

Supporting Information

A Facile, Regioselective and Controllable Bromination of Aromatic Amines Using CuBr₂/Oxone[®] System

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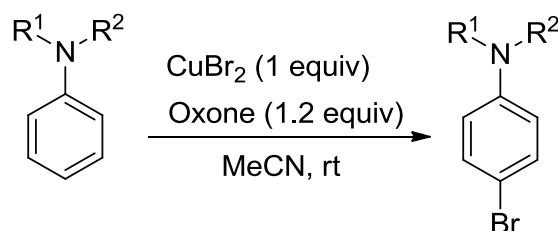
1. General information.

^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 400 spectrometer. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and coupling constant (Hz). Mass spectra were obtained on a Bruker Daltonics Inc. APEXII FT-ICR. Melting points were measured with an X-4 micro melting-point apparatus and uncorrected.

All reactions were carried out with oven-dried glassware in air unless stated otherwise. All reagents and solvents were purchased commercially and used without further purification. All yields refer to isolated yields (average of two run) of compounds estimated to be > 95% pure as determined by ^1H NMR. The known compounds were partly characterized by melting points, MS, ^1H NMR, and compared to authentic samples or the literature data. New compounds were characterized by ^1H and ^{13}C NMR, MS, and Elemental analysis.

2. Experimental procedures

2.1 General procedure for monobromination of aromatic amines



An oven-dried 50-mL three necked flask was charged with the amine (1 mmol), cupric bromide (0.5 mmol), and Oxone[®] (1.2 mmol). After acetonitrile (8 mL) was added via syringe, the mixture was stirred for 3 h at room temperature until the starting amine were consumed completely (monitored by TLC). Saturated sodium carbonate (5 mL) was added, with stirring for 5 min, and then 10 mL of water was added. The aqueous layer was extracted with ethyl acetate (15 mL $\times$ 3). The combined

organic layers were washed with brine, dried over anhydrous MgSO_4 , and evaporated under reduced pressure. The residue was purified by column chromatography.

2.2 General procedure for polybromination of aromatic amines

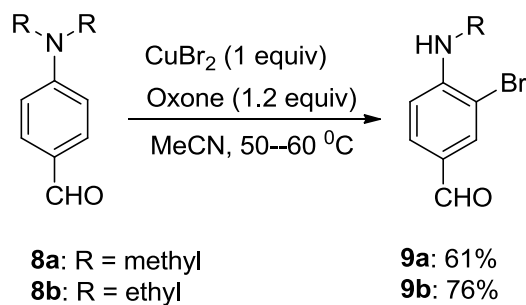
Procedure A: An oven-dried 50-mL three necked flask was charged with the amine (1 mmol), cupric bromide (2.5 mmol) and Oxone[®] (6 mmol), and then acetonitrile (10 mL) was added via syringe. The reaction mixture was stirred at room temperature. The reaction was monitored by TLC and quenched according to the time as mentioned in the text. Then the mixture was filtered through a pad of silica gel, and the filtrate was washed with ethyl acetate (20 mL $\times$ 2). The combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography.

Procedure B: An oven-dried 50-mL three necked flask was charged with the amine (1 mmol), cupric bromide (1–3 mmol) and Oxone[®] (1.2–6 mmol), and then acetonitrile (10 mL) was added via syringe. The reaction mixture was stirred at room temperature for 10 h. The reaction mixture was worked-up as described above in Procedure A.

2.3 General procedure for chlorination of aromatic amines

According to the procedure as described for the mono-bromination of aromatic amines in the 2.1 section except in place of cupric bromide with hydrated cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$).

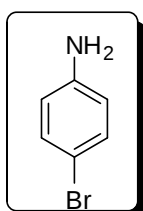
2.4 Synthesis of 2-bromo-4-(*N*-methylamino)benzaldehyde and 2-bromo-4-(*N*-methylamino)benzaldehyde



An oven-dried 50 mL three necked flask was charged with **8a** or **8b** (1 mmol), cupric bromide (0.5 mmol), Oxone (1.2 mmol), and acetonitrile (8 mL). Then the mixture was heated at 50–60 °C with stirring for 16 h. The reaction mixture was cooled down to room temperature, and filtered through a pad of silica gel. The filtrate was washed with ethyl acetate (20 mL × 2), and the combined organic phases were evaporated under reduced pressure. The residue was purified by column chromatography with petroleum/ethyl acetate to give the desired product **9a** (61%) and **9b** (76%), respectively.

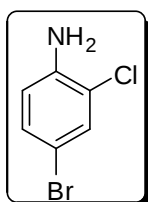
3. Characterization data for the compounds

4-Bromoaniline (2b) (CAS Registry No. 106-40-1)¹.



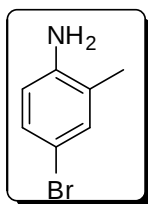
Brown solid: mp 62–64 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.23 (dd, *J* = 6 Hz, 2 Hz, 2H), 6.56 (dd, *J* = 6 Hz, 2 Hz, 2H), 3.64 (br. s, 2H). MS (EI, *m/z*, rel.%): 171 (*M*⁺, 100%), 173 ([*M*+2]⁺, 85%).

4-Bromo-2-chloroaniline (2c) (CAS Registry No. 38762-41-3).



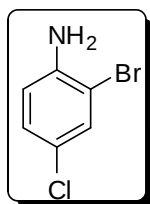
Brown solid: mp 70–71 °C (lit.² mp 70.5-72°C). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 2 Hz, 1H), 7.16 (dd, *J* = 8.8 Hz, 2 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 4.02 (br. s, 2H). MS (EI, *m/z*, rel.%): 205 (*M*⁺, 80%), 207 ([*M*+2]⁺, 100%), 207 ([*M*+4]⁺, 20%).

4-Bromo-2-methylaniline (2d) (CAS Registry No. 583-75-5)¹.



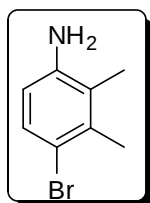
Brown solid: mp 58–60 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.15 (d, *J* = 2 Hz, 1H), 7.11 (dd, *J* = 8.4 Hz, 2 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 3.57 (br. s, 2H), 2.12 (s, 3H). MS (EI, *m/z*, rel.%): 185 (*M*⁺, 100%), 187 ([*M*+2]⁺, 85%).

2-Bromo-4-chloroaniline (2e) (CAS Registry No. 873-38-1).



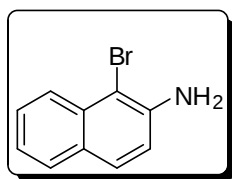
Brown solid: mp 66–68 °C (lit.². mp 63-65°C). ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 4.04 (br. s, 2H). MS (EI, *m/z*, rel.%): 205 (*M*⁺, 75%), 207 ([*M*+2]⁺, 100%), 207 ([*M*+4]⁺, 20%).

4-Bromo-2,3-dimethylaniline (2f) (CAS Registry No. 22364-25-6).



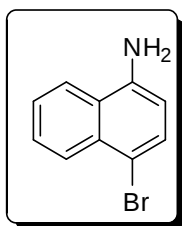
Brown solid: mp 212–214 °C (lit.³. mp 214 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.19 (d, *J* = 8.8 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 1H), 3.56 (br. s, 2H), 2.37 (s, 3H), 2.12 (s, 3H). MS (EI, *m/z*, rel.%): 199 (*M*⁺, 100%), 201 ([*M*+2]⁺, 85%).

1-Bromo-2-naphthylamine (2g) (CAS Registry No. 20191-75-7)¹.



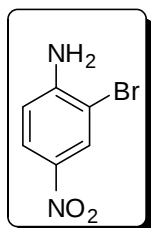
Colorless solid: mp 62–64 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 5.6 Hz, 1H), 4.32 (br. s, 2H). MS (EI, *m/z*, rel.%): 221 (*M*⁺, 100%), 223 ([*M*+2]⁺, 95%).

4-Bromo-1-naphthylamine (2h) (CAS Registry No. 2298-07-9)¹.



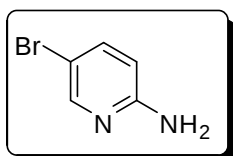
Colorless solid: mp 100–102 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8 Hz, 1H), 7.56–7.41 (m, 3H), 6.64 (d, *J* = 8 Hz, 1H), 4.16 (br. s, 2H). MS (EI, *m/z*, rel.%): 221 (*M*⁺, 100%), 223 ([*M*+2]⁺, 95%).

2-Bromo-4-nitroaniline (2i) (CAS Registry No. 13296-94-1)



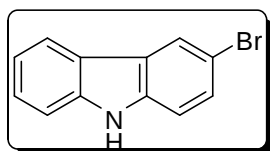
Yellow solid: mp 103–104 °C (lit.⁴ mp 102–104 °C). ¹H NMR (300 MHz, CDCl₃): δ 8.36 (d, *J* = 2.4 Hz, 1H), 8.02 (dd, *J* = 8.9 Hz, 2.4 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 4.87 (br. s, 2H). MS (EI, *m/z*, rel.%): 216 (*M*⁺, 80%), 218 ([*M*+2]⁺, 75%).

2-Amino-5-bromopyridine (2j) (CAS Registry No. 1072-97-5)⁵.



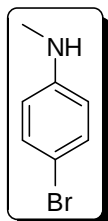
Brown solid: mp 135–137 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 2 Hz, 1H), 7.48 (dd, *J* = 8.8 Hz, 2 Hz, 1H), 6.40 (d, *J* = 8.8 Hz, 1H), 4.42 (br. s, 2H). MS (EI, *m/z*, rel.%): 172 (*M*⁺, 100%), 174 ([*M*+2]⁺, 90%).

3-Bromocarbazole (2k) (CAS Registry No. 1592-95-6)¹.



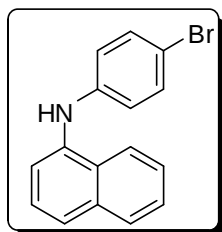
Colorless solid. mp 193–195 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.18 (s, 1H), 8.03 (br. s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.49 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.44–7.42 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26–7.23 (m, 1H). MS (EI, *m/z*, rel.%): 245 (*M*⁺, 100%), 247 ([*M*+2]⁺, 95%).

4-Bromo-*N*-methylaniline (2m) (CAS Registry No. 6911-87-1)⁶.



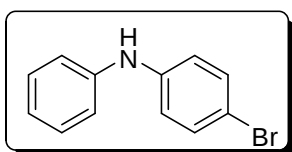
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 3.76 (br. s, 1H), 2.80 (s, 3H). MS (EI, *m/z*, rel.%): 185 (*M*⁺, 100%), 187 ([*M*+2]⁺, 85%).

(*p*-Bromophenyl)(1-naphthyl)amine (2a) (CAS Registry No. 1331748-61-8).



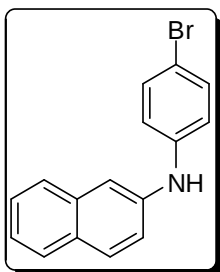
Yellow oil. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.34 (s, 1H), 8.27 (d, $J = 8.8$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.71–7.66 (m, 2H), 7.59 (t, $J = 8$ Hz, 1H), 7.27–7.23 (m, 2H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 2H), 6.88 (t, $J = 7.2$ Hz, 1H). MS (EI, m/z , rel.%): 297 (M^+ , 100%), 299 ($[\text{M}+2]^+$, 85%).

4-Bromodiphenylamine (2n) (CAS Registry No. 54446-36-5).



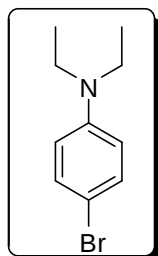
Colorless solid: mp 85–86 $^{\circ}\text{C}$ (lit.⁷ mp 88 $^{\circ}\text{C}$). ^1H NMR (400 MHz, CDCl_3): δ 7.33 (d, $J = 6.8$ Hz, 2H), 7.29–7.24 (m, 2H), 7.04 (d, $J = 7.6$ Hz, 2H), 6.93 (t, $J = 2.4$ Hz, 1H), 6.92 (d, $J = 6.8$ Hz, 2H), 5.68 (br. s, 1H). MS (EI, m/z , rel.%): 247 (M^+ , 100%), 249 ($[\text{M}+2]^+$, 85%).

(*p*-Bromophenyl)(2-naphthyl)amine (2o) (CAS Registry No. 70539-21-8).



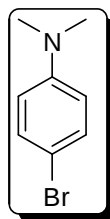
Colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8$ Hz, 1H), 7.65 (d, $J = 8.8$ Hz, 1H), 7.52 (t, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 8.8$ Hz, 1H), 7.35–7.31 (m, 3H), 7.18 (d, $J = 7.6$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.45 (br. s, 1H). MS (EI, m/z , rel.%): 297 (M^+ , 100%), 299 ($[\text{M}+2]^+$, 95%).

***N,N*-Diethyl-4-bromoaniline (2p)** (CAS Registry No. 2052-06-4)⁸.



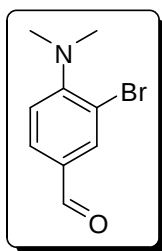
Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 8.4$ Hz, 2H), 3.31 (q, $J = 6.8$ Hz, 4H), 1.13 (t, $J = 6.8$ Hz, 6H). MS (EI, m/z , rel.%): 227 (M^+ , 25%), 229 ($[\text{M}+2]^+$, 25%).

***N,N*-Dimethyl-4-bromoaniline (2q)** (CAS Registry No. 586-77-6)⁸.



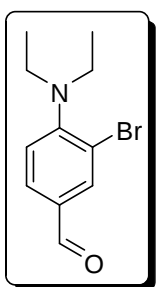
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (d, *J* = 9.2 Hz, 2H), 6.60 (d, *J* = 9.2 Hz, 2H), 2.92 (s, 6H). MS (EI, *m/z*): 199 (*M*⁺, 95%), 201 ([*M*+2]⁺, 100%).

3-Bromo-4-(dimethylamino)benzaldehyde (2r) (CAS Registry No. 56479-63-1)⁹.



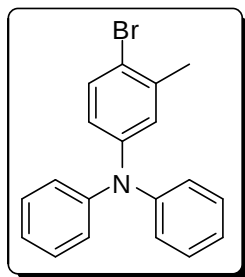
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 8.02 (d, *J* = 2 Hz, 1H), 7.72 (dd, *J* = 8.4 Hz, 2 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 2.94 (s, 6H). MS (EI, *m/z*, rel.%): 227 (*M*⁺, 70%), 229 ([*M*+2]⁺, 75%).

3-Bromo-4-(diethylamino)benzaldehyde (2s) (CAS Registry No. 872183-50-1).



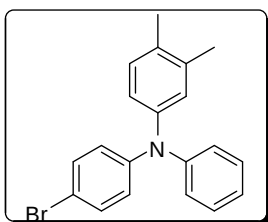
Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 9.81 (s, 1H), 8.04 (d, *J* = 2 Hz, 1H), 7.72 (dd, *J* = 8.4 Hz, 2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.27 (q, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.2 Hz, 6H). MS (EI, *m/z*, rel.%): 240 ([*M*-152]⁺, 100%), 255 (*M*⁺, 10%), 257 ([*M*+2]⁺, 10%).

4-Bromo-3-methyltriphenylamine (2t) (CAS Registry No. 717880-57-4).



Colorless solid: mp126–128 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.43 (d, *J* = 8.8 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 4H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.69 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 2.20 (s, 3H). MS (EI, *m/z*, rel.%): 337 (*M*⁺, 100%), 339 ([*M*+2]⁺, 85%).

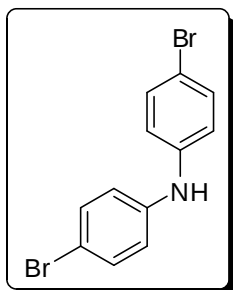
4-Bromo-3',4'-dimethyltriphenylamine (2u) (CAS Registry No. 1372114-32-3).



Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.28–7.24 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.98–6.82 (m, 4H),

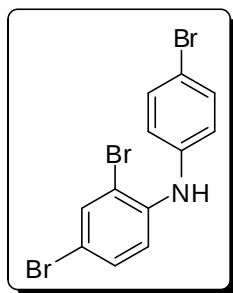
6.80 (d, $J = 2$ Hz, 3H), 2.33 (s, 3H), 1.98 (s, 3H). MS (EI, m/z , rel.%): 351 (M^+ , 100%), 353 ($[M+2]^+$, 90%).

4,4'-Dibromodiphenylamine (3n) (CAS Registry No. 16292-17-4).



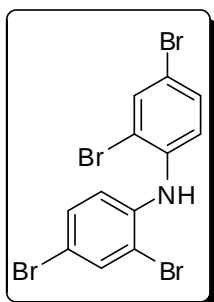
Yellow solid: mp 105–107 °C (lit¹⁰. mp 106 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, $J = 8.4$ Hz, 4H), 6.91 (d, $J = 8.4$ Hz, 4H), 5.67 (br.s, 1H). MS (EI, m/z , rel.%): 325 (M^+ , 50%), 327 ($[M+2]^+$, 100%), 329 ($[M+4]^+$, 45%).

2,4,4'-Tribromodiphenylamine (4n) (CAS Registry No. 81090-61-1).



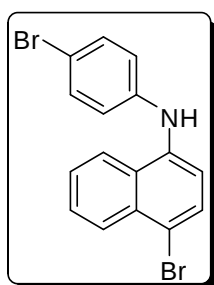
Yellow solid: mp 94–96 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, $J = 2$ Hz, 1H), 7.42 (dd, $J = 6.8$ Hz, 2H, 2H), 7.26 (dd, $J = 8.8$ Hz, 2H, 1H), 7.04 (d, $J = 8.8$ Hz, 1H), 6.99 (dd, $J = 6.8$ Hz, 2H, 2H), 5.97 (br.s, 1H). MS (EI, m/z , rel.%): 403 (M^+ , 40%), 405 ($[M+2]^+$, 100%), 407 ($[M+4]^+$, 90%), 409 ($[M+6]^+$, 35%).

2,2',4,4'-Tetrabromodiphenylamine (5n) (CAS Registry No. 38573-62-5).



Colorless solid: mp 184–186 °C (lit¹¹. mp 189-190 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, $J = 2.4$ Hz, 2H), 7.32 (dd, $J = 8.8$ Hz, 2 Hz, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 6.31 (s, 1H). MS (EI, m/z , rel.%): 481 (M^+ , 15%), 483 ($[M+2]^+$, 60%), 485 ($[M+4]^+$, 100%), 487 ($[M+6]^+$, 55%), 489 ($[M+8]^+$, 12%).

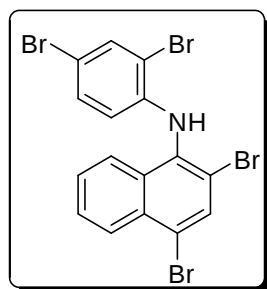
(4-Bromophenyl)(1-(4-bromonaphthyl))amine (3a).



Colorless solid: mp 108–109 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, $J = 8.8$ Hz, 1H), 8.0 (d, $J = 4.4$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H, 2H), 7.19 (d, $J = 8.0$ Hz, 1H), 6.82 (d, $J = 8.8$ Hz,

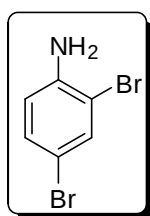
2H); ^{13}C NMR (100 MHz, CDCl_3): δ 143.55, 138.20, 132.79, 132.25, 129.86, 129.11, 127.91, 127.65, 126.65, 122.24, 118.88, 117.16, 112.73. MS (EI, m/z , rel.%): 375 (M^+ , 50%), 377 ($[\text{M}+2]^+$, 100%), 379 ($[\text{M}+4]^+$, 40%). Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{Br}_2\text{N}$: C, 50.96; H, 2.94; N, 3.71%; found: C, 51.19; H, 3.04; N, 3.62%.

(2,4-Dibromophenyl)(1-(2,4-dibromonaphthyl))amine (5a).



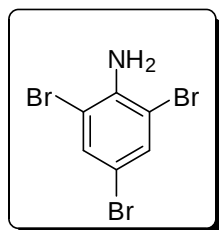
Colorless solid: mp 146–148 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, $J = 7.2$ Hz, 1H), 8.04 (s, 1H), 7.87 (d, $J = 7.2$ Hz, 1H), 7.68–7.48 (m, 3H), 7.03 (d, $J = 7.2$ Hz, 1H), 6.17 (s, 1H), 5.94 (d, $J = 8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 142.16, 135.05, 134.74, 133.16, 132.28, 132.05, 131.14, 128.39, 128.15, 128.09, 124.61, 121.67, 119.60, 115.64, 111.24, 110.96. MS (EI, m/z , rel.%): 531 (M^+ , 10%), 533 ($[\text{M}+2]^+$, 50%), 535 ($[\text{M}+4]^+$, 75%), 537 ($[\text{M}+6]^+$, 40%), 539 ($[\text{M}+8]^+$, 10%). Anal. Calcd. for $\text{C}_{16}\text{H}_9\text{Br}_4\text{N}$: C, 35.93; H, 1.70; N, 2.62%; found: C, 35.72; H, 1.87; N, 2.77%.

2,4-Dibromoaniline (3b) (CAS Registry No. 615-57-6)



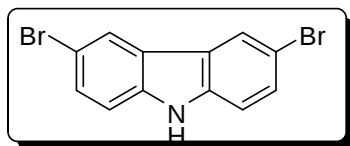
Brown solid: mp 77–79 $^{\circ}\text{C}$ (lit¹². mp 78-80 $^{\circ}\text{C}$). ^1H NMR (400 MHz, CDCl_3): δ 7.51 (s, 1H), 7.17 (d, $J = 8.4$ Hz, 1 H), 6.62 (d, $J = 8.8$ Hz, 1H), 4.08 (br. s, 2H). MS (EI, m/z , rel.%): 249 (M^+ , 30%), 251($[\text{M}+2]^+$, 50%), 253 ($[\text{M}+4]^+$, 25%).

2,4,6-Tribromoaniline (4b) (CAS Registry No. 147-82-0)



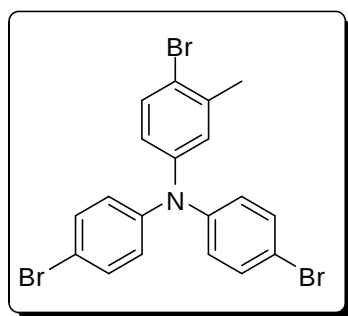
Brown solid: mp 120–122 $^{\circ}\text{C}$ (lit¹¹. mp 121-123 $^{\circ}\text{C}$). ^1H NMR (400 MHz, CDCl_3): δ 7.50 (s, 2H), 4.55 (br. s, 2H). MS (EI, m/z , rel.%): 327 (M^+ , 20%), 329 ($[\text{M}+2]^+$, 95%), 331 ($[\text{M}+4]^+$, 100%), 333 ($[\text{M}+6]^+$, 20%).

3,6-Dibromocarbazole (3k) (CAS Registry No. 6825-20-3).



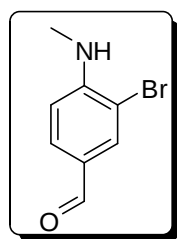
Colorless solid: mp 193–195 °C (lit¹³. mp 210–211 °C);
¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, *J* = 1.6 Hz, 2H),
 8.08 (br. s, 1H), 7.52 (dd, *J* = 8.4 Hz, 1.6 Hz, 2H), 7.29
 (d, *J* = 8.4 Hz, 2H). MS (EI, *m/z*): 323 (*M*⁺, 40%), 325 ([*M*+2]⁺, 100%), 327 ([*M*+4]⁺,
 40%).

4,4'-Tribromo-3-methyltriphenylamine (4t)



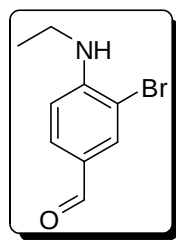
Colorless solid: mp 107–109 °C. ¹H NMR (400 MHz,
 CDCl₃): δ 7.38 (d, *J* = 6.4 Hz, 1H), 7.36–7.30 (m, 4H),
 7.05–7.02 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 4H), 6.73 (dd, *J*
 = 6.8 Hz, 2.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ
 147.69, 147.30, 138.79, 132.99, 129.45, 126.20, 124.62,
 124.43, 123.14, 117.86, 23.13. MS (EI, *m/z*, rel.%): 417 (*M*⁺-80, 100%), 493(*M*⁺,
 15%), 495 ([*M*+2]⁺, 45%), 497 ([*M*+4]⁺, 40%), 499 ([*M*+6]⁺, 15%). Anal. Calcd. for
 C₁₉H₁₄Br₃N: C, 46.01; H, 2.84; N, 2.82%; found: C, 46.22; H, 2.97; N, 2.87%.

3-Bromo-4-(methylamino)benzaldehyde (6r) (CAS Registry No. 28164-48-9)¹⁴.



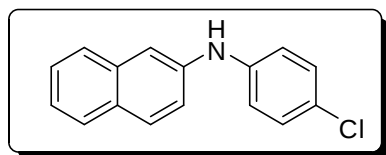
colorless solid: mp 64–66 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.67 (s,
 1H), 7.93 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H),
 5.03 (br. s 1H), 2.97 (s, 3H). MS (EI, *m/z*, rel.%): 213 (*M*⁺, 65%),
 215 ([*M*+2]⁺, 60%).

3-Bromo-4-(ethylamino)benzaldehyde (6s) (CAS Registry No. 532440-31-6).



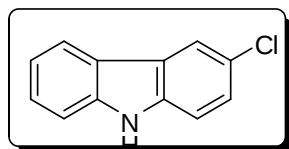
Yellow oil, ¹H NMR (400 MHz, CDCl₃): δ 9.66 (s, 1H), 7.93 (d, *J* = 2
 Hz, 1H), 7.66 (dd, *J* = 8.4 Hz, 2 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H),
 4.90 (br. s 1H), 3.29 (q, 7.2 Hz), 1.33 (t, 7.2 Hz). MS (EI, *m/z*, rel.%):
 227 (*M*⁺, 30%), 229 ([*M*+2]⁺, 30%).

(4-chlorophenyl)(2-naphthyl)amine (CAS Registry No.55566-60-4).



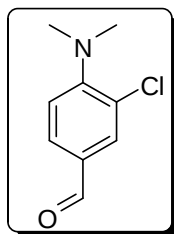
Colorless solid: mp 100–101 °C (lit.¹⁵ mp 101 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 7.37–7.35 (m, 3H), 7.18 (dd, *J* = 8.0 Hz, 0.8 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.37 (br. s, 1H). MS (EI, *m/z*, rel.%): 218 (*M*⁺-35, 100%), 253 (*M*⁺, 75%), 255([*M*+2]⁺, 20%).

3-Chlorocarbazole (CAS Registry No. 2732-25-4)



Colorless solid. mp 198–200 °C (lit.¹⁶ mp 200 °C). ¹H NMR (400 MHz, CDCl₃): δ 8.02–8.06 (m, 3H), 7.43–7.45 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.36 (t, *J* = 1.6 Hz, 2H), 7.25–7.20 (m, 1H). MS (EI, *m/z*, rel.%): 201 (*M*⁺, 100%), 203 ([*M*+2]⁺, 30%).

4-(Dimethylamino)-3-chlorobenzaldehyde (CAS Registry No. 56479-63-1).



Colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 9.80 (s, 1H), 7.82 (d, *J* = 1 Hz, 1H), 6.67 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 2.96 (s, 6H). MS (EI, *m/z*, rel.%): 183 (*M*⁺, 100%), 185 ([*M*+2]⁺, 35%).

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