# Supporting Information

**BF₃-Et₂O Promoted Bifunctionalization of Aldehydes for the Synthesis of Arylmethyl Substituted Organophosphorus Compounds**

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**General Information.** All chemicals were obtained from Sigma-Aldrich, Tokyo Chemical Industry and S. D. Fine, the progress of the reactions was monitored by thin-layer chromatography (TLC) on pre-coated silica-gel plates using Merck Silica Gel 60 F$_{254}$, Cat. No. 1.05554.0007 and visualized by short-wave ultraviolet light. Column chromatography was performed by hand using silica-gel (100–200 mesh, Silicycle).$^1$H, $^{13}$C, NMR spectra were recorded on Bruker-Advance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (DMSO-d$_6$: 2.5 ppm and 3.4 ppm. Carbon nuclear magnetic resonance spectra $^{13}$C NMR solvent DMSO-d$_6$: 39.90-40 ppm) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) down field from tetramethylsilane and are referenced to the carbon resonance of the solvent. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines respectively.

![Chemical Reaction](image)

**General procedure for synthesis of Compounds (3a-3l):**

To a 30 ml glass vial were added benzaldehyde (1.0 mmol) and diphenyl phosphite (1.5 mmol) in acetonitrile ACN (10ml). Then boron trifluoride diethyl etherate (1.5 mmol) was added dropwise. The reaction mixture was heated to 80 °C in an oil bath for 8 hour. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml× 2) and washed with H$_2$O (50 ml × 2).
The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

**General procedure for synthesis of Compounds (5a-5l):**

![Chemical reaction diagram]

To a 30 ml glass vial were added benzaldehyde (1.0 mmol), and diphenyl phosphite 2 (1.0 mmol), in acetonitrile ACN (10ml). Then boron trifluoride diethyl etherate (1.5 mmol), was added dropwise. After 20 minutes was added substituted phenol (1.0 mmol) and the reaction mixture was heated to 80 °C in an oil bath for 8 hour. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml× 2) and washed with H$_2$O (50 ml × 2). The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

**Optimization Table 2.**

<table>
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<th>BF$_3$-OEt$_2$ (mmol)</th>
<th>5a (% yield)</th>
<th>3a (% yield)</th>
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<td>1.5</td>
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<td>1.0</td>
<td>1.5</td>
<td>51</td>
<td>29</td>
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</tbody>
</table>
Conditions: Addition of benzaldehyde 1a (1 mmol), diphenyl phosphite 2 (0.3 mmol) in 10 mL of ACN, followed by addition of BF$_3$-OEt$_2$ (1.5 mmol) and then add external phenol after 20 minutes (1.0 mmol) at 80 °C for 8 h.

**General procedure for synthesis of Compounds (7a-7l):**

![Chemical Reaction](image)

To a 30 ml glass vial were added benzaldehyde (1.0 mmol), and diphenyl phosphite 2 (1.0 mmol), in acetonitrile ACN (10ml). Then boron trifluoride diethyl etherate (1.5 mmol), was added dropwise. After that was added aliphatic thiol 6 (1.0 mmol) and the reaction mixture was heated to 80 °C in an oil bath for 8 hour. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml× 2) and washed with H$_2$O (50 ml × 2). The organic layer was dried.
over anhydrous Na$_2$SO$_4$, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

**General procedure for synthesis of Compounds 10 and 12:** To a 30 ml glass vial were added 1 (1.0 mmol), diphenyl phosphite 2 (1 mmol) and indole 9 or 11 (1 mmol) in acetonitrile (ACN). The boron trifluoride diethyl etherate (1.5 mmol) was added dropwise to the reaction mixture. The reaction mixture was heated to 80 °C in an oil bath for 8 hours. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml × 2) and washed with H$_2$O (50 ml × 2). The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) to get the desired product 10 and 12 respectively.

**General procedure for synthesis of Compounds 13:**
To a 50 ml oven dried round bottom flask were added PCl₃ (0.4 mmol), and 2-methoxyphenol (3.2 mmol). The reaction mixture was stirred at ambient temperature for 1 hour after which tris(2-methoxyphenyl) phosphite was formed (confirmed by LC-MS). After that 1-2 drops of water was added to the same reaction mixture. Then benzaldehyde 1 and boron trifluoride diethyl etherate (1.5 mmol) were slowly added to the reaction mixture. The reaction mixture was heated to 80 °C in an oil bath for 8 hours. After completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml × 2) and washed with H₂O (50 ml × 2). The organic layer was dried over anhydrous Na₂SO₄, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

General procedure for synthesis of Compounds (8a-8i): Control Experiment (I)

To a 30 ml glass vial were added benzaldehyde (1.0 mmol), and diphenyl phosphite 2 (1.0 mmol), in acetonitrile ACN (10ml). Then boron trifluoride diethyl etherate (1.5 mmol), was added dropwise. The reaction mixture was heated to 80 °C in an oil bath for 8 hour. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled down to room temperature, extracted with ethyl acetate (25 ml × 2) and washed with H₂O (50 ml × 2).
The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

**NMR Characterization data:**

**Diphenyl ((4-hydroxyphenyl 4-methoxyphenyl) methyl) phosphonate(3a):**

![Structure of 3a](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (185mg, 81%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.56 (s, 1H), 7.61 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 7.8$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 4H), 7.15 (t, $J = 7.3$ Hz, 2H), 6.97 (d, $J = 8.5$ Hz, 2H), 6.86 (m, 6H), 5.13 (d, $J = 25.9$ Hz, 1H), 3.73 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 158.93 (s), 157.17 (s), 150.60 (s), 150.52 (s), 131.01 (s), 130.92 (s), 130.19 (d, $J = 1.5$ Hz), 129.01 (d, $J = 4.6$ Hz), 126.96 (d, $J = 4.9$ Hz), 125.55 (s), 120.90 (d, $J = 3.7$ Hz), 115.93 (s), 114.53 (s), 55.54 (s), 48.49 (d, $J = 139.1$ Hz).

$^{31}$P NMR (162 MHz, DMSO) $\delta$ 19.98 (s).

HRMS (ESI): m/z calcd. For C$_{26}$H$_{24}$O$_5$P$^+$ [M+1]$^+$ 447.1361; found: 447.1364.

**Diphenyl ((4-hydroxyphenyl) (2-methoxyphenyl) methyl) phosphonate(3b)**

![Structure of 3b](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (180 mg, 78%) as a colourless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (m, 1H), 7.33 – 7.25 (m, 4H), 7.17 (m, 4H), 7.00 (d, $J = 1.0$ Hz, 3H), 6.87 – 6.78 (m, 5H), 6.54 (d, $J =$
8.5 Hz, 2H), 5.43 (d, J = 25.8 Hz, 1H), 3.75 (s, 3H). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 131.00 (s), 130.92 (s), 130.12 (s), 130.09 – 130.03 (d), 129.53 (s), 129.49 (s), 128.73 (s), 125.08 (s), 124.58 – 124.23 (d), 120.81 (d, J = 1.6 Hz), 120.75 (s), 120.71 (s), 115.96 (s), 110.86 (s), 55.65 (s), 41.23 (d, J = 142.5 Hz).

\(^{31}\text{P NMR}\) (162 MHz, CDCl\(_3\)) \(\delta\) 19.68 (s).

HRMS (ESI): m/z calcd. For C\(_{26}\)H\(_{24}\)O\(_5\)P\(+[\text{M+1}]^+\) 447.1361: found: 447.1367.

**Diphenyl ((3,4-dimethoxyphenyl) (4-hydroxyphenyl) methyl) phosphonate (3c):**

![Image of compound 3c](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 24:76); (190mg, 76%) as a colourless oil. \(^1\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.55 (s, 1H), 7.49 (m, 2H), 7.29 (m, 4H), 7.26 – 7.22 (m, 2H), 7.15 (t, J = 7.4 Hz, 2H), 6.97 (d, J = 8.6 Hz, 1H), 6.92 – 6.80 (m, 6H), 5.10 (d, J = 25.8 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H).

\(^{13}\text{C NMR}\) (101 MHz, DMSO) \(\delta\) 157.15 (d, J = 1.7 Hz), 150.86 – 150.30 (m), 149.02 (s), 148.55 (d, J = 1.9 Hz), 130.96 (d, J = 8.3 Hz), 130.18 (s), 129.29 (d, J = 4.2 Hz), 126.87 (d, J = 5.1 Hz), 125.55 (s), 122.00 (d, J = 8.6 Hz), 120.86 (d, J = 3.8 Hz), 115.90 (s), 113.82 (d, J = 9.3 Hz), 112.42 (s), 55.95 (s), 55.92 (s), 48.80 (d, J = 138.9 Hz). \(^{31}\text{P NMR}\) (162 MHz, DMSO) \(\delta\) 19.85 (s).

HRMS (ESI): m/z calcd. For C\(_{27}\)H\(_{26}\)O\(_6\)P\(+[\text{M+1}]^+\) 475.1310: found: 475.1305.

**Diphenyl ((4-hydroxyphenyl) (3,4,5-trimethoxyphenyl) methyl) phosphonate (3d):**

![Image of compound 3d](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 32:68); (207mg, 79%) as a colourless oil. \(^1\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.53 (s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.30 (m, 4H), 7.16 (m, 2H), 6.98 (s, 2H), 6.88 (d, J = 8.1 Hz, 4H), 6.81 (d, J = 8.4 Hz, 2H), 5.10 (d, J = 25.5 Hz, 1H), 3.72 (s, 3H), 3.65 (s, 3H). \(^{13}\text{C NMR}\) (101 MHz, DMSO) \(\delta\) 157.25 (s), 153.29 (s), 150.69 (d, J = 9.7 Hz), 150.52 (d, J = 10.0 Hz),
137.28 (s), 132.47 (d, $J = 3.7$ Hz), 130.95 (d, $J = 8.0$ Hz), 130.20 (s), 130.11 (s), 126.55 (s), 126.49 (s), 125.56 (d, $J = 4.3$ Hz), 120.81 (d, $J = 3.9$ Hz), 115.93 (s), 107.39 (d, $J = 9.0$ Hz), 60.49 (s), 56.30 (s), 49.36 (d, $J = 138.5$ Hz).

$^{31}$P NMR (162 MHz, DMSO) $\delta$ 19.28 (s).

HRMS (ESI): m/z calcd. For C$_{28}$H$_{28}$O$_7$P [M+1]$^+$ 507.1573: found: 507.1569.

Diphenyl ((3-hydroxy-4-methoxyphenyl) (4-hydroxyphenyl) methyl) phosphonate (3e):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 25:75); (180mg, 78%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.51 (s, 1H), 9.13 (s, 1H), 7.46 (m, 2H), 7.28 (m, 4H), 7.18 – 7.12 (m, 3H), 7.07 – 7.01 (m, 1H), 6.93 – 6.77 (m, 7H), 4.99 (d, $J = 25.8$ Hz, 1H), 3.75 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 157.12 (s), 150.58 (d, $J = 9.7$ Hz), 147.45 (s), 146.92 (s), 130.97 (d, $J = 8.6$ Hz), 130.17 (d, $J = 1.9$ Hz), 129.46 (d, $J = 4.5$ Hz), 127.04 (d, $J = 4.9$ Hz), 125.53 (d, $J = 3.1$ Hz), 120.93 (t, $J = 3.7$ Hz), 120.72 (d, $J = 9.2$ Hz), 117.12 (d, $J = 8.3$ Hz), 115.85 (s), 112.75 (s), 56.08 (s), 48.70 (d, $J = 139.2$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 20.00 (s). HRMS (ESI): m/z calcd. For C$_{26}$H$_{24}$O$_6$P [M+1]$^+$ 463.1310: found: 463.1313.

Diphenyl ((3-bromo-4-methoxyphenyl) (4-hydroxyphenyl) methyl) phosphonate(3f):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (186 mg, 71%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.64 (s, 1H), 7.80 (t, $J = 1.8$ Hz, 1H), 7.64 (m, 1H), 7.44 (dd, $J = 8.6$, 1.6 Hz, 2H), 7.34 – 7.24 (m, 4H), 7.13 (m, 3H), 6.92 – 6.86 (m, 2H), 6.84 – 6.77 (m, 4H), 5.17 (d, $J = 25.8$ Hz, 1H), 3.81 (s,
\(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 157.25 (s), 155.08 (s), 150.46 (d, \(J = 4.5\) Hz), 150.36 (d, \(J = 4.5\) Hz), 134.01 (d, \(J = 9.1\) Hz), 130.95 (d, \(J = 8.4\) Hz), 130.68 (d, \(J = 4.2\) Hz), 130.24 (d, \(J = 6.3\) Hz), 126.41 (d, \(J = 5.1\) Hz), 125.68 (d, \(J = 4.1\) Hz), 120.77 (d, \(J = 3.9\) Hz), 116.05 (s), 113.23 (s), 110.93 (s), 56.68 (s), 47.76 (d, \(J = 139.5\) Hz).

\(^{31}\)P NMR (162 MHz, DMSO) \(\delta\) 19.28 (s).

HRMS (ESI): m/z calcd. For C\(_{26}\)H\(_{23}\)BrO\(_{5}\)P [M+1]+ 525.0466. found: 525.0469.

**Diphenyl (bis(4-hydroxyphenyl) methyl) phosphonate(3g):**

![Diagram of Diphenyl (bis(4-hydroxyphenyl) methyl) phosphonate](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 20:80); (164mg, 76%) as a colourless oil. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.49 (s, 2H), 7.47 – 7.41 (m, 4H), 7.29 (t, \(J = 7.9\) Hz, 4H), 7.15 (t, \(J = 7.2\) Hz, 2H), 6.87 – 6.74 (m, 8H), 5.00 (d, \(J = 26.0\) Hz, 1H). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 157.04 (s), 150.61 (s), 150.51 (s), 130.97 (s), 130.88 (s), 130.16 (s), 127.17 (s), 127.12 (s), 125.51 (s), 120.89 (d, \(J = 4.0\) Hz), 115.86 (s), 48.57 (d, \(J = 138.8\) Hz).\(^{31}\)P NMR (162 MHz, DMSO) \(\delta\) 20.11 (s). HRMS (ESI): m/z calcd. For C\(_{25}\)H\(_{22}\)O\(_{5}\)P [M+1]+ 433.1205. found: 433.1203.

**Diphenyl ((4-hydroxyphenyl(5-methylfuran-2-yl) methyl) phosphonate(3h):**

![Diagram of Diphenyl ((4-hydroxyphenyl(5-methylfuran-2-yl) methyl) phosphonate](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (174mg, 77%) as a colourless oil. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.51 (s, 1H), 7.33 (m, 6H), 7.18 (m, 2H), 7.00 – 6.95 (m, 2H), 6.85 – 6.74 (m, 4H), 6.39 (s, 1H), 6.06 (d, \(J = 2.3\) Hz, 1H), 5.21 (d, \(J = 26.9\) Hz, 1H), 2.20 (s, 3H). \(^{13}\)C NMR (101 MHz, DMSO) \(\delta\) 157.42 (s), 151.82 (s), 150.57 (d, \(J = 5.6\) Hz), 147.70 (s), 131.18 (d, \(J = 6.9\) Hz), 130.23 (d, \(J = 8.8\) Hz), 125.61 (d, \(J = 6.1\) Hz), 124.13 (d, \(J = 6.4\) Hz), 120.83 (d, \(J = 4.2\) Hz), 120.75 (d, \(J = 4.0\) Hz),
115.81 (s), 110.10 (d, J = 6.3 Hz), 107.34 (s), 43.83 (d, J = 141.9 Hz), 13.70 (s).\textsuperscript{31}P NMR (162 MHz, DMSO) δ 18.25 (s). \textbf{HRMS} (ESI): m/z calcd. For C\textsubscript{24}H\textsubscript{22}O\textsubscript{5}P [M+1]\textsuperscript{+} 421.1205. found: 421.1199.

\textbf{Diphenyl (S)-((4-hydroxyphenyl) (5-methylthiophen-2-yl) methyl) phosphonate(3i):}

![Diphenyl (S)-((4-hydroxyphenyl) (5-methylthiophen-2-yl) methyl) phosphonate(3i)](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (176mg, 76%) as a colourless oil. \textbf{\textsuperscript{1}H NMR} (400 MHz, DMSO) δ 9.54 (s, 1H), 7.43 (m, 2H), 7.32 (m, 4H), 7.22 – 7.12 (m, 2H), 7.07 (t, J = 3.2 Hz, 1H), 6.96 (m, 2H), 6.78 (d, J = 8.5 Hz, 4H), 6.70 (m, 1H), 5.40 (d, J = 26.5 Hz, 1H), 2.40 (s, 3H) \textbf{\textsuperscript{13}C NMR} (101 MHz, DMSO) δ 157.40 (d, J = 2.2 Hz), 150.51 (d, J = 10.0 Hz), 139.70 (d, J = 2.9 Hz), 136.35 (d, J = 5.1 Hz), 131.03 (s), 130.96 (s), 130.29 (s), 130.16 (s), 127.68 (d, J = 8.7 Hz), 126.18 (s), 125.62 (d, J = 9.2 Hz), 120.88 (d, J = 3.9 Hz), 120.77 (d, J = 4.0 Hz), 115.84 (s), 44.80 (d, J = 142.1 Hz), 15.33 (s).\textsuperscript{31}P NMR (162 MHz, DMSO) δ 17.72 (s). \textbf{HRMS} (ESI): m/z calcd. For C\textsubscript{24}H\textsubscript{21}O\textsubscript{4}PS [M+1]\textsuperscript{+} 437.0976: found: 437.0976.

\textbf{Diphenyl ((6-bromobenzo[d] [1,3] dioxol-5-yl) (4-hydroxyphenyl) methyl) phosphonate(3j):}

![Diphenyl ((6-bromobenzo[d] [1,3] dioxol-5-yl) (4-hydroxyphenyl) methyl) phosphonate(3j)](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 22:78); (193mg, 72%) as a colourless oil. \textbf{\textsuperscript{1}H NMR} (400 MHz, DMSO) δ 9.58 (s, 1H), 7.54 (d, J = 1.7 Hz, 1H), 7.44 – 7.26 (m, 7H), 7.24 – 7.12 (m, 2H), 6.91 (dd, J = 7.6, 1.0 Hz, 2H), 6.86 – 6.73 (m, 4H), 6.10 (m, 2H), 5.21 (d, J = 26.3 Hz, 1H). \textbf{\textsuperscript{13}C NMR} (101 MHz, DMSO) δ 157.51 (s), 150.40 (s), 150.30 (s), 150.22 (s), 148.01 (d, J = 27.7 Hz), 131.07 (d, J = 7.9 Hz),
130.33 (d, $J = 11.7$ Hz), 128.67 (s), 125.80 (d, $J = 9.0$ Hz), 124.73 (s), 120.68 (d, $J = 4.0$ Hz), 116.14 (s), 115.83 (s), 115.69 (s), 113.25 (s), 110.03 (s), 102.83 (s), 48.00 (d, $J = 141.6$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 18.25 (s). HRMS (ESI): m/z calcd. For C$_{26}$H$_{21}$BrO$_6$P [M+1]$^+$ 539.0259: found: 539.0264.

**Diphenyl ((5-(2-chlorophenyl) furan-2-yl) (4-hydroxyphenyl) methyl) phosphonate(3k):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 23:77); (136mg, 71%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.56 (s, 1H), 7.70 (m, 1H), 7.55 (m, 1H), 7.48 (m, 2H), 7.44 – 7.38 (m, 1H), 7.36 – 7.27 (m, 5H), 7.17 (d, $J = 4.5$ Hz, 2H), 7.12 (d, $J = 3.4$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 6.70 (t, $J = 3.2$ Hz, 1H), 5.47 (d, $J = 26.8$ Hz, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 157.61 (s), 150.56 (s), 150.47 – 150.40 (d), 149.94 (s), 149.53 (s), 131.28 (d, $J = 10.6$ Hz), 130.28 (d, $J = 7.5$ Hz), 129.36 (s), 128.59 (s), 128.04 (s), 125.71 (s), 123.69 – 123.63 (d), 123.59 (s), 120.73 (t, $J = 4.3$ Hz), 115.96 (s), 112.61 (s), 111.66 (s), 43.88 (d, $J = 141.6$ Hz). $^{31}$P NMR (162 MHz, DMSO) $\delta$ 15.81 (s). HRMS (ESI): m/z calcd. For C$_{29}$H$_{23}$ClO$_5$P [M+1]$^+$ 517.0972: found: 517.0966.

**Diphenyl ((3-bromobenzo[b]thiophen-2-yl) (4-hydroxyphenyl) methyl) phosphonate(3l):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 21:79); (190mg, 69%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.68 (s, 1H), 8.07 (d, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.58 – 7.42 (m, 4H), 7.30 (t, $J = 7.7$ Hz, 4H),
7.17 (m, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.3 Hz, 4H), 5.54 (d, J = 25.9 Hz, 1H).  
\[\text{\textsuperscript{13}C NMR (101 MHz, DMSO) } \delta \text{ 157.85 (s), 150.30 (d, J = 9.5 Hz), 150.09 (s), 137.89 (s), 137.03 (s), 134.83 (s), 131.25 (d, J = 7.4 Hz), 130.36 (d, J = 9.8 Hz), 126.56 (s), 126.23 (s), 125.93 (d, J = 6.7 Hz), 123.87 (s), 123.54 (s), 123.24 (s), 120.69 (d, J = 2.6 Hz), 116.26 (s), 109.07 (d, J = 15.1 Hz), 45.74 (d, J = 145.8 Hz).}\]

\[\text{\textsuperscript{31}P NMR (162 MHz, DMSO) } \delta \text{ 15.68 (s).}\]

HRMS (ESI): m/z calcd. For C\textsubscript{27}H\textsubscript{21}BrO\textsubscript{4}PS [M+1]\textsuperscript{+} 551.0082: found: 551.0083.

**Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (4-methoxyphenyl) methyl) phosphonate (5a):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (198mg, 79%) as a colourless oil.  
\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.72 (s, 1H), 7.44 (d, J = 8.5 Hz, 2H), 7.20 – 7.09 (m, 4H), 7.04 (m, 2H), 6.86 (d, J = 7.6 Hz, 2H), 6.80 (m, 4H), 6.68 (s, 1H), 6.48 (s, 1H), 5.04 (d, J = 27.6 Hz, 1H), 3.72 (s, 3H), 3.13 – 2.97 (m, 1H), 2.12 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H).}\]

\[\text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) } \delta \text{ 158.77 (d, J = 2.4 Hz), 154.28 (s), 150.51 (dd, J = 10.1, 6.5 Hz), 145.94 (d, J = 12.3 Hz), 132.11 (d, J = 5.8 Hz), 130.95 (d, J = 7.6 Hz), 129.55 (d, J = 6.1 Hz), 127.99 (d, J = 5.6 Hz), 125.05 (s), 123.72 (s), 121.80 (s), 121.07 – 120.24 (d), 115.21 (s), 114.12 (s), 113.53 (s), 112.71 (s), 55.28 (s), 44.21 (d, J = 139.9 Hz), 28.73 (s), 23.84 (d, J = 17.8 Hz), 15.64 (s).}\]

\[\text{\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) } \delta \text{ 20.00 (s).}\]

HRMS (ESI): m/z calcd. For C\textsubscript{30}H\textsubscript{32}O\textsubscript{5}P [M+1]\textsuperscript{+} 503.1987: found: 503.1992.

**Diphenyl ((4-hydroxy-5-isopropyl-2-methylphenyl) (4-methoxyphenyl) methyl) phosphonate (5b):**
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (196mg, 79%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.28 (s, 1H), 7.81 (d, $J = 0.7$ Hz, 1H), 7.49 (m, 2H), 7.33 – 7.24 (m, 4H), 7.14 (t, $J = 7.4$ Hz, 2H), 6.95 (d, $J = 8.7$ Hz, 2H), 6.85 (m, 4H), 6.65 (s, 1H), 5.03 (d, $J = 27.0$ Hz, 1H), 3.72 (s, 3H), 3.29 – 3.14 (m, 1H), 2.17 (s, 3H), 1.16 (m, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 158.87 (d, $J = 2.2$ Hz), 153.87 (s), 150.61 (dd, $J = 10.0$, 2.5 Hz), 135.00 (d, $J = 13.5$ Hz), 132.22 (s), 131.32 (d, $J = 7.6$ Hz), 153.87 (s), 150.61 (dd, $J = 10.0$, 2.5 Hz), 135.00 (d, $J = 13.5$ Hz), 132.22 (s), 131.32 (d, $J = 7.6$ Hz), 130.13 (d, $J = 2.2$ Hz), 128.01 (d, $J = 5.4$ Hz), 127.18 (d, $J = 5.4$ Hz), 120.81 (dd, $J = 7.3$, 4.0 Hz), 117.63 (s), 114.42 (s), 55.50 (s), 45.02 (d, $J = 139.7$ Hz), 26.68 (s), 23.03 (d, $J = 5.0$ Hz), 19.55 (s). $^{31}$P NMR (162 MHz, DMSO) δ 20.57 (s). HRMS (ESI): m/z calcd. For C$_{30}$H$_{32}$O$_5$P [M+1]$^+$ 503.1987: found: 503.1993.

Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (naphthalen-2-yl) methyl) phosphonate(5c):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (190mg, 71%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.33 (s, 1H), 8.33 (d, $J = 8.6$ Hz, 1H), 7.96 (m, 2H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.69 (s, 1H), 7.65 – 7.49 (m, 3H), 7.31 (t, $J = 7.9$ Hz, 2H), 7.17 (t, $J = 7.8$ Hz, 3H), 7.05 (t, $J = 7.3$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.77 (s, 1H), 6.63 (d, $J = 8.4$ Hz, 2H), 6.05 (d, $J = 27.7$ Hz, 1H), 3.36 – 3.21 (m, 1H), 2.09 (s, 3H), 1.13 (d, $J = 6.3$ Hz, 3H), 0.78 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 155.52 (s), 150.84 – 150.18 (d), 146.27 (d, $J = 11.9$ Hz), 134.04 (s), 132.90 (d, $J = 4.2$ Hz), 132.40 (s), 131.48 (d, $J = 9.8$ Hz), 130.26 (s), 130.05 (s), 129.84 (s), 129.44 (s), 128.98 (d, $J = 6.5$ Hz), 128.48 (s), 127.01 (s), 126.26 (s), 125.82 (s), 125.70 (s), 125.40 (s), 123.62 (s), 123.05 (d, $J = 3.5$ Hz), 121.68 (s), 121.00 (d, $J = 3.8$ Hz), 120.48 (d, $J = 4.1$ Hz), 115.71 (s), 112.74 (s), 39.96 (d, $J = 41.9$, 21.0 Hz). 28.66 (s), 24.43 (d, $J = 6.9$ Hz), 16.33 (s). $^{31}$P NMR (162 MHz, DMSO) δ 20.53 (s). HRMS (ESI): m/z calcd. For C$_{33}$H$_{32}$O$_4$P [M+1]$^+$ 523.2038: found: 523.2039.

Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (3,4,5-trimethoxyphenyl) methyl) phosphonate(5d):
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 28:72); (216mg, 81%) as a colourless oil. **^1H NMR** (400 MHz, DMSO) δ 9.37 (s, 1H), 7.74 (s, 1H), 7.35 – 7.25 (m, 4H), 7.14 (t, J = 7.4 Hz, 2H), 6.97 (d, J = 7.5 Hz, 4H), 6.93 – 6.85 (m, 3H), 5.27 (d, J = 27.2 Hz, 1H), 3.73 (s, 6H), 3.69 (s, 3H), 3.46 – 3.36 (m, 1H), 2.19 (s, 3H), 1.22 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.7 Hz, 3H). **^13C NMR** (101 MHz, DMSO) δ 155.56 (s), 153.26 (s), 150.92 (d, J = 9.7 Hz), 150.69 (d, J = 9.9 Hz), 146.10 (d, J = 11.8 Hz), 137.49 (s), 132.42 (d, J = 4.2 Hz), 131.88 (s), 130.10 (d, J = 7.6 Hz), 125.47 (d, J = 10.7 Hz), 123.00 (d, J = 3.5 Hz), 121.88 (s), 120.70 (t, J = 4.1 Hz), 112.52 (s), 107.90 (d, J = 8.5 Hz), 60.50 (s), 56.32 (s), 44.71 (d, J = 139.4 Hz), 28.52 (s), 24.45 (d, J = 41.2 Hz), 16.26 (s). **^31P NMR** (162 MHz, DMSO) δ 19.96 (s). **HRMS** (ESI): m/z calcd. For C_{32}H_{36}O_7P [M+1]^+ 563.2199: found: 563.2202.

**Diphenyl ((5-(2-chlorophenyl)furan-2-yl) (4-hydroxy-2-isopropyl-5-methylphenyl)methyl)phosphonate (5e):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 23:77); (217mg, 73%) as a colourless oil. **^1H NMR** (400 MHz, DMSO) δ 9.41 (s, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.56 (d, J = 1.3 Hz, 1H), 7.50 (dd, J = 8.0, 1.1 Hz, 1H), 7.40 – 7.25 (m, 6H), 7.20 – 7.06 (m, 5H), 6.85 (d, J = 5.9 Hz, 3H), 6.78 (t, J = 3.0 Hz, 1H), 5.48 (d, J = 27.6 Hz, 1H), 3.34 (m, 1H), 2.12 (s, 3H), 1.26 – 1.14 (m, 6H). **^13C NMR** (101 MHz, DMSO) δ 155.91 (s), 150.68 (s), 150.59 (s), 150.50 (s), 150.28 (d, J = 2.4 Hz), 149.52 (d, J = 2.4 Hz), 145.84 (d, J = 8.9 Hz), 132.46 (s), 131.21 (s), 130.24 (d, J = 8.3 Hz), 129.33 (d, J = 14.0 Hz), 128.59 (s), 127.94 (s), 125.68 (d, J = 7.6 Hz), 122.02 (s), 120.77 (d, J = 4.2 Hz), 120.57 (d, J
= 4.1 Hz), 120.26 (d, J = 5.4 Hz), 112.60 (s), 112.15 (s), 111.77 (d, J = 6.2 Hz), 28.82 (s), 24.88 (s), 23.45 (s), 16.23 (s). $^{31}$P NMR (162 MHz, DMSO) δ 16.08 (s).

**Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (5-methylfuran-2-yl) methyl) phosphonate (5f):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (186mg, 78%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.33 (s, 1H), 7.40 – 7.33 (m, 3H), 7.32 – 7.25 (m, 2H), 7.18 (m, J = 21.3, 11.0, 3.8 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.82 – 6.75 (m, 3H), 6.43 (t, J = 2.9 Hz, 1H), 6.05 (d, J = 2.2 Hz, 1H), 5.22 (d, J = 27.7 Hz, 1H), 3.31 – 3.18 (m, 1H), 2.19 (s, 3H), 2.07 (s, 3H), 1.14 (m, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 155.67 (d, J = 2.5 Hz), 151.73 (d, J = 2.3 Hz), 150.60 (dd, J = 13.5, 9.9 Hz), 148.94 (d, J = 1.2 Hz), 145.67 (d, J = 9.0 Hz), 132.35 (d, J = 4.7 Hz), 130.22 (d, J = 6.9 Hz), 125.61 (d, J = 6.8 Hz), 121.83 (d, J = 2.5 Hz), 120.81 (d, J = 4.0 Hz), 120.59 (d, J = 4.1 Hz), 112.02 (s), 110.27 (d, J = 5.8 Hz), 107.36 (s), 40.82 – 39.14 (d), 28.67 (s), 24.84 (s), 23.41 (s), 16.19 (s), 13.70 (s). $^{31}$P NMR (162 MHz, DMSO) δ 16.08 (s). HRMS (ESI): m/z calcd. For C$_{33}$H$_{31}$O$_5$PCl [M+1]$^+$ 573.1598: found: 573.1593.

**Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (5-methylfuran-2-yl) methyl) phosphonate (5g):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (187mg, 76%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.36 (s, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.36 (dd, J = 11.1, 4.7 Hz, 2H), 7.28 (m, J = 10.9, 4.8 Hz, 2H), 7.23 – 7.09 (m, 3H), 7.02 (m, 2H), 6.78 (m, 3H), 6.70 (d, J = 2.3 Hz, 1H), 5.38 (d, J = 27.7 Hz, 1H),
3.31 – 3.16 (m, 1H), 2.39 (s, 3H), 2.08 (s, 3H), 1.17 (d, $J = 6.6$ Hz, 3H), 1.10 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 155.69 (d, $J = 1.9$ Hz), 150.66 (d, $J = 2.5$ Hz), 150.57 (d, $J = 2.3$ Hz), 145.59 (d, $J = 10.5$ Hz), 139.74 (d, $J = 3.0$ Hz), 136.89 (d, $J = 4.9$ Hz), 131.93 (s), 130.28 (s), 130.15 (s), 127.75 (d, $J = 8.4$ Hz), 125.61 (d, $J = 9.2$ Hz), 122.82 (d, $J = 3.9$ Hz), 121.86 (d, $J = 1.6$ Hz), 120.84 (d, $J = 4.1$ Hz), 120.62 (d, $J = 4.1$ Hz), 112.14 (s), 40.94 – 39.18 (d), 28.65 (s), 24.57 (s), 23.85 (s), 16.28 (s), 15.32 (s). $^{31}$P NMR (162 MHz, DMSO) δ 17.94 (s).

HRMS (ESI): m/z calcd. For C$_{28}$H$_{30}$O$_4$PS [M+1]$^+$ 493.1602: found: 493.1601.

Diphenyl ((4-hydroxy-2,3-dimethylphenyl) (4-methoxyphenyl) methyl) phosphonate(5h):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (184mg, 77%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.34 (s, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.46 (m, 2H), 7.33 – 7.24 (m, 4H), 7.14 (dt, $J = 11.9$, 7.3 Hz, 2H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.78 (m, 3H), 5.10 (d, $J = 27.4$ Hz, 1H), 3.72 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 158.83 (s), 154.73 (s), 150.65 (d, $J = 10.0$ Hz), 150.50 (d, $J = 10.0$ Hz), 136.84 (d, $J = 13.2$ Hz), 131.43 (d, $J = 7.7$ Hz), 130.17 (d, $J = 6.0$ Hz), 128.15 (d, $J = 5.4$ Hz), 127.09 (s), 125.60 (s), 125.43 (s, $J = 17.6$ Hz), 125.32 (s), 123.69 (s), 120.90 (d, $J = 3.8$ Hz), 120.76 (d, $J = 4.0$ Hz), 114.39 (s), 112.55 (s), 55.54 (s), 45.36 (d, $J = 139.7$ Hz), 15.92 (s), 12.76 (s). $^{31}$P NMR (162 MHz, DMSO) δ 20.70 (s). HRMS (ESI): m/z calcd. For C$_{28}$H$_{28}$O$_5$P [M+1]$^+$ 475.1674: found: 475.1679.

Diphenyl ((4-hydroxy-3-methylphenyl) (4-methoxyphenyl) methyl) phosphonate(5i):
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (174mg, 74%) as a colourless oil. \textsuperscript{1}H NMR (400 MHz, DMSO) δ 9.40 (s, 1H), 7.56 (m, 2H), 7.33 – 7.25 (m, 6H), 7.14 (t, J = 7.4 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.1 Hz, 4H), 6.79 (d, J = 8.9 Hz, 1H), 5.03 (d, J = 25.9 Hz, 1H), 3.73 (s, 3H), 2.11 (s, 3H). \textsuperscript{13}C NMR (101 MHz, DMSO) δ 158.87 (s), 155.18 (s), 150.63 (d, J = 2.9 Hz), 150.53 (d, J = 2.9 Hz), 132.13 (d, J = 9.0 Hz), 130.94 (d, J = 8.6 Hz), 130.16 (d, J = 1.8 Hz), 129.06 (d, J = 4.6 Hz), 128.05 (d, J = 8.3 Hz), 126.76 (d, J = 4.9 Hz), 125.51 (s), 124.48 (s), 120.90 – 120.84 (d), 115.14 (s), 114.49 (s), 55.53 (s), 48.57 (d, J = 138.9 Hz), 16.55 (s). \textsuperscript{31}P NMR (162 MHz, DMSO) δ 19.95 (s). HRMS (ESI): m/z calcd. For C\textsubscript{27}H\textsubscript{26}O\textsubscript{5}P [M+1] \textsuperscript{+} 461.1518: found: 461.1514.

**Diphenyl ((4-hydroxy-2-methylphenyl) (4-methoxyphenyl) methyl) phosphonate(5j):**

![Structure](image)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (174mg, 75%) as a colourless oil. \textsuperscript{1}H NMR (400 MHz, DMSO) δ 9.42 (s, 1H), 7.76 (dd, J = 8.5, 1.6 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.29 (m, 4H), 7.15 (q, J = 7.2 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.84 (m, 4H), 6.76 – 6.69 (m, 1H), 6.65 (s, 1H), 5.03 (d, J = 26.9 Hz, 1H), 3.73 (s, 3H), 2.22 (s, 3H). \textsuperscript{13}C NMR (101 MHz, DMSO) δ 158.91 (s), 156.92 (s), 150.54 (t, J = 9.7 Hz), 138.39 (d, J = 12.9 Hz), 131.38 (d, J = 7.9 Hz), 130.42 (s), 130.21 (d, J = 4.6 Hz), 128.01 (d, J = 5.2 Hz), 125.58 (d, J = 12.5 Hz), 120.83 (dd, J = 6.5, 4.0 Hz), 117.99 (s), 114.47 (s), 113.50 (s), 55.54 (s), 44.61 (d, J = 140.0 Hz), 20.10 (s). \textsuperscript{31}P NMR (162 MHz, DMSO) δ 20.33 (s). HRMS (ESI): m/z calcd. For C\textsubscript{27}H\textsubscript{26}O\textsubscript{5}P [M+1] \textsuperscript{+} 461.1518: found: 461.1513.

**Diphenyl (R)-((3-chloro-4-hydroxyphenyl) (4-methoxyphenyl) methyl) phosphonate(5k):**
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 26:74); (170mg, 71%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 9.67 (s, 1H), 7.74 – 7.66 (m, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.30 (t, $J = 7.7$ Hz, 4H), 7.15 (t, $J = 7.3$ Hz, 2H), 7.06 – 6.88 (m, 8H), 5.19 (d, $J = 25.9$ Hz, 1H), 3.73 (s, 3H). $^{31}$P NMR (162 MHz, DMSO) δ 19.57 (s).

$^{13}$C NMR (101 MHz, DMSO) δ 159.00 (s), 157.31 (s), 150.70 (s), 150.60 (s), 131.08 (s), 131.00 (s), 130.18 (s), 130.17 (s), 129.03 (d, $J = 4.5$ Hz), 127.00 (s), 125.55 (s), 120.94 (s), 116.04 (s), 114.57 (s), 55.49 (s), 48.73 (d, $J = 139.3$ Hz). $^{31}$P NMR (162 MHz, DMSO) δ 19.57 (s). HRMS (ESI): m/z calcd. For C$_{26}$H$_{23}$NO$_7$P [M+1]$^+$ 492.1212: found: 492.1219.

Diphenyl ((3,5-di-tert-butyl-4-hydroxyphenyl) (4-methoxyphenyl) methyl) phosphonate(5i):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 10:90); (220mg, 79%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 7.58 (m, 2H), 7.40 (d, $J = 1.7$ Hz, 2H), 7.35 – 7.27 (m, 2H), 7.25 – 7.08 (m, 4H), 6.99 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H), 6.92 – 6.87 (m, 2H), 6.67 (dd, $J = 7.6$, 0.9 Hz, 2H), 5.08 (d, $J = 25.7$ Hz, 1H), 3.74 (s, 3H), 1.34 (s, 18H). $^{13}$C NMR (101 MHz, DMSO) δ 158.87 (s), 153.59 (s), 150.80 (s), 150.71 (s), 150.55 (s), 150.45 (s), 139.79 (s), 130.87 (d, $J = 8.4$ Hz), 130.19 (s), 129.92 (s), 129.04 (s), 127.34 (d, $J = 4.8$ Hz), 126.27 (d, $J = 8.6$ Hz), 125.53 (s), 125.33 (s), 120.87 (d, $J = 4.0$ Hz), 120.71 (d, $J = 4.0$ Hz), 114.50 (s), 55.54 (s), 49.18 (d, $J = 137.5$ Hz), 35.04 (s),
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (390mg, 83%) as a colourless oil. 

**$^{1}H$ NMR (400 MHz, DMSO) $\delta$**: 7.52 (m, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.25 – 7.19 (m, 1H), 7.16 (d, $J = 8.3$ Hz, 3H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 4.88 (d, $J = 20.9$ Hz, 1H), 3.76 (s, 3H), 2.77 – 2.55 (m, 2H), 1.55 – 1.40 (m, 2H), 1.33 – 1.07 (m, 6H), 0.81 (t, $J = 7.0$ Hz, 3H). 

**$^{13}C$ NMR (101 MHz, DMSO) $\delta$**: 159.42 (d, $J = 2.4$ Hz), 150.62 (dd, $J = 9.8$, 4.3 Hz), 131.12 (d, $J = 7.0$ Hz), 130.30 (s), 130.17 (s), 127.14 (d, $J = 4.5$ Hz), 125.64 (d, $J = 12.4$ Hz), 120.95 (d, $J = 4.2$ Hz), 120.76 (d, $J = 4.2$ Hz), 114.39 (s), 55.57 (s), 44.08 (d, $J = 148.9$ Hz), 32.43 (d, $J = 6.6$ Hz), 31.18 (s), 28.79 (s), 28.18 (s), 22.42 (s), 14.31 (s).

**$^{31}P$ NMR (162 MHz, DMSO) $\delta$**: 16.16 (s).

**HRMS (ESI):** m/z calcd. For C$_{26}$H$_{31}$O$_4$PS $[M+1]^+$ 471.1759: found: 471.1761.

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The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (390mg, 83%) as a colourless oil. 

**$^{1}H$ NMR (400 MHz, DMSO) $\delta$**: 7.69 (m, 1H), 7.38 (m, 2H), 7.35 – 7.25 (m, 6H), 7.14 (t, $J = 7.3$ Hz, 1H), 7.03 (d, $J = 7.7$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 5.03 (d, $J = 20.8$ Hz, 1H), 3.76 (s, 3H), 2.67 (d, $J = 6.0$ Hz, 1H), 2.61 – 2.47 (m, 1H), 1.53 – 1.40 (m, 2H), 1.30 – 1.10 (m, 6H), 0.81 (t, $J = 7.0$ Hz, 3H). 

**$^{13}C$ NMR (101 MHz, DMSO) $\delta$**: 156.85 (d, $J = 8.3$ Hz), 150.66 (t, $J = 9.9$ Hz), 130.34 (s), 130.26 (s), 130.11 (s), 129.83 (s), 125.60 (d, $J = 12.0$ Hz), 123.29 (d, $J = 2.7$ Hz), 121.13 (s), 120.79 (d, $J = 4.1$ Hz), 120.55 (d, $J = 4.0$ Hz), 111.54 (s), 56.15 (s), 36.65 (d, $J = 151.7$ Hz), 32.70 (d, $J = 5.9$ Hz), 31.05 (s), 28.79 (s), 28.18 (s), 22.42 (s), 14.31 (s).
Hz), 31.19 (s), 28.81 (s), 28.04 (s), 22.40 (s), 14.26 (s). **31P NMR** (162 MHz, DMSO) δ 15.90 (s). **HRMS** (ESI): m/z calcd. For C_{26}H_{31}O_{4}PS [M+1]⁺ 471.1759: found: 471.1763.

**Diphenyl ((3,4-dimethoxyphenyl) (hexylthio) methyl) phosphonate(7c):**

![Chemical structure of Diphenyl ((3,4-dimethoxyphenyl) (hexylthio) methyl) phosphonate(7c)]

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (430mg, 86%) as a colourless oil.

**1H NMR** (400 MHz, DMSO) δ 7.43 – 7.35 (m, 2H), 7.30 (t, J = 7.9 Hz, 2H), 7.19 (m, J = 19.0, 11.6, 6.5 Hz, 6H), 6.96 (m, 3H), 4.87 (d, J = 20.8 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.70 – 2.54 (m, 2H), 1.51 (m, 2H), 1.32 – 1.10 (m, 6H), 0.81 (t, J = 7.0 Hz, 3H).

**13C NMR** (101 MHz, DMSO) δ 154.21 – 149.67 (m), 149.08 (dd, J = 8.7, 1.7 Hz), 130.19 (d, J = 15.2 Hz), 127.38 (d, J = 4.4 Hz), 125.59 (d, J = 13.4 Hz), 122.46 (d, J = 7.6 Hz), 120.91 (d, J = 4.0 Hz), 120.72 (d, J = 3.9 Hz), 113.50 (d, J = 6.8 Hz), 112.03 (s), 55.89 (d, J = 2.7 Hz), 44.54 (d, J = 148.5 Hz), 32.46 (d, J = 6.5 Hz), 31.22 (s), 28.82 (s), 28.23 (s), 22.46 (s), 14.27 (s). **31P NMR** (162 MHz, DMSO) δ 16.05 (s).

**HRMS** (ESI): m/z calcd. For C_{27}H_{34}O_{5}PS [M+1]⁺ 501.1865: found: 501.1869.

**Diphenyl -((hexylthio)(4-hydroxy-3-methoxyphenyl) methyl) phosphonate(7d):**

![Chemical structure of Diphenyl -((hexylthio)(4-hydroxy-3-methoxyphenyl) methyl) phosphonate(7d)]

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (399mg, 82%) as a colourless oil.

**1H NMR** (400 MHz, DMSO) δ 9.21 (s, 1H), 7.39 (m, 2H), 7.30 (m, 2H), 7.24 – 7.12 (m, 5H), 7.00 (m, 1H), 6.93 (t, J = 9.0 Hz, 3H), 4.76 (d, J = 20.7 Hz, 1H), 3.78 (s, 3H), 2.76 – 2.51 (m, 2H), 1.67 – 1.40 (m, 2H), 1.33 – 1.12 (m, 6H), 0.82 (t, J = 7.0 Hz, 3H).

**13C NMR** (101 MHz, DMSO) δ 150.72 (s), 150.64 (s), 148.06 (d, J = 2.6 Hz), 147.06 (s), 130.26 (s), 130.11 (s), 127.46 (d, J = 4.4 Hz), 125.61 (d, J = 11.2 Hz), 120.99 (d, J = 4.0 Hz), 120.82 (d, J = 3.9 Hz), 116.99 (d, J = 6.1 Hz), 112.33 (s), 56.03 (s), 44.51 (d, J = 149.0 Hz), 32.46 (d, J = 6.4 Hz), 31.22 (s), 28.83 (s), 28.24 (s), 22.46 (s), 14.31 (s). **31P NMR** (162 MHz, DMSO) δ 16.27 (s).

**HRMS** (ESI): m/z calcd. For C_{26}H_{32}O_{5}PS [M+1]⁺ 487.1708: found: 487.1710.

**Diphenyl -((3,4-dihydroxyphenyl) (hexylthio)methyl) phosphonate(7e):**
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (392mg, 83%) as a colourless oil. **^1H NMR** (400 MHz, DMSO) δ 9.12 (s, 1H), 9.03 (s, 1H), 7.38 (t, J = 7.3 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.24 - 7.12 (m, 4H), 7.08 (s, 1H), 6.91 (d, J = 7.9 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 6.78 - 6.73 (m, 1H), 4.67 (d, J = 20.5 Hz, 1H), 2.61 (m, 2H), 1.55 - 1.37 (m, 2H), 1.32 - 1.13 (m, 6H), 0.88 - 0.71 (t, 3H). **^13C NMR** (101 MHz, DMSO) δ 150.69 (d, J = 9.8 Hz), 145.83 (d, J = 2.4 Hz), 145.77 (s), 130.26 (s), 130.11 (s), 125.60 (d, J = 12.3 Hz), 121.28 (d, J = 8.1 Hz), 121.00 (d, J = 4.1 Hz), 120.83 (d, J = 4.0 Hz), 117.12 (d, J = 6.3 Hz), 115.80 (s), 44.55 (d, J = 149.4 Hz), 32.40 (d, J = 6.4 Hz), 31.20 (s), 28.83 (s), 28.23 (s), 14.32 (s). **^31P NMR** (162 MHz, DMSO) δ 16.49 (s).

**HRMS (ESI):** m/z calcd. For C_{25}H_{30}O_{5}PS [M+1]^+ 473.1552: found: 473.152.

**Diphenyl-((hexylthio)(3,4,5-trimethoxyphenyl) methyl) phosphonate(7f):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 21:79); (456mg, 86%) as a colourless oil. **^1H NMR** (400 MHz, DMSO) δ 7.40 (t, J = 7.9 Hz, 2H), 7.34 - 7.26 (m, 2H), 7.21 (m, 3H), 7.15 (d, J = 7.4 Hz, 1H), 6.92 (m, 4H), 4.86 (d, J = 20.9 Hz, 1H), 3.71 (s, 6H), 3.67 (s, 3H), 2.75 - 2.58 (m, 2H), 1.64 - 1.44 (m, 2H), 1.32 - 1.06 (m, 6H), 0.80 (t, J = 6.9 Hz, 3H). **^13C NMR** (101 MHz, DMSO) δ 153.19 (d, J = 1.4 Hz), 150.81 (s), 150.70 (d, J = 2.8 Hz), 150.59 (s), 137.69 (s), 130.87 (d, J = 3.9 Hz), 130.33 (s), 130.08 (s), 125.63 (d, J = 19.9 Hz), 120.85 (d, J = 4.2 Hz), 120.57 (d, J = 4.1 Hz), 107.42 (d, J = 7.3 Hz), 60.46 (s), 56.27 (s), 45.05 (d, J = 147.6 Hz), 32.63 (d, J = 6.7 Hz), 31.19 (s), 28.81 (s), 28.15 (s), 22.42 (s), 14.27 (s). **^31P NMR** (162 MHz, DMSO) δ 15.65 (s). **HRMS (ESI):** m/z calcd. For C_{28}H_{36}O_{6}PS [M+1]^+ 531.1970: found: 531.1970.

**Diphenyl (S)-((hexylthio)(1H-indol-3-yl) methyl) phosphonate(7g):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 24:76); (374mg, 86%) as a colourless oil. **^1H NMR** (400 MHz, DMSO) δ 11.21 (d, J = 2.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 2.5 Hz, 1H), 7.39 (m, J = 10.5, 6.5, 5.2 Hz, 3H), 7.29 - 7.10 (m, 7H), 7.07 - 7.00 (m, 1H), 6.93 - 6.85 (m, 2H), 5.14 (d, J = 19.8 Hz,
1H), 2.80 – 2.68 (m, 1H), 2.58 (dt, J = 12.5, 7.2 Hz, 1H), 1.47 (m, J = 14.3, 7.2, 3.1 Hz, 2H), 1.27 – 1.10 (m, 6H), 0.79 (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 150.81 (d, J = 9.9 Hz), 150.66 (s), 136.56 (s), 130.20 (d, J = 15.5 Hz), 126.69 (d, J = 8.1 Hz), 126.09 (d, J = 7.3 Hz), 125.55 (d, J = 11.1 Hz), 122.01 (s), 120.97 (d, J = 4.1 Hz), 120.80 (d, J = 4.1 Hz), 119.90 (s), 119.32 (s), 112.16 (s), 106.95 (d, J = 3.6 Hz), 36.77 (d, J = 155.4 Hz), 32.18 (d, J = 4.1 Hz), 31.16 (s), 28.87 (s), 28.24 (s), 22.39 (s), 14.32 (s).

31P NMR (162 MHz, DMSO) δ 16.68 (s).

HRMS (ESI): m/z calcd. For C27H31NO3PS [M+1]+ 480.1762: found: 480.1769.

Diphenyl (S)-((4-methoxyphenyl) (octylthio) methyl) phosphonate(7h):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 09:91); (414mg, 83%) as a colourless oil. 1H NMR (400 MHz, DMSO) δ 7.59 (m, 2H), 7.41 – 7.34 (m, 2H), 7.32 – 7.25 (m, 2H), 7.25 – 7.18 (m, 3H), 7.13 (dd, J = 13.8, 6.5 Hz, 1H), 6.97 (d, J = 8.6 Hz, 4H), 4.89 (d, J = 20.9 Hz, 1H), 3.75 (s, 3H), 2.74 – 2.56 (m, 2H), 1.60 – 1.44 (m, 2H), 1.31 – 1.16 (m, 10H), 0.86 (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 159.49 (d, J = 2.2 Hz), 150.71 (dd, J = 9.8, 4.2 Hz), 131.13 (d, J = 7.1 Hz), 130.16 (s), 127.07 (d, J = 4.4 Hz), 125.54 (d, J = 12.0 Hz), 120.95 (d, J = 4.0 Hz), 120.77 (d, J = 3.9 Hz), 114.31 (s), 55.45 (s), 44.35 (d, J = 148.9 Hz), 32.49 (d, J = 6.5 Hz), 31.77 (s), 29.11 (s), 29.02 (s), 28.89 (s), 28.59 (s), 22.62 (s), 14.33 (s). 31P NMR (162 MHz, DMSO) δ 16.06 (s).


Diphenyl (S)-((4-methoxyphenyl) (pentylthio)methyl) phosphonate(7i):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (370mg, 81%) as a colourless oil. 1H NMR (400 MHz, DMSO) δ 7.54 (dd, J = 8.8, 2.0 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.29 (t, J = 7.9 Hz, 2H), 7.24 – 7.11 (m, 4H), 6.99 – 6.90 (m, 4H), 4.89 (d, J = 20.8 Hz, 1H), 3.75 (s, 3H), 2.73 – 2.55 (m, 2H), 1.50 (p, J = 7.2 Hz, 2H), 1.32 – 1.12 (m, 4H), 0.80 (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 159.44 (d, J = 2.6 Hz), 150.70 (d, J = 4.3 Hz), 150.60 (d, J = 4.0 Hz), 131.12 (d, J = 7.0 Hz), 130.28 (s), 130.14 (s), 127.13 (d, J = 4.5 Hz), 125.62 (d, J = 12.5 Hz), 120.94 (d, J = 4.0 Hz), 120.76 (d, J = 4.1 Hz), 114.39 (s), 55.55 (s), 44.17 (d, J = 148.9 Hz), 32.42 (d, J = 6.5 Hz), 30.74 (s), 28.54 (s), 22.09 (s), 14.21 (s). 31P NMR (162 MHz, DMSO) δ 16.16 (s). HRMS (ESI): m/z calcd. For C25H30O4PS [M+1]+ 457.1602: found: 457.1603.

Diphenyl (S)-((butylthio)(4-methoxyphenyl) methyl) phosphonate(7j):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (370mg, 81%) as a colourless oil.
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 0.8:92); (354mg, 80%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 7.50 (m, 2H), 7.43 – 7.36 (m, 2H), 7.30 (t, $J = 7.9$ Hz, 2H), 7.22 (s, 1H), 7.19 – 7.11 (m, 3H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 4.87 (d, $J = 20.8$ Hz, 1H), 3.76 (s, 3H), 2.78 – 2.52 (m, 2H), 1.47 (m, 2H), 1.28 (m, $J = 13.0, 8.1, 5.0$ Hz, 3H), 0.80 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 159.40 (d, $J = 2.5$ Hz), 150.61 (s), 150.55 (s), 131.10 (d, $J = 7.1$ Hz), 130.28 (d, $J = 14.2$ Hz), 127.11 (d, $J = 4.6$ Hz), 125.67 (d, $J = 12.8$ Hz), 120.94 (d, $J = 4.0$ Hz), 120.75 (d, $J = 4.0$ Hz), 114.41 (s), 55.60 (s), 44.00 (d, $J = 4.0$ Hz), 32.06 (s, 3H), 30.88 (s), 21.66 (s), 13.86 (s).

$^{31}$P NMR (162 MHz, DMSO) δ 16.20 (s).

HRMS (ESI): m/z calcd. For C$_{24}$H$_{28}$O$_4$PS [M+1]$^+$ 443.1446: found: 443.1455.

Diphenyl (S)-((4-methoxyphenyl) (propylthio) methyl) phosphonate(7k):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (335mg, 84%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 7.96 – 6.43 (m, 15H), 4.95 (d, $J = 19.5$ Hz, 1H), 2.56 (d, $J = 40.2$ Hz, 2H), 1.38 (d, $J = 116.9$ Hz, 2H), 0.85 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 159.40 (d, $J = 2.5$ Hz), 150.61 (s), 150.55 (s), 131.10 (d, $J = 7.1$ Hz), 130.28 (d, $J = 14.2$ Hz), 127.11 (d, $J = 4.6$ Hz), 125.67 (d, $J = 12.8$ Hz), 120.94 (d, $J = 4.0$ Hz), 120.75 (d, $J = 4.0$ Hz), 114.41 (s), 55.60 (s), 44.00 (d, $J = 4.0$ Hz), 32.06 (s, 3H), 30.88 (s), 21.66 (s), 13.86 (s). $^{31}$P NMR (162 MHz, DMSO) δ 16.00 (s).

HRMS (ESI): m/z calcd. For C$_{22}$H$_{24}$O$_3$PS [M+1]$^+$ 399.1184: found: 399.1188.

Diphenyl (S)-((benzylthio)(4-methoxyphenyl) methyl) phosphonate(7l):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 10:90); (352mg, 74%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) δ 7.45 – 7.36 (m, 3H), 7.35 – 7.21 (m, 8H), 7.16 (t, $J = 7.0$ Hz, 1H), 7.10 (d, $J = 8.6$ Hz, 2H), 6.97 (t, $J = 5.9$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 4.62 (d, $J = 20.5$ Hz, 1H), 3.93 (m, 1H), 3.77 (s, 3H), 3.75 – 3.69 (m, 1H). $^{13}$C NMR (101 MHz, DMSO) δ 159.51 (s), 150.54 (s), 137.33 (s), 131.11 (d,
$J = 6.8 \text{ Hz}$), 130.41 (s), 130.25 (s), 129.53 (s), 129.04 (s), 127.77 (s), 126.40 (s), 125.76 (d, $J = 13.4 \text{ Hz}$), 120.87 (d, $J = 4.0 \text{ Hz}$), 120.69 (d, $J = 4.1 \text{ Hz}$), 114.59 (s), 55.64 (s), 44.06 (d, $J = 148.7 \text{ Hz}$), 36.41 (s). $^{31}$P NMR (162 MHz, DMSO) δ 15.60 (s).

**HRMS (ESI): m/z calcd. For C$_{27}$H$_{26}$O$_{4}$PS [M+1]$^+$ 477.1289: found: 477.1293.**

Diphenyl ((1H-indol-3-yl 4-methoxyphenyl) methyl) phosphonate (10):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 13:87); (136mg, 83%) as a colourless oil. $^{1}$H NMR (400 MHz, DMSO) δ 11.21 (d, $J = 2.1 \text{ Hz}$, 1H), 7.75 – 7.67 (m, 2H), 7.62 (dd, $J = 8.8, 2.2 \text{ Hz}$, 2H), 7.42 (d, $J = 8.1 \text{ Hz}$, 1H), 7.28 (t, $J = 7.9 \text{ Hz}$, 4H), 7.13 (m, 3H), 7.05 – 6.97 (m, 1H), 6.91 (dd, $J = 11.6, 4.7 \text{ Hz}$, 4H), 6.82 (d, $J = 8.6 \text{ Hz}$, 2H), 5.43 (d, $J = 26.3 \text{ Hz}$, 1H), 3.71 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 158.88 (d, $J = 2.8 \text{ Hz}$), 150.75 (d, $J = 5.9 \text{ Hz}$), 150.65 (d, $J = 7.1 \text{ Hz}$), 130.16 (d, $J = 1.8 \text{ Hz}$), 128.75 (d, $J = 5.8 \text{ Hz}$), 127.19 (d, $J = 12.6 \text{ Hz}$), 125.49 (d, $J = 9.5 \text{ Hz}$), 124.70 (s), 121.97 (s), 120.95 (d, $J = 3.8 \text{ Hz}$), 120.82 (d, $J = 4.1 \text{ Hz}$), 119.19 (d, $J = 14.1 \text{ Hz}$), 114.28 (s), 112.06 (s), 109.46 (d, $J = 5.1 \text{ Hz}$), 55.53 (s), $\delta$ 40.98 (d, $J = 79.0 \text{ Hz}$). $^{31}$P NMR (162 MHz, DMSO) δ 20.20 (s). HRMS (ESI): m/z calcd. For C$_{28}$H$_{25}$NO$_{4}$P [M+1]$^+$ 470.1521: found: 470.1526.

Diphenyl (S)-((4-methoxy-2-methylphenyl) (2-methoxyphenyl) methyl) phosphonate (12):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 09:91); (350 mg, 74%) as a colourless oil. $^{1}$H NMR (400 MHz, DMSO) δ 7.94 – 7.79 (m, 1H), 7.48 (d, $J = 6.8 \text{ Hz}$, 2H), 7.28 (m, 4H), 7.16 (d, $J = 4.7 \text{ Hz}$, 2H), 6.93 (d, $J = 8.6 \text{ Hz}$, 2H), 6.88 – 6.77 (m, 6H), 5.07 (d, $J = 26.8 \text{ Hz}$, 1H), 3.73 (s, 6H), 2.28 (d, $J = 14.1 \text{ Hz}$, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 158.95 (s), 158.73 (s), 150.60 (s), 150.44 (d, $J = 10.2 \text{ Hz}$), 138.60 (d, $J = 13.0 \text{ Hz}$), 131.82 (s), 131.37 (d, $J = 7.9 \text{ Hz}$), 130.26 (s), 130.19 (s), 127.75 (d, $J = 5.5 \text{ Hz}$), 127.07 (d, $J = 2.9 \text{ Hz}$), 125.60 (d, $J = 13.0 \text{ Hz}$), 120.80 (d, $J = 4.2 \text{ Hz}$), 120.74 (d, $J = 4.0 \text{ Hz}$), 116.73 (s), 114.50 (s), 114.23 (s), 111.90 (s), 55.58 (s), 55.47 (s), 44.63 (d, $J = 140.0 \text{ Hz}$), 20.13 (s). $^{31}$P NMR (162 MHz, DMSO) δ 20.04 (s). HRMS (ESI): m/z calcd. For C$_{28}$H$_{28}$O$_{5}$P [M+1]$^+$ 475.1624: found: 475.1681.

bis(2-methoxyphenyl) (S)-((4-hydroxy-3-methoxyphenyl) (phenyl) methyl) phosphonate (13a):
**31P NMR** (162 MHz, DMSO) δ 19.22 (s).

**HRMS** (ESI): m/z calcd. For C_{29}H_{30}O_{8}P [M+1]+: 537.1678 found: 537.1682.

**4,4’-((2-chlorophenyl) methylene) diphenol(8a):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (254mg, 82%) as a colourless oil. **1H NMR** (400 MHz, Acetone) δ 8.34 (s, 2H), 7.42 (m 1H), 7.30 – 7.23 (m, 2H), 7.01 (m, 1H), 6.90 (t, J = 5.6 Hz, 4H), 6.80 (t, J = 5.6 Hz, 4H), 5.80 (s, 1H). **13C NMR** (101 MHz, Acetone) δ 155.92 (s), 142.64 (s), 133.97 (s), 133.80 (s), 131.02 (s), 130.28 (s), 129.47 (s), 127.73 (s), 126.70 (s), 115.05 (s), 51.77 (s). **HRMS** (ESI): m/z calcd. For C_{19}H_{16}ClO_{2} [M+1]+: 311.0839. found: 311.0841.

**4,4’-((4-chlorophenyl) methylene) diphenol(8b):**

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (254mg, 82%) as a colourless oil. **1H NMR** (400 MHz, Acetone) δ 8.34 (s, 2H), 7.42 (m 1H), 7.30 – 7.23 (m, 2H), 7.01 (m, 1H), 6.90 (t, J = 5.6 Hz, 4H), 6.80 (t, J = 5.6 Hz, 4H), 5.80 (s, 1H). **13C NMR** (101 MHz, Acetone) δ 155.92 (s), 142.64 (s), 133.97 (s), 133.80 (s), 131.02 (s), 130.28 (s), 129.47 (s), 127.73 (s), 126.70 (s), 115.05 (s), 51.77 (s). **HRMS** (ESI): m/z calcd. For C_{19}H_{16}ClO_{2} [M+1]+: 311.0839. found: 311.0841.

**31P NMR** (162 MHz, DMSO) δ 19.22 (s).

**HRMS** (ESI): m/z calcd. For C_{29}H_{30}O_{8}P [M+1]+: 537.1678 found: 537.1682.
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (251 mg, 81%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.31 (s, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.08 (t, $J = 6.9$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 4H), 6.70 (d, $J = 8.6$ Hz, 4H), 5.37 (s, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 156.14 (s), 144.58 (s), 134.61 (s), 131.14 (s), 131.01 (s), 130.28 (s), 128.56 (s), 115.56 (s), 54.07 (s). HRMS (ESI): m/z calcd. For C$_{19}$H$_{16}$ClO$_2$ [M+1]$^+$: 311.0839. found: 311.0841.

4,4'-(4-nitropheryl) methylene) diphenol(8c):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 20:80); (253 mg, 79%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.34 (s, 2H), 8.25 – 8.06 (m, 2H), 7.33 (t, $J = 10.0$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 4H), 6.78 – 6.67 (m, 4H), 5.55 (s, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 156.35 (s), 153.65 (s), 146.22 (s), 133.78 (s), 130.54 (s), 130.37 (s), 123.90 (s), 115.70 (s), 54.40 (s). HRMS (ESI): m/z calcd. For C$_{19}$H$_{16}$NO$_4$ [M+1]$^+$: 322.1079 found: 322.1084.

4-(bis(4-hydroxyphenyl) methyl) benzonitrile(8d):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (234 mg, 78%) as a colourless oil. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.35 (s, 2H), 7.75 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 6.87 (d, $J = 8.5$ Hz, 4H), 6.70 (d, $J = 8.5$ Hz, 4H), 5.48 (s, 1H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 156.29 (s), 151.41 (s), 133.88 (s), 132.63 (s), 130.35 (s), 119.40 (s), 115.65 (s), 109.22 (s), 54.62 (s). HRMS (ESI): m/z calcd. For C$_{20}$H$_{16}$NO$_2$ [M+1]$^+$: 302.1181. found: 302.1188.

4,4'-(3-(trifluoromethyl) phenyl) methylene) diphenol(8e):
The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (251mg, 73%) as a colourless oil. \(^{1}\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.35 (s, 2H), 7.53 (dt, \(J = 15.6, 7.8\) Hz, 2H), 7.43 – 7.31 (m, 2H), 6.90 (d, \(J = 8.5\) Hz, 4H), 6.72 (d, \(J = 8.5\) Hz, 4H), 5.52 (s, 1H). \(^{13}\text{C NMR}\) (101 MHz, DMSO) \(\delta\) 156.25 (s), 147.04 (s), 134.23 (s), 133.47 (s), 130.32 (s), 129.72 (s), 125.50 (d, \(J = 3.8\) Hz), 123.24 (d, \(J = 3.7\) Hz), 120.79 (s), 115.67 (s), 54.31 (s). \(^{19}\text{F NMR}\) (377 MHz, DMSO) \(\delta\) -61.15 (s). HRMS (ESI): m/z calcd. For \(\text{C}_{20}\text{H}_{16}\text{F}_{3}\text{O}_{2}\) [M+1] \(^{+}\): 345.1102. found: 345.1110.

4,4'-(4-fluorophenyl) methylene) diphenol(8f):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (238mg, 81%) as a colourless oil. \(^{1}\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.29 (s, 2H), 7.13 – 7.05 (m, 4H), 6.86 (d, \(J = 8.5\) Hz, 4H), 6.73 – 6.64 (m, 4H), 5.37 (s, 1H). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 166.91 (s), 164.51 (s), 160.80 (s), 146.43 (s), 139.69 (s), 135.78 (d, \(J = 8.0\) Hz), 134.99 (s), 120.19 (d, \(J = 8.6\) Hz), 119.94 (s), 58.65 (s). \(^{19}\text{F NMR}\) (377 MHz, DMSO) \(\delta\) -103.61 (dt, \(J = 8.3, 5.5\) Hz). HRMS (ESI): m/z calcd. For \(\text{C}_{19}\text{H}_{16}\text{FO}_{2}\) [M+1] \(^{+}\): 295.1134. found: 295.1139.

4,4'-(3-fluorophenyl) methylene) diphenol(8g):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (235mg, 80%) as a colourless oil. \(^{1}\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.37 (s, 2H), 7.32 (td, \(J = 8.0, 6.4\) Hz, 1H), 7.01 (td, \(J = 8.3, 2.3\) Hz, 1H), 6.92 (d, \(J = 7.7\) Hz, 1H), 6.88 (d, \(J = 8.5\) Hz, 4H), 6.82 (m, 1H), 6.72 – 6.66 (m, 4H), 5.39 (s, 1H). \(^{13}\text{C NMR}\) (101 MHz, DMSO) \(\delta\) 163.79 (s), 161.37 (s), 156.18 (s), 148.59 (d, \(J = 6.8\) Hz), 134.41 (s), 130.49 (d, \(J = 8.3\) Hz), 130.27 (s), 125.48 (s), 115.90 (d, \(J = 21.3\) Hz), 115.55 (s), 113.16 (d, \(J = 20.9\) Hz), 54.35 (s). \(^{19}\text{F NMR}\) (377 MHz, CDCl\(_3\)) \(\delta\) -110.46 (td, \(J = 5.3, 3.0\) Hz). HRMS (ESI): m/z calcd. For \(\text{C}_{19}\text{H}_{16}\text{FO}_{2}\) [M+1] \(^{+}\): 295.1134. found: 295.1139.

4,4'-(4-bromophenyl) methylene) diphenol(8h):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (277mg, 77%) as a colourless oil. \(^{1}\text{H NMR}\) (400 MHz, DMSO) \(\delta\) 9.30 (s, 2H), 7.51 – 7.41 (m, 2H), 7.02 (d, \(J = 8.4\) Hz, 2H), 6.86 (t, \(J = 5.6\) Hz, 4H), 6.73 – 6.65 (m, 4H), 5.36 (s, 1H). \(^{13}\text{C NMR}\) (101 MHz, DMSO) \(\delta\) 156.13 (s), 145.03 (s), 134.52 (s), 131.52 (d, \(J = 7.0\) Hz).
Hz), 130.28 (s), 119.49 (s), 115.54 (s), 54.09 (s). HRMS (ESI): m/z calcd. For C_{19}H_{15}BrO_2 [M+1]^+: 355.0334. found: 355.0341.

4,4'-(2-bromophenyl) methylene) diphenol (8i):

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 17:83); (258mg, 75%) as a colourless oil. \(^1\)H NMR (400 MHz, DMSO) δ 9.33 (s, 2H), 7.60 (dd, \(J = 7.9, 1.2\) Hz, 1H), 7.30 (dd, \(J = 7.5, 1.2\) Hz, 1H), 7.16 (d, \(J = 1.7\) Hz, 1H), 6.93 (m, 1H), 6.81 (m, 4H), 6.71 – 6.67 (m, 4H), 5.64 (s, 1H). \(^{13}\)C NMR (101 MHz, DMSO) δ 156.19 (s), 144.19 (s), 133.40 (s), 133.28 (s), 131.41 (s), 130.50 (s), 128.67 (s), 127.98 (s), 125.04 (s), 115.58 (s), 54.32 (s). HRMS (ESI): m/z calcd. For C_{19}H_{15}BrO_2 [M+1]^+: 355.0334. found: 355.0341.

\(^1\)H NMR, \(^{13}\)C\(^{\{1\}}\) NMR, and \(^{31}\)PNMR spectra:

\(^1\)H NMR (400 MHz, DMSO-d_6) of 3a
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 3a

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3a
$^{31}\text{P NMR (400 MHz, CDCl}_3\text{)}$ of 3b

$^1\text{H NMR (400 MHz, DMSO-d}_6\text{)}$ of 3c
$^{13}$C NMR (101 MHz, DMSO- $d_6$) of 3c

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3c
$^1$H NMR (400 MHz, DMSO-d$_6$) of 3d

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 3d
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3d

$^1$H NMR (400 MHz, DMSO-$d_6$) of 3e
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 3e

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3e
$^1$H NMR (400 MHz, DMSO-d$_6$) of 3f

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 3f
$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 3f

$^1$H NMR (400 MHz, DMSO-d$_6$) of 3g
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 3g

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3g
$^1$H NMR (400 MHz, DMSO-d$_6$) of 3h

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 3h
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3h

$^1$H NMR (400 MHz, DMSO-$d_6$) of 3i
$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 3i

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 3i
$^1$H NMR (400 MHz, DMSO-d$_6$) of 3j

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 3j
$^{31}\text{P NMR (400 MHz, DMSO-d}_6\text{) of 3j}$

$^{1}\text{H NMR (400 MHz, DMSO-d}_6\text{) of 3k}$
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 3k

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3k
$^1$H NMR (400 MHz, DMSO-d$_6$) of 3l

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 3l
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 3I
$^{1}H$ NMR (400 MHz, CDCl$_3$-$d_6$) of 5a

$^{13}C$ NMR (101 MHz, CDCl$_3$- $d_6$) of 5a
$^{31}$P NMR (400 MHz, CDCl$_3$-d$_6$) of 5a

$^1$H NMR (400 MHz, DMSO-d$_6$) of 5b
$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 5b

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 5b
$^1$H NMR (400 MHz, DMSO-$d_6$) of 5c

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5c
$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 5c

$^1$H NMR (400 MHz, DMSO-d$_6$) of 5d
$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 5d

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 5d
$^1$H NMR (400 MHz, DMSO-$d_6$) of 5e

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5e
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5e

$^1$H NMR (400 MHz, DMSO-$d_6$) of 5f
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5f

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5f
$^1$H NMR (400 MHz, DMSO-$d_6$) of 5g

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5g
$^{31}\text{P NMR (400 MHz, DMSO-d}_6\text{) of 5g}$

$^{1}\text{H NMR (400 MHz, DMSO-d}_6\text{) of 5h}$
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5h

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5h
$^1$H NMR (400 MHz, DMSO-$d_6$) of 5i

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5i
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5i

$^1$H NMR (400 MHz, DMSO-$d_6$) of 5j
$^{13}$C NMR (101 MHz, DMSO- $d_6$) of 5j

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5j
$^1$H NMR (400 MHz, DMSO-$d_6$) of 5k

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5k
$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 5k

$^1$H NMR (400 MHz, DMSO-d$_6$) of 5l
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 5l

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 5l
$^1$H NMR (400 MHz, DMSO-$d_6$) of 7a

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7a
$^3$P NMR (400 MHz, DMSO-$d_6$) of 7a

$^1$H NMR (400 MHz, DMSO-$d_6$) of 7b
$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 7b

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 7b
$^1$H NMR (400 MHz, DMSO-$d_6$) of 7c

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7c
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7c

$^1$H NMR (400 MHz, DMSO-$d_6$) of 7d
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7d

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7d
$^1$H NMR (400 MHz, DMSO-$d_6$) of 7e

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7e
$^{31}\text{P} \text{ NMR (400 MHz, DMSO-d}_6\text{) of 7e}$

$^{1}\text{H} \text{ NMR (400 MHz, DMSO-d}_6\text{) of 7f}$
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7f

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7f
$^1$H NMR (400 MHz, DMSO-d$_6$) of 7g

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 7g
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7g

$^1$H NMR (400 MHz, DMSO-$d_6$) of 7h
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7h

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7h
$^1$H NMR (400 MHz, DMSO-d$_6$) of 7i

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 7i
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7i

$^1$H NMR (400 MHz, DMSO-$d_6$) of 7j
$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 7j

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 7j
$^1$H NMR (400 MHz, DMSO-$d_6$) of 7k

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 7k
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7k

$^1$H NMR (400 MHz, DMSO-$d_6$) of 7l
$^{13}$C NMR (101 MHz, DMSO- $d_6$) of 7l

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 7l
$^1$H NMR (400 MHz, DMSO-d$_6$) of 10

$^{31}$P NMR (400 MHz, DMSO-d$_6$) of 10
$^{13}$C NMR (101 MHz, DMSO- $d_6$) of 10

$^1$H NMR (400 MHz, DMSO-$d_6$) of 12
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 12

$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 12
$^1$H NMR (400 MHz, DMSO-d$_6$) of 13a

$^{13}$C NMR (101 MHz, DMSO- d$_6$) of 13a
$^{31}$P NMR (400 MHz, DMSO-$d_6$) of 13a

$^1$H NMR (400 MHz, DMSO-$d_6$) of 13b
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 13b

31P NMR (400 MHz, DMSO-$d_6$) of 13b
$^1$H NMR (400 MHz, Acetone-$d_6$) of 8a

$^{13}$C NMR (101 MHz, Acetone- $d_6$) of 8a
$^1$H NMR (400 MHz, DMSO-$d_6$) of 8b

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8b
$^1$H NMR (400 MHz, DMSO-$d_6$) of 8c

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8c
$^1$H NMR (400 MHz, DMSO-$d_6$) of 8d

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8d
$^1$H NMR (400 MHz, DMSO-d$_6$) of 8e

$^{13}$C NMR (101 MHz, DMSO-d$_6$) of 8e
$^{19}$F NMR (377 MHz, DMSO-$d_6$) of 8e

$^1$H NMR (400 MHz, DMSO-$d_6$) of 8f
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8f

$^{19}$F NMR (377 MHz, DMSO-$d_6$) of 8f
$^1$H NMR (400 MHz, DMSO-$d_6$) of 8g

$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8g
$^{19}$F NMR (377 MHz, CDCl$_3$) of 8g

$^1$H NMR (400 MHz, DMSO-d$_6$) of 8h
$^{13}$C NMR (101 MHz, DMSO- $d_6$) of 8h

$^1$H NMR (400 MHz, DMSO-$d_6$) of 8i
$^{13}$C NMR (101 MHz, DMSO-$d_6$) of 8i