HI-Catalyzed Hydroamination and Hydroarylation of Alkenes

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Abstract: Aromatic amines react with alkenes in the presence of catalytic amounts of aqueous HI to give mixtures of the corresponding hydroamination and hydroarylation products. While the hydroamination reaction is the preferred pathway for aliphatic alkenes, the hydroarylation reaction becomes more important when styrenes are used as substrates. In general, the electronic properties of the alkene and the amine strongly influence the efficiency and the selectivity of the reaction.

Key words: alkenes, aminations, amines, homogeneous catalysis, iodine

The hydroamination of alkenes represents an environmentally friendly and economically desirable process. As a consequence, there has been much effort towards the development of corresponding catalytic processes. While the use of metal complexes and bases as catalysts has attracted most of the attention,[1] Brønsted acids have only recently been used as hydroamination catalysts,[2,3] although selected metal-catalyzed hydroaminations did use acids as co-catalysts.[1,4] Furthermore, some of the metal catalysts used for hydroaminations (e.g. $TiCl_4$)[5] are supposed to liberate at least protons under the reaction conditions and therefore may initiate proton-catalyzed reactions. Furthermore, it must be mentioned that hydroaminations of alkenes have been successfully achieved in the presence of heterogeneous acidic catalysts.[6]

The major problem with proton-catalyzed hydroaminations of alkenes is the fact that amines are more basic than alkenes. Consequently, alkenes are usually not protonated to give carbenium ions in the presence of amines. However, from a mechanistic point of view, the formation of carbenium ions from alkenes is essential for proton-catalyzed hydroaminations since these intermediates need to be trapped by nucleophilic amines. In order to achieve sufficient degrees of alkene protonation under the reaction conditions, amines (or amine derivatives) with decreased basicity such as anilines,[3] amides, carbamates and sulfonamides[2] have been used most widely for proton-catalyzed hydroaminations of alkenes.

As catalysts, strong Brønsted acids have been used and best results have been reported with TfOH (CF_3SO_3H) by Hartwig et al.[2a] and $PhNH_3B(C_6F_5)_4{\cdot}Et_2O$ by Bergman et al.[3] However, to the best of our knowledge, simple hydrogen halides have not been used successfully as catalysts for hydroamination reactions. In contrast, several examples can be found in the literature where attempted additions of anilines to alkenes in the presence of catalytic amounts of preformed anilinium hydrochlorides have failed.[5] This observation is in agreement with the results of Bergman et al., who found an increase in activity for acid catalysts with decreasing anion coordination ability of the conjugate base. However, Hickinbottom reported more than 70 years ago that very small amounts of hydroamination products can be isolated from reactions of anilines with cyclohexene or styrene at 220–250 °C in the presence of more or less stoichiometric amounts of anilinium hydrochloride.[7]

In this article we wish to report that readily available and inexpensive hydrogen iodide can be used as hydroamination catalyst. Initial experiments were performed with styrene (**1**) and aniline (**2**). Typically, the reaction mixture consisting of 5 mol% of aqueous HI (c = 57%), **1**, **2** (5 equiv) and toluene was heated for several hours in a sealed Schlenk tube. Subsequently, the mixture was analyzed by GC-MS and two products **3a** and **3b** were separately isolated by flash chromatography as pure compounds. The results are summarized in Table 1. First of all, it must be mentioned that besides the desired hydroamination product **3a** the *ortho*-hydroarylation product **3b** was obtained as by-product in all reactions. This finding is in agreement with Bergman's results[3] and the fact that **3a** is principally known to undergo an acid-catalyzed Hofmann–Martius rearrangement at elevated temperatures.[8] It is also in agreement with results obtained for $TiCl_4$-catalyzed reactions.[5b] However, as can be seen from Table 1, the reaction conditions (temperature and time) do not strongly influence the ratio of **3a**:**3b**. This is in contrast to $PhNH_3B(C_6F_5)_4{\cdot}Et_2O$-catalyzed reactions where long reaction times favor the formation of hydroarylation products.[3] While these established results can easily be explained by an acid-catalyzed Hofmann–Martius rearrangement of initially formed hydroamination product, the steady ratio of **3a**:**3b** observed in our case of HI-catalyzed reactions suggests that the hydroamination and hydroarylation product are formed in parallel. Interestingly, the corresponding *para*-hydroarylation product can only be detected in trace amounts (<1%) by GC-MS. Furthermore, side products formed by acid-catalyzed polymerization of styrene could not be detected by GC-MS analysis and NMR spectroscopy. While reactions performed at 135 °C need 36–48 hours to reach 100% con-

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version, reactions go to completion within six hours at 150 °C. Furthermore, the reactions can be performed with two, four or five equivalents of aniline with comparable results.

In order to compare the performance of various styrenes and anilines in HI-catalyzed hydroamination/hydroarylation reactions we chose the reaction conditions of entry 4 in Table 1 (135 °C, 24 h, 5 equiv aniline) and performed reactions with five styrenes **1**, **4**–**7** and four anilines **2**, **8**–**10**. The results are summarized in Table 2.

Entries 1–4 and 7–10 in Table 2 indicate that the hydroamination/hydroarylation ratio is significantly shifted towards the hydroarylation product when 4-chloroaniline (**8**) is used instead of aniline (**2**). Starting from electron-deficient CF_3-substituted styrene **6**, the desired products could only be obtained in poor yields (entries 7 and 8). However, both reactions showed 100% conversion after 24 hours and the poor yields can be explained by the formation of a polymer during the course of the reactions. Due to the fact that the alkene unit in **6** is electron poor, protonation of the alkene can obviously not compete with a possible anionic polymerization of **6** initiated by the amine or iodide ions. The opposite should be true for reactions of MeO-substituted electron-rich styrene **5** (entries 5 and 6). However, the easy formation of a resonance-stabilized benzylic cation from **5** or the corresponding hydroamination products **14a**, **15a** is probably responsible for the fact that at 135 °C only hydroarylation products **14b**, **15b** and significant amounts of polymerized material could be obtained (cationic polymerization). The poor yield (26%) obtained for the reaction of **5** with aniline (**2**) could be improved to 61% (**14a** + **14b**) when the reaction was performed at 45 °C. In this case, even a small amount of the hydroamination product (**14a**/**14b**, 5:95) could be detected. While the electron neutral styrenes **1**, **4** and **7** proved to react more smoothly under the reaction conditions the use of 3,5-(CF_3)-disubstituted aniline **10** (entry 12) did not result in the exclusive formation of the hydroamination product **21a** as reported before.[3,5b] Furthermore, side products formed by acid-catalyzed polymerization of styrenes **1**, **4** and **7** could only be detected in trace amounts.

With these results in hand, we focused on HI-catalyzed reactions of anilines **2**, **8**–**10** with norbornene **22**. All reactions were performed at 135 °C for 24 hours in the presence of 5 mol% of HI. The results are summarized in Table 3.

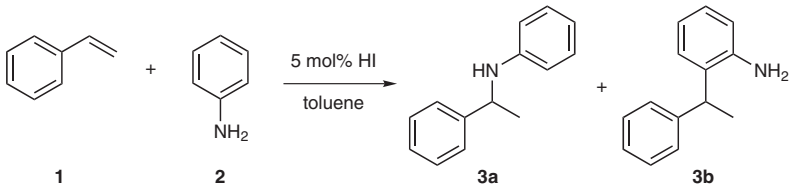
First of all, it can be seen from Table 3 that all anilines reacted successfully with norbornene (**22**) under the chosen conditions to give *exo*-addition products exclusively (confirmed by NOESY of **26a**). Usually, mixtures of hydroamination and hydroarylation products were obtained but in the case of 3,5-(CF_3)-disubstituted aniline **10**, the hydroamination product **26a** was the sole product (entry 6). While the yield was only moderate for electron rich anisidine (**9**, entry 5), the electron neutral and poor deriv-

Biographical Sketches

Klaudia Marcseková was born in Nové Zámky, Slovakia in 1969. After studying chemistry at the Universities of Jena (1987–1991), Bratislava (1991–1992) and Heidelberg (1992–2004), she received her diploma degree in 2004. Since then she has been working for her Ph.D. thesis in the group of Prof. Sven Doye. Her research interests are enantioselective hydroamination reactions and the development of novel hydroamination catalysts.

Sven Doye was born in Berlin, Germany in 1967. Between 1986 and 1990 he studied chemistry at the Technical University of Berlin. He received his diploma degree in 1990 from the same University and his Ph.D. in 1993 from the University of Hannover. During his graduate studies under the supervision of Prof. Winterfeldt, he worked on the stereoselective synthesis of the sesquiterpene (–)-myltaylenol. Between 1994 and 1996 he spent two years in industry working for BASF AG in Ludwigshafen, Germany. After a subsequent year of post doctoral research at the Massachusetts Institute of Technology in Cambridge, USA, with Prof. S. L. Buchwald (1996–1997), he returned to the University of Hannover in 1998. Since then he has been working independently on the development of catalytic hydroamination reactions. From October 2003 to September 2006 he was Professor of Organic Chemistry at the University of Heidelberg, Germany and since September 2006 he has been Professor of Organic Chemistry at the University of Oldenburg, Germany. From September 2002 to January 2003 he was also Guest Professor at Cardiff University, Wales, UK.

Table 1 HI-Catalyzed Hydroaminations of Styrene (**1**) with Aniline (**2**)



1 **2** **3a** **3b**

Entry	Temp (°C)	Time (h)	**2** (equiv)	Yield **3a** + **3b** (%)[a]	Ratio **3a/3b** (GC-MS)	Yield **3a** (%)[b]	Yield **3b** (%)[b]
1	105	24	5	10	68:32	–	–
2	120	24	5	50	63:57	32	17
3	135	15	5	33	69:31	–	–
4	135	24	5	82	65:35	53	28
5	135	36	5	86	64:36	54	31
6	135	48	5	98	57:43	56	42
7	135	24	4	82	68:32	56	26
8	135	24	2	74	70:30	42	25
9	150	3	5	60	68:32	40	18
10	150	6	5	97	66:34	64	32
11	150	12	5	98	64:36	64	34
12	150	24	5	98	67:33	65	32

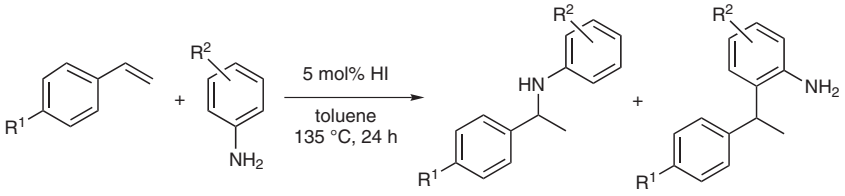
[a] Reaction conditions: alkene (4.70 mmol), amine (23.5 mmol), HI (c = 57% in H_2O, 0.235 mmol, 5 mol%), toluene (0.5 mL). Yields refer to an isolated mixture of **3a** and **3b**.
[b] Yields refer to isolated pure compounds.

atives **2**, **8** and **10** gave better results. Especially interesting is the fact that the reaction between norbornene (**22**) and aniline (**2**) also worked in the presence of 25 mol% 2,6-di-*tert*-butyl-4-methylpyridine, albeit with slightly reduced overall yield (entry 2). The inhibition of a reaction caused by the addition of this pyridine base (25 mol%) has been suggested to provide evidence for a proton-catalyzed process.[3,9] Although we do not have any doubts that the reactions described in this publication are proton-catalyzed, we performed an additional control experiment in the presence of 5 mol% Et_3N (entry 3).[3] Surprisingly, even in this case, the reaction is not completely inhibited.

Finally, we focused on the HI-catalyzed reaction of aniline (**2**) with cyclohexene (**27**). The results are presented in Table 4. Although product formation is observed at 135 °C, the reaction is relatively slow and long reaction times (1–3 weeks) are required to obtain the desired products in reasonable yields (entries 1 and 2). As observed with norbornene, the selectivity for the hydroamination product was good (>85:15) in all experiments.

In summary, we have shown that aromatic amines react with alkenes in the presence of catalytic amounts of aqueous HI to give mixtures of the corresponding hydroamination and hydroarylation products. While the hydroamination reaction is the preferred pathway for aliphatic alkenes, the hydroarylation reaction becomes more important when styrenes are used as substrates. In general, the electronic properties of the alkene and the amine strongly influence the efficiency and the selectivity of the reaction. Since some selectivities observed for the HI-catalyzed reactions described in this publication differ dramatically from results reported for comparable $PhNH_3B(C_6F_5)_4{\cdot}Et_2O$-catalyzed reactions,[3] it is probably necessary to consider the role of the conjugate base in mechanistic discussions of acid-catalyzed hydroamination/hydroarylation processes. For example, it is imaginable that the HI-catalyzed process consists of an initial HI-addition to the alkene and a subsequent nucleophilic substitution of the iodide by the amine. Further studies addressing these issues are currently underway in our laboratories. With regard to scope and limitations, the HI-catalyzed process seems to be comparable to $TiCl_4$-catalyzed hydroaminations of styrenes and norbornene reported by Ackermann et al.[5] This suggests that these reactions are also proton-catalyzed reactions and not Ti-catalyzed reactions as claimed by the authors.

Table 2 HI-Catalyzed Hydroaminations of Styrenes with Aromatic Amines



1, **4–7** **2**, **8–10** **3a**, **11a–21a** **3b**, **11b–21b**

Entry	Alkene	R^1	Amine	R^2	Yield **a** (%)[a]	Yield **b** (%)[a]	Yield **a** + **b** (%) (calcd)	Ratio **a**/**b** (calcd)
1	**1**	H	**2**	H	53 (**3a**)	28 (**3b**)	81	65:35
2			**8**	4-Cl	27 (**11a**)	41 (**11b**)	86[b]	40:60
3	**4**	Me	**2**	H	44 (**12a**)	36 (**12b**)	80	55:45
4			**8**	4-Cl	9[c] (**13a**)	66 (**13b**)	75	12:88
5	**5**	OMe	**2**	H	– (**14a**)	26 (**14b**)	26	0:100
6			**8**	4-Cl	– (**15a**)	83 (**15b**)	83	0:100
7	**6**	CF_3	**2**	H	10 (**16a**)	– (**16b**)	10	100:0
8			**8**	4-Cl	15 (**17a**)	17 (**17b**)	32	47:53
9	**7**	F	**2**	H	57 (**18a**)	25 (**18b**)	82	70:30
10			**8**	4-Cl	47 (**19a**)	37 (**19b**)	84	56:44
11			**9**	4-OMe	15 (**20a**)	20 (**20b**)	38[d]	45:55
12			**10**	3,5-$(CF_3)_2$	–[e] (**21a**)	–[e] (**21b**)	60	67:33[f]

[a] Reaction conditions: alkene (4.70 mmol), amine (23.50 mmol), HI (c = 57% in H_2O, 0.235 mmol, 5 mol%), toluene (0.5 mL), 135 °C, 24 h. Unless otherwise noted, yields refer to isolated pure compounds.
[b] In addition to pure **11a** and **11b**, a mixture of **11a** and **11b** [18%, **a**/**b** = 42:58 (GC)] was obtained after chromatography.
[c] Contaminated with traces of polymerized material.
[d] In addition to pure **20a** and **20b**, a mixture of **20a** and **20b** [3%, **a**/**b** = 71:29 (GC)] was obtained after chromatography.
[e] The products **21a** and **21b** could not be separated by chromatography.
[f] Determined by GC.

All reactions were performed under an inert atmosphere of argon in dry sealed Schlenk tubes (Duran glassware, 100 mL, ∅ 30 mm) equipped with Teflon stopcocks and magnetic stirring bars (15 × 4.5 mm). All compounds were purchased from commercial sources (Acros Organics, Fluka) and were used without further purification. Unless otherwise noted, yields refer to isolated yields of pure compounds as gauged by TLC analysis, ^{1}H and ^{13}C NMR spectroscopy. All products were characterized by ^{1}H NMR, ^{13}C NMR, IR, and mass spectra. Additional characterization data were obtained by CHN elemental analysis and/or high-resolution mass spectrometry (HRMS). NMR spectra were recorded on the following spectrometers: Bruker Avance DRX 300, Bruker AC 300, Bruker Avance DRX 500. All ^{1}H NMR spectra are reported in δ ppm relative to the signal for $CDCl_3$ at 7.26 ppm or TMS at 0.00 ppm. All ^{13}C NMR spectra are reported in δ ppm relative to the central line of the triplet for $CDCl_3$ at 77.0 ppm. IR spectra were recorded on a Bruker Vector 22 spectrometer using an attenuated total reflection (ATR) method. Mass spectra were recorded on a JEOL JMS-700 or a Finnigan TSQ 700 (EI) spectrometer with an ionization potential of 70 eV. Elemental analyses were carried out on an Elementar Vario EL machine. GC-MS analyses were performed on a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with a Hewlett Packard HP 5972 Series I Mass Selective Detector. PE: light petroleum ether (bp 40–60 °C).

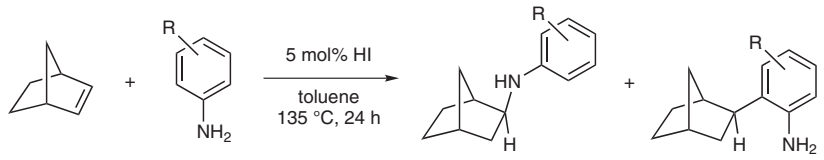
HI-Catalyzed Hydroamination and Hydroalkylation of Alkenes; General Procedure A

Under argon, the amine (23.5 mmol), the alkene (4.70 mmol), toluene (0.5 mL), and aq HI solution (0.03 mL, c = 57% in H_2O, 0.235 mmol, 5 mol%) were placed in a Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred at 135 °C for 24 h. After the mixture had been cooled to r.t., a crude mixture of products was obtained by filtration through SiO_2 (40 g, PE–EtOAc, 2:1). The product ratio was determined by GC-MS. Purification by flash chromatography (SiO_2, 200 g) gave the isolated pure products.

HI-Catalyzed Hydroamination and Hydroalkylation of Alkenes; General Procedure B

Under argon, the amine (23.50 mmol), the alkene (4.70 mmol), toluene (0.5 mL), and aq HI solution (0.03 mL, c = 57% in H_2O, 0.235 mmol, 5 mol%) were placed in a Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred at 135 °C for 24 h. After the mixture had been cooled to

Table 3 HI-Catalyzed Hydroaminations of Norbornene (**22**) with Aromatic Amines

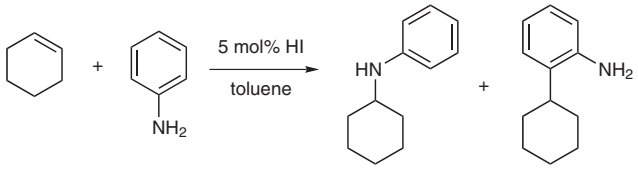


22 **2**, **8**–**10** **23a**–**26a** **23b**–**26b**

Entry	Amine	R	Yield **a** + **b** (%)[a]	Ratio **a**/**b** (GC)	Yield **a** (%)[b]	Yield **b** (%)[b]
1	**2**	H	73[c]	78:22	58 (**23a**)	15 (**23b**)
2	**2**	H	48[d]	82:18	39 (**23a**)	9 (**23b**)
3	**2**	H	34[e]	77:23	27 (**23a**)	7 (**23b**)
4	**8**	4-Cl	77	87:23	65 (**24a**)	12 (**24b**)
5	**9**	4-OMe	54	70:30	34 (**25a**)	20 (**25b**)
6	**10**	3,5-$(CF_3)_2$	64	100:0	64 (**26a**)	– (**26b**)

[a] Reaction conditions: norbornene (**22**, 4.70 mmol), amine (23.50 mmol), HI (*c* = 57% in H_2O, 0.235 mmol, 5 mol%), toluene (0.5 mL), 135 °C, 24 h. Yield refers to an isolated mixture of **a** and **b**.
[b] Yields refer to isolated pure compounds.
[c] The reaction was performed with C_6D_6.
[d] The reaction was performed in the presence of 25 mol% of 2,6-di-*tert*-butyl-4-methylpyridine.
[e] The reaction was performed in the presence of 5 mol% of Et_3N.

Table 4 HI-Catalyzed Hydroaminations of Cyclohexene (**27**) with Aniline (**2**)



27 **2** **28a** **28b**

Entry	Temp (°C)	Time (h)	Yield **28a** + **28b** (%)[a]	Ratio **28a**/**28b** (GC-MS)	Yield **28a** (%)[b]	Yield **28b** (%)[b]
1	135	168	21	87:13	18	2
2	135	504	59	86:14	47	6
3	150	70	17	88:12	–[c]	–[c]

[a] Reaction conditions: Alkene (4.70 mmol), amine (23.5 mmol), HI (*c* = 57% in H_2O, 0.235 mmol, 5 mol%), toluene (0.5 mL). Yields refer to an isolated mixture of **28a** and **28b**.
[b] Yields refer to isolated pure compounds.
[c] Due to the low yield, the products were not separated.

r.t., purification by flash chromatography (SiO_2, 200 g) gave the isolated pure products.

Amines 3a/3b

The general procedure A was used to synthesize amines **3a** and **3b** from styrene (**1**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **3a** (495 mg, 53%) and amine **3b** (258 mg, 28%) were obtained as brown oils.

3a

IR (neat): 3411 3053, 3023, 2968, 2924, 2867, 1602, 1505, 1450, 1352, 1280, 750, 697 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.8 Hz, 3 H), 4.04 (br s, 1 H), 4.48 (q, *J* = 6.8 Hz, 1 H), 6.51 (d, *J* = 7.5 Hz, 2 H), 6.64 (t, *J* = 7.4 Hz, 1 H), 7.08 (t, *J* = 8.5 Hz, 2 H), 7.19–7.38 (m, 5 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.0 (CH_3), 53.5 (CH), 113.3 (CH), 117.2 (CH), 125.8 (CH), 126.9 (CH), 128.6 (CH), 129.1 (CH), 145.2 (C), 147.2 (C).

HRMS: *m*/*z* (%) calcd for [$C_{14}H_{15}N^+$]: 197.1204; found: 197.1196 (68).

Anal. Calcd for $C_{14}H_{15}N$ (197.3): C, 85.24; H, 7.66; N, 7.10. Found: C, 85.22; H, 7.71; N, 7.02.

3b

IR (neat): 3444, 3367, 3060, 3024, 2967, 2931, 1621, 1495, 1452, 1296, 1026, 751, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.62 (d, *J* = 7.2 Hz, 3 H), 4.08 (q, *J* = 7.0 Hz, 1 H), 6.64 (dd, *J* = 7.9, 1.3 Hz, 1 H), 6.85 (dt, *J* = 7.5, 1.3 Hz, 1 H), 7.09 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.18–7.31 (m, 6 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.8 (CH_3), 40.2 (CH), 116.2 (CH), 118.8 (CH), 126.4 (CH), 127.2 (CH), 127.3 (CH), 127.5 (CH), 128.8 (CH), 129.8 (C), 144.2 (C), 145.6 (C).

HRMS: *m*/*z* (%) calcd for [$C_{14}H_{15}N^+$]: 197.1204; found: 197.1214 (94).

Anal. Calcd for $C_{14}H_{15}N$ (197.3): C, 85.24; H, 7.66; N, 7.10. Found: C, 85.12; H, 7.72; N, 7.12.

Amines 11a/11b

The general procedure B was used to synthesize amines **11a** and **11b** from styrene (**1**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **11a** (299 mg, 27%), a mixture of isomers **11a** and **11b** (192 mg, 18%), and amine **11b** (446 mg, 41%) were obtained as brown oils.

11a

IR (neat): 3418, 3026, 2967, 1600, 1500, 1450, 1316, 1295, 1253, 1206, 1178, 1142, 1090, 815, 762, 701 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.51 (d, *J* = 6.8 Hz, 3 H), 4.06 (br s, 1 H), 4.43 (q, *J* = 6.8 Hz, 1 H), 6.41 (d, *J* = 8.9 Hz, 2 H), 7.02 (d, *J* = 8.9 Hz, 2 H), 7.18–7.34 (m, 5 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.0 (CH_3), 53.6 (CH), 114.4 (CH), 121.9 (C), 125.8 (CH), 127.0 (CH), 128.7 (CH), 128.9 (CH), 144.7 (C), 145.7 (C).

HRMS: *m*/*z* (%) calcd for [$C_{14}H_{14}{}^{37}ClN^+$]: 233.0785; found: 233.0772 (14); calcd for [$C_{14}H_{14}{}^{35}ClN^+$]: 231.0815; found: 231.0813 (46).

Anal. Calcd for $C_{14}H_{14}ClN$ (231.7): C, 72.57; H, 6.09; N, 6.04. Found: C, 72.80; H, 6.11; N, 6.02.

11b

IR (neat): 3448, 3372, 2968, 1622, 1600, 1490, 1451, 1413, 1282, 1147, 1080, 877, 816, 760, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.2 Hz, 3 H), 3.42 (br s, 2 H), 4.01 (q, *J* = 7.0 Hz, 1 H), 6.55 (d, *J* = 8.5 Hz, 1 H), 7.04 (dd, *J* = 8.3, 2.3 Hz, 2 H), 7.16–7.33 (m, 6 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.8 (CH_3), 40.3 (CH), 117.2 (CH), 123.5 (C), 126.7 (CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 128.9 (CH), 131.4 (C), 142.9 (C), 144.8 (C).

HRMS: *m*/z (%) calcd for [$C_{14}H_{14}{}^{37}ClN^+$]: 233.0785; found: 233.0789 (29); calcd for [$C_{14}H_{14}{}^{35}ClN^+$]: 231.0815; found: 231.0809 (95).

Anal. Calcd for $C_{14}H_{14}ClN$ (231.7): C, 72.57; H, 6.09; N, 6.04. Found: C, 72.83; H, 6.17; N, 5.97.

Amines 12a/12b

The general procedure B was used to synthesize amines **12a** and **12b** from 1-methyl-4-vinylbenzene (**4**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **12a** (435 mg, 44%) and amine **12b** (357 mg, 36%) were obtained as brown oils.

12a

IR (neat): 3410, 3050, 3018, 2966, 2923, 1603, 1504, 1449, 1429, 1318, 1277, 1257, 817, 749, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (d, *J* = 6.7 Hz, 3 H), 2.29 (s, 3 H), 3.93 (br s, 1 H), 4.42 (q, *J* = 6.6 Hz, 1 H), 6.48 (d, *J* = 6.7 Hz, 2 H), 6.61 (t, *J* = 7.3 Hz, 1 H), 7.03–7.24 (m, 6 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.0 (CH_3), 25.0 (CH_3), 53.1 (CH), 113.2 (CH), 117.1 (CH), 125.7 (CH), 129.0 (CH), 129.3 (CH), 136.3 (C), 142.2 (C), 147.3 (C).

HRMS: *m*/*z* (%) calcd for [$C_{15}H_{17}N^+$]: 211.1361; found: 211.1356 (38).

Anal. Calcd for $C_{15}H_{17}N$ (211.3): C, 85.26; H, 8.11; N, 6.63. Found: C, 85.50; H, 8.16; N, 6.41.

12b

IR (neat): 3442, 3367, 3020, 2966, 2929, 2872, 1622, 1581, 1511, 1495, 1453, 1295, 1266, 820, 750, 529 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 7.2 Hz, 3 H), 2.29 (s, 3 H), 3.38 (br s, 2 H), 4.01 (q, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 7.7 Hz, 1 H), 6.83 (t, *J* = 7.5 Hz, 1 H), 7.00–7.11 (m, 5 H), 7.27 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 20.1 (CH_3), 21.8 (CH_3), 39.8 (CH), 116.1 (CH), 118.6 (CH), 127.1 (CH), 127.1 (CH), 127.3 (CH), 129.4 (CH), 129.9 (C), 135.8 (C), 142.6 (C), 144.3 (C).

HRMS: *m*/*z* (%) calcd for [$C_{15}H_{17}N^+$]: 211.1361; found: 211.1359 (51).

Anal. Calcd for $C_{15}H_{17}N$ (211.3): C, 85.26; H, 8.11; N, 6.63; Found: C, 85.36; H, 8.15; N, 6.44.

Amine 13b

The general procedure B was used to synthesize amine **13b** from 1-methyl-4-vinylbenzene (**4**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 10:1), amine **13a** (102 mg, 9%) and amine **13b** (758 mg, 66%) were obtained as brown oils.

13b

IR (neat): 3448, 3371, 3022, 2968, 2931, 2876, 1731, 1622, 1512, 1489, 1454, 1413, 1281, 1147, 1104, 1049, 876, 817, 650, 557 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 7.1 Hz, 3 H), 2.30 (s, 3 H), 3.42 (br s, 2 H), 3.97 (q, *J* = 7.1 Hz, 1 H), 6.54 (d, *J* = 8.4 Hz, 1 H), 7.01–7.25 (m, 6 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.0 (CH_3), 21.8 (CH_3), 39.9 (CH), 117.2 (CH), 123.4 (C), 127.0 (CH), 127.1 (CH), 127.2 (CH), 129.6 (CH), 131.6 (C), 136.2 (C), 141.7 (C), 142.9 (C).

HRMS: *m*/*z* (%) calcd for [$C_{15}H_{16}{}^{37}ClN^+$]: 247.0942; found: 247.0959 (33); calcd for [$C_{15}H_{16}{}^{35}ClN^+$]: 245.0971; found: 245.0947 (93).

Anal. Calcd for $C_{15}H_{16}ClN$ (245.7): C, 73.31; H, 6.56; N, 5.70. Found: C, 73.07; H, 6.71; N, 5.40.

Amine 14b

The general procedure B was used to synthesize amine **14b** from 1-methoxy-4-vinylbenzene (**5**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 10:1), amine **14b** (282 mg, 26%) was obtained as a colorless oil.

IR (neat): 3444, 3366, 2964, 2932, 1621, 1581, 1511, 1495, 1455, 1300, 1246, 1177, 1030, 832, 751 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 7.2 Hz, 3 H), 3.40 (br s, 2 H), 3.76 (s, 3 H), 4.02 (q, *J* = 7.0 Hz, 1 H), 6.63 (dd, *J* = 7.8, 1.2 Hz, 1 H), 6.79–6.86 (m, 3 H), 7.04–7.13 (m, 3 H), 7.26 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.9 (CH_3), 39.4 (CH), 55.2 (CH_3), 114.1 (CH), 116.2 (CH), 118.7 (CH), 127.1 (CH), 127.2 (CH), 128.4 (CH), 130.1 (C), 137.6 (C), 144.3 (C), 158.1 (C).

HRMS: *m/z* (%) calcd for [$C_{15}H_{17}NO^+$]: 227.1310; found: 227.1309 (69).

Anal. Calcd for $C_{15}H_{17}NO$ (227.3): C, 79.26; H, 7.54; N, 6.16. Found: C, 79.05; H, 7.55; N, 6.14.

Amine 15b

The general procedure B was used to synthesize amine **15b** from 1-methoxy-4-vinylbenzene (**5**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **15b** (1.018 g, 83%) was obtained as a brown oil.

IR (neat): 3448, 3369, 2966, 2933, 2853, 1732, 1614, 1511, 1489, 1460, 1413, 1245, 1178, 1033, 877, 833, 815 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.57 (d, *J* = 7.3 Hz, 3 H), 3.43 (br s, 2 H), 3.77 (s, 3 H), 3.96 (q, *J* = 6.8 Hz, 1 H), 6.54 (d, *J* = 8.3 Hz, 1 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 7.02 (dd, *J* = 8.3, 2.0 Hz, 1 H), 7.09 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 21.8 (CH_3), 39.5 (CH), 55.2 (CH_3), 114.2 (CH), 117.2 (CH), 123.4 (C), 126.9 (CH), 127.1 (CH), 128.3 (CH), 131.7 (C), 136.7 (C), 142.9 (C), 158.3 (C).

HRMS: *m/z* (%) calcd for [$C_{15}H_{16}{}^{37}ClNO^+$]: 263.0891; found: 263.0908 (17); calcd for [$C_{15}H_{16}{}^{35}ClNO^+$]: 261.0920; found: 261.0916 (55).

Anal. Calcd for $C_{15}H_{16}ClNO$ (261.8): C, 68.83; H, 6.16; N, 5.35. Found: C, 68.68; H, 6.26; N, 5.40.

Amine 16a

The general procedure B was used to synthesize amine **16a** from 1-(trifluoromethyl)-4-vinylbenzene (**6**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 10:1), amine **16a** (125 mg, 10%) was obtained as a colorless oil.

IR (neat): 3410, 3053, 2971, 2929, 2871, 1619, 1603, 1506, 1419, 1327, 1258, 1209, 1164, 1123, 1016, 841, 751, 693 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 6.9 Hz, 3 H), 4.05 (br s, 1 H), 4.53 (q, *J* = 6.9 Hz, 1 H), 6.47 (d, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.3 Hz, 1 H), 7.09 (dd, *J* = 8.3, 7.3 Hz, 2 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 25.1 (CH_3), 53.3 (CH), 113.3 (CH), 117.7 (CH), 124.2 (C, q, *J* = 272.2 Hz), 125.7 (CH, q, *J* = 3.8 Hz), 126.2 (CH), 129.2 (CH), 129.2 (C, q, *J* = 32.0 Hz), 146.8 (C), 149.5 (C).

HRMS: *m/z* (%) calcd for [$C_{15}H_{14}F_3N^+$]: 265.1078; found: 265.1084 (45).

Anal. Calcd for $C_{15}H_{14}F_3N$ (265.3): C, 67.91; H, 5.32; N, 5.28; Found: C, 67.63; H, 5.34; N, 4.95.

Amines 17a/17b

The general procedure B was used to synthesize amines **17a** and **17b** from 1-(trifluoromethyl)-4-vinylbenzene (**6**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **17a** (213 mg, 15%) and amine **17b** (245 mg, 17%) were obtained as brown oils.

17a

IR (neat): 3422, 2971, 2928, 2871, 1619, 1601, 1500, 1418, 1325, 1164, 1127, 1067, 1017, 841, 816 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 6.8 Hz, 3 H), 4.10 (br s, 1 H), 4.46 (q, *J* = 6.6 Hz, 1 H), 6.37 (d, *J* = 9.0 Hz, 2 H) 7.02 (d, *J* = 8.9 Hz, 2 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.56 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 24.9 (CH_3), 53.4 (CH), 114.4 (CH), 122.3 (C), 124.3 (C, q, *J* = 247.0 Hz), 125.8 (CH, q, *J* = 3.8 Hz), 126.1 (CH), 129.0 (CH), 129.4 (C, q, *J* = 32.4 Hz), 145.3 (C), 149.0 (C).

HRMS: *m/z* (%) calcd for [$C_{15}H_{13}{}^{37}ClF_3N^+$]: 301.0659; found: 301.0677 (24); calcd for [$C_{15}H_{13}{}^{35}ClF_3N^+$]: 299.0689; found: 299.0683 (65).

Anal. Calcd for $C_{15}H_{13}ClF_3N$ (299.7): C, 60.11; H, 4.37; N, 4.67. Found: C, 60.05; H, 4.41; N, 4.63.

17b

IR (neat): 3447, 3372, 3040, 2976, 2933, 2876, 1620, 1491, 1421, 1414, 1327, 1283, 1161, 1115, 1070, 1018, 885, 875, 843, 816, 614 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.2 Hz, 3 H), 3.38 (br s, 2 H), 4.07 (q, *J* = 7.2 Hz, 1 H), 6.56 (d, *J* = 8.3 Hz, 1 H), 7.05 (dd, *J* = 8.3, 2.5 Hz, 1 H), 7.22 (d, *J* = 2.3 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.6 (CH_3), 40.0 (CH), 117.5 (CH), 123.7 (C), 124.2 (C, q, *J* = 272.2 Hz), 125.9 (CH, q, *J* = 3.8 Hz), 127.2 (CH), 127.5 (CH), 127.8 (CH), 129.0 (C, q, *J* = 32.4 Hz), 130.4 (C), 142.8 (C), 149.0 (C).

HRMS: *m/z* (%) calcd for [$C_{15}H_{13}{}^{37}ClF_3N^+$]: 301.0659; found: 301.0675 (30); calcd for [$C_{15}H_{13}{}^{35}ClF_3N^+$]: 299.0689; found: 299.0707 (100).

Anal. Calcd for $C_{15}H_{13}ClF_3N$ (299.7): C, 60.11; H, 4.37; N, 4.67. Found: C, 60.14; H, 4.48; N, 4.73.

Amines 18a/18b

The general procedure B was used to synthesize amines **18a** and **18b** from 1-fluoro-4-vinylbenzene (**7**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **18a** (576 mg, 57%) and amine **18b** (254 mg, 25%) were obtained as colorless oils.

18a

IR (neat): 3407, 3053, 2967, 2931, 2870, 1604, 1508, 1451, 1429, 1340, 1257, 1180, 1093, 835, 751, 693 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.45 (d, *J* = 6.8 Hz, 3 H), 3.98 (br s, 1 H), 4.43 (q, *J* = 6.8 Hz, 1 H), 6.47 (d, *J* = 7.7 Hz, 2 H), 6.64 (t, *J* = 7.4 Hz, 1 H), 6.97 (t, *J* = 8.7 Hz, 2 H), 7.08 (dd, *J* = 8.7, 7.4 Hz, 2 H), 7.29 (dd, *J* = 7.4, 5.5 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.1 (CH_3), 52.8 (CH), 113.3 (CH), 115.4 (CH, d, *J* = 21.4 Hz), 117.4 (CH), 127.3 (CH, d, *J* = 8.2 Hz), 129.1 (CH), 140.9 (C, d, *J* = 3.3 Hz), 147.1 (C), 161.7 (C, d, *J* = 244.3 Hz).

HRMS: *m/z* (%) calcd for [$C_{14}H_{14}FN^+$]: 215.1110; found: 215.1099 (55).

Anal. Calcd for $C_{14}H_{14}FN$ (215.3): C, 78.11; H, 6.56; N, 6.51. Found: C, 78.08; H, 6.55; N, 6.47.

18b

IR (neat): 3453, 3373, 3064, 3035, 2968, 2932, 2874, 1622, 1602, 1508, 1496, 1453, 1295, 1221, 1158, 1097, 1015, 751, 553 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 7.2 Hz, 3 H), 3.40 (br s, 2 H), 4.05 (q, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 7.9 Hz, 1 H), 6.84 (dd, *J* = 7.5, 7.4 Hz, 1 H), 6.95 (t, *J* = 8.7 Hz, 2 H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1 H), 7.14 (dd, *J* = 8.7, 5.5 Hz, 2 H), 7.25 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.9 (CH_3), 39.4 (CH), 115.5 (CH, d, *J* = 20.9 Hz), 116.3 (CH), 118.8 (CH), 127.1 (CH), 127.4 (CH), 128.8 (CH, d, *J* = 7.7 Hz), 129.5 (C), 141.3 (C, d, *J* = 3.3 Hz), 144.1 (C), 161.4 (C, d, *J* = 244.3 Hz).

HRMS: *m/z* (%) calcd for [$C_{14}H_{14}FN^+$]: 215.1110; found: 215.1094 (44).

Anal. Calcd for $C_{14}H_{14}FN$ (215.3): C, 78.11; H, 6.56; N, 6.51. Found: C, 77.99; H, 6.58; N, 6.54.

Amines 19a/19b

The general procedure B was used to synthesize amines **19a** and **19b** from 1-fluoro-4-vinylbenzene (**7**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 2:1), amine **19a** (550 mg, 47%) and amine **19b** (433 mg, 37%) were obtained as brown oils.

19a

IR (neat): 3421, 2969, 2926, 2870, 1729, 1600, 1507, 1316, 1253, 1093, 836, 816, 506 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 6.7 Hz, 3 H), 4.02 (br s, 1 H), 4.41 (q, *J* = 6.7 Hz, 1 H), 6.21 (d, *J* = 8.9 Hz, 2 H), 6.96–7.05 (m, 4 H), 7.29 (dd, *J* = 8.4, 5.3 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.1 (CH_3), 53.0 (CH), 114.4 (CH), 115.5 (CH, d, *J* = 21.5 Hz), 122.1 (C), 127.3 (CH, d, *J* = 8.3 Hz), 129.0 (CH), 140.3 (C, d, *J* = 3.5 Hz), 145.6 (C), 161.8 (C, d, *J* = 245.0 Hz).

HRMS: *m/z* (%) calcd for [$C_{14}H_{13}{}^{37}ClFN^+$]: 251.0691; found: 251.0725 (15); calcd for [$C_{14}H_{13}{}^{35}ClFN^+$]: 249.0721; found: 249.0735 (51).

Anal. Calcd for $C_{14}H_{13}ClFN$ (249.7): C, 67.34; H, 5.25; N, 5.61. Found: C, 67.82; H, 5.35; N, 5.32.

19b

IR (neat): 3458, 3381, 2970, 2932, 2876, 1890, 1730, 1623, 1602, 1507, 1489, 1455, 1413, 1282, 1222, 1158, 1096, 878, 837, 819, 650, 555, 502 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.8 Hz, 3 H), 3.41 (br s, 2 H), 4.00 (q, *J* = 6.9 Hz, 1 H), 6.56 (d, *J* = 8.3 Hz, 1 H), 6.97 (dd, *J* = 8.8, 8.3 Hz, 2 H), 7.04 (dd, *J* = 8.3, 2.5 Hz, 1 H), 7.13 (dd, *J* = 8.3, 5.4 Hz, 2 H), 7.21 (d, *J* = 2.0 Hz, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 21.8 (CH_3), 39.5 (CH), 115.7 (CH, d, *J* = 21.7 Hz), 117.3 (CH), 123.6 (C), 127.1 (CH), 127.2 (CH), 128.8 (CH, d, *J* = 8.5 Hz), 131.1 (C), 140.4 (C, d, *J* = 2.8 Hz), 142.8 (C), 161.5 (C, d, *J* = 244.9 Hz).

HRMS: *m/z* (%) calcd for [$C_{14}H_{13}{}^{37}ClFN^+$]: 251.0691; found: 251.0705 (23); calcd for [$C_{14}H_{13}{}^{35}ClFN^+$]: 249.0721; found: 249.0733 (75).

Anal. Calcd for $C_{14}H_{13}ClFN$ (249.7): C, 67.34; H, 5.25; N, 5.61. Found: C, 67.53; H, 5.28; N, 5.60.

Amines 20a/20b

The general procedure B was used to synthesize amines **20a** and **20b** from 1-fluoro-4-vinylbenzene (**7**) and 4-methoxybenzenamine (**9**). After purification by flash chromatography (PE–EtOAc, 2:1), amine **20a** (168 mg, 15%), a mixture of isomers **20a** and **20b** (36 mg, 3%), and amine **20b** (227 mg, 20%) were obtained as brown oils.

20a

IR (neat): 3398, 2964, 2931, 2833, 1603, 1511, 1464, 1373, 1236, 1038, 1016, 835, 820 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.46 (d, *J* = 6.8 Hz, 3 H), 3.68 (s, 3 H), 4.38 (q, *J* = 6.6 Hz, 1 H), 6.44 (d, *J* = 6.8 Hz, 2 H), 6.69 (d, *J* = 6.8 Hz, 2 H), 6.98 (t, *J* = 8.7 Hz, 2 H), 7.31 (dd, *J* = 8.5, 5.3 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 25.2 (CH_3), 53.7 (CH), 55.7 (CH_3), 114.7 (CH), 114.8 (CH), 115.4 (CH, d, *J* = 21.4 Hz), 127.4 (CH, d, *J* = 7.7 Hz), 141.9 (C, d, *J* = 3.3 Hz), 141.3 (C), 152.1 (C), 161.7 (C, d, *J* = 244.3 Hz).

HRMS: *m/z* (%) calcd for [$C_{15}H_{16}FNO^+$]: 245.1216; found: 245.1210 (100).

Anal. Calcd for $C_{15}H_{16}FNO$ (245.1): C, 73.45; H, 6.57; N, 5.71. Found: C, 73.58; H, 6.65; N, 5.63.

20b

IR (neat): 3430, 3359, 2966, 2934, 2832, 1892, 1604, 1506, 1464, 1430, 1285, 1221, 1159, 1016, 875, 838 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 7.2 Hz, 3 H), 3.23 (br s, 2 H), 3.78 (s, 3 H), 4.08 (q, *J* = 7.2 Hz, 1 H), 6.61 (d, *J* = 8.5 Hz, 1 H), 6.68 (dd, *J* = 8.7, 2.8 Hz, 1 H), 6.87 (d, *J* = 2.8 Hz, 1 H), 6.96 (t, *J* = 8.7 Hz, 2 H), 7.15 (dd, *J* = 8.7, 5.5 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 21.9 (CH_3), 39.5 (CH), 55.7 (CH_3), 111.8 (CH), 114.1 (CH), 115.5 (CH, d, *J* = 20.9 Hz), 117.3 (CH), 128.9 (CH, d, *J* = 7.7 Hz), 131.7 (C), 137.7 (C), 141.1 (C, d, *J* = 2.7 Hz), 153.1 (C), 161.4 (C, d, *J* = 244.8 Hz).

HRMS: *m/z* (%) calcd for [$C_{15}H_{16}FNO^+$]: 245.1216; found: 245.1197 (100).

Anal. Calcd for $C_{15}H_{16}FNO$ (245.1): C, 73.45; H, 6.57; N, 5.71. Found: C, 73.08; H, 6.64; N, 5.90.

Amines 23a/23b

The general procedure A was used to synthesize amines **23a** and **23b** from norbornene (**22**) and aniline (**2**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **23a** (510 mg, 58%) and amine **23b** (136 mg, 15%) were obtained as brown oils.

23a

IR (neat): 3407, 3049, 2952, 2869, 1601, 1604, 1452, 1427, 1356, 1305, 1277, 1254, 1180, 1155, 1115, 1032, 992, 747, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.12–1.26 (m, 4 H), 1.44 (d, *J* = 9.8 Hz, 1 H), 1.50–1.61 (m, 2 H), 1.82 (ddd, *J* = 12.8, 7.7, 2.3 Hz, 1 H), 2.28 (m, 2 H), 3.23 (dd, *J* = 7.5, 4.1 Hz, 1 H), 3.56 (br s, 1 H), 6.57 (d, *J* = 7.7 Hz, 2 H), 6.67 (t, *J* = 7.4 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 26.4 (CH_2), 28.5 (CH_2), 35.3 (CH_2), 35.6 (CH), 41.1 (CH_2), 41.2 (CH), 56.6 (CH), 113.1 (CH), 116.9 (CH), 129.2 (CH), 147.6 (C).

HRMS: *m/z* (%) calcd for [$C_{13}H_{17}N^+$]: 187.1361; found: 187.1351 (100).

Anal. Calcd for $C_{13}H_{17}N$ (187.3): C, 83.37; H, 9.15; N, 7.48. Found: C, 83.25; H, 9.16; N, 7.52.

23b

IR (neat): 3470, 3378, 3022, 2951, 2868, 1619, 1581, 1495, 1454, 1296, 1260, 1034, 747 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, *J* = 9.8 Hz, 1 H), 1.30–1.40 (m, 2 H), 1.52–1.72 (m, 4 H), 1.80 (ddd, *J* = 11.5, 8.9, 2.1 Hz, 1 H), 2.36 (br s, 1 H), 2.47–2.48 (m, 1 H), 2.58 (dd, *J* = 8.9, 5.5 Hz, 1 H), 3.63 (br s, 2 H), 6.68 (d, *J* = 7.7 Hz, 1 H), 6.75 (t, *J* = 7.4 Hz, 1 H), 7.01 (t, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ = 26.3 (CH_2), 30.3 (CH_2), 36.3 (CH_2), 36.9 (CH), 37.8 (CH_2), 40.4 (CH), 42.0 (CH), 115.5 (CH), 118.3 (CH), 125.3 (CH), 126.3 (CH), 131.5 (C), 144.0 (C).

HRMS: *m/z* (%) calcd for [$C_{13}H_{17}N^+$]: 187.1361; found: 187.1356 (100).

Anal. Calcd for $C_{13}H_{17}N$ (187.3): C, 83.37; H, 9.15; N, 7.48. Found: C, 83.21; H, 9.18; N, 7.47.

Amines 24a/24b

The general procedure A was used to synthesize amines **24a** and **24b** from norbornene (**22**) and 4-chlorobenzenamine (**8**). After purification by flash chromatography (PE–EtOAc, 10:1), amine **24a** (675 mg, 65%) and amine **24b** (125 mg, 12%) were obtained as brown oils.

24a

IR (neat): 3412, 2953, 2910, 2870, 1600, 1498, 1322, 1314, 1305, 1278, 1263, 1251, 1178, 1121, 1090, 814 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.13–1.22 (m, 4 H), 1.42 (d, *J* = 9.8 Hz, 1 H), 1.47–1.57 (m, 2 H), 1.80 (ddd, *J* = 12.2, 7.3, 2.0 Hz, 1 H), 2.24 (br s, 1 H), 2.28 (br s, 1 H), 3.16–3.17 (m, 1 H), 3.55 (br s, 1 H), 6.46 (d, *J* = 8.8 Hz, 2 H), 7.08 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 26.3 (CH_2), 28.4 (CH_2), 35.3 (CH_2), 35.6 (CH), 41.0 (CH_2), 41.1 (CH), 56.7 (CH), 114.1 (CH), 121.4 (C), 129.0 (CH), 146.1 (C).

HRMS: *m*/*z* (%) calcd for [$C_{13}H_{16}{}^{37}ClN^+$]: 223.0942, found 223.0949 (35); calcd for [$C_{13}H_{16}{}^{35}ClN^+$]: 221.0971; found: 221.0961 (100).

Anal. Calcd for $C_{13}H_{16}ClN$ (221.7): C, 70.42; H, 7.27; N, 6.32. Found: C, 70.95; H, 7.37; N, 6.14.

24b

IR (neat): 3478, 3389, 2956, 2869, 1620, 1489, 1453, 1413, 1315, 1298, 1279, 1143, 1092, 880, 850, 813, 650, 551 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.25–1.36 (m, 3 H), 1.48–1.51 (m, 2 H), 1.53–1.70 (m, 2 H), 1.77–1.81 (m, 1 H), 2.37 (br s, 1 H), 2.43 (br s, 1 H), 2.51–2.53 (m, 1 H), 3.62 (br s, 2 H), 6.58 (d, *J* = 8.3 Hz, 1 H), 6.95 (dd, *J* = 8.3, 1.2 Hz, 1 H), 7.08 (d, *J* = 1.2 Hz, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 29.1 (CH_2), 30.2 (CH_2), 36.2 (CH_2), 36.9 (CH), 37.8 (CH_2), 40.3 (CH), 42.0 (CH), 116.5 (CH), 123.1 (C), 125.5 (CH), 126.0 (CH), 133.2 (C), 142.6 (C).

HRMS: *m*/*z* (%) calcd for [$C_{13}H_{16}{}^{37}ClN^+$]: 223.0942; found: 223.0940 (28); calcd for [$C_{13}H_{16}{}^{35}ClN^+$]: 221.0971; found: 221.0972 (100).

Anal. Calcd for $C_{13}H_{16}ClN$ (221.7): C, 70.42; H, 7.27; N, 6.32. Found: C, 70.76; H, 7.30; N, 6.31.

Amines 25a/25b

The general procedure A was used to synthesize amines **25a** and **25b** from norbornene (**22**) and 4-methoxybenzenamine (**9**). After purification by flash chromatography (PE–EtOAc, 5:1), amine **25a** (344 mg, 34%) and amine **25b** (204 mg, 20%) were obtained as brown oils.

25a

IR (neat): 3397, 2951, 2909, 2869, 2830, 1620, 1511, 1464, 1452, 1441, 1356, 1302, 1235, 1179, 1156, 1118, 1103, 1040, 818, 749 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.12–1.22 (m, 4 H), 1.43 (d, *J* = 9.7 Hz, 1 H), 1.46–1.55 (m, 2 H), 1.78 (ddd, *J* = 12.7, 7.7, 2.3 Hz, 1 H), 2.25 (m, 2 H), 3.15–3.17 (m, 1 H), 3.25 (br s, 1 H), 3.72 (s, 3 H), 6.52 (d, *J* = 8.7 Hz, 2 H), 6.76 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 26.5 (CH_2), 28.5 (CH_2), 35.2 (CH_2), 35.6 (CH), 41.0 (CH_2), 41.1 (CH), 55.8 (CH_3), 57.4 (CH), 114.4 (CH), 114.9 (CH), 141.9 (C), 151.8 (C).

HRMS: *m*/*z* (%) calcd for [$C_{14}H_{19}NO^+$]: 217.1467; found: 217.1460 (100).

Anal. Calcd for $C_{14}H_{19}NO$ (217.3): C, 77.38; H, 8.81; N, 6.45. Found: C, 77.61; H, 8.89; N, 6.48.

25b

IR (neat): 3443, 3362, 2951, 2869, 2830, 1607, 1585, 1499, 1466, 1453, 1430, 1285, 1245, 1225, 1156, 1137, 1040, 876, 809 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 9.4 Hz, 1 H), 1.29–1.38 (m, 2 H), 1.51–1.68 (m, 4 H), 1.77–1.82 (m, 1 H), 2.36 (br s, 1 H), 2.43 (br s, 1 H), 2.58–2.60 (m, 1 H), 3.35 (br s, 2 H), 3.75 (s, 3 H), 6.58 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.62 (d, *J* = 8.4 Hz, 1 H), 6.77 (d, *J* = 2.7 Hz, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 29.2 (CH_2), 30.2 (CH_2), 36.3 (CH_2), 36.9 (CH), 38.0 (CH_2), 40.6 (CH), 42.1 (CH), 55.7 (CH_3), 110.6 (CH), 112.6 (CH), 116.3 (CH), 133.6 (C), 137.7 (C), 152.7 (C).

HRMS: *m*/*z* (%) calcd for [$C_{14}H_{19}NO^+$]: 217.1467; found: 217.1491 (100).

Anal. Calcd for $C_{14}H_{19}NO$ (217.3): C, 77.38; H, 8.81; N, 6.45. Found: C, 77.61; H, 8.89; N, 6.48.

Amine 26a

The general procedure A was used to synthesize amine **26a** from norbornene (**22**) and 3,5-bis(trifluoromethyl)aniline (**10**). After purification by flash chromatography (PE–EtOAc, 10:1), amine **26a** (976 mg, 64%) was obtained as a colorless oil.

IR (neat): 3437, 2959, 2879, 1622, 1516, 1474, 1429, 1395, 1358, 1327, 1308, 1276, 1175, 1131, 1103, 1095, 1030, 861, 845, 701, 683 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.19–1.24 (m, 4 H), 1.44 (d, *J* = 9.5 Hz, 1 H), 1.50–1.62 (m, 2 H), 1.86 (ddd, *J* = 12.2, 7.3, 2.0 Hz, 1 H), 2.25 (br s, 1 H), 2.32 (br s, 1 H), 3.25 (m, 1 H), 4.00 (br s, H), 6.87 (s, 2 H), 7.11 (s, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 26.4 (CH_2), 28.4 (CH_2), 35.5 (CH_2), 35.8 (CH), 41.0 (CH_2), 41.4 (CH), 56.5 (CH), 109.7 (CH, q, *J* = 3.8 Hz), 112.1 (CH), 112.2 (CH), 123.8 (C, q, *J* = 272.2 Hz), 132.4 (C, q, *J* = 33.0 Hz), 148.2 (C).

HRMS: *m*/*z* (%) calcd for [$C_{15}H_{15}F_6N^+$]: 323.1109; found: 323.1155 (53).

Anal. Calcd for $C_{15}H_{15}F_6N$ (323.3): C, 55.73; H, 4.68; N, 4.33. Found: C, 56.04; H, 4.77; N, 4.62.

Amines 28a/28b

The general procedure A was used to synthesize amines **28a** and **28b** from cyclohexene (**27**) and aniline (**2**). The reaction time was 7 d (168 h). After purification by flash chromatography (PE–EtOAc, 100:1), amine **28a** (145 mg, 18%) and amine **28b** (20 mg, 2%) were obtained as orange oils.

28a

IR (neat): 3398, 3050, 3019, 2929, 2853, 1601, 1505, 1449, 1431, 1319, 1255, 1178, 1149, 1117, 748, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.08–1.26 (m, 3 H), 1.31–1.39 (m, 2 H), 1.62–1.76 (m, 3 H), 2.02–2.05 (m, 2 H), 3.23 (ddd, *J* = 17.6, 10.3, 4.0 Hz, 1 H), 3.47 (br s, 1 H), 6.56 (d, *J* = 7.8 Hz, 2 H), 6.64 (t, *J* = 7.3 Hz, 1 H), 7.13 (t, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 25.0 (CH_2), 25.9 (CH_2), 33.4 (CH_2), 51.6 (CH), 113.1 (CH), 116.7 (CH), 129.2 (CH), 147.3 (C).

HRMS: *m*/*z* (%) calcd for [$C_{12}H_{17}N^+$]: 175.1361; found: 175.1368 (48).

Anal. Calcd for $C_{12}H_{17}N$ (175.3): C, 82.23; H, 9.78; N, 7.99. Found: C, 82.45; H, 9.47; N, 8.32.

28b

IR (neat): 3466, 3375, 3022, 2926, 2852, 1620, 1582, 1496, 1452, 1293, 1255, 748 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.33–1.49 (m, 5 H), 1.70–1.98 (m, 5 H), 2.40–2.55 (m, 1 H), 3.66 (br s, 2 H), 6.68 (d, *J* = 7.8 Hz, 1 H), 6.77 (t, *J* = 7.3 Hz, 1 H), 7.01 (br t, *J* = 7.6 Hz, 1 H), 7.11 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, DEPT, $CDCl_3$): δ = 26.4 (CH_2), 27.2 (CH_2), 32.8 (CH_2), 38.4 (CH), 115.9 (CH), 119.1 (CH), 126.0 (CH), 126.5 (CH), 132.0 (C), 143.3 (C).

HRMS: *m*/*z* (%) calcd for [$C_{12}H_{17}N^+$]: 175.1361; found: 175.1347 (100).

Anal. Calcd for $C_{12}H_{17}N$ (175.3): C, 82.23; H, 9.78; N, 7.99. Found: C, 82.51; H, 9.38; N, 8.28.

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