3-(1-Naphthyl)-2-propenoate, *Z*-3n. ^{1}H NMR: δ 3.52 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 5.24 (s, 1H, =CH), 7.45−7.57 (m, 4H, arom), 7.87−8.05 (m, 3H, arom). ^{13}C NMR: δ 168.7, 165.8 (CO_2CH_3, C3), 133.1, 131.8, 128.4, 127.5, 127.3, 126.5, 125.1, 124.9 (arom), 99.6 (C2), 57.7 (OCH_3), 50.9 (OCH_3). IR ($CHCl_3$): ν 1715, 1640, 1600, 1515, 1440. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.83. Found: C, 74.23; H, 5.98.

Methyl *E*-3-(1-Naphthyl)-2-propenoate, *E*-3n. ^{1}H NMR: δ 3.42 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.55 (s, 1H, =CH), 7.40−7.48 (m, 4H, arom), 7.72−7.88 (m, 3H, arom). ^{13}C NMR: δ 170.6, 166.4 (CO_2CH_3, C3), 133.2, 133.1, 130.6, 129.3, 128.2, 126.3, 126.2, 125.7, 124.8, 124.5 (arom), 94.5 (C2), 56.2 (OCH_3), 50.7 (OCH_3). IR ($CHCl_3$): ν 1725, 1630, 1600, 1585, 1465. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.83. Found: C, 74.20; H, 6.02.

Methyl 3-(2-Furyl)-2-propenoate, 3o. In this case the reaction was instantaneous at room temperature. From 0.73 g (2.4 mmol) of complex **1k** and 0.14 g (1.0 mmol) of ylide **2a** was obtained an *E*/*Z* mixture (1:1) of vinyl ethers **3o** which were separated by chromatography (15:1 hexanes/EtOAc) to yield 0.08 g (19%) of the *Z* isomer (colorless oil) and 0.20 g (41%) of the *E* isomer (colorless oil).

Methyl *Z*-3-(2-Furyl)-2-propenoate, *Z*-3o. ^{1}H NMR: δ 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.24 (s, 1H, =CH), 6.49 (dd, 1H, J_1 = 3.3 Hz, fur.), 7.25 (dd, 1H, J_1 = 3.9 Hz, J_2 = 3.3 Hz, fur.), 7.50 (t, 1H, J = 1.5 Hz, fur.). ^{13}C NMR: δ 166.5, 159.0 (CO_2CH_3, C3), 146.8, 143.6, 115.3, 111.3 (fur.), 91.8 (C2), 56.1 (OCH_3), 51.2 (OCH_3). Anal. Calcd for $C_9H_{10}O_4$: C, 59.32; H, 5.54. Found: C, 59.40; H, 5.27.

Methyl *E*-3-(2-Furyl)-2-propenoate, *E*-3o. ^{1}H NMR: δ 3.74 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 5.82 (s, 1H, CH=), 6.46−6.48 (m, 1H, fur.), 6.77 (d, 1H, J = 3.3 Hz, fur.), 7.46−7.47 (m, 1H, fur.). ^{13}C NMR: δ 165.3, 158.6 (CO_2CH_3, C3), 149.4 (fur.), 144.5 (fur.), 112.4 (fur.), 111.8 (fur.), 97.4 (C2), 62.0 (OCH_3), 51.0 (OCH_3). Anal. Calcd for $C_9H_{10}O_4$: C, 59.32; H, 5.54. Found: C, 59.11; H, 5.25.

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