Selectfluor-induced C(sp²)-O Coupling Reaction of N-substituted Anilines with Hydroxylamine Derivatives

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1. General and Experimental Information

Melting points were determined using a digital melting point apparatus and uncorrected. $^1$H NMR spectra were recorded at 400, 500 and 600MHz using TMS as internal standard, $^{13}$C NMR spectra were recorded at 100, 125 and 150 MHz using TMS as internal standard. All chemical shifts were reported as $\delta$ values (ppm) relative to TMS and observed coupling constants ($J$) are given in Hertz (Hz). Mass spectra were measured with a HRMS-ESI instrument. All chemical reagents were purchased from commercial source and without prior purification. Column Chromatography was performed on silica gel (200-300 mesh) and the elution was performed with $n$-hexane/ethyl acetate.

(i) General Procedure for the synthesis of 2a-2s2, 6ab-6gb (2a as example):

A suspension of N-substituted anilines 1a (0.5 mmol), NHPI (0.6 mmol) and Selectfluor (1.0 mmol) in CH$_3$CN was stirred at 40 °C for 2 h. After cooling, water (10 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and then concentrated under reduced pressure. The residues were purified by flash column chromatography ($n$-hexane-EtOAc) to afford the desired product 2a.

(ii) General Procedure for the Synthesis of 2t’-2z3’ (2t’ as example)

A suspension of 2t (Prepared according to (i)), NH$_2$OH·HCl (1.5 mmol) and K$_2$CO$_3$ (1.5 mmol) in MeOH:CHCl$_3$(1:2)(6 mL) was stirred at 25 °C for 16 h. When the reaction was finished, water (10 mL) was added and the mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and then Ac$_2$O (3.0 mmol), DMAP (0.05 mmol) was added. After being stirred for 2 h at 25 °C, the organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ($n$-hexane-EtOAc) to afford the desired product 2t’.
2、Characterization Data for the products

2a: white solid; yield 85% (138 mg); m.p. 152.8-153.6 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.96-7.93\) (m, 2H), 7.88-7.85 (m, 2H), 7.16 (d, \(J = 7.8\) Hz, 1H), 6.99 (d, \(J = 7.8\) Hz, 1H), 6.84 (s, 1H), 3.33 (s, 3H), 2.33 (s, 3H), 2.02 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 171.5, 162.6, 153.7, 140.2, 135.1, 129.3, 128.9, 128.8, 125.7, 124.1, 113.7, 36.2, 22.0, 21.5\). HRMS: C\(_{18}\)H\(_{17}\)N\(_2\)O\(_4\) [M+H]\(^+\); calculated: 325.1183, found: 325.1183.

2b: white solid; yield 65% (112 mg); m.p. 176.2-176.6 °C; \(^1\)H NMR (600 MHz, DMSO-\(d^6\)): \(\delta 7.98-7.90\) (m, 4H), 7.85 (s, 1H), 7.54 (d, \(J = 8.4\) Hz, 1H), 7.32 (d, \(J = 7.8\) Hz, 1H), 3.16 (s, 3H), 1.88 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 169.9, 163.3, 154.9, 135.4, 134.5, 131.8, 129.9, 129.7, 125.4, 124.1, 114.6, 35.9, 22.2\). HRMS: C\(_{17}\)H\(_{13}\)N\(_2\)O\(_4\)ClNa [M+Na]\(^+\); calculated: 367.0456, found: 367.0453.

2c: white solid; yield 60% (116 mg); m.p. 174.0-174.5 °C; \(^1\)H NMR (500 MHz, DMSO-\(d^6\)): \(\delta 8.16-7.73\) (m, 5H), 7.46 (s, 2H), 3.15 (s, 3H), 1.88 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 169.9, 163.4, 154.9, 135.4, 132.1, 130.3, 129.8, 128.4, 124.1, 122.6, 117.2, 35.8, 22.2\). HRMS: C\(_{17}\)H\(_{13}\)N\(_2\)O\(_4\)BrNa [M+Na]\(^+\); calculated: 410.9951, found: 410.9938.
**2d**: white solid; yield 77% (130 mg); m.p. 160.4-160.9 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.97-7.94 (m, 2H), 7.88-7.86 (m, 2H), 7.19 (d, $J$ = 7.8 Hz, 1H), 7.02 (d, $J$ = 7.8, 1H), 6.86 (s, 1H), 3.34 (s, 3H), 2.62 (q, $J$ = 7.8 Hz, 2H), 2.03 (s, 3H), 1.21 (t, $J$ = 7.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.5, 162.7, 153.9, 146.5, 135.1, 129.4, 129.1, 128.8, 124.3, 124.1, 112.7, 36.2, 28.7, 22.0, 15.2. HRMS: C$_{19}$H$_{18}$N$_2$NaO$_4$[M+Na]$^+$; calculated: 361.1159, found: 361.1156.

**2e**: white solid; yield 72% (132 mg); m.p. 166.3-167.1 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.98-7.95 (m, 2H), 7.89-7.86 (m, 2H), 7.22-7.19 (m, 2H), 7.05 (s, 1H), 3.35 (s, 3H), 2.03 (s, 3H), 1.28 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.5, 162.9, 153.6, 153.5, 135.1, 129.0, 128.8, 124.1, 122.2, 110.6, 36.2, 35.0, 31.2, 22.1. HRMS: C$_{21}$H$_{22}$N$_2$NaO$_4$[M+Na]$^+$; calculated: 389.1472, found: 389.1469.

**2f**: white solid; yield 75% (132 mg); m.p. 145.8-146.4 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.96-7.94 (m, 2H), 7.88-7.86 (m, 2H), 7.20 (d, $J$ = 7.8 Hz, 1H), 7.05 (d, $J$ = 7.8 Hz, 1H), 6.87 (s, 1H), 3.34 (s, 3H), 2.90-2.83 (m, 1H),
2.03 (s, 3H), 1.21 (d, \( J = 7.2 \) Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 171.6, 162.8, 153.8, 151.1, 135.1, 129.4, 129.1, 128.8, 124.1, 122.7, 111.6, 36.2, 34.1, 23.8, 22.1. HRMS: C\(_{20}\)H\(_{20}\)N\(_2\)NaO\(_4\)[M+Na]\(^+\); calculated: 375.1315, found: 375.1305.

![2g](image)

**2g**: white solid; yield 80% (154 mg); m.p. 174.5-175.6 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta \) 7.97-7.94 (m, 2H), 7.88-7.85 (m, 2H), 7.51-7.49 (m, 2H), 7.43-7.35 (m, 5H), 7.22 (s, 1H), 3.40 (s, 3H), 2.10 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 171.4, 162.7, 154.3, 143.2, 139.4, 135.2, 130.6, 130.0, 128.9, 128.8, 128.2, 127.2, 124.2, 123.8, 112.1, 36.2, 22.2. HRMS: C\(_{23}\)H\(_{18}\)N\(_2\)NaO\(_4\)[M+Na]\(^+\); calculated: 409.1159, found: 409.1140.

![2h](image)

**2h**: white solid; yield 35% (68 mg); m.p. 171.2-172.0 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.99-7.93 (m, 4H), 7.82 (s, 1H), 7.57 (d, \( J = 7.6 \) Hz, 1H), 7.51 (d, \( J = 8.8 \) Hz, 1H), 3.20 (s, 3H), 1.92 (s, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 169.8, 163.1, 153.8, 135.6, 133.0, 132.9, 132.4, 129.3, 124.2, 116.2, 35.9, 22.2. HRMS: C\(_{17}\)H\(_{13}\)BrN\(_2\)NaO\(_4\)[M+Na]\(^+\); calculated: 410.9951, found: 410.9951.

![2i](image)

**2i**
2i: white solid; yield 31% (53 mg); m.p. 174.0-175.0 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99-7.94 (m, 4H), 7.71 (s, 1H), 7.58 (d, $J = 9.2$ Hz, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 3.20 (s, 3H), 1.92 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.8, 163.1, 153.4, 135.6, 132.2, 130.3, 130.0, 129.3, 128.6, 124.2, 115.9, 35.9, 22.2. HRMS: C$_{17}$H$_{13}$ClN$_2$NaO$_4$[M+Na]$^+$; calculated: 367.0456, found: 367.0441.

![2i](image)

2j: white solid; yield 39% (63 mg); m.p. 153.0-154.0 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.93-7.90 (m, 2H), 7.86-7.82 (m, 2H), 7.09-7.08 (m, 2H), 6.94 (d, $J = 9.0$ Hz, 1H), 3.33 (s, 3H), 2.34 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.3, 162.6, 152.6, 135.1, 135.0, 131.3, 130.0, 129.9, 128.8, 124.0, 113.4, 36.2, 22.0, 20.5. HRMS: C$_{18}$H$_{17}$N$_2$O$_4$[M+H]$^+$; calculated: 325.1183, found: 325.1181.

![2j](image)

2k: white solid; yield 43% (67 mg); m.p. 153.7-154.3 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.95-7.93 (m, 2H), 7.87-7.85 (m, 2H), 7.33-7.28 (m, 2H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 3.36 (s, 3H), 2.03 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.3, 162.6, 154.2, 135.1, 131.6, 129.8, 129.6, 128.7, 125.1, 124.1, 113.3, 36.1, 22.0. HRMS: C$_{17}$H$_{15}$N$_2$O$_4$[M+H]$^+$; calculated: 311.1026, found: 311.1030.

![2k](image)

2k': white solid; yield 23% (54 mg); m.p. 186.7-187.0 °C; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.98-7.93 (m, 4H), 7.89-7.84 (m, 4H), 7.25 (d, $J = 6.0$ Hz,
1H), 7.04 (d, J = 2.4 Hz, 1H), 6.90 (d, J = 4.8 Hz, 1H), 3.33 (s, 3H), 2.04 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.5, 162.7, 162.4, 159.1, 155.2, 135.3, 135.2, 130.7, 128.8, 128.7, 128.1, 124.3, 124.2, 109.3, 101.6, 36.2, 22.1. HRMS: C$_{25}$H$_{18}$N$_3$O$_7$[M+H]$^+$; calculated: 472.1139, found: 472.1130.

![Diagram](image1)

(2l)

2l: white solid; yield 41% (77 mg); m.p. 178.5-179.2 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.95-7.92 (m, 2H), 7.88-7.84 (m, 2H), 7.34-7.27 (m, 2H), 7.18 (t, J = 11.4 Hz, 1H), 7.03 (d, J = 12.6 Hz, 1H), 3.34 (s, 3H), 2.33-2.26 (m, 1H), 1.92-1.89 (m, 1H), 1.76-1.48 (m, 6H), 1.24-1.19 (m, 2H), 1.07-0.98 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 177.1, 162.5, 154.1, 135.1, 130.9, 129.9, 129.4, 128.8, 124.7, 124.1, 112.5, 41.6, 36.2, 29.9, 29.0, 25.7, 25.4. HRMS: C$_{22}$H$_{22}$N$_2$NaO$_4$ [M+Na]$^+$; calculated: 401.1472, found: 401.1491.

![Diagram](image2)

(2l')

2l': white solid; yield 24% (65 mg); m.p. 142.0-143.1 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.97-7.92 (m, 4H), 7.89-7.84 (m, 4H), 7.22 (d, J = 13.2 Hz, 1H), 7.01 (d, J = 6.3 Hz, 1H), 6.88 (dd, J$_1$ = 13.2 Hz, J$_2$ = 6.3 Hz, 1H), 3.30 (s, 3H), 2.31-2.27 (m, 1H), 1.78-1.76 (m, 1H), 1.59-1.47 (m, 5H), 1.24-1.08 (m, 2H), 0.92-0.89 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 177.2, 162.7, 162.3, 159.0, 155.1, 135.3, 135.2, 130.7, 128.8, 128.6, 127.4, 124.3, 124.2, 108.8, 101.0, 41.4, 36.4, 29.9, 29.0, 25.7, 25.6, 25.3. HRMS: C$_{30}$H$_{25}$N$_3$NaO$_7$ [M+Na]$^+$; calculated: 562.1585, found: 562.1577.

![Diagram](image3)

(2m)

2m: white solid; yield 71% (120 mg); m.p. 151.4-151.7 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.97-7.94 (m, 2H), 7.89-7.86 (m, 2H), 7.12 (d, J = 8.4 Hz,
1H), 6.98 (d, J = 7.8 Hz, 1H), 6.82 (s, 1H), 3.97-3.92 (m, 1H), 3.76-3.70 (m, 1H), 2.34 (s, 3H), 2.02 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.1, 162.6, 153.9, 140.2, 135.1, 130.4, 128.8, 127.0, 125.3, 124.1, 113.0, 43.2, 22.4, 21.4, 13.1. HRMS: C$_{19}$H$_{19}$N$_2$O$_4$ [M+H]$^+$; calculated: 339.1339, found: 339.1348.

$^{2n}$: white solid; yield 81% (148 mg); m.p. 144.5-145.0 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.94-7.93 (m, 2H), 7.87-7.85 (m, 2H), 7.11 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 3.94-3.89 (m, 1H), 3.64-3.59 (m, 1H), 2.32 (s, 3H), 2.01 (s, 3H), 1.62-1.54 (m, 2H), 1.40-1.33 (m, 2H), 0.93 (t, J = 7.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.2, 162.6, 153.9, 140.1, 135.1, 130.4, 128.8, 127.4, 125.3, 124.1, 113.0, 48.1, 30.0, 22.4, 21.5, 20.2, 13.9. HRMS: C$_{21}$H$_{23}$N$_2$O$_4$ [M+H]$^+$; calculated: 367.1652, found: 367.1660.

$^{2o}$: white solid; yield 74% (125 mg); m.p. 164.3-165.0 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.97-7.94 (m, 2H), 7.88-7.85 (m, 2H), 7.14 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.84 (s, 1H), 3.34 (s, 3H), 2.37-2.31 (m, 4H), 2.20-2.14 (m, 1H), 1.13 (t, J = 7.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 174.7, 162.6, 153.8, 140.1, 135.1, 129.6, 128.8, 128.5, 125.6, 124.1, 113.6, 36.2, 27.1, 21.5, 9.5. HRMS: C$_{19}$H$_{18}$N$_2$O$_4$Na [M+Na]$^+$; calculated: 361.1159, found: 361.1153.

$^{2p}$: white solid; yield 84% (148 mg); m.p. 180.5-181.0 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.93-7.91 (m, 2H), 7.85-7.83 (m, 2H), 7.13 (d, J = 8.0 Hz,
1H), 6.98 (d, J = 7.5 Hz, 1H), 6.80 (s, 1H), 3.31 (s, 3H), 2.63-2.58 (m, 1H), 2.31 (s, 3H), 1.14 (d, J = 6.5 Hz, 3H), 1.05 (d, J = 6.5 Hz, 3H). ^13^C NMR (125 MHz, CDCl$_3$) δ 178.1, 162.5, 153.7, 140.0, 135.1, 129.5, 128.7, 128.2, 125.4, 124.0, 113.1, 36.2, 31.2, 21.4, 20.0, 19.4. HRMS: C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$; calculated: 353.1496, found: 353.1497.

(2q)

2q: white solid; yield 88% (155 mg); m.p. 169.0-169.5 °C; ^1H NMR (500 MHz, CDCl$_3$): δ 7.95-7.92 (m, 2H), 7.87-7.83 (m, 2H), 7.12 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.82 (s, 1H), 3.32 (s, 3H), 2.32-2.25 (m, 4H), 2.15-2.09 (m, 1H), 1.72-1.61 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H). ^13^C NMR (125 MHz, CDCl$_3$) δ 173.9, 162.6, 153.7, 140.1, 135.1, 129.6, 128.8, 128.5, 125.5, 124.1, 113.5, 36.1, 35.6, 21.5, 18.6, 13.9. HRMS: C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$; calculated: 353.1496, found: 353.1497.

(2r)

2r: white solid; yield 76% (149 mg); m.p. 170.0-170.5 °C; ^1H NMR (600 MHz, CDCl$_3$): δ 7.95-7.93 (m, 2H), 7.86-7.85 (m, 2H), 7.13 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 3.31 (s, 3H), 2.34-2.29 (m, 4H), 1.90-1.88 (m, 1H), 1.76-1.46 (m, 6H), 1.23-1.20 (m, 2H), 1.06-1.00 (m, 1H). ^13^C NMR (150 MHz, CDCl$_3$) δ 177.2, 162.6, 153.7, 140.0, 135.1, 129.5, 128.8, 128.3, 125.4, 124.1, 113.0, 41.5, 36.3, 29.9, 29.0, 25.8, 25.7, 25.4, 21.5. HRMS: C$_{20}$H$_{25}$N$_2$O$_4$ [M+H]$^+$; calculated: 393.1809, found: 393.1823.

(2s1)

2s1: white solid; yield 65% (121 mg); m.p. 129.1-129.9 °C; ^1H NMR (500 MHz, CDCl$_3$): δ 7.98-7.94 (m, 2H), 7.90-7.86 (m, 2H), 7.42 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.80 (s, 1H), 3.31 (s, 3H), 2.63-2.58 (m, 1H), 2.31 (s, 3H), 1.14 (d, J = 6.5 Hz, 3H), 1.05 (d, J = 6.5 Hz, 3H). ^13^C NMR (125 MHz, CDCl$_3$) δ 178.1, 162.5, 153.7, 140.0, 135.1, 129.5, 128.7, 128.2, 125.4, 124.0, 113.1, 36.2, 31.2, 21.4, 20.0, 19.4. HRMS: C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$; calculated: 353.1496, found: 353.1497.
1H), 6.95 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H), 3.44 (s, 3H), 3.27 (q, J = 7.5 Hz, 2H), 2.29 (s, 3H), 1.43 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.6, 154.5, 140.4, 135.2, 132.9, 128.7, 125.4, 124.5, 124.2, 112.6, 46.2, 38.5, 21.4, 8.1. HRMS: C$_{18}$H$_{19}$N$_2$O$_5$S [M+H]$^+$; calculated: 375.1009, found: 375.1007.

![Image](2s2)

**2s2**: white solid; yield 70% (136 mg); m.p. 136.3-137.0 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 8.00-7.97 (m, 2H), 7.91-7.88 (m, 2H), 7.43 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 6.76 (s, 1H), 3.45 (s, 3H), 3.25-3.22 (m, 2H), 2.31 (s, 3H), 1.98-1.91 (m, 2H), 1.07 (t, J = 7.8 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 162.6, 154.6, 140.5, 135.2, 133.0, 128.8, 125.4, 124.6, 124.2, 112.5, 53.4, 38.3, 21.5, 17.1, 13.1. HRMS: C$_{19}$H$_{21}$N$_2$O$_5$S [M+H]$^+$; calculated: 389.1166, found: 389.1180.

![Image](2t')

**2t'**: white solid; yield 85% (145 mg); m.p. 134.2-134.8 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.49 (d, J = 7.2 Hz, 2H), 7.27-7.20 (m, 3H), 6.95 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.2 Hz, 1H), 6.51 (s, 1H), 3.48 (s, 3H), 2.38 (s, 6H), 2.28 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.1, 168.9, 152.2, 139.4, 135.7, 130.3, 129.8, 129.1, 128.5, 127.7, 124.8, 111.4, 37.4, 24.6, 21.5. HRMS: C$_{19}$H$_{21}$N$_2$O$_4$ [M+H]$^+$; calculated: 341.1496, found: 341.1498.

![Image](2u')

**2u'**: white solid; yield 76% (135 mg); m.p. 155.5-156.1 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.40 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 7.2 Hz, 1H), 6.76 (d, J = 7.2 Hz, 1H), 6.54 (s, 1H), 3.44 (s, 3H), 2.41 (s, 6H), 2.29 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.1, 169.0, 152.2,
140.0, 139.3, 132.7, 130.3, 129.4, 128.6, 128.3, 124.8, 111.3, 37.5, 24.6, 21.5, 21.3. HRMS: C_{20}H_{23}N_{2}O_{4} [M+H]^+; calculated: 355.1652, found: 355.1654.

![2v']

2v': white solid; yield 60% (107 mg); m.p. 134.3-134.9 °C; 'H NMR (600 MHz, CDCl₃): δ 7.54-7.52 (m, 2H), 6.91-6.88 (m, 3H), 6.77 (d, J = 7.8 Hz, 1H), 6.54 (s, 1H), 3.45 (s, 3H), 2.41 (s, 6H), 2.29 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.2, 168.8, 163.4 (d, J_{C-F} = 248.7 Hz), 152.2, 139.7, 131.7, 130.9 (d, J_{C-F} = 8.4 Hz), 130.2, 129.0, 124.9, 114.8 (d, J_{C-F} = 21.6 Hz), 111.5, 37.6, 24.7, 21.5. HRMS: C_{19}H_{22}FN_{2}O_{4} [M+H]^+; calculated: 359.1402, found: 359.1397.

![2w']

2w': white solid; yield 74% (138 mg); m.p. 152.8-153.2 °C; 'H NMR (600 MHz, CDCl₃): δ 7.46 (d, J = 7.2 Hz, 2H), 7.18 (d, J = 6.6 Hz, 2H), 6.89 (d, J = 6.6 Hz, 1H), 6.76 (d, J = 6.6 Hz, 1H), 6.54 (s, 1H), 3.44 (s, 3H), 2.40 (s, 6H), 2.29 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.1, 168.8, 152.2, 139.8, 135.9, 134.0, 130.2, 130.0, 128.8, 128.0, 125.0, 111.5, 37.6, 24.7, 21.5. HRMS: C_{19}H_{20}FN_{2}O_{4}Cl [M+H]^+; calculated: 375.1106, found: 375.1102.

![2x']

2x': white solid; yield 69% (144 mg); m.p. 159.8-160.2 °C; 'H NMR (600 MHz, CDCl₃): δ 7.40 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.54 (s, 1H), 3.45 (s, 3H), 2.42 (s, 6H), 2.30 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.2, 168.8, 152.2, 139.8, 134.5, 131.0, 130.2, 128.8, 125.0, 124.3, 111.5, 37.5, 24.7, 21.6.
HRMS: C_{19}H_{20}N_{2}O_{4}Br [M+H]^+; calculated: 419.0601, found: 419.0611.

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\begin{align*}
\text{2y’} & : \text{white solid; yield 85\% (150 mg); m.p. 124.4-124.8 } ^\circ \text{C; } ^1\text{H NMR (600 MHz, CDCl}_3\text{): } \delta 7.33 \text{ (s, 1H), 7.19 \text{ (s, 1H), 7.03 \text{ (s, 2H), 6.92 (d, } J = 6.0 \text{ Hz, 1H), 6.73 \text{ (d, } J = 6.0 \text{ Hz, 1H), 6.50 \text{ (s, 1H), 3.45 (s, 3H), 2.36 (s, 6H), 2.25 (s, 3H), 2.23 (s, 3H). } ^{13}\text{C NMR (150 MHz, CDCl}_3\text{): } \delta 171.3, 168.9, 152.2, 139.3, 137.4, 135.6, 130.5, 130.3, 129.2, 127.4, 125.5, 124.8, 111.3, 37.3, 24.6, 21.5, 21.1. } HRMS: C_{20}H_{23}N_{2}O_{4} [M+H]^+; calculated: 355.1652, found: 355.1657.
\end{align*}
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\begin{align*}
\text{2z1’} & : \text{white solid; yield 67\% (137 mg); m.p. 150.8-151.4 } ^\circ \text{C; } ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.75 \text{ (d, } J = 8.5 \text{ Hz, 2H), 7.50 \text{ (d, } J = 8.5 \text{ Hz, 2H), 6.92 \text{ (d, } J = 8.0 \text{ Hz, 1H), 6.84 \text{ (d, } J = 8.0 \text{ Hz, 1H), 6.59 \text{ (s, 1H), 3.29 (s, 3H), 2.41 (s, 6H), 2.33 (s, 3H). } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{): } \delta 154.7, 140.7, 139.1, 138.2, 130.1, 129.3, 129.0, 124.7, 124.5, 111.6, 38.3, 24.7, 21.6. } HRMS: C_{18}H_{19}N_{2}O_{5}ClSNa [M+Na]^+; calculated: 433.0595, found: 433.0588.
\end{align*}
\]

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\begin{align*}
\text{2z2’} & : \text{white solid; yield 65\% (144 mg); m.p. 143.0-144.0 } ^\circ \text{C; } ^1\text{H NMR (600 MHz, CDCl}_3\text{): } \delta 7.96 \text{ (d, } J = 7.8 \text{ Hz, 2H), 7.80 \text{ (d, } J = 8.4 \text{ Hz, 2H), 6.95 \text{ (d, } J = 8.4 \text{ Hz, 1H), 6.86 \text{ (d, } J = 7.8 \text{ Hz, 1H), 6.61 \text{ (s, 1H), 3.34 (s, 3H), 2.40 (s, 6H), 2.35 (s, 3H). } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{): } \delta 154.6, 143.3, 140.8, 134.3 \text{ (q, } J_{C-F} = 32.9 \text{ Hz), 130.3, 128.0, 126.2 \text{ (q, } J_{C-F} = 3.6 \text{ Hz), 124.6, 124.4, 123.3 \text{ (d, } J_{C-F} = 271.4 \text{ Hz), 111.7, 38.4, 24.6, 21.6. } HRMS: C_{19}H_{19}F_{3}N_{2}O_{5}SNa [M+Na]^+; calculated: 467.0859, found: 467.0874.
\end{align*}
\]
2z3': white solid; yield 76% (148 mg); m.p. 148.4-149.1 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.71 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.59 (s, 1H), 3.28 (s, 3H), 2.46 (s, 3H), 2.42 (s, 6H), 2.33 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 169.5, 154.7, 143.4, 140.3, 136.7, 130.1, 129.6, 127.7, 125.2, 124.4, 111.5, 38.3, 24.7, 21.6, 21.5. HRMS: C₁₉H₂₂N₂O₅SNa [M+Na]⁺; calculated: 413.1142, found: 413.1129.

6ab: ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.85 (s, 2H), 6.82 (s, 1H), 3.27 (s, 3H), 2.36 (s, 3H), 1.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 164.9, 153.7, 140.2, 132.8, 129.3, 128.8, 125.7, 113.7, 36.2, 22.0, 21.5. HRMS: C₁₄H₁₄N₂NaO₄ [M+Na]⁺; calculated: 297.0850, found: 297.0850.

6fb: ¹H NMR (400 MHz, CDCl₃) δ 7.17 (d, J = 8.0 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.92-6.77 (m, 3H), 3.28 (s, 3H), 2.93-2.84 (m, 1H), 1.96 (s, 3H), 1.24 (d, J = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 165.0, 153.8, 151.1, 132.8, 129.4, 129.0, 122.8, 111.5, 36.2, 34.1, 23.8, 23.7, 22.0. HRMS: C₁₆H₁₈N₂NaO₄ [M+Na]⁺; calculated: 325.1148, found: 325.1159.

6gb: ¹H NMR (400 MHz, CDCl₃) δ 7.57–7.50 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.43–7.37 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 1.6 Hz, 1H),
6.86 (s, 2H), 3.34 (s, 3H), 2.03 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
171.4, 164.9, 154.3, 143.2, 139.5, 132.9, 130.5, 129.9, 129.0, 128.2, 127.2,
123.8, 112.1, 36.2, 22.1. HRMS: C$_{19}$H$_{16}$N$_2$NaO$_4$ [M+Na]$^+$; calculated:
359.1002, found: 359.0990.
Copies of NMR Spectra