Aryl Nitrenium Ions from N-Alkyl-N-arylamino-diazonium Precursors:

Synthesis and Reactivity

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A. Synthesis of triazenes 2

Typical reaction conditions for the synthesis of triazenes 2. To a stirred solution of diisopropylamine (1.1 mmol) in THF (5 mL, 0.2M) was added n-BuLi solution in hexanes (2.50–2.57 M, 1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. The appropriate carbonitrile (1.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Aryl azide (1.20 mmol) dissolved in HPMA (1.2 mL) was added dropwise, and then the resulting mixture was warmed to rt. After an hour, alkyllating or acylating reagent (1.5 mmol) was added dropwise, while the reaction flask was submerged in a water bath to avoid excessive heat generation. The resulting mixture was stirred for an hour, then concentrated under reduced pressure. The resulting crude mixture was partitioned between Et₂O (50 mL) and water (50 ml). The organic layer was separated, and the aqueous later was further extracted with Et₂O (2 × 30 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL). The resulting crude material was dried (Na₂SO₄), filtered, concentrated, and purified by automated column chromatography (silica gel, 10% EtOAc in hexanes) to afford triazene (2a–2aa).

1-(3-Methyl-3-phenyltriaz-1-en-1-yl)cyclohexanecarbonitrile (2a): white solid, mp 64–66 °C (hexanes); IR (neat) 1600, 1474, 1450 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.32 (m, 4H), 7.10 (tt, J = 7.2, 1.3 Hz, 1H), 3.44 (s, 3H), 2.15–2.00 (m, 2H), 1.90-1.82 (m, 4H), 1.81–1.67 (m, 3H), 1.42–1.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.1, 129.4, 123.8, 121.3, 116.8, 66.4, 36.4, 32.1, 25.0, 22.8; HRMS calcd for C₁₄H₁₉N₄ [M+H]+: 243.1610, found 243.1620.

2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2b): brown oil; IR (neat) 1599, 1471, 1446 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.71–7.64 (m, 2H), 7.51–7.35 (m, 7H), 7.15 (tt, J = 7.3, 1.2 Hz, 1H), 3.52 (s, 3H), 2.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 140.0, 129.4, 123.8, 121.3, 116.8, 66.4, 36.4, 32.1, 25.0, 22.8; HRMS calcd for C₁₆H₁₇N₄ [M+H]+: 265.1453, found 265.1445.

1-(3-(2-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)cyclohexanecarbonitrile (2c): white solid, mp 67–70 °C (hexanes); IR (neat) 1596, 1505, 1467, 1452 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.16 (m, 2H), 7.07–6.86 (m, 2H), 3.87 (s, 3H), 3.33 (s, 3H), 2.24–2.00 (m, 2H), 1.91–1.78 (m, 4H), 1.78–1.63 (m, 3H), 1.40–1.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 134.9, 127.6, 126.0, 121.5, 121.2, 112.3, 65.6, 55.9, 36.4, 25.0, 22.9; HRMS calcd for C₁₅H₂₁N₄O [M+H]+: 273.1715, found 273.1710.
1-(3-(3-Methoxyphenyl)-3-methyltriaz-1-en-yl)cyclohexanecarbonitrile (2d): yellow oil; IR (neat) 1602, 1477 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26 (t, \(J = 8.2\) Hz, 1H), 7.05 (t, \(J = 2.3\) Hz, 1H), 6.97 (ddd, \(J = 8.2, 2.5, 0.9\) Hz, 1H), 3.84 (s, 3H), 3.43 (s, 3H), 2.13–2.01 (m, 2H), 1.87 (ddd, \(J = 10.7, 9.5, 5.4, 2.1\) Hz, 4H), 1.81–1.68 (m, 2H), 1.44–1.22 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.6, 146.3, 130.1, 121.1, 109.3, 109.0, 102.8, 66.6, 55.5, 36.4, 32.0, 24.9, 22.8; HRMS calcd for C\(_{15}\)H\(_{21}\)N\(_4\)O [M+H]\(^+\): 273.1715, found 273.1717.

1-(3-Methyl-3-phenyltriaz-1-en-yl)cyclopentanecarbonitrile (2e): pale yellow solid, mp 55–57 °C (hexanes); IR (neat) 1599, 1474, 1450 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44–7.31 (m, 4H), 7.09 (tt, \(J = 7.2, 1.3\) Hz, 1H), 3.42 (s, 3H), 2.40–2.08 (m, 3H), 1.99–1.80 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.0, 129.3, 123.7, 122.1, 116.7, 70.0, 39.5, 32.0, 24.4; HRMS calcd for C\(_{13}\)H\(_{17}\)N\(_4\) [M+H]\(^+\): 229.1453, found 229.1449.

2-(3-(2-Chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2f): pale yellow oil; IR (neat) 1594, 1472 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68–7.60 (m, 2H), 7.46–7.36 (m, 3H), 7.30–7.24 (m, 2H), 7.23–7.17 (m, 1H), 3.42 (s, 3H), 1.98 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.9, 140.1, 130.7, 129.2, 128.9, 128.5, 128.2, 127.7, 126.4, 126.1, 120.7, 67.2, 37.8, 29.2; HRMS calcd for C\(_{16}\)H\(_{16}\)ClN\(_4\) [M+H]\(^+\): 299.1063, found 299.1057.

2-(3-(3-Chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2g): orange-yellow oil; IR (neat) 1596, 1476, 1466 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.69–7.58 (m, 2H), 7.44–7.35 (m, 2H), 7.35–7.27 (m, 1H), 7.27–7.16 (m, 1H), 7.00–6.89 (m, 2H), 3.81 (s, 3H), 3.38 (s, 3H), 1.96 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.6, 140.5, 134.5, 128.8, 128.4, 127.7, 126.2, 126.0, 121.1, 112.2, 66.9, 55.5, 37.4, 29.3; HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_4\)O [M+H]\(^+\): 295.1559, found 295.1551.
2-(3-(3-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2i): orange-yellow oil; IR (neat) 1602, 1474, 1466, cm−1; 1H NMR (400 MHz, CDCl3) δ 7.66–7.56 (m, 2H), 7.46–7.37 (m, 2H), 7.37–7.31 (m, 1H), 7.25 (t, J = 8.2 Hz, 1H), 7.11–7.04 (m, 1H), 6.97 (dd, J = 8.4, 2.2 Hz, 1H), 6.66 (dd, J = 8.4, 2.4 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 2.02 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.6, 146.2, 139.9, 130.1, 129.0, 128.6, 126.2, 120.8, 109.7, 109.0, 102.9, 68.0, 55.5, 32.4, 29.1; HRMS calcd for C17H19N4O [M+H]+: 295.1559, found 295.1554.

2-(3-Acetyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2j): brown oil; IR (neat) 1716, 1513, 1374 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.50–7.40 (m, 3H), 7.39– 7.29 (m, 5H), 7.06– 6.99 (m, 2H), 2.68 (s, 3H), 1.89 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 173.1, 138.0, 134.9, 129.5, 129.4, 129.1, 128.8, 125.8, 119.0, 70.0, 28.6, 22.9; HRMS calcd for C17H17N4O [M+H]+: 293.1402, found 293.1391.

2-(3-Ethyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2k): pale yellow oil; IR (neat) 1599, 1474, 1447 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.60 (dt, J = 6.9, 1.4 Hz, 2H), 7.45–7.35 (m, 4H), 7.35–7.26 (m, 3H), 7.06 (t, J = 7.4 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.98 (s, 3H), 1.17 (t, J = 7.1 Hz, 2H), 1.71–1.55 (m, 2H), 1.36 (tq, J = 14.8, 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 143.8, 140.0, 129.4, 128.9, 128.5, 126.0, 120.7, 116.4, 67.8, 39.7, 28.0, 10.9; HRMS calcd for C17H19N4 [M+H]+: 279.1610, found 279.1605.

2-(3-Butyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2l): red-orange oil; IR (neat) 1598, 1474, 1447 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.68–7.57 (m, 2H), 7.48–7.39 (m, 4H), 7.39–7.31 (m, 3H), 7.10 (tt, J = 7.2, 1.2 Hz, 1H), 4.19–4.01 (m, 2H), 2.01 (s, 3H), 1.71–1.55 (m, 2H), 1.36 (tq, J = 14.8, 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 144.3, 140.1, 129.5, 129.0, 128.6, 126.2, 123.8, 120.9, 116.6, 68.0, 44.6, 29.2, 27.9, 20.6, 14.0; HRMS calcd for C19H23N4 [M+H]+: 307.1923, found 307.1937.

2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2-phenylbutanenitrile (2m): orange-yellow oil; IR (neat) 1599, 1474, 1447 cm−1; 1H NMR (400 MHz, CDCl3) δ 7.66–7.60 (m, 2H), 7.44–7.36 (m, 4H), 7.36–7.29 (m, 3H), 7.08 (tt, J = 7.4, 1.2 Hz, 1H), 3.47 (s, 3H), 2.32 (A of ABX3, JAB = 13.6, JAX = 7.2 Hz, 1H), 2.26 (B of ABX3, JAB = 13.6, JBX = 7.2 Hz, 1H), 1.02 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 144.8,
139.1, 129.3, 128.8, 128.5, 126.4, 123.8, 119.6, 116.8, 73.5, 35.7, 32.3, 9.2; HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{N}_{4}$ $[\text{M+H}]^+$: 279.1610, found 279.1595.

2-Methyl-2-(3-methyl-3-phenyltriaz-1-en-1-yl)propanenitrile ($2n$): yellow oil; IR (neat) 1600, 1475, 1451 cm$^{-1}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.46–7.31 (m, 4H), 7.11 (tt, $J$ = 6.8, 1.4 Hz, 1H), 3.44 (s, 3H), 1.68 (s, 6H); $^1\text{C}$ NMR (100 MHz, CDCl$_3$) $\delta$ 145.0, 129.4, 123.9, 122.3, 116.9, 60.7, 32.2, 27.6; HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{N}_{4}$ $[\text{M+H}]^+$: 203.1297, found 203.1287.

2-(3-(2-Methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-methylpropanenitrile ($2o$): off-white solid, mp 78–79 °C; IR (neat) 1596, 1505, 1468 cm$^{-1}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.21 (m, 2H), 7.02–6.94 (m, 2H), 3.87 (s, 3H), 3.33 (s, 3H), 1.66 (s, 6H); $^1\text{C}$ NMR (100 MHz, CDCl$_3$) $\delta$ 152.7, 127.7, 126.0, 122.6, 121.2, 112.2, 100.2, 60.0, 55.9, 37.2, 27.6; HRMS calcd for $\text{C}_{12}\text{H}_{17}\text{N}_{4}\text{O}$ $[\text{M+H}]^+$: 233.1402, found 233.1411.

2-(3-Methyl-3-phenyltriaz-1-en-1-yl)-2,2-diphenylacetonitrile ($2p$): off-white solid, mp 98–102 °C; IR (neat) 1598, 1470, 1445 cm$^{-1}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.60–7.50 (m, 4H), 7.47–7.41 (m, 3H), 7.40–7.27 (m, 7H), 7.09 (tt, $J$ = 7,4, 1.2 Hz, 1H), 3.54 (s, 3H); $^1\text{C}$ NMR (100 MHz, CDCl$_3$) $\delta$ 144.8, 140.3, 129.4, 128.9, 128.7, 127.5, 124.1, 119.7, 117.0, 74.8, 32.7; HRMS calcd for $\text{C}_{21}\text{H}_{19}\text{N}_{4}$ $[\text{M+H}]^+$: 327.1610, found 327.1599.

1-(3-methyl-3-(p-tolyl)triaz-1-en-1-yl)cyclohexane-1-carbonitrile ($2q$): off-white solid, mp 103–105 °C (hexanes); IR (neat) 1612, 1516, 1470 cm$^{-1}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.32–7.26 (m, 2H), 7.19–7.12 (m, 2H), 3.41 (s, 3H), 2.33 (s, 3H), 2.14–2.02 (m, 2H), 1.94–1.79 (m, 4H), 1.79–1.65 (m, 3H), 1.40–1.28 (m, 1H); $^1\text{C}$ NMR (100 MHz, CDCl$_3$) $\delta$ 142.8, 133.4, 129.9, 121.3, 117.0, 66.2, 36.5, 32.4, 25.0, 22.8, 20.9; HRMS calcd for $\text{C}_{13}\text{H}_{21}\text{N}_{4}$ $[\text{M+H}]^+$: 257.1766, found 257.1783.

1-(3-(4-methoxyphenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile ($2r$): white solid, mp 45–46 °C (hexanes); IR (neat) 1612, 1516, 1470 cm$^{-1}$; $^1\text{H}$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.34–7.28 (m, 2H),
6.94–6.86 (m, 2H), 3.80 (s, 3H), 3.40 (s, 3H), 2.12–2.02 (m, 2H), 1.93–1.79 (m, 4H), 1.79–1.66 (m, 3H), 1.39–1.25 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.4, 138.9, 121.4, 118.6, 114.6, 66.1, 55.7, 36.4, 32.9, 24.9, 22.8. HRMS calcd for C$_{15}$H$_{21}$N$_4$O [M+H]$^+$: 273.1715, found 273.1704.

1-(3-(4-((tert-butyl)phenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (2s): white solid, mp 81–82 °C (hexanes); IR (neat) 1610, 1516, 1467 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41–7.36 (m, 2H), 7.36–7.31 (m, 2H), 3.42 (s, 3H), 2.14–2.02 (m, 2H), 1.86 (dtt, $J$ = 14.0, 8.6, 2.9 Hz, 4H), 1.79–1.66 (m, 4H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.8, 142.7, 126.2, 121.3, 116.7, 66.3, 36.4, 34.5, 32.3, 31.6, 25.0, 22.8; HRMS calcd for C$_{18}$H$_{27}$N$_4$ [M+H]$^+$: 299.2236, found 299.2223.

1-(3-(4-chlorophenyl)-3-methyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (2t): white solid, mp 108–109 °C (hexanes); IR (neat) 1596, 1496, 1474 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39–7.28 (m, 4H), 3.41 (s, 3H), 2.13–2.01 (m, 2H), 1.91–1.83 (m, 4H), 1.82–1.69 (m, 3H), 1.42–1.26 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.6, 129.4, 128.9, 121.0, 117.8, 66.6, 36.3, 32.0, 24.9, 22.8; HRMS calcd for C$_{14}$H$_{18}$ClN$_4$ [M+H]$^+$: 277.1220, found 277.1230.

2-(3-(3,4-dimethylphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2u): brown oil; IR (neat) 1613, 1466, 1446 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67–7.59 (m, 2H), 7.45–7.37 (m, 2H), 7.37–7.30 (m, 1H), 7.22–7.17 (m, 1H), 7.17–7.07 (m, 2H), 3.46 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 2.00 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.0, 140.3, 137.7, 132.5, 130.4, 128.9, 128.5, 126.2, 121.1, 118.6, 114.8, 67.5, 32.9, 29.2, 20.4, 19.2; HRMS calcd for C$_{18}$H$_{21}$N$_4$ [M+H]$^+$: 293.1766, found 293.1747.

2-(3-methyl-3-(p-tolyl)triaz-1-en-1-yl)-2-phenylpropanenitrile (2v): orange oil; IR (neat) 1612, 1516, 1470 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32–7.26 (m, 2H), 7.19–7.12 (m, 2H), 3.41 (s, 3H), 2.33 (s, 3H), 2.14–2.02 (m, 2H), 1.94–1.79 (m, 4H), 1.79–1.65 (m, 3H), 1.40–1.28 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.8, 133.4, 129.9, 121.3, 117.0, 66.2, 36.5, 32.4, 25.0, 22.8, 20.9; HRMS calcd for C$_{17}$H$_{18}$N$_4$ [M+H]$^+$: 279.1610, found 279.1591.
2-(3-(4-methoxyphenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2w): brown oil; IR (neat) 1512, 1462, 1245 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64–7.61 (m, 1H), 7.44–7.38 (m, 1H), 7.36–7.31 (m, 2H), 6.93–6.89 (m, 1H), 3.80 (s, 3H), 3.47 (s, 3H), 2.00 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.7, 140.3, 138.8, 128.9, 128.5, 126.2, 121.1, 118.8, 114.6, 67.5, 55.8, 33.3, 29.3; HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_4\)O [M+H]\(^+\): 295.1559, found 295.1542.

2-(3-(4-((\textit{tert}-butyl)phenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2x): colorless oil; IR (neat) 1610, 1516, 1465 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64–7.60 (m, 2H), 7.43–7.32 (m, 7H), 3.48 (s, 3H), 2.00 (s, 3H), 1.32 (s, 9H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.1, 142.6, 140.2, 129.0, 128.6, 126.3, 126.2, 121.0, 116.9, 67.6, 34.5, 32.7, 31.6, 29.2; HRMS calcd for C\(_{20}\)H\(_{25}\)N\(_4\) [M+H]\(^+\): 321.2079, found 321.2058.

2-(3-(4-chlorophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2y): brown oil; IR (neat) 1596, 1496, 1474 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64–7.59 (m, 2H), 7.45–7.29 (m, 7H), 3.47 (s, 3H), 2.01 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.5, 139.8, 129.4, 129.3, 129.0, 128.7, 126.2, 120.7, 118.0, 68.0, 32.4, 29.2; HRMS calcd for C\(_{16}\)H\(_{16}\)ClN\(_4\) [M+H]\(^+\): 299.1063, found 299.1043.

2-(3-(4-bromophenyl)-3-methyltriaz-1-en-1-yl)-2-phenylpropanenitrile (2z): yellow oil; IR (neat) 1591, 1492, 1472 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.65–7.58 (m, 2H), 7.50–7.27 (m, 7H), 3.47 (s, 3H), 2.02 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.0, 139.7, 132.4, 129.1, 128.8, 126.2, 120.7, 118.3, 116.8, 68.0, 32.3, 29.1; HRMS calcd for C\(_{16}\)H\(_{16}\)BrN\(_4\) [M+H]\(^+\): 343.0558, found 343.0537.

1-(3-(pent-4-en-1-yl)-3-phenyltriaz-1-en-1-yl)cyclohexane-1-carbonitrile (2aa): yellow oil; IR (neat) 1641, 1599, 1479, 1452 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47–7.30 (m, 4H), 7.09 (tt, \(J\) = 7.1, 1.3 Hz, 1H), 5.83 (ddt, \(J\) = 17.2, 10.4, 6.6 Hz, 1H), 5.21–4.91 (m, 2H), 4.15–3.94 (m, 2H), 2.14–2.02 (m, 4H), 1.92–1.81 (m, 4H), 1.81–1.66 (m, 5H), 1.42–1.29 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.4, 137.7, 129.5, 123.5, 121.3, 116.5, 115.5, 66.4, 44.0, 36.3, 31.4, 25.0, 24.6, 22.8. HRMS calcd for C\(_{18}\)H\(_{25}\)N\(_4\) [M+H]\(^+\): 297.2079, found 297.2063.
B. Characterization of Triazenes 3 Obtained as minor isomer

All compounds listed in section B were obtained as minor isomer, and only the characteristic $^1$H NMR peaks were given. For the full characterization of 3a and 3b, see section C.

1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclohexanecarbonitrile (3a): see section C

2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3b): see section C

1-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexanecarbonitrile (3c):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.92 (s, 3H), 3.30 (s, 3H).

1-(3-(3-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexanecarbonitrile (3d):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.26 (s, 3H).

1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclopentanecarbonitrile (3e):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.21 (s, 3H).

2-(3-(2-Chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3f):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.09 (s, 3H), 2.25 (s, 3H).
2-(3-(3-Chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3g):
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.04 (s, 3H), 2.25 (s, 3H).

![Structure of 3g](image)

2-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3h):
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.93 (s, 3H), 3.07 (s, 3H), 2.25 (s, 3H).

![Structure of 3h](image)

2-(3-(3-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3i):
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.84 (s, 3H), 3.03 (s, 3H), 2.25 (s, 3H).

![Structure of 3i](image)

2-(1-Acetyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3j): not observed.

2-(1-Ethyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3k):
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.61 (A of ABX \(J_{AB} = 14.0\), \(J_{AX} = 7.0\) Hz, 1H), 3.52 (A of ABX \(J_{AB} = 13.9\), \(J_{AX} = 7.0\) Hz, 1H), 2.20 (s, 3H).

![Structure of 3k](image)

2-(3-Butyl-3-phenyltriaz-1-en-1-yl)-2-phenylpropanenitrile (3l):
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.26 (t, \(J = 6.5\) Hz, 2H), 1.78–1.71 (m, 2H), 1.51–1.41 (m, 1H), 0.96 (t, \(J = 7.4\) Hz, 3H).

![Structure of 3l](image)

2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylbutanenitrile (3m): not observed.
2-Methyl-2-(1-methyl-3-phenyltriaz-2-en-1-yl)propanenitrile (3n):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.23 (s, 3H), 1.88 (s, 6H).

2-(3-(2-Methoxyphenyl)-1-methyltriaz-2-en-1-yl)2-methylpropanenitrile (3o):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.92 (s, 3H), 3.28 (s, 3H), 1.87 (s, 6H).

2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2,2-diphenylacetonitrile (3p): not observed.

1-(1-methyl-3-(p-tolyl)triaz-2-en-1-yl)cyclohexane-1-carbonitrile (3q):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.22 (s, 3H).

1-(3-(4-methoxyphenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (3r):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.82 (s, 3H), 3.20 (s, 3H).

1-(3-(4-(tert-butyl)phenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (3s):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.23 (s, 3H).
1-(3-(4-chlorophenyl)-1-methyltriaz-2-en-1-yl)cyclohexane-1-carbonitrile (3t):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.25 (s, 3H).

(E)-2-(3-(3,4-dimethylphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3u):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.99 (s, 3H).

2-(1-methyl-3-(p-tolyl)triaz-2-en-1-yl)-2-phenylpropanenitrile (3v):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.00 (s, 3H), 2.04 (s, 3H).

2-(3-(4-methoxyphenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3w):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.60 (s, 3H), 2.86 (s, 3H).

2-(3-(4-(tert-butyl)phenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3x):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.00 (s, 3H), 2.25 (s, 3H).

2-(3-(4-chlorophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3y):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.02 (s, 3H), 2.24 (s, 3H).

2-(3-(4-bromophenyl)-1-methyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3z):
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.02 (s, 3H), 2.25 (s, 3H).
C. Synthesis of Triazene 3

Typical reaction conditions for the synthesis of triazenes 3. To a stirred solution of diisopropylamine (1.1 mmol) in THF (5 mL, 0.2M) was added n-BuLi solution in hexanes (2.50–2.57 M, 1.05 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. The appropriate carbonitrile (1.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Aryl azide (1.20 mmol) dissolved in HPMA (1.2 mL) was added dropwise, and then the resulting mixture was warmed to rt. After an hour, alkylating or acylating reagent (1.5 mmol) was added dropwise, while the reaction flask was submerged in a water bath to avoid excessive heat generation. The resulting mixture was stirred for an hour, then concentrated under reduced pressure. The resulting crude mixture was partitioned between Et₂O (50 mL) and water (50 mL). The organic layer was separated, and the aqueous layer was further extracted with Et₂O (2 × 30 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL). The resulting crude material was dried (Na₂SO₄), filtered, concentrated, and purified by automated column chromatography (silica gel, 10% EtOAc in hexanes) to afford triazenes (3a, 3b).

1-(1-Methyl-3-phenyltriaz-2-en-1-yl)cyclohexanecarbonitrile (3a): colorless oil; IR (neat) 1596, 1465, 1442 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.48–7.42 (m, 2H), 7.40–7.30 (m, 2H), 7.25–7.17 (m, 1H), 3.25 (s, 3H), 2.50–2.39 (m, 2H), 2.05 (ddd, J = 13.6, 11.5, 3.7 Hz, 2H), 1.95–1.83 (m, 2H), 1.81–1.66 (m, 3H), 1.41–1.29 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 128.6, 126.4, 120.9, 119.1, 62.9, 34.5, 30.8, 24.3, 22.3; HRMS calcd for C₂₁H₁₉N₄ [M+H]⁺: 243.1610, found 243.1606.

2-(1-Methyl-3-phenyltriaz-2-en-1-yl)-2-phenylpropanenitrile (3b): colorless oil; IR (neat) 1597, 1465, 1444 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.49 (m, 4H), 7.48–7.34 (m, 5H), 7.29–7.22 (m, 1H), 3.03 (s, 3H), 2.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 138.9, 129.5, 129.4, 129.2, 127.2, 125.5, 121.5, 119.4, 66.6, 33.5, 28.8; HRMS calcd for C₁₆H₁₇N₄ [M+H]⁺: 265.1453, found 265.1461.

D. Synthesis of cyclohexenecarboxyimidamide 4a

N’-phenylcyclohex-1-ene-1-carboximidamide (4a) To a stirred solution of diisopropylamine (0.31 mL, 2.2 mmol) in THF (10 mL) was added 2.45M n-BuLi solution in hexanes (0.86, 2.1 mmol) at -78 °C. The resulting mixture was stirred for 20 min at -78 °C. Cyclohexanecarbonitrile (0.24 mL, 2.0 mmol) was added dropwise at -78 °C, and subsequently stirred for 20 minutes. Phenyl azide (290 mg, 2.4 mmol) dissolved in THF (2.4 mL) was added dropwise, and then the resulting mixture was stirred at -78 °C for 30 min. Then the reaction mixture was warmed to rt. After an hour, sat. aq. NH₄Cl solution (5 mL) was added. The resulting crude mixture extracted with Et₂O (3 × 20 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL). The resulting crude material was dried (Na₂SO₄), filtered, concentrated, and purified by automated column chromatography (silica gel, 90:9:1 CH₂Cl₂/MeOH/NH₄OH) to afford 4a (327 mg); brown oil; RF = 0.29 (90:9:1 CH₂Cl₂/MeOH/NH₄OH); IR (neat) 1621, 1581 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.43–6.40 (m, 1H), 4.32 (s, 2H), 2.40–2.35 (m, 2H), 2.21–2.15 (m, 2H), 1.75–1.61 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 149.5, 134.4, 130.4, 129.6, 129.5, 123.0, 121.9, 121.9, 25.7, 25.4, 22.5, 21.9; HRMS calcd for C₁₁H₁₇N₂ [M+H]⁺: 201.1392, found 201.1408.
E. Optimization of α-arylation conditions

a. Optimization of para-selective arylation conditions

![Reaction Scheme]

<table>
<thead>
<tr>
<th>entry</th>
<th>acid</th>
<th>solvent</th>
<th>conditions</th>
<th>yield(7a)</th>
<th>crude nmr ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BF$_3$·OEt$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>41%</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>BF$_3$·OEt$_2$</td>
<td>MeCN</td>
<td>0 ºC, 1h</td>
<td>43%</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>BF$_3$·OEt$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>-20 ºC, 1h</td>
<td>39%</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>BF$_3$·OEt$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>-45 ºC, 1h</td>
<td>22%</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>BF$_3$·OEt$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>-78 ºC, 1h</td>
<td>0%</td>
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</tr>
<tr>
<td>6</td>
<td>BF$_3$·OEt$_2$</td>
<td>EtOAc</td>
<td>0 ºC, 1h</td>
<td>34%</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>BF$_3$·OEt$_2$</td>
<td>CHCl$_3$</td>
<td>0 ºC, 1h</td>
<td>21%</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>BF$_3$·OEt$_2$</td>
<td>ether</td>
<td>0 ºC, 1h</td>
<td>7%</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>BF$_3$·OEt$_2$</td>
<td>acetone</td>
<td>0 ºC, 1h</td>
<td>7%</td>
<td>63</td>
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<tr>
<td>10</td>
<td>BF$_3$·OEt$_2$</td>
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<td>0 ºC, 1h</td>
<td>28%</td>
<td>91</td>
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<tr>
<td>11</td>
<td>TiCl$_4$</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>—%[b]</td>
<td>59</td>
</tr>
<tr>
<td>12</td>
<td>SnCl$_4$</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>20%</td>
<td>84</td>
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<tr>
<td>13</td>
<td>BBr$_3$</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>32%</td>
<td>overlap with impurity</td>
</tr>
<tr>
<td>14</td>
<td>AlCl$_3$</td>
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<td>0 ºC, 1h</td>
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<td>55</td>
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<tr>
<td>15</td>
<td>MgCl$_2$</td>
<td>CH$_2$Cl$_2$</td>
<td>rt, 1h</td>
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<td>56</td>
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<tr>
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<td>HfCl$_4$</td>
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<td>0 ºC, 1h</td>
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<td>58</td>
</tr>
<tr>
<td>17</td>
<td>ZrCl$_4$</td>
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<td>0 ºC, 1h</td>
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<td>72</td>
</tr>
<tr>
<td>18</td>
<td>Sc(OTf)$_3$</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>19%</td>
<td>95[c]</td>
</tr>
<tr>
<td>19</td>
<td>MeOTf</td>
<td>CH$_2$Cl$_2$</td>
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<td>0%</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>TMSOTf</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>TFA</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>37%[d]</td>
<td>62</td>
</tr>
<tr>
<td>22</td>
<td>CSA</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>10%</td>
<td>58</td>
</tr>
<tr>
<td>23</td>
<td>TfOH</td>
<td>CH$_2$Cl$_2$</td>
<td>0 ºC, 1h</td>
<td>26%</td>
<td>62</td>
</tr>
<tr>
<td>24</td>
<td>TfOH</td>
<td>MeOH</td>
<td>0 ºC, 1h</td>
<td>22%</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>toluene</td>
<td>reflux</td>
<td>—%[b]</td>
<td></td>
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</tr>
<tr>
<td>26</td>
<td>aceton</td>
<td>reflux</td>
<td>—%[b]</td>
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<tr>
<td>27</td>
<td>CuCl</td>
<td>MeCN/water</td>
<td>rt, 18 h</td>
<td>15%[d]</td>
<td>100</td>
</tr>
</tbody>
</table>

[a] reaction conditions: 2 (0.25 mmol), solvent (0.2M), acid (0.3 mmol) [b] the existence of the product in the complex mixture was confirmed by crude $^1$H NMR. However, not isolated. [c] large amount of unidentified side product produced. [d] The yields were inconsistent under given conditions. Average yield from 23–52%
b. Optimization of ortho-selective arylation conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>conditions</th>
<th>yield</th>
<th>crude nmr ratio</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>CH$_2$Cl$_2$</td>
<td>0 °C - rt, 1h</td>
<td>39%</td>
<td>45 35 30</td>
</tr>
<tr>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>rt, 1h</td>
<td>38%</td>
<td>42 31 27</td>
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<td>3</td>
<td>CH$_2$Cl$_2$</td>
<td>-20 °C, 1h</td>
<td>36%</td>
<td>40 35 25</td>
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<tr>
<td>4</td>
<td>CH$_2$Cl$_2$</td>
<td>-45 °C, 1h</td>
<td>41%</td>
<td>38 35 27</td>
</tr>
<tr>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>0 °C, 18h</td>
<td>48%</td>
<td>45 32 22</td>
</tr>
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<td>6</td>
<td>toluene</td>
<td>0 °C - rt, 1h</td>
<td>-%[b]</td>
<td>42 24 35</td>
</tr>
<tr>
<td>7</td>
<td>THF</td>
<td>0 °C - rt, 1h</td>
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</tr>
<tr>
<td>8</td>
<td>ether</td>
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<td>-%[b]</td>
<td>42 19 39</td>
</tr>
<tr>
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<tr>
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<td>54 24 22</td>
</tr>
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<td>MeOH</td>
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<td>12</td>
<td>CF$_3$CH$_2$OH</td>
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<td>41 39 20</td>
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<tr>
<td>14</td>
<td>(CF$_3$)$_2$CH$_2$OH[d]</td>
<td>0 °C - rt, 1h</td>
<td>38%</td>
<td>50 41 9</td>
</tr>
</tbody>
</table>

[a] reaction conditions: 2 (0.25 mmol), solvent (0.2M), acid (0.3 mmol) [b] not isolated. [c] 10 mol% of TFA was used. [d] Acidic solvent promoted the reaction without acid. [d] reaction proceed without acid.
F. The para-selective arylation of α-carbonitriles

Typical reaction conditions for the synthesis of α-(4-aminoaryl)carbonitrile products 7. To a solution of triazene (0.25 mmol) in CH₂Cl₂ (0.2M, 1.25 mL) at 0 °C was added BF₃•OEt₂ (0.3 mmol) dropwise. Gentle bubbling continued for approximately 3 to 5 minutes. The resulting mixture was continued stirring for an hour at 0 °C. The reaction solution gradually turned brown or black. The reaction mixture was quenched with 1M NaOH (3 mL), and the aq. layer was extracted 3 times with CH₂Cl₂ (5 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated. The resulting crude material was purified by automated column chromatography (SiO₂, 20% EtOAc/hexanes) to afford the corresponding α-(4-aminoaryl)carbonitrile products (7a–7p, 7aa).

1-(4-(Methylamino)phenyl)cyclohexanecarbonitrile (7a): white solid, mp 91–95 °C; IR (neat) 3413, 2229, 1615 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.26 (m, 2H), 6.64–6.57 (m, 2H), 3.77 (bs, 1H), 2.84 (s, 3H), 2.24–2.06 (m, 2H), 1.92–1.75 (m, 5H), 1.74–1.63 (m, 2H), 1.33–1.18 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 130.1, 126.6, 123.5, 112.6, 43.5, 37.7, 30.8, 25.3, 23.9; HRMS calcd for C₁₄H₁₉N₂ [M+H]+: 215.1548, found 215.1558.

2-(4-(Methylamino)phenyl)-2-phenylpropanenitrile (7b): brown oil; IR (neat) 3413, 2233, 1613 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.22 (m, 5H), 7.20–7.12 (m, 2H), 6.61–6.48 (m, 2H), 3.79 (bs, 1H), 2.81 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 142.4, 129.5, 128.9, 127.8, 127.8, 126.7, 124.1, 112.5, 45.6, 30.7, 28.5; HRMS calcd for C₁₆H₁₇N₂ [M+H]+: 237.1392, found 237.1392.

1-(3-Methoxy-4-(methylamino)phenyl)cyclohexanecarbonitrile (7c): off-white solid, mp 76–79 °C; IR (neat) 3431, 2231, 1613 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.97 (dd, J = 8.2, 2.2 Hz, 1H), 6.88 (d, J = 2.1 Hz, 1H), 6.56 (d, J = 8.3 Hz, 1H), 4.26 (bs, 1H), 3.87 (s, 3H), 2.86 (s, 3H), 2.24–2.09 (m, 2H), 1.89–1.79 (m, 5H), 1.78–1.65 (m, 2H), 1.36–1.16 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.0, 139.1, 129.5, 123.5, 118.1, 109.0, 107.3, 55.7, 43.8, 37.8, 30.5, 25.3, 23.9; HRMS calcd for C₁₅H₂₁N₂O [M+H]+: 245.1654, found 245.1656.

1-(2-Methoxy-4-(methylamino)phenyl)cyclohexanecarbonitrile (7d): yellow solid, mp 100–102 °C; IR (neat) 3402, 2230, 1614 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, J = 8.2 Hz, 1H), 6.19 (q, J = 2.3 Hz,
3H), 6.17 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 2.84 (s, 3H), 2.34 (ddt, J = 13.5, 3.1, 1.7 Hz, 2H), 1.91–1.75 (m, 5H), 1.69 (td, J = 12.7, 3.9 Hz, 2H), 1.31–1.23 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 158.8, 150.5, 126.8, 123.3, 118.2, 104.1, 97.3, 55.6, 40.3, 35.1, 30.84, 25.58, 23.61; HRMS calcd for C15H21N2O [M+H]+: 245.1654, found 245.1656.

1-(4-(Methylamino)phenyl)cyclopentanecarbonitrile (7e): off-white solid, mp 76–78 °C; IR (neat) 3399, 2222, 1612 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.29–7.20 (m, 2H), 6.64–6.52 (m, 2H), 3.78 (bs, 1H), 2.83 (s, 3H), 2.49–2.36 (m, 2H), 2.11–1.95 (m, 4H), 1.93–1.81 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 148.9, 128.1, 127.1, 125.2, 112.6, 47.1, 40.4, 30.8, 24.2; HRMS calcd for C13H17N2 [M+H]+: 201.1392, found 201.1398.

2-(3-Chloro-4-(methylamino)phenyl)-2-phenylpropanenitrile (7f): brown oil; IR (neat) 3421, 2235, 1610 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.40–7.33 (m, 4H), 7.33–7.27 (m, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.17 (dd, J = 8.5, 2.3 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 4.41 (q, J = 5.1 Hz, 1H), 2.90 (d, J = 5.2 Hz, 3H), 2.04 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 144.7, 141.8, 129.8, 129.1, 128.0, 127.5, 126.6, 126.5, 123.7, 119.2, 110.6, 45.4, 30.5, 28.4; HRMS calcd for C16H16ClN2 [M+H]+: 271.1002, found 271.0996.

2-(2-Chloro-4-(methylamino)phenyl)-2-phenylpropanenitrile (7g): brown oil; IR (neat) 3412, 2235, 1608 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.36 (d, J = 8.6 Hz, 1H), 7.34–7.23 (m, 5H), 6.61 (d, J = 2.6 Hz, 1H), 6.54 (dd, J = 8.6, 2.6 Hz, 1H), 2.82 (s, 4H), 2.05 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 150.4, 142.4, 135.4, 128.8, 128.8, 127.5, 125.9, 124.3, 122.6, 114.9, 110.6, 45.0, 30.6, 30.0; HRMS calcd for C16H16ClN2 [M+H]+: 271.1002, found 271.1000.

2-(3-Methoxy-4-(methylamino)phenyl)-2-phenylpropanenitrile (7h): brown oil; IR (neat) 3430, 2233, 1612 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 7.44–7.20 (m, 5H), 6.88 (dd, J = 8.2, 2.2 Hz, 1H), 6.69 (d, J = 2.1 Hz, 1H), 6.52 (d, J = 8.2 Hz, 1H), 4.28 (bs, 1H), 3.76 (s, 3H), 2.84 (s, 3H), 2.04 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 147.0, 142.3, 139.2, 128.9, 128.6, 127.8, 126.7, 124.2, 119.4, 108.6, 108.4, 55.6, 45.9, 30.4, 28.6; HRMS calcd for C17H19N2O [M+H]+: 267.1497, found 267.1501.
2-(2-Methoxy-4-(methylamino)phenyl)-2-phenylpropanenitrile (7i): brown oil; IR (neat) 3410, 2235, 1613 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38–7.18 (m, 5H), 7.15 (d, \(J = 8.5\) Hz, 1H), 6.21 (dd, \(J = 8.4, 2.3\) Hz, 1H), 6.11 (d, \(J = 2.3\) Hz, 1H), 3.85 (s, 1H), 3.56 (s, 3H), 2.83 (s, 3H), 1.99 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.5, 151.1, 143.3, 128.4, 127.7, 127.0, 125.8, 123.8, 117.3, 103.7, 97.5, 55.6, 42.9, 30.8, 28.5; HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_2\)O \([\text{M+H}]^+:\) 267.1497, found 267.1499.

N-(4-(1-Cyano-1-phenylethyl)phenyl)acetamide (7j): yellow oil; IR (neat) 3300, 1672, 1601 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53–7.48 (m, 2H), 7.47 (s, 1H), 7.38–7.34 (m, 4H), 7.33–7.28 (m, 3H), 2.16 (s, 3H), 2.06 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.7, 141.4, 137.8, 137.0, 129.1, 128.2, 127.6, 126.7, 123.6, 120.3, 45.9, 28.3, 24.8; HRMS calcd for C\(_{17}\)H\(_{20}\)N\(_3\)O \([\text{M+NH}_4]^+:\) 282.1606, found 282.1598.

2-(4-(Ethylamino)phenyl)-2-phenylpropanenitrile (7k): pale brown oil; IR (neat) 3396, 2233, 1612 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43–7.21 (m, 5H), 7.17–7.05 (m, 2H), 3.66 (bs, 1H), 3.13 (q, \(J = 7.1\) Hz, 2H), 2.02 (s, 3H), 1.23 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.1, 142.4, 129.4, 128.9, 127.8, 127.8, 126.7, 124.1, 112.7, 45.6, 38.5, 28.5, 15.0; HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_2\) \([\text{M+H}]^+:\) 251.1548, found 251.1560.

2-(4-(Butylamino)phenyl)-2-phenylpropanenitrile (7l): brown oil; IR (neat) 3400, 2234, 1613 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47–7.23 (m, 5H), 7.18–7.10 (m, 2H), 6.58–6.49 (m, 2H), 3.69 (bs, 1H), 3.13 (q, \(J = 7.1\) Hz, 2H), 2.02 (s, 3H), 1.67–1.49 (m, 2H), 1.48–1.33 (m, 2H), 0.95 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.2, 142.4, 129.3, 128.9, 127.8, 127.8, 126.7, 124.1, 112.7, 45.6, 43.7, 31.7, 28.5, 20.4, 14.1; HRMS calcd for C\(_{19}\)H\(_{23}\)N\(_2\) \([\text{M+H}]^+:\) 279.1861, found 279.1877.

2-(4-(Methylamino)phenyl)-2-phenylbutanenitrile (7m): pale yellow oil; IR (neat) 3413, 2233, 1613 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42–7.29 (m, 4H), 7.28–7.22 (m, 1H), 7.21–7.12 (m, 2H), 6.60–6.51 (m, 2H), 2.81 (s, 3H), 2.36 (p, \(J = 7.3\) Hz, 2H), 1.04 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.9,
141.1, 128.9, 128.5, 128.10, 127.7, 127.1, 122.9, 112.5, 52.0, 33.1, 30.8, 10.4; HRMS calcd for C_{17}H_{19}N_{2} [M+H]^+: 251.1548, found 251.1553.

2-Methyl-2-(4-(methylamino)phenyl)propanenitrile (7n): pale yellow oil; IR (neat) 3410, 2234, 1615 cm^{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.44–7.13 (m, 1H), 6.76–6.30 (m, 1H), 2.83 (s, 2H), 1.68 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 148.9, 129.9, 126.2, 125.3, 112.6, 36.4, 30.8, 29.4; HRMS calcd for C\textsubscript{11}H\textsubscript{15}N\textsubscript{2} [M+H]^+: 175.1235, found 175.1228.

2-(3-Methoxy-4-(methylamino)phenyl)-2-methylpropanenitrile (7o): colorless oil; IR (neat) 3428, 2233, 1614 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta 6.95 (dd, J = 8.2, 2.2 Hz, 1H), 6.85 (d, J = 2.2 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H), 2.86 (s, 3H), 1.70 (s, 6H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \delta 147.0, 139.1, 129.3, 125.4, 117.6, 109.0, 106.8, 55.7, 36.8, 30.5, 29.5; HRMS calcd for C\textsubscript{12}H\textsubscript{17}N\textsubscript{2}O [M+H]^+: 205.1341, found 205.1356.

2-(4-(Methylamino)phenyl)-2,2-diphenylacetonitrile (7p): yellow solid, mp 109–112 °C; IR (neat) 3416, 2235, 1613 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.38–7.28 (m, 6H), 7.27–7.19 (m, 3H), 7.03–6.92 (m, 2H), 6.59–6.50 (m, 2H), 3.85 (bs, 1H), 2.82 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 149.1, 141.1, 129.9, 129.0, 128.7, 128.5, 128.1, 124.1, 112.3, 57.0, 30.7; HRMS calcd for C\textsubscript{21}H\textsubscript{19}N\textsubscript{2} [M+H]^+: 299.1548, found 299.1555.

1-(4-(pent-4-en-1-ylamino)phenyl)cyclohexane-1-carbonitrile (5aa): yellow oil; IR (neat) 3394, 1599 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.32–7.21 (m, 2H), 6.61–6.56 (m, 2H), 5.84 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.06 (dq, J = 17.2, 1.7 Hz, 1H), 5.00 (ddt, J = 10.2, 2.2, 1.3 Hz, 1H), 3.70 (s, 1H), 3.13 (t, J = 7.1 Hz, 2H), 2.22–2.06 (m, 4H), 1.90–1.77 (m, 5H), 1.76–1.64 (m, 4H), 1.34–1.16 (m, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 148.0, 138.1, 130.0, 126.6, 123.5, 115.4, 112.9, 43.51, 43.48, 37.7, 31.4, 28.8, 25.3, 23.9; HRMS calcd for C\textsubscript{18}H\textsubscript{25}N\textsubscript{2} [M+H]^+: 269.2018, found 269.2003.
G. The ortho-selective arylation of α-carbonitriles

Typical reaction conditions for the synthesis of benzoamidine products 8. To a solution of triazene 2 (0.20 mmol) in Methanol (0.2M, 1.0 mL) at 0 °C was added trifluoroacetic acid (0.5 mmol) dropwise. Gentle bubbling continued for approximately 3 to 5 minutes. The resulting mixture was kept in a refrigerator at 0 °C for 12 h. The reaction mixture was quenched with 1M NaOH (3 mL), and the aq. layer was extracted 3 times with dichloromethane (3 × 5 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated. The resulting crude material was purified by automated column chromatography (SiO₂, eluted with 90:9:1 CH₂Cl₂:MeOH:NH₄OH) to afford the corresponding benzoamidine (8q–8z).

1'-methylspiro[cyclohexane-1,3'-indolin]-2'-imine (8a): colorless oil; IR (neat) 1644, 1604 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd, J = 7.6, 1.2 Hz, 1H), 7.24 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 6.92 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 6.76 (dd, J = 7.8, 1.4 Hz, 1H), 3.23 (s, 3H), 1.92–1.76 (m, 6H), 1.69–1.59 (m, 4H), 1.58–1.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.8, 145.0, 135.3, 127.8, 124.6, 120.1, 107.0, 48.3, 35.6, 27.3, 25.3, 21.6; HRMS calcd for C₁₄H₁₉N₂ [M+H]⁺: 215.1548, found 215.1538.

1',5'-dimethylspiro[cyclohexane-1,3'-indolin]-2'-imine (8q): yellow solid, mp 109-112 °C; IR (neat) 1641, 1610, 1596 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.04 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 3.21 (s, 3H), 2.34 (s, 3H), 1.94–1.75 (m, 5H), 1.71–1.57 (m, 4H), 1.57–1.48 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.9, 142.7, 135.5, 129.4, 127.9, 125.7, 106.6, 48.4, 35.6, 27.4, 25.3, 21.6, 21.4. HRMS calcd for C₁₅H₂₁N₂ [M+H]⁺: 229.1705, found 229.1697.

1'-methyl-4'-methyl)imidino-[1,1'-bi(cyclohexane)]-2',5'-diene-1-carbonitrile (10q): pale yellow oil; IR (neat) 1656, 1607, 1591 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.74 (dd, J = 10.5, 2.0 Hz, 1H), 6.46 (dd, J = 10.5, 2.8 Hz, 1H), 6.39 (dd, J = 10.2, 2.0 Hz, 1H), 6.26 (dd, J = 10.3, 2.8 Hz, 1H), 3.35 (s, 3H), 1.99 (dd, J = 13.2, 1.6 Hz, 1H), 1.91 (dd, J = 13.2, 1.6 Hz, 1H), 1.81–1.71 (m, 2H), 1.64 (m, 2H), 1.36 (s, 3H), 1.36–1.23 (m, 3H), 1.07 (dtt, J = 12.8, 12.8, 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 158.5, 143.2, 138.6, 132.1, 121.9, 119.1, 47.1, 44.9, 38.2, 30.9, 30.5, 25.3, 23.5, 23.5, 23.0; HRMS calcd for C₁₅H₂₁N₂ [M+H]⁺: 229.1705, found 229.1692.
5'-methoxy-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-ime (8r): colorless oil; IR (neat) 1592 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 2.5 Hz, 1H), 6.77 (dd, J = 8.5, 2.5 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.20 (s, 3H), 1.91–1.75 (m, 5H), 1.71–1.57 (m, 4H), 1.57–1.44 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 154.1, 138.9, 136.6, 113.5, 110.9, 106.5, 56.1, 48.5, 35.4, 27.3, 25.2, 21.5; HRMS calcd for C₁₅H₂₁N₂O [M+H]⁺: 245.1654, found 245.1643.

1'-methoxy-4'-(methylimino)-[1,1'-bi(cyclohexane)]-2',5'-diene-1-carbonitrile (10r): colorless oil; IR (neat) 1642, 1596 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.97 (dd, J = 10.7, 2.1 Hz, 1H), 6.60 (dd, J = 10.4, 2.1 Hz, 1H), 6.41 (dd, J = 10.7, 2.8 Hz, 1H), 6.23 (dd, J = 10.3, 2.8 Hz, 1H), 3.45 (s, 3H), 3.18 (s, 3H), 2.08 (d, J = 13.5 Hz, 1H), 1.97 (d, J = 13.4 Hz, 1H), 1.83–1.70 (m, 3H), 1.70–1.55 (m, 2H), 1.29 (tdd, J = 13.2, 3.7, 2.0 Hz, 2H), 1.14–1.03 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 138.4, 136.4, 133.8, 122.3, 121.7, 52.6, 48.9, 39.0, 30.3, 30.0, 25.5, 23.1, 23.1; HRMS calcd for C₁₅H₂₁N₂O [M+H]⁺: 245.1654, found 245.1647.

5'-[(tert-butyl)-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-ime (8s): white solid, mp 107–111 °C; IR (neat) 1640, 1611, 1594 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 2.0 Hz, 1H), 7.27 (dd, J = 8.0, 1.8 Hz, 2H), 6.68 (d, J = 8.1 Hz, 1H), 3.21 (s, 3H), 1.94–1.77 (m, 5H), 1.73–1.59 (m, 4H), 1.59–1.48 (m, 1H), 1.34 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 177.0, 143.1, 142.7, 135.2, 124.2, 122.0, 106.1, 48.4, 35.6, 34.6, 31.9, 27.3, 25.4, 21.8; HRMS calcd for C₁₈H₂₇N₂ [M+H]⁺: 271.2174, found 271.2157.

5'-chloro-1'-methylspiro[cyclohexane-1,3'-indolin]-2'-ime (8t): white solid, mp 53–58 °C; IR (neat) 1643, 1599, 1594 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 2.1 Hz, 1H), 7.21 (dd, J = 8.3, 2.1 Hz, 1H), 6.66 (d, J = 8.3 Hz, 1H), 3.22 (s, 3H), 1.92–1.77 (m, 5H), 1.73–1.57 (m, 4H), 1.56–1.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.3, 143.6, 136.9, 127.6, 125.4, 125.1, 107.7, 48.6, 35.4, 27.6, 25.1, 21.5; HRMS calcd for C₁₄H₁₈ClN₂ [M+H]⁺: 249.1159, found 249.1159.
1,3,5,6-tetramethyl-3-phenylindolin-2-imine (8u): yellow oil; IR (neat) 1645, 1618 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.33-7.19\) (m, 5H), 6.74 (s, 1H), 6.61 (s, 1H), 3.29 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H), 1.72 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 176.9, 143.4, 143.2, 136.4, 133.7, 128.9, 128.8, 127.2, 126.8, 124.8, 108.7, 53.2, 27.5, 25.4, 20.4, 19.5\); HRMS calcd for C\(_{18}\)H\(_{21}\)N\(_2\) [M+H]\(^+\): 265.1705, found 265.1694.

1,3,4,5-tetramethyl-3-phenylindolin-2-imine (8u') not separable from 8u. \(^1\)H NMR (400 MHz, CDCl\(_3\), diagnostic peaks only) \(\delta 7.07\) (d, \(J = 7.9\) Hz, 1H), 3.25 (s, 3H), 2.17 (s, 3H), 1.78 (s, 3H).

1,3,5-trimethyl-3-phenylindolin-2-imine (8v): white solid, mp 87-89 °C; IR (neat) 1644, 1594 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.34-7.27\) (m, 2H), 7.26-7.19 (m, 3H), 7.02 (dd, \(J = 7.8, 1.7\) Hz, 1H), 6.78 (d, \(J = 1.6\) Hz, 1H), 6.69 (d, \(J = 7.9\) Hz, 1H), 3.29 (s, 3H), 2.24 (s, 3H), 1.73 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 176.6, 143.0, 142.9, 136.4, 130.6, 128.8, 128.5, 127.3, 126.8, 124.4, 106.9, 53.3, 27.6, 25.3, 21.1\); HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_2\) [M+H]\(^+\): 251.1548, found 251.1537.

5-methoxy-1,3-dimethyl-3-phenylindolin-2-imine (8w): brown oil; IR (neat) 1644, 1596 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.33-7.27\) (m, 2H), 7.27-7.19 (m, 3H), 6.78 (d, \(J = 8.5, 2.5\) Hz, 1H), 6.70 (d, \(J = 8.5\) Hz, 1H), 6.61 (d, \(J = 2.5\) Hz, 1H), 3.72 (s, 3H), 3.29 (s, 3H), 1.74 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 176.5, 155.2, 142.7, 139.2, 137.6, 128.9, 127.4, 126.8, 112.5, 111.3, 107.2, 56.0, 53.6, 27.7, 25.3\); HRMS calcd for C\(_{17}\)H\(_{19}\)N\(_2\)O [M+H]\(^+\): 267.1497, found 267.1480.

5-(tert-butyl)-1,3-dimethyl-3-phenylindolin-2-imine (8x): pale yellow oil; IR (neat) 1645, 1615, 1595 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.33-7.27\) (m, 2H), 7.26-7.19 (m, 4H), 7.02 (d, \(J = 1.9\) Hz, 1H), 6.73 (d, \(J = 8.2\) Hz, 1H), 3.29 (s, 3H), 1.75 (s, 3H), 1.25 (s, 9H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 176.8, 144.4, 143.1, 143.0, 135.9, 128.8, 127.3, 126.8, 124.8, 120.8, 106.5, 53.5, 34.6, 31.8, 27.5, 25.5\); HRMS calcd for C\(_{20}\)H\(_{25}\)N\(_2\) [M+H]\(^+\): 293.2018, found 293.2001.
5-chloro-1,3-dimethyl-3-phenylindolin-2-imine (8y): yellow solid, mp 107–111 °C; IR (neat) 1646, 1604 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.34–7.23 (m, 3H), 7.22–7.17 (m, 3H), 6.93 (d, \(J = 2.1\) Hz, 1H), 6.71 (d, \(J = 8.3\) Hz, 1H), 3.30 (s, 3H), 1.74 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.1, 143.9, 142.0, 137.9, 129.0, 128.2, 127.7, 126.7, 126.3, 124.0, 108.0, 53.3, 27.7, 25.3; HRMS calcd for C\(_{16}\)H\(_{16}\)ClN\(_2\) [M+H]\(^+\): 271.1002, found 271.0986.

5-bromo-1,3-dimethyl-3-phenylindolin-2-imine (8z): dark brown oil; IR (neat) 1649, 1600 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38–7.24 (m, 4H), 7.23–7.17 (m, 2H), 7.06 (d, \(J = 2.0\) Hz, 1H), 6.67 (d, \(J = 8.3\) Hz, 1H), 3.29 (s, 3H), 1.73 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 176.0, 144.4, 142.0, 138.3, 131.1, 129.0, 127.7, 126.8, 126.7, 113.5, 108.6, 53.3, 27.6, 25.3; HRMS calcd for C\(_{16}\)H\(_{16}\)BrN\(_2\) [M+H]\(^+\): 315.0497, found 315.0478.
H. Crossover Experiment with a mixture of 2c and 2n

Two substrates, 2c and 2n, which have similar reactivity toward the α-arylation reaction, were subjected to a crossover experiment. A mixture of 2c and 2n (1:1) was submitted to typical reaction conditions (see S14). The ^1H NMR spectrum of the resulting crude mixture was carefully compared with the known spectra of 7c, 7a, 7n, and 7o. The observed ratio of 7c:7a:7n:7o was ca. 4:1:4:1 (see below).
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