

Chan–Evans–Lam Amination of Boronic Acid Pinacol (BPin) Esters:

Overcoming the Aryl Amine Problem

Julien C. Vantourout,^a Robert P. Law,^b Albert Isidro-Llobet,^b Stephen J. Atkinson,^b and Allan

J. B. Watson*^a

^a Department of Pure and Applied Chemistry, WestCHEM, University of Strathclyde,

Glasgow, G1 1XL (UK). E-mail: allan.watson.100@strath.ac.uk

^b GlaxoSmithKline, Medicines Research Centre, Gunnels Wood Road, Stevenage, SG1 2NY

(UK).

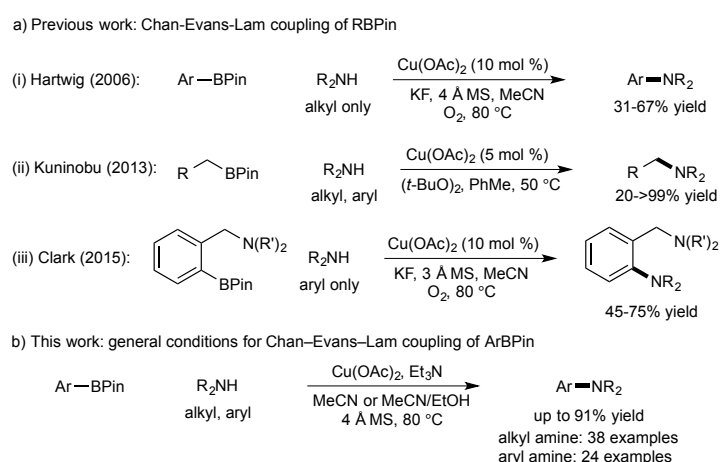
Abstract

The Chan-Evans-Lam reaction is a valuable C-N bond forming process. However, aryl boronic acid pinacol (BPin) ester reagents can be difficult coupling partners that often deliver low yields, in particular in reactions with aryl amines. Herein we report effective reaction conditions for the Chan-Evans-Lam amination of aryl BPin with alkyl and aryl amines. A mixed MeCN/EtOH solvent system was found to enable effective C-N bond formation using aryl amines while EtOH is not required for the coupling of alkyl amines.

Transition metal-mediated C-N bond formation is an essential transformation that enables the preparation of valuable amine products.¹ The Buchwald–Hartwig reaction² (mediated by Pd) and Chan–Evans–Lam (CEL) reaction^{3,4} (mediated by Cu) are two related methods that are widely practiced. The CEL reaction is particularly favored due to several advantages it can offer versus its Pd counterpart, such as the lower cost and toxicity of the metal as well as its tolerance of aerobic conditions. This process typically couples a boronic acid with an amine under mild conditions to deliver a new C-N bond (Scheme 1) and has seen considerable development. Despite this, a significant and routinely encountered problem with the CEL amination reaction is that aryl boronic acid pinacol (BPin) esters and aryl amines are generally very poor substrates. Enabling the effective amination of aryl BPin esters is highly

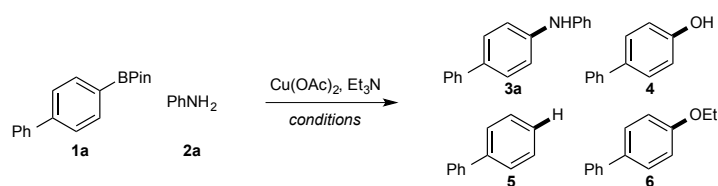
desired due to the increased stability and accessibility of these species with respect to the parent boronic acids.⁴

In relation to this BPin problem, Hartwig has developed specific reaction conditions for the CEL reaction of aryl BPin that are moderately effective with alkyl amines but not with aryl amines (Scheme 1a (i)).⁵ Koninobu has shown alkyl BPin substrates will undergo reaction with alkyl and aryl amines; however, aryl BPin species are not tolerated (Scheme 1a (ii)).⁶ More recently, Clark has shown that substrates capable of chelation can be used to facilitate CEL of specific substrates (Scheme 1a (iii)).⁷ Herein we report a simple set of general reaction conditions that promote the efficient CEL reaction of aryl BPin esters and aryl amines (Scheme 1b). These conditions also operate effectively for the coupling of alkyl amines, providing the first set of general conditions for this previously troublesome process.



Scheme 1. Approaches to Chan-Evans-Lam coupling of RBPIn.

Our initial investigation of the aryl amine/aryl BPin coupling was performed using a benchmark reaction between aniline (**1a**) and biphenyl BPin (**2a**) (Table 1). We began with standard CEL conditions (entry 1) to establish a general reactivity profile for this process, which gave 16% yield of the desired amine product **3a**, highlighting the problem with these substrates. In addition to **3a**, we observed the expected by-product of this reaction, phenol **4** (1%). Conversion to product almost doubled when heating under reflux in CH_2Cl_2 (entry 2).

Table 1. Reaction optimization.^a

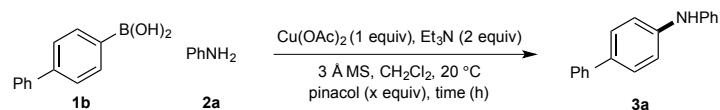
entry	reaction conditions	3a:4:5:6 (%) ^b
1	CH ₂ Cl ₂ , 0.25 M, 25 °C	16:1:0:--
2	CH ₂ Cl ₂ , 0.25 M, 40 °C	31:2:5:--
3	MeCN, 0.25 M, 60 °C	39:8:6:--
4	MeCN, 0.25 M, 80 °C	44:14:11:--
5	MeCN, 0.25 M, 3 Å MS, 80 °C	58:6:3:--
6	MeCN, 1.0 M, 3 Å MS, 80 °C	71:2:0:--
7	EtOH, 0.25 M, 60 °C	43:12:15:38
8	MeCN:EtOH (20:1), 1.0 M, 3 Å MS, 80 °C	82:6:3:7
9	MeCN:EtOH (20:1), 1.0 M, 3 Å MS, O ₂ , 80 °C ^c	21:2:0:0

^a **1a** (1.0 equiv, 0.3 mmol), **2a** (2 equiv, 0.6 mmol), Cu(OAc)₂ (1 equiv, 0.3 mmol), Et₃N (2 equiv, 0.6 mmol), solvent, air, 24 h. ^b Determined by HPLC analysis using an internal standard. Mass balance is returned starting material. ^c Using 10 mol % Cu(OAc)₂.

A survey of reaction solvents was useful (a broad range of solvents was evaluated, see ESI). Replacement of CH₂Cl₂ with MeCN allowed access to higher reaction temperatures and provided a small increase in conversion to **3a** with increases in formation of **4** and the emergence of **5**, the product of protodeboronation, also noted (entries 3 and 4). Addition of molecular sieves reduced the levels of phenolic by-product **4** (entry 5) and increasing the reaction concentration boosted the yield of **3a** further, providing relatively good efficiency (entry 6). In addition to lowering production of phenol by-product **4**, removal of H₂O by addition of molecular sieves was observed to decrease formation of protodeboronation by-product **5**, as expected.⁸ During the solvent survey, use of alcoholic media such as EtOH led

to a significant quantity of the corresponding ether product **6** as expected;^{3a,b,4d,e,9} however, a competitive quantity of **3a** was produced and, more importantly, complete conversion of **1a** was observed for the first time (entry 7). This increase in reactivity may be attributable to an increase in mono-nuclear Cu(OAc)₂ from the paddlewheel dimer, [Cu(OAc)₂]₂.¹⁰ To limit the production of **6** while attempting to retain this increase in reactivity, mixtures of MeCN:EtOH were evaluated (see ESI). At 20:1 MeCN:EtOH, the formation of **6** was lowered significantly and this provided an efficient system for the coupling of **1a** and **2a** (entry 8). Unfortunately, attempts to render the process catalytic were unsuccessful – using 10 mol % Cu(OAc)₂ under an O₂ atmosphere led to only 21% conversion to **3a** (entry 9).

The reason for the lack of efficiency under catalytic reaction conditions was intriguing since several literature methods report moderate to good efficiency using catalytic Cu(OAc)₂ under an O₂ atmosphere.¹¹ In this regard, a series of control experiments using boronic acid **1b**, aniline **2a**, and stoichiometric CEL reaction conditions were informative (Table 2).

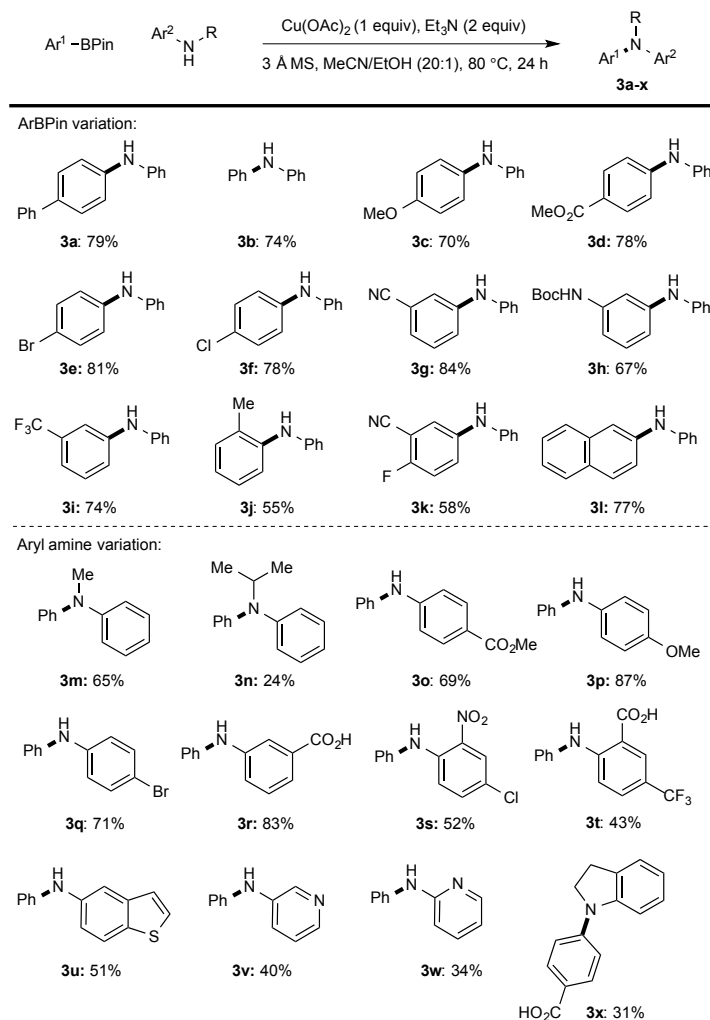
Table 2. The inhibitory effect of pinacol on CEL reactions of boronic acid **1b**.^a

entry	pinacol	time	3a (%) ^b
1	---	6 h	41
2	---	24 h	70
3	1 equiv added at 0 h	6 h	11
4	1 equiv added at 0 h	24 h	12
5	1 equiv added at 6 h	6 h	46
6	1 equiv added at 6 h	24 h	50

^a **1b** (1.0 equiv, 0.25 mmol), **2a** (2 equiv, 0.5 mmol), Cu(OAc)₂ (1 equiv, 0.25 mmol), Et₃N (2 equiv, 0.5 mmol), CH₂Cl₂ (1 mL), air, 20 °C. ^b Determined by HPLC analysis using an internal standard.

The CEL reaction of **1b** with **2a** proceeds well in the absence of pinacol, as expected (entries 1 and 2). However, addition of stoichiometric pinacol at various time points immediately impedes the reaction. Specifically, addition of pinacol at t = 0 h leads to *ca.* 10% conversion over 6 h and this does not improve over an additional 18 h of reaction time (entries 3 and 4). Similarly, addition of pinacol at t = 6 h immediately halts the reaction at *ca.* 50% conversion (entries 5 and 6). The origin of this effect is unclear; however, diols are known to form stable complexes with Cu(II).¹² We therefore speculate that pinacol, released as a by-product as the reactions of BPin substrates progress, inhibits catalyst turnover and therefore reaction efficiency. Accordingly, stoichiometric Cu(OAc)₂ are required with BPin substrates.

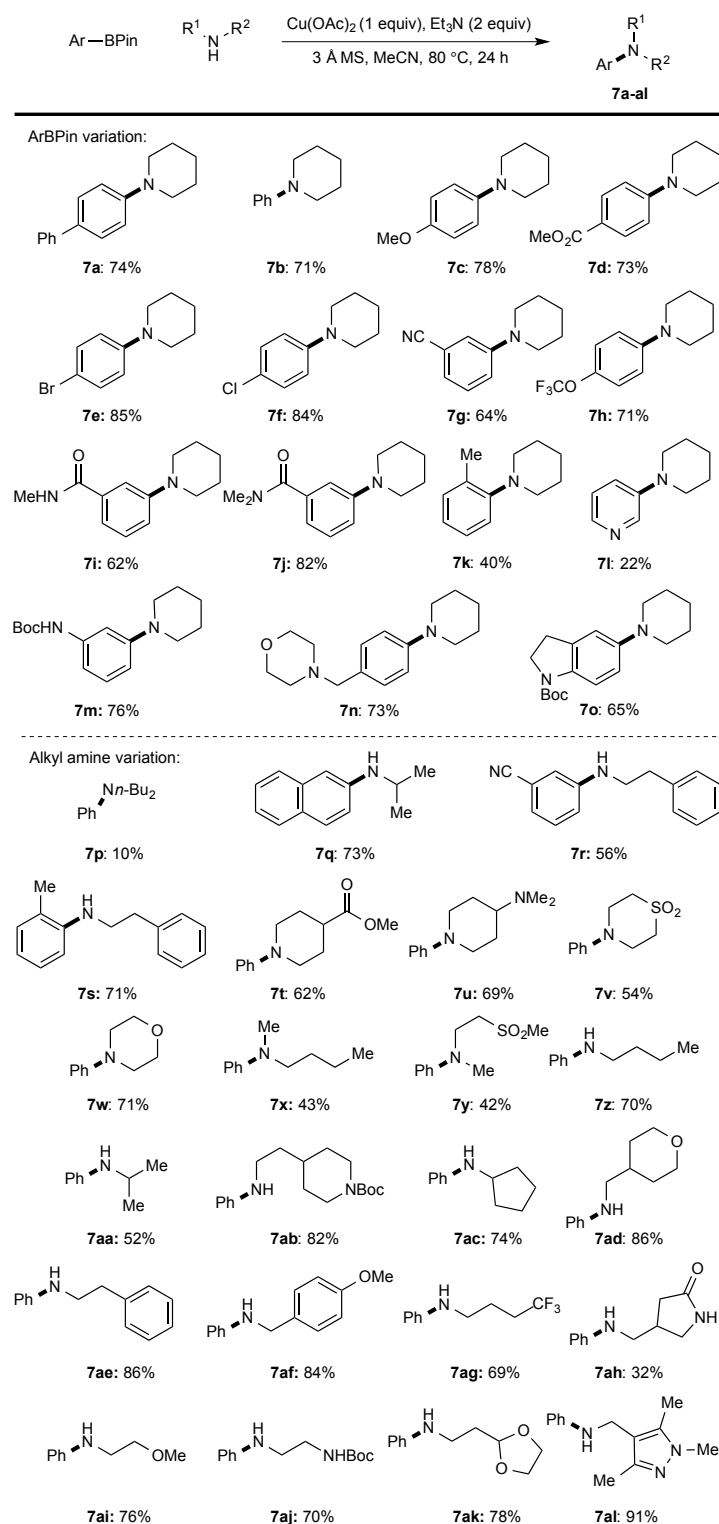
Based on this, we proceeded to evaluate the generality of the optimum stoichiometric conditions (entry 8). Application of the developed protocol to a range of ArBPIn and aniline substrates showed the conditions to be broadly applicable (Scheme 2).



Scheme 2. Scope of the developed CEL reaction conditions to a range of aryl BPIn and aryl amine substrates. Isolated yields.

The reaction conditions tolerated functionality on both the aryl BPIn and aryl amine components. Electron-rich (**3c**, **3h**, **3j**), -neutral (**3a**, **3b**, **3l**), and -withdrawing groups (**3d-g**, **3i**, **3k**) were tolerated on the ArBPIn. The aryl amine was also broadly tolerant of functionality and substitution (**3m-x**). Yields were generally >70% with some diminished yields observed with specific components, in particular heterocycles (**3u**, **3w**) and secondary aryl amines (**3n**, **3x**).

Pleasingly, the developed conditions were also found to be applicable to alkyl amines (Scheme 3). In this case, the addition of EtOH was not necessary to achieve good levels of reaction efficiency. Once more, a good diversity of BPin (**7a-o**) and amine (**7p-7al**) components was tolerated. Similar trends were observed with some heterocyclic (**7l**) and secondary amines (**7p**) delivering lower yields. While the product **7ah** was isolated in relatively low yield due to competing arylation of the lactam, the reaction of other amides and carbamates were more chemoselective (*e.g.*, **7i**, **7m**, **7aj**). Taking the combined scope of aryl and alkyl amine, the developed reaction conditions allow the effective and general Chan-Evans-Lam amination of aryl BPin.



Scheme 3. Scope of the developed CEL reaction conditions to a range of aryl BPIn and alkyl amine substrates. Isolated yields.

Conclusions

In summary, a straightforward set of reaction conditions has been developed that allow the efficient Chan–Evans–Lam coupling of aryl BPIn and aryl amines. These conditions are also

suitable for the coupling of alkyl amines. This provides the first general set of reaction conditions for the CEL reaction of aryl BPin reagents.

Experimental Section

General information. All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Purification was carried out according to standard laboratory methods. EtOAc and petroleum ether 40-60° for purification purposes were used as obtained from suppliers without further purification. Reactions were carried out using capped 5 mL microwave vials (reactions for Table 1, Scheme 2, and Scheme 3). Glassware was oven-dried (150 °C) and purged with N₂ before use. Purging refers to a vacuum/nitrogen-refilling procedure. Room temperature was generally *ca.* 20 °C. Reactions were carried out at elevated temperatures using a temperature-regulated hotplate/stirrer. 3 Å molecular sieves were purchased from Aldrich Chemical Company in powdered form, and activated and stored in a oven at 150 °C until their use.

Purification and Analysis. Thin layer chromatography was carried out using silica plates coated with fluorescent indicator UV254. These were analyzed under 254 nm UV light or developed using potassium permanganate solution. ¹⁹F NMR spectra were obtained at 282 MHz. ¹H and ¹³C NMR spectra were obtained at 400 MHz and 101 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are reported in Hz with CDCl₃ referenced at 7.27 ppm (¹H) and 77.36 ppm (¹³C) and DMSO-d₆ referenced at 2.50 ppm (¹H) and 39.52 ppm (¹³C). High-resolution mass spectra were obtained using a quadropole time-of-flight (Q-TOF) machine with electrospray ionization. Reverse phase HPLC data were obtained using a C18 column. Analysis was performed using a gradient method, eluting with 5–80% MeCN/H₂O over 16 minutes at a flow rate of 2 mL/min. Samples for HPLC analysis were prepared through the addition of 2 mL of caffeine standard to the reaction mixture. The resulting solution was then stirred before the removal of a 200 µL aliquot. The aliquot was diluted to 1 mL with MeCN. A 200 µL aliquot of the diluted solution was then filtered and

further diluted with 800 μL MeCN and 500 μL H₂O for HPLC analysis against established conversion factors.

General procedure for the Chan–Evans–Lam amination of boronic acid pinacol (BPin) esters with aryl amines. A solution of aryl BPin (1 equiv, 0.30 mmol, 1 M), aryl amine (2 equiv, 0.60 mmol), Cu(OAc)₂ (1 equiv, 0.30 mmol, 54 mg), Et₃N (2 equiv, 0.60 mmol, 61 mg, 84 μL), and powdered activated 3 Å molecular sieves in MeCN-EtOH (20:1 ratio, 300 μL) was sealed into an oven dried round-bottomed 5 mL microwave vial under air and stirred at 80 °C (preheated sand bath, sand temperature) for 24 h. The reaction mixture was allowed to cool to room temperature, filtered through Celite, and the filtrate was evaporated to give a residue that was purified by silica chromatography (EtOAc/petroleum ether with 1% Et₃N modifier). Appropriate fractions were evaporated to afford the desired product.

General procedure for the Chan–Evans–Lam amination of boronic acid pinacol (BPin) esters with alkyl amines. A solution of aryl BPin (1 equiv, 0.20 mmol, 0.5 M), alkyl amine (2 equiv, 0.40 mmol), Cu(OAc)₂ (1 equiv, 0.20 mmol, 36 mg), Et₃N (2 equiv, 0.40 mmol, 41 mg, 56 μL), and powdered activated 3 Å molecular sieves in MeCN (400 μL) was sealed in an oven dried round-bottomed 5 mL microwave vial under air and stirred at 80 °C (preheated sand bath, sand temperature) for 24 h. The reaction mixture was allowed to cool to room temperature, filtered through Celite, and the filtrate was evaporated to give a residue that was purified by silica chromatography (EtOAc/petroleum ether with 1% Et₃N modifier). Appropriate fractions were evaporated to afford the desired product.

N-Phenyl-[1,1'-biphenyl]-4-amine (**3a**).¹³ Orange solid (57 mg, 79% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 110-111 °C. ¹H NMR (400 MHz; DMSO-d₆): δ 6.86 (t, J = 7.3 Hz, 1H), 7.12-7.17 (m, 4H), 7.27-7.28 (m, 3H), 7.42 (t, J = 7.6 Hz, 2H), 7.55-7.63 (m, 4H), 8.30 (br. s., 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 117.2, 117.6, 119.6, 120.4, 126.2, 126.8, 127.8, 129.3, 129.7, 131.6, 140.5, 143.5. LCMS (ESI): t_R = 1.43 min, [M+H]⁺ 246.2. HRMS (ESI): (C₁₈H₁₆N) [M+H]⁺ requires

246.1277, found $[M+H]^+$ 246.1279. ν_{\max} (neat): 3372, 1596, 1523, 1505, 1485, 1323, 846, 759, 745, 693 cm^{-1} .

Diphenylamine (3b).¹⁴ White solid (38 mg, 74% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 51-52 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.81 (t, $J = 7.3$ Hz, 2H), 7.05-7.07 (m, 4H), 7.20-7.24 (m, 4H), 8.10 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 116.7, 119.6, 129.1, 143.4. LCMS (ESI): $t_R = 1.21$ min, $[M+H]^+$ 170.2. HRMS (ESI): (C₁₂H₁₂N) $[M+H]^+$ requires 170.0964, found $[M+H]^+$ 170.0965. ν_{\max} (neat): 3407, 3383, 3042, 1595, 1519, 1494, 1458, 1418, 1316, 1242, 1172, 876, 743, 689 cm^{-1} .

4-Methoxy-N-phenylaniline (3c).¹⁵ Yellow solid (42 mg, 70% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 104-105 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 3.71 (s, 3H), 6.70 (t, $J = 7.3$ Hz, 1H), 6.85-6.92 (m, 4H), 7.03-7.05 (m, 2H), 7.13-7.15 (m, 2H), 7.79 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 55.2, 114.5, 114.8, 118.2, 120.3, 129.0, 136.1, 145.1, 153.8. LCMS (ESI): $t_R = 1.17$ min, $[M+H]^+$ 200.3. HRMS (ESI): (C₁₃H₁₄NO) $[M+H]^+$ requires 200.1070, found $[M+H]^+$ 200.1073. ν_{\max} (neat): 3388, 1596, 1501, 1443, 1316, 1298, 1249, 1181, 1033, 812, 750, 695 cm^{-1} .

Methyl-4-(phenylamino)benzoate (3d).¹⁶ White solid (54 mg, 78% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 108-109 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 3.78 (s, 3H), 6.99 (t, $J = 7.3$ Hz, 1H), 7.05-7.07 (m, 2H), 7.17-7.20 (m, 2H), 7.30-7.34 (m, 2H), 7.78-7.82 (m, 2H), 8.74 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 51.4, 113.9, 119.0, 119.4, 121.9, 129.2, 131.0, 141.2, 148.5, 165.9. LCMS (ESI): $t_R = 1.17$ min, $[M+H]^+$ 228.2. HRMS (ESI): (C₁₄H₁₄NO₂) $[M+H]^+$ requires 228.1019, found $[M+H]^+$ 228.1023. ν_{\max} (neat): 3334, 1687, 1589, 1532, 1496, 1433, 1344, 1281, 1251, 1172, 1109, 851, 767, 747, 692 cm^{-1} .

4-Bromo-N-phenylaniline (3e).¹⁷ White solid (60 mg, 81% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 88-89 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.87 (t, *J* = 7.5 Hz, 1H), 6.99-7.01 (m, 2H), 7.06-7.08 (m, 2H), 7.23-7.27 (m, 2H), 7.34-7.37 (m, 2H), 8.27 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 110.0, 117.4, 118.0, 120.3, 129.2, 131.7, 142.6, 143.0. LCMS (ESI): t_R = 1.34 min, [M+H]⁺ 250.1. HRMS (ESI): (C₁₂H₁₁BrN) [M+H]⁺ requires 248.0069, found [M+H]⁺ 248.0076. ν_{max} (neat): 3401, 1579, 1500, 1481, 1312, 1070, 803, 748, 704, 690 cm⁻¹.

4-Chloro-N-phenylaniline (3f).¹⁷ Colourless solid (48 mg, 78% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 65-66 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.86 (t, *J* = 7.2 Hz, 1H), 7.04-7.08 (m, 4H), 7.23-7.27 (m, 4 H), 8.25 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 117.2, 117.7, 120.2, 122.5, 128.9, 129.2, 142.5, 142.7. LCMS (ESI): t_R = 1.32 min, [M+H]⁺ 204.2. HRMS (ESI): (C₁₂H₁₁ClN) [M+H]⁺ requires 204.0575, found [M+H]⁺ 204.0579. ν_{max} (neat): 3402, 1585, 1500, 1482, 1443, 1394, 1307, 1298, 1171, 1069, 874, 804, 749, 710, 690 cm⁻¹.

3-(Phenylamino)benzotrile (3g).¹⁸ Colourless solid (49 mg, 84% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 95-96 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.95 (t, *J* = 7.4 Hz, 1H), 7.12-7.14 (m, 2H), 7.15-7.19 (m, 1H), 7.28-7.32 (m, 4H), 7.33-7.39 (m, 1H), 8.52 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 111.9, 117.6, 118.3, 119.1, 120.2, 121.4, 122.2, 129.3, 130.4, 141.7, 144.7. LCMS (ESI): t_R = 1.15 min, [M+H]⁺ 195.2. HRMS (ESI): (C₁₃H₁₁N₂) [M+H]⁺ requires 195.0917, found [M+H]⁺ 195.0921. ν_{max} (neat): 3338, 2233, 1592, 1533, 1495, 1482, 1416, 1338, 1303, 1153, 993, 962.1, 863, 778, 763, 711, 695, 677 cm⁻¹.

tert-Butyl-(3-(phenylamino)phenyl)carbamate (3h). Colourless solid (57 mg, 67% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 87–

88 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 1.47 (s, 9H), 6.67 (t, J = 7.1 Hz, 1H), 6.80 (m, 1H), 6.90 (m, 1H), 7.04-7.07 (m, 3H), 7.19-7.23 (m, 2H), 7.32 (s, 1H), 8.08 (s, 1H), 9.18 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 28.1, 78.7, 106.6, 109.9, 110.7, 116.7, 119.4, 129.0, 140.3, 143.4, 143.6, 152.7 (1 signal not observed). LCMS (ESI): t_{R} = 1.29 min, $[\text{M}+\text{H}]^+$ 285.2. HRMS (ESI): ($\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_2$) $[\text{M}+\text{H}]^+$ requires 285.1598, found $[\text{M}+\text{H}]^+$ 285.1604. ν_{max} (neat): 3331, 1692, 1595, 1526, 1497, 1450, 1398, 1368, 1275, 1247, 1153, 1053, 859, 761, 696 cm^{-1} .

N-Phenyl-3-(trifluoromethyl)aniline (**3i**).¹⁸ Colourless oil (53 mg, 74% yield). Purification: silica chromatography, 0-5% (EtOAc + 1% Et₃N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 6.93 (t, J = 7.3 Hz, 1H), 7.07-7.14 (m, 3H), 7.27-7.32 (m, 4H), 7.40-7.42 (m, 1H), 8.51 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 111.5 (q, $J_{\text{C-F}}$ = 4.2 Hz), 115.0 (q, $J_{\text{C-F}}$ = 4.2 Hz), 118.2, 118.9 (q, $J_{\text{C-F}}$ = 1 Hz), 121.2, 125.6 (q, $J_{\text{C-F}}$ = 273 Hz), 129.5, 129.8, 130.4 (q, $J_{\text{C-F}}$ = 35 Hz), 142.0, 144.7. ^{19}F -NMR (282 MHz, DMSO- d_6): δ -61.5 (s). LCMS (ESI): t_{R} = 1.34 min, $[\text{M}+\text{H}]^+$ 238.2. HRMS (ESI): ($\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}$) $[\text{M}+\text{H}]^+$ requires 238.0838, found $[\text{M}+\text{H}]^+$ 238.0841. ν_{max} (neat): 3404, 1658, 1049, 1023, 999, 824, 761 cm^{-1} .

3-Methyl-*N*-phenylaniline (**3j**).¹⁸ Yellow oil (30 mg, 55%). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 2.19 (s, 3H), 6.74 (t, J = 7.5 Hz, 1H), 6.86-6.91 (m, 3H), 7.10-7.19 (m, 5H), 7.33 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 17.9, 116.0, 118.7, 119.7, 121.8, 126.4, 128.9, 129.4, 130.8, 141.3, 145.0. LCMS (ESI): t_{R} = 1.29 min, $[\text{M}+\text{H}]^+$ 184.2. HRMS (ESI): ($\text{C}_{13}\text{H}_{14}\text{N}$) $[\text{M}+\text{H}]^+$ requires 184.1121, found $[\text{M}+\text{H}]^+$ 184.1123. ν_{max} (neat): 3407, 3383, 3042, 1595, 1519, 1494, 1458, 1418, 1318, 1242, 1172, 1083, 1023, 993, 876, 846 cm^{-1} .

2-Fluoro-5-(phenylamino)benzotrile (**3k**). Colourless solid (37 mg, 58% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 90–91 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 6.93 (t, J = 7.3 Hz, 1H), 7.07-7.10 (m, 2H), 7.26-

7.30 (m, 2H), 7.35-7.37 (m, 3H), 8.43 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 100.1 (d, $J_{C-F} = 2.8$ Hz), 114.2, 117.3 (d, $J_{C-F} = 24$ Hz), 117.6, 119.5 (d, $J_{C-F} = 253$ Hz), 123.3 (d, $J_{C-F} = 8$ Hz), 129.3, 141.1, 142.1, 154.7, 157.2. ^{19}F -NMR (282 MHz, DMSO- d_6): δ -121.2 (s). LCMS (ESI): $t_R = 1.18$ min, $[\text{M}+\text{H}]^+$ 213.2. HRMS (ESI): ($\text{C}_{13}\text{H}_{10}\text{FN}_2$) $[\text{M}+\text{H}]^+$ requires 213.0828, found $[\text{M}+\text{H}]^+$ 213.0823. ν_{max} (neat): 3345, 3039, 2243, 1595, 1533, 1493, 1402, 1348, 1241, 1226, 1171, 818, 755, 718, 693 cm^{-1} .

N-Phenylnaphthalen-2-amine (**3l**).¹⁹ Colourless solid (51 mg, 77% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 107–108 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 6.89 (t, $J = 7.2$ Hz, 1H), 7.18-7.21 (m, 6H), 7.26-7.29 (m, 1H), 7.45 (d, $J = 8.3$ Hz 1H), 7.66 (d, $J = 8.1$ Hz 1H), 7.73-7.78 (m, 2H), 8.38 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 108.9, 117.3, 119.9, 120.1, 122.7, 126.1, 126.2, 127.3, 128.1, 128.7, 129.2, 134.3, 141.3, 143.0. LCMS (ESI): $t_R = 1.35$ min, $[\text{M}+\text{H}]^+$ 220.2. HRMS (ESI): ($\text{C}_{16}\text{H}_{14}\text{N}$) $[\text{M}+\text{H}]^+$ requires 220.1121, found $[\text{M}+\text{H}]^+$ 220.1127. ν_{max} (neat): 3401, 1596, 1496, 1304, 854, 737, 690 cm^{-1} .

N-Methyl-*N*-phenylaniline (**3m**).²⁰ Colourless oil (36 mg, 65% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 3.25 (s, 3H), 6.94 (t, $J = 7.2$ Hz, 2H), 6.97-7.00 (m, 4H), 7.25-7.29 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 120.0, 121.1, 129.1, 148.6 (one signal obscured by DMSO signals). LCMS (ESI): $t_R = 1.36$ min, $[\text{M}+\text{H}]^+$ 184.2. HRMS (ESI): ($\text{C}_{13}\text{H}_{14}\text{N}$) $[\text{M}+\text{H}]^+$ requires 184.1121, found $[\text{M}+\text{H}]^+$ 184.1123. ν_{max} (neat): 3036, 1584, 1493, 1340, 1271, 1251, 1185, 1156, 1130, 1091, 1074, 1023, 991, 864, 747, 722, 690 cm^{-1} .

N-Isopropyl-*N*-phenylaniline (**3n**).²¹ Colourless oil (15 mg, 24% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 1.07 (d, $J = 4.1$ Hz, 6H), 4.30 (sept, $J = 2.3$ Hz, 1H), 6.78-6.81 (m, 4H), 6.94-6.98 (t, $J = 7.5$

Hz, 2H), 7.24-7.28 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 21.4, 48.3, 122.0, 123.1, 129.8, 146.8. LCMS (ESI): $t_{\text{R}} = 1.52$ min, $[\text{M}+\text{H}]^+$ 212.2. HRMS (ESI): ($\text{C}_{15}\text{H}_{18}\text{N}$) $[\text{M}+\text{H}]^+$ requires 212.1434, found $[\text{M}+\text{H}]^+$ 212.1425. ν_{max} (neat): 3042, 1586, 1498, 1340, 1242, 1183, 1132, 1092, 1088, 993, 880, 777, 710, 690 cm^{-1} .

Methyl-4-(phenylamino)benzoate (3o).¹⁵ White solid (54 mg, 69% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et_3N)/petroleum ether. M.pt.: 108-109 $^{\circ}\text{C}$. ^1H NMR (400 MHz, DMSO- d_6): δ 3.78 (s, 3H), 6.99 (t, $J = 7.3$ Hz, 1H), 7.05-7.07 (m, 2H), 7.17-7.20 (m, 2H), 7.30-7.34 (m, 2H), 7.78-7.82 (m, 2H), 8.74 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 51.4, 113.9, 119.0, 119.4, 121.9, 129.2, 131.0, 141.2, 148.5, 165.9. LCMS (ESI): $t_{\text{R}} = 1.17$ min, $[\text{M}+\text{H}]^+$ 228.2. HRMS (ESI): ($\text{C}_{14}\text{H}_{14}\text{NO}_2$) $[\text{M}+\text{H}]^+$ requires 228.1019, found $[\text{M}+\text{H}]^+$ 228.1023. ν_{max} (neat): 3334, 1687, 1589, 1532, 1496, 1433, 1344, 1281, 1251, 1172, 1109, 851, 767, 747, 692 cm^{-1} .

4-Methoxy-N-phenylaniline (3p).¹⁶ Yellow solid (52 mg, 87% yield). M.pt.: 104-105 $^{\circ}\text{C}$. Purification: silica chromatography, 0-3% (EtOAc + 1% Et_3N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 3.71 (s, 3H), 6.69 (t, $J = 7.3$ Hz, 1H), 6.85-6.92 (m, 4H), 7.03-7.05 (m, 2H), 7.13-7.15 (m, 2H), 7.79 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 55.2, 114.5, 114.8, 118.2, 120.3, 129.0, 136.1, 145.1, 153.8. LCMS (ESI): $t_{\text{R}} = 1.17$ min, $[\text{M}+\text{H}]^+$ 200.3. HRMS (ESI): ($\text{C}_{13}\text{H}_{14}\text{NO}$) $[\text{M}+\text{H}]^+$ requires 200.1070, found $[\text{M}+\text{H}]^+$ 200.1073. ν_{max} (neat): 3388, 1596, 1501, 1443, 1316, 1298, 1249, 1181, 1033, 812, 750, 695 cm^{-1} .

4-Bromo-N-phenylaniline (3q).¹⁷ White solid (53 mg, 71% yield). M.pt.: 88-89 $^{\circ}\text{C}$. Purification: silica chromatography, 0-3% (EtOAc + 1% Et_3N)/petroleum ether. ^1H NMR (400 MHz, DMSO- d_6): δ 6.87 (t, $J = 7.5$ Hz, 1H), 6.99-7.01 (m, 2H), 7.06-7.08 (m, 2H), 7.23-7.27 (m, 2H), 7.34-7.36 (m, 2H), 8.27 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 110.0, 117.4, 118.0, 120.3, 129.2, 131.7, 142.6, 143.0. LCMS (ESI): $t_{\text{R}} = 1.34$ min, $[\text{M}+\text{H}]^+$ 250.1.

HRMS (ESI): (C₁₂H₁₁BrN) [M+H]⁺ requires 248.0069, found [M+H]⁺ 248.0076. ν_{\max} (neat): 3401, 1579, 1500, 1481, 1312, 1070, 803, 748, 704, 690 cm⁻¹.

3-(Phenylamino)benzoic acid (3r).²² White solid (53 mg, 83% yield). Purification: silica chromatography, 0-30% (EtOAc + 1% AcOH)/petroleum ether. M.pt.: 140-141 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.88 (t, *J* = 7.1 Hz, 1H), 7.09-7.11 (m, 2H), 7.27-7.33 (m, 5H), 7.65 (s, 1H), 8.33 (s, 1H), 12.81 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 116.5, 117.5, 120.1, 120.2, 120.4, 129.2, 129.3, 131.7, 142.7, 143.9, 167.4. LCMS (ESI): *t*_R = 1.01 min, [M+H]⁺ 214.2. HRMS (ESI): (C₁₃H₁₂NO₂) [M+H]⁺ requires 214.0863, found [M+H]⁺ 214.0865. ν_{\max} (neat): 3407, 2989, 1686, 1593, 1512, 1463, 1427, 1296, 1279, 996, 934, 882, 786, 749, 698, 681, 664 cm⁻¹.

4-Chloro-2-nitro-N-phenylaniline (3s). Red solid (39 mg, 52% yield). Purification: silica chromatography, 0-15% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 59-61 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 7.16-7.23 (m, 2H), 7.31-7.33 (m, 2H), 7.41-7.43 (m, 2H), 7.48-7.52 (m, 1H), 8.12 (s, 1H), 9.40 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 118.7, 120.8, 124.0, 125.0, 125.2, 129.5, 133.4, 135.6, 138.9, 141.0. LCMS (ESI): *t*_R = 1.38 min, [M+H]⁺ 249.1. HRMS (ESI): (C₁₂H₁₀ClN₂O₂) [M+H]⁺ requires 249.0425, found [M+H]⁺ 249.0432. ν_{\max} (neat): 3338, 1618, 1593, 1566, 1526, 1498, 1456, 1407, 1345, 1246, 1213, 1148, 1074, 902, 885, 849, 819, 766, 759, 725, 694, 667 cm⁻¹.

2-(Phenylamino)-5-(trifluoromethyl)benzoic acid (3t). White solid (36 mg, 43% yield). Purification: silica chromatography, 0-25% (EtOAc + 1% AcOH)/petroleum ether. M.pt.: 77-78 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 7.20-7.23 (m, 2H), 7.32-7.33 (m, 2H), 7.41-7.45 (m, 2H), 7.64-7.67 (m, 1H), 8.14 (s, 1H), 9.97 (s, 1H), 13.57 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 111.5, 113.7, 116.7 (q, *J*_{C-F} = 24 Hz), 123.1, 124.7, 125.7, 129.6, 130.3(dt, *J*_{C-F} = 168 Hz, 7.3 Hz), 139.0, 150.1, 168.9 (1 signal not observed). ¹⁹F-NMR (282 MHz, DMSO-

d₆): δ -60.1 (s). LCMS (ESI): $t_R = 1.41$ min, $[M+H]^+$ 282. HRMS (ESI): (C₁₄H₁₁F₃NO₂) $[M+H]^+$ requires 282.0736, found $[M+H]^+$ 282.0739. ν_{\max} (neat): 3330, 2901, 1666, 1592, 1577, 1524, 1499, 1435, 1417, 1321, 1243, 1139, 1068, 904, 823, 792, 758, 745, 682, 662 cm⁻¹.

N-Phenylbenzo[*b*]thiophen-5-amine (**3u**). Grey solid (33 mg, 51% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 120-121 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.81 (t, $J = 7.3$ Hz, 1H), 7.08-7.11 (m, 3H), 7.21-7.23 (m, 2H), 7.33 (d, $J = 6.3$ Hz, 1H), 7.57 (d, $J = 6.2$ Hz, 1H), 6.67 (d, $J = 6.7$ Hz, 1H), 7.81 (d, $J = 6.7$ Hz, 1H), 8.17 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 110.1, 116.3, 117.1, 119.4, 122.9, 123.6, 127.7, 129.1, 130.9, 140.5, 143.9 (1 signal not observed). LCMS (ESI): $t_R = 1.33$ min, $[M+H]^+$ 226.1. HRMS (ESI): (C₁₄H₁₂NS) $[M+H]^+$ requires 226.0685, found $[M+H]^+$ 226.0686. ν_{\max} (neat): 3376, 3053, 1667, 1596, 1512, 1497, 1433, 1344, 1298, 1267, 1246, 1201, 1153, 1086, 1049, 1028, 892, 861, 825, 802, 745, 712, 670 cm⁻¹.

N-Phenylpyridin-3-amine (**3v**).²³ White solid (20 mg, 40% yield). Purification: silica chromatography, 0-50% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 140-141 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.72 (t, $J = 7.2$ Hz, 1H), 6.82-6.87 (m, 2H), 7.23-7.27 (m, 2H), 7.54 (m, 1H), 7.67 (m, 2H), 8.15 (s, 1H), 8.96 (s, 1H). ¹³C NMR (101 MHz, DMSO-d₆): δ 110.6, 114.1, 117.9, 120.2, 128.5, 137.1, 141.7, 147.1, 155.8. LCMS (ESI): $t_R = 0.36$ min, $[M+H]^+$ 171.2. HRMS (ESI): (C₁₁H₁₁N₂) $[M+H]^+$ requires 171.0917, found $[M+H]^+$ 171.0915. ν_{\max} (neat): 3008, 1667, 1588, 1574, 1530, 1493, 1464, 1442, 1430, 1327, 1253, 1159, 1148, 1159, 992, 768, 747, 695 cm⁻¹.

N-Phenylpyridin-2-amine (**3w**).²⁴ White solid (17 mg, 34% yield). Purification: silica chromatography, 0-50% (EtOAc + 1% Et₃N)/petroleum ether. M.pt.: 140-141 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.71 (t, $J = 7.2$ Hz, 1H), 6.81-6.87 (m, 2H), 7.23-7.27 (m, 2H), 7.54

(t, $J = 7.4$ Hz, 1H), 7.66 (m, 2H), 8.14 (s, 1H), 8.95 (s, 1H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 110.6, 114.1, 117.9, 120.2, 128.5, 137.1, 141.7, 147.1, 155.8. LCMS (ESI): $t_R = 0.36$ min, $[\text{M}+\text{H}]^+$ 171.2. HRMS (ESI): ($\text{C}_{11}\text{H}_{11}\text{N}_2$) $[\text{M}+\text{H}]^+$ requires 171.0917, found $[\text{M}+\text{H}]^+$ 171.0915. ν_{max} (neat): 3088, 1589, 1537, 1494, 1464, 1444, 1327, 992, 770, 748, 696 cm^{-1} .

4-(Indolin-1-yl)benzoic acid (3x). Grey solid (20 mg, 31% yield). Purification: silica chromatography, 0-40% (EtOAc + 1% AcOH)/petroleum ether. M.pt.: 139-140 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 3.09 (t, $J = 7.2$ Hz, 2H), 3.94 (t, $J = 7.7$ Hz, 2H), 6.71-6.75 (m, 1H), 7.13-7.15 (m, 1H), 7.16-7.19 (m, 4H), 7.85-7.88 (m, 2H) (1 signal not observed). ^{13}C NMR (101 MHz, DMSO- d_6): δ 27.4, 51.4, 108.1, 115.3, 118.8, 125.0, 126.9, 130.2, 131.4, 144.4, 146.0, 169.1, 178.8. LCMS (ESI): $t_R = 1.15$ min, $[\text{M}+\text{H}]^+$ 240.1. HRMS (ESI): ($\text{C}_{15}\text{H}_{14}\text{NO}_2$) $[\text{M}+\text{H}]^+$ requires 240.1019, found $[\text{M}]^+$ 240.1007. ν_{max} (neat): 3341, 2861, 1684, 1594, 1568, 1529, 1511, 1482, 1457, 1402, 1320, 1295, 1187, 1170, 928, 790, 740, 708 cm^{-1} .

1-([1,1'-Biphenyl]-4-yl)piperidine (7a).²⁵ White solid (35 mg, 74% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et_3N)/cyclohexane. ^1H NMR (400 MHz, CDCl_3): δ 1.55-1.64 (m, 2H), 1.67-1.76 (m, 4H), 3.20 (t, $J = 5.1$ Hz, 4H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.25-7.27 (m, 1 H), 7.35-7.41 (m, 2H), 7.49 (d, $J = 8.8$ Hz, 2H) 7.54-7.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.4, 25.8, 50.4, 116.4, 126.3, 126.5, 127.6, 128.7, 131.6, 141.1, 151.4. LCMS (ESI): $t_R = 0.89$ min, $[\text{M}+\text{H}]^+$ 238.3. ν_{max} (neat): 2934, 2814, 1604, 1525, 1488, 1448, 1384, 1337, 1236, 1125, 917, 820, 760, 718, 691 cm^{-1} .

1-Phenylpiperidine (7b). Colourless oil (23 mg, 71% yield).²⁶ Purification: silica chromatography, 0-1% (EtOAc + 1% Et_3N)/cyclohexane. ^1H NMR (400 MHz, CDCl_3): δ 1.53-1.61 (m, 2H), 1.66-1.75 (m, 4H), 3.15 (t, $J = 5.4$ Hz, 4H), 6.78-6.84 (m, 1H), 6.93 (dd, $J = 8.7, 0.9$ Hz, 2H), 7.20-7.27 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.4, 25.9, 50.7, 116.5,

119.1, 129.0, 152.3. LCMS (ESI): $t_R = 1.29$ min, $[M+H]^+$ 162.3. ν_{\max} (neat): 2932, 2853, 2805, 1597, 1493, 1450, 1384, 1334, 1235, 1220, 1131, 1025, 993, 916, 859, 753, 690 cm^{-1} .

1-(4-Methoxyphenyl)piperidine (7c).²⁶ Off-white gum (30 mg, 78% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.50-1.58 (m, 2H), 1.67-1.75 (m, 4H), 3.02 (t, $J = 5.4$ Hz, 4H), 3.76 (s, 3H), 6.82 (d, $J = 9.0$ Hz, 2H), 6.91 (d, $J = 9.0$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 24.2, 26.2, 52.3, 55.6, 114.4, 118.7, 147.0, 153.6. LCMS (ESI): $t_R = 1.21$ min, $[M+H]^+$ 121.3. ν_{\max} (neat): 2934, 2802, 1510, 1453, 1243, 1182, 1121, 1041, 920, 823 cm^{-1} .

Methyl 4-(piperidin-1-yl)benzoate (7d).²⁷ White solid (32 mg, 73% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.59-1.72 (m, 6H), 3.32 (t, $J = 4.6$ Hz, 4H), 3.85 (s, 3H), 6.84 (d, $J = 9.0$ Hz, 2H), 7.89 (d, $J = 9.0$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 24.4, 25.4, 48.8, 51.5, 113.6, 118.7, 131.2, 154.5, 167.2. LCMS (ESI): $t_R = 1.28$ min, $[M+H]^+$ 220.3. ν_{\max} (neat): 2847, 2843, 1704, 1606, 1516, 1436, 1287, 1247, 1191, 1110, 964, 916, 827, 771, 694 cm^{-1} .

1-(4-Bromophenyl)piperidine (7e).²⁸ White solid (41 mg, 85% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.54-1.61 (m, 2H), 1.64-1.73 (m, 4H), 3.12 (t, $J = 5.4$ Hz, 4H), 6.79 (d, $J = 9.0$ Hz, 2H), 7.31 (d, $J = 9.0$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 24.2, 25.7, 50.4, 111.1, 118.0, 131.7, 151.2. LCMS (ESI): $t_R = 1.46$ min, $[M+H]^+$ 240.2. ν_{\max} (neat): 2941, 2858, 2817, 1588, 1494, 1450, 1387, 1340, 1280, 1243, 1223, 1127, 992, 917, 860, 808 cm^{-1} .

1-(4-Chlorophenyl)piperidine (7f).²⁹ White solid (33 mg, 84% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 67-69 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.51-1.61 (m, 2H), 1.65-1.74 (m, 4H), 3.11 (t, $J = 5.4$ Hz, 4H), 6.82-6.85(m,

2H), 7.15-7.20 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.2, 25.7, 50.6, 117.6, 123.9, 128.8, 150.8. LCMS (ESI): $t_{\text{R}} = 1.43$ min, $[\text{M}+\text{H}]^+$ 196.3. ν_{max} (neat): 2940, 2810, 1596, 1492, 1441, 1383, 1338, 1242, 1223, 1127, 993, 916, 858, 808, 747 cm^{-1} .

1-(3-Cyanophenyl)piperidine (7g).³⁰ Off-white gum (24 mg, 64% yield). Purification: silica chromatography, 0-2.5% (EtOAc + 1% Et_3N)/cyclohexane. ^1H NMR (400 MHz, CDCl_3): δ 1.58-1.74 (m, 6H), 3.19 (t, $J = 5.4$ Hz, 4H), 7.03 (d, $J = 7.3$ Hz, 1H), 7.07-7.12 (m, 2H), 7.25-7.31 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.1, 25.4, 49.7, 112.9, 118.6, 119.5, 120.1, 121.7, 129.7, 151.9. LCMS (ESI): $t_{\text{R}} = 1.25$ min, $[\text{M}+\text{H}]^+$ 187.3. ν_{max} (neat): 2937, 2861, 2216, 1595, 1572, 1493, 1438, 1383, 1247, 1123, 996, 955, 784, 688 cm^{-1} .

1-(4-(Trifluoromethoxy)phenyl)piperidine (7h). Colourless oil (35 mg, 71% yield). Purification: silica chromatography, 0-1% (EtOAc + 2% Et_3N)/cyclohexane. ^1H NMR (400 MHz, CDCl_3): δ 1.52-1.62 (m, 2H), 1.65-1.74 (m, 4H), 3.13 (t, $J = 5.4$ Hz, 4H), 6.88 (d, $J = 9.0$ Hz, 2H), 7.08 (dd, $J = 9.2, 0.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.2, 25.8, 50.7, 116.9, 120.7 (q, $J_{\text{C-F}} = 255.3$ Hz), 121.8, 141.6 (q, $J_{\text{C-F}} = 2.0$ Hz), 151.0. ^{19}F NMR (282 MHz, CDCl_3): δ -58.32 (s). LCMS (ESI) $t_{\text{R}} = 1.48$ min, $[\text{M}+\text{H}]^+$ 246.3. HRMS (ESI): ($\text{C}_{12}\text{H}_{15}\text{F}_3\text{NO}$) $[\text{M}+\text{H}]^+$ requires 246.1100, found $[\text{M}+\text{H}]^+$ 246.1101. ν_{max} (neat): 2938, 1509, 1260, 1232, 1206, 1155, 1131, 1026, 920, 835, 807 cm^{-1} .

N-Methyl-3-(piperidin-1-yl)benzamide (7i). Off-white solid (27 mg, 62% yield). Purification: silica chromatography, 0-35% (EtOAc + 1% Et_3N)/cyclohexane. M.pt.: 96-98 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 1.53-1.62 (m, 2H), 1.64-1.73 (m, 4H), 2.98 (d, $J = 4.9$ Hz, 3H), 3.19 (t, $J = 5.1$ Hz, 4H), 6.27 (br. s., 1H), 7.02 (ddd, $J = 8.3, 2.7, 1.0$ Hz, 1H), 7.05-7.10 (m, 1H), 7.24 (t, $J = 7.8$ Hz, 1H), 7.35-7.39 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 24.2, 25.7, 26.8, 50.3, 114.9, 116.5, 119.0, 129.0, 135.6, 152.3, 168.8. LCMS (ESI): $t_{\text{R}} = 0.91$ min, $[\text{M}+\text{H}]^+$ 219.3. HRMS (ESI): ($\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}$) $[\text{M}+\text{H}]^+$ requires 219.1492, found $[\text{M}+\text{H}]^+$ 219.1492. ν_{max} (neat):

3315, 2934, 2854, 2806, 1636, 1598, 1576, 1543, 1489, 1443, 1365, 1343, 1239, 1127, 940, 755, 693 cm⁻¹.

N,N-Dimethyl-3-(piperidin-1-yl)benzamide (**7j**). Off-white gum (38 mg, 82% yield). Purification: silica chromatography, 0-30% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.51-1.63 (m, 2H), 1.65-1.74 (m, 4H), 2.97 (br. s., 3H), 3.09 (br. s., 3H), 3.17 (t, *J* = 5.6 Hz, 4H), 6.79 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.91-6.97 (m, 2H), 7.20-7.25 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 24.3, 25.7, 35.2, 39.5, 50.3, 114.7, 117.2, 117.2, 128.9, 137.2, 152.1, 172.2. LCMS (ESI): t_R = 1.00 min, [M+H]⁺ 233.4. HRMS (ESI): (C₁₄H₂₁N₂O) [M+H]⁺ requires 233.1648, found [M+H]⁺ 233.1648. ν_{max} (neat): 2932, 2854, 1635, 1599, 1575, 1485, 1444, 1389, 1267, 1244, 1096, 994, 911, 749 cm⁻¹.

1-(o-Tolyl)piperidine (**7k**).³¹ Off-white gum (14 mg, 40% yield). Purification: silica chromatography, 0-0.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.54-1.60 (m, 2H), 1.66-1.74 (m, 4H), 2.30 (s, 3H), 2.83 (t, *J* = 4.9 Hz, 4H), 6.94 (ddd, *J* = 7.3, 1.0 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.11-7.18 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 17.8, 24.5, 26.6, 53.4, 119.0, 122.6, 126.4, 130.9, 132.7, 153.0. LCMS (ESI): t_R = 1.52 min, [M+H]⁺ 176.3. ν_{max} (neat): 2933, 2852, 2801, 1599, 1491, 1451, 1442, 1379, 1326, 1227, 1124, 1106, 1028, 923, 759, 723 cm⁻¹.

3-(Piperidin-1-yl)pyridine (**7l**).³² Brown gum (7 mg, 22% yield). Purification: silica chromatography, 0-75% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.55-1.65 (m, 2H), 1.67-1.76 (m, 4H), 3.19 (t, *J* = 5.4 Hz, 4H), 7.13 (ddd, *J* = 8.6, 4.6, 0.7 Hz, 1H), 7.18 (ddd, *J* = 8.3, 2.7, 1.5 Hz, 1H), 8.05 (dd, *J* = 4.5, 1.3 Hz, 1H), 8.31 (d, *J* = 2.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 24.1, 25.6, 49.9, 122.6, 123.3, 139.0, 140.0, 147.7. LCMS (ESI): t_R = 0.94 min, [M+H]⁺ 163.3. ν_{max} (neat): 2935, 2854, 2810, 1582, 1488, 1451, 1424, 1384, 1346, 1245, 1131, 919, 859, 797, 707 cm⁻¹.

tert-Butyl (3-(piperidin-1-yl)phenyl)carbamate (**7m**). White solid (42 mg, 76% yield). Purification: silica chromatography, 0-5% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 94-95 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.51 (s, 9 H), 1.53-1.60 (m, 2H), 1.68 (dt, *J* = 11.2, 5.6 Hz, 4H), 3.14 (t, *J* = 5.6 Hz, 4H), 6.44 (br. s., 1H), 6.60 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.08 (br. s., 1H), 7.09-7.14 (m, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 24.4, 25.8, 28.4, 50.5, 80.2, 106.6, 109.3, 111.3, 129.3, 139.2, 152.7, 153.0. LCMS (ESI): *t*_R = 1.36 min, [M+H]⁺ 277.3. HRMS (ESI): (C₁₆H₂₅N₂O₂) [M+H]⁺ requires 277.1911, found [M+H]⁺ 277.1914. *v*_{max} (neat): 3328, 2933, 1698, 1607, 1532, 1497, 1443, 1366, 1236, 1155, 1053, 1026, 979, 954, 901, 861, 768, 692 cm⁻¹.

4-(4-(Piperidin-1-yl)benzyl)morpholine (**7n**). Colourless oil (38 mg, 73% yield). Purification: silica chromatography, 0-45% (EtOAc + 2% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.53-1.61 (m, 2H), 1.66-1.75 (m, 4H), 2.42 (t, *J* = 4.6 Hz, 4H), 3.14 (t, *J* = 5.1 Hz, 4H), 3.41 (s, 2H), 3.69 (t, *J* = 4.9 Hz, 4H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 24.3, 25.9, 50.7, 53.6, 63.0, 67.1, 116.2, 128.0, 130.0, 151.4. LCMS (ESI): *t*_R = 1.17 min, [M+H]⁺ 261.4. HRMS (ESI): (C₁₆H₂₅N₂O) [M+H]⁺ requires 261.1961, found [M+H]⁺ 261.1961. *v*_{max} (neat): 2932, 2853, 2804, 1613, 1515, 1453, 1237, 1118, 1006, 915, 866 cm⁻¹.

tert-Butyl 5-(piperidin-1-yl)indoline-1-carboxylate (**7o**). Off-white solid (39 mg, 65% yield). Purification: silica chromatography, 0-7% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 88-91 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.51-1.56 (m, 2H), 1.55 (s, 9H), 1.66-1.76 (m, 4H), 2.98-3.08 (m, 6H), 3.94 (br. s., 2H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.80 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 0.5H), 7.74 (d, *J* = 8.2 Hz, 0.5H). ¹³C NMR (126 MHz, CDCl₃): δ 24.2, 26.0, 27.3, 27.8, 28.5, 47.5, 47.7, 52.2, 52.3, 80.0, 81.1, 114.7, 114.8, 114.9, 116.0, 116.4, 131.7, 132.7, 135.3, 136.4, 148.3, 152.5, 152.8. LCMS (ESI): *t*_R = 1.50 min, [M+H]⁺ 303.3. HRMS (ESI): (C₁₈H₂₇N₂O₂)

$[M+H]^+$ requires 303.2037, found $[M+H]^+$ 303.2069. ν_{\max} (neat): 2932, 2855, 2793, 1692, 1494, 1453, 1380, 1366, 1331, 1244, 1174, 1140, 1127, 1018, 950, 862, 813, 762 cm^{-1} .

N,N-Dibutylaniline (7p).³³ Brown oil (4 mg, 10% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃) δ 0.95 (t, $J = 7.3$ Hz, 6H), 1.29-1.40 (m, 4H), 1.52-1.62 (m, 4H), 3.22-3.29 (m, 4H), 6.58-6.67 (m, 3H), 7.15-7.22 (m, 2H). LCMS (ESI): $t_R = 1.64$ min, $[M+H]^+$ 206.4. Matches data from Barker, T. J.; Jarvo, E. R. *J. Am. Chem. Soc.*, **2009**, *131*, 15598–15599.

N-Isopropyl-naphthalen-2-amine (7q).³⁴ Brown oil (27 mg, 73% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.26 (d, $J = 6.3$ Hz, 6H), 3.58 (br. s., 1H), 3.75 (sept, $J = 6.3$ Hz, 1H), 6.78 (d, $J = 2.4$ Hz, 1H), 6.82 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.16 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 1H), 7.33 (ddd, $J = 8.3, 6.9, 1.2$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 1H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 22.9, 44.3, 105.0, 118.3, 121.8, 125.8, 126.2, 127.3, 127.6, 128.9, 135.3, 145.1. LCMS (ESI): $t_R = 1.31$ min, $[M+H]^+$ 186.3. ν_{\max} (neat): 3403, 2966, 1627, 1603, 1522, 1485, 1398, 1361, 1225, 1191, 828, 807, 744 cm^{-1} .

3-(Phenethylamino)benzotrile (7r). Off-white solid (25 mg, 56% yield). Purification: silica chromatography, 0-3% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 61-63 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.92 (t, $J = 7.0$ Hz, 2H), 3.35-3.45 (m, 2H), 3.88 (br. s., 1H), 6.73-6.81 (m, 2H), 6.95 (dt, $J = 7.5, 1.1$ Hz, 1H), 7.17-7.28 (m, 4H), 7.30-7.36 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 35.2, 44.6, 113.0, 115.0, 117.3, 119.4, 120.8, 126.7, 128.7, 128.8, 129.9, 138.6, 148.2. LCMS (ESI): $t_R = 1.26$ min, $[M+H]^+$ 223.3. HRMS (ESI): (C₁₅H₁₅N₂) $[M+H]^+$ requires 223.1230, found $[M+H]^+$ 223.1231. ν_{\max} (neat): 3392, 3028, 2930, 2857, 2227, 1602, 1583, 1514, 1493, 1428, 1335, 1303, 780, 751, 700, 682 cm^{-1} .

2-Methyl-N-phenethylaniline (7s). Yellow gum (30 mg, 71% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 2.02 (s, 3H), 2.96 (t, *J* = 6.8 Hz, 2H), 3.44 (t, *J* = 6.8 Hz, 2H), 3.51 (br. s., 1H), 6.62-6.70 (m, 2H), 7.03 (d, *J* = 7.1 Hz, 1H), 7.09-7.16 (m, 1H), 7.20-7.27 (m, 3H), 7.28-7.35 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 17.3, 35.5, 45.0, 109.9, 117.0, 122.1, 126.4, 127.1, 128.6, 128.8, 130.1, 139.4, 145.9. LCMS (ESI): *t*_R = 1.39 min, [M+H]⁺ 212.3. HRMS (ESI): (C₁₅H₁₈N) [M+H]⁺ requires 212.1434, found [M+H]⁺ 212.1435. *ν*_{max} (neat): 3419, 3023, 2920, 2853, 1606, 1587, 1514, 1473, 1453, 1317, 1263, 1130, 1052, 746, 700 cm⁻¹.

Methyl 1-phenylpiperidine-4-carboxylate (7t). Light yellow oil (27 mg, 62% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.81-1.93 (m, 2H), 1.97-2.07 (m, 2H), 2.45 (tt, *J* = 11.1, 4.0 Hz, 1H), 2.78 (td, *J* = 11.9, 2.9 Hz, 2H), 3.64 (dt, *J* = 12.7, 3.3 Hz, 2H), 3.70 (s, 3H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 7.21-7.28 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 28.1, 41.0, 49.3, 51.7, 116.7, 119.7, 129.1, 151.6, 175.3. LCMS (ESI): *t*_R = 1.15 min, [M+H]⁺ 220.3. HRMS (ESI): (C₁₃H₁₈NO₂) [M+H]⁺ requires 220.1332, found [M+H]⁺ 220.1338. *ν*_{max} (neat): 2951, 2811, 1733, 1598, 1496, 1448, 1388, 1314, 1251, 1194, 1168, 1043, 922, 757, 694 cm⁻¹.

N,N-Dimethyl-1-phenylpiperidin-4-amine (7u). Yellow solid (28 mg, 69% yield). Purification: silica chromatography, 0-7% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 45-48 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.64 (qd, *J* = 12.1, 3.9 Hz, 2H), 1.89-1.97 (m, 2H), 2.24-2.31 (m, 1H), 2.32 (s, 6H), 2.71 (td, *J* = 12.3, 2.6 Hz, 2H), 3.68-3.77 (m, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.94 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.20-7.28 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 28.3, 41.7, 49.2, 62.2, 116.5, 119.4, 129.0, 151.5. LCMS (ESI): *t*_R = 0.97 min, [M+H]⁺ 205.3. HRMS (ESI): (C₁₃H₂₁N₂) [M+H]⁺ requires 205.1699, found [M+H]⁺ 205.1701. *ν*_{max} (neat): 2945, 2770, 1600, 1499, 1378, 1220, 1190, 1153, 1065, 1040, 994, 918, 757, 692 cm⁻¹.

4-Phenylthiomorpholine 1,1-dioxide (7v). White solid (23 mg, 54% yield). Purification: silica chromatography, 0-35% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 123-124 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.05-3.14 (m, 4H), 3.79-3.88 (m, 4H), 6.86-6.97 (m, 3H), 7.26-7.34 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 47.7, 50.6, 116.4, 120.9, 129.8, 147.7. LCMS (ESI): t_R = 0.78 min, [M+H]⁺ 212.3. HRMS (ESI): (C₁₀H₁₄NO₂S) [M+H]⁺ requires 212.0740, found [M+H]⁺ 212.0737. ν_{max} (neat): 2930, 1598, 1498, 1309, 1384, 1276, 1227, 1176, 1121, 975, 858, 756, 694 cm⁻¹.

4-Phenylmorpholine (7w).³⁵ White solid (23 mg, 71% yield). Purification: silica chromatography, 0-2% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 54-55 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.16 (t, *J* = 4.9 Hz, 4H), 3.86 (t, *J* = 4.9 Hz, 4H), 6.85-6.94 (m, 3H), 7.26-7.31 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 49.4, 67.0, 115.7, 120.0, 129.2, 151.3. LCMS (ESI): t_R = 0.92 min, [M+H]⁺ 164.3. ν_{max} (neat): 2953, 2844, 1603, 1501, 1453, 1331, 1263, 1239, 1123, 1067, 925, 758, 695 cm⁻¹.

N-Butyl-N-methylaniline (7x).³³ Off-white gum (14 mg, 43% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.29-1.40 (m, 2H), 1.49-1.60 (m, 2H), 2.91 (s, 3H), 3.30 (t, *J* = 7.3 Hz, 2H), 6.63-6.72 (m, 3H), 7.18-7.26 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 14.0, 20.4, 28.9, 38.3, 52.5, 112.1, 115.8, 129.2, 149.4. LCMS (ESI): t_R = 1.42 min, [M+H]⁺ 164.3. ν_{max} (neat): 2958, 2869, 1600, 1507, 1366, 1207, 746, 691 cm⁻¹.

N-Methyl-N-(2-(methylsulfonyl)ethyl)aniline (7y). Colourless oil (18 mg, 42% yield). Purification: silica chromatography, 0-35% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 2.91 (s, 3H), 2.98 (s, 3H), 3.25 (t, *J* = 6.8 Hz, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 6.76-6.84 (m, 3H), 7.25-7.31 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 38.8, 42.1, 46.7, 51.4, 113.2, 118.2, 129.6, 148.1. LCMS (ESI): t_R = 0.82 min, [M+H]⁺ 214.2. HRMS (ESI):

(C₁₀H₁₆NO₂S) [M+H]⁺ requires 214.0896, found [M+H]⁺ 214.0899. ν_{\max} (neat): 2927, 1600, 1505, 1362, 1362, 1301, 1134, 955, 752, 695 cm⁻¹.

N-Butylaniline (**7z**).³⁶ Colourless oil (21 mg, 70% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 0.95 (t, *J*=7.3 Hz, 3H), 1.37-1.48 (m, 2H), 1.55-1.64 (m, 2H), 3.10 (t, *J* = 7.1 Hz, 2H), 3.53 (br. s., 1H), 6.59 (d, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 7.13-7.20 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 13.9, 20.3, 31.7, 43.7, 112.7, 117.1, 129.2, 148.6. LCMS (ESI): *t*_R = 1.26 min, [M+H]⁺ 150.3. ν_{\max} (neat): 3414, 2958, 2869, 1603, 1506, 1320, 1262, 1179, 747, 692 cm⁻¹.

N-Isopropylaniline (**7aa**).³⁷ Off-white oil (14 mg, 52% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.20 (d, *J* = 6.4 Hz, 6H), 3.37 (br. s., 1H), 3.62 (sept, *J* = 6.3 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 7.11-7.18 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 23.0, 44.2, 113.3, 117.0, 129.3, 147.5. LCMS (ESI): *t*_R = 1.12 min, [M+H]⁺ 136.2. ν_{\max} (neat): 3397, 2696, 1603, 1506, 1317, 1256, 1179, 748, 693 cm⁻¹.

tert-Butyl 4-(2-(phenylamino)ethyl)piperidine-1-carboxylate (**7ab**). Off-white solid (50 mg, 82% yield). Purification: silica chromatography, 0-10% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 92-94 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.06-1.23 (m, 2H), 1.46 (s, 9H), 1.52-1.60 (m, 3H), 1.69 (d, *J* = 13.0 Hz, 2H), 2.69 (t, *J* = 12.2 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 3.53 (br. s., 1H), 4.01-4.16 (m, 2H), 6.59 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 8.4, 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 28.5, 32.2, 33.9, 36.3, 41.3, 44.0, 79.3, 112.7, 117.3, 129.3, 148.4, 154.9. LCMS (ESI): *t*_R = 1.39 min, [M+H]⁺ 305.3. HRMS (ESI): (C₁₈H₂₉N₂O₂) [M+H]⁺ requires 305.2224, found [M+H]⁺ 305.2231. ν_{\max} (neat): 3375, 2922, 2850, 1675, 1602, 1507, 1423, 1365, 1278, 1244, 1166, 1143, 1090, 968, 866, 747, 693 cm⁻¹.

N-Cyclopentylaniline (7ac).³⁸ Off-white gum (24 mg, 74% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.40-1.53 (m, 2H), 1.55-1.78 (m, 4H), 1.95-2.08 (m, 2H), 3.61 (br. s., 1H), 3.73-3.82 (m, 1H), 6.59 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 7.10-7.20 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 24.1, 33.6, 54.7, 113.2, 116.9, 129.2, 148.1. LCMS (ESI): t_R = 1.27 min, [M+H]⁺ 162.3. ν_{max} (neat): 3397, 2955, 2868, 1602, 1504, 1429, 1313, 1180, 747, 692 cm⁻¹.

N-((Tetrahydro-2H-pyran-4-yl)methyl)aniline (7ad).³⁹ Off-white oil (33 mg, 86% yield). Purification: silica chromatography, 0-9% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.30-1.43 (m, 2H), 1.66-1.75 (m, 2H), 1.78-1.91 (m, 1H), 3.03 (d, *J* = 6.6 Hz, 2H), 3.39 (td, *J* = 11.8, 2.1 Hz, 2H), 3.71 (br. s., 1H), 3.94-4.03 (m, 2H), 6.60 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.66 - 6.72 (m, 1H), 7.13 - 7.20 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 31.1, 34.9, 50.0, 67.8, 112.7, 117.3, 129.3, 148.3. LCMS (ESI): t_R = 1.02 min, [M+H]⁺ 192.3. ν_{max} (neat): 3372, 2929, 2843, 1603, 1508, 1327, 1264, 1141, 1091, 1014, 984, 853, 749, 693 cm⁻¹.

N-Phenethylaniline (7ae).⁴⁰ Off-white gum (34 mg, 86% yield). Purification: silica chromatography, 0-1.5% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 2.91 (t, *J* = 7.0 Hz, 2H), 3.40 (t, *J* = 7.0 Hz, 2H), 3.66 (br. s., 1H), 6.61 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.70 (tt, *J* = 7.3, 1.0 Hz, 1H), 7.14-7.26 (m, 5H), 7.28-7.34 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 35.6, 45.1, 113.0, 117.5, 126.4, 128.6, 128.8, 129.3, 139.3, 148.0. LCMS (ESI): t_R = 1.31 min, [M+H]⁺ 198.3. ν_{max} (neat): 3409, 3025, 2928, 2861, 1602, 1506, 1454, 1319, 1262, 1180, 748, 693 cm⁻¹.

N-(4-Methoxybenzyl)aniline (7af).⁴¹ Yellow oil (36 mg, 84% yield). Purification: silica chromatography, 0-2% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 3.80 (s, 3H), 3.92 (br. s., 1H), 4.25 (s, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.14-7.20 (m, 2H), 7.28 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (101 MHz,

CDCl₃): δ 47.8, 55.3, 112.9, 114.1, 117.5, 128.8, 129.2, 131.4, 148.2, 158.9. LCMS (ESI): t_R = 1.22 min, [M-H]⁻ 212.2. ν_{\max} (neat): 3416, 3011, 2927, 2835, 1603, 1509, 1465, 1431, 1302, 1246, 1177, 1033, 824, 750, 693 cm⁻¹.

N-(4,4,4-Trifluorobutyl)aniline (**7ag**).³⁹ Yellow oil (28 mg, 69% yield). Purification: silica chromatography, 0-1% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 1.81-1.93 (m, 2H), 2.12-2.28 (m, 2H), 3.21 (t, J = 7.0 Hz, 2H), 3.59 (br. s., 1H), 6.60 (dd, J = 8.7, 0.9 Hz, 2H), 6.68-6.76 (m, 1H), 7.13-7.22 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 22.2 (q, J_{C-F} = 2.7 Hz), 31.5 (q, J_{C-F} = 28.6 Hz), 42.7, 112.8, 117.8, 127.1 (q, J_{C-F} = 275.8 Hz), 129.4, 147.8. ¹⁹F NMR (282 MHz, CDCl₃): δ -66.14 (t, J = 10.4 Hz, 3F). LCMS (ESI): t_R = 1.21 min, [M+H]⁺ 204.3. ν_{\max} (neat): 3414, 2948, 1604, 1508, 1391, 1316, 1295, 1250, 1225, 1144, 1028, 750, 693 cm⁻¹.

4-((Phenylamino)methyl)pyrrolidin-2-one (**7ah**). Off-white solid (12 mg, 32% yield). Purification: silica chromatography, 0-100% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 95-98 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.16 (dd, J = 17.1, 6.1 Hz, 1H), 2.51 (dd, J = 16.9, 8.8 Hz, 1H), 2.72-2.85 (m, 1H), 3.15-3.26 (m, 3H), 3.55 (dd, J = 9.5, 8.1 Hz, 1H), 3.77 (br. s., 1H), 6.28 (br. s., 1H), 6.61 (d, J = 7.8 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 7.18 (t, J = 7.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 34.3, 34.6, 45.9, 47.7, 112.8, 117.9, 129.4, 147.7, 177.6. LCMS (ESI): t_R = 0.71 min, [M+H]⁺ 191.3. HRMS: (C₁₁H₁₅N₂O) [M+H]⁺ requires 191.1179, found [M+H]⁺ 191.1176. ν_{\max} (neat): 3335, 2924, 1682, 1602, 1499, 1321, 1262, 750, 694 cm⁻¹.

N-(2-Methoxyethyl)aniline (**7ai**).³⁷ Yellow oil (23 mg, 76% yield). Purification: silica chromatography, 0-6% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 3.28 (t, J = 5.3 Hz, 2H), 3.38 (s, 3H), 3.60 (t, J = 5.3 Hz, 2H), 4.00 (br. s., 1H), 6.60-6.66 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 7.13-7.20 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 43.5, 58.7, 71.1,

113.1, 117.6, 129.2, 148.2. LCMS (ESI): $t_R = 0.90$ min, $[M+H]^+$ 152.3. ν_{\max} (neat): 3401, 2891, 1603, 1507, 1459, 1320, 1277, 1193, 1117, 749, 693 cm^{-1} .

tert-Butyl (2-(phenylamino)ethyl)carbamate (7aj). Off-white solid (33 mg, 70% yield). Purification: silica chromatography, 0-12% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 83-85 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.45 (s, 9H), 3.22-3.29 (m, 2H), 3.32-3.41 (m, 2H), 3.94 (br. s., 1H), 4.77 (br. s., 1H), 6.61 (d, $J = 8.3$ Hz, 2H), 6.71 (t, $J = 7.3$ Hz, 1H), 7.13-7.21 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 28.4, 40.2, 44.4, 79.6, 112.8, 117.6, 129.3, 148.0, 156.4. LCMS (ESI): $t_R = 1.11$ min, $[M+H]^+$ 237.4. HRMS: (C₁₃H₂₁N₂O₂) $[M+H]^+$ requires 237.1598, found $[M+H]^+$ 237.1602. ν_{\max} (neat): 3380, 2977, 1691, 1604, 1509, 1366, 1253, 1169, 989, 749, 693 cm^{-1} .

N-(2-(1,3-Dioxolan-2-yl)ethyl)aniline (7ak). Light brown oil (30 mg, 78% yield). Purification: silica chromatography, 0-6% (EtOAc + 1% Et₃N)/cyclohexane. ¹H NMR (400 MHz, CDCl₃): δ 2.01 (td, $J = 6.4, 4.5$ Hz, 2H), 3.27 (t, $J = 6.5$ Hz, 2H), 3.83-3.91 (m, 2H), 3.93-4.01 (m, 2H), 4.05 (br. s., 1H), 4.98 (t, $J = 4.5$ Hz, 1H), 6.61 (d, $J = 7.8$ Hz, 2H), 6.68 (t, $J = 7.3$ Hz, 1H), 7.16 (dd, $J = 8.3, 7.3$ Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 33.1, 39.3, 64.9, 103.8, 112.8, 117.3, 129.2, 148.4. LCMS (ESI): $t_R = 0.95$ min, $[M+H]^+$ 194.3. HRMS (ESI): (C₁₁H₁₆NO₂) $[M+H]^+$ requires 194.1176, found $[M+H]^+$ 194.1177. ν_{\max} (neat): 3400, 2884, 1603, 1508, 1413, 1319, 1266, 1180, 1139, 1031, 944, 750, 694 cm^{-1} .

N-((1,3,5-Trimethyl-1H-pyrazol-4-yl)methyl)aniline (7al).⁴² White solid (39 mg, 91% yield). Purification: silica chromatography, 0-100% (EtOAc + 1% Et₃N)/cyclohexane. M.pt.: 106-107 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.21 (s, 3H), 2.21 (s, 3H), 3.41 (br. s., 1H), 3.72 (s, 3H), 3.99 (s, 2H), 6.65 (dd, $J = 8.4, 0.9$ Hz, 2H), 6.69-6.75 (m, 1H), 7.16-7.23 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 9.6, 11.7, 35.8, 38.1, 112.7, 113.5, 117.4, 129.3, 137.6, 146.3,

148.4. LCMS (ESI): $t_R = 0.98$ min, $[M+H]^+$ 216.3. ν_{\max} (neat): 3300, 2925, 2823, 1601, 1511, 1470, 1436, 1384, 1317, 1256, 1177, 1150, 1098, 1069, 990, 870, 750, 697 cm^{-1} .

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Supporting Information. Data from solvent and concentration optimization, NMR, LCMS, HRMS, and IR spectra for characterization.

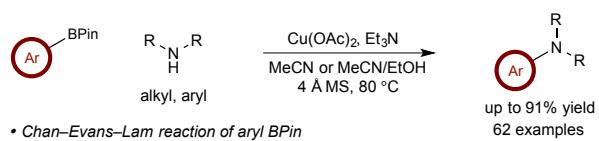
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- *Chan–Evans–Lam reaction of aryl BPin*
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- *Broad substrate scope*