Supporting Information

Regioselective Radical Arylation: Silver-Mediated Synthesis of 3-Phosphorylated-Coumarins, Quinolin-2(1*H*)-one and Benzophosphole Oxides

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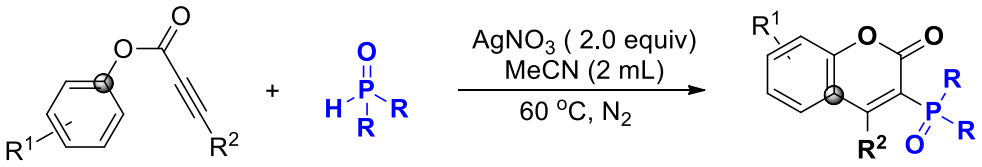
1. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063–0.2 mm). Melting points were measured on a Yanaco Micro Melting Point Apparatus. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR were recorded on a Variance VNMR 400 or Bruker AV-600 spectrometer in $CDCl_3$. For ^{1}H NMR spectra, data are quoted in the following order: chemical shift (δ) in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.26 ppm). Multiplicities are indicated s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets); coupling constants (*J*) are in Hertz (Hz). For proton-decoupled ^{13}C NMR spectra, chemical shifts (δ) are also quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR (KBr disc) and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are recorded using electrospray ionization (ESI). X-ray crystallographic data were collected using SMART APEX II X-ray diffractometer. Compounds **1a-1g**, **4a-4f**, were prepared according to the previous reported procedures.[1] **2a-2h** were prepared according to the previous reported procedures.[2] **6** was prepared according to the previous reported procedures.[3]

2. General procedure the hydrophosphinylative cyclization of phenyl propiolate



1a-1i
0.40 mmol

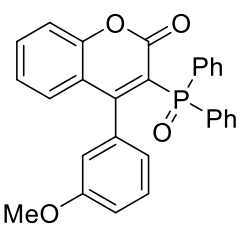
2
0.48 mmol

3a-3x
R^1=Aryl-, alkyl-

Aryl alkynoates **1a-1i** (0.40 mmol, 1.0 equiv), arylphosphine oxide **2** (0.48 mmol, 1.2 equiv), $AgNO_3$ (0.80 mmol, 2.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere, MeCN (2 mL) as solvent was then added. The mixture was stirred for 24-48h at 60℃. After the aryl alkynoates **1** was completely consumed (monitored by TLC), the crude mixture was directly purified by flash column chromatography on silica gel (EtOAc/petroleum ether 1:1) to give the desired products **3a-3l**.

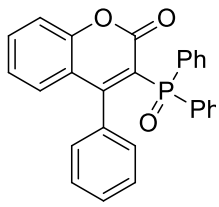
3-(diphenylphosphoryl)-4-(3-methoxyphenyl)-2*H*-chromen-2-one (3a)[4]

Yellow oil (123 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.68 (m, 4H), 7.55 (s, 1H), 7.47–7.23 (m, 8H), 7.16 (s, 2H), 6.91 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H), 6.70 (s, 1H), 3.71 (s, 3H); ^{13}C NMR



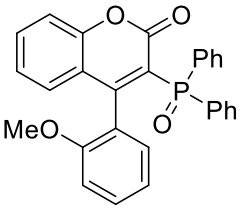
(100 MHz, $CDCl_3$): δ 165.3 (d, *J* = 5.2 Hz), 159.5 (d, *J* = 13.1 Hz), 158.7, 154.2, 134.6 (d, *J* = 4.4 Hz), 133.7, 133.5 (d, *J* = 10.8 Hz), 132.4 (d, *J* = 10.8 Hz), 131.5, 131.4 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 10.1 Hz), 128.9 (d, *J* = 22.3 Hz), 128.2 (d, *J* = 4.0 Hz), 128.0 (d, *J* = 4.0 Hz), 124.3, 121.0, 120.5 (d, *J* = 9.3 Hz), 118.8 (d, *J* = 1.4 Hz), 116.7, 114.7, 114.0, 55.0; ^{31}P NMR (243 MHz, $CDCl_3$): δ 23.8; IR (neat): *v* = 3062, 2929, 1720, 1594, 1535, 1481, 1437, 1335, 1241, 1194, 756 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_3P]^+$ $[M+H]^+$: 453.1250, found: 453.1256.

3-(diphenylphosphoryl)-4-phenyl-2*H*-chromen-2-one (3b)[4]



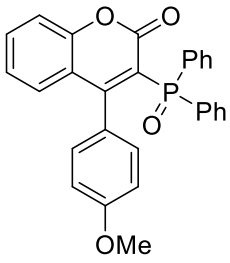
White solid (143.5 mg, 85% yield); m.p. 81-82 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 10.0 Hz, 4H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 7H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 6.4 Hz, 2H), 7.21 – 7.10 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.9 (d, *J* = 5.2 Hz), 159.6 (d, *J* = 13.4 Hz), 154.3, 133.7, 133.6 (d, *J* = 4.3 Hz), 133.4, 132.3, 131.6 (d, *J* = 3.1 Hz), 131.5, 128.9 (d, *J* = 15.6 Hz), 128.2 (d, *J* = 4.6 Hz), 128.0 (d, *J* = 29.2 Hz), 124.4, 120.8 (d, *J* = 9.4 Hz), 119.3, 118.3, 116.7; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.4; IR (neat): *v* = 3061, 2924, 2856, 1719, 1598, 1536, 1485, 1440, 1198, 1114, 914, 746 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{27}H_{20}O_3P]^+$ $[M+H]^+$: 423.1145, found: 423.1153.

3-(diphenylphosphoryl)-4-(2-methoxyphenyl)-2*H*-chromen-2-one (3c)



Yellow oil (91.7 mg, 51% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.83-7.71 (m, 4H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.51–7.30 (m, 8H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.11–7.00 (m, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.4 (d, *J* = 5.0 Hz), 159.6 (d, *J* = 13.6 Hz), 155.9, 154.2, 133.37, 133.35 (d, *J* = 48.0 Hz), 132.3 (d, *J* = 48.0 Hz), 131.56 (d, *J* = 16.0 Hz), 131.57 (d, *J* = 4.0 Hz), 131.6 (d, *J* = 16.0 Hz), 131.3 (dd, *J* = 16.5, 2.8 Hz), 130.7, 129.4, 128.2 (d, *J* = 18.7 Hz), 127.9 (d, *J* = 7.1 Hz), 127.7, 124.2, 122.6 (d, *J* = 4.1 Hz), 120.5 (d, *J* = 11.7 Hz), 120.1, 116.6, 110.2, 55.0; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.4; IR (neat): *v* = 3061, 2924, 2854, 1738, 1591, 1487, 1439, 1338, 1250, 1193, 1161, 793 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_4P]^+$ $[M+H]^+$: 453.1250, found: 453.1251.

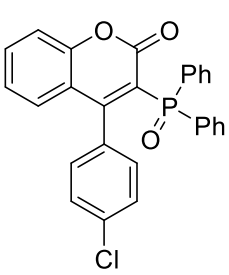
3-(diphenylphosphoryl)-4-(4-methoxyphenyl)-2*H*-chromen-2-one (3d)[4]



Yellow solid (130.0 mg, 72% yield); m.p. 114-115 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 12.2, 7.7 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47–7.41 (m, 2H), 7.36 (dd, *J* = 21.2, 7.9 Hz, 5H), 7.24–7.10 (m, 4H), 6.87 (d, *J* = 7.9 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (d, *J* = 5.3), 160.2, 159.7 (d, *J* = 13.4 Hz), 154.3, 133.7 (d, *J* = 13.9 Hz), 132.7, 131.41 (d, *J* = 10.0 Hz), 131.41 (d, *J* = 3.0 Hz), 130.1, 128.8, 128.1 (d, *J* = 12.7 Hz), 125.7 (d, *J* = 4.4 Hz), 124.3, 122.0 (d, *J* = 9.3 Hz), 119.4, 118.3, 116.8, 113.4, 55.2; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.2; IR (neat): *v* = 3060, 2926, 1719, 1602, 1507, 1443, 1339, 1251, 1188, 854, 743 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_4P]^+$

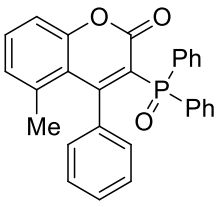
$[M+H]^+$: 453.1250, found: 453.1253.

4-(4-chlorophenyl)-3-(diphenylphosphoryl)-2*H*-chromen-2-one (3e)[4]



Yellow solid (125 mg, 68% yield); m.p. 242-243 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 12.4, 7.7 Hz, 4H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 6.9 Hz, 2H), 7.45–7.32 (m, 7H), 7.17 (d, *J* = 8.2 Hz, 3H), 7.09 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6 (d, *J* = 5.0 Hz), 159.3 (d, *J* = 13.1 Hz), 154.3, 135.1, 133.9, 133.1, 132.0, 131.9, 131.7 (d, *J* = 2.9 Hz), 131.5 (d, *J* = 10.3 Hz), 129.6, 128.5, 128.3, 128.2, 124.5, 120.5 (d, *J* = 9.1 Hz), 116.8; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.8; IR (neat): *v* = 3063, 2927, 2225, 1721, 1599, 1536, 1486, 1193, 1105, 740 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{27}H_{19}ClO_3P]^+$ $[M+H]^+$: 457.0755, found: 457.0767.

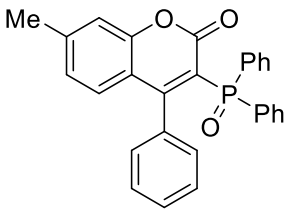
3-(diphenylphosphoryl)-8-methyl-4-phenyl-2*H*-chromen-2-one (3f)



3f

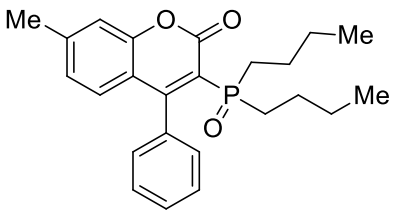
Yellow oil (86 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.69 (m, 4H), 7.60–7.29 (m, 9H), 7.22 (dd, *J* = 14.5, 6.5 Hz, 2H), 7.13 (dd, *J* = 15.0, 7.6 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz , $CDCl_3$): δ 166.1 (d, *J* = 5.3 Hz), 159.6 (d, *J* = 13.7 Hz), 154.1, 134.7, 133.7, 133.5 (d, *J* = 3.9 Hz), 133.0 (d, *J* = 8.0 Hz), 131.9 (d, *J* = 9.3 Hz), 131.51, 131.50 (t, *J* = 20.0 Hz), 129.2 (d, *J* = 74.4 Hz), 128.0, 128.04 (d, *J* = 25.0 Hz), 127.5, 125.2, 124.5, 120.1 (d, *J* = 9.5 Hz), 118.6 (d, *J* = 101.0 Hz), 116.6, 20.0; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.5; IR (neat): *v* = 3063, 2925, 1719, 1598, 1538, 1441, 1330, 1260, 1194, 1116, 915, 741 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_3P]^+$ $[M+H]^+$: 437.1301, found: 437.1307.

4-(cyclohexa-2,4-dien-1-yl)-3-(diphenylphosphoryl)-6-methyl-2*H*-chromen-2-one (3g)



Yellow solid (101mg, 58% yield); m.p. 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (m, 4H), 7.49–7.43 (m, 2H), 7.39 (d, *J* = 6.8 Hz, 7H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.14 (s, 1H), 6.97 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (d, *J* = 5.4 Hz), 159.8 (d, *J* = 13.7 Hz), 154.4, 145.5, 133.7 (d, *J* = 4.5 Hz), 133.6, 132.5, 131.5, 131.4 (d, *J* = 2.6 Hz), 128.6 (d, *J* = 36.1 Hz), 128.2, 128.1, 128.0, 127.7, 125.6, 118.4 (d, *J* = 9.2 Hz), 116.7, 21.7; ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.4; IR (neat): *v* =3059, 2924, 1718, 1614, 1526, 1439, 1341, 1264, 1196, 1114, 916, 734 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_3P]^+$ $[M+H]^+$: 437.1301, found: 437.1304.

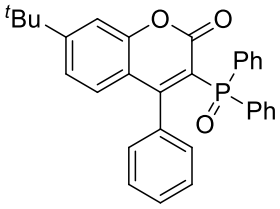
3-(dibutylphosphoryl)-7-methyl-4-phenyl-2*H*-chromen-2-one (3h)



Yellow oil (73.8 mg, 47% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.42 (m, 3H), 7.23–7.18 (m, 2H), 7.17 (s, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 2.44 (s, 3H), 2.21–2.08 (m, 2H), 2.01–1.87 (m, 2H), 1.66–1.53 (m, 2H), 1.49–1.31 (m, 6H), 0.86 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CDCl3): δ 166.1 (d, J = 3.6 Hz), 160.4 (d,

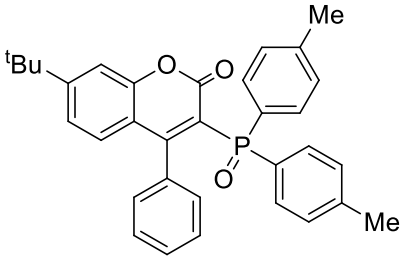
J = 14.5 Hz), 153.9, 145.2, 133.9 (d, J = 3.6 Hz), 128.4, 127.8, 127.5, 125.7, 118.9, 118.8, 116.7(d, *J* = 7.8 Hz), 115.8, 29.4 (d, *J* = 71.6 Hz), 24.1 (d, *J* = 16.1 Hz),, 23.7 (d, *J* = 4.3 Hz), 21.7 (d, *J* = 10.3 Hz), 13.6 (d, *J* = 4.4 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ 43.8; IR (neat): ν = 3053, 2947, 1709, 1609, 1532, 1456, 1336, 1198, 1088, 906, 782 cm-1; HRMS (ESI) Exact mass calculated for $[C_{24}H_{29}NaO_3P]^+$ $[M+Na]^+$: 419.1747, found: 419.1746.

6-(tert-butyl)-3-(diphenylphosphoryl)-4-phenyl-2*H*-chromen-2-one (3i)



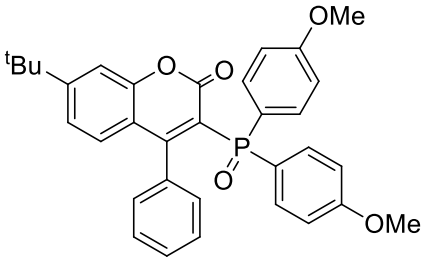
Yellow solid (116 mg, 61% yield); m.p. 225-228 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (m, 4H), 7.46 (t, *J* = 7.1 Hz, 2H), 7.37 (dd, *J* = 14.8, 7.9 Hz, 8H), 7.22 (dd, *J* = 12.6, 6.6 Hz, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz , $CDCl_3$) : δ 165.8 (d, *J* = 5.3 Hz), 159. 9 (d, *J* = 13.5 Hz), 158.6, 154.3, 133.7 (d, *J* = 4.3 Hz), 133.6, 132.5, 131.5 (d, *J* = 10.3 Hz), 128.6 (d, *J* = 47.5 Hz), 128.2 (d, *J* = 6.7 Hz), 128.0, 127.7, 122.0, 118.4 (d, *J* = 9.4 Hz), 117.9, 116.9, 113.4, 35.3, 30.8; ^{31}P NMR (243 MHz, $CDCl_3$) : δ 24.6; IR (neat) : *v* = 3062, 2962, 1719, 1607, 1522, 1341, 1198, 1111, 1003, 915, 736 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{31}H_{28}O_3P]^+$ $[M+H]^+$: 479.1771, found: 479.1776.

7-(tert-butyl)-3-(di-p-tolylphosphoryl)-4-phenyl-2*H*-chromen-2-one (3j)



Yellow oil (121.9 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 12.4, 8.0 Hz, 4H), 7.42 – 7.35 (m, 3H), 7.33 (d, *J* = 1.3 Hz, 1H), 7.22 (s, 1H), 7.19 (d, *J* = 8.3 Hz, 6H), 7.03(d, *J* = 8.5 Hz, 1H), 2.35 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3(d, *J* = 5.2 Hz), 159.8(d, *J* = 13.5 Hz), 158.3, 154.2, 141.7(d, *J* = 2.7 Hz), 133.8(d, *J* = 4.2 Hz), 131.5(q, *J* = 10.9 Hz), 130.4, 129.7, 129.2, 128.6(q, *J* = 24.6 Hz), 127.6(d, *J* = 8.8 Hz), 127.5, 121.8(d, *J* = 6.2 Hz), 118.3(t, *J* = 7.2 Hz), 117.2, 113.3(d, *J* = 14.4 Hz), 35.2, 30.7(q, *J* = 7.3 Hz), 21.4(q, *J* = 12.0 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ 25.1; IR (neat): *v* = 3030, 2962, 2220, 1719, 1612, 1523, 1404, 1340, 916, 812, 731 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{33}H_{31}NaO_3P]^+$ $[M+Na]^+$: 529.1903, found: 529.1892.

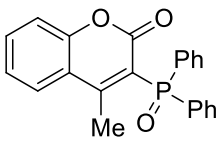
3-(bis(4-methoxyphenyl)phosphoryl)-7-(tert-butyl)-4-phenyl-2*H*-chromen-2-one (3k)



Yellow oil (132.5 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 12.0, 8.7 Hz, 4H), 7.14 (d, *J* = 6.4 Hz, 3H), 7.06 (s, 1H), 6.95 (d, *J* = 6.0 Hz, 2H), 6.92 (s, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.63 (dd, *J* = 8.5, 1.7 Hz, 4H), 3.54 (s, 6H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0 (d, *J* = 5.0 Hz), 162.0 (d, *J* = 2.5 Hz), 160.0 (d, *J* = 13.5 Hz), 158.3, 154.2, 134.0 (d, *J* = 54.2 Hz), 133.3 (q, *J* = 11.8 Hz), 128.2, 128.1 (d, *J* = 14.9 Hz), 127.6 (d, *J* = 16 Hz), 125.1, 123.9, 121.8 (d, *J* = 11.3 Hz), 118.5 (d, *J* = 9.9 Hz), 117.5, 113.4 (q, *J* = 15.6 Hz), 55.1 (q, *J* = 18.1 Hz), 35.2, 30.88, 30.80, 30.7 (q, *J* = 7.8 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ 24.3; IR (neat): *v* = 3064, 2961, 2218, 1718, 1596, 1503, 1295, 1252, 1182, 1113, 731 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{33}H_{31}NaO_5P]^+$ $[M+Na]^+$: 561.1801,

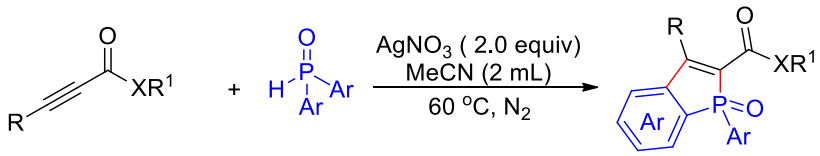
found: 561.1792.

3-(diphenylphosphoryl)-4-methyl-2*H*-chromen-2-one (3l)



Yellow oil (105 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.70 (m, 4H), 7.59 (d, *J* = 6.7 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 4H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 20.4 Hz, 1H), 2.35 (d, *J* = 13.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.2 (d, *J* = 25.3 Hz), 152.4, 151.5, 150.2, 132.6 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 10.0 Hz), 130.0, 129.9, 129.8, 129.5, 128.9 (d, *J* = 12.1 Hz), 126.1, 121.4, 15.8 (d, *J* = 8.1 Hz); ^{31}P NMR (243 MHz, $CDCl_3$): δ 31.4; IR (neat): ν = 3063, 2933, 2840, 1717, 1599, 1539, 1335, 1192, 1114, 913, 743 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{22}H_{18}O_3P]^+$ $[M+H]^+$: 361.0988, found: 361.0991.

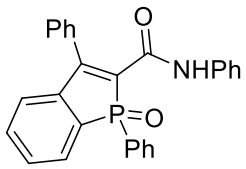
3. General procedure the hydrophosphinylative cyclization of propynoic acid amide



4 0.40 mmol + **2** 0.48 mmol → **5a-5k** X = O, NH

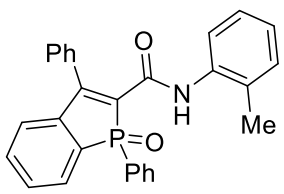
Propynoic alkyl ester **1j-1m** or aryl propargyl amide **4a-4e** (0.40 mmol, 1.0 equiv), arylphosphine oxide **2** (0.48 mmol, 1.2 equiv), $AgNO_3$ (0.80 mmol, 2.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere, MeCN (2 mL) as solvent was then added. The mixture was stirred for 24-48 h at 60℃. After the **4** was completely consumed (monitored by TLC), the crude mixture was directly purified by flash column chromatography on silica gel (EtOAc/petroleum ether 1:1) to give the desired products **5a-5k**.

3-(diphenylphosphoryl)-4-phenylquinolin-2(1*H*)-one (5a)[5]



Yellow solid (161.6 mg, 95% yield); m.p. 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.84–7.69 (m, 3H), 7.59–7.46 (m, 8H), 7.44 (t, *J* = 7.3 Hz, 4H), 7.22 (dd, *J* = 14.4, 6.7 Hz, 3H), 7.03 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, *J* = 12.7 Hz), 158.9 (d, *J* = 14.8 Hz), 142.7 (d, *J* = 26.2 Hz), 137.6, 133.4 (d, *J* = 2.0 Hz), 132.9 (d, *J* = 2.8 Hz), 131.0, 130.9, 129.5, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 128.2, 127.6, 126.1, 126.0, 124.3, 120.0; ^{31}P NMR (243 MHz, $CDCl_3$): δ 39.9; IR (neat): *v* = 3236, 3057, 2924, 1666, 1599, 1544, 1441, 1319, 1190, 1117, 742 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{27}H_{21}NO_2P]^+$ $[M+H]^+$: 422.1304, found: 422.1315.

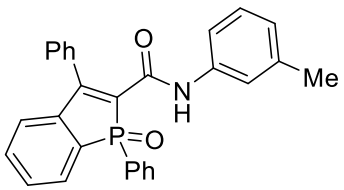
3-(diphenylphosphoryl)-8-methyl-4-phenylquinolin-2(1*H*)-one (5b)



Yellow solid (104.4 mg, 60% yield); m.p. 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86–7.69 (m, 3H), 7.62–7.42 (m, 10H), 7.14–6.93 (m, 4H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, *J* = 12.6 Hz), 159.3 (d, *J* = 17.8 Hz), 143.9 (d, *J* = 26.2 Hz), 135.9, 133.5 (d,

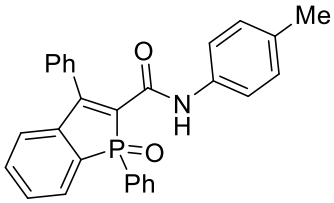
J = 2.0 Hz), 132.9 (d, *J* = 4.0 Hz), 131.12, 131.08, 131.01, 131.00, 130.3, 129.5, 129.4, 129.3, 129.2, 129.1, 128.6, 128.3, 126.5, 126.15, 126.06, 124.6, 122.0, 17.7; ^{31}P NMR (243 MHz, $CDCl_3$): δ 40.0; IR (neat): *v* = 3205, 3059, 2924, 2855, 1669, 1530, 1450, 1308, 1190, 1117, 914, 741 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{23}NO_2P]^+$ $[M+H]^+$: 436.1461, found: 436.1466.

3-(diphenylphosphoryl)-7-methyl-4-phenylquinolin-2(1*H*)-one (5c)



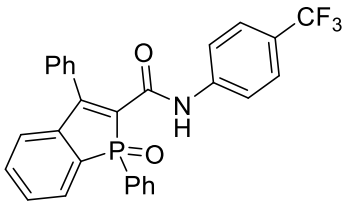
Yellow solid (104.5 mg, 60% yield); m.p. 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.87–7.70 (m, 3H), 7.51 (dt, *J* = 16.1, 7.6 Hz, 10H), 7.34 (s, 1H), 7.23–7.09 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (d, *J* = 13.8 Hz), 159.0 (d, *J* = 18.1 Hz), 142.9 (d, *J* = 26.2 Hz), 138.8, 137.6, 133.5 (d, *J* = 32.0 Hz), 132.9 (d, *J* = 2.9 Hz), 132.8, 132.7, 131.1, 130.1, 129.52, 129.48, 129.4, 129.2, 129.1, 128.6, 128.2, 126.1, 126.0, 125.1, 120.6, 117.0, 21.4; ^{31}P NMR (243 MHz, $CDCl_3$): δ 40.0; IR (neat): *v* = 3062, 2924, 2316, 1673, 1553, 1491, 1443, 1313, 1190, 1117, 732 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{23}NO_2P]^+$ $[M+H]^+$: 436.1461, found: 436.1466.

3-(diphenylphosphoryl)-6-methyl-4-phenylquinolin-2(1*H*)-one (5d)



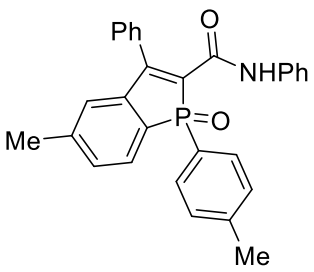
Yellow solid (146.2 mg, 84% yield); m.p. 87-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.85–7.68 (m, 3H), 7.55–7.39 (m, 9H), 7.36–7.20 (m, 4H), 7.03 (t, *J* = 7.8 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, *J* = 12.4 Hz), 158.6 (d, *J* = 18.1 Hz), 142.7 (d, *J* = 26.0 Hz), 135.1, 133.9, 133.4 (d, *J* = 1.9 Hz), 132.8 (d, *J* = 2.9 Hz), 131.0, 130.9, 129.5, 129.4, 129.3, 129.2(One carbon is missing due to the single overlap), 129.1, 129.0, 128.5, 128.2, 126.0, 125.9, 119.9, 20.8; ^{31}P NMR (243 MHz, $CDCl_3$): δ 39.8; IR (neat): *v* = 3053, 2924, 1667, 1601, 1526, 1319, 1251, 1191, 1115, 817, 705 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{23}NO_2P]^+$ $[M+H]^+$: 436.1461, found: 436.1469.

3-(diphenylphosphoryl)-4-phenyl-6-(trifluoromethyl)quinolin-2(1*H*)-one (5e)



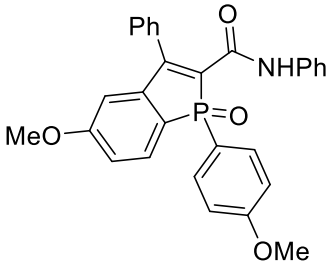
Yellow solid (171.1 mg, 87% yield); m.p. 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (s, 1H), 7.76 (d = 12.4, 7.6 Hz, 3H), 7.52 (t, *J* = 10.0 Hz, 8H), 7.50 (s, 6H), 7.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 (d, *J* = 12.8 Hz), 159.9 (d, *J* = 17.7 Hz), 142.7 (d, *J* = 25.9 Hz), 140.7, 133.6 (d, *J* = 1.8 Hz), 133.1 (d, *J* = 2.8 Hz), 132.5, 132.4, 131.5, 131.3, 131.2, 131.0, 130.9, 129.7, 129.54, 129.45, 129.3, 129.1, 128.6, 128.2, 126.4, 126.3, 126.1 (q, *J* = 3.7 Hz), 119.6; ^{31}P NMR (243 MHz, $CDCl_3$): δ 40.0; ^{19}F NMR (565 MHz, $CDCl_3$): δ -62.2; IR (neat): *v* = 3049, 2929, 1674, 1604, 1541, 1411, 1323, 1181, 1117, 1067, 841, 732 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{20}F_3NO_2P]^+$ $[M+H]^+$: 490.1178, found: 490.1182.

3-(di-p-tolylphosphoryl)-4-phenylquinolin-2(1*H*)-one (5f)



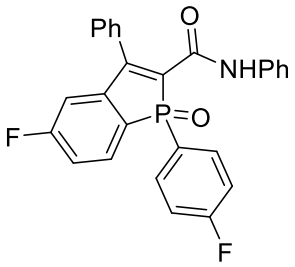
Yellow solid (95.2 mg, 53% yield); m.p. 281-283 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 7.73–7.58 (m, 3H), 7.48 (dd, *J* = 19.1, 11.4 Hz, 7H), 7.31 (s, 1H), 7.25–7.19 (m, 3H), 7.10–6.97 (m, 3H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 160.3 (d, *J* = 12.7 Hz), 158.7 (d, *J* = 18.0 Hz), 144.3 (d, *J* = 2.1 Hz), 143.6 (d, *J* = 2.9 Hz), 143.2, 143.0, 137.7, 131.6, 131.5, 131.1, 131.0, 129.9, 129.8, 129.4, 128.7, 128.5, 128.2, 126.9, 126.8, 124.2, 120.0, 21.9, 21.6; ^{31}P NMR (243 MHz, $CDCl_3$): δ 40.0; IR (neat) : *v* = 3049, 2926, 2859, 1670, 1599, 1544, 1391, 1319, 1253, 1186, 912, 740 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{29}H_{25}NO_2P]^+$ $[M+H]^+$: 450.1617, found: 450.1620.

3-(bis(4-methoxyphenyl)phosphoryl)-4-phenylquinolin-2(1*H*)-one (5g)



Yellow solid (95 mg, 50% yield); m.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 7.66 (dd, *J* = 19.1, 9.8 Hz, 3H), 7.52–7.40 (m, 7H), 7.22 (t, *J* = 8.6 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 9.5 Hz, 3H), 6.74 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0 (d, *J* = 1.8 Hz), 163.3 (d, *J* = 3.0 Hz), 160.3 (d, *J* = 12.2 Hz), 157.6 (d, *J* = 17.4 Hz), 145.4 (d, *J* = 28.0 Hz), 137.7, 133.0 (td, *J* =26.7 Hz, *J* =5.8 Hz), 131.0, 130.9, 129.4, 128.7, 128.5, 128.2, 124.2, 120.0, 114.8, 114.6, 114.1, 114.0, 113.4, 113.3, 55.6, 55.3; ^{31}P NMR (243 MHz, $CDCl_3$): δ 38.9; IR (neat): *v* = 3051, 2939, 2844, 1667, 1592, 1499, 1315, 1254, 1183, 1115, 910, 740 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{29}H_{25}NO_4P]^+$ $[M+H]^+$: 482.1516, found: 482.1525.

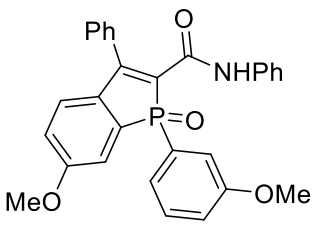
3-(bis(4-fluorophenyl)phosphoryl)-4-phenylquinolin-2(1*H*)-one (5h)



Yellow solid (90 mg, 49% yield); m.p. 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 7.86 –7.60 (m, 3H), 7.55 (s, 2H), 7.49 (s, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.26–7.20 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3 (d, *J* = 48.5 Hz), 164.8 (d, *J* = 44.9 Hz), 159.8 (d, *J* = 12.2 Hz), 156.9 (d, *J* = 19.1 Hz), 146.0 (d, *J* = 8.7 Hz), 145.7 (d, *J* = 8.9 Hz), 137.4, 133.7, 133.66 (d, *J* = 3.6 Hz), 133.5, 131.9, 131.8, 131.5 (d, *J* = 3.0), 131.4 (d, *J* = 1.0), 130.0, 128.9, 128.8, 128.1, 124.5, 120.0, 118.0 (d, *J* = 12.0 Hz), 117.8 (d, *J* = 12.0 Hz), 116.9 (d, *J* = 14.0 Hz), 116.7 (d, *J* = 14.0 Hz), 114.3 (d, *J* = 12.0), 114.0 (d, *J* = 12.0); ^{31}P NMR (243 MHz, $CDCl_3$) : δ 37.1; ^{19}F NMR (565 MHz, $CDCl_3$): δ -103.0, -104.4; IR (neat) : *v* = 3060, 1667, 1593, 1548, 1499, 1444, 1321, 1195, 1112, 910, 740 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{27}H_{19}F_2NO_2P]^+$ $[M+H]^+$: 458.1116, found: 458.1124.

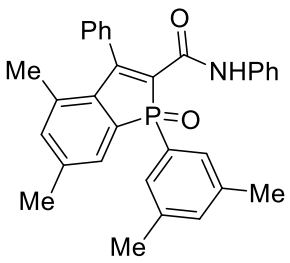
3-(bis(3-methoxyphenyl)phosphoryl)-4-phenylquinolin-2(1*H*)-one (5i)

Colorless solid (101 mg, 52% yield); m.p. 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.50 (s, 1H), 7.51 (s, 3H), 7.47 (s, 2H), 7.39 (d, *J* = 7.8 Hz, 3H), 7.31 – 7.23 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 8.6 Hz,



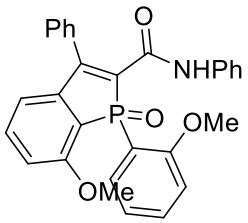
1H), 7.09 – 6.98 (m, 2H), 6.96 (d, J = 8.6 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 13.8 Hz), 160.3 (d, J = 12.6 Hz), 159.8 (d, J = 15.7 Hz), 159.6 (d, J = 17.9 Hz), 137.7, 134.8 (d, J = 25.9 Hz), 134.0, 133.0, 132.9, 130.4, 130.3, 129.5, 128.8, 128.6, 128.1, 127.5 (d, J = 12.8 Hz), 124.2, 122.7 (d, J = 11.2 Hz), 119.9, 118.8 (d, J = 2.5 Hz), 118.76, 118.5 (dd, J = 66.7 Hz, J = 2.5 Hz)), 115.6 (dd, J = 78.8 Hz, J = 10.9 Hz)), 55.81, 55.40; ^{31}P NMR (243 MHz, $CDCl_3$): δ 39.07; IR (neat): ν = 3060, 2923, 2851, 1748, 1662, 1596, 1548, 1480, 1432, 1315, 1242, 1185, 1036, 912, 854, 743 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{29}H_{25}NO_4P]^+$ $[M+H]^+$: 482.1516, found: 482.1527.

3-(bis(3,5-dimethylphenyl)phosphoryl)-4-phenylquinolin-2(1*H*)-one (5j)



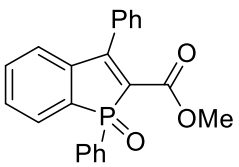
Yellow solid (147 mg, 77% yield); m.p. 254-256 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.50 (d, J = 7.5 Hz, 4H), 7.41 (s, 1H), 7.36 (d, J = 8.7 Hz, 4H), 7.30 (s, 1H), 7.18 (d, J = 9.6 Hz, 3H), 7.06–6.94 (m, 2H), 2.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, J = 17.7 Hz), 160.4 (d, J = 12.0 Hz), 141.6, 141.5, 138.9, 138.7, 138.2 (d, J = 1.9 Hz), 137.8, 137.6, 137.4, 136.8 (d, J = 13.3 Hz), 134.7 (d, J = 3.0 Hz), 129.2, 128.8, 128.7, 128.4 (d, J = 10.9 Hz), 128.2 (d, J = 10.1 Hz), 127.9, 126.3, 124.0, 119.9, 21.3, 21.14, 21.07, 20.98; ^{31}P NMR (243 MHz, $CDCl_3$): δ 36.0; IR (neat): ν = 3045, 2926, 2857, 1671, 1601, 1545, 1443, 1318, 1257, 1183, 909, 743 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{31}H_{29}NO_2P]^+$ $[M+H]^+$: 478.1930, found: 478.1926.

3-(bis(2-methoxyphenyl)phosphoryl)-4-phenylquinolin-2(1*H*)-one (5k)



Yellow solid (91.8 mg, 48% yield); m.p. 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.10 (dd, J = 14.4, 7.6 Hz, 1H), 7.45 (dd, J = 19.6, 7.7 Hz, 9H), 7.21 (t, J = 7.4 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.00 (t, J = 7.3 Hz, 1H), 6.94 (t, J = 7.0 Hz, 1H), 6.85–6.75 (m, 2H), 3.82 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (d, J = 4.6 Hz), 160.5 (d, J = 3.0 Hz), 160.8, 157.5, 157.3, 145.1 (d, J = 24.6 Hz), 138.1, 135.1, 135.05, 134.5 (d, J = 1.9 Hz), 133.5 (d, J = 14.0 Hz), 129.0, 128.7, 128.3 (d, J = 5.9 Hz), 123.9, 121.1 (d, J = 12.2 Hz), 119.8, 118.6 (d, J = 11.5 Hz), 116.9, 116.6, 115.8, 113.5 (d, J = 6.3 Hz), 111.1(d, J = 6.9 Hz), 56.1, 55.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 42.2; IR (neat) : ν = 3056, 2932, 2849, 1670, 1587, 1472, 1266, 1181, 911, 743 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{29}H_{25}NO_4P]^+$ $[M+H]^+$: 482.1516, found: 482.1523.

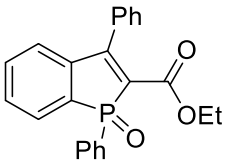
methyl 1,3-diphenylphosphindole-2-carboxylate 1-oxide (5l)



Yellow oil (72.5 mg, 50% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ7.81–7.70 (m, 3H), 7.58–7.50 (m, 6H), 7.46 (s, 2H), 7.39 (s, 2H), 7.22 (s, 1H), 3.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5 (d, J = 18.5 Hz), 163.0 (d, J = 12.3 Hz), 142.1 (d, J = 24.9 Hz), 133.1, 133.0, 132.9 (d, J = 8.1 Hz), 132.5 (d, J = 2.7 Hz), 131.8 (d, J =10.7 Hz), 131.0 (d, J = 11.0 Hz), 129.5 (d, J = 9.6 Hz), 129.4, 128.8 (d, J = 12.9 Hz), 128.3, 127.9, 126.5 (d, J =

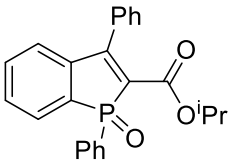
10.5 Hz), 126.1, 125.5, 52.0; ^{31}P NMR (243 MHz, $CDCl_3$) δ 35.8; IR (neat) : ν = 3059, 2925, 2849, 1720, 1561, 1487, 1314, 1219, 1077, 758, 703 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{22}H_{18}O_3P]^+$ $[M+H]^+$: 361.0988, found: 361.0992.

ethyl 1,3-diphenylphosphindole-2-carboxylate 1-oxide (5m)



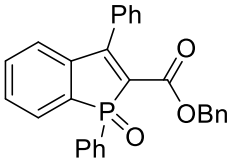
Yellow gum (99.1 mg, 66% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83–7.70 (m, 3H), 7.58–7.48 (m, 6H), 7.46 (s, 2H), 7.39 (s, 2H), 7.23 (s, 1H), 4.11–3.94 (m, 2H), 0.97 (d, J = 4.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.8 (d, J = 18.3 Hz), 162.4 (d, J = 12.3 Hz), 142.2 (d, J = 24.9 Hz), 133.0, 132.9, 132.8, 132.3 (d, J = 2.6 Hz), 131.6 (d, J =10.7 Hz), 131.0 (d, J = 11.0 Hz), 129.4 (d, J = 9.6 Hz), 129.2, 128.6 (d, J = 12.8 Hz), 128.2, 127.8, 126.6, 126.3 (d, J = 10.5 Hz), 125.9, 60.7, 13.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ 35.8; IR (neat) : ν = 3060, 2984, 1714, 1562, 1444, 1311, 1217, 1079, 758, 703 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{23}H_{20}O_3P]^+$ $[M+H]^+$: 375.1145, found: 375.1149.

isopropyl 1,3-diphenylphosphindole-2-carboxylate 1-oxide (5n)



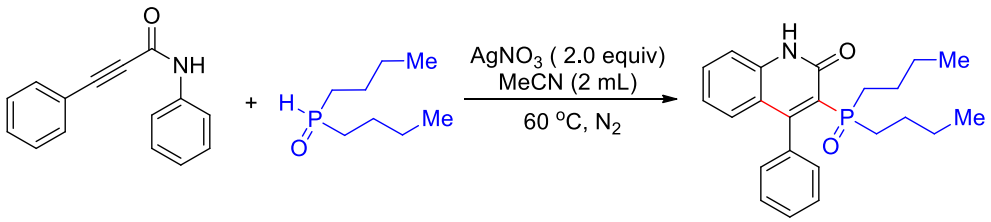
Yellow solid (120.3 mg, 78% yield); m.p. 142-144 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$): δ7.82–7.69 (m, 3H), 7.52 (m, 6H), 7.45 (s, 2H), 7.38 (s, 2H), 7.21 (s, 1H), 4.85 (d, J = 5.8 Hz, 1H), 1.08 (d, J = 25.7 Hz, 3H), 0.82 (d, J = 64.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.2 (d, J = 18.3 Hz), 162.0 (d, J = 12.5 Hz), 142.2 (d, J = 25.1 Hz), 133.1 (d, J =13.0 Hz), 133.0, 132.2 (d, J = 2.6 Hz), 131.5 (d, J =10.5 Hz), 131.0 (d, J = 11.0 Hz), 129.4 (d, J = 9.6 Hz), 129.1, 128.7 (d, J = 28.2 Hz), 128.5, 128.1, 127.8, 127.1, 126.5, 126.2 (d, J = 10.4 Hz), 68.6, 21.3, 21.2; ^{31}P NMR (243 MHz, $CDCl_3$) δ 35.7; IR (neat) : ν = 3061, 2981, 1711, 1560, 1446, 1307, 1217, 1076, 756, 705 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{24}H_{22}O_3P]^+$ $[M+H]^+$: 389.1301, found: 389.1305.

benzyl 1,3-diphenylphosphindole-2-carboxylate 1-oxide (5o)



Yellow oil (160.6 mg, 92% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ7.75–7.67 (m, 3H), 7.49 (m, 6H), 7.37 (s, 4H), 7.21 (s, 2H), 7.17 (d, J = 6.7 Hz, 2H), 6.90 (d, J = 6.0 Hz, 2H), 5.12 (d, J = 12.6 Hz, 1H), 4.96 (d, J = 12.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.2 (d, J = 18.2 Hz), 162.2 (d, J = 12.3 Hz), 142.0 (d, J = 24.8 Hz), 135.1, 133.0, 132.9, 132.8, 132.2, 131.7 (d, J =10.7 Hz), 131.0 (d, J = 11.0 Hz), 129.4 (d, J = 9.6 Hz), 129.3, 128.6 (d, J = 12.9 Hz), 128.1 (d, J = 22.2 Hz), 127.8, 127.65, 127.60, 126.4 (d, J = 10.4 Hz), 126.2, 125.5, 66.3; ^{31}P NMR (243 MHz, $CDCl_3$) δ 35.7; IR (neat) : ν = 3061, 2931, 1719, 1559, 1446, 1310, 1215, 1161, 1076, 753, 702 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{28}H_{22}O_3P]^+$ $[M+H]^+$: 437.1301, found: 437.1300.

4. Procedure the phosphinylative cyclization of *N*,3-diphenylpropiolamide with dibutylphosphine oxide

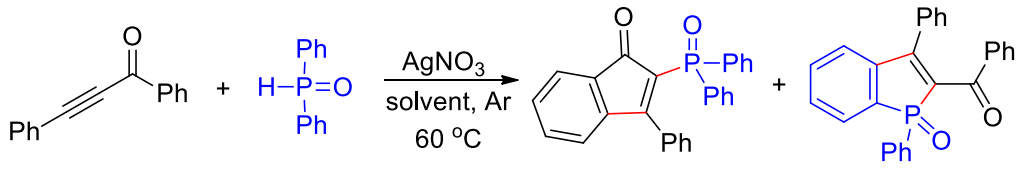


5 **2h** **6**, 80% yield

N,3-diphenylpropiolamide **5** (0.40 mmol, 1.0 equiv), dibutylphosphine oxide **2h** (0.48 mmol, 1.2 equiv), $AgNO_3$ (0.80 mmol, 2.0 equiv) and a stir bar were added to a sealed tube under a nitrogen atmosphere, MeCN (2 mL) as solvent was then added. The mixture was stirred for 48 h at 60℃. After the **5** was completely consumed (monitored by TLC), the crude mixture was directly purified by flash column chromatography on silica gel (EtOAc/petroleum ether 1:1) to give the desired products **3-(dibutylphosphoryl)-4-phenylquinolin-2(1*H*)-one (6)** as Yellow oil (122,0 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.64 (d, *J* = 18.2 Hz, 1H), 7.48 (s, 2H), 7.35 (s, 2H), 7.30 (d, *J* = 2.8 Hz, 3H), 7.13 (d, *J* = 5.7 Hz, 1H), 2.06 (s, 1H), 1.97 (dd, *J* = 17.6, 9.4 Hz, 3H), 1.60 (m, 4H), 1.44–1.35 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, *J* = 16.1 Hz), 145.2 (d, *J* = 3.7 Hz), 137.1, 133.6 (d, *J* = 13.8 Hz), 132.0 (d, *J* = 78.2 Hz), 130.2, 129.3, 129.0, 128.9, 127.4 (d, *J* = 38.1 Hz), 125.0, 124.0, 120.3, 28.4 (d, *J* = 68.9 Hz), 24.1 (d, *J* = 15.0 Hz), 23.5 (d, *J* = 34.5 Hz), 13.6; ^{31}P NMR (243 MHz, $CDCl_3$): δ 42.1; IR (neat): *v* = 3030, 2953, 1664, 1602, 1543, 1448, 1314, 1162, 906, 752 cm^{-1}; HRMS (ESI) Exact mass calculated for $[C_{23}H_{28}NNaO_2P]^+$ $[M+Na]^+$: 404.1750, found: 404.1687.

5. The reaction of 1,3-diphenylprop-2-yn-1-one 6 with 2a

The reaction of 1,3-diphenylprop-2-yn-1-one **6** with **2a** gave an inseparable mixture **7** and **8** in 58% combined yield (in 1:1 ratio).



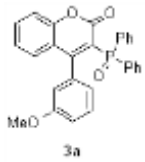
6 **2a** **7** **7**:**8** = 1:1 58% combined yield **8**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75–7.70 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.46 (s, 0H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 2H), 7.23 (d, *J* = 4.6 Hz, 1H), 7.19 (s, 1H), 7.13 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.93, 194.86, 193.17, 193.12, 173.45, 173.41, 156.09, 155.98, 144.49, 144.40, 141.77, 141.61, 136.86, 133.57, 133.22, 133.12, 133.07, 132.55, 132.53, 132.50, 131.47, 131.40, 131.23, 131.16, 131.11, 130.63, 130.56, 130.35, 129.57, 129.49, 128.82, 128.74, 128.53, 128.16, 128.08, 127.94, 125.33, 125.26, 123.31, 123.25; ^{31}P NMR (243 MHz, $CDCl_3$): δ 18.3, 38.2; HRMS (ESI) Exact mass calculated for $[C_{27}H_{19}O_2P]^+$ $[M+Na]^+$: 429.1020, found: 429.1008.

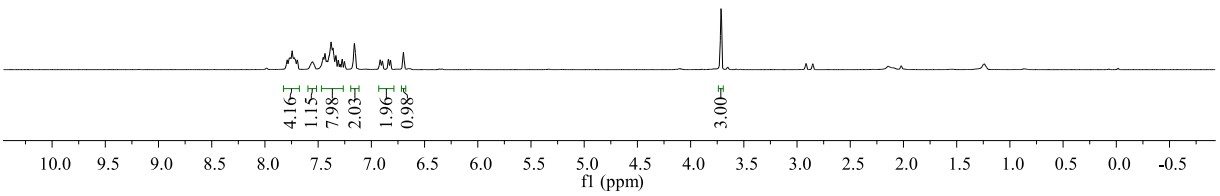
6. References

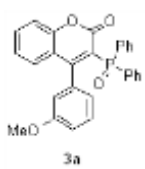
1. (a) W. Gao, T. Liu, B. Zhang, X. Li, W Wei, Q. Liu, J. Tian and H. Chang, *J. Org. Chem*., 2016, *81*, 11297–11304; (b) K. Park, T. Palani, A. Pyo and S. Lee. *Tetrahedron Lett*., 2012, **53**, 733–737; (c) T. Kawate, N. Iwase, M. Shimizu, S. A. Stanley, Samantha. Wellington, E. Kazyanskaya, D. T. Hung, *Bioorg. Med. Chem. Lett*. 2013, **23**, 6052-6059; (d) V. Lellek and H.-J. Hansen, *Helv. Chim. Acta*, 2001, **84**, 3548–3580.
2. (a) C. C, Chen, and J. Waser, *Chem. Commun*., 2014, **50**, 12923–12926; (b) P. Peng, L. Peng, G. Wang, F. Wang, Y. Luo, and A. Lei, *Org. Chem. Front*., 2016, **3**, 749–752; (c) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett*. 2005, **19**, 4277–4280.
3. K. Okamoto, T. Shimbayashi, E. Tamura, K. Ohe, *Org. Lett*. 2015, **17**, 5843–5845.
4. D. Liu, J.-Q. Chen, X.-Z. Wang, P.-F. Xu, *Adv. Synth. Catal*. **2017**, *359*, 2773–2777.
5. P. Zhang, Y. Gao, L. Zhang, Z. Li, Y. Liu, G. Tang, Y. Zhao, *Adv. Synth. Catal*. **2016**, *358*, 138–142.

7. ^{1}H NMR, ^{13}C NMR, ^{32}P, and ^{19}F NMR spectra of products

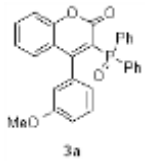


3a





3a


Ph
Ph
MeO

3a

23.84
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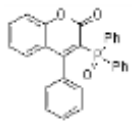
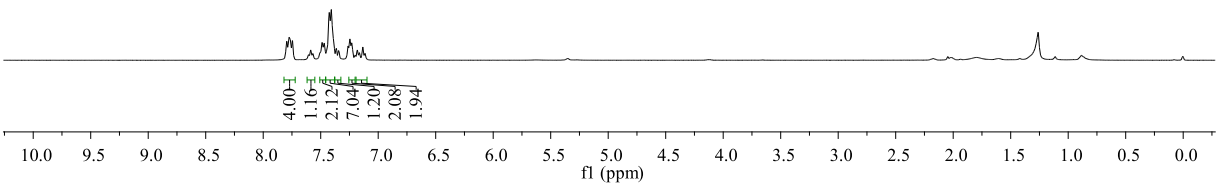
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Ph
Ph

3b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2.12
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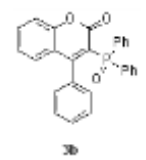
1.20
2.08
1.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3b

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165.87
159.53
154.28
131.58
128.27
128.22
128.09
127.80
124.37
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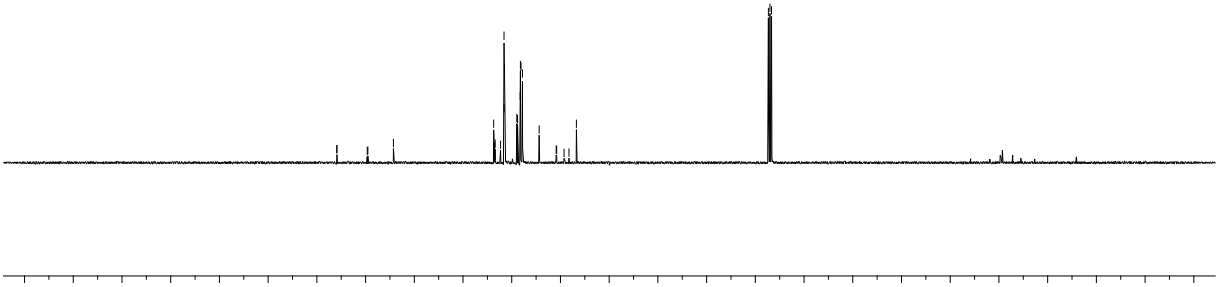
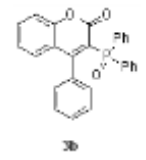
120.78
119.26
118.25
116.73
77.32
77.00
76.68



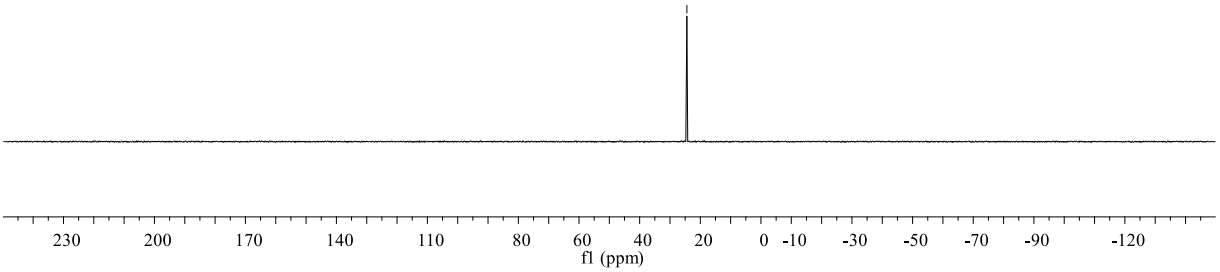
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



3b

24.43



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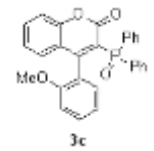
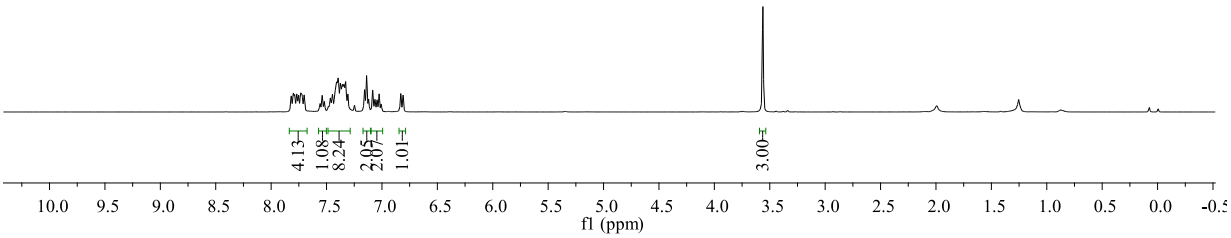
f1 (ppm)


Ph
P
Ph
O
MeO
O
O

3c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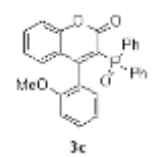
8.24
2.05
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
P
Ph
O
MeO
O
O

3c

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163.38
159.67
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155.88
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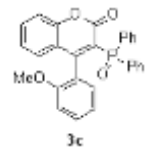
131.49
131.23
129.35
127.93
124.22
120.56
116.58
110.21
77.32
77.00
76.68
54.99
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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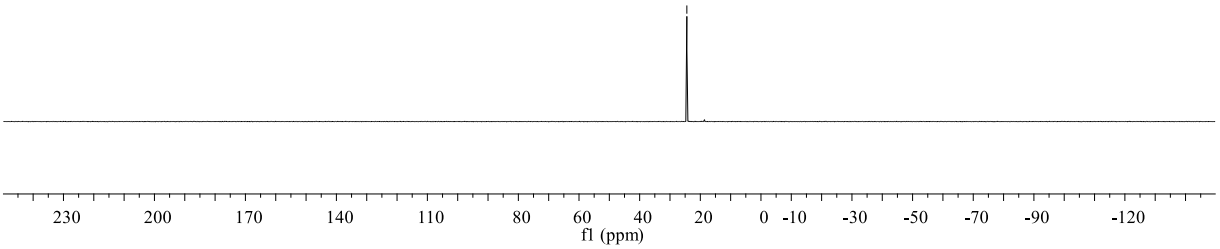
O
Ph
P
Ph
O
MeO

3c

24.44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60
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20
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-10
-30
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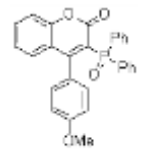
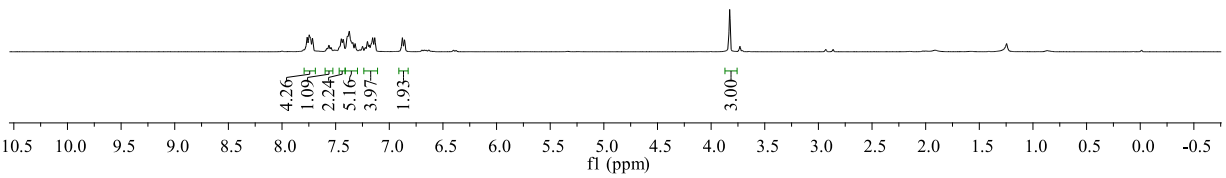
-70
-90
-120
f1 (ppm)


O
O
Ph
P
Ph
O
OMe

3d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8.5
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6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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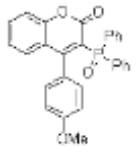
0.5
0.0
-0.5
f1 (ppm)



3d

165.79
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131.44
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113.33
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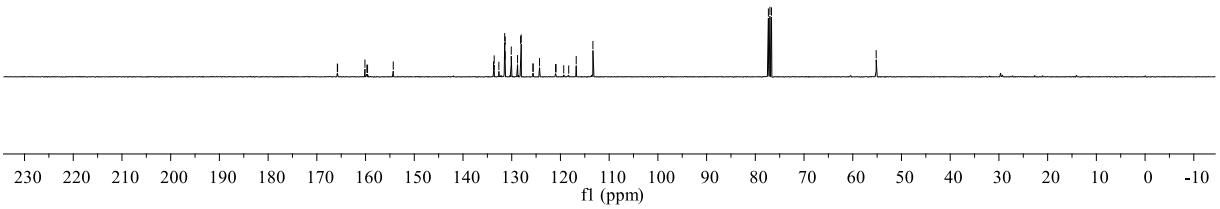
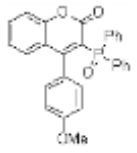
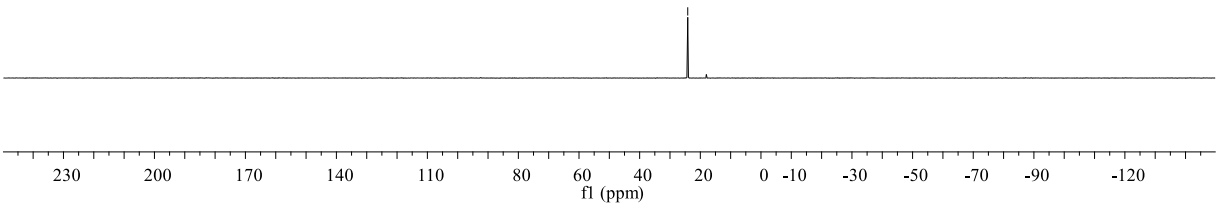
77.00
76.68
55.19

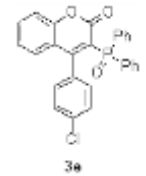




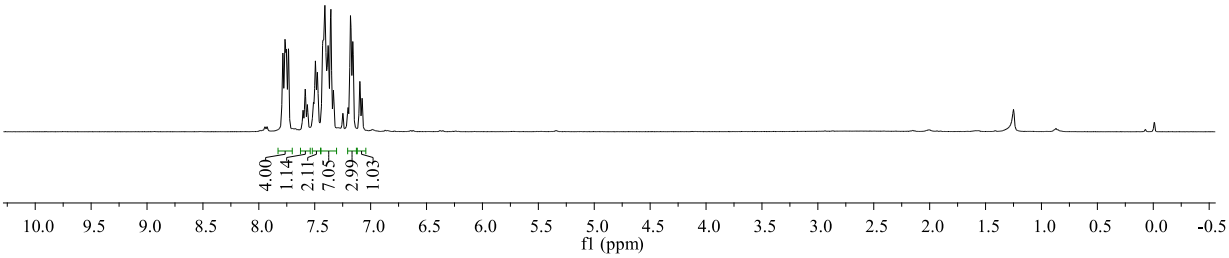
3d

24.15





3e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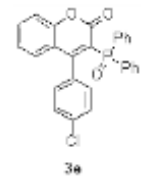
2.11
7.05
2.99
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



3e

164.62
164.57
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154.27
131.69
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128.45
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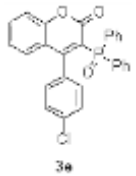
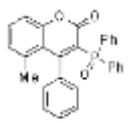
124.49
120.55
120.45
116.83
77.32
77.00
76.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

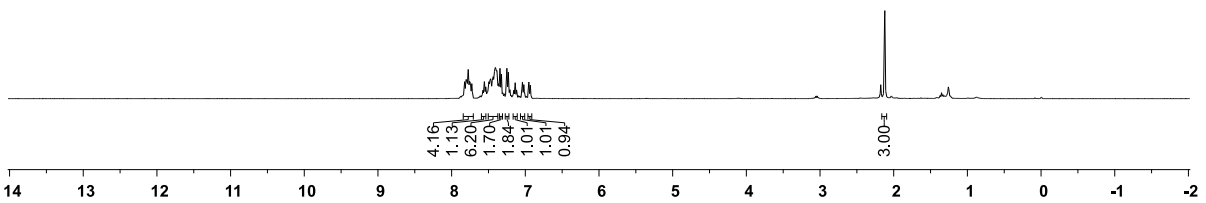


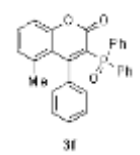
3e

24.75
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)



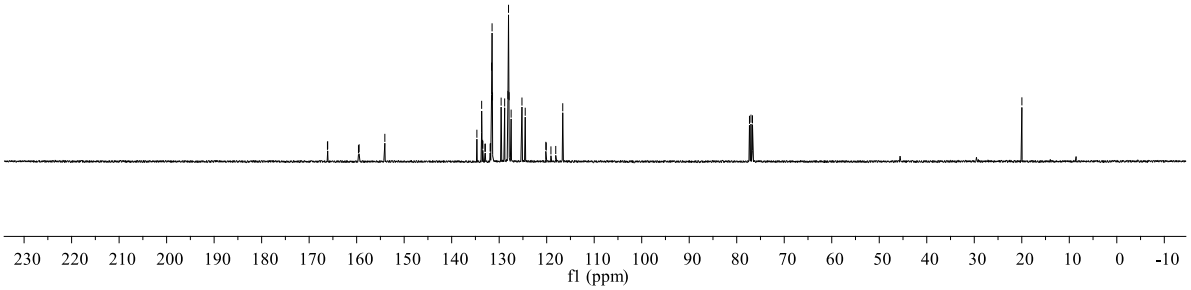
3f


4.16
1.13
6.20
1.70
1.84
1.01
1.01
0.94
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2



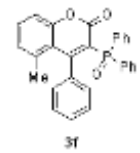
3f

166.15
166.10
159.48
154.07
133.69
131.50
128.85
127.91
124.52
120.18
120.09
119.10
118.09
116.62
77.32
77.00
76.68
19.98



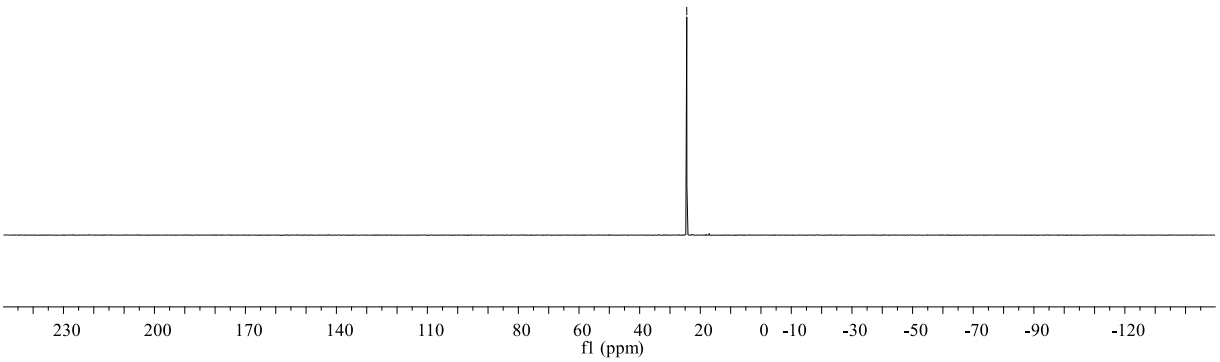
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



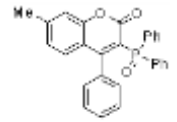
3f

24.46

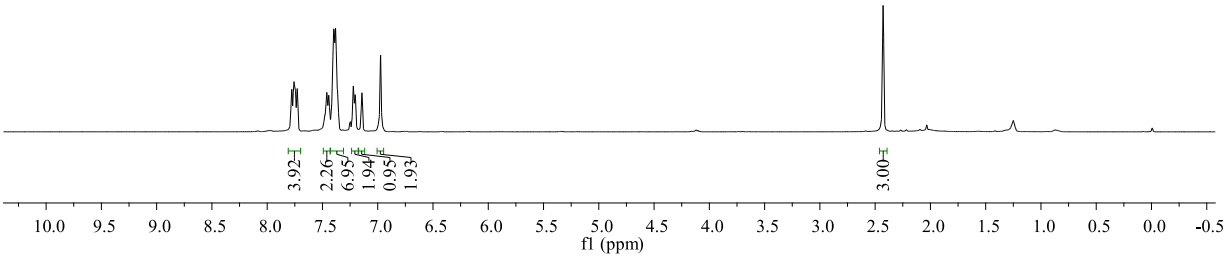


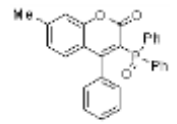
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120

f1 (ppm)


Me
Ph
P
Ph
O
O

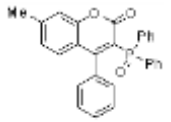
3g


3.92
2.26
6.95
1.94
0.95
1.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Me
Ph
P
Ph
O
O

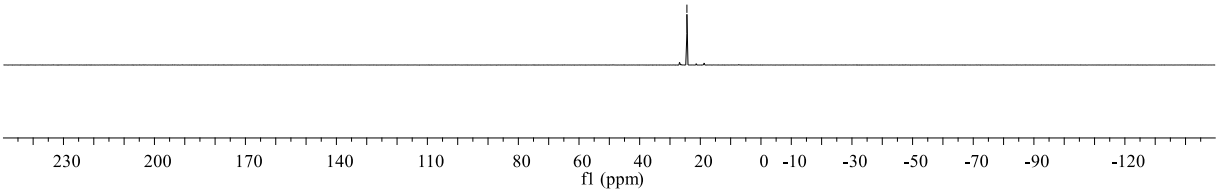
3g

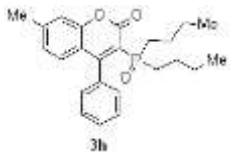
165.89
165.84
159.71
154.35
145.48
131.51
128.81
128.10
125.58
118.48
118.39
116.73
77.32
77.00
76.68
21.72
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Ph
Ph
O
O

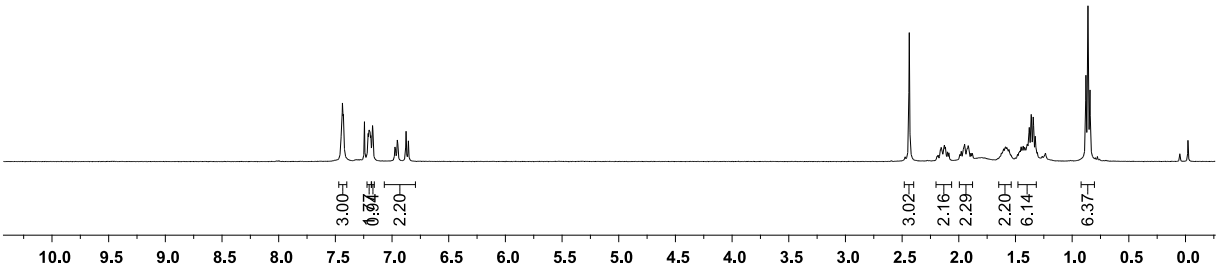
3g

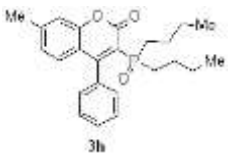
24.42


230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Me
O
O
Me
Me
O

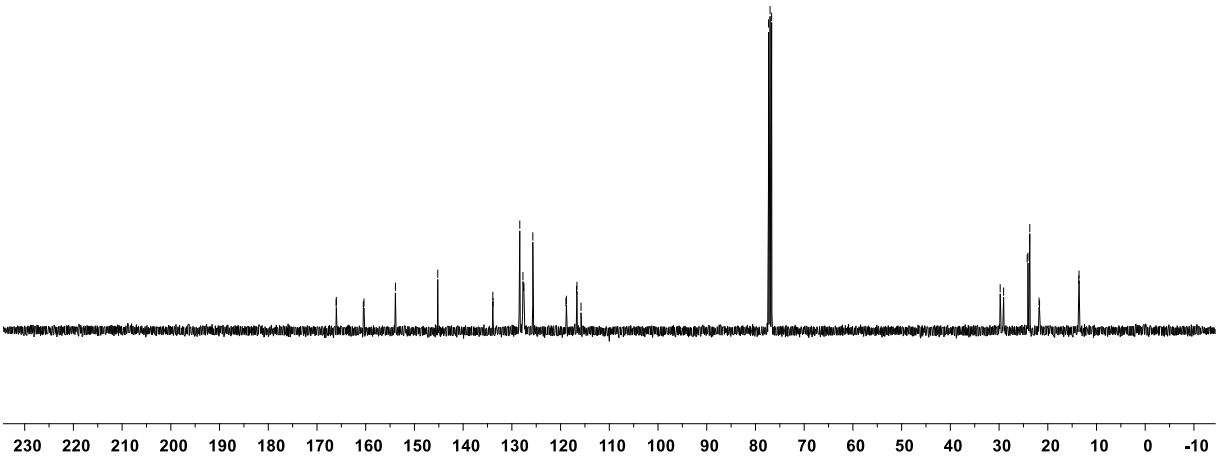
3h

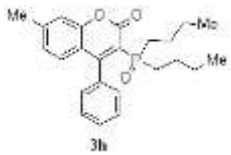

3.00
2.20
3.02
2.16
2.29
2.20
6.14
6.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



3h

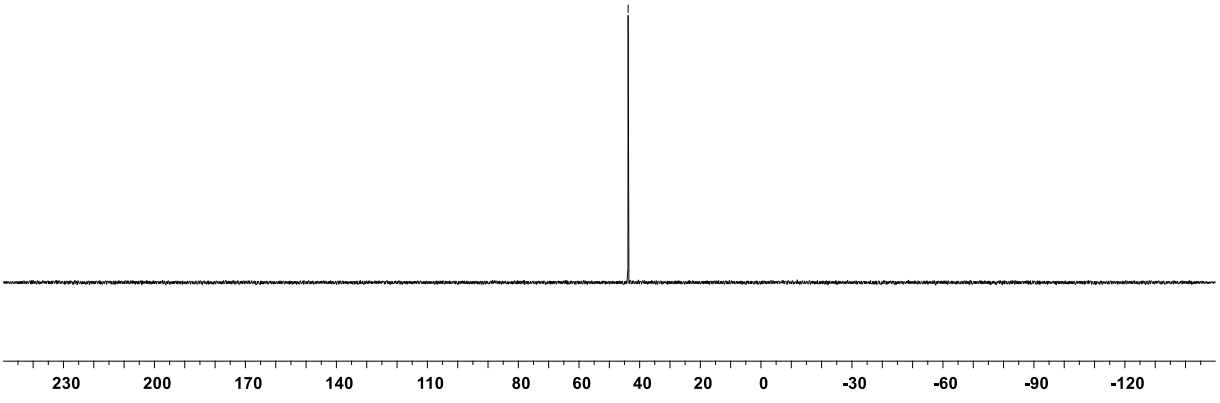
166.1
166.0
160.3
153.9
145.2
133.9
133.9
125.7
118.9
118.8
116.7
116.6
115.8
77.3
77.0
76.7
29.8
29.1
23.7
13.6
13.6

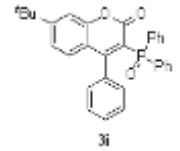




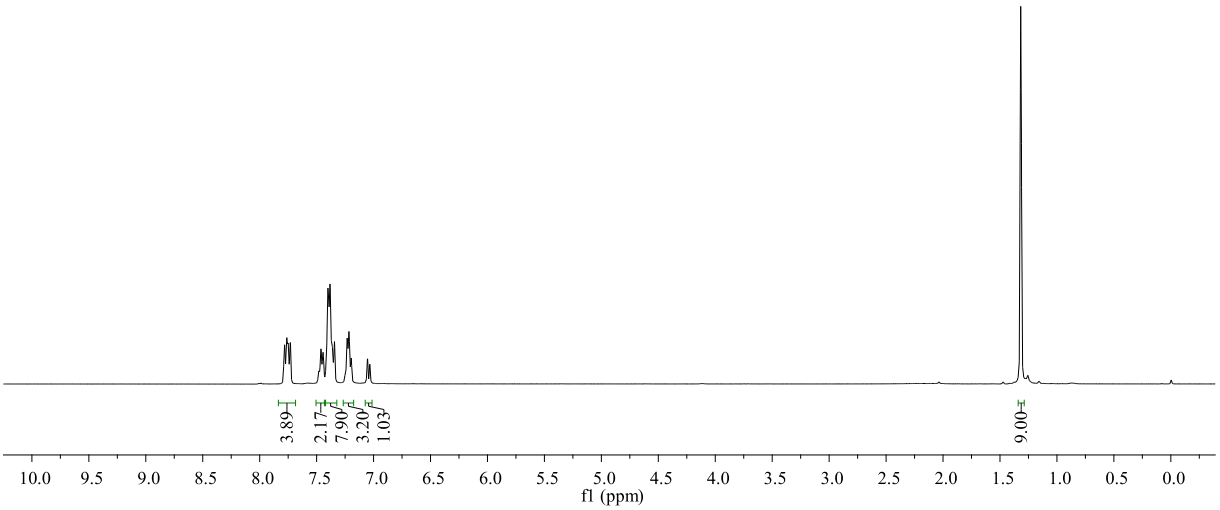
3h

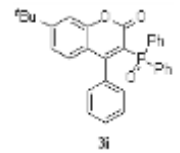
43.8





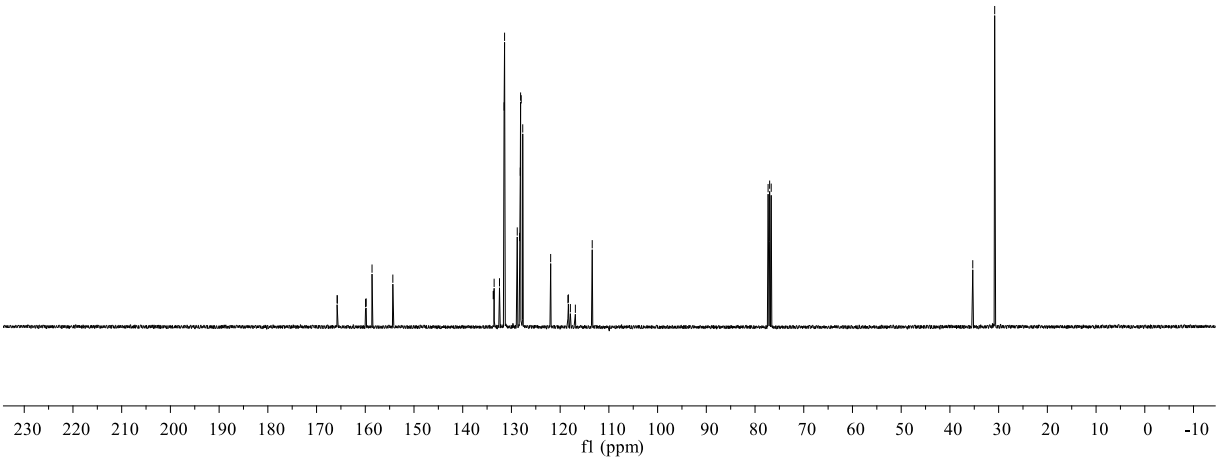
3i

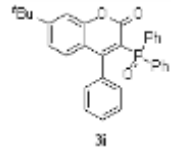




3i

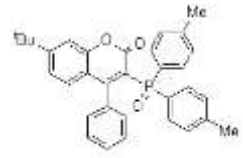
165.78
165.73
159.94
159.81
158.61
154.34
133.55
131.41
128.19
127.68
121.95
118.40
118.31
117.90
116.88
113.42
77.32
77.00
76.68
35.31
30.81



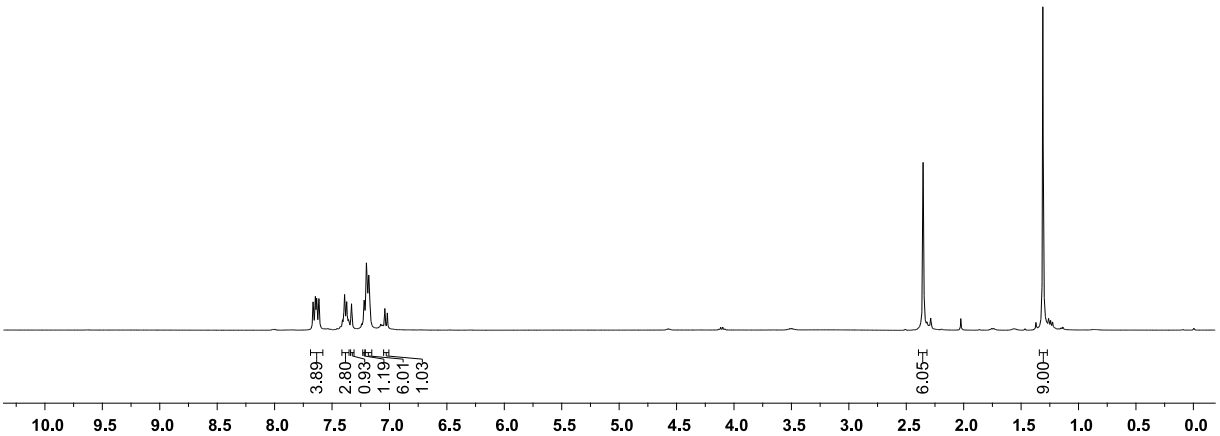

tBu
O
O
Ph
P
O
Ph

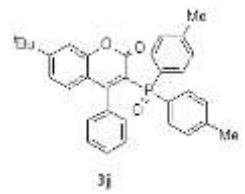
3i

24.59
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Me
tBu
O
O
P
O
Me

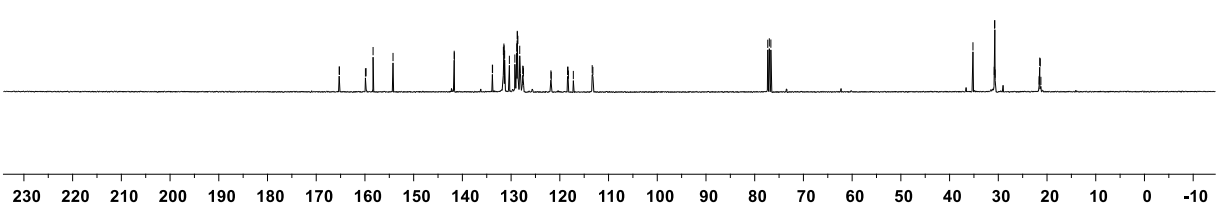
3j

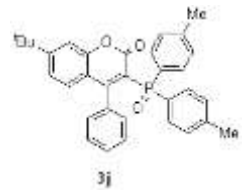

3.89
2.80
0.93
1.19
6.01
1.03
6.05
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



3j

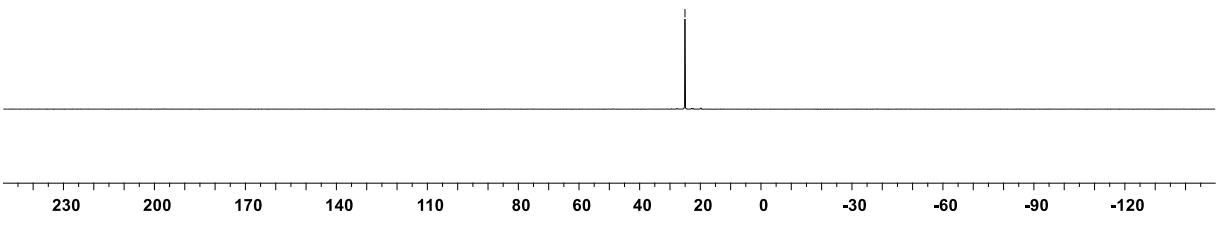
165.3
165.2
158.3
154.2
141.7
141.7
129.2
127.5
121.8
118.4
118.3
118.2
117.2
113.4
113.2
77.3
77.0
76.7
35.2
30.7
21.6
21.5
21.4
21.3

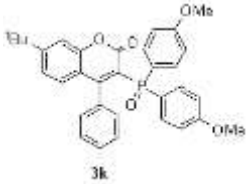




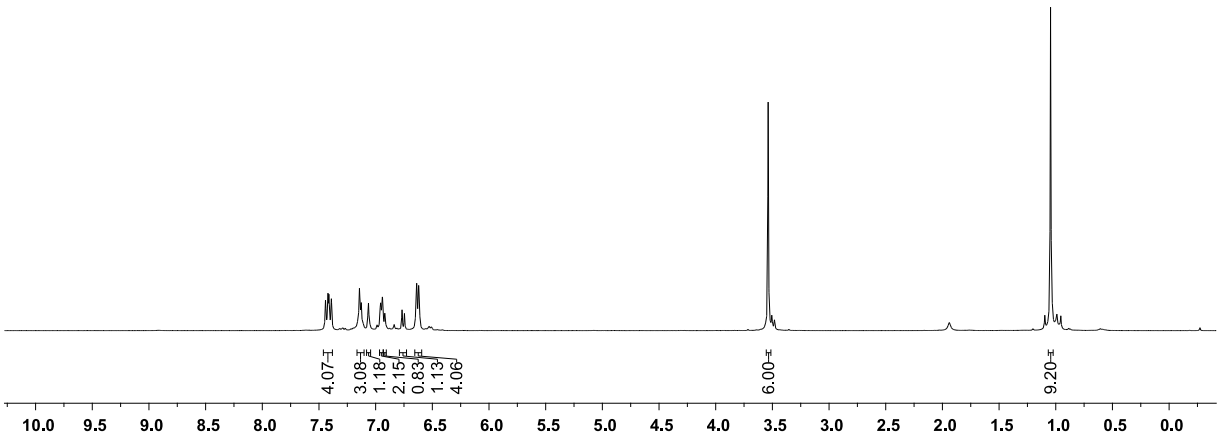
3j

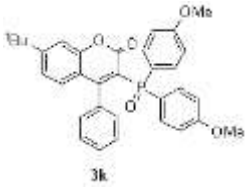
25.1



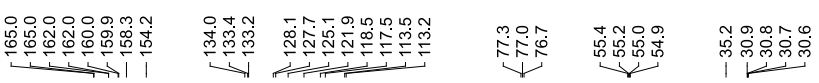

OMe
tBu
O
O
P
O
OMe

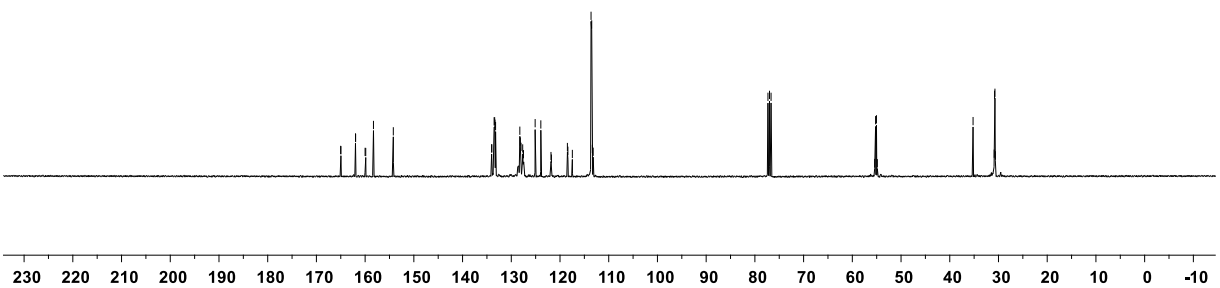
3k

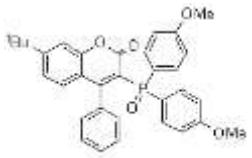

4.07
3.08
1.18
2.15
0.83
1.13
4.06
6.00
9.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


OMe
tBu
O
O
P
O
OMe

3k

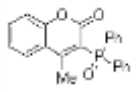

165.0
165.0
162.0
162.0
160.0
159.9
158.3
154.2
134.0
133.4
133.2
128.1
127.7
125.1
121.9
118.5
117.5
113.5
113.2
77.3
77.0
76.7
55.4
55.2
55.0
54.9
35.2
30.9
30.8
30.7
30.6


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

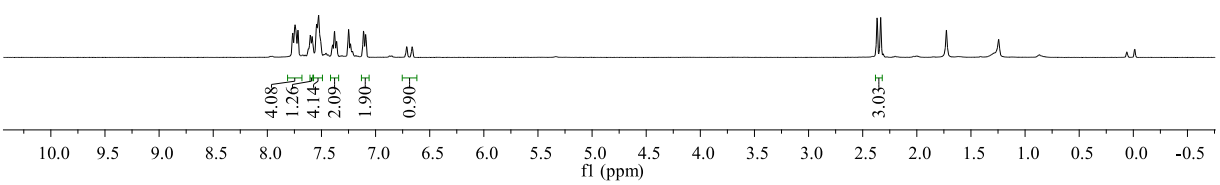

OMe
OMe

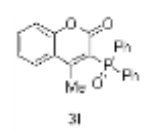
3k

24.3
230
200
170
140
110
80
60
40
20
0
-30
-60
-90
-120


Ph
Ph
Me

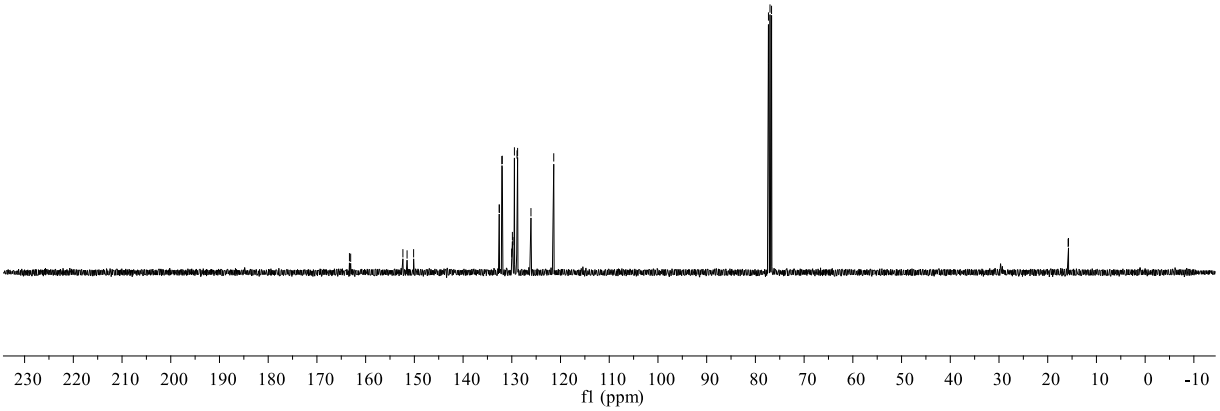
3l


4.08
1.26
4.14
2.09
1.90
0.90
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

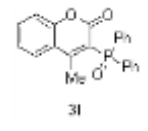


3l

163.32
163.07
152.35
151.50
150.15
132.05
129.76
128.93
126.07
121.39
77.32
77.00
76.68
15.81
15.73

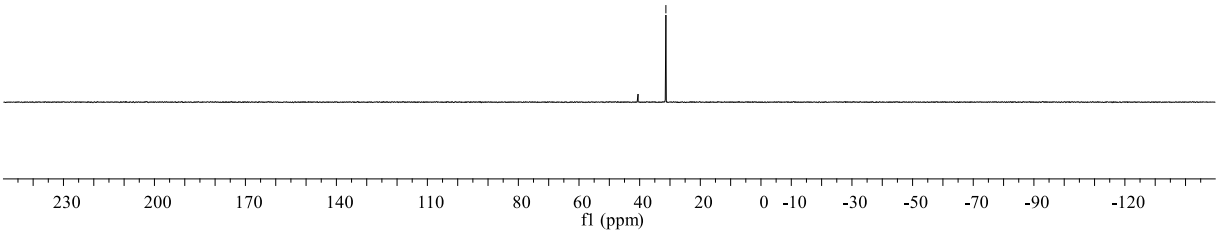


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

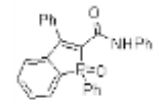


3l

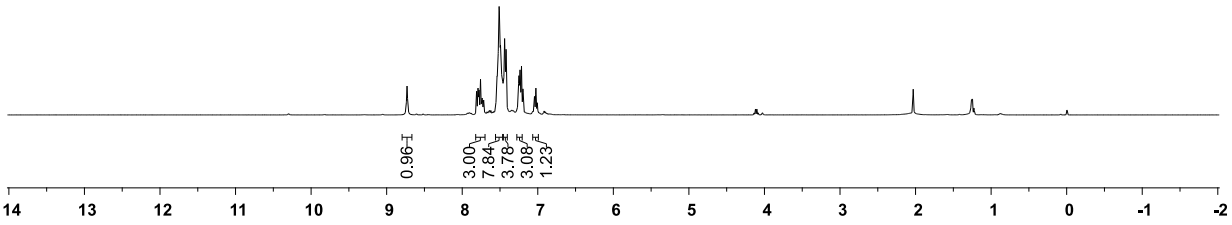
31.35

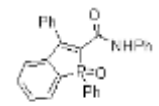


230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120
f1 (ppm)

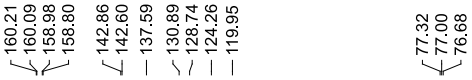

Ph
O
NHPh
P=O
Ph

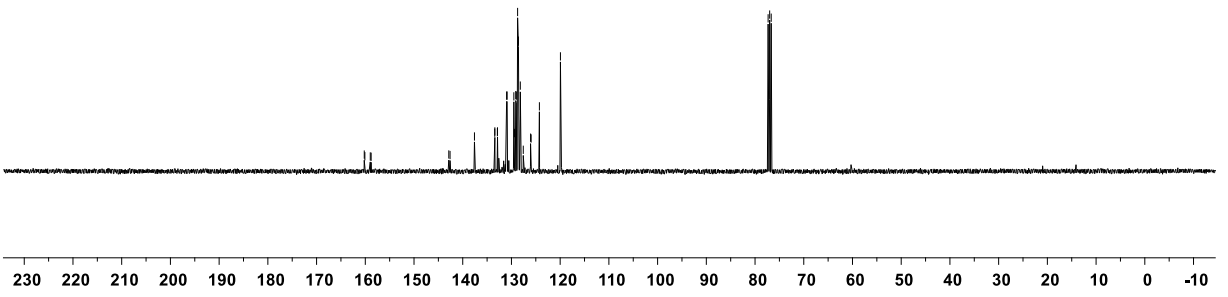
5a

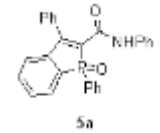

0.96
3.00
7.84
3.78
3.08
1.23
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2


Ph
O
NHPh
P=O
Ph

5a

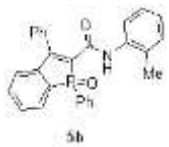

160.21
160.09
158.98
158.80
142.86
142.60
137.59
130.89
128.74
124.26
119.95
77.32
77.00
76.68


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

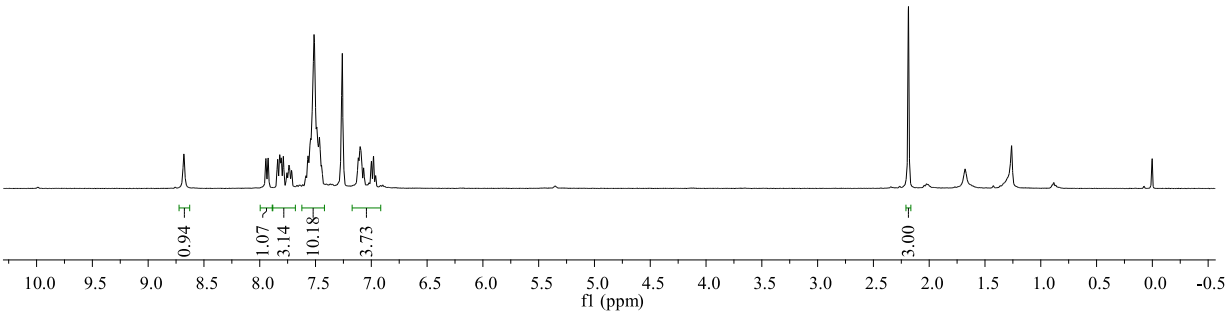

Ph
O
NHPh
P=O
Ph

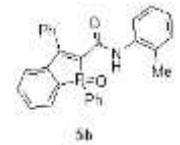
5a

39.85
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Ph
O
N
H
Me
P=O
Ph

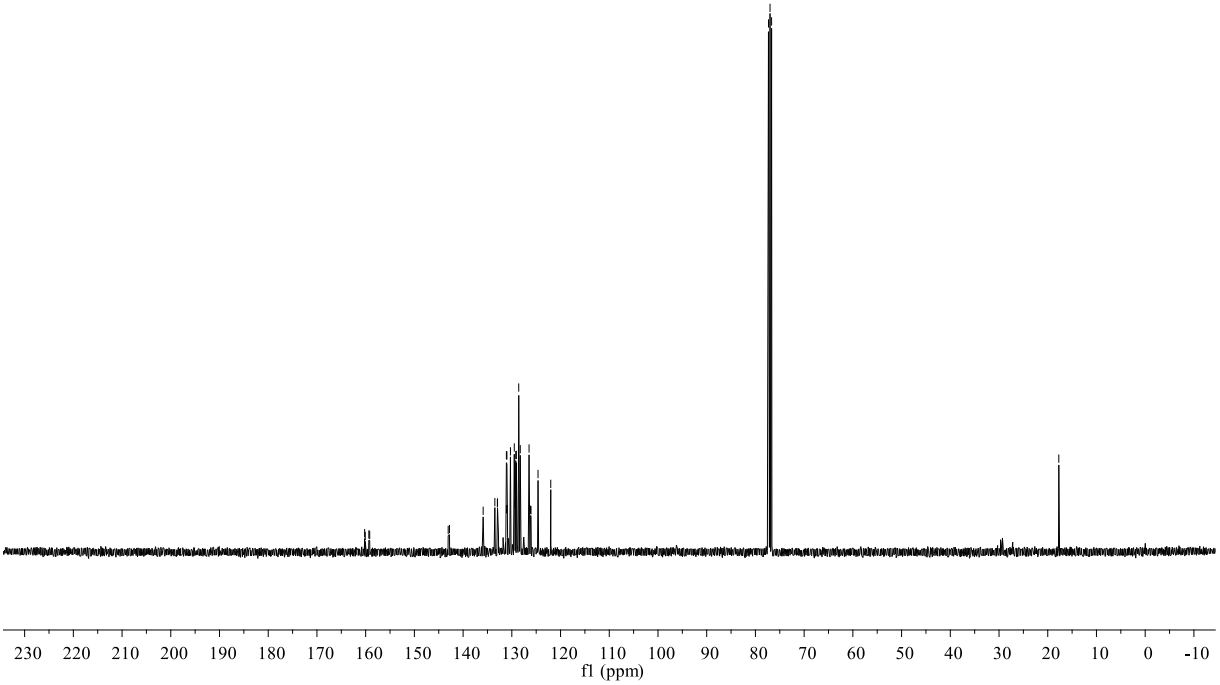
5b

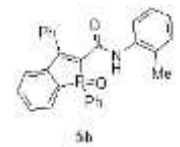

0.94
1.07
3.14
10.18
3.73
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



5b

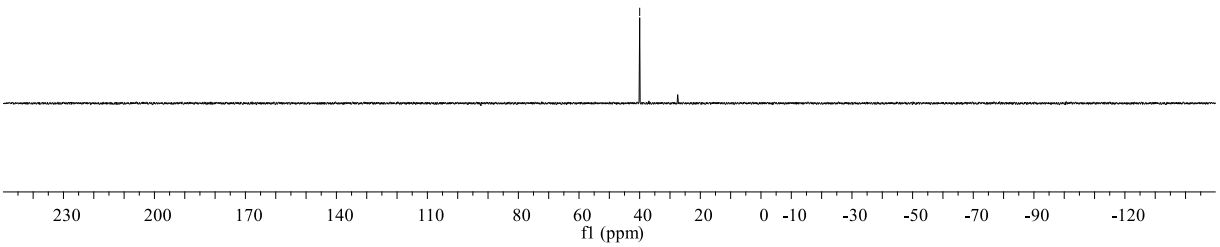
160.21
160.08
159.35
159.17
143.06
142.80
131.12
130.28
129.35
129.20
128.58
126.46
126.06
122.01
77.32
77.00
76.68
17.73

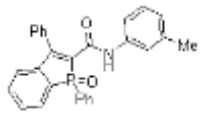




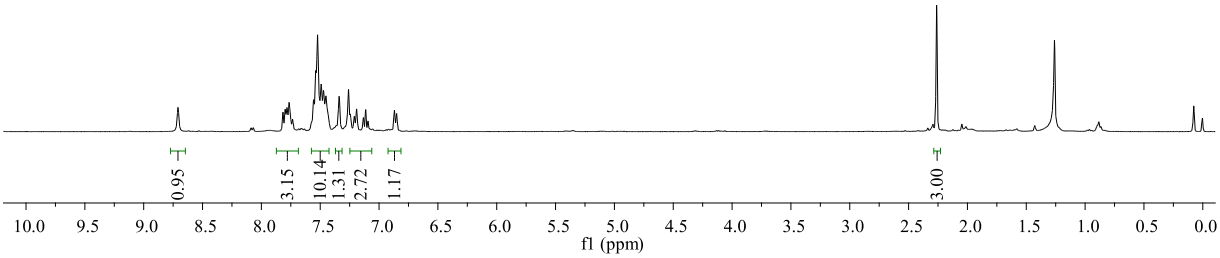
5b

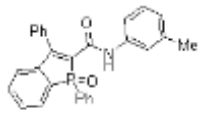
39.99




Ph
O
N
H
Me
P=O
Ph

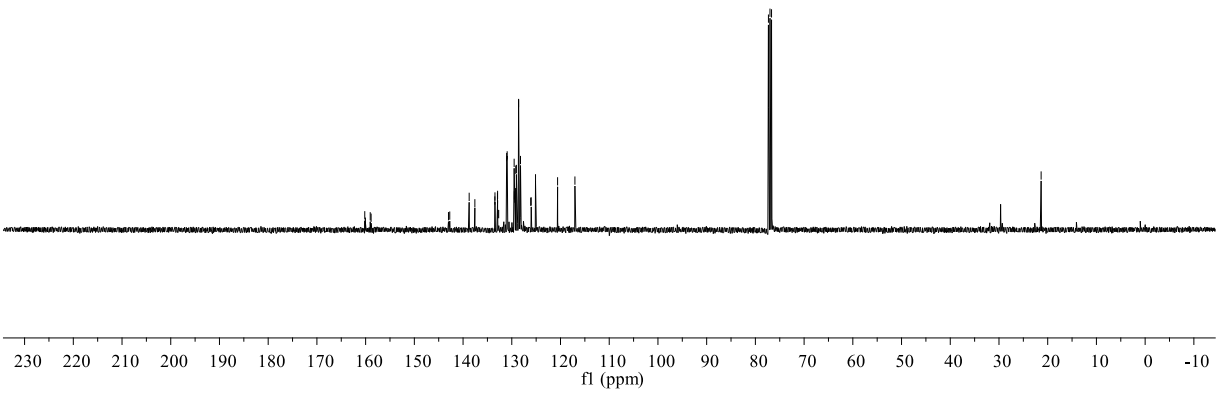
5c

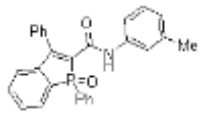

0.95
3.15
10.14
1.31
2.72
1.17
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
O
N
H
Me
P=O
Ph

5c

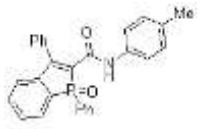

160.18
160.04
159.06
158.87
132.94
132.69
129.51
129.18
128.21
125.13
120.60
117.04
77.32
77.00
76.68
21.35


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

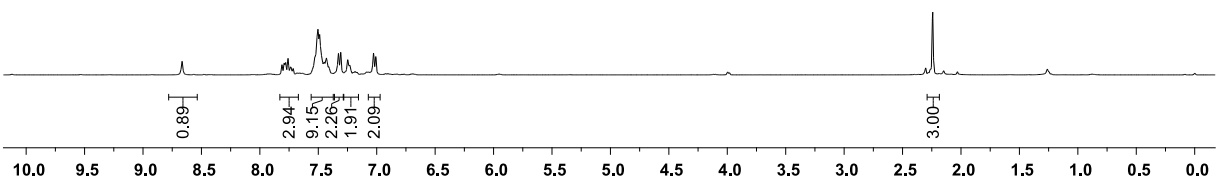

Ph
O
N
H
Me
P=O
Ph

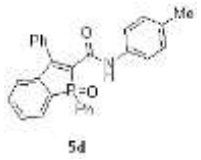
5c

39.93
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Me
Ph
O
N
H
P=O
Ph

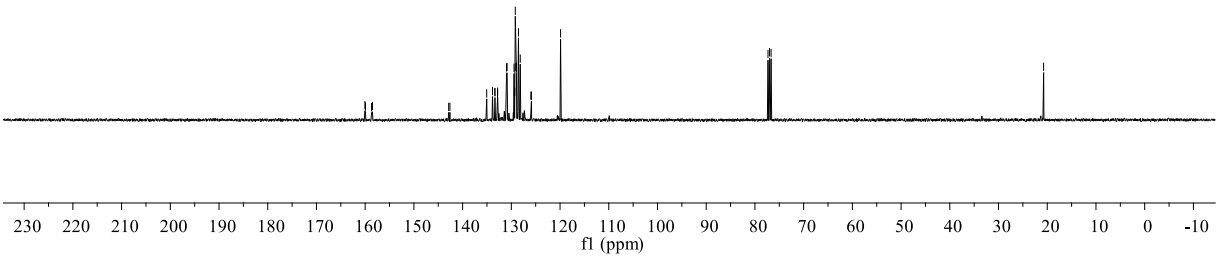
5d


0.89
2.94
9.15
2.26
1.91
2.09
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



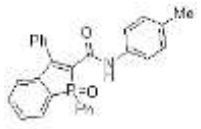
5d

160.06
159.93
158.69
158.51
142.86
142.60
132.81
129.19
125.88
119.89
77.32
77.00
76.68
20.75



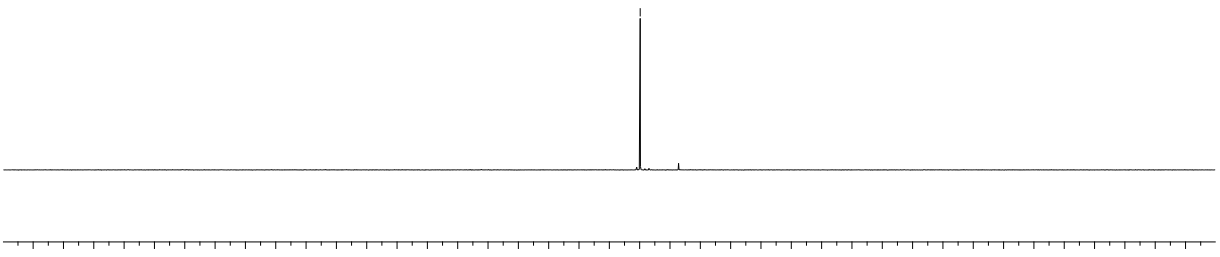
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



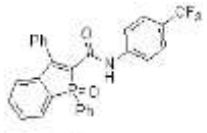
5d

39.83

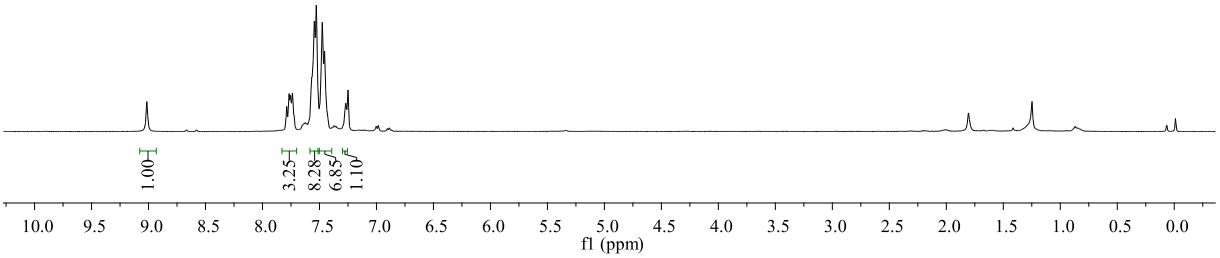


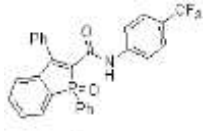
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120

f1 (ppm)


Ph
O
N
H
P=O
Ph
OPh

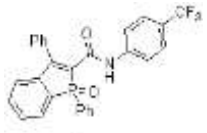
5e


1.00
3.25
8.28
6.85
1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
O
N
H
P=O
Ph
OPh

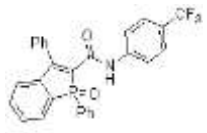
5e

160.59
160.46
159.93
159.76
142.82
142.56
140.71
129.72
128.64
119.59
77.32
77.00
76.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



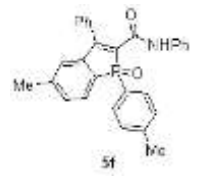
5e

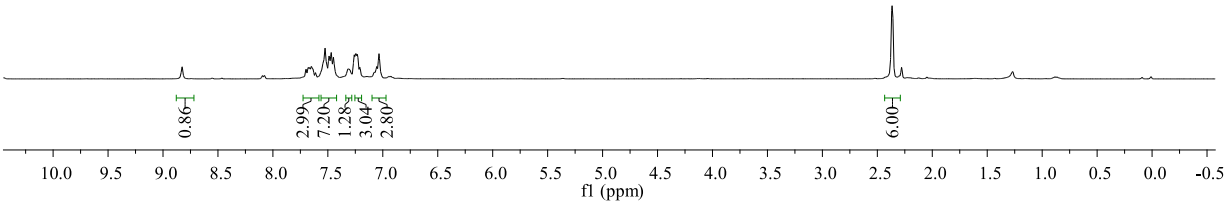
39.99
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)

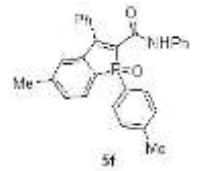


5e

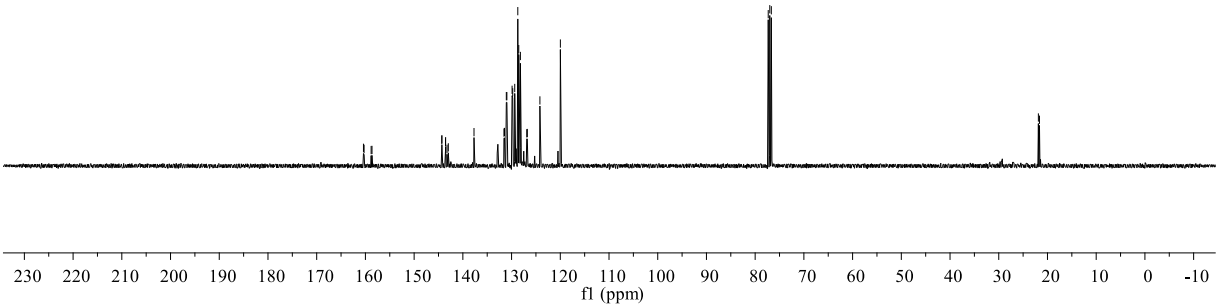
-62.15
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
f1 (ppm)

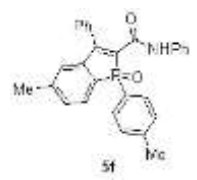






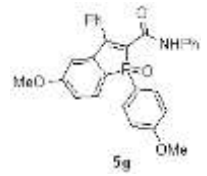
160.40
160.27
158.83
158.65
143.56
142.98
137.71
129.35
128.72
128.52
128.19
126.88
126.77
124.18
119.98
77.32
77.00
76.68
21.87
21.64



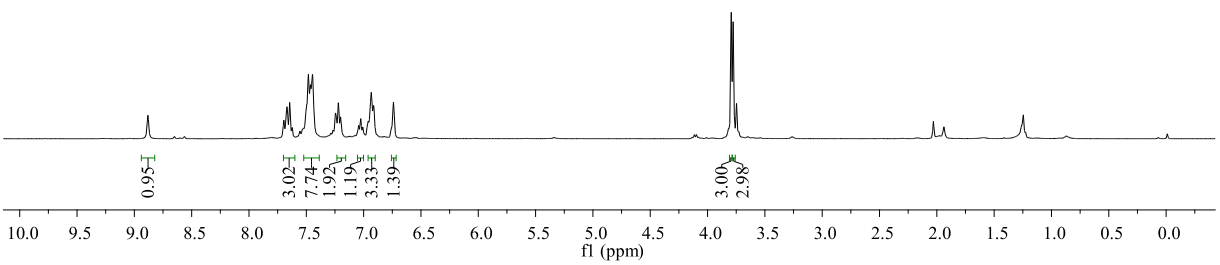

Ph
O
NHPh
Me
P=O
Me

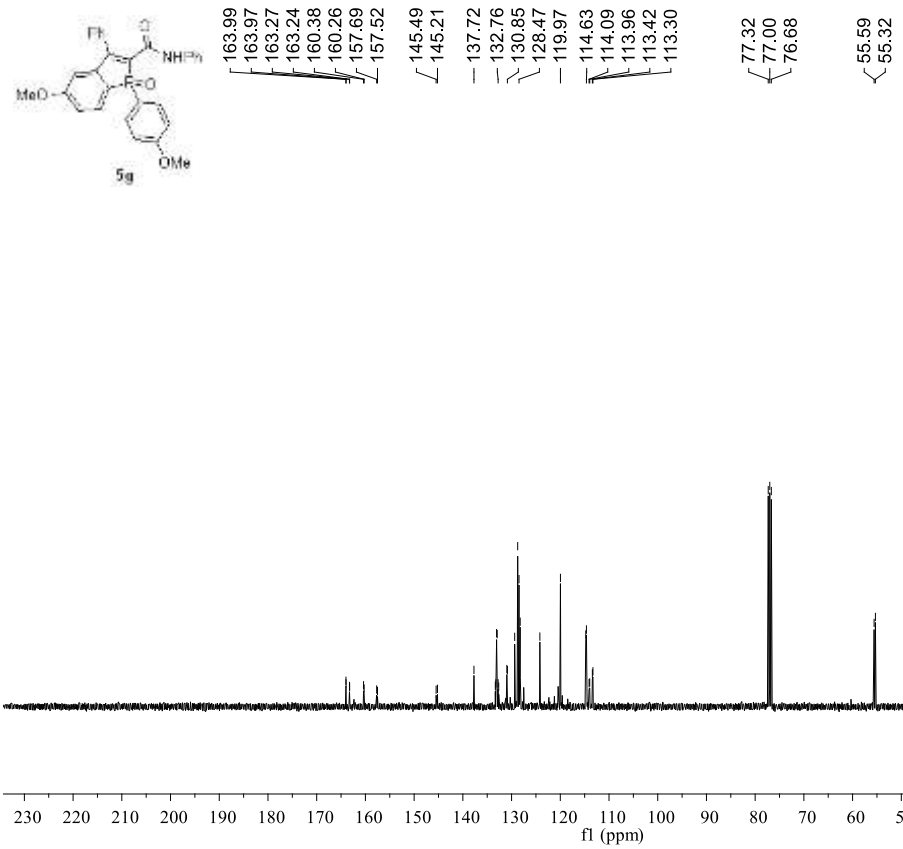
5f

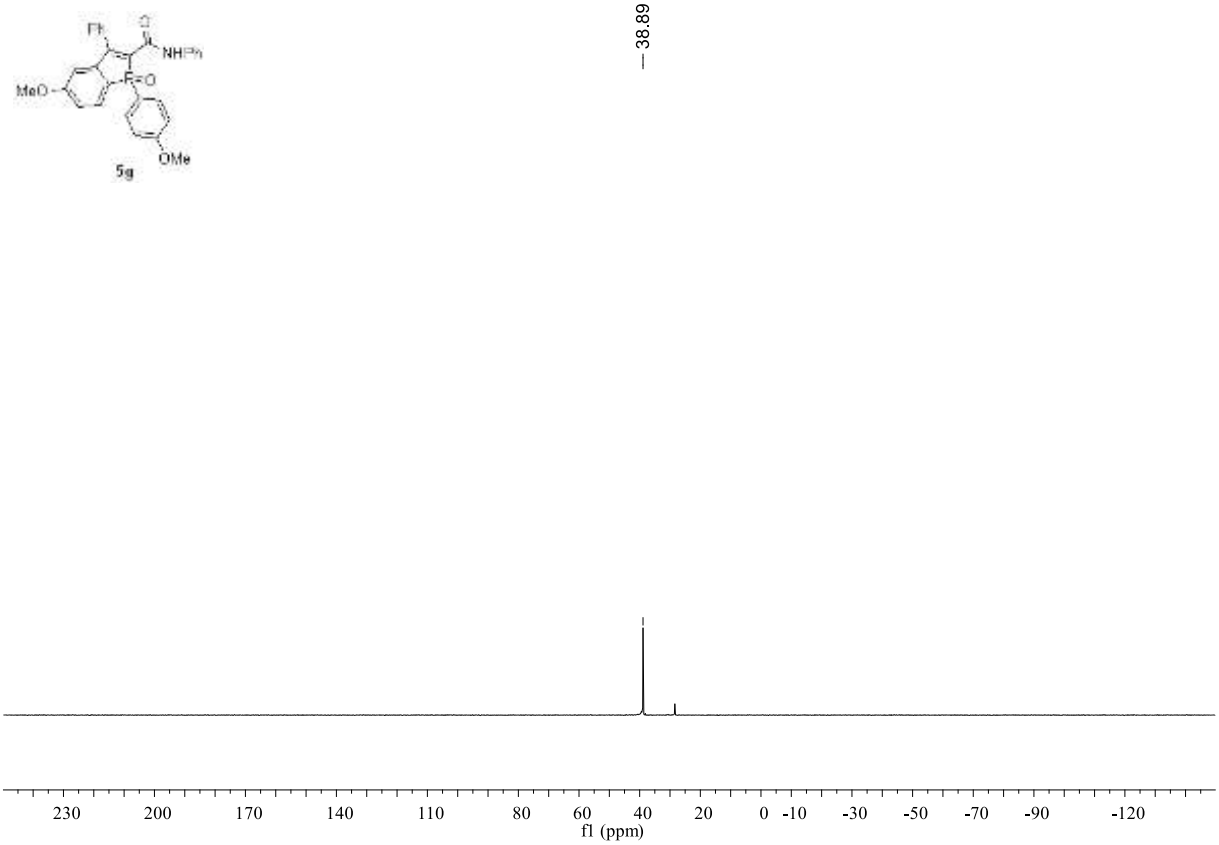
39.98
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)

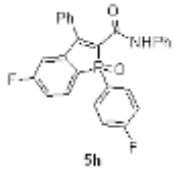

Ph
O
NHPh
MeO
P=O
OMe

5g

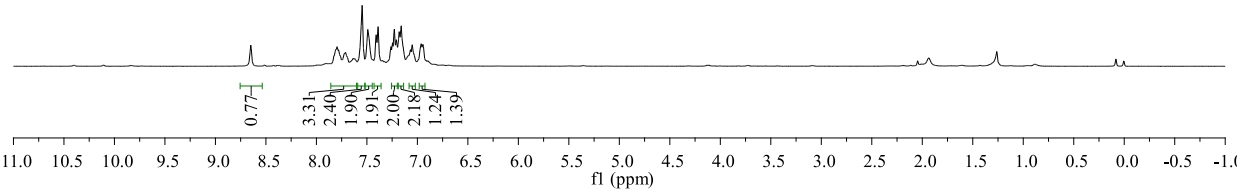

0.95
3.02
7.74
1.92
1.19
3.33
1.39
3.00
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

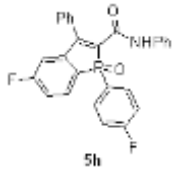

MeO
NHPh
OMe
5g
163.99
163.97
163.27
163.24
160.38
160.26
157.69
157.52
145.49
145.21
137.72
132.76
130.85
128.47
119.97
114.63
114.09
113.96
113.42
113.30
77.32
77.00
76.68
55.59
55.32
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
NHPh
OMe
5g
38.89
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120
f1 (ppm)

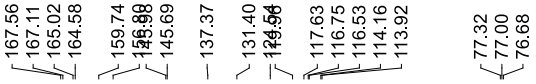

Ph
O
NHPh
F
P=O
F

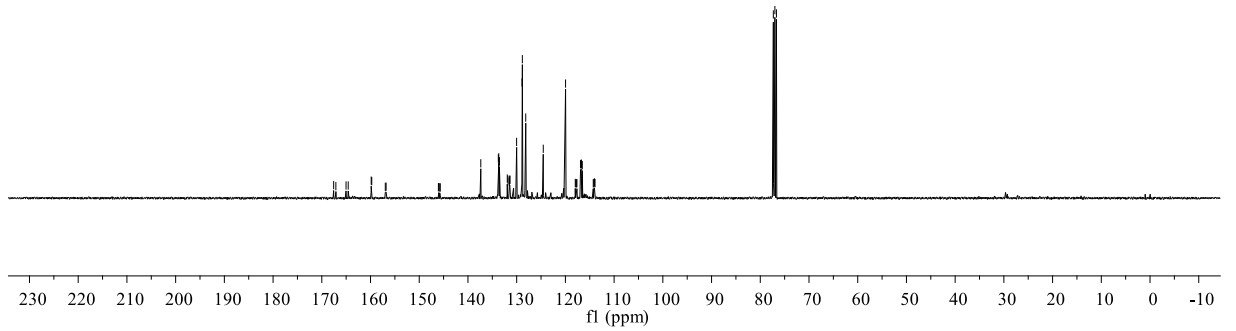
5h

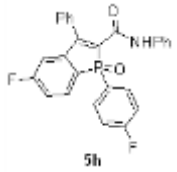

0.77
3.31
2.40
1.90
1.91
2.00
2.18
1.24
1.39
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Ph
O
NHPh
F
P=O
F

5h

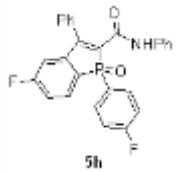

167.56
167.11
165.02
164.58
159.74
145.69
137.37
131.40
117.63
116.75
116.53
114.16
113.92
77.32
77.00
76.68


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
O
NHPh
P=O
F
F

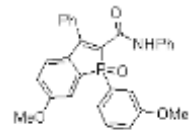
5h

37.13
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)

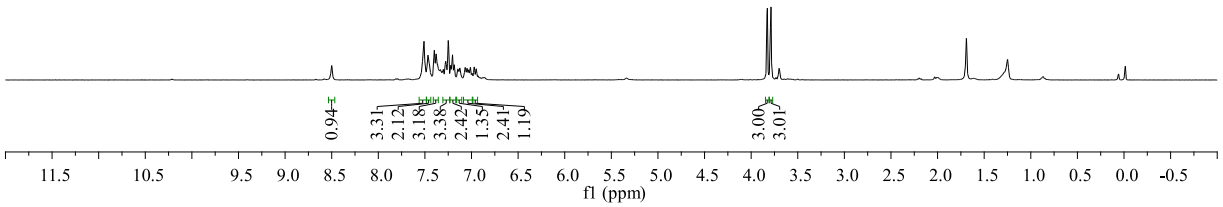

Ph
O
NHPh
P=O
F
F

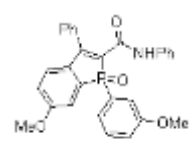
5h

-103.00
-104.41
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

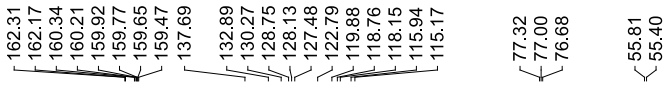

Ph
O
NHPh
P=O
MeO
OMe

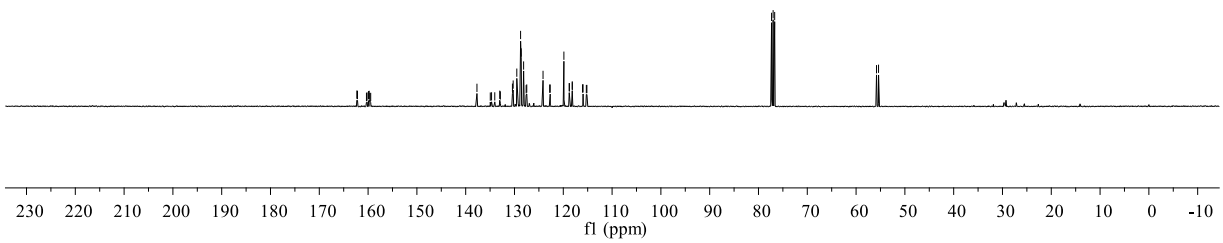
5i

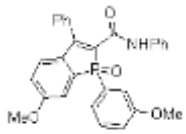

0.94
3.31
2.12
3.18
3.38
2.42
1.35
2.41
1.19
3.00
3.01
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Ph
O
NHPh
P=O
MeO
OMe

5i

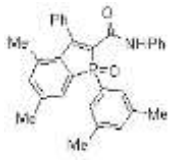

162.31
162.17
160.34
160.21
159.92
159.77
159.65
159.47
137.69
132.89
130.27
128.75
128.13
127.48
122.79
119.88
118.76
118.15
115.94
115.17
77.32
77.00
76.68
55.81
55.40


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

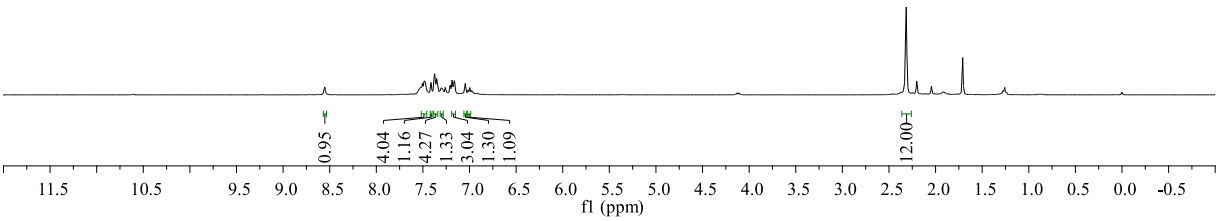

Ph
O
NHPh
P=O
MeO
OMe

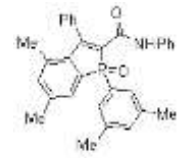
5i

39.07
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)

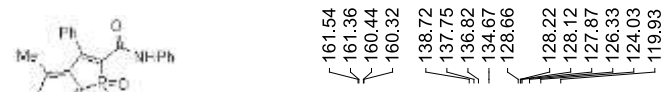

Ph
O
NHPh
Me
P=O
Me
Me
Me

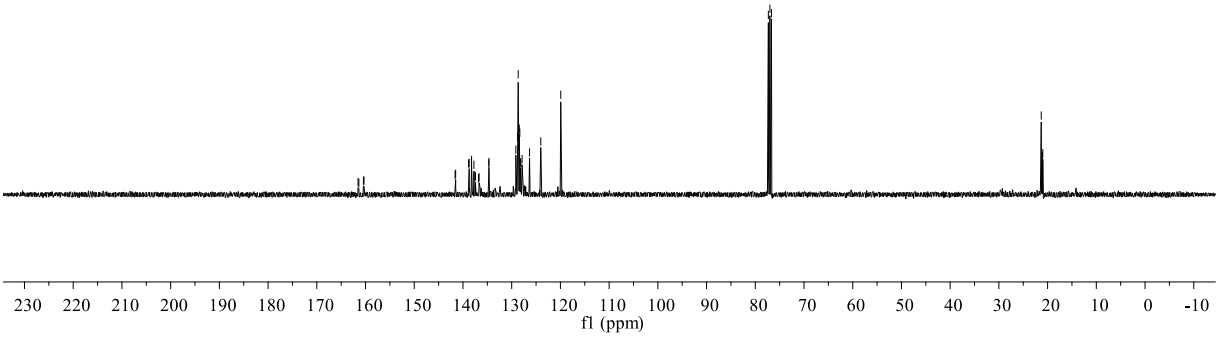
5j

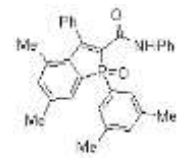

0.95
4.04
1.16
4.27
1.33
3.04
1.30
1.09
12.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Ph
O
NHPh
Me
P=O
Me
Me
Me

5j

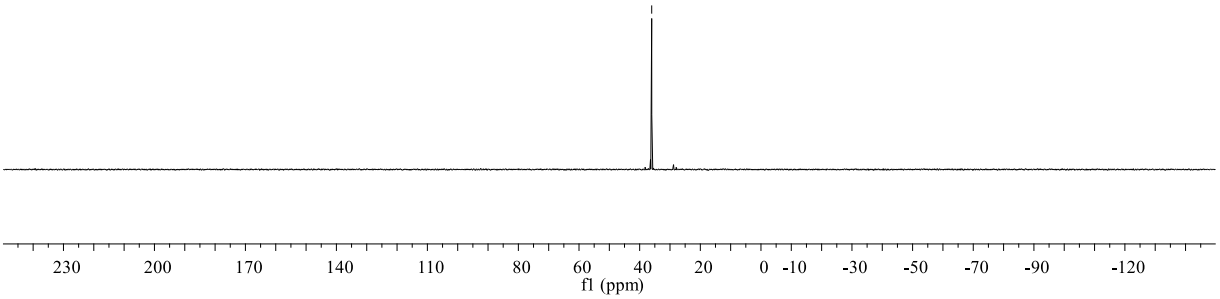

161.54
161.36
160.44
160.32
138.72
137.75
136.82
134.67
128.66
128.22
128.12
127.87
126.33
124.03
119.93
77.32
77.00
76.68
21.31
21.14
21.07
20.98

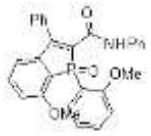

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
O
NHPh
Me
P=O
Me
Me
Me

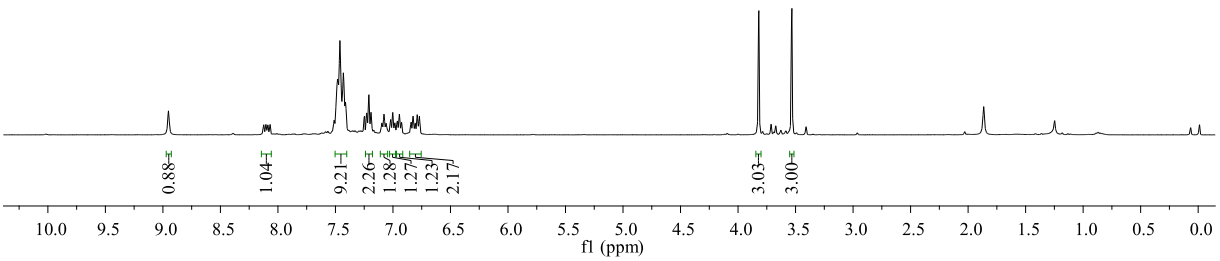
5j

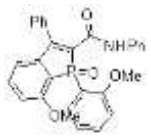

36.03


230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120
f1 (ppm)


Ph
O
NHPh
P=O
OMe
OMe

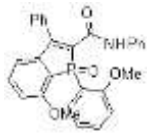
5k


0.88
1.04
9.21
2.26
1.28
1.27
1.23
2.17
3.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
O
NHPh
P=O
OMe
OMe

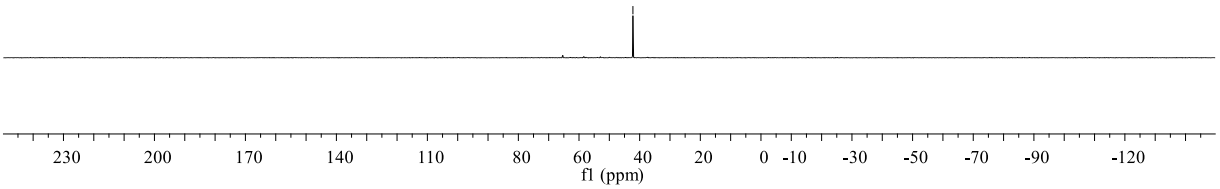
5k

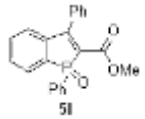
160.96
160.91
160.83
160.50
160.47
157.50
157.31
145.21
144.97
134.48
133.38
116.61
115.83
113.52
113.46
111.09
111.02
77.32
77.00
76.68
56.05
55.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
O
NHPh
P=O
OMe
OMe

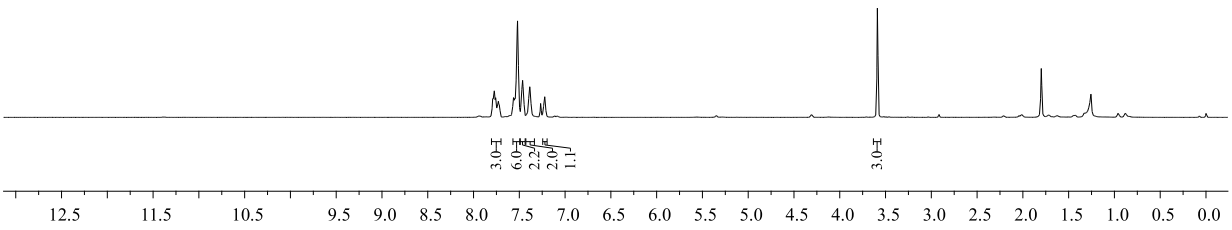
5k

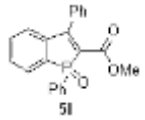
42.22


230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120
f1 (ppm)


Ph
O
OMe
P
O
Ph

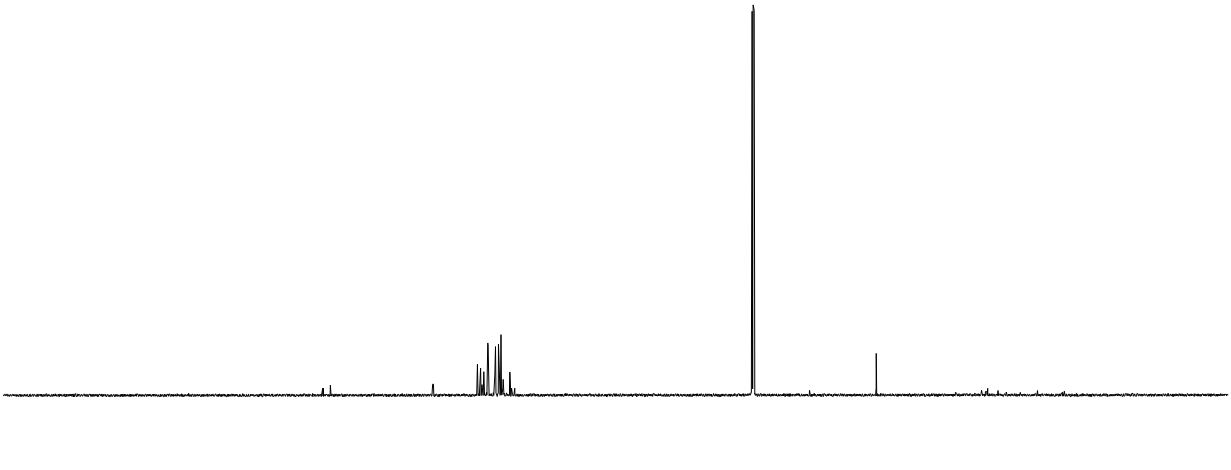
5l


3.0
6.0
2.2
2.0
1.1
3.0
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

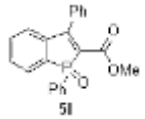


5l

164.6
164.4
163.0
162.9
142.2
142.0
133.1
131.0
129.6
129.4
128.7
127.9
126.5
125.5
77.2
77.0
76.8
52.0

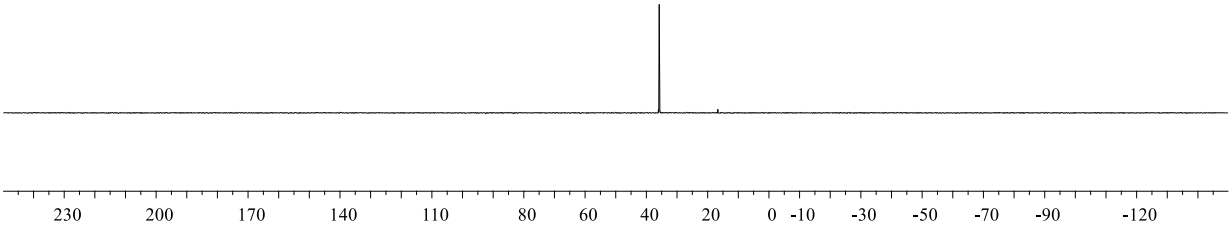


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

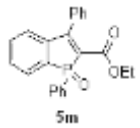


5l

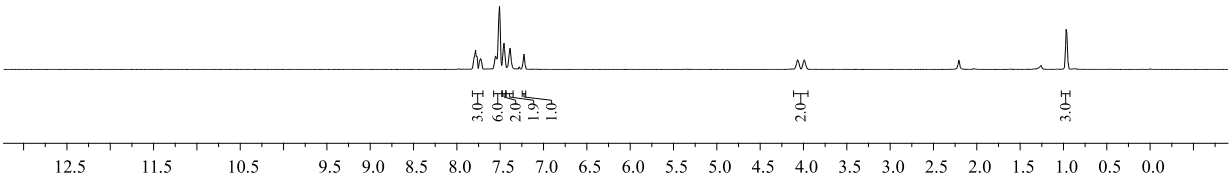
35.8

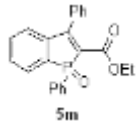


230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120


Ph
O
OEt
P
O
Ph

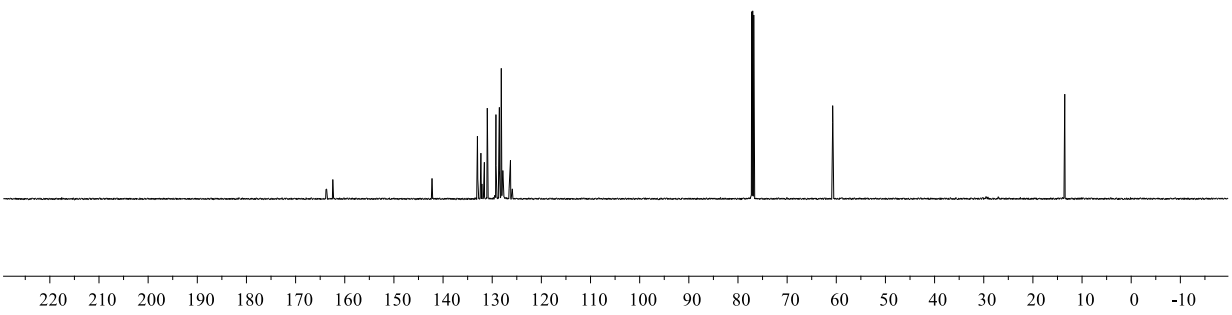
5m

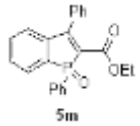

3.0
6.0
2.0
1.9
1.0
2.0
3.0
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


Ph
O
OEt
P
O
Ph

5m


163.8
163.7
162.4
162.3
142.2
142.1
133.0
131.0
129.4
129.2
128.5
127.8
126.4
125.9
77.2
77.0
76.8
60.7
13.5

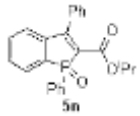

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



5m

35.8

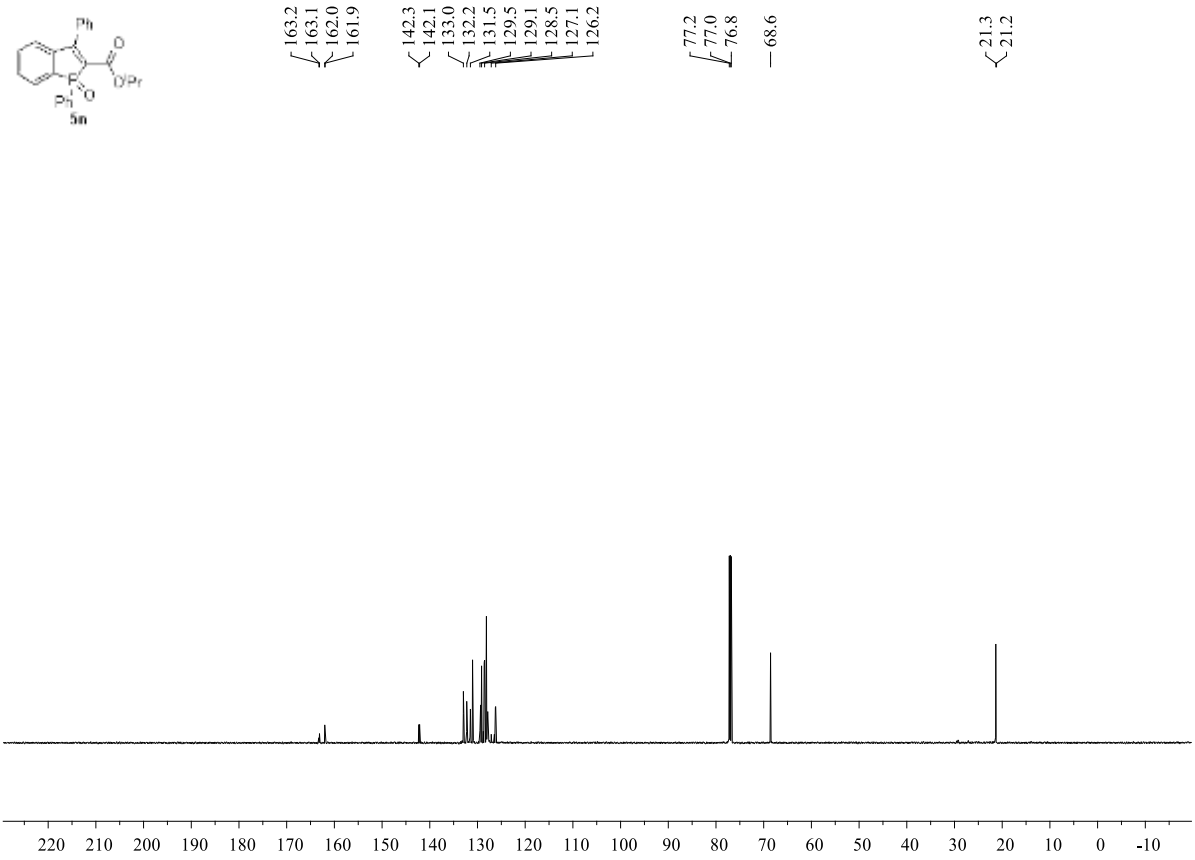
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120

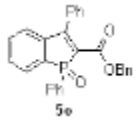


5n

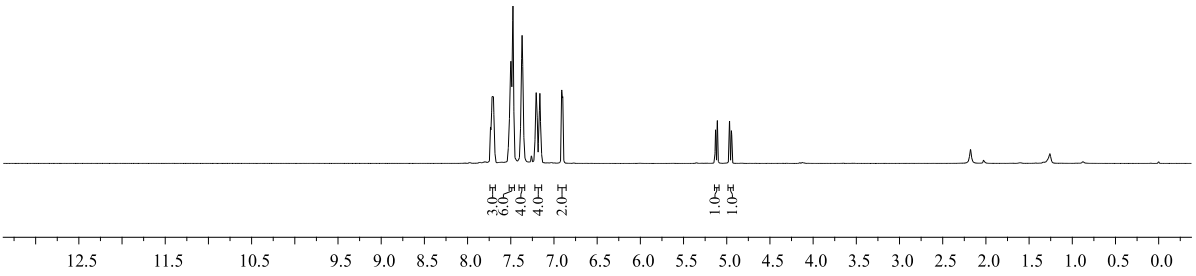
3.0 6.0 2.0 2.0 1.0 1.0 3.0 3.0

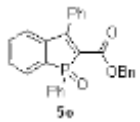
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


Ph
O
OiPr
P
O
Ph
5m
163.2
163.1
162.0
161.9
142.3
142.1
133.0
132.2
131.5
129.5
129.1
128.5
127.1
126.2
77.2
77.0
76.8
68.6
21.3
21.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
35.7
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120



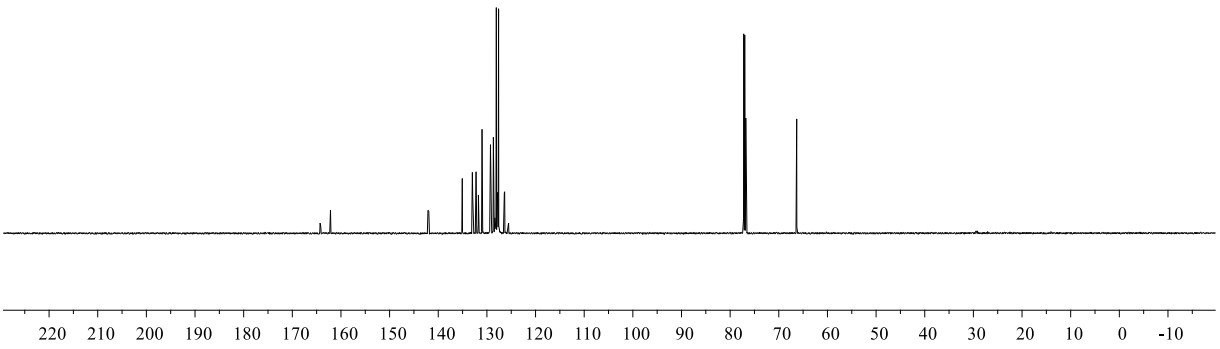
5o

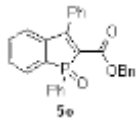




5o

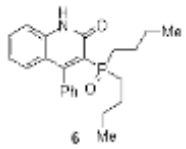
164.3
164.2
162.2
162.2
142.1
141.9
132.2
130.9
129.3
128.7
128.2
127.8
127.6
126.3
77.2
77.0
76.8
66.3



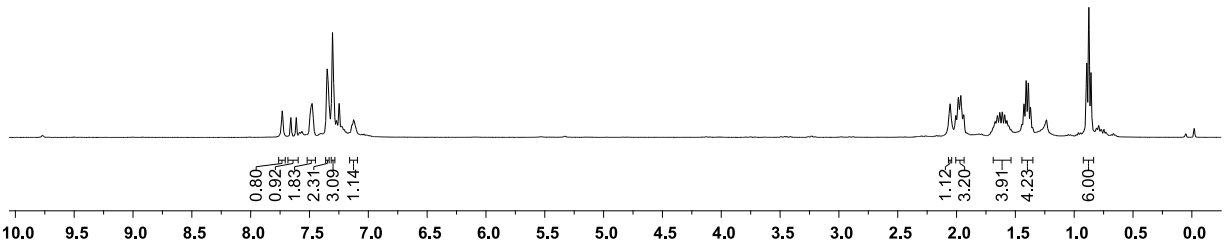

Ph
O
OBn
P
O
Ph

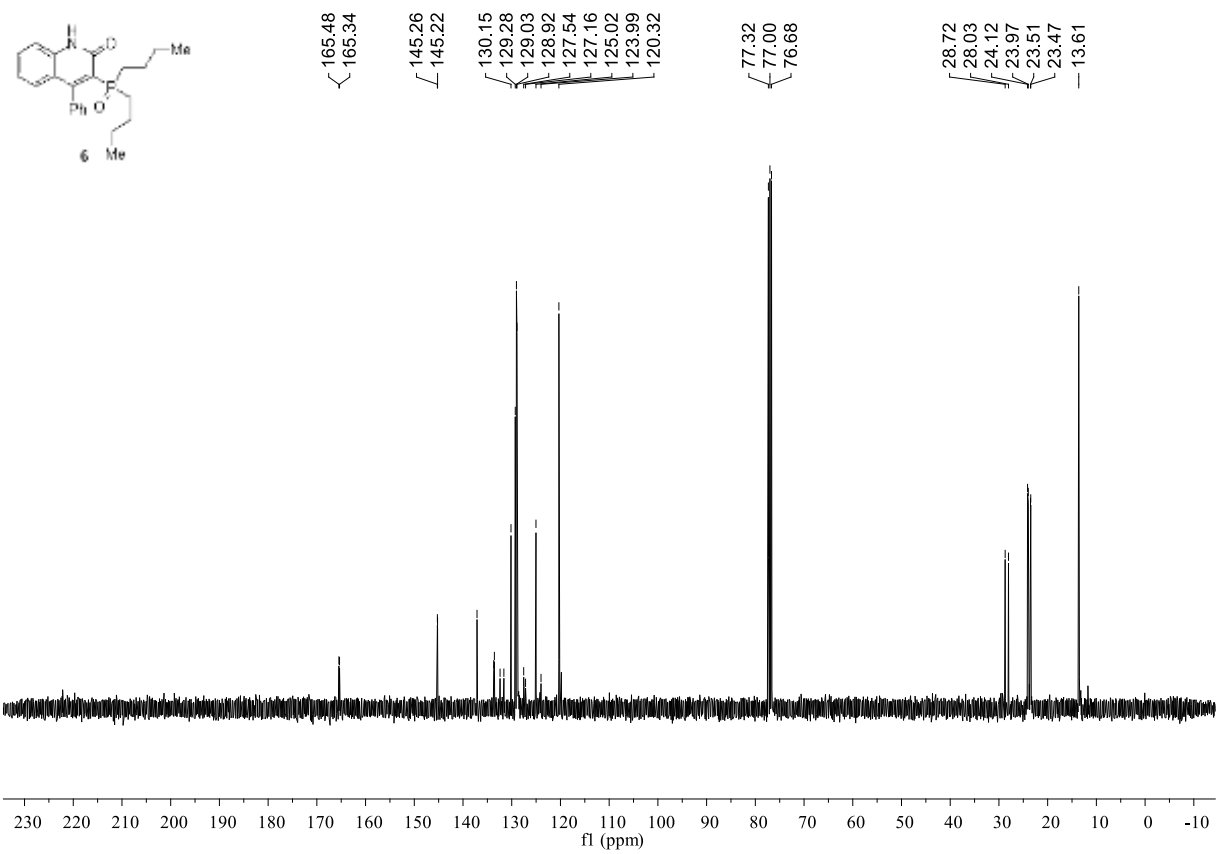
5e

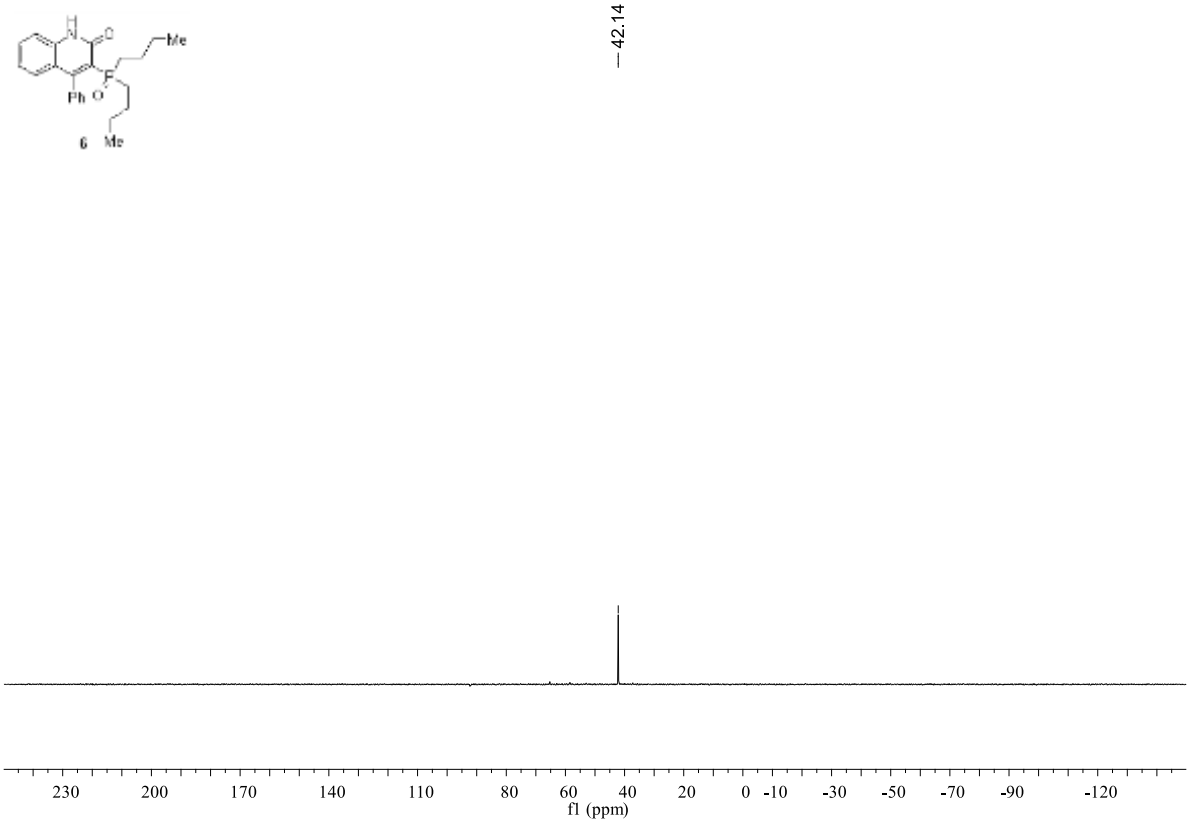
35.7
230
200
170
140
110
80
60
40
20
0
-10
-30
-50
-70
-90
-120

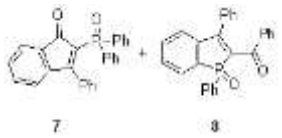

H
N
O
Me
P
Ph
O
Me

6

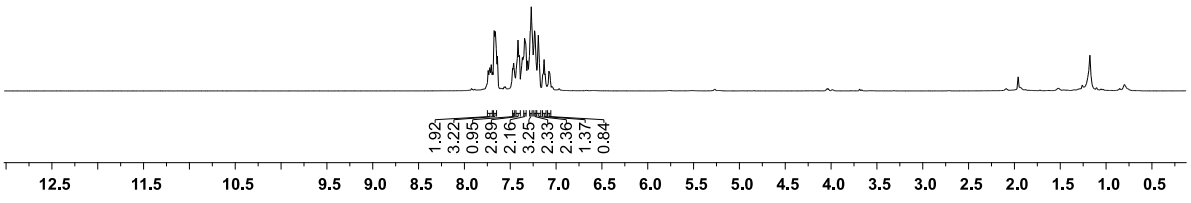

0.80
0.92
1.83
2.31
3.09
1.14
1.12
3.20
3.91
4.23
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

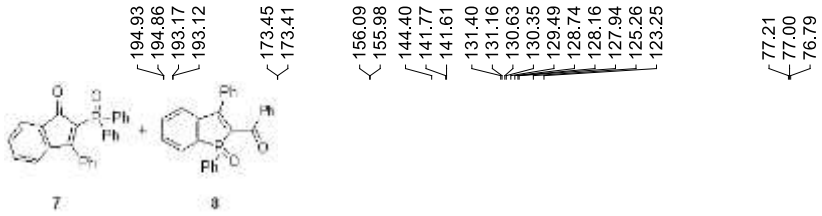

165.48
165.34
145.26
145.22
130.15
129.28
129.03
128.92
127.54
127.16
125.02
123.99
120.32
77.32
77.00
76.68
28.72
28.03
24.12
23.97
23.51
23.47
13.61
Me
Ph
O
P
6
Me
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


42.14
Me
Ph
O
P
6
Me
230 200 170 140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -120
f1 (ppm)

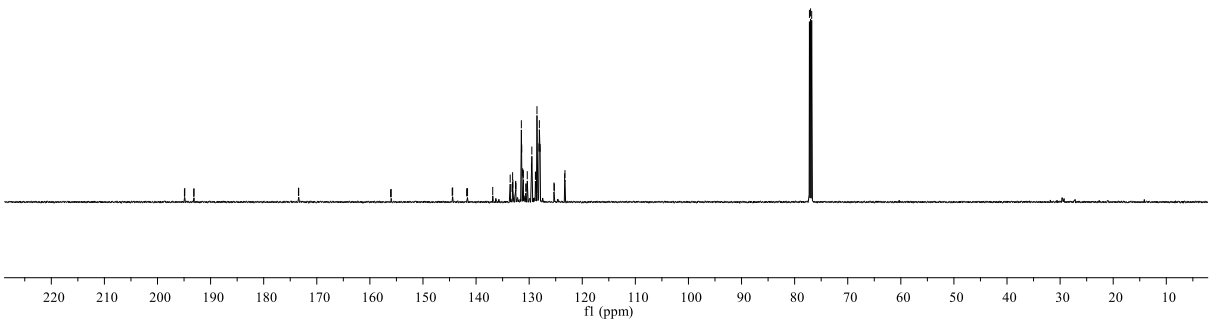


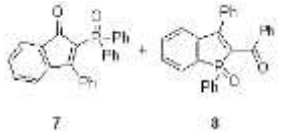
7 8


1.92
3.22
0.95
2.89
2.16
3.25
2.33
2.36
1.37
0.84
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


194.93
194.86
193.17
193.12
173.45
173.41
156.09
155.98
144.40
141.77
141.61
131.40
131.16
130.63
130.35
129.49
128.74
128.16
127.94
125.26
123.25
77.21
77.00
76.79

7 8

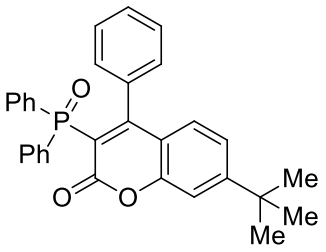

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

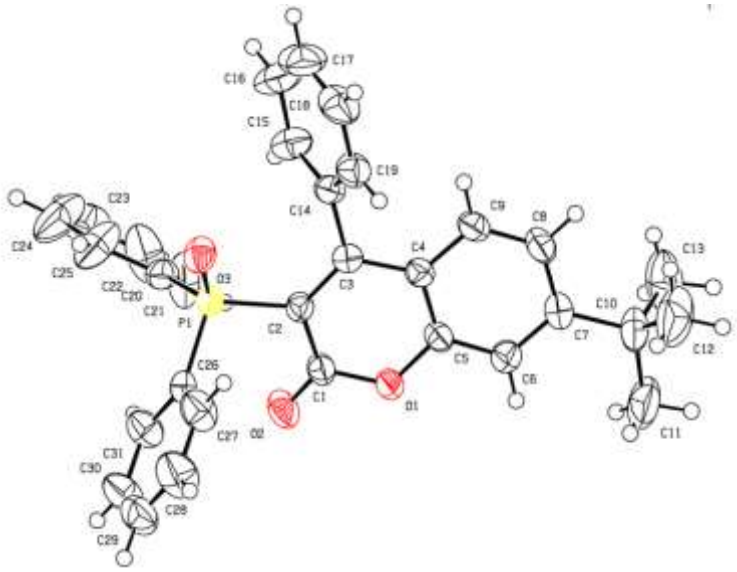


7 8

8. X-ray Structure of 3i

Slow diffusion of petrol ether into a solution of **3i** in EtOAc gave crystals that were suitable for X-ray diffraction:



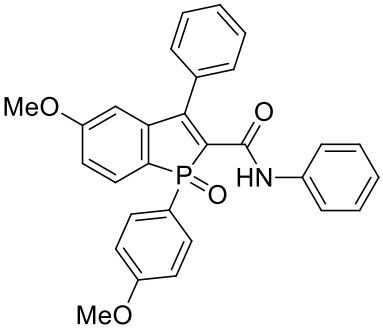


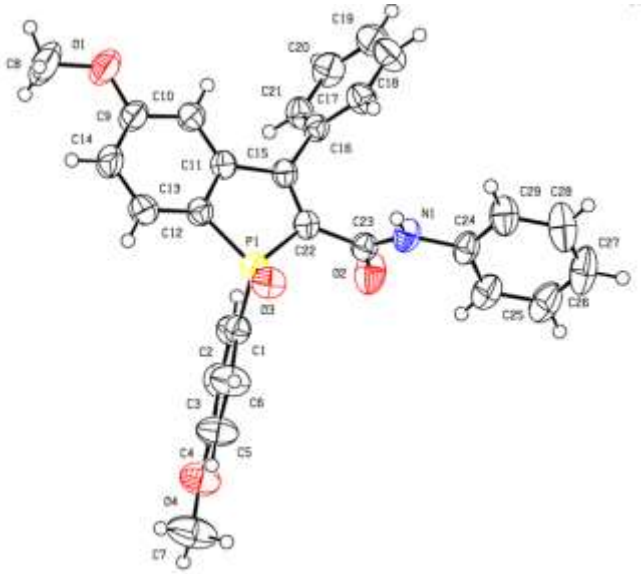
3i: CCDC 1921050

	Product		
Empirical formula	$C_{31}H_{27}O_3P$	Crystal size(mm)	0.24 x 0.24 x 0.20
		θ range for data collection	2.40 to 27.41 °
Formula weight	478.50	*h*, *k*, *l* ranges	-22<=h<=22, -14<=k<=17, -14<=l<=14
Temperature(K)	273(2)	Reflections collected / unique	5795 / 3909 [R(int) = 0.0565]
Wavelength(Å)	0.71073	Completeness	99.7%
Crystal system space group	monoclinic p 1 21/c 1	Absorption correction	None
Unit cell dimensions	a = 17.0617(8) Å b = 13.6110(6) Å c = 11.3034(6) Å α = 90° β = 106.030(2) ° γ = 90°	Data / restraints / parameters	5795/ 0 / 319
Volume(Å^3)	2522.9(2)	Goodness-of-fit on F^2	1.052
Z Calculated density(g·cm^{-3})	4 1.260	Final *R* indices [I>2σ (I)]	R_1 = 0.0565, wR_2 = 0.1596
Absorption coefficient(mm^{-1})	0.140	*R* indices (all data)	R_1 = 0.0933, wR_2 = 0.1298
F(000)	1008.9	Largest diff. peak and hole(e·Å^{-3})	0.601 and -0.405

9. X-ray Structure of 5g

Slow diffusion of petrol ether into a solution of **5g** in EtOAc gave crystals that were suitable for X-ray diffraction:



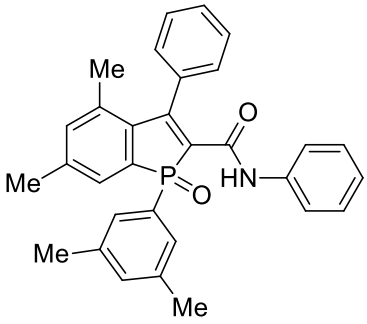


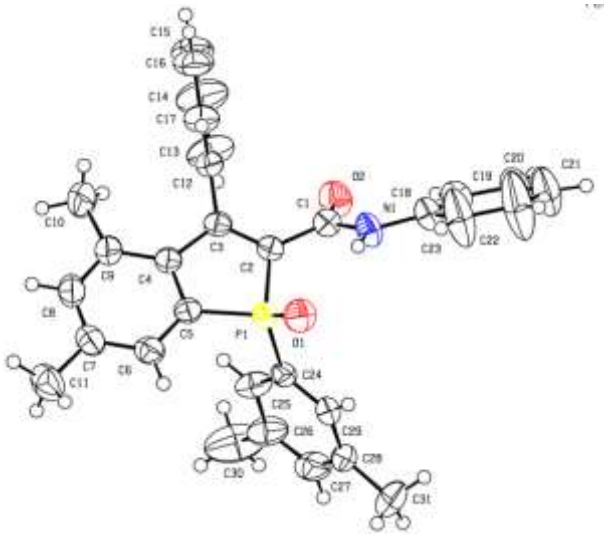
5g: CCDC 1921043

	Product		
Empirical formula	$C_{29}H_{24}NO_4P$	Crystal size(mm)	0.28 x 0.26 x 0.24
Formula weight	481.49	θ range for data collection	2.40 to 24.67 °
Temperature(K)	273	*h*, *k*, *l* ranges	-23<=h<=29, -13<=k<=14, -26<=l<=26
Wavelength(Å)	0.71073	Reflections collected / unique	5688 / 3639 [R(int) = 0.0552]
Crystal system	monoclinic	Completeness	99.7%
space group	C 1 2/c 1	Absorption correction	None
Unit cell dimensions	a = 22.6531(10) Å b = 11.2558(4) Å c = 20.1149(9) Å α = 90° β = 105.379(1) ° γ = 90°	Data / restraints / parameters	5688/ 0 / 318
Volume(Å^3)	4945.2(4)	Goodness-of-fit on F^2	1.076
Z	8		
Calculated density(g·cm^{-3})	1.293	Final *R* indices [I>2σ (I)]	R_1 = 0.1032, wR_2 = 0.1239
Absorption coefficient(mm^{-1})	0.147	*R* indices (all data)	R_1 = 0.0552, wR_2 = 0.1457
F(000)	2017.8	Largest diff. peak and hole(e·Å^{-3})	0.379 and -0.595

10. X-ray Structure of 5j

Slow diffusion of petrol ether into a solution of **5j** in EtOAc gave crystals that were suitable for X-ray diffraction:





5j: CCDC 1921051

	Product		
Empirical formula	$C_{31}H_{28}NO_2P$	Crystal size(mm)	0.28 x 0.24 x 0.24
		θ range for data collection	2.37 to 24.71 °
Formula weight	477.51	h, k, l ranges	-13<=h<=13, -13<=k<=13, -16<=l<=16
Temperature(K)	273(2)	Reflections collected / unique	6000/ 2961 [R(int) = 0.0468]
Wavelength(Å)	0.71073	Completeness	99.1%
Crystal system space group	triclinic P -1	Absorption correction	None
Unit cell dimensions	a = 10.4035(16) Å b = 10.5900(16) Å c = 13.0053(19) Å α = 89.785(5)° β = 77.673(5) ° γ = 69.240(4)°	Data / restraints / parameters	6000 / 0 / 315
Volume(Å^3)	1304.9(3)	Goodness-of-fit on F^2	1.049
Z Calculated density(g·cm^{-3})	2 1.215	Final R indices [I>2σ (I)]	R_1 = 0.0769, wR_2 = 0.1530
Absorption coefficient(mm^{-1})	0.133	R indices (all data)	R_1 = 0.1858, wR_2 = 0.1994
F(000)	348.0	Largest diff. peak and hole(e·Å^{-3})	0.736 and -0.658