Supporting Information

Transition-Metal-Free Dehydrogenation Coupling of Pyridinium through Self-Promoted Hydride Transfer Process

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**General methods.** Anhydrous THF, Et₂O were distilled over sodium and benzophenone ketyl under nitrogen atmosphere; Et₃N, DCM and MeCN were refluxed with CaH₂ and freshly distilled prior to use; anhydrous MeOH and EtOH were distilled over magnesium under nitrogen atmosphere; all other solvents and reagents were used from commercial sources without further purifications. All reactions sensitive to air or moisture were carried out under argon or nitrogen atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted.

The silica gel (200-300 meshes) was used for column chromatography. Thin layer chromatographies (TLC) were carried out on GF254 plates (0.25 mm layer thickness). ¹H NMR, ¹³C NMR and ¹⁹F NMR experiments were performed on Bruker AM-300, Bruker AM-400 or DRX-600 NMR spectrometer at ambient temperature. The residual solvent protons (¹H) or the solvent carbons (¹³C) were used as internal standards. ¹H NMR data were presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). Chemical shifts (δ) were given in ppm with reference to solvent signals [¹H NMR: CDCl₃ (7.26), CD₃OD (3.31), D₂O (4.79), DMSO-d₆ (2.50); ¹³C NMR: CDCl₃ (77.16), CD₃OD (49.86)], DMSO-d₆ (39.52). The following abbreviations are used in reporting NMR data: s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet. HRMS (ESI) was taken on Agilent 6540 Q-TOF spectrometer.
General procedures for preparation of pyridinium

\[
\text{HO-CH}_{2}-\text{CH}_{2}-\text{Br} + \text{MeO} \rightarrow \text{HO-CH}_{2}-\text{CH}_{2}-\text{N}^+\text{MeO}^- \text{Br}^{-}
\]

A mixture of phenylethyl bromide (230 mg, 1 mmol) and 3-acetylpyridine (363 mg, 3 mmol) was stirred at 70 °C without solvent for 3 h. After the reaction mixture was cooled to room temperature, the solid was collected by filtration and washed with Et₂O (3 × 20 mL) then petroleum ether (3 × 20 mL). The residue yellow solid was dried at 40°C under vacuum to yield pyridinium 1 (343 mg, 98.3% yield) as a yellow powder.

\[
\begin{align*}
\text{H NMR (400 MHz, D}_{2}\text{O}) & \delta 8.94 (d, J = 8.1 \text{ Hz}, 1\text{H}), 8.87 (s, 1\text{H}), 8.79 (d, J = 6.1 \text{ Hz}, 1\text{H}), 8.11 (dd, J = 7.9, 6.3 \text{ Hz}, 1\text{H}), 6.89 (d, J = 8.8 \text{ Hz}, 1\text{H}), 6.53 (m, 2\text{H}), 4.90 (t, J = 6.4 \text{ Hz}, 2\text{H}), 3.80 (s, 3\text{H}), 3.21 (t, J = 6.3 \text{ Hz}, 2\text{H}), 2.60 (s, 3\text{H}). \\
\text{C NMR (100 MHz, D}_{2}\text{O}) & \delta 196.1, 147.0, 146.8, 145.2, 144.6, 135.2, 128.3, 121.3, 115.8, 112.9, 63.6, 55.9, 35.9, 26.3. \\
\text{HRMS (ESI) calcd. for C}_{16}\text{H}_{18}\text{NO}_{3} [M]^{+} & 272.1281, \text{ found 272.1285.}
\end{align*}
\]

3a. Light pink powder (97.8% yield). \(\text{H NMR (400 MHz, D}_{2}\text{O}) \delta 8.97 (bri, 2\text{H}), 8.82 (d, J = 6.1 \text{ Hz}, 1\text{H}), 8.13 (dd, J = 8.5, 6.2 \text{ Hz}, 1\text{H}), 7.21 (t, J = 7.9 \text{ Hz}, 1\text{H}), 6.80 (dd, J = 8.1, 2.1 \text{ Hz}, 1\text{H}), 6.65 (d, J = 7.5 \text{ Hz}, 1\text{H}), 6.52 (s, 1\text{H}), 4.97 (t, J = 6.4 \text{ Hz}, 2\text{H}), 3.30 (t, J = 6.4 \text{ Hz}, 2\text{H}), 2.64 (s, 3\text{H}). \text{C NMR (100 MHz, D}_{2}\text{O}) \delta 196.1, 156.0, 147.0, 144.7, 137.2, 135.3, 130.7, 128.4, 121.0, 115.7, 114.5, 63.3, 36.4, 26.4. \text{HRMS (ESI) calcd. for C}_{15}\text{H}_{16}\text{NO}_{2} [M]^{+} 242.1176, \text{ found 242.1170.}
\]

4a. Yellow foam. (89.0% yield) \(\text{H NMR (300 MHz, D}_{2}\text{O}) \delta 8.95 (d, J = 6.1 \text{ Hz}, 1\text{H}), 8.75 (d, J = 8.1 \text{ Hz}, 1\text{H}), 8.59 (s, 1\text{H}), 8.14 (dd, J = 7.9, 6.3 \text{ Hz}, 1\text{H}), 7.69 (dd, J = 10.1, 4.4 \text{ Hz}, 1\text{H}), 7.46 (m, 4\text{H}), 7.10 (t, J = 7.9 \text{ Hz}, 1\text{H}), 6.72 (dd, J = 8.2, 1.8 \text{ Hz}, 1\text{H}), 6.52 (d, J = 7.6 \text{ Hz}, 1\text{H}), 6.43 (d, J = 1.8 \text{ Hz}, 1\text{H}), 4.87 (t, J = 6.2 \text{ Hz}, 2\text{H}), 3.21 (t, J = 6.2 \text{ Hz}, 2\text{H}). \text{C NMR (75 MHz, D}_{2}\text{O}) \delta 192.2, 156.0, 146.6, 146.1, 145.3, 137.0, 136.3, 134.8, 134.1, 130.6, 129.9, 129.0, 128.5, 120.8, 115.5, 114.5, 63.3, 36.4.
HRMS (ESI) calcd. for C_{26}H_{18}NO_2 [M]^+ 304.1332, found 304.1334.

5a. White powder (93.5% yield). ^1H NMR (400 MHz, D_2O) δ 8.92 (m, 2H), 8.88 (d, J = 8.4 Hz, 1H), 8.22 (t, J = 6.8 Hz 1H), 6.93 (d, J = 8.8 Hz, 1H), 6.54 (m, 2H), 4.94 (t, J = 6.4 Hz, 2H), 3.83 (s, 3H), 3.24 (t, J = 6.4 Hz, 2H). ^13C NMR (100 MHz, D_2O) δ 147.5, 147.0, 145.3, 143.0 (m), 142.6 (m), 130.3 (q, J_{C-F} = 24.3 Hz), 128.9, 128.1, 121.1, 121.0 (q, J_{C-F} = 178.8 Hz.), 115.7, 113.1, 63.9, 56.0, 35.9. ^19F NMR (376 MHz, D_2O) δ -63.31. HRMS (ESI) calcd. for C_{15}H_{15}F_3NO_2 [M]^+ 298.1049, found 298.1055.

6a. Yellow foam (93.5% yield). ^1H NMR (400 MHz, D_2O) δ 9.01 (d, J = 6.1 Hz, 1H), 8.81 (d, J = 8.1 Hz, 1H), 8.52 (s, 1H), 8.21 (dd, J = 7.8, 6.4 Hz, 1H), 7.76 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H), 6.82 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 1.9 Hz, 1H), 6.45 (dd, J = 8.2, 1.9 Hz, 1H), 4.89 (t, J = 6.1 Hz, 2H), 3.73 (s, 3H), 3.20 (t, J = 6.1 Hz, 2H). ^13C NMR (100 MHz, D_2O) δ 192.3, 146.9, 146.7, 146.1, 145.3, 145.3, 136.2, 134.9, 134.2, 129.9, 129.0, 128.5, 128.1, 121.1, 115.7, 112.8, 63.5, 55.8, 35.9. HRMS (ESI) calcd. for C_{21}H_{20}NO_3 [M]^+ 334.1438, found 334.1448.

7a. White powder (91.7% yield). ^1H NMR (400 MHz, D_2O) δ 8.86 (s, 1H), 8.82 (d, J = 8.2 Hz, 1H), 8.70 (d, J = 6.0 Hz, 1H), 8.05 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.55 (s, 1H), 6.50 (d, J = 8.2 Hz, 1H), 4.88 (t, J = 6.4 Hz, 2H), 3.80 (s, 3H), 3.20 (t, J = 6.3 Hz, 2H). ^13C NMR (100 MHz, D_2O) δ 165.5, 146.8, 146.3, 145.2, 144.0, 143.8, 133.3, 128.3, 128.0, 121.1, 115.8, 112.9, 63.6, 55.9, 35.8. HRMS (ESI) calcd. for C_{15}H_{17}N_2O_3 [M]^+ 273.1234, found 273.1241.
8a. White powder (88.7% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 9.16 (s, 1H), 8.89 (d, $J$ = 8.2 Hz, 1H), 8.83 (d, $J$ = 6.2 Hz, 1H), 8.15 (t, $J$ = 6.2 Hz, 1H), 6.92 (d, $J$ = 8.2 Hz, 1H), 6.59 (d, $J$ = 1.9 Hz, 1H), 6.54 (dd, $J$ = 8.2, 1.9 Hz, 1H), 4.92 (t, $J$ = 6.5 Hz, 2H), 3.83 (s, 3H), 3.23 (t, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 148.9, 147.8, 146.9, 145.3, 128.6, 127.9, 121.2, 115.8, 113.5, 113.0, 112.9, 64.1, 55.9, 35.7. HRMS (ESI) calcd. for C$_{15}$H$_{13}$N$_2$O$_2$ [M]$^+$ 255.1128, found 255.1133.

9a. White powder (76.5% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 8.96 (m, 2H), 8.78 (d, $J$ = 6.1 Hz, 1H), 8.09 (dd, $J$ = 8.5, 6.2 Hz, 1H), 6.89 (d, $J$ = 8.2 Hz, 1H), 6.55 (d, $J$ = 1.8 Hz, 1H), 6.52 (dd, $J$ = 8.2, 1.9 Hz, 1H), 4.90 (t, $J$ = 6.4 Hz, 2H), 3.99 (s, 3H), 3.81 (s, 3H), 3.22 (t, $J$ = 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 163.1, 147.2, 146.9, 145.3, 145.4, 145.2, 130.1, 128.2, 121.2, 115.8, 112.9, 63.6, 55.9, 53.8, 35.8. HRMS (ESI) calcd. for C$_{16}$H$_{18}$NO$_4$ [M]$^+$ 288.1230, found 288.1234.

10a. White powder (80.5% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 8.80 (d, $J$ = 7.6 Hz, 1H), 8.48 (d, $J$ = 6.0 Hz, 1H), 7.80 (t, $J$ = 8.0 Hz, 1H), 6.93 (m, 1H), 6.57 (dd, $J$ = 4.1, 2.2 Hz, 2H), 4.92 (t, $J$ = 6.5 Hz, 2H), 4.02 (s, 3H), 3.84 (s, 3H), 3.20 (t, $J$ = 6.5 Hz, 2H), 2.90 (s, 3H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 165.3, 156.5, 147.8, 146.8, 146.3, 145.1, 132.0, 128.4, 124.7, 121.3, 115.9, 112.9, 60.2, 55.9, 53.9, 34.5, 17.1. HRMS (ESI) calcd. for C$_{17}$H$_{20}$NO$_4$ [M]$^+$ 302.1387, found 302.1391.
Yellow powder (72.5% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 9.01 (d, $J = 8.2$ Hz, 1H), 8.67 (d, $J = 5.5$ Hz, 1H), 8.32 (t, $J = 9.9$ Hz, 2H), 8.17 (t, $J = 7.7$ Hz, 1H), 7.96 (t, $J = 7.5$ Hz, 1H), 7.75 (t, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 7.3$ Hz, 1H), 6.30 (brs, 2H), 5.20 (brs, 2H), 3.73 (s, 3H), 3.23 (brs, 2H).

$^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 148.1, 147.7, 146.6, 144.9, 137.7, 135.7, 130.7, 129.9, 129.0, 120.9, 118.1, 115.6, 112.7, 59.0, 55.8, 34.4. HRMS (ESI) calcd. for C$_{18}$H$_{18}$NO$_2$ [M]$^+$ 280.1332, found 280.1336.

Yellow powder (89.3% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 9.39 (d, $J = 8.7$ Hz, 1H), 8.80 (d, $J = 5.2$ Hz, 1H), 8.38 (d, $J = 9.1$ Hz, 1H), 8.32 (d, $J = 7.6$ Hz, 1H), 8.03 (dd, $J = 8.8$, 8.0 Hz, 1H), 7.90 (dd, $J = 8.7$, 5.8 Hz, 1H), 6.78 (d, $J = 8.2$ Hz, 1H), 6.36 (d, $J = 1.9$ Hz, 1H), 6.33 (dd, $J = 8.2$, 1.9 Hz, 1H), 5.28 (t, $J = 6.3$ Hz, 2H), 3.78 (s, 3H), 3.29 (t, $J = 6.3$ Hz, 2H).

$^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 149.0, 147.1, 146.7, 145.0, 138.9, 135.6, 134.1, 129.2, 128.9, 124.4, 121.9, 121.0, 118.2, 115.6, 112.7, 59.7, 55.9, 34.5. HRMS (ESI) calcd. for C$_{18}$H$_{17}$BrNO$_2$ [M]$^+$ 358.0437, found 358.0441.

Yellow powder (87.5% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 8.93 (d, $J = 8.0$ Hz, 1H), 8.63 (dd, $J = 5.4$ Hz, 1H), 8.03 (m, 2H), 7.73 (dd, $J = 8.3$, 5.9 Hz, 1H), 7.63 (d, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 6.33 (m, 2H), 5.47 (t, $J = 6.5$ Hz, 2H), 4.10 (s, 3H), 3.73 (s, 3H), 3.10 (t, $J = 6.5$ Hz, 2H).

$^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 150.3, 149.9, 147.7, 146.3, 144.6, 132.1, 130.4, 129.6, 129.1, 122.4, 121.2, 120.9, 116.1, 115.6, 112.3, 64.6, 56.6, 55.8, 36.7. HRMS (ESI) calcd. for C$_{19}$H$_{20}$NO$_3$ [M]$^+$ 310.1438, found 310.1442.

Yellow powder (87.5% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 9.13 (d, $J = 8.4$ Hz, 1H), 8.94 (d, $J = 5.5$ Hz, 1H), 8.68 (dd, $J = 9.7$, 4.2 Hz, 1H), 8.18 (dd, $J = 8.0$, 2.6 Hz, 1H), 8.15 (m, 1H), 7.94 (dd, $J = 8.2$, 5.9 Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 6.43 (d, $J = 1.6$ Hz, 1H), 6.35 (dd, $J = 8.1$, 1.6 Hz, 1H), 5.32 (t, $J = 6.6$ Hz, 2H), 3.78
(s, 3H), 3.28 (t, $J = 6.7$ Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 163.9 (d, $J_{C-F} = 252.8$ Hz), 150.9, 149.4, 149.3 (d, $J_{C-F} = 5.1$ Hz), 148.9, 137.3, 134.0 (d, $J_{C-F} = 10.7$ Hz), 130.5, 127.8 (d, $J_{C-F} = 26.6$ Hz), 124.4, 124.2 (d, $J_{C-F} = 9.4$ Hz), 121.9, 117.5, 116.2 (d, $J_{C-F} = 23.1$ Hz), 113.8, 61.9, 57.2, 37.1. $^{19}$F NMR (376 MHz, CD$_3$OD) $\delta$ -108.84 (s). HRMS (ESI) calcd. for C$_{18}$H$_{17}$FNO$_2$ [M]$^+$ 298.1238, found 298.1240.

16a. Yellow powder (91.4% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 9.12 (s, 1H), 8.31 (brs, 2H), 8.15 (m, 3H), 7.93 (m, 1H), 6.74 (d, $J = 8.2$ Hz, 1H), 6.48 (d, $J = 1.6$ Hz, 1H), 6.44 (dd, $J = 8.2$, 1.6 Hz, 1H), 4.90 (t, $J = 6.3$ Hz, 2H), 3.72 (s, 3H), 3.23 (t, $J = 6.3$ Hz, 2H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 148.8, 146.6, 145.0, 137.4, 137.1, 133.7, 131.3, 129.7, 128.8, 127.2, 127.1, 126.2, 121.0, 115.7, 112.7, 62.7, 55.9, 35.8. HRMS (ESI) calcd. for C$_{18}$H$_{18}$NO$_2$ [M]$^+$ 280.1332, found 280.1337.

17a. Yellow foam (67.8% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 9.06 (s, 1H), 8.41 (d, $J = 6.9$ Hz, 1H), 8.27 (d, $J = 6.9$ Hz, 1H), 7.80 (t, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 8.3$ Hz, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 6.68 (d, $J = 8.2$ Hz, 1H), 6.48 (d, $J = 1.8$ Hz, 1H), 6.40 (dd, $J = 8.2$, 1.7 Hz, 1H), 4.88 (t, $J = 6.3$ Hz, 2H), 4.02 (s, 3H), 3.69 (s, 3H), 3.21 (t, $J = 6.3$ Hz, 2H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 154.1, 148.1, 146.6, 145.0, 137.4, 137.1, 133.7, 131.3, 129.7, 128.8, 127.2, 127.1, 126.2, 121.0, 115.7, 112.7, 62.7, 55.9, 35.7. HRMS (ESI) calcd. for C$_{19}$H$_{20}$NO$_3$ [M]$^+$ 310.1438, found 310.1442.

18a. Yellow foam (65.5% yield). $^1$H NMR (400 MHz, D$_2$O) $\delta$ 8.94 (s, 1H), 8.19 (d, $J = 6.2$ Hz, 1H), 8.06 (d, $J = 6.8$ Hz, 1H), 7.89 (t, $J = 8.2$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.10 (d, $J = 8.1$ Hz, 1H), 6.52 (d, $J = 8.2$ Hz, 1H), 6.36 (d, $J = 1.8$ Hz, 1H), 6.25 (dd, $J = 8.2$, 1.8 Hz, 1H), 4.77 (t, $J = 6.3$ Hz, 2H), 3.92 (s, 3H), 3.61 (s, 3H), 3.07 (t, $J = 6.3$ Hz, 2H). $^{13}$C NMR (100 MHz, D$_2$O) $\delta$ 157.4, 146.5, 145.0, 144.2, 138.8, 137.8,
133.9, 128.5, 125.3, 120.9, 119.1, 118.3, 115.4, 112.3, 109.3, 62.4, 56.3, 55.7, 35.7. HRMS (ESI) calcd. for C_{19}H_{20}NO_3 [M]^+ 310.1438, found 310.1444.

19a. Yellow foam (75.8% yield). \(^1\)H NMR (400 MHz, D\(_2\)O) \(\delta\) 8.91 (s, 1H), 8.27 (brs, 2H), 8.03 (d, \(J = 9.0\) Hz, 1H), 7.95 (d, \(J = 9.0\) Hz, 1H), 6.72 (m, 1H), 6.41 (s, 2H), 4.89 (t, \(J = 6.0\) Hz, 2H), 4.05 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.20 (t, \(J = 5.2\) Hz, 2H). \(^{13}\)C NMR (100 MHz, D\(_2\)O) \(\delta\) 151.2, 146.4, 144.9, 143.4, 143.3, 131.4, 131.3, 128.3, 126.0, 125.8, 123.8, 122.5, 120.7, 115.3, 112.1, 62.6, 62.0, 56.6, 55.5, 35.6. HRMS (ESI) calcd. for C_{20}H_{22}NO_4 [M]^+ 340.1543, found 340.1553.

20a. Yellow powder (92.5% yield). \(^1\)H NMR (400 MHz, D\(_2\)O) \(\delta\) 9.18 (s, 1H), 8.56 (d, \(J = 7.0\) Hz, 1H), 8.44 (t, \(J = 7.8\) Hz, 2H), 8.15 (d, \(J = 8.3\) Hz, 1H), 7.80 (t, \(J = 8.0\) Hz, 1H), 6.75 (d, \(J = 8.2\) Hz, 1H), 6.47 (d, \(J = 1.8\) Hz, 1H), 6.44 (dd, \(J = 8.2, 1.8\) Hz, 1H), 4.94 (t, \(J = 6.3\) Hz, 2H), 3.72 (s, 3H), 3.24 (t, \(J = 6.3\) Hz, 2H). \(^{13}\)C NMR (100 MHz, D\(_2\)O) \(\delta\) 149.3, 146.7, 145.1, 140.5, 136.5, 135.1, 131.9, 129.8, 128.7, 128.4, 125.6, 121.2, 121.0, 115.7, 112.8, 62.9, 55.9, 35.7. HRMS (ESI) calcd. for C_{18}H_{17}BrNO_2 [M]^+ 358.0437, found 358.0443.
General procedures for dehydrogenation coupling reaction

To a solution of pyridinium 1 (70 mg, 0.2 mmol) and Na$_2$CO$_3$ (25 mg, 0.24 mmol) in MeOH (8 mL) was stirred at 50 °C under air atmosphere for 2 h. The mixture was concentrated in vacuum to give the residue, which was subjected to flash chromatographic column (dichloromethane/methanol = 10:1) to afford product 2 (53 mg, 76.1 %) as an orange powder. $^1$H NMR (400 MHz, CD$_3$OD) δ 9.08 (s, 1H), 8.57 (dd, $J = 8.9$, 1.0 Hz, 1H), 8.29 (d, $J = 9.0$ Hz, 1H), 7.44 (s, 1H), 6.62 (s, 1H), 4.65 (t, $J = 6.8$ Hz, 2H), 3.91 (s, 3H), 3.13 (t, $J = 6.8$ Hz, 2H), 2.66 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 195.3, 156.4, 154.2, 150.7, 147.9, 144.9, 134.5, 133.6, 125.4, 118.8, 117.2, 112.6, 57.9, 57.4, 27.8, 27.7. HRMS (ESI) calcd. for C$_{16}$H$_{16}$NO$_3$ [M]$^+$ 270.1125, found 270.1127.

3. Yellow powder (72.1% yield). $^1$H NMR (400 MHz, CD$_3$OD) δ 9.28 (s, 1H), 8.78 (dd, $J = 8.7$, 1.5 Hz, 1H), 8.45 (d, $J = 8.8$ Hz, 1H), 8.08 (d, $J = 8.8$ Hz, 1H), 6.93 (dd, $J = 8.8$, 2.3 Hz, 1H), 6.84 (d, $J = 1.8$ Hz, 1H), 4.80 (t, $J = 8.0$ Hz, 2H), 3.28 (t, $J = 8.0$ Hz, 2H), 2.71 (s, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 195.3, 156.4, 154.2, 150.7, 147.9, 144.9, 134.5, 133.6, 125.4, 118.8, 117.2, 112.6, 57.9, 57.4, 27.8, 27.7. HRMS (ESI) calcd. for C$_{15}$H$_{14}$NO$_2$ [M]$^+$ 240.1019, found 240.1019.

4. Yellow powder (74.1% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.25 (s, 1H), 8.72 – 8.63 (m, 1H), 8.59 (d, $J = 8.7$ Hz, 1H), 8.19 (d, $J = 8.8$ Hz, 1H), 7.93 (d, $J = 7.4$ Hz, 2H), 7.80 (t, $J = 7.4$ Hz, 1H), 7.66 (t, $J = 7.7$ Hz, 2H), 6.96 (dd, $J = 8.7$, 2.2 Hz, 1H), 6.88 (d, $J = 1.8$ Hz, 1H), 4.78 (t, $J = 6.6$ Hz, 2H), 3.24 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 191.2, 164.1, 151.3, 146.1, 144.6, 140.1, 135.7, 134.6, 132.2, 131.2, 130.6, 129.6, 123.2, 117.0, 116.6, 115.6, 54.7, 26.4. HRMS (ESI) calcd. for C$_{20}$H$_{16}$NO$_2$ [M]$^+$ 302.1176, found 302.1181.
5. Orange powder (70.4% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 9.29 (s, 1H), 8.69 (m, 2H), 7.71 (s, 1H), 6.92 (s, 1H), 4.79 (t, $J = 8.0$ Hz, 2H), 4.01 (s, 3H), 3.24 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 156.7, 155.1, 150.7, 145.1 (q, $J_{C\text{-}F} = 3.2$ Hz), 143.1 (m), 134.6, 127.5 (q, $J_{C\text{-}F} = 24.6$ Hz), 126.3, 124.2 (q, $J_{C\text{-}F} = 180.0$ Hz), 118.5, 117.2, 112.7, 57.9, 57.5, 27.6. $^{19}$F NMR (376 MHz, CD$_3$OD) $\delta$ -64.30. HRMS (ESI) calcd. for C$_{15}$H$_{13}$F$_3$NO$_2$ [M]$^+$ 296.0893, found 296.0895.

6. Orange powder (78.0% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.71 (s, 1H), 8.36 (d, $J = 8.7$ Hz, 1H), 8.18 (d, $J = 9.0$ Hz, 1H), 7.88 (d, $J = 7.4$ Hz, 2H), 7.73 (t, $J = 7.4$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 2H), 7.33 (s, 1H), 6.48 (s, 1H), 4.55 (t, $J = 6.6$ Hz, 2H), 3.88 (s, 3H), 3.09 (t, $J = 6.6$ Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 192.7, 159.2, 153.8, 151.3, 148.3, 145.8, 137.8, 135.9, 134.9, 133.5, 132.0, 131.0, 125.0, 117.6, 117.3, 112.2, 57.8, 57.3, 28.0. HRMS (ESI) calcd. for C$_{21}$H$_{18}$NO$_3$ [M]$^+$ 332.1281, found 332.1283.

7. Orange powder (58.2% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.84 (s, 1H), 8.44 (dd, $J = 9.0, 1.6$ Hz, 1H), 8.18 (d, $J = 9.1$ Hz, 1H), 7.33 (s, 1H), 6.50 (s, 1H), 4.56 (t, $J = 8.0$ Hz, 2H), 3.87 (s, 3H), 3.08 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 166.2, 152.8, 152.1, 145.4, 142.1, 134.6, 127.6, 123.1, 117.7, 110.3, 56.4, 56.3, 27.4. HRMS (ESI) calcd. for C$_{15}$H$_{15}$N$_2$O$_3$ [M]$^+$ 271.1077, found 271.1079.
8. Orange powder (64.4% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.75 (s, 1H), 8.11 – 7.97 (m, 2H), 7.20 (s, 1H), 6.38 (s, 1H), 4.44 (t, $J$ = 8.0 Hz, 2H), 3.83 (s, 3H), 3.04 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 173.3, 153.8, 152.5, 149.1, 142.1, 136.9, 122.9, 119.1, 115.9, 109.3, 109.2, 103.0, 56.0, 55.8, 27.6. HRMS (ESI) calcd. for C$_{15}$H$_{13}$N$_2$O$_2$ [M]$^+$ 253.0972, found 253.0971.

9. Orange powder (62.0% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.91 (s, 1H), 8.41 (dd, $J$ = 9.0, 1.5 Hz, 1H), 8.13 (d, $J$ = 9.1 Hz, 1H), 7.29 (s, 1H), 6.46 (s, 1H), 4.55 (t, $J$ = 8.0 Hz, 2H), 3.98 (s, 3H), 3.86 (s, 3H), 3.06 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 170.2, 164.5, 153.4, 153.3, 146.6, 141.9, 135.8, 122.5, 122.3, 118.6, 110.4, 109.6, 56.1, 55.9, 53.4, 27.7. HRMS (ESI) calcd. for C$_{16}$H$_{16}$NO$_4$ [M]$^+$ 286.1074, found 286.1076.

10. Yellow powder (66% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.54 (d, $J$ = 8.9 Hz, 1H), 8.21 (d, $J$ = 9.0 Hz, 1H), 7.43 (s, 1H), 6.66 (s, 1H), 4.59 (t, $J$ = 8.0 Hz, 2H), 3.99 (s, 3H), 3.92 (s, 3H), 3.08 (t, $J$ = 8.0 Hz, 2H), 3.04 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 166.1, 157.2, 154.1, 151.7, 144.2, 134.2, 126.2, 121.3, 116.6, 110.8, 56.5, 53.7, 50.0, 27.1, 18.4. HRMS (ESI) calcd. for C$_{17}$H$_{18}$NO$_4$ [M]$^+$ 300.1230, found 300.1234.

11. Yellow powder (63.2% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.40 (d, $J$ = 9.2 Hz, 1H), 7.37 (s, 1H), 6.36 (s, 1H), 3.97 (s, 3H), 3.04 (s, 3H).

S11
Hz, 1H), 8.22 (d, J = 8.9 Hz, 1H), 8.14 (d, J = 9.3 Hz, 1H), 8.00 (d, J = 7.0 Hz, 1H), 7.93 (t, J = 8.0 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.35 (s, 1H), 6.46 (s, 1H), 4.75 (t, J = 8.0 Hz, 2H), 3.87 (s, 3H), 3.12 (t, J = 8.0 Hz, 2H).

13C NMR (100 MHz, CD3OD) δ 154.5, 152.4, 145.3, 141.2, 136.4, 135.9, 132.3, 129.8, 129.2, 122.5, 121.7, 119.1, 118.0, 117.6, 112.7, 57.4, 48.6, 28.2. HRMS (ESI) calcd. for C18H16NO2 [M]+ 278.1176, found 278.1176.

**12.** Red powder (69.6% yield). 1H NMR (600 MHz, CD3OD) δ 8.59 (d, J = 9.6 Hz, 1H), 8.17 (d, J = 9.7 Hz, 2H), 7.88 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 7.1 Hz, 2H), 7.30 (s, 1H), 4.70 (t, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.10 (t, J = 7.0 Hz, 2H). 13C NMR (150 MHz, CD3OD) δ 174.3, 154.6, 153.6, 142.6, 140.7, 138.1, 135.4, 132.4, 126.8, 125.9, 122.9, 119.7, 118.1, 111.3, 111.3, 56.9, 48.3, 28.7. HRMS (ESI) calcd. for C18H15BrNO2 [M]+ 356.0281, found 356.0278.

**13.** Red powder (77.8% yield). 1H NMR (400 MHz, CD3OD) δ 8.39 (d, J = 9.1 Hz, 1H), 8.12 (d, J = 9.2 Hz, 1H), 7.56 (m, 3H), 7.39 (s, 1H), 6.54 (s, 1H), 5.10 (t, J = 8.0 Hz, 2H), 4.09 (s, 3H), 3.89 (s, 3H), 3.04 (t, J = 8.0 Hz, 2H). 13C NMR (100 MHz, CD3OD) δ 168.9, 155.4, 153.4, 152.5, 144.0, 137.8, 132.4, 130.8, 129.9, 123.8, 121.8, 118.6, 117.9, 114.0, 111.8, 58.3, 57.1, 53.6, 29.3. HRMS (ESI) calcd. for C19H18NO3 [M]+ 308.1281, found 308.1284.

**14.** Red powder (75.2% yield). 1H NMR (600 MHz, CD3OD) δ 8.33 (d, J = 9.3 Hz, 1H), 8.25 (dd, J = 9.5, 3.9 Hz, 1H), 8.16 (d, J = 9.3 Hz, 1H), 7.79 – 7.66 (m, 2H), 7.31 (s, 1H), 6.43 (s, 1H), 4.72 (t, J = 7.0 Hz, 2H), 3.85 (s, 3H), 3.10 (t, J = 7.0 Hz, 2H). 13C NMR (150 MHz, CD3OD) δ 173.3, 162.2 (d, JCF = 164.5 Hz), 154.5, 153.6, 142.1 (d, JCF = 2.4 Hz), 138.0, 137.3, 129.6 (d, JCF = 6.4 Hz), 123.7 (d, JCF = 16.7 Hz), 122.7, 121.1 (d, JCF = 5.7 Hz), 119.5, 115.9 (d, JCF = 15.2 Hz), 111.4, 111.3, 56.9, 48.3, 28.6. 19F NMR (376 MHz, CD3OD) δ -112.29. HRMS (ESI) calcd. for
C_{15}H_{15}FNO_2 [M]^+ 296.1081, found 296.1082.

15. Orange powder (82.0% yield). \(^1\)H NMR (400 MHz, D_2O) \(\delta\) 8.74 (d, \(J = 9.0\) Hz, 1H), 8.59 (s, 1H), 8.50 (d, \(J = 9.3\) Hz, 1H), 8.38 (d, \(J = 9.4\) Hz, 1H), 8.19 (d, \(J = 9.1\) Hz, 1H), 7.38 (s, 1H), 6.90 (s, 1H), 4.84 (t, \(J = 6.9\) Hz, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 3.18 (t, \(J = 6.8\) Hz, 2H). \(^{13}\)C NMR (100 MHz, D_2O) \(\delta\) 166.4, 153.0, 152.9, 147.6, 145.3, 140.3, 134.1, 132.4, 129.1, 126.6, 120.0, 117.9, 117.7, 114.5, 111.3, 55.9, 53.2, 46.9, 25.0. HRMS (ESI) calcd. for C_{20}H_{18}NO_4 [M]^+ 336.1230, found 336.1230.

16. Orange powder (78.3% yield). \(^1\)H NMR (400 MHz, CD_3OD) \(\delta\) 8.60 (m, 1H), 8.00 (m, 3H), 7.82 (dd, \(J = 8.2, 7.0\) Hz, 1H), 7.63 (d, \(J = 6.8\) Hz, 1H), 7.21 (s, 1H), 6.53 (s, 1H), 4.43 (t, \(J = 6.0\) Hz, 2H), 3.79 (s, 3H), 2.98 (t, \(J = 6.0\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CD_3OD) \(\delta\) 171.5, 155.4, 153.7, 140.9, 138.0, 136.2, 135.9, 133.0, 131.5, 129.5, 127.3, 120.0, 119.5, 116.3, 111.5, 56.9, 55.7, 29.1. HRMS (ESI) calcd. for C_{18}H_{16}NO_2 [M]^+ 278.1176, found 278.1178.

17. Red powder (73.2% yield). \(^1\)H NMR (400 MHz, CD_3OD) \(\delta\) 8.47 (d, \(J = 6.6\) Hz, 1H), 8.39 (d, \(J = 6.8\) Hz, 1H), 8.31 (d, \(J = 8.6\) Hz, 1H), 7.96 (t, \(J = 8.3\) Hz, 1H), 7.62 (d, \(J = 7.8\) Hz, 1H), 7.61 (s, 1H), 7.02 (s, 1H), 4.71 (t, \(J = 8.0\) Hz, 2H), 4.15 (s, 3H), 3.97 (s, 3H), 3.18 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CD_3OD) \(\delta\) 157.2, 155.4, 154.8, 149.5, 136.4, 136.1, 133.8, 133.4, 128.4, 123.4, 119.4, 118.9, 118.0, 117.0, 115.1, 58.1, 57.8, 56.9, 28.4. HRMS (ESI) calcd. for C_{19}H_{18}NO_3 [M]^+ 308.1281, found 308.1281.
18. Orange powder (70.8% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.93 (dd, $J = 9.5$, 6.1 Hz, 2H), 7.54 (t, $J = 6.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 1H), 6.75 (s, 1H), 6.46 (s, 1H), 4.37 (brs, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 3.03 (brs, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 171.0, 160.9, 154.9, 152.9, 142.8, 137.9, 136.1, 135.5, 121.0, 119.7, 117.9, 117.9, 117.9, 115.2, 112.3, 112.3, 56.9, 56.9, 55.0, 28.9. HRMS (ESI) calcd. for C$_{19}$H$_{18}$NO$_3$ [M]$^+$ 308.1281, found 308.1280.

19. Orange powder (66.8% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.29 (d, $J = 6.6$ Hz, 1H), 8.04 (m, 3H), 7.20 (s, 1H), 6.92 (s, 1H), 4.64 (brs, 2H), 4.11 (s, 3H), 3.85 (s, 3H), 3.38 (s, 3H), 3.22 (brs, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 155.7, 155.1, 153.7, 148.4, 148.1, 136.7, 134.2, 134.1, 126.7, 126.4, 124.6, 122.5, 120.9, 120.2, 115.2, 62.7, 58.7, 57.8, 56.6, 28.2. HRMS (ESI) calcd. for C$_{20}$H$_{20}$NO$_4$ [M]$^+$ 338.1387, found 338.1388.

20. Red powder (75.3% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 8.79 (d, $J = 8.7$ Hz, 1H), 8.61 (d, $J = 7.1$ Hz, 1H), 8.48 (d, $J = 7.6$ Hz, 1H), 8.42 (d, $J = 7.0$ Hz, 1H), 7.91 (t, $J = 8.2$ Hz, 1H), 7.56 (s, 1H), 7.06 (s, 1H), 4.75 (t, $J = 8.0$ Hz, 2H), 3.98 (s, 3H), 3.22 (t, $J = 8.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 156.0, 155.6, 149.7, 141.2, 140.2, 138.1, 136.4, 133.3, 132.6, 129.0, 124.0, 123.2, 119.3, 118.4, 117.0, 57.9, 56.9, 28.2. HRMS (ESI) calcd. for C$_{18}$H$_{17}$BrNO$_2$ [M]$^+$ 356.0281, found 356.0280.
**Controlled reaction in the absence of oxygen**

![Chemical structure](image)

To an oven dried Schlenk tube equipped with a stir-bar in the glovebox, pyridinium 1 (0.20 mmol, 70 mg) and Na₂CO₃ (0.24 mmol, 25 mg) were added. Dry MeOH (8 mL) was added to the mixture by syringe. The Schlenk tube was moved out of the glove box and stirred at 50 °C for 2 h. After 2 hours, pyridinium 1 was completely consumed (monitored by TLC). The reaction solution was concentrated in vacuum to give the residue, which was subjected to flash chromatographic column (dichloromethane/methanol = 20:1 to 10:1) to afford coupling product 2 (34 mg, 48.8% yield) as an orange powder and 1,4-dihydropyridine 21 (25 mg, 45.9% yield) as a yellow oil.

**Compound 21:** ¹H NMR (400 MHz, CD₃OD) δ 6.90 (s, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.72 (d, J = 1.8 Hz, 1H), 6.67 (dd, J = 8.1, 1.8 Hz, 1H), 5.86 (d, J = 8.1 Hz, 1H), 4.95 (m, 1H), 3.81 (s, 3H), 3.44 (t, J = 6.6 Hz, 2H), 2.93 (d, J = 1.2 Hz, 2H), 2.74 (t, J = 6.6 Hz, 2H), 1.96 (s, 3H). ¹³C NMR (100 MHz, CD₃OD) δ 198.5, 148.7, 148.7, 148.6, 133.2, 129.7, 122.4, 118.2, 113.8, 109.3, 109.1, 57.7, 57.3, 37.4, 24.2, 23.1. HRMS (ESI) calcd. for C₁₉H₁₇NO₃ ([M+H]+) 274.1438, found 274.1441.

**Hydrogen transfer trapping experiment**

![Chemical structure](image)

A flame-dried, round-bottom flask was charged with pyridinium 1 (0.2 mmol, 70 mg), Na₂CO₃ (0.3 mmol, 32 mg), and pyridinium 22 (0.4 mmol, 105 mg) in dry MeOH (8 mL). The reaction mixture was allowed to be vacuumed and purged with argon-blowing for 20 min. After stirring for 12 h at 50 °C, the reaction mixture was concentrated in vacuum. The residue was subjected to flash chromatographic column (dichloromethane/methanol = 20:1 to 15:1 to 10:1) to afford dehydrogenation coupling product 2 (16 mg, 23.0% yield) as an orange powder, 1,4-dihydropyridine 21 (4 mg, 7.3% yield) as a yellow oil, and another 1,4-dihydropyridine 23 (4 mg, 14.6% yield) as a yellow oil.

**Compound 23:** ¹H NMR (400 MHz, CDCl₃) δ 6.89 (s, 1H), 5.66 (d, J = 7.9 Hz, 1H), 4.89 (m, 1H), 3.05 (brs, 2H), 2.99 (s, 3H), 2.15 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 195.0, 144.1, 128.7, 109.0, 106.9, 41.2, 24.1, 21.4. HRMS (ESI) calcd. for C₈H₁₂NO ([M+H]+) 138.0913, found 138.0911.
Dynamic NMR experiment

To an oven dried 25mL of round-bottom flask were added pyridinium 1 (0.1 mmol, 35 mg) and Na$_2$CO$_3$ (0.12 mmol, 13 mg) in the glovebox. Methanol (10 mL) was also added by syringe. Then, the sealed round-bottom flask was moved out of the glove box and stirred at 50 °C for 2 h. 1 mL of this reaction solution was taken out respectively at different time points (0 min, 15 min, 45 min, 90 min, and 120 min) and was concentrated in vacuum to give the residue which was immediately dissolved in CD$_3$OD to perform $^1$H NMR experiments. The NMR analysis showed that in the meantime consumption of pyridinium 1, equal amounts of coupling product 2 and 1,4-dihydropyridine 21 appeared simultaneously.
Deuterium labeling experiment

To a solution of protected 2-bromopyridine 21a (12.0 g, 49.6 mmol) in dry THF (100 mL) was added dropwise a solution of n-BuLi (23.0 mL, 2.4 M solution in hexanes, 55.2 mmol) at −78 °C under argon atmosphere. The mixture was stirred for an additional 1 h. D$_2$O (99.8%, 11.3 mL, 500 mmol) was then added dropwise at −78 °C. The reaction mixture was stirred for another 1 h at room temperature. Then 150 mL of 4 mol/L HCl was added to the reaction mixture. The result solution was warmed to 80 °C for 1 h. The mixture was cooled to 0 °C and saturated sodium bicarbonate solution was slowly added to bring the pH of the solution to ~7 and the resulting solution was extracted with ethyl acetate (3 × 150 mL). The combined organic phases were washed with brine (200 mL) and dried over Na$_2$SO$_4$. The solvents were removed under reduced pressure and the crude mixture was then purified by flash chromatography over silica gel (petroleum ether/ethyl acetate = 2:1) to afford 3.98 g (66% over 2 steps) of deuterated pyridine 21b as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 9.14 (s, 1H), 8.20 (dd, $J$ = 8.0, 2.1 Hz, 1H), 7.40 (d, $J$ = 7.9 Hz, 1H), 2.61 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.8, 150.0, 135.56, 132.4, 123.6, 26.81. HRMS (ESI) calcd. for C$_7$H$_7$DNO ([M+H]$^+$) 123.0663, found 123.0665.

A suspension of phenylethyl bromide 1a (231 mg, 1.0 mmol) and deuterated pyridine 21b (363 mg, 3.0 mmol) was stirred at 70 °C without solvents for 3 h. The mixture was cooled to room temperature. The solid was collected by filtration and washed with Et$_2$O (3 × 20 mL) then petroleum ether (3 × 20 mL). The residue yellow solid was dried at 40°C in vacuum to yield pyridinium 1-[D] (342 mg, 0.97 mmol, 97.2% yield) as a yellow powder. $^1$H NMR (300 MHz, D$_2$O) δ 8.95 (d, $J$ = 8.0 Hz, 1H), 8.87 (s, 1H), 8.12 (d, $J$ = 8.0 Hz, 1H), 6.89 (d, $J$ = 8.2 Hz, 1H), 6.54 (br, 2H), 4.91 (t, $J$ = 6.0 Hz, 2H), 3.81 (s, 3H), 3.22 (t, $J$ = 5.8 Hz, 2H), 2.62 (s, 3H). $^{13}$C NMR (75 MHz, D$_2$O) δ 196.1, 146.8, 145.2, 144.6, 135.2, 128.3, 128.2,
121.3, 115.8, 112.9, 63.5, 55.9, 35.9, 26.3. HRMS (ESI) calcd. for C_{16}H_{17}DNO_{3} [M]^+ 273.1344, found 273.1349.

To an oven dried Schlenk tube equipped with a stir-bar, 1-[D] (0.20 mmol, 70 mg), Na_{2}CO_{3} (0.24 mmol, 25 mg) were added in the glovebox. Dry MeOH (8 mL) was added to the mixture by injection syringe in the glove box. The result solution was stirred for 2 h in the glove box at 50 °C. The schlenk tube was moved out of the glove box and the reaction mixture was concentrated in vacuum to give the residue, which was subjected to flash chromatographic column (dichloromethane/methanol = 20:1 to 10:1) to afford coupling product 2 (32 mg, 46.6% yield) as an orange powder and 1,4-dihydropyridine 21-[D] (23 mg, 42.2% yield) as a yellow oil. Compound 21-[D]: \^1H NMR (400 MHz, CD_{3}OD) \(\delta\) 6.90 (s, 1H), 6.84 (d, \(J = 8.1 \text{ Hz, } 1\text{H}\)), 6.74 (dd, \(J = 8.1, 2.0 \text{ Hz, } 1\text{H}\)), 4.94 (m, 1H), 3.80 (s, 3H), 3.44 (t, \(J = 6.6 \text{ Hz, } 2\text{H}\)), 2.92 (m, 1H), 2.73 (t, \(J = 6.6 \text{ Hz, } 2\text{H}\)), 1.96 (s, 3H). \(^{13}\text{C} \) NMR (100 MHz, MeOD) \(\delta\) 198.51, 148.74, 148.65, 148.62, 133.25, 122.38, 118.17, 113.81, 109.14, 109.04, 57.69, 57.34, 37.40, 24.22, 23.05. HRMS (ESI) calcd. for C_{16}H_{19}DNO_{3} ([M+H]^+) 275.1500, found 275.1508.

Aromatization of 1,4-dihydropyridine 3

A solution of 3 (55 mg, 0.2 mmol) and HBr (0.25 mmol) in MeOH (6 mL) was stirred at 50°C under oxygen atmosphere for 2 h. The reaction mixture was concentrated in vacuum to give the residue, which was subjected to flash chromatographic column (dichloromethane/methanol = 5:1) to afford pyridinium 1 (52 mg, 73.5% yield).
Copies of $^1$H NMR and $^{13}$C NMR spectra

![NMR Spectra](image-url)
19F NMR (376 MHz, D2O)
$^{19}$F NMR (376 MHz, D$_2$O)
$^{19}$F NMR (376 MHz, CD$_3$OD)
HO
MeO
11

HO
MeO
11
\[ ^{19}\text{F} \text{NMR (376 MHz, CD}_3\text{OD)} \]