Supporting Information for

Synthesis of Phosphaisocoumarins via Iodocyclization

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General Information. NMR spectra were all recorded on a Varian Mercury300 spectrometer using CDCl₃ as the solvent. The ¹H NMR spectra used CDCl₃ (with TMS) as the internal reference at 7.27ppm. ³¹P NMR spectra used the 85% H₃PO₄ as the external reference. MS spectra were determined using a HP5989A mass spectrometer. IR spectra were measured on a Y-Zoom Cursor instrument. Starting materials **1** were formed from the Pd-catalyzed cross-coupling reaction¹ of the corresponding aryl perfluoroalkanesulfonates with alkynes.

General procedures for the preparation of 4-iodophosphaisocoumarins **2**

4-Iodophosphaisocoumarins **2** were prepared according to two different procedures by I₂ or ICl (method A or B).

Method A: This procedure was used for all the following compounds **2** except **2c** and **2i**. A mixture of **1** (0.5 mmol) and I₂ (1.0 mmol) was dissolved in 5ml CHCl₃. After stirring at room temperature for 12 h, the reaction mixture was then diluted with EtOAc and washed with 5% aqueous Na₂S₂O₃. The organic phase was washed with brine, dried (Na₂SO₄), and evaporated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc as eluent to give the corresponding product **2**.

Method B: This procedure was used for the preparation of **2c** and **2i**. To the ester alkyne **1** (0.1mmol) was added ICl (0.12mmol) in 1.2ml CH₂Cl₂ and the resulting mixture was stirred in the dark under nitrogen at room temperature for 10h. The reaction mixture was then diluted with EtOAc and washed with 5% aqueous Na₂S₂O₃. The organic phase was washed with brine, dried (Na₂SO₄), and evaporated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc as eluent to give the corresponding product **2**.

The isolated yield and the spectra data for **2a-2j** are as follows:

1-Ethoxy-3-phenyl-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (**2a**)

Yield: 83%. A pale yellow solid, mp: 115.2-115.9°C. ¹H NMR: 7.47-8.02 (m, 9H), 4.26-4.37 (m, 2H), 1.38 (t, J=6.9Hz, 3H); ³¹P NMR: 8.15; MS (EI): m/z: 412 (M⁺, 100), 384 (57), 257 (3), 239 (18), 165 (34), 105 (31), 77 (28); IR (KBr, cm⁻¹): 2985, 1607, 1588, 1462, 1389, 1272, 1234, 1168, 1061, 1017, 938, 858; Anal. Calcd. for C₁₆H₁₄PO₃I: C, 46.62, H 3.43. Found: C, 46.56, H, 3.42.

3-Butyl-1-ethoxy-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (**2b**)

Yield: 70%. A pale yellow solid, mp: 61-62°C. ¹H NMR: 7.61-7.82 (m, 3H), 7.39-7.45 (m, 1H), 4.18-4.25 (m, 2H), 2.79-2.97 (m, 2H), 1.67-1.72 (m, 2H), 1.41-1.48 (m, 2H), 1.33 (t, J=7.2Hz, 3H), 0.97 (t, J=7.2Hz, 3H); ³¹P NMR: 10.33; MS

(EI): m/z: 392 (M^+ , 100), 363 (10), 237 (95), 219 (28), 195 (49), 179 (14), 102 (10), 77 (8); IR (KBr, cm^{-1}): 2980, 1593, 1465, 1442, 1262, 1151, 1090, 1031, 969, 771; Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{PO}_3\text{I}$: C, 42.87, H, 4.64. Found: C, 42.99, H, 4.65.

1-Ethoxy-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2c)

Yield: 35%. A white solid, mp: 50-51°C. ^1H NMR: 7.47-7.85 (m, 4H), 7.20 (dd, $J_1=18.0\text{Hz}$, $J_2=2.1\text{Hz}$, 1H), 4.18-4.30 (m, 2H), 1.36 (dt, $J_1=7.2\text{Hz}$, $J_2=2.1\text{Hz}$, 3H); ^{31}P NMR: 13.06; MS (EI): m/z: 336 (M^+ , 88), 308 (100), 209 (9), 165 (32), 153 (99), 105 (17), 77 (9); IR (KBr, cm^{-1}): 2968, 1593, 1385, 1255, 1220, 1154, 1030, 974; Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{IPO}_3$: C, 35.74, H, 3.00. Found: C, 35.65, H, 2.97.

7-Chloro-1-ethoxy-3- (4-ethyl-phenyl)-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2d)

Yield: 64%. A white solid, mp: 145-146°C; ^1H NMR: 7.79-7.92 (m, 2H), 7.55-7.64 (m, 3H), 7.27-7.30 (m, 2H), 4.25-4.35 (m, 2H), 2.74 (q, $J=7.5\text{Hz}$, 2H), 1.38 (t, $J=6.9\text{Hz}$, 3H), 1.29 (t, $J=7.2\text{Hz}$, 3H); ^{31}P NMR: 8.64; MS (EI): m/z: 474 (M^+ , 100), 446 (52), 431 (16), 319 (4), 291 (19), 255 (5), 189 (12), 105 (5), 78 (8); IR (KBr, cm^{-1}): 2966, 1638, 1460, 1277, 1261, 1161, 1027, 1017, 969, 824; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{PO}_3\text{ClI}$: C, 45.54, H, 3.62. Found: C, 45.55, H, 3.68.

7-Chloro-1-ethoxy-3-phenyl-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2e)

Yield: 67%. A yellow solid, mp: 160.5-161.1°C. ^1H NMR: 7.48-7.96 (m, 8H), 4.29-4.39 (m, 2H), 1.40 (dt, $J_1=6.9\text{Hz}$, $J_2=1.8\text{Hz}$, 3H); ^{31}P NMR: 5.65; MS (EI): m/z: 446 (M^+ , 100), 418 (70), 291 (4), 273 (14), 263 (36), 199 (21), 163 (24), 105 (36), 77 (45); IR (KBr, cm^{-1}): 2996, 1608, 1588, 1464, 1390, 1277, 1261, 1160, 1062, 1029, 945, 822; Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{PO}_3\text{ClI}$: C, 43.03, H, 2.94. Found: C, 43.06, H, 2.85.

3-Butyl-4-iodo-7-chloro-1-ethoxy-benzo[c][1, 2] oxaphosphinine 1-oxide (2f)

Yield: 64%. A pale yellow solid, mp: 53-54°C. ^1H NMR: 7.71-7.78 (m, 2H), 7.54-7.58 (m, 1H), 4.22-4.27 (m, 2H), 2.78-2.93 (m, 2H), 1.63-1.69 (m, 2H), 1.41-1.49 (m, 2H), 1.36 (dt, $J_1=7.2\text{Hz}$, $J_2=2.1\text{Hz}$, 3H); 0.97 (dt, $J_1=7.2\text{Hz}$, $J_2=2.4\text{Hz}$, 3H); ^{31}P NMR: 9.47; MS (EI): m/z: 426 (M^+ , 67), 397 (4), 271 (100), 253 (23), 229 (49), 105 (24), 77 (15); IR (KBr, cm^{-1}): 2985, 1595, 1464, 1387, 1282, 1267, 1157, 1031, 967, 825; Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{PO}_3\text{ClI}$: C, 39.41, H, 4.02. Found: C, 39.36, H, 3.91.

7-Chloro-4-iodo-3-cyclopropyl-1-ethoxy-benzo[c][1, 2] oxaphosphinine 1-oxide (2g)

Yield: 76%. A white solid, mp: 105-106°C; ^1H NMR: 7.68-7.75 (m, 2H), 7.53-7.57 (m, 1H), 4.14-4.25 (m, 2H), 2.47-2.57 (m, 1H), 1.34 (t, $J=6.9\text{Hz}$, 3H), 1.14-1.21 (m, 1H), 0.90-1.02 (m, 3H); ^{31}P NMR: 9.28; MS (EI): m/z: 410 (M^+ , 75), 283 (35), 255 (100), 237 (27), 220 (16), 209 (29), 175 (16), 139 (14), 99 (6), 75 (6); IR (KBr, cm^{-1}): 2981, 1585, 1460, 1390, 1273, 1251, 1160, 1020, 956, 825; Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{PO}_3\text{ClI}$: C, 38.03, H, 3.20. Found: C, 38.07, H, 3.33.

7-Chloro-1-ethoxy-3- methoxymethyl-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2h)

Yield: 46%. A white solid, mp: 100-101°C; ^1H NMR: 7.71-7.82 (m, 2H), 7.59-7.63 (m, 1H), 4.69 (dd, $J_1=12.9\text{Hz}$, $J_2=1.8\text{Hz}$, 1H), 4.49 (d, $J=12.9\text{Hz}$, 1H), 4.23-4.36 (m, 2H), 3.49 (d, $J=0.3\text{Hz}$, 3H), 1.36 (t, $J=6.9\text{Hz}$, 3H); ^{31}P NMR: 8.27; MS (EI): m/z: 414 (M^+ , 40), 384 (33), 287 (100), 259 (84), 231 (39), 199 (35), 136 (19), 101 (8), 75 (8); IR (KBr, cm^{-1}): 2990, 1739, 1597, 1456, 1385, 1287, 1267, 1163, 1088, 1013, 967; Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{PO}_4\text{ClI}$: C, 34.76, H, 3.17. Found: C, 34.84, H, 3.27.

7-Chloro-1-ethoxy-3- trimethylsilyl-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2i)

Yield: 82%. A pale yellow solid, mp: 118-119°C; ^1H NMR: 7.56-7.78 (m, 3H), 4.16-4.26 (m, 2H), 1.36 (t, $J=6.9\text{Hz}$, 3H), 0.45 (s, 9H). ^{31}P NMR: 9.36; MS (EI): m/z : 442 (M^+ , 100), 427 (17), 399 (97), 272 (55), 244 (77), 215 (8), 149 (27), 137 (19), 75 (27); IR (KBr, cm^{-1}): 2985, 1460, 1386, 1281, 1262, 1162, 1028, 968, 929; Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{PO}_3\text{IClSi}$: C, 35.27, H, 3.87. Found: C, 35.21, H, 3.92.

1-Ethoxy-7-methoxy-3--phenyl-4-iodobenzo[c][1, 2] oxaphosphinine 1-oxide (2j)

Yield: 93%. A white solid, mp: 145-146°C, yield: ^1H NMR: 7.86 (t, $J=8.1\text{Hz}$, 1H), 7.60-7.64 (m, 2H), 7.18-7.45 (m, 5H), 4.22-4.32 (m, 2H), 3.92 (s, 3H), 1.37 (t, $J=7.2\text{Hz}$, 3H); ^{31}P NMR: 14.538; MS (EI): m/z : 442 (M^+ , 100), 414 (62), 287 (5), 269 (6), 259 (34), 195 (4), 105 (9), 77 (12); IR (KBr, cm^{-1}): 2970, 1600, 1485, 1389, 1257, 1158, 1060, 1018, 935, 830; Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{PO}_4\text{I}$: C, 46.17, H, 3.65. Found: C, 46.35, H, 3.67.

Procedure for the preparation of 1-Ethoxy -3--phenyl-4-phenylethynylbenzo[c][1, 2] oxaphosphinine 1-oxide 8

To a mixture of **2a** (0.105g, 0.25 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (9mg, 0.0128mmol), CuI (4mg, 0.021mmol) and Et_3N (1.5ml), was added dropwise phenylacetylene (0.04ml, 0.366mmol) at room temperature. After stirring at 50°C for 4h under nitrogen, the reaction mixture was diluted with EtOAc and washed with aqueous NH_4Cl until neutral and brine, dried (Na_2SO_4), and evaporated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc as eluent to give the corresponding product **9** as a yellow solid, mp: 132-133°C, yield: 82%. ^1H NMR: 7.35-8.19 (m, 14H), 4.22-4.32 (m, 2H), 1.34 (t, $J=7.2\text{Hz}$, 3H); ^{31}P NMR: 13.26; MS (EI): m/z : 386 (M^+ , 100), 357 (34), 339 (27), 292 (33), 265 (42), 189 (8), 105 (26), 77 (36); IR (KBr, cm^{-1}): 2980, 2205, 1651, 1471, 1385, 1278, 1242, 1154, 1106, 1090, 1077, 1017, 947; Anal. Calcd. for $\text{C}_{24}\text{H}_{29}\text{PO}_3$: C, 74.60, H, 4.96. Found: C, 74.38, H, 4.97.

Referencee

(1) Chen, Q-Y.; Yang, Z-Y. *Tetrahedron Lett.* **1986**, 27, 1171-1174.