Supporting Information for:

A Photoredox Coupling Reaction of Benzylboronic Esters

and Carbonyl Compounds in Batch and Flow

Yiding Chen[†], Oliver May[†], David C. Blakemore[‡] and Steven V. Ley^{†*}

[†] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

‡ Medicine Design, Pfizer Inc., Eastern Point Road, Groton, Connecticut 06340, United States

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General Information

All procedures below were conducted under inert nitrogen atmosphere unless stated otherwise. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros and Fluorochem and were used as supplied unless stated otherwise. Acetone was purchased from Sima-Aldrich and used as supplied. Methanol were distilled from CaO under inert gas prior to use. Work-up solvents were employed directly from commercial sources, i.e. Sigma-Aldrich unless stated otherwise. Petroleum ether refers to the fractions of petrol collected between 40-60 °C b.p.

Reactions were monitored *via* thin layer chromatography (TLC) on pre-coated glass backed plates (Merck Kieselgel 60 F_{254}). Products were visualized by UV light (254 nm) and/or with KMnO₄ stain. Flash column chromatography was conducted using a Biotage SPX system with single use disposable silica columns of the appropriate size (SiliaSep Flash Cartridges 4 or 12 g 40-60 μ m ISO04/012).

¹H NMR, ¹³C NMR were obtained from a 600 MHz Bruker DRX-600 Spectrometer or a 400 MHz Bruker Avance DPX-400 Spectrometer. ¹⁹F NMR data were obtained from a 400 MHz Bruker Avance DPX-400 Spectrometer. ¹H NMR were generally obtained with 32 scans at 298 K with a sweep width of 10776 Hz. ¹³C NMR were generally obtained with 256 scans at 298 K with a sweep width of 40650 Hz. ¹⁹F NMR were generally obtained with 32 scans at 298 K with a sweep width of 40650 Hz. ¹⁹F NMR were generally obtained with 32 scans at 298 K with a sweep width of 131579 Hz. Chemical shifts (δ) are referenced to the residual solvent as CDCl₃ in the unit of parts per million (ppm). Coupling constants *J* are quoted in the unit of hertz (Hz). Proton and carbon multiplicity are recorded as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br), or combinations thereof. All compounds examined were dried *in vacuo* to remove residual solvents. Spectra are assigned as fully as possible, using ¹H-TCOSY, DEPT-135, HSQC and ¹H NOESY where appropriate to facilitate structural determination. Multiple signals arising from (pseudo)axial/equatorial positions are distinguished using suffix as for example Ha and H_b. ¹H NMR signals are reported to two decimal places and ¹³C signals to one decimal place.

Low resolution mass spectra (LRMS) were recorded on an Advion Expression CMS spectrometer. High resolution mass spectrometry (HRMS) was performed on either a Waters Micromass LCT Premier spectrometer or performed by the Mass Spectrometry Service for the Department of Chemistry at the University of Cambridge. Infra-red spectra were recorded neat on a Perkin-Elmer Spectrum One FTIR spectrometer with a universal ATR sampling accessory, selected peaks are reported.

The UV/Vis experiments were operated on a Shimadzu RF-6000 Spectro Fluorophotometer Melting points were recorded on a Stanford Research Systems OptiMelt Automated Melting Point System.

All compounds listed in the paper are >98% purity. Some products appear to be very hydroscopic therefore contain 0.2 - 0.5 mol equivalents of water (2 - 5 wt%) present in the ¹H NMR spectra as shown below. Inseparable impurities are noted.

Photochemical experiments were performed magnetically stirred in 5 mL glass test-tubes, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm) using a coiled commercial LED strip (1 m, from LEDXON, PN: 9009083) with a total power output of 14.4 W. To maintain a constant reaction temperature of 35°C, the setup was cooled by a constant air flow from a clip fan (Figure S1).



Figure S1: General set-up of the batch reaction

Screening of various conditions

For a detailed procedure, see General Procedure A.

Screening of photocatalysts

	Bpin + H S0% Quinuclidine	→ CI
MeO	CI Acetone : MeOH	MeO
Entry	Photocatalyst (2 mol%)	Yield
1	{Ir[dF(CF ₃)ppy] ₂ (dtbpy)}PF ₆	40%
2	[Ir(dtbbpy)(ppy) ₂]PF ₆	36%
3	9-Mesityl-10-methylacridinium tetrafluoroborate	22%
4	9-Mesityl-10-methylacridinium perchlorate	4%
5	[Ru(bpy) ₃]Cl ₂	0%
6	N/A	0%

Reaction conditions: 0.1 mmol 4-methoxybenzylboronic acid pinacol ester, 0.15 mmol 4chlorobenzaldehyde, 0.05 mmol quinuclidine, 0.5 mL acetone and 0.5 mL methanol, 35 °C, 8 h. NMR yields measured with 1,3,5-trimethoxybenzene as internal standard

Screen of bases

MeO	$\begin{array}{c} & \begin{array}{c} O \\ Bpin \end{array} + H \\ & \begin{array}{c} O \\ H \\ & \end{array} \end{array} \begin{array}{c} 2 \text{ mol\% } \{Ir[dF(CF_3)ppy]_2(dtbpy) \\ \hline Additives \end{array} \\ \hline Acetone : MeOH \\ 1:1 \end{array}$	PF ₆ MeOOH
Entry	Additives	Yield
1	50 mol % 3-Quinuclidinol	57%
2	20 mol% 3-Quinuclidinol	54%
3	50 mol% 3-Quinuclidinol + 20 mol% Sc(OTf) ₃	46%
4	50 mol% Lutidine	0%
5	50 mol% DMAP	31%
6	20 mol% DIPEA	45%
7	20 mol% DBN	20%
8	20 mol% TMEDA	38%
9	100 mol% K ₂ CO ₃	10%

Reaction conditions: 0.1 mmol 4-methoxybenzylboronic acid pinacol ester, 0.15 mmol 4chlorobenzaldehyde, 2 mol% {Ir[dF(CF₃)ppy]₂(dtbpy)}PF₆, 0.5 mL acetone, 0.5 mL methanol, 35 °C, 8 h. NMR yields measured with 1,3,5-trimethoxybenzene as internal standard

Screening of solvents and concentration

MeO	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	ОН
Entry	Solvent(s) (Concentration)*	Yield
1	Acetone and Methanol 1:1 (0.05 M)	86% (84%)**
2	Acetone and Methanol 1:1 (0.2 M)	37%
3	Methanol (0.1 M)	28%
4	Acetone (0.1M)	24%
5	Acetonitrile (0.1 M)	19%
6	Dichloromethane (0.1 M)	46%
7	Acetone and tBuOH 1:1 (0.1 M)	55%
8	Acetone and isopropanol 1:1 (0.1 M)	44%
9	Acetone and methanol 5:1 (0.1 M)	48%
10	Dimethylacetamide (0.1 M)	44%
11	Acetone and toluene (0.05 M)	32%
12	Acetone and HFIP (0.05 M)***	20%

Reaction conditions: 0.1 mmol 4-methoxybenzylboronic acid pinacol ester, 0.15 mmol 4chlorobenzaldehyde, 2 mol% $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$, 20 mol% 3-quniuclidinol, 35 °C, 8 h. NMR yield measured with 1,3,5-trimethoxybenzene as internal standard

* Concentration measured against boronic ester

** Isolated yield

***HFIP: Hexafluoro-2-propanol

Cross-coupling products of benzylboronic esters with aldehydes and imines

Flow adaptation: Vapourtec UV-150 photoreactor



1-(4-Bromophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3a

In a 10 mL test tube was charged with 4-methoxybenzylboronic acid pinacol ester (50 mg, 0.2 mmol, 1.0 eq.), 4-chlorobenzaldehyde (42 mg, 0.3 mmol, 1.5 eq.), 3-quinuclidinol (5.1 mg, 0.04 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (4.4 mg, 0.004 mmol, 2 mol%). The tube was vacuumed and backfilled with nitrogen three time, and the reagents were then dissolved in 1:1 mixture of methanol and acetone (4 mL) before purged with dry nitrogen gas for 10 min.

The clear yellow solution was then pumped through a Vapourtec UV-150TM reactor (10 mL, FEP tubing) while irradiate by a 420 nm blue LED lamp (output power: 17W) at a flow rate of 0.1 mL/min. The reactor temperature was held at 35 °C with air cooling. Once the reaction mixture has fully be taken up by the reactor, the input was switched to a 1:1 mixture of methanol and acetone, to push the remaining reaction mixture through the reactor. The reaction mixture was collected over the period of reaction, and solvent was removed under vacuum. The resulting residue was purified with flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a pale-yellow solid (36 mg, 70%). Analytical data obtained were the same as the batch reaction.

Flow adaptation and Large-scale synthesis: Uniqsis PhotoSyn reactor



1-(4-Bromophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3ak

In a 500 mL pear-shaped flask was charged with 4-methoxybenzylboronic acid pinacol ester (2.48 g, 10.0 mmol, 1.0 eq.), 4-bromobenzaldehyde (2.77 g, 15.0 mmol, 1.5 eq.), 3-quinuclidinol (254 mg, 2.0 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(224 mg, 0.2 mmol, 2 mol%)$. The flask was vacuumed and backfilled with nitrogen three time, and the reagents were then dissolved in 1:1 mixture of methanol and acetone (200 mL) before purged with dry nitrogen gas for 15 min. The flow system was controlled by LabVIEW v. 2018. The front panel and block diagram are shown below (Figure S2 and Figure S3).



Figure S2: LabVIEW Front Panel. 1. Pump connection address using either TCP/IP or COM port; 2. Flow rate input; 3. Reaction time (minutes); 4. Emergency stop; 5. Pump pressure (bar); 6. UVvis display of selected wavelengths.

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Figure S3: LabVIEW Block diagram. **1.** Initialise Knauer pump using user defined COM port; **2.** Set initial flow rate to 0; **3.** Start pump; **4.** Manually select a flow rate ; **5.** Get pump pressure value as an integer, convert to double and divide by 10 to get the reading in Bar; **6.** Get current time and subtract from start time to give current time in seconds; **7.** Create an array of time in seconds and pressure and plot to an XY graph; **8.** Stop pumps; **9.** Close serial connection; **10.** Display any error codes; **11.** Read delimited spreadsheet, convert to an array and select columns 4, 6, 8 and 10; **12.** Create a new array containing selected wavelengths; **13.** Set reaction run time in minutes to stop reaction after time has elapse or stop using stop button; **14.** Combine arrays of time and UV wavelength and plot to an XY graph. **15.** Update values every 500 ms.

The clear yellow solution was then pumped through a Uniqsis PhotosynTM reactor (PFA, 20 mL, 1/16" OD tubing) at a flow rate of 0.33 mL/min. The reactor temperature was held at 25 °C with water cooling and was detected by an infrared thermometer. The output stream was monitored by a Uniqsis Flow-UVTM in-line UV-Vis detector. Once the reaction mixture has fully be taken up by the reactor, the input was switched to a 1:1 mixture of methanol and acetone, to push the remaining reaction mixture through the reactor. The reaction mixture was collected over the period of reaction, and solvent was removed under vacuum. The resulting residue was purified with flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a pale-yellow solid (1.69 g, 55%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.45 (d, *J* = 8.4 Hz, 2H, *H*_{Ar}), 7.18 (d, *J* = 8.4 Hz, 2H, *H*_{Ar}), 7.06 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.83 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.78 (dd, *J* = 8.2, 5.2 Hz, 1H, CHOH), 3.78 (s, 3H, OC*H*₃), 2.93 (dd, *J* = 13.8, 5.2 Hz, 1H, *CH*_aCHOH), 2.88 (dd, *J* = 13.8, 8.2 Hz, 1H, *CH*_bCHOH), 2.20 (br s, 1H, O*H*); ¹³**C NMR** (151 MHz, CDCl₃) δ 158.5, 142.9, 131.5 (*C*_{Ar}H), 130.6 (*C*_{Ar}H), 129.5, 127.8 (*C*_{Ar}H), 121.3, 114.1 (*C*_{Ar}H), 74.8 (CHOH), 55.3 (OCH₃), 45.2 (*C*H₂CHOH). **LRMS** (ESI, m/z) 307.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₄⁷⁹BrO⁺ [M-OH]⁺ 289.0223, found 289.0222. **IR** v max (film): 3433, 2933, 2835, 1683, 1610, 1585, 1510, 1486, 1439, 1382, 1328, 1300, 1244, 1176, 1069, 1034, 1008, 823 cm⁻¹. **M.p.**: 78 – 80 °C.

General Procedure A for the cross-coupling reaction



1-(4-Chlorophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3a

In a 5 mL glass test tube was charged with 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and {Ir[dF(CF₃)ppy]₂(dtbpy)}PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The reagents were dissolved in 1:1 mixture of methanol and acetone (2 mL) before purged with dry nitrogen gas for 10 min. The resulting solution was then irradiated with a commercial blue LED strip (14.4 W, 450 nm) for 8 hours with stirring, the reaction temperature was maintained at 30 – 35 °C using a clip fan. Upon completion the mixture was concentrated and purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (22 mg, 84%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 4H, *H*_{Ar}), 7.10 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.87 (d, J = 8.4 Hz, 1H, *H*_{Ar}), 4.86 (td, *J* = 5.2, 2.8 Hz, 1H, CHOH), 3.82 (s, 3H, OCH₃), 2.98 (dd, *J* = 13.8, 5.2 Hz, 1H, CH_aCHOH), 2.91 (dd, *J* = 13.8, 8.4 Hz, 1H, CH_bCHOH), 1.99 (d, *J* = 2.8 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.6, 142.4, 133.3, 130.6 (*C*_{Ar}H), 129.5, 128.6 (*C*_{Ar}H), 127.5 (*C*_{Ar}H), 114.2 (*C*_{Ar}H), 74.9 (CHOH), 55.4 (OCH₃), 45.4 (CH₂CHOH). **LRMS** (ESI, m/z) 285.1 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₅O₂³⁵ClNa⁺ [M+Na]⁺ 285.0653, found 285.0651. **IR** v max (film): 3377, 2934, 1612, 1512, 1491, 1464, 1301, 1246, 1178, 1090, 1035, 1013, 829 cm⁻¹. **M.p.**: 81 – 83 °C (lit. 83 – 85 °C).¹



1-(4-Chlorophenyl)-2-(p-tolyl)ethan-1-ol 3b

General Procedure A was followed using 4-methylbenzylboronic acid pinacol ester (23 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02

mmol, 20 mol%) and {Ir[dF(CF₃)ppy]₂(dtbpy)}PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (19 mg, 77%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 4H, *H*_{Ar}), 7.15 – 7.04 (m, 4H, *H*_{Ar}), 4.85 (ddd, *J* = 8.3, 4.9, 2.9 Hz, 1H, CHOH), 2.98 (dd, *J* = 13.7, 4.9 Hz, 1H, C*H*_aCHOH), 2.90 (dd, *J* = 13.7, 8.3 Hz, 1H, C*H*_bCHOH), 2.33 (s, 3H, C*H*₃), 1.95 (d, *J* = 2.9 Hz, 1H, CHO*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 142.4, 136.5, 134.5, 133.3, 129.5 (*C*_{Ar}H), 129.5 (*C*_{Ar}H), 128.6 (*C*_{Ar}H), 127.4 (*C*_{Ar}H), 74.8 (CHOH), 45.9 (C*H*₂CHOH), 21.2 (CH₃). **LRMS** (ESI, m/z) 247.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₅O³⁵ClNa⁺ [M+Na]⁺ 269.0704, found 269.0703. **IR** v max (film): 3411, 2916, 1596, 1515, 1491, 1408, 1090, 1042, 1013, 827, 794, 778 cm⁻¹. **M.p.**: 47 – 49 °C. The data presented are consistent with literature precedent.²



1-(4-Chlorophenyl)-2-(o-tolyl)ethan-1-ol 3c

General Procedure A was followed using 2-methylbenzylboronic acid pinacol ester (23 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (16 mg, 65%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.27 (m, 4H, H_{Ar}), 7.19 – 7.10 (m, 4H, H_{Ar}), 4.88 (ddd, J = 8.1, 5.5, 2.6 Hz, 1H, CHOH), 3.05 – 2.93 (m, 2H, CH₂CHOH), 2.29 (s, 3H, CH₃), 1.95 (d, J = 2.8 Hz, 1H, CHOH); ¹³**C NMR** (100 MHz, CDCl₃) δ 13C NMR (100 MHz, CDCl₃) δ 142.6, 136.9, 136.0, 133.4, 130.7 (C_{Ar} H), 130.4 (C_{Ar} H), 128.7 (C_{Ar} H), 127.3 (C_{Ar} H), 127.1 (C_{Ar} H), 126.3 (C_{Ar} H), 73.9 (CHOH), 43.5 (CH₂CHOH), 19.7 (CH₃). **LRMS** (ESI, m/z) 269.1 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₅O³⁵ClNa⁺ [M+Na]⁺ 269.0704, found 269.0705. **IR** ν max (film): 3468, 3196, 1603, 1511, 1101, 1037, 798 cm⁻¹. **M.p.**: 76 – 79 °C.



1-(4-Chlorophenyl)-2-(naphthalen-1-yl)ethan-1-ol 3d

General Procedure A was followed using (1-naphthylmethyl)boronic acid pinacol ester (26 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a white solid (17 mg, 60%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.09 (dd, J = 8.5, 1.2 Hz, 1H, H_{Naphth}), 7.92 – 7.87 (m, 1H, H_{Naphth}), 7.79 (d, J = 8.2 Hz, 1H, H_{Naphth}), 7.56 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H, H_{Naphth}), 7.52 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H, H_{Naphth}), 7.40 (dd, J = 8.2, 7.0 Hz, 1H, H_{Naphth}), 7.37 – 7.31 (m, 4H, H_{Ar}), 7.30 – 7.28 (m, 1H, H_{Naphth}), 5.05 (ddd, J = 8.9, 4.6, 2.5 Hz, 1H, CHOH), 3.50 (dd, J = 14.0, 4.6 Hz, 1H, CH_aCHOH), 3.37 (dd, J = 14.0, 8.9 Hz, 1H, CH_bCHOH), 1.95 (d, J = 2.5 Hz, 1H, CHOH); ¹³**C NMR** (100 MHz, CDCl₃) δ 13C NMR (151 MHz, CDCl₃) δ 142.6, 134.2, 133.8, 133.5, 132.2, 129.1 (C_{Naphth} H), 128.7(C_{Ar} H), 128.1 (C_{Naphth} H), 127.9 (C_{Naphth} H), 127.4 (C_{Ar} H), 126.4 (C_{Naphth} H), 125.9 (C_{Naphth} H), 123.7 (C_{Naphth} H), 73.9 (CHOH), 43.5 (CH₂CHOH). **HRMS** (ESI) calcd for C₁₈H₁₄³⁵Cl⁺</sup> [M-OH]⁺ 265.0779, found 265.0783. **IR** v max (film): 3748, 3432, 3047, 2338, 2202, 1611, 1597, 1503, 1491, 1397, 1088, 1013, 775 cm⁻¹.



1-(4-Chlorophenyl)-2-phenylethan-1-ol 3e

General Procedure A was followed using benzylboronic acid pinacol ester (22 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (11 mg, 47%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.36 – 7.28 (m, 5H, *H*_{Ar}), 7.27 – 7.22 (m, 2H, *H*_{Ar}), 7.20 – 7.14 (m, 2H, *H*_{Ar}), 4.89 (ddd, *J* = 8.2, 5.1, 2.9 Hz, 1H, CHOH), 3.02 (dd, *J* = 13.6, 5.1 Hz, 1H, C*H*_aCHOH), 2.96 (dd, *J* = 13.6, 8.2 Hz, 1H, C*H*_bCHOH), 1.95 (d, *J* = 2.9 Hz, 1H, CHO*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 142.4, 137.7, 133.4, 129.7 (*C*_{Ar}H), 128.8 (*C*_{Ar}H), 128.7 (*C*_{Ar}H), 127.4 (*C*_{Ar}H), 126.9 (*C*_{Ar}H), 74.8 (CHOH), 46.3 (*C*H₂CHOH). **LRMS** (ESI, m/z) 255.2 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₃O³⁵CINa⁺ [M+Na]⁺ 255.0547, found 255.0545. **IR** v max (film): 3400, 3338, 3026, 2923, 1493, 1454, 1090, 1013, 829, 747, 700 cm⁻¹. The data presented are consistent with literature precedent.³

1-(4-Chlorophenyl)-2-[4-(trifluoromethoxy)phenyl]ethan-1-ol 3f

General Procedure A was followed using 4-(trifluoromethoxy)benzylboronic acid pinacol ester (30 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (15 mg, 46%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.32 (d, J = 8.2 Hz, 2H, H_{Ar}), 7.25 (d, J = 8.2 Hz, 2H, H_{Ar}), 7.18 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.14 (d, J = 8.4 Hz, 2H, H_{Ar}), 4.87 (td, J = 6.6, 2.8 Hz, 1H, CHOH), 2.98 (d, J = 6.6 Hz, 2H, CH₂CHOH), 1.95 (d, J = 2.8 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 148.2, 142.1, 136.5, 133.6, 131.0 (C_{Ar}H), 128.8 (C_{Ar}H), 127.4 (C_{Ar}H), 121.1 (C_{Ar}H), 120.6 (q, ¹ $J_{C-F} = 256.9$ Hz, C_{Ar-F}), 74.7 (CHOH), 45.3 (CH₂CHOH); ¹⁹**F NMR** (376 MHz, CDCl₃) δ -57.9. **LRMS** (ESI, m/z) 317.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₁OClF₃⁺ [M-OH]⁺ 299.0445, found 299.0450. **IR** v max (film): 3462, 3311, 2334, 1509, 1262, 1223, 1162, 1093, 1014, 830 cm⁻¹. **M.p.**: 58 – 60 °C.



1,2-Bis(4-chlorophenyl)ethan-1-ol 3g

General Procedure A was followed using 4-chlorobenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (11 mg, 42%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.34 (d, J = 8.5 Hz, 2H, H_{Ar}), 7.30 – 7.24 (m, 4H, H_{Ar}), 7.10 (d, J = 8.4 Hz, 2H, H_{Ar}), 4.88 (t, J = 6.6 Hz, 1H, CHOH), 2.99 (d, J = 6.6 Hz, 2H, CH₂CHOH), 1.93 (d, J = 3.0 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 142.1, 136.1, 133.6, 132.8, 131.0 (C_{Ar} H), 128.8 (C_{Ar} H), 128.8 (C_{Ar} H), 127.4 (C_{Ar} H), 74.7 (CHOH), 45.3 (CH₂CHOH). **LRMS** (ESI, m/z) 267.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₁O³⁵Cl₂⁻ [M-H]⁻ 265.1087, found 265.1082. The data presented are consistent with literature precedent.²



1-(4-Chlorophenyl)-2-(3-fluorophenyl)ethan-1-ol 3h

General Procedure A was followed using 3-fluorobenzylboronic acid pinacol ester (24 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (5 mg, 20%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.41 – 7.19 (m, 5H, *H*_{Ar}), 7.02 – 6.80 (m, 3H, *H*_{Ar}), 4.89 (td, *J* = 6.7, 2.8 Hz, 1H, CHOH), 2.98 (d, *J* = 6.7 Hz, 2H, CH₂CHOH), 1.93 (d, *J* = 2.8 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 166.2 (d, ¹*J*_{C-F} = 187.6 Hz, *C*_{Ar-F})142.1, 140.3 (d, ³*J*_{C-F} = 7.2 Hz, *C*_{Ar-F}), 133.6, 130.1 (d, ³*J*_{C-F} = 8.6 Hz, *C*_{Ar-F}H), 128.8 (*C*_{Ar}H), 127.4 (*C*_{Ar}H), 125.3 (d, ⁴*J*_{C-F} = 2.7 Hz, *C*_{Ar-F}H),

116.5 (d, ${}^{2}J_{C-F} = 21.1$ Hz, $C_{Ar-F}H$), 113.83 (d, ${}^{2}J_{C-F} = 20.8$ Hz, $C_{Ar-F}H$), 74.5 (CHOH), 45.8 (CH₂CHOH); ¹⁹F NMR (376 MHz, CDCl₃) δ -113.2. LRMS (ESI, m/z) 251.3 ([M+H]⁺, 100%); HRMS (ESI) calcd for C₁₄H₁₁OFCl⁻ [M-H]⁻ 249.0482, found 249.0479. IR v max (film): 3423, 3358, 2925, 1617, 1589, 1490, 1448, 1252, 1141, 1091, 1013, 829, 779, 751, 694 cm⁻¹.



Methyl 4-[2-(4-chlorophenyl)-2-hydroxyethyl]benzoate 3i

General Procedure A was followed using methyl 4-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)methyl]benzoate (28 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (10 mg, 34%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 7.30 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 7.24 (d, *J* = 8.3 Hz, 2H, *H*_{Ar}), 7.22 (d, *J* = 8.3 Hz, 2H, *H*_{Ar}), 4.92 (ddd, *J* = 7.8, 5.6, 3.0 Hz, 1H, CHOH), 3.91 (s, 3H, C*H*₃), 3.07 (dd, *J* = 13.7, 7.8 Hz, 1H, C*H*_aCHOH), 3.03 (dd, *J* = 13.7, 5.6 Hz, 1H, C*H*_bCHOH), 1.93 (d, *J* = 3.0 Hz, 1H, O*H*); ¹³C **NMR** (151 MHz, CDCl₃) δ 167.1 (COOCH₃), 143.1, 142.0, 133.6, 129.9 (C_{Ar}H), 129.7 (C_{Ar}H), 128.8, 128.8 (C_{Ar}H), 127.4 (C_{Ar}H), 74.6 (CHOH), 52.2 (COOCH₃), 46.0 (CH₂CHOH). **LRMS** (ESI, m/z) 291.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₄O₂³⁵Cl⁺ [M-OH]⁺ 273.0682, found 273.0685. **IR** v max (film): 3493, 3001, 2360, 1695, 1593, 1423, 1295, 668 cm⁻¹. **M.p.**: 118 – 120 °C.



1-(4-Chlorophenyl)-2-(phenylthio)ethan-1-ol 3j

General Procedure A was followed using 4,4,5,5,-tetramethyl-2-phenylsulfanylmethyl-1,3,2dioxaborolane (25 mg, 0.1 mmol, 1.0 eq.), 4-chlorobenzaldehyde (21 mg, 0.15 mmol, 1.5 eq.), 3quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and {Ir[dF(CF₃)ppy]₂(dtbpy)}PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 - 20% EtOAc in petroleum ether) to give the titled product as a colourless oil (4 mg, 16%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H, H_{Ar}), 7.36 – 7.23 (m, 7H, H_{Ar}), 4.69 (dt, J = 9.4, 3.0 Hz, 1H, CHOH), 3.29 (dd, J = 13.8, 3.6 Hz, 1H, C H_a CHOH), 3.04 (dd, J = 13.9, 9.4 Hz, 1H, C H_b CHOH), 2.86 (d, J = 2.5 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 140.7, 134.6, 133.82, 130.7 (C_{Ar} H), 129.4 (C_{Ar} H), 128.9 (C_{Ar} H), 127.4 (C_{Ar} H), 127.2 (C_{Ar} H), 71.1 (CHOH), 44.4 (CH₂CHOH). **LRMS** (ESI, m/z) 265.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₃O³⁵ClSNa⁺ [M+Na]⁺ 287.0268, found 287.0266. **IR** v max (film): 3515, 3438, 3250, 1512, 1090, 1008, 739, 691 cm⁻¹. The data presented are consistent with literature precedent.⁴



2-(4-Methoxyphenyl)-1-(o-tolyl)ethan-1-ol 3k

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *o*-tolualdehyde (18 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆(2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (19 mg, 78%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.54 (dd, J = 7.6, 1.5 Hz, 1H, H_{Ar}), 7.28 – 7.23 (m, 1H, H_{Ar}), 7.19 (td, J = 7.4, 1.5 Hz, 1H, H_{Ar}), 7.16 – 7.09 (m, 3H, H_{Ar}), 6.85 (d, J = 8.6 Hz, 2H, H_{Ar}), 5.08 (ddd, J = 8.7, 4.3, 2.8 Hz, 1H, CHOH), 3.80 (s, 3H, OCH₃), 2.96 (dd, J = 13.9, 4.3 Hz, 1H, CH_aCHOH), 2.86 (dd, J = 13.8, 8.7 Hz, 1H, CH_bCHOH), 2.29 (s, 3H, CCH₃), 1.87 (d, J = 2.8 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.6, 142.2, 134.5, 130.6 (C_{Ar}H), 130.4, 130.4 (C_{Ar}H), 127.4 (C_{Ar}H), 126.5 (C_{Ar}H), 125.4 (C_{Ar}H), 114.1 (C_{Ar}H), 72.0 (CHOH), 55.4 (OCH₃), 44.24 (CH₂CHOH), 19.2 (CCH₃). **LRMS** (ESI, m/z) 243.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₈O₂Na⁺ [M+Na]⁺ 265.1199, found 265.1196. **IR** v max (film): 338, 2915, 1611, 1583, 1512, 1463, 1441, 1300, 1246, 1177, 1112, 1036, 821, 758 cm⁻¹. **M.p.**: 71 – 73 °C.



1-(2-Bromophenyl)-2-(4-methoxyphenyl)ethan-1-ol 31

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *o*-bromobenzaldehyde (28 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a colourless oil (24 mg, 78%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (dd, J = 7.8, 1.8 Hz, 1H, H_{Ar}), 7.54 (dd, J = 7.8, 1.2 Hz, 1H, H_{Ar}), 7.35 (td, J = 7.5, 1.2 Hz, 1H, H_{Ar}), 7.22 (d, J = 8.5 Hz, 2H, H_{Ar}), 7.15 (td, J = 7.8, 1.8 Hz, 1H, H_{Ar}), 6.88 (d, J = 8.6 Hz, 2H, H_{Ar}), 5.21 (dt, J = 9.2, 3.2 Hz, 1H, CHOH), 3.81 (s, 3H, OCH₃), 3.15 (dd, J = 14.0, 3.2 Hz, 1H, CH_{a} CHOH), 2.68 (dd, J = 14.0, 9.2 Hz, 1H, CH_{b} CHOH), 2.02 (d, J = 3.2 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.7, 143.0, 132.7 (C_{Ar} H), 130.6 (C_{Ar} H), 130.2, 129.0 (C_{Ar} H), 127.9 (C_{Ar} H), 127.4 (C_{Ar} H), 121.9, 114.2 (C_{Ar} H), 74.3 (CHOH), 55.4 (OCH₃), 43.6 (CH₂CHOH). **LRMS** (ESI, m/z) 307.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₄⁷⁹BrO⁺ [M-OH]⁺ 289.0223, found 289.0221. **IR** v max (film): 3329, 2948, 1512, 1459, 1403, 1112, 1020, 880 cm⁻¹.



tert-Butyl {2-[1-hydroxy-2-(4-methoxyphenyl)ethyl]phenyl}carbamate 3m

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *tert*-butyl (2-formylphenyl)carbamate (34 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a colourless oil (26 mg, 76%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.06 – 7.82 (m, 2H, *H*_{Ar}), 7.32 – 7.21 (m, 1H, *H*_{Ar}), 7.11 (d, *J* = 8.5 Hz, 3H, *H*_{Ar}), 7.00 (td, *J* = 7.5, 1.2 Hz, 1H, *H*_{Ar}), 6.86 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.88 (ddd, *J* = 8.8,

5.3, 2.8 Hz, 1H, CHOH), 3.80 (s, 3H, OCH₃), 3.11 (dd, J = 13.7, 8.8 Hz, 1H, CH_aCHOH), 3.04 (dd, J = 13.8, 5.3 Hz, 1H, CH_bCHOH), 2.27 (d, J = 2.8 Hz, 1H, OH), 1.53 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 153.5, 137.3, 130.6 (C_{Ar}H), 129.6, 128.7 (C_{Ar}H), 127.5 (C_{Ar}H), 123.2 (C_{Ar}H), 122.0, 114.3 (C_{Ar}H), 80.2 (C(CH₃)₃), 75.8 (CHOH), 55.4 (OCH₃), 42.1 (CH₂CHOH), 28.6 (C(CH₃)₃). LRMS (ESI, m/z) 366.3 ([M+Na]⁺, 100%); HRMS (ESI) calcd for C₂₀H₂₅NO₄Na⁺ [M+Na]⁺ 366.1681, found 366.1677. IR v max (film): 3320, 2934, 1967, 1726, 1590, 1513, 1448, 1367, 1302, 1246, 1159, 1037, 755 cm⁻¹.



3-(1-Hydroxy-2-(4-methoxyphenyl)ethyl)benzonitrile 3n

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3-formylbenzonitrile (20 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a colourless oil (21 mg, 82%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.65 (s, 1H, *H*_{Ar}), 7.56 (dt, *J* = 8.0, 1.8 Hz, 2H, *H*_{Ar}), 7.44 (t, *J* = 7.7 Hz, 1H, *H*_{Ar}), 7.07 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.85 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.89 (dd, *J* = 8.5, 4.8 Hz, 1H, CHOH), 3.80 (s, 3H, OCH₃), 2.98 (dd, *J* = 13.8, 4.8 Hz, 1H, CH_aCHOH), 2.88 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_bCHOH), 2.08 (d, *J* = 2.9 Hz, 1H, OH); ¹³C **NMR** (100 MHz, CDCl₃) δ 158.8, 145.3, 131.3 (C_{Ar}H), 130.6 (C_{Ar}H), 130.5 (C_{Ar}H), 129.8 (C_{Ar}H), 129.2 (C_{Ar}H), 128.9, 119.0, 114.3 (C_{Ar}H), 112.6, 74.5 (CHOH), 55.4 (OCH₃), 45.4 (CH₂CHOH). **LRMS** (ESI, m/z) 254.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₅O₂NNa⁺ [M+Na]⁺ 276.0995, found 276.0991. **IR** v max (film): 3426, 2910, 2232, 1612, 1584, 1513, 1440, 1301, 1246, 1178, 1108, 1035, 817, 692 cm⁻¹.



2-(4-Methoxyphenyl)-1-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethan-1-ol 3o General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (35 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (22 mg, 63%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.82 (s, 1H, *H*_{Ar}), 7.74 (d, *J* = 7.2 Hz, 1H, *H*_{Ar}), 7.47 (d, *J* = 7.7 Hz, 1H, *H*_{Ar}), 7.36 (t, *J* = 7.4 Hz, 1H, *H*_{Ar}), 7.14 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 6.85 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.94 – 4.83 (m, 1H, CHOH), 3.80 (s, 3H, OCH₃), 3.01 (dd, *J* = 13.8, 4.3 Hz, 1H, C*H*_aCHOH), 2.91 (dd, *J* = 13.8, 8.9 Hz, 1H, C*H*_bCHOH), 1.92 (d, *J* = 3.0 Hz, 1H, O*H*), 1.36 (s, 12H, C(C*H*₃)₂); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.5, 143.3, 134.2 (*C*_{Ar}H), 132.3 (*C*_{Ar}H), 130.6 (*C*_{Ar}H), 130.3, 129.0 (*C*_{Ar}H), 128.0 (*C*_{Ar}H), 126.1, 114.1 (*C*_{Ar}H), 84.0 (*C*(CH₃)₂), 75.6 (CHOH), 55.4 (OCH₃), 45.3 (CH₂CHOH), 25.0 (C(CH₃)₂). **LRMS** (ESI, m/z) 377.3 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₂₁H₂₇O₄BNa⁺ [M+Na]⁺ 377.1895, found 377.1891. **IR** v max (film): 3439, 2976, 1609, 1512, 1429, 1358, 1317, 1246, 1143, 1109, 1036, 964, 857, 710 cm⁻¹.



3-[1-Hydroxy-2-(4-methoxyphenyl)ethyl]phenol 3p

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3-hydroxybenzaldehyde (18 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 60% EtOAc in petroleum ether) to give the titled product as a colourless oil (18 mg, 73%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.20 (t, *J* = 7.9 Hz, 1H, *H*_{Ar}), 7.10 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.88 (d, *J* = 7.7 Hz, 1H, *H*_{Ar}), 6.86 – 6.80 (m, 3H, *H*_{Ar}), 6.74 (dd, *J* = 7.9, 2.6 Hz, 1H, *H*_{Ar}), 5.25 (br s, 1H, ArO*H*), 4.80 (dd, *J* = 8.5, 4.8 Hz, 1H, CHOH), 3.79 (s, 3H, OC*H*₃), 2.98 (dd, *J* = 13.8, 4.8 Hz, 1H, C*H*_aCHOH), 2.89 (dd, *J* = 13.8, 8.5 Hz, 1H, C*H*_bCHOH), 2.09 (br s, 1H, CHO*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.5, 155.9, 145.8, 130.6 (*C*_{Ar}H), 129.9, 129.8 (*C*_{Ar}H), 118.5 (*C*_{Ar}H), 114.7 (*C*_{Ar}H), 114.1 (*C*_{Ar}H), 112.9 (*C*_{Ar}H), 75.3 (*C*HOH), 55.4 (OCH₃), 45.1 (*C*H₂CHOH). **LRMS** (ESI, m/z) 245.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₅O₂⁺ [M-OH]⁺ 227.1067, found 227.1065. **IR** v max (film): 3348, 2936, 2836, 1610, 1591, 1512, 1457, 1301, 1245, 1178, 1153, 110, 1033, 819, 789, 698 cm⁻¹.



1,2-Bis(4-methoxyphenyl)ethan-1-ol 3q

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 4-anisaldehyde (20 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆(2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (11 mg, 44%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.23 (m, 2H, *H*_{Ar}), 7.09 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 6.88 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.83 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.81 (ddd, *J* = 7.9, 5.5, 2.6 Hz, 1H, CHOH), 3.81 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 2.97 (dd, *J* = 13.7, 5.5 Hz, 1H, C*H*_aCHOH), 2.94 (dd, *J* = 13.7, 7.9 Hz, 1H, C*H*_bCHOH), 1.89 (d, *J* = 2.6 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 159.2, 158.5, 136.2, 130.6 (*C*_{Ar}H), 130.2, 127.3 (*C*_{Ar}H), 114.1 (*C*_{Ar}H), 113.9 (*C*_{Ar}H), 75.2 (CHOH), 55.4 (OCH₃), 55.4 (OCH₃), 45.3 (CH₂CHOH). **LRMS** (ESI, m/z) 281.1 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₈O₃Na⁺ [M+Na]⁺ 281.1148, found 281.1143. **IR** v max (film): 3389, 2938, 2836, 1612, 1585, 1512, 1464, 1301, 1245, 1176, 1105, 1034, 830 cm⁻¹. **M.p.**: 111– 113 °C (lit.: 113). The data presented are consistent with literature precedent.⁵



2-(4-Methoxyphenyl)-1-[4-(trifluoromethyl)phenyl]ethan-1-ol 3r

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 4-(trifluoromethyl)benzaldehyde (26 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a white solid (23 mg, 79%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.60 (d, J = 8.1 Hz, 2H, H_{Ar}), 7.46 (d, J = 8.1 Hz, 2H, H_{Ar}), 7.09 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.85 (d, J = 8.8 Hz, 2H, H_{Ar}), 4.92 (q, J = 3.9 Hz, 1H, CHOH), 3.80 (s, 3H, OCH₃), 3.00 (dd, J = 13.8, 4.7 Hz, 1H, CH_aCHOH), 2.89 (dd, J = 13.8, 8.5 Hz, 1H, CH_bCHOH), 2.04 (d, J = 2.9 Hz, 1H, OH); ¹³C **NMR** (100 MHz, CDCl₃) δ 158.7, 147.8, 130.6 (C_{Ar}H), 129.8 (q, ² $J_{C-F} = 32.4$ Hz, C_{Ar-F}), 129.26, 126.3 (C_{Ar-F}H), 125.5 (q, ³ $J_{C-F} = 3.8$ Hz, C_{Ar-F}), 124.3 (q, ¹ $J_{C-F} = 271.8$ Hz, C_{Ar-F}), 114.2 (C_{Ar}H), 74.9 (CHOH), 55.4 (OCH₃), 45.4 (CH₂CHOH); ¹⁹F **NMR** (376 MHz, CDCl₃) δ -63.4. **HRMS** (ESI) calcd for C₁₆H₁₅O₂F₃Na⁺ [M+Na]⁺ 319.0916, found 319.0916. **IR** v max (film): 3254, 2963, 2844, 1611, 1514, 1467, 1421, 1329, 1250, 1159, 1121, 1069, 1034, 840, 814 cm⁻¹. **M.p.**: 97 – 99 °C. The data presented are consistent with literature precedent.⁶



1-{4-[1-Hydroxy-2-(4-methoxyphenyl)ethyl]phenyl}ethan-1-one 3s

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 4-acetylbenzaldehyde (23 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a white solid (13 mg, 49%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.4 Hz, 2H, *H*_{Ar}), 7.43 (d, *J* = 8.3 Hz, 2H, *H*_{Ar}), 7.09 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.84 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 4.92 (dd, *J* = 8.4, 4.7 Hz, 1H, CHOH), 3.80 (s, 3H, OC*H*₃), 3.01 (dd, *J* = 13.8, 4.7 Hz, 1H, C*H*_aCHOH), 2.91 (dd, *J* = 13.8, 8.4 Hz, 1H, C*H*_bCHOH), 2.61 (s, 3H, COC*H*₃), 2.02 (d, *J* = 3.0 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 259.1 (COCH₃), 158.7, 149.2, 136.5, 130.7 (C_{Ar}H), 129.3, 128.6 (C_{Ar}H), 126.2 (C_{Ar}H), 114.2 (C_{Ar}H), 75.0 (CHOH), 55.4 (OCH₃), 45.3 (CH₂CHOH), 26.8 (COCH₃). **LRMS** (ESI, m/z) 271.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₇H₁₈O₃Na⁺ [M+Na]⁺ 293.1148, found 293.1144. **IR** v max (film): 3509, 3333, 2915, 1667, 1606, 1511, 1413, 1360, 1272, 1242, 1178, 1057, 1030, 834 cm⁻¹. **M.p.**: 128 – 130 °C.



Methyl 3-[1-hydroxy-2-(p-tolyl)ethyl]benzoate 3t

General Procedure A was followed using 4-methylbenzylboronic acid pinacol ester (23 mg, 0.1 mmol, 1.0 eq.), methyl 3-formylbenzoate (24 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (16 mg, 59%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.07 (s, 1H, *H*_{Ar}), 7.96 (dt, *J* = 7.8, 1.5 Hz, 1H, *H*_{Ar}), 7.56 (dt, *J* = 7.6, 1.6 Hz, 1H, *H*_{Ar}), 7.42 (t, *J* = 7.7 Hz, 1H, *H*_{Ar}), 7.16 – 7.07 (m, 4H, *H*_{Ar}), 4.93 (dt, *J* = 9.0, 3.7 Hz, 1H, C*H*OH), 3.93 (s, 3H, COOC*H*₃), 3.04 (dd, *J* = 13.7, 4.4 Hz, 1H, C*H*_aCHOH), 2.92 (dd, *J* = 13.7, 9.0 Hz, 1H, C*H*_bCHOH), 2.33 (s, 3H, CC*H*₃), 2.02 (d, *J* = 3.0 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 167.2 (COOCH₃), 144.4, 136.6, 134.6, 130.7 (C_{Ar}H), 130.4, 129.5 (C_{Ar}H), 129.5 (C_{Ar}H), 128.9 (C_{Ar}H), 128.6 (C_{Ar}H), 127.2 (C_{Ar}H), 75.0 (CHOH), 52.3 (COOCH₃), 45.9 (CH₂CHOH), 21.2 (CCH₃). **LRMS** (ESI, m/z) 271.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₇H₁₇O₃⁻ [M-H]⁻ 269.1178, found 269.1176. **IR** v max (film): 3455, 2947, 1722, 1515, 1433, 1286, 1201, 1108, 1055, 794, 759, 696 cm⁻¹.



1-[4-(Methylthio)phenyl]-2-(p-tolyl)ethan-1-ol 3u

General Procedure A was followed using 4-methylbenzylboronic acid pinacol ester (23 mg, 0.1 mmol, 1.0 eq.), 4-(methylthio)benzaldehyde (23 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (18 mg, 71%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.20 (m, 4H, H_{Ar}), 7.14 – 7.04 (m, 4H, H_{Ar}), 4.84 (ddd, J = 8.3, 4.8, 2.8 Hz, 1H, CHOH), 2.99 (dd, J = 13.7, 4.8 Hz, 1H), 2.92 (dd, J = 13.7, 8.3 Hz, 1H, C H_b CHOH), 2.49 (s, 3H, SC H_3), 2.33 (s, 3H, CC H_3), 1.91 (d, J = 2.8 Hz, 1H, OH); ¹³C **NMR** (100 MHz, CDCl₃) δ 141.0, 137.7, 136.4, 134.9, 129.5 (C_{Ar} H) 129.4 (C_{Ar} H), 126.8 (C_{Ar} H), 126.6 (C_{Ar} H), 75.1 (CHOH), 45.8 (CH₂CHOH), 21.2 (SCH₃), 16.1 (CCH₃). **HRMS** (ESI) calcd for C₁₆H₁₇S⁺ [M-OH]⁺ 241.1045, found 241.1047. **IR** v max (film): 3438, 2917, 2835, 1515, 1489, 1423, 1107, 1040, 817 cm⁻¹. **M.p**.: 90 – 92 °C.



N-Benzyl-2-(4-methoxyphenyl)-1-phenylethan-1-amine 3v

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *N*-benzylidenebenzylamine (29 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a colourless oil (22 mg, 70%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.39 – 7.31 (m, 4H, H_{Ar}), 7.29 – 7.25 (m, 3H, H_{Ar}), 7.21 (t, J = 7.2 Hz, 1H, H_{Ar}), 7.15 – 7.11 (m, 2H, H_{Ar}), 7.02 (d, J = 8.4 Hz, 2H, H_{Ar}), 6.80 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.85 (dd, J = 8.7, 5.5 Hz, 1H, CHNH), 3.80 (s, 3H, OCH₃), 3.66 (d, J = 13.6 Hz, 1H, CH_aNH), 3.47 (d, J = 13.6 Hz, 1H, CH_aNH), 2.91 (dd, J = 13.7, 5.5 Hz, 1H, CH_aCHOH), 2.84 (dd, J = 13.7, 8.7

Hz, 1H, C*H*_bCHOH), 1.66 (br s, 1H, N*H*); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 144.0, 140.7, 131.0, 130.4 (*C*_{Ar}H), 128.5 (*C*_{Ar}H), 128.4 (*C*_{Ar}H), 128.1 (*C*_{Ar}H), 127.6 (*C*_{Ar}H), 127.2 (*C*_{Ar}H), 126.9 (*C*_{Ar}H), 113.9 (*C*_{Ar}H), 63.9 (*C*HNH), 55.4 (OCH₃), 51.5 (*C*H₂NH), 44.6 (*C*H₂CHNH). LRMS (ESI, m/z) 318.3 ([M+H]⁺, 100%); HRMS (ESI) calcd for C₂₂H₂₄NO⁺ [M+H]⁺ 318.1858, found 318.1855. IR v max (film): 3590, 3026, 2917, 2356, 1611, 1511, 1453, 1247, 1177, 1035, 699 cm⁻¹.



N-[2-(4-Methoxyphenyl)-1-phenylethyl]-2-methylpropan-2-amine 3w

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *N*-benzylidene-*tert*-butylamine (24 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (16 mg, 56%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H, *H*_{Ar}), 7.30 – 7.24 (m, 2H, *H*_{Ar}), 7.21 – 7.16 (m, 1H, *H*_{Ar}), 7.05 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 6.80 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 3.94 (dd, *J* = 9.0, 5.5 Hz, 1H, C*H*NH), 3.79 (s, 3H, OC*H*₃), 2.86 (dd, *J* = 13.6, 5.5 Hz, 1H, C*H*_aNH), 2.64 (dd, *J* = 13.6, 9.0 Hz, 1H, C*H*_bNH), 1.39 (br s, 1H, N*H*), 0.84 (s, 9H, C(C*H*₃)₃); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.3, 147.8, 131.5, 130.4 (*C*_{Ar}H), 128.2 (*C*_{Ar}H), 127.3 (*C*_{Ar}H), 126.5 (*C*_{Ar}H), 113.8 (*C*_{Ar}H), 59.4 (CHNH), 55.4 (OCH₃), 51.3 (*C*(CH₃)₃), 46.4 (*C*H₂CHNH), 30.1 (C(*C*H₃)₃). **LRMS** (ESI, m/z) 284.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₉H₂₆NO⁺ [M+H]⁺ 284.2014, found 284.2012. **IR** v max (film): 3786, 2957, 2345, 1611, 1512, 1453, 1388, 1364, 1301, 1246, 1177, 1036, 823, 758, 700 cm⁻¹.



2-(4-Methoxyphenyl)-*N*-methyl-1-phenylethan-1-amine 3x

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *N*-benzylidenemethylamine (18 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg,

0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a colourless oil (19 mg, 80%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.37 – 7.23 (m, 5H, *H*_{Ar}), 7.05 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.81 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 3.79 (s, 3H, OC*H*₃), 3.68 (dd, *J* = 8.4, 5.6 Hz, 1H, C*H*NH), 2.90 (dd, *J* = 13.7, 5.6 Hz, 1H, C*H*_aNH), 2.82 (dd, *J* = 13.6, 8.4 Hz, 1H, C*H*_bNH), 2.21 (s, 3H, NC*H*₃), 1.70 (br s, 1H, N*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.3, 143.6, 131.0, 130.4 (*C*_{Ar}H), 128.5 (*C*_{Ar}H), 127.5 (*C*_{Ar}H), 127.2 (*C*_{Ar}H), 114.0 (*C*_{Ar}H), 67.2 (*C*HNH), 55.4 (OCH₃), 44.4 (*C*H₂CHNH), 34.8 (NCH₃). **LRMS** (ESI, m/z) 242.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₂₀NO⁺ [M+H]⁺ 242.1545, found 242.1547. **IR** v max (film): 3297, 2172, 1632, 1512, 1248, 1038, 798, 700 cm⁻¹.



2-(4-Methoxyphenyl)-1-(perfluorophenyl)ethan-1-ol 3y

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2,3,4,5,6-pentafluorobenzaldehyde (29 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a white solid (13 mg, 42%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.08 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.83 (d, J = 8.6 Hz, 2H, H_{Ar}), 5.24 (q, J = 7.1 Hz, 1H, CHOH), 3.79 (s, 3H, OCH₃), 3.25 (dd, J = 13.7, 8.0 Hz, 1H, CH_aCHOH), 3.05 (dd, J = 13.7, 6.5 Hz, 1H, CH_bCHOH), 2.24 (d, J = 6.9 Hz, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.9, 146.2, 139.5, 138.8, 131.1, 130.3 (C_{Ar} H), 128.3, 116.2, 114.4 (C_{Ar} H), 113.3, 67.7 (CHOH), 55.4 (OCH₃), 42.4 (CH₂CHOH); ¹⁹**F NMR** (376 MHz, CDCl₃) δ -144.2 - -144.5 (m), -155.9 (t, J = 21.0 Hz), -162.6 - -163.3 (m). **LRMS** (ESI, m/z) 341.3 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₅H₁₁O₂F₅Na⁺ [M+Na]⁺ 341.0571, found 341.0566. **IR** v max (film): 3422, 2938, 2837, 1653, 1612, 1503, 1466, 1420, 1302, 1248, 1178, 1121, 1035, 997, 953, 882, 821 cm⁻¹. **M.p.**: 78 – 80 °C.



1-Mesityl-2-(4-methoxyphenyl)ethan-1-ol 3z

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), mesitaldehyde (22 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a colourless oil (14 mg, 50%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.14 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.85 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.83 (s, 2H, *H*_{Ar}), 5.25 (ddd, *J* = 9.1, 5.1, 2.6 Hz, 1H, CHOH), 3.80 (s, 3H, OCH₃), 3.15 (dd, *J* = 13.8, 9.1 Hz, 1H, C*H*_aCHOH), 2.94 (dd, *J* = 13.8, 5.1 Hz, 1H, C*H*_bCHOH), 2.39 (s, 6H, C*H*₃), 2.26 (s, 3H, C*H*₃), 1.75 (d, *J* = 2.6 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.5, 136.8, 136.2, 136.1, 131.0, 130.5 (*C*_{Ar}H), 130.3 (*C*_{Ar}H), 114.1 (*C*_{Ar}H), 73.0 (*C*HOH), 55.4 (OCH₃), 41.5 (*C*H₂CHOH), 20.9 (*C*H₃), 20.9 (2 × CH₃). **HRMS** (ESI) calcd for C₁₈H₂₁O₂⁻ [M-H]⁻ 269.1542, found 269.1541. **IR** v max (film): 3331, 2946, 2835, 1512, 1449, 1412, 1113, 1040, 970, 835 cm⁻¹.



2-(4-methoxyphenyl)-1-(pyridin-2-yl)ethan-1-ol 3aa

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2-pyridinecarboxaldehyde (16 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 60% EtOAc in petroleum ether) to give the titled product as a white solid (18 mg, 80%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.57 (dt, *J* = 4.9, 1.2 Hz, 1H, *H*_{Pyridine}), 7.65 (td, *J* = 7.6, 1.8 Hz, 1H, *H*_{Pyridine}), 7.21 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H, *H*_{Pyridine}), 7.14 (d, *J* = 7.9 Hz, 1H, *H*_{Pyridine}), 7.09 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.83 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.95 (s, 1H, CHOH), 3.91 (d, *J* = 5.3 Hz, 1H, OH), 3.81 (s, 3H, OCH₃), 3.08 (dd, *J* = 13.7, 5.4 Hz, 1H, CH_aCHOH), 2.99 (dd, *J* = 13.7, 7.4 Hz, 1H,

CH_bCHOH); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 158.4, 148.5 (C_{Pyridine}H), 136.5 (C_{Pyridine}H), 130.7 (C_{Ar}H), 129.8, 122.5 (C_{Pyridine}H), 120.9 (C_{Pyridine}H), 113.9 (C_{Ar}H), 74.3 (CHOH), 55.4 (OCH₃), 44.4 (CH₂CHOH). **LRMS** (ESI, m/z) 230.4 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₆O₂N⁺ [M+H]⁺ 230.1176, found 230.1173. **IR** v max (film): 3120, 2907, 2833, 1713, 1598, 1510, 1465, 1435, 1336, 1302, 1242, 1177, 1111, 1035, 1006, 828, 805, 755 cm⁻¹. **M.p.**: 113 – 115 °C.



2-(4-Methoxyphenyl)-1-(pyridin-3-yl)ethan-1-ol 3ab

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3-pyridinecarboxaldehyde (16 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 60% EtOAc in petroleum ether) to give the titled product as a white solid (21 mg, 92%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.51 (d, J = 2.4 Hz, 1H, $H_{Pyridine}$), 8.49 (dd, J = 5.0, 1.8 Hz, 1H, $H_{Pyridine}$), 7.67 (dt, J = 7.9, 1.8 Hz, 1H, $H_{Pyridine}$), 7.26 (td, J = 5.0, 2.4 Hz, 1H, $H_{Pyridine}$), 7.08 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.84 (d, J = 8.6 Hz, 2H, H_{Ar}), 4.89 (dd, J = 8.2, 5.2 Hz, 1H, CHOH), 3.79 (s, 3H, OCH₃), 2.99 (dd, J = 13.7, 5.2 Hz, 1H, CH_{a} CHOH), 2.93 (dd, J = 13.7, 8.2 Hz, 1H, CH_{b} CHOH), 2.39 (br s, 1H, OH); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.7, 149.0 ($C_{Pyridine}$ H), 148.0 ($C_{Pyridine}$ H), 139.2, 133.8 ($C_{Pyridine}$ H), 130.7 (C_{Ar} H), 129.2, 123.5 ($C_{Pyridine}$ H), 114.2 (C_{Ar} H), 73.3 (CHOH), 55.4 (OCH₃), 45.3 (CH₂CHOH). **LRMS** (ESI, m/z) 230.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₆O₂N⁺ [M+H]⁺ 230.1176, found 230.1174. **IR** v max (film): 3332, 3194, 2907, 1611, 1583, 1512, 1464, 1428, 130, 1246, 1178, 1108, 1032, 814, 714 cm⁻¹. **M.p.**: 117 – 119 °C.



6-[1-Hydroxy-2-(4-methoxyphenyl)ethyl]-2-(methylthio)nicotinonitrile 3ac

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1

mmol, 1.0 eq.), 6-formyl-2-(methylthio)nicotinonitrile (27 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a white solid (26 mg, 86%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.73 (d, *J* = 7.9 Hz, 1H, *H*_{Pyridine}), 7.01 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.95 (d, *J* = 7.9 Hz, 1H, *H*_{Pyridine}), 6.82 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 5.02 – 4.86 (m, 1H, CHOH), 3.79 (s, 3H, OCH₃), 3.25 (d, *J* = 6.0 Hz, 1H, OH), 3.11 (dd, *J* = 13.8, 5.3 Hz, 1H, CH_aCHOH), 2.97 (dd, *J* = 13.8, 7.2 Hz, 1H, CH_bCHOH), 2.58 (s, 3H, SCH₃); ¹³C **NMR** (151 MHz, CDCl₃) δ 165.3, 162.8, 158.7, 141.0 (*C*_{Pyridine}H), 130.7 (*C*_{Ar}H), 128.7, 115.7 (*C*N), 115.5 (*C*_{Pyridine}H), 114.1 (*C*_{Ar}H), 105.9, 74.5 (CHOH), 55.4 (OCH₃), 43.7 (CH₂CHOH), 13.3 (SCH₃). **LRMS** (ESI, m/z) 301.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₇N₂O₂S⁺ [M+H]⁺ 301.1011, found 301.1005. **IR** v max (film): 3477, 2929, 2834, 2224, 1611, 1572, 1511, 1425, 1358, 1301, 1245, 1177, 1071, 1033, 907, 834, 788 cm⁻¹. **M.p.**: 112 – 115 °C.



2-(4-Isocyanophenyl)-1-(pyridin-3-yl)ethan-1-ol 3ad

General Procedure A was followed using 4-isocyanobenzylboronic acid pinacol ester (24 mg, 0.1 mmol, 1.0 eq.), 3-pyridinecarboxaldehyde (16 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a white solid (7 mg, 33%).

¹**H NMR** (400 MHz, CDCl₃) δ 8.58 – 8.52 (m, 2H, *H*_{Pyridine}), 7.65 (d, *J* = 7.9 Hz, 1H, *H*_{Pyridine}), 7.59 (d, *J* = 7.8 Hz, 2H, *H*_{Ar}), 7.29 (dd, *J* = 7.9, 4.7 Hz, 3H, *H*_{Pyridine} + *H*_{Ar}), 4.99 (dd, *J* = 7.8, 5.3 Hz, 1H, CHOH), 3.15 – 3.04 (m, 2H, CH₂CHOH); ¹³**C NMR** (100 MHz, CDCl₃) δ 165.6, 149.6 (*C*_{Pyridine}H), 147.9 (*C*_{Pyridine}H), 143.0, 138.6, 133.7 (*C*_{Pyridine}H), 132.4 (*C*_{Ar}H), 130.6 (*C*_{Ar}H), 123.7 (*C*_{Pyridine}H), 111.0, 72.8 (CHOH), 45.8 (*C*H₂CHOH). **LRMS** (ESI, m/z) 225.1 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₄H₁₃ON₂⁺ [M+H]⁺ 225.1028, found 225.1026. **IR** v max (film): 3399, 3334, 2925, 1607, 1512, 1432, 1095, 1004, 814 cm⁻¹. **M.p.**: 118 – 120 °C.



tert-Butyl 2-[1-hydroxy-2-(4-methoxyphenyl)ethyl]-1H-pyrrole-1-carboxylate 3ae

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), *N*-Boc-pyrrole-2-carboxaldehyde (29 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and {Ir[dF(CF₃)ppy]₂(dtbpy)}PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 50% EtOAc in petroleum ether) to give the titled product as a pale-yellow oil (19 mg, 61%). The product is not stable under air. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.13 (m, 3H, *H*_{Pyrrole} + *H*_{Ar}), 6.83 (d, *J* = 8.6 Hz, 2H), 6.22 – 6.17 (m, 1H, *H*_{Pyrrole}), 6.09 (t, *J* = 3.4 Hz, 1H, *H*_{Pyrrole}), 5.10 (dt, *J* = 8.5, 5.6 Hz, 1H, CHOH), 3.90 (d, *J* = 5.6 Hz, 1H, OH), 3.79 (s, 3H, OCH₃), 3.15 (dd, *J* = 13.8, 5.5 Hz, 1H, CH_aCHOH), 3.08 (dd, *J* = 13.8, 8.5 Hz, 1H, CH_bCHOH), 1.60 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 144.2, 137.8, 131.2, 130.5 (C_{Ar}H), 122.1 (C_{Pyrrole}H), 113.8 (C_{Ar}H), 112.0 (C_{Pyrrole}H), 110.5 (C_{Pyrrole}H), 84.7 (C(CH₃)₃), 68.2 (CHOH), 55.4 (OCH₃), 40.8 (CH₂CHOH), 28.1 (C(CH₃)₃). LRMS (ESI, m/z) 340.4 ([M+Na]⁺, 100%); HRMS (ESI) calcd for C₁₈H₂₃O₄NNa⁺ [M+Na]⁺ 340.1519, found 340.1517. IR v max (film): 2977, 2341, 1737, 1605, 1511, 1467, 1393, 1369, 1325, 1249, 1173, 1121, 1066, 1034, 961, 847, 727 cm⁻¹.



2-(4-Methoxyphenyl)-1-(pyrimidin-5-yl)ethan-1-ol 3af

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), pyrimidine-5-carboxaldehyde (16 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 45% EtOAc in petroleum ether) to give the titled product as a white solid (18 mg, 76%).

¹**H NMR** (400 MHz, CDCl₃) δ 9.12 (s, 1H, *H*_{Pyrimidine}), 8.67 (s, 2H, *H*_{Pyrimidine}), 7.08 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.85 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 4.92 (ddd, *J* = 8.2, 5.2, 3.0 Hz, 1H, CHOH), 3.79 (s, 3H, OC*H*₃), 3.02 (dd, *J* = 13.8, 5.2 Hz, 1H, C*H*_aCHOH), 2.96 (dd, *J* = 13.8, 8.2 Hz, 1H, C*H*_bCHOH), 2.41 (d, *J* = 3.0 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 159.0, 158.1 (*C*_{Pyrimidine}H), 155.0 (*C*_{Thiophene}H), 136.6, 130.7 (*C*_{Ar}H), 128.2, 114.5 (*C*_{Ar}H), 71.4 (CHOH), 55.4 (OCH₃), 45.1 (*C*_{H2}CHOH). **LRMS** (ESI, m/z) 253.2 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₃H₁₄O₂N₂Na⁺ [M+Na]⁺ 253.0947, found 253.0945. **IR** v max (film): 3303, 2936, 2835, 1611, 1567, 1512, 1439, 1408, 1301, 1247, 1178, 1110, 1064, 1034, 821, 727 cm⁻¹. **M.p.**: 105 – 107 °C.



1-(2-Chloroquinolin-3-yl)-2-(4-methoxyphenyl)ethan-1-ol 3ag

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2-chloroquinoline-3-carbaldehyde (29 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 50% EtOAc in petroleum ether) to give the titled product as a white solid (18 mg, 59%).

¹**H** NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H, *H*_{Quinoline}), 8.02 (d, *J* = 8.5 Hz, 1H, *H*_{Quinoline}), 7.83 (dd, *J* = 8.2, 1.4 Hz, 1H, *H*_{Quinoline}), 7.72 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H, *H*_{Quinoline}), 7.56 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H, *H*_{Quinoline}), 7.23 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 6.88 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 5.32 (dd, *J* = 8.8, 2.8 Hz, 1H, *CH*OH), 3.80 (s, 4H, OC*H*₃), 3.32 (dd, *J* = 14.0, 3.0 Hz, 1H, *CH*_aCHOH), 2.72 (dd, *J* = 14.0, 9.1 Hz, 1H, *CH*_bCHOH), 2.37 (s, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 148.7, 147.1, 135.9 (*C*_{Quinoline}H), 135.7, 130.7 (*C*_{Ar}H), 130.4 (*C*_{Quinoline}H), 129.6, 128.3 (*C*_{Quinoline}H), 127.8 (*C*_{Quinoline}H), 127.6, 127.3 (*C*_{Quinoline}H), 114.3 (*C*_{Ar}H), 71.8 (*C*HOH), 55.4 (O*C*H₃), 43.7 (*C*H₂CHOH). **LRMS** (ESI, m/z) 314.1 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₈H₁₇O₂N³⁵Cl⁺ [M+H]⁺ 314.0948, found 314.0945. **IR** v max (film): 3376, 2922, 2835, 2359, 1612, 1511, 1491, 1398, 1327, 1246, 1177, 1138, 1037, 818, 782, 754 cm⁻¹. **M.p.**: 111 – 113 °C.



2-(4-Methoxyphenyl)-1-(thiazol-2-yl)ethan-1-ol 3ah

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2-thiazolecarboxaldehyde (17 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 40% EtOAc in petroleum ether) to give the titled product as a white solid (16 mg, 68%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.75 (d, J = 3.2 Hz, 1H, H_{Thiazole}), 7.29 (d, J = 3.2 Hz, 1H, H_{Thiazole}), 7.14 (d, J = 8.5 Hz, 2H, H_{Ar}), 6.85 (d, J = 8.5 Hz, 2H, H_{Ar}), 5.18 (dt, J = 8.5, 4.3 Hz, 1H, CHOH), 3.79 (s, 3H, OCH₃), 3.30 (dd, J = 13.9, 4.3 Hz, 1H, CH_aCHOH), 3.04 (dd, J = 13.9, 8.5 Hz, 1H, CH_bCHOH), 2.86 (d, J = 4.7 Hz, 1H, OH); ¹³C **NMR** (100 MHz, CDCl₃) δ 174.2, 158.8, 142.5 (C_{Thiazole} H), 130.8 (C_{Ar} H), 128.7, 119.1 (C_{Thiazole} H), 114.2 (C_{Ar} H), 73.1 (CHOH), 55.4 (OCH₃), 43.8 (CH₂CHOH). **LRMS** (ESI, m/z) 236.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₂H₁₄O₂NS⁺ [M+H]⁺ 236.0745, found 236.0745. **IR** v max (film): 3397, 3245, 2358, 1611, 1513, 1247, 1178, 1035, 787, 669 cm⁻¹. **M.p.**: 98 – 100 °C.



2-(4-Methoxyphenyl)-1-{5-[1-methyl-5-(trifluoromethyl)-1*H*-pyrazol-3-yl]thiophen-2-yl}ethan-1-ol 3ai

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 5-[1-methyl-5-(trifluoromethyl)-1*H*-pyrazol-3-yl]thiophene-2-carbaldehyde (39 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a white solid (21 mg, 54%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.16 – 7.10 (m, 3H, *H*_{Ar}), 6.87 – 6.83 (m, 3H, *H*_{Ar}), 6.77 (s, 1H, *H*_{Ar}), 5.08 (dd, *J* = 8.0, 5.3 Hz, 1H, CHOH), 4.00 (s, 3H, NCH₃), 3.79 (s, 3H, OCH₃), 3.11 (dd, *J* = 13.8,

5.3 Hz, 1H, C*H*_aCHOH), 3.06 (dd, J = 13.8, 8.0 Hz, 1H, C*H*_bCHOH), 2.13 (br s, 1H, O*H*); ¹³C NMR (151 MHz, CDCl₃) δ 158.7, 147.7, 145.9, 134.3, 133.3 (q, ²*J*_{C-F} = 39.1 Hz, *C*_{Ar-F}), 130.6 (*C*_{Ar}H), 129.4, 124.6 (*C*_{Ar}H), 123.9 (*C*_{Ar}H), 120.0 (q, ¹*J*_{C-F} = 268.9 Hz, *C*_{Ar-F}), 114.2 (*C*_{Ar}H), 104.4 (d, ³*J*_{C-F} = 2.3 Hz, *C*_{Ar-F}H), 71.6 (*C*HOH), 55.4 (OCH₃), 45.2 (*C*H₂CHOH), 38.2 (d, ³*J*_{C-F} = 2.1 Hz, N*C*_{Ar-F}H₃); ¹⁹F NMR (376 MHz, CDCl₃) δ -60.6. LRMS (ESI, m/z) 383.1 ([M+H]⁺, 100%); HRMS (ESI) calcd for C₁₈H₁₈N₂O₂F₃S⁺ [M+H]⁺ 383.1041, found 383.1032. IR v max (film):3363, 2923, 2316, 1611, 1545, 1513, 1421, 1273, 1247, 1196, 1180, 1158, 1128, 1035, 804, 711 cm⁻¹. M.p.: 104 – 106 °C.



2-(4-Methoxyphenyl)-1-(thiophen-2-yl)ethan-1-ol 3aj

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2-thiophenecarboxaldehyde (17 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (11 mg, 48%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.29 – 7.23 (m, 1H, *H*_{Thiophene}), 7.14 (d, *J* = 8.3 Hz, 2H, *H*_{Ar}), 6.99 – 6.92 (m, 2H, *H*_{Thiophene}), 6.85 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 5.11 (t, *J* = 7.3 Hz, 1H, CHOH), 3.79 (s, 3H, OC*H*₃), 3.11 (dd, *J* = 13.8, 5.1 Hz, 1H, C*H*_aCHOH), 3.04 (dd, *J* = 13.8, 8.2 Hz, 1H, C*H*_bCHOH), 2.09 (d, *J* = 3.4 Hz, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.7, 147.8, 130.6 (*C*_{Ar}H), 129.6, 126.8 (*C*_{Thiophene}H), 124.7 (*C*_{Thiophene}H), 124.0 (*C*_{Thiophene}H), 114.1 (*C*_{Ar}H), 71.5 (*C*HOH), 55.4 (OCH₃), 45.4 (*C*H₂CHOH). **LRMS** (ESI, m/z) 257.3 ([M+Na]⁺, 100%); **HRMS** (ESI) calcd for C₁₃H₁₄O₂SNa⁺ [M+Na]⁺ 257.0607, found 257.0604. **IR** v max (film): 3749, 3400, 2918, 1611, 1512, 1463, 1301, 1246, 1178, 1033, 831, 701 cm⁻¹.

Cross-coupling products of benzylboronic esters with ketones



1-(4-Methoxyphenyl)-2-phenylpropan-2-ol 5a

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), acetophenone (18 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 20% EtOAc in petroleum ether) to give the titled product as a colourless oil (13 mg, 54%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H, *H*_{Ar}), 7.35 – 7.30 (m, 2H, *H*_{Ar}), 7.26 – 7.20 (m, 1H, *H*_{Ar}), 6.90 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.75 (d, *J* = 8.7 Hz, 2H, *H*_{Ar}), 3.77 (s, 3H, OC*H*₃), 3.08 (d, *J* = 13.5 Hz, 1H, C*H*_aCCH₃), 2.96 (d, *J* = 13.5 Hz, 1H, C*H*_bCCH₃), 1.84 (br s, 1H, O*H*), 1.56 (s, 3H, C*H*₃); ¹³**C NMR** (100 MHz, CDCl₃) δ 158.6, 147.8, 131.7 (*C*_{Ar}H), 128.8, 128.2 (*C*_{Ar}H), 126.8 (*C*_{Ar}H), 125.2 (*C*_{Ar}H), 113.7 (*C*_{Ar}H), 74.6 (CH₂CCH₃), 55.3 (OCH₃), 49.7 (CH₂CCH₃), 29.5 (CCH₃). **LRMS** (ESI, m/z) 243.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₇O₂⁻ [M-H]⁻ 241.1234, found 241.1229. **IR** v max (film): 3519, 3410, 2934, 1611, 1512, 1445, 1247, 1179, 1035, 819, 700 cm⁻¹. The data presented are consistent with literature precedent.⁷



2-(2,6-Difluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5b

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2',6'-difluoroacetophenone (24 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (9 mg, 32%).
¹**H NMR** (600 MHz, CDCl₃) δ 7.21 – 7.12 (m, 1H, H_{Ar}), 6.87 (d, J = 8.8 Hz, 2H, H_{Ar}), 6.84 – 6.76 (m, 2H, H_{Ar}), 6.73 (d, J = 8.8 Hz, 2H, H_{Ar}), 3.76 (s, 3H, OCH₃), 3.20 (d, J = 13.5 Hz, 1H, CH_aCOH), 3.13 – 3.07 (m, 1H, OH), 3.02 (d, J = 13.5 Hz, 1H, CH_bCOH), 1.75 (t, J = 1.1 Hz, 3H, CCH₃); ¹³**C NMR** (151 MHz, CDCl₃) δ 160.7 (dd, ¹ $J_{C-F} = 246.8$, 8.9 Hz, C_{Ar-F}), 158.6, 131.3 (C_{Ar} H), 128.7, 128.6, 122.0, 113.7 (C_{Ar} H), 112.6 (d, ² $J_{C-F} = 29.7$ Hz, C_{Ar-F}), 76.1 (CH₂COH), 55.3 (OCH₃), 48.6 (CH₂COH), 28.6 (CCH₃); ¹⁹**F NMR** (376 MHz, CDCl₃) δ -110.5. **HRMS** (ESI) calcd for C₁₆H₁₅F₂O⁻ [M-OH]⁺ 261.1091, found 261.1096. **IR** ν max (film): 3373, 2343, 2183, 1513, 1464, 1250, 987, 787 cm⁻¹.



2-(2-Fluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5c

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2'-fluoroacetophenone (21 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (12 mg, 44%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.32 (td, J = 8.1, 1.7 Hz, 1H, H_{Ar}), 7.25 – 7.19 (m, 1H, H_{Ar}), 7.09 – 6.99 (m, 2H, H_{Ar}), 6.90 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.74 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.75 (s, 3H, OCH₃), 3.29 (d, J = 13.7 Hz, 1H, C H_a COH), 3.04 (d, J = 13.7 Hz, 1H, C H_b COH), 2.08 (d, J = 1.8 Hz, 1H, OH), 1.63 (s, 3H, CCH₃); ¹³C **NMR** (151 MHz, CDCl₃) δ 158.8, 158.6, 134.1, 131.5 (C_{Ar} H), 128.8, 128.7 (d, $^2J_{C-F} = 17.8$ Hz, C_{Ar-F}), 127.6 (d, $^3J_{C-F} = 4.5$ Hz, C_{Ar-F}), 124.1 (d, $^3J_{C-F} = 3.2$ Hz, C_{Ar-F}), 116.0 (d, $^1J_{C-F} = 23.9$ Hz, C_{Ar-F}), 113.8 (C_{Ar} H), 73.7 (CH₂COH), 55.3 (OCH₃), 47.2 (d, $^4J_{C-F} = 4.0$ Hz, CH₂COH), 28.3 (d, $^4J_{C-F} = 3.9$ Hz, CCH₃); ¹⁹F **NMR** (376 MHz, CDCl₃) δ -112.8. **HRMS** (ESI) calcd for C₁₆H₁₈FO₂⁺ [M+H]⁺ 261.1291, found 261.1285. **IR** ν max (film): 3492, 2915, 2341, 1612, 1512, 1485, 1447, 1247, 1178, 1036, 811, 758 cm⁻¹.



2-[3,5-Bis(trifluoromethyl)phenyl]-1-(4-methoxyphenyl)propan-2-ol 5d

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3',5'-bis(trifluoromethyl)acetophenone (38 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a colourless oil (24 mg, 64%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 (d, J = 1.7 Hz, 2H, H_{Ar}), 7.77 (s, 1H, H_{Ar}), 6.91 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.80 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.78 (s, 3H, OCH₃), 3.03 (d, J = 13.6 Hz, 1H, CH_aCOH), 2.98 (d, J = 13.6 Hz, 1H, CH_bCOH), 1.98 (s, 1H, OH), 1.59 (s, 3H, CCH₃); ¹³**C NMR** (151 MHz, CDCl₃) δ 159.0, 150.5, 131.6 (C_{Ar} H), 131.4 (m, C_{Ar} H-F), 127.5, 125.7, 123.6 (q, $J_{C-F} = 272.3$ Hz, C_{C-F}), 120.8 (m, C_{Ar} H-F), 114.1 (C_{Ar} H), 74.3 (CH₂COH), 55.4 (OCH₃), 49.6 (CH₂COH), 29.4 (CCH₃). ¹⁹**F NMR** (376 MHz, CDCl₃) δ -62.7. **HRMS** (ESI) calcd for C₁₈H₁₅O₂F₆⁻ [M-H]⁻ 377.0976, found 377.0978. **IR** ν max (film): 3564, 3491, 2945, 2339, 1612, 1513, 1468, 1376, 1278, 1170, 1130, 1037, 899, 844, 708, 682 cm⁻¹.



3-[2-Hydroxy-1-(4-methoxyphenyl)propan-2-yl]phenol 5e

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 3-hydroxyacetophenone (20 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (9 mg, 35%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.20 (t, J = 7.9 Hz, 1H, H_{Ar}), 6.96 – 6.87 (m, 4H, H_{Ar}), 6.76 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.71 (ddd, J = 8.0, 2.5, 0.9 Hz, 1H, H_{Ar}), 4.92 (br s, 1H, ArOH), 3.77 (s, 3H, OCH₃), 3.07 (d, J = 13.6 Hz, 1H, CH_aCOH), 2.94 (d, J = 13.6 Hz, 1H, CH_aCOH), 1.87 (s, 1H, COH),

1.53 (s, 3H, CC*H*₃); ¹³C **NMR** (151 MHz, CDCl₃) δ 158.6, 155.6, 149.9, 131.7 (*C*_{Ar}H), 129.5 (*C*_{Ar}H), 128.6, 117.7 (*C*_{Ar}H), 113.7 (*C*_{Ar}H), 113.6 (*C*_{Ar}H), 112.4 (*C*_{Ar}H), 74.6 (CH₂COH), 55.3 (OCH₃), 49.5 (CH₂COH), 29.6 (CCH₃). **LRMS** (ESI, m/z) 259.1 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₁₆H₁₉O₃⁺ [M+H]⁺ 259.1334, found 259.1323. **IR** v max (film): 3306, 2150, 1609, 1512, 1448, 1248, 1178, 1003, 704 cm⁻¹.



1-(4-Methoxyphenyl)-2-(naphthalen-1-yl)propan-2-ol 5f

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 1-acetonaphthone (26 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆(2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (11 mg, 36%).

¹**H NMR** (600 MHz, CDCl₃) δ 8.88 (d, J = 8.6 Hz, 1H, H_{Naphth}), 7.90 (d, J = 8.6 Hz, 1H, H_{Naphth}), 7.78 (d, J = 8.0 Hz, 1H, H_{Naphth}), 7.56 (ddd, J = 8.6, 6.7, 1.5 Hz, 1H, H_{Naphth}), 7.50 (ddd, J = 8.0, 6.7, 1.2 Hz, 1H, H_{Naphth}), 7.43 (dd, J = 7.3, 1.2 Hz, 1H, H_{Naphth}), 7.35 (t, J = 7.7 Hz, 1H, H_{Naphth}), 6.85 (d, J = 8.5 Hz, 2H, H_{Ar}), 6.72 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.75 (s, 3H, OCH₃), 3.55 (d, J = 13.6 Hz, 1H, CH_aCOH), 3.32 (d, J = 13.6 Hz, 1H, CH_bCOH), 2.09 (s, 1H, OH), 1.79 (s, 3H, CCH₃); ¹³C **NMR** (151 MHz, CDCl₃) δ 158.5, 142.3, 135.0, 131.7 (C_{Ar}H), 131.0, 129.5 (C_{Naphth}H), 129.3, 128.8 (C_{Naphth}H), 127.1 (C_{Naphth}H), 125.6 (C_{Naphth}H), 125.3 (C_{Naphth}H), 125.0 (C_{Naphth}H), 124.2 (C_{Naphth}H), 113.6 (C_{Ar}H), 76.3 (CH₂COH), 55.3 (OCH₃), 47.8 (CH₂COH), 29.6 (CCH₃). **HRMS** (ESI) calcd for C₂₀H₁₉O⁺ [M-OH]⁺ 275.1430, found 275.1434. **IR** v max (film): 3650, 3466, 2331, 2167, 1996, 1611, 1511, 1298, 1247, 779 cm⁻¹. The data presented are consistent with literature precedent.⁸



1,1,1-Trifluoro-3-(4-methoxyphenyl)-2-phenylpropan-2-ol 5g

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2,2,2-trifluoroacetophenone (26 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (15 mg, 49%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.49 (m, 2H, *H*_{Ar}), 7.42 – 7.32 (m, 3H, *H*_{Ar}), 6.89 (d, *J* = 8.7 Hz, 2H, *H*_{Ar}), 6.73 (d, *J* = 8.7 Hz, 2H, *H*_{Ar}), 3.74 (s, 3H, OC*H*₃), 3.47 – 3.27 (m, 2H, C*H*₂COH), 2.41 (s, 1H, O*H*); ¹³**C NMR** (100 MHz, CDCl₃) δ 159.2, 137.4, 131.9 (*C*_{Ar}H), 128.6 (*C*_{Ar}H), 128.4 (*C*_{Ar}H), 126.6 (q, ⁴*J*_{C-F} = 1.5 Hz, *C*_{Ar-F}H), 124.9, 125.7 (q, ¹*J*_{C-F} = 285.7 Hz, *C*_{Ar-F}), 114.0 (*C*_{Ar}H), 55.3 (OCH₃), 41.1 (*C*H₂COH). One carbon is not detectable due to peak overlapping. ¹⁹**F NMR** (376 MHz, CDCl₃) δ -78.2. **HRMS** (ESI) calcd for C₁₆H₁₄OF₃⁺ [M-OH]⁺ 279.0997, found 279.0996. **IR** v max (film): 3454, 2932, 1974, 1612, 1514, 1449, 1249, 1156, 1073, 1034, 962, 831, 759, 701 cm⁻¹. The data presented are consistent with literature precedent.⁹



2-(4-Methoxyphenyl)-1,1-diphenylethan-1-ol 5h

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), benzophenone (27 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a white solid (18 mg, 59%).

¹**H NMR** (400 MHz, CDCl₃) δ 7.49 – 7.40 (m, 4H, H_{Ar}), 7.31 (t, J = 7.5 Hz, 4H, H_{Ar}), 7.23 (t, J = 7.3 Hz, 2H, H_{Ar}), 6.81 (d, J = 8.7 Hz, 2H, H_{Ar}), 6.70 (d, J = 8.7 Hz, 2H, H_{Ar}), 3.74 (s, 3H, OCH₃), 3.60 (s, 2H, CH₂COH), 2.32 (s, 1H, OH); ¹³C **NMR** (100 MHz, CDCl₃) δ 158.7, 146.8, 132.0 (C_{Ar} H), 128.2 (C_{Ar} H), 127.7, 127.0 (C_{Ar} H), 126.3 (C_{Ar} H), 113.7 (C_{Ar} H), 77.9 (CH₂COH), 55.3 (OCH₃), 47.2 (CH₂COH). **HRMS** (ESI) calcd for C₂₁H₁₉O⁺ [M-OH]⁺ 287.1436, found 287.1430. **IR** v max (film): 3560, 3030, 2932, 1610, 1582, 1511, 1493, 1446, 1346, 1302, 1247, 1178, 1110, 1033, 827, 776,

699 cm⁻¹. **M.p.**: 135 – 138 °C (lit.: 138 °C). The data presented are consistent with literature precedent.¹⁰



1-(2-Chlorophenyl)-1-(4-chlorophenyl)-2-(p-tolyl)ethan-1-ol 5i

General Procedure A was followed using 4-methylbenzylboronic acid pinacol ester (23 mg, 0.1 mmol, 1.0 eq.), 2,4'-dichlorobenzophenone (38 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a colourless oil (24 mg, 66%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.70 – 7.52 (m, 1H, *H*_{Ar}), 7.40 – 7.30 (m, 1H, *H*_{Ar}), 7.25 – 7.21 (m, 4H, *H*_{Ar}), 7.15 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.94 (d, *J* = 7.8 Hz, 2H, *H*_{Ar}), 6.74 (d, *J* = 7.8 Hz, 2H, *H*_{Ar}), 3.99 (d, *J* = 13.1 Hz, 1H, C*H*_aCOH), 3.45 (d, *J* = 13.1 Hz, 1H, C*H*_bCOH), 2.95 (s, 1H, O*H*), 2.27 (s, 3H, C*H*₃); ¹³**C NMR** (151 MHz, CDCl₃) δ 144.1, 142.7, 136.4, 133.1, 132.6, 132.4, 131.5 (*C*_{Ar}H), 130.9 (*C*_{Ar}H), 129.1 (*C*_{Ar}H), 128.7 (*C*_{Ar}H), 128.6 (*C*_{Ar}H), 128.2 (*C*_{Ar}H), 128.1 (*C*_{Ar}H), 126.8 (*C*_{Ar}H), 77.9 (CH₂COH), 44.8 (*C*H₂COH), 21.2 (*C*H₃). **HRMS** (ESI) calcd for C₂₁H₁₇Cl₂⁺ [M-OH]⁺ 339.0702, found 339.0706. **IR** v max (film): 3547, 2927, 2148, 1514, 1489, 1435, 1238, 1093, 1014, 828, 780, 747 cm⁻¹. **M.p.**: 106 – 109 °C.



2-(4-Methoxyphenyl)-1-phenyl-1-(pyridin-2-yl)ethan-1-ol 5j

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 2-benzoylpyridine (28 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was

purified *via* flash column chromatography (0 - 30%) EtOAc in petroleum ether) to give the titled product as a white solid (26 mg, 85%).

¹**H** NMR (600 MHz, CDCl₃) δ 8.41 (ddd, J = 4.9, 1.7, 1.0 Hz, 1H, $H_{Pyridine}$), 7.64 (td, J = 7.8, 1.7 Hz, 1H, $H_{Pyridine}$), 7.66 – 7.54 (m, 2H, H_{Ar}), 7.44 (d, J = 7.8 Hz, 1H, $H_{Pyridine}$), 7.33 (t, J = 7.7 Hz, 2H, H_{Ar}), 7.24 (t, J = 7.3 Hz, 1H, H_{Ar}), 7.12 (ddd, J = 7.4, 4.9, 1.1 Hz, 1H, $H_{Pyridine}$), 6.88 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.66 (d, J = 8.6 Hz, 2H, H_{Ar}), 5.38 (s, 1H, OH), 3.73 (s, 3H, OCH₃), 3.65 (d, J = 13.6 Hz, 1H, $CH_{a}COH$), 3.55 (d, J = 13.6 Hz, 1H, $CH_{b}COH$); ¹³C NMR (151 MHz, CDCl₃) δ 163.2, 158.2, 147.3 (C_{Ar} H), 146.4, 136.8 (C_{Ar} H), 131.8 (C_{Ar} H), 128.6, 128.3 (C_{Ar} H), 127.1 (C_{Ar} H), 126.3 (C_{Ar} H), 122.0 (C_{Ar} H), 121.1 (C_{Ar} H), 113.3 (C_{Ar} H), 77.6 (CH₂COH), 55.2 (OCH₃), 46.5 (CH₂COH). LRMS (ESI, m/z) 306.3 ([M+H]⁺, 100%); HRMS (ESI) calcd for C₂₀H₂₀NO₂⁺ [M+H]⁺ 306.1494, found 306.1489. IR v max (film): 3381, 3030, 2929, 1611, 1590, 1512, 1446, 1395, 1301, 1246, 1178, 1115, 1034, 828, 756, 700 cm⁻¹. M.p.: 140 – 143 °C.



9-(4-Methoxybenzyl)-9H-xanthen-9-ol 5k

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 9-xanthone (29 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and { $Ir[dF(CF_3)ppy]_2(dtbpy)$ }PF₆ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a white solid (17 mg, 55%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.64 (dd, J = 7.8, 1.7 Hz, 2H, H_{Ar}), 7.27 (ddd, J = 8.2, 7.2, 1.7 Hz, 2H, H_{Ar}), 7.16 (ddd, J = 7.8, 7.2, 1.2 Hz, 2H, H_{Ar}), 6.96 (dd, J = 8.2, 1.2 Hz, 2H, H_{Ar}), 6.52 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.34 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.69 (s, 3H, OCH₃), 3.11 (s, 2H, CH₂COH), 2.50 (s, 1H, OH); ¹³**C NMR** (151 MHz, CDCl₃) δ 158.4, 150.6, 131.5 (C_{Ar}H), 128.9 (C_{Ar}H), 127.7, 126.7 (C_{Ar}H), 126.7, 123.2 (C_{Ar}H), 116.0 (C_{Ar}H), 113.0 (C_{Ar}H), 70.4 (CH₂COH), 55.2 (OCH₃), 52.3 (CH₂COH). **LRMS** (ESI, m/z) 319.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₂₁H₁₉O₃⁺ [M+H]⁺

319.1334, found 319.1326. **IR** v max (film): 3363, 2927, 1655, 1605, 1509, 1479, 1452, 1301, 1277, 1250, 1176, 1101, 1034, 824, 761 cm⁻¹. **M.p.**: 57 – 60 °C.



9-(4-Methoxybenzyl)-9H-thioxanthen-9-ol 5l

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 9-thioxanthenone (32 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 10% EtOAc in petroleum ether) to give the titled product as a white solid (25 mg, 75%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.54 – 7.50 (m, 2H, H_{Ar}), 7.44 (dd, J = 7.6, 1.4 Hz, 2H, H_{Ar}), 7.24 (td, J = 7.4, 1.7 Hz, 2H, H_{Ar}), 7.21 (td, J = 7.4, 1.4 Hz, 2H, H_{Ar}), 6.66 (d, J = 8.6 Hz, 2H, H_{Ar}), 6.58 (d, J = 8.6 Hz, 2H, H_{Ar}), 3.75 (s, 3H, OCH₃), 3.02 (s, 2H, CH₂COH), 2.56 (s, 1H, OH); ¹³**C NMR** (151 MHz, CDCl₃) δ 158.6, 139.8, 131.8 (C_{Ar} H), 130.3, 127.6, 127.2 (C_{Ar} H), 126.5 (C_{Ar} H), 126.3 (C_{Ar} H), 125.7 (C_{Ar} H), 113.3 (C_{Ar} H), 75.5 (CH₂COH), 55.3 (OCH₃), 42.9 (CH₂COH). **LRMS** (ESI, m/z) 335.1 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₂₁H₁₉O₂S [M+H]⁺ 335.1106, found 335.1103. **IR** ν max (film): 3450, 2834, 2361, 1611, 1584, 1511, 1459, 1439, 1302, 1247, 1178, 1110, 1036, 827, 752, 736 cm⁻¹. **M.p.**: 115 – 117 °C.



9-(4-Methoxybenzyl)-9H-fluoren-9-ol 5m

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), 9-fluorenone (27 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6$ (2.2 mg, 0.002 mmol, 2 mol%). The crude mixture was

purified *via* flash column chromatography (0 - 5%) EtOAc in petroleum ether) to give the titled product as a white solid (27 mg, 90%).

¹**H NMR** (600 MHz, CDCl₃) δ 7.46 (dd, J = 7.4, 1.0 Hz, 2H, H_{Ar}), 7.27 – 7.23 (m, 2H, H_{Ar}), 7.22 – 7.20 (m, 2H, H_{Ar}), 7.18 – 7.15 (m, 2H, H_{Ar}), 6.82 (d, J = 8.5 Hz, 2H, H_{Ar}), 6.60 (d, J = 8.5 Hz, 2H, H_{Ar}), 3.66 (s, 3H, OCH₃), 3.15 (s, 2H, CH₂COH), 2.08 (s, 1H, OH); ¹³**C NMR** (151 MHz, CDCl₃) δ 158.4, 148.5, 139.5, 131.8 (C_{Ar} H), 129.0 (C_{Ar} H), 128.6, 127.7 (C_{Ar} H), 124.4 (C_{Ar} H), 120.1 (C_{Ar} H), 113.1 (C_{Ar} H), 82.5 (CH₂COH), 55.3 (OCH₃), 45.1 (CH₂COH). **LRMS** (ESI, m/z) 303.2 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₂₁H₁₉O₂⁺ [M+H]⁺ 303.1385, found 303.1389. **IR** v max (film): 3417, 2920, 1610, 1512, 1449, 1301, 1248, 1179, 1037, 824, 759, 737 cm⁻¹. **M.p.**: 87 – 89 °C (lit.: 110 – 111 °C). The data presented are consistent with literature precedent except melting point.¹¹



N-(cyclohexylcarbamoyl)-4-(2-hydroxy-1-(4-methoxyphenyl)propan-2-

yl)benzenesulfonamide 5n

General Procedure A was followed using 4-methoxybenzylboronic acid pinacol ester (25 mg, 0.1 mmol, 1.0 eq.), acetohexamide (49 mg, 0.15 mmol, 1.5 eq.), 3-quinuclidinol (2.5 mg, 0.02 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(2.2 mg, 0.002 mmol, 2 mol%)$. The crude mixture was purified *via* flash column chromatography (0 – 30% EtOAc in petroleum ether) to give the titled product as a white solid (26 mg, 59%). The yield was adjusted to account for 10% acetohexamide that we were not able to separate from the product.

¹**H NMR** (600 MHz, CDCl₃) δ 7.82 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 7.55 (d, *J* = 8.5 Hz, 2H, *H*_{Ar}), 6.87 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.77 (d, *J* = 8.6 Hz, 2H, *H*_{Ar}), 6.50 (d, *J* = 8.0 Hz, 1H, N*H*), 3.77 (s, 3H, OC*H*₃), 3.62 (q, *J* = 9.4 Hz, 1H, NHC*H*), 3.05 (d, *J* = 13.7 Hz, 1H, C*H*_aCOH), 2.97 (d, *J* = 13.7 Hz, 1H, C*H*_bCOH), 2.01 (s, 1H, O*H*), 1.88 – 1.77 (m, 2H, NHCHC*H*_aCH₂), 1.71 – 1.65 (m, 2H, NHCHC*H*_bCH₂), 1.56 (s, 3H, CC*H*₃), 1.34 (m, 6H, NHCHCH₂C*H*₂ + NHCHCH₂CH₂C*H*₂C*H*₂); ¹³C **NMR** (151 MHz, CDCl₃) δ 158.9, 154.4, 150.5, 137.8, 131.6 (C_{Ar}H), 127.7, 126.9 (C_{Ar}H), 126.4 (C_{Ar}H), 114.0 (C_{Ar}H), 74.6 (CH₂COH), 55.4 (OCH₃), 49.5 (CH₂COH), 49.4 (NHCH), 33.0 (NHCH*C*H₂), 29.5 (C*C*H₃), 25.51 (NHCHCH₂*C*H₂), 24.7 (NHCHCH₂CH₂CH₂). **LRMS** (ESI, m/z) 447.3 ([M+H]⁺, 100%); **HRMS** (ESI) calcd for C₂₃H₃₁O₅N₂S [M+H]⁺ 447.1954, found 447.1937. **IR** v max (film): 3372, 2927, 2354, 1676, 1611, 1513, 1459, 1332, 1250, 1163, 1036 cm⁻¹. **M.p.**: 70 − 73 °C.

On-Off Test



General Procedure A was followed with 4-methoxybenzylboronic acid pinacol ester (50 mg, 0.2 mmol, 1.0 eq.), 4-chlorobenzaldehyde (42 mg, 0.3 mmol, 1.5 eq.), 3-quinuclidinol (5.1 mg, 0.04 mmol, 20 mol%) and $\{Ir[dF(CF_3)ppy]_2(dtbpy)\}PF_6(4.4 mg, 0.004 mmol, 2 mol%)$. The LED light source was switched off at 1 and 3 h into the reaction, and subsequently switched back on at 2 and 4 h into the reaction respectively. Samples were taken at the beginning of the reaction as well as 1, 2, 3, 4 and 10 h time point. At 10 h point little starting material was detected therefore the reaction was quenched. The yields shown were NMR yields calculated with 1,3,5-trimethoxybenzene as internal standard.



On-Off Reaction

Stern-Volmer Experiments

Stock solutions (1:1 MeOH/acetone) of photocatalyst (0.02 mM), 3-quinuclidinol (16 mM), 4chlorobenzaldehyde (16 mM) and 4-methoxybenzyl pinacol boronic ester (16 mM) were diluted and prepared into appropriate concentrations. The concentration of photocatalyst was kept at 0.01 mM. Samples were irradiated at 380 nm and emission was detected at 545 mM.







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Spectroscopic data



¹H and ¹³C NMR spectrum of **1-(4-bromophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3ak**



¹H and ¹³C NMR spectrum of 1-(4-chlorophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3a



¹H and ¹³C NMR spectrum of **1-(4-chlorophenyl)-2-(***p***-tolyl)ethan-1-ol 3b**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1-(4-chlorophenyl)-2-(o-tolyl)ethan-1-ol 3c



¹H and ¹³C NMR spectrum of 1-(4-chlorophenyl)-2-(naphthalen-1-yl)ethan-1-ol 3d



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1-(4-chlorophenyl)-2-phenylethan-1-ol 3e



¹H and ¹³C NMR spectrum of 1-(4-chlorophenyl)-2-[4-(trifluoromethoxy)phenyl]ethan-1-ol 3f



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 FI (ppm)

¹⁹F NMR spectra of 1-(4-chlorophenyl)-2-[4-(trifluoromethoxy)phenyl]ethan-1-ol 3f



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1,2-bis(4-chlorophenyl)ethan-1-ol 3g



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1-(4-chlorophenyl)-2-(3-fluorophenyl)ethan-1-ol 3h



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 fl (ppm)

¹⁹F NMR spectra of 1-(4-chlorophenyl)-2-(3-fluorophenyl)ethan-1-ol 3h



¹H and ¹³C NMR spectrum of methyl 4-[2-(4-chlorophenyl)-2-hydroxyethyl]benzoate 3i



¹H and ¹³C NMR spectrum of 1-(4-chlorophenyl)-2-(phenylthio)ethan-1-ol 3j



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)-1-(***o***-tolyl)ethan-1-ol 3k**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1-(2-bromophenyl)-2-(4-methoxyphenyl)ethan-1-ol 3l





¹H and ¹³C NMR spectrum of **3-(1-hydroxy-2-(4-methoxyphenyl)ethyl)benzonitrile 3n**



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-[3-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)phenyl]ethan-1-ol 3o



¹H and ¹³C NMR spectrum of **3-(1-hydroxy-2-(4-methoxyphenyl)ethyl)phenol 3p**



¹H and ¹³C NMR spectrum of **1,2-bis(4-methoxyphenyl)ethan-1-ol 3q**



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-[4-(trifluoromethyl)phenyl]ethan-1-ol 3r



0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -25 11 (ppm)

¹⁹F NMR spectra of **2-(4-methoxyphenyl)-1-[4-(trifluoromethyl)phenyl]ethan-1-ol 3r**



¹H and ¹³C NMR spectrum of 1-{4-[1-hydroxy-2-(4-methoxyphenyl)ethyl]phenyl}ethan-1-one

3s


¹H and ¹³C NMR spectrum of methyl 3-[1-hydroxy-2-(*p*-tolyl)ethyl]benzoate 3t



¹H and ¹³C NMR spectrum of **1-[4-(methylthio)phenyl]-2-(***p***-tolyl)ethan-1-ol 3u**



 1 H and 13 C NMR spectrum of *N*-benzyl-2-(4-methoxyphenyl)-1-phenylethan-1-amine 3v



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of N-[2-(4-methoxyphenyl)-1-phenylethyl]-2-methylpropan-2-

amine 3w



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)**-*N*-methyl-1-phenylethan-1-amine **3**x



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)-1-(perfluorophenyl)ethan-1-ol 3y**



¹⁹F NMR spectra of **2-(4-methoxyphenyl)-1-(perfluorophenyl)ethan-1-ol 3y**



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of 1-mesityl-2-(4-methoxyphenyl)ethan-1-ol 3z



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-(pyridin-2-yl)ethan-1-ol 3aa



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-(pyridin-3-yl)ethan-1-ol 3ab



¹H and ¹³C NMR spectrum of **6-[1-hydroxy-2-(4-methoxyphenyl)ethyl]-2-**

(methylthio)nicotinonitrile 3ac



¹H and ¹³C NMR spectrum of **2-(4-isocyanophenyl)-1-(pyridin-3-yl)ethan-1-ol 3ad**



¹H and ¹³C NMR spectrum of *tert*-Butyl 2-[1-hydroxy-2-(4-methoxyphenyl)ethyl]-1*H*-pyrrole-1-carboxylate 3ae



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-(pyrimidin-5-yl)ethan-1-ol 3af



¹H and ¹³C NMR spectrum of 1-(2-chloroquinolin-3-yl)-2-(4-methoxyphenyl)ethan-1-ol 3ag



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)-1-(thiazol-2-yl)ethan-1-ol 3ah**



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)-1-{5-[1-methyl-5-(trifluoromethyl)-1***H***-pyrazol-3-yl]thiophen-2-yl}ethan-1-ol 3ai**



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 fl (ppm)

¹⁹F NMR spectra of **2-(4-methoxyphenyl)-1-{5-[1-methyl-5-(trifluoromethyl)-1***H***-pyrazol-3-yl]thiophen-2-yl}ethan-1-ol 3ai**



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-(thiophen-2-yl)ethan-1-ol 3aj



¹H and ¹³C NMR spectrum of 1-(4-methoxyphenyl)-2-phenylpropan-2-ol 5a



¹H and ¹³C NMR spectrum of 2-(2,6-difluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5b



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 fl (ppm)

¹⁹F NMR spectra of 2-(2,6-difluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5b



¹H and ¹³C NMR spectrum of 2-(2-fluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5c



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 fl (ppm)

¹⁹F NMR spectra of **2-(2-fluorophenyl)-1-(4-methoxyphenyl)propan-2-ol 5c**



¹H and ¹³C NMR spectrum of **2-[3,5-bis(trifluoromethyl)phenyl]-1-(4-methoxyphenyl)propan-**

2-ol 5d



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 FI (ppm)

¹⁹F NMR spectra of **2-[3,5-bis(trifluoromethyl)phenyl]-1-(4-methoxyphenyl)propan-2-ol 5d**



¹H and ¹³C NMR spectrum of **3-[2-hydroxy-1-(4-methoxyphenyl)propan-2-yl]phenol 5e**



¹H and ¹³C NMR spectrum of 1-(4-methoxyphenyl)-2-(naphthalen-1-yl)propan-2-ol 5f



¹H and ¹³C NMR spectrum of 1,1,1-trifluoro-3-(4-methoxyphenyl)-2-phenylpropan-2-ol 5g



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 FI (ppm)

¹⁹F NMR spectra of 1,1,1-trifluoro-3-(4-methoxyphenyl)-2-phenylpropan-2-ol 5g



¹H and ¹³C NMR spectrum of **2-(4-methoxyphenyl)-1,1-diphenylethan-1-ol 5h**



¹H and ¹³C NMR spectrum of 1-(2-chlorophenyl)-1-(4-chlorophenyl)-2-(*p*-tolyl)ethan-1-ol 5i



¹H and ¹³C NMR spectrum of 2-(4-methoxyphenyl)-1-phenyl-1-(pyridin-2-yl)ethan-1-ol 5j



¹H and ¹³C NMR spectrum of **9-(4-methoxybenzyl)-9***H***-xanthen-9-ol 5**k



¹H and ¹³C NMR spectrum of **9-(4-methoxybenzyl)-9***H***-thioxanthen-9-ol 5***l*



 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectrum of **9-(4-methoxybenzyl)-9H-fluoren-9-ol 5m**


methoxyphenyl)propan-2-yl)benzenesulfonamide 5n