Supporting Information

Pd-Catalyzed Cascade Reaction of N-H Insertion and Oxidative Dehydrogenative Aromatization: A New Entry to 2-Amino-phenols

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Table of Contents

1. General procedures and characterizing data
2. $^1$H and $^{13}$C NMR spectra
General Information
All experiments were conducted under air unless otherwise noted. Flasks were flame dried and cooled under nitrogen before use. All solvents were dried appropriately. 1,4-dioxane was dried by refluxing from sodium under nitrogen. For column chromatography, 200-300 mesh silica gel was employed. $^1$H NMR and $^{13}$C NMR were recorded on 400MHz or 500 MHz spectrometer in CDCl$_3$ or DMSO-$d_6$ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS(0 ppm). HRMS were performed using atmospheric pressure chemical ionization (APCI) with a ion-trap analyzer or electron impact mode (EI) with a TOF mass analyzer. IR spectra were recorded on a FTIR-8400S FTIR spectrometer. Melting points were not corrected. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All the diazo compounds were prepared according to the references.[1][2]

Typical procedure for Pd-catalyzed cascade reaction of N-H insertion and oxidative dehydrogenative aromatization
A reaction tube was charged with palladium(II) catalyst (10 mol%), aniline (0.5 mmol) and 1,4-dioxane (3 mL), then 6-diazo-2-cyclohexenone (0.75 mmol) was added, and the reaction mixture was stirred at 60 °C for 3 h under air. After the mixture was cooled to room temperature, solvents were removed under vacuum. The residue was purified by column chromatography on silica gel to give the desired product.

2-(phenylamino)phenol (3a) [1]
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as dark brown oil (yield 90%, 83.3 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25-7.18 (m, 3H), 7.10 (t, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.89 (t, $J = 6.9$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 5.79 (s, 1H), 5.26 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.1, 145.5, 129.5, 129.1, 126.1, 124.7, 121.0, 120.3, 115.9, 115.4. MS (ESI) 186.2 (M+H)$^+$.  

2-((4-(tert-butylphenylamino)phenol (3b)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as brown oil (yield 83%, 100.2 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 (s, 2H), 7.18 (d, $J = 7.4$ Hz, 1H), 7.12 – 7.05 (m, 1H), 6.98 (d, $J = 7.0$ Hz, 1H), 6.88 (t, $J = 6.8$ Hz, 1H), 6.74 (d, $J = 7.6$ Hz, 2H), 5.77 (s, 1H), 5.20 (s, 1H), 1.29 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.8, 143.4, 142.8, 129.7, 126.2, 125.7, 124.3, 121.0, 115.9, 115.3, 77.3, 77.0, 76.8, 34.1, 31.5. HRMS
(EI) calcd for C₁₆H₁₅NO 241.1467, found: 241.1470. IR (KBr, cm⁻¹): 2960, 1607, 1516, 827, 746.

2-((4-methoxyphenyl)amino)phenol (3e) [⁴]
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as brown oil (yield 85%, 91.5 mg); ¹H NMR (400 MHz, DMSO) δ 9.39 (s, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.97-6.95 (m, 1H), 6.82-6.77 (m, 4H), 6.64-6.61 (m, 2H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 154.7, 149.6, 139.5, 132.1, 124.8, 122.4, 121.1, 119.1, 115.5, 114.9, 55.7. MS (ESI) 216.2 (M+H)⁺

2-(mesitylamino)phenol (3d) [⁵]
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as brown oil (yield 80%, 90.9 mg); ¹H NMR (400 MHz, CDCl₃) δ 6.93 (s, 2H), 6.84 (s, 1H), 6.71 (s, 2H), 6.27 (s, 1H), 2.30 (s, 3H), 2.16 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 134.5, 129.3, 121.4, 114.8, 77.3, 77.0, 76.8, 20.9, 18.1. MS (ESI) 228.2 (M+H)⁺

2-((4-chlorophenyl)amino)phenol (3e)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a brown solid (yield 74%, 81.3 mg); Mp: 79-81 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.16 (t, J = 7.2 Hz, 3H), 7.10 (t, J = 7.7 Hz, 1H), 6.98 (d, J = 7.9 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.6 Hz, 2H), 5.66 (s, 1H), 5.30 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 144.0, 129.3, 128.8, 126.2, 125.1, 124.4, 121.2, 117.1, 115.5. HRMS (APCI) calcd for C₁₂H₁₁ClNO (M+H)⁺ 220.0524, found: 220.0531. IR (KBr, cm⁻¹): 2924, 1591, 1456, 1091, 820, 748.

2-((4-(trifluoromethyl)phenyl)amino)phenol (3f)
The title compound was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 3/1) to afford pure product as a brown solid (yield 46%, 58.2 mg); Mp: 100-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.2 Hz, 2H),
7.21-7.14 (m, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.2 Hz, 2H), 5.59 (s, 1H), 5.53 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.2, 148.5, 127.5, 127.1, 126.8, 125.9, 125.4, 123.2, 121.3, 115.8, 114.7. HRMS (APCI) calcd for C$_{13}$H$_{11}$F$_2$NO (M+H)$^+$ 254.0787, found: 254.0789. IR (KBr, cm$^{-1}$): 2926, 1620, 1458, 1327, 1113, 1067, 831, 750.

5-methyl-2-(phenylamino)phenol (3g)$[^6]$  
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a brown solid (yield 88%, 87.7 mg); mp: 63-65 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (t, J = 7.8 Hz, 2H), 7.04 (d, J = 7.9 Hz, 1H), 6.86-6.83 (m, 2H), 6.70 (d, J = 8.0 Hz, 3H), 5.84 (s, 1H), 5.06 (s, 1H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.1, 146.4, 137.4, 129.5, 126.1, 125.8, 121.7, 121.7, 119.8, 115.7, 115.1. MS (ESI) 200.2 (M+H)$^+$

5-methyl-2-(p-tolylamino)phenol (3h)$[^7]$  
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a brown solid (yield 85%, 90.6 mg); mp: 63-65 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.01 (d, J = 7.4 Hz, 3H), 6.82 (s, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 7.8 Hz, 2H), 5.89 (s, 1H), 4.97 (s, 1H), 2.32 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.8, 143.7, 136.9, 129.8, 129.3, 126.4, 125.4, 121.4, 115.7, 115.5, 21.1, 20.4. MS (ESI) 214.2 (M+H)$^+$

4-((2-hydroxy-4-methylphenyl)amino)benzonitrile (3i)  
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford pure product as a grey solid (yield 53%, 59.4 mg); mp: 139-141 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 7.9 Hz, 1H), 6.85 (s, 1H), 6.77 – 6.72 (m, 3H), 5.58 (s, 1H), 5.49 (s, 1H), 2.34 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.9, 133.7, 133.6, 125.2, 120.9, 120.4, 117.4, 117.3, 114.1, 114.0, 21.1. HRMS (EI) calcd for C$_{14}$H$_{12}$N$_2$O 224.0950, found: 224.0948. IR (KBr, cm$^{-1}$): 2924, 1595, 1458, 1377, 752.
6-methyl-2-(phenylamino)-3-(prop-1-en-2-yl)phenol (3j)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford pure product as a yellow solid (yield 70%, 83.8 mg); mp: 54-56 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.19 (t, $J = 7.6$ Hz, 2H), 7.03 (d, $J = 7.7$ Hz, 1H), 6.84 (t, $J = 7.3$ Hz, 1H), 6.72 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 2H), 6.08 (s, 1H), 5.16 (s, 1H), 5.09 (s, 1H), 4.81 (s, 1H), 2.31 (s, 3H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.2, 146.3, 143.2, 139.2, 129.6, 128.4, 124.2, 123.2, 119.9, 119.3, 115.3, 114.5, 24.4, 15.8. HRMS (EI) caledd for C$_{16}$H$_{17}$NO 239.1310, found: 239.1311. IR (KBr, cm$^{-1}$): 3337, 2920, 1601, 1495, 1418, 1306, 1209, 1036, 908, 743, 689.

![chemical structure](image1.png)

6-methyl-3-(prop-1-en-2-yl)-2-(p-tolylamino)phenol (3k)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford pure product as brown oil (yield 73%, 92.5 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.00 (t, $J = 7.7$ Hz, 3H), 6.71 (d, $J = 7.7$ Hz, 1H), 6.52 (d, $J = 7.7$ Hz, 2H), 6.08 (s, 1H), 5.28 (s, 1H), 5.08 (s, 2H), 4.81 (s, 1H), 2.29 (s, 3H), 2.24 (s, 3H), 1.86 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.1, 143.8, 143.3, 138.9, 130.0, 129.2, 128.1, 124.5, 123.1, 119.3, 115.3, 114.7, 77.3, 77.0, 76.8, 24.2, 20.5, 15.9. HRMS (EI) caledd for C$_{17}$H$_{19}$NO 253.1467, found: 253.1469. IR (KBr, cm$^{-1}$): 3379, 2920, 1614, 1514, 1427, 1219, 1036, 895, 812.

![chemical structure](image2.png)

2-((4-chlorophenyl)amino)-6-methyl-3-(prop-1-en-2-yl)phenol (3l)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford pure product as brown oil (yield 60%, 82.1 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.16 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 7.7$ Hz, 1H), 6.56 (d, $J = 8.0$ Hz, 2H), 6.02 (s, 1H), 5.32 (s, 1H), 5.18 (s, 1H), 5.11 (s, 1H), 4.81 (s, 1H), 2.32 (s, 3H), 1.88 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 151.1, 145.0, 143.0, 139.2, 129.3, 128.7, 124.7, 123.7, 123.4, 119.5, 115.8, 115.5, 77.3, 77.0, 76.8, 24.2, 15.9. HRMS (EI) caledd for C$_{16}$H$_{16}$ClN$_{2}$O 273.0920, found: 273.0925. IR (KBr, cm$^{-1}$): 3370, 2920, 1608, 1504, 1210, 1036, 899.

![chemical structure](image3.png)

2-(benzylamino)phenol (5a) $^{[8]}$
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford pure product as brown oil (yield 63%, 58.7 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 (t, $J = 7.5$ Hz, 2H), 7.03 (d, $J = 7.6$ Hz, 1H), 6.84 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 7.5$ Hz, 1H), 6.62 (d, $J = 7.5$ Hz, 2H), 6.08 (s, 1H), 5.16 (s, 1H), 5.09 (s, 1H), 4.81 (s, 1H), 2.31 (s, 3H), 1.86 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.1, 143.1, 139.2, 129.3, 128.7, 124.7, 123.6, 123.4, 119.5, 115.8, 115.5, 77.3, 77.0, 76.8, 24.2, 15.9. HRMS (EI) caledd for C$_{16}$H$_{16}$N$_{2}$O 273.0920, found: 273.0925. IR (KBr, cm$^{-1}$): 3370, 2920, 1608, 1504, 1210, 1036, 899.
ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 80%, 79.7 mg). Mp: 69-71 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.33 (m, 4H), 7.28 (d, \(J = 6.8\) Hz, 1H), 6.83 (t, \(J = 7.0\) Hz, 1H), 6.73 (d, \(J = 7.2\) Hz, 1H), 6.68-6.63 (m, 2H), 4.59 (s, 1H), 4.35 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.4, 139.3, 136.9, 128.6, 127.6, 127.2, 121.8, 117.8, 114.3, 112.5, 48.6. MS (ESI) 200.2 (M+H)\(^+\).

![Image](image1.png)

**2-((4-methylbenzyl)amino)phenol (5b)**
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 82%, 87.4 mg). Mp: 71-73 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (d, \(J = 7.6\) Hz, 1H), 7.16 (d, \(J = 7.6\) Hz, 1H), 6.84 (t, \(J = 7.0\) Hz, 1H), 6.74-6.62 (m, 3H), 4.61 (s, 1H), 4.31 (s, 2H), 2.35 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 143.5, 137.1, 136.8, 136.4, 129.3, 127.6, 121.7, 117.7, 114.3, 112.5, 48.3, 21.1. HRMS (EI) calcd for C\(_{16}\)H\(_{15}\)NO 213.1154, found: 213.1156. IR (KBr, cm\(^{-1}\)): 2922, 1610, 1514, 1487, 1250, 1111, 802, 741. IR (KBr, cm\(^{-1}\)): 2924, 1622, 1529, 1454, 1242, 1126, 798, 689.

![Image](image2.png)

**2-((4-fluorobenzyl)amino)phenol (5c)**
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 75%, 81.5 mg). Mp: 75-77 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.33 (m, 2H), 7.03 (t, \(J = 8.6\) Hz, 2H), 6.83 (t, \(J = 7.4\) Hz, 1H), 6.73 (d, \(J = 8.0\) Hz, 1H), 6.63 (d, \(J = 6.8\) Hz, 2H), 4.60 (s, 1H), 4.32 (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 163.0, 161.1, 143.3, 136.8, 129.1, 129.0, 121.7, 117.8, 115.5, 115.3, 114.3, 112.3, 47.8. HRMS (EI) calcd for C\(_{17}\)H\(_{12}\)FNO 217.0903, found: 217.0907. IR (KBr, cm\(^{-1}\)): 2926, 1603, 1510, 1223, 1155, 822, 743.

![Image](image3.png)

**2-((1-phenylethyl)amino)phenol (5d)**\(^{[9]}\)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 71%, 75.7 mg). Mp: 122-124 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 (d, \(J = 7.6\) Hz, 2H), 7.31 (t, \(J = 7.4\) Hz, 2H), 7.24-7.20 (m, 1H), 6.69 (s, 2H), 6.57 (s, 1H), 6.44 (d, \(J = 7.2\) Hz, 1H), 4.46 (s, 2H), 1.53 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.2, 143.5, 135.9, 128.6, 126.9, 125.9, 121.5, 117.7, 114.1, 113.7, 53.9, 24.9. MS (ESI) 214.2 (M+H)\(^+\).

![Image](image4.png)
2-(benzhydrylamino)phenol (5e) \[^{10}\]

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 66%, 90.9 mg). Mp: 128-130 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 7.2\) Hz, 4H), 7.34 (t, \(J = 7.2\) Hz, 4H), 7.26-7.23 (m, 2H), 6.71 (d, \(J = 7.6\) Hz, 2H), 6.59 (t, \(J = 7.2\) Hz, 1H), 6.45 (d, \(J = 7.6\) Hz, 1H), 5.50 (s, 1H), 4.68 (s, 1H), 4.58 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.1, 143.0, 136.3, 128.7, 127.5, 127.3, 121.7, 117.6, 114.2, 113.2, 63.1. MS (ESI) 276.2 (M+H\(^+\)).

2-(dodecylamino)phenol (5f)

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as light green solid (yield 79%, 109.6 mg). Mp: 70-72 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.86 (s, 1H), 6.69 (d, \(J = 7.2\) Hz, 2H), 6.62 (s, 1H), 4.38 (s, 2H), 3.10 (s, 2H), 1.64 (t, \(J = 7.2\) Hz, 2H), 1.27 (s, 16H), 0.88 (t, \(J = 6.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.7, 137.3, 121.6, 117.4, 114.3, 112.4, 44.5, 31.9, 29.7, 29.6, 29.5, 29.4, 27.2, 22.7, 14.1. HRMS (EI) calcd for C\(_{18}\)H\(_{31}\)NO 277.2406, found: 277.2403. IR (KBr, cm\(^{-1}\)): 2920, 1605, 1512, 1230, 825, 749.

2-(cyclohexylamino)phenol (5g) \[^{11}\]

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a brown solid (yield 84%, 80.3 mg). Mp: 65-67 °C; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.19 (s, 1H), 6.61 (dd, \(J = 16.7, 7.7\) Hz, 2H), 6.49 (d, \(J = 7.7\) Hz, 1H), 6.36 (t, \(J = 7.5\) Hz, 1H), 4.15 (s, 1H), 3.17 (s, 1H), 1.91 (d, \(J = 10.9\) Hz, 2H), 1.67 (d, \(J = 13.0\) Hz, 2H), 1.57 (d, \(J = 12.4\) Hz, 1H), 1.32 (dd, \(J = 24.4, 12.2\) Hz, 2H), 1.21-1.09 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.0, 135.5, 128.4, 121.3, 118.4, 114.9, 52.8, 33.4, 26.0, 25.0. MS (ESI) 192.2 (M+H\(^+\)).

2-(tert-butylamino)phenol (5h) \[^{12}\]

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a brown solid (yield 84%, 80.3 mg). Mp: 65-67 °C; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.19 (s, 1H), 6.61 (dd, \(J = 16.7, 7.7\) Hz, 2H), 6.49 (d, \(J = 7.7\) Hz, 1H), 6.36 (t, \(J = 7.5\) Hz, 1H), 4.15 (s, 1H), 3.17 (s, 1H), 1.91 (d, \(J = 10.9\) Hz, 2H), 1.67 (d, \(J = 13.0\) Hz, 2H), 1.57 (d, \(J = 12.4\) Hz, 1H), 1.32 (dd, \(J = 24.4, 12.2\) Hz, 2H), 1.21-1.09 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.0, 135.5, 128.4, 121.3, 118.4, 114.9, 52.8, 33.4, 26.0, 25.0. MS (ESI) 192.2 (M+H\(^+\)).
ether/ethyl acetate = 50/1) to afford pure product as a yellow solid (yield 60%, 49.6 mg). Mp: 80-82 °C; 1H NMR (400 MHz, CDCl3) δ 7.05-7.00 (m, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.78 (t, J = 7.4 Hz, 1H), 1.21 (s, 9H); 13C NMR (125 MHz, CDCl3) δ 153.1, 131.0, 126.9, 125.6, 119.4, 113.9, 53.3, 29.7. MS (ESI) 166.2 (M+H)+.

2-((2-(1H-indol-3-yl)ethyl)amino)phenol (5i)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a white solid (yield 77%, 97.1 mg). Mp: 84-86 °C; 1H NMR (400 MHz, CDCl3) δ 7.99 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.07 (s, 1H), 6.87 (t, J = 6.4 Hz, 1H), 6.73 (dd, J = 7.2 Hz, 2H), 6.64 (d, J = 7.2 Hz, 1H), 4.42 (s, 2H), 3.47 (s, 2H), 3.12 (t, J = 6.8 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 143.9, 136.4, 127.4, 122.1, 122.0, 119.4, 118.8, 117.9, 114.4, 113.5, 112.8, 111.2, 44.5, 25.3. HRMS (EI) calcd for C16H16N2O 252.1263, found: 252.1269. IR (KBr, cm⁻¹): 3396, 2912, 1599, 1510, 1456, 1231, 1128, 750, 739.

2-(((4-fluorobenzyl)amino)-5-methylphenol (5j)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a yellow solid (yield 70%, 80.9 mg). Mp: 117-119 °C; 1H NMR (400 MHz, CDCl3) δ 7.34-7.31 (m, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.61-6.55 (m, 3H), 4.26 (s, 2H), 2.21 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 163.4, 160.9, 144.4, 136.2, 134.0, 129.1, 121.8, 115.5, 115.3, 113.7, 48.5, 20.6. HRMS (EI) calcd for C14H14FNO 231.1059, found: 231.1062. IR (KBr, cm⁻¹): 3039, 1614, 1522, 1244, 1126, 818.

2-(((4-methoxybenzyl)amino)-5-methylphenol (5k)
The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a yellow solid (yield 78%, 94.9 mg). Mp: 100-102 °C; 1H NMR (400 MHz, CDCl3) δ 7.29 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.62 (s, 1H), 6.57 (s, 1H), 4.22 (s, 2H), 3.80 (s, 3H), 2.21 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 163.3, 160.8, 144.1, 129.2, 129.1, 121.7, 115.5, 115.3, 113.6, 102.1. HRMS (EI) calcd for C15H17NO2 243.1259, found: 243.1255. IR (KBr, cm⁻¹): 3390, 1620, 1529, 1512, 1236, 1128, 1018, 825, 798.
2-((tert-butyldimethylsilyloxy)ethyl)amino)-5-methylphenol (5)  

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as a white solid (yield 88%, 123.8 mg). Mp: 83-85 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.69-6.59 (m, 3H), 3.80 (t, \(J = 5.2\) Hz, 2H), 3.16 (s, 2H), 2.22 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 146.1, 133.9, 129.7, 121.2, 115.8, 115.6, 61.9, 48.0, 25.9, 20.7, 18.3, -5.34. HRMS (EI) calcd for C\(_{13}\)H\(_{27}\)NO\(_2\)Si 281.1811, found: 281.1812. IR (KBr, cm\(^{-1}\)): 3033, 2161, 1624, 1510, 1210, 1110, 815, 780.

**Procedure for the synthesis of 3a’ (the controlled experiment)**

Under a nitrogen atmosphere, a reaction tube was charged with palladium(II) catalyst (10 mol%), aniline (0.5 mmol) and 1,4-dioxane (3 mL), then 6-diazo-2-cyclohexenone (0.75 mmol) was added, and the reaction mixture was stirred at 60 °C for 3 h. After the mixture was cooled to room temperature, solvents were removed under vacuum. The residue was purified by column chromatography on silica gel to give the desired product.

![Cyclohexanone structure](image)

6-(phenylamino)cyclohex-2-enone (3a’)

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) to afford pure product as brown oil (yield 93%, 87.1 mg, Scheme 3); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (t, \(J = 7.9\) Hz, 2H), 7.03 – 6.99 (m, 1H), 6.74 (t, \(J = 7.3\) Hz, 1H), 6.67 (d, \(J = 7.9\) Hz, 2H), 6.14 (dd, \(J = 10.0, 2.6\) Hz, 1H), 5.02 (s, 1H), 4.01 (dd, \(J = 13.6, 4.4\) Hz, 1H), 2.69-2.49 (m, 3H), 1.89-1.78 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 150.2, 147.0, 129.8, 128.2, 118.1, 112.9, 59.5, 30.4, 26.0. HRMS (EI) calcd for C\(_{13}\)H\(_{15}\)NO 187.0997, found: 187.0995.

**Procedure for the reaction of 1a with phenol**

A reaction tube was charged with palladium(II) catalyst (10 mol%), phenol (0.5 mmol) and 1,4-dioxane (3 mL), then 6-diazo-2-cyclohexenone (0.75 mmol) was added, and the reaction mixture was stirred at 60 °C for 12 h under air.

**Procedure for the synthesis of Murrayafoline A\(^{[6]}\)\(^{[13]}\)**

A reaction tube was charged with palladium(II) chloride (1 mmol), aniline (2a) (10 mmol) and 1,4-dioxane (20 mL), then 6-diazo-2-cyclohexenone (15 mmol) was added, and the reaction mixture was stirred at 60 °C for 5 h under air. After the mixture was cooled to room temperature, solvents were removed under vacuum. The residue was purified by column chromatography on silica gel to give the desired product. A
mixture of the purified product (3g), MeI (3 equiv.) and K₂CO₃ (5 equiv.) in anhydrous acetone (35 mL) was heated to 60 °C for 2.5 h. After cooling to room temperature, the resulting mixture was filtered through a pad of celite, eluting with ethyl acetate. The solvent was removed under vacuum to give the methylation intermediates in quantitative yield. Then the methylation intermediates, K₂CO₃ (0.1 equiv.), Pd(OAc)₂ (0.05 equiv.) and pivalic acid were added to a reaction tube. The tube was placed in an oil bath (110 °C) and the mixture was stirred under air for 14 h. The solution is then cooled to rt, diluted with CH₂Cl₂, washed with a saturated aqueous solution of Na₂CO₃, dried over MgSO₄, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to give the desired product.

![Structure](image)

1-methoxy-3-methyl-9H-carbazole[^6][^13]

The title compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1) to afford pure product as yellow oil (yield 57%, 1.2 g); ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.47 (s, 1H), 7.43-7.38 (m, 2H), 7.22-7.19 (m, 1H), 6.73 (s, 1H), 3.98 (s, 3H), 2.53 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.5, 139.5, 129.4, 128.1, 125.6, 124.3, 123.6, 120.4, 119.1, 112.5, 110.8, 107.6, 55.4, 21.7.

References:
3a

400MHz, CDCl₃
100MHz, CDCl$_3$

3a
**3b**

400MHz, CDCl₃
$^{13}$C NMR Spectral Data for Compounds

<table>
<thead>
<tr>
<th>ppm</th>
<th>150.841</th>
<th>143.425</th>
<th>142.810</th>
<th>129.670</th>
<th>126.222</th>
<th>125.699</th>
<th>124.251</th>
<th>120.968</th>
<th>115.889</th>
<th>115.313</th>
<th>77.737</th>
<th>77.302</th>
<th>31.502</th>
</tr>
</thead>
</table>

$^{13}$C NMR Spectrum for Compound 3b

125MHz, CDCl$_3$
OH

H

\[ 3c \]

OMe

400 MHz, DMSO-\(d_6\)
3c

125MHz, CDCl₃
400MHz, CDCl₃

OH

3d

1.00

1.99

2.21

6.24

3.28

1.05

2.300

6.714

6.837

6.929

7.258

-0.002

-2.300

-2.160

-7.258

-6.929

-6.837

-6.714

-6.272
125MHz, CDCl$_3$
OH
N
Cl

3e

400MHz, CDCl₃
$^1$H (ppm)

-150.795
-144.000
129.323
128.750
126.188
125.131
124.408
121.187
117.099
115.479

115.479
117.099
121.187
124.408
125.131
126.188
128.750
129.323
130.000
210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440

$^3$e

100MHz, CDCl$_3$
400MHz, CDCl₃
$3g$

400MHz, CDCl$_3$
$3g$

$100\text{MHz, CDCl}_3$
OH
N
3h

400MHz, CDCl₃
$\text{3h}$

$125\text{MHz, CDCl}_3$
$^1$H NMR (125 MHz, DMSO-$d_6$)

![NMR spectrum of compound 3i](image-url)

$3j$

400MHz, CDCl$_3$
$^{1}J_{HH}$ (ppm)

- 151.167
- 146.313
- 143.178
- 139.199
- 129.577
- 128.345
- 124.205
- 123.176
- 119.864
- 119.335
- 119.335
- 115.306
- 114.510

- 15.811
- 24.374

100MHz, CDCl$_3$

$3j$
f1 (ppm)

-100102030405060708090100110120130140150160170180190200210

15.888
20.493
24.221
76.777
77.031
77.285
114.665
115.263
119.309
123.122
124.494
128.143
129.217
129.956
138.868
143.271
143.778
151.045
21.093

12S1

3k

125 MHz, CDCl₃
3I

400 MHz, CDCl$_3$
125MHz, CDCl₃
5a

OH
H

400MHz, CDCl₃
5a
100MHz, CDCl₃
OH

5b

400MHz, CDCl₃
125MHz, CDCl₃
400MHz, CDCl₃
$5c$

$125$MHz, CDCl$_3$
OH

H

\mathbf{5d}

400MHz, CDCl$_3$
125MHz, CDCl₃
400MHz, CDCl₃
100MHz, CDCl₃
$5f$

$400\text{MHz, CDCl}_3$
$5f$

125 MHz, CDCl$_3$
125MHz, CDCl$_3$
400MHz, CDCl$_3$
125MHz, CDCl₃
$\text{f1 (ppm)}$

- 143.948
- 136.367
- 127.426
- 122.140
- 119.408
- 117.863
- 118.804
- 114.350
- 113.845
- 111.90

- 44.522
- 25.281

$\text{f1 (ppm)}$
400MHz, CDCl₃
$\text{**S53**}$
400MHz, CDCl₃
125MHz, CDCl$_3$
400MHz, CDCl₃
125MHz, CDCl₃
$3a^*$

$400\text{MHz, CDCl}_3$

1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4 6.6 6.8 7.0 7.2

f$_1$ (ppm)
100MHz, CDCl₃
400MHz, CDCl₃
$100\text{MHz, CDCl}_3$