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Phospholane-Catalyzed Wittig Reaction

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We identified 2-phenylisophosphindoline 2-oxide as a suitable and potentially tunable catalyst for the catalytic Wittig reaction of aldehydes with activated organohalides. This catalyst was obtained by a straightforward two-step synthesis. Trimethoxysilane proved to be an efficient reducing agent for the in situ generation and regeneration of the catalyst from the corresponding phosphane oxide. Sodium carbonate was identified as a suitable base for the transformation. It is noteworthy that the particle size of the sodium carbonate had a tremendous effect on the outcome of the reaction. Under the optimized reaction conditions, 23 aldehydes were converted into the corresponding alkenes in high isolated yields of up to 88 %. Moreover, an asymmetric catalytic Wittig reaction was performed for the desymmetrization of a prochiral diketone.

Introduction

Phosphorus-based reagents are versatile, important compounds that are utilized in numerous organic transformations.[1] The Wittig,[2] Appel,[3] and Mitsunobu[4] reactions are three examples of frequently employed methods that are based on phosphanes. Nevertheless, the phosphane oxides that form as byproducts in these reactions often hamper the purification of the desired products and lead to an increase in the associated costs as a result of low atom economy.[5] In addition to the numerous immobilization approaches,[6] the regeneration of the phosphane is performed under harsh reaction conditions or by the utilization of highly toxic phosgene.[7] A promising alternative involves the in situ reduction of the phosphane oxide and the use of catalytic amounts of the phosphane.[8]

Carbonyl olefinations are one of the fundamental and most frequently employed transformations in organic synthesis.[1c,9] Hence, the development of catalytic Wittig reactions is a challenging yet worthy task. Despite the drawbacks described above, this long known reaction is the most commonly used method to convert aldehydes and ketones into the corresponding olefins, even on multigram scales, to provide products with high regio- and *E*/*Z*-selectivity.[10] The first examples of catalytic Wittig-type reactions utilized arsenic-[11] and telluride-based[12] catalysts. One major issue in the development of catalytic Wittig reactions involves the compatibility of the reducing agent, which is used for the in situ reduction of the phosphane oxide, with the other reagents and products.

Various systems for the reduction of phosphane oxides into their corresponding phosphanes have been reported. For example, these systems include aluminum hydrides,[13] SmI_2/hexamethylphosphoric triamide (HMPA),[14] $TiCp_2Cl_2$/Mg,[15] Bi/TiO_2,[16] $InBr_3$/1,1,3,3-tetramethyldisilazane (TMDS),[17] $SiCl_4$,[18] electroreductions,[19] and $(COCl)_2$/Hantzsch ester.[20] Nevertheless, these procedures are not suitable, as the reaction conditions and necessary reagents are incompatible with the components of a Wittig reaction. Recently, organosilanes in combination with specially designed phospholes and phospholanes were utilized for the in situ reduction to enable the performance of the catalytic Appel,[8h] Staudinger,[21] and Wittig reactions.[8b,8j,8k,8o] A recently published life cycle assessment (LCA) by Huijbregts et al. indicates that ecological factors such as the cumulative energy demand and greenhouse gas emissions might be reduced under certain conditions by applying these methods.[22] The development of catalytic variations of the above-mentioned phosphorus-based transformations can generally be categorized into redox-shuttled and redox-neutral approaches (Scheme 1).[5]

In redox-shuttled processes, the oxidation state of the catalyst changes from P^{III} in the phosphane into P^{V} in the corresponding oxide, whereas in redox-neutral processes, the oxidation state remains constant throughout the catalytic cycle. The redox-shuttled process was established by O'Brien for catalytic Wittig reactions.[8b,8j,8k,8o] Furthermore, van Delft et al. developed catalytic Appel, Staudinger, and aza-Wittig reactions by using this strategy.[8h,8i,8l] Catalytic diaza-Wittig reactions and catalytic amide formations have been recently reported.[23] Marsden established the redox-neutral strategy for a catalytic aza-Wittig[24] reaction, as Denton utilized it for catalytic Appel reactions.[8e–8g] The phospholane structure is a common motif for catalysts in both redox-shuttled and redox-neutral pro-

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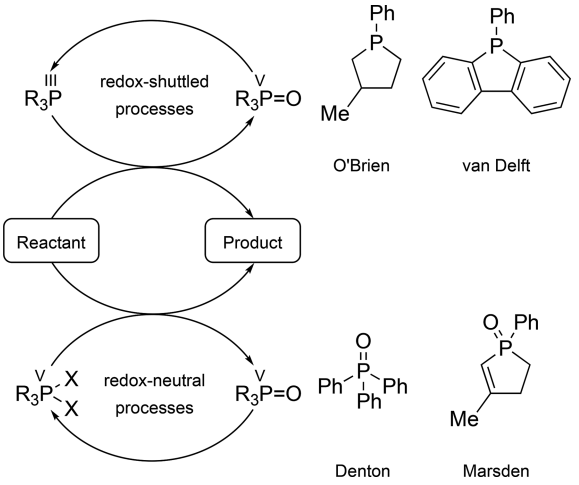
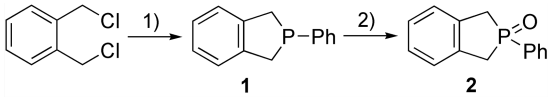


Scheme 1. General approaches to catalytic processes utilizing phosphorus-based organocatalysts and selected examples of organophosphorus catalysts.

cesses (Scheme 1). Moreover, it is well-known that modifications to the basic framework and the introduction of substituents have a great impact on the catalytic activity of those catalysts. We are interested in the synthesis and application of phosphorus-based organocatalysts.[25] In this context, we recently reported the first asymmetric catalytic Wittig reaction that utilizes catalytic amounts of chiral phosphanes.[8n] Promising results were also obtained with phospholane derivatives such as 1,2-bis[(2*S*,5*S*)-2,5-dimethylphospholano]benzene (*S*,*S*-Me-DuPhos). Hence, we envisioned phospholane derivative **1** to be a potentially tunable catalyst for catalytic Wittig reactions (Scheme 2).



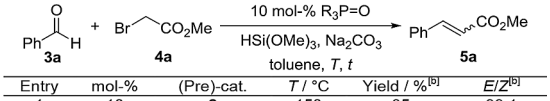
Scheme 2. Preparation of 2-phenylisophosphindoline 2-oxide (**2**). Reagents and conditions: (1) (a) Mg, tetrahydrofuran (THF), 23 °C, 16 h; (b) $PhPCl_2$, THF, 23 °C, 3 h. (2) H_2O_2 (10%), acetone, reflux, 1 h, 49% over two steps.

Results and Discussion

Initially, we prepared the desired product **2** by a two-step synthesis starting from α,α′-dichloro-*ortho*-xylene.[26] However, phospholane **1** is air sensitive and partially oxidized during purification or when stored under ambient conditions. Hence, **1** was converted into the corresponding bench-stable and easy-to-handle phospholane oxide **2**.

As a proof of principle, we chose the conversion of benzaldehyde (**3a**) and methyl bromoacetate (**4a**) into methyl phenylpropenoate (**5a**) as the model reaction to evaluate various reaction conditions and potential catalysts for the catalytic Wittig reaction (Table 1). In our initial studies, several phosphanes and phosphane oxides in addition to compound **2** as well as numerous silanes, bases, solvents, and temperatures over a range of 100–150 °C were examined by employing them in the model reaction. We identified $HSi(OMe)_3$ and Na_2CO_3 as a suitable reducing agent and base, respectively. The utilization of Na_2CO_3 as a base in catalytic Wittig reactions has been previously reported by O'Brien and co-workers.[8b,8k] However, in our hands, our very promising initial results were difficult to reproduce, and the yields varied under the same reaction conditions between 12 and 85%. However, a cautious investigation revealed the significance of the grain size of Na_2CO_3 on the outcome of the reaction. A detailed evaluation of the influence of the particle size of Na_2CO_3 revealed that ground Na_2CO_3 with a grain size of 125–250 μm gave reproducible and excellent yields of approximately 85%. In contrast, Na_2CO_3 that had a particle size between 125 and 1000 μm afforded varying yields in the above-mentioned range (Supporting Information). Under our initial reaction conditions, the utilization of **2** as a catalyst led to **5a** in yields up to 85% (Table 1, Entry 1). Other cyclic and acyclic phosphanes and phosphane oxides gave the desired product **5a** in yields of 5–71% (Table 1, Entries 2–6). Further optimization studies led to a decrease in the amount of the precatalyst to 5 mol-%, the retention of toluene as the solvent of choice, a lower reaction temperature of 125 °C, and a reaction time of 16 h (Table 1, Entry 7). A further decrease in the amount of precatalyst to 2.5 mol-% resulted in a decreased yield of 52% (Table 1, Entry 8).

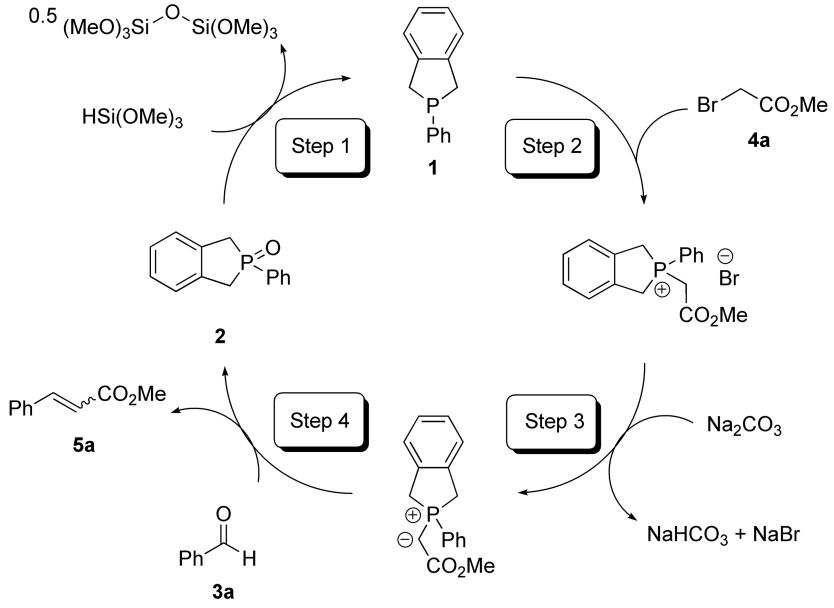
Table 1. Utilization of different phosphorus-based catalysts in the model reaction of **3a** with **4a**.[a]



Entry	mol-%	(Pre)-cat.	*T* / °C	Yield / %[b]	*E*/*Z*[b]
1	10	**2**	150	85	99:1
2	10	Ph_3P	150	5	86:14
3	10	Bu_3P	150	39	87:13
4	10	$Bu_3P=O$	150	21	88:12
5	10	$Et_3P=O$	150	28	88:12
6	10		150	71	99:1
7[c]	5	**2**	125	84	80:20
8[c]	2.5	**2**	125	52	83:17

[a] Screening reactions were performed on a 1.5 mmol scale. Reagents and conditions: R_3P or $R_3P=O$ (catalytic amount), benzaldehyde (**3a**, 0.5 M in toluene, 1.0 equiv.), methyl bromoacetate (**4a**, 1.2 equiv.), trimethoxysilane (2.0 equiv.), Na_2CO_3 (1.5 equiv.), 24 h. [b] Calculated/determined by GC analysis using *n*-hexadecane as the internal standard. [c] 16 h.

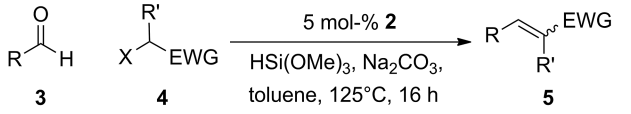
Under the reaction conditions, we propose that precatalyst **2** is initially reduced by treatment with trimethoxysilane to give the corresponding phosphane **1** (Scheme 3). The formation of hexamethyldisilicate, as the only byproduct from the phosphane oxide reduction, was detected by GC–MS analysis and can easily be separated from the product upon the conclusion of the reaction. In situ formation of the corresponding phosphonium salt in step 2 and subsequent deprotonation in step 3 leads to the Wittig ylide. Finally, the conversion of aldehyde **3a** in the last step regenerates phosphane oxide **2** and releases the desired olefinic product **5a**. At this point, we want to highlight that the complete catalytic cycle consists in total of four steps. Hence, the conver-



Scheme 3. The four consecutive reaction steps of the catalytic Wittig reaction.

sion and selectivity of each step of the catalytic cycle must be >95% in average to finally provide **5a** in 85% yield.

We were then interested in the scope and limitations of the catalytic Wittig reaction under our standard conditions. Hence, we examined the reaction of various aromatic, heteroaromatic, and aliphatic aldehydes **3** with halo-substituted derivatives **4** to yield the desired alkenes **5** (Scheme 4).



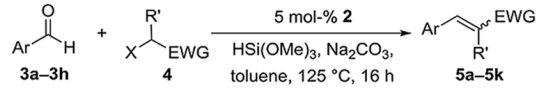
Scheme 4. Evaluation of the scope and limitations of the catalytic Wittig reaction under standard reaction conditions (EWG = electron-withdrawing group).

We began by studying the conversion of aromatic aldehydes **3a**–**3f** and methyl bromoacetate (**4a**) into the corresponding alkenes **5a**–**5f** (Table 2, Entries 1–7). The employment of benzaldehyde (**3a**) yielded methyl 3-phenylpropenoate (**5a**) in 82% isolated yield (Table 2, Entry 1). The utilization of methyl chloroacetate (**4b**) or iodoacetate (**4c**) led to significantly lower yields of 24 and 30%, respectively. The reaction of 2-naphthaldehyde (**3b**) with **4a** afforded the corresponding olefin **5b** in 82% yield (Table 2, Entry 2). Moreover, substituted benzaldehydes that have electron-donating or -withdrawing groups could be converted with similar efficiency into **5c** in 83% yield, **5d** and **5e**, both in 76% isolated yield, and *tert*-butyl derivative **5f** in 60% yield (Table 2, Entries 3–6). The reaction of methoxy-substituted benzaldehydes **3g**–**3i** gave the desired products **5g**–**5i** in up to 87% yield (Table 2, Entries 7–9). The employment of other activated halogenated compounds is also possible. For example, the conversion of *meta*-anisaldehyde (**3h**) with bromoacetonitrile and methyl 2-bromopropionate led to the corresponding olefins **5j** and **5k** in 84 and 54% yield, respectively (Table 2, Entries 10 and 11). The moderate yield of **5k** might be attributed to steric effects. Notably, when the reaction was performed under harsher conditions (i.e., 10 mol-% **2**, 150 °C, 24 h), products **5a**–**5f** were obtained with a higher (*E*) selectivity but with slightly lower yields. Notably, the *E*/*Z* selectivities were in contrast to the levels of selectivity obtained by the same substrates in other catalytic Wittig transformations.[8b,8j–8n] Here, the selectivities are higher when the amount of catalyst and the reaction temperature is increased (Table 2, Entries 1–6). One explanation for this might be that some equilibration is occurring at 125 °C. The *E*/*Z* ratio of product **5a** (83:17) did not change significantly when it was stirred in the presence of 5 mol-% **2** and $HSi(OMe)_3$ in toluene at 125 °C for 16 h.

The scope of the substrates for this reaction is not restricted to aromatic aldehydes. We also successfully employed heteroaromatic and aliphatic aldehydes (Table 3). The corresponding heteroaromatic products **5l**–**5o** were obtained in good to excellent isolated yields of 72–88%. In contrast, quinoline derivative **5p** was obtained in only 22% yield. This drastic drop in the yield of **5p** compared to **5b** and **5l**–**5o** might be attributed to the pyridine moiety, which can participate in a side reaction such as an alkylation as a result of the Lewis base nature of the nitrogen atom. Aliphatic aldehydes and **4a** were converted into olefins **5q**–**5w** in slightly lower yields of 66–78%.

Recently, we reported the first enantioselective catalytic Wittig reaction.[8n] So far, there are very few examples of stoichiometric modifications to this reaction.[27] We examined the desymmetrization of prochiral diketone **6** in the presence of a catalytic amount of a chiral phosphane to give bicyclic olefin **7** (Scheme 5). In the context of this work, we

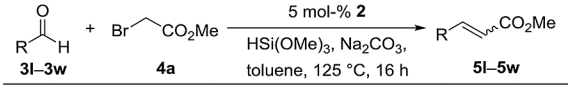
Table 2. Substrate study of the catalytic Wittig reaction with different aryl aldehydes and organohalides.[a]



Entry	Aldehyde	Product	Yield / %	*E*/*Z*
1	**3a**	**5a**	82[b] (85)[c]	83:17 99:1[c]
2	**3b**	**5b**	82 (80)[c]	86:14 (98:2)[c]
3	**3c**	**5c**	83 (81)[c]	76:24 (92:8)[c]
4	**3d**	**5d**	76 (70)[c]	80:20 (90:10)[c]
5	**3e**	**5e**	76 (72)[c]	85:15 (94:6)[c]
6	**3f**	**5f**	60 (55)[c]	81:19 (97:3)[c]
7	**3g**	**5g**	65	81:19
8	**3h**	**5h**	87	83:17
9	**3i**	**5i**	65	87:13
10	**3h**	**5j**	84	83:17
11	**3h**	**5k**	54	89:11

[a] Reactions were conducted on a 1–2 mmol scale. Reagents and conditions: aldehyde **3** (0.5 M in toluene, 1.0 equiv.), organohalide (1.2 equiv.), 2-phenylisophosphindoline 2-oxide (**2**, 5 mol-%), trimethoxysilane (2.0 equiv.), Na_2CO_3 (1.5 equiv.), 125 °C, 16 h. Isolated yields are reported. *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy. [b] The use of methyl chloroacetate (**4b**) or iodoacetate (**4c**) instead of **4a** led to 24 and 30% yield, respectively, of the product. [c] Reagents and conditions: aldehyde **3** (0.5 M in toluene, 1.0 equiv.), methyl bromoacetate (**4a**) (1.2 equiv.), 2-phenylisophosphindoline 2-oxide (**2**, 10 mol-%), trimethoxysilane (2.0 equiv.), Na_2CO_3 (1.5 equiv.), 150 °C, 24 h, yields and *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy.

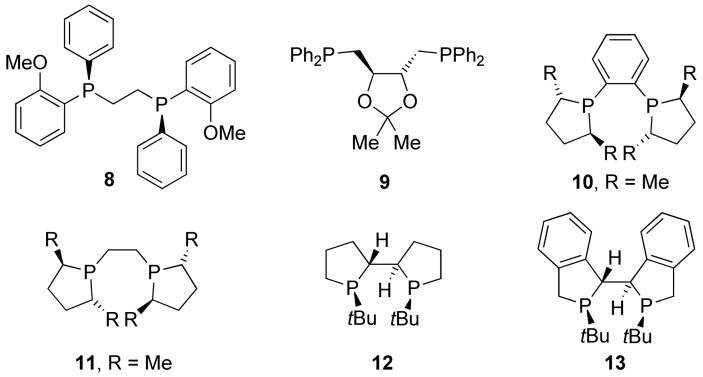
Table 3. Substrate scope for the reaction of heteroaromatic and aliphatic substrates **3l**–**3w** with methyl bromoacetate (**4a**).[a]



Entry	Aldehyde	Product	Yield / %	*E*/*Z*
1	**3l**	**5l**	72	71:29
2	**3m**	**5m**	87	86:14
3	**3n**	**5n**	78	74:26
4	**3o**	**5o**	88	>99:1
5	**3p**	**5p**	22	95:5
6	**3q**	**5q**	73	79:21
7	**3r**	**5r**	78	95:5
8	**3s**	**5s**	72	83:17
9	**3t**	**5t**	70	79:21
10	**3u**	**5u**	66	80:20
11	**3v**	**5v**	74	78:22
12	**3w**	**5w**	70	81:19

[a] Reagents and conditions: aldehyde **3** (0.5 M in toluene, 1.0 equiv.), organohalide (1.2 equiv.), 2-phenylisophosphindoline 2-oxide (**2**, 5 mol-%), trimethoxysilane (2.0 equiv.), Na_2CO_3 (1.5 equiv.), 125 °C, 16 h. Isolated yields are reported. *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy.

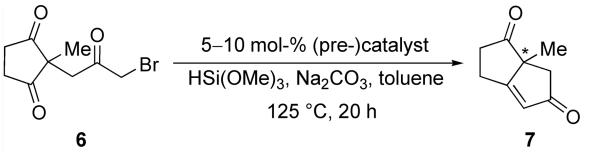
were interested in the further elaboration of this reaction by screening potential chiral catalysts **8**–**10** under thermal conditions (Table 4). Precatalyst **2** gave the desired product **7** in 72% yield and with the expected 1:1 mixture of enantiomers (Table 4, Entry 1). (*R*,*R*)-1,2-Ethanediylbis-



Scheme 5. Chiral phosphane catalysts for the enantioselective catalytic Wittig reaction.

[(2-methoxyphenyl)phenylphosphane] [(*R*,*R*)-DIPAMP, **8**] and (4*R*,5*R*)-4,5-bis[(diphenylphosphanyl)methyl]-2,2-dimethyl-1,3-dioxolane [(*R*,*R*)-DIOP, **9**] gave the desired product **7** in low yields and with low enantioselectivities (Table 4, Entries 2 and 3).

Table 4. Screening chiral catalysts **8**–**13** in the enantioselective catalytic Wittig reaction.



Entry	Catalyst	mol-%	Yield / %	*ee* / %[a]	*er* [*R*/*S*][a]
1	**2**	10	72[b]	0	50:50
2	**8**	5	<20[c]	8	54:46
3	**9**	5	29[b]	1	55:45
4	**10**	5	8[c]	86	81:19
5	**11**	5	53[c]	36	68:32
6	**12**	5	<5[c]	32	34:66
7	**13**	5	50[b]	62	81:19

[a] The *ee* values and enantiomeric ratios (*er*) were determined by chiral GC–MS analysis. [b] Isolated yield after column chromatography. [c] The yields were determined by ^{1}H NMR analysis of the reaction mixture.

Nevertheless, high enantioselectivity can be obtained in the presence of catalytic amounts of (*S*,*S*)-Me-DuPhos (**10**) which afforded an excellent enantiomeric excess (*ee*) value of 86% (Table 4, Entry 4). However, the yield was <10%. The employment of 1,2-bis[(2*R*,5*R*)-2,5-dimethylphospholano]ethane [(*R*,*R*)-Me-BPE, **11**] gave the desired product **7** in 53% yield with an enantiomeric excess value of 36% (Table 4, Entry 5). This result indicates that both good yields and selectivities ought to be achievable in general. Catalyst **12** gave **7** in 32%*ee* (Table 4, Entry 6). Interestingly, chiral phosphane **13** contains a subunit of our model catalyst **2**. In the presence of **13**, the desired product **7** was obtained in 50% yield and 62%*ee* (Table 4, Entry 6).

Conclusions

As initially envisioned, 2-phenylisophosphindoline 2-oxide (**2**) acts as an efficient precatalyst in the catalytic Wittig reaction. Na_2CO_3 was employed as a base in combination with trimethoxysilane as the in situ reducing agent. The particle size of Na_2CO_3 was identified as a crucial factor for the reproducibility of the reaction. Hexamethyldisilicate was produced as the only byproduct of the phosphane oxide reduction. Aromatic, heteroaromatic, and aliphatic aldehydes underwent the reaction with methyl bromoacetate and bromoacetonitrile to afford products in yields up to 88%. This is especially remarkable because the four steps of the catalytic cycle must successfully proceed with an average yield of about 97% for each step. In attempts towards an asymmetric catalytic Wittig reaction for the desymmetrization of a prochiral diketone, a yield of up to 53% and an *ee* value of up to 86% were obtained.

Experimental Section

General Methods: All reagents were purchased from commercial sources and used without further purification, with the exception of benzaldehyde, which was freshly distilled. Toluene and THF were freshly distilled from sodium/benzophenone. To obtain reproducible results, it is important to use sodium carbonate with a small particle size (125–250 μm).

2-Phenylisophosphindoline 2-Oxide (2): THF (10 mL) was added to magnesium turnings (3.6 g, 0.15 mol), which were then activated with 1,2-dibromoethane (0.24 mL) at 23 °C. The solvent was removed in vacuo, and fresh THF (40 mL) was added again. A solution of 1,2-bis(chloromethyl)benzene (6.4 g, 37 mmol) in THF (450 mL) was added to this mixture over a period of 3.5 h at 23 °C, and the greenish solution was stirred for another 15 h. This Grignard solution was poured dropwise and simultaneously with a solution of phenyldichlorophosphane (6.6 g, 37 mmol) in THF (100 mL) into vigorously stirred THF (100 mL) over a period of 1.5 h. The yellowish mixture was then stirred at 23 °C for an additional 3 h. Subsequently, a satd. aqueous NH_4Cl solution (300 mL) was added, and the aqueous layer was extracted with Et_2O (3× 150 mL). The combined organic layers were dried with $MgSO_4$, and the solvents were removed. The crude product was dissolved in acetone (100 mL) and cooled to 0 °C, and an aqueous H_2O_2 solution (10 wt.-%, 78 mL) was added slowly. The mixture was allowed to reach 23 °C and was then heated at reflux for 1 h. All of the volatiles were removed in vacuo. The residue was dried with $MgSO_4$ in CH_2Cl_2 and purified by flash column chromatography (ethyl acetate/ethanol, 20:1) to afford **2** (4.1 g, 49%) as a pale orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.33–3.63 (m, 4 H,

CH_2), 7.30–7.64 (m, 9 H, ArH) ppm. ^{13}C NMR: δ = 35.4 (d, $J_{C,P}$ = 67.6 Hz, 2× CH_2), 127.3 (d, $J_{C,P}$ = 15.2 Hz, 2× CH), 128.0 (d, $J_{C,P}$ = 1.0 Hz, 2× CH), 128.7 (d, $J_{C,P}$ = 11.7 Hz, 2× CH), 129.7 (d, $J_{C,P}$ = 9.5 Hz, 2× CH), 132.2 (d, $J_{C,P}$ = 2.7 Hz, CH), 133.4 (C), 135.6 (d, $J_{C,P}$ = 10.1 Hz, 2× C) ppm. ^{31}P NMR: δ = 56.01 ppm. MS (EI, 70 eV): *m*/*z* (%) = 228 (100) $[M]^+$, 165 (15), 104 (65), 103 (22), 78 (21), 77 (18). HRMS (EI): calcd. for $C_{14}H_{13}OP$ $[M]^+$ 228.0699; found 228.0697.

General Procedure (GP1) for the Catalytic Wittig Reaction: A 15 mL Ace pressure tube that was equipped with a stir bar was charged with 2-phenylisophosphindoline 2-oxide (**2**, 0.08 mmol, 5 mol-%), aldehyde **3** (0.5 M in toluene, 1.5 mmol, 1.0 equiv.), Na_2CO_3 (2.3 mmol, 1.5 equiv.), organohalide **4** (1.8 mmol, 1.2 equiv.), and $HSi(OMe)_3$ (3.0 mmol, 2.0 equiv.). The tube was then purged with argon and sealed with an O-ring cap, and the reaction mixture was heated at 125 °C for 16 h. After cooling to 23 °C, purification was performed by flash chromatography [SiO_2; cyclohexane/ethyl acetate (EtOAc)].

Methyl 3-Phenylpropenoate (5a): By following GP1, benzaldehyde (**3a**, 161 mg, 1.52 mmol), methyl bromoacetate (**4a**, 279 mg, 1.82 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.08 mmol), Na_2CO_3 (242 mg, 2.28 mmol), and $HSi(OMe)_3$ (371 mg, 3.04 mmol) were combined in toluene (3.0 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5a** (203 mg, 82%; *E*/*Z*, 83:17) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.82 (s, 3 H, CH_3), 6.46 (d, *J* = 16.0 Hz, 1 H, CH), 7.38–7.43 (m, 3 H, ArH), 7.51–7.56 (m, 2 H, ArH), 7.72 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.6 (CH_3), 117.7 (CH), 128.0 (2× CH), 128.8 (2× CH), 130.2 (CH), 134.2 (C), 144.7 (CH), 167.3 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 162 (51) $[M]^+$, 161 (25), 131 (100) $[M^+ – OMe]$, 103 (62) $[M^+ – CO_2Me]$, 102 (16), 77 (35).

Methyl 3-(2-Naphthyl)propenoate (5b): By following GP1, 2-naphthaldehyde (**3b**, 339 mg, 2.17 mmol), methyl bromoacetate (**4a**, 398 mg, 2.60 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 25 mg, 0.11 mmol), Na_2CO_3 (345 mg, 3.26 mmol), and $HSi(OMe)_3$ (530 mg, 4.34 mmol) were combined in toluene (4.3 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5b** (378 mg, 82%; *E*/*Z*, 86:14) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.85 (s, 3 H, CH_3), 6.57 (d, *J* = 16.0 Hz, 1 H, CH), 7.48–7.54 (m, 2 H, CH), 7.66–7.70 (m, 1 H), 7.80–7.91 (m, 4 H), 7.93–7.97 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.5 (CH_3), 117.7 (CH), 123.3 (CH), 126.5 (CH), 127.0 (CH), 127.6 (CH), 128.4 (CH), 128.5 (CH), 129.8 (CH), 131.7 (C), 133.1 (C), 134.0 (C), 144.7 (CH), 167.3 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 212 (100) $[M]^+$, 211 (14), 182 (14), 181 (94) $[M^+ – OMe]$, 153 (52) $[M^+ – CO_2Me]$, 152 (78), 151 (21), 127 (13), 76 (27). $C_{14}H_{12}O_2$ (212.25): calcd. C 79.22, H 5.70; found C 79.16, H 5.63.

Methyl 3-(4-Methoxycarbonylphenyl)propenoate (5c): By following GP1, 4-(methoxycarbonyl)benzaldehyde (**3c**, 262 mg, 1.59 mmol), methyl bromoacetate (**4a**, 292 mg, 1.91 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 18 mg, 0.08 mmol), Na_2CO_3 (253 mg, 2.39 mmol), and $HSi(OMe)_3$ (389 mg, 3.18 mmol) were combined in toluene (3.2 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5c** (290 mg, 83%; *E*/*Z*, 76:24) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.83 (s, 3 H, CH_3), 3.94 (s, 3 H, CH_3), 6.53 (d, *J* = 16.1 Hz, 1 H, CH), 7.57–7.62 (m, 2 H, ArH), 7.72 (d, *J* = 16.1 Hz, 1 H, CH), 8.01–8.08 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.5 (CH_3), 51.9 (CH_3), 119.9 (CH), 127.6 (2× CH), 129.8 (2× CH), 131.1 (C), 138.3 (C), 143.1 (CH), 166.0 (C=O), 166.6 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 220 (52) $[M]^+$, 205 (16) $[M^+ – Me]$, 189 (100) $[M^+ – OMe]$, 161 (17) $[M^+ – CO_2Me]$, 145 (19), 115 (12), 102 (22). $C_{12}H_{12}O_4$ (220.22): calcd. C 65.45, H 5.49; found C 65.16, H 5.33.

Methyl 3-(4-Chlorophenyl)propenoate (5d): By following GP1, 4-chlorobenzaldehyde (**3d**, 248 mg, 1.76 mmol), methyl bromoacetate (**4a**, 323 mg, 2.11 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 20 mg, 0.09 mmol), Na_2CO_3 (280 mg, 2.64 mmol), and $HSi(OMe)_3$ (430 mg, 3.52 mmol) were combined in toluene (3.5 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5d** (262 mg, 76%; *E*/*Z*, 80:20) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.82 (s, 3 H, CH_3), 6.42 (d, *J* = 16.0 Hz, 1 H, CH), 7.35–7.39 (m, 2 H, ArH), 7.45–7.48 (m, 2 H, ArH), 7.65 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.5 (CH_3), 118.2 (CH), 128.9 (2× CH), 129.0 (2× CH), 132.7 (C), 135.9 (C), 143.1 (CH), 166.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 198 (17) $[M]^+$, 196 (51) $[M]^+$, 167 (33), 165 (100) $[M^+ – OMe]$, 137 (32) $[M^+ – CO_2Me]$, 102 (31), 101 (30), 75 (19). $C_{10}H_9ClO_2$ (196.63): calcd. C 61.08, H 4.61; found C 60.99, H 4.33.

Methyl 3-[(1,1′-Biphenyl)-4-yl]propenoate (5e): By following GP1, 4-phenylbenzaldehyde (**3e**, 273 mg, 1.50 mmol), methyl bromoacetate (**4a**, 275 mg, 1.80 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.07 mmol), Na_2CO_3 (238 mg, 2.18 mmol), and $HSi(OMe)_3$ (426 mg, 3.49 mmol) were combined in toluene (3.0 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5e** (272 mg, 76%; *E*/*Z*, 85:15) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.84 (s, 3 H, CH_3), 6.49 (d, *J* = 16.0 Hz, 1 H, CH), 7.36–7.42 (m, 1 H, ArH), 7.44–7.50 (m, 2 H, ArH), 7.59–7.66 (m, 6 H, ArH), 7.75 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.6 (CH_3), 117.5 (CH), 126.9 (2× CH), 127.4 (2× CH), 127.8 (CH), 128.5 (2× CH), 128.8 (2× CH), 133.2 (C), 140.0 (C), 143.0 (C), 144.3 (CH), 167.4 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 238 (100) $[M]^+$, 207 (62) $[M^+ – OMe]$, 178 (76) $[M^+ – CO_2Me]$, 165 (30), 152 (25), 89 (25).

Methyl 3-(4-*tert*-Butylphenyl)propenoate (5f): By following GP1, 4-*tert*-butylbenzaldehyde (**3f**, 230 mg, 1.42 mmol), methyl bromoacetate (**4a**, 261 mg, 1.71 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.07 mmol), Na_2CO_3 (226 mg, 2.13 mmol), and $HSi(OMe)_3$ (347 mg, 2.84 mmol) were combined in toluene (2.8 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5f** (186 mg, 60%; *E*/*Z*, 81:19) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, CH_3), 3.81 (s, 3 H, CH_3), 6.42 (d, *J* = 16.0 Hz, 1 H, CH), 7.41–7.50 (m, 4 H, ArH), 7.70 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9 (3× CH_3), 34.6 (C), 51.3 (CH_3), 116.7 (CH), 125.7 (2× CH), 127.8 (2× CH), 131.5 (C), 144.5 (CH), 153.5 (C), 167.2 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 218 (20) $[M]^+$, 203 (100) $[M^+ – Me]$, 128 (10).

Methyl 3-(4-Methoxyphenyl)propenoate (5g): By following GP1, 4-methoxybenzaldehyde (**3g**, 202 mg, 1.48 mmol), methyl bromoacetate (**4a**, 217 mg, 1.42 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 18 mg, 0.08 mmol), Na_2CO_3 (232 mg, 2.18 mmol), and $HSi(OMe)_3$ (288 mg, 2.36 mmol) were combined in toluene (3.0 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5g** (186 mg, 65%; *E*/*Z*, 81:19) as a yellowish solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 6.32 (d, *J* = 15.9 Hz, 1 H, CH), 6.89–6.93 (m, 2 H, ArH), 7.47–7.50 (m, 2 H, ArH), 7.66 (d, *J* = 15.9 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.5 (CH_3), 55.2 (CH_3), 114.2 (2× CH), 115.2 (CH), 127.0 (C), 129.6 (2× CH), 144.4 (CH), 161.3

(C), 167.6 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 192 (71) $[M]^+$, 161 (100) $[M^+ – OMe]$, 133 (31) $[M^+ – CO_2Me]$, 89 (16).

Methyl 3-(3-Methoxyphenyl)propenoate (5h): By following GP1, 3-methoxybenzaldehyde (**3h**, 161 mg, 1.18 mmol), methyl bromoacetate (**4a**, 217 mg, 1.42 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 14 mg, 0.06 mmol), Na_2CO_3 (188 mg, 2.36 mmol), and $HSi(OMe)_3$ (288 mg, 2.36 mmol) were combined in toluene (2.4 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5h** (198 mg, 87%, *E*/*Z*, 83:17) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.82 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 6.44 (d, *J* = 16.0 Hz, 1 H, CH), 6.93–6.96 (m, 1 H, ArH), 7.04–7.06 (m, 1 H, ArH), 7.12–7.14 (m, 1 H, ArH), 7.29–7.34 (m, 1 H, ArH), 7.67 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.5 (CH_3), 55.1 (CH_3), 112.9 (CH), 116.0 (CH), 117.9 (CH), 120.6 (CH), 129.7 (CH), 135.6 (C), 144.6 (CH), 159.8 (C), 167.2 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 192 (81) $[M]^+$, 191 (20), 161 (100) $[M^+ – OMe]$, 133 (22) $[M^+ – CO_2Me]$, 118 (26), 90 (15), 89 (15), 77 (11).

Methyl 3-(2-Methoxyphenyl)propenoate (5i): By following GP1, 2-methoxybenzaldehyde (**3i**, 157 mg, 1.15 mmol), methyl bromoacetate (**4a**, 262 mg, 1.71 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 13 mg, 0.06 mmol), Na_2CO_3 (191 mg, 1.80 mmol), and $HSi(OMe)_3$ (273 mg, 2.23 mmol) were combined in toluene (2.4 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5i** (144 mg, 65%, *E*/*Z*, 87:13) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 3.90 (s, 3 H, CH_3), 6.55 (d, *J* = 16.2 Hz, 1 H, CH), 6.87–7.00 (m, 2 H, ArH), 7.33–7.39 (m, 1 H, ArH), 7.50–7.53 (m, 1 H, ArH), 8.01 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.4 (CH_3), 55.27 (CH_3), 111.0 (CH), 118.1 (CH), 120.5 (CH), 123.2 (C), 128.7 (CH), 131.4 (CH), 140.1 (CH), 158.2 (C), 167.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 192 (31) $[M]^+$, 161 (100) $[M^+ – OMe]$, 118 (21), 105 (17). $C_{11}H_{12}O_3$ (192.21): calcd. C 68.74, H 6.29; found C 68.54, H 6.14.

3-(3-Methoxy)phenylpropene Nitrile (5j): By following GP1, 3-methoxybenzaldehyde (**3h**, 208 mg, 1.53 mmol), bromoacetonitrile (220 mg, 1.84 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 14 mg, 0.06 mmol), Na_2CO_3 (197 mg, 1.86 mmol), and $HSi(OMe)_3$ (303 mg, 2.48 mmol) were combined in toluene (2.9 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5j** (165 mg, 84%; *E*/*Z*, 83:17) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.84 (s, 3 H, CH_3), 5.88 (d, *J* = 16.6 Hz, 1 H, CH), 6.94–7.14 (m, 3 H), 7.30–7.44 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 55.2 (CH_3), 96.5 (CH), 112.3 (CH), 116.7 (CH), 118.0 (C), 119.8 (CH), 130.0 (CH), 134.7 (C), 150.3 (CH), 159.8 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 159 (100) $[M]^+$, 158 (11), 131 (21), 130 (28), 129 (27), 128 (14) $[M^+ – OMe]$, 116 (28), 102 (21), 89 (37), 63 (15). $C_{10}H_9NO$ (159.19): calcd. C 75.45, H 5.70, N 8.80; found C 75.73, H 5.44, N 8.59.

Methyl 2-Methyl-3-(3-methoxyphenyl)propenoate (5k): By following GP1, 3-methoxybenzaldehyde (**3h**, 206 mg, 1.51 mmol), methyl 2-bromopropionate (307 mg, 1.84 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.07 mmol), Na_2CO_3 (240 mg, 2.26 mmol), and $HSi(OMe)_3$ (380 mg, 3.11 mmol) were combined in toluene (2.9 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5k** (168 mg, 54%; *E*/*Z*, 89:11) as a yellowish oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 1.5 Hz, 3 H, CH_3), 3.83 (s, 6 H, CH_3), 6.86–6.91 (m, 1 H), 6.92–6.95 (m, 1 H), 6.98–7.02 (m, 1 H), 7.29–7.35 (m, 1 H), 7.67 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 52.0 (CH_3), 55.1 (CH_3), 113.8 (CH), 115.0 (CH), 122.0 (CH), 128.4 (C), 129.3 (CH), 137.1 (C), 138.7 (CH), 159.3 (C), 169.0 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 206 (72) $[M]^+$, 175 (25) $[M^+ – OMe]$, 146 (100) $[M^+ – CO_2Me]$, 131 (22), 115 (33), 103 (28), 91 (23).

Methyl 3-(2-Furanyl)propenoate (5l): By following GP1, furan-2-carbaldehyde (**3l**, 155 mg, 1.61 mmol), methyl bromoacetate (**4a**, 296 mg, 1.93 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 18 mg, 0.08 mmol), Na_2CO_3 (256 mg, 2.41 mmol), and $HSi(OMe)_3$ (393 mg, 3.22 mmol) were combined in toluene (3.2 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5l** (177 mg, 72%; *E*/*Z*, 71:29) as an orange oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.79 (s, 3 H, CH_3), 6.32 (d, *J* = 15.7 Hz, 1 H, CH), 6.46–6.48 (m, 1 H, ArH), 6.60–6.63 (m, 1 H, ArH), 7.44 (d, *J* = 15.7 Hz, 1 H, CH), 7.48–7.49 (m, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.6 (CH_3), 112.2 (CH), 114.7 (CH), 115.3 (CH), 131.1 (CH), 144.7 (CH), 150.8 (C), 167.4 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 152 (50) $[M]^+$, 121 (100) $[M^+ – OMe]$, 65 (43).

Methyl 3-(2-Thienyl)propenoate (5m): By following GP1, 2-thienylcarbaldehyde (**3m**, 204 mg, 1.82 mmol), methyl bromoacetate (**4a**, 335 mg, 2.19 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 21 mg, 0.09 mmol), Na_2CO_3 (289 mg, 2.73 mmol), and $HSi(OMe)_3$ (445 mg, 3.64 mmol) were combined in toluene (3.6 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5m** (265 mg, 87%; *E*/*Z*, 86:14) as a reddish oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.80 (s, 3 H, CH_3), 6.25 (d, *J* = 15.7 Hz, 1 H, CH), 7.04–7.08 (m, 1 H, ArH), 7.25–7.27 (m, 1 H, ArH), 7.37–7.39 (m, 1 H, ArH), 7.80 (dt, *J* = 15.7 Hz, *J* = 0.7 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.5 (CH_3), 116.3 (CH), 127.9 (CH), 128.3 (CH), 130.8 (CH), 137.1 (CH), 139.3 (C), 167.1 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 168 (60) $[M]^+$, 137 (100) $[M – OMe]^+$, 109 (40) $[M – CO_2Me]^+$, 65 (18).

Methyl 3-(2-Benzofuranyl)propenoate (5n): By following GP1, benzofuran-2-carbaldehyde (**3n**, 250 mg, 1.71 mmol), methyl bromoacetate (**4a**, 314 mg, 2.05 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 20 mg, 0.09 mmol), Na_2CO_3 (272 mg, 2.57 mmol), and $HSi(OMe)_3$ (418 mg, 3.42 mmol) were combined in toluene (3.4 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5n** (269 mg, 78%; *E*/*Z*, 74:26) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.83 (s, 3 H, CH_3), 6.59 (d, *J* = 15.6 Hz, 1 H, CH), 6.90–6.95 (m, 1 H, ArH), 7.22–7.28 (m, 1 H, ArH), 7.33–7.40 (m, 1 H, ArH), 7.45–7.52 (m, 1 H, ArH), 7.54–7.61 (m, 2 H, ArH, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.7 (CH_3), 111.1 (CH), 111.3 (CH), 118.3 (CH), 121.6 (CH), 123.2 (CH), 126.3 (CH), 128.2 (C), 131.3 (CH), 152.1 (C), 155.4 (C), 167.0 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 202 (82) $[M]^+$, 171 (100) $[M^+ – OMe]$, 143 (16) $[M^+ – CO_2Me]$, 115 (47), 89 (12). $C_{12}H_{10}O_3$ (202.21): calcd. C 71.28, H 4.98; found C 71.22, H 5.15.

Methyl 3-(2-Benzothiophenyl)propenoate (5o): By following GP1, benzothiophene-2-carbaldehyde (**3o**, 146 mg, 0.90 mmol), methyl bromoacetate (**4a**, 165 mg, 1.08 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 10 mg, 0.05 mmol), Na_2CO_3 (143 mg, 1.35 mmol), and $HSi(OMe)_3$ (220 mg, 1.80 mmol) were combined in toluene (1.8 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5o** (172 mg, 88%; *E*/*Z*, >99:1) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 6.32 (d, *J* = 15.6 Hz, 1 H, CH), 7.36–7.40 (m, 2 H, ArH), 7.47–7.48 (m, 1 H, ArH), 7.75–7.82 (m, 2 H, ArH), 7.86–7.92 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.8 (CH_3), 119.0 (CH), 122.4 (CH), 124.4 (CH), 124.8 (CH), 126.2 (CH), 128.7 (CH), 137.8 (CH), 139.4 (C), 139.5 (C), 140.1 (C), 166.9 (C=O) ppm. MS (EI,

70 eV): *m*/*z* (%) = 218 (100) $[M]^+$, 187 (94) $[M^+ – OMe]$, 159 (19) $[M^+ – CO_2Me]$, 158 (25), 115 (85), 79 (16).

Methyl 3-(Quinolin-2-yl)propenoate (5p): By following GP1, quinoline-2-carbaldehyde (**3p**, 295 mg, 1.88 mmol), methyl bromoacetate (**4a**, 345 mg, 2.26 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 21 mg, 0.09 mmol), Na_2CO_3 (299 mg, 2.82 mmol), and $HSi(OMe)_3$ (459 mg, 3.76 mmol) were combined in toluene (3.8 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5p** (90 mg, 22%; *E*/*Z*, 95:5) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, CH_3), 7.03 (d, J = 16.0 Hz, 1 H, CH), 7.56–7.60 (m, 1 H, ArH), 7.62–7.64 (m, 1 H, ArH), 7.74–7.78 (m, 1 H, ArH), 7.82–7.85 (m, 1 H, ArH), 7.93 (d, J = 16.0 Hz, 1 H, CH), 8.13–8.16 (m, 1 H, ArH), 8.20–8.22 (m, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.9 (CH_3), 120.3 (CH), 123.2 (CH), 127.3 (CH), 127.5 (CH), 128.0 (C), 129.8 (CH), 130.0 (CH), 136.7 (CH), 144.3 (CH), 148.2 (C), 153.0 (C), 166.9 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 213 (66) $[M]^+$, 198 (16) $[M^+ – Me]$, 182 (85) $[M^+ – OMe]$, 155 (100), 154 (80) $[M^+ – CO_2Me]$, 129 (32), 128 (64), 127 (18), 101 (22), 77 (30).

Methyl 5-(5-Methylfur-2-yl)hex-2-enoate (5q): By following GP1, 3-(5-methylfur-2-yl)butanal (**3q**, 184 mg, 1.21 mmol), methyl bromoacetate (**4a**, 222 mg, 1.45 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 14 mg, 0.06 mmol), Na_2CO_3 (296 mg, 1.82 mmol), and $HSi(OMe)_3$ (296 mg, 2.42 mmol) were combined in toluene (2.4 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5q** (185 mg, 73%; *E*/*Z*, 79:21) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 1.25 (d, J = 7.0 Hz, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.33–2.44 (m, 1 H, CH_2), 2.55–2.65 (m, 1 H, CH_2), 2.89–3.00 (m, 1 H, CH), 3.73 (s, 3 H, CH_3), 5.83–5.88 (m, 3 H, 2 ArH, CH), 6.87–6.97 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 13.4 (CH_3), 18.5 (CH_3), 32.3 (CH), 38.2 (CH_2), 51.3 (CH_3), 104.6 (CH), 105.6 (CH), 122.4 (CH), 147.0 (CH), 150.4 (C), 157.0 (C), 166.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 208 (4) $[M]^+$, 109 (100) $[M^+ – C_3H_4CO_2Me]$. IR [attenuated total reflectance (ATR)]: $\tilde{\nu}$ = 2951 (w), 1721 (vs), 1657 (m), 1613 (w), 1566 (w), 1436 (m), 1270 (m), 1216 (s), 1164 (vs), 1112 (m), 1019 (s), 957 (m), 940 (m), 780 (s), 720 (m) cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{16}O_3$ 208.1094; found 208.1090. $C_{12}H_{16}O_3$ (208.26): calcd. C 69.21, H 7.74; found C 69.19, H 7.65.

Methyl 4,4-(Diphenyl)but-2-enoate (5r): By following GP1, diphenylacetaldehyde (**3r**, 330 mg, 1.68 mmol), methyl bromoacetate (**4a**, 308 mg, 2.02 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 19 mg, 0.08 mmol), Na_2CO_3 (267 mg, 2.52 mmol), and $HSi(OMe)_3$ (411 mg, 3.36 mmol) were combined in toluene (3.3 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5r** (331 mg, 78%; *E*/*Z*, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 3.74 (s, 3 H, CH_3), 4.90 (d, J = 7.3 Hz, 1 H, CH), 5.76 (dd, J = 15.6 Hz, J = 1.5 Hz, 1 H, CH), 7.16–7.36 (m, 10 H, 10 ArH), 7.42–7.52 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 51.4 (CH_3), 53.3 (CH), 122.4 (CH), 126.8 (2× CH), 128.5 (4× CH), 128.6 (4× CH), 141.4 (2× C), 150.1 (CH), 166.7 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 252 (14) $[M]^+$, 221 (15) $[M^+ – OMe]$, 193 (93) $[M^+ – CO_2Me]$, 192 (100), 191 (39), 178 (29), 165 (33), 115 (93), 91 (18).

Methyl 5-Phenylpent-2-enoate (5s): By following GP1, 3-phenylpropanal (**3s**, 210 mg, 1.57 mmol), methyl bromoacetate (**4a**, 288 mg, 1.88 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 18 mg, 0.08 mmol), Na_2CO_3 (250 mg, 2.36 mmol), and $HSi(OMe)_3$ (384 mg, 3.14 mmol) were combined in toluene (3.1 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 20:1) afforded **5s** (216 mg, 72%; *E*/*Z*, 83:17) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 2.50–2.59 (m, 2 H, CH_2), 2.76–2.82 (t, J = 7.7 Hz, 2 H, CH_2), 3.74 (s, 3 H, CH_3), 5.87 (dt, J = 15.7 Hz, J = 1.6 Hz, 1 H, CH), 7.03 (dt, J = 15.7 Hz, J = 6.8 Hz, 1 H, CH), 7.17–7.25 (m, 3 H, ArH), 7.27–7.34 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 33.9 (CH_2), 34.3 (CH_2), 51.4 (CH_3), 121.4 (CH), 126.1 (CH), 128.3 (2× CH), 128.5 (2× CH), 140.7 (C), 148.3 (CH), 167.0 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 190 (1) $[M]^+$, 158 (8) $[M^+ – OMe]$, 130 (15) $[M^+ – CO_2Me]$, 91 (100).

Methyl Non-2-enoate (5t): By following GP1, heptanal (**3t**, 181 mg, 1.59 mmol), methyl bromoacetate (**4a**, 292 mg, 1.91 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 18 mg, 0.079 mmol), Na_2CO_3 (253 mg, 2.39 mmol), and $HSi(OMe)_3$ (389 mg, 3.18 mmol) were combined in toluene (3.2 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5t** (190 mg, 70%; *E*/*Z*, 79:21) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 0.86–0.92 (m, 3 H, CH_3), 1.24–1.51 (m, 8 H, CH_2), 2.16–2.24 (m, 2 H, CH_2), 3.73 (s, 3 H, CH_3), 5.82 (dt, J = 15.7 Hz, J = 1.6 Hz, 1 H, CH), 6.98 (dt, J = 15.7 Hz, J = 7.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 14.0 (CH_3), 22.5 (CH_2), 27.9 (CH_2), 28.7 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 51.3 (CH_3), 120.7 (CH), 149.5 (CH), 167.1 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 139 (34) $[M^+ – OMe]$, 138 (32), 113 (37) $[M^+ – C_4H_9]$, 101 (18), 100 (21), 96 (51), 87 (100), 81 (32), 74 (34), 69 (39), 55 (72).

Methyl Trideca-2,12-dienoate (5u): By following GP1, undec-10-enal (**3u**, 249 mg, 1.48 mmol), methyl bromoacetate (**4a**, 272 mg, 1.78 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.07 mmol), Na_2CO_3 (235 mg, 2.22 mmol), and $HSi(OMe)_3$ (362 mg, 2.96 mmol) were combined in toluene (3.0 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5u** (220 mg, 66%; *E*/*Z*, 80:20) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 1.25–1.50 (m, 12 H, CH_2), 2.00–2.09 (m, 2 H, CH_2), 2.16–2.24 (m, 2 H, CH_2), 3.73 (s, 3 H, CH_3), 4.90–5.04 (m, 2 H, CH_2), 5.75–5.89 (m, 2 H, CH), 6.98 (dt, J = 15.6 Hz, J = 7.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 27.9 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 32.1 (CH_2), 33.7 (CH_2), 51.2 (CH_3), 114.1 (CH), 120.7 (CH), 139.0 (CH), 149.6 (CH), 167.1 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 224 (1) $[M]^+$, 150 (33), 142 (17), 135 (15), 121 (22), 113 (65), 109 (28), 100 (37), 95 (51), 87 (49), 81 (95), 67 (63), 55 (100), 41 (76).

Methyl 5,7,7-Trimethyloct-2-enoate (5v): By following GP1, 3,5,5-trimethylhexanal (**3v**, 213 mg, 1.50 mmol), methyl bromoacetate (**4a**, 275 mg, 1.80 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 17 mg, 0.08 mmol), Na_2CO_3 (238 mg, 2.25 mmol), and $HSi(OMe)_3$ (367 mg, 3.00 mmol) were combined in toluene (3.0 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 10:1) afforded **5v** (219 mg, 1.10 mmol, 74%; *E*/*Z*, 78:22) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer): δ = 0.90 (s, 9 H, 3× CH_3), 0.92–0.97 (m, 3 H, CH_3), 1.00–1.31 (m, 2 H, CH_2), 1.58–1.77 (m, 1 H, CH), 2.00–2.32 (m, 2 H, CH_2), 3.74 (s, 3 H, CH_3), 5.82 (dt, J = 15.5 Hz, J = 1.5 Hz, 1 H, CH), 6.95 (dt, J = 15.6 Hz, J = 7.5 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 22.3 (CH_3), 28.8 (CH), 29.8 (3× CH_3), 30.9 (C), 41.8 (CH_2), 50.3 (CH_2), 51.1 (CH_3), 121.9 (CH), 148.3 (CH), 166.7 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 2953 (m), 2905 (m), 2869 (w), 1724 (vs), 1657 (m), 1468 (m), 1436 (m), 1395 (w), 1363 (m), 1309 (s), 1270 (w), 1226 (w), 1195 (s), 1162 (s), 1128 (m), 1101 (m), 1043 (m), 982 (s), 921 (m), 816 (m), 718 (m) cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{22}O_2$ 198.1614; found 198.1617.

Methyl 6-(5,5-Dimethyl-1,3-dioxanyl)-hex-2-enoate (5w): By following GP1, 4-(5,5-dimethyl-1,3-dioxanyl)butanal (**3w**, 266 mg,

1.43 mmol), methyl bromoacetate (**4a**, 262 mg, 1.72 mmol), 2-phenylisophosphindoline 2-oxide (**2**, 16 mg, 0.07 mmol), Na_2CO_3 (227 mg, 2.15 mmol), and $HSi(OMe)_3$ (349 mg, 2.86 mmol) were combined in toluene (2.9 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 5:1) afforded **5w** (243 mg, 70%; *E*/*Z*, 81:19) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ = 0.71 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.53–1.72 (m, 4 H, CH_2), 2.18–2.26 (m, 2 H, CH_2), 3.38–3.44 (m, 2 H, OCH_2), 3.56–3.61 (m, 2 H, OCH_2), 3.71 (s, 3 H, CH_3), 4.40–4.45 (m, 1 H, CH), 5.82 (dt, J = 15.6 Hz, J = 1.6 Hz, 1 H, CH), 6.96 (dt, J = 15.6 Hz, J = 6.9 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, major isomer): δ = 21.6 (CH_3), 22.1 (CH_2), 22.8 (CH_3), 29.9 (C), 31.8 (CH_2), 34.0 (CH_2), 51.1 (CH_3), 77.0 (2× CH_2), 101.5 (CH), 121.0 (CH), 148.9 (CH), 166.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 242 (1) $[M]^+$, 241 (8), 141 (21), 125 (52), 115 (100), $[M^+ - C_7H_{11}O_2]$, 97 (13), 81 (17), 69 (73), 56 (42). IR (ATR): $\tilde{\nu}$ = 2952 (m), 2846 (w), 1721 (vs), 1656 (m), 1436 (m), 1394 (w), 1312 (m), 1270 (s), 1195 (s), 1165 (s), 1132 (vs), 1110 (s), 1039 (m), 1017 (s), 980 (s), 940 (w), 923 (m), 855 (m), 817 (m), 784 (s), 719 (m), 665 (m) cm^{-1}. $C_{13}H_{22}O_4$ (242.31): calcd. C 64.44, H 9.15; found C 64.06, H 9.18.

General Procedure (GP2) for the Asymmetric Catalytic Wittig Reaction, Compound 7: A 15 mL Ace pressure tube that was equipped with a stir bar was charged with the phosphane or phosphane oxide (0.05 mmol, 5 mol-%), triketone **6** (0.5 M in toluene, 1.0 mmol, 1.0 equiv.), Na_2CO_3 (1.5 equiv., 1.5 mmol), and $HSi(OMe)_3$ (2.0 mmol, 2.0 equiv.). The tube was then purged with argon and sealed with an O-ring cap, and the reaction mixture was heated at 125 °C for 20 h. After cooling to 23 °C, the reaction mixture was filtered through a short plug of silica (ethyl acetate) and then purified by flash column chromatography [SiO_2; cyclohexane/ethyl acetate (EtOAc)].

Synthesis of (*R*)-Bis-nor Wieland–Miescher Ketone (*R*-7): By following GP2, (1*R*,1′*R*,2*S*,2′*S*)-2,2′-di-*tert*-butyl-2,3,2′,3′-tetrahydro-1*H*,1′*H*-(1,1′)biisophosphindolyl [(*R*,*R*,*S*,*S*)-DuanPhos, **13**, 10 mg, 0.026 mmol, 5 mol-%), Na_2CO_3 (80 mg, 0.75 mmol), carbonyl compound **6** (128 mg, 0.518 mmol), and $HSi(OMe)_3$ (125 mg, 1.02 mmol) were combined in toluene (1.1 mL). Purification by flash chromatography (SiO_2; cyclohexane/EtOAc, 1:1) afforded product (*R*)-**7** (39 mg, 50%, 62%*ee*) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 2.28–2.64 (m, 3 H, CH_2), 2.91–3.20 (m, 3 H, CH_2), 5.97 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.2 (CH_3), 24.4 (CH_2), 38.3 (CH_2), 44.7 (CH_2), 56.7 (C), 126.1 (CH), 184.7 (C), 207.6 (C=O), 212.5 (C=O) ppm.

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