Supporting Information

Ir(III)-Catalyzed ortho C-H Alkylations of (Hetero)aromatic Aldehydes Using Alkyl Boron Reagents

Xiao-Yang Chen*† and Erik J. Sorensen*
Department of Chemistry, Princeton University, Princeton, New Jersey, 08544, United States
*Email: xc3@princeton.edu; ejs@princeton.edu

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General Information

All commercially available reagents were purchased from Alfa Aesar, Ark Pharm Inc., Combi-Blocks, Enamine Building Blocks, Fisher Scientific, Frontier Scientific, Oakwood Chemicals, Sigma Aldrich, and TCI America, and were used directly without further purifications. \([\text{Cp}^*\text{IrCl}_2]_2\) was synthesized from \(\text{IrCl}_3\) and \(\text{Cp}^*\) according to a known procedure.\(^1\) Dichloroethane and acetic acid were freeze-pump-thawed three times before use. Other reaction solvents were purified according to the method of Grubbs.\(^2\) Reactions were monitored by thin layer chromatography (TLC) carried out on 250 μm Merck silica gel plates (60 F254) containing a fluorescent indicator (254 nm). Visualization of the developed TLC plate was performed by irradiation with UV light. Organic solvents were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath (25 °C). Filtration was performed using Celite®. Preparative thin layer chromatography was undertaken using Analtech Uniplate silica gel chromatography plates containing a fluorescent indicator (254 nm) (20x20 cm, 250, 500 or 1000 micron). Flash column chromatography was performed using Silicycle SiliaFlash P60 silica gel (60 Å pore size, 40 – 63 μm particle size, 230 – 400 mesh).

\(^1\)H NMR spectra were recorded on a Bruker 500 (500 MHz) and are referenced relative to residual CHCl₃ (in CDCl₃) proton signals at δ 7.26 ppm. Data for \(^1\)H spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent), integration, coupling constant (Hz) and assignment. \(^13\)C NMR spectra were recorded on a Bruker 500 (126 MHz) and are referenced relative to residual CHCl₃ (in CDCl₃) at δ 77.16 ppm. Data for \(^13\)C NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. \(^19\)F NMR spectra were recorded on a Bruker 300 (282 MHz). Data for \(^19\)F NMR spectra are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a 30000-200 cm⁻¹ diamond and are reported in terms of frequency of absorption (cm⁻¹). High-resolution mass spectra were obtained from Princeton University Mass Spectrometry Facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization). X-ray crystallographic analyses were performed using Bruker SMART APEX DUO diffractometer equipped with a copper or molybdenum X-ray tube on a Bruker Kappa APEX-II CCD diffractometer.
Experimental Procedures and Characterization Data

Syntheses of Substrates

Synthesis of 1-tosyl-1H-indole-3-carbaldehyde (S1)

Following a previously reported procedure,\textsuperscript{3} a 25 mL oven-dried round bottom flask equipped with a magnetic stir bar was charged with 1H-indole-3-carbaldehyde (0.29 g, 2.0 mmol). The flask was capped with a rubber septum before being evacuated and filled with argon three times. Anhydrous DCM (5 mL) was added, and the reaction flask was cooled to 0 °C, followed by the addition of Et\textsubscript{3}N (0.56 mL, 4.0 mmol). The resulting mixture was stirred at 0 °C for 10 min before TsCl (0.42 g, 2.2 mmol) was added. The solution was allowed to warm to r.t. and stirred for 16 h. After this time, the reaction was quenched with water (10 mL) and saturated aqueous NaHCO\textsubscript{3} (10 mL), and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent removed \textit{in vacuo}. Purification was undertaken by flash silica gel column chromatography using hexane/EtOAc (4:1) as the eluting solvent to give the product as a white solid (0.53 g, 88%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 10.10 (s, 1H), 8.25 (dt, J = 7.7, 1.0 Hz, 1H), 8.23 (s, 1H), 7.95 (dt, J = 8.3, 1.0 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.43 – 7.34 (m, 2H), 7.31 – 7.28 (m, 2H), 2.38 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 185.49, 146.31, 136.36, 135.35, 134.47, 130.47, 127.38, 126.45, 126.42, 125.20, 122.75, 122.50, 113.38, 21.82. MS-ESI m/z 300.0678 ([M + H]\textsuperscript{+}, C\textsubscript{16}H\textsubscript{14}NO\textsubscript{3}S, calc. 300.0689). IR (neat): 2961, 2933, 2873, 1739, 1668, 1539, 1434, 1377.

Synthesis of 1-tosyl-1H-pyrrole-2-carbaldehyde (S2)

Following a previously reported procedure,\textsuperscript{4} a 25 mL oven-dried round bottom flask equipped with a magnetic stir bar was charged with 1H-pyrazole-2-carbaldehyde (0.19 g, 2.0 mmol). The flask was capped with a rubber septum before being evacuated and filled with argon three times. Anhydrous THF (5 mL) was added, and the reaction flask was cooled to 0 °C, followed by the addition of NaH (60% in mineral oil, 0.12 g, 3.0 mmol). The resulting mixture was stirred at 0 °C for 10 min before TsCl (0.57 g, 3.0 mmol) was added. The solution was allowed to warm to r.t. and stirred for 12 h. After this time, the reaction was quenched with water (10 mL) and saturated aqueous NH\textsubscript{4}Cl (10 mL), and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent removed \textit{in vacuo}. Purification was undertaken...
by flash silica gel column chromatography using hexane/EtOAc/DCM (5:1:1) as the eluting solvent to give the product as a light orange solid (0.46 g, 93%). \( ^1 \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 9.97 (s, 1H), 7.85 – 7.75 (m, 2H), 7.62 (dd, \( J = 3.1, 1.8 \text{ Hz}, 1\text{H} \)), 7.32 (dt, \( J = 7.2, 0.9 \text{ Hz}, 2\text{H} \)), 7.16 (dd, \( J = 3.8, 1.7 \text{ Hz}, 1\text{H} \)), 6.40 (t, \( J = 3.4 \text{ Hz}, 1\text{H} \)), 2.42 (s, 3H). \( ^{13} \text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) 179.12, 146.10, 135.33, 133.63, 130.29, 129.58, 127.63, 124.63, 112.54, 21.85. MS-ESI m/z 250.0536 ([M + H]+, \( \text{C}_{12}\text{H}_{12}\text{NO}_{3}\)S, calc. 250.0532). IR (neat): 3137, 3124, 1732, 1689, 1666, 1593, 1538, 1422, 1363, 1250.

Synthesis of 1-cyclopentene-1-carboxaldehyde (S3)

Following a previously reported procedure,\(^5\) to a solution of sodium periodate (28.3 g, 0.13 mol) in water (250 mL) was added an Et\(_2\)O solution (150 mL) of 1,2-cyclohexanediol (12.0 g, 0.103 mol). The solution was stirred for 30 min at r.t., followed by the addition of 20% aqueous KOH (40 mL). The reaction mixture was stirred for 1 h. The layers were separated, and the organic layer was washed with water, brine, dried over Na\(_2\)SO\(_4\) and the solvent removed in vacuo. Kugelrohr distillation (50 °C, 1 mmHg) gave the desired product as a colorless oil (4.5 g, 46%). \( ^1 \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 9.79 (s, 1H), 6.87 (ddd, \( J = 4.4, 2.8, 1.8 \text{ Hz}, 1\text{H} \)), 2.60 (ddt, \( J = 7.7, 5.0, 2.5 \text{ Hz}, 2\text{H} \)), 2.52 (tt, \( J = 6.6, 2.1 \text{ Hz}, 2\text{H} \)), 1.99 (p, \( J = 7.6 \text{ Hz}, 2\text{H} \)). \( ^{13} \text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) 190.04, 153.30, 148.05, 33.81, 28.44, 23.05.

Synthesis of 2-benzylacrylaldehyde (S4)

Following a previously reported procedure,\(^6\) hydrocinnamaldehyde (2.6 mL, 20 mmol), formaldehyde (37% aqueous solution, 1.8 mL, 24 mmol) and dimethylamine hydrochloride (1.96 g, 24 mmol) were placed in a round bottom flask and stirred at 70 °C for 24 h. After cooling to r.t., the reaction was diluted with \( \text{H}_2\text{O} \) (20 mL) and extracted with DCM (3 x 20 mL). The combined organic layer was washed with brine, dried over Na\(_2\)SO\(_4\) and the solvent removed in vacuo. Purification was undertaken by flash silica gel column chromatography using hexane/Et\(_2\)O (25:1) as the eluting solvent to give the product as a colorless oil (1.39 g, 47%). \( ^1 \text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 9.61 (s, 1H), 7.31 (dd, \( J = 8.1, 6.8 \text{ Hz}, 2\text{H} \)), 7.25 – 7.21 (m, 1H), 7.21 – 7.18 (m, 2H), 6.11 (d, \( J = 1.6 \text{ Hz}, 1\text{H} \)), 6.07 (d, \( J = 0.9 \text{ Hz}, 1\text{H} \)), 3.58 (s, 2H). \( ^{13} \text{C NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) 194.09, 149.80, 138.21, 135.34, 129.23, 128.63, 126.53, 34.22. MS-ESI m/z 147.0807 ([M + H]+, \( \text{C}_{10}\text{H}_{11}\text{O} \), calc. 147.0804). IR (neat): 3029, 2928, 2824, 1690, 1496, 1454.
Synthesis of ethyl 5-formylhex-5-enoate (S5)

Following a previously reported procedure, to a solution of oxalyl chloride (1.7 mL, 20 mmol) in DCM (15 mL) was added DMSO (4.3 mL, 60 mmol) dropwise at -78 °C. The solution was stirred for 15 min before ethyl 6-hydroxyhexanoate (1.6 mL, 10 mmol) and Et₃N (15.6 mL, 0.112 mol) were added at the same temperature. The solution was allowed to warm to r.t. followed by the addition of methylene-N,N-dimethylammonium chloride (1.9 g, 20 mmol). After 15 h of stirring at r.t., the mixture was diluted with DCM (30 mL), washed with saturated aqueous NaHCO₃, brine, dried over Na₂SO₄, and the solvent removed in vacuo. Purification was undertaken by flash silica gel column chromatography using hexane/EtOAc (8:1) as the eluting solvent to give the product as a light-yellow oil (1.5 g, 89%).

1H NMR (500 MHz, CDCl₃) δ 9.53 (d, J = 1.7 Hz, 1H), 6.28 (d, J = 1.6 Hz, 1H), 6.03 (s, 1H), 4.15 – 4.08 (m, 2H), 2.33 – 2.26 (m, 4H), 1.84 – 1.75 (m, 2H), 1.24 (td, J = 7.1, 1.7 Hz, 3H).

13C NMR (126 MHz, CDCl₃) δ 194.60, 173.35, 149.43, 134.65, 60.48, 33.79, 27.27, 23.06, 14.36. MS-ESI m/z 193.0825 ([M + Na]⁺, C₉H₁₄NaO₃, calc. 193.0835). IR (neat): 3029, 2938, 2825, 1734, 1694, 1454, 1374, 1245.
Optimization Experiments

**Table S1. Evaluation of Catalysts**

| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|-----------------|
| 1     | none                                 | 58              |
| 2     | no [Cp*IrCl$_2$]$_2$                  | 0               |
| 3     | [Cp*RhCl$_2$]$_2$ instead of [Cp*IrCl$_2$]$_2$ | 26 (mono:di 1:1.6) |
| 4     | [Ru($p$-cymene)Cl$_2$]$_2$ instead of [Cp*IrCl$_2$]$_2$ | 4 (mono) |

**Table S2. Evaluation of Additives**

| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|-----------------|
| 1     | none                                 | 58              |
| 2     | AgSbF$_6$ instead of AgNTf$_2$        | 44              |
| 3     | AgPF$_6$ instead of AgNTf$_2$         | 50              |
| 4     | AgBF$_4$ instead of AgNTf$_2$         | 32              |

**Table S3. Evaluation of Oxidants**
| entry | variation from the standard condition | yield of 1c (%) |
|-------|---------------------------------------|-----------------|
| 1     | none                                  | 58              |
| 2     | AgOAc instead of AgF                  | 0               |
| 3     | AgTFA instead of AgF                  | 0               |
| 4     | AgOTs instead of AgF                  | 36 (mono:di 1:5) |
| 5     | AgOTf instead of AgF                  | 10              |
| 6     | Ag$_2$CO$_3$ instead of AgF           | 0               |
| 7     | Ag$_3$PO$_4$ instead of AgF           | 18              |
| 8     | PhI(OAc)$_2$ instead of AgF           | 0               |
| 9     | benzoquinone instead of AgF           | 0               |
| 10    | K$_2$S$_2$O$_8$ instead of AgF        | 10              |
| 11    | Oxone® instead of AgF                 | 0               |
| 12    | 2,4,6-trimethyl-F-pyridinium OTf instead of AgF | 46 |
| 13    | 2,4,6-trimethyl-F-pyridinium BF$_4$ instead of AgF | 8 |
| 14    | NFSI instead of AgF                   | 40              |
| 15    | Selectfluor® instead of AgF           | 30              |
| 16    | Ce(SO$_4$)$_2$ instead of AgF         | 6               |
| 17    | Cu(OAc)$_2$ instead of AgF            | 6               |

Table S4. Evaluation of Catalyst/Additive Loadings and Reaction Time

| entry | variation from the standard condition | yield of 1c (%) |
|-------|---------------------------------------|-----------------|
| 1     | none                                  | 58              |
| 2     | [Cp*IrCl$_2$)$_2$ (4 mol%), AgNTf$_2$ (16 mol %), 24 h | 68              |
Table S5. Evaluation of Solvents

| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|----------------|
| 1     | none                                 | 68             |
| 2     | DCE/HFIP (9:1) instead of DCE         | 10             |
| 3     | with 5 equiv of TFA                  | 12 (mono:di 2:1)|
| 4     | HFIP instead of DCE                  | 0              |
| 5     | PhCl instead of DCE                  | 52             |
| 6     | PhCF₃ instead of DCE                 | 50             |
| 7     | toluene instead of DCE               | 30             |
| 8     | DCM instead of DCE                   | 36             |
| 9     | chloroform instead of DCE            | 40             |
| 10    | MeCN instead of DCE                  | 0              |
| 11    | THF instead of DCE                   | 58             |
| 12    | 1,4-dioxane instead of DCE           | 42             |
| 13    | DMF instead of DCE                   | 0              |
| 14    | MeOH instead of DCE                  | 0              |
| 15    | AcOH instead of DCE                  | 72 (mono:di 1:17)|
Table S6. Evaluation of Catalytic Ligands

\[
\begin{align*}
\text{Br} & \quad \text{H} & \quad \text{O} & \quad \text{Br} & \quad \text{n-Bu} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{n-Bu}
\end{align*}
\]

\[
\begin{align*}
\text{L1} \ (62\%) & \quad \text{L2} \ (60\%) & \quad \text{L3} \ (22\%) & \quad \text{L4} \ (50\%) & \quad \text{L5} \ (56\%)
\end{align*}
\]

\[
\begin{align*}
\text{L6} \ (50\%) & \quad \text{L7} \ (68\%) & \quad \text{L8} \ (16\%) & \quad \text{L9} \ (12\%) & \quad \text{L10} \ (38\%)
\end{align*}
\]

\[
\begin{align*}
\text{L11} \ (32\%) & \quad \text{L12} \ (30\%) & \quad \text{L13} \ (30\%) & \quad \text{L14} \ (6\%) & \quad \text{No TDG} \ (0\%)
\end{align*}
\]

Table S7. Evaluation of the Reaction Concentration and Temperature

\[
\begin{align*}
\text{Br} & \quad \text{H} & \quad \text{O} & \quad \text{Br} & \quad \text{n-Bu} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{n-Bu}
\end{align*}
\]

\[
\begin{align*}
\text{L7}
\end{align*}
\]
| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|----------------|
| 1     | none                                 | 68             |
| 2     | 0.15 M instead of 0.1 M              | 62             |
| 3     | 0.2 M instead of 0.1 M               | 50             |
| 4     | 0.067 M instead of 0.1 M             | 68             |
| 5     | 60 ºC instead of 80 ºC               | 40             |
| 6     | 100 ºC instead of 80 ºC              | 72             |

**Table S8. Evaluation of the Amounts of AgF and n-BuBF₃K**

![Chemical structure](image)

| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|----------------|
| 1     | none                                 | 72             |
| 2     | AgF (4 equiv), n-BuBF₃K (3 equiv)    | 78 (94)        |

[a] AcOH (0.1 M) was used as the reaction solvent

**Table S9. Evaluation of Scale-up Reactions**

![Chemical structure](image)

| entry | variation from the standard condition | yield of 1c (%) |
|-------|--------------------------------------|----------------|
| 1     | None (0.1 mmol scale)                | 94             |
| 2     | 0.3 mmol scale                       | 88             |
| 3     | 0.3 mmol scale (20 mL scintillation vial with a cross-shaped stir-bar) | 94             |
Standard Procedures

General Procedure for the Optimization Experiments (using Table S8, entry 2 as an example)

A 10-mL oven-dried microwave-vial equipped with a magnetic stir bar was charged with \([\text{Cp}^*\text{IrCl}_2]_2\) (3.2 mg, 0.004 mmol), 4-bromobenzaldehyde (18.5 mg, 0.10 mmol), AgF (50.8 mg, 0.40 mmol) and \(n\)-BuBF\(_3\)K (49.2 mg, 0.30 mmol). The vial was transferred to a glovebox filled with N\(_2\), wherein AgNTf\(_2\) (6.2 mg, 0.016 mmol) and aniline (1.8 \(\mu\)L, 0.020 mmol) were added. The vial was sealed with a PTFE-lined aluminum cap and taken out of the glovebox. Degassed DCE or AcOH (1 mL) was added through a syringe, and the vial was heated in a pie-block at 100 ºC under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite\(^\circ\) and washed with EtOAc (10 mL). The filtrate was then concentrated \textit{in vacuo} before CH\(_2\)Br\(_2\) (6.95 \(\mu\)L, 0.1 mmol) was added. The yield of the desired product was determined by crude \(^1\)H NMR using CH\(_2\)Br\(_2\) as the internal standard.

Note: All control experiments were conducted on a 0.1 mmol scale unless otherwise noted, and changes were made based on the “standard condition” described above.

General Procedure A for the (Hetero)aromatic Aldehyde Substrate Scope Experiments (using 1a as an example)

\[
\text{[Cp}^*\text{IrCl}_2]_2 (4 \text{ mol %}) \quad \text{AgNTf}_2 (16 \text{ mol %}) \quad \text{L7 (20 mol %)} \\
\text{n-BuBF}_3\text{K (3.0 equiv)} \quad \text{AgF (4.0 equiv)} \quad \text{AcOH (0.1 M)} \quad 100 \degree \text{C}, \text{N}_2, 24 \text{ h}
\]

A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with \([\text{Cp}^*\text{IrCl}_2]_2\) (9.6 mg, 0.012 mmol), AgF (0.152 g, 1.20 mmol) and \(n\)-BuBF\(_3\)K (0.147 g, 0.90 mmol). The vial was transferred to a glovebox filled with N\(_2\), wherein AgNTf\(_2\) (18.6 mg, 0.048 mmol), 4-fluorobenzaldehyde (32.2 \(\mu\)L, 0.30 mmol) and aniline (5.6 \(\mu\)L, 0.060 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed AcOH (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 ºC under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite\(^\circ\) and washed with EtOAc (15 mL). The filtrate was then concentrated \textit{in vacuo} and the resulting residue was purified by flash silica gel column chromatography using hexane/Et\(_2\)O (50:1) as the eluting solvent.
General Procedure B for the Potassium Alkyl Trifluoroborate Scope Experiments (using 3a as an example)

A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with \([\text{Cp}^*\text{IrCl}_2]_2\) (9.6 mg, 0.012 mmol), 2-chloroisocoticinaldehyde (42.5 mg, 0.30 mmol), AgF (0.152 g, 1.20 mmol) and \(n\)-BuBF\(_3\)K (0.147 g, 0.90 mmol). The vial was transferred to a glovebox filled with N\(_2\), wherein AgNTf\(_2\) (18.6 mg, 0.048 mmol) and aniline (5.6 \(\mu\)L, 0.060 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed AcOH (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite\(^\circledR\) and washed with EtOAc (15 mL). The filtrate was then concentrated \textit{in vacuo} and the resulting residue was purified by flash silica gel column chromatography using hexane/Et\(_2\)O (10:1) as the eluting solvent.

General Procedure C for the \(\alpha,\beta\)-Unsaturated Aldehyde Scope Experiments (using 4a as an example)

A 20-mL oven-dried scintillation vial equipped with a cross-shaped stir bar was charged with \([\text{Cp}^*\text{IrCl}_2]_2\) (12.0 mg, 0.015 mmol), AgF (0.114 g, 0.90 mmol), crotonic acid (7.7 mg, 0.09 mmol) and \(n\)-BuBF\(_3\)K (98.4 mg, 0.60 mmol). The vial was transferred to a glovebox filled with N\(_2\), wherein AgNTf\(_2\) (23.3 mg, 0.060 mmol), 1-cyclopentene-1-carboxaldehyde (29.5 \(\mu\)L) and 4-(trifluoromethyl)aniline (11.3 \(\mu\)L, 0.090 mmol) were added. The vial was capped tightly with a PTFE-lined green cap and taken out of the glovebox. Degassed DCE (3 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 24 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite\(^\circledR\) and washed with EtOAc (15 mL). The filtrate was then concentrated \textit{in vacuo} and the resulting residue was purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the eluting solvent.
Substrate Scope Experiments

This compound was synthesized from 4-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (50:1) as the eluting solvent to give the product as a yellow oil (60.3 mg, 85%). \( ^1H \) NMR (500 MHz, CDCl₃) δ 10.48 (s, 1H), 6.79 (d, \( J = 9.4 \) Hz, 2H), 3.06 – 2.73 (m, 4H), 1.67 – 1.49 (m, 4H), 1.40 (q, \( J = 7.4 \) Hz, 4H), 0.94 (t, \( J = 7.3 \) Hz, 6H). \( ^13C \) NMR (126 MHz, CDCl₃) δ 191.98, 164.82 (d, \( J = 254.8 \) Hz), 150.13 (d, \( J = 8.8 \) Hz), 128.41 (d, \( J = 2.7 \) Hz), 115.66 (d, \( J = 20.8 \) Hz), 34.36, 33.58 (d, \( J = 1.4 \) Hz), 22.79, 14.04. \(^{19}F\) NMR (282 MHz, CDCl₃) δ -105.91 (t, \( J = 9.5 \) Hz). MS-ESI m/z 237.1645 ([M + H]⁺, C₁₅H₂₂FO, calc. 237.1649). IR (neat): 2960, 2933, 2874, 1694, 1596, 1459, 1282.

This compound was synthesized from 4-chlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (50:1) as the eluting solvent to give the product as a light-yellow oil (65.9 mg, 87%). \( ^1H \) NMR (500 MHz, CDCl₃) δ 10.48 (s, 1H), 7.08 (s, 2H), 2.96 – 2.76 (m, 4H), 1.55 (ddt, \( J = 10.1, 7.9, 3.5 \) Hz, 4H), 1.46 – 1.35 (m, 4H), 0.93 (t, \( J = 7.3 \) Hz, 6H). \( ^13C \) NMR (126 MHz, CDCl₃) δ 192.45, 148.17, 138.66, 130.33, 128.87, 34.45, 33.29, 22.79, 14.01. MS-ESI m/z 253.1342 ([M + H]⁺, C₁₅H₂₂ClO, calc. 253.1354). IR (neat): 2959, 2932, 2873, 1695, 1579, 1465, 1403.

This compound was synthesized from 4-bromobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (50:1) as the eluting solvent to give the product as a light-yellow solid (83.5 mg, 94%). \( ^1H \) NMR (500 MHz, CDCl₃) δ 10.49 (s, 1H), 7.26 (s, 2H), 2.96 – 2.80 (m, 4H), 1.66 – 1.48 (m, 4H), 1.39 (q, \( J = 7.4 \) Hz, 4H), 0.94 (t, \( J = 7.3 \) Hz, 6H). \( ^13C \) NMR (126 MHz, CDCl₃) δ 192.75, 148.15, 131.87, 130.79, 127.65, 34.52, 33.24, 22.82, 14.03. MS-ESI m/z 297.0839 ([M + H]⁺, C₁₅H₂₂BrO, calc. 297.0849). IR (neat): 2959, 2931, 2872, 1695, 1579, 1465, 1403.
This compound was synthesized from 4-(trifluoromethyl)benzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et2O (50:1) as the eluting solvent to give the product as a light-yellow solid (76.6 mg, 89%). 1H NMR (500 MHz, CDCl3) δ 10.59 (s, 1H), 7.34 (s, 2H), 2.98 – 2.88 (m, 4H), 1.58 (td, J = 7.5, 6.9, 3.9 Hz, 4H), 1.46 – 1.36 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 193.27, 146.46, 135.09 (q, J = 1.2 Hz), 133.70 (q, J = 32.2 Hz), 125.45 (q, J = 272.9 Hz), 34.55, 33.33, 22.82, 13.97. 19F NMR (282 MHz, CDCl3) δ -63.36. MS-ESI m/z 287.1609 ([M + H]+, C16H22F3O, calc. 287.1617). IR (neat): 2959, 2935, 2874, 2862, 1697, 1578, 1466, 1411, 1350, 1323.

This compound was synthesized from methyl-4-formylbenzoate following general procedure A and purified by flash silica gel column chromatography using hexane/Et2O (33:1) as the eluting solvent to give the product as a white solid (82.5 mg, 99%). 1H NMR (500 MHz, CDCl3) δ 10.59 (s, 1H), 7.74 (s, 2H), 3.93 (s, 3H), 3.02 – 2.82 (m, 4H), 1.62 – 1.53 (m, 4H), 1.40 (h, J = 7.4 Hz, 4H), 0.93 (t, J = 7.3 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 193.80, 166.60, 145.83, 135.78, 133.06, 129.76, 52.53, 34.62, 33.28, 22.83, 14.04. MS-ESI m/z 277.1793 ([M + H]+, C17H22O3, calc. 277.1798). IR (neat): 2958, 2932, 2873, 1727, 1697, 1570, 1458, 1436, 1297.

This compound was synthesized from 4-formylbenzonitrile following general procedure A and purified by flash silica gel column chromatography using hexane/Et2O (50:1) as the eluting solvent to give the product as a yellow oil (25.3 mg, 35%). 1H NMR (500 MHz, CDCl3) δ 10.56 (s, 1H), 7.38 (s, 2H), 2.96 – 2.83 (m, 4H), 1.56 (tt, J = 7.9, 6.5 Hz, 4H), 1.39 (dq, J = 14.6, 7.4 Hz, 4H), 0.93 (t, J = 7.4 Hz, 6H). 13C NMR (126 MHz, CDCl3) δ 193.05, 146.30, 135.90, 132.04, 118.28, 115.70, 34.30, 32.93, 22.71, 13.97. MS-ESI m/z 244.1692 ([M + H]+, C16H22NO, calc. 244.1696). IR (neat): 2959, 2932, 2873, 2727, 1697, 1570, 1458, 1436, 1297.
This compound was synthesized from 3-(trifluoromethyl)benzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K, and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a light-yellow oil (58.8 mg, 85%). 

\[
\text{IR (neat): 2962, 2935, 2875, 1710, 1618, 1577, 1467, 1333, 1270.}
\]

\[
\text{MS-ESI m/z 231.0993 ([M + H]^+}, \text{ C}_{12}\text{H}_{14}\text{F}_3\text{O, calc. 231.0991}). \text{ IR (neat): 2962, 2935, 2875, 1710, 1618, 1577, 1467, 1333, 1270.}
\]

This compound was synthesized from methyl-3-formylbenzoate following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K, and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a light-yellow oil (59.9 mg, 91%). 

\[
\text{IR (neat): 2958, 2933, 2873, 1727, 1705, 1609, 1437, 1293, 1262.}
\]

This compound was synthesized from 4-bromo-3-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (50:1) as the eluting solvent to give the product as a light-yellow oil (82.3 mg, 87%). 

\[
\text{IR (neat): 2958, 2933, 2873, 1727, 1705, 1609, 1437, 1293, 1262.}
\]
This compound was synthesized from 3,4-dichlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et$_2$O (50:1) as the eluting solvent to give the product as a white solid (77.7 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.45 (s, 1H), 7.24 (s, 1H), 3.10 – 3.03 (m, 2H), 2.85 – 2.79 (m, 2H), 1.54 (qt, $J$ = 7.5, 3.2 Hz, 4H), 1.46 (q, $J$ = 7.3 Hz, 2H), 1.39 (dt, $J$ = 14.9, 7.3 Hz, 2H), 0.94 (dt, $J$ = 15.1, 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.68, 145.03, 144.76, 137.49, 132.42, 131.46, 130.32, 34.26, 32.87, 32.51, 30.36, 23.03, 22.75, 13.99, 13.93. MS-ESI m/z 287.0960 ([M + H]$^+$, C$_{15}$H$_{21}$ClO, calc. 287.0964). IR (neat): 2953, 2927, 2871, 1693, 1562, 1464, 1378.

This compound was synthesized from 4-bromo-3-chlorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et$_2$O (50:1) as the eluting solvent to give the product as a light-yellow solid (86.4 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.45 (s, 1H), 7.42 (s, 1H), 3.16 – 3.01 (m, 2H), 2.88 – 2.73 (m, 2H), 1.58 – 1.50 (m, 4H), 1.49 – 1.41 (m, 2H), 1.37 (dt, $J$ = 14.6, 7.4 Hz, 2H), 0.94 (dt, $J$ = 14.8, 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.89, 144.75, 144.74, 133.68, 133.29, 133.09, 128.42, 34.31, 32.79, 32.51, 30.78, 23.03, 22.76, 14.00, 13.94. MS-ESI m/z 331.0453 ([M + H]$^+$, C$_{15}$H$_{21}$BrClO, calc. 331.0459). IR (neat): 2956, 2928, 2871, 1693, 1562, 1464, 1375.
This compound was synthesized from 3-bromo-4-fluorobenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (50:1) as the eluting solvent to give the product as a light-yellow oil (82.8 mg, 88%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.43 (s, 1H), 6.90 (d, \(J = 9.1\) Hz, 1H), 3.16 – 3.06 (m, 2H), 2.93 – 2.83 (m, 2H), 1.55 (dddd, \(J = 16.0, 9.0, 7.9, 3.4\) Hz, 4H), 1.51 – 1.44 (m, 2H), 1.39 (hd, \(J = 7.3\) Hz, 2H), 0.95 (dt, \(J = 18.8, 7.3\) Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 192.09, 161.11 (d, \(J = 253.8\) Hz), 147.92 (d, \(J = 1.1\) Hz), 147.80 (d, \(J = 8.7\) Hz), 130.16 (d, \(J = 3.0\) Hz), 116.31 (d, \(J = 22.9\) Hz), 111.01 (d, \(J = 19.6\) Hz), 34.12, 33.23 (d, \(J = 1.4\) Hz), 32.70, 32.08 (d, \(J = 2.4\) Hz), 23.02, 22.73, 14.01, 13.95. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -95.11 (d, \(J = 9.1\) Hz). MS-ESI m/z 315.0748 ([M + H]\(^+\), \(\text{C}_{15}\text{H}_{21}\text{BrFO}\), calc. 315.0754). IR (neat): 2958, 2930, 2872, 1697, 1571, 1456, 1379, 1297.

This compound was synthesized from 3-fluoro-4-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a light-yellow solid (71.3 mg, 89%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.37 (d, \(J = 0.9\) Hz, 1H), 6.64 (d, \(J = 8.0\) Hz, 1H), 3.93 (s, 3H), 2.99 (td, \(J = 7.9, 2.7\) Hz, 2H), 2.93 – 2.89 (m, 2H), 1.55 (ddq, \(J = 10.6, 7.6, 5.6\) Hz, 4H), 1.41 (hd, \(J = 7.3, 3.5\) Hz, 4H), 0.94 (td, \(J = 7.3, 4.4\) Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 191.34 (d, \(J = 2.8\) Hz), 151.08 (d, \(J = 12.3\) Hz), 148.81 (d, \(J = 241.9\) Hz), 144.40 (d, \(J = 3.9\) Hz), 134.09 (d, \(J = 13.0\) Hz), 124.77 (d, \(J = 2.4\) Hz), 112.43 (d, \(J = 1.9\) Hz), 56.16, 34.95 (d, \(J = 1.1\) Hz), 33.69, 33.41, 24.52 (d, \(J = 5.4\) Hz), 22.88, 14.07, 14.02. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -141.13 – -145.92 (m). MS-ESI m/z 267.1744 ([M + H]\(^+\), \(\text{C}_{16}\text{H}_{24}\text{FO}_2\), calc. 267.1755). IR (neat): 2957, 2928, 2871, 1688, 1602, 1564, 1492, 1463, 1300.

This compound was synthesized from 4-methoxy-3-(trifluoromethyl)benzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O.
(20:1) as the eluting solvent to give the product as a yellow oil (77.4 mg, 99%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.13 (s, 1H), 8.04 (s, 1H), 6.83 (s, 1H), 3.97 (s, 3H), 3.08 – 3.02 (m, 2H), 1.60 (tt, $J = 7.9$, 5.7 Hz, 2H), 1.42 (h, $J = 7.4$ Hz, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 189.67, 161.12 (q, $J = 1.5$ Hz), 152.71 (d, $J = 1.0$ Hz), 131.26 (q, $J = 5.1$ Hz), 126.36, 123.22 (q, $J = 272.2$ Hz), 117.29 (q, $J = 31.9$ Hz), 113.81, 56.33, 34.30, 32.75, 22.76, 13.94. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -62.65. MS - ESI m/z 261.1088 ([M + H]$^+$, C$_{13}$H$_{16}$F$_3$O$_2$, calc. 261.1097). IR (neat): 2960, 2934, 2874, 1700, 1619, 1568, 1505, 1467, 1427, 1396, 1335, 1306, 1257.

This compound was synthesized from methyl 5-formyl-2-methoxybenzoate following general procedure A and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (74.0 mg, 99%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.07 (s, 1H), 8.28 (s, 1H), 6.79 (s, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.05 – 2.97 (m, 2H), 1.62 – 1.52 (m, 2H), 1.39 (h, $J = 7.3$ Hz, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 190.31, 165.45, 162.85, 152.61, 137.14, 126.54, 117.98, 113.90, 56.36, 52.19, 33.98, 32.99, 22.72, 13.93. MS-ESI m/z 251.1263 ([M + H]$^+$, C$_{14}$H$_{19}$O$_4$, calc. 251.1278). IR (neat): 2957, 2872, 1733, 1696, 1607, 1558, 1499, 1465, 1436, 1384, 1328, 1262.

This compound was synthesized from 4-fluoro-3-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et$_2$O (33:1) as the eluting solvent to give the product as a light-yellow oil (41.0 mg, 51%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.42 (s, 1H), 6.83 (d, $J = 12.1$ Hz, 1H), 3.90 (d, $J = 1.5$ Hz, 3H), 2.98 – 2.93 (m, 2H), 2.87 – 2.83 (m, 2H), 1.58 – 1.46 (m, 4H), 1.46 – 1.34 (m, 4H), 0.97 – 0.90 (m, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.44, 158.02 (d, $J = 255.6$ Hz), 144.10 (d, $J = 10.3$ Hz), 143.23 (d, $J = 8.2$ Hz), 141.94 (d, $J = 3.5$ Hz), 128.88 (d, $J = 2.9$ Hz), 116.72 (d, $J = 19.2$ Hz), 61.68 (d, $J = 5.7$ Hz), 34.35, 34.25, 33.11 (d, $J = 1.2$ Hz), 25.59 (d, $J = 2.4$ Hz), 23.14, 22.77, 14.06, 14.03. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -121.66 (d, $J = 12.1$ Hz). MS-ESI m/z 267.1741 ([M + H]$^+$, C$_{18}$H$_{24}$FO$_2$, calc. 267.1755). IR (neat): 2959, 2933, 2873, 1695, 1579, 1480, 1310.
This compound was synthesized from 4-chloro-3-methoxybenzaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtO (33:1) as the eluting solvent to give the product as a light-yellow oil (35.3 mg, 42%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.44 (s, 1H), 7.13 (s, 1H), 3.84 (s, 3H), 2.98 – 2.92 (m, 2H), 2.86 – 2.81 (m, 2H), 1.58 – 1.47 (m, 4H), 1.47 – 1.34 (m, 4H), 0.94 (td, $J$ = 7.3, 6.1 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.88, 152.79, 142.62, 141.23, 132.80, 131.88, 130.34, 61.32, 34.52, 34.44, 32.92, 26.10, 23.21, 22.80, 14.05, 13.99. MS-ESI m/z 283.1448 ([M + H]$^+$, C$_{16}$H$_{24}$ClO$_2$, calc. 283.1459). IR (neat): 2959, 2932, 2872, 1695, 1576, 1556, 1464, 1394, 1263.

This compound was synthesized from 4-chloro-2-fluorobenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a light-yellow oil (41.3 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.44 (s, 1H), 7.11 – 7.00 (m, 2H), 3.01 – 2.91 (m, 2H), 1.57 – 1.50 (m, 2H), 1.45 – 1.36 (m, 2H), 0.94 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 188.02 (d, $J$ = 10.5 Hz), 166.19 (d, $J$ = 261.0 Hz), 149.02, 140.48 (d, $J$ = 12.6 Hz), 127.24 (d, $J$ = 3.4 Hz), 120.80 (d, $J$ = 5.2 Hz), 114.72 (d, $J$ = 25.4 Hz), 33.34, 33.33, 22.80, 14.02. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -116.55 – -120.63 (m). MS-ESI m/z 215.0625 ([M + H]$^+$, C$_{11}$H$_{13}$ClFO, calc. 215.0633). IR (neat): 2959, 2930, 2873, 1700, 1601, 1564, 1465, 1408, 1263.

This compound was synthesized from 4-bromo-2-fluorobenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a light-yellow oil (74.2 mg, 95%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.44 (s, 1H), 7.24 – 7.19 (m, 2H), 2.99 – 2.94 (m, 2H), 1.57 – 1.49 (m, 2H), 1.44 – 1.36 (m, 2H), 0.94 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR
This compound was synthesized from 2-fluoro-4-methoxybenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K, and purified by preparative thin layer chromatography using hexane/EtOAc (15:1) as the eluting solvent to give the product as a light-yellow oil (47.2 mg, 75%). ¹H NMR (500 MHz, CDCl₃) δ 10.34 (d, J = 1.6 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 6.48 (dt, J = 12.9, 2.1 Hz, 1H), 3.84 (d, J = 1.7 Hz, 3H), 3.02–2.92 (m, 2H), 1.56–1.47 (m, 2H), 1.39 (h, J = 7.0 Hz, 2H), 0.92 (td, J = 7.3, 1.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 187.50 (d, J = 10.6 Hz), 168.29 (d, J = 257.7 Hz), 164.73 (d, J = 13.5 Hz), 149.42 (d, J = 1.7 Hz), 115.83 (d, J = 4.9 Hz), 112.95 (d, J = 2.6 Hz), 99.13 (d, J = 25.7 Hz), 55.85, 33.88 (d, J = 2.3 Hz), 33.32, 22.80, 14.04. ¹⁹F NMR (282 MHz, CDCl₃) δ -117.68 (d, J = 13.0 Hz). MS-ESI m/z 211.1121 ([M + H]+, C₁₂H₁₆FO₂, calc. 211.1129). IR (neat): 2958, 2932, 2872, 1693, 1570, 1464, 1435, 1419, 1338, 1283.

This compound was synthesized from 4-bromo-2-methylbenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K, and purified by preparative thin layer chromatography using hexane/EtOAc (20:1) as the eluting solvent to give the product as a yellow oil (17.8 mg, 23%). ¹H NMR (500 MHz, CDCl₃) δ 10.52 (s, 1H), 7.26 (s, 2H), 2.94–2.86 (m, 2H), 2.56 (s, 3H), 1.62–1.52 (m, 2H), 1.39 (h, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 192.67, 148.36, 143.05, 132.75, 131.88, 131.02, 127.75, 34.72, 32.92, 22.77, 20.91, 14.00. MS-ESI m/z 255.0383 ([M + H]+, C₁₂H₁₆BrO, calc. 255.0379). IR (neat): 2958, 2930, 2872, 1693, 1574, 1464, 1380, 1241.
This compound was synthesized from 4-fluoro-2-methoxybenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\(^3\)K, and purified by flash silica gel column chromatography using hexane/Et\(_2\)O (33:1) as the eluting solvent to give the product as a light-yellow oil (52.6 mg, 83\%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.50 (s, 1H), 6.53 (s, 1H), 6.51 (s, 1H), 3.87 (s, 3H), 2.96 – 2.91 (m, 2H), 1.51 (p, \(J = 8.1, 7.6\) Hz, 2H), 1.38 (h, \(J = 7.3\) Hz, 2H), 0.92 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 190.62, 166.27 (d, \(J = 254.7\) Hz), 165.29 (d, \(J = 11.4\) Hz), 150.32 (d, \(J = 10.4\) Hz), 119.67 (d, \(J = 2.8\) Hz), 110.05 (d, \(J = 21.1\) Hz), 97.26 (d, \(J = 25.5\) Hz), 56.17, 33.94 (d, \(J = 1.7\) Hz), 33.27, 22.83, 14.05. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -101.47 (t, \(J = 10.1\) Hz). MS-ESI m/z 211.1137 ([M + H]\(^+\), C\(_{12}\)H\(_{16}\)FO\(_2\), calc. 211.1129). IR (neat): 2959, 2934, 2873, 1687, 1593, 1458, 1429, 1409, 1311.

This compound was synthesized from 2-methoxy-4-(trifluoromethyl)benzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\(^3\)K, and purified by flash silica gel column chromatography using hexane/Et\(_2\)O (33:1) as the eluting solvent to give the product as a yellow oil (67.9 mg, 87\%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.60 (s, 1H), 7.08 (s, 1H), 7.03 (d, \(J = 1.6\) Hz, 1H), 3.94 (s, 3H), 2.98 – 2.89 (m, 2H), 1.58 – 1.48 (m, 2H), 1.39 (h, \(J = 7.3\) Hz, 2H), 0.93 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 191.73, 162.97, 147.86, 135.26 (q, \(J = 32.4\) Hz), 125.56 (d, \(J = 1.3\) Hz), 123.51 (q, \(J = 273.1\) Hz), 119.94 (q, \(J = 3.8\) Hz), 105.91 (q, \(J = 3.8\) Hz), 56.20, 33.63, 22.89, 14.01. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -63.57. MS-ESI m/z 261.1091 ([M + H]\(^+\), C\(_{13}\)H\(_{16}\)FO\(_2\), calc. 261.1097). IR (neat): 2960, 2935, 2874, 1696, 1582, 1477, 1459, 1427, 1409, 1347, 1327, 1304.

This compound was synthesized from 2-methoxy-4-nitrobenzaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\(^3\)K, and purified by flash silica
gel column chromatography using hexane/EtO (25:1) as the eluting solvent to give the product as a yellow solid (66.5 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.58 (s, 1H), 7.68 (d, $J = 2.0$ Hz, 1H), 7.64 (d, $J = 2.1$ Hz, 1H), 4.00 (s, 3H), 3.03 – 2.87 (m, 2H), 1.58 – 1.50 (m, 2H), 1.39 (h, $J = 7.3$ Hz, 2H), 0.92 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 191.34, 163.06, 150.63, 148.36, 127.53, 117.82, 104.04, 56.57, 33.56, 33.42, 22.77, 13.96. MS-ESI m/z 238.1073 ([M + H]$^+$, C$_{12}$H$_{16}$NO, calc. 238.1074). IR (neat): 3101, 2963, 2944, 2896, 2875, 2855, 1684, 1590, 1530, 1474, 1456, 1429, 1401, 1349, 1331, 1299, 1277.

This compound was synthesized from 2-fluoroisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtO (20:1) as the eluting solvent to give the product as a light-yellow oil (17.7 mg, 25%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.51 (s, 1H), 7.98 (s, 1H), 2.95 – 2.69 (m, 4H), 1.59 – 1.50 (m, 4H), 1.40 (ddt, $J = 14.8$, 11.5, 7.3 Hz, 4H), 0.93 (td, $J = 7.3$, 3.1 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.47 (d, $J = 4.1$ Hz), 161.64 (d, $J = 237.7$ Hz), 146.75 (d, $J = 14.2$ Hz), 142.68 (d, $J = 4.4$ Hz), 135.57 (d, $J = 5.2$ Hz), 124.71 (d, $J = 31.5$ Hz), 34.44 (d, $J = 1.2$ Hz), 33.06, 29.53, 24.71, 22.81, 22.63, 13.93, 13.91. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -76.11. MS-ESI m/z 238.1600 ([M + H]$^+$, C$_{14}$H$_{21}$FNO, calc. 238.1602). IR (neat): 2961, 2933, 2874, 1708, 1592, 1560, 1457, 1397, 1282.

This compound was synthesized from 2-chloroisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtO (33:1) as the eluting solvent to give the product as a yellow oil (64.3 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.95 – 2.89 (m, 2H), 2.80 – 2.74 (m, 2H), 1.59 – 1.48 (m, 4H), 1.43 (dt, $J = 14.7$, 7.3 Hz, 2H), 1.35 (dt, $J = 14.6$, 7.4 Hz, 2H), 0.92 (dt, $J = 15.7$, 7.3 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.92, 151.08, 149.32, 141.58, 136.51, 135.98, 34.16, 32.33, 29.57, 28.96, 22.95, 22.62, 13.87, 13.84. MS-ESI m/z 254.1296 ([M + H]$^+$, C$_{14}$H$_{21}$ClNO, calc. 254.1306). IR (neat): 2960, 2932, 2873, 1709, 1545, 1466, 1371.
This compound was synthesized from 2-bromoisonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a yellow oil (67.0 mg, 75%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 10.46 (s, 1H), 8.14 (s, 1H), 2.94 – 2.87 (m, 2H), 2.77 – 2.71 (m, 2H), 1.53 (ddtd, J = 15.4, 9.9, 7.5, 5.5 Hz, 4H), 1.47 – 1.39 (m, 2H), 1.36 (h, J = 7.3 Hz, 2H), 0.92 (dt, J = 19.9, 7.3 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 192.93, 149.84, 144.28, 141.36, 138.08, 136.76, 34.07, 32.44, 31.21, 29.52, 22.96, 22.61, 13.86, 13.83. MS-ESI m/z 298.0814 ([M + H]\(^+\), C\(_{14}\)H\(_{21}\)BrNO, calc. 298.0801). IR (neat): 2959, 2931, 2873, 1708, 1542, 1465, 1430, 1367.

This compound was synthesized from isonicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a light-yellow oil (65.3 mg, 99%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 10.54 (s, 1H), 8.39 (s, 2H), 2.90 – 2.78 (m, 4H), 1.57 – 1.50 (m, 4H), 1.36 (h, J = 7.4 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 193.26, 150.19, 137.99, 137.58, 34.43, 29.98, 22.67, 13.88. MS-ESI m/z 220.1686 ([M + H]\(^+\), C\(_{14}\)H\(_{22}\)NO, calc. 220.1696). IR (neat): 2959, 2931, 2873, 1706, 1465, 1414.

This compound was synthesized from 6-chloronicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a light-yellow oil (10.6 mg, 14%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 10.51 (s, 1H), 7.09 (s, 1H), 3.09 – 3.03 (m, 2H), 2.93 – 2.87 (m, 2H), 1.72 – 1.63 (m, 2H), 1.61 – 1.52 (m, 2H), 1.47 – 1.36 (m, 4H), 0.94 (td, J = 7.3, 2.1 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 191.51, 166.59, 157.58, 154.05, 126.72, 123.85, 35.65, 33.15, 33.04, 32.89, 22.90, 22.80, 14.02, 13.96. MS-ESI m/z 254.1296 ([M + H]\(^+\), C\(_{14}\)H\(_{21}\)ClNO, calc. 254.1306). IR (neat): 2963, 2935, 2874, 1700, 1596, 1566, 1546, 1466, 1379.
This compound was synthesized from 6-(trifluoromethyl)nicotinaldehyde following general procedure A and purified by flash silica gel column chromatography using hexane/EtO (50:1) as the eluting solvent to give the product as a yellow oil (62.8 mg, 73%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.60 (s, 1H), 7.41 (s, 1H), 3.15 – 3.08 (m, 2H), 2.99 – 2.92 (m, 2H), 1.73 – 1.64 (m, 2H), 1.59 (tt, $J = 7.9, 6.5$ Hz, 2H), 1.42 (hd, $J = 7.4, 2.4$ Hz, 4H), 0.94 (td, $J = 7.4, 5.2$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.05, 165.33, 156.21, 149.67 (q, $J = 34.3$ Hz), 130.19 (d, $J = 1.1$ Hz), 121.20 (q, $J = 274.8$ Hz), 120.24 (q, $J = 2.9$ Hz), 35.71, 33.41, 33.04, 32.76, 22.82, 13.97, 13.91. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -68.62. MS - ESI m/z 288.1580 ([M + H]$^+$, C$_{15}$H$_{21}$F$_3$NO, calc. 288.1570). IR (neat): 2961, 2934, 2875, 1704, 1593, 1563, 1458, 1390, 1360.

This compound was synthesized from 4-quinolinecarboxaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K, and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (53.6 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.89 (s, 1H), 8.86 (s, 1H), 8.69 (dd, $J = 8.4, 1.5$ Hz, 1H), 8.11 (dd, $J = 8.2, 1.4$ Hz, 1H), 7.70 (ddd, $J = 8.3, 6.8, 1.4$ Hz, 1H), 7.62 (ddd, $J = 8.4, 6.8, 1.4$ Hz, 1H), 3.13 – 3.02 (m, 2H), 1.74 – 1.61 (m, 2H), 1.43 (h, $J = 7.4$ Hz, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 193.28, 153.93, 147.77, 137.88, 134.00, 129.98, 129.19, 128.99, 124.31, 124.03, 35.20, 29.85, 22.66, 13.91. MS-ESI m/z 214.1225 ([M + H]$^+$, C$_{14}$H$_{16}$NO, calc. 214.1226). IR (neat): 2959, 2931, 2872, 1696, 1502, 1461.

This compound was synthesized from 4-isooquinolinecarboxaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF$_3$K, and purified by flash silica gel column chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (52.3 mg, 82%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.82 (s, 1H), 9.29 (d, $J = 0.8$ Hz, 1H), 9.00 (dq, $J = 8.7, 0.9$ Hz, 1H), 7.94 (dt, $J = 8.1, 1.1$ Hz, 1H), 7.78 (ddd, $J = 8.5, 6.9, 1.4$ Hz, 1H), 7.59 (ddd, $J = 8.0, 6.9, 1.1$ Hz, 1H), 3.34 – 3.20 (m, 2H), 1.85 – 1.71 (m, 2H), 1.44 (h, $J = 7.4$ Hz, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.98, 162.45, 157.17, 133.54, 133.30, 128.35, 127.45, 127.39, 124.44, 121.85, 34.82, 33.97, 22.80, 13.98. MS-ESI m/z 214.1226 ([M + H]$^+$, C$_{14}$H$_{16}$NO, calc. 214.1226). IR (neat): 2959, 2930, 2872, 1685, 1619, 1573, 1494, 1428, 1376.
This compound was synthesized from \textbf{S1} following general procedure A \textit{with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\textsubscript{3}K}, and purified by flash silica gel column chromatography using hexane/EtOAc (10:1) as the eluting solvent to give the product as a yellow oil (28.8 mg, 27%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 10.27 (s, 1H), 8.29 – 8.23 (m, 1H), 8.21 – 8.15 (m, 1H), 7.70 (d, \(J = 8.7\) Hz, 2H), 7.38 – 7.32 (m, 2H), 7.28 – 7.21 (m, 2H), 3.41 – 3.36 (m, 2H), 2.36 (s, 3H), 1.79 (tt, \(J = 8.4, 6.2\) Hz, 2H), 1.48 (h, \(J = 7.6\) Hz, 2H), 0.97 (t, \(J = 7.6\) Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 185.83, 153.11, 145.88, 136.11, 135.80, 130.30, 126.63, 126.39, 125.22, 121.49, 119.17, 114.63, 34.42, 26.01, 22.87, 21.78, 13.84. MS-ESI m/z 356.1308 ([M + H]\textsuperscript{+}, C\textsubscript{20}H\textsubscript{22}N\textsubscript{O}\textsubscript{3}S, calc. 356.1315). IR (neat): 2959, 2931, 2872, 1739, 1707, 1667, 1597, 1454, 1376, 1245.

This compound was synthesized from \textbf{S2} following general procedure A \textit{with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\textsubscript{3}K}, and purified by flash silica gel column chromatography using hexane/EtOAc (30:1) as the eluting solvent to give the product as a yellow solid (78.6 mg, 86%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 10.12 (s, 1H), 7.74 (d, \(J = 8.4\) Hz, 2H), 7.52 (d, \(J = 3.2\) Hz, 1H), 7.33 – 7.29 (m, 2H), 6.28 (d, \(J = 3.1\) Hz, 1H), 2.85 – 2.68 (m, 2H), 2.41 (s, 3H), 1.56 – 1.46 (m, 2H), 1.31 (h, \(J = 7.4\) Hz, 2H), 0.89 (t, \(J = 7.3\) Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 180.11, 145.79, 143.50, 135.63, 130.24, 128.87, 128.59, 127.39, 114.08, 31.95, 26.89, 22.57, 21.83, 14.00. MS-ESI m/z 306.1168 ([M + H]\textsuperscript{+}, C\textsubscript{16}H\textsubscript{20}N\textsubscript{O}\textsubscript{3}S, calc. 306.1158). IR (neat): 2959, 2931, 2872, 1739, 1707, 1667, 1597, 1454, 1376, 1245.

This compound was synthesized from 5-nitro-2-furaldehyde following general procedure A \textit{with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF\textsubscript{3}K}, and purified by flash silica gel column chromatography using hexane/EtOAc (25:1) as the eluting solvent to give the product as a yellow oil (40.4 mg, 68%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 9.88 (d, \(J = 0.6\) Hz, 1H), 7.27 (s, 1H), 2.90 – 2.82 (m, 2H), 1.67 – 1.58 (m, 2H), 1.39 (h, \(J = 7.4\) Hz, 2H), 0.94 (t, \(J = 7.4\) Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 179.56, 152.22, 146.88, 137.82, 113.08, 31.55, 24.62, 22.30, 13.80. MS-ESI m/z 198.0750 ([M + H]\textsuperscript{+}, C\textsubscript{9}H\textsubscript{12}NO\textsubscript{4}, calc. 198.0761). IR (neat): 3132, 2962, 2932, 2874, 1741, 1694, 1588, 1540,
This compound was synthesized from 5-chloro-2-thiophenecarboxaldehyde following general procedure A with the exception of using 3 equiv of AgF and 2 equiv of n-BuBF₃K, and purified by flash silica gel column chromatography using hexane/EtOAc (50:1) as the eluting solvent to give the product as a yellow oil (47.8 mg, 79%). ¹H NMR (500 MHz, CDCl₃) δ 9.91 (s, 1H), 6.85 (s, 1H), 2.91 – 2.87 (m, 2H), 1.67 – 1.59 (m, 2H), 1.38 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 181.14, 152.94, 141.07, 136.78, 130.14, 33.41, 28.37, 22.43, 13.92. MS-ESI m/z 203.0287 ([M + H]+, C₉H₁₂ClOS, calc. 203.0292). IR (neat): 2961, 2933, 2873, 1741, 1662, 1431, 1377.

This compound was synthesized using potassium methyltrifluoroborate as the alkylating reagent following general procedure B and purified by preparative thin layer chromatography using hexane/EtOAc (2:1) as the eluting solvent to give the product as a light yellow solid (9.2 mg, 18%). ¹H NMR (500 MHz, CDCl₃) δ 10.56 (s, 1H), 8.20 (s, 1H), 2.59 (s, 3H), 2.48 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 192.84, 151.73, 149.60, 141.36, 131.72, 16.44, 15.57. MS-ESI m/z 170.0373 ([M + H]+, C₈H₉ClNO, calc. 170.0367). IR (neat): 2962, 2934, 2874, 1700, 1596, 15.57. MS-ESI m/z 198.0692 ([M + H]+, C₁₀H₁₃ClNO, calc. 198.0680). IR (neat): 2969, 2936, 2875, 1709, 1596, 1463, 1378, 1365.
This compound was synthesized using potassium n-hexyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as an orange oil (78.2 mg, 84%). ¹H NMR (500 MHz, CDCl₃) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.94 – 2.88 (m, 2H), 2.79 – 2.74 (m, 2H), 1.59 – 1.49 (m, 4H), 1.40 (ddt, J = 14.5, 10.7, 5.7 Hz, 2H), 1.29 (dqd, J = 14.5, 7.8, 7.2, 3.0 Hz, 10H), 0.90 – 0.83 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 192.90, 151.07, 149.31, 141.55, 136.53, 136.02, 32.05, 31.57, 31.49, 30.21, 29.85, 29.50, 29.24, 29.18, 22.64, 22.62, 14.13, 14.12. MS-ESI m/z 310.1920 ([M + H]⁺, C₁₈H₂₉ClNO, calc. 310.1932). IR (neat): 2961, 2932, 2873, 2860, 1709, 1596, 1466, 1370.

This compound was synthesized using potassium n-octyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a white solid (88.8 mg, 81%). ¹H NMR (500 MHz, CDCl₃) δ 10.49 (s, 1H), 8.16 (s, 1H), 2.94 – 2.88 (m, 2H), 2.80 – 2.73 (m, 2H), 1.54 (tdd, J = 15.0, 9.8, 6.5 Hz, 4H), 1.43 – 1.36 (m, 2H), 1.36 – 1.20 (m, 18H), 0.86 (td, J = 6.9, 3.7 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 192.90, 151.08, 149.32, 141.55, 136.54, 136.03, 32.09, 31.93, 31.90, 30.26, 29.86, 29.85, 29.53, 29.37, 29.29, 29.28, 29.27, 29.25, 22.75, 22.73, 14.20, 14.18. MS-ESI m/z 366.2544 ([M + H]⁺, C₂₂H₃₇ClNO, calc. 366.2558). IR (neat): 2958, 2929, 2856, 1716, 1578, 1467, 1374, 1283.

This compound was synthesized using potassium (cyclopentylmethyl)trifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et₂O (33:1) as the eluting solvent to give the product as a yellow oil (23.3 mg, 25%). ¹H NMR (500 MHz, CDCl₃) δ 10.52 (s, 1H), 8.18 (s, 1H), 3.04 (d, J = 7.4 Hz, 2H), 2.80 (d, J = 7.4 Hz, 2H), 2.06 (tt, J = 9.3, 7.1 Hz, 1H), 1.96 (ddt, J = 14.3, 7.1, 1.6 Hz, 1H), 1.69 – 1.62 (m, 8H), 1.56 – 1.46 (m, 4H), 1.25 (tt, J = 11.4, 8.1, 4.8 Hz, 2H), 1.17 (dddd, J = 16.4, 12.0, 9.1, 4.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 193.56, 151.25, 149.58, 142.35, 135.67, 135.43,
This compound was synthesized using potassium (cyclohexylmethyl)trifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et$_2$O (33:1) as the eluting solvent to give the product as a yellow oil (64.0 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.47 (s, 1H), 8.12 (s, 1H), 2.89 (d, $J = 7.0$ Hz, 2H), 2.66 (d, $J = 7.1$ Hz, 2H), 1.71 – 1.65 (m, 4H), 1.64 – 1.60 (m, 6H), 1.59 (d, $J = 3.2$ Hz, 1H), 1.39 (dtq, $J = 14.3$, 7.0, 3.5 Hz, 1H), 1.18 – 1.10 (m, 6H), 1.06 (td, $J = 11.9$, 11.5, 2.9 Hz, 2H), 0.95 (qd, $J = 11.7$, 3.5 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 193.52, 151.57, 150.04, 142.84, 134.57, 134.56, 40.10, 39.54, 37.20, 35.72, 33.13, 33.11, 26.39, 26.35, 26.20. MS-ESI m/z 334.1928 ([M + H]$^+$, C$_{20}$H$_{29}$ClNO, calc. 334.1932). IR (neat): 2961, 2930, 2872, 1709, 1596, 1449, 1369.

This compound was synthesized using potassium (3,3-dimethylbutyl)trifluoroborate as the alkylating reagent following general procedure B with the exception of using DCE as the solvent and a lower reaction temperature (80 °C), and purified by preparative thin layer chromatography using hexane/EtOAc (10:1) as the eluting solvent to give the product as a yellow solid (4.7 mg, 5%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.49 (s, 1H), 8.17 (s, 1H), 2.99 – 2.86 (m, 2H), 2.83 – 2.70 (m, 2H), 1.51 – 1.34 (m, 4H), 1.00 (s, 9H), 0.97 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 192.68, 151.01, 149.37, 141.39, 137.41, 136.56, 46.87, 44.03, 31.07, 31.02, 29.25, 29.15, 25.40, 24.92. MS-ESI m/z 310.1923 ([M + H]$^+$, C$_{18}$H$_{29}$ClNO, calc. 310.1932). IR (neat): 2960, 2934, 2873, 1697, 1595, 1459, 1364.

This compound was synthesized using potassium phenethyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/Et$_2$O (10:1) as the eluting solvent to give the product as a yellow solid (85.3 mg, 81%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.02 (s, 1H), 8.16 (s, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 4H), 7.04 (s, 1H), 6.90 (s, 1H), 6.86 – 6.78 (m, 4H), 6.76 – 6.68 (m, 4H), 6.66 – 6.60 (m, 4H), 6.56 – 6.50 (m, 4H), 6.46 – 6.40 (m, 4H), 6.36 – 6.30 (m, 4H), 6.26 – 6.20 (m, 4H), 6.16 – 6.10 (m, 4H), 6.06 – 6.00 (m, 4H), 5.96 – 5.90 (m, 4H), 5.86 – 5.80 (m, 4H), 5.76 – 5.70 (m, 4H), 5.66 – 5.60 (m, 4H), 5.56 – 5.50 (m, 4H), 5.46 – 5.40 (m, 4H), 5.36 – 5.30 (m, 4H), 5.26 – 5.20 (m, 4H), 5.16 – 5.10 (m, 4H), 5.06 – 5.00 (m, 4H), 4.96 – 4.90 (m, 4H), 4.86 – 4.80 (m, 4H), 4.76 – 4.70 (m, 4H), 4.66 – 4.60 (m, 4H), 4.56 – 4.50 (m, 4H), 4.46 – 4.40 (m, 4H), 4.36 – 4.30 (m, 4H), 4.26 – 4.20 (m, 4H), 4.16 – 4.10 (m, 4H), 4.06 – 4.00 (m, 4H), 3.96 – 3.90 (m, 4H), 3.86 – 3.80 (m, 4H), 3.76 – 3.70 (m, 4H), 3.66 – 3.60 (m, 4H), 3.56 – 3.50 (m, 4H), 3.46 – 3.40 (m, 4H), 3.36 – 3.30 (m, 4H), 3.26 – 3.20 (m, 4H), 3.16 – 3.10 (m, 4H), 3.06 – 3.00 (m, 4H), 2.96 – 2.90 (m, 4H), 2.86 – 2.80 (m, 4H), 2.76 – 2.70 (m, 4H), 2.66 – 2.60 (m, 4H), 2.56 – 2.50 (m, 4H), 2.46 – 2.40 (m, 4H), 2.36 – 2.30 (m, 4H), 2.26 – 2.20 (m, 4H), 2.16 – 2.10 (m, 4H), 2.06 – 2.00 (m, 4H), 1.96 – 1.90 (m, 4H), 1.86 – 1.80 (m, 4H), 1.76 – 1.70 (m, 4H), 1.66 – 1.60 (m, 4H), 1.56 – 1.50 (m, 4H), 1.46 – 1.40 (m, 4H), 1.36 – 1.30 (m, 4H), 1.26 – 1.20 (m, 4H), 1.16 – 1.10 (m, 4H), 1.06 – 1.00 (m, 4H), 0.96 – 0.90 (m, 4H), 0.86 – 0.80 (m, 4H), 0.76 – 0.70 (m, 4H), 0.66 – 0.60 (m, 4H), 0.56 – 0.50 (m, 4H), 0.46 – 0.40 (m, 4H), 0.36 – 0.30 (m, 4H), 0.26 – 0.20 (m, 4H), 0.16 – 0.10 (m, 4H), 0.06 – 0.00 (m, 4H). MS-ESI m/z 368.1606 ([M + H]$^+$, C$_{18}$H$_{25}$ClNO, calc. 368.1619). IR (neat): 2961, 2972, 2872, 1709, 1595, 1457, 1369.
7.21 – 7.17 (m, 2H), 7.14 – 7.10 (m, 2H), 3.28 – 3.22 (m, 2H), 3.07 (dd, \(J = 8.9, 6.7 \text{ Hz}, 2\text{H}\)), 2.94 – 2.89 (m, 2H), 2.85 (dd, \(J = 8.9, 6.7 \text{ Hz}, 2\text{H}\)). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 192.16, 151.38, 149.82, 142.33, 140.29, 140.01, 134.98, 134.35, 128.76, 126.62, 126.61, 37.96, 35.65, 31.78, 31.31.

This compound was synthesized using potassium 3-acetoxypropyltrifluoroborate as the alkylating reagent following general procedure B and purified by flash silica gel column chromatography using hexane/EtOAc (2:1) as the eluting solvent to give the product as a yellow oil (86.9 mg, 85%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 10.47 (s, 1H), 8.19 (s, 1H), 4.10 (t, \(J = 6.2 \text{ Hz}, 2\text{H}\)), 4.05 (t, \(J = 6.2 \text{ Hz}, 2\text{H}\)), 3.04 – 2.96 (m, 2H), 2.89 – 2.81 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.89 (dd, \(J = 15.9, 12.3, 8.0, 6.1 \text{ Hz}, 4\text{H}\)). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 191.48, 152.53, 150.74, 141.80, 133.08, 132.78, 126.27 (q, \(J = 277.0 \text{ Hz}\)), 126.24 (q, \(J = 277.0 \text{ Hz}\)), 35.43 (q, \(J = 29.0 \text{ Hz}\)), 33.34 (q, \(J = 29.3 \text{ Hz}\)), 22.97 (q, \(J = 3.4 \text{ Hz}\)), 22.22 (q, \(J = 3.4 \text{ Hz}\)). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -66.31 (t, \(J = 10.4 \text{ Hz}\)) -66.66 (t, \(J = 10.4 \text{ Hz}\)). MS-ESI m/z 334.0416 ([M + H]\(^+\), \(\text{C}_{12}\text{H}_{11}\text{ClF}_{6}\text{NO}\), calc. 334.0428). IR (neat): 2962, 2934, 2874, 1698, 1595, 1459, 1307.
This compound was synthesized from S3 following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1) as the eluting solvent to give the product as a yellow oil (8.0 mg, 18%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.00 (s, 1H), 2.62 – 2.53 (m, 6H), 1.85 (p, $J = 7.8$ Hz, 2H), 1.54 – 1.46 (m, 2H), 1.35 (p, $J = 7.6$ Hz, 2H), 0.93 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 188.32, 167.28, 138.52, 38.52, 30.63, 30.35, 28.33, 22.69, 21.51, 13.99. MS-ESI m/z 153.1273 ([M + H]$^+$, C$_{10}$H$_{17}$O, calc. 153.1274).

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{4b} \\
n-\text{Bu}
\end{array}
\]

This compound was synthesized from 1-cyclohexene-1-carboxaldehyde following general procedure C without the addition of crotonic acid, and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then hexane/DCM (1:1) as the eluting solvent to give the product as a yellow oil (6.0 mg, 12%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.12 (s, 1H), 2.55 – 2.49 (m, 2H), 2.25 (td, $J = 6.2$, 2.2 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.64 – 1.58 (m, 4H), 1.50 (ddd, $J = 12.9$, 5.9, 3.6 Hz, 2H), 1.36 (p, $J = 7.5$ Hz, 2H), 0.93 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 191.16, 161.03, 133.72, 32.43, 32.32, 32.08, 22.88, 22.32, 22.31, 21.86, 14.04. MS-ESI m/z 167.1433 ([M + H]$^+$, C$_{11}$H$_{19}$O, calc. 167.1430).

\[
\begin{array}{c}
\text{O} \\
\text{Ph} \\
\text{H} \\
n-\text{Bu} \\
n-\text{Bu} \\
\text{4c}
\end{array}
\]

This compound was synthesized from S4 following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then hexane/DCM (1:1) as the eluting solvent to give the product as a yellow oil (9.1 mg, 12%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.18 (s, 1H), 7.23 (t, $J = 7.6$ Hz, 2H), 7.16 – 7.12 (m, 1H), 7.11 – 7.08 (m, 2H), 3.64 (s, 2H), 2.64 – 2.56 (m, 2H), 2.27 (dd, $J = 9.6$, 6.6 Hz, 2H), 1.53 (ddd, $J = 12.6$, 5.9, 3.5 Hz, 2H), 1.40 (p, $J = 7.5$ Hz, 2H), 1.33 (td, $J = 7.8$, 6.3, 3.6 Hz, 4H), 0.94 (t, $J = 7.5$ Hz, 3H), 0.91 – 0.84 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 191.43, 165.81, 140.55, 135.38, 128.42, 128.13, 125.87, 35.31, 33.35, 30.80, 30.63, 30.30, 23.29, 23.06, 14.04, 14.02. MS-ESI m/z 259.2038 ([M + H]$^+$, C$_{18}$H$_{27}$O, calc. 259.2056).

\[
\begin{array}{c}
\text{EtO} \\
\text{O} \\
n-\text{Bu} \\
n-\text{Bu} \\
\text{4d}
\end{array}
\]

This compound was synthesized from S5 following general procedure C and purified by preparative thin layer chromatography using hexane/EtOAc (5:1), then DCM as the eluting solvent to give the product as a yellow oil (6.3 mg, 7%). $^1$H NMR (500 MHz, CDCl$_3$) δ 10.06 (s, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 2.64 – 2.56 (m, 2H), 2.27 (dd, $J = 9.6$, 6.6 Hz, 2H), 1.53 (ddd, $J = 12.6$, 5.9, 3.5 Hz, 2H), 1.40 (p, $J = 7.5$ Hz, 2H), 1.33 (td, $J = 7.8$, 6.3, 3.6 Hz, 4H), 0.94 (t, $J = 7.5$ Hz, 3H), 0.91 – 0.84 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 191.43, 165.81, 140.55, 135.38, 128.42, 128.13, 125.87, 35.31, 33.35, 30.80, 30.63, 30.30, 23.29, 23.06, 14.04, 14.02. MS-ESI m/z 259.2038 ([M + H]$^+$, C$_{18}$H$_{27}$O, calc. 259.2056).
Hz, 2H), 2.61 – 2.43 (m, 2H), 2.37 – 2.20 (m, 6H), 1.66 – 1.58 (m, 2H), 1.51 – 1.32 (m, 8H), 1.27 – 1.23 (m, 3H), 0.93 (dt, J = 8.4, 7.2 Hz, 6H).\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \textsuperscript{δ} 191.56, 173.71, 164.59, 136.02, 60.40, 34.67, 34.33, 33.33, 30.80, 30.57, 24.78, 24.75, 23.30, 22.99, 14.40, 14.10, 14.02. MS-ESI m/z 305.2075 ([M + H]\textsuperscript{+}, C\textsubscript{17}H\textsubscript{30}NaO\textsubscript{3}, calc. 305.2087).
Mechanistic Studies

Following a previously reported procedure, 4-fluorobenzaldehyde (1.07 mL, 10.0 mmol) was dissolved in anhydrous DCM (10 mL) along with 3Å molecular sieves in a 50-mL oven-dried round bottom flask equipped with a magnetic stir bar under an argon atmosphere. To this solution was added aniline (0.91 mL, 10.0 mmol). The reaction was stirred at r.t. for 2 h, at which point Na₂SO₄ was added with subsequent filtration. The solvent was removed in vacuo to give the product as a white solid (1.83 g, 92%).

\[
\begin{align*}
\text{H}_{\text{NMR}} (500 \text{ MHz, CDCl}_3) & \delta 8.43 (s, 1H), 7.94 - 7.88 (m, 2H), 7.42 - 7.37 (m, 2H), 7.27 - 7.13 (m, 5H). \\
\text{C NMR} (126 \text{ MHz, CDCl}_3) & \delta 164.84 (d, J = 252.1 \text{ Hz}), 158.99, 151.98, 132.70 (d, J = 3.0 \text{ Hz}), 130.92 (d, J = 8.8 \text{ Hz}), 129.33, 126.16, 120.97, 116.09 (d, J = 21.9 \text{ Hz}). \\
\text{F NMR} (282 \text{ MHz, CDCl}_3) & \delta -108.12 (tt, J = 8.5, 5.5 \text{ Hz}). \\
\text{MS-ESI m/z} & 200.0870 ([M + H]^+, \text{C}_{13}\text{H}_{11}\text{FN}, \text{calc.} 200.0870). \\
\text{IR (neat):} & 3066, 2878, 1625, 1586, 1505, 1483, 1235, 1218.
\end{align*}
\]

Following a previously reported procedure with slight modifications, NaOAc (73.8 mg, 0.90 mmol) and [Cp*IrCl₂]₂ (119.5 mg, 0.15 mmol) were added to a solution of imine I (59.8 mg, 0.30 mmol) in anhydrous DCE (10 mL) in a 25-mL oven-dried round bottom flask equipped with a magnetic stir bar under an argon atmosphere. The mixture was stirred at 60 °C for 8 h, then filtered through a pad of Celite®. The filtrate was evaporated in vacuo and purified by preparative thin layer chromatography using DCM/EtOAc (100:1) as the eluting solvent to yield the iridacycle as a red solid (109.1 mg, 63%). Single crystal was obtained by slow diffusion of pentane to a solution of iridacycle II in DCM at -20 °C.\text{H NMR} (500 MHz, CDCl₃) δ 8.26 (s, 1H), 7.61 (dd, J = 8.3, 5.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.49 (dd, J = 9.5, 2.4 Hz, 1H), 7.39 (dd, J = 8.5, 7.2 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.72 (td, J = 8.7, 2.5 Hz, 1H), 1.46 (s, 15H). \text{C NMR} (126 MHz, CDCl₃) δ 173.96, 173.62 (d, J = 6.3 Hz), 165.00 (d, J = 257.2 Hz), 151.63, 143.43 (d, J = 1.4 Hz), 131.47 (d, J = 9.6 Hz), 129.08, 127.39, 122.51, 121.16 (d, J = 17.7 Hz), 109.62 (d, J = 23.7 Hz), 89.41, 8.76. \text{F NMR} (282 MHz, CDCl₃) δ -106.35 (td, J = 9.2, 5.6 Hz). \text{MS-ESI m/z} 526.1532 ([M]⁺, \text{C}_{23}\text{H}_{24}\text{F}_3\text{IrN}, \text{calc.} 526.1517). \text{IR (neat):} 2914, 1599, 1585, 1539, 1484, 1447, 1380, 1343, 1242, 1230.

Following a previously reported procedure,\text{H NMR} (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.94 – 7.88 (m, 2H), 7.42 – 7.37 (m, 2H), 7.27 – 7.13 (m, 5H). \text{C NMR} (126 MHz, CDCl₃) δ 164.84 (d, J = 252.1 Hz), 158.99, 151.98, 132.70 (d, J = 3.0 Hz), 130.92 (d, J = 8.8 Hz), 129.33, 126.16, 120.97, 116.09 (d, J = 21.9 Hz). \text{F NMR} (282 MHz, CDCl₃) δ -108.12 (tt, J = 8.5, 5.5 Hz). \text{MS-ESI m/z} 200.0870 ([M + H]^+, \text{C}_{13}\text{H}_{11}\text{FN}, \text{calc.} 200.0870). \text{IR (neat):} 3066, 2878, 1625. 1586. 1505, 1483, 1235, 1218.
Following a previously reported procedure with slight modifications,\textsuperscript{10} iridacycle II (56.1 mg, 0.10 mmol) was added to a 25-mL oven-dried round bottom flask equipped with a magnetic stir bar under air. The flask was then transferred to a glovebox filled with N\textsubscript{2}, wherein AgNTf\textsubscript{2} (39.2 mg, 0.101 mmol) was added. The flask was sealed with a rubber septum and taken out of the glovebox. Anhydrous acetonitrile (5 mL) was added, and the reaction mixture was stirred at r.t. for 6 h, and then filtered through a pad of Celite\textsuperscript{®}. The filtrate was evaporated \textit{in vacuo} to give iridacycle III as a light orange solid (84.7 mg, quantitative). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.42 (s, 1H), 7.77 (dd, J = 8.4, 5.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.43 (dd, J = 8.9, 2.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.31 (m, 2H), 6.89 (td, J = 8.6, 2.4 Hz, 1H), 2.51 (s, 3H), 1.50 (s, 15H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 176.85, 166.67 (d, J = 6.5 Hz), 165.44 (d, J = 260.5 Hz), 149.62, 143.87 (d, J = 1.8 Hz), 132.95 (d, J = 9.7 Hz), 130.07, 128.74, 122.19, 121.44 (d, J = 18.9 Hz), 120.13, 119.99 (q, J = 321.6 Hz), 111.67 (d, J = 23.4 Hz), 92.08, 8.65, 4.04. \textsuperscript{19}F NMR (282 MHz, CDCl\textsubscript{3}) δ -78.67, -103.40 (dd, J = 8.9, 5.6 Hz). MS-ESI m/z 567.1770 ([M]\textsuperscript{+}, C\textsubscript{25}H\textsubscript{27}FlrN\textsubscript{2}, calc. 567.1782). IR (neat): 2947, 2837, 1604, 1589, 1546, 1488, 1452, 1350, 1227.

A 10-mL oven-dried microwave-vial equipped with a magnetic stir bar was charged with iridacycle III (84.7 mg, 0.10 mmol), AgF (50.8 mg, 0.40 mmol) and n-BuBF\textsubscript{3}K (49.2 mg, 0.30 mmol). The vial was sealed with a PTFE-lined aluminum cap, evacuated and filled with argon three times. Degassed AcOH (1 mL) was added through a syringe, and the vial was heated in a pie-block at 100 °C under vigorous stirring for 12 h. After cooling to r.t., the reaction mixture was filtered through a pad of Celite\textsuperscript{®} and washed with EtOAc (10 mL). The filtrate was then concentrated \textit{in vacuo} and the resulting residue was purified by flash silica gel column chromatography using hexane/Et\textsubscript{2}O (50:1) as the eluting solvent to give the product as a yellow oil (6.1 mg, 26%).
Decarbonylation

Following a previously reported procedure,11 a 10-mL oven-dried microwave vial equipped with a magnetic stir bar was charged with PPh3 (6.6 mg, 0.025 mmol). The vial was transferred to a glovebox filled with N2, wherein [Ir(cod)Cl]2 (8.4 mg, 0.0125 mmol) was added. The vial was sealed with a PTFE-lined aluminum cap and taken out of the glovebox. A solution of the di-alkylation product 2b (0.5 mmol) in 1,4-dioxane (0.5 mL) was added to the vial via a syringe. The resulting mixture was degassed by the freeze–pump-thaw method for three times and kept under nitrogen atmosphere. The reaction mixture was then heated to 140 °C and stirred for 72 h. The crude product was purified by flash silica gel column chromatography using hexane/EtOAc (50:1) as the eluting solvent to give the product as a colorless oil (97.4 mg, 86%).

$\text{H NMR (500 MHz, CDCl}_3\text{)} \delta 8.01 (d, J = 2.4 \text{ Hz}, 1\text{H}), 7.31 (d, J = 2.5 \text{ Hz}, 1\text{H}), 2.67 - 2.61 (m, 2\text{H}), 2.56 - 2.49 (m, 2\text{H}), 1.61 - 1.51 (m, 4\text{H}), 1.34 (d, J = 2.1, 7.4 \text{ Hz}, 4\text{H}), 0.91 (dt, J = 12.9, 7.4 \text{ Hz}, 6\text{H}).$

$\text{13C NMR (126 MHz, CDCl}_3\text{)} \delta 148.57, 146.88, 138.84, 137.17, 136.04, 33.28, 32.84, 31.91, 31.44, 22.50, 22.25, 13.92, 13.88.$

MS-ESI m/z 226.1357 ([M]+, C13H21ClN, calc. 226.1357). IR (neat): 2957, 2930, 2860, 1561, 1465, 1427, 1405, 1379.
$^1$H, $^{13}$C and $^{19}$F NMR Spectra of New Compounds
n-Bu

O

H

n-Bu

1a

f1 (ppm)

5.91
4.07
4.23
4.12
2.01
1.00
0.92
0.94
0.95
1.38
1.39
1.41
1.42
1.56
1.56
1.57
1.58
1.58
1.59
1.59
2.91
2.92
2.93
2.93
2.94
6.79
6.80
7.26
Cl3

CD

10.48
1s

F
O=H
n-Bu

Br

F
O=H
n-Bu

Br

1s

-14.01
22.80
33.22
33.24
33.38
76.91
77.41
117.55
117.74
121.11
121.16
128.70
128.79
130.19
130.21
149.02
164.82
166.91
188.14
188.22

-118.54
-118.53
-118.50
-118.49
**3a**

**3b**
14.35
16.22
22.73
23.20
76.91
77.16
77.41
137.02
137.80
141.35
148.92
150.97
192.85
6.15
10.30
2.10
4.12
2.06
2.04
0.98
1.00
0.84
0.85
0.85
0.86
0.86
1.56
1.56
1.56
1.57
1.57
1.58
2.75
2.76
2.76
2.76
2.78
2.89
2.90
2.91
2.91
2.92
7.26
8.16
10.49

3b

3c
$f_1 \text{(ppm)}$

3i

$\text{AcO-} \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{OAc}
\end{array}$

3j

$\text{F}_2\text{C-} \begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{N} \\
\text{CF}_3
\end{array}$
X-ray Crystallographic Data

A translucent intense orange prism-like specimen of C$_{23}$H$_{24}$ClIrN, approximate dimensions 0.113 mm x 0.166 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Table 1: Data collection details for PDJXC7a.

| Axis | dx/mm | 20/° | ω/° | φ/° | χ/° | Wid th/° | Frames | Time/s | Wavelength/Å | Voltage/kV | Current/mA | Temperature/K |
|------|-------|------|-----|-----|-----|----------|--------|--------|-------------|------------|------------|---------------|
| Omega | 33.991 | 35.93 | -130.07 | 0.00 | 54.74 | 0.50 | 303 | 1.50 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | 102.00 | 54.74 | 0.50 | 303 | 1.50 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | -54.00 | 54.74 | 0.50 | 303 | 1.50 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | 51.00 | 54.74 | 0.50 | 303 | 1.50 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | 153.00 | 54.74 | 0.50 | 303 | 1.50 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | -105.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 35.93 | -130.07 | -156.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 20.93 | -145.07 | 0.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 20.93 | -145.07 | 180.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 20.93 | -145.07 | 270.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |
| Omega | 33.991 | 20.93 | -145.07 | 90.00 | 54.74 | 0.50 | 303 | 1.00 | 0.71073 | 50 | 1.0 | n/a |

A total of 4053 frames were collected. The total exposure time was 1.29 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 61710 reflections to a maximum θ angle of 33.14° (0.65 Å resolution), of which 7679 were independent (average redundancy 8.036, completeness = 99.8%, R$_{int}$ = 5.68%, R$_{sig}$ = 2.95%) and 7162 (93.27%) were greater than 2σ(F$^2$). The final cell constants of $a = 9.2681(5)$ Å, $b = 10.4733(5)$ Å, $c = 10.8722(5)$ Å, $α = 82.9875(15)^°$, $β = 85.2833(17)^°$, $γ = 74.7986(16)^°$, volume = 1009.40(9) Å$^3$, are based upon the refinement of the XYZ-centroids of 9791 reflections above 20 σ(I) with 5.245° < 2θ < 72.76°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.728. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2540 and 0.5170.
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, C_{23}H_{24}ClIrN. The final anisotropic full-matrix least-squares refinement on F^2 with 249 variables converged at R1 = 2.17\%, for the observed data and wR2 = 4.83\% for all data. The goodness-of-fit was 1.089. The largest peak in the final difference electron density synthesis was 2.289 e/Å^3 and the largest hole was -0.813 e/Å^3 with an RMS deviation of 0.145 e/Å^3. On the basis of the final model, the calculated density was 1.846 g/cm^3 and F(000), 544 e^-.

Table 2. Sample and crystal data for PDJXC7a.

| Identification code | PDJXC7a |
|---------------------|---------|
| Chemical formula    | C_{23}H_{24}ClIrN |
| Formula weight      | 561.08 g/mol |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal size        | 0.113 x 0.166 x 0.280 mm |
| Crystal habit       | translucent intense orange prism |
| Crystal system      | triclinic |
| Space group         | P -1 |
| Unit cell dimensions| a = 9.2681(5) Å  \[\alpha = 82.9875(15)^\circ\]  
b = 10.4733(5) Å  \[\beta = 85.2833(17)^\circ\]  
c = 10.8722(5) Å  \[\gamma = 74.7986(16)^\circ\]  |
| Volume              | 1009.40(9) Å^3 |
| Z                   | 2 |
| Density (calculated)| 1.846 g/cm^3 |
| Absorption coefficient| 6.733 mm^-1 |
| F(000)              | 544 |

Table 3. Data collection and structure refinement for PDJXC7a.

| Theta range for data collection | 2.03 to 33.14^\circ |
| Index ranges                   | -14\leq h \leq 14, -16\leq k \leq 16, -16\leq l \leq 16 |
| Reflections collected          | 61710 |
| Independent reflections        | 7679 [R(int) = 0.0568] |
| Coverage of independent reflections | 99.8\% |
| Absorption correction          | multi-scan |
| Max. and min. transmission     | 0.5170 and 0.2540 |
| Structure solution technique   | direct methods |
| Structure solution program     | SHELXT (Sheldrick, 2016) |
| Refinement method              | Full-matrix least-squares on F^2 |
| Refinement program             | SHELXL-2014/7 (Sheldrick, 2014) |
| Function minimized             | \Sigma w(F_o^2 - F_e^2)^2 |
| Data / restraints / parameters | 7679 / 0 / 249 |
| Goodness-of-fit on F^2         | 1.089 |
\[ \Delta/\sigma_{\text{max}} \] 0.003

**Final R indices**

7162 data; I>2\(\sigma(I)\) R1 = 0.0217, wR2 = 0.0474

all data R1 = 0.0251, wR2 = 0.0483

**Weighting scheme**

w=1/[\(\sigma^2(Fo^2)\)+0.0197P+0.7300P]

where P=(\(Fo^2\)+2\(Fc^2\))/3

**Largest diff. peak and hole** 2.289 and -0.813 e\(\text{Å}^{-3}\)

**R.M.S. deviation from mean** 0.145 e\(\text{Å}^{-3}\)

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**Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å\(^2\)) for PDJXC7a.**

U(eq) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

|     | x/a       | y/b       | z/c       | U(eq)    |
|-----|-----------|-----------|-----------|----------|
| Ir1 | 0.55443(2)| 0.72803(2)| 0.24316(2)| 0.00981(2)|
| Cl1 | 0.63266(6)| 0.92600(5)| 0.16797(5)| 0.01514(9)|
| F1  | 0.00695(17)| 0.64414(16)| 0.55593(15)| 0.0248(3)|
| N1  | 0.3843(2) | 0.84803(17)| 0.34651(16)| 0.0112(3)|
| C1  | 0.6572(2)| 0.73178(19)| 0.40039(18)| 0.0115(3)|
| C2  | 0.8082(3)| 0.6775(2) | 0.4245(2) | 0.0145(4)|
| C3  | 0.8588(3)| 0.6973(2) | 0.5352(2) | 0.0158(4)|
| C4  | 0.7708(3)| 0.7677(2) | 0.6255(2) | 0.0159(4)|
| C7  | 0.4159(2)| 0.8663(2) | 0.45616(18)| 0.0122(3)|
| C6  | 0.5659(2)| 0.8050(2) | 0.49199(18)| 0.0115(3)|
| C5  | 0.6211(3)| 0.8225(2) | 0.60365(19)| 0.0142(4)|
| C8  | 0.2401(2)| 0.9115(2) | 0.3000(2) | 0.0135(4)|
| C9  | 0.1103(3)| 0.9019(2) | 0.3707(2) | 0.0179(4)|
| C10 | 0.9719(3)| 0.9621(3) | 0.3216(3) | 0.0241(5)|
| C11 | 0.9629(3)| 0.0320(3) | 0.2049(3) | 0.0243(5)|
| C12 | 0.0933(3)| 0.0412(2) | 0.1348(2) | 0.0209(4)|
| C13 | 0.2318(3)| 0.9798(2) | 0.1815(2) | 0.0158(4)|
| C14 | 0.4418(3)| 0.5780(2) | 0.2141(2) | 0.0146(4)|
| C15 | 0.4455(3)| 0.6566(2) | 0.0952(2) | 0.0196(4)|
| C16 | 0.5974(3)| 0.6487(2) | 0.0589(2) | 0.0210(5)|
| C17 | 0.6922(3)| 0.5633(2) | 0.1510(2) | 0.0167(4)|
| C18 | 0.5942(2)| 0.5160(2) | 0.24591(19)| 0.0126(4)|
| C19 | 0.3032(3)| 0.5574(2) | 0.2853(3) | 0.0228(5)|
| C20 | 0.3147(4)| 0.7255(3) | 0.0192(3) | 0.0358(8)|
| C21 | 0.6519(5)| 0.7184(3) | 0.9426(2) | 0.0382(8)|
| C22 | 0.8596(3)| 0.5167(3) | 0.1397(3) | 0.0274(6)|
| C23 | 0.6444(3)| 0.4134(2) | 0.3528(2) | 0.0191(4)|
### Table 5. Bond lengths (Å) for PDJXC7a.

| Bond                    | Length (Å) |
|-------------------------|------------|
| Ir1-C1                  | 2.033(2)   |
| Ir1-C18                 | 2.150(2)   |
| Ir1-C14                 | 2.167(2)   |
| Ir1-C15                 | 2.264(2)   |
| F1-C3                   | 1.365(3)   |
| N1-C8                   | 1.430(3)   |
| C1-C6                   | 1.415(3)   |
| C2-H2                   | 0.95       |
| C4-C5                   | 1.384(3)   |
| C7-C6                   | 1.434(3)   |
| C8-C13                  | 1.393(3)   |
| C9-C10                  | 1.391(3)   |
| C10-C11                 | 1.383(4)   |
| C11-C12                 | 1.393(4)   |
| C12-C13                 | 1.384(3)   |
| C13-H13                 | 0.95       |
| C14-C15                 | 1.448(3)   |
| C15-C16                 | 1.415(4)   |
| C16-C17                 | 1.445(4)   |
| C17-C18                 | 1.446(3)   |
| C18-C23                 | 1.498(3)   |
| C19-H19B                | 0.98       |
| C20-H20A                | 0.98       |
| C20-H20C                | 0.98       |
| C21-H21B                | 0.98       |
| C22-H22A                | 0.98       |
| C22-H22C                | 0.98       |
| C23-H23B                | 0.98       |

### Table 6. Bond angles (°) for PDJXC7a.

| Bond                    | Angle (°) |
|-------------------------|-----------|
| C1-Ir1-N1               | 77.75(8)  |
| N1-Ir1-C18              | 124.96(7) |
| N1-Ir1-C17              | 163.46(8) |
| C1-Ir1-C14              | 124.57(8) |
| C18-Ir1-C14             | 39.03(8)  |
| C1-Ir1-C16              | 141.89(10)|
| C18-Ir1-C16             | 64.01(8)  |

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| Bond Length (Å)                  | C14-Ir1-C16 | N1-Ir1-C15 | C17-Ir1-C15 | C16-Ir1-C15 | N1-Ir1-C11 | C17-Ir1-C11 | C16-Ir1-C11 | C7-N1-C8 | C8-N1-Ir1 | C2-C1-Ir1 | C3-C2-C1 | C1-C2-H2 | F1-C3-C2 | C3-C4-C5 | C5-C4-H4 | N1-C7-H7 | C5-C6-C1 | C1-C6-C7 | C4-C5-H5 | C13-C8-C9 | C9-C8-N1 | C10-C9-H9 | C11-C10-C9 | C9-C10-H10 | C10-C11-H11 | C13-C12-C11 | C11-C12-H12 | C12-C13-H13 | C18-C14-C15 | C15-C14-C19 | C15-C14-Ir1 | C16-C15-C14 | C14-C15-C20 | C14-C15-Ir1 | C15-C16-C17 | C17-C16-C21 | C17-C16-Ir1 | C16-C17-C18 | C18-C17-C22 | C18-C17-Ir1 |
|---------------------------------|-------------|------------|------------|------------|------------|------------|------------|-----------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|                                | 63.38(9)    | 107.42(9)  | 63.74(9)   | 36.72(10)  | 87.05(5)   | 109.04(6)  | 93.30(6)   | 120.48(18)| 122.81(13)| 127.47(15)| 118.8(2)   | 120.6     | 117.6(2)  | 117.6(2)  | 121.2     | 121.7     | 122.7(2)  | 113.62(18)| 120.4     | 120.6(2)  | 120.50(19)| 120.5     | 120.6(2)  | 119.7     | 120.0     | 120.0(2)  | 119.9     | 120.2     | 108.0(2)  | 125.3(2)  | 74.58(12)  | 107.5(2)  | 126.8(3)  | 67.34(12)  | 109.62(19)| 125.2(3)  | 68.26(12) | 106.8(2) | 126.6(2)  | 70.01(11)  |
C14-C18-C17 107.95(19)  C14-C18-C23 126.6(2)
C17-C18-C23 125.3(2)  C14-C18-Ir1 71.12(11)
C17-C18-Ir1 70.77(12)  C23-C18-Ir1 126.93(15)
C14-C19-H19A 109.5  C14-C19-H19B 109.5
H19A-C19-H19B 109.5  C14-C19-H19C 109.5
H19A-C19-H19C 109.5  H19B-C19-H19C 109.5
C15-C20-H20A 109.5  C15-C20-H20B 109.5
H20A-C20-H20B 109.5  C15-C20-H20C 109.5
H20A-C20-H20C 109.5  H20B-C20-H20C 109.5
C16-C21-H21A 109.5  C16-C21-H21B 109.5
H21A-C21-H21B 109.5  C16-C21-H21C 109.5
H21A-C21-H21C 109.5  H21B-C21-H21C 109.5
C17-C22-H22A 109.5  C17-C22-H22B 109.5
H22A-C22-H22B 109.5  C17-C22-H22C 109.5
H22A-C22-H22C 109.5  H22B-C22-H22C 109.5
C18-C23-H23A 109.5  C18-C23-H23B 109.5
H23A-C23-H23B 109.5  C18-C23-H23C 109.5
H23A-C23-H23C 109.5  H23B-C23-H23C 109.5

| Table 7. Torsion angles (°) for PDJXC7a. |
|----------------------------------------|
| C6-C1-C2-C3 | 0.5(3) | Ir1-C1-C2-C3 | 176.28(16) |
| C1-C2-C3-F1 | -179.49(19) | C1-C2-C3-C4 | -0.1(3) |
| F1-C3-C4-C5 | 179.41(19) | C2-C3-C4-C5 | 0.1(3) |
| C8-N1-C7-C6 | -176.44(18) | Ir1-N1-C7-C6 | 1.9(2) |
| C2-C1-C6-C5 | -0.8(3) | Ir1-C1-C6-C5 | -177.12(16) |
| C2-C1-C6-C7 | 175.23(18) | Ir1-C1-C6-C7 | -1.1(2) |
| N1-C7-C6-C5 | 175.48(19) | N1-C7-C6-C1 | -0.5(3) |
| C3-C4-C5-C6 | -0.4(3) | C1-C6-C5-C4 | 0.8(3) |
| C7-C6-C5-C4 | -174.9(2) | C7-N1-C8-C13 | 130.8(2) |
| Ir1-N1-C8-C13 | -47.4(2) | C7-N1-C8-C9 | -51.0(3) |
| Ir1-N1-C8-C9 | 130.82(18) | C13-C8-C9-C10 | -0.3(3) |
| N1-C8-C9-C10 | -178.5(2) | C8-C9-C10-C11 | -0.8(4) |
| C9-C10-C11-C12 | 0.8(4) | C10-C11-C12-C13 | 0.4(4) |
| C11-C12-C13-C8 | -1.6(3) | C9-C8-C13-C12 | 1.5(3) |
| N1-C8-C13-C12 | 179.7(2) | C18-C14-C15-C16 | -3.3(2) |
| C19-C14-C15-C16 | -179.0(2) | Ir1-C14-C15-C16 | 58.97(15) |
| C18-C14-C15-C20 | 172.5(2) | C19-C14-C15-C20 | -3.2(4) |
| Ir1-C14-C15-C20 | -125.2(2) | C18-C14-C15-Ir1 | -62.26(14) |
| C19-C14-C15-Ir1 | 122.1(2) | C14-C15-C16-C17 | 1.5(2) |
| C20-C15-C16-C17 | -174.4(2) | Ir1-C15-C16-C17 | 58.67(15) |
Table 8. Anisotropic atomic displacement parameters (Å²) for PDJXC7a.

The anisotropic atomic displacement factor exponent takes the form: \(-2\pi^2 [ h^2 a^* U_{11} + \ldots + 2h k a^* b^* U_{12} ] \)

|       | U_{11}     | U_{22}     | U_{33}     | U_{23}     | U_{13}     | U_{12}     |
|-------|------------|------------|------------|------------|------------|------------|
| Ir1   | 0.01495(4) | 0.00801(3) | 0.00732(3) | -0.00095(2)| 0.00039(2) | -0.00464(2)|
| C11   | 0.0194(2)  | 0.0132(2)  | 0.0147(2)  | 0.00080(16)| 0.00042(17)| -0.00897(18)|
| F1    | 0.0197(7)  | 0.0266(8)  | 0.0270(8)  | -0.0008(6) | -0.0102(6) | -0.0019(6) |
| N1    | 0.0144(8)  | 0.0088(7)  | 0.0109(7)  | 0.0006(6)  | -0.0006(6) | -0.0049(6) |
| C1    | 0.0160(9)  | 0.0081(8)  | 0.0108(8)  | 0.0003(6)  | 0.0004(7)  | -0.0048(7) |
| C2    | 0.0165(10) | 0.0120(9)  | 0.0148(9)  | -0.0011(7) | -0.0021(7) | -0.0028(7) |
| C3    | 0.0172(10) | 0.0115(9)  | 0.0176(9)  | 0.0022(7)  | -0.0054(8) | -0.0021(7) |
| C4    | 0.0259(11) | 0.0116(9)  | 0.0113(8)  | 0.0021(7)  | -0.0042(8) | -0.0074(8) |
| C7    | 0.0158(9)  | 0.0106(8)  | 0.0101(8)  | -0.0023(6) | 0.0030(7)  | -0.0038(7) |
| C6    | 0.0168(9)  | 0.0089(8)  | 0.0089(8)  | -0.0003(6) | 0.0004(7)  | -0.0040(7) |
| C5    | 0.0229(11) | 0.0101(8)  | 0.0100(8)  | -0.0004(7) | -0.0020(7) | -0.0048(7) |
| C8    | 0.0148(9)  | 0.0105(8)  | 0.0162(9)  | -0.0022(7) | -0.0016(7) | -0.0044(7) |
| C9    | 0.0164(10) | 0.0172(10) | 0.0200(10) | -0.0022(8) | 0.0013(8)  | -0.0047(8) |
| C10   | 0.0140(10) | 0.0256(12) | 0.0333(13) | -0.0041(10)| 0.0003(9)  | -0.0060(9) |
| C11   | 0.0166(11) | 0.0244(12) | 0.0323(13) | -0.0023(10)| -0.0081(9) | -0.0043(9) |
| C12   | 0.0218(11) | 0.0190(10) | 0.0232(11) | -0.0006(9) | -0.0094(9) | -0.0058(9) |
| C13   | 0.0174(10) | 0.0151(9)  | 0.0165(9)  | -0.0011(7) | -0.0031(8) | -0.0068(8) |
| C14   | 0.0203(10) | 0.0092(8)  | 0.0169(9)  | -0.0034(7) | -0.0023(8) | -0.0069(7) |
| C15   | 0.0346(13) | 0.0121(9)  | 0.0151(9)  | -0.0033(7) | -0.0099(9) | -0.0079(9) |
|      |   \( U_{11} \)   |   \( U_{22} \)   |   \( U_{33} \)   |   \( U_{23} \)   |   \( U_{13} \)   |   \( U_{12} \)   |
|------|----------------|----------------|----------------|----------------|----------------|----------------|
| C16  | 0.0440(15)     | 0.0144(9)      | 0.0076(8)      | -0.0052(7)     | 0.0044(9)      | -0.0126(10)   |
| C17  | 0.0241(11)     | 0.0136(9)      | 0.0139(9)      | -0.0067(7)     | 0.0085(8)      | -0.0081(8)    |
| C18  | 0.0170(9)      | 0.0092(8)      | 0.0118(8)      | -0.0017(6)     | 0.0016(7)      | -0.0041(7)    |
| C19  | 0.0158(10)     | 0.0186(10)     | 0.0365(13)     | -0.0081(10)    | 0.0026(9)      | -0.0077(8)    |
| C20  | 0.056(2)       | 0.0194(12)     | 0.0350(15)     | -0.0065(11)    | -0.0318(14)    | -0.0044(12)   |
| C21  | 0.082(3)       | 0.0254(13)     | 0.0116(10)     | -0.0030(9)     | 0.0111(13)     | -0.0254(15)   |
| C22  | 0.0246(12)     | 0.0274(13)     | 0.0339(14)     | -0.0176(11)    | 0.0161(11)     | -0.0120(10)   |
| C23  | 0.0247(12)     | 0.0121(9)      | 0.0195(10)     | 0.0021(8)      | -0.0011(8)     | -0.0044(8)    |

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\( \text{Å}^2 \)) for PDJXC7a.
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