Supporting Information for "Synthesis and biological evaluation of *N*-phosphorylated derivatives of 3-(4-aminophenyl)-coumarin-7-*O*-sulfamate as new steroid sulfatase inhibitors "

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1. Material and methods

Thionyl chloride, 4-nitrophenylacetic acid, potassium carbonate, 2,4-dihydroxybenzaldehyde, sodium hydrosulfite, chlorosulfonyl isocyanate, *N*,*N*-dimethylacetamide, formic acid, dimethylchlorophosphate, diethylchlorophosphate, diphenylchlorophosphate are commercially available from Aldrich. Di-*i*-propylchlorophosphate, di-*n*-butylchlorophosphate, dibenzylchlorophosphate, 2-chloro-[1,3,2]dioxaphosphinane 2-oxide, 2-chloro-5,5-dimethyl-[1,3,2]dioxaphosphinane 2-oxide were obtained according to literature procedures [J. Acharya, A.K. Gupta, P.D. Shakya and M.P. Kaushik, *Tetr. Lett.*, 2005, **46**, 5293–5295; H. Vothi, S. Halm, C. Nguyen, I. Bae and J. Kim, *Fire Mater.*, 2014, **38**, 36–45]. Pyridine, dichloromethane and acetone were dried and distilled using standard procedures. Melting points (uncorrected) were determined with a Stuart Scientific SMP30 apparatus. NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer. Chemical shifts are reported in ppm relative to the residue solvent peak (DMSO-d6 2.49 ppm for ^{1}H, 39.5 ppm for ^{13}C) or to an external standard (85% H_3PO_4 = 0 for ^{31}P). Coupling constants are given in Hertz. IR spectra were measured on Nicolet 8700. Elemental analysis was performed using CHNS-Carlo Erba EA-1108. Mass spectra were recorded on Agilent *6540 Accurate Mass Q-TOF* LC/*MS* Systems. Column chromatography was performed using silica gel 60 (230-400 mesch, Merck). Preparative thin-layer chromatography was performed with Polygram SIL G/UV254 silica gel (Macherey- Nagel GmbH & Co. KG, Düren, Germany).

2. Preparation of 7-hydroxy-3-(4-nitrophenyl)-coumarin 7

$SOCl_2$ (54.12 g, 33 mL) was added to a solution of 4-nitrophenylacetic acid (7.25 g, 40 mmol) in dry CH_2Cl_2 (33 mL), and the suspension was refluxed for 4 h. The resulting solution was evaporated, the residue was dissolved in dry acetone (200 mL) and 2,4-dihydroxybenzaldehyde (4.24 g, 40 mmol) was added. The mixture was refluxed with anhydrous K_2CO_3 (22.08 g, 160 mmol) for 4 h. Then, acetone was removed under reduced pressure and cold water (400 mL) was added. 3 N HCl was added until the solution became acidic. The resulting precipitate was filtered, washed with water and recrystallized from ethanol to give desired product **7**.

Yield 68%; mp 298-299 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3201, 1685, 1588, 1508, 1415, 1336, 1286, 1219, 1169, 1118, 993, 848; ^{1}H NMR δ_H (500 MHz, DMSO) 10.81 (1H, s, OH), 8.39 (1H, s, CH), 8.28 (2H, d, *J* 8.8, Ar-H), 8.00 (2H, d, *J* 8.3, Ar-H), 7.64 (1H, d, *J* 8.8, Ar-H), 6.85 (1H, d, *J* 8.8, Ar-H), 6.77 (1H, s, Ar-H); ^{13}C NMR (101 MHz, DMSO), δ (ppm): 162.9, 160.3, 156.1, 147.3, 143.9, 142.5, 131.3, 129.9, 124.0, 120.4, 114.4, 112.4, 102.5. Anal. Calcd for: $C_{15}H_9NO_5$: C, 63.61; H, 3.20; N, 4.95. Found: C, 63.70; H, 3.27; N, 4.84%. HRMS (m/z) $[M-H]^-$ calcd 282.0402. Found 282.0444.

3. Preparation of 3-(4-aminophenyl)-7-hydroxy-coumarin 8

7-hydroxy-3-(4-nitrophenyl)-coumarin **7** (7.08 g, 25 mmol) was added to a mixture of acetone (1300 mL) and water (650 mL) and resulting solution was heated to 50 ^{o}C (until the solution became completely transparent). Next, sodium hydrosulfite (43.53 g, 250 mmol) was added (in three potion)

and the reaction mixture was heated to reflux. After 2 h, acetone was evaporated. Resulting precipitate was filtered, washed with water and recrystallized from acetone to give desired product **8**.

Yield 58%; mp 292-295 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3338, 3278, 1670, 1608, 1565, 1507, 1467, 1333, 1284, 1211, 1162, 1132, 994, 846; ^{1}H NMR δ_H (500 MHz, DMSO) 10.45 (1H, s, OH), 7.94 (1H, s, CH), 7.53 (1H, d, *J* 8.3, Ar-H), 7.41 (2H, d, *J* 8.8, Ar-H), 6.77 (1H, d, *J* 8.8, Ar-H), 6.71 (1H, s, Ar-H), 6.59 (2H, d, *J* 8.8, Ar-H), 5.43 (2H, br s, NH_2); ^{13}C NMR (101 MHz, DMSO), δ (ppm): 137.6, 137.5, 131.4, 126.0, 114.8, 106.5, 106.2, 99.9, 99.4, 90.6, 90.4, 89.6, 78.8. Anal. Calcd for: $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.01; H, 4.41; N, 5.65%. HRMS (m/z) [M-H]$^-$ calcd 252.0661. Found 252.0705.

4. General method for the synthesis of *N*-phosphorylated derivatives of 3-(4-aminophenyl)-7-hydroxy-coumarin 9a-h

The corresponding chlorophosphate (3.0 mmol) was added to a solution of 3-(4-aminophenyl)-7-hydroxy-coumarin **8** (380 mg, 1.5 mmol) in dry pyridine (4.5 mL). The reaction mixture was stirred under nitrogen atmosphere for 24 h. Next, the solvent was evaporated and the resulting residue was purified by column chromatography using CH_2Cl_2 : MeOH 50 : 1 as an eluent to give the desired products **9a-h**.

3-[4-(dimethoxy-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9a. Yield 71%, mp 214.0-216.2 ^{o}C; ν_{max} (KBr)/cm^{-1} 3238, 1708, 1601, 1515, 1466, 1210, 1118, 969, 826, 623; ^{1}H NMR δ_H (400 MHz, DMSO) 10.58 (1H, s, OH), 8.27 (1H, d, *J* 9.2, NH), 8.06 (1H, s, CH), 7.58 (3H, d, *J* 8.1, Ar-H), 7.07 (2H, d, *J* 9.2, Ar-H), 6.81 (1H, d, *J* 8.5, Ar-H), 6.75 (1H, s, Ar-H), 3.67 (6H, d, *J* 11.0, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 161.3, 160.7, 155.1, 141.2, 140.1, 130.2, 129.5, 128.0, 122.4, 117.2 (d, J_{P-C} 7.6), 113.8, 112.6, 102.1, 53.4 (d, J_{P-C} 5.4); ^{31}P NMR δ_P (162 MHz, DMSO) 5.05. Anal. calcd for: $C_{17}H_{16}NO_6P$: C, 56.52; H 4.46; N, 3.88. Found: C, 56.43; H, 4.51; N, 3.85%. HRMS (*m/z*) [M+H]+ calcd 362.0794, found 362.0809.

3-[4-(diethoxy-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9b. Yield 75%, mp 217.0-219.4 ^{o}C; ν_{max} (KBr)/cm^{-1} 3218, 1687, 1606, 1516, 1468, 1208, 1126, 964, 834, 624; ^{1}H NMR δ_H (400 MHz, DMSO) 10.60 (1H, s, OH), 8.20 (1H, d, *J* 9.4, NH), 8.07 (1H, s, CH), 7.57 (3H, dd, *J* 8.6, 2.9, Ar-H), 7.07 (2H, d, *J* 8.8, Ar-H), 6.81 (1H, dd, *J* 8.5, 2.3, Ar-H), 6.74 (1H, d, *J* 2.2, Ar-H), 4.11-3.92 (4H, m, CH_2), 1.24 (6H, t, *J* 7.1, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 161.3, 160.7, 155.1, 141.5, 140.0, 130.2, 129.4, 127.8, 122.4, 117.2 (d, J_{P-C} 7.6), 113.8, 112.6, 102.1, 62.5 (d, J_{P-C} 5.1), 16.5 (d, J_{P-C} 6.6); ^{31}P NMR δ_P (162 MHz, DMSO) 2.12. Anal. calcd for: $C_{19}H_{20}NO_6P$: C, 58.61; H 5.18; N, 3.60. Found: C, 58.57; H, 5.11; N, 3.57%. HRMS (*m/z*) [M+H]+ calcd 390.1107, found 390.1130.

3-[4-(diisopropyl-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9c. Yield 66%, mp 164.4-168.3 ^{o}C; ν_{max} (KBr)/cm^{-1} 3278, 1703, 1611, 1518, 1466, 1215, 1128, 958, 835, 624; ^{1}H NMR δ_H (400 MHz, DMSO) 10.58 (1H, s, OH), 8.12 (1H, d, *J* 9.4, NH), 8.07 (1H, s, CH), 7.61-7.54 (3H, m, Ar-H), 7.06 (2H, d, *J* 8.8, Ar-H), 6.81 (1H, dd, *J* 8.5, 2.3, Ar-H), 6.74 (1H, d, *J* 2.2, Ar-H), 4.59-4.47 (2H, m, CH), 1.29 (6H, d, *J* 6.2, CH_3), 1.19 (6H, d, *J* 6.2, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 161.3, 160.7, 155.0, 141.8, 140.0, 130.1, 129.3, 127.5, 122.4, 117.2 (d, J_{P-C} 7.6), 113.8, 112.6, 102.1, 71.0 (d, J_{P-C} 5.1), 24.1 (d, J_{P-C} 4.4), 23.9

(d, J_{P-C} 5.1); ^{31}P NMR δ_P (162 MHz, DMSO) -0.08. Anal. calcd for: $C_{21}H_{24}NO_6P$: C, 60.43; H 5.80; N, 3.36. Found: C, 60.47; H, 5.71; N, 3.31%. HRMS (*m/z*) [M+H]+ calcd 418.1420, found 418.1433.

3-[4-(di-*n*-butyl-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9d. Yield 63%, mp 163.1-166.1 ^{o}C; ν_{max} (KBr)/cm^{-1} 3252, 1713, 1605, 1518, 1467, 1214, 1122, 966, 832, 622; ^{1}H NMR δ_H (400 MHz, DMSO) 10.61 (1H, s, OH), 8.19 (1H, d, *J* 9.5, NH), 8.07 (1H, s, CH), 7.58 (3H, dd, *J* 8.6, 3.0, Ar-H), 7.06 (2H, d, *J* 8.7, Ar-H), 6.81 (1H, dd, *J* 8.5, 2.2, Ar-H), 6.75 (1H, d, *J* 2.2, Ar-H), 4.05-3.87 (4H, m, CH_2), 1.58 (4H, quint, *J* 6.7, CH_2), 1.34 (4H, sext, *J* 7.5, CH_2), 0.86 (6H, t, *J* 7.4, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 161.4, 160.7, 155.1, 141.4, 140.0, 130.1, 129.4, 127.8, 122.4, 117.1 (d, J_{P-C} 7.5), 113.8, 112.6, 102.1, 66.0 (d, J_{P-C} 5.3), 32.2 (d, J_{P-C} 6.7), 18.7, 13.9; ^{31}P NMR δ_P (162 MHz, DMSO) 2.45. Anal. calcd for: $C_{24}H_{30}NO_6P$: C, 62.74; H 6.58; N, 3.05. Found: C, 62.60; H, 6.65; N, 2.99%. HRMS (*m/z*) [M+H]+ calcd 446.1733, found 446.1759.

3-[4-(diphenoxy-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9e. Yield 78%, mp 229.8-232.0 ^{o}C; ν_{max} (KBr)/cm^{-1} 3215, 1684, 1604, 1517, 1464, 1193, 1130, 956, 836, 624; ^{1}H NMR δ_H (400 MHz, DMSO) 10.61 (1H, s, OH), 9.04 (1H, d, *J* 10.3, NH), 8.11 (1H, s, CH), 7.66 (2H, d, *J* 8.2, Ar-H), 7.59 (1H, d, *J* 8.4, Ar-H), 7.52-7.36 (4H, m, Ar-H), 7.35-7.16 (8H, m, Ar-H), 6.82 (1H, d, *J* 8.2, Ar-H), 6.76 (1H, s, Ar-H); ^{13}C NMR δ_C (101 MHz, DMSO) 161.4, 160.6, 155.2, 150.5 (d, J_{P-C} 6.3), 140.4, 140.1, 130.5, 130.2, 129.7, 128.8, 125.8, 122.2, 120.6 (d, J_{P-C} 4.7), 117.8 (d, J_{P-C} 8.1), 113.8, 112.6, 102.2; ^{31}P NMR δ_P (162 MHz, DMSO) -6.93. Anal. calcd for: $C_{27}H_{20}NO_6P$: C, 66.81; H 4.15; N, 2.89. Found: C, 66.70; H, 4.18; N, 2.93%. HRMS (*m/z*) [M+H]+ calcd 486.1107, found 486.1123.

3-[4-(dibenzyloxy-phosphorylamino)-phenyl]-7-hydroxy-coumarin 9f. Yield 78%, mp 245.0-250.0 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3215, 1704, 1605, 1518, 1456, 1199, 1127, 966, 843, 625; ^{1}H NMR δ_H (400 MHz, DMSO) 10.58 (1H, s, OH), 8.46 (1H, d, *J* 9.5, NH), 8.07 (1H, s, CH), 7.58 (3H, dd, *J* 8.6, 3.3, Ar-H), 7.40-7.29 (10H, m, Ar-H), 7.12 (2H, d, *J* 8.7, Ar-H), 6.81 (1H, dd, *J* 8.5, 2.3, Ar-H), 6.75 (1H, d, *J* 2.2, Ar-H), 5.12-4.98 (4H, m, CH_2); ^{13}C NMR δ_C (101 MHz, DMSO) 161.4, 160.7, 155.1, 141.1, 140.1, 136.7 (d, J_{P-C} 7.75), 130.2, 129.4, 128.9, 128.7, 128.2, 128.1, 122.4, 117.5 (d, J_{P-C} 7.7), 113.8, 112.6, 102.1, 67.9 (d, J_{P-C} 4.9); ^{31}P NMR δ_P (162 MHz, DMSO) 2.77. Anal. calcd for: $C_{29}H_{24}NO_6P$: C, 67.83; H 4.71; N, 2.73. Found: C, 67.71; H, 4.77; N, 2.71%. HRMS (*m/z*) [M+H]+ calcd 514.1420, found 514.1431.

3-{4-(2-oxo-2λ^5-[1,3,2]dioxaphophinan-2-ylamino)-phenyl}-7-hydroxy-coumarin 9 g. Yield 60%, mp 262.8-266.0 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3215, 1706, 1602, 1514, 1461, 1227, 1122, 961, 828, 632; ^{1}H NMR δ_H (400 MHz, DMSO) 10.61 (1H, s, OH), 8.27 (1H, d, *J* 10.8, NH), 8.07 (1H, s, CH), 7.58 (3H, dd, *J* 8.6, 2.9, Ar-H), 7.08 (2H, d, *J* 8.7, Ar-H), 6.81 (1H, dd, *J* 8.5, 2.3, Ar-H), 6.75 (1H, d, *J* 2.2, Ar-H), 4.46-4.29 (4H, m, CH_2), 2.13-1.86 (2H, m, CH_2); ^{13}C NMR δ_C (101 MHz, DMSO) 161.3, 160.7, 155.1, 141.1, 140.1, 130.2, 129.5, 128.0, 122.4, 117.4 (d, J_{P-C} 7.6), 113.8, 112.6, 102.1, 68.6 (d, J_{P-C} 6.6), 26.2 (d, J_{P-C} 6.9); ^{31}P NMR δ_P (162 MHz, DMSO) -4.11. Anal. calcd for: $C_{18}H_{16}NO_6P$: C, 57.91; H 4.32; N, 3.75. Found: C, 57.99; H, 4.29; N, 3.62%. HRMS (*m/z*) [M+H]+ calcd 374.0794, found 374.0805.

3-{4-(5,5-dimethyl-2-oxo-2λ^5-[1,3,2]dioxaphophinan-2-ylamino)-phenyl}-7-hydroxy-coumarin 9h. Yield 65%, mp 234.5-237.6 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3234, 1713, 1606, 1518, 1468, 1218, 1123, 985, 833, 622; ^{1}H NMR δ_H (400 MHz, DMSO) 10.61 (1H, s, OH), 8.24 (1H, d, *J* 10.6, NH), 8.06

(1H, s, CH), 7.65-7.54 (3H, m, Ar-H), 7.10 (2H, d, *J* 8.7, Ar-H), 6.82 (1H, dd, *J* 8.5, 2.3, Ar-H), 6.75 (1H, d, *J* 2.2, Ar-H), 4.12-3.92 (4H, m, CH_2), 1.14 (3H, s, CH_3), 0.89 (3H, s, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 161.4, 160.7, 155.1, 141.1, 140.1, 130.2, 129.5, 128.2, 122.4, 117.7 (d, J_{P-C} 7.5), 113.8, 112.6, 102.2, 77.2 (d, J_{P-C} 6.4), 32.3 (d, J_{P-C} 5.9), 21.6, 20.5; ^{31}P NMR δ_P (162 MHz, DMSO) -4.52. Anal. calcd for: $C_{20}H_{20}NO_6P$: C, 59.85; H 5.02; N, 3.49. Found: C, 59.77; H, 5.06; N, 3.40%. HRMS (*m/z*) [M+H]+ calcd 402.1107, found 402.1111.

5. General method for the synthesis of *N*-phosphorylated derivatives of 3-(4-aminophenyl)-coumarin-7-*O*-sulfamate 10a-h

A mixture of formic acid (96 mg, 1.54 mmol) and *N*,*N*-dimethyl acetamide (1.4 mg, 0.016 mmol) was added to a stirred solution of chlorosulfonyl isocyanate (212 mg, 1.50 mmol) in dry dichloromethane (0.5 mL) at 40 ^{o}C within a period of 3.5 h. Then, a stirred solution of *N*-phosphorylated derivatives of 7-hydroxy-3-phenylcoumarin **9a-h** (253 mg, 1.00 mmol) in *N*,*N*-dimethyl acetamide (3.4 mL) was added to the mixture. The mixture was stirred at ambient temperature overnight and then poured onto water (10 mL). Eventually, a white precipitate was formed. The suspension was stirred at ambient temperature for another 2 hours. The resulting precipitate was filtered, washed with water and recrystallized from acetonitrile to give desired product **10a-h**.

3-[4-(dimethoxy-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10a. Yield 87%, mp 205.8-208.9 ^{o}C; ν_{max} (KBr)/cm^{-1} 3323, 1683, 1618, 1520, 1464, 1384, 1195, 1119, 931, 835, 771, 618; ^{1}H NMR δ_H (400 MHz, DMSO) 8.34 (1H, d, *J* 9.3, NH), 8.26 (2H, s, NH_2), 8.21 (1H, s, CH), 7.84 (1H, d, *J* 8.3, Ar-H), 7.64 (2H, d, *J* 7.8, Ar-H), 7.36 (1H, s, Ar-H), 7.29 (1H, d, *J* 8.5, Ar-H), 7.10 (2H, d, *J* 7.7, Ar-H), 3.67 (6H, d, *J* 11.2, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.6, 152.2, 141.9, 138.8, 130.0, 129.8, 127.3, 126.5, 119.1, 118.5, 117.3 (d, J_{P-C} 7.6), 109.9, 53.4 (d, J_{P-C} 5.3); ^{31}P NMR δ_P (162 MHz, DMSO) 4.92. Anal. calcd for: $C_{17}H_{17}N_2O_8PS$: C, 46.37; H 3.89; N, 6.36; S, 7.28. Found: C, 46.49; H, 3.92; N, 6.30; S, 7.19%. HRMS (*m/z*) [M+H]+ calcd 441.0521, found 441.0534.

3-[4-(diethoxy-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10b. Yield 84%, mp 206.0-208.1 ^{o}C; ν_{max} (KBr)/cm^{-1} 3307, 1683, 1616, 1517, 1466, 1383, 1192, 1125, 932, 831, 773, 617; ^{1}H NMR δ_H (400 MHz, DMSO) 8.30-8.24 (3H, m, NH, NH_2), 8.22 (1H, s, CH), 7.84 (1H, d, *J* 8.6, Ar-H), 7.63 (2H, d, *J* 8.6, Ar-H), 7.35 (1H, d, *J* 2.2, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.10 (2H, d, *J* 8.8, Ar-H), 4.11-3.94 (4H, m, CH_2), 1.24 (6H, t, *J* 7.1, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.5, 152.2, 142.2, 138.7, 130.0, 129.7, 127.0, 126.5, 119.1, 118.5, 117.2 (d, J_{P-C} 7.6), 109.9, 62.6 (d, J_{P-C} 5.1), 16.5 (d, J_{P-C} 6.6); ^{31}P NMR δ_P (162 MHz, DMSO) 1.98. Anal. calcd for: $C_{19}H_{21}N_2O_8PS$: C, 48.72; H 4.52; N, 5.98; S, 6.85. Found: C, 48.85; H, 4.47; N, 5.91; S, 6.94%. HRMS (*m/z*) [M+H]+ calcd 469.0834, found 469.0854.

3-[4-(diisopropyl-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10c. Yield 77%, mp 321.1-328.1 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3331, 1686, 1616, 1516, 1467, 1375, 1194, 1115, 935, 830, 775, 619; ^{1}H NMR δ_H (400 MHz, DMSO) 8.26 (2H, s, NH_2), 8.22 (1H, s, CH), 8.20 (1H, d, *J* 9.4, NH), 7.84 (1H, d, *J* 8.6, Ar-H), 7.63 (2H, d, *J* 8.6, Ar-H), 7.35 (1H, d, *J* 2.2, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.09 (2H, d, *J* 8.8, Ar-H), 4.61-4.48 (2H, m, CH), 1.30 (6H, d, *J* 6.2, CH_3), 1.20 (6H, d, *J* 6.2, CH_3); ^{13}C NMR

δ_C (101 MHz, DMSO) 160.0, 153.5, 152.2, 142.5, 138.6, 130.0, 129.6, 126.8, 126.5, 119.1, 118.5, 117.2 (d, J_{P-C} 7.6), 109.9, 71.1 (d, J_{P-C} 5.1), 24.1 (d, J_{P-C} 4.4), 23.9 (d, J_{P-C} 5.0); ^{31}P NMR δ_P (162 MHz, DMSO) -0.24. Anal. calcd for: $C_{21}H_{25}N_2O_8PS$: C, 50.80; H 5.08; N, 5.64; S, 6.46. Found: C, 50.74; H, 5.17; N, 5.71; S, 6.43%. HRMS (*m/z*) [M+H]+ calcd 497.1148, found 497.1160.

3-[4-(di-*n*-butyl-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10d. Yield 90%, mp 186.9-189.5 ^{o}C; ν_{max} (KBr)/cm^{-1} 3240, 1701, 1615, 1518, 1463, 1384, 1187, 1117, 928, 830, 777, 621; ^{1}H NMR δ_H (400 MHz, DMSO) 8.30-8.24 (3H, m, NH, NH_2), 8.22 (1H, s, CH), 7.85 (1H, d, *J* 8.6, Ar-H), 7.63 (2H, d, *J* 8.6, Ar-H), 7.35 (1H, d, *J* 2.2, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.10 (2H, d, *J* 8.8, Ar-H), 4.05-3.88 (4H, m, CH_2), 1.58 (4H, quint, *J* 6.8, CH_2), 1.34 (4H, sext, *J* 7.7, CH_2),0.86 (6H, t, *J* 7.4, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.5, 152.2, 142.1, 138.7, 130.0, 129.7, 127.0, 126.5, 119.1, 118.5, 117.2 (d, J_{P-C} 7.7), 109.9, 66.1 (d, J_{P-C} 5.2), 32.2 (d, J_{P-C} 6.7), 18.7, 13.9; ^{31}P NMR δ_P (162 MHz, DMSO) 2.31. Anal. calcd for: $C_{24}H_{31}N_2O_8PS$: C, 53.52; H 5.80; N, 5.20; S, 5.95. Found: C, 53.61; H, 5.83; N, 5.15; S, 6.02%. HRMS (*m/z*) [M+H]+ calcd 525.1461, found 525.1471.

3-[4-(diphenoxy-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10e. Yield 86%, mp 170.3-174.6 ^{o}C; ν_{max} (KBr)/cm^{-1} 3253, 1680, 1616, 1518, 1456, 1384, 1185, 1116, 941, 831, 763, 620; ^{1}H NMR δ_H (400 MHz, DMSO) 9.12 (1H, d, *J* 10.4, NH), 8.31-8.24 (3H, m, NH_2, CH), 7.85 (1H, d, *J* 8.6, Ar-H), 7.72 (2H, d, *J* 8.6, Ar-H), 7.47-7.39 (4H, m , Ar-H), 7.36 (1H, d, *J* 2.1, Ar-H), 7.33-7.21 (9H, m, Ar-H); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.6, 152.3, 150.4 (d, J_{P-C} 6.3), 140.8, 139.1, 130.5, 130.1, 130.0, 128.1, 126.3, 125.9, 120.6 (d, J_{P-C} 4.7), 119.2, 118.5, 117.8 (d, J_{P-C} 8.0), 109.9; ^{31}P NMR δ_P (162 MHz, DMSO) -7.05. Anal. calcd for: $C_{27}H_{21}N_2O_8PS$: C, 57.45; H 3.75; N, 4.96; S, 5.68. Found: C, 57.49; H, 3.65; N, 5.00; S, 5.71%. HRMS (*m/z*) [M+H]+ calcd 565.0835, found 565.0848.

3-[4-(dibenzyloxy-phosphorylamino)-phenyl]-coumarin-7-*O*-sulfamate 10f. Yield 92%, mp 171.2-175.5 ^{o}C; ν_{max} (KBr)/cm^{-1} 3223, 1700, 1614, 1518, 1456, 1390, 1187, 1116, 938, 843, 759, 621; ^{1}H NMR δ_H (400 MHz, DMSO) 8.54 (1H, d, *J* 9.5, NH), 8.27 (2H, s, NH_2), 8.21 (1H, s, CH), 7.85 (1H, d, *J* 8.6, Ar-H), 7.63 (2H, d, *J* 8.6, Ar-H), 7.41-7.32 (11H, m, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.14 (2H, d, *J* 8.8, Ar-H), 5.13-4.96 (4H, m, CH_2); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.6, 152.2, 141.8, 138.8, 136.7 (d, J_{P-C} 7.57), 130.0, 129.7, 128.9, 128.7, 128.2, 127.3, 126.5, 119.1, 118.5, 117.5 (d, J_{P-C} 7.7), 109.9, 68.0 (d, J_{P-C} 4.7); ^{31}P NMR δ_P (162 MHz, DMSO) 2.62. Anal. calcd for: $C_{29}H_{25}N_2O_8PS$: C, 58.78; H 4.25; N, 4.73; S, 5.41. Found: C, 58.89; H, 4.33; N, 4.60; S, 5.37%. HRMS (*m/z*) [M+H]+ calcd 593.1148, found 593.1160.

3-{4-(2-oxo-2λ^5-[1,3,2]dioxaphophinan-2-ylamino)-phenyl}-coumarin-7-*O*-sulfamate 10 g. Yield 82%, mp 213.5-216.0 ^{o}C (with decomposition); ν_{max} (KBr)/cm^{-1} 3326, 1683, 1617, 1518, 1465, 1383, 1192, 1117, 930, 827, 771, 618; ^{1}H NMR δ_H (400 MHz, DMSO) 8.35 (1H, d, *J* 10.8, NH), 8.32-8.15 (3H, m, NH_2, CH), 7.85 (1H, d, *J* 8.6, Ar-H), 7.65 (2H, d, *J* 8.6, Ar-H), 7.36 (1H, d, *J* 2.2, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.11 (2H, d, *J* 8.7, Ar-H), 4.47-4.28 (4H, m, CH_2), 2.15-1.86 (2H, m, CH_2); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.6, 152.2, 141.9, 138.8, 130.0, 129.8, 127.3, 126.5, 119.1, 118.5, 117.4 (d, J_{P-C} 7.6), 109.9, 68.7 (d, J_{P-C} 6.2), 26.22 (d, J_{P-C} 6.9); ^{31}P NMR δ_P (162 MHz, DMSO) -4.29. Anal. calcd for: $C_{18}H_{17}N_2O_8PS$: C, 47.79; H 3.79; N, 6.19; S, 7.09. Found: C, 47.69; H, 3.90; N, 6.14; S, 7.05%. HRMS (*m/z*) [M+H]+ calcd 453.0521, found 453.0534.

3-{4-(5,5-dimethyl-2-oxo-2λ^5-[1,3,2]dioxaphophinan-2-ylamino)-phenyl}-7-coumarin-7-*O*-sulfamate 10h. Yield 88%, mp 225.4-227.3 ^{o}C; ν_{max} (KBr)/cm^{-1} 3328, 1686, 1614, 1518, 1468, 1384, 1188, 1112, 937, 834, 767, 620; ^{1}H NMR δ_H (400 MHz, DMSO) 8.31 (1H, d, *J* 10.6, NH), 8.26 (2H, s, NH_2), 8.23 (1H, s, CH), 7.85 (1H, d, *J* 8.6, Ar-H), 7.65 (2H, d, *J* 8.6, Ar-H), 7.36 (1H, d, *J* 2.2, Ar-H), 7.29 (1H, dd, *J* 8.5, 2.3, Ar-H), 7.13 (2H, d, *J* 8.7, Ar-H), 4.12-3.93 (4H, m, CH_2), 1.15 (3H, s, CH_3), 0.89 (3H, s, CH_3); ^{13}C NMR δ_C (101 MHz, DMSO) 160.0, 153.6, 152.2, 141.8, 138.8, 130.0, 129.8, 127.4, 126.5, 119.1, 118.5, 117.6 (d, J_{P-C} 7.6), 109.9, 77.2 (d, J_{P-C} 6.4), 32.3 (d, J_{P-C} 5.9), 21.6, 20.5; ^{31}P NMR δ_P (162 MHz, DMSO) -4.69. Anal. calcd for: $C_{20}H_{21}N_2O_8PS$: C, 50.50; H 4.41; N, 5.83; S, 6.67. Found: C, 50.61; H, 4.43; N, 5.71; S, 6.75%. HRMS (*m/z*) [M+H]+ calcd 481.0835, found 481.0848.