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 F₂₅₄, 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).¹H, ¹³C, 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-d₆: 2.5 ppm and 3.4 ppm. Carbon nuclear magnetic resonance spectra ¹³C NMR solvent DMSO-d₆: 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.



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 0 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 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 (5a-5l):



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 0 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 Na₂SO₄, concentrated via rotary evaporation, and purified by column chromatography on silica gel (petroleum ether: ethyl acetate) as a liquid.

Optimization Table 2.

Ar 1	OH + Ar 4	H ^P OPI H ^P OPI BF <u>3,Et2</u> O ACN, 80 ⁰ C	PhO PhO Nu ₁ Ar	Ar P Nu ₂ +	OPh OP Nu ₁ Ar 3
entry	2	4a	BF3-OEt2 (mmol)	5a (%yield)	3a(%yield)
1	2.0	1.0	1.5	39	43
2	1.5	1.0	1.5	45	37
3	1.3	1.0	1.5	51	29

4	1.2	1.0	1.5	57	19
5	1.1	1.0	1.5	68	14
6	1.0	1.0	1.5	81	11
7	0.8	1.0	1.5	64	8
8	1.0	1.0	2.0	72	13
9	1.0	1.0	2.5	63	9
10	1.0	1.0	3.0	59	7
11	1.0	1.5	1.5	76	11
12	1.0	0.8	1.5	71	18
13	1.0	0.5	1.5	64	21
14	1.0	0.3	1.5	58	26

Conditions: Addition of benzaldehyde **1a** (1 mmol), diphenyl phosphite **2** (0.3 mmol) in 10 mL of ACN, followed by addition of BF₃-OEt₂ (1.5 mmol) and then add external phenol after 20 minutes (1.0 mmol) at 80 $^{\circ}$ C for 8 h.

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



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 $^{\circ}$ 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 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 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 0 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 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) 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 ambedient 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 $^{\circ}$ 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 $^{\circ}$ 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 Na₂SO₄, 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):



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (185mg, 81%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 19.98 (s). HRMS (ESI): m/z calcd. For C₂₆H₂₄O5P⁺ [M+1]⁺ 447.1361: found: 447.1364. **Diphenyl ((4-hydroxyphenyl) (2-methoxyphenyl) methyl) phosphonate(3b)**



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 19:81); (180 mg, 78%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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).³¹P NMR (162 MHz, CDCl₃) δ 19.68 (s). HRMS (ESI): m/z calcd. For C₂₆H₂₄O5P⁺ [M+1] ⁺447.1361: found: 447.1367.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 24:76); (190mg, 76%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 19.85 (s). HRMS (ESI): m/z calcd. For C₂₇H₂₆O₆P [M+1]⁺475.1310: found: 475.1305.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 32:68); (207mg, 79%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 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, 6H), 3.65 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 19.28 (s). **HRMS** (ESI): m/z calcd. For C₂₈H₂₈O₇P [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. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 20.00 (s). HRMS (ESI): m/z calcd. For C₂₆H₂₄O₆P [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) δ 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,

3H).). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 19.28 (s). **HRMS** (ESI): m/z calcd. For C₂₆H₂₃BrO₅P [M+1]⁺ 525.0466. found: 525.0469.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 20:80); (164mg, 76%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 20.11 (s). HRMS (ESI): m/z calcd. For C₂₅H₂₂O₅P [M+1]⁺433.1205. found: 433.1203.

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



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) δ 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) δ 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).³¹P NMR (162 MHz, DMSO) δ 18.25 (s). **HRMS** (ESI): m/z calcd. For C₂₄H₂₂O₅P [M+1] ⁺ 421.1205. found: 421.1199.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (176mg, 76%) as a colourless oil. ¹H 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) ¹³C 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).³¹P NMR (162 MHz, DMSO) δ 17.72 (s). HRMS (ESI): m/z calcd. For C₂₄H₂₁O₄PS [M+1]⁺437.0976: found: 437.0976.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 22:78); (193mg, 72%) as a colourless oil. 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). 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).³¹P NMR (162 MHz, DMSO) δ 18.25 (s). HRMS (ESI): m/z calcd. For C₂₆H₂₁BrO₆P [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. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 15.81 (s). HRMS (ESI): m/z calcd. For C₂₉H₂₃ClO₅P [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) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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).³¹P NMR (162 MHz, DMSO) δ 15.68 (s). HRMS (ESI): m/z calcd. For C₂₇H₂₁BrO₄PS [M+1] + 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. ¹H NMR (400 MHz, CDCl₃) δ 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). ¹³C NMR (101 MHz, CDCl₃) δ 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).³¹P NMR (162 MHz, CDCl₃) δ 20.00 (s). HRMS (ESI): m/z calcd. For C₃₀H₃₂O₅P [M+1] + 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. ¹H 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). ¹³C 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), 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).³¹P NMR (162 MHz, DMSO) δ 20.57 (s). HRMS (ESI): m/z calcd. For C₃₀H₃₂O₅P [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. ¹H 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). ¹³C 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), 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).³¹P NMR (162 MHz, DMSO) δ 20.53 (s). HRMS (ESI): m/z calcd. For C₃₃H₃₂O₄P [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 C₃₂H₃₆O₇P [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). **HRMS** (ESI): m/z calcd. For C₃₃H₃₁O₅PCl [M+1]⁺573.1598: found: 573.1593.

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. ¹H 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). ¹³C 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), 148.04 (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).³¹P NMR (162 MHz, DMSO) δ 16.75 (s). HRMS (ESI): m/z calcd. For C₂₈H₃₀O₅P [M+1]⁺477.1831: found: 477.1832.

Diphenyl ((4-hydroxy-2-isopropyl-5-methylphenyl) (5-methylthiophen-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). ¹³C 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).³¹P NMR (162 MHz, DMSO) δ 17.94 (s). HRMS (ESI): m/z calcd. For C₂₈H₃₀O₄PS [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. ¹H 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) s). ¹³C 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).³¹P NMR (162 MHz, DMSO) δ 20.70 (s). HRMS (ESI): m/z calcd. For C₂₈H₂₈O₅P [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. ¹H 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). ¹³C 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).³¹P NMR (162 MHz, DMSO) δ 19.95 (s). HRMS (ESI): m/z calcd. For C₂₇H₂₆O₅P [M+1]⁺461.1518: found: 461.1514.





The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 18:82); (174mg, 75%) as a colourless oil. ¹H 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). ¹³C 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).³¹P NMR (162 MHz, DMSO) δ 20.33 (s). HRMS (ESI): m/z calcd. For C₂₇H₂₆O₅P [M+1] ⁺ 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). ³¹P NMR (162 MHz, DMSO) δ 19.57 (s). ¹³C 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). ³¹P NMR (162 MHz, DMSO) δ 19.57 (s). **HRMS** (ESI): m/z calcd. For C₂₆H₂₃NO₇P [M+1] ⁺ 492.1212: found: 492.1219.





The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 10:90); (220mg, 79%) as a colourless oil. ¹H 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). ¹³C 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),

30.72 (s). ³¹P NMR (162 MHz, DMSO) δ 20.10 (s). **HRMS** (ESI): m/z calcd. For C₃₄H₄₀O₅P [M+1]⁺559.2613: found: 559.2615.

Diphenyl -((hexylthio)(4-methoxyphenyl) methyl) phosphonate(7a):



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) δ 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**CNMR**(101 MHz,) δ 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) δ 16.16 (s). **HRMS** (ESI): m/z calcd. For C₂₆H₃₁O₄PS [M+1]⁺ 471.1759: found: 471.1761.





The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (390mg, 84%) as a colourless oil.¹**H NMR** (400 MHz, DMSO) δ 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) δ 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), 31.19 (s), 28.81 (s), 28.04 (s), 22.40 (s), 14.26 (s). ³¹**P NMR** (162 MHz, DMSO) δ 15.90 (s). **HRMS** (ESI): m/z calcd. For C₂₆H₃₁O₄PS [M+1] ⁺ 471.1759: found: 471.1763. **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 C₂₇H₃₄O₅PS [M+1]⁺ 501.1865: found: 501.1869.

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.¹**H 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). ¹³**C 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). ³¹**P NMR** (162 MHz, DMSO) δ 16.27 (s). **HRMS** (ESI): m/z calcd. For C₂₆H₃₂O₅PS [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), 22.44 (s), 14.32 (s).³¹P NMR (162 MHz, DMSO) δ 16.49 (s). HRMS (ESI): m/z calcd. For C₂₅H₃₀O₅PS [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 C₂₈H₃₆O₆PS [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. ¹**H 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), 7.97 - 7.00 (m, 1H), 6.93 - 6.85 (m, 2H), 5.14 (d, *J* = 19.8 Hz, 1H), 7.99 (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), 7.99 (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), 7.99 (m, *J* = 10.5, 6.5) (m, *J* = 10.5) (m, J =

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). ¹³**C 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). ³¹**P 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. ¹**H 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). ¹³**C 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), 130.04 (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). ³¹**P NMR** (162 MHz, DMSO) δ 16.06 (s). **HRMS** (ESI): m/z calcd. For C₂₈H₃₆O₄PS [M+1]⁺ 499.2072: found: 499.2077.

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 = 08:92); (354mg, 80%) as a colourless oil. ¹H 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). ¹³C 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* = 148.8 Hz), 32.06 (d, *J* = 6.4 Hz), 30.88 (s), 21.66 (s), 13.86 (s). ³¹P NMR (162 MHz, DMSO) δ 16.20 (s). HRMS (ESI): m/z calcd. For C₂₄H₂₈O₄PS [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. ¹H 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). ¹³C NMR (101 MHz, DMSO) δ 150.59 (d, *J* = 9.8, 4.0 Hz), 135.71 (d, *J* = 4.4 Hz), 130.34 (s), 130.18 (s), 129.96 (d, *J* = 6.9 Hz), 128.99 (d, *J* = 1.1 Hz), 128.41 (d, *J* = 2.3 Hz), 125.70 (d, *J* = 14.1 Hz), 120.97 (d, *J* = 4.0 Hz), 120.74 (d, *J* = 4.1 Hz), 44.77 (d, *J* = 147.7 Hz), 34.66 (d, *J* = 6.6 Hz), 22.32 (s), 13.55 (s). ³¹P NMR (162 MHz, DMSO) δ 16.00 (s). HRMS (ESI): m/z calcd. For C₂₂H₂₄O₃PS [M+1]⁺ 399.1184: found: 399.1188. Diphenyl (S)-((benzylthio)(4-methoxyphenyl) methyl) phosphonate(71):



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 10:90); (352mg, 74%) as a colourless oil. ¹H 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). ¹³C NMR (101 MHz, DMSO) δ 159.51 (s), 150.54 (s), 137.33 (s), 131.11 (d,

J = 6.8 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 Hz), 120.87 (d, J = 4.0 Hz), 120.69 (d, J = 4.1 Hz), 114.59 (s), 55.64 (s), 44.06 (d, J = 148.7 Hz), 36.41 (s). ³¹P NMR (162 MHz, DMSO) δ 15.60 (s). **HRMS** (ESI): m/z calcd. For C₂₇H₂₆O₄PS [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. ¹H NMR (400 MHz, DMSO) δ 11.21 (d, J = 2.1 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.62 (dd, J = 8.8, 2.2 Hz, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.28 (t, J = 7.9 Hz, 4H), 7.13 (m, 3H), 7.05 – 6.97 (m, 1H), 6.91 (dd, J = 11.6, 4.7 Hz, 4H), 6.82 (d, J = 8.6 Hz, 2H), 5.43 (d, J = 26.3 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 158.88 (d, J = 2.8 Hz), 150.75 (d, J = 5.9 Hz), 150.65 (d, J = 5.8 Hz), 136.24 (s), 131.15 (d, J = 7.1 Hz), 130.16 (d, J = 1.8 Hz), 128.75 (d, J = 5.8 Hz), 127.19 (d, J = 12.6 Hz), 125.49 (d, J = 9.5 Hz), 124.70 (s), 121.97 (s), 120.95 (d, J = 3.8 Hz), 120.82 (d, J = 4.1 Hz), 119.19 (d, J = 14.1 Hz), 114.28 (s), 112.06 (s), 109.46 (d, J = 5.1 Hz), 55.53 (s), δ 40.98 (d, J = 79.0 Hz).³¹P NMR (162 MHz, DMSO) δ 20.20 (s). HRMS (ESI): m/z calcd. For C₂₈H₂₅NO₄P [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. ¹H NMR (400 MHz, DMSO) δ 7.94 – 7.79 (m, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.28 (m, 4H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.88 – 6.77 (m, 6H), 5.07 (d, *J* = 26.8 Hz, 1H), 3.73 (s, 6H), 2.28 (d, *J* = 14.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO) δ 158.95 (s), 158.73 (s), 150.60 (s), 150.44 (d, *J* = 10.2 Hz), 138.60 (d, *J* = 13.0 Hz), 131.82 (s), 131.37 (d, *J* = 7.9 Hz), 130.26 (s), 130.19 (s), 127.75 (d, *J* = 5.5 Hz), 127.07 (d, *J* = 2.9 Hz), 125.60 (d, *J* = 13.0 Hz), 120.80 (d, *J* = 4.2 Hz), 120.74 (d, *J* = 4.0 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 Hz), 20.13 (s). ³¹P NMR (162 MHz, DMSO) δ 20.04 (s). HRMS (ESI): m/z calcd. For C₂₈H₂₈O₅P [M+1]⁺ 475.1674: found: 475.1681.

bis(2-methoxyphenyl) (S)-((4-hydroxy-3-methoxyphenyl) (phenyl) methyl) phosphonate (13a):



¹**H NMR** (400 MHz, DMSO) δ 9.16 (s, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.32 – 7.22 (m, 6H), 7.19 – 7.12 (m, 3H), 6.97 (d, J = 8.3 Hz, 1H), 6.94 – 6.80 (m, 5H), 5.09 (d, J = 25.7 Hz, 1H), 3.74 (s, 6H), 3.72 (s, 3H). ¹³**C NMR** (101 MHz, DMSO) δ 157.17 (s), 150.63 (d, J = 10.0 Hz), 149.05 (s), 148.62 (s), 147.95 (s), 147.53 (s), 146.97 (s), 146.48 (s), 130.98 (d, J = 8.4 Hz), 130.17 (s), 129.22 (s), 127.13 (d, J = 41.9 Hz), 125.53 (s), 122.09 (s), 120.86 (d, J = 3.4 Hz), 117.13 (d, J = 7.7 Hz), 115.91 (s), 114.32 (d, J = 8.9 Hz), 113.96 (d, J = 8.9 Hz), 112.78 (s), 112.47 (s), 56.09 (s), 55.97 (s), 48.99 (d, J = 138.8 Hz). ³¹**P NMR** (162 MHz, DMSO) δ 19.65 (s). **HRMS** (ESI): m/z calcd. For C₂₈H₂₈O₇P [M+1] +: 507.1573found: 507.1579.

bis(2-methoxyphenyl) (S)-((4-hydroxy-3-methoxyphenyl) (4-methoxyphenyl) methyl) phosphonate (13b):



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 40:60); (396 mg, 73%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 9.21 (s, 1H), 7.37 – 7.22 (m, 6H), 7.14 (m, 2H), 7.07 (m, 2H), 7.00 – 6.92 (m, 5H), 5.22 – 5.12 (d, 1H), 3.78 (s, 3H), 3.75 (s, 6H), 3.70 (s, 3H).¹³C NMR (101 MHz, DMSO) δ 153.28 (s), 150.77 (s), 150.67 (s), 150.55 (s), 147.94 (s), 146.56 (d, J = 2.0 Hz), 137.34 (s), 132.40 (d, J = 3.9 Hz), 130.15 (d, J = 7.8 Hz), 127.00 (d, J = 5.3 Hz), 125.54 (d, J = 4.0 Hz), 122.37 (d, J = 8.5 Hz), 120.79 (d, J = 1.6 Hz), 116.14 (s), 115.94 (s), 114.26 (d, J = 8.7 Hz), 107.42 (d, J = 8.9 Hz), 60.50 (s), 56.32 (s), 49.63 (d, J = 138.3 Hz). ³¹P NMR (162 MHz, DMSO) δ 19.22 (s). HRMS (ESI): m/z calcd. For C₂₉H₃₀O₈P [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 C₁₉H₁₆ClO₂ [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 = 16:84); (251mg, 81%) as a colourless oil. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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 C₁₉H₁₆ClO₂ [M+1]⁺: 311.0839. found: 311.0841.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 20:80); (253mg, 79%) as a colourless oil. ¹**H NMR** (400 MHz, DMSO) δ 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) δ 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 C₁₉H₁₆NO₄ [M+1]⁺: 322.1079found: 322.1084.

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



The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 16:84); (234mg, 78%) as a colourless oil. ¹**H NMR** (400 MHz, DMSO) δ 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) δ 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 C₂₀H₁₆NO₂ [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. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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). ¹⁹F NMR (377 MHz, DMSO) δ -61.15 (s). HRMS (ESI): m/z calcd. For C₂₀H₁₆F₃O₂ [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**H NMR** (400 MHz, DMSO) δ 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**C NMR** (101 MHz, CDCl₃) δ 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**F NMR** (377 MHz, DMSO) δ -103.61 (dt, *J* = 8.3, 5.5 Hz). **HRMS** (ESI): m/z calcd. For C₁₉H₁₆FO₂ [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. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 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). ¹⁹F NMR (377 MHz, CDCl₃) δ -110.46 (td, *J* = 5.3, 3.0 Hz). HRMS (ESI): m/z calcd. For C₁₉H₁₆FO₂ [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. ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (101 MHz, DMSO) δ 156.13 (s), 145.03 (s), 134.52 (s), 131.52 (d, *J* = 7.0

Hz), 130.28 (s), 119.49 (s), 115.54 (s), 54.09 (s). **HRMS** (ESI): m/z calcd. For C₁₉H₁₆BrO₂ [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). ¹³C 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 C₁₉H₁₆BrO₂ [M+1] ⁺: 355.0334. found: 355.0341.



¹H NMR, ¹³C{¹H} NMR, and ³¹PNMR spectra:



¹H NMR (400 MHz, DMSO-d₆) of 3b



 $^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3b





^{31}P NMR (400 MHz, CDCl₃) of 3b



¹H NMR (400 MHz, DMSO-d₆) of 3c



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3c



 ^{31}P NMR (400 MHz, DMSO-d₆) of 3c



^1H NMR (400 MHz, DMSO-d_6) of 3d



¹³C NMR (101 MHz, DMSO- d₆) of 3d





$^{\rm 31}P$ NMR (400 MHz, DMSO-d_6) of 3d



¹H NMR (400 MHz, DMSO-d₆) of 3e







³¹P NMR (400 MHz, DMSO-d₆) of 3e


¹H NMR (400 MHz, DMSO-d₆) of 3f



 $^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3f





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

^{31}P NMR (400 MHz, DMSO-d_6) of 3f



¹H NMR (400 MHz, DMSO-d₆) of 3g



^{13}C NMR (101 MHz, DMSO- d_6) of 3g



³¹P NMR (400 MHz, DMSO-d₆) of 3g



¹H NMR (400 MHz, DMSO-d₆) of 3h



¹³C NMR (101 MHz, DMSO- d₆) of 3h



$^{\rm 31}P$ NMR (400 MHz, DMSO-d_6) of 3h



¹H NMR (400 MHz, DMSO-d₆) of 3i



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3i



 31 P NMR (400 MHz, DMSO-d₆) of 3i



150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 3j



 $^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3j



^{31}P NMR (400 MHz, DMSO-d_6) of 3j



^1H NMR (400 MHz, DMSO-d_6) of 3k



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 3k



 ^{31}P NMR (400 MHz, DMSO-d_6) of 3k



¹H NMR (400 MHz, DMSO-d₆) of 3I





¹³C NMR (101 MHz, DMSO- d₆) of 3I



^{31}P NMR (400 MHz, DMSO-d_6) of 31



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, CDCl₃-d₆) of 5a





140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 5b



¹³C NMR (101 MHz, DMSO- d₆) of 5b



 ^{31}P NMR (400 MHz, DMSO-d₆) of 5b







^{31}P NMR (400 MHz, DMSO-d_6) of 5c





$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 5d



 ^{31}P NMR (400 MHz, DMSO-d₆) of 5d



¹H NMR (400 MHz, DMSO-d₆) of 5e



 $^{\rm 13}C$ NMR (101 MHz, DMSO- $d_6)$ of 5e





$^{\rm 31}P$ NMR (400 MHz, DMSO-d_6) of 5e



¹H NMR (400 MHz, DMSO-d₆) of 5f



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 5f



³¹P NMR (400 MHz, DMSO-d₆) of 5f



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 5g



$^{\rm 13}C$ NMR (101 MHz, DMSO- $d_6)$ of 5g





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





 ^{31}P NMR (400 MHz, DMSO-d₆) of 5h





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

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



¹H NMR (400 MHz, DMSO-d₆) of 5j





$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 5j



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



¹H NMR (400 MHz, DMSO-d₆) of 5k



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



¹H NMR (400 MHz, DMSO-d₆) of 5I



$^{\rm 13}{\rm C}$ NMR (101 MHz, DMSO- d_6) of 5I



 ^{31}P NMR (400 MHz, DMSO-d_6) of 5I





¹H NMR (400 MHz, DMSO-d₆) of 7a



159.43 (150.69) (150.65) (120.65) (1

- 55.57 - 55.57 - 43.34 - 43.34 - 23.46 - 23.4





³¹P NMR (400 MHz, DMSO-d₆) of 7a



¹H NMR (400 MHz, DMSO-d₆) of 7b









-5 -10 -15 -20



¹H NMR (400 MHz, DMSO-d₆) of 7c

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



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 f1 (ppm)

¹H NMR (400 MHz, DMSO-d₆) of 7d







150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 7e


$^{\rm 31}P$ NMR (400 MHz, DMSO-d_6) of 7e



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 7f



150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 7g



^{31}P NMR (400 MHz, DMSO-d_6) of 7g



150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 7h



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 7h



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 7i



^{31}P NMR (400 MHz, DMSO-d_6) of 7i





¹H NMR (400 MHz, DMSO-d₆) of 7j



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 7j



 ^{31}P NMR (400 MHz, DMSO-d_6) of 7j



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

¹H NMR (400 MHz, DMSO-d₆) of 7k



³¹P NMR (400 MHz, DMSO-d₆) of 7k



140 130 120 110 100 90 80 70 60 50 40 30 20 10 -10 -20 -40 -50 -60 -70 -80 -90 0 -30

¹H NMR (400 MHz, DMSO-d₆) of 7I



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 7I



¹H NMR (400 MHz, DMSO-d₆) of 10



 ^{31}P NMR (400 MHz, DMSO-d_6) of 10



140 130 120 110 100 80 70 60 50 30 20 10 -10 -20 -50 -60 -70 -80 -90 90 40 0 -30 -40

$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 10



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

$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 12



 ^{31}P NMR (400 MHz, DMSO-d_6) of 12



150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70

¹H NMR (400 MHz, DMSO-d₆) of 13a



¹³C NMR (101 MHz, DMSO- d₆) of 13a





^{31}P NMR (400 MHz, DMSO-d_6) of 13a



$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 13b



³¹P NMR (400 MHz, DMSO-d₆) of 13b



¹H NMR (400 MHz, Acetone-d₆) of 8a



¹³C NMR (101 MHz, Acetone- d₆) of 8a



¹H NMR (400 MHz, DMSO-d₆) of 8b



1 H NMR (400 MHz, DMSO-d₆) of 8c



 ^{13}C NMR (101 MHz, DMSO- d₆) of 8c



¹H NMR (400 MHz, DMSO-d₆) of 8d



¹H NMR (400 MHz, DMSO-d₆) of 8e





$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 8f



^1H NMR (400 MHz, DMSO-d_6) of 8g



 $^{\rm 13}C$ NMR (101 MHz, DMSO- $d_6)$ of 8g



$^{19}\mathsf{F}\,\mathsf{NMR}$ (377 MHz, CDCl₃) of 8g



$^{\rm 13}C$ NMR (101 MHz, DMSO- $d_6)$ of 8h



10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 f1(ppm)

$^{\rm 13}C$ NMR (101 MHz, DMSO- d_6) of 8i



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