

**MS 4A-PROMOTED AQUEOUS PHOSPHO-ALDOL-BROOK
REARRANGEMENT REACTION OF ISATINS**

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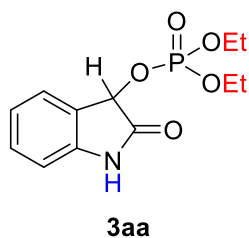
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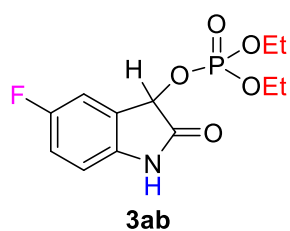
1. Compounds Data

1. diethyl (2-oxoindolin-3-yl) phosphate, **3aa**^{1,2}



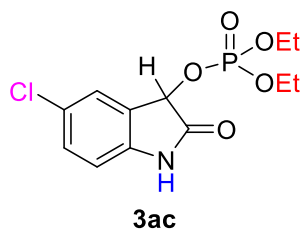
Yield: 100%. Pale yellow oil. ¹H NMR (CDCl₃, δ): 9.00 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.28–7.25 (m, 1H), 7.04 (td, *J* = 17.1, 9.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 5.58 (d, *J* = 13.9 Hz, 1H), 4.31–4.17 (m, 4H), 1.39–1.32 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): 174.0, 141.8, 130.6, 126.1, 124.6, 122.9, 110.6, 72.8, 72.7, 64.5 (dd, *J*_{C,P} = 6.2, 30.5 Hz), 16.0. IR (neat, cm⁻¹): 3261, 2988, 2933, 2912, 1735, 1654, 1624, 1473, 1444, 1395, 1370, 1327, 1255, 1182, 1104, 1035, 976, 909, 871, 817, 754.

2. diethyl (5-fluoro-2-oxoindolin-3-yl) phosphate, **3ab**¹



Yield: 100%. Orange oil. ¹H NMR (CDCl₃, δ): 8.79 (s, 1H), 7.28–7.27 (m, 1H), 6.98 (t, *J* = 8.7 Hz, 1H), 6.82–6.80 (m, 1H), 5.56 (d, *J* = 13.6 Hz, 1H), 4.27–4.18 (m, 4H), 1.40–1.35 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): 173.8 (d, *J*_{C,F} = 6.5 Hz), 160.0, 158.1, 137.5, 126.0 (dd, *J*_{C,F} = 2.5, 8.3 Hz), 117.2 (d, *J*_{C,F} = 23.4 Hz), 114.1 (d, *J*_{C,F} = 25.1 Hz), 111.3 (d, *J*_{C,F} = 7.8 Hz), 72.6, 64.8 (dd, *J*_{C,P} = 6.2, 27.5 Hz), 16.0. IR (neat, cm⁻¹): 3225, 2987, 2933, 1732, 1633, 1614, 1487, 1395, 1257, 1195, 1166, 1140, 1109, 1038, 986, 909, 861, 819.

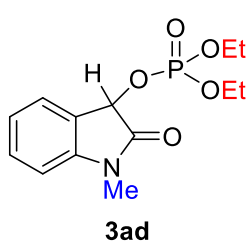
3. 5-chloro-2-oxoindolin-3-yl diethyl phosphate, **3ac**¹



Yield: 32%. Yellow oil. ¹H NMR (CDCl₃, δ): 8.31 (s, 1H), 7.51 (s, 1H), 7.27–7.25 (m, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.54 (d, *J* = 13.9 Hz, 1H), 4.29–4.19 (m, 4H), 1.40–1.35 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): 173.2, 139.9, 130.6, 128.4, 126.6,

126.1, 111.4, 72.2, 64.8 (dd, $J_{C,P} = 6.1, 26.1$ Hz), 16.0. IR (neat, cm^{-1}): 3449, 2984, 2926, 2850, 1735, 1622, 1477, 1458, 1444, 1394, 1257, 1182, 1123, 1039, 978, 819.

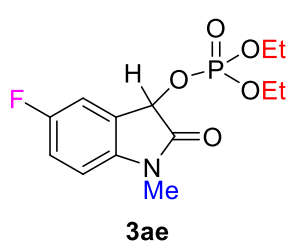
4. diethyl (1-methyl-2-oxoindolin-3-yl) phosphate, **3ad**



Yield: 81%. Yellow oil. ^1H NMR (CDCl_3 , δ): 7.57 (d, $J = 7.3$ Hz, 1H), 7.36 (td, $J = 15.4, 7.8$ Hz, 1H), 7.1 (td, $J = 15.4, 7.3$ Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 5.60 (d, $J = 11.8$ Hz, 1H), 4.34–4.15 (m, 4H), 3.19 (s, 3H), 1.41–1.32 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3):

171.9, 144.2, 130.6, 126.0, 124.2, 123.1, 108.5, 72.3, 64.6 (dd, $J_{C,P} = 6.0, 42.3$ Hz), 26.3, 16.0 (dd, $J_{C,P} = 3.5, 7.1$ Hz). IR (neat, cm^{-1}): 3490, 3060, 2985, 2934, 2912, 1735, 1617, 1495, 1473, 1376, 1355, 1329, 1262, 1213, 1165, 1130, 1093, 1024, 905, 881, 801, 754, 697, 637, 605.

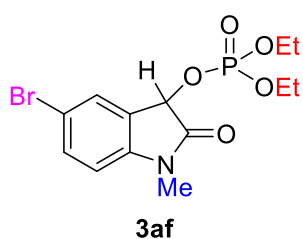
5. diethyl (5-fluoro-1-methyl-2-oxoindolin-3-yl) phosphate, **3ae**



Yield: 91%. Yellow oil. ^1H NMR (CDCl_3 , δ): 7.35 (d, $J = 7.3$ Hz, 1H), 7.07 (td, $J = 17.4, 8.7$ Hz, 1H), 6.76–6.75 (m, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 5.57 (d, $J = 12.1$ Hz, 1H), 4.32–4.17 (m, 4H), 3.19 (s, 3H), 1.42–1.34 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3):

171.6, 160.3, 158.3, 140.1. 125.6, 117.0 (d, $J_{C,F} = 23.6$ Hz), 114.3 (d, $J_{C,F} = 25.4$ Hz), 109.1, 72.0, 64.8 (dd, $J_{C,P} = 15.7, 41.1$ Hz), 26.4, 16.0. IR (neat, cm^{-1}): 3479, 3066, 2986, 2934, 2913, 1732, 1625, 1614, 1495, 1471, 1456, 1368, 1329, 1274, 1230, 1145, 1103, 1024, 954, 820, 769, 692.

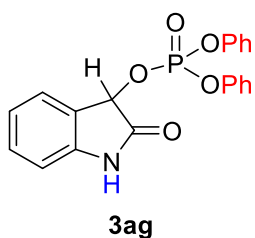
6. 5-bromo-1-methyl-2-oxoindolin-3-yl diethyl phosphate, **3af**



Yield: 82%. Yellow oil. ^1H NMR (CDCl_3 , δ): 7.69 (s, 1H), 7.49 (d, $J = 8.1$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 5.57 (d, $J = 12.3$ Hz, 1H), 4.32–4.18 (m, 4H), 3.18 (s, 3H), 1.41–1.35 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3): 171.3, 143.2, 133.4, 129.2, 126.0,

115.7, 109.9, 71.7, 64.8 (dd, $J_{\text{C,P}} = 6.1, 36.5$ Hz), 26.4. IR (neat, cm^{-1}): 3464, 2984, 2932, 1735, 1611, 1490, 1363, 1326, 1267, 1212, 1103, 1025, 984, 904, 874, 810, 657.

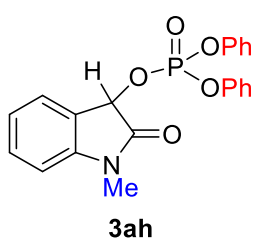
7. 2-oxoindolin-3-yl diphenyl phosphate, **3ag**



Yield: 34%. Yellow oil. ^1H NMR (CDCl_3 , δ): 8.29 (s, 1H), 7.36–7.20 (m, 12H), 6.95 (td, $J = 15.0, 7.5$ Hz, 1H), 6.79 (d, $J = 7.8$ Hz, 1H), 5.78 (d, $J = 12.8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 172.8 (d, $J_{\text{C,P}} = 6.4$ Hz), 150.4 (dd, $J_{\text{C,P}} = 11.8, 26.6$ Hz), 141.5,

130.8, 129.8 (d, $J_{\text{C,P}} = 4.2$ Hz), 126.3, 125.6 (d, $J_{\text{C,P}} = 5.0$ Hz), 123.7 (d, $J_{\text{C,P}} = 3.8$ Hz), 123.0, 120.4 (dd, $J_{\text{C,P}} = 1.5, 11.0$ Hz), 110.4, 73.8 (d, $J_{\text{C,P}} = 5.9$ Hz). IR (neat, cm^{-1}): 3252, 1716, 1682, 1622, 1590, 1488, 1471, 1196, 1163, 1070, 1025, 952, 753, 689.

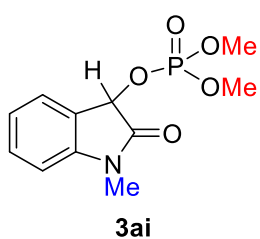
8. 1-methyl-2-oxoindolin-3-yl diphenyl phosphate, **3ah**^{3,4}



Yield: 32%. Yellow oil. ^1H NMR (CDCl_3 , δ): 7.35–7.20 (m, 12H), 6.99 (td, $J = 15.0, 7.5$ Hz, 1H), 6.80 (d, $J = 7.5$ Hz, 1H), 5.79 (d, $J = 11.7$ Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): 171.1 (d, $J_{\text{C,P}} = 7.2$ Hz), 150.5 (dd, $J_{\text{C,P}} = 14.5, 29.5$ Hz), 144.3, 130.9,

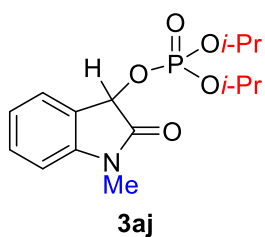
129.7, 126.1, 125.6, 123.1, 120.5 (dd, $J_{\text{C,P}} = 5.9, 15.4$ Hz), 115.3, 108.5, 73.5 (d, $J_{\text{C,P}} = 6.1$ Hz), 26.4. IR (neat, cm^{-1}): 3060, 2967, 1729, 1617, 1586, 1487, 1472, 1378, 1278, 1262, 1190, 1165, 1092, 1037, 1023, 1009, 973, 957, 905, 766, 690, 609.

9. dimethyl (1-methyl-2-oxoindolin-3-yl) phosphate, **3ai**



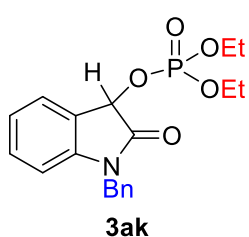
Yield: 73%. Yellow oil. ^1H NMR (CDCl_3 , δ): 7.55 (d, $J = 7.2$ Hz, 1H), 7.37 (td, $J = 15.4, 7.7$ Hz, 1H), 7.11 (td, $J = 15.4, 7.2$ Hz, 1H), 6.83 (d, $J = 7.7$ Hz, 1H), 5.59 (d, $J = 11.7$ Hz, 1H), 3.93 (d, $J = 11.3$ Hz, 3H), 3.82 (d, $J = 11.3$ Hz, 3H), 3.20 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): 171.8 (d, $J_{\text{C,P}} = 6.9$ Hz), 144.2, 130.7, 125.9, 124.0 (d, $J_{\text{C,P}} = 3.3$ Hz), 123.2, 108.6, 72.4 (d, $J_{\text{C,P}} = 5.5$ Hz), 55.0 (d, $J_{\text{C,P}} = 49.1$ Hz), 54.6 (d, $J_{\text{C,P}} = 36.9$ Hz), 26.3. IR (neat, cm^{-1}): 3484, 2959, 2856, 1735, 1617, 1495, 1472, 1377, 1356, 1331, 1272, 1188, 1094, 1028, 914, 852, 809, 756, 697.

10. diisopropyl (1-methyl-2-oxoindolin-3-yl) phosphate, **3aj**



Yield: 89%. Pale yellow oil. ^1H NMR (CDCl_3 , δ): 7.60 (d, $J = 7.4$ Hz, 1H), 7.37–7.34 (m, 1H), 7.11–7.07 (m, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 5.60 (d, $J = 11.9$ Hz, 1H), 4.87–4.80 (m, 1H), 4.74–4.67 (m, 1H), 3.19 (s, 3H), 1.42–1.38 (dd, $J = 15.7, 6.1$ Hz, 6H), 1.34–1.32 (dd, $J = 6.1, 1.6$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3): 172.0 (d, $J_{\text{C,P}} = 7.4$ Hz), 144.1, 130.5, 126.1, 124.3, 123.0, 108.4, 73.5 (d, $J_{\text{C,P}} = 6.3$ Hz), 73.2 (d, $J_{\text{C,P}} = 6.3$ Hz), 72.2 (d, $J_{\text{C,P}} = 5.6$ Hz), 26.2, 23.7 (m). IR (neat, cm^{-1}): 3480, 2981, 2936, 1738, 1615, 1495, 1471, 1376, 1354, 1329, 1261, 1143, 1130, 1092, 1006, 909, 797, 753, 697.

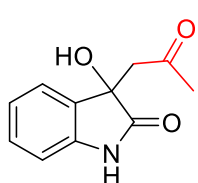
11. 1-benzyl-2-oxoindolin-3-yl diethyl phosphate, **3ak**⁴



Yield: 17%. Pale yellow oil. ^1H NMR (CDCl_3 , δ): 7.57 (d, $J = 7.3$ Hz, 1H), 7.34–7.22 (m, 7H), 7.07–7.04 (m, 1H), 6.71 (d, $J = 7.9$ Hz, 1H), 5.70 (d, $J = 11.9$ Hz, 1H), 4.92 (d, $J = 15.6$ Hz, 1H), 4.83 (d, $J = 15.6$ Hz, 1H), 4.36–4.17 (m, 4H), 1.43–1.33 (m, 6H). ^{13}C NMR

(125 MHz, CDCl₃): 172.0 (d, $J_{C,P}$ = 7.2 Hz), 143.3, 135.1, 130.5, 128.8, 127.8, 127.3, 126.0, 124.2, 123.2, 109.5, 72.3 (d, $J_{C,P}$ = 5.6 Hz), 64.7 (d, $J_{C,P}$ = 6.1 Hz), 64.4 (d, $J_{C,P}$ = 5.8 Hz), 44.0, 16.1 (d, $J_{C,P}$ = 4.5 Hz), 16.0 (d, $J_{C,P}$ = 4.5 Hz). IR (neat, cm⁻¹): 3450, 3061, 3030, 2984, 2926, 2853, 1735, 1616, 1489, 1467, 1457, 1368, 1264, 1173, 1103, 1021, 753, 697.

12. 3-hydroxy-3-(2-oxopropyl)indolin-2-one, **3am**⁵

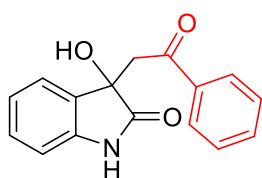


3am

Yield: 92%. White solid. ¹H NMR (CDCl₃, δ): 7.45 (s, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.21–7.18 (m, 1H), 7.00–6.96 (m, 1H), 6.80 (d, J = 7.8 Hz, 1H), 4.28 (s, 1H), 3.11 (d, J = 17.0 Hz, 1H), 2.90 (d, J = 17.0 Hz, 1H), 2.12 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): 206.6, 176.5, 139.3, 131.0,

129.0, 123.3, 122.1, 109.2, 73.3, 47.5, 30.4. IR (neat, cm⁻¹): 3365, 3317, 2897, 1717, 1621, 1484, 1470, 1362, 1333, 1181, 1113, 1088, 1060, 1014, 779, 760, 621, 591, 554, 496, 477.

13. 3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one, **3an**⁶



3an

Yield: 90%. White solid. ¹H NMR (CDCl₃, δ): 7.88 (d, J = 7.7 Hz, 2H), 7.58–7.55 (m, 1H), 7.45–7.41 (m, 3H), 7.34–7.31 (m, 1H), 7.05–7.02 (m, 1H), 6.86 (d, J = 7.7 Hz, 1H), 4.44 (s, 1H), 3.81 (d, J = 17.3 Hz, 1H), 3.49 (d, J = 17.3 Hz, 1H), 3.24 (s, 3H). ¹³C NMR

(125 MHz, CDCl₃): 198.5, 176.1, 143.6, 136.4, 133.8, 130.0, 128.7, 128.1, 124.0, 123.1, 108.5, 74.5, 44.3, 26.3. IR (neat, cm⁻¹): 3384, 3317, 2933, 1686, 1616, 1497, 1469, 1384, 1353, 1228, 1114, 1093, 1069, 1031, 1023, 996, 767, 685, 606, 554.

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3. ^1H NMR and ^{13}C NMR Spectra

