Polymer-supported Organotin Reagents for Regioselective Halogenation of Aromatic Amines

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General

All starting materials were obtained from commercial suppliers and used without further purification. Dibutylphenyltin hydride was obtained using an already described procedure.^{s1} Diethyl ether and THF were distilled from sodium/benzophenone ketyl and cyclohexane was distilled over calcium hydride.

¹H and ¹³C NMR spectra were recorded on a spectrometer operating at 300 MHz for ¹H and 75.5 MHz for ¹³C in CDCl₃ solution. Chemical shifts (δ) are expressed in ppm downfield to the tetramethylsilane (TMS) as the internal standard and coupling constants (J) are expressed in Hertz.

Solid state MAS NMR experiments were performed at room temperature on a spectrometer operating at 186.5 MHz for ¹¹⁹Sn using a 4 mm double-bearing probehead. ¹¹⁹Sn MAS spectra were acquired with ¹H TPPM decoupling^{s2} during acquisition and a MAS frequency of 10 kHz. Repetition time was set to 20 s for quantitative purpose since ¹¹⁹SnT₁ were measured in the order of 3 s. Spectra were referenced to Me₄Sn using Ph₄Sn as a secondary reference (−97.35 ppm).^{s3}

Mass spectra were recorded in EI (70 eV) in GC-MS mode: the m/z values are given for meaningful signals and in the case of isotopic patterns containing Br, the given abundance refers to the higher peak.

IR spectra were recorded on a FT-IR spectrometer from 400 mg dry KBr pellets with 4 mg of substance or 10 mg of polymer. Polystyrene bands (cm^{−1}):^{s4} aromatic C–H stretchings, 3082, 3059, 3025; aliphatic C–H stretchings, 2921, 2850; weak overtone bands, 1942, 1870, 1802, 1719 (monosubstituted aromatic rings); aromatic C–C stretchings: 1601, 1586, 1493, 1452; weak in-plane aromatic C–H bending band, 1028; out-of-plane aromatic C–H bending bands, 759, 698 (monosubstituted aromatic rings).

Elemental analyses were carried out by the CNRS Analysis Central Laboratory, Vernaison, France, in order to calculate tin and halogen loadings on the resins.

ICP-MS analyses were performed with an ICP operating at 1350 W and all parameters were optimized to obtain the maximum sensitivity (ions optics, flow rates, glassware position...).

(s1) Ruel, G.; The, N. K.; Dumartin, G.; Delmond, B.; Pereyre, M. *J. Organomet. Chem.* **1993**, *444*, C18–C20.

(s2) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* **1995**, *103*, 6951–6958.

(s3) Dumartin, G.; Kharboutli, J.; Delmond, B.; Pereyre, M.; Biesemans, M.; Gielen, M.; Willem, R. *Organometallics* **1996**, *15*, 19–23.

(s4) Mercier, F. A. G.; Biesemans, M.; Altmann, R.; Willem, R.; Pintelon, R.; Schoukens, J.; Delmond, B.; Dumartin, G. *Organometallics* **2001**, *20*, 958–962.

Nebulization was performed with a nebulizer working at around 1 mL.min⁻¹. A fully quantified analytical method was set up, using 8 points of calibration between 0 and 1 ppb of tin. The material has been dissolved in 3 mL of a mixture of 2% nitric acid and acetone and interferences of the matrix have been studied in order to correct the analytical results. No internal reference was used but the stability over time had been checked up every 5 samples, and memory effect had been checked up between each sample.

Synthesis

Synthesis of poly(4-chlorobutyl)styrene 1^{s1}

To a suspension of Amberlite XE 305 (6.0 g) in dry cyclohexane (15 mL) were added successively, under argon, TMEDA (8.7 mL, 57.7 mmol) and a solution of *n*-butyllithium (2.5 M in hexanes, 27.7 mL, 69.2 mmol). The reaction mixture was heated at 65°C for 4 h. The resin was then washed under argon with dry cyclohexane (8 × 20 mL) and this procedure (TMEDA, *n*-butyllithium) was repeated once. The orange resulting lithiated polymer was then washed under argon with dry THF (12 × 20 mL). 1-Bromo-4-chlorobutane (7.9 mL, 68.6 mmol) was added, at 0°C under argon, on the lithiated polymer suspension in dry THF (50 mL). The mixture was stirred at room temperature for 18 h then the resulting polymer was successively washed with a mixture of 1:1 THF/H₂O (40 mL), THF (6 × 40 mL), absolute ethanol (4 × 40 mL) and dried *in vacuo* (0.5 mbar) at 60°C for 5 h. Polymer **1** was obtained as a white resin (7.8 g) and was found to contain 2.21 mmol of C–Cl/g. Anal. Found: C, 82.59; H, 7.72; Cl, 7.86; Br, 0.43. IR (KBr) ν 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1028, 759, 698, 650, 539 cm⁻¹.

Synthesis of poly[4-(dibutylphenylstannyl)butyl]styrene 2^{s1}

To a solution of lithium diisopropylamide (30.5 mmol) in dry THF was slowly added, at 0°C under argon, dibutylphenyltin hydride (8.62 g, 27.7 mmol). The resulting mixture was stirred for 1 h at 0°C and subsequently added at 0°C under argon to the dry polymer **3** (6.0 g). The mixture was allowed to warm up to room temperature and stirred for 18 h. The resulting polymer was successively washed with a mixture of 1:1 THF/H₂O (60 mL), THF (6 × 60 mL), absolute ethanol (4 × 60 mL) and dried *in vacuo* (0.5 mbar) at 60°C for 5 h. Polymer **2** was obtained as a white resin (10.4 g) and was found to contain 1.33 mmol of Sn/g. Anal. Found: C, 74.87; H, 7.12; Sn, 15.76; Cl, <0.20. ¹¹⁹Sn MAS NMR (186.5 MHz) δ_{Sn} -20 ppm; IR (KBr) ν 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1073, 1028, 759, 726, 698 cm⁻¹.

Synthesis of poly[4-(dibutyliodostannyl)butyl]styrene 3a^{s1}

A solution of iodine (3.81 g, 15.0 mmol) in absolute ethanol (50 mL) was added to the polymer **2** (10.0 g) and the resulting mixture was stirred at 60°C for 18 h in the dark. The polymer was successively washed with a mixture of 1:1 THF/aqueous Na₂S₂O₃ (60 mL), THF (6 × 60 mL), absolute ethanol (4 × 60 mL) and dried *in vacuo* (0.5 mbar) at 60°C for 5 h. Polymer **3a** was obtained as a pale yellow resin (10.7 g) and was found to contain 1.16 mmol of Sn–I/g. Anal. Found: C, 63.22; H, 7.00; Sn, 14.30; I, 14.78. ¹¹⁹Sn MAS NMR (186.5 MHz) δ_{Sn} 104 ppm; IR (KBr) ν 3082, 3059, 3025, 2921, 2850, 1942, 1870, 1802, 1719, 1601, 1586, 1493, 1452, 1073, 1028, 759, 698 cm⁻¹.

General procedure for the bromination of aromatic amines.

To a solution of aromatic amine **4** (2.4 mmol) in anhydrous diethyl ether (32 mL) was added dropwise, at –78°C under argon, a solution of *n*-butyllithium (2.5 M in hexanes, 0.96 mL, 2.4 mmol). The resulting mixture was stirred for 1 h at –78°C and then added to the dry polymer **3a** (2.07 g, 2.4 mmol). The resulting heterogeneous mixture was stirred for 18 h at room temperature before adding bromine (1.0 M in CH₂Cl₂, 2.4 mL, 2.4 mmol) at –78°C. The mixture was stirred for 1 h at –78°C and 1 h at room temperature, and the polymer was filtered. The resin was at first washed with diethyl ether (6 × 40 mL), then with THF (6 × 40 mL) and absolute ethanol (4 × 40 mL), and dried *in vacuo* (0.5 mbar) at 60°C for 5 h before reuse. Polymer **3b** was obtained as a blue-brown resin and was found to contain 1.31 mmol of Sn–Br/g. Anal. Found: C, 65.64; H, 7.38; Sn, 15.54; Br, 10.80; I, 0.46. ¹¹⁹Sn MAS NMR (186.5 MHz) δ_{Sn} 157 ppm; IR (KBr) ν 3082, 3059, 3025, 2921, 2851, 1943, 1870, 1800, 1719, 1601, 1586, 1493, 1452, 1073, 1028, 759, 698 cm⁻¹. The ethereal filtrate was then successively washed with a saturated solution of NaHCO₃ (50 mL) and brine (50 mL), dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel.

Characterization of 4-bromoarylamines 7a-i

All compounds **7a-i** were obtained following the general procedure for the bromination of aromatic amines.

4-bromoaniline 7a.^{s5} Compound **7a** was obtained from aniline **4a** (2.43 mmol) as a pale brown solid after chromatography (9:1, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.18): 317 mg, 76%; mp

(s5) Berrier, C.; Jacquesy, J. C.; Renoux, A. *Bull. Soc. Chim. Fr.* **1990**, 127, 93–97.

62-63°C; ^1H NMR (300 MHz, CDCl_3) δ_{H} 3.66 (br s, 2H), 6.56 (dd, $J = 6.6$ Hz, $J = 2.1$ Hz, 2H), 7.23 (dd, $J = 6.6$ Hz, $J = 2.1$ Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ_{C} 110.2, 116.7, 132.0, 145.4; MS-EI m/z (relative intensity) 173/171 (100), 92 (86), 91 (10), 86.5/85.5 (10), 65 (76), 63 (15), 45.5 (14), 39 (18); IR (KBr) ν 3474, 3283, 1613, 1592, 1488, 1287, 827, 605, 503 cm^{-1} .

2,4-dibromoaniline.^{s6} ^1H NMR (300 MHz, CDCl_3) δ_{H} 4.10 (br s, 2H), 6.64 (d, $J = 8.4$ Hz, 1H), 7.20 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H), 7.53 (d, $J = 2.4$ Hz, 1H); MS-EI m/z (relative intensity) 253/251/249 (100), 172/170 (20), 91 (24), 90 (37), 63 (26).

2,4,6-tribromoaniline.^{s6} ^1H NMR (300 MHz, CDCl_3) δ_{H} 4.57 (br s, 2H), 7.51 (s, 2H); MS-EI m/z (relative intensity) 333/331/329/327 (100), 252/250/248 (34), 171/169 (23), 170/168 (37), 166.5/165.5/164.5/163.5 (15), 90 (41), 89 (27), 85.5/84.5 (25), 63 (49), 62 (54), 61 (32), 52 (22), 44.5 (30).

4-bromo-2-nitroaniline 7b.^{s7} Compound **7b** was obtained from 2-nitroaniline **4b** (2.34 mmol) as an orange solid after chromatography (8:2, petroleum ether/AcOEt, 1% Et_3N , $R_f = 0.33$): 281 mg, 55%; mp 113-114°C; ^1H NMR (300 MHz, CDCl_3) δ_{H} 6.09 (br s, 2H), 6.72 (d, $J = 8.7$ Hz, 1H), 7.43 (dd, $J = 8.7$ Hz, $J = 2.4$ Hz, 1H), 8.27 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ_{C} 107.9, 120.3, 128.4, 132.4, 138.5, 143.5; MS-EI m/z (relative intensity) 218/216 (100), 188/186 (8), 172/170 (45), 145/143 (19), 91 (56), 90 (52), 64 (25), 63 (46), 52 (24); IR (KBr) ν 3472, 3342, 3093, 1638, 1559, 1500, 1456, 1403, 1365, 1338, 1249, 886, 814 cm^{-1} .

4-bromo-2-iodoaniline 7c. Compound **7c** was obtained from 2-iodoaniline **4c** (2.48 mmol) as a brown solid after chromatography (8:2, petroleum ether/AcOEt, 1% Et_3N , $R_f = 0.55$): 340 mg, 46%; mp 70-71°C; ^1H NMR (300 MHz, CDCl_3) δ_{H} 4.11 (br s, 2H), 6.62 (d, $J = 8.4$ Hz, 1H), 7.22 (dd, $J = 8.4$ Hz, $J = 2.1$ Hz, 1H), 7.73 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ_{C} 84.1, 109.9, 115.5, 132.1, 140.4, 145.9; MS-EI m/z (relative intensity) 299/297 (100), 172/170 (36), 145/143 (14), 127 (10), 91 (65), 90 (54), 64 (42), 63 (86), 62 (33), 52 (42), 41 (19), 38 (23); IR (KBr) ν 3384, 3288, 3175, 3070, 3046, 1617, 1573, 1475, 1386, 1022, 871, 810 cm^{-1} .

2,4-dibromo-6-iodoaniline. ^1H NMR (300 MHz, CDCl_3) δ_{H} 7.54 (d, $^4J = 2.1$ Hz, 1H), 7.70 (d, $^4J = 2.1$ Hz, 1H).

(s6) Choi, H. Y.; Chi, D. Y. *J. Am. Chem. Soc.* **2001**, *123*, 9202–9203.

(s7) Dirk, S. M.; Tour, J. M. *Tetrahedron* **2003**, *59*, 287–293.

4-bromo-2-fluoroaniline 7d.^{s8} Compound **7d** was obtained from 2-fluoroaniline **4d** (2.4 mmol) as an orange solid after chromatography (9:1, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.3): 320 mg, 70%; ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.54 (br s, 2H), 6.58 (dd, J = 8.5 Hz, J = 9.3 Hz, 1H), 6.98 (ddd, J = 2.1 Hz, J = 8.5 Hz, J = 1.1 Hz, 1H), 7.06 (dd, J = 2.1 Hz, J = 10.5 Hz, 1H).

4-bromo-2-methoxyaniline 7e. Compound **7e** was obtained from 2-methoxyaniline **4e** (1.2 mmol) as a brown solid after chromatography (85:15, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.31): 178 mg, 73%; mp 60-61°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.78 (br s, 2H), 3.84 (s, 3H), 6.58 (d, J = 8.4 Hz, 1H), 6.88-6.91 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 55.7, 109.6, 113.7, 115.7, 123.7, 135.3, 147.9; MS-EI m/z (relative intensity) 203/201 (92), 188/186 (100), 160/158 (41), 107 (17), 93 (7), 91 (7), 90 (8), 79 (24), 78 (26), 63 (10), 52 (35), 51 (25); IR (KBr) ν 3248, 3298, 3180, 3103, 2958, 2927, 2904, 2854, 2830, 1615, 1583, 1504, 1283, 1227, 1029, 860, 830, 809 cm⁻¹.

2,4-dibromo-6-methoxyaniline. ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.84 (s, 3H), 4.20 (br s, 2H), 6.82 (d, J = 2.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H); MS-EI m/z (relative intensity) 283/281/279 (85), 268/266/264 (100), 240/238/236 (24), 159/157 (6), 158/156 (5), 93 (7), 90 (10), 78 (33), 75 (15), 51 (20).

4-bromo-3-methoxyaniline 7f. Compound **7f** was obtained from 3-methoxyaniline **4f** (1.2 mmol) as a brown solid after chromatography (75:25, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.17): 110 mg, 45%; mp 93-94°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.71 (br s, 2H), 3.83 (s, 3H), 6.18 (dd, J = 8.4 Hz, J = 2.7 Hz, 1H), 6.25 (d, J = 2.7 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 56.0, 99.5, 99.6, 108.5, 133.4, 147.2, 156.4; MS-EI m/z (relative intensity) 203/201 (100), 160/158 (23), 122 (22), 107 (13), 94 (25), 93 (20), 92 (91), 79 (23), 78 (22), 65 (24), 52 (20), 51 (17).

2-bromo-5-methoxyaniline. ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.75 (s, 3H), 4.07 (br s, 2H), 6.23 (dd, J = 8.7 Hz, J = 2.7 Hz, 1H), 6.32 (d, J = 2.7 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H); MS-EI m/z (relative intensity) 203/201 (100), 173/171 (15), 160/158 (22), 94 (23), 93 (72), 92 (22), 79 (17), 78 (16), 61 (17), 52 (23), 51 (18).

2,4-dibromo-5-methoxyaniline. MS-EI m/z (relative intensity) 283/281/279 (100), 240/238/236 (24), 172/170 (16), 93 (19), 90 (13), 78 (23), 52 (12), 51 (13).

(s8) Data in good agreement with those from Sigma-Aldrich.

2-bromo-4-methoxyaniline 7g.^{s9} Compound **7g** was obtained from 4-methoxyaniline **4g** (1.2 mmol) as a brown liquid after chromatography (85:15, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.28): 129 mg, 53%; ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.72 (s, 3H), 3.80 (br s, 2H), 6.72 (m, 2H), 7.00 (d, J = 2.4 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 55.9, 109.6, 115.1, 116.7, 117.5, 138.0, 152.7; MS-EI m/z (relative intensity) 203/201 (66), 188/186 (100), 160/158 (22), 90 (7), 79 (19), 78 (15), 52 (44); IR (neat) ν 3442, 3358, 3203, 2999, 2949, 2832, 1623, 1600, 1499, 1440, 1275, 1230, 1212, 1037, 865 cm⁻¹.

2,6-dibromo-4-methoxyaniline. ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.72 (s, 3H), 4.19 (br s, 2H), 7.01 (s, 2H); MS-EI m/z (relative intensity) 283/281/279 (52), 268/266/264 (100), 240/238/236 (10), 78 (26), 52 (20).

1-amino-4-bromonaphthalene 7h.^{s10} Compound **7h** was obtained from 1-aminonaphthalene **4h** (2.34 mmol) as a purple solid after chromatography (8:2, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.16): 218 mg, 42%; mp 101-102°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 4.18 (br s, 2H), 6.66 (d, J = 8.1 Hz, 1H), 7.48-7.61 (m, 3H), 7.81 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.1 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 110.2, 111.4, 121.2, 124.8, 125.6, 127.2, 127.8, 130.1, 132.3, 142.1; MS-EI m/z (relative intensity) 223/221 (100), 142 (21), 141 (5), 140 (11), 115 (67), 114 (15), 111.5/110.5 (8), 70.5 (19); IR (KBr) ν 3417, 3316, 1626, 1514, 1450, 1372, 1273, 807 cm⁻¹.

1-amino-2,4-dibromonaphthalene. ¹H NMR (300 MHz, CDCl₃) δ_{H} 4.67 (br s, 2H), 7.51-7.62 (m, 2H), 7.78-7.81 (m, 2H), 8.17 (dd, J = 8.7 Hz, J = 1.2 Hz, 1H).

4-bromoacetanilide 7i.^{s10} Compound **7i** was obtained from acetanilide **4i** (1.58 mmol) as a white solid after chromatography (6:4, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.18): 229 mg, 68%; mp 167-168°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 2.17 (s, 3H), 7.20 (br s, 1H), 7.41 (s, 4H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 24.6, 116.9, 121.4, 132.0, 136.9, 168.3; MS-EI m/z (relative intensity) 215/213 (23), 173/171 (87), 92 (56), 91 (20), 65 (44), 64 (25), 63 (34), 43 (100), 39 (20); IR (KBr) ν 3304, 3265, 3193, 3123, 1671, 1604, 1588, 1535, 1488, 1393, 1370, 1314, 1260, 823, 745 cm⁻¹.

(s9) Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797–11810.

(s10) Smith, M. B.; Guo, L. C.; Okeyo, S.; Stenzel, J.; Yanella, J.; LaChapelle, E. *Org. Lett.* **2002**, *4*, 2321–2323.

General procedure for the iodination of aromatic amines.

To a solution of aromatic amine **4** (2.4 mmol) in anhydrous diethyl ether (32 mL) was added dropwise, at -78°C under argon, a solution of *n*-butyllithium (2.5 M in hexanes, 0.96 mL, 2.4 mmol). The resulting mixture was stirred for 1 h at -78°C and then added to the dry polymer **3a** (2.07 g, 2.4 mmol). The resulting heterogeneous mixture was stirred for 18 h at room temperature before adding a solution of ICl (3.6 mmol) in diethyl ether (10 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for 24 h in the dark before filtration of the polymer. The resin was at first washed with diethyl ether (6×40 mL), then with THF (6×40 mL) and absolute ethanol (4×40 mL), and dried *in vacuo* (0.5 mbar) at 60°C for 5 h before reuse. Polymer **3c** was obtained as a brown resin and was found to contain 1.36 mmol of Sn–Cl/g. Anal. Found: C, 68.99; H, 7.71; Sn, 16.12; Cl, 5.52; I, <0.20. ^{119}Sn MAS NMR (186.5 MHz) δ_{Sn} 170 ppm; IR (KBr) ν 3082, 3058, 3025, 2920, 2851, 1942, 1870, 1800, 1719, 1601, 1586, 1493, 1452, 1071, 1028, 759, 698 cm^{-1} . The ethereal filtrate was then successively washed with a saturated solution of NaHCO_3 (50 mL) and brine (50 mL), dried over MgSO_4 , and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel.

Characterization of 4-iodoarylamines 8a-h

All compounds **8a-h** were obtained following the general procedure for the iodination of aromatic amines.

4-iodoaniline 8a.^{s11} Compound **8a** was obtained from aniline **4a** (2.43 mmol) as a brown solid after chromatography (9:1, petroleum ether/AcOEt, 1% Et_3N , $R_f = 0.15$): 324 mg, 61%; mp $64-65^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ_{H} 3.68 (br s, 2H), 6.45–6.50 (m, 2H), 7.38–7.43 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ_{C} 79.4, 117.3, 137.9, 146.0; MS-EI m/z (relative intensity) 219 (100), 127 (5), 109.5 (6), 92 (58), 65 (57), 63 (14); IR (KBr) ν 3405, 3300, 3200, 3058, 3028, 1629, 1583, 1484, 1275, 816 cm^{-1} .

4-iodo-2-nitroaniline 8b.^{s12} Compound **8b** was obtained from 2-nitroaniline **4b** (2.4 mmol) as an orange solid after chromatography (8:2, petroleum ether/AcOEt, 1% Et_3N , $R_f = 0.31$): 399 mg, 63%; mp $121-122^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ_{H} 6.09 (br s, 2H), 6.61 (d, $J = 8.7$ Hz, 1H), 7.56 (dd, $J = 8.7$ Hz, $J = 2.1$ Hz, 1H), 8.43 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ_{C}

(s11) Edgar, K. J.; Falling, S. N. *J. Org. Chem.* **1990**, *55*, 5287–5291.

(s12) Price, D. W., Jr.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497–2518.

75.9, 120.6, 133.1, 134.3, 143.7, 144.0; MS-EI m/z (relative intensity) 264 (100), 234 (4), 218 (27), 127 (5), 91 (55), 90 (15), 64 (21), 63 (24), 52 (20); IR (KBr) ν 3491, 3379, 1614, 1610, 1554, 1491, 1460, 1335, 1249, 1232, 811 cm^{-1} .

2-fluoro-4-iodoaniline 8d.^{s13} Compound **8d** was obtained from 2-fluoroaniline **4d** (2.4 mmol) as a pale red solid after chromatography (9:1, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.29): 379 mg, 67%; mp 52-53°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 3.74 (br s, 2H), 6.53 (dd, J = 8.4 Hz, J = 9.0 Hz, 1H), 7.21 (ddd, J = 1.8 Hz, J = 8.4 Hz, J = 0.9 Hz, 1H), 7.28 (dd, J = 1.8 Hz, J = 10.5 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 77.3, 118.4, 124.1 (d, J = 21.1 Hz), 133.3, 134.5 (d, J = 12.8 Hz), 149.8-153.1 (d, J = 243.9 Hz); MS-EI m/z (relative intensity) 237 (100), 127 (4), 118.5 (6), 110 (48), 90 (24), 83 (41), 63 (16), 57 (14); IR (KBr) ν 3418, 3330, 3213, 1622, 1575, 1494, 1409, 1291, 1204, 871, 817 cm^{-1} .

1-amino-4-iodonaphthalene 8h. Compound **8h** was obtained from 1-aminonaphthalene **4h** (2.4 mmol) as a red solid after chromatography (85:15, petroleum ether/AcOEt, 1% Et₃N, R_f = 0.37): 286 mg, 44%; mp 82-83°C; ¹H NMR (300 MHz, CDCl₃) δ_{H} 4.20 (br s, 2H), 6.56 (d, J = 7.8 Hz, 1H), 7.46-7.58 (m, 2H), 7.75 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ_{C} 85.7, 111.2, 121.3, 124.6, 125.6, 127.7, 132.8, 134.5, 137.5, 143.2; MS-EI m/z (relative intensity) 269 (100), 142 (31), 140 (10), 134.5 (4), 115 (33); IR (KBr) ν 3448, 3364, 3047, 1595, 1566, 1512, 1385, 1301, 1138, 823, 758 cm^{-1} .

(s13) Glendenning, M. E., Goodby, J. W., Hird, M., Toyne, K. J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 481–491.