DDQ-mediated direct C(sp³)–H phosphorylation of xanthene derivatives

Qian Chen,*a,b Xiaofeng Wang,a Guodian Yu,a Chunxiao Wen,a and Yanping Huoa

aSchool of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China; bKey Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510640, China

*qianchen@gdut.edu.cn

SUPPORTING INFORMATION

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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\(_3\) (\(\delta\) 7.26 ppm) for \(^1\)H NMR and CDCl\(_3\) (\(\delta\) 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

1a 1b 1c 1d 1e 1f 1g 1h 1i 1j 1k 1l 1m

2a 2b 2c 2d 2e 2f 2g 2h 2i 2j 2k 2l 2m

S3
3. General procedure for the phosphorylation reaction

To a solution of 9H-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 Na₂SO₃ solution (15 mL) and extracted with ethyl acetate (3×15 mL). The extracts were combined and dried over anhydrous Na₂SO₄. 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(9H-xanthen-9-yl)phosphine oxide (3aa):**

![3aa]

White solid (110 mg, 96%): mp 253–254 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 29.8; HRMS (ESI-TOF) \textit{m/z}: [M + H]\(^+\) calcd for C\(_{25}\)H\(_{20}\)O\(_2\)P 383.1195, found 383.1189.

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

![3ab]

White solid (107 mg, 87%): mp 218–220 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)): \(\delta\) 30.2; HRMS (ESI-TOF) \textit{m/z}: [M + H]\(^+\) calcd for C\(_{27}\)H\(_{24}\)O\(_2\)P 411.1508, found 411.1516.
Di([1,1'-biphenyl]-4-yl)(9H-xanthen-9-yl)phosphine oxide (3ac):

\[
\text{Ph} \begin{array}{c}
\text{P} \\
\text{O} \\
\text{Ph}
\end{array}
\text{3ac}
\]

White solid (67 mg, 42%): mp 253–255 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 30.1; HRMS (ESI-TOF) \(m/z\): [M + H]^+ calcd for C\(_{37}\)H\(_{28}\)O\(_2\)P 535.1821, found 535.1825.

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

\[
\text{Cl} \begin{array}{c}
\text{P} \\
\text{O} \\
\text{Cl}
\end{array}
\text{3ad}
\]

White solid (98 mg, 72%): mp 243–245 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 28.5; HRMS (ESI-TOF) \(m/z\): [M + Na]^+ calcd for C\(_{25}\)H\(_{17}\)Cl\(_2\)O\(_2\)PNa 473.0235, found 473.0236.
Bis(4-fluorophenyl)(9H-xanthen-9-yl)phosphine oxide (3ae):

![3ae]

White solid (83 mg, 66%): mp 208–209 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 28.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -106.0; HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) calcd for C\(_{25}\)H\(_{18}\)F\(_2\)O\(_2\)P 419.1007, found 419.1009.

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

![3af]

White solid (98 mg, 63%): mp 242–244 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 27.5; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -63.3; HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) calcd for C\(_{27}\)H\(_{18}\)F\(_6\)O\(_2\)P 519.0943, found 519.0950.
Di-\textit{m}-tolyl(9\textit{H}-xanthen-9-yl)phosphine oxide (3ag):

![Chemical Structure of 3ag]

White solid (91 mg, 74\%): mp 202–204 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$): $\delta$ 30.2; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{27}$H$_{24}$O$_2$P 411.1508, found 411.1509.

Bis(3-methoxyphenyl)(9\textit{H}-xanthen-9-yl)phosphine oxide (3ah):

![Chemical Structure of 3ah]

White solid (104 mg, 78\%): mp 183–184 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$
Bis(3-fluorophenyl)(9H-xanthen-9-yl)phosphine oxide (3ai):

![3ai]

White solid (110 mg, 88%): mp 204–205 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 27.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.0; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{27}$H$_{24}$O$_4$P 443.1407, found 443.1411.

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

![3aj]

White solid (81 mg, 66%): mp 218–219 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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), 129.0 (d, $J$ = 92.5 Hz), 128.0 (d, $J$ = 92.5 Hz), 127.7 (dd, $J$ = 8.0, 3.3 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$_3$) $\delta$ 27.7; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -111.0; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{25}$H$_{18}$F$_2$O$_2$P 419.1007, found 419.1009.
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$_3$) $\delta$ 38.0; HRMS (ESI-TOF) $m/z$: [M + H$^+$] calcd for C$_{27}$H$_{24}$O$_2$P 411.1508, found 411.1508.

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

![Structure of Bis(3,5-dimethylphenyl)(9H-xanthen-9-yl)phosphine oxide](image)

White solid (79 mg, 60%): mp 219–220 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 31.3; HRMS (ESI-TOF) $m/z$: [M + H$^+$] calcd for C$_{29}$H$_{28}$O$_2$P 439.1821, found 439.1821.

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

![Structure of Di(naphthalen-1-yl)(9H-xanthen-9-yl)phosphine oxide](image)

White solid (136 mg, 94%): mp 249–250 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 40.5; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{33}\)H\(_{24}\)O\(_2\)P 483.1508, found 483.1509.

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

![Chemical Structure](image)

Colorless oil (78 mg, 82%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 20.9; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{17}\)H\(_{20}\)O\(_4\)P 319.1094, found 319.1092.

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

![Chemical Structure](image)

Colorless oil (70 mg, 80%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 152.3 (d, \( J = 5.3 \) Hz), 130.0 (d, \( J = 4.4 \) 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\(_3\)) \( \delta \) 40.5; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{17}\)H\(_{20}\)O\(_4\)P 319.1094, found 319.1092.
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); \(^{31}\text{P} \) NMR (162 MHz, CDCl\(_3\)) \( \delta \) 23.3; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{15}\)H\(_{16}\)O\(_4\)P 291.0781, found 291.0779.

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

\[
\begin{align*}
\text{PrO-P-OPr} \\
\text{3ap}
\end{align*}
\]

Colorless oil (68 mg, 65%): \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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); \(^{31}\text{P} \) NMR (162 MHz, CDCl\(_3\)) \( \delta \) 19.0; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{19}\)H\(_{24}\)O\(_4\)P 347.1407, found 347.1410.

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

\[
\begin{align*}
\text{BuO-P-OBu} \\
\text{3aq}
\end{align*}
\]

Colorless oil (73 mg, 65%): \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 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; \(^{31}\text{P} \) NMR (162 MHz, CDCl\(_3\)) \( \delta \) 20.8; HRMS (ESI-TOF) \( m/z \): [M + H]\(^+\) calcd for C\(_{21}\)H\(_{28}\)O\(_4\)P 375.1720, found 375.1720.
Diphenyl (9H-xanthen-9-yl)phosphonate (3ar):

![3ar]

White solid (57 mg, 46%): mp 155–157 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 13.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{25}$H$_{20}$O$_4$P 415.1094, found 415.1095.

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

![3ba]

White solid (63 mg, 53%): mp 234–235 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 30.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{26}$H$_{22}$O$_2$P 397.1352, found 397.1352.
(3-Fluoro-9H-xanthen-9-yl)diphenylphosphine oxide (3ca):

White solid (52 mg, 43%): mp 241–242 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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), 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$_3$) $\delta$ 29.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.5 (d, $J$ = 5.1 Hz); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcld for C$_{25}$H$_{19}$FO$_2$P 401.1101, found 401.1099.

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

White solid (62 mg, 45%): mp 250–251 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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\(_3\)) \( \delta \) 29.7; HRMS (ESI-TOF) \( m/z \): [M + H\(^+\)] calcd for C\(_{25}\)H\(_{19}\)BrO\(_2\)P 461.0301, found 461.0303.

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

![Structure](image)

White solid (117 mg, 85%): mp 193–195 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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):

![Structure](image)

White solid (133 mg, 94%): mp 189–191 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 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$_3$) $\delta$ 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$_3$) $\delta$ 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):

Yellow solid (115 mg, 72%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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,
= 4.0 Hz), 114.1, 113.3 (d, \( J = 2.4 \text{ Hz} \)), 55.2, 50.3, 49.6 (d, \( J = 63.3 \text{ Hz} \)); 
\( ^{31} \text{P NMR} \) (162 MHz, CDCl\(_3\)) \( \delta \) 26.9; HRMS (ESI-TOF) \( \text{m/z} \): \([\text{M} + \text{Na}]^+\) calcd for C\(_{33}\)H\(_{28}\)NO\(_2\)PNa 524.1750, found 524.1761.

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

![Diagram of 3ja]

Yellow solid (159 mg, 96%): \( \text{mp 274–275 °C} \); \( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.52–7.46 (m, 6H), 7.40–7.33 (m, 6H), 7.06–6.99 (m, 4H), 6.89 (d, \( J = 8.4 \text{ Hz} \), 2H), 6.84–6.78 (m, 2H), 6.37 (d, \( J = 8.1 \text{ Hz} \), 2H), 5.02 (d, \( J = 18.4 \text{ Hz} \), 1H), 4.24 (s, 2H); 
\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 141.8 (d, \( J = 3.7 \text{ Hz} \)), 135.7, 132.5 (d, \( J = 8.4 \text{ Hz} \)), 131.9, 131.8 (d, \( J = 2.7 \text{ Hz} \)), 130.5 (d, \( J = 4.3 \text{ Hz} \)), 129.8 (d, \( J = 93.4 \text{ Hz} \)), 128.3 (d, \( J = 3.3 \text{ Hz} \)), 127.9, 127.8, 120.9 (d, \( J = 2.7 \text{ Hz} \)), 120.7, 118.0 (d, \( J = 4.1 \text{ Hz} \)), 113.1 (d, \( J = 2.4 \text{ Hz} \)), 50.4, 49.4 (d, \( J = 63.1 \text{ Hz} \)); \( ^{31} \text{P NMR} \) (162 MHz, CDCl\(_3\)) \( \delta \) 27.5; HRMS (ESI-TOF) \( \text{m/z} \): \([\text{M} + \text{Na}]^+\) calcd for C\(_{32}\)H\(_{25}\)BrNOPNa 572.0749, found 572.0756.

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

![Diagram of 3ka]

White solid (107 mg, 90%): \( \text{mp 280–282 °C} \); \( ^{1} \text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 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, \( J = 8.1 \text{ Hz} \), 2H), 4.95 (d, \( J = 19.1 \text{ Hz} \), 1H), 2.71 (s, 3H); 
\( ^{13} \text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 142.9 (d, \( J = 3.6 \text{ Hz} \)), 132.3 (d, \( J = 8.4 \text{ Hz} \)), 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; 31P NMR (162 MHz, CDCl3) δ 26.3; HRMS (ESI-TOF) m/z: [M + H]+ calcd for C26H23NOP 396.1512, found 396.1513.

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

White solid (47 mg, 38%): mp 254–256 °C; 1H NMR (400 MHz, CDCl3) 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); 13C NMR (100 MHz, CDCl3) 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); 31P NMR (162 MHz, CDCl3) δ 31.9; HRMS (ESI-TOF) m/z: [M + H]+ calcd for C28H26OP 409.1716, found 409.1716.

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

White solid (105 mg, 96%): mp 157–159 °C; 1H NMR (400 MHz, CDCl3) 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), 7.21–7.13 (m, 2H), 7.10–7.02 (m, 2H), 6.55–6.47 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 172.1 (d, J = 2.7 Hz), 151.4 (d, J = 2.7 Hz), 147.7 (d, J = 2.7 Hz), 137.1 (d, J = 2.7 Hz), 131.8 (d, J = 2.7 Hz), 131.2 (d, J = 2.7 Hz), 130.8 (d, J = 2.7 Hz), 130.4 (d, J = 2.7 Hz), 129.5 (d, J = 6.2 Hz), 129.4 (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 = 6.2 Hz), 38.7 (d, J = 2.6 Hz), 34.2 (d, J = 5.1 Hz), 33.6 (d, J = 3.2 Hz); 31P NMR (162 MHz, CDCl3) δ 30.7; HRMS (ESI-TOF) m/z: [M + H]+ calcd for C28H26OP 409.1716, found 409.1716.
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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 24.2; HRMS (ESI-TOF) \(m/z\): [M + Na\(^+\)] calcd for C\(_{21}\)H\(_{20}\)NO\(_3\)PNa 388.1073, found 388.1070.

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

![Image of 3fo structure]

White solid (109 mg, 96%): mp 154–155 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 24.2; HRMS (ESI-TOF) \(m/z\): [M + Na\(^+\)] calcd for C\(_{22}\)H\(_{22}\)NO\(_3\)PNa 402.1230, found 402.1221.

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

![Image of 3go structure]
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$_3$PNa 464.1386, found 464.1386.

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

![Dimethyl (10-methyl-9,10-dihydroacridin-9-yl)phosphonate (3ko)](image)

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$_3$PNa 326.0917, found 326.0914.

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

![Dimethyl (9H-thioxanthen-9-yl)phosphonate (3mo)](image)

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$_3$) $\delta$ 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$_3$) $\delta$ 23.7; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{15}$H$_{16}$O$_3$PS 307.0552, found 307.0548.

References:


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

**Top Panel:** 
- Chemical structure of compound **MeO-P-OMe** with annotations for **3fo** and **Me**. 
- NMR spectrum with peaks at 142.57, 142.53, 138.08, 137.28, 130.67, 129.79, 128.64, 128.70, 127.73, 120.59, 114.23, and 114.20 ppm. 

**Bottom Panel:** 
- Chemical structure of compound **MeO-P-OMe** with annotations for **3fo** and **Me**. 
- NMR spectrum with peaks at -24.18 ppm.