

Supplementary Materials for
Copper-catalyzed oxidative C(sp³)-H/C(sp²)-H cross-coupling en route
to carbocyclic rings

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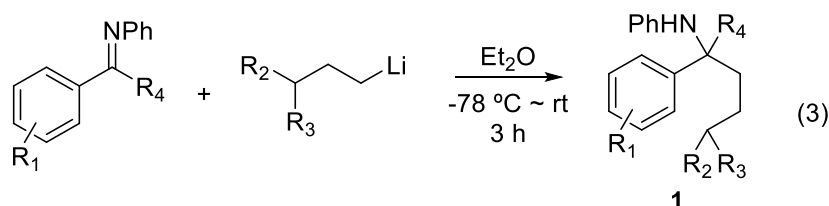
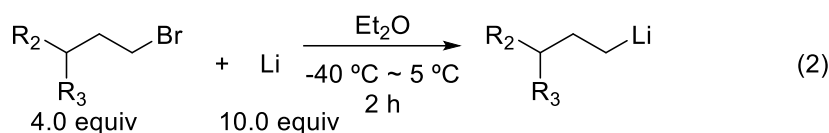
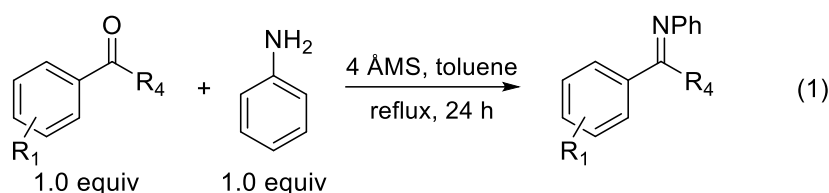
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I. General Information: Instrumentation, Materials.

Instrumentation. ^1H NMR spectra were recorded at ambient temperature on Bruker-400 (400 MHz) spectrometers and are referenced relative to the residual protons in CDCl_3 at δ 7.26 ppm or $(\text{CD}_3)_2\text{SO}-d_6$ at δ 2.50 ppm. Data for ^1H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, ap = apparent), integration, and coupling constant (Hz). ^{13}C NMR spectra were recorded at ambient temperature on Bruker-400 (100 MHz) spectrometers and are referenced relative to CDCl_3 at δ 77.16 ppm or $(\text{CD}_3)_2\text{SO}-d_6$ at δ 39.25 ppm. The ^{13}C NMR spectra were obtained with ^1H decoupling. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. High resolution mass spectra were recorded on P-SIMS-Gly of BrukerDaltonics Inc. using ESI-TOF (electrospray ionization-time of flight).

Materials. Copper diacetate was purchased from Shanghai DEMO Medical Tech Co., Ltd. and used as received. Silver carbonate was purchased from Adamas Reagent Co., Ltd. and used as received. 1,2-dichloroethane was purchased from Sinopharm Chemical Reagent Co., Ltd. Other commercial reagents were purchased from commercial suppliers and used without further purification.

II. Preparation of Substrates.



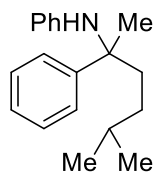
General procedure (A) for the synthesis of substrates.

Step 1: Preparation of imine. To an oven-dried round-bottom bottle equipped with a magnetic stir bar was added ketone (1.0 equiv), aniline (1.0 equiv), 4 ÅMS (0.2 g/mmol) and toluene (2.0 M). The mixture was then reflux for 24 h. After completion, it was allowed to cool to room temperature, and was directly filtered through a short pad of Celite®, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

Step 2: Preparation of lithium reagent. The bromide (4.0 equiv) in Et₂O (4.0 M) was added dropwise to a vigorously stirred suspension of lithium rods (10.0 equiv) in Et₂O (4.0 M) at -40 °C under N₂ atmosphere. And the mixture was allowed to warm up to 5 °C and stirred for 2 h. The resulting blackish suspension was then used immediately.

Step 3: Preparation of the substates. The freshly prepared lithium reagent was added dropwise to a vigorously stirred solution of imine in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 3 h (but with **1g**, **1j**, **1n**, the stirring temperature was -40°C). After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to give the substrate **1**.

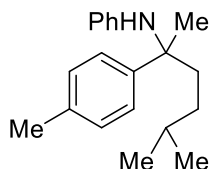
***N*-(5-methyl-2-phenylhexan-2-yl)aniline (1a)**



Prepared according to general procedure (A) from acetophenone and 1-bromo-3-methylbutane to provide the title compound **1a** as a colorless oil (1.17 g, 4.4 mmol, 88% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 6.9 Hz, 1H),

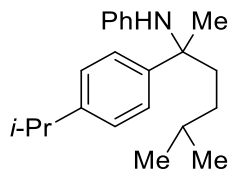
6.98 (t, $J = 7.7$ Hz, 2H), 6.58 (t, $J = 7.3$ Hz, 1H), 6.31 (d, $J = 7.9$ Hz, 2H), 3.99 (s, 1H), 1.83 (dtd, $J = 19.6, 13.2, 8.4$ Hz, 2H), 1.62 (s, 3H), 1.51 – 1.32 (m, 1H), 1.09 (dd, $J = 15.9, 7.4$ Hz, 2H), 0.81 (d, $J = 7.0$ Hz, 3H), 0.80 (d, $J = 7.0$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 146.2, 128.8, 128.5, 126.3, 126.3, 117.0, 115.4, 58.4, 42.4, 32.7, 28.4, 25.7, 22.8, 22.7. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 268.2065, found 268.2062.

***N*-(5-methyl-2-(*p*-tolyl)hexan-2-yl)aniline (1b)**



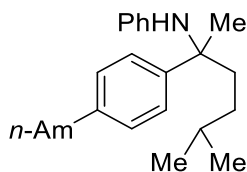
Prepared according to general procedure (A) from 1-(*p*-tolyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1b** as a colorless oil (1.26 g, 4.5 mmol, 90% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.04 – 6.95 (m, 2H), 6.60 (t, $J = 7.2$ Hz, 1H), 6.40 – 6.29 (m, 2H), 4.00 (s, 1H), 2.35 (s, 3H), 1.83 (dddd, $J = 36.0, 13.2, 9.3, 7.5$ Hz, 2H), 1.62 (s, 3H), 1.51 – 1.35 (m, 1H), 1.11 (dt, $J = 9.5, 7.1$ Hz, 2H), 0.84 (d, $J = 6.7$ Hz, 3H), 0.81 (d, $J = 6.7$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 143.8, 135.7, 129.2, 128.7, 126.2, 117.0, 115.4, 58.2, 42.4, 32.7, 28.4, 25.8, 22.8, 22.7, 21.1. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 282.2222, found 282.2222.

***N*-(2-(4-isopropylphenyl)-5-methylhexan-2-yl)aniline (1c)**



Prepared according to general procedure (A) from 1-(4-isopropylphenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1c** as a colorless oil (1.21 g, 3.9 mmol, 78% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.8$ Hz, 2H), 7.19 (d, $J = 7.8$ Hz, 2H), 7.02 (t, $J = 7.5$ Hz, 2H), 6.62 (t, $J = 7.3$ Hz, 1H), 6.37 (d, $J = 8.0$ Hz, 2H), 4.02 (s, 1H), 3.04 – 2.83 (m, 1H), 1.87 (dtd, $J = 21.6, 13.0, 6.2$ Hz, 2H), 1.64 (s, 3H), 1.54 – 1.37 (m, 1H), 1.28 (d, $J = 6.9$ Hz, 6H), 1.15 (dd, $J = 15.9, 7.7$ Hz, 2H), 0.86 (d, $J = 7.0$ Hz, 3H), 0.83 (d, $J = 7.0$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.7, 146.4, 144.2, 128.8, 126.4, 126.1, 116.9, 115.4, 58.2, 42.1, 33.7, 32.7, 28.4, 26.0, 24.1, 22.8, 22.7. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{32}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 310.2535, found 310.2537.

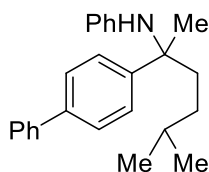
***N*-(5-methyl-2-(4-pentylphenyl)hexan-2-yl)aniline (1d)**



Prepared according to general procedure (A) from 1-(4-pentylphenyl)ethan-1-one and

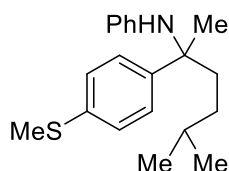
1-bromo-3-methylbutane to provide the title compound **1d** as a colorless oil (1.08 g, 3.2 mmol, 64% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.7 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 2H), 4.02 (s, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.02 – 1.74 (m, 2H), 1.74 – 1.57 (m, 5H), 1.49 – 1.41 (m, 1H), 1.40 – 1.30 (m, 4H), 1.14 (dd, *J* = 15.8, 7.3 Hz, 2H), 0.92 (t, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 7.4 Hz, 3H), 0.83 (d, *J* = 7.4 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.3, 144.0, 140.8, 128.7, 128.4, 126.1, 116.9, 115.4, 58.2, 42.3, 35.6, 32.7, 31.8, 31.2, 28.4, 25.8, 22.8, 22.7, 22.7, 14.2. HRMS (ESI) calcd. for C₂₄H₃₆N [M+H]⁺ *m/z* 338.2848, found 338.2844.

***N*-(2-([1,1'-biphenyl]-4-yl)-5-methylhexan-2-yl)aniline (1e)**



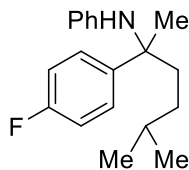
Prepared according to general procedure (A) from 1-([1,1'-biphenyl]-4-yl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1e** as a white solid (1.65 g, 4.8 mmol, 96% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.62 (m, 2H), 7.62 – 7.52 (m, 4H), 7.50 – 7.41 (m, 2H), 7.39 – 7.31 (m, 1H), 7.08 – 6.98 (m, 2H), 6.68 – 6.56 (m, 1H), 6.46 – 6.35 (m, 2H), 4.06 (s, 1H), 2.03 – 1.79 (m, 2H), 1.69 (s, 3H), 1.54 – 1.40 (m, 1H), 1.17 (dt, *J* = 9.0, 6.8 Hz, 2H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.2, 146.0, 140.9, 139.0, 128.8, 128.8, 127.2, 127.1, 127.1, 126.7, 117.1, 115.4, 58.3, 42.3, 32.7, 28.4, 25.8, 22.8, 22.7. HRMS (ESI) calcd. for C₂₅H₃₀N [M+H]⁺ *m/z* 344.2378, found 344.2379.

***N*-(5-methyl-2-(4-(methylthio)phenyl)hexan-2-yl)aniline (1f)**



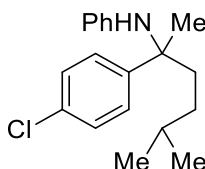
Prepared according to general procedure (A) from 1-(4-(methylthio)phenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1f** as a yellow oil (0.80 g, 2.6 mmol, 52% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 7.9 Hz, 2H), 3.99 (s, 1H), 2.49 (s, 3H), 1.94 – 1.70 (m, 2H), 1.61 (s, 3H), 1.50 – 1.34 (m, 1H), 1.09 (dd, *J* = 16.0, 7.4 Hz, 2H), 0.83 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 7.2 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 143.8, 135.9, 128.8, 126.9, 126.6, 117.1, 115.4, 58.2, 42.5, 32.7, 28.4, 25.6, 22.8, 22.7, 15.9. HRMS (ESI) calcd. for C₂₀H₂₈NS [M+H]⁺ *m/z* 314.1942, found 314.1940.

***N*-(2-(4-fluorophenyl)-5-methylhexan-2-yl)aniline (1g)**



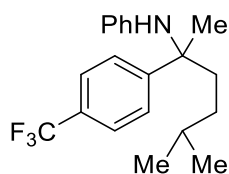
Prepared according to general procedure (A) from 1-(4-fluorophenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1g** as a yellow oil (0.97 g, 3.4 mmol, 67% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.38 (m, 2H), 7.07 – 6.96 (m, 4H), 6.70 – 6.57 (m, 1H), 6.38 – 6.27 (m, 2H), 4.00 (s, 1H), 1.83 (dddd, $J = 19.0, 13.2, 9.6, 7.2$ Hz, 2H), 1.63 (s, 3H), 1.51 – 1.34 (m, 1H), 1.19 – 1.01 (m, 2H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.82 (d, $J = 6.8$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 161.6 (d, $J = 245.4$ Hz), 146.0, 142.5 (d, $J = 3.0$ Hz), 128.8, 128.0 (d, $J = 7.1$ Hz), 117.3, 115.4, 115.2 (d, $J = 21.2$ Hz), 58.1, 42.6, 32.7, 28.4, 25.7, 22.7, 22.6. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{25}\text{NF}$ $[\text{M}+\text{H}]^+$ m/z 286.1971, found 286.1967.

***N*-(2-(4-chlorophenyl)-5-methylhexan-2-yl)aniline (1h)**



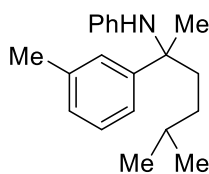
Prepared according to general procedure (A) from 1-(4-chlorophenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1h** as a colorless oil (1.14 g, 3.8 mmol, 76% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.35 (m, 2H), 7.33 – 7.26 (m, 2H), 7.05 – 6.96 (m, 2H), 6.62 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.34 – 6.26 (m, 2H), 3.98 (s, 1H), 1.91 – 1.69 (m, 2H), 1.61 (s, 3H), 1.49 – 1.35 (m, 1H), 1.07 (ddd, $J = 10.9, 8.5, 6.4$ Hz, 2H), 0.82 (d, $J = 6.6$ Hz, 3H), 0.80 (d, $J = 6.6$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 145.4, 132.1, 128.9, 128.6, 127.9, 117.3, 115.4, 58.1, 42.5, 32.6, 28.4, 25.6, 22.7, 22.6. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{25}\text{NCl}$ $[\text{M}+\text{H}]^+$ m/z 302.1676, found 302.1677.

***N*-(5-methyl-2-(4-(trifluoromethyl)phenyl)hexan-2-yl)aniline (1j)**



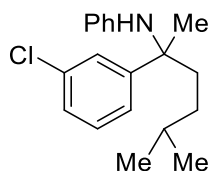
Prepared according to general procedure (A) from 1-(4-(trifluoromethyl)phenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1j** as a yellow oil (1.17 g, 3.5 mmol, 70% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.55 (m, 4H), 7.03 (t, $J = 7.8$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.31 (d, $J = 7.9$ Hz, 2H), 4.04 (s, 1H), 1.87 (dtd, $J = 17.0, 13.2, 8.3$ Hz, 2H), 1.67 (s, 3H), 1.50 – 1.40 (m, 1H), 1.11 (dd, $J = 16.2, 7.2$ Hz, 2H), 0.85 (d, $J = 6.7$ Hz, 3H), 0.83 (d, $J = 6.7$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 151.2, 145.7, 128.9, 128.7 (q, $J = 32.3$ Hz), 126.7, 125.5 (q, $J = 4.0$ Hz), 124.5 (q, $J = 273.7$ Hz), 117.5, 115.4, 58.5, 42.3, 32.6, 28.4, 25.7, 22.7, 22.6. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{25}\text{NF}_3$ $[\text{M}+\text{H}]^+$ m/z 336.1939, found 336.1938.

***N*-(5-methyl-2-(*m*-tolyl)hexan-2-yl)aniline (**1k**)**



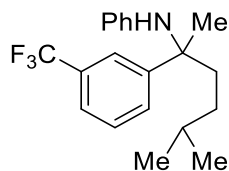
Prepared according to general procedure (A) from 1-(*m*-tolyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1k** as a colorless oil (1.12 g, 4.0 mmol, 80% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.18 (m, 1H), 7.09 – 6.95 (m, 3H), 6.65 – 6.55 (m, 1H), 6.38 – 6.29 (m, 2H), 3.99 (s, 1H), 2.36 (s, 3H), 1.93 – 1.76 (m, 2H), 1.62 (s, 3H), 1.44 (dt, J = 13.3, 6.6 Hz, 1H), 1.12 (dt, J = 9.4, 7.1 Hz, 2H), 0.84 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 147.0, 146.3, 137.9, 128.7, 128.3, 127.1, 126.9, 123.4, 117.0, 115.5, 58.3, 42.2, 32.7, 28.4, 25.8, 22.8, 22.7, 21.9. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 282.2222, found 282.2221.

***N*-(2-(3-chlorophenyl)-5-methylhexan-2-yl)aniline (**1m**)**



Prepared according to general procedure (A) from 1-(3-chlorophenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1m** as a colorless oil (0.81 g, 2.7 mmol, 54% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (t, J = 1.9 Hz, 1H), 7.36 (dt, J = 7.5, 1.6 Hz, 1H), 7.23 (d, J = 7.3 Hz, 1H), 7.20 (dt, J = 8.0, 1.7 Hz, 1H), 7.00 (dd, J = 8.4, 7.0 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.30 (d, J = 8.0 Hz, 2H), 3.97 (s, 1H), 1.81 (dtd, J = 19.5, 13.3, 8.5 Hz, 2H), 1.60 (s, 3H), 1.49 – 1.35 (m, 1H), 1.08 (dd, J = 15.9, 7.5 Hz, 2H), 0.82 (d, J = 6.7 Hz, 3H), 0.80 (d, J = 6.7 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 149.4, 145.8, 134.5, 129.8, 128.9, 126.6, 126.5, 124.6, 117.4, 115.5, 58.3, 42.2, 32.6, 28.4, 25.6, 22.7, 22.6. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{25}\text{NCl}$ $[\text{M}+\text{H}]^+$ m/z 302.1676, found 302.1672.

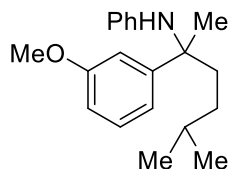
***N*-(5-methyl-2-(3-(trifluoromethyl)phenyl)hexan-2-yl)aniline (**1n**)**



Prepared according to general procedure (A) from 1-(3-(trifluoromethyl)phenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1n** as a yellow oil (0.70 g, 2.1 mmol, 42% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, J = 1.8, 0.9 Hz, 1H), 7.75 (dt, J = 7.8, 1.5 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.69 (tq, J = 7.4, 1.1 Hz, 1H), 6.41 – 6.32 (m, 2H), 4.07 (s, 1H), 1.92 (dddd, J = 20.6, 16.8, 13.3, 8.3 Hz, 2H), 1.71 (s, 3H), 1.55 – 1.45 (m, 1H), 1.17 (dd, J = 16.2, 7.3 Hz, 2H), 0.89 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 148.3, 145.7, 130.8 (q, J = 32.3 Hz),

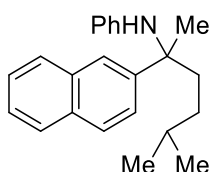
130.0, 129.0, 128.9, 124.5 (q, $J = 272.7$ Hz), 123.4 (q, $J = 4.0$ Hz), 122.9 (q, $J = 4.0$ Hz), 117.6, 115.5, 58.4, 42.1, 32.6, 28.3, 25.8, 22.7, 22.6. HRMS (ESI) calcd. for $C_{20}H_{25}NF_3$ $[M+H]^+$ m/z 336.1939, found 336.1935.

***N*-(2-(3-methoxyphenyl)-5-methylhexan-2-yl)aniline (1o)**



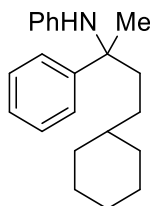
Prepared according to general procedure (A) from 1-(3-methoxyphenyl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1o** as a colorless oil (1.40 g, 4.7 mmol, 94% total yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, $J = 7.9$ Hz, 1H), 7.09 – 7.03 (m, 2H), 7.03 – 6.96 (m, 2H), 6.78 (dd, $J = 8.1, 2.3$ Hz, 1H), 6.64 – 6.55 (m, 1H), 6.34 (dd, $J = 8.5, 1.1$ Hz, 2H), 3.98 (s, 1H), 3.79 (s, 3H), 1.94 – 1.72 (m, 2H), 1.61 (s, 3H), 1.48 – 1.38 (m, 1H), 1.10 (dt, $J = 8.6, 7.4$ Hz, 2H), 0.83 (d, $J = 7.0$ Hz, 3H), 0.81 (d, $J = 7.0$ Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 148.8, 146.2, 129.4, 128.7, 118.8, 117.1, 115.4, 112.6, 111.1, 58.4, 55.3, 42.3, 32.7, 28.4, 25.6, 22.7, 22.6. HRMS (ESI) calcd. for $C_{20}H_{28}NO$ $[M+H]^+$ m/z 298.2171, found 298.2167.

***N*-(5-methyl-2-(naphthalen-2-yl)hexan-2-yl)aniline (1p)**



Prepared according to general procedure (A) from 1-(naphthalen-2-yl)ethan-1-one and 1-bromo-3-methylbutane to provide the title compound **1p** as a yellow solid (0.41 g, 1.3 mmol, 26% total yield). 1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.79 (m, 4H), 7.72 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.55 – 7.46 (m, 2H), 7.04 – 6.94 (m, 2H), 6.62 (tt, $J = 7.2, 1.1$ Hz, 1H), 6.43 – 6.36 (m, 2H), 4.11 (s, 1H), 2.04 – 1.90 (m, 2H), 1.77 (s, 3H), 1.52 – 1.42 (m, 1H), 1.26 – 1.06 (m, 2H), 0.85 (d, $J = 6.6$ Hz, 3H), 0.84 (d, $J = 6.6$ Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 144.7, 133.6, 132.4, 128.8, 128.3, 128.3, 127.6, 125.9, 125.6, 125.2, 124.6, 117.2, 115.5, 58.6, 42.4, 32.8, 28.4, 25.5, 22.7, 22.7. HRMS (ESI) calcd. for $C_{23}H_{28}N$ $[M+H]^+$ m/z 318.2222, found 318.2223.

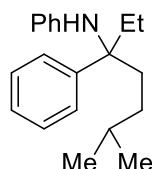
***N*-(4-cyclohexyl-2-phenylbutan-2-yl)aniline (1q)**



Prepared according to general procedure (A) from acetophenone and (2-bromoethyl)cyclohexane to provide the title compound **1q** as a colorless oil (1.07 g, 3.5

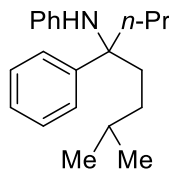
mmol, 70% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.45 (m, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.00 (t, $J = 7.7$ Hz, 2H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.33 (d, $J = 8.0$ Hz, 2H), 4.02 (s, 1H), 1.99 – 1.77 (m, 2H), 1.74 – 1.57 (m, 8H), 1.25 – 1.02 (m, 6H), 0.94 – 0.69 (m, 2H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 146.1, 128.7, 128.4, 126.3, 126.2, 117.0, 115.3, 58.3, 41.8, 38.0, 33.4, 33.3, 31.2, 26.7, 26.4, 26.4, 25.6. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{30}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 308.2378, found 308.2375.

***N*-(6-methyl-3-phenylheptan-3-yl)aniline (1s)**



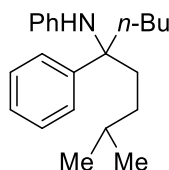
Prepared according to general procedure (A) from propiophenone and 1-bromo-3-methylbutane to provide the title compound **1s** as a colorless oil (1.35 g, 4.8 mmol, 96% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.44 (m, 2H), 7.38 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 7.02 – 6.92 (m, 2H), 6.58 (tt, $J = 7.4, 1.1$ Hz, 1H), 6.35 – 6.25 (m, 2H), 3.96 (s, 1H), 2.18 – 1.74 (m, 4H), 1.48 – 1.32 (m, 1H), 1.12 – 0.92 (m, 2H), 0.85 – 0.70 (m, 9H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.1, 146.1, 128.8, 128.3, 126.8, 126.3, 116.9, 115.2, 60.9, 35.1, 32.2, 29.7, 28.3, 22.8, 22.6, 7.8. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 282.2222, found 282.2218.

***N*-(7-methyl-4-phenyloctan-4-yl)aniline (1t)**



Prepared according to general procedure (A) from 1-phenylbutan-1-one and 1-bromo-3-methylbutane to provide the title compound **1t** as a colorless oil (0.90 g, 3.1 mmol, 62% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.44 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 – 7.19 (m, 1H), 7.01 – 6.92 (m, 2H), 6.61 – 6.55 (m, 1H), 6.33 – 6.25 (m, 2H), 3.95 (s, 1H), 2.10 – 1.91 (m, 2H), 1.92 – 1.71 (m, 2H), 1.44 – 1.35 (m, 1H), 1.24 – 1.10 (m, 2H), 1.10 – 0.99 (m, 2H), 0.88 – 0.71 (m, 9H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 146.2, 128.8, 128.3, 126.7, 126.3, 116.9, 115.2, 60.8, 40.5, 35.4, 32.2, 28.4, 22.8, 22.6, 16.6, 14.6. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{30}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 296.2378, found 296.2380.

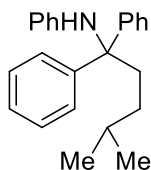
***N*-(2-methyl-5-phenylnonan-5-yl)aniline (1u)**



Prepared according to general procedure (A) from 1-phenylpentan-1-one and

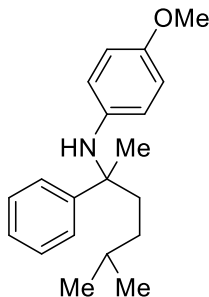
1-bromo-3-methylbutane to provide the title compound **1u** as a white solid (1.21 g, 3.9 mmol, 78% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.44 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.8 Hz, 2H), 6.58 (t, J = 7.3 Hz, 1H), 6.30 (d, J = 8.0 Hz, 2H), 3.96 (s, 1H), 2.12 – 1.94 (m, 2H), 1.93 – 1.78 (m, 2H), 1.45 – 1.34 (m, 1H), 1.31 – 1.18 (m, 2H), 1.18 – 1.08 (m, 2H), 1.09 – 1.00 (m, 2H), 0.88 – 0.70 (m, 9H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 146.2, 128.7, 128.3, 126.8, 126.29, 116.9, 115.2, 60.7, 37.7, 35.4, 32.2, 28.4, 25.5, 23.1, 22.8, 22.6, 14.2. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{32}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 310.2535, found 310.2535.

***N*-(4-methyl-1,1-diphenylpentyl)aniline (1v)**



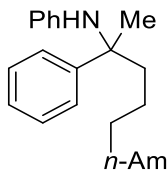
Prepared according to general procedure (A) from benzophenone and 1-bromo-3-methylbutane to provide the title compound **1v** as a white solid (0.63 g, 1.9 mmol, 38% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.51 (m, 4H), 7.36 – 7.27 (m, 4H), 7.23 – 7.16 (m, 2H), 7.05 – 6.95 (m, 2H), 6.64 (tt, J = 7.3, 1.1 Hz, 1H), 6.45 – 6.36 (m, 2H), 4.53 (s, 1H), 2.62 – 2.47 (m, 2H), 1.51 – 1.43 (m, 1H), 1.13 – 1.00 (m, 2H), 0.78 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz,) δ 146.2, 146.1, 128.7, 128.5, 126.8, 126.5, 117.8, 116.2, 65.2, 35.4, 32.7, 28.4, 22.7. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 330.2222, found 330.2218.

4-methoxy-*N*-(5-methyl-2-phenylhexan-2-yl)aniline (1y)



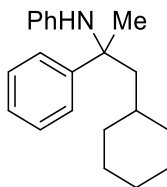
Prepared according to general procedure (A) from acetophenone, aniline and 1-bromo-3-methylbutane to provide the title compound **1y** as a colorless oil (1.31 g, 4.4 mmol, 88% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, J = 8.3, 1.1 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.71 – 6.56 (m, 2H), 6.30 (d, J = 8.9 Hz, 2H), 3.73 (s, 1H), 3.68 (s, 3H), 2.00 – 1.71 (m, 2H), 1.59 (s, 3H), 1.49 – 1.36 (m, 1H), 1.19 – 1.02 (m, 2H), 0.83 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 152.0, 147.2, 140.2, 128.4, 126.4, 126.3, 117.0, 114.4, 58.6, 55.7, 42.3, 32.8, 28.4, 25.7, 22.8, 22.7. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 298.2171, found 298.2168.

***N*-(2-phenyldecan-2-yl)aniline (1ag)**



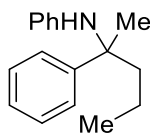
Prepared according to general procedure (A) from acetophenone and 1-bromooctane to provide the title compound **1ag** as a colorless oil (1.08 g, 3.5 mmol, 70% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.25 – 7.18 (m, 1H), 6.98 (t, J = 7.6 Hz, 2H), 6.58 (t, J = 7.3 Hz, 1H), 6.31 (d, J = 8.0 Hz, 2H), 4.01 (s, 1H), 1.95 – 1.72 (m, 2H), 1.63 (s, 3H), 1.34 – 1.12 (m, 12H), 0.86 (t, J = 6.8 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 146.2, 128.8, 128.5, 126.3, 126.3, 117.0, 115.4, 58.4, 44.7, 32.0, 30.1, 29.6, 29.4, 25.7, 23.8, 22.8, 14.3. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{32}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 310.2535, found 310.2530.

***N*-(1-cyclohexyl-2-phenylpropan-2-yl)aniline (1ah)**



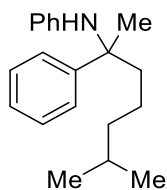
Prepared according to general procedure (A) from acetophenone and (bromomethyl)cyclohexane to provide the title compound **1ah** as a colorless oil (1.35 g, 4.6 mmol, 92% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.45 (m, 2H), 7.37 – 7.29 (m, 2H), 7.26 – 7.21 (m, 1H), 7.05 – 6.96 (m, 2H), 6.66 – 6.57 (m, 1H), 6.38 – 6.29 (m, 2H), 4.05 (s, 1H), 1.75 (dd, J = 7.9, 4.8 Hz, 2H), 1.70 (s, 3H), 1.64 – 1.51 (m, 3H), 1.50 – 1.31 (m, 3H), 1.24 – 1.01 (m, 3H), 0.98 – 0.82 (m, 2H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.7, 146.2, 128.8, 128.4, 126.4, 126.4, 117.0, 115.5, 59.0, 53.1, 35.6, 35.4, 33.5, 26.6, 26.5, 26.3, 25.5. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 294.2222, found 294.2222.

***N*-(2-phenylpentan-2-yl)aniline (1ai)**



Prepared according to general procedure (A) from acetophenone and 1-bromopropane to provide the title compound **1ai** as a colorless oil (0.76 g, 3.2 mmol, 64% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.43 (m, 2H), 7.37 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.04 – 6.93 (m, 2H), 6.59 (tq, J = 7.4, 1.0 Hz, 1H), 6.31 (dq, J = 7.7, 0.9 Hz, 2H), 4.01 (s, 1H), 2.00 – 1.69 (m, 2H), 1.64 (s, 3H), 1.37 – 1.15 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.7, 146.2, 128.8, 128.5, 126.4, 126.3, 117.0, 115.3, 58.5, 47.1, 25.8, 17.2, 14.6. HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 240.1752, found 240.1748.

***N*-(6-methyl-2-phenylheptan-2-yl)aniline (1am)**



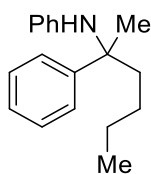
Prepared according to general procedure (A) from acetophenone and 1-bromo-4-methylpentane to provide the title compound **1am** as a colorless oil (1.29 g, 4.6 mmol, 92% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (dd, J = 8.3, 1.1 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (tt, J = 6.5, 1.1 Hz, 1H), 7.09 – 6.97 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.40 – 6.29 (m, 2H), 4.05 (s, 1H), 1.99 – 1.75 (m, 2H), 1.68 (s, 3H), 1.50 (dp, J = 13.3, 6.7 Hz, 1H), 1.26 (dddt, J = 13.5, 11.7, 5.6, 2.8 Hz, 2H), 1.17 – 1.06 (m, 2H), 0.83 (dd, J = 6.6, 3.2 Hz, 6H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 146.2, 128.8, 128.5, 126.3, 126.3, 117.0, 115.4, 58.5, 44.8, 39.3, 27.8, 25.7, 22.7, 22.6, 21.5. HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 282.2222, found 282.2221.

General procedure (B) for the synthesis of the substrates.

Step 1: Preparation of imine. The imine was prepared according to *Step 1* of general procedure (A).

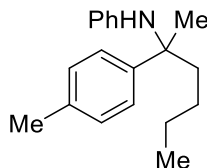
Step 2: Preparation of the substrates. Butyllithium (2.5 M in hexane, 4.0 equiv) was added dropwise to a vigorously stirred solution of imine in Et_2O (1.0 M) at -78°C under N_2 atmosphere and stirred at room temperature for 3 h (but with **1ac**, **1ae**, **1af**, the stirring temperature was -40°C). After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by column chromatography on silica gel to give the substrate **1**.

N-(2-phenylhexan-2-yl)aniline (**1z**)



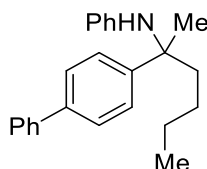
Prepared according to general procedure (B) from acetophenone to provide the title compound **1z** as a colorless oil (1.16 g, 4.6 mmol, 92% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.48 (m, 2H), 7.37 (dd, J = 10.7, 4.6 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.10 – 7.00 (m, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.37 (dd, J = 8.6, 1.2 Hz, 2H), 4.07 (s, 1H), 2.01 – 1.77 (m, 2H), 1.70 (s, 3H), 1.39 – 1.15 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 146.2, 128.8, 128.5, 126.3, 126.3, 117.0, 115.4, 58.4, 44.6, 26.0, 25.7, 23.1, 14.2. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 254.1909, found 254.1904.

N-(2-(*p*-tolyl)hexan-2-yl)aniline (**1aa**)



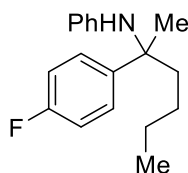
Prepared according to general procedure (B) from 1-(p-tolyl)ethan-1-one to provide the title compound **1aa** as a colorless oil (1.01 g, 3.8 mmol, 76% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.59 (td, J = 7.4, 1.0 Hz, 1H), 6.34 (dd, J = 8.6, 1.0 Hz, 2H), 4.00 (s, 1H), 2.34 (s, 3H), 1.83 (dtd, J = 19.8, 13.3, 7.8 Hz, 2H), 1.62 (s, 3H), 1.34 – 1.13 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.3, 143.8, 135.8, 129.2, 128.8, 126.2, 116.9, 115.4, 58.2, 44.6, 26.0, 25.8, 23.2, 21.1, 14.2. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 268.2065, found 268.2063.

***N*-(2-([1,1'-biphenyl]-4-yl)hexan-2-yl)aniline (1ab)**



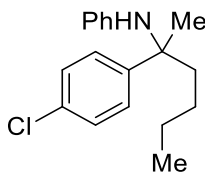
Prepared according to general procedure (B) from 1-([1,1'-biphenyl]-4-yl)ethan-1-one to provide the title compound **1ab** as a white solid (1.02 g, 3.1 mmol, 62% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.61 (m, 2H), 7.61 – 7.51 (m, 4H), 7.45 (dd, J = 10.5, 4.8 Hz, 2H), 7.40 – 7.30 (m, 1H), 7.11 – 6.94 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.39 (d, J = 8.0 Hz, 2H), 4.06 (s, 1H), 2.01 – 1.78 (m, 2H), 1.69 (s, 3H), 1.39 – 1.17 (m, 4H), 0.87 (t, J = 6.7 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.2, 146.0, 141.0, 139.0, 128.8, 127.2, 127.1, 127.1, 126.8, 117.1, 115.4, 58.3, 44.5, 26.0, 25.8, 23.2, 14.2. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 330.2222, found 330.2221.

***N*-(2-(4-fluorophenyl)hexan-2-yl)aniline (1ac)**



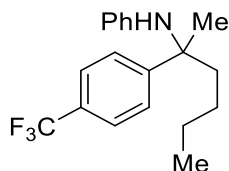
Prepared according to general procedure (B) from 1-(4-fluorophenyl)ethan-1-one to provide the title compound **1ac** as a yellow oil (1.00 g, 3.7 mmol, 74% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.38 (m, 2H), 7.02 (dd, J = 12.4, 4.8 Hz, 4H), 6.72 – 6.54 (m, 1H), 6.33 (dd, J = 8.6, 1.0 Hz, 2H), 4.02 (s, 1H), 2.02 – 1.71 (m, 2H), 1.65 (s, 3H), 1.37 – 1.05 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 161.6 (d, J = 244.4 Hz), 146.0, 142.4 (d, J = 3.0 Hz), 128.8, 127.9 (d, J = 8.1 Hz), 117.2, 115.4, 115.2 (d, J = 21.2 Hz), 58.1, 44.7, 26.0, 25.7, 23.1, 14.1. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{NF}$ $[\text{M}+\text{H}]^+$ m/z 272.1815, found 272.1813.

***N*-(2-(4-chlorophenyl)hexan-2-yl)aniline (1ad)**



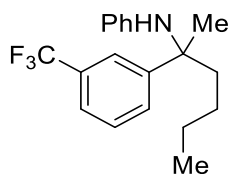
Prepared according to general procedure (B) from 1-(4-chlorophenyl)ethan-1-one to provide the title compound **1ad** as a colorless oil (0.92 g, 3.2 mmol, 64% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.42 (dd, $J = 7.2, 1.5$ Hz, 2H), 7.31 (dd, $J = 5.0, 3.8$ Hz, 2H), 7.03 (td, $J = 7.4, 2.2$ Hz, 2H), 6.69 – 6.61 (m, 1H), 6.33 (dd, $J = 8.6, 1.0$ Hz, 2H), 4.02 (s, 1H), 1.96 – 1.73 (m, 2H), 1.65 (s, 3H), 1.33 – 1.15 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 145.4, 132.2, 128.9, 128.6, 127.9, 117.3, 115.4, 58.2, 44.5, 26.0, 25.6, 23.1, 14.1. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{NCl}$ $[\text{M}+\text{H}]^+$ m/z 288.1519, found 288.1513.

***N*-(2-(4-(trifluoromethyl)phenyl)hexan-2-yl)aniline (1ae)**



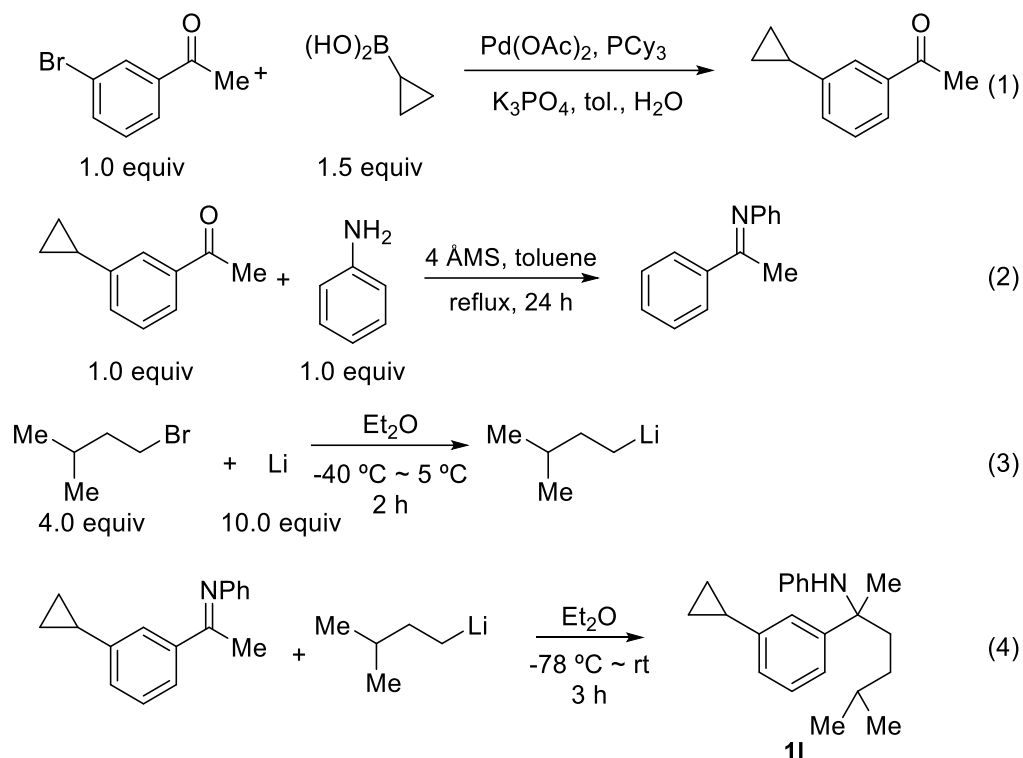
Prepared according to general procedure (B) from 1-(4-(trifluoromethyl)phenyl)ethan-1-one to provide the title compound **1ae** as a yellow oil (1.00 g, 3.1 mmol, 62% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.55 (m, 4H), 7.06 – 6.96 (m, 2H), 6.63 (ddt, $J = 8.4, 7.4, 1.1$ Hz, 1H), 6.33 – 6.25 (m, 2H), 4.04 (s, 1H), 1.97 – 1.71 (m, 2H), 1.66 (s, 3H), 1.35 – 1.11 (m, 4H), 0.85 (t, $J = 7.0$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 151.1, 145.7, 128.9, 128.7 (q, $J = 32.3$ Hz), 126.7, 125.5 (q, $J = 4.0$ Hz), 124.5 (q, $J = 272.7$ Hz), 117.5, 115.4, 58.5, 44.4, 25.9, 25.7, 23.1, 14.1. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NF}_3$ $[\text{M}+\text{H}]^+$ m/z 322.1783, found 322.1778.

***N*-(2-(3-(trifluoromethyl)phenyl)hexan-2-yl)aniline (1af)**



Prepared according to general procedure (B) from 1-(3-(trifluoromethyl)phenyl)ethan-1-one to provide the title compound **1af** as a yellow oil (0.55 g, 1.7 mmol, 34% total yield). ^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.64 (m, 2H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.05 – 6.96 (m, 2H), 6.63 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.34 – 6.25 (m, 2H), 4.02 (s, 1H), 1.99 – 1.73 (m, 2H), 1.66 (s, 3H), 1.32 – 1.12 (m, 4H), 0.84 (t, $J = 7.0$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 145.7, 130.8 (q, $J = 32.3$ Hz), 130.0, 129.0, 128.9, 124.5 (q, $J = 273.7$ Hz), 123.4 (q, $J = 4.0$ Hz), 122.9 (q, $J = 4.0$ Hz), 117.5, 115.5, 58.4, 44.2, 25.9, 25.8, 23.0, 14.1. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NF}_3$ $[\text{M}+\text{H}]^+$ m/z 322.1783, found 322.1778.

Synthesis of *N*-(2-(3-cyclopropylphenyl)-5-methylhexan-2-yl)aniline (1l)



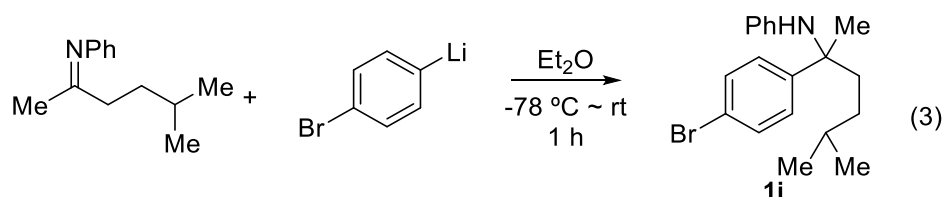
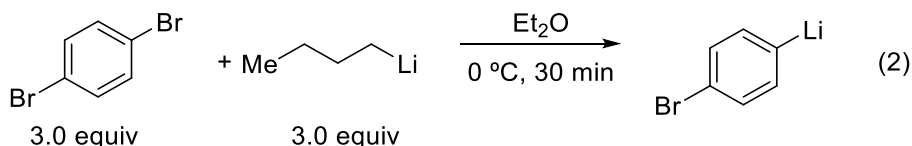
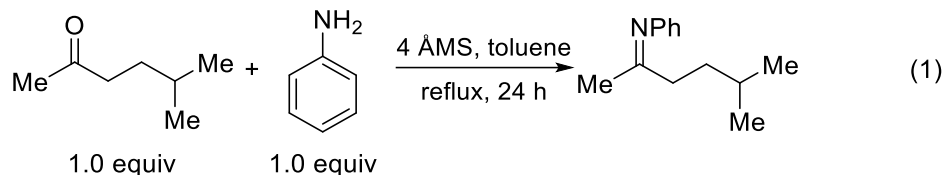
Step 1: Preparation of 1-(3-cyclopropylphenyl)ethan-1-one. The ketone was prepared according to a patent^[1]. To a mixture of 1-(3-bromophenyl)ethan-1-one (10.0 mmol, 1.0 equiv), cyclopropylboronic acid (1.5 equiv), K₃PO₄ (3.0 equiv) and PCy₃ (0.2 equiv) in toluene/H₂O (0.2 M, 100:1) was added Pd(OAc)₂ (0.1 equiv) under N₂. The reaction was heated at 100 °C for 15 h. After completion, it was allowed to cool to rt and washed with water. The aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄. After concentrated under vacuum, the crude was purified by column chromatography on silica gel to provide the ketone as a colorless oil (1.55 g, 9.7 mmol, 97% total yield).

Step 2: Preparation of N,1-diphenylethan-1-imine. The imine was prepared according to Step 1 of general procedure (A).

Step 3: Preparation of the lithium reagent. The lithium reagent was prepared according to Step 2 of general procedure (A).

Step 4: Preparation of N-(2-(3-cyclopropylphenyl)-5-methylhexan-2-yl)aniline (11**).** Prepared according to Step 3 of general procedure (A) to provide the title compound **11** as a colorless oil (1.35 g, 4.4 mmol, 88% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.24 (m, 1H), 7.24 – 7.16 (m, 2H), 7.05 – 6.96 (m, 2H), 6.94 – 6.85 (m, 2H), 6.65 – 6.57 (m, 1H), 6.35 (dd, *J* = 8.6, 1.0 Hz, 2H), 3.99 (s, 1H), 1.97 – 1.74 (m, 3H), 1.62 (s, 3H), 1.50 – 1.38 (m, 1H), 1.21 – 1.04 (m, 2H), 1.01 – 0.89 (m, 2H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.71 – 0.64 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 146.9, 146.3, 144.0, 128.8, 128.3, 123.9, 123.5, 123.1, 117.0, 115.5, 58.4, 42.2, 32.7, 28.4, 25.9, 22.8, 22.7, 15.8, 9.5, 9.5. HRMS (ESI) calcd. for C₂₂H₃₀N [M+H]⁺ *m/z* 308.2378, found 308.2368.

Synthesis of *N*-(2-(4-bromophenyl)-5-methylhexan-2-yl)aniline (**1i**).

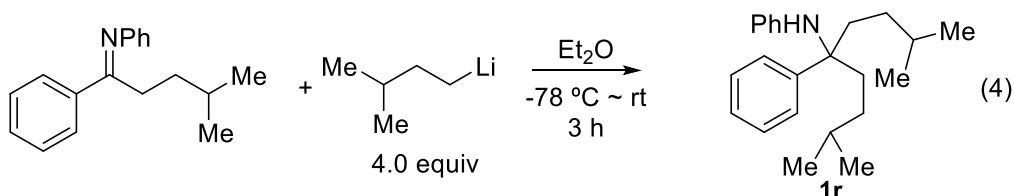
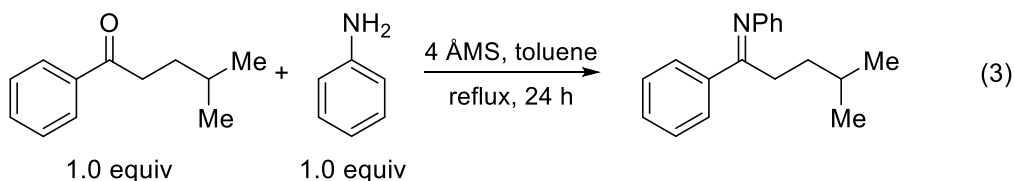
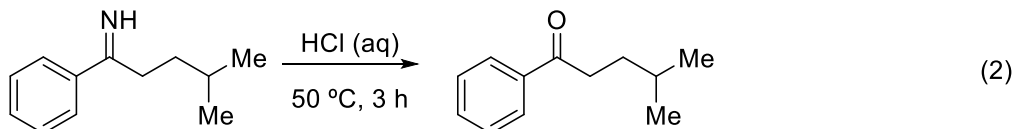
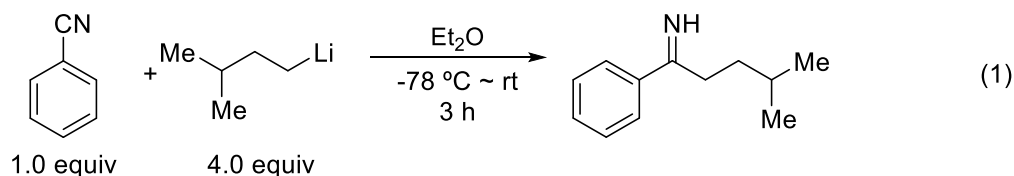


Step 1: Preparation of 5-methyl-N-phenylhexan-2-imine. The imine was prepared according to Step 1 of general procedure (A).

Step 2: Preparation of (4-bromophenyl)lithium. Butyllithium (2.5 M in hexane, 3.0 equiv) was added dropwise to a vigorously stirred solution of 1,4-dibromobenzene in Et₂O (1.0 M) at 0 °C under N₂ atmosphere and stirred for another 30 min. After completion, the resulting blackish suspension was then used immediately.

Step 3: Preparation of 1i. The freshly prepared lithium reagent was added dropwise to a vigorously stirred solution of imine in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 1 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1i** as a white solid (0.69 g, 2.0 mmol, 10% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.36 (m, 2H), 7.32 (dd, *J* = 9.1, 2.4 Hz, 2H), 6.98 (tt, *J* = 7.8, 2.3 Hz, 2H), 6.60 (tt, *J* = 7.4, 1.8 Hz, 1H), 6.29 (dt, *J* = 8.9, 1.9 Hz, 2H), 3.95 (s, 1H), 1.94 – 1.66 (m, 2H), 1.59 (s, 3H), 1.49 – 1.32 (m, 1H), 1.13 – 0.99 (m, 2H), 0.81 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 145.8, 131.5, 128.8, 128.3, 120.3, 117.3, 115.4, 58.2, 42.4, 32.6, 28.3, 25.5, 22.7, 22.6. HRMS (ESI) calcd. for C₁₉H₂₅NBr [M+H]⁺ *m/z* 346.1170, found 346.1166.

Synthesis of *N*-(2,8-dimethyl-5-phenylnonan-5-yl)aniline (**1r**).



Step 1: Preparation of 4-methyl-1-phenylpentan-1-imine. The freshly prepared isopentyllithium was added dropwise to a vigorously stirred solution of benzonitrile in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 3 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was used directly.

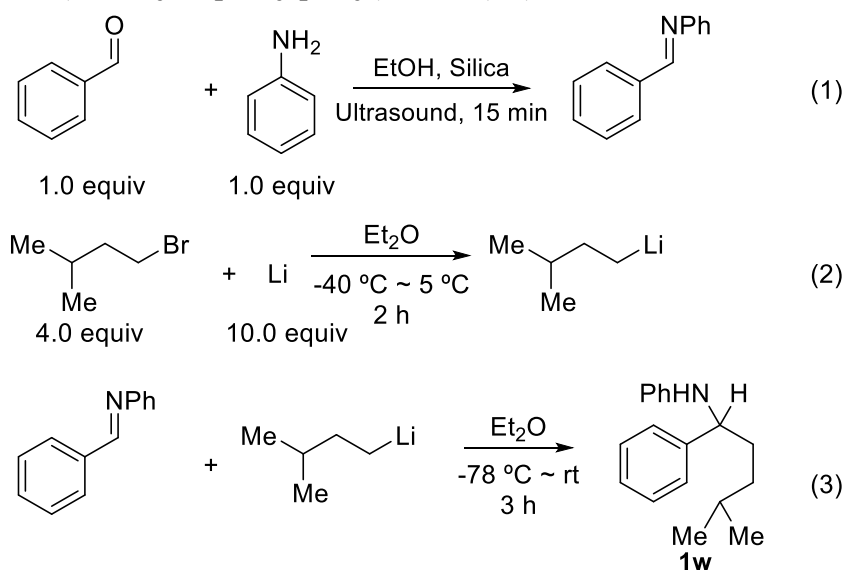
Step 2: Hydrolysis of 4-methyl-1-phenylpentan-1-imine. The prepared crude of *Step 1* was mixed with dilute hydrochloric acid and stirred at 50 °C for 3 h. After completion, EtOAc was added and the organic layer was separated, the aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was used directly without further purification.

Step 3: Preparation of 4-methyl-N,1-diphenylpentan-1-imine. To an oven-dried round-bottom bottle equipped with a magnetic stir bar was added 4-methyl-1-phenylpentan-1-one (1.0 equiv), aniline (1.0 equiv), 4 ÅMS (0.2 g/mmol) and toluene (2.0 M). The mixture was then reflux for 24 h. After completion, it was allowed to cool to room temperature, and was directly filtered through a short pad of Celite®, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

Step 4: Preparation of N-(2,8-dimethyl-5-phenylnonan-5-yl)aniline (1r). The freshly prepared lithium reagent was added dropwise to a vigorously stirred solution of 4-methyl-N,1-diphenylpentan-1-imine in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 3 h. After completion, the reaction was quenched with water.

The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1r** as a colorless oil (0.65 g, 2.0 mmol, 40% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.43 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.03 – 6.91 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 1H), 2.01 (ddd, *J* = 13.2, 11.1, 5.7 Hz, 2H), 1.85 (ddd, *J* = 13.2, 10.8, 5.8 Hz, 2H), 1.49 – 1.32 (m, 2H), 1.13 – 0.94 (m, 4H), 0.82 (d, *J* = 6.7 Hz, 6H), 0.77 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 146.4, 146.2, 128.7, 128.3, 126.8, 126.3, 116.9, 115.3, 60.7, 35.4, 32.2, 28.4, 22.8, 22.6. HRMS (ESI) calcd. for C₂₃H₃₄N [M+H]⁺ *m/z* 324.2691, found 324.2692.

Synthesis of *N*-(4-methyl-1-phenylpentyl)aniline (**1w**).

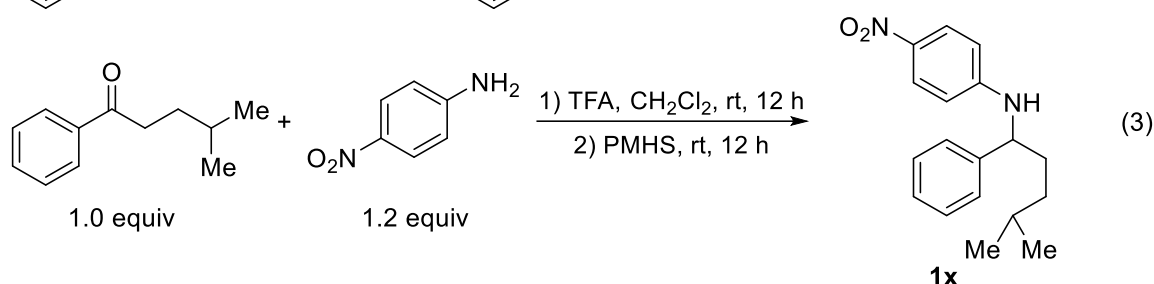
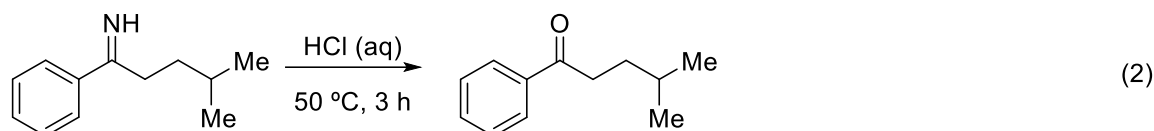
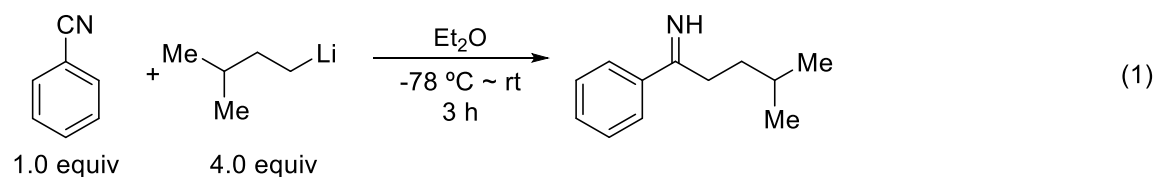


Step 1: Preparation of *N*,1-diphenylmethanimine. The imine was prepared according to the method developed by Guzen^[2]. To an oven-dried round-bottom bottle was added benzaldehyde (1.0 equiv), aniline (1.0 equiv), silica (0.3 g/mmol) and EtOH (0.3 M). The mixture was then placed under ultrasound irradiation for 15 min. After completion, it was filtered, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

Step 2: Preparation of lithium reagent. The lithium reagent was prepared according to Step 2 of general procedure (A).

Step 3: Preparation of the *N*-(4-methyl-1-phenylpentyl)aniline (1w**).** The same as Step 3 of general procedure (A) used *N*,1-diphenylmethanimine to provide the title compound **1w** as a colorless oil (0.83 g, 3.3 mmol, 66% total yield). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 4H), 7.25 – 7.17 (m, 1H), 7.13 – 7.02 (m, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.04 (s, 1H), 1.87 – 1.68 (m, 2H), 1.64 – 1.43 (m, 1H), 1.40 – 1.12 (m, 2H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 147.6, 144.5, 129.2, 128.7, 127.0, 126.5, 117.2, 113.3, 58.6, 37.0, 35.6, 28.1, 22.7, 22.6. HRMS (ESI) calcd. for C₁₈H₂₄N [M+H]⁺ *m/z* 254.1909, found 254.1905.

Synthesis of *N*-(4-methyl-1-phenylpentyl)-4-nitroaniline (**1x**).



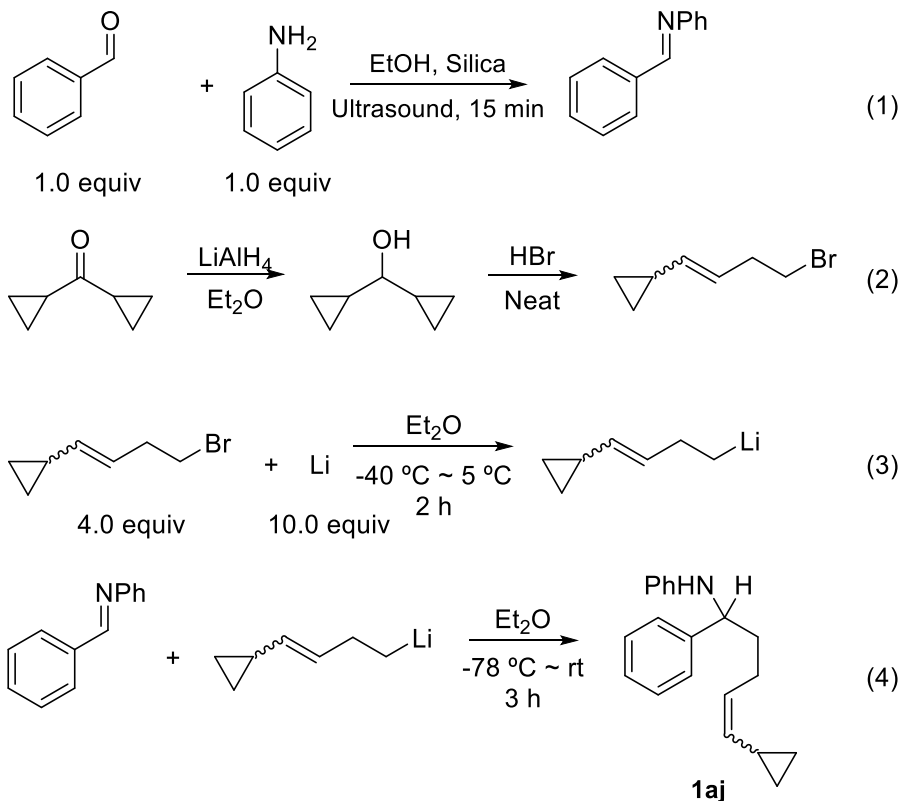
Step 1: Preparation of 4-methyl-1-phenylpentan-1-imine. The freshly prepared isopentyllithium was added dropwise to a vigorously stirred solution of benzonitrile in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 3 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was used directly.

Step 2: Hydrolysis of 4-methyl-1-phenylpentan-1-imine. The prepared crude of *Step 1* was mixed with dilute hydrochloric acid and stirred at 50 °C for 3 h. After completion, EtOAc was added and the organic layer was separated, the aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was used directly without further purification.

Step 3: Preparation of *N*-(4-methyl-1-phenylpentyl)-4-nitroaniline (1x**).** The substrate **1x** was prepared according to the method developed by Patel^[3]. To a stirred solution of 4-methyl-1-phenylpentan-1-one (1.0 equiv) and 4-nitroaniline (1.2 equiv) in dichloromethane (2.0 M) was added TFA (1.0 M). The mixture was stirred at room temperature for 12 h. PMHS [2.0 equiv of – MeSi(H)O– unit, average Mn: 1700–3200] was then added and the resulting mixture was again stirred for 12 h at rt. After completion, the reaction mixture was basified with 1 M aq sodium hydroxide to pH 8 and extracted with dichloromethane for 3 times. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1y** as a yellow solid (0.75 g, 2.5 mmol, 25% total yield). ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.92 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.23 (m, 3H), 6.51 – 6.39 (m, 2H), 4.90 (d, *J* = 6.1 Hz, 1H), 4.36 (q, *J* = 6.6 Hz, 1H), 1.91 – 1.77 (m, 2H), 1.63 – 1.47 (m, 1H), 1.40 – 1.10 (m,

2H), 0.89 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 152.6, 142.5, 138.2, 129.0, 127.7, 126.4, 126.3, 111.9, 58.5, 36.6, 35.4, 28.1, 22.7, 22.6. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ m/z 299.1760, found 299.1759.

Synthesis of *N*-(5-cyclopropyl-1-phenylpent-4-en-1-yl)aniline (**1aj**).



Step 1: Preparation of *N*,1-diphenylmethanimine. The imine was prepared according to the method developed by Guzen^[1]. To an oven-dried round-bottom bottle was added benzaldehyde (1.0 equiv), aniline (1.0 equiv), Silica (0.3 g/mmol) and EtOH (0.3 M). The mixture was then placed under ultrasound irradiation for 15 min. After completion, it was filtered, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

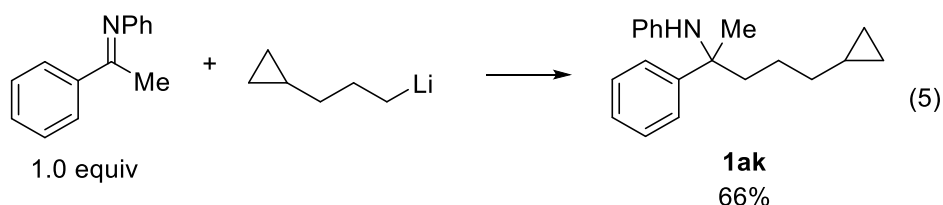
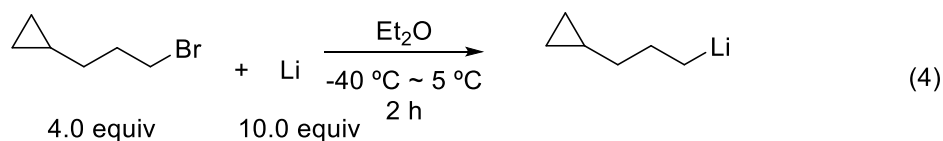
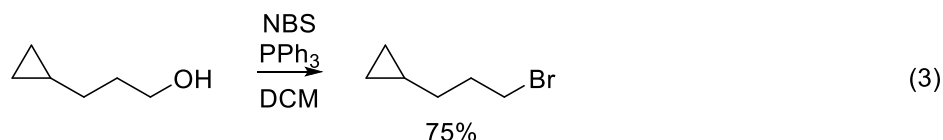
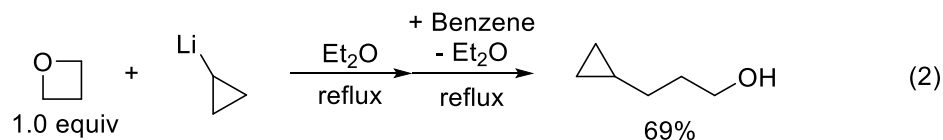
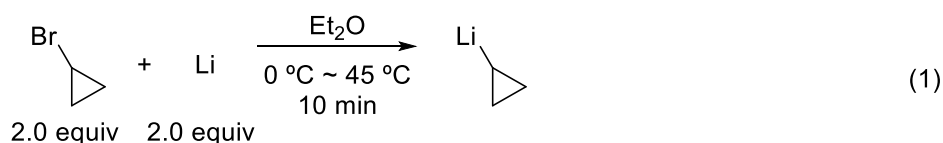
Step 2: Preparation of (4-bromobut-1-en-1-yl)cyclopropane. The bromide was prepared according to the method developed by Fifer^[4] and Kataoka^[5]. Dicyclopropylmethanone (1.0 equiv) dissolved in Et₂O (1.0 M) was added dropwise to a vigorously stirred suspension of LiAlH₄ (1.2 equiv) in Et₂O (1.0 M) at 0 °C under N₂ atmosphere and stirred for another 1 h at that temperature. After completion, the reaction was quenched with the sequential dropwise addition of water (0.05 mL/mmol), 10% NaOH (0.05 mL/mmol) and water (0.15 mL/mmol). The system was then filtered through Celite[®], diluted with Et₂O, washed with water and the organic layer was dried over Na₂SO₄ and concentrated under vacuum. The crude was used directly. At 0 °C under N₂ atmosphere, HBr (5.0 equiv) was added to a vigorously stirred neat phase of the newly prepared dicyclopropylmethanol and stirred for 15 min. After completion, the system was extracted with hexane (0.2 mL/mmol) for 3 times and the combined organic layer was washed with brine and NaHCO₃ (aq.), dried over Na₂SO₄. After evaporation, the

crude was distilled (104~105 °C, 17 mmHg) to give 7.0 g (90%) a mixture of (*E*)- and (*Z*)-(4-bromobut-1-en-1-yl)cyclopropane.

Step 3: Preparation of (4-cyclopropylbut-3-en-1-yl)lithium. The lithium reagent was prepared according to *Step 2* of general procedure (A).

Step 4: Preparation of N-(5-cyclopropyl-1-phenylpent-4-en-1-yl)aniline (1aj). Prepared according to *Step 2* of general procedure (A) to provide the substrates **1aj** as a colorless oil (0.55 g, 2.0 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.27 (m, 4.6H), 7.25 – 7.18 (m, 1.15H), 7.14 – 7.04 (m, 2.3H), 6.65 – 6.62 (m, 1.15H), 6.56 – 6.48 (m, 2.3H), 5.52 (dt, *J* = 15.1, 6.7 Hz, 1H), 5.43 – 5.22 (m, 0.15H), 4.97 (dd, *J* = 15.3, 8.6 Hz, 1H), 4.79 (dd, *J* = 19.3, 8.9 Hz, 0.15H), 4.38 (t, *J* = 6.9 Hz, 0.15H), 4.33 (t, *J* = 6.8 Hz, 1H), 4.11 (s, 1.15H), 2.28 – 2.25 (m, 0.3H), 2.18 – 2.00 (m, 2H), 1.97 – 1.76 (m, 2.3H), 1.48 – 1.41 (m, 0.15H), 1.41 – 1.28 (m, 1H), 0.77 – 0.58 (m, 2.15H), 0.39 – 0.23 (m, 2.15H); ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 147.5, 144.1, 135.2, 135.1, 129.1, 128.6, 126.9, 126.8, 126.8, 126.5, 126.4, 117.1, 113.3, 113.2, 57.8, 57.7, 38.8, 38.6, 29.3, 24.5, 13.6, 9.8, 6.9, 6.9, 6.5, 6.4. HRMS (ESI) calcd. for C₂₀H₂₄N [M+H]⁺ *m/z* 278.1909, found 278.1904.

Synthesis of *N*-(5-cyclopropyl-2-phenylpentan-2-yl)aniline (**1ak**).



Step 1 & 2: Preparation of 3-cyclopropylpropan-1-ol. The alcohol was prepared according to the method developed by Wagner^[6]. Bromocyclopropane (2.0 equiv) in Et₂O (5.0 M) was added dropwise to a vigorously stirred suspension of lithium shot (2.0 equiv) in Et₂O (5.0 M) under an argon atmosphere. The resulting brown suspension of cyclopropyllithium and lithium

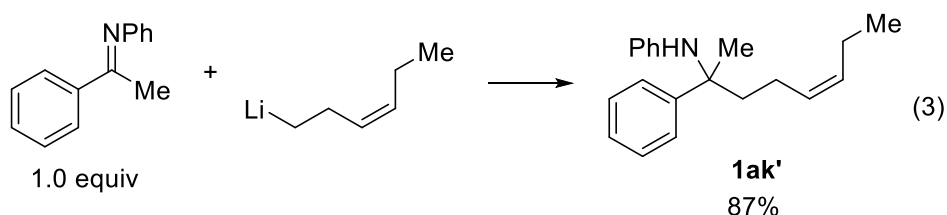
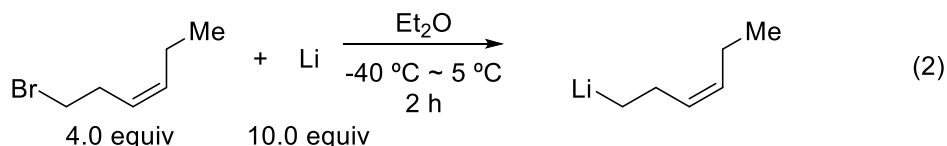
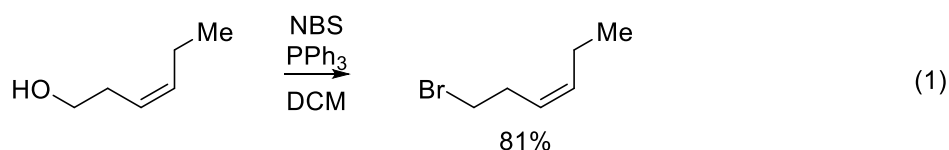
bromide was refluxed an additional 10 min and was then cooled in an ice bath. A solution of trimethylene oxide (1.0 equiv) in Et₂O (5.0 M) was added dropwise over 5 min. The resulting solution was allowed to stand at room temperature for 10 min and was then refluxed for 1 h. After 1.2 mL/mmol of benzene was added, the ether was distilled off and the solution was refluxed for 3.5 h. The cooled solution was treated with saturated aqueous ammonium chloride. The resulting aqueous layer was extracted once with Et₂O. The combined benzene and Et₂O solution was dried over Na₂SO₄. After evaporation, the crude was distilled (76 °C, 17 Torr) to give the 3-cyclopropylpropan-1-ol as a colorless oil (1.3 g, 13 mmol, 69%).

Step 3: Preparation of (3-bromopropyl)cyclopropane. The bromide was prepared according to the method developed by a patent^[7]. To a solution of 3-cyclopropylpropan-1-ol (1.0 equiv) in CH₂Cl₂ (0.5 M) was added PPh₃ (1.0 equiv) and NBS (1.0 equiv) at -20 °C. The reaction mixture was stirred at -20 °C to rt for overnight. The reaction was quenched by addition of water and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄. After evaporation, the crude was purified by column chromatography on silica gel to provide the bromide as a colorless oil (1.70 g, 10.5 mmol, 75%).

Step 4: Preparation of (3-cyclopropylpropyl)lithium. The lithium reagent was prepared according to Step 2 of general procedure (A).

Step 5: Preparation of N-(5-cyclopropyl-2-phenylpentan-2-yl)aniline (1ak). Prepared according to Step 3 of general procedure (A) to provide the substrates **1ak** as a colorless oil (0.56 g, 2.0 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.45 (m, 2H), 7.33 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.08 – 6.93 (m, 2H), 6.60 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.41 – 6.29 (m, 2H), 4.03 (s, 1H), 2.08 – 1.76 (m, 2H), 1.66 (s, 3H), 1.38 – 1.29 (m, 2H), 1.15 – 1.09 (m, 2H), 0.66 – 0.50 (m, 1H), 0.42 – 0.28 (m, 2H), -0.02 – -0.16 (m, 2H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.8, 146.2, 128.8, 128.5, 126.4, 126.3, 117.0, 115.4, 58.5, 44.5, 35.1, 25.8, 23.9, 10.9, 4.6, 4.6. HRMS (ESI) calcd. for C₂₀H₂₆N [M+H]⁺ *m/z* 280.2065, found 280.2063.

Synthesis of (Z)-N-(2-phenyloct-5-en-2-yl)aniline (1ak').

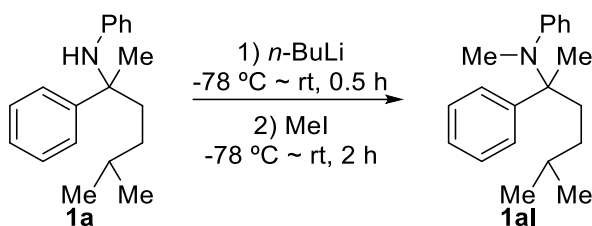


Step 1: Preparation of (Z)-1-bromohex-3-ene. The bromide was prepared according to *Step 3* of the synthesis of **1ak** using (Z)-hex-3-en-1-ol to provide the bromide as a colorless oil (13.2 g, 81 mmol, 81%).

Step 4: Preparation of (Z)-hex-3-en-1-yl lithium. The lithium reagent was prepared according to *Step 2* of general procedure (A).

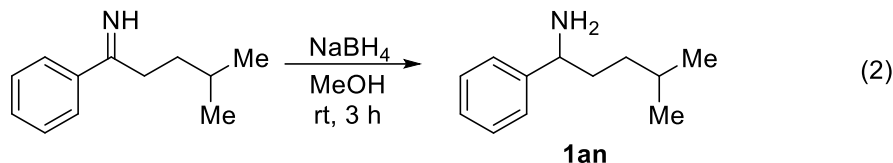
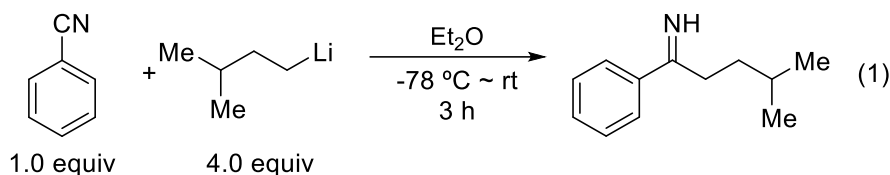
Step 5: Preparation of (Z)-N-(2-phenyloct-5-en-2-yl)aniline (1ak'). Prepared according to *Step 3* of general procedure (A) to provide the substrates **1ak'** as a colorless oil (2.43 g, 8.7 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 2H), 5.37 – 5.24 (m, 2H), 4.07 (s, 1H), 2.16 – 1.76 (m, 6H), 1.66 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.6, 146.1, 132.4, 128.8, 128.5, 128.4, 126.5, 126.2, 117.2, 115.4, 58.5, 43.8, 26.3, 21.8, 20.5, 14.4. HRMS (ESI) calcd. for C₂₀H₂₅NNa [M+Na]⁺ *m/z* 302.1885, found 302.1889.

Synthesis of *N*-methyl-*N*-(5-methyl-2-phenylhexan-2-yl)aniline (**1al**).



Butyllithium (2.5 M in hexane, 3.0 equiv) was added dropwise to a vigorously stirred solution of **1a** in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred for another 30 min at rt, then MeI (3.0 equiv) in Et₂O (1.0 M) was added to the above mixture at -78 °C under N₂ atmosphere and stirred for another 2 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1al** as a colorless oil (1.21 g, 4.3 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.18 – 7.12 (m, 2H), 6.96 – 6.86 (m, 3H), 2.79 (s, 3H), 1.99 – 1.78 (m, 2H), 1.51 (s, 3H), 1.40 – 1.30 (m, 1H), 1.07 – 0.81 (m, 2H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 6.6 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 147.5, 128.1, 128.0, 126.9, 126.2, 124.4, 121.4, 63.6, 39.6, 37.5, 33.7, 28.6, 22.7, 22.7, 22.4. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 282.2222, found 282.2217.

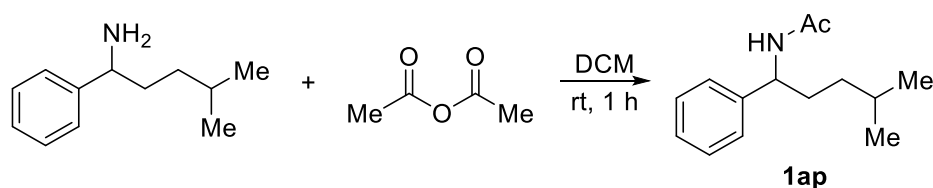
Synthesis of 4-methyl-1-phenylpentan-1-amine (**1an**).



Step 1: Preparation of 4-methyl-1-phenylpentan-1-imine. The same as Step 1 from the synthesis of **1v**.

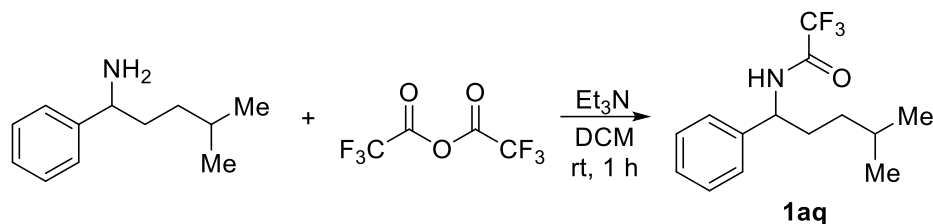
Step 2: Reduction of imine. The prepared crude of Step 1 was dissolved in MeOH (0.5 M) and cooled to 0 °C. NaBH₄ (3.0 equiv) was added in several portions and the resulting mixture was allowed to warm to room temperature and stirred for 3 h. After completion, the reaction was quenched with saturated aqueous solution of ammonium chloride. The mixture was diluted with DCM and separated. The aqueous phase was extracted with DCM for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1an** as a colorless oil (4.67 g, 26.4 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 3.83 (t, *J* = 6.9 Hz, 1H), 1.65 (dtd, *J* = 8.7, 6.7, 1.4 Hz, 2H), 1.55 – 1.49 (m, 3H), 1.24 (ddt, *J* = 13.2, 10.0, 6.9 Hz, 1H), 1.07 (ddt, *J* = 13.3, 9.0, 6.7 Hz, 1H), 0.86 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.9, 128.5, 126.9, 126.4, 56.7, 37.6, 35.9, 28.2, 22.7, 22.7. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 178.1596, found 178.1593.

Synthesis of *N*-(4-methyl-1-phenylpentyl)acetamide (**1ap**).



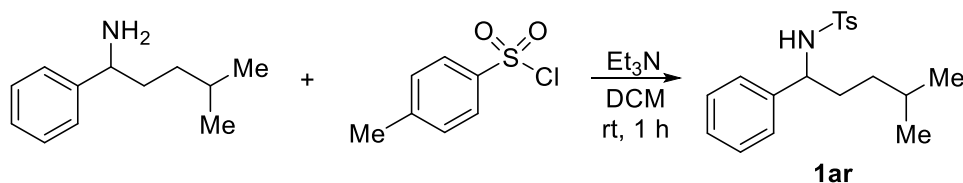
1an was dissolved in DCM (0.2 M) and cooled to 0 °C, acetic anhydride (1.2 equiv) was added dropwise. Then the system was allowed to warm to room temperature and stirred for 1 h. After completion, the reaction was quenched with water. The mixture was diluted with DCM and separated. The aqueous phase was extracted with DCM for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1ap** as a colorless oil (2.11 g, 9.6 mmol, 96%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.15 (m, 5H), 6.55 – 6.51 (m, 1H), 4.90 (q, *J* = 7.6 Hz, 1H), 1.93 (d, *J* = 1.8 Hz, 3H), 1.76 (tq, *J* = 13.6, 7.5 Hz, 2H), 1.53 (tt, *J* = 13.1, 6.6 Hz, 1H), 1.30 – 1.02 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 169.5, 142.7, 128.6, 127.2, 126.6, 53.8, 35.4, 34.2, 27.9, 23.3, 22.6, 22.5. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 220.1701, found 220.1700.

Synthesis of *N*-(4-methyl-1-phenylpentyl)acetamide (**1aq**).



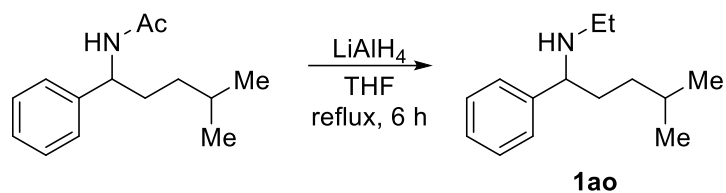
1an and Et₃N (1.2 equiv) were dissolved in DCM (0.2 M) and cooled to 0 °C, Trifluoroacetic anhydride (1.2 equiv) was added dropwise. Then the system was allowed to warm to room temperature and stirred for 1 h. After completion, the reaction was quenched with water. The mixture was diluted with DCM and separated. The aqueous phase was extracted with DCM for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1aq** as a white solid (1.19 g, 4.4 mmol, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H), 7.34 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 6.69 (s, 1H), 4.93 (q, *J* = 7.7 Hz, 1H), 1.96 – 1.80 (m, 2H), 1.56 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.17 (dddt, *J* = 45.0, 13.3, 10.0, 6.5 Hz, 2H), 0.87 (d, *J* = 6.6 Hz, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 156.6 (q, *J* = 37.1 Hz), 140.3, 129.1, 128.2, 126.7, 116.0 (q, *J* = 289.2 Hz), 54.9, 35.2, 33.5, 27.9, 22.6, 22.5. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 274.1419, found 274.1420.

Synthesis of 4-methyl-*N*-(4-methyl-1-phenylpentyl)benzenesulfonamide (**1ar**).



1an and Et₃N (1.2 equiv) were dissolved in DCM (0.2 M) and cooled to 0 °C, Tosyl chloride (1.2 equiv) was added dropwise. Then the system was allowed to warm to room temperature and stirred for 1 h. After completion, the reaction was quenched with water. The mixture was diluted with DCM and separated. The aqueous phase was extracted with DCM for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1ar** as a white solid (1.45 g, 4.4 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.05 (m, 5H), 7.01 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.44 (d, *J* = 7.7 Hz, 1H), 4.22 (q, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 1.89 – 1.56 (m, 2H), 1.42 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.21 – 1.07 (m, 1H), 1.03 – 0.87 (m, 1H), 0.77 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 142.9, 141.2, 137.8, 129.3, 128.4, 127.2, 127.1, 126.6, 58.7, 35.6, 35.0, 27.7, 22.5, 21.5. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 332.1684, found 332.1681.

Synthesis of *N*-ethyl-4,4-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (**1ao**).

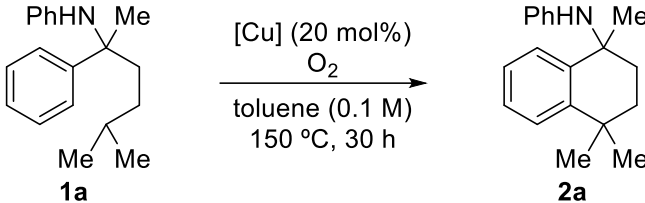


1ap was dissolved in THF (0.1 M) and cooled to 0 °C, lithium aluminium hydride (5.0 equiv) was added in several portions. Then the system was allowed to reflux for 6 h. After completion, the reaction was quenched with aqueous saturated sodium potassium tartrate solution. The mixture was diluted with EtOAc and separated. The aqueous phase was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to provide the substrates **1ao** as a colorless oil (0.84 g, 4.1 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.17 (m, 5H), 3.58 – 3.45 (m, 1H), 2.58 – 2.33 (m, 2H), 1.83 – 1.55 (m, 2H), 1.48 (tq, *J* = 13.1, 6.6 Hz, 1H), 1.31 (s, 1H), 1.16 (tt, *J* = 11.7, 5.8 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H), 1.01 – 0.93 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 128.3, 127.3, 126.9, 64.0, 42.0, 36.2, 35.6, 28.2, 22.7, 22.6, 15.5. HRMS (ESI) calcd. for C₂₀H₂₈N [M+H]⁺ *m/z* 206.1909, found 206.1907.

III. Copper-catalyzed oxidative C(sp³)-H/ C(sp²)-H cross-coupling en route to carbocyclic rings

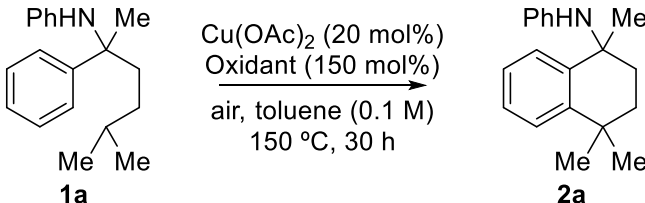
Reaction Optimization

Table S1 | Copper Catalyst Screening

					
entry	[Cu]	yield % ^b	entry	[Cu]	yield % ^b
1	CuCl	0	7	CuBr ₂	0
2	CuBr	0	8	CuSO ₄	0
3	CuCN	0	9	Cu(OTf) ₂	0
4	Cu ₂ O	0	10	Cu(BF ₄) ₂	0
5	CuCl ₂	0	11	Cu(acac) ₂	12
6	Cu	9	12	Cu(TFA) ₂	0

^aConditions: **1a** (0.1 mmol, 1 equiv), Cat. (20 mol%), solvent (0.1 M), 150 °C, 30 h. ^bDetermined by TLC and isolated yield.

Table S2 | Oxidant Screening

					
entry	Oxidant	yield % ^b	entry	Oxidant	yield % ^b
1	TEMPO	0	8	Selectfluor	0
2	PIDA	0	9	DDQ	0
3	(NH ₄) ₂ S ₂ O ₈	0	10	FeCl ₃	0
4	Na ₂ S ₂ O ₈	0	11	Ag ₂ CO ₃	49
5	Ce(SO ₄) ₂	0	12	AgOAc	38
6	BQ	0	13	AgNO ₃	0
7	NFSI	0	14	Ag ₂ O	9
			15	BPO	0

^aConditions: **1a** (0.1 mmol, 1 equiv), Cat. (20 mol%), oxidant (150 mol%), solvent (0.1 M), 150 °C, 30 h. ^bDetermined by TLC and isolated yield.

Table S3 | Solvent Screening

1a $\xrightarrow[\text{air, solvent (0.1 M), 150 °C, 30 h}]{\text{Cu(OAc)}_2 \text{ (20 mol\%)}, \text{Ag}_2\text{CO}_3 \text{ (150 mol\%)}}$ 2a					
entry	solvent	yield % ^b	entry	solvent	yield % ^b
1	EtOAc	0	9	EtOH	0
2	CHCl ₃	0	10	<i>o</i> -xylene	trace
3	CCl ₄	0	11	<i>m</i> -xylene	trace
4	1,2-DCE	72	12	<i>p</i> -xylene	trace
5	MeCN	0	13	mesitylene	0
6	DMSO	0	14	PhCl	trace
7	DMF	0	15	PhCF ₃	55
8	Acetone	0	16	Dioxane	0

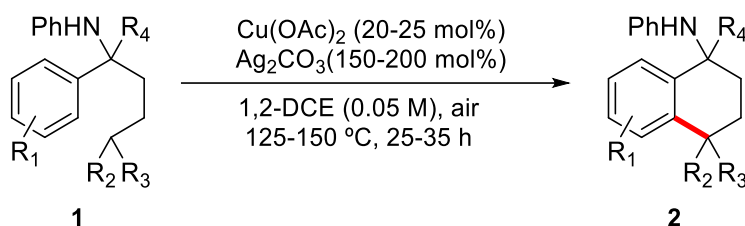
^aConditions: **1a** (0.1 mmol, 1 equiv), Cat. (20 mol%), oxidant (150 mol%), solvent (0.1 M), 150 °C, 30 h. ^bDetermined by TLC and isolated yield.

Table S4 | Final Variation

1a $\xrightarrow[\text{air, 1,2-DCE (0.1 M), 150 °C, 30 h}]{\text{Cu(OAc)}_2 \text{ (20 mol\%)}, \text{Ag}_2\text{CO}_3 \text{ (150 mol\%)}}$ 2a					
entry	variation	yield % ^b			
1	135 °C	81			
2	135 °C, 0.5 M 1,2-DCE	85			
3	135 °C, 0.5 M 1,2-DCE, 25 h	92			
4	entry 3, 10% Cu(OAc) ₂	87			
5	entry 3, 5% Cu(OAc) ₂	83			
6	entry 3, 100% Ag ₂ CO ₃	83			
7	entry 3, 200% Ag ₂ CO ₃	85			
8	entry 3, 12 h	77			
9	entry 3, 120 °C	60			

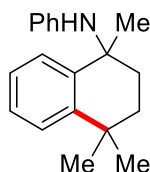
^aConditions: **1a** (0.1 mmol, 1 equiv), Cat. (20 mol%), oxidant (150 mol%), solvent (0.1 M), 150 °C, 30 h. ^bDetermined by TLC and isolated yield.

Substrate Screening



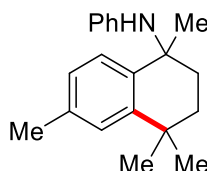
General procedure (C) for the copper-catalyzed oxidative C(sp³)-H/ C(sp²)-H cross-coupling en route to carbocyclic rings. To an oven-dried 35 mL screw-cap sealed tube equipped with a magnetic stir bar was added Cu(OAc)₂ (20 mol%), Ag₂CO₃ (150 mol%), substrate **1** (0.1 mmol, 1.0 equiv) and 1,2-dichloroethane (2.0 mL) at air atmosphere. The vessel was then sealed with a Teflon screw-cap and placed into a preheated oil bath at 135 °C for 25 h. After completion, the reaction mixture was allowed to cool to room temperature, and was directly filtered through a short pad of silica gel washed with EtOAc. The filtrate was concentrated under vacuum and purified by chromatography on silica gel to obtain the corresponding product **2**.

1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2a**)



Prepared according to general procedure (C) using **1a** to provide the title compound **2a** as a colorless oil (24.4 mg, 0.92 mmol, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.23 (td, *J* = 7.6, 1.5 Hz, 1H), 7.14 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.66 – 6.57 (m, 1H), 6.33 – 6.24 (m, 2H), 4.04 (s, 1H), 2.72 (td, *J* = 13.9, 3.4 Hz, 1H), 1.98 (td, *J* = 14.0, 3.2 Hz, 1H), 1.72 (dt, *J* = 13.8, 3.8 Hz, 1H), 1.57 (s, 3H), 1.50 (dt, *J* = 13.6, 3.7 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 144.7, 141.2, 128.9, 126.9, 126.9, 126.8, 126.4, 117.2, 115.3, 55.8, 36.4, 34.0, 33.9, 32.1, 31.6, 30.1. HRMS (ESI) calcd. for C₁₉H₂₄N [M+H]⁺ *m/z* 266.1909, found 266.1907.

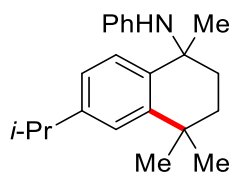
1,4,4,6-tetramethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2b**)



Prepared according to general procedure (C) (but for 20 h) using **1b** to provide the title compound **2b** as a colorless oil (24.3 mg, 0.87 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.96 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.62 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.34 – 6.27 (m, 2H), 4.02 (s, 1H), 2.68 (td, *J* = 13.8, 3.3 Hz, 1H), 2.35 (s, 3H), 1.95 (td, *J* = 14.0, 3.3 Hz, 1H), 1.70 (ddd, *J* = 13.8, 4.3, 3.4 Hz, 1H), 1.55 (s, 3H), 1.48 (ddd, *J* = 13.6, 4.4, 3.3 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ

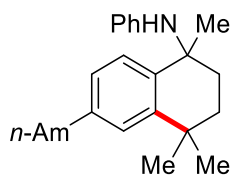
146.0, 144.4, 138.2, 136.2, 128.8, 127.5, 127.4, 126.8, 117.1, 115.3, 55.7, 36.5, 34.0, 33.9, 32.1, 31.6, 30.1, 21.5. HRMS (ESI) calcd. for C₂₀H₂₆N [M+H]⁺ *m/z* 280.2065, found 280.2065.

6-isopropyl-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2c)



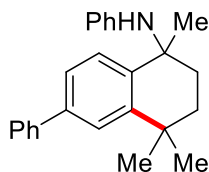
Prepared according to general procedure (C) using **1c** to provide the title compound **2c** as a colorless oil (23.0 mg, 0.75 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 7.04 – 6.96 (m, 3H), 6.61 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.33 – 6.26 (m, 2H), 4.00 (s, 1H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.66 (td, *J* = 13.7, 3.3 Hz, 1H), 1.93 (td, *J* = 13.8, 3.2 Hz, 1H), 1.69 (ddd, *J* = 13.8, 4.6, 3.3 Hz, 1H), 1.57 (s, 3H), 1.48 (ddd, *J* = 13.5, 4.6, 3.2 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.26 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 144.6, 141.3, 128.8, 127.1, 126.8, 126.0, 117.1, 115.5, 58.0, 46.8, 35.8, 34.1, 32.2, 32.1, 26.2, 17.0, 14.7. HRMS (ESI) calcd. for C₂₂H₃₀N [M+H]⁺ *m/z* 308.2378, found 308.2377.

1,4,4-trimethyl-6-pentyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2d)



Prepared according to general procedure (C) using **1d** to provide the title compound **2d** as a colorless oil (26.8 mg, 0.80 mmol, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.94 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.60 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.31 – 6.24 (m, 2H), 4.00 (s, 1H), 2.65 (td, *J* = 13.7, 3.3 Hz, 1H), 2.58 (dd, *J* = 8.9, 6.7 Hz, 2H), 1.93 (td, *J* = 13.8, 3.2 Hz, 1H), 1.72 – 1.65 (m, 1H), 1.65 – 1.59 (m, 2H), 1.55 (s, 3H), 1.47 (ddd, *J* = 13.5, 4.4, 3.2 Hz, 1H), 1.37 (s, 3H), 1.36 – 1.33 (m, 4H), 1.32 (s, 3H), 0.91 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 144.4, 141.2, 138.4, 128.8, 126.7, 126.7, 117.1, 115.4, 55.7, 36.5, 35.9, 34.0, 33.7, 32.1, 31.8, 31.5, 31.2, 30.2, 22.7, 14.2. HRMS (ESI) calcd. for C₂₄H₃₄N [M+H]⁺ *m/z* 336.2691, found 336.2688.

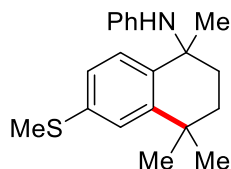
1,4,4-trimethyl-*N*,6-diphenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2e)



Prepared according to general procedure (C) using **1e** to provide the title compound **2e** as a colorless oil (22.5 mg, 0.66 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.62 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.10 – 7.01 (m, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.36

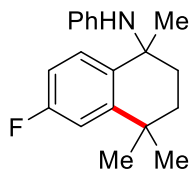
(d, $J = 8.0$ Hz, 2H), 4.09 (s, 1H), 2.76 (td, $J = 13.9, 3.2$ Hz, 1H), 2.04 (td, $J = 14.1, 3.1$ Hz, 1H), 1.77 (dt, $J = 14.0, 3.8$ Hz, 1H), 1.63 (s, 3H), 1.54 (dt, $J = 13.7, 3.8$ Hz, 1H), 1.50 (s, 3H), 1.42 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.8, 145.0, 141.4, 140.4, 139.5, 128.9, 128.9, 128.8, 127.4, 127.2, 125.7, 125.3, 117.3, 115.4, 55.8, 36.4, 34.2, 33.8, 32.1, 31.6, 30.1. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 342.2222, found 342.2217.

1,4,4-trimethyl-6-(methylthio)-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2f)



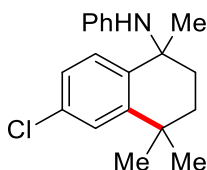
Prepared according to general procedure (C) using **1f** to provide the title compound **2f** as a white solid (21.5 mg, 0.69 mmol, 69%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 6.47 (d, $J = 8.3$ Hz, 1H), 6.35 (d, $J = 2.0$ Hz, 1H), 6.12 (dd, $J = 8.3, 1.9$ Hz, 1H), 6.01 (t, $J = 7.7$ Hz, 2H), 5.54 (t, $J = 7.3$ Hz, 1H), 5.39 (d, $J = 8.0$ Hz, 2H), 4.97 (s, 1H), 1.74 – 1.60 (m, 1H), 1.58 (s, 3H), 1.05 (td, $J = 14.2, 3.0$ Hz, 1H), 0.77 (dt, $J = 14.5, 3.8$ Hz, 1H), 0.58 (s, 3H), 0.53 – 0.49 (m, 1H), 0.48 (s, 3H), 0.42 (s, 3H).; ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 146.0, 144.6, 138.2, 135.2, 127.9, 126.7, 123.8, 123.6, 115.2, 114.1, 54.2, 35.5, 33.4, 32.8, 31.4, 30.6, 28.5, 14.4. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{NS}$ $[\text{M}+\text{H}]^+$ m/z 312.1786, found 312.1790.

6-fluoro-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2g)



Prepared according to general procedure (C) using **1g** to provide the title compound **2g** as a yellow oil (20.1 mg, 0.71 mmol, 71%). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 8.8, 6.2$ Hz, 1H), 7.07 – 6.95 (m, 3H), 6.81 (td, $J = 8.4, 2.7$ Hz, 1H), 6.66 – 6.58 (m, 1H), 6.25 (dd, $J = 8.5, 1.2$ Hz, 2H), 3.99 (s, 1H), 2.66 (td, $J = 13.9, 3.3$ Hz, 1H), 1.95 (td, $J = 14.1, 3.3$ Hz, 1H), 1.70 (dt, $J = 13.9, 3.7$ Hz, 1H), 1.52 (s, 3H), 1.46 (ddd, $J = 13.7, 4.2, 3.3$ Hz, 1H), 1.36 (s, 3H), 1.31 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 161.9 (d, $J = 244.4$ Hz), 147.1 (d, $J = 7.1$ Hz), 145.7, 136.9 (d, $J = 3.0$ Hz), 128.9, 128.8 (d, $J = 8.1$ Hz), 117.4, 115.4, 113.8 (d, $J = 21.2$ Hz), 113.2 (d, $J = 20.2$ Hz), 55.6, 36.2, 34.4, 34.0, 32.0, 31.4, 23.0. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NF}$ $[\text{M}+\text{H}]^+$ m/z 284.1815, found 284.1812.

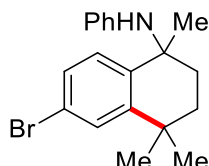
6-chloro-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2h)



Prepared according to general procedure (C) using **1h** to provide the title compound **2h** as a

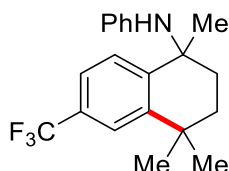
yellow solid (23.0 mg, 0.77 mmol, 77%). ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, J = 8.5 Hz, 1H), 7.32 (d, J = 2.2 Hz, 1H), 7.08 (dd, J = 8.5, 2.2 Hz, 1H), 7.04 – 6.96 (m, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.25 (dd, J = 8.5, 1.2 Hz, 2H), 3.99 (s, 1H), 2.67 (td, J = 14.0, 3.4 Hz, 1H), 1.95 (td, J = 14.1, 3.3 Hz, 1H), 1.69 (dt, J = 13.9, 3.7 Hz, 1H), 1.51 (s, 3H), 1.45 (dt, J = 13.7, 3.7 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 145.6, 139.9, 132.6, 128.9, 128.6, 127.0, 126.8, 117.5, 115.4, 55.6, 36.2, 34.4, 33.9, 31.9, 31.5, 29.9. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NCl}$ $[\text{M}+\text{H}]^+$ m/z 300.1519, found 300.1511.

6-bromo-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2i)



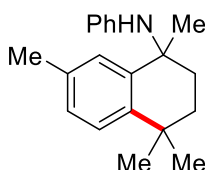
Prepared according to general procedure (C) using **1i** to provide the title compound **2i** as a white solid (23.8 mg, 0.69 mmol, 69%). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 2.1 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.23 (dd, J = 8.5, 2.1 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.29 – 6.23 (m, 2H), 4.00 (s, 1H), 2.68 (td, J = 14.0, 3.3 Hz, 1H), 1.95 (td, J = 14.1, 3.2 Hz, 1H), 1.70 (dt, J = 13.9, 3.6 Hz, 1H), 1.52 (s, 3H), 1.46 (dt, J = 13.6, 3.6 Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 147.2, 145.5, 140.4, 130.0, 129.7, 129.0, 128.9, 120.9, 117.5, 115.4, 55.6, 36.2, 34.3, 33.9, 31.9, 31.5, 29.8. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NBr}$ $[\text{M}+\text{H}]^+$ m/z 344.1014, found 344.1011.

1,4,4-trimethyl-*N*-phenyl-6-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-amine (2j)



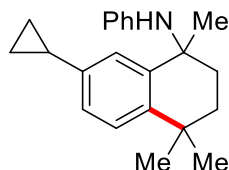
Prepared according to general procedure (C) using **1j** to provide the title compound **2j** as a colorless oil (14.0 mg, 0.42 mmol, 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 8.3 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.35 (dd, J = 8.3, 1.9 Hz, 1H), 7.04 – 6.96 (m, 2H), 6.67 – 6.58 (m, 1H), 6.27 – 6.19 (m, 2H), 4.04 (s, 1H), 2.72 (td, J = 14.0, 3.4 Hz, 1H), 1.98 (td, J = 14.2, 3.3 Hz, 1H), 1.73 (dt, J = 13.9, 3.7 Hz, 1H), 1.54 (s, 3H), 1.49 (dt, J = 13.7, 3.6 Hz, 1H), 1.42 (s, 3H), 1.34 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.5, 145.4, 145.4, 129.1 (q, J = 32.3 Hz), 129.0, 127.5, 127.3 (q, J = 273.7 Hz), 124.0 (q, J = 4.0 Hz), 123.2 (q, J = 4.0 Hz), 117.7, 115.4, 55.8, 36.1, 34.3, 33.9, 31.9, 31.6, 29.8. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{23}\text{NF}_3$ $[\text{M}+\text{H}]^+$ m/z 334.1783, found 334.1778.

1,4,4,7-tetramethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2k)



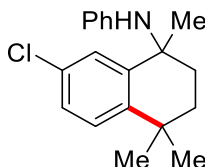
Prepared according to general procedure (C) using **1k** to provide the title compound **2k** as a colorless oil (23.4 mg, 0.84 mmol, 84%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.02 (m, 3H), 6.69 – 6.60 (m, 1H), 6.34 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.02 (s, 1H), 2.71 (td, *J* = 13.8, 3.1 Hz, 1H), 2.29 (s, 3H), 1.96 (td, *J* = 13.9, 3.0 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.58 (s, 3H), 1.53 – 1.43 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 141.7, 141.1, 135.7, 128.8, 127.9, 127.1, 126.8, 117.2, 115.6, 55.8, 36.4, 33.9, 33.7, 32.1, 31.6, 30.2, 21.3. HRMS (ESI) calcd. for C₂₀H₂₆N [M+H]⁺ *m/z* 280.2065, found 280.2062.

7-cyclopropyl-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2l**)



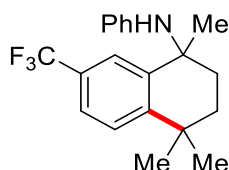
Prepared according to general procedure (C) using **1l** to provide the title compound **2l** as a colorless oil (25.3 mg, 0.83 mmol, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.90 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.32 (dd, *J* = 8.6, 1.0 Hz, 2H), 3.97 (s, 1H), 2.68 (td, *J* = 13.8, 3.2 Hz, 1H), 2.01 – 1.87 (m, 1H), 1.86 – 1.76 (m, 1H), 1.73 – 1.65 (m, 1H), 1.57 (s, 3H), 1.48 (ddd, *J* = 13.5, 4.2, 3.3 Hz, 1H), 1.38 (s, 3H), 1.31 (s, 3H), 0.88 (ddd, *J* = 8.4, 3.7, 1.8 Hz, 2H), 0.69 – 0.62 (m, 1H), 0.61 – 0.54 (m, 1H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 141.8, 141.7, 141.1, 128.8, 126.9, 124.3, 123.7, 117.3, 115.6, 55.9, 36.3, 33.9, 33.8, 32.1, 31.6, 30.3, 15.2, 9.4, 9.1. HRMS (ESI) calcd. for C₂₂H₂₈N [M+H]⁺ *m/z* 306.2222, found 306.2213.

7-chloro-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2m**)



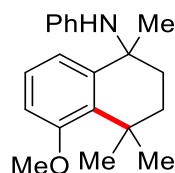
Prepared according to general procedure (C) using **1m** to provide the title compound **2m** as a yellow solid (22.4 mg, 0.75 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.65 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.29 (dd, *J* = 8.5, 0.7 Hz, 2H), 3.99 (s, 1H), 2.69 (td, *J* = 14.0, 3.4 Hz, 1H), 1.94 (td, *J* = 14.1, 3.3 Hz, 1H), 1.70 (dt, *J* = 13.9, 3.8 Hz, 1H), 1.53 (s, 3H), 1.45 (dt, *J* = 13.7, 3.7 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.6, 143.6, 143.2, 132.2, 128.9, 128.6, 127.2, 126.7, 117.6, 115.6, 55.8, 36.1, 33.9, 33.9, 32.0, 31.5, 29.8. HRMS (ESI) calcd. for C₁₉H₂₃NCl [M+H]⁺ *m/z* 300.1519, found 300.1523.

1,4,4-trimethyl-*N*-phenyl-7-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-amine (**2n**)



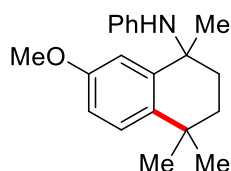
Prepared according to general procedure (C) using **1n** to provide the title compound **2n** as a colorless oil (15.0 mg, 0.45 mmol, 45%). ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.83 (m, 1H), 7.45 (dt, *J* = 8.4, 5.2 Hz, 2H), 7.05 – 6.94 (m, 2H), 6.69 – 6.59 (m, 1H), 6.28 – 6.19 (m, 2H), 3.99 (s, 1H), 2.69 (td, *J* = 14.0, 3.4 Hz, 1H), 1.97 (ddd, *J* = 14.2, 10.9, 3.4 Hz, 1H), 1.72 (dt, *J* = 14.0, 3.7 Hz, 1H), 1.54 (s, 3H), 1.48 (ddd, *J* = 13.6, 4.0, 3.3 Hz, 1H), 1.39 (d, *J* = 5.3 Hz, 3H), 1.32 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 148.7, 145.5, 142.5, 128.9, 128.7 (q, *J* = 32.3 Hz), 124.4 (q, *J* = 272.7 Hz), 124.0 (q, *J* = 4.0 Hz), 123.6 (q, *J* = 4.0 Hz), 127.6, 117.9, 115.7, 55.9, 36.0, 34.4, 34.0, 31.9, 31.4, 29.8. HRMS (ESI) calcd. for C₂₀H₂₃NF₃ [M+H]⁺ *m/z* 334.1783, found 334.1780.

5-methoxy-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2o)



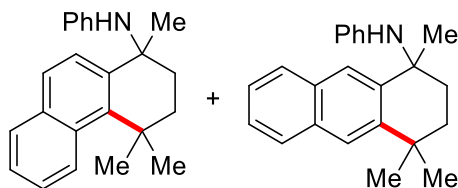
Prepared according to general procedure (C) using **1o** to provide the title compound **2o** as a white solid (17.7 mg, 0.60 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (dd, *J* = 6.4, 1.5 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.77 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.63 – 6.56 (m, 1H), 6.27 – 6.20 (m, 2H), 4.05 (s, 1H), 3.87 (s, 3H), 2.67 (td, *J* = 13.9, 3.2 Hz, 1H), 1.97 (td, *J* = 14.2, 3.1 Hz, 1H), 1.65 (dt, *J* = 13.8, 3.6 Hz, 1H), 1.59 (s, 3H), 1.50 (s, 3H), 1.46 – 1.38 (m, 4H).; ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 146.2, 143.9, 133.2, 129.1, 127.5, 120.0, 117.4, 115.5, 110.2, 56.4, 55.5, 39.3, 34.4, 33.9, 30.8, 30.2, 27.0. HRMS (ESI) calcd. for C₂₀H₂₆NO [M+H]⁺ *m/z* 296.2014, found 296.2013.

7-methoxy-1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2o')



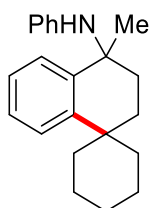
Prepared according to general procedure (C) using **1o** to provide the title compound **2o'** as a white solid (10.3 mg, 0.35 mmol, 35%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 9.7 Hz, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.78 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 1H), 3.70 (s, 3H), 2.66 (td, *J* = 13.9, 3.2 Hz, 1H), 1.91 (td, *J* = 14.0, 3.1 Hz, 1H), 1.66 (dt, *J* = 13.9, 3.9 Hz, 1H), 1.54 (s, 3H), 1.44 (dt, *J* = 13.7, 3.7 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 145.9, 142.8, 137.0, 128.8, 128.0, 117.3, 115.6, 113.3, 111.1, 56.1, 55.3, 36.4, 33.9, 33.5, 32.3, 31.7, 30.2. HRMS (ESI) calcd. for C₂₀H₂₆NO [M+H]⁺ *m/z* 296.2014, found 296.2015.

1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydrophenanthren-1-amine (2p) + 1,4,4-trimethyl-*N*-phenyl-1,2,3,4-tetrahydroanthracen-1-amine (2p')



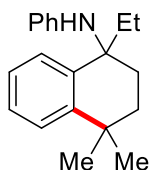
Prepared according to general procedure (C) using **1p** to provide the title compound **2p** and **2p'** as a mixture (**2p**:**2p'**=2.5:1, yellow solid, 18.9 mg, 0.60 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 8.7 Hz, 2.5H), 8.12 (s, 1H), 7.89 (s, 1H), 7.81 (dd, *J* = 8.3, 4.5 Hz, 5H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 2.5H), 7.55 – 7.33 (m, 7.5H), 6.98 (dd, *J* = 11.4, 4.6 Hz, 2.5H), 6.93 (dd, *J* = 11.2, 4.6 Hz, 5H), 6.60 (dt, *J* = 14.6, 7.3 Hz, 3.5H), 6.35 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 8.0 Hz, 5H), 4.13 (s, 3.5H), 2.91 – 2.76 (m, 3.5H), 2.18 – 2.02 (m, 3.5H), 1.86 (dt, *J* = 14.0, 3.8 Hz, 2.5H), 1.82 – 1.76 (m, 8.5H), 1.74 (s, 7.5H), 1.70 (s, 7.5H), 1.64 (s, 3H), 1.59 – 1.50 (m, 6.5H), 1.44 (s, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 145.8, 143.8, 140.3, 140.2, 139.6, 134.3, 132.7, 132.3, 132.1, 129.4, 128.9, 128.9, 128.1, 127.8, 127.3, 127.3, 125.8, 125.6, 125.5, 125.5, 125.2, 124.7, 124.6, 117.3, 115.7, 115.1, 56.6, 56.3, 41.1, 36.4, 35.1, 34.9, 34.4, 33.5, 32.9, 32.8, 32.5, 30.1, 29.3, 28.1. HRMS (ESI) calcd. for C₂₃H₂₆N [M+H]⁺ *m/z* 316.2065, found 316.2067.

4'-methyl-*N*-phenyl-3',4'-dihydro-2'*H*-spiro[cyclohexane-1,1'-naphthalen]-4'-amine (**2q**)



Prepared according to general procedure (C) using **1q** to provide the title compound **2q** as a colorless oil (18.9 mg, 0.62 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.60 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.27 – 6.21 (m, 2H), 4.02 (s, 1H), 2.58 (td, *J* = 13.9, 3.2 Hz, 1H), 2.35 (ddd, *J* = 14.1, 4.5, 3.2 Hz, 1H), 2.09 (td, *J* = 12.6, 4.4 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.78 (d, *J* = 12.2 Hz, 1H), 1.70 – 1.42 (m, 11H), 1.42 – 1.25 (m, 1H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 145.4, 142.0, 128.8, 127.0, 126.8, 126.7, 126.4, 117.2, 115.4, 55.6, 40.2, 37.2, 37.1, 33.7, 29.5, 27.9, 26.3, 22.4, 21.8. HRMS (ESI) calcd. for C₂₂H₂₈N [M+H]⁺ *m/z* 306.2222, found 306.2221.

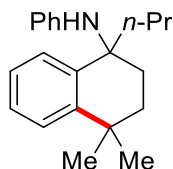
1-ethyl-4,4-dimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2s**)



Prepared according to general procedure (C) using **1s** to provide the title compound **2s** as a yellow solid (22.0 mg, 0.79 mmol, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.22 (ddd, *J* = 7.9, 7.2, 1.5 Hz, 1H), 7.11 (ddd, *J* = 7.9,

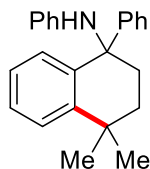
7.1, 1.4 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.60 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.29 (ddd, $J = 7.9, 2.3, 1.2$ Hz, 2H), 4.04 (s, 1H), 2.68 – 2.48 (m, 1H), 1.98 – 1.75 (m, 3H), 1.71 – 1.58 (m, 2H), 1.39 (s, 3H), 1.34 (s, 3H), 1.02 (t, $J = 7.5$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 144.8, 141.1, 128.8, 127.2, 127.1, 126.8, 126.0, 117.1, 115.5, 57.9, 36.7, 35.7, 34.1, 32.2, 32.1, 25.6, 8.3. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 280.2065, found 280.2064.

4,4-dimethyl-*N*-phenyl-1-propyl-1,2,3,4-tetrahydronaphthalen-1-amine (2t)



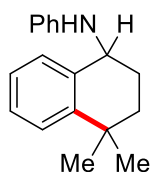
Prepared according to general procedure (C) using **1t** to provide the title compound **2t** as a yellow solid (19.6 mg, 0.67 mmol, 67%). ^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.40 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.25 – 7.20 (m, 1H), 7.15 – 7.09 (m, 1H), 7.05 – 6.96 (m, 2H), 6.61 (tt, $J = 7.2, 1.1$ Hz, 1H), 6.32 – 6.25 (m, 2H), 4.08 (s, 1H), 2.60 (dt, $J = 13.2, 3.9$ Hz, 1H), 1.93 (dt, $J = 15.6, 3.9$ Hz, 1H), 1.88 – 1.73 (m, 2H), 1.72 – 1.60 (m, 2H), 1.60 – 1.43 (m, 2H), 1.41 (s, 3H), 1.35 (s, 3H), 0.98 (t, $J = 7.2$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 144.6, 141.3, 128.8, 127.1, 126.8, 126.0, 117.1, 115.5, 58.0, 46.8, 35.8, 34.1, 32.2, 32.1, 26.2, 17.0, 14.7. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 294.2222, found 294.2219.

4,4-dimethyl-*N*,1-diphenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2v)



Prepared according to general procedure (C) using **1v** to provide the title compound **2v** as a white solid (29.4 mg, 0.90 mmol, 90%). ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.35 – 7.22 (m, 6H), 7.18 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.10 – 7.00 (m, 3H), 6.63 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.44 – 6.37 (m, 2H), 4.36 (s, 1H), 2.97 (ddd, $J = 13.5, 10.4, 2.8$ Hz, 1H), 2.16 (ddd, $J = 13.8, 8.0, 2.8$ Hz, 1H), 1.64 (ddd, $J = 13.8, 8.0, 2.8$ Hz, 1H), 1.44 (ddd, $J = 13.6, 10.4, 2.8$ Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 146.1, 145.5, 139.7, 129.5, 128.8, 128.3, 127.8, 127.5, 127.1, 127.0, 126.2, 117.2, 115.8, 63.0, 35.1, 34.1, 32.1, 32.0, 29.2. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 328.2065, found 328.2063.

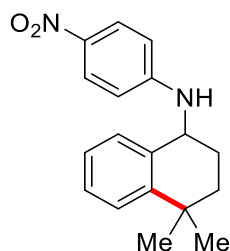
4,4-dimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2w)



Prepared according to general procedure (C) (but at 125 °C) using **1w** to provide the title compound **2w** as a colorless oil (18.8 mg, 0.75 mmol, 75%). ^1H NMR (400 MHz, CDCl_3) δ

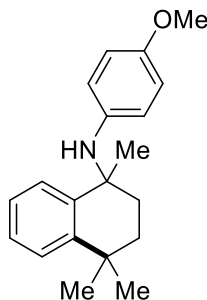
7.39 (ddd, $J = 7.6, 4.7, 1.3$ Hz, 2H), 7.27 (td, $J = 7.6, 1.5$ Hz, 1H), 7.24 – 7.19 (m, 2H), 7.17 (td, $J = 7.4, 1.4$ Hz, 1H), 6.76 – 6.67 (m, 3H), 4.61 (t, $J = 5.1$ Hz, 1H), 3.88 (s, 1H), 2.12 – 1.92 (m, 2H), 1.87 (ddd, $J = 13.2, 10.2, 2.9$ Hz, 1H), 1.64 (ddd, $J = 13.6, 7.8, 3.0$ Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 146.4, 137.2, 129.5, 129.3, 127.7, 126.8, 126.1, 117.2, 112.9, 52.1, 35.3, 34.0, 31.8, 31.6, 25.4. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 252.1752, found 252.1750.

4,4-dimethyl-*N*-(4-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-amine (2x)



Prepared according to general procedure (C) using **1x** to provide the title compound **2x** as a yellow solid (15.1 mg, 0.51 mmol, 51%). ^1H NMR (400 MHz, CDCl_3) δ 8.19 – 8.05 (m, 2H), 7.40 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.35 – 7.27 (m, 1H), 7.17 (ddd, $J = 8.1, 7.0, 1.4$ Hz, 1H), 6.67 – 6.55 (m, 2H), 4.69 (t, $J = 5.2$ Hz, 1H), 2.10 (dddd, $J = 13.3, 10.2, 4.7, 3.0$ Hz, 1H), 2.02 – 1.91 (m, 1H), 1.83 (ddd, $J = 13.3, 10.2, 2.9$ Hz, 1H), 1.68 (ddd, $J = 13.7, 7.9, 3.0$ Hz, 1H), 1.36 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.5, 146.5, 138.1, 135.1, 129.0, 128.4, 127.2, 126.8, 126.4, 111.3, 52.1, 35.1, 34.0, 31.7, 31.5, 25.3. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ m/z 297.1603, found 297.1591.

N-(4-methoxyphenyl)-1,4,4-trimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (2y)



Prepared according to general procedure (C) using **1y** to provide the title compound **2y** as a colorless solid (22.4 mg, 0.69 mmol, 69%). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.37 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.23 (td, $J = 7.6, 1.5$ Hz, 1H), 7.19 – 7.12 (m, 1H), 6.69 – 6.57 (m, 2H), 6.31 – 6.21 (m, 2H), 3.72 (s, 1H), 3.69 (s, 3H), 2.59 (td, $J = 13.7, 3.2$ Hz, 1H), 1.94 (td, $J = 13.8, 3.0$ Hz, 1H), 1.70 (dt, $J = 13.7, 3.6$ Hz, 1H), 1.54 (s, 3H), 1.52 – 1.43 (m, 1H), 1.39 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.2, 144.8, 141.6, 139.9, 127.1, 126.8, 126.3, 117.3, 114.4, 56.1, 55.7, 36.3, 34.1, 33.7, 32.0, 31.6, 30.4. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 296.2014, found 296.2013.

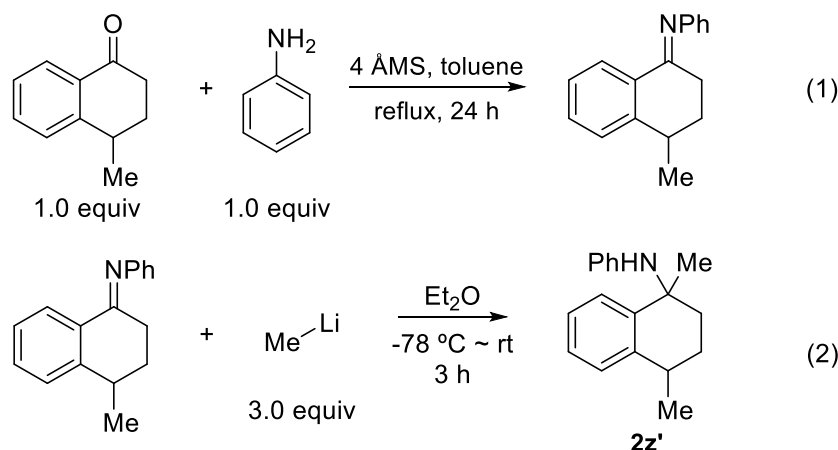
General procedure (D) for the copper-catalyzed oxidative C(sp³)-H/ C(sp²)-H cross-coupling en route to carbocyclic rings. To an oven-dried 35 mL screw-cap sealed tube

equipped with a magnetic stir bar was added Cu(OAc)₂ (25 mol%), Ag₂CO₃ (200 mol%), substrate **1** (0.1 mmol, 1.0 equiv) and 1,2-dichloroethane (2.0 mL) at air atmosphere. The vessel was then sealed with a Teflon screw-cap and placed into a preheated oil bath at 150 °C for 35 h. After completion, the reaction mixture was allowed to cool to room temperature, and was directly filtered through a short pad of silica gel washed with EtOAc. The filtrate was concentrated under vacuum and purified by chromatography on silica gel to obtain the corresponding product **2**.

Determination of d.r. of **2z-ah**.

The d.r. of **2z-ah** were determined by ¹H NMR and ¹³C NMR analysis. The spectra showed that all these compounds gave only one set of peaks, which means only single diastereoisomer was obtained in all cases. To further confirm this result, we have synthesized the pilot product **2z** (labeled as **2z'**) from racemic cyclic ketone as shown below.

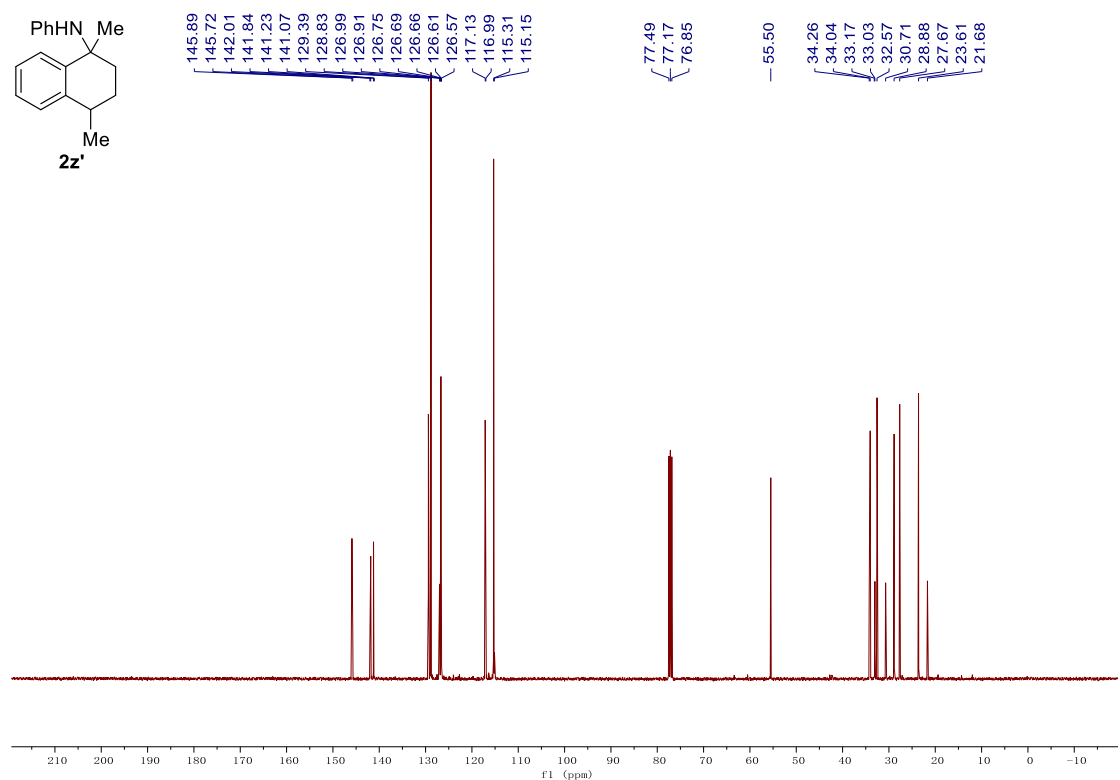
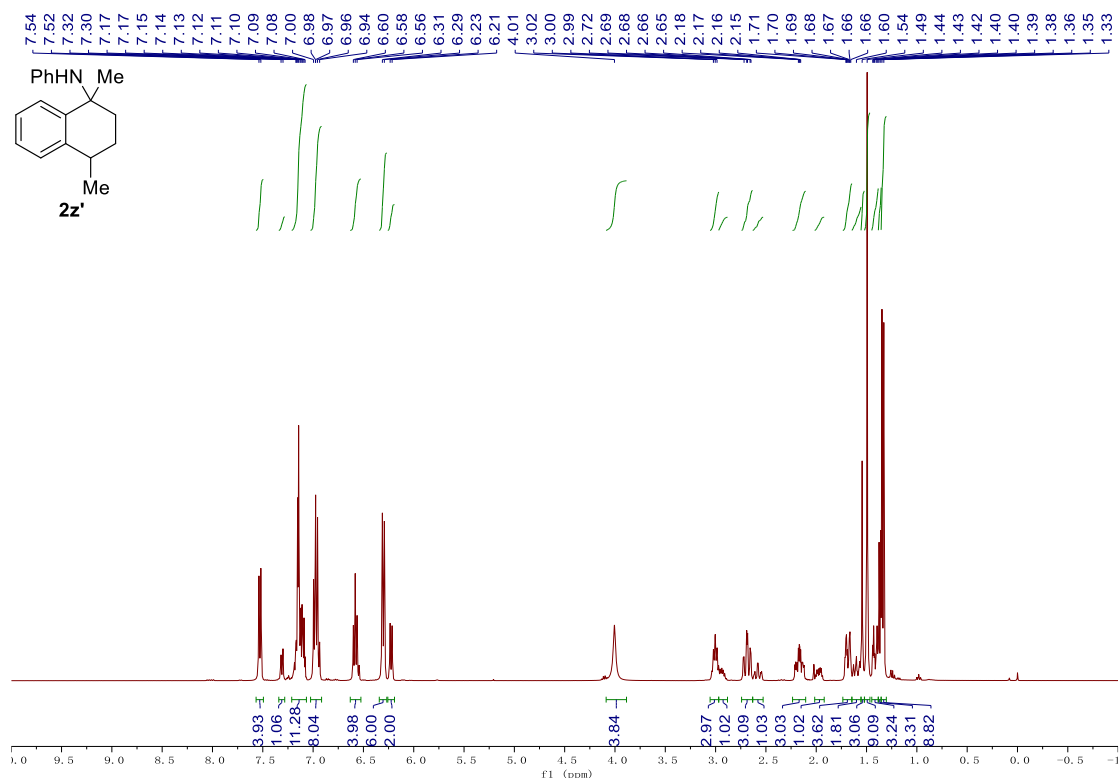
Synthesis of 1,4-dimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2z'**).

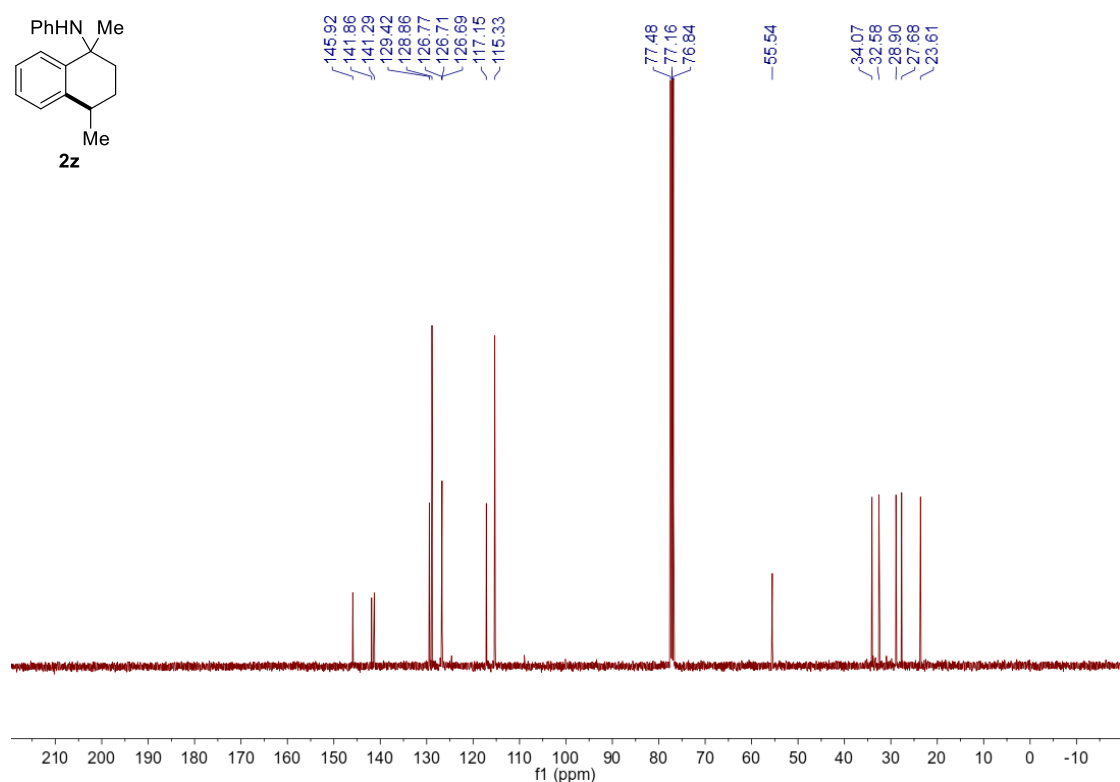
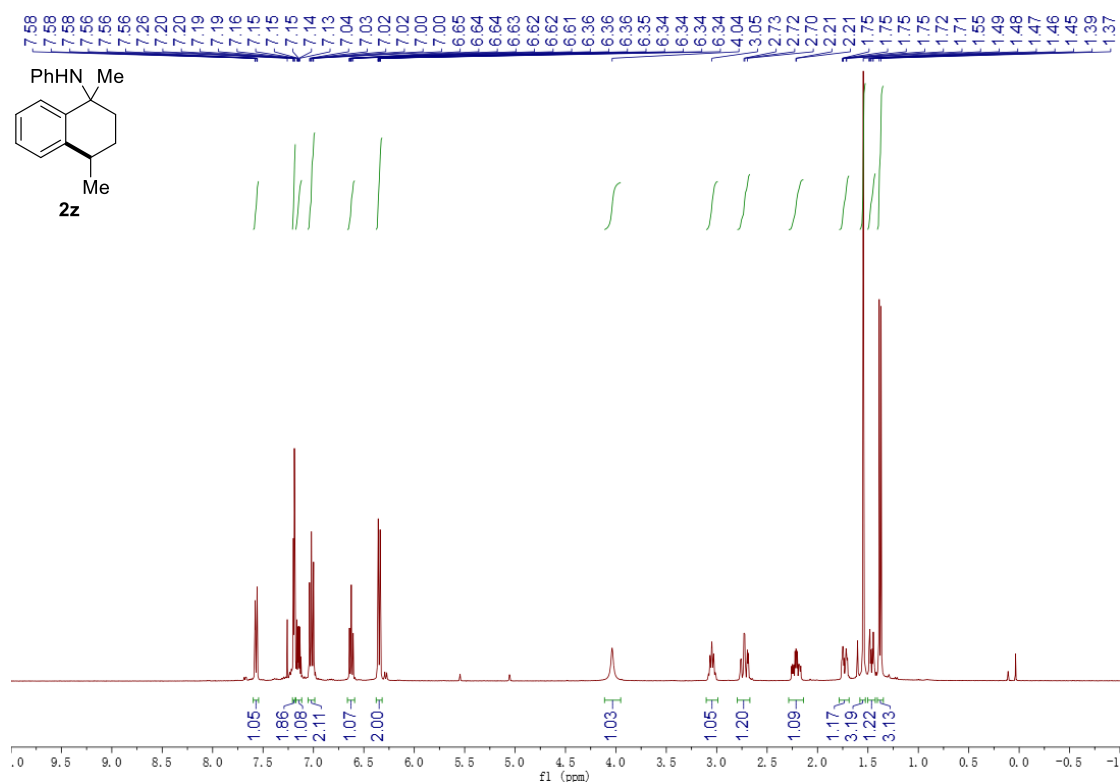


Step 1: Preparation of imine. To an oven-dried round-bottom bottle equipped with a magnetic stir bar was added 4-methyl-3,4-dihydronaphthalen-1(2H)-one (1.0 equiv), aniline (1.0 equiv), 4 ÅMS (0.2 g/mmol) and toluene (2.0 M). The mixture was then reflux for 24 h. After completion, it was allowed to cool to room temperature, and was directly filtered through a short pad of Celite®, washed with EtOAc. The filtrate was concentrated under vacuum and was used directly.

Step 2: Preparation of **2z'.** Methyl lithium (1.6 M in Et₂O) was added dropwise to a vigorously stirred solution of imine in Et₂O (1.0 M) at -78 °C under N₂ atmosphere and stirred at room temperature for 3 h. After completion, the reaction was quenched with water. The resulting aqueous layer was extracted with EtOAc for 3 times and the combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The crude was purified by column chromatography on silica gel to give **2z'** as a white solid (0.45 g, 1.8 mmol, 36% yield; 3:1 dr). ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.52 (m, 4H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.32 – 6.94 (m, 11H), 7.03 – 6.91 (m, 8H), 6.60 – 6.54 (m, 4H), 6.30 (d, *J* = 7.8 Hz, 6H), 6.22 (d, *J* = 7.8 Hz, 2H), 4.01 (m, 4H), 3.04 – 2.97 (m, 3H), 2.97 – 2.91 (m, 1H), 2.69 (td, *J* = 13.7, 3.4 Hz, 3H), 2.58 (td, *J* = 13.5, 3.1 Hz, 1H), 2.17 (tdd, *J* = 13.8, 5.6, 3.3 Hz, 3H), 1.97 (dp, *J* = 14.1, 4.6 Hz, 1H), 1.69 (dq, *J* = 13.6, 3.5 Hz, 3H), 1.64 – 1.54 (m, 2H), 1.54 (s, 3H), 1.49 (s, 9H), 1.41 (dt, *J* = 13.7, 3.7 Hz, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.34 (d, *J* = 7.3 Hz, 9H).; ¹³C NMR (101

MHz, CDCl₃) δ 145.9, 145.7, 142.0, 141.8, 141.2, 141.1, 129.4, 128.8, 127.0, 126.9, 126.8, 126.7, 126.7, 126.6, 126.6, 117.1, 117.0, 115.3, 115.2, 55.5, 34.3, 34.0, 33.2, 33.0, 32.6, 30.7, 28.9, 27.7, 23.6, 21.7. HRMS (ESI) calcd. for C₁₇H₂₃ [M+H]⁺ m/z 252.1752, found 252.1752.

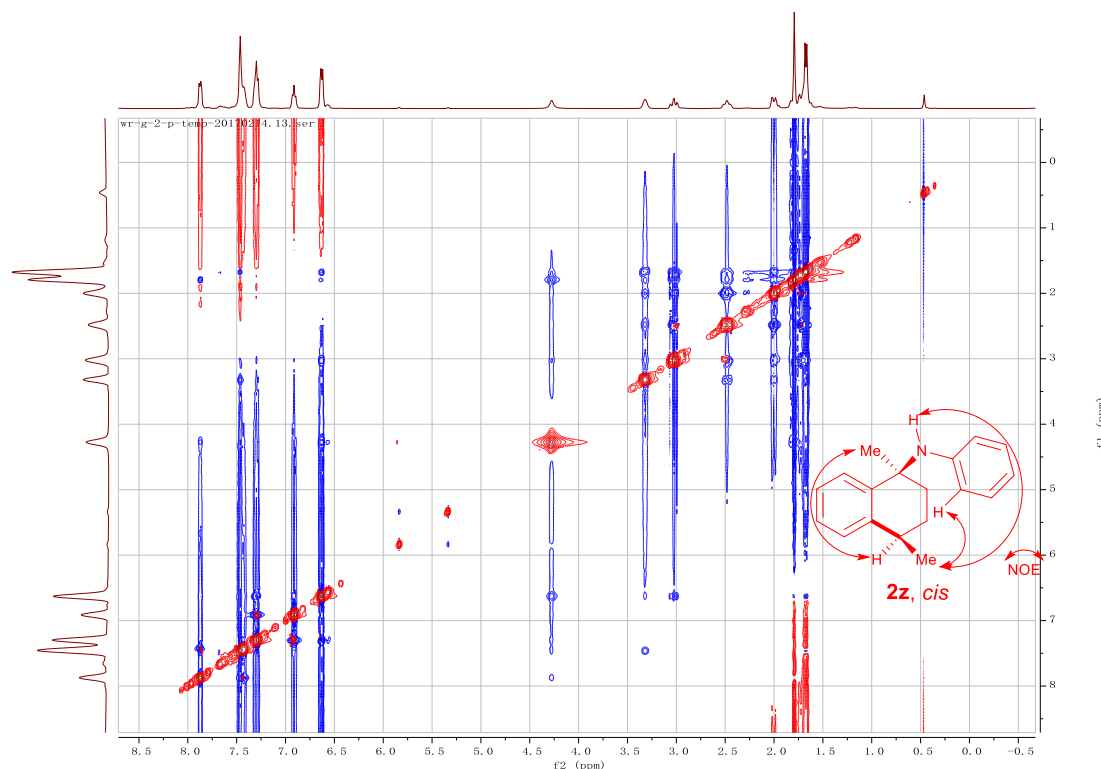




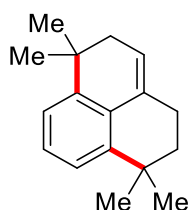
The ¹H NMR analysis of **2z'** showed two sets of peaks that belong to both diastereoisomers with 3:1 d.r., and the major one was consistent with **2z** made using our method. Therefore, because all the spectra of **2z-ah** synthesized from our method showed only one set of peaks, it can be inferred that only single diastereoisomers were afforded in all these cases. What's more, the mixture of diastereoisomers of **2z'** could not be separated through the same

separation method as our general procedure (D).

To further identify the diastereomer, NOESY spectrum was conducted with product **2z**, which indicated that the relative configuration is *cis*.

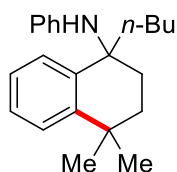


1,1,6,6-tetramethyl-2,3,5,6-tetrahydro-1*H*-phenalene (**2r**)



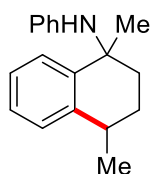
Prepared according to general procedure (D) (but at 135 °C) using **1r** to provide the title compound **2r** as a colorless oil (9.7 mg, 0.43 mmol, 43%). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 5.64 (tt, *J* = 4.5, 1.6 Hz, 1H), 2.51 (ddt, *J* = 8.0, 6.1, 1.6 Hz, 2H), 2.18 (dt, *J* = 4.2, 1.8 Hz, 2H), 1.74 – 1.68 (m, 2H), 1.32 (s, 6H), 1.26 (s, 6H).; ¹³C NMR (101 MHz, CDCl₃) δ 144.6, 144.0, 133.5, 129.3, 127.3, 124.0, 121.4, 120.4, 38.6, 38.4, 34.6, 34.1, 31.3, 28.9, 27.7. HRMS (ESI) calcd. for C₁₇H₂₃ [M+H]⁺ *m/z* 227.1800, found 227.1796.

1-butyl-4,4-dimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2u**)



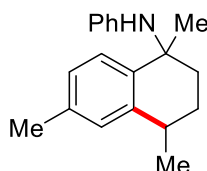
Prepared according to general procedure (D) (but at 135 °C) using **1u** to provide the title compound **2u** as a white solid (9.8 mg, 0.32 mmol, 32%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.14 – 7.06 (m, 1H), 6.98 (t, *J* = 7.8 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 1H), 2.57 (td, *J* = 14.2, 13.2, 3.8 Hz, 1H), 1.96 – 1.79 (m, 2H), 1.77 – 1.57 (m, 3H), 1.53 – 1.40 (m, 2H), 1.40 – 1.31 (m, 8H), 0.94 (t, *J* = 7.1 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 144.6, 141.5, 128.8, 127.1, 127.1, 126.8, 126.1, 117.1, 115.5, 58.0, 44.2, 35.8, 34.1, 32.2, 32.1, 26.0, 25.9, 23.3, 14.3. HRMS (ESI) calcd. for C₂₂H₃₀N [M+H]⁺ *m/z* 308.2378, found 308.2373.

1,4-dimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2z**)



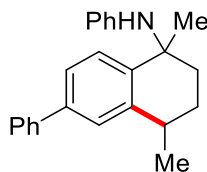
Prepared according to general procedure (D) using **1z** to provide the title compound **2z** as a colorless oil (15.5 mg, 0.62 mmol, 62% yield; single diastereoisomer). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.19 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.18 – 7.10 (m, 1H), 7.06 – 6.99 (m, 2H), 6.62 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.38 – 6.31 (m, 2H), 4.04 (s, 1H), 3.10 – 2.99 (m, 1H), 2.73 (td, *J* = 13.8, 3.5 Hz, 1H), 2.21 (tdd, *J* = 13.8, 5.8, 3.3 Hz, 1H), 1.73 (dddd, *J* = 13.7, 4.3, 3.4, 2.2 Hz, 1H), 1.55 (s, 3H), 1.46 (dt, *J* = 13.5, 3.8 Hz, 1H), 1.38 (d, *J* = 7.2 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 141.9, 141.3, 129.4, 128.9, 126.8, 126.7, 126.7, 117.2, 115.4, 55.6, 34.1, 32.6, 29.0, 27.7, 23.6. HRMS (ESI) calcd. for C₁₈H₂₂N [M+H]⁺ *m/z* 252.1752, found 252.1751.

1,4,6-trimethyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2aa**)



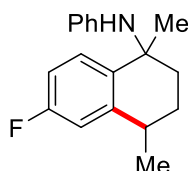
Prepared according to general procedure (D) using **1aa** to provide the title compound **2aa** as a colorless oil (11.1 mg, 0.42 mmol, 42% yield; single diastereoisomer). ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.04 – 6.93 (m, 4H), 6.61 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.37 – 6.33 (m, 2H), 4.01 (s, 1H), 3.05 – 2.93 (m, 1H), 2.69 (td, *J* = 13.7, 3.5 Hz, 1H), 2.33 (s, 3H), 2.18 (tdd, *J* = 13.9, 5.8, 3.3 Hz, 1H), 1.70 (dddd, *J* = 13.7, 4.3, 3.4, 2.2 Hz, 1H), 1.52 (s, 3H), 1.47 – 1.40 (m, 1H), 1.35 (d, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 141.1, 138.9, 136.1, 129.9, 128.8, 127.7, 126.7, 117.1, 115.4, 55.4, 34.1, 32.6, 29.0, 27.8, 23.6, 21.2. HRMS (ESI) calcd. for C₁₉H₂₄N [M+H]⁺ *m/z* 266.1909, found 266.1912.

1,4-dimethyl-*N*,6-diphenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**2ab**)



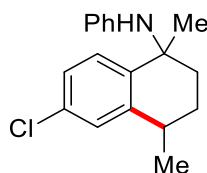
Prepared according to general procedure (D) using **1ab** to provide the title compound **2ab** as a colorless oil (15.0 mg, 0.46 mmol, 46% yield; single diastereoisomer). ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.58 (m, 3H), 7.46 – 7.29 (m, 5H), 7.05 – 6.98 (m, 2H), 6.61 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.40 – 6.34 (m, 2H), 4.05 (s, 1H), 3.17 – 3.01 (m, 1H), 2.72 (td, $J = 13.8, 3.5$ Hz, 1H), 2.22 (tdd, $J = 13.8, 5.8, 3.3$ Hz, 1H), 1.74 (dtd, $J = 13.7, 3.9, 2.2$ Hz, 1H), 1.56 (s, 3H), 1.46 (dt, $J = 13.6, 3.7$ Hz, 1H), 1.39 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 141.7, 141.1, 141.1, 139.4, 128.9, 128.8, 128.1, 127.3, 127.2, 127.1, 125.6, 117.3, 115.4, 55.5, 34.0, 32.8, 28.9, 27.8, 23.7. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 328.2065, found 328.2062.

6-fluoro-1,4-dimethyl-N-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2ac)



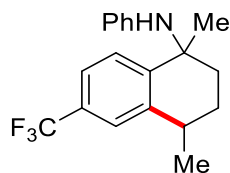
Prepared according to general procedure (D) using **1ac** to provide the title compound **2ac** as a yellow oil (12.1 mg, 0.45 mmol, 45% yield; single diastereoisomer). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (dd, $J = 8.7, 6.0$ Hz, 1H), 7.05 – 6.98 (m, 2H), 6.90 – 6.79 (m, 2H), 6.63 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.36 – 6.29 (m, 2H), 3.99 (s, 1H), 3.06 – 2.94 (m, 1H), 2.68 (td, $J = 13.7, 3.5$ Hz, 1H), 2.18 (tdd, $J = 13.8, 5.8, 3.3$ Hz, 1H), 1.77 – 1.67 (m, 1H), 1.51 (d, $J = 0.8$ Hz, 3H), 1.44 (dddd, $J = 13.7, 4.3, 3.4, 0.7$ Hz, 1H), 1.36 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 161.6 (d, $J = 245.4$ Hz), 145.8, 143.6 (d, $J = 7.1$ Hz), 137.6 (d, $J = 3.0$ Hz), 128.9, 128.8 (d, $J = 8.1$ Hz), 117.4, 115.4, 115.3 (d, $J = 20.2$ Hz), 114.0 (d, $J = 21.2$ Hz), 55.3, 34.1, 32.9, 32.9, 28.9, 27.7, 23.4. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{NF}$ $[\text{M}+\text{H}]^+$ m/z 270.1658, found 270.1655.

6-chloro-1,4-dimethyl-N-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2ad)



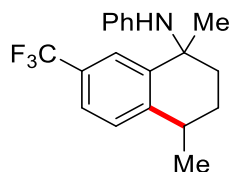
Prepared according to general procedure (D) using **1ad** to provide the title compound **2ad** as a colorless oil (15.1 mg, 0.53 mmol, 53% yield; single diastereoisomer). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.4$ Hz, 1H), 7.15 (d, $J = 2.3$ Hz, 1H), 7.08 (dd, $J = 8.4, 2.3$ Hz, 1H), 7.04 – 6.97 (m, 2H), 6.62 (tt, $J = 7.2, 1.1$ Hz, 1H), 6.34 – 6.26 (m, 2H), 3.98 (s, 1H), 2.99 (p, $J = 6.7$ Hz, 1H), 2.67 (td, $J = 13.8, 3.5$ Hz, 1H), 2.17 (tdd, $J = 13.9, 5.7, 3.4$ Hz, 1H), 1.78 – 1.66 (m, 1H), 1.49 (s, 3H), 1.42 (dt, $J = 13.6, 3.8$ Hz, 1H), 1.35 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.6, 143.3, 140.5, 132.2, 129.2, 128.9, 128.5, 127.0, 117.5, 115.4, 55.3, 34.1, 32.6, 28.7, 27.6, 23.5. HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{NCl}$ $[\text{M}+\text{H}]^+$ m/z 286.1363, found 286.1360.

1,4-dimethyl-*N*-phenyl-6-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-amine (2ae)



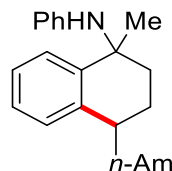
Prepared according to general procedure (D) using **1ae** to provide the title compound **2ae** as a yellow oil (14.0 mg, 0.44 mmol, 44% yield; single diastereoisomer). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.05 – 6.96 (m, 2H), 6.67 – 6.58 (m, 1H), 6.32 – 6.24 (m, 2H), 4.04 (s, 1H), 3.08 (p, *J* = 6.7 Hz, 1H), 2.72 (td, *J* = 13.9, 3.5 Hz, 1H), 2.21 (tdd, *J* = 13.9, 5.8, 3.4 Hz, 1H), 1.74 (dtd, *J* = 13.9, 3.8, 2.1 Hz, 1H), 1.51 (s, 3H), 1.46 (dt, *J* = 13.6, 3.7 Hz, 1H), 1.37 (d, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 146.1, 145.4, 142.0, 129.0, 128.9 (q, *J* = 32.3 Hz), 127.4, 126.4 (q, *J* = 4.0 Hz), 124.5 (q, *J* = 272.7 Hz), 123.5 (q, *J* = 4.0 Hz), 117.6, 115.3, 55.5, 34.1, 32.6, 28.5, 27.5, 23.6. HRMS (ESI) calcd. for C₁₉H₂₁NF₃ [M+H]⁺ *m/z* 320.1626, found 320.1621.

1,4-dimethyl-*N*-phenyl-7-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-amine (2af)



Prepared according to general procedure (D) using **1af** to provide the title compound **2af** as a yellow oil (14.3 mg, 0.45 mmol, 45% yield; single diastereoisomer). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.64 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.33 – 6.27 (m, 2H), 3.98 (s, 1H), 3.07 (p, *J* = 6.8 Hz, 1H), 2.70 (td, *J* = 13.8, 3.5 Hz, 1H), 2.19 (tdd, *J* = 13.9, 5.7, 3.4 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.52 (d, *J* = 0.7 Hz, 3H), 1.48 – 1.40 (m, 1H), 1.35 (d, *J* = 7.3 Hz, 3H).; ¹³C NMR (101 MHz, CDCl₃) δ 145.6, 145.3, 143.1, 130.1, 129.0 (q, *J* = 32.3 Hz), 128.9, 124.5 (q, *J* = 273.7 Hz), 124.0 (q, *J* = 4.0 Hz), 123.4 (q, *J* = 4.0 Hz), 117.8, 115.7, 55.6, 34.2, 32.7, 28.6, 27.4, 23.4. HRMS (ESI) calcd. for C₁₉H₂₁NF₃ [M+H]⁺ *m/z* 320.1626, found 320.1629.

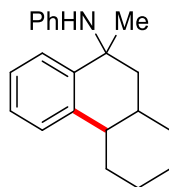
1-methyl-4-pentyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (2ag)



Prepared according to general procedure (D) using **1ag** to provide the title compound **2ag** as a colorless oil (12.3 mg, 0.40 mmol, 40% yield; single diastereoisomer). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.09 (m, 3H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.32 (d, *J* = 8.1 Hz, 2H), 4.03 (s, 1H), 2.78 (dt, *J* = 10.4, 5.1 Hz, 1H), 2.64 (td, *J* = 13.9, 3.3 Hz, 1H), 2.13 – 1.98 (m, 1H), 1.95 – 1.83 (m, 1H), 1.82 – 1.60 (m, 2H), 1.52 (s, 3H), 1.46 –

1.24 (m, 7H), 0.91 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 141.9, 141.1, 129.8, 128.8, 126.8, 126.7, 126.5, 117.1, 115.3, 55.6, 38.1, 36.9, 34.3, 32.1, 29.0, 28.0, 23.9, 22.8, 14.3. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{29}\text{NNa}$ $[\text{M}+\text{Na}]^+$ m/z 330.2198, found 330.2202.

9-methyl-*N*-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-9-amine (2ah)



Prepared according to general procedure (D) using **1ah** to provide the title compound **2ah** as a colorless oil (10.5 mg, 0.36 mmol, 36% yield; single diastereoisomer). ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.54 (m, 1H), 7.38 – 7.34 (m, 1H), 7.29 – 7.18 (m, 2H), 7.15 – 7.08 (m, 2H), 6.71 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.58 – 6.53 (m, 2H), 3.95 (s, 1H), 2.58 – 2.48 (m, 1H), 2.47 – 2.38 (m, 1H), 2.33 – 2.20 (m, 1H), 2.01 – 1.89 (m, 1H), 1.81 – 1.68 (m, 2H), 1.62 (s, 3H), 1.55 – 1.38 (m, 3H), 1.37 – 1.22 (m, 2H), 1.20 – 1.06 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 143.3, 140.4, 128.9, 126.7, 126.5, 124.8, 117.8, 116.6, 54.9, 42.4, 42.4, 37.2, 34.1, 33.3, 30.5, 26.6, 26.0. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 292.2065, found 292.2064.

Substituent Group Effects on Nitrogen.

To test the substituent group effects on nitrogen, several substrates were synthesized and subjected to the standard conditions. The results are showed in Fig. S1 as below:

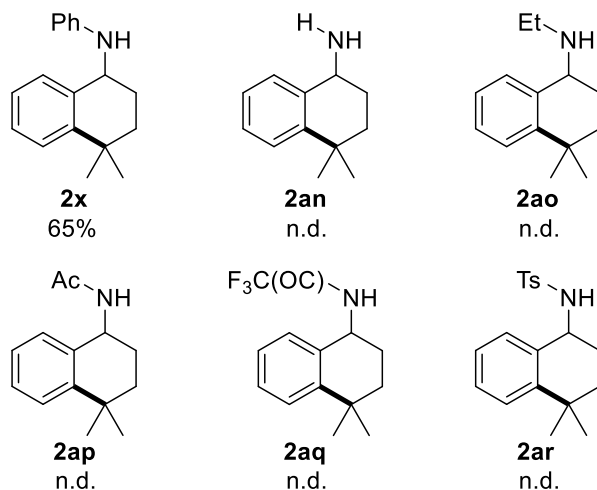
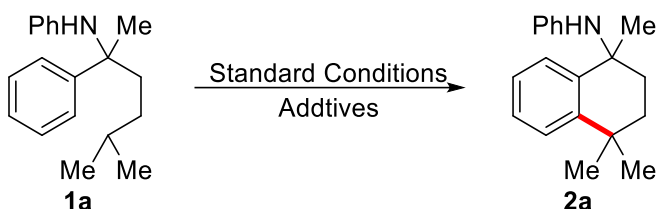


Figure S1 | Effects of Different Substituent Group on Nitrogen.^a

^aReaction conditions: Reactions performed on the substrate (0.1 mmol), $\text{Cu}(\text{OAc})_2$ (20 mol%) and Ag_2CO_3 (1.5 equiv) in 1,2-DCE (2.0 mL) at 135 °C for 25 h; n.r., no reaction; n.d., not detected.

IV. Mechanism Details.

Table S5 | Radical Inhibitor Effect

		
entry	Additives	yield ^b
1	TEMPO (1.0 eq.)	trace
2	TEMPO (0.5 eq.)	trace
3	TEMPO (0.3 eq.)	10%
4	Galvinoxyl (1.0 eq.)	0
5	Galvinoxyl (0.5 eq.)	0
6	Galvinoxyl (0.3 eq.)	10%
7	BHT (1.0 eq.)	0
8	BHT (0.5 eq.)	0
9	BHT (0.3 eq.)	20%

^aDetermined by TLC and isolating.

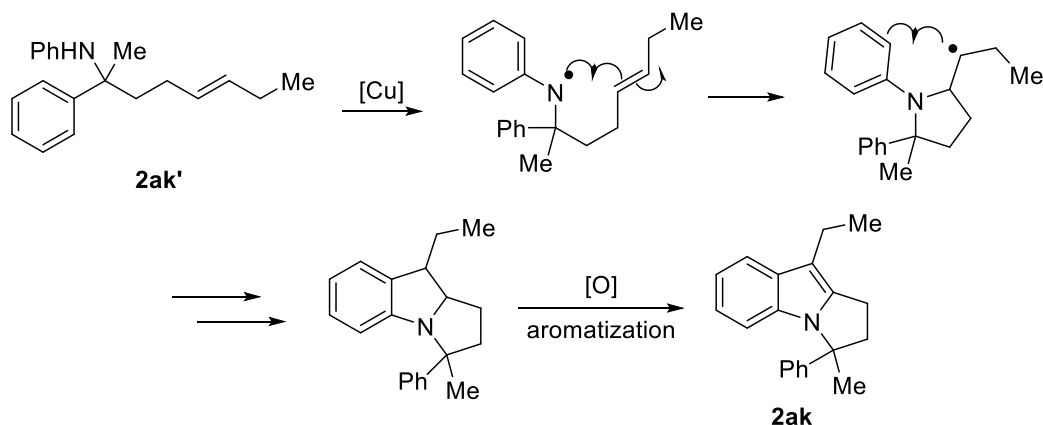
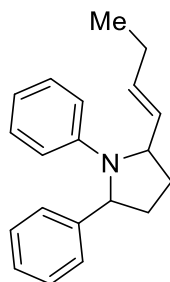


Figure S2 | Mechanism supplementary. A pathway from **2ak'** to **2ak**.

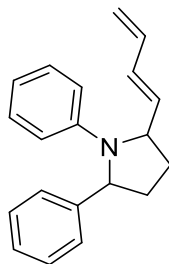
(*E*)-2-(but-1-en-1-yl)-1,5-diphenylpyrrolidine (**2aj-1**)



Prepared according to general procedure (C) (but at 150 °C for 9 h) using **1aj** to provide the title compound **2aj-1** as a colorless oil (7.8 mg, 0.28 mmol, 14%). ¹H NMR (400 MHz, CDCl₃) δ

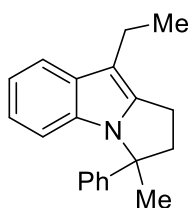
7.30 – 7.22 (m, 2H), 7.22 – 7.15 (m, 1H), 7.15 – 7.11 (m, 2H), 7.10 – 7.02 (m, 2H), 6.55 (t, $J = 7.3$ Hz, 1H), 6.50 – 6.42 (m, 2H), 5.59 (ddd, $J = 15.5, 6.9, 5.9$ Hz, 1H), 5.42 (ddt, $J = 15.3, 6.0, 1.5$ Hz, 1H), 4.92 (d, $J = 8.3$ Hz, 1H), 4.56 (t, $J = 7.0$ Hz, 1H), 2.54 (dddd, $J = 14.4, 12.1, 8.4, 6.3$ Hz, 1H), 2.34 – 2.17 (m, 1H), 2.11 – 1.96 (m, 2H), 1.79 (dd, $J = 12.0, 6.2$ Hz, 1H), 1.69 (dd, $J = 12.1, 6.2$ Hz, 1H), 0.96 (t, $J = 7.4$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.5, 144.3, 133.3, 129.3, 128.7, 128.5, 126.6, 126.2, 115.2, 113.9, 62.4, 60.6, 33.1, 30.0, 25.4, 13.9. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 278.1909, found 278.1912.

(E)-2-(buta-1,3-dien-1-yl)-1,5-diphenylpyrrolidine (2aj-2)



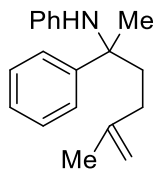
Prepared according to general procedure (C) (but at 150 °C for 9 h) using **1aj** to provide the title compound **2aj-2** as a colorless oil (9.9 mg, 0.36 mmol, 18%). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.12 (m, 2H), 7.12 – 7.05 (m, 2H), 6.58 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.52 – 6.42 (m, 2H), 6.42 – 6.26 (m, 1H), 6.14 (ddq, $J = 15.3, 10.4, 0.8$ Hz, 1H), 5.76 (ddd, $J = 15.2, 5.9, 0.7$ Hz, 1H), 5.14 (dd, $J = 16.9, 1.7$ Hz, 1H), 5.04 (dd, $J = 10.0, 1.7$ Hz, 1H), 4.98 (d, $J = 8.2$ Hz, 1H), 4.73 – 4.60 (m, 1H), 2.54 (dddd, $J = 13.6, 12.0, 8.3, 6.3$ Hz, 1H), 2.31 (dddd, $J = 14.0, 12.2, 8.1, 6.2$ Hz, 1H), 1.83 (ddt, $J = 11.9, 6.1, 1.0$ Hz, 1H), 1.76 (ddt, $J = 12.2, 6.3, 1.0$ Hz, 1H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.2, 144.0, 136.6, 135.4, 131.3, 128.8, 128.6, 126.7, 126.2, 116.7, 115.6, 113.8, 62.5, 60.3, 33.2, 29.8. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 276.1752, found 276.1748.

9-ethyl-3-methyl-3-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indole (2ak)



Prepared according to general procedure (C) (but at 150 °C for 9 h) using **1ak** to provide the title compound **2ak** as a colorless oil (9.9 mg, 0.36 mmol, 18%). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.31 – 7.19 (m, 3H), 7.08 – 6.99 (m, 3H), 6.98 – 6.90 (m, 2H), 3.10 – 2.86 (m, 2H), 2.78 (q, $J = 7.6$ Hz, 2H), 2.67 (t, $J = 7.2$ Hz, 2H), 2.00 (s, 3H), 1.32 (t, $J = 7.6$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 145.5, 140.7, 132.9, 131.8, 128.6, 127.1, 125.4, 119.9, 118.7, 118.5, 110.5, 107.8, 65.7, 47.2, 25.8, 22.5, 18.2, 15.1. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 276.1752, found 276.1750.

N-(5-methyl-2-phenylhex-5-en-2-yl)aniline (3a)



Colorless oil (13.0 mg, 0.49 mmol, 49%). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.45 (m, 2H), 7.39 – 7.29 (m, 2H), 7.28 – 7.20 (m, 1H), 7.07 – 6.95 (m, 2H), 6.62 (tt, $J = 7.3, 1.1$ Hz, 1H), 6.39 – 6.31 (m, 2H), 4.84 – 4.59 (m, 2H), 4.05 (s, 1H), 2.17 – 1.88 (m, 4H), 1.67 (s, 3H), 1.65 (t, $J = 1.1$ Hz, 3H).; ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 146.1, 145.8, 128.8, 128.6, 126.5, 126.3, 117.3, 115.5, 110.0, 58.5, 42.3, 32.1, 26.1, 22.8. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ m/z 266.1909, found 266.1911.

V. References.

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VI. Spectroscopic Data (NMR Spectrum).

