Supplementary Information

Remarkable Electron-Withdrawing Effect of Ph₂P(O)-Ethynyl Group: Ph₂P(O)-Ethynyl-Substituted Aryl Halides and Copper Acetylides for Tailor-Made Sonogashira Couplings

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I. General Information.

All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. Toluene was distilled from sodium. Diisopropylamine were distilled from CaH$_2$. Dry tetrahydrofuran (THF) was purchased from Wako Chemicals. Pd(PPh$_3$)$_4$ was prepared according to the reported method. Silica gel was used for column chromatography. The other materials were purchased from commercial sources and used without additional purification. NMR spectra was recorded at 25 °C on 300 and 500 MHz instruments in CDCl$_3$ and calibrated with tetramethysilane (TMS) as an internal reference. Mass spectra were recorded on MALDI-TOF mass spectrometers. Melting points (m.p.) were measured on a GTO-250RS instrument.

II. Procedure and Characterization.

Synthesis of 13.$^1$

To a flask were added CuI (190.4 mg, 1.0 mmol), Ph$_2$PCl (1.8 mL, 10.0 mmol), trimethylsilylacetylene (1.7 mL, 12.0 mmol), triethylamine (2.8 mL, 20.0 mmol) and toluene (30.0 mL), and the mixture was stirred under nitrogen at 80 °C for 24 h. After workup with AcOEt/water, the organic layer was washed with aqueous NH$_4$Cl and brine, and dried over MgSO$_4$. After filtration, the solvents were evaporated. The crude product was used for next step without purification. To the crude product were added THF (20.0 mL) and then 30% H$_2$O$_2$ (5.0 mL) at 0 °C, and the mixture was stirred under air at rt for 13 h. After workup with CH$_2$Cl$_2$/water, the organic layer was washed with brine, and dried over MgSO$_4$. After filtration, the solvents were evaporated. The crude product was used for next step without purification. To the crude product were added water (0.5 mL) and THF (50.0 mL), and then TBAF (1.0 M in THF, 1.0 mL, 1.0 mmol) at 0 °C, and the mixture was stirred under air at rt for 5 h. After the solvents were evaporated, the crude product was subjected to...
column chromatography on silica gel (hexane/AcOEt, 1:1) to give 13 (1.63 g, 72% yield in 3 steps) in a pure form.

13: white powder; 1H NMR (500 MHz, CDCl₃): δ 3.33 (d, J = 9.8 Hz, 1H), 7.48-7.52 (m, 4H), 7.56-7.59 (m, 2H), 7.83-7.87 (m, 4H).

Synthesis of 1 and 29² by Sonogashira coupling (representative procedure for 1).

A toluene solution (5 mL) of 1,4-diiodobenzene 2 (659.8 mg, 2.0 mmol), 13 (226.2 mg, 1.0 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:1) to afford 1 in a pure form (184.1 mg, 43% yield).

1: yellow powder, m.p. 163-166 °C; 1H NMR (500 MHz, CDCl₃): δ 7.31 (d, J = 8.2 Hz, 2H), 7.49-7.52 (m, 4H), 7.56-7.59 (m, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.86-7.91 (m, 4H); 13C NMR (75 MHz, CDCl₃): δ 83.94 (d, J = 167.0 Hz), 97.28, 103.74 (d, J = 29.4 Hz), 118.70 (d, J = 3.5 Hz), 128.27 (d, J = 13.4 Hz), 130.40 (d, J = 11.2 Hz), 131.94 (d, J = 3.1 Hz), 132.18 (d, J = 121.6 Hz), 133.19 (d, J = 1.8 Hz), 137.31; 3¹P NMR (121 MHz, CDCl₃): δ 9.87; HRMS (MALDI-TOF) calcd for C₂₀H₁₅IOP (M+H⁺): 428.9905, found 428.9934.

29: pale-yellow powder, m.p. 112-114 °C; 1H NMR (500 MHz, CDCl₃): δ 7.14 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.50-7.61 (m, 7H), 7.89 (d, J = 8.0 Hz, 1H), 7.96-8.00 (m, 4H).

Synthesis of 20³ and 21³ (representative procedure for 21).
A toluene solution (10 mL) of 1,3-diethynylbenzene (126.2 mg, 1.0 mmol), CuI (19.0 mg, 0.1 mmol), Ph₂PCl (220.6 μL, 1.2 mmol) and Et₃N (277.2 μL, 2.0 mmol) was stirred under nitrogen at 80 °C for 8 h. After usual workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine, and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was used for next step without purification. To a THF solution (10.0 mL) of crude product was added H₂O₂aq (30%, 2.5 mL, 20.0 mmol) at 0 °C and the mixture was stirred at rt for 2 h. After workup with CH₂Cl₂ and water, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:1) to afford 21 in a pure form (146.8 mg, 45% yield).

21:³ white powder; m.p. 111-113 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.12 (s, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.49-7.52 (m, 4H), 7.55-7.58 (m, 4H), 7.71 (s, 1H), 7.87-7.91 (m, 4H).

20:³ white powder; m.p. 145-147 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.24 (s, 1H), 7.48-7.52 (m, 6H), 7.54-7.58 (m, 4H), 7.87-7.91 (m, 4H).

Synthesis of 7.⁴

A toluene solution (5 mL) of ethynylbenzene (102.1 mg, 1.0 mmol), 1-bromo-4-iodobenzene (311.2 mg, 1.1 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at rt
for 15 h. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane) to afford 7 in a pure form (213.4 mg, 83% yield).

**Synthesis of 12.**

A DMF solution (5 mL) of 1-bromo-3,7-dimethyloctane (243.3 mg, 1.1 mmol), 4-bromophenol (173.0 mg, 1.0 mmol) and K₂CO₃ (414 mg, 3.0 mmol) was stirred under nitrogen at 80 °C for overnight. After workup with CH₂Cl₂ and dilute HClaq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH₂Cl₂, 6:1) to afford 12 in a pure form (291.3 mg, 93% yield).

**Synthesis of 19.**

A toluene solution (10 mL) of 1,4-diiodobenzene (329.9 mg, 1.0 mmol), 13 (497.7 mg, 2.2 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (AcOEt) to afford 19 in a pure form (384.3 mg, 73% yield).

19: white powder, m.p. 264-266 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.50-7.53 (m, 8H), 7.57-7.61 (m, 8H), 7.87-7.91 (m, 8H); ¹³C NMR (75 MHz, CDCl₃): δ 85.78 (d, J
Competitive Sonogashira coupling of 1 vs 2 with 3.

![Chemical structures of 1, 2, 3, 4, and 5]

A toluene solution (5.0 mL) of 1 (214.1 mg, 0.5 mmol), 2 (165.0 mg, 0.5 mmol), 3 (66.1 mg, 0.5 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for overnight. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH₂Cl₂, 10:1, and hexane/AcOEt, 1.5:1) to afford 4 in a pure form (157.8 mg, 73% yield) and 5 in a pure form (36.8 mg, 22% yield) and recover 1 in a pure form (47.1 mg, 22% yield) and 2 in a pure form (128.7 mg, 78% yield).

4: pale-yellow powder, m.p. 187-189 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.84 (s, 3H), 6.89 (d, J = 9.2 Hz, 2H), 7.47-7.53 (m, 8H), 7.56-7.59 (m, 4H), 7.88-7.93 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 55.25 (d, J = 4.9 Hz), 84.25 (d, J = 167.9 Hz), 87.36, 92.94, 104.94 (d, J = 30.1 Hz), 114.04, 114.54, 118.88 (d, J = 4.7 Hz), 126.15, 128.64 (d, J = 13.4 Hz), 130.90 (d, J = 10.8 Hz), 131.37, 132.26 (d, J = 2.8 Hz), 132.36 (d, J = 1.9 Hz), 132.83 (d, J = 121.9 Hz), 133.16, 159.96; ³¹P NMR (121 MHz, CDCl₃): δ 9.78; HRMS (FAB) calcd for C₂⁹H₂₂O₂P (M+H⁺): 433.1357, found 433.1355.

5: white powder, ¹H NMR (300 MHz, CDCl₃): δ 3.83 (s, 3H), 6.88 (d, J = 8.8 Hz,
Competitive Sonogashira coupling of 6 vs 7 with 3.

A toluene solution (5.0 mL) of 6 (190.6 mg, 0.5 mmol), 7 (128.6 mg, 0.5 mmol), 3 (66.1 mg, 0.5 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for overnight. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH₂Cl₂, 10:1, and hexane/AcOEt, 1.5:1) to afford 4 in a pure form (164.3 mg, 76% yield) and 8 in a pure form (15.4 mg, 10% yield) and recover 6 in a pure form (24.8 mg, 13% yield) and 7 in a pure form (114.4 mg, 89% yield).

8: white powder, ¹H NMR (500 MHz, CDCl₃): δ 3.84 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.35-7.38 (m, 3H), 7.47-7.55 (m, 8H).

Competitive Sonogashira coupling of 6 vs 9 with 3.

A toluene solution (5.0 mL) of 6 (190.6 mg, 0.5 mmol), 9 (190.6 mg, 0.5 mmol), 3 (66.1 mg, 0.5 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for overnight. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH₂Cl₂, 10:1, and hexane/AcOEt, 1.5:1) to afford 4 in a pure form (164.3 mg, 56% yield) and 10 in a pure form (15.4 mg, 20% yield) and recover 6 in a pure form (24.8 mg, 22% yield) and 9 in a pure form (114.4 mg, 75% yield).
(66.1 mg, 0.5 mmol), Pd(PPh3)4 (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for overnight. After workup with CH2Cl2 and NH4Claq, the combined organic layer was washed with brine and dried over MgSO4. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography silica gel (hexane/AcOEt, 1:1) to afford a mixture of 4, 10 and remaining starting compounds 6, 9. 1H NMR analysis of the mixture indicated the formations of 4 in 56% yield and 10 in 20% yield and recoveries of 6 in 22% and 9 in 75% (using 1, 4-dioxane as an internal standard).

10: white powder; m.p. 151-152 °C; 1H NMR (500 MHz, CDCl3): δ 3.84 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.49-7.54 (m, 5H), 7.56-7.58 (m, 3H), 7.74 (s, 1H), 7.88-7.93 (m, 4H).

Competitive Sonogashira coupling of 11 vs 12 with 13.

A toluene solution (10.0 mL) of 11 (234.0 mg, 1.0 mmol), 12 (313.3 mg, 1.0 mmol), 13 (226.2 mg, 1.0 mmol), Pd(PPh3)4 (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH2Cl2 and NH4Claq, the combined organic layer was washed with brine and dried over MgSO4. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH2Cl2, 10:1, and hexane/AcOEt, 1:1) to recover 12 (307.0 mg, 98% yield) and afford 14 in a pure form (232.6 mg, 70% yield).

14: white powder; m.p. 125-126 °C; 1H NMR (500 MHz, CDCl3): δ 3.84 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.49-7.56 (m, 8H), 7.88-7.92 (m, 4H).
Synthesis of 17a, 17b and 17c by Sonogashira coupling (representative procedure for 17a).

\[
\begin{align*}
\text{Pd(PPh}_3\text{)}_4 & \quad \text{(5 mol\%)} \\
\text{CuI} & \quad \text{(5 mol\%)} \\
\text{toluene, i-Pr}_2\text{NH} & \\
80^\circ\text{C, 15 h} & \quad \text{to 17a, 45\% (Rf = 0.34)} \\
& \quad \text{17b, 72\% (Rf = 0.41)} \\
& \quad \text{17c, 82\% (Rf = 0.36)} \\
\end{align*}
\]

A toluene solution (5 mL) of 16a (339.5 mg, 1.2 mmol), 13 (226.2 mg, 1.0 mmol), Pd(PPh3)4 (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH2Cl2 and NH4Claq, the combined organic layer was washed with brine and dried over MgSO4. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:1) to afford 17a in a pure form (171.5 mg, 45% yield).

17a: white powder, m.p. 88-89 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.29-7.35 (m, 2H), 7.49-7.52 (m, 4H), 7.55-7.58 (m, 2H), 7.61-7.64 (m, 2H), 7.94-7.98 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 86.76 (d, \(J = 166.3\) Hz), 102.63 (d, \(J = 29.5\) Hz), 122.05 (d, \(J = 3.8\) Hz), 125.87 (d, \(J = 2.1\) Hz), 127.04, 128.39 (d, \(J = 13.7\) Hz), 130.70 (d, \(J = 11.2\) Hz), 131.54, 132.07 (d, \(J = 3.1\) Hz), 132.40, 132.46 (d, \(J = 121.9\) Hz), 134.16 (d, \(J = 1.9\) Hz); ³¹P NMR (121 MHz, CDCl₃): δ 10.08; HRMS (MALDI-TOF) calcd for C₂₀H₁₅BrO₂P (M+H⁺): 381.0044, found 381.0061.

17b (=9):³ white powder; m.p. 98-99 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.26 (t, \(J = 8.0\) Hz, 1H), 7.49-7.54 (m, 5H), 7.56-7.60 (m, 3H), 7.74 (s, 1H), 7.86-7.91 (m, 4H).

17c (=6):¹ white powder; m.p. 154-155 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, \(J = 8.6\) Hz, 2H), 7.49-7.59 (m, 8H), 7.86-7.91 (m, 4H).

Synthesis of 18a, 18b and 18c by Sonogashira coupling (representative procedure for 19).
A toluene solution (5.0 mL) of 3 (158.6 mg, 1.2 mmol), 17a (381.2 mg, 1.0 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH₂Cl₂ and NH₄Cl aq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1.5:1) to afford 18a in a pure form (324.3 mg, 75% yield).

18a: yellow powder, m.p.140-142 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.82 (s, 3H), 6.78 (d, J = 8.6 Hz, 2H), 7.27-7.34 (m, 3H), 7.35-7.44 (m, 5H), 7.47-7.50 (m, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.94-7.97 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 55.18 (d, J = 4.6 Hz), 85.90, 85.98 (d, J = 169.1 Hz), 94.73, 103.82 (d, J = 30.1 Hz), 113.85, 114.37, 121.88 (d, J = 4.1 Hz), 127.21 (d, J = 1.9 Hz), 127.63, 128.54 (d, J = 13.4 Hz), 130.25, 130.84 (d, J = 11.2 Hz), 131.81, 132.03 (d, J = 2.8 Hz), 132.86 (d, J = 1.8 Hz), 132.91 (d, J = 121.6 Hz), 133.20, 159.81; ³¹P NMR (121 MHz, CDCl₃): δ 9.86; HRMS (MALDI-TOF) calcd for C₂₉H₂₂O₂P (M+H⁺): 433.1357, found 433.1362.

18b (=10):³ white powder; m.p. 151-152 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.84 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.47 (d, J = 8.8 Hz, 2H), 7.49-7.54 (m, 5H), 7.56-7.58 (m, 3H), 7.74 (s, 1H), 7.88-7.93 (m, 4H).

18c (=4): as described in above

Sonogashira coupling of 16c with an excess amount of 13.
A toluene solution (5 mL) of 16c (141.4 mg, 0.5 mmol), 13 (226.2 mg, 1.0 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for 15 h. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (AcOEt) to afford 17c in a pure form (183.0 mg, 96% yield) and 19 (0.01 mmol, 2% NMR yield (using 1, 4-dioxane as an internal standard)).

17c: as described in above

**Competitive Sonogashira coupling of 20 vs 13 with 11.**

A toluene solution (5.0 mL) of 20 (163.2 mg, 0.5 mmol), 13 (113.1 mg, 0.5 mmol), 11 (117.0 mg, 0.5 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and diisopropylamine (0.25 mL) was stirred under nitrogen at 80 °C for overnight. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1.5:1) to afford 4 in a pure form (149.2 mg, 69% yield) and 14 in a pure form (29.9 mg, 18% yield).
Synthesis of 23 and 24 by click reaction (representative procedure for 23).

An acetone solution (10 mL) of 21 (326.3 mg, 1.0 mmol), benzyl azide (159.8 mg, 1.2 mmol), CuI (19.0 mg, 0.1 mmol) and DIPEA (340.1 μL, 2.0 mmol) was stirred under nitrogen at rt for 2 h. After workup with CH₂Cl₂ and water, the organic layer was dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:2) to give 23 in a pure form (363.0 mg, 79% yield).

23: white powder; m.p. 114-115 °C; ¹H NMR (500 MHz, CDCl₃): δ 5.59 (s, 2H), 7.32-7.33 (m, 2H), 7.38-7.44 (m, 4H), 7.48-7.58 (m, 7H), 7.68 (s, 1H), 7.88-7.92 (m, 5H), 8.02 (s, 1H).

24: white powder; m.p. 157-158°C; ¹H NMR (400 MHz, CDCl₃): δ 5.57 (s, 2H), 7.29-7.32 (m, 2H), 7.36-7.39 (m, 3H), 7.43-7.48 (m, 4H), 7.49-7.55 (m, 2H), 7.85-7.91 (m, 4H), 8.08 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 54.41, 128.53 (d, J = 13.4 Hz), 129.27 (d, J = 13.4 Hz), 130.77 (d, J = 23.9 Hz), 131.49 (d, J = 10.5 Hz), 131.85, 132.14 (d, J = 2.8 Hz), 132.95, 133.44, 141.52, 142.88; MRMS (MALDI-TOF) calcd for C₂₁H₁₉N₃OP (M+H⁺): 360.1266, found 360.1262.

Synthesis of 28.
To a THF solution (10 mL) of 17a (381.2 mg, 1.0 mmol) was added t-BuOK (134.6 mg, 1.2 mmol). After the mixture was stirred for 2 h under nitrogen at rt, 29 (342.6 mg, 0.8 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), toluene (16 mL) and diisopropylamine (0.5 mL) was added sequentially. The mixture was stirred under nitrogen at rt for 36 h. After workup with CH₂Cl₂ and NH₄Cl aq, the organic layer was washed with brine, and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 2:1) to give 28 in a pure form (238.7 mg, 62% yield, based on iodide).

28: white powder; m.p. 126-129 °C; ^1H NMR (500 MHz, CDCl₃): δ 7.17-7.20 (m, 2H), 7.28-7.30 (m, 1H), 7.33-7.38 (m, 5H), 7.44-7.48 (m, 3H), 7.58-7.60 (m, 1H), 7.65 (d, J = 3.4 Hz, 1H), 7.66 (d, J = 4.2 Hz, 1H), 7.90-7.95 (m, 4H); ^13C NMR (75 MHz, CDCl₃): δ 86.33 (d, J = 168.6 Hz), 91.19, 92.66, 103.37 (d, J = 30.4 Hz), 122.15 (d, J = 4.1 Hz), 124.55, 125.50, 126.39 (d, J = 1.8 Hz), 126.94, 128.39, 128.44 (d, J = 13.7 Hz), 129.78, 130.28, 130.85 (d, J = 11.2 Hz), 132.04 (d, J = 2.8 Hz), 132.28, 132.32, 132.79 (d, J = 121.9 Hz), 133.00 (d, J = 2.2 Hz), 133.55; ^31P NMR (121 MHz, CDCl₃): δ 9.91; HRMS (MALDI-TOF) calcd for C₂₈H₁₉BrOP (M+H⁺): 481.0357, found 481.0396.

Synthesis of 30.
To a THF solution (10 mL) of 28 (240.6 mg, 0.5 mmol) was added t-BuOK (67.3 mg, 0.6 mmol). After the mixture was stirred for 2 h under nitrogen at rt, 29 (149.9 mg, 0.35 mmol), Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol), toluene (16 mL) and diisopropylamine (0.25 mL) was added sequentially. The mixture was stirred under nitrogen at rt for 48 h. After workup with CH₂Cl₂ and NH₄Claq, the organic layer was washed with brine, and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1.5:1) and recrystallization from THF/hexane to give 30 in a pure form (114.0 mg, 56% yield, based on iodide).

30: white powder; m.p. 129-131 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.16-7.31 (m, 8H), 7.34-7.38 (m, 2H), 7.40-7.44 (m, 3H), 7.54 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.62-7.66 (m, 3H), 7.88-7.92 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 86.46 (d, J = 168.5 Hz), 91.14, 92.11, 92.36, 93.03, 103.53 (d, J = 30.0 Hz), 122.48 (d, J = 4.1 Hz), 124.98, 125.28, 125.44, 125.51, 126.39 (d, J = 2.0 Hz), 127.03, 127.06, 128.33, 128.40-128.48 (m), 128.53 (d, J = 11.3 Hz), 128.56, 129.62 (d, J = 3.5 Hz), 130.30, 130.94 (d, J = 11.3 Hz), 132.06, 132.24, 132.47, 132.92 (d, J = 122.0 Hz), 133.10, 133.63; ³¹P NMR (121 MHz, CDCl₃): δ 6.89; HRMS (MALDI-TOF) calcd for C₃₆H₂₃BrOP (M+H⁺): 581.0670, found 581.0641.

**Synthesis of 25²**.
To a THF solution (5 mL) of 30 (58.1 mg, 0.1 mmol) was added t-BuOK (13.5 mg, 0.12 mmol). After the mixture was stirred for 2 h under nitrogen at rt, the resulted reaction mixture was added to a toluene solution (8 mL) of Pd(PPh3)4 (5.8 mg, 0.005 mmol), CuI (1 mg, 0.005 mmol) and diisopropylamine (0.05 mL) via syringe over 6 minutes. The mixture was stirred under nitrogen at 80 °C for 15 h. After workup with CH2Cl2 and NH4Claq, the organic layer was washed with brine, and dried over MgSO4. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH2Cl2, 8:1) to give 25 in a pure form (20.4 mg, 68% yield).

25: pale-green powder; m.p. 209-210 °C; 1H NMR (500 MHz, CDCl3): δ 7.17-7.20 (m, 6H), 7.33-7.37 (m, 6H); 13C NMR (125 MHz, CDCl3): δ 92.79, 126.61, 128.52, 131.98.

Synthesis of starting compound 31.

A solution of BuLi (1.6 M in hexane, 2.1 mL, 3.3 mmol) was added dropwise to a stirring suspension of 9,10-dibromoanthracene (1008.1 mg, 3.0 mmol) in 40 mL of THF at -78 °C, and the resulting mixture was stirred for 3 h at -78 °C. To the resulting clear red solution, a solution of iodine (989.8 mg, 3.9 mmol) in 10.0 mL of THF was added dropwise, and the resulting mixture was stirred for 1 h at -78 °C, and then allowed to warm to room temperature for overnight. The resulting mixture was
concentrated in vacuo to approximately 10% of the initial volume, and 20% aqueous solution of Na$_2$S$_2$O$_3$ was added. A yellow crystalline precipitate was filtered, washed successively with dilute Na$_2$S$_2$O$_3$ solution, water, and cold ethanol, and dried in vacuo. Recrystallization from toluene afforded 31 in a pure form (907.8 mg, 79% yield).

31: $^9$ yellow fiber-like crystal, $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.59-7.63 (m, 4H), 8.52-8.56 (m, 4H).

**Synthesis of 32.**

![Synthesis of 32](image)

A toluene solution (20.0 mL) of 31 (383.0 mg, 1.0 mmol), 13 (339.3 mg, 1.5 mmol), Pd(PPh$_3$)$_4$ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 18 h. After workup with CH$_2$Cl$_2$ and NH$_4$Claq, the combined organic layer was washed with brine and dried over MgSO$_4$. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:1) to afford 32 in a pure form (298.4 mg, 62% yield).

32: white powder, m.p. 195-196 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.54-7.58 (m, 4H), 7.60-7.67 (m, 6H), 8.03-8.07 (m, 4H), 8.47 (d, $J = 8.6$ Hz, 2H), 8.59 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 94.87 (d, $J = 165.8$ Hz), 102.44 (d, $J = 29.5$ Hz), 113.90 (d, $J = 4.1$ Hz), 126.42, 127.65, 127.83, 128.05, 128.50, 128.79 (d, $J = 12.9$ Hz), 129.99, 131.06 (d, $J = 11.4$ Hz), 132.41, 133.05 (d, $J = 121.9$ Hz), 133.94 (d, $J = 2.1$ Hz); $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 6.33; HRMS (MALDI-TOF) calcd for C$_{28}$H$_{19}$BrOP (M+H$^+$): 481.0357, found 481.0323.

**Synthesis of 33 and 35 (representative procedure for 33).**
A toluene solution (20.0 mL) of 3 (198.2 mg, 1.5 mmol), 32 (481.3 mg, 1.0 mmol), Pd(PPh₃)₄ (57.8 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol) and diisopropylamine (0.5 mL) was stirred under nitrogen at 80 °C for 18 h. After workup with CH₂Cl₂ and NH₄Claq, the combined organic layer was washed with brine and dried over MgSO₄. After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/AcOEt, 1:1) to afford 33 in a pure form (420.7 mg, 79% yield).

33: white powder, m.p. 180-181 °C; ¹H NMR (500 MHz, CDCl₃): δ 3.89 (s, 3H), 7.00 (d, J = 8.8 Hz, 2H), 7.54-7.58 (m, 4H), 7.60-7.65 (m, 6H), 7.72 (d, J = 8.6 Hz, 2H), 8.04-8.08 (m, 4H), 8.45-8.47 (m, 2H), 8.69-8.70 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 55.36 (d, J = 4.6 Hz), 84.94, 94.89 (d, J = 167.5 Hz), 103.14 (d, J = 29.4 Hz), 104.35, 113.22 (d, J = 4.6 Hz), 114.22 (d, J = 8.3 Hz), 114.94, 122.28, 126.40, 126.78, 127.53 (d, J = 3.6 Hz), 127.94, 128.76 (d, J = 13.4 Hz), 131.07 (d, J = 11.3 Hz), 131.40, 132.35, 133.21 (d, J = 122.0 Hz), 133.24 (d, J = 1.5 Hz), 133.32, 160.26; ³¹P NMR (121 MHz, CDCl₃): δ 7.31; HRMS (MALDI-TOF) calcd for C₃₇H₂₆O₂P (M+H⁺): 533.1670, found 533.1642.

35: white powder, m.p. 249-150 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.11 (t, J = 7.3 Hz, 4H), 7.17 (d, J = 7.6 Hz, 4H), 7.32 (t, J = 7.8 Hz, 4H), 7.54-7.58 (m, 4H), 7.60-7.64 (m, 8H), 8.04-8.08 (m, 4H), 8.45-8.47 (m, 2H), 8.68-8.70 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 85.51, 94.92 (d, J = 167.5 Hz), 103.20 (d, J = 29.5 Hz),
104.84, 113.19, 115.27, 121.94 (d, \( J = 8.2 \) Hz), 122.38, 123.87 (m), 125.22 (m), 126.46, 126.82, 127.59 (d, \( J = 5.2 \) Hz), 127.98, 128.78 (d, \( J = 13.3 \) Hz), 129.48 (m), 131.10 (d, \( J = 11.3 \) Hz), 131.46, 132.78 (d, \( J = 3.0 \) Hz), 132.84 (d, \( J = 121.0 \) Hz), 133.31, 133.72, 146.93, 148.70; \(^{31}\)P NMR (121 MHz, CDCl\(_3\)): \( \delta \) 7.26; HRMS (MALDI-TOF) calcd for C\(_{48}\)H\(_{32}\)NOP (M\(^+\)): 669.2222, found 669.2263.

**Synthesis of 26 and 27:**

![Synthesis diagram]

To a THF solution (15.0 mL) of 33 (266.3 mg, 0.5 mmol) was added t-BuOK (78.5 mg, 0.7 mmol). After the mixture was stirred for 3.5 h under nitrogen at rt, 4-iodobenzonitrile 34 (171.8 mg, 0.75 mmol), Pd(PPh\(_3\))\(_4\) (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol), toluene (20.0 mL) and diisopropylamine (0.25 mL) was added sequentially. The mixture was stirred under nitrogen at 80 °C overnight. After workup with CH\(_2\)Cl\(_2\) and NH\(_4\)Claq, the organic layer was washed with brine, and dried over MgSO\(_4\). After filtration, the solvents were evaporated. The crude product was subjected to column chromatography on silica gel (hexane/CH\(_2\)Cl\(_2\), 4:1) to give 26 in a pure form (169.1 mg, 78% yield).

26: white powder, m.p. 234-235 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 3.89 (s, 3H), 6.98 (d, \( J = 8.8 \) Hz, 2H), 7.60-7.66 (m, 4H), 7.69-7.72 (m, 4H), 7.80 (d, \( J = 8.2 \) Hz, 2H), 8.56-8.60 (m, 2H), 8.65-8.70 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 55.40 (d, \( J = 5.3 \) Hz), 85.17, 91.02, 100.17, 103.40, 111.55, 114.23, 115.28, 116.35, 118.58,
120.28, 126.71, 127.18, 127.48, 128.26, 131.75, 131.98, 132.18, 132.28, 133.24, 160.13; HRMS (MALDI-TOF) calcd for C_{32}H_{19}NO (M^+): 433.1467, found 433.1422.

27: white powder, m.p. 190-191 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.09-7.12 (m, 4H), 7.18 (d, \(J = 7.6\) Hz, 4H), 7.32 (t, \(J = 7.9\) Hz, 4H), 7.58-7.69 (m, 8H), 7.95 (d, \(J = 7.6\) Hz, 1H), 8.02 (s, 1H), 8.65-8.67 (m, 2H), 8.69-8.71 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 85.77, 88.09, 100.28, 103.42, 115.84, 116.82, 119.71, 122.15, 122.20, 123.75, 123.76 (q, \(J = 272.3\) Hz), 124.38, 125.11 (q, \(J = 2.1\) Hz), 126.66, 126.92, 127.02, 127.41, 128.26 (q, \(J = 3.6\) Hz), 129.07, 129.46 (m), 131.12 (q, \(J = 32.5\) Hz), 131.79, 132.20, 132.67, 134.69 (d, \(J = 1.5\) Hz), 147.04, 148.39; HRMS (MALDI-TOF) calcd for C_{43}H_{26}F_{3}N (M^+): 613.2017, found 613.2003.

### III. References


IV. $^1$H NMR and $^{13}$C NMR Charts
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![1H NMR spectrum](image)
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\[ \text{MgO} \text{H}_{2} + \text{P} \rightarrow \text{MgO} \text{H}_{2} \text{P} \]

'H NMR
$^{31}$P NMR
1H NMR

H₂O
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Ph$_3$(O)P=O=P(O)Ph$_2$
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![NMR Spectrogram](image)

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- Temperature: 298 K

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**Chemical Structures**

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- **H2O**: 
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  - **O**: Oxygen atom

**Additional Notes**

- **Remarks**: None