Supporting Information

Photoredox-mediated Remote C(sp³)-H Heteroarylation of Free Alcohols

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1. Reagents

All commercial materials were used as received unless otherwise noted. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ($\lambda_{\text{max}} = 254$ nm). Flash chromatography was performed using Silica gel (200–300 mesh) purchased from Qingdao Haiyang Chemical Co., China. [Bis(trifluoroacetoxy)iodo]benzene (PhI(OTFA)$_2$, 7), and (diaacetoxyiodo)benzene (PhI(OAc)$_2$,) were purchased from sigma-aldrich®. Acetoxybenziodoxole (BI–OAc, 1)$^{[1]}$, perfluorohydroxylbenziodoxole (PFBI–OH, 2)$^{[2]}$ and hydroxylbenziodoxole (BI–OH, 5)$^{[1]}$ were synthesized according to reported procedures and used as freshly prepared. [Ru(bpy)$_3$]Cl$_2$ (98%, Ru > 15.75%, Energy Chemical) and HFIP (99.0%, ACS grade, J&K Chemical) were used as received unless otherwise noted.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm). Peaks recorded are relative to internal standards: TMS ($\delta = 0.00$) for $^1$H and CDCl$_3$ ($\delta = 77.00$) for $^{13}$C spectra. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, br s = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999–2, made from clear borosilicate glass) unless otherwise noted, sealed with PTFE cap on bench top. The energy saver CFL bulb (23 W, MINI SPIRAL, SOFT WHITE) was purchased from SATCO®.
3. Synthesis of PFBI-OAc 6

PFBI-OH 2 (2.0 g, 6.0 mmol, 1.0 equiv) was heated in Ac₂O (4 mL) to reflux until the solution turned clear (without suspension). The mixture was heated for another 15 min, then left to cool down and slightly yellowish crystals started to form. The crystallization was continued at room temperature over night under Ar. The crystal were then collected and dried overnight under high vacuum to give compound 6 (1.4 g, ~64%). **Note:** compound 6 is very sensitive to moisture, and easily hydrolyzed to form PFBI-OH 2 and acetic acid. **1H NMR** (500 MHz, DMSO-d6) δ 2.21 (s, 3H); **13C NMR** (125 MHz, DMSO-d6) δ 179.28, 24.42; **19F NMR** (470 MHz, DMSO-d6) δ -137.27—137.38(m, 1F), -139.12—139.24(m, 1F), -144.36—144.52(m, 1F), -148.99—149.12(m, 1F).
4. *N*-Heteroaromatic substrates

![Chemical Structures](image)

**Scheme S2.** List of all *N*-heteroaromatic substrates used in this study

All *N*-heteroaromatics substrated were commercial available and used as received unless otherwise noted.
5. Alcohol substrates

Compositions 3, 4b-2, 4c-2, 4d-2, 4e-2, 4f-2, 4g-2, 4h-2, 4i-2, 4j-2, 4k-2, 4l-2, 4m-2, 4n-2, 4o-2, 4p-2, 4q-2, 4r-2, 4s-2, 4t-2, 4u-2, 4v-2, 26-2 and 31 were commercial available and used as received.

5.1 Synthesis of alkane substrates 4i-2:

To a solution of acetone (20 mL) and water (10 mL), 7-bromo-heptan-1-ol (1.0 g, 5.8 mmol) and sodium azide (1.89 g, 29.0 mmol) were added. The reaction mixture was stirred at ambient temperature for 72 hours. After removal of the organic solvent in vacuo, the residual aqueous solution was extracted with EtOAc (50 mL x 3). The combined organic phase was washed with brine, dried over Na2SO4 and filtrated. The
filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:4) to afford compound 4i-2 (0.80 g, 88%) as a colorless oil. R_f = 0.23 (1:4 ethyl acetate/hexanes). Spectra data are consistent with those reported in the literature.\cite{3}

5.2 Synthesis of alkane substrates 4j-2:

To a solution of ethyl 7-bromoheptanoate (2.44 g, 10 mmol) in DMF (15 mL), sodium phenolate (3.50 g, 30 mmol) was added, and the mixture was stirred for 2 hour at room temperature. Then the reaction mixture was poured into brine (200 mL) and extracted with Et_2O (50 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo and the residue was dissolved in THF (50 mL). To the resulting solution, LiAlH_4 (760 mg, 20 mmol) was carefully added portionwise at 0 °C. After completing the addition of LiAlH_4, the reaction mixture was further stirred at 0 °C for another 1 hour. Then water (1 mL) was added carefully into the reaction solution at 0 °C to quench the reaction. After removal of the organic solvent in vacuo, 30 mL of 1M HCl (aq.) and EtOAc (50 mL) were added into the residue. The aqueous phase was further extracted with EtOAc (50 mL x 2). The combined organic phase was washed with brine, dried over Na_2SO_4 and filtrated. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:3) to afford compound 4j-2 (1.71 g, 82% for 2 steps) as a colorless oil. R_f = 0.15 (1:4 ethyl acetate/hexanes). Spectra data are consistent with those reported in the literature.\cite{4}
5.3 Synthesis of alkane substrates 4l-2:

To a solution of 4-iodobenzoic acid (3.73 g, 15 mmol) in DMF (15 mL), potassium hydroxide (0.84 g, 15 mmol) was added, and the mixture was stirred for 10 minutes at room temperature. 9-Bromononan-1-ol (2.23 g, 10 mmol) was added into the suspension, then the mixture was heated to 120 °C and stirred for another 1 hour. After being cooled to room temperature, the resulting clear solution was poured into brine (200 mL) and extracted with Et₂O (50 mL x 3). The combined organic phase was dried over Na₂SO₄ and filtrated. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1:3) to afford compound 4l-2 (3.27 g, 82%) as a white solid. Rₛ = 0.20 (1:4 ethyl acetate/hexanes). ¹H NMR (500 MHz, CDCl₃) δ 7.81–7.79 (m, 2H), 7.75–7.73 (m, 2H), 4.30 (t, J = 6.7 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 1.78–1.72 (m, 2H), 1.59–1.54 (m, 2H), 1.46–1.33 (m, 11H); ¹³C NMR (125 MHz, CDCl₃) δ 166.15, 137.64, 130.96, 129.92, 100.53, 65.34, 62.96, 32.70, 29.40, 29.27, 29.12, 28.59, 25.93, 25.66; HRMS Calcd for C₁₆H₂₄IO₃ [M+H⁺]: 391.0770, Found: 391.0780.

6. Optimization for alkylation of N-heteroarenes with alcohols

All screening reactions were carried out at a 0.4 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2). The vials were purged with Ar for 1 min, sealed with PTEF cap and stirred on bench top. Stock solution of Ru(bpy)₃Cl₂ in HFIP was used if necessary. A 23 W compact household fluorescent bulb was positioned 10 cm aside from the reaction vials.

4-Chloroquinoline 4 (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol 3 and other specified
reagents were dispersed in 0.5 mL of solvent containing photocatalyst. The mixture was stirred at specified temperature with light irradiation for 24 h. After removal of the solvent in vacuo, the residue was dissolved in 3 mL of CDCl$_3$ along with Cl$_2$CHCHCl$_2$ (20 μL) as an internal standard for $^1$H NMR analysis. The composition of reaction mixture was analyzed based on the integration of methenyl group peaks at 3.15–3.07 (m, 1H) for compound 4a.

**Evaluation of the loading of PFBI-OH 2:**

| Entry | PFBI-OH (equiv) | Yield (%) NMR |
|-------|-----------------|---------------|
| 1     | 1.20            | 63            |
| 2     | 1.25            | 65            |
| 3     | 1.30            | 75            |
| 4     | 1.35            | 84(80)*       |
| 5     | 1.40            | 76            |
| 6     | 1.45            | 72            |
| 7     | 1.50            | 70            |

* Isolated yield.

**Evaluation of the loading of alcohol 3:**

| Entry | Alkanol (equiv) | Yield (%) NMR |
|-------|-----------------|---------------|
| 1     | 1.0             | 42            |
| 2     | 1.25            | 57            |
| 3     | 1.50            | 84(80)*       |
| 4     | 1.75            | 86(81)*       |
| 5     | 2.0             | 86(81)*       |

* Isolated yield.
Screening of photocatalysts:

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\[
\begin{array}{ccc}
\text{Entry} & \text{Photocatalyst} & \text{Yield (%), NMR} \\
1 & \text{Ru(bpy)}_3\text{Cl}_2 & 84(80)^a \\
2 & \text{Ir(ppy)}_3 & 13 \\
3 & \text{[Ir(dF(CF}_3\text{ppy)}_2(dtbpy)]PF}_6 & 32 \\
4 & \text{[Ir(dF(CF}_3\text{ppy)}_2(bppy)]PF}_6 & 33 \\
5 & \text{[Ir(ppy)}_2(dtbpy)]PF}_6 & 16 \\
\end{array}
\]

^a Isolated yield.
```

Evaluation of the loading of photocatalyst Ru(bpy)_3Cl_2:

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\[
\begin{array}{ccc}
\text{Entry} & \text{Ru(bpy)}_3\text{Cl}_2 (\text{mol}%) & \text{Yield (%), NMR} \\
1 & 0 & <2 (ND) \\
2 & 0.25 & 70 \\
3 & 0.5 & 84(80)^a \\
4 & 1.0 & 61 \\
\end{array}
\]

^a Isolated yield.
```


**Screening of oxidants:**

![Chemical structure and reaction scheme](image)

The optimized conditions as following: 4-chloroquinoline 4 (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol 3 (53.0 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH 2 (181.2 mg, 0.54 mmol, 1.35 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 24 h.

| Entry | Oxidant | Yield (%) | NMR |
|-------|---------|-----------|-----|
| 1     | Bi-OH   | 3         |     |
| 2     | Bi-OAc  | 25        |     |
| 3     | PFBI-OH | 84(80)    |     |
| 4     | PFBI-OAc| 30        |     |
| 5     | PIDA    | 28        |     |
| 6     | PIFA    | 4         |     |

*a* Isolated yield.

**Evaluation of solvents:**

![Chemical structure and reaction scheme](image)

| Entry | Solvent       | Yield (%) | NMR |
|-------|---------------|-----------|-----|
| 1     | HFIP (0.5 mL) | 84(80)*   |     |
| 2     | TFE           | 38        |     |
| 3     | DCM           | 3         |     |
| 4     | CH₃CN         | 4         |     |
| 5     | THF           | <1        |     |
| 6     | DMF           | <1        |     |
| 7     | HFIP/DCM (v/v 1:5) | 8    |     |

*a* Isolated yield.
7. General procedure and substrate scope

**General procedure:** N-heteroaromatic substrate (0.4 mmol, 1.0 equiv), alcohols (0.6 mmol, 1.5 equiv) and PFBI-OH (0.54 mmol, 1.35 equiv) were added to a solution of Ru(bpy)$_2$Cl$_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 24 h. (NOTE: the vials were placed approximately 5 cm away from the CFL bulb. The reaction temperature was kept at around 30 ± 1 °C, owing to the radiation of light source. Stirring rate: 500 rpm). The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K$_2$CO$_3$ (approximate 80 mg), and the resulting mixture was vigorously stirred for 5 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.

![Scheme S7.](image)

**Compound 4a** was isolated in 80% yield (80.2 mg) as a colorless oil following the general procedure. **$^1$H NMR** (500 MHz, CDCl$_3$) δ 8.18 (dd, $J$ = 8.3, 0.6 Hz, 1H), 8.05 (d, $J$ = 8.4 Hz, 1H), 7.77–7.69 (m, 1H), 7.59–7.56 (m, 1H), 7.40 (s, 1H), 3.67–3.59 (m, 2H), 3.15–3.07 (m, 1H), 2.39 (br s, 1H), 1.96–1.89 (m, 1H), 1.81–1.74 (m, 1H), 1.67–
1.58 (m, 1H), 1.52–1.44 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.58, 148.14, 142.82, 130.19, 128.82, 126.63, 124.94, 123.74, 119.58, 62.02, 42.06, 32.81, 30.43, 20.54; HRMS Calcd for C$_{14}$H$_{17}$ClNO $[M+H]^+$: 250.0999, Found: 250.1001.

Compound 4b was isolated in 83% yield (87.5 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.19 (dd, J = 8.4, 1.1 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.38 (s, 1H), 3.64–3.56 (m, 2H), 2.92–2.86 (m, 1H), 2.02 (br s, 1H), 1.89–1.77 (m, 4H), 1.60–1.52 (m, 1H), 1.46–1.39 (m, 1H), 0.85 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.65, 148.29, 142.78, 130.22, 129.00, 126.70, 125.04, 123.84, 120.08, 62.34, 49.77, 31.24, 30.50, 28.47, 12.01; HRMS Calcd for C$_{15}$H$_{19}$ClNO$_4$ $[M+H]^+$: 264.1155, Found: 264.1163.

Compound 4c was isolated in 84% yield (93.4 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (dd, J = 8.4, 1.0 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.60–7.57 (m, 1H), 7.37 (s, 1H), 3.63–3.55 (m, 2H), 3.01–2.95 (m, 1H), 2.12 (br s, 1H), 1.88–1.82 (m, 2H), 1.81–1.67 (m, 2H), 1.60–1.52 (m, 1H), 1.46–1.38 (m, 1H), 1.35–1.24 (m, 1H), 1.23–1.14 (m, 1H), 0.87 (t, J = 7.3 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.85, 148.27, 142.77, 130.21, 128.99, 126.69, 125.03, 123.83, 120.04, 62.32, 47.91, 37.78, 31.56, 30.50, 20.63, 14.08; HRMS Calcd for C$_{16}$H$_{21}$ClNO$_4$ $[M+H]^+$: 278.1312, Found: 278.1318.
Compound 4d was isolated in 76% yield (122.5 mg) as a white solid following the general procedure. 

\[ ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta \ 8.19 \ (dd, \ J = 8.4, 0.6 \text{ Hz, 1H}), \ 8.06 \ (d, \ J = 8.4 \text{ Hz, 1H}), \ 7.75–7.72 \ (m, \ 1H), \ 7.60–7.57 \ (m, \ 1H), \ 7.37 \ (s, \ 1H), \ 3.63–3.55 \ (m, \ 2H), \ 2.99–2.93 \ (m, \ 1H), \ 1.90 \ (br \ s, \ 1H), \ 1.88–1.81 \ (m, \ 2H), \ 1.80–1.69 \ (m, \ 2H), \ 1.60–1.51 \ (m, \ 1H), \ 1.45–1.37 \ (m, \ 1H), \ 1.31–1.11 \ (m, \ 20 \ H), \ 0.87 \ (t, \ J = 7.0 \text{ Hz, 3H}); \ ]

\[ ^{13}C \text{NMR} \ (125 \text{ MHz, CDCl}_3) \delta \ 165.89, \ 148.42, \ 142.76, \ 130.22, \ 129.18, \ 126.71, \ 125.10, \ 123.88, \ 120.15, \ 62.57, \ 48.24, \ 35.69, \ 31.86, \ 31.60, \ 30.58, \ 29.66, \ 29.60, \ 29.57, \ 29.52, \ 29.41, \ 29.30, \ 27.50, \ 22.64, \ 14.08; \ ]

HRMS Calcd for C\text{25}H\text{39}ClNO [M+H]\(+\): 404.2720, Found: 404.2708.

Compound 4e was isolated in 62% yield (72.6 mg) as a white solid following the general procedure. 

\[ ^1H \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta \ 8.19 \ (dd, \ J = 8.4, 0.9 \text{ Hz, 1H}), \ 8.06 \ (d, \ J = 8.4 \text{ Hz, 1H}), \ 7.75–7.72 \ (m, \ 1H), \ 7.60–7.57 \ (m, \ 1H), \ 7.38 \ (s, \ 1H), \ 3.63–3.55 \ (m, \ 2H), \ 3.11–3.05 \ (m, \ 1H), \ 1.85–1.80 \ (m, \ 2H), \ 1.77–1.72 \ (m, \ 1H), \ 1.59–1.51 \ (m, \ 2H), \ 1.46–1.35 \ (m, \ 2H), \ 0.92 \ (d, \ J = 6.5 \text{ Hz, 3H}), \ 0.86 \ (d, \ J = 6.6 \text{ Hz, 3H}); \ ]

\[ ^{13}C \text{NMR} \ (125 \text{ MHz, CDCl}_3) \delta \ 165.93, \ 148.48, \ 142.74, \ 130.24, \ 129.23, \ 126.74, \ 125.11, \ 123.90, \ 120.21, \ 62.70, \ 45.95, \ 44.88, \ 32.04, \ 30.55, \ 25.73, \ 23.22, \ 22.22; \ ]

HRMS Calcd for C\text{17}H\text{23}ClNO [M+H]\(+\): 292.1468, Found: 292.1460.
Compound 4f was isolated in 77% yield (104.2 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J = 8.3$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 7.77–7.74 (m, 1H), 7.62–7.59 (m, 1H), 7.37 (s, 1H), 7.24–7.22 (m, 2H), 7.16–7.11 (m, 3H), 3.63–3.54 (m, 2H), 3.05–2.99 (m, 1H), 2.63–2.55 (m, 1H), 2.52–2.47 (m, 1H), 2.20–2.13 (m, 1H), 2.10–2.03 (m, 1H), 1.96–1.84 (m, 2H), 1.78 (br s, 1H), 1.60–1.51 (m, 1H), 1.45–1.37 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.23, 148.52, 142.85, 141.95, 130.32, 129.23, 128.28, 128.27, 126.84, 125.75, 125.15, 123.92, 120.39, 62.53, 47.76, 37.25, 33.74, 31.58, 30.47; HRMS Calcd for C$_{21}$H$_{23}$ClNO [M+H$^+$]: 340.1468, Found: 340.1458.

\[
R_f = 0.44, \text{ 50% EtOAc in Hexane}
\]

Compound 4g was isolated in 64% yield (73.8 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.19 (dd, $J = 8.3$, 0.4 Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.76–7.73 (m, 1H), 7.62–7.58 (m, 1H), 7.40 (s, 1H), 3.64–3.55 (m, 2H), 3.15–3.09 (m, 1H), 2.17–2.06 (m, 3H), 2.02–1.81 (m, 4H), 1.70 (br s, 1H), 1.62–1.53 (m, 1H), 1.46–1.38 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.38, 148.64, 142.81, 130.32, 129.30, 126.90, 125.17, 123.92, 120.85, 83.86, 68.81, 62.52, 46.82, 34.01, 31.18, 30.45, 16.56; HRMS Calcd for C$_{17}$H$_{19}$ClNO [M+H$^+$]: 288.1155, Found: 288.1148.

\[
R_f = 0.60, \text{ 50% EtOAc in Hexane}
\]

Compound 4h was isolated in 65% yield (82.3 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.3$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.76–7.73 (m, 1H), 7.61–7.58 (m, 1H), 7.37 (s, 1H), 5.74 (ddt, $J = 17.0$, 10.2, 6.7 Hz, 1H), 4.94 (d, $J = 17.0$ Hz, 1H), 4.89 (d, $J = 10.2$ Hz, 1H), 3.63–3.55 (m
2H), 3.00–2.94 (m, 1H), 2.00–1.96 (m, 2H), 1.91–1.70 (m, 5H), 1.59–1.51 (m, 1H), 1.45–1.26 (m, 4H), 1.21–1.13 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.73, 148.43, 142.81, 138.79, 130.27, 129.20, 126.77, 125.12, 123.91, 120.17, 114.29, 62.64, 48.18, 35.49, 33.50, 31.60, 30.57, 28.90, 26.96; HRMS Calcd for C$_{19}$H$_{23}$ClNO [M+H$^+$]: 318.1625, Found: 318.1616.

![Chemical Structure of 4i](image)

$R_f=0.38$, 50% EtOAc in Hexane

Compound 4i was isolated in 76% yield (96.6 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, $J=8.3$ Hz, 1H), 8.05 (d, $J=8.4$ Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.58 (m, 1H), 7.37 (s, 1H), 6.91–6.88 (m, 1H), 6.84–6.83 (m, 2H), 3.91 (t, $J=6.2$ Hz, 2H), 3.63–3.55 (m, 2H), 3.07–3.01 (m, 1H), 2.11 (br s, 1H), 1.89–1.84 (m, 4H), 1.81–1.73 (m, 1H), 1.67–1.52 (m, 2H), 1.46–1.38 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.81, 143.02, 130.38, 129.20, 126.93, 125.15, 123.92, 120.08, 62.46, 51.29, 47.70, 32.47, 31.65, 30.43, 26.82; HRMS Calcd for C$_{16}$H$_{20}$ClNaO [M+H$^+$]: 319.1326, Found: 319.1313.

![Chemical Structure of 4j](image)

$R_f=0.41$, 50% EtOAc in Hexane

Compound 4j was isolated in 60% yield (88.5 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, $J=8.3$ Hz, 1H), 8.06 (d, $J=8.4$ Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.40 (s, 1H), 6.91–6.88 (m, 1H), 6.84–6.83 (m, 2H), 3.91 (t, $J=6.2$ Hz, 2H), 3.63–3.56 (m, 2H), 3.07–3.01 (m, 1H), 2.11 (br s, 1H), 1.89–1.84 (m, 4H), 1.81–1.73 (m, 1H), 1.67–1.52 (m, 2H), 1.46–1.38 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.20, 158.83, 148.46, 142.96, 130.35, 129.35, 129.21, 126.87, 125.17, 123.93, 120.51, 120.25, 114.38, 67.47, 62.60, 47.85, 31.95, 31.68, 30.51, 27.21; HRMS Calcd for C$_{22}$H$_{25}$ClNO$_2$ [M+H$^+$]: 370.1574, Found: 370.1553.
Compound 4k was isolated in 70% yield (115.0 mg) as a white solid following the general procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.18 (d, \(J = 8.3\) Hz, 1H), 8.03 (d, \(J = 8.4\) Hz, 1H), 7.75–7.71 (m, 1H), 7.61–7.58 (m, 1H), 7.38 (s, 1H), 7.34–7.30 (m, 5H), 5.09 (br s, 1H), 5.04 (s, 2H), 3.63–3.55 (m, 2H), 3.26–3.19 (m, 1H), 3.08–3.02 (m, 2H), 2.02–1.98 (m, 2H), 1.94–1.83 (m, 3H), 1.57–1.48 (m, 1H), 1.46–1.38 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 164.65, 156.35, 148.36, 143.12, 136.52, 130.42, 129.09, 128.40, 127.96, 126.98, 125.14, 123.93, 120.16, 66.49, 62.21, 45.36, 38.98, 35.23, 31.20, 30.31; HRMS Calcd for C\(_{23}\)H\(_{26}\)ClN\(_2\)O\(_3\) [M+H\(^+\)]: 413.1632, Found: 413.1614.

Compound 4l was isolated in 73% yield (160.8 mg) as a white solid following the general procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.18 (dd, \(J = 8.4, 0.8\) Hz, 1H), 8.05 (d, \(J = 8.4\) Hz, 1H), 7.78–7.76 (m, 2H), 7.75–7.72 (m, 1H), 7.71–7.69 (m, 2H), 7.61–7.58 (m, 1H), 7.37 (s, 1H), 4.24 (t, \(J = 6.6\) Hz, 2H), 3.63–3.55 (m, 2H), 3.00–2.94 (m, 1H), 1.92 (br s, 1H), 1.88–1.66 (m, 6H), 1.59–1.50 (m, 1H), 1.47–1.31 (m, 4H), 1.29–1.17 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.02, 165.52, 148.40, 142.79, 137.56, 130.88, 130.79, 130.26, 129.77, 129.14, 126.77, 125.06, 123.87, 120.08, 100.52, 65.16, 62.49, 48.11, 35.46, 31.61, 30.50, 28.41, 27.15, 26.07; HRMS Calcd for C\(_{25}\)H\(_{28}\)ClINO\(_3\) [M+H\(^+\)]: 552.0802, Found: 552.0772.
Compound 4m was isolated in 80% yield (83.1 mg) as a white solid following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 8.3$, 0.9 Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.76–7.73 (m, 1H), 7.62–7.59 (m, 1H), 7.35 (s, 1H), 6.43 (br s, 1H), 3.76–3.67 (m ,2H), 3.56–3.50 (m, 1H), 3.01–2.93 (m, 1H), 2.50–2.45 (m, 1H), 2.18–2.07 (m, 2H), 2.04–1.98 (m, 1H), 1.85–1.76 (m, 1H), 1.69–1.63 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.19, 147.46, 143.29, 130.70, 128.35, 127.00, 124.86, 123.89, 119.55, 59.92, 46.53, 39.73, 38.22, 25.12, 24.95; HRMS Calcd for C$_{15}$H$_{17}$ClNO [M+H$^+$]: 262.0999, Found: 262.0993.

![Rf = 0.51, 50% EtOAc in Hexane](image)

Compound 4n was isolated in 83% yield (91.7 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 8.4$, 1.0 Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.57 (m, 1H), 7.45 (s, 1H), 4.07 (br s, 1H), 3.59–3.54 (m, 1H), 3.53–3.48 (m ,1H), 3.11–3.06 (m, 1H), 2.67–2.59 (m, 1H), 2.31–2.25 (m, 1H), 2.10–2.04 (m, 1H), 1.90–1.76 (m, 4H), 1.61–1.54 (m, 1H), 1.49–1.42 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.65, 147.90, 142.95, 130.50, 128.73, 126.83, 125.02, 123.86, 120.49, 60.84, 53.19, 41.43, 38.49, 34.48, 33.70, 24.84; HRMS Calcd for C$_{16}$H$_{19}$ClNO [M+H$^+$]: 276.1155, Found: 276.1147.

![Rf = 0.51, 50% EtOAc in Hexane](image)

Compound 4o was isolated in 91% yield (105.2 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 8.4$, 1.0 Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.57 (m, 1H), 7.41 (s, 1H), 3.58–3.51 (m, 2H), 2.71 (td, $J = 11.5$, 3.5 Hz, 1H), 2.60 (br s, 1H), 2.12–2.04 (m ,1H), 2.01–1.95 (m, 2H), 1.89–1.81 (m, 2H), 1.57–1.46 (m, 1H), 1.47–1.31 (m, 4H), 1.25–1.18 (m, 1H); $^{13}$C
NMR (125 MHz, CDCl$_3$) δ 165.94, 148.28, 142.97, 130.41, 128.92, 126.80, 125.08, 123.91, 120.72, 60.39, 52.68, 37.54, 37.46, 34.61, 32.50, 26.35, 26.14; HRMS Calcd for C$_{17}$H$_{21}$ClNO [M+H$^+$]: 290.1312, Found: 290.1301.

Scheme S8.

R$_f$ = 0.33, 25% EtOAc in Hexane

Compound 4p-major was isolated in 37% yield (43.0 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.60–7.57 (m, 1H), 7.43 (s, 1H), 3.47 (ddd, J = 16.8, 10.7, 5.2 Hz, 2H), 3.22–3.15 (m, 1H), 2.23–2.17 (m, 1H), 1.55–1.49 (m, 1H), 1.48–1.44 (m, 1H), 1.40–1.26 (m, 4H), 1.35 (d, J = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.58, 148.15, 143.00, 130.49, 128.87, 126.88, 125.09, 123.93, 120.67, 65.31, 40.58, 39.18, 37.48, 34.53, 22.35, 20.12, 14.40; HRMS Calcd for C$_{17}$H$_{23}$ClNO [M+H$^+$]: 292.1468, Found: 292.1464.

R$_f$ = 0.28, 25% EtOAc in Hexane

Compound 4p-minor was isolated in 34% yield (38.8 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.44 (s, 1H), 3.59 (dd, J = 10.9, 4.5 Hz, 1H), 3.44 (dd, J = 10.9, 6.8 Hz, 1H), 3.35–3.28 (m, 1H), 1.96–1.90 (m, 1H),
1.75–1.66 (m, 1H), 1.50–1.43 (m, 1H), 1.37 (d, $J = 7.0$ Hz, 3H), 1.32–1.17 (m, 4H), 0.82 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.74, 148.02, 143.19, 130.46, 128.99, 126.88, 125.09, 123.92, 119.68, 65.87, 39.46, 38.69, 38.17, 33.99, 21.62, 19.98, 14.28; HRMS Calcd for C$_{17}$H$_{23}$ClNO [M+H$^+$]: 292.1468, Found: 292.1464.

\[ \text{Rf} = 0.81, \text{25\% EtOAc in Hexane} \]

Compound 4p' was isolated in 16\% yield (17.0 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (dd, $J = 8.3$, 0.5 Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.74–7.71 (m, 1H), 7.59–7.56 (m, 1H), 7.36 (s, 1H), 2.98–2.92 (m, 1H), 1.78–1.66 (m, 4H), 1.33–1.23 (m, 2H), 1.21–1.11 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.44, 148.67, 142.42, 130.06, 129.40, 126.55, 125.10, 123.88, 120.18, 48.41, 37.82, 20.76, 14.18; HRMS Calcd for C$_{16}$H$_{21}$ClN [M+H$^+$]: 262.1363, Found: 262.1368.

\[ \text{Rf} = 0.45, \text{50\% EtOAc in Hexane} \]

Compound 4q was isolated in 68\% yield (72.3 mg) as a colorless oil following the general procedure, 36 h. The two diastereoisomers were obtained as an inseparable mixture. The $dr$ ratio was determined by the integration of peaks at 3.85–3.78 ppm (m, 1H) for one isomer and 3.77–3.71 ppm (m, 1H) for the other isomer. Data for one diastereoisomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 3.85–3.78 (m, 1H), 3.13–3.06 (m, 1H), 2.02–1.90 (m, 1H), 1.86–1.80 (m, 1H), 1.40–1.30 (m, 2H), 1.38 (d, $J = 7.0$ Hz, 3H), 1.16 (d, $J = 6.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.60, 148.44, 142.80, 130.32, 129.20, 126.73, 125.10, 123.89, 119.88, 67.94, 42.49, 36.99, 32.46, 23.43, 20.93; Data for the other diastereoisomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$
8.19 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 3.77–3.71 (m, 1H), 3.13–3.06 (m, 1H), 2.02–1.90 (m, 1H), 1.79–1.72 (m, 1H), 1.56–1.48 (m, 2H), 1.38 (d, J = 7.0 Hz, 3H), 1.15 (d, J = 6.0 Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 166.52, 148.35, 142.89, 130.25, 129.15, 126.76, 125.10, 123.89, 119.88, 67.64, 42.41, 37.13, 32.58, 23.53, 21.01; HRMS Calcd for C\(_{15}\)H\(_{19}\)ClNO \([\text{M+H}^+]\) \(=\) 264.1155, Found: 264.1154.

\[\text{R}_f = 0.15, 25\% \text{ EtOAc in Hexane}\]

Compound 4\(r\) was isolated in 44% yield (53.8 mg) as a colorless oil following the general procedure. The two diastereoisomers were obtained as an inseparable mixture. The \(dr\) ratio was determined by the integration of peaks at 7.41 ppm (s, 1H) for one isomer and 7.39 ppm (s, 1H) for the other isomer. Data for one diastereoisomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.18 (dd, J = 8.4, 0.9 Hz, 1H), 8.05 (d, J = 5.7 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 4.23–4.14 (m, 3H), 3.15–3.07 (m, 1H), 2.05–1.49 (m, 4H), 1.38 (d, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 174.98, 166.16, 148.50, 142.85, 130.28, 129.26, 126.78, 125.13, 123.89, 119.79, 70.42, 61.60, 42.32, 32.25, 31.57, 20.67, 14.15; Data for the other diastereoisomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.18 (dd, J = 8.4, 0.9 Hz, 1H), 8.07 (d, J = 5.7 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.39 (s, 1H), 4.23–4.14 (m, 3H), 3.15–3.07 (m, 1H), 2.05–1.49 (m, 4H), 1.38 (d, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 175.02, 166.15, 148.43, 142.89, 130.26, 129.26, 126.78, 125.13, 123.89, 119.64, 70.25, 61.57, 42.23, 32.12, 31.72, 20.97, 14.11; HRMS Calcd for C\(_{17}\)H\(_{21}\)ClNO\(_3\) \([\text{M+H}^+]\) \(=\) 322.1210, Found: 322.1204.

\[\text{R}_f = 0.50, 80\% \text{ EtOAc in Hexane}\]
Compound 4t was isolated in 63% yield (59.0 mg) as a colorless oil following the general procedure, 3 equiv of 1-butanol 4t-2 and 2 equiv of PFBI-OH 2 were used, 36 h. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.19 (dd, $J$ = 8.3, 0.8 Hz, 1H), 8.05 (d, $J$ = 8.4 Hz, 1H); 7.76–7.73 (m, 1H), 7.61–7.58 (m, 1H), 7.41 (s, 1H), 3.71 (t, $J$ = 6.3 Hz, 2H), 3.01 (t, $J$ = 7.5 Hz, 2H), 2.45 (br s, 1H), 1.98–1.92 (m, 2H), 1.73–1.67 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.43, 148.40, 142.84, 130.46, 128.91, 126.82, 124.95, 123.94, 121.45, 62.24, 38.08, 32.13, 25.34; HRMS Calcd for C$_{13}$H$_{15}$ClNO [M+H$^+$]: 236.0842, Found: 236.0840.

$R_f$ = 0.50, 80% EtOAc in Hexane

Compound 4u was isolated in 74% yield (74.5 mg) as a colorless oil following the general procedure, 3 equiv of 3-methyl-1-butanol 4u-2 and 2 equiv of PFBI-OH 2 were used, 36 h. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, $J$ = 8.2 Hz, 1H), 8.02 (d, $J$ = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.59–7.56 (m, 1H), 7.37 (s, 1H), 3.80–3.75 (m, 1H), 3.73–3.69 (m, 1H), 3.65 (br s, 1H), 2.99 (dd, $J$ = 13.8, 6.8 Hz, 1H), 2.82 (dd, $J$ = 13.8, 7.0 Hz, 1H), 2.36–2.27 (m, 1H), 1.65–1.58 (m, 2H), 0.99 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.64, 148.23, 142.65, 130.42, 128.77, 126.81, 124.85, 123.89, 122.12, 60.34, 45.31, 39.26, 30.47, 20.34; HRMS Calcd for C$_{14}$H$_{17}$ClNO [M+H$^+$]: 250.0999, Found: 250.0993.

$R_f$ = 0.50, 80% EtOAc in Hexane

Compound 8 was isolated in 70% yield (64.1 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, $J$ = 8.4 Hz, 1H), 7.95 (d, $J$ = 8.2 Hz, 1H), 7.68–7.65 (m, 1H), 7.52–7.49 (m, 1H), 7.15 (s, 1H), 3.66–3.57 (m, 2H), 3.14–3.07 (m, 1H), 2.69 (s, 3H), 2.51 (br s, 1H), 1.99–1.91 (m, 1H), 1.81–1.74 (m, 1H),...
1.68–1.59 (m, 1H), 1.52–1.44 (m, 1H), 1.37 (d, J = 6.9 Hz, 3H); \( ^{13}C \text{ NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 166.19, 147.21, 144.68, 129.19, 129.09, 126.99, 125.55, 123.55, 120.23, 62.51, 42.13, 32.88, 30.64, 21.03, 18.84; \( \text{HRMS} \) Calcd for C\(_{15}\)H\(_{20}\)NO \[M+H\]^+: 230.1545, Found: 230.1537.

\[
\text{R}_f = 0.32, \text{ 50\% EtOAc in Hexane}
\]

Compound 9 was isolated in 71% yield (65.6 mg) as a colorless oil following the general procedure. \( ^{1}H \text{ NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 8.04 (d, J = 8.4 Hz, 2H), 7.67–7.64 (m, 1H), 7.50–7.47 (m, 1H), 7.17 (s, 1H), 3.65 (t, J = 6.4 Hz, 2H), 3.61–3.56 (m, 1H), 2.72 (s, 3H), 1.91–1.84 (m, 1H), 1.82–1.75 (m, 1H), 1.69 (br s, 1H), 1.67–1.58 (m, 1H), 1.57–1.50 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H); \( ^{13}C \text{ NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 158.59, 153.46, 147.93, 129.26, 128.90, 125.39, 122.72, 118.41, 62.46, 33.38, 33.07, 30.64, 25.28, 21.17; \( \text{HRMS} \) Calcd for C\(_{15}\)H\(_{20}\)NO [M+H\(^+\)]: 230.1545, Found: 230.1537.

\[
\text{R}_f = 0.20, \text{ 50\% EtOAc in Hexane}
\]

Compound 10 was isolated in 63% yield (65.0 mg) as a colorless oil following the general procedure. \( ^{1}H \text{ NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 8.34 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.58–7.55 (m, 1H), 7.49 (s, 1H), 3.67–3.59 (m, 2H), 3.22–3.15 (m, 1H), 2.74 (s, 3H), 2.28 (br s, 1H), 2.02–1.94 (m, 1H), 1.85–1.77 (m, 1H), 1.69–1.61 (m, 1H), 1.54–1.46 (m, 1H), 1.41 (d, J = 6.9 Hz, 3H); \( ^{13}C \text{ NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 201.71, 165.99, 148.52, 143.67, 129.80, 129.35, 127.39, 125.16, 122.31, 118.55, 62.56, 42.33, 32.78, 30.60, 30.17, 20.87; \( \text{HRMS} \) Calcd for C\(_{16}\)H\(_{20}\)NO\(_2\) [M+H\(^+\)]: 258.1494, Found: 258.1493.
R_f = 0.34, 60% Acetone in Hexane

Compound 11 was isolated in 62% yield (60.7 mg) as a colorless oil following the general procedure. ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 8.5 Hz, 2H), 7.70 (ddd, J = 8.2, 6.9, 1.0 Hz, 1H), 7.55 (dd, J = 8.2, 6.9, 1.0 Hz, 1H), 7.18 (s, 1H), 4.89 (s, 2H), 3.66–3.59 (m, 3H), 1.92–1.85 (m, 1H), 1.82–1.75 (m, 1H), 1.67–1.58 (m, 1H), 1.58–1.49 (m, 1H), 1.39 (d, J = 6.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.62, 154.30, 146.98, 129.54, 129.27, 126.55, 126.10, 122.99, 114.74, 64.14, 62.72, 33.37, 33.31, 30.60, 21.21; HRMS Calcd for C₁₅H₂₀NO₂ [M+H⁺]: 246.1494, Found: 246.1489.

R_f = 0.16, 50% EtOAc in Hexane

Compound 12 was isolated in 80% yield (68.9 mg) as a colorless oil following the general procedure. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, J = 5.6 Hz, 1H), 8.23 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.68–7.65 (m, 1H), 7.61–7.58 (m, 1H), 7.50 (d, J = 5.6 Hz, 1H), 3.87–3.80 (m, 2H), 3.63–3.52 (m, 2H), 2.21–2.14 (m, 1H), 1.89 (br s, 1H), 1.86–1.79 (m, 1H), 1.70–1.61 (m, 1H), 1.53–1.45 (m, 1H), 1.41 (d, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.39, 141.68, 136.37, 129.68, 127.53, 126.98, 126.72, 124.64, 119.07, 62.64, 35.95, 31.96, 30.92, 21.17; HRMS Calcd for C₁₄H₁₈NO [M+H⁺]: 216.1388, Found: 216.1380.

R_f = 0.50, 50% EtOAc in Hexane

Compound 13 was isolated in 62% yield (61.3 mg) as a colorless oil following the general procedure. ¹H NMR (500 MHz, CDCl₃) δ 10.24 (s, 1H), 8.30–8.28 (m, 1H),
8.23 (s, 1H), 8.03–8.00 (m, 1H), 7.78–7.75 (m, 2H), 3.90–3.83 (m, 1H), 3.66–3.57 (m, 2H), 2.29–2.21 (m, 1H), 1.90–1.83 (m, 1H), 1.71–1.62 (m, 2H), 1.56–1.49 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 194.34, 166.33, 145.77, 135.85, 130.47, 129.80, 128.83, 124.86, 119.71, 62.82, 36.26, 31.88, 30.92, 20.97; HRMS Calcd for C$_{15}$H$_{18}$NO$_2$ [M+H$^+$]: 244.1338, Found: 244.1337.

$\text{R}_f = 0.50$, 50% EtOAc in Hexane

Compound 14 was isolated in 74% yield (87.4 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.67 (s, 1H), 8.24–8.20 (m, 2H), 7.80–7.77 (m, 1H), 7.68–7.65 (m, 1H), 3.83–3.76 (m, 1H), 3.63–3.55 (m, 2H), 2.17–2.10 (m, 1H), 1.84–1.78 (m, 1H), 1.67–1.59 (m, 2H), 1.52–1.44 (m, 1H), 1.40 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.05, 143.48, 134.89, 130.93, 128.05, 127.91, 126.86, 124.98, 117.62, 62.70, 35.92, 32.02, 30.83, 21.06; HRMS Calcd for C$_{14}$H$_{17}$BrNO [M+H$^+$]: 294.0494, Found: 294.0491.

$\text{R}_f = 0.41$, 50% EtOAc in Hexane

Compound 15 was isolated in 69% yield (94.0 mg) as a light brown oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.48 (d, J = 5.7 Hz, 1H), 8.33 (s, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 5.7 Hz, 1H), 3.87–3.80 (m, 1H), 3.62–3.51 (m, 2H), 2.19–2.12 (m, 1H), 1.86–1.79 (m, 1H), 1.68–1.59 (m, 1H), 1.53–1.43 (m, 1H), 1.40 (d, J = 7.0 Hz, 3H), 1.40 (s, 12H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.34, 141.72, 135.63, 135.58, 131.65, 127.89, 123.52, 119.49, 84.26, 62.68, 35.93, 31.94, 30.91, 24.87, 24.52, 21.20; HRMS Calcd for C$_{20}$H$_{29}$BNO$_3$ [M+H$^+$]: 342.2240,
Found: 342.2250.

\[ R_f = 0.74, 50\% \text{EtOAc in Hexane} \]

Compound 16 was isolated in 84\% yield (88.8 mg) as a colorless oil following the general procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.66 (d, \(J = 8.2\) Hz, 1H), 8.54 (d, \(J = 8.0\) Hz, 1H), 8.32 (d, \(J = 8.3\) Hz, 1H), 8.12 (d, \(J = 7.7\) Hz, 1H), 7.84–7.81 (m, 1H), 7.72–7.68 (m, 2H), 7.63–7.60 (m, 1H), 3.90–3.84 (m, 1H), 3.64–3.59 (m, 1H), 3.55–3.50 (m, 1H), 2.43–2.36 (m, 1H), 2.34 (br s, 1H), 1.90–1.83 (m, 1H), 1.79–1.71 (m, 1H), 1.60–1.52 (m, 1H), 1.46 (d, \(J = 6.9\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 164.97, 143.42, 133.03, 130.10, 129.54, 128.51, 127.17, 126.29, 125.58, 124.97, 123.33, 122.54, 121.79, 62.46, 36.56, 30.98, 30.91, 21.18; HRMS Calcd for C\(_{18}\)H\(_{20}\)NO \([\text{M+H}^+\]): 266.1545, Found: 266.1557.

\[ R_f = 0.22, \text{EtOAc} \]

Compound 17 was isolated in 72\% yield (62.0 mg) as a colorless oil following the general procedure. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.39 (s, 1H), 8.19 (d, \(J = 7.9\) Hz, 1H), 7.98–7.87 (m, 3H), 3.83–3.76 (m, 1H), 3.68–3.61 (m, 2H), 2.48 (br s, 1H), 2.31–2.24 (m, 1H), 1.95–1.88 (m, 1H), 1.72–1.64 (m, 1H), 1.62–1.54 (m, 1H), 1.50 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 150.16, 132.64, 132.40, 131.78, 127.15, 126.23, 125.33, 123.42, 62.57, 35.39, 31.92, 30.81, 20.70; HRMS Calcd for C\(_{13}\)H\(_{17}\)N\(_2\)O \([\text{M+H}^+\]): 217.1341, Found: 217.1343.

\[ R_f = 0.25, 50\% \text{EtOAc in Hexane} \]
Compound 18 was isolated in 63% yield (58.0 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.01–7.96 (m, 2H), 7.66–7.65 (m, 2H), 3.66–3.57 (m, 2H), 3.35–3.28 (m, 1H), 2.79 (s, 3H), 2.16–2.09 (m, 1H), 1.89 (br s, 1H), 1.81–1.74 (m, 1H), 1.70–1.62 (m, 1H), 1.53–1.45 (m, 1H), 1.35 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 160.22, 152.82, 141.21, 140.58, 128.86, 128.68, 128.60, 128.17, 62.70, 37.25, 31.50, 30.77, 22.79, 20.15; HRMS Calcd for C$_{14}$H$_{19}$N$_2$O [M+H$^+$]: 231.1497, Found: 231.1501.

$R_f = 0.26$, EtOAc

Compound 19 was isolated in 58% yield (80.3 mg) as a pale yellow following the general procedure, 3.0 equiv of 1-pentanol and 2.0 equiv of PFBI-OH were used, 36 h. $^1$H NMR (500 MHz, CDCl$_3$) δ 9.50 (s, 1H), 8.42 (s, 1H), 7.74 (d, $J = 7.6$ Hz, 2H), 7.58–7.56 (m, 1H), 7.46–7.43 (m, 2H), 7.39 (d, $J = 3.4$ Hz, 1H), 6.48 (s, 1H), 3.64–3.57 (m, 3H), 2.09 (br s, 1H), 1.90–1.83 (m, 1H), 1.68–1.61 (m, 1H), 1.56–1.50 (m, 2H), 1.30 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 152.40, 142.33, 138.55, 136.49, 135.81, 134.23, 129.49, 126.30, 114.90, 106.48, 106.25, 62.38, 33.97, 31.94, 30.10, 21.26; HRMS Calcd for C$_{18}$H$_{21}$N$_2$O$_3$S [M+H$^+$]: 345.1273, Found: 345.1281.

$R_f = 0.57$, 50% EtOAc in Hexane

Compound 20 was isolated in 66% yield (58.3 mg) as a colorless oil following the general procedure, 24 h. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, $J = 8.1$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.46–7.43 (m, 1H), 7.36–7.33 (m, 1H), 3.69–3.62 (m, 2H), 3.37–3.30 (m, 1H), 2.01–1.93 (m, 1H), 1.89–1.82 (m, 2H), 1.73–1.56 (m, 2H), 1.48 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 177.67, 152.87, 134.56, 125.88, 124.68, 122.56, 121.56, 62.47, 39.16, 33.60, 30.33, 21.39; HRMS Calcd for C$_{12}$H$_{16}$NOS [M+H$^+$]: 222.0953, Found: 222.0957.
Compound 21 was isolated in 49% yield (43.0 mg) as a colorless oil following the general procedure, 24 h. \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.42 (d, \(J = 5.2\) Hz, 1H), 7.12 (s, 1H), 7.10 (dd, \(J = 5.2, 1.6\) Hz, 1H), 3.65–3.57 (m, 2H), 2.95–2.88 (m, 1H), 2.47 (br s, 1H), 1.87–1.80 (m, 1H), 1.71–1.63 (m, 1H), 1.62–1.54 (m, 1H), 1.49–1.41 (m, 1H), 1.31 (s, 9H), 1.30 (d, \(J = 6.7\) Hz, 3H); \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 165.78, 160.57, 148.68, 118.46, 118.39, 62.72, 41.54, 34.67, 33.16, 30.71, 30.55, 21.01; \textbf{HRMS} Calcd for C\textsubscript{14}H\textsubscript{24}NO [M\textsuperscript{+}H\textsuperscript{+}]: 222.1858, Found: 222.1865.

\[ \text{Scheme S9} \]

Compound 22 was isolated in 62% yield (55.0 mg) as a colorless oil following the general procedure, an inseparable mixture. Data for \textbf{22-major}: \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 9.13 (s, 1H), 8.21 (dd, \(J = 8.2, 2.2\) Hz, 1H), 7.25 (d, \(J = 8.2\) Hz, 1H), 3.94 (s, 3H), 3.65–3.58 (m, 2H), 3.04–2.97 (m, 1H), 2.10 (br s, 1H), 1.88–1.81 (m, 1H), 1.74–1.67 (m, 1H), 1.61–1.52 (m, 1H), 1.47–1.38 (m, 1H), 1.32 (d, \(J = 6.9\) Hz, 3H); \textbf{\textsuperscript{13}C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 170.82, 165.87, 150.36, 137.55, 123.70, 121.23, 62.57, 52.23, 41.74, 32.95, 30.54, 20.65; Data for \textbf{22-minor}: \textbf{\textsuperscript{1}H NMR} (500 MHz, CDCl\textsubscript{3}) \(\delta\) 8.69 (dd, \(J = 4.7, 1.8\) Hz, 1H), 8.07 (dd, \(J = 7.9, 1.8\) Hz, 1H), 7.18 (dd, \(J = 7.9, 4.7\) Hz, 1H), 3.92 (s, 3H), 3.79–3.72 (m, 1H), 3.65–3.58 (m, 2H), 1.99–1.91 (m, 1H), 1.67–1.62
(m, 2H), 1.47–1.38 (m, 1H), 1.29 (d, J = 6.7 Hz, 3H); \textbf{^{13}C NMR} (125 MHz, CDCl$_3$) $\delta$
167.50, 166.48, 151.86, 137.95, 125.68, 120.51, 62.57, 52.41, 36.79, 32.40, 30.59, 20.58; \textbf{HRMS} Calcd for C$_{12}$H$_{18}$NO$_3$ [M+H$^+$]: 224.1287, Found: 224.1291.

$\text{R}_f = 0.32$, EtOAc

Compound 23 was isolated in 76% yield (79.2 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol 4t-2 and 2.0 equiv of PFBI-OH were used, 36 h. \textbf{^1H NMR} (500 MHz, CDCl$_3$) $\delta$ 8.45 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.78–7.72 (m, 2H), 4.04 (s, 3H), 3.69 (t, J = 6.1 Hz, 2H), 3.44 (t, J = 7.3 Hz, 2H), 2.60 (br s, 1H), 2.10–2.04 (m, 2H), 1.78–1.73 (m, 2H); \textbf{^{13}C NMR} (125 MHz, CDCl$_3$) $\delta$ 166.39, 162.45, 140.12, 135.76, 130.58, 129.40, 128.87, 128.36, 125.37, 122.92, 61.84, 52.74, 34.40, 32.48, 24.54; \textbf{HRMS} Calcd for C$_{15}$H$_{18}$NO$_3$ [M+H$^+$]: 260.1287, Found: 260.1290.

$\text{R}_f = 0.40$, EtOAc

Compound 24 was isolated in 65% yield (65.0 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol 4t-2 and 2.0 equiv of PFBI-OH were used, 36 h. \textbf{^1H NMR} (500 MHz, CDCl$_3$) $\delta$ 8.04 (dd, J = 9.2, 5.3 Hz, 1H), 7.79 (dd, J = 9.2, 2.8 Hz, 1H), 7.50 (td, J = 8.9, 2.8 Hz, 1H), 7.43 (s, 1H), 3.71 (t, J = 6.3 Hz, 2H), 2.99 (t, J = 7.6 Hz, 2H), 2.44 (br s, 1H), 1.96–190 (m, 2H), 1.72–1.66 (m, 2H); \textbf{^{13}C NMR} (125 MHz, CDCl$_3$) $\delta$ 161.75 (d, J = 2.6 Hz), 160.72 (d, J = 248.8 Hz), 145.47, 141.97 (d, J = 5.5 Hz), 131.52 (d, J = 9.1 Hz), 125.81 (d, J = 10.2 Hz), 122.04, 120.55 (d, J = 25.6 Hz), 107.77 (d, J = 24.3 Hz), 62.18, 37.99, 32.09, 25.39; \textbf{HRMS} Calcd for C$_{13}$H$_{14}$ClFNO [M+H$^+$]: 254.0748, Found: 254.0762.
Compound 25 was isolated in 60% yield (52.9 mg) as a colorless oil following the general procedure, 3.0 equiv of 1-butanol 4t-2 and 2.0 equiv of PFBI-OH were used, 36 h. \textbf{1H NMR} (500 MHz, CDCl$_3$) δ 8.71 (br s, 1H), 7.39 (s, 1H), 7.35 (d, \(J = 4.4\) Hz, 1H), 3.70 (t, \(J = 6.3\) Hz, 2H), 2.93 (t, \(J = 7.6\) Hz, 2H), 2.18 (br s, 1H), 1.90–1.84 (m, 2H), 1.69–1.63 (m, 2H); \textbf{13C NMR} (125 MHz, CDCl$_3$) δ 163.61, 150.04, 138.68 (q, \(J = 33.6\) Hz), 122.83 (q, \(J = 273.2\) Hz), 118.47, 116.75, 62.27, 37.69, 32.02, 25.67; \textbf{HRMS} Calcd for C$_{10}$H$_{13}$F$_3$NO [M+H$^+$]: 220.0949, Found: 220.0960.

Quinoxyfen 26-1 (125.3 mg, 0.4 mmol, 1.0 equiv), alcohol 26-2 (166.4 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH (181.4 mg, 0.54 mmol, 1.35 equiv) were added to a solution of Ru(bpy)$_3$Cl$_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (1.0 mL). The reaction vial was purged with Ar for 1 min and sealed with PTFE cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 24 h. The solvent was removed \textit{in vacuo} and the residue was dissolved in DCM (3 mL). To the solution was added K$_2$CO$_3$ (approximate 80 mg), and the resulting mixture was vigorously stirred for 5 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated \textit{in vacuo} and the residue was purified by preparative thin layer chromatography to afford the desired compound 26 in 67% yield (155.6 mg) as a colorless oil. \textbf{1H NMR} (500 MHz, CDCl$_3$) δ 7.96 (d, \(J = 2.0\) Hz, 1H), 7.52 (d, \(J = 2.0\) Hz, 1H), 7.18–7.09 (m, 4H), 6.49 (s, 1H), 3.58–3.50 (m, 2H), 2.79–2.73 (m, 1H), 1.99 (br s, 1H), 1.74–1.66 (m, 2H), 1.61–1.56 (m, 3H), 1.53–1.45 (m, 1H), 1.37–1.16 (m, 5H), 1.22 (s, 12H), 0.69 (t, \(J = 7.8\) Hz, 2H); \textbf{13C NMR} (125 MHz, CDCl$_3$) δ 168.62,
162.25, 159.81 (d, J = 244.3 Hz), 151.20, 150.27 (d, J = 2.6 Hz), 134.86, 129.89, 128.72, 127.39, 121.82, 121.75, 117.10, 117.00, 116.91, 106.42, 82.84, 62.60, 48.09, 35.30, 32.33, 31.19, 30.49, 27.15, 24.75, 23.77, 11.03; HRMS Calcd for C_{30}H_{38}BCl_2FNO_4 [M+H^+]: 576.2255, Found: 576.2275.

**R_f = 0.46, 5% MeOH in DCM**

Compound 27 was isolated in 53% yield (94.5 mg) as a colorless oil following the general procedure. $^1$H NMR (500 MHz, CDCl_3) $\delta$ 7.72 (s, 1H), 5.13 (br s, 2H), 4.18 (t, J = 6.9 Hz, 2H), 4.14 (d, J = 4.7 Hz, 4H), 3.67–3.59 (m, 2H), 3.49 (br s, 1H), 2.85 (br s, 1H), 2.27–2.20 (m, 1H), 2.12 (t, J = 7.1 Hz, 2H), 2.07 (s, 6H), 2.04–1.93 (m, 5H), 1.83–1.76 (m, 1H), 1.62–1.54 (m, 1H), 1.48–1.40 (m, 1H); $^{13}$C NMR (125 MHz, CDCl_3) $\delta$ 170.90, 165.33, 159.64, 152.73, 140.84, 126.90, 84.15, 68.44, 63.63, 62.35, 41.24, 40.86, 34.90, 32.46, 30.44, 30.30, 28.75, 20.82, 16.70; HRMS Calcd for C_{22}H_{32}N_5O_5 [M+H^+]: 446.2403, Found: 446.2417.

**R_f = 0.26, EtOAc**

Compound 28 was isolated in 78% yield (172.3 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol 4t-2 and 2.0 equiv of PFBI-OH were used, 36 h. $^1$H NMR (500 MHz, CDCl_3) $\delta$ 8.34 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H), 7.79 (s, 2H), 7.75 (ddd, J = 8.4, 6.9, 1.0 Hz, 1H), 7.62 (ddd, J = 8.4, 6.9, 0.8 Hz, 1H), 5.75 (d, J = 7.4 Hz, 1H), 4.94–4.88 (m, 1H), 3.71 (t, J = 6.2 Hz, 2H), 3.47–3.31 (m, 6H), 2.61 (br s, 1H), 2.04–1.98 (m, 2H), 1.77–1.71 (m, 2H), 0.93 (d, J = 6.6 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl_3) $\delta$ 171.55, 160.85, 152.03, 141.23, 136.13, 134.86, 132.46 (q, J_{C-F} = 33.9 Hz), 130.20, 127.79, 126.86, 126.68, 126.02, 125.98, 125.96, 123.31, 122.93 (hept, J_{C-F} = 3.6 Hz), 122.84 (q, J_{C-F} = 272.8 Hz), 77.54,
62.22, 54.30, 36.34, 34.19, 32.33, 25.08, 24.43, 14.86; **HRMS** Calcd for C_{28}H_{27}F_{6}N_{2}O_{4} [M+H\textsuperscript{+}]: 569.1875, Found: 569.1905.

Camptothecin 29-1 (139.9 mg, 0.4 mmol, 1.0 equiv), 1-butanol 4t-2 (89.7 mg, 1.2 mmol, 3 equiv) and PFBI-OH (268.8 mg, 0.8 mmol, 2 equiv) were added to a solution of Ru(bpy)_{3}Cl_{2} (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (1.0 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 \degree C under the fluorescent light irradiation (23 W) for 36 h. The solvent was removed in vacuo and the residue was purified by preparative thin layer chromatography on silica gel to afford the desired compound 29 in 58% yield (98.4 mg) as a light yellow solid. **\textsuperscript{1}H NMR** (500 MHz, CDCl_{3}) \(\delta\) 8.19 (d, \(J = 8.4\) Hz, 1H), 8.11 (d, \(J = 8.4\) Hz, 1H), 7.79–7.76 (m, 1H), 7.65–7.63 (m, 2H), 5.73 (d, \(J = 16.2\) Hz, 1H), 5.29 (d, \(J = 16.2\) Hz, 1H), 5.25 (s, 2H), 3.95 (s, 1H), 3.74 (t, \(J = 6.0\) Hz, 2H), 3.22 (t, \(J = 7.8\) Hz, 2H), 1.96–1.83 (m, 4H), 1.80–1.74 (m, 2H), 1.73 (br s, 1H), 1.03 (t, \(J = 7.4\) Hz, 3H); **\textsuperscript{13}C NMR** (125 MHz, CDCl_{3}) \(\delta\) 173.88, 157.62, 151.74, 150.23, 149.35, 146.98, 144.13, 130.60, 130.05, 127.71, 127.24, 127.17, 123.57, 118.46, 98.04, 72.77, 66.30, 62.15, 49.65, 32.52, 31.58, 29.59, 26.28, 7.82; **HRMS** Calcd for C_{24}H_{25}N_{2}O_{5} [M+H\textsuperscript{+}]: 421.1763, Found: 421.1790.

8. Mechanism studies

8.1 Alcoholysis of PFBI-OH 2 for preparation of PFBI-OBu 30

![Scheme S10](image-url)
To the solution of 1-butanol 4t-2 (46.0 mg, 0.6 mmol, 1.5 equiv) in HFIP (1.0 mL), PFBI-OH 2 (134.4 mg, 0.4 mmol, 1.0 equiv) were added. The reaction vial was sealed with PTEF cap, and stirred at 30 °C for 24 h. The solvent was removed in vacuo to afford the desired compound 30 in 92% yield (145.0 mg) as a white solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.36 (t, \(J = 6.6\) Hz, 2H), 1.64–1.57 (m, 2H), 1.45–1.38 (m, 2H), 0.96 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 76.43 (d, \(J = 4.2\) Hz), 34.96, 18.70, 13.81; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -134.41—134.50 (m, 1F), -142.01—142.10 (m, 1F), -143.12—143.23 (m, 1F), -146.07—146.17 (m, 1F); Compound 30 underwent hydrolysis under aqueous conditions for HRMS analysis procedure, affording PFBI-OH 2. HRMS Calcd for C\(_7\)H\(_2\)F\(_4\)IO\(_3\) \([\text{M+H}^+]\): 336.8985, Found: 336.8990.

8.2 PFBI-OBu 30 as alkylation reagent

![Scheme S11.](image)

4-Chloroquinoline 4 (65.2 mg, 0.4 mmol, 1.0 equiv) and PFBI-OBu 30 (316.0 mg, 0.8 mmol, 2 equiv) were added to a solution of Ru(bpy)_3Cl_2 (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 36 h. The solvent was removed in vacuo and the residue was dissolved in DCM (3 mL). To the solution was added K\(_2\)CO\(_3\) (approximate 120 mg), and the resulting mixture was vigorously stirred for 5 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography (ethyl acetate) to afford compound 4s in 49% yield (46.0 mg).
8.3 $^1$H NMR monitored alcoholsysis procedure of PFBI-OH with 4t-2

Three parallel reactions were conducted. To the solution of 1-butanol 4t-2 (46.0 mg, 0.44 mmol, 1.1 equiv) in HFIP (1.0 mL), PFBI-OH 2 (134.4 mg, 0.4 mmol, 1.0 equiv)
was added. The reaction vial was sealed with PTEF cap, and stirred at 30 °C for 2, 4 and 6 hours, respectively. After removal of the solvent *in vacuo* (water bath for rotary evaporation, 40 °C), the residue was dissolved in 3 mL of CDCl₃ for ¹H NMR analysis. The results indicated that PFBI-OBu 30 formed *in situ* after the mixture of PFBI-OH 2 and 1-butanol 4t-2 in HFIP, and increased gradually as the extension of reaction time.

**8.4 The Stern-Volmer quenching experiments**

The luminescence quenching experiments were carried out on a fluorescence spectrophotometer. To a glass cuvette with a PTEF cap, photocatalyst [Ru(bpy)₃]Cl₂, quencher PFBI-OBu 30 or compound 4, and HFIP were added to obtain a total volume of 200 µL. Before determination, the solution was degassed by three freeze-pump-thaw cycles and backfilled with argon. The concentration of [Ru(bpy)₃]Cl₂ was 1.0 × 10⁻⁴ M. All samples were irradiated at 452 nm, and emission was determined at 568 nm. It should be noted that all samples were measured within 1 minute after preparation. The results showed that the excited state of Ru (I) * can be quenched by PFBI-OBu 30, while no obvious change of Ru (I) * luminescence in the presence of variable concentrations of compound 4 was observed. (NOTE: I₀ is emission intensity of Ru (I) * without quencher; I is emission intensity of Ru (I) * in presence of a quencher.)

![Graph](image)

**Figure S2.** Stern-Volmer quenching experiment for PFBI-OBu 30.
8.5 Alkoxyl radical-induced β-C-Cscission in Minisci alkylation reaction

4-Chloroquinoline 4 (65.2 mg, 0.4 mmol, 1.0 equiv), *iso*butanol 31 (46.0 mg, 6 mmol, 1.5 equiv) and PFBI-OH (0.54 mmol, 1.35 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 12 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 80 mg), and the resulting mixture was vigorously stirred for 5 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography to afford compound 32 in 76% yield (62.3 mg) as a colorless oil.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 8.18 \text{ (dd, } J = 8.4, 0.9 \text{ Hz, 1H), 8.07–8.05 (m, 1H), 7.73 } \]
(ddd, $J = 8.4, 6.9, 1.4$ Hz, 1H), $7.57$ (ddd, $J = 8.2, 6.9, 1.2$ Hz, 1H), $7.43$ (s, 1H), $3.27$–$3.19$ (m, 1H), $1.39$ (d, $J = 6.9$ Hz, 6H). Spectra data are consistent with those reported in the literature.[5]

9. Light ON/OFF experiments

![Scheme S13.](image)

4-Chloroquinoline 4 (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol 3 (52.8 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH (181.4 mg, 0.54 mmol, 1.35 equiv) were added to a solution of Ru(bpy)$_3$Cl$_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap. The reactions were stirred at 30 °C under the fluorescent light irradiation (23 W), and kept in the dark in 1 h intervals. After each interval, one vial was take out. After removal of the solvent in vacuo, the residue was dissolved in 3 mL of CDCl$_3$ along with Cl$_2$CHCHCl$_2$ (20 μL) as an internal standard for $^1$H NMR analysis.

| Vial | Time (h)/condition | Yield (%)$^a$ |
|------|-------------------|--------------|
| 1    | 0-1/hv            | 5            |
| 2    | 0-1/hv            | 5            |
| 3    | 0-1/hv            | 14           |
| 4    | 0-1/hv, 1-2/dark  | 14           |
| 5    | 0-1/hv, 1-2/dark  | 18           |
| 6    | 0-1/hv, 1-2/dark  | 18           |

$^a$ NMR yield, average of three experiments
Figure S4. Light ON/OFF experiments using 3 and 4.

10. References

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11. NMR spectra
