Electronic Supplementary Information

Intramolecular Addition of Benzyl Anion to Alkyne

Utilizing [1,2]-Phospha-Brook Rearrangement
under Brønsted Base Catalysis

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Contents

General Information S1
Experimental Procedure S2
Analytical Data S6

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR Spectra of 1 – 8 S16
General Information

Unless otherwise noted, the reactions were carried out with dried glassware under argon atmosphere. $^1$H NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard (CDCl$_3$: 7.26 ppm, TMS: 0.00 ppm; CD$_3$OD: 3.31 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. $^{13}$C NMR spectra were recorded on a JEOL JNM-ECA600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl$_3$: 77.0 ppm; CD$_3$OD: 49.0 ppm). $^{31}$P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H$_3$PO$_4$ solution as an external standard (0.0 ppm in CDCl$_3$). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF$_{254}$, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40-50 μm; Kanto Chemical Co., Inc.). High resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T FT-ICR-MS spectrometer at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

Materials: Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Dichloromethane, tetrahydrofuran and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under argon atmosphere.
Experimental Procedure

Procedure for Preparation of Biaryl Compounds 1.

Synthesis of 1a is representative as shown in Scheme S1.

Scheme S1. Synthesis of 1a

Synthesis of S1

2-Bromoiodobenzene (3.8 mL, 30 mmol) and ethynyltrimethylsilane (4.4 mL, 32 mmol) were sequentially added to a solution of palladium acetate (0.13 g, 0.60 mmol), triphenylphosphine (0.47 g, 1.8 mmol) and copper iodide (0.23 g, 1.2 mmol) in Et₃N (60 mL). The resulting mixture was stirred at ambient temperature for 11 h, and then sat. aq. NH₄Cl was added. The product was extracted with AcOEt, and the combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The crude product was purified by silica gel column chromatography (hexane) afforded S1 (7.6 g, 30 mmol, >99%) as a pale yellow oil.

Synthesis of S2

To a solution of S1 (5.1 g, 20 mmol) in THF (40 mL) was added dropwise a solution of nBuLi (1.6 M in hexane, 15 mL, 24 mmol) at −78 °C. After stirred for 2.5 h, triisopropyl borate (6.9 mL, 30 mmol) was added to the solution in one portion at that temperature. The resulting mixture was then allowed to warm to room temperature and was stirred for 12 h. The reaction was quenched with 2N aq. HCl, and the mixture was stirred for 10 min before the extraction of the product with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and
evaporated. The crude mixture was purified by recrystallization from hexane to afford S2 (3.0 g, 14 mmol, 70%) as a white crystal.

**Synthesis of S3**

\[
\begin{align*}
\text{Br-CHO} + \text{SiMe}_3 - & \text{S2} \\
& \begin{array}{c}
\text{1.1 eq.}
\end{array}
\end{align*}
\]

A mixture of palladium acetate (0.11 g, 0.50 mmol), DPPF (0.42 g, 0.75 mmol) and K₂CO₃ (2.8 g, 20 mmol) in 1,2-DME (30.0 mL) was stirred at room temperature for 30 min. 2-Bromobenzaldehyde (1.2 mL, 10 mmol) and S2 (2.4 g, 11 mmol) were sequentially added, and the resulting mixture was then heated at reflux for 4 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 10:1) to yield S3 (2.7 g, 9.8 mmol, 98%) as a yellow oil.

**Synthesis of S4**

\[
\begin{align*}
\text{S3} \quad \text{K₂CO₃ (3.0 eq.)} \\
\text{MeOH, rt, 9 h} \quad \text{H} \\
\end{align*}
\]

A mixture of S3 (2.7 g, 9.8 mmol) and K₂CO₃ (4.1 g, 29 mmol) in MeOH (20 mL) was stirred at room temperature for 9 h. Sat. aq. NH₄Cl was added, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 10:1) to provide S4 (1.9 g, 9.3 mmol, 95%) as a yellow oil.

**Synthesis of 1a**

\[
\begin{align*}
\text{S4} \quad \text{PdCl₂(PPh₃)₂ (2.0 mol%)} \\
\text{Et₃N/DMF, rt, 3 h} \quad \text{Ar} \quad \text{1a} \\
\text{Ar} = 4-\text{NO}_2-\text{C₆H₄} \\
\end{align*}
\]

I-iodo-4-nitrobenzene (0.52 g, 2.1 mmol) and a solution of S4 (0.41 g, 2.0 mmol) in DMF (2.0 mL) were sequentially added to a solution of dichlorobis(triphenylphosphine)palladium (28 mg, 0.040 mmol) and copper iodide (15 mg, 0.080 mmol) in Et₃N (2.0 mL). The resulting mixture was stirred at ambient temperature for 3 h, and then sat. aq. NH₄Cl was added. The product was extracted with AcOEt, and the combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 5:1) to afford 1a (0.47 g, 1.4 mmol, 72%) as a yellow solid.
General Procedure for Intramolecular Cyclization Catalyzed by Phosphazene Base P2-tBu.

The reaction of 1a with diethyl phosphite (2) is representative (Table 1, entry 15). To a solution of 1a (82 mg, 0.25 mmol) and diethyl phosphite (2) (32 µL, 0.25 mmol) in CH₂Cl₂ (10 mL) was added a solution of P2-tBu in THF (2.0 M, 13 µL, 0.25 mmol). The resulting mixture was then stirred at room temperature for 6 h. The reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was dried over Na₂SO₄ and evaporated. The residue was purified by column chromatography (hexane/AcOEt = 3:2 to 1:1) to provide 4a (99 mg, 0.21 mmol, 86%) as a yellow solid.

Procedure for Transformation of 3a by Friedel-Crafts Reaction (Scheme 4a).

The reaction of 3a with anisole is representative. To a solution of 3a (46 mg, 0.10 mmol) and anisole (33 µL, 0.30 mmol) in CH₂Cl₂ (1.0 mL) was added TfOH (30 mg, 0.20 mmol) at 0 °C. After stirred at that temperature for 2 h, the reaction was quenched with sat. aq. NaHCO₃, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The crude mixture was purified by column chromatography (hexane/AcOEt = 10:1 to 5:1) to afford 6a (37 mg, 0.088 mmol, 88%) as a white solid.

Procedure for Transformation of 3a by Pd-Catalyzed Cross-Coupling Reaction (Scheme 4b).

The reaction of 3a with phenylboronic acid is representative. A mixture of palladium acetate (1.1 mg, 5.0 µmol), triphenylphosphine (3.9 mg, 0.015 mmol) and K₂CO₃ (28 mg, 0.20 mmol) in 1,2-dioxane (0.50 mL) was stirred at room temperature for 30 min. A solution of 3a (46 mg, 0.10 mmol) in 1,4-dioxane (0.50 mL) and phenylboronic acid (18 mg, 0.15 mmol) were sequentially added, and the
resulting mixture was then heated at 100 °C for 5 h. After cooled to room temperature, the reaction was quenched with sat. aq. NH₄Cl, and the product was extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and evaporated. The crude mixture was purified by column chromatography (hexane/ AcOEt = 20:1 to 15:1) to provide 6b (29 mg, 0.074 mmol, 74%) as a white solid.
2-Formyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1a):

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 9.0$ Hz, 2H), 7.45 (dd, $J = 7.8, 0.6$ Hz, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.48 (dd, $J = 7.8, 7.2$ Hz, 1H), 7.53 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.59 (dd, $J = 7.8, 7.8$ Hz, 1H), 7.68 (dd, $J = 7.8, 0.6$ Hz, 1H), 7.70 (dd, $J = 7.8, 7.8$ Hz, 1H), 8.10 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.11 (d, $J = 9.0$ Hz, 2H), 9.92 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 91.6, 93.3, 122.6, 123.5, 127.0, 128.4, 128.5, 129.5, 130.3, 131.2, 131.9, 132.2, 133.6 (2C), 134.2, 140.8, 143.8, 147.0, 191.6; IR (ATR): 2843, 2755, 2217, 1695, 1596, 1519, 1343, 1198, 1107 cm$^{-1}$; HRMS (ESI) Calcd for C$_{21}$H$_{13}$NO$_3$ [M+Na]$^+$ 350.0788, Found 350.0788.

5-Fluoro-2-formyl-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1b):

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.15 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.24-7.29 (m, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.51 (ddd, $J = 7.8, 7.8, 1.8$ Hz, 1H), 7.54 (ddd, $J = 7.8, 7.8, 1.8$ Hz, 1H), 7.69 (d, $J = 7.8$ Hz, 1H), 8.11-8.15 (m, 1H), 8.13 (d, $J = 8.4$ Hz, 2H), 9.83 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 91.9, 92.7, 115.9 (d, $J = 23.1$ Hz), 118.1 (d, $J = 23.1$ Hz), 122.4, 123.6, 128.9, 129.3, 129.6, 129.9 (d, $J = 10.1$ Hz), 130.1, 130.8, 131.9, 132.4, 139.4, 146.5 (d, $J = 8.6$ Hz), 147.1, 165.6 (d, $J = 254.3$ Hz), 189.9; IR (ATR): 3078, 2849, 2758, 2218, 1693, 1597, 1578, 1518, 1343, 1191, 1107 cm$^{-1}$; HRMS (ESI) Calcd for C$_{25}$H$_{15}$FNO$_3$ [M+Na]$^+$ 368.0693, Found 368.0693.

2-Formyl-5-methoxy-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1c):

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.91 (s, 3H), 6.89 (d, $J = 2.4$ Hz, 1H), 7.08 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.31 (d, $J = 9.0$ Hz, 2H), 7.46 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.48 (ddd, $J = 7.8, 7.2, 1.2$ Hz, 1H), 7.52 (ddd, $J = 7.2, 7.2, 1.2$ Hz, 1H), 7.67 (dd, $J = 7.8, 1.2$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.12 (d, $J = 9.0$ Hz, 2H), 9.77 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 55.7, 91.6, 93.2, 114.3, 115.9, 122.5, 123.5, 127.8, 128.4, 129.4, 129.5, 129.6, 130.2, 131.9, 132.2, 140.8, 146.1, 147.0, 163.6, 190.3; IR (ATR): 2973, 2916, 2841, 2760, 2218, 1684, 1594, 1517, 1342, 1238, 1091, 933 cm$^{-1}$; HRMS (ESI) Calcd for C$_{26}$H$_{15}$NO$_4$ [M+Na]$^+$ 380.0893, Found 380.0893.

2-Formyl-4-methoxy-2'-(4-nitrophenyl)ethynyl-1,1'-biphenyl (1d):

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.94 (s, 3H), 7.25 (dd, $J = 8.4, 3.0$ Hz, 1H), 7.33 (d, $J = 9.0$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.42 (dd, $J = 7.8, 0.6$ Hz, 1H), 7.45 (ddd, $J = 7.8, 7.8, 1.2$ Hz, 1H), 7.51 (ddd, $J = 7.8, 7.8, 1.2$ Hz, 1H), 7.58 (d, $J = 3.0$ Hz, 1H), 7.67 (dd, $J = 7.8, 0.6$ Hz, 1H), 8.13 (d, $J = 9.0$ Hz, 2H), 9.88 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 55.7, 91.5, 93.5, 109.6, 121.0, 122.8, 123.5, 128.1, 129.5, 129.6, 130.7, 132.0, 132.3, 132.6, 135.1, 136.7, 140.5, 147.0, 159.6, 191.5; IR (ATR): 3077, 2940, 2847, 2752, 2217, 1691, 1597, 1519, 1472, 1343, 1279, 1164 cm$^{-1}$; HRMS (ESI) Calcd for C$_{26}$H$_{15}$NO$_4$ [M+Na]$^+$ 380.0893, Found 380.0893.
3-Chloro-2-formyl-2′-(4-nitrophenyl)ethynyl-1,1′-biphenyl (1e):

\[
\begin{align*}
{^1}H \text{ NMR} (600 MHz, CDCl}_3: & \delta 7.31 (dd, J = 4.2, 4.2 Hz, 1H), 7.34 (d, J = 9.0 Hz, 2H), 7.37 (dd, J = 7.8, 1.2 Hz, 1H), 7.45 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.50 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 7.54-7.58 (m, 2H), 7.63 (dd, J = 7.8, 1.2 Hz, 1H), 8.15 (d, J = 9.0 Hz, 2H), 10.2 (s, 1H); \\
{^{13}}C \text{ NMR} (150 MHz, CDCl}_3: & \delta 91.7, 93.4, 121.4, 123.6, 128.2, 129.4, 129.5, 130.1, 130.6, 131.7, 131.9, 132.0, 132.2, 133.0, 135.3, 141.7, 144.1, 147.0, 190.0; \text{ IR (ATR): } 3109, 3068, 2851, 2763, 2217, 1704, 1594 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcld for C}_{21}H_{12}ClNO_3 [M+Na]^+ 384.0398, \text{ Found 384.0398.}
\end{align*}
\]

5′-Chloro-2-formyl-2′-(4-nitrophenyl)ethynyl-1,1′-biphenyl (1f):

\[
\begin{align*}
{^1}H \text{ NMR} (600 MHz, CDCl}_3: & \delta 7.27 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.47 (s, 1H), 7.45-7.48 (m, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.61 (dd, J = 7.8, 7.8 Hz, 1H), 7.72 (dd, J = 7.8, 7.8 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 9.92 (s, 1H); \text{ IR (ATR): } 2985, 2917, 2845, 2215, 1697, 1596, 1519, 1343, 1236 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcld for C}_{21}H_{12}ClNO_3 [M+Na]^+ 384.0398, \text{ Found 384.0398.}
\end{align*}
\]

2-Formyl-2′-(4-nitrophenyl)ethynyl-5′-trifluoromethyl-1,1′-biphenyl (1g):

\[
\begin{align*}
{^1}H \text{ NMR} (600 MHz, CDCl}_3: & \delta 7.30 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 7.2 Hz, 1H), 7.64 (dd, J = 7.2, 7.2 Hz, 1H), 7.72-7.76 (m, 3H), 7.79 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 9.91 (s, 1H); \text{ IR (ATR): } 2848, 2754, 2223, 1697, 1612, 1596, 1520, 1173, 1125 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcld for C}_{21}H_{12}F_3NO_3 [M+Na]^+ 418.0662, \text{ Found 418.0661.}
\end{align*}
\]

4′,5′-Dioxymethylene-2-formyl-2′-(4-Nitrophenyl)ethynyl-1,1′-biphenyl (1h):

\[
\begin{align*}
{^1}H \text{ NMR} (600 MHz, CDCl}_3: & \delta 6.11 (s, 2H), 6.91 (s, 1H), 7.08 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.40 (dd, J = 7.8, 0.6 Hz, 1H), 7.57 (ddd, J = 7.8, 7.8, 0.6 Hz, 1H), 7.68 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 8.07 (dd, J = 7.8, 1.2 Hz, 1H), 8.09 (d, J = 8.4 Hz, 2H), 9.95 (s, 1H); \text{ IR (ATR): } 2900, 2845, 2207, 1693, 1593, 1516, 1475, 1340, 1223, 1036 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcld for C}_{21}H_{12}NO_3 [M+Na]^+ 394.0686, \text{ Found 394.0686.}
\end{align*}
\]

2-Formyl-1-[2-(4-nitrophenyl)ethylidencyanophthalene (1i):

\[
\begin{align*}
{^1}H \text{ NMR} (600 MHz, CDCl}_3: & \delta 6.89 (d, J = 9.0 Hz, 2H), 7.48 (ddd, J = 7.8, 6.6, 1.2 Hz, 1H), 7.51 (dd, J = 6.6, 2.4 Hz, 1H), 7.57-7.62 (m, 3H), 7.64 (ddd, J = 7.8, 6.6, 1.2 Hz, 1H), 7.77 (dd, J = 6.6, 2.4 Hz, 1H), 7.96-8.00 (m, 3H), 8.02 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 9.0 Hz, 1H), 9.90 (s, 1H); \text{ IR (ATR): } 2900, 2845, 2207, 1693, 1593, 1516, 1475, 1340, 1223, 1036 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcld for C}_{21}H_{12}NO_3 [M+Na]^+ 394.0686, \text{ Found 394.0686.}
\end{align*}
\]
1-(2-Formyl)phenyl-2-(4-nitrophenyl)ethynlnaphthalene (1j):

{\text{\textsuperscript{1}}H NMR (600 MHz, CDCl\textsubscript{3}) \text{\textdelta} 7.21 (d, J = 9.0 Hz, 2H), 7.45-7.48 (m, 3H), 7.54-7.59 (m, 1H), 7.69 (ddd, J = 8.4, 8.4, 0.6 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.71 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 8.10 (d, J = 9.0 Hz, 2H), 8.20 (dd, J = 7.8, 0.6 Hz, 1H), 9.66 (s, 1H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \text{\textdelta} 92.6, 94.1, 120.4, 123.5, 126.4, 127.2, 127.4, 127.5, 127.6, 128.3, 128.69, 129.6, 131.9, 132.0, 132.5, 133.3, 133.7, 135.1, 139.4, 142.3, 146.9, 191.4; IR (ATR): 3057, 2839, 2746, 2206, 1697, 1596, 1517, 1341, 1195, 1108, 854 cm\textsuperscript{-1}; HRMS (ESI) Calcd for C\textsubscript{25}H\textsubscript{15}NO\textsubscript{3} [M+Na]\textsuperscript{+} 400.0944, Found 400.0944.

2-(2-Formyl)phenyl-3-(4-nitrophenyl)ethynlnaphthalene (1k):

{\text{\textsuperscript{1}}H NMR (600 MHz, CDCl\textsubscript{3}) \text{\textdelta} 7.29 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.59-7.64 (m, 3H), 7.73 (dd, J = 7.8, 7.8 Hz, 1H), 7.88-7.94 (m, 3H), 8.11-8.15 (m, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.23 (s, 1H), 9.96 (s, 1H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \text{\textdelta} 91.8, 93.8, 120.2, 123.6, 127.0, 127.5, 127.8, 128.0, 128.1, 128.5, 129.6 (2C), 131.6, 131.9, 132.5, 132.7, 133.0, 133.6, 134.6, 137.0, 143.7, 147.0, 191.6; IR (ATR): 3057, 2923, 2851, 2752, 2213, 1693, 1595, 1516, 1340, 1236, 1091, 893 cm\textsuperscript{-1}; HRMS (ESI) Calcd for C\textsubscript{25}H\textsubscript{15}NO\textsubscript{3} [M+Na]\textsuperscript{+} 400.0944, Found 400.0944.

2-(2-Formyl)phenyl-1-(4-nitrophenyl)ethynlnaphthalene (1l):

{\text{\textsuperscript{1}}H NMR (600 MHz, CDCl\textsubscript{3}) \text{\textdelta} 7.39 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.63 (dd, J = 7.8, 7.8 Hz, 1H), 7.65 (dd, J = 7.8, 7.8 Hz, 1H), 7.72 (dd, J = 7.2, 7.2 Hz, 1H), 7.74 (dd, J = 7.2, 7.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 9.0 Hz, 2H), 8.46 (d, J = 8.4 Hz, 1H), 9.95 (s, 1H); \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \text{\textdelta} 91.6, 96.8, 119.9, 123.6, 126.3, 127.0, 127.3, 127.5, 128.1, 128.45, 128.51, 129.6, 129.7, 131.4, 131.9, 132.6, 132.8, 133.6, 134.4, 139.8, 144.4, 147.0, 191.6; IR (ATR): 3056, 2924, 2851, 2756, 2207, 1693, 1594, 1517, 1436, 1340, 1104 cm\textsuperscript{-1}; HRMS (ESI) Calcd for C\textsubscript{25}H\textsubscript{15}NO\textsubscript{3} [M+Na]\textsuperscript{+} 400.0944, Found 400.0944.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3a):

{\text{\textsuperscript{1}}H NMR (600 MHz, CDCl\textsubscript{3}) \text{\textdelta} 1.05 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 3.86 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.91 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.99 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.09 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.50 (dd, J = 7.8, 7.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.73 (dd, J = 7.8, 7.2 Hz, 1H), 7.62-7.68 (m, 2H), 7.91 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 8.00 (s, 1H), 8.18 (d, J = 8.4 Hz, 2H), 8.70 (d, J = 7.8 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H); \textsuperscript{31}P NMR (243 MHz, CDCl\textsubscript{3}) \text{\textdelta} -0.77; \textsuperscript{13}C NMR (150 MHz, CDCl\textsubscript{3}) \text{\textdelta} 15.7 (d, J = 7.2 Hz), 15.9 (d, J = 7.2 Hz), 63.99 (d, J = 5.8 Hz), 64.04 (d, J = 7.1 Hz), 79.1, 122.5, 123.3, 123.7 (2C), 125.0, 126.7, 126.8, 127.1, 146.8, 192.1; IR (ATR): 3104, 3061, 2849, 2736, 2218, 1691, 1677, 1595, 1518, 1342, 1233, 1106 cm\textsuperscript{-1}; HRMS (ESI) Calcd for C\textsubscript{25}H\textsubscript{15}NO\textsubscript{3} [M+Na]\textsuperscript{+} 400.0944, Found 400.0944.
127.7, 127.8, 128.0, 128.5, 129.1, 130.7, 131.1, 132.1, (d, J = 2.9 Hz), 146.9 (d, J = 5.7 Hz), 147.5; IR (ATR): 3080, 3070, 2983, 2930, 2908, 2372, 2336, 1604, 1522, 1497, 1451, 1348, 1270, 1165, 1108, 1032, 998 cm⁻¹; HRMS (ESI) Caled for C_{23}H_{25}NO_3P [M+Na]^+ 488.1234, Found 488.1234.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]- 3-fluorophenanthrene (3b)

\[ \text{H NMR (600 MHz, CDCl}_3) \delta 1.04 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 3.85 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 3.90 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 4.00 (ddq, } J = 9.6, 7.2, 7.2 Hz, 1H), 4.09 (ddq, } J = 9.6, 7.2, 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.41 (ddd, J = 8.4, 8.4, 2.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.62-7.66 (m, 1H), 7.91-7.96 (m, 2H), 7.97 (s, 1H), 8.18 (d, J = 8.4 Hz, 2H), 8.29 (dd, J = 10.8, 2.4 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H); \]

\[ {^31}P \text{ NMR (243 MHz, CDCl}_3) \delta -0.77; {^{13}}C \text{ NMR (150 MHz, CDCl}_3) \delta 15.8 (d, J = 5.9 Hz), 16.0 (d, J = 7.2 Hz), 64.0 (d, J = 5.7 Hz), 64.1 (d, J = 5.7 Hz), 79.0, 107.9 (d, J = 21.6 Hz), 116.2 (d, J = 24.5 Hz), 123.6, 123.8, 125.1, 126.8, 127.4, 127.5, 127.8, 128.8, 130.5 (d, J = 4.4 Hz), 131.2, 131.3, 131.5, 132.4 (d, J = 8.6 Hz), 146.8 (d, J = 5.7 Hz), 147.6, 162.2 (d, J = 245.6 Hz); IR (ATR): 3082, 2985, 2909, 1630, 1605, 1523, 1504, 1452, 1348, 1271, 1178, 1032, 999, 899 cm⁻¹; HRMS (ESI) Caled for C_{23}H_{25}NO_3P [M+Na]^+ 506.1139, Found 506.1139.

9-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-2-methoxyphenanthrene (3d):

\[ \text{H NMR (600 MHz, CDCl}_3) \delta 1.04 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 3.85 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 3.92 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 3.98 (s, 3H), 4.00 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 4.10 (ddq, } J = 10.2, 7.2, 7.2 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 3.0 Hz, 1H), 7.34 (dd, J = 9.0, 3.0 Hz, 1H), 7.43 (dd, J = 7.8, 7.2 Hz, 1H), 7.59 (dd, J = 7.8, 7.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 8.17 (d, J = 8.4 Hz, 2H), 8.58 (d, J = 9.0 Hz, 1H), 8.62 (d, J = 7.8 Hz, 1H); \]

\[ {^31}P \text{ NMR (243 MHz, CDCl}_3) \delta -0.79; {^{13}}C \text{ NMR (150 MHz, CDCl}_3) \delta 15.8 (d, J = 5.7 Hz), 16.0 (d, J = 7.2 Hz), 55.5, 64.0 (d, J = 5.9 Hz), 64.1 (d, J = 5.7 Hz), 79.0(d, J = 3.0 Hz), 109.0, 118.3, 122.9, 123.7, 124.2, 124.9, 125.0, 125.8, 126.8, 127.5, 127.6, 127.8, 131.3, 132.2, 132.8(d, J = 2.9 Hz), 147.0(d, J = 5.7 Hz), 147.6, 158.6; IR (ATR): 3080, 2983, 2937, 2909, 2840, 1605, 1522, 1347, 1269, 1231, 1033, 998 cm⁻¹; HRMS (ESI) Caled for C_{28}H_{25}NO_3P [M+Na]^+ 518.1339, Found 518.1339.

1-Chloro-9-[diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3e):

\[ \text{H NMR (600 MHz, CDCl}_3) \delta 1.14 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H), 3.95-4.03 (m, 3H), 4.07 (ddq, } J = 9.6, 7.2, 7.2 Hz, 1H), 7.16 (d, J = 9.0 Hz, 1H), 7.53 (dd, J = 7.8, 7.8 Hz, 1H), 7.63 (dd, J = 7.8, 7.8 Hz, 1H), 7.64-7.67 (m, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 8.18 (d, J = 9.0 Hz, 2H), 8.53 (s, 1H), 8.63 (d, J = 7.8 Hz, 1H), 8.73 (d, J = 7.8 Hz, 1H); \]

\[ {^31}P \text{ NMR (243 MHz, CDCl}_3) \delta -0.91; {^{13}}C \text{ NMR (150 MHz, CDCl}_3) \delta 15.9 (d, J = 7.2 Hz), 16.0 (d, J = 8.6 Hz), 64.16 (d, J = 7.1 Hz), 64.20 (d, J = 7.2 Hz), 79.0, 121.6, 123.1, 123.7, 123.8, 125.1, 127.3, 127.5, 127.6, 128.1, 128.2, 128.4, 130.8, 132.3, 133.2, 133.7 (d, J = 4.4 Hz), 146.7 (d, J = 5.7 Hz); IR (ATR): 3079, 2984, 2909, 1606, 1523, 1448, 1348, 1273, 1024, 999 cm⁻¹; HRMS (ESI) Caled for C_{23}H_{25}CINO_3P [M+Na]^+ 522.0844, Found 522.0844.

S9
3-Chloro-10-[diethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3f):

$^1$H NMR (600 MHz, CDCl₃) $\delta$ 1.05 (t, $J = 7.2$ Hz, 3H), 1.23 (t, $J = 7.2$ Hz, 3H), 3.86 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 3.91 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 4.01 (ddq, $J = 10.2$, 7.2, 7.2 Hz, 1H), 4.10 (ddq, $J = 10.2$, 7.2, 7.2 Hz, 1H), 7.05 (d, $J = 9.0$ Hz, 1H), 7.44 (dd, $J = 9.0$, 1.2 Hz, 1H), 7.62 (d, $J = 9.0$ Hz, 2H), 7.69 (dd, $J = 7.8$, 7.8 Hz, 1H), 7.74 (dd, $J = 7.8$, 7.8 Hz, 1H), 7.87 (d, $J = 9.0$ Hz, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.97 (s, 1H), 8.18 (d, $J = 9.0$ Hz, 2H), 8.61 (d, $J = 9.0$ Hz, 1H), 8.69 (d, $J = 1.2$ Hz, 1H); $^{31}$P NMR (243 MHz, CDCl₃) $\delta$ −0.73; $^{13}$C NMR (150 MHz, CDCl₃) $\delta$ 15.8 (d, $J = 7.2$ Hz), 16.0 (d, $J = 7.2$ Hz), 64.1 (d, $J = 5.9$ Hz), 64.2 (d, $J = 5.7$ Hz), 79.2, 122.7, 123.1, 123.8, 126.6, 126.9, 127.3, 127.7, 127.8, 128.1, 128.5, 129.2, 129.8, 131.1, 131.9 (d, $J = 4.4$ Hz), 132.5, 133.1, 146.7 (d, $J = 5.9$ Hz), 147.7; IR (ATR): 2984, 2908, 1734, 1605, 1524, 1349, 1321, 1277, 1124, 1034, 1000 cm⁻¹; HRMS (ESI) Calcd for C₂₅H₂₃ClNO₆P [M+Na]$^+$ 522.0844, Found 522.0844; CCDC No. 1546787. A single crystal for single-crystal X-ray diffraction analysis was obtained by recrystallization from hexane/AcOEt.

Figure S1. ORTEP diagram of 3f. Hydrogens are omitted for clarity.

10-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-3-trifluoromethylphenanthrene (3g):

$^1$H NMR (600 MHz, CDCl₃) $\delta$ 1.05 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 3H), 3.86 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 3.91 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 4.02 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 4.11 (ddq, $J = 9.6$, 7.2, 7.2 Hz, 1H), 7.11 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.73 (dd, $J = 7.8$, 7.8 Hz, 1H), 7.80 (dd, $J = 7.8$, 7.8 Hz, 1H), 8.00 (d, $J = 7.8$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 8.11 (s, 1H), 8.20 (d, $J = 9.0$ Hz, 2H), 8.72 (d, $J = 7.8$ Hz, 1H), 9.00 (s, 1H); $^{31}$P NMR (243 MHz, CDCl₃) $\delta$ −0.71; $^{13}$C NMR (150 MHz, CDCl₃) $\delta$ 15.8 (d, $J = 7.2$ Hz), 16.0 (d, $J = 7.2$ Hz), 64.1 (d, $J = 5.7$ Hz), 64.2 (d, $J = 5.9$ Hz), 79.0, 120.8 (q, $J = 2.9$ Hz), 122.6, 122.7 (q, $J = 2.9$ Hz), 123.8, 124.2 (q, $J = 270.0$ Hz), 126.0, 127.7, 128.0, 128.45, 128.47 (q, $J = 33.0$ Hz), 129.4, 130.4, 130.47, 130.54, 130.9, 131.0, 131.8 (d, $J = 4.4$ Hz), 146.5 (d, $J = 7.2$ Hz), 147.7; IR (ATR): 2984, 2908, 1734, 1605, 1524, 1349, 1321, 1277, 1124, 1034, 1000 cm⁻¹; HRMS (ESI) Calcd for C₂₆H₂₃F₃NO₆P [M+Na]$^+$ 556.1107, Found 556.1107.
10-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]-2,3-dioxymethylenephenanthrene (3h):

\[
\begin{align*}
\text{IR (ATR)}: & 3054, 2985, 2907, 1605, 1523, 1503, 1474, 1348, 1266, 1244, 1217, 1033, 999 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{25}\text{H}_{29}\text{NO}_3\text{P [M+Na]}^+ 532.1131, \text{Found 532.1131.}
\end{align*}
\]

5-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[c]phenanthrene (3i):

\[
\begin{align*}
\text{IR (ATR)}: & 2985, 2907, 1605, 1523, 1503, 1474, 1348, 1266, 1244, 1217, 1033, 999 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{25}\text{H}_{29}\text{NO}_3\text{P [M+Na]}^+ 532.1390, \text{Found 532.1390.}
\end{align*}
\]

6-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[c]phenanthrene (3j):

\[
\begin{align*}
\text{IR (ATR)}: & 3054, 2985, 2907, 1605, 1523, 1503, 1474, 1348, 1266, 1244, 1217, 1033, 999 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{25}\text{H}_{29}\text{NO}_3\text{P [M+Na]}^+ 538.1390, \text{Found 538.1390.}
\end{align*}
\]
6-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]benzo[a]anthracene (3k):

\[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 1.05 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H), 3.90 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 3.95 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.01 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 4.10 (ddq, J = 10.2, 7.2, 7.2 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.52 (ddd, J = 8.4, 8.4, 1.2 Hz, 1H), 7.56 (ddd, J = 8.4, 8.4, 1.2 Hz, 1H), 7.67 (dd, J = 8.4, 8.4 Hz, 1H), 7.72-7.78 (m, 1H), 7.75 (d, J = 9.0 Hz, 2H), 7.89 (s, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 3.6 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 9.0 Hz, 2H), 8.41 (s, 1H), 8.84 (d, J = 8.4 Hz, 1H), 9.22 (s, 1H); \text{31P NMR (243 MHz, CDCl}_3\text{)} \delta -0.61; \text{13C NMR (150 MHz, CDCl}_3\text{)} \delta 15.8 (d, J = 5.7 Hz), 16.0 (d, J = 7.2 Hz), 64.05 (d, J = 5.7 Hz), 64.09 (d, J = 4.4 Hz), 79.0, 122.3, 122.8, 123.7, 124.0, 126.2, 126.3, 126.9, 127.4, 127.9, 127.98, 128.02, 128.1, 128.3, 129.2, 130.5, 131.0, 131.47, 131.52, 132.3 (d, J = 4.4 Hz), 146.9 (d, J = 5.9 Hz), 147.6; \text{IR (ATR): } 3057, 2984, 2932, 2908, 2867, 1606, 1522, 1347, 1269, 1031, 1000, 970 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{29}H_{34}NO_8P[M+Na]^+ 538.1390, Found 538.1390.

5-[Diethoxyphosphoryloxy(4-nitrophenyl)methyl]chrysene (3l):

\[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 0.81 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 6.6 Hz, 3H), 3.62-3.77 (m, 3H), 3.89-3.97 (m, 1H), 7.44 (dd, J = 7.2, 7.2 Hz, 1H), 7.58 (dd, J = 7.2, 7.2 Hz, 1H), 7.70-7.73 (m, 1H), 7.77 (dd, J = 7.8, 7.8 Hz, 1H), 7.79-7.83 (m, 2H), 7.99 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 9.0 Hz, 2H), 8.10-8.23 (m, 1H), 8.22 (d, J = 9.0 Hz, 2H), 8.31 (s, 1H), 8.75 (d, J = 9.0 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H); \text{31P NMR (243 MHz, CDCl}_3\text{)} \delta -1.1; \text{13C NMR (150 MHz, CDCl}_3\text{)} \delta 15.6 (d, J = 7.2 Hz), 15.8 (d, J = 7.2 Hz), 63.9 (d, J = 5.7 Hz), 63.9 (d, J = 7.2 Hz), 78.7, 121.4, 123.2, 123.8, 126.0, 126.4, 127.0, 127.4, 127.5, 127.7, 128.1, 128.7, 129.2, 129.3 (2C), 129.8, 130.3 (2C), 131.2, 133.2, 133.7, 147.5 (d, J = 7.2 Hz), 147.8; \text{IR (ATR): } 3593, 3056, 2983, 2907, 1604, 1522, 1347, 1270, 1166, 1106, 1032, 1004, 982 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{30}H_{36}NO_8P[M+Na]^+ 538.1390, Found 538.1390.

9-[Dimethoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3m):

\[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 3.52 (d, J = 10.8 Hz, 3H), 3.70 (d, J = 11.4 Hz, 3H), 7.12 (d, J = 9.0 Hz, 1H), 7.50 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.62-7.68 (m, 4H), 7.73 (ddd, J = 7.8, 7.2, 1.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.96 (dd, J = 7.8, 1.2 Hz, 1H), 8.01 (s, 1H), 8.18 (d, J = 9.0 Hz, 2H), 8.69 (d, J = 7.8 Hz, 1H), 8.74 (d, J = 8.4 Hz, 1H); \text{31P NMR (243 MHz, CDCl}_3\text{)} \delta 1.65; \text{13C NMR (150 MHz, CDCl}_3\text{)} \delta 54.39 (d, J = 5.7 Hz), 54.44 (d, J = 5.7 Hz), 79.4, 122.6, 123.4, 123.8, 124.9, 126.86, 126.90, 127.2, 127.8, 127.9, 128.0, 128.5, 129.2, 130.7, 130.8, 131.2, 132.1, 132.0 (d, J = 3.0 Hz), 146.8 (d, J = 5.7 Hz), 147.7; \text{IR (ATR): } 2956, 2918, 2853, 1606, 1523, 1451, 1348, 1272, 1187, 1042, 1000, 854 \text{ cm}^{-1}; \text{HRMS (ESI) Calcd for C}_{25}H_{29}NO_8P[M+Na]^+ 460.0920, Found 460.0920.

9-[Diisopropoxyphosphoryloxy(4-nitrophenyl)methyl]phenanthrene (3n):

\[ \delta 1.00 (d, J = 6.0 Hz, 3H), 1.139 (d, J = 6.0 Hz, 3H), 1.143 (d, J = 6.0 Hz, 3H), 1.29 (d, J = 6.0 Hz, 3H), 4.47 (dsep, J = 7.2, 6.0 Hz, 1H), 4.61 (dsep, J = 7.2, 6.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.49 (dd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.62 (dd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.65 (dd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.71 (dd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.93 (dd,
2-Diethoxyphosphoryl(hydroxy)methyl-2’-(4-nitrophenoxy)ethyl-1,1’-biphenyl (4a):

Mixture of diastereomers. The ratio is 74:26.

\[ J = 8.4, 1.2 \text{ Hz}, 1H \], 7.95 (dd, \( J = 8.4, 1.2 \text{ Hz}, 1H \)), 8.01 (s, 1H), 8.16 (d, \( J = 9.0 \text{ Hz}, 2H \)), 8.69 (d, \( J = 8.4 \text{ Hz}, 1H \)), 8.73 (d, \( J = 8.4 \text{ Hz}, 1H \)); \(^{31}\)P NMR (243 MHz, CDCl\(_3\)) \( \delta = 2.42 \); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 23.2 \) (d, \( J = 5.9 \text{ Hz} \)), 23.4 (d, \( J = 5.9 \text{ Hz} \)), 23.5 (d, \( J = 4.4 \text{ Hz} \)), 72.8 (d, \( J = 5.7 \text{ Hz} \)), 72.9 (d, \( J = 5.7 \text{ Hz} \)), 78.9, 122.5, 123.3, 123.6, 125.0, 126.6, 126.7, 127.0, 127.6, 127.85, 127.90, 128.6, 129.0, 130.66, 130.72, 131.1, 132.4 (d, \( J = 4.4 \text{ Hz} \)), 147.2 (d, \( J = 5.7 \text{ Hz} \)), 147.5; IR (ATR): 3046, 2980, 2936, 2871, 1604, 1522, 1452, 1347, 1258, 1107, 989 cm\(^{-1}\); HRMS (ESI) Calcd for C\(_{27}\)H\(_{35}\)NO\(_3\)P [M+Na]\(^+\) 516.1546, Found 516.1546.

9-[(4-Methoxyphenyl)(4-nitrophenoxy)methyl]phenanthrene (6a):

\(^{1}\)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 3.81 \) (s, 3H), 6.29 (s, 1H), 6.87 (d, \( J = 8.4 \text{ Hz}, 2H \)), 7.06 (d, \( J = 8.4 \text{ Hz}, 2H \)), 7.10 (s, 1H), 7.33 (d, \( J = 9.0 \text{ Hz}, 2H \)), 7.51 (dd, \( J = 8.4, 7.8 \text{ Hz}, 1H \)), 7.55 (dd, \( J = 7.8, 7.2 \text{ Hz}, 1H \)), 7.64 (d, \( J = 8.4, 8.4 \text{ Hz}, 1H \)), 7.65 (dd, \( J = 7.8, 7.2 \text{ Hz}, 1H \)), 7.68
(d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 9.0 Hz, 2H), 8.68 (d, J = 7.8 Hz, 1H), 8.75 (d, J = 7.8 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 52.5, 55.2, 114.2, 122.4, 123.3, 123.7, 124.8, 126.5, 126.81, 126.84, 126.9, 128.68, 128.74, 129.9, 130.4, 130.6, 130.7, 130.9, 131.1, 133.8, 137.0, 146.6, 151.7, 158.5; IR (ATR): 3076, 2933, 2836, 1606, 1510, 1346, 1249, 1179, 1111, 1036 cm⁻¹; HRMS (ESI) Calcd for C26H21NO3 [M+Na⁺] 442.1414, Found 442.1413.

9-[(4-Nitrophenyl)(phenyl)methyl]phenanthrene (6b):

$^1$H NMR (600 MHz, CDCl3) δ 6.34 (s, 1H), 7.10 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.30 (dd, J = 7.8, 7.8 Hz, 1H), 7.34-7.36 (m, 5H), 7.51 (dd, J = 7.8, 7.2 Hz, 1H), 7.55 (dd, J = 7.8, 7.2 Hz, 1H), 7.63 (dd, J = 7.8, 7.2 Hz, 1H), 7.65 (dd, J = 7.8, 7.2 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 8.16 (d, J = 8.4 Hz, 2H), 8.67 (d, J = 7.8 Hz, 1H), 8.75 (d, J = 7.8 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 53.3, 122.4, 123.3, 123.7, 124.8, 126.5, 126.8, 126.89, 126.94, 127.2, 128.78, 128.85 (2c), 129.7, 130.0, 130.5, 130.7, 131.0, 131.1, 136.7, 141.8, 146.7, 151.3; IR (ATR): 3077, 3061, 3028, 2927, 2853, 1600, 1518, 1494, 1345, 1110 cm⁻¹; HRMS (ESI) Calcd for C27H19NO2 [M+] 412.1308, Found 412.1308.

9-[(4-Nitrophenyl)(4-trifluoromethylphenyl)methyl]phenanthrene (6c):

$^1$H NMR (600 MHz, CDCl3) δ 6.40 (s, 1H), 7.07 (s, 1H), 7.28 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 9.0 Hz, 2H), 7.52 (dd, J = 8.4, 7.2 Hz, 1H), 7.57 (dd, J = 7.8, 7.2 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.65 (dd, J = 8.4, 7.8 Hz, 1H), 7.67 (d, J = 8.4, 7.2 Hz, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 9.0 Hz, 2H), 8.69 (d, J = 8.4 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 53.0, 122.5, 123.4, 123.9, 124.0 (q, J = 270 Hz), 124.5, 125.8 (q, J = 2.9 Hz), 126.7, 126.99, 127.03, 127.2, 128.8, 129.0, 129.5 (q, J = 31.7 Hz), 129.99, 130.02, 130.4, 130.5, 130.96, 131.04, 135.8, 145.9, 146.9, 150.1; IR (ATR): 3077, 2921, 1597, 1519, 1346, 1324, 1165, 1124, 1112, 1068, 1018 cm⁻¹; HRMS (ESI) Calcd for C28H18F3NO2 [M+Na⁺] 480.1182, Found 480.1182.

9-[(4-Nitrophenyl)(tosylamido)methyl]phenanthrene (7):

$^1$H NMR (600 MHz, CDCl3) δ 2.24 (s, 3H), 5.46 (d, J = 7.2 Hz, 1H), 6.30 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 7.8 Hz, 2H), 7.24 (s, 1H), 7.48 (d, J = 9.0 Hz, 2H), 7.45-7.51 (m, 3H), 7.57 (ddd, J = 7.8, 7.2, 1.2 Hz, 1H), 7.60-7.69 (m, 4H), 8.08 (d, J = 9.0 Hz, 2H), 8.62 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H); 13C NMR (150 MHz, CDCl3) δ 21.3, 59.0, 122.4, 123.6, 123.8, 123.9, 126.9, 127.0, 127.1, 127.2, 127.6, 128.36, 128.44, 128.5, 128.8, 129.4, 130.3, 130.6, 131.2, 131.9, 136.7, 143.8, 147.36, 147.38; IR (ATR): 3269, 2959, 2925, 2853, 1599, 1520, 1450, 1346, 1158, 1090 cm⁻¹; HRMS (ESI) Calcd for C28H23N2O4S [M+Na⁺] 505.1193, Found 505.1193.
9-[(4-Methoxyphenylsulfanyl)(4-nitrophenyl)methyl]phenanthrene (8):

\[
\text{Ar} \quad \text{S} \quad \text{OMe}
\]

\[
\text{Ar} = \text{4-NO}_2\text{-C}_6\text{H}_4
\]

\[^{1}\text{H NMR (600 MHz, CDCl}_3\text{)} \delta 3.75 (s, 3H), 6.10 (s, 1H), 6.76 (d, } J = 9.0 \text{ Hz, 2H), 7.29 (d, } J = 9.0 \text{ Hz, 2H), 7.54 (d, } J = 9.0 \text{ Hz, 2H), 7.55 (dd, } J = 7.8, 7.8 \text{ Hz, 1H), 7.63 (dd, } J = 7.8, 7.2 \text{ Hz, 1H), 7.64 (dd, } J = 7.8, 7.2 \text{ Hz, 1H), 7.68 (dd, } J = 7.8, 7.2 \text{ Hz, 1H), 7.92 (d, } J = 7.8 \text{ Hz, 1H), 7.98 (d, } J = 7.8 \text{ Hz, 1H), 8.06 (s, 1H), 8.09 (d, } J = 9.0 \text{ Hz, 2H), 8.67 (d, } J = 7.8 \text{ Hz, 1H), 8.74 (d, } J = 7.8 \text{ Hz, 1H); }^{13}\text{C NMR (150 MHz, CDCl}_3\text{)} \delta 55.3, 55.9, 114.7, 122.5, 123.5, 123.7, 124.1, 125.1, 126.6, 126.8, 127.0, 127.3, 128.0, 128.9, 129.4, 129.8, 130.2, 131.1 (2C), 133.0, 134.8, 146.9, 148.7, 159.8; \text{ IR (ATR): } 3075, 2938, 2836, 1592, 1519, 1493, 1345, 1287, 1248, 1173, 1105, 1031 \text{ cm}^{-1}; \text{ HRMS (ESI) Calcd for C}_{28}\text{H}_{21}\text{NO}_3\text{S [M+Na]}^+ 474.1134, \text{ Found 474.1134.}