DDQ-mediated direct C(sp^3)–H phosphorylation of xanthene derivatives

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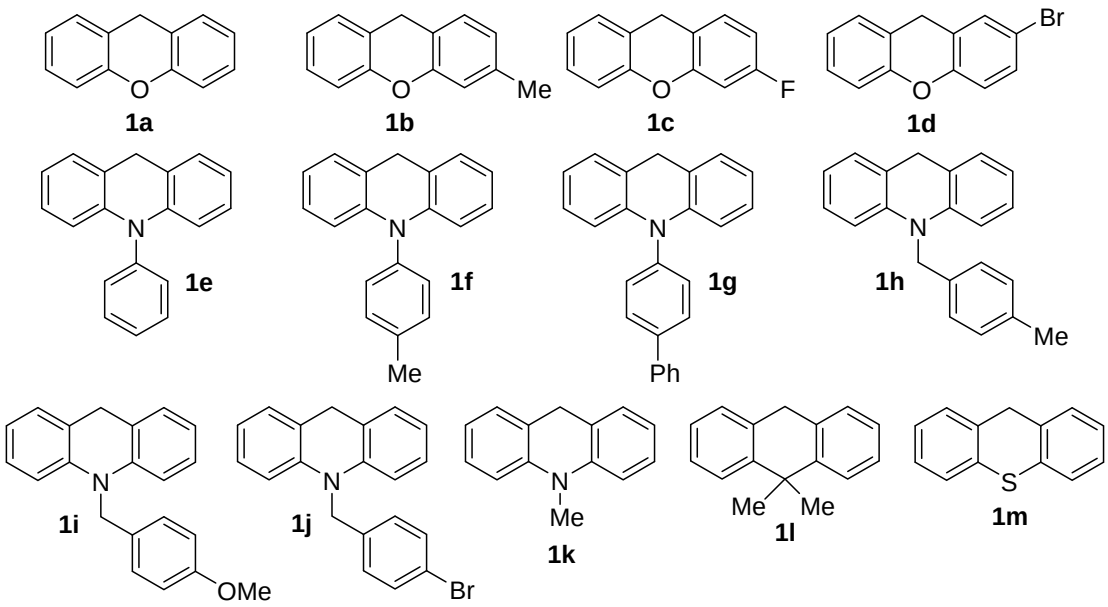
SUPPORTING INFORMATION

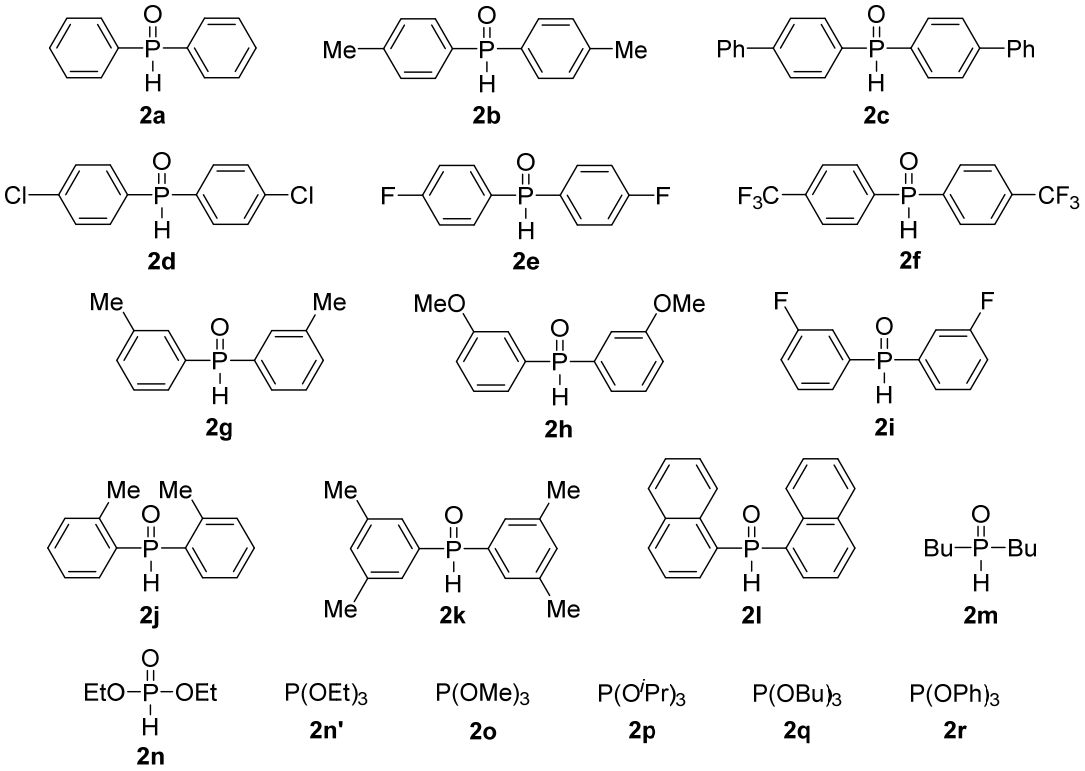
Content:

1. General information

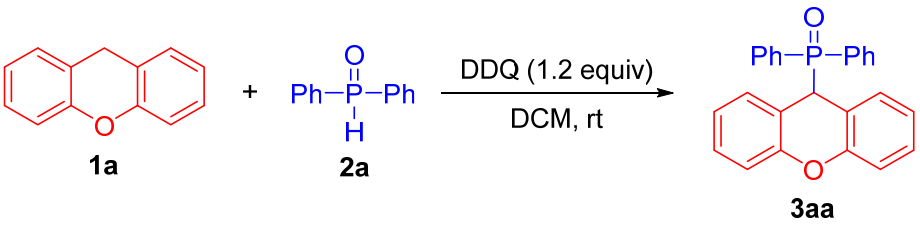
Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Petroleum ether refers to the petroleum fraction b.p. 60~90 °C. Xanthenes were prepared according to the literature.[1] Dihydroacridines, dihydroanthracenes and thioxanthenes were prepared according to the literature.[2] All reactions were carried out in an oven-dried thick-walled glassware. Flash chromatography was performed using the indicated solvent system on silica gel standard grade (200~300 mesh). ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 (100 MHz) spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker 400 (162 MHz) spectrometer. ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker 400 (376 MHz) spectrometer. Chemical shifts were reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF. Melting points (mp) were uncorrected and measured on micro melting point apparatus. Abbreviations for signal coupling are as follows: s = singlet, d = doublet; t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad.

2. Overview of substrates numbering





3. General procedure for the phosphorylation reaction

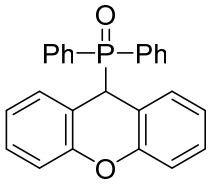


1a **2a** **3aa**

To a solution of 9*H*-xanthene **1a** (55 mg, 0.3 mmol) in DCM (2 mL) was added DDQ (82 mg, 0.36 mmol). After stirring for 20 min at room temperature, diphenylphosphine oxide **2a** (121 mg, 0.6 mmol) was added. The resulting mixture was stirred at room temperature for 8 h. The reaction was then quenched with saturated aqueous Na_2SO_3 solution (15 mL) and extracted with ethyl acetate (3×15 mL). The extracts were combined and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (3:2) to afford the desired **3aa** (110 mg, 96%) as a white solid.

4. Characterizations of compounds 3

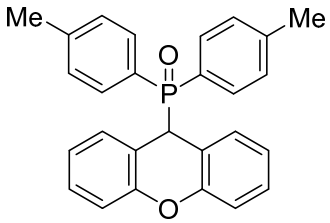
Diphenyl(9*H*-xanthen-9-yl)phosphine oxide (3aa):



3aa

White solid (110 mg, 96%): mp 253–254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.46 (m, 6H), 7.38–7.33 (m, 4H), 7.20–7.11 (m, 2H), 6.98–6.84 (m, 6H), 4.91 (d, J = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J = 4.7 Hz), 132.2 (d, J = 8.4 Hz), 131.9 (d, J = 2.7 Hz), 130.1 (d, J = 3.5 Hz), 129.6 (d, J = 95.9 Hz), 128.6 (d, J = 3.1 Hz), 128.0 (d, J = 11.4 Hz), 122.8 (d, J = 2.7 Hz), 117.0 (d, J = 4.7 Hz), 116.3 (d, J = 2.7 Hz), 45.5 (d, J = 64.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{20}O_2P$ 383.1195, found 383.1189.

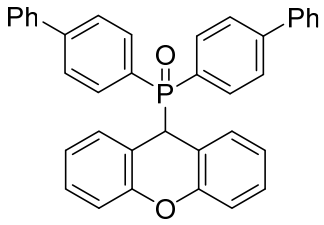
Di-*p*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3ab):



3ab

White solid (107 mg, 87%): mp 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 10.6, 8.1 Hz, 4H), 7.19–7.14 (m, 6H), 6.98–6.93 (m, 2H), 6.90 (d, J = 7.6 Hz, 4H), 4.87 (d, J = 17.8 Hz, 1H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J = 4.4 Hz), 142.4 (d, J = 2.7 Hz), 132.2 (d, J = 8.8 Hz), 130.2 (d, J = 3.6 Hz), 128.8 (d, J = 11.8 Hz), 128.5 (d, J = 3.1 Hz), 126.3 (d, J = 98.0 Hz), 122.8 (d, J = 2.8 Hz), 117.3 (d, J = 4.7 Hz), 116.3 (d, J = 2.8 Hz), 45.4 (d, J = 64.0 Hz), 21.6 (d, J = 1.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{24}O_2P$ 411.1508, found 411.1516.

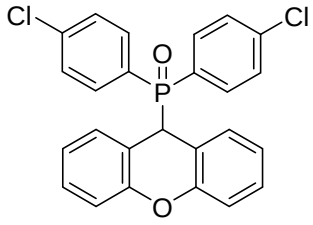
Di([1,1'-biphenyl]-4-yl)(9*H*-xanthen-9-yl)phosphine oxide (3ac):



3ac

White solid (67 mg, 42%): mp 253–255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 12H), 7.50–7.45 (m, 4H), 7.42–7.38 (m, 2H), 7.22–7.17 (m, 2H), 7.05–7.02 (m, 2H), 6.95–6.89 (m, 4H), 4.99 (d, J = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 4.4 Hz), 144.7 (d, J = 2.8 Hz), 139.8, 132.7 (d, J = 8.8 Hz), 130.3 (d, J = 3.5 Hz), 128.9, 128.8 (d, J = 3.0 Hz), 128.2, 128.0 (d, J = 96.2 Hz), 127.2, 126.8 (d, J = 11.7 Hz), 123.0 (d, J = 2.6 Hz), 117.0 (d, J = 4.7 Hz), 116.5 (d, J = 2.7 Hz), 45.6 (d, J = 64.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{37}H_{28}O_2P$ 535.1821, found 535.1825.

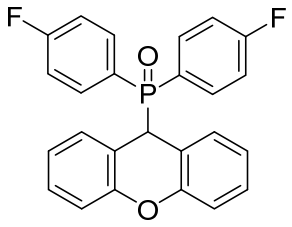
Bis(4-chlorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ad):



3ad

White solid (98 mg, 72%): mp 243–245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 4H), 7.37–7.32 (m, 4H), 7.23–7.16 (m, 2H), 6.98–6.89 (m, 6H), 4.88 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J = 4.4 Hz), 138.9 (d, J = 3.4 Hz), 133.4 (d, J = 9.2 Hz), 130.1 (d, J = 3.6 Hz), 129.0 (d, J = 3.2 Hz), 128.6 (d, J = 12.0 Hz), 127.7 (d, J = 96.7 Hz), 123.1 (d, J = 2.7 Hz), 116.6 (d, J = 2.9 Hz), 116.5 (d, J = 4.8 Hz), 45.5 (d, J = 65.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{17}Cl_2O_2PNa$ 473.0235, found 473.0236.

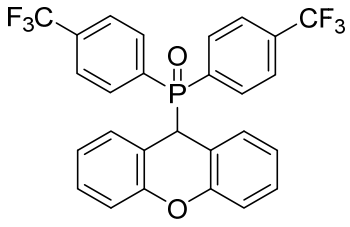
Bis(4-fluorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ae):



3ae

White solid (83 mg, 66%): mp 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.44 (m, 4H), 7.21–7.15 (m, 2H), 7.09–7.02 (m, 4H), 6.97–6.88 (m, 6H), 4.86 (d, J = 18.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (dd, J = 254, 3.3 Hz), 152.5 (d, J = 4.4 Hz), 134.6 (dd, J = 9.3, 9.3 Hz), 130.1 (d, J = 3.6 Hz), 128.9 (d, J = 3.2 Hz), 125.2 (dd, J = 98.6, 3.4 Hz), 123.0 (d, J = 2.8 Hz), 116.7 (d, J = 4.8 Hz), 116.4 (d, J = 2.9 Hz), 115.6 (dd, J = 21.3, 12.5 Hz), 45.7 (d, J = 65.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{18}F_2O_2P$ 419.1007, found 419.1009.

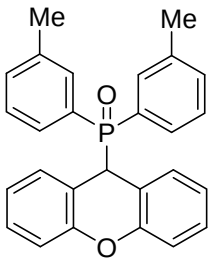
Bis(4-(trifluoromethyl)phenyl)(9*H*-xanthen-9-yl)phosphine oxide (3af):



3af

White solid (98 mg, 63%): mp 242–244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.62 (m, 8H), 7.25–7.19 (m, 2H), 6.97–6.91 (m, 6H), 4.97 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J = 4.5 Hz), 134.3 (d, J = 3.0 Hz), 133.5 (d, J = 93.8 Hz), 132.6 (d, J = 8.8 Hz), 130.1 (d, J = 3.7 Hz), 129.3 (d, J = 3.3 Hz), 125.1 (dq, J = 11.3, 3.7 Hz), 123.4 (d, J = 272 Hz), 123.3 (d, J = 2.8 Hz), 116.7 (d, J = 2.9 Hz), 116.0 (d, J = 4.9 Hz), 45.6 (d, J = 64.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{18}F_6O_2P$ 519.0943, found 519.0950.

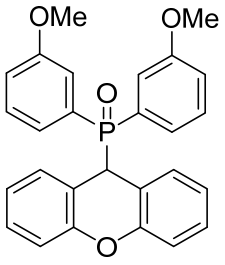
Di-*m*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3ag):



3ag

White solid (91 mg, 74%): mp 202–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 5H), 7.20–7.14 (m, 3H), 7.13–7.06 (m, 2H), 6.91–6.78 (m, 6H), 4.81 (d, J = 17.5 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 4.3 Hz), 137.9 (d, J = 11.3 Hz), 132.9 (d, J = 8.2 Hz), 132.7 (d, J = 2.9 Hz), 130.2 (d, J = 3.5 Hz), 129.3 (d, J = 94.6 Hz), 129.2 (d, J = 8.8 Hz), 128.5 (d, J = 3.1 Hz), 127.8 (d, J = 12.2 Hz), 122.8 (d, J = 2.7 Hz), 117.2 (d, J = 4.7 Hz), 116.3 (d, J = 2.8 Hz), 45.5 (d, J = 63.5 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{24}O_2P$ 411.1508, found 411.1509.

Bis(3-methoxyphenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ah):

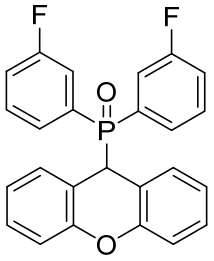


3ah

White solid (104 mg, 78%): mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.20–7.07 (m, 6H), 7.04 (dd, J = 8.2, 2.2 Hz, 2H), 6.97–6.92 (m, 4H), 6.91–6.87 (m, 2H), 4.90 (d, J = 17.0 Hz, 1H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 14.3 Hz), 152.7 (d, J = 4.2 Hz), 130.8 (d, J = 95.1 Hz), 130.2 (d, J = 3.5 Hz), 129.3 (d, J = 13.7 Hz), 128.6 (d, J = 3.1 Hz), 124.3 (d, J = 8.6 Hz), 122.9 (d, J = 2.6 Hz), 118.8 (d, J = 2.6 Hz), 117.0 (d, J = 4.8 Hz), 116.6 (d, J = 9.3 Hz), 116.4 (d, J = 2.7 Hz), 55.4 , 45.4 (d, J = 62.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ

30.3; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{27}H_{24}O_4P$ 443.1407, found 443.1411.

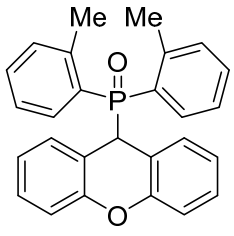
Bis(3-fluorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ai):



3ai

White solid (110 mg, 88%): mp 204–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.21 (m, 4H), 7.18–7.10 (m, 6H), 6.91–6.83 (m, 6H), 4.84 (d, J = 17.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (dd, J = 250, 16.1 Hz), 152.6 (d, J = 4.5 Hz), 130.2 (d, J = 7.3 Hz), 130.1 (d, J = 7.7 Hz), 129.6 (dd, J = 94.8, 3.5 Hz), 127.8 (dd, J = 8.0, 3.3 Hz), 123.1 (d, J = 2.8 Hz), 119.5 (dd, J = 21.1, 2.6 Hz), 119.2 (d, J = 9.3 Hz), 119.0 (d, J = 9.2 Hz), 116.6 (d, J = 2.9 Hz), 116.3 (d, J = 4.8 Hz), 45.5 (d, J = 65.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{25}H_{18}F_2O_2P$ 419.1007, found 419.1009.

Di-*o*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3aj):

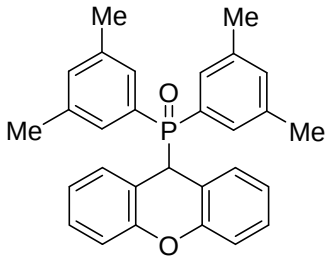


3aj

White solid (81 mg, 66%): mp 218–219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 12.6, 7.8 Hz, 2H), 7.39–7.31 (m, 2H), 7.21–7.10 (m, 6H), 7.05–6.98 (m, 4H), 6.90–6.83 (m, 2H), 5.17 (d, J = 16.3 Hz, 1H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (d, J = 4.1 Hz), 143.9 (d, J = 7.4 Hz), 132.2 (d, J = 10.5 Hz), 132.0 (d, J = 11.4 Hz), 131.7 (d, J = 2.7 Hz), 130.0 (d, J = 3.4 Hz), 129.4 (d, J = 92.5 Hz),

128.5 (d, *J* = 2.9 Hz), 124.8 (d, *J* = 12.1 Hz), 123.0 (d, *J* = 2.6 Hz), 117.8 (d, *J* = 4.5 Hz), 116.6 (d, *J* = 2.6 Hz), 44.6 (d, *J* = 62.6 Hz), 21.4 (d, *J* = 3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.0; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{24}O_2P$ 411.1508, found 411.1508.

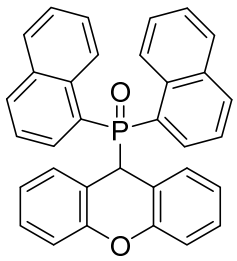
Bis(3,5-dimethylphenyl)(9*H*-xanthen-9-yl)phosphine oxide(3ak):



3ak

White solid (79 mg, 60%): mp 219–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.14 (m, 2H), 7.14–7.05 (m, 6H), 7.00–6.96 (m, 2H), 6.93–6.88 (m, 4H), 4.92 (d, *J* = 17.6 Hz, 1H), 2.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, *J* = 4.3 Hz), 137.6 (d, *J* = 12.1 Hz), 133.6 (d, *J* = 2.9 Hz), 130.3 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 8.5 Hz), 128.9 (d, *J* = 94.3 Hz), 128.5 (d, *J* = 3.1 Hz), 122.8 (d, *J* = 2.7 Hz), 117.3 (d, *J* = 4.7 Hz), 116.2 (d, *J* = 2.8 Hz), 45.3 (d, *J* = 63.1 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{28}O_2P$ 439.1821, found 439.1821.

Di(naphthalen-1-yl)(9*H*-xanthen-9-yl)phosphine oxide (3al):

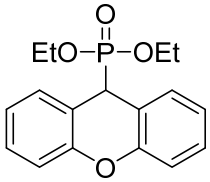


3al

White solid (136 mg, 94%): mp 249–250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.59 (dd, *J* = 14.8, 7.1 Hz, 2H), 7.42–7.34 (m, 2H), 7.32–7.28 (m, 2H), 7.25–7.18 (m, 2H), 7.03–6.93 (m,

2H), 6.85–6.83 (m, 2H), 6.73–6.71 (m, 2H), 6.61–6.57 (m, 2H), 5.43 (d, *J* = 17.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, *J* = 4.3 Hz), 134.5 (d, *J* = 7.7 Hz), 133.9 (d, *J* = 9.0 Hz), 133.2 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 10.6 Hz), 129.9 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 0.5 Hz), 128.5 (d, *J* = 3.0 Hz), 127.3 (d, *J* = 3.7 Hz), 127.2, 126.9 (d, *J* = 91.2 Hz), 126.2, 123.9 (d, *J* = 13.8 Hz), 122.9 (d, *J* = 2.6 Hz), 117.7 (d, *J* = 4.6 Hz), 116.5 (d, *J* = 2.7 Hz), 45.3 (d, *J* = 63.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.5; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{24}O_2P$ 483.1508, found 483.1509.

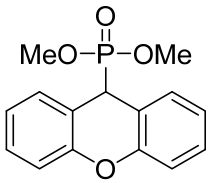
Diethyl (9*H*-xanthen-9-yl)phosphonate (3an):



3an

Colorless oil (78 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.22–7.15 (m, 2H), 7.04–6.98 (m, 4H), 4.40 (d, *J* = 24.7 Hz, 1H), 3.86–3.76 (m, 4H), 1.08 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 5.3 Hz), 130.1 (d, *J* = 4.4 Hz), 128.7 (d, *J* = 3.6 Hz), 123.1 (d, *J* = 3.2 Hz), 117.2 (d, *J* = 8.2 Hz), 116.5 (d, *J* = 3.4 Hz), 63.0 (d, *J* = 7.5 Hz), 40.4 (d, *J* = 141 Hz), 16.2 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.9; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{20}O_4P$ 319.1094, found 319.1092.

Dimethyl (9*H*-xanthen-9-yl)phosphonate (3ao):

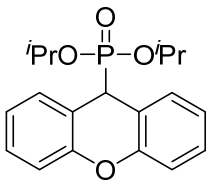


3ao

Colorless oil (70 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 2H), 7.30–7.24 (m, 2H), 7.11–7.07 (m, 4H), 4.51 (d, *J* = 24.7 Hz, 1H), 3.54 (d, *J* = 10.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 5.3 Hz), 130.0 (d, *J* = 4.4 Hz),

128.8 (d, J = 3.6 Hz), 123.3 (d, J = 3.2 Hz), 116.9 (d, J = 8.2 Hz), 116.6 (d, J = 3.4 Hz), 53.7 (d, J = 7.4 Hz), 40.0 (d, J = 141 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}O_4P$ 291.0781, found 291.0779.

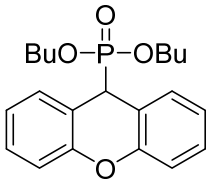
Diisopropyl (9*H*-xanthen-9-yl)phosphonate (3ap):



3ap

Colorless oil (68 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 7.26–7.20 (m, 2H), 7.09–7.01 (m, 4H), 4.46–4.34 (m, 3H), 1.14 (dd, J = 15.9, 6.2 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2 (d, J = 5.2 Hz), 130.4 (d, J = 4.3 Hz), 128.5 (d, J = 3.6 Hz), 122.9 (d, J = 3.2 Hz), 117.4 (d, J = 8.2 Hz), 116.4 (d, J = 3.3 Hz), 71.7 (d, J = 7.9 Hz), 40.9 (d, J = 143 Hz), 23.7 (dd, J = 45.9, 4.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}O_4P$ 347.1407, found 347.1410.

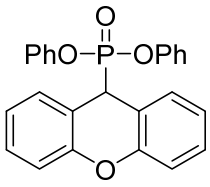
Dibutyl (9*H*-xanthen-9-yl)phosphonate (3aq):



3aq

Colorless oil (73 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.28–7.23 (m, 2H), 7.11–7.03 (m, 4H), 4.48 (d, J = 24.7 Hz, 1H), 3.83–3.76 (m, 4H), 1.52–1.43 (m, 4H), 1.29–1.22 (m, 4H), 0.85 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J = 5.3 Hz), 130.2 (d, J = 4.4 Hz), 128.7 (d, J = 3.6 Hz), 123.1 (d, J = 3.1 Hz), 117.3 (d, J = 8.2 Hz), 116.5 (d, J = 3.3 Hz), 66.6 (d, J = 7.7 Hz), 40.3 (d, J = 141 Hz), 32.5 (d, J = 5.8 Hz), 18.5, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{28}O_4P$ 375.1720, found 375.1720.

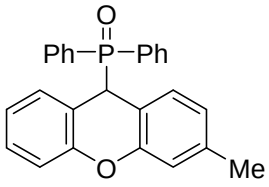
Diphenyl (9*H*-xanthen-9-yl)phosphonate (3ar):



3ar

White solid (57 mg, 46%): mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.36–7.29 (m, 2H), 7.22–7.11 (m, 8H), 7.10–7.04 (m, 2H), 6.82–6.78 (m, 4H), 4.91 (d, J = 23.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J = 5.6 Hz), 150.5 (d, J = 10.4 Hz), 130.4 (d, J = 4.6 Hz), 129.5, 129.2 (d, J = 3.8 Hz), 124.9 (d, J = 0.7 Hz), 123.4 (d, J = 3.4 Hz), 120.2 (d, J = 4.3 Hz), 116.9 (d, J = 3.6 Hz), 116.0 (d, J = 8.5 Hz), 40.7 (d, J = 143 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{20}O_4P$ 415.1094, found 415.1095.

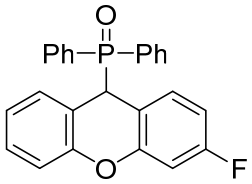
(3-Methyl-9*H*-xanthen-9-yl)diphenylphosphine oxide (3ba):



3ba

White solid (63 mg, 53%): mp 234–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.41 (m, 6H), 7.34–7.26 (m, 4H), 7.11–7.05 (m, 1H), 6.90–6.86 (m, 1H), 6.84–6.77 (m, 2H), 6.74 (dd, J = 7.8, 2.0 Hz, 1H), 6.67–6.60 (m, 2H), 4.83 (d, J = 17.4 Hz, 1H), 2.20 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, J = 4.3 Hz), 152.5 (d, J = 4.4 Hz), 138.9 (d, J = 3.3 Hz), 132.3 (d, J = 1.5 Hz), 132.2 (d, J = 1.4 Hz), 132.0 (d, J = 2.6 Hz), 130.2 (d, J = 3.5 Hz), 129.8 (d, J = 3.4 Hz), 129.5 (d, J = 94.9 Hz), 129.4 (d, J = 94.8 Hz), 128.9 (d, J = 13.0 Hz), 128.6 (d, J = 3.1 Hz), 128.2, 128.1, 123.8 (d, J = 2.6 Hz), 122.8 (d, J = 2.8 Hz), 117.1 (d, J = 4.6 Hz), 116.8 (d, J = 2.9 Hz), 116.4 (d, J = 2.8 Hz), 113.8 (d, J = 4.7 Hz), 45.0 (d, J = 64.3 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}O_2P$ 397.1352, found 397.1352.

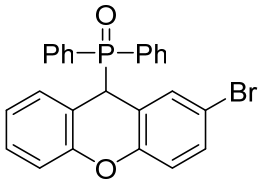
(3-Fluoro-9*H*-xanthen-9-yl)diphenylphosphine oxide (3ca):



3ca

White solid (52 mg, 43%): mp 241–242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.47 (m, 6H), 7.44–7.34 (m, 4H), 7.18–7.15 (m, 1H), 6.96–6.87 (m, 4H), 6.65–6.57 (m, 2H), 4.88 (d, J = 17.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (dd, J = 247, 3.3 Hz), 153.3 (dd, J = 12.2, 4.1 Hz), 152.2 (d, J = 4.4 Hz), 132.2 (d, J = 4.4 Hz), 132.1 (d, J = 4.4 Hz), 131.2 (d, J = 3.4 Hz), 131.1 (d, J = 3.4 Hz), 130.1 (d, J = 3.5 Hz), 129.4 (d, J = 95.3 Hz), 129.0 (d, J = 95.1 Hz), 128.8 (d, J = 3.1 Hz), 128.2 (dd, J = 11.4, 8.2 Hz), 123.2 (d, J = 2.7 Hz), 116.8 (d, J = 4.5 Hz), 116.4 (d, J = 2.8 Hz), 112.8 (dd, J = 4.7, 3.3 Hz), 110.2 (d, J = 2.6 Hz), 110.0 (d, J = 2.6 Hz), 104.0 (d, J = 2.8 Hz), 103.8 (d, J = 2.8 Hz), 44.8 (d, J = 64.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5 (d, J = 5.1 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{19}FO_2P$ 401.1101, found 401.1099.

(2-Bromo-9*H*-xanthen-9-yl)diphenylphosphine oxide (3da):

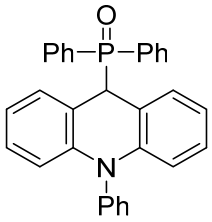


3da

White solid (62 mg, 45%): mp 250–251 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.51 (m, 6H), 7.46–7.35 (m, 4H), 7.29–7.23 (m, 1H), 7.20–7.13 (m, 1H), 6.95–6.85 (m, 4H), 6.80 (d, J = 8.7 Hz, 1H), 4.81 (d, J = 16.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J = 4.3 Hz), 151.8 (d, J = 4.3 Hz), 132.8 (d, J = 3.5 Hz), 132.4 (d, J = 3.0 Hz), 132.3 (d, J = 3.4 Hz), 132.2 (d, J = 8.7 Hz), 132.1 (d, J = 8.8 Hz), 131.6 (d, J = 2.9 Hz), 130.1 (d, J = 3.4 Hz), 129.8 (d, J = 86.8 Hz) 129.7 (d, J = 95.8 Hz), 128.9 (d, J = 3.0 Hz), 128.4 (d, J = 1.4 Hz), 128.3 (d, J = 1.4 Hz), 123.2 (d, J = 2.5 Hz), 119.0

(d, J = 4.7 Hz), 118.0 (d, J = 2.6 Hz), 116.4 (d, J = 2.6 Hz), 116.2 (d, J = 4.9 Hz), 115.0 (d, J = 3.3 Hz), 45.3 (d, J = 63.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{19}BrO_2P$ 461.0301, found 461.0303.

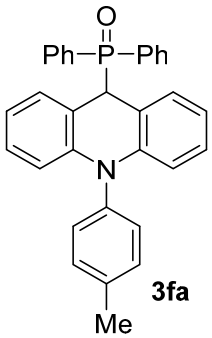
Diphenyl(10-phenyl-9,10-dihydroacridin-9-yl)phosphine oxide (3ea):



3ea

White solid (117 mg, 85%): mp 193–195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 8H), 7.43–7.33 (m, 5H), 7.00–6.90 (m, 4H), 6.78–6.70 (m, 4H), 6.06 (d, J = 8.2 Hz, 2H), 5.14 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7 (d, J = 3.5 Hz), 140.0, 132.6 (d, J = 8.4 Hz), 131.6 (d, J = 2.7 Hz), 130.8, 130.4, 130.3 (d, J = 4.0 Hz), 130.0 (d, J = 92.3 Hz), 128.1, 128.0 (d, J = 11.1 Hz), 127.7 (d, J = 3.1 Hz), 120.4 (d, J = 2.7 Hz), 115.4 (d, J = 4.6 Hz), 113.9 (d, J = 2.5 Hz), 49.1 (d, J = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{25}NOP$ 458.1668, found 458.1659.

Diphenyl(10-(*p*-tolyl)-9,10-dihydroacridin-9-yl)phosphine oxide (3fa):

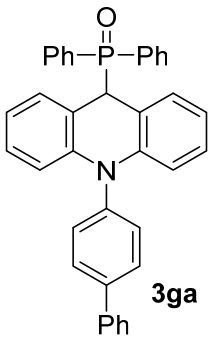


3fa

White solid (133 mg, 94%): mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 6H), 7.38–7.33 (m, 4H), 7.28–7.26 (m, 2H), 7.00–6.90 (m, 4H), 6.77–6.71 (m, 2H), 6.58 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 8.2 Hz, 2H), 5.15 (d, J =

18.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, J = 3.6 Hz), 137.9, 137.2, 132.6 (d, J = 8.4 Hz), 131.6 (d, J = 2.7 Hz), 131.1, 130.4, 130.3 (d, J = 4.0 Hz), 130.0 (d, J = 92.3 Hz), 128.0 (d, J = 11.1 Hz), 127.7 (d, J = 3.2 Hz), 120.3 (d, J = 2.7 Hz), 115.3 (d, J = 4.5 Hz), 113.9 (d, J = 2.5 Hz), 49.1 (d, J = 63.9 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{26}NOPNa$ 494.1644, found 494.1643.

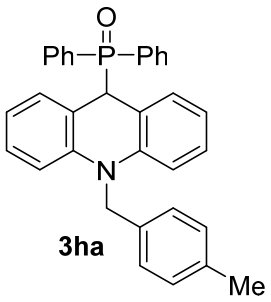
(10-([1,1'-Biphenyl]-4-yl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ga):



3ga

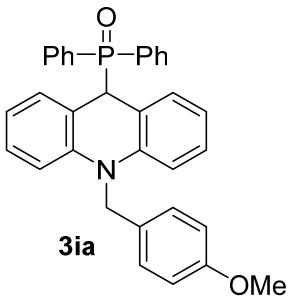
Yellow solid (115 mg, 72%): mp 218–220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.57–7.46 (m, 8H), 7.42–7.35 (m, 5H), 7.02–6.95 (m, 4H), 6.82–6.74 (m, 4H), 6.17 (d, J = 8.1 Hz, 2H), 5.18 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, J = 3.6 Hz), 141.0, 140.2, 139.2, 132.7 (d, J = 8.4 Hz), 131.8 (d, J = 2.7 Hz), 131.1, 130.5 (d, J = 4.0 Hz), 129.9 (d, J = 93.1 Hz), 129.2, 128.9, 128.1 (d, J = 11.2 Hz), 127.9 (d, J = 3.1 Hz), 127.7, 127.1, 120.6 (d, J = 2.7 Hz), 115.4 (d, J = 4.6 Hz), 114.1 (d, J = 2.4 Hz), 49.1 (d, J = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{37}H_{29}NOP$ 534.1981, found 534.1978.

(10-(4-Methylbenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ha):



Yellow solid (140 mg, 96%): mp 258–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.44 (m, 6H), 7.39–7.34 (m, 4H), 7.09–6.98 (m, 6H), 6.90–6.88 (m, 2H), 6.83–6.79 (m, 2H), 6.42 (d, J = 8.4 Hz, 2H), 5.01 (d, J = 19.0 Hz, 1H), 4.24 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1 (d, J = 3.5 Hz), 136.4, 133.5, 132.5 (d, J = 8.3 Hz), 131.7 (d, J = 2.7 Hz), 130.3 (d, J = 4.3 Hz), 130.1 (d, J = 92.6 Hz), 129.4, 128.2 (d, J = 3.3 Hz), 127.8 (d, J = 11.2 Hz), 125.8, 120.6 (d, J = 2.8 Hz), 118.0 (d, J = 4.0 Hz), 113.3 (d, J = 2.4 Hz), 50.7, 49.6 (d, J = 63.3 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{33}H_{28}NOPNa$ 508.1801, found 508.1802.

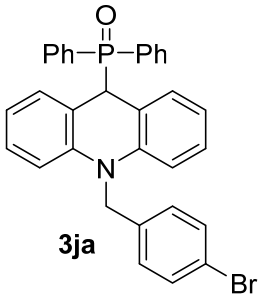
(10-(4-Methoxybenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ia):



Yellow solid (143 mg, 95%): mp 261–263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 6H), 7.40–7.33 (m, 4H), 7.06–6.99 (m, 4H), 6.92–6.90 (m, 2H), 6.84–6.75 (m, 4H), 6.43 (d, J = 8.0 Hz, 2H), 5.00 (d, J = 18.9 Hz, 1H), 4.23 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.0 (d, J = 3.6 Hz), 132.5 (d, J = 8.4 Hz), 131.7 (d, J = 2.6 Hz), 130.3 (d, J = 4.4 Hz), 129.5 (d, J = 92.5 Hz), 128.3, 128.2 (d, J = 3.3 Hz), 127.7 (d, J = 11.3 Hz), 126.9, 120.6 (d, J = 2.8 Hz), 118.0 (d, J

= 4.0 Hz), 114.1, 113.3 (d, *J* = 2.4 Hz), 55.2, 50.3, 49.6 (d, *J* = 63.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{33}H_{28}NO_2PNa$ 524.1750, found 524.1761.

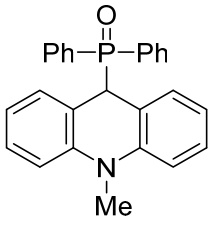
(10-(4-Bromobenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ja):



3ja

Yellow solid (159 mg, 96%): mp 274–275 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 6H), 7.40–7.33 (m, 6H), 7.06–6.99 (m, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.84–6.78 (m, 2H), 6.37 (d, *J* = 8.1 Hz, 2H), 5.02 (d, *J* = 18.4 Hz, 1H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (d, *J* = 3.7 Hz), 135.7, 132.5 (d, *J* = 8.4 Hz), 131.9, 131.8 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 4.3 Hz), 129.8 (d, *J* = 93.4 Hz), 128.3 (d, *J* = 3.3 Hz), 127.9, 127.8, 120.9 (d, *J* = 2.7 Hz), 120.7, 118.0 (d, *J* = 4.1 Hz), 113.1 (d, *J* = 2.4 Hz), 50.4, 49.4 (d, *J* = 63.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{32}H_{25}BrNOPNa$ 572.0749, found 572.0756.

(10-Methyl-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ka):

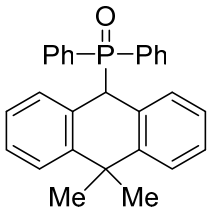


3ka

White solid (107 mg, 90%): mp 280–282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 6H), 7.35–7.28 (m, 4H), 7.21–7.15 (m, 2H), 7.05–7.01 (m, 2H), 6.88–6.81 (m, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 4.95 (d, *J* = 19.1 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9 (d, *J* = 3.6 Hz), 132.3 (d, *J* = 8.4 Hz), 131.5 (d,

J = 2.3 Hz), 130.3 (d, *J* = 92.4 Hz), 130.2 (d, *J* = 4.4 Hz), 128.1 (d, *J* = 3.0 Hz), 127.6 (d, *J* = 11.3 Hz), 120.5 (d, *J* = 2.4 Hz), 118.5 (d, *J* = 3.8 Hz), 112.2 (d, *J* = 1.8 Hz), 50.2 (d, *J* = 63.6 Hz), 32.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{23}NOP$ 396.1512, found 396.1513.

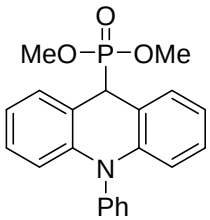
(10,10-Dimethyl-9,10-dihydroanthracen-9-yl)diphenylphosphine oxide (3la):



3la

White solid (47 mg, 38%): mp 254–256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.44 (m, 8H), 7.40–7.33 (m, 4H), 7.27–7.22 (m, 2H), 6.95–6.88 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 5.13 (d, *J* = 16.5 Hz, 1H), 1.62 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1 (d, *J* = 5.1 Hz), 132.5 (d, *J* = 8.3 Hz), 131.7 (d, *J* = 2.7 Hz), 130.8 (d, *J* = 94.9 Hz), 129.5 (d, *J* = 3.9 Hz), 128.1 (d, *J* = 11.4 Hz), 127.9 (d, *J* = 6.2 Hz), 127.4 (d, *J* = 3.5 Hz), 126.9 (d, *J* = 3.3 Hz), 125.1 (d, *J* = 3.2 Hz), 50.2 (d, *J* = 60.2 Hz), 38.7 (d, *J* = 2.6 Hz), 34.2 (d, *J* = 5.1 Hz), 33.6 (d, *J* = 3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{28}H_{26}OP$ 409.1716, found 409.1716.

Dimethyl (10-phenyl-9,10-dihydroacridin-9-yl)phosphonate (3eo):

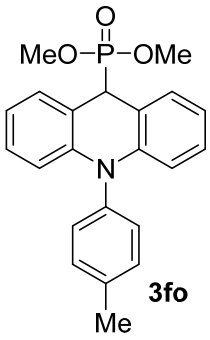


3eo

White solid (105 mg, 96%): mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.50 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.41–7.37 (m, 2H), 7.31–7.24 (m,

2H), 7.05–6.98 (m, 2H), 6.91 (dd, *J* = 7.3, 7.3 Hz, 2H), 6.30 (d, *J* = 8.2 Hz, 2H), 4.68 (d, *J* = 24.9 Hz, 1H), 3.56 (d, *J* = 10.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (d, *J* = 4.2 Hz), 140.5, 131.1, 130.7, 129.9 (d, *J* = 5.2 Hz), 128.3, 127.9 (d, *J* = 3.6 Hz), 120.7 (d, *J* = 3.1 Hz), 115.7 (d, *J* = 7.9 Hz), 114.2 (d, *J* = 3.0 Hz), 53.5 (d, *J* = 7.6 Hz), 43.5 (d, *J* = 140 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{21}H_{20}NO_3PNa$ 388.1073, found 388.1070.

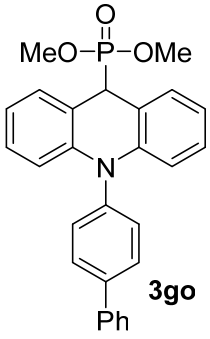
Dimethyl (10-(*p*-tolyl)-9,10-dihydroacridin-9-yl)phosphonate (3fo):



3fo

White solid (109 mg, 96%): mp 154–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 2H), 7.28–7.22 (m, 4H), 7.04–6.97 (m, 2H), 6.90 (dd, *J* = 7.3, 7.3 Hz, 2H), 6.33 (d, *J* = 8.2 Hz, 2H), 4.67 (d, *J* = 24.9 Hz, 1H), 3.55 (d, *J* = 10.5 Hz, 6H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (d, *J* = 4.1 Hz), 138.1, 137.7, 131.3, 130.7, 129.8 (d, *J* = 5.2 Hz), 127.8 (d, *J* = 3.6 Hz), 120.6 (d, *J* = 3.1 Hz), 115.6 (d, *J* = 8.0 Hz), 114.2 (d, *J* = 3.0 Hz), 53.5 (d, *J* = 7.5 Hz), 43.5 (d, *J* = 140 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.2; HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calcd for $C_{22}H_{22}NO_3PNa$ 402.1230, found 402.1221.

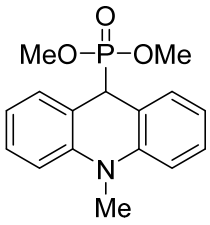
Dimethyl (10-([1,1'-biphenyl]-4-yl)-9,10-dihydroacridin-9-yl)phosphonate (3go):



3go

White solid (99 mg, 75%): mp 66–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 2H), 7.72–7.67 (m, 2H), 7.54–7.38 (m, 5H), 7.32–7.27 (m, 2H), 7.09–7.01 (m, 2H), 6.94 (dd, *J* = 7.3, 7.3 Hz, 2H), 6.41 (d, *J* = 8.2 Hz, 2H), 4.70 (d, *J* = 24.9 Hz, 1H), 3.58 (d, *J* = 10.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5 (d, *J* = 4.2 Hz), 141.2, 140.1, 139.7, 131.4, 129.9 (d, *J* = 5.2 Hz), 129.3, 128.9, 127.9 (d, *J* = 3.6 Hz), 127.7, 127.1, 120.8 (d, *J* = 3.1 Hz), 115.8 (d, *J* = 8.0 Hz), 114.3 (d, *J* = 3.0 Hz), 53.6 (d, *J* = 7.5 Hz), 43.5 (d, *J* = 140 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.2; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{27}H_{24}NO_3PNa$ 464.1386, found 464.1386.

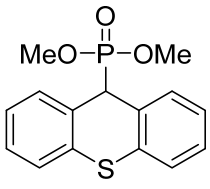
Dimethyl (10-methyl-9,10-dihydroacridin-9-yl)phosphonate (3ko):



3ko

White solid (66 mg, 72%): mp 90–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 4H), 6.95 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 4.56 (d, *J* = 25.4 Hz, 1H), 3.50 (d, *J* = 10.5 Hz, 6H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, *J* = 4.4 Hz), 129.7 (d, *J* = 5.7 Hz), 128.3 (d, *J* = 3.8 Hz), 120.7 (d, *J* = 3.2 Hz), 118.3 (d, *J* = 7.3 Hz), 112.4 (d, *J* = 3.0 Hz), 53.5 (d, *J* = 7.4 Hz), 44.2 (d, *J* = 140 Hz), 33.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.1; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{16}H_{18}NO_3PNa$ 326.0917, found 326.0914.

Dimethyl (9*H*-thioxanthen-9-yl)phosphonate (3mo):



3mo

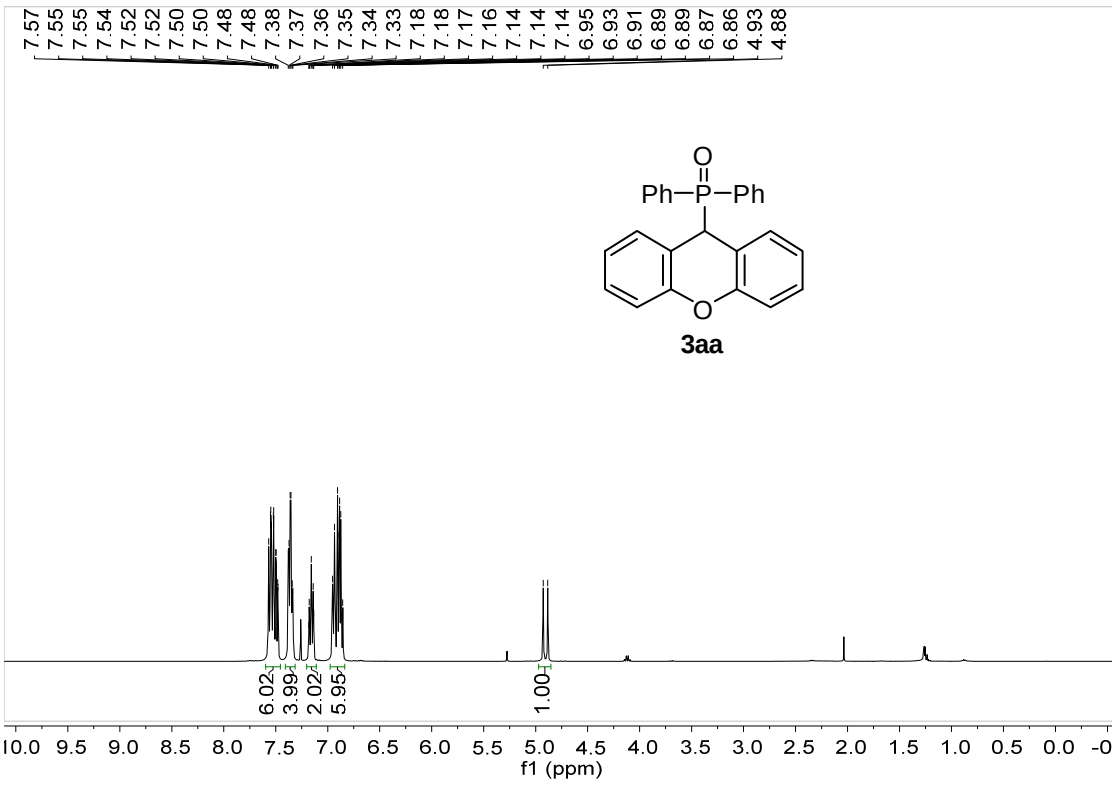
White solid (42 mg, 46%): mp 181–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24

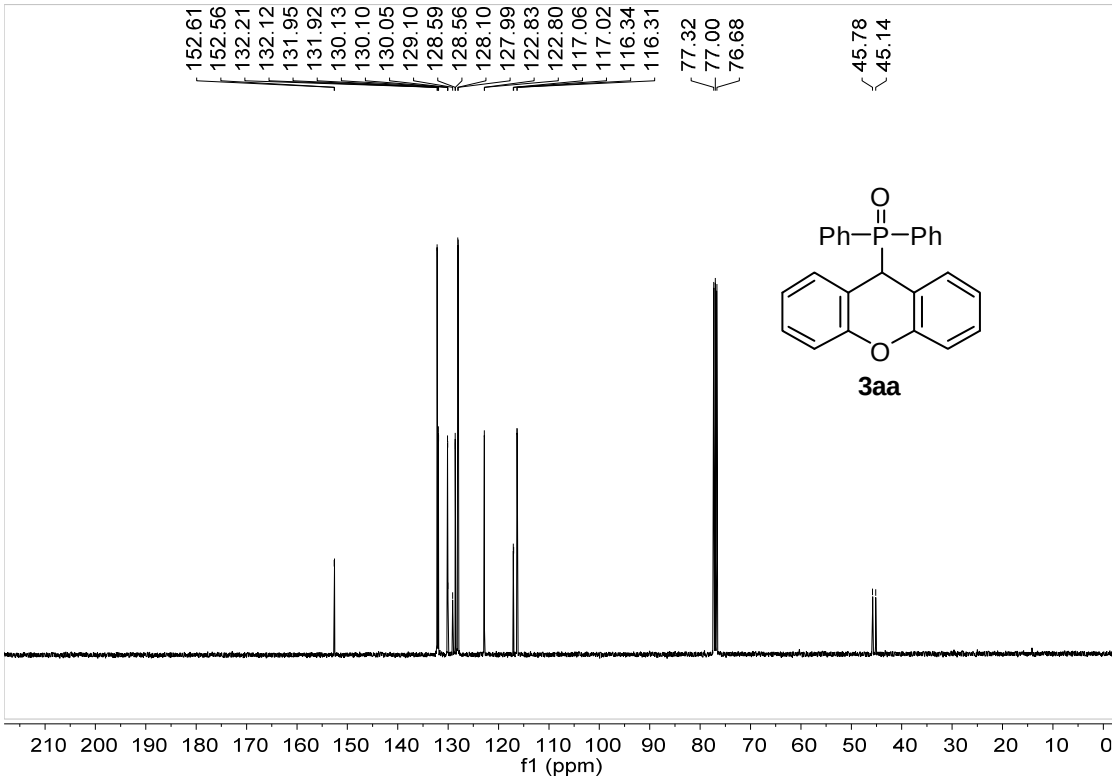
(m, 4H), 7.18–7.12 (m, 4H), 4.63 (d, J = 28.3 Hz, 1H), 3.44 (d, J = 10.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J = 6.1 Hz), 130.6 (d, J = 5.7 Hz), 128.9 (d, J = 7.3 Hz), 127.8 (d, J = 3.9 Hz), 126.6 (d, J = 3.4 Hz), 126.5 (d, J = 3.2 Hz), 53.5 (d, J = 7.2 Hz), 48.9 (d, J = 137 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}O_3PS$ 307.0552, found 307.0548.

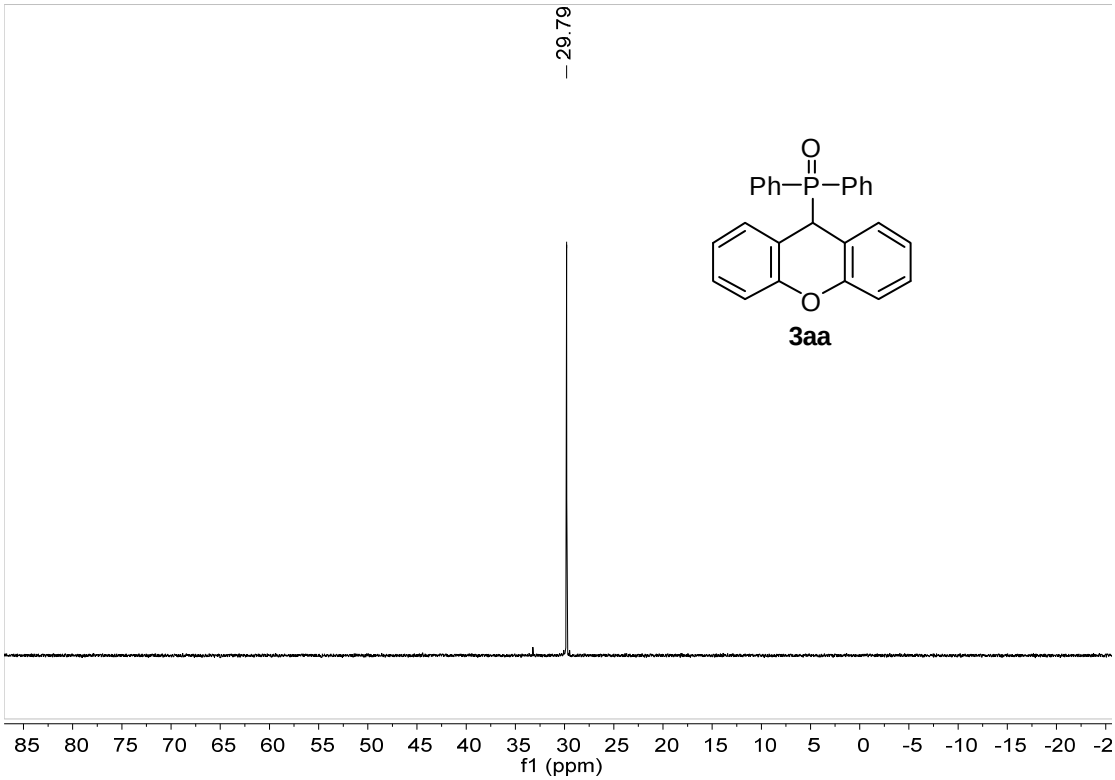
References:

1. Menéndez, C. A.; Nador, F.; Radivoy, G.; Gerbino, D. C. *Org. Lett.* **2014**, *16*, 2846.
2. Pintér, Á.; Sud, A.; Sureshkumar, D.; Klussmann, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 5004.

5. Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra for compounds 3



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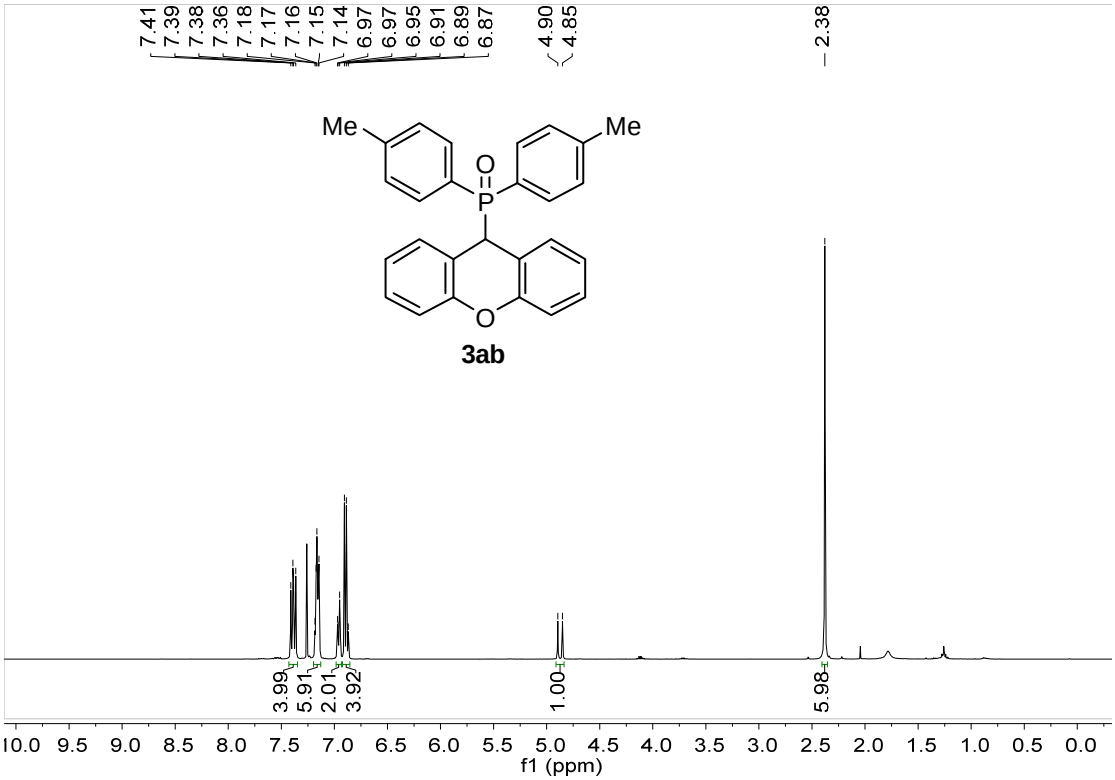
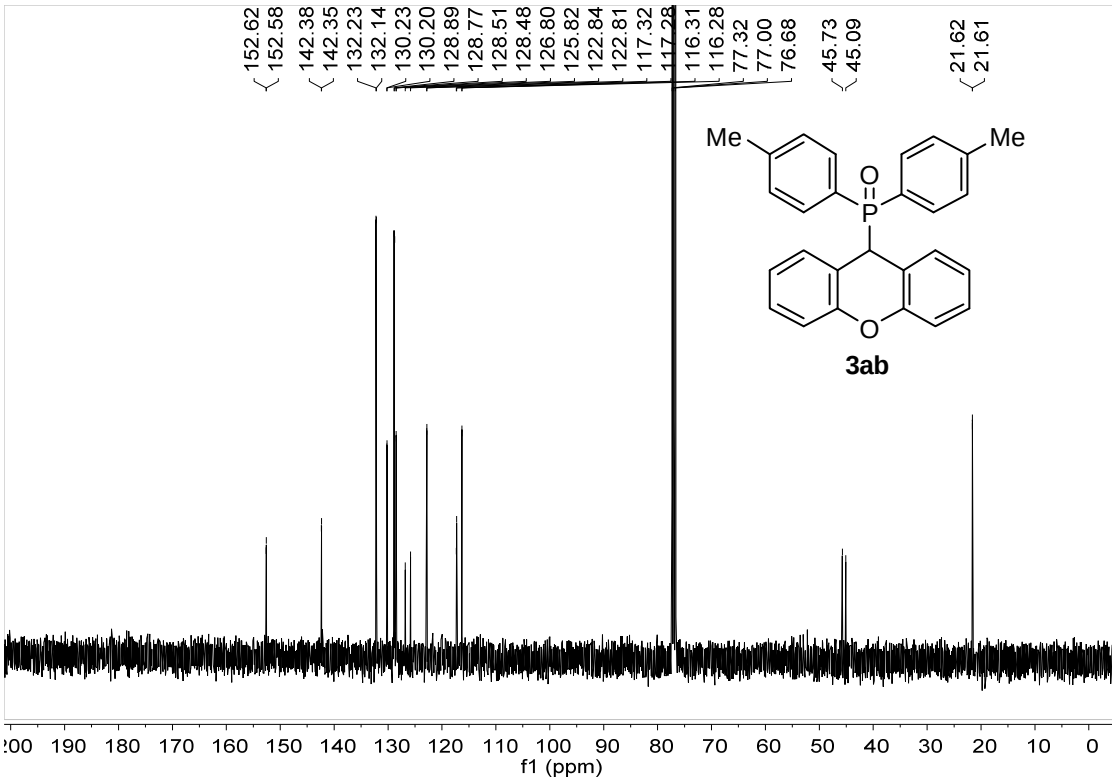
Ph—P—Ph
O
3aa
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -2
f1 (ppm)


7.41
7.39
7.38
7.36
7.18
7.17
7.16
7.15
7.14
6.97
6.97
6.95
6.91
6.89
6.87
4.90
4.85
2.38
Me
Me
O
P
O
3ab
3.99
5.91
2.01
3.92
1.00
5.98
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)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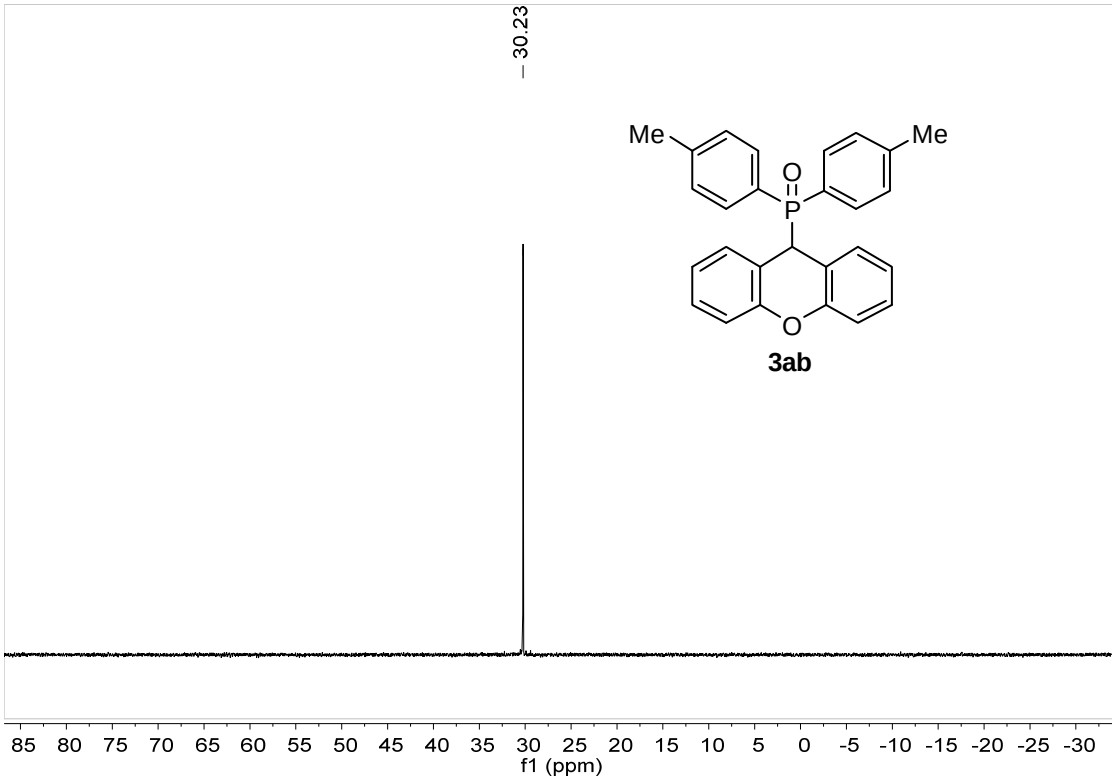
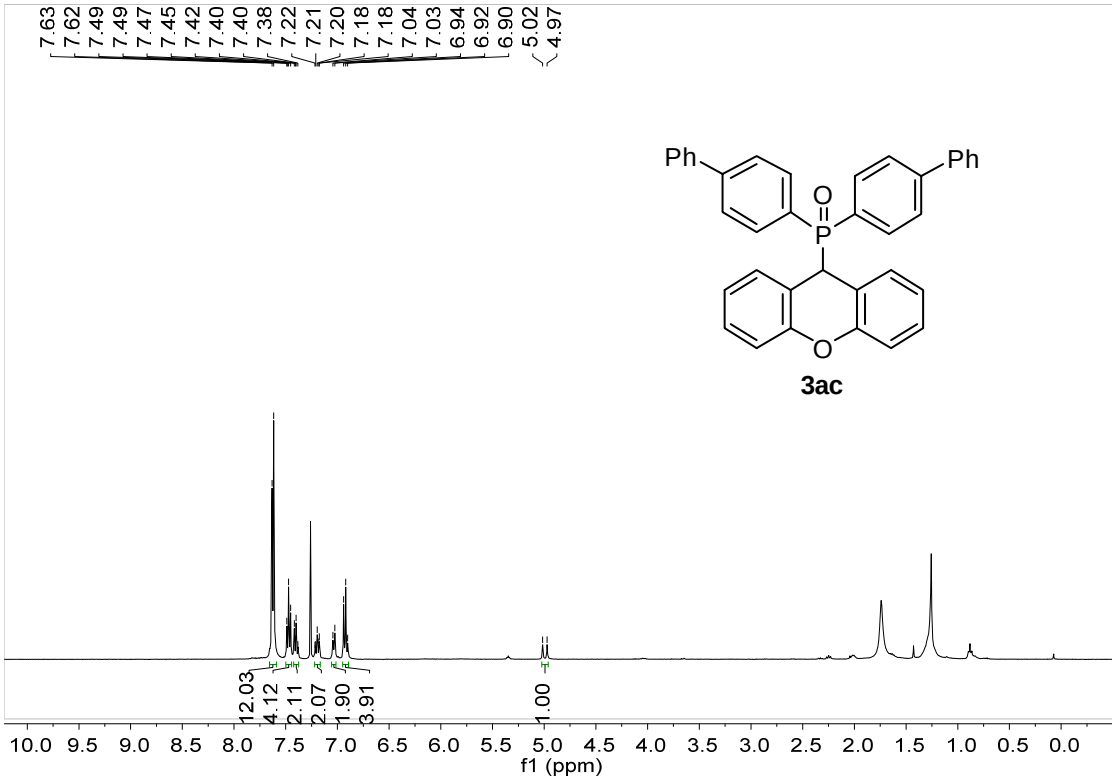
152.58
142.38
142.35
132.23
132.14
130.23
130.20
128.89
128.77
128.51
128.48
126.80
125.82
122.84
122.81
117.32
117.28
116.31
116.28
77.32
77.00
76.68
45.73
45.09
21.62
21.61
Me
Me
O
P
O
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


30.23
Me
Me
O
P
O
3ab
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)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7.62
7.49
7.49
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7.40
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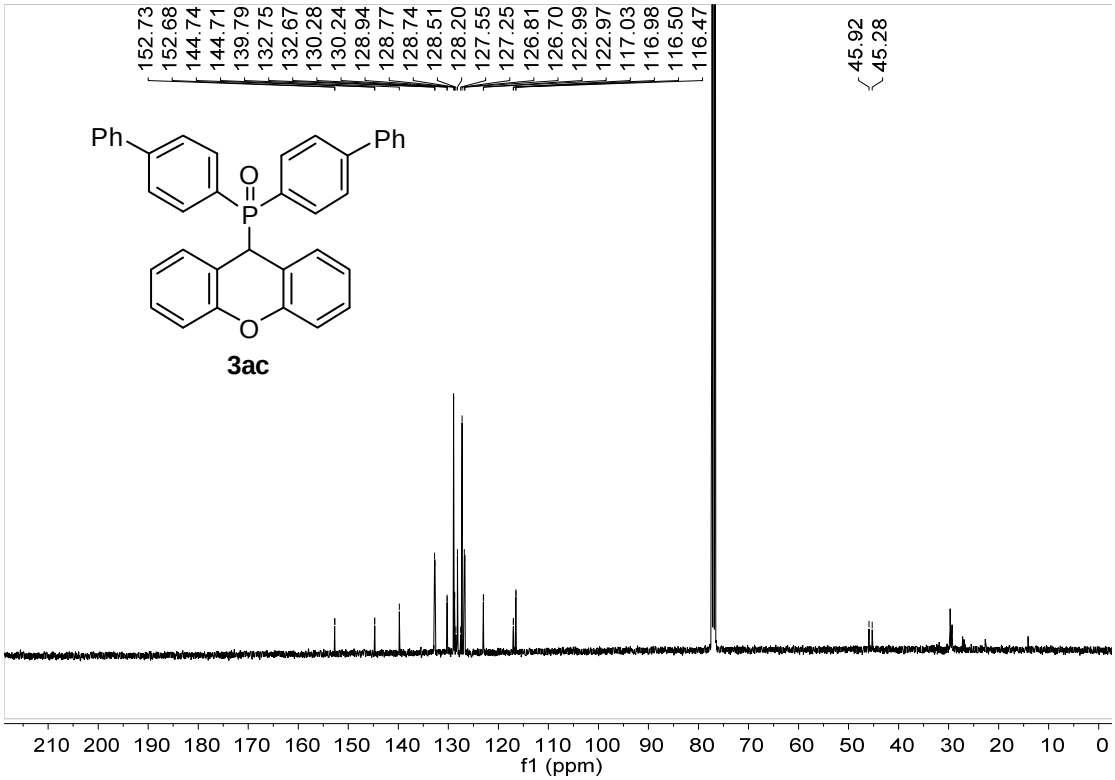
7.22
7.21
7.20
7.18
7.18
7.04
7.03
6.94
6.92
6.90
5.02
4.97
Ph
Ph
O
P
O
3ac
12.03
4.12
2.11
2.07
1.90
3.91
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.24
128.94
128.77
128.74
128.51
128.20
127.55
127.25
126.81
126.70
122.99
122.97
117.03
116.98
116.50
116.47
45.92
45.28
Ph
Ph
O
P
O
3ac
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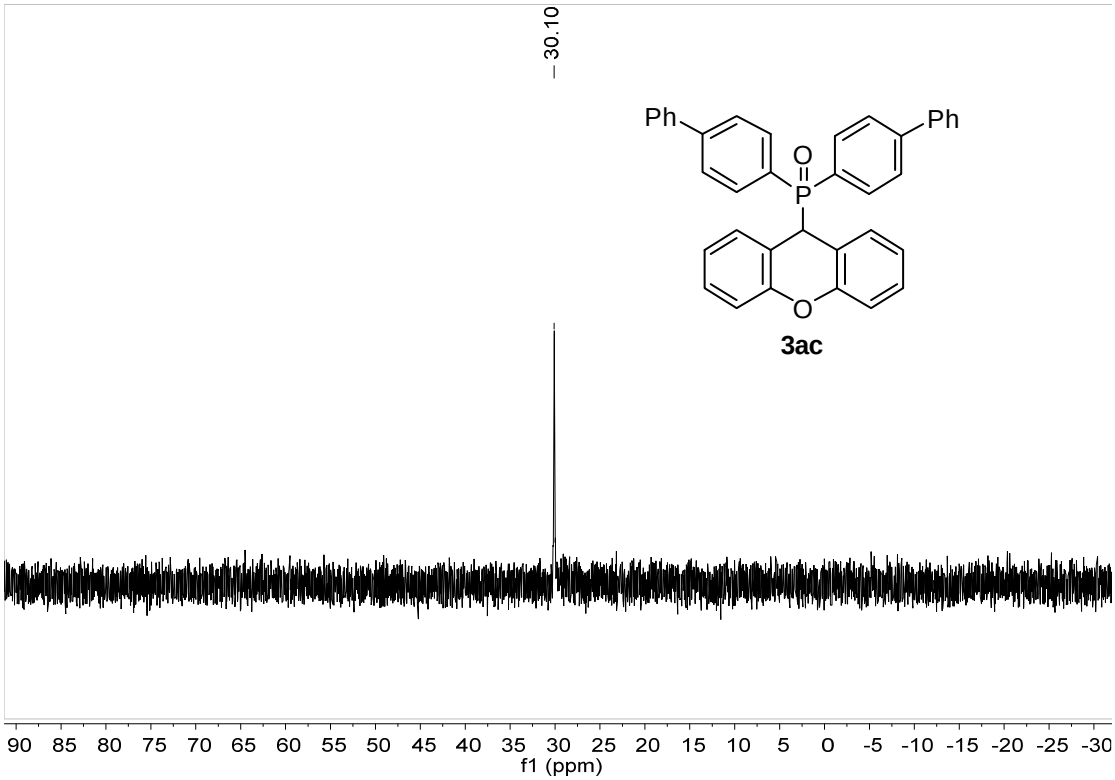
f1 (ppm)


30.10
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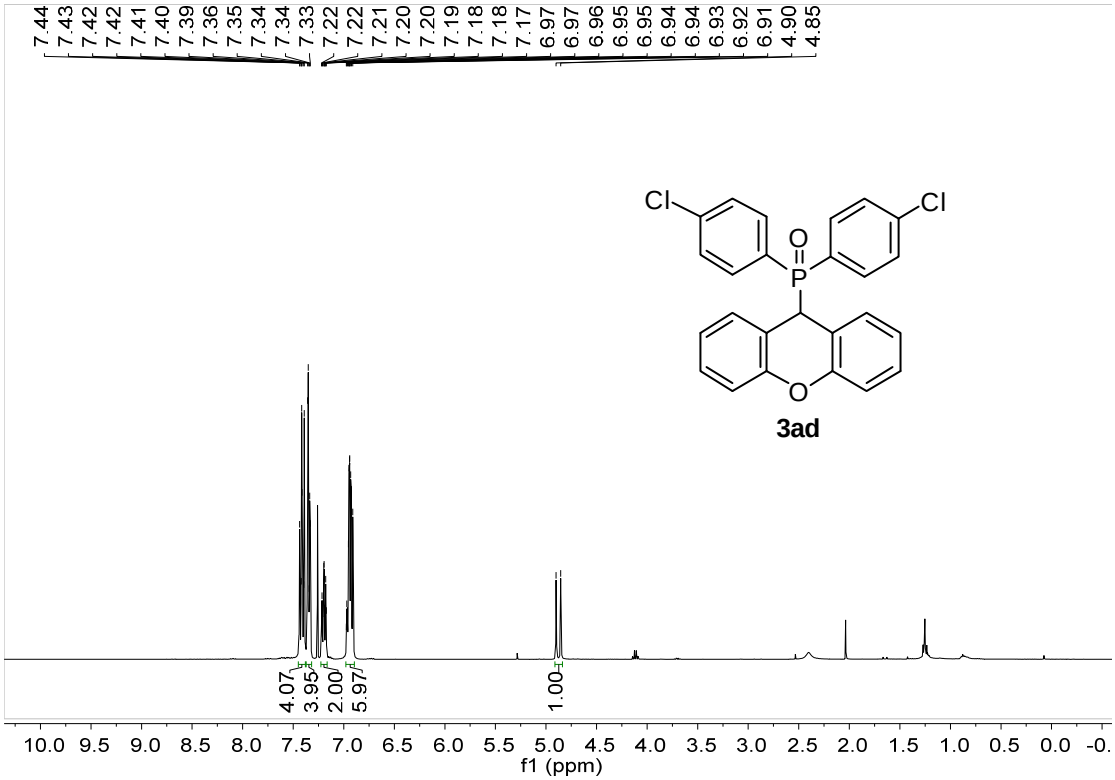
Ph
O
P
O
3ac
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)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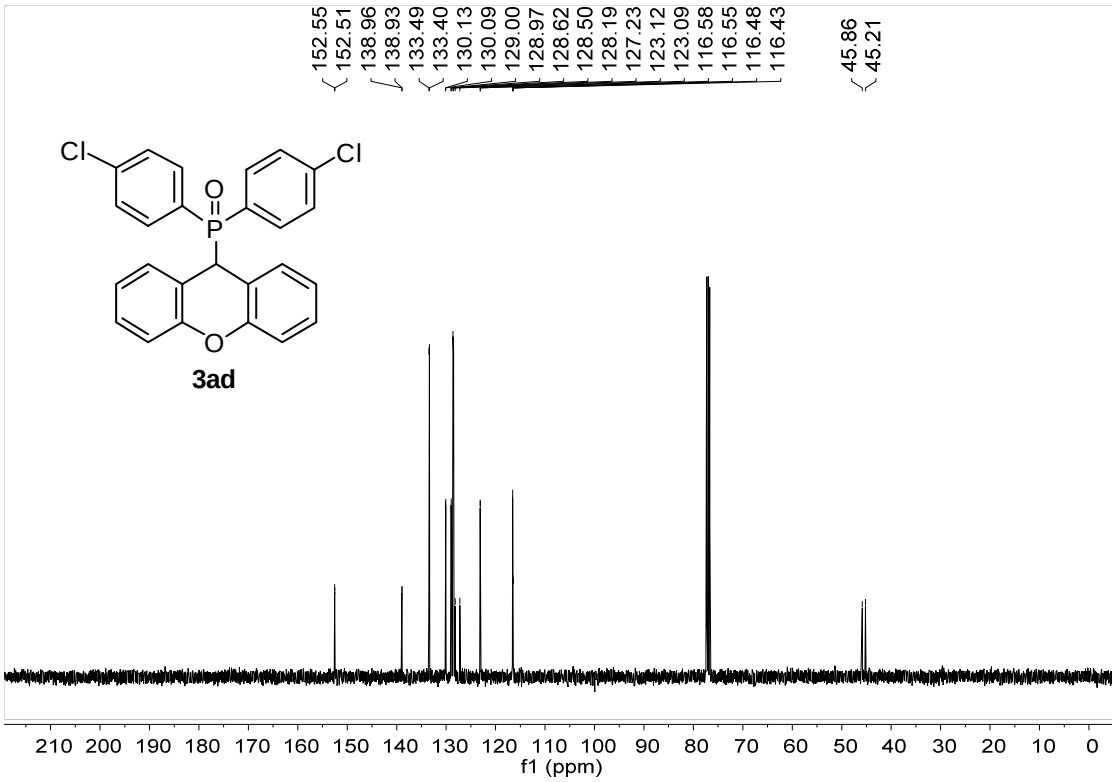
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.93
6.92
6.91
4.90
4.85
Cl
Cl
O
P
O
3ad
4.07
3.95
2.00
5.97
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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127.23
123.12
123.09
116.58
116.55
116.48
116.43
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45.21
Cl
Cl
O
P
O
3ad
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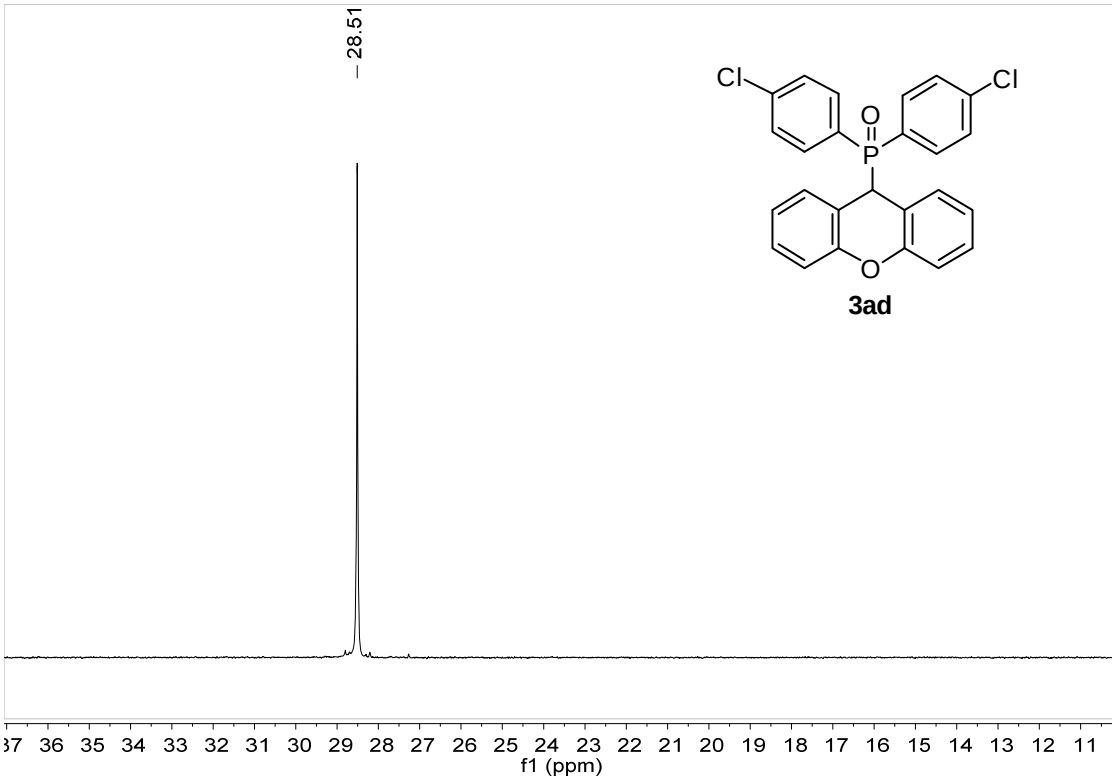
f1 (ppm)


28.51
Cl
Cl
O
P
O
3ad
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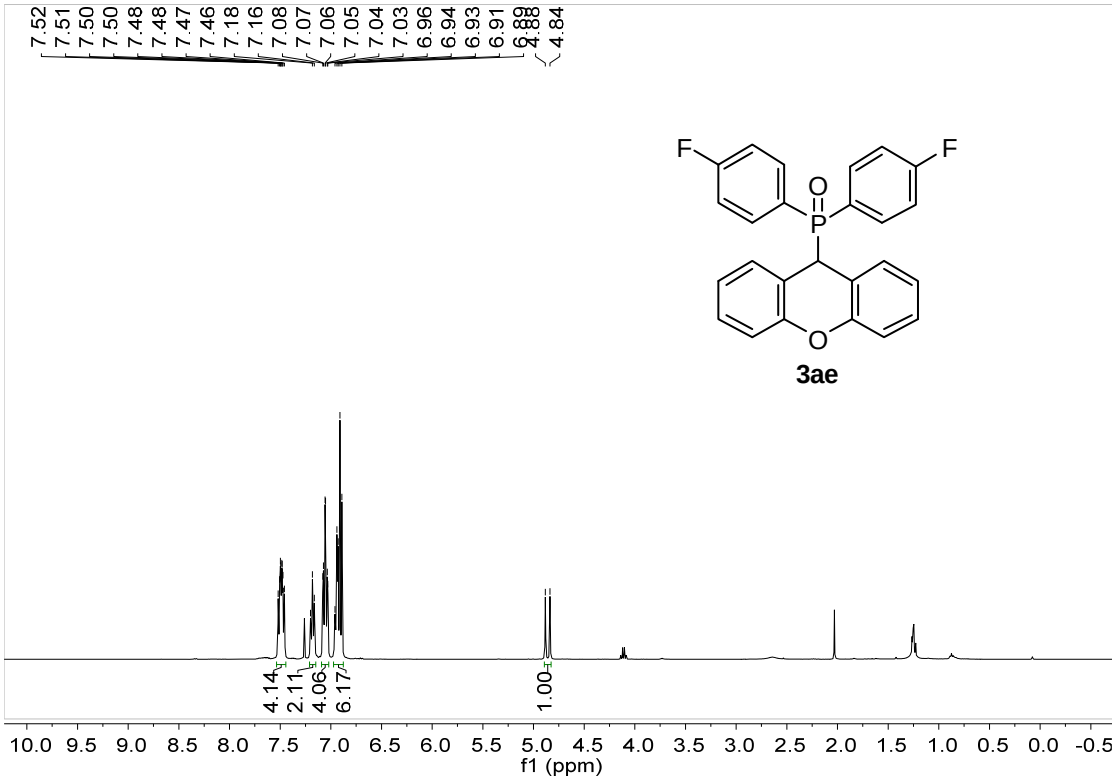
f1 (ppm)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7.16
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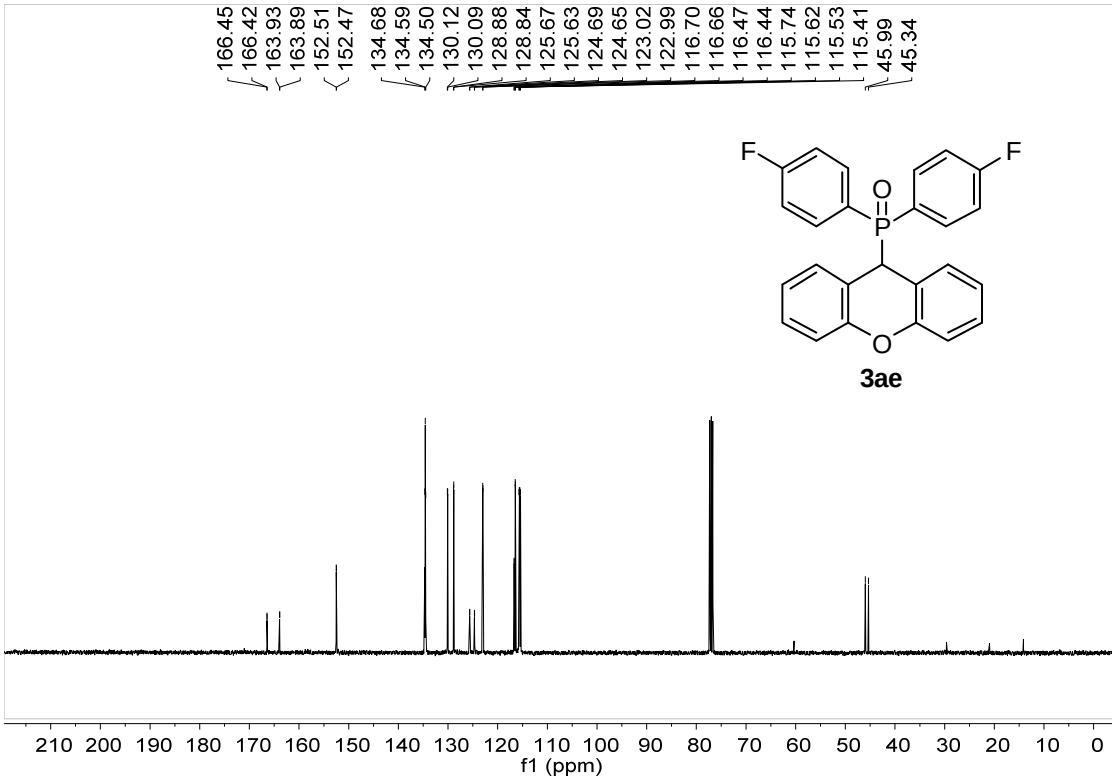
7.05
7.04
7.03
6.96
6.94
6.93
6.91
6.89
6.88
4.84
F
F
O
P
O
3ae
4.14
2.11
4.06
6.17
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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116.47
116.44
115.74
115.62
115.53
115.41
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F
O
P
O
3ae
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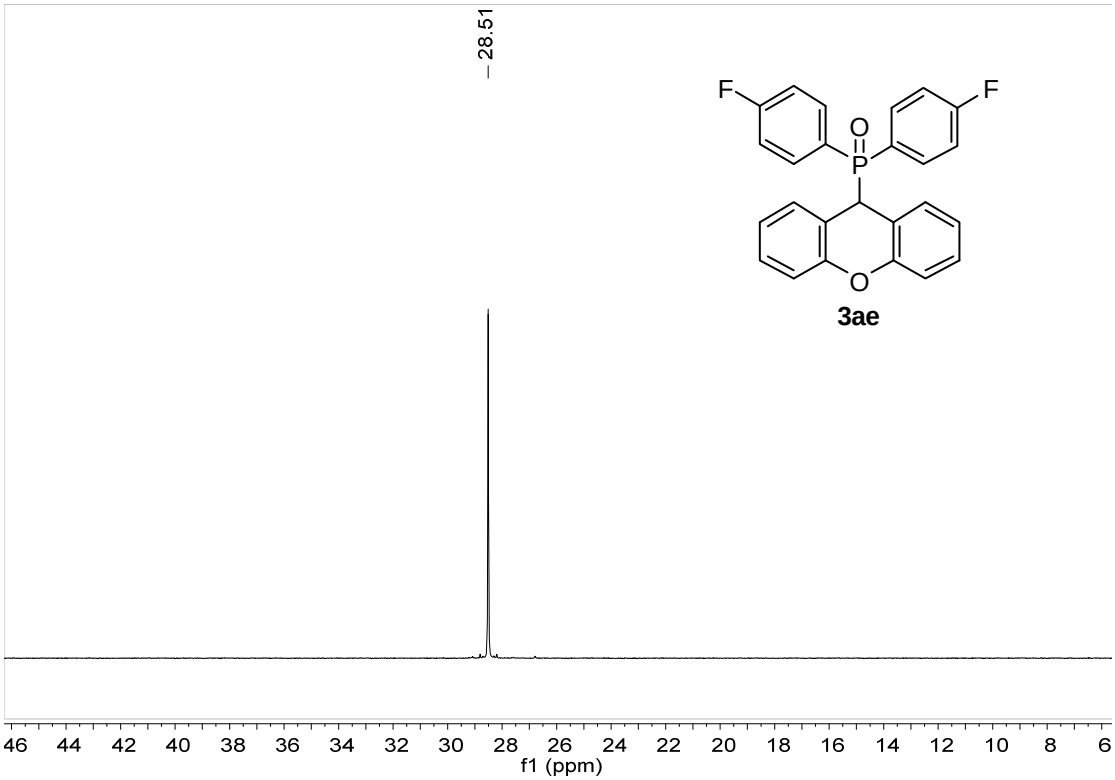
f1 (ppm)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F
F
O
P
O
3ae
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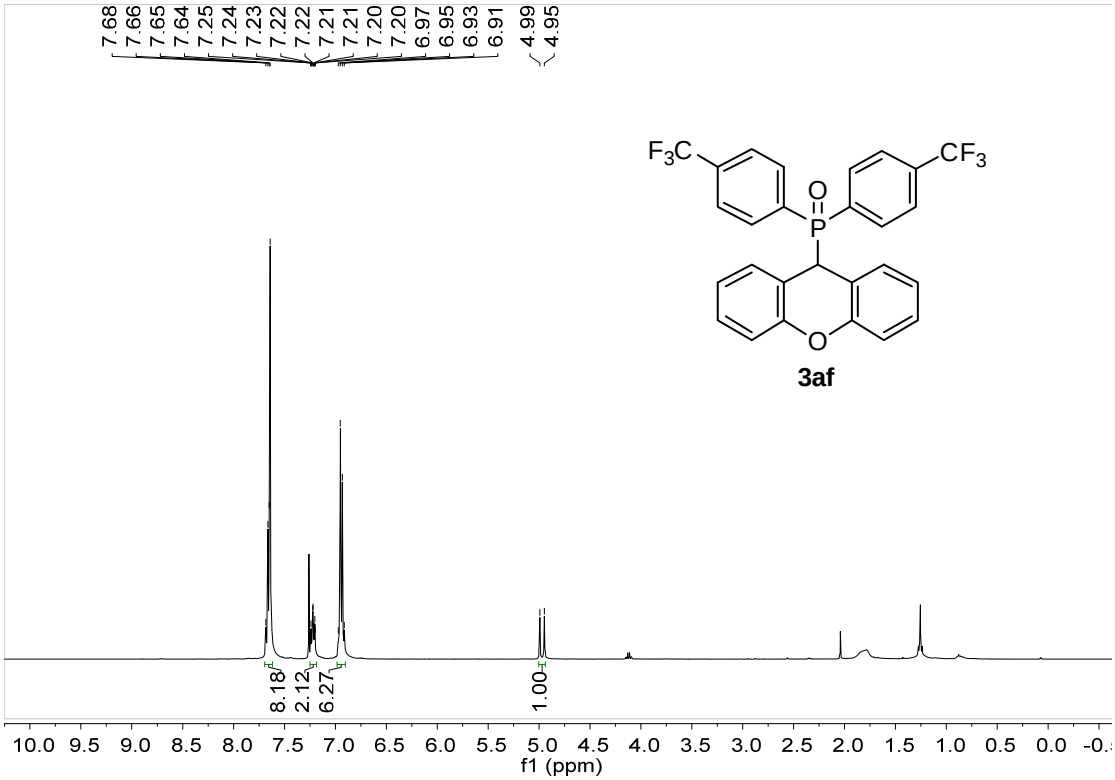
f1 (ppm)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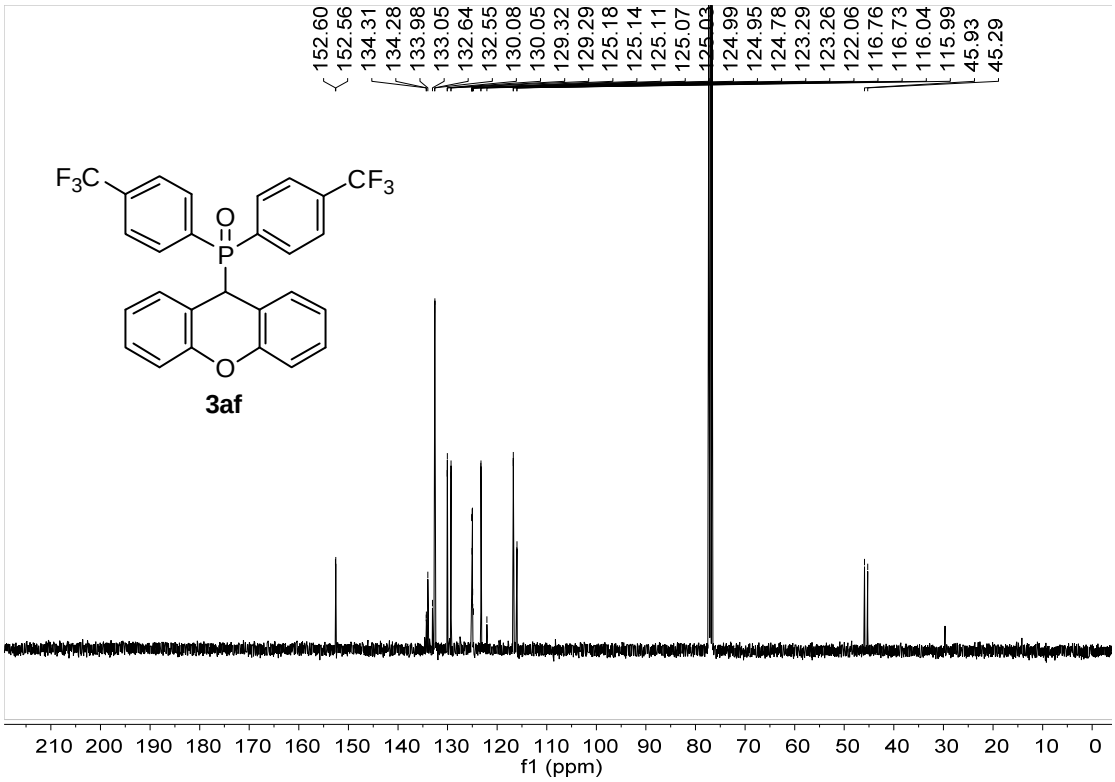
7.20
6.97
6.95
6.93
6.91
4.99
4.95
F3C
CF3
O
P
O
3af
8.18
2.12
6.27
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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152.56
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133.05
132.64
132.55
130.08
130.05
129.32
129.29
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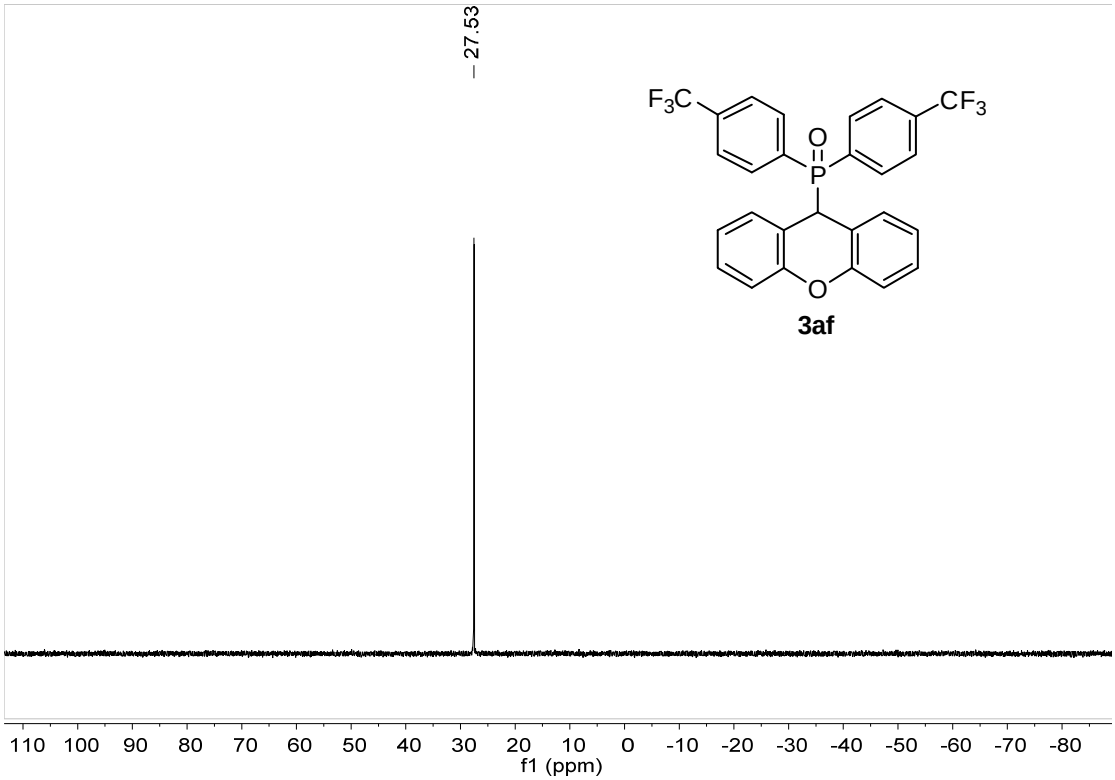
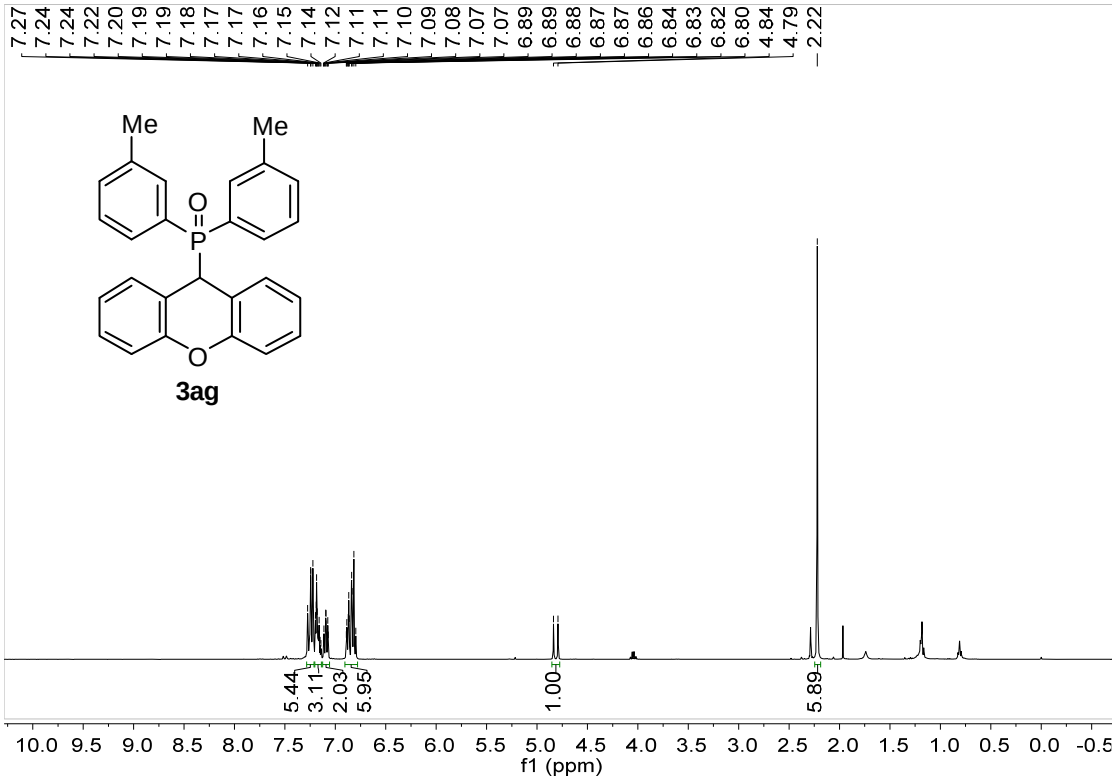
125.14
125.11
125.07
125.03
124.99
124.95
124.78
123.29
123.26
122.06
116.76
116.73
116.04
115.99
45.93
45.29
F3C
CF3
O
P
O
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


27.53
F3C
CF3
O
P
O
3af
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


7.27
7.24
7.24
7.22
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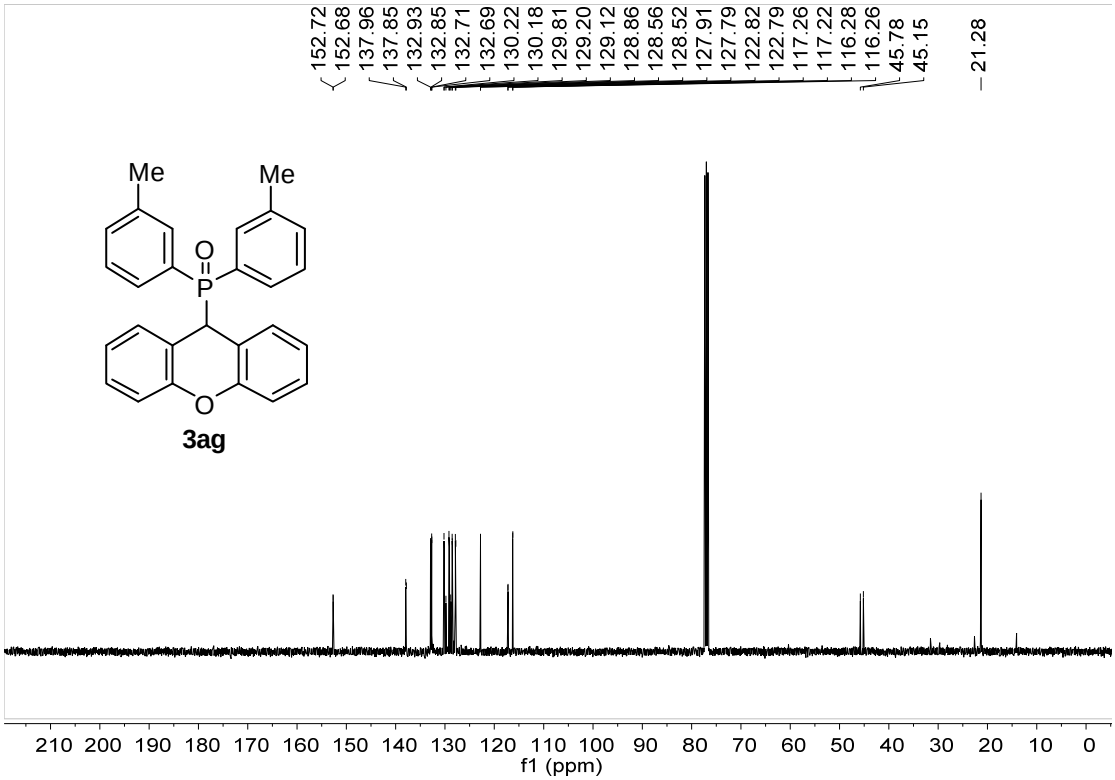
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.12
7.11
7.11
7.10
7.09
7.08
7.07
7.07
6.89
6.89
6.88
6.87
6.87
6.86
6.84
6.83
6.82
6.80
4.84
4.79
2.22
Me
Me
O
P
O
3ag
5.44
3.11
2.03
5.95
1.00
5.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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152.68
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137.85
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132.85
132.71
132.69
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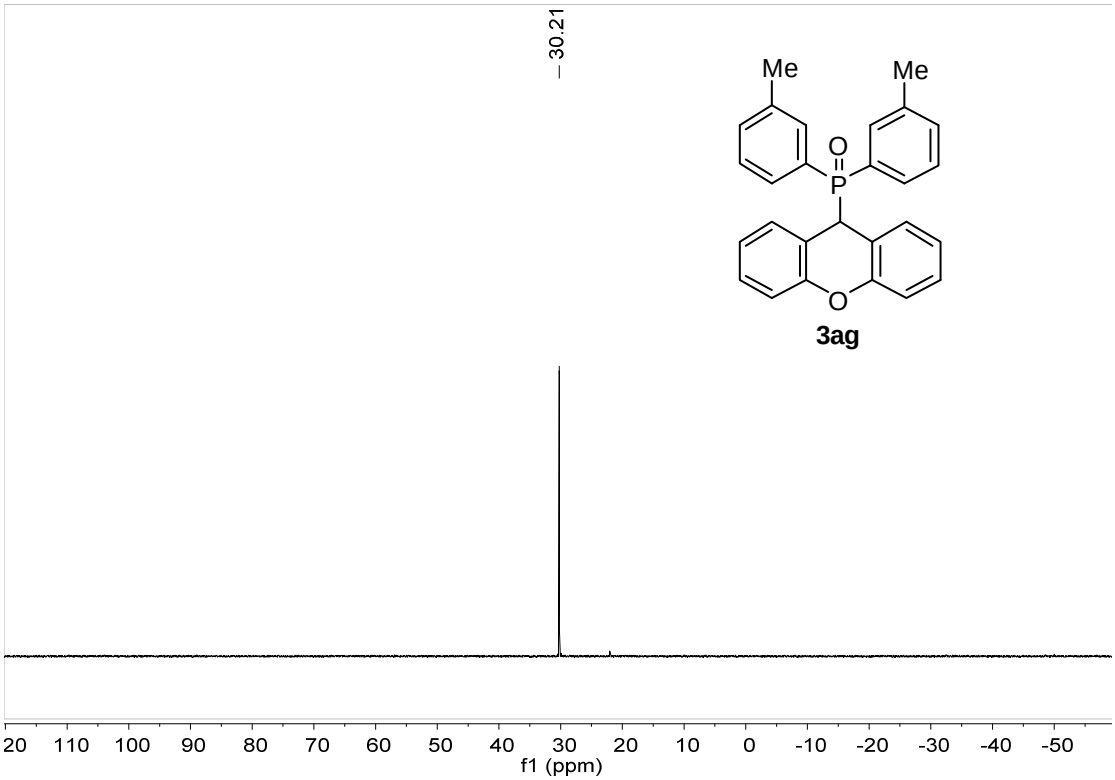
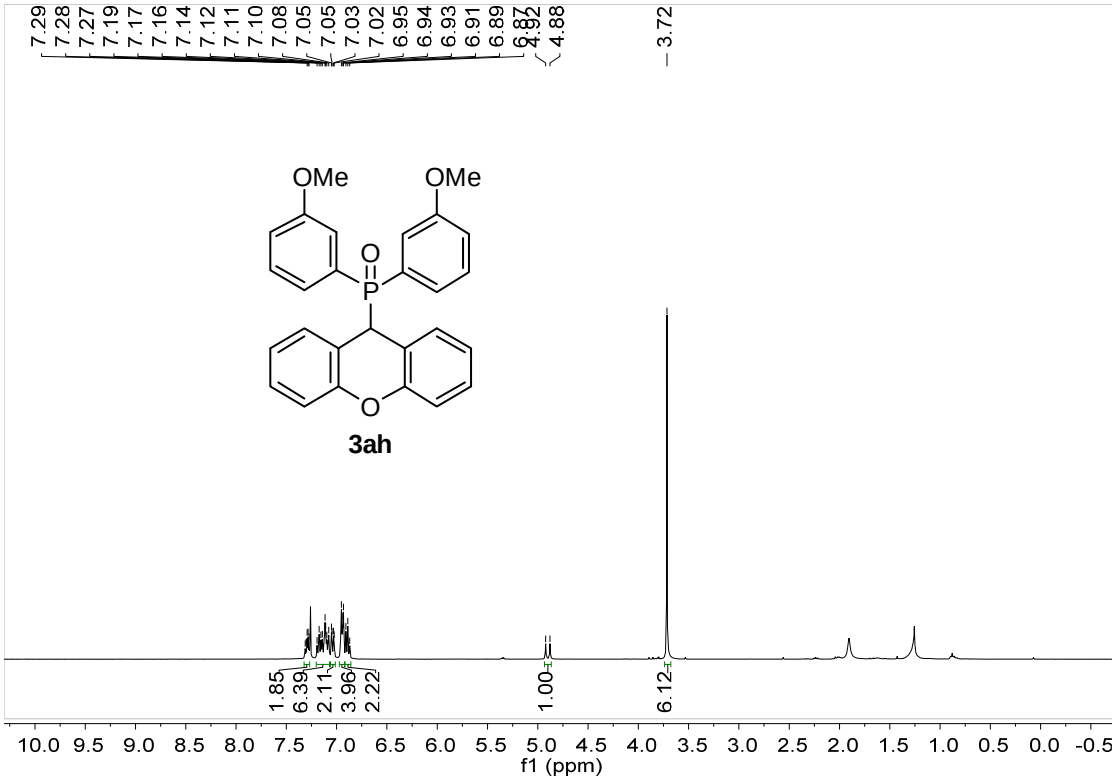
130.18
129.81
129.20
129.12
128.86
128.56
128.52
127.91
127.79
122.82
122.79
117.26
117.22
116.28
116.26
45.78
45.15
21.28
Me
Me
O
P
O
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


30.21
Me
Me
O
P
O
3ag
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)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7.28
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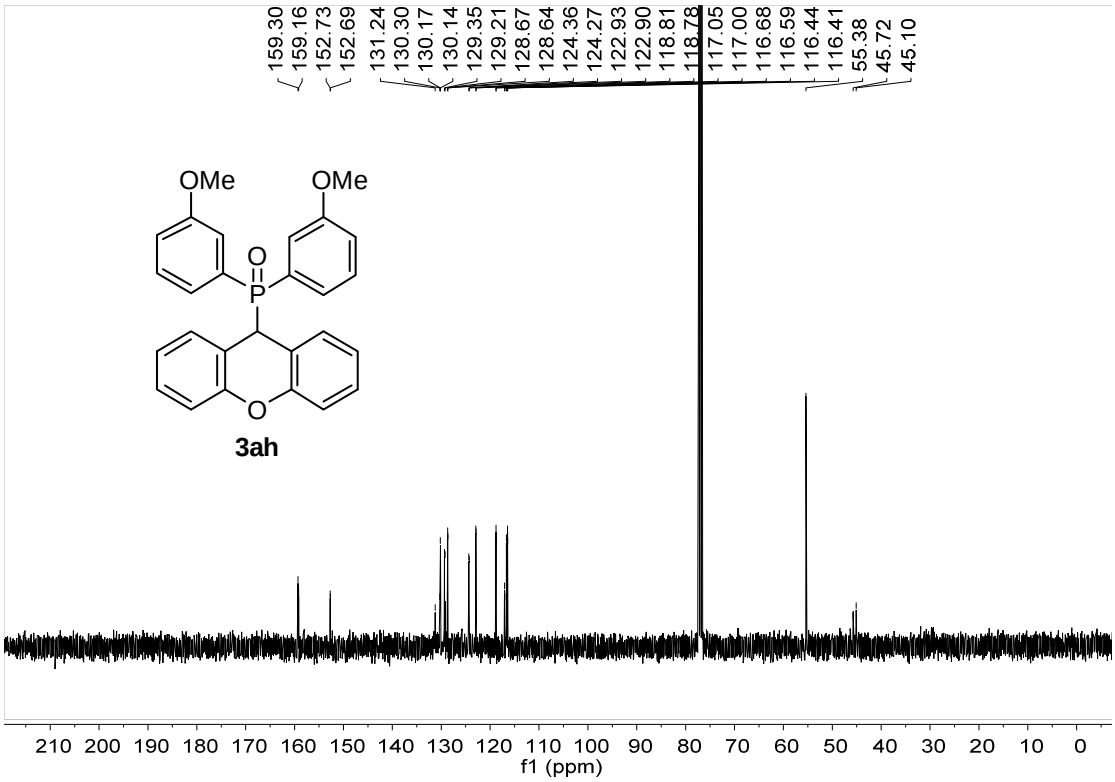
7.16
7.14
7.12
7.11
7.10
7.08
7.05
7.05
7.03
7.02
6.95
6.94
6.93
6.91
6.89
4.92
4.88
3.72
OMe
OMe
O
P
O
3ah
1.85
6.39
2.11
3.96
2.22
1.00
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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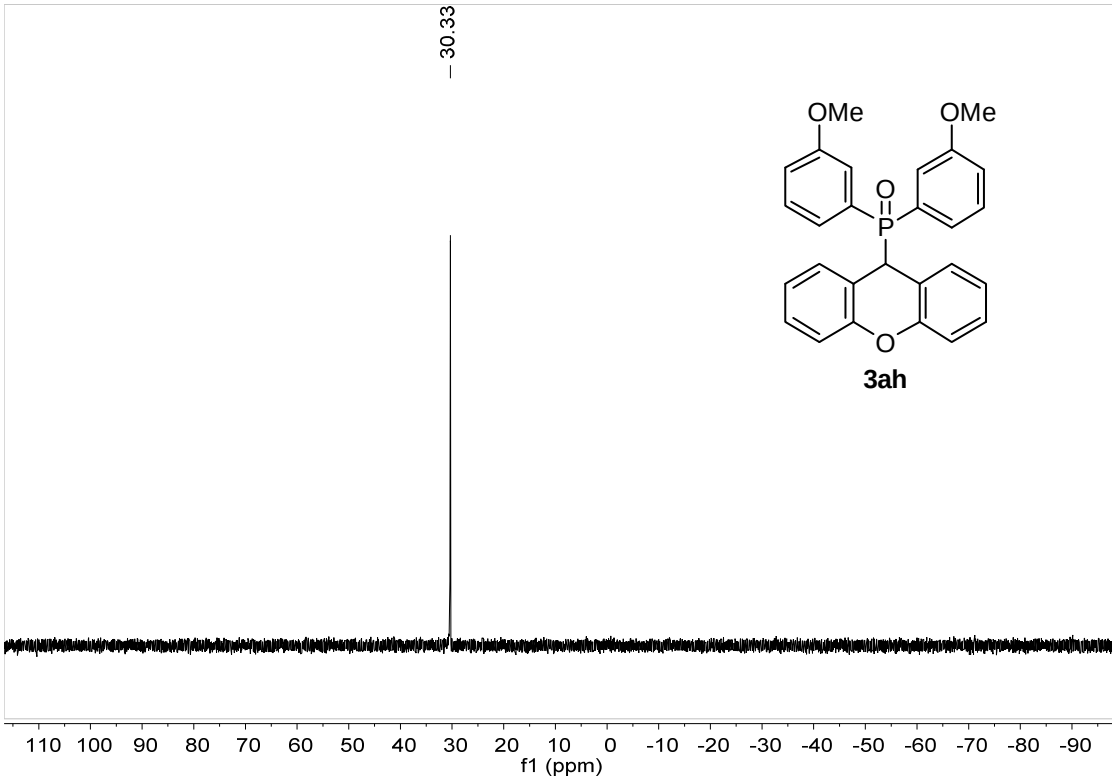
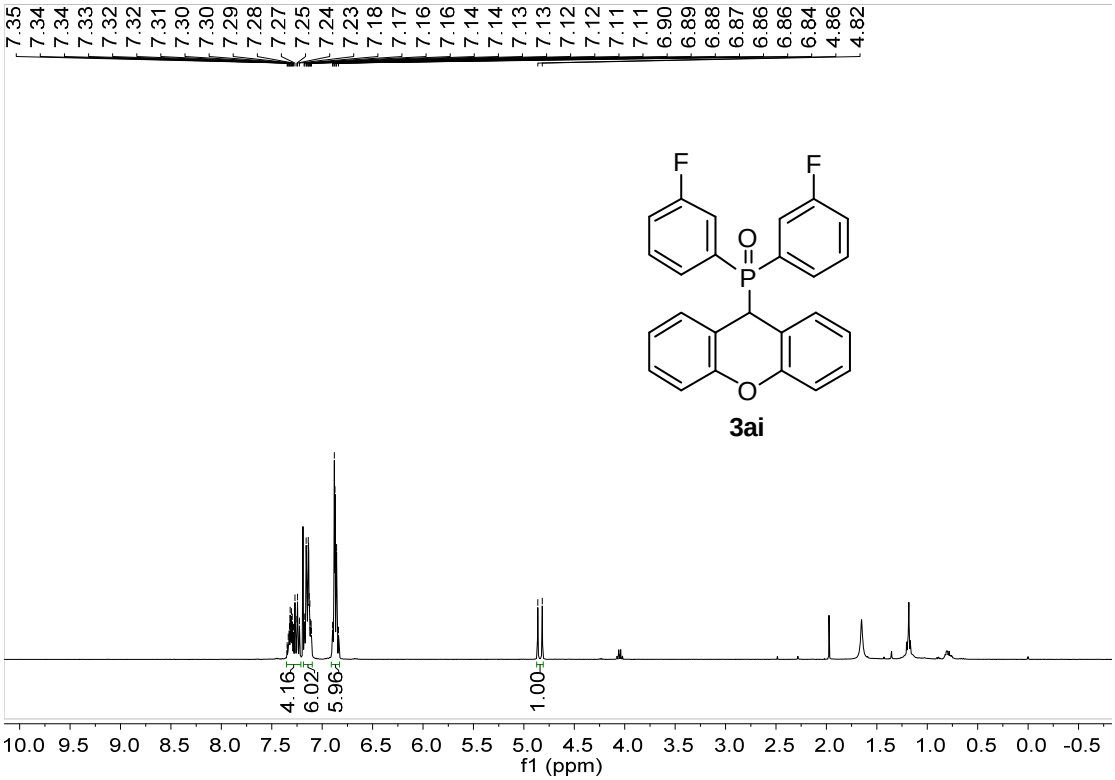
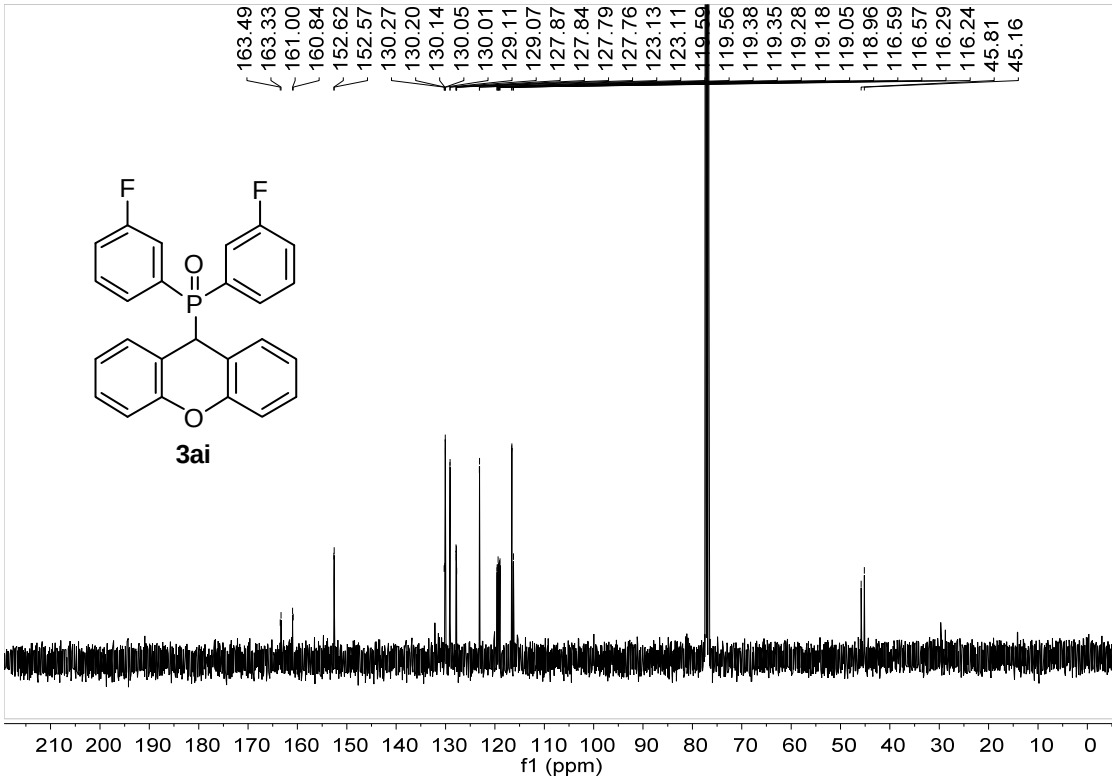
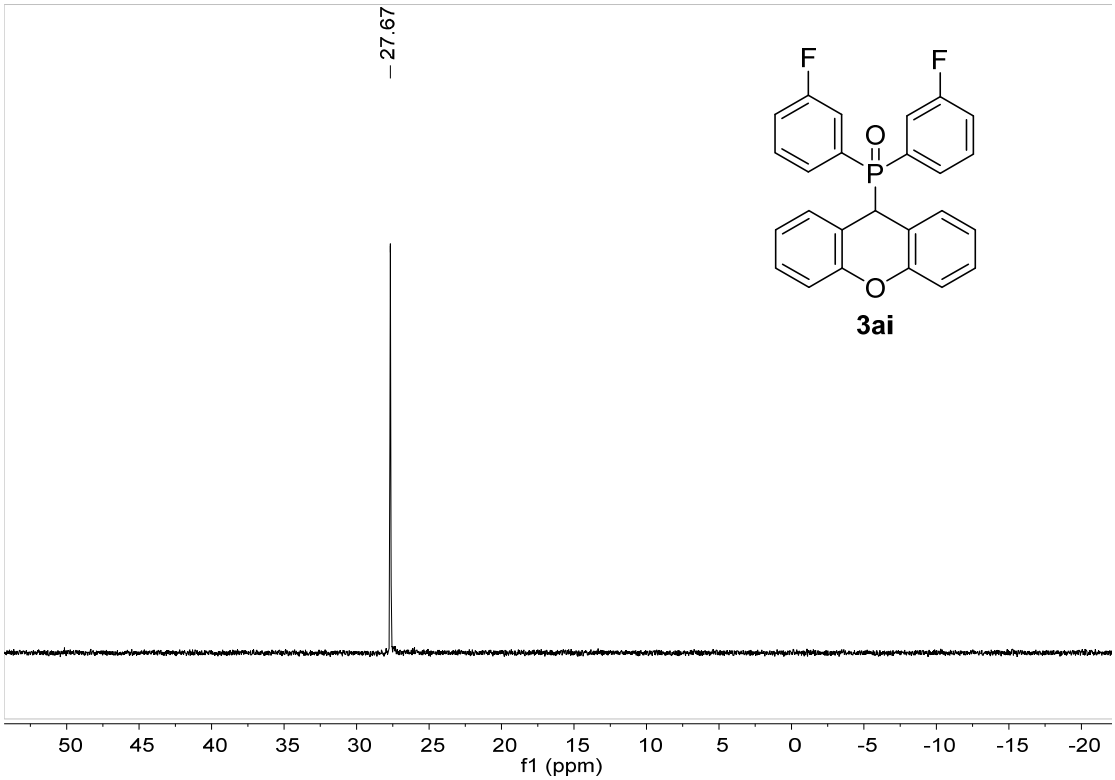
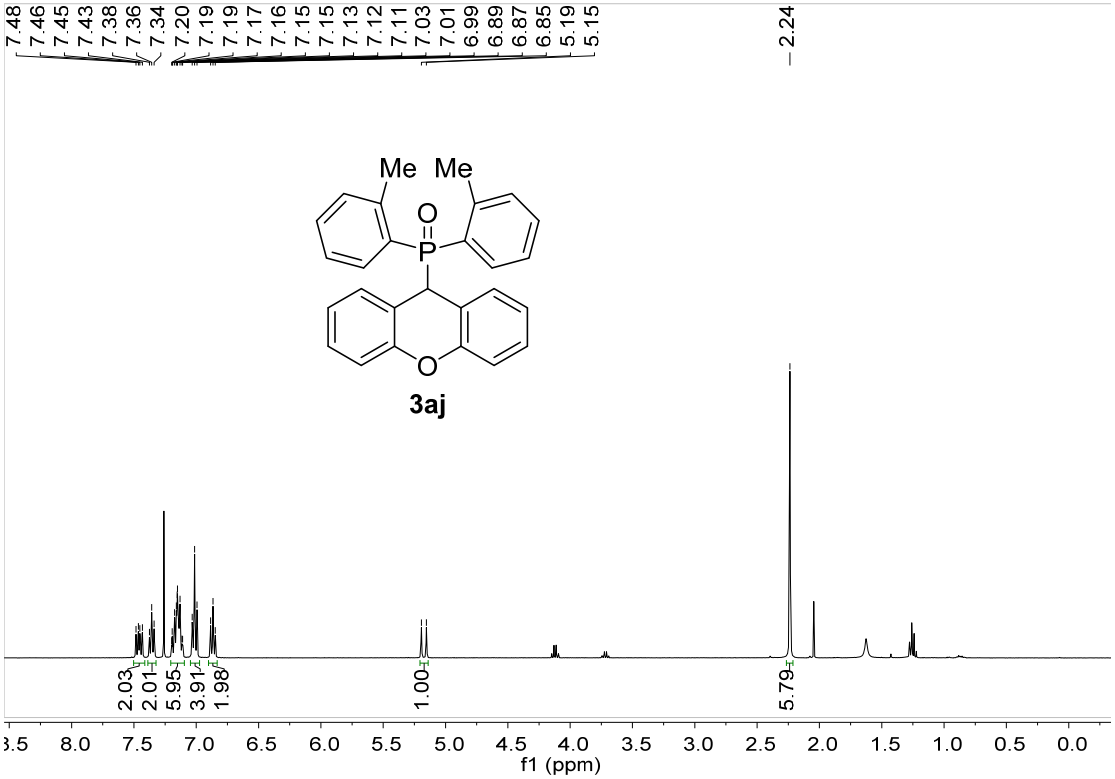
159.16
152.73
152.69
131.24
130.30
130.17
130.14
129.35
129.21
128.67
128.64
124.36
124.27
122.93
122.90
118.81
118.78
117.05
117.00
116.68
116.59
116.44
116.41
55.38
45.72
45.10
OMe
OMe
O
P
O
3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

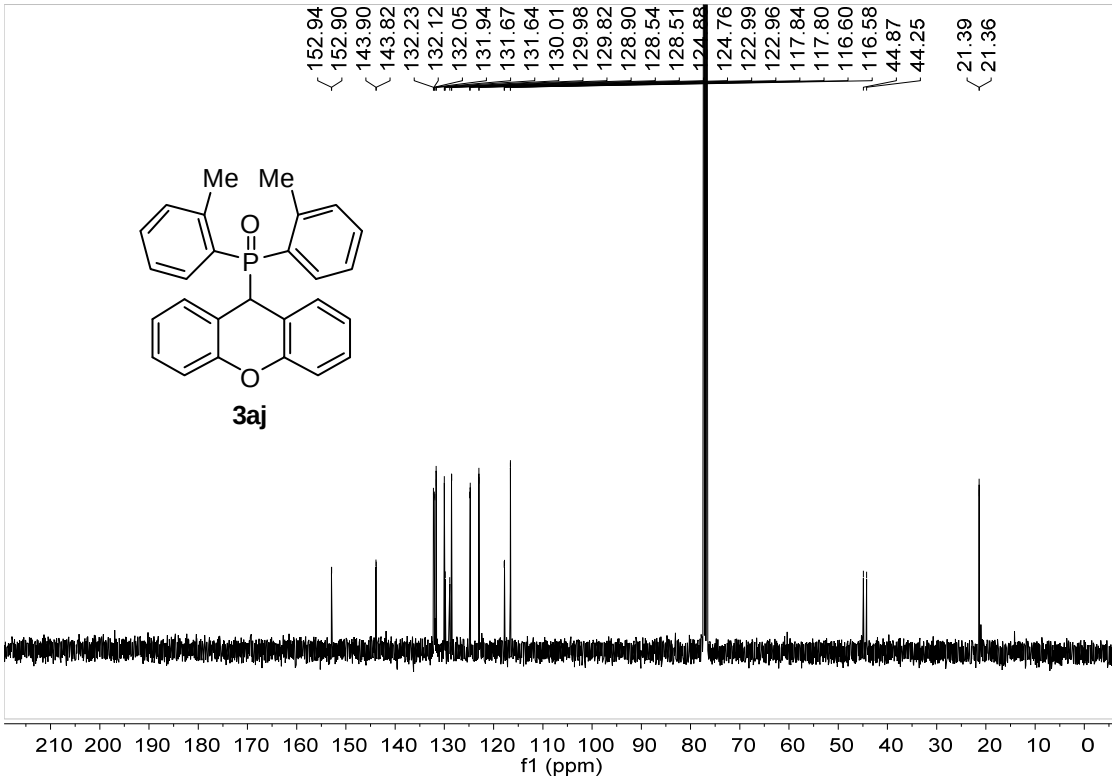

30.33
OMe
OMe
O
P
O
3ah
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.25 7.24 7.23 7.18 7.17 7.16 7.16 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.11 6.90 6.89 6.88 6.87 6.86 6.86 6.84 4.86 4.82
F
F
O
P
O
3ai
4.16
6.02
5.96
1.00
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)


163.49 163.33 161.00 160.84 152.62 152.57 130.27 130.20 130.14 130.05 130.01 129.11 129.07 127.87 127.84 127.79 127.76 123.13 123.11 119.59 119.56 119.38 119.35 119.28 119.18 119.05 118.96 116.59 116.57 116.29 116.24 45.81 45.16
F
F
O
P
O
3ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


27.67
F
F
O
P
O
3ai
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)


7.48
7.46
7.45
7.43
7.38
7.36
7.34
7.20
7.19
7.19
7.17
7.16
7.15
7.15
7.13
7.12
7.11
7.03
7.01
6.99
6.89
6.87
6.85
5.19
5.15
2.24
Me Me
O
P
O
3aj
2.03
2.01
5.95
3.91
1.98
1.00
5.79
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)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152.90
143.90
143.82
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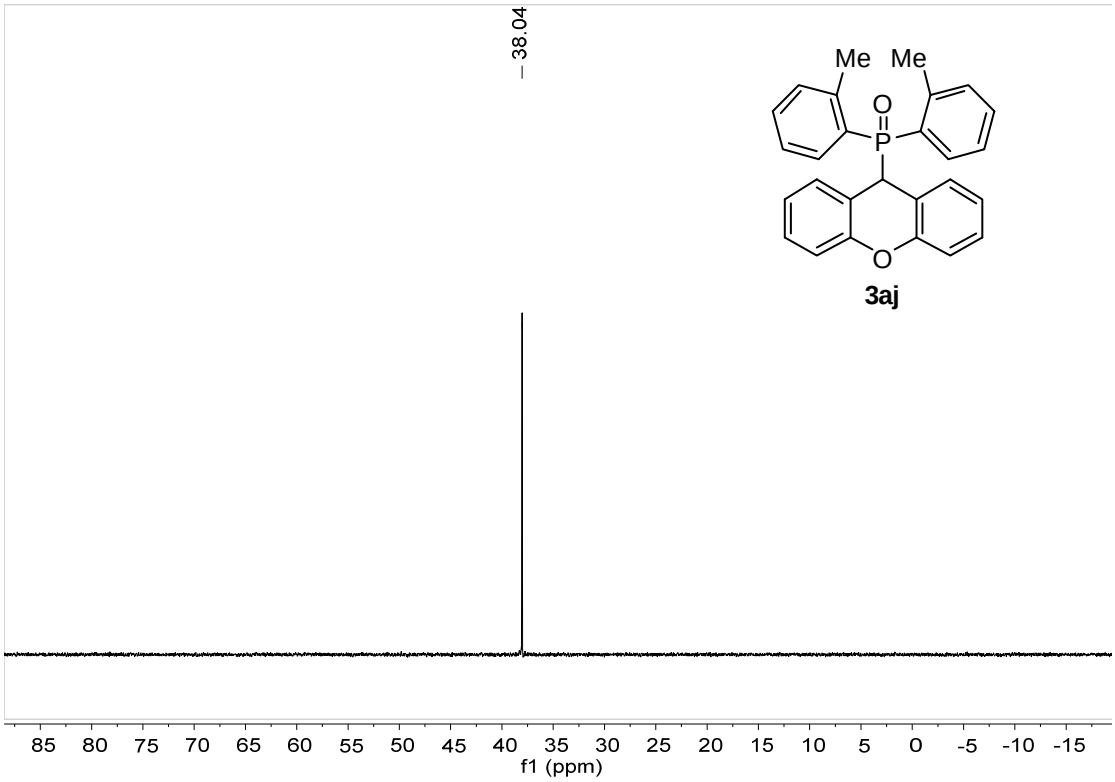
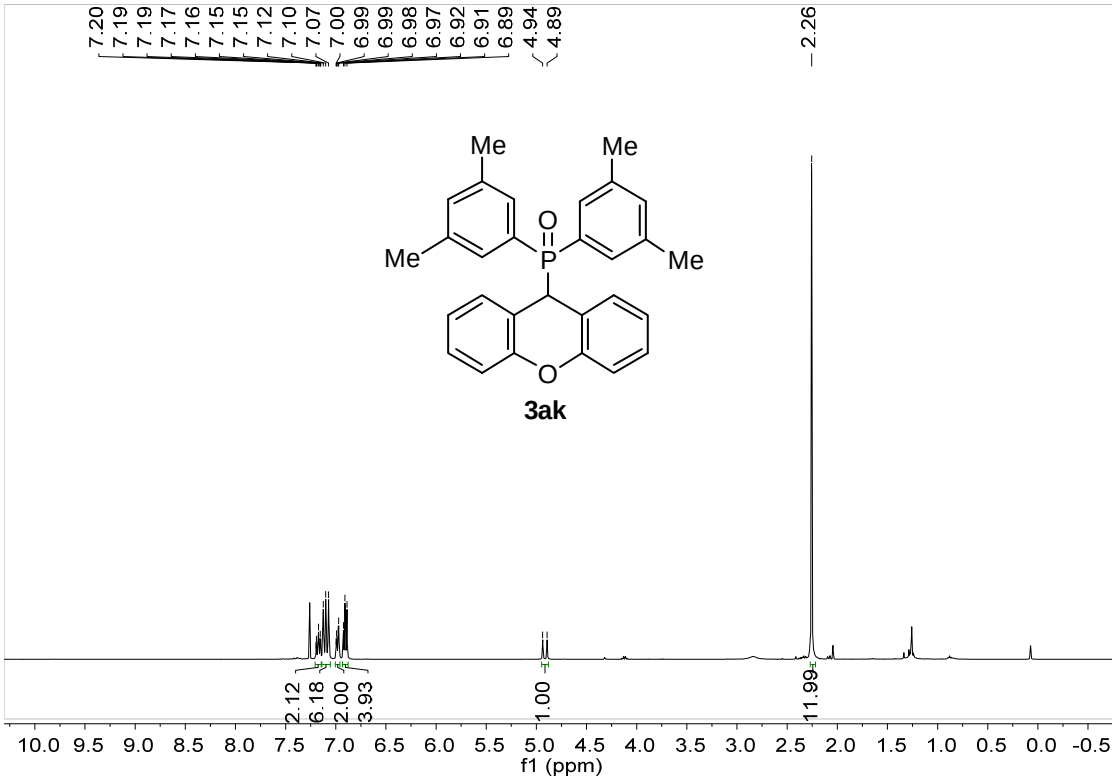
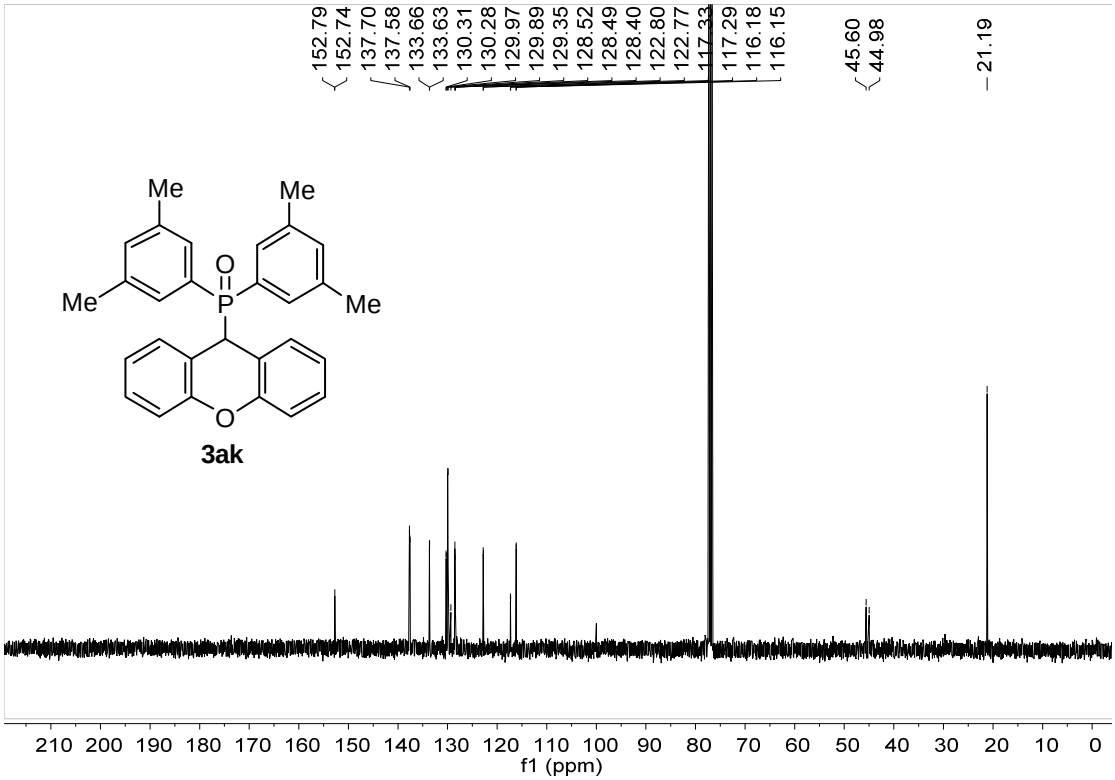
132.12
132.05
131.94
131.67
131.64
130.01
129.98
129.82
128.90
128.54
128.51
124.88
124.76
122.99
122.96
117.84
117.80
116.60
116.58
44.87
44.25
21.39
21.36
Me Me
O
P
O
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


38.04
Me Me
O
P
O
3aj
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)


7.20
7.19
7.19
7.17
7.16
7.15
7.15
7.12
7.10
7.07
7.00
6.99
6.99
6.98
6.97
6.92
6.91
6.89
4.94
4.89
2.26
Me
Me
Me
Me
O
P
O
3ak
2.12
6.18
2.00
3.93
1.00
11.99
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)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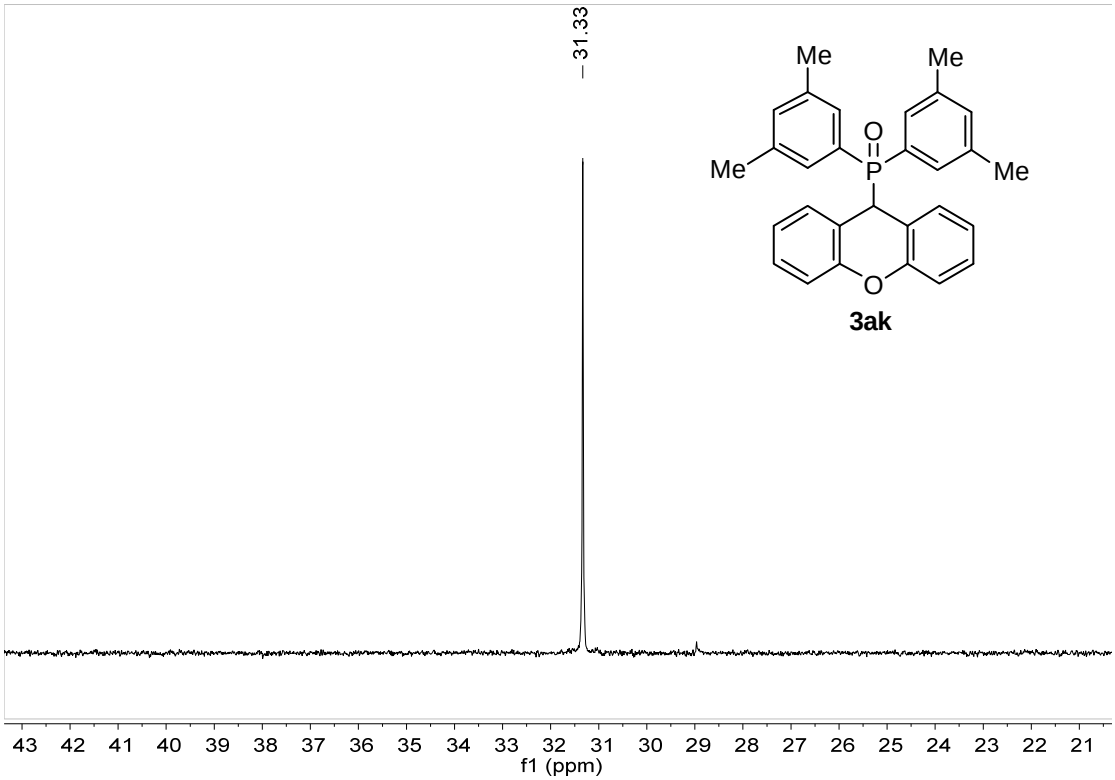
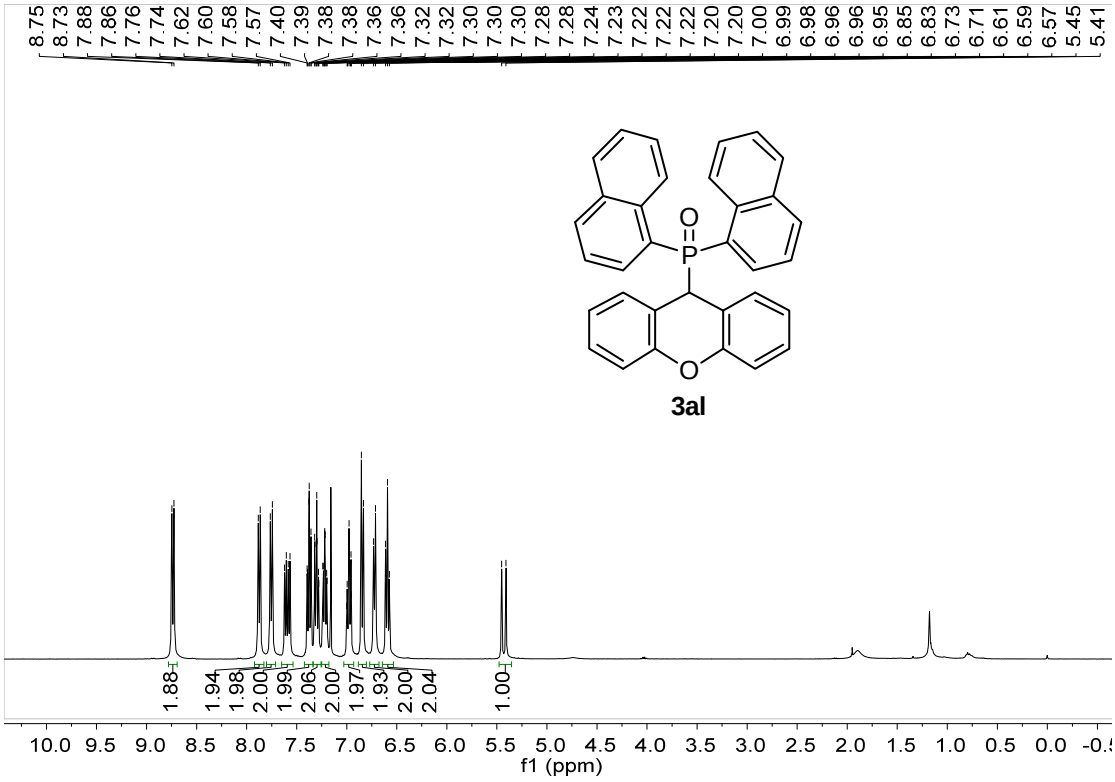
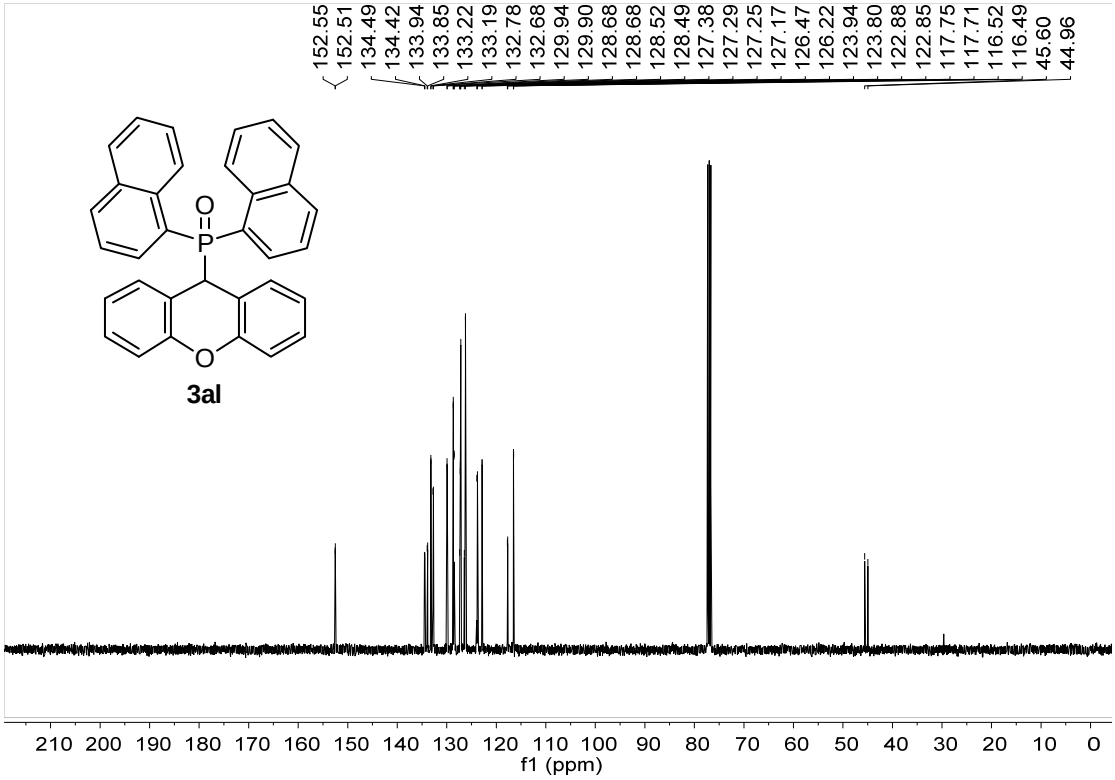
129.89
129.35
128.52
128.49
128.40
122.80
122.77
117.33
117.29
116.18
116.15
45.60
44.98
21.19
Me
Me
Me
Me
O
P
O
3ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


31.33
Me
Me
Me
Me
O
P
O
3ak
43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21
f1 (ppm)


8.75 8.73 7.88 7.86 7.76 7.74 7.62 7.60 7.58 7.57 7.40 7.39 7.38 7.38 7.36 7.36 7.32 7.32 7.30 7.30 7.28 7.28 7.24 7.23 7.22 7.22 7.20 7.20 7.00 6.99 6.98 6.96 6.96 6.95 6.85 6.83 6.73 6.71 6.61 6.59 6.57 5.45 5.41
O
P
O
3al
1.88 1.94 1.98 2.00 1.99 2.06 2.00 1.97 1.93 2.00 2.04 1.00
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)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132.68
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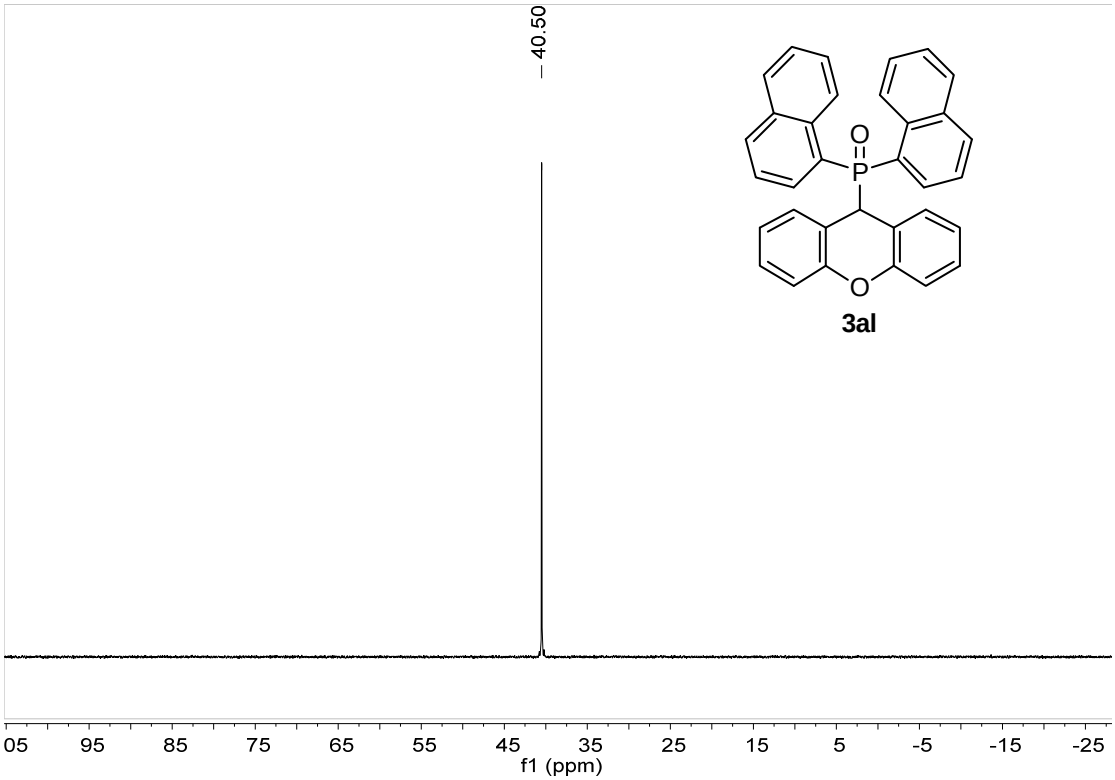
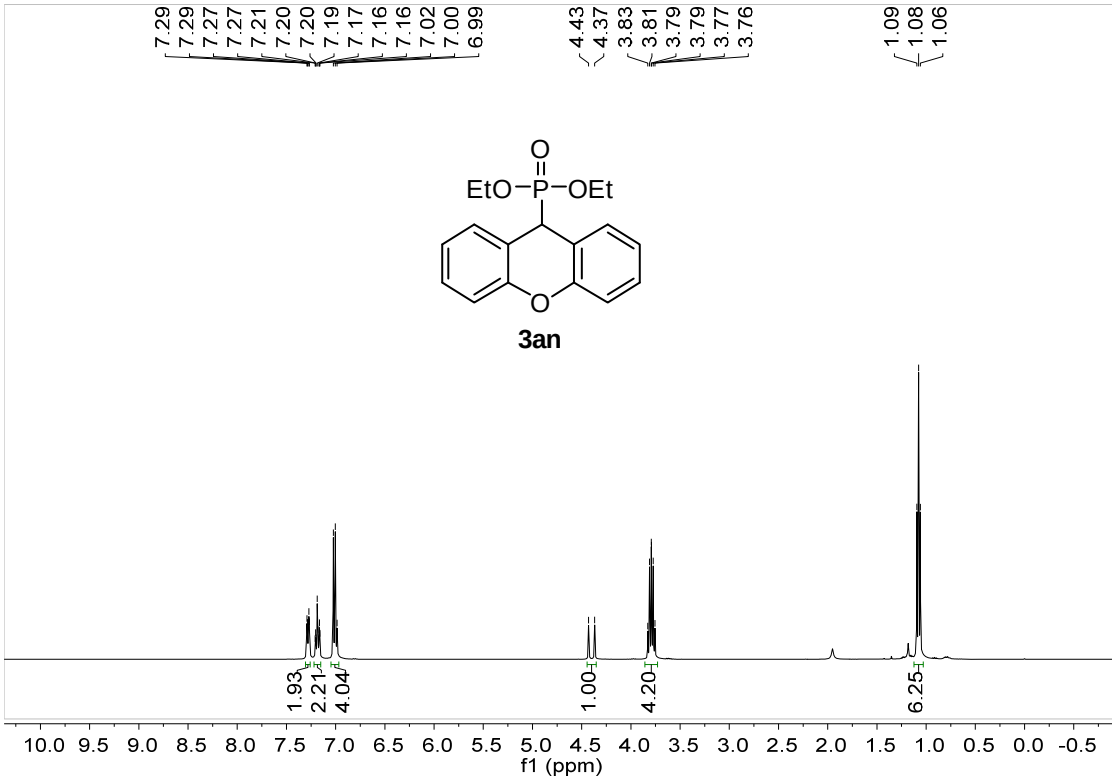
129.90
128.68
128.68
128.52
128.49
127.38
127.29
127.25
127.17
126.47
126.22
123.94
123.80
122.88
122.85
117.75
117.71
116.52
116.49
45.60
44.96
O
P
O
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


40.50
O
P
O
3al
05 95 85 75 65 55 45 35 25 15 5 -5 -15 -25
f1 (ppm)


7.29
7.29
7.27
7.27
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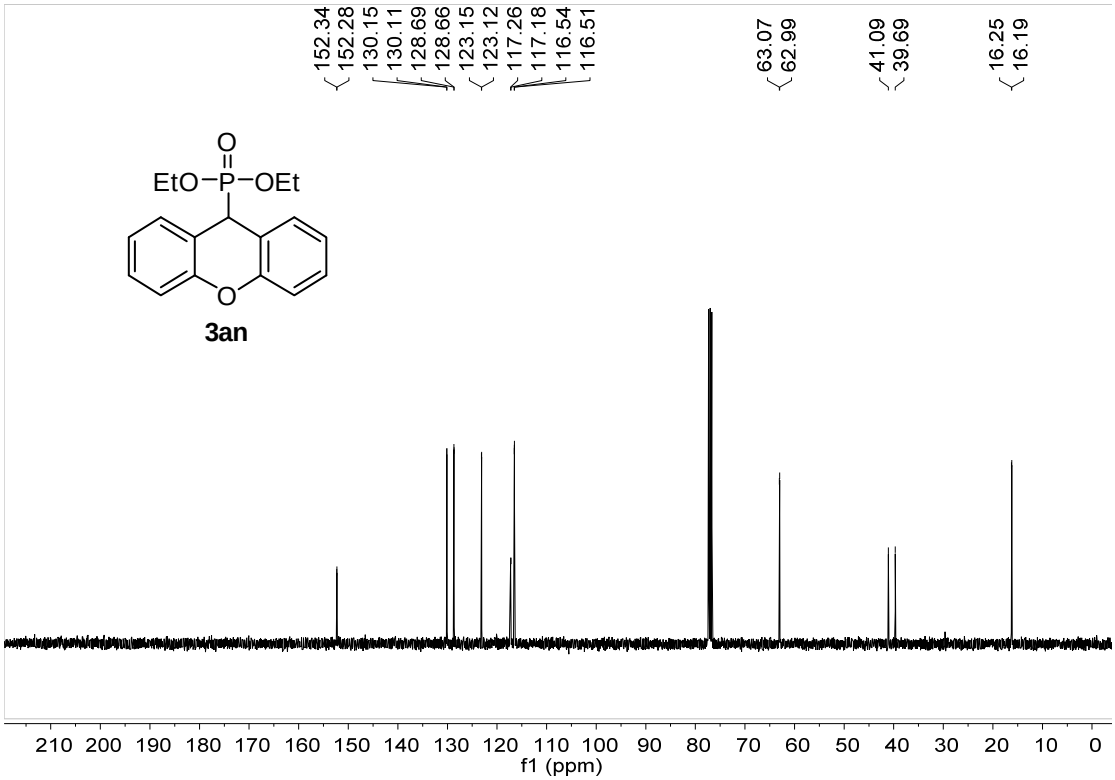
7.20
7.20
7.19
7.17
7.16
7.16
7.02
7.00
6.99
4.43
4.37
3.83
3.81
3.79
3.79
3.77
3.76
1.09
1.08
1.06
O
EtO−P−OEt
O
3an
1.93
2.21
4.04
1.00
4.20
6.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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130.11
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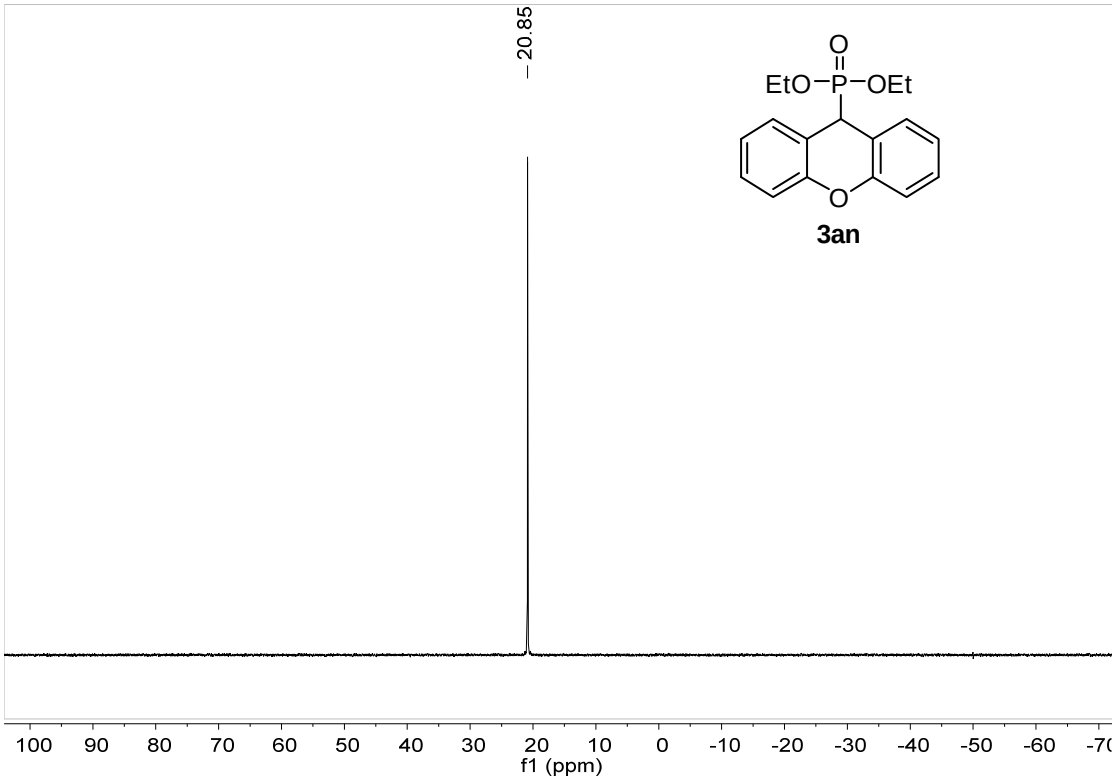
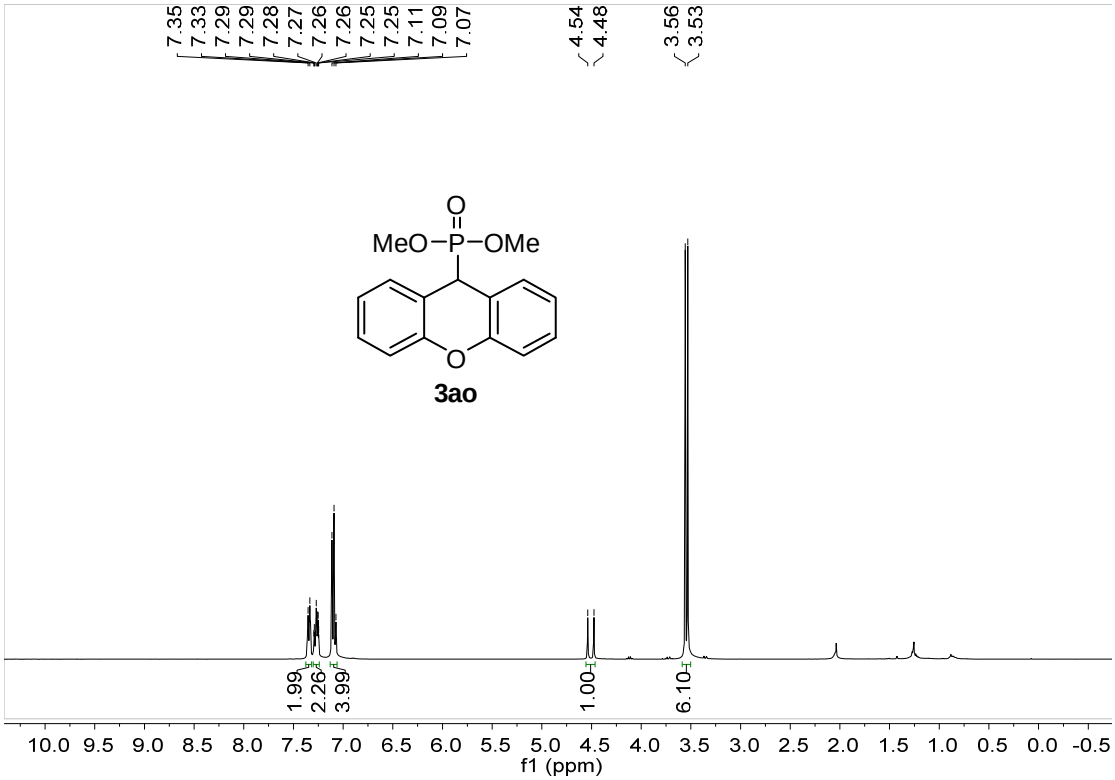
128.66
123.15
123.12
117.26
117.18
116.54
116.51
63.07
62.99
41.09
39.69
16.25
16.19
O
EtO−P−OEt
O
3an
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


20.85
EtO−P−OEt
O
O
3an
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)


7.35
7.33
7.29
7.29
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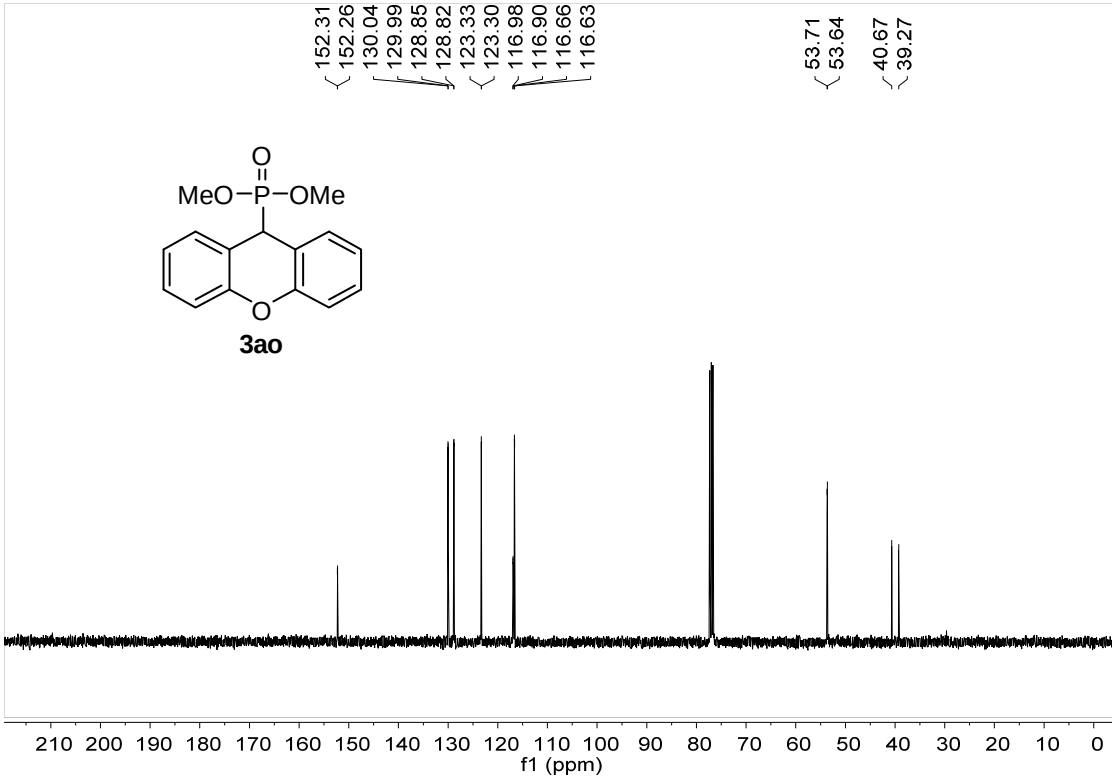
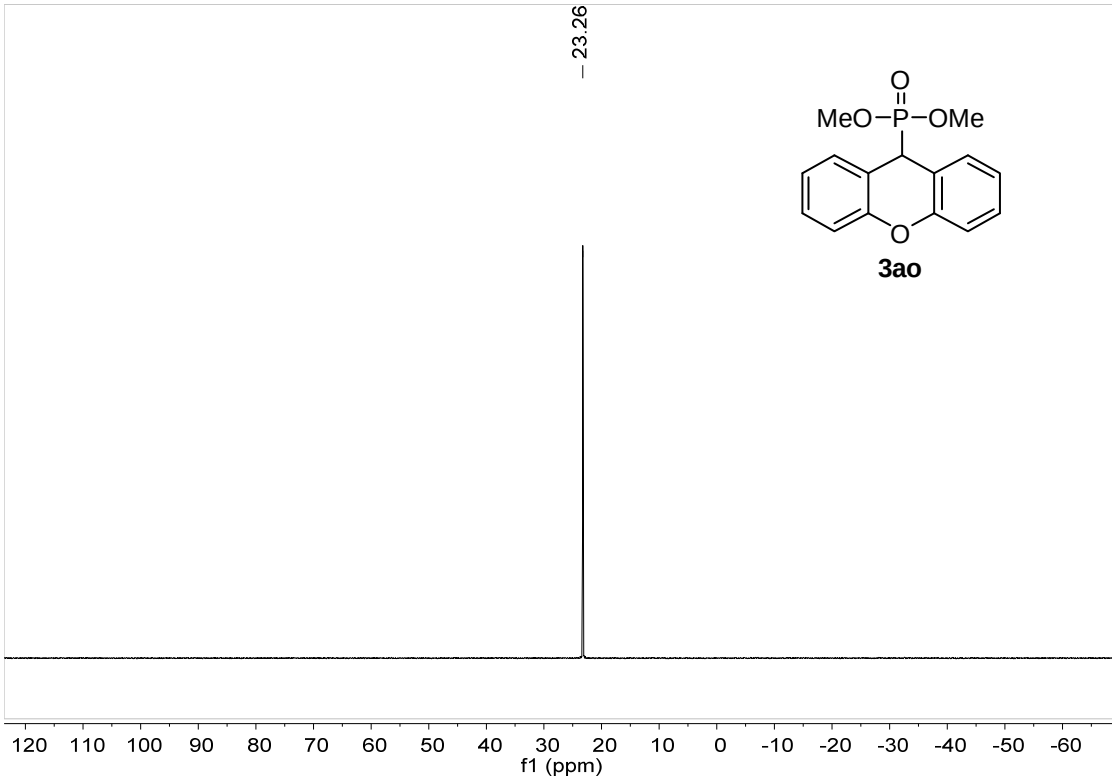
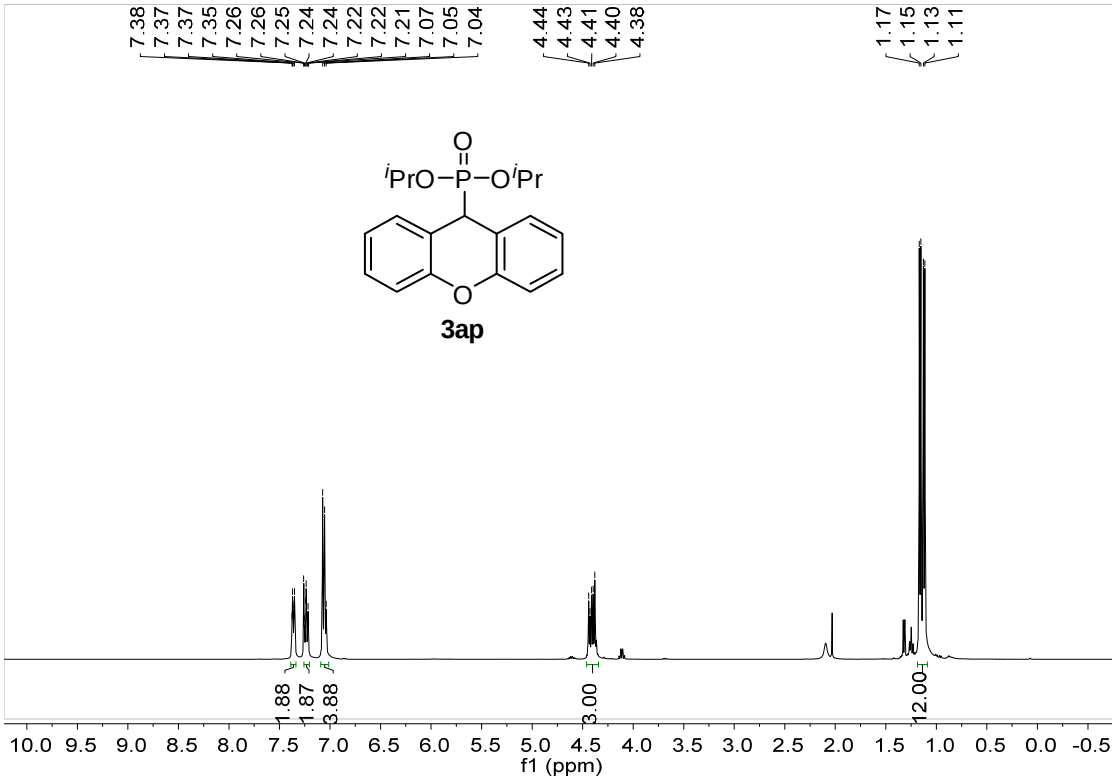
7.27
7.26
7.26
7.25
7.25
7.11
7.09
7.07
4.54
4.48
3.56
3.53
MeO−P−OMe
O
O
3ao
1.99
2.26
3.99
1.00
6.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.31
152.26
130.04
129.99
128.85
128.82
123.33
123.30
116.98
116.90
116.66
116.63
53.71
53.64
40.67
39.27
O
MeO–P–OMe
O
3ao
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23.26
O
MeO–P–OMe
O
3ao
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)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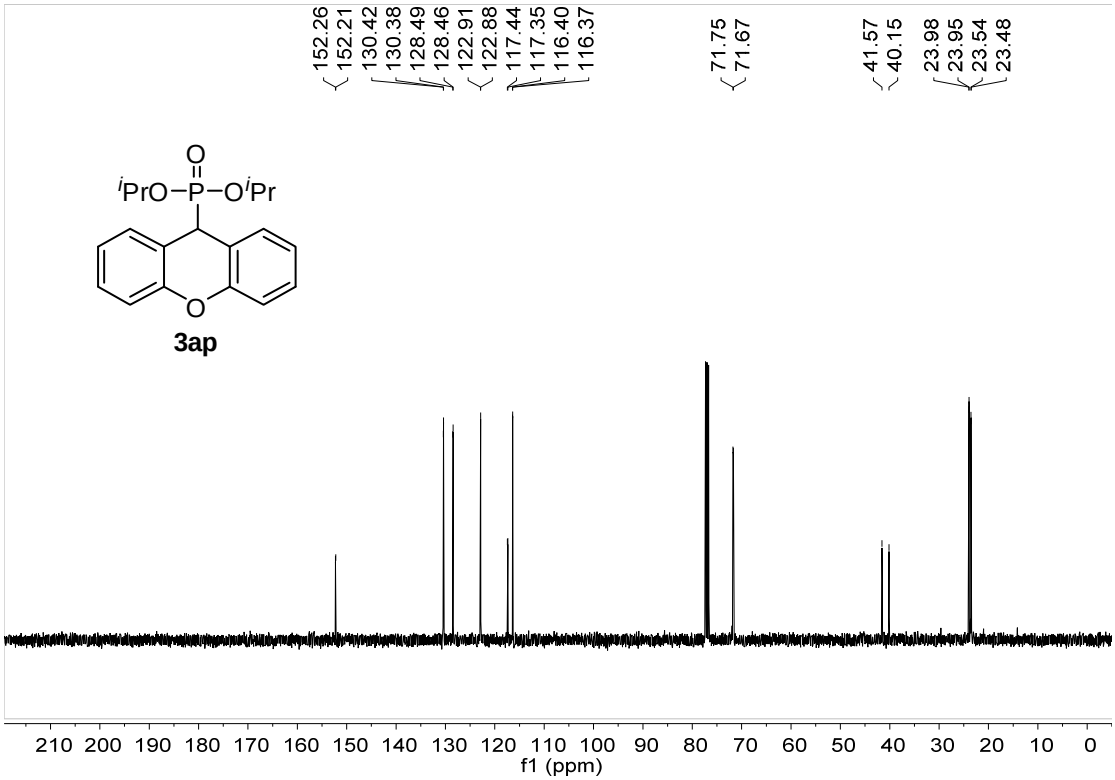
7.26
7.25
7.24
7.24
7.22
7.22
7.21
7.07
7.05
7.04
4.44
4.43
4.41
4.40
4.38
1.17
1.15
1.13
1.11
O
iPrO–P–OiPr
O
3ap
1.88
1.87
3.88
3.00
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.88
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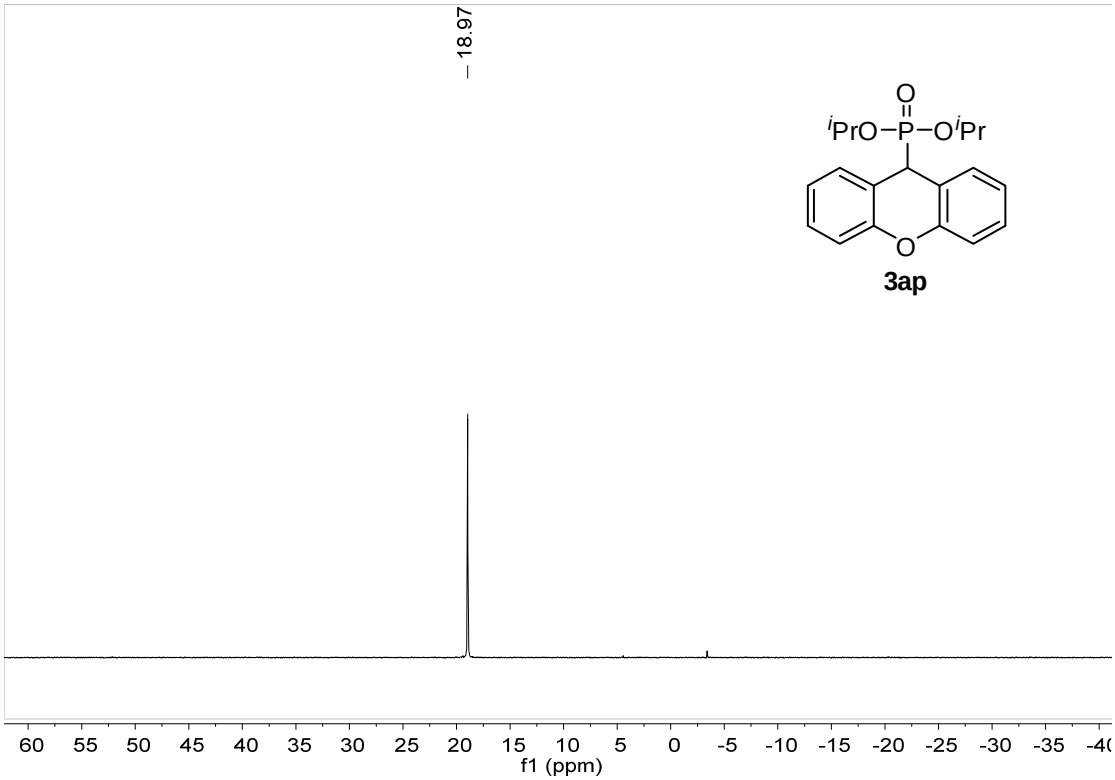
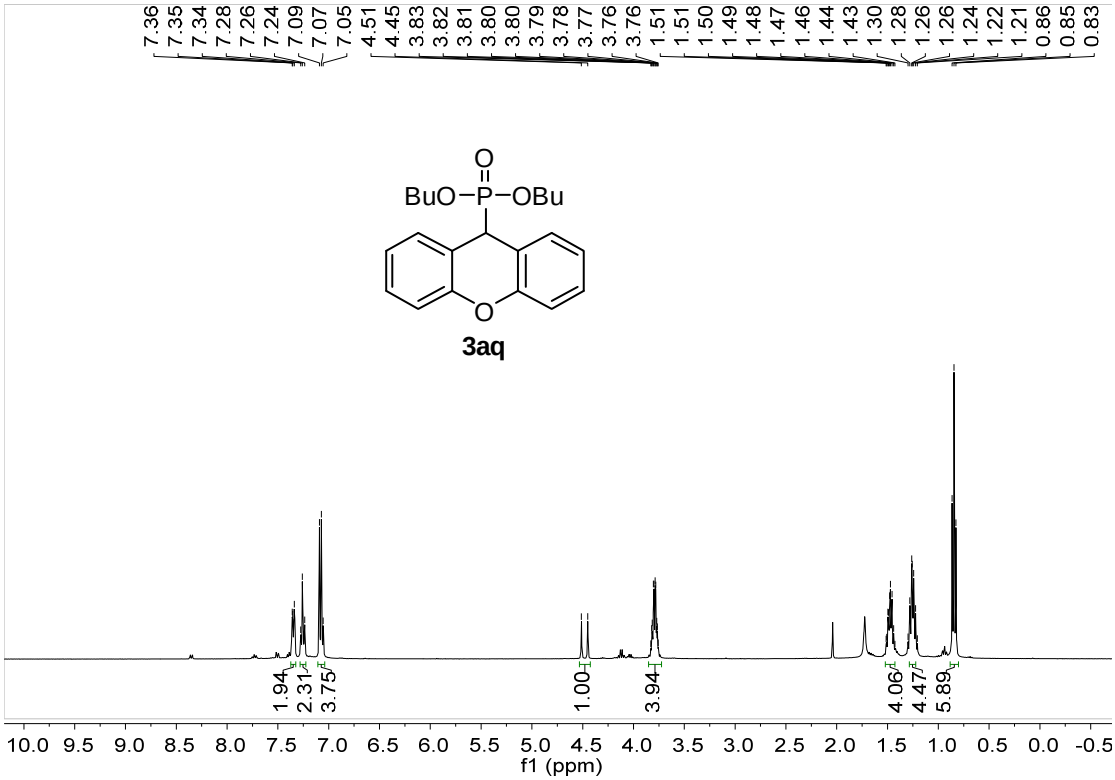
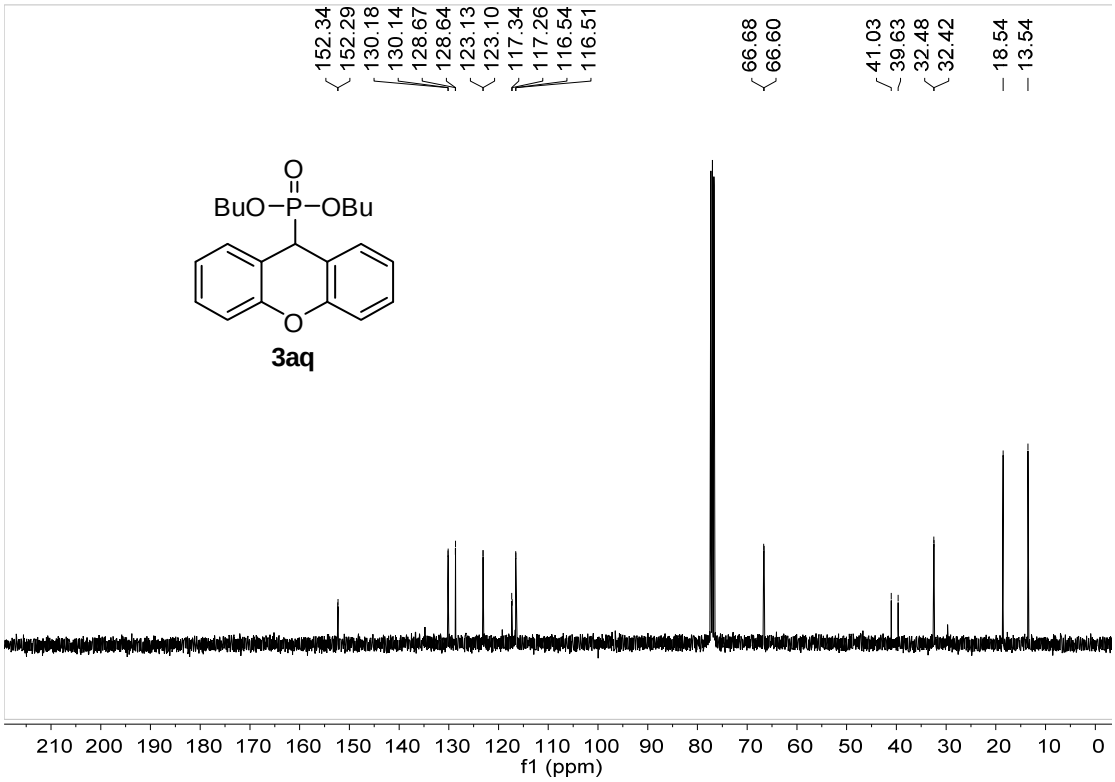
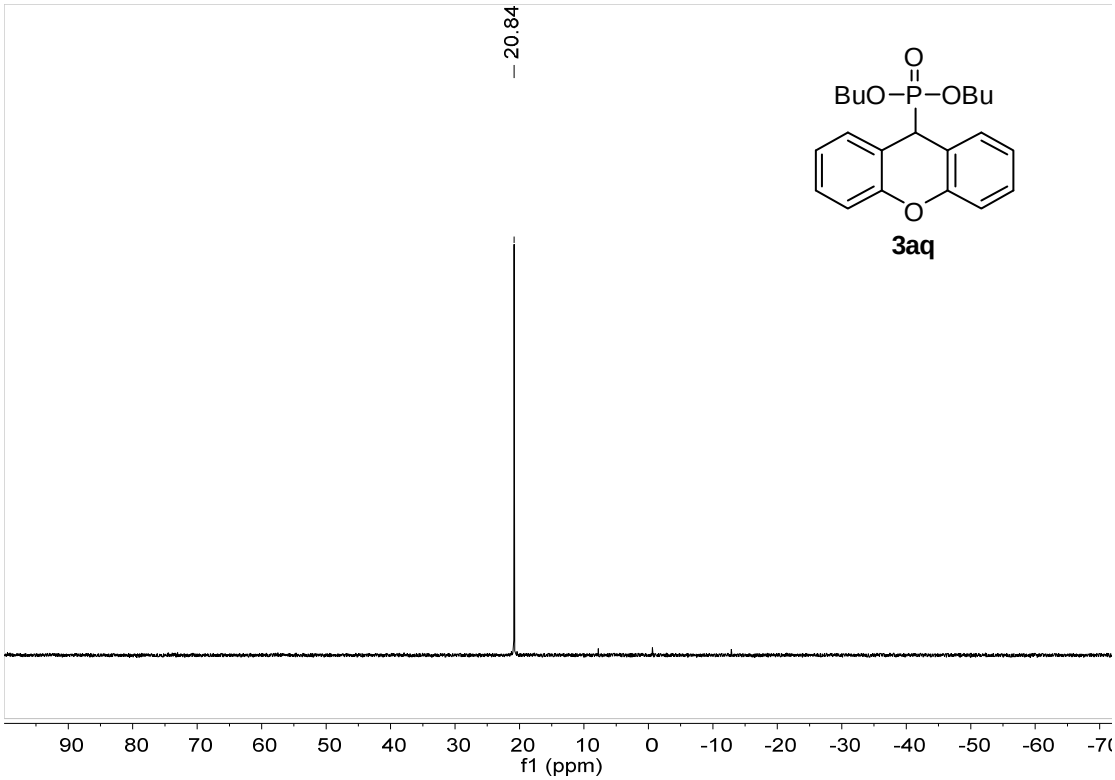
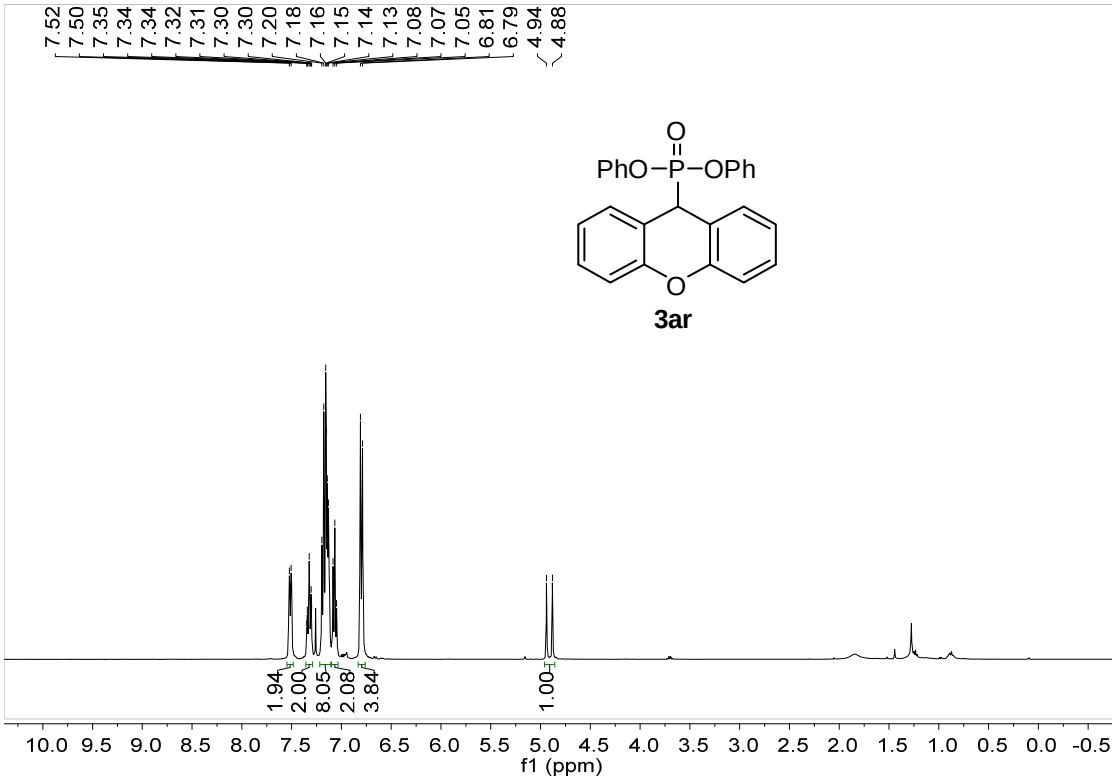
117.35
116.40
116.37
71.75
71.67
41.57
40.15
23.98
23.95
23.54
23.48
O
iPrO–P–OiPr
O
3ap
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

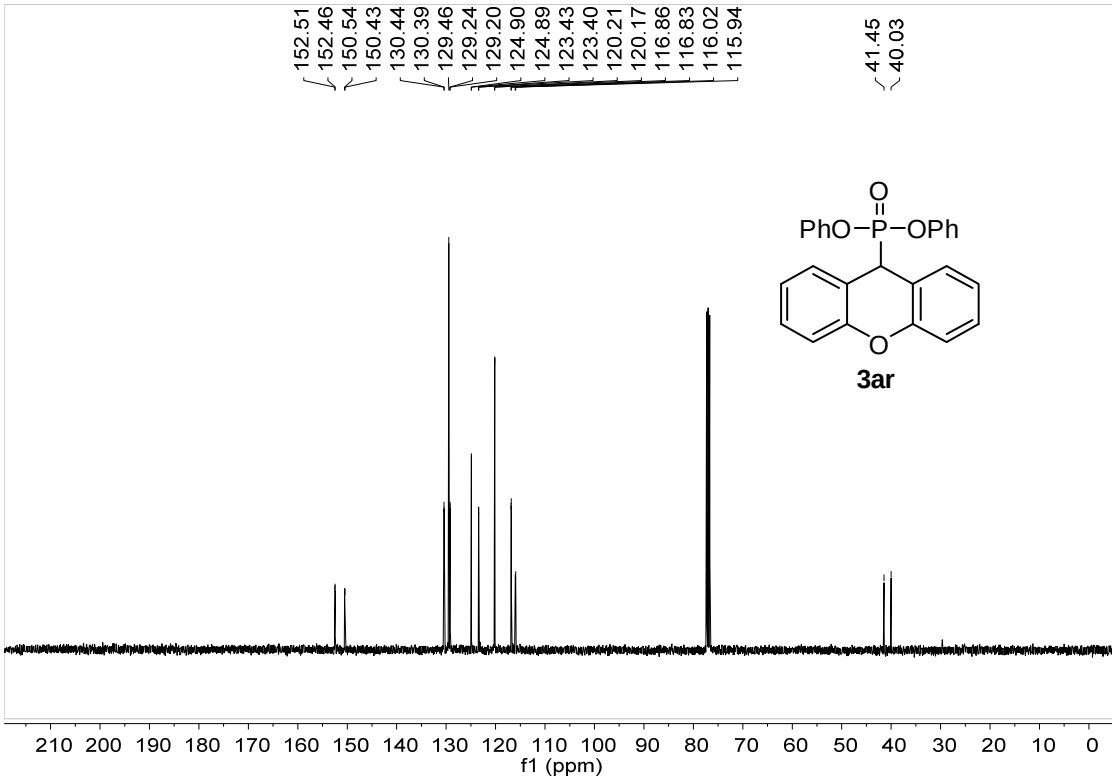

18.97
O
iPrO–P–OiPr
O
3ap
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

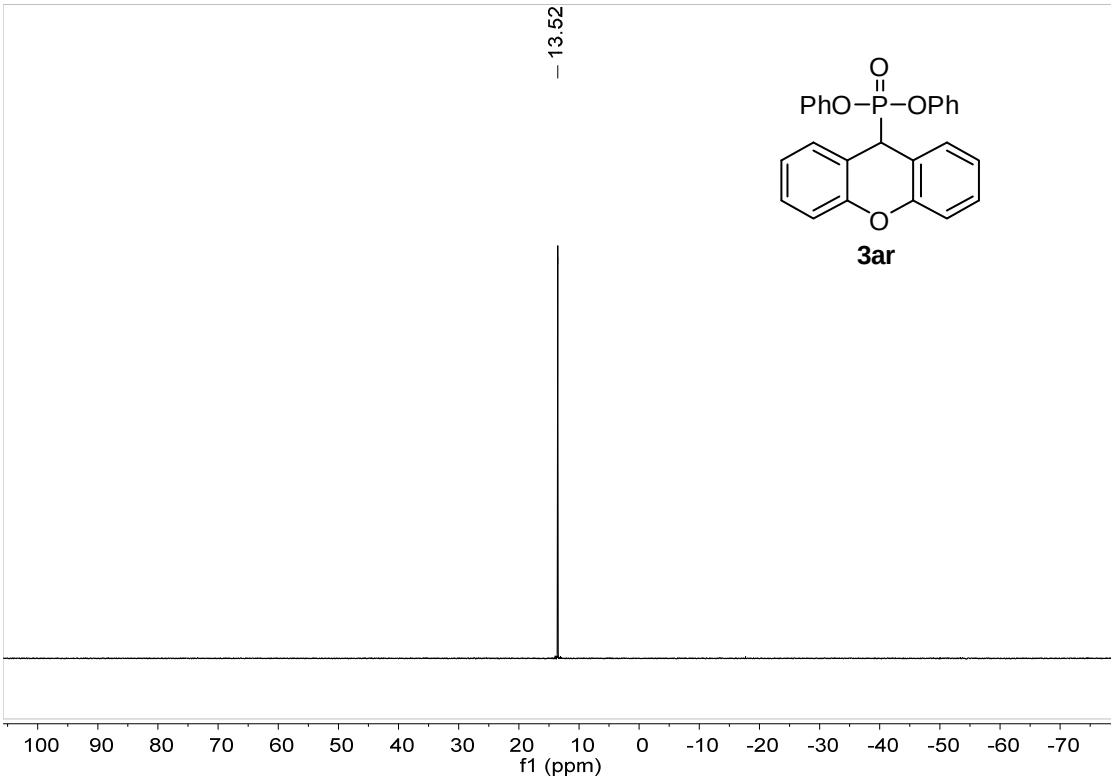

7.36 7.35 7.34 7.28 7.26 7.24 7.09 7.07 7.05 4.51 4.45 3.83 3.82 3.81 3.80 3.80 3.79 3.78 3.77 3.76 3.76 1.51 1.51 1.50 1.49 1.48 1.47 1.46 1.44 1.43 1.30 1.28 1.26 1.26 1.24 1.22 1.21 0.86 0.85 0.83
O
BuO–P–OBu
O
3aq
1.94 2.31 3.75 1.00 3.94 4.06 4.47 5.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

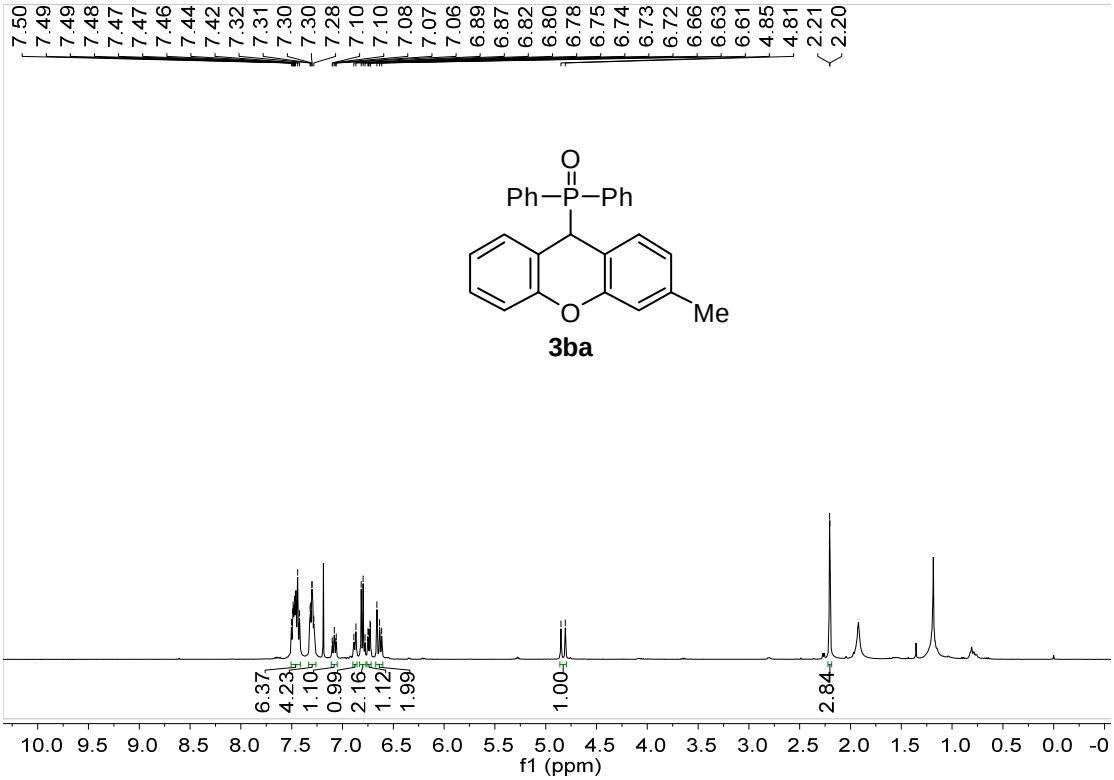

152.34
152.29
130.18
130.14
128.67
128.64
123.13
123.10
117.34
117.26
116.54
116.51
66.68
66.60
41.03
39.63
32.48
32.42
18.54
13.54
O
BuO−P−OBu
O
3aq
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

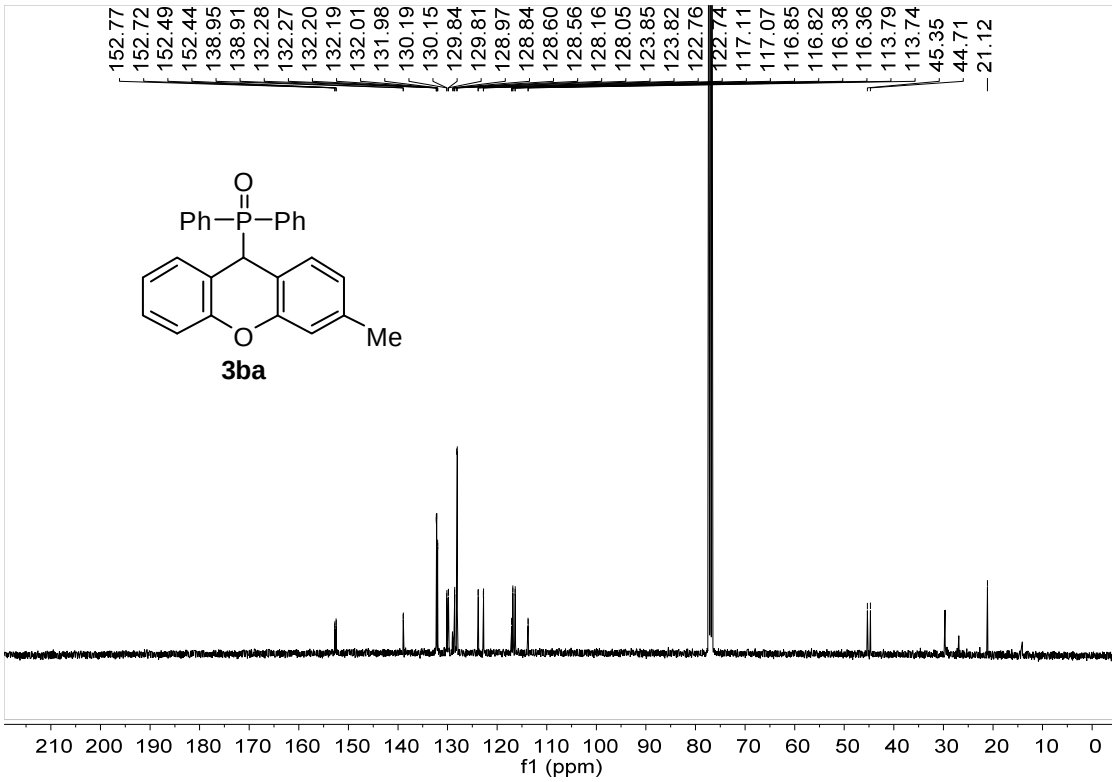

20.84
O
BuO−P−OBu
O
3aq
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -7
f1 (ppm)

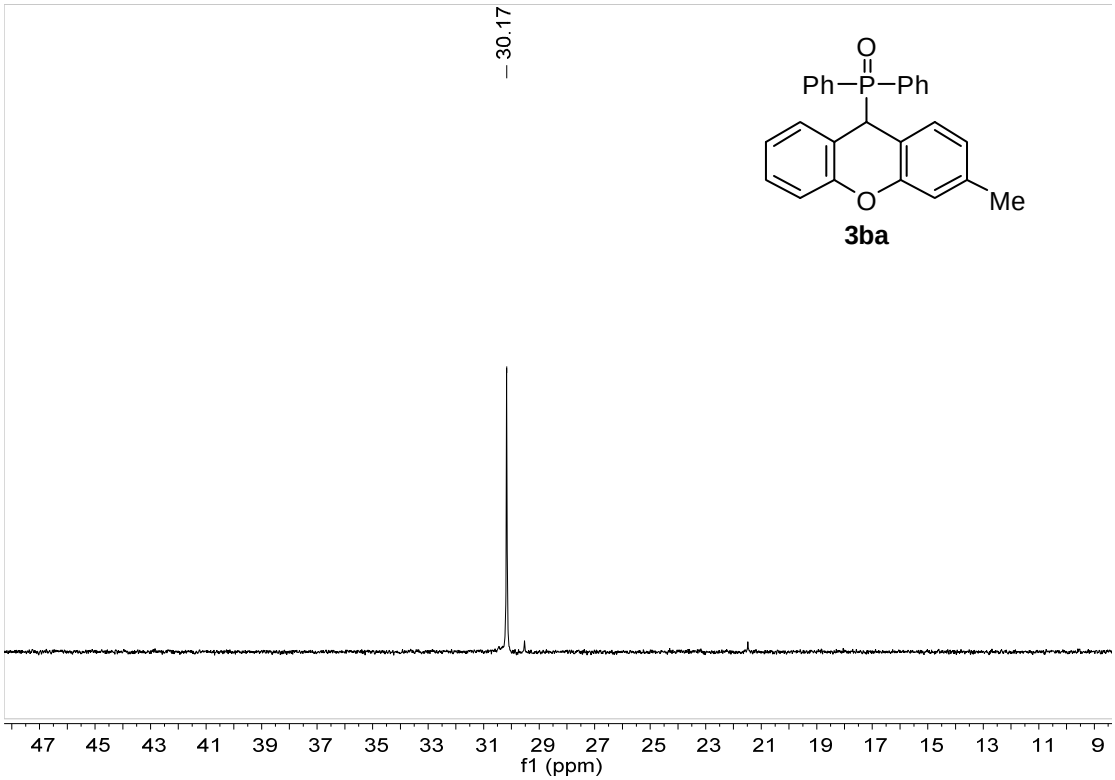

7.52
7.50
7.35
7.34
7.34
7.32
7.31
7.30
7.30
7.20
7.18
7.16
7.15
7.14
7.13
7.08
7.07
7.05
6.81
6.79
4.94
4.88
O
PhO−P−OPh
O
3ar
1.94
2.00
8.05
2.08
3.84
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

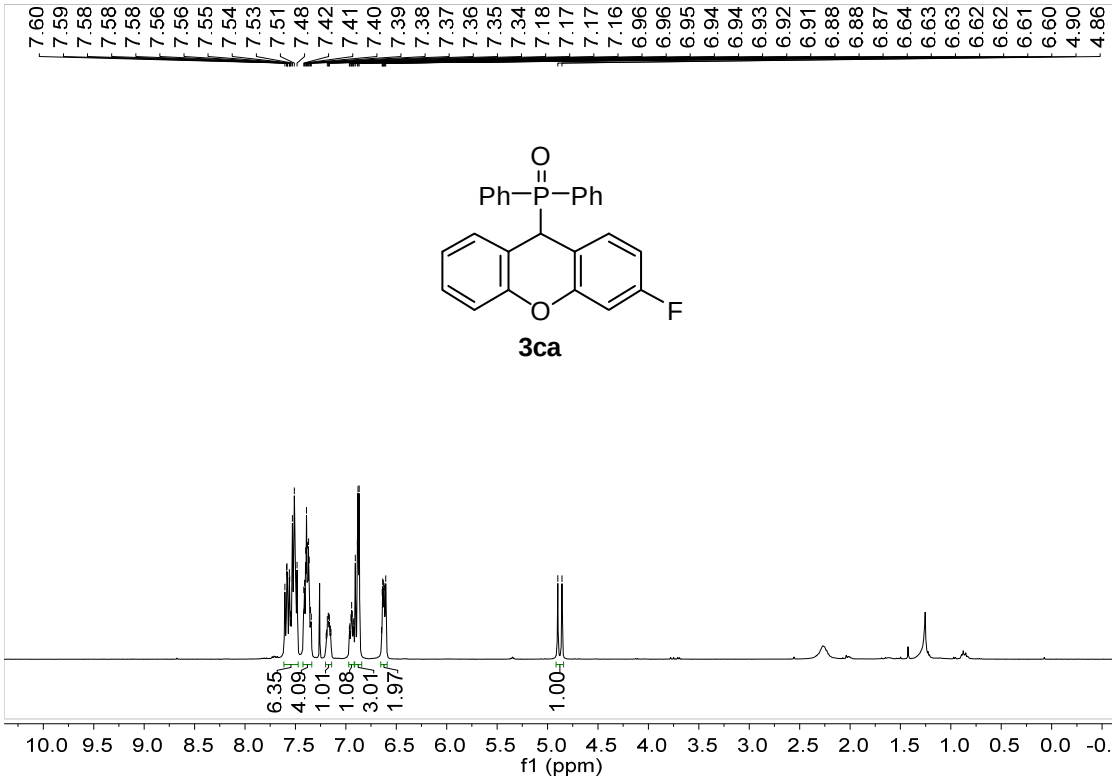

152.51
152.46
150.54
150.43
130.44
130.39
129.46
129.24
129.20
124.90
124.89
123.43
123.40
120.21
120.17
116.86
116.83
116.02
115.94
41.45
40.03
O
PhO−P−OPh
O
3ar
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

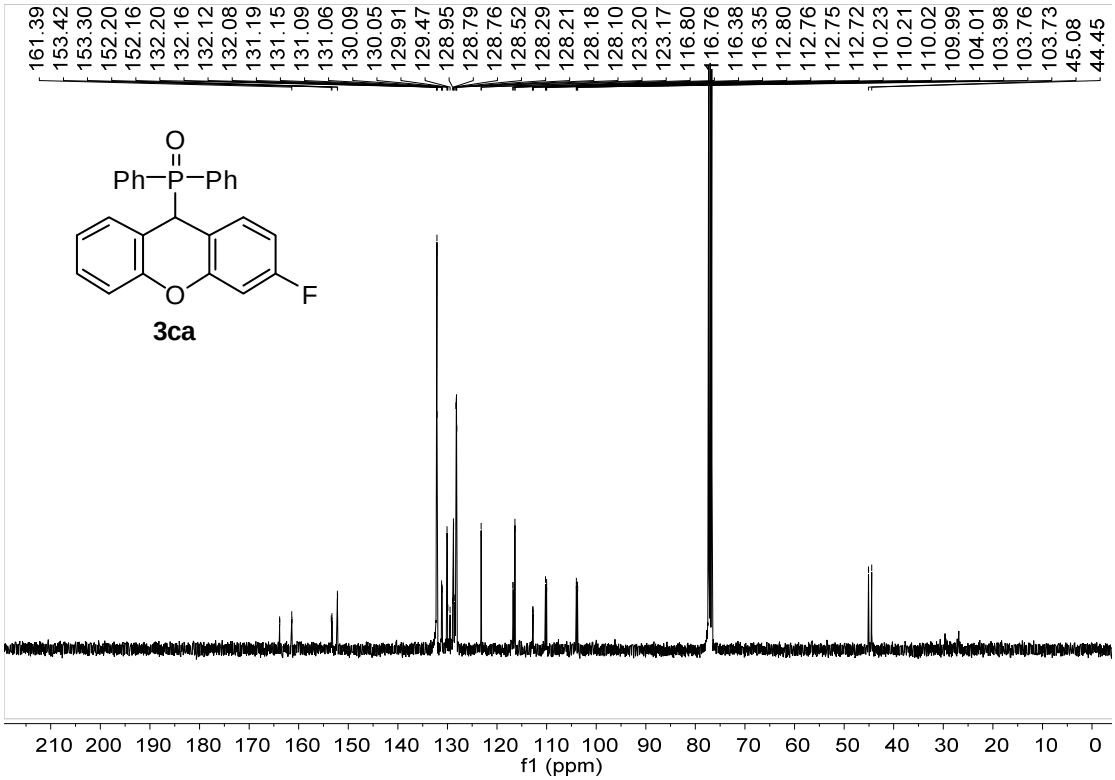

13.52
O
PhO–P–OPh
O
3ar
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

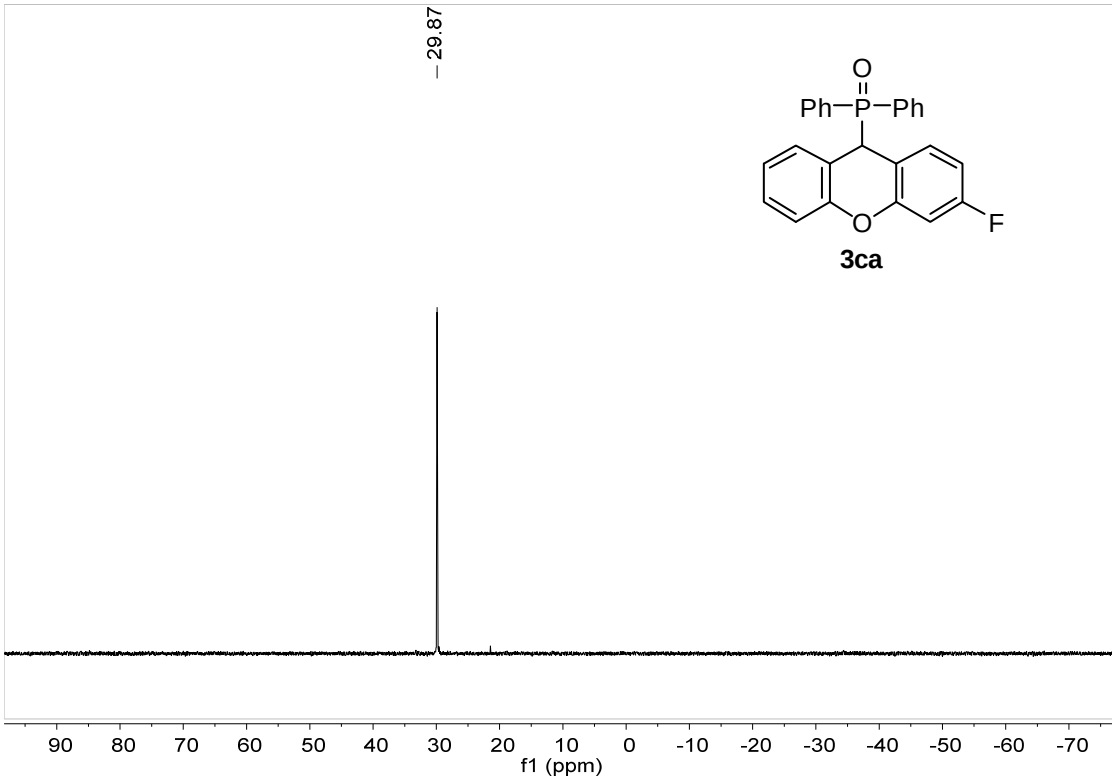

7.50 7.49 7.49 7.48 7.47 7.47 7.46 7.44 7.42 7.32 7.31 7.30 7.30 7.28 7.10 7.10 7.08 7.07 7.06 6.89 6.87 6.82 6.80 6.78 6.75 6.74 6.73 6.72 6.66 6.63 6.61 4.85 4.81 2.21 2.20
O
Ph–P–Ph
O
Me
3ba
6.37 4.23 1.10 0.99 2.16 1.12 1.99 1.00 2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

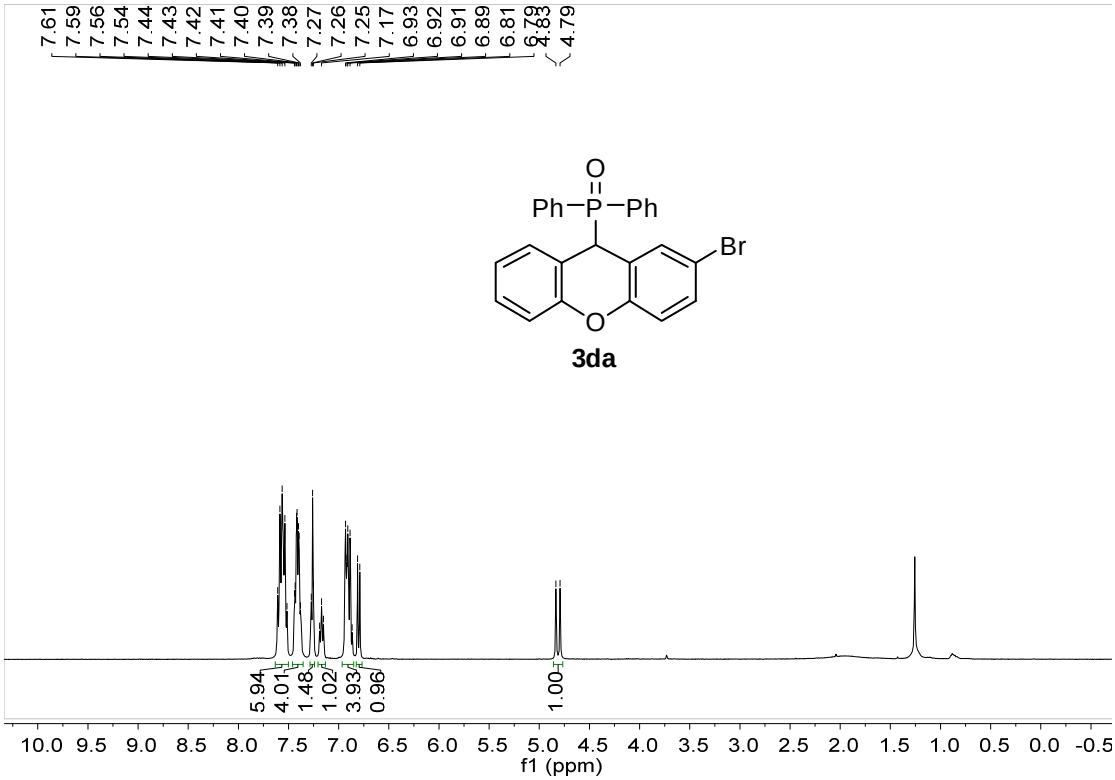

152.77
152.72
152.49
152.44
138.95
138.91
132.28
132.27
132.20
132.19
132.01
131.98
130.19
130.15
129.84
129.81
128.97
128.84
128.60
128.56
128.16
128.05
123.85
123.82
122.76
122.74
117.11
117.07
116.85
116.82
116.38
116.36
113.79
113.74
45.35
44.71
21.12
O
Ph—P—Ph
O
Me
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

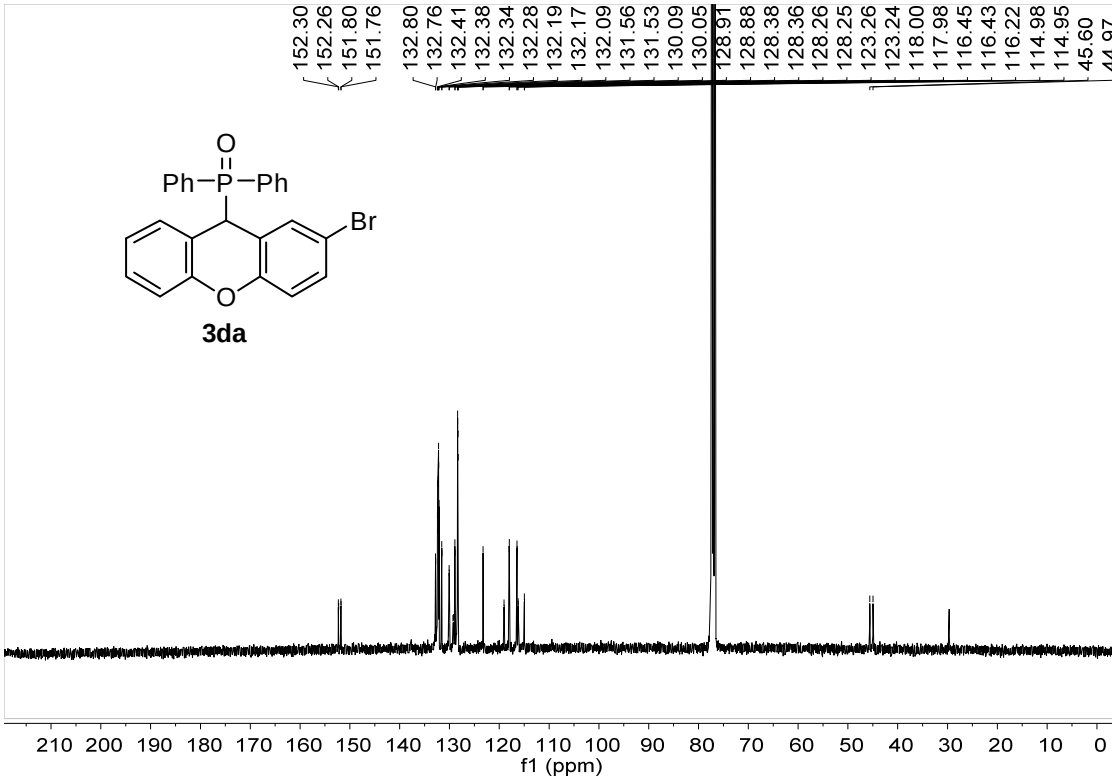

30.17
O
Ph—P—Ph
O
Me
3ba
47 45 43 41 39 37 35 33 31 29 27 25 23 21 19 17 15 13 11 9
f1 (ppm)

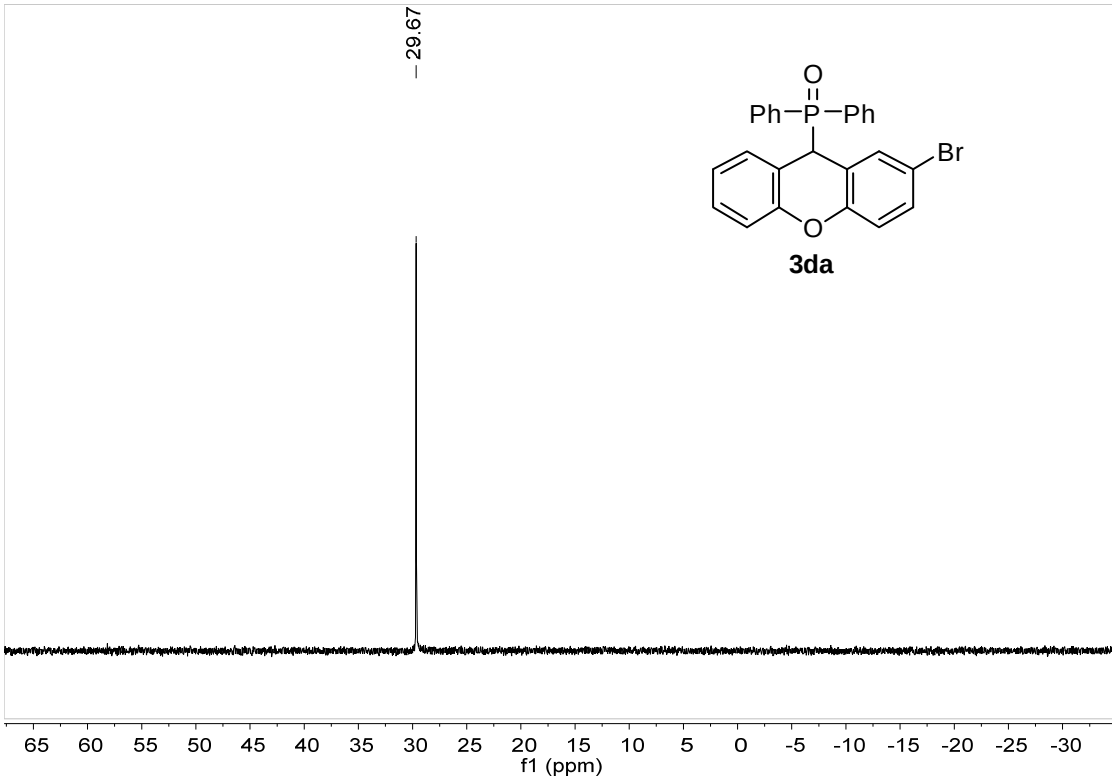

7.60 7.59 7.58 7.58 7.58 7.56 7.56 7.55 7.54 7.53 7.51 7.48 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.18 7.17 7.17 7.16 6.96 6.96 6.95 6.94 6.94 6.93 6.92 6.91 6.88 6.88 6.87 6.64 6.63 6.63 6.62 6.62 6.61 6.60 4.90 4.86
O
Ph—P—Ph
O
F
3ca
6.35 4.09 1.01 1.08 3.01 1.97 1.00
10.0 9.5 9.0 8.5 8.0 7.5 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.
f1 (ppm)

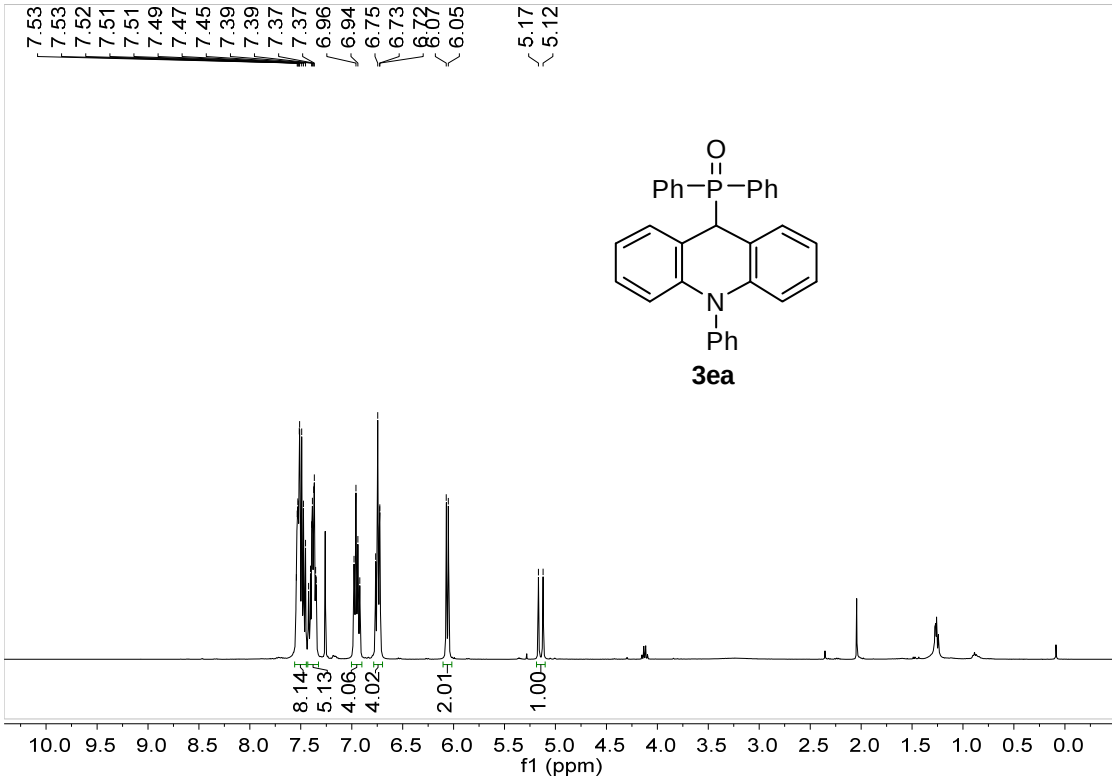

161.39 153.42 153.30 152.20 152.16 132.20 132.16 132.12 132.08 131.19 131.15 131.09 131.06 130.09 130.05 129.91 129.47 128.95 128.79 128.76 128.52 128.29 128.21 128.18 128.10 123.20 123.17 116.80 116.76 116.38 116.35 112.80 112.76 112.75 112.72 110.23 110.21 110.02 109.99 104.01 103.98 103.76 103.73 45.08 44.45
O
Ph—P—Ph
O
F
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

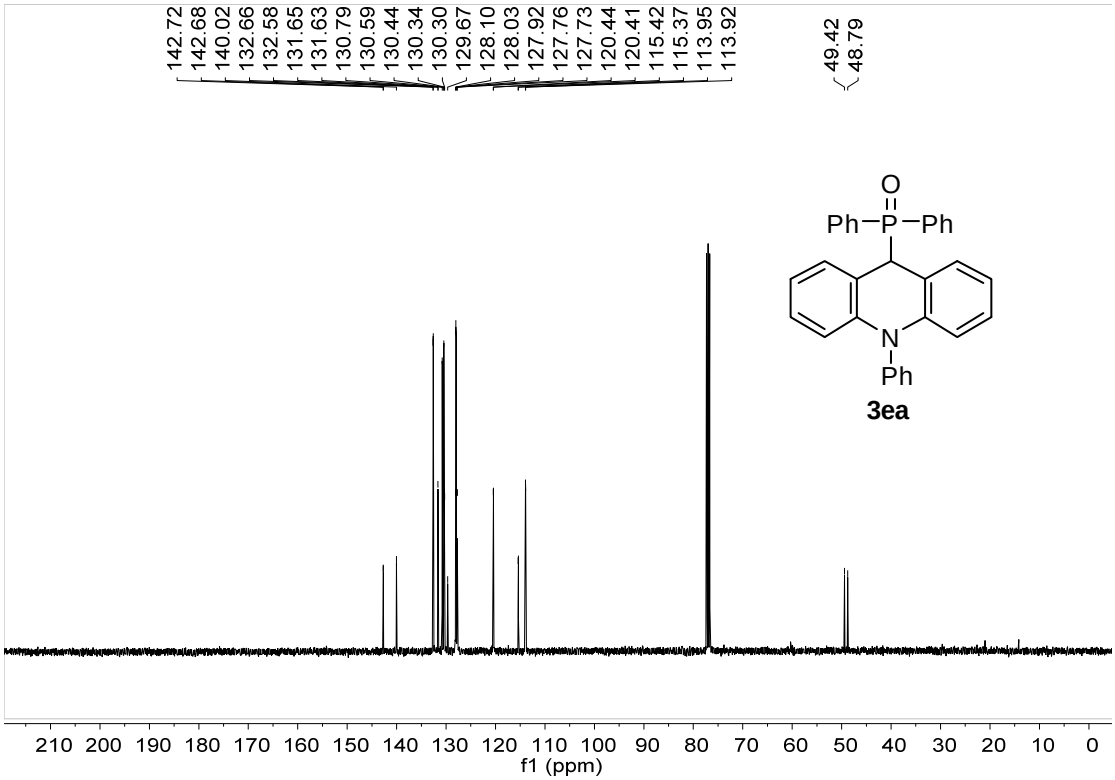

29.87
O
Ph—P—Ph
O
F
3ca
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

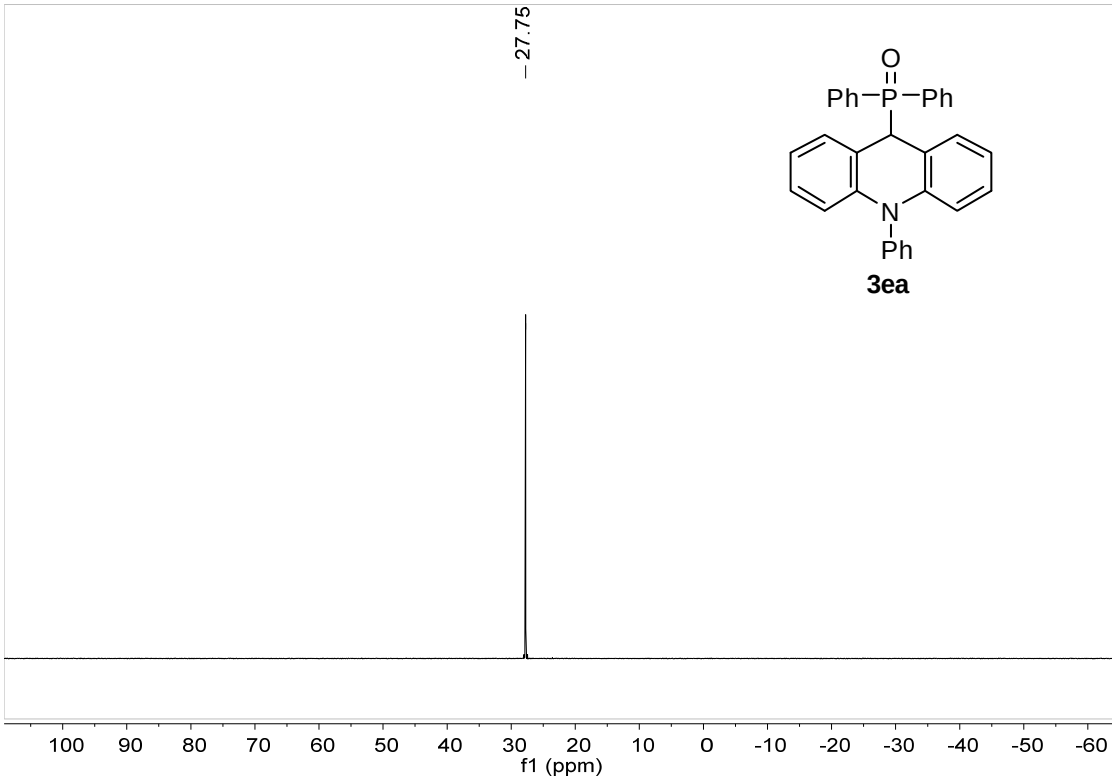

7.61
7.59
7.56
7.54
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.27
7.26
7.25
7.17
6.93
6.92
6.91
6.89
6.81
6.79
4.83
4.79
O
Ph—P—Ph
Br
O
3da
5.94
4.01
1.48
1.02
3.93
0.96
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


152.30
152.26
151.80
151.76
132.80
132.76
132.41
132.38
132.34
132.28
132.19
132.17
132.09
131.56
131.53
130.09
130.05
128.91
128.88
128.38
128.36
128.26
128.25
123.26
123.24
118.00
117.98
116.45
116.43
116.22
114.98
114.95
45.60
O
Ph–P–Ph
Br
O
3da
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


29.67
O
Ph–P–Ph
Br
O
3da
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)


7.53
7.53
7.52
7.51
7.51
7.49
7.47
7.45
7.39
7.39
7.37
7.37
6.96
6.94
6.75
6.73
6.72
6.07
6.05
5.17
5.12
O
Ph—P—Ph
N
Ph
3ea
8.14
5.13
4.06
4.02
2.01
1.00
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)


142.72
142.68
140.02
132.66
132.58
131.65
131.63
130.79
130.59
130.44
130.34
130.30
129.67
128.10
128.03
127.92
127.76
127.73
120.44
120.41
115.42
115.37
113.95
113.92
49.42
48.79
O
Ph—P—Ph
N
Ph
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


27.75
O
Ph—P—Ph
N
Ph
3ea
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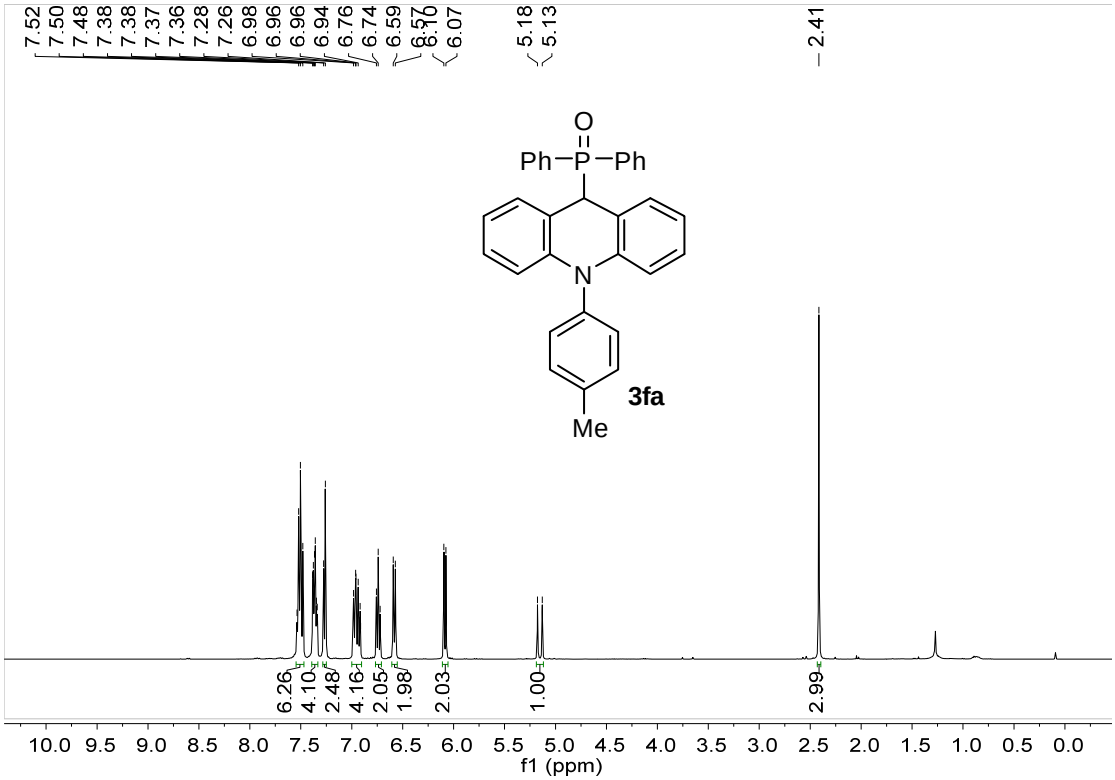
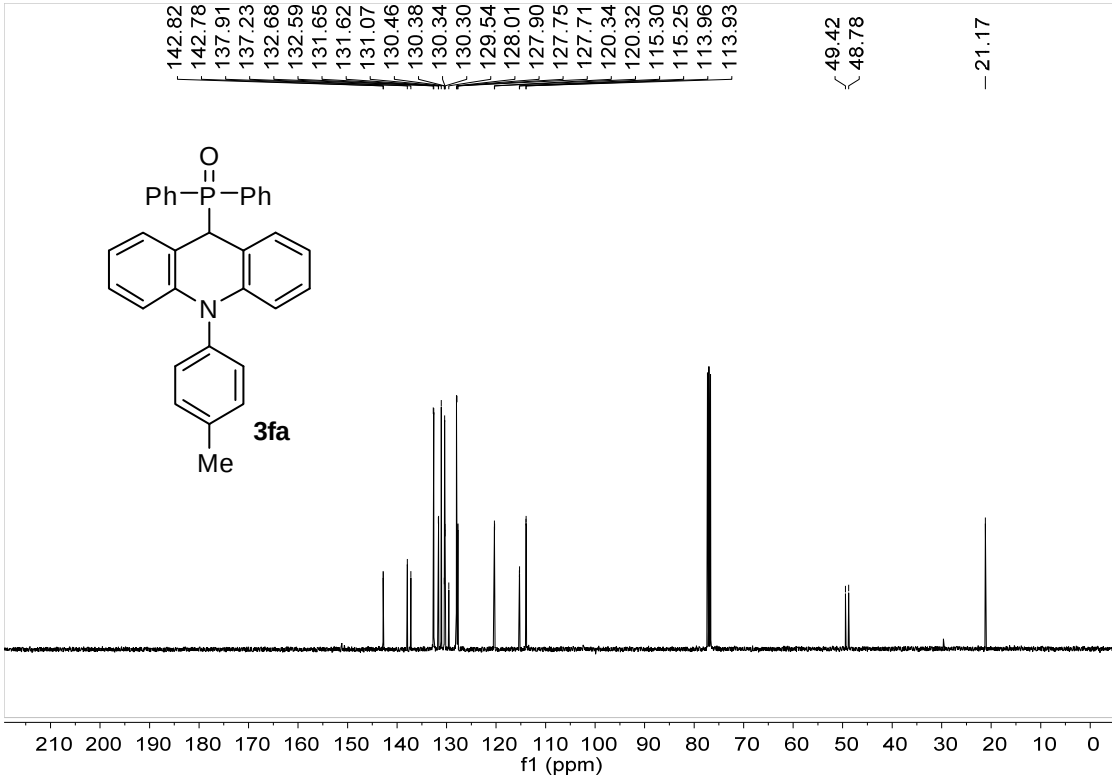
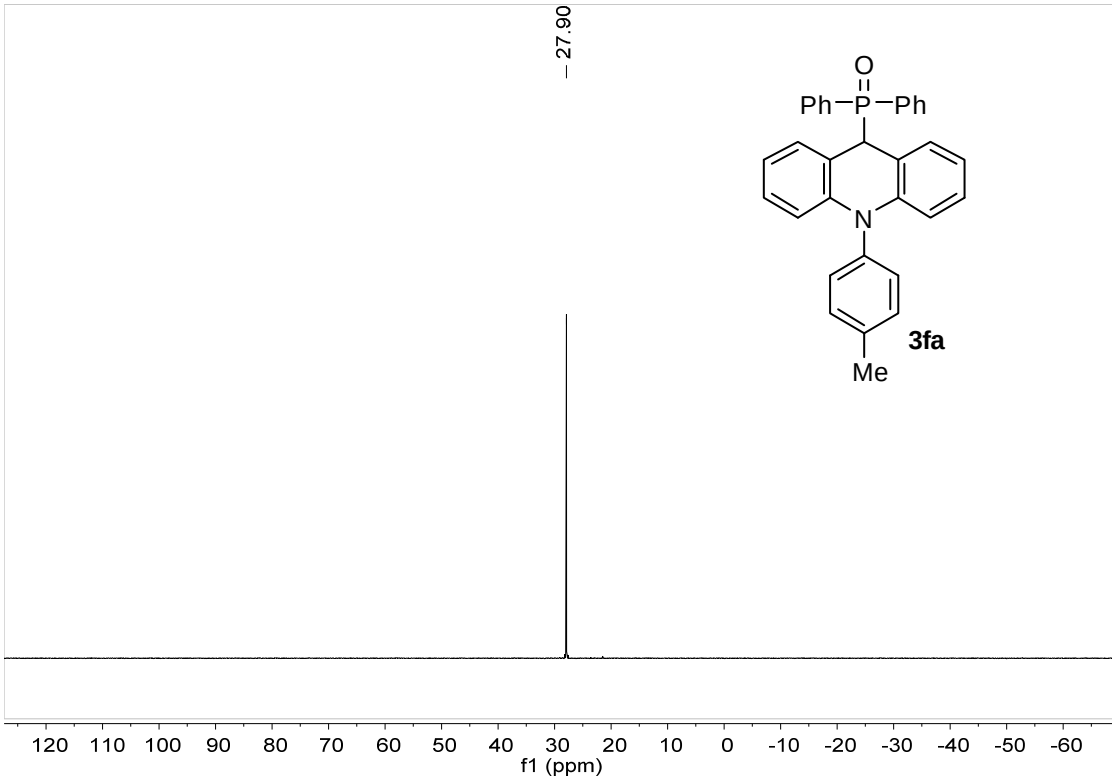
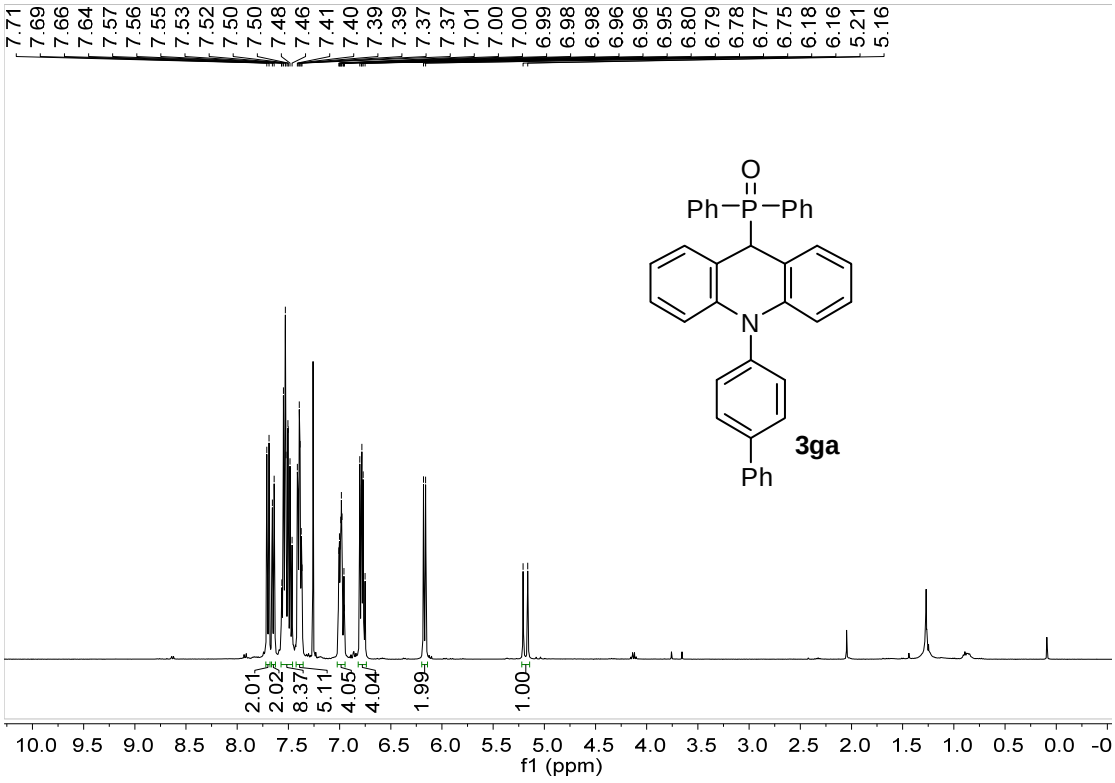
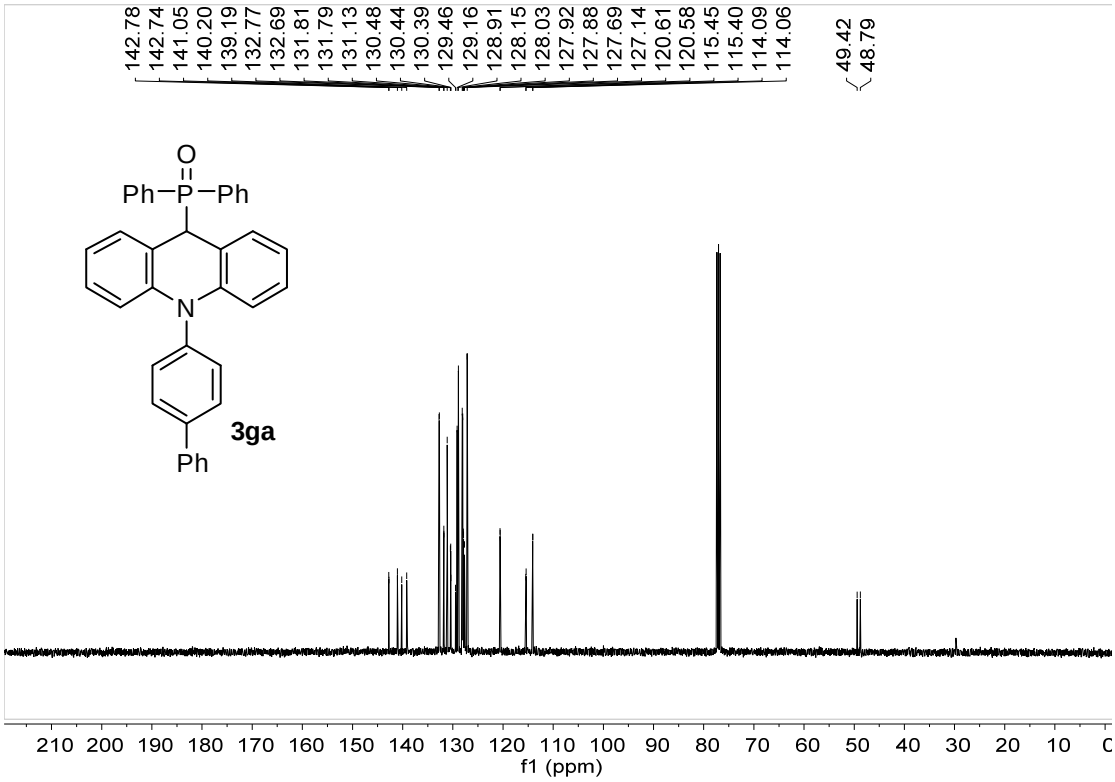
f1 (ppm)

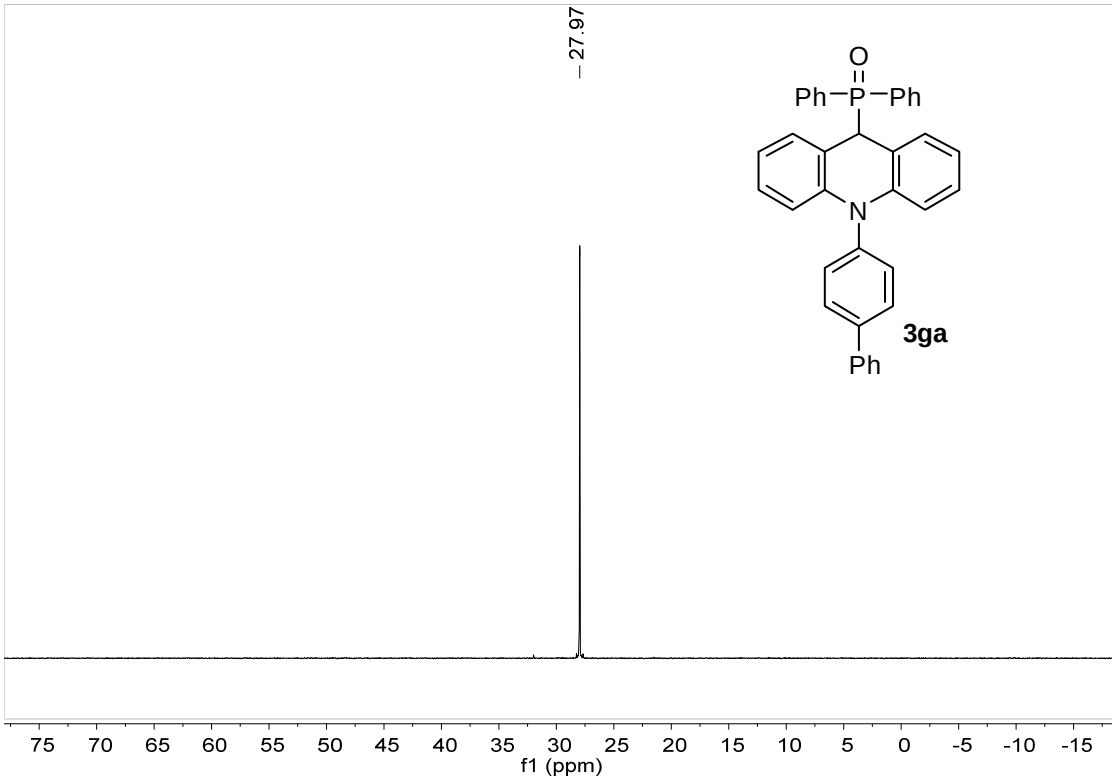

7.52
7.50
7.48
7.38
7.38
7.37
7.36
7.28
7.26
6.98
6.96
6.96
6.94
6.76
6.74
6.59
6.57
6.10
6.07
5.18
5.13
2.41
O
Ph—P—Ph
N
3fa
Me
6.26
4.10
2.48
4.16
2.05
1.98
2.03
1.00
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

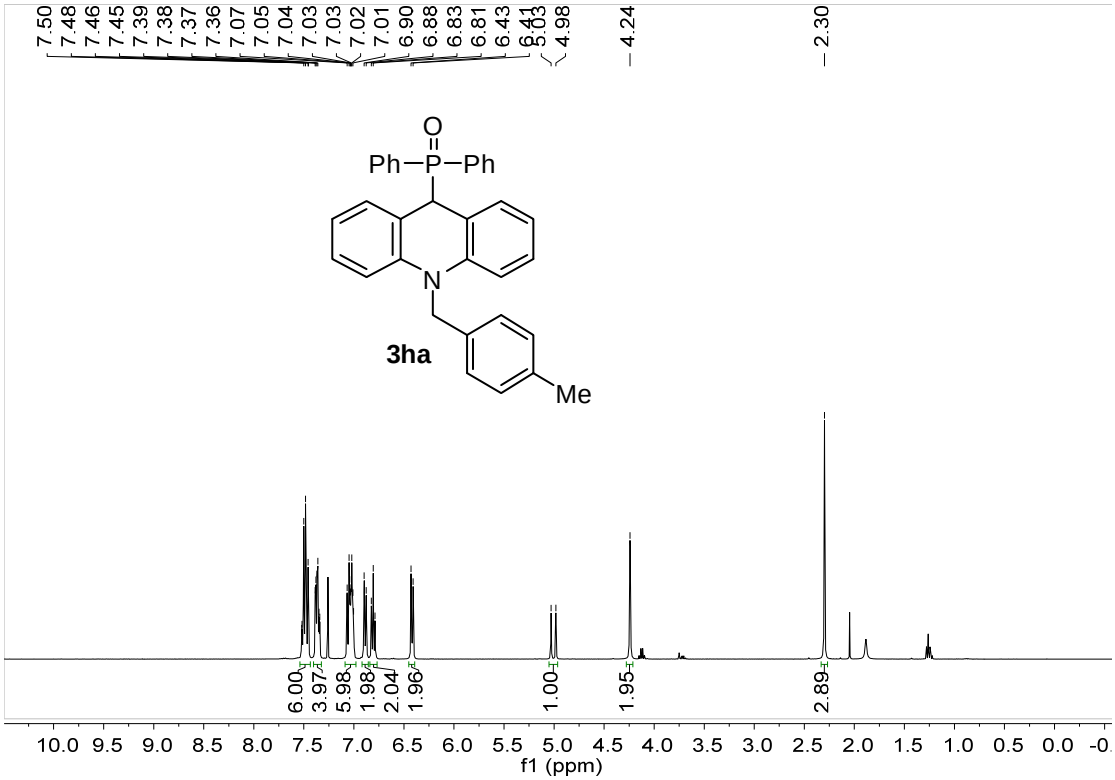

142.82
142.78
137.91
137.23
132.68
132.59
131.65
131.62
131.07
130.46
130.38
130.34
130.30
129.54
128.01
127.90
127.75
127.71
120.34
120.32
115.30
115.25
113.96
113.93
49.42
48.78
21.17
O
Ph—P—Ph
N
Me
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

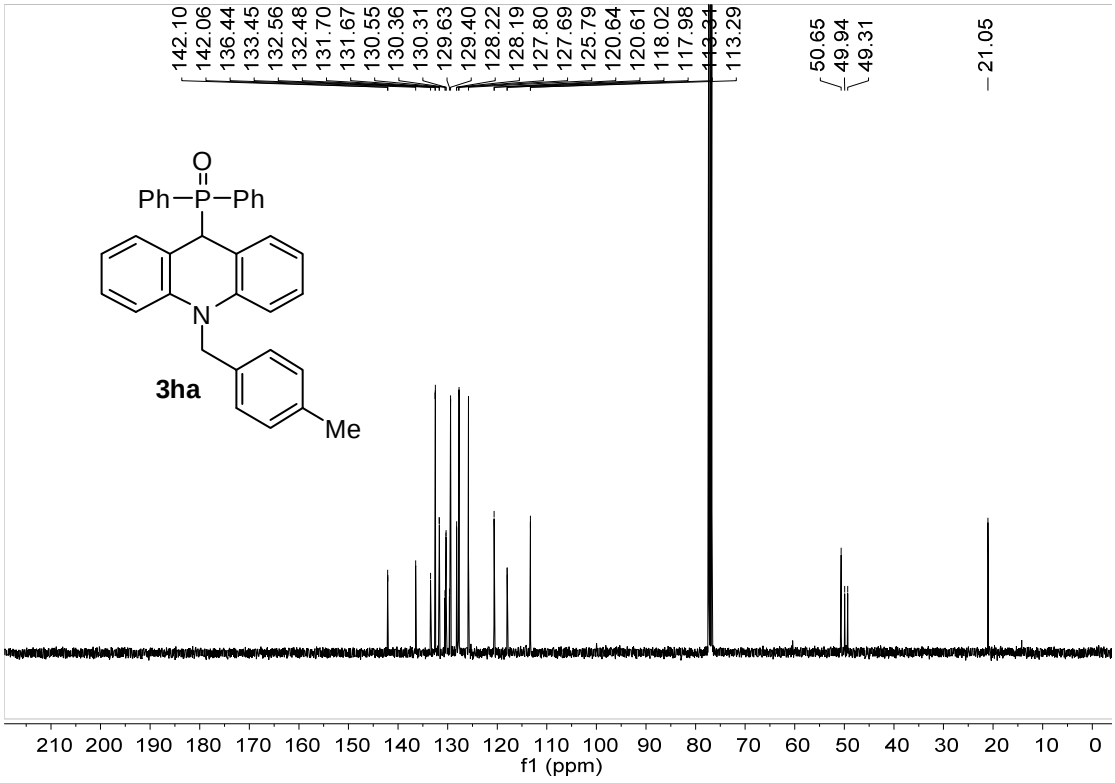

27.90
O
Ph—P—Ph
N
Me
3fa
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)

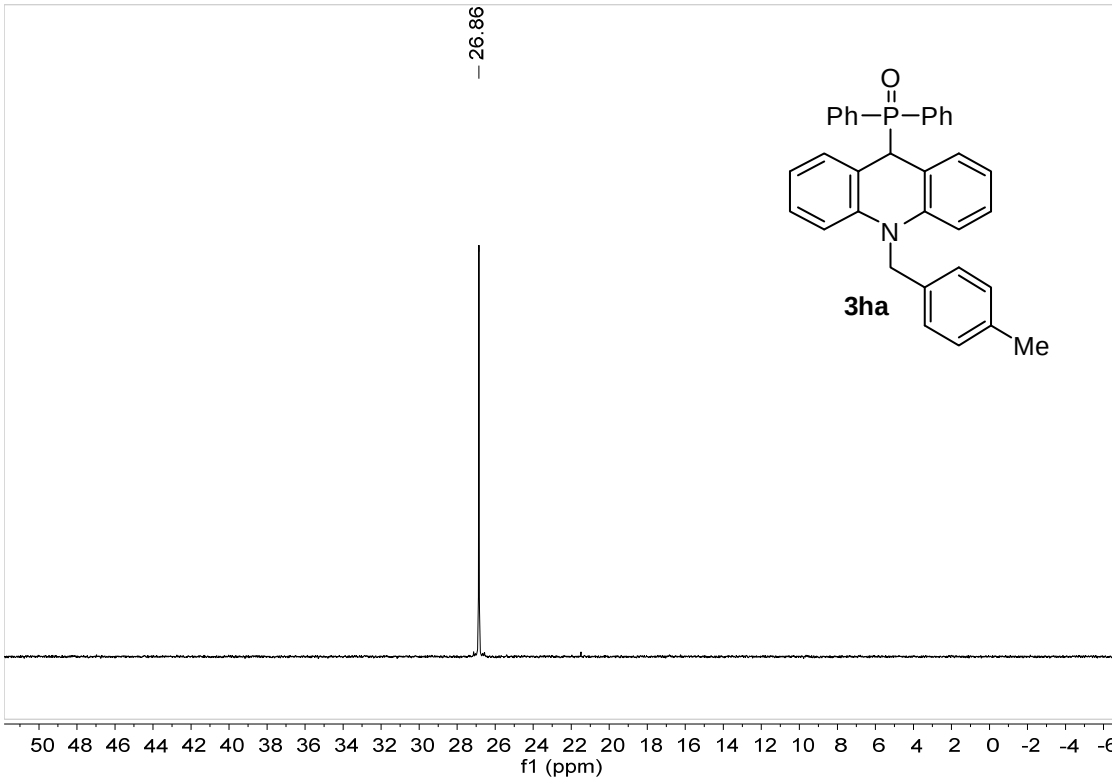

7.71 7.69 7.66 7.64 7.57 7.56 7.55 7.53 7.52 7.50 7.50 7.48 7.46 7.41 7.40 7.39 7.39 7.37 7.37 7.01 7.00 7.00 6.99 6.98 6.98 6.96 6.96 6.95 6.80 6.79 6.78 6.77 6.75 6.18 6.16 5.21 5.16
O
Ph—P—Ph
N
3ga
Ph
2.01 2.02 8.37 5.11 4.05 4.04 1.99 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

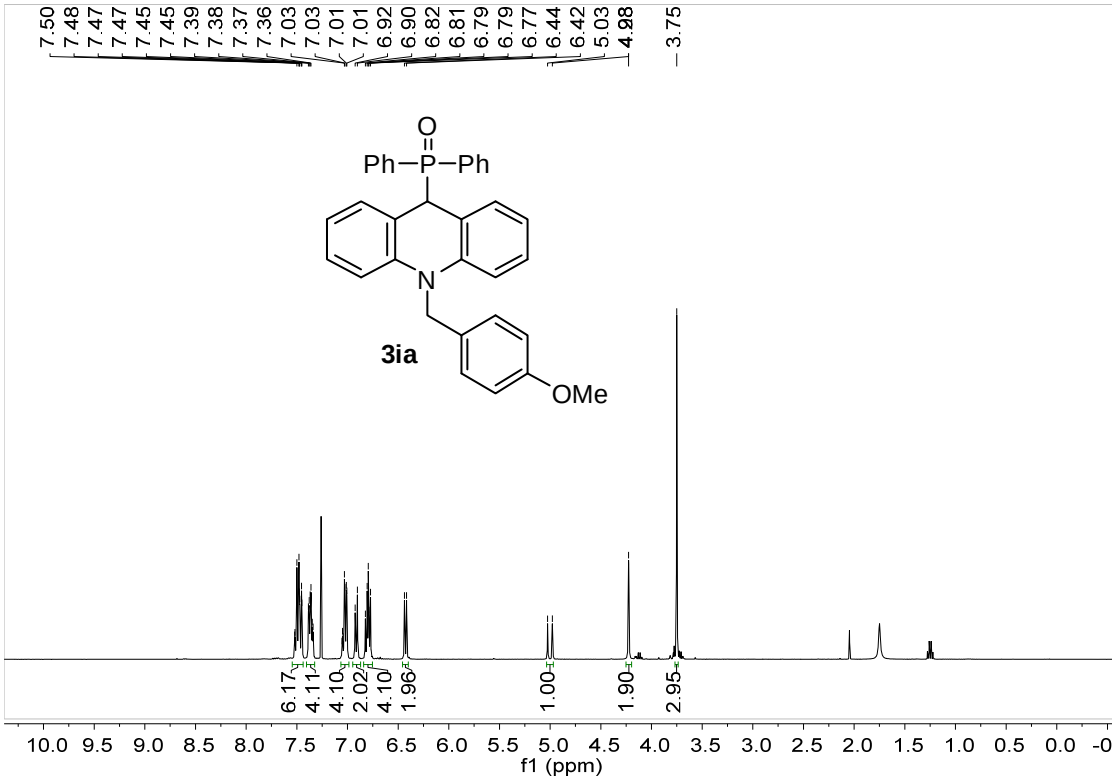

142.78 142.74 141.05 140.20 139.19 132.77 132.69 131.81 131.79 131.13 130.48 130.44 130.39 129.46 129.16 128.91 128.15 128.03 127.92 127.88 127.69 127.14 120.61 120.58 115.45 115.40 114.09 114.06
49.42 48.79
O
Ph—P—Ph
N
3ga
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

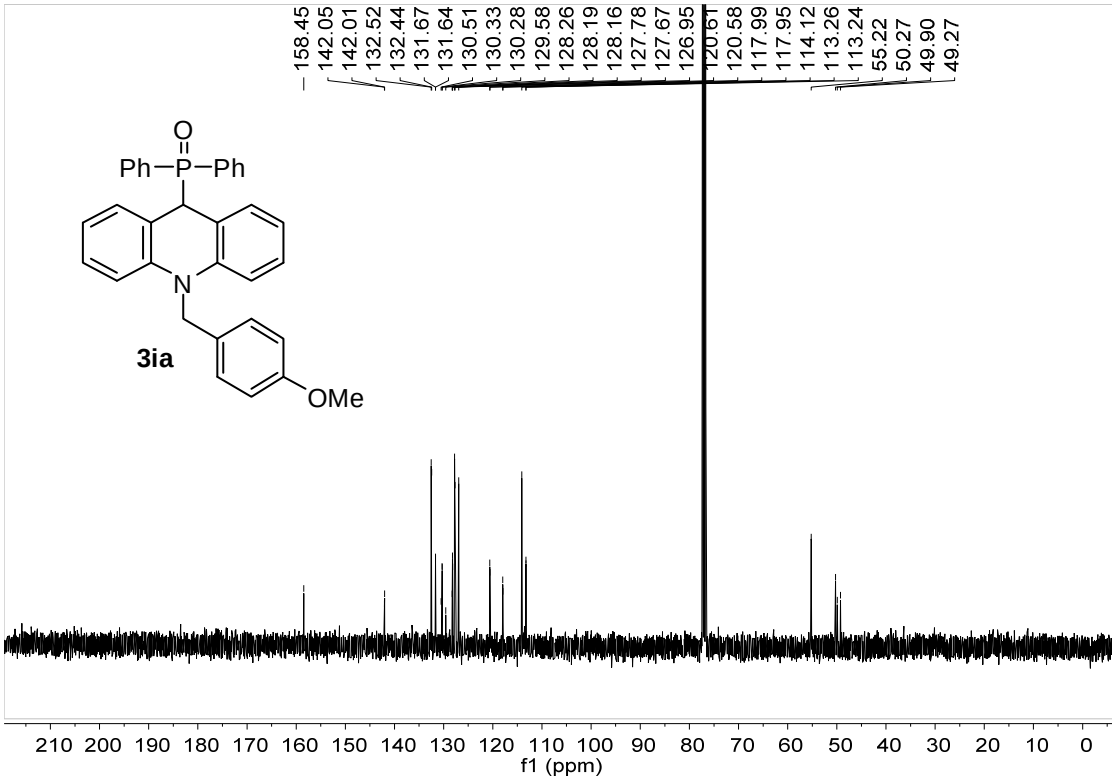

27.97
O
Ph—P—Ph
N
Ph
3ga
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

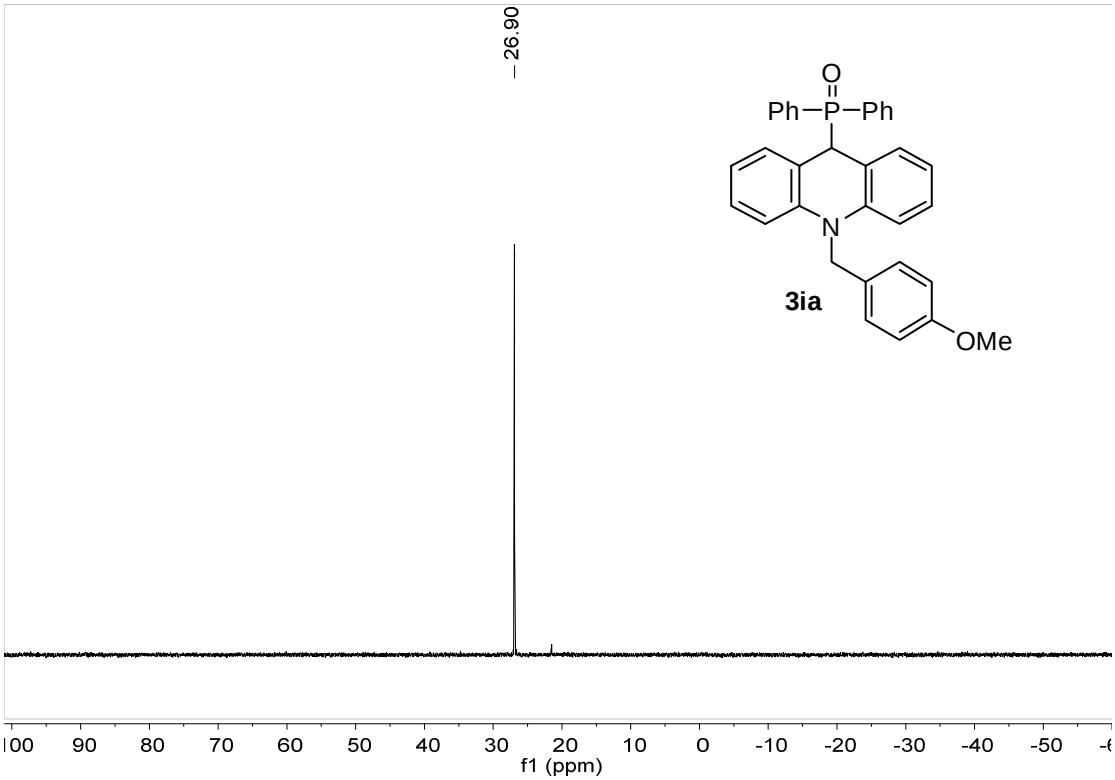

7.50 7.48 7.46 7.45 7.39 7.38 7.37 7.36 7.07 7.05 7.04 7.03 7.03 7.02 7.01 6.90 6.88 6.83 6.81 6.43 6.41 5.03 4.98
4.24
2.30
O
Ph—P—Ph
N
3ha
Me
6.00 3.97 5.98 1.98 2.04 1.96 1.00 1.95 2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

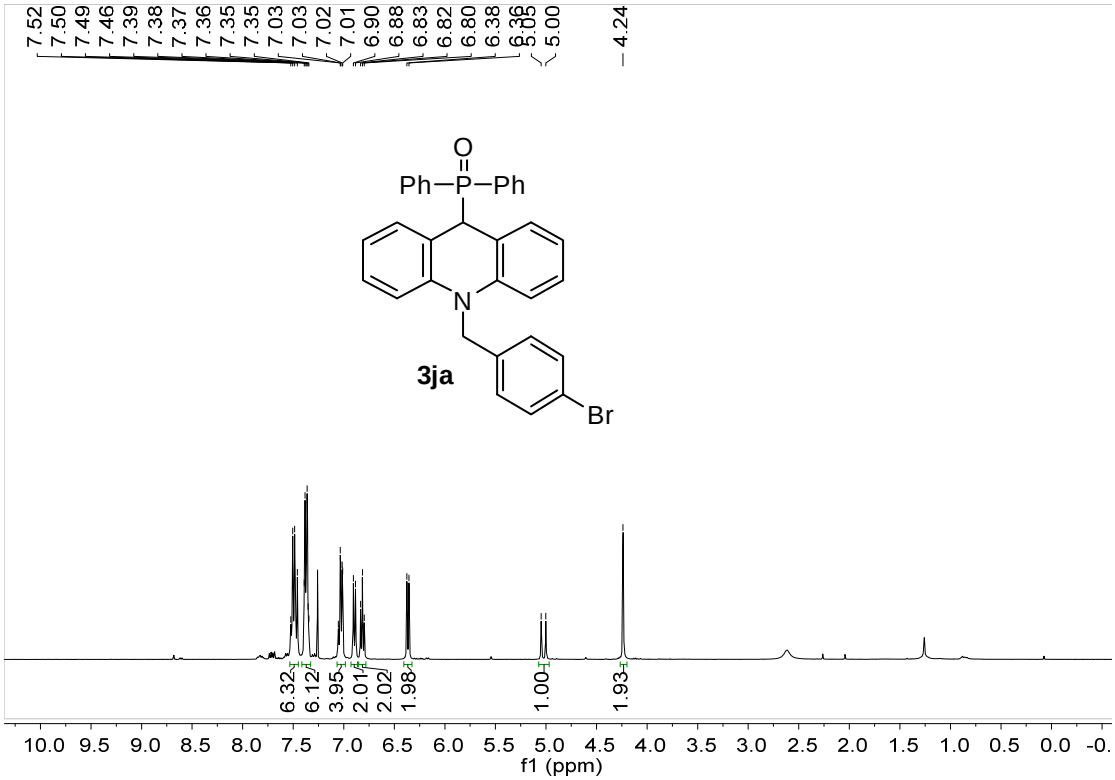

142.10
142.06
136.44
133.45
132.56
132.48
131.70
131.67
130.55
130.36
130.31
129.63
129.40
128.22
128.19
127.80
127.69
125.79
120.64
120.61
118.02
117.98
113.29
50.65
49.94
49.31
21.05
O
Ph—P—Ph
N
3ha
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

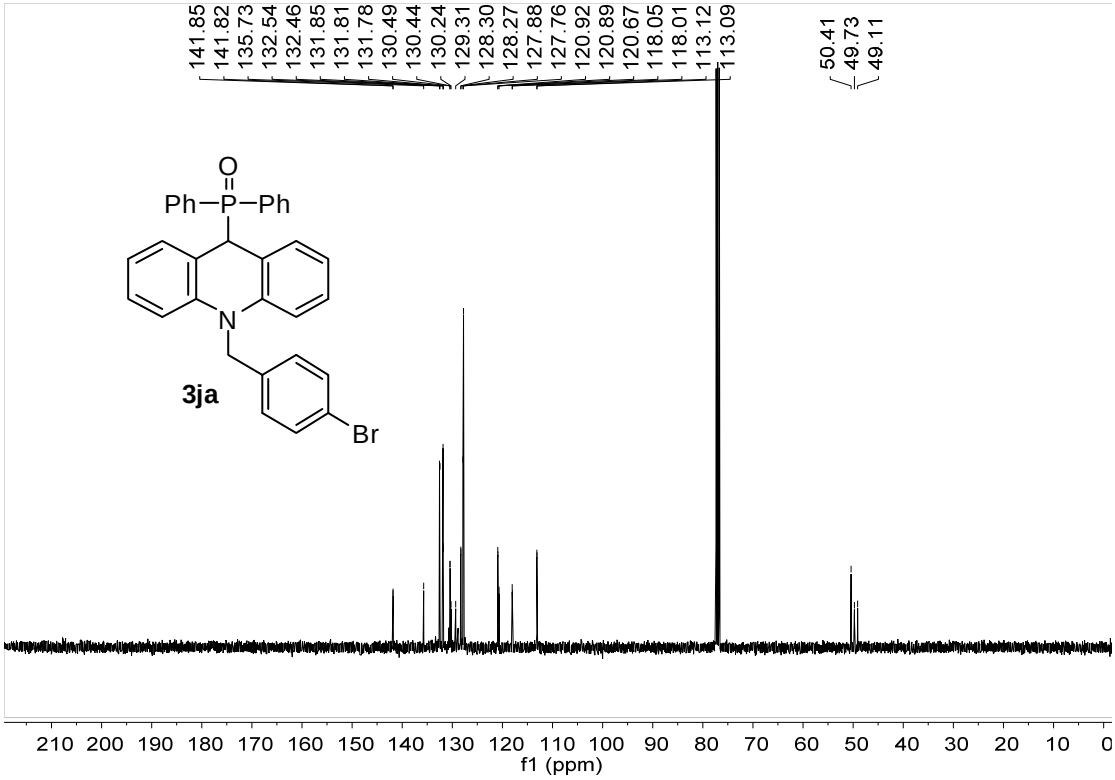

26.86
O
Ph—P—Ph
N
3ha
Me
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4
f1 (ppm)

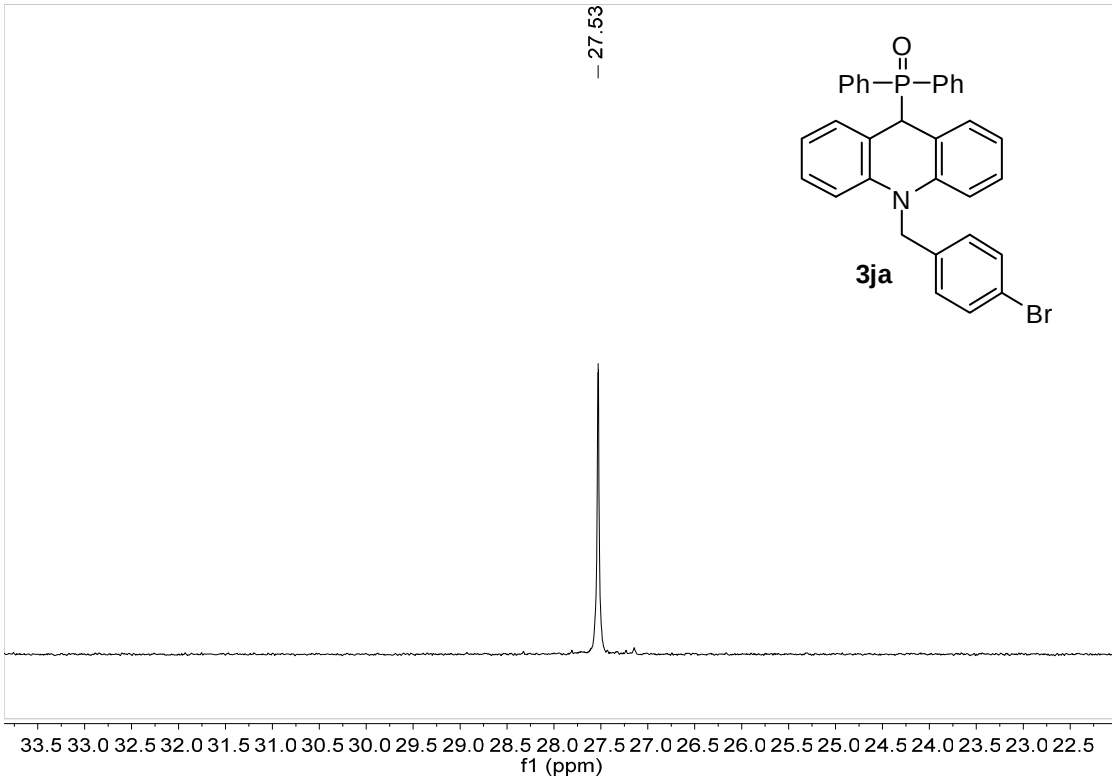

7.50
7.48
7.47
7.47
7.45
7.45
7.39
7.38
7.37
7.36
7.03
7.03
7.01
7.01
6.92
6.90
6.82
6.81
6.79
6.79
6.77
6.44
6.42
5.03
4.98
3.75
O
Ph—P—Ph
N
3ia
OMe
6.17
4.11
4.10
2.02
4.10
1.96
1.00
1.90
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

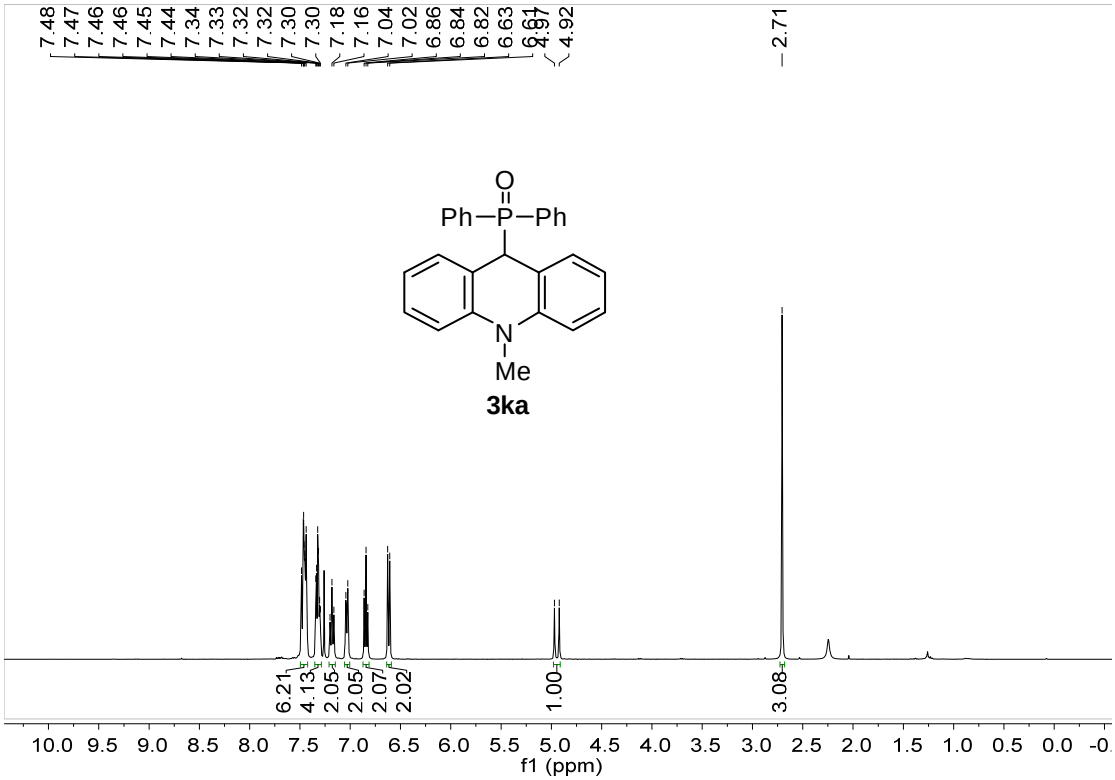

158.45
142.05
142.01
132.52
132.44
131.67
131.64
130.51
130.33
130.28
129.58
128.26
128.19
128.16
127.78
127.67
126.95
120.61
120.58
117.99
117.95
114.12
113.26
113.24
55.22
50.27
49.90
49.27
O
Ph—P—Ph
N
3ia
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

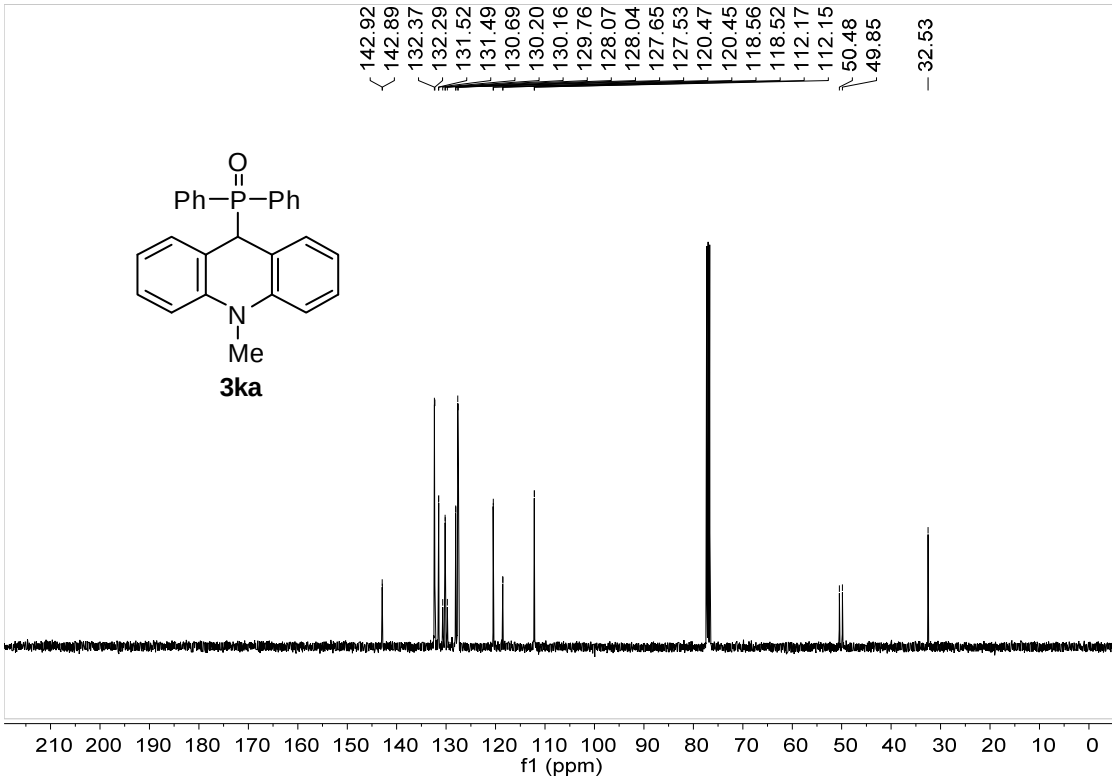

26.90
O
Ph—P—Ph
N
3ia
OMe
f1 (ppm)

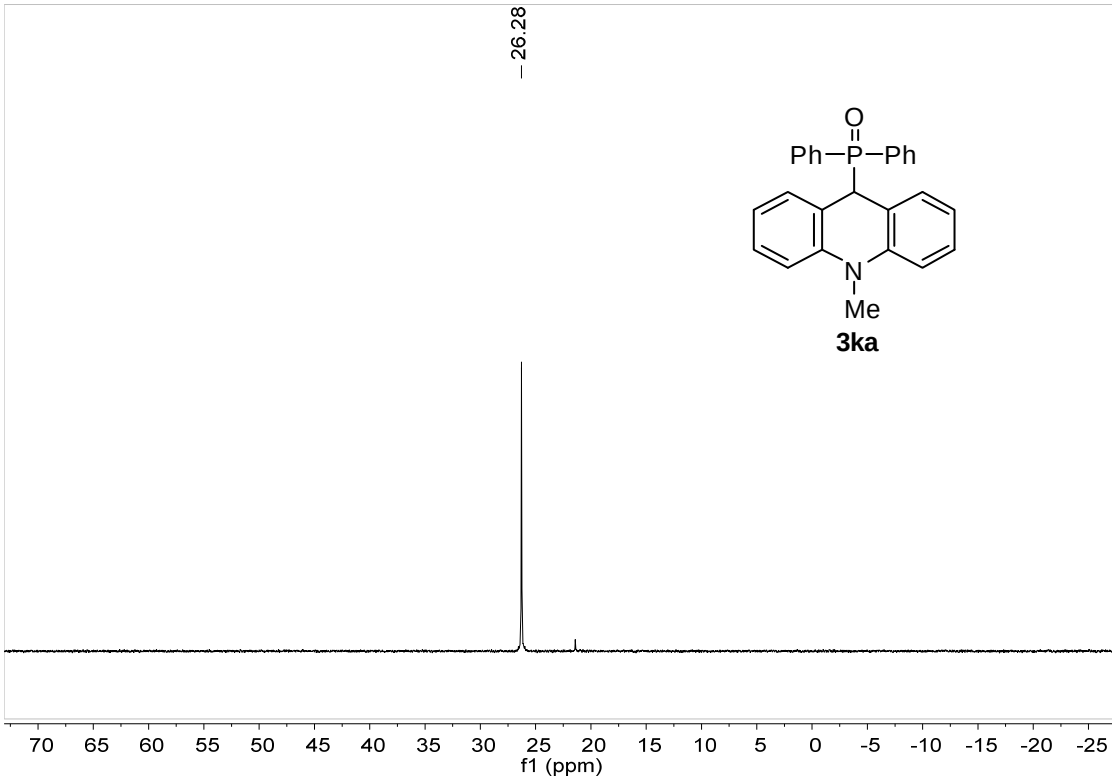

7.52
7.50
7.49
7.46
7.39
7.38
7.37
7.36
7.35
7.35
7.03
7.03
7.02
7.01
6.90
6.88
6.83
6.82
6.80
6.38
6.36
5.05
5.00
4.24
O
Ph—P—Ph
N
3ja
Br
6.32
6.12
3.95
2.01
2.02
1.98
1.00
1.93
f1 (ppm)

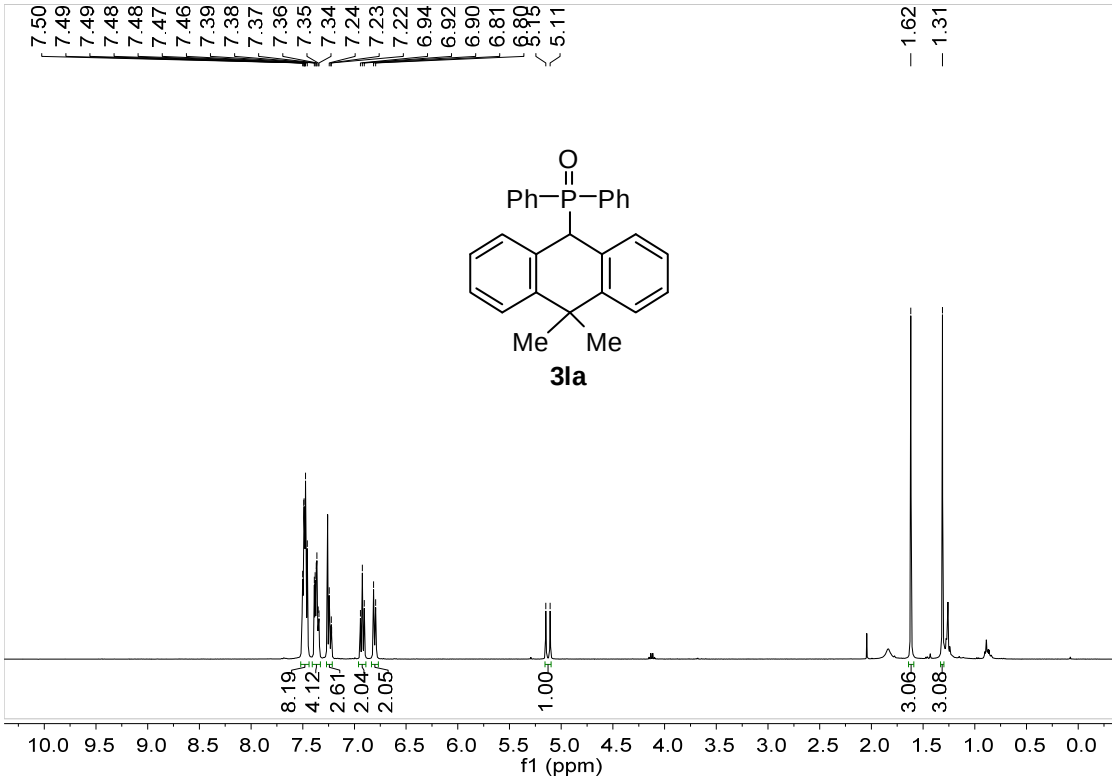

141.85
141.82
135.73
132.54
132.46
131.85
131.81
131.78
130.49
130.44
130.24
129.31
128.30
128.27
127.88
127.76
120.92
120.89
120.67
118.05
118.01
113.12
113.09
50.41
49.73
49.11
O
Ph—P—Ph
N
3ja
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

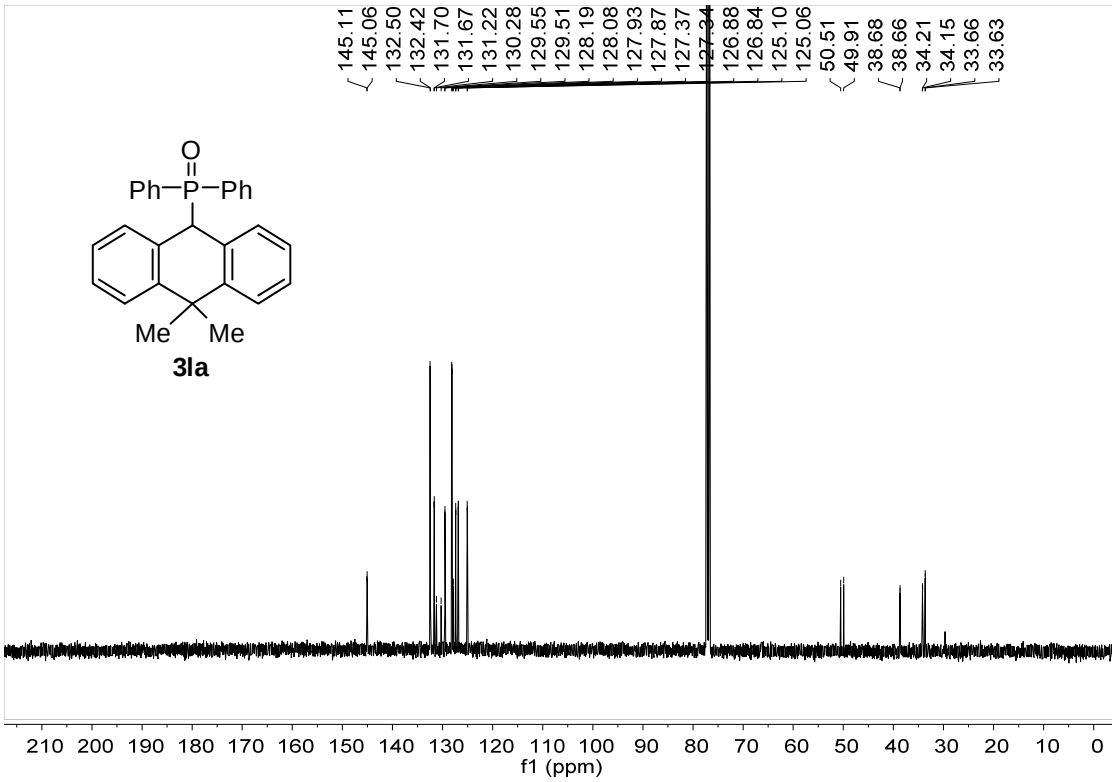

27.53
O
Ph—P—Ph
N
3ja
Br
33.5 33.0 32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0 25.5 25.0 24.5 24.0 23.5 23.0 22.5
f1 (ppm)

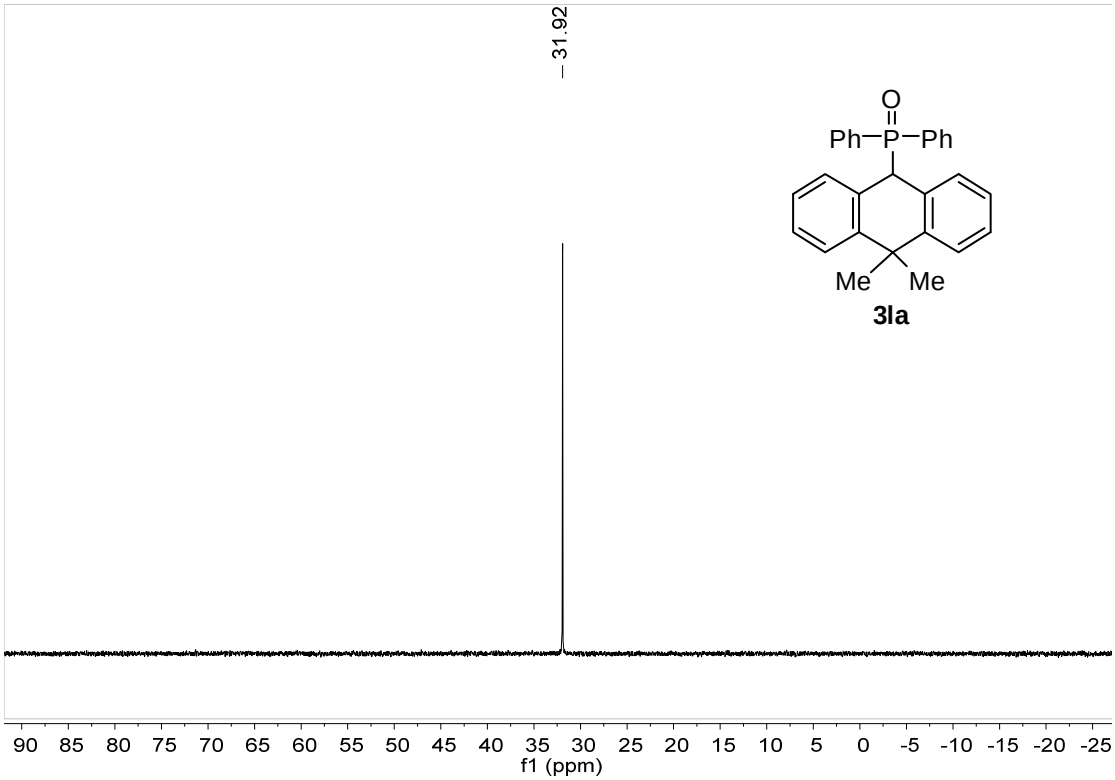

7.48
7.47
7.46
7.46
7.45
7.44
7.34
7.33
7.32
7.32
7.30
7.30
7.18
7.16
7.04
7.02
6.86
6.84
6.82
6.63
6.61
4.97
4.92
2.71
O
Ph—P—Ph
N
Me
3ka
6.21
4.13
2.05
2.05
2.07
2.02
1.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

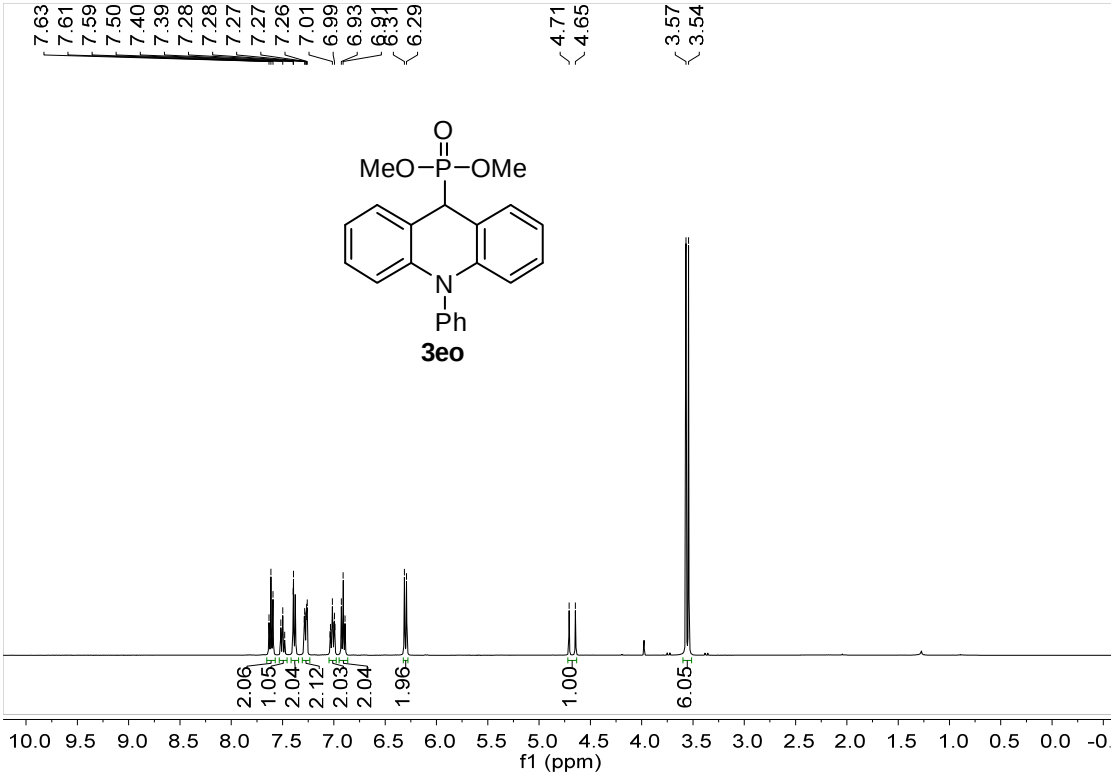

142.92
142.89
132.37
132.29
131.52
131.49
130.69
130.20
130.16
129.76
128.07
128.04
127.65
127.53
120.47
120.45
118.56
118.52
112.17
112.15
50.48
49.85
32.53
O
Ph—P—Ph
N
Me
3ka
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

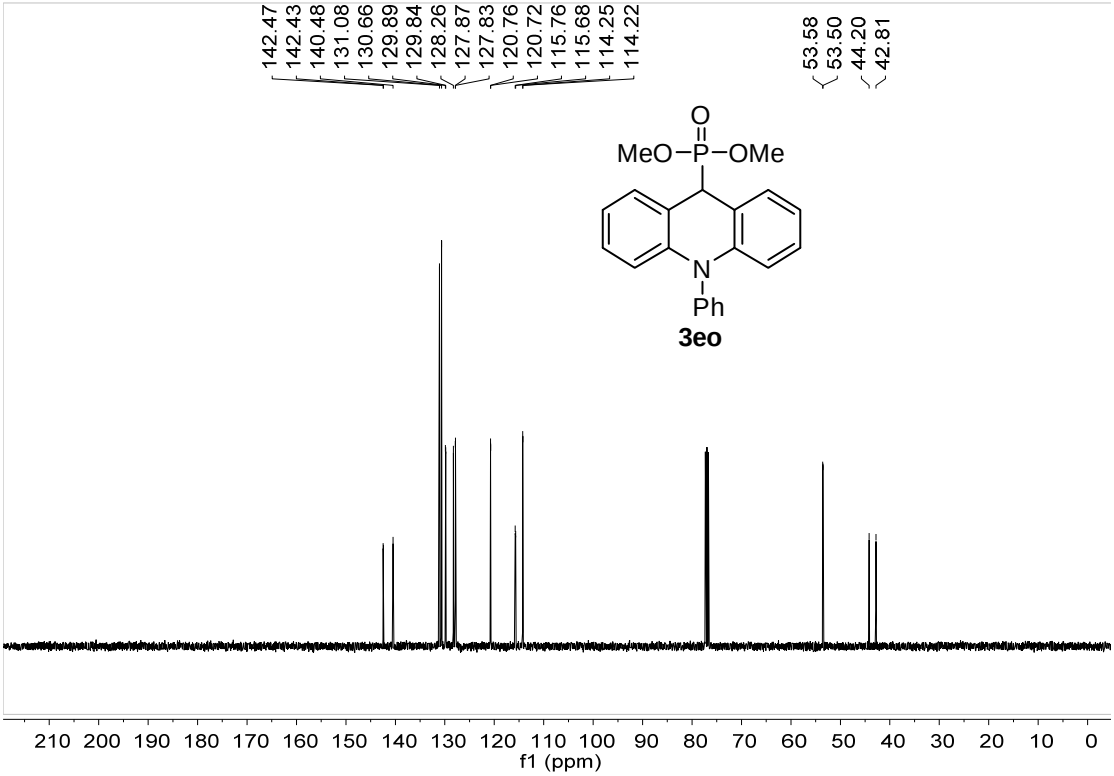

26.28
O
Ph—P—Ph
N
Me
3ka
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)


7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.39
7.38
7.37
7.36
7.35
7.34
7.24
7.23
7.22
6.94
6.92
6.90
6.81
6.80
5.15
5.11
1.62
1.31
O
Ph—P—Ph
Me Me
3la
8.19
4.12
2.61
2.04
2.05
1.00
3.06
3.08
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)


145.11
145.06
132.50
132.42
131.70
131.67
131.22
130.28
129.55
129.51
128.19
128.08
127.93
127.87
127.37
127.34
126.88
126.84
125.10
125.06
50.51
49.91
38.68
38.66
34.21
34.15
33.66
33.63
O
Ph—P—Ph
Me Me
3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


31.92
O
Ph—P—Ph
Me Me
3la
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)


7.63
7.61
7.59
7.50
7.40
7.39
7.28
7.28
7.27
7.27
7.26
7.01
6.99
6.93
6.91
6.31
6.29
4.71
4.65
3.57
3.54
O
MeO−P−OMe
N
Ph
3eo
2.06
1.05
2.04
2.12
2.03
2.04
1.96
1.00
6.05
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)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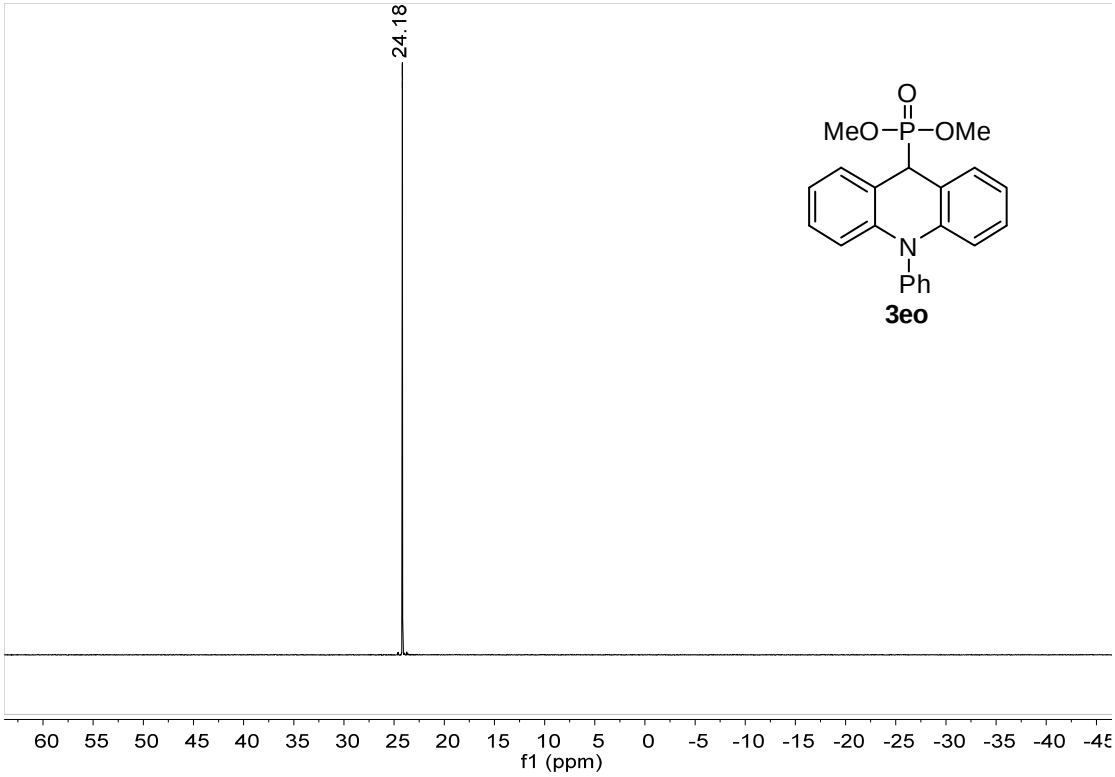
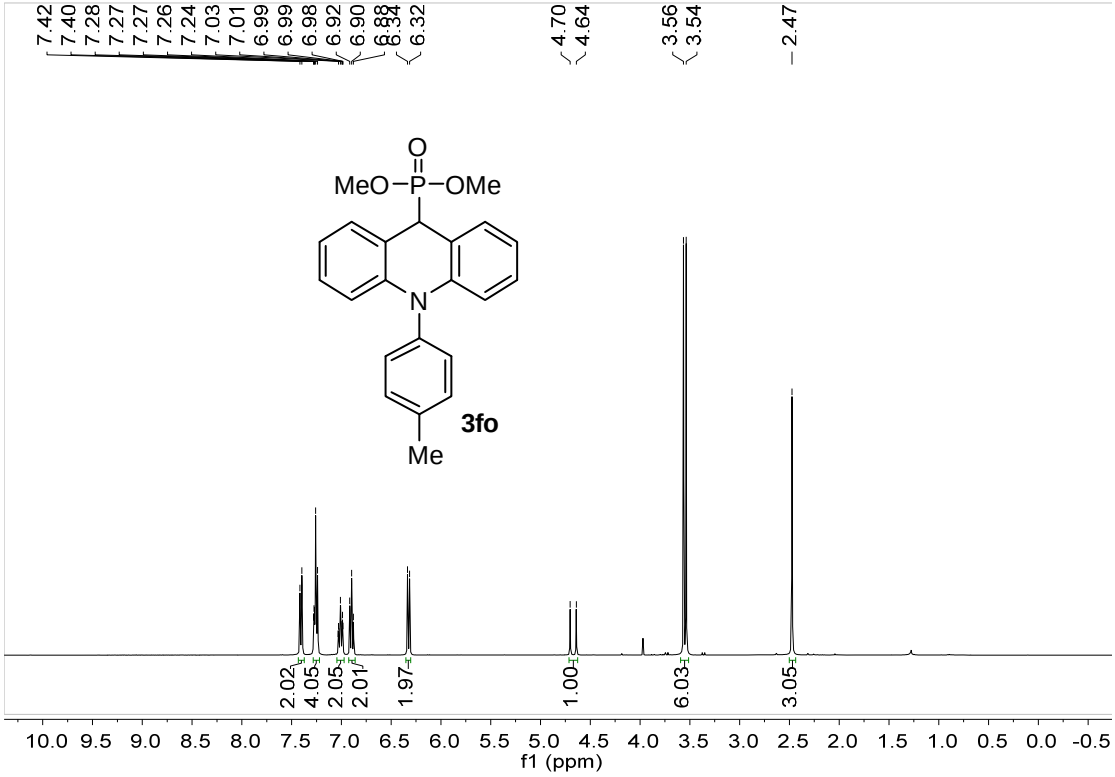
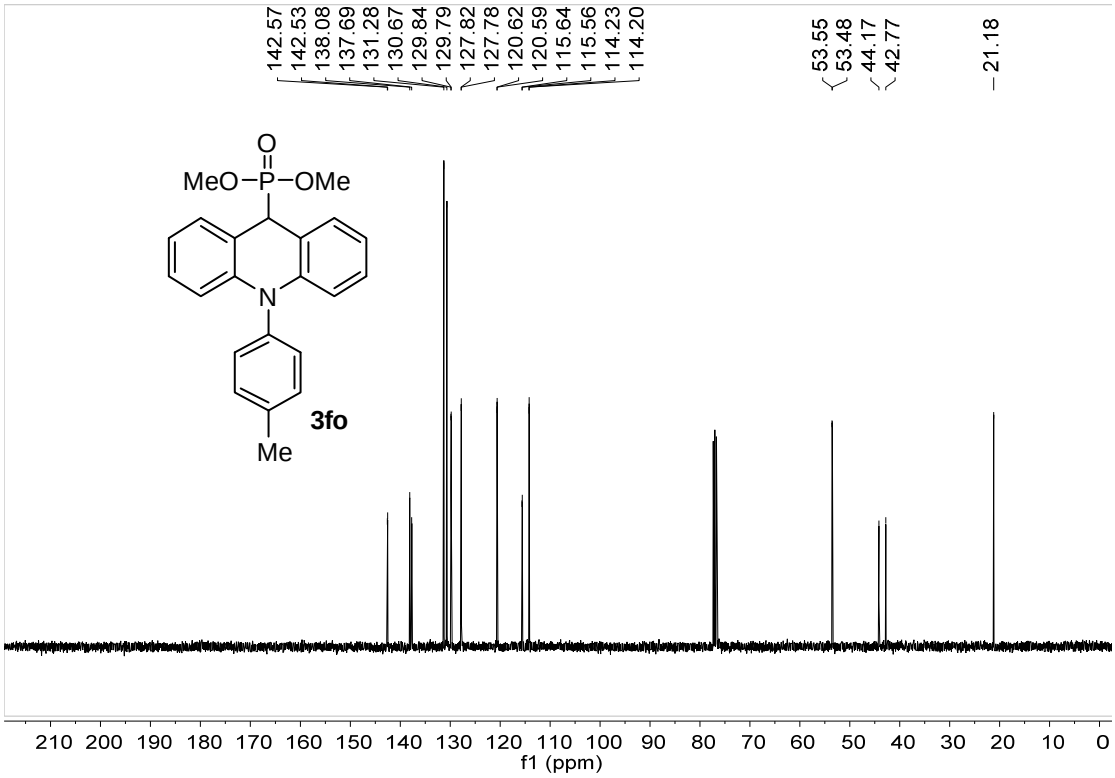
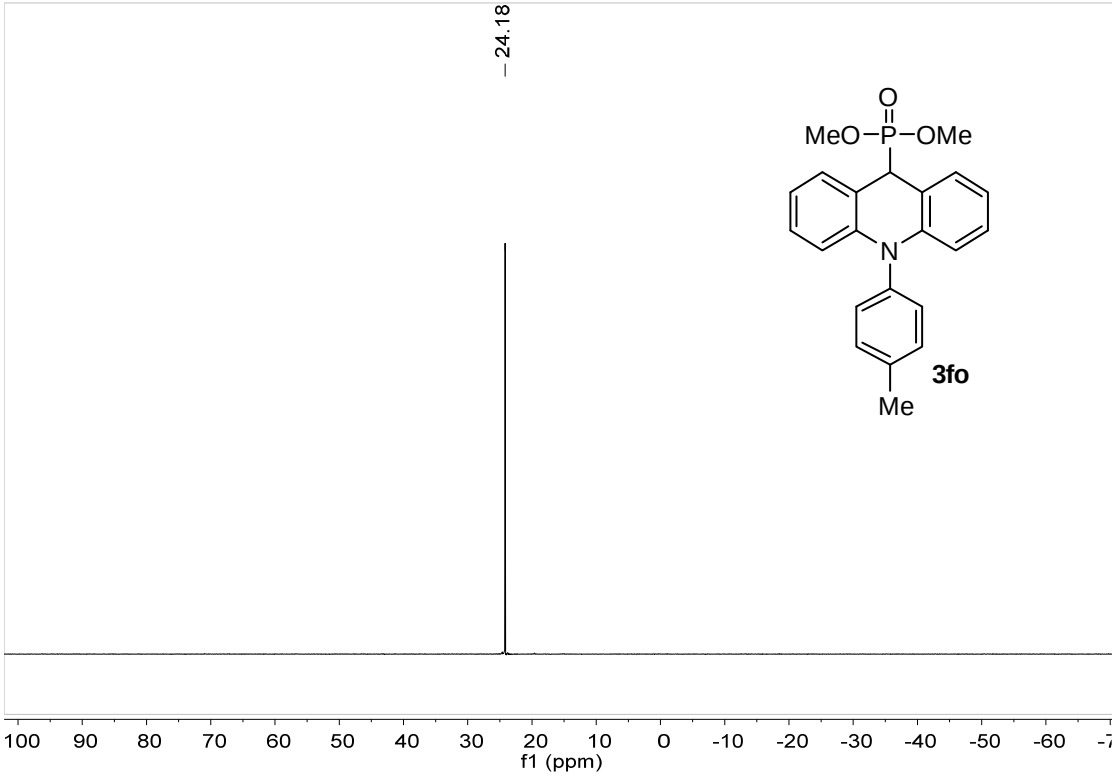
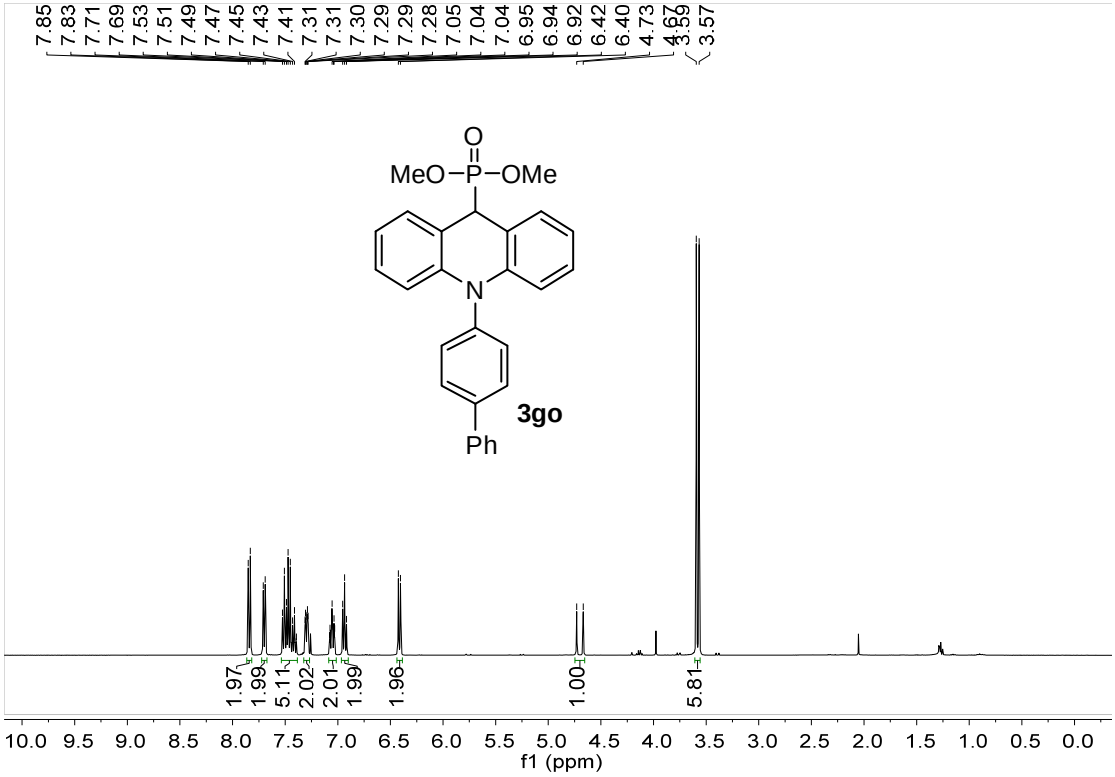
142.43
140.48
131.08
130.66
129.89
129.84
128.26
127.87
127.83
120.76
120.72
115.76
115.68
114.25
114.22
53.58
53.50
44.20
42.81
O
MeO−P−OMe
N
Ph
3eo
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


24.18
O
MeO–P–OMe
N
Ph
3eo
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)


7.42
7.40
7.28
7.27
7.27
7.26
7.24
7.03
7.01
6.99
6.99
6.98
6.92
6.90
6.34
6.32
4.70
4.64
3.56
3.54
2.47
O
MeO–P–OMe
N
3fo
Me
2.02
4.05
2.05
2.01
1.97
1.00
6.03
3.05
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)


142.57
142.53
138.08
137.69
131.28
130.67
129.84
129.79
127.82
127.78
120.62
120.59
115.64
115.56
114.23
114.20
53.55
53.48
44.17
42.77
21.18
MeO−P−OMe
O
N
Me
3fo
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


24.18
MeO−P−OMe
O
N
Me
3fo
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60
f1 (ppm)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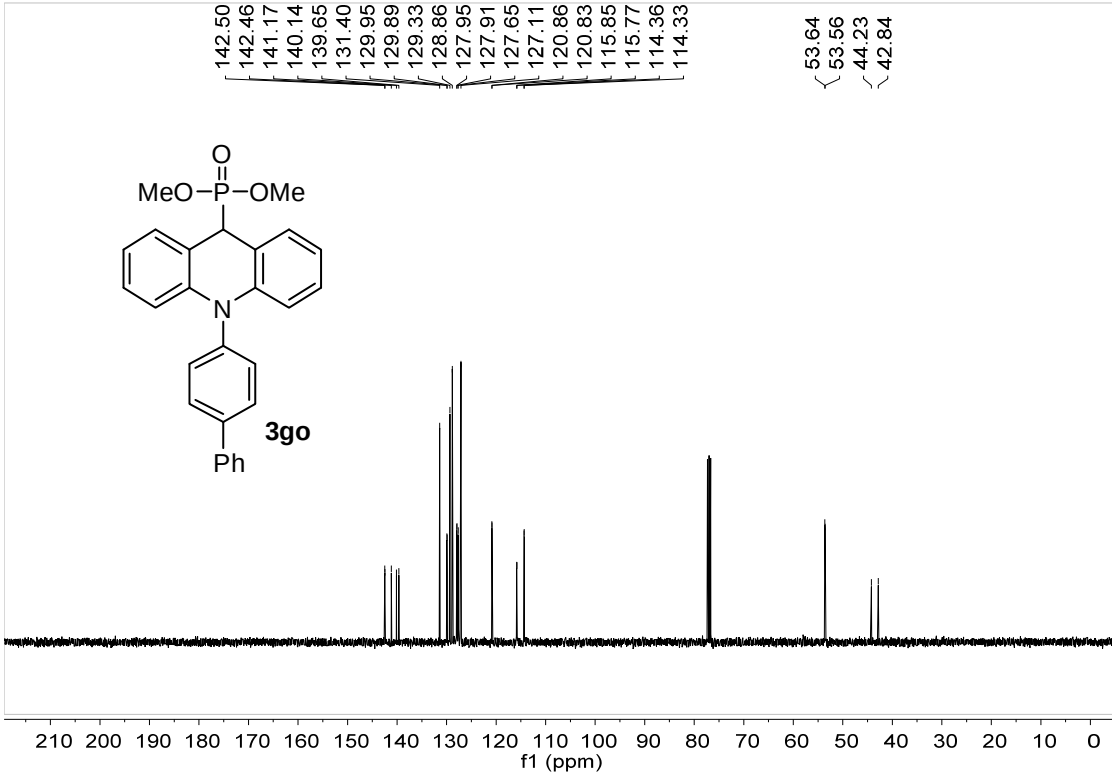
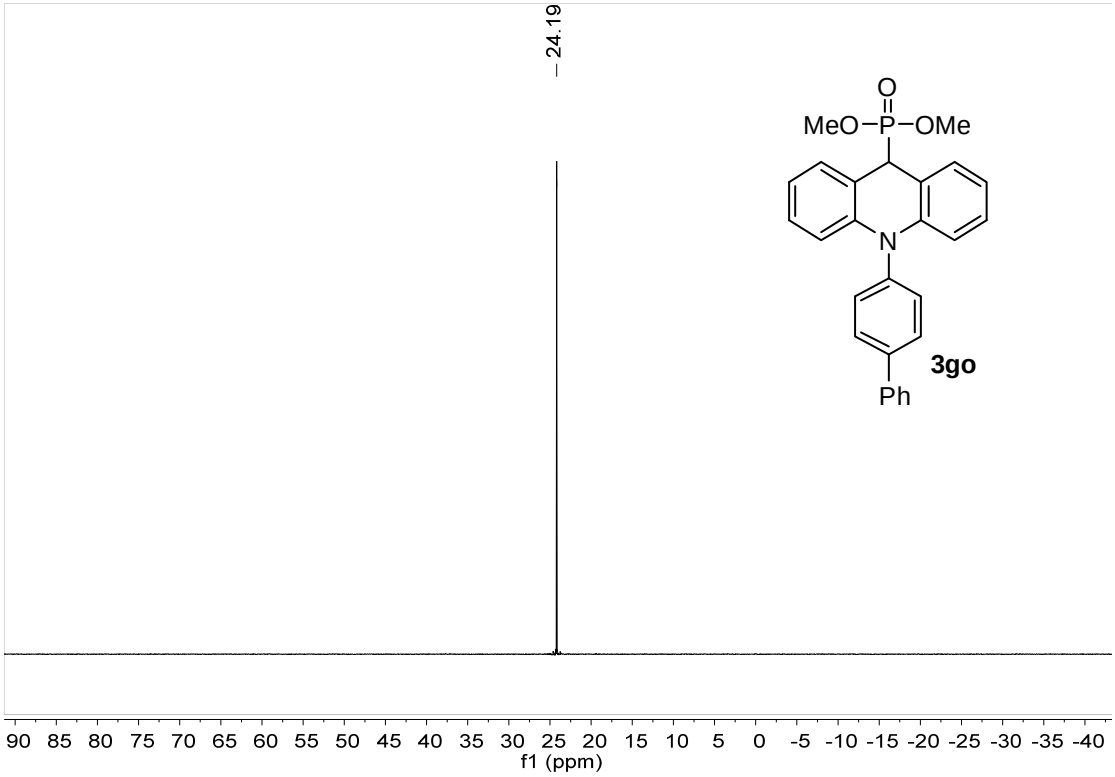
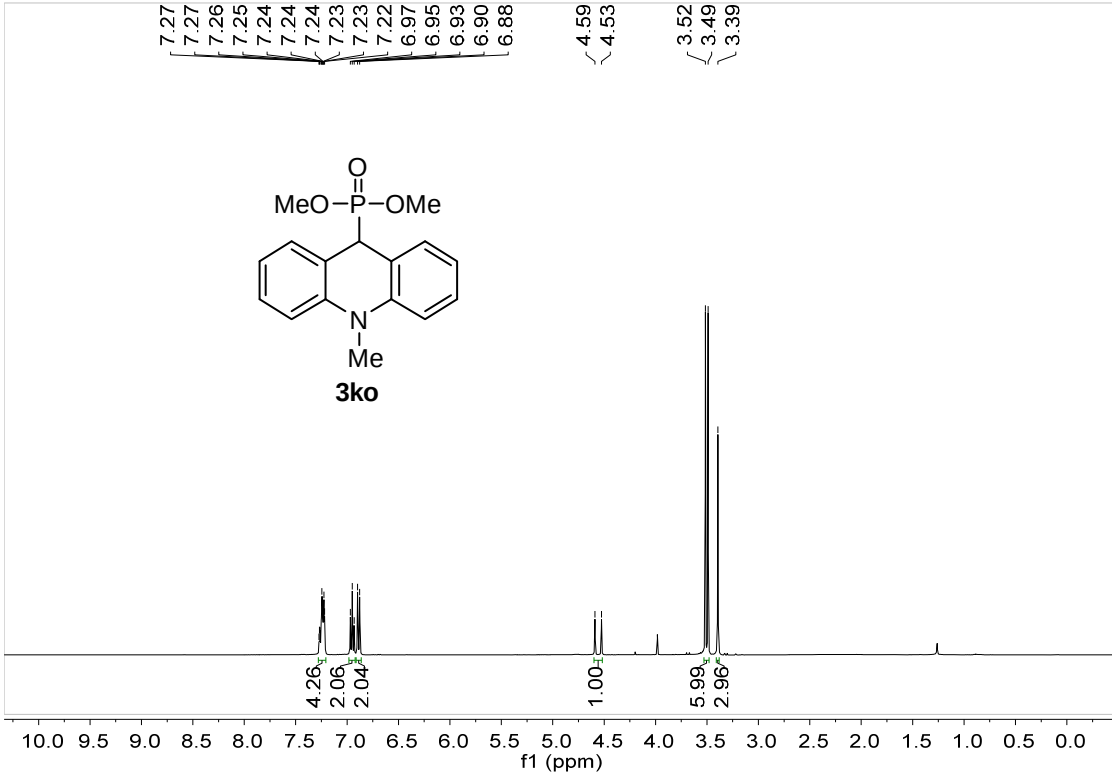
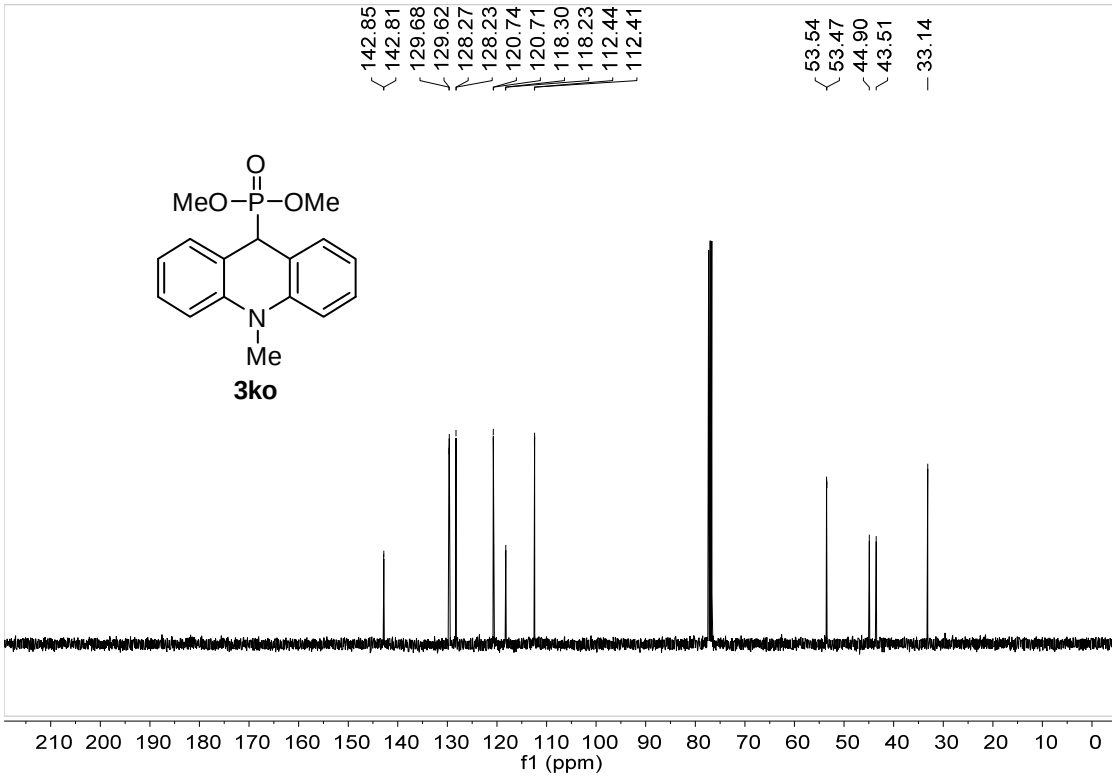
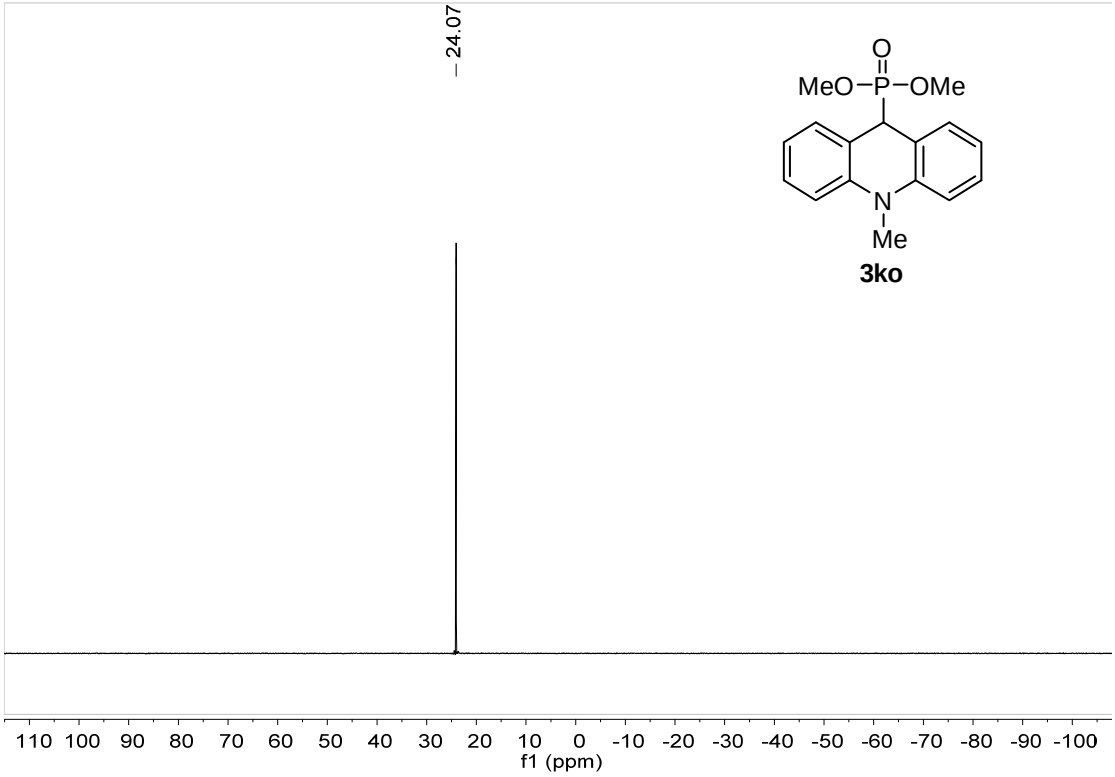
7.83
7.71
7.69
7.53
7.51
7.49
7.47
7.45
7.43
7.41
7.31
7.31
7.30
7.29
7.29
7.28
7.05
7.04
7.04
6.95
6.94
6.92
6.42
6.40
4.73
4.67
3.59
3.57
O
MeO−P−OMe
N
3go
Ph
1.97
1.99
5.11
2.02
2.01
1.99
1.96
1.00
5.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

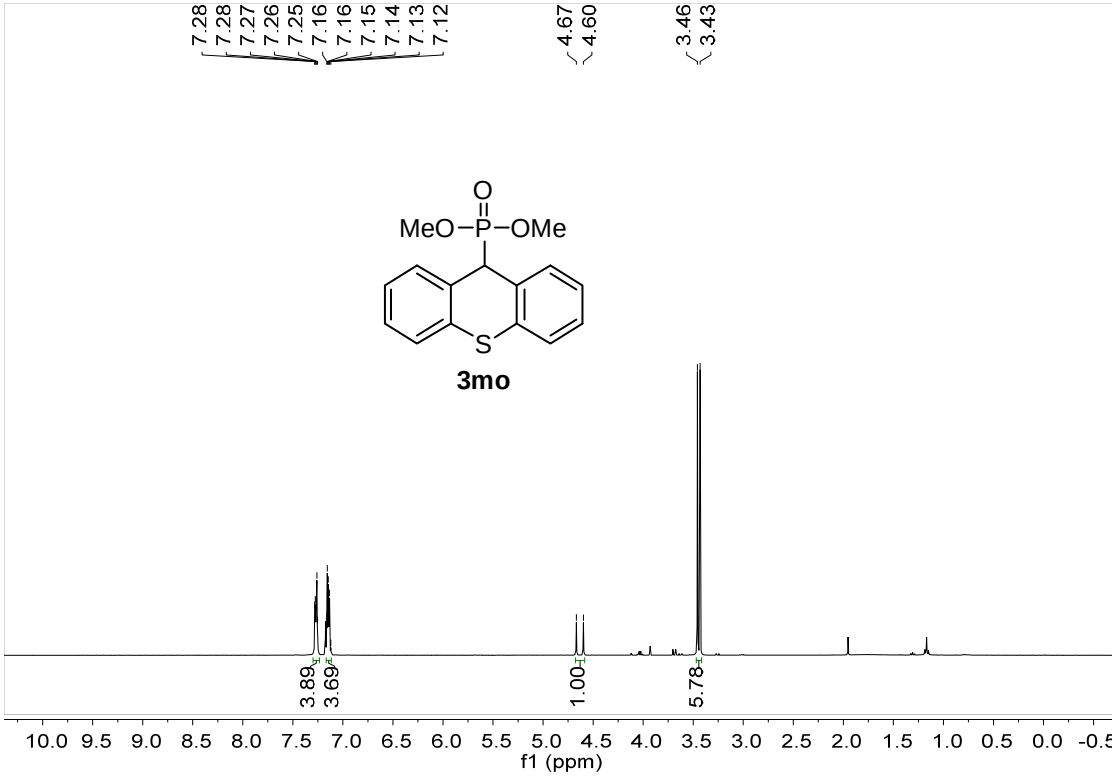

142.50
142.46
141.17
140.14
139.65
131.40
129.95
129.89
129.33
128.86
127.95
127.91
127.65
127.11
120.86
120.83
115.85
115.77
114.36
114.33
53.64
53.56
44.23
42.84
O
MeO−P−OMe
N
3go
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

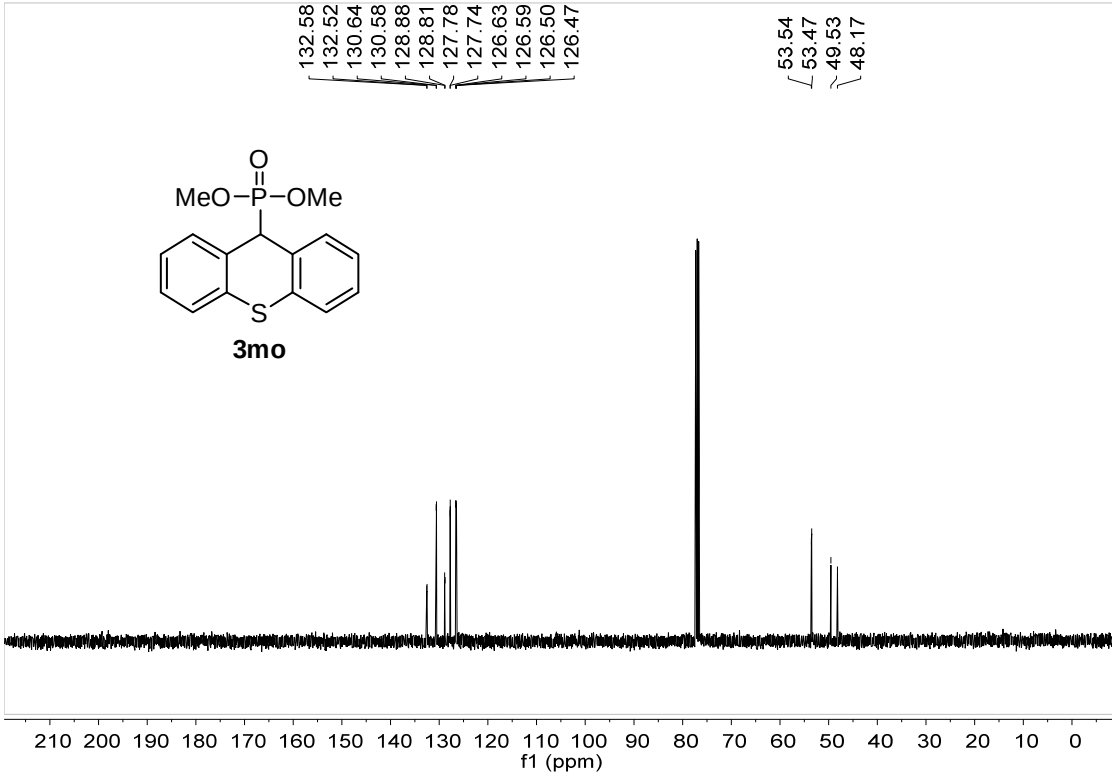

24.19
O
MeO–P–OMe
N
Ph
3go
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

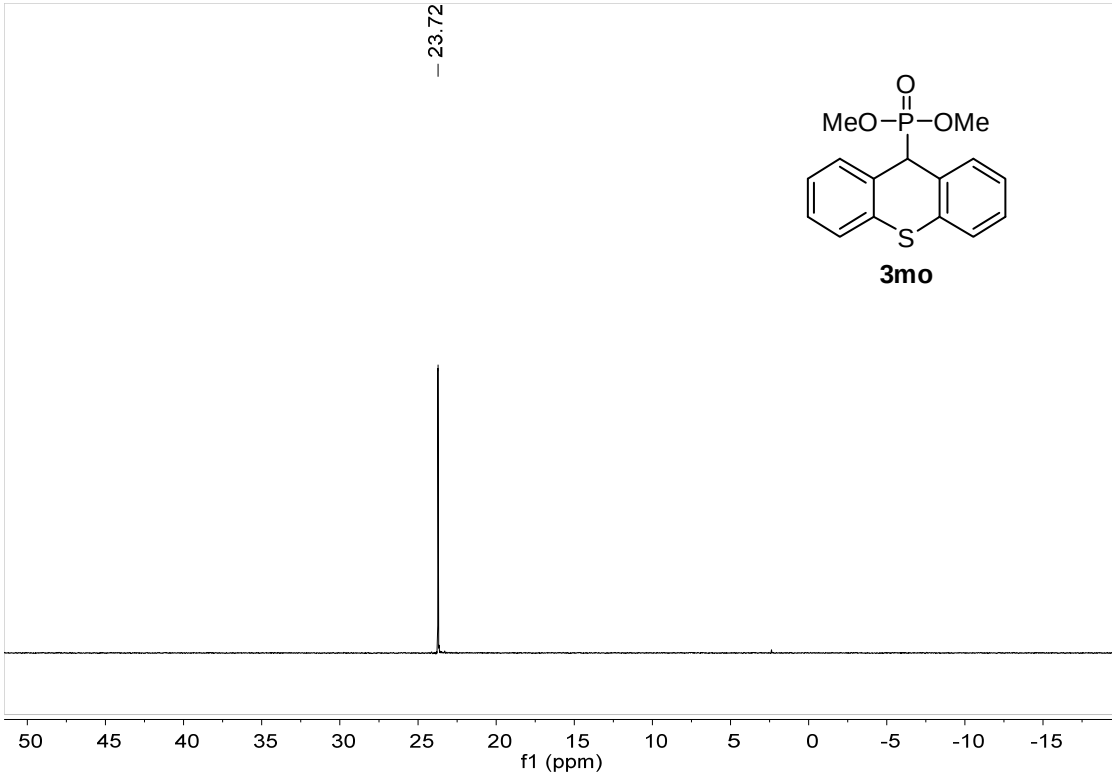

7.27
7.27
7.26
7.25
7.24
7.24
7.24
7.23
7.23
7.22
6.97
6.95
6.93
6.90
6.88
4.59
4.53
3.52
3.49
3.39
O
MeO–P–OMe
N
Me
3ko
4.26
2.06
2.04
1.00
5.99
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.85
142.81
129.68
129.62
128.27
128.23
120.74
120.71
118.30
118.23
112.44
112.41
53.54
53.47
44.90
43.51
33.14
O
MeO–P–OMe
N
Me
3ko
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


24.07
O
MeO–P–OMe
N
Me
3ko
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)


7.28
7.28
7.27
7.26
7.25
7.16
7.16
7.15
7.14
7.13
7.12
4.67
4.60
3.46
3.43
O
MeO–P–OMe
S
3mo
3.89
3.69
1.00
5.78
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)


132.58
132.52
130.64
130.58
128.88
128.81
127.78
127.74
126.63
126.59
126.50
126.47
53.54
53.47
49.53
48.17
O
MeO–P–OMe
S
3mo
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


23.72
O
MeO–P–OMe
S
3mo
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
f1 (ppm)