Palladium(0)-Catalyzed Cyclopropane C-H Bond Functionalization: Synthesis of Quinoline and Tetrahydroquinoline Derivatives

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General Considerations

Reactions were set-up on the bench top and carried out under an argon atmosphere unless otherwise noted. HPLC Grade THF and toluene were dried and purified via solvent purification system. DCE was purchased from Aldrich in Sure-Seal bottles and used without further purification. Mesitylene was purchased from Aldrich, stored over molecular sieves and used without further purification. Pd(OAc)$_2$, PCy$_3$·HBF$_4$, PtBu$_2$Me·HBF$_4$, Cs$_2$CO$_3$ and CsOPiv were stored in a dessicator and were weighed to air. K$_3$PO$_4$, NaOtBu and KOrBu were stored in a glovebox and small quantities were removed prior to their use. Cyclopropylamine was distilled and stored under argon. All other reagents and solvents were used without further purification.

New compounds (starting materials and products) were characterized by $^1$H NMR and $^{13}$C NMR using 300 MHz or 400 MHz spectrometers. Copies of the $^1$H and $^{13}$C spectra can be found at the end of the supporting information. Spectra were calibrated according to residual solvent peaks (CDCl$_3$). $^{13}$C NMR spectra were obtained with $^1$H decoupling. For most starting materials, spectra were obtained at 55 °C (due to rotamers). IR spectra, melting point (when applicable) and, in most cases, HRMS were also obtained.

Synthesis and Characterization of Cyclopropylaniline Starting Materials

General Procedure A for the Preparation of $N$-Cyclopropylbenzenamines

\[
\begin{array}{c}
\text{R} \quad \text{X} \\
\text{NH}_2 \\
\end{array} \quad \xrightarrow{\text{EtO, OTMS}} \quad \xrightarrow{\text{1. AcOH, MeOH}} \quad \text{R} \quad \overset{\text{2. NaBH}_4, \text{BF}_3\cdot\text{OEt}_2, \text{THF}}{\text{X}} \\
\]

**Step 1.** To a solution of the desired 2-haloaniline (1.00 equiv) in AcOH (3.00 equiv) and MeOH (1.5M) at room temperature under argon was added (1-ethoxycyclopropoxy)trimethylsilane (1.20 equiv) dropwise. The mixture was stirred at reflux for 24 h then concentrated under reduced pressure.

**Step 2.** To a solution of NaBH$_4$ (2.00 equiv) in THF (0.50 M) at 0 °C was added BF$_3$·OEt$_2$ (2.00 equiv) dropwise. The resulting mixture was stirred for 1 h after which time the crude concentrated mixture from Step 1 was added dropwise as a solution in a minimal amount of THF. The solution was brought to room temperature and then stirred at reflux for 24 h. The reaction was quenched by the slow addition of H$_2$O and the crude product was extracted with Et$_2$O (x3), washed with brine, dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.
General Procedure B for the Preparation of N-Cyclopropylbenzenamines

![Chemical structure](image)

To a solution of the desired 1-bromo-2-fluoroarene (1.00 equiv) and K$_2$CO$_3$ (1.10 equiv) in DMSO (0.45 M) was added cyclopropylamine (3.00 equiv). The resulting mixture was heated at 55 °C for 16 h. The crude product was extracted with Et$_2$O (x3), washed with brine, dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure C for the Preparation of N-Cyclopropylbenzenamines

![Chemical structure](image)

Prepared according to a literature procedure.$^1$ A solution of Cu(OAc)$_2$ (1.00 equiv) and bipyridine (1.00 equiv) in DCE (0.12 M) at 70 °C was added to a room temperature suspension of the desired 2-haloaniline (1.00 equiv), cyclopropylboronic acid (2.00 equiv) and Na$_2$CO$_3$ (2.00 equiv) in DCE (0.6 M). The mixture was heated at 70 °C until the reaction was judged to be complete by TLC (1-4 hours). After cooling to room temperature, an aqueous solution of NH$_4$OH (25%) was added. The organic layer was separated and the aqueous layer was extracted with DCM (x3). The combined organic layers were washed with brine, dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

General Procedure for the Protection of N-Cyclopropylbenzenamines

![Chemical structure](image)

A solution of N-cyclopropylbenzenamine (1.00 equiv) in the desired chloroformate (0.4 M) was heated at 70 °C for 2.5 to 24 h (until judged complete by TLC). The reaction was slowly poured over H$_2$O and the crude product was extracted with CHCl$_3$ (x3), dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.
2-Bromo-N-cyclopropylbenzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-bromoaniline (3.44 g, 20.0 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 2.49 g (59% yield) of an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.41 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.21 (ddd, $J = 8.1$, 7.3, 1.4 Hz, 1H), 7.07 (ddd, $J = 8.1$, 1.5 Hz, 1H), 6.61 (ddd, $J = 7.6$, 7.6, 1.5 Hz, 1H), 4.73 (br s, 1H), 2.45 (tt, $J = 6.7$, 3.4 Hz, 1H), 0.85-0.73 (m, 2H), 0.64-0.53 (m, 2H).

Methyl 2-bromophenylcyclopropylcarbamate (1a) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropylbenzenamine (1.27 g, 5.97 mmol, 1.00 equiv) and methyl chloroformate (15 mL, 0.40 M). The product was purified by silica gel flash chromatography (20% Et$_2$O in petroleum ether) to afford 1.42 g (88% yield) of a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.61 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.31 (ddd, $J = 7.6$, 7.6, 1.5 Hz, 1H), 7.16 (ddd, $J = 7.9$, 7.5, 1.7 Hz, 1H), 7.11 (br d, $J = 7.7$ Hz, 1H), 3.65 (br s, 3H), 3.15-3.09 (m, 1H), 0.74 (d, $J = 5.8$ Hz, 2H), 0.63-0.58 (m, 2H).

R$_f$ 0.23 (20% Et$_2$O in petroleum ether).

2-Bromo-N-cyclopropyl-5-methylbenzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-bromo-5-methylaniline (0.67 mL, 5.4 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 963 mg (66% yield) of an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293 K, TMS) $\delta$ 7.27 (d, $J = 8.0$ Hz, 1H), 6.88 (dd, $J = 2.1$, 0.5 Hz, 1H), 6.44 (ddd, $J = 8.0$, 2.1, 0.6 Hz, 1H), 4.66 (br s, 1H), 2.43 (tt, $J = 6.7$, 3.4 Hz, 1H), 2.31 (s, 3H), 0.85-0.72 (m, 2H), 0.64-0.52 (m, 2H).

R$_f$ 0.23 (20% Et$_2$O in petroleum ether).
Methyl 2-bromo-5-methylphenylcyclopropylcarbamate (1b) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-5-methylbenzenamine (300 mg, 1.33 mmol, 1.00 equiv) and methyl chloroformate (3.3 mL, 0.40 M). The product was purified by silica gel flash chromatography (25% Et₂O in petroleum ether) to afford 291 mg (77% yield) of a clear oil.

¹H NMR (300 MHz, CDCl₃, 328K, TMS) δ 7.46 (d, J = 8.1 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.93 (s, 1H), 3.70 (s, 3H), 3.15-3.08 (m, 1H), 2.31 (s, 3H), 0.75-0.71 (m, 2H), 0.65-0.58 (m, 2H).

¹³C NMR (75 MHz, CDCl₃, 328K, TMS) δ 156.7, 140.7, 138.4, 132.9, 131.0, 129.7, 120.7, 53.0, 31.3, 20.9, 7.6.

HRMS Calculated for C₁₁H₁₁NOBr (M⁺ - OCH₃) 252.0024, Found 252.0027.

IR (ν max/cm⁻¹) 3410, 3008, 2972, 2921, 1598, 1502, 1305, 1017 cm⁻¹. Rf 0.60 (100% petroleum ether).

Benzyl 2-bromo-5-methylphenylcyclopropylcarbamate (1b‘) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-5-methylbenzenamine (300 mg, 1.33 mmol, 1.00 equiv) and benzyl chloroformate (3.3 mL, 0.40 M). The product was purified by silica gel flash chromatography (60% CH₂Cl₂ in petroleum ether) to afford 323 mg (68% yield) of a yellow oil.

¹H NMR (300 MHz, CDCl₃, 328K, TMS) δ 7.47 (d, J = 8.0 Hz, 1H), 7.32-7.23 (m, 5H), 6.98-6.93 (m, 2H), 5.18 (s, 2H), 3.20-3.12 (m, 1H), 2.30 (s, 3H), 0.77-0.61 (m, 4H).

¹³C NMR (75 MHz, CDCl₃, 328K, TMS) δ 156.2, 140.7, 138.4, 137.0, 132.9, 131.0, 129.8, 128.5, 127.9, 127.7, 120.7, 67.5, 31.2, 20.9, 7.7.

HRMS Calculated for C₁₁H₁₁NO₂Br (M⁺ - CH₂C₆H₅) 267.9973, Found 267.9941.

IR (ν max/cm⁻¹) 3014, 2953, 1718, 1442, 1340, 1091, 1021 cm⁻¹. Rf 0.35 (30% Et₂O in petroleum ether).

2-Bromo-5-methoxybenzenamine Prepared according to a modified literature procedure.² To a mixture of concentrated HCl (0.15 M, 17 mL) and glacial acetic acid (0.15 M, 17 mL) at 0 °C was added 1-bromo-4-methoxy-2-nitrobenzene (600 mg, 2.59 mmol, 1.00 equiv). Zinc powder (4.31 g) was then added portionwise over 1h after which point the reaction mixture was stirred for an additional 15 minutes at 0 °C and then quenched by addition of concentrated ammonium hydroxide until slightly
basic. The crude product was extracted with CH\textsubscript{2}Cl\textsubscript{2} (x3), washed with brine, dried with MgSO\textsubscript{4} and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (15% Et\textsubscript{3}O in petroleum ether) to afford 522 mg (80% yield) of a brown oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293K, TMS) \(\delta\) 7.27 (d, \(J \approx 8.8\) Hz, 1H), 6.33 (d, \(J \approx 2.8\) Hz, 1H), 6.23 (dd, \(J \approx 8.8, 2.8\) Hz, 1H), 3.89 (br s, 1H), 3.74 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293K, TMS) \(\delta\) 160.0, 144.8, 132.9, 105.6, 101.3, 100.5, 55.4. HRMS Calculated for C\textsubscript{7}H\textsubscript{8}NOBr (M\textsuperscript{+}) 200.9789, Found 200.9773.

IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3481, 3374, 3006, 2943, 1492, 1301, 1210 cm\textsuperscript{-1}.

R\textsubscript{f} 0.25 (15% Et\textsubscript{2}O in petroleum ether).

2-Bromo-N-cyclopropyl-5-methoxybenzenamine General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-bromo-5-methoxyaniline (400 mg, 1.98 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (3% Et\textsubscript{2}O in petroleum ether) to afford 318 mg (66% yield) of a pale pink oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 293K, TMS) \(\delta\) 7.28 (d, \(J \approx 8.7\) Hz, 1H), 6.64 (d, \(J \approx 2.9\) Hz, 1H), 6.20 (dd, \(J \approx 8.7, 2.9\) Hz, 1H), 4.69 (br s, 1H), 3.80 (s, 3H), 2.43 (tt, \(J \approx 6.7, 3.4\) Hz, 1H), 0.81 - 0.72 (m, 2H), 0.67 - 0.61 (m, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 293K, TMS) \(\delta\) 160.2, 146.6, 132.5, 103.3, 100.6, 99.5, 55.5, 25.2, 7.6. HRMS Calculated for C\textsubscript{9}H\textsubscript{9}NOBr (M\textsuperscript{+} - CH\textsubscript{3}) 227.9847, Found 227.9837.

IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3397, 3091, 2961, 1600, 1215, 1016 cm\textsuperscript{-1}.

R\textsubscript{f} 0.47 (4% Et\textsubscript{2}O in petroleum ether).

Methyl 2-bromo-5-methoxyphenylcyclopropylcarbamate (1c) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-5-methoxybenzenamine (200 mg, 0.826 mmol, 1.00 equiv) and methyl chloroformate (2.1 mL, 0.40 M). The product was purified by silica gel flash chromatography (40% Et\textsubscript{3}O in petroleum ether) to afford 190 mg (77% yield) of a white solid.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 328K, TMS) \(\delta\) 7.47 (d, \(J \approx 8.8\) Hz, 1H), 6.73 (dd, \(J \approx 8.8, 3.0\) Hz, 1H), 6.67 (d, \(J \approx 3.0\) Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.11 (tt, \(J \approx 7.1, 3.7\) Hz, 1H), 0.76-0.72 (m, 2H), 0.67-0.61 (m, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, 328K, TMS) \(\delta\) 159.7, 156.7, 141.8, 133.4, 116.4, 114.8, 114.7, 55.8, 53.1, 31.3, 7.7. HRMS Calculated for C\textsubscript{12}H\textsubscript{14}NO\textsubscript{3}Br (M\textsuperscript{+}) 301.0114, Found 301.0137.

IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3012, 2954, 2838, 1718, 1593, 1340, 1230 cm\textsuperscript{-1}.

R\textsubscript{f} 0.18 (30% Et\textsubscript{3}O in petroleum ether).

Melting point 64-66 °C
2-Bromo-N-cyclopropyl-5-(trifluoromethyl)benzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-bromo-5-(trifluoromethyl)aniline (0.60 mL, 4.2 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 710 mg (61% yield) of a clear oil.

\[ \delta 7.49 \ (dd, J = 8.2, 0.7 \text{ Hz}, 1H), 7.24 \ (d, J = 2.0 \text{ Hz}, 1H), 6.85 - 6.82 \ (m, 1H), 4.90 \ (br \ s, 1H), 2.51 - 2.45 \ (m, 1H), 0.88 - 0.79 \ (m, 2H), 0.62 - 0.58 \ (m, 2H). \]

\[ \text{IR (}\nu_{\text{max}}/\text{cm}^{-1}\text{)} 3419, 3096, 3010, 2978, 1600, 1437, 1334, 1276, 1128, 1081 \text{ cm}^{-1}. \]

Rf 0.48 (100% petroleum ether).

Methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate (1d)  General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-5-(trifluoromethyl)benzenamine (550 mg, 1.96 mmol, 1.0 equiv) and methyl chloroformate (5.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (15% Et₂O in petroleum ether) to afford 575 mg (87% yield) of a yellow oil.

\[ \delta 7.75 \ (d, J = 8.2 \text{ Hz}, 1H), 7.41 \ (br \ d, J = 8.3 \text{ Hz}, 1H), 7.39 \ (br \ s, 1H), 3.73 \ (br \ s, 3H), 3.14 \ (tt, J = 7.2, 3.8 \text{ Hz}, 1H), 0.81 - 0.76 \ (m, 2H), 0.62 \ (br \ s, 2H). \]

\[ \text{HRMS Calculated for C}_{11}\text{H}_{8}\text{NOBrF}_3 (M^+) 287.9870, \text{Found} 287.9861. \]

IR (\nu_{\text{max}}/\text{cm}^{-1}) 3419, 3096, 3010, 2978, 1600, 1437, 1334, 1276, 1081, 1016, 822 cm⁻¹. Rf 0.21 (10% Et₂O in petroleum ether).

2-Bromo-N-cyclopropyl-5-fluorobenzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-bromo-5-fluoroaniline (1.00 g, 5.26 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 696 mg (57% yield) of a clear oil.
**Methyl 2-bromo-5-fluorphenylcyclopropylcarbamate (1e)**  
*General procedure for the protection of N-cyclopropylbenzenamines* was followed using 2-bromo-N-cyclopropyl-5-fluorobenzenamine (550 mg, 2.39 mmol, 1.00 equiv) and methyl chloroformate (6.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (15% Et₂O in petroleum ether) to afford 586 mg (85% yield) of a yellow oil.

**2-Bromo-N-cyclopropyl-4-nitrobenzenamine**  
*General procedure B for the preparation of N-cyclopropylbenzenamines* was followed using 2-bromo-1-fluoro-4-nitrobenzene (1.00 g, 4.55 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% Et₂O in petroleum ether) to afford 1.05 g (90% yield) of a yellow solid.
Methyl 2-bromo-4-nitrophenylcyclopropylcarbamate (1f) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-4-nitrobenzenamine (800 mg, 3.11 mmol, 1.00 equiv) and methyl chloroformate (8.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (gradient from 20% to 30% EtOAc in petroleum ether) to afford 358 mg (37% yield) of a yellow solid.

^1H NMR (400 MHz, CDCl₃, 293K, TMS) δ 8.49 (d, J = 2.5 Hz, 1H), 8.19 (dd, J = 8.7, 2.6 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 3.72 (br s, 3H), 3.13 (tt, J = 7.0, 3.6 Hz, 1H), 0.82-0.80 (m, 2H), 0.59 (br s, 2H).

^13C NMR (75 MHz, CDCl₃, 293K, TMS) δ 155.8, 147.2, 147.1, 130.6, 128.8, 124.7, 123.3, 53.4, 31.2, 8.1.

HRMS Calculated for C₁₀H₈N₂O₃Br (M⁺ - OCH₃) 284.9698, Found 284.9680.

IR (νmax/cm⁻¹) 3099, 3014, 2957, 1729, 1527, 1345 cm⁻¹. Rf 0.24 (20% EtOAc in petroleum ether). Melting point 87-89 °C

3-Bromo-4-(cyclopropylamino)benzonitrile General procedure B for the preparation of N-cyclopropylbenzenamines was followed using 3-bromo-4-fluorobenzonitrile (1.00 g, 4.55 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% Et₂O in petroleum ether) to afford 0.954 g (89% yield) of a white solid.

^1H NMR (400 MHz, CDCl₃, 293K, TMS) δ 7.64 (s, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 5.18 (br s, 1H), 2.52-2.47 (m, 1H), 0.93-0.81 (m, 2H), 0.67-0.55 (m, 2H). ^13C NMR (100 MHz, CDCl₃, 293K, TMS) δ 149.1, 135.7, 132.8, 119.1, 112.1, 108.3, 100.3, 24.9, 7.8. HRMS Calculated for C₁₀H₉N₂Br (M⁺) 235.9949, Found 235.9924. IR (νmax/cm⁻¹) 3404, 3091, 3007, 2221, 1596, 1334, 1192, 815 cm⁻¹. Rf 0.28 (10% Et₂O in petroleum ether). Melting point 100-101 °C

Methyl 2-bromo-4-cyanophenylcyclopropylcarbamate (1g) General procedure for the protection of N-cyclopropylbenzenamines was followed using 3-bromo-4-(cyclopropylamino)benzonitrile (700 mg, 2.95 mmol, 1.00 equiv) and methyl chloroformate (7.0 mL, 0.40 M). The product was purified by silica gel flash chromatography (25% EtOAc in petroleum ether) to afford 674 mg (77% yield) of a white solid.
1H NMR (400 MHz, CDCl₃, 293K, TMS) δ 7.92 (d, J = 1.8 Hz, 1H), 7.63 (dd, J = 8.1, 1.9 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 3.71 (br s, 3H), 3.11 (tt, J = 7.1, 3.6 Hz, 1H), 0.81-0.79 (m, 2H), 0.57 (br s, 2H).

13C NMR (75 MHz, CDCl₃, 328K, TMS) δ 155.9, 145.7, 136.9, 131.9, 131.0, 124.9, 116.9, 112.9, 53.3, 31.2, 30.9, 8.0.

HRMS Calculated for C₁₁H₈N₂OBr (M⁺ - OCH₃) 264.9800, Found 264.9767.

IR (ν max/cm⁻¹) 3529, 3096, 3014, 2955, 2233, 1725, 1442, 1340, 1214, 534 cm⁻¹.

Rf 0.28 (25% EtOAc in petroleum ether).

Bromo-N-cyclopropyl-3-methylaniline General procedure C for the preparation of N-cyclopropylbenzenamines was followed using 2-bromo-3-methylaniline (0.37 mL, 3.0 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% hexanes) to afford 350 mg (52% yield) of a clear oil.

1H NMR (400 MHz, CDCl₃, 293K) δ 7.09 (dd, J = 7.8, 7.8 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 7.4 Hz, 1H), 4.89 (br s, 1H), 2.45-2.40 (m, 1H), 2.35 (s, 3H), 0.78-0.70 (m, 2H), 0.62-0.56 (m, 2H).

13C NMR (100 MHz, CDCl₃, 293K) δ 145.8, 138.2, 127.5, 119.4, 111.9, 110.1, 25.4, 23.6, 7.5.

IR (ν max/cm⁻¹) 3404, 2922, 1595, 1469, 1323, 1016, 766 cm⁻¹. Rf 0.36 (100% hexanes).

Melting point 66-68 ºC.

B N C O₂Me

Methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate (1h) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclopropyl-3-methylaniline (590 mg, 2.61 mmol, 1.0 equiv) and methyl chloroformate (5.2 mL, 0.50 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 632 mg (85% yield) of a white solid.

1H NMR (400 MHz, CDCl₃, 328K) δ 7.22-7.16 (m, 2H), 6.94 (dd, J = 6.8, 2.6 Hz, 1H), 3.70 (br s, 3H), 3.15 (tt, J = 7.2, 3.8 Hz, 1H), 2.46 (s, 3H), 0.78-0.68 (m, 2H), 0.65-0.60 (m, 2H). 13C NMR (100 MHz, CDCl₃, 328K) δ 156.7, 141.1, 139.6, 129.6, 127.6, 127.2, 126.7, 126.5, 30.0, 23.7, 7.4.

IR (ν max/cm⁻¹) 3013, 2953, 1722, 1469, 1442, 1340, 1217, 1087, 550 cm⁻¹. Rf 0.18 (10% EtOAc in hexanes).
2-Chloro-N-cyclopropylbenzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-chloroaniline (2.1 mL, 20 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 2.0 g (60% yield) of a yellow oil.

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\text{H NMR (400 MHz, CDCl}_3, 293K, \text{TMS}) \ \delta 7.23 (dd, J = 7.9, 1.5 Hz, 1H), 7.16 (dd, J = 8.1, 7.3, 1.5 Hz, 1H), 7.08 (dd, J = 8.1, 1.6 Hz, 1H), 6.66 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 4.72 (s, 1H), 2.44 (tt, J = 6.7, 3.4 Hz, 1H), 0.84-0.71 (m, 2H), 0.63-0.51 (m, 2H).
\]

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\text{C NMR (100 MHz, CDCl}_3, 293K, \text{TMS}) \ \delta 144.7, 129.1, 127.8, 118.9, 117.8, 112.7, 25.1, 7.6.
\]

HRMS Calculated for C\(_9\)H\(_{10}\)NCl (M\(^+\)) 167.0502, Found 167.0500.

IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3408, 3288, 2957, 2898, 1595, 1036, 747 cm\(^{-1}\).

RF 0.35 (100% petroleum ether).

Methyl 2-chlorophenylcyclopropylcarbamate (i)  General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-chloro-N-cyclopropylbenzenamine (175 mg, 1.04 mmol, 1.00 equiv) and methyl chloroformate (4.7 mL, 0.22 M). The product was purified by silica gel flash chromatography (20% Et\(_2\)O in petroleum ether) to afford 219 mg (93% yield) of a pale yellow oil.

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\text{H NMR (400 MHz, CDCl}_3, 328K, \text{TMS}) \ \delta 7.48-7.44 (m, 1H), 7.32-7.22 (m, 2H), 7.17-7.13 (m, 1H), 3.73 (s, 3H), 3.15 (tt, J = 7.1, 3.6 Hz, 1H), 0.81-0.74 (m, 2H), 0.65-0.59 (m, 2H).
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\text{C NMR (100 MHz, CDCl}_3, 293K, \text{TMS}) \ \delta 156.8, 139.2, 133.3, 130.1, 130.0, 128.5, 127.4, 53.0, 31.0, 7.5.
\]

HRMS Calculated for C\(_{10}\)H\(_9\)NOCl (M\(^-\)OCH\(_3\)) 194.0373, Found 194.0354. IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3100, 3018, 2956, 1719, 1442, 1341, 753 cm\(^{-1}\). RF 0.30 (20% Et\(_2\)O in petroleum ether).

(4-Chloro-3-iodophenoxy)triisopropylsilane  To a solution of 4-chloro-2-iodophenol (1.00 g, 3.93 mmol, 1.00 equiv) and imidazole (401 mg, 5.90 mmol, 1.50 equiv) in DMF (20 mL, 0.20 M) at room temperature was added triisopropylsilyl chloride (1.7 mL, 7.9 mmol, 2.0 equiv) via syringe. The resulting solution was stirred at room temperature for four hours. The crude reaction mixture was then diluted with H\(_2\)O and extracted with Et\(_2\)O (x3). The combined organic layers were washed with brine, dried with MgSO\(_4\), and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (gradient 0 to 5% EtOAc in hexanes) to afford 1.49 g (93% yield) of a clear oil.

\[
\text{H NMR (400 MHz, CDCl}_3, 293K) \ \delta 7.36 (d, J = 2.8 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 6.77 (dd, J = 8.7, 2.8 Hz, 1H), 1.26-1.17 (m, 3H), 1.07 (d, J = 6.8 Hz, 18H).
\]

\[
\text{C NMR (100 MHz, CDCl}_3, \text{TMS}) \ \delta 156.8, 139.2, 133.3, 130.1, 130.0, 128.5, 127.4, 53.0, 31.0, 7.5.
\]
293K) δ 154.9, 131.3, 130.3, 129.1, 120.9, 97.7, 17.8, 12.6. IR (ν_max/cm⁻¹) 3063, 2946, 2867, 1579, 1461, 1283, 1230, 932, 883, 686 cm⁻¹. R_f 0.60 (100% hexanes).

2-Chloro-N-cyclopropyl-5-((triisopropylsilyl)oxy)aniline An oven-dried test tube equipped with a magnetic stir bar and a teflon septum was charged with BrettPhos Palladacycle Precatalyst¹ (24.3 mg, 0.0304 mmol, 1.00 mol%), BrettPhos³ (16.3 mg, 0.0304 mmol, 1.00 mol%) and NaOtBu (351 mg, 3.65 mmol, 1.2 equiv). The test tube was evacuated and backfilled with argon (x3). (4-Chloro-3-iodophenoxy)triisopropylsilane (1.25g, 3.04 mmol, 1.00 equiv) was then added as a solution in toluene (3.0 mL, 1.0 M) followed by cyclopropylamine (0.25 mL, 3.7 mmol, 1.2 equiv). The resulting mixture was stirred at room temperature for 12 hours after which point it was diluted with EtOAc. After addition of H₂O, the organic layer was separated and the aqueous layer was extracted with EtOAc (x3). The combined organic layers were washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (gradient 0 to 2% EtOAc in hexanes) to afford 508 mg (49% yield) of a yellow oil.

¹H NMR (400 MHz, CDCl₃, 293K) δ 7.04 (d, J = 8.6 Hz, 1H), 6.66 (d, J = 2.8 Hz, 1H), 6.22 (dd, J = 8.5, 2.8 Hz, 1H), 4.64 (br s, 1H), 2.44-2.38 (m, 1H), 1.31-1.22 (m, 3H), 1.12 (d, J = 7.0 Hz, 18H), 0.83-0.70 (m, 2H), 0.63-0.55 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 293K) δ 155.8, 145.2, 129.0, 110.9, 109.4, 104.6, 24.9, 17.9, 12.7, 7.3. IR (ν_max/cm⁻¹) 3417, 3089, 2945, 2867, 1599, 1505, 1464, 1426, 1308, 1196, 1009, 883, 686 cm⁻¹. R_f 0.27 (100% hexanes).

Methyl (2-chloro-5-((triisopropylsilyl)oxy)phenyl)(cyclopropyl)carbamate (1j) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-chloro-N-cyclopropyl-5-((triisopropylsilyl)oxy)aniline (450 mg, 1.32 mmol, 1.00 equiv) and methyl chloroformate (3.0 mL, 0.44 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 398 mg (76% yield) of a clear oil.

¹H NMR (400 MHz, CDCl₃, 328K) δ 7.24 (d, J = 8.8 Hz, 1H), 6.77 (dd, J = 8.7, 2.8 Hz, 1H), 6.65 (d, J = 2.8 Hz, 1H), 3.69 (br s, 3H), 3.10 (tt, J = 7.2, 3.8 Hz, 1H), 1.29-1.20 (m, 3H), 1.11 (d, J = 7.1 Hz, 18H), 0.77-0.72 (m, 2H), 0.61-0.57 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 328K) δ 156.6, 155.3, 139.7, 130.0, 125.2, 121.9, 120.1, 52.8, 31.0, 17.8, 12.7, 7.3. IR (ν_max/cm⁻¹) 2947, 2868, 1728, 1595, 1480, 1337, 1259 cm⁻¹. R_f 0.32 (10% EtOAc in hexanes).
2-Chloro-N-cyclopropyl-4-(trifluoromethyl)benzenamine  General procedure A for the preparation of N-cyclopropylbenzenamines was followed using 2-chloro-4-(trifluoromethyl)aniline (0.57 mL, 4.1 mmol, 1.0 equiv). The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 0.56 mg (29% yield) of a clear oil.

1H NMR (400 MHz, CDCl$_3$, 293K, TMS) $\delta$ 7.31 (dd, $J = 8.2, 0.7$ Hz, 1H), 7.26 (d, $J = 2.6$ Hz, 1H), 6.91 (ddt, $J = 8.2, 1.4, 0.7$ Hz, 1H), 4.88 (br s, 1H), 2.47 (tt, $J = 6.7, 3.4$ Hz, 1H), 0.87-0.82 (m, 2H), 0.61-0.57 (m, 2H).

13C NMR (100 MHz, CDCl$_3$, 293K, TMS) $\delta$ 145.0, 130.2 (q, $J_{CF} = 32$ Hz), 129.3, 124.2 (q, $J_{CF} = 270$ Hz), 122.0, 114.2 (q, $J_{CF} = 4.2$ Hz), 108.9 (q, $J_{CF} = 4.1$ Hz), 24.9, 7.7.

HRMS Calculated for C$_{10}$H$_9$NF$_3$Cl (M$^+$) 235.0376, Found 235.0353.

IR ($\nu_{\text{max}}$/cm$^{-1}$) 3422, 3097, 2981, 1511, 1278 cm$^{-1}$.

R$_f$ 0.39 (100% petroleum ether).

Methyl 2-chloro-4-(trifluoromethyl)phenylcyclopropylcarbamate (1k) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-chloro-N-cyclopropyl-4-(trifluoromethyl)benzenamine (450 mg, 1.91 mmol, 1.00 equiv) and methyl chloroformate (3.8 mL, 0.50 M). The product was purified by silica gel flash chromatography (10% Et$_2$O in petroleum ether) to afford 350 mg (62% yield) of a clear oil.

1H NMR (400 MHz, CDCl$_3$, 293K, TMS) $\delta$ 7.56 (d, $J = 8.4$ Hz, 1H), 7.51-7.48 (m, 1H), 7.40 (br s, 1H), 3.70 (br s, 3H), 3.10 (tt, $J = 7.1, 3.6$ Hz, 1H), 0.80-0.77 (m, 2H), 0.61-0.55 (m, 2H). 13C NMR (75 MHz, CDCl$_3$, 328K, TMS) $\delta$ 156.5, 140.4, 137.6, 130.8, 130.4 (q, $J_{CF} = 33$ Hz), 127.4 (q, $J_{CF} = 3.6$ Hz), 125.3 (q, $J_{CF} = 4.0$ Hz), 123.5 (q, $J_{CF} = 271$ Hz), 53.3, 31.2, 8.0. HRMS Calculated for C$_{11}$H$_{8}$NOF$_3$Cl (M$^+$ - OCH$_3$) 264.0217, Found 264.0204. IR ($\nu_{\text{max}}$/cm$^{-1}$) 3024, 2958, 1727, 1646, 1336, 1131 cm$^{-1}$. R$_f$ 0.25 (10% Et$_2$O in petroleum ether).

Methyl 3-chloro-4-(cyclopropylamino)benzoate General procedure C for the preparation of N-cyclopropylbenzenamines was followed using methyl 4-amino-3-chlorobenzoate (742 mg, 4.00 mmol, 1.00 equiv). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 427 mg (47% yield) of a white solid.
**Methyl 3-chloro-4-(cyclopropyl(methoxycarbonyl)amino)benzoate (II)**

General procedure for the protection of N-cyclopropylbenzenamines was followed using methyl 3-chloro-4-(cyclopropylamino)benzoate (563 mg, 2.50 mmol, 1.00 equiv) and methyl chloroformate (5.0 mL, 0.50 M). The product was purified by silica gel flash chromatography (20% EtOAc in hexanes) to afford 472 mg (67% yield) of a yellow solid.

**Synthesis and Characterization of Starting Materials 5, 7a, 8 and 10**

1-Bromo-2-(vinlyloxy)naphthalene. Prepared according to a modified literature procedure. A solution of 1-bromonaphthalen-2-ol (5.59 g, 24.0 mmol, 1.00 equiv) and 1,2-dibromoethane (3.1 mL, 36 mmol, 1.5 equiv) in water (20 mL) was stirred under reflux for 30 min. A 3N aqueous solution of sodium hydroxide (10.4 mL, 31.2 mmol, 1.30 equiv) was then added dropwise via an addition funnel.
The reaction mixture was then stirred at reflux for 16 h, cooled to room temperature, extracted with CH₂Cl₂, washed with water and brine, dried with MgSO₄ and concentrated under reduced pressure. The resulting crude product was then dissolved in dry THF (20 mL) and slowly added via syringe to a solution of potassium tert-butoxide (2.69 g, 24.0 mmol, 1.00 equiv) in THF (60 mL) at 0 °C under argon. The reaction mixture was stirred at room temperature for 16 h, quenched with water, extracted with EtOAc, washed with water and brine, dried with MgSO₄ and concentrated under reduced pressure. The residue was passed over a plug of silica gel to provide 1.1 g of crude 1-bromo-2-(vinlyoxy)naphthalene (Rf = 0.39, 100% petroleum ether).

1-Bromo-2-cyclopropoxynaphthalene (5) To a solution of diethylzinc (1M in hexanes, 8.0 mL, 8.0 mmol, 2.0 equiv) in dichloroethane (20 mL) at -5 °C under argon was added dropwise, and very slowly, a solution of trifluoroacetic acid (592 µL, 8.00 mmol, 2.00 equiv) in dichloroethane (10 mL). The reaction mixture was stirred for 20 min then a solution of diiodomethane (643 µL, 8.00 mmol, 2.00 equiv) in dichloroethane (10 mL) was added dropwise. The reaction mixture was again stirred for 20 min then a solution of 1-bromo-2-(vinlyoxy)naphthalene (1.00 g, 4.00 mmol, 1.00 equiv) in dichloroethane (10 mL) was added dropwise. The mixture was allowed to warm to room temperature and then stirred until the reaction was judged to be complete by TLC. The reaction was then quenched at 0 °C by addition of a saturated solution of NH₄Cl (stir for 1 h). The crude product was then extracted with CH₂Cl₂, washed with water and brine, dried with MgSO₄, concentrated under reduced pressure and purified by silica gel flash chromatography to give 613 mg of 5.

1H NMR (400 MHz, CDCl₃, 293K, TMS) δ 8.21 (dd, J = 8.6, 0.8 Hz, 1H), 7.79 (dd, J = 9.1, 9.1 Hz, 2H), 7.60 (d, J = 9.0 Hz, 1H), 7.55 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 7.39 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 3.99-3.94 (m, 1H), 0.95-0.90 (m, 2H), 0.89-0.83 (m, 2H). 13C NMR (100 MHz, CDCl₃, 293K, TMS) δ 153.4, 133.1, 129.9, 128.6, 128.0, 127.6, 126.1, 124.3, 115.3, 108.4, 52.5, 52.6. HRMS Calculated for C₁₃H₁₁OBr (M⁺) 261.9993, Found 261.9988. Rf 0.44 (5% Et₂O in petroleum ether).
Methyl 1H-indole-1-carboxylate Prepared according to a literature procedure. To a solution of indole (1.17 g, 10.0 mmol, 1.00 equiv) in DMF (33 mL, 0.30 M) at room temperature under an atmosphere of argon was added NaH (0.505 g, 20.0 mmol, 2.00 equiv). The resulting mixture was stirred at room temperature for 30 min after which point methyl chloroformate (1.16 mL, 15.0 mmol, 1.50 equiv) was added via syringe. The mixture was allowed to stir until the reaction was judged to be complete by TLC. The reaction was quenched by the slow addition of H₂O. The crude product was extracted with EtOAc (x3), washed with brine, dried with MgSO₄ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 1.52 g (87% yield) of a clear oil.

¹H NMR (400 MHz, CDCl₃, 293K) δ 8.21 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 3.6 Hz, 1H), 7.59 (dd, J = 7.8, 0.6 Hz, 1H), 7.36 (dd, J = 7.8, 7.8 Hz, 1H), 7.27 (ddd, J = 7.5, 7.5, 0.4 Hz, 1H), 6.62 (d, J = 3.7 Hz, 1H), 4.06 (s, 3H).

Exhibited spectral data identical to a previous report.

Methyl 1,6b-dihydrocyclopropa[b]indole-2(1H)-carboxylate (7a) To a solution of diethylzinc (1M in hexanes, 5.0 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (5.0 mL) at 0°C under argon was added dropwise, and very slowly, a solution of trifluoroacetic acid (0.37 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (2.5 mL). The reaction mixture was stirred for 20 min then a solution of diiodomethane (0.40 mL, 5.0 mmol, 2.0 equiv) in dichloromethane (2.5 mL) was added dropwise. The reaction mixture was again stirred for 20 min then a solution of methyl 1H-indole-1-carboxylate (0.438 g, 2.50 mmol, 1.00 equiv) in dichloromethane (2.5 mL) was added dropwise. The mixture was allowed to warm to room temperature and then stirred until the reaction was judged to be complete by TLC. The reaction was then quenched at 0°C by addition of a saturated solution of NH₄Cl (stir for 30 min). The crude product was then extracted with CH₂Cl₂ (x3), washed with water and brine, dried with MgSO₄, concentrated under reduced pressure and purified by silica gel flash chromatography (50% CH₂Cl₂ in hexanes) to give 180 mg (38% yield) of a white solid.

¹H NMR (400 MHz, CDCl₃, 293K) δ 7.86 (br s, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.18 (dd, J = 7.7, 7.7 Hz, 1H), 6.98 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 4.18 (br s, 1H), 3.90 (br s, 3H), 2.65 (ddd, J = 8.6, 6.6, 4.0 Hz, 1H), 1.09-1.07 (m, 1H), 0.29-0.28 (m, 1H).

Exhibited spectral data identical to a previous report.
2-Bromo-N-cyclobutylaniline  Prepared according to a literature procedure.\textsuperscript{8} To a solution of 2-bromoaniline (2.70 g, 15.7 mmol, 1.10 equiv) in THF at room temperature under an atmosphere of argon was added cyclobutanone (1.00 g, 14.3 mmol, 1.00 equiv) via syringe followed by NaBH(OAc)$_3$ (4.54 g, 21.4 mmol, 1.50 equiv), portionwise. AcOH (0.82 mL, 14.3 mmol, 1.00 equiv) was then added via syringe. The resulting mixture was stirred at room temperature for 3 days. The crude product was extracted with Et$_2$O (x3), washed with brine, dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (100% hexanes) to afford 1.63 g (50% yield) of a clear oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 7.45 (dd, $J = 7.7$, 1.5 Hz, 1H), 7.19 (ddd, $J = 7.5$, 7.5, 1.4 Hz, 1H), 6.61-6.57 (m, 2H), 4.47 (br s, 1H), 3.97 (sextuplet, $J = 6.7$ Hz, 1Hz), 2.53-2.46 (m, 2H), 2.00-1.78 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$, 293K) $\delta$ 144.0, 132.3, 128.4, 117.6, 111.6, 109.3, 48.7, 31.0, 15.3.

IR ($\nu_{\text{max}}$/cm$^{-1}$) 3406, 3066, 2980, 2935, 1595, 1507, 1319, 1170, 1017, 741 cm$^{-1}$. $R_f$ 0.47 (100% hexanes).

Methyl (2-bromophenyl)(cyclobutyl)carbamate (8) General procedure for the protection of N-cyclopropylbenzenamines was followed using 2-bromo-N-cyclobutylaniline (1.50 g, 6.63 mmol, 1.00 equiv) and methyl chloroformate (13.0 mL, 0.51 M). The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 1.60 g (85% yield) of a white solid.

$^1$H NMR (400 MHz, CDCl$_3$, 328K) $\delta$ 7.65 (dd, $J = 7.8$, 1.0 Hz, 1H), 7.35 (ddd, $J = 7.6$, 7.6, 0.7 Hz, 1H), 7.22-7.16 (m, 2H), 4.72 (br s, 1H), 3.66 (br s, 3H), 2.22-2.15 (m, 2H), 1.95 (quintet, $J = 10.0$ Hz, 1H), 1.83 (quintet, $J = 10.1$ Hz, 1H), 1.66-1.51 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, 328K) $\delta$ 155.4, 138.7, 133.4, 131.6, 129.1, 128.0, 125.8, 52.9, 52.8, 29.7, 28.7, 15.1. IR ($\nu_{\text{max}}$/cm$^{-1}$) 2988, 2951, 1714, 1442, 1322, 1293, 1039 cm$^{-1}$. $R_f$ 0.24 (10% EtOAc in hexanes). Melting point 46-47 °C.
2-Bromo-1-(1-cyclopropylethoxy)-4-nitrobenzene (10) 1-Cyclopropylethanol (0.37 mL, 3.8 mmol, 1.1 equiv) was added dropwise via syringe to a solution of KH (0.500 g, 3.75 mmol, 1.10 equiv) in THF (23 mL, 0.15 M) at 0 °C under an atmosphere of argon. The resulting mixture was stirred for 10 minutes after which time 2-bromo-1-fluoro-4-nitrobenzene (0.750 g, 3.41 mmol, 1.00 equiv) was added and the solution was brought to room temperature. Once judged complete by TLC, the reaction was quenched by slow addition of water. The crude product was extracted with CH$_2$Cl$_2$ (x3), washed with brine, dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (3% Et$_2$O in petroleum ether) to afford 0.819 g (84% yield) of a pale yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$, 328K) $\delta$ 8.46 (d, $J = 2.8$ Hz, 1H), 8.15 (dd, $J = 9.1$, 2.8 Hz, 1H), 6.92 (dd, $J = 9.2$, 0.5 Hz, 1H), 4.13 (quintet, $J = 6.4$ Hz, 1H), 1.46 (d, $J = 6.2$ Hz, 3H), 1.21 (tdt, $J = 8.3$, 6.9, 5.1 Hz, 1H), 0.65-0.56 (m, 2H), 0.48-0.32 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, 328K) $\delta$ 160.0, 141.1, 129.3, 124.4, 113.3, 113.2, 80.0, 19.5, 16.5, 3.5, 2.1. $R_f$ 0.27 (3% Et$_2$O in petroleum ether).

General Procedures and Characterization for Arylation Products

General Procedure A for Arylation at sp$^3$ C–H Bonds of Cyclopropanes – Quinoline Synthesis

A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), Pd(OAc)$_2$ (5.00 mol%), PtBu$_3$Me·HBF$_4$ (10.0 mol%), K$_3$PO$_4$ (1.50 equiv) and CsOPiv (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to 0 °C and diluted with THF (0.20 M) after which point DDQ (1.20 equiv) was added. The mixture was then brought to room temperature.
temperature and stirred until the reaction was judged complete by TLC. The crude product was extracted with CH\textsubscript{2}Cl\textsubscript{2} (x3), dried with MgSO\textsubscript{4} and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

**General Procedure B for Arylation at sp\textsuperscript{3} C–H Bonds of Cyclopropanes – Quinoline Synthesis**

\[
\begin{array}{c}
\text{O} \quad \text{OR'} \\
\text{R} \quad \text{Cl} \\
\text{N} \\
\text{Br} \\
\text{O} \quad \text{OR'}
\end{array}
\xrightarrow{i. \text{Pd(OAc)}_2 (5 \text{ mol\%}), \text{PCy}_3 \cdot \text{HBF}_4 (10 \text{ mol\%}), \text{Cs}_2 \text{CO}_3 (1.5 \text{ equiv}), \text{PivOH, Mes}}
\text{R} \quad \text{N} \\
\text{H} \\
\text{R'} \\
\text{O} \quad \text{OR'}
\xrightarrow{\text{ii. DDQ, THF}}
\text{R} \quad \text{N} \\
\text{H} \\
\text{R'} \\
\text{O} \quad \text{OR'}
\]

A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), Pd(OAc)\textsubscript{2} (5.00 mol\%), PCy\textsubscript{3} \cdot \text{HBF}_4 (10.0 mol\%), Cs\textsubscript{2}CO\textsubscript{3} (1.50 equiv) and PivOH (30.0 mol\%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to 0 °C and diluted with THF (0.20 M) after which point DDQ (1.20 equiv) was added. The mixture was then brought to room temperature and stirred until the reaction was judged complete by TLC. The crude product was extracted with CH\textsubscript{2}Cl\textsubscript{2} (x3), dried with MgSO\textsubscript{4} and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

**General Procedure C for Arylation at sp\textsuperscript{3} C–H Bonds of Cyclopropanes – Tetrahydroquinoline Synthesis**

\[
\begin{array}{c}
\text{O} \quad \text{OR'} \\
\text{R} \quad \text{Br} \\
\text{N} \\
\text{CO}_2\text{Me} \\
\text{O} \quad \text{OR'}
\end{array}
\xrightarrow{i. \text{Pd(OAc)}_2 (5 \text{ mol\%}), \text{PtBu}_2\text{Me} \cdot \text{HBF}_4 (10 \text{ mol\%}), \text{K}_3\text{PO}_4, \text{CsOPiv, Mes}}
\text{R} \quad \text{N} \\
\text{CO}_2\text{Me}
\xrightarrow{\text{ii. Pd/C, EtOAc, H}_2}
\text{R} \quad \text{N} \\
\text{CO}_2\text{Me}
\]

A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), Pd(OAc)\textsubscript{2} (5.00 mol\%), PtBu\textsubscript{2}Me \cdot \text{HBF}_4 (10.0 mol\%), K\textsubscript{3}PO\textsubscript{4} (1.50 equiv) and CsOPiv (30.0 mol\%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to room temperature and diluted with EtOAc (0.20 M) after which point Pd/C (10 mol\%) was added. The mixture was then vigorously stirred under H\textsubscript{2} bubbling for 10 minutes after which point the reaction was stirred under an atmosphere of H\textsubscript{2} (no bubbling) until judged complete by TLC. The crude product was filtered over celite and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.
General Procedure D for Arylation at sp$^3$ C–H Bonds of Cyclopropanes – Tetrahydroquinoline

Synthesis

A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with the starting material (if a solid, 1.00 equiv), Pd(OAc)$_2$ (5.00 mol%), PCy$_3$HBF$_4$ (10.0 mol%), Cs$_2$CO$_3$ (1.50 equiv) and PivOH (30.0 mol%). The vial was purged with argon. The starting material (if a liquid, 1.00 equiv) was added as a solution in mesitylene (0.20 M). The resulting mixture was placed in a preheated bath and stirred for the indicated time. The reaction was then cooled to room temperature and diluted with EtOAc (0.20 M) after which point Pd/C (10 mol%) was added. The mixture was then vigorously stirred under H$_2$ bubbling for 10 minutes after which point the reaction was stirred under an atmosphere of H$_2$ (no bubbling) until judged complete by TLC. The crude product was filtered over celite and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

Quinoline (3a) Synthesized according to General Procedure A using methyl 2-bromophenylcyclopropylcarbamate 1a (110 mg, 0.409 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et$_2$O in petroleum ether) to afford 46 mg (87% yield) of an orange oil. Synthesized according to General Procedure B using methyl 2-chlorophenylcyclopropylcarbamate 1i (92.3 mg, 0.409 mmol, 1.00 equiv) at 140 °C for 4 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et$_2$O in petroleum ether) to afford 40 mg (76% yield) of an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K, TMS) δ 8.93 (dd, $J = 4.1$, 1.4 Hz, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 8.12 (d, $J = 8.6$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.72 (ddd, $J = 8.4$, 7.0, 1.4 Hz, 1H), 7.58-7.52 (m, 1H), 7.40 (dd, $J = 8.3$, 4.2 Hz, 1H).

Commercially available - CAS#: 91-22-5.
7-Methylquinoline (3b) Synthesized according to General Procedure A using methyl 2-bromo-5-methylphenylcyclopropylcarbamate 1b (128 mg, 0.450 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et₂O in petroleum ether) to afford 43 mg (67% yield) of an orange oil. Synthesized according to General Procedure A using benzyl 2-bromo-5-methylphenylcyclopropylcarbamate 1b' (162 mg, 0.450 mmol, 1.00 equiv) at 90 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (40% Et₂O in petroleum ether) to afford 38 mg (59% yield) of an orange oil.

\(^{1}\)H NMR (400 MHz, CDCl₃, 293K, TMS) δ 8.87 (dd, \(J = 4.2, 1.5\) Hz, 1H), 8.10 (dd, \(J = 8.2, 1.6\) Hz, 1H), 7.88 (d, \(J = 8.3\) Hz, 1H), 7.38 (dd, \(J = 8.3, 1.6\) Hz, 1H), 2.57 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl₃, 293K, TMS) δ 150.5, 148.7, 139.9, 135.8, 128.9, 128.6, 127.5, 126.5, 120.4, 22.0.

HRMS Calculated for C₁₀H₉N (M⁺) 143.0735, Found 143.0727.

IR (ν max/cm⁻¹) 3048, 2924, 1627, 1503 cm⁻¹. R_f 0.20 (30% Et₂O in petroleum ether).

7-Methoxyquinoline (3c) Synthesized according to General Procedure A using methyl 2-bromo-5-methoxyphenylcyclopropylcarbamate 1c (150 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (70% Et₂O in petroleum ether) to afford 73 mg (91% yield) of a yellow oil.

\(^{1}\)H NMR (400 MHz, CDCl₃, 293K, TMS) δ 8.83 (d, \(J = 3.1\) Hz, 1H), 8.06 (dd, \(J = 8.2, 1.3\) Hz, 1H), 7.69 (d, \(J = 9.0\) Hz, 1H), 7.42 (d, \(J = 2.4\) Hz, 1H), 7.26 (dd, \(J = 7.8, 4.7\) Hz, 1H), 7.20 (dd, \(J = 9.0, 2.5\) Hz, 1H), 3.95 (s, 3H).

Exhibited spectral data identical to a previous report. 9

7-(Trifluoromethyl)quinoline (3d) Synthesized according to General Procedure A using methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate 1d (169 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 20 h). The product was purified by silica gel flash chromatography (15% EtOAc and 15% toluene in hexanes) to afford 77 mg (78% yield) of a white solid.

\(^{1}\)H NMR (400 MHz, CDCl₃, 293K) δ 9.01 (d, \(J = 3.1\) Hz, 1H), 8.41 (br s, 1H), 8.21 (d, \(J = 8.3\) Hz, 1H), 7.94 (d, \(J = 8.4\) Hz, 1H), 7.71 (dd, \(J = 8.5, 1.6\) Hz, 1H), 7.51 (dd, \(J = 8.3, 4.2\) Hz, 1H).

Exhibited spectral data identical to a previous report. 10
7-Fluoroquinoiline (3e) Synthesized according to General Procedure A using methyl 2-bromo-5-fluorophenylcyclopropycarbamate 1e (144 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 2 h). The product was purified by silica gel flash chromatography (15% EtOAc and 15% toluene in hexanes) to afford 54 mg (73% yield) of a yellow oil.

\[ ^1H \text{NMR (400 MHz, CDCl}_3, 293K) \delta 8.89 \text{ (dd, } J = 4.2, 1.6 \text{ Hz, 1H)}, 8.13 \text{ (dd, } J = 8.3, 1.0 \text{ Hz, 1H)}, 7.79 \text{ (dd, } J = 9.0, 6.0 \text{ Hz, 1H)}, 7.71 \text{ (dd, } J = 10.1, 2.5 \text{ Hz, 1H)}, 7.37 - 7.29 \text{ (m, 2H).} \]

13C NMR (100 MHz, CDCl3, 293K) δ 162.9 (d, \( J_F = 249 \text{ Hz} \)), 151.3, 149.1 (d, \( J_F = 12 \text{ Hz} \)), 136.0, 129.8 (d, \( J_F = 10 \text{ Hz} \)), 125.3 (d, \( J_F = 1 \text{ Hz} \)), 120.4 (d, \( J_F = 3 \text{ Hz} \)), 117.2 (d, \( J_F = 26 \text{ Hz} \)), 113.0 (d, \( J_F = 20 \text{ Hz} \)). IR (\( \nu_{max}/cm^{-1} \)) 3055, 3005, 2927, 1630, 1507, 1322, 1258, 1108 cm\(^{-1}\). Rf 0.19 (15% EtOAc and 15% toluene in hexanes).

6-Nitroquinoiline (3f) Synthesized according to General Procedure A using methyl 2-bromo-4-nitrophenylylcyclopropylcarbamate 1f (129 mg, 0.409 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 8 h). The product was purified by silica gel flash chromatography (40% EtOAc in petroleum ether) to afford 44 mg (61% yield) of a yellow solid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3, 293K, TMS) \delta 9.11 \text{ (dd, } J = 4.2, 1.7 \text{ Hz, 1H}), 8.81 \text{ (d, } J = 2.5 \text{ Hz, 1H)}, 8.49 \text{ (dd, } J = 9.3, 2.5 \text{ Hz, 1H}), 8.38-8.36 \text{ (m, 1H)}, 8.25 \text{ (d, } J = 9.3 \text{ Hz, 1H}), 7.59 \text{ (dd, } J = 8.4, 4.2 \text{ Hz, 1H).} \]

Exhibited spectral data identical to a previous report.\(^{11}\)

Quinoline-6-carbonitrile (3g) Synthesized according to General Procedure A using methyl 2-bromo-4-cyanophenylcyclopropylcarbamate 1g (133 mg, 0.450 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (45% EtOAc in petroleum ether) to afford 45 mg (65% yield) of a beige solid.

\[ ^1H \text{NMR (400 MHz, CDCl}_3, 293K, TMS) \delta 9.05 \text{ (dd, } J = 4.2, 1.5 \text{ Hz, 1H}), 8.24-8.21 \text{ (m, 2H)}, 8.19 \text{ (d, } J = 8.8 \text{ Hz, 1H}), 7.86 \text{ (dd, } J = 8.7, 1.8 \text{ Hz, 1H}), 7.54 \text{ (dd, } J = 8.3, 4.2 \text{ Hz, 1H).} \]

\[ ^13C \text{NMR (100 MHz, CDCl}_3, 293K, TMS) \delta 153.4, 149.3, 136.5, 134.2, 131.2, 130.3, 127.7, 122.9, 118.6, 110.5. \]

HRMS Calculated for C10H6N2 (M+) 154.0531, Found 154.0529. IR (\( \nu_{max}/cm^{-1} \)) 3050, 2230, 1496, 1321, 1216, 838, 755 cm\(^{-1}\). Rf 0.19 (45% EtOAc in petroleum ether). Melting point 131-132 ºC.
5-Methylquinoline (3h) Synthesized according to General Procedure A using methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate 1h (142 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 16 h (DDQ oxidation at room temperature for 3.5 h). The product was purified by silica gel flash chromatography (30% EtOAc in hexanes) to afford 62 mg (87% yield) of an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) δ 8.90 (d, $J = 3.1$ Hz, 1H), 8.31 (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 8.5$ Hz, 1H), 7.58 (dd, $J = 7.1$, 7.1 Hz, 1H), 7.40 (dd, $J = 8.5$, 4.2 Hz, 1H), 7.35 (d, $J = 7.0$ Hz, 1H), 2.67 (s, 3H).

Exhibited spectral data identical to a previous report.

7-((Triisopropylsilyl)oxy)quinoline (3j) Synthesized according to General Procedure B using methyl (2-chloro-5-((triisopropylsilyl)oxy)phenyl)(cyclopropyl)carbamate 1j (128 mg, 0.322 mmol, 1.00 equiv) at 140 °C for 3.5 h (DDQ oxidation at room temperature for 2 h). The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford 83 mg (85% yield) of a red oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) δ 8.83 (dd, $J = 4.3$, 1.7 Hz, 1H), 8.07 (dd, $J = 8.3$, 1.2 Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.50 (d, $J = 2.4$ Hz, 1H), 7.25 (dd, $J = 8.2$, 4.3 Hz, 1H), 7.20 (dd, $J = 8.8$, 2.4 Hz, 1H), 1.40-1.29 (m, 3H), 1.14 (d, $J = 7.4$ Hz, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$, 328K) δ 157.2, 150.5, 149.7, 135.7, 128.7, 123.7, 123.0, 119.0, 115.7, 17.9, 12.7. IR ($\nu_{\text{max}}$/cm$^{-1}$) 3062, 2945, 2868, 1619, 1499, 1322, 1271, 1211, 1072, 969, 836 cm$^{-1}$.

R$_f$ 0.13 (5% EtOAc in hexanes).

6-(Trifluoromethyl)quinoline (3k) Synthesized according to General Procedure B using methyl 2-chloro-4-(trifluoromethyl)phenylcyclopropylcarbamate 1k (120 mg, 0.409 mmol, 1.00 equiv) at 140 °C for 8 h (DDQ oxidation at room temperature for 2.5 h). The product was purified by silica gel flash chromatography (30% Et$_2$O in petroleum ether) to afford 42 mg (52% yield) of a yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) δ 9.03 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.43 (d, $J = 0.8$ Hz, 1H), 8.23 (dd, $J = 8.4$, 0.9 Hz, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 7.73 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.53 (dd, $J = 8.3$, 4.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$, 293K, TMS) δ 151.9, 147.4, 136.1, 131.4 (q, $J_F = 32.4$ Hz), 129.8, 129.2, 127.5 (q, $J_F = 4.4$ Hz), 124.1 (q, $J_F = 271$ Hz), 123.1, 122.4 (q, $J_F = 3.1$ Hz). HRMS Calculated for C$_{10}$H$_7$NF$_3$ (M$^+$) 197.0452, Found 197.0456. IR ($\nu_{\text{max}}$/cm$^{-1}$) 3060, 1510, 1321, 1153, 1145, 1117, 933, 842 cm$^{-1}$. R$_f$ 0.26 (30% Et$_2$O in petroleum ether). Melting point 60-62 °C.
Methyl quinoline-6-carboxylate (3I) Synthesized according to General Procedure B using methyl 3-chloro-4-[(cyclopropyl(methoxycarbonyl)amino)benzoate 1I (143 mg, 0.500 mmol, 1.00 equiv) at 140 °C for 3 h (DDQ oxidation at room temperature for 3 h). The product was purified by silica gel flash chromatography (50% EtOAc in hexanes) to afford 77 mg (82% yield) of an orange solid.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 8.98 (dd, $J = 4.2$, 1.7 Hz, 1H), 8.57 (d, $J = 1.8$ Hz, 1H), 8.27 (dd, $J = 8.8$, 1.9 Hz, 1H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.12 (d, $J = 8.8$ Hz, 1H), 7.45 (dd, $J = 8.3$, 4.2 Hz, 1H), 3.97 (s, 3H).

Exhibited spectral data identical to a previous report.$^{13}$

Methyl 3,4-dihydroquinoline-1(2H)-carboxylate (4a) Synthesized according to General Procedure C using methyl 2-bromophenylcyclopropylcarbamate 1a (135 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 13 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 78 mg (82% yield) of a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 7.65 (br d, $J = 7.9$ Hz, 1H), 7.16-7.12 (m, 1H), 7.08-7.06 (m, 1H), 6.99 (ddd, $J = 7.4$, 7.4, 1.2 Hz, 1H), 3.78 (s, 3H), 3.76-3.73 (m, 2H), 2.76 (t, $J = 6.6$ Hz, 2H), 1.93 (tt, $J = 6.4$, 6.4 Hz, 2H).

Exhibited spectral data identical to a previous report.$^{14}$

Methyl 7-(trifluoromethyl)-3,4-dihydroquinoline-1(2H)-carboxylate (4d) Synthesized according to General Procedure C using methyl 2-bromo-5-(trifluoromethyl)phenylcyclopropylcarbamate 1d (84.5 mg, 0.250 mmol, 1.00 equiv) at 110 °C for 15 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 29 mg (45% yield) of a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 8.07 (br s, 1H), 7.25 (dd, $J = 7.9$, 1.1 Hz, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 3.83 (s, 3H), 3.81-3.78 (m, 2H), 2.82 (t, $J = 6.5$ Hz, 2H), 1.98 (dd, $J = 12.6$, 6.3 Hz, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$, 293K) $\delta$ 155.1, 138.5, 133.4, 129.0, 128.5 (q, $J_F = 32.1$ Hz), 124.1 (q, $J_F = 271$ Hz), 120.7 (q, $J_F = 3.7$ Hz), 119.9 (q, $J_F = 3.7$ Hz), 53.1, 44.8, 27.5, 23.0. IR ($\nu_{\text{max}}$/cm$^{-1}$) 2957, 1714, 1511, 1435, 1328, 1122, 1079 cm$^{-1}$. R$_f$ 0.19 (10% EtOAc in hexanes).
Methyl 5-methyl-3,4-dihydroquinoline-1(2H)-carboxylate (4h) Synthesized according to General Procedure C using methyl (2-bromo-3-methylphenyl)(cyclopropyl)carbamate 1h (142 mg, 0.500 mmol, 1.00 equiv) at 110 °C for 13 h. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to afford 102 mg (99% yield) of a clear oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 7.43 (d, $J = 7.9$ Hz, 1H), 7.06 (dd, $J = 7.8$, 7.8 Hz, 1H), 6.91 (d, $J = 7.4$ Hz, 1H), 3.76 (s, 3H), 3.75-3.72 (m, 2H), 2.65 (t, $J = 6.9$ Hz, 2H), 2.21 (s, 3H), 2.00-1.93 (m, 2H).

Exhibited spectral data identical to a previous report.

Dimethyl 3,4-dihydroquinoline-1,6(2H)-dicarboxylate (4l) Synthesized according to General Procedure D using methyl 3-chloro-4-(cyclopropyl(methoxycarbonyl)amino)benzoate 1l (143 mg, 0.500 mmol, 1.00 equiv) at 140 °C for 3 h. The product was purified by silica gel flash chromatography (15% EtOAc in hexanes) to afford 119 mg (95% yield) of a clear oil.

$^1$H NMR (400 MHz, CDCl$_3$, 293K) $\delta$ 7.83 (br s, 2H), 7.79 (br s, 1H), 3.90 (s, 3H), 3.84-3.78 (m, 2H), 3.83 (s, 3H), 2.82 (t, $J = 6.5$ Hz, 2H), 1.96 (dt, $J = 12.5$, 6.3 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$, 293K) $\delta$ 166.8, 155.1, 142.4, 130.2, 129.4, 127.5, 124.7, 123.1, 53.1, 51.9, 45.2, 27.5, 23.0. IR ($\nu_{max}$/cm$^{-1}$) 2953, 2847, 1717, 1611, 1440, 1283, 1192, 1109 cm$^{-1}$. $R_f$ 0.27 (20% EtOAc in hexanes).

$^{1H}$-benzo[f]chromene (6) A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with 1-bromo-2-cyclopropoxynaphthalene 5 (148 mg, 0.563 mmol, 1.00 equiv), Pd(OAc)$_2$ (6.3 mg, 2.82 x 10$^{-2}$ mmol, 5.00 mol%), PCy$_3$-HBF$_4$ (20.7 mg, 5.63 x 10$^{-2}$ mmol, 10.0 mol%), Cs$_2$CO$_3$ (275 mg, 0.845 mmol, 1.50 equiv) and PivOH (17.3 mg, 0.169 mmol, 30.0 mol%). The vial was purged with argon. Mesitylene (2.8 mL, 0.2 M) was then added and the resulting mixture was placed in a preheated oil bath at 110 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH$_2$Cl$_2$ (x3), dried with MgSO$_4$ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (100% petroleum ether) to afford 91 mg (91% yield) of a pale yellow solid.
\[ \delta_{\text{H}} \] NMR (300 MHz, CDCl\textsubscript{3}, 293K, TMS) \( \delta \) 7.81 (dd, \( J = 8.1, 1.3 \) Hz, 1H), 7.72-7.66 (m, 2H), 7.54 (ddd, \( J = 8.4, 6.9, 1.5 \) Hz, 1H), 7.43 (ddd, \( J = 8.1, 6.9, 1.2 \) Hz, 1H), 7.09 (d, \( J = 8.8 \) Hz, 1H), 6.61 (dt, \( J = 6.3, 2.0 \) Hz, 1H), 5.15 (dt, \( J = 6.3, 3.5 \) Hz, 1H), 3.69 (dd, \( J = 3.4, 2.0 \) Hz, 2H).

Exhibited spectral data identical to a previous report.\textsuperscript{15}

\[
\begin{align*}
\text{Methyl 2,2a-dihydro-1H-cyclobuta[b]indole-3(7bH)-carboxylate} & \quad (9) \\
\text{A 4 mL screw-cap vial} & \quad \text{equipped with a magnetic stir bar} \\
& \quad \text{and a teflon septum was charged with} \\
& \quad \text{methyl} \quad (2 \quad \text{bromophenyl})(\text{cyclobutyl})\text{carbamate} \\
& \quad 8 \quad (142 \quad \text{mg, 0.500 mmol, 1.00 equiv}), \\
& \quad \text{Pd(OAc)} \textsubscript{2} \quad (5.6 \quad \text{mg, 0.025 mmol, 5.0 mol%)}, \\
& \quad \text{PCy} \textsubscript{3} \cdot \text{HBF} \textsubscript{4} \quad (18.4 \quad \text{mg, 0.050 mmol, 10.0 mol%)}, \\
& \quad \text{Cs} \textsubscript{2} \text{CO} \textsubscript{3} \quad (244 \quad \text{mg, 0.750 mmol, 1.50 equiv}) \quad \text{and PivOH} \quad (15.3 \quad \text{mg, 0.150 mmol, 30.0 mol%)}. \\
& \quad \text{The vial was evacuated and backfilled with argon. This procedure was repeated 3 times.} \\
& \quad \text{Mesitylene} \quad (2.5 \quad \text{mL, 0.2 M}) \quad \text{was then added and the resulting mixture was placed in a preheated oil bath at} \quad 140 \quad ^{\circ} \text{C} \quad \text{and stirred for 16 h. The reaction was then cooled to room temperature} \\
& \quad \text{and the crude product was extracted with CH}_{2} \text{Cl}_{2} \quad (x3), \quad \text{dried with MgSO} \textsubscript{4} \quad \text{and concentrated under reduced pressure.} \\
& \quad \text{The product was purified by silica gel flash chromatography (5% EtOAc in hexanes) to afford} \quad 66 \quad \text{mg (65% yield) of an orange oil.} \\
\[
\begin{align*}
\text{1H NMR} & \quad (400 \quad \text{MHz, CDCl}\textsubscript{3}, 328K) \quad \delta \quad 7.86 \quad \text{(br s, 1H)}, \quad 7.22 \quad \text{(dd,} \quad J = 7.7, 7.7 \quad \text{Hz, 1H)}, \quad 7.14 \quad \text{(d,} \quad J = 7.4 \quad \text{Hz, 1H)}, \quad 7.00 \quad \text{(ddd,} \quad J = 7.4, 7.4, 0.9 \quad \text{Hz, 1H)}, \quad 4.86 \quad \text{(br s, 1H)}, \quad 3.98-3.93 \quad \text{(m, 1H)}, \quad 3.83 \quad \text{(s, 3H)}, \\
& \quad 2.66-2.49 \quad \text{(m, 2H)}, \quad 2.29-2.21 \quad \text{(m, 1H)}, \quad 2.06-1.98 \quad \text{(m, 1H)}. \\
\text{13C NMR} & \quad (100 \quad \text{MHz, CDCl}\textsubscript{3}, 293K) \quad \delta \quad 153.1, \quad 143.6, \quad 135.6, \quad 127.8, \quad 124.5, \quad 122.9, \quad 115.2, \quad 58.4, \quad 52.4, \quad 40.9, \quad 29.3, \quad 26.6. \quad \text{IR (}v_{\text{max}}/\text{cm}^{-1}) \quad 2989, \quad 2949, \quad 1715, \quad 1602, \quad 1383, \quad 1067, \quad 762 \quad \text{cm}^{-1}. \quad R_{f} \quad 0.24 \quad \text{(5% EtOAc in hexanes).}
\end{align*}
\]

2-Methyl-5-nitro-2H-spiro[benzofuran-3,1'-cyclopropane] \quad (11) \quad \text{and} \quad 2\text{-methyl-6-nitro-1,1a,2,7b-tetrahydrocyclopropa[c]chromene} \quad (12) \quad \text{A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged with} \\
\quad 2\text{-bromo-1-(1-cyclopropylethoxy)-4-nitrobenzene} \quad 10 \quad (150 \quad \text{mg, 0.524 mmol, 1.00 equiv}), \\
\quad \text{Pd(OAc)} \textsubscript{2} \quad (5.9 \quad \text{mg, 0.0262 mmol, 5.00 mol%)}, \\
\quad \text{PCy} \textsubscript{3} \cdot \text{HBF} \textsubscript{4} \quad (19.3 \quad \text{mg, 0.0524 mmol, 10.0 mol%)}, \\
\quad \text{Cs} \textsubscript{2} \text{CO} \textsubscript{3} \quad (188 \quad \text{mg, 0.577 mmol, 1.10 equiv}) \quad \text{and PivOH} \quad (16.1 \quad \text{mg, 0.157 mmol, 30.0 mol%)}. \\
\quad \text{The vial was evacuated and backfilled with argon. This procedure was repeated 3 times.} \\
\quad \text{Mesitylene} \quad (3.1 \quad \text{mL, 0.17 M}) \quad \text{was then added and the resulting mixture was placed in a preheated oil bath at} \quad 140 \quad ^{\circ} \text{C} \quad \text{and stirred for 16 h. The reaction was then cooled to room temperature and the crude product} \\
\quad \text{was extracted with} \quad \text{CH}_{2} \text{Cl}_{2} \quad (x3), \quad \text{dried with MgSO} \textsubscript{4} \quad \text{and concentrated under reduced pressure. The}
product was purified by silica gel flash chromatography (gradient from 3% to 4% Et₂O in petroleum ether) to afford 72 mg (67% yield) of a yellow solid as an inseparable mixture of 11 and 12 in a 3:1 ratio.

\(^{1}H\) NMR (400 MHz, CDCl₃, 328K, TMS) \(\delta 8.14\) (d, \(J = 2.4\) Hz, 1H, 12), 8.07 (dd, \(J = 8.8, 2.4\) Hz, 1H, 11), 7.96 (dd, \(J = 8.8, 2.4\) Hz, 1H, 12), 7.55 (d, \(J = 2.4\) Hz, 1H, 11), 6.83 (d, \(J = 8.8\) Hz, 1H, 12), 6.79 (d, \(J = 8.8\) Hz, 1H, 11), 4.98 (q, \(J = 6.4\) Hz, 1H, 11), 4.65 (qd, \(J = 6.5, 0.8\) Hz, 1H, 12), 2.07 (td, \(J = 8.5, 4.4\) Hz, 1H, 12), 1.67 (tdd, \(J = 8.3, 5.6, 1.2\) Hz, 1H, 12), 1.35 (d, \(J = 6.4\) Hz, 3H, 11), 1.31-0.93 (m, remaining 9H, 11 and 12).

\(^{13}C\) NMR (100 MHz, CDCl₃, 293K, TMS) Product 11: \(\delta 165.0, 142.0, 134.7, 125.0, 115.3, 108.6, 85.7, 28.4, 18.1, 15.4, 13.8\). Product 12: \(\delta 156.0, 141.7, 128.1, 123.9, 122.4, 118.3, 69.6, 22.6, 20.5, 12.0, 11.8\).

Characterization of the 1,2-Dihydroquinoline Intermediate

Methyl quinoline-1(4H)-carboxylate (2a) A 4 mL screw-cap vial equipped with a magnetic stir bar and a teflon septum was charged Pd(OAc)₂ (3.9 mg, 1.7 x 10⁻² mmol, 5.0 mol%), PCy₃-HBF₄ (12.7 mg, 3.47 x 10⁻² mmol, 10.0 mol%), Cs₂CO₃ (124 mg, 0.380 mmol, 1.10 equiv) and PivOH (10.6 mg, 0.104 mmol, 30.0 mol%). The vial was purged with argon. Methyl 2-chlorophenylecyclopropylcarbamate 1i (78.0 mg, 0.346 mmol, 1.00 equiv) was then added as a 0.2 M solution in mesitylene and the resulting mixture was placed in a preheated oil bath at 140 °C and stirred for 16 h. The reaction was then cooled to room temperature and the crude product was extracted with CH₂Cl₂ (x3), dried with MgSO₄ and concentrated under reduced pressure. The product was purified by silica gel flash chromatography (4% Et₂O in petroleum ether) to afford 53 mg (82% yield) of a pale yellow solid.

\(^{1}H\) NMR (400 MHz, CDCl₃, 293K, TMS) \(\delta 7.93\) (d, \(J = 8.3\) Hz, 1H), 7.21 (t, \(J = 7.6\) Hz, 1H), 7.12-7.06 (m, 2H), 6.94 (d, \(J = 7.6\) Hz, 1H), 5.33 (dt, \(J = 7.8, 4.0\) Hz, 1H), 3.87 (d, \(J = 0.6\) Hz, 3H), 3.34 (d, \(J = 3.7\) Hz, 2H). \(^{13}C\) NMR (100 MHz, CDCl₃, 293K, TMS) \(\delta 153.4, 136.8, 128.3, 128.0, 127.0, 126.4, 125.0, 121.7, 109.6, 53.3, 27.6\). IR (\(\nu_{\text{max}}/\text{cm}^{-1}\)) 3028, 2959, 1730, 1667, 1460, 1334 cm⁻¹. Rₜ 0.29 (5% Et₂O in petroleum ether).
Experimental References


