Supplementary Materials

$t$-BuONa-mediated direct C-H halogenation of electron-deficient (hetero)arenes

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1. General Information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H and $^{13}$C NMR spectra were recorded at 25 °C on a Varian 600 MHz or 500 MHz or 300 MHz for $^1$H, at 150 MHz or 125 MHz or 75 MHz for $^{13}$C respectively in CDCl$_3$ or DMSO-$d_6$. Chemical shifts are reported in ppm relative to the residual signals of the deuterated solvents as the internal standard (CDCl$_3$: δ $^1$H = 7.26, δ $^13$C = 77.16 ppm) and (DMSO-$d_6$: δ $^1$H = 2.50, δ $^13$C = 40.45 ppm). $^1$H NMR spectra were recorded using TMS as internal standard, $^{13}$C NMR spectra were recorded using an internal reference. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, $J$, are reported in Hertz. High-resolution mass-spectra were obtained on an Agilent 1100 LCMsD mass spectrometer. Melting points (mp) are uncorrected.

2. Preparation of Halogenated (Hetero)Arenes

2.1 Iodination of (Hetero)Arenes

General procedure for iodination

Representative procedure for the preparation of 3a: To a solution of benzothiazole (138 mg, 1 mmol) in DMF (5 mL) were added perfluorobutyl iodide (381 mg, 1.1 mmol) and sodium $t$-butoxide (48 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. After the starting material benzothiazole 1a was consumed as indicated by TLC, the solution was poured into water and then extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel: 200-300 mesh, petroleum ether : ethyl acetate = 60:1-30:1) to give 2-iodobenzothiazole 3a (258 mg, 99%) as a white solid ($R_f$ = 0.49, petroleum ether : ethyl acetate = 30:1).

2.2 Bromination of (Hetero)Arenes

General procedure for bromination
Representative procedure for the preparation of 4a: To a solution of benzothiazole (138 mg, 1 mmol) in DMF (0.5 mL) were added carbon tetrabromide (365 mg, 1.1 mmol) and sodium t-butoxide (384 mg, 4 mmol). The mixture was stirred at room temperature for 25 min. After the starting material benzothiazole 1a was consumed as indicated by TLC, the solution was poured into water and then extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel: 200-300 mesh, petroleum ether : ethyl acetate = 60:1-30:1) to give 2-bromobenzothiazole 4a (198 mg, 93%) as a pale yellow solid ($R_f$ = 0.46, petroleum ether : ethyl acetate = 30:1).

2.3 Chlorination of (Hetero)Arenes

General procedure for chlorination

Representative procedure for the preparation of 5a: To a solution of benzothiazole (138 mg, 1 mmol) in DMF (0.5 mL) were added carbon tetrachloride (169 mg, 1.1 mmol) and sodium t-butoxide (384 mg, 4 mmol). The mixture was stirred at room temperature for 25 min. After the starting material benzothiazole 1a was consumed as indicated by TLC, the solution was poured into water and then extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel: 200-300 mesh, petroleum ether : ethyl acetate = 60:1-30:1) to give 2-chlorobenzothiazole 5a (148 mg, 88%) as a light tan oil ($R_f$ = 0.47, petroleum ether : ethyl acetate = 30:1).
Scheme S1. Proposed Mechanism for the Tribromomethylation and Trichloromethylation of Pentafluorobenzene.

3. Light-mediated Cross-coupling of Halogenated Heteroarenes

General procedure for the Light-mediated Cross-coupling of 2-iodobenzothiazole with (Hetero)Arenes

An over-dried vial, equipped with a magnetic stirring bar, is charged with 2-iodobenzothiazole (261 mg, 1 mmol), 1,10-phenanthroline (18 mg), 1,3,5-trimethoxybenzene (841 mg, 5 mmol), potassium tert-butoxide (449 mg, 4 mmol) in DMF (2 mL). The reaction mixture was then degassed via three cycles of freeze-pump-thaw, backfilling with nitrogen after each cycle. After the reaction mixture was degassed, the vial was placed approximately 2 cm away from a 36 W fluorescent lamp. The mixture was stirred at room temperature. After the starting material 2-iodobenzothiazole was consumed as indicated by TLC, the reaction mixture was poured into water and then extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic phase was washed with water (3 x 10 mL), dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel: 200-300 mesh, petroleum ether : ethyl acetate = 50:1-25:1 ) to give 2-(2,4,6-trimethoxyphenyl)benzothiazole 8a ( 235 mg, 78%) as a white solid ($R_f = 0.35$, petroleum ether : ethyl acetate = 5:1).
4. Analytical Data for Compounds 3-8

2-iodobenzothiazole (3a)

\[
\begin{array}{c}
\text{S} \\
\text{N-I} \\
\end{array}
\]

258 mg, 99% yield; White solid; m. p. 78-80 °C. \(^1\)H NMR (600 MHz, CDCl₃): \(\delta = 7.35-7.43\) (m, 2H), 7.80-7.81 (m, 1H), 8.01-8.02 (m, 1H);
\(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta = 105.9, 120.5, 122.6, 125.7, 126.4, 139.2, 154.2\);
HRMS (ESI) (m/z): Calcd for C₇H₄N(S) (M+H)\(^+\): 261.9187, found: 261.9192.

2-iodobenzoxazole (3b)

\[
\begin{array}{c}
\text{O} \\
\text{N-I} \\
\end{array}
\]

240 mg, 98% yield; White solid; m. p. 86-90 °C (dec.). \(^1\)H NMR (300 MHz, CDCl₃): \(\delta = 7.23-7.31\) (m, 2H), 7.46-7.51 (m, 1H), 7.64-7.71 (m, 1H);
\(^{13}\)C NMR (125 MHz, CDCl₃): \(\delta = 108.2, 110.1, 119.2, 124.6, 125.3, 142.6, 153.9\);
HRMS (ESI) (m/z): Calcd for C₇H₄NO (M+H)\(^+\): 245.9416, found: 245.9422.

2-iodo-N-methylbenzimidazole (3c)

\[
\begin{array}{c}
\text{N} \\
\text{I} \\
\end{array}
\]

208 mg, 81% yield; White solid; m. p. 118-119 °C. \(^1\)H NMR (600 MHz, CDCl₃): \(\delta = 3.66\) (s, 3H), 7.18-7.19 (m, 2H), 7.23 (d, \(J = 4.2\) Hz, 1H), 7.69 (d, \(J = 4.8\) Hz, 1H);
\(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta = 33.6, 104.5, 109.3, 119.0, 122.1, 122.9, 136.1, 145.3\);
HRMS (ESI) (m/z): Calcd for C₈H₇IN₂ (M+H)\(^+\): 258.9732, found: 258.9741.

1,4-dibromo-2-iodo-3-nitrobenzene (3d)
387 mg, 95% yield; White solid; m. p. 111-112 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.50-7.53 (m, 1H), 7.60-7.63 (m, 1H);

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 95.1, 111.0, 131.2, 134.0, 134.2, 156.8;

HRMS (ESI) (m/z): Calcd for C$_6$H$_2$Br$_2$NO (M+H)$^+$: 407.7555, found: 407.7559.

Pentafluorobenzene (3e)

291 mg, 99% yield; colorless oil;

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 65.9 (td, $J_1$ = 28.5 Hz, $J_2$ = 4.5 Hz ), 136.0-136.3 (m), 137.7-138.0 (m), 140.5-140.7 (m), 142.2-142.4 (m), 146.2-146.4 (m), 147.8-148.0 (m);

HRMS (ESI) (m/z): Calcd for C$_6$F$_5$I (M+H)$^+$: 294.9043, found: 294.9052.

2,5-diiodothiazole (3f)

330 mg, 98% yield; White solid; m. p. 107-109 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.63 (s, 1H);

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 74.7, 104.0, 152.6;

HRMS (ESI) (m/z): Calcd for C$_3$H$_2$I$_2$NS (M+H)$^+$: 337.7997, found: 337.7993.

2,4-diiodo-5-phenyloxazole (3g)

373 mg, 94% yield; White solid; m. p. 81-82 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.32 (t, $J$ = 7.2
Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H);

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 100.2, 124.1, 124.9, 126.8, 128.9, 129.0, 157.4;

HRMS (ESI) (m/z): Calcd for C$_9$H$_5$I$_2$NO (M+H)$^+$ : 397.8539, found: 397.8532.

2,6-diiodopyridine 1-oxide (3h)

321 mg, 93% yield; White solid; m. p. 175-176 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 6.56 (t, $J =$ 6.0 Hz, 1H), 7.89 (d, $J$ = 3.0 Hz, 2H);

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 108.2, 125.4, 137.3;

HRMS (ESI) (m/z): Calcd for C$_5$H$_3$I$_2$NO (M+H)$^+$ : 347.8382, found: 347.8387.

2-iodo-1-methylimidazole (3i)

72 mg, 35% yield; White solid; m. p. 88-89 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 3.53 (s, 3H), 6.95 (d, $J$ = 1.2 Hz, 1H), 6.97 (d, $J$ = 1.2 Hz, 1H);

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 36.6, 90.8, 124.1, 132.2;

HRMS (ESI) (m/z): Calcd for C$_4$H$_5$I$_2$N (M+H)$^+$ : 208.9576, found: 208.9571.

2,5-diiodo-1-methyl-1H-imidazole (3j)

210 mg, 63% yield; White solid; m. p. 150-152 °C. $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ = 3.59 (s, 3H), 7.11 (s, 1H);

$^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ = 37.7, 75.8, 93.9, 139.1;

HRMS (ESI) (m/z): Calcd for C$_4$H$_5$I$_2$N (M+H)$^+$ : 334.8542, found: 334.8545.
2-bromobenzothiazole (4a)

199 mg, 93 % yield; pale yellow solid; m. p. 38-39 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.37\text{-}7.48\) (m, 2H), 7.77\text{-}7.80 (m, 1H), 7.96\text{-}7.99 (m, 1H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 120.9, 122.8, 125.7, 126.6, 137.3, 138.9, 152.3\);

HRMS (ESI) (m/z): Calcd for C\(_7\)H\(_4\)BrN\(_2\)S(M+H)\(^+\) : 213.9326, found: 213.9331.

2-bromobenzoxazole (4b)

175 mg, 89% yield; yellow oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.28\text{-}7.35\) (m, 2H), 7.47\text{-}7.52 (m, 1H), 7.64\text{-}7.70 (m, 1H); The \(^{13}\)C NMR spectrum and HRMS were not provided in view that compound 4b is very sensitive to light and heat. It can be easily decomposed at room temperature.

2-bromo-1-methylbenzimidazole (4c)

179 mg, 85 % yield; white solid; m. p. 103-104 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.78\) (s, 3H), 7.22\text{-}7.26 (m, 1H), 7.28\text{-}7.33 (m, 2H), 7.67\text{-}7.72 (m, 1H);

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 31.6, 109.2, 119.2, 122.4, 123.0, 130.3, 135.9, 142.9\);

HRMS (ESI) (m/z): Calcd for C\(_8\)H\(_7\)BrN\(_2\) (M+H)\(^+\) : 210.9871, found: 210.9869.

2-bromo-1-methylimidazole (4d)

101 mg, 63% yield; red brown oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.61\) (s, 3H), 6.96 (d, \(J = 1.2\) Hz, 1H), 6.98 (d, \(J = 1.2\) Hz, 1H);
$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 34.4, 119.7, 123.1, 129.3;

HRMS (ESI+) (m/z): Calcd for C$_4$H$_5$BrN (M+H)$^+$: 160.9714, found: 160.9722.

**2,5-dibromothiazole (4e)**

\[
\text{Br} \quad \text{S} \quad \text{Br}
\]

187 mg, 77 % yield; white solid; m. p. 45-47 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.52 (s, 1H);

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 110.6, 135.8, 144.0;

HRMS (ESI) (m/z): Calcd for C$_3$HBr$_2$NS (M+H)$^+$: 243.8254, found: 243.8251.

**2,4-dibromo-5-phenyloxazole (4f)**

\[
\text{Ph} \quad \text{O} \quad \text{Br}
\]

245 mg, 81 % yield; yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): δ = 7.29-7.33 (m, 1H), 7.33-7.43 (m, 2H), 7.55 (d, J = 9.0 Hz, 2H);

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 123.5, 123.6, 126.3, 128.4, 128.5, 132.0, 154.8;

HRMS (ESI) (m/z): Calcd for C$_9$H$_5$Br$_2$NO (M+H)$^+$: 303.8796, found: 303.8792.

**2-chlorobenzothiazole (5a)**

\[
\text{Cl} \quad \text{N} \quad \text{S}
\]

149 mg, 88 % yield; light brownish oil; $^1$H NMR (600 MHz, CDCl$_3$): δ = 7.33-7.44 (m, 2H), 7.69-7.70 (m, 1H), 7.90-7.91 (m, 1H);

$^{13}$C NMR (150 MHz, CDCl$_3$): δ = 121.0, 122.8, 125.7, 126.6, 136.0, 150.9, 153.1;

HRMS (ESI) (m/z): Calcd for C$_7$H$_4$ClNS (M+H)$^+$: 169.9831, found: 169.9835.

**2-chloro-1-methylbenzoimidazole (5b)**
85.1 mg, 51% yield; White solid; m. p. 117-118 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.77 (s,1H), 7.24-7.27 (m, 1H), 7.29-7.33 (m, 2H), 7.67-7.70 (m, 1H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 30.4, 109.2, 119.3, 122.6, 123.1, 135.6, 140.9, 141.6;

HRMS (ESI) (m/z): Calcd for C$_7$H$_4$ClNO (M+H)$^+$: 167.0376, found: 167.0371.

2,4-dichloro-5-phenyloxazole (5c)

135 mg, 63 % yield; yellow oil; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.32-7.36 (m, 1H), 7.39-7.44 (m, 2 H), 7.58 (d, $J$ = 9.0 Hz, 2H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 122.8, 123.5, 124.3, 126.4, 128.5, 128.6, 128.7, 153.2;

HRMS (ESI) (m/z): Calcd for C$_9$H$_5$Cl$_2$N$_2$O (M+H)$^+$: 213.9826, found: 213.9833.

1,2,3,4,5-pentafluoro-6-(tribromomethyl)benzene (6)

383 mg, 92 % yield; colorless oil;

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 20.3-20.4 (m), 102.3 (t, $J$ = 22.5 Hz), 119.8 (t, $J$ = 12.8 Hz), 142.4-142.6 (m), 144.0-144.3 (m), 145.6-145.9 (m);

HRMS (ESI) (m/z): Calcd for C$_7$Br$_3$F$_3$ (M+H)$^+$: 418.7528, found: 418.7536.

1,2,3,4,5-pentafluoro-6-(trichloromethyl)benzene (7)
218 mg, 77 % yield; colorless oil;

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 58.4$ (t, $J = 2.25$ Hz), 117.7 (t, $J = 13.5$ Hz), 142.6-143.0 (m), 143.2-143.6 (m), 144.3-144.6 (m), 144.9-145.3 (m);

HRMS (ESI) (m/z): Calcd for C$_7$Cl$_3$F$_5$ (M+H)$^+$ : 284.9064, found: 284.9058.

2-(2, 4, 6-trimethoxyphenyl)benzothiazole (8a)

223 mg, 74% yield; White solid; m. p. 118-119 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 3.77$ (s, 6H), 3.86 (s, 3H), 6.20 (s, 2H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.5$ Hz, 1H), 7.89 (d, $J = 9.0$ Hz, 1H), 8.12 (d, $J = 9.0$ Hz, 1H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 55.4, 55.9, 90.6, 104.9, 121.1, 123.2, 124.5, 125.3, 136.4, 153.1, 159.6, 161.9, 162.7$;

HRMS (ESI) (m/z): Calcd for C$_{16}$H$_{15}$NO$_3$S [M+H]$^+$ : 302.0851 found: 302.0855.

2-(1-methyl-1H-indol-2-yl)benzothiazole (8b)

206 mg, 78% yield; White solid; m. p. 140-142 °C NMR (300 MHz, CDCl$_3$): $\delta = 4.28$ (s, 3H), 7.13-7.22 (m, 2H), 7.32-7.50 (m, 4H), 7.66 (d, $J = 9.0$ Hz, 1H), 7.86 (d, $J = 6.0$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 1H);

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 32.2, 107.2, 110.0, 120.5, 121.2, 121.5, 123.1, 126.2, 132.1, 134.4, 139.7, 154.2, 160.5$;

HRMS (ESI) (m/z): Calcd for C$_{16}$H$_{12}$NS (M+H)$^+$ : 256.0799, found: 256.0794.
5. Copies of $^1$H and $^{13}$C NMR Spectra for Compounds 3-8