Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201801582

Link to VoR: http://dx.doi.org/10.1002/adsc.201801582

10.1002/adsc.201801582

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Copper-Catalyzed Intermolecular Hydroamination of Arylamines or Aza-Heterocycles with Nitrostyrene Derivatives

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Received:

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract. A new copper-catalyzed protocol for the intermolecular anti-Markovnikov addition of arylamines or heterocycles to terminal and unsymmetrical 1,2-disubstituted vinylarenes has been developed. The direct hydroamination is catalyzed by a readily available *N*-heterocyclic carbene-based copper complex and KO*t*-Bu, and the use of MeOH as an additive enhances the reactivity. The method provides a broad range of new and versatile amine compounds bearing various functional groups in good to excellent yields.

Keywords: Copper catalysis; hydroamination; anti-Markovnikov selectivity; vinylarenes; *N*-heterocyclic carbene

Introduction

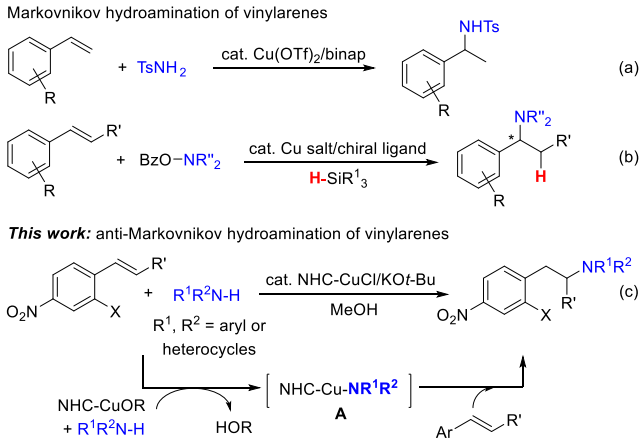
Hydroamination of a carbon-carbon double bond or triple bond is one of the most atom efficient and simple routes for synthesizing various amines.[1] Due to the significance of nitrogen-containing compounds in organic synthesis and medicinal chemistry, a number of efficient and selective catalytic systems for the hydroamination of unsaturated compounds with nucleophilic amines such as alkylamines, (hetero)arylamines, amides, carbamates, and sulfonamides have been intensively studied. In particular, early- and late-transition metal catalysts have played an important role in promoting these transformations and controlling the chemo-, regio- and stereoselectivities.[2]

Among the numerous metal-catalyzed hydroamination reactions, the copper-catalyzed direct addition of amines to alkenes is an attractive and practical method for the synthesis of aliphatic amines as it uses a relatively inexpensive, environmentally benign and easy-to-handle copper catalyst and easily accessible alkene substrates. In the past decade, a variety of copper catalysts have been utilized for intramolecular and intermolecular hydroamination reactions of alkenes,[3],[4] alkynes,[5] and allenes.[6] Compared to the catalytic processes related to intramolecular hydroaminations, the corresponding intermolecular reactions have been less studied since controlling the regioselectivity (Markovnikov vs. anti-Markovnikov selectivity) is challenging. To date, only a few examples of Cu-catalyzed direct intermolecular hydroaminations of unsymmetrical alkenes have been reported,[3] and general approaches for accessing anti-Markovnikov amine products remain rare. The regioselectivity of Cu-catalyzed hydroaminations is known to be influenced by the catalytic system. For example, Hii and coworkers explored the first intermolecular hydroamination of vinylarenes with arylsulfonamides promoted by copper(II) triflate and a phosphine ligand.[3c] The reaction was thought to be catalyzed by an acidic proton generated from the copper triflate system, resulting in Markovnikov selectivity (Scheme 1a).[7] On the other hand, Gunnoe and coworkers described the anti-Markovnikov addition of aniline to styrene derivatives by using a well-defined copper-amido catalyst[8] complexed with an *N*-heterocyclic carbene (NHC) ligand.[3a] Although these two reported reactions are efficient and highly regioselective, the methods still suffer from some limitations: the NHC-Cu catalyst requires a multistep synthesis, the substrate scope is limited to only terminal styrenes, and the amine sources are limited to compounds such as tosyl or nosyl amides, aniline and benzylamines. Therefore, the development of a new copper-catalyzed system with a broader substrate scope and improved operational simplicity is of practical and synthetic interest.

As an alternative approach regarding the Cu-catalyzed amination reaction with unsymmetrical alkenes, Miura, Buchwald and coworkers[9] independently pioneered copper-hydride-catalyzed formal hydroaminations using *O*-benzoylhydroxylamines as electrophilic amine sources and hydrosilanes as copper hydride sources (Scheme 1b).[10] This methodology allows the synthesis of

Markovnikov amine products from vinylarenes with high regio- and enantioselectivity.[11]

In our previous studies, we demonstrated an aza-Michael addition of (hetero)aryl amines to α,β-unsaturated carbonyls catalyzed by a copper complex generated in situ from the reaction of a phosphine or an imidazolinium salt with CuCl and KO*t*-Bu under mild conditions.[12] As a continuation of our studies on the synthesis of amine compounds from alkenes using a copper catalyst, we report herein an efficient and mild Cu-catalyzed intermolecular anti-Markovnikov hydroamination of vinylarenes with arylamines or heterocycles (Scheme 1c). A readily prepared NHC-CuCl species in the presence of KO*t*-Bu and MeOH promoted the addition of the amine to various mono- and 1,2-disubstituted vinylarenes, providing various novel arylamine and azole products in good to excellent yields.

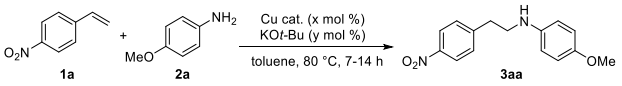


Scheme 1. Cu-catalyzed regioselective hydroamination reactions

Results and Discussion

We commenced our studies with 4-nitrostyrene (**1a**) and 4-methoxyaniline (**2a**) as the model substrates, as shown in Table 1. Guided by our previous studies on aza-Michael reactions,[12] we initially attempted the addition of amine **2a** to **1a** in the presence of **IPrCuCl** and KO*t*-Bu in toluene at ambient temperature. However, the reaction did not proceed (<2% of **3aa**). When the reaction temperature was increased to 80 °C, desired aminated product **3aa** was obtained in 30% yield with >98% anti-Markovnikov selectivity (entry 1). The result shown in entry 2 indicated that the use of MeOH as an additive promoted the amination and improved the yield of **3aa** (63%). It is noteworthy that previous work on Cu-catalyzed intramolecular hydroamination of aminoalkenes by Sawamura and coworkers has shown that MeOH as a protic solvent plays an significant role in enhancing yield due to the rapid protonation of the copper-carbon bond generated in situ.[4a] To optimize the catalytic system, various imidazolium salts **L1**-**L4** as NHC precursors were examined, but reaction conditions using a preformed **IPrCuCl** species were more efficient (entries 3-6). Under these reaction conditions using imidazolium salts **L1**-**L4**, it was found that 11-49% of nitrostyrene **1a** was decomposed presumably owing to polymerization. As the concentration of the reaction solution increased, the amination proceeded more effectively (entries 7-8). Complete conversion was observed within 7 hours in the presence of 5 mol % **IPrCuCl** and the reaction generated only anti-Markovnikov product **3aa** (>98% yield, entry 8). When the amination was performed under non-inert conditions, the efficiency was significantly reduced, affording the desired amine **3aa** in 41% yield along with decomposition of 37% of nitrostyrene **1a** (entry 9). As illustrated in entries 10-12 of Table 1, the NHC ligand, CuCl, and KO*t*-Bu were all essential for promoting the addition of the amine to nitrostyrene **1a**. Based on these results, we assumed that the NHC-copper amido complex **A** in Scheme 1,[8],[13] the key catalytic species, might be generated from the reaction of the in situ-formed NHC-CuO*t*-Bu species with aniline. The copper-amido species **A** was selectively inserted into nitrostyrene **1a** to form a C-N bond at the terminal carbon of the double bond, creating a C-Cu bond on the internal carbon. Then, the alkylcopper intermediate reacted with aniline to regenerate the Cu-amido species with concomitant release of the aminated product. As suggested by Sawamura and coworkers,[4a] at this stage, the importance of methanol can be explained by the assumption that MeOH reacts more efficiently with the alkylcopper intermediate than with the aniline substrate, facilitating the regeneration of the catalytic species.

Table 1. Optimization of hydroamination of 4-methoxyaniline (**2a**) to 4-nitrostyrene[a]



entry	Cu catalyst (mol %)	KO*t*-Bu (mol %)	MeOH (equiv)	conc. (M)	time (h)	conv (%)[b]	yield (%)[b]
1	**IPrCuCl** (10)	10	0	0.2	14	30	30
2	**IPrCuCl** (10)	10	1	0.2	14	68	63
3	**L1** + CuCl (10)	20	1	0.2	14	64	53
4	**L2** + CuCl (10)	20	1	0.2	14	85	36
5	**L3** + CuCl (10)	20	1	0.2	14	58	32
6	**L4** + CuCl (10)	20	1	0.2	14	68	43
7	**IPrCuCl** (5)	5	1	0.6	7	81	80
8	**IPrCuCl** (5)	5	1	1.0	7	>98	>98
9[c]	**IPrCuCl** (5)	5	1	1.0	7	78	41
10	**IPrCuCl** (5)	0	0	1.0	7	<2	<2
11	**CuCl** (5)	5	0	1.0	7	<2	<2
12	no	5	0	1.0	7	58	<2

[a]Reaction conditions: nitrostyrene **1a** (0.2 mmol), aniline **2a** (0.24 mmol), toluene (0.2-1.0 M) under N_2. 10 mol % of **L1**-**L4** was used. [b]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c]The reaction was carried out under open air conditions.

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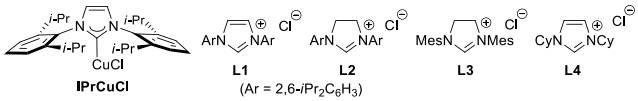
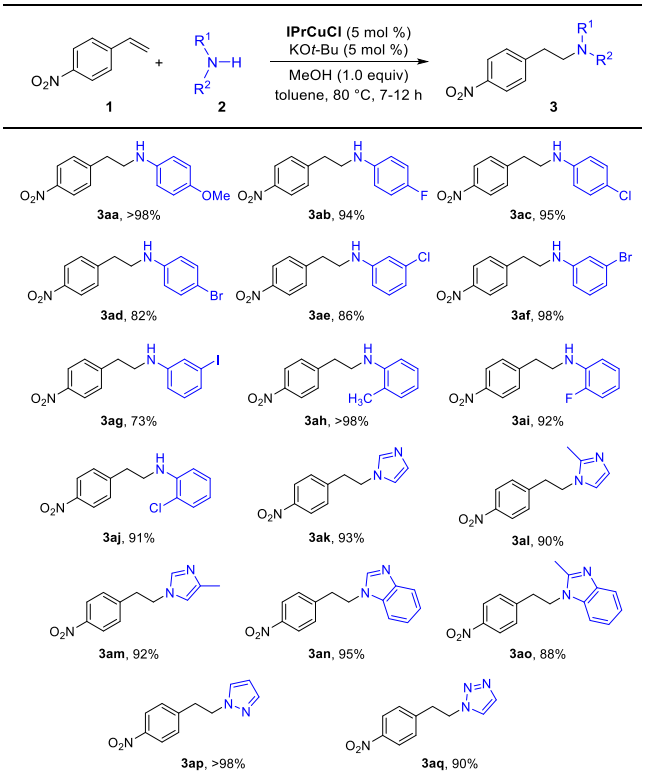


With the optimal conditions in hand, we explored the generality of the amination. A range of arylamines and heterocycles were efficiently and selectively added to nitrostyrene **1a** with a catalyst loading of 5 mol % and 1 equiv MeOH, as depicted in Table 2. The Cu-catalyzed hydroamination reactions with aniline derivatives bearing methoxy, methyl, or halogen groups at the *para*, *meta*, and *ortho* positions proceeded well, affording corresponding amine products **3aa**-**3aj** in good to excellent yields (up to >98%). Notably, sterically demanding anilines **2h**-**2j** with substituents at the *ortho* position required a longer reaction time (7 h vs. 12 h). Substrates with heterocyclic substituents including imidazole **2k**, methyl imidazoles **2l**-**2m**, benzimidazoles **2n**-**2o**, pyrazole **2p**, and triazole **2q**, which have served as valuable building blocks for biologically active molecules, were also successfully transformed to the desired amines (**3ak**-**3aq**) in 88 to >98% yields. Notably, 4-methyl-*1H*-imidazole (**2m**) was selectively added to nitrostyrene **1a**, affording only 4-methylimidazole product **3am** (vs. 5-methylimidazole) presumably due to steric hindrance.[14] However, these catalytic reaction conditions were not effective in the hydroamination with halogen-substituted styrenes. When the catalytic reaction was carried out with *p*-chlorostyrene or *p*-bromostyrene using **2a**, the reaction did not proceed (2% conv).

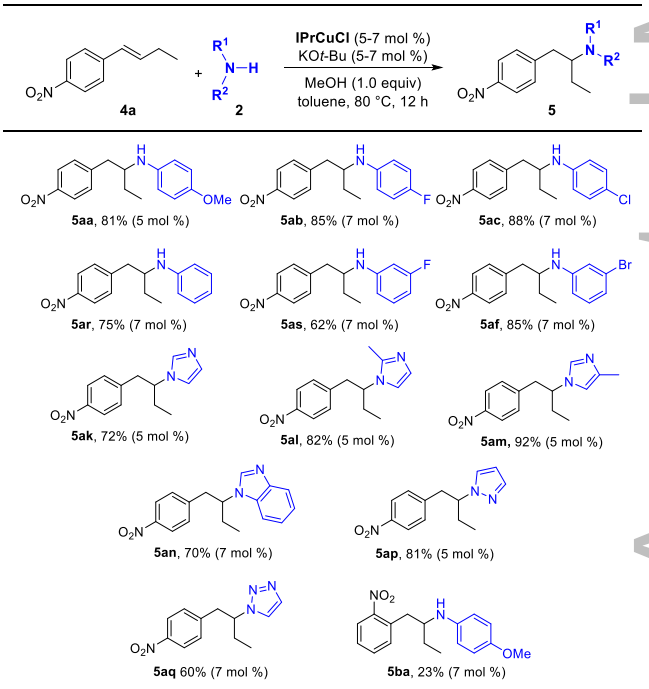
Table 2. Cu-catalyzed hydroamination of 4-nitrostyrene with various anilines and azoles[a],[b]



[a]Reaction conditions: nitrostyrene **1a** (0.40 mmol), amine **2** (0.48 mmol), MeOH (0.40 mmol), **IPrCuCl** (5 mol %), KO*t*-Bu (5 mol %), toluene (1.0 M) under N_2. [b]Yields of the isolated products. The reaction time was 7 h for **3aa**-**3ag** and 12 h for **3ah**-**3aq**.

Next, we investigated the addition of amines to challenging unsymmetrical 1,2-disubstituted alkenes, which are rarely studied as substrates for Cu-catalyzed intermolecular hydroaminations, as illustrated in Table 3. To our delight, when *p*-nitro-(*E*)-*β*-ethyl styrene (**4a**) was treated with 4-methoxyaniline under the established reaction conditions, only desired regioisomer **5aa** was produced, albeit less efficiently (81% yield of **5aa** vs. >98% yield of **3aa**) and more slowly (12 h vs. 7 h) compared with the addition to nitrostyrene **1a**. Various anilines with fluoro, chloro, and bromo substituents at the *para* or *meta* positions of the phenyl group were employed in this catalytic reaction, and desired amines **5ab**-**5af** were obtained in 62-88% yields. In addition, the Cu-catalyzed reactions of a variety of heterocycles including imidazoles, pyrazole, and triazole with *β*-ethyl styrene **4a** provided corresponding amines **5ak**-**5aq** in moderate to good yields (60-92%). However, the reaction with a sterically demanding *ortho*-nitrostyrene (**4b**) was not effective using these catalytic reaction conditions, affording amine product **5ba** in only 23% yield.

Table 3. Cu-catalyzed hydroamination of **4a** with anilines and azoles [a],[b]



[a]Reaction conditions: *β*-ethyl styrene **4a** (0.40 mmol), amine **2** (0.48 mmol), MeOH (0.40 mmol), **IPrCuCl** (5-7 mol %), KO*t*-Bu (5-7 mol %), toluene (1.0 M) under N_2. [b]Yields of the isolated products.

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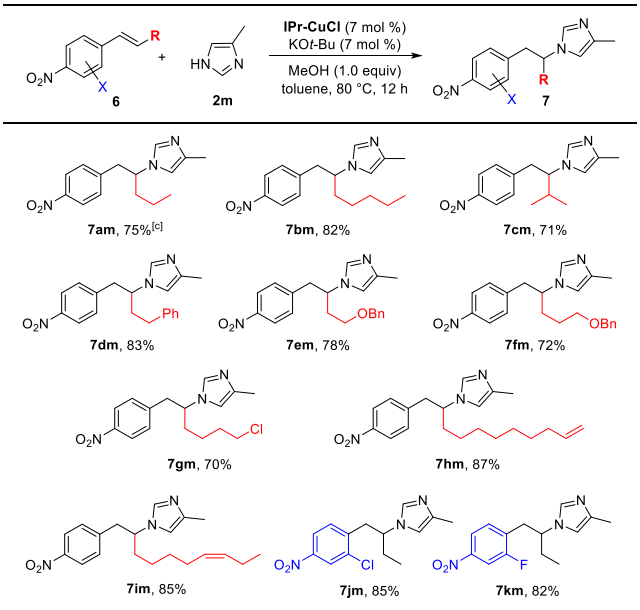
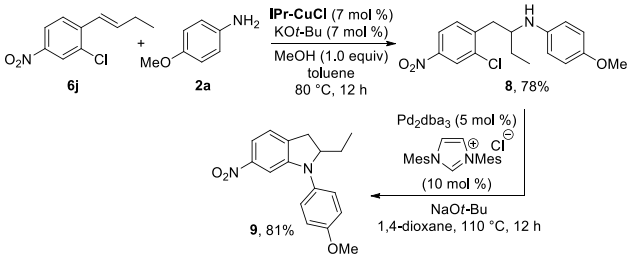
Encouraged by the successful Cu-catalyzed regioselective hydroamination of unsymmetrical alkene **4** with anilines and heterocycles, we extended the substrate scope to a variety of *β*-substituted styrene derivatives **6**, as shown in Table 4. All transformations were highly regioselective in that 4-methylimidazole (**2m**) was added at the *β*-position of vinylarenes **6**, providing only the anti-Markovnikov 4-methylimidazole products (**7am**-**7km**). Alkenes **6a**-**6d**, with *p*-nitrophenyl and various alkyl substituents such as propyl, pentyl, isopropyl, and phenethyl groups, were successfully converted to corresponding amine products **7am**-**7dm** in 71%-83% yields. This copper-catalyzed reaction is tolerant of functional groups such as a chloro, benzyl ether, and alkene substituents on the substrates, affording new and versatile functionalized amine products **7em**-**7im** in 70-87% yields. When *p*-nitro-(*E*)-*β*-ethyl styrenes **6j**-**6k** bearing a chloro or a fluoro group at the *ortho* position of the phenyl moiety were subjected to the catalytic reaction conditions, aminations with **2m** also proceeded well and gave desired amines **7jm**-**7km**, which could be utilized for further organic transformations, in good yields (82-85%).

Table 4. Cu-catalyzed hydroamination of various *β*-substituted styrenes with **2m**[a],[b]



[a]Reaction conditions: styrene **6** (0.40 mmol), methylimidazole **2m** (0.48 mmol), MeOH (0.40 mmol), **IPrCuCl** (7 mol %), KO*t*-Bu (7 mol %), toluene (1.0 M) under N_2. [b]Yields of the isolated products. [c]5 mol % of **IPrCuCl** was used.

The utility of the amine products obtained from our newly developed hydroamination was demonstrated in the synthesis of indoline **9**, as shown in Scheme 2.[15] The Cu-catalyzed hydroamination of *β*-substituted styrene **6j** (with 2-chloro and 4-nitro substituents on the phenyl group) with *p*-anisidine (**2a**) produced amine **8** in 78% yield, which underwent a Pd-catalyzed cyclization to afford indoline **9** in 81% yield.



Scheme 2. Synthesis of indoline **9**

Conclusion

We have developed an efficient and anti-Markovnikov-selective copper-catalyzed intermolecular hydroamination of nitrostyrene derivatives with various arylamines and heterocycles. A readily accessible NHC-based copper catalyst combined with KO*t*-Bu plays a key role in promoting the addition of relatively less nucleophilic arylamines or heterocycles to monosubstituted and even unsymmetrical 1,2-disubstituted vinylarenes with high anti-Markovnikov selectivity (>99:1). The catalytic process enables the synthesis of new and synthetically versatile amine compounds, including aniline, imidazole, pyrazole, and triazole derivatives, in good to excellent yields. The use of inexpensive and easy-to-handle copper catalysts, the good functional group tolerance, the high efficiency, the excellent regioselectivity, the broad substrate scope and the operational simplicity make the developed methodology attractive and practical. Further studies of the catalytic addition of amines to other types of alkenes are ongoing in our laboratory.

Experimental Section

General: Infrared (IR) spectra were recorded on a ABB MB3000 FT-IR spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 ppm). High-resolution mass spectra (HRMS) were performed at the Korea Basic Science Institute for technical assistance using an electrospray ionization (ESI) time-of-flight mass spectrometer. Unless otherwise noted, all reactions were carried out with distilled solvents under an atmosphere of dry N_2 in oven-dried (130 °C) glassware. Toluene and 1,4-dioxane were purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. Acetonitrile was purified by distillation from CaH_2 immediately prior to use. Methyl alcohol was purified by distillation from sodium immediately prior to use. All work-up and purification procedures were carried out with reagent grade solvents in air. An **IPrCuCl** complex was synthesized according to reported experimental procedures.[16] A variety of vinylarenes were prepared according to reported experimental procedures.[17]

Representative experimental procedure for the synthesis of NO_2-substituted styrenes

(*E*)-1-(But-1-en-1-yl)-4-nitrobenzene (4a). 4-Nitrobenzaldehyde (1.06 g, 6.42 mmol), butyraldehyde (0.720 mL, 8.03 mmol), malononitrile (1.06 g, 16.1 mmol) and acetonitrile (40 mL) were added into a 100 mL round-bottom flask, and then acetic acid (0.689 mL, 12.0 mmol) was added. The reaction was allowed to stir for 10 min, and then ammonium acetate (0.619 mg, 8.03 mmol) was added to the mixture, which was allowed to stir at 80 °C for an additional 5 h. After that time, the reaction solution was allowed to cool to room temperature and filtered to remove the precipitate. The filtrate was concentrated *in vacuo* and partitioned between water (50 mL) and ethyl acetate (50 mL x 3). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified using silica gel column chromatography (EtOAc:hexanes = 1:10) to afford the desired (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 600 mg, 3.39 mmol, 53% yield) as light-yellow oil. This compound has been previously reported and spectra data match described. [17] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.50-6.38 (m, 2H), 2.27 (quint, *J* = 7.5 Hz, 2H), 1.10 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.2, 144.4, 137.8, 127.0, 126.2, 123.8, 26.1, 13.0.

Representative experimental procedure for Cu-catalyzed hydroamination of vinylarenes

4-Methoxyaniline (59.1 mg, 0.480 mmol), **IPrCuCl** (9.63 mg, 0.0200 mmol) and KO*t*-Bu (2.24 mg, 0.0200 mmol) were added to a vial (4 mL) charged with a magnetic bar in a glove box. The vial was sealed with a cap (phenolic open top cap with gray PTFE/silicone) and removed from the glove box. Then, the vial was purged with N_2 gas for 5 min and toluene (0.2 mL) was added. After premixing for 30 min, a solution of (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (70.9 mg, 0.400 mmol) in toluene (0.2 mL) was added to the mixture, which was allowed to stir at 80 °C for 12 h. After that time, the reaction solution was quenched by adding saturated aqueous NH_4Cl (1 mL) and washed with EtOAc (3 mL x 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3) to afford the desired product, 4-methoxy-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (**5aa**, 97.3 mg, 0.324 mmol, 81% yield), as a yellow solid.

4-Methoxy-*N*-(4-nitrophenethyl)aniline (3aa). Compound **3aa** was synthesized from 4-methoxyaniline (**2a**, 59.1 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 99% yield (108 mg, 0.396 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). This compound has been previously reported and spectra data match described.[18] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 3.45 (br s, 1H), 3.42 (t, *J* = 6.9 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.4, 147.5, 146.7, 141.6, 129.6, 123.7, 114.9, 114.3, 55.6, 45.4, 35.4.

4-Fluoro-*N*-(4-nitrophenethyl)aniline (3ab). Compound **3ab** was synthesized from 4-fluoroaniline (**2b**, 45.5 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 94% yield (97.9 mg, 0.376 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 66-67 °C; **IR** (neat): 3364 (m), 3078 (w), 2924 (m), 1605 (m), 1504 (s), 1404 (m), 1342 (s), 1281 (m), 1211 (s), 1111 (m), 825 (s), 748 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.62-6.58 (m, 2H), 3.67 (br s, 1H), 3.47 (t, *J* = 6.8 Hz, 2H) 3.06 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.3, 146.7, 145.6, 143.9, 129.6, 123.7 (J_{C-F} = 41.4 Hz), 115.7 (J_{C-F} = 22.3 Hz), 113.7 (J_{C-F} = 7.5 Hz), 45.0, 35.2; **HRMS** (EI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2O_2$ 261.1039, Found 261.1041.

4-Chloro-*N*-(4-nitrophenethyl)aniline (3ac). Compound **3ac** was synthesized from 4-chloroaniline (**2c**, 61.2 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 95% yield (105 mg, 0.380 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). This compound has been previously reported and spectra data match described.[18] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.74 (br s, 1H), 3.44 (t, *J* = 6.8 Hz, 2H) 3.02 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 146.7, 146.0, 129.6, 129.1, 123.7, 122.2, 114.0, 44.5, 35.1.

4-Bromo-*N*-(4-nitrophenethyl)aniline (3ad). Compound **3ad** was synthesized from 4-bromoaniline (**2d**, 82.6 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 82% yield (105 mg, 0.328 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 70-71 °C; **IR** (neat): 3394 (m), 3078 (w), 2924 (m), 1589 (m), 1504 (s), 1404 (m), 1342 (s), 1296 (m), 1180 (m), 1111 (m), 849 (m), 818 (s), 725 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 3.70 (br s, 1H), 3.44 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 146.7, 146.4, 132.0, 129.6, 123.7, 114.4, 109.2, 44.4, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}BrN_2O_2$ 321.0239, Found 321.0237.

3-Chloro-*N*-(4-nitrophenethyl)aniline (3ae). Compound **3ae** was synthesized from 3-chloroaniline (**2e**, 50.7 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 86% yield (95.2 mg, 0.344 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 71-72 °C; **IR** (neat): 3310 (m), 3070 (w), 2924 (m), 1597 (s), 1512 (m), 1342 (s), 1265 (m), 1165 (s), 1088 (m), 849 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.70 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.59 (dd, *J* = 1.5, 1.5 Hz, 1H), 6.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.79 (br s, 1H), 3.45 (t, *J* = 6.7 Hz, 2H) 3.03 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.6, 147.0, 146.8, 135.2, 130.4, 129.7, 123.9, 117.7, 112.4, 111.3, 44.2, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2O_2$ 277.0744, Found 277.0744.

3-Bromo-*N*-(4-nitrophenethyl)aniline (3af). Compound **3af** was synthesized from 3-bromoaniline (**2f**, 82.6 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 98% yield (126 mg, 0.392 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 77-78 °C; **IR** (neat): 3402 (m), 3078 (w), 2924 (m), 1589 (s), 1512 (s), 1504 (s), 1404 (m), 1335 (s), 1304 (m), 1173 (m), 1111 (m), 1060 (m), 849 (s), 764 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.03 (t, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 6.52 (dd, *J* = 8.2, 1.5 Hz, 1H), 3.80 (br s, 1H), 3.44 (t, *J* = 6.8 Hz, 2H) 3.02 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.8, 147.0, 146.8, 130.6, 129.6, 123.8, 123.4, 120.4, 115.3, 111.6, 44.1, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}BrN_2O_2$ 321.0239, Found 321.0240.

3-Iodo-*N*-(4-nitrophenethyl)aniline (3ag). Compound **3ag** was synthesized from 3-iodoaniline (**2g**, 105 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 73% yield (108 mg, 0.293 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 103-104 °C; **IR** (neat): 3394 (m), 3070 (w), 2924 (m), 1582 (s), 1512 (s), 1474 (m), 1335 (s), 1234 (m), 1168 (m), 1080 (m), 1034 (m), 980 (m), 849 (s), 764 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.95 (s, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.56

(dt, *J* = 7.7, 1.2 Hz, 1H), 3.71 (br s, 1H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.02 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.6, 146.8, 130.8, 129.6, 126.7, 123.9, 121.3, 112.3, 95.3, 44.2, 35.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}IN_2O_2$ 369.0100, Found 369.0097.

2-Methyl-*N*-(4-nitrophenethyl)aniline (3ah). Compound **3ah** was synthesized from *o*-toluidine (**2h**, 51.0 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 99% yield (101.5 mg, 0.396 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 75-76 °C; **IR** (neat): 3371 (m), 3063 (w), 2932 (m), 1597 (s), 1512 (s), 1466 (m), 1342 (s), 1281 (m), 1149 (m), 1111 (m), 1049 (m), 849 (s), 748 (s), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.75-6.70 (m, 2H), 3.58 (br s, 1H), 3.54 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.09 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.4, 146.7, 145.3, 130.3, 129.6, 127.2, 123.7, 122.0, 117.3, 109.6, 44.2, 35.1, 17.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O_2$ 257.1290, Found 257.1294.

2-Fluoro-*N*-(4-nitrophenethyl)aniline (3ai). Compound **3ai** was synthesized from 2-fluoroaniline (**2i,** 44.7 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 92% yield (95.8 mg, 0.368 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 73-74 °C; **IR** (neat): 3379 (m), 3070 (w), 2924 (m), 1605 (m), 1512 (s), 1443 (m), 1335 (s), 1250 (m), 1188 (m), 1111 (m), 1034 (m), 918 (m), 849 (m), 741 (s), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.05-6-97 (m, 2H), 6.76-6.66 (m, 2H), 3.95 (br s, 1H), 3.50 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.6 (J_{C-F} = 239 Hz), 146.9, 146.8, 135.9 (J_{C-F} = 11.6 Hz), 129.6, 124.7 (J_{C-F} = 3.9 Hz), 123.9, 117.2 (J_{C-F} = 6.8 Hz), 114.7 (J_{C-F} = 18.3 Hz), 112.1 (J_{C-F} = 2.9 Hz), 44.2, 35.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}FN_2O_2$ 261.1039, Found 261.1036.

2-Chloro-*N*-(4-nitrophenethyl)aniline (3aj). Compound **3aj** was synthesized from 2-chloroaniline (**2j**, 50.5 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 91% yield (101 mg, 0.366 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 84-85 °C; **IR** (neat): 3394 (m), 3063 (w), 2924 (m), 1597 (m), 1512 (s), 1458 (m), 1342 (s), 1296 (m), 1180 (m), 1095 (m), 1026 (m), 926 (w), 849 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.27 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.19 (td, *J* = 7.8, 1.2 Hz, 1H), 6.66-6.72 (m, 2H), 4.35 (br s, 1H), 3.52 (t, *J* = 7.0 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 146.8, 143.3, 129.7, 129.3, 127.9, 123.9, 119.4, 117.7, 111.2, 44.2, 35.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2O_2$ 277.0744, Found 277.0748.

1-(4-Nitrophenethyl)-1*H*-imidazole (3ak). Compound **3ak** was synthesized from 1*H*-imidazole (**2k**, 32.7 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 93% yield (80.8 mg, 0.372 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 61-62 °C; **IR** (neat): 3109 (m), 2970 (m), 2924 (m), 1605 (m), 1504 (s), 1412 (m), 1342 (s), 1234 (m), 1180 (m), 1103 (m), 1080 (m), 918 (m), 841 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.13 (d, *J* = 8.6 Hz, 2H), 7.29 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.03 (s, 1H), 6.82 (s, 1H), 4.23 (t, *J* = 6.8 Hz, 2H), 3.16 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.1, 145.0, 137.0, 129.9, 129.5, 124.0, 118.6, 47.6, 37.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}N_3O_2$ 218.0930, Found 218.0935.

2-Methyl-1-(4-nitrophenethyl)-1*H*-imidazole (3al). Compound **3al** was synthesized from 2-methyl-1*H*-imidazole (**2l**, 39.4 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 90% yield (83.3 mg, 0.360 mmol) as a light yellow solid. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 58-59°C; **IR** (neat): 3094 (m), 2924 (m), 2839 (m), 1936 (w), 1597 (m), 1504 (s), 1427 (m), 1335 (s), 1288 (m), 1149 (m), 1111 (m), 1034 (m), 840 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 1H), 6.71 (s, 1H), 4.12 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.1, 145.0, 144.4, 129.6, 127.6, 123.9, 118.7, 46.7, 37.2, 12.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{14}N_3O_2$ 232.1086, Found 232.1091.

4-Methyl-1-(4-nitrophenethyl)-1*H*-imidazole (3am). Compound **3am** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 92% yield (85.1 mg, 0.368 mmol) as an orange solid. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 52-53°C; **IR** (neat): 3094 (m), 2916 (m), 2854 (m), 1605 (m), 1512 (s), 1450 (m), 1342 (s), 1227 (m), 1165 (m), 1111 (m), 1034 (m), 856 (m), 818 (m), 756 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.22-7.19 (m, 3H), 6.55 (s, 1H), 4.15 (t, *J* = 6.8 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.2, 145.1, 139.0, 136.1, 129.5, 124.0, 115.0, 47.6, 37.6, 13.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{14}N_3O_2$ 232.1086, Found 232.1096.

1-(4-Nitrophenethyl)-1*H*-benzo[*d*]imidazole (3an). Compound **3an** was synthesized from 1*H*-benzo[*d*]imidazole (**2n**, 56.7 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 95% yield (102 mg, 0.380 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (2% MeOH in EtOAc). mp 138-139 °C; **IR** (neat): 3078 (m), 2924 (m), 2839 (m), 1597 (m), 1512 (s), 1404 (m), 1335 (s), 1281 (m), 1219 (m), 1111 (m), 1034 (m), 856 (m), 825 (w), 741 (s), 694 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.78 (br s, 1H), 7.56 (s, 1H), 7.33-7.27 (m, 3H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.43 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 6.7 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.1, 143.8, 142.8, 133.2, 129.5, 123.9, 123.1, 122.3, 120.5, 109.3, 45.7, 35.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{14}N_3O_2$ 268.1086, Found 268.1083.

2-Methyl-1-(4-nitrophenethyl)-1*H*-benzo[*d*]imidazole (3ao). Compound **3ao** was synthesized from 2-methyl-1*H*-benzo[*d*]imidazole (**2o**, 63.4 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 88% yield (99.0 mg, 0.352 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (5% MeOH in EtOAc). mp 139-140 °C; **IR** (neat): 3086 (m), 2916 (m), 2847 (m), 1605 (m), 1512 (s), 1458 (m), 1404 (m), 1335 (s), 1281 (m), 1149 (m), 1111 (m), 1011 (m), 841 (m), 748 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 5.1 Hz, 1H), 7.27 (br s, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.38 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 6.7 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.3, 146.9, 145.2, 142.5, 134.3, 129.7, 123.8, 122.2, 122.0, 119.2, 108.8, 44.4, 35.2, 13.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{16}N_3O_2$ 282.1243, Found 282.1254.

1-(4-Nitrophenethyl)-1*H*-pyrazole (3ap). Compound **3ap** was synthesized from 1*H*-pyrazole (**2p**, 32.7 mg, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 99% yield (86.0 mg, 0.396 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 82-83 °C; **IR** (neat): 3109 (m), 2932 (m), 2854 (m), 2847 (w), 1597 (m), 1512 (s), 1450 (w), 1396 (m), 1342 (s), 1281 (m), 1188 (w), 1157 (w), 1095 (m), 1041 (m), 964 (m), 918 (w), 856 (m), 733 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 8.5 Hz, 2H), 7.51 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.13 (s, 1H), 6.15-6.14 (m, 1H), 4.37 (t, *J* = 6.8 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.9, 139.8, 129.6, 129.5, 123.7, 105.3, 52.5, 36.4. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{12}N_3O_2$ 218.0930, Found 218.0933.

1-(4-Nitrophenethyl)-1*H*-1,2,3-triazole (3aq). Compound **3aq** was synthesized from 1*H*-1,2,3-triazole (**2q**, 27.8 µL, 0.480 mmol) and 1-nitro-4-vinylbenzene (**1a**, 51.0 µL, 0.400 mmol) in 90% yield (78.6 mg, 0.360 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 114-115 °C; **IR** (neat): 3016 (m), 2962 (m), 2854 (m), 1597 (m), 1512 (s), 1458 (m), 1342 (s), 1211 (m), 1111 (m), 1072 (m), 1026 (m), 856 (m), 810 (m), 733 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.61 (s, 1H), 7.36 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.67 (t, *J* = 7.0 Hz, 2H), 3.35 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.2, 144.7, 133.7, 129.6, 123.9, 123.7, 50.4, 36.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{11}N_4O_2$ 219.0882, Found 219.0886.

4-Methoxy-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (5aa). Compound **5aa** was synthesized from 4-methoxyaniline (**2a**, 59.1 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 81% yield (97.3 mg, 0.324 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 63-64 °C; **IR** (neat): 3394 (m), 3040 (w), 2955 (m), 2908 (m), 1597 (m), 1504 (s), 1342 (s), 1227 (s), 1180 (w), 1149 (m), 1111 (m), 1034 (s), 856 (m), 802 (s), 741 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.57-3.51 (m, 1H), 3.17 (br s, 1H), 2.97-2.88 (m, 2H), 1.57-1.54 (m, 1H), 1.43-1.38 (m, 1H), 0.99 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.0, 146.9, 146.5, 141.3, 130.2, 123.4, 115.0, 114.6, 56.1, 55.7, 39.8, 27.0, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_3$ 301.1552, Found 301.1557.

4-Fluoro-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (5ab). Compound **5ab** was synthesized from 4-fluoroaniline (**2b**, 45.5 µL, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 85% yield (98.0 mg, 0.340 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 3410 (m), 3070 (w), 2962 (m), 2870 (m), 1512 (s), 1404 (w), 1342 (s), 1219 (s), 1149 (m), 1111 (m), 1011 (s), 856 (m), 818 (s), 748 (m), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 6.9 (td, *J* = 8.6, 1.1 Hz, 2H), 6.52 (ddd, *J* = 8.8, 4.2, 1.1 Hz, 2H), 3.58-3.52 (m, 1H), 3.32 (br s, 1H), 2.96 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.90 (dd, *J* = 13.7, 5.5 Hz, 1H), 1.64-1.54 (m, 1H), 1.41 (dquint, *J* = 14.2, 7.3 Hz, 1H), 1.00 (td, *J* = 7.3, 1.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 156.7 (J_{C-F} = 235 Hz), 146.6, 146.6, 143.5, 130.2, 123.5, 115.8 (J_{C-F} = 22.2 Hz), 114.0 (J_{C-F} = 6.8 Hz), 55.8, 39.7, 27.0, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}FN_2O_2$ 289.1352, Found 289.1353.

4-Chloro-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (5ac). Compound **5ac** was synthesized from 4-chloroaniline (**2c**, 42.8 µL, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 88% yield (107 mg, 0.352 mmol) as an orange oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 3402 (m), 3078 (w), 2962 (m), 2878 (m), 1597 (m), 1512 (s), 1404 (w), 1342 (s), 1180 (m), 1103 (m), 1011 (s), 856 (m), 818 (s), 748 (m), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.12 (td, *J* = 8.6, 3.2 Hz, 2H), 6.52 (ddd, *J* = 8.8, 4.2, 1.1 Hz, 2H), 3.58 (br s, 1H), 3.44 (s, 1H), 2.97 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.90 (dd, *J* = 13.7, 5.5 Hz, 1H), 1.64-1.54 (m, 1H), 1.41 (dquint, *J* = 14.2, 7.3 Hz, 1H), 1.00 (td, *J* = 7.3, 1.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.6, 146.4, 145.7, 130.2, 129.3, 123.5, 121.9, 114.1, 55.2, 39.7, 27.0, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}ClN_2O_2$ 305.1057, Found 305.1057.

***N*-(1-(4-Nitrophenyl)butan-2-yl)aniline (5ar).** Compound **5ar** was synthesized from aniline (**2r**, 44.0 µL, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 75% yield (81.1 mg, 0.300 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 3410 (m), 3325 (m), 2962 (m), 2870 (m), 1597 (m), 1512 (s), 1342 (s), 1180 (m), 1111 (m), 964 (w), 856 (m), 784 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.20 (td, *J* = 7.3, 0.9 Hz, 2H), 6.71 (td, *J* = 7.3, 0.9 Hz, 1H), 6.61 (dd, *J* = 7.7, 0.9 Hz, 2H), 3.67-3.61 (m, 1H), 3.44 (br s, 1H), 2.98 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.93 (dd, *J* = 13.7, 6.0 Hz, 1H), 1.64-1.55 (m, 1H), 1.46-1.35 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.1, 146.7, 146.6, 130.3, 129.5, 123.4, 117.4, 113.1, 55.0, 39.8, 27.0, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{19}N_2O_2$ 271.1447, Found 271.1452.

3-Fluoro-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (5as). Compound **5as** was synthesized from 3-fluoroaniline (**2s**, 46.0 µL, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 62% yield (71.5 mg, 0.248 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 54-55 °C; **IR** (neat): 3394 (m), 3078 (w), 2924 (m), 2854 (m), 1620 (s), 1520 (s), 1481 (m), 1335 (s), 1288 (m), 1142 (s), 1111 (m), 1018 (m), 856 (m), 810 (m), 748 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.10 (td, *J* = 8.2, 6.6 Hz, 1H), 6.39 (td, *J* = 8.2, 2.3 Hz, 1H), 6.34 (ddd, *J* = 8.2, 2.3, 0.9 Hz, 1H), 6.28 (dt, *J* = 11.9, 2.3 Hz, 1H), 3.61-3.56 (m, 1H), 3.55 (br s, 1H), 2.98 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.91 (dd, *J* = 13.7, 5.5 Hz, 1H), 1.65-1.56 (m, 1H), 1.47-1.36 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 164.2 (J_{C-F} = 243 Hz), 149.1, 149.0, 146.3, 130.5 (J_{C-F} = 10.6 Hz), 130.2, 123.5, 108.9, 103.8 (J_{C-F} = 21.2 Hz), 99.7 (J_{C-F} = 26.1 Hz), 55.1, 39.8, 27.1, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}FN_2O_2$ 289.1352, Found 289.1352.

3-Bromo-*N*-(1-(4-nitrophenyl)butan-2-yl)aniline (5af). Compound **5af** was synthesized from 3-bromoaniline (**2f**, 54.3 µL, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 85% yield (119 mg, 0.340 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 3402 (m), 3070 (w), 2970 (m), 2916 (m), 1597 (m), 1512 (s), 1342 (s), 1281 (w), 1234 (m), 1142 (w), 1111 (m), 1011 (m), 849 (m), 764 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.01 (dd, J = 7.8, 7.8 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.71 (s, 1H), 6.49 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.59 (br s, 1H), 3.53 (s, 1H), 2.98 (dd, *J* = 13.3, 5.5 Hz, 1H), 2.89 (dd, *J* = 13.3, 5.5 Hz, 1H), 1.66-1.56 (m, 1H), 2.98 (dquint, *J* = 14.4, 7.3 Hz, 1H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.5, 146.6, 146.3, 130.7, 130.3, 123.5, 123.4, 120.1, 115.5, 111.7, 54.9, 39.8, 27.1, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}BrN_2O_2$ 349.0552, Found 349.0552.

1-(1-(4-Nitrophenyl)butan-2-yl)-1*H*-imidazole (5ak). Compound **5ak** was synthesized from 1*H*-imidazole (**2k**, 32.7 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 72% yield (70.6 mg, 0.289 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 49-50 °C; **IR** (neat): 3109 (m), 2967 (m), 2924 (m), 1605 (m), 1512 (s), 1412 (m), 1342 (s), 1273 (m), 1180 (m), 1111 (m), 1080 (m), 918 (m), 856 (m), 802 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 1H), 7.80-7.06 (m, 3H), 6.87 (s, 1H), 4.09-4.01 (m, 1H), 3.18 (dd, *J* = 13.3, 4.5 Hz, 1H), 3.06 (dd, *J* = 13.3, 10.5 Hz, 1H), 1.96-1.83 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 144.8, 136.4, 129.8, 129.5, 123.8, 116.2, 61.3, 42.7, 28.7, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O_2$ 246.1243, Found 246.1245.

2-Methyl-1-(1-(4-nitrophenyl)butan-2-yl)-1*H*-imidazole (5al). Compound **5al** was synthesized from 2-methyl-1*H*-imidazole (**2l**, 39.4 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 82% yield (85.1 mg, 0.328 mmol) as a yellow solid. The crude product

was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 49-50 °C; **IR** (neat): 3109 (m), 2962 (m), 2878 (m), 1605 (m), 1512 (s), 1458 (m), 1420 (m), 1342 (s), 1273 (m), 1157 (m), 1111 (m), 1011 (m), 987 (m), 941 (m), 856 (m), 802 (m), 741 (s), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.97 (s, 1H), 6.91 (s, 1H), 4.03-3.96 (m, 1H), 3.13 (dd, *J* = 13.3, 4.5 Hz, 1H), 2.98 (dd, *J* = 13.3, 10.5 Hz, 1H), 1.96-1.83 (m, 5H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.1, 144.9, 129.6, 128.2, 123.7, 114.3, 59.4, 42.7, 29.0, 12.9, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}N_3O_2$ 260.1399, Found 260.1403.

4-Methyl-1-(1-(4-nitrophenyl)butan-2-yl)-1*H*-imidazole (5am). Compound **5am** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 92% yield (95.4 mg, 0.368 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 3101 (m), 2970 (m), 2878 (m), 1605 (m), 1512 (s), 1458 (m), 1342 (s), 1281 (m), 1157 (m), 1111 (m), 1057 (w), 972 (w), 910 (m), 856 (m), 810 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.05-7.03 (m, 3H), 6.59 (s, 1H), 3.92 (tt, *J* = 9.5, 4.9 Hz, 1H), 3.10 (dd, *J* = 13.7, 4.5 Hz, 1H), 2.99 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.14 (s, 3H), 1.88-1.76 (m, 2H) 0.81 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.8, 145.6, 145.1, 129.5, 124.1, 123.6, 123.0, 61.2, 42.5, 28.6, 13.8, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{18}N_3O_2$ 260.1399, Found 260.1401.

1-(1-(4-Nitrophenyl)butan-2-yl)-1*H*-benzo[*d*]imidazole (5an). Compound **5an** was synthesized from 1*H*-benzo[*d*]imidazole (**2n**, 56.7 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 70% yield (82.7 mg, 0.280 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). mp 103-104 °C; **IR** (neat): 3070 (m), 2962 (m), 2870 (m), 2361 (m), 1605 (m), 1512 (s), 1404 (m), 1342 (s), 1281 (m), 1203 (m), 1111 (m), 1072 (w), 1011 (m), 856 (m), 741 (s), 710 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.77-7.74 (m, 1H), 7.68 (s, 1H), 7.36-7.33 (m, 1H), 7.25-7.20 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 4.42-4.37 (m, 1H), 3.32 (dd, *J* = 14.2, 7.8 Hz, 1H), 3.27 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.15-2.01 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.7, 144.8, 143.9, 141.5, 132.9, 129.5, 123.5, 122.8, 122.1, 120.5, 110.0, 60.0, 40.6, 27.1, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{18}N_3O_2$ 296.1399, Found 296.1397.

1-(1-(4-Nitrophenyl)butan-2-yl)-1*H*-pyrazole (5ap). Compound **5ap** was synthesized from 1*H*-pyrazole (**2p**, 32.7 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 81% yield (80.0 mg, 0.326 mmol) as a light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 2962 (m), 2924 (m), 2870 (m), 1605 (m), 1520 (s), 1466 (m), 1404 (m), 1342 (s), 1281 (m), 1103 (m), 1049 (m), 933 (w), 856 (m), 802 (m), 748 (s), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.01 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 1H), 7.05 (s, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.09 (s, 1H), 4.18-4.11 (m, 1H), 3.36 (dd, *J* = 13.7, 10.1 Hz, 1H), 3.13 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.11-2.07 (m, 1H), 1.91-1.88 (m, 1H), 0.79 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.6, 146.1, 139.6, 129.6, 129.4, 123.4, 104.5, 65.8, 41.7, 28.4, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O_2$ 246.1243, Found 246.1245.

1-(1-(4-Nitrophenyl)butan-2-yl)-1*H*-1,2,3-triazole (5aq). Compound **5aq** was synthesized from 1*H*-1,2,3-triazole (**2q**, 33.2 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-4-nitrobenzene (**4a**, 70.9 mg, 0.400 mmol) in 60% yield (59.2 mg, 0.240 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 58-59 °C; **IR** (neat): 2962 (m), 2924 (m), 2854 (m), 1605 (m), 1512 (s), 1458 (m), 1420 (m), 1342 (s), 1149 (m), 1111 (m), 957 (m), 864 (m), 810 (s), 741 (m), 710 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.55 (s, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 4.76 (tt, *J* = 9.8, 4.9 Hz, 1H), 3.44 (dd, *J* = 14.0, 9.8 Hz, 1H), 3.24 (dd, *J* =14.0, 4.8 Hz, 1H), 2.19-2.11 (m, 1H), 1.96 (ddd, *J* = 14.2, 7.3, 4.6 Hz, 1H), 0.80 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.8, 145.3, 133.8, 129.6, 123.6, 68.5, 41.2, 28.5, 10.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}N_4O_2$ 247.1195, Found 247.1199.

4-Methoxy-*N*-(1-(2-nitrophenyl)butan-2-yl)aniline (5ba). Compound **5ba** was synthesized from 4-methoxyaniline (**2a**, 59.1 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-2-nitrobenzene (**4b**, 70.9 mg, 0.400 mmol) in 23% yield (27.6 mg, 0.0920 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). **IR** (neat): 3402 (m), 2962 (m), 2932 (m), 1612 (m), 1512 (s), 1458 (w), 1350 (m), 1242 (s), 1180 (w), 1142 (w), 1041 (m), 856 (w), 818 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.47 (td, *J* = 7.7, 1.3 Hz, 1H), 7.38-7.30 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 8.7, 3.6 Hz, 2H), 3.72 (s, 3H), 3.57 (quint, *J* = 6.4 Hz, 1H), 3.27 (br s, 1H), 3.13-3.11 (m, 2H), 1.67-1.48 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.8, 150.0, 141.8, 134.4, 132.8, 132.5, 127.2, 124.6, 114.8, 114.3, 56.6, 55.7, 37.8, 28.0, 10.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_3$ 301.1552, Found 301.1560.

4-Methyl-1-(1-(4-nitrophenyl)pentan-2-yl)-1*H*-imidazole (7am). Compound **7am** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-nitro-4-(pent-1-en-1-yl)benzene (**6a**, 76.5 mg, 0.400 mmol) in 75% yield (82.0 mg, 0.300 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2947 (m), 2870 (m), 2800 (w), 1605 (m), 1520 (s), 1450 (m), 1420 (w), 1342 (s), 1281 (w), 1219 (m), 1157 (m), 1111 (m), 1018 (m), 856 (m), 818 (s), 748 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.09 (s, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.59 (s, 1H), 4.03 (quint, *J* = 4.5 Hz, 1H), 3.10 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.02 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.18 (s, 3H), 1.84-1.76 (m, 2H), 1.22 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.88 (td, *J* = 7.4, 1.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.8, 145.1, 138.9, 135.5, 129.5, 123.7, 112.4, 59.3, 42.8, 37.5, 19.2, 13.8, 13.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{20}N_3O_2$ 274.1556, Found 274.1559.

4-Methyl-1-(1-(4-nitrophenyl)heptan-2-yl)-1*H*-imidazole (7bm). Compound **7bm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(hept-1-en-1-yl)-4-nitrobenzene (**6b**, 87.7 mg, 0.400 mmol) in 82% yield (98.9 mg, 0.328 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2932 (m), 2862 (m), 1605 (m), 1520 (s), 1458 (m), 1342 (s), 1288 (w), 1157 (m), 1111 (m), 1003 (m), 972 (w), 858 (m), 818 (s), 702 (m), 741 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 4.06-3.99 (m, 1H), 3.12 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.03 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.20 (s, 3H), 1.85-1.80 (m, 2H), 1.26-1.25 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 145.1, 139.1, 135.5, 129.6, 123.8, 112.5, 59.6, 43.0, 35.5, 31.3, 25.7, 22.4, 13.9 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{24}N_3O_2$ 302.1869, Found 302.1871.

4-Methyl-1-(3-methyl-1-(4-nitrophenyl)butan-2-yl)-1*H*-imidazole (7cm). Compound **7cm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(3-methylbut-1-en-1-yl)-4-nitrobenzene (**6c**, 76.5 mg, 0.400 mmol) in 71% yield (77.6 mg, 0.284 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2978 (m), 2878 (m), 2824 (w), 1605 (m), 1512 (s), 1412 (w), 1342 (s), 1281 (m), 1165 (m), 1111 (m), 1011 (w), 972 (m), 941 (w), 849 (m), 725 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.07-7.05 (m, 3H), 6.59 (s, 1H), 3.73-3.67 (m, 1H), 3.28 (dd, *J* = 13.7, 3.7 Hz, 1H), 2.98 (dd,

J = 13.7, 11.0 Hz, 1H), 2.19 (s, 3H), 2.12-2.03 (m, 1H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.6, 138.8, 136.0, 129.4, 123.8, 113.2, 66.1, 39.6, 33.5, 20.2, 19.0, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{20}N_3O_2$ 274.1556, Found 274.1557.

4-methyl-1-(1-(4-nitrophenyl)-4-phenylbutan-2-yl)-1*H*-imidazole (7dm). Compound **7dm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-nitro-4-(4-phenylbut-1-en-1-yl)benzene (**6d**, 101 mg, 0.400 mmol) in 83% yield (111 mg, 0.332 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2908 (m), 2862 (m), 1605 (m), 1566 (w), 1512 (s), 1450 (w), 1412 (w), 1342 (s), 1281 (m), 1157 (m), 1111 (m), 1003 (w), 918 (w), 856 (m), 818 (w), 748 (m), 702 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 1H), 7.10-7.09 (m, 2H), 7.07 (s, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.64 (s, 1H), 4.05-3.98 (m, 1H), 3.11 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.05 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.63-2.56 (m, 1H), 2.50-2.42 (m, 1H), 2.24 (s, 3H), 2.21-2.15 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 144.8, 140.0, 139.4, 135.7, 129.5, 128.6, 128.3, 126.4, 123.7, 112.3, 58.4, 43.0, 36.7, 31.9, 13.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{22}N_3O_2$ 336.1712, Found 336.1710.

1-(4-(Benzyloxy)-1-(4-nitrophenyl)butan-2-yl)-4-methyl-1*H*-imidazole (7em). Compound **7em** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(4-(benzyloxy)but-1-en-1-yl)-4-nitrobenzene (**6e**, 113 mg, 0.400 mmol) in 78% yield (114 mg, 0.312 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2862 (m), 2800 (w), 1605 (m), 1512 (s), 1443 (m), 1342 (s), 1281 (m), 1157 (m), 1111 (m), 1011 (m), 926 (m), 856 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.37-7.26 (m, 5H), 7.09 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.57 (s, 1H), 4.40 (s, 2H), 4.40-4.34 (m, 2H), 3.47 (dt, *J* = 9.5, 4.6 Hz, 1H), 3.13 (dd, *J* = 14.2, 5.1 Hz, 1H), 3.04 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.21-2.13 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 144.9, 139.1, 137.8, 135.8, 129.6, 128.4, 127.9, 127.8, 123.7, 112.5, 73.3, 65.6, 56.0, 42.4, 35.8, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{24}N_3O_3$ 366.1818, Found 366.1816.

1-(5-(Benzyloxy)-1-(4-nitrophenyl)pentan-2-yl)-4-methyl-1*H*-imidazole (7fm). Compound **7fm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(5-(benzyloxy)pent-1-en-1-yl)-4-nitrobenzene (**6f**, 119 mg, 0.400 mmol) in 72% yield (110 mg, 0.290 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2862 (m), 2800 (w), 1605 (m), 1512 (s), 1443 (m), 1342 (s), 1281 (m), 1157 (m), 1111 (m), 1011 (m), 926 (m), 856 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.38-7.29 (m, 5H), 7.08 (s, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.59 (s, 1H), 4.46 (s, 2H), 4.09-4.07 (m, 1H), 3.48-3.40 (m, 2H), 3.11 (dd, *J* = 13.9, 4.9 Hz, 1H), 3.00 (dd, *J* = 13.7, 9.3Hz, 1H), 2.19 (s, 3H), 2.02-1.90 (m, 2H), 1.53-1.50 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.1, 139.1, 138.2, 135.7, 129.6, 128.5, 127.8, 127.7, 123.8, 112.4, 73.0, 69.2, 59.3, 42.8, 32.5, 26.0, 13.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{26}N_3O_3$ 380.1974, Found 380.1970.

1-(6-Chloro-1-(4-nitrophenyl)hexan-2-yl)-4-methyl-1*H*-imidazole (7gm). Compound **7gm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(6-chlorohex-1-en-1-yl)-4-nitrobenzene (**6g**, 95.9 mg, 0.400 mmol) in 70% yield (90.1 mg, 0.280 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2947 (m), 2870 (m), 1605 (m), 1558 (w), 1520 (s), 1450 (w), 1342 (s), 1265 (s), 1157 (m), 1111 (m), 1065 (w), 856 (m), 818 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.16 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.61 (s, 1H), 4.08-4.03 (m, 1H), 3.51-3.47 (m, 2H), 3.15 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.05 (dd, *J* = 13.7, 9.1 Hz, 1H), 2.22 (s, 3H), 1.88 (q, *J* = 7.6 Hz, 2H), 1.44-1.25 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 144.8, 139.3, 135.5, 129.6, 123.8, 112.4, 59.5, 44.4, 42.9, 34.8, 31.9, 23.4, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{21}ClN_3O_2$ 322.1322, Found 322.1331.

4-Methyl-1-(1-(4-nitrophenyl)undec-10-en-2-yl)-1*H*-imidazole (7hm). Compound **7hm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-nitro-4-(undeca-1,10-dien-1-yl)benzene (**6h**, 109 mg, 0.400 mmol) in 87% yield (124 mg, 0.349 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2932 (m), 2862 (m), 1605 (m), 1597 (s), 1520 (s), 1481 (m), 1342 (s), 1250 (m), 1203 (s), 1149 (s), 1111 (m), 1065 (m), 972 (m), 941 (m), 702 (s), 856 (m), 818 (s), 741 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.12 (s, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.60 (s, 1H), 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.98 (dd, *J* = 17.0, 2.3 Hz, 1H), 4.93 (dd, *J* = 10.2, 2.3 Hz, 1H), 4.03 (tt, *J* = 8.9, 5.5 Hz, 1H), 3.12 (dd, *J* = 13.8, 4.6 Hz, 1H), 3.03 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.21 (s, 3H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.84-1.80 (m, 2H), 1.36-1.12 (m, 10H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.1, 139.0, 135.5, 129.6, 123.8, 123.8, 114.2, 112.4, 59.6, 42.9, 35.5, 33.7, 29.1, 29.0, 28.9, 28.7, 26.0, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{30}N_3O_2$ 356.2338, Found 356.2331.

(*Z*)-4-Methyl-1-(1-(4-nitrophenyl)dec-7-en-2-yl)-1*H*-imidazole (7im). Compound **7im** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and 1-((1*E*,7*Z*)-deca-1,7-dien-1-yl)-4-nitrobenzene (**6i**, 104 mg, 0.400 mmol) in 85% yield (116 mg, 0.340 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2939 (m), 2862 (m), 1605 (m), 1520 (s), 1450 (m), 1342 (s), 1288 (m), 1157 (m), 1111 (m), 1072 (w), 1003 (w), 972 (w), 856 (s), 810 (m), 741 (s), 702 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.09 (s, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 1H), 5.36-5.32 (m, 1H), 5.27-5.22 (m, 1H), 4.05-3.98 (m, 1H), 3.11 (dd, *J* = 13.8, 5.1 Hz, 1H), 3.03 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.20 (s, 3H), 2.02-1.94 (m, 4H), 1.85-1.80 (m, 2H), 1.33-1.20 (m, 4H), 0.92 (t, 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 146.9, 145.1, 139.1, 135.5, 132.1, 129.6, 128.3, 123.8, 112.4, 59.5, 42.9, 35.4, 29.1, 26.7, 25.6, 20.5, 14.3, 13.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{28}N_3O_2$ 342.2182, Found 342.2186.

1-(1-(2-Chloro-4-nitrophenyl)butan-2-yl)-4-methyl-1*H*-imidazole (7jm). Compound **7jm** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-2-chloro-4-nitrobenzene (**6j**, 84.7 mg, 0.400 mmol) in 85% yield (100 mg, 0.340 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2970 (m), 2878 (m), 1589 (m), 1520 (s), 1350 (s), 1242 (s), 1157 (m), 1119 (m), 1041 (m), 895 (m), 810 (s), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.23 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.11 (s, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.62 (s, 1H), 4.07 (dq, *J* = 9.4, 4.7 Hz, 1H), 3.37 (dd, *J* = 13.7, 4.6 Hz, 1H), 3.02 (dd, *J* = 13.5, 9.8 Hz, 1H), 2.19 (s, 3H), 1.95-1.90 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.3, 142.6, 139.1, 135.6, 134.6, 131.4, 124.7, 121.8, 112.3, 59.1, 40.7, 28.8, 13.8, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}ClN_3O_2$ 294.1009, Found 294.1013.

1-(1-(2-Fluoro-4-nitrophenyl)butan-2-yl)-4-methyl-1*H*-imidazole (7km). Compound **7km** was synthesized from 4-methyl-1*H*-imidazole (**2m**, 39.4 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-2-fluoro-4-nitrobenzene (**6k**, 78.0 mg, 0.400 mmol) in 82% yield (91.0 mg, 0.328 mmol) as a yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 2970 (m), 2878 (m), 1605 (m), 1528 (s), 1435 (w), 1420 (w), 1350 (s), 1234 (m), 1165 (m), 1072 (m), 1003 (m), 949 (m), 879 (m), 810 (s), 742 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz):

δ 7.88 (dd, *J* = 9.6, 2.3 Hz, 1H), 7.84 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.14 (s, 1H), 6.97 (t, *J* = 8.2 Hz, 1H), 6.62 (s, 1H), 4.02 (tt, *J* = 9.5, 4.9 Hz, 1H), 3.24 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.97 (dd, *J* = 14.4, 9.8 Hz, 1H), 2.17 (s, 3H), 1.93-1.81 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 160.2 (J_{C-F} = 250 Hz), 147.8 (J_{C-F} = 9.6 Hz), 138.9, 135.5, 132.2 (J_{C-F} = 16.4 Hz), 131.5 (J_{C-F} = 5.8 Hz), 119.3 (J_{C-F} = 3.9 Hz), 112.4, 111.2 (J_{C-F} = 27.9 Hz), 59.8, 36.3, 28.7, 13.7, 10.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}FN_3O_2$ 278.1305, Found 278.1298.

***N*-(1-(2-Chloro-4-nitrophenyl)butan-2-yl)-4-methoxyaniline (8).** Compound **8** was synthesized from 4-methoxyaniline (**2a,** 59.1 mg, 0.480 mmol) and (*E*)-1-(but-1-en-1-yl)-2-chloro-4-nitrobenzene (**6j**, 84.7 mg, 0.400 mmol) in 78% yield (104 mg, 0.311 mmol) as a yellow solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3). mp 55-56 °C; **IR** (neat): 3394 (w), 2970 (m), 2932 (m), 2862 (w), 1682 (w), 1512 (s), 1466 (w), 1350 (s), 1242 (m), 1180 (w), 1119 (m), 1041 (m), 895 (m), 818 (s), 741 (m), cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 2.3 Hz, 1H), 8.01 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H), 3.63 (quint, *J* = 6.4 Hz, 1H), 3.23 (br s, 1H), 3.07-2.98 (m, 2H), 1.69-1.59 (m, 1H), 1.52 (dquint, *J* = 14.1, 7.2 Hz, 1H), 1.00 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.1, 146.7, 145.1, 141.4, 135.0, 132.0, 124.5, 121.5, 114.9, 114.6, 55.7, 55.6, 38.9, 27.8, 10.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{20}ClN_2O_3$ 335.1162, Found 335.1158.

Experimental procedure for Pd-catalyzed cyclization of 8

2-Ethyl-1-(4-methoxyphenyl)-6-nitroindoline (9). In a glove box, tris(dibenzylideneacetone) dipalladium (0) (2.70 mg, 2.98 x 10^{-3} mmol), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (2.0 mg, 5.97 x 10^{-3} mmol) and NaO*t*-Bu (8.6 mg, 0.0896 mmol) were added into a vial (8 mL) charged with a magnetic bar, and the vial was sealed with a cap (phenolic open top cap with gray PTFE/silicone). After being removed from the glove box, the vial was purged with N_2 gas for 10 min, and 1,4-dioxane (0.2 mL) was added. And then a solution of aminated product 8 (20.0 mg, 0.0597 mmol) in 1,4-dioxane (0.2 mL) was added at 0 °C. The phenolic open-top cap was changed to a closed cap and the reaction mixture was heated at 110 °C and stirred for 12 h. The mixture was filtered through a plug of silica gel and washed with CH_2Cl_2. The organic filtrate was concentrated *in vacuo*. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:3) to afford 2-ethyl-1-(4-methoxyphenyl)-6-nitroindoline (**9**, 14.3 mg, 0.0479 mmol, 81% yield) as a yellow solid. mp 59-60 °C; **IR** (neat): 2978 (m), 2870 (m), 2839 (w), 1620 (w), 1512 (s), 1443 (w), 1381 (w), 1342 (s), 1288 (m), 1242 (m), 1180 (w), 1119 (m), 1072 (w), 1034 (m), 949 (w), 849 (m), 810 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.16-7.13 (m, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 4.22 (qd, *J* = 9.2, 3.2 Hz, 1H), 3.86 (s, 3H), 3.30 (dd, *J* = 16.7, 8.9 Hz, 1H), 2.90 (ddd, *J* = 16.9, 9.6, 1.4 Hz, 1H), 1.76 (ddd, *J* = 13.7, 7.3, 3.2 Hz, 1H), 1.61-1.53 (m, 1H), 0.91 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.4, 152.5, 148.4, 136.6, 134.8, 126.4. 124.1, 115.1, 113.6, 100.8, 67.3, 55.5, 33.8, 26.2, 9.1; **HRMS** (EI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{18}N_2NaO_3$ 321.1215, Found 321.1215.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) (NRF-2017R1A2B4008310). This work was also partially supported by the Bio & Medical Technology Development Program of the National Research Foundation (NRF) and was funded by the Korean government (MSIP&MOHW) (NRF-2015M3A9E6029594).

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