Supporting Information

Stereoselective Synthesis of (Z)-Allyl Alcohols Through Coinage-metal Catalyzed Nucleophilic Addition of Benzo[d]isoxazoles with Unactivated Propargyl Alcohols

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1. General experimental methods

Unless otherwise noted, commercial reagents were purchased from commercial suppliers and were used as received. All solvents were dried and distilled according to standard procedures before use. The flash column chromatography was performed using silica gel (60 Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35 ºC. Nuclear magnetic resonance (NMR) spectra were recorded in parts per million (ppm) from internal trimethylsilane (TMS) on the δ scale. High resolution mass spectrometry (HRMS) spectra analysis was performed by electrospray ionization (ESI-micrOTOF). EPR spectra were recorded on a Bruker X-band A200 spectrometer. The secondary propargyl alcohols were prepared according to reported procedure.[1]

2. General procedure for the preparation of (Z)-3a.

To a stirred solution of propargyl alcohol 1a (0.5 mmol) in anhydrous toluene (3.0 mL) was added Ph$_3$PAuCl (0.025 mmol), AgOAc (0.05 mmol) and Li$_2$CO$_3$ (0.5 mmol) at room temperature. The reaction was purged with N$_2$, and then benzo[d]isoxazole 2a (0.75 mmol) dissolved in toluene (1.0 mL) was added via a syringe. The reaction was raised to 80 °C for about 4-6 h. After completion of the reaction as indicated by TLC, the reaction was allowed to cool to room temperature, diluted with ethyl acetate (5.0 mL), and extracted. The combined organic phase was washed with brine, dried over Na$_2$SO$_4$, and concentrated to give the crude residue, which was purified by silica column chromatography (elute: petroleum ether/ethyl acetate = 20/1, v/v) to give the desired product 3a as a yellow solid.

The other allyl alcohols 3b-3x were prepared according to their procedures similar to 3a.

(Z)-2-((3-Hydroxy-1-phenyl-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3a)

Yield 135 mg, 79%; yellow solid, mp: 105-106 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.54-7.51 (m, 1H), 7.41-7.36 (m, 2H), 7.24-7.16 (m, 6H), 7.04 (d, J = 7.6 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 8.8 Hz, 1H), 6.04 (d, J = 8.8 Hz, 1H), 5.60 (d, J = 8.4 Hz, 1H), 2.24 (br, 1H), 2.23 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.8, 148.8, 139.8, 137.6, 134.3, 133.9, 133.5, 133.4, 129.3, 128.8, 125.9, 122.3, 121.1, 116.1, 115.5, 102.2, 68.9, 21.1. HRMS calcd. for C$_{23}$H$_{20}$NO$_2$ (M+H)$^+$: 342.1489, found: 342.1487.
(Z)-2-((3-Hydroxy-1,3-di-p-tolylprop-1-en-1-yl)oxy)benzonitrile (3b)

Yield 145 mg, 82%; yellow solid, mp: 118-119 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.51-7.49 (m, 1H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.22-7.15 (m, 3H), 7.02 (d, $J = 8.0$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.90 (t, $J = 7.6$ Hz, 1H), 6.68 (d, $J = 8.8$ Hz, 1H), 5.97 (d, $J = 8.4$ Hz, 1H), 5.57 (d, $J = 8.4$ Hz, 1H), 2.33 (br, 1H), 2.22 (s, 3H), 2.19 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 158.9, 148.9, 139.9, 139.3, 137.5, 134.3, 133.7, 133.6, 130.6, 129.41, 126.0, 125.8, 122.2, 120.2, 116.2, 115.5, 102.1, 68.9, 21.2, 21.1. HRMS calcd. for C$_{24}$H$_{22}$NO$_2$ (M+H)$^+$: 356.1645, found: 356.1647.

(Z)-2-((3-Hydroxy-1-(4-methoxyphenyl)-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3c)

Yield 156 mg, 84%; yellow solid, mp: 127-128 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.61-7.59 (m, 1H), 7.39 (d, $J = 8.8$ Hz, 2H), 7.32-7.25 (m, 3H), 7.12 (d, $J = 7.6$ Hz, 2H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.80-6.77 (m, 3H), 5.99 (d, $J = 8.8$ Hz, 1H), 5.65 (d, $J = 8.8$ Hz, 1H), 3.75 (s, 3H), 2.37 (br, 1H), 2.31 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 160.3, 158.9, 148.7, 140.0, 137.5, 134.3, 133.7, 129.3, 127.3, 125.9, 122.2, 119.2, 116.1, 115.5, 114.2, 102.1, 68.9, 55.3, 21.1. HRMS calcd. for C$_{24}$H$_{22}$NO$_3$ (M+H)$^+$: 372.1594, found: 372.1592.
(Z)-2-((1-(4-Butylphenyl)-3-hydroxy-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3d)
Yield 177 mg, 89%; yellow solid, mp: 133-134 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53-7.52 (m, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.24-7.16 (m, 3H), 7.04 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.00 (d, $J = 8.4$ Hz, 1H), 5.59 (d, $J = 8.4$ Hz, 1H), 2.49-2.44 (m, 2H), 2.23 (s, 3H), 1.50-1.41 (m, 2H), 1.25-1.18 (m, 2H), 0.81 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.9, 149.0, 144.4, 139.8, 137.6, 134.3, 133.8, 130.7, 129.3, 128.8, 126.0, 125.7, 122.2, 120.1, 116.1, 115.5, 102.1, 69.0, 35.4, 33.3, 22.3, 21.1, 13.9. HRMS calcd. for C$_{27}$H$_{28}$NO$_2$ (M+H)$^+$: 398.2115, found: 398.2113.

(Z)-2-((1-(4-Fluorophenyl)-3-hydroxy-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3e)
Yield 122 mg, 68%; yellow solid, mp: 138-139 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63-7.60 (m, 1H), 7.47-7.42 (m, 2H), 7.30-7.26 (m, 3H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.97 (t, $J = 8.6$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 1H), 6.05 (d, $J = 8.8$ Hz, 1H), 5.66 (d, $J = 8.8$ Hz, 1H), 2.31 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.1 (d, $^1J = 248$ Hz), 158.5, 147.9, 139.7, 137.7, 134.3, 133.8, 133.7, 129.5, 129.4, 127.8, 125.9, 122.4, 121.0, 115.8 (d, $^2J = 21$ Hz), 115.4, 102.3, 68.9, 21.1. HRMS calcd. for C$_{23}$H$_{19}$FNO$_2$ (M+H)$^+$: 360.1394, found: 360.1392.
(Z)-2-((3-Hydroxy-3-(p-tolyl)-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxy)benzonitrile (3f)

Yield 112 mg, 55%; yellow solid, mp: 147-148 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65-7.63 (m, 1H), 7.59-7.53 (m, 4H), 7.35-7.30 (m, 1H), 7.28 (d, \(J = 8.0\) Hz, 2H), 7.14 (d, \(J = 8.0\) Hz, 2H), 7.05 (t, \(J = 7.6\) Hz, 1H), 6.73 (d, \(J = 8.4\) Hz, 1H), 6.24 (d, \(J = 8.4\) Hz, 1H), 5.70 (d, \(J = 2.2\) Hz, 8.6 Hz, 1H), 2.32 (br, 1H), 2.32 (s, 3H). 

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.0, 158.3, 147.4, 139.4, 138.0, 134.7, 134.3, 129.5, 126.0, 125.9, 125.8, 125.6 (q, \(^1\)J = 270 Hz), 123.4, 122.7, 118.7, 115.8, 115.2, 102.4, 69.0, 21.1. HRMS calcd. for C\(_{24}\)H\(_{19}\)F\(_3\)NO\(_2\) (M+H): 410.1362, found: 410.1364.

(Z)-2-((1-(4-Bromophenyl)-3-hydroxy-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3g)

Yield 156 mg, 74%; yellow solid, mp: 141-142 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63-7.60 (m, 1H), 7.41 (d, \(J = 8.6\) Hz, 2H), 7.32 (d, \(J = 8.8\) Hz, 2H), 7.27 (d, \(J = 7.6\) Hz, 2H), 7.13 (d, \(J = 7.6\) Hz, 2H), 7.03 (t, \(J = 7.6\) Hz, 1H), 7.00-6.98 (m, 1H), 6.73 (d, \(J = 8.8\) Hz, 1H), 6.12 (d, \(J = 8.4\) Hz, 1H), 5.67 (d, \(J = 8.8\) Hz, 1H), 2.32 (s, 3H), 2.31 (br, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.5, 147.85, 139.55, 137.8, 134.3, 133.9, 132.4, 132.0, 129.4, 127.3), 126.5, 126.0, 123.4, 122.5, 121.7, 115.3, 102.3, 68.9, 21.1. HRMS calcd. for C\(_{24}\)H\(_{19}\)BrNO\(_2\) (M+H): 420.0594, found: 420.0596.
(Z)-4-Chloro-2-((3-hydroxy-1-phenyl-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3h)

Yield 136 mg, 73%; yellow oil.

$\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.52 (d, J = 2.5 \text{ Hz, 1H}), 7.44-7.41 (m, 2H), 7.30-7.22 (m, 5H), 7.20-7.17 (m, 1H), 7.11 (d, J = 7.9 \text{ Hz, 2H}), 6.67 (d, J = 9.0 \text{ Hz, 1H}), 6.12 (d, J = 8.5 \text{ Hz, 1H}), 5.64 (d, J = 8.5 \text{ Hz, 1H}), 2.42 (br, 1H), 2.30 (s, 3H).

$\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 157.4, 148.6, 139.7, 137.7, 134.3, 133.1, 132.9, 129.4, 129.4, 128.9, 127.2, 126.1, 125.8, 121.5, 116.9, 114.8, 103.5, 69.0, 21.1. $\text{HRMS}$ calcd. for C$_{23}$H$_{19}$ClNO$_2$(M+H)$^+$: 376.1099, found: 376.1089.

(Z)-4-Chloro-2-((3-hydroxy-1-(thiophen-3-yl)-3-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3i)

Yield 123 mg, 65%; yellow oil.

$\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.50 (d, J = 2.4 \text{ Hz, 1H}), 7.20-7.15 (m, 5H), 7.07-7.04 (m, 3H), 6.68 (d, J = 9.0 \text{ Hz, 1H}), 5.97 (d, J = 8.6 \text{ Hz, 1H}), 5.51 (d, J = 8.6 \text{ Hz, 1H}), 2.24 (s, 3H), 2.23 (br, 1H).

$\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 157.6, 145.2, 139.4, 137.9, 134.6, 132.9, 132.1, 129.4, 127.4, 127.1, 126.0, 124.9, 123.5, 120.2, 118.0, 116.6, 103.2, 68.9, 21.1. $\text{HRMS}$ calcd. for C$_{21}$H$_{17}$ClNO$_2$S(M+H)$^+$: 382.0663, found: 382.0654.
(Z)-2-(((3-(2-Bromo-5-methoxyphenyl)-3-hydroxy-1-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3j)
Yield 164 mg, 73%; yellow solid, mp: 149-150 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49-7.44 (m, 1H), 7.26-7.21 (m, 3H), 7.14-7.09 (m, 1H), 7.10 (d, $J = 2.8$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 1H), 6.56-6.53 (m, 1H), 5.95 (d, $J = 8.0$ Hz, 1H), 5.84 (d, $J = 8.0$ Hz, 1H), 3.68 (s, 3H), 2.78 (br, 1H), 2.19 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.3, 158.6, 150.3, 142.9, 139.5, 134.9, 134.1, 133.5, 130.5, 129.5, 126.7, 125.9, 122.2, 118.5, 115.9, 115.3, 113.5, 112.3, 102.2, 68.6, 55.5, 21.3. HRMS calcd. for C$_{24}$H$_{21}$BrNO$_3$ (M+H)$^+$: 450.0699, found: 450.0697.

(Z)-2-(((3-(4-Bromophenyl)-3-hydroxy-1-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3k)
Yield 136 mg, 65%; yellow solid, mp: 135-136 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.26-7.17 (m, 6H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 5.91 (d, $J = 8.6$ Hz, 1H), 5.60 (d, $J = 8.6$ Hz, 1H), 2.74 (br, 1H), 2.20 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 149.5, 141.7, 139.6, 134.4, 133.8, 131.7, 130.2, 129.6, 127.8, 125.8, 122.4, 121.6, 120.5, 119.4, 115.5, 102.0, 68.5, 21.3. HRMS calcd. for C$_{23}$H$_{19}$BrNO$_2$ (M+H)$^+$: 420.0594, found: 420.0589.

(Z)-2-(((1,3-Bis(4-bromophenyl)-3-hydroxyprop-1-en-1-yl)oxy)-4-methoxybenzonitrile (3l)
Yield 128 mg, 50%; yellow solid, mp: 131-132 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.79 (d, \(J = 8.8\) Hz, 1H), 7.61-7.55 (m, 2H), 7.50-7.44 (m, 4H), 7.31-7.29 (m, 2H), 6.75 (d, \(J = 8.8\) Hz, 1H), 6.39 (d, \(J = 8.4\) Hz, 1H), 6.19 (s, 1H), 5.90 (s, 1H), 5.41-5.35 (m, 1H), 3.76 (br, 1H), 3.63 (s, 3H).

\(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 164.6, 159.9, 146.2, 143.5, 135.9, 132.7, 132.4, 131.6, 128.9, 127.7, 123.5, 122.9, 120.8, 116.7, 109.0, 101.8, 93.5, 67.5, 56.2.

HRMS calcd. for C\(_{23}\)H\(_{19}\)Br\(_2\)NO\(_3\) (M+H\(^+\)): 513.9648, found: 513.9653.

(Z)-2-((3-(2-Bromophenyl)-3-hydroxy-1-((\(p\)-tolyl)prop-1-en-1-yl)oxy)-4-chlorobenzonitrile (3m)

Yield 195 mg, 85%; yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.51 (m, 1H), 7.40 (d, \(J = 2.5\) Hz, 1H), 7.36-7.34 (m, 1H), 7.23-7.18 (m, 3H), 7.07-7.04 (m, 1H), 7.01-6.97 (m, 3H), 6.55 (d, \(J = 9.0\) Hz, 1H), 5.97 (d, \(J = 8.1\) Hz, 1H), 5.89 (d, \(J = 8.1\) Hz, 1H), 2.75 (br, 1H), 2.20 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 157.3, 150.0, 141.8, 139.7, 134.1, 133.0, 132.8, 130.2, 129.6, 129.2, 128.4, 127.9, 127.1, 125.9, 122.2, 119.0, 117.2, 114.8, 103.5, 68.5, 21.3.

HRMS calcd. for C\(_{23}\)H\(_{18}\)BrClNO\(_2\) (M+H\(^+\)): 454.0204, found: 454.0225.

(Z)-2-((3-(2-Bromophenyl)-3-hydroxy-1-((\(p\)-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3n)

Yield 170 mg, 81%; yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.63-7.60 (m, 1H), 7.56 (d, \(J = 7.7\) Hz, 1H), 7.45 (d, \(J = 7.9\) Hz, 1H), 7.35-7.33 (m, 2H), 7.31-7.21 (m, 2H), 7.09-7.07 (m, 3H), 6.96 (t, \(J =\)
7.9 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 6.08-6.00 (m, 2H), 5.28 (br, 1H), 2.29 (s, 3H).

\[^{13}\text{C NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 158.6, 150.3, 141.7, 139.5, 134.5, 134.1, 133.6, 133.0, 130.5, 129.5, 129.2, 128.4, 127.9, 125.9, 122.2, 118.5, 116.6, 116.7, 115.8, 102.1, 68.6, 21.3. **HRMS** calcd. for C\(_{23}\)H\(_{19}\)BrNO\(_2\)(M+H): 420.0599, found: 420.0586.

![Chemical structure](Z)-2-((3-(4-Bromo-3-fluorophenyl)-3-hydroxy-1-(\(p\)-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3o)

Yield 131 mg, 60%; yellow oil.

\[^{1}\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.55-7.53 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.27-7.23 (m, 3H), 7.13-7.10 (m, 1H), 7.03-7.01 (m, 2H), 6.99-6.94 (m, 2H), 6.90-6.86 (m, 1H), 6.67 (d, J = 8.5 Hz, 1H), 5.87 (d, J = 8.6 Hz, 1H), 5.62 (d, J = 8.6 Hz, 1H), 2.22 (s, 3H). **13C NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 160.4 (d, \(J = 242\) Hz), 150.0, 144.6, 139.7, 134.3, 133.8, 133.5, 130.0, 129.6, 125.8, 122.8, 122.5, 118.9, 115.5, 114.1 (d, \(J = 23\) Hz), 113.9, 108.0, 107.8, 102.1, 67.9, 21.2. **HRMS** calcd. for C\(_{23}\)H\(_{18}\)BrFNO\(_2\)(M+H): 438.0499, found: 438.0494.

![Chemical structure](Z)-2-((3-Hydroxy-1-(\(p\)-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)oxy)benzonitrile (3p)

Yield 107 mg, 53%; yellow solid, mp: 146-147 °C.

\[^{1}\text{H NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, J = 7.6 Hz, 1H), 7.60-7.51 (m, 4H), 7.35-7.33 (m, 1H), 7.31-7.25 (m, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.00 (d, J = 8.6 Hz, 1H), 5.80 (d, J = 8.4 Hz, 1H), 2.52 (br, 1H), 2.29 (s, 3H). **13C NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 158.6, 149.9, 146.7, 139.7, 134.3, 133.8, 130.1, 129.6, 126.3, 125.9,
125.5, 124.8 (q, ^1J = 268 Hz), 122.8, 122.4, 119.3, 116.0, 115.5, 102.2, 68.5, 21.2.

**HRMS** calcd. for C$_{24}$H$_{19}$F$_3$NO$_2$ (M+H)$^+$: 410.1362, found: 410.1360.

![Chemical structure](image)

(Z)-2-((3-Hydroxy-3-(naphthalen-1-yl)-1-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile

(3q)

Yield 98 mg, 50%; yellow solid, mp: 131-132 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (d, $^1J = 8.4$ Hz, 1H), 7.81 (d, $^1J = 7.8$ Hz, 1H), 7.74 (d, $^1J = 8.0$ Hz, 1H), 7.70 (d, $^1J = 7.2$ Hz, 1H), 7.59 (d, $^1J = 1.4$ Hz, 7.7 Hz, 1H), 7.58 -7.49 (m, 1H), 7.47 (d, $^1J = 7.2$ Hz, 1H), 7.44-7.39 (m, 1H), 7.34 (d, $^1J = 8.0$ Hz, 2H), 7.24-7.18 (m, 1H), 7.06 (d, $^1J = 8.0$ Hz, 2H), 6.97 (t, $^1J = 7.6$ Hz, 1H), 6.70 (d, $^1J = 8.4$ Hz, 1H), 6.41 (d, $^1J = 8.4$ Hz, 1H), 6.20 (d, $^1J = 8.4$ Hz, 1H), 2.28 (br, 1H), 2.27 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.8, 149.4, 139.4, 138.5, 134.1, 133.9, 133.7, 130.4, 129.5, 128.7, 128.5, 126.3, 125.8, 125.4, 124.0, 123.8, 122.2, 119.8, 116.1, 115.6, 102.2, 67.2, 21.2. **HRMS** calcd. for C$_{27}$H$_{22}$NO$_2$ (M+H)$^+$: 392.1645, found: 392.1647.

![Chemical structure](image)

(Z)-2-((3-Hydroxy-3-(naphthalen-2-yl)-1-(p-tolyl)prop-1-en-1-yl)oxy)benzonitrile

(3r)

Yield 110 mg, 56%; yellow solid, mp: 136-137 °C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80-7.75 (m, 4H), 7.58 (d, $^1J = 7.6$ Hz, 1H), 7.52 (d, $^1J = 8.6$ Hz, 1H), 7.44-7.41 (m, 2H), 7.35 (d, $^1J = 8.0$ Hz, 2H), 7.24-7.18 (m, 1H), 7.06 (d, $^1J = 8.0$ Hz, 2H), 6.95 (t, $^1J = 7.6$ Hz, 1H), 6.73 (d, $^1J = 8.4$ Hz, 1H), 6.13 (d, $^1J = 8.6$ Hz, 1H), 5.86 (d, $^1J = 8.6$ Hz, 1H), 2.58 (br, 1H), 2.27 (s, 3H). $^{13}$C NMR (100 MHz,
CDCl$_3$ $\delta$ 158.8, 149.3, 140.1, 139.4, 134.3, 133.7, 133.3, 133.0, 130.5, 129.5, 128.5, 128.1, 127.7, 126.2, 125.9, 124.8, 124.2, 122.2, 120.0, 116.2, 115.5, 102.1, 69.3, 21.3. 

**HRMS** calcd. for C$_{27}$H$_{22}$NO$_2$ (M+H)$^+$: 392.1645, found: 392.1647.

(Z)-2-((3-Hydroxy-1-((p-tolyl)hex-1-en-1-yl)oxy)benzonitrile (3s)

Yield 125 mg, 82%; yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 7.6 Hz, 1H), 7.29-7.24 (m, 3H), 7.02 (d, $J$ = 8.0 Hz, 2H), 6.91 (t, $J$ = 7.6 Hz, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H), 5.77 (d, $J$ = 8.6 Hz, 1H), 4.54-4.52 (m, 1H), 2.22 (s, 3H), 2.01 (br, 1H), 1.65-1.53 (m, 1H), 1.52-1.42 (m, 1H), 1.41-1.25 (m, 2H), 0.82 (t, $J$ = 7.2 Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.0, 149.2, 139.2, 134.3, 133.8 130.7, 129.5, 125.7, 122.1, 120.6, 116.1, 115.2, 102.1, 66.6, 39.5, 21.3, 18.6, 14.0. 

**HRMS** calcd. for C$_{20}$H$_{22}$NO$_2$ (M+H)$^+$: 308.1645, found: 308.1647.

(Z)-2-(((3-Cyclohexyl-3-hydroxy-1-((p-tolyl)prop-1-en-1-yl)oxy)benzonitrile (3t)

Yield 161 mg, 93%; yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.49 (m, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.27-7.22 (m, 1H), 7.02 (d, $J$ = 8.0 Hz, 2H), 6.91 (t, $J$ = 7.6 Hz, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H), 5.77 (d, $J$ = 9.2 Hz, 1H), 4.25-4.23 (m, 1H), 2.22 (s, 3H), 1.81-1.32 (m, 4H), 1.23-1.02 (m, 4H), 0.97-0.95 (m, 2H), 0.83-0.72 (m, 2H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.0, 149.9, 139.2, 134.3, 133.7, 130.8, 129.5, 125.7, 122.1, 119.3, 116.1,

A mixture of compound 3a (0.30 mmol) and K$_2$CO$_3$ (0.45 mmol), H$_2$O$_2$ (0.60 mmol) in DMSO (1.5 mL) was stirred at room temperature overnight. TLC monitored the reaction upon completion. Water (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (10 mL x 3). The combined organic solution was washed with brine, dried over MgSO$_4$, and concentrated. The crude product was purified through silica gel column chromatography (PE/EA = 2/1, v/v) to give the product 4 as a colorless oil.

(Z)-2-(((3-Hydroxy-1-phenyl-3-((p-tolyl)prop-1-en-1-yl)oxy)benzamide (4)

Yield 72 mg, 67%; colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15-8.12 (m, 1H), 7.66 (s, 1H), 7.35 (br, 2H), 7.22-7.09 (m, 6H), 7.07-7.00 (m, 2H), 6.98-6.96 (m, 1H), 6.71 (d, $J$ = 8.2 Hz, 1H), 6.15 (d, $J$ = 8.4 Hz, 1H), 6.08 (d, $J$ = 7.0 Hz, 1H), 5.52 (d, $J$ = 8.4 Hz, 1H), 2.29 (br, 1H), 2.24 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.7, 155.2, 148.4, 140.0, 137.8, 136.4, 133.4, 132.7, 129.4, 129.2, 128.8, 128.7, 126.1, 125.6, 122.5, 121.0, 115.1, 69.1, 21.1. HRMS calcd. for C$_{23}$H$_{22}$NO$_3$(M+H)$^+$: 360.1594, found: 360.1587.
5. NMR spectra of the (Z)-allyl alcohols 3.

3a
3b

[Chemical structure and NMR spectrum image]

S15
$3e$

![Chemical structure diagram 1](image1)

![Chemical structure diagram 2](image2)
3f
3n
3r

\[
\text{Structure 3r}
\]

\[
\text{N}
\]

\[
\text{Me}
\]

\[
\text{CH}
\]

\[
\text{N}
\]

\[
\text{Me}
\]

\[
\text{CH}
\]

\[
\text{N}
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\[
\text{Me}
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\text{CH}
\]

\[
\text{N}
\]

\[
\text{Me}
\]

\[
\text{CH}
\]

\[
\text{N}
\]

\[
\text{Me}
\]

\[
\text{CH}
\]
6. X-ray diffraction analysis of compound 3l.
**Table S1.** Crystal data and structure refinement for tj20180413a.

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<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
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<tr>
<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>293(2) K</td>
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<td>Wavelength</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>b = 10.2392(7) Å 76.617(6)°</td>
</tr>
<tr>
<td></td>
<td>c = 10.9408(7) Å 79.659(5)°</td>
</tr>
<tr>
<td>Volume</td>
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<tr>
<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<tr>
<td>Absorption coefficient</td>
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<tr>
<td>F(000)</td>
<td>512</td>
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<td>Crystal size</td>
<td>? x ? x ? mm³</td>
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<tr>
<td>Theta range for data collection</td>
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</tr>
<tr>
<td>Index ranges</td>
<td>-11&lt;=h&lt;=11, -11&lt;=k&lt;=12, -12&lt;=l&lt;=13</td>
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<tr>
<td>Reflections collected</td>
<td>5434</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>Completeness to theta = 25.099°</td>
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<tr>
<td>Absorption correction</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<td>R indices (all data)</td>
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<tr>
<td>Extinction coefficient</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.875 and -0.879 e.Å⁻³</td>
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</table>