Supporting Information
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Cu (II)-Catalyzed C-N Coupling of Aryl Halides and N-nucleophiles Promoted by Quebrachitol or Diethylene Glycol

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<sup>a</sup> Standard conditions: bromobenzene (1.28 mmol), aniline (1.53 mmol), QCT (0.26 mmol), base (3.85 mmol), solvent (3 mL), under argon atmosphere at 110 °C for 12 h. “+” adding QCT; “-” no adding QCT. <sup>b</sup> Isolated yield. <sup>c</sup> The loading of 1a was 5 gram.
Copies of the $^1$H NMR and $^{13}$C NMR of 3a-3u and 4a-4o

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Chemical Formula: C_{13}H_{14}F_3NO
Exact Mass: 281.1027

Counts vs. Mass-to-Charge (m/z)
Figure S31. \( N\)-(4-Methoxyphenyl)-2-methyl-3-(trifluoromethyl)aniline (4j)
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Figure S38. o-Toluidine (5b)
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Figure S52. 2-Amino-4-methylbenzoic acid (5p)
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Figure S53. 1-(4-Aminophenyl)ethan-1-one (5q)
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Figure S54. 5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-amine (5r)
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Molecular Weight: 94.1170
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Radical clock related spectrum
Exact Mass: 140.0841
Procedures, Characterization Data, and References

General Information
All starting materials, reagents, and solvents are commercially available and used without further purification. Melting points were determined with a X-4 apparatus and are uncorrected. The nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 400 MHz spectrometer in CDCl₃ or DMSO-d₆ by using tetramethylsilane (TMS) as an internal standard. Electrospray ionization mass spectrometry (ESI-MS) analyses were recorded with an Agilent 1100 Series MSD Trap SL (Santa Clara, CA, USA). The reactions were monitored by thin-layer chromatography (TLC: HG/T2354-92, GF254), and compounds were visualized on TLC with UV light.

Synthesis of 3a–v; General Procedure A
To a solution of aliphatic amine (1.53 mmol), Cu(OAc)₂·H₂O (0.13 mmol), QCT (0.26 mmol), K₂CO₃ (3.85 mmol) in DMSO (3 mL) were added aryl halides (1.28 mmol). The flask was evacuated and backfilled with argon (3×), and the resulting mixture was heated in a oil bath with appropriate temperature under rapid stirring for the indicated time. After the complete consumption of aryl halide as monitored by TLC, the flask was cooled to r.t. The flask was opened to air, and the reaction mixture (if the product was acidic, the mixture was acidified) was extracted with ethyl acetate (3×10 mL), and the organic layer was washed with water (2×10 mL) and once with brine (10 mL), dried with magnesium sulfate and concentrated in vacuo. The product was purified by column chromatography on silica gel.

Synthesis of 4a–p; General Procedure B
To a solution of aromatic amine (1.53 mmol), Cu(OAc)₂·H₂O (0.13 mmol), K₂CO₃ (3.84 mmol) in DEG (3 mL) were added aryl halides (1.28 mmol). The flask was evacuated and backfilled with argon (3×), and the resulting mixture was heated in a oil bath with appropriate temperature under rapid stirring for the indicated time. After the complete consumption of aryl halide as monitored by TLC, the flask was cooled to r.t. The flask was opened to air, and the reaction mixture (if the product was acidic, the mixture was acidified) was extracted with ethyl acetate (3×10 mL), and the organic layer was washed with water (2×10 mL) and once with brine (10 mL), dried with magnesium sulfate and concentrated in vacuo. The product was purified by column chromatography on silica gel.

Synthesis of 5a–z, 5aa; General Procedure C
To a sealed reaction vessel were added ammonia (aq, 25%) (1.8 mL, 12.8 mmol), Cu(OAc)₂·H₂O (0.13 mmol), QCT (0.26 mmol) in NMP (1.8 mL) and aryl halides (1.28 mmol). The resulting mixture was heated in an oil bath with appropriate temperature under rapid stirring for the indicated time. After complete consumption of the aryl halide as monitored by TLC, the reaction vessel was cooled to r.t. It was opened to air, and the reaction mixture was extracted with ethyl acetate (3×10 mL), and the organic layer was washed with water (2×10 mL) and once with brine (10 mL), dried with magnesium sulfate and concentrated in vacuo. The product was purified by column chromatography on silica gel.
According to the general procedure A, 3a was obtained as a light-yellow oil (0.19 g, 93%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.26–7.21\) (m, 2 H), 6.94–6.91 (m, 2 H), 6.83–6.79 (m, 1 H), 3.14 (t, \(J = 5.4\) Hz, 4 H), 1.73–1.67 (m, 4 H), 1.59–1.53 (m, 2 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 152.3, 129.0, 119.2, 116.6, 50.7, 25.9, 24.4\).

According to the general procedure A, 3b was obtained as a solid (0.25 g, 96%). M.p. 69–70 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.75–7.73\) (dd, \(J = 8.2, 1.6\) Hz, 1 H), 7.46–7.41 (m, 1 H), 7.15–7.12 (dd, \(J = 8.3, 1.0\) Hz, 1 H), 6.98–6.94 (m, 1 H), 3.03 (t, \(J = 5.3\) Hz, 4 H), 1.75–1.69 (m, 4 H), 1.62–1.56 (m, 2 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 147.0, 142.7, 133.4, 126.0, 120.9, 120.6, 53.0, 26.0, 24.0\).

According to the general procedure A, 3c was obtained as a yellow solid (0.25 g, 94%). M.p. 95 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.14–8.11\) (m, 2 H), 6.92 (d, \(J = 9.4\) Hz, 2 H), 3.44 (t, \(J = 4.8\) Hz, 4 H), 1.78–1.67 (m, 6 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 154.8, 137.6, 126.1, 112.5, 48.5, 25.2, 24.2\).

According to the general procedure A, 3d was obtained as a red oil (0.22 g, 90%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.93\) (br, 2 H), 6.85–6.82 (m, 2 H), 3.76 (s, 3 H), 3.03 (t, \(J = 5.0\) Hz, 4 H), 1.73 (br, 4 H), 1.57–1.53 (m, 2 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 153.8, 147.1, 118.9, 114.4, 55.6, 52.5, 26.1, 24.1\).

According to the general procedure A, 3e was obtained as a white solid (0.23 g, 92%). M.p. 60–63 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.19\) (d, \(J = 8.7\) Hz, 2 H), 6.86 (br, 2 H), 3.12 (t, \(J = 5.2\) Hz, 4 H), 1.76–1.70 (m, 4 H), 1.58–1.57 (m, 2 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 150.8, 128.8, 123.9, 117.7, 50.7, 25.7, 24.2\).

According to the general procedure A, 3f was obtained as a brown oil (0.18 g, 85%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.93\) (br, 2 H), 6.85–6.82 (m, 2 H), 3.76 (s, 3 H), 3.03 (t, \(J = 5.0\) Hz, 4 H), 1.57–1.53 (m, 2 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 153.8, 147.1, 118.9, 114.4, 55.6, 52.5, 26.1, 24.1\).

According to the general procedure A; solid (0.22 g, 90%). M.p. 164–165 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.13–8.11\) (m, 2 H), 6.49–6.46 (m, 2 H), 3.42–3.39 (m, 4 H), 2.09–2.06 (m, 4 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 151.9, 136.6, 126.3, 110.4, 47.9, 25.4\).

According to the general procedure A, 3h was obtained as an off-white solid (0.20 g, 95%). M.p. 45–47 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.31–7.26\) (m, 2 H), 6.94–6.88 (m, 3 H), 3.87 (t, \(J = 4.5\) Hz, 4 H), 3.17 (t, \(J = 4.8\) Hz, 4 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 151.3, 129.2, 120.1, 115.7, 67.0, 49.4\).

According to the general procedure A (0.21 g, 91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.10\) (d, \(J = 8.4\) Hz, 2 H), 6.85 (d, \(J = 6.8\) Hz, 2 H), 3.86 (br, 4 H), 3.11 (t, \(J = 4.4\) Hz, 4 H), 2.28 (s, 3 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)): \(\delta = 149.2, 129.8, 121.1, 116.6, 67.0, 50.0, 21.8\).

According to the general procedure A, 3j was obtained as an off-white solid (0.24 g, 80%). M.p. 65–75 °C. \(^1\)H
NMR (400 MHz, CDCl₃): δ = 6.92–6.88 (m, 2 H), 6.86–6.83 (m, 2 H), 3.77 (s, 3 H), 3.67 (t, J = 5.3 Hz, 2 H), 3.13–3.11 (m, 4 H), 2.72–2.70 (m, 4 H), 2.65–2.62 (t, J = 5.4 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ = 153.9, 145.6, 118.3, 114.5, 59.3, 57.7, 55.6, 53.0, 50.7.

N,N-Diethylaniline (3k):[11] According to the general procedure A, 3k was obtained as a light yellow liquid (0.18 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ = 7.23–7.18 (m, 2 H), 6.69–6.61 (m, 3 H), 3.37–3.32 (q, J = 14.1, 7.0 Hz, 4 H), 1.15 (t, J = 7.1 Hz, 6 H). ¹³C NMR (101 MHz, CDCl₃): δ = 147.9, 129.3, 115.4, 111.9, 44.4, 12.6.

(S)-4-Methyl-N-(1-phenylethyl)aniline (3l):[12] According to the general procedure A, 3l was obtained as an off-white solid (0.22 g, 82%). M.p. 101–104 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.37–7.35 (m, 2 H), 7.32–7.28 (m, 2 H), 7.23–7.19 (m, 1 H), 6.91 (d, J = 8.2 Hz, 2 H), 6.47 (d, J = 8.2 Hz, 2 H), 4.48–4.43 (q, J = 13.5, 6.8 Hz, 1 H), 2.18 (s, 3 H), 1.53 (d, J = 6.7 Hz, 3 H). ¹³C NMR (101 MHz, DMSO-d₆): δ = 145.5, 141.1, 129.7, 128.7, 126.9, 126.4, 125.9, 113.5, 53.8, 25.1, 20.4.

2-[(4-Nitrophenyl)amino]ethan-1-ol (3m):[13] According to the general procedure A, 3m was obtained as a yellow solid (0.19 g, 83%). M.p. 93–96 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.05 (d, J = 9.2 Hz, 2 H), 7.35 (t, J = 5.0 Hz, 1 H), 6.73 (d, J = 9.3 Hz, 2 H), 4.86 (t, J = 5.4 Hz, 1 H), 3.65–3.61 (q, J = 11.2, 5.6 Hz, 2 H), 3.31–2.27 (q, J = 11.4, 5.7 Hz, 2 H). ¹³C NMR (101 MHz, DMSO-d₆): δ = 155.3, 136.0, 126.7, 111.3, 59.8, 45.5.

1-[4-(4-Nitrophenyl)piperazin-1-yl]ethan-1-one (3n):[14] According to the general procedure A, 3n was obtained as a yellow solid (0.29 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ = 8.16–8.12 (m, 2 H), 6.85–6.81 (m, 2 H), 3.81 (t, J = 4.9 Hz, 2 H), 3.68–3.66 (m, 2 H), 3.48–3.44 (m, 4 H), 2.16 (s, 3 H). ¹³C NMR (101 MHz, CDCl₃): δ = 169.2, 154.4, 139.1, 126.0, 125.9, 113.5, 47.0, 46.9, 45.5, 40.7, 21.3.

4-Chloro-2-(cyclohexylamino)benzoic acid (3o): According to the general procedure A, 3o was obtained as a white solid (0.28 g, 87%). M.p. 173–176 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.04 (br, 1 H), 7.77 (d, J = 8.5 Hz, 1 H), 6.77 (d, J = 1.6 Hz, 1 H), 6.54–6.51 (dd, J = 8.5, 1.8 Hz, 1 H), 3.46 (br, 1 H), 1.91–1.88 (m, 2 H), 1.68–1.64 (m, 2 H), 1.58–1.55 (m, 1 H), 1.46–1.35 (m, 2 H), 1.30–1.18 (m, 3 H). ¹³C NMR (101 MHz, DMSO-d₆): δ = 170.0, 151.2, 139.8, 134.1, 114.2, 111.2, 109.1, 49.8, 32.6, 31.1, 25.7, 24.4.

3-Nitro-4-(piperidin-1-yl)benzoic acid (3p):[15] According to the general procedure A, 3p was obtained as a white solid (0.29 g, 90%). ¹H NMR (400 MHz, CDCl₃): δ = 8.50 (d, J = 2.1 Hz, 1 H), 8.07–8.05 (dd, J = 8.8, 2.1 Hz, 1 H), 6.77 (d, J = 1.6 Hz, 1 H), 6.54–6.51 (dd, J = 8.5, 1.8 Hz, 1 H), 3.46 (br, 1 H), 1.91–1.88 (m, 2 H), 1.68–1.64 (m, 2 H), 1.58–1.55 (m, 1 H), 1.46–1.35 (m, 2 H), 1.30–1.18 (m, 3 H). ¹³C NMR (101 MHz, CDCl₃): δ = 170.3, 147.9, 139.3, 134.6, 129.7, 119.2, 118.7, 51.9, 25.6, 23.8.

4-(Cyclohexylamino)-3-nitrobenzoic acid (3q):[16] According to the general procedure A, 3q was obtained as a white solid (0.28 g, 82%). M.p. >300 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 8.62 (s, 1 H), 8.25 (d, J = 7.6 Hz, 1 H), 7.97 (d, J = 7.3 Hz, 1 H), 7.18 (d, J = 7.8 Hz, 1 H), 3.7 (br, 1 H), 1.97–1.95 (m, 2 H), 1.70 (m, 2 H), 1.62–1.59 (m, 1 H), 1.48–1.35 (m, 4 H), 1.26–1.24 (m, 1 H). ¹³C NMR (101 MHz, CDCl₃): δ = 166.8, 146.7, 136.7, 130.7, 129.0, 118.2, 115.3, 51.0, 32.3, 25.4, 24.5.

3-(Phenylamino)propanoic acid (3r):[17] According to the general procedure A, 3r
was obtained as a colorless oil (0.19 g, 88%). ¹H NMR (400 MHz, DMSO-d₆): δ = 12.17 (br, 1 H), 7.09–7.04 (m, 2 H), 6.57–6.51 (m, 3 H), 5.58 (br, 1 H), 3.24 (t, J = 6.9 Hz, 2 H), 2.48 (t, J = 6.9 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ = 172.7, 147.9, 128.3, 115.2, 111.4, 38.2, 33.1.

**Phenyl-D-valine (3s):** According to the general procedure A, 3s was obtained as a white solid (0.21 g, 85%). M.p. 112–114 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 12.17 (br, 1 H), 7.09–7.04 (m, 2 H), 6.57–6.51 (m, 3 H), 5.58 (br, 1 H), 3.24 (t, J = 6.9 Hz, 2 H), 2.48 (t, J = 6.9 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ = 172.7, 147.9, 128.3, 115.2, 111.4, 38.2, 33.1.

**tert-Butylphenyl-D-valinate (3t):** According to the general procedure A, 3t was obtained as a white solid (0.27 g, 86%). M.p. 64–66 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.17–7.13 (m, 2 H), 6.72–6.69 (m, 1 H), 6.64–6.62 (m, 2 H), 4.12 (br, 1 H), 3.75 (d, J = 5.3 Hz, 1 H), 2.15–2.04 (m, 1 H), 1.42 (s, 9 H), 1.05–1.01 (q, J = 8.9, 6.9 Hz, 6 H). ¹³C NMR (101 MHz, CDCl₃): δ = 172.8, 147.6, 129.2, 117.9, 113.6, 81.5, 62.9, 31.5, 28.1, 19.0, 18.7.

**(4-Nitrophenyl)glycine (3u):** According to the general procedure A, 3u was obtained as a brown solid (0.22 g, 88%). M.p. 224–226 °C. ¹H NMR (400 MHz, DMSO-d₆): δ = 12.83 (br, 1 H), 8.02 (d, J = 9.2 Hz, 2 H), 7.44 (t, J = 5.6 Hz, 1 H), 6.68 (d, J = 9.1 Hz, 2 H), 3.99 (d, J = 6.0 Hz, 2 H). ¹³C NMR (101 MHz, DMSO-d₆): δ = 171.8, 154.7, 136.8, 126.5, 111.7, 44.5.

**1-[2-(Allyloxy)phenyl)piperidine (3v):** According to the general procedure A, 3v was obtained as a colorless oil (0.21 g, 75%). ¹H NMR (400 MHz, CDCl₃): δ = 12.17 (br, 1 H), 7.09–7.04 (m, 2 H), 6.57–6.51 (m, 3 H), 5.58 (br, 1 H), 3.24 (t, J = 6.9 Hz, 2 H), 2.48 (t, J = 6.9 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃): δ = 172.7, 147.9, 128.3, 115.2, 111.4, 38.2, 33.1.

**4-Methoxy-N-(4-nitrophenyl)aniline (4a):** According to the general procedure B, 4a was obtained as (0.15 g, 70%). M.p. 148–149 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.10 (d, J = 9.2 Hz, 2 H), 7.17 (d, J = 8.9 Hz, 2 H), 6.95 (d, J = 8.9 Hz, 2 H), 6.77 (d, J = 9.2 Hz, 2H), 6.11 (br, 1H), 3.83 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 151.4, 143.2, 137.2, 122.3, 121.4, 118.6, 116.6, 113.3, 68.9, 52.3, 26.5, 24.6.

**4-Nitro-N-phenylaniline (4b):** According to the general procedure B (0.16 g, 57%). M.p. 124–126 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.14–8.10 (m, 2 H), 7.41–7.36 (m, 2 H), 7.22–7.15 (m, 3 H), 6.96–6.92 (m, 2 H), 6.27 (br, 1 H). ¹³C NMR (101 MHz, CDCl₃): δ = 150.3, 139.8, 139.5, 129.8, 126.3, 125.5, 115.0, 112.7, 55.6.

**N-(4-Methoxyphenyl)-3-nitroaniline (4c):** According to the general procedure B (0.31 g, 75%). M.p. 115–116 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.64 (t, J = 8.6 Hz, 1 H), 7.61–7.59 (m, 1 H), 7.30 (t, J = 8.1 Hz, 1 H), 7.13–7.08 (m, 3 H), 6.93–6.91 (m, 2 H), 5.77 (br, 1 H), 3.83 (s, 3 H). ¹³C NMR (101 MHz, CDCl₃): δ = 155.7, 149.3, 147.6, 134.5, 130.8, 123.0, 120.5, 115.3, 112.3, 107.5, 55.7.

**5,5,8,8-Tetramethyl-N-(2-nitrophenyl)-5,6,7,8-tetrahydronaphthalen-2-amine (4d):** According to the general procedure B (0.29 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ = 9.48 (br, 1 H), 8.21–8.19 (dd, J = 8.6, 1.5 Hz, 1 H), 7.36–7.32 (m, 2 H), 7.22–7.15 (m, 3 H), 6.96–6.92 (m, 2 H), 6.27 (br, 1 H). ¹³C NMR (101 MHz, CDCl₃): δ = 151.4, 143.2, 137.2, 122.3, 121.4, 118.6, 116.6, 113.3, 68.9, 52.3, 26.5, 24.6.
7.21–7.19 (dd, J = 8.7, 1.1 Hz, 1 H), 7.18 (d, J = 2.3 Hz, 1 H), 7.06–7.03 (dd, J = 8.4, 2.4 Hz, 1 H), 6.75–6.71 (m, 1 H), 1.71 (s, 4 H), 1.30 (s, 6 H), 1.28 (s, 6 H). 13C NMR (101 MHz, CDCl3): δ = 146.7, 143.7, 142.7, 135.8, 135.6, 132.8, 127.8, 126.7, 122.6, 122.0, 117.0, 116.1, 35.0, 34.9, 34.5, 34.1, 31.9, 31.8.

2-Methyl-N-phenylaniline (4e):[24] According to the general procedure B (0.15 g, 62%). 1H NMR (400 MHz, CDCl3): δ = 7.26–7.18 (m, 4 H), 7.15–7.11 (m, 1 H), 6.96–6.87 (m, 4 H), 5.37 (br, 1 H), 2.25 (s, 3 H). 13C NMR (101 MHz, CDCl3): δ = 144.0, 141.3, 131.0, 129.3, 128.4, 126.8, 122.0, 120.5, 118.9, 116.9, 20.7.

4-Methyl-N-phenylaniline (4f):[25] According to the general procedure B, 4f was obtained as an off-white solid (0.17 g, 74%). M.p. 85–86 °C. 1H NMR (400 MHz, CDCl3): δ = 7.23–7.22 (m, 2 H), 7.10–7.07 (m, 2 H), 7.02–7.00 (m, 4 H), 6.88 (t, J = 7.6 Hz, 1 H), 5.64 (br, 1 H), 2.30 (s, 3 H). 13C NMR (101 MHz, CDCl3): δ = 144.0, 140.3, 130.9, 129.9, 129.3, 120.3, 118.9, 116.9, 20.7.

4-Fluoro-N-phenylaniline (4g):[26] According to the general procedure B, 4g was obtained as a brown oil (0.17 g, 72%). 1H NMR (400 MHz, CDCl3): δ = 7.27–7.21 (m, 2 H), 7.07–7.02 (m, 2 H), 7.00–6.91 (m, 4 H), 6.88 (t, J = 6.4 Hz, 1 H), 5.28 (br, 1 H). 13C NMR (101 MHz, CDCl3): δ = 158.1 (d, J = 241.4 Hz), 143.9, 138.9 (d, J = 3.0 Hz), 129.4, 120.5 (d, J = 7.0 Hz), 116.8, 116.0 (d, J = 22.2 Hz).

4-Chloro-N-phenylaniline (4h):[27] According to the general procedure B, 4h was obtained as a brown solid (36 mg, 11%). M.p. 57–60 °C. 1H NMR (400 MHz, CDCl3): δ = 7.29–7.25 (m, 2 H), 7.21–7.19 (m, 2 H), 7.06–7.04 (m, 2 H), 7.00–6.94 (m, 3 H). 13C NMR (101 MHz, CDCl3): δ = 142.8, 142.0, 129.5, 129.4, 125.6, 121.6, 121.6, 118.9, 118.2.

4-Methoxy-N-phenylaniline (4i):[28] According to the general procedure B (0.21 g, 85%). M.p. 99–101 °C. 1H NMR (400 MHz, CDCl3): δ = 7.22 (t, J = 7.4 Hz, 2 H), 7.10 (br, 2 H), 6.99–6.85 (m, 5 H), 3.80 (s, 3 H). 13C NMR (101 MHz, CDCl3): δ = 155.3, 145.2, 135.8, 129.3, 122.2, 119.6, 115.7, 114.7, 55.6.

N-(4-Methoxyphenyl)-2-methyl-3-(trifluoromethyl)aniline (4j): According to the general procedure B (0.21 g, 58%). 1H NMR (400 MHz, CDCl3): δ = 7.18–7.09 (m, 3 H), 7.00 (br, 2 H), 6.89–6.87 (m, 2 H), 3.81 (s, 3 H), 2.33 (s, 3 H). 13C NMR (101 MHz, CDCl3): δ = 155.8, 145.1, 135.5, 130.9, 129.9 (J = 29.1 Hz), 123.2, 118.4, 117.2 (J = 6.0 Hz), 114.9, 55.6, 13.2 (J = 2.3 Hz). HRMS (ESI): m/z [M – H]– calcd for C15H13F3NO: 280.0955; found: 280.0962.

N-Phenyl-(1,1'-biphenyl)-4-amine (4k):[29] According to the general procedure B, 4k was obtained as a yellow solid (0.24 g, 76%). M.p. 113 °C. 1H NMR (400 MHz, CDCl3): δ = 7.57–7.50 (m, 4 H), 7.41 (t, J = 7.5 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 3 H), 7.13 (br, 3 H), 6.96 (br, 1 H). 13C NMR (101 MHz, CDCl3): δ = 142.9, 142.6, 140.9, 133.8, 129.4, 128.8, 128.0, 126.6, 126.5, 121.3, 118.1, 117.8.

1-(4-(Phenylamino)phenyl)ethan-1-one (4l):[30] According to the general procedure B, 4l was obtained as a yellow solid (0.24 g, 76%). M.p. 105–106 °C, 1H NMR (400 MHz, CDCl3): δ = 7.89–7.85 (m, 2 H), 7.37–7.32 (m, 2 H), 7.20–7.17 (m, 2 H), 7.11–7.06 (m, 1 H), 7.01–6.98 (m, 2 H), 2.53 (s, 3 H). 13C NMR (101 MHz, CDCl3): δ = 196.5, 148.5, 141.1, 140.7, 130.7, 129.5, 129.0, 123.3, 120.7, 114.4, 26.2.

2-(Phenylamino)benzoic acid (4m):[31] According to the general procedure B, 4m was obtained as a white solid (0.19 g, 70%). M.p. 182–184 °C. 1H NMR (400 MHz,
DMSO-d$_6$): $\delta = 9.67$ (br, 1 H), 7.92–7.89 (dd, $J = 8.0, 1.6$ Hz, 1 H), 7.41–7.34 (m, 3 H), 7.25–7.22 (m, 3 H), 7.07 (t, $J = 7.2$ Hz, 1 H), 6.78 (t, $J = 7.8$ Hz, 1 H). $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta = 170.4, 147.5, 141.0, 134.6, 132.4, 130.0, 123.6, 121.8, 117.9, 114.2, 113.1.$

3-(Phenylamino)benzoic acid (4n): According to the general procedure B, 4n was obtained as an off-white solid (0.19 g, 70%). M.p. 107–114 °C. $^{1}$H NMR (400 MHz, DMSO-d$_6$): $\delta = 12.83$ (br, 1 H), 8.35 (s, 1 H), 7.64 (s, 1 H), 7.38–7.30 (m, 2 H), 7.29–7.16 (m, 3 H), 7.09 (d, $J = 7.7$ Hz, 2 H), 6.88 (t, $J = 7.3$ Hz, 1 H). $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta = 170.4, 147.5, 141.0, 134.6, 132.4, 130.0, 123.6, 121.8, 117.9, 114.2, 113.1.$

2-{2-[(2,6-Dichlorophenyl)amino]phenyl}acetic acid (4o): According to the general procedure B, 4o was obtained as a white solid (0.27 g, 72%). M.p. 158–159 °C. $^{1}$H NMR (400 MHz, DMSO-d$_6$): $\delta = 12.71$ (br, 1 H), 7.53 (d, $J = 7.6$ Hz, 2 H), 7.25–7.16 (m, 3 H), 7.05 (t, $J = 7.0$ Hz, 1 H), 6.89 (t, $J = 6.6$ Hz, 1 H), 6.32 (t, $J = 7.5$ Hz, 1 H), 3.72 (s, 2 H). $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta = 173.8, 143.1, 137.6, 131.4, 130.5, 129.6, 128.0, 126.0, 124.4, 121.3, 116.5, 38.3.$

2-(Allyloxy)-N-phenylaniline (4p): According to the general procedure B, 4p was obtained as a brown oil (0.23 g, 80%). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31–7.25$ (m, 3 H), 7.16–7.14 (m, 2 H), 6.96–6.78 (m, 4 H), 6.18 (br, 1 H), 6.14–6.04 (m, 1 H), 5.44–5.38 (dq, $J = 17.2, 3.1, 1.6$ Hz, 1 H), 5.32–5.28 (dq, $J = 10.5, 2.7, 1.3$ Hz, 1 H), 4.61–4.59 (dt, $J = 8.9, 1.4$ Hz, 2 H).

Aniline (5a): According to the general procedure C, 5a was obtained as a brown oil (0.11 g, 90%). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 7.17–7.12$ (m, 2 H), 6.77–6.73 (m, 1 H), 6.69–6.66 (m, 2 H), 3.46 (br, 2 H). GC-MS: 93 [M].

o-Toluidine (5b): According to the general procedure C, 5b was obtained as a brown oil (0.12 g, 88%). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 7.03$ (t, $J = 7.4$ Hz, 2 H), 6.72–6.68 (m, 1 H), 6.67 (d, $J = 7.8$ Hz, 1 H), 3.57 (br, 2 H), 2.16 (s, 3 H). GC-MS: 107 [M].

4-Isopropylaniline (5c): According to the general procedure C, 5c was obtained as a reddish brown oil (0.15 g, 89%). $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 7.03–7.01$ (m, 2 H), 6.65–6.61 (m, 2 H), 3.34 (br, 2 H), 2.85–2.75 (m, 1 H), 1.20 (d, $J = 6.9$ Hz, 6 H). GC-MS: 135 [M].

4-Methoxyaniline (5d): According to the general procedure C, 5d was obtained as a grey white solid (0.13 g, 80%). M.p. 57–59 °C. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 6.75–6.71$ (m, 2 H), 6.65–6.61 (m, 2 H), 3.73 (s, 3 H), 3.39 (br, 2 H). HRMS (ESI/Q-TOF): $m/z$ [M + H]$^+$ calcd for C$_7$H$_{10}$NO: 124.0762; found: 124.0760.

2-Aminophenol (5e): According to the general procedure C, 5e was obtained as a light grey solid (0.10 g, 70%). M.p. 172–173 °C. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 6.81–6.67$ (m, 4 H), 4.64 (br, 1 H), 3.65 (br, 2 H). HRMS (ESI/Q-TOF): $m/z$ [M + H]$^+$ calcd for C$_6$H$_8$NO: 110.0606; found: 110.0602.

4-Aminophenol (5f): According to the general procedure C, 5f was obtained as a white solid (87 mg, 62%). M.p. 186–188 °C. $^{1}$H NMR (400 MHz, CDCl$_3$): $\delta = 6.68–6.66$ (m, 2 H), 6.61–6.59 (m, 2 H), 4.28 (br, 1 H), 3.42 (br, 2 H). HRMS (ESI/Q-TOF): $m/z$ [M + H]$^+$ calcd for C$_6$H$_8$NO: 110.0606; found: 110.0599.

4-Aminobenzenethiol (5g): According to the general procedure C, 5g was obtained
as a yellow solid (0.12 g, 73%). M.p. 43–45 °C. 1H NMR (400 MHz, CDCl3): δ = 7.25–7.22 (m, 2 H), 6.57–6.53 (m, 2 H), 3.72 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M – H]– calcd for C6H6NS: 124.0221; found: 124.0230.

4-Nitroaniline (5h):[41] According to the general procedure C, 5h was obtained as a yellow solid (0.17 g, 96%). M.p. 144–147 °C. 1H NMR (400 MHz, CDCl3): δ = 8.06 (d, J = 9.0 Hz, 2 H), 6.64–6.61 (m, 2 H), 4.41 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M – H]– calcd for C6H5N2O2: 137.0351; found: 137.0361.

4-Aminobenzonitrile (5i):[42] According to the general procedure C, 5i was obtained as an orange solid (0.14 g, 90%). M.p. 85–86 °C. 1H NMR (400 MHz, CDCl3): δ = 7.41–7.38 (m, 2 H), 6.66–6.63 (m, 2 H), 4.24 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M – H]– calcd for C7H5N2: 117.0453; found: 117.0461.

3-(Trifluoromethyl)aniline (5j):[43] According to the general procedure C, 5j was obtained as a pale yellow liquid (0.20 g, 95%). 1H NMR (400 MHz, CDCl3): δ = 7.22 (d, J = 7.8 Hz, 1 H), 6.70–6.97 (m, 1 H), 6.89–6.88 (m, 1 H), 6.82–6.80 (m, 1 H), 3.82 (br, 2 H). GC-MS: 161 [M].

4-Fluoroaniline (5k):[44] According to the general procedure C, 5k was obtained as a pale-yellow liquid (0.13 g, 93%). 1H NMR (400 MHz, CDCl3): δ = 6.88–6.81 (m, 2 H), 6.63–6.58 (m, 2 H), 3.49 (br, 2 H). GC-MS: 111 [M].

3,5-Bis(trifluoromethyl)aniline (5l):[45] According to the general procedure C, 5l was obtained as a pale-yellow liquid (0.28 g, 95%). 1H NMR (400 MHz, CDCl3): δ = 7.21 (s, 1 H), 7.03 (s, 2 H), 4.06 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M – H]– calcd for C8H4F6N: 228.0248; found: 228.0269.

2-Chloro-6-methylaniline (5m):[46] According to the general procedure C, 5m was obtained as a purple liquid (0.15 g, 82%). 1H NMR (400 MHz, CDCl3): δ = 7.14–7.12 (m, 1 H), 6.96–9.64 (m, 1 H), 6.61 (t, J = 7.8 Hz, 1 H), 3.99 (br, 2 H), 2.19 (s, 3 H). GC-MS: 141 [M].

2-(Trifluoromethoxy)aniline (5n):[47] According to the general procedure C, 5n was obtained as a pale yellow liquid (0.19 g, 82%). 1H NMR (400 MHz, CDCl3): δ = 7.14–7.12 (m, 1 H), 7.09–7.05 (m, 1 H), 6.78 (dd, J =8.0, 1.6 Hz, 1 H), 6.74–6.70 (m, 1 H), 3.84 (br, 2 H). GC-MS: 177 [M].

2-Amino-4-methylbenzoic Acid (5p):[48] According to the general procedure C, 5p was obtained as a grey solid (0.16 g, 89%). M.p. 145 °C. 1H NMR (400 MHz, CDCl3): δ = 7.95–7.92 (m, 1 H), 7.33–7.29 (m, 1 H), 6.70–6.66 (m, 2 H). HRMS (ESI/Q-TOF): m/z [M – H]– calcd for C8H8NO2: 150.0555; found: 150.0574.

1-(4-Aminophenyl)ethan-1-one (5q):[50] According to the general procedure C, 5q was obtained as a light yellow solid (0.15 g, 86%). M.p. 103–105 °C. 1H NMR (400 MHz, CDCl3): δ = 7.79 (d, J = 8.5 Hz, 2 H), 6.64 (d, J = 8.5 Hz, 2 H), 4.20 (br, 2 H), 2.50 (s, 3 H). GC-MS: 135 [M].

5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-amine (5r):[51] According to
the general procedure C, 5r was obtained as a brown oil (0.20 g, 75%). 1H NMR (400 MHz, CDCl3): δ = 7.09 (d, J = 8.4 Hz, 1 H), 6.63 (d, J = 2.5 Hz, 1 H), 6.52 (dd, J = 8.4, 2.5 Hz, 1 H), 3.29 (br, 2 H), 1.64 (s, 4 H), 1.25 (s, 6 H), 1.23 (s, 6 H). GC-MS: 203 [M]

Naphthalen-1-amine (5s): According to the general procedure C, 5s was obtained as a white solid (0.15 g, 82%). M.p. 43–45 °C. 1H NMR (400 MHz, CDCl3): δ = 7.79–7.76 (m, 2 H), 7.46–7.39 (m, 2 H), 7.31–7.24 (m, 2 H), 6.74 (dd, J = 6.9, 1.6 Hz, 1 H), 4.08 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M + H]^+ calcd for C10H10N: 144.0813; found: 144.0809.

Quinolin-5-amine (5t): According to the general procedure C, 5t was obtained as a grey solid (0.16 g, 85%). M.p. 107–110 °C. 1H NMR (400 MHz, CDCl3): δ = 8.88 (dd, J = 4.2, 1.6 Hz, 1 H), 8.18–8.15 (m, 1 H), 7.57 (d, J = 8.4 Hz, 1 H), 7.50 (t, J = 7.4 Hz, 1 H), 7.34–7.31 (m, 1 H), 6.81 (dd, J = 7.4, 1.0 Hz, 1 H), 4.17 (br, 2 H). HRMS (ESI/Q-TOF): m/z [M + H]^+ calcd for C9H9N2: 145.0766; found: 145.0757.

4-Methylpyridin-2-amine (5u): According to the general procedure C, 5u was obtained as a yellow solid (0.12 g, 88%). M.p. 106–107 °C. 1H NMR (400 MHz, CDCl3): δ = 7.94 (dd, J = 5.0, 1.1 Hz, 1 H), 7.27–7.25 (m, 1 H), 6.62–6.59 (m, 1 H), 4.43 (br, 2 H), 2.12 (s, 3 H). GC-MS: 108 [M].

2-Aminonicotinic acid (5v): According to the general procedure C, 5v was obtained as a white solid (0.13 g, 72%). M.p. 107–110 °C. 1H NMR (400 MHz, CDCl3): δ = 8.18–8.16 (m, 1 H), 8.05–8.02 (m, 1 H), 7.20 (br, 1 H), 6.62–6.59 (m, 1 H). HRMS (ESI/Q-TOF): m/z [M + Na]^+ calcd for C6H6N2NaO2: 161.0327; found: 161.0331.

Pyridin-4-amine (5w): According to the general procedure C, 5w was obtained as a white solid (90 mg, 75%). M.p. 158 °C. 1H NMR (400 MHz, CDCl3): δ = 8.21–8.19 (m, 2 H), 6.52–6.50 (m, 2 H), 4.23 (br, 2 H). GC-MS: 94 [M].

Pyridin-2-amine (5x): According to the general procedure C, 5x was obtained as a white solid (94 mg, 78%). M.p. 56–58 °C. 1H NMR (400 MHz, CDCl3): δ = 8.06–8.05 (m, 1 H), 7.42–7.37 (m, 1 H), 6.63–6.60 (m, 1 H), 6.49–6.46 (m, 1 H), 4.58 (br, 2 H). GC-MS: 108 [M].

4-Methylpyridin-3-amine (5y): According to the general procedure C, 5y was obtained as a brown solid (0.11 g, 80%). M.p. 105 °C. 1H NMR (400 MHz, CDCl3): δ = 8.01 (s, 1 H), 7.93 (d, J = 4.8 Hz, 1 H), 6.94 (d, J = 4.8 Hz, 1 H), 3.64 (br, 2 H), 2.12 (s, 3 H). HRMS (ESI/Q-TOF): m/z [M + H]^+ calcd for C6H9N2: 109.0766; found: 109.0759.

1,2,3,4-Tetrahydroacridin-9-amine (5z): According to the general procedure C, 5z was obtained as a white solid (0.12 g, 48%). M.p. 177–179 °C. 1H NMR (400 MHz, CDCl3): δ = 7.89 (d, J = 8.1 Hz, 1 H), 7.70–7.68 (m, 1 H), 7.58–7.54 (m, 1 H), 7.38–7.34 (m, 1 H), 4.66 (br, 2 H), 3.03 (t, J = 6.2 Hz, 2 H), 2.61 (t, J = 6.0 Hz, 2 H), 1.98–1.89 (m, 4 H). HRMS (ESI/Q-TOF): m/z [M + H]^+ calcd for C13H15N2: 199.1235; found: 199.1229.

2-(Allyloxy)aniline (5aa): According to the general procedure C, 5aa was obtained as brown oil (0.14 g, 72%). 1H NMR (400 MHz, CDCl3): δ = 6.81–6.77 (m, 2 H), 6.73–6.67 (m, 2 H), 6.12–6.03 (m, 1 H), 5.42 (dq, J = 17.2, 3.2, 1.6 Hz, 1 H), 5.26 (dq, J = 10.5, 2.8, 1.4 Hz, 1 H), 4.55 (dt, J = 5.3, 1.5 Hz, 2 H), 3.64 (br, 2 H). GC-MS: 149 [M].
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