Supporting Information

Nonconventional Difluoroalkylation of C(sp2)–H Bonds Through Hydroarylation

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General information

Unless otherwise noted, [RhCp*Cl₂]₂, anhydrous DCM, DCE were purchased from commercial suppliers and used as received. All reactions were carried out under air atmosphere unless otherwise stated. Reactions were monitored through thin layer chromatography. Subsequent to elution, spots were visualized using UV radiation (254 nm) on 254 nm. Further visualization was possible using basic solution of potassium permanganate or acidic solution of ceric molybdate as stain, followed by heating on a hot plate. Flash chromatography was performed using silica gel with distilled solvents. HRMS spectra were recorded on a Waters Q-Tof Permier Spectrometer. ¹H NMR and ¹³C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of SiMe₄ (δ 0.00, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); hept (heptet); dd (doublet of doublet); ddd (doublet of doublet of doublet); td (triplet of doublet); m (multiplet); ddt (doublet of doublet of triplet) and etc. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (¹³C NMR) are reported as δ in units of parts per million (ppm) downfield from CHCl₃ (δ 7.26) and relative to the signal of chloroform-d (δ 77.00, triplet).

Experimental section

Substrates preparation

General Procedure for Synthesis of 1a-1i, 1n-1v:



Synthetic procedure: Following a procedure from Ackermann et al., ¹⁻³ an ovendried RBF was charged with indole (10 mmol, 1 equiv) in DMF, following by portionwise adding of NaH (60% dispersion in mineral oil, 440 mg, 11 mmol, 1.1 equiv) at 0 °C. After sitrring for 30 min at 0 °C, 2-chloropyrimidine (1.37g, 12 mml, 1.2equiv) was added. The resulting mixture was stirred at 130 °C for 24 h. Then the mixture was cooled to room temperature, washed with water and extracted with EtOAc. After dring over Na₂SO₄, the organic phase was concentrated and purified by column chromatgraphy on sillca gel (eluent = petroleum ether/EtOAc = 10/1) to afford **1a-1i**, **1n-1v** as white solid.

General reaction scheme for 1j synthesis:



Synthetic procedure: a) Under nitrogen atmosphere, an oven-dried 50 mL schlenk tube was charged with 1-(pyrimidin-2-yl)-1-indole-4-carbaldehyde (377 mg, 1.7 mmol, 1 equiv) and CH₃OH (10 mL). The solution was cooled to 0 °C and NaBH₄ (96.5 mg, 2.6 mmol, 1.5 equiv) was added. After the mixture stirring from 0 °C to room temperature for 2 h, water was added carefully and after the gas evolution

ceased, the reaction mixture was evaporated under reduced pressure to remove MeOH. The remained aqueous layer was extracted with ethylacetate $(3 \times 20 \text{ mL})$. The combined organic layers were dried over MgSO₄ and after filtration the solvent was removed under reduced pressure. The residue was obtained in 99% yield as a white solid and directly used in the next step without further purification. b) In a three-neck 35 mL RBF (1-(pyrimidin-2-yl)-1-indol-4-yl)methanol (113 mg, 0.5 mmol, 1 equiv) was dissolved in dry THF. DMAP (spatula tip) and NEt₃ (0.16 mL, 1.1 mmol, 2.2 equiv) wered added. The mixture was cooled to 0 °C under N₂ with an ice/water bath. Acetic anhydride (102 mg, 1.0 mmol, 2 equiv) was added dropwise. Then the ice bath was removed and the reaction mixture was allowed to stir at ambient temperature for 3 h when TLC analysis indicated full conversion of the starting material. The reaction mixture was filtered through a silica plug and diluted with EtOAc (10 mL) and washed with H_2O (2 × 10 mL). The aqueous phase was extracted with EtOAc (2×10 mL), and the combined organic phase was dried over Na₂SO₄. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent = petroleum ether/EtOAc = 10/1) to give 1j (114 mg, 0.43 mmol, 86%) as a white solid.

General reaction scheme for 11 synthesis:



Synthetic procedure: a) To a suspension of $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) in 8 mL DME was added 4-bromoindole (392 mg, 2 mmol), and the mixture was stirred for 15 min under room temperature. A solution of phenylboronic acid (293 mg, 2.4 mmol, 1 equiv) in 5 mL of ethanol was added and the mixture was stirred for 10 min under the same conditions. A solution of potassium carbonate (415 mg,

3 mmol, 1.25 equiv) in 10 mL of water was added to above mixture and the resulting reaction mixture was heated at reflux for 3-4 hours under the N₂ atmosphere. After the end of the reaction was established by TLC, the reaction was diluted by water, extracted with ethyl acetate. The organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated under vacuum. The product was purified by silica gel column (eluent = petroleum ether/EtOAc = 10/1) to afford 4-phenyl-1*H*-indole (309 mg, 1.6 mmol, 80%) as a yellow oil.

b) **11** was synthetized from 4-phenyl-1*H*-indole following the above general synthetic procedure of **1a** and obtained as a gray solid (399 mg, 1.47 mmol, 92%).

General reaction scheme for 1k synthesis:



Synthetic procedure: Following a procedure from Frank Glorius et al.,⁴ 5-Bromo-1-(pyrimidin-2-yl)-1*H*-indole (329 1.20 mmol. equiv), mg, 1 bis(pinacolato)diboron (366 mg, 1.44 mmol, 1.20 equiv), [1,1 ' bis(diphenylphosphino)ferrocene]dichloropalladium(II) (43.9 mg, 0.06 mmol, 5.0mol%) and KOAc (353 mg, 3.60 mmol, 3.0 equiv.) were dissolved in DMSO (2.4 mL). The reaction was heated at 110 °C for 14 h. The reaction mixture was filtered through Celite with additional EtOAc, then washed consecutively with water and brine. After drying the organic layer and removing the solvent in vacuo, the pure product was obtained by column chromatography (eluent = petroleum ether/EtOAc = 10/1). 1k was obtained in 67% yield as a white solid.

General reaction scheme for 1m synthesis:



Synthetic procedure: Following a procedure from Frank Glorius et al.,⁴ 5-Bromo-1-(pyrimidin-2-yl)-1*H*-indole (329 mg, 1.20 mmol, 1 equiv), phenylboronic acid 1.28 pinacol (262)mg, mmol, 1.07 equiv) and [1,1'ester bis(diphenylphosphino)ferrocene]dichloropalladium(II) (43.9 mg, 0.06 mmol, 5.0 mol %) were dissolved in 1,2-dimethoxyethane (12 mL). An aqueous solution of Na₂CO₃ (2 M, 1.2 mL, 2.4 mmol, 2.0 equiv.) was added and the reaction was heated at 85 °C for 15 h. The reaction mixture was filtered through Celite with additional EtOAc, then washed consecutively with water and brine. After drying the organic layer and removing the solvent in vacuo, the pure product was obtained by column chromatography(eluent = petroleum ether/EtOAc = 10/1). 1m was obtained in 63% yield as a yellow solid.

General reaction scheme for 1w-1z synthesis:



Synthetic procedure: A mixture of indole (0.59 g, 5.0 mmol, 1 equiv), 2bromopyridine (0.95 g, 6.0 mmol, 1.2 equiv), KOH (0.70 g, 12.5 mmol, 2.5 equiv) in DMSO (6 mL) was vigorouslystirred at 120 °C under N₂ atmosphere for 30 h. After cooling the mixture to room temperature, the reaction mixture was diluted with EtOAc (40 mL) and washed with H₂O (2 × 30 mL). The aqueous phase was extracted with EtOAc (2 × 30 mL), and the combined organic phase was dried over Na₂SO₄. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (eluent = petroleum ether/EtOAc = 20/1) to give 1w (0.84 g, 4.3 mmol, 86%) as a yellow oil.

General reaction scheme for 1aa and 1ab synthesis:



Synthetic procedure: 1aa (1.18 g, 8.1 mmol, 81%) and **1ab** (1.22 g, 7.7 mmol, 77%) were synthetized from 2pyrrole (10 mmol) following the above general synthetic procedure of **1a**.

General Procedure for Synthesis of 2a-2f:



Synthetic procedure: a) Following a procedure from Alison R Cochrane et.al.,⁵ a solution of 2,2,2-trifluoroethanol (10 mmol, 1 equiv) and triethylamine (5 mL, 36 mmol), DMAP in CH₂Cl₂ (10 mL) was cooled to 0 °C. Sulfonylchloride (12 mmol, 1.2 equiv) was added dropwise, and the solution was allowed to stired at 0 °C for 1 h, then warmed to room temperature and stirred for overnight. Water (20 mL) was added, The CH₂Cl₂ layer was separated and washed with brine (20 mL), dried over Na₂SO₄, filtered, and evaporated. The crude were directly used in the next step without further purification.



2,2,2-trifluoroethyl 2,4,6-triisopropylbenzenesulfonate **2a'** was obtained in 98% yield (3.60 g, 9.8 mmol) as a white solid.



2,2,2-trifluoroethyl 2,4,6-trimethylbenzenesulfonate **2b'** was obtained in 83% yield (2.34 g, 8.3 mmol) as a white solid.



2,2,2-trifluoroethyl 4-methoxybenzenesulfonate **2c'** was obtained in 90% yield (2.43 g, 9.0 mmol) as a white solid.



2,2,2-trifluoroethyl benzenesulfonate **2e'** was obtained in 80% yield (1.92 g, 8.0 mmol) as a colorless liquid.



2,2,2-trifluoroethyl 4-(trifluoromethyl)benzenesulfonate **2f'** was obtained in 90% yield (2.77 g, 9.0 mmol) as a white solid.

b) Method A: Following a procedure from Alison R Cochrane et.al. To a solution of 2,2,2-trifluoroethyl sulfonate (5 mmol, 1 equiv) in THF (50 mL) at -78 °C was added dropwise 2.5 M *n*-butyllithium in hexanes (4.6 mL, 11.5 mmol, 2.3 equiv). After stirring under N₂ atmosphere at -78 °C for 1 h, the solution was neutralized with a mixture of THF/H₂O (1:1, 30 mL). Water (20 mL) was added, and the organic phase was extracted with EtOAc (2×30 mL), dried over Na₂SO₄, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (eluent = petroleum ether/EtOAc = 30/1) to give products **2**.

Method B: Preparation of LDA solution in THF: To a stirred solution of freshly distilled diisopropylamine (0.7 mL, 6 mmol) in anhydrous 5 mL of THF was added a solution of *n*-butyllithium (2.7 mL, 6.6 mmol, 2.5 M solution in hexane) at -78 °C under N₂ atmosphere. The prepared solution of LDA was slowly warmed to 0°C and stirred for 10 min and cooled again to -78 °C. To the LDA solution was added dropwise a solution of sulfonate (5 mmol) in 25 mL of THF for 20 min. The reaction mixture was stirred at the same temperature for 30 min and quenched by addition of THF/H₂O (1:1, 30mL). The solution was concentrated under reduced pressure and then the mixture was cooled to room temperature, washed with water and extracted with EtOAc. After dried over Na₂SO₄, the organic phase was concentrated and purified by column chromatgraphy on sillca gel (eluent = petroleum ether/EtOAc = 30/1) to afford products **2**.

Method C: The same as method A, except that the base used was replaced by LIHMDS.



2,2-difluorovinyl 2,4,6-triisopropylbenzenesulfonate **2a** was synthetized following the method A. This compound was obtained in 73% yield (1.26 g, 7.3 mmol) as a white solid.



2,2-difluorovinyl 2,4,6-trimethylbenzenesulfonate 2b was synthetized following

the method A. This compound was obtained in 85% yield (1.11 g, 8.5 mmol) as a white solid.



2,2-difluorovinyl 4-methoxybenzenesulfonate **2c** was synthetized following the method B. This compound was obtained in 92% yield (1.15 g, 9.2 mmol) as a white solid.



2,2-difluorovinyl benzenesulfonate **2e** was synthetized following the method B. This compound was obtained in 90% yield (0.99 g, 9.0 mmol) as a Colorless liquid.



2,2-difluorovinyl 4-(trifluoromethyl)benzenesulfonate **2f** was synthetized following the method C. This compound was obtained in 65% yield (0.94 g, 6.5 mmol) as a colorless oil.

Procedure for Synthesis of RhCp*(MeCN)₃(SbF₆)₂:

Synthetic procedure: Following a procedure from Rovis et al.,⁴ an oven-dried Schlenk tube was charged with AgSbF₆ (0.687 g, 2 mmol). After refilling with N₂, MeCN (2.5 mL, 0.2 M) was added in through syring, followed by adding [RhCp*Cl₂]₂ (0.309 g, 0.5 mmol) in one portion. After stirring for 4 h, the reaction

mixture was transfered into a centrifuge tube and spun for 2 min. The yellow supernatant was collected and 1 mL MeCN was added to the tube and spun again. This procedure was repeated until the superntant become colorless. The combined solution was concentrated to affored the product as yellow solid.

Hydroarylation reaction:



General procedure: An oven-dried Schlenk tube with a magnetic stirring bar was charged with **1** (0.1 mmol), RhCp*(MeCN)₃(SbF₆)₂ (0.005 mmol), 2,2-difluorovinyl arenesulfonates **2** (0.3 mmol) and solvent DCE (3 mL) was added through syringe and the tube was sealed with a teflon cap. After stirring at 50 °C for 12 h or more (monitored by TLC), the mixture was put through a celite plug. The solvent was removed in vacuo and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate 10:1 v/v) to afford the product **3**.

Large scale reaction:

Follow the general procedure: An oven-dried Schlenk tube with a magnetic stirring bar was charged with **1a** (3.0 mmol, 1 equiv), RhCp*(MeCN)₃(SbF₆)₂ (0.15 mmol), 2,2-difluorovinyl 2,4,6-triisopropylphenylsulfonates **2a** (9.0 mmol, 3.0 equiv) and solvent DCE (90 mL) was added through syringe and the tube was sealed with a teflon cap. After stirring at 50 °C for 24 h, the mixture was put through a celite plug. The solvent was removed in vacuo and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate 10:1 v/v) to afford the product **3aa** (723.7 mg, 1.52 mmol, 51%).

Substrates giving no desired products:



Control Experiments:



General procedure: An oven-dried Schlenk tube with a magnetic stirring bar was charged with **1** (0.1 mmol), RhCp*(MeCN)₃(SbF₆)₂ (0.005 mmol), 2,2-difluorovinyl arenesulfonates **2a** (0.3 mmol) and solvent DCE (3 mL) was added through syringe and the tube was sealed with a teflon cap. After stirring at 50 °C for 3.5 h, the mixture was put through a celite plug. The solvent was removed in vacuo and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate 10:1 v/v) to afford substrate **1** the product **3**.







General procedure: An oven-dried Schlenk tube with a magnetic stirring bar was charged with **1** (0.1 mmol), RhCp*(MeCN)₃(SbF₆)₂ (0.005 mmol), 2,2-difluorovinyl arenesulfonates **2a** (0.3 mmol), CH₃COOD (or CH₃COOH) (1.0 mmol, 10 equiv) and solvent DCE (3 mL) was added through syringe and the tube was sealed with a teflon cap. After stirring at 50 °C for 3.5 h, the mixture was put through a celite plug. The solvent was removed in vacuo and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ ethyl acetate 10:1 v/v) to afford substrate **1** the product **3**.



Characterization of structurally novel compounds (1-(pyrimidin-2-yl)-1*H*-indol-4-yl)methyl acetate



Following general procedure, **1j** was obtained as a white solid (114 mg, 0.43 mmol, 86%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.85$ (d, J = 8.3 Hz, 1H), 8.74 (d, J = 4.8 Hz, 2H), 8.35 (d, J = 3.8 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 7.11 (t, J = 4.8 Hz, 1H), 6.83 (dd, J = 3.7, 0.8 Hz, 1H), 5.45 (s, 2H), 2.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 171.1$, 158.1, 157.6, 135.4, 130.3, 127.4,

126.2, 123.6, 122.5, 116.6, 116.4, 104.7, 64.7, 21.0; **HRMS (ESI, m/z):** cacld for $C_{15}H_{14}O_2N_3$ [M+H]⁺:268.1086, found:268.1091.

4-phenyl-1-(pyrimidin-2-yl)-1*H*-indole



Following general procedure, **11** was obtained as a gray solid (399 mg, 1.47 mmol, 92%). ¹H NMR (400 MHz, CDCl₃): δ = 8.85 (dd, J = 8.4, 0.9 Hz, 1H), 8.73 (d, J = 4.8 Hz, 2H), 8.32 (d, J = 3.8 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.54 – 7.47 (m, 2H), 7.46 – 7.37 (m, 2H), 7.31 (dd, J = 7.4, 1.0 Hz, 1H), 7.07 (t, J = 4.8 Hz, 1H), 6.88 (dd, J

 $= 3.8, 0.8 \text{ Hz}, 1\text{H}); {}^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3):\delta = 158.1, 157.7, 140.8, 135.7, 134.6, 129.4, 128.9, 128.5, 127.0, 126.1, 123.9, 122.2, 116.2, 115.3, 106.2; \text{HRMS} (ESI, m/z): cacld for C_{18}\text{H}_{14}\text{N}_3 [M+H]^+:272.1188, found:272.1187.$

2-(2-methyl-1*H*-pyrrol-1-yl)pyrimidine

Following general procedure, **1y** was obtained as a brown oil (1.22 g, 7.7 mmol, 77%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.63$ (d, J = 4.8 Hz, 2H), 7.72 (dd, J = 3.4, 2.0 Hz, 1H), 7.04 (t, J = 4.8 Hz, 1H), 6.20 (t, J = 3.2 Hz, 1H), 6.08 – 6.01 (m, 1H), 2.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.9$, 157.8, 131.1, 120.3, 116.7, 112.0, 109.7, 16.6; HRMS (ESI, m/z): cacld for C₉H₁₀N₃ [M+H]⁺:160.0875, found:160.0872.

2,2,2-trifluoroethyl 2,4,6-triisopropylbenzenesulfonatee



Following general procedure, **2a'** was obtained as a white solid (98%). ¹H NMR (400 MHz, CDCl₃): δ = 7.21 (s, 2H), 4.39 (q, *J* = 8.0 Hz, 2H), 4.07 (hept, *J* = 6.7 Hz, 2H), 2.92 (hept, *J* = 7.2 Hz, 1H), 1.28 – 1.25 (m, 18H); ¹⁹F NMR (376 MHz, CDCl₃): δ = -73.4 (t, *J* = 7.8 Hz, 3F); ¹³C NMR

(100 MHz, CDCl₃): $\delta = 154.6$, 151.1, 128.3, 122.1 (q, J = 277.7 Hz), 63.5 (q, J =

38.0 Hz), 34.3, 29.8, 24.6, 23.5; HRMS (ESI, m/z): cacld for C₁₇H₂₆F₃O₃S [M+H]⁺: 367.1555, found: 367.1554.

2,2,2-trifluoroethyl 2,4,6-trimethylbenzenesulfonate



Following general procedure, **2b'** was obtained as a white solid (83%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.01$ (s, 2H), 4.30 (q, J = 8.0 Hz, 2H), 2.63 (s, 6H), 2.33 (s, 3H); ¹⁹F NMR

(376 MHz, CDCl₃): $\delta = -73.6$ (t, J = 8.1 Hz, 3F); ¹³C NMR (100 MHz, CDCl₃): δ = 144.3, 140.2, 131.9, 129.4, 120.0 (q, J = 277.9 Hz), 63.8 (q, J = 37.9 Hz), 22.5, 21.1; **HRMS (ESI, m/z):** cacld for $C_{11}H_{14}F_{3}O_{3}S$ [M+H]⁺: 283.0616, found: 283.0615.

2,2,2-trifluoroethyl 4-methoxybenzenesulfonate



Following general procedure, **2c'** was obtained as a white solid (90%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.90 - 7.83$ (m, 2H), 7.06 - 7.00 (m, 2H), 4.33 (q, J = 7.9 Hz, 2H), 3.90

(s, 3H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -73.8$ (t, J = 8.1 Hz, 3F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 164.4$, 130.4, 125.9, 121.9 (q, J = 277.7 Hz), 114.7, 64.4 (q, J = 38.1 Hz), 55.8; HRMS (ESI, m/z): cacld for C₉H₁₀F₃O₄S [M+H]⁺: 271.0252, found: 271.0251.

2,2,2-trifluoroethyl benzenesulfonate



Following general procedure, **2e'** was obtained as a colorless liquid (80%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.95 - 7.88$ (m, 2H), 7.74 - 7.67 (m, 1H), 7.63 - 7.54 (m, 2H), 4.36 (q, J =

7.9 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -73.9$ (t, J = 7.8 Hz, 3F); ¹³C **NMR (100 MHz, CDCl₃):** $\delta = 134.7, 134.6, 129.5, 127.9, 121.8$ (q, J = 277.6 Hz), 64.6 (q, J = 38.2 Hz); HRMS (ESI, m/z): cacld for C₈H₈F₃O₃S [M+H]⁺: 241.0146, found: 241.0143.

2,2,2-trifluoroethyl 4-(trifluoromethyl)benzenesulfonate



Following general procedure, **2f'** was obtained as a white solid (90%). ¹**H** NMR (400 MHz, CDCl₃): $\delta = 8.08$ (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 4.45 (g, J = 7.8

Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -63.4$ (s, 3F), -73.8 (t, J = 7.8 Hz, 3F); ¹³C NMR (100 MHz, CDCl₃): δ = 138.57, 136.22 (q, J = 33.4 Hz), 128.59, 126.69 (q, J = 3.7 Hz), 122.9 (q, J = 273.2 Hz), 121.7 (q, J = 277.7 Hz), 64.93 (q,

J = 38.4 Hz; **HRMS (ESI, m/z):** cacld for C₉H₇F₆O₃S [M+H]⁺: 309.0020, found: 309.0012.

2,2-difluorovinyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, 2a was obtained as a white solid (73%). ¹H NMR (400 MHz, CDCl₃): δ = 7.22 (s, 2H), 6.10 (dd, J = 14.6, 3.7 Hz, 1H), 4.08 (hept, J = 6.8 Hz, 2H), 2.93 (hept, J = 6.9 Hz, 1H), 1.29 – 1.25 (m, 18H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -90.3$ (dd, J = 52.6, 14.6 Hz), -

109.3 (dd, J = 52.6, 3.9 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 156.8$ (dd, J =294.8, 283.7 Hz), 154.8, 151.5, 128.1, 124.0, 100.3 (dd, *J* = 60.0, 15.2 Hz), 34.3, 29.9, 24.6, 23.5; **HRMS (ESI, m/z):** cacld for C₁₇H₂₅F₂O₃S [M+H]⁺: 347.1492, found: 347.1492.

2,2-difluorovinyl 2,4,6-trimethylbenzenesulfonate



Following general procedure, 20 was compared to $\delta = 7.01$ (s, 2H), $\delta = 7.01$ (s, 2H), $\delta = 6.06$ (dd, J = 14.7, 3.9 Hz, 1H), 2.64 (s, 6H), 2.33 (s, 3H); $\delta = 7.01$ (s, 2H), $\delta = 7.01$ (s, 2 Following general procedure, 2b was obtained as a white ¹⁹F NMR (376 MHz, CDCl₃): δ = -90.5 (dd, J = 52.2, 14.7

Hz), -109.1 (dd, J = 52.2, 3.9 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 156.88$ (dd, J = 294.8, 284.2 Hz), 144.47, 140.63, 131.85, 129.10, 100.24 (dd, J = 59.6, 15.2 Hz), 22.52 , 21.07; **HRMS (ESI, m/z):** cacld for C₁₁H₁₃F₂O₃S [M+H]⁺: 263.0553, found: 263.0559.

2,2-difluorovinyl 4-methoxybenzenesulfonate



Following general procedure, **2c** was obtained as a white solid (92%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.91 - 7.82$ (m, 2H), 7.08 - 6.99 (m, 2H), 6.07 (dd, J = 14.4, 3.9 Hz,

1H), 3.91 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -90.5$ (dd, J = 50.6, 14.5 Hz, 1F), -108.9 (dd, J = 51.0, 4.1 Hz, 1F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 164.5$, 157.0 (dd, J = 295.2, 284.2 Hz), 130.7, 125.2, 114.6, 100.8 (dd, J = 59.7, 15.2 Hz), 55.8; HRMS (ESI, m/z): cacld for cacld for $C_9H_8F_2O_4SNa$ [M+Na]⁺: 273.0009, found: 273.0000.

2,2-difluorovinyl benzenesulfonate

Following general procedure, **2e** was obtained as a colorless liquid (90%). ¹H NMR (400 MHz, CDCl₃): $\delta = 7.98 - 7.91$ (m, 2H), 7.77 - 7.70 (m, 1H), 7.61 (t, J = 7.7 Hz, 2H), 6.10 (dd, J = 14.3, 3.9 Hz, 1H).; ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -90.4$ (dd, J = 49.9, 14.2 Hz), -108.6 (dd, J = 50.2, 4.0 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 157.0$ (dd, J = 295.5, 284.8 Hz), 134.8, 134.2, 129.4, 128.4, 100.9(dd, J = 60.0, 15.2 Hz); HRMS (ESI, m/z): cacld for C₈H₇F₂O₃S [M+H]⁺: 221.0084, found: 221.0090.

2,2-difluorovinyl 4-(trifluoromethyl)benzenesulfonate

F₃C F F Solid (65%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.09$ (d, J F Solid (65%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.09$ (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 6.15 (dd, J = 14.1, 4.0 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -63.4$ (s, 3F), -89.2 (dd, J = 48.5, 14.2 Hz, 1F), -107.6 (dd, J = 48.5, 4.0 Hz, 1F); ¹³C NMR (100 MHz, CDCl₃): δ = 157.03 (dd, J = 295.6, 285.7 Hz), 137.85, 136.37 (q, J = 33.4 Hz), 128.97, 126.62 (q, J = 3.7 Hz), 122.9 (q, J = 273.3 Hz), 100.90 (dd, J = 60.3, 15.3 Hz);

HRMS (ESI, m/z): cacld for C₉H₆F₅O₃S [M+H]⁺: 288.9958, found: 288.9960.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate

N F N N

Following general procedure, **3aa** was obtained as a white solid (38.0 mg, 0.07 mmol, 70%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 8.30 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.21 (td,

J = 7.5, 1.1 Hz, 1H), 7.17 (s, 2H), 7.12 (t, J = 4.8 Hz, 1H), 6.73 (s, 1H), 4.39 (t, J = 12.7 Hz, 2H), 4.04 (hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.8 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.0, 158.0, 154.4, 150.8, 137.2, 131.0, 129.2$ (t, J = 2.0 Hz), 128.5, 123.9, 123.6, 123.6 (t, J = 276.8 Hz), 122.0, 120.4, 117.3, 114.1, 110.4, 36.1 (t, J = 28.5 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for cacld for C₂₉H₃₄F₂N₃O₃S [M+H]⁺: 542.2289, found: 542.2296.

2,2-difluoro-2-(4-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, **3ba** was obtained as a white solid (45.5 mg, 0.082 mmol, 82%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 8.13 (d, J = 8.4 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.12 (t, J = 4.8 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.76 (s, 1H), 4.40 (t, J = 12.8 Hz, 2H), 4.06

(hept, J = 6.8 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 2.53 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.4, 150.8, 137.0, 131.0, 129.7, 128.6 (t, J = 2.0 Hz), 128.2, 123.9, 123.7, 123.6 (t, J = 276.7 Hz), 122.4, 117.2, 111.6, 108.8, 36.2 (t, J = 28.3 Hz), 34.2, 29.5, 24.4, 23.5, 18.5; HRMS (ESI, m/z): cacld for cacld for C₃₀H₃₆F₂N₃O₃S [M+H]⁺: 556.2445, found: 556.2444.

2,2-difluoro-2-(5-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ca** was obtained as a white solid (38.8 mg, 0.068 mmol, 68%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.71$ (d, J = 4.8 Hz, 2H), 8.21 (d, J = 8.5 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.17 (s, 2H), 7.13 – 7.06 (m,

2H), 6.65 (s, 1H), 4.39 (t, J = 12.7 Hz, 2H), 4.05 (hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 2.45 (s, 3H), 1.26 (d, J = 7.0 Hz, 6H), 1.21 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 12.7 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.4, 150.8, 135.5, 131.4, 131.1, 129.2 (t, J = 1.8 Hz), 128.8, 125.1, 123.9, 123.7 (t, J = 276.8 Hz), 120.1, 117.0, 114.0, 110.2, 36.3 (t, J = 28.3 Hz), 34.2, 29.5, 24.4, 23.5, 21.2; HRMS (ESI, m/z): cacld for C₃₀H₃₆F₂N₃O₃S [M+H]⁺: 556.2445, found: 556.2443.

2,2-difluoro-2-(6-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3da** was obtained as a colorless oil (40.4 mg, 0.073 mmol, 73%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.74$ (d, J = 4.8 Hz, 2H), 8.11 (s, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.18 (s, 2H), 7.12 (t, J = 4.8 Hz,

1H), 7.08 - 7.02 (m, 1H), 6.68 (s, 1H), 4.36 (t, J = 12.8 Hz, 2H), 4.05 (hept, J = 6.7 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 2.49 (s, 3H), 1.27 (d, J = 6.9 Hz, 6H),

1.21 (d, J = 6.8 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.8$ (t, J = 12.8 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.0$, 154.4, 150.8, 137.5, 133.5, 131.0, 128.5 (t, J = 1.9 Hz), 126.3, 123.9, 123.6 (t, J = 276.8 Hz), 123.6, 120.0, 117.1, 114.0, 110.3, 36.1 (t, J = 28.3 Hz), 34.2, 29.5, 24.4, 23.4, 22.0; HRMS (ESI, m/z): cacld for C₃₀H₃₆F₂N₃O₃S [M+H]⁺: 556.2445, found: 556.2440.

2,2-difluoro-2-(7-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ea** was obtained as a yellow oil (33.4 mg, 0.060 mmol, 60%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.81$ (d, J = 4.8 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 4.9 Hz, 1H), 7.18 (s, 2H), 7.11 (t, J = 7.5

Hz, 1H), 7.04 – 6.99 (m, 1H), 6.69 (s, 1H), 4.02 (hept, J = 6.8 Hz, 2H), 3.92 (t, J = 12.8 Hz, 2H), 2.92 (hept, J = 7.0 Hz, 1H), 1.99 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.0$ (t, J = 12.8 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.4$, 158.0, 154.5, 150.8, 136.6, 131.0, 129.5 (t, J = 1.7 Hz), 129.0, 126.1, 124.0, 123.2 (t, J = 276.2 Hz), 122.2, 121.6, 119.1, 118.5, 108.2, 34.5 (t, J = 29.1 Hz), 34.2, 29.5, 24.4, 23.5, 20.4; HRMS (ESI, m/z): cacld for C₃₀H₃₆F₂N₃O₃S [M+H]⁺: 556.2445, found: 556.2437.

2,2-difluoro-2-(4-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3fa** was obtained as a white solid (46.1 mg, 0.081 mmol, 81%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 7.88 (d, J = 8.4 Hz, 1H), 7.20 (t, J = 8.2 Hz, 1H), 7.16 (s, 2H), 7.12 (t, J = 4.8 Hz, 1H), 6.85 (s, 1H), 6.64 (d, J = 7.9 Hz, 1H), 4.36 (t, J = 12.9 Hz, 2H), 4.03 (hept, J = 6.8 Hz, 2H), 3.94 (s, 3H), 2.91

(hept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.01$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.1, 154.4, 152.6, 150.8, 138.5, 131.1, 127.6 (t, J = 1.8 Hz), 124.4, 123.9, 123.5 (t, J = 276.9 Hz), 119.0, 117.4, 107.5, 107.3, 102.1, 55.3, 36.0 (t, J = 28.2 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₀H₃₆F₂N₃O₄S [M+H]⁺: 572.2395, found: 572.2394.

2,2-difluoro-2-(5-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ga** was obtained as a white solid (36.3 mg, 0.064 mmol, 64%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.70$ (d, J = 4.8 Hz, 2H), 8.26 (d, J = 9.1 Hz, 1H), 7.17 (s, 2H), 7.08 (t, J = 4.8 Hz, 1H), 7.02 (d, J = 2.6 Hz, 1H), 6.91 (dd, J = 9.1, 2.6 Hz, 1H), 6.67

(s, 1H), 4.40 (t, J = 12.7 Hz, 2H), 4.05 (hept, J = 6.7 Hz, 2H), 3.86 (s, 3H), 2.91 (hept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.7 Hz, 12H); ¹⁹F **NMR (376 MHz, CDCl₃):** $\delta = -66.6$ (t, J = 12.8 Hz, 2F); ¹³C **NMR (100 MHz, CDCl₃):** $\delta = 158.0, 158.0, 155.4, 154.4, 150.8, 132.1, 131.0, 129.8$ (t, J = 2.0 Hz), 129.2, 123.9, 123.6 (t, J = 276.8 Hz), 117.0, 115.3, 113.0, 110.3, 102.3, 55.6, 36.3 (t, J = 28.4 Hz), 34.2, 29.5, 24.4, 23.5; **HRMS (ESI, m/z):** cacld for C₃₀H₃₆F₂N₃O₄S [M+H]⁺: 572.2395, found: 572.2388.

2,2-difluoro-2-(6-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ha** was obtained as a colorless oil (41.1 mg, 0.072 mmol, 72%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 7.93 (d, J = 2.3 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.17 (s,

2H), 7.11 (t, J = 4.8 Hz, 1H), 6.87 (dd, J = 8.6, 2.3 Hz, 1H), 6.65 (s, 1H), 4.36 (t, J = 12.8 Hz, 2H), 4.04 (hept, J = 6.7 Hz, 2H), 3.87 (s, 3H), 2.91 (hept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.8 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.9$ (t, J = 12.7 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 157.4, 154.4, 150.8, 138.1, 131.1, 128.0 (t, J = 1.9 Hz), 123.9, 123.6 (t, J = 276.6 Hz), 122.6, 120.7, 117.1, 111.2, 110.4, 98.7, 55.7, 36.2 (t, J = 28.4 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₀H₃₆F₂N₃O₄S [M+H]⁺: 572.2395, found: 572.2392.

2-(4-(benzyloxy)-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, **3ia** was obtained as a white solid (50.7 mg, 0.078 mmol, 78%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.74$ (d, J = 4.8 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.32 (m, 1H), 7.23 – 7.17 (m, 3H), 7.12 (t, J = 4.8 Hz, 1H), 6.94

(s, 1H), 6.72 (d, J = 7.9 Hz, 1H), 5.23 (s, 2H), 4.39 (t, J = 13.0 Hz, 2H), 4.06 (hept, J = 6.7 Hz, 2H), 2.92 (hept, J = 6.9 Hz, 1H), 1.27 (d, J = 7.0 Hz, 6H), 1.22 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.0$ (t, J = 13.0 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.4, 151.8, 150.8, 138.7, 137.3, 131.0, 128.4, 127.7, 127.6 (t, J = 1.7 Hz), 127.3, 124.4, 123.9, 123.5 (t, J = 276.9 Hz), 119.4, 117.3, 107.7, 107.5, 103.6, 70.0, 36.0 (t, J = 28.2 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₆H₄₀F₂N₃O₄S [M+H]⁺: 648.2708, found: 648.2707.

(2-(1,1-difluoro-2-(((2,4,6-triisopropylphenyl)sulfonyl)oxy)ethyl)-1-(pyrimidin-2-yl)-1*H*-indol-4-yl)methyl acetate



Following general procedure, **3ja** was obtained as a colorless oil (30.2 mg, 0.049 mmol, 49%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.77$ (d, J = 4.8 Hz, 2H), 8.30 (d, J = 8.2 Hz, 1H), 7.32 – 7.22 (m, 2H), 7.22 – 7.15 (m, 3H), 6.85 (s, 1H), 5.41 (s, 2H), 4.43 (t, J = 12.8 Hz, 2H), 4.05 (hept, J = 6.7 Hz, 2H), 2.93 (hept, J = 6.9 Hz, 1H), 2.13 (s, 3H), 1.28

(d, J = 7.0 Hz, 6H), 1.22 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 171.0$, 158.1, 157.9, 154.5, 150.8, 137.4, 131.0, 129.7 (t, J = 1.8 Hz), 127.4, 127.1, 124.0, 123.6, 123.5 (t, J = 276.7 Hz), 122.4, 117.5, 114.5, 108.3, 64.5, 36.1 (t, J = 28.5 Hz), 34.2, 29.5, 24.4, 23.4, 21.0; HRMS (ESI, m/z): cacld for C₃₂H₃₈F₂N₃O₅S [M+H]⁺: 614.2500, found: 614.2505.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, **3ka** was obtained as a white solid (24.4 mg, 0.037 mmol, 37%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.75$ (d, J = 4.8 Hz, 2H), 8.24 (d, J = 8.4 Hz, 1H), 8.05 (s, 1H), 7.70 (dd, J = 8.5, 1.2 Hz, 1H), 7.18 – 7.10 (m, 3H), 6.70 (s, 1H), 4.36 (t, J = 8.5)

12.7 Hz, 2H), 4.01 (hept, J = 6.7 Hz, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 1.37 (s, 12H), 1.25 (d, J = 6.9 Hz, 6H), 1.18 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 12.6 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.4, 150.8, 139.3, 131.0, 129.9, 129.3 (t, J = 2.2 Hz), 128.1, 128.0, 124.0, 123.6 (t, J = 276.7 Hz), 117.4, 113.4, 110.7, 83.6, 36.1 (t, J = 28.4 Hz), 34.2, 29.7,

29.5, 24.9, 24.4, 23.5; **HRMS (ESI, m/z):** cacld for C₃₅H₄₄BF₂N₃O₅SNa [M+Na]⁺: 690.2960, found: 690.2963.

2,2-difluoro-2-(4-phenyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3la** was obtained as a yellow oil (42.9 mg, 0.070 mmol, 70%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.67$ (d, J = 4.8 Hz, 2H), 8.23 - 8.15 (m, 1H), 7.57 - 7.51 (m, 2H), 7.44 - 7.35 (m, 2H), 7.32 - 7.23 (m, 2H), 7.20 - 7.15 (m, 1H), 7.09 - 7.04 (m, 3H), 6.81 (s, 1H),

4.29 (t, J = 12.9 Hz, 2H), 3.92 (hept, J = 6.8 Hz, 2H), 2.80 (hept, J = 6.9 Hz, 1H), 1.15 (d, J = 7.0 Hz, 6H), 1.08 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.8$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.4, 150.8, 140.6, 137.7, 134.2, 131.0, 129.5 (t, J = 1.9 Hz), 128.8, 128.5, 127.0, 126.7, 123.9, 123.5 (t, J = 276.8 Hz), 122.1, 117.5, 113.1, 109.8, 36.1 (t, J = 28.4Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₅H₃₈F₂N₃O₃S [M+H]⁺: 618.2580, found: 618.2591.

2,2-difluoro-2-(5-phenyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ma** was obtained as a white solid (40.8 mg, 0.066 mmol, 66%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.75$ (d, J = 4.8 Hz, 2H), 8.39 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 1.7 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.55 (dd, J = 8.7, 1.9 Hz, 1H), 7.51 – 7.42 (m, 2H),

7.37 – 7.31 (m, 1H), 7.18 (s, 2H), 7.14 (t, J = 4.8 Hz, 1H), 6.79 (s, 1H), 4.43 (t, J = 12.7 Hz, 2H), 4.06 (hept, J = 6.7 Hz, 2H), 2.92 (hept, J = 7.0 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.7 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.1$, 158.0, 154.5, 150.8, 141.8, 136.7, 135.4, 131.0, 129.9 (t, J = 2.3 Hz), 129.0, 128.7, 127.3, 126.6, 124.0, 123.6 (t, J = 276.8 Hz), 123.3, 118.8, 117.3, 114.5, 110.7, 36.2 (t, J = 28.4 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₃₅H₃₈F₂N₃O₃S [M+H]⁺: 618.2591, found: 618.2592.

methyl 2-(1,1-difluoro-2-(((2,4,6-triisopropylphenyl)sulfonyl)oxy)ethyl)-1-(pyrimidin-2-yl)-1*H*-indole-4-carboxylate



Following general procedure, **3na** was obtained as a white solid (20.2 mg, 0.034 mmol, 34%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.77$ (d, J = 4.9 Hz, 2H), 8.48 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.5 Hz, 1H), 7.42 (s, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.21 – 7.12 (m, 3H), 4.41 (t, J = 12.8 Hz, 2H), 4.07

- 3.92 (m, 5H), 2.90 (hept, J = 6.7 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.18 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.5$, 158.2, 157.8, 154.5, 150.9, 138.0, 131.4, 131.0, 128.2, 125.2, 124.0, 123.4 (t, J = 278.8 Hz), 122.9, 121.4, 118.8, 117.8, 111.2, 51.8, 36.1 (t, J = 27.4 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₁H₃₆F₂N₃O₅S [M+H]⁺: 600.2344, found: 600.2342.

methyl 2-(1,1-difluoro-2-(((2,4,6-triisopropylphenyl)sulfonyl)oxy)ethyl)-1-(pyrimidin-2-yl)-1*H*-indole-5-carboxylate



Following general procedure, **30a** was obtained as a yellow oil (29.4 mg, 0.049 mmol, 49%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.77$ (d, J = 4.8 Hz, 2H), 8.31 – 8.23 (m, 2H), 7.96 (dd, J = 8.8, 1.8 Hz, 1H), 7.17 (d, J = 13.7 Hz, 3H), 6.78 (s, 1H), 4.37 (t, J = 13.7 Hz, 3H), 6.78 (s, 1H), 70.78 (s, 1H), 7

12.4 Hz, 2H), 4.00 (hept, J = 6.7 Hz, 2H), 3.93 (s, 3H), 2.90 (hept, J = 6.7 Hz, 1H), 1.25 (d, J = 7.0 Hz, 6H), 1.18 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.5$ (t, J = 13.4 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 167.6$, 158.3, 157.7, 154.5, 150.8, 139.7, 130.9, 130.8 (t, J = 2.4 Hz), 128.1, 124.9, 124.0, 123.9, 123.4 (t, J = 278.8 Hz), 122.9, 117.9, 113.8, 110.8, 51.9, 36.0 (t, J = 28.9 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₃₁H₃₆F₂N₃O₅S [M+H]⁺: 600.2344, found: 600.2348.

2,2-difluoro-2-(5-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3pa** was obtained as a white solid (31.4 mg, 0.056 mmol, 56%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 8.28 (dd, J = 9.2, 4.6 Hz, 1H), 7.23 – 7.12 (m, 4H), 7.01 (td, J = 9.2, 2.6 Hz, 1H), 6.68 (s, 1H), 4.39 (t, J = 12.5 Hz, 2H), 4.03

(hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9, 6.5 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H),

1.20 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.5$ (t, J = 12.6 Hz, 2F), -121.9 (ddd, J = 9.0, 9.0, 4.6 Hz, 1F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.9$ (d, J = 237.7 Hz), 158.1, 157.8, 154.5, 150.8, 133.6, 130.9, 130.9 (t, J = 2.0 Hz), 129.1 (d, J = 10.1 Hz), 124.0, 123.5 (t, J = 276.7 Hz), 117.4, 115.4 (d, J = 9.0 Hz), 111.5 (d, J = 25.1 Hz), 110.0 (d, J = 4.1 Hz), 105.4 (d, J = 23.6 Hz), 36.2 (t, J = 28.6 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₂₉H₃₃F₃N₃O₃S [M+H]⁺: 560.2195, found: 560.2196.

2,2-difluoro-2-(6-fluoro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3qa** was obtained as a colorless oil (37.0 mg, 0.066 mmol, 66%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 8.10 (dd, J = 11.1, 2.4 Hz, 1H), 7.46 (dd, J = 8.6, 5.5 Hz, 1H), 7.20 –

7.10 (m, 3H), 6.97 (td, J = 8.9, 2.4 Hz, 1H), 6.70 (s, 1H), 4.39 (t, J = 12.6 Hz, 2H), 4.04 (hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 5H), 1.20 (d, J = 6.7 Hz, 11H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.6 Hz, 2F), -118.4 (ddd, J = 10.9, 9.5, 5.5 Hz, 1F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 160.7$ (d, J = 238.4 Hz), 158.1, 157.9, 154.5, 150.8, 137.3 (d, J = 12.9 Hz), 131.0, 129.7 (t, J = 4.2 Hz), 129.7 (d, J = 4.1 Hz), 124.9, 124.0, 123.5 (t, J = 276.6 Hz), 120.9 (d, J = 10.0 Hz), 117.4, 110.5 (d, J = 24.4 Hz), 110.2, 101.6 (d, J = 28.9 Hz), 36.2 (t, J = 28.6 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₂₉H₃₃F₃N₃O₃S [M+H]⁺: 560.2195, found: 560.2194.

2-(4-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ra** was obtained as a white solid (35.5 mg, 0.062 mmol, 62%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.76$ (d, J = 4.8 Hz, 2H), 8.21 - 8.14 (m, 1H), 7.22 - 7.14 (m, 5H), 6.83 (s, 1H), 4.39 (t, J = 12.6 Hz, 2H), 4.02 (hept, J = 6.7 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.25

(d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.6 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.7, 154.5, 150.8, 137.8, 130.9, 130.1 (t, J = 2.1 Hz), 127.2, 125.5, 124.2, 124.0, 123.4 (t, J = 276.6 Hz), 121.8, 117.8, 112.8, 108.3, 36.1 (t, J = 28.7 Hz), 34.2, 29.5, 24.4, 23.4; HRMS (ESI, m/z): cacld for C₂₉H₃₂ClF₂N₃O₃SNa [M+Na]⁺: 598.1719, found: 598.1720.

2-(5-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, **3sa** was obtained as a white solid (24.8 mg, 0.043 mmol, 43%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.76$ (d, J = 4.9 Hz, 2H), 8.22 (d, J = 8.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.21 – 7.09 (m, 4H), 6.78 (s, 1H), 4.38 (t, J = 12.6 Hz, 2H), 4.01 (hept, J = 6.7

Hz, 2H), 2.90 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 7H), 1.19 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.7 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.8, 154.5, 150.8, 137.4, 130.9, 130.1 (t, J = 2.0 Hz), 129.0, 124.9, 124.5, 124.0, 123.3 (t, J = 276.6 Hz), 117.8, 114.1, 113.2, 110.1, 36.1 (t, J = 28.8 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₂₉H₃₃ClF₂N₃O₃S [M+H]⁺: 576.1899, found: 576.1896.

2-(4-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ta** was obtained as a white solid (32.9 mg, 0.053 mmol, 53%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.76$ (d, J = 4.8 Hz, 2H), 8.26 - 8.19 (m, 1H), 7.36 (dd, J = 7.7, 0.8 Hz, 1H), 7.20 - 7.09 (m, 4H), 6.78 (s, 1H), 4.38 (t, J = 12.6 Hz, 2H), 4.01 (hept, J = 6.7 Hz, 2H),

2.90 (hept, J = 6.8 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.6$ (t, J = 12.6 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.8, 154.5, 150.8, 137.4, 130.9, 130.1 (t, J = 2.1 Hz), 129.0, 124.9, 124.5, 124.0, 123.3 (t, J = 276.6 Hz), 117.8, 114.1, 113.3, 110.1, 36.1 (t, J = 28.7 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₂₉H₃₃BrF₂N₃O₃S [M+H]⁺: 620.1394, found: 620.1393.

2-(5-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ua** was obtained as a colorless oil (29.5 mg, 0.048 mmol, 48%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.64$ (d, J = 4.8 Hz, 2H), 8.10 (d, J = 8.9 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 8.9, 2.0 Hz, 1H), 7.09 – 7.03 (m, 3H), 6.56 (s, 1H),

4.29 (t, J = 12.5 Hz, 2H), 3.93 (hept, J = 6.7 Hz, 2H), 2.82 (hept, J = 6.9 Hz, 1H), 1.17 (d, J = 6.9 Hz, 6H), 1.10 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃):

δ = -66.5 (t, J = 12.5 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃):δ = 158.1, 157.7, 154.5, 150.8, 135.8, 130.9, 130.6 (t, J = 2.2 Hz), 130.2, 126.4, 124.0, 123.4 (t, J = 276.6 Hz), 122.8, 117.6, 115.9, 115.2, 109.5, 36.2 (t, J = 28.7 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₂₉H₃₃BrF₂N₃O₃S [M+H]⁺: 620.1394, found: 620.1399.

2-(6-bromo-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)-2,2-difluoroethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3va** was obtained as a white solid (32.3 mg, 0.051 mmol, 51%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.75$ (d, J = 4.8 Hz, 2H), 8.52 (s, 1H), 7.44 – 7.37 (m, 1H), 7.34 – 7.28 (m, 1H), 7.19 – 7.11 (m,

3H), 6.69 (s, 1H), 4.37 (t, J = 12.5 Hz, 2H), 4.02 (hept, J = 6.8 Hz, 2H), 2.91 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.8 Hz, 12H); ¹⁹F **NMR (376 MHz, CDCl₃):** $\delta = -66.6$ (t, J = 12.5 Hz, 2F); ¹³C **NMR (100 MHz, CDCl₃):** $\delta = 158.2$, 157.7, 154.5, 150.8, 137.7, 130.9, 130.0 (t, J = 2.1 Hz), 127.3, 125.3, 124.0, 123.4 (t, J = 276.7 Hz), 121.4, 117.6, 117.4, 117.3, 110.1, 36.2 (t, J = 28.5 Hz), 34.2, 29.5, 24.4, 23.5; **HRMS (ESI, m/z):** cacld for C₂₉H₃₃BrF₂N₃O₃S [M+H]⁺: 620.1394, found: 620.1389.

2,2-difluoro-2-(1-(pyridin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate

^{OTrisyl} Following general procedure, **3wa** was obtained as a brown solid (23.5 mg, 0.044 mmol, 44%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.60$ (dd, J = 5.3, 1.8 Hz, 1H), 7.88 (td, J = 7.7, 1.9 Hz, 1H), 7.61 (dd, J = 6.6, 2.1 Hz, 1H), 7.48 (d, J = 8.0

Hz, 1H), 7.37 – 7.28 (m, 2H), 7.22 – 7.14 (m, 4H), 6.73 (s, 1H), 4.05 – 3.93 (m, 4H), 2.91 (hept, J = 6.8 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.9$ (t, J = 12.6 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 154.5$, 150.9, 150.8, 149.5, 138.5, 137.2, 131.0, 129.0 (t, J = 2.2 Hz), 128.0, 124.0, 123.4 (t, J = 276.2 Hz), 122.8, 122.1, 121.2, 121.0, 120.7, 110.1, 107.1, 34.6 (t, J = 29.2 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₃₀H₃₅F₂N₂O₃S [M+H]⁺: 541.2336, found: 541.2332.

2,2-difluoro-2-(4-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6-triisopropylbenzenesulfonate



Following general procedure, **3xa** was obtained as a colorless liquid (28.9 mg, 0.051 mmol, 51%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.59$ (dd, J = 4.9, 1.9 Hz, 1H), 7.86 (td, J = 7.8, 1.9 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.16 (s, 2H), 7.11 (t, J = 8.1 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.83 (s, 1H), 6.58 (d, J = 7.8 Hz, 1H), 4.05 –

3.91 (m, 7H), 2.91 (hept, J = 7.0 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.2$ (t, J = 12.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 154.4$, 153.1, 151.0, 150.7, 149.5, 138.6, 138.4, 131.0, 127.4 (t, J = 1.9 Hz), 123.9, 123.6, 123.4 (t, J = 276.5 Hz), 122.1, 121.2, 118.6, 104.4, 103.5, 100.9, 55.3, 34.6 (t, J = 29.0 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₃₁H₃₇F₂N₂O₄S [M+H]⁺: 571.2442, found: 571.2448.

2,2-difluoro-2-(5-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3ya** was obtained as a colorless liquid (25.9 mg, 0.045 mmol, 45%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.60$ (dd, J = 5.0, 1.8 Hz, 1H), 7.88 (td, J = 7.7, 2.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.19 (s, 2H), 7.09 (d, J = 2.5 Hz,

1H), 6.86 (dd, J = 9.0, 2.5 Hz, 1H), 6.67 (s, 1H), 4.08 – 3.93 (m, 4H), 3.88 (s, 3H), 2.93 (hept, J = 6.9 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.7 Hz, 12H); ¹⁹**F NMR (376 MHz, CDCl₃):** $\delta = -66.9$ (t, J = 12.7 Hz, 2F); ¹³**C NMR (100 MHz, CDCl₃):** $\delta = 154.9$, 154.5, 151.0, 150.8, 149.5, 138.5, 132.3, 131.0, 129.5 (t, J = 2.1 Hz), 128.6, 123.9, 123.4 (t, J = 276.4 Hz), 121.9, 120.8, 112.7, 111.0, 106.8, 102.4, 55.8, 34.7 (t, J = 29.1 Hz), 34.2, 29.5, 24.4, 23.5; **HRMS (ESI, m/z):** cacld for C₃₁H₃₇F₂N₂O₄S [M+H]⁺: 571.2442, found: 571.2443.

2,2-difluoro-2-(6-methoxy-1-(pyridin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3za** was obtained as a colorless liquid (21.5 mg, 0.038 mmol, 38%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.60$ (dd, J = 5.0, 1.8 Hz, 1H), 7.87 (td, J = 7.7, 2.0 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.33

- 7.28 (m, 1H), 7.15 (s, 2H), 6.86 – 6.78 (m, 2H), 6.63 (s, 1H), 4.05 – 3.85 (m, 4H), 3.78 (s, 3H), 2.90 (hept, J = 6.9 Hz, 1H), 1.25 (d, J = 6.8 Hz, 6H), 1.18 (d, J = 6.7 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): δ = -67.1 (t, J = 12.7 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): δ = 156.9, 154.5, 151.0, 150.7, 149.6, 138.6, 138.0, 131.0, 127.8 (t, J = 2.0 Hz), 123.9, 123.4 (t, J = 276.4 Hz), 122.3, 122.1, 121.3, 121.1, 110.4, 107.0, 94.4, 55.7, 34.6 (t, J = 29.2 Hz), 34.2, 29.5, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₃₁H₃₇F₂N₂O₄S [M+H]⁺: 571.2442, found: 571.2440.

(1-(pyrimidin-2-yl)-1*H*-pyrrole-2,5-diyl)bis(2,2-difluoroethane-2,1-diyl) bis(2,4,6-triisopropylbenzenesulfonate)



Following general procedure, **3aaa** was obtained as a yellow oil (33.4 mg, 0.040 mmol, 40%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.66$ (d, J = 4.8 Hz, 2H), 7.18 – 7.10 (m, 5H), 6.22 (s, 2H), 4.02 – 3.90 (m, 8H),

2.90 (hept, J = 6.9 Hz, 2H), 1.25 (d, J = 6.9 Hz, 12H), 1.18 (d, J = 6.7 Hz, 24H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.8$ (t, J = 12.9 Hz, 4F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.3$, 157.5, 154.4, 150.7, 131.0, 124.0 (t, J = 1.7 Hz), 123.9, 123.4 (t, J = 276.3 Hz), 118.5, 113.3, 34.8 (t, J = 28.8 Hz), 34.2, 29.4, 24.4, 23.5; HRMS (ESI, m/z): cacld for C₄₂H₅₆F₄N₃O₆S₂ [M+H]⁺: 838.3533, found: 838.3536.

2,2-difluoro-2-(5-methyl-1-(pyrimidin-2-yl)-1*H*-pyrrol-2-yl)ethyl 2,4,6triisopropylbenzenesulfonate



Following general procedure, **3aba** was obtained as a white solid (23.8 mg, 0.047 mmol, 47%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.71$ (d, J = 4.8 Hz, 1H), 7.18 – 7.13 (m, 2H), 6.16 (d, J = 3.4 Hz, 1H), 5.95 (dd, J = 3.4, 1.1 Hz, 1H), 4.03

- 3.89 (m, 4H), 2.90 (hept, J = 6.9 Hz, 1H), 2.35 (s, 3H), 1.25 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.8 Hz, 12H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -68.0$ (t, J = 13.2 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.8, 154.3, 150.7, 132.2, 131.1, 123.9, 123.6 (t, J = 276.5 Hz), 121.5 (t, J = 1.7 Hz), 118.2, 113.1, 109.1, 34.9 (t, J = 28.5 Hz), 34.2, 29.4, 24.4, 23.5, 14.6; HRMS (ESI, m/z): cacld for C₂₆H₃₄F₂N₃O₃S [M+H]⁺: 506.2290, found: 506.2290.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 2,4,6trimethylbenzenesulfonate



Following general procedure, **3ab** was obtained as a white solid (31.1 mg, 0.068 mmol, 68%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.73$ (d, J = 4.8 Hz, 2H), 8.29 (dd, J = 8.3, 1.0 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.32 – 7.25 (m, 1H), 7.24 – 7.18 (m, 1H), 7.12 (t, J = 4.8 Hz, 1H), 6.85 (s, 2H), 6.59 (s, 1H), 4.31 (t, J = 12.0 Hz, 2H), 2.46 (s, 6H), 2.29 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -67.0$ (t, J = 11.9 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.0$,

157.9, 144.0, 139.9, 137.1, 131.9, 131.7, 129.2 (t, J = 3.2 Hz), 128.5, 123.6, 123.4 (t, J = 276.6 Hz), 122.0, 120.3, 117.2, 114.2, 110.2, 35.9 (t, J = 28.9 Hz), 22.3, 21.1; **HRMS (ESI, m/z):** cacld for C₂₃H₂₂F₂N₃O₃S [M+H]⁺: 458.1350, found: 458.1346.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)ethyl benzenesulfonate



Following general procedure, **3ac** was obtained as a yellow oil (12.1 mg, 0.029 mmol, 29%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.81$ (d, J = 4.8 Hz, 2H), 8.31 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.9 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.35 – 7.17 (m, 5H), 6.56 (s, 1H), 4.31 (t, J = 11.2 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 11.2 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.9,

137.2, 136.7, 134.1, 128.9, 128.8, 128.3, 127.7, 123.7, 123.1 (t, J = 278.2 Hz), 122.0, 120.3, 117.5, 114.1, 110.4, 35.5 (t, J = 29.0 Hz); **HRMS (ESI, m/z):** cacld for C₂₀H₁₆F₂N₃O₃S [M+H]⁺: 416.0880, found: 416.0878.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 4methylbenzenesulfonate



Following general procedure, **3ad** was obtained as a white solid (18.6 mg, 0.043 mmol, 43%). ¹H NMR (400 MHz, **CDCl₃):** $\delta = 8.83 - 8.76$ (m, 2H), 8.31 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.7 Hz, 1H), 7.36 - 7.27

(m, 1H), 7.27 – 7.16 (m, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H), 4.30 (t, J = 11.2 Hz, 2H), 2.34 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃): $\delta = -66.7$ (t, J = 11.2 Hz, 2F); ¹³C NMR (100 MHz, CDCl₃): $\delta = 158.2$, 157.9, 145.4, 137.2, 133.6, 129.4, 128.9 (t, J = 3.7 Hz), 128.3, 127.8, 123.6, 123.0 (t, J = 277.9 Hz), 121.9, 120.2, 117.4, 114.1, 110.4, 35.5 (t, J = 35.5 Hz), 21.6; HRMS (ESI, m/z): cacld for C₂₁H₁₇F₂N₃O₃SNa [M+Na]⁺: 452.0856, found: 452.0858.

2,2-difluoro-2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)ethyl 4methoxybenzenesulfonate



Following general procedure, **3ae** was obtained as a colorless oil (21.2 mg, 0.048 mmol, 48%). ¹H NMR (400 MHz, **CDCl₃**): $\delta = 8.79$ (d, J = 4.8 Hz, 2H), 8.28 (dd, J = 8.4, 1.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.51 – 7.46 (m, 1H), 7.29 (ddd, J = 8.4, 7.1, 1.3 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.66 – 6.60 (m, 2H), 6.53 (s, 1H), 4.26 (t, J = 11.1 Hz, 2H), 3.75 (s, 3H); ¹⁹F

NMR (376 MHz, CDCl₃): δ = -67.0 (t, *J* = 11.1 Hz, 2F); ¹³C **NMR (100 MHz, CDCl₃):** δ = 163.9, 158.2, 157.9, 137.2, 130.1, 129.0 (t, *J* = 3.8 Hz), 128.3, 127.9, 123.6, 122.9 (t, *J* = 277.5 Hz), 121.9, 120.3, 117.5, 114.1, 113.9, 110.4, 55.6, 35.5 (t, *J* = 29.3 Hz); **HRMS (ESI, m/z):** cacld for C₂₁H₁₇F₂N₃O₄SNa [M+Na]⁺: 468.0806, found: 468.0809.

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