Supplementary Information

for

Efficacious *N*-Protection of *O*-Aryl Sulfamates with 2,4-Dimethoxybenzyl Groups

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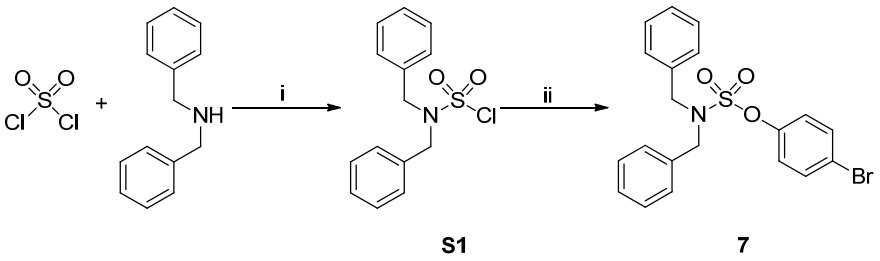
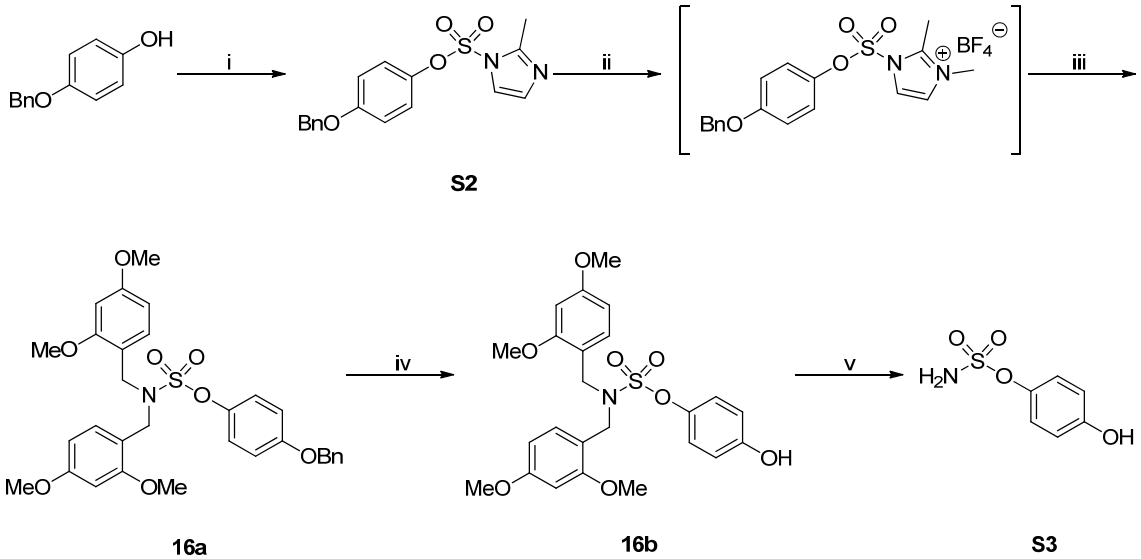
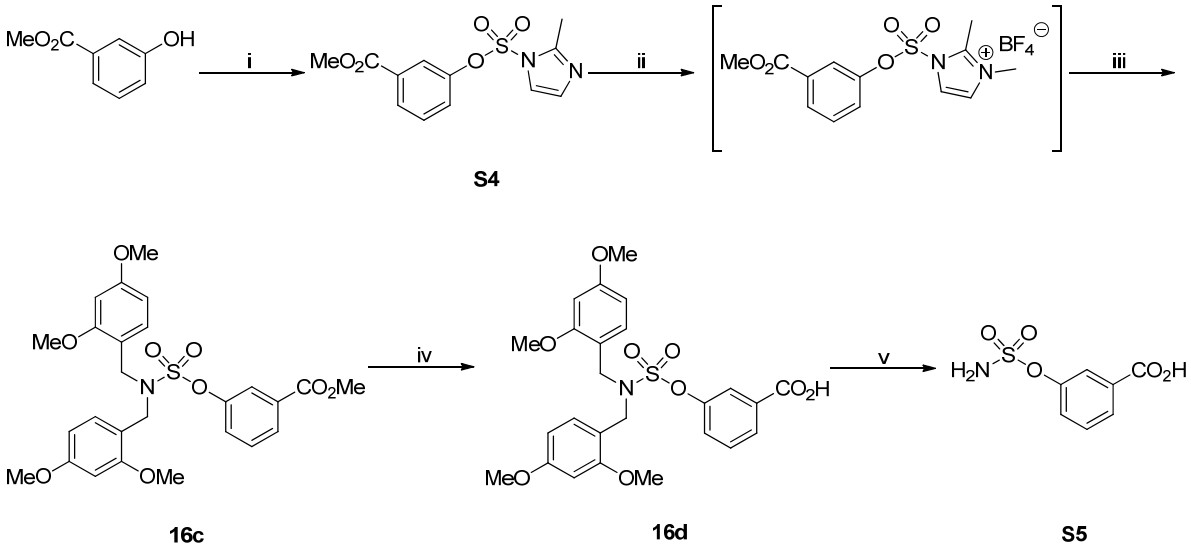
1- Supplemental synthetic schemes.



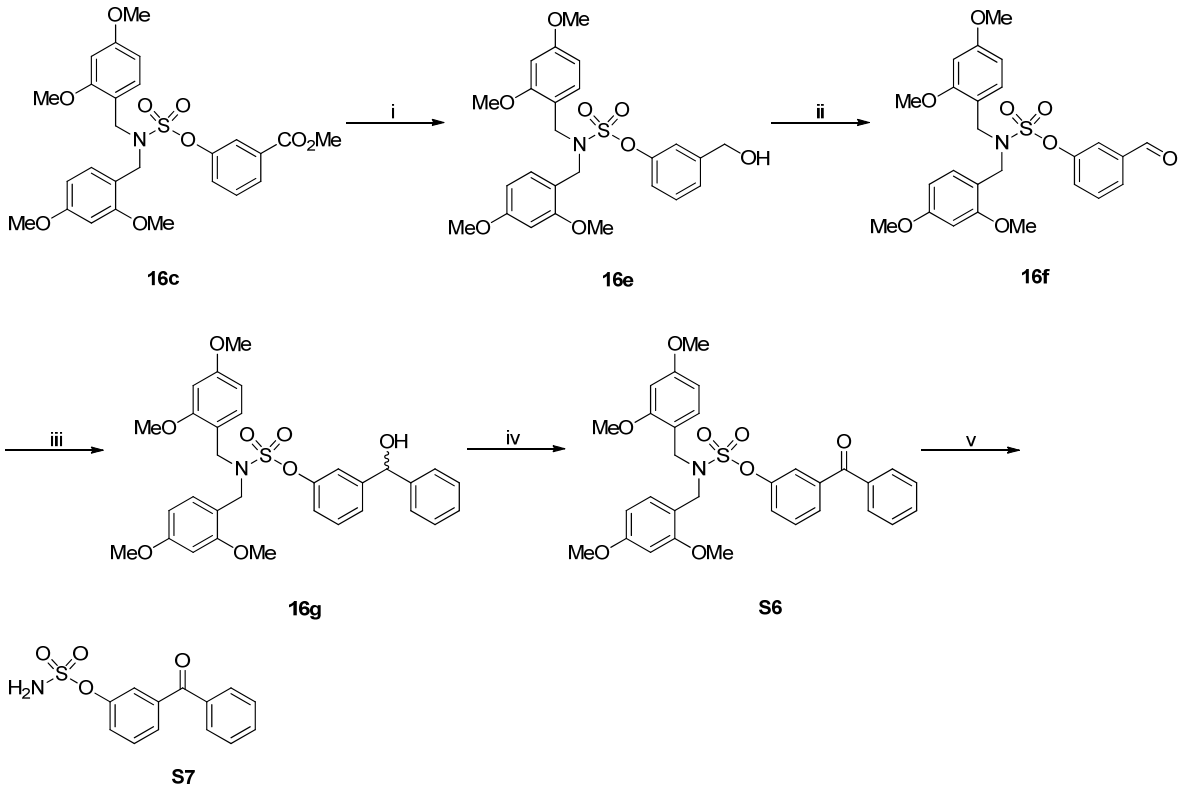
Scheme S1: Synthesis of 4-bromophenyl *O*-bis-benzylsulfamate using *N*,*N*-bis-benzylsulfamoyl chloride **S1** [*Reagents and conditions*: i, pyridine, diethyl ether, -78 °C to room temp., 4 h, 10%; ii, 4-bromophenol, caesium carbonate, THF, 67 °C, 16 h, 40%].



Scheme S2: Synthesis of 4-hydroxyphenyl *O*-sulfamate **S3** [*Reagents and conditions*: i, caesium carbonate, 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**), MeCN, microwave heating (120 °C, 15 min), 96%; ii, trimethyloxonium tetrafluoroborate, DCM, 0 °C to room temp., 8 h; iii, **2**, DCM/MeCN, 42 °C, 24 h, 61 %; iv, H_2, Pd/C (10 %), MeOH, 50 °C, 24 h, 85%; v, 10% TFA, DCM, room temp., 2 h, 86%].

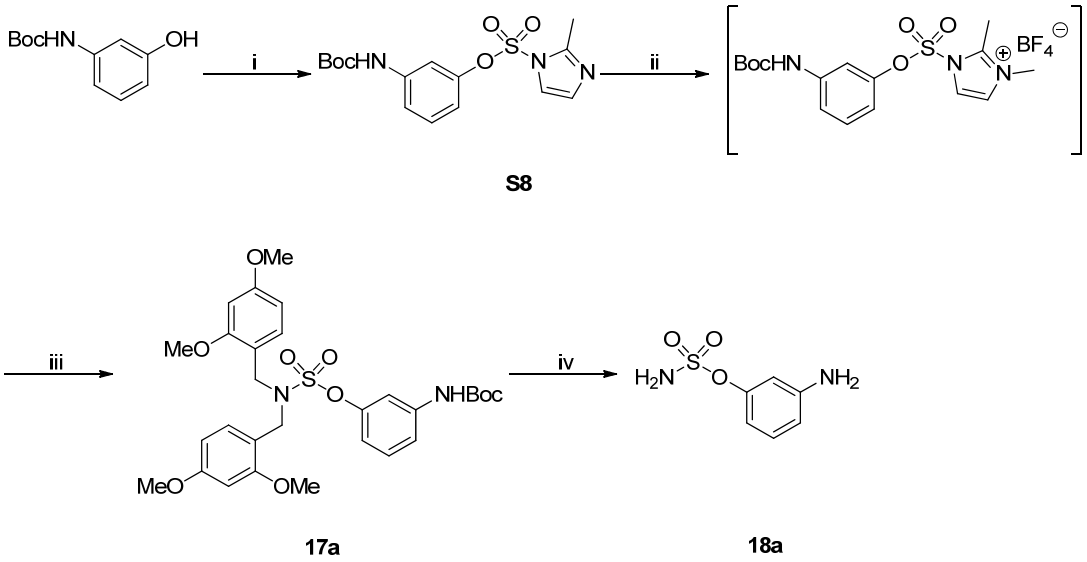


Scheme S3: Synthesis of 3-(sulfamoyloxy)benzoic acid **S5** [*Reagents and conditions*: i, caesium carbonate, 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**), MeCN, microwave heating (120 °C, 15 min), 92%; ii, trimethyloxonium tetrafluoroborate, DCM, 0 °C to room temp., 8 h; iii, **2**, DCM/MeCN, 42 °C, 24 h, 64 %; iv, LiOH, H_2O/THF, 60 °C, 24 h, 85%; v, 10% TFA, DCM, RT, 2 h, 89%].

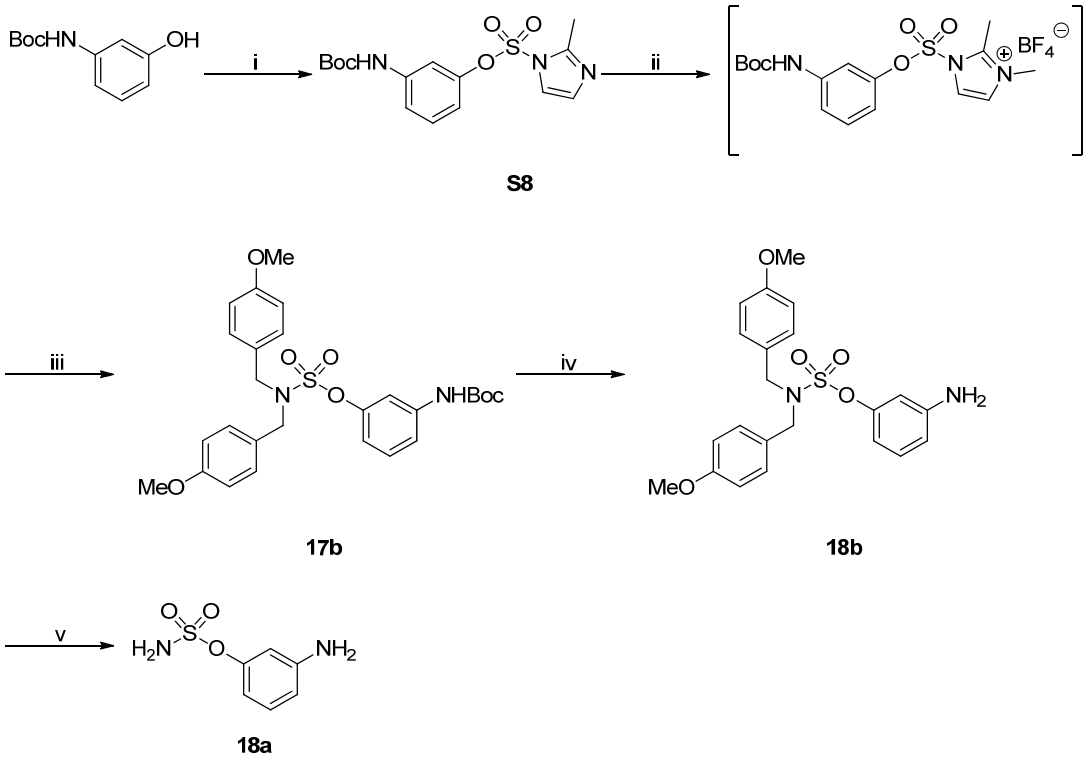


Scheme S4: Synthesis of 3-benzoylphenyl *O*-sulfamate **S7** [*Reagents and conditions*: i, Lithium aluminium hydride (2.0 M in THF), THF, 0 °C, 2 h, 84%; (ii) MnO_2,

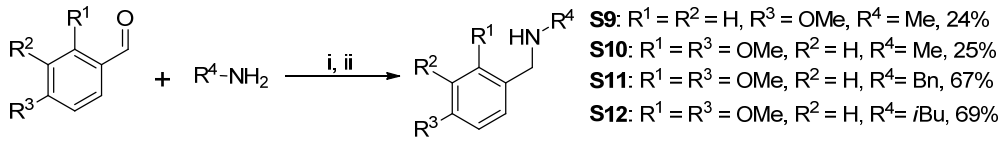
DCM, room temp., 16 h, 89%; (iii) phenylmagnesium bromide (1.0 M in THF), THF, 0 °C to room temp., 2 h, 88%; (iv) MnO_2, DCM, RT, 16 h, 84 %; (v) 10% TFA, DCM, RT, 2 h, 87%].



Scheme S5: Synthesis of 3-aminophenyl *O*-sulfamate **18a** via bis-*N*-2,4-dimethoxybenzyl protected sulfamate [*Reagents and conditions*: i, caesium carbonate, 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**), MeCN, microwave heating (120 °C, 15 min), 84%; ii, trimethyloxonium tetrafluoroborate, DCM, 0 °C to room temp., 8 h; iii, **2**, DCM/MeCN, 42 °C, 24 h, 58 %; iv, 10% TFA, DCM, RT, 2 h, 70%].



Scheme S6: Synthesis of 3-aminophenyl *O*-sulfamate **18a** via bis-*N*-4-methoxybenzyl protected sulfamate [*Reagents and conditions*: i, caesium carbonate, 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**), MeCN, microwave heating (120 °C, 15 min), 84%; ii, trimethyloxonium tetrafluoroborate, DCM, 0 °C to room temp., 8 h; iii, **1**, DCM/MeCN, 42 °C, 24 h, 70 %; iv, 10% TFA, DCM, room temp., 2 h, 94%; v, 50% TFA, DCM, 42 °C, 24 h, 88%].



S9: $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Me$, 24%
S10: $R^1 = R^3 = OMe$, $R^2 = H$, $R^4 = Me$, 25%
S11: $R^1 = R^3 = OMe$, $R^2 = H$, $R^4 = Bn$, 67%
S12: $R^1 = R^3 = OMe$, $R^2 = H$, $R^4 = i$Bu, 69%

Scheme S7: Synthesis of methoxy-substituted benzylamines [*Reagents and conditions*: i, EtOH, heat at reflux, 4 h; ii, $NaBH_4$, room temp., 16 h].

2- Experimental procedures

Materials and methods

Chemicals and solvents were obtained from reputable suppliers. Solvents were either dried by standard techniques or purchased as anhydrous. Petrol was reagent grade (bp range 40–60 °C). All reactions that required an inert or dry atmosphere were carried out under nitrogen, which was dried by passage through a column of phosphorus pentoxide. Glassware was dried in an oven prior to use. Reactions needing microwave irradiation were carried out in an Initiator^{TM} Sixty Biotage apparatus. Column chromatography was carried out using 40-60 μm mesh silica in glass columns under medium pressure or with a Biotage SP4 flash purification system using KP-Sil™ silica. Thin layer chromatography (TLC) was performed on 20 mm pre-coated plates of silica gel (Merck, silica gel 60F254); visualisation was made using ultraviolet light (254 nm). NMR spectra were recorded on a Bruker BioSpin UltraShield Plus (500 MHz for ^{1}H; 125 MHz for ^{13}C) using deuterated solvent as lock. IR spectra were recorded on a Bio-Rad FTS 3000MX diamond ATR. UV analysis was performed using a Hitachi U-2000 spectrophotometer. LCMS was carried out on a Waters Acquity UPLC system with PDA and ELSD operating in positive and negative ion electrospray mode, employing an Acquity UPLC BEH C18, 1.7 μm, 2.1 × 50 mm column with 0.1% formic acid and acetonitrile (5-95%) for gradient elution. HRMS were measured using a Finnigan MAT 95 XP or a Finnigan MAT 900 XLT by the EPSRC National Mass Spectrometry Service Centre (Swansea).

4-Methoxyphenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5b)

Compound **5b** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (364 mg, 1.61 mmol), caesium carbonate (289 mg, 0.89 mmol), 4-methoxyphenol (100 mg, 0.81 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (210 mg, 97%): R_f 0.26 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 273.5; IR (film) ν_{max}/cm^{-1} 1595, 1552, 1500, 1416, 1206, 1141, 1029; δ_H (500 MHz, $CDCl_3$) 2.44 (s, 3H, C*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 6.82 (s, 4H, 4 ×Ar*H*), 6.88 (d, *J* = 1.7 Hz, 1H, H$_{imidazole}$), 7.13 (d, *J* = 1.7 Hz,

1H, $H_{imidazole}$); δ_C (126 MHz, $CDCl_3$) 15.03, 55.80, 115.15, 120.50, 122.66, 128.02, 142.45, 146.97, 159.33; HRMS (ESI) calcd for $C_{11}H_{13}N_2O_4S$ $[M+H]^+$: 269.0591; found 269.0591

4-Chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5c)

Compound **5c** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (218 mg, 0.96 mmol), caesium carbonate (173 mg, 0.53 mmol), 4-chlorophenol (62 mg, 0.48 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (123 mg, 93%): R_f 0.35 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 264.5; IR (film) ν_{max}/cm^{-1} 1553, 1483, 1422, 1207, 1145, 1044, 1014; δ_H (500 MHz, $CDCl_3$) 2.49 (s, 3H, C*H*$_3$), 6.87 (d, *J* = 9.0 Hz, 2H, H-2, 6), 6.89 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.12 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.33 (d, *J* = 9.0 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 15.09, 120.51, 123.09, 128.23, 130.53, 134.59, 146.84, 147.39; HRMS (ESI) calcd for $C_{10}H_{10}ClN_2O_3S$ $[M+H]^+$: 273.0095; found 273.0101

3-Chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5d)

Compound **5d** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (429 mg, 1.89 mmol), caesium carbonate (340 mg, 1.04 mmol), 3-chlorophenol (100 µL, 122 mg, 0.48 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (214 mg, 83%): R_f 0.33 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 265.0; IR (film) ν_{max}/cm^{-1} 1583, 1554, 1423, 1207, 1152, 1044; δ_H (500 MHz, $CDCl_3$) 2.51 (s, 3H, C*H*$_3$), 6.79 (ddd, *J* = 8.1, 2.3, 1.0 Hz, 1H, H-6), 6.90 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.03 (dd, *J* = 2.1, 2.1 Hz, 1H, H-2), 7.14 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.29 (dd, *J* = 8.1, 8.1 Hz, 1H, H-5), 7.38 – 7.32 (m, 1H, H-4); δ_C (126 MHz, $CDCl_3$) 15.09, 119.84, 120.50, 122.55, 128.25, 129.07, 131.08, 135.79, 146.84, 149.20; LRMS (ESI^+) *m/z* 273.4, 275.1 $[M+H]^+$

2-Chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5e)

Compound **5e** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (218 mg, 0.96 mmol), caesium carbonate (173 mg, 0.53 mmol), 2-chlorophenol (50 µL, 62 mg, 0.48 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (119 mg, 90%): R_f 0.33 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 264.5; IR (film) ν_{max}/cm^{-1} 1555, 1474, 1424, 1193, 1170, 1043; δ_H (500 MHz, $CDCl_3$) 2.56 (s, 3H, C*H*$_3$), 6.89 (d, *J* = 1.9 Hz, 1H, $H_{imidazole}$), 7.09 – 7.07 (m, 1H, Ar*H*), 7.10 (d, *J* = 2.1 Hz, 1H, $H_{imidazole}$), 7.36 – 7.26 (m, 2H, 2 × Ar*H*), 7.52 – 7.40 (m, 1H, Ar*H*); δ_C (126 MHz, $CDCl_3$) 15.28, 120.41, 123.81, 127.49, 128.20, 128.36, 129.35, 131.38, 145.30, 146.98; HRMS (ESI) calcd for $C_{10}H_{10}ClN_2O_3S$ $[M+H]^+$: 273.0095; found 273.0101

2,6-Dimethylphenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5f)

Compound **5f** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (370 mg, 1.64 mmol), caesium carbonate (293 mg, 0.90 mmol), 2,6-dimethylphenol (100 mg, 0.82 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a white solid (203 mg, 93%): R_f 0.30 (petrol:EtOAc – 8:2); mp: 55.0-57.0 °C; λ_{max} (EtOH)/nm 262.5; IR (film) ν_{max}/cm^{-1} 1551, 1473, 1419, 1205, 1046; δ_H (500 MHz, $CDCl_3$) 2.07 (s, 6H, 2 × C*H*$_3$), 2.55 (s, 3H, C*H*$_3$), 6.93 (d, *J* = 1.5 Hz, 1H, $H_{imidazole}$), 7.06 (d, *J* = 7.4 Hz, 2H, H-3, 5), 7.16 – 7.10 (m, 1H, H-4), 7.21 (d, *J* = 1.6 Hz, 1H, $H_{imidazole}$); δ_C (126 MHz, $CDCl_3$) 15.18, 16.33, 120.12, 127.91, 128.13, 129.84, 131.67, 146.58, 147.87; HRMS (ESI) calcd for $C_{12}H_{15}N_2O_3S$ $[M+H]^+$: 267.0798; found 267.0803

4-Nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5h)

Compound **5h** was synthesised according to general procedure C, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (4.07 g, 18.0 mmol), caesium carbonate (644 mg, 1.98 mmol), 4-nitrophenol (250 mg, 1.80 mmol) and acetonitrile (20 mL). The crude brown oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as an off-white solid (418 mg, 82%): R_f 0.29 (petrol:EtOAc – 3:1); mp: 113.0-115.0 °C; λ_{max} (EtOH)/nm 253.5; IR (film) ν_{max}/cm^{-1}

1618, 1588, 1553, 1525, 1424, 1346, 1208, 1145, 1045; δ_H (500 MHz, $CDCl_3$) 2.57 (s, 3H, CH_3), 6.92 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.13 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.16 (d, *J* = 9.2 Hz, 2H, H-2, 6), 8.27 (d, *J* = 9.2 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 15.19, 120.48, 122.94, 126.11, 128.55, 146.79, 147.32, 152.83; HRMS (ESI) calcd for $C_{10}H_{10}N_3O_5S$ $[M+H]^+$: 284.0336; found 284.0341

3-Nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5i)

Compound **5i** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (651 mg, 2.87 mmol), caesium carbonate (515 mg, 1.58 mmol), 3-nitrophenol (200 mg, 1.44 mmol) and acetonitrile (20 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a yellow solid (294 mg, 72%): R_f 0.27 (petrol:EtOAc – 3:1); mp: 70.5-72.5 °C; λ_{max} (EtOH)/nm 249.0; IR (film) ν_{max}/cm^{-1} 1557, 1522, 1418, 1351, 1193, 1160, 1045; δ_H (500 MHz, $CDCl_3$) 2.57 (s, 3H, C*H*$_3$), 6.93 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.14 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.26 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 1H, H-6), 7.60 (dd, *J* = 8.3, 8.3 Hz, 1H, H-5), 7.92 (dd, *J* = 2.3, 2.3 Hz, 1H, H-2), 8.26 (ddd, *J* = 8.2, 2.1, 1.0 Hz, 1H, H-4); δ_C (126 MHz, $CDCl_3$) 15.20, 117.79, 120.44, 123.55, 127.74, 128.59, 131.28, 146.84, 149.00, 149.15; HRMS (ESI) calcd for $C_{10}H_{10}N_3O_5S$ $[M+H]^+$: 284.0336; found 284.0337

2-Nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5j)

Compound **5j** was synthesised according to general procedure C, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (4.88 g, 21.6 mmol), caesium carbonate (773 mg, 2.37 mmol), 2-nitrophenol (300 mg, 2.16 mmol) and acetonitrile (20 mL). The crude brown oil was purified by column chromatography (DCM:MeOH - 1:0 → 99:1) to yield the *title compound* as a yellow solid (428 mg, 70%): R_f 0.20 (DCM:MeOH – 99:1); mp: 55.5-57.5 °C; λ_{max} (EtOH)/nm 245.0; IR (film) ν_{max}/cm^{-1} 1600, 1532, 1425, 1339, 1208, 1151, 1045; δ_H (500 MHz, $CDCl_3$) 2.56 (s, 3H, C*H*$_3$), 6.93 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.11 (dd, *J* = 8.2, 1.3 Hz, 1H, H-6), 7.12 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.59 – 7.51 (m, 1H, H-4), 7.66 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H, H-5), 8.08 (dd, *J* = 8.2, 1.7 Hz, 1H, H-3); δ_C (126 MHz, $CDCl_3$) 15.23, 120.26, 124.43,

126.76, 128.59, 129.21, 134.99, 141.17, 142.38, 147.14; HRMS (ESI) calcd for $C_{10}H_{10}N_3O_5S$ $[M+H]^+$: 284.0336; found 284.0340

4-Cyanophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5k)

Compound **5k** was synthesised following two different procedures.

1st procedure: Compound **5k** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (760 mg, 3.36 mmol), caesium carbonate (602 mg, 1.85 mmol), 4-cyanophenol (200 mg, 1.68 mmol) and acetonitrile (20 mL). The crude yellow solid was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a white solid (261 mg, 59%).

2nd procedure: Compound **5k** was synthesised according to general procedure C, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (950 mg, 4.20 mmol), caesium carbonate (150 mg, 0.46 mmol), 4-cyanophenol (50 mg, 042 mmol) and acetonitrile (5 mL). The crude yellow solid was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a white solid (88 mg, 80%); R_f 0.28 (petrol:EtOAc – 7:3); mp: 102.5-104.5 °C; λ_{max} (EtOH)/nm 268.5; IR (film) ν_{max}/cm^{-1} 2239, 1601, 1555, 1498, 1417, 1206, 1144, 1048; δ_H (500 MHz, $CDCl_3$) 2.54 (s, 3H, C*H*$_3$), 6.91 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.09 (d, *J* = 8.7 Hz, 1H, H-2, 6), 7.12 (d, *J* = 1.8 Hz, 1H, $H_{imidazole}$), 7.70 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 15.14, 113.11, 117.20, 120.45, 123.02, 128.49, 134.60, 146.77, 151.62; HRMS (ESI) calcd for $C_{11}H_{10}N_3O_3S$ $[M+H]^+$: 264.0437; found 264.0442

2-Cyanophenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5l)

Compound **5l** was synthesised according to general procedure C, using the following reagents: 1,1'-sulfonylbis(2-methyl-1H-imidazole) (**4**) (4.75 g, 21.0 mmol), caesium carbonate (752 mg, 2.31 mmol), 2-cyanophenol (250 mg, 2.10 mmol) and acetonitrile (20 mL). The crude brown oil was purified by column chromatography (DCM:MeOH - 1:0 → 99:1) to yield the *title compound* as a yellow solid (398 mg, 72%): R_f 0.18 (DCM:MeOH – 99:1); mp: 96.5-98.5 °C; λ_{max} (EtOH)/nm 271.5; IR (film) ν_{max}/cm^{-1} 1608, 1555, 1510, 1487, 1424, 1207, 1151, 1045; δ_H (500 MHz, $CDCl_3$) 2.60 (s, 3H,

C*H*$_3$), 6.93 (d, *J* = 1.8 Hz, 1H, H$_{imidazole}$), 7.14 (d, *J* = 1.8 Hz, 1H, H$_{imidazole}$), 7.25 (dd, *J* = 8.6, 1.1 Hz, 1H, H-6), 7.49 (ddd, *J* = 7.6, 7.6, 1.1 Hz, 1H, H-4), 7.67 (ddd, *J* = 8.4, 7.7, 1.7 Hz, 1H, H-5), 7.71 (dd, *J* = 7.7, 1.7 Hz, 1H, H-3); δ_C (126 MHz, $CDCl_3$) 15.35, 107.99, 113.57, 120.40, 123.15, 128.64, 128.92, 134.45, 134.78, 147.16, 149.52; HRMS (ESI) calcd for $C_{11}H_{10}N_3O_3S$ $[M+H]^+$: 264.0437; found 264.0442

4-(Trifluoromethyl)phenyl 2-methyl-1*H*-imidazole-1-sulfonate, (5m)

Compound **5m** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (837 mg, 3.70 mmol), caesium carbonate (663 mg, 2.04 mmol), 4-(trifluoromethyl)phenol (300 mg, 1.85 mmol) and acetonitrile (20 mL). The crude orange oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (454 mg, 80%): R_f 0.32 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 259.5; IR (film) ν_{max}/cm^{-1} 1613, 1555, 1508, 1427, 1323, 1211, 1173, 1127; δ_H (500 MHz, CDCl3) 2.52 (s, 3H, C*H*$_3$), 6.91 (d, *J* = 1.8 Hz, 1H, H$_{imidazole}$), 7.08 (d, *J* = 8.4 Hz, 2H, H-2, 6), 7.13 (d, *J* = 1.8 Hz, 1H, H$_{imidazole}$), 7.66 (d, *J* = 8.5 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 15.11, 120.50, 122.42, 123.33 (d, *J* = 272.5 Hz), 127.86 (q, *J* = 3.7 Hz), 128.38, 131.09 (q, *J* = 33.4 Hz), 146.82, 151.18; δ_F (471 MHz, $CDCl_3$) -62.62 (CF_3); LRMS (ESI^+) *m/z* 308.1 $[M+H]^+$

4-Chlorophenyl bis(4-methoxybenzyl)sulfamate, (8c)

Compound **8c** was synthesised according to general procedure H, using the following reagents: 4-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5c**) (300 mg, 1.10 mmol), trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol), DCM (11.0 mL), acetonitrile (5.5 mL) and bis(4-methoxybenzyl)amine (**1**) (283 mg, 1.10 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 9:1) to yield the *title compound* as a clear oil (399 mg, 81%): R_f 0.33 (petrol:EtOAc – 9:1); λ_{max} (EtOH)/nm 274.5; IR (film) ν_{max}/cm^{-1} 1612, 1588, 1512, 1484, 1370, 1248, 1170, 1032; δ_H (500 MHz, $CDCl_3$) 3.82 (s, 6H, 2 × OC*H*$_3$), 4.30 (s, 4H, 2 × ArC*H*$_2$), 6.88 (d, *J* = 8.7 Hz, 4H, H-3', 5'), 7.06 (d, *J* = 8.9 Hz, 2H, H-2, 6), 7.20 (d, *J* = 8.7 Hz, 4H, H-2', 6'), 7.30 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 50.36, 55.45,

114.17, 123.46, 126.74, 129.87, 130.52, 132.35, 148.86, 159.70; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5S$ $[M+NH_4]^+$: 465.1245; found 465.1244

3-Chlorophenyl bis(4-methoxybenzyl)sulfamate, (8d)

Compound **8d** was synthesised according to general procedure H, using the following reagents: 3-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5d**) (300 mg, 1.10 mmol), trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol), DCM (11.0 mL), acetonitrile (5.5 mL) and bis(4-methoxybenzyl)amine (**1**) (283 mg, 1.10 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 9:1) to yield the *title compound* as a clear oil (355 mg, 72%): R_f 0.32 (petrol:EtOAc – 9:1); λ_{max} (EtOH)/nm 274.5; IR (film) ν_{max}/cm^{-1} 1611, 1586, 1512, 1371, 1248, 1167, 1032; δ_H (500 MHz, $CDCl_3$) 3.83 (s, 6H, 2 × OC*H*$_3$), 4.32 (s, 4H, 2 × ArC*H*$_2$), 6.89 (d, *J* = 8.7 Hz, 4H, H-3', 5'), 7.06 (dd, *J* = 2.1, 2.1 Hz, 1H, Ar*H*), 7.10 (ddd, *J* = 7.9, 2.3, 1.4 Hz, 1H, Ar*H*), 7.22 (d, *J* = 8.7 Hz, 4H, H-2', 6'), 7.26 – 7.23 (m, 1H, Ar*H*), 7.28 (dd, *J* = 7.9, 7.9 Hz, 1H, Ar*H*); δ_C (126 MHz, $CDCl_3$) 50.41, 55.45, 114.21, 120.33, 122.64, 126.70, 127.05, 130.51, 130.53, 135.02, 150.77, 159.72; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5S$ $[M+NH_4]^+$: 465.1245; found 465.1244

2-Chlorophenyl bis(4-methoxybenzyl)sulfamate, (8e)

Compound **8e** was synthesised according to general procedure H, using the following reagents: 2-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5e**) (300 mg, 1.10 mmol), trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol), DCM (11.0 mL), acetonitrile (5.5 mL) and bis(4-methoxybenzyl)amine (**1**) (283 mg, 1.10 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 9:1) to yield the *title compound* as a clear oil (384 mg, 78%): R_f 0.29 (petrol:EtOAc – 9:1); λ_{max} (EtOH)/nm 274.0; IR (film) ν_{max}/cm^{-1} 1612, 1586, 1514, 1359, 1166, 1054; δ_H (500 MHz, $CDCl_3$) 3.81 (s, 6H, 2 × OC*H*$_3$), 4.42 (s, 4H, 2 × ArC*H*$_2$), 6.86 (d, *J* = 8.7 Hz, 4H, H-3', 5'), 7.24 – 7.19 (m, 5H, H-2', 6' & H-5), 7.30 (ddd, *J* = 8.0, 8.0, 1.7 Hz, 1H, H-4), 7.44 (dd, *J* = 8.0, 1.6 Hz, 1H, H-6), 7.52 (dd, *J* = 8.2, 1.5 Hz, 1H, H-3); δ_C (126 MHz, $CDCl_3$) 50.58, 55.44, 114.13, 123.61, 126.83, 127.23, 127.51, 128.07, 130.47, 130.95, 146.59, 159.61; HRMS (ESI) calcd for $C_{22}H_{26}ClN_2O_5S$ $[M+NH_4]^+$: 465.1245; found 465.1244

2,6-Dimethylphenyl bis(4-methoxybenzyl)sulfamate, (8f)

Compound **8f** was synthesised according to general procedure H, using the following reagents: 2,6-dimethylphenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5f**) (300 mg, 1.13 mmol), trimethyloxonium tetrafluoroborate (167 mg, 1.13 mmol), DCM (11.3 mL), acetonitrile (5.7 mL) and bis(4-methoxybenzyl)amine (**1**) (290 mg, 1.13 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 9:1) to yield the *title compound* as a clear oil (310 mg, 62%): R_f 0.32 (petrol:EtOAc – 9:1); λ_{max} (EtOH)/nm 274.5; IR (film) ν_{max}/cm^{-1} 1612, 1513, 1363, 1247, 1175, 1032; δ_H (500 MHz, $CDCl_3$) 2.42 (s, 6H, 2 × C*H*$_3$), 3.82 (s, 6H, 2 × OC*H*$_3$), 4.46 (s, 4H, 2 × ArC*H*$_2$), 6.88 (d, *J* = 8.7 Hz, 4H, H-3', 5'), 7.07 (s, 3H, 3 × Ar*H*), 7.27 (d, *J* = 8.7 Hz, 4H, H-2', 6'); δ_C (126 MHz, $CDCl_3$) 17.75, 50.35, 55.44, 114.14, 126.70, 127.13, 129.51, 130.35, 132.45, 147.89, 159.58; HRMS (ESI) calcd for $C_{24}H_{31}N_2O_5S$ $[M+NH_4]^+$: 459.1948; found 459.1949

4-Methoxyphenyl bis(2,4-dimethoxybenzyl)sulfamate, (9b)

Compound **9b** was synthesised according to general procedure H, using the following reagents: 4-methoxyphenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5b**) (350 mg, 1.30 mmol), trimethyloxonium tetrafluoroborate (193 mg, 1.30 mmol), DCM (13 mL), acetonitrile (6.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (414 mg, 1,30 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a pale yellow oil (428 mg, 65%): R_f 0.30 (petrol:EtOAc – 3:1); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1502, 1463, 1367, 1208, 1156, 1032; δ_H (500 MHz, $CDCl_3$) 3.72 (s, 6H, 2 × OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.43 (s, 4H, 2 × ArC*H*$_2$), 6.37 (d, *J* = 2.4 Hz, 2H, H-3'), 6.42 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 6.79 (d, *J* = 9.1 Hz, 2H, H-3, 5), 7.00 (d, *J* = 9.1 Hz, 2H, H-2, 6), 7.26 (d, *J* = 8.4 Hz, 2H, H-6'); δ_C (126 MHz, $CDCl_3$) 46.97, 55.21, 55.51, 55.70, 98.21, 104.06, 114.50, 116.84, 123.16, 131.05, 143.93, 157.87, 158.52, 160.65; HRMS (ESI) calcd for $C_{25}H_{30}NO_8S$ $[M+H]^+$: 504.1687; found 504.1677

4-Chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9c)

Compound **9c** was synthesised according to general procedure H, using the following reagents: 4-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5c**) (300 mg, 1.10 mmol), trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol), DCM (11.0 mL), acetonitrile (5.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (349 mg, 1,10 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (352 mg, 63%): R_f 0.32 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1508, 1484, 1370, 1208, 1156, 1035; δ_H (500 MHz, $CDCl_3$) 3.73 (s, 6H, 2 × OC*H*$_3$), 3.80 (s, 6H, 2 × OC*H*$_3$), 4.44 (s, 4H, 2 × ArC*H*$_2$), 6.39 (d, *J* = 2.4 Hz, 2H, H-3'), 6.43 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 6.98 (d, *J* = 8.9 Hz, 2H, H-2, 6), 7.24 (d, *J* = 9.0 Hz, 4H, H-3, 5 & H-6'); δ_C (126 MHz, $CDCl_3$) 47.08, 55.25, 55.54, 98.29, 104.09, 116.60, 123.46, 129.62, 131.11, 148.92, 158.58, 160.80; HRMS (ESI) calcd for $C_{24}H_{27}ClNO_7S$ $[M+H]^+$: 508.1191; found 508.1181

3-Chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9d)

Compound **9d** was synthesised according to general procedure H, using the following reagents: 3-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5d**) (300 mg, 1.10 mmol), trimethyloxonium tetrafluoroborate (163 mg, 1.10 mmol), DCM (11.0 mL), acetonitrile (5.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (349 mg, 1,10 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (341 mg, 61%): R_f 0.31 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1587, 1508, 1467, 1371, 1208, 1156, 1034; δ_H (500 MHz, $CDCl_3$) 3.75 (s, 6H, 2 × OC*H*$_3$), 3.81 (s, 6H, 2 × OC*H*$_3$), 4.45 (s, 4H, 2 × ArC*H*$_2$), 6.41 (d, *J* = 2.4 Hz, 2H, H-3'), 6.45 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 6.91 (dd, *J* = 2.0, 2.0 Hz, 1H, H-2), 7.03 (ddd, *J* = 7.9, 2.2, 1.4 Hz, 1H, H-6), 7.20 – 7.16 (m, 1H, H-4), 7.22 (dd, *J* = 8.0, 8.0 Hz, 1H, H-5), 7.26 (d, *J* = 8.3 Hz, 2H, H-6'); δ_C (126 MHz, $CDCl_3$) 47.28, 55.27, 55.54, 98.36, 104.12, 116.62, 120.36, 122.63, 126.69, 130.27, 131.23, 134.72, 150.85, 158.62, 160.84; HRMS (ESI) calcd for $C_{24}H_{27}ClNO_7S$ $[M+H]^+$: 508.1191; found 508.1187

2-Chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9e)

Compound **9e** was synthesised according to general procedure H, using the following reagents: 2-chlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5e**) (350 mg, 1.28 mmol), trimethyloxonium tetrafluoroborate (190 mg, 1.28 mmol), DCM (13 mL), acetonitrile (6.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (407 mg, 1,28 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (444 mg, 68%): R_f 0.30 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 276.5; IR (film) ν_{max}/cm^{-1} 1614, 1589, 1508, 1473, 1372, 1207, 1157, 1034; δ_H (500 MHz, $CDCl_3$) 3.71 (s, 6H, 2 × OC*H*$_3$), 3.78 (s, 6H, 2 × OC*H*$_3$), 4.56 (s, 4H, 2 × ArC*H*$_2$), 6.35 (d, *J* = 2.4 Hz, 2H, H-3'), 6.40 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.16 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H, Ar*H*), 7.23 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H, Ar*H*), 7.27 (d, *J* = 8.4 Hz, 2H, H-6'), 7.40 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar*H*), 7.43 (dd, *J* = 8.2, 1.6 Hz, 1H, Ar*H*); δ_C (126 MHz, $CDCl_3$) 47.07, 55.20, 55.51, 98.16, 104.07, 116.55, 123.61, 127.16, 127.22, 127.87, 130.77, 130.91, 146.73, 158.51, 160.65; HRMS (ESI) calcd for $C_{24}H_{27}ClNO_7S$ $[M+H]^+$: 508.1191; found 508.1183

2,6-Dimethylphenyl bis(2,4-dimethoxybenzyl)sulfamate, (9f)

Compound **9f** was synthesised according to general procedure H, using the following reagents: 2,6-dimethylphenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5f**) (300 mg, 1.13 mmol), trimethyloxonium tetrafluoroborate (167 mg, 1.13 mmol), DCM (11.5 mL), acetonitrile (5.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (358 mg, 1,13 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a white solid (345 mg, 61%): R_f 0.25 (petrol:EtOAc – 85:15); mp: 92.5-94.5 °C; λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1612, 1608, 1510, 1466, 1364, 1289, 1204, 1188, 1027; δ_H (500 MHz, $CDCl_3$) 2.35 (s, 6H, 2 × C*H*$_3$), 3.72 (s, 6H, 2 × OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.60 (s, 4H, 2 × ArC*H*$_2$), 6.37 (d, *J* = 2.4 Hz, 2H, H-3'), 6.43 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.02 (s, 3H, 3 × Ar*H*), 7.33 (d, *J* = 8.4 Hz, 2H, H-6'); δ_C (126 MHz, $CDCl_3$) 17.60, 46.83, 55.22, 55.52, 98.18, 104.09, 116.84, 126.41, 129.32, 130.70, 132.54, 147.95, 158.46, 160.57; HRMS (ESI) calcd for $C_{26}H_{32}NO_7S$ $[M+H]^+$: 502.1894; found 502.1894

2,6-Dichlorophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9g)

Compound **9g** was synthesised according to general procedure H, using the following reagents: 2,6-dichlorophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5g**) (350 mg, 1.14 mmol), trimethyloxonium tetrafluoroborate (169 mg, 1.14 mmol), DCM (11.4 mL), acetonitrile (5.7 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (362 mg, 1.14 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a yellow oil (389 mg, 63%): R_f 0.31 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.5; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1508, 1440, 1382, 1207, 1157, 1035; δ_H (500 MHz, $CDCl_3$) 3.71 (s, 6H, 2 × OC*H*$_3$), 3.78 (s, 6H, 2 × OC*H*$_3$), 4.60 (s, 4H, 2 × ArC*H*$_2$), 6.35 (d, *J* = 2.4 Hz, 2H, H-3'), 6.40 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.10 (t, *J* = 8.1 Hz, 1H, H-4), 7.30 (d, *J* = 8.4 Hz, 2H, H-6'), 7.33 (d, *J* = 8.1 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 47.20, 55.18, 55.50, 98.09, 104.02, 116.55, 127.35, 129.43, 130.23, 130.98, 144.26, 158.52, 160.64; HRMS (ESI) calcd for $C_{24}H_{26}Cl_2NO_7S$ $[M+H]^+$: 542.0802; found 542.0793

4-Nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9h)

Compound **9h** was synthesised according to general procedure H, using the following reagents: 4-nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5h**) (300 mg, 1.06 mmol), trimethyloxonium tetrafluoroborate (157 mg, 1.06 mmol), DCM (10.5 mL), acetonitrile (5.3 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (337 mg, 1,06 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a yellow oil (340 mg, 62%): R_f 0.29 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 275.0; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1507, 1374, 1346, 1206, 1156, 1033; δ_H (500 MHz, $CDCl_3$) 3.75 (s, 6H, 2 × OC*H*$_3$), 3.81 (s, 6H, 2 × OC*H*$_3$), 4.48 (s, 4H, 2 × ArC*H*$_2$), 6.40 (d, *J* = 2.4 Hz, 2H, H-3'), 6.44 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.16 (d, *J* = 9.2 Hz, 2H, H-2, 6), 7.24 (d, *J* = 8.3 Hz, 2H, H-6'), 8.15 (d, *J* = 9.2 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 47.36, 55.30, 55.56, 98.37, 104.12, 116.26, 122.36, 125.36, 131.24, 145.55, 155.12, 158.65, 160.99; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_9S$ $[M+H]^+$: 519.1432; found 519.1413

3-Nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9i)

Compound **9i** was synthesised according to general procedure H, using the following reagents: 3-nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5i**) (200 mg, 0.71 mmol),

trimethyloxonium tetrafluoroborate (104 mg, 0.71 mmol), DCM (7.1 mL), acetonitrile (3.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (225 mg, 0.71 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a yellow oil (208 mg, 57%): R_f 0.27 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 273.0; IR (film) ν_{max}/cm^{-1} 1612, 1589, 1530, 1507, 1351, 1206, 1157, 1033; δ_H (500 MHz, $CDCl_3$) 3.78 (s, 6H, 2 × OC*H*$_3$), 3.82 (s, 6H, 2 × OC*H*$_3$), 4.49 (s, 4H, 2 × ArC*H*$_2$), 6.43 (d, *J* = 2.3 Hz, 2H, H-3'), 6.45 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.26 (d, *J* = 8.2 Hz, 2H, H-6'), 7.46 (dd, *J* = 8.1, 7.6 Hz, 1H, H-5), 7.51 – 7.48 (m, 1H, H-6), 7.65 (dd, *J* = 2.1, 2.1 Hz, 1H, H-2), 8.06 (ddd, *J* = 7.7, 2.2, 1.5 Hz, 1H, H-4); δ_C (126 MHz, $CDCl_3$) 47.52, 55.33, 55.54, 98.40, 104.18, 116.39, 117.70, 121.28, 128.61, 130.16, 131.35, 148.75, 150.63, 158.67, 160.98; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_9S$ $[M+H]^+$: 519.1432; found 519.1409

2-Nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9j)

Compound **9j** was synthesised according to general procedure H, using the following reagents: 2-nitrophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5j**) (250 mg, 0.88 mmol), trimethyloxonium tetrafluoroborate (131 mg, 0.88 mmol), DCM (8.8 mL), acetonitrile (4.4 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (281 mg, 0.88 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a yellow oil (279 mg, 61%): R_f 0.30 (petrol:EtOAc – 3:1); λ_{max} (EtOH)/nm 276.5; IR (film) ν_{max}/cm^{-1} 1611, 1589, 1532, 1508, 1355, 1208, 1158, 1034; δ_H (500 MHz, $CDCl_3$) 3.73 (s, 6H, 2 × OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.55 (s, 4H, 2 × ArC*H*$_2$), 6.36 (d, *J* = 2.4 Hz, 2H, H-3'), 6.40 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.24 (d, *J* = 8.4 Hz, 2H, H-6'), 7.34 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H, H-4), 7.52 (dd, *J* = 8.2, 1.5 Hz, 1H, H-6), 7.60 – 7.54 (m, 1H, H-5), 7.92 (dd, *J* = 8.2, 1.6 Hz, 1H, H-3); δ_C (126 MHz, $CDCl_3$) 47.29, 55.23, 55.50, 98.19, 104.06, 116.25, 124.54, 125.80, 126.48, 131.01, 134.17, 142.66, 143.14, 158.57, 160.75; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_9S$ $[M+H]^+$: 519.1432; found 519.1409

4-Cyanophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9k)

Compound **9k** was synthesised according to general procedure H, using the following reagents: 4-cyanophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5k**) (300 mg, 1.14

mmol), trimethyloxonium tetrafluoroborate (169 mg, 1.14 mmol), DCM (11.5 mL), acetonitrile (5.7 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (362 mg, 1,14 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a white solid (358 mg, 63%): R_f 0.28 (petrol:EtOAc – 3:1); mp: 113.0-115.0 °C; λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 2229, 1606, 1509, 1367, 1303, 1204, 1156, 1030; δ_H (500 MHz, $CDCl_3$) 3.74 (s, 6H, 2 × OCH_3), 3.81 (s, 6H, 2 × OCH_3), 4.47 (s, 4H, 2 × ArCH_2), 6.41 (d, *J* = 2.4 Hz, 2H, H-3'), 6.44 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.13 (d, *J* = 8.8 Hz, 2H, H-2, 6), 7.24 (d, *J* = 8.3 Hz, 2H, H-6'), 7.59 (d, *J* = 8.8 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 47.27, 55.29, 55.57, 98.37, 104.14, 110.12, 116.30, 118.26, 122.69, 131.18, 133.85, 153.74, 158.64, 160.95; HRMS (ESI) calcd for $C_{25}H_{27}N_2O_7S$ $[M+H]^+$: 499.1533; found 499.1530

2-Cyanophenyl bis(2,4-dimethoxybenzyl)sulfamate, (9l)

Compound **9l** was synthesised according to general procedure H, using the following reagents: 2-cyanophenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5l**) (300 mg, 1.14 mmol), trimethyloxonium tetrafluoroborate (169 mg, 1.14 mmol), DCM (11.5 mL), acetonitrile (5.7 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (362 mg, 1,14 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a clear oil (341 mg, 60%): R_f 0.26 (petrol:EtOAc – 3:1); λ_{max} (EtOH)/nm 276.5; IR (film) ν_{max}/cm^{-1} 2236, 1613, 1592, 1508, 1450, 1374, 1208, 1157, 1033; δ_H (500 MHz, $CDCl_3$) 3.73 (s, 6H, 2 × OCH_3), 3.79 (s, 6H, 2 × OCH_3), 4.61 (s, 4H, 2 × ArCH_2), 6.36 (d, *J* = 2.3 Hz, 2H, H-3'), 6.40 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.27 (d, *J* = 8.4 Hz, 2H, H-6'), 7.30 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, H-4), 7.53 – 7.50 (m, 1H, H-6), 7.59 – 7.55 (m, 1H, H-5), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H, H-3); δ_C (126 MHz, $CDCl_3$) 47.43, 55.24, 55.51, 98.21, 104.10, 107.18, 115.26, 116.33, 122.72, 126.34, 131.09, 133.73, 134.23, 151.76, 158.59, 160.76; HRMS (ESI) calcd for $C_{25}H_{30}N_3O_7S$ $[M+NH_4]^+$: 516.1799; found 516.1796

4-(Trifluoromethyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate, (9m)

Compound **9m** was synthesised according to general procedure H, using the following reagents: 4-(trifluoromethyl)phenyl 2-methyl-1*H*-imidazole-1-sulfonate (**5m**) (350

mg, 1.14 mmol), trimethyloxonium tetrafluoroborate (169 mg, 1.14 mmol), DCM (11.4 mL), acetonitrile (5.7 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (362 mg, 1.14 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a yellow oil (408 mg, 66%): R_f 0.32 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.5; IR (film) ν_{max}/cm^{-1} 1613, 1592, 1508, 1373, 1323, 1208, 1157, 1121, 1036; δ_H (500 MHz, $CDCl_3$) 3.74 (s, 6H, 2 × OC*H*$_3$), 3.80 (s, 6H, 2 × OC*H*$_3$), 4.47 (s, 4H, 2 × ArC*H*$_2$), 6.40 (d, *J* = 2.4 Hz, 2H, H-3'), 6.44 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.15 (d, *J* = 8.1 Hz, 2H, H-2, 6), 7.25 (d, *J* = 8.4 Hz, 2H, H-6'), 7.55 (d, *J* = 8.5 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 47.17, 55.25, 55.53, 98.32, 104.08, 116.44, 122.23, 123.91 (d, *J* = 272.0 Hz), 126.96 (q, *J* = 3.7 Hz), 128.50 (d, *J* = 32.9 Hz), 131.16, 152.96, 158.62, 160.87; δ_F (471 MHz, $CDCl_3$) -62.23 (CF_3); HRMS (ESI) calcd for $C_{25}H_{27}F_3NO_7S$ $[M+H]^+$: 542.1450; found 542.1455

4-Methoxyphenyl sulfamate, (15b)

Compound **15b** was synthesised following two different procedures.

1st procedure: Compound **15b** was synthesised according to general procedure F, using the following reagents: 4-methoxyphenyl bis(2,4-dimethoxybenzyl)sulfamate (**9b**) (250 mg, 0.50 mmol), DCM (4.5 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 65:35) to yield the *title compound* as an off-white solid (91 mg, 90%).

2nd procedure: Compound **15b** was synthesised according to general procedure G, using the following reagents: 4-methoxyphenyl bis(4-methoxybenzyl)sulfamate (**8b**) (250 mg, 0.56 mmol), DCM (2.8 mL) and TFA (2.8 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 0:1) to yield the *title compound* as an off-white solid (107 mg, 93%): R_f 0.33 (petrol:EtOAc – 65:35); δ_H (500 MHz, DMSO) 3.76 (s, 3H, OC*H*$_3$), 6.99 (d, *J* = 9.1 Hz, 2H, H-3, 5), 7.20 (d, *J* = 9.1 Hz, 2H, H-2, 6), 7.87 (s, 2H, N*H*$_2$); LRMS (ESI^-) *m/z* 202.1 $[M-H]^-$; ^1H NMR data were identical to literature data.[1]

4-Chlorophenyl sulfamate, (15c)

Compound **15c** was synthesised following two different procedures.

1st procedure: Compound **15c** was synthesised according to general procedure F, using the following reagents: 4-chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9c**) (200 mg, 0.39 mmol), DCM (3.5 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a white solid (69 mg, 84%).

2nd procedure: Compound **15c** was synthesised according to general procedure G, using the following reagents: 4-chlorophenyl bis(4-methoxybenzyl)sulfamate (**8c**) (250 mg, 0.56 mmol), DCM (2.8 mL) and TFA (2.8 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 0:1) to yield the *title compound* as a white solid (105 mg, 90%): R_f 0.30 (petrol:EtOAc – 8:2); δ_H (500 MHz, DMSO) 7.30 (d, *J* = 8.8 Hz, 2H, H-2, 6), 7.53 (d, *J* = 8.8 Hz, 2H, H-3, 5), 8.07 (s, 2H, N*H*$_2$); LRMS (ESI$^-$) *m/z* 206.1, 208.1 [M-H]$^-$; ^{1}H NMR data were identical to literature data.[1]

3-Chlorophenyl sulfamate, (15d)

Compound **15d** was synthesised following two different procedures.

1st procedure: Compound **15d** was synthesised according to general procedure F, using the following reagents: 3-chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9d**) (200 mg, 0.39 mmol), DCM (3.5 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a white solid (74 mg, 90%).

2nd procedure: Compound **15d** was synthesised according to general procedure G, using the following reagents: 3-chlorophenyl bis(4-methoxybenzyl)sulfamate (**8d**) (250 mg, 0.56 mmol), DCM (2.8 mL) and TFA (2.8 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 0:1) to yield the *title compound* as a white solid (100 mg, 86%): R_f 0.29 (petrol:EtOAc – 8:2); δ_H (500 MHz, DMSO) 7.27 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H, H-6), 7.37 (dd, *J* = 2.2, 2.2 Hz, 1H, H-2), 7.42 (ddd, *J* = 8.1, 2.1, 1.1 Hz, 1H, H-4), 7.53 – 7.46 (m, 1H, H-5), 8.13 (s, 2H, N*H*$_2$); LRMS (ESI$^-$) *m/z* 206.0, 208.1 [M-H]$^-$; ^{1}H NMR data were identical to literature data.[2]

2-Chlorophenyl sulfamate, (15e)

Compound **15e** was synthesised following two different procedures.

1st procedure: Compound **15e** was synthesised according to general procedure F, using the following reagents: 2-chlorophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9e**) (200 mg, 0.39 mmol), DCM (3.5 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as an off-white solid (66 mg, 81%).

2nd procedure: Compound **15e** was synthesised according to general procedure G, using the following reagents: 2-chlorophenyl bis(4-methoxybenzyl)sulfamate (**8e**) (250 mg, 0.56 mmol), DCM (2.8 mL) and TFA (2.8 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 0:1) to yield the *title compound* as an off-white solid (107 mg, 92%): R_f = 0.29 (petrol:EtOAc – 8:2); mp: 63.0-65.0 °C; λ_{max} (EtOH)/nm 266.5; IR (film) ν_{max}/cm^{-1} 3350, 3264, 1566, 1473, 1377, 1179, 1059; δ_H (500 MHz, DMSO) 7.33 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 1H, Ar*H*), 7.45 – 7.41 (m, 1H, Ar*H*), 7.50 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar*H*), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 8.26 (s, 2H, NH_2); δ_C (126 MHz, DMSO) 123.79, 126.42, 127.75, 128.41, 130.61, 146.12; HRMS (ESI) calcd for $C_6H_5ClNO_3S$ $[M-H]^-$: 205.9684; found 205.9684

2,6-Dimethylphenyl sulfamate, (15f)

Compound **15f** was synthesised following two different procedures.

1st procedure: Compound **15f** was synthesised according to general procedure F, using the following reagents: 2,6-dimethylphenyl bis(2,4-dimethoxybenzyl)sulfamate (**9f**) (250 mg, 0.50 mmol), DCM (4.5 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a white solid (90 mg, 90%).

2nd procedure: Compound **15f** was synthesised according to general procedure G, using the following reagents: 2,6-dimethylphenyl bis(4-methoxybenzyl)sulfamate (**8f**) (200 mg, 0.45 mmol), DCM (2.3 mL) and TFA (2.3 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 0:1) to yield the *title compound* as a white solid (84 mg, 92%): R_f 0.28 (petrol:EtOAc – 8:2); δ_H (500 MHz, DMSO) 2.32 (s, 6H, 2 × CH_3), 7.13 – 7.02 (m, 3H, Ar*H*), 8.04 (s, 2H, NH_2); LRMS (ESI^-) *m/z* 200.1 $[M-H]^-$; ^{1}H NMR data were identical to literature data.[3]

2,6-Dichlorophenyl sulfamate, (15g)

Compound **15g** was synthesised according to general procedure F, using the following reagents: 2,6-dichlorophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9g**) (250 mg, 0.46 mmol), DCM (4.1 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as an off-white solid (100 mg, 89%): R_f 0.27 (petrol:EtOAc – 3:1); λ_{max} (EtOH)/nm 269.5; IR (film) ν_{max}/cm^{-1} 3352, 3280, 1576, 1544, 1441, 1373, 1227, 1173, 1066; δ_H (500 MHz, DMSO) 7.32 (t, *J* = 8.1 Hz, 1H, H-4), 7.57 (d, *J* = 8.2 Hz, 2H, H-3, 5), 8.40 (s, 2H, N*H*$_2$); δ_C (126 MHz, DMSO) 128.24, 129.37, 129.53, 143.46; HRMS (ESI) calcd for $C_6H_4Cl_2NO_3S$ $[M-H]^-$: 239.9294; found 239.9291

4-Nitrophenyl sulfamate, (15h)

Compound **15h** was synthesised according to general procedure F, using the following reagents: 4-nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9h**) (250 mg, 0.48 mmol), DCM (4.3 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a yellow solid (84 mg, 80%): R_f = 0.30 (petrol:EtOAc – 7:3); δ_H (500 MHz, DMSO) 7.53 (d, *J* = 9.2 Hz, 2H, H-2, 6), 8.35 (d, *J* = 9.1 Hz, 2H, H-3, 5), 8.36 (s, 2H, N*H*$_2$); ^{1}H NMR data were identical to literature data.[1, 2]

3-Nitrophenyl sulfamate, (15i)

Compound **15i** was synthesised according to general procedure F, using the following reagents: 3-nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9i**) (150 mg, 0.29 mmol), DCM (2.6 mL) and TFA (0.3 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a pale orange solid (55 mg, 87%): R_f = 0.30 (petrol:EtOAc – 7:3); δ_H (500 MHz, DMSO) 7.76 – 7.73 (m, 1H, H-6), 7.78 (dd, *J* = 8.0, 8.0 Hz, 1H, H-5), 8.11 (dd, *J* = 2.2, 2.2 Hz, 1H, H-2), 8.22 (ddd, *J* = 8.0, 2.2, 1.3 Hz, 1H, H-4), 8.26 (s, 2H, N*H*$_2$); ^{1}H NMR data were identical to literature data.[2]

2-Nitrophenyl sulfamate, (15j)

Compound **15j** was synthesised according to general procedure F, using the following reagents: 2-nitrophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9j**) (200 mg, 0.39 mmol), DCM (3.5 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a pale orange solid (34 mg, 40%): R_f = 0.28 (petrol:EtOAc – 7:3); δ_H (500 MHz, DMSO) 7.58 – 7.54 (m, 1H, H-4), 7.59 – 7.57 (m, 1H, H-6), 7.82 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H, H-5), 8.05 (dd, *J* = 8.1, 1.6 Hz, 1H, H-3), 8.40 (s, 2H, N*H*$_2$); ^{1}H NMR data were identical to literature data.[4]

4-Cyanophenyl sulfamate, (15k)

Compound **15k** was synthesised according to general procedure F, using the following reagents: 4-cyanophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9k**) (200 mg, 0.40 mmol), DCM (3.6 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 65:35) to yield the *title compound* as a white solid (73 mg, 92%): R_f = 0.29 (petrol:EtOAc – 65:35); δ_H (500 MHz, DMSO) 7.47 (d, *J* = 8.7 Hz, 2H, H-2, 6), 7.98 (d, *J* = 8.7 Hz, 2H, H-3, 5), 8.28 (s, 2H, N*H*$_2$); LRMS (ESI$^-$) *m/z* 199.1 [M+H]$^-$; ^{1}H NMR data were identical to literature data.[1]

2-Cyanophenyl sulfamate, (15l)

Compound **15l** was synthesised according to general procedure F, using the following reagents: 2-cyanophenyl bis(2,4-dimethoxybenzyl)sulfamate (**9l**) (200 mg, 0.40 mmol), DCM (3.6 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 65:35) to yield the *title compound* as an off-white solid (68 mg, 86%): R_f 0.30 (petrol:EtOAc – 65:35); mp: 82.0-84.0 °C; λ_{max} (EtOH)/nm 281.0; IR (film) ν_{max}/cm^{-1} 3366, 3243, 2247, 1602, 1558, 1487, 1450, 1385, 1162, 1098; δ_H (500 MHz, DMSO) 7.51 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H, H-4), 7.59 (dd, *J* = 8.5, 1.0 Hz, 1H, H-6), 7.82 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H, H-5), 7.95 (dd, *J* = 7.7, 1.7 Hz, 1H, H-3), 8.50 (s, 2H, N*H*$_2$); δ_C (126 MHz, DMSO) 106.61, 115.29, 122.79, 127.14, 134.14, 135.02, 151.10; HRMS (ESI) calcd for $C_7H_5N_2O_3S$ [M-H]$^-$: 197.0026; found 197.0027

4-(Trifluoromethyl)phenyl sulfamate, (15m)

Compound **15m** was synthesised according to general procedure F, using the following reagents: 4-(trifluoromethyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate (**9m**) (250 mg, 0.46 mmol), DCM (4.1 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as an off-white solid (100 mg, 90%): R_f 0.28 (petrol:EtOAc – 3:1); δ_H (500 MHz, DMSO) 7.50 (d, *J* = 8.5 Hz, 2H, H-2, 6), 7.87 (d, *J* = 8.7 Hz, 2H, H-3, 5), 8.21 (s, 2H, N*H*$_2$); LRMS (ESI$^-$) *m/z* 240.1 $[M-H]^-$; ^{1}H NMR data were identical to literature data.[1]

4-(Benzyloxy)phenyl bis(2,4-dimethoxybenzyl)sulfamate, (16a)

Compound **16a** was synthesised according to general procedure H, using the following reagents: 4-(benzyloxy)phenyl 2-methyl-1*H*-imidazole-1-sulfonate (**S2**) (450 mg, 1.31 mmol), trimethyloxonium tetrafluoroborate (193 mg, 1.31 mmol), DCM (13.0 mL), acetonitrile (6.5 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (416 mg, 1.31 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (461 mg, 61%): R_f = 0.30 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1591, 1501, 1369, 1208, 1155, 1035; δ_H (500 MHz, $CDCl_3$) 3.72 (s, 6H, 2 × OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.43 (s, 4H, 2 × ArC*H*$_2$), 5.02 (s, 2H, ArC*H*$_2$), 6.37 (d, *J* = 2.3 Hz, 2H, H-3'), 6.42 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 6.87 (d, *J* = 9.1 Hz, 2H, 2 × Ar*H*), 7.00 (d, *J* = 9.1 Hz, 2H, 2 × Ar*H*), 7.26 (d, *J* = 8.3 Hz, 2H, H-6'), 7.36 – 7.31 (m, 1H, Ar*H*), 7.44 – 7.36 (m, 4H, 4 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 46.98, 55.21, 55.52, 70.50, 98.21, 104.04, 115.48, 116.83, 123.19, 127.61, 128.21, 128.76, 131.06, 136.81, 144.10, 157.08, 158.52, 160.65; HRMS (ESI) calcd for $C_{31}H_{34}NO_8S$ $[M+H]^+$: 580.2000; found 580.1991

4-Hydroxyphenyl bis(2,4-dimethoxybenzyl)sulfamate, (16b)

4-(Benzyloxy)phenyl bis(2,4-dimethoxybenzyl)sulfamate (**16a**) (300 mg, 0.52 mmol) in MeOH (10.5 mL) was subjected to palladium catalyzed hydrogenation using an H-Cube® reactor and a 10% Pd/C CatCart. The reaction mixture was heated at 60 °C for 24 h. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 65:35) to yield the *title compound* as a clear oil (215 mg, 85%): R_f = 0.31

(petrol:EtOAc – 65:35); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1592, 1505, 1360, 1208, 1157, 1034; δ_H (500 MHz, $CDCl_3$) 3.72 (s, 6H, 2 × OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.43 (s, 4H, 2 × OC*H*$_3$), 5.10 (s, 1H, O*H*), 6.38 (d, *J* = 2.4 Hz, 2H, H-3'), 6.42 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 6.70 (d, *J* = 9.0 Hz, 2H, H-3, 5), 6.93 (d, *J* = 9.0 Hz, 2H, H-2, 6), 7.25 (d, *J* = 8.4 Hz, 2H, H-6'); δ_C (126 MHz, $CDCl_3$) 47.00, 55.23, 55.54, 98.25, 104.10, 116.05, 116.80, 123.36, 131.04, 143.92, 154.05, 158.53, 160.67; HRMS (ESI) calcd for $C_{24}H_{28}NO_8S$ $[M+H]^+$: 490.1530; found 490.1527

Methyl 3-((*N*,*N*-bis(2,4-dimethoxybenzyl)sulfamoyl)oxy)benzoate. (16c)

Compound **16c** was synthesised according to general procedure H, using the following reagents: methyl 3-(((2-methyl-1*H*-imidazol-1-yl)sulfonyl)oxy)benzoate (**S4**) (750 mg, 2.53 mmol), trimethyloxonium tetrafluoroborate (374 mg, 2.53 mmol), DCM (25.3 mL), acetonitrile (12.7 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (805 mg, 2.53 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a clear oil (845 mg, 64%): R_f 0.30 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1725, 1613, 1588, 1508, 1372, 1287, 1267, 1208, 1157, 1035; δ_H (500 MHz, $CDCl_3$) 3.74 (s, 6H, 2 × OC*H*$_3$), 3.80 (s, 6H, 2 × OC*H*$_3$), 3.91 (s, 3H, CO_2C*H*$_3$), 4.47 (s, 4H, 2 × ArC*H*$_2$), 6.39 (d, *J* = 2.4 Hz, 2H, H-3'), 6.43 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.26 (d, *J* = 8.3 Hz, 2H, H-6'), 7.31 (ddd, *J* = 8.1, 2.3, 1.2 Hz, 1H, H-4), 7.37 (dd, *J* = 8.1, 7.6 Hz, 1H, H-5), 7.65 (dd, *J* = 1.9, 1.9 Hz, 1H, H-2), 7.89 (ddd, *J* = 7.7, 1.3, 1.3 Hz, 1H, H-6); δ_C (126 MHz, $CDCl_3$) 47.11, 52.42, 55.24, 55.50, 98.31, 104.07, 116.59, 123.18, 126.68, 127.60, 129.60, 131.13, 131.85, 150.42, 158.58, 160.77, 166.08; HRMS (ESI) calcd for $C_{26}H_{30}NO_9S$ $[M+H]^+$: 532.1636; found 532.1626

3-((*N*,*N*-bis(2,4-dimethoxybenzyl)sulfamoyl)oxy)benzoic acid, (16d)

To methyl 3-((*N*,*N*-bis(2,4-dimethoxybenzyl)sulfamoyl)oxy)benzoate (**16c**) in THF (5 mL) was added a 2 M aqueous solution of lithium hydroxide (2.8 mL, 5.65 mmol). The resulting mixture was heated at 60 °C for 18 h. Upon completion, the mixture was acidified to pH 3 using a 4 M aqueous solution of HCl. The reaction was then diluted with water (20 mL) and extracted with EtOAc (3 × 25 mL). The pooled organic extracts were washed with water (30 mL) and brine (30 mL), dried over

$MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (DCM:MeOH:AcOH - 1:0 → 950:49:1) to yield the *title compound* as a clear oil (249 mg, 85%): R_f = 0.32 (DCM:MeOH:AcOH - 1:0 → 950:49:1); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1696, 1613, 1587, 1508, 1371, 1291, 1266, 1208, 1157, 1034; δ_H (500 MHz, $CDCl_3$) 3.76 (s, 6H, 2 × OC*H*$_3$), 3.81 (s, 6H, 2 × OC*H*$_3$), 4.49 (s, 4H, 2 × ArC*H*$_2$), 6.41 (d, *J* = 2.3 Hz, 2H, H-3'), 6.44 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 7.27 (d, *J* = 8.4 Hz, 2H, H-6'), 7.45 – 7.39 (m, 2H, H-4 & H-5), 7.68 (dd, *J* = 1.9, 1.9 Hz, 1H, H-2), 7.98 – 7.93 (m, 1H, H-6); δ_C (126 MHz, $CDCl_3$) 47.23, 55.28, 55.52, 98.37, 104.14, 116.59, 123.79, 127.65, 128.15, 129.78, 130.91, 131.21, 150.52, 158.62, 160.83, 170.61; HRMS (ESI) calcd for $C_{25}H_{28}NO_9S$ $[M+H]^+$: 518.1479; found 518.1474

3-(Hydroxymethyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate, (16e)

To methyl 3-((*N*,*N*-bis(2,4-dimethoxybenzyl)sulfamoyl)oxy)benzoate (**16c**) (500 mg, 0.94 mmol) in THF (8 mL), cooled at 0 °C, was added dropwise a lithium aluminiumhydride solution (2.0 M in THF, 0.52 mL). The resulting solution was stirred at 0 °C for 2 h. Upon completion, the reaction was quenched by addition of Rochelle's salt (20 mL). The aqueous layer was extracted with EtOAc (3 × 30 mL). The pooled organic extracts were washed with water and brine (30 mL, respectively), dried over $MgSO_4$ and concentrated *in vacuo*. The crude solid was purified by column chromatography (petrol:EtOAc - 1:0 → 1:1) to yield the *title compound* as a clear oil (400 mg, 84%): R_f 0.35 (petrol:EtOAc – 1:1); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1588, 1508, 1367, 1208, 1158, 1034; δ_H (500 MHz, $CDCl_3$) 1.77 (t, *J* = 6.1 Hz, 1H, CH_2OH), 3.73 (s, 6H, 2 × OC*H*$_3$), 3.80 (s, 6H, 2 × OC*H*$_3$), 4.46 (s, 4H, 2 × ArC*H*$_2$), 4.63 (d, *J* = 5.8 Hz, 2H, C*H*$_2$OH), 6.39 (d, *J* = 2.4 Hz, 2H, H-3'), 6.43 (dd, *J* = 8.4, 2.4 Hz, 2H, H-5'), 6.99 (s, 1H, H-2), 7.08 – 7.02 (m, 1H, Ar*H*), 7.21 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.26 (d, *J* = 8.4 Hz, 2H, H-6'), 7.29 (dd, *J* = 7.8, 7.8 Hz, 1H, H-5); δ_C (126 MHz, $CDCl_3$) 47.02, 55.25, 55.54, 64.76, 98.27, 104.10, 116.77, 120.31, 121.07, 124.72, 129.71, 131.11, 142.99, 150.67, 158.59, 160.69; HRMS (ESI) calcd for $C_{25}H_{30}NO_8S$ $[M+H]^+$: 504.1687; found 504.1684

3-Formylphenyl bis(2,4-dimethoxybenzyl)sulfamate, (16f)

To 3-(hydroxymethyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate (**16e**) (300 mg, 3.60 mmol) in anhydrous DCM (10 mL) was added manganese dioxide (518 mg, 5.96 mmol). The resulting solution was stirred at room temperature for 16 h. Upon completion, the heterogeneous mixture was filtered through Celite and washed with DCM (15 mL). The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a clear oil (266 mg, 89%): R_f 0.30 (petrol:EtOAc – 7:3); λ_{max} (EtOH)/nm 275.5; IR (film) ν_{max}/cm^{-1} 1703, 1616, 1588, 1507, 1361, 1208, 1173, 1031; δ_H (500 MHz, $CDCl_3$) 3.75 (s, 6H, 2 × OC*H*$_3$), 3.81 (s, 6H, 2 × OC*H*$_3$), 4.48 (s, 4H, 2 × ArC*H*$_2$), 6.40 (d, *J* = 2.3 Hz, 2H, H-3'), 6.44 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.26 (d, *J* = 8.4 Hz, 2H, H-6'), 7.40 – 7.37 (m, 1H, H-6), 7.41 (dd, *J* = 1.7, 1.7 Hz, 1H, H-2), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H, H-5), 7.72 (ddd, *J* = 7.6, 1.2, 1.2 Hz, 1H, H-4), 9.91 (s, 1H, CHO); δ_C (126 MHz, $CDCl_3$) 47.28, 55.29, 55.53, 98.40, 104.20, 116.60, 122.95, 127.43, 128.14, 130.30, 131.23, 137.94, 151.09, 158.66, 160.88, 191.02; HRMS (ESI) calcd for $C_{25}H_{28}NO_8S$ $[M+H]^+$: 502.1530; found 502.1519

3-(Hydroxy(phenyl)methyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate, (16g)

To methyl 3-formylphenyl bis(2,4-dimethoxybenzyl)sulfamate (**16f**) (200 mg, 0.40 mmol) in THF (10 mL), cooled at 0 °C, was added dropwise a phenyl magnesium bromide solution (1.0 M in THF, 1.2 mL). The resulting solution was stirred at 0 °C for 3 h. Upon completion, the reaction was quenched by addition of a 1 M HCl solution (4 mL) and diluted with water (10 mL). The aqueous layer was extracted with EtOAc (3 × 25 mL). The pooled organic extracts were washed with water and brine (30 mL, respectively), dried over $MgSO_4$ and concentrated *in vacuo*. The crude solid was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a clear oil (203 mg, 88%): R_f 0.25 (petrol:EtOAc – 7:3); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1588, 1508, 1368, 1208, 1157, 1034; δ_H (500 MHz, $CDCl_3$) 2.25 (d, *J* = 3.6 Hz, 1H, CHO*H*), 3.71 (s, 6H, 2 × OC*H*$_3$), 3.79 (s, 6H, 2 × OC*H*$_3$), 4.42 (s, 4H, 2 × ArC*H*$_2$), 5.76 (d, *J* = 3.0 Hz, 1H, C*H*OH), 6.38 (d, *J* = 2.4 Hz, 2H, H-3'), 6.41 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.08 – 7.02 (m, 2H, 2 × Ar*H*), 7.23 – 7.19 (m, 1H, Ar*H*), 7.29 – 7.23 (m, 4H, 4 × Ar*H*), 7.33 (d, *J* = 4.4 Hz, 4H, 4 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 47.00, 55.24, 55.53, 75.84, 98.29, 104.09, 116.75, 120.02, 121.13, 124.48, 126.73, 127.92, 128.73, 129.68, 131.10, 143.43,

145.87, 150.65, 158.58, 160.69; HRMS (ESI) calcd for $C_{31}H_{32}NO_8S$ $[M-H]^-$: 578.1843; found 578.1857

3-((*tert*-Butoxycarbonyl)amino)phenyl bis(2,4-dimethoxybenzyl)sulfamate, (17a)

Compound **17a** was synthesised according to general procedure H, using the following reagents: 3-((*tert*-butoxycarbonyl)amino)phenyl 2-methyl-1*H*-imidazole-1-sulfonate (**S8**) (300 mg, 0.85 mmol), trimethyloxonium tetrafluoroborate (126 mg, 0.85 mmol), DCM (8.5 mL), acetonitrile (4.3 mL) and bis(2,4-dimethoxybenzyl)amine (**2**) (270 mg, 0.85 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a pale yellow oil (290 mg, 58%): R_f 0.28 (petrol:EtOAc – 3:1); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1727, 1613, 1591, 1508, 1367, 1208, 1155, 1129, 1035; δ_H (500 MHz, $CDCl_3$) 1.52 (s, 9H, C(CH_3)$_3$), 3.71 (s, 6H, 2 × OCH_3), 3.80 (s, 6H, 2 × OCH_3), 4.45 (s, 4H, 2 × ArCH_2), 6.37 (d, J = 2.4 Hz, 2H, H-3'), 6.43 (dd, J = 8.4, 2.4 Hz, 2H, H-5'), 6.79 (ddd, J = 8.1, 2.3, 1.0 Hz, 1H, H-6), 7.03 (dd, J = 2.2, 2.2 Hz, 1H, H-2), 7.20 (dd, J = 8.2, 8.2 Hz, 1H, H-5), 7.26 (d, J = 8.4 Hz, 2H, H-6'), 7.31 – 7.27 (m, 1H, H-4); δ_C (126 MHz, $CDCl_3$) 28.45, 47.00, 55.22, 55.52, 80.96, 98.23, 104.06, 112.21, 116.21, 116.29, 116.79, 129.87, 131.09, 139.63, 150.89, 152.44, 158.58, 160.67; HRMS (ESI) calcd for $C_{29}H_{40}N_3O_9S$ $[M+NH_4]^+$: 606.2480; found 606.2476

3-((*tert*-Butoxycarbonyl)amino)phenyl bis(4-methoxybenzyl)sulfamate, (17b)

Compound **17b** was synthesised according to general procedure H, using the following reagents: 3-((*tert*-butoxycarbonyl)amino)phenyl 2-methyl-1*H*-imidazole-1-sulfonate (**S8**) (350 mg, 0.99 mmol), trimethyloxonium tetrafluoroborate (146 mg, 0.99 mmol), DCM (9.9 mL), acetonitrile (5.0 mL) and bis(4-methoxybenzyl)amine (**1**) (255 mg, 0.99 mmol). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a pale yellow oil (365 mg, 70%): R_f 0.33 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 274.5; IR (film) ν_{max}/cm^{-1} 1727, 1612, 1513, 1367, 1246, 1156, 1032; δ_H (500 MHz, $CDCl_3$) 1.52 (s, 9H, C(CH_3)$_3$), 3.82 (s, 6H, 2 × OCH_3), 4.32 (s, 4H, 2 × ArCH_2), 6.47 (s, 1H, N*H*Boc), 6.86 (d, J = 8.7 Hz, 5H, 5 × Ar*H*), 7.20 (d, J = 8.7 Hz, 4H, H-2', 6'), 7.21 – 7.25 (m, 3H, 3 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 28.44, 50.44, 55.44, 112.18, 114.11, 116.22,

116.49, 126.97, 130.03, 130.56, 139.85, 150.84, 152.41, 159.59; HRMS (ESI) calcd for $C_{27}H_{36}N_3O_7S$ $[M+NH_4]^+$: 546.2268; found 546.2256

3-Aminophenyl sulfamate, (18a)

Compound **18a** was synthesised following two different procedures.

1st procedure: Compound **18a** was synthesised according to general procedure F, using the following reagents: 3-((*tert*-butoxycarbonyl)amino)phenyl bis(2,4-dimethoxybenzyl)sulfamate (**17a**) (150 mg, 0.25 mmol), DCM (2.3 mL) and TFA (0.3 mL). The crude product was purified by column chromatography (DCM:MeOH - 1:0 → 96:4) to yield the *title compound* as a white solid (34 mg, 70%).

2nd procedure: Compound **18a** was synthesised according to general procedure G, using the following reagents: 3-aminophenyl bis(4-methoxybenzyl)sulfamate (**18b**) (200 mg, 0.47 mmol), DCM (2.4 mL) and TFA (2.4 mL). The crude product was purified by column chromatography (DCM:MeOH - 1:0 → 96:4) to yield the *title compound* as a white solid (78 mg, 88%): R_f 0.30 (DCM:MeOH – 96:4); mp: 95.0-97.0 °C; λ_{max} (EtOH)/nm 238.5, 288.5; IR (film) ν_{max}/cm^{-1} 3409, 3328, 1612, 1488, 1357, 1187, 1126; δ_H (500 MHz, DMSO) 5.34 (s, 2H, N*H*$_2$), 6.38 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.57 – 6.41 (m, 2H, 2 × Ar*H*), 7.03 (dd, *J* = 8.0, 8.0 Hz, 1H, H-5), 7.84 (s, 2H, N*H*$_2$); δ_C (126 MHz, DMSO) 107.06, 108.68, 111.88, 129.60, 150.17, 151.17; HRMS (ESI) calcd for $C_6H_9N_2O_3S$ $[M+H]^+$: 189.0328; found 189.0328

3-Aminophenyl bis(4-methoxybenzyl)sulfamate, (18b)

3-((*tert*-Butoxycarbonyl)amino)phenyl bis(4-methoxybenzyl)sulfamate (**17a**) (300 mg, 0.57 mmol) was solubilized in a 10% TFA/DCM mixture (5 mL). The resulting solution was stirred at room temperature for 2 h. Upon completion, the solvent was removed *in vacuo*. The crude residue was dissolved in EtOAc (20 mL), washed with sat. aq. $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 25 mL). The pooled organic extracts were washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a pale yellow oil (230 mg, 94%): R_f 0.28 (petrol:EtOAc – 7:3); λ_{max} (EtOH)/nm 275.0, 281.5; IR (film) ν_{max}/cm^{-1} 1611, 1585, 1512, 1491, 1365, 1246, 1173, 1030; δ_H (500 MHz, $CDCl_3$) 3.73 (s, 2H,

NH_2), 3.82 (s, 6H, 2 × OCH_3), 4.30 (s, 4H, 2 × ArCH_2), 6.46 (dd, *J* = 2.2, 2.2 Hz, 1H, H-2), 6.53 (ddd, *J* = 8.1, 2.3, 0.8 Hz, 1H, Ar*H*), 6.56 (ddd, *J* = 8.2, 2.3, 0.8 Hz, 1H, Ar*H*), 6.87 (d, *J* = 8.7 Hz, 4H, H-3', 5'), 7.09 (dd, *J* = 8.1, 8.1 Hz, 1H, H-5), 7.20 (d, *J* = 8.7 Hz, 4H, H-2', 6'); δ_C (126 MHz, $CDCl_3$) 50.40, 55.45, 108.45, 111.55, 113.36, 114.11, 127.07, 130.32, 130.55, 147.99, 151.46, 159.60; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_5S$ $[M+H]^+$: 429.1479; found 429.1476

4-Bromophenyl 4-methoxybenzyl(methyl)sulfamate, (19a)

Compound **19a** was synthesised according to general procedure D, using the following reagents: 1-((4-bromophenoxy)sulfonyl)-2,3-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (**6**) (600 mg, 1.43 mmol), 1-(4-methoxyphenyl)-*N*-methylmethanamine (**S9**) (217 mg, 1.43 mmol) and acetonitrile (11.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a white solid (532 mg, 96%): R_f 0.34 (petrol:EtOAc – 85:15); mp: 65.0-67.0 °C; λ_{max} (EtOH)/nm 274.0; IR (film) ν_{max}/cm^{-1} 1613, 1585, 1512, 1483, 1368, 1197, 1153; δ_H (500 MHz, $CDCl_3$) 2.83 (s, 3H, NCH_3), 3.82 (s, 3H, OCH_3), 4.35 (s, 2H, ArCH_2), 6.89 (d, *J* = 8.7 Hz, 2H, H-3', 5'), 7.15 (d, *J* = 8.9 Hz, 2H, H-2, 6), 7.23 (d, *J* = 8.7 Hz, 2H, H-2', 6'), 7.51 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 35.24, 54.77, 55.46, 114.26, 120.20, 123.80, 126.76, 130.10, 132.98, 149.38, 159.78; HRMS (ESI) calcd for $C_{15}H_{20}BrN_2O_4S$ $[M+NH_4]^+$: 403.0322; found 403.0328

4-Bromophenyl 2,4-dimethoxybenzyl(methyl)sulfamate, (19b)

Compound **19b** was synthesised according to general procedure D, using the following reagents: 1-((4-bromophenoxy)sulfonyl)-2,3-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (**6**) (600 mg, 1.43 mmol), 1-(2,4-dimethoxyphenyl)-*N*-methylmethanamine (**S10**) (260 mg, 1.43 mmol) and acetonitrile (11.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a clear oil (566 mg, 95%): R_f 0.32 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1509, 1481, 1372, 1197, 1155, 1034; δ_H (500 MHz, $CDCl_3$) 2.87 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.40 (s, 2H, ArCH_2), 6.49 – 6.44 (m, 2H, H-3' & H-5'), 7.12 (d, *J*

= 8.9 Hz, 2H, H-2, 6), 7.21 (d, *J* = 8.2 Hz, 1H, H-6'), 7.48 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 35.80, 49.26, 55.49, 55.56, 98.56, 104.47, 115.61, 120.00, 123.84, 131.52, 132.86, 149.48, 158.84, 161.16; HRMS (ESI) calcd for $C_{16}H_{22}BrN_2O_5S$ $[M+NH_4]^+$: 433.0427; found 433.0422

4-Bromophenyl benzyl(2,4-dimethoxybenzyl)sulfamate, (19c)

Compound **19c** was synthesised according to general procedure D, using the following reagents: 1-((4-bromophenoxy)sulfonyl)-2,3-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (**6**) (600 mg, 1.43 mmol), *N*-benzyl-1-(2,4-dimethoxyphenyl)methanamine (**S11**) (369 mg, 1.43 mmol) and acetonitrile (11.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a clear oil (629 mg, 89%): R_f 0.33 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1588, 1509, 1481, 1370, 1196, 1155, 1039; δ_H (500 MHz, $CDCl_3$) 3.77 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 4.39 (s, 2H, ArC*H*$_2$), 4.41 (s, 2H, ArC*H*$_2$), 6.42 (d, *J* = 2.3 Hz, 1H, H-3'), 6.45 (dd, *J* = 8.3, 2.4 Hz, 1H, H-5'), 6.91 (d, *J* = 8.9 Hz, 2H, H-2, 6), 7.26 (d, *J* = 8.3 Hz, 1H, H-6'), 7.35 – 7.28 (m, 5H, 5 × Ar*H*), 7.39 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 46.06, 52.07, 55.33, 55.58, 98.45, 104.43, 115.85, 119.95, 123.86, 128.02, 128.59, 128.73, 132.38, 132.72, 135.83, 149.38, 158.80, 161.22; HRMS (ESI) calcd for $C_{22}H_{26}BrN_2O_5S$ $[M+NH_4]^+$: 509.0740; found 509.0739

4-Bromophenyl 2,4-dimethoxybenzyl(isobutyl)sulfamate, (19d)

Compound **19d** was synthesised according to general procedure D, using the following reagents: 1-((4-bromophenoxy)sulfonyl)-2,3-dimethyl-1*H*-imidazol-3-ium tetrafluoroborate (**6**) (600 mg, 1.43 mmol), *N*-(2,4-dimethoxybenzyl)-2-methylpropan-1-amine (**S12**) (321 mg, 1.43 mmol) and acetonitrile (11.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 9:1) to yield the *title compound* as a clear oil (560 mg, 85%): R_f 0.27 (petrol:EtOAc – 9:1); λ_{max} (EtOH)/nm 277.0; IR (film) ν_{max}/cm^{-1} 1613, 1588, 1509, 1482, 1368, 1197, 1154, 1033; δ_H (500 MHz, $CDCl_3$) 0.88 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 2.02 – 1.89 (m, 1H, C*H*(CH$_3$)$_2$), 3.04 (d, *J* = 7.5 Hz, 2H, C*H*$_2$CH), 3.81 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 4.50 (s, 2H, ArC*H*$_2$), 6.49 – 6.43 (m, 2H, H-3' & H-5'), 7.01 (d, *J* = 8.9 Hz,

2H, H-2, 6), 7.33 (d, *J* = 8.2 Hz, 1H, H-6'), 7.43 (d, *J* = 8.9 Hz, 2H, H-3, 5); δ_C (126 MHz, $CDCl_3$) 20.05, 26.97, 47.07, 55.41, 55.56, 56.49, 98.42, 104.43, 116.17, 119.73, 123.74, 132.36, 132.73, 149.63, 158.81, 161.15; HRMS (ESI) calcd for $C_{19}H_{28}BrN_2O_5S$ $[M+NH_4]^+$: 475.0897; found 475.0887

[1,1'-Biphenyl]-4-yl 4-methoxybenzyl(methyl)sulfamate, (20a)

Compound **20a** was synthesised according to general procedure E, using the following reagents: 4-bromophenyl 4-methoxybenzyl(methyl)sulfamate (**19a**) (400 mg, 1.04 mmol), potassium carbonate (429 mg, 3.11 mmol), phenyl boronic acid (189 mg, 1.55 mmol), tetrakis(triphenylphosphine)palladium(0) (120 mg, 0.10 mmol) and acetonitrile (20 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a yellow solid (345 mg, 87%): R_f 0.35 (petrol:EtOAc – 85:15); mp: 103.5-105.5 °C; λ_{max} (EtOH)/nm 251.0; IR (film) ν_{max}/cm^{-1} 1609, 1594, 1512, 1485, 1460, 1373, 1180, 1151, 1032; δ_H (500 MHz, $CDCl_3$) 2.86 (s, 3H, NC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 4.38 (s, 2H, ArC*H*$_2$), 6.88 (d, *J* = 8.6 Hz, 2H, H-3", 5"), 7.25 (d, *J* = 8.6 Hz, 2H, H-2", 6"), 7.40 – 7.33 (m, 3H, H-4' & H-3, 5), 7.45 (dd, *J* = 7.6, 7.6 Hz, 2H, H-2', 5'), 7.57 (dd, *J* = 8.3, 1.2 Hz, 2H, H-2', 6'), 7.61 (d, *J* = 8.8 Hz, 2H, H-2, 6); δ_C (126 MHz, $CDCl_3$) 35.25, 54.78, 55.45, 114.25, 122.30, 127.00, 127.26, 127.75, 128.59, 129.02, 130.10, 140.08, 140.10, 149.76, 159.73; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4S$ $[M+NH_4]^+$: 401.1530; found 401.1533

[1,1'-Biphenyl]-4-yl 2,4-dimethoxybenzyl(methyl)sulfamate, (20b)

Compound **20b** was synthesised according to general procedure E, using the following reagents: 4-bromophenyl 2,4-dimethoxybenzyl(methyl)sulfamate (**19b**) (400 mg, 0.96 mmol), potassium carbonate (398 mg, 2.88 mmol), phenyl boronic acid (176 mg, 1.44 mmol), tetrakis(triphenylphosphine)palladium(0) (111 mg, 0.10 mmol) and acetonitrile (19 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a yellow oil (358 mg, 90%): R_f 0.34 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 251.0; IR (film) ν_{max}/cm^{-1} 1613, 1591, 1509, 1485, 1371, 1207, 1154, 1034; δ_H (500 MHz, $CDCl_3$) 2.90 (s, 3H, NC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 4.43 (s, 2H, ArC*H*$_2$), 6.49 – 6.44 (m,

2H, H-3" & H-5"), 7.25 (d, *J* = 8.1 Hz, 1H, H-6"), 7.33 (d, *J* = 8.7 Hz, 2H, H-3, 5), 7.39 – 7.35 (m, 1H, H-4'), 7.45 (dd, *J* = 7.6, 7.6 Hz, 2H, H-3', 5'), 7.61 – 7.54 (m, 4H, H-2, 6 & H-2', 6'); δ_C (126 MHz, $CDCl_3$) 35.78, 49.22, 55.50, 55.53, 98.56, 104.49, 115.82, 122.33, 127.24, 127.69, 128.48, 128.99, 131.47, 139.87, 140.18, 149.87, 158.86, 161.09; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_5S$ $[M+NH_4]^+$: 431.1635; found 431.1638

[1,1'-Biphenyl]-4-yl benzyl(2,4-dimethoxybenzyl)sulfamate, (20c)

Compound **20c** was synthesised according to general procedure E, using the following reagents: 4-bromophenyl benzyl(2,4-dimethoxybenzyl)sulfamate (**19c**) (400 mg, 0.81 mmol), potassium carbonate (337 mg, 2.44 mmol), phenyl boronic acid (149 mg, 1.22 mmol), tetrakis(triphenylphosphine)palladium(0) (94 mg, 0.08 mmol) and acetonitrile (16 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a pale yellow oil (350 mg, 87%): R_f 0.35 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 251.5; IR (film) ν_{max}/cm^{-1} 1613, 1591, 1509, 1485, 1369, 1208, 1154, 1039; δ_H (500 MHz, $CDCl_3$) 3.76 (s, 3H, OC*H*$_3$), 3.79 (s, 3H, OC*H*$_3$), 4.44 (s, 2H, ArC*H*$_2$), 4.45 (s, 2H, ArC*H*$_2$), 6.42 (d, *J* = 2.3 Hz, 1H, H-3"), 6.45 (dd, *J* = 8.4, 2.4 Hz, 1H, H-5"), 7.14 (d, *J* = 8.3 Hz, 2H, H-3, 5), 7.39 – 7.27 (m, 7H, 7 × Ar*H*), 7.44 (dd, *J* = 7.6, 7.6 Hz, 2H, H-3', 5'), 7.51 (d, *J* = 8.5 Hz, 2H, H-2, 6), 7.55 (d, *J* = 7.8 Hz, 2H, H-2', 6'); δ_C (126 MHz, $CDCl_3$) 46.02, 52.07, 55.31, 55.53, 98.42, 104.43, 116.00, 122.33, 127.22, 127.65, 127.93, 128.36, 128.53, 128.74, 128.97, 132.36, 136.00, 139.75, 140.19, 149.83, 158.82, 161.14; HRMS (ESI) calcd for $C_{28}H_{31}N_2O_5S$ $[M+NH_4]^+$: 507.1948; found 507.1947

[1,1'-Biphenyl]-4-yl 2,4-dimethoxybenzyl(isobutyl)sulfamate, (20d)

Compound **20d** was synthesised according to general procedure E, using the following reagents: 4-bromophenyl 2,4-dimethoxybenzyl(isobutyl)sulfamate (**19d**) (400 mg, 0.87 mmol), potassium carbonate (362 mg, 2.62 mmol), phenyl boronic acid (160 mg, 1.31 mmol), tetrakis(triphenylphosphine)palladium(0) (101 mg, 0.09 mmol) and acetonitrile (17 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 85:15) to yield the *title compound* as a clear oil (340 mg, 85%): R_f 0.36 (petrol:EtOAc – 85:15); λ_{max} (EtOH)/nm 252.0; IR (film) ν_{max}/cm^{-1}

1613, 1592, 1509, 1485, 1366, 1208, 1152, 1032; δ_H (500 MHz, $CDCl_3$) 0.89 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 2.02 – 1.92 (m, 1H, C*H*(CH_3)$_2$), 3.09 (d, *J* = 7.4 Hz, 2H, CH_2CH), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.54 (s, 2H, ArCH_2), 6.46 (d, *J* = 2.4 Hz, 1H, H-3"), 6.48 (dd, *J* = 8.3, 2.4 Hz, 1H, H-5"), 7.23 (d, *J* = 8.7 Hz, 2H, H-3, 5), 7.37 – 7.32 (m, 1H, H-4'), 7.39 (d, *J* = 8.3 Hz, 1H, H-6"), 7.44 (dd, *J* = 7.6, 7.6 Hz, 2H, H-3', 5'), 7.58 – 7.51 (m, 4H, H-2, 6 & H-2', 6'); δ_C (126 MHz, $CDCl_3$) 20.08, 27.00, 47.07, 55.40, 55.52, 56.51, 98.38, 104.41, 116.34, 122.22, 127.22, 127.61, 128.39, 128.96, 132.32, 139.61, 140.25, 149.99, 158.79, 161.04

[1,1'-Biphenyl]-4-yl methylsulfamate, (21a)

Compound **21a** was synthesised following two different procedures.

1st procedure: Compound **21a** was synthesised according to general procedure F, using the following reagents: [1,1'-biphenyl]-4-yl 2,4-dimethoxybenzyl(methyl)sulfamate (**20b**) (250 mg, 0.60 mmol), DCM (5.4 mL) and TFA (0.6 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a pale yellow solid (151 mg, 95%).

2nd procedure: Compound **21a** was synthesised according to general procedure G, using the following reagents: [1,1'-biphenyl]-4-yl 4-methoxybenzyl(methyl)sulfamate (**20a**) (250 mg, 0.65 mmol), DCM (3.3 mL) and TFA (3.3 mL). The crude product was purified by column chromatography (petrol:DCM - 1:0 → 1:9) to yield the *title compound* as a pale yellow solid (165 mg, 96%): R_f 0.30 (petrol:EtOAc – 8:2); mp: 114.5-116.5 °C; λ_{max} (EtOH)/nm 250.0; IR (film) ν_{max}/cm^{-1} 3299, 1599, 1516, 1484, 1351, 1171, 1134, 1085; δ_H (500 MHz, DMSO) 2.75 (d, *J* = 4.7 Hz, 3H, NCH_3), 7.42 – 7.34 (m, 3H, H-3, 5 & H-4'), 7.48 (dd, *J* = 7.7, 7.7 Hz, 2H, H-3', 5'), 7.67 (dd, *J* = 8.2, 1.1 Hz, 2H, H-2', 6'), 7.75 (d, *J* = 8.7 Hz, 2H, H-2, 6), 8.28 (q, *J* = 4.6 Hz, 1H, N*H*); δ_C (126 MHz, DMSO) 29.21, 122.51, 126.77, 127.70, 128.18, 129.03, 138.76, 139.08, 149.34; HRMS (ESI) calcd for $C_{13}H_{12}NO_3S$ $[M-H]^-$: 262.0543; found 262.0537

[1,1'-Biphenyl]-4-yl benzylsulfamate, (21b)

Compound **21b** was synthesised according to general procedure F, using the following reagents: [1,1'-biphenyl]-4-yl benzyl(2,4-dimethoxybenzyl)sulfamate (**20c**) (250 mg, 0.51 mmol), DCM (4.5 mL) and TFA (0.5 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a pale yellow solid (166 mg, 96%): R_f 0.33 (petrol:EtOAc – 8:2); mp: 113.0-115.0 °C; λ_{max} (EtOH)/nm 251.5; IR (film) ν_{max}/cm^{-1} 3274, 1599, 1518, 1485, 1454, 1448, 1348, 1153, 1092, 1076; δ_H (500 MHz, DMSO) 4.33 (d, *J* = 6.0 Hz, 2H, ArC*H*$_2$), 7.31 – 7.28 (m, 1H, Ar*H*), 7.32 (d, *J* = 8.7 Hz, 2H, H-3, 5), 7.38 – 7.34 (m, 4H, 4 × Ar*H*), 7.41 – 7.37 (m, 1H, H-4'), 7.48 (dd, *J* = 7.7, 7.7 Hz, 2H, H-3', 5'), 7.67 (dd, *J* = 8.3, 1.1 Hz, 2H, H-2', 6'), 7.73 (d, *J* = 8.8 Hz, 2H, H-2, 6), 8.98 (t, *J* = 6.0 Hz, 1H, N*H*); δ_C (126 MHz, DMSO) 46.67, 122.46, 126.76, 127.48, 127.80, 128.12, 128.40, 129.02, 137.37, 138.73, 139.08, 149.35; HRMS (ESI) calcd for $C_{19}H_{16}NO_3S$ [M-H]$^-$: 338.0856; found 338.0843

[1,1'-Biphenyl]-4-yl isobutylsulfamate, (21c)

Compound **21c** was synthesised according to general procedure F, using the following reagents: [1,1'-biphenyl]-4-yl isobutyl(2,4-dimethoxybenzyl)sulfamate (**20d**) (250 mg, 0.55 mmol), DCM (5.0 mL) and TFA (0.6 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a pale orange solid (156 mg, 93%): R_f 0.34 (petrol:EtOAc – 8:2); mp: 98.5-100.5 °C; λ_{max} (EtOH)/nm 250.5; IR (film) ν_{max}/cm^{-1} 3293, 1599, 1517, 1486, 1351, 1143, 1078; δ_H (500 MHz, DMSO) 0.88 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.81 – 1.70 (m, 1H, C*H*(CH$_3$)$_2$), 2.92 (dd, *J* = 6.8, 5.9 Hz, 2H, C*H*$_2$CH), 7.41 – 7.34 (m, 3H, H-3, 5 & H-4'), 7.48 (dd, *J* = 7.7, 7.7 Hz, 2H, H-3', 5'), 7.67 (dd, *J* = 8.3, 1.1 Hz, 2H, H-2', 6'), 7.75 (d, *J* = 8.7 Hz, 2H, H-2, 6), 8.43 (t, *J* = 5.8 Hz, 1H, N*H*); δ_C (126 MHz, DMSO) 19.79, 28.05, 50.67, 122.45, 126.74, 127.67, 128.12, 129.02, 138.64, 139.10, 149.43; HRMS (ESI) calcd for $C_{16}H_{18}NO_3S$ [M-H]$^-$: 304.1013; found 304.1004

Dibenzylsulfamoyl chloride, (S1)

To sulfuryl chloride (0.41 mL, 0.68 g, 5.06 mmol) in Et_2O (10 mL), cooled at -78 °C, was added dropwise over 35 min a solution of dibenzylamine (0.97 mL, 1.0 g, 5.06 mmol) and pyridine (0.41 mL, 0.40 g, 5.06 mmol) in Et_2O (10 mL). The resulting

mixture was stirred at -78 °C for 3 h and for an additional 2 h at room temperature. The mixture was filtered through Celite and concentrated *in vacuo*. The crude solid was purified by column chromatography (petrol:EtOAc - 1:0 → 98:2) to yield the *title compound* as a white solid (150 mg, 10%): R_f 0.58 (petrol:EtOAc – 97:3); mp: 65.5-67.5 °C; IR (film) ν_{max}/cm^{-1} 1494, 1451, 1383, 1173, 1039; δ_H (500 MHz, $CDCl_3$) 4.40 (s, 4H, ArC*H*$_2$), 7.23 – 7.16 (m, 4H, 4 × Ar*H*), 7.30 – 7.24 (m, 6H, 6 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 53.12, 128.75, 128.89, 129.42, 133.15

4-(Benzyloxy)phenyl 2-methyl-1*H*-imidazole-1-sulfonate, (S2)

Compound **S2** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (678 mg, 3.00 mmol), caesium carbonate (537 mg, 1.65 mmol), 4-(benzyloxy)phenol (300 mg, 1.50 mmol) and acetonitrile (20 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a clear oil (500 mg, 96%): R_f 0.38 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 273.0; IR (film) ν_{max}/cm^{-1} 1595, 1552, 1499, 1418, 1206, 1144, 1044; δ_H (500 MHz, $CDCl_3$) 2.43 (s, 3H, C*H*$_3$), 5.03 (s, 2H, ArC*H*$_2$), 6.86 – 6.78 (m, 2H, 2 × Ar*H*), 6.88 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 6.95 – 6.87 (m, 2H, 2 × Ar*H*), 7.13 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.37 – 7.32 (m, 1H, Ar*H*), 7.39 (d, *J* = 4.4 Hz, 4H, 4 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 15.03, 70.61, 116.14, 120.51, 122.71, 127.61, 128.04, 128.42, 128.83, 136.19, 142.58, 146.97, 158.47; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_4S$ $[M+H]^+$: 345.0904; found 345.0904

4-Hydroxyphenyl sulfamate, (S3)

Compound **S3** was synthesised according to general procedure F, using the following reagents: 4-hydroxyphenyl bis(2,4-dimethoxybenzyl)sulfamate (**16b**) (150 mg, 0.31 mmol), DCM (2.8 mL) and TFA (0.3 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 1:1) to yield the *title compound* as a pale red solid (50 mg, 86%): R_f 0.35 (petrol:EtOAc – 1:1); mp: 138.0-140.0 °C; λ_{max} (EtOH)/nm 277.5; IR (film) ν_{max}/cm^{-1} 3371, 3232, 1601, 1551, 1504, 1364, 1150; δ_H (500 MHz, DMSO) 6.78 (d, *J* = 9.0 Hz, 2H, 2 × Ar*H*), 7.07 (d, *J* = 9.0 Hz, 2H, 2 × Ar*H*), 7.88 (brs, 2H, N*H*$_2$), 9.41 (brs, 1H, O*H*); δ_C (126 MHz, DMSO) 115.75,

123.32, 142.37, 155.82; HRMS (ESI) calcd for $C_6H_6NO_4S$ $[M-H]^-$: 188.0023; found 188.0023

Methyl 3-(((2-methyl-1*H*-imidazol-1-yl)sulfonyl)oxy)benzoate, (S4)

Compound **S4** was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (149 mg, 0.66 mmol), caesium carbonate (118 mg, 0.36 mmol), methyl 3-hydroxybenzoate (50 mg, 0.33 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 3:1) to yield the *title compound* as a clear oil (90 mg, 92%): R_f 0.20 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 272.0; IR (film) ν_{max}/cm^{-1} 1727, 1585, 1554, 1422, 1296, 1266, 1205, 1151, 1045; δ_H (500 MHz, $CDCl_3$) 2.49 (s, 3H, C*H*$_3$), 3.92 (s, 3H, CO_2CH_3), 6.89 (d, *J* = 1.5 Hz, 1H, $H_{imidazole}$), 7.08 (dd, *J* = 8.2, 2.4 Hz, 1H, H-4), 7.13 (d, *J* = 1.6 Hz, 1H, $H_{imidazole}$), 7.45 (dd, *J* = 8.0, 8.0 Hz, 1H, H-5), 7.66 (dd, *J* = 2.1, 2.1 Hz, 1H, H-2), 8.04 (d, *J* = 7.8 Hz, 1H, H-6); δ_C (126 MHz, $CDCl_3$) 15.08, 52.80, 120.43, 122.99, 125.88, 128.25, 129.70, 130.49, 132.82, 146.85, 148.98, 165.20; HRMS (ESI) calcd for $C_{15}H_{20}N_3O_5S$ $[M+H]^+$: 354.1118; found 354.1124

3-(Sulfamoyloxy)benzoic acid, (S5)

Compound **S5** was synthesised according to general procedure F, using the following reagents: 3-((*N*,*N*-bis(2,4-dimethoxybenzyl)sulfamoyl)oxy)benzoic acid (**16d**) (200 mg, 0.39 mmol), DCM (3.5 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (DCM:MeOH:AcOH - 1:0 → 90:9:1) to yield the *title compound* as a white solid (75 mg, 89%): R_f 0.28 (DCM:MeOH:AcOH - 1:0 → 90:9:1); mp: 162.0-164.0 °C; λ_{max} (EtOH)/nm 274.5; IR (film) ν_{max}/cm^{-1} 3374, 3281, 1681, 1587, 1451, 1366, 1302, 1166, 1101; δ_H (500 MHz, DMSO) 7.52 (ddd, *J* = 8.1, 2.5, 1.0 Hz, 1H, H-4), 7.60 (dd, *J* = 7.9, 7.9 Hz, 1H, H-5), 7.82 (dd, *J* = 2.0, 2.0 Hz, 1H, H-2), 7.90 (ddd, *J* = 7.8, 1.3, 1.3 Hz, 1H, H-6), 8.09 (s, 2H, N*H*$_2$), 13.25 (brs, 1H, CO_2H); δ_C (126 MHz, DMSO) 122.93, 126.87, 127.45, 130.20, 132.64, 150.15, 166.40; HRMS (ESI) calcd for $C_7H_6NO_5S$ $[M-H]^-$: 215.9961; found 215.9962

3-Benzoylphenyl bis(2,4-dimethoxybenzyl)sulfamate, (S6)

To 3-(hydroxy(phenyl)methyl)phenyl bis(2,4-dimethoxybenzyl)sulfamate (**16g**) (462 mg, 0.80 mmol) in DCM (15 mL) was added manganese oxide (693 mg, 7.97 mmol). The resulting solution was stirred at room temperature for 16 h. Upon completion, the heterogeneous mixture was filtered through Celite and washed with DCM (20 mL). The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as a clear oil (386 mg, 84%): R_f 0.33 (petrol:EtOAc – 7:3); λ_{max} (EtOH)/nm 252.0; IR (neat) ν_{max}/cm^{-1} 1735, 1660, 1612, 1588, 1507, 1455, 1371, 1275, 1208, 1158, 1036; δ_H (500 MHz, $CDCl_3$) 3.72 (s, 6H, 2 × OC*H*$_3$), 3.78 (s, 6H, 2 × OC*H*$_3$), 4.47 (s, 4H, 2 × ArC*H*$_2$), 6.37 (d, *J* = 2.4 Hz, 2H, H-3'), 6.40 (dd, *J* = 8.3, 2.4 Hz, 2H, H-5'), 7.25 (d, *J* = 8.3 Hz, 2H, H-6'), 7.39 – 7.35 (m, 1H, Ar*H*), 7.45 – 7.41 (m, 2H, H-2 & H-5), 7.53 – 7.47 (m, 2H, H-3", 5"), 7.65 – 7.57 (m, 1H, H-4"), 7.66 (ddd, *J* = 7.7, 1.3, 1.3 Hz, 1H, Ar*H*), 7.78 (dd, *J* = 8.3, 1.4 Hz, 2H, H-2", 6"); δ_C (126 MHz, $CDCl_3$) 47.20, 55.25, 55.51, 98.36, 104.09, 116.55, 123.58, 126.06, 127.97, 128.55, 129.67, 130.23, 131.12, 132.88, 137.16, 139.18, 150.34, 158.59, 160.80, 195.36; HRMS (ESI) calcd for $C_{31}H_{32}NO_8S$ $[M+H]^+$: 578.1843; found 578.1839

3-Benzoylphenyl sulfamate, (S7)

Compound **S7** was synthesised according to general procedure F, using the following reagents: 3-benzoylphenyl bis(2,4-dimethoxybenzyl)sulfamate (**S6**) (200 mg, 0.35 mmol), DCM (3.2 mL) and TFA (0.4 mL). The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 65:35) to yield the *title compound* as a pale orange solid (84 mg, 87%): R_f 0.33 (petrol:EtOAc – 65:35); m.p. 68.5-70.5 °C; λ_{max} (EtOH)/nm 252.0; IR (neat) ν_{max}/cm^{-1} 3358, 3257, 1648, 1577, 1439, 1365, 1282, 1169, 1158; δ_H (500 MHz, DMSO) 7.62 – 7.55 (m, 3H, 3 × Ar*H*), 7.63 (dd, *J* = 2.0, 2.0 Hz, 1H, H-2), 7.67 (dd, *J* = 7.8, 7.8 Hz, 1H, H-5), 7.74 – 7.69 (m, 2H, 2 × Ar*H*), 7.82 – 7.75 (m, 2H, 2 × Ar*H*), 8.11 (s, 2H, N*H*$_2$); δ_C (126 MHz, DMSO) 123.20, 126.67, 127.83, 128.70, 129.72, 130.26, 133.04, 136.48, 138.50, 149.93, 194.58; HRMS (ESI) calcd for $C_{13}H_{12}NO_4S$ $[M+H]^+$: 278.0482; found 278.0482

3-((*tert*-Butoxycarbonyl)amino)phenyl 2-methyl-1*H*-imidazole-1-sulfonate, (S8)

Compound (**S8**) was synthesised according to general procedure B, using the following reagents: 1,1'-sulfonylbis(2-methyl-1*H*-imidazole) (**4**) (216 mg, 0.96 mmol), caesium carbonate (171 mg, 0.53 mmol), *N*-Boc-3-aminophenol (100 mg, 0.48 mmol) and acetonitrile (5 mL). The crude yellow oil was purified by column chromatography (petrol:EtOAc - 1:0 → 8:2) to yield the *title compound* as a pale yellow solid (142 mg, 84%): R_f 0.30 (petrol:EtOAc – 8:2); mp: 108.0-110.0 °C; λ_{max} (EtOH)/nm 276.0; IR (film) ν_{max}/cm^{-1} 1724, 1601, 1556, 1494, 1425, 1204, 1152, 1049; δ_H (500 MHz, $CDCl_3$) 1.51 (s, 9H, C(CH_3)$_3$), 2.48 (s, 3H, CH_3), 6.54 – 6.47 (m, 1H, H-6), 6.57 (s, 1H, N*H*Boc), 6.88 (d, *J* = 1.7 Hz, 1H, $H_{imidazole}$), 7.18 – 7.10 (m, 2H, $H_{imidazole}$ & H-2), 7.23 (dd, *J* = 8.2, 8.2 Hz, 1H, H-5), 7.32 (d, *J* = 7.9 Hz, 1H, H-4); δ_C (126 MHz, $CDCl_3$) 15.09, 28.40, 81.54, 111.65, 115.26, 118.00, 120.54, 128.05, 130.51, 140.52, 146.91, 149.48, 152.21; HRMS (ESI) calcd for $C_{15}H_{20}N_3O_5S$ $[M+H]^+$: 354.1118; found 354.1124

1-(4-Methoxyphenyl)-*N*-methylmethanamine, (S9)

Compound **S9** was synthesised according to general procedure A, using the following reagents: methylamine 8.03 M in EtOH (3.07 mL, 24.7 mmol), 4-methoxybenzaldehyde (3.0 mL, 3.36 g, 24.7 mmol), sodium borohydride (1.03 g, 27.1 mmol) and ethanol (12 mL). The crude product was purified by column chromatography (DCM:MeOH:NH_3 - 1:0:0 → 90:9:1) to yield the *title compound* as a clear liquid (0.90 g, 24%): R_f 0.24 (DCM:MeOH:NH_3 – 90:9:1); δ_H (500 MHz, $CDCl_3$) 1.18 (s, 1H, N*H*), 2.44 (s, 3H, NCH_3), 3.68 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3), 6.86 (d, *J* = 8.6 Hz, 2H, H-3, 5), 7.23 (d, *J* = 8.8 Hz, 2H, H-2, 6); ^{1}H NMR data were identical to literature data.[1]

1-(2,4-Dimethoxyphenyl)-*N*-methylmethanamine, (S10)

Compound **S10** was synthesised according to general procedure A, using the following reagents: methylamine 8.03 M in EtOH (2.25 mL, 18.1 mmol), 2,4-dimethoxybenzaldehyde (3.0 g, 18.1 mmol), sodium borohydride (0.75 g, 19.9 mmol) and ethanol (9 mL). The crude product was purified by column chromatography (DCM:MeOH:NH_3 - 1:0:0 → 90:9:1) to yield the *title compound* as a yellow liquid (0.82 g, 25%): R_f 0.22 (DCM:MeOH:NH_3 – 90:9:1); λ_{max} (EtOH)/nm 276.5; IR (film)

ν_{max}/cm^{-1} 1612, 1588, 1505, 1462, 1288, 1206, 1154, 1034; δ_H (500 MHz, $CDCl_3$) 2.03 (s, 1H, N*H*), 2.40 (s, 3H, NCH_3), 3.68 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.43 (dd, *J* = 8.1, 2.4 Hz, 1H, H-5), 6.45 (d, *J* = 2.4 Hz, 1H, H-3), 7.12 (d, *J* = 8.1 Hz, 1H, H-6); δ_C (126 MHz, $CDCl_3$) 35.80, 50.90, 55.40, 55.48, 98.63, 103.68, 120.73, 130.69, 158.76, 160.20

_N_-Benzyl-1-(2,4-dimethoxyphenyl)methanamine, (S11)

Compound **S11** was synthesised according to general procedure A, using the following reagents: benzylamine (1.97 mL, 1.93 g, 18.1 mmol), 2,4-dimethoxybenzaldehyde (3.0 g, 18.1 mmol), sodium borohydride (0.75 g, 19.9 mmol) and ethanol (9 mL). The crude product was purified by column chromatography (EtOAc:petrol - 1:0 → 1:1) to yield the *title compound* as a clear oil (3.12 g, 67%): R_f 0.33 (EtOAc:petrol – 1:1); λ_{max} (EtOH)/nm 276.5; IR (film) ν_{max}/cm^{-1} 1612, 1588, 1506, 1453, 1287, 1207, 1155, 1034; δ_H (500 MHz, $CDCl_3$) 1.82 (s, 1H, N*H*), 3.75 (s, 2H, ArCH_2), 3.77 (s, 2H, ArCH_2), 3.81 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.44 (dd, *J* = 8.1, 2.4 Hz, 1H, H-5), 6.47 (d, *J* = 2.3 Hz, 1H, H-3), 7.14 (d, *J* = 8.1 Hz, 1H, H-6), 7.26 – 7.21 (m, 1H, H-4'), 7.38 – 7.29 (m, 4H, 4 × Ar*H*); δ_C (126 MHz, $CDCl_3$) 48.50, 53.09, 55.39, 55.51, 98.68, 103.74, 121.05, 126.87, 128.31, 128.42, 130.62, 140.83, 158.83, 160.18; HRMS (ESI) calcd for $C_{16}H_{20}NO_4$ $[M+H]^+$: 258.1489; found 258.1486

_N_-(2,4-Dimethoxybenzyl)-2-methylpropan-1-amine, (S12)

Compound **S12** was synthesised according to general procedure A, using the following reagents: isobutylamine (1.80 mL, 1.32 g, 18.1 mmol), 2,4-dimethoxybenzaldehyde (3.0 g, 18.1 mmol), sodium borohydride (0.75 g, 19.9 mmol) and ethanol (9 mL). The crude product was purified by column chromatography (EtOAc:MeOH - 1:0 → 95:5) to yield the *title compound* as a clear liquid (2.80 g, 69%): R_f 0.25 (EtOAc:MeOH – 95:5); λ_{max} (EtOH)/nm 276.5; IR (film) ν_{max}/cm^{-1} 1613, 1589, 1506, 1463, 1287, 1207, 1153, 1037; δ_H (500 MHz, $CDCl_3$) 0.89 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.49 (s, 1H, N*H*), 1.81 – 1.72 (m, 1H, C*H*(CH$_3$)$_2$), 2.38 (d, *J* = 6.8 Hz, 2H, CH_2CH), 3.70 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.43 (dd, *J* = 8.1, 2.4 Hz, 1H, H-5), 6.45 (d, *J* = 2.4 Hz, 1H, H-3), 7.13 (d, *J* = 8.1 Hz,

1H, H-6); δ_C (126 MHz, $CDCl_3$) 20.84, 28.40, 49.21, 55.37, 55.47, 57.43, 98.64, 103.71, 121.42, 130.42, 158.73, 160.04

Sulfamoyl chloride

Formic acid (0.55 g, 0.45 mL, 12 mmol) was added dropwise to neat chloridesulfonyl isocyanate (1.6 g, 1.0 mL, 12 mmol) at 0 °C. The resulting white slurry was stirred at room temperature for 3 h to give sulfamoyl chloride as a white solid. Addition of toluene (6.0 mL) yielded a stock solution (2 mmol/mL) of the reagent that was used in the next step without any further purification.

3-Bromophenylsulfamate

To 3-bromophenol (1.0 g, 6.0 mmol) in DMA (6.0 mL), a fresh stock solution of sulfamoyl chloride in toluene (6.0 mL, 12 mmol) was added dropwise at 0 °C. The resulting mixture was allowed to reach room temperature and stirred overnight. The reaction was quenched by addition of water (6.0 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by MPLC (from PE 100% to PE/EtOAc 70:30) yielded the title compound as. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* as an off-white solid (1.31 g, 87%): R_f 0.2 (petrol:EtOAc – 8:2); λ_{max} (EtOH)/nm 267.0; IR (film) ν_{max}/cm^{-1} 1164, 1364, 1462, 1578, 3276, 3374; δ_H (500 MHz; $CDCl_3$) 4.98 (brs, NH_2, 2H), 7.30 (m, 1H, Ar*H*), 7.31 (m, 1H, Ar*H*), 7.49 (m, 1H, Ar*H*), 7.52 (m, 1H, Ar*H*); δ_C (125 MHz; $CDCl_3$) 121.0, 125.5, 130.7, 131.1, 150.3; HRMS (ESI) calcd for $C_6H_5BrNO_3S$ $[M-H]^-$: 249.9179; found 249.9182

[1,1'-biphenyl]-3-yl sulfamate

To 3-bromophenyl sulfamate (53 mg, 0.210 mmol) in DME (0.5 mL) was added aq. Na_2CO_3 2 M (0.2 mL, 0.4 mmol). The resulting solution was sparged with nitrogen for 15 min. Phenyl boronic acid (24 mg,0.20 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) DCM complex (10 mg, 0.013 mmol) were added. The mixture was heated at 80 °C for 20 min under microwave irradiation. Upon completion, the reaction was distributed between EtOAc (20 mL)

and water (20 mL). The EtOAc phase was separated and the aqueous phase was extracted with EtOAc (3 × 25 mL). The pooled organic extracts were washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (petrol:EtOAc - 1:0 → 7:3) to yield the *title compound* (11 mg, 22%) as a white solid: R_f 0.30 (petrol:EtOAc – 7:3); λ_{max} (EtOH)/nm 248 nm; IR (film) ν_{max}/cm^{-1} 1150, 1263, 1275, 1364, 1415, 1573, 1586, 2923, 3103, 3211, 3311, 3621; δ_H (500 MHz; $CDCl_3$) 5.01 (s, NH_2, 2H), 7.30 (ddd, *J* = 1.1, 2.3, 8.1 Hz, 1H, Ar*H*), 7.38 (m, 1H, Ar*H*), 7.45 (m, 2H, H-3' and H-5'), 7.47 (m, 1H, Ar*H*), 7.55 (m, 1H, Ar*H*), 7,55 (m, 1H, Ar*H*), 7.57 (m, 2H, H-2' and H-6'); δ_C (125 MHz; $CDCl_3$) 120.8, 120.9, 126.1, 127.3, 128.2, 129.1, 130.3, 139.7, 143.6, 150.6; LRMS (ES^-) *m/z* 248.2 $[M-H]^-$; HRMS (ESI) calcd for $C_{12}H_{10}NO_3S$ $[M-H]^-$: 248.0387; found 248.0391

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