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Manganese(III)-Mediated Selective Diphenylphosphinoyl Radical Reaction of 1,4-Diaryl-1-butynes for the Synthesis of 2-Phosphinoylated 3,4-Dihydronaphathalenes

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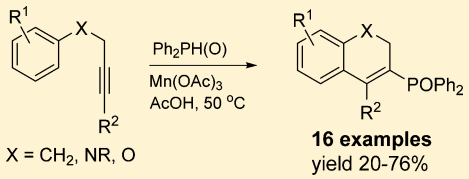
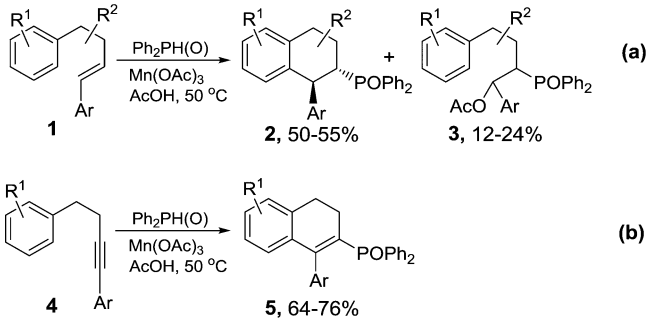
Supporting Information

ABSTRACT: A diphenylphosphinoyl radical-initiated sequential reaction of 1,4-diaryl-1-butynes and analogues is developed for the synthesis of 2-phosphinoylated 3,4-dihydronaphathalenes and related compounds.



Formation of a carbon−phosphorus bond by the reaction of phosphorus radicals is a subject with both mechanistic and synthetic interests.[1] The reaction of phosphinoyl radicals [$R_2P(O)^•$] is much less abundant than that of phosphinyl [$R_2P^•$] and phosphonyl [$(RO)_2P(O)^•$] radicals.[1a] The generation of phosphinoyl radical [$R_2P(O)^•$] from diphenyl- or dialkylphosphine oxide has been reported by the Tailades group[2] using Et_3B, and the Parsons and the Jany groups using azo compounds.[3] We have recently introduced the $(RO)_2PH(O)/Mn(OAc)_3$ system to generate phosphonyl radicals for the phosphonation of arenes and conjugate alkenes/alkynes.[4] We also developed the $Ph_2PH(O)/Mn(OAc)_3$ system for the generation of diphenylphosphinoyl radical to react with 1,4-diaryl-1-butenes **1** for the preparation of phosphinoylated tetrahydronaphathalenes **2** (Scheme 1, a).[5] This is a novel P-radical addition and cyclization sequence, but it suffers from the generation of a significant amount of uncyclized byproduct **3**. Introduced in this paper is the reaction of diphenylphosphinoyl radical with 1,4-diaryl-1-butynes **4** to form 2-phosphinoylated 3,4-dihydronaphathalenes **5** without the formation of acyclic byproduct (Scheme 1, b).

Scheme 1. Novel Diphenylphosphinoyl Radical-Initiated Reactions



The reaction of diphenylphosphinoyl radical with the model compound, 1,4-diphenyl-1-butyne **4a**, was carried out under the optimized condition developed for the reactions of 1,4-diphenylbutenes **1**.[5] A mixture of 1 equiv of **4a**, 2 equiv of $Ph_2PH(O)$, and 3 equiv of $Mn(OAc)_3$ in acetic acid was heated at 50 °C for 20 min to afford phosphinoylated dihydronaphathalene **5a** in 76% isolated yield, and no acyclic phosphinoylated byproduct was observed (Scheme 2, a). The reaction of 1-phenyl-3-(4-chlorophenyl)propyne **6a** gave desired phosphinoylated indene **7** in 8% yield, whereas phosphinoylated acyclic compounds **8a** (60%) and **8b** (10%) were the major products (Scheme 2, b). Similarly, the reaction of 1-(4-chlorophenyl)-5-phenylpentyne **9** gave benzo[7]anuulene **10** in 20% yield together with acyclic compounds **11a** (20%) and **11b** (18%) (Scheme 2, c). The reactions of 3-phenylpropyne and 4-phenylbutyne were also attempted, which gave a mixture containing polymeric phosphinoylated compounds. Results from the reactions of different alkynes indicate that the cyclization of the phosphinoylated vinyl radical is more favorable for the formation of six-membered dihydronaphathalene **5a** than for five-membered indene **7** or seven-membered

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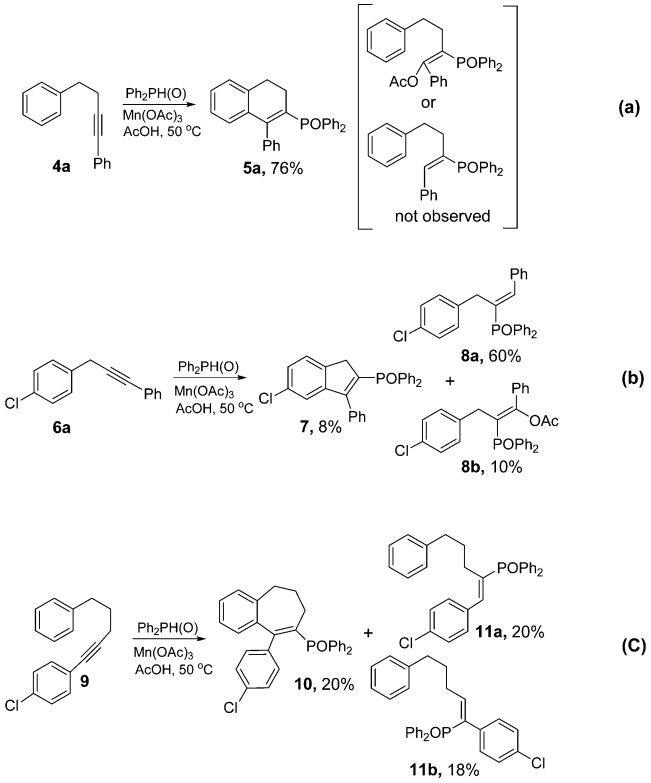
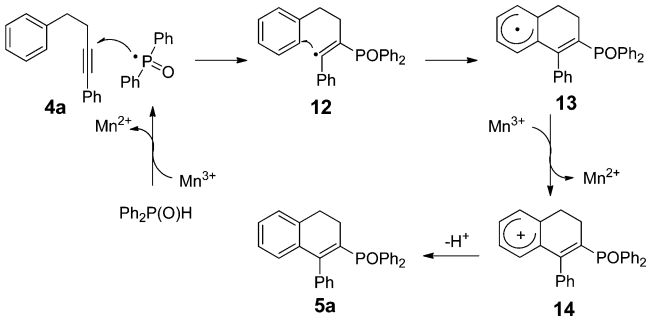
Scheme 2. Reactions of Diphenylphosphinoyl Radical with Different Diphenylalkynes



benzo[7]anuulene **10** ring systems. Without the phenyl group at the 1-position, the vinyl radicals are highly reactive for oxidation and polymerization instead of cyclization.[6]

A mechanism for the reaction of **4a** with 1,4-diphenyl-1-butyne is proposed in Scheme 3. Phosphinoyl radical selectively

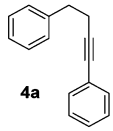
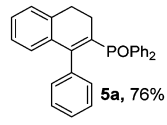
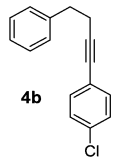
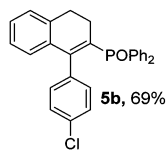
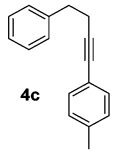
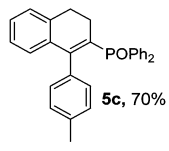
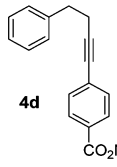
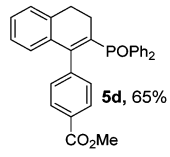
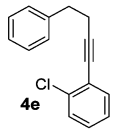
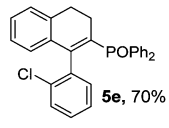
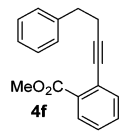
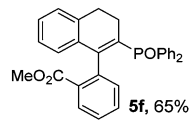
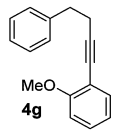
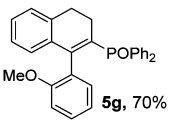
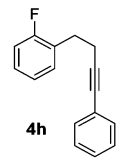
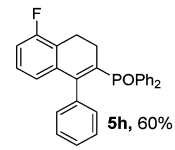
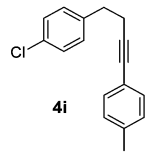
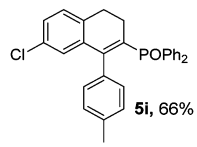
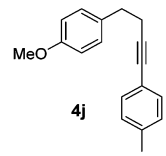
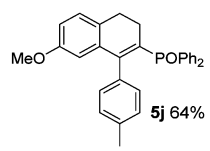
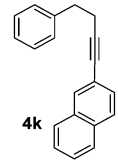
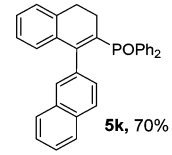
Scheme 3. Proposed Reaction Mechanism



adds to the 2-position of **4a** to form vinyl radical **12**, which is stabilized by the 1-phenyl group. Radical **12** is cyclized to form **13** and then carbocation **14** after oxididation with $Mn(OAc)_3$. Deprotonation of **14** gave product **5a**. No acyclic phosphinoylation byproducts observed from this reaction indicates that the terminal phenyl group is important to stabilize the vinyl radical **12** and facilitate the cyclization.[6] The structure of **5a** has been confirmed by single crystal X-ray analysis.

The electronic effect of the substitution group on two phenyl rings of 1,4-diaryl-1-butynes **4** was explored. The results shown in Table 1 indicate that neither electron-donating nor electron-withdrawing groups have a significant impact on the product yield (entries 1−10). It was also found that steric effect at the

Table 1. Reactions of 1,4-Diarylalkynes 4

entry	alkyne **4**	product **5** and yield
1	 **4a**	 **5a**, 76%
2	 **4b**	 **5b**, 69%
3	 **4c**	 **5c**, 70%
4	 **4d**	 **5d**, 65%
5	 **4e**	 **5e**, 70%
6	 **4f**	 **5f**, 65%
7	 **4g**	 **5g**, 70%
8	 **4h**	 **5h**, 60%
9	 **4i**	 **5i**, 66%
10	 **4j**	 **5j** 64%
11	 **4k**	 **5k**, 70%

ortho-position of 1-phenyl of **4** has limited effect on the product yield (entries 5−7). The reaction of 1-naphthyl-4-phenylbutyne

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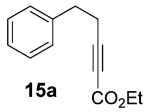
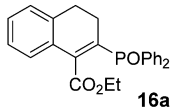
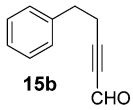
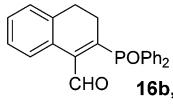
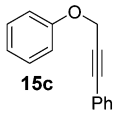
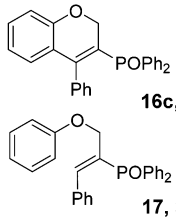
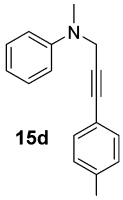
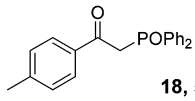
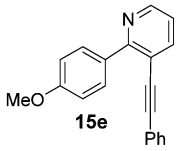
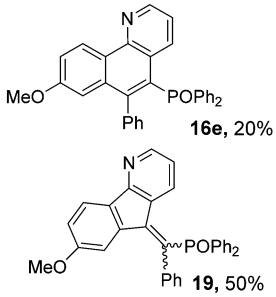
4k was also attempted and gave expected product **5k** in good yield (entry 11).

Good results obtained from the phosphinoyl radical reaction of 1,4-diphenyl-1-butynes encouraged us to broaden the study on substrate scope. 4-Phenylbutynes with ester and aldehyde substituents at the 1-position gave desired products **16a** and **16b** in good yields (Table 2, entries 1 and 2). The replacement

Table 2. Reactions of Alkynes 15

entry	alkyne **15**	product and yield
1	 **15a**	 **16a** 65%
2	 **15b**	 **16b**, 58%
3	 **15c**	 **16c**, 30% **17**, 32%
4	 **15d**	 **18**, 50%
5	 **15e**	 **16e**, 20% **19**, 50%

of a carbon in 1,4-diarylbutynes **4** with a heteroatom such as O or N was attempted. The reaction of **15c** gave desired product **16c** in 30% yield together with acyclic byproduct **17** in 32% yield (entry 3). The structure of **16c** was confirmed by single crystal X-ray analysis. The reaction of 1-(*p*-tolyl)-3-*N*-methylanilinopropyne **15d** gave **18** as a major product (entry 4). It is plausible for the diphenylphosphinoyl radical to add to the alkyne to give the vinyl radical, which could be oxidized to the vinyl acetate as in the formation of **8b**. Hydrolysis of the enol acetate would give the ketone, which could undergo a retro-Mannich reaction losing $PhMeN{=}CH_2^+$ to give **18**. The reaction of **15e** bearing a fused pyridyl unit gave desired six-membered cyclization product **16e** in 20% yield together with compound **19**, which is derived from the addition of phosphinoyl radical to the sp-carbon close to the phenyl ring.

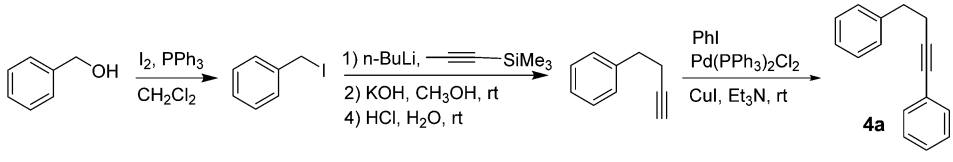
In summary, we have expanded our recently discovered phosphinoyl radical addition and cyclization sequence for the reaction of 1,4-diarylbutynes in the synthesis of 2-phosphinoylated 3,4-dihydronaphthalenes. This reaction has been further extended for analogue substrates for the synthesis of indene, benzo[7]anuulene, and other heterocyclic skeletons.

EXPERIMENTAL SECTION

General Methods. ^{1}H (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were determined in $CDCl_3$, and chemical shifts are reported in ppm from internal TMS (δ). High resolution mass spectra were recorded on a TOF machine (EI). Flash column chromatography was performed with 300−400 mesh silica gel. All of the reagents were used directly as obtained commercially unless otherwise noted. Manganese triacetate,[7] but-1-yne-1,4-diyldibenzene,[8] 1-chloro-4-(3-phenylprop-2-yn-1-yl)-benzene (**6a**),[9] ethyl-5-phenylpent-2-ynoate (**15a**),[10] 5-phenylpent-2-ynal (**15b**),[11] (3-phenoxyprop-1-yn-1-yl)-benzene (**15c**),[12] *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline (**15d**),[13] and 2-(4-methoxyphenyl)-3-(phenylethynyl) pyridine (**15e**)[14] were prepared according to the reported procedures.

Synthesis of Diarylalkynes 4a and 9. *General Procedure for the Synthesis of but-1-yne-1,4-diyldibenzene (**4a**) (Scheme 4).* To a solution of PPh_3 (1.73 g, 6.6 mmol) in CH_2Cl_2 (20 mL) was added resublimed iodine (1.67 g, 6.6 mmol). After 5 min of stirring at room temperature, a solution of phenylmethanol (0.69 g, 6.4 mmol) in CH_2Cl_2 (8 mL) was added to the reaction mixture and stirred for additional 12 h. The reaction mixture was diluted with diethyl ether (15 mL) and then washed with aqueous 5% $NaHCO_3$ (10 mL × 3) and brine (10 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to give a crude product that was purified by flash column chromatography (silica gel, petroleum ether) to afford the benzyl iodide (1.25 g, 90%) as a yellow solid. To a solution of 1-trimethylsilyl-1-propyne (0.41 g, 3.6 mmol) in dry THF (30 mL) was added *n*-BuLi (2.5 M in hexane, 1.32 mL, 3.3 mmol) at −78 °C. After 2 h of stirring at this temperature, benzyl iodide (0.65 g, 3.0 mmol) in dry THF (10 mL) was added to the reaction mixture and stirred at −78 °C for 1 h. The reaction mixture was warmed to room temperature, quenched with brine (30 mL), and then extracted with diethyl ether (30 mL × 2). The combined organic layer was concentrated under vacuum to give crude product [4-(4-methoxyphenyl)-1-butynyl]trimethylsilane. To the resulting silane were added 20 mL of methanol and KOH (0.20 g, 3.6 mmol). After being stirred overnight, the solution was neutralized with 1 N HCl (5.0 mL) and then extracted with diethyl ether (15 mL × 3). The organic layer was dried over $MgSO_4$, concentrated under vacuum, and purified by flash column chromatography (silica gel, petroleum 40:1 ether/EtOAc) to afford but-3-yn-1-ylbenzene (0.31g, 80%) as a colorless oil. To a mixture of but-3-yn-1-ylbenzene (0.26 g, 2.0 mmol), Et_3N (30 mL), $PdCl_2(PPh_3)_2$ (0.028 g, 0.040 mmol), and iodobenzene (0.49 g, 2.4 mmol) (stirring for 3 min beforehand) was added CuI (3.8 mg, 0.020 mmol). The Ar-flushed flask was sealed, and the mixture was stirred at room temperature for 12 h. The reaction mixture was filtered and washed with saturated aqueous NaCl solution (10 mL × 2), and the

Scheme 4



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filtrate was extracted with diethyl ether (15 mL × 3). The combined organic layer was dried over $MgSO_4$ and concentrated under vacuum. The resulting crude product was purified by flash column chromatography (silica gel, 40:1 petroleum ether/EtOAc) to give **4a** (0.35 g, 85%) as a clear yellow liquid. The Pd-catalyzed coupling reaction of pent-4-yn-1-ylbenzene and 1-chloro-4-iodobenzene was used for the synthesis of **9**.

Preparation of 2-Phosphinoylated 3,4-Dihydronaphthalenes 5a−k, Their Derivatives, and Byproducts. *General Procedure.* To a solution of acetic acid (10 mL), but-1-yne-1,4-diyldibenzene (1.0 mmol), and diphenylphosphine oxide (2 mmol) was added $Mn(OAc)_3$ (3 mmol) in 10 portions at 50 °C. After 20 min the reaction was complete, and the acetic acid was removed under vacuum. To the residue was added water (20 mL), and the solution was extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by flash chromatography (silica gel, 9:1 petroleum ether/EtOAc) to afford phosphinoylated dihydronaphthalene **5a**.

*Diphenyl(1-phenyl-3,4-dihydronaphthalen-2-yl)phosphine Oxide (**5a**).* White solid, mp 146−147 °C, 76% yield (308.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.67 (m, 4H), 7.34−7.43 (m, 2H), 7.26−7.34 (m, 4H), 7.16−7.24 (m, 2H), 7.01−7.11 (m, 3H), 6.92−7.00 (m, 3H), 6.64 (d, J = 7.7 Hz, 1H), 2.92 (t, J = 6.0 Hz, 2H), 2.58−2.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3 (d, J = 8.2 Hz), 137.4 (d, J = 6.8 Hz), 137.2, 136.2 (d, J = 13.7 Hz), 134.6, 133.5, 131.7 (d, J = 9.7 Hz), 131.4, 130.5, 129.4, 129.2, 128.5 (d, J = 12.0 Hz), 128.1, 127.9, 127.7 (d, J = 8.0 Hz), 126.9, 28.4 (d, J = 6.2 Hz), 26.6 (d, J = 10.5 Hz). HRMS (EI-TOF) m/z: (M^+) calcd for $C_{28}H_{23}OP$ 406.1487, found 406.1485 (M^+, 70.00).

*(1-(4-Chlorophenyl)-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5b**).* White solid, mp 111−112 °C, 69% yield (303.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.62 (m, 4H), 7.40−7.46 (m, 2 H), 7.29−7.36 (m, 4 H), 7.16−7.24 (m, 2 H), 7.06 (t, J = 8.0 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 2 H), 6.89 (d, J = 8.0 Hz, 2 H), 6.62 (d, J = 8.0 Hz, 1 H), 2.90 (t, J = 8.0 Hz, 2 H), 2.58−2.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (d, J = 7.6 Hz), 136.7, 135.5 (d, J = 7.0 Hz), 135.2 (d, J = 13.7 Hz), 133.8, 133.4, 132.7, 131.4, 131.3 (d, J = 10.0 Hz), 131.1, 129.2, 128.7, 128.2 (d, J = 12.0 Hz), 127.6, 127.4 (d, J = 6.0 Hz), 126.5, 27.8 (d, J = 6.2 Hz), 26.2 (d, J = 10.3 Hz). HRMS (EI-TOF) m/z: (M^+) calcd for $C_{28}H_{22}ClOP$ 440.1097, found 440.1102.

*Diphenyl(1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)phosphine Oxide (**5c**).* White solid, mp 105−106 °C, 70% yield (294.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.63 (m, 4H), 7.34−7.42 (m, 2H), 7.24−7.36 (m, 4H), 7.16−7.22 (m, 1H), 7.01−7.09 (m, 1H), 6.82 (d, J = 7.5 Hz, 2H), 6.74 (d, J = 7.5 Hz, 2H), 6.69 (d, J = 7.5 Hz, 1H), 2.90 (t, J = 6.0 Hz, 2H), 2.57−2.68 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5 (d, J = 8.2 Hz), 137.5 (d, J = 4.8 Hz), 136.4 (d, J = 13.7 Hz), 134.8, 134.65 (d, J = 7.0 Hz), 133.7, 132.0 (d, J = 9.6 Hz), 131.4, 130.6, 129.6, 129.3, 128.8 (d, J = 6.0 Hz), 128.6, 128.4, 127.9, 127.1, 28.7 (d, J = 5.9 Hz), 26.7 (d, J = 10.5 Hz), 21.7. HRMS (EI-TOF) m/z: (M^+) calcd for $C_{29}H_{25}OP$ 420.1643, found 420.1643.

*Methyl 4-(2-(Diphenylphosphoryl)-3,4-dihydronaphthalen-1-yl)-benzoate (**5d**).* White solid, mp 152−153 °C, 65% yield (301.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.53−7.64 (m, 4H), 7.35−7.44 (m, 2H), 7.24−7.34 (m, 4H), 7.15−7.24 (m, 2H), 6.97−7.10 (m, 3H), 6.54 (d, J = 7.8 Hz, 1H), 3.88 (s, 3H), 2.89 (t, J = 6.0 Hz, 2H), 2.54−2.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 150.3 (d, J = 7.0 Hz), 142.6 (d, J = 6.1 Hz), 137.1, 135.5 (d, J = 13.2 Hz), 134.1, 133.1, 131.8 (d, J = 10.0 Hz), 131.6, 130.6, 129.6, 129.3, 129.1, 128.7, 128.6, 127.8, 127.0, 52.4, 28.3 (d, J = 5.1 Hz), 26.7 (d, J = 10.2 Hz). HRMS (EI-TOF) m/z: (M^+) calcd for $C_{30}H_{25}O_3P$ 464.1541, found 464.1541.

*(1-(2-Chlorophenyl)-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5e**).* White solid, mp 120−121 °C; 70% yield (308.1 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.68 (m, 4H), 7.37−7.48 (m, 3H), 7.28−7.36 (m, 3H), 7.14−7.27 (m, 2H), 7.03−7.10 (m, 2H), 6.95−7.02 (m, 2H), 6.81−6.86 (m, 1H), 6.60 (d, J = 7.7 Hz, 1H), 2.90 (t, J = 6.0 Hz, 2H), 2.56−2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (d, J = 7.5 Hz), 139.3 (d, J = 6.6 Hz), 137.2, 135.6 (d, J = 13.3 Hz), 134.2, 133.9, 133.2, 131.8, 131.7, 130.7, 130.2, 129.8, 129.4, 129.1, 128.7 (d, J = 12.0 Hz), 128.2, 127.9, 127.1, 28.4 (d, J = 5.6 Hz), 26.8 (d, J = 10.2 Hz). HRMS (EI-TOF) m/z: (M^+) calcd for $C_{28}H_{22}ClOP$ 440.1097, found 440.1099.

*Methyl 2-(2-(Diphenylphosphoryl)-3,4-dihydronaphthalen-1-yl)-benzoate (**5f**).* White solid; mp 159−160 °C, 65% yield (302.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.77 (m, 3H), 7.49−7.58 (m, 2H), 7.42 (d, J = 6.6 Hz, 1H), 7.34−7.41 (m, 2H), 7.27−7.33 (m, 2H), 7.18−7.25 (m, 4H), 7.13−7.16 (m, 2H), 6.93−7.02 (m, 1H), 6.40 (d, J = 7.5 Hz, 1H), 3.63 (s, 3H), 2.79−3.06 (m, 2H), 2.44−2.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 151.6 (d, J = 7.0 Hz), 139.5, 136.9, 136.1, 132.5, 131.9, 131.8, 131.7 (d, J = 5.0 Hz), 131.5 (d, J = 3.0 Hz), 131.2, 130.7, 128.9, 128.6 (d, J = 12.0 Hz), 128.3, 128.1 (d, J = 7.0 Hz), 127.4, 126.7, 126.5, 51.9, 28.1 (d, J = 6.3 Hz), 26.6 (d, J = 10.8 Hz). HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{30}H_{26}O_3P$ 465.1619, found 465.1633.

*(1-(2-Methoxyphenyl)-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5g**).* White solid, mp 109−110 °C, 70% yield (306.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.70 (m, 2H), 7.45−7.55 (m, 3H), 7.35−7.41 (m, 1H), 7.27−7.34 (m, 3H), 7.13−7.20 (m, 3H), 6.93−7.04 (m, 3H), 6.62−6.72 (m, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.30 (d, J = 8.0 Hz, 1H), 3.48 (s, 3H), 2.90 (t, J = 8.0 Hz, 2H), 2.56−2.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 147.7 (d, J = 5.0 Hz), 136.9, 135.4 (d, J = 13.0 Hz), 131.8 (d, J = 8.0 Hz), 131.5 (d, J = 8.0 Hz), 131.3, 131.0, 129.8, 128.9, 128.2 (d, J = 10.0 Hz), 127.9 (d, J = 11.0 Hz), 127.5, 127.0, 126.7, 126.3, 120.1, 109.9, 54.7, 28.2, 26.1 (d, J = 8.9 Hz). HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{29}H_{26}O_2P$ 437.1675, found 437.1670.

*(5-Fluoro-1-phenyl-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5h**).* White solid, mp 107−108 °C, 60% yield (255.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.55 (m, 4H), 7.27−7.34 (m, 2H), 7.14−7.25 (m, 5H), 6.83−6.96 (m, 6H), 6.30−6.35 (m, 1H), 2.78−2.89 (m, 2H), 2.45−2.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.8, 150.2 (d, J = 3.0 Hz), 150.1 (d, J = 2.0 Hz), 137.7 (d, J = 5.0 Hz), 137.6 (d, J = 5.0 Hz), 136.7 (d, J = 7.0 Hz), 133.7, 132.7, 131.3 (d, J = 10.0 Hz), 131.0, 130.0, 128.1 (d, J = 12.0 Hz), 127.4, 126.8 (d, J = 8.0 Hz), 123.4, 115.8 (d, J = 22.0 Hz), 25.3 (d, J = 10.0 Hz), 19.4 (d, J = 3.0 Hz). HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{28}H_{23}FOP$ 425.1470, found 425.1465.

*(7-Chloro-1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5i**).* White solid, mp 121−122 °C, 66% yield (300.4 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.61 (m, 4H), 7.33−7.42 (m, 2H), 7.23−7.32 (m, 4H), 7.13−7.18 (m, 1H), 7.07−7.12 (m, 1H), 6.79 (d, J = 7.8 Hz, 2H), 6.74 (d, J = 7.8 Hz, 2H), 6.66 (s, 1H), 2.84 (t, J = 6.0 Hz, 2H), 2.55−2.66 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0 (d, J = 6.2 Hz), 137.8, 137.5, 135.4, 134.3, 133.5, 132.9, 132.4, 131.6 (d, J = 8.0 Hz), 131.1, 130.1, 128.9, 128.7, 128.5, 128.3, 127.8, 27.7, 26.4 (d, J = 8.8 Hz), 21.4. HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{29}H_{25}ClOP$ 455.1331, found 455.1335.

*(7-Methoxy-1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)-diphenylphosphine Oxide (**5j**).* White solid, mp 123−124 °C; 64% yield (288.8 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.62 (m, 4H), 7.33−7.42 (m, 2H), 7.22−7.32 (m, 4H), 7.06−7.14 (m, 1H), 6.81 (d, J = 6.0 Hz, 2H), 6.76−6.78 (m, 1H), 6.72 (d, J = 6.0 Hz, 2H), 6.27 (s, 1H), 3.59 (s, 3H), 2.83 (t, J = 6.0 Hz, 2H), 2.54−2.66 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 151.2 (d, J = 8.2 Hz), 137.1, 134.5, 134.1 (d, J = 6.8 Hz), 133.1, 131.7, 131.6, 131.0, 130.2, 129.6 (d, J = 6.8 Hz), 129.4, 128.5 (d, J = 6.8 Hz), 128.2, 114.6, 113.8, 55.4, 27.4 (d, J = 5.3 Hz), 26.8 (d, J = 10.5 Hz), 21.4. HRMS (ESI-TOF) m/z: (M + H)$^+$ calcd for $C_{30}H_{28}O_2P$ 451.1827, found 451.1834.

*3,4-Dihydro-[1,2′-binaphthalen]-2-yl)diphenylphosphine Oxide (**5k**).* White solid, mp 169−170 °C; 70% yield (320.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.73 (m, 1H), 7.46−7.62 (m, 6H), 7.34−7.45 (m, 3H), 7.20−7.25 (m, 3H), 7.05−7.19 (m, 5H), 6.96−7.04 (m, 2H), 6.63−6.73 (m, 1H), 2.92−3.07 (m, 2H), 2.67−2.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5 (d, J = 8.1 Hz), 137.0, 135.6 (d, J = 13.5 Hz), 134.5 (d, J = 6.8 Hz), 132.4 (d, J = 6.1 Hz), 131.2 (d, J = 9.0 Hz), 130.7, 130.0, 129.8, 129.1, 128.4, 128.1, 128.0,

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127.8, 127.6, 127.4 (d, J = 2.3 Hz), 127.2, 126.5, 126.1, 125.8, 28.1 (d, J = 6.0 Hz), 26.2 (d, J = 10.2 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{32}H_{26}OP$ 457.1721, found 457.1716.

*(E)-(3-(4-Chlorophenyl)-1-phenylprop-1-en-2-yl)-diphenylphosphine Oxide (**8a**).* Yellow oil, 60% yield (257.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.71 (m, 2H), 7.38−7.52 (m, 8H), 7.28−7.35 (m, 5H), 7.04−7.10 (m, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.85−6.90 (m, 2H), 6.80−6.84 (m, 1H), 3.79 (d, J = 108.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1(d, J = 10.6 Hz), 133.0, 132.3, 131.8 (d, J = 15.3 Hz), 131.0, 130.3, 129.8 (d, J = 7.2 Hz), 129.0 (d, J = 11.0 Hz), 128.8, 128.6 (d, J = 7.5 Hz), 128.3, 128.1 (d, J = 7.1 Hz), 127.6, 123.7 (d, J = 8.8 Hz), 31.6 (d, J = 8.6 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{27}H_{23}ClOP$ 429.1175, found 429.1140.

*(9-(4-Chlorophenyl)-6,7-dihydro-5H-benzo[7]annulen-8-yl)-diphenylphosphine Oxide (**10**).* Colorless oil; 20% yield (95.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.76 (m, 2H), 7.61−7.67 (m, 1H), 7.52−7.57 (m, 1H), 7.39−7.50 (m, 5H), 7.29−7.35 (m, 1H), 7.06−7.23 (m, 6H), 6.99 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 6.8 Hz, 1H), 2.30−2.50 (m, 3H), 2.22−2.28 (m, 1H), 1.51−1.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (d, J = 22.5 Hz), 143.9 (d, J = 27.8 Hz), 141.3, 134.5, 133.0, 132.3 (d, J = 9.0 Hz), 131.0 (d, J = 6.6 Hz), 130.3, 129.8, 129.1 (d, J = 7.5 Hz), 128.8 (d, J = 11.3 Hz), 128.5 (d, J = 6.2 Hz), 128.2 (d, J = 8.2 Hz), 125.9, 125.7, 123.1 (d, J = 10.9 Hz), 35.4, 23.0, 25.9 (d, J = 9.8 Hz). HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{29}H_{24}ClNaOP$ 477.1151, found 477.1131.

*(E)-(1-(4-Chlorophenyl)-5-phenylpent-1-en-2-yl)-diphenylphosphine Oxide (**11a**).* Colorless oil, 20% yield (95.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.62 (m, 4H), 7.30−7.34 (m, 2H), 7.18−7.26 (m, 7H), 7.13−7.17 (m, 2H), 7.06−7.12 (m, 1H), 6.95 (d, J = 6.8 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 2.35−2.44 (m, 2H), 2.14−2.26 (m, 2H), 1.65−1.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.1 (d, J = 4.5 Hz), 141.6, 135.8, 134.2 (d, J = 3.8 Hz), 133.8, 133.4, 132.0 (d, J = 4.3 Hz), 131.4, 131.3, 130.9, 128.3 (d, J = 4.0 Hz), 128.2, 127.6, 125.8, 36.8, 35.4, 31.7. HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{29}H_{26}ClNaOP$ 479.1307, found 479.1304.

*Ethyl-2-(diphenylphosphoryl)-3,4-dihydronaphthalene-1-carboxylate (**16a**).* Yellow oil, 65% yield (276.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.70 (m, 6H), 7.50−7.55 (m, 2H), 7.38−7.44 (m, 2H), 7.27−7.31 (m, 3H), 7.18−7.23 (m, 1H), 4.08−4.26 (m, 2H), 3.46−3.53 (m, 2H), 2.88−3.08 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (d, J = 12.4 Hz), 163.0 (d, J = 12.4 Hz), 138.7 (d, J = 19.5 Hz), 137.9, 130.7, 129.7, 129.3 (d, J = 8.3 Hz), 128.5 (d, J = 8.3 Hz), 127.0 (d, J = 7.3 Hz), 126.0, 126.0 (d, J = 2.3 Hz), 123.9, 121.3 (d, J = 8.3 Hz), 60.7, 34.9, 29.7 (d, J = 7.5 Hz), 13.7. HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{25}H_{23}NaO_3P$ 425.1283, found 425.1275.

*2-(Diphenylphosphoryl)-3,4-dihydronaphthalene-1-carbaldehyde (**16b**).* Yellow oil, 55% yield (197.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H), 7.67−7.81 (m, 6H), 7.57−7.62 (m, 2H), 7.48−7.54 (m, 4H), 7.13−7.21 (m, 2H), 2.68−2.73 (m, 2H), 2.26−2.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9 (d, J = 8.0 Hz), 148.4 (d, J = 5.3 Hz), 136.6, 132.6, 131.7 (d, J = 10.0 Hz), 129.8, 128.9 (d, J = 12.2 Hz), 128.5, 128.4, 128.3, 127.6 (d, J = 3.6 Hz), 126.9, 126.1, 27.5 (d, J = 10.2 Hz), 27.2 (d, J = 6.3 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{23}H_{20}O_2P$ 359.1201, found 359.1191.

*Diphenyl(4-phenyl-2H-chromen-3-yl)phosphine Oxide (**16c**).* White solid, mp 121−122 °C,30% yield (122.7 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.66 (m, 4H), 7.36−7.44 (m, 2H), 7.27−7.35 (m, 4H), 7.03−7.11 (m, 2H), 6.90−7.10 (m, 5H), 6.78−6.85 (m, 1H), 6.62−6.67 (m, 1H), 4.89 (d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 149.3 (d, J = 6.0 Hz), 134.9 (d, J = 4.0 Hz), 133.2, 131.8, 131.5, 131.3, 131.2, 129.8, 128.3, 128.1 (d, J = 7.5 Hz), 127.9, 127.5, 125.0 (d, J = 10.5 Hz), 121.5, 116.0, 65.2 (d, J = 17.2 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{27}H_{22}O_2P$ 409.1357, found 409.1363.

*(8-Methoxy-6-phenylbenzo[h]quinolin-5-yl)diphenylphosphine Oxide (**16e**).* Yellow oil, 20% yield (101.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (d, J = 8.8 Hz, 1H), 9.05−9.15 (m, 1H), 8.92 (d, J = 4.0 Hz, 1H), 7.34−7.43 (m, 6H), 7.31 (d, J = 7.2 Hz, 2H), 7.17−7.23 (m, 4H), 7.04−7.09 (m, 1H), 6.96 (d, J = 4.4 Hz, 4H), 6.54 (d, J = 2.4 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 148.5, 137.3 (d, J = 6.4 Hz), 136.0, 135.1, 134.9, 134.6, 131.7, 131.6, 130.9, 130.9, 128.6, 128.4, 128.3, 128.1, 128.0, 127.8, 126.4, 120.3, 118.9, 109.1, 55.1. HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{32}H_{24}NNaO_2P$ 508.1442, found 508.1438.

*(3-Phenoxy-1-phenylprop-1-en-2-yl)diphenylphosphine Oxide (**17**).* White solid, mp 233−234 °C, 32% yield (131.6 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.64 (m, 4H), 7.37−7.40 (m, 5H), 7.24−7.36 (m, 8H), 6.87−6.96 (m, 1H), 6.75−6.85 (m, 3H), 4.47 (d, J = 15.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (d, J = 9.5 Hz), 140.8 (d, J = 14.3 Hz), 140.2 (d, J = 7.5 Hz), 133.3, 132.1, 131.9, 131.6 (d, J = 10.5 Hz), 131.3, 129.2, 128.5, 128.2, 128.1 (d, J = 2.8 Hz), 127.7, 127.5, 62.9 (d, J = 8.7 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{27}H_{24}O_2P$ 411.1514, found 411.1505.

*2-(Diphenylphosphoryl)-1-(p-tolyl)ethanone (**18**).* White solid, mp 152−153 °C,50% yield (167.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.76−7.85 (m, 4H), 7.50−7.55 (m, 2H), 7.42−7.49 (m, 4H), 7.21 (d, J = 8.0 Hz, 2H), 4.12 (d, J = 12.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 144.6, 134.4, 132.4, 132.1, 131.4, 131.1 (d, J = 10.0 Hz), 129.3 (d, J = 18.0 Hz), 128.5 (d, J = 12.0 Hz), 43.1 (d, J = 58.0 Hz), 21.6. HRMS (ESI-TOF) m/z: $(M + H)^+$ calcd for $C_{21}H_{20}O_2P$ 335.1201, found 335.1195.

*((7-Methoxy-5H-indeno[1,2-b]pyridin-5-ylidene)(phenyl)methyl)-diphenylphosphine Oxide (**19**).* Yellow oil, 50% yield (254.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73−8.78 (m, 1H), 7.64−7.68 (m, 1H), 7.54−7.63 (m, 3H), 7.48−7.53 (m, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.36−7.42 (m, 2H), 7.26−7.35 (m, 3H), 7.23 (d, J = 6.8 Hz, 2H), 7.06−7.15 (m, 3H), 6.83−6.89 (m, 1H), 6.72 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 157.1, 149.8, 147.9 (d, J = 22.5 Hz), 143.4, 143.1, 138.8, 136.6, 135.3, 133.1, 132.5, 132.1 (d, J = 6.2 Hz), 131.1 (d, J = 10.8 Hz), 130.7 (d, J = 7.5 Hz), 129.1 (d, J = 4.5 Hz), 128.53, 128.49, 128.3 (d, J = 1.4 Hz), 123.9 (d, J = 10.5 Hz), 122.0, 113.8, 55.2. HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{32}H_{24}NNaO_2P$ 508.1442, found 508.1433.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **5a−k**, **8a**, **10**, **11a**, **16a−c**, **16e**, **17**, **18**, and **19**, X-ray ellipsoid plot of compounds **5a**, **16c**, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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