Copper-Mediated Synthesis of Drug-like Bicyclopentanes

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1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armairego.\(^1\) All solvents were purified according to the method of Grubbs.\(^2\) Additionally, all inorganic bases were ground prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (Fluka, 230–400 mesh) according to the method of Still.\(^3\) Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or KMnO\(_4\) stain. \(^1\)H NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz and are internally referenced to residual protic CDCl\(_3\) (\(\delta\) 7.26 ppm), (CD\(_3\))\(_2\)CO (\(\delta\) 2.05 ppm), C\(_6\)D\(_6\) (\(\delta\) 7.16 ppm), CD\(_3\)OD (\(\delta\) 3.31 ppm), CD\(_3\)CN (\(\delta\) 1.94 ppm) or (CD\(_3\))\(_2\)SO (\(\delta\) 2.50 ppm). Data for \(^1\)H NMR are reported as follows: chemical shift (\(\delta\) ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, qd = quartet of doublets, br = broad), coupling constant (Hz), and integration. \(^13\)C NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz (125 MHz) and data are reported in terms of chemical shift relative to CDCl\(_3\) (\(\delta\) 77.16 ppm), (CD\(_3\))\(_2\)CO (\(\delta\) 29.84 ppm and 206.26 ppm), C\(_6\)D\(_6\) (\(\delta\) 128.06 ppm), CD\(_3\)OD (\(\delta\) 49.00 ppm), CD\(_3\)CN (\(\delta\) 1.32 ppm and 118.26 ppm) or (CD\(_3\))\(_2\)SO (\(\delta\) 39.52 ppm). \(^19\)F NMR spectra were recorded on a Bruker NanoBay 400 MHz (376 MHz) or 300 MHz (282 MHz). \(^31\)P NMR spectra were recorded on a Bruker UltraShield Plus Avance III 500 MHz (121 MHz). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm\(^{-1}\)). High Resolution Mass Spectra were obtained from the Princeton University Mass Spectral Facility.
2) Preparation of Iodomesitylene Dicarboxylates (without purification)⁴

\[
\begin{align*}
\text{MesI(OAc)₂} & \quad \text{toluene, 50 °C} \\
\text{carboxylic acid} & \quad \text{no purification}
\end{align*}
\]

A 500 mL round-bottom flask was charged with iodomesitylene diacetate (10 mmol), carboxylic acid (20.5–21 mmol, 2.05–2.10 equiv.), and 200 mL toluene. The flask was attached to a rotary evaporator with the water bath heated to 50 °C and the solvent (and the generated acetic acid) was removed over a time period of ~10 min. A second 150 mL aliquot of toluene was added to the flask and the evaporation step was repeated. Repeat the evaporation step for two more times with 100 mL toluene each time. The products are typically generated in >99% yield. After further removal of residual toluene under high-vac, these iodomesitylene dicarboxylates can be directly used in the three-component coupling reactions without purification.

3) Preparation of Propellane (solution in Et₂O)⁵

\[
\begin{align*}
\text{Br-Br-Cl} & \quad \text{2.0 equiv (n-BuLi or PhLi)} \\
\text{Bu}_2\text{O/Et}_2\text{O} & \quad \text{–78 °C, then 0 °C}
\end{align*}
\]

Charge a flame-dried flask equipped with a stir bar with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane. Add 10 mL Et₂O and 20 mL n-Bu₂O. Cool to –78 °C (a white suspension will form). Add 5 mL n-BuLi (11.0 M in hexanes, 2.0 equiv) slowly dropwise. The mixture was stirred at –78 °C for 15 minutes, then warm to 0 °C and stirring for another 2 hours. Fit the reaction flask with a flask to flask vacuum distillation piece attached to a receiving flask cooled to –78 °C. Use a pump to slowly pull the system down to ~10 Torr and hold at this pressure for 10 minutes. This should distill over the Et₂O and propellane. The concentration can be checked by NMR by taking a 100 uL aliquot of the stock solution and determining the ratio of propellane to an added standard, such as mesitylene (45%-55% yield, typically concentrations are 0.8-1.3 M with this protocol).
This solution should be kept at a –20 °C freezer, and the propellane is stable for at least several months.

Alternatively, PhLi (2.0 equiv) can also be employed (addition of PhLi into the reaction solution at –45 ºC) for the preparation of propellane giving similar yield and concentration.
4) Reaction Optimization

To an 8 mL vial equipped with a stir bar was added photocatalyst Ir(ppy)$_3$ (0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (11.8 mg, 0.06 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyrano-4-carboxylate) (2.0 equiv), copper salt and ligand. Solvent (2.0 mL) was added and then base (3.0 equiv) was added to the mixture. The solution was degassed by sparging with nitrogen for 5 minutes. The stock solution of propellane (0.8 M in Et$_2$O, 1.5 equiv) was then added before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 3 cm away, with cooling fan to keep the reaction at ~35 ºC) for 1 hour. The reaction was quenched by exposure to air. 1,3-Benzodioxole (internal standard) was added then the reaction mixture was analyzed by $^1$H NMR.

**Figure S1** Evaluation of different copper sources and ligands. Yields determined by $^1$H NMR.
Figure S2 Evaluation of copper loading. Yields determined by $^1$H NMR.

*Note: further increases in copper loading generally do not improve the reaction yield.

| copper loading | yield |
|----------------|-------|
| 60 mol%        | 80%   |
| 50 mol%        | 76%   |
| 40 mol%        | 66%   |
| 30 mol%        | 64%   |
| 20 mol%        | 30%   |

Figure S3 Evaluation of different copper(II) diketonates. Yields determined by $^1$H NMR.

| copper(II) diketonates         | yield |
|--------------------------------|-------|
| $\text{MeO}_2\text{C} = \text{Me}$ | $\text{Cu}^{2+}$ | 80%   |
| $\text{i-PrO}_2\text{C} = \text{i-Pr}$ | $\text{Cu}^{2+}$ | 60%   |
| $\text{i-BuO}_2\text{C} = \text{i-Bu}$ | $\text{Cu}^{2+}$ | 62%   |
| $\text{O}_2\text{C} = \text{i-Pr}$ | $\text{Cu}^{2+}$ | 56%   |
**Figure S4** Evaluation of different solvents. Yields determined by $^1$H NMR.

| solvent  | yield  |
|----------|--------|
| dioxane  | 80%    |
| THF      | 78%    |
| DME      | 76%    |
| MeCN     | 58%    |
| acetone  | 50%    |
| EtOAc    | 62%    |
| DMSO     | 36%    |

**Figure S5** Evaluation of different bases. Yields determined by $^1$H NMR.

| base      | yield  |
|-----------|--------|
| BTMG      | 80%    |
| TMG       | 46%    |
| BTTP      | 76%    |
| DBU       | 80%    |
| $\text{K}_2\text{CO}_3$ | 30%    |
| $\text{Na}_2\text{CO}_3$ | 26%    |
5) Control Experiments

![Chemical structure](image)

| $X$ equiv | $Y$ equiv | $Z$ equiv | yield |
|----------|----------|----------|-------|
| 1.0      | 1.5      | 2.0      | 80%   |
| 1.0      | 1.5      | 1.5      | 72%   |
| 1.0      | 1.0      | 1.5      | 60%   |
| 1.0      | 1.0      | 1.0      | 50%   |
| 2.0      | 1.5      | 1.0      | 62%   |

**Figure S6** Evaluation of the stoichiometry of the reactants. Yields determined by $^1$H NMR.

| deviations from standard | yield |
|--------------------------|-------|
| none                     | 80%   |
| no photocatalyst, light only | 48% |
| no photocatalyst, no light | 0% |
| no Cu                     | 0%    |
| no base                   | 24%   |
| with integrated photoreactor, 5 minutes | 72% |

**Figure S7** Control experiments for three-component coupling. Yields determined by $^1$H NMR.
As shown in Figures S7, S8, and S9, although light [no photocatalyst] can slightly promote the degradation of iodosmestylenic dicarboxylate and give some product, irradiation with blue LEDs in the presence of a photocatalyst is essential for the desired three-component coupling to occur generally. See section 12 of the Supplementary Information for further discussion and UV-Vis experiments.
6) Reactivity Studies of Different Radicals.

Figure S10 Competition studies using azaindole as substrate: BCP radical vs. other alkyl radicals.
Yields determined by $^1$H NMR.

Figure S11 Competition studies using indazole as substrate: BCP radical vs. other alkyl radicals.
Yields determined by $^1$H NMR.
Figure S12 Comparison of the reactivity of different alkyl radical toward three component coupling. Yields determined by $^1$H NMR.

As demonstrated in Figure S10 and S11 BCP radicals are trapped by copper faster than other alkyl radicals across multiple nucleophile classes. As shown in Figure S12, a clear trend is observed demonstrating that as the $s$-character of the radical increases the proportion of direct two-component coupling concomitantly increases.\textsuperscript{6}
7) General Procedure for Three-Component Coupling

To a 40 mL vial equipped with a stir bar was added Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv) and Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv). 1,4-Dioxane (10.0 mL) was added and then BTMG (0.18 mL, 0.90 mmol, 3.0 equiv) was added to the mixture. The solution was degassed by sparging with nitrogen for 5-10 minutes. The stock solution of propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv) was then added before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 3 cm away, with cooling fan to keep the reaction at ~35 ºC) for 1 hour. The reaction mixture was removed from the light, diluted with EtOAc, washed with aqueous ammonia (1.0 M, 15 mL) [or alternatively 0.1M EDTA (aq)] to remove copper. The aqueous layer was extracted with three portions of EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel to afford the desired coupling product.

**Note 1:** for aniline substrates, directly mixing the N-nucleophile with iodomesitylene dicarboxylate neat can sometimes lead to decomposition of the nucleophiles. Therefore, aniline substrates were added to the reaction solution last.

**Note 2:** In general, attempting to form the iodonium dicarboxylates *in-situ* from the corresponding carboxylic acids leads to lower yields.

Using different batches of propellane (with slightly different concentration: 0.8-1.3 M) did not affect the efficiency of the three-component coupling.
General Procedure (A) for α-Acylation Substrate

To a 40 mL vial equipped with a stir bar was added Ir(ppy)$_3$ (2 mol%) and CuCl (55 mol%). Dioxane is added (volume giving a concentration of 0.033 M for the N-nucleophile) followed by 2,4-butanedione (acac; 50 mol%) and BTMG (3.0 equiv). The vial is then sonicated and a green-yellow suspension forms. 6-Bromo-1H-pyrrolo[3,2-b]pyridine (1.0 equiv) is then added and a green-brown suspension will form (color change is dependent on nucleophile). The solution was degassed by sparging with nitrogen for 5-10 minutes. The stock solution of propellane is added (1.5 equiv, solution in Et$_2$O) as well as the alkyl bromide (2.0 equiv) before sealing with parafilm. The reaction was stirred and irradiated using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 3 cm away, with cooling fan to keep the reaction at ~35 ºC) for 1 hour (if using the integrated photoreactor, it’s done in 15 minutes). The reaction mixture was removed from the light, diluted with EtOAc, washed with aqueous ammonia (1.0 M, 15 mL) [or alternatively 0.1M EDTA (aq)] solution to remove copper. The aqueous layer was extracted with three portions of EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel to afford the desired coupling product.

Note: For some nucleophiles, using Cu(acac)$_2$ may give a higher yield.

General Procedure (B) for Amino-Trifluoromethylation of [1.1.1]Propellane

To an 40 mL vial equipped with a stir bar was added Cu(acac)$_2$ (30 mol%) and 6-Bromo-1H-pyrrolo[3,2-b]pyridine (2.0 equiv). Dioxane is added followed by BTMG (3.0 equiv), and the solution is stirred for 15 minutes to pre-complex the nucleophile. The stock solution
of propellane (1.0 equiv, solution in Et₂O) is added, followed by Togni II (2.0 equiv, 60 wt% on celite). The reaction is stirred at room temperature and should be complete within 5-10 minutes (it should become very dark when finished and will warm up). The reaction mixture is then diluted with EtOAc and washed with 0.1M EDTA solution to remove copper. The aqueous layer was extracted with three portions of EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel to afford the desired coupling product.

**Note:** copper loading between 30-60 mol% is equally effective for the trifluoromethylation.

**Reaction Setup**

**Figure S13** Two 34 W Kessil KSH150B Blue LED Grow Light 150 are positioned 3 cm away from the vials on both sides of the box covered with aluminum foil. A cooling fan is used to keep the reaction at approximately 35 °C.
8) Experimental Data

8.1 Iodonium dicarboxylates

**Iodomesitylene bis-2-(1-(tert-butoxycarbonyl)azetidin-3-yl)acetate**

Prepared following the general procedure outlined above using 2-(1-(tert-butoxycarbonyl)azetidin-3-yl)acetic acid.

**1H NMR (500 MHz, CDCl₃)** $\delta$ 7.10 (s, 2H), 3.97 (t, $J = 8.5$ Hz, 4H), 3.49 (dd, $J = 8.9, 5.5$ Hz, 4H), 2.78-2.71 (m, 2H), 2.68 (s, 6H), 2.51 (d, $J = 7.8$ Hz, 4H), 2.36 (s, 3H), 1.41 (s, 18H).

**13C NMR (125 MHz, CDCl₃)** $\delta$ 176.59, 156.40, 143.62, 141.33, 129.84, 129.14, 79.51, 54.44 (br), 38.35, 28.50, 26.85, 25.88, 21.35.

**IR (film)** $\nu_{\text{max}}$ 2974, 2882, 1696, 1655, 1398, 1365, 1144, 857 cm$^{-1}$.

**Iodomesitylene bis-N-(tert-butoxycarbonyl)azetidine-3-carboxylate**

Prepared following the general procedure outlined above using 1-(tert-butoxycarbonyl)azetidine-3-carboxylic acid.

**1H NMR (500 MHz, CDCl₃)** $\delta$ 7.11 (s, 2H), 4.02-3.85 (m, 8H), 3.22 (ddd, $J = 15.0, 8.5, 6.4$ Hz, 2H), 2.70 (s, 6H), 2.35 (s, 3H), 1.41 (s, 18H).

**13C NMR (125 MHz, CDCl₃)** $\delta$ 177.25, 156.20, 143.84, 141.49, 130.07, 129.14, 79.88, 52.39 (br), 31.65, 28.46, 26.83, 21.36.

**IR (film)** $\nu_{\text{max}}$ 2976, 2893, 1737, 1699, 1393, 1366, 1140, 855 cm$^{-1}$. 
Iodomesitylene bis-3,3-difluorocyclobutane-1-carboxylate
Prepared following the general procedure outlined above using 3,3-difluorocyclobutane-1-carboxylic acid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.11 (s, 2H), 2.87-2.80 (m, 2H), 2.70 (s, 6H), 2.71-2.63 (m, 8H), 2.37 (s, 3H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 178.01, 143.79, 141.49, 130.14, 129.29, 118.99 (dd, \(J = 285.9, 273.8\) Hz), 39.45 (t, \(J = 24.1\) Hz), 26.78, 25.97 (dd, \(J = 13.8, 5.4\) Hz), 21.38.

IR (film) \(\nu_{max}\) 2963, 2844, 1658, 1357, 1297, 1250, 1160, 896 cm\(^{-1}\).

Iodomesitylene bis-1-(\(\text{tert}\)-butoxycarbonyl)pyrrolidine-3-carboxylate
Prepared following the general procedure outlined above using 1-(\(\text{tert}\)-butoxycarbonyl)pyrrolidine-3-carboxylic acid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.09 (s, 2H), 3.54-3.20 (m, 8H), 2.98-2.86 (m, 2H), 2.69 (s, 6H), 2.35 (s, 3H), 2.03-1.94 (m, 4H), 1.43 (s, 18H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)), rotameric, minor rotamer in brackets[ ] \(\delta\) 177.78, 154.35, 143.45, 141.31, 129.96, 129.10, 79.41, 48.67 [48.45], [45.37] 45.06, 43.05, 29.39, [28.81], 28.49, 26.64, 21.23.

IR (film) \(\nu_{max}\) 2977, 2932, 1735, 1693, 1653, 1396, 1366, 1160, 1124, 850 cm\(^{-1}\).
Iodomesitylene bis-1-\((\text{tert}-\text{butoxycarbonyl})\text{piperidine}-3\)-carboxylate

Prepared following the general procedure outlined above using 1-\((\text{tert}-\text{butoxycarbonyl})\text{piperidine}-3\)-carboxylic acid.

\(^1\text{H NMR (500 MHz, CDCl}_3\) \(\delta\) 7.07 (s, 2H), 4.28-3.76 (m, 4H), 2.79-2.61 (m, 4H) 2.68 (s, 6H), 2.36-2.31 (m, 2H), 2.31 (s, 3H), 1.97-1.90 (m, 2H), 1.63-1.57 (m, 2H), 1.50-1.42 (m, 2H), 1.44-1.31 (m, 2H), 1.41 (s, 18H).

\(^{13}\text{C NMR (125 MHz, CDCl}_3\), rotameric, minor rotamer in brackets[}] \(\delta\) 178.38, 154.79, 143.31, 141.39, 129.76, 129.11, 79.70, [46.66] 45.84, 44.54 [43.50], 41.63, 28.50, 28.18, 26.74, 24.66, 21.30.

\(\text{IR (film)}\) \(\nu_{\text{max}}\) 2976, 2934, 1732, 1692, 1656, 1422, 1241, 1169, 1149, 856 cm\(^{-1}\).
Iodomesitylene bis-tetrahydro-2H-pyran-3-carboxylate
Prepared following the general procedure outlined above using tetrahydro-2H-pyran-3-carboxylic acid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.08 (s, 2H), 3.87 (ddd, $J$ = 11.3, 4.2, 1.6 Hz, 2H), 3.76 (dt, $J$ = 10.2, 3.0 Hz, 2H), 3.41 (dd, $J$ = 11.3, 9.5 Hz, 2H), 3.40-3.31 (m, 2H), 2.68 (s, 6H) 2.54-2.44 (m, 2H), 2.36 (s, 3H) 1.94-1.83 (m, 2H), 1.68-1.44 (m, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 177.98, 143.27, 141.40, 129.88, 129.08, 69.62, 68.15, 41.78, 26.72, 26.69, 25.10, 21.32.

IR (film) $\nu_{\text{max}}$ 2946, 2848, 1729, 1647, 1301, 1190, 1087, 1011, 913, 855 cm$^{-1}$.

Iodomesitylene bis-pivalate
Prepared following the general procedure outlined above using pivalic acid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.06 (s, 2H), 2.70 (s, 6H), 2.35 (s, 3H), 1.06 (s, 18H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 183.61, 142.65, 141.40, 130.25, 128.83, 39.18, 27.90, 26.52, 21.32.

IR (film) $\nu_{\text{max}}$ 2970, 2870, 1646, 1478, 1291, 1278, 1177, 1157, 889 cm$^{-1}$. 
Iodomesitylene bis-3-methyloxetane-3-carboxylate

Prepared following the general procedure outlined above using 3-methyloxetane-3-carboxylic acid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.10 (s, 2H), 4.79 (d, $J = 5.9$ Hz, 4H), 4.29 (d, $J = 5.9$ Hz, 4H), 2.73 (s, 6H), 2.37 (s, 3H), 1.48 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 179.34, 143.60, 141.46, 130.40, 129.23, 80.47, 44.44, 26.70, 22.54, 21.36.

IR (film) $\nu_{\text{max}}$ 2965, 2876, 1731, 1651, 1454, 1301, 1161, 981, 839 cm$^{-1}$.

Iodomesitylene bis-1-(tert-butoxycarbonyl)-3-methylazetidine-3-carboxylate

Prepared following the general procedure outlined above using 1-(tert-butoxycarbonyl)-3-methylazetidine-3-carboxylic acid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.09 (s, 2H), 4.03 (brs, 4H), 3.55 (d, $J = 8.5$ Hz, 4H), 2.69 (s, 6H), 2.35 (s, 3H), 1.44 (s, 3H), 1.40 (s, 18H), 1.39 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 179.44, 156.42, 143.61, 141.44, 130.30, 129.26, 79.75, 59.18 (br), 38.59, 28.47, 26.69, 23.37, 21.35.

IR (film) $\nu_{\text{max}}$ 2974, 2887, 1701, 1451, 1394, 1366, 1169, 1105, 856 cm$^{-1}$.
Iodomesitylene bis-1-methylocyclohexane-1-carboxylate
Prepared following the general procedure outlined above using 1-methylocyclohexane-1-carboxylic acid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.05 (s, 2H), 2.71 (s, 6H), 2.35 (s, 3H), 1.91-1.82 (m, 4H), 1.47-1.38 (m, 6H), 1.27-1.14 (m, 6H), 1.11-1.03 (m, 4H), 1.00 (s, 6H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 182.82, 142.62, 141.39, 130.46, 128.72, 43.88, 36.32, 27.05, 26.70, 25.90, 23.53, 21.31.

IR (film) \(v_{\text{max}}\) 2927, 2855, 1641, 1450, 1310, 1218, 1164, 1133, 850 cm\(^{-1}\).

Iodomesitylene bis-4-methyltetrahydro-2H-pyran-4-carboxylate
Prepared following the general procedure outlined above using 4-methyltetrahydro-2H-pyran-4-carboxylic acid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.08 (s, 2H), 3.69 (dt, \(J = 11.8, 4.0\) Hz, 4H), 3.29 (ddd, \(J = 11.7, 10.5, 2.5\) Hz, 4H), 2.71 (s, 6H), 2.36 (s, 3H), 1.95-1.83 (m, 4H), 1.35 (ddd, \(J = 14.2, 10.6, 4.2\) Hz, 4H), 1.08 (s, 6H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 181.57, 143.22, 141.33, 130.60, 128.72, 65.62, 41.53, 36.11, 27.01, 26.75, 21.35.

IR (film) \(v_{\text{max}}\) 2957, 2853, 1643, 1457, 1300, 1229, 1157, 1106, 1034 cm\(^{-1}\).
Iodomesitylene bis-1-((tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylate

Prepared following the general procedure outlined above using 1-((tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylic acid.

$^{1}H$ NMR (500 MHz, CDCl$_3$) $\delta$ 7.07 (s, 2H), 3.86-3.52 (m, 4H), 2.85-2.73 (m, 4H), 2.69 (s, 6H), 2.35 (s, 3H), 1.92-1.83 (m, 4H), 1.42 (s, 18H), 1.24-1.15 (m, 4H), 1.06 (s, 6H).

$^{13}C$ NMR (125 MHz, CDCl$_3$) rotameric, minor rotamer in brackets[] $\delta$ 181.43, 154.98, 143.24, 141.27, 130.30, 128.98, 79.47, 42.39, [41.90] 41.09, 35.29 [34.51], 28.57, 26.77, 26.60, 21.33.

IR (film) $\nu_{max}$ 2972, 2923, 1691, 1653, 1421, 1240, 1158, 1109, 971 cm$^{-1}$. 
8.2 Radical Precursor Scope

**tert-Butyl 3-((3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)methyl)azetidine-1-carboxylate (13)**

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodositylene di-tert-butyl 3,3’-((bis(oxy))bis(2-oxoethane-2,1-diyl))bis(azetidine-1-carboxylate) (405 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (25-35% EtOAc/hexanes), followed by another flash chromatography (15-20% acetone/hexanes) provided the title compound (65 mg, 50% yield) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.49 (s, 1H), 7.90 (s, 1H), 7.25 (d, $J = 3.3$ Hz, 1H), 6.66 (d, $J = 3.1$ Hz, 1H), 4.08 (t, $J = 8.3$ Hz, 2H), 3.60 (dd, $J = 8.5$, 5.6 Hz, 2H), 2.64-2.55 (m, 1H), 2.24 (s, 6H), 2.00 (d, $J = 7.7$ Hz, 2H), 1.45 (s, 9H).

$^{13}$C NMR (125 MHz, Acetone-$d_6$) δ 156.68, 146.84, 143.84, 132.00, 130.54, 121.07, 113.47, 103.17, 78.98, 56.17 (br), 54.94 (br), 53.65, 50.43, 35.98, 35.06, 28.55, 28.00.

IR (film) $v_{max}$ 2973, 2877, 1697, 1415, 1142, 907, 782 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{21}$H$_{27}$BrN$_3$O$_2$ ([M+H]$^+$) 432.1281, found 432.1278.
6-Bromo-1-(3-isopropylbicyclo[1.1.1]pent-1-yl)-1H-pyrrolo[3,2-\textbf{b}]pyridine (14)
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-\textbf{b}]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(2-methylpropanoate) (252 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (55 mg, 60% yield) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J$ = 1.9 Hz, 1H), 7.92 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.28 (d, $J$ = 3.3 Hz, 1H), 6.64 (dd, $J$ = 3.3, 0.7 Hz, 1H), 2.18 (s, 6H), 1.94 (hept, $J$ = 6.8 Hz, 1H), 0.95 (d, $J$ = 6.8 Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.93, 144.01, 130.36, 129.48, 120.42, 112.81, 102.79, 50.87, 49.29, 41.84, 27.30, 19.30.

IR (film) $\nu_{\text{max}}$ 2959, 2873, 1414, 1320, 1281, 1245, 1137, 906, 782, 725 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{15}$H$_{18}$BrN$_2$ ([M+H]$^+$) 305.0648, found 305.0644.
6-Bromo-1-(3-(pentan-3-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (15)
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(2-ethylbutanoate) (286 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (77 mg, 77% yield) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.47 (d, $J = 1.8$ Hz, 1H), 8.05-7.87 (m, 1H), 7.26 (d, $J = 3.4$ Hz, 1H), 6.68-6.57 (m, 1H), 2.24 (s, 6H), 1.50-1.27 (m, 5H), 0.94 (t, $J = 7.4$ Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.88, 144.01, 130.34, 129.43, 120.42, 112.77, 102.74, 52.40, 49.55, 40.86, 40.29, 23.87, 12.13.

IR (film) $\nu_{\text{max}}$ 2967, 2873, 1415, 1281, 1245, 906, 782, 726 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{22}$BrN$_2$ ([M+H]$^+$) 333.0961, found 333.0951.
tert-Butyl 3-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)azetidine-1-carboxylate (16)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene 1,1'-di-tert-butyl O$_2$-bis(azetidine-1,3-dicarboxylate) (388 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (25-30% EtOAc/hexanes), followed by another flash chromatography (10-15% acetone/hexanes) provided the title compound (56 mg, 45% yield) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.50 (s, 1H), 7.92 (s, 1H), 7.28 (d, $J$ = 3.3 Hz, 1H), 6.68 (d, $J$ = 3.0 Hz, 1H), 4.04 (t, $J$ = 8.5 Hz, 2H), 3.70 (dd, $J$ = 8.6, 5.3 Hz, 2H), 2.86-2.81 (m, 1H), 2.32 (s, 6H), 1.45 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 156.54, 145.88, 144.22, 130.25, 129.47, 120.44, 112.99, 103.21, 79.79, 51.44, 50.14, 37.99, 28.54, 28.07.

IR (film) $\nu_{max}$ 2975, 2880, 1696, 1415, 1247, 1141, 907, 729 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{20}$H$_{25}$BrN$_3$O$_2$ ([M+H]$^+$) 418.1125, found 418.1123.
6-Bromo-1-(3-(3,3-difluorocyclobutyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (17)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(3,3-difluorocyclobutane-1-carboxylate) (310 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes) provided the title compound (76 mg, 72% yield) as a yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.50 (s, 1H), 7.95-7.89 (m, 1H), 7.26 (d, $J$ = 2.9 Hz, 1H), 6.66 (d, $J$ = 2.9 Hz, 1H), 2.73-2.66 (m, 2H), 2.56-2.46 (m, 1H), 2.42-2.32 (m, 2H), 2.28 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.93, 144.24, 130.18, 129.42, 120.32, 119.49 (dd, $J_{C,F} = 283.0, 275.1$ Hz), 112.96, 103.18, 52.11, 51.48, 49.76, 38.06 (dd, $J_{C,F} = 23.4, 22.3$ Hz), 22.41 (dd, $J_{C,F} = 11.8, 7.1$ Hz).

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -83.73 (d, $J$ = 193.3 Hz, 1F), -94.14 (d, $J$ = 193.3 Hz, 1F).

IR (film) $\nu_{max}$ 2979, 2878, 1503, 1415, 1281, 1163, 905, 882, 782, 727 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{16}$BrF$_2$N$_2$ ([M+H]$^+$) 353.0459, found 353.0459.
6-Bromo-1-(3-cyclopentylbicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (18)
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene dicyclopentanecarboxylate (283 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (5-10% EtOAc/hexanes) provided the title compound (63 mg, 63% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.67-8.42 (m, 1H), 8.08-7.82 (m, 1H), 7.28 (d, $J = 3.3$ Hz, 1H), 6.65 (d, $J = 3.2$ Hz, 1H), 2.19 (s, 6H), 2.18-2.13 (m, 1H), 1.75-1.71 (m, 2H), 1.65-1.58 (m, 4H), 1.35-1.29 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.71, 143.85, 130.56, 129.56, 120.68, 112.76, 102.69, 51.79, 49.89, 39.84, 38.89, 29.69, 25.81.

IR (film) $\nu_{\text{max}}$ 2951, 2869, 1415, 1282, 1245, 907, 782 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$BrN$_2$ ([M+H]$^+$) 331.0804, found 331.0802.
(±)-tert-Butyl 3-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate (19)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene 1,1′-di-tert-butyl O$_3$O$_3$-bis(pyrrolidine-1,3-dicarboxylate) (405 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (30-40% EtOAc/hexanes), followed by another flash chromatography (5-10% EtOAc/CH$_2$Cl$_2$) provided the title compound (72 mg, 55% yield, rotameric) as a colorless oil.

(Mixture of rotamers) $^1$H NMR (500 MHz, CDCl$_3$) δ 8.49 (s, 1H), 7.93 (s, 1H), 7.28 (d, $J$ = 3.3 Hz, 1H), 6.69 (d, $J$ = 3.0 Hz, 1H), 3.52-3.43 (m, 2H), 3.41-3.29 (m, 1H), 3.21-3.05 (m, 1H), 2.52-2.47 (m, 1H), 2.27 (s, 6H), 2.02-1.98 (m, 1H), 1.77-1.64 (m, 1H), 1.48 & 1.47 (s, 9H).

(Mixture of rotamers) $^{13}$C NMR (125 MHz, CDCl$_3$) δ 154.70, 154.62, 145.89, 144.20, 130.24, 129.44, 120.40, 112.94, 103.13, 103.09, 79.51, 52.06, 49.61, 48.91, 48.59, 45.88, 45.60, 38.23, 37.29, 29.27, 28.70, 28.68, 28.62, 28.57.

IR (film) $\nu_{\text{max}}$ 2979, 2884, 1689, 1413, 1248, 1167, 876, 730 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{21}$H$_{27}$BrN$_3$O$_2$ ([M+H]$^+$) 432.1281, found 432.1278.
(±)-tert-Butyl 3-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (20)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene 1,1'-di-tert-butyl $O^9,O^3$-bis(piperidine-1,3-dicarboxylate) (422 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes), followed by another flash chromatography (5-10% EtOAc/CH$_2$Cl$_2$) provided the title compound (82 mg, 61% yield) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 7.90 (s, 1H), 7.27 (s, 1H), 6.66 (d, $J = 2.9$ Hz, 1H), 3.94 (brs, 1H), 2.86-2.70 (m, 1H), 2.54 (brs, 1H), 2.25 (s, 6H), 1.92-1.66 (m, 4H), 1.48 (s, 9H), 1.46-1.44 (m, 1H), 1.27-1.18 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 154.99, 145.77, 143.98, 130.39, 129.58, 120.53, 112.86, 102.98, 79.76, 51.72, 49.40, 46.63 (br), 44.51 (br), 38.70, 34.72, 28.62, 27.90, 24.75.

IR (film) $\nu_{max}$ 2976, 1687, 1416, 1243, 1115, 906, 730 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{22}$H$_{20}$BrN$_3$O$_2$ ([M+H]$^+$) 446.1438, found 446.1426.
(±)-6-Bromo-1-(3-(tetrahydro-2H-pyran-3-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (21)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-3-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes) provided the title compound (64 mg, 62% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.52 (s, 1H), 7.92 (s, 1H), 7.27-7.26 (m, 1H), 6.69-6.63 (m, 1H), 3.94-3.90 (m, 2H), 3.40-3.30 (m, 1H), 3.16 (t, $J$ = 10.7 Hz, 1H), 2.24 (s, 6H), 1.99-1.83 (m, 2H), 1.69-1.61 (m, 2H), 1.33-1.25 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.68, 143.94, 130.41, 129.52, 120.58, 112.86, 102.92, 70.66, 68.23, 51.75, 49.44, 37.82, 34.94, 26.89, 25.44.

IR (film) $\nu_{\text{max}}$ 2981, 2915, 1415, 1308, 1089, 907, 782, 728 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$BrN$_2$O ([M+H]$^+$) 347.0754, found 347.0744.
6-Bromo-1-(3-cycloheptyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (22)
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene dicycloheptanecarboxylate (317 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (59 mg, 55% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.47 (s, 1H), 7.91 (s, 1H), 7.25 (d, $J$ = 3.3 Hz, 1H), 6.63 (d, $J$ = 3.1 Hz, 1H), 2.16 (s, 6H), 1.80-1.66 (m, 5H), 1.64-1.57 (m, 2H), 1.54-1.39 (m, 4H), 1.25-1.19 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.89, 143.99, 130.36, 129.40, 120.42, 112.77, 102.73, 51.21, 49.57, 41.55, 38.44, 31.24, 28.56, 26.39.

IR (film) $\nu_{\text{max}}$ 2915, 2853, 1415, 1282, 1245, 906, 880, 782, 725 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{24}$BrN$_2$ ([M+H]$^+$) 359.1117, found 359.1113.
6-Bromo-1-(3-(tert-butyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (23)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(2,2-dimethylpropanoate) (269 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (72 mg, 75% yield) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 2.0$ Hz, 1H), 8.21-7.60 (m, 1H), 7.26 (d, $J = 3.4$ Hz, 1H), 6.82-6.24 (m, 1H), 2.17 (s, 6H), 0.97 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.97, 144.02, 130.36, 129.48, 120.43, 112.84, 102.84, 49.88, 48.59, 45.31, 29.16, 26.44.

IR (film) $v_{\text{max}}$ 2957, 2871, 1502, 1414, 1311, 1205, 905, 782, 725 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{20}$BrN$_2$ ([M+H]$^+$) 319.0804, found 319.0809.
6-Bromo-1-(3-(3-methyloxetan-3-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (24)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(3-methyloxetane-3-carboxylate) (286 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-25% EtOAc/hexanes) provided the title compound (73 mg, 73% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 7.99-7.89 (m, 1H), 7.29 (d, $J = 3.3$ Hz, 1H), 6.68 (d, $J = 2.8$ Hz, 1H), 4.57 (d, $J = 5.8$ Hz, 2H), 4.43 (d, $J = 5.9$ Hz, 2H), 2.35 (s, 6H), 1.36 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.85, 144.15, 130.31, 129.51, 120.48, 112.96, 103.19, 79.38, 50.42, 49.48, 41.19, 38.15, 21.04.

IR (film) $\nu_{max}$ 2961, 2870, 1415, 1316, 1202, 979, 906, 782 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{18}$BrN$_2$O ([M+H]$^+$) 333.0597, found 333.0599.
tert-Butyl 3-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-3-methylazetidine-1-carboxylate (25)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene 1,1'-di-tert-butyl $O^3,O^3$-bis(3-methylazetidine-1,3-dicarboxylate) (405 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (25-35% EtOAc/hexanes) provided the title compound (90 mg, 70% yield) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 7.91 (s, 1H), 7.27 (d, $J = 3.3$ Hz, 1H), 6.66 (d, $J = 3.1$ Hz, 1H), 3.81 (d, $J = 8.4$ Hz, 2H), 3.61 (d, $J = 8.4$ Hz, 2H), 2.30 (s, 6H), 1.45 (s, 9H), 1.30 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 156.66, 145.97, 144.25, 130.19, 129.48, 120.36, 113.05, 103.26, 79.77, 57.71 (br), 56.47 (br), 50.22, 49.44, 41.77, 32.69, 28.53, 21.95.

IR (film) $\nu_{\text{max}}$ 2974, 2878, 1694, 1380, 1135, 1103, 907, 730 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{21}$H$_{27}$BrN$_3$O$_2$ ([M+H]$^+$) 432.1281, found 432.1282.
6-Bromo-1-(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (26)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodositylene bis(1-methylcyclohexane-1-carboxylate) (317 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (86 mg, 80% yield) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.47 (s, 1H), 7.96-7.84 (m, 1H), 7.26 (d, $J$ = 3.2 Hz, 1H), 6.64 (d, $J$ = 2.9 Hz, 1H), 2.16 (s, 6H), 1.68-1.38 (m, 5H), 1.35-1.11 (m, 5H), 0.94 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.88, 143.96, 130.40, 129.48, 120.46, 112.74, 102.74, 49.55, 48.83, 45.94, 33.98, 31.16, 26.34, 22.01, 19.99.

IR (film) $\nu_{\text{max}}$ 2918, 1414, 1304, 1244, 1188, 905, 782, 725 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{24}$BrN$_2$ ([M+H]$^+$) 359.1117, found 359.1119.
6-Bromo-1-(3-(4-methyltetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (27)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(4-methyltetrahydro-2H-pyran-4-carboxylate) (319 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (25-30% EtOAc/hexanes) provided the title compound (82 mg, 76% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 1.7$ Hz, 1H), 7.94-7.86 (m, 1H), 7.26 (d, $J = 3.4$ Hz, 1H), 6.64 (d, $J = 3.3$ Hz, 1H), 3.83 (ddd, $J = 11.6$, 4.2, 2.5 Hz, 2H), 3.60 (td, $J = 11.7$, 2.1 Hz, 2H), 2.20 (s, 6H), 1.66 (td, $J = 12.9$, 4.7 Hz, 2H), 1.22 (d, $J = 15.0$ Hz, 2H), 1.07 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.90, 144.07, 130.33, 129.45, 120.41, 112.83, 102.95, 63.95, 49.43, 49.07, 45.41, 33.78, 29.36, 19.39.

IR (film) $v_{max}$ 2969, 2915, 1502, 1414, 1309, 1101, 905, 782, 729 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{18}$H$_{22}$BrN$_2$O ([M+H]$^+$) 361.0910, found 361.0904.
tert-Butyl 4-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-4-methylpiperidine-1-carboxylate (28)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene 1,1′-di-tert-butyl $O^4, O^1$-bis(4-methylpiperidine-1,4-dicarboxylate) (438 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (25-35% EtOAc/hexanes) provided the title compound (94 mg, 68% yield) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 8.11-7.78 (m, 1H), 7.27 (d, $J = 3.3$ Hz, 1H), 6.66 (d, $J = 2.9$ Hz, 1H), 3.94 (brs, 2H), 2.95 (brs, 2H), 2.21 (s, 6H), 1.52-1.49 (m, 2H), 1.47 (s, 9H), 1.32-1.24 (m, 2H), 1.03 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 154.97, 145.86, 144.05, 130.33, 129.46, 120.43, 112.82, 102.96, 79.58, 49.57, 48.97, 45.26, 40.26 (br), 39.52 (br), 33.16, 30.14, 28.58, 18.90.

IR (film) $\nu_{\text{max}}$ 2973, 1688, 1416, 1247, 1162, 906, 780 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{23}$H$_{31}$BrN$_3$O$_2$ ([M+H]$^+$) 460.1594, found 460.1596.
1-(3-((1s,3s)-Adamant-1-yl)bicyclo[1.1.1]pentan-1-yl)-6-bromo-1H-pyrrolo[3,2-b]pyridine (29)

Prepared following the general procedure outlined above using Ir(ppy)₃ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(adamantane-1-carboxylate) (363 mg, 0.60 mmol, 2.0 equiv), Cu(acac)₂ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et₂O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes), followed by another flash chromatography (10-15% acetone/hexanes) provided the title compound (62 mg, 52% yield) as a white solid.

^1H NMR (500 MHz, CDCl₃) δ 8.48 (d, J = 1.7 Hz, 1H), 8.04-7.86 (m, 1H), 7.28 (d, J = 3.3 Hz, 1H), 6.70-6.57 (m, 1H), 2.14 (s, 6H), 2.02 (s, 3H), 1.74 (d, J = 12.2 Hz, 3H), 1.64 (d, J = 11.9 Hz, 3H), 1.55-1.47 (m, 6H).

^13C NMR (125 MHz, CDCl₃) δ 145.84, 143.92, 130.50, 129.56, 120.59, 112.75, 102.72, 49.04, 48.92, 44.82, 38.92, 36.91, 30.46, 28.26.

IR (film) νmax 2902, 2847, 1415, 1288, 1245, 906, 781, 730 cm⁻¹.

HRMS (ESI-TOF) m/z calcd. for C₂₂H₂₆BrN₂ ([M+H]⁺) 397.1274, found 397.1271.
Methyl 4-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)bicyclo[2.2.2]octane-1-carboxylate (30)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene $O'^1, O'^4, 4'$-dimethyl bis(bicyclo[2.2.2]octane-1,4-dicarboxylate) (401 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-20% EtOAc/hexanes), followed by reverse phase chromatography provided the title compound (64 mg, 50% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.48 (s, 1H), 7.89 (s, 1H), 7.26 (d, $J = 4.8$ Hz, 1H), 6.64 (d, $J = 2.9$ Hz, 1H), 3.66 (s, 3H), 2.14 (s, 6H), 1.92-1.75 (m, 6H), 1.57-1.43 (m, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 178.44, 145.94, 144.12, 130.32, 129.46, 120.43, 112.84, 102.90, 51.89, 49.83, 49.11, 43.12, 38.74, 29.05, 28.19, 27.53.

IR (film) $\nu_{max}$ 2946, 2917, 1728, 1416, 1299, 1247, 1073, 906, 783 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{22}$H$_{26}$BrN$_2$O$_2$ ([M+H]$^+$) 429.1172, found 429.1174.
(±)-tert-Butyl 3-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-4-oxopiperidine-1-carboxylate (31)

Prepared following the general procedure (A) outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), N-Boc-3-bromo-4-piperidone (167 mg, 0.60 mmol, 2.0 equiv), CuCl (16.3 mg, 0.17 mmol, 0.55 equiv), acetoacetone (15.4 µL, 0.15 mmol, 0.5 equiv), BTMG (0.19 mL, 0.90 mmol, 3.0 equiv), propellane (1.09 M in Et$_2$O, 0.41 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Purification by reversed-phase chromatography (35-90% MeCN/H$_2$O) provided the title compound (84 mg, 60% yield) as an off-white solid.

$^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 8.80 (s, 1H), 7.76 (s, 1H), 6.73 (d, $J = 3.4$ Hz, 1H), 6.69 (d, $J = 3.3$ Hz, 1H), 3.64 (brs, 0.3H), 3.34 (brs, 1.4H), 3.05 (brs, 0.3H) 2.99 (dd, $J = 13.3, 7.8$ Hz, 2H), 2.12 (s, 1H), 1.93 (t, $J = 6.3$ Hz, 2H), 1.81 (s, 6H), 1.45 (s, 9H).

$^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 205.30, 154.13, 146.85, 144.76, 129.93, 129.54, 119.96, 113.52, 103.90, 80.11, 52.64, 49.71, 48.65, 45.66, 43.45, 40.78, 34.80, 28.44.

IR (film) $\nu_{max}$ 2921, 1690 (humped), 1416, 1241, 1163, 907, 782, 731 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{22}$H$_{27}$BrN$_3$O$_3$ ([M+H]$^+$) 460.1230, found 460.1234.
(±)-tert-Butyl 2-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)propanoate (32)
Prepared following the general procedure (A) outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), tert-butyl 2-bromopropionate (100 µL, 0.60 mmol, 2.0 equiv), CuCl (16.3 mg, 0.17 mmol, 0.55 equiv), acetoacetone (15.4 µL, 0.15 mmol, 0.5 equiv), BTMG (0.19 mL, 0.90 mmol, 3.0 equiv), propellane (1.09 M in Et$_2$O, 0.41 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Purification by flash chromatography (10-40% EtOAc/hexanes) provided the title compound (71 mg, 61% yield) as an off-white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.48 (s, 1H), 7.90 (d, $J$ = 1.3 Hz, 1H), 7.26 (d, $J$ = 2.6 Hz, 1H), 6.65 (d, $J$ = 2.7 Hz, 1H), 2.70 (q, $J$ = 7.0 Hz, 1H), 2.30 (s, 6H), 1.48 (s, 9H), 1.17 (d, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.08, 145.81, 144.10, 130.36, 129.51, 120.47, 112.91, 103.02, 80.92, 52.33, 49.46, 40.11, 38.12, 28.34, 14.11.

IR (film) $\nu_{max}$ 2977, 1723, 1415, 1280, 1246, 1151, 906, 727 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{24}$BrN$_2$O$_2$ ([M+H]$^+$) 391.1016, found 391.1017.
2-(3-(6-Bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-2,2-difluoroacetic acid (33)

Prepared following the general procedure (A) outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), ethyl bromodifluoroacetate (77 µL, 0.60 mmol, 2.0 equiv), CuCl (16.3 mg, 0.17 mmol, 0.55 equiv), acetoacetone (15.4 µL, 0.15 mmol, 0.5 equiv), BTMG (0.19 mL, 0.90 mmol, 3.0 equiv), propellane (1.09 M in Et$_2$O, 0.41 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Following the reaction, mesitylene (13.9 µL, 0.1 mmol, 0.333 equiv) was added and the yield was determined by $^1$H-NMR to be 85%. The compound was then hydrolyzed and subjected to reversed-phase chromatography [0-100% MeCN/H$_2$O (0.1% TFA)] and thereby isolated as the carboxylic acid half TFA salt (25 mg, 18% yield) as a white solid.

$^1$H NMR (500 MHz, CD$_3$OD) $\delta$ 8.39 (d, $J = 2.0$ Hz, 1H), 8.20 (dd, $J = 2.0$, 0.9 Hz, 1H), 7.58 (d, $J = 3.4$ Hz, 1H), 6.61 (dd, $J = 3.4$, 0.9 Hz, 1H), 2.55 (s, 6H).

$^{13}$C NMR (125 MHz, CD$_3$OD) $\delta$ 169.40 (t, $J = 27$ Hz), 146.69, 144.44, 132.75, 130.97, 122.39, 115.29 (t, $J = 249.2$ Hz), 113.7, 103.1, 52.74 (t, $J = 3.1$ Hz), 50.30 (t, $J = 2.7$ Hz), 37.55 (t, $J = 37.4$ Hz).

$^{19}$F NMR (376 MHz, CD$_3$OD) $\delta$ -76.96 (TFA, 1.5F), -110.29 (Product, 2F).

IR (film) $\nu_{max}$ 3400 (br), 2925, 1650 (humped), 1417, 1282, 1196, 1132, 911, 722 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{14}$H$_{12}$BrF$_2$N$_2$O$_2$ ([M+H]$^+$) 357.0045, found 357.0040.
(±)-Methyl 4-(1-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)ethyl)benzoate (34)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), methyl 4-(1-bromoethyl)benzoate (146 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes) provided the title compound (59 mg, 46% yield) as a yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.47 (s, 1H), 8.02 (d, $J$ = 8.3 Hz, 2H), 7.83 (s, 1H), 7.26 (d, $J$ = 8.2 Hz, 2H), 7.20 (d, $J$ = 3.2 Hz, 1H), 6.62 (d, $J$ = 3.0 Hz, 1H), 3.92 (s, 3H), 3.18 (q, $J$ = 7.0 Hz, 1H), 2.21-2.10 (m, 6H), 1.39 (d, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 167.08, 148.60, 145.89, 144.13, 130.19, 129.91, 129.44, 128.71, 127.43, 120.29, 112.88, 103.01, 52.21, 51.58, 50.14, 41.21, 39.46, 16.93.

IR (film) $\nu_{\text{max}}$ 2922, 1720, 1416, 1281, 1110, 907, 711 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{22}$H$_{22}$BrN$_2$O$_2$ ([M+H]$^+$) 425.0859, found 425.0822.
6-Bromo-1-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (35)
Prepared following the general procedure (B) outlined above using 6-bromo-1H-pyrrolo[3,2-b]pyridine (118 mg, 0.60 mmol, 2.0 equiv), Cu(acac)\(_2\) (23.6 mg, 0.09 mmol, 0.30 equiv), BTMG (0.19 mL, 0.90 mmol, 3.0 equiv), propellane (1.04 M in Et\(_2\)O, 0.29 mL, 0.30 mmol, 1.0 equiv), Togni reagent II (60wt% on celite, 316 mg, 0.6 mmol, 2.0 equiv) and 1,4-dioxane (3.0 mL). Purification by flash chromatography (10-30% EtOAc/hexanes) provided the title compound (99.3 mg, 68% yield) as an off-white solid.

\(^1\text{H} \text{NMR (500 MHz, CD}_3\text{CN) }\delta 8.50 \text{ (s, 1H), 8.12 \text{ (s, 1H), 7.46 \text{ (d, } J = 3.2 \text{ Hz, 1H), 6.63 \text{ (d, } J = 3.3 \text{ Hz, 1H), 2.68 \text{ (s, 6H).}}}

\(^{13}\text{C} \text{NMR (125 MHz, CD}_3\text{CN) }\delta 147.00, 144.99, 131.85, 130.16, 124.57 \text{ (q, } J = 273.4 \text{ Hz), 121.09, 113.79, 103.98, 52.35 \text{ (q, } J = 2.0 \text{ Hz), 49.94 \text{ (q, } J = 2.3 \text{ Hz), 35.21 \text{ (q, } J = 39.6 \text{ Hz).}}

\(^{19}\text{F} \text{NMR (376 MHz, CD}_3\text{CN) }\delta -71.78.

IR (film) \nu_{\text{max}} 2930, 1525, 1420, 1401, 1175, 1132, 910, 782, 730 \text{ cm}^{-1}.

HRMS (ESI-TOF) m/z calcd. for C\(_{13}\)H\(_{11}\)BrF\(_3\)N\(_2\) ([M+H]\(^+\)) 331.0052, found 331.0049.
6-Bromo-1-(3-(phenylsulfonyl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (36)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), S-phenyl benzenesulfonothioate (263 mg, 1.05 mmol, 3.5 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.94 mL, 0.75 mmol, 2.5 equiv), and THF (10.0 mL). Purification by flash chromatography (40-50% EtOAc/hexanes) provided the title compound (50 mg, 41% yield) as a brown solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.51 (s, 1H), 7.95 (d, $J$ = 8.5 Hz, 2H), 7.79-7.69 (m, 2H), 7.68-7.59 (m, 2H), 7.16 (d, $J$ = 3.4 Hz, 1H), 6.67 (d, $J$ = 3.2 Hz, 1H), 2.67 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.05, 144.91, 136.61, 134.50, 129.67, 129.62, 128.77, 120.00, 113.53, 104.47, 53.85, 49.74, 49.41.

IR (film) $\nu_{\text{max}}$ 2956, 1515, 1417, 1308, 1140, 909, 722, 689 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{18}$H$_{16}$BrN$_2$O$_2$S ([M+H]$^+$) 403.0110, found 403.0116.
8.2 Nucleophile Scope

6-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pent-1-yl)-1H-pyrrolo[3,2-b]pyridine (37)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (30-40% EtOAc/hexanes) provided the title compound (78 mg, 75% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.49 (s, 1H), 7.92 (s, 1H), 7.28 (d, $J = 3.3$ Hz, 1H), 6.66 (d, $J = 2.9$ Hz, 1H), 4.04 (dd, $J = 11.2$, 3.9 Hz, 2H), 3.47-3.37 (m, 2H), 2.22 (s, 6H), 1.84 (tt, $J = 11.9$, 3.6 Hz, 1H), 1.64-1.57 (m, 2H), 1.38 (qd, $J = 12.6$, 4.4 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.91, 144.10, 130.30, 129.44, 120.38, 112.85, 102.93, 67.73, 50.97, 49.53, 40.16, 34.16, 29.55.

IR (film) $\nu_{\text{max}}$ 2980, 2914, 1502, 1416, 1245, 1089, 906, 782 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$BrN$_2$O ([M+H]$^+$) 347.0754, found 347.0744.
4-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pent-1-yl)-1H-pyrrolo[2,3-c]pyridine (38)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 4-bromo-1H-pyrrolo[2,3-c]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.3 M in Et$_2$O, 0.35 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1,3,5-Trimethoxybenzene was then added as an internal standard to determine the $^1$H-NMR yield (72%). Purification by flash chromatography (45-55% EtOAc/hexanes) provided the title compound (60 mg, 58% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 8.90 (s, 1H), 8.77 (s, 1H), 6.64 (d, $J = 3.1$ Hz, 1H), 6.55 (d, $J = 3.1$ Hz, 1H), 3.90 (dt, $J = 11.0$, 3.2 Hz, 2H), 3.11 (m, 2H), 1.54 (s, 6H), 1.21–1.09 (m, 1H), 0.96 (m, 4H).

$^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 140.60, 134.88, 133.72, 133.26, 129.90, 113.12, 101.56, 67.58, 50.49, 49.37, 39.48, 34.05, 29.59.

IR (film) $\nu_{\text{max}}$ 2908, 1492, 1438, 1284, 1240, 1146, 1085, 889, 771 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$BrN$_2$O ([M+H]$^+$) 347.0754, found 347.0750.
4-Chloro-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[2,3-b]pyridine (39)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 4-chloro-1H-pyrrolo[2,3-b]pyridine (46 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.3 M in Et$_2$O, 0.35 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1,3,5-Trimethoxybenzene was then added as an internal standard to determine the $^1$H-NMR yield (60%). Purification by flash chromatography (0-2% Acetone/CH$_2$Cl$_2$) provided the title compound (43 mg, 47% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.20 (d, $J$ = 5.2 Hz, 1H), 7.19 (d, $J$ = 3.6 Hz, 1H), 7.08 (d, $J$ = 5.2 Hz, 1H), 6.52 (d, $J$ = 3.6 Hz, 1H), 4.02 (dd, $J$ = 11.6, 4.4 Hz, 2H), 3.41 (td, $J$ = 11.8, 2.0 Hz, 2H), 2.28 (s, 6H), 1.81 (tt, $J$ = 12.1, 3.8 Hz, 1H), 1.59 (d, $J$ = 10.3 Hz, 2H), 1.38 (qd, $J$ = 12.4, 4.4 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.71, 143.32, 135.87, 127.08, 120.66, 116.05, 98.17, 67.88, 51.08, 48.81, 40.58, 34.38, 29.67.

IR (film) $\nu_{\text{max}}$ 2967, 2914, 1591, 1551, 1414, 1281, 1089, 889, 820 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$ClN$_2$O ([M+H]$^+$) 303.1259, found 303.1254.
6-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-indazole (40)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-indazole (59 mg, 0.30 mmol, 1.0 equiv), iodositylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.3 M in Et$_2$O, 0.35 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Purification by flash chromatography (15-25% EtOAc/hexanes) provided the title compound (75 mg, 72% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.96 (d, $J = 1.1$ Hz, 1H), 7.74 (dt, $J = 1.6, 0.7$ Hz, 1H), 7.58 (dd, $J = 8.5, 0.7$ Hz, 1H), 7.24 (dd, $J = 7.2, 1.6$ Hz, 1H), 4.04 (dd, $J = 11.6, 4.7$ Hz, 2H), 3.42 (td, $J = 11.9, 2.0$ Hz, 2H), 2.31 (s, 6H), 1.85 (tt, $J = 11.9, 3.9$ Hz, 1H), 1.61 (dd, $J = 12.9, 2.3$ Hz, 2H), 1.40 (qd, $J = 12.3, 4.5$ Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.03, 133.83, 124.45, 123.37, 122.40, 120.89, 113.07, 67.84, 51.28, 50.87, 40.54, 34.29, 29.64.

IR (film) $\nu_{max}$ 2917, 1730, 1608, 1462, 1419, 1227, 1089, 911, 896 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$BrN$_2$O ([M+H]$^+$) 347.0754, found 347.0747.
Methyl 1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-indazole-4-carboxylate (41)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), methyl 1H-indazole-4-carboxylate (53 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.3 M in Et$_2$O, 0.35 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Purification by flash chromatography (15-40% EtOAc/hexanes) provided the title compound (63 mg, 64% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.50 (d, $J = 0.9$ Hz, 1H), 7.92 (d, $J = 7.2$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.42 (dd, $J = 8.4$, 7.2 Hz, 1H), 4.04 (dd, $J = 12.0$, 4.9 Hz, 2H), 4.01 (s, 3H), 3.42 (td, $J = 11.9$, 2.0 Hz, 2H), 2.33 (s, 6H), 1.86 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.62 (d, $J = 12.8$ Hz, 2H), 1.40 (qd, $J = 12.0$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.88, 139.78, 134.46, 125.77, 124.38, 123.10, 123.05, 115.14, 67.84, 52.33, 51.36, 50.99, 40.57, 34.28, 29.63.

IR (film) $v_{\text{max}}$ 2922, 1719, 1606, 1447, 1415, 1283, 1266, 1175, 755 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{23}$N$_2$O$_3$ ([M+H]$^+$) 327.1703, found 327.1699.
2-Phenyl-1-(3-(tetrahydro-2H-pyran-4-yl))bicyclo[1.1.1]pentan-1-yl-1H
benzo[d]imidazole (42)

Prepared following the general procedure outlined above using Ir(ppy)_3 (3.9 mg, 6.0 µmol, 0.02 equiv), 2-phenyl-1H-benzo[d]imidazole (58 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(TMHD)_2 (77 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et_2O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes) provided the title compound (83 mg, 81% yield) as a colorless oil.

_1H NMR (500 MHz, CDCl_3) _δ_ 7.83-7.72 (m, 1H), 7.63-7.61 (m, 1H), 7.58-7.54 (m, 2H), 7.52-7.44 (m, 3H), 7.34-7.27 (m, 2H), 3.95 (dd, _J_ = 11.4, 4.3 Hz, 2H), 3.32 (td, _J_ = 12.1, 1.9 Hz, 2H), 2.04 (s, 6H), 1.67 (tt, _J_ = 11.9, 3.8 Hz, 1H), 1.49-1.40 (m, 2H), 1.32-1.19 (m, 2H).

_13C NMR (125 MHz, CDCl_3) _δ_ 154.32, 142.95, 135.82, 132.04, 130.29, 129.82, 127.95, 122.85, 122.49, 120.09, 111.72, 67.67, 52.19, 49.10, 41.16, 34.01, 29.41.

IR (film) _ν_ max 2915, 2844, 1453, 1369, 1211, 1089, 894, 744, 701 cm⁻¹.

HRMS (ESI-TOF) m/z calcd. for C_{23}H_{25}N_2O ([M+H]^+) 345.1961, found 345.1958.
6-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrazolo[4,3-b]pyridine (43)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrazolo[4,3-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-25% EtOAc/hexanes) provided the title compound (56 mg, 54% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.57 (d, $J = 1.7$ Hz, 1H), 8.19 (s, 1H), 8.04 (s, 1H), 4.02 (dd, $J = 11.2$, 4.1 Hz, 2H), 3.41 (t, $J = 11.0$ Hz, 2H), 2.29 (s, 6H), 1.85 (tt, $J = 11.8$, 3.7 Hz, 1H), 1.65-1.55 (m, 2H), 1.38 (qd, $J = 12.6$, 4.4 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.79, 140.59, 134.79, 132.72, 120.16, 117.94, 67.76, 51.26, 50.91, 40.59, 34.19, 29.58.

IR (film) $\nu_{\text{max}}$ 2919, 2843, 1587, 1434, 1265, 1089, 919, 777 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{19}$BrN$_3$O ([M+H]$^+$) 348.0706, found 348.0693.
5-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrazolo[3,4-b]pyridine (44)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 5-bromo-1H-pyrazolo[3,4-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-20% EtOAc/hexanes) provided the title compound (48 mg, 46% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.61-8.45 (m, 1H), 8.15 (d, $J = 2.1$ Hz, 1H), 7.93 (s, 1H), 4.02 (dd, $J = 11.2$, 4.1 Hz, 2H), 3.41 (t, $J = 11.8$ Hz, 2H), 2.34 (s, 6H), 1.84 (tt, $J = 11.8$, 3.7 Hz, 1H), 1.60 (d, $J = 14.5$ Hz, 2H), 1.39 (qd, $J = 12.6$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 149.70, 149.13, 131.70, 131.59, 117.52, 112.79, 67.87, 51.36, 49.97, 40.80, 34.36, 29.66.

IR (film) $v_{max}$ 2919, 2843, 1478, 1435, 1266, 1089, 895, 768 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{19}$BrN$_3$O ([M+H]$^+$) 348.0706, found 348.0695.
5-Bromo-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-indole (45)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 5-bromo-1H-indole (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.05 M in Et$_2$O, 0.43 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1,3,5-Trimethoxybenzene was then added as an internal standard to determine the $^1$H-NMR yield (68%). Purification by flash chromatography (0-5% EtOAc/toluene) provided the title compound (60 mg, 57% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.73 (d, $J = 1.9$ Hz, 1H), 7.38 (d, $J = 8.7$ Hz, 1H), 7.26 (dd, $J = 8.7$, 1.9 Hz, 1H), 7.05 (d, $J = 3.2$ Hz, 1H), 6.40 (d, $J = 3.0$ Hz, 1H), 4.03 (dd, $J = 11.2$, 3.7 Hz, 2H), 3.41 (td, $J = 11.9$, 2.0 Hz, 2H), 2.21 (s, 6H), 1.82 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.59 (d, $J = 13.0$ Hz, 2H), 1.38 (qd, $J = 13.3$, 12.8, 4.6 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 134.61, 131.06, 127.47, 124.51, 123.56, 113.07, 112.41, 101.07, 67.84, 50.92, 49.69, 40.14, 34.30, 29.63.

IR (film) $\nu_{\text{max}}$ 2933, 1458, 1279, 1240, 1157, 1085, 886, 757, 723 cm$^{-1}$.

A high-resolution mass spectrum could not be obtained for this compound, however, a lower resolution mass spectrum is reported below:

**MS (EI-QUAD)** m/z calcd. for C$_{18}$H$_{20}$BrNO: 345.1/347.1 (1:1), found 345.1/347.1 (1:1).
1-(3-(Tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-indole-3-carbonitrile (46)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (4.6 mg, 7.0 µmol, 0.02 equiv), 1H-indole-3-carbonitrile (50 mg, 0.35 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (353 mg, 0.70 mmol, 2.0 equiv), Cu(acac)$_2$ (55 mg, 0.21 mmol, 0.6 equiv), BTMG (0.22 mL, 1.05 mmol, 3.0 equiv), propellane (1.05 M in Et$_2$O, 0.70 mL, 0.74 mmol, 1.5 equiv), and 1,4-dioxane (9.8 mL). Purification by flash chromatography (15-40% EtOAc/hexanes) provided the title compound (56 mg, 55% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 8.1$ Hz, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.55 (s, 1H), 7.35-7.28 (m, 2H), 4.04 (dd, $J = 11.8$, 4.9 Hz, 2H), 3.42 (td, $J = 11.9$, 2.0 Hz, 2H), 2.26 (s, 6H), 1.85 (tt, $J = 11.9$, 3.8 Hz, 1H), 1.60 (d, $J = 13.3$ Hz, 2H), 1.38 (qd, $J = 12.1$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 135.29, 133.38, 128.49, 124.00, 122.36, 120.19, 115.95, 112.10, 86.17, 67.75, 51.00, 49.98, 40.23, 34.13, 29.55.

IR (film) $\nu_{\text{max}}$ 2927, 2851, 2212, 1727, 1525, 1460, 1228, 1086, 748 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{21}$N$_2$O ([M+H]$^+$) 293.1648, found 293.1643.
9-(3-(Tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-9H-pyrido[2,3-b]indole (47)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 9H-pyrido[2,3-b]indole (50 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.0 M in Et$_2$O, 0.45 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Purification by flash chromatography (60-100% EtOAc/hexanes) provided the title compound (67 mg, 70% yield) as a yellow solid.

$^1$H NMR (500 MHz, DMSO) δ 9.16 (s, 1H), 8.41 (s, 1H), 8.27 (d, $J = 7.8$ Hz, 1H), 8.15 (d, $J = 5.0$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.59 (td, $J = 7.8$, 1.3 Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 3.91 (dd, $J = 11.2$, 4.0 Hz, 2H), 3.37-3.29 (m, 2H), 2.51 (s, 6H), 1.83 (tt, $J = 11.8$, 3.8 Hz, 1H), 1.59 (d, $J = 12.7$ Hz, 2H), 1.28 (qd, $J = 13.2$, 12.8, 4.4 Hz, 2H).

$^{13}$C NMR (125 MHz, DMSO) δ 140.66, 138.96, 136.38, 133.41, 128.57, 128.00, 121.94, 120.97, 120.01, 114.68, 111.56, 66.74, 51.36, 49.03, 40.92, 33.59, 29.24.

IR (film) $\nu_{\text{max}}$ 2910, 2841, 1622, 1463, 1347, 1325, 1230, 1091, 757 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{21}$H$_{23}$N$_2$O ([M+H]$^+$) 319.1805, found 319.1801.
3-Bromo-9-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pent-1-yl)-9H-carbazole (48)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 3-bromo-9H-carbazole (74 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTTP (0.28 mL, 0.90 mmol, 3.0 equiv), propellane (1.3 M in Et$_2$O, 0.35 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1,3,5-Trimethoxybenzene was then added as an internal standard to determine the $^1$H-NMR yield (69%). Purification by flash chromatography (0-5% CH$_2$Cl$_2$/toluene) provided the title compound (66 mg, 56% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (s, 1H), 8.01 (d, $J$ = 7.8 Hz, 1H), 7.67 (d, $J$ = 8.4 Hz, 1H), 7.54 (d, $J$ = 8.8 Hz, 1H), 7.50-7.40 (m, 2H), 7.24 (t, $J$ = 7.5 Hz, 1H), 4.05 (dd, $J$ = 11.4, 4.4 Hz, 2H), 3.43 (t, $J$ = 12.8 Hz, 2H), 2.48 (s, 6H), 1.85 (tt, $J$ = 11.8, 3.8 Hz, 1H), 1.63 (d, $J$ = 13.9 Hz, 2H), 1.42 (qd, $J$ = 12.4, 4.4 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.07, 139.35, 128.36, 126.47, 125.42, 122.98, 122.57, 120.47, 119.81, 112.25, 112.09, 110.96, 67.86, 52.03, 49.87, 41.68, 34.39, 29.65.

IR (film) $v_{max}$ 2913, 1620, 1469, 1442, 1327, 1272, 1230, 1088, 726 cm$^{-1}$.

A high-resolution mass spectrum could not be obtained for this compound, however, a lower resolution mass spectrum is reported below:

**MS (EI-QUAD)** m/z calcd. for C$_{22}$H$_{22}$BrNO: 395.1/397.1 (1:1), found 394.8/397.0 (1:1).
Methyl 1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrole-3-carboxylate (49)
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), methyl 1H-pyrrole-3-carboxylate (38 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-20% EtOAc/hexanes), followed by another flash chromatography (5-15% EtOAc/toluene) provided the title compound (44 mg, 53% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 (t, $J = 1.8$ Hz, 1H), 6.62 (t, $J = 2.5$ Hz, 1H), 6.56 (dd, $J = 2.8$, 1.6 Hz, 1H), 4.00 (dd, $J = 11.2$, 4.1 Hz, 2H), 3.79 (s, 3H), 3.38 (t, $J = 11.0$ Hz, 2H), 2.01 (s, 6H), 1.77 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.54 (d, $J = 14.8$ Hz, 2H), 1.32 (qd, $J = 12.5$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.36, 124.12, 119.68, 116.12, 110.30, 67.76, 51.19, 50.76, 49.88, 38.64, 34.07, 29.56.

IR (film) $\nu_{max}$ 3123, 2914, 2841, 1698, 1538, 1262, 1091, 886, 764 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{22}$NO$_3$ ([M+H]$^+$) 276.1594, found 276.1576.
1-(1-(3-(Tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrol-2-yl)ethan-1-one (50)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 1-(1H-pyrrol-2-yl)ethan-1-one (33 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). 1,3-Benzodioxole was then added as an internal standard to determine the $^1$H-NMR yield (62%). Purification by flash chromatography (10-20% EtOAc/hexanes) provided the title compound (36 mg, 46% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 6.98 (dd, $J = 4.0$, 1.8 Hz, 1H), 6.88 (dd, $J = 2.7$, 1.8 Hz, 1H), 6.11 (dd, $J = 4.0$, 2.6 Hz, 1H), 4.11-3.89 (m, 2H), 3.38 (td, $J = 11.9$, 2.1 Hz, 2H), 2.42 (s, 3H), 2.16 (s, 6H), 1.76 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.61-1.47 (m, 2H), 1.40-1.31 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 186.95, 131.94, 128.83, 121.62, 107.72, 67.91, 51.59, 50.82, 39.05, 34.24, 29.66, 27.46.

IR (film) $v_{max}$ 2918, 2844, 1660, 1409, 1270, 1089, 893, 740 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{22}$NO$_2$ ([M+H]$^+$) 260.1645, found 260.1649.
3-(4-Chlorophenyl)-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pent-1-yl)-1H-pyrazole (51)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 3-(4-chlorophenyl)-1H-pyrazole (54 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-20% EtOAc/hexanes) provided the title compound (54 mg, 55% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.1$ Hz, 2H), 7.42 (d, $J = 2.3$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 6.50 (d, $J = 2.3$ Hz, 1H), 4.01 (dd, $J = 11.4$, 4.4 Hz, 2H), 3.39 (td, $J = 11.9$, 2.0 Hz, 2H), 2.13 (s, 6H), 1.80 (tt, $J = 11.9$, 3.8 Hz, 1H), 1.56 (d, $J = 12.8$ Hz, 2H), 1.35 (qd, $J = 12.5$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.09, 133.33, 132.18, 129.09, 128.77, 127.13, 102.92, 67.77, 51.22, 50.76, 38.98, 34.09, 29.55.

IR (film) $\nu_{\text{max}}$ 2916, 2843, 1494, 1417, 1252, 1088, 1013, 891, 756 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{22}$ClN$_2$O ([M+H]$^+$) 329.1415, found 329.1434.
6-Bromo-3,3-dimethyl-1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1,3-dihydro-2H-pyrrolo[3,2-b]pyridin-2-one (52)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-3,3-dimethyl-1,3-dihydro-2H-pyrrolo[3,2-b]pyridin-2-one (72 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-20% EtOAc/hexanes) provided the title compound (76 mg, 65% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (d, $J = 1.9$ Hz, 1H), 7.40 (d, $J = 1.9$ Hz, 1H), 4.05-3.98 (m, 2H), 3.38 (t, $J = 11.8$ Hz, 2H), 2.25 (s, 6H), 1.77 (ddt, $J = 12.0$, 8.0, 3.9 Hz, 1H), 1.55 (d, $J = 13.0$ Hz, 2H), 1.38 (s, 6H), 1.37-1.29 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 180.15, 154.72, 143.40, 138.07, 119.03, 118.56, 67.80, 51.21, 46.63, 44.63, 42.18, 34.31, 29.54, 22.72.

IR (film) $\nu_{\text{max}}$ 2926, 2847, 1731, 1586, 1413, 1324, 1138, 967, 879, 693 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{19}$H$_{24}$BrN$_2$O$_2$ ([M+H]$^+$) 391.1016, found 391.1013.
2-Chloro-N-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)nicotinamide (53)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 2-chloronicotinamide (47 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(II) bis-(2-isobutrylcyclohexanone) (72 mg, 0.18 mmol, 0.6 equiv), BTTP (0.27 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (50-70% EtOAc/hexanes) provided the title compound (48 mg, 52% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.42 (dd, $J = 4.7$, 2.0 Hz, 1H), 8.07 (dd, $J = 7.6$, 2.0 Hz, 1H), 7.31 (dd, $J = 7.6$, 4.7 Hz, 1H), 6.96 (s, 1H), 4.02-3.91 (m, 2H), 3.35 (td, $J = 11.9$, 2.0 Hz, 2H), 2.00 (s, 6H), 1.70 (tt, $J = 11.8$, 3.9 Hz, 1H), 1.60-1.45 (m, 2H), 1.35-1.24 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.68, 150.98, 147.15, 139.81, 131.34, 122.86, 67.80, 50.69, 45.86, 41.12, 34.32, 29.54.

IR (film) $\nu_{\text{max}}$ 3256, 2914, 2846, 1657, 1532, 1398, 1251, 1087, 877 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{20}$ClN$_2$O$_2$ ([M+H]$^+$) 307.1208, found 307.1203.
Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 4-(trifluoromethyl)benzamide (57 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(II) bis-(2-isobutylcyclohexanone) (72 mg, 0.18 mmol, 0.6 equiv), BTTP (0.27 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes) provided the title compound (61 mg, 60% yield) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.1$ Hz, 2H), 6.79 (s, 1H), 3.97 (dd, $J = 11.1$, 4.3 Hz, 2H), 3.35 (td, $J = 11.9$, 2.0 Hz, 2H), 1.99 (s, 6H), 1.69 (ddt, $J = 11.8$, 7.6, 3.8 Hz, 1H), 1.57-1.45 (m, 2H), 1.28 (qd, $J = 12.5$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.41, 137.94, 133.25 (q, $J_{C,F} = 32.7$ Hz), 127.48, 125.64 (q, $J_{C,F} = 3.7$ Hz), 123.76 (q, $J_{C,F} = 272.5$ Hz), 67.82, 50.66, 46.07, 41.08, 34.33, 29.56.

$^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -62.95.

IR (film) $\nu_{\text{max}}$ 3287, 2914, 2847, 1647, 1534, 1324, 1126, 1065, 859, 732 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{18}$H$_{21}$F$_3$NO$_2$ ([M+H]$^+$) 340.1519, found 340.1523.
\(N\)-(3-(Tetrahydro-2\(H\)-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-3( trifluoromethyl)pyridin-2-amine (55)

Prepared following the general procedure outlined above using Ir(ppy)\(_3\) (3.9 mg, 6.0 \(\mu\)mol, 0.02 equiv), 3-(trifluoromethyl)pyridin-2-amine (49 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2\(H\)-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)\(_2\) (47 mg, 0.18 mmol, 0.6 equiv), BTTP (0.27 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et\(_2\)O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). 1,3-Benzodioxole was then added as an internal standard to determine the \(^1\)H-NMR yield (62%). Purification by flash chromatography (5-10% EtOAc/hexanes), followed by another flash chromatography (5-10% acetone/pentane) provided the title compound (49 mg, 52% yield) as a white solid.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.27 (d, \(J = 4.9\) Hz, 1H), 7.62 (d, \(J = 7.6\) Hz, 1H), 6.63 (dd, \(J = 7.5, 5.2\) Hz, 1H), 5.25 (s, 1H), 3.99 (dd, \(J = 11.4, 4.3\) Hz, 2H), 3.45-3.23 (m, 2H), 1.98 (s, 6H), 1.70 (td, \(J = 11.8, 6.0\) Hz, 1H), 1.56-1.49 (m, 2H), 1.33 (qd, \(J = 12.6, 4.5\) Hz, 2H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 154.63, 151.76, 134.81 (q, \(J_{C,F} = 5.1\) Hz), 124.52 (q, \(J_{C,F} = 271.5\) Hz), 111.92, 108.62 (q, \(J_{C,F} = 31.2\) Hz), 67.98, 50.58, 47.40, 41.24, 34.59, 29.74.

\(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -63.60.

IR (film) \(\nu_{\text{max}}\) 3479, 2915, 2846, 1584, 1474, 1305, 1087, 1024, 770 cm\(^{-1}\).

HRMS (ESI-TOF) m/z calcd. for C\(_{16}\)H\(_{20}\)F\(_3\)N\(_2\)O ([M+H]\(^+\)) 313.1522, found 313.1526.
N-(2-Bromophenyl)-3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-amine (56)

Prepared following the general procedure outlined above using Ir(ppy)_3 (3.9 mg, 6.0 µmol, 0.02 equiv), 2-bromoaniline (52 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)_2 (47 mg, 0.18 mmol, 0.6 equiv), BTTP (0.27 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et_2O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (2-5% EtOAc/hexanes) provided the title compound (78 mg, 80% yield) as a white solid.

^1H NMR (500 MHz, CDCl_3) δ 7.41 (dd, J = 7.9, 1.5 Hz, 1H), 7.16 (ddd, J = 8.6, 7.4, 1.5 Hz, 1H), 6.96 (dd, J = 8.2, 1.5 Hz, 1H), 6.59 (td, J = 7.6, 1.5 Hz, 1H), 4.81 (s, 1H), 4.03-3.94 (m, 2H), 3.38 (td, J = 11.9, 2.0 Hz, 2H), 1.94 (s, 6H), 1.71 (tt, J = 11.9, 3.9 Hz, 1H), 1.53 (ddd, J = 13.1, 4.1, 1.9 Hz, 2H), 1.38-1.29 (m, 2H).

^13C NMR (125 MHz, CDCl_3) δ 143.84, 132.54, 128.22, 118.37, 113.25, 109.83, 67.86, 50.26, 48.81, 40.41, 34.43, 29.62.

IR (film) ν_max 3336, 2909, 1594, 1500, 1315, 1237, 1087, 1020, 879, 742 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for C_{16}H_{21}BrNO ([M+H]^+) 322.0801, found 322.0810.
2-((3-(Tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)amino)benzonitrile (57)

Prepared following the general procedure outlined above using \text{Ir(ppy)$_3$} (3.9 mg, 6.0 µmol, 0.02 equiv), 2-aminobenzonitrile (35 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), \text{Cu(acac)$_2$} (47 mg, 0.18 mmol, 0.6 equiv), \text{BTTP} (0.27 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (8-12% EtOAc/hexanes), followed by another flash chromatography (5-10% acetone/pentane) provided the title compound (57 mg, 71% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44-7.34 (m, 2H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.70 (td, $J = 7.6$, 1.0 Hz, 1H), 5.03 (s, 1H), 4.04-3.90 (m, 2H), 3.38 (td, $J = 11.9$, 2.0 Hz, 2H), 1.95 (s, 6H), 1.72 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.53 (ddd, $J = 12.9$, 4.1, 2.0 Hz, 2H), 1.36-1.29 (m, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 149.24, 133.99, 132.87, 117.98, 117.17, 112.43, 96.17, 67.85, 50.47, 48.36, 40.61, 34.37, 29.61.

IR (film) $\nu_{\text{max}}$ 3340, 2970, 2915, 2219, 1605, 1578, 1462, 1246, 1086, 761 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{20}$NaN$_2$O ([M+Na]$^+$) 291.1468, found 291.1464.
1,1-Diphenyl-N-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)methanimine (58)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), diphenylmethanimine (54 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (0-3% EtOAc/hexanes, containing 2% Et$_3$N) provided the title compound (80 mg, 80% yield) as a white solid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.63-7.56 (m, 2H), 7.41 (dd, $J = 5.0$, 1.7 Hz, 3H), 7.38-7.33 (m, 1H), 7.30 (dd, $J = 8.2$, 6.7 Hz, 2H), 7.18-7.12 (m, 2H), 3.96-3.85 (m, 2H), 3.33-3.12 (m, 2H), 1.55 (s, 6H), 1.54-1.49 (m, 1H), 1.37 (ddd, $J = 13.0$, 3.9, 1.9 Hz, 2H), 1.16 (ddd, $J = 13.3$, 12.0, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.54, 139.84, 138.00, 130.25, 128.40, 128.31, 128.29, 128.13, 128.01, 67.89, 54.75, 52.36, 41.07, 34.58, 29.46.

IR (film) $\nu_{\text{max}}$ 2960, 2906, 1622, 1444, 1237, 1089, 777, 695 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{23}$H$_{26}$NO ([M+H]$^+$) 332.2009, found 332.2014.
4-Bromo-N-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)benzenesulphonamide (59)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 4-bromobenzenesulphonamide (71 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-20% acetone/pentane) provided the title compound (56 mg, 48% yield) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.74 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 5.30 (s, 1H), 3.93 (ddt, $J = 11.6$, 4.6, 1.1 Hz, 2H), 3.30 (td, $J = 12.0$, 2.1 Hz, 2H), 1.68 (s, 6H), 1.58 (dd, $J = 11.9$, 3.8 Hz, 1H), 1.44-1.35 (m, 2H), 1.18 (dtd, $J = 13.3$, 12.1, 4.6 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 140.53, 132.35, 128.84, 127.62, 67.69, 50.74, 45.67, 40.19, 34.09, 29.46.

IR (film) $\nu_{\text{max}}$ 3261, 2970, 2847, 1575, 1331, 1248, 1160, 1090, 1011, 739 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{20}$BrNaNO$_3$S ([M+Na]$^+$) 408.0240, found 408.0245.
4-Chloro-N-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)benzenesulfonamide (60)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 4-chlorobenzenesulfonamide (57 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(tetrahydro-2H-pyran-4-carboxylate) (303 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-20% acetone/pentane) provided the title compound (51 mg, 50% yield) as a colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H), 5.49 (s, 1H), 3.96-3.86 (m, 2H), 3.30 (td, $J = 12.0$, 2.1 Hz, 2H), 1.67 (s, 6H), 1.59 (tt, $J = 11.9$, 3.9 Hz, 1H), 1.39 (ddd, $J = 13.0$, 4.2, 2.0 Hz, 2H), 1.17 (dtd, $J = 13.5$, 12.0, 4.6 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 139.95, 139.21, 129.41, 128.77, 67.71, 50.77, 45.73, 40.22, 34.12, 29.48.

IR (film) $\nu_{\text{max}}$ 3263, 2971, 2914, 1478, 1391, 1331, 1247, 1160, 1087, 753 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{16}$H$_{20}$ClNaNO$_3$S ([M+Na]$^+$) 364.0745, found 364.0757.
Methyl 2-(3-(diethoxyphosphoryl)bicyclo[1.1.1]pentan-1-yl)-2-methylpropanoate (61)

Prepared following a modified version of procedure (A) outlined above using Ir(ppy)$_3$ (4.6 mg, 7.0 µmol, 0.02 equiv), diethyl phosphite (45 mg, 0.35 mmol, 1.0 equiv), methyl 2-bromoisobutyrate (91 µL, 0.70 mmol, 2.0 equiv), Cu(TMHD)$_2$ (90 mg, 0.21 mmol, 0.60 equiv), BTMG (0.22 mL, 1.05 mmol, 3.0 equiv), propellane (1.04 M in Et$_2$O, 0.50 mL, 0.4553 mmol, 1.5 equiv), and 1,4-dioxane (9.8 mL). Purification by flash chromatography (20-100% EtOAc/hexanes) provided the title compound (71 mg, 67% yield) as yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) δ 4.14-4.03 (m, 4H), 3.66 (s, 3H), 1.93 (s, 6H), 1.31 (t, $J$ = 7.1 Hz, 6H), 1.11 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.05, 61.91 (d, $J$ = 6.4 Hz), 51.80, 48.87 (d, $J$ = 2.5 Hz), 48.59, 42.70 (d, $J$ = 24.3 Hz), 29.99 (d, $J$ = 162.4 Hz), 21.52 (d, $J$ = 1.1 Hz), 16.72 (d, $J$ = 5.8 Hz).

$^{31}$P NMR (121 MHz, CDCl$_3$) δ 19.96.

IR (film) $\nu_{\text{max}}$ 2981, 1731, 1470, 1271, 1253, 1153, 1056, 1024, 961 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{14}$H$_{26}$PO$_5$ ([M+H]$^+$) 305.1512, found 305.1512.
Methyl 2-(3-((4-methoxyphenyl)thio)bicyclo[1.1.1]pentan-1-yl)-2-methylpropanoate (62)

Prepared following a modified version of procedure (A) outlined above using Ir(ppy)$_3$ (4.6 mg, 7.0 µmol, 0.02 equiv), $p$-methoxythiophenol (43 µL, 0.35 mmol, 1.0 equiv), methyl 2-bromo-isobutryrate (91 µL, 0.70 mmol, 2.0 equiv), Cu(acac)$_2$ (55 mg, 0.21 mmol, 0.60 equiv), BTMG (0.22 mL, 1.05 mmol, 3.0 equiv), propellane (1.05 M in Et$_2$O, 0.50 mL, 0.53 mmol, 1.5 equiv), and 1,4-dioxane (9.8 mL). Following the reaction, mesitylene was added as an internal standard and the yield was determined using a calibrated UPLC trace (50% yield). The compound could be purified via multiple rounds of chromatography and was isolated as a clear oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H), 3.62 (s, 3H), 1.72 (s, 6H), 1.08 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 176.27, 159.79, 136.26, 124.19, 114.49, 55.43, 51.73, 51.50, 45.80, 42.51, 40.96, 22.05.

IR (film) $\nu_{max}$ 2977, 1731, 1592, 1493, 1245, 1200, 1150, 1032, 830 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{17}$H$_{23}$SO$_3$ ([M+H]$^+$) 307.1362, found 307.1364.
Methyl 2-methyl-2-(3-(tritylthio)bicyclo[1.1.1]pentan-1-yl)propanoate (63)

Prepared following a modified version of procedure (A) outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), triphenylmethanethiol (83 mg, 0.30 mmol, 1.0 equiv), methyl 2-bromoisobutyrate (78 µL, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.60 equiv), BTMG (0.19 mL, 0.90 mmol, 3.0 equiv), propellane (1.05 M in Et$_2$O, 0.43 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). Following the reaction, mesitylene was added as an internal standard and the yield was determined using a calibrated UPLC trace (33% yield). This compound could not be purified. $^1$H- and $^{13}$C-NMR spectra of semi-pure material are shown below in the spectral data. We were able to confirm the product structure from these spectra as well as high-resolution mass spectrometry.

HRMS (ESI-TOF) m/z calcd. for C$_{29}$H$_{30}$SO$_2$Na ([M+Na]$^+$) 365.1859, found 365.1862.

8.3 Drug and Natural Product Scope

(4aR,6aS,6bR,10S,12aS,14bR)-2-(3-(6-Bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2H)-one (64)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv),
iodomesitylene diglycyrrhetinlate (711 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-20% acetone/pentane) provided the title compound (107 mg, 52% yield, d.r. = 1.6:1) as a yellow solid.

(Mixture of diastereoisomers) $^1$H NMR (500 MHz, CDCl$_3$) δ 8.49 (s, 1H), 7.92 (s, 1H), 7.29-7.27 (m, 1H), 6.68-6.66 (m, 1H), 5.63 (brs, 0.59H), 5.61 (brs, 0.36H), 3.25-3.20 (m, 1H), 2.81-2.76 (m, 1H), 2.36-2.28 (m, 6H), 2.18 (s, 1.96H), 2.16 (s, 1.20H), 2.06-2.00 (m, 2H), 1.87-1.81 (m, 2H), 1.70-1.64 (m, 3H), 1.55-1.38 (m, 9H), 1.14 (s, 6H), 1.01 (s, 3H), 0.95-0.93 (m, 3H), 0.91-0.87 (m, 3H), 0.81 (s, 3H), 0.71-0.68 (m, 1H).

(Mixture of diastereoisomers) $^{13}$C NMR (125 MHz, CDCl$_3$) δ 200.36, 200.32, 169.88, 169.77, 145.81, 144.06, 130.41, 130.34, 129.47, 128.55, 120.50, 120.45, 112.88, 112.83, 103.02, 102.92, 78.86, 61.97, 61.93, 55.08, 52.11, 49.33, 48.82, 47.76, 46.96, 45.75, 45.55, 45.48, 43.63, 43.47, 43.29, 41.56, 39.42, 39.27, 39.24, 37.23, 36.88, 35.87, 32.93, 32.88, 32.54, 32.28, 32.17, 32.13, 30.68, 28.84, 28.59, 28.50, 28.23, 27.43, 27.31, 26.47, 26.39, 23.66, 23.30, 18.87, 18.85, 18.80, 18.54, 17.61, 16.55, 16.52, 15.73.

IR (film) $\nu_{max}$ 3398, 2925, 2869, 1653, 1416, 1207, 908, 730 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{41}$H$_{50}$BrN$_2$O$_2$ ([M+H]$^+$) 687.3520, found 687.3512.
(3S,6aR,6bS,8aS,12aR,14bR)-8a-(3-(6-Bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)-4,4,6a,6b,11,11,14b-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12a,14,14a,14b-icosahydropicen-3-ol (65)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodositylene dioleanolate (694 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-30% EtOAc/hexanes), followed by preparative TLC (25% acetone/pentane) provided the title compound (78 mg, 39% yield, d.r. > 20:1) as a pale yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 (s, 1H), 7.97 (s, 1H), 7.31 (d, $J$ = 3.3 Hz, 1H), 6.71 (d, $J$ = 3.1 Hz, 1H), 5.32 (brs, 1H), 3.22 (dd, $J$ = 11.1, 4.9 Hz, 1H), 2.30 (s, 6H), 2.29-2.27 (m, 1H), 1.95-1.70 (m, 7H), 1.68-1.50 (m, 11H), 1.41-1.34 (m, 2H), 1.21 (s, 3H), 1.12-1.07 (m, 1H), 1.00 (s, 3H), 0.96 (s, 3H), 0.94 (s, 3H), 0.90 (s, 6H), 0.79 (s, 3H), 0.75-0.72 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.74, 144.24, 143.87, 143.54, 129.51, 122.20, 120.62, 112.72, 102.67, 79.11, 55.32, 52.26, 48.73, 48.25, 47.82, 45.75, 42.41, 42.29, 40.17, 39.00, 38.93, 37.03, 34.41, 33.57, 33.20, 32.51, 32.27, 30.89, 28.25, 27.39, 26.86, 26.71, 25.01, 24.74, 23.79, 18.45, 17.93, 16.00, 15.79.

IR (film) $v_{\text{max}}$ 3382, 2930, 1461, 1417, 1284, 908, 732 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{41}$H$_{58}$BrN$_2$O ([M+H]$^+$) 673.3727, found 673.3710.
6-Bromo-1-(3-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (66)

Prepared following the general procedure outlined above using Ir(ppy)_3 (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene digemfibrozilate (488 mg, 0.60 mmol, 2.0 equiv), Cu(acac)_2 (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et_2O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (10-15% EtOAc/hexanes) provided the title compound (98 mg, 70% yield) as a pale yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 1H), 7.93 (s, 1H), 7.28 (d, J = 3.3 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.70-6.62 (m, 3H), 3.96 (t, J = 6.3 Hz, 2H), 2.32 (s, 3H), 2.22 (s, 6H), 2.20 (s, 3H), 1.86-1.77 (m, 2H), 1.52-1.44 (m, 2H), 0.98 (s, 6H).

^13C NMR (125 MHz, CDCl_3) δ 157.09, 145.81, 143.95, 136.66, 130.48, 129.56, 123.64, 120.86, 120.59, 112.80, 112.10, 102.83, 68.47, 50.17, 48.80, 45.52, 35.63, 31.41, 24.86, 23.54, 21.57, 16.00.

IR (film) v_max 2960, 2873, 1509, 1415, 1265, 1130, 906, 782 cm^{-1}.

HRMS (ESI-TOF) m/z calcd. for C_{26}H_{32}BrN_2O ([M+H]^+) 467.1693, found 467.1697.
2-(3-(1-Oxoisindolin-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoic acid (S1)

Prepared following the general procedure outlined above using Ir(ppy)₃ (3.9 mg, 6.0 µmol, 0.02 equiv), isoindolin-1-one (40 mg, 0.30 mmol, 1.0 equiv), methyl 2-bromopropionate (100 mg, 0.60 mmol, 2.0 equiv), Cu(II) bis-(2-isobutyrylcyclohexanone) (72 mg, 0.18 mmol, 0.6 equiv), BTTP (0.18 mL, 0.60 mmol, 2.0 equiv), propellane (0.8 M in Et₂O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (20-25% EtOAc/hexanes) provided the title compound (77 mg, 90% yield) as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.44-7.35 (m, 2H), 4.31 (s, 2H), 3.67 (s, 3H), 2.73 (q, J = 7.0 Hz, 1H), 2.15 (s, 6H), 1.14 (d, J = 7.1 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 174.57, 168.60, 140.81, 133.38, 131.42, 128.09, 123.62, 122.77, 51.73, 51.60, 48.65, 47.33, 39.50, 38.61, 13.97.

IR (film) νₘₚₙ 3495, 2977, 2877, 1732, 1685, 1400, 1262, 1199, 855, 734 cm⁻¹.

HRMS (ESI-TOF) m/z calcd. for C₁₇H₂₀NO₃ ([M+H]⁺) 286.1438, found 286.1444.
2-(3-(1-Oxoisindolin-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoic acid (67)

To a solution of the ester S1 (77 mg, 0.27 mmol, 1.0 equiv.) in a mixture of 1,4-dioxane (1.5 mL) and water (1.0 mL) was added NaOH (28 mg, 0.70 mmol, 2.6 equiv.) in water (0.5 mL). The resulting mixture was stirred overnight, then acidified to pH 3.0 (with aqueous 1.0 M HCl solution), extracted with CH₂Cl₂ for three times, and washed with brine. The combined organic layers were dried (Na₂SO₄), filtered, and concentrated in vacuo to provide the title compound (69 mg, 95% yield) as a white solid.

**¹H NMR (500 MHz, CDCl₃)** δ 7.81 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.47-7.39 (m, 2H), 4.36 (s, 2H), 2.80 (q, J = 7.0 Hz, 1H), 2.23 (s, 6H), 1.20 (d, J = 7.0 Hz, 3H).

**¹³C NMR (125 MHz, CDCl₃)** δ 178.90, 168.96, 140.89, 133.36, 131.61, 128.24, 123.86, 122.82, 51.88, 48.91, 47.42, 39.51, 38.50, 13.96.

**IR (film)** ν max 2977, 2916, 1732, 1647, 1415, 1262, 1185, 740 cm⁻¹.

**HRMS (ESI-TOF)** m/z calcd. for C₁₆H₁₇NaNO₃ ([M+Na]⁺) 294.1101, found 294.1108.
Gram scale synthesis

**tert-Butyl (3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)carbamate (S2)**

Prepared following the general procedure (B) outlined above using *tert*-butyl carbamate (2.68 g, 22.9 mmol, 2.0 equiv), Cu(acac)$_2$ (900 mg, 3.43 mmol, 0.30 equiv), BTMG (7.3 mL, 34.3 mmol, 3.0 equiv), propellane (1.04 M in Et$_2$O, 11 mL, 11.4 mmol, 1.0 equiv), Togni reagent II (60wt% on celite, 12 g, 23 mmol, 2.0 equiv) and 1,4-dioxane (100 mL). Purification by flash chromatography (0-20% EtOAc/hexanes) provided the title compound (1.9 g, 64% yield) as a white solid.

*Note:* Run for 45 min.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.97 (s, 1H), 2.22 (s, 6H), 1.48 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 154.61, 123.42 (q, $J = 274.0$ Hz), 80.08, 51.36, 45.52 (q, $J = 2.3$ Hz), 34.86 (q, $J = 34.7$ Hz), 28.34.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -71.35.

IR (film) $\nu_{max}$ 3326, 2986, 1687, 1512, 1404, 1279, 1164, 1119, 998 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_6$H$_9$F$_3$N [–Boc Fragmentation] ([M+H]$^+$) 152.0682, found 152.0685.
3-(Trifluoromethyl)bicyclo[1.1.1]pentan-1-amine hydrochloride (68)

Boc-protected amine **S2** (1.6 g, 6.4 mmol) was dissolved in EtOAc (20 mL) and cooled to 0 °C. 16 mL of HCl (4.0 M in Dioxane) was slowly added and the reaction warmed to r.t. Product 68 was directly filtered out and dried under vacuum (1.12 g, 94% yield, white solid).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.19 (s, 3H), 2.25 (s, 6H).

$^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 122.84 (q, $J = 274.4$ Hz), 50.21 (q, $J = 2.1$ Hz), 43.11 (q, $J = 2.2$ Hz), 34.26 (q, $J = 39.3$ Hz).

$^{19}$F NMR (282 MHz, DMSO-$d_6$) $\delta$ -69.69.

Spectroscopic data matches with previously reported data.$^7$
5-Methyl-N-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)isoxazole-4-carboxamide (69)

Compound 68 (10 mg, 0.05 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (0.2 mL) and triethylamine (16.4 µL, 2.2 equiv) was added. 5-Methylisoxazole-4-carbonyl chloride (7.8 mg, 0.05 mmol, 1.0 equiv) was then added and the reaction stirred for one hour. The mixture was then diluted with Et₂O, washed first with 0.1 M HCl, then saturated NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated to give the title compound as a white solid (11.9 mg, 85% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.28 (s, 1H), 6.14 (s, 1H), 2.76 (s, 3H), 2.35 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 173.42, 161.27, 147.45, 123.08 (q, J = 273.7 Hz), 111.17, 51.76 (q, J = 2.2 Hz), 45.63 (q, J = 2.5 Hz), 35.71 (q, J = 39.5 Hz), 12.55.

¹⁹F NMR (282 MHz, CDCl₃) δ -71.36.

IR (film) ν max 3290, 2929, 1646, 1616, 1531, 1401, 1176, 1123, 700 cm⁻¹.

HRMS (ESI-TOF) m/z calcd. for C₁₁H₁₂F₃N₂O₂ ([M+H]+) 261.0845, found 261.0847.
(S)-3-((2-(3-(6-bromo-1H-pyrrolo[3,2-b]pyridin-1-yl)bicyclo[1.1.1]pentan-1-yl)propan-2-yl)hex-5-en-2-one (S3)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis(2-((1R,3R)-3-acetyl-2,2-dimethylcyclobutyl)acetate) (387 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (0.8 M in Et$_2$O, 0.56 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (10.0 mL). Purification by flash chromatography (15-20% EtOAc/hexanes) provided the title compound (91 mg, 76% yield) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J$ = 1.9 Hz, 1H), 7.89 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.25 (d, $J$ = 3.3 Hz, 1H), 6.64 (dd, $J$ = 3.3, 0.7 Hz, 1H), 5.75-5.59 (m, 1H), 5.19-4.90 (m, 2H), 2.68 (dd, $J$ = 11.6, 2.8 Hz, 1H), 2.39 (td, $J$ = 12.6, 11.6, 8.1 Hz, 1H), 2.35-2.30 (m, 1H), 2.27 (s, 6H), 2.17 (s, 3H), 1.04 (s, 3H), 1.01 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 212.40, 145.87, 144.12, 135.79, 130.21, 129.40, 120.30, 117.10, 112.88, 103.05, 58.09, 51.14, 48.63, 44.96, 34.66, 34.59, 33.64, 23.93, 21.05.

IR (film) $\nu_{\text{max}}$ 2972, 1708, 1414, 1248, 1195, 906, 783, 728 cm$^{-1}$.

HRMS (ESI-TOF) m/z calcd. for C$_{21}$H$_{26}$BrN$_2$O ([M+H]$^+$) 401.1223, found 401.1219.
6-bromo-1-(3-(1-(pyrimidin-2-yl)piperidin-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-pyrrolo[3,2-b]pyridine (S4)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 6-bromo-1H-pyrrolo[3,2-b]pyridine (59 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis-1-(pyrimidin-2-yl)piperidine-4-carboxylate (395 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (0.18 mL, 0.90 mmol, 3.0 equiv), propellane (1.05 M in Et$_2$O, 0.43 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.333 equiv) was then added and the yield determined by $^1$H-NMR to be 64%. Purification of this compound proved challenging. Flash chromatography (10% acetone/toluene) enabled isolation of only semi-pure material as a yellow oil, the data for which are reported below.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.47 (brs, 1H), 8.36-8.22 (m, 2H), 7.89 (d, $J = 1.1$ Hz, 1H), 7.25 (d, $J = 3.5$ Hz, 1H), 6.63 (dd, $J = 3.4$, 0.9 Hz, 1H), 6.46 (t, $J = 4.7$ Hz, 1H), 4.86 (dt, $J = 13.3$, 2.4 Hz, 2H), 2.86 (td, $J = 13.0$, 2.6 Hz, 2H), 2.20 (s, 6H), 1.87 (tt, $J = 11.9$, 3.7 Hz, 1H), 1.79-1.69 (m, 2H), 1.25 (qd, $J = 12.6$, 4.3 Hz, 2H).

$^{13}$C NMR (quantitative) (125 MHz, CDCl$_3$) $\delta$ 161.66 (1C), 157.87 (2C), 145.90 (1C), 144.09 (1C), 130.31 (1C), 129.46 (1C), 120.40 (1C), 112.86 (1C), 109.62 (1C), 102.93 (1C), 51.16 (3C), 49.50 (1C), 43.79 (2C), 40.17 (1C), 35.56 (1C), 28.78 (2C).

MS (ESI-Quad) 424.1, 426.1 (1:1).
1-(3-(tetrahydro-2H-pyran-4-yl)bicyclo[1.1.1]pentan-1-yl)-1H-indazole-3-carboxamide (S5)

Prepared following the general procedure outlined above using Ir(ppy)$_3$ (3.9 mg, 6.0 µmol, 0.02 equiv), 1H-indazole-3-carboxamide (48 mg, 0.30 mmol, 1.0 equiv), iodomesitylene bis-tetrahydro-2H-pyran-4-carboxylate (310 mg, 0.60 mmol, 2.0 equiv), Cu(acac)$_2$ (47 mg, 0.18 mmol, 0.6 equiv), BTMG (64 µL, 0.30 mmol, 1.0 equiv), propellane (1.05 M in Et$_2$O, 0.43 mL, 0.45 mmol, 1.5 equiv), and 1,4-dioxane (8.4 mL). 1, 3, 5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.333 equiv) was then added and the yield determined by $^1$H-NMR to be 60%. Purification by reversed-phase chromatography (10-100% MeCN/H$_2$O) followed by preparative TLC (20% acetone/toluene) enabled isolation of a portion of the product as a white solid to confirm the regiochemical outcome. The data below are consistent with functionalization of the indazole, as previously observed.$^4$ Only one regioisomer was observed by UHPLC-MS analysis of the reaction mixture.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J = 8.2$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.40 (t, $J = 7.7$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 6.92 (s, 1H), 5.51 (s, 1H), 4.04 (dd, $J = 11.2$, 4.4 Hz, 2H), 3.42 (td, $J = 11.8$, 2.0 Hz, 2H), 2.32 (s, 6H), 1.86 (tt, $J = 11.8$, 3.9 Hz, 1H), 1.65-1.57 (m, 2H), 1.40 (qd, $J = 12.4$, 4.5 Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.62, 140.78, 137.11, 126.95, 123.42, 123.04, 122.93, 110.45, 67.81, 51.38, 51.23, 40.49, 34.24, 29.62.

IR (film) $\nu_{\text{max}}$ 3471, 3294, 2916, 1673, 1593, 1480, 1227, 1088, 893, 731 cm$^{-1}$.

HRMS (EI-TOF) m/z calcd. for C$_{18}$H$_{21}$N$_3$O$_2$ ([M-e$^{-}\cdot$]) 311.16338, found 311.16283.
9) Additional Examples

As shown in the above reaction, gem-dimethylcyclobutyl acetic acid was employed in the three-component coupling. The only observed coupled product is the ring-opening product\(^8\), which is consistent with the proposition that a primary alkyl radical was generated in the reaction.

Compound S4 was prepared following the general procedure outlined above.

Compound S5 was prepared following the general procedure outlined above, and only indazole functionalization was observed.
These reactions were performed on 0.05 mmol scale following the general procedure outlined above and the yields were determined by $^{19}$F NMR with an internal standard (1,4-difluorobenzene).

**Effect of alkynes on reaction outcome:**

| alkyne added            | yield |
|-------------------------|-------|
| none                    | 76%   |
| C≡CCl, 4 equiv          | 50%   |
| TMS—Me, 4 equiv         | 72%   |
| Et—Et, 4 equiv          | 71%   |

While internal alkynes are well-tolerated, terminal alkynes do suppress the yield somewhat. Alkenes do not impact reaction efficiency.
10) Metabolism Assays

10.1 Experimental Procedure

Pooled human liver microsomes (BD Ultrapool; pooled male and female), pooled rat liver microsomes (male Sprague Dawley rats), pooled mouse liver microsomes (male CD mice), dog liver microsomes (male beagle), monkey liver microsomes (male cyno) and guinea pig liver microsomes (male Dunkin Hartley) are purchased from a reputable commercial supplier. Microsomes are stored at –80 °C prior to use. Microsomes should be thawed and kept on ice no longer than 30 min prior to initiation of incubation. Pre-incubation times should be kept to a minimum and no longer than 5 min before initiation of reaction.

Microsomes (final protein concentration 0.5 mg/mL), 0.1 M phosphate buffer pH 7.4 containing 1 mM MgCl₂ and test compound (final substrate concentration 1 µM; final DMSO concentration 0.05 %) are pre-incubated at 37 °C prior to the addition of NADPH (final concentration 1 mM) to initiate the reaction. The final incubation volume is 500 µL. Three species specific control compounds are included with each species (as defined by the Janssen guidance document). All incubations are performed singularly for each test compound.

At 6 time points (0, 5, 10, 20, 40 and 60 min) reactions are stopped by the removal of 50 µL of the incubation mixture into methanol. The incubation plates are centrifuged at 2,500 rpm for 20 min at 4 °C to precipitate the protein.

10.2 Quantitative Analysis

Following protein precipitation, the sample supernatants are combined in cassettes of up to 8 compounds and analysed using Cyprotex standard LC-MS/MS conditions.

10.3 Data Analysis

From a plot of ln peak area ratio (compound peak area/internal standard peak area) against time, the gradient of the line is determined. Subsequently, half-life, intrinsic clearance, hepatic clearance (ClH) are calculated using the equations & parameters outlined in the Janssen guidance document.
Three control compounds per species are included in the assay and if the values for these compounds are not within the specified limits the results are rejected and the experiment repeated.
II) Cyclic Voltammetry Data

Cyclic voltammetry was performed on a CH Instruments Electrochemical Analyzer (CHI600E). A 0.005 M CH$_3$CN solution of the iodomesitylene dicyclohexanecarboxylate was prepared with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and the solution was sparged with N$_2$ for 15 minutes. The cyclic voltammogram was obtained using a glassy carbon working electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). Data was collected with a scan rate of 0.1 V/s.

![iodomesitylene dicarboxylate](image)

**Figure S14** Cyclic voltammogram of the THP iodonium dicarboxylate shows an irreversible reduction event at $-0.82$ V vs. SCE in CH$_3$CN.
12) UV-Vis Experiments

To probe the difference in photocatalytic reactivity between different classes of substrates, such as azaindoles and amides, relevant UV-Vis spectra of representative compounds and complexes were obtained in dioxane at the following concentrations for each component: N-nucleophiles (0.01M), organic base [either BTMG or BTTP] (0.03M), copper(II) diketonate complex (0.006M), iodonium dicarboxylate (0.02M). Four sets of overlaid UV-Vis spectra are shown below in figures S15-S18, along with the components present in the mixture. To obtain this data, the “initial mixtures/solutions” were prepared by measuring the necessary components into glass cuvettes, then degassing the samples via nitrogen bubbling for 5 minutes. Initial UV-Vis spectra were then measured for each of the four systems. Next, iodonium dicarboxylate was added to each cuvette, and new UV-Vis spectra obtained. A final spectrum was obtained for each sample after allowing them to age for a period of five minutes. The UV-Vis spectrum of the iodonium dicarboxylate was obtained separately at the same concentration and is shown in each set of overlaid spectra below.

Figure S15: Spectra of Cu/azaindole complex before and after iodonium dicarboxylate
**Figure S16:** Spectra of Cu/amide complex before and after iodonium dicarboxylate addition
Figure S17: Spectra of azaindole/BTMG before and after iodonium dicarboxylate addition
Figure S18: Spectra of Cu(acac)$_2$ before and after iodonium dicarboxylate addition

Discussion

As can be seen in figure S15, subtle changes in the UV-Vis spectrum occur after addition of iodonium dicarboxylate to the copper azaindole complex. Similar changes are not seen either in the case of the analogous copper amide complex formed under the reaction conditions (Fig S16) or in the case Cu(acac)$_2$ alone (S18). Furthermore, substantial changes in the spectrum of azaindole/BTMG are observed after addition of the iodonium dicarboxylate (S17). This evidence supports the formation of a new photoactive species in the case of azaindole which is not formed with the amide substrate. It is therefore possible that this new species is responsible for initiating a successful three-component coupling when using azaindole even without photocatalyst, while the amide substrate, which does not appear to form a similar species, does require photocatalyst to achieve sufficient reactivity.
13) References

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14) Spectral Data
13 - $^1$H NMR (300 MHz, CDCl$_3$)

13 - $^{13}$C NMR (125 MHz, Acetone-$_d$_6)
1H NMR (500 MHz, CDCl3)

13C NMR (125 MHz, CDCl3)
17. $^1$H NMR (500 MHz, CDCl$_3$)

18. $^{13}$C NMR (125 MHz, CDCl$_3$)
$^{17}$F NMR (310 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
(S)-2H NMR (500 MHz, CDCl₃)

(S)-13C NMR (125 MHz, CDCl₃)
21. ¹H NMR (500 MHz, CDCl₃)

22. ¹³C NMR (125 MHz, CDCl₃)
23. $^1$H NMR (500 MHz, CDCl$_3$)

24. $^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
25 - $^1$H NMR (300 MHz, CDCl$_3$)

26 - $^{13}$C NMR (125 MHz, CDCl$_3$)
24 - $^1$H NMR (500 MHz, CDCl$_3$)

25 - $^{13}$C NMR (125 MHz, CDCl$_3$)
29. $^1$H NMR (300 MHz, CDCl$_3$)

29. $^{13}$C NMR (125 MHz, CDCl$_3$)
**33 derivative: 1H NMR (500 MHz, CD3OD)**

- 8.39
- 8.20
- 6.61
- 3.31
- 2.55

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**33 derivative: 13C NMR (125 MHz, CD3OD)**

- 169.41
- 146.49
- 132.75
- 120.97
- 115.30
- 113.70
- 103.14
- 53.75
- 37.55
33 derivative - $^1$H NMR (376 MHz, CD$_3$OD)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)

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39. $^1$H NMR (500 MHz, CDCl$_3$)

39. $^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (300 MHz, CDCl₃)

$^{13}C$ NMR (125 MHz, CDCl₃)
43. $^1$H NMR (500 MHz, CDCl$_3$)

43. $^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, DMSO-$_d_6$)

$^{13}$C NMR (125 MHz, DMSO-$_d_6$)
49. $^1$H NMR (500 MHz, CDCl$_3$)

49. $^{13}$C NMR (125 MHz, CDCl$_3$)
54. 1H NMR (500 MHz, CDCl₃)

54. 13C NMR (125 MHz, CDCl₃)
$^3$H NMR (300 MHz, CDCl$_3$)
$^7$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (125 MHz, CDCl₃)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (121 MHz, CDCl$_3$)

$^6^1$
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\[ \text{H NMR (500 MHz, CDCl}_3) \]

\[ \text{C NMR (125 MHz, CDCl}_3) \]
63. $^1$H NMR (500 MHz, CDCl$_3$)

64. $^{13}$C NMR (125 MHz, CDCl$_3$)
mixture of diastereomers, d.r. = 1:6:1

$^1$H NMR (590 MHz, CDCl$_3$)

mixture of diastereomers, d.r. = 1:6:1

$^1$C NMR (121 MHz, CDCl$_3$)
85 - $^1$H NMR (100 MHz, CDCl$_3$)

85 - $^{13}$C NMR (125 MHz, CDCl$_3$)
66. $^1$H NMR (500 MHz, CDCl$_3$)

68. $^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)

For the full description, please refer to the original document.
$^7$Li NMR (3% Me$_6$Si, CDCl$_3$)
$^3$H NMR (300 MHz, CDCl$_3$)

$^1$H NMR (125 MHz, CDCl$_3$)
$^{77}$Se NMR (392 MHz, CDCl$_3$)
$^{1}H$-NMR (500 MHz, CDCl$_3$)

$^{13}C$-NMR (125 MHz, CDCl$_3$)
SS \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3})

SS \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3})