Supplementary Materials for

Practical olefin hydroamination with nitroarenes

Jinghan Gui, Chung-Mao Pan, Ying Jin, Tian Qin, Julian C. Lo, Bryan J. Lee, Steven H. Spergel, Michael E. Mertzman, William J. Pitts, Thomas E. La Cruz, Michael A. Schmidt, Nitin Darvatkar, Swaminathan R. Natarajan, Phil S. Baran*

*Corresponding author. E-mail: pbaran@scripps.edu

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Practical Olefin Hydroamination with Nitroarenes

Jinghan Gui,1 Chung-Mao Pan,1† Ying Jin,1† Tian Qin,1 Julian C. Lo,1 Bryan J. Lee,1 Steven H. Spergel,2 Michael E. Mertzman,2 William J. Pitts,2 Thomas E. La Cruz,3 Michael A. Schmidt,3 Nitin Darvatkar,4 Swaminathan R. Natarajan,4 and Phil S. Baran1*

1Department of Chemistry, The Scripps Research Institute, 10550 N. Torrey Pines Rd., La Jolla, CA 92037

2Discovery Chemistry, Bristol-Myers Squibb, Provinceline Road and Route 206, P.O. Box 4000, Princeton, NJ 08543, United States

3Chemical Development, Bristol-Myers Squibb, 1 Squibb Drive, New Brunswick, NJ 08903, United States

4Kemxtree LLC, 1370 Hamilton Street, Somerset, NJ 08873, United States

†These authors contributed equally to this work.

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**General Experimental.** Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically \(^1\text{H NMR}\) homogeneous material, unless otherwise stated. Reactions were monitored by LC-MS or thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using shortwave UV light as the visualizing agent and an acidic solution of vanillin and heat, \(p\)-anisaldehyde and heat, Dragendorff\’s reagent, iodine (mixed with silica gel), or KMnO\(_4\) and heat as developing agents. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.043 – 0.063 mm). NMR spectra were recorded on Bruker AVIII-600, DRX-500, AV-400, and DPX-400 instruments and were calibrated using residual undeuterated solvent as an internal reference (CDCl\(_3\): 7.26 ppm \(^1\text{H NMR}\), 77.2 ppm \(^{13}\text{C NMR}\); MeOH-d\(_4\): 3.31 ppm \(^1\text{H NMR}\), 29.8 ppm \(^{13}\text{C NMR}\); acetone-d\(_6\): 2.05 ppm \(^1\text{H NMR}\), 29.8 ppm \(^{13}\text{C NMR}\); C\(_6\)D\(_6\): 7.16 ppm \(^1\text{H NMR}\), 128.1 ppm \(^{13}\text{C NMR}\); DMSO-d\(_6\): 2.50 ppm \(^1\text{H NMR}\), 39.5 ppm \(^{13}\text{C NMR}\)). The following abbreviations were used to explain NMR peak multiplicities: \(s\) = singlet, \(d\) = doublet, \(t\) = triplet, \(q\) = quartet, \(m\) = multiplet, \(br\) = broad. High–resolution mass spectra (HRMS) were recorded on an Agilent LCMS TOF mass spectrometer using electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and were uncorrected.
A possible mechanism that accounts for the formation of the hydroamination product and the various side products observed over the course of our studies is depicted in Fig. S1A. In accordance with previous studies (25, 26), an Fe hydride species formed in situ would convert olefin $\text{S4}$ to the alkyl radical $\text{S5}$. This presumably takes place in the presence of additional ligands and under specific reaction conditions.
though a hydrogen atom transfer event, as suggested by Shenvi et al. (28, 31), who were the first to propose that this phenomenon, largely associated with organometallic chemistry (43-46), is operative in Mukaiyama-type hydrofunctionalizations. Additionally, the Fe hydride would reduce the nitroarenes to their corresponding nitrosarenes (e.g., S2), which could either undergo further reduction to the aniline byproduct S3, or productively form adducts with either one or two equivalents of alkyl radical S5 to afford hydroxylamine S6 or N,O-alkylated product S7, respectively. The formation of S6 from S2 might proceed via two possible pathways (Fig. S1B): addition of one equivalent of alkyl radical S5 to nitrosoarene S2 gives an oxygen-centered radical S17, which could be reduced to hydroxylamine anion S18 via a single-electron transfer process. Protonation of S18 by the solvent would afford hydroxylamine S6. Alternatively, S6 might also be derived from a proton transfer process between a LnFe\textsuperscript{m−1}-H species and oxygen-centered radical intermediate S17. Then, hydroxylamine S6 thus formed would be reduced by the LnFe\textsuperscript{m−1} species to the desired secondary amine S8 in a process that regenerates the LnFe\textsuperscript{m} catalyst. The desired S8 could also be generated by reduction of the N,O-alkylated product S7 by Zn and HCl.

The proposed mechanism was supported by a variety of control experiments and other mechanistic studies (Fig. S1C). In the absence of a donor olefin under the standard reaction conditions, 1-nitronaphthalene 8 was reduced to 1-naphthylamine 11, a byproduct often observed in this reaction. Although 11 could be an intermediate in the reaction pathway, resubjection of 11 to the reaction conditions with olefin A present did not result in the formation of the desired hydroaminated product 9, suggesting that 11 was not involved in a productive pathway and that either the nitro- or nitrosoarene (S1 or S2, respectively) was involved in the C–N bond formation event. Using nitrosobenzene (S2) instead of nitrobenzene (S1) also yielded S10 (35%) and S11 (11%) in a similar proportion to that observed when nitrobenzene (S1) was used, implicating the nitroso species as an intermediate en route to the hydroaminated product.

Additionally, Co(acac)$_2$ and Mn(dpm)$_3$, failed to both reduce the nitroarene to the corresponding aniline in the absence of olefin (Fig. S2) and effect the hydroamination process in the presence of olefin (entry 6-7, Figure 1B in main text). As these two other catalysts are known to generate radicals from olefins in the presence of PhSiH$_3$, these
results suggest that direct radical addition to the nitroarene is not operative and that instead the nitroarene is reduced to the nitrosoarene prior to alkyl radical addition and C–N bond formation in the Fe(acac)₃-based system.

The nature of the alkyl radical addition to the nitrosoarene was probed by quenching the reaction after 2 min. Hydroxylamine S13 could be isolated following work up and purification, consistent with nucleophilic attack at the nitrogen atom. Furthermore, stirring the isolated S13 with Fe(acac)₃ and PhSiH₃ in EtOH resulted in reduction to the secondary amine 16, supporting the transformation of S6 to S8 in Fig. S1A. However, when 2-allylnitrobenzene (S14) was subjected to the reaction conditions using degassed EtOH under an inert oxygen-free atmosphere (to preclude a Mukaiyama-type hydration pathway), the amino alcohol S15 was isolated in 58% yield. Such a product could arise from an intramolecular alkyl radical attack on the oxygen atom of the nitrosoarene to give a 6-membered ring followed by N–O bond reduction, suggesting that the alkyl radical attack could also occur at the oxygen atom of the nitrosoarene. Interestingly, indoline S16, resulting from alkyl radical attack at the nitrogen atom, was not isolated from this reaction mixture. Based on these results, it seems likely that the specific pathway (N vs. O attack on the nitrosoarene) leading to the formation of S7 and S8 is case dependent.
General Procedure for the Olefin Hydroamination with Nitroarenes.

General Procedure A (with Zn-HCl reduction stage):
To a solution of the nitro compound (0.1 mmol, 1 equiv) and Fe(acac)₃ (10.6 mg, 0.03 mmol, 30 mol%) in EtOH (0.50 mL, 0.2 M) was added donor olefin (0.3 mmol, 3 equiv), and PhSiH₃ (24.6 µL, 0.2 mmol, 2 equiv) [CAUTION: gas evolution (presumably H₂) is occasionally observed upon addition of PhSiH₃. In larger scale, slow addition of PhSiH₃ may be preferred]. The resulting mixture was heated in an oil bath preheated to 60 °C with stirring for 1 h. The reaction mixture was then cooled to room temperature and Zn (130 mg, 2 mmol, 20 equiv) and 2N HCl (1 ml) was added to the reaction mixture. After stirring at 60 °C for another 1 h, the reaction mixture was cooled to room temperature and filtered through Celite®. After the filter cake was washed with EtOAc, the filtrate was neutralized with sat. NaHCO₃ (aq) and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was then purified on SiO₂ to furnish the desired amine product.

General Procedure B (without Zn-HCl reduction stage):
To a solution of the nitro compound (0.1 mmol, 1 equiv) and Fe(acac)₃ (10.6 mg, 0.03 mmol, 30 mol%) in EtOH (0.50 mL, 0.2 M) was added donor olefin (0.3 mmol, 3 equiv), and PhSiH₃ (24.6 µL, 0.2 mmol, 2 equiv) [CAUTION: gas evolution (presumably H₂) is occasionally observed upon addition of PhSiH₃. In larger scale, slow addition of PhSiH₃ may be preferred]. The resulting mixture was heated in an oil bath preheated to 60 °C with stirring for 1 h. The reaction mixture was then cooled to room temperature, diluted with brine and extracted with Et₂O three times. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was then purified on SiO₂ to furnish the desired amine product.

General Procedure C (using isobutylene as donor olefin):
A solution of the nitro compound (0.35 mmol, 1 equiv) and Fe(acac)₃ (37.1 mg, 0.105 mmol, 30 mol%) in EtOH (1.75 mL, 0.2 M) was cooled to −78 °C, followed by addition
of isobutylene (pre-condensed at –78 °C) (100 µL, 1.05 mmol, 3 equiv). The reaction mixture was stirred for 2 min at –78 °C followed by addition of PhSiH₃ (86.2 uL, 0.7 mmol, 2 equiv). The resulting solution was warmed up to rt, then heated in an oil bath preheated to 60 °C with stirring for 1 h. The reaction mixture was then cooled to room temperature and Zn (130 mg, 2 mmol, 20 equiv) and 2N HCl (1 ml) was added to the reaction mixture. After stirring at 60 °C for another 1 h, the reaction mixture was cooled to room temperature and filtered through Celite®. After the filter cake was washed with EtOAc, the filtrate was neutralized with sat. NaHCO₃ (aq) and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting crude product was then purified on SiO₂ to furnish the desired amine product.

**General Procedure D (decagram scale, provided by Kemxtree):**
A 1 L multi-neck round bottom flask equipped with a magnetic stir bar was charged with 10 g of nitro compound, 0.3 equiv of Fe(acac)₃ and 3.0 equiv of olefin in 300 mL of ethanol at room temperature. The resulting reddish-orange solution was kept in an oil bath and heated to 60 °C and 2 equiv of PhSiH₃ was added slowly over 10 min while maintaining the temperature at 60 °C. Then, the reaction mixture was heated at 60 °C for 1 h and the progress of the reaction was monitored by TLC and LC-MS. After the reaction mixture was cooled to room temperature, 2N HCl (1 mL for 0.1 mmol scale) was added, followed by careful addition of zinc powder (20 equiv). After heating at 60 °C for another 1 h, the reaction mixture was brought to room temperature, diluted with 200 mL of EtOAc and thereafter with 300 mL of saturated NaHCO₃ solution. Reaction suspension was filtered over a pad of Celite® and the layers were separated. The aqueous layer was extracted with EtOAc (300 mL x 3). Combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was then purified on SiO₂ to furnish the desired amine product.
Photographic Guide for the Olefin Hydroamination with Nitroarenes.
Photographic Guide for General Procedure A/B.

Fig. S3. Left: Nitro compound and Fe(acac)$_3$ were added to the reaction vial; Right: EtOH, donor olefin and PhSiH$_3$ were added next.

Fig. S4. Left: The reaction mixture was heated at 60 °C for 1 h; Right: The reaction mixture after 1 h.
Fig. S5. Left: Zn and 2N HCl were added at room temperature; Right: The reaction mixture was heated at 60 °C for another 1 h.

Fig. S6. Left: Reaction mixture after stirred at 60 °C for 5 min; Right: Reaction mixture after stirred at 60 °C for 1 h.
**Photographic Guide for General Procedure C.**

**Fig. S7.** Left: Filtering the reaction mixture through Celite® and washing with EtOAc; Right: Extraction with EtOAc after neutralized with sat. NaHCO₃ (aq).

**Fig. S8.** Instructions for adding condensed isobutylene to the reaction:

1) Left: condensed isobutylene liquid at –78 °C;
2) Middle: reaction vial/syringe/needle pre-cooled at –78 °C for 5 min;
3) Right: condensed isobutylene quickly transferred to the reaction vial using pre-cooled syringe and needle.
Photographic Guide for General Procedure D (provided by Kemxtree).

Fig. S9. Left: Nitro compound, Fe(acac)$_3$ and olefin in EtOH were added to a round bottom flask at room temperature; Right: Reddish-orange reaction mixture.

Fig. S10. Left: The reaction mixture was kept in an oil bath and heated to 60 °C; Right: 2 equiv of PhSiH$_3$ was added slowly over 10 min at 60 °C.
**Fig. S11.** Left: Reaction mixture after heating at 60 °C for 1 h; Right: Zn and 2N HCl were added and reaction mixture was heated at 60 °C for 1 h.

**Fig. S12.** Left: Filtration of reaction mixture over a pad of Celite®; Right: Separation of reaction mixture after filtration.
**Troubleshooting: Frequently Asked Questions.**

**Question 1:**
How do you purify the products: flash chromatography or preparative TLC? Do you occasionally try to work up the crude mixture with Boc₂O (or CbzCl, or other similar reagents) to facilitate the separation?

**Answer:**
We use both column chromatography and preparative TLC for purification purposes. In simple reaction systems, we prefer to use column chromatography. (Note: For products with extremely low or high polarity, 5% Et₃N is added to the eluent to avoid mass loss during column chromatography.) In cases where the products are difficult to purify using column chromatography, we use preparative TLC instead. Furthermore, you could protect the products as Boc or Cbz derivatives, but we would consider these to be “purification methods of last resort.”

**Question 2:**
How do you monitor this reaction?

**Answer:**
This reaction could be easily monitored by TLC or LC-MS. For these two methods, we normally take two samples from the reaction mixture: the first sample after 1 h (that is, before adding Zn-HCl) and the second sample after 2 h (that is, after 1 h of Zn-HCl reduction).

**Question 3:**
I have an acid sensitive substrate, can I use a weaker acid than HCl in the second stage?

**Answer:**
In this case, you could use saturated NH₄Cl (aq) (1 mL for 0.1 mmol scale reaction) instead of HCl in the second stage. In some cases, you might also get a decent yield for the acid sensitive substrates using the one-step procedure (General procedure B, without Zn-HCl stage), such as compound **123** shown in Figure 4B (main text).

**Question 4:**
Regarding the Zn-HCl reduction, how do you determine whether that stage is necessary?

**Answer:**

Most of the time, it is very easy to tell if the Zn-HCl stage is beneficial from the two LC-MS results mentioned above:

1) In cases where the bis-alkylated byproduct is fully transformed into the desired product in the Zn-HCl stage and no severe product decomposition is observed, Zn-HCl reduction is needed. A representative example is shown in Fig. S13, in which both the desired product and bis-alkylated byproduct were formed after 1 h (top trace; before the Zn-HCl stage). After the Zn-HCl stage (bottom trace), only the desired product was present in the reaction mixture and no bis-alkylated byproduct was detected. Therefore, in this case, the Zn-HCl reduction was necessary.

![Fig. S13. LC-MS trace of a representative substrate for which the Zn-HCl stage is needed.](image)

Below are two representative TLC plates for the substrates of this kind (Fig. S14).
Fig. S14. TLC plates of the reactions with 75% and 43% yields (SM: starting material; 1h: reaction system before Zn-HCl stage; 2h: reaction system after Zn-HCl stage).

2) In cases where the bis-alkylated byproduct remains unchanged during the Zn-HCl stage (N-O bond not cleaved), or severe product decomposition is observed, or problems related to functional group tolerance occur (for example, in some 2-halopyridine substrates), the Zn-HCl stage is not needed. In the example illustrated by Fig. S15, both the desired product and the bis-alkylated byproduct were formed after 1 h (top trace; before the Zn-HCl stage). After the Zn-HCl stage (bottom trace), both the desired product and the bis-alkylated byproduct remained unchanged. In this case, the Zn-HCl reduction was not necessary.

Fig. S15. LC-MS trace of a representative substrate for which the Zn-HCl stage is ineffective (due to an N-O bond cleavage problem).
In another example (Fig. S16), both the desired product and the bis-alkylated byproduct were formed after 1 h (top trace; before Zn-HCl stage). After the Zn-HCl stage (bottom trace), severe and obvious product decomposition was observed. In this case, the Zn-HCl reduction should not be conducted.

![Fig. S16. LC-MS trace of a representative substrate for which the Zn-HCl stage is detrimental (due to product decomposition)](image)

Below is one representative TLC plate for the substrate of this kind (Fig. S17).

![Fig. S17. TLC plate of a representative substrate for which the Zn-HCl stage is detrimental (SM: starting material; 1h: reaction system before Zn-HCl stage; 2h: reaction system after Zn-HCl stage).](image)
Experimental Procedures and Characterization Data for Substrates

**1-(4-Fluorophenyl)-4-nitro-1\textit{H}-indazole (106).** The product was synthesized following the literature procedure (39).

$R_f = 0.33$ (silica gel, 10:1 hexanes:Et$_2$O);

**Melting Point:** 178.1 – 180.3 °C;

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.84 (s, 1 H), 8.23 (d, $J = 7.7$ Hz, 1 H), 7.98 (d, $J = 8.4$ Hz, 1 H), 7.73 – 7.62 (m, 2 H), 7.57 (t, $J = 8.1$ Hz, 1 H), 7.32 – 7.26 (m, 2 H) ppm;

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 162.1 (d, $J = 248.7$ Hz), 141.0, 140.8, 135.3 (d, $J = 2.7$ Hz), 134.9, 126.6, 125.7 (d, $J = 8.7$ Hz), 119.1, 118.3, 117.2, 116.9 (d, $J = 23.9$ Hz) ppm;

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –113.2 ppm;

HRMS (ESI-TOF, m/z): calcld for C$_{13}$H$_9$FN$_3$O$_2$ [M+H]$^+$ 258.0673; found 258.0665.

**tert-Butyl 4-(methyl(3-nitropyridin-2-yl)amino)piperidine-1-carboxylate (109).** 2-Chloro-3-nitropyridine (173 mg, 1.1 mmol, 1.1 equiv), tert-butyl 4-(methylamino)piperidine-1-carboxylate (214 mg, 1.0 mmol, 1.0 equiv), potassium carbonate (276 mg, 2.0 mmol, 2.0 equiv) and 10 mL acetonitrile were placed in flask. The mixture was stirred under reflux for 12 h. After filtration, the solution was concentrated \textit{in vacuo}. The residue was purified by flash column chromatography (SiO$_2$, 10:1 dichloromethane:EtOAc) furnished amine 108 as a thick yellow oil (322 mg, 88%).

$R_f = 0.35$ (silica gel, 4:1 hexanes:EtOAc);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27 (dd, $J = 4.5$, 1.7 Hz, 1 H), 8.09 (dd, $J = 8.1$, 1.7 Hz, 1 H), 6.66 (dd, $J = 8.1$, 4.5 Hz, 1 H), 4.60 (tt, $J = 11.9$, 4.0 Hz, 1 H), 4.24 (br s, 2 H), 2.83 (t, $J = 13.2$ Hz, 2 H), 2.65 (s, 3 H), 1.88 – 1.78 (m, 2 H), 1.77 – 1.64 (m, 2 H), 1.46 (s, 9 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 154.8, 153.2, 151.3, 135.7, 132.1, 112.2, 79.8, 56.1, 43.5 (br), 33.5, 29.0, 28.6 ppm;

HRMS (ESI-TOF, m/z): calcld for C$_{16}$H$_{25}$N$_4$O$_4$ [M+H]$^+$ 337.1870; found 337.1863.
8-Butylidene-1,4-dioxaspiro[4.5]decane (S18). To a cooled solution (–78 °C) of butyltriphenylphosphium bromide (800 mg, 2.0 mol, 1.0 equiv) in 2 mL THF, "BuLi solution (1.1 mL, 1.9 M in THF, 2.0 mmol, 1.0 equiv) was added dropwise over 10 min, followed by warming to 0 °C. After stirring at 0 °C for 30 min, the reaction was cooled to –78 °C. 1,4-Cyclohexanedione monoethylene acetal (296.7 mg, 1.90 mmol, 0.95 equiv) in 1.5 mL THF was added dropwise and then the reaction was slowly warmed to room temperature overnight. The reaction was quenched with saturated NH₄Cl solution, and extracted with EtOAc three times. The combined organic layers were washed with brine and dried over Na₂SO₄. After removal of solvent, the residue was purified by flash column chromatography (SiO₂, 30:1 hexanes:EtOAc), furnishing protected alkene S18 as a colorless oil (249 mg, 67%).

\[ R_f = 0.68 \text{ (silica gel, 10:1 hexanes:EtOAc);} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta 5.13 (t, J = 7.2 \text{ Hz, 1 H}), 3.95 (s, 4 H), 2.28 – 2.18 (m, 4 H), 1.99 – 1.92 (m, 2 H), 1.68 – 1.60 (m, 4 H), 1.38 – 1.28 (m, 2 H), 0.89 – 0.85 (t, J = 7.4 \text{ Hz, 3 H}) \text{ ppm;} \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3\text{): } \delta 136.9, 123.0, 109.2, 64.4, 36.5, 35.7, 33.7, 29.6, 25.2, 23.3, 13.8 \text{ ppm;} \]

\[ \text{HRMS (ESI-TOF, m/z): calcd for C}_{12}\text{H}_{21}\text{O}_2 [M+H]^+ 197.1536; found 197.1535.} \]

4-Butylidenecyclohexan-1-one (114). 5 g SiO₂, 1 mL 20% H₂SO₄ aqueous solution and 10 mL dichloromethane were placed in a flask and stirred for 30 min at room temperature. The acetal S18 (249 mg, 1.3 mmol, 1 equiv) was dissolved in 2 mL dichloromethane and added into the suspension solution. After the mixture was stirred at room temperature for 2 h, the silica gel was removed by filtration. The resulting solution was concentrated \textit{in vacuo} and purified by flash column chromatography (SiO₂, 30:1 hexanes:EtOAc) furnished deprotected alkene 114 as a colorless oil (168 mg, 87%).

\[ R_f = 0.63 \text{ (silica gel, 10:1 hexanes:EtOAc);} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{): } \delta 5.32 (t, J = 7.3 \text{ Hz, 1 H}), 2.50 – 2.42 (m, 4 H), 2.39 – 2.34 (m, 4 H), 2.00 (dt, J = 7.4 \text{ Hz, 2 H}), 1.37 (tq, J = 7.4, 7.4 Hz, 2 H), 0.89 (t, J = 7.4 \text{ Hz, 3 H}) \text{ ppm;} \]
\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3) : \delta 211.9, 134.1, 125.5, 42.1, 41.1, 34.4, 29.8, 26.3, 23.0, 13.9 \text{ ppm; } \]

**HRMS (ESI-TOF, } m/z): \text{ calcd for } C_{10}H_{17}O [M+H]^+ 153.1274; \text{ found 153.1269.} \]
Experimental Procedures and Characterization Data for Products.

Benzyl 4-((3-cyano-4-((2-hydroxyethyl)amino)phenyl)amino)-4-methylpiperidine-1-carboxylate (1). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 1:3→0:1 hexanes:EtOAc) furnished amine 1 as a colorless oil (28.6 mg, 70%).

\[ R_f = 0.28 \] (silica gel, 1:3 hexanes:EtOAc);

\[ ^1H \text{ NMR} (500 \text{ MHz, acetone-}d_6, 40 ^\circ\text{C}): \delta 7.40 – 7.34 (m, 4 H), 7.32 – 7.29 (m, 1 H), 7.09 (dd, \( J = 8.9, 2.7 \text{ Hz}, 1 \text{ H} \)), 6.98 (d, \( J = 2.7 \text{ Hz}, 1 \text{ H} \)), 6.73 (d, \( J = 8.9 \text{ Hz}, 1 \text{ H} \)), 5.12 (s, 2 H), 4.87 (br s, 1 H), 3.85 (br s, 1 H), 3.79 – 3.77 (m, 2 H), 3.66 – 3.61 (m, 2 H), 3.55 – 3.51 (m, 2 H), 3.32 (td, \( J = 5.5, 5.5 \text{ Hz}, 2 \text{ H} \)), 1.82 – 1.78 (m, 2 H), 1.58 – 1.52 (m, 2 H), 1.21 (s, 3 H) ppm;

\[ ^{13}C \text{ NMR} (151 \text{ MHz, acetone-}d_6): \delta 155.7, 146.5, 138.6, 137.7, 129.8, 129.4, 128.7, 128.7, 124.8, 118.6, 113.2, 96.8, 67.3, 61.0, 53.0, 46.8, 41.0, 38.2, 26.8 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C₂₃H₂₉N₄O₃ \([\text{M+H}]^+\) 409.2234; found 409.2237.

3-Methyl-3-(naphthalen-1-ylamino)butan-1-ol (9). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 5:1→3:1 hexanes:EtOAc) furnished amine 9 as a colorless oil (14.5 mg, 63%).

\[ R_f = 0.45 \] (silica gel, 2:1 hexanes:EtOAc);

\[ ^1H \text{ NMR} (600 \text{ MHz, CDCl}_3): \delta 7.87 – 7.84 (m, 1 H), 7.83 – 7.77 (m, 1 H), 7.49 – 7.40 (m, 2 H), 7.39 – 7.32 (m, 2 H), 7.10 (dd, \( J = 7.2, 1.2 \text{ Hz}, 1 \text{ H} \)), 3.98 (t, \( J = 5.9 \text{ Hz}, 2 \text{ H} \)), 2.05 (t, \( J = 5.9 \text{ Hz}, 2 \text{ H} \)), 1.42 (s, 6 H) ppm;

\[ ^{13}C \text{ NMR} (151 \text{ MHz, CDCl}_3): \delta 141.0, 134.7, 129.0, 126.8, 126.1, 125.7, 125.3, 120.9, 120.2, 113.5, 60.3, 55.4, 43.5, 28.1 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C₁₅H₂₀N₂O [\text{M+H}]^+ 230.1539; found 230.1533.
3-(((4-Hydroxy-2-methylbutan-2-yl)(naphthalen-1-yl)amino)oxy)-3-methylbutan-1-ol (10). For entry 2 in Figure 1B: On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO$_2$, 5:1→3:1→1:1 hexanes:EtOAc) furnished bis-alkylated byproduct 10 as a white solid (13.5 mg, 41%), together with aniline product 9 (9.7 mg, 42%) and 1-naphthylamine 11 (2.2 mg, 15%).

$R_f = 0.18$ (silica gel, 1:1 hexanes:EtOAc);

**Melting Point:** 127.1 – 129.8 °C;

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 8.52 (d, $J = 8.4$ Hz, 1 H), 7.80 (d, $J = 7.4$ Hz, 1 H), 7.72 (d, $J = 7.5$ Hz, 1 H), 7.69 (d, $J = 8.1$ Hz, 1 H), 7.48 – 7.44 (m, 2 H), 7.44 – 7.41 (m, 1 H), 3.82 – 3.77 (m, 1 H), 3.71 – 3.66 (m, 2 H), 3.61 – 3.57 (m, 1 H), 2.08 – 2.04 (m, 1 H), 1.89 – 1.84 (m, 1 H), 1.77 – 1.68 (m, 2 H), 1.31 (s, 3 H), 1.11 (s, 3 H), 1.01 (s, 3 H), 0.78 (s, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 149.0, 135.3, 133.2, 128.9, 126.9, 126.5, 126.2, 126.0, 125.9, 124.9, 80.8, 63.9, 60.3, 59.5, 45.3, 42.2, 26.9, 26.2, 25.0, 23.8 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{20}$H$_{30}$NO$_3$ [M+H]$^+$ 332.2220; found 332.2219.

3-Methyl-N-(1-methylcyclohexyl)aniline (12). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 20:1→10:1 hexanes:Et$_2$O) furnished amine 12 as a colorless oil (8.3 mg, 40%).

$R_f = 0.42$ (silica gel, 10:1 hexanes:Et$_2$O);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.00 (t, $J = 7.7$ Hz, 1 H), 6.68 (s, 1 H), 6.66 (d, $J = 8.0$ Hz, 1 H), 6.60 (d, $J = 7.5$ Hz, 1 H), 2.24 (s, 3 H), 1.78 – 1.74 (m, 2 H), 1.65 – 1.60 (m, 2 H), 1.51 – 1.44 (m, 6 H), 1.23 (s, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 147.5, 139.3, 129.5, 121.6, 121.4, 117.9, 54.7, 39.2, 27.0, 26.8, 23.3, 21.7 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{14}$H$_{22}$N [M+H]$^+$ 204.1747; found 204.1749.
N-(tert-Butyl)-2,3-dihydro-1H-inden-4-amine (13). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO₂, 100:1→40:1 hexanes:EtOAc) furnished amine 13 as a colorless oil (33 mg, 50%).

\[ R_f = 0.52 \] (silica gel, 20:1 hexanes:EtOAc);

\(^1\text{H NMR (600 MHz, MeOH-d₄)}: \delta 6.97 (t, J = 7.7 \text{ Hz}, 1 \text{ H}), 6.75 (d, J = 8.0 \text{ Hz}, 1 \text{ H}), 6.70 (d, J = 7.3 \text{ Hz}, 1 \text{ H}), 2.88 (t, J = 7.5 \text{ Hz}, 2 \text{ H}), 2.74 (t, J = 7.3 \text{ Hz}, 2 \text{ H}), 2.05 \text{ (quintet, } J = 7.4 \text{ Hz}, 2H), 1.31 \text{ (s, 9 H) ppm;}

\(^{13}\text{C NMR (151 MHz, MeOH-d₄)}: \delta 145.9, 143.7, 134.1, 127.8, 116.9, 116.8, 53.3, 34.4, 31.0, 30.3, 25.8 \text{ ppm;}

HRMS (ESI-TOF, m/z): calcd for C₁₃H₂₀N [M+H]⁺ 190.1590; found 190.1589.

N-(2,3-Dimethylbutan-2-yl)-2,3-dihydro-1H-inden-4-amine (14). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 100:1 hexanes: Et₂O) furnished amine 14 as a colorless oil (10.0 mg, 46%).

\[ R_f = 0.71 \] (silica gel, 10:1 hexanes: Et₂O);

\(^1\text{H NMR (600 MHz, MeOH-d₄)}: \delta 6.92 (t, J = 7.8 \text{ Hz}, 1 \text{ H}), 6.68 (d, J = 7.8 \text{ Hz}, 1 \text{ H}), 6.58 (d, J = 7.8 \text{ Hz}, 1 \text{ H}), 2.87 (t, J = 7.8 \text{ Hz}, 2 \text{ H}), 2.67 (t, J = 7.2 \text{ Hz}, 2 \text{ H}), 2.22 – 2.18 (m, 1 \text{ H}), 2.08 – 2.04 (m, 2 \text{ H}), 1.27 (s, 6 \text{ H}), 0.94 (d, J = 6.6 \text{ Hz}, 6 \text{ H) ppm;}

\(^{13}\text{C NMR (151 MHz, MeOH-d₄)}: \delta 145.5, 144.1, 131.5, 127.8, 114.8, 113.8, 53.3, 34.4, 34.3, 30.6, 25.5, 25.3, 17.8 \text{ ppm;}


N-(tert-Butyl)-9H-fluoren-2-amine (15). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO₂, 30:1→10:1 hexanes:EtOAc) furnished amine 15 as a colorless oil (39.1 mg, 47%).

\[ R_f = 0.63 \] (silica gel, 20:3 hexanes:EtOAc);
1H NMR (600 MHz, acetone-d₆): δ 7.62 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 8.2 Hz, 1 H), 7.44 (d, J = 7.4 Hz, 1 H), 7.26 (t, J = 7.4 Hz, 1 H), 7.13 (t, J = 7.2 Hz, 1 H), 7.01 (s, 1 H), 6.81 (dd, J = 8.2, 2.0 Hz, 1 H), 3.78 (s, 2 H), 1.37 (s, 9 H) ppm;
13C NMR (151 MHz, acetone-d₆): δ 148.3, 145.4, 143.4, 143.1, 132.1, 127.4, 125.5, 125.4, 120.9, 119.0, 116.5, 113.6, 51.7, 37.4, 30.3 ppm;

N-(1-Methylcyclopentyl)-4-(methylthio)aniline (16). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 50:1→30:1 hexanes:EtOAc) furnished amine 16 as a colorless oil (14.5 mg, 66%).

Rᶠ = 0.47 (silica gel, 8:1 hexanes:EtOAc);
1H NMR (600 MHz, acetone-d₆): δ 7.13 (d, J = 9.0 Hz, 2 H), 6.67 (d, J = 8.4 Hz, 2 H), 4.89 (s, 1 H), 2.35 (s, 3 H), 1.99 – 1.96 (m, 2 H), 1.76 – 1.66 (m, 6 H), 1.40 (s, 3 H) ppm;
13C NMR (151 MHz, acetone-d₆): δ 147.6, 132.2, 123.4, 116.2, 61.9, 41.1, 26.1, 25.1, 19.3 ppm;
HRMS (ESI-TOF, m/z): calcd for C₁₃H₂₀NS [M+H]⁺ 222.1311, found 222.1316.

N-(tert-Butyl)-4-(methylthio)aniline (17). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO₂, 20:1→10:1 hexanes:EtOAc) furnished amine 17 as a colorless oil (50.0 mg, 73%) (47).

Rᶠ = 0.34 (silica gel, 10:1 hexanes:EtOAc);
1H NMR (600 MHz, MeOH-d₄): δ 7.15 (d, J = 8.6 Hz, 2 H), 6.83 (d, J = 8.6 Hz, 2 H), 2.39 (s, 3 H), 1.26 (s, 9 H) ppm;
13C NMR (151 MHz, MeOH-d₄): δ 146.2, 130.7, 129.3, 121.7, 52.9, 30.0, 18.1 ppm;
HRMS (ESI-TOF, m/z): calcd for C₁₁H₁₈NS [M+H]⁺ 196.1154; found 196.1151.
4-(Methylthio)-N-(2,4,4-trimethylpentan-2-yl)aniline (18). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 100:1→50:1 hexanes:EtOAc) furnished amine 18 as a colorless oil (14.4 mg, 57%).

\[ R_f = 0.55 \] (silica gel, 10:1 hexanes:EtOAc);

\(^1^H\) NMR (600 MHz, acetone-\(d_6\)): \(\delta 7.11\) (d, \(J = 8.6\) Hz, 2 H), 6.70 (d, \(J = 8.6\) Hz, 2 H), 4.57 (s, 1 H), 2.34 (s, 3 H), 1.75 (s, 2 H), 1.39 (s, 6 H), 1.01 (s, 9 H) ppm;

\(^{13}\)C NMR (151 MHz, acetone-\(d_6\)): \(\delta 147.7, 131.8, 123.8, 117.2, 55.5, 52.5, 32.5, 32.0, 31.1, 19.1\) ppm;

HRMS (ESI-TOF, m/z): calcd for C\(_{15}\)H\(_{26}\)NS [M+H]\(^+\) 252.1780; found 252.1784.

\(N\)-(2,3-Dimethylbutan-2-yl)-4-(methylthio)aniline (19). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 50:1→30:1 hexanes:EtOAc) furnished amine 19 as a colorless oil (11.8 mg, 53%).

\[ R_f = 0.47 \] (silica gel, 8:1 hexanes:EtOAc);

\(^1^H\) NMR (600 MHz, acetone-\(d_6\)): \(\delta 7.11\) (d, \(J = 8.4\) Hz, 2 H), 6.95 (d, \(J = 8.4\) Hz, 2 H), 4.55 (s, 1 H), 2.37 (s, 3 H), 2.26 – 2.22 (m, 1 H), 1.26 (s, 6 H), 0.93 (d, \(J = 6.6\) Hz, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, acetone-\(d_6\)): \(\delta 147.6, 131.8, 124.3, 117.5, 57.1, 35.7, 25.2, 19.0, 18.0\) ppm;

HRMS (ESI-TOF, m/z): calcd for C\(_{13}\)H\(_{22}\)NS [M+H]\(^+\) 224.1467, found 224.1475.

\(N\)-(tert-Butyl)benzo[\(d\)][1,3]dioxol-5-amine (20). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO₂, 5:1→4:1 hexanes:EtOAc) furnished amine 20 as a colorless oil (41.6 mg, 60%).

\[ R_f = 0.40 \] (silica gel, 4:1 hexanes:EtOAc);

\(^1^H\) NMR (600 MHz, acetone-\(d_6\)): \(\delta 6.61\) (d, \(J = 8.3\) Hz, 1 H), 6.44 (d, \(J = 1.9\) Hz, 1 H), 6.30 (dd, \(J = 8.3, 2.0\) Hz, 1 H), 5.85 (s, 2 H), 1.24 (s, 9 H) ppm;
N-(2,3,3-Trimethylbutan-2-yl)benzo[d][1,3]dioxol-5-amine (21). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 12:1 hexanes:EtOAc) furnished amine 21 as a colorless oil (10.6 mg, 45%).

$R_f = 0.72$ (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.64 (d, $J = 8.4$ Hz, 1 H), 6.51 (d, $J = 2.4$ Hz, 1 H), 6.39 (dd, $J = 8.4$, 2.4 Hz, 1 H), 5.86 (s, 2 H), 1.09 (s, 6 H), 1.02 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 148.9, 144.1, 142.5, 117.3, 108.6, 106.7, 102.1, 60.9, 38.7, 26.2, 23.4 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{14}$H$_{22}$NO$_2$ [M+H]$^+$ 236.1645, found 236.1648.

N-(tert-Pentyl)benzo[d][1,3]dioxol-5-amine (22). On 0.35 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 20:1→10:1 hexanes:EtOAc) furnished amine 22 as a colorless oil (29.8 mg, 41%).

$R_f = 0.61$ (silica gel, 4:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.60 (d, $J = 8.3$ Hz, 1 H), 6.42 (d, $J = 1.2$ Hz, 1 H), 6.26 (dd, $J = 7.5$, 1.5 Hz, 1 H), 5.84 (s, 2 H), 1.60 (q, $J = 7.4$ Hz, 2 H), 1.19 (s, 6 H), 0.88 (t, $J = 7.5$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 148.7, 143.7, 141.0, 111.1, 108.7, 101.6, 101.3, 54.6, 34.6, 28.2, 8.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{12}$H$_{18}$NO$_2$ [M+H]$^+$ 208.1332; found 208.1338.

N-(1-(Benzyloxy)-2-methylpropan-2-yl)benzo[d][1,3]dioxol-5-amine (23). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 15:1→5:1 hexanes:EtOAc) furnished amine 23 as a colorless oil (15.2 mg, 51%).
\( R_f = 0.50 \) (silica gel, 3:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): \( \delta 7.38 – 7.33 \) (m, 4 H), 7.30 – 7.28 (m, 1 H), 6.65 (d, \( J = 8.4 \) Hz, 1 H), 6.54 (d, \( J = 2.4 \) Hz, 1 H), 6.43 (dd, \( J = 8.4, 1.8 \) Hz, 1 H), 5.88 (s, 2 H), 4.52 (s, 2 H), 3.25 (s, 2 H), 1.17 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)) \( \delta \) 149.1, 145.0, 140.5, 139.7, 129.4, 128.9, 128.7, 117.7, 108.7, 106.8, 102.3, 77.3, 74.3, 56.7, 25.4 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{18}\)H\(_{22}\)NO\(_3\) [M+H]\(^+\) 300.1594, found 300.1603.

\( \text{N-}(\text{tert-Butyl})-4\text{-methoxyaniline} \) (24). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO\(_2\), 30:1\( \rightarrow \)20:1 hexanes:EtOAc) furnished amine 24 as a colorless oil (35.1 mg, 56%).

\( R_f = 0.45 \) (silica gel, 10:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, acetone-\(d_6\)): \( \delta 6.80 \) (d, \( J = 8.8 \) Hz, 2 H), 6.72 (d, \( J = 8.8 \) Hz, 2 H), 3.70 (s, 3 H), 1.22 (s, 9 H) ppm;

\(^{13}\)C NMR (151 MHz, acetone-\(d_6\)) \( \delta \) 154.4, 141.9, 122.1, 114.7, 55.6, 52.1, 30.4 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{11}\)H\(_{18}\)NO [M+H]\(^+\) 180.1383; found 180.1381.

\( 4\)-\( \text{Methoxy-\(N\)-(2,3,3-trimethylbutan-2-yl)aniline} \) (25). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO\(_2\), 20:1\( \rightarrow \)10:1 hexanes:Et\(_2\)O) furnished amine 25 as a colorless oil (9.3 mg, 40%).

\( R_f = 0.45 \) (silica gel, 10:1 hexanes:Et\(_2\)O);

\(^1\)H NMR (600 MHz, acetone-\(d_6\)): \( \delta 6.84 \) (d, \( J = 8.7 \) Hz, 2 H), 6.74 (d, \( J = 8.7 \) Hz, 2 H), 3.71 (s, 3 H), 1.09 (s, 6 H), 1.03 (s, 9 H) ppm;

\(^{13}\)C NMR (151 MHz, acetone-\(d_6\)) \( \delta \) 155.4, 141.3, 125.3, 114.4, 59.7, 55.6, 38.4, 26.0, 23.2 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{14}\)H\(_{24}\)NO [M+H]\(^+\) 222.1852; found 222.1856.

\( 4\)-\( \text{Methoxy-\(N\)-(2-methylpentan-2-yl)aniline} \) (26). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO\(_2\), 20:1\( \rightarrow \)20:3
hexanes:EtOAc) furnished amine 26 as a colorless oil (11.4 mg, 55%).

On decagram scale (65.3 mmol 4-nitroanisole) conducted at Kemxtree, general procedure D was followed and purification by flash column chromatography provided amine 26 (5.1 g, 38%, unoptimized yield).

\[ R_f = 0.33 \] (silica gel, 20:3 hexanes:EtOAc);

\[ ^1H \text{ NMR (600 MHz, acetone-}d_6\text{)}: \delta 6.76 (d, J = 8.8 \text{ Hz, } 2 \text{ H}), 6.71 (d, J = 8.8 \text{ Hz, } 2 \text{ H}), 3.67 (s, 3 \text{ H}), 1.54 – 1.51 (m, 2 \text{ H}), 1.43 – 1.36 (m, 2 \text{ H}), 1.20 (s, 6 \text{ H}), 0.87 (t, J = 7.3 \text{ Hz, } 3 \text{ H}) \text{ ppm;} \]

\[ ^13C \text{ NMR (151 MHz, acetone-}d_6\text{)}: \delta 154.0, 142.0, 121.1, 114.8, 55.6, 54.4, 45.0, 28.7, 18.0, 15.0 \text{ ppm;} \]

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{13}\)H\(_{22}\)NO \([M+H]^+\) 208.1696; found 208.1697.

4-Methoxy-N-(tert-pentyl)aniline (27). On decagram scale (65.3 mmol 4-nitroanisole) conducted at Kemxtree, general procedure D was followed and purification by flash column chromatography (SiO\(_2\), 10:1 hexanes:EtOAc) provided amine 27 as a brown oil (5.2 g, 41%, unoptimized yield).

\[ R_f = 0.41 \] (silica gel, 5:1 hexanes:EtOAc);

\[ ^1H \text{ NMR (400 MHz, MeOD-}d_4\text{)}: \delta 6.91 (d, J = 8.9 \text{ Hz, } 1 \text{ H}), 6.78 (d, J = 8.9 \text{ Hz, } 1 \text{ H}), 3.73 (s, 3 \text{ H}), 1.50 (q, J = 7.5 \text{ Hz, } 2 \text{ H}), 1.12 (s, 6 \text{ H}), 0.92 (t, J = 7.5 \text{ Hz, } 3 \text{ H}) \text{ ppm;} \]

\[ ^13C \text{ NMR (101 MHz, MeOD-}d_4\text{)}: \delta 156.8, 139.6, 125.6, 114.9, 56.3, 55.9, 35.0, 27.3, 9.0 \text{ ppm;} \]

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{12}\)H\(_{20}\)NO \([M+H]^+\) 194.1539; found 194.1540.

2-Methoxy-5-methyl-N-(2,3,3-trimethylbutan-2-yl)aniline (28).

On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO\(_2\), 80:1→50:1 hexanes:Et\(_2\)O) furnished amine 28 as a colorless oil (9.3 mg, 40%).

\[ R_f = 0.50 \] (silica gel, 10:1 hexanes:Et\(_2\)O);
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.80 (d, $J = 2.4$ Hz, 1 H), 6.74 (d, $J = 8.4$ Hz, 1 H), 6.57 (dd, $J = 7.8$, 1.8 Hz, 1 H), 3.80 (s, 3 H), 2.22 (s, 3 H), 1.20 (s, 6 H), 1.06 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 149.8, 137.4, 130.9, 121.0, 120.8, 111.3, 60.5, 56.3, 39.3, 26.0, 23.2, 21.2 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{15}$H$_{26}$NO [M+H]$^+$ 236.2009, found 236.2018.

2-Methoxy-5-methyl-$N$-(2-methylpentan-2-yl)aniline (29). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 100:1 hexanes:EtOAc, with addition of ca. 2% NEt$_3$) furnished amine 29 as a colorless oil (14.3 mg, 65%).

$R_f$ = 0.81 (silica gel, 20:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.73 – 6.65 (m, 2 H), 6.40 (d, $J = 8.1$ Hz, 1 H), 4.19 (s, 1 H), 3.79 (s, 3 H), 2.22 (s, 3 H), 1.69 – 1.66 (m, 2 H), 1.37 – 1.33 (m, 2 H), 1.31 (s, 6 H), 0.90 (t, $J = 7.2$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 146.9, 137.7, 130.5, 117.4, 115.3, 110.7, 56.2, 53.8, 44.7, 28.7, 21.5, 18.1, 15.0 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{14}$H$_{24}$NO [M+H]$^+$ 222.1852; found 222.1852.

2-Methoxy-5-methyl-$N$-(1-methylcyclopentyl)aniline (30). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 70:1→60:1 hexanes:Et$_2$O) furnished amine 30 as a colorless oil (11.0 mg, 50%).

$R_f$ = 0.34 (silica gel, 10:1 hexanes:Et$_2$O);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.70 (d, $J = 7.8$ Hz, 1 H), 6.66 (d, $J = 2.4$ Hz, 1 H), 6.47 (dd, $J = 8.4$, 1.2 Hz, 1 H), 3.78 (s, 3 H), 2.22 (s, 3 H), 1.94 – 1.91 (m, 2 H), 1.78 – 1.61 (m, 6 H), 1.35 (s, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 148.0, 137.1, 130.9, 119.0, 116.9, 111.0, 62.8, 56.1, 41.4, 26.5, 25.2, 21.3 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{14}$H$_{22}$NO [M+H]$^+$ 220.1696, found 220.1698.
$N$-(1-(Benzyloxy)-2-methylpropan-2-yl)-2,3-dihydro-$1H$-inden-4-amine (31). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 50:1 hexanes:EtOAc, with addition of ca. 2% NEt$_3$) furnished amine 31 as a colorless oil (16.5 mg, 56%).

$R_f$ = 0.70 (silica gel, 20:1 hexanes:EtOAc);

$^{1}H$ NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.39 – 7.17 (m, 5 H), 6.96 (t, $J$ = 7.7 Hz, 1 H), 6.75 (d, $J$ = 8.0 Hz, 1 H), 6.71 (d, $J$ = 7.4 Hz, 1 H), 4.51 (s, 2 H), 3.40 (s, 2 H), 2.87 (t, $J$ = 7.5 Hz, 2 H), 2.69 (t, $J$ = 7.3 Hz, 2 H), 2.02 (quintet, $J$ = 7.5 Hz, 2 H), 1.29 (s, 6 H) ppm;

$^{13}C$ NMR (151 MHz, MeOH-$d_4$): $\delta$ 146.0, 143.7, 139.7, 134.2, 129.4, 128.7, 128.6, 127.9, 117.1, 116.7, 78.4, 74.3, 56.2, 34.4, 30.8, 25.7, 25.6 ppm;


$N$-(1-(Benzyloxy)-2-methylpropan-2-yl)-9$H$-fluoren-2-amine (32). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 25:1 → 15:1 hexanes:EtOAc) furnished amine 32 as a colorless oil (17.4 mg, 51%).

$R_f$ = 0.62 (silica gel, 5:1 hexanes:EtOAc);

$^{1}H$ NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.66 (d, $J$ = 7.8 Hz, 1 H), 7.59 (d, $J$ = 8.4 Hz, 1 H), 7.47 (d, $J$ = 7.2 Hz, 1 H), 7.35 – 7.26 (m, 6 H), 7.19 (ddd, $J$ = 7.8, 7.2, 1.2 Hz, 1 H), 7.09 (d, $J$ = 1.8 Hz, 1 H), 6.92 (dd, $J$ = 7.8, 1.8 Hz, 1 H), 4.53 (s, 2 H), 3.78 (s, 2 H), 3.36 (s, 2 H), 1.29 (s, 6 H) ppm;

$^{13}C$ NMR (151 MHz, MeOH-$d_4$): $\delta$ 146.3, 145.5, 144.0, 143.2, 139.7, 136.4, 129.4, 128.9, 128.6, 127.7, 126.6, 125.8, 121.5, 120.9, 119.8, 119.0, 77.5, 74.3, 56.4, 37.6, 25.8 ppm;


$N$-(1-(benzyloxy)-2-methylpropan-2-yl)-4-(trifluoromethyl)aniline (33). On 0.1 mmol scale, general procedure A was followed and purification by flash column
chromatography (SiO₂, 10:1→4:1 hexanes:EtOAc) furnished amine 33 as a colorless oil (17.8 mg, 55%).

\( R_f = 0.61 \) (silica gel, 4:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): \( \delta \) 7.32 – 7.26 (m, 7 H), 6.81 (d, \( J = 8.4 \) Hz, 2 H), 4.53 (s, 2 H), 3.48 (s, 2 H), 1.36 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): \( \delta \) 151.7, 139.7, 129.3, 128.8, 128.6, 126.6 (q, \( J = 4.5 \) Hz), 126.6 (q, \( J = 268.9 \) Hz), 119.4 (q, \( J = 33.2 \) Hz), 116.4, 77.3, 74.3, 55.1, 25.5 ppm;

\(^{19}\)F NMR (376 MHz, MeOH-\(d_4\)): \( \delta \) –62.8 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{18}\)H\(_{21}\)F\(_3\)NO \([\text{M+H}]^+\) 324.1570, found 324.1576.

\( N-\left(2-\left(\text{1-(Benzyloxy)-2-methylpropan-2-yl)amino}\right)-4\text{-methoxyphenyl}\right)\text{acetamide (34).} \) On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO₂, 2:1→1:2 hexanes:EtOAc) furnished amine 34 as a colorless oil (15.5 mg, 45%).

\( R_f = 0.22 \) (silica gel, 1:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): \( \delta \) 7.41 – 7.24 (m, 5 H), 7.05 (d, \( J = 8.7 \) Hz, 1 H), 6.60 (d, \( J = 2.8 \) Hz, 1 H), 6.43 (dd, \( J = 8.6, 2.8 \) Hz, 1 H), 4.56 (s, 2 H), 3.73 (s, 3 H), 3.39 (s, 2 H), 1.90 (s, 3 H), 1.27 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): \( \delta \) 172.9, 160.1, 143.7, 139.6, 129.5, 128.9, 128.8 (2C), 122.2, 107.3, 106.2, 79.0, 74.5, 56.1, 55.7, 25.2, 22.8 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{20}\)H\(_{27}\)N\(_2\)O\(_3\) \([\text{M+H}]^+\) 343.2016; found 343.2017.

\( N-\left(3\text{-methoxy-5-}\left(\text{2-methylpentan-2-yl)amino}\right)\text{phenyl}\right)\text{acetamide (35).} \) On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO₂, 6:1→1:1 hexanes:EtOAc) furnished amine 35 as a white solid (13.2 mg, 50%).

\( \text{Melting Point: } 90.2 – 91.5 \degree \text{C}; \)

\( R_f = 0.47 \) (silica gel, 1:1 hexanes:EtOAc);
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.96 (d, $J = 9.0$ Hz, 1 H), 6.51 (d, $J = 3.0$ Hz, 1 H), 6.31 (dd, $J = 9.0$, 3.0 Hz, 1 H), 3.75 (s, 3 H), 1.64 – 1.62 (m, 2 H), 1.39 – 1.35 (m, 2 H), 1.27 (s, 6 H), 0.92 (t, $J = 7.2$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 173.0, 160.4, 144.4, 129.0, 120.0, 104.3, 103.6, 55.7, 54.9, 45.4, 28.4, 22.8, 18.3, 15.0 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{15}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 265.1911, found 265.1916.

$N$-(4-(tert-Butylamino)phenyl)acetamide (36). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 20:1→10:1 hexanes:EtOAc) furnished amine 36 as a colorless oil (12.0 mg, 58%).

$R_f$ = 0.30 (silica gel, 10:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.33 (d, $J = 8.8$ Hz, 2 H), 6.89 (d, $J = 8.8$ Hz, 2 H), 2.09 (s, 3 H), 1.24 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 171.3, 144.0, 133.4, 122.8, 122.2, 55.3, 30.0, 23.6 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{12}$H$_{19}$N$_2$O [M+H]$^+$ 207.1492; found 207.1493.

$N$-(4-(2,4,4-Trimethylpentan-2-yl)amino)phenyl)acetamide (37). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 3:1→1:1 hexanes:EtOAc) furnished amine 37 as a colorless oil (13.1 mg, 50%).

$R_f$ = 0.30 (silica gel, 1:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.27 – 7.22 (m, 2 H), 6.77 – 6.70 (m, 2 H), 2.07 (s, 3 H), 1.68 (s, 2 H), 1.34 (s, 6 H), 1.00 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 169.4, 143.2, 128.9, 120.8, 117.6, 54.5, 51.8, 30.6, 30.2, 28.8, 21.6 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{16}$H$_{27}$N$_2$O [M+H]$^+$ 263.2118; found 263.2117.

$N$-(3-Methyl-4-(2,4,4-trimethylpentan-2-yl)amino)phenyl)acetamide (38). On 0.1 mmol scale, general procedure A was followed and purification by flash column
chromatography (SiO₂, 2:1→1:1 hexanes:EtOAc) furnished amine 38 as a colorless oil (12.1 mg, 44%).

\[ R_f = 0.33 \] (silica gel, 1:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): \( \delta \) 7.17 (d, \( J = 2.4 \text{ Hz}, 1 \text{ H} \)), 7.15 (dd, \( J = 8.6, 2.4 \text{ Hz}, 1 \text{ H} \)), 6.82 (d, \( J = 8.6 \text{ Hz}, 1 \text{ H} \)), 2.10 (s, 3 H), 2.07 (s, 3 H), 1.76 (s, 2 H), 1.40 (s, 6 H), 1.02 (s, 9 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): \( \delta \) 171.2, 143.1, 129.6, 125.7, 124.5, 120.3, 116.2, 56.5, 53.8, 32.6, 32.0, 31.0, 23.5, 18.6 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{17}\)H\(_{29}\)N\(_2\)O \([\text{M+H}]^+\) 277.2274; found 277.2277.

N-(4-((1-Methylcyclohexyl)amino)phenyl)acetamide (39). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO\(_2\), 3:1→2:1 hexanes:EtOAc) furnished amine 39 as a colorless oil (16.3 mg, 66%). On decagram scale (55.6 mmol \( N \)-(4-nitrophenyl)acetamide) conducted at Kemxtree, general procedure D was followed and purification by flash column chromatography provided amine 26 (6.5 g, 48%, unoptimized yield).

\[ R_f = 0.34 \] (silica gel, 2:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): \( \delta \) 7.28 (d, \( J = 8.8 \text{ Hz}, 2 \text{ H} \)), 6.83 (d, \( J = 8.8 \text{ Hz}, 2 \text{ H} \)), 2.08 (s, 3 H), 1.76 – 1.72 (m, 2 H), 1.64 – 1.61 (m, 2 H), 1.50 – 1.45 (m, 6 H), 1.22 (s, 3 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): \( \delta \) 171.3, 144.2, 132.1, 122.4, 122.3, 55.0, 39.1, 27.0, 26.6, 23.5, 23.3 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{15}\)H\(_{23}\)N\(_2\)O \([\text{M+H}]^+\) 247.1805; found 247.1807.

N-(3-Methoxy-5-((1-methylcyclohexyl)amino)phenyl)acetamide (40). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO\(_2\), 6:1→1:1 hexanes:EtOAc) furnished amine 40 as a white solid (17.8 mg, 65%).

\[ R_f = 0.44 \] (silica gel, 1:1 hexanes: EtOAc);

Melting Point: 83.6 – 85.3 °C;
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.94 (d, $J = 9.0$ Hz, 1 H), 6.48 (d, $J = 3.0$ Hz, 1 H), 6.27 (dd, $J = 8.4$, 2.4 Hz, 1 H), 3.74 (s, 3 H), 2.13 (s, 3 H), 1.92 – 1.88 (m, 2 H), 1.54 – 1.47 (m, 8 H), 1.32 (s, 3 H) ppm;

$^{13}$C NMR (101 MHz, MeOH-$d_4$): $\delta$ 173.1, 160.5, 144.3, 129.3, 119.6, 103.9, 103.1, 55.7, 54.2, 39.0, 27.5, 26.9, 23.1, 22.7 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{16}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 277.1911, found 277.1914.

1-Cyclopropyl-2-(2-methoxy-4-((2-methyl-1-phenylpropan-2-yl)amino)phenoxy)ethan-1-one (41). On 0.05 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 5:1 $\rightarrow$ 3:1 hexanes:EtOAc) furnished amine 41 as a colorless oil (10.8 mg, 61%).

$R_f = 0.08$ (silica gel, 5:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 7.26 – 7.22 (m, 2 H), 7.21 – 7.15 (m, 3 H), 6.77 (d, $J = 8.6$ Hz, 1 H), 6.51 (d, $J = 2.6$ Hz, 1 H), 6.39 (dd, $J = 8.6$, 2.6 Hz, 1 H), 4.62 (s, 2 H), 3.78 (s, 3 H), 2.45 – 2.41 (m, 1 H), 1.25 (s, 6 H), 0.98 – 0.90 (m, 4 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 207.9, 151.6, 144.2, 141.3, 139.6, 131.5, 128.5, 126.8, 118.0, 109.2, 104.5, 76.4, 56.0, 54.8, 47.0, 28.7, 17.2, 11.1 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{22}$H$_{28}$NO$_3$ [M+H]$^+$ 354.2064; found 354.2066.

1-Cyclopropyl-2-(2-methoxy-4-((1-methylcyclopentyl)amino)phenoxy)ethanone (42). On 0.05 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 10:1 $\rightarrow$ 2:1 hexanes:EtOAc) furnished amine 42 as a colorless oil (7.3 mg, 48%).

$R_f = 0.42$ (silica gel, 2:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.73 (d, $J = 8.4$ Hz, 1 H), 6.39 (d, $J = 3.0$ Hz, 1 H), 6.19 (dd, $J = 8.4$, 3.0 Hz, 1 H), 4.57 (s, 2 H), 3.76 (s, 3 H), 2.44 – 2.40 (m, 1 H), 1.96 – 1.94 (m, 2 H), 1.76 – 1.63 (m, 6 H), 1.36 (s, 3 H), 0.93 – 0.92 (m, 4 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 208.2, 152.0, 144.8, 140.5, 118.6, 107.2, 102.5, 76.8, 62.2, 56.1, 41.3, 26.5, 25.1, 17.3, 11.2 ppm;
Benzyl 4-((4-(2-cyclopropyl-2-oxoethoxy)-3-methoxyphenyl) amino)-4-methylpiperidine-1-carboxylate (43). On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO2, 8:1→1:1 hexanes:EtOAc) furnished amine 43 as a colorless oil (21.5 mg, 47%).

\[ R_f = 0.47 \] (silica gel, 4:2:0.2 hexanes:EtOAc:MeOH);

\[ {^1}H \text{ NMR (400 MHz, MeOH-}d_4\text{)}: \delta 7.38 – 7.31 (m, 5 H), 6.76 (d, } J = 8.4 \text{ Hz, 1 H), 6.56 (d, } J = 2.4 \text{ Hz, 1 H), 6.40 (dd, } J = 8.4, 2.4 \text{ Hz, 1 H), 5.13 (s, 2 H), 4.73 (s, 2 H), 3.82 (s, 3 H), 3.58 (br s, 4 H), 2.37 – 2.30 (m, 1 H), 1.90 – 1.84 (m, 2 H), 1.60 – 1.54 (m, 2 H), 1.26 (s, 3 H), 1.05 – 0.99 (m, 4 H) ppm]

\[ {^{13}}C \text{ NMR (151 MHz, MeOH-}d_4\text{)}: \delta 210.1, 157.0, 151.7, 143.1, 143.0, 138.2, 129.5, 129.1, 128.8, 117.8, 113.0, 107.4, 76.6, 68.2, 56.3, 53.3, 41.4, 38.3, 26.0, 17.8, 11.9 \text{ ppm;}

HRMS (ESI-TOF, m/z): calcd for C_{26}H_{33}N_2O_5 [M+H]^+ 453.2384, found 453.2382.

1-(4-((1-Methylcyclopentyl)amino)phenyl)propan-2-one (44). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 20:1→5:1 hexanes:EtOAc) furnished amine 44 as a colorless oil (12.0 mg, 52%).

\[ R_f = 0.31\text{ (silica gel, 5:1 hexanes:EtOAc)};\]

\[ {^1}H \text{ NMR (600 MHz, MeOH-}d_4\text{): } \delta 6.95 (d, } J = 8.4 \text{ Hz, 2 H), 6.71 (d, } J = 8.4 \text{ Hz, 2 H), 3.58 (s, 2 H), 2.11 (s, 3 H), 1.96 – 1.93 (m, 2 H), 1.78 – 1.66 (m, 6 H), 1.35 (s, 3 H) ppm;\]

\[ {^{13}}C \text{ NMR (151 MHz, MeOH-}d_4\text{): } \delta 210.6, 147.6, 130.9, 124.4, 117.7, 62.7, 50.8, 41.3, 28.9, 26.3, 25.2 \text{ ppm;}

HRMS (ESI-TOF, m/z): calcd for C_{16}H_{22}NO [M+H]^+ 232.1696, found 232.1704.

1-(4-((1-Methylcyclohexyl)amino)phenyl)propan-2-one (45). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 20:1→5:1 hexanes:EtOAc) furnished amine 45 as a colorless oil (15.0 mg, 61%).
Rf = 0.30 (silica gel, 5:1 hexanes:EtOAc);

1H NMR (600 MHz, MeOH-d4): δ 6.98 (d, J = 8.4 Hz, 2 H), 6.81 (d, J = 8.4 Hz, 2 H), 3.60 (s, 2 H), 2.12 (s, 3 H), 1.81 – 1.77 (m, 2 H), 1.64 – 1.60 (m, 2 H), 1.52 – 1.40 (m, 6 H), 1.25 (s, 3 H) ppm;

13C NMR (151 MHz, MeOH-d4) δ 210.3, 146.8, 130.7, 126.1, 120.4, 54.6, 50.7, 39.1, 29.0, 27.0, 26.8, 23.3 ppm;

HRMS (ESI-TOF, m/z): calcd for C16H24NO [M+H]+ 246.1852, found 246.1859.

1-(4-((tert-Pentylamino)phenyl)propan-2-one (46). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 10:1→5:1 hexanes:EtOAc) furnished amine 46 as a colorless oil (8.8 mg, 40%).

Rf = 0.62 (silica gel, 3:1 hexanes:EtOAc);

1H NMR (600 MHz, MeOH-d4): δ 6.98 (d, J = 8.4 Hz, 2 H), 6.81 (d, J = 8.5 Hz, 2 H), 3.60 (s, 2 H), 2.12 (s, 3 H), 1.64 (q, J = 7.5 Hz, 2 H), 1.24 (s, 6 H), 0.90 (t, J = 7.5 Hz, 3 H) ppm;

13C NMR (151 MHz, MeOH-d4): δ 210.3, 147.1, 130.8, 126.0, 120.0, 55.2, 50.7, 34.7, 29.0, 27.9, 8.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C14H22NO [M+H]+ 220.1696; found 220.1697.

1-(4-((1-(Benzyloxy)-2-methylpropan-2-yl)amino)phenyl)propan-2-one (47). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 20:1→5:1 hexanes:EtOAc) furnished amine 47 as a colorless oil (19.8 mg, 64%).

Rf = 0.45 (silica gel, 3:1 hexanes:EtOAc);

1H NMR (600 MHz, MeOH-d4): δ 7.33 – 7.32 (m, 4 H), 7.29 – 7.26 (m, 1 H), 7.01 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 2 H), 4.51 (s, 2 H), 3.63 (s, 2 H), 3.33 (s, 2 H), 2.12 (s, 3 H), 1.21 (s, 6 H) ppm;

13C NMR (151 MHz, MeOH-d4): δ 210.0, 146.1, 139.7, 130.8, 129.4, 128.9, 128.6, 128.1, 122.4, 77.6, 74.3, 56.1, 50.7, 29.1, 25.6 ppm;
HRMS (ESI-TOF, m/z): calcd for C$_{20}$H$_{26}$NO$_2$ [M+H]$^+$ 312.1958, found 312.1967.

1-(4-(Octan-2-ylamino)phenyl)propan-2-one (48). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 30:1→10:1 hexanes:EtOAc:MeOH) furnished amine 48 as a colorless oil (11.8 mg, 45%).

$R_f$ = 0.51 (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-d$_6$): $\delta$ 6.96 (d, $J = 8.4$ Hz, 2 H), 6.58 (d, $J = 8.4$ Hz, 2 H), 4.57 (s, 1 H), 3.53 (s, 2 H), 3.48 – 3.45 (m, 1 H), 2.06 (s, 3H), 1.62 – 1.57 (m, 1 H), 1.46 – 1.40 (m, 2 H), 1.34 – 1.28 (m, 7 H), 1.16 (d, $J = 6.0$ Hz, 3 H), 0.89 (t, $J = 6.0$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-d$_6$): $\delta$ 206.7, 148.4, 131.0, 122.9, 113.8, 50.5, 49.0, 37.9, 32.8, 28.9, 27.1, 23.4, 21.1, 21.0, 14.5 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{17}$H$_{28}$NO [M+H]$^+$ 262.2165, found 262.2173.

1-(4-(Cyclopentylamino)phenyl)propan-2-one (49). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 30:1→10:1 hexanes:EtOAc) furnished amine 49 as a colorless oil (10.7 mg, 50%).

$R_f$ = 0.46 (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (400 MHz, MeOH-d$_4$): $\delta$ 6.95 (d, $J = 8.4$ Hz, 2 H), 6.62 (d, $J = 8.4$ Hz, 2 H), 3.75 (quintet, $J = 6.2$ Hz, 1 H), 3.56 (s, 2 H), 2.08 (s, 3 H), 2.03 – 1.98 (m, 2 H), 1.77 – 1.74 (m, 2 H), 1.65 – 1.61 (m, 2 H), 1.52 – 1.47 (m, 2 H) ppm.

$^{13}$C NMR (151 MHz, MeOH-d$_4$): $\delta$ 210.7, 149.1, 131.0, 123.6, 115.0, 55.9, 50.8, 34.0, 28.8, 25.0 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{14}$H$_{20}$NO [M+H]$^+$ 218.1539, found 218.1540.

Ethyl 4-(2-aminoethyl)-N-(1-methylcyclohexyl)aniline (50). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography
(SiO₂, 30:15:1:1 hexanes:DCM:MeOH:NEt₃) furnished amine 50 as a colorless oil (8.9 mg, 38%).

\[ R_f = 0.20 \] (silica gel, 3:1:0.5:1 hexanes:EtOAc:MeOH:NEt₃);

\[ ^1H \text{ NMR (600 MHz, MeOH-}d_4\text{): } \delta \text{ 7.03 (d, } J = 8.4 \text{ Hz, 2 H), 6.85 (d, } J = 8.4 \text{ Hz, 2 H), 2.95 (t, } J = 7.2 \text{ Hz, 2 H), 2.74 (t, } J = 7.2 \text{ Hz, 2 H), 1.80 – 1.77 (m, 2 H), 1.66 – 1.62 (m, 2 H), 1.53 – 1.47 (m, 6 H), 1.25 (s, 3 H) ppm} \]

\[ ^13C \text{ NMR (151 MHz, MeOH-}d_4\text{): } \delta \text{ 144.4, 128.4, 128.1, 119.1, 52.9, 41.6, 37.3, 35.3, 28.9, 25.1, 21.4 ppm;} \]


2-((2-Hydroxyethyl)amino)-5-((2,3,3-trimethylbutan-2-yl)amino)benzonitrile (51). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 65:15:1→55:20:1 hexanes:EtOAc:MeOH) furnished amine 51 as a light yellow oil (15.9 mg, 58%).

\[ R_f = 0.36 \] (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

\[ ^1H \text{ NMR (600 MHz, acetone-}d_6\text{): } \delta \text{ 7.12 (dd, } J = 9.0, 3.0 \text{ Hz, 1 H), 7.03 (d, } J = 2.4 \text{ Hz, 1 H), 6.74 (d, } J = 8.4 \text{ Hz, 1 H), 4.97 (s, 1 H), 4.03 (s, 1 H), 3.80 (t, } J = 6.0 \text{ Hz, 2 H), 3.35 – 3.33 (m, 2 H), 1.09 (s, 6 H), 1.04 (s, 9 H) ppm.} \]

\[ ^13C \text{ NMR (151 MHz, MeOH-}d_4\text{): } \delta \text{ 147.9, 137.7, 133.1, 128.7, 118.9, 112.9, 96.5, 61.3, 60.8, 46.7, 38.6, 26.1, 23.2 ppm;} \]

HRMS (ESI-TOF, m/z): calcd for C₁₆H₂₆NO₃ [M+H]⁺ 276.2070, found 276.2078.

2-((2-Hydroxyethyl)amino)-5-((2-methyl-1-phenylpropan-2-yl)amino)benzonitrile (52). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 60:15:1→50:20:1 hexanes:EtOAc:MeOH) furnished amine 52 as a light yellow oil (24.3 mg, 79%).

\[ R_f = 0.26 \] (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

\[ ^1H \text{ NMR (600 MHz, MeOH-}d_4\text{): } \delta \text{ 7.27 – 7.24 (m, 2 H), 7.21 – 7.20 (m, 1 H), 7.17 – 7.15 (m, 2 H), 7.13 (dd, } J = 9.0, 3.0 \text{ Hz, 1 H), 7.02 (d, } J = 2.4 \text{ Hz, 1 H), 6.77 (d, } J = 9.0} \]
Hz, 1 H), 3.75 (t, J = 5.4 Hz, 2 H), 3.33 (t, J = 5.4 Hz, 2 H), 2.81 (s, 2 H), 1.12 (s, 6 H) ppm.

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 145.9, 139.7, 138.5, 131.6, 128.7, 127.0, 123.3, 118.7, 113.5, 113.4, 96.9, 61.1, 55.4, 48.1, 46.9, 28.3 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{19}$H$_{24}$N$_3$O [M+H]$^+$ 310.1914, found 310.1915.

2-((2-Hydroxyethyl)amino)-5-(octan-2-ylamino)benzonitrile (53). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 60:15:1 $\rightarrow$ 50:20:1 hexanes:EtOAc:MeOH) furnished amine 53 as a yellow oil (17.9 mg, 62%).

$R_f$ = 0.31 (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.87 (dd, J = 9.0, 3.0 Hz, 1 H), 6.71 (d, J = 9.0 Hz, 1 H), 6.68 (d, J = 3.0 Hz, 1 H), 4.65 (s, 1 H), 4.28 (s, 1 H), 3.96 (s, 1 H), 3.77 – 3.75 (m, 2 H), 3.38 – 3.36 (m, 1 H), 3.29 – 3.26 (m, 2 H), 1.55 – 1.25 (m, 10 H), 0.87 (t, J = 6.6 Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 144.7, 141.0, 123.5, 119.1, 117.7, 114.6, 97.6, 61.2, 50.7, 47.1, 37.6, 32.9, 30.4, 27.0, 23.5, 20.4, 14.3 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{17}$H$_{28}$N$_3$O [M+H]$^+$ 290.2227, found 290.2231.

5-((10-Hydroxydecan-2-yl)amino)-2-((2-hydroxyethyl)amino)benzonitrile (54). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 60:15:1 $\rightarrow$ 50:20:1 hexanes:EtOAc:MeOH) furnished amine 54 as a yellow oil (17.8 mg, 53%).

$R_f$ = 0.43 (silica gel, 3:2:0.5 hexanes:EtOAc:MeOH);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 6.89 (dd, J = 9.0, 3.0 Hz, 1 H), 6.73 (d, J = 9.0 Hz, 1 H), 6.71 (d, J = 3.0 Hz, 1 H), 3.73 (t, J = 5.4 Hz, 2 H), 3.53 (t, J = 5.4 Hz, 2 H), 3.31 – 3.29 (m, 1 H), 3.27 (t, J = 5.4 Hz, 2 H), 1.54 – 1.40 (m, 3 H), 1.39 – 1.33 (m, 11 H), 1.12 (d, J = 6.6 Hz, 3 H) ppm;
13C NMR (151 MHz, MeOH-d4): δ 144.8, 141.2, 123.7, 119.3, 117.8, 114.7, 97.8, 63.0, 61.4, 50.8, 47.2, 37.7, 33.7, 30.8, 30.7, 30.5, 27.1, 26.9, 20.6 ppm;

5-(Cyclopentylamino)-2-((2-hydroxyethyl)amino)benzonitrile (55). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 60:15:1→50:30:1 hexanes:EtOAc:MeOH) furnished amine 55 as a light yellow oil (15.3 mg, 62%).

Rf = 0.19 (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

1H NMR (400 MHz, acetone-d6): δ 6.95 (dd, J = 8.8, 2.8 Hz, 1 H), 6.72 (d, J = 9.2 Hz, 1 H), 6.67 (d, J = 2.8, 1 H), 3.76 (t, J = 5.6 Hz, 2 H), 3.73 – 3.70 (m, 1 H), 3.27 (dt, J = 5.6, 5.6 Hz, 2 H), 1.99 – 1.92 (m, 2 H), 1.72 – 1.65 (m, 2 H), 1.63 – 1.56 (m, 2 H), 1.49 – 1.44 (m, 2 H) ppm;
13C NMR (151 MHz, acetone-d6): δ 144.2, 141.6, 122.5, 119.2, 115.7, 114.4, 97.6, 61.3, 56.0, 47.3, 34.0, 24.9 ppm;

5-(Cyclohexylamino)-2-((2-hydroxyethyl)amino)benzonitrile (56). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 60:15:1→50:20:1 hexanes:EtOAc:MeOH) furnished amine 56 as a yellow oil (10.5 mg, 41%).

Rf = 0.32 (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

1H NMR (600 MHz, acetone-d6): δ 6.88 (dd, J = 9.0, 3.0 Hz, 1 H), 6.72 – 6.70 (m, 2 H), 4.65 (s, 1 H), 4.35 (s, 1 H), 3.76 (t, J = 5.4 Hz, 2 H), 3.27 (dt, J = 5.4, 5.4 Hz, 2 H), 3.19 – 3.16 (m, 1 H), 2.00 – 1.98 (m, 2 H), 1.75 – 1.72 (m, 2 H), 1.64 – 1.60 (m, 1 H), 1.42 – 1.34 (m, 2 H), 1.29 – 1.11 (m, 3 H) ppm;
13C NMR (151 MHz, acetone-d6): δ 143.9, 141.6, 122.3, 118.9, 115.7, 114.2, 97.4, 61.0, 52.8, 47.1, 33.9, 26.8, 25.7 ppm;
3-((9H-Fluoren-2-yl)amino)-3-methylbutan-1-ol (57). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 7:1→1:1 hexanes:EtOAc) furnished amine 57 as a colorless oil (14.8 mg, 55%).

\[ R_f = 0.43 \] (silica gel, 1:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): δ 7.63 (d, \(J = 7.2\) Hz, 1 H), 7.57 (d, \(J = 8.4\) Hz, 1 H), 7.45 (d, \(J = 7.8\) Hz, 1 H), 7.27 (t, \(J = 7.8\) Hz, 1 H), 7.16 (t, \(J = 7.2\) Hz, 1 H), 7.08 (s, 1 H), 6.88 (dd, \(J = 7.8, 1.8\) Hz, 1 H), 3.79 (s, 2 H), 3.75 (t, \(J = 7.2\) Hz, 2 H), 1.93 (t, \(J = 7.2\) Hz, 2 H), 1.33 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): δ 147.2, 145.7, 143.8, 143.4, 135.0, 127.7, 126.2, 125.7, 121.0, 119.6, 119.5, 116.8, 59.9, 54.8, 44.3, 37.6, 28.8 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{18}\)H\(_{22}\)NO \([M+H]^+\) 268.1696, found 268.1695.

3-((2,3-Dihydro-1H-inden-5-yl)amino)-3-methylbutan-1-ol (58). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 10:1→4:1 hexanes:EtOAc) furnished amine 58 as a colorless oil (15.1 mg, 69%).

\[ R_f = 0.43 \] (silica gel, 2:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): δ 6.95 (t, \(J = 7.8\) Hz, 1 H), 6.73 (d, \(J = 7.8\) Hz, 1 H), 6.64 (d, \(J = 7.2\) Hz, 1 H), 3.74 (t, \(J = 7.2\) Hz, 2 H), 3.33 (t, \(J = 5.4\) Hz, 2 H), 2.87 (t, \(J = 7.2\) Hz, 2 H), 2.71 (t, \(J = 7.2\) Hz, 2 H), 2.05 (quintet, \(J = 7.2\) Hz, 2 H), 1.92 (t, \(J = 7.2\) Hz, 2 H), 1.34 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)): δ 145.8, 144.0, 132.9, 127.9, 115.9, 114.8, 59.8, 54.8, 44.8, 34.4, 31.0, 28.6, 25.7 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{14}\)H\(_{22}\)NO \([M+H]^+\) 220.1696, found 220.1695.

3-Methyl-3-((4-(methylthio)phenyl)amino)butan-1-ol (59). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 5:1→3:1 hexanes:EtOAc) furnished amine 59 as a colorless oil (13.4 mg, 60%).

\[ R_f = 0.43 \] (silica gel, 2:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)): δ 6.95 (t, \(J = 7.8\) Hz, 1 H), 6.73 (d, \(J = 7.8\) Hz, 1 H), 6.64 (d, \(J = 7.2\) Hz, 1 H), 3.74 (t, \(J = 7.2\) Hz, 2 H), 3.33 (t, \(J = 5.4\) Hz, 2 H), 2.87 (t, \(J = 7.2\) Hz, 2 H), 2.71 (t, \(J = 7.2\) Hz, 2 H), 2.05 (quintet, \(J = 7.2\) Hz, 2 H), 1.92 (t, \(J = 7.2\) Hz, 2 H), 1.34 (s, 6 H) ppm.

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)) δ 145.8, 144.0, 132.9, 127.9, 115.9, 114.8, 59.8, 54.8, 44.8, 34.4, 31.0, 28.6, 25.7 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{14}\)H\(_{22}\)NO \([M+H]^+\) 220.1696, found 220.1695.
$R_f = 0.17$ (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 7.12 (d, $J = 8.7$ Hz, 2 H), 6.75 (d, $J = 8.6$ Hz, 2 H), 3.72 (t, $J = 6.8$ Hz, 2 H), 2.36 (s, 3 H), 1.89 (t, $J = 6.8$ Hz, 2 H), 1.32 (s, 6 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 147.3, 131.5, 125.1, 118.0, 59.4, 53.9, 44.6, 28.7, 18.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{12}$H$_{20}$NOS [M+H]$^+$ 226.1260; found 226.1255.

2-Methyl-2-((4-(trifluoromethyl)phenyl)amino)propan-1-ol (60). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 1:1→1:2 hexanes:EtOAc) furnished amine 60 as a colorless oil (14.8 mg, 60%).

$R_f = 0.35$ (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.33 (d, $J = 9.0$ Hz, 2 H), 6.81 (d, $J = 8.4$ Hz, 2 H), 3.69 (t, $J = 7.2$ Hz, 2 H), 2.01 (t, $J = 7.2$ Hz, 2 H), 1.39 (s, 6 H) ppm.

$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 151.8, 127.0 (q, $J = 3.5$ Hz), 126.7 (q, $J = 253.7$ Hz), 118.6 (q, $J = 31.7$ Hz), 115.3, 59.5, 53.5, 43.7, 28.6 ppm;

$^{19}$F NMR (376 MHz, MeOH-$d_4$): $\delta$ –61.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{12}$H$_{17}$F$_3$NO [M+H]$^+$ 248.1257, found 248.1262.

2,4-Dimethyl-4-(m-tolylamino)pentan-2-ol (61). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 4:1→7:3 hexanes:EtOAc) furnished amine 61 as a colorless oil (12.4 mg, 57%).

$R_f = 0.60$ (silica gel, 7:3 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.99 – 6.96 (m, 1 H), 6.64 – 6.62 (m, 2 H), 6.51 – 6.50 (m, 1 H), 2.20 (s, 3 H), 1.86 (s, 2 H), 1.38 (s, 6 H), 1.30 (s, 6 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 147.9, 138.7, 129.3, 119.7, 116.0, 110.9, 71.6, 55.5, 53.2, 32.5, 30.1, 21.7 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{14}$H$_{24}$NO [M+H]$^+$ 222.1852, found 222.1850.

(R)-7-((4-Methoxyphenyl)amino)-3,7-dimethyloctan-1-ol (62)
Conducted at Bristol-Myers Squibb, Process Department). On 1.0 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 1:1 hexanes:EtOAc) furnished amine 62 as a light pink oil (201.6 mg, 72%).

\[ R_f = 0.20 \] (silica gel, 1:1 hexanes:EtOAc);
\[ \left[ \alpha \right]^{23}_D = -3.6^\circ \] (c 1.1, MeOH);

\[ ^1H \text{ NMR (500 MHz, } C_6D_6) : \delta 6.78 \text{ (d, } J = 8.4 \text{ Hz, 2 H}), 6.70 \text{ (d, } J = 8.5 \text{ Hz, 2 H}), 3.53 - 3.41 \text{ (m, 2 H)}, 3.38 \text{ (s, 3 H)}, 1.63 - 1.16 \text{ (m, 9 H)}, 1.10 \text{ (s, 6 H)}, 1.10 - 1.01 \text{ (m, 1 H)}, 0.84 \text{ (d, } J = 6.4 \text{ Hz, 3 H}) \text{ ppm;}\]

\[ ^{13} \text{C NMR (101 MHz, } C_6D_6) : \delta 154.9, 140.9, 122.5, 114.9, 61.2, 55.5, 54.6, 42.9, 40.6, 38.4, 30.1, 28.8, 22.2, 20.2 \text{ ppm;}\]

HRMS (ESI-TOF, m/z): calcd for C_{17}H_{30}NO_{2} [M+H]^+ 280.2271; found 280.2270.

(3-((1-Methylcyclopentyl)amino)phenyl)boronic acid (63). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 50:30:1 hexanes:DCM:MeOH) furnished amine 63 as a colorless oil (12.0 mg, 55%).

\[ R_f = 0.31 \] (silica gel, 4:1:1:0.1 hexanes:acetone:DCM:MeOH);

\[ ^1H \text{ NMR (600 MHz, acetone-}d_6) : \delta 7.20 \text{ (d, } J = 2.4 \text{ Hz, 1 H }), 7.09 \text{ (d, } J = 7.2 \text{ Hz, 1 H }), 7.05 \text{ (t, } J = 7.2 \text{ Hz, 1 H }), 6.91 \text{ (s, 1 H)}, 6.75 \text{ (dd, } J = 8.4, 1.2 \text{ Hz, 1 H}), 2.01 - 1.98 \text{ (m, 2 H)}, 1.76 - 1.73 \text{ (m, 2 H)}, 1.70 - 1.65 \text{ (m, 4 H)}, 1.39 \text{ (s, 3 H}) \text{ ppm;}\]

\[ ^{13} \text{C NMR (151 MHz, acetone-}d_6) : \delta 147.8, 128.8, 123.0, 121.8, 117.9, 61.9, 41.2, 26.3, 25.0 \text{ ppm. The boron-bound carbon was not observed due to quadrupolar relaxation;}\]

\[ ^{11} \text{B NMR (160 MHz, acetone-}d_6) : \delta 9.6 \text{ ppm;}\]

HRMS (ESI-TOF, m/z): calcd for C_{12}H_{19}BNO_{2} [M+H]^+ 220.1503, found 220.1507.

(3-((1-(Benzyloxy)-2-methylpropan-2-yl)amino)phenyl)boronic acid (64). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 50:30:1 hexanes:DCM:MeOH) furnished amine 64 as a colorless oil (13.4 mg, 45%).
\[ R_f = 0.31 \text{ (silica gel, 4:1:1:0.1 hexanes:acetone:DCM:MeOH)}; \]

\[^1\text{H} \text{ NMR (600 MHz, acetone-}d_6)\]: \( \delta \) 7.39 – 7.33 (m, 5 H), 7.31 – 7.28 (m, 1 H), 7.26 – 7.23 (m, 1 H), 7.12 – 7.09 (m, 1 H), 6.99 (s, 1 H), 6.90 – 6.88 (m, 1 H), 4.56 (s, 2 H), 3.46 (s, 2 H), 1.34 (s, 6 H) ppm;

\[^{13}\text{C} \text{ NMR (151 MHz, acetone-}d_6)\]: \( \delta \) 147.6, 139.9, 129.2, 128.8, 128.5, 128.3, 125.2, 124.8, 121.0, 78.3, 73.9, 55.0, 25.8 ppm. The boron-bound carbon was not observed due to quadrupolar relaxation;

\[^{11}\text{B} \text{ NMR (160 MHz, acetone-}d_6)\]: \( \delta \) 9.6 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{17}\)H\(_{23}\)BNO\(_3\) [M+H]\(^+\) 300.1766, found 300.1774.

\[
\text{(3-((2,3-Dimethylbutan-2-yl)amino)phenyl)boronic acid (65). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO}_2, 50:30:1 hexanes:DCM:MeOH) furnished amine 65 as a colorless oil (9.3 mg, 42%).} \]

\[ R_f = 0.35 \text{ (silica gel, 4:1:1:0.1 hexanes:acetone:DCM:MeOH)}; \]

\[^1\text{H} \text{ NMR (600 MHz, acetone-}d_6)\]: \( \delta \) 7.27 (d, \( J = 1.8 \text{ Hz}, 1 \text{ H} \)), 7.14 (d, \( J = 7.2 \text{ Hz}, 1 \text{ H} \)), 7.05 (t, \( J = 7.8 \text{ Hz}, 1 \text{ H} \)), 6.93 (s, 1 H), 6.83 (ddd, \( J = 7.8, 2.4, 1.2 \text{ Hz}, 1 \text{ H} \)), 2.23 (septet, \( J = 6.9 \text{ Hz}, 1 \text{ H} \)), 1.25 (s, 6 H), 0.92 (d, \( J = 7.2 \text{ Hz}, 6 \text{ H} \)) ppm;

\[^{13}\text{C} \text{ NMR (151 MHz, acetone-}d_6)\]: \( \delta \) 147.9, 128.8, 123.8, 123.3, 119.5, 57.0, 35.9, 25.4, 18.1 ppm. The boron-bound carbon was not observed due to quadrupolar relaxation.

\[^{11}\text{B} \text{ NMR (160 MHz, acetone-}d_6)\]: \( \delta \) 9.5 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{12}\)H\(_{21}\)BNO\(_2\) [M+H]\(^+\) 222.1660, found 222.1664.

\[
\text{4-\((\text{ tert-Butylamino})\text{phenyl trifluoromethanesulfonate (66). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO}_2, 20:1 \rightarrow 10:1 \text{ hexanes:acetone}) furnished amine 66 as a colorless oil (52.1 mg, 50%).} \]

\[ R_f = 0.48 \text{ (silica gel, 4:1 hexanes:acetone)}; \]

\[^1\text{H} \text{ NMR (600 MHz, MeOH-}d_4)\]: \( \delta \) 7.05 (d, \( J = 9.1 \text{ Hz}, 2 \text{ H} \)), 6.82 (d, \( J = 9.1 \text{ Hz}, 2 \text{ H} \)), 1.34 (s, 9 H) ppm;
$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 149.0, 142.4, 122.6, 120.2 (q, $J = 320.0$ Hz), 118.1, 52.1, 29.8 ppm;

$^{19}$F NMR (376 MHz, MeOH-$d_4$): $\delta$ –73.6 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{11}$H$_{15}$F$_3$NO$_3$S [M+H]$^+$ 298.0719; found 298.0723.

4-((2-Methylpentan-2-yl)amino)phenyl trifluoromethanesulfonate (67). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 30:1→10:1 hexanes:EtOAc) furnished amine 67 as a colorless oil (16.0 mg, 49%). $R_f = 0.61$ (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 7.11 (d, $J = 9.0$ Hz, 2 H), 6.84 (d, $J = 9.0$ Hz, 2 H), 5.03 (s, 1 H), 1.71 – 1.68 (m, 2 H), 1.39 – 1.34 (m, 2 H), 1.33 (s, 6 H), 0.88 (t, $J = 7.2$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 149.1, 141.1, 122.6, 119.8 (q, $J = 320.1$ Hz), 116.1, 54.1, 44.1, 28.3 (q, $J = 7.6$ Hz), 18.0, 14.9 ppm;

$^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –73.6 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{13}$H$_{19}$F$_3$NO$_3$S [M+H]$^+$ 326.1032, found 326.1033.

4-((1-Methylcyclohexyl)amino)phenyl trifluoromethanesulfonate (68). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 30:1 hexanes:EtOAc) furnished amine 68 as a colorless oil (18.7 mg, 61%). $R_f = 0.66$ (silica gel, 4:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 7.12 (d, $J = 9.0$ Hz, 2 H), 6.87 (d, $J = 9.0$ Hz, 2 H), 4.90 (s, 1 H), 1.97 – 1.95 (m, 2 H), 1.62 – 1.47 (m, 8 H), 1.35 (s, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 148.8, 141.1, 122.6, 119.8 (q, $J = 320.1$ Hz), 116.4, 53.7, 38.5, 26.8, 26.6, 22.8 ppm;

$^{19}$F NMR (376 MHz, acetone-$d_6$): $\delta$ –73.6 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{14}$H$_{19}$F$_3$NO$_3$S [M+H]$^+$ 338.1032, found 338.1037.
4-((1-(Benzyloxy)-2-methylpropan-2-yl)amino)phenyl trifluoromethanesulfonate (69). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 25:1→10:1 hexanes:EtOAc) furnished amine 69 as a colorless oil (24.6 mg, 61%).

\[ R_f = 0.52 \] (silica gel, 4:1 hexanes:EtOAc);

\[ ^{1}H \text{ NMR (600 MHz, acetone-}d_6\text{): } \delta 7.35 – 7.28 \text{ (m, 5 H), 7.12 (d, } J = 9.6 \text{ Hz, 2 H), 6.89 (d, } J = 9.0 \text{ Hz, 2 H), 5.05 (s, 1 H), 4.56 (s, 2 H), 3.52 (s, 2 H), 1.38 (s, 6 H) ppm; } \]

\[ ^{13}C \text{ NMR (151 MHz, acetone-}d_6\text{): } \delta 148.8, 141.7, 139.8, 129.2, 128.5, 128.4, 122.6, 119.8 \text{ (q, } J = 320.1 \text{ Hz), 117.2, 77.7, 73.8, 54.9, 25.4 \text{ ppm; } } \]

\[ ^{19}F \text{ NMR (376 MHz, acetone-}d_6\text{): } \delta –73.6 \text{ ppm; } \]

HRMS (ESI-TOF, \( m/z \)): calcd for C₁₈H₂₁F₃NO₄S \([M+H]⁺ 404.1138\), found 404.1141.

4-((4-Hydroxy-2,4-dimethylpentan-2-yl)amino)phenyl trifluoromethanesulfonate (70). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 10:1→5:1 hexanes:EtOAc) furnished amine 70 as a colorless oil (28.5 mg, 80%).

\[ R_f = 0.24 \] (silica gel, 3:1 hexanes:EtOAc);

\[ ^{1}H \text{ NMR (600 MHz, MeOH-}d_4\text{): } \delta 7.06 \text{ (d, } J = 9.0 \text{ Hz, 2 H), 6.80 (d, } J = 9.6 \text{ Hz, 2 H), 1.90 (s, 2 H), 1.42 (s, 6 H), 1.30 (s, 6 H) ppm; } \]

\[ ^{13}C \text{ NMR (151 MHz, MeOH-}d_4\text{): } \delta 148.9, 142.4, 122.7, 120.4 \text{ (q, } J = 320.1 \text{ Hz), 118.2, 72.7, 55.6, 52.7, 31.8, 30.2 \text{ ppm; } } \]

\[ ^{19}F \text{ NMR (376 MHz, acetone-}d_6\text{): } \delta –75.2 \text{ ppm; } \]

HRMS (ESI-TOF, \( m/z \)): calcd for C₁₄H₂₁F₃NO₄S \([M+H]⁺ 356.1138\), found 356.1140.

3-((3,5-Difluorophenyl)amino)-3-methylbutan-1-ol (71). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 7:1→5:1 hexanes:EtOAc) furnished amine 71 as a colorless oil (16.1 mg, 75%).

\[ R_f = 0.33 \] (silica gel, 5:1 hexanes:EtOAc);
1H NMR (600 MHz, MeOH-d$_4$): δ 6.30 – 6.21 (m, 2 H), 6.06 (tt, $J$ = 9.3, 2.2 Hz, 1 H), 3.66 (t, $J$ = 7.4 Hz, 2 H), 1.95 (t, $J$ = 7.4 Hz, 2 H), 1.34 (s, 6 H) ppm;

13C NMR (151 MHz, MeOH-d$_4$): δ 165.3 (dd, $J$ = 241.3, 16.4 Hz), 151.3 (t, $J$ = 13.5 Hz), 98.5 (dd, $J$ = 22.7, 5.9 Hz), 91.8 (t, $J$ = 26.6 Hz), 59.5, 53.7, 43.7, 28.6 ppm;

19F NMR (376 MHz, MeOH-d$_4$): δ –113.4 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{11}$H$_{16}$NO [M+H]$^+$ 126.1194; found 126.1196.

**4-((3,5-Difluorophenyl)amino)-2,4-dimethylpentan-2-ol (72).** On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 7:1 $\rightarrow$ 5:1 hexanes:EtOAc) furnished amine 72 as a colorless oil (13.5 mg, 56%).

R$_f$ = 0.33 (silica gel, 5:1 hexanes:EtOAc);

1H NMR (600 MHz, MeOH-d$_4$): δ 6.23 – 6.21 (m, 2 H), 6.05 (tt, $J$ = 9.0, 2.4 Hz, 1 H), 1.90 (s, 2 H), 1.42 (s, 6 H), 1.28 (s, 6 H) ppm;

13C NMR (151 MHz, MeOH-d$_4$): δ 165.25 (dd, $J$ = 241.2, 16.4 Hz), 151.2 (t, $J$ = 13.4 Hz), 98.7 (dd, $J$ = 22.6, 5.8 Hz), 91.7 (t, $J$ = 26.6 Hz), 72.5, 55.2, 52.4, 31.4, 30.0 ppm;

19F NMR (376 MHz, MeOH-d$_4$): δ –113.4 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{13}$H$_{20}$F$_2$NO [M+H]$^+$ 244.1507; found 244.1502.

**3-Methyl-3-((perfluorophenyl)amino)butan-1-ol (73).** On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 5:1 $\rightarrow$ 3:1 hexanes:EtOAc) furnished amine 73 as a colorless oil (16.2 mg, 60%).

R$_f$ = 0.45 (silica gel, 3:1 hexanes:EtOAc);

1H NMR (600 MHz, acetone-d$_6$): δ 4.51 (s, 1 H), 3.86 – 3.83 (m, 3 H), 1.85 (t, $J$ = 6.0 Hz, 2 H), 1.23 (s, 6 H) ppm;

13C NMR (151 MHz, acetone-d$_6$): δ 144.7 (m), 143.1 (m), 139.7 (m), 138.1 (m), 136.4 (m), 122.9 (m), 59.5, 57.6, 45.8, 27.9 ppm;

19F NMR (376 MHz, acetone-d$_6$): δ –149.5 (m), –166.1 (m), –167.1 (m) ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{11}$H$_{13}$F$_5$NO [M+H]$^+$ 270.0912; found 270.0913.
N-(tert-Butyl)-2-chloroaniline (74). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO₂, 200:1→100:1 hexanes:DCM) furnished amine 74 as a colorless oil (26.9 mg, 42%) (48).

\[ R_f = 0.27 \] (silica gel, 40:1 hexanes:DCM);

H NMR (600 MHz, acetone-d₆): δ 7.23 (d, J = 7.8 Hz, 1 H), 7.11 (t, J = 7.5 Hz, 1 H), 7.04 (d, J = 8.4 Hz, 1 H), 6.61 (t, J = 7.5 Hz, 1 H), 4.37 (s, 1 H), 1.39 (s, 9 H) ppm;

C NMR (151 MHz, MeOH-d₄): δ 144.1, 130.3, 128.4, 122.7, 119.4, 117.5, 52.7, 30.1 ppm;

HRMS (ESI-TOF, m/z): calcd for C₁₀H₁₅ClN [M+H]+ 184.0888; found 184.0889.

N-(1-(Benzyloxy)-2-methylpropan-2-yl)-2-chloroaniline (75). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 40:1 hexanes:EtOAc) furnished amine 75 as a colorless oil (14.4 mg, 50%).

\[ R_f = 0.80 \] (silica gel, 6:1 hexanes:EtOAc);

H NMR (600 MHz, MeOH-d₄): δ 7.36 – 7.27 (m, 5 H), 7.25 (dd, J = 8.4, 1.2 Hz, 1 H), 7.08 (ddd, J = 7.8, 7.2, 1.2 Hz, 1 H), 7.03 (dd, J = 8.4, 1.2 Hz, 1 H), 6.67 (ddd, J = 7.8, 7.2, 1.8 Hz, 1 H), 4.56 (s, 2 H), 3.46 (s, 2 H), 1.35 (s, 6 H) ppm;

C NMR (151 MHz, MeOH-d₄): δ 144.2, 139.6, 130.4, 129.3, 128.7, 128.6, 128.4, 123.1, 119.7, 117.8, 78.7, 74.3, 55.7, 25.1 ppm;

HRMS (ESI-TOF, m/z): calcd for C₁₇H₂₁ClNO [M+H]+ 290.1306, found 290.1311.

3-((2-Chlorophenyl)amino)-3-methylbutan-1-ol (76). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 7:1→5:1 hexanes:EtOAc) furnished amine 76 as a colorless oil (12.8 mg, 60%).

\[ R_f = 0.53 \] (silica gel, 2:1 hexanes:EtOAc);

H NMR (600 MHz, acetone-d₆): δ 7.24 (dd, J = 7.8, 1.2 Hz, 1 H), 7.12 (dd, J = 7.8, 7.8 Hz, 1 H), 7.05 (dd, J = 8.4, 1.2 Hz, 1 H), 6.61 (ddd, J = 7.8, 7.8, 1.8 Hz, 1 H), 5.00 (s, 1
4-((2-Chlorophenyl)amino)-2,4-dimethylpentan-2-ol (77). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 20:1→8:1 hexanes:EtOAc) furnished amine 77 as a colorless oil (14.8 mg, 61%).

\[ R_f = 0.34 \text{ (silica gel, 6:1 hexanes:EtOAc)}; \]

\[ {^1}H \text{ NMR (600 MHz, acetone-}d_6) : \delta 7.21 \text{ (d,} J = 7.8 \text{ Hz, 1 H}), 7.08 \text{ (t,} J = 7.8 \text{ Hz, 1 H}), 7.03 \text{ (d,} J = 8.4 \text{ Hz, 1 H}), 6.56 \text{ (t,} J = 7.8 \text{ Hz, 1 H}), 6.02 \text{ (s, 1 H)}, 3.89 \text{ (s, 1 H)}, 1.94 \text{ (s, 2 H)}, 1.51 \text{ (s, 6 H)}, 1.34 \text{ (s, 6 H) ppm}; \]

\[ {^{13}}C \text{ NMR (151 MHz, MeOH-}d_4) : \delta 144.2, 130.4, 128.2, 122.3, 118.5, 116.9, 72.5, 55.7, 53.7, 31.5, 30.1 \text{ ppm}; \]

\[ \text{HRMS (ESI-TOF,} m/z) : \text{calcd for C}_{13}H_{21}ClNO \left[ {\text{M+H}}^+ \right] 242.1306, \text{ found 242.1311.} \]

3-((4-Bromophenyl)amino)-3-methylbutan-1-ol (78). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 2:1→1:1 hexanes:EtOAc) furnished amine 78 as a colorless oil (14.9 mg, 58%). On decagram scale (65.3 mmol 1-bromo-4-nitrobenzene) conducted at Kemxtree, general procedure D was followed but with 3 equiv of prenol B (15.1 mL) instead of isoprenol A as donor olefin. Purification by flash column chromatography provided amine 78 (4.0 g, 31%, unoptimized yield).

\[ R_f = 0.34 \text{ (silica gel, 4:2:0.5 hexanes:EtOAc:MeOH)}; \]

\[ {^1}H \text{ NMR (600 MHz, MeOH-}d_4) : \delta 7.19 \text{ (d,} J = 8.4 \text{ Hz, 2 H}), 6.72 \text{ (d,} J = 8.4 \text{ Hz, 2 H}), 3.69 \text{ (t,} J = 7.2 \text{ Hz, 2 H}), 1.90 \text{ (t,} J = 7.2 \text{ Hz, 2 H}), 1.30 \text{ (s, 6 H) ppm}; \]

\[ {^{13}}C \text{ NMR (151 MHz, MeOH-}d_4) : \delta 147.6, 132.5, 120.2, 110.9, 59.7, 54.0, 44.0, 28.7 \text{ ppm}; \]

\[ \text{HRMS (ESI-TOF,} m/z) : \text{calcd for C}_{11}H_{17}BrNO \left[ {\text{M+H}}^+ \right] 258.0488, \text{ found 258.0482.} \]
N-(1-(Benzyloxy)-2-methylpropan-2-yl)-4-bromoaniline (79). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 20:1→10:1 hexanes:EtOAc) furnished amine 79 as a colorless oil (15.0 mg, 45%).

\[ R_f = 0.48 \] (silica gel, 5:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, MeOH-\(d_4\)) \(\delta\) 7.33 – 7.27 (m, 5 H), 7.21 (d, \(J = 8.4\) Hz, 2 H), 6.75 (d, \(J = 8.4\) Hz, 2 H), 4.51 (s, 2 H), 3.36 (s, 2 H), 1.27 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)) \(\delta\) 147.0, 139.7, 132.5, 129.4, 128.9, 128.6, 122.2, 112.6, 77.4, 74.3, 55.7, 25.6 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{17}\)H\(_{21}\)BrNO [M+H]\(^+\) 334.0801; found 334.0798.

4-Bromo-N-(2,3-dimethylbutan-2-yl)aniline (80). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 20:1→10:1 hexanes:EtOAc) furnished amine 80 as a colorless oil (10.5 mg, 41%). On decagram scale (49.5 mmol 1-bromo-4-nitrobenzene) conducted at Kemxtree, general procedure D was followed and purification by flash column chromatography provided amine 80 (3.8 g, 30%, unoptimized yield).

\[ R_f = 0.48 \] (silica gel, 8:1 hexanes:EtOAc);

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.20 (d, \(J = 8.8\) Hz, 2 H), 6.58 (d, \(J = 8.8\) Hz, 2 H), 3.53 (br s, 1 H), 2.10 (septet, \(J = 6.8\) Hz, 1 H), 1.23 (s, 6 H), 0.91 (d, \(J = 6.8\) Hz, 6 H) ppm;

\(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta\) 146.1, 131.8, 118.1, 109.3, 56.8, 35.4, 25.0, 17.7 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{12}\)H\(_{19}\)BrN [M+H]\(^+\) 256.0695; found 256.0688.

4-Iodo-N-(2-methyl-1-phenylpropan-2-yl)aniline (81). On 0.1 mmol scale, general procedure B was followed but with 3 equiv of PhSiH\(_3\) (36.9 µL) and 2 equiv of (2-methylallyl)benzene (30.0 µL), and purification by flash column chromatography (SiO₂, 200:1→100:1 hexanes:Et\(_2\)O) furnished amine 81 as a colorless oil (15.4 mg, 44%).

\[ R_f = 0.35 \] (silica gel, 20:1 hexanes:Et\(_2\)O);
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.41 – 7.36 (m, 2 H), 7.22 – 7.20 (m, 2 H), 7.18 – 7.14 (m, 1 H), 7.11 – 7.08 (m, 2 H), 6.66 – 6.61 (m, 2 H), 2.96 (s, 2 H), 1.27 (s, 6 H) ppm;
$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 148.3, 139.6, 138.6, 131.7, 128.8, 127.2, 119.8, 78.5, 55.0, 46.3, 28.5 ppm;
HRMS (ESI-TOF, $m/z$): calcd for C$_{16}$H$_{19}$IN [M+H]$^+$ 352.0557; found 352.0559.

Ethyl 4-((1-methylcyclopentyl)amino)-1H-pyrrole-2-carboxylate (82). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 1-methylcyclopentene (52.6 µL), and purification by flash column chromatography (SiO$_2$, 8:1→1:1 hexanes:EtOAc) furnished amine 82 as a yellow oil (12.8 mg, 54%).

$R_f$ = 0.18 (silica gel, 2:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 6.84 (dd, $J$ = 3.0, 1.8 Hz, 1 H), 6.30 (dd, $J$ = 3.0, 1.8 Hz, 1 H), 4.23 (q, $J$ = 7.2 Hz, 2 H), 1.82 – 1.75 (m, 4 H), 1.66 – 1.62 (m, 2H), 1.51 – 1.47 (m, 2 H), 1.28 (t, $J$ = 7.2 Hz, 3 H), 1.25 (s, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$) $\delta$ 162.8, 132.4, 121.6, 117.8, 112.2, 64.5, 61.1, 40.1, 26.6, 24.9, 14.8 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{13}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 237.1598, found 237.1600.

Ethyl 4-((2-methyl-1-phenylpropan-2-yl)amino)-1H-pyrrole-2-carboxylate (83). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 2-methyl-3-phenyl-1-propene (75.0 µL), and purification by flash column chromatography (SiO$_2$, 8:1→1:1 hexanes:EtOAc) furnished amine 83 as a yellow oil (16.0 mg, 56%).

$R_f$ = 0.19 (silica gel, 2:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.28 – 7.25 (m, 2 H), 7.21 – 7.16 (m, 3 H), 6.70 (d, $J$ = 1.8 Hz, 1 H), 6.60 (d, $J$ = 1.8 Hz, 1 H), 4.29 (q, $J$ = 7.2 Hz, 2 H), 2.76 (s, 2 H), 1.35 (t, $J$ = 7.2 Hz, 3 H), 1.07 (s, 6 H) ppm;
Ethyl 4-((2-methyl-1-phenylpropan-2-yl)amino)-1H-pyrrole-2-carboxylate (84). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 2-methyl-1-pentene (61.7 µL), and purification by flash column chromatography (SiO$_2$, 8:1→1:1 hexanes:EtOAc) furnished amine 84 as a yellow oil (12.7 mg, 53%).

$R_f$ = 0.18 (silica gel, 2:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): δ 6.65 (s, 1 H), 6.56 (s, 1 H), 4.27 (q, $J$ = 7.2 Hz, 2 H), 1.39 – 1.37 (m, 4 H), 1.34 (t, $J$ = 7.2 Hz, 3 H), 1.10 (s, 6 H), 0.92 (t, $J$ = 4.2 Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): δ 162.8, 131.2, 121.5, 119.0, 113.3, 61.1, 55.4, 44.8, 27.3, 18.5, 15.1, 14.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{13}$H$_{23}$N$_2$O$_2$ [M+H]$^+$ 239.1754, found 239.1758.

5-(tert-Butylamino)benzo[d]thiazol-2(3H)-one (85). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO$_2$, 2:1→1:1 hexanes:EtOAc) furnished amine 85 as a colorless oil (42.1 mg, 54%).

$R_f$ = 0.36 (silica gel, 1:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): δ 7.00 (d, $J$ = 2.2 Hz, 1 H), 6.95 (d, $J$ = 8.6 Hz, 1 H), 6.77 (dd, $J$ = 8.5, 2.3 Hz, 1 H), 1.29 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): δ 170.2, 144.6, 129.0, 125.1, 118.4, 112.4, 112.3, 52.1, 30.3 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{11}$H$_{15}$N$_2$O$_2$S [M+H]$^+$ 223.0900; found 223.0895.

6-((2,3-Dimethylbutan-2-yl)amino)benzo[d]thiazol-2(3H)-one (86). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 2:1→1:1 hexanes:EtOAc) furnished amine 86 as a colorless oil (24.8 mg, 50%).
$R_f = 0.28$ (silica gel, 1:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 7.00 (d, $J = 2.1$ Hz, 1 H), 6.95 (d, $J = 8.6$ Hz, 1 H), 6.77 (dd, $J = 8.6$, 2.2 Hz, 1 H), 2.15 (hept, $J = 6.8$ Hz, 1 H), 1.23 (s, 6 H), 0.94 (d, $J = 6.8$ Hz, 6 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 170.4, 144.7, 128.6, 125.3, 117.7, 112.5, 111.5, 57.4, 36.0, 25.3, 18.0 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{13}$H$_{19}$N$_2$OS [M+H]$^+$ 251.1213; found 251.1210.

Ethyl 5-((2-methyl-1-phenylpropan-2-yl)amino)-1H-indole-2-carboxylate (87). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 2-methyl-3-phenyl-1-propene (75.0 µL), and purification by flash column chromatography (SiO$_2$, 10:1→5:1 hexanes:EtOAc) furnished amine 87 as a yellow oil (20.0 mg, 60%).

$R_f = 0.41$ (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.30 (d, $J = 8.4$ Hz, 1 H), 7.27 – 7.24 (m, 3 H), 7.21 – 7.16 (m, 3 H), 7.07 (d, $J = 0.6$ Hz, 1 H), 6.99 (dd, $J = 8.4$, 1.2 Hz, 1 H), 4.38 (q, $J = 7.2$ Hz, 2 H), 2.88 (s, 2 H), 1.41 (t, $J = 7.2$ Hz, 3 H), 1.18 (s, 6 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 160.9, 140.4, 138.4, 132.1, 130.1, 127.7, 127.2, 127.0, 125.4, 120.7, 112.0, 107.9, 106.6, 59.6, 53.8, 46.0, 27.1, 13.4 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{21}$H$_{25}$N$_2$O$_2$ [M+H]$^+$ 337.1911, found 337.1920.

Ethyl 5-((1-methylcyclopentyl)amino)-1H-indole-2-carboxylate (88). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 1-methylcyclopentene (52.6 µL), and purification by flash column chromatography (SiO$_2$, 10:1→4:1 hexanes:EtOAc) furnished amine 88 as a light brown amorphous solid (13.1 mg, 46%).

$R_f = 0.32$ (silica gel, 3:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.29 (d, $J = 8.8$ Hz, 1 H), 7.12 (d, $J = 1.8$ Hz, 1 H), 7.03 (d, $J = 0.8$ Hz, 1 H), 6.95 (dd, $J = 8.8$, 2.1 Hz, 1 H), 4.37 (q, $J = 7.1$ Hz, 2 H), 1.94 –
1.90 (m, 2 H), 1.83 – 1.77 (m, 2 H), 1.73 – 1.68 (m, 2 H), 1.65 – 1.61 (m, 2 H), 1.40 (t, \( J = 7.1 \text{ Hz}, 3 \text{ H} \)), 1.29 (s, 3 H) ppm;

\(^{13}\text{C NMR} (151 \text{ MHz, } \text{MeOH-d}_4)\): \( \delta \) 163.6, 140.6, 135.1, 129.1, 128.9, 122.7, 113.4, 112.4, 108.5, 64.5, 61.7, 40.9, 26.5, 24.9, 14.7 ppm;

\text{HRMS (ESI-TOF, } m/z \text{): calcd for } \text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_2 \{M+H\}^+ 287.1754; \text{ found } 287.1757.

**Ethyl 1-benzyl-5-((1-methylcyclopentyl)amino)-1H-indole-2-carboxylate (89).** On 0.05 mmol scale, general procedure A was followed but with 3 equiv of PhSiH\(_3\) (18.5 \( \mu \text{L} \)) and 5 equiv of 1-methylcyclopentene (26.4 \( \mu \text{L} \)) and purification by flash column chromatography (SiO\(_2\), 20:1 \( \rightarrow \) 10:1 hexanes:EtOAc) furnished amine 89 as a brown oil (9.5 mg, 50%).

\( R_f = 0.19 \) (silica gel, 5:1 hexanes:EtOAc);

\(^1\text{H NMR} (600 \text{ MHz, } \text{MeOH-d}_4)\): \( \delta \) 7.27 – 7.19 (m, 4 H), 7.19 – 7.15 (m, 1 H), 7.11 (d, \( J = 2.0 \text{ Hz}, 1 \text{ H} \)), 7.01 – 6.99 (m, 2 H), 6.94 (dd, \( J = 8.9, 2.2 \text{ Hz}, 1 \text{ H} \)), 5.80 (s, 2 H), 4.29 (q, \( J = 7.1 \text{ Hz}, 2 \text{ H} \)), 1.94 – 1.91 (m, 2 H), 1.81 – 1.79 (m, 2 H), 1.71 – 1.63 (m, 4 H), 1.33 (t, \( J = 7.1 \text{ Hz}, 3 \text{ H} \)), 1.31 (s, 3 H) ppm;

\(^{13}\text{C NMR} (151 \text{ MHz, acetone-d}_6)\): \( \delta \) 162.7, 143.0, 140.2, 134.9, 129.4, 128.0, 127.9, 127.4, 120.3, 112.4, 110.5, 105.6, 62.4, 61.0, 48.3, 41.1, 26.3, 25.1, 14.8 ppm;

\text{HRMS (ESI-TOF, } m/z \text{): calcd for } \text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_2 \{M+H\}^+ 377.2224; \text{ found } 377.2218.

**Ethyl 5-((1-(benzyloxy)-2-methylpropan-2-yl)amino)-1H-pyrazole-3-carboxylate (90).** On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH\(_3\) (36.9 \( \mu \text{L} \)) and 5 equiv of ((2-methylallyloxy)methyl)benzene (86.5 \( \mu \text{L} \)), and purification by flash column chromatography (SiO\(_2\), 3:1 \( \rightarrow \) 2:1 \( \rightarrow \) 1:1 hexanes:EtOAc) furnished amine 90 as a colorless oil (20.0 mg, 63%).

\( R_f = 0.23 \) (silica gel, 2:1 hexanes:EtOAc);

\(^1\text{H NMR} (600 \text{ MHz, acetone-d}_6)\): \( \delta \) 7.35 – 7.32 (m, 4 H), 7.28 – 7.25 (m, 1 H), 6.12 (s, 1 H), 4.54 (s, 2 H), 4.27 (q, \( J = 7.2 \text{ Hz}, 2 \text{ H} \)), 3.47 (s, 2 H), 1.31 (t, \( J = 6.6 \text{ Hz}, 3 \text{ H} \)), 1.30 (s, 6 H) ppm;
**13C NMR (151 MHz, acetone-\textit{d}_6):** δ 139.8, 129.1, 128.3, 128.2, 97.0, 77.9, 73.7, 61.0, 54.9, 25.1, 14.6 ppm (three carbon undetected due to free pyrazole ring);

**HRMS (ESI-TOF, \textit{m/z}):** calcd for C$_{17}$H$_{24}$N$_3$O$_3$ [M+H]$^+$ 318.1812; found 318.1821.

**Ethyl 1-(4-methoxyphenyl)-6-(4-((2-methyl-1-phenylpropan-2-yl)amino)phenyl)-7-oxo-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-c]pyridine-3-carboxylate (91).** On 0.025 mmol scale, general procedure B was followed but with 2 equiv of PhSiH$_3$ (6.2 µL) and 2 equiv of (2-methylallyl)benzene (7.5 µL), and purification by preparative TLC (SiO$_2$, 20:1 DCM:EtOAc) furnished amine 91 as a colorless oil (3.2 mg, 24%), together with recovered starting material (3.6 mg, 33%). $R_f$ = 0.52 (silica gel, 10:1 DCM:EtOAc);

**1H NMR (600 MHz, acetone-\textit{d}_6):** δ 7.53 (d, $J$ = 13.2 Hz, 2 H), 7.25 – 7.12 (m, 7 H), 6.98 (d, $J$ = 13.8 Hz, 2 H), 6.84 (d, $J$ = 13.2 Hz, 2 H), 4.37 (q, $J$ = 10.8 Hz, 2 H), 4.08 (t, $J$ = 9.9 Hz, 2 H), 3.85 (s, 3 H), 3.27 (t, $J$ = 9.9 Hz, 2 H), 3.02 (s, 2 H), 1.38 (t, $J$ = 10.8 Hz, 3 H), 1.30 (s, 6 H) ppm;

**13C NMR (151 MHz, acetone-\textit{d}_6):** δ 162.7, 160.8, 157.7, 146.9, 139.9, 139.6, 134.6, 134.2, 133.1, 131.6, 128.7, 127.9, 127.7, 127.6, 127.0, 116.5, 114.3, 61.3, 56.0, 54.7, 52.4, 46.3, 28.7, 22.6, 14.8 ppm;

**HRMS (ESI-TOF, \textit{m/z}):** calcd for C$_{32}$H$_{35}$N$_4$O$_4$ [M+H]$^+$ 539.2653; found 539.2647.

**6-Methoxy-N-(2-methylpentan-2-yl)pyridin-3-amine (92).** On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 10:1→5:1 hexanes:EtOAc) furnished amine 92 as a colorless oil (12.8 mg, 62%).

$R_f$ = 0.58 (silica gel, 3:1 hexanes:EtOAc);

**1H NMR (600 MHz, acetone-\textit{d}_6):** δ 7.73 (d, $J$ = 2.9 Hz, 1 H), 7.25 (dd, $J$ = 8.8, 2.9 Hz, 1 H), 6.58 (d, $J$ = 8.2 Hz, 1 H), 3.80 (s, 3 H), 1.57 – 1.49 (m, 2 H), 1.47 – 1.37 (m, 2 H), 1.21 (s, 6 H), 0.90 (t, $J$ = 7.3 Hz, 3 H) ppm;
$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 159.1, 138.9, 137.9, 132.6, 110.8, 54.7, 53.3, 45.1, 28.6, 18.1, 15.1 ppm;
HRMS (ESI-TOF, $m/z$): calcd for C$_{12}$H$_{21}$N$_2$O [$M+H]^+$ 209.1648; found 209.1648.

4-((6-Methoxypyridin-3-yl)amino)-2,4-dimethylpentan-2-ol (93). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 3:1 $\rightarrow$ 1:1 hexanes:EtOAc) furnished amine 93 as a colorless oil (13.7 mg, 58%).

$R_f$ = 0.32 (silica gel, 10:1 hexanes:EtOAc);
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.80 (d, $J$ = 2.9 Hz, 1 H), 7.40 (dd, $J$ = 8.8, 2.9 Hz, 1 H), 6.70 (d, $J$ = 8.8 Hz, 1 H), 3.85 (s, 3 H), 1.78 (s, 2 H), 1.33 (s, 6 H), 1.26 (s, 6 H) ppm;
$^{13}$C NMR (151 MHz, MeOH-$d_4$): $\delta$ 161.4, 141.4, 137.2, 136.4, 111.0, 72.5, 57.1, 54.1, 52.1, 32.7, 29.6 ppm;
HRMS (ESI-TOF, $m/z$): calcd for C$_{13}$H$_{23}$N$_2$O$_2$ [$M+H]^+$ 239.1754; found 239.1753.

2-Methoxy-N-(1-methylcyclopentyl)pyridin-3-amine (94). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 50:1 $\rightarrow$ 30:1 hexanes:EtOAc) furnished amine 94 as a colorless oil (11.1 mg, 54%).

$R_f$ = 0.48 (silica gel, 8:1 hexanes:EtOAc);
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.43 (dd, $J$ = 4.8, 1.2 Hz, 1 H), 6.84 (dd, $J$ = 7.8, 1.8 Hz, 1 H), 6.71 (dd, $J$ = 7.8, 4.8 Hz, 1 H), 4.31 (s, 1 H), 3.96 (s, 3 H), 1.98 – 1.95 (m, 2 H), 1.77 – 1.69 (m, 6 H), 1.40 (s, 3 H) ppm;
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 153.0, 131.9, 131.4, 117.1, 116.5, 60.9, 53.4, 40.4, 25.7, 24.6 ppm
HRMS (ESI-TOF, $m/z$): calcd for C$_{12}$H$_{19}$N$_2$O [$M+H]^+$ 207.1492, found 207.1496.

2-Methoxy-N-(1-methylcyclohexyl)pyridin-3-amine (95). On 0.1 mmol scale, general procedure A was followed and purification by flash column
chromatography (SiO2, 50:1→30:1 hexanes:EtOAc) furnished amine 95 as a colorless oil (13.8 mg, 63%). 

\[ R_f = 0.52 \] (silica gel, 8:1 hexanes:EtOAc);

\[ ^1H \text{ NMR (600 MHz, CDCl}_3\text{)}: \delta 7.45 (d, J = 4.2 \text{ Hz, 1 H}), 6.92 (d, J = 7.2 \text{ Hz, 1 H}), 6.70 \text{ (dd, J = 7.8, 4.8 \text{ Hz, 1 H}), 4.26 (s, 1 H), 3.97 (s, 3 H), 1.91 – 1.90 (m, 2 H), 1.52 – 1.48 (m, 8 H), 1.34 (s, 3 H) ppm; } \]

\[ ^{13}C \text{ NMR (151 MHz, CDCl}_3\text{)}: \delta 153.2, 132.1, 131.3, 117.5, 117.0, 53.5, 52.7, 37.7, 26.7, 25.9, 22.2 \text{ ppm; } \]

HRMS (ESI-TOF, \textit{m/z}): calcd for C_{13}H_{21}N_{2}O [M+H]^+ 221.1648, found 221.1649.

6-Methoxy-N-(2-methyl-1-phenylpropan-2-yl)pyridin-3-amine (96). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 10:1→4:1 hexanes:EtOAc) furnished amine 96 as a colorless oil (15.3 mg, 60%).

\[ R_f = 0.38 \] (silica gel, 3:1 hexanes:EtOAc);

\[ ^1H \text{ NMR (600 MHz, MeOH-d}_4\text{)}: \delta 7.76 (d, J = 3.0 \text{ Hz, 1 H}), 7.36 (dd, J = 9.0, 3.0 \text{ Hz, 1 H}), 7.27 – 7.24 (m, 2 H), 7.21 – 7.16 (m, 3 H), 6.71 (d, J = 9.0 \text{ Hz, 1 H}), 3.86 (s, 3 H), 2.85 (s, 2 H), 1.16 (s, 6 H) ppm; \]

\[ ^{13}C \text{ NMR (151 MHz, MeOH-d}_4\text{)}: \delta 160.6, 139.6, 139.5, 138.0, 135.1, 131.7, 128.9, 127.3, 111.1, 56.2, 54.1, 48.4, 27.7 \text{ ppm; } \]

HRMS (ESI-TOF, \textit{m/z}): calcd for C_{16}H_{21}N_{2}O [M+H]^+ 257.1648, found 257.1653.

N-(1-(benzyloxy)-2-methylpropan-2-yl)-6-methoxypyridin-3-amine (97). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 10:1→4:1 hexanes:EtOAc) furnished amine 97 as a colorless oil (21.4 mg, 75%).

\[ R_f = 0.38 \] (silica gel, 3:1 hexanes:EtOAc);
$^1$H NMR (600 MHz, MeOH-$d_4$): $\delta$ 7.78 (d, $J = 3.0$ Hz, 1 H), 7.37 – 7.33 (m, 5 H), 7.30 – 7.28 (m, 1 H), 6.67 (d, $J = 8.4$ Hz, 1 H), 4.52 (s, 2 H), 3.85 (s, 3 H), 3.25 (s, 2 H), 1.18 (s, 6 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$) $\delta$ 161.8, 142.1, 139.8, 137.4, 137.3, 129.5, 129.1, 128.8, 111.1, 77.3, 74.5, 56.6, 54.3, 25.5 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{17}$H$_{23}$N$_2$O$_2$ [M+H]$^+$ 287.1754, found 287.1757.

$N$-(tert-Butyl)pyridin-3-amine (98). On 0.35 mmol scale, general procedure C was followed and purification by flash column chromatography (SiO$_2$, 40:1 → 20:1 EtOAc:MeOH) furnished amine 98 as a light yellow oil (25.1 mg, 47%) (49).

$R_f = 0.33$ (silica gel, 20:1 EtOAc:MeOH);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 8.10 (s, 1 H), 7.82 (d, $J = 4.5$ Hz, 1 H), 7.14 – 7.10 (m, 1 H), 7.03 (dd, $J = 8.3$, 4.6 Hz, 1 H), 1.35 (s, 9 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 144.7, 139.9, 138.8, 123.9, 121.8, 51.6, 30.3 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_9$H$_{15}$N$_2$ [M+H]$^+$ 151.1230; found 151.1231.

$N$-(2-Methylpentan-2-yl)pyridin-3-amine (99). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 2:1 → 1:1 hexanes:EtOAc) furnished amine 99 as a colorless oil (8.1 mg, 45%).

$R_f = 0.33$ (silica gel, 1:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): $\delta$ 8.10 (s, 1 H), 7.80 (s, 1 H), 7.12 – 7.11 (m, 1 H), 7.04 – 7.00 (m, 1 H), 1.68 – 1.64 (m, 2 H), 1.41 – 1.33 (m, 2 H), 1.30 (s, 6 H), 0.87 (t, $J = 7.3$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 144.8, 139.4, 138.5, 124.0, 121.4, 54.0, 44.1, 28.3, 18.0, 14.8 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{11}$H$_{19}$N$_2$ [M+H]$^+$ 179.1543; found 179.1542.

$N$-(2-Methyl-1-phenylpropan-2-yl)pyridin-3-amine (100). On 0.1 mmol scale, general procedure A was followed and purification by
flash column chromatography (SiO₂, 10:1→1:1 hexanes:EtOAc) furnished amine 100 as a colorless oil (9.8 mg, 43%).

\( R_f = 0.23 \) (silica gel, 2:1 hexanes:EtOAc);

\(^1\)H NMR (500 MHz, MeOH-\(d_4\)) \( \delta \): 8.05 (d, \( J = 3.0 \) Hz, 1 H), 7.81 (dd, \( J = 4.5, 1.5 \) Hz, 1 H), 7.29 (ddd, \( J = 8.5, 3.0, 1.5 \) Hz, 1 H), 7.25 – 7.18 (m, 4 H), 7.13 – 7.11 (m, 2 H), 3.05 (s, 2 H), 1.34 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\(d_4\)) \( \delta \): 145.7, 139.4, 138.5, 137.6, 131.6, 128.8, 127.3, 125.2, 123.2, 55.0, 46.2, 28.4 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C₁₅H₁₉N \([M+H]^+\) 227.1543, found 227.1550.

3-((2-Methoxypyridin-3-yl)amino)-3-methylbutan-1-ol (101). On 0.1 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 3:1→2:1 hexanes:EtOAc) furnished amine 101 as a colorless oil (13.5 mg, 64%).

\( R_f = 0.25 \) (silica gel, 3:1 hexanes:EtOAc);

\(^1\)H NMR (600 MHz, acetone-\(d_6\)) \( \delta \): 7.37 (dd, \( J = 5.0, 1.6 \) Hz, 1 H), 7.03 (dd, \( J = 7.7, 1.6 \) Hz, 1 H), 6.72 (dd, \( J = 7.7, 4.9 \) Hz, 1 H), 4.74 (s, 1 H), 3.88 (s, 3 H), 3.70 (m, 2 H), 3.61 (m, 1 H), 1.94 (t, \( J = 6.8 \) Hz, 2 H), 1.38 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, acetone-\(d_6\)) \( \delta \): 153.8, 132.9, 132.3, 118.0, 117.9, 59.2, 53.5, 53.4, 44.5, 28.2 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C₁₁H₁₉N₂O₂ \([M+H]^+\) 211.1441; found 211.1443.

6-Chloro-N-(1-methylcyclohexyl)pyridin-3-amine (102). On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO₂, 10:1→5:1 hexanes:EtOAc) furnished amine 102 as a colorless oil (9.4 mg, 42%).

\( R_f = 0.33 \) (silica gel, 5:1 heanes:EtOAc);

\(^1\)H NMR (600 MHz, acetone-\(d_6\)) \( \delta \): 7.91 (d, \( J = 3.1 \) Hz, 1 H), 7.22 (dd, \( J = 8.7, 3.2 \) Hz, 1 H), 7.09 (d, \( J = 8.7 \) Hz, 1 H), 4.83 (s, 1 H), 1.93 – 1.91 (m, 2 H), 1.64 – 1.32 (m, 8 H), 1.32 (s, 3 H) ppm;
**13C NMR (151 MHz, acetone-d$_6$):** δ 144.1, 138.4, 138.0, 125.5, 124.4, 53.8, 38.4, 26.8, 26.5, 22.7 ppm;

**HRMS (ESI-TOF, m/z):** calcd for C$_{12}$H$_{18}$ClN$_2$ [M+H]$^+$ 225.1153; found 225.1152.

6-Methoxy-N-(1-methylcyclohexyl)pyridin-3-amine (103). On 0.1 mmol scale, general procedure A was followed, and purification by flash column chromatography (SiO$_2$, 10:1→5:1 hexanes:EtOAc) furnished amine 103 as a colorless oil (14.6 mg, 66%).

**R$_f$ = 0.52** (silica gel, 3:1 hexanes:EtoAc);

**1H NMR (600 MHz, acetone-d$_6$):** δ 7.75 (d, $J = 2.9$ Hz, 1 H), 7.27 (dd, $J = 8.8$, 2.9 Hz, 1 H), 6.59 (d, $J = 8.7$ Hz, 1 H), 3.80 (s, 3 H), 1.80 – 1.62 (m, 4 H), 1.54 – 1.30 (m, 6 H), 1.18 (s, 3 H) ppm;

**13C NMR (151 MHz, acetone-d$_6$):** δ 158.1, 137.6, 137.2, 131.8, 109.7, 53.1, 52.2, 38.0, 26.6, 25.7, 21.9 ppm;

**HRMS (ESI-TOF, m/z):** calcd for C$_{13}$H$_{21}$N$_2$O [M+H]$^+$ 221.1648; found 221.1648.

2-((6-Chloropyridin-3-yl)amino)-2-methylpropan-1-ol (104). On 0.1 mmol scale, general procedure B was followed and purification by flash column chromatography (SiO$_2$, 1:1→1:2 hexanes:EtoAc) furnished amine 104 as a colorless oil (14.5 mg, 68%).

**R$_f$ = 0.17** (silica gel, 2:1 hexanes:EtoAc);

**1H NMR (600 MHz, acetone-d$_6$):** δ 7.87 (d, $J = 3.1$ Hz, 1 H), 7.21 (dd, $J = 8.7$, 3.1 Hz, 1 H), 7.11 (d, $J = 8.7$ Hz, 1 H), 5.22 (s, 1 H), 3.73 (m, 2 H), 3.66 (t, $J = 4.6$ Hz, 1 H), 1.94 (t, $J = 6.9$ Hz, 2 H), 1.37 (s, 6 H) ppm;

**13C NMR (151 MHz, acetone-d$_6$):** δ 142.7, 137.2, 136.2, 124.2, 123.0, 57.7, 52.5, 42.8, 26.8 ppm;

**HRMS (ESI-TOF, m/z):** calcd for C$_{10}$H$_{16}$ClN$_2$O [M+H]$^+$ 215.0946; found 215.0945.

4-((6-Chloropyridin-3-yl)amino)-2,4-dimethylpentan-2-ol (105). On 0.1 mmol scale, general procedure B was followed and purification by preparative TLC (SiO$_2$, 3:1 DCM:Eto) furnished amine 105 as a colorless oil (10.7 mg, 44%).
N-(2-((1-(4-Fluorophenyl)-1H-indazol-4-yl)amino)-2-methyl propyl)benzamide (108). On 0.1 mmol scale, general procedure A was followed and purification by preparative TLC (SiO₂, 3:1 hexanes:EtOAc) furnished amine 108 as a pale yellow oil (20.8 mg, 52%) (39).

\[ R_f = 0.52 \text{ (silica gel, 1:1 hexanes:EtOAc);} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\text{):} \delta 8.23 (s, 1 H), 7.79 (d,} J = 7.6 \text{ Hz, 2 H), 7.66 (dd,} J = 8.7, 4.8 \text{ Hz, 2 H), 7.50 (t,} J = 7.3 \text{ Hz, 1 H), 7.42 (t,} J = 7.5 \text{ Hz, 2 H), 7.25 – 7.17 (m, 3 H), 6.96 (d,} J = 8.3 \text{ Hz, 1 H), 6.65 (br s, 1 H), 6.46 (d,} J = 7.7 \text{ Hz, 1 H), 5.35 (br s, 1 H), 3.75 (d,} J = 6.2 \text{ Hz, 2 H), 1.53 (s, 6 H) ppm;} \]

\[ ^13 \text{C NMR (151 MHz, CDCl}_3\text{):} \delta 169.1, 161.2 (d,} J = 245.9 \text{ Hz), 140.3 (d,} J = 19.3 \text{ Hz), 140.2, 136.7, 134.1, 132.9, 132.0, 129.0, 128.9, 127.1, 124.7 (d,} J = 8.4 \text{ Hz), 116.8, 116.3 (d,} J = 22.7 \text{ Hz), 102.7, 99.1, 55.7, 50.3, 25.2 \text{ ppm;} \]

\[ ^19 \text{F NMR (376 MHz, CDCl}_3\text{):} \delta –115.7 \text{ ppm;} \]

HRMS (ESI-TOF, m/z): calcd for C₂₄H₂₄FN₄O [M+H]^+ 403.1929; found 403.1930.

tert-Butyl 4-(methyl(3-(tert-pentylamino)pyridin-2-yl)amino) piperidine-1-carboxylate (111). On 0.1 mmol scale, general procedure B was followed but with 5 equiv alkene (53.0 µL) and 3 equiv PhSiH₃ (36.9 µL). Purification by preparative TLC (SiO₂, 5:1 hexanes:EtOAc) furnished amine 111 as a pale yellow oil (15.5 mg, 41%) (36).

\[ R_f = 0.38 \text{ (silica gel, 4:1 hexanes:EtOAc);} \]
$^1$H NMR (400 MHz, acetone-$d_6$): δ 7.59 (dd, $J = 4.7$, 1.6 Hz, 1 H), 7.10 (dd, $J = 8.1$, 1.6 Hz, 1 H), 6.87 (dd, $J = 8.0$, 4.7 Hz, 1 H), 4.91 (br s, 1 H), 4.00 (d, $J = 13.2$ Hz, 2 H), 3.21 (tt, $J = 10.8$, 3.7 Hz, 1 H), 2.85 – 2.70 (m, 2 H), 2.56 (s, 3 H), 1.79 – 1.68 (m, 4 H), 1.52 – 1.43 (m, 2 H), 1.43 (s, 9 H), 1.32 (s, 6 H), 0.86 (t, $J = 7.5$ Hz, 3 H) ppm;

$^{13}$C NMR (151 MHz, acetone-$d_6$): δ 155.0, 152.5, 138.6, 135.0, 121.0, 118.5, 79.3, 58.6, 53.5, 43.6 (br), 36.0, 34.0, 30.4, 28.6, 27.7, 8.7 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{21}$H$_{37}$N$_4$O$_2$ [M+H]$^+$ 377.2911; found 377.2916.

4-Butyl-4-(phenylamino)cyclohexan-1-one (113). On 0.1 mmol scale, general procedure A was followed and purification by preparative TLC (SiO$_2$, 5:1 hexanes:Et$_2$O) furnished amine 113 as a colorless oil (8.8 mg, 36%) ($\Delta$).

$R_f = 0.33$ (silica gel, 10:1 hexanes:Et$_2$O);

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.17 (t, $J = 7.8$ Hz, 2 H), 6.80 – 6.73 (m, 3 H), 3.49 (br s, 1 H), 2.67 – 2.57 (m, 2 H), 2.34 – 2.24 (m, 4 H), 1.89 – 1.79 (m, 2 H), 1.74 – 1.68 (m, 2 H), 1.34 – 1.20 (m, 4 H), 0.84 (t, $J = 6.9$ Hz, 3 H) ppm;

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 211.6, 146.5, 129.4, 118.7, 116.7, 55.0, 37.9, 37.1, 36.3, 25.7, 23.1, 14.2 ppm;

HRMS (ESI-TOF, $m/z$): calcd for C$_{16}$H$_{24}$NO [M+H]$^+$ 246.1852; found 246.1860.

1-(4-Methoxyphenyl)-2,2,6-trimethylpiperidine (116). On 0.1 mmol scale, general procedure A was followed but with 3 equiv of PhSiH$_3$ (36.9 µL) and 5 equiv of 6-methyl-5-hepten-2-one (73.8 µL), and purification by flash column chromatography (SiO$_2$, 100:1→50:1→20:1 hexanes:EtOAc) furnished amine 116 as a colorless oil (10.0 mg, 43%).

$R_f = 0.53$ (silica gel, 10:1 hexanes:EtOAc);

$^1$H NMR (600 MHz, acetone-$d_6$): δ 7.05 (d, $J = 8.3$ Hz, 2 H), 6.83 (d, $J = 8.9$ Hz, 2 H), 3.78 (s, 3 H), 3.36 – 3.26 (m, 1 H), 1.79 – 1.65 (m, 2 H), 1.63 – 1.51 (m, 3 H), 1.35 – 1.18 (m, 1 H), 1.08 (s, 3 H), 0.84 (s, 3 H), 0.67 (d, $J = 6.0$ Hz, 3 H) ppm;
$^{13}$C NMR (151 MHz, acetone-$d_6$): $\delta$ 158.1, 141.5, 132.1, 113.7, 55.6, 55.2, 50.9, 42.1, 37.3, 33.1, 23.6, 21.8, 17.9 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{15}$H$_{24}$NO [M+H]$^+$ 234.1852; found 234.1851.

4-((2-Chlorophenyl)amino)-4-methylpentan-2-one (118)

(Conducted at Bristol-Myers Squibb, Medicinal Chemistry Department). On 0.3 mmol scale, general procedure A was followed and purification by ISCO silica gel flash chromatography (0 – 50% EtOAc in hexanes) furnished amine 118 as a colorless oil (27.7 mg, 41%).

$R_f$ = 0.39 (silica gel, 10:1 hexanes:EtOAc);

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.28 (dd, $J =$ 7.9, 1.5 Hz, 1 H), 7.18 – 7.09 (m, 1 H), 7.07 – 6.99 (m, 1 H), 6.70 – 6.57 (m, 1 H), 4.88 (s, 1 H), 2.88 (s, 2 H), 2.07 (s, 3 H), 1.39 (s, 6 H) ppm;

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 207.9, 142.2, 129.2, 127.7, 119.9, 117.4, 114.9, 52.7, 51.9, 31.8, 27.5 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{12}$H$_{17}$NOCl [M+H]$^+$ 226.0993; found 226.0993.

N-(2-((2-Methyl-4-oxopentan-2-yl)amino)phenyl)acetamide (120)

(Conducted at Bristol-Myers Squibb, Medicinal Chemistry Department). On 0.3 mmol scale, general procedure A was followed and purification by ISCO silica gel flash chromatography (0 – 50% EtOAc in hexanes) furnished amine 120 as a colorless oil (32.7 mg, 44%).

$R_f$ = 0.20 (silica gel, 1:1 hexanes:EtOAc);

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.24 (s, 1 H), 7.26 (dd, $J =$ 7.8, 1.1 Hz, 1 H), 7.06 – 6.95 (m, 2 H), 6.77 – 6.69 (m, 1 H), 4.42 (s, 1 H), 2.75 (s, 2 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.27 (s, 6 H) ppm;

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 208.8, 169.1, 140.3, 128.8, 126.1, 126.0, 119.4, 119.2, 53.6, 53.5, 32.5, 28.1, 23.8 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{14}$H$_{21}$N$_2$O$_2$ [M+H]$^+$ 249.1598; found 249.1597.
3-((2-Acetamidophenyl)amino)-3-methylbutanamide (121)  
(Conducted at Bristol-Myers Squibb, Medicinal Chemistry Department). On 0.3 mmol scale, general procedure A was followed and purification by ISCO silica gel flash chromatography (0 – 10% methanol in dichloromethane) furnished amine 121 as a colorless crystalline solid (29.9 mg, 40%). 

\[ R_f = 0.35 \] (silica gel, 10:1 DCM:MeOH);

**Melting Point:** 162.0-165.0 °C (EtOAc);

**\(^1\)H NMR (400 MHz, DMSO-\(d_6\)):** \( \delta \) 9.32 (s, 1 H), 7.50 (br s, 1 H), 7.29 (d, \( J = 7.5 \) Hz, 1 H), 7.07 – 6.92 (m, 3 H), 6.76 – 6.66 (m, 1 H), 4.97 (s, 1 H), 2.30 (s, 2 H), 2.05 (s, 3 H), 1.27 (s, 6 H) ppm.

**\(^1\)C NMR (101 MHz, DMSO-\(d_6\)):** \( \delta \) 173.2, 168.6, 140.0, 128.4, 125.6, 125.3, 118.8, 118.4, 53.1, 47.1, 27.3, 23.3 ppm.

**HRMS (ESI-TOF, \( m/z \)):** calcd for C\(_{13}\)H\(_{20}\)N\(_3\)O\(_2\) [M+H]\(^+\) 250.1550; found 250.1550.

Ethyl 3-((2-acetamidophenyl)amino)-3-methylbutanoate (122)  
(Conducted at Bristol-Myers Squibb, Medicinal Chemistry Department). On 0.3 mmol scale, general procedure B was followed and purification by ISCO silica gel flash chromatography (0 – 70% EtOAc in hexanes) furnished amine 122 as a colorless oil (33.4 mg, 40%). 

\[ R_f = 0.22 \] (silica gel, 1:1 hexanes:EtOAc);

**\(^1\)H NMR (400 MHz, DMSO-\(d_6\)):** \( \delta \) 9.24 (s, 1 H), 7.27 (dd, \( J = 7.8, 1.0 \) Hz, 1 H), 7.06 – 6.94 (m, 2 H), 6.79 – 6.71 (m, 1 H), 4.41 (s, 1 H), 4.06 (q, \( J = 7.1 \) Hz, 2 H), 2.57 (s, 2 H), 2.05 (s, 3 H), 1.30 (s, 6 H), 1.15 (t, \( J = 7.1 \) Hz, 3 H) ppm;

**\(^1\)C NMR (101 MHz, DMSO-\(d_6\)):** \( \delta \) 170.9, 168.5, 139.6, 128.5, 125.6, 125.3, 119.3, 119.0, 59.7, 53.0, 45.9, 27.4, 23.3, 14.0 ppm;

**HRMS (ESI-TOF, \( m/z \)):** calcd for C\(_{15}\)H\(_{23}\)N\(_2\)O\(_3\) [M+H]\(^+\) 279.1703; found 279.1703.
Medicinal Chemistry Department). On 0.3 mmol scale, general procedure B was followed and purification by ISCO silica gel flash chromatography (0 – 70% EtOAc in hexanes) furnished amine 123 as a colorless oil (37.9 mg, 41%).

\[ R_f = 0.48 \] (silica gel, EtOAc);

\(^1\text{H NMR} (400\text{ MHz, DMSO-}d_6)\): \(\delta\) 9.21 (s, 1 H), 7.11 (dd, \(J = 7.8, 1.4\) Hz, 1 H), 7.04 – 6.95 (m, 1 H), 6.89 (dd, \(J = 8.2, 1.2\) Hz, 1 H), 6.70 – 6.59 (m, 1 H), 4.61 (t, \(J = 5.0\) Hz, 1 H), 4.37 (s, 1 H), 3.52 (dq, \(J = 9.5, 7.1\) Hz, 2 H), 3.41 (dq, \(J = 9.6, 7.1\) Hz, 2 H), 2.03 (s, 3 H), 1.88 (d, \(J = 5.1\) Hz, 2 H), 1.26 (s, 6 H), 1.08 (t, \(J = 7.0\) Hz, 6 H) ppm;

\(^1\text{C NMR} (101\text{ MHz, DMSO-}d_6)\): \(\delta\) 168.5, 140.9, 126.4 (2C), 125.8, 117.1, 116.6, 100.2, 60.4, 52.0, 44.7, 28.1, 23.2, 15.2 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{17}\)H\(_{29}\)N\(_2\)O\(_3\) [M+H]\(^+\) 309.2173; found 309.2173.

Methyl 1-(4-methoxyphenyl)-6-(4-((2-(methyl-d\(_2\))-propan-2-yl-1,1,1,3,3,3-d\(_6\))amino)phenyl)-7-oxo-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-c]pyridine-3-carboxylate (124). On 0.05 mmol scale, general procedure B was followed but with 3 equiv of PhSiH\(_3\) (18.5 \(\mu\)L) and 5 equiv of isobutylene-d\(_8\) (16.3 \(\mu\)L). Purification by preparative TLC (SiO\(_2\), 1:1 hexanes:EtOAc) furnished amine 124 as a pale yellow oil (6.6 mg, 27%).

\[ R_f = 0.48 \] (silica gel, 1:1 hexanes:EtOAc);

\(^1\text{H NMR} (400\text{ MHz, MeOH-}d_4)\): \(\delta\) 7.47 (d, \(J = 8.9\) Hz, 2 H), 7.10 (d, \(J = 8.7\) Hz, 2 H), 6.99 (d, \(J = 8.9\) Hz, 2 H), 6.86 (d, \(J = 8.7\) Hz, 2 H), 4.41 (q, \(J = 7.1\) Hz, 2 H), 4.06 (t, \(J = 6.7\) Hz, 2 H), 3.84 (s, 3 H), 3.28 (t, \(J = 6.8\) Hz, 2 H), 1.41 (t, \(J = 7.1\) Hz, 3 H), 1.29 (m, 1 H) ppm;

\(^1\text{C NMR} (151\text{ MHz, MeOH-}d_4)\): \(\delta\) 163.3, 161.6, 159.0, 140.2, 134.7, 134.5, 134.0, 128.4, 127.9, 127.5, 120.1, 114.7, 62.2, 56.0, 53.1, 52.2, 29.3 (m), 29.1 (m), 22.6, 14.6 ppm;

HRMS (ESI-TOF, \(m/z\)): calcd for C\(_{26}\)H\(_{23}\)D\(_8\)N\(_4\)O\(_4\) [M+H]\(^+\) 471.2842; found 471.2845.
N-(2-(Methyl-d2)propan-2-yl)-1,1,1,3,3,3-d6-4-(methylthio)aniline (125). On 0.35 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO2, 4:1 hexanes:EtOAc) furnished amine 125 as a pale yellow oil (54.4 mg, 77%).

\[ R_f = 0.65 \] (silica gel, 4:1 hexanes:EtOAc);

\[^1H\text{ NMR (600 MHz, MeOH-d}_4\text{): } \delta 7.15 \text{ (d, } J = 8.6 \text{ Hz, 2 H), 6.83 \text{ (d, } J = 8.6 \text{ Hz, 2 H),} \]

\[ 2.38 \text{ (s, 3 H), 1.22 (m, 1 H) ppm;} \]

\[^{13}C\text{ NMR (151 MHz, MeOH-d}_4\text{): } \delta 146.3, 130.7, 129.2, 121.6, 52.4, 29.3 \text{ (quintet, } J = 19.3 \text{ Hz), 29.1 \text{ (septet, } J = 17.9 \text{ Hz), 18.1 ppm;} \]

HRMS (ESI-TOF, m/z): calcd for C11H10D8NS [M+H]^+ 204.1657; found 204.1660.

3-Methoxy-4-(3-methyl-1H-1,2,4-triazol-1-yl)-N-(1-methylcyclohexyl)aniline (126) (Conducted at Bristol-Myers Squibb, Process Department). On 0.5 gram scale (2.1 mmol), general procedure A was followed and purification by flash column chromatography (SiO2, 40:1 DCM:MeOH) furnished amine 126 as a thick, slightly pink oil (307.7 mg, 48%).

\[ R_f = 0.42 \] (silica gel, 19:1 DCM:MeOH);

\[^1H\text{ NMR (500 MHz, CDCl}_3\text{): } \delta 8.32 \text{ (s, 1 H), 7.31 \text{ (d, } J = 8.7 \text{ Hz, 1 H), 6.35 \text{ (d, } J = 8.5,1 \text{ Hz), 6.31 \text{ (s, 1 H), 3.78 \text{ (s, 3 H), 3.78 – 3.74 (m, 1 H), 2.45 \text{ (s, 3 H), 1.87 (m, 2 H), 1.51 (m, 7 H), 1.35 (m, 4 H) ppm;} \]

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\text{): } \delta 160.2, 152.4, 147.9, 144.5, 125.7, 116.8, 107.8, 99.5, 55.6, 53.3, 38.1, 26.8, 25.6, 22.0, 13.9 ppm; \]

HRMS (ESI-TOF, m/z): calcd for C17H25N4O [M+H]^+ 301.2023; found 301.2025.

N-(2-Methyl-1-phenylpropan-2-yl)cyclopentanamine (127). On 0.2 mmol scale, general procedure A was followed and purification by preparative TLC (SiO2, 9:1 DCM:MeOH) furnished amine 127 as a colorless film (5.3 mg, 24%).

\[ R_f = 0.31 \] (silica gel, 9:1 DCM:MeOH);
$^1$H NMR (400 MHz, MeOH-$d_4$): δ 7.37 – 7.26 (m, 5 H), 3.90 – 3.82 (m, 1 H), 3.00 (s, 2 H), 2.27 – 2.19 (m, 2 H), 1.88 – 1.81 (m, 2 H), 1.77 – 1.66 (m, 4 H), 1.31 (s, 6 H) ppm;
$^{13}$C NMR (151 MHz, MeOH-$d_4$): δ 136.0, 131.9, 129.6, 128.6, 62.0, 56.1, 45.5, 33.1, 24.9, 24.1 ppm;
HRMS (ESI-TOF, m/z): calcd for C$_{15}$H$_{24}$N [M+H]$^+$ 218.1903; found 218.1904.

2,3-Dimethyl-N-phenethylbutan-2-amine (128). On 0.2 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO$_2$, 92:8 DCM:MeOH) furnished amine 128 as a white film (10.2 mg, 20%).

$R_f$ = 0.24 (silica gel, 95:5 DCM:MeOH);

$^1$H NMR (400 MHz, MeOH-$d_4$): δ 7.37 – 7.25 (m, 5 H), 3.20 – 3.16 (m, 2 H), 3.02 – 2.95 (m, 2 H), 2.02 (septet, $J$ = 6.9 Hz, 1 H), 1.30 (s, 6 H), 0.99 (d, $J$ = 6.8 Hz, 6 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): δ 138.0, 130.0, 129.7, 128.3, 43.5, 34.5, 34.1, 30.7, 21.2, 17.2 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{14}$H$_{24}$N [M+H]$^+$ 206.1903; found 206.1904.

$N^1$-(2-Methyl-1-phenylpropan-2-yl)-$N^2$-phenylethane-1,2-diamine (129). On 0.1 mmol scale, general procedure A was followed and purification by preparative TLC (SiO$_2$, 2:2:0.5 hexanes:EtOAc:MeOH) furnished amine 129 as a pale yellow oil (5.6 mg, 21%).

$R_f$ = 0.51 (silica gel, 2:2:0.5 hexanes:EtOAc:MeOH);

$^1$H NMR (600 MHz, MeOH-$d_4$): δ 7.25 – 7.19 (m, 3 H), 7.16 – 7.12 (m, 4 H), 6.68 – 6.64 (m, 3 H), 3.30 (t, $J$ = 6.0 Hz, 2 H), 2.93 (t, $J$ = 6.0 Hz, 2 H), 2.76 (s, 2 H), 1.10 (s, 6 H) ppm;

$^{13}$C NMR (151 MHz, MeOH-$d_4$): δ 150.0, 138.9, 131.6, 130.1, 129.1, 127.4, 118.3, 114.1, 49.6, 47.0, 44.4, 42.0, 26.3 ppm;

HRMS (ESI-TOF, m/z): calcd for C$_{18}$H$_{25}$N$_2$ [M+H]$^+$ 269.2012; found 269.2011.

$N^1$-(1-Methylcyclohexyl)-$N^2$-phenylethane-1,2-diamine (130). On 0.1 mmol scale, general procedure A was followed and
purification by preparative TLC (SiO₂, 2:2:0.5 hexanes:EtOAc:MeOH) furnished amine 130 as a pale yellow oil (5.8 mg, 25%).

\( R_f = 0.22 \) (silica gel, 2:2:0.5 hexanes:EtOAc:MeOH);

\(^1\)H NMR (600 MHz, MeOH-\( d_4 \)): \( \delta \) 7.15 – 7.13 (m, 2 H), 6.70 – 6.66 (m, 3 H), 3.35 (t, \( J = 6.0 \) Hz, 2 H), 2.97 (t, \( J = 6.0 \) Hz, 2 H), 1.64 – 1.45 (m, 8 H), 1.36 – 1.30 (m, 2 H), 1.22 (s, 3 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\( d_4 \)): \( \delta \) 149.6, 130.2, 118.7, 114.2, 49.6, 43.4, 41.0, 36.7, 26.5, 23.1, 22.3 ppm;


On 0.4 mmol scale, general procedure A was followed and purification by flash column chromatography (SiO₂, 10:1→3:1→2:3 hexanes:EtOAc) furnished amine S10 as a colorless oil (25.1 mg, 35%), together with bisalkylated adduct S11 as a colorless oil (11.8 mg, 11%).

3-Methyl-3-(phenylamino)butan-1-ol (S10).

\( R_f = 0.42 \) (silica gel, 2:3 hexanes:EtOAc);

\(^1\)H NMR (500 MHz, MeOH-\( d_4 \)): \( \delta \) 7.17 – 7.14 (m, 2 H), 6.88 (dd, \( J = 10.2, 1.2 \) Hz, 2 H), 6.81 – 6.78 (m, 1 H), 3.74 (t, \( J = 8.4 \) Hz, 2 H), 1.90 (t, \( J = 8.4 \) Hz, 2 H), 1.30 (s, 6 H) ppm;

\(^{13}\)C NMR (151 MHz, MeOH-\( d_4 \)): \( \delta \) 147.8, 129.7, 120.6, 120.4, 59.8, 54.5, 44.3, 28.7 ppm;

HRMS (ESI-TOF, \( m/z \)): calcd for C\(_{11}\)H\(_{18}\)NO [M+H]\(^+\) 180.1383, found 180.1391.

3-(((4-hydroxy-2-methylbutan-2-yl)(phenyl)amino)oxy)-3-methylbutan-1-ol (S11).

\( R_f = 0.25 \) (silica gel, 2:3 hexanes: EtOAc);

\(^1\)H NMR (500 MHz, MeOD-\( d_4 \)): \( \delta \) 7.27 – 7.24 (m, 3 H), 7.12 – 7.09 (m, 2 H), 3.78 – 3.71 (m, 2 H), 3.70 – 3.60 (m, 2 H), 1.86 – 1.79 (m, 1 H), 1.77 – 1.71 (m, 2 H), 1.69 – 1.64 (m, 1 H), 1.21 (s, 3 H), 1.12 (s, 3 H), 1.05 (s, 3 H), 0.88 (s, 3 H) ppm;
\[ ^{13}\text{C NMR (151 MHz, MeOD-}\text{d}_4): \delta 152.5, 128.5, 127.4, 126.2, 80.9, 62.4, 60.0, 59.5, 45.3, 42.2, 27.3, 26.1, 25.4, 25.1 \text{ ppm;} \]

HRMS (ESI-TOF, m/z): calcd for C\text{16}H\text{28}NO\text{3} [M+H]\text{^+}: 282.2069, found: 282.2064.

On 0.4 mmol scale, general procedure B was followed but the reaction was quenched after 2 min. Purification by flash column chromatography (SiO\text{2}, 10:1→4:1 hexanes:EtOAc) furnished amine S\text{13} as a light pink oil (20.7 mg, 22%).

\textit{N-(1-Methylcyclopentyl)-N-(4-(methylthio)phenyl)hydroxylamine (S\text{13}).}

\[ R_f = 0.38 \text{ (silica gel, 7:1 hexanes:EtOAc);} \]

\[ ^1\text{H NMR (600 MHz, MeOH-}\text{d}_4): \delta 7.22 \text{ (d, } J = 8.7 \text{ Hz, } 2 \text{ H}), 7.17 \text{ (d, } J = 8.7 \text{ Hz, } 2 \text{ H),} \]

2.45 (s, 3 H), 2.10 – 2.03 (m, 2 H), 1.79 – 1.77 (m, 2 H), 1.66 – 1.64 (m, 2 H), 1.45 – 1.41 (m, 2 H), 1.06 (s, 3 H) ppm;

\[ ^{13}\text{C NMR (151 MHz, MeOH-}\text{d}_4): \delta 150.2, 134.9, 127.7, 125.0, 73.2, 38.9, 24.7, 20.6, 16.6 \text{ ppm;} \]

HRMS (ESI-TOF, m/z): calcd for C\text{13}H\text{20}NO\text{S} [M+H]\text{^+} 238.1260, found 238.1260.

On 0.043 mmol scale, general procedure B was followed without addition of any donor olefin, and purification by flash column chromatography (SiO\text{2}, 10:1→4:1 hexanes:EtOAc) furnished amine 16 as a colorless oil (8.5 mg, 89%) and recovered starting material (0.9 mg, 9%).
A solution of the nitro compound S14 (7.5 mg, 0.046 mmol, 1 equiv) and Fe(acac)$_3$ (4.9 mg, 0.0138 mmol, 30 mol%) in EtOH (0.25 mL) was degassed by argon bubbling for 15 min. Then, PhSiH$_3$ (11.3 µL, 0.092 mmol, 2 equiv) was added to the reaction under argon. After heating in an oil bath preheated to 60 °C with stirring for 1 h, the reaction mixture was cooled to room temperature, diluted with brine and extracted with Et$_2$O three times. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude product was then purified by flash column chromatography (SiO$_2$, 2:1→1:1 hexanes:EtOAc) to furnish amine S15 as a colorless oil (4.0 mg, 58%), whose spectroscopic data was identical to that reported in the literature (50).
Heat Energy Evaluation (taking the reaction to form product 126 as example).

Since a nitro aromatic compound (potentially energetic) is used as a starting material and thermal events were qualitatively observed for this transformation, we decided to study the reaction heat flow (2 g scale) in a 400 mL Easymax reactor with the jacket temperature set at 20 °C to gauge the severity of any possible thermal event. At 10% of the reactor capacity, when a single charge of each reagent was introduced into the process stream, no dramatic temperature spikes were observed, with the exception being a ~2 °C internal temperature rise upon silane addition. The heat energy slowly dissipated over a 2 h period as the reaction reached completion. These results alleviated concerns of an induction period and the possibility of a runaway thermal event should the scale of the reaction be increased to >1 g, but active batch cooling should always be implemented for any on scale processing.

![Temperature profile of the amination reaction.](image)

**Fig. S18.** Temperature profile of the amination reaction.
X-ray crystallographic data for 93.

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). A 0.115 x 0.053 x 0.044 mm red block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 175(2) K using f and v scans. Crystal-to-detector distance was 40 mm using variable exposure time (30s or 60s) depending on q with a scan width of 1.0°. Data collection was 100% complete to 25.00° in q. A total of 75632 reflections were collected covering the indices, -14<=h<=13, -23<=k<=23, -18<=l<=18. 6312 reflections were found to be symmetry independent, with a Rint of 0.0793. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S1-S3.

<table>
<thead>
<tr>
<th>Table S1. Crystal data and structure refinement for 93.</th>
</tr>
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<tbody>
<tr>
<td>Identification code</td>
</tr>
<tr>
<td>Empirical formula</td>
</tr>
</tbody>
</table>

Fig. S19. X-ray crystallographic structure of 93.
Table S2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for CCDC 1050751. U(eq) is defined as one third of the trace of the orthogonalized Uᵢⱼ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
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<tr>
<td>O(1)</td>
<td>1944(2)</td>
<td>11742(1)</td>
<td>4132(1)</td>
<td>25(1)</td>
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Table S3. Bond lengths [Å] and angles [°] for CCDC 1050751.

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<thead>
<tr>
<th>Bond</th>
<th>Length/°</th>
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<tbody>
<tr>
<td>O(1)-C(2)</td>
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<tr>
<td>O(1)-C(1)</td>
<td>1.4336(18)</td>
</tr>
<tr>
<td>O(2)-C(7)</td>
<td>1.4438(18)</td>
</tr>
<tr>
<td>N(1)-C(2)</td>
<td>1.3181(19)</td>
</tr>
<tr>
<td>N(1)-C(3)</td>
<td>1.3549(18)</td>
</tr>
<tr>
<td>N(2)-C(4)</td>
<td>1.4383(18)</td>
</tr>
<tr>
<td>N(2)-C(5)</td>
<td>1.505(2)</td>
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<tr>
<td>C(2)-C(13)</td>
<td>1.392(2)</td>
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<tr>
<td>C(3)-C(4)</td>
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<tr>
<td>C(4)-C(12)</td>
<td>1.398(2)</td>
</tr>
<tr>
<td>C(5)-C(8)</td>
<td>1.531(2)</td>
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<tr>
<td>C(5)-C(11)</td>
<td>1.538(2)</td>
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<tr>
<td>C(5)-C(6)</td>
<td>1.5469(19)</td>
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<td>C(6)-C(7)</td>
<td>1.543(2)</td>
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<tr>
<td>C(7)-C(9)</td>
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<td>Bond/Distance</td>
<td>Value</td>
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<td>------------------</td>
<td>-------------</td>
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<tr>
<td>C(12)-C(13)</td>
<td>1.376(2)</td>
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<td>C(2)-O(1)-C(1)</td>
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<td>116.31(13)</td>
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<td>C(4)-N(2)-C(5)</td>
<td>115.92(12)</td>
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<tr>
<td>N(1)-C(2)-O(1)</td>
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<tr>
<td>N(1)-C(3)-C(4)</td>
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<td>C(8)-C(5)-C(11)</td>
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<td>N(2)-C(5)-C(6)</td>
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<td>C(8)-C(5)-C(6)</td>
<td>107.32(12)</td>
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<td>C(11)-C(5)-C(6)</td>
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<td>C(7)-C(6)-C(5)</td>
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<td>115.28(12)</td>
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<td>C(9)-C(7)-C(6)</td>
<td>107.68(12)</td>
</tr>
<tr>
<td>C(13)-C(12)-C(4)</td>
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<tr>
<td>C(12)-C(13)-C(2)</td>
<td>118.52(14)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:
X-ray crystallographic data for 121.

Fig. S20. X-ray crystallographic structure of 121.

Single crystal X-ray diffraction analysis has established the chemical structure for CCDC 1050750 as the 2-amino substituted phenylacetamide shown above. The crystalline structure is neat (non-solvated/anhydrous) and belongs to the monoclinic $P2_1/c$ space group with a single conformer in the asymmetric unit ($Z' = 1$). The twist of the butanamide towards the acetamide is stabilized by the intramolecular hydrogen bond interaction of the acetamide NH and the butanamide carbonyl groups ($d_{N\cdots O} = 2.74\text{Å}$). This combined with the sp$^3$ geometry of the aniline causes the H-bonded ring to be undulated where the conformation can best be described as an envelope. Molecules are assembled into 2D layers which are stacked perpendicular to the (001) crystallographic set of planes. This supramolecular motif is supported by an intermolecular hydrogen bond network formed through the terminal NH$_2$ group which serves as a hydrogen bond donor to both the acetamide carbonyl and aniline N ($d_{N\cdots O} = 3.15\text{Å}$, $d_{N\cdots N} = 2.87\text{Å}$), respectively propagating along the [100] and [010] directions in the crystals. The aniline NH group is not engaged in any intermolecular interactions as a hydrogen bond donor.

*Treatment of Hydrogen Atoms*: The position of the aniline hydrogen observed from the difference maps was used to determine its coordinates. The positions of all other hydrogen atoms, although also observed in the difference maps, were calculated from an idealized geometry with standard bond lengths and angles. All hydrogen positions were refined using a riding model.

<table>
<thead>
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<th>Table S4. Crystal data and structure refinement for 121.</th>
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<tbody>
<tr>
<td>Refcode</td>
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S85
<table>
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<th>Property</th>
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</thead>
<tbody>
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<td>Formula weight</td>
<td>249.31</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space Group</td>
<td>$P2_1/c$</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 9.1681(2),\text{Å}$, $a = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 12.6016(2),\text{Å}$, $b = 100.3440(10)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 11.8485(2),\text{Å}$, $g = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$V = 1346.64(4),\text{Å}^3$</td>
</tr>
<tr>
<td>No. of molecules/cell</td>
<td>$Z = 4; Z' = 1$</td>
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<tr>
<td>Calculated crystal density</td>
<td>1.230 g cm$^{-3}$</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.686 mm$^{-1}$</td>
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<tr>
<td>Crystal growth</td>
<td>EtOAc, reflux to room temp.</td>
</tr>
<tr>
<td>Crystal morphology</td>
<td>colorless prisms</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>0.120 x 0.100 x 0.030</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>RT (~296K)</td>
</tr>
<tr>
<td>$q_{\text{max}}$ ($^\circ$)</td>
<td>61.357 (Cu Ka)</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>10610</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2079 [R(int) = 0.0240]</td>
</tr>
<tr>
<td>No. of observed reflections ($I \geq 2s$)</td>
<td>1834</td>
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<tr>
<td>No. of parameters refined</td>
<td>167</td>
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<td>No. of reflections used</td>
<td>2079</td>
</tr>
<tr>
<td>$-0.219 \leq \Delta\rho \leq 0.310$ e/Å$^3$</td>
<td></td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0382, wR2 = 0.1027</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0427, wR2 = 0.1057</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.069</td>
</tr>
</tbody>
</table>
HN

Me

Me

NHAc

36
\begin{align*}
\text{NHAc} & \quad \text{OMe} \\
\text{Me} & \quad \text{NHAc}
\end{align*}

\text{f1 (ppm)}

\begin{align*}
10.5 & \quad 10.0 & \quad 9.5 & \quad 9.0 & \quad 8.5 & \quad 8.0 & \quad 7.5 & \quad 7.0 & \quad 6.5 & \quad 6.0 & \quad 5.5 & \quad 5.0 & \quad 4.5 & \quad 4.0 & \quad 3.5 & \quad 3.0 & \quad 2.5 & \quad 2.0 & \quad 1.5 & \quad 1.0 & \quad 0.5 & \quad 0.0 & \quad -0.5 & \quad -1.0
\end{align*}
\[
\begin{align*}
&\text{H} \\
&\text{N} \\
&\text{O} \\
&\text{H} \\
&\text{Bu} \\
&113
\end{align*}
\]
References


doi:10.1021/ol026200s