Supplementary Information

Ruthenium polypyridyl complex-catalysed aryl alkoxylation of styrenes: Improving reactivity using a continuous-flow photo-microreactor

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Table of Contents

General information S1
General Procedure for aryl alkoxylation of olefins with Flow Microreactor S2
Preparation of aryldiazonium tetrafluoroborate S2
Picture S1. The glass chip during the reaction S3
Picture S2. The LEDs array S3
Picture S3. General reaction setup S3
Scheme S1. Reaction without Ru complex S4
Scheme S2. Reaction efficiency of the flow reaction compared with batch reaction S4
Figure S1. The wave length and spectral irradiance of LED S4
Characterization of prepared 3 and 4 S5
References S13
1H and 13C NMR Spectra of 3 and 4 S14
**General Information**

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received.

Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 mm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and ceric ammonium molybdate solution stain.

NMR spectra were recorded on a JEOL ECA 500 spectrometer (400 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR), and are internally referenced to residual protio solvent signals or TMS (note: CDCl$_3$ referenced at $\delta$ 7.26 and 77.0 ppm respectively, TMS referenced at $\delta$ 0 and 0 ppm respectively). Data for $^1$H NMR are reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets), coupling constant (Hz), integration, and assignment. Data for $^{13}$C NMR are reported in terms of chemical shifts ($\delta$ ppm).

IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$).

High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and are reported as m/z (M+H+, relative intensity).

Melting points were measured on a Yanagimoto micro melting point apparatus without correlation.

Glass (borosilicate glass) Chip for microreactor was from Dexerials Corporation.
General Procedure for aryldiazonium tetrafluoroborate

A solution of aryldiazonium tetrafluoroborate (0.35 mol/L) in MeCN and a solution of styrene (0.7 mol/L, 2.0 equiv) and Ru(bpy)$_3$Cl$_2$・6H$_2$O (1.75 x 10$^{-3}$ mol/L, 0.5 mol%) in MeOH were degassed via Freeze-Pump-Thaw (FPT) cycling for three times and backfilled with Ar. The two solutions were introduced into different channels respectively by using a syringe pump. Both streams were mixed in the channel of the reactor chip. Light (450 nm) from an LED array (sum: 1.20 W x 2) was used to irradiate the flow from a distance of 1.5 cm from the chip surface. The residue was filtrated through silica gel, washed with CHCl$_3$, concentrated in vacuo. The resulting mixture was purified by flash column chromatography on silica gel ($n$-hexane : EtOAc = 40 : 1) to give product.

General Procedure for aryldiazonium tetrafluoroborate

A solution of aryldiazonium tetrafluoroborate (0.35 mol/L) in MeCN and a solution of styrene (0.7 mol/L, 2.0 equiv) and Ru(bpy)$_3$Cl$_2$・6H$_2$O (1.75 x 10$^{-3}$ mol/L, 0.5 mol%) in DMF were degassed via Freeze-Pump-Thaw (FPT) cycling for three times and backfilled with Ar. The two solutions were introduced into different channels respectively by using a syringe pump. Both streams were mixed in the channel of the reactor chip. Light (450 nm) from an LED array (sum: 1.20 W x 2) was used to irradiate the flow from a distance of 1.5 cm from the chip surface. The residue was diluted with EtOAc, washed with water, dried with MgSO$_4$, and concentrated in vacuo. The resulting mixture was purified by flash column chromatography on silica gel ($n$-hexane : EtOAc = 40 : 1) to give product.

Preparation of aryldiazonium tetrafluoroborate

To a round-bottom flask, a solution of water (2.0 mL) and conc. HCl (2.0 mL) (1:1) was added to a mixture of aniline derivatives (10.0 mmol, 1.0 equiv) and conc. HCl (3.0 mL) at 0 °C. To this solution, a solution of NaNO$_2$ (1.1 equiv) in 1.5 mL of water was added dropwise and stirred for 30 min at 0 °C. After that, an ice cold solution of 45% aq. HBF$_4$ (10 mL) was added slowly to the reaction mixture and stirred for 15 min at 0 °C. The resulting solid precipitate was filtered and washed with ice cold water, dried under a vacuum desiccator, and stored at freezer.
Picture S1. The glass chip during the reaction

Picture S2. Picture for LEDs array (40 mm x 65 mm; 0.05 W x 4 x 6; 450 nm)

Picture S3. General reaction setup
Scheme S1. Reaction without Ru complex

![Scheme S1](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>yield (%)</th>
<th>The reaction with Ru cat.; yield (%)</th>
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<tr>
<td>1</td>
<td>p-cyano</td>
<td>71</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>p-nitro</td>
<td>&lt;10</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>p-methoxy</td>
<td>n.d.</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>p-methyl</td>
<td>n.d.</td>
<td>41</td>
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Scheme S2. Reaction efficiency of the flow reaction compared with batch reaction

![Scheme S2](image)

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<th>conc. (mol/L)</th>
<th>2 conc. (mol/L)</th>
<th>3</th>
<th>yieldflow (%)</th>
<th>STY (g h⁻¹L⁻¹)</th>
<th>yieldbatch (%)</th>
<th>STY (g h⁻¹L⁻¹)</th>
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<td>4-CNC₆H₄</td>
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<td>3aa</td>
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<td>46</td>
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<tr>
<td>2</td>
<td>1b</td>
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<td>0.70</td>
<td>3ba</td>
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<td>42</td>
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<tr>
<td>3</td>
<td>1c</td>
<td>4-BuC₆H₄</td>
<td>0.35</td>
<td>0.70</td>
<td>3ca</td>
<td>40</td>
<td>147</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>4-MeOC₆H₄</td>
<td>0.35</td>
<td>0.70</td>
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<td>192.8</td>
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Figure S1. The wave length and spectral irradiance of LED

![Figure S1](image)
4-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (3aa)

78% yield, 80 mg, 0.27 mmol (based on 0.35 mmol scale)
Yellow oil
**TLC (SiO$_2$)**: $R_f = 0.36$ (n-hexane:ethyl acetate =10:1).

$^1$H NMR: (400 MHz, CDCl$_3$): $\delta$ 7.53 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.15 (d, $J = 8.7$ Hz, 2H), 4.29 (dd, $J = 8.2$ Hz, 5.0 Hz, 1H), 3.16 (s, 3H), 3.11 (dd, $J = 13.7$ Hz, 8.2 Hz, 1H), 2.93 (dd, $J = 13.7$ Hz, 5.0 Hz, 1H), 1.32 (s, 9H).

$^{13}$C NMR: (100 MHz, CDCl$_3$): $\delta$ 150.9, 144.5, 137.8, 131.8, 130.2, 126.3, 125.3, 119.1, 110.0, 83.9, 56.7, 44.8, 34.5, 31.3.

4-[2-Methoxy-2-(4-methylphenyl)ethyl]benzonitrile (3ab)

69% yield, 61 mg, 0.24 mmol (based on 0.35 mmol scale)
White solid
**TLC (SiO$_2$)**: $R_f = 0.22$ (n-hexane:ethyl acetate =10:1).

m.p.: 70.2-71.9 ºC

$^1$H NMR: (400 MHz, CDCl$_3$): $\delta$ 7.52 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 4.28 (dd, $J = 7.8$ Hz, 5.5 Hz, 1H), 3.16 (s, 3H), 3.12 (dd, $J = 13.7$ Hz, 7.8 Hz, 1H), 2.93 (dd, $J = 13.7$ Hz, 5.5 Hz, 1H), 2.35 (s, 3H).

$^{13}$C NMR: (100 MHz, CDCl$_3$): $\delta$ 144.2, 137.7, 137.6, 131.8, 130.3, 129.1, 126.3, 119.1, 110.0, 84.0, 56.6, 44.8, 21.1.

**HRMS**: $m/z$ (DART) calcd for C$_{17}$H$_{18}$NO$^+$ (M+H)$^+$ 252.1383, found 252.1387.

**FTIR**: (neat): 2927, 2823, 2228, 1609, 1512, 1449, 1414, 1350, 1178, 1097, 1021, 817 cm$^{-1}$
4-[2-Methoxy-2-(2-methylphenyl)ethyl]benzonitrile (3ac)

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{NC} & \quad \text{OMe}
\end{align*}
\]

62% yield, 55 mg, 0.22 mmol (based on 0.35 mmol scale)

White solid

**TLC (SiO\textsubscript{2}):** $R_f = 0.22$ ($n$-hexane:ethyl acetate =10:1).

**m.p.:** 51.5-53.0 °C

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.53 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.24-7.17 (m, 4H), 7.12 (d, $J = 7.8$ Hz, 1H), 4.59 (dd, $J = 7.8$ Hz, 4.8 Hz , 1H), 3.16 (s, 3H), 3.06 (dd, $J = 13.7$ Hz, 7.8 Hz , 1H), 2.92 (dd, $J = 13.7$ Hz, 4.8 Hz , 1H), 2.20 (s, 3H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): $\delta$ 144.3, 138.9, 135.2, 131.8, 130.4, 130.2, 127.5, 126.4, 125.8, 119.1, 110.1, 80.4, 56.7, 43.8, 18.9.

**HRMS:** $m/z$ (DART) calcd for C\textsubscript{17}H\textsubscript{18}NO\textsuperscript{+} (M+H)\textsuperscript{+} 252.1383, found 252.1373.

**FTIR:** (neat): 2930, 2823, 2228, 1608, 1507, 1462, 1178, 1093, 825, 762, 734 cm\textsuperscript{-1}

4-[2-Methoxy-2-(4-methoxyphenyl)ethyl]benzonitrile (3ad)

\[
\begin{align*}
\text{OMe} & \quad \text{OMe} \\
\text{NC} & \quad \text{OMe}
\end{align*}
\]

56% yield, 53 mg, 0.20 mmol (based on 0.35 mmol scale)

White solid

**TLC (SiO\textsubscript{2}):** $R_f = 0.13$ ($n$-hexane:ethyl acetate =10:1).

**m.p.:** 73.7-75.7 °C

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.52 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.12 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 4.26 (dd, $J = 7.8$ Hz, 6.0 Hz , 1H), 3.81 (s, 3H), 3.15 (s, 3H), 3.13 (dd, $J = 13.7$ Hz, 7.8 Hz , 1H), 2.93 (dd, $J = 13.7$ Hz, 6.0 Hz , 1H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): $\delta$ 159.3, 144.2, 132.7, 131.8, 130.4, 130.2, 127.9, 126.4, 125.8, 119.1, 113.8, 110.0, 83.7, 56.5, 55.2, 44.8.

**HRMS:** $m/z$ (DART) calcd for C\textsubscript{16}H\textsubscript{14}NO\textsuperscript{+} (M-MeOH+H)\textsuperscript{+} 236.1070, found 236.1061.

**FTIR:** (neat): 2934, 2837, 2227, 1610, 1512, 1464, 1415, 1304, 1247, 1174, 1095, 1034, 835, 775 cm\textsuperscript{-1}
4-[2-Methoxy-2-(4-chlorophenyl)ethyl] benzonitrile (3ae)

60% yield, 57 mg, 0.21 mmol (based on 0.35 mmol scale)

Yellow solid

**TLC (SiO$_2$):** R$_f$ = 0.16 (n-hexane:ethyl acetate =10:1).

**m.p.:** 79.5-81.3 ºC

**$^1$H NMR:** (400 MHz, CDCl$_3$): δ 7.53 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 4.30 (dd, J = 7.8 Hz, 5.5 Hz, 1H), 3.17 (s, 3H), 3.11 (dd, J = 13.7 Hz, 7.8 Hz, 1H), 2.92 (dd, J = 13.7 Hz, 5.5 Hz, 1H).

**$^{13}$C NMR:** (100 MHz, CDCl$_3$): δ 143.6, 139.3, 133.6, 131.9, 130.3, 128.7, 128.0, 119.0, 110.2, 83.5, 56.8, 44.6.

**HRMS:** m/z (DART) calcd for C$_{16}$H$_{15}$ClNO$^+$ (M+H)$^+$ 272.0837, found 272.0847.

**FTIR:** (neat): 2932, 2824, 2731, 2228, 1608, 1507, 1490, 1465, 1410, 1346, 1290, 1250, 1178, 1091, 1015, 833, 743 cm$^{-1}$

4-[2-Methoxy-2-(4-bromophenyl)ethyl]benzonitrile (3af)

45% yield, 51 mg, 0.16 mmol (based on 0.35 mmol scale)

Colorless and crystalline solid

**TLC (SiO$_2$):** R$_f$ = 0.13 (n-hexane:ethyl acetate =10:1).

**m.p.:** 103.9-105.4 ºC

**$^1$H NMR:** (400 MHz, CDCl$_3$): δ 7.53 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 4.29 (dd, J = 7.8 Hz, 5.5 Hz, 1H), 3.17 (s, 3H), 3.10 (dd, J = 13.7 Hz, 7.8 Hz, 1H), 2.92 (dd, J = 13.7 Hz, 5.5 Hz, 1H).

**$^{13}$C NMR:** (100 MHz, CDCl$_3$): δ 143.5, 139.8, 131.9, 131.6, 130.3, 128.3, 121.7, 119.0, 110.2, 83.5, 56.8, 44.6.

**HRMS:** m/z (EI+) calcd for C$_{15}$H$_{11}$BrN$^+$ (M-MeOH+H)$^+$ 284.0075, found 284.0067.

**FTIR:** (neat): 2986, 2931, 2824, 2227, 1608, 1592, 1507, 1485, 1404, 1344, 1297, 1228, 1178, 1095, 1071, 1011, 880, 830, 776, 746, 720 cm$^{-1}$
1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-4-methylbenzene (3ba)

41% yield, 41 mg, 0.14 mmol (based on 0.35 mmol scale)

Orange oil

**TLC (SiO$_2$):** $R_f$ = 0.47 (n-hexane:ethyl acetate = 10:1).

**$^1$H NMR:** (400 MHz, CDCl$_3$): $\delta$ 7.35 (d, $J$ = 8.2 Hz, 2H), 7.19 (d, $J$ = 8.2 Hz, 2H), 7.05 (m, 4H), 4.28 (dd, $J$ = 8.2 Hz, 8.5 Hz, 1H), 3.17 (s, 3H), 3.04 (dd, $J$ = 14.2 Hz, 8.2 Hz, 1H), 2.84 (dd, $J$ = 14.2 Hz, 5.0 Hz, 1H), 1.33 (s, 9H).

**$^{13}$C NMR:** (100 MHz, CDCl$_3$): $\delta$ 150.5, 138.9, 136.0, 135.6, 129.3, 128.9, 126.5, 125.3, 85.0, 56.9, 44.5, 34.6, 31.5, 21.2.

**HRMS:** m/z (DART) calcd for C$_{19}$H$_{23}$+ (M-MeOH+H)$^+$ 251.1794, found 251.1788.

**FTIR:** (neat): 2963, 2867, 2820, 2969, 1612, 1515, 1463, 1409, 1363, 1308, 1269, 1231, 1202, 1156, 1098, 1040, 1022, 1005, 977, 942, 880, 831, 810, 797, 756, 712, 692, 672 cm$^{-1}$

1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-4-tert-butylbenzene (3ca)

40% yield, 46 mg, 0.14 mmol (based on 0.35 mmol scale)

Brown crystalline solid

**TLC (SiO$_2$):** $R_f$ = 0.47 (n-hexane:ethyl acetate = 10:1).

**m.p.:** 68.1-69.9 °C

**$^1$H NMR:** (400 MHz, CDCl$_3$): $\delta$ 7.35 (d, $J$ = 8.5 Hz, 2H), 7.28 (d, $J$ = 8.2 Hz, 2H), 7.21 (d, $J$ = 8.5 Hz, 2H), 7.11 (d, $J$ = 8.2 Hz, 2H), 4.31 (dd, $J$ = 8.5 Hz, 4.6 Hz, 1H), 3.17 (s, 3H), 3.04 (dd, $J$ = 14.2 Hz, 8.5 Hz, 1H), 2.84 (dd, $J$ = 14.2 Hz, 4.6 Hz, 1H), 1.32 (s, 9H), 1.30 (s, 9H).

**$^{13}$C NMR:** (100 MHz, CDCl$_3$): $\delta$ 150.4, 148.8, 139.0, 136.0, 128.9, 126.3, 125.2, 125.0, 84.7, 56.8, 44.3, 34.5, 34.4, 31.4.

**HRMS:** m/z (DART) calcd for C$_{22}$H$_{29}$+ (M-MeOH+H)$^+$ 293.2264, found 293.2260.

**FTIR:** (neat): 2963, 2868, 1510, 1464, 1410, 1364, 1269, 1203, 1102, 1020, 834 cm$^{-1}$
1-Methoxy-4-[2-methoxy-2-(4-tert-butylphenyl)ethyl]benzene (3da)

\[
\text{MeO} \quad \text{MeO} \quad \text{MeO}
\]

35% yield, 37 mg, 0.12 mmol (based on 0.35 mmol scale)

Yellow oil

**TLC (SiO\textsubscript{2}):** $R_f = 0.41$ (n-hexane:ethyl acetate =10:1).

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.34 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 2H), 4.25 (dd, $J = 8.0$ Hz, 5.3 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H), 3.03 (dd, $J = 14.0$ Hz, 8.0 Hz, 1H), 2.82 (dd, $J = 14.0$ Hz, 5.3 Hz, 1H), 1.32 (s, 9H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): $\delta$ 157.9, 150.4, 138.7, 131.0, 130.3, 126.4, 125.1, 113.4, 85.0, 56.8, 55.2, 43.9, 34.5, 31.4.

**HRMS:** m/z (DART) calcd for C\textsubscript{19}H\textsubscript{23}O\textsuperscript{+} (M-MeOH+H)$^+$ 267.1743, found 267.1745.

**FTIR:** (neat): 2961, 2905, 2868, 2835, 1613, 1585, 1512, 1464, 1442, 1408, 1363, 1301, 1246, 1203, 1177, 1098, 1038, 998, 978, 879, 833, 802, 756, 715, 692, 672 cm\textsuperscript{-1}

1-[1-Methoxy-2-phenylethyl]-4-tert-butylbenzene (3ea)

\[
\text{MeO}
\]

62% yield, 58 mg, 0.22 mmol (based on 0.35 mmol scale)

Yellow crystalline solid

**TLC (SiO\textsubscript{2}):** $R_f = 0.45$ (n-hexane:ethyl acetate =10:1).

**m.p.:** 39.7-40.7 °C

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.34 (d, $J = 8.3$ Hz, 2H), 7.25 (t, $J = 7.0$ Hz, 2H), 7.21-7.17 (m, 3H), 7.15 (d, $J = 7.0$ Hz, 2H), 4.31 (dd, $J = 8.2$ Hz, 5.0 Hz, 1H), 3.17 (s, 3H), 3.08 (dd, $J = 13.7$ Hz, 8.2 Hz, 1H), 2.88 (dd, $J = 13.7$ Hz, 5.0 Hz, 1H), 1.32 (s, 9H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): $\delta$ 150.5, 138.9, 138.7, 129.4, 128.1, 126.4, 126.1, 125.2, 124.2, 84.8, 56.8, 44.8, 34.5, 31.4.

**HRMS:** m/z (DART) calcd for C\textsubscript{18}H\textsubscript{21}O\textsuperscript{+} (M-MeOH+H)$^+$ 237.1638, found 237.1645.

**FTIR:** (neat): 3029, 2964, 2868, 2821, 1605, 1510, 1496, 1454, 1409, 1363, 1269, 1202, 1100, 1078, 1031, 874, 833, 750, 701 cm\textsuperscript{-1}
1-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]-4-nitrobenzene (3fa)  

\[
\text{\includegraphics[width=1in]{1-5-3.jpg}}
\]

66% yield, 72 mg, 0.23 mmol (based on 0.35 mmol scale)

Yellow solid

**TLC (SiO\textsubscript{2}):** \(R_f = 0.40\) (n-hexane:ethyl acetate =10:1).

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.11 (d, \(J = 8.7\) Hz, 2H), 7.36 (d, \(J = 8.2\) Hz, 2H), 7.29 (d, \(J = 8.7\) Hz, 2H), 7.16 (d, \(J = 8.2\) Hz, 2H), 4.32 (dd, \(J = 8.2\) Hz, 5.0 Hz, 1H), 3.16 (dd, 13.7 Hz, 8.2 Hz, 1H), 3.17 (s, 3H), 2.99 (dd, \(J = 13.7\) Hz, 5.0 Hz, 1H), 1.33 (s, 9H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): \(\delta\) 151.0, 146.7, 146.5, 137.7, 130.3, 126.3, 125.4, 123.3, 83.9, 56.8, 44.5, 34.6, 31.4.

2-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (3ga)  

\[
\text{\includegraphics[width=1in]{2-5-3.jpg}}
\]

58% yield, 59 mg, 0.20 mmol (based on 0.35 mmol scale)

Yellow oil

**TLC (SiO\textsubscript{2}):** \(R_f = 0.40\) (n-hexane:ethyl acetate =10:1).

**\textsuperscript{1}H NMR:** (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.61 (d, \(J = 8.2\) Hz, 1H), 7.47 (dd, \(J = 8.2\) Hz, 6.8 Hz, 1H), 7.37 (d, \(J = 8.2\) Hz, 2H), 7.30 (dd, \(J = 7.8\) Hz, 6.8 Hz, 1H), 7.29 (d, \(J = 7.8\) Hz, 1H), 7.24 (d, \(J = 8.2\) Hz, 2H), 4.42 (dd, \(J = 8.7\) Hz, 4.6 Hz, 1H), 3.22 (dd, 14.2 Hz, 8.7 Hz, 1H), 3.17 (s, 3H), 3.13 (dd, \(J = 14.2\) Hz, 4.6 Hz, 1H), 1.33 (s, 9H).

**\textsuperscript{13}C NMR:** (100 MHz, CDCl\textsubscript{3}): \(\delta\) 150.8, 142.8, 137.9, 132.6, 132.3, 131.1, 126.7, 126.2, 125.4, 118.2, 112.8, 83.4, 56.9, 43.4, 34.5, 31.4.
4-[2-Ethoxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (4a)

54% yield, 58 mg, 0.19 mmol (based on 0.35 mmol scale)
Yellow oil

\textbf{TLC (SiO}_2\textbf{):} R_f = 0.26 (n-hexane:ethyl acetate =10:1).

\textbf{\textsuperscript{1}H NMR:} (400 MHz, CDCl}_3\textbf{:} \delta 7.52 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 4.37 (dd, J = 8.2 Hz, 5.0 Hz, 1H), 3.38 (dq, J = 9.2 Hz, 6.9 Hz, 1H), 3.21 (dq, J = 9.2 Hz, 7.3 Hz, 1H), 3.11 (dd, J = 13.7 Hz, 8.2 Hz, 1H), 2.91 (dd, J = 13.7 Hz, 5.0 Hz, 1H), 1.32 (s, 9H), 1.10 (dd, J = 7.3 Hz, 6.9 Hz, 3H).

\textbf{\textsuperscript{13}C NMR:} (100 MHz, CDCl}_3\textbf{:} \delta 150.7, 144.7, 136.8, 131.7, 130.3, 126.1, 125.3, 119.2, 109.9, 82.1, 64.2, 44.9, 34.5, 31.4, 15.2.

\textbf{HRMS:} m/z (DART) calcd for C\textsubscript{19}H\textsubscript{20}N\textsuperscript{+} (M-EtOH+H)\textsuperscript{+} 262.1590, found 262.1590.

\textbf{FTIR:} (neat): 2965, 2903, 2228, 1917, 1615, 1549, 1465, 1363, 1332, 1269, 1222, 1178, 1158, 1091, 950, 925, 884, 838, 738, 683 cm\textsuperscript{-1}

4-[2-Isopropoxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (4b)

47% yield, 51 mg, 0.16 mmol (based on 0.35 mmol scale)
Yellow sticky oil

\textbf{TLC (SiO}_2\textbf{):} R_f = 0.26 (n-hexane:ethyl acetate =10:1).

\textbf{\textsuperscript{1}H NMR:} (400 MHz, CDCl}_3\textbf{:} \delta 7.53 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 4.47 (dd, J = 8.5 Hz, 4.7 Hz, 1H), 3.41 (sep, J = 6.1 Hz, 1H), 3.04 (dd, J = 13.7 Hz, 8.5 Hz, 1H), 2.88 (dd, J = 13.7 Hz, 4.7 Hz, 1H), 1.32 (s, 9H), 1.05 (d, J = 6.1 Hz, 3H), 0.91 (d, J = 6.1 Hz, 3H).

\textbf{\textsuperscript{13}C NMR:} (100 MHz, CDCl}_3\textbf{:} \delta 150.5, 144.9, 139.4, 131.6, 130.4, 126.1, 125.2, 119.2, 109.8, 79.4, 69.0, 45.5, 34.5, 31.4, 23.3, 20.9.

\textbf{HRMS:} m/z (DART) calcd for C\textsubscript{19}H\textsubscript{20}N\textsuperscript{+} (M-PrOH+H)\textsuperscript{+} 262.1581, found 262.1581.

\textbf{FTIR:} (neat): 2967, 2870, 2228, 1608, 1506, 1465, 1413, 1376, 1331, 1269, 1176, 1139, 1123, 1072, 1017, 964, 836 cm\textsuperscript{-1}
4-[2-Benzylxyloxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (4c)

![Chemical structure of 4c]

42% yield, 54 mg, 0.15 mmol (based on 0.35 mmol scale)
White solid

**TLC (SiO$_2$)**: $R_f = 0.22$ (n-hexane:ethyl acetate =10:1).

**m.p.**: 91.2-93.0 °C

**$^1$H NMR** (400 MHz, CDCl$_3$): δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.29-7.21 (m, 7H), 7.10-7.08 (m, 2H), 4.47 (dd, $J = 8.7$ Hz, 4.6 Hz, 1H), 4.45 (d, $J = 12.0$ Hz, 1H), 4.16 (d, $J = 12.0$ Hz, 1H), 3.15 (dd, $J = 13.8$ Hz, 8.7 Hz, 1H), 2.96 (dd, $J = 13.8$ Hz, 4.6 Hz, 1H), 1.34 (s, 9H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$): δ 151.0, 144.5, 138.1, 138.0, 131.8, 130.4, 128.2, 127.6, 127.5, 126.4, 125.4, 119.2, 109.9, 81.3, 70.3, 45.0, 34.6, 31.4.

**HRMS**: $m/z$ (DART) calcd for C$_{19}$H$_{20}$N$^+$ (M-BnOH+H)$^+$ 262.1590, found 262.1579.

**FTIR** (neat): 2963, 2867, 2228, 1608, 1507, 1455, 1413, 1363, 1269, 1204, 1073, 1018, 838, 736 cm$^{-1}$

[2-(4-cyanobenzene)-1-(4-tert-butylphenyl)ethyl]formate (4d)

![Chemical structure of 4d]

45% yield, 49 mg, 0.16 mmol (based on 0.35 mmol scale)
orange sticky oil

**TLC (SiO$_2$)**: $R_f = 0.17$ (n-hexane:ethyl acetate =10:1).

**$^1$H NMR** (400 MHz, CDCl$_3$): δ 8.00 (s, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.25-7.21 (m, 4H), 6.05 (dd, $J = 8.2$ Hz, 6.0 Hz, 1H), 3.29 (dd, $J = 13.7$ Hz, 8.2 Hz, 1H), 3.15 (dd, $J = 13.7$ Hz, 6.0 Hz, 1H), 1.31 (s, 9H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$): δ 160.0, 151.7, 142.3, 135.5, 132.1, 130.3, 126.3, 125.6, 118.8, 110.7, 75.5, 42.7, 34.6, 31.3.

**HRMS**: $m/z$ (DART) calcd for C$_{19}$H$_{20}$N$^+$ (M-OCOH+H)$^+$ 262.1590, found 262.1595.

**FTIR** (neat): 2963, 2870, 2228, 1928, 1720, 1609, 1508, 1476, 1463, 1414, 1364, 1313, 1270, 1158, 1110, 1051, 1021, 984, 953, 889, 832, 776, 683 cm$^{-1}$
Reference
NMR spectra of 3aa

p-tert-butylstyrene-product proton.esp

Chemical Shift (ppm) vs Normalized Intensity

Normalized Intensity

Normalized Intensity

p-tert-butylstyrene-product carbon.esp

Chemical Shift (ppm) vs Normalized Intensity

Normalized Intensity
NMR spectra of 3ab

p-methylstyrene-product proton.esp

Chemical Shift (ppm)

Normalized Intensity

2.95 1.10 0.99 2.94 1.03 2.09 2.13 2.12 2.07 7.53 7.51 7.22 7.13 7.10

p-methylstyrene-product carbon.esp

Chemical Shift (ppm)

Normalized Intensity

144.23 137.70 137.62 131.81 130.26 129.14 126.57 119.11 109.98 83.99 77.00 76.68 56.62 44.77 21.14
NMR spectra of 3ae

Chemical Shift (ppm)
Normalized Intensity

Chemical Shift (ppm)
Normalized Intensity
NMR spectra of 3af

- p-bromostyrene -product proton.esp

- p-bromostyrene -product carbon.esp
NMR spectra of 3ba

**p-methylbenzene diazonium salt-product proton.esr**

**Chemical Shift (ppm)**

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

**Normalized Intensity**

- 9.04
- 7.37
- 4.38
- 1.00
- 0.1

**Chemical Shift (ppm)**

10 9 8 7 6 5 4 3 2 1 0

**Normalized Intensity**

- 9.04
- 7.37
- 4.38
- 1.00
- 0.1

**p-methylbenzene diazonium salt-product carbon.esr**

**Chemical Shift (ppm)**

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

**Normalized Intensity**

- 150.53
- 138.93
- 156.93
- 135.60
- 129.34
- 126.49
- 84.99
- 77.44
- 77.12
- 76.80
- 56.91
- 44.49
- 34.62
- 21.17

**Chemical Shift (ppm)**

0 10 20 30 40 50 60 70 80 90 100

**Normalized Intensity**

- 150.53
- 138.93
- 156.93
- 135.60
- 129.34
- 126.49
- 84.99
- 77.44
- 77.12
- 76.80
- 56.91
- 44.49
- 34.62
- 21.17
NMR spectra of 3da

- p-methoxybenzene diazoniumsalt-product proton.esp

- p-methoxybenzene diazoniumsalt-product carbon.esp
NMR spectra of 3ea

benez diazoniumsalt-product proton.esp

Chemical Shift (ppm)

Normalized Intensity

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

10 9 8 7 6 5 4 3 2 1 0

Chemical Shift (ppm)

Normalized Intensity

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

180 160 140 120 100 80 60 40 20 0

benzene diazoniumsalt-product carbon.esp

Chemical Shift (ppm)

Normalized Intensity

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

180 160 140 120 100 80 60 40 20 0
NMR spectra of 3fa

\( p\)-nitrobenzene diazonium salt-proton.esp

\( p\)-nitrobenzene diazonium salt-carbon.esp

Chemical Shift (ppm)
Normalized Intensity
NMR spectra of 3ga

- o-cyanobenzene diazoniumsalt-product proton.esp

- o-cyanobenzene diazoniumsalt-product carbon.esp
NMR spectra of 4a

EtOH-product proton.esp

EtOH-product carbon.esp
NMR spectra of 4b

IPA-product proton.esp

Normalized Intensity

Chemical Shift (ppm)

Normalized Intensity

Chemical Shift (ppm)

IPA-product carbon.esp

Normalized Intensity

Chemical Shift (ppm)