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Olefin-Metathesis-Based Synthesis of Furans by an RCM/Deprotonation/Phosphorylation Sequence and Their Diels–Alder Reactions

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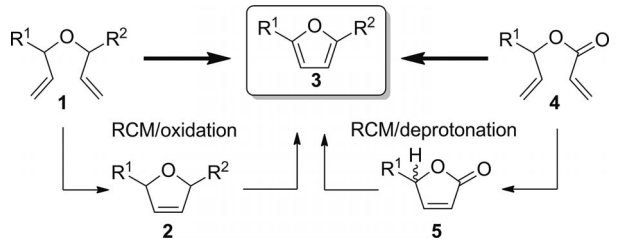
Butenolides, obtained by ring-closing metathesis (RCM) of acrylates, undergo quantitative deprotonation with amide bases. Trapping of the resulting anions with electrophiles, for example, chlorophosphates, give furans. Subsequent Diels–Alder reaction and acid-catalysed rearrangement of the resulting oxabicyclonorbornadienes give substituted benzenes.

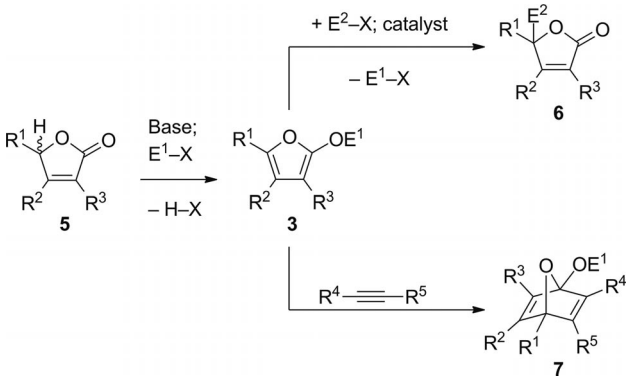
Introduction

The synthesis of aromatic and heteroaromatic compounds from acyclic precursors using olefin metathesis is a rapidly expanding field.[1,2] Reactions previously described in the literature can be classified as assisted tandem catalytic[3] RCM/aromatization sequences,[4–6] one-flask sequences comprising an Ru-catalysed RCM step followed by an oxidation[7–10] or elimination reaction,[11–13] and two-step procedures involving isolation of the RCM product, which is then converted into an aromatic compound.[14,15] Due to the significance of substituted furans as synthetic intermediates and as structural elements in various drugs and drug candidates, we started to explore metathesis-based routes for the synthesis of these aromatic heterocycles. Very recently we disclosed a one-flask RCM/oxidation sequence for the synthesis of 2-substituted and 2,5-disubstituted furans **3** starting from diallyl ethers **1** that proceeds via dihydrofurans **2**.[10] Although this sequence requires oxidants such as DDQ or chloranil for the aromatization, no oxidation is necessary for the aromatization of lactones **5**, which result from the RCM of acrylates **4**. Instead, deprotonation and subsequent trapping of the vinylogous enolates should give 2-oxygenated furans **3** (Scheme 1).

The deprotonation of butenolides **5** and the subsequent trapping as masked furan-2-ols **3** has mostly been limited to unsubstituted 2(5*H*)-furanone[16] or simple 4-substituted derivatives (Scheme 2).[17,18] In particular, the corresponding 2-(silyloxy)furans (**3**, $E^1 = SiR_3$) have been used as vinylogous nucleophiles in alkylation reactions with allyl bromides[19,20] or organocatalytic vinylogous Michael[21] and aldol reactions to give 5-substituted butenolides **6**.[22] Although numerous Diels–Alder reactions of furans have been reported in the literature,[23] the number of examples using masked furan-2-ols is rather limited.[24] For example, a [4 + 2] cycloaddition of a 2-(aryloxy)furan followed by acid-induced aromatization has been used in the synthesis of diaryl ethers,[25] which are important structural motifs in many natural products and drugs.[26,27]



Scheme 1. RCM/oxidation vs. RCM/deprotonation for the synthesis of substituted furans.



Scheme 2. Metallation/trapping sequence for the synthesis of masked furan-2-ols and prospective transformations.

In this work we have investigated an olefin-metathesis-based synthesis of masked 5-substituted furan-2-ols that relies on the RCM of acrylates **4**, their metallation and trapping with an appropriate electrophile as well as their subse-

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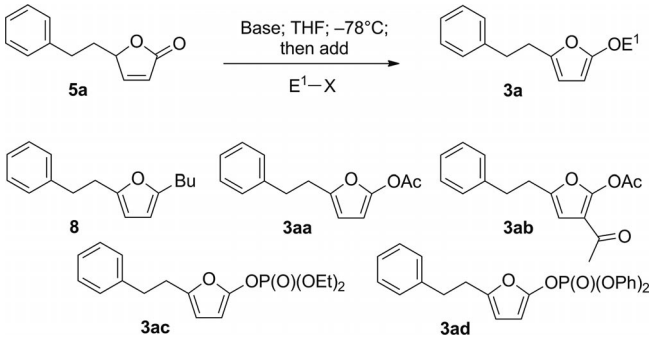
quent conversion into multiple-substituted benzenes by acid-induced rearrangement of cycloadducts **7**.

Results and Discussion

Optimization of the Deprotonation/Trapping Sequence

The deprotonation/electrophilic trapping sequence was optimized with lactone **5a** as the test substrate, which was synthesized by ring-closing metathesis of the corresponding acrylate **4a** under the optimized conditions previously disclosed by us.[28] Initially, we tested a combination of weak amine bases and the strong and presumably hard acylating agent, acetyl bromide, to achieve a selective *O*-acylation of lactone **5a** under concomitant aromatization to the 2-acetoxyfuran **3aa** (Table 1).

Table 1. Optimization of the deprotonation/electrophilic trapping sequence.



Entry	Base[a]	E^1–X[a]	Products (yields [%])
1	NEt_3	$H_3CC(O)Br$	–[b]
2	pyridine	$H_3CC(O)Br$	–[b]
3	BuLi	$H_3CC(O)Br$	**8** (51)
4[c]	LDA	$H_3CC(O)Br$	**3aa** (10), **3ab** (31)
5	LDA	Ac_2O	**3aa** (28)
6	LDA	Tf_2O	–[d]
7	LDA	*p*TsCl	–[d]
8	LDA	H_3CSO_2Cl	–[d]
9	LDA	$ClP(O)(OEt)_2$	**3ac** (46–54)
10	LDA	$ClP(O)(OPh)_2$	**3ad** (46–60)
11	NaHMDS	$ClP(O)(OPh)_2$	**3ad** (76–89)

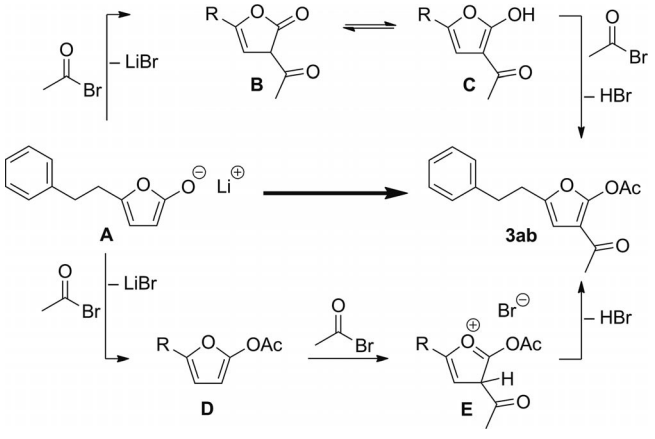
[a] 1.1 equiv. of base and 1.1 equiv. of trapping reagent in THF were used in all experiments unless otherwise stated. [b] No conversion; only unreacted starting material was recovered. [c] 2.2 equiv. of base and 2.0 equiv. of acetyl bromide were used. [d] Complex mixture of products was detected by ^{1}H NMR spectroscopy of the crude reaction mixture.

Neither triethylamine nor pyridine led to a noticeable conversion, as judged from the ^{1}H NMR spectra of the crude mixtures (Entries 1 and 2). It has previously been reported that various organolithium reagents react with 3,5-disubstituted butenolides under nucleophilic attack at the 2-position rather than deprotonation.[29] This was confirmed for **5a**, which reacts with butyllithium after aqueous workup to give the 2,5-dialkyl-substituted furan **8** in fair yield (Entry 3). Next, an excess of in situ prepared LDA was used as base with an excess of acetyl bromide in THF (Entry 4). Under these conditions, the desired 2-acetoxyfuran **3aa** was isolated in low yield along with a significant amount of the diacetylated furan **3ab**. Unfortunately, the combination of THF as solvent and acetyl bromide as trapping reagent always led to the formation of significant amounts of 1-acetoxy-4-bromobutane, a THF cleavage product, even at –78 °C. We were surprised by this observation as the cleavage of THF with acetyl bromide had previously been reported to require ambient temperature and Zeise's salt as a catalyst.[30] In an attempt to improve the selectivity of the reaction and to avoid the formation of the THF cleavage product, we tested a combination of LDA and acetic anhydride as acetylating agent (Entry 5). These conditions resulted in the selective and quantitative formation of **3aa**, based on the ^{1}H NMR spectrum of the crude reaction mixture. Unfortunately, the isolated yield never exceeded 30%, irrespective of the purification method. Even more disappointing was the use of triflic anhydride, *p*-toluenesulfonyl chloride and methanesulfonyl chloride as trapping reagents (Entries 6–8). In all these cases, complete consumption of the starting material and the formation of complex mixtures were observed. From the ^{1}H NMR spectra of the crude reaction mixtures, we could obtain no evidence for the formation of the expected furans.

A breakthrough was eventually achieved with chlorophosphates. After deprotonation of **5a** with a slight excess of LDA and treatment of the reaction mixture with diethyl or diphenyl chlorophosphate, the furan-2-yl phosphates **3ac** or **3ad**, respectively, were isolated in acceptable yields of between 46 and 60% (Entries 9 and 10). The yields of **3ad** could be further improved to 76–89% by replacing LDA by NaHMDS in combination with diphenyl chlorophosphate (Entry 11).

Acetyl Bromide versus Acetic Anhydride as Trapping Reagents

Although the isolated yields of the 2-acetoxyfurans were disappointingly low in the test reactions (Table 1, Entries 4 and 5), we were intrigued by the distinctive reactivities of acetyl bromide and acetic anhydride. Two mechanisms may explain the formation of the 3-acetylated furan **3ab** (Scheme 3). The metallated butenolide **A** first reacts as an

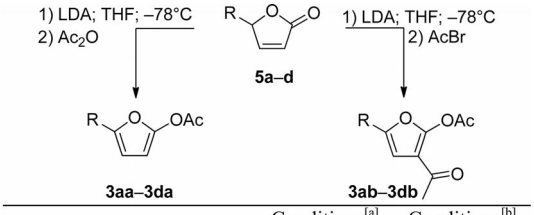


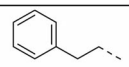
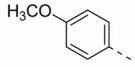
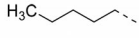
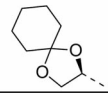
Scheme 3. Proposed mechanism for the formation of diacetylated furans.

enolate by undergoing acetylation at the 3-position to give **B** and its tautomer **C**, which then undergoes *O*-acetylation to yield **3ab**. Alternatively, **A** is first *O*-acetylated, and the 2-acetoxyfuran **D** (i.e., **3aa**) then undergoes electrophilic 3-acetylation to give **3ab**, which proceeds via the σ complex **E**. Although electrophilic substitution reactions of furans at the 3-position are rare, we favour the latter scenario, because with a hard electrophile like acetyl bromide rapid *O*-acylation of **A** appears to be more likely than *C*-acylation. Furthermore, the oxygen atom at C-2 should enhance the electron density at C-3, thereby facilitating electrophilic attack at this position. This assumption is supported by the observation that 2-methoxyfurans undergo electrophilic bromination at C-3.[31] Also in line with this scenario is the fact that no acetylation at C-3 was observed with the weaker electrophile acetic anhydride.

Lactones **5b**–**d** gave very similar results under these acylating conditions. With LDA and acetic anhydride, the corresponding 2-acetoxyfurans **3ba**, **3ca** and **3da** were the only products; however, purification by column chromatography or Kugelrohr distillation resulted in extensive decomposition and rather low isolated yields of 20–30%. Similarly to **5a**, the reactions of metallated **5b** and **5c** with acetyl bromide gave mixtures of mono- and diacetylated products in comparable isolated yields and product ratios. Lactone **5d** with an acetal-protected diol moiety underwent decomposition to a complex mixture of products. This observation underlines the high Lewis acidity of acetyl bromide (Table 2).

Table 2. Deprotonation/electrophilic trapping sequence for lactones **5a**–**d** with acetic anhydride or acetyl bromide.



Entry	R	5	Conditions[a] product (yield)	Conditions[b] product (yield)
1		**5a**	**3aa** (28%)	**3aa** (10%) **3ab** (31%)
2		**5b**	**3ba** (23%)	**3ba** (9%) **3bb** (20%)
3		**5c**	**3ca** (24%)	**3ca** (5%) **3cb** (27%)
4		**5d**	**3da** (25%)	–[c]

[a] Acetic anhydride as trapping reagent. [b] Acetyl bromide as trapping reagent. [c] Complex mixture of products.

The constitution of trisubstituted furans **3ab**–**3cb** was not obvious from routine NMR spectra, and therefore a 2D NOE spectrum was recorded for **3bb**, which revealed a strong NOE between 4-H and 2′-H of the 4-methoxyphenyl substituent (Figure 1).

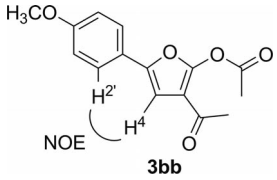


Figure 1. NOE interaction for **3bb**.

2-Furanyl Phosphates: Synthesis and Diels–Alder Reactions

The optimized conditions for the aromatization of lactone **5a** (Table 1, Entry 11) were next applied to other lactones. The ^{1}H NMR spectra of all crude reaction mixtures revealed a full conversion of the starting materials and the highly selective formation of the expected 2-furanyl phosphates. Although the test compound **3ad** could be isolated after chromatography in yields varying between 76 and 89%, we were surprised that the isolated yields for the other examples were greatly diminished due to hydrolysis upon contact with silica. In some cases the starting material **5** was recovered, in others a complex mixture of products was formed. For this reason we decided to characterize the crude 2-furanyl phosphates obtained after aqueous workup of the reaction mixture by NMR spectroscopy and convert them directly into 7-oxanorbornadienes **7** by Diels–Alder reaction with dimethyl acetylenedicarboxylate (DMAD). These products turned out to be stable to chromatography on silica and could be fully characterized. Not unexpectedly, **7e** was obtained as a mixture of diastereomers in a ratio of approximately 3:1 (Table 3).

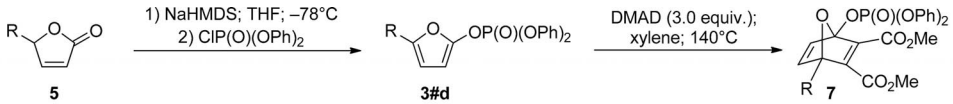
Lewis Acid Mediated Rearrangement of 7-Oxanorbornadienes

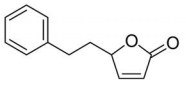
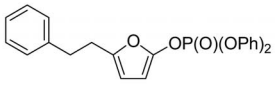
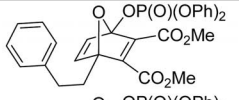
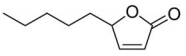
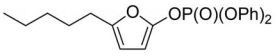
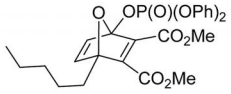
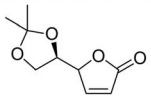
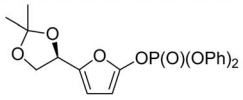
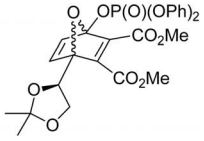
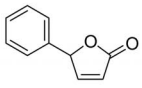
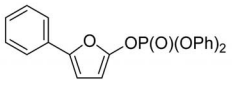
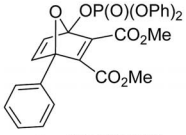
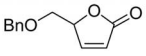
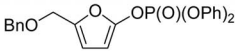
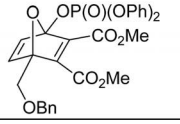
Several ring-opening reactions to six-membered carbacycles have been reported for the Diels–Alder adducts of furans. Base-induced rearrangement[32] or Rh-catalysed nucleophilic ring-opening[33] gives functionalized cyclohexadienes stereoselectively, whereas treatment of 7-oxanorbornadienes with Brønsted or Lewis acids normally results in rearrangement to phenols.[34–36] The gold-catalysed[37] rearrangement of furans with a pendant alkyne side-chain also gives phenols, but proceeds via an arene oxide rather than a Diels–Alder adduct.[38,39]

A few examples of the Diels–Alder reactions of furans with electron-donating substituents at the 2-position and subsequent rearrangement to phenols have been reported. For example, as shown in Scheme 4, 2-methoxyfuran (**9**) was found to undergo a cycloaddition reaction with hexafluorobutyne (**10**) to give **11**, which rearranges thermally, even in the absence of acid, to phenol **12**.[40]

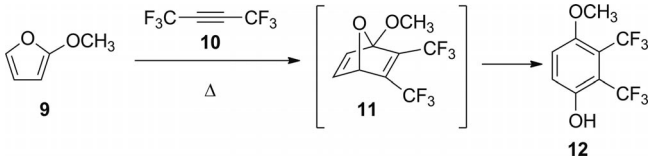
In this particular case, the rearrangement is facilitated by the electron-donating character of the 2-methoxy substituent. The electron-withdrawing nature of the phosphate group will most likely contribute to the stability of the cycloaddition products **7** described in this work. Equally important for the stability of these cycloadducts should be the

Table 3. Synthesis of 2-furanyl phosphates **3#d** and their Diels–Alder reactions to 7-oxanorbornadienes **7**.



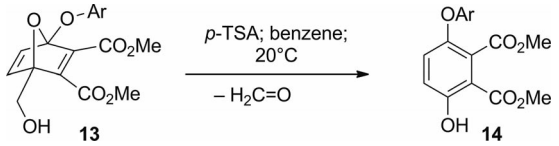
Entry	Lactone	5	2-Furanyl phosphate	3[a]	Diels–Alder adduct	7	Yield[b]
1		**5a**		**3ad**[c]		**7a**	69–82%
2		**5c**		**3cd**		**7c**	63–82%
3		**5e**		**3ed**		**7e**[d]	45–55%
4		**5f**		**3fd**		**7f**	52–58%
5		**5g**		**3gd**		**7g**	55–62%

[a] Conversion of **5** into the corresponding furanyl phosphate **3** was quantitative based on ^{1}H NMR spectroscopy of the crude reaction mixtures. [b] Range of yields was obtained for three experiments, yields are calculated for the sequence starting from lactones **5**. [c] Isolated yields of analytically pure **3ad**, purified by chromatography on silica, varied between 76 and 89%. [d] Isolated as a 3:1 mixture of diastereomers.



Scheme 4. Diels–Alder reaction of 2-methoxyfuran and thermal rearrangement to a phenol.[40]

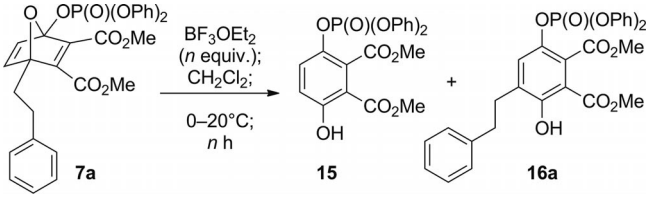
absence of a proton at C-5 of the furan precursor. It has, for instance, been shown that Diels–Alder adducts **13** of 2-(aryloxy)furans with a hydroxymethyl substituent at C-5 are stable, but that in the presence of an acid the side-chain is cleaved to formaldehyde with concomitant rearrangement to phenol **14** (Scheme 5).[25]



Scheme 5. Fragmentation of hydroxymethyl-substituted Diels–Alder adduct.[25]

To investigate the effect of different C-5 side-chains on the course of acid-mediated ring-cleavage reactions, the bicyclic phosphates **7a**,**c**,**f**,**g** were treated with $BF_3{\cdot}OEt_2$ in dichloromethane. In the case of **7a**, two products **15** and **16a** were isolated in ratios of 1:4 to 1:2 in varying yields, depending on the reaction time and the amount of Lewis acid used (Table 4).

Table 4. $BF_3{\cdot}OEt_2$-mediated cleavage of **7a**.

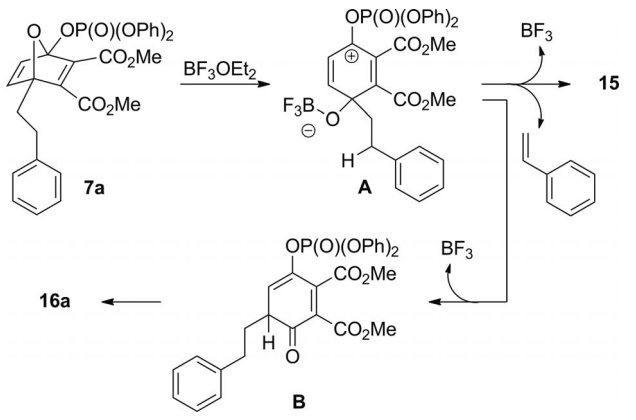


Entry	$BF_3{\cdot}OEt_2$ [equiv.]	Time [h]	Yield [%]	
			15	**16a**
1	1.5	24	12	58
2[a]	1.5	5	23	55
3	2.5	18.5	20	77
4[b]	1.1	18.5	27	63

[a] 14% of unreacted starting material was recovered. [b] 5% of unreacted starting material was recovered.

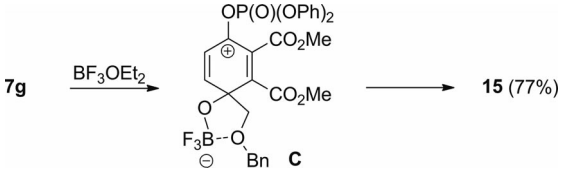
Compound **15** was easily identified by the presence of a pair of doublets in the aromatic region. It results from a dealkylation reaction, presumably with the formation of styrene as a byproduct, by a mechanism that involves Lewis acid mediated cleavage of the bicyclic ring system to give the stabilized carbenium ion **A**, which then undergoes deprotonation at the benzylic position and cleavage of the C–

C bond with concomitant reconstitution of aromaticity. The formation of **16a** can be explained by a competing pathway resembling the NIH shift,[41] which was originally proposed as a pathway to rationalize the oxidative metabolism of arenes. Thus, the alkyl chain migrates to the *ortho* position to give cyclohexadienone **B**, which rapidly tautomerizes to the phenol **16a** (Scheme 6).



Scheme 6. Mechanism for the competing formation of **15** and **16a** from **7a**.

We then investigated the reactions of **7c**, **7f** and **7g** under these conditions. Although for **7f** a complex mixture of products was obtained, treatment of the (benzyloxy)methyl-substituted derivative **7g** with BF_3·OEt_2 resulted in the exclusive formation of the dealkylation product **15**, which was isolated in 77% yield. The rearrangement product resulting from a 1,2-shift of the (benzyloxy)methyl substituent could not even be detected in trace amounts (Scheme 7). Presumably, a chelate **C** is formed that allows facile debenzylation and subsequent fragmentation to formaldehyde and phenol **15**.



Scheme 7. BF_3·OEt_2-mediated cleavage of **7g**.

Remarkably, the pentyl-substituted derivative **7c** rearranges under otherwise identical conditions to **16c** in 79% yield. The dealkylation product **15** was observed only in very minor amounts in all experiments starting from **7c**. For this derivative, a structural elucidation based on 2D NMR techniques was achieved. Unfortunately, 2D NOE experiments were ambiguous, and we therefore conducted HMBC experiments. Relevant couplings between protons and carbon atoms across two or three bonds are depicted in Figure 2.

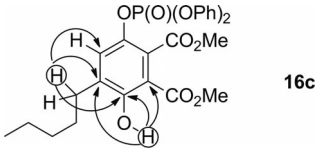


Figure 2. HMBC experiments for **16c**.

Conclusions

Metallation of α,β-unsaturated γ-butyrolactones and trapping of the resulting vinylogous enolates with appropriate electrophiles yielded 5-substituted furan-2-ol derivatives. Chlorophosphates are particularly well suited as trapping reagents, giving the corresponding furanyl phosphates. These compounds readily underwent [4+2] cycloaddition reactions to 7-oxanorbornadienes, which are remarkably stable and can be isolated. Finally, the reactions of these bicyclic products with Lewis acids were studied. Two competing pathways, a rearrangement and an elimination, were observed under the reaction conditions. Remarkably, the phosphate remains intact in both cases. This is potentially useful for synthetic applications such as Pd-catalysed arylation reactions.

Experimental Section

General: All experiments were conducted in dry reaction vessels under dry nitrogen. Solvents were purified by standard procedures. ^{1}H NMR spectra were obtained with a Bruker DRX 300 spectrometer at 300 MHz in $CDCl_3$ with $CHCl_3$ (δ = 7.26 ppm) as internal standard. Coupling constants (J) are given in Hz. Signal assignments refer to the numbering schemes detailed in the Supporting Information. ^{13}C NMR spectra were recorded with a Bruker DRX 300 spectrometer at 75 MHz in $CDCl_3$ with $CDCl_3$ (δ = 77.0 ppm) as internal standard. IR spectra were recorded with a Nicolet Impact 400 D spectrometer as films in NaCl or KBr plates or as KBr discs. Wavenumbers (ν) are given in cm^{-1}. EI mass spectra were obtained at 70 eV with a GC TOF micromass spectrometer (Micromass Manchester Waters Inc.). ESI mass spectra were obtained with a Q-TOF micromass spectrometer (Micromass Manchester Waters Inc.).

General Procedure for the Synthesis of 2-Furanyl Phosphates 3#d: In a flame-dried and nitrogen-flushed reaction vessel, NaHMDS (1.1 equiv.) was dissolved in dry THF and cooled to –78 °C. A solution of the appropriate lactone **5** (1.0 equiv.) was dissolved in dry THF (5 mL/mmol) and added dropwise. The reaction mixture was stirred at –78 °C for 15 min, and then diphenyl chlorophosphate (1.1 equiv.) was added to the reaction mixture, which was stirred for another 45 min. After completion of the reaction, the mixture was quenched by the addition of water. After phase separation, the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents removed in vacuo. The residue was suspended in a mixture of hexane and *tert*-butyl methyl ether, filtered and the solvents were again removed in vacuo. The resulting crude product was sufficiently pure for subsequent reactions without any further purification.

5-Phenethylfuran-2-yl Diphenyl Phosphate (3ad): By applying the general procedure, the title compound was obtained from **5a**

(500 mg, 2.7 mmol). ^{1}H NMR spectroscopy of the crude reaction mixture indicated complete conversion into **3ad**. For this particular example, analytically pure **3ad** (1.02 g, 2.4 mmol, 89%) was obtained by column chromatography on silica with only a slightly reduced yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.33 (5 H, Aryl), 7.31–7.14 (10 H, Aryl), 5.88 (d, J = 3.2 Hz, 1 H, 9-H), 5.63 (dd, J = 3.1, 2.3 Hz, 1 H, 8-H), 2.94–2.80 (4 H, 5-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 148.1, 148.0, 140.7, 129.8, 128.3, 128.2, 126.0, 125.8, 120.0, 106.5, 90.2, 34.0, 29.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –17.7 ppm. HRMS (EI): calcd. for $C_{24}H_{21}O_5P$ $[M]^+$ 420.1127; found 420.1113. $C_{24}H_{21}O_5P$ (420.39): calcd. C 68.6, H 5.0; found C 68.4, H 4.9.

5-Pentylfuran-2-yl Diphenyl Phosphate (3cd): By applying the general procedure, the title compound was obtained from **5c** (82 mg, 0.5 mmol). ^{1}H NMR spectroscopy of the crude reaction mixture indicated complete conversion into **3cd**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.18 (10 H, Aryl), 5.88 (d, J = 3.1 Hz, 1 H, 8-H), 5.62 (dd, J = 3.1, 2.4 Hz, 1 H, 7-H), 2.51 (t, J = 7.5 Hz, 2 H, 5-H), 1.63–1.52 (2 H, 4-H), 1.40–1.25 (4 H, 2-H, 3-H), 0.95–0.85 (3 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 149.8, 149.4, 147.9, 130.1, 129.9, 126.4, 125.9, 120.4, 120.1, 105.8, 90.1, 31.2, 27.8, 27.4, 22.3, 13.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –17.7 ppm.

(*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)furan-2-yl Diphenyl Phosphate (3ed): By applying the general procedure, the title compound was obtained from **5e** (98 mg, 0.5 mmol). ^{1}H NMR spectroscopy of the crude reaction mixture indicated complete conversion into **3ed**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.19 (10 H, Aryl), 6.29 (d, J = 3.3 Hz, 1 H, 8-H), 5.72 (dd, J = 3.3, 2.2 Hz, 1 H, 7-H), 4.96 (dd, J = 7.1, 6.9 Hz, 1 H, 5-H), 4.18 (dd, J = 8.4, 6.5 Hz, 1 H, 4-Ha), 4.01 (dd, J = 8.3, 7.5 Hz, 1 H, 4-Hb), 1.46 (s, 3 H, 1-H/2-H), 1.43 (s, 3 H, 2-H/1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 149.9, 149.7, 144.7, 130.1, 129.9, 126.4, 125.9, 120.4, 120.1, 110.1, 90.7, 71.1, 67.6, 26.3, 25.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –18.1 ppm.

Diphenyl 5-Phenylfuran-2-yl Phosphate (3fd): By applying the general procedure, the title compound was obtained from **5f** (85 mg, 0.5 mmol). ^{1}H NMR spectroscopy of the crude reaction mixture indicated complete conversion into **3fd**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.51 (2 H, Aryl), 7.46–7.21 (13 H, Aryl), 6.56 (d, J = 3.4 Hz, 1 H, 7-H), 5.86 (dd, J = 3.4, 2.2 Hz, 1 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 149.8, 149.3, 146.8, 130.1, 129.9, 129.7, 128.6, 127.3, 126.4, 125.9, 120.4, 120.1, 106.0, 92.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –17.9 ppm.

5-[(Benzyloxy)methyl]furan-2-yl Diphenyl Phosphate (3gd): By applying the general procedure, the title compound was obtained from **5g** (108 mg, 0.5 mmol). ^{1}H NMR spectroscopy of the crude reaction mixture indicated complete conversion into **3gd**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.10 (15 H, Aryl), 6.19 (d, J = 3.3 Hz, 1 H, 9-H), 5.67 (dd, J = 3.3, 2.2 Hz, 1 H, 8-H), 4.46 (s, 2 H, 5-H), 4.31 (s, 2 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 149.7, 144.7, 131.7, 130.1, 129.9, 128.4, 127.9, 127.7, 126.4, 125.9, 120.4, 120.1, 111.1, 90.7, 71.8, 63.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –17.9 ppm.

General Procedure for the Diels–Alder Reactions of Furanyl Phosphates 3#d: The appropriate crude or purified furanyl phosphate **3#d** was dissolved in xylene (2 mL/mmol). DMAD (3.0 equiv.) was added, and the reaction mixture was heated at 135 °C. After complete consumption of the starting material, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel with a mixture of hexane and *tert*-butyl methyl ether as eluent.

Dimethyl 1-[(Diphenoxyphosphoryl)oxy]-4-phenethyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7a): By starting from purified **3ad** (968 mg, 2.3 mmol), the title compound **7a** (1.14 g, 2.0 mmol, 88%) was obtained by applying the general procedure after purification by column chromatography on silica gel with a mixture of hexane/*tert*-butyl methyl ether (3:1) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.16 (16 H, Aryl, 9-H), 6.98 (dd, J = 5.2, 1.0 Hz, 1 H, 8-H), 3.78 (s, 3 H, 14-H/16-H), 3.69 (s, 3 H, 16-H/14-H), 2.69 (dd, J = 8.3, 8.1 Hz, 2 H, 5-H), 2.64–2.42 (2 H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 162.4, 153.1, 151.3, 150.3, 146.6, 142.5, 141.0, 129.6, 128.4, 126.1, 125.5, 120.3, 111.8, 91.4, 52.4, 52.2, 31.0, 30.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.1 ppm. IR (neat): $\tilde{\nu}$ = 1718, 1589, 1488, 1282, 1178, 1009, 957, 844, 754, 688 cm^{-1}. HRMS (EI): calcd. for $C_{30}H_{27}O_9P$ $[M]^+$ 562.1387; found 562.1393. $C_{30}H_{27}O_9P$ (562.50): calcd. C 64.1, H 4.8; found C 63.9, H 4.8.

Dimethyl 1-[(Diphenoxyphosphoryl)oxy]-4-pentyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7c): The title compound was obtained from crude **3cd** [synthesized from **5c** (82 mg, 0.5 mmol) as described above] by applying the general procedure. After purification by column chromatography on silica with hexane/*tert*-butyl methyl ether mixtures (3:1 to 1:1) as eluent, **7c** (183 mg, 0.4 mmol, 82% based on **5c**) was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.16 (11 H, Aryl, 8-H), 6.99 (d, J = 5.2 Hz, 1 H, 7-H), 3.79 (s, 3 H, 13-H/15-H), 3.66 (s, 3 H, 15-H/13-H), 2.25–2.08 (2 H, 5-H), 1.47–1.20 (6 H, 2-H, 3-H, 4-H), 0.92–0.84 (3 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.3, 162.3, 153.9, 150.7, 150.3, 146.8, 142.1, 129.7, 125.4, 120.3, 111.7, 92.0, 52.4, 52.2, 31.8, 28.8, 24.5, 22.4, 13.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.1 ppm. IR (neat): $\tilde{\nu}$ = 1717, 1589, 1488, 1435, 1282, 1179, 1162, 1009, 956, 883, 754, 687 cm^{-1}. HRMS (EI): calcd. for $C_{27}H_{29}O_9P$ $[M]^+$ 528.1544; found 528.1555. HRMS (ESI): calcd. for $C_{27}H_{29}O_9PNa$ $[M + Na]^+$ 551.1447; found 551.0958. $C_{27}H_{29}O_9P$ (528.49): calcd. C 61.4, H 5.5; found C 61.1, H 5.6.

Dimethyl 1-[(*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-4-[(diphenoxyphosphoryl)oxy]-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7e): The title compound was obtained from crude **3ed** [synthesized from **5e** (98 mg, 0.5 mmol) as described above] by applying the general procedure. After purification by column chromatography on silica with hexane/*tert*-butyl methyl ether mixtures (2:1 to 1:1) as eluent, **7e** (104 mg, 0.2 mmol, 45% based on **5e**) was isolated as a 1:1 mixture of diastereomers. Partial separation of the diastereomers was achieved by careful chromatography. Analytical data of the less polar diastereomer: $[a]_D^{21}$ = –14.8 (c = 6, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.16 (12 H, Aryl, 7-H, 8-H), 4.93 (t, J = 6.2 Hz, 1 H, 4-H), 4.13 (dd, J = 8.6, 6.9 Hz, 1 H, 3-Ha), 3.97 (dd, J = 8.6, 5.7 Hz, 1 H, 3-Hb), 3.78 (s, 3 H, 13-H/15-H), 3.67 (s, 3 H, 15-H/13-H), 1.39 (br. s, 3 H, 1-H/2-H], 1.38 (br. s, 3 H, 2-H/1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 161.8, 152.5, 150.2, 144.8, 142.3, 142.2, 129.7, 125.6, 120.4, 111.8, 110.5, 91.2, 72.4, 65.9, 52.6, 52.3, 25.9, 25.3 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.2 ppm. IR (neat): $\tilde{\nu}$ = 1720, 1589, 1488, 1436, 1285, 1257, 1182, 1162, 1010, 961, 843, 770, 689 cm^{-1}. HRMS (EI): calcd. for $C_{27}H_{27}O_{11}PNa$ $[M]^+$ 558.1286; found 558.1278. $C_{27}H_{27}O_{11}P$ (558.47): calcd. C 58.1, H 4.9; found C 57.9, H 4.8. Analytical data for the more polar diastereomer of **7e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.15 (10 H, Aryl, 8-H), 6.98 (br. d, J = 5.3 Hz, 1 H, 7-H), 4.94 (dd, J = 6.4, 6.4 Hz, 1 H, 5-H), 4.11 (dd, J = 8.6, 6.9 Hz, 1 H, 4-Ha), 3.96 (dd, J = 8.6, 6.0 Hz, 1 H, 4-Hb), 3.81 (s, 3 H, 13-H/15-H), 3.67 (s, 3 H, 15-H/13-H), 1.37 (br. s, 3 H, 1-H/2-H), 1.36 (br. s, 3 H, 2-H/1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 161.9, 152.5, 150.3, 149.9, 144.8,

143.2, 129.7, 125.6, 120.3, 111.9, 110.5, 91.6, 72.3, 65.5, 52.5, 52.3, 25.9, 25.4 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.3 ppm.

Dimethyl 1-[(Diphenoxyphosphoryl)oxy]-4-phenyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7f): The title compound was obtained from crude **3fd** [synthesized from **5f** (85 mg, 0.5 mmol) as described above] by applying the general procedure. After purification by column chromatography on silica with hexane/*tert*-butyl methyl ether mixtures (3:1 to 1:1) as eluent, **7f** (125 mg, 0.2 mmol, 52% based on **5f**) was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (dd, J = 5.3, 1.1 Hz, 1 H, 6-H), 7.46–7.16 (16 H, Aryl, 7-H), 3.68 (s, 3 H, 12-H/14-H), 3.62 (s, 3 H, 14-H/12-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6, 161.8, 156.8, 150.3, 147.6, 145.6, 142.4, 132.7, 129.6, 129.1, 128.5, 126.9, 125.6, 120.4, 111.9, 91.7, 52.3, 52.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.0 ppm. IR (neat): $\tilde{\nu}$ = 1721, 1589, 1488, 1435, 1284, 1184, 1162, 1011, 951, 756, 688, 555 cm^{-1}. HRMS (EI): calcd. for $C_{28}H_{23}O_9P$ $[M]^+$ 534.1074; found 534.1042. $C_{28}H_{23}O_9P$ (534.45): calcd. C 62.9, H 4.3; found C 62.7, H 4.1.

Dimethyl 1-[(Benzyloxy)methyl]-4-[(diphenoxyphosphoryl)oxy]-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7g): The title compound was obtained from crude **3gd** [synthesized from **5g** (108 mg, 0.5 mmol) as described above] by applying the general procedure. After purification by column chromatography on silica with hexane/*tert*-butyl methyl ether mixtures (1:1) as eluent, **7g** (168 mg, 0.3 mmol, 55% based on **5g**) was isolated. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.17 (16 H, Aryl, 9-H), 7.07 (dd, J = 5.3, 0.9 Hz, 1 H, 8-H), 4.60 (dd, J = 12.0, 8.3 Hz, 1 H, 5-Ha), 4.57 (dd, J = 12.0, 8.3 Hz, 1 H, 5-Hb), 4.19 (dd, J = 11.8, 9.4 Hz, 1 H, 6-Ha), 4.16 (dd, J = 11.8, 9.4 Hz, 1 H, 6-Hb), 3.74 (s, 3 H, 14-H/16-H), 3.68 (s, 3 H, 16-H/14-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 162.0, 152.5, 150.3, 149.9, 144.5, 142.3, 137.5, 129.6, 128.3, 127.7, 125.6, 120.4, 112.1, 73.6, 66.0, 52.4, 52.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.2 ppm. IR (neat): $\tilde{\nu}$ = 1720, 1589, 1488, 1436, 1283, 1183, 1162, 1010, 956, 844, 754, 688, 561 cm^{-1}. HRMS (EI): calcd. for $C_{30}H_{27}O_{10}P$ $[M]^+$ 578.1360; found 578.1363. $C_{30}H_{27}O_{10}P$ (578.50): calcd. C 62.3, H 4.7; found C 62.1, H 4.6.

General Procedure for Lewis Acid Mediated Ring-Opening Reactions of Diels–Alder Adducts 7: In a flame-dried and nitrogen-flushed reaction vessel, the appropriate precursor **7** was dissolved in dry CH_2Cl_2 and cooled to 0 °C. Then $BF_3{\cdot}Et_2O$ (1.5 equiv.) was added, and the reaction mixture was stirred at 0 °C. After completion of the reaction, the mixture was quenched by the addition of a solution of saturated aqueous NH_4Cl. After phase separation, the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, filtered, and the solvents removed with a rotary evaporator. The residue was purified by column chromatography on silica gel using a mixture of hexane/*tert*-butyl methyl ether as eluent.

Dimethyl 6-[(Diphenoxyphosphoryl)oxy]-3-hydroxy-4-phenethylphthalate (16a): By applying the general procedure, **7a** (311 mg, 0.6 mmol) was converted into a mixture of **16a** and **15** in a ratio of approximately 4:1. The products were separated by column chromatography on silica gel with a mixture of hexane/*tert*-butyl methyl ether (5:1 to 3:1) as eluent. Yield of the less polar product **16a**: 238 mg (0.4 mmol, 77%); yield of the more polar product **15**: 55 mg (0.12 mmol, 20%). Analytical data for **16a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.14 (s, 1 H, 21-H), 7.40–7.15 (16 H, Aryl), 3.91 (s, 3 H, 14-H/16-H), 3.70 (s, 3 H, 16-H/14-H), 2.96–2.80 (4 H, 5-H, 6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1, 165.8, 157.3, 150.2, 141.1, 138.9, 133.6, 129.8, 128.3, 127.2, 125.9, 125.6, 120.1, 120.0, 108.9, 53.0, 52.4, 34.9, 31.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.7 ppm. IR (neat): $\tilde{\nu}$ = 1739, 1678, 1589, 1488, 1431, 1347, 1299, 1182, 1162, 1062, 1010, 947, 752, 688 cm^{-1}. HRMS (ESI): calcd. for $C_{30}H_{28}O_9P$ $[M + H]^+$ 563.1471; found 563.1426. $C_{30}H_{27}O_9P$ (562.50): calcd. C 64.1, H 4.8; found C 64.0, H 4.6.

Dimethyl 6-[(Diphenoxyphosphoryl)oxy]-3-hydroxy-4-pentylphthalate (16c): By applying the general procedure, **7c** (94 mg, 0.2 mmol) was converted into the title compound **16c**. The crude product was purified by column chromatography on silica gel using a hexane/*tert*-butyl methyl ether mixture (5:1) as eluent. Yield of **16c**: 74 mg (0.1 mmol, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.07 (s, 1 H, 20-H), 7.40–7.16 (11 H, Aryl), 3.89 (s, 3 H, 13-H/15-H), 3.69 (s, 3 H, 15-H/13-H), 2.61 (dd, J = 7.9, 7.5 Hz, 2 H, 5-H), 1.60–1.47 (2 H, 4-H), 1.36–1.25 (4 H, 2-H, 3-H), 0.87 (t, J = 6.7 Hz, 3 H, 1-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.2, 165.9, 157.3, 150.4, 138.9, 134.9, 129.8, 127.1, 125.7, 120.2, 120.1, 108.8, 52.9, 52.4, 31.4, 29.7, 28.5, 22.4, 13.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.6 ppm. IR (neat): $\tilde{\nu}$ = 1739, 1678, 1589, 1488, 1432, 1345, 1299, 1247, 1205, 1182, 1161, 1060, 1009, 947, 878, 844, 804, 754, 687 cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{30}O_9P$ $[M + H]^+$ 529.1627; found 529.1598. $C_{27}H_{29}O_9P$ (528.49): calcd. C 61.4, H 5.5; found C 61.4, H 5.6.

Dimethyl 3-[(Diphenoxyphosphoryl)oxy]-6-hydroxyphthalate (15): By applying the general procedure, **7g** (303 mg, 0.5 mmol) was converted into the title compound **15**. The crude product was purified by column chromatography on silica gel using hexane/*tert*-butyl methyl ether mixtures (6:1 to 3:1) as eluent. Yield of **15**: 184 mg (0.4 mmol, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.80 (s, 1 H, 15-H), 7.57 (d, J = 9.3 Hz, 1 H, Aryl), 7.40–7.18 (10 H, Aryl), 7.02 (d, J = 9.3 Hz, 1 H, Aryl), 3.91 (s, 2 H, 7-H/8-H), 3.71 (s, 3 H, 8-H/7-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 165.2, 158.9, 150.4, 139.5, 129.9, 127.6, 125.7, 120.1, 120.0, 115.3, 109.5, 53.1, 52.5 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.6 ppm. IR (neat): $\tilde{\nu}$ = 1739, 1681, 1589, 1487, 1456, 1335, 1299, 1248, 1204, 1182, 1161, 1118, 1023, 1009, 992, 952, 863, 754, 687 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{19}O_9P$ $[M]^+$ 458.0767; found 458.0750. $C_{22}H_{19}O_9P$ (458.36): calcd. C 57.7, H 4.2; found C 57.9, H 4.2.

Supporting Information (see footnote on the first page of this article): Experimental details and ^{1}H and ^{13}C NMR spectra for all new compounds.

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