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P-Arylation of Dialkyl Phosphites and Secondary Phosphine Oxides with Arynes

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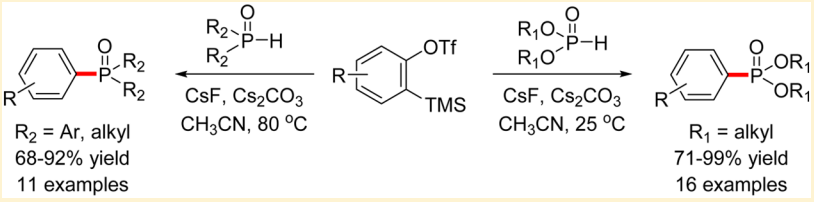
Supporting Information

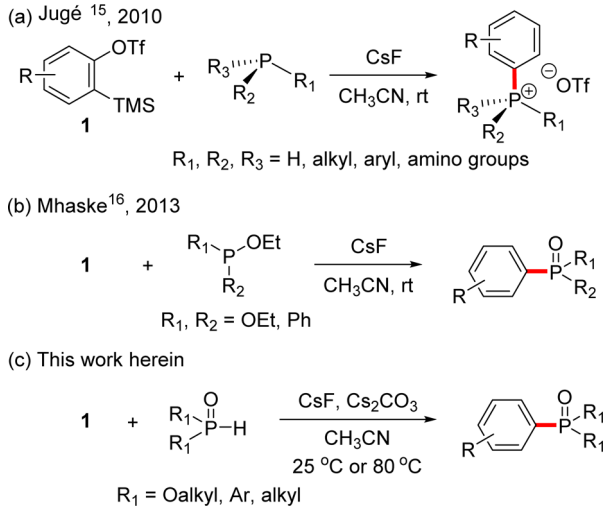


ABSTRACT: The novel P-arylation of dialkyl phosphites and secondary phosphine oxides with arynes has been achieved. The reactions produce dialkyl arylphosphonates in 71−99% yield and tertiary phosphine oxides in 68−92% yield under mild conditions.

Organophosphorus compounds have been of particular interest due to their broad applications in organic synthesis,[1] materials,[2] bioorganic and medical chemistry,[3] coordination chemistry and catalysis,[4] and flame retardants.[5] The synthesis of various organophosphorus compounds has been well-documented. For examples, the Michaelis−Arbuzov reaction provides an efficient protocol for the synthesis of alkylphosphonates,[6] and the transition-metal-catalyzed Arbuzov or Hirao C−P bond construction reaction has been developed for the synthesis of arylphosphonates and their derivatives.[7] It is noteworthy that trivalent arylphosphines, which have been widely used in metal-catalyzed reactions as ligands[8] and organic synthesis,[9] can be facilely prepared by a reduction of phosphine oxides.[10]

With the above background and our recent investigations on the behaviors of arynes,[11] we became interested in studying transition-metal-free P-arylation of organophosphorus compounds under mild conditions. Arynes undergo facile insertion into various σ-bonds for the formation of carbon−carbon and carbon−heteroatom bonds due to the strong electrophilicity of the highly strained carbon−carbon triple bond.[12,13] Recently, various transition-metal-free C−P bond formation reactions via arynes have been well-developed.[14−17] In 2010, Jugé and co-workers reported an arylation of phosphines with arynes generated *in situ* from 2-(trimethylsilyl)aryl triflates (Kobayashi precursors[18]) for the synthesis of quaternary and P-stereogenic phosphonium triflates (Scheme 1a).[15] In 2013, Mhaske and co-workers reported an arylation of P(III) nucleophiles for the synthesis of aryl-phosphonates, aryl-phosphinates, and aryl-phosphine oxides via the Michaelis−Arbuzov type reaction involving arynes using Kobayashi precursors (Scheme 1b).[16] However, to our knowledge, the arylation of dialkyl phosphites and secondary phosphine oxides with arynes was rarely investigated. Mhaske and co-workers described that the reaction of diethyl phosphite with benzyne afforded diethyl phenylphosphonate only in trace amounts.[16] It is noteworthy that Jugé and co-workers recently described one example of the *O*-bromophenylation of a secondary phosphine oxide using 1,2-dibromobenzene as the aryne precursor with *n*-BuLi at −78 °C.[17] Herein, we report a novel P-arylation of dialkyl phosphites and secondary phosphine oxides with arynes, which affords dialkyl arylphosphonates and tertiary phosphine oxides in good to high yields under mild conditions (Scheme 1c). In addition, the reaction mechanism has also been investigated.

Scheme 1. P-Arylation via Arynes Using Kobayashi Precursors



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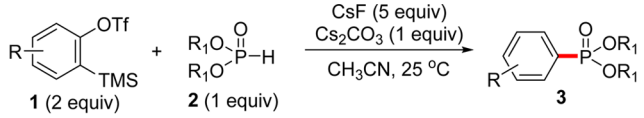
We first carried out the reactions of Kobayashi benzyne precursor **1a** with diethyl phosphite **2a** in the presence of CsF or KF/18-crown-6 in CH_3CN or THF at room temperature (25 °C), while the desired diethyl phenylphosphonate **3a** was obtained in poor yields. We then turned to the addition of inorganic bases based on previous research[19] and our recent study,[11b] which described that a few aryne reactions required their promotion. Thus, we envisioned that the addition of an inorganic base would enhance the nucleophilicity of dialkyl phosphites. To test this hypothesis, we then examined the reaction of **1a** with **2a** in the presence of CsF with the addition of Cs_2CO_3. To our delight, the yield of **3a** significantly increased. With Cs_2CO_3 (1 equiv) as the base and CsF (5 equiv) as the fluoride source, the reaction of diethyl phosphite **2a** with benzyne precursor **1a** (2 equiv) in CH_3CN at 25 °C for 24 h afforded diethyl phenylphosphonate **3a** in a maximum 85% isolated yield (Table 1).

We then set out to explore the generality of this method for P-arylation of dialkyl phosphites with aryne precursors under the optimized conditions. The reactions of various arynes (generated from aryne precursors **1a–h**) with a variety of dialkyl phosphites **2** led to the formation of the desired products **3b–p** in 71–99% yields (Table 1), whereas treatment of diphenyl phosphite with **1a** gave the corresponding product in poor yield (<5%). To our surprise, P-arylation with an unsymmetrical aryne generated from 4-methoxy-2-(trimethylsilyl)phenyl triflate **1d** regioselectively afforded the *para* isomer (**3k** or **3l**) as a single product. In contrast, P-arylation with similarly unsymmetrical aryne (generated from **1e** or **1f**) produced **3m** or **3n** with two regioisomers (*meta*-**3**/*para*-**3** = 2:1), which is in good agreement with our recent studies on the insertion of arynes into the C–H and O–H bond.[11a,b] Similarly, both aryne precursor **1g** for 1,2-didehydronaphthalene and 4,6-dimethyl-substituted aryne precursor **1h** afforded the desired products **3o** (α/β = 2:1) and **3p**/**3p′** (1:4) with two regioisomers, respectively, which further suggested that these reactions involved an aryne mechanism. In contrast, the previously reported P-arylation of triethyl phosphite with **1g** gave the β-isomer (α/β = 1:40) regioselectively.[16] This difference in regioselectivity might be explained by the steric hindrance of the bulky triethyl phosphite.

Having succeeded in P-arylation of dialkyl phosphites, we were encouraged to explore the P-arylation of secondary phosphine oxides. However, the reaction of diphenylphosphine oxide **4a** with benzyne precursor **1a** under the same conditions gave the desired triphenylphosphine oxide **5a** in only 19% yield. When the reaction was carried out with excess amounts of Cs_2CO_3 (3 equiv) at 80 °C, the yield of **5a** was significantly increased (84% yield). Thus, the arylation of diarylphosphine oxides **4a–c** with aryne precursors **1a–c** led to the formation of the desired products **5b–i** in 68–90% yields under the same conditions (Table 2). It is noteworthy that sterically hindered triarylphosphine oxides **5h** and **5i** can be obtained in good yields. Similarly, the reaction of dialkylphosphine oxide **4d** and **4e** with benzyne smoothly afforded dialkyl(phenyl)phosphine oxide **5j** and **5k** in high yield, respectively.

To elucidate the hydrogen source of the *ortho*-position on **3** or **5**, we carried out deuterium labeling studies (Scheme 2a).

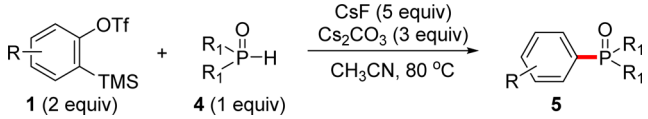
Table 1. Scope of the Reactions of Dialkyl Phosphites with Arynes[a,b,c]



entry	aryne precursor	product(s), yield
1	**1a**, R = H **1b**, R = Me	**3a**, R = H, R_1 = Et, (85%)
2		**3b**, R = H, R_1 = Me, (83%)
3		**3c**, R = H, R_1 = ^{i}Pr, (71%)
4		**3d**, R = H, R_1 = Bu, (88%)
5		**3e**, R = H, R_1 = ^{i}Bu, (99%)
6		**3f**, R = H, R_1 = Bn, (78%)
7		**3g**, R = Me, R_1 = Et, (75%)
8		**3h**, R = Me, R_1 = ^{i}Bu, (80%)
9	**1c**	**3i**, R_1 = Et, (77%)
10		**3j**, R_1 = ^{i}Bu, (84%)
11	**1d**: R = OMe	**3k**, R = OMe, R_1 = Et, (85%, *para* only)
12	**1e**: R = Me	**3l**, R = OMe, R_1 = ^{i}Bu, (97%, *para* only)
13	**1f**: R = ^{t}Bu	**3m**, R = Me, R_1 = ^{i}Bu, (98%, *m*/*p* = 2:1)
14		**3n**, R = ^{t}Bu, R_1 = ^{i}Bu, (97%, *m*/*p* = 2:1)
15	**1g**	**3o**, (86%, α/β = 2:1)
16	**1h**	(98%, **3p**/**3p′** = 1:4)

[a]Reaction conditions: **1** (0.68 mmol), **2** (0.34 mmol), CsF (1.7 mmol), Cs_2CO_3 (0.34 mmol), CH_3CN (3.4 mL), 24–48 h. [b]Isolated yield based on **2**. [c]Isomer ratio was determined by ^{1}H or ^{31}P NMR.

Table 2. Scope of the Reactions of Secondary Phosphine Oxides with Arynes[a,b]



entry	R_1	aryne precursor	product	yield (%)
1	phenyl	**1a**	**5a**	84
2		**1b**	**5b**	80
3		**1c**	**5c**	68
4	4-Me-phenyl	**1a**	**5d**	90
5		**1b**	**5e**	84
6		**1c**	**5f**	79
7	3,5-dimethyl-phenyl	**1a**	**5g**	82
8		**1b**	**5h**	72
9		**1c**	**5i**	79
10	butyl	**1a**	**5j**	92
11	cyclopentyl	**1a**	**5k**	85

[a]Reaction conditions: **1** (0.68 mmol), **2** (0.34 mmol), CsF (1.7 mmol), Cs_2CO_3 (1.0 mmol), CH_3CN (3.4 mL), 15 h. [b]Isolated yield based on **4**.

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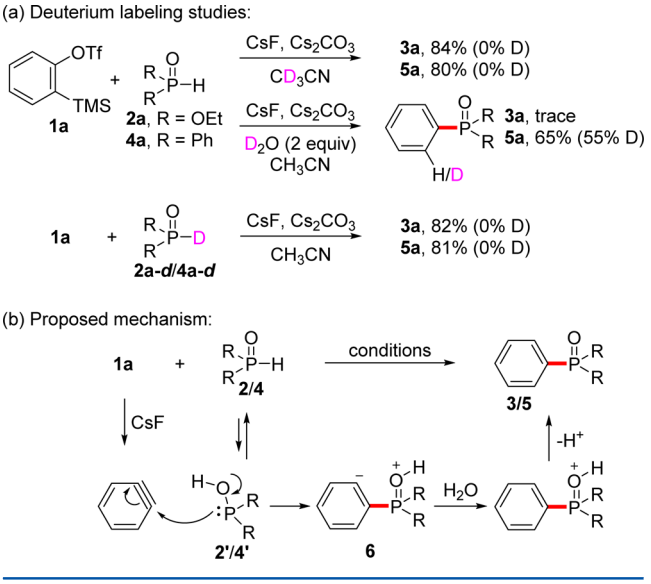
Scheme 2. Mechanistic Study



When **2a** or **4a** reacted with benzyne in acetonitrile-d_3, **3a-*d*** or **5a-*d*** was not detected. When the reaction was performed with the addition of D_2O (2 equiv), the desired product **5a** was formed in 65% yield with 55% D incorporation at the *ortho*-position, while only trace amounts of **3a** were detected under the same conditions. We then carried out the reaction of **1a** with **2a-*d*** or **4a-*d***, and the reaction afforded **3a** or **5a** with no incorporation of D at the *ortho*-position. These observations clearly indicated that trace amounts of water in hygroscopic CsF/Cs_2CO_3 served as the proton source reacting with aryl anion intermediate **6** formed by the nucleophilic addition of phosphine to benzyne (Scheme 2b). Similarly, previous Michaelis–Arbuzov-type reaction involving arynes showed that the hydrated water of TBAF served as the proton source.[14c] At this point, the base Cs_2CO_3, which is stronger than CsF, probably increases the concentration of the P(III) form through the tautomerization of the P(V) phosphinylidene **2**/**4**.[20] The experimental results of the reactions of dialkyl phosphites (up to 99% yield, 25 °C), diphenyl phosphite (<5% yield, 25 °C), or diarylphosphine oxides (up to 90% yield, 80 °C, excess Cs_2CO_3) with benzyne indicate that initial tautomerization rates decrease in the order $Ar_2P(O)H/(PhO)_2P(O)H > (AlkO)_2P(O)H$, which are in good agreement with the literature.[20b]

In conclusion, we have developed a highly efficient P-arylation method of dialkyl phosphites and secondary phosphine oxides, which provides a facile protocol for the synthesis of arylphosphonates and tertiary phosphine oxides. This property of arynes should lead to new and useful applications in organic synthesis.

EXPERIMENTAL SECTION

General Details. All reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe/septa techniques. Acetonitrile was distilled from calcium hydride. THF was distilled from sodium. Petroleum ether refers to the petroleum fraction bp 40–60 °C. Commercial reagents were used without purification unless otherwise noted. Kobayashi aryne precursors **1** were prepared according to the literature.[18] Flash chromatography was performed using the indicated solvent system on silica gel standard grade 60 (230–400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. ^{31}P NMR spectra were recorded on a 162 MHz spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF. Melting points are uncorrected. The known compounds **3a**,[16] **3b**,[16] **3c**,[7c] **3d**,[16] **3e**,[21] **3f**,[7c] **3g**,[7d] **3i**,[16] **3k**,[7c] **5a**,[16] **5c**,[16] **5d**,[7g] **5g**,[7f] and **5j**[22] showed characterization data in full agreement with previously reported data.

General Procedure for the Synthesis of Dialkyl Arylphosphonates 3. To a solution of 2-(trimethylsilyl)phenyl triflate **1a** (203 mg, 0.68 mmol) and diethyl phosphite **2a** (47 mg, 0.34 mmol) in acetonitrile (3.4 mL) was added cesium carbonate (111 mg, 0.34 mmol) and cesium fluoride (258 mg, 1.7 mmol) under a nitrogen atmosphere. The mixture was stirred at 25 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to give the pure product **3a** (62 mg, 85%).

General Procedure for the Synthesis of Tertiary Phosphine Oxides 5. To a solution of 2-(trimethylsilyl)phenyl triflate **1a** (203 mg, 0.68 mmol) and diphenylphosphine oxide **4a** (69 mg, 0.34 mmol) in acetonitrile (3.4 mL) was added cesium carbonate (326 mg, 1.0 mmol) and cesium fluoride (258 mg, 1.7 mmol) under a nitrogen atmosphere. The mixture was stirred at 80 °C for 15 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to give the pure product **5a** (79 mg, 84%).

*Diethyl Phenylphosphonate (**3a**).* Thick oil (62 mg, 85%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.75 (m, 2H), 7.57–7.52 (m, 1H), 7.50–7.42 (m, 2H), 4.20–4.01 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (CH, d, J = 3.0 Hz), 131.9 (CH, d, J = 9.9 Hz), 128.4 (CH, d, J = 14.7 Hz), 128.6 (C, d, J = 187 Hz), 62.3 (CH_2, d, J = 6.0 Hz), 16.4 (CH_3, d, J = 6.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.8.

*Dimethyl Phenylphosphonate (**3b**).* Thick oil (52 mg, 83%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.77 (m, 2H), 7.60–7.54 (m, 1H), 7.51–7.46 (m, 2H), 3.76 (d, J = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (CH, d, J = 3.1 Hz), 131.6 (CH, d, J = 9.8 Hz), 128.2 (CH, d, J = 15.1 Hz), 126.7 (C, d, J = 189 Hz), 52.4 (CH_3, d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.6.

*Diisopropyl Phenylphosphonate (**3c**).* Thick oil (58 mg, 71%):[7c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.75 (m, 2H), 7.57–7.48 (m, 1H), 7.48–7.40 (m, 2H), 4.81–4.56 (m, 2H), 1.36 (d, J = 6.2 Hz, 6H), 1.21 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9 (CH, d, J = 3.0 Hz), 131.7 (CH, d, J = 9.8 Hz), 130.0 (C, d, J = 188 Hz), 128.3 (CH, d, J = 15.0 Hz), 70.7 (CH, d, J = 5.6 Hz), 24.1 (CH_3, d, J = 4.0 Hz), 23.8 (CH_3, d, J = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.6.

*Dibutyl Phenylphosphonate (**3d**).* Thick oil (81 mg, 88%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.54–7.52 (m, 1H), 7.46–7.42 (m, 2H), 4.12–3.95 (m, 4H), 1.69–1.60 (m, 4H), 1.39 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3 (CH, d, J = 3.0 Hz), 131.7 (CH, d, J = 9.7 Hz), 128.4 (CH, d, J = 15.4 Hz), 128.3 (C, d, J = 188 Hz), 65.8 (CH_2, d, J = 5.7 Hz), 32.4 (CH_2, d, J = 6.5 Hz), 18.7 (CH_2), 13.5 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.8.

*Diisobutyl Phenylphosphonate (**3e**).* Thick oil (91 mg, 99%):[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.77 (m, 2H), 7.58–7.51 (m, 1H), 7.48–7.43 (m, 2H), 3.91–3.71 (m, 4H), 1.99–1.89 (m, 2H), 0.92 (dd, J = 6.7, 1.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (CH, d, J = 3.0 Hz), 131.7 (CH, d, J = 9.7 Hz), 129.3 (C, d, J = 188 Hz), 128.4 (CH, d, J = 15.0 Hz), 71.9 (CH_2, d, J = 6.0 Hz), 29.2 (CH, d, J = 6.7 Hz), 18.7 (CH_3, d, J = 0.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.5.

*Dibenzyl Phenylphosphonate (**3f**).* Thick oil (90 mg, 78%):[7c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 2H), 7.58–7.51 (m, 1H), 7.46–7.42 (m, 2H), 7.34–7.27 (m, 10H), 5.14–5.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (CH, d, J = 6.9 Hz), 132.4 (CH, d, J = 3.1 Hz), 131.8 (CH, d, J = 10.0 Hz), 128.8 (C, d, J = 190 Hz), 128.6 (CH), 128.4 (CH), 128.3 (CH, d, J = 15.0 Hz), 127.9 (C, d, J = 189 Hz), 67.5 (CH_2, d, J = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7.

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J. Org. Chem. 2016, 81, 276–281

*Diethyl (3,4-Dimethylphenyl)phosphonate (**3g**).* Thick oil (62 mg, 75%):[7d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 13.2 Hz, 1H), 7.52 (dd, J = 13.3, 7.8 Hz, 1H), 7.21 (dd, J = 7.7, 4.4 Hz, 1H), 4.17−3.98 (m, 4H), 2.29 (s, 6H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6 (C, d, J = 3.3 Hz), 136.9 (C, d, J = 15.3 Hz), 132.8 (CH, d, J = 10.5 Hz), 129.7 (CH, d, J = 15.8 Hz), 129.3 (CH, d, J = 9.7 Hz), 125.3 (C, d, J = 189 Hz), 61.9 (CH_2, d, J = 5.3 Hz), 19.9 (CH_3), 19.6 (CH_3), 16.3 (CH_3, d, J = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.9.

*Diisobutyl (3,4-Dimethylphenyl)phosphonate (**3h**).* Thick oil (81 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 13.2 Hz, 1H), 7.50 (dd, J = 11.8, 7.6 Hz, 1H), 7.20 (dd, J = 7.7, 4.4 Hz, 1H), 3.86−3.69 (m, 4H), 2.29 (s, 6H), 1.97−1.90 (m, 2H), 0.91 (dd, J = 6.7, 2.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (C, d, J = 3.2 Hz), 136.8 (C, d, J = 15.4 Hz), 132.9 (CH, d, J = 10.4 Hz), 129.7 (CH, d, J = 15.7 Hz), 129.3 (CH, d, J = 9.5 Hz), 125.3 (C, d, J = 190 Hz), 71.8 (CH_2, d, J = 6.0 Hz), 29.2 (CH, d, J = 6.8 Hz), 19.9 (CH_3), 19.6 (CH_3), 18.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{27}PO_3Na$ 321.1590; Found 321.1595.

*Diethyl (2,5-Dimethylphenyl)phosphonate (**3i**).* Thick oil (63 mg, 77%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 14.7 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.16−7.10 (m, 1H), 4.21−3.99 (m, 4H), 2.51 (s, 3H), 2.33 (s, 3H), 1.32 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (C, d, J = 10.0 Hz), 134.9 (C, d, J = 14.9 Hz), 134.5 (CH, d, J = 10.5 Hz), 133.1 (CH, d, J = 3.1 Hz), 131.1 (CH, d, J = 15.7 Hz), 126.4 (C, d, J = 183 Hz), 61.8 (CH_2, d, J = 5.4 Hz), 20.9 (CH_3), 20.6 (CH_3), 16.3 (CH_3, d, J = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0.

*Diisobutyl (2,5-Dimethylphenyl)phosphonate (**3j**).* Thick oil (85 mg, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 16.2 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 7.16−7.10 (m, 1H), 3.88−3.71 (m, 4H), 2.51 (s, 3H), 2.34 (s, 3H), 1.98−1.91 (m, 2H), 0.93 (d, J = 6.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (C, d, J = 9.8 Hz), 134.9 (C, d, J = 14.9 Hz), 134.6 (CH, d, J = 10.5 Hz), 133.1 (CH, d, J = 3.1 Hz), 131.1 (CH, d, J = 15.6 Hz), 126.4 (C, d, J = 182 Hz), 71.7 (CH_2, d, J = 6.1 Hz), 29.2 (CH, d, J = 6.9 Hz), 20.8 (CH_3), 20.7 (CH_3, d, J = 3.4 Hz), 18.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{27}PO_3Na$ 321.1590; Found 321.1595.

*Diethyl (4-Methoxyphenyl)phosphonate (**3k**).* Thick oil (70 mg, 85%):[7c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 12.7, 8.7 Hz, 2H), 6.99−6.94 (m, 2H), 3.84 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (C, d, J = 3.4 Hz), 133.7 (CH, d, J = 11.3 Hz), 119.6 (C, d, J = 195 Hz), 114.0 (CH, d, J = 16.0 Hz), 61.9 (CH_2, d, J = 6.5 Hz), 55.3 (CH_3), 16.3 (CH_3, d, J = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7.

*Diisobutyl (4-Methoxyphenyl)phosphonate (**3l**).* Thick oil (99 mg, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 14.9, 9.1 Hz, 2H), 6.96 (dd, J = 11.7, 2.9 Hz, 2H), 3.84 (s, 3H), 3.83−3.69 (m, 4H), 1.96−1.90 (m, 2H), 0.91 (dd, J = 6.7, 2.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (C, d, J = 3.4 Hz), 133.7 (CH, d, J = 11.2 Hz), 119.6 (C, d, J = 196 Hz), 113.4 (CH, d, J = 16.0 Hz), 71.8 (CH_2, d, J = 6.0 Hz), 55.3 (CH_3), 29.2 (CH, d, J = 6.5 Hz), 18.7 (CH_3, d, J = 1.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{25}PO_4Na$ 323.1383; Found 323.1390.

*Diisobutyl m-Tolylphosphonate (**m-3m**) and Diisobutyl p-Tolylphosphonate (**p-3m**).* Thick oil (95 mg, 98%). Two isomers in ∼2:1 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) ***m*-3m**: δ 7.62 (d, J = 13.7 Hz, 1H), 7.56 (dd, J = 7.2, 1.6 Hz, 1H), 7.34 (dd, J = 5.3, 4.2 Hz, 2H), 3.85−3.69 (m, 4H), 2.39 (s, 3H), 2.02−1.87 (m, 2H), 0.91 (dd, J = 6.7, 2.0 Hz, 12H); ***p*-3m**: δ 7.68 (dd, J = 13.1, 8.1 Hz, 2H), 7.29−7.24 (m, 2H), 3.86−3.71 (m, 4H), 2.39 (s, 3H), 2.02−1.87 (m, 2H), 0.92 (dd, J = 6.7, 2.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) ***m*-3m**: δ 138.2 (C, d, J = 15.0 Hz), 133.0 (CH, d, J = 3.2 Hz), 132.3 (CH, d, J = 9.9 Hz), 128.8 (CH, d, J = 9.5 Hz), 128.5 (C, d, J = 187 Hz), 128.3 (CH, d, J = 15.7 Hz), 71.9 (CH_2, d, J = 6.1 Hz), 29.2 (CH, d, J = 6.7 Hz), 21.6 (CH_3), 18.7 (CH_3, d, J = 0.9 Hz); ***p*-3m**: δ 142.9 (C, d, J = 3.1 Hz), 131.8 (CH, d, J = 10.1 Hz), 129.2 (CH, d, J = 15.4 Hz), 125.1 (C, d, J = 191 Hz), 71.9 (CH_2, d, J = 6.1 Hz), 29.2 (CH, d, J = 6.7 Hz), 21.3 (CH_3), 18.7 (CH_3, d, J = 0.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) ***m*-3m**: δ 19.0; ***p*-3m**: δ 19.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{25}PO_3Na$ 307.1434; Found 307.1438.

*Diisobutyl (3-(tert-Butyl)phenyl)phosphonate (**m-3n**) and Diisobutyl (4-(tert-Butyl)phenyl)phosphonate (**p-3n**).* Thick oil (108 mg, 97%). Two isomers in ∼2:1 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) ***m*-3n**: δ 7.81 (d, J = 15.9 Hz, 1H), 7.61−7.54 (m, 2H), 7.39−7.34 (m, 1H), 3.86−3.72 (m, 4H), 1.98−1.88 (m, 2H), 1.31 (s, 9H), 0.90 (dd, J = 6.5, 1.1 Hz, 12H); ***p*-3n**: δ 7.71 (dd, J = 12.9, 8.5 Hz, 2H), 7.47−7.44 (m, 2H), 3.88−3.70 (m, 4H), 2.00−1.86 (m, 2H), 1.32 (s, 9H), 0.91 (dd, J = 6.7, 1.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) ***m*-3n**: δ 151.4 (C, d, J = 13.9 Hz), 129.3 (CH, d, J = 3.1 Hz), 128.8 (CH, d, J = 9.6 Hz), 128.6 (CH, d, J = 10.6 Hz), 128.1 (CH, d, J = 15.8 Hz), 127.8 (C, d, J = 186 Hz), 71.8 (CH_2, d, J = 6.4 Hz), 31.1 (CH_3), 29.1 (CH, d, J = 6.8 Hz), 18.7 (CH_3, d, J = 1.6 Hz); ***p*-3n**: δ 155.7 (C, d, J = 3.2 Hz), 131.6 (CH, d, J = 10.1 Hz), 125.6 (C, d, J = 189 Hz), 125.4 (CH, d, J = 15.2 Hz), 71.8 (CH_2, d, J = 6.2 Hz), 31.2 (CH_3), 29.1 (CH, d, J = 6.8 Hz), 18.7 (CH_3, d, J = 1.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) ***m*-3n**: δ 19.3; ***p*-3n**: δ 19.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{31}PO_3Na$ 349.1903; Found 349.1900.

*Diisobutyl Naphthalen-1-ylphosphonate (**α-3o**) and Diisobutyl Naphthalen-2-ylphosphonate (**β-3o**).* Thick oil (94 mg, 86%). Two isomers in ∼2:1 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) ***α*-3o**: δ 8.52 (d, J = 8.5 Hz, 1H), 8.29−8.20 (m, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 25.1 Hz, 1H), 7.76 (d, J = 19.4 Hz, 1H), 7.59−7.49 (m, 2H), 3.95−3.86 (m, 4H), 2.06−1.89 (m, 2H), 0.94 (dd, J = 6.7, 2.8 Hz, 12H); ***β*-3o**: δ 8.43 (d, J = 15.2 Hz, 1H), 7.98−7.86 (m, 3H), 7.82−7.70 (m, 1H), 7.62−7.49 (m, 2H), 3.82−3.73 (m, 4H), 2.05−1.91 (m, 2H), 0.90 (dd, J = 6.7, 2.4 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) ***α*-3o**: δ 134.6 (C, d, J = 9.1 Hz), 133.6 (C, d, J = 1.5 Hz), 133.6 (CH, d, J = 2.7 Hz), 132.7 (CH, d, J = 2.4 Hz), 128.7 (CH, d, J = 1.9 Hz), 128.2 (CH), 127.4 (CH), 126.6 (CH, d, J = 15.4 Hz), 124.7 (C, d, J = 187 Hz), 124.5 (CH, d, J = 16.1 Hz), 72.1 (CH_2, d, J = 5.9 Hz), 29.1 (CH, d, J = 6.8 Hz), 18.8 (CH_3); ***β*-3o**: δ 135.0 (C), 134.0 (C, d, J = 10.2 Hz), 132.4 (CH, d, J = 16.6 Hz), 128.9 (CH), 128.3 (CH, d, J = 18.6 Hz), 128.29 (CH), 127.8 (CH), 126.8 (CH), 126.5 (CH, d, J = 9.8 Hz), 125.4 (C, d, J = 178 Hz), 72.1 (CH_2, d, J = 5.9 Hz), 29.2 (CH, d, J = 6.9 Hz), 18.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) ***α*-3o**: δ 19.1; ***β*-3o**: δ 19.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{25}PO_3Na$ 343.1434; Found 343.1435.

*Diisobutyl (3,5-Dimethylphenyl)phosphonate (**3p**) and Diisobutyl (2,4-Dimethylphenyl)phosphonate (**3p′**).* Thick oil (99 mg, 98%). Two isomers in ∼1:4 ratio: ^{1}H NMR (400 MHz, $CDCl_3$) **3p**: δ 7.80 (dd, J = 14.1, 8.3 Hz, 1H), 7.07−7.05 (m, 2H), 3.90−3.68 (m, 4H), 2.53 (s, 3H), 2.35 (s, 3H), 1.99−1.89 (m, 2H), 0.93 (dd, J = 6.7, 1.9 Hz, 12H); **3p′**: δ 7.42 (s, 1H), 7.39 (s, 1H), 7.16 (s, 1H), 3.88−3.70 (m, 4H), 2.35 (s, 6H), 2.00−1.90 (m, 2H), 0.93 (dd, J = 6.7, 1.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) **3p**: δ 142.8 (C, d, J = 3.1 Hz), 141.6 (C, d, J = 10.6 Hz), 134.1 (CH, d, J = 10.8 Hz), 132.0 (CH, d, J = 15.4 Hz), 126.1 (CH, d, J = 15.3 Hz), 125.1 (C, d, J = 108 Hz), 71.7 (CH_2, d, J = 6.1 Hz), 29.3 (CH, d, J = 6.7 Hz), 21.4 (CH_3), 21.1 (CH_3), 18.7 (CH_3); **3p′**: δ 138.1 (C, d, J = 15.8 Hz), 134.1 (C, d, J = 3.9 Hz), 129.4 (CH, d, J = 9.7 Hz), 127.9 (C, d, J = 187 Hz), 71.9 (CH_2, d, J = 6.0 Hz), 29.2 (CH, d, J = 6.7 Hz), 21.2 (CH_3), 18.7 (CH_3, d, J = 0.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) **3p**: δ 20.4; **3p′**: δ 19.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{27}PO_3Na$ 321.1590; Found 321.1595.

*Triphenylphosphine Oxide (**5a**).* White amorphous solid (79 mg, 84%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.61 (m, 6H), 7.58−7.52 (m, 3H), 7.51−7.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (C, d, J = 103 Hz), 132.0 (CH, d, J = 9.9 Hz), 131.9 (CH, d, J = 2.7 Hz), 128.5 (CH, d, J = 12.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1.

*(3,4-Dimethylphenyl)diphenylphosphine Oxide (**5b**).* White amorphous solid (83 mg, 80%): mp 113−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 4H), 7.55−7.49 (m, 3H), 7.47−7.42 (m, 4H), 7.32−7.27 (m, 1H), 7.2−7.19 (m, 1H), 2.30 (s, 3H), 2.27 (d, J = 7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2 (C, d, J = 2.9 Hz), 137.2 (C, d, J = 12.3 Hz), 133.4 (C, d, J = 100 Hz), 133.0 (CH, d, J = 9.8 Hz), 132.0 (CH, d, J = 9.9 Hz), 131.9 (CH, d, J = 2.7 Hz), 129.7

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J. Org. Chem. 2016, 81, 276−281

(CH, d, J = 2.8 Hz), 129.9 (C, d, J = 110 Hz), 129.6 (CH), 128.5 (CH, d, J = 12.1 Hz), 19.9 (CH_3), 19.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{19}PONa$ 329.1066; Found 329.1069.

*(2,5-Dimethylphenyl)diphenylphosphine Oxide (**5c**).* White amorphous solid (71 mg, 68%):[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.62 (m, 4H), 7.56−7.51 (m, 2H), 7.48−7.43 (m, 4H), 7.22 (d, J = 7.8 Hz, 1H), 7.17−7.14 (m, 1H), 6.88 (d, J = 14.4 Hz, 1H), 2.36 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0 (C, d, J = 8.1 Hz), 134.7 (C, d, J = 12.8 Hz), 133.9 (CH, d, J = 12.5 Hz), 132.9 (C, d, J = 104 Hz), 132.8 (CH, d, J = 2.7 Hz), 131.9 (CH, d, J = 9.7 Hz), 131.8 (CH), 131.7 (CH, d, J = 2.8 Hz), 130.4 (C, d, J = 103 Hz), 128.5 (CH, d, J = 12.0 Hz), 21.2 (CH_3, d, J = 4.7 Hz), 20.9 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7.

*Phenyldi-p-tolylphosphine Oxide (**5d**).* White amorphous solid (94 mg, 90%):[7g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.61 (m, 2H), 7.55−7.47 (m, 5H), 7.43−7.39 (m, 2H), 7.23 (d, J = 6.6 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3 (C, d, J = 2.6 Hz), 133.1 (C, d, J = 104 Hz), 132.3 (CH, d, J = 10.2 Hz), 132.1 (CH, d, J = 10.2 Hz), 131.8 (CH, d, J = 2.5 Hz), 129.3 (C, d, J = 106 Hz), 129.2 (CH, d, J = 12.5 Hz), 128.4 (CH, d, J = 12.1 Hz), 21.6 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3.

*(3,4-Dimethylphenyl)di-p-tolylphosphine Oxide (**5e**).* White amorphous solid (95 mg, 84%): mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.48 (m, 5H), 7.30−7.28 (m, 1H), 7.26−7.23 (m, 4H), 7.20−7.15 (m, 1H), 2.39 (s, 6H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1 (C, d, J = 2.5 Hz), 140.9 (C, d, J = 6.1 Hz), 137.0 (C, d, J = 12.2 Hz), 133.0 (C, d, J = 9.8 Hz), 132.1 (CH, d, J = 10.2 Hz), 131.3 (C, d, J = 146 Hz), 130.5 (C, d, J = 106 Hz), 129.7 (CH, d, J = 3.1 Hz), 129.5 (CH, d, J = 6.0 Hz), 129.1 (CH, d, J = 12.4 Hz), 21.6 (CH_3), 19.9 (CH_3), 19.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}PONa$ 357.1379; Found 357.1383.

*(2,5-Dimethylphenyl)di-p-tolylphosphine Oxide (**5f**).* White amorphous solid (90 mg, 79%): mp 146−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.49 (m, 4H), 7.27−7.24 (m, 4H), 7.21 (d, J = 7.7 Hz, 1H), 7.17−7.12 (m, 1H), 6.89 (d, J = 14.2 Hz, 1H), 2.40 (s, 6H), 2.36 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0 (C, d, J = 2.7 Hz), 139.9 (C, d, J = 8.1 Hz), 134.5 (C, d, J = 12.6 Hz), 133.9 (CH, d, J = 12.5 Hz), 132.6 (CH, d, J = 2.5 Hz), 131.9 (CH, d, J = 10.1 Hz), 131.7 (CH, d, J = 11.0 Hz), 130.9 (C, d, J = 102 Hz), 129.9 (C, d, J = 101 Hz), 129.2 (CH, d, J = 12.4 Hz), 21.6 (CH_3), 21.2 (CH_3, d, J = 4.6 Hz), 21.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}PONa$ 357.1379; Found 357.1383.

*Bis(3,5-dimethylphenyl)(phenyl)phosphine Oxide (**5g**).* White amorphous solid (93 mg, 82%):[7f] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.62 (m, 2H), 7.54−7.50 (m, 1H), 7.47−7.42 (m, 2H), 7.26 (d, J = 12 Hz, 4H), 7.16 (s, 2H), 2.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (C, d, J = 12.7 Hz), 133.6 (CH, d, J = 2.8 Hz), 132.8 (C, d, J = 103 Hz), 132.1 (C, d, J = 104 Hz), 132.3 (CH, d, J = 9.9 Hz), 131.9 (CH, d, J = 2.7 Hz), 129.6 (CH, d, J = 9.8 Hz), 128.3 (CH, d, J = 12.0 Hz), 21.2 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7.

*(3,4-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine Oxide (**5h**).* White amorphous solid (89 mg, 72%): mp 90−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 12.0 Hz, 1H), 7.31−7.25 (m, 5H), 7.20−7.17 (m, 1H), 7.14 (s, 2H), 2.31 (s, 15H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 (C, d, J = 2.8 Hz), 138.0 (C, d, J = 12.7 Hz), 136.9 (C, d, J = 12.2 Hz), 133.4 (CH, d, J = 2.8 Hz), 133.3 (C, d, J = 106 Hz), 133.0 (CH, d, J = 9.6 Hz), 130.5 (C, d, J = 104 Hz), 129.6 (CH, d, J = 9.8 Hz), 129.6 (CH, d, J = 1.2 Hz), 128.7 (CH, d, J = 11.4 Hz), 21.3 (CH_3), 19.9 (CH_3), 19.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{27}PONa$ 385.1692; Found 385.1698.

*(2,5-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine Oxide (**5i**).* White amorphous solid (97 mg, 79%): mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.11 (m, 8H), 6.88 (d, J = 14.2 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 6H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9 (C, d, J = 8.0 Hz), 138.0 (C, d, J = 12.6 Hz), 134.4 (C, d, J = 12.7 Hz), 133.9 (CH, d, J = 12.6 Hz), 133.4 (CH, d, J = 2.8 Hz), 132.3 (C, d, J = 102 Hz), 132.5 (CH, d, J = 2.6 Hz), 131.6 (CH, d, J = 11.0 Hz), 130.8 (C, d, J = 102 Hz), 129.4 (CH, d, J = 9.7 Hz), 21.3 (CH_3), 21.2 (CH_3), 21.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{27}PONa$ 385.1692; Found 385.1698.

*Dibutyl(phenyl)phosphine Oxide (**5j**).* Thick oil (74 mg, 92%):[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.52−7.48 (m, 1H), 7.44−7.37 (m, 2H), 2.36 (br, 2H), 2.08−1.80 (m, 4H), 1.57−1.31 (m, 6H), 0.78 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (CH, d, J = 2.6 Hz), 131.1 (C, d, J = 126 Hz), 130.5 (CH, d, J = 9.1 Hz), 128.7 (CH, d, J = 11.4 Hz), 28.8 (CH_2, d, J = 69.2 Hz), 23.9 (CH_2, d, J = 15.3 Hz), 23.3 (CH_2, d, J = 4.0 Hz), 13.3 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.8.

*Dicyclopentyl(phenyl)phosphine Oxide (**5k**).* Thick oil (76 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.68 (m, 2H), 7.51−7.46 (m, 1H), 7.42−7.38 (m, 2H), 2.36−2.28 (m, 2H), 2.01−1.76 (m, 4H), 1.70−1.41 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8 (CH, d, J = 2.4 Hz), 131.3 (CH, d, J = 2.4 Hz), 130.1 (C, d, J = 127 Hz), 128.3 (CH, d, J = 10.7 Hz), 37.5 (CH, d, J = 71.2 Hz), 27.0 (CH_2), 26.5 (CH_2, d, J = 9.6 Hz), 26.0 (CH_2), 25.9 (CH_2, d, J = 10.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{23}PONa$ 285.1379; Found 285.1385.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02308.

Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra for **3** and **5** (PDF)

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Notes

The authors declare no competing financial interest.

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J. Org. Chem. 2016, 81, 276−281