Pd-catalysed Regio- and Stereo-Controlled C-2 β-Fluorovinylation of Indoles

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General Experimental Details

Techniques

Manipulations involving air and moisture-sensitive materials were conducted employing standard Schlenk-line and glovebox techniques, using vacuum lines attached to a double manifold with greaseless J. Youngs valves equipped with an oil pump (0.1 mmHg) under an atmosphere of dry nitrogen. All glassware was dried overnight before use, in a 180 °C oven and then allowed to cool under vacuum at 0.05 mbar. The removal of solvents in vacuo was achieved using a Büchi rotary evaporator (bath temperatures up to 40 °C) at a pressure of 15 mmHg (diaphragm pump), or at 0.05 mbar (oil pump) on a vacuum line at room temperature. The addition of < 200 μ L of liquids was via a Gilson PIPETMAN p20, for larger volumes standard syringe practices were employed.

Solvents

Anhydrous ethyl acetate was purchased from Sigma Aldrich and used under nitrogen atmosphere. Other solvents for anhydrous conditions, were dried by storage over activated molecular sieves (3Å) under nitrogen, with THF (tetrahydrofuran), dichloromethane (DCM), acetonitrile (MeCN), hexane, and diethyl ether (Et2O) dried using an Anhydrous Engineering alumina column drying system situated in the University of Bristol's chemistry department, and collected into Strauss flasks, using a gas-tight J. Youngs valve, containing activated molecular sieves. Molecular sieves were activated by heating to 300 °C under vacuum for 30 minutes, followed by cooling (still under vacuum). Deuterated solvents for NMR analysis were purchased from Sigma Aldrich.

Reagents

All reagents were purchased from TCI UK, Apollo Scientific, Sigma Aldrich, Alfa Aesar or Fluorochem and used as received.

Chromatography

TLC analysis was performed on Merck Silica gel 60F254 glass-backed plates. Visualisation was achieved by UV fluorescence (254 nm) or staining with basic KMnO4 or PMA. Flash column chromatography was conducted using Merck 60 silica: 230-400 mesh (40-63 μ m) or using an automated flash purification system (Biotage Selekt or Buchi Pure C-850 Flashprep) using Biotage Sfar Duo prepacked columns of size 5 g, 25 g or 50 g.

Analysis

NMR spectra were recorded on Bruker Nano 400 or Bruker Advance III HD 500 cryo spectrometers. Chemical shifts (δ) are quoted in parts per million (ppm), referenced to the residual solvent peak (1H and 13C NMR) and coupling constants (J) are given in Hz. Multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. NMR shifts for novel compounds have been assigned with the use of the appropriate 2D NMR experiments, such as COSY, HSQC and HMBC. Infrared spectra were recorded using a Perkin Elmer Spectrum Two FTIR spectrometer.

Compound naming

Compound names were generated by ChemDraw Professional 20.0 (PerkinElmer) following IUPAC nomenclature.

¹⁹F NMR Calibration

The ¹⁹F NMR are internally referenced to $CFCI_3$ and externally to 4,4'-difluoro-biphenyl as internal standard (with 16 scan and 10s relaxation delay)

Use of HF reagents (Warning)

The hazards of hydrogen fluoride solutions are well-categorised. Therefore, personal protection is of utmost importance. It is advised to wear two pairs of nitrile gloves when handling, and if the gloves come into contact with HF, they are removed immediately, and the area affected is washed thoroughly with water, then with Hexafluorine solutionTM. Calcium glucanoate gel is applied to the area and medical attention is sought. It is advised that Hexafluorine solutionTM and calcium glucanoate gel is kept nearby.

If HF has spilled on gloves:

Note: Time is of the essence as exposure to HF is a life-threatening emergency.

· Immediately remove gloves and wash area thoroughly with water

• If any HF has penetrated through gloves, then rub calcium glucanoate gel into the area for several minutes, reapplying once an hour for several hours.

If HF has been spilled on skin:

• Immediately wash the area with hexafluorine solution and large quantities of water for 5 minutes • Then rub calcium gluconate gel into the area for several minutes

• Monitor area for 15 minutes and if redness and swelling develop, proceed to the closest A&E.

Optimisation Studies

Catalyst optimisation

To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with catalyst (0.005 mmol, 0.05 equiv), *N*-methylindole (13.12 mg, 0.1 mmol, 1.0 equiv.), and fluorovinyliodane (0.1 mmol, 1.0 equiv., 49 mg). Solvent 1mL was added and reaction was allowed to stir at room temperature. After 12h, reaction mixture was diluted with ethyl acetate 4mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with ethylacetate (3 x). The combined organic layers were evaporated to ~1-2 mL volume, and 4,4'-difluoro-1,1'-biphenyl was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.

\bigcirc		Ales Me consci sc	at (5 mol%) lvent, rt , 12h	Ph F N
1	a Entry	2a Catalyst (x mol%)	Solvent	Yield ^[b]
	1	Pd(OAc) ₂ (5)	AcOH	54
	2	PdBr ₂ (5)	AcOH	50
	3	$(CH_3CN)_2PdCl_2$ (5)	AcOH	30
	4	Pd(OCOCF3)2 (5)	AcOH	32
	5	PEPSI (5)	AcOH	nr
	6	Pd(dppf)Cl ₂ (5)	AcOH	10
	7	Pd2(dba)3 (5)	EtOAc	23
	8	Pd(PPh ₃) ₄ (5)	EtOAc	50
	9	Cu(OTf) ₂ (10)	EtOAc	13
	10	Cu(OTf) ₂ (10)	DCE	14

[a] Reaction conditions: **1** (0.1mmol), **2** (0.1mmol), catalyst (5 mol%) in 1 mL solvent at room temperature for 12 h. [b] ¹⁹FNMR yield using 4,4'-difluorobiphenyl as internal standard.

Solvent optimisation

To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with $Pd(OAc)_2$ (0.005 mmol, 0.05 equiv), *N*-methylindole (13.12 mg, 0.1 mmol, 1.0 equiv.), and fluorovinyliodane (0.1 mmol, 1.0 equiv., 49 mg). Solvent 1mL was added and reaction was allowed to stir at room temperature. After 12h, reaction mixture was diluted with ethyl acetate 4mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with ethylacetate (3 x). The combined organic layers were evaporated to ~1-2 mL volume, and 4,4'-difluoro-1,1'-biphenyl was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.

		Pd(OAc) ₂ (5 mol%) Me 2a		Ph F N Sa	
	Entry	Catalyst (x mol%)	Solvent	Yield ^[b]	
	1	Pd(OAc) ₂ (5)	DCE	29	
	2	Pd(OAc) ₂ (5)	DCM	27	
	3	Pd(OAc) ₂ (5)	MeOH	12	
	4	Pd(OAc) ₂ (5)	HFIP	35	
	5	Pd(OAc) ₂ (5)	MeCN	10	
	6	Pd(OAc) ₂ (5)	EtOAc	64	

[a] Reaction conditions: **1** (0.1mmol), **2** (0.1mmol), $Pd(OAc)_2$ (5 mol%) in 1 mL solvent at room temperature for 12 h. [b] ¹⁹FNMR yield using 4,4'-difluorobiphenyl as internal standard.

Optimisation with additives

To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with $Pd(OAc)_2$ (0.005 mmol, 0.05 equiv), *N*-methylindole (13.12 mg, 0.1 mmol, 1.0 equiv.), fluorovinyliodane (0.1 mmol, 1.0 equiv., 49 mg) and additive (2equiv.). Ethyl acetate 1mL was added and reaction was allowed to stir at room temperature. After 12h, reaction mixture was diluted with ethyl acetate 4mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with ethylacetate (3 x). The combined organic layers were evaporated to ~1-2 mL volume, and 4,4'-difluoro-1,1'-biphenyl was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.

Û	Ta [BF4] Me 2a		es N P Me 2a	d(OAc) ₂ (5 mol%) EtOAc, additive rt , 12h	Ph F N F N 3a	
	-	Entry	Catalyst (x mol%)	Additive	Yield ^[b]	
	•	1	Pd(OAc) ₂ (5)	Acetic acid	60	
		2	Pd(OAc) ₂ (5)	TFA	14	
		3	Pd(OAc) ₂ (5)	TsOH	11	
		4	Pd(OAc) ₂ (5)	Triflic acid	10	
	-	[a] Poact	ion conditions: 1 (0 1	mmo 2 (0.1 mmc)	D D D D D D D D D D D D D D D D D D D	

[a] Reaction conditions: 1 (0.1mmol), 2 (0.1mmol), Pd(OAc)₂
(5 mol%) in 1 mL ethyl acetate at room temperature for 12 h.
[b] ¹⁹FNMR yield using 4,4'-difluorobiphenyl as internal standard.

Optimisation with time, temperature and catalyst loading

Variation in yield with catalyst loading and temperature were monitored by following above standard conditions and the results summarised below.

$\hat{\square}$	\sim		Pd(OAc) ₂ EtOA	(x mol%) c, t ⁰ C	F _{Ma} N
V	1a [']	[BF ₄ ⁻] Mé 2a			3a
	Entry	Catalyst (x mol%)	Time (h)	Temperature (⁰ C)	Yield ^[b]
•	9	Pd(OAc) ₂ (10)	12	rt	65
	10	Pd(OAc) ₂ (2)	12	rt	42
	11	Pd(OAc) ₂ (5)	7	40	72
	12	Pd(OAc) ₂ (5)	12	50	55
	13	Pd(OAc) ₂ (5)	4	50	74
	13 ^c	Pd(OAc) ₂ (5)	4	50	80
	13 ^d	Pd(OAc) ₂ (5)	4	50	69

[a] Reaction conditions: **1** (0.1mmol), **2** (0.1mmol), Pd(OAc)₂ (x mol%) in 1 mL ethyl acetate. [b] ¹⁹FNMR yield using 4,4'-difluorobiphenyl as internal standard. [c] 1.5 equiv. **2**. [d] 1.5 equiv. **1**

Optimisation with different arenes in the iodonium salts

To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.005 mmol, 0.05 equiv), *N*-methylindole (13.12 mg, 0.1 mmol, 1.0 equiv.) and fluorovinyliodane (0.1 mmol, 1.0 equiv.). ethyl acetate 1mL was added and reaction was allowed to stir at 50 °C. After 4 h, reaction mixture was diluted with ethyl acetate 4mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with ethylacetate (3 x). The combined organic layers were evaporated to ~1-2 mL volume, and 4,4'-difluoro-1,1'-biphenyl was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.



General Procedures

General Procedures 1: Synthesis of *N*-substituted pyrrole

Pyrrole substrates **4a** and **4b** were purchased from Aldrich and used as received. Substrates **4c** and **4d** were synthesized as described.¹



A mixture of hexane-2,5-dione (1.2 equiv, 6 mmol), aniline (1.0 equiv, 5 mmol), and sulfamic acid (0.05 equiv, 0.25 mol) was stirred at room temperature under solvent-free conditions for 30 min. After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was diluted with diethyl ether. The ether layer was washed with brine, dried (MgSO₄), and concentrated in vacuo. The residue was purified by silica-gel column chromatography (5% ethyl acetate in hexane) to afford the pure product.

General Procedures 2a: Synthesis of Z-fluorovinyl iodonium salts

z-Fluorovinyl iodane were prepared by following two sets of conditions developed in our lab.²



Conditions A

To an HDPE vial equipped with a stirrer bar, was added aryl iodide (1.1 equiv.), Selectfluor (1.5 equiv.), and Ag_2CO_3 (0.1 equiv.). The vial was wrapped in aluminium foil before being placed in a -20 °C cooling bath. Solvent (MeNO2 or dimethyl carbonate) was added in the amount specified to give a 0.125 M concentration of alkyne. Pyridine.9HF (4 equiv.) was added drop-wise, and the reaction was left to stir for 5 minutes. Alkyne (1 equiv.) was added slowly, and the reaction mixture was allowed to warm to room temperature, at which it was stirred for 24 hours. Distilled water (half the reaction volume) was added to the reaction mixture, which was then transferred into a separating funnel, along with a further rinse of the vial with dimethyl carbonate. The aqueous and organic layers were separated, and the aqueous phase was extracted with dimethyl carbonate (2 x). The aqueous phase was slowly poured into a saturated aqueous solution of NaHCO₃. The combined organic extracts were washed with a saturated aqueous solution of NaBF₄, and twice with distilled water, then evaporated under reduced pressure. To the resulting crude product was added either Et₂O or pentane (10-15 mL per mmol of alkyne added at the start of the reaction). The suspension was sonicated for 10-15 minutes, then carefully decanted (leaving behind the (Z)-FVI). This trituration process was typically repeated 1-3 times. Evaporation of the residual solvent yielded the Z-fluorovinyl iodonium Salt.

Conditions B

To an HDPE vial equipped with a stirrer bar, was added aryl iodide (1.1 equiv.), Selectfluor (1.5 equiv.), K_2CO_3 (3 equiv.), and Ag_2CO_3 (0.1 equiv.). The vial was wrapped in aluminium foil before being placed in a -20 °C cooling bath. Nitromethane was added in the amount specified to give a 0.125 M concentration of alkyne. Pyridine.9HF (4 equiv.) was added drop-wise, and the reaction was left to stir for 5-10 minutes. Alkyne (1 equiv.) was added slowly, and the reaction mixture was allowed to warm to room temperature. The procedure from this point onwards is identical to that under "Conditions A".



General Procedures 2b: Synthesis of *E*-fluorovinyl iodonium salts

E-Fluorovinyl iodane were synthesized as described in ref. 3.



To an HDPE vial equipped with a stirrer bar were added PhI (0.612 g, 3.0 mmol, 1.5 equiv), Py-HF (1.144 g, 40 mmol, 20 equiv), *m*-CPBA (0.688 g, 3.0 mmol, 1.5 equiv), and CH₂Cl₂ (8 mL). The mixture was stirred at room temperature for 3 h, and then alkyne **1** (2.0 mmol, 1.0 equiv) was added at this temperature. After the mixture was cooled to -78 °C, BF₃·Et₂O (1.0 mL, 8.0 mmol, 4 equiv) was added, and the mixture stirred for 10 min. The reaction mixture was warmed to room temperature and stirred for 20 min. The reaction mixture was poured into water (25 mL) and extracted with CH₂Cl₂ (10 mL × 3). The combined organic layer was washed with an aqueous solution (20 mL) of NaBF₄ (1.096 g, 10.0 mmol, 5 equiv) and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was submitted to column chromatography on silica gel. Organic compounds containing *m*-chlorobenzoic acid were first eluted with hexane/EtOAc (9:1), and β-fluorovinyliodonium salts were eluted with EtOAc.

General Procedures 3a: Synthesis of fluorovinylated indole



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with $Pd(OAc)_2$ (0.010 mmol, 0.05 equiv), indole (1.5-3.0 equiv.)[1.5 equiv for *N*-methylindole and 3.0 equiv for N-H indole], and fluorovinyliodane (0.2 mmol, 1.0 equiv.). Dry ethylacetate 2 mL was added and reaction was allowed to stir at rt-50 °C for 3-6 h. After completion of reaction, mixture was diluted with ethyl acetate 4 mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 times). The combined organic layers were evaporated, and the mixture was purified by silica gel column chromatography using pentane/ethylacetate (95:5) to get the pure compound.

General Procedures 3b: Synthesis of 2-fluorovinylated tryptophol



In a 10 mL flame-driedd Schlenk tube equipped with a stirrer bar was added $Cu(OTf)_2$ (0.020 mmol, 0.10 equiv), tryptophol (0.3 mmol, 1.5 equiv.), and DCM 2 mL under argon. The reaction was cooled to 0 °C and stirred for 5 minutes. Fluorovinyliodane (0.2 mmol, 1.0 equiv.) was added, and the reaction was left to stir for 5 minutes at 0 °C. The reaction mixture was then allowed to warm to room temperature, at which it was stirred for 30 minutes. After completion of reaction, mixture was diluted with DCM (5 mL) and quenched by the addition of saturated aqueous solution of NaHCO₃(5 mL). The aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of DCM (3 times). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The mixture was purified by silica gel column chromatography using pentane/ethylacetate (95:5) to afford the desire product.

General Procedures 3c: Synthesis of fluorovinylated Pyrole



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.01 mmol, 0.05 equiv), pyrrole (1.5-3.0 equiv.)[1.5 equiv for *N*-methylpyrole and 3.0 equiv for N-*H* pyrole]. Dry ethylacetate 2mL was added and reaction was allowed to stir at room temperature for 3-4 h. After completion of reaction, mixture was diluted with ethyl acetate 4 mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 times). The combined organic layers were evaporated, and the mixture was purified by neutral alumina column chromatography using pentane/ethylacetate (97:3) to get the pure compound.



In a 10 mL flame-driedd Schlenk tube equipped with a stirrer bar was added $Cu(OTf)_2$ (0.020mmol, 0.10 equiv), Trimethoxybenzene (0.3 mmol, 1.5 equiv.), Fluorovinyliodane (0.2 mmol, 1.0 equiv.) and DCE 2mL under nitrogen. The reaction was Heated to 70 °C for 4 hours. After completion of reaction, mixture was diluted with DCM (5 mL) and quenched by the addition of saturated aqueous solution of NaHCO₃ (5 mL). The aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of DCM (3 times). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The mixture was purified by neutral alumina column chromatography using pentane/ethylacetate (95:5) to afford the desire product.

General Procedures 4: Synthesis of ketone compound



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.01 mmol, 0.05 equiv), indole (1.5-3.0 equiv.)[1.5 equiv for *N*-methylindole and 3.0 equiv for N-H indole], and fluorovinyliodane (0.2 mmol, 1.0 equiv.). Acetic acid 2 mL was added and reaction was allowed to stir at rt for 16 h and then heated at 70 °C for 8 h. After completion of reaction, mixture was quenched with saturated solution of NaHCO₃. Ethyl acetate 10mL was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 time). The combined organic layers were evaporated, and the mixture was purified by silica gel column chromatography using pentane/ethylacetate (90:10) to get the pure compound.

General Procedures 5: Synthesis of di-ketone compound



In a pressure tube equipped with stirrer bar fluoro-vinylindole (0.2 mmol, 1 equiv) acid (0.5 mmol, 2.5 equiv) was added and the reaction mixture was allowed to heat at 50 °C for 24 h. After completion of reaction (TLC), the reaction mixture was transferred into round bottom flask and evaporated to get crude product. The crude product was purified by silica gel column chromatography using pentane/ethylacetate (90:10).

General Procedures 6: Synthesis of 2-(phenylethynyl)-1H-indole

HF elimination reaction was performed as described in ref. 4.



A 10 ml flame-dried pressure tube was charged with *t*-BuOK (68.9 mg, 0.4 mmol) and (*Z*)-2-(2-fluoro-2-phenylvinyl)-1*H*-indole (0.1 mmol) followed by adding anhydrous THF (1.0 ml) through syringe and then closed tightly. After stirring at 100 °C for 24 hours, saturated ammonium chloride (2 ml) was added and the resulting mixture was extracted with dichloromethane (2x5 ml). Removal of the solvent in vacuo and purification of the residue by silica gel column chromatography using pentane/ethylacetate (95:5) afforded the desired product.

General Procedures 7: Synthesis of (*Z*)-2-(2,5-diphenylpent-1-en-1-yl)-1methyl-1*H*-indole

Coupling reaction was performed as described in ref. 5.



To a solution of fluoro-vinylindole (29.3 mg, 0.1 mmol) and Pd(PPh₃)₄ (5.8 mg, 0.005 mmol, 5 mol%) in diethyl ether in a flame-dried Schlenk tube was added dropwise a solution of PhMgBr in THF (0.24 mmol, 2.4 equiv) at room temperature under an argon atmosphere. The mixture was stirred for 2 h at 40 °C. After completion (monitored by TLC) of the reaction, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with water and brine, then dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The crude residue was then purified by column chromatography on silica gel using pentane/ethylacetate (98:2) as the eluent to afford target product **16a** as a colorless oil (58% yield).

General Procedures 8: Reaction with vinyl iodane



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.005 mmol, 0.05 equiv), *N*-methylindole (0.15 mmol, 1.5 equiv., 19 mg), and vinyl iodane (0.1 mmol, 1.0 equiv., 45 mg). Dry ethylacetate 1 mL was added and reaction was allowed to stir at rt-50 °C for 3-6 h. After completion of reaction, mixture was diluted with ethyl acetate 4 mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 times). The combined organic layers were evaporated, and the mixture was purified by silica gel column chromatography using pentane/ethylacetate (95:5) to get the pure compound.

General Procedures 9: Synthesis of fluoroalkene



To a 10 mL dried glass vial equipped with a stirrer bar, was added (*Z*)-(3-((*N*-cyclopropyl-4methylphenyl)sulfonamido)-2-fluoroprop-1-en-1-yl)(mesityl)iodonium BF4 (301 mg, 0.5 mmol, 1 equiv.) and methanol (5 mL). The solution was cooled to 0 °C and sodium borohydride (38 mg, 1 mmol, 2 equiv.) was added. The mixture was allowed to stir for 5 hours before adding water (5 mL) and DCM (10 mL). The aqueous and organic layers were separated, and the aqueous phase was extracted with DCM (3 x). The combined organic extracts were filtered and evaporated under reduced pressure. The resulting crude was subjected to flash-column chromatography (0 to 25% EtOAc in pentane) to afford the product as a white solid (130 mg, 77%).

General Procedures 10a: Reaction with fluoroalkene



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.005 mmol, 0.05 equiv), indole (0.15 mmol, 1.5 equiv., 17 mg), and *N*-cyclopropyl-*N*-(2-fluoroallyl)-4-methylbenzenesulfonamide (0.1 mmol, 1.0 equiv., 27 mg). Dry ethylacetate 1 mL was added and reaction was allowed to stir at 70 °C for 12 h. After 12 h, 4,4'-difluoro-1,1'-biphenyl as NMR standard was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.

General Procedures 10b: Reaction with fluoroalkene (with oxidant)

Coupling reaction was performed as described in ref. 7.



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with $Pd(OAc)_2$ (0.010 mmol, 0.05 equiv), copper acetate (0.18 mmol, 1.8 equiv, 33 mg) indole (0.15 mmol, 1.5 equiv., 17 mg), and *N*-cyclopropyl-*N*-(2-fluoroallyl)-4-methylbenzenesulfonamide (0.1 mmol, 1.0 equiv., 27 mg). DMF (0.9 mL) and DMSO (0.1 mL) was added and reaction was allowed to stir at 70 °C for 12 h. After 12 h, 4,4'-difluoro-1,1'-biphenyl as NMR standard was added. The mixture was analysed by ¹⁹F NMR to determine NMR yields by integration relative to 4,4'-difluoro-1,1'-biphenyl.

Reactivity of E-FVI

Reaction of indole with E-FVI



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.010 mmol, 0.05 equiv), indole (0.6 mmol, 3.0 equiv., 70 mg) and E-fluorovinyliodane (0.2 mmol, 1.0 equiv., 104 mg). Dry ethylacetate 2 mL was added and reaction was allowed to stir at rt-50 °C for 4 h. After completion of reaction, mixture was diluted with ethyl acetate 4 mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 times). The combined organic layers were evaporated, and the mixture was purified by silica gel column chromatography using pentane/ethylacetate (95:5) to get **3ao** in 52% yield.

Reaction of pyrrole with E-FVI



To a 10 mL dried Schlenk tube equipped with a stirrer bar was charged with Pd(OAc)₂ (0.010 mmol, 0.05 equiv), pyrrole (0.6 mmol, 3.0 equiv., 57 mg) and E-fluorovinyliodane (0.2 mmol, 1.0 equiv., 104 mg). Dry ethylacetate 2 mL was added and reaction was allowed to stir at rt-50 °C for 4 h. After completion of reaction, mixture was diluted with ethyl acetate 4 mL and filtered through a short pad of celite and transferred into a separating funnel. Distilled water (4 mL) was added to the separating funnel and the aqueous and organic layers were separated, and the aqueous phase was extracted with 5 mL of ethylacetate (3 times). The combined organic layers were evaporated, and the mixture was purified by silica gel column chromatography using pentane/ethylacetate (98:2) to get **5i** in 39% yield.

Kinetics experiment with Pd(0) and Pd (II)

Kinetics study of reaction were performed at 0.05 mmol scale with $Pd_2(dba)_3$ and $Pd(OAc)_2$ at 25 °C. Indole (1.0 equiv, 0.05 mmol) and FVI (1.0 equiv, 0.05 mmol) and Pd-catalyst (0.0025 mmol) were added in NMR tube and the data were recorded after every 100 second.



The study revealed that the reaction started immidiately with Pd(0), however became sluggish later on.



The reaction with Pd(OAc)₂ showed significant progress with time.



An intermediate was noticed during reaction which get converted into the product when worked up with water.

Deuterium Experiment

Synthesis of deuterated indole

Deuterated indole was synthesized as described in ref. 6.



A solution of N-methyl indoles in deuterated acetic acid (CD_3CO_2D) (0.1 M) was heated at 150 °C for 110 h in a sealed tube. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 95:5) to give deuterated indoles 84% yield (71% deuteration at C-2 position).



Two different reactions, one with non-deuterated indole and other with deuterated indole were performed in a 10 mL dried Schlenk tube following the standard procedure (general procedure 3a).

After 20 minutes both the reactions were quenched by adding 4 mL of distilled water and aqueous layer was extracted with 4 mL of ethyl acetate (3 times). The combine organic layer was concentrated to 1 mL and ¹⁹FNMR yield was recorded separately for both the crude products using 4,4'-difluoro-1,1'- biphenyl as NMR standard.



Competitive reaction between fluorovinyl iodane and vinyl iodane



To a 10 mL dried Schlenk tube equipped with a stirrer bar was added $Pd(OAc)_2$ (0.005 mmol, 0.05 equiv), *N*-methylindole (0.10 mmol, 1.0 equiv., 13 mg), vinyl iodane **11a** (0.1 mmol, 1.0 equiv., 45 mg) and fluorovinyl iodane **1x** (0.1 mmol, 1.0 equiv., 47 mg). Dry ethylacetate 1 mL was added and reaction was allowed to stir at rt for 20 minutes. After 20 minutes, reaction was quenched with 4 mL of water and extracted with 5 mL of ethyl acetate. The organic layer was evaporated to 1 mL in *vacua* and ¹⁹FNMR yield of crude product was recorded.

Competitive reaction between N-methylindole and 1-H indole



To a 10 mL dried Schlenk tube equipped with a stirrer bar was added $Pd(OAc)_2$ (0.005 mmol, 0.05 equiv), *N*-methylindole **2a** (0.10 mmol, 1.0 equiv., 13 mg), 1-*H*-lindole **2b** (0.10 mmol, 1.0 equiv., 12 mg) and fluorovinyl iodane **1a** (0.1 mmol, 1.0 equiv., 49 mg). Dry ethylacetate 1 mL was added and reaction was allowed to stir at rt for 20 minutes. After 20 minutes, reaction was quenched with 4 mL of water and extracted with 5 mL of ethyl acetate. The organic layer was evaporated to 1 mL in *vacua* and ¹⁹FNMR yield of crude product was recorded.

Stability of flurovinylindole

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole subjected to below mentioned conditions to check the hydrolytic stability.



Entry	Conditions	Results
1	Stirred in acetic acid for 6 h at rt	20% Decomposition of compound 3a was noticed
2	Stirred in acetic acid for 6 h at 70 $^{\rm 0}{\rm C}$	Decomposition of compound 3a was noticed, no spot for ketone 14a
3	Stirred in acetic acid and 10 eq water for 6h at rt	Decomposition of compound 3a was noticed, no spot for ketone 14a
4	Stirred in acetic acid and 10 eq water for 6h at 70 $^{\rm 0}{\rm C}$	Decomposition of compound 3a was noticed, no spot for ketone 14a
5	Stirred with K_2CO_3 (1 eq) in ethyl acetate for 6 h at rt	Decomposition of compound 3a was noticed, with 2-3 faint spot on TLC

Plausible mechanism for fluorovinylation of indole



Plausible mechanism for diketone compound



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Spectral data

1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole (4c)



Compound **4c** was prepared according to general procedure 1 using hexane-2,5-dione (685 mg, 6 mmol), 4-methoxyaniline (616 mg, 5 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a yellow solid (674 mg, 67%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.16 (d, J = 8.9 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 5.91 (s, 1H), 3.88 (s, 2H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.0, 131.9, 129.3, 129.1, 114.3, 105.4, 55.6, 13.1.

HRMS (ESI+) calc: [M]⁺ (C₁₃H₁₅ON 201.1148; measured: 201.1144 = 1.99 ppm

difference.

IR (neat) vmax/cm⁻¹: 2940, 1510, 1404, 1296, 1238, 1163, 842, 769, 559.

 $R_f = 0.44$ (5% EtOAc/pentane).

1-cyclopropyl-2,5-dimethyl-1H-pyrrole (4d)

Compound **4d** was prepared according to general procedure 1 using hexane-2,5-dione (685 mg, 6 mmol), cyclopropanamine (285 mg, 5 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a yellow solid (399 mg, 59%).

 ^1H NMR (400 MHz, CDCl_3) δ 5.63 (s, 2H), 2.80 (tt, J = 7.0, 4.1 Hz, 1H), 2.20 (s, 6H), 0.94 – 0.88 (m, 2H), 0.87 – 0.80 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 130.3, 105.3, 25.7, 13.5, 7.4.

HRMS (ESI+) calc: $[M]^+$ (C₉H₁₃N) 135.1043; measured: 135.1039 = 2.96 ppm

difference.

IR (neat) vmax/cm⁻¹: 2921, 1520, 1410, 1371, 1030, 747, 563.

 $\mathbf{R}_{f} = 0.7 (5\% \text{ EtOAc/pentane}).$

(Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(4-nitrophenyl)iodonium BF₄(1g)



Compound **1g** was prepared according to general procedure 2a (condition b) using pent-4-yn-1-ylbenzene (288 mg, 2.0 mmol) and 1-iodo-4-nitrobenzene (548 mg, 2.20 mmol) and purified by trituration with pentane to yield a yellow sticky solid (419 mg, 42%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.23 – 8.17 (m, 4H), 7.29 – 7.25 (m, 2H), 7.21 – 7.17 (m, 1H), 7.13 – 7.11 (m, 2H), 6.58 (d, J = 32.9 Hz, 1H), 2.62 – 2.55 (m, 4H), 1.89 (h, J = 7.0 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 174.6 (d, J = 281.3 Hz), 150.2, 140.4, 136.5, 128.8, 128.6, 126.7, 126.5, 116.9, 75.0 (d, J = 21.5 Hz), 34.6, 31.7 (d, J = 23.4 Hz), 27.0.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -61.35 (dt, J = 33.9, 17.3 Hz), -144.57 - -144.62 (BF₄).

HRMS (ESI+) calc: [M]⁺ (C₁₇H₁₆FINO2) 412.0204; measured: 412.0191 = 3.16 ppm

difference.

IR (neat) vmax/cm⁻¹: 3114, 1651, 1525, 1466, 1351, 1308, 1010, 995, 846, 733, 520.

(Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(4-(trifluoromethyl)phenyl)iodonium BF₄(1h)



Compound **1h** was prepared according to general procedure 2a (condition b) using pent-4-yn-1-ylbenzene (288 mg, 2.0 mmol) and 1-iodo-4-(trifluoromethyl)benzene (598 mg, 2.20 mmol) and purified by trituration with pentane to yield a white sticky solid (449 mg, 43%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.16 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.14 – 7.11 (m, 2H), 6.59 (d, J = 33.0 Hz, 1H), 2.64 – 2.54 (m, 4H), 1.90 (h, J = 7.0 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 174.2 (d, J = 280.6 Hz), 140.5, 135.9, 134.6 (q, J = 33.5 Hz), 128.9 (q, J = 3.7 Hz), 128.7, 128.6, 126.4, 123.1 (q, J = 273.2 Hz), 114.7, 75.0 (d, J = 21.7 Hz), 34.6, 31.7 (d, J = 23.5 Hz), 27.0.

 $^{19}\textbf{F}$ NMR (377 MHz, CDCl_3) δ -62.08 (dt, J = 33.7, 17.1 Hz), -63.35 (s), -144.62 - -144.68 (BF_4).

HRMS (ESI+) calc: $[M]^+$ (C₁₈H₁₆F₄I) 435.0227; measured: 435.0209 = 4.14 ppm

difference.

IR (neat) vmax/cm⁻¹: 3104, 1641, 1594, 1400, 1323, 1133, 1066, 834, 703.

(Z)-(2-cyclopropyl-2-fluorovinyl)(mesityl)iodonium BF₄(1k)



Compound **1k** was prepared according to general procedure 2a (condition b) using ethynylcyclopropane (132 mg, 2.0 mmol) and 2-iodo-1,3,5-trimethylbenzene (541 mg, 2.20 mmol) and purified by trituration with pentane to yield a white sticky solid (476.51 mg, 57%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.06 (s, 2H), 6.28 (d, J = 34.0 Hz, 1H), 2.64 (s, 6H), 2.33 (s, 3H), 1.92 (dp, J = 24.7, 6.7 Hz, 1H), 0.99 (d, J = 6.6 Hz, 4H).

¹³**C NMR** (101 MHz, CDCl₃) δ 173.9 (d, J = 270.3 Hz), 144.3, 142.5, 130.3, 119.5, 67.6 (d, J = 24.4 Hz), 27.0 (d, J = 1.3 Hz), 21.1, 12.9 (d, J = 26.2 Hz), 8.0 (d, J = 1.7 Hz).

¹⁹**F NMR** (377 MHz, CDCl₃) δ -79.96 (dd, J = 34.1, 24.7 Hz), -148.07 - -148.13 (BF₄).

HRMS (ESI+) calc: [M]⁺ (C₁₂H₁₇FI) 331.0353; measured: 331.0339 = 4.23 ppm

difference.

IR (neat) vmax/cm⁻¹: 3110, 1633, 1456, 1381, 1191, 1069, 1029, 921, 855, 734.





Compound **1n** was prepared according to general procedure 2a (condition b) using (1I,2S,4S)-1-isopropyl-4-methyl-2-(prop-2-yn-1-yloxy)cyclohexane (389 mg, 2.0 mmol) and 2-iodo-1,3,5trimethylbenzene (541 mg, 2.20 mmol) and purified by trituration with pentane to yield a yellow sticky solid (557 mg, 51%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.08 (s, 2H), 6.45 (d, J = 33.6 Hz, 1H), 4.37 – 4.19 (m, 2H), 3.10 (td, J = 10.6, 4.2 Hz, 1H), 2.66 (s, 6H), 2.34 (s, 3H), 2.06 – 1.93 (m, 2H), 1.65 – 1.57 (m, 2H), 1.33 – 1.16 (m, 4H), 0.91 – 0.83 (m, 7H), 0.65 (d, J = 6.9 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 170.0 (d, J = 278.9 Hz), 144.6, 142.7, 130.4, 119.0, 81.0, 74.2 (d, J = 19.4 Hz), 65.0 (d, J = 31.6 Hz), 48.1, 40.0, 34.4, 31.5, 27.2, 25.8, 23.4, 22.3, 21.2, 20.9, 16.2.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -76.76 (dt, J = 33.6, 9.2 Hz) -147.59 - -147.65 (BF₄).

HRMS (ESI+) calc: [M+H]⁺ (C₂₂H₃₃FIO) 459.1555; measured: 459.1545 = 2.18 ppm

difference.

(E)-(2-fluorododec-1-en-1-yl)(phenyl)iodonium BF₄(1ab)

+ [BF₄-]

Compound **1ab** was prepared according to general procedure 2b using Dodecyne (166 mg, 1 mmol) and iodobenzene (306 mg, 1.50 mmol) and purified using silica gel chromatography (90% EtOAc/pentane) to yield a colourless oil (286 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.97 (d, J = 8 Hz, 2H), 7.63 – 7.59 (m, 1H), 7.47 (dd, J = 8.4, 7.2 Hz, 2H), 6.72 (d, J = 14.4 Hz, 1H), 2.79 (dt, J = 22.2, 7.6 Hz, 2H), 1.50 (q, J = 7.1 Hz, 2H), 1.28 – 1.20 (m, 14H), 0.88 (t, J = 7 Hz 3H).

These data are consistent with those previously reported.³

N-cyclopropyl-N-(2-fluoroallyl)-4-methylbenzenesulfonamide (11a)



Compound **11a** was prepared according to general procedure 9 using (*Z*)-(3-((*N*-cyclopropyl-4-methylphenyl)sulfonamido)-2-fluoroprop-1-en-1-yl)(mesityl)iodonium BF₄ (301 mg, 0.5 mmol) and Sodium borohydride (38 mg, 1.0 mmol) and purified using silica gel chromatography (90% EtOAc/pentane) to yield a white solid (286 mg, 60%).

¹**H NMR** (500 MHz, CDCl₃) δ 7.78 – 7.77 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.72 (dd, J = 16.3, 3.2 Hz, 1H), 4.56 (dd, J = 47.9, 3.1 Hz, 1H), 3.96 (d, J = 14.6 Hz, 2H), 2.46 (s, 3H), 2.14 (ttd, J = 6.9, 3.7, 1.0 Hz, 1H), 0.93 – 0.89 (m, 2H), 0.73 – 0.69 (m, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 161.6 (d, *J* = 261.1 Hz), 143.8, 135.5, 129.6, 128.0, 94.0 (d, *J* = 17.6 Hz), 50.7 (d, *J* = 31.8 Hz), 30.7, 21.7, 7.7.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -100.65 (dq, *J* = 47.9, 15.1 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₃H₁₆FNO₂S) 270.0959; measured: 270.0953 = 2.22 ppm difference.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (3a)



Compound **3a** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (20 mg, 0.15 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (4% EtOAc/pentane) to yield a colourless oil (22 mg, 74%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, J = 7.8 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.17 (m, 5H), 7.08 (ddd, J = 8.1, 6.9, 1.1 Hz, 1H), 6.84 (d, J = 2.5 Hz, 1H), 5.63 (d, J = 36.6 Hz, 1H), 3.69 (s, 3H), 2.73 (t, J = 7.6 Hz, 2H), 2.44 (dt, J = 17.6, 7.5 Hz, 2H), 1.99 (p, J = 7.6 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 162.1 (d, J = 269.7 Hz), 141.6, 136.9, 132.4, 128.6, 128.6, 128.3, 126.2, 121.6, 120.5, 119.7, 109.1, 102.6 (d, J = 11.8 Hz), 96.0 (d, J = 11.4 Hz), 35.1, 32.7 (d, J = 25.6 Hz), 29.8, 28.0.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -94.43 (dt, J = 36.1, 17.7 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₀H₂₀NF) 294.1653; measured: 294.1642 = 3.74 ppm difference.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-1-benzyl-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3d)



Compound **3d** was prepared according to general procedure 3a using 1-benzyl-1*H*-indole (62 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless oil (16 mg, 44%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.63 (dd, J = 7.2, 1.7 Hz, 1H), 7.29 – 7.24 (m, 5H), 7.23 – 7.18 (m, 2H), 7.15 – 7.08 (m, 4H), 7.01 – 6.99 (m, 2H), 6.95 (d, J = 2.5 Hz, 1H), 5.52 (d, J = 36.5 Hz, 1H), 5.35 (s, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.34 (dt, J = 17.8, 7.3 Hz, 2H), 1.90 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 162.3 (d, J = 270.1 Hz), 141.5, 137.9, 136.7, 132.2, 129.0, 128.60, 128.56, 128.5, 127.5, 126.10, 126.01, 122.0, 120.7, 120.1, 109.4, 103.3 (d, J = 12.3 Hz), 96.1 (d, J = 11.2 Hz), 46.6, 34.9, 32.5 (d, J = 25.7 Hz), 27.8.

19F NMR (376 MHz, CDCl₃) δ -93.91 (dt, J = 36.3, 18.0 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₆H₂₄FN) 370.1966; measured: 370.1949 = 4.59 ppm difference.

IR (neat) vmax/cm⁻¹: 2990, 2907, 1692, 1453, 1067, 880, 560.

 $\mathbf{R}_{f} = 0.4$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3e)



Compound **3e** was prepared according to general procedure 3a using 1*H*-indole (35 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless oil (18mg, 63%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.64 (s, 1H), 7.47 (dq, J = 7.8, 0.9 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.16 – 7.07 (m, 4H), 7.00 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.32 (d, J = 2.1 Hz, 1H), 5.61 (d, J = 40.8 Hz, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.34 (dt, J = 18.6, 7.5 Hz, 2H), 1.89 (tt, J = 8.5, 6.8 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 160.6 (d, J = 261.2 Hz), 141.6, 136.7, 131.9, 128.6, 128.1, 126.2, 122.4, 120.4, 120.1, 110.8, 102.6 (d, J = 3.4 Hz), 98.8 (d, J = 10.0 Hz), 35.1, 32.1 (d, J = 26.4 Hz), 27.95.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -103.0 (dtd, J = 40.7, 18.6, 6.1 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₉H₁₈NF) 280.1496; measured: 280.1488 = 2.86 ppm difference.

IR (neat) v_{max}/ cm⁻¹: 3021, 2959, 1376, 1070, 1027.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-(p-tolyl)-1H-indole (3f)



Compound **3f** was prepared according to general procedure 3a using 5-(p-tolyl)-1*H*-indole (62 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (18 mg, 48%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.65 (s, 1H), 7.66 (dt, J = 1.7, 0.8 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.18 – 7.12 (m, 5H), 6.35 (d, J = 2.0 Hz, 1H), 5.61 (d, J = 40.8 Hz, 1H), 2.65 (t, J = 7.6 Hz, 2H), 2.39 – 2.30 (m, 5H), 1.90 (p, J = 7.6 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 160.7 (d, J = 261.4 Hz), 141.5, 139.8, 136.1, 133.5, 132.6, 129.5, 128.6, 128.6, 127.3, 126.2, 122.3, 118.6, 110.9, 102.8, 98.8 (d, J = 9.8 Hz), 35.1, 32.1 (d, J = 26.1 Hz), 27.9, 21.2.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -102.7 (dtd, J = 40.8, 18.6, 6.1 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₆H₂₄NF) 370.1966; measured: 370.1967 = 0.27 ppm difference.

IR (neat) vmax/cm⁻¹: 2924, 1692, 1454, 1321, 1066, 800, 700.

 $\mathbf{R}_{f} = 0.4$ (5% EtOAc/pentane).



Compound **3g** was prepared according to general procedure 3a using 5-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (20 mg, 68%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.54 (s, 1H), 7.26 – 7.20 (m, 3H), 7.17– 7.11 (m, 4H), 6.91 (dd, J = 8.3, 1.7 Hz, 1H), 6.23 (s, 1H), 5.58 (d, J = 40.9 Hz, 1H), 2.64 (t, J = 7.6 Hz, 2H), 2.37 – 2.28 (m, 5H), 1.88 (p, J = 7.6 Hz, 1H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 160.3 (d, J = 261.1 Hz), 141.6, 135.0, 132.0, 129.2, 128.6, 128.6, 128.3, 126.2, 124.1, 120.1, 110.4, 102.2, 98.9 (d, J = 10.0 Hz), 35.1, 32.1 (d, J = 26.4 Hz), 27.9, 21.6.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -103.3 (dtd, J = 40.8, 18.5, 6.0 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₂₀NF) 294.1653; measured: 294.1640 = 4.42 ppm difference.

IR (neat) v_{max}/ cm⁻¹: 2923, 1449, 1312, 1029, 842, 791, 548.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-methoxy-1H-indole (3h)



Compound **3h** was prepared according to general procedure 3a using 5-methoxy-1*H*-indole (44 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (22 mg, 70%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.59 (s, 1H), 7.32 – 7.28 (m, 2H), 7.23 – 7.19 (m, 4H), 7.00 (d, J = 2.4 Hz, 1H), 6.83 (dd, J = 8.8, 2.4 Hz, 1H), 6.32 (d, J = 2.1 Hz, 1H), 5.65 (d, J = 40.8 Hz, 1H), 3.84 (s, 3H), 2.71 (t, J = 7.6 Hz, 2H), 2.40 (dt, J = 18.6, 7.5 Hz, 2H), 1.95 (p, J = 7.5 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ : 160.4 (d, J = 261.1 Hz), 154.4, 141.6, 132.6, 131.9 (d, J = 3.3 Hz), 128.6, 128.5, 126.2, 112.7, 111.5, 102.4 (d, J = 3.3 Hz), 102.0, 98.8 (d, J = 10.0 Hz), 56.0, 35.1, 32.1 (d, J = 26.3 Hz), 28.0.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -102.9 (dtd, J = 40.8, 18.7, 6.0 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₂₀FNO) 310.1602; measured: 310.1603 = 0.32 ppm difference.

IR (neat) vmax/cm⁻¹: 3473, 2924, 1482, 1449, 1198, 1141, 1032, 848, 790, 699, 551.

 $\mathbf{R}_{\mathbf{f}} = 0.3$ (5% EtOAc/pentane).

(Z)-4-(benzyloxy)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3i)



Compound **3i** was prepared according to general procedure 3a using 4-(benzyloxy)-1*H*-indole (134 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (45 mg, 58%).

¹**H NMR** (400 MHz, CDCl₃) δ : 8.64 (s, 1H), 7.43 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 7.15 – 7.10 (m, 3H), 6.99 (t, J = 7.9 Hz, 1H), 6.90 (dt, J = 8.2, 0.9 Hz, 1H), 6.48 – 6.46 (m, 2H), 5.58 (d, J = 40.9 Hz, 1H), 5.13 (s, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.32 (dt, J = 18.7, 7.4 Hz, 2H), 1.87 (p, J = 7.6 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ : 160.2 (d, J = 260.5 Hz), 152.4, 141.6, 138.1 (d, J = 3.3 Hz), 137.8, 130.6, 128.6, 128.6, 127.8, 127.5, 126.2, 123.2, 119.2, 104.5, 101.3, 100.2 (d, J = 3.2 Hz), 98.8 (d, J = 9.9 Hz), 70.1, 35.0, 32.0 (d, J = 26.4 Hz), 27.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -103.7 (dtd, J = 41.0, 18.9, 6.2 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₆H₂₄FNO) 386.1915; measured: 386.1908 = 1.81 ppm difference.

IR (neat) vmax/cm⁻¹: 3025, 2924, 1700, 1604, 1580, 1504, 1453, 1251, 1088, 907.

 $\mathbf{R}_{\mathbf{f}} = 0.3$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-7-methoxy-1H-indole (3j)



Compound **3j** was prepared according to general procedure 3a using 7-methoxy-1*H*-indole (88 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (42 mg, 68%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.78 (s, 1H), 7.25 – 7.21 (m, 2H), 7.15 – 7.12 (m, 3H), 7.08 (dt, J = 8.0, 0.8 Hz, 1H), 6.91 (t, J = 7.8 Hz, 1H), 6.55 (dd, J = 7.7, 0.8 Hz, 1H), 6.30 (d, J = 2.3)

Hz, 1H), 5.59 (d, J = 40.5 Hz, 1H), 3.89 (s, 3H), 2.65 (t, J = 7.6 Hz, 2H), 2.33 (dt, J = 18.6, 7.4 Hz, 2H), 1.92 – 1.85 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 160.4 (d, J = 261.6 Hz), 145.9, 141.6, 131.6, 129.3, 128.6, 128.6, 127.2, 126.2, 120.3, 113.2, 102.8 (d, J = 3.3 Hz), 102.3, 98.8 (d, J = 10.1 Hz), 55.5, 35.1, 32.1 (d, J = 26.2 Hz), 27.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -102.7 (dtd, J = 40.5, 18.5, 5.4 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₀H₂₀FNO) 310.1602; measured: 310.1603 =0.32 ppm difference

IR (neat) vmax/cm⁻¹: 3489, 2928, 1693, 1580, 1407, 1327, 1254, 1095, 729.

R_f = 0.7 (10% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-iodo-1H-indole (3k)



Compound **3k** was prepared according to general procedure 3a using 5-iodo-1*H*-indole (73 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (12 mg, 29%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.72 (s, 1H), 7.87 (d, J = 1.7 Hz, 1H), 7.40 (dd, J = 8.6, 1.7 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.22 – 7.18 (m, 3H), 7.11 (d, J = 8.4 Hz, 1H), 6.29 (d, J = 2.1 Hz, 1H), 5.65 (d, J = 40.6 Hz, 1H), 2.71 (t, J = 7.6 Hz, 2H), 2.44 – 2.36 (m, 2H), 1.96 (q, J = 7.6 Hz, 2H).

¹³**C NMR** (151 MHz, CDCl₃) δ 161.3 (d, J = 262.4 Hz), 141.4, 135.7 (d, J = 3.0 Hz), 132.8, 130.7, 130.6, 129.1, 128.6, 128.6, 126.2, 112.7, 101.6 (d, J = 3.1 Hz), 98.4 (d, J = 9.8 Hz), 83.4, 35.1, 32.1 (d, J = 26.3 Hz), 27.9.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -101.42 (dtd, J = 40.4, 18.8, 6.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₉H₁₇FIN) 406.0462; measured: 406.0476 = 3.45 ppm difference.

IR (neat) vmax/cm⁻¹: 2920, 1450, 1304, 1111, 883, 790, 698, 506.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-5-bromo-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3)



Compound **3I** was prepared according to general procedure 3a using 5-bromo-1*H*-indole (59 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (15mg, 42%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.73 (s, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.29 (q, J = 7.5 Hz, 2H), 7.29 – 7.18 (m, 5H), 6.31 (d, J = 2.1 Hz, 1H), 5.65 (d, J = 40.5 Hz, 1H), 2.71 (t, J = 7.6 Hz, 2H), 2.40 (dt, J = 18.5, 7.4 Hz, 2H), 1.95 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 161.3 (d, J = 262.5 Hz), 141.4, 135.2 (d, J = 3.1 Hz), 133.2(d, J = 1.1 Hz), 129.8, 128.6, 128.6, 126.2, 125.2, 122.8 (d, J = 1.2 Hz), 113.2, 112.1, 101.2 (d, J = 3.3 Hz), 98.5 (d, J = 9.8 Hz), 35.1, 32.0 (d, J = 26.1 Hz), 27.9.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -101.42 (dtd, J = 40.5, 18.8, 6.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₉H₁₇BrFN) 358.0601; measured: 358.0611 = 2.79 ppm difference.

IR (neat) vmax/cm⁻¹: 2975, 2898, 1405, 1242, 1047, 861, 408

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-5-fluoro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3m)



Compound **3m** was prepared according to general procedure 3a using 5-fluoro-1H-indole (41 mg, 0.3 mmol) and (Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (18mg, 61%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.70 (s, 1H), 7.31 (dd, J = 8.5, 6.4 Hz, 2H), 7.25 – 7.17 (m, 5H), 6.91 (td, J = 9.1, 2.5 Hz, 1H), 6.35 (d, J = 2.1 Hz, 1H), 5.66 (d, J = 40.6 Hz, 1H), 2.72 (t, J = 7.6 Hz, 2H), 2.41 (dt, J = 18.6, 7.5 Hz, 2H), 1.96 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 161.9 (d, J = 262.2 Hz), 158.0 (d, J = 234.2 Hz), 141.5, 133.7, 133.1 (d, J = 3.1 Hz), 128.63, 128.60, 128.4 (d, J = 10.3 Hz), 126.2, 111.3 (d, J = 9.7 Hz), 110.7 (d, J = 26.4 Hz), 105.1 (dd, J = 23.6, 1.2 Hz), 102.6 (dd, J = 4.8, 3.2 Hz), 98.6 (d, J = 9.8 Hz), 35.1, 32.0 (d, J = 26.1 Hz), 27.9.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -101.78 (dtd, J = 40.5, 18.6, 6.1 Hz), -124.55 (td, J = 9.5, 4.3 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₉H₁₇NF₂) 298.1402; measured: 298.1389 = 4.36 ppm difference.

IR (neat) vmax/cm⁻¹: 3473, 2924, 1484, 1448, 1178, 1129, 861, 698, 552.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-4-chloro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole (3n)



Compound **3n** was prepared according to general procedure 3a using 4-chloro-1*H*-indole (91 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2

mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (23 mg, 37%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.84 (s, 1H), 7.36 – 7.32 (m, 2H), 7.27 – 7.23 (m, 4H), 7.11 (d, J = 0.6 Hz, 1H), 7.10 (d, J = 1.2 Hz, 1H), 6.51 (d, J = 2.2 Hz, 1H), 5.73 (d, J = 40.6 Hz, 1H), 2.75 (t, J = 7.6 Hz, 2H), 2.45 (dt, J = 19.1, 7.5 Hz, 2H), 2.00 (p, J = 7.6 Hz, 2H).

 $^{13}\textbf{C}$ NMR (126 MHz, CDCl₃) δ 161.3 (d, J = 262.4 Hz), 141.4, 137.2 (d, J = 3.1 Hz), 132.5, 128.63, 128.61, 127.0, 126.2, 125.70 (d, J = 1.4 Hz), 122.9, 119.8, 109.3, 101.0 (d, J = 3.2 Hz), 98.5 (d, J = 9.8 Hz), 35.0, 32.0 (d, J = 26.1z Hz), 27.9.

¹⁹**FNMR** (376 MHz, CDCl₃) δ -101.57 (dtd, J = 40.6, 18.8, 6.5 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₉H₁₇CIFN) 314.1106; measured: 314.1106 = 0 ppm difference.

IR (neat) vmax/cm⁻¹: 3356, 2947, 1097, 1615, 1435, 1257, 1123, 769, 700.

 $\mathbf{R}_{\mathbf{f}} = 0.3$ (5% EtOAc/pentane).

(Z)-4-chloro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (30)



Compound **30** was prepared according to general procedure 3a using 4-chloro-1-methyl-1*H*-indole (50 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (32 mg, 48%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.31 - 7.27 (m, 2H), 7.23 - 7.19 (m, 3H), 7.17 - 7.13 (m, 1H), 7.07 (dd, J = 4.5, 0.9 Hz, 2H), 6.91 (d, J = 2.4 Hz, 1H), 5.61 (d, J = 36.1 Hz, 1H), 3.68 (s, 3H), 2.75 - 2.71 (m, 2H), 2.44 (dt, J = 17.7, 7.5 Hz, 2H), 1.99 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 162.9 (d, J = 271.3 Hz), 141.5, 137.7, 133.2, 128.6, 128.6, 127.1, 126.2, 125.8, 122.1, 119.5, 107.8, 101.1 (d, J = 12.2 Hz), 95.7 (d, J = 11.5 Hz), 35.1, 32.7 (d, J = 25.5 Hz), 30.2, 28.0.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -92.9 (dtd, J = 36.0, 17.8, 2.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₁₉CIFN) 328.1263; measured: 328.1252= 3.35 ppm difference.

IR (neat) vmax/cm⁻¹: 2932, 1685, 1600, 1453, 1283, 1124, 763, 564.

 $\mathbf{R}_{\mathbf{f}} = 0.4$ (5% EtOAc/pentane).

Methyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-5-carboxylate (3p)



Compound **3p** was prepared according to general procedure 3a using methyl 1*H*-indole-5-carboxylate (105 mg, 0.6 mmol) and (Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium

BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (28 mg, 42%).

¹**H NMR** (500 MHz, CDCl₃) δ 8.92 (s, 1H), 8.35 (dt, J = 1.5, 0.8 Hz, 1H), 7.91 (dd, J = 8.6, 1.6 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.26 – 7.22 (m, 3H), 6.50 (s, 1H), 5.72 (d, J = 40.5 Hz, 1H), 3.95 (s, 3H), 2.75 (t, J = 7.6 Hz, 2H), 2.48 – 2.40 (m, 2H), 1.99 (p, J = 7.6 Hz, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 168.3, 161.3 (d, J = 262.4 Hz), 141.4, 139.2 (d, J = 2.8 Hz), 133.4 (d, J = 1.1 Hz), 128.62, 128.59, 127.7, 126.2, 123.4 (d, J = 1.2 Hz), 122.2, 110.4, 103.5 (d, J = 3.3 Hz), 98.5 (d, J = 9.7 Hz), 52.0, 35.0, 32.0 (d, J = 26.0 Hz), 27.9.

19F NMR (376 MHz, CDCl₃) δ -101.11 – -101.93 (m).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₁H₂₀FNO₂) 338.1551; measured: 338.1560 = 3.25 ppm difference

IR (neat) vmax/cm⁻¹: 3356, 2947, 1097, 1615, 1435, 1257, 1123, 769, 700.

 $\mathbf{R}_{f} = 0.3$ (5% EtOAc/pentane).

Ethyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-4-carboxylate (3q)



Compound **3q** was prepared according to general procedure 3a using ethyl 1*H*-indole-4carboxylate (114 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (21 mg, 30%).

¹**H NMR** (500 MHz, CDCl₃) δ 8.91 (d, J = 6.0 Hz, 1H), 7.91 (dd, J = 7.6, 0.9 Hz, 1H), 7.55 (dt, J = 8.1, 1.0 Hz, 1H), 7.34 (dd, J = 8.6, 6.6 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.07 (d, J = 2.1 Hz, 1H), 5.78 (d, J = 40.7 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.46 (dt, J = 18.8, 7.4 Hz, 2H), 2.00 (p, J = 7.6 Hz, 2H), 1.48 (d, J = 14.3 Hz, 3H).

¹³**C NMR** (126 MHz, CDCl₃) δ 167.7, 161.6 (d, J = 262.8 Hz), 141.4, 137.5 (d, J = 3.0 Hz), 134.0, 128.67, 128.61, 127.7, 126.2, 123.5, 121.5, 121.4, 115.3, 104.0 (d, J = 2.9 Hz), 98.8 (d, J = 9.6 Hz), 60.7, 35.0, 32.1 (d, J = 26.1 Hz), 27.9, 14.6.

19FNMR (376 MHz, CDCl₃) δ -101.00 (dtd, J = 42.5, 18.9, 6.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₂H₂₂FNO₂) 352.1707; measured: 352.1691 = 4.54 ppm difference.

IR (neat) vmax/cm⁻¹: 3378, 2927, 1691, 1497, 1341, 1270, 1187, 752.

 $\mathbf{R}_{f} = 0.6$ (10% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indol-5-ol (3r)



Compound **3r** was prepared according to general procedure 3a using 1*H*-indol-5-ol (40 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (50 mg, 0.1 mmol)

and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (13 mg, 44%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.63 (s, 1H), 7.36 – 7.30 (m, 2H), 7.27 – 7.21 (m, 4H), 6.98 (d, J = 2.4 Hz, 1H), 6.77 (dd, J = 8.6, 2.4 Hz, 1H), 6.31 (d, J = 2.1 Hz, 1H), 5.67 (d, J = 40.8 Hz, 1H), 4.55 (s, 1H), 2.75 (t, J = 7.6 Hz, 2H), 2.43 (dt, J = 18.8, 7.4 Hz, 2H), 1.99 (p, J = 7.6 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 160.5 (d, J = 261.6 Hz), 149.6, 141.4, 132.9, 131.9 (d, J = 3.4 Hz), 128.7, 128.5, 126.1, 112.1, 111.3, 104.6, 101.9 (d, J = 3.2 Hz), 98.7 (d, J = 10.0 Hz), 34.9, 31.9 (d, J = 26.2 Hz), 27.8.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -102.60 (dtd, J = 40.8, 18.7, 6.0 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₂₀FNO) 332.1421; measured: 332.1414 = 2.11 ppm difference.

IR (neat) vmax/cm⁻¹: 3401, 2930, 1692, 1451, 1182, 699, 468, 408.

 $\mathbf{R}_{f} = 0.3$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-3-methyl-1H-indole (3s)



Compound **3s** was prepared according to general procedure 3a using 3-methyl-1*H*-indole (79 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (35 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.64 (d, J = 6.5 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.34 – 7.32 (m, 3H), 7.25 – 7.20 (m, 3H), 7.21 – 7.16 (m, 1H), 7.10 (t, J = 7.5 Hz, 1H), 5.73 (d, J = 41.3 Hz, 1H), 2.74 (t, J = 7.6 Hz, 2H), 2.45 (dt, J = 19.0, 7.5 Hz, 2H), 2.30 (s, 3H), 1.99 (p, J = 7.6 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 159.9 (d, J = 260.2 Hz), 141.6, 136.0 (d, J = 3.3 Hz), 128.6, 128.6, 128.4, 128.2, 126.2, 122.5, 119.3, 118.7, 110.5, 109.8 (d, J = 2.9 Hz), 96.7 (d, J = 9.9 Hz), 35.1, 32.3 (d, J = 26.6 Hz), 28.1, 8.8.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -104.97 (dtd, J = 41.1, 19.0, 6.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₂₀NF) 294.1653; measured: 294.1654 = 0.34 ppm difference.

IR (neat) vmax/cm⁻¹: 2948, 1394, 1317, 1062, 699.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-2-(2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indol-3-yl)ethan-1-ol (3t)



Compound **3t** was prepared according to general procedure 3b using 2-(1*H*-indol-3-yl)ethan-1-ol (97 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (25 mg, 39%).

¹**H NMR** (500 MHz, CDCl₃) δ 8.76 (d, J = 6.7 Hz, 1H), 7.55 (dd, J = 7.9, 1.0 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.23 – 7.18 (m, 4H), 7.10 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 5.78 (d, J = 41.0 Hz, 1H), 3.85 (t, J = 6.4 Hz, 2H), 3.02 (t, J = 6.4 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.44 (dt, J = 19.1, 7.5 Hz, 2H), 1.98 (ddd, J = 15.1, 8.3, 6.9 Hz, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 160.8 (d, J = 261.5 Hz), 141.5, 136.2 (d, J = 3.1 Hz), 129.6 (d, J = 1.9 Hz), 128.64, 128.62, 127.7, 126.2, 122.8, 119.7, 118.7 (d, J = 1.3 Hz), 110.8, 110.2 (d, J = 2.9 Hz), 96.5 (d, J = 9.4 Hz), 63.1, 35.1, 32.3 (d, J = 26.5 Hz), 28.0, 27.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -103.51 (dtd, J = 41.0, 19.1, 6.9 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₁H₂₂FNO) 324.1758; measured: 324.1773 = 4.63 ppm difference.

IR (neat) vmax/cm⁻¹: 3441, 2926, 1690, 1495, 1455, 1313, 1043, 742, 700.

 $\mathbf{R}_{f} = 0.4$ (5% EtOAc/pentane).

(Z)-2-(2-(2-fluoro-2-phenylvinyl)-1H-indol-3-yl)ethan-1-ol (3u)

Compound **3u** was prepared according to general procedure 3b using 2-(1*H*-indol-3-yl)ethan-1-ol (97 mg, 0.6 mmol) and (*Z*)-(2-fluoro-2-phenylvinyl)(mesityl)iodonium BF₄ (91 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (42 mg, 75%).

¹**H NMR** (500 MHz, CDCl₃) δ 8.97 (d, J = 6.4 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.64 – 7.61 (m, 1H), 7.48 – 7.45 (m, 2H), 7.42 – 7.40 (m, 2H), 7.31 – 7.24 (m, 1H), 7.16 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.63 (d, J = 41.1 Hz, 1H), 3.93 (t, J = 6.4 Hz, 2H), 3.17 (t, J = 6.4 Hz, 2H).

¹³**C NMR** (126 MHz, CDCl₃) δ 156.8 (d, J = 251.7 Hz), 136.6 (d, J = 3.5 Hz), 132.0 (d, J = 27.7 Hz), 129.9 (d, J = 2.3 Hz), 129.3, 128.9 (d, J = 2.3 Hz), 127.8, 124.1 (d, J = 7.8 Hz), 123.4, 119.9, 118.8 (d, J = 1.5 Hz), 112.7 (d, J = 3.3 Hz), 111.0, 95.5 (d, J = 11.3 Hz), 63.1, 28.1.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -118.06 (dd, J = 41.1, 7.0 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₈H₁₆FNO) 282.1289; measured: 282.1279 = 3.54 ppm

IR (neat) vmax/cm⁻¹: 3463, 2933, 1494, 1447, 1317, 1036, 1006, 761, 739, 466.

 $\mathbf{R}_{\mathbf{f}} = 0.4$ (5% EtOAc/pentane).

(Z)-2-(2-fluorododec-1-en-1-yl)-1-methyl-1H-indole (3v)

Compound **3v** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluorododec-1-en-1-yl)(mesityl)iodonium BF₄ (104 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (42 mg, 66%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.49 (dt, J = 7.9, 1.0 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.11 – 7.07 (m, 1H), 6.99 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 6.75 (d, J = 2.5 Hz, 1H), 5.55 (d, J = 36.6 Hz, 1H), 3.61 (s, 3H), 2.32 (dt, J = 17.8, 7.5 Hz, 2H), 1.60 – 1.51 (m, 2H), 1.29 – 1.16 (m, 15H), 0.83 – 0.79 (m, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 162.7 (d, J = 269.6 Hz), 136.9, 132.6 (d, J = 2.2 Hz), 128.4, 121.6, 120.5, 119.7, 109.1, 102.5 (d, J = 11.9 Hz), 95.6 (d, J = 11.6 Hz), 33.3 (d, J = 25.5 Hz), 32.0, 29.8, 29.7, 29.7, 29.5, 29.5, 29.1, 26.5, 22.8, 14.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -94.0 (dtd, J = 36.3, 17.8, 2.5 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₁H₃₀FN) 316.2435; measured: 316.2428 = 2.21 ppm

difference.

IR (neat) vmax/cm⁻¹: 2925, 2852, 1723, 1466, 1265, 1102, 733.

 $\mathbf{R}_{\mathbf{f}} = 0.7$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1-methyl-1H-indole (3w)



Compound **3w** was prepared according to general procedure 3b using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-3,3-dimethylbut-1-en-1-yl)(mesityl)iodonium BF₄ (87 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (35 mg, 75%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.49 (dt, J = 7.9, 1.0 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.09 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 6.99 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.75 (d, J = 2.7 Hz, 1H), 5.60 (d, J = 37.7 Hz, 1H), 3.61 (s, 3H), 1.19 (s, 9H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 169.5 (d, J = 272.8 Hz), 137.0, 132.8, 128.4, 121.5, 120.5, 119.7, 109.1, 102.4 (d, J = 12.6 Hz), 92.2 (d, J = 12.4 Hz), 35.8 (d, J = 23.0 Hz), 29.8, 27.5 (d, J = 2.6 Hz).

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -102.4 (dd, J = 37.7, 2.6 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₅H₁₈FNO) 232.1496; measured: 232.1485 = 4.73 ppm difference.

IR (neat) vmax/cm⁻¹: 2964, 1682, 1462, 1301, 1072, 870, 776, 506.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(Z)-2-(2-cyclopropyl-2-fluorovinyl)-1-methyl-1H-indole (3x)


Compound **3x** was prepared according to general procedure 3b using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-cyclopropyl-2-fluorovinyl)(mesityl)iodonium BF₄ (84 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (30 mg, 69%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.48 (dt, J = 7.8, 1.0 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.09 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.99 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.69 (dt, J = 2.7, 0.7 Hz, 1H), 5.64 (d, J = 36.2 Hz, 1H), 3.62 (s, 3H), 1.62 (dtt, J = 21.6, 8.3, 5.2 Hz, 1H), 0.87 – 0.83 (m, 2H), 0.81 – 0.75 (m, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ : 162.1 (d, J = 264.8 Hz), 136.9, 132.8 (d, J = 3.0 Hz), 128.4, 121.5, 120.4, 119.7, 109.1, 102.3 (d, J = 11.8 Hz), 94.0 (d, J = 13.3 Hz), 29.8, 13.4 (d, J = 28.3 Hz), 5.6 (d, J = 2.1 Hz).

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -108.2 (ddd, J = 36.1, 21.1, 2.7 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₄H₁₄FN) 216.1183; measured: 216.1183 = 0 ppm difference.

IR (neat) vmax/cm⁻¹: 2978, 1394, 1250, 1062, 895.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(Z)-2-(2-cyclohexyl-2-fluorovinyl)-1-methyl-1H-indole (3y)



Compound **3y** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-cyclohexyl-2-fluorovinyl)(mesityl)iodonium BF₄ (92 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (40 mg, 78%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.49 (dt, J = 7.8, 1.0 Hz, 1H), 7.19 – 7.17 (m, 1H), 7.09 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 6.99 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 5.52 (d, J = 37.6 Hz, 1H), 3.61 (s, 3H), 2.25 (ddd, J = 14.8, 7.2, 3.8 Hz, 1H), 1.95 – 1.90 (m, 2H), 1.79 – 1.74 (m, 2H), 1.68 – 1.63 (m, 1H), 1.36 – 1.14 (m, 5H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 166.6 (d, J = 271.0 Hz), 137.0, 132.7 (d, J = 2.0 Hz), 128.4, 121.5, 120.5, 119.7, 109.1, 102.4 (d, J = 12.1 Hz), 93.5 (d, J = 11.6 Hz), 41.7 (d, J = 23.7 Hz), 30.2, 30.2, 29.8, 26.1, 26.0.

¹⁹**F NMR** (377 MHz, CDCl₃) δ : -98.5 (ddd, J = 37.6, 14.8, 2.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₇H₂₀NF) 258.1653; measured: 258.1652 = 0.39 ppm

IR (neat) vmax/cm⁻¹: 2929, 2854, 1721, 1466, 1317, 741.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).



Compound **3z** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(4-(benzyloxy)-2-fluorobut-1-en-1-yl)(mesityl)iodonium BF₄ (102 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (14 mg, 22%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.58 (d, J = 7.9 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.31 – 7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 5.75 (d, J = 36.7 Hz, 1H), 4.57 (s, 2H), 3.75 (t, J = 6.4 Hz, 2H), 3.68 (s, 3H), 2.72 (dt, J = 17.6, 6.4 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 138.2, 136.9, 132.3, 128.6, 128.3, 127.9, 127.9, 121.7, 120.6, 119.7, 102.8 (d, J = 12.0 Hz), 97.3 (d, J = 10.8 Hz), 73.3, 66.5, 34.1 (d, J = 25.8 Hz), 29.8.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -95.45 (dt, J = 35.7, 17.2 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₀H₂₀FNO) 310.1602; measured: 310.1611 = 2.9 ppm

IR (neat) vmax/cm⁻¹: 2937, 2857, 1733, 1546, 1426, 1217, 760.

 $\mathbf{R}_{\mathbf{f}} = 0.5$ (5% EtOAc/pentane).

2-((*Z*)-2-fluoro-3-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)-1-methyl-1*H*-indole (3aa)



Compound **3aa** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.15 mmol) and ((*Z*)-2-fluoro-3-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)(mesityl)iodonium BF₄ (109 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (24 mg, 35%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.60 (dt, J = 7.9, 1.0 Hz, 1H), 7.29 (dd, J = 8.3, 1.0 Hz, 1H), 7.20 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.09 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.92 (d, J = 2.2 Hz, 1H), 5.97 (d, J = 35.9 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.16 – 4.10 (m, 1H), 3.73 (s, 3H), 3.25 (td, J = 10.6, 4.2 Hz, 1H), 2.29 (pd, J = 7.0, 2.7 Hz, 1H), 2.15 (dtd, J = 12.1, 3.6, 1.8 Hz, 1H), 1.71 – 1.63 (m, 2H), 1.44 – 1.21 (m, 3H), 1.07 – 0.99 (m, 1H), 0.98 – 0.93 (m, 6H), 0.91 – 0.85 (m, 1H), 0.82 (d, J = 7.0 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 158.4 (d, J = 270.6 Hz), 137.1, 131.7 (d, J = 2.8 Hz), 128.2, 122.0, 120.8, 119.8, 109.2, 103.5 (d, J = 12.0 Hz), 97.7 (d, J = 8.7 Hz), 79.9, 66.9 (d, J = 31.4 Hz), 48.4, 40.5, 34.6, 31.7, 29.8, 25.9, 23.5, 22.5, 21.1, 16.4.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -104.49 (dtd, J = 35.9, 13.5, 2.3 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₂H₃₀FNO) 344.2384; measured: 344.2373 = 3.20 ppm difference.

IR (neat) vmax/cm⁻¹: 2952, 2920, 1462, 1317, 1235, 1084, 784, 748.

 $\mathbf{R}_{\mathbf{f}} = 0.5$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)isoindoline-1,3-dione (3ab)



Compound **3ab** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.15 mmol)and (*Z*)-(3-(1,3-dioxoisoindolin-2-yl)-2-fluoroprop-1-en-1-yl)(mesityl)iodonium BF₄ (108 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (21 mg, 31%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.90 (dd, J = 5.5, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.0 Hz, 2H), 7.57 (dt, J = 8.0, 1.0 Hz, 1H), 7.19 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.07 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 6.08 (d, J = 34.9 Hz, 1H), 4.61 (d, J = 16.4 Hz, 2H), 3.73 (s, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 167.7, 154.4 (d, J = 271.3 Hz), 137.2, 134.4, 132.1, 131.0, 128.1, 123.8, 122.3, 120.9, 119.9, 109.3, 104.1 (d, J = 12.2 Hz), 99.8 (d, J = 9.2 Hz), 39.3 (d, J = 30.4 Hz), 29.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -103.93 (dtd, J = 35.0, 16.4, 2.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₁₅FN₂O₂) 335.1190; measured: 335.1191 = 0.30 ppm difference.

IR (neat) vmax/cm⁻¹: 2922, 1773, 1715, 1466, 1388, 1103, 949, 731, 530.

 $\mathbf{R}_{f} = 0.6$ (15% EtOAc/pentane).

(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-N-(4-fluorobenzyl)-4-nitrobenzenesulfonamide (3ac)

Compound **3ac** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (20 mg, 0.15 mmol) and (*Z*)-(2-fluoro-3-((*N*-(4-fluorobenzyl)-4-nitrophenyl)sulfonamido)prop-1-en-1-yl)(mesityl)iodonium BF₄ (70 mg, 0.1 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless sticky solid (37 mg, 74%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.34 – 8.30 (m, 2H), 8.05 – 8.03 (m, 2H), 7.56 (dt, J = 7.9, 1.0 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.28 – 7.20 (m, 2H), 7.11 – 7.04 (m, 3H), 6.69 (d, J = 2.4 Hz, 1H), 5.70 (d, J = 35.4 Hz, 1H), 4.47 (s, 2H), 4.12 (d, J = 18.7 Hz, 2H), 3.63 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 162.8 (d, J = 247.8 Hz), 153.85 (d, J = 271.4 Hz), 150.0, 145.7, 137.1, 130.3 (d, J = 8.0 Hz), 129.9 (d, J = 3.2 Hz), 128.5, 127.8, 124.3, 122.7, 120.9, 120.2, 116.0, 115.8, 109.2, 104.4 (d, J = 12.4 Hz), 101.1 (d, J = 9.2 Hz), 50.3, 47.7zz (d, J = 26.6 Hz), 29.7.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -103.9 (dtd, J = 35.1, 18.6, 2.5 Hz), -113.1 (tt, J = 8.5, 5.2 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₅H₂₁F₂N₃O₄S) 498.1294; measured: 498.1273 = 4.22 ppm

difference.

IR (neat) vmax/cm⁻¹: 2958, 1603, 1529, 1348, 1163, 854, 743, 605, 571.

 $\mathbf{R}_{\mathbf{f}} = 0.5$ (25% EtOAc/pentane).

(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide (3ad)



Compound **3ad** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (20 mg, 0.15 mmol) and (*Z*)-(2-fluoro-3-((4-methylphenyl)sulfonamido)prop-1-en-1-yl)(mesityl)iodonium BF₄ (56 mg, 0.1 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless sticky solid (11 mg, 30%).

¹**H NMR** (400 MHz, CDCl₃) δ : 7.69 (d, J = 8.4 Hz, 2H), 7.48 (dt, J = 7.9, 1.0 Hz, 1H), 7.20 – 7.17 (m, 3H), 7.13 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.01 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 5.73 (d, J = 35.6 Hz, 1H), 3.86 (ddd, J = 13.8, 6.5, 0.7 Hz, 2H), 3.55 (s, 3H), 2.25 (s, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) $\delta:$ 155.0 (d, J = 268.5 Hz), 143.9, 137.0, 129.8, 129.7, 127.9, 127.1, 126.5, 122.2, 120.7, 119.8, 109.1, 103.8 (d, J = 12.1 Hz), 98.6 (d, J = 9.1 Hz), 44.5 (d, J = 31.4 Hz), 29.6, 21.4.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -105.0 (dtd, J = 35.7, 13.7, 2.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₉H₁₉FN₂O₂S) 359.1240; measured: 359.1224 = 4.46 ppm difference.

IR (neat) vmax/cm⁻¹: 3664, 2978, 1394, 1251, 1062.

 $\mathbf{R}_{f} = 0.5$ (25% EtOAc/pentane).

(Z)-N-(2-fluoro-3-(1-methyl-1*H*-indol-2-yl)allyl)-*N*-(4-fluorophenyl)-4methylbenzenesulfonamide (3ae)



Compound **3ae** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-3-((*N*-(4-fluorophenyl)-4-methylphenyl)sulfonamido)prop-1-en-1-yl)(mesityl)iodonium BF₄ (131 mg, 0.2 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless sticky solid (54 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.57 – 7.53 (m, 3H), 7.28 – 7.23 (m, 3H), 7.19 (ddd, J = 8.3, 6.9, 1.2 Hz, 1H), 7.12 – 7.07 (m, 3H), 7.02 – 6.96 (m, 2H), 6.79 (d, J = 2.3 Hz, 1H), 5.78 (d, J = 34.9 Hz, 1H), 4.48 (d, J = 15.4 Hz, 2H), 3.60 (s, 3H), 2.43 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 158.8 (d, J = 472.8 Hz), 144.1, 137.2, 135.8, 134.9 (d, J = 3.3 Hz), 131.4 (d, J = 8.8 Hz), 130.9, 129.7, 128.0, 127.9, 122.4, 120.8, 120.0, 116.5, 116.2, 109.3, 103.9 (d, J = 11.8 Hz), 100.3 (d, J = 9.5 Hz), 53.1 (d, J = 29.6 Hz), 29.8, 21.7.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -102.8 (dtd, J = 35.3, 15.3, 2.4 Hz), -112.1 (tt, J = 8.0, 4.8 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₅H₂₂NF₂N2O₂S) 453.1443; measured: 453.1459 = 3.53 ppm

IR (neat) vmax/cm⁻¹: 2977, 1394, 1257, 1063, 879, 551.

 $\mathbf{R}_{f} = 0.5$ (15% EtOAc/pentane).

(Z)-N-(4-bromophenyl)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4methylbenzenesulfonamide (3af)



Compound **3af** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (20 mg, 0.15 mmol) and (Z)-(3-((N-(4-bromophenyl)-4-methylphenyl)sulfonamido)-2-fluoroprop-1-en-1-yl)(mesityl)iodonium BF₄ (65 mg, 0.1 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless sticky solid (33 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.57 – 7.52 (m, 3H), 7.45 – 7.41 (m, 2H), 7.28 – 7.23 (m, 3H), 7.19 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.07 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.03 – 6.99 (m, 2H), 6.78 (d, J = 2.3 Hz, 1H), 5.79 (d, J = 35.0 Hz, 1H), 4.48 (d, J = 15.1 Hz, 2H), 3.60 (s, 3H), 2.43 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 154.8 (d, J = 270.7 Hz), 144.0, 138.0, 137.0, 135.5, 132.5, 130.8, 130.7, 129.7, 127.9, 127.7, 122.5, 122.3, 120.7, 119.9, 109.2, 103.8 (d, J = 11.9 Hz), 100.2 (d, J = 9.4 Hz), 52.6 (d, J = 29.9 Hz), 29.7, 21.6.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -102.9 (dtd, J = 35.1, 15.0, 2.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₅H₂₂BrFN₂O₂S) 513.0642; measured: 513.0618 = 4.68 ppm

difference.

IR (neat) vmax/cm⁻¹: 2914, 1483, 1348, 1318, 1157, 1071, 877, 750, 583, 545.

 $\mathbf{R}_{f} = 0.5 (15\% \text{ EtOAc/pentane}).$

(Z)-N-cyclopropyl-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide (3ag)



Compound **3ag** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (20 mg, 0.15 mmol) and (*Z*)-(3-((N-cyclopropyl-4-methylphenyl)sulfonamido)-2-fluoroprop-1en-1-yl)(mesityl)iodonium BF₄ (60 mg, 0.1 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless sticky solid (28 mg, 70%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.78 - 7.75 (m, 2H), 7.58 (dt, J = 7.9, 1.0 Hz, 1H), 7.30 - 7.27 (m, 2H), 7.21 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.09 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 6.79 (d, J = 2.3 Hz, 1H), 5.96 (d, J = 35.2 Hz, 1H), 4.16 (d, J = 16.4 Hz, 2H), 3.71 (s, 3H), 2.41 (s, 3H), 2.22 (dtd, J = 6.8, 3.2, 1.2 Hz, 1H), 0.93 (td, J = 4.3, 3.1 Hz, 2H), 0.77 - 0.70 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 156.5 (d, J = 272.7 Hz), 143.9, 135.5, 129.7, 128.1, 128.0, 122.3, 120.8, 120.0, 109.3, 103.9 (d, J = 12.1 Hz), 99.8 (d, J = 9.6 Hz), 52.0 (d, J = 28.9 Hz), 30.9, 29.9, 21.7, 8.0.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -100.7 (dt, J = 34.0, 16.4 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₂H₂₃FN₂O₂S) 399.1537; measured: 399.1519 = 4.51 ppm difference.

IR (neat) vmax/cm⁻¹: 2943, 1598, 1466, 1323, 1157, 815, 666, 547.

 $\mathbf{R}_{f} = 0.5$ (15% EtOAc/pentane).

(Z)-3-fluoro-4-(1-methyl-1H-indol-2-yl)but-3-en-2-one (3ah)



Compound **3ah** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-3-oxobut-1-en-1-yl)(mesityl)iodonium BF₄ (67 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (13 mg, 30%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 (dt, J = 8.0, 1.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.22 (d, J = 2.0 Hz, 1H), 7.13 (ddd, J = 8.0, 6.4, 1.5 Hz, 1H), 7.05 (d, J = 33.7 Hz, 1H), 3.81 (s, 3H), 2.45 (d, J = 3.8 Hz, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 192.0 (d, J = 34.0 Hz), 154.5 (d, J = 274.1 Hz), 138.5, 130.1 (d, J = 5.0 Hz), 128.1, 124.2, 121.9, 120.6, 109.7, 108.7 (d, J = 15.1 Hz), 104.1 (d, J = 8.2 Hz), 29.9, 25.8 (d, J = 1.5 Hz).

¹⁹**F NMR** (377 MHz, CDCl₃) δ -119.71 (dqd, J = 33.7, 3.8, 2.0 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₃H₁₂FNO) 218.0976; measured: 218.0972 = 1.83 ppm difference.

IR (neat) vmax/cm⁻¹: 2976, 1677, 1624, 1461, 1394, 1324, 1255, 1065, 869.

 $\mathbf{R}_{\mathbf{f}} = 0.5$ (5% EtOAc/pentane).

Ethyl (z)-2-fluoro-3-(1-methyl-1H-indol-2-yl)acrylate (3ai)



Compound **3ai** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(3-ethoxy-2-fluoro-3-oxoprop-1-en-1-yl)(mesityl)iodonium BF₄ (73 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (16 mg, 32%).

¹**H NMR** (400 MHz, CDCl₃) δ : 7.66 – 7.63 (m, 1H), 7.33 – 7.25 (m, 2H), 7.19 (d, J = 2.0 Hz, 1H), 7.15 – 7.07 (m, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 161.4 (d, J = 32.6 Hz), 147.2 (d, J = 270.4 Hz), 138.2, 129.9 (d, J = 5.1 Hz), 128.0, 123.9, 121.7, 120.5, 109.7, 108.2 (d, J = 14.7 Hz), 106.7 (d, J = 7.5 Hz), 62.1, 29.9, 14.4.

¹⁹**F NMR** (376 MHz, CDCl₃) δ: -121.3 (d, J = 32.4 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₄H₁₄FNO₂) 248.1081; measured: 248.1072 = 3.63 ppm

difference.

IR (neat) vmax/cm⁻¹: 2991, 1716, 1661, 1461, 1367, 1255, 1095, 790, 752, 646.

 $\mathbf{R}_{f} = 0.5 (5\% \text{ EtOAc/pentane}).$

(Z)-2-(2-fluoro-2-phenylvinyl)-1-methyl-1H-indole (3aj)



Compound **3aj** was prepared according to general procedure 4 using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-2-phenylvinyl)(mesityl)iodonium BF₄ (91 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (29 mg, 58%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.61 – 7.60 (m, 2H), 7.55 (dt, J = 7.8, 1.0 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.18 – 7.16 (m, 1H), 7.03 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.99 (d, J = 2.6 Hz, 1H), 6.40 (d, J = 36.5 Hz, 1H), 3.73 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 158.1 (d, J = 260.8 Hz), 137.5, 132.5 (d, J = 7.4 Hz), 129.3, 128.9 (d, J = 2.3 Hz), 128.5, 124.3, 124.2, 122.2, 120.9, 120.0, 109.2, 104.1 (d, J = 13.7 Hz), 95.2 (d, J = 13.2 Hz), 29.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ : -108.7 (dd, J = 36.4, 2.4 Hz).

HRMS (EI+) calc: [M+H]⁺ (C₁₇H₁₄NF) 252.1183; measured: 252.1185 = 0.79 ppm

IR (neat) vmax/cm⁻¹: 2920, 1463, 1318, 1075, 1014, 760, 886, 612.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-2-phenylvinyl)-1H-indole (3ak)



Compound **3ak** was prepared according to general procedure 3a using 1*H*-indole (70 mg, 0.6 mmol) and (*Z*)-(2-fluoro-2-phenylvinyl)(mesityl)iodonium BF₄ (91 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (25 mg, 51%).

¹**H NMR** (400 MHz, CDCl₃) δ: 8.89 (s, 1H), 7.65 – 7.58 (m, 3H), 7.45 – 7.37 (m, 4H), 7.21 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.10 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 6.61 (d, J = 2.1 Hz, 1H), 6.50 (d, J = 40.8 Hz, 1H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 156.7 (d, J = 251.7 Hz), 137.1, 132.1, 131.8, 129.2, 128.9 (d, J = 2.3 Hz), 128.1, 124.1, 124.0, 123.0, 120.6, 120.3, 110.9, 104.8 (d, J = 3.7 Hz), 97.9 (d, J = 11.9 Hz).

¹⁹**F NMR** (376 MHz, CDCl₃) δ : -117.6 (dd, J = 40.9, 6.2 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₆H₁₂NF) 238.1027; measured: 238.1022 = 2.10 ppm

IR (neat) vmax/cm⁻¹: 3437, 2979, 1410, 1283, 1077, 785, 749, 608.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-2-(4-fluorophenyl)vinyl)-1-methyl-1H-indole (3al)



Compound **3al** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl)(mesityl)iodonium BF₄ (94 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (38 mg, 70%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.59 – 7.54 (m, 3H), 7.24 – 7.21 (m, 1H), 7.14 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.07 – 7.01 (m, 3H), 6.97 (dt, J = 2.8, 0.7 Hz, 1H), 6.31 (d, J = 36.4 Hz, 1H), 3.72 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ : 163.4 (d, J = 249.9 Hz), 157.3 (d, J = 262.4 Hz), 137.5, 132.4, 128.4, 126.2, 122.3, 120.9, 120.0, 116.1 (d, J = 2.1 Hz), 115.9 (d, J = 2.1 Hz), 109.2, 104.1 (d, J = 13.7 Hz), 95.0 (d, J = 11.1 Hz), 29.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ : -108.1 (dd, J = 36.5, 2.3 Hz), -111.3 (dddd, J = 13.7, 8.5, 5.2, 1.6 Hz).

HRMS (EI+) calc: [M+H]⁺ (C₁₇H₁₃F₂N) 270.1085; measured: 270.1089 = 1.48 ppm difference.

IR (neat) vmax/cm⁻¹: 2952, 1600, 1505, 1467, 1223, 1071, 831, 735, 515.

 $\mathbf{R}_{\mathbf{f}} = 0.6$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)-1-methyl-1H-indole (3am)



Compound **3am** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)(mesityl)iodonium BF₄ (104 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (40 mg, 62%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.78 – 7.75 (m, 2H), 7.68 – 7.61 (m, 3H), 7.32 – 7.29 (m, 1H), 7.26 – 7.22 (m, 1H), 7.14 – 7.10 (m, 2H), 6.57 (d, J = 36.1 Hz, 1H), 3.81 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ 156.31 (d, J = 260.4 Hz), 137.5, 131.7, 130.9, 130.5, 128.2, 125.7 (q, J = 3.62 Hz), 125.0 (q, J = 271.7 Hz), 124.2, 124.1, 122.6, 121.0, 120.1, 109.2, 105.0 (d, J = 14.2 Hz), 97.2 (d, J = 12.9 Hz), 29.8.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -110.0 (dd, J = 36.0, 2.8 Hz), -62.71.

HRMS (ESI+) calc: $[M+H]^+$ (C₁₈H₁₃F₄N) 320.1057; measured: 320.1042 = 4.69 ppm difference.

IR (neat) vmax/cm⁻¹: 2963, 1613, 1463, 1319, 1112, 1066, 825, 735, 614.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-2-(2-fluoro-2-(thiophen-3-yl)vinyl)-1-methyl-1H-indole (3an)



Compound **3an** was prepared according to general procedure 3a using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-2-(thiophen-3-yl)vinyl)(mesityl)iodonium BF₄ (92 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (36 mg, 70%).

¹**H NMR** (400 MHz, CDCl₃) δ: 7.54 (dt, J = 7.9, 1.0 Hz, 1H), 7.49 (dt, J = 3.0, 1.0 Hz, 1H), 7.30 (dt, J = 5.1, 2.9 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.15 – 7.11 (m, 1H), 7.03 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.94 (s, 1H), 6.20 (d, J = 36.5 Hz, 1H), 3.71 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃) δ: 155.1 (d, J = 257.9 Hz), 137.3, 134.7 (d, J = 29.6 Hz), 132.2 (d, J = 3.1 Hz), 128.3, 126.9 (d, J = 2.1 Hz), 123.9 (d, J = 6.6 Hz), 122.1 (d, J = 4.7 Hz), 122.0, 120.7, 119.8, 109.0, 103.7 (d, J = 13.2 Hz), 94.9 (d, J = 12.4 Hz), 29.8.

¹⁹**F NMR** (377 MHz, CDCl₃) δ : -105.5 (dd, J = 36.4, 2.9 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₅H₁₂FNS) 258.0747; measured: 258.0745 = 0.77 ppm difference.

IR (neat) vmax/cm⁻¹: 2978, 1394, 1250, 1061, 892.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(E)-2-(2-fluorododec-1-en-1-yl)-1H-indole (3ao)



Compound **3ao** was prepared according to general procedure 3a using 1*H*-indole (70 mg, 0.6 mmol) and (*E*)-(2-fluorododec-1-en-1-yl)(mesityl)iodonium BF₄ (104 mg, 0.2 mmol) and purified using silica gel chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (31 mg, 52%).

 $\label{eq:homoson} {}^{1}\textbf{H} \ \textbf{NMR} \ (400 \ \text{MHz}, \ \text{CDCI}_3) \ \delta: \ 7.77 \ (s, \ 1\text{H}), \ 7.49 \ (dq, \ J = 7.7, \ 0.9 \ \text{Hz}, \ 1\text{H}), \ 7.24 \ (dq, \ J = 8.0, \ 1.0 \ \text{Hz}, \ 1\text{H}), \ 7.10 \ -7.00 \ (m, \ 2\text{H}), \ 6.31 \ (dt, \ J = 2.0, \ 0.9 \ \text{Hz}, \ 1\text{H}), \ 6.02 \ (dd, \ J = 20.2, \ 0.8 \ \text{Hz}, \ 1\text{H}), \ 2.53 \ (dt, \ J = 23.3, \ 7.6 \ \text{Hz}, \ 2\text{H}), \ 1.63 \ -1.55 \ (m, \ 2\text{H}), \ 1.35 \ -1.19 \ (m, \ 14\text{H}), \ 0.82 \ -0.79 \ (m, \ 3\text{H}).$

¹³**C NMR** (101 MHz, CDCl₃) δ : 164.5 (d, J = 256.5 Hz), 136.2, 131.8 (d, J = 15.8 Hz), 129.0, 122.1, 120.3, 110.6, 101.6 (d, J = 3.7 Hz), 99.9 (d, J = 33.1 Hz), 32.0, 30.1 (d, J = 26.5 Hz), 29.7, 29.7, 29.5, 29.5, 29.4, 26.3, 22.8, 14.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ: -95.0 (td, J = 23.4, 20.1 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₂₀H₂₈FN) 302.2279; measured: 302.2275 = 1.32 ppm difference.

IR (neat) vmax/cm⁻¹: 2991, 2904, 1394, 1250 1062, 891, 749.

 $\mathbf{R}_{f} = 0.8$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1,2,5-trimethyl-1H-pyrrole (5a)



Compound **5a** was prepared according to general procedure 3c using 1,2,5-trimethyl-1*H*-pyrrole (33 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (30 mg, 56%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.21 – 7.16 (m, 2H), 7.12 – 7.08 (m, 3H), 6.10 (dd, J = 3.5, 1.1 Hz, 1H), 5.25 (d, J = 40.5 Hz, 1H), 3.26 (s, 3H), 2.61 – 2.57 (m, 2H), 2.22 (dt, J = 18.2, 7.3 Hz, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 1.84 – 1.76 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 156.90 (d, J = 257.7 Hz), 142.2, 128.7, 128.5, 125.9, 112.1, 105.7 (d, J = 9.4 Hz), 99.3 (d, J = 12.1 Hz), 35.1, 32.5 (d, J = 27.0 Hz), 30.3, 28.4, 12.4, 10.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -109.07 (dtd, J = 40.3, 18.3, 3.6 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₈H₂₂FN) 272.1809; measured: 272.1806 = 1.10 ppm difference.

IR (neat) vmax/cm⁻¹: 2922, 1699, 1453, 1378, 1259, 1064, 699.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole (5b)



Compound **5b** was prepared according to general procedure 3c using 1-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole (60 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (32 mg, 44%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.22 – 7.17 (m, 2H), 7.13 – 7.08 (m, 3H), 7.00 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.28 – 6.18 (m, 1H), 5.30 (d, J = 40.5 Hz, 1H), 3.76 (s, 3H), 2.66 – 2.57 (m, 2H), 2.25 (dt, J = 18.3, 7.5 Hz, 2H), 1.91 (s, 3H), 1.88 (s, 3H), 1.82 (t, J = 7.5 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 159.1, 157.3 (d, J = 258.1 Hz), 142.2, 131.6, 129.4, 129.3, 128.7, 128.5, 126.5, 125.9, 114.4, 112.7, 106.2 (d, J = 9.4 Hz), 99.2 (d, J = 11.9 Hz), 55.6, 35.1, 32.5 (d, J = 26.8 Hz), 28.4, 12.9, 10.9.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -108.44 (dtd, J = 40.3, 18.3, 3.6 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₄H₂₆FNO) 364.2071; measured: 364.2065 = 1.65 ppm difference.

IR (neat) vmax/cm⁻¹: 2920, 1511, 1453, 1292, 1245, 1033, 833, 699, 583.

 $\mathbf{R}_{f} = 0.5$ (5% EtOAc/pentane).

(Z)-1-cyclopropyl-3-(2-fluoro-5-phenylpent-1-en-1-yl)-2,5-dimethyl-1H-pyrrole (5c)



Compound **5c** was prepared according to general procedure 3c using 1-cyclopropyl-2,5dimethyl-1*H*-pyrrole (41 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (20 mg, 34%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.29 (m, 2H), 7.23 – 7.20 (m, 3H), 6.19 (d, J = 3.5 Hz, 1H), 5.35 (d, J = 40.6 Hz, 1H), 2.89 (tt, J = 7.0, 4.1 Hz, 1H), 2.73 – 2.69 (m, 2H), 2.38 – 2.30 (m, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 1.95 – 1.88 (m, 2H), 1.07 – 1.01 (m, 2H), 0.90 (dt, J = 4.0, 1.6 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 157.1 (d, J = 257.9 Hz), 142.2, 130.4 (d, J = 2.3 Hz), 128.7, 128.4, 127.6, 125.9, 112.3, 106.2 (d, J = 9.2 Hz), 99.1 (d, J = 12.1 Hz), 35.1, 32.5 (d, J = 27.1 Hz), 28.4, 25.8, 13.4, 11.1, 7.7.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -108.90 (dtd, J = 40.3, 18.4, 3.3 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₀H₂₄FN) 298.1966; measured: 298.1961 = 1.68 ppm difference.

IR (neat) vmax/cm⁻¹: 2938, 1657, 1453, 1394, 1228, 1052, 742, 699.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-2,5-dimethyl-1H-pyrrole (5d)

Compound **5d** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (40 mg, 58%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 (s, 1H), 7.23 – 7.19 (m, 2H), 7.14 – 7.11 (m, 3H), 6.10 – 6.08 (m, 1H), 5.25 (d, J = 40.6 Hz, 1H), 2.63 – 2.60 (m, 2H), 2.24 (dt, J = 18.1, 7.3 Hz, 2H), 2.14 (s, 3H), 2.11 (s, 3H), 1.83 (dtd, J = 9.3, 7.8, 6.7 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 157.1 (d, J = 257.9 Hz), 142.2, 128.7, 128.5, 126.1, 125.9, 123.5, 113.3, 106.6 (d, J = 9.3 Hz), 99.0 (d, J = 12.4 Hz), 35.2, 32.4 (d, J = 27.0 Hz), 28.4, 13.0, 11.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -108.93 (dtd, J = 40.3, 18.2, 3.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₇H₂₀NF) 258.1653; measured: 258.1645 = 3.10 ppm difference.

IR (neat) vmax/cm⁻¹: 3668, 2978, 1394, 1251, 1061, 891.

 $\mathbf{R}_{f} = 0.6$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-2,5-dimethyl-1H-pyrrole (5e)

Compound **5e** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*Z*)-(2-fluoro-3,3-dimethylbut-1-en-1-yl)(mesityl)iodonium BF₄ (87 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (24 mg, 62%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.38 (s, 1H), 6.10 – 6.09 (m, 1H), 5.29 (d, J = 41.8 Hz, 1H), 2.14 (d, J = 0.9 Hz, 3H), 2.12 (s, 3H), 1.11 (d, J = 0.8 Hz, 9H).

¹³**C NMR** (101 MHz, CDCl₃) δ 164.7 (d, J = 261.0 Hz), 128.1, 126.1, 123.7, 113.3, 106.5 (d, J = 10.2 Hz), 94.9 (d, J = 13.2 Hz), 35.2 (d, J = 24.4 Hz), 27.8 (d, J = 2.5 Hz), 13.0, 11.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -116.59 (dd, J = 41.7, 3.7 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₂H₁₈FN) 196.1496; measured: 196.1499 = 1.53 ppm difference.

IR (neat) vmax/cm⁻¹: 3572, 2970, 1636, 1394, 1068, 866.

 $\mathbf{R}_{f} = 0.8$ (5% EtOAc/pentane).

(Z)-3-(2-cyclohexyl-2-fluorovinyl)-2,5-dimethyl-1H-pyrrole (5f)

Compound **5f** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*Z*)-(2-cyclohexyl-2-fluorovinyl)(mesityl)iodonium BF₄ (92 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (29 mg, 65%).

 ^1H NMR (400 MHz, CDCl₃) δ 7.49 (s, 1H), 6.20 – 6.18 (m, 1H), 5.31 (s, 1H), 2.26 – 2.18 (m, 7H), 1.97 – 1.94 (m, 2H), 1.84 – 1.81 (m, 2H), 1.74 – 1.70 (m, 1H), 1.41 – 1.24 (m, 5H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 161.8 (d, J = 259.2 Hz), 126.1 (d, J = 2.5 Hz), 123.5, 113.3, 106.5 (d, J = 9.5 Hz), 96.2 (d, J = 12.4 Hz), 41.4 (d, J = 25.0 Hz), 30.5, 30.4, 26.2, 26.1, 13.0, 11.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -112.91 (ddd, J = 41.8, 15.4, 3.6 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₄H₂₀F) 222.1653; measured: 222.1648 = 2.25 ppm

difference.

IR (neat) vmax/cm⁻¹: 2927, 2854, 1638, 1448, 1157, 1002.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-2-(4-fluorophenyl)vinyl)-2,5-dimethyl-1H-pyrrole (5g)

Compound **5g** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl)(mesityl)iodonium BF₄ (94 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (28 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (s, 1H), 7.55 – 7.50 (m, 2H), 7.04 (t, J = 8.7 Hz, 2H), 6.30 (s, 1H), 6.12 (d, J = 40.3 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H).

¹³**C NMR** (126 MHz, CDCl₃) δ 162.4 (d, J = 247.2 Hz), 153.2 (d, J = 248.7 Hz), 130.3 (dd, J = 28.5, 3.3 Hz), 126.6 (d, J = 2.8 Hz), 125.6 (d, J = 1.7 Hz), 125.2 (t, J = 7.6 Hz), 115.5 (dd, J = 21.9, 2.1 Hz), 113.5, 106.7 (d, J = 10.1 Hz), 99.08 (dd, J = 14.0, 2.1 Hz), 13.0, 11.5.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -114.18 (t, J = 7.8 Hz), -121.33 (d, J = 40.2 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₄H₁₃F₂N) 234.1082; measured: 234.1089 = 2.99 ppm difference.

IR (neat) vmax/cm⁻¹: 3668, 2978, 1506, 1394, 1231, 1061, 833.

 $\mathbf{R}_{\mathbf{f}} = 0.5$ (5% EtOAc/pentane).

(Z)-3-(2-fluoro-2-(thiophen-3-yl)vinyl)-2,5-dimethyl-1H-pyrrole (5h)



Compound **5h** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*Z*)-(2-fluoro-2-(thiophen-3-yl)vinyl)(mesityl)iodonium BF₄ (92 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (27 mg, 62%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.50 – 7.49 (m, 1H), 7.26 (dt, J = 3.1, 1.0 Hz, 1H), 7.21 (dt, J = 5.1, 3.0 Hz, 1H), 7.14 (dt, J = 5.0, 1.2 Hz, 1H), 6.21 – 6.19 (m, 1H), 5.94 (d, J = 40.3 Hz, 1H), 2.19 (s, 3H), 2.16 (d, J = 0.9 Hz, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 151.5 (d, J = 246.8 Hz), 136.2 (d, J = 30.6 Hz), 126.6 (d, J = 2.6 Hz), 126.2 (d, J = 2.1 Hz), 125.3 (d, J = 1.6 Hz), 124.0 (d, J = 6.6 Hz), 119.1 (d, J = 4.6 Hz), 113.4, 106.7 (d, J = 9.8 Hz), 99.2 (d, J = 12.9 Hz), 13.0, 11.4.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -118.17 (dt, J = 40.6, 3.5 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₁₂H₁₂FNS) 222.0747; measured: 222.0752 = 2.25 ppm difference.

IR (neat) vmax/cm⁻¹: 3680, 2978, 1394, 1062, 891.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(E)-3-(2-fluorododec-1-en-1-yl)-2,5-dimethyl-1H-pyrrole (5i)



Compound **5i** was prepared according to general procedure 3c using 2,5-dimethyl-1*H*-pyrrole (57 mg, 0.6 mmol) and (*E*)-(2-fluorododec-1-en-1-yl)(mesityl)iodonium BF₄ (104 mg, 0.2 mmol) and purified using neutral alumina chromatography (5% EtOAc/pentane) to yield a colourless sticky solid (22 mg, 39%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.44 (s, 1H), 5.84 (d, J = 22.9 Hz, 1H), 5.68 (d, J = 2.7 Hz, 1H), 2.38 (dt, J = 23.8, 7.7 Hz, 2H), 2.15 (s, 3H), 2.08 (s, 3H), 1.56 – 1.47 (m, 2H), 1.32 – 1.19 (m, 14H), 0.83 – 0.79 (m, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 160.0 (d, J = 244.6 Hz), 126.1, 124.4 (d, J = 5.6 Hz), 112.6 (d, J = 13.6 Hz), 105.2 (d, J = 1.6 Hz), 100.8 (d, J = 30.0 Hz), 32.1, 29.8, 29.7, 29.6, 29.5, 29.53, 29.4 (d, J = 27.8 Hz), 26.6, 22.8, 14.3, 13.0, 11.3.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -104.46 (q, J = 23.6 Hz).

HRMS (ESI+) calc: [M+H]⁺ (C₁₈H₃₁FN) 280.2441; measured: 280.2432 = 3.2 ppm difference.

IR (neat) vmax/cm⁻¹: 3668, 2971, 1723, 1393, 1251, 1062, 894.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(Z)-N-(2-fluoro-3-(1-methyl-1*H*-pyrrolo[2,3-b]pyridin-2-yl)allyl)-*N*-(4-fluorophenyl)-4methylbenzenesulfonamide (7a)



Compound **7a** was prepared according to general procedure 3a using 1-methyl-1*H*-pyrrolo[2,3-b]pyridine (40 mg, 0.3 mmol) and (*E*)-(2-fluorododec-1-en-1-yl)(mesityl)iodonium BF₄ (131 mg, 0.2 mmol) at 70 °C and purified using neutral alumina chromatography (40% EtOAc/pentane) to yield a colourless sticky solid (25 mg, 27%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.18 (dd, J = 4.7, 1.6 Hz, 1H), 7.73 (dd, J = 7.9, 1.5 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.18 (t, J = 1.1 Hz, 1H), 7.02 – 6.99 (m, 2H), 6.94 – 6.88 (m, 4H), 6.64 (d, J = 2.2 Hz, 1H), 5.72 (d, J = 34.9 Hz, 1H), 4.40 (d, J = 14.8 Hz, 2H), 3.74 (s, 3H), 2.43 (s, 3H).

¹³**C NMR** (126 MHz, CDCl₃) δ 162.4 (d, J = 249.2 Hz), 156.3 (d, J = 272.5 Hz), 144.2, 143.4, 135.6, 134.8 (d, J = 3.3 Hz), 131.2 (d, J = 8.8 Hz), 129.8, 129.7 (d, J = 1.3 Hz), 128.5, 127.9, 120.7, 116.5, 116.34, 116.31, 101.7 (d, J = 12.6 Hz), 99.9 (d, J = 9.0 Hz), 53.0, 52.8, 28.2, 21.7.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -101.23 (dt, J = 32.2, 14.7 Hz), -111.94 (tt, J = 8.2, 4.8 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₄H₂₁F₂N₃O₂S) 454.1395; measured: 454.1378 = 3.74 ppm difference.

IR (neat) vmax/cm⁻¹: 2935,1597, 1505, 1348, 1162, 1091, 812, 1552.

 $\mathbf{R}_{f} = 0.5 (50\% \text{ EtOAc/pentane}).$

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1,3,5-trimethoxybenzene (9a)



Compound **9a** was prepared according to general procedure 3d using 1,3,5-trimethoxy benzene (51 mg, 0.3 mmol) and (Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using neutral alumina chromatography (40% EtOAc/pentane) to yield a colourless sticky solid (32 mg, 48%).

¹**H NMR** (600 MHz, CDCl₃) δ 6.18 (s, 2H), 5.39 (d, J = 40.1 Hz, 1H), 3.84 (s, 3H), 3.84 (s, 6H), 2.76 (t, J = 7.34 Hz, 2H), 2.39 (dt, J = 16.8, 7.3 Hz, 1H), 1.96 (p, J = 7.4 Hz, 1H).

¹³**C NMR** (151 MHz, CDCl₃) δ 160.7, 159.7 (d, J = 263.0 Hz), 158.7, 142.3, 128.7, 128.5, 125.9, 104.1, 96.9 (d, J = 14.2 Hz), 90.9, 56.0, 55.5, 34.9, 32.2 (d, J = 27.3 Hz), 28.1.

¹⁹**F NMR** (377 MHz, CDCl₃) δ -97.62 (dt, J = 40.1, 16.8 Hz).

HRMS (ESI+) calc: [M]⁺ (C₂₀H₂₃O₃F) 330.1626; measured: 330.1620 = 1.82 ppm difference.

IR (neat) vmax/cm⁻¹: 2975,1606, 1454, 1410, 1228, 1061, 889.

 $\mathbf{R}_{f} = 0.7$ (5% EtOAc/pentane).

(E)-2-(4-fluorostyryl)-1-methyl-1H-indole (13a)



Compound **13a** was prepared according to general procedure 8 using 1-methyl-1*H*-indole (39 mg, 0.15 mmol) and (*E*)-(4-fluorostyryl)(mesityl)iodonium BF₄ (45 mg, 0.1 mmol) and purified using silica gel column chromatography (40% EtOAc/pentane) to yield a colourless sticky solid (19 mg, 74%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.51 (dt, J = 7.9, 1.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.24 – 7.21 (m, 1H), 7.15 – 6.97 (m, 6H), 6.71 (d, J = 0.8 Hz, 1H), 3.74 (s, 3H).

¹⁹**F NMR** (377 MHz, CDCl₃) δ -113.73 (tt, *J* = 8.6, 5.4 Hz).

These data are consistent with those previously reported.

1-(1-Methyl-1H-indol-2-yl)-5-phenylpentan-2-one (14a)



Compound **14a** was prepared according to general procedure 4 using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluoro-5-phenylpent-1-en-1-yl)(mesityl)iodonium BF₄ (99 mg, 0.2 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (24 mg, 41%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.49 (dt, J = 7.8, 1.0 Hz, 1H), 7.22 – 7.09 (m, 5H), 7.04 – 7.00 (m, 3H), 6.28 (d, J = 0.8 Hz, 1H), 3.75 (s, 2H), 3.54 (s, 3H), 2.51 – 2.47 (m, 2H), 2.43 (t, J = 7.3 Hz, 2H), 1.81 (p, J = 7.4 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 206.9, 141.5, 137.9, 133.2, 128.6, 128.5, 127.8, 126.1, 121.5, 120.4, 119.8, 109.3, 102.1, 42.3, 40.8, 35.0, 30.0, 25.2.

HRMS (ESI+) calc: [M+H]⁺ (C₂₀H₂₁NO) 292.1696; measured: 292.1693 = 1.03 ppm difference.

IR (neat) vmax/cm⁻¹: 2930, 1712, 1601, 1453, 1115, 848, 739, 699.

 $\mathbf{R}_{f} = 0.5 (15\% \text{ EtOAc/pentane}).$

1-(1-Methyl-1H-indol-2-yl)dodecan-2-one (14b)

Me

Compound **14b** was prepared according to general procedure 4 using 1-methyl-1*H*-indole (39 mg, 0.3 mmol) and (*Z*)-(2-fluorododec-1-en-1-yl)(mesityl)iodonium BF₄ (104 mg, 0.2 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (24 mg, 38%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (dt, J = 7.8, 1.0 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.20 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.09 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.39 (d, J = 0.9 Hz, 1H), 3.85 (s, 2H), 3.64 (s, 3H), 2.48 (t, J = 7.4 Hz, 2H), 1.29 – 1.23 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 207.3, 133.2, 127.7, 121.4, 120.2, 119.6, 109.2, 101.9, 42.2, 41.6, 31.9, 29.9, 29.5, 29.4, 29.4, 29.1, 23.7, 22.7, 14.1.

HRMS (ESI+) calc: $[M+H]^+$ (C₂₁H₃₁NO) 314.2478; measured: 314.2476 = 0.6 ppm difference.

IR (neat) vmax/cm⁻¹: 2920, 1715, 1557, 1464, 1052, 743, 725.

 $\mathbf{R}_{f} = 0.6$ (15% EtOAc/pentane).

1-(3-Acetyl-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one (15a)



Compound **15a** was prepared according to general procedure 5 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (58 mg, 0.2 mmol) and acetic acid (36 mg, 0.6 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (27 mg, 40%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.89 – 7.87 (m, 1H), 7.39 – 7.36 (m, 1H), 7.29 (dt, J = 6.4, 3.7 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.18 – 7.13 (m, 3H), 4.40 (s, 2H), 3.68 (s, 3H), 2.71 – 2.67 (m, 5H), 2.62 (t, J = 7.6 Hz, 2H), 1.94 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃) δ 206.1, 194.8, 141.8, 141.6, 137.2, 128.6, 128.5, 126.0, 126.0, 122.6, 122.3, 120.7, 114.5, 110.3, 42.2, 40.7, 35.2, 31.8, 29.9, 25.2.

HRMS (ESI+) calc: $[M+H]^+$ (C₂₂H₂₃NO₂) 334.1802; measured: 334.1795 = 2.09 ppm difference.

IR (neat) vmax/cm⁻¹: 2974, 1719, 1640, 1511, 1416, 1213, 1088, 738, 700, 503.

 $\mathbf{R}_{f} = 0.6$ (15% EtOAc/pentane).

1-(1-Methyl-3-(2,2,2-trifluoroacetyl)-1H-indol-2-yl)-5-phenylpentan-2-one (15b)



Compound **15b** was prepared according to general procedure 5 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (58 mg, 0.1 mmol) and 2,2,2-trifluoroacetic acid (68 mg, 0.6 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (44 mg, 57%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.98 (ddt, J = 5.4, 2.7, 1.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.18 (tt, J = 8.0, 1.5 Hz, 3H), 4.34 (s, 2H), 3.72 (s, 3H), 2.74 (t, J = 7.3 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H), 1.98 (p, J = 7.5 Hz, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl₃) δ 204.7, 175.5 (q, J = 36.6 Hz), 147.1, 141.6, 137.3, 128.6, 128.5, 126.1, 124.3, 123.7, 123.6, 121.0 (q, J = 5.2 Hz), 117.3 (q, J = 289.5 Hz), 110.3, 108.5, 42.5, 41.0, 35.1, 30.4, 25.0.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -74.62.

HRMS (ESI+) calc: $[M+H]^+$ ($C_{22}H_{20}NO_2F_3$) 387.1441; measured: 387.1435 = 1.55 ppm

difference.

IR (neat) vmax/cm⁻¹: 2934, 1708, 1644, 1484, 1348, 1158, 1072, 878, 748, 583, 545. **R**_f = 0.4 (15% EtOAc/pentane).

1-(3-(2,2-Difluoro-2-phenylacetyl)-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one (15c)



Compound **15c** was prepared according to general procedure 5 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (58 mg, 0.1 mmol) and 2,2-difluoro-2-phenylacetic acid (103 mg, 0.6 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (35 mg, 38%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.81 (d, J = 8.2 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.34 (m, 4H), 7.28 – 7.23 (m, 3H), 7.19 – 7.4 (m, 4H), 4.30 (s, 2H), 3.69 (s, 3H), 2.71 (t, J = 7.3 Hz, 2H), 2.63 (t, J = 7.6 Hz, 2H), 1.95 (p, J = 7.5 Hz, 2H).

¹³**C NMR** (151 MHz, CDCl₃) δ 205.3, 185.3 (t, J = 32.6 Hz), 145.6, 141.7, 137.3, 133.61 (t, J = 25.4 Hz), 131.2, 130.9, 128.8, 128.73, 128.7, 128.5, 126.4 (t, J = 5.6 Hz), 126.1, 124.8, 123.2, 122.9, 122.3 (t, J = 6.8 Hz), 117.0 (t, J = 250.7 Hz), 111.0, 110.0, 42.2, 41.1, 35.2, 30.3, 25.1.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -97.00.

HRMS (ESI+) calc: [M+H]⁺ (C₂₈H₂₅NO₂F₂) 446.1926; measured: 446.1921 = 1.12 ppm difference.

IR (neat) vmax/cm⁻¹: 2944, 1720, 1645, 1453, 1410, 1262, 1051, 748, 698.

 $\mathbf{R}_{f} = 0.5$ (15% EtOAc/pentane).

1-(3-(2,2-Difluoroacetyl)-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one (15d)



Compound **15d** was prepared according to general procedure 5 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (58 mg, 0.1 mmol) and 2,2-difluoroacetic acid (58 mg, 0.6 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (33 mg, 44%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.89 – 7.88 (m, 1H), 7.44 – 7.42 (m, 1H), 7.39 – 7.35 (m, 2H), 7.30 – 7.28 (m, 2H), 7.22 – 7.18 (m, 3H), 6.47 (t, J = 54.1 Hz, 1H), 4.42 (s, 2H), 3.75 (s, 3H), 2.76 (t, J = 7.3 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.00 (p, J = 7.4 Hz, 2H).

 $^{13}\textbf{C}$ NMR (151 MHz, CDCl₃) δ 205.1, 183.0 (t, J = 24.9 Hz), 145.5, 141.6, 137.4, 128.7, 128.5, 126.1, 124.7, 123.5, 123.5, 120.9 (t, J = 4.0 Hz), 110.51, 110.5 (t, J = 250.8 Hz), 110.3, 42.5, 40.9, 35.2, 30.4, 25.1.

¹⁹**F NMR** (376 MHz, CDCl₃) δ -126.17 (d, J = 54.1 Hz).

HRMS (ESI+) calc: $[M+H]^+$ (C₂₂H₂₁NO₂F₂) 370.1613; measured: 370.1607 = 1.62 ppm

difference.

IR (neat) vmax/cm⁻¹: 2947, 1722, 1654, 1453, 1405, 1258, 1060, 746.

 $R_f = 0.5$ (15% EtOAc/pentane).

2-(phenylethynyl)-1H-indole (16aj)



Compound **16aj** was prepared according to general procedure 6 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (29.3 mg, 0.1 mmol) and PhMgBr (0.24 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (17 mg, 77%).

 ^1H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 7.61 (dd, J = 7.9, 1.0 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.39 – 7.33 (m, 4H), 7.25 – 7.22 (m, 1H), 7.13 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.84 (dd, J = 2.1, 1.0 Hz, 1H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl_3) δ 136.3, 131.6, 128.8, 128.6, 127.9, 123.7, 122.7, 121.0, 120.6, 118.9, 110.9, 109.0, 92.7, 81.9.

HRMS (ESI+) calc: [M+H]⁺ (C₁₆H₁₁N) 218.0964; measured: 218.0962 = 0.92 ppm

difference.

IR (neat) vmax/cm⁻¹: 3378, 2975, 1596, 1397, 1062, 797, 1074, 748, 529.

(Z)-2-(2,5-diphenylpent-1-en-1-yl)-1-methyl-1H-indole (17a)



Compound **17a** was prepared according to general procedure 7 using (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole (29.3 mg, 0.1 mmol) and PhMgBr (0.24 mmol) and purified using silica gel chromatography (10% EtOAc/pentane) to yield a colourless oil (21 mg, 58%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.26 – 7.23 (m, 2H), 7.22 – 7.18 (m, 5H), 7.14 – 7.08 (m, 6H), 7.03 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 6.89 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.39 (s, 1H), 3.56 (s, 3H), 2.63 – 2.59 (m, 2H), 2.54 (td, J = 7.5, 1.3 Hz, 2H), 1.76 – 1.68 (m, 2H).

 $^{13}\textbf{C}$ NMR (101 MHz, CDCl_3) δ 142.3, 138.8, 137.8, 134.1, 128.6, 128.6, 128.5, 128.5, 126.0, 121.3, 120.2, 119.8, 119.4, 109.2, 98.0, 35.5, 33.0, 31.0, 29.9.

HRMS (MALDI+) calc: [M+Na]⁺ (C₂₆H₂₅N) 374.1879; measured: 374.1871 = 2.14 ppm

difference.

IR (neat) vmax/cm⁻¹: 2923, 1701, 1602, 1465, 1368, 1239, 1074, 743, 699.

NMR spectra of novel compound



1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole





S63



(Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(4-nitrophenyl)iodonium BF4





(Z)-(2-fluoro-5-phenylpent-1-en-1-yl)(4-(trifluoromethyl)phenyl)iodonium BF₄





S66



f1 (ppm)



S68











(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole


(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole





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



(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole







(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-(p-tolyl)-1H-indole





(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-methyl-1H-indole



(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-methyl-1*H*-indole





(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-methoxy-1H-indole



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

8.64	7.43 7.43 7.15 7.15 7.15 7.15 6.99 6.99 6.48 6.48 6.48	5.58	5.13	2.63	2.32	1.87
		I			I.	

(Z)-4-(benzyloxy)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole







(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-7-methoxy-1H-indole



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



(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-iodo-1H-indole



¹H NMR (400 MHz, CDCl₃)



(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-5-iodo-1H-indole





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

8.70	7.31 7.25 7.17 6.91	6.35 6.34	5.66	2.72	2.41	1.96
	121	Y				

(Z)-5-fluoro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole







7.131 7.127 7.127 7.127 7.127 7.127 6.91 - 5.61 - 3.68 - 3.68

(Z)-4-chloro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole



(Z)-4-chloro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole



¹³C NMR (101 MHz, CDCl₃)



-92.9

(Z)-4-chloro-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1-methyl-1H-indole



Methyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-5-carboxylate





Methyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-5-carboxylate



Methyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-5-carboxylate





Ethyl (Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indole-4-carboxylate





S94

- 160.5	- 149.6	- 141.4	132.9 131.9 128.7 128.5 128.5	-112.1	- 104.6 - 101.9 - 98.7	-34.9 -31.9
				N		(())

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-1H-indol-5-ol



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

8.64	7.52 7.34 7.30 7.25 7.21 7.16 7.10	5.73	2.74	2.44 2.30	1.99
			1	11	

(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-3-methyl-1H-indole



(Z)-2-(2-fluoro-5-phenylpent-1-en-1-yl)-3-methyl-1H-indole





- 3.17

(Z)-2-(2-(2-fluoro-2-phenylvinyl)-1H-indol-3-yl)ethan-1-ol



¹H NMR (500 MHz, CDCl₃)



(Z)-2-(2-(2-fluoro-2-phenylvinyl)-1H-indol-3-yl)ethan-1-ol





(Z)-2-(2-fluorododec-1-en-1-yl)-1-methyl-1H-indole



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



(Z)-2-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1-methyl-1H-indole



 $(Z) \hbox{-} 2 \hbox{-} (2 \hbox{-} fluoro \hbox{-} 3, 3 \hbox{-} dimethylbut \hbox{-} 1 \hbox{-} en \hbox{-} 1 \hbox{-} yl) \hbox{-} 1 \hbox{-} methyl \hbox{-} 1 H \hbox{-} indole$



(Z)-2-(2-fluoro-3,3-dimethylbut-1-en-1-yl)-1-methyl-1H-indole





(Z)-2-(2-cyclopropyl-2-fluorovinyl)-1-methyl-1H-indole





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



ii (ppm)

(Z)-2-(2-cyclohexyl-2-fluorovinyl)-1-methyl-1H-indole





0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 f1 (ppm) -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 2-((*Z*)-2-fluoro-3-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)-1-methyl-1*H*-indole



2-((Z)-2-fluoro-3-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)-1-methyl-1H-indole


2-((*Z*)-2-fluoro-3-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)-1-methyl-1*H*-indole



(Z)-2-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)isoindoline-1,3-dione





(Z)-2-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)isoindoline-1,3-dione



$\begin{array}{c} 8.34\\ 8.36\\ 8.05\\ 8.05\\ 8.03\\ 7.35\\ 7.35\\ 7.35\\ 7.23\\ 7.23\\ 7.20\\ -6.69\\ -6.69\\ -6.69\\ -6.69\\ -1.26\\ -1.26\\ -1.26\\ \end{array}$

(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-N-(4-fluorobenzyl)-4-nitrobenzenesulfonamide



(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-N-(4-fluorobenzyl)-4-nitrobenzenesulfonamide



--113.1

(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-N-(4-fluorobenzyl)-4-nitrobenzenesulfonamide





(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide



7.57 7.53 7.129 6.79 6.79 6.79 6.79 6.79 6.79 6.79 - 2.43 - 2.43

(Z)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-N-(4-fluorophenyl)-4-methylbenzenesulfonamide



(*Z*)-N-(2-fluoro-3-(1-methyl-1*H*-indol-2-yl)allyl)-*N*-(4-fluorophenyl)-4methylbenzenesulfonamide



-100 f1 (ppm) 0 -10 -30 -70 -80 -120 -140 -150 -170 -200 -20 -40 -50 -60 -90 -110 -130 -160 -190 -180 7.57 7.55 7.45 7.45 7.41 7.23 7.23 7.19 7.07 7.07 7.03 6.99 6.99 - 5.79 4.48 - 3.60 - 2.43

(Z)-N-(4-bromophenyl)-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide





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

7,7,7 7,75 7,730 7,209 7,009 ~ 6,79 ~ 6,79 ~ 6,79 ~ 6,79 ~ 6,79 ~ 6,79 ~ 6,79 ~ 6,79 ~ 2,41 ~ 2,21 ~ 2,21 ~ 0,03

(Z)-N-cyclopropyl-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide



(Z)-N-cyclopropyl-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide



(Z)-N-cyclopropyl-N-(2-fluoro-3-(1-methyl-1H-indol-2-yl)allyl)-4-methylbenzenesulfonamide







Ethyl (z)-2-fluoro-3-(1-methyl-1H-indol-2-yl)acrylate



____29.9

(Z)-2-(2-fluoro-2-phenylvinyl)-1-methyl-1H-indole



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

- 8.89 7.55 7.55 7.57 7.57 7.57 7.10 7.10 7.110





¹H NMR (400 MHz, CDCl₃)



— 1.54

(Z)-2-(2-fluoro-2-phenylvinyl)-1H-indole





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

(Z)-2-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)-1-methyl-1H-indole



(Z)-2-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)-1-methyl-1*H*-indole



- 155.1 137.3 1127.3 128.3 128.3 122.3 122.0 119.8 - 04.9 - 94.9

(Z)-2-(2-fluoro-2-(thiophen-3-yl)vinyl)-1-methyl-1H-indole



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 f1 (ppm) -110 -120 -130 -140 -150 -160 -170 -180 -190 -2(

7.77 7.49 7.18 7.118 7.10	6.31	2.53	1.63 1.55 1.47 1.47 1.19 0.82 0.79
15551			51777 57

(E)-2-(2-fluorododec-1-en-1-yl)-1H-indole



-95.0

(E)-2-(2-fluorododec-1-en-1-yl)-1H-indole



- 156.9 - 142.2 - 142.2 - 142.2 - 128.7 - 128.5 - 112.1 - 105.7



(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1,2,5-trimethyl-1H-pyrrole





--109.07

(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1,2,5-trimethyl-1H-pyrrole



-5.30 -5.30 -5.30 -5.30 -5.30 -5.30 -5.30

2.63 2.59 -2.25 1.87 1.87 1.87 1.82

-3.76

(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole



(Z)-3-(2-fluoro-5-phenylpent-1-en-1-yl)-1-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole

-108.44



(Z)-1-cyclopropyl-3-(2-fluoro-5-phenylpent-1-en-1-yl)-2,5-dimethyl-1H-pyrrole



S133



(Z)-1-cyclopropyl-3-(2-fluoro-5-phenylpent-1-en-1-yl)-2,5-dimethyl-1H-pyrrole









S137



(Z)-3-(2-cyclohexyl-2-fluorovinyl)-2,5-dimethyl-1H-pyrrole





S140





(Z)-3-(2-fluoro-2-(thiophen-3-yl)vinyl)-2,5-dimethyl-1H-pyrrole





(E)-3-(2-fluorododec-1-en-1-yl)-2,5-dimethyl-1H-pyrrole



- 5.72 - 4.40 - 2.33 - 3.64 -- 8.18

(Z)-N-(2-fluoro-3-(1-methyl-1H-pyrrolo[2,3-b]pyridin-2-yl)allyl)-N-(4-fluorophenyl)-4methylbenzenesulfonamide



101.7 162.4 156.3 144.2 143.4 135.6 135.6 134.8 123.8 129.7 129.8 129.7 129.7 120.7 120.7 116.5 116.5 116.3 53.0 28.2 21.7

(Z)-N-(2-fluoro-3-(1-methyl-1H-pyrrolo[2,3-b]pyridin-2-yl)allyl)-N-(4-fluorophenyl)-4methylbenzenesulfonamide



¹³C NMR (126 MHz, CDCl₃)








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



-- 3.74





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



1-(1-Methyl-1H-indol-2-yl)-5-phenylpentan-2-one







1-(3-Acetyl-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one



7.98	7.41 7.37 7.36 7.31 7.29 7.18 7.18	4.34	3.72	2.74	1.98 1.98
				17	\sim

1-(1-Methyl-3-(2,2,2-trifluoroacetyl)-1H-indol-2-yl)-5-phenylpentan-2-one



1-(1-Methyl-3-(2,2,2-trifluoroacetyl)-1H-indol-2-yl)-5-phenylpentan-2-one





1-(3-(2,2-Difluoro-2-phenylacetyl)-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one





1-(3-(2,2-Difluoroacetyl)-1-methyl-1H-indol-2-yl)-5-phenylpentan-2-one





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

2-(phenylethynyl)-1H-indole





(Z)-2-(2,5-diphenylpent-1-en-1-yl)-1-methyl-1H-indole



(Z)-2-(2,5-diphenylpent-1-en-1-yl)-1-methyl-1H-indole

