Deboronative Cyanation of Alkyltrifluoroborates via Photoredox Catalysis

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Supporting Information

Table of Contents

1. General Information..........................................................................................................................S2

2. Preparation of [Ru(bpy)]_3(PF_6)_2..........................................................................................S2

3. Preparation of Substrates.............................................................................................................S3

4. Reaction Optimization Studies....................................................................................................S10

5. General Procedure for Deboronative Cyanation Reaction......................................................S12

6. Competitive Experiments...........................................................................................................S18

7. Regioselective Hydrocyanation of the Alkene..........................................................................S18

8. Mechanism Studies.....................................................................................................................S19

9. References.................................................................................................................................S22

10. NMR spectra..............................................................................................................................S23
1. General Information

Materials

All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. CH$_3$CN, CH$_2$Cl$_2$, HFIP and MeOH were purchased from Sigma-Aldrich and used without any purification. Acetone was purchased from Sinopharm Chemical Reagent. Ir(ppy)$_3$ was purchased from Wuhan Zhuoxin Technology Co., Ltd.

Analytic Methods

$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR spectra were recorded on a Bruker Advance 600 spectrometer at the ambient temperature in CDCl$_3$, d$_6$-DMSO or D$_2$O. Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for $^{13}$C NMR are reported in terms of chemical shift (δ ppm). Data for $^{19}$F NMR are reported in terms of chemical shift (δ ppm). Gas Chromatography-Mass Spectrometer (GC-MS) analyses were performed on a Thermo Trace 1300 ISQ Series GC-MS System. GC-MS method: initial temp.: 50 °C (hold for 1 min), rate: 40 °C/min, final temp.: 250 °C (hold for 12 min). Room-temperature Electron Spin Resonance (ESR) spectra were obtained using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band). Microwave power employed was 5 mW; sweep width ranged from 2000 to 4000 G. Modulation frequency and modulation amplitude were 100 kHz and 3.5 G, respectively. Column chromatography was performed using 50-500 mesh silica gel. High-resolution mass spectra (HRMS) were recorded on an ACQUITY UPLC LCT Premier XE spectrometer with ESI mode. Organic solutions were concentrated under reduced pressure on a BUCHI rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Preparation of [Ru(bpy)$_3$](PF$_6$)$_2$

To a 250 mL round-bottomed flask was charged with RuCl$_3$ (540 mg, 2.6 mmol), 2,2’-bipyridine (2.5 g, 16 mmol) and EtOH (100 mL). The reaction mixture was heated to reflux for 12 h under nitrogen. After cooling to room temperature, KPF$_6$ (1.9 g, 10 mmol) was added, and the solid was collected by vacuum filtration. The red solid was washed with water and then washed through the fritted funnel with acetone to removed excess ruthenium salts. The acetone eluent was diluted with Et$_2$O to precipitate the ruthenium complex. The resulting red solid was filtered and dried overnight in vacuo. Spectral data corresponds to that previously reported.$^1$
3. Preparation of Substrates

I. General Procedure for the Preparation of 1b-d, 1i, 1j, 1o, 1p, 1u, 8

Alkene (10.0 mmol) in THF (2 mL) was added dropwise to a solution of BH$_3$•THF (20 mL, 20 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred for 2 h at room temperature and H$_2$O (2.0 mL) was slowly added. After stirring for additional 3 h at room temperature, the reaction mixture was concentrated in vacuo, diluted with ethyl acetate (30 mL), and washed with saturated aqueous bicarbonate (20 mL) and brine (20 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated to approximately 5 mL. Petroleum ether was then added. The resultant precipitate was washed with petroleum ether and dried under vacuum to afford the alkylboronic acid as white solid or thick oil. A 100 mL round-bottomed flask equipped with a stir bar was charged with the alkylboronic acid and MeOH (20 mL). To the flask was added KHF$_2$ (15 mL, 3.91 g, 50 mmol), and the resulting suspension was stirred for 2 h and then concentrated to dryness. The residue, a white solid, was extracted with hot acetone (3 × 30 mL), and the combined filtered extracts were concentrated to approximately 5 mL. Ether was added and the resultant precipitate was collected and dried to afford the potassium trifluoroborate as a white solid.

II. General Procedure for the Preparation of 1e-h, 1k-n, 1s, 1t, 1v-x, 1z

Cul (190 mg, 1.0 mmol), PPh$_3$ (341 mg, 1.3 mmol), LiOMe (760 mg, 20.0 mmol), and bis(pinacolato)diboron (3.80 g, 15.0 mmol) were added to a 100 mL round-bottomed flask equipped with a stir bar. The vessel was evacuated and filled with nitrogen gas three times. DMF (40 mL) and the alkyl bromide (10.0 mmol) were added by syringe under a nitrogen atmosphere. The resulting reaction mixture was stirred vigorously at 25 ºC for 18 h. The reaction mixture was diluted with EtOAc and filtered through silica gel. Then the mixture was washed with saturated aqueous brine (3 × 100 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and purified by column chromatography to afford the pinacol ester.

III. General Procedure for the Preparation of 1y, 1ab

CuCl (30 mg, 0.3 mmol), NaOt-Bu (86 mg, 0.9 mmol) and DPEphos ligand (162 mg, 0.3 mmol) were added to a 100 mL round-bottomed flask equipped with a stir bar. The vessel was evacuated and filled with nitrogen gas three times. THF (8.0 mL) were added under nitrogen. The reaction mixture was stirred vigorously at 25 °C for 18 h. The reaction mixture was then diluted with EtOAc and filtered through silica gel. Then the mixture was filtered with saturated aqueous brine (3 × 100 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and purified by column chromatography to afford the pinacol ester.
purified by flash column chromatography to afford pinacol ester as yellow oil.

**IV. Procedure for the Preparation of 1q**

\[\text{Me} = \text{CH}_2\text{OH} \quad \text{HO} \quad \text{Bpin} \quad \text{DCC, DMAP} \quad \text{DCM} \quad \text{r.t.} \quad \text{Me} \quad \text{Me} \quad \text{O} \quad \text{Bpin} \]

To a stirred solution of but-2-yn-1-ol (0.54 mL, 7.2 mmol), 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoic acid (1.15 g, 4.8 mmol) and DMAP (33.6 mg, 0.276 mmol) in anhydrous DCM (10 mL) was added DCC (1.09 g, 5.2 mmol) separately at room temperature. After stirring for 12 h, the mixture was filtered and washed with 1 M HCl, saturated NaHCO₃ aqueous and brine, respectively. After dried over Na₂SO₄, the crude product was concentrated and purified by flash column chromatography to afford pinacol ester as yellow oil.

**V. Procedure for the Preparation of 1ab**

\[\text{Fe(acac)}_3 (706, 2.0 \text{ mmol}) \quad \text{and bis(pinacolato)dboron (8.9 g, 35.0 mmol) were added to a 100 mL round-bottomed flask equipped with a stir bar. The vessel was evacuated and filled with nitrogen gas three times. THF (50 mL) was added, followed by TMEDA (8 mL of a 4\% (v/v) solution of TMEDA (0.32 mL) in THF, 2.0 mmol). Next, ethylmagnesium bromide (15 mL (3M in Et}_2\text{O), 45.0 mmol) was added dropwise to the reaction mixture at a rate of one drop/sec. Finally, 1-bromoadamantane (10.0 mmol) was added to the reaction mixture at once. The reaction mixture was stirred at room temperature for 12 h.} \]

Mixture was filtered (washed with Et₂O) and concentrated under reduced pressure. The crude residue was purified by silica flash chromatography to afford the desired pinacol ester.

**VI. General Procedure for the Preparation of alkyl trifluoroborates from alkylboronic acids and esters**

\[\text{To the solution of alkylboronic acids or esters (10 mmol) in methanol (20 mL) was added saturated aqueous KHF}_2 (15 mL, 3.91 g, 50 mmol). The resulting suspension was stirred for 2 h and then concentrated to dryness. The residue, a white solid, was extracted with hot acetone (3 \times 30 mL), and the combined filtered extracts were concentrated to approximately 5 mL. Diethyl ether was added and the resultant precipitate was collected and dried to afford the potassium trifluoroborate as a white solid.\]
Potassium (phenethyl)trifluoroborate (1a)
Following general procedure VI, 1a was obtained as a white solid (10 mmol scale, 1.74 g, 82% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 7.19 (dd, J = 10.2, 4.4 \text{ Hz, 2H}), 7.13 (d, J = 6.7 \text{ Hz, 2H}), 7.06 (d, J = 7.1 \text{ Hz, 1H}), 2.42 (s, 2H), 0.30 (s, 2H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 148.0, 127.8, 127.7, 124.3, 32.1.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (564 MHz, } d_6\text{-DMSO)} & \delta -137.7.
\end{align*}
\]

Potassium (4-methylphenethyl)trifluoroborate (1b)
Following general procedure I, 1b was obtained as a white solid (10 mmol scale, 1.94 g, 86% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 6.99 (s, 4H), 2.39 – 2.34 (m, 2H), 2.23 (s, 3H), 0.32 – 0.18 (m, 2H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 144.9, 132.9, 128.4, 127.5, 31.6, 20.6.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (564 MHz, } d_6\text{-DMSO)} & \delta -137.7.
\end{align*}
\]

Potassium (4-(tert-butyl)phenethyl)trifluoroborate (1c)
Following general procedure I, 1c was obtained as a white solid (10 mmol scale, 2.09 g, 78% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 7.20 (d, J = 7.2 \text{ Hz, 2H}), 7.03 (t, J = 7.2 \text{ Hz, 2H}), 2.40 – 2.32 (m, 2H), 1.24 (s, 9H), 0.25 (t, J = 14.8 \text{ Hz, 2H}).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 146.4, 144.8, 127.3, 124.5, 33.9, 31.5.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (564 MHz, } d_6\text{-DMSO)} & \delta -137.7.
\end{align*}
\]

Potassium (4-chlorophenethyl)trifluoroborate (1d)
Following general procedure I, 1d was obtained as a white solid (10 mmol scale, 1.85 g, 75% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 7.23 (d, J = 8.3 \text{ Hz, 2H}), 7.14 (d, J = 8.1 \text{ Hz, 2H}), 2.45 – 2.35 (m, 2H), 0.27 (s, 2H).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 147.0, 129.6, 128.9, 127.8, 31.5.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (564 MHz, } d_6\text{-DMSO)} & \delta -137.8.
\end{align*}
\]

Potassium (4-(1,3-dioxoisindolin-2-yl)butyl)trifluoroborate (1e)
Following general procedure II and VI, 1e was obtained as a white solid (10 mmol scale, 1.79 g, 58% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 7.84 (dt, J = 12.8, 7.2 \text{ Hz, 4H}), 3.50 (t, J = 7.3 \text{ Hz, 2H}), 1.55 – 1.44 (m, 2H), 1.11 (dt, J = 15.8, 8.0 \text{ Hz, 2H}), -0.05 (dd, J = 14.6, 6.8 \text{ Hz, 2H}).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 167.9, 134.4, 131.6, 123.0, 38.1, 31.8, 23.1.
\end{align*}
\]

\[
\begin{align*}
\text{F NMR (564 MHz, } d_6\text{-DMSO)} & \delta -132.2.
\end{align*}
\]

Potassium (3-phenoxypropyl)trifluoroborate (1f)
Following general procedure II and VI, 1f was obtained as a white solid (10 mmol scale, 1.47 g, 61% yield).

\[
\begin{align*}
\text{H NMR (600 MHz, } d_6\text{-DMSO)} & \delta 7.25 (t, J = 7.9 \text{ Hz, 2H}), 6.86 (d, J = 7.8 \text{ Hz, 3H}), 3.87 – 3.80 (m, 2H), 1.57 (dd, J = 15.0, 7.7 \text{ Hz, 2H}), 0.02 (d, J = 6.0 \text{ Hz, 2H}).
\end{align*}
\]

\[
\begin{align*}
\text{C NMR (151 MHz, } d_6\text{-DMSO)} & \delta 158.9, 129.3, 119.8, 114.3, 70.7, 25.2.
\end{align*}
\]
Potassium (3-(4-cyanophenoxy)propyl)trifluoroborate (1g)
Following general procedure II and VI, 1g was obtained as a white solid (10 mmol scale, 1.39 g, 52% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.72 (d, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.7$ Hz, 2H), 3.94 (t, $J = 7.4$ Hz, 2H), 1.58 (dt, $J = 14.1$, 6.9 Hz, 2H), 0.03 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 162.5, 134.1, 119.3, 115.4, 102.0, 71.4, 25.0. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -137.0.

Potassium (3-(4-bromophenoxy)propyl)trifluoroborate (1h)
Following general procedure II and VI, 1h was obtained as a white solid (10 mmol scale, 1.77 g, 55% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.39 (d, $J = 8.9$ Hz, 2H), 6.83 (t, $J = 6.1$ Hz, 2H), 3.82 (t, $J = 7.4$ Hz, 2H), 1.62 – 1.50 (m, 2H), 0.01 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 158.3, 131.9, 116.6, 111.1, 71.1, 25.1. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -137.1.

Potassium (((1S, 2S, 5S)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)methyl)trifluoroborate (1i)
Following general procedure I, 1i was obtained as a white solid (10 mmol scale, 1.93 g, 79% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 2.19 (dd, $J = 14.3$, 6.9 Hz, 1H), 1.98 (s, 1H), 1.91 – 1.75 (m, 4H), 1.75 – 1.66 (m, 1H), 1.42 (dq, $J = 9.9$, 7.0 Hz, 1H), 1.12 (s, 3H), 0.99 (s, 3H), 0.74 (d, $J = 9.0$ Hz, 1H), 0.14 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 48.6, 41.1, 3.32, 38.2, 34.1, 28.5, 26.9, 25.0, 23.2. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -134.6.

Potassium (2,2-diphenylethyl)trifluoroborate (1j)
Following general procedure I, 1j was obtained as a white solid (10 mmol scale, 2.3 g, 80% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.20 (d, $J = 7.2$ Hz, 4H), 7.14 (dt, $J = 12.5$, 6.2 Hz, 4H), 7.00 (dt, $J = 13.2$, 5.8 Hz, 2H), 3.95 (t, $J = 7.3$ Hz, 1H), 0.80 (dd, $J = 12.1$, 6.0 Hz, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 150.1, 127.7, 127.5, 124.4, 48.1. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -134.6.

Potassium (4-((thiophene-2-carbonyl)oxy)butyl)trifluoroborate (1k)
Following general procedure II and VI, 1k was obtained as a white solid (10 mmol scale, 1.31 g, 45% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.92 (d, $J = 4.0$ Hz, 1H), 7.77 (d, $J = 3.6$ Hz, 1H), 7.20 (t, $J = 4.1$ Hz, 1H), 4.18 (t, $J = 6.7$ Hz, 2H), 1.63 – 1.55 (m, 2H), 1.28 – 1.19 (m, 2H), -0.01 (d, $J = 3.6$ Hz, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 161.5, 133.6, 133.4, 133.3, 128.3, 65.5, 31.8, 21.8. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.9.

Potassium (5-(4-(ethoxycarbonyl)phenoxy)pentyl)trifluoroborate (1l)
Following general procedure II and VI, 1l was obtained as a white solid (10 mmol scale, 1.31 g, 45% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.88 (d, $J = 8.7$ Hz, 2H), 7.07 – 6.95 (m, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.99 (t, $J = 6.7$ Hz, 2H), 1.73 – 1.62 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 5H), 1.18 (d, $J = 7.1$ Hz, 2H), -0.03 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 165.4, 162.6, 131.1, 121.7, 114.3, 68.1, 60.2, 29.1, 28.9, 25.3, 14.2. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.8.
Potassium (5-ethoxy-5-oxopentyl)trifluoroborate (1m)

Following general procedure II and VI, 1m was obtained as a white solid (10 mmol scale, 1.42 g, 60% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 4.01 (q, $J = 7.1$ Hz, 2H), 2.17 (t, $J = 7.5$ Hz, 2H), 1.43 (p, $J = 7.5$ Hz, 2H), 1.16 (t, $J = 7.1$ Hz, 3H), 1.14 – 1.08 (m, 2H), -0.04 – -0.14 (m, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 173.7, 59.6, 34.4, 28.6, 25.5, 14.4. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.9.

Potassium (3-((2,6-difluorobenzoyl)oxy)propyl)trifluoroborate (1n)

Following general procedure II and VI, 1n was obtained as a white solid (10 mmol scale, 1.78 g, 58% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.62 (dq, $J = 14.1$, 7.0 Hz, 1H), 7.23 (td, $J = 8.4$, 4.8 Hz, 2H), 4.24 – 4.14 (m, 2H), 1.53 (s, 2H), -0.00 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 160.9, 159.3 (dd, $J = 252.6$, 6.7 Hz), 133.5 (t, $J = 10.7$ Hz), 112.5, 112.2, 69.4, 24.8. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -112.3 (t, $J = 7.3$ Hz), -137.3.

Potassium decyltrifluoroborate (1o)

Following general procedure I, 1o was obtained as a white solid (10 mmol scale, 2.06 g, 83% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 1.29 – 1.13 (m, 14H), 1.10 (d, $J = 4.2$ Hz, 2H), 0.85 (t, $J = 6.9$ Hz, 3H), -0.08 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 33.2, 31.3, 29.5, 29.3, 29.2, 28.8, 25.6, 22.1, 13.9. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.8.

Potassium (11-bromoundecyl)trifluoroborate (1p)

Following general procedure I, 1p was obtained as a white solid (10 mmol scale, 2.39 g, 70% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 3.51 (t, $J = 6.5$ Hz, 2H), 1.85 – 1.72 (m, 2H), 1.36 (dd, $J = 14.2$, 6.9 Hz, 2H), 1.32 – 1.13 (m, 12H), 1.11 (d, $J = 4.8$ Hz, 2H), -0.08 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 35.2, 33.2, 32.2, 29.5, 29.2, 29.1, 28.9, 28.1, 27.5, 25.6. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.7.

Potassium (6-(but-2-yn-1-yloxy)-6-oxohexyl)trifluoroborate (1q)

Following general procedure IV and VI, 1q was obtained as a white solid (10 mmol scale, 1.07 g, 39% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 4.62 (d, $J = 2.3$ Hz, 2H), 2.24 (t, $J = 7.5$ Hz, 2H), 1.82 (d, $J = 2.1$ Hz, 3H), 1.49 – 1.43 (m, 2H), 1.20 – 1.14 (m, 2H), 1.11 (dt, $J = 15.0$, 7.4 Hz, 2H), -0.08 (dq, $J = 13.1$, 6.4 Hz, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 172.6, 83.0, 74.2, 52.0, 33.6, 32.5, 25.4, 24.9, 3.2. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.9.

Potassium cyclohexyltrifluoroborate (1r)

Following general procedure VI, 1r was obtained as a white solid (10 mmol scale, 1.2 g, 63% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 1.57 (d, $J = 9.3$ Hz, 3H), 1.49 (d, $J = 13.2$ Hz, 2H), 1.12 – 0.97 (m, 3H), 0.89 (q, $J = 12.3$ Hz, 2H), -0.03 (s, 1H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 28.9, 28.3, 27.5. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -144.3.
Potassium (1-(tert-butoxycarbonyl)piperidin-4-yl)trifluoroborate (1s)

Following general procedure II and VI, 1e was obtained as a white solid (10 mmol scale, 1.51 g, 52% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 3.85 (s, 2H), 3.35 (dd, $J = 5.7, 2.3$ Hz, 2H), 2.48 (t, $J = 29.1$ Hz, 2H), 1.37 (s, 9H), 1.01 (q, $J = 12.5$ Hz, 2H), 0.11 (s, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) $\delta$ 159.1, 83.7, 48.5, 30.3, 29.6.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) $\delta$ -144.6.

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Potassium (1-tosylpiperidin-4-yl)trifluoroborate (1t)

Following general procedure II and VI, 1t was obtained as a white solid (5 mmol scale, 1.04 g, 60% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 7.56 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 3.50 (d, $J = 10.8$ Hz, 2H), 2.39 (s, 3H), 1.94 (t, $J = 10.6$ Hz, 2H), 1.52 – 1.43 (m, 2H), 1.18 (qd, $J = 12.7, 3.8$ Hz, 2H), -0.16 (ddd, $J = 11.6, 8.0, 3.9$ Hz, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) $\delta$ 142.9, 132.7, 129.6, 127.4, 48.0, 27.3, 21.0.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) $\delta$ -144.6.

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Potassium (cyclododecyl)trifluoroborate (1u)

Following general procedure I, 1u was obtained as a white solid (10 mmol scale, 2.33 g, 85% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 1.46 – 1.13 (m, 18H), 1.08 (qt, $J = 13.3, 6.5$ Hz, 4H), 0.11 (d, $J = 4.8$ Hz, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) $\delta$ 26.1, 24.0, 23.7, 23.6, 23.5, 23.0.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) $\delta$ -136.7.

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Potassium (4-(3-benzoylphenoxy)butan-2-yl)trifluoroborate (1v)

Following general procedure II and VI, 1v was obtained as a white solid (5 mmol scale, 0.76 g, 42% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 7.72 (d, $J = 8.7$ Hz, 2H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.02 (d, $J = 8.6$ Hz, 2H), 4.11 – 4.02 (m, 2H), 1.74 (ddd, $J = 15.5, 13.2, 6.7$ Hz, 1H), 1.41 (td, $J = 13.7, 7.6$ Hz, 1H), 0.74 (d, $J = 7.2$ Hz, 3H), 0.27 (s, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) $\delta$ 194.4, 163.0, 137.9, 132.2, 131.9, 129.2, 128.6, 128.4, 114.2, 68.9, 16.8.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) $\delta$ -143.7.

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Potassium (4-(4-methoxyphenoxy)butan-2-yl)trifluoroborate (1w)

Following general procedure II and VI, 1v was obtained as a white solid (5 mmol scale, 0.76 g, 42% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 6.80 (q, $J = 9.1$ Hz, 4H), 3.91 – 3.81 (m, 2H), 3.67 (s, 3H), 1.73 – 1.62 (m, 1H), 1.32 (dt, $J = 14.0, 7.9$ Hz, 1H), 0.71 (d, $J = 7.2$ Hz, 3H), 0.22 (s, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) $\delta$ 153.2, 152.9, 115.2, 114.6, 68.8, 55.4, 33.4, 16.9.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) $\delta$ -143.7.

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Potassium (4-(4-cyanophenoxy)butan-2-yl)trifluoroborate (1x)

Following general procedure II and VI, 1x was obtained as a white solid (10 mmol scale, 1.12 g, 40% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ 7.72 (d, $J = 8.7$ Hz, 2H), 7.03 (d, $J = 8.7$ Hz, 2H), 4.04 (dd, $J = 15.3, 6.4$ Hz, 2H), 1.75
- 1.66 (m, 1H), 1.38 (dd, $J = 13.7$, 6.2 Hz, 1H), 0.72 (d, $J = 7.2$ Hz, 3H), 0.26 (d, $J = 4.5$ Hz, 1H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 162.6, 134.1, 119.3, 115.4, 101.9, 69.0, 33.0, 16.8. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -143.7.

Potassium (1-methyl-3-oxocyclopentyl)trifluoroborate (1y)

Following general procedure III and VI, 1y was obtained as a white solid (10 mmol scale, 0.98 g, 48% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 2.13 – 1.83 (m, 4H), 1.40 (d, $J = 17.6$ Hz, 1H), 1.21 (t, $J = 8.6$ Hz, 1H), 0.79 (s, 3H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 223.2, 50.1, 37.3, 32.9, 24.5.

$^{19}$F NMR (376 MHz, $d_6$-DMSO) δ -144.0.

Potassium (4-((2-(4-isobutylphenyl)propanoyl)oxy)butan-2-yl)trifluoroborate (1z)

Following general procedure II and VI, 1z was obtained as a white solid (10 mmol scale, 1.73 g, 51% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.16 (d, $J = 7.7$ Hz, 2H), 7.09 (d, $J = 7.8$ Hz, 2H), 4.05 – 3.88 (m, 2H), 3.67 (q, $J = 7.1$ Hz, 1H), 2.40 (d, $J = 7.1$ Hz, 2H), 1.84 – 1.76 (m, 1H), 1.54 – 1.45 (m, 1H), 1.34 (d, $J = 7.1$ Hz, 3H), 1.18 – 1.11 (m, 1H), 0.85 (d, $J = 6.6$ Hz, 6H), 0.63 (t, $J = 6.7$ Hz, 3H), 0.10 (s, 1H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 173.9, 139.6, 138.1, 129.0, 127.0, 65.5, 44.3, 44.2, 32.6, 29.6, 22.2, 18.6, 16.5. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -144.0.

Potassium ((3r,5r,7r)-adamantan-1-yl)trifluoroborate (1aa)

Following general procedure V and VI, 1aa was obtained as a white solid (10 mmol scale, 0.6 g, 25% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 1.68 (s, 3H), 1.61 (q, $J = 11.7$ Hz, 6H), 1.43 (s, 6H).

$^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 45.5, 39.0, 38.7, 36.3, 30.5, 28.4.

$^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -152.7.

Potassium (1-methyl-3-oxocyclohexyl)trifluoroborate (1ab)

Following general procedure III and VI, 1ab was obtained as a white solid (10 mmol scale, 0.98 g, 45% yield).

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 2.18 (d, $J = 13.3$ Hz, 1H), 2.14 – 2.04 (m, 1H), 2.02 – 1.92 (m, 1H), 1.89 – 1.80 (m, 1H), 1.76 – 1.51 (m, 3H), 1.20 – 1.09 (m, 1H), 0.61 (s, 3H). $^{13}$C NMR (151 MHz, $d_2$o) δ 227.0, 52.5, 43.7, 34.7, 26.6, 23.6. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -150.0.

Potassium (4-phenylbutyl)trifluoroborate (8)

$^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.21 (t, $J = 7.1$ Hz, 2H), 7.11 (dd, $J = 14.6$, 7.4 Hz, 3H), 2.48 (d, $J = 9.3$ Hz, 2H), 1.44 (d, $J = 6.8$ Hz, 2H), 1.14 (d, $J = 4.5$ Hz, 2H), -0.04 (s, 2H). $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 143.2, 128.2, 128.0, 125.2, 35.8, 35.3, 25.4. $^{19}$F NMR (564 MHz, $d_6$-DMSO) δ -136.8.
4. Reaction Optimization Studies

Supplementary Fig. S1
**Supplementary Table S1: Screening of the solvent**

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<tr>
<th>entry</th>
<th>solvent</th>
<th>GC yield (%)(^b)</th>
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<tr>
<td>1(^c)</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>68</td>
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<tr>
<td>3</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
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<td>4</td>
<td>Acetone/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>trace</td>
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<tr>
<td>5</td>
<td>EtOAc/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>trace</td>
</tr>
<tr>
<td>6(^d)</td>
<td>HFIP/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>THF/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
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</tr>
<tr>
<td>8</td>
<td>MeOH/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>trace</td>
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<tr>
<td>9</td>
<td>Acetone/CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (2:1)</td>
<td>43</td>
</tr>
<tr>
<td>10(^d)</td>
<td>HFIP/CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (2:1)</td>
<td>51</td>
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</table>

\(^a\) Reaction conditions: 1a (0.2 mmol, 1 equiv), 2b (0.3 mmol, 1.5 equiv), [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.004 mmol, 2 mol %), BI-OAc (0.4 mmol, 2 equiv), TFA (2 equiv), under air atmosphere, 24 h at room temperature with 2 × 9 W blue LEDs irradiation, unless otherwise stated.

\(^b\) GC yields with 2-phenylacetonitrile as an internal standard added after the reaction. \(^c\) Reaction conducted under N<sub>2</sub> atmosphere. \(^d\) HFIP = Hexafluoro-2-propanol.

**Supplementary Table S2: Screening of the amount of BI-OAc**

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<th>TsCN (equiv)</th>
<th>TFA (equiv)</th>
<th>BI-OAc (equiv)</th>
<th>solvent</th>
<th>GC yield of 3a (%)</th>
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<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>26</td>
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<tr>
<td>2</td>
<td>3</td>
<td>2</td>
<td>3</td>
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<td>63</td>
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<tr>
<td>3</td>
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<td>none</td>
<td>3</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O (1:1)</td>
<td>62</td>
</tr>
<tr>
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<tr>
<td>5</td>
<td>3</td>
<td>none</td>
<td>2</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;/Acetone (2:1)</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 1r (0.2 mmol, 1 equiv), 2b, [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (0.004 mmol, 2 mol %), BI-OAc, TFA, under air atmosphere, 24 h at room temperature with 2 × 9 W blue LEDs irradiation, unless otherwise stated. \(^b\) GC yields with 2-phenylacetonitrile as an internal standard added after the reaction.
5. General Procedure for Deboronative Cyanation Reaction

Method A (primary alkyltrifluoroborates): To a 5 mL vial was sequentially added alkyltrifluoroborates 1 (0.2 mmol), TsCN 2b (54.3 mg, 0.3 mmol), \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) (3.8 mg, 2 mol %), BI-OAc (183.6 mg, 0.6 mmol). Then CH$_2$Cl$_2$ (1 mL), H$_2$O (1 mL) and TFA (30 μL, 0.4 mmol) were added. The reaction mixture was stirred for 24 h at room temperature with blue LEDs (2 × 9 W) irradiation. Upon completion, the reaction mixture was purified by column chromatography (silica gel, ethyl acetate/petroleum ether) yielded the desired product.

Method B (secondary and tertiary alkyltrifluoroborates): To a 5 mL vial was sequentially added alkyltrifluoroborates 1 (0.2 mmol), TsCN 2b (108.6 mg, 0.6 mmol), \([\text{Ru(bpy)}_3](\text{PF}_6)_2\) (3.8 mg, 2 mol %), BI-OAc (183.6 mg, 0.6 mmol). Then CH$_2$Cl$_2$ (1 mL) and H$_2$O (1 mL) were added. The reaction mixture was stirred for 24 h at room temperature with blue LEDs (2 × 9 W) irradiation. Upon completion, the reaction mixture was purified by column chromatography (silica gel, ethyl acetate/petroleum ether) yielded the desired product.

3-Phenylpropanenitrile (3a)
Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (0.2 mmol scale: 18.7 mg, 71% yield, 1 mol scale: 89.1 mg, 68% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.35 (t, $J = 7.5$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 2H), 2.96 (t, $J = 7.4$ Hz, 2H), 2.62 (t, $J = 7.4$ Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 138.0, 128.8, 128.2, 119.1, 31.5, 19.3. GC-MS (m/z): 131.04. Spectral data corresponds to that previously reported.$^6$

3-(p-Tolyl)propanenitrile (3b)
Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (18 mg, 62% yield).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.13 (q, $J = 8.0$ Hz, 4H), 2.92 (t, $J = 7.4$ Hz, 2H), 2.59 (t, $J = 7.4$ Hz, 2H), 2.33 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 136.8, 135.0, 129.5, 128.1, 119.2, 31.1, 21.0, 19.5. GC-MS (m/z): 145.14. Spectral data corresponds to that previously reported.$^7$

3-(4-(tert-Butyl)phenyl)propanenitrile (3c)
Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired
product as a colorless oil (21 mg, 56% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 8.1$ Hz, 2H), 2.93 (t, $J = 7.5$ Hz, 2H), 2.60 (t, $J = 7.4$ Hz, 2H), 1.31 (s, 9H). 13C NMR (151 MHz, CDCl$_3$) $\delta$ 150.1, 134.9, 127.9, 125.7, 119.3, 34.4, 31.3, 31.0, 19.3. HRMS (ESI) m/z calcd for C$_{13}$H$_{18}$N [M+H]: 188.1434; found: 188.1439.

3-(4-Chlorophenyl)propanenitrile (3d)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (22.3 mg, 67% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 2.93 (t, $J = 7.3$ Hz, 2H), 2.61 (t, $J = 7.3$ Hz, 2H).

13C NMR (151 MHz, CDCl$_3$) $\delta$ 136.3, 133.1, 129.6, 129.0, 118.8, 30.9, 19.3.

GC-MS (m/z): 165.09. Spectral data corresponds to that previously reported.

5-(1,3-Dioxoisindolin-2-yl)pentanenitrile (3e)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 2:1) to give the desired product as a white solid (24.2 mg, 53% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 5.3$, 3.1 Hz, 2H), 7.78 – 7.58 (m, 2H), 3.73 (t, $J = 6.8$ Hz, 2H), 2.42 (t, $J = 7.1$ Hz, 2H), 1.88 – 1.82 (m, 2H), 1.71 (dt, $J = 14.6$, 7.2 Hz, 2H).

13C NMR (151 MHz, CDCl$_3$) $\delta$ 168.3, 134.1, 131.9, 123.3, 119.2, 36.6, 27.6, 22.6, 16.6.

GC-MS (m/z): 228.14. Spectral data corresponds to that previously reported.

4-Phenoxybutanenitrile (3f)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 20:1) to give the desired product as a colorless oil (23.2 mg, 72% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.29 (t, $J = 7.6$ Hz, 2H), 6.97 (t, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 8.5$ Hz, 2H), 4.07 (t, $J = 5.7$ Hz, 2H), 2.59 (t, $J = 7.1$ Hz, 2H), 2.18 – 2.08 (m, 2H).

13C NMR (151 MHz, CDCl$_3$) $\delta$ 158.3, 129.5, 121.2, 119.2, 114.4, 65.1, 25.4, 14.2.

GC-MS (m/z): 161.12. Spectral data corresponds to that previously reported.

4-(3-Cyanopropoxy)benzonitrile (3g)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (25.7 mg, 69% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 8.8$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 4.14 (t, $J = 5.7$ Hz, 2H), 2.62 (t, $J = 7.0$ Hz, 2H), 2.22 – 2.14 (m, 2H).

13C NMR (151 MHz, CDCl$_3$) $\delta$ 161.5, 134.0, 119.0, 118.8, 115.1, 104.5, 65.6, 25.1, 14.1.

GC-MS (m/z): 186.12. Spectral data corresponds to that previously reported.

4-(4-Bromophenoxy)butanenitrile (3h)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 20:1) to give the desired product as a colorless oil (24 mg, 50% yield).

1H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.7$ Hz, 2H), 6.76 (d, $J = 8.7$ Hz, 2H), 4.03 (t, $J = 5.7$ Hz, 2H), 2.58 (t, $J = 7.1$ Hz, 2H), 2.16 – 2.09 (m, 2H).

13C NMR (151 MHz, CDCl$_3$) $\delta$ 157.4, 132.3, 119.0, 116.2, 113.4, 65.4, 25.3, 14.1.

GC-MS (m/z): 239.03 (Br$^{79}$); 241.03 (Br$^{81}$). Spectral data corresponds to that previously reported.
2-((1S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)acetonitrile (3i)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (17.2 mg, 53% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.50 – 2.34 (m, 4H), 2.12 (ddd, $J = 13.3$, 11.8, 6.5 Hz, 1H), 2.03 (t, $J = 4.9$ Hz, 1H), 2.00 – 1.92 (m, 2H), 1.92 – 1.83 (m, 1H), 1.49 (ddd, $J = 16.7$, 11.4, 6.1 Hz, 1H), 1.22 (s, 3H), 1.01 (s, 3H), 0.94 (d, $J = 9.9$ Hz, 1H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 119.5, 119.4, 45.1, 40.8, 38.6, 37.8, 33.0, 29.7, 27.7, 25.7, 24.2, 22.9, 21.4. GC-MS (m/z): 163.20. Spectral data corresponds to that previously reported.

3,3-Diphenylpropanenitrile (3j)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (32.4 mg, 78% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33 (t, $J = 7.5$ Hz, 4H), 7.28 – 7.22 (m, 6H), 4.38 (t, $J = 7.7$ Hz, 1H), 3.03 (d, $J = 7.7$ Hz, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 141.1, 128.8, 127.5, 127.3, 118.4, 47.1, 24.2. GC-MS (m/z): 207.11. Spectral data corresponds to that previously reported.

4-Cyanobutyl thiophene-2-carboxylate (3k)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (28.5 mg, 68% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 3.6$ Hz, 1H), 7.57 (d, $J = 4.9$ Hz, 1H), 7.11 (t, $J = 4.3$ Hz, 1H), 4.34 (t, $J = 6.1$ Hz, 2H), 2.44 (t, $J = 7.1$ Hz, 2H), 1.95 – 1.89 (m, 2H), 1.86 – 1.79 (m, 2H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 162.0, 133.5, 133.4, 132.5, 127.8, 119.3, 63.8, 27.7, 22.3, 16.9. GC-MS (m/z): 209.08. Spectral data corresponds to that previously reported.

Ethyl 4-((5-cyanopentyl)oxy)benzoate (3l)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (40.2 mg, 77% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.99 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.03 (t, $J = 6.2$ Hz, 2H), 2.40 (t, $J = 7.0$ Hz, 2H), 1.89 – 1.81 (m, 2H), 1.80 – 1.72 (m, 2H), 1.66 (dt, $J = 15.2$, 7.6 Hz, 2H), 1.38 (q, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.3, 162.5, 131.5, 122.9, 119.5, 113.9, 67.4, 60.6, 28.3, 25.3, 25.1, 17.1, 14.3. HRMS (ESI) m/z calcd for C$_{15}$H$_{20}$NO$_3$ [M+H]$^+$: 262.1438; found: 262.1258.

Ethyl 5-cyanopentanoate (3m)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 20:1) to give the desired product as a colorless oil (14 mg, 45% yield).

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 4.13 (q, $J = 7.1$ Hz, 2H), 2.36 (dt, $J = 12.5$, 7.2 Hz, 4H), 1.83 – 1.75 (m, 2H), 1.74 – 1.67 (m, 2H), 1.25 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.7, 119.3, 60.5, 33.3, 24.8, 23.9, 17.0, 14.2. HRMS
(ESI) m/z calcd for C_{14}H_{14}NO_2[M+H]^+: 156.1019; found: 156.0979.

3-Cyanopropyl 2,6-difluorobenzoate (3n)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a colorless oil (37 mg, 82% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.45 (t, J = 7.0 Hz, 1H), 6.98 (t, J = 8.4 Hz, 2H), 4.48 (t, J = 5.7 Hz, 2H), 2.56 (t, J = 7.2 Hz, 2H), 2.18 – 2.11 (m, 2H). ^13C NMR (151 MHz, CDCl_3) δ 161.6, 161.1 (dd, J = 256.9, 5.9 Hz), 133.2 (t, J = 10.6 Hz), 118.7, 112.1 (d, J = 21.8 Hz), 112.1 (d, J = 21.8 Hz), 63.3, 24.8, 14.1. HRMS (ESI) m/z calcd for C_{11}H_{10}F_2NO_2[M+H]^+: 226.0680; found: 226.0676.

Undecanenitrile (3o)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (22.3 mg, 66% yield).

^1H NMR (600 MHz, CDCl_3) δ 2.34 (t, J = 7.1 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.47 – 1.41 (m, 2H), 1.29 (dd, J = 15.3, 9.5 Hz, 12H), 0.88 (t, J = 6.9 Hz, 3H).

^13C NMR (151 MHz, CDCl_3) δ 119.9, 31.8, 29.4, 29.3, 29.2, 28.7, 28.6, 25.3, 17.1, 14.1. GC-MS (m/z): 167.25. Spectral data corresponds to that previously reported.

12-Bromododecanenitrile (3p)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (31.2 mg, 60% yield).

^1H NMR (600 MHz, CDCl_3) δ 3.41 (t, J = 6.9 Hz, 2H), 2.34 (t, J = 7.1 Hz, 2H), 1.92 – 1.79 (m, 2H), 1.69 – 1.63 (m, 2H), 1.43 (tt, J = 14.4, 7.2 Hz, 4H), 1.29 (s, 10H).

^13C NMR (151 MHz, CDCl_3) δ 119.8, 119.4, 34.0, 32.7, 29.3, 29.2, 28.7, 28.6, 28.1, 25.3, 17.1. HRMS (ESI) m/z calcd for C_{12}H_{23}BrN [M+H]^+: 260.1008; found: 260.1005.

But-2-yn-1-yl 6-cyanohexanoate (3q)

Following method A, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a colorless oil (17.6 mg, 46% yield).

^1H NMR (600 MHz, CDCl_3) δ 4.64 (s, 2H), 2.39 – 2.32 (m, 4H), 1.85 (s, 3H), 1.71 – 1.64 (m, 4H), 1.52 – 1.45 (m, 2H).

^13C NMR (151 MHz, CDCl_3) δ 172.6, 119.5, 83.2, 73.0, 52.8, 33.6, 28.0, 25.0, 23.9, 17.0, 3.6. HRMS (ESI) m/z calcd for C_{11}H_{16}NO_2[M+H]^+: 194.1176; found: 194.1181.

tert-Butyl 4-cyanopiperidine-1-carboxylate (3s)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (32.4 mg, 77% yield).

^1H NMR (600 MHz, CDCl_3) δ 3.65 (ddd, J = 13.4, 7.1, 3.5 Hz, 2H), 1.85 (s, 3H), 1.71 – 1.64 (m, 4H), 1.52 – 1.45 (m, 2H).

^13C NMR (151 MHz, CDCl_3) δ 172.6, 119.5, 83.2, 73.0, 52.8, 33.6, 28.0, 25.0, 23.9, 17.0, 3.6. HRMS (ESI) m/z calcd for C_{11}H_{16}NO_2[M+H]^+: 194.1176; found: 194.1181.

1-Tosylpiperidine-4-carbonitrile (3t)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a white solid (27.5 mg, 52% yield).

^1H NMR (600 MHz, CDCl_3) δ 3.65 (ddd, J = 13.4, 7.1, 3.5 Hz, 2H), 1.85 (s, 3H), 1.71 – 1.64 (m, 4H), 1.52 – 1.45 (m, 2H).

^13C NMR (151 MHz, CDCl_3) δ 172.6, 119.5, 83.2, 73.0, 52.8, 33.6, 28.0, 25.0, 23.9, 17.0, 3.6. GC-MS (m/z): 210.21. Spectral data corresponds to that previously reported.
\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 7.9\) Hz, 2H), 7.32 (d, \(J = 7.9\) Hz, 2H), 3.12 (s, 4H), 2.74 – 2.67 (m, 1H), 2.44 (s, 3H), 2.04 – 1.94 (m, 2H), 1.94 – 1.86 (m, 2H). \[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 144.0, 132.7, 129.8, 127.5, 120.3, 43.8, 27.9, 25.3, 21.5. GC-MS (m/z): 264.18. Spectral data corresponds to that previously reported.9

Cyclododecanecarbonitrile (3u)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a colorless oil (22 mg, 57% yield).

\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 2.64 (s, 1H), 1.78 – 1.63 (m, 4H), 1.54 (dt, \(J = 11.6, 6.4\) Hz, 2H), 1.48 – 1.37 (m, 4H), 1.29 (d, \(J = 45.8\) Hz, 12H).

\[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 123.2, 27.1, 26.4, 23.6, 23.4, 23.2, 23.1, 21.8.

GC-MS (m/z): 193.25. Spectral data corresponds to that previously reported.

4-(3-Benzoylphenoxy)-2-methylbutanenitrile (3v)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a colorless oil (24 mg, 43% yield).

\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 8.7\) Hz, 2H), 7.76 (d, \(J = 7.4\) Hz, 2H), 7.57 (t, \(J = 7.4\) Hz, 1H), 7.48 (t, \(J = 7.6\) Hz, 2H), 6.97 (d, \(J = 8.7\) Hz, 2H), 4.21 (dd, \(J = 11.1, 5.3\) Hz, 2H), 3.01 (dd, \(J = 15.0, 7.1\) Hz, 1H), 2.15 – 2.05 (m, 2H), 1.43 (d, \(J = 7.1\) Hz, 3H).

\[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 195.5, 161.9, 138.1, 132.5, 131.9, 130.5, 129.7, 128.2, 122.2, 113.9, 64.7, 33.5, 22.5, 17.9. HRMS (ESI) m/z calcd for C\(_{18}\)H\(_{18}\)NO\(_2\)[M+H]+: 280.1332; found: 280.1338.

4-(4-Methoxyphenoxy)-2-methylbutanenitrile (3w)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 20:1) to give the desired product as a colorless oil (15.2 mg, 37% yield).

\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 6.91 – 6.75 (m, 4H), 4.10 – 4.03 (m, 2H), 3.77 (s, 3H), 2.99 (dq, \(J = 14.3, 7.1\) Hz, 1H), 2.15 – 1.92 (m, 2H), 1.40 (d, \(J = 7.1\) Hz, 3H).

\[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 154.1, 152.5, 122.5, 115.4, 114.6, 65.1, 55.7, 33.8, 22.4, 17.9. HRMS (ESI) m/z calcd for C\(_{12}\)H\(_{16}\)NO\(_2\)[M+H]+: 206.1176; found: 206.1178.

4-(3-Cyanobutoxy)benzonitrile (3x)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (34.8 mg, 87% yield).

\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 8.6\) Hz, 2H), 6.96 (d, \(J = 8.8\) Hz, 2H), 4.25 – 4.11 (m, 2H), 3.05 – 2.94 (m, 1H), 2.14 – 2.05 (m, 2H), 1.43 (d, \(J = 7.1\) Hz, 3H).

\[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 161.5, 134.0, 122.1, 119.0, 115.1, 104.4, 64.9, 33.4, 22.5, 17.9. HRMS (ESI) m/z calcd for C\(_{12}\)H\(_{13}\)N\(_2\)O[M+H]+: 201.1022; found: 201.1025.

1-Methyl-3-oxocyclopentane-1-carbonitrile (3y)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (34.8 mg, 87% yield).

\[^1\]H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 2.75 (d, \(J = 18.2\) Hz, 2H), 2.56 – 2.47 (m, 2H), 2.44 – 2.36 (m, 1H), 2.26 (d, \(J = 18.2\) Hz, 1H), 2.07 – 2.00 (m, 1H), 1.55 (s, 3H).

\[^13\]C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 212.9, 123.6, 49.8, 36.4, 35.0, 34.9, 24.7. GC-MS (m/z): 264.18. Spectral data corresponds to that previously reported.9
S17

(m/z): 123.11. Spectral data corresponds to that previously reported.¹⁷

![3-Cyanobutyl 2-(4-isoobutylphenyl)propanoate (3z)](image)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 10:1) to give the desired product as a colorless oil (27 mg, 47% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.18 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 4.29 (dt, J = 11.3, 5.5 Hz, 1H), 4.13 (ddd, J = 12.6, 8.2, 4.7 Hz, 1H), 3.70 (q, J = 7.1 Hz, 1H), 2.45 (d, J = 7.2 Hz, 3H), 1.87 (ddt, J = 20.2, 13.6, 5.9 Hz, 2H), 1.77 (ddd, J = 14.1, 9.6, 5.6 Hz, 1H), 1.51 – 1.47 (m, 3H), 1.25 (d, J = 7.3 Hz, 1H), 1.20 (d, J = 7.1 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 174.3, 140.7, 137.6, 129.3, 127.0, 122.1, 61.1, 45.0, 44.9, 32.8, 30.2, 22.3, 22.1, 18.1, 17.6. HRMS (ESI) m/z calcd for C₁₈H₂₆NO₂[M+H]+: 288.1958; found: 288.1956.

¹-Adamantanecarbonitrile (3aa)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 50:1) to give the desired product as a white solid (19 mg, 59% yield).

¹H NMR (600 MHz, CDCl₃) δ 2.04 (d, J = 7.1 Hz, 9H), 1.73 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 125.2, 39.8, 35.7, 30.1, 27.0. GC-MS (m/z): 161.16. Spectral data corresponds to that previously reported.¹⁸

¹-Methyl-3-oxocyclohexane-1-carbonitrile (3ab)

Following method B, the resulting mixture was purified by flash chromatography (PE: EA = 5:1) to give the desired product as a colorless oil (1 mmol scale: 61.7 mg, 45% yield).

¹H NMR (600 MHz, DMSO) δ 2.59 – 2.47 (m, 2H), 2.38 – 2.30 (m, 1H), 2.24 (d, J = 14.1 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.84 – 1.72 (m, 2H), 1.38 (s, 3H). ¹³C NMR (151 MHz, DMSO) δ 207.18, 123.38, 50.39, 39.64, 36.91, 34.26, 25.60, 22.44. GC-MS (m/z): 137.14. Spectral data corresponds to that previously reported.¹⁹
6. Competitive Experiments

\[
\text{Ph-BF}_3\text{K} \quad 4, \ 0.1 \ \text{mmol} \quad + \quad \text{Ph-BF}_3\text{K} \quad 1\text{a}, \ 0.1 \ \text{mmol} \quad \xrightarrow{\text{Method A}} \quad \text{Ph-CN} \quad 5 \quad 7\% \ \text{yield} \quad + \quad \text{Ph-CN} \quad 3\text{a} \quad 58\% \ \text{yield}
\]

\[
\text{Ph-BF}_3\text{K} \quad 4, \ 0.1 \ \text{mmol} \quad + \quad \text{Ph-BF}_3\text{K} \quad 1\text{r}, \ 0.1 \ \text{mmol} \quad \xrightarrow{\text{Method B}} \quad \text{Ph-CN} \quad 5 \quad 1\% \ \text{yield} \quad + \quad \text{Ph-CN} \quad 3\text{r} \quad 42\% \ \text{yield}
\]

Fig. S2

7. Regioselective hydrocyanation of the alkene

To a 5 mL vial was sequentially added alkyltrifluoroborates 8 (0.2 mmol), TsCN 2b (54.3 mg, 0.3 mmol), [Ru(bpy)$_3$](PF$_6$)$_2$ (3.8 mg, 2 mol %), BI-OAc (183.6 mg, 0.6 mmol). Then CH$_2$Cl$_2$ (1 mL), H$_2$O (1 mL) and TFA (30 μL, 0.4 mmol) were added. The reaction mixture was stirred for 24 h at room temperature with blue LEDs (2 × 9 W) irradiation. Upon completion, the reaction mixture was purified by column chromatography (silica gel, ethyl acetate/petroleum ether) yielded the desired product as a colorless oil (23 mg, 72% yield).

5-Phenylpentanenitrile (9)

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.22 – 7.15 (m, 3H), 2.66 (t, $J = 7.5$ Hz, 2H), 2.34 (t, $J = 7.1$ Hz, 2H), 1.83 – 1.75 (m, 2H), 1.68 (dt, $J = 14.7$, 7.2 Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 141.1, 128.4, 128.3, 126.0, 119.6, 34.9, 30.2, 24.8, 17.0. GC-MS (m/z): 159.17. Spectral data corresponds to that previously reported.
8. Mechanism Studies

a) TEMPO-trapping experiment

\[ 2a + 2b \xrightarrow{\text{Method A}} 3a, 0\% \quad \text{yield} \]

GC-MS analysis of the reaction mixture:

![GC-MS analysis graph]

Fig. S3

S19
\[ \text{1H NMR analysis of 10} \]

2,2,6,6-tetramethyl-1-phenethoxypiperidine(10)

Colorless oil (10 mg, 19% yield). \( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\)) \( \delta \) 7.28 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.23 (d, \( J = 7.4 \text{ Hz}, 2\text{H} \)), 7.19 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 3.94 (t, \( J = 7.0 \text{ Hz}, 2\text{H} \)), 2.82 (t, \( J = 7.0 \text{ Hz}, 2\text{H} \)), 1.61 – 1.54 (m, 2H), 1.41 (d, \( J = 4.5 \text{ Hz}, 4\text{H} \)), 1.07 (s, 12H). GC-MS (m/z): 261.31. Spectral data corresponds to that previously reported.\(^{21}\)

b) ESR experiment with PBN

To a 5 mL vial was sequentially added Potassium (phenethyl)trifluoroborate \( 1\text{a} \) (42.4 mg, 0.2 mmol), TsCN \( 2\text{b} \) (54.3 mg, 0.3 mmol), PBN (N-benzyldiene-tert-butylamine N-oxide) (88.5 mg, 0.5 mmol), \( \text{[Ru(bpy)}_3\text{](PF}_6\text{)}_2 \) (3.8 mg, 2 mol %), BI-OAc (183.6 mg, 0.6 mmol). Then CH\(_2\text{Cl}_2\) (1 mL), H\(_2\text{O}\) (1 mL) and TFA (30 \( \mu\text{L}, 0.4 \text{ mmol} \)) were added. The reaction mixture was stirred for 24 h at room temperature with blue LEDs (2 × 9 W) irradiation. Upon completion, the reaction mixture was analysis by ESR.
c) GC-MS analysis of the reaction mixture of 3x

2 mol % [Ru(bpy)]_3[PF_6]_2
3 equiv BI-OAc
CH_2Cl_2/H_2O, rt blue LEDs

RT: 0.22 - 15.09

Fig. S4
9. References

10. NMR data

Potassium (phenethyl)trifluoroborate (1a)
Potassium (4-methylphenethyl)trifluoroborate (1b)
Potassium (4-(tert-butyl)phenethyl)trifluoroborate (1c)
Potassium (4-chlorophenethyl)trifluoroborate (1d)
Potassium (4-(1,3-dioxoisooindolin-2-yl)butyl)trifluoroborate (1e)
Potassium (3-phenoxypropyl)trifluoroborate (1f)

$\text{H NMR (600 MHz, } d_2\text{-DMSO)}$

$^{19}\text{F NMR (564 MHz, } d_2\text{-DMSO)}$
Potassium (3-(4-cyanophenoxy)propyl)trifluoroborate (1g)
Potassium (3-(4-bromophenoxy)propyl)trifluoroborate (1h)

$\text{BF}_3\text{K}$

$^1\text{H NMR (600 MHz, }\text{d}_2\text{-DMSO})$

$^1\text{F NMR (564 MHz, }\text{d}_2\text{-DMSO})$

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S33
Potassium \(((1S)-6,6\text{-dimethylbicyclo}[3.1.1]\text{heptan-2-yl})\text{methyl})\text{trifluoroborate} \ (1i)\)
Potassium (2,2-diphenylethyl)trifluoroborate (1j)
Potassium (4-((thiophene-2-carbonyl)oxy)butyl) trifluoroborate (1k)
Potassium (5-(4-(ethoxycarbonyl)phenoxy)penty1)trifluoroborate (11)
$^{13}C$ NMR (151 MHz, $d_{6}$-DMSO)

$^{19}F$ NMR (564 MHz, $d_{6}$-DMSO)
Potassium (5-ethoxy-5-oxopentyl)trifluoroborate (1m)
Potassium (3-((2,6-difluorobenzoyl)oxy)propyl)trifluoroborate (1n)
Potassium decyltrifluoroborate (10)
Potassium (11-bromoundecyl)trifluoroborate (1p)
Potassium (6-(but-2-yn-1-yloxy)-6-oxohexyl)trifluoroborate (1q)
Potassium cyclohexyltrifluoroborate (1r)
Potassium (1-(tert-butoxycarbonyl)piperidin-4-yl)trifluoroborate (1s)
Potassium trifluoro(1-tosylpiperidin-4-yl)borate (1t)
$^{13}C$ NMR (151 MHz, $d_6$ DMSO)

$^{19}F$ NMR (594 MHz, $d_2$ DMSO)
Potassium (cyclododecyl)trifluoroborate (1u)
Potassium (4-(3-benzoylphenoxy)butan-2-yl)trifluoroborate (1v)
Potassium trifluoro(4-(4-methoxyphenoxy)butan-2-yl)borate (1w)
Potassium (4-(4-cyanophenoxy)butan-2-yl)trifluoroborate (1x)

$^1$H NMR (500 MHz, $d_2$-DMSO)
Potassium trifluoro(1-methyl-3-oxocyclopentyl)borate (1y)
Potassium trifluoro(4-((2-(4-isobutylphenyl)propanoyl)oxy)butan-2-yl)borate (1z)
Potassium ((3r,5r,7r)-adamantan-1-yl)trifluoroborate (1aa)
Potassium trifluoro(1-methyl-3-oxocyclohexyl)borate (1ab)
Potassium trifluoro(4-phenylbutyl)borate (8)

$\text{${}^{1}H$ NMR (500 MHz, $d_6$-DMSO)}$

$\text{${}^{13}C$ NMR (151 MHz, $d_6$-DMSO)}$

S65
$^{19}$F NMR (504 MHz, $d_6$ DMSO)
3-Phenylpropanenitrile (3a)
3-(p-Tolyl)propanitrile (3b)
3-(4-(tert-Butyl)phenyl)propanenitrile (3c)
3-(4-Chlorophenyl)propanenitrile (3d)
5-(1,3-Dioxoisindolin-2-yl)pentanenitrile (3e)
4-Phenoxybutanenitrile (3f)
4-(3-Cyanopropoxy)benzonitrile (3g)
4-(4-Bromophenoxy)butanenitrile (3h)
2-((1S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-yl)acetonitrile (3i)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
3,3-Diphenylpropanenitrile (3j)
4-Cyanobutyl thiophene-2-carboxylate (3k)
Ethyl 4-((5-cyanopentyl)oxy)benzoate (3I)
Ethyl 5-cyanopentanoate (3m)
3-Cyanopropyl 2,6-difluorobenzoate (3n)
Undecanitrile (3o)
12-Bromododecanitrile (3p)

$\text{Br}$

$\text{H NMR (600 MHz, CDCl}_3$)

$\text{CN}$

$\Delta_\text{NMR (151 MHz, CDCl}_3$)

$\text{CN}$

$\Delta$
But-2-yn-1-yl 6-cyanohexanoate (3q)
**tert-Butyl 4-cyanopiperidine-1-carboxylate (3s)**

**$^1$H NMR (600 MHz, CDCl$_3$)**

**$^{13}$C NMR (151 MHz, CDCl$_3$)**
Cyclododecanecarbonitrile (3u)
4-(3-Benzoylphenoxy)-2-methylbutanenitrile (3v)
4-(4-Methoxyphenoxy)-2-methylbutanenitrile (3w)
4-(3-Cyanobutoxy)benzonitrile (3x)
1-Methyl-3-oxocyclopentane-1-carbonitrile (3y)
3-Cyanobutyl 2-(4-isobutylphenyl)propanoate (3z)
1-Adamantanecarbonitrile (3aa)
1-Methyl-3-oxocyclohexane-1-carbonitrile (3ab)
5-Phenylpentanenitrile (9)