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Multicomponent *C*-Alkylation Reactions of Aromatic Aldimines with Trialkylboranes Reagents

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Dedicated to Professor Luis Castedo

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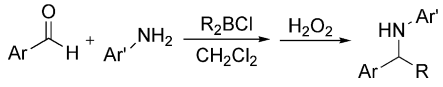
The one-pot three-component reaction of an aryl aldehyde, an arylamine, and a trialkylborane in the presence of hydrogen peroxide afforded the alkylated arylamines **1** in good yields via oxidized imine–borane complexes. In addition, the versatility of our procedure has been confirmed by the use of enolizable aldehydes, alkylic amines, and cyclic imines.

Introduction

Alkylic 1,2-addition to the carbon–nitrogen double bond is a useful tool for preparing a variety of alkylated amines. However, the low electrophilicity displayed by the imino group and the formation of reductive coupling products are severe disadvantages of these addition reactions.[1] In these reactions, organometallic reagents are typically used to generate the carbon–carbon bond, but the reactions of organometallics with imines are often accompanied by the enolization of substrates bearing acidic α protons. Recently, free-radical reactions have also emerged as a valuable tool for C=N alkylation. The 1,2-addition to the C=N bond using radicals as alkylating agents has been studied as both intra- and intermolecular processes.[2] The limited data available in the literature on the intermolecular addition reaction highlights the low reactivity of the C=N bond. Nevertheless, the low reactivity of imines can be overcome either by attaching activating substituents to the nitrogen atom or by using a Lewis acid as an external activator.

The intermolecular radical alkylation of activated imine derivatives can be performed by usingthe Et_3B/air/RI alkylating system;[3] the ethyl radical generated from triethylborane abstracts iodine from the alkyl iodide to produce a new carbon-centered alkyl radical. However, the scope of this method is limited to the generation of radicals that are more stable than the ethyl radical, that is, secondary, tertiary, and stabilized alkyl radicals. Such a limitation is usually overcome by using stoichiometric amounts of tributyltin hydride[4] as a source of tin radicals which are able to abstract the halogen atom efficiently from the alkyl halide. A novel dimethylzinc/air radical initiation system able to act as an efficient source of unstable methyl radicals has recently been developed.[5] Two further drawbacks of the radical addition reaction are the low reactivity and yields attainable with nonactivated imines in comparison with those reported for other derivatives such as oxime ethers,[3a,3b,3e,3g] hydrazones,[3b,3d–3f] or tosylimines.[3c,3g,5]

We recently described a new one-pot alkylative amination reaction involving three components, which are benzaldehyde, an aniline, and a dialkylchloroborane as alkylating agent (Scheme 1). In this reaction, the chloroborane reagent acts both as a Lewis acid catalyst in the formation of the imine and as a chain donor to the C=N bond.[6]



Scheme 1. General one-pot alkylation reaction with R_2BCl.

As a continuation of this previous investigation, we focused in this work on the use of trialkylboranes as chain donors for the nonactivated imine group with the aim of developing a general one-pot procedure for the alkylative amination reaction. To the best of our knowledge a similar one-pot reaction has previously been described only for activated oxime ethers in the presence of a strong Lewis acid catalyst using Et_3B or Et_3B/RI as the alkylating agent.[7] It is noteworthy that our methodology is the first example of a one-pot alkylative amination process for nonactivated imines using a wide variety of trialkylboranes as alkylating agents. Such a broad choice of trialkylboranes, which allows

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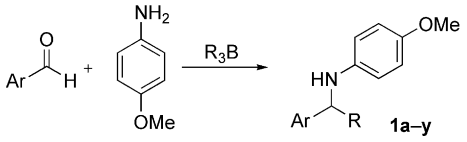
the addition of different alkyl groups (either primary or secondary) to the C=N bond in good yield, is perhaps the foremost advantage of this reaction.

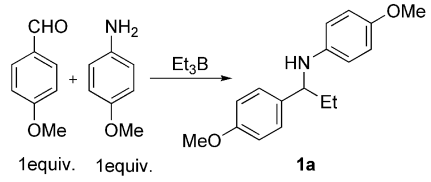
Results and Discussion

We herein report our preliminary results for the one-pot reaction between R_3B, *p*-methoxyaniline, and aromatic aldehydes with different substitution patterns (Scheme 2). To establish the basics for this reaction, a study was initially carried out using *p*-anisaldehyde, *p*-methoxyaniline, and a 1 M solution of commercially available triethylborane (Et_3B) in hexane as the starting compounds. In general, the reactions were performed in dichloromethane at 25 °C using equimolar amounts of amine and aldehyde. We studied the reactions under various experimental conditions (Table 1), including varying the amount of added Et_3B (1–3 mmol) and the influence of co-reagents. The first observation was that no reaction occurs in the absence of co-reagents. Even an excess of Et_3B had no perceivable beneficial effect; the imine–borane complex was the only observed reaction product in this case.



Scheme 2. General alkylation reaction.

Table 1. Synthesis of amine **1a** by the three-component reaction.[a]



Entry	Et_3B [equiv.]	co-reagent	Yield [%][b]
1	1	–	<5
2	1	O_2	10
3	1	H_2O_2[c]	15
4	2	–	<5
5	2	O_2	25
6	2	H_2O_2[c]	35
7	3	–	<5
8	3	O_2	polyalkylated[d]
9	3	H_2O_2[c]	90–95

[a] Reactions carried out with equimolar amounts of aldehyde and amine for 96 h. [b] Yields of compound **1a** were determined by ^{1}H NMR spectroscopy with an estimated detection limit of 5% (yields quoted as <5% for no detection). [c] 1 Equiv. of H_2O_2. [d] A mixture of polyalkylated products plus compound **1a** was observed.

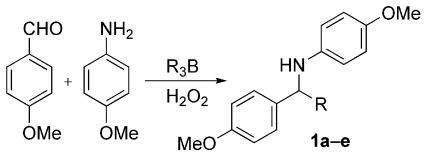
A more detailed assessment of the influence of co-reagents on the alkylation reaction was attained by evaluating separately the effects of H_2O_2 and O_2 on the reaction yield (Table 1). It was found that although the alkyl(aryl)amine **1a** was produced in the presence of both co-reagents, only H_2O_2 afforded good yields when the quantity of Et_3B was increased (entries 3, 6, and 9). This methodology is very useful because the use of H_2O_2 allows us to adjust the amount of co-reagent employed to enable the reaction to proceed more cleanly.

The second observation was that the overall yield was much higher when 3 equiv. of Et_3B and 1 equiv. of H_2O_2 were used (Table 1, entry 9). Under such conditions the reaction showed good regioselectivity and only the imine-ethylated product **1a** was obtained. In contrast, a mixture of **1a** and polyalkylated amines was obtained when oxygen was used instead of H_2O_2 (Table 1, entry 8).

A double role, as Lewis acid catalyst for the formation of the imine and as chain donor to the carbon–nitrogen double bond, is assumed to be played by Et_3B in this reaction. Furthermore the imine activation is thought to proceed via the formation of an imino–borane complex.

Reported examples are limited to the addition of Et_3B to the activated C=N bond. However, our procedure offers an alternative method for introducing a primary or secondary alkyl group. To evaluate the influence of the alkyl group of R_3B on the efficiency of the reaction, *p*-anisaldehyde, *p*-methoxyaniline, and different primary and secondary alkylating agents were assayed. The results obtained from the reactions with different R_3B (R = *n*Bu, *s*Bu, *n*-Hex, and Chx; Chx = cyclohexyl) are summarized in Table 2.

Table 2. Synthesis of the amines **1a**–**e** by the three-component reactions with different R_3B.[a]



Entry	R	Time [h]	Amine	Yield [%][b]
1	Et	96	**1a**	95 (90)
2	*n*Bu	85	**1b**	85 (80)
3	*n*-Hex	85	**1c**	85 (79)
4	Chx	72	**1d**	95 (89)
5	*s*Bu	72	**1e**	95 (91)

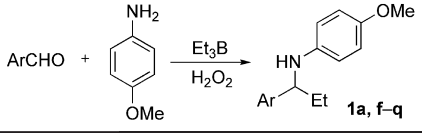
[a] Reactions carried out with equimolar amounts of aldehyde and amine, 3 equiv. of R_3B, and 1 equiv. of H_2O_2. [b] Yields of compounds **1a**–**e** were determined by ^{1}H NMR spectroscopy with an estimated detection limit of 5%. The yields obtained after purification by silica gel chromatography are given in parentheses.

The desired alkylated amines were obtained in good yields (Table 2, entries 1–5) even when primary trialkylboranes were used (Table 2, entries 1–3). With secondary trialkylboranes, a shorter reaction time was required for completion than with primary trialkylboranes (Table 2, entries 4 and 5). These results show that the limitations of the alkylation associated with the generation of primary alkyl radicals by the standard tin-free method (triethylborane/iodoalkane)[5] may be circumvented by using this methodology. An additional advantage of the method is that a wide variety of trialkylboranes can be prepared in situ by the hydroboration of alkenes. In fact, both Hex_3B and Chx_3B were

prepared and directly used, yielding the corresponding amines without any detrimental effect (Table 2, entries 3 and 4).

To delineate the scope of the present method, a number of aryl aldehydes were studied in the reaction of *p*-methoxyaniline and Et_3B, including a set of substituted benzaldehydes and some representative heterocyclic aldehydes (Table 3). In all cases, the alkylated amines **1a**,**f**–**q** were obtained in good or very good yields. As expected, the reactivity of the benzaldehydes was found to be significantly influenced by the electronic effect of the substituent. Electron-withdrawing groups led to a significant decrease in the reaction rate and required higher quantities of Et_3B for completion (Table 3, entries 6–10), whereas exactly the opposite effects were exerted by electron-releasing groups (Table 3, entries 2–5). Moreover, the highest alkylating rates were observed for benzaldehydes bearing a methoxy substituent at the *ortho* position (Table 3, entries 4 and 5). The favorable effect of the *o*-methoxy group may be associated with the occurrence of a coordinating state involving the oxygen and boron atoms; such an interaction would provide higher stability to the amine–borane complex and faster release of the ethyl radicals. The reaction was also perfectly applicable to heterocyclic aromatic aldehydes (Table 3, entries 11–13), rendering good yields in the desired ethylated amines. The particularly high reactivities observed with 2-furfural and 2-pyridinecarbaldehyde may be related to the presence of the heteroatom at the vicinal position with respect to the amine group, which would allow a coordination interaction similar to that in *o*-methoxybenzaldehyde.

Table 3. Synthesis of the amines **1a**,**f**–**q** by the three-component reaction.

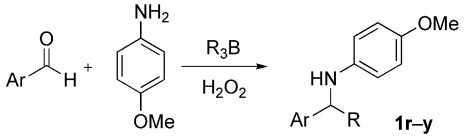


Entry	Ar	Et_3B [equiv.]	Time [h]	Amine	Yield [%][a]
1	C_6H_5	3	126	**1f**	70
2	4-$MeOC_6H_4$	3	96	**1a**	90
3	3-$MeOC_6H_4$	3	96	**1g**	91
4	2-$MeOC_6H_4$	3	48	**1h**	93
5	2,3-$(MeO)_2C_6H_3$	3	48	**1i**	90
6	4-FC_6H_4	4	168	**1j**	82
7	4-ClC_6H_4	4	168	**1k**	81
8	4-MeC_6H_4	4	126	**1l**	89
9	4-NCC_6H_4	4	126	**1m**	80
10	4-$NO_2C_6H_4$	4	126	**1n**	82
11	2-furyl	3	48	**1o**	79
12	4-pyridyl	3	75	**1p**	76
13	2-pyridyl	3	72	**1q**	70

[a] Yields after purification by silica gel chromatography.

Encouraged by the above results, we turned our attention to the combined effect of the aldehyde substitution pattern and the nature of the trialkylborane used as the alkylating agent. A representative selection of the aldehydes listed in Table 3 was chosen to study the reaction of *p*-methoxyaniline with either nBu_3B or sBu_3B (Table 4) using the same reaction conditions as established above. As can be seen in Table 4, the two trialkylboranes reacted efficiently to afford good yields of the alkylated amine; sBu_3B (entries 2, 4, 6, and 8) reacted faster than the primary nBu_3B. With regard to the influence of the aldehyde substitution pattern, the results obtained were similar to those observed with Et_3B; reactions involving aryl aldehyde derivatives with electron-withdrawing substituents needed longer periods of time to be completed (Table 4, entries 5–8). Also, here *o*-methoxybenzaldehyde showed the highest reactivity (Table 4, entries 1 and 2) with both nBu_3B and sBu_3B, which is in full agreement with the results described above for Et_3B.

Table 4. Synthesis of the amines **1r**–**y** by the three-component reaction.



Entry	Ar	R	Time [h]	Amine	Yield [%][a]
1	2-$MeOC_6H_4$	*n*Bu	<48	**1r**	82
2		*s*Bu	28	**1s**	91
3	3-$MeOC_6H_4$	*n*Bu	85	**1t**	80
4		*s*Bu	72	**1u**	90
5	4-FC_6H_4	*n*Bu	120	**1v**	70
6		*s*Bu	96	**1w**	82
7	4-ClC_6H_4	*n*Bu	120	**1x**	72
8		*s*Bu	96	**1y**	83

[a] Isolated yields after silica gel chromatography.

The versatility of this alkylation method was evidenced by its application to enolizable aldehydes, alkylic amines, and cyclic imines. Thus, the amines shown in Figure 1 were synthesized by using the standard procedure with slight modifications.

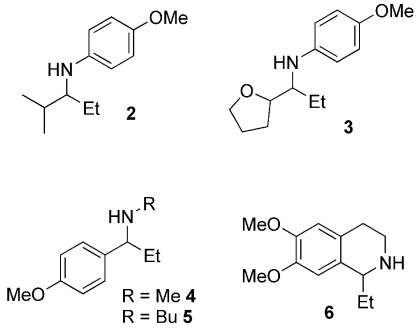


Figure 1. Synthesis of the amines **2**–**6** by the three-component reaction.

The one-pot reaction between *p*-methoxyaniline, Et_3B, and the enolizable aldehyde, 2-methylpropanal, afforded the expected amine **2** in 35% yield. Further experimentation

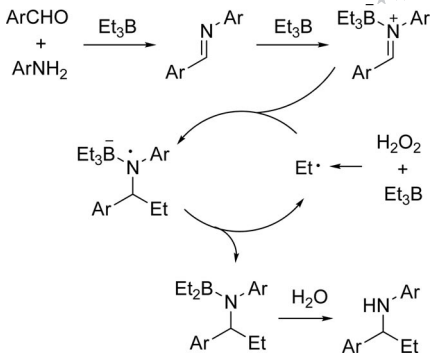
revealed that the yield of the amine could be significantly increased if the alkylation addition was performed with the previously formed imine. In this way amine **2** was obtained in 70% yield after 48 h. The extension of this reaction to other enolizable aldehydes is under investigation.

To test the effect of a heteroatom at the position vicinal to the amine group in the reaction with enolizable aldehydes, we next investigated the one-pot reaction with tetrahydro-2-furancarbaldehyde, *p*-methoxyaniline, and Et_3B. Although reaction times of 2–6 days were used in most of these experiments, conversion was almost complete after 20 min with an 80% yield of the amine **3**. Note that 1,2-stereoinduction was detected at room temperature with the formation of an 87:13 mixture of the ethylated amine **3**. The presence of the chelate-forming Lewis acid may explain the higher reactivity observed in the 1,2-stereoinduction.

Subsequently we examined the reactivity of aliphatic amines with *p*-methoxybenzaldehyde and Et_3B. The one-pot reaction using $MeNH_2$ and $BuNH_2$ failed to give the expected products **4** and **5**; the imine–borane complex was obtained instead. The low reactivity of these aliphatic imines was overcome by Lewis acid activation. Two equivalents of $BF_3{\cdot}OEt_2$ were required for a successful one-pot addition to give the desired alkylated amines **4** and **5** (38 and 40% yields, respectively). On the other hand, when we carried out the alkylation addition with the preformed imine in the presence of 2 equiv. of $BF_3{\cdot}OEt_2$, the yield was increased significantly so that amines **4** and **5** were obtained in 80 and 83% yields, respectively.

We next chose the 3,4-dihydro-6,7-dimethoxyisoquinoline as a model substrate to investigate the influence of reaction conditions on the ethyl addition to endocyclic imines. Again activation with 2 equiv. of $BF_3{\cdot}OEt_2$ was found to be essential in the reaction with Et_3B. Under these conditions the ethylated amine **6** was obtained in 60% yield.

Our studies on the mechanism of this reaction initially focused on the standard one-pot reaction between *p*-methoxyaniline, *p*-anisaldehyde, and Et_3B (3 equiv.). First observations showed that under a stream of oxygen the reaction was not reliable and polyalkylated compounds were the main products. A second feature to note is that the addition of radical scavengers such as cumene or AIBN inhibited in part the alkylation reaction. Moreover, when the reaction was performed with $BF_3{\cdot}Et_2O$ as the catalyst for imine formation, the amount of trialkylborane required could be reduced to 2 equiv. All these results suggest the mechanism for the one-pot procedure that is illustrated in Scheme 3. Accordingly, Et_3B must act not only as an alkylating agent, but also as a Lewis acid catalyst for imine formation and activation. Thus, the first equivalent of Et_3B would be used for the formation of the imine. The imine formed would be activated by the second equivalent of Et_3B through the formation of an imine–borane complex, and the third equivalent of Et_3B would act as the radical initiator. In agreement with previously reported studies,[8] a free-radical chain mechanism is proposed in which the generated alkyl radical playing the role of chain carrier is regenerated in the propagation step.



Scheme 3. Proposed mechanism for the alkylative amination reaction.

Conclusions

A one-pot alkylative amination reaction of aryl aldehyde derivatives that involves three components with trialkylborane as the alkylating agent has been developed. The reaction can be applied to differently substituted aldehydes as well as to hetaryl aldehydes, as well as being used to attach primary and secondary alkyl chains depending on the radical stability. The broad applicability of the procedure was ascertained by extending this reaction to enolizable aldehydes and aliphatic amines. Additional studies to ascertain the detailed mechanism of the reaction and to extend its synthetic potential to different types of nonactivated imines are underway in our laboratory.

Experimental Section

General: EI-MS spectra were recorded with an HP-MS 5988A spectrometer operating at 70 eV and HRMS spectra with a VG Autospec spectrometer. Infrared spectra were obtained with an ATR accessory (MIRacle ATR, PIKE Technologies, USA) coupled to a FTIR Jasco FT/IR–4100 spectrometer. All spectra were recorded in the range 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. NMR spectra were registered with a Bruker AC 200 instrument at 200 MHz for ^1H and 50.3 MHz for ^{13}C or a Bruker ARX 400 instrument at 400 MHz for ^1H and 100.6 MHz for ^{13}C. Chemical shifts are given relative to residual $CHCl_3$ (δ_H = 7.24 ppm) and $CDCl_3$ (δ_C = 77.0 ppm). All solvents were dried and distilled prior to use. Reactions were monitored by TLC using silica gel 60 F_{254} (Merck); aliquots were removed after 2, 4, 8, 24 h, and 2 d and so forth. Products were purified by column chromatography using 0.040–0.063 mm silica gel (Merck 9385). All experiments were performed under an inert atmosphere (Ar) in oven-dried glassware sealed with a rubber septum and with anhydrous solvents. Triethyl-, tributyl-, and tri-*sec*-butylborane were purchased from Aldrich Chemical Co., whereas trihexyl- and tricyclohexylborane were synthesized as previously from borane in THF and the corresponding alkene.[9] Tetrahydrofuran-2-carbaldehyde was obtained from tetrahydrofuran-2-methanol according to the previously described procedure.[10]

General Procedure for the One-Pot Reaction of Aldehyde, Amine, and Trialkylborane: Trialkylborane (3 mmol) was added to a solution of aldehyde (1 mmol) and amine (1 mmol) in dichloromethane and the reaction mixture was left to stir for 2 h at room temperature. An aqueous solution of hydrogen peroxide (0.1 mL, 33%) was

then added and the mixture stirred for 2–7 d. The crude reaction was concentrated to dryness under reduced vacuum. The ^{1}H NMR spectrum of the residue exhibited signals corresponding to the almost exclusive presence of the expected amines. The residue was purified by column chromatography (SiO_2, 10% ethyl acetate in hexane) to yield the alkylated amines **1a**–**1y**, **2**, and **3** in 70–93% yields.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)propyl]amine (1a):**[11] Yield 244 mg, 90%, colorless oil. R_f = 0.66 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3400, 3036, 2959, 2932, 1609, 1508, 1460, 1440, 1378, 1299, 1231 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.21 (d, J = 7.5 Hz, 2 H, 2′-H, 6′-H), 6.82 (d, J = 7.5 Hz, 2 H, 3′-H, 5′-H), 6.66 (d, J = 8.8 Hz, 2 H, 3′′-H, 5′′-H), 6.45 (d, J = 8.8 Hz, 2 H, 2′′-H, 6′′-H), 4.08 (t, J = 6.8 Hz, 1 H, 1-H), 3.76 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 1.85–1.68 (m, 2 H, CH_2), 0.92 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2 (C-4′), 152.0 (C-4′′), 141.9 (C-1′′), 135.2 (C-1′), 127.4 (C-2′, C-6′), 114.5, 114.3, 113.5 (6 × CH_{Ar}), 60.3 (C-1), 55.4, 54.8 (2 × OCH_3), 30.9 (CH_2), 10.4 (CH_3) ppm. MS (EI): m/z (%) = 271 (12) [M]$^+$, 242 (34), 149 (92), 121 (100), 91 (38), 77 (39). HRMS: calcd. for $C_{17}H_{21}NO_2$ 271.1572; found 271.1566.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)pentyl]amine (1b):** Yield 239 mg, 80%, colorless oil. R_f = 0.73 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3401, 3010, 2954, 2930, 1604, 1508, 1462, 1440, 1378, 1238 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H), 6.90 (d, J = 8.8 Hz, 2 H, 3′-H, 5′-H), 6.74 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.52 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.22 (t, J = 6.7 Hz, 1 H, 1-H), 3.83 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 1.86–1.70 (m, 2 H, CH_2), 1.46–1.29 (m, 4 H, 2 × CH_2), 0.92 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.3 (C-4′), 151.6 (C-4′′), 141.8 (C-1′′), 136.5 (C-1′), 127.3 (C-2′, C-6′), 114.6, 114.4, 113.7 (6 × CH_{Ar}), 58.4 (C-1), 55.6, 55.1 (2 × OCH_3), 38.7, 28.4, 22.6 (3 × CH_2), 13.9 (CH_3) ppm. MS (EI): m/z (%) = 300 (6), 299 (30) [M]$^+$, 243 (17), 242 (100), 177 (26), 121 (83). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1876.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)heptyl]amine (1c):**[6] Yield 258 mg, 79%, colorless oil. R_f = 0.75 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3404, 3005, 2953, 2927, 2833, 1585, 1504, 1462, 1440, 1377, 1236 cm^{-1}. The NMR spectral data have previously been reported by us. MS (EI): m/z (%) = 328 (1), 327 (14) [M]$^+$, 243 (11), 242 (63), 205 (18), 134 (11), 123 (15), 122 (11), 121 (100). HRMS: calcd. for $C_{21}H_{29}NO_2$ 327.2198; found 327.2188.

***N*-[1-Cyclohexyl-1-(4-methoxyphenyl)methyl]-*N*-(4-methoxyphenyl)-amine (1d):**[6] Yield 289 mg, 89%, colorless liquid. R_f = 0.78 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3401, 3040, 2923, 2850, 1609, 1547, 1508, 1461, 1450, 1236 cm^{-1}. The NMR spectral data have previously been reported by us. MS (EI): m/z (%) = 325 (4) [M]$^+$, 243 (18), 242 (100), 134 (14), 121 (76). HRMS: calcd. for $C_{21}H_{27}NO_2$ 325.2042; found 325.2047.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-methoxyphenyl)-2-methylbutyl]-amine (1e)**

Isomer a: Yield 137 mg, 46%, colorless oil. R_f = 0.73 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3413, 3062, 2993, 2961, 1608, 1585, 1508, 1458, 1379, 1239 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.17 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 6.81 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.65 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.42 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.14 (d, J = 4.9 Hz, 1 H, 1-H), 3.75 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 1.81–1.65 (m, 1 H, CH), 1.58–1.27 (m, 1 H, CH_2), 1.24–1.06 (m, 1 H, CH_2), 0.89 (t, J = 6.5 Hz, 3 H, CH_2-CH_3), 0.87 (d, J = 6.5 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.2 (C-4′), 151.6 (C-4′′), 142.1 (C-1′′), 135.1 (C-1′), 127.9 (C-2′, C-6′), 114.6, 114.2, 113.5 (6 × CH_{Ar}), 61.8 (C-1), 56.6, 55.1 (2 × OCH_3), 41.9 (CH), 26.6 (CH_2), 14.5, 12.0 (2 × CH_3) ppm. MS (EI): m/z (%) = 299 (8) [M]$^+$, 243 (16), 242 (100), 177 (5), 121 (19). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1891.

Isomer b: Yield 137 mg, 46%, colorless oil. R_f = 0.68 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3408, 3018, 2967, 2920, 1611, 1509, 1458, 1240 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.9 Hz, 2 H, 2′-H, 6′-H), 6.78 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.61–6.59 (m, 4 H, CH_{Ar}), 4.10 (d, J = 5.7 Hz, 1 H, 1-H), 3.74 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 1.99–1.81 (m, 1 H, CH), 1.62–1.42 (m, 1 H, CH_2), 1.20–1.03 (m, 1 H, CH_2), 0.89 (t, J = 6.5 Hz, 3 H, CH_2-CH_3), 0.87 (d, J = 6.5 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.1 (C-4′), 151.7 (C-4′′), 141.6 (C-1′′), 134.0 (C-1′), 128.2 (C-2′, C-6′), 114.5, 114.4, 113.3 (6 × CH_{Ar}), 62.9 (C-1), 55.5, 54.9 (2 × OCH_3), 41.2 (CH), 25.4 (CH_2), 15.7, 11.6 (2 × CH_3) ppm. MS (EI): m/z (%) = 299 (8) [M]$^+$, 243 (16), 242 (100), 177 (5), 121 (19). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1895.

***N*-(4-Methoxyphenyl)-*N*-[1-phenylpropyl]amine (1f):**[11] Yield 169 mg, 70%, colorless oil. R_f = 0.75 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3400, 3059, 3025, 2961, 2930, 1601, 1582, 1509, 1451, 1379, 1294 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.15 (m, 5 H, CH_{Ar}), 6.67 (d, J = 8.6 Hz, 2 H, 3′′-H, 5′′-H), 6.43 (d, J = 8.6 Hz, 2 H, 2′′-H, 6′′-H), 4.14 (t, J = 6.9 Hz, 1 H, 1-H), 3.62 (s, 3 H, OCH_3), 1.89–1.72 (m, 2 H, CH_2), 0.93 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8 (C-4′′), 143.9, 141.6 (C-1′, C-1′′), 128.4, 126.8, 126.5, 114.7, 114.5 (9 × CH_{Ar}), 60.6 (C-1), 55.7 (OCH_3), 31.6 (CH_2), 10.7 (CH_3) ppm. MS (EI): m/z (%) = 242 (3), 241 (20) [M]$^+$, 213 (15), 212 (100). HRMS: calcd. for $C_{14}H_{17}NO_2$ 241.1467; found 241.1461.

***N*-(4-Methoxyphenyl)-*N*-[1-(3-methoxyphenyl)propyl]amine (1g):** Yield 247 mg, 91%, colorless oil. R_f = 0.68 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3397, 3020, 2959, 2933, 1598, 1509, 1454, 1379, 1294 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, J = 8.1 Hz, 1 H, 5′-H), 6.92 (d, J = 8.1 Hz, 1 H, 6′-H), 6.88 (d, J = 2.5 Hz, 1 H, 2′-H), 6.75 (dd, J = 8.1, J = 2.5 Hz, 1 H, 4′-H), 6.67 (d, J = 8.6 Hz, 2 H, 3′′-H, 5′′-H), 6.47 (d, J = 8.6 Hz, 2 H, 2′′-H, 6′′-H), 4.11 (t, J = 6.5 Hz, 1 H, 1-H), 3.77 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 1.85–1.73 (m, 2 H, CH_2), 0.94 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.8 (C-3′), 151.8 (C-4′′), 146.0 (C-1′), 141.8 (C-1′′), 129.4 (C-5′), 118.9 (C-6′), 114.7, 114.4 (4 × CH_{Ar}), 112.3, 111.8 (C-2′, C-4′), 60.5 (C-1), 55.7, 55.0 (2 × OCH_3), 31.6 (CH_2), 10.8 (CH_3) ppm. MS (EI): m/z (%) = 272 (4), 271 (23) [M]$^+$, 243 (15), 242 (100), 121 (14). HRMS: calcd. for $C_{17}H_{21}NO_2$ 272.1606; found 272.1607.

***N*-(4-Methoxyphenyl)-*N*-[1-(2-methoxyphenyl)propyl]amine (1h):** Yield 252 mg, 93%, colorless oil. R_f = 0.71 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3378, 3025, 2963, 2931, 1592, 1577, 1509, 1462, 1374, 1231 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (d, J = 7.5 Hz, 1 H, 6′-H), 7.16 (t, J = 7.5 Hz, 1 H, 4′-H), 6.87–6.84 (m, 2 H, 3′-H, 5′-H), 6.66 (d, J = 8.9 Hz, 2 H, 3′′-H, 5′′-H), 6.47 (d, J = 8.9 Hz, 2 H, 2′′-H, 6′′-H), 4.55 (t, J = 6.7 Hz, 1 H, 1-H), 3.86 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 1.86–1.72 (m, 2 H, CH_2), 0.93 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0 (C-2′), 151.7 (C-4′′), 141.7 (C-1′′), 131.5 (C-1′), 127.6, 127.2 (C-4′, C-6′), 120.6 (C-5′), 114.6, 114.5 (4 × CH_{Ar}), 110.4 (C-3′), 55.6, 55.2 (2 × OCH_3), 55.0 (C-1), 29.5 (CH_2), 11.0 (CH_3) ppm. MS (EI): m/z (%) = 272 (12), 271 (66)

$[M]^+$, 243 (60), 242 (100), 149 (40), 121 (79). HRMS: calcd. for $C_{17}H_{21}NO_2$ 271.1572; found 271.1572.

***N*-(4-Methoxyphenyl)-*N*-[1-(2,3-dimethoxyphenyl)propyl]amine (1i):** Yield 271 mg, 90%, colorless oil. R_f = 0.66 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3396, 2961, 2933, 1618, 1585, 1509, 1476, 1378, 1229 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.96 (t, J = 8.1 Hz, 1 H, 5′-H), 6.85 (dd, J = 8.1, J = 1.6 Hz, 1 H, 4′-H), 6.77 (dd, J = 8.1, J = 1.6 Hz, 1 H, 6′-H), 6.67 (d, J = 8.6 Hz, 2 H, 3′′-H, 5′′-H), 6.51 (d, J = 8.6 Hz, 2 H, 2′′-H, 6′′-H), 4.57 (t, J = 6.7 Hz, 1 H, 1-H), 3.90 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 1.80 (m, 2 H, CH_2), 0.96 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 151.6 (C-4′′, C-3′), 146.6 (C-2′), 141.8 (C-1′′), 137.4 (C-1′), 123.9, 118.9, 114.7, 114.3, 110.6 (7 × CH_{Ar}), 60.6 (C-1), 55.6, 55.5, 54.7 (3 × OCH_3), 30.4 (CH_2), 11.1 (CH_3) ppm. MS (EI): m/z (%) = 302 (7), 301 (34) $[M]^+$, 273 (17), 272 (100). HRMS: calcd. for $C_{18}H_{23}NO_3$ 301.1678; found 301.1676.

***N*-[1-(4-Fluorophenyl)propyl]-*N*-(4-methoxyphenyl)amine (1j):** Yield 212 mg, 82%, colorless oil. R_f = 0.68 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3404, 3045, 2963, 2932, 1602, 1506, 1461, 1379, 1279, 1235 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.27 (dd, J = 8.5, $J_{F,H}$ = 5.5 Hz, 2 H, 2′-H, 6′-H), 6.97 (t, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.66 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.42 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.11 (t, J = 6.7 Hz, 1 H, 1-H), 3.67 (s, 3 H, OCH_3), 1.87–1.64 (m, 2 H, CH_2), 0.90 (t, J = 7.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7 (d, $^1J_{F,C}$ = 243.2 Hz, C-4′), 152.0 (C-4′′), 141.3, 139.6 (C-1′, C-1′′), 127.9 (d, $^3J_{F,C}$ = 8 Hz, C-2′, C-6′), 115.2 (d, $^2J_{F,C}$ = 20.8 Hz, C-3′, C-5′), 114.7, 114.6 (4 × CH_{Ar}), 60.1 (C-1), 55.7 (OCH_3), 31.6 (CH_2), 10.7 (CH_3) ppm. MS (EI): m/z (%) = 260 (5), 259 (27) $[M]^+$, 231 (17), 230 (100), 123 (13), 109 (40). HRMS: calcd. for $C_{16}H_{18}FNO$ 259.1372; found 259.1372.

***N*-[1-(4-Chlorophenyl)propyl]-*N*-(4-methoxyphenyl)amine (1k):** Yield 223 mg, 81%, colorless oil. R_f = 0.71 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3404, 3020, 2964, 2931, 2874, 1617, 1592, 1509, 1488, 1460, 1380, 1230 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.24 (s, 4 H, CH_{Ar}), 6.65 (d, J = 8.8 Hz, 2 H, 3′′-H, 5′′-H), 6.40 (d, J = 8.8 Hz, 2 H, 2′′-H, 6′′-H), 4.08 (t, J = 6.8 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 1.87–1.64 (m, 2 H, CH_2), 0.92 (t, J = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.0 (C-4′′), 142.6, 141.4, 132.4 (3 × $C_{quat,Ar}$), 128.6, 127.9, 114.7, 114.5 (8 × CH_{Ar}), 60.0 (C-1), 55.7 (OCH_3), 31.6 (CH_2), 10.6 (CH_3) ppm. MS (EI): m/z (%) = 277 (8), 275 (25) $[M]^+$, 248 (40), 247 (6), 246 (100), 127 (8), 125 (24). HRMS: calcd. for $C_{16}H_{18}ClNO$ 275.1077; found 275.1080.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-methylphenyl)propyl]amine (1l):**[12] Yield 227 mg, 89%, colorless oil. R_f = 0.75 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3401, 2960, 2925, 2853, 1606, 1509, 1460, 1450, 1377, 1240 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.0 Hz, 2 H, 3′-H, 5′-H), 7.09 (d, J = 8.0 Hz, 2 H, 2′-H, 6′-H), 6.66 (d, J = 8.5 Hz, 2 H, 3′′-H, 5′′-H), 6.46 (d, J = 8.5 Hz, 2 H, 2′′-H, 6′′-H), 4.09 (t, J = 6.8 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 2.29 (s, 3 H, CH_3), 1.85–1.71 (m, 2 H, CH_2), 0.91 (t, J = 7.3 Hz, 3 H, CH_2-*CH*$_3$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.6 (C-4′′), 139.8, 136.6, 136.5 (3 × $C_{quat,Ar}$), 129.1, 126.7, 115.7, 114.6 (8 × CH_{Ar}), 61.4 (C-1), 55.6 (OCH_3), 30.9 (CH_2), 21.0 (*CH*$_3$), 10.7 (CH_2-*CH*$_3$) ppm. MS (EI): m/z (%) = 256 (6), 255 (31) $[M]^+$, 227 (23), 226 (100), 123 (15), 105 (40). HRMS: calcd. for $C_{17}H_{21}NO$ 255.1623; found 255.1621.

4-[1-(Methoxyanilino)propyl]benzonitrile (1m):[13] Yield 213 mg, 80%, colorless oil. R_f = 0.58 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3402, 3045, 2963, 2929, 2366, 1604, 1509, 1461, 1382, 1235 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.2 Hz, 2 H, 3′-H, 5′-H), 7.43 (d, J = 8.2 Hz, 2 H, 2′-H, 6′-H), 6.66 (d, J = 8.7 Hz, 2 H, 3′′-H, 5′′-H), 6.38 (d, J = 8.7 Hz, 2 H, 2′′-H, 6′′-H), 4.15 (t, J = 6.4 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 1.85–1.67 (m, 2 H, CH_2), 0.94 (t, J = 7.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.1 (C-4′′), 150.1, 141.0 (C-1′, C-1′′), 132.3, 127.3 (4 × CH_{Ar}), 118.9 (C-4′), 114.7, 114.4 (4 × CH_{Ar}), 110.6 (CN), 60.2 (C-1), 55.6 (OCH_3), 31.5 (CH_2), 10.6 (CH_3) ppm. MS (EI): m/z (%) = 267 (4), 266 (21) $[M]^+$, 238 (23), 237 (100), 122 (11). HRMS: calcd. for $C_{17}H_{18}N_2O$ 266.1419; found 266.1411.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-nitrophenyl)propyl]amine (1n):** Yield 234 mg, 82%, colorless oil. R_f = 0.62 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3405, 3025, 2964, 2932, 1596, 1508, 1460, 1380, 1230 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.9 Hz, 2 H, 3′-H, 5′-H), 7.49 (d, J = 8.9 Hz, 2 H, 2′-H, 6′-H), 6.65 (d, J = 8.8 Hz, 2 H, 3′′-H, 5′′-H), 6.39 (d, J = 8.8 Hz, 2 H, 2′′-H, 6′′-H), 4.24 (t, J = 6.6 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 1.87–1.75 (m, 2 H, CH_2), 0.95 (t, J = 7.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.3, 152.2, 146.9 (3 × $C_{quat,Ar}$), 140.9 (C-1′′), 127.3, 123.8, 114.7, 114.4 (8 × CH_{Ar}), 60.1 (C-1), 55.6 (OCH_3), 31.5 (CH_2), 10.6 (CH_3) ppm. MS (EI): m/z (%) = 287 (7), 286 (39) $[M]^+$, 258 (16), 257 (100), 122 (17). HRMS: calcd. for $C_{16}H_{18}N_2O_3$ 286.1317; found 286.1310.

***N*-[1-(2-Furyl)propyl]-*N*-(4-methoxyphenyl)amine (1o):** Yield 182 mg, 79%, colorless oil. R_f = 0.66 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3400, 3030, 2963, 2932, 1617, 1509, 1461, 1441, 1380, 1230 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34 (d, J = 1.8 Hz, 1 H, 5′-H), 6.76 (d, J = 9.2 Hz, 2 H, 3′′-H, 5′′-H), 6.60 (d, J = 9.2 Hz, 2 H, 2′′-H, 6′′-H), 6.29 (dd, J = 3.1, J = 1.8 Hz, 1 H, 4′-H), 6.16 (d, J = 3.1 Hz, 1 H, 3′-H), 4.32 (t, J = 6.7 Hz, 1 H, 1-H), 3.73 (s, 3 H, OCH_3), 1.98–1.46 (m, 2 H, CH_2), 0.97 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.3 (C-2′), 152.2 (C-4′′), 141.4, 141.3 (C-5′, C-1′′), 114.9, 114.6 (4 × CH_{Ar}), 109.9 (C-4′), 105.9 (C-3′), 55.6, 54.4 (C-1′, OCH_3), 28.0 (CH_2), 10.4 (CH_3) ppm. MS (EI): m/z (%) = 232 (11), 231 (65) $[M]^+$, 203 (19), 202 (100), 123 (24), 109 (16), 107 (15). HRMS: calcd. for $C_{14}H_{17}NO_2$ 231.1259; found 231.1256.

***N*-(4-Methoxyphenyl)-*N*-[1-(4-pyridyl)propyl]amine (1p):** Yield 184 mg, 76%, colorless oil. R_f = 0.20 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3400, 3033, 2964, 2931, 1600, 1560, 1509, 1460, 1361, 1231 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 6.0 Hz, 2 H, 2′-H, 6′-H), 7.25 (d, J = 6.0 Hz, 2 H, 3′-H, 5′-H), 6.66 (d, J = 8.5 Hz, 2 H, 3′′-H, 5′′-H), 6.39 (d, J = 8.5 Hz, 2 H, 2′′-H, 6′′-H), 4.13 (t, J = 6.6 Hz, 1 H, 1-H), 3.65 (s, 3 H, OCH_3), 1.98–1.46 (m, 2 H, CH_2), 0.94 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 152.1 (C-4′, C-4′′), 149.7 (C-2′, C-6′), 140.9 (C-1′′), 121.8 (C-3′, C-5′), 114.7, 114.3 (4 × CH_{Ar}), 59.5 (C-1), 55.6 (OCH_3), 31.0 (CH_2), 10.5 (CH_3) ppm. MS (EI): m/z (%) = 243 (3), 242 (21) $[M]^+$, 214 (14), 213 (100). HRMS: calcd. for $C_{15}H_{18}NO_2$ 242.1419; found 242.1425.

***N*-(4-Methoxyphenyl)-*N*-[1-(2-pyridyl)propyl]amine (1q):** Yield 169 mg, 70%, colorless oil. R_f = 0.42 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3272, 3105, 3075, 3035, 3005, 2952, 2930, 1615, 1590, 1507, 1459, 1381, 1250 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (dd, J = 5.9, J = 1.6 Hz, 1 H, 6′-H), 7.59 (dt, J = 7.5, J = 1.6 Hz, 1 H, 4′-H), 7.29 (d, J = 7.5 Hz, 1 H, 3′-H), 7.13 (dd, J = 7.5, J = 5.9 Hz, 1 H, 5′-H), 6.67 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.51 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.30 (t, J = 6.6 Hz, 1 H, 1-H), 3.67 (s, 3 H, OCH_3), 1.93–1.79 (m, 2 H, CH_2), 0.92 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 163.0 (C-2′), 151.9 (C-4′′), 149.2 (C-6′), 141.5 (C-1′′), 136.5 (C-4′), 121.9, 121.3 (C-3′, C-5′), 114.7, 114.6 (4 × CH_{Ar}), 61.5 (C-1), 55.6 (OCH_3), 29.9 (CH_2), 10.5 (CH_3) ppm. MS (EI): *m/z* (%) = 243 (3), 242 (13) $[M]^+$, 214 (14), 213 (100). HRMS: calcd. for $C_{15}H_{18}NO_2$ 242.1419; found 242.1424.

***N*-(4-Methoxyphenyl)-*N*-[1-(2-methoxyphenyl)pentyl]amine (1r):** Yield 245 mg, 82%, colorless oil. R_f = 0.77 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3403, 3020, 2954, 2931, 1617, 1587, 1509, 1461, 1377, 1284 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 7.8 Hz, 1 H, 6′-H), 7.17 (t, *J* = 7.8 Hz, 1 H, 4′-H), 6.87–6.85 (m, 2 H, 5′-H, 3′-H), 6.68 (d, *J* = 8.1 Hz, 2 H, 3′′-H, 5′′-H), 6.49 (d, *J* = 8.1 Hz, 2 H, 2′′-H, 6′′-H), 4.63 (t, *J* = 6.7 Hz, 1 H, 1-H), 3.87 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 1.84–1.68 (m, 2 H, CH_2), 1.38–1.27 (m, 4 H, 2 × CH_2), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (C-2′), 151.7 (C-4′′), 141.7 (C-1′′), 131.9 (C-1′), 127.5, 127.1 (C-4′, C-6′), 120.6 (C-5′), 114.7, 114.4 (4 × CH_{Ar}), 110.4 (C-3′), 55.6, 55.2 (2 × OCH_3), 53.5 (C-1), 36.5, 28.6, 22.5 (3 × CH_2), 13.9 (CH_3) ppm. MS (EI): *m/z* (%) = 300 (8), 299 (35) $[M]^+$, 243 (50), 242 (100), 177 (3), 121 (72). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1872.

***N*-(4-Methoxyphenyl)-*N*-[1-(2-methoxyphenyl)-2-methylbutyl]-amine (1s)**

Isomer a: Yield 137 mg, 46%, colorless oil. R_f = 0.85 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3407, 3060, 3031, 3001, 2959, 2932, 1617, 1587, 1509, 1459, 1380, 1284 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 7.8 Hz, 1 H, 6′-H), 7.15 (t, *J* = 7.8 Hz, 1 H, 4′-H), 6.85–6.81 (m, 2 H, 5′-H, 3′-H), 6.64 (d, *J* = 7.5 Hz, 2 H, 3′′-H, 5′′-H), 6.44 (br. s, 2 H, 2′′-H, 6′′-H), 4.58 (br. s, 1 H, 1-H), 3.85 (s, 3 H, OCH_3), 3.65 (br. s, 3 H, OCH_3), 1.88–1.82 (m, 1 H, CH), 1.47–1.37 (m, 1 H, CH_2), 1.27–1.16 (m, 1 H, CH_2), 0.90 (t, *J* = 7.1 Hz, 3 H, CH_2-CH_3), 0.89 (d, *J* = 7.1 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0 (C-2′), 151.8 (C-4′′), 142.1 (C-1′′), 131.4 (C-1′), 128.4, 127.8 (C-4′, C-6′), 120.3 (C-5′), 114.5 (4 × CH_{Ar}), 110.3 (C-3′), 55.9 (C-1), 55.2 (2 × OCH_3), 39.4 (CH), 26.9 (CH_2), 14.9 (CH-CH_3), 11.7 (CH_2-CH_3) ppm. MS (EI): *m/z* (%) = 299 (7) $[M]^+$, 243 (27), 242 (100), 121 (13). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1882.

Isomer b: Yield 137 mg, 46%, colorless oil. R_f = 0.80 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3397, 3020, 2959, 2930, 1598, 1586, 1509, 1461, 1378, 1288 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.8 Hz, 1 H, 4′-H), 7.13 (d, *J* = 7.8 Hz, 1 H, 6′-H), 6.85–6.82 (m, 2 H, 3′-H, 5′-H), 6.64 (d, *J* = 8.6 Hz, 2 H, 3′′-H, 5′′-H), 6.46 (br. s, 2 H, 2′′-H, 6′′-H), 4.45 (br. s, 1 H, 1-H), 3.85 (s, 3 H, OCH_3), 3.66 (br. s, 3 H, OCH_3), 1.87–1.79 (m, 1 H, CH), 1.72–1.66 (m, 1 H, CH_2), 1.26–1.12 (m, 1 H, CH_2), 0.89 (t, *J* = 7.2 Hz, 3 H, CH_2-CH_3), 0.82 (d, *J* = 7.2 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3 (C-2′), 151.6 (C-4′′), 142.4 (C-1′′), 131.4 (C-1′), 128.3, 127.5 (C-4′, C-6′), 120.3 (C-5′), 114.6 (4 × CH_{Ar}), 110.4 (C-3′), 57.0 (C-1), 55.7, 55.3 (2 × OCH_3), 39.8 (CH), 25.3 (CH_2), 16.3 (CH-CH_3), 11.7 (CH_2-CH_3) ppm. MS (EI): *m/z* (%) = 299 (13) $[M]^+$, 243 (48), 242 (100), 121 (24). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1896.

***N*-(4-Methoxyphenyl)-*N*-[1-(3-methoxyphenyl)pentyl]amine (1t):** Yield 239 mg, 80%, colorless oil. R_f = 0.73 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3401, 3020, 2995, 2953, 2931, 1598, 1509, 1484, 1377, 1233 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 7.8 Hz, 1 H, 5′-H), 6.90 (d, *J* = 7.8 Hz, 1 H, 6′-H), 6.87 (d, *J* = 2.4 Hz, 1 H, 2′-H), 6.74 (dd, *J* = 7.8, *J* = 2.4 Hz, 1 H, 4′-H), 6.66 (d, *J* = 8.9 Hz, 2 H, 3′′-H, 5′′-H), 6.47 (d, *J* = 8.9 Hz, 2 H, 2′′-H, 6′′-H), 4.16 (t, *J* = 6.7 Hz, 1 H, 1-H), 3.77 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 1.78–1.71 (m, 2 H, CH_2), 1.39–1.24 (m, 4 H, 2 × CH_2), 0.94 (t, *J* = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7 (C-3′), 152.1 (C-4′′), 146.0 (C-1′), 141.1 (C-1′′), 129.4 (C-5′), 118.9 (C-6′), 114.6 (4 × CH_{Ar}), 112.2, 111.9 (C-4′, C-2′), 59.5 (C-1), 55.6, 55.1 (2 × OCH_3), 38.3, 28.5, 22.6 (3 × CH_2), 13.9 (CH_3) ppm. MS (EI): *m/z* (%) = 300 (6), 299 (27) $[M]^+$, 243 (53), 242 (100), 121 (30). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1876.

***N*-(4-Methoxyphenyl)-*N*-[1-(3-methoxyphenyl)-2-methylbutyl]-amine (1u)**

Isomer a: Yield 134 mg, 45%, colorless oil. R_f = 0.78 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3411, 3011, 2959, 2931, 1606, 1584, 1509, 1454, 1379, 1221 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (t, *J* = 8.1 Hz, 1 H, 5′-H), 6.87 (d, *J* = 8.1 Hz, 1 H, 6′-H), 6.83 (d, *J* = 2.5 Hz, 1 H, 2′-H), 6.72 (dd, *J* = 8.1, *J* = 2.5 Hz, 1 H, 4′-H), 6.65 (d, *J* = 8.9 Hz, 2 H, 3′′-H, 5′′-H), 6.43 (d, *J* = 8.9 Hz, 2 H, 2′′-H, 6′′-H), 4.16 (d, *J* = 4.8 Hz, 1 H, 1-H), 3.76 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 1.79–1.73 (m, 1 H, CH), 1.53–1.43 (m, 1 H, CH_2), 1.24–1.12 (m, 1 H, CH_2), 0.91 (t, *J* = 7.1 Hz, 3 H, CH_2-CH_3), 0.88 (d, *J* = 7.1 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.6 (C-3′), 151.7 (C-4′′), 145.2 (C-1′), 142.1 (C-1′′), 129.1 (C-5′), 119.5 (C-6′), 114.7, 114.2 (4 × CH_{Ar}), 113.2, 111.5 (C-2′, C-4′), 62.4 (C-1), 55.7, 55.1 (2 × OCH_3), 41.8 (CH), 26.8 (CH_2), 14.5 (CH-CH_3), 11.9 (CH_2-CH_3) ppm. MS (EI): *m/z* (%) = 300 (2), 299 (11) $[M]^+$, 243 (17), 242 (100), 121 (4). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1885.

Isomer b: Yield 134 mg, 45%, colorless oil. R_f = 0.75 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3405, 3010, 2960, 2932, 1599, 1584, 1509, 1461, 1380, 1232 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 7.9 Hz, 1 H, 5′-H), 6.86 (d, *J* = 7.9 Hz, 1 H, 6′-H), 6.82 (d, *J* = 2.4 Hz, 1 H, 2′-H), 6.71 (dd, *J* = 7.9, *J* = 2.4 Hz, 1 H, 4′-H), 6.65 (d, *J* = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.42 (d, *J* = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.06 (d, *J* = 6.1 Hz, 1 H, 1-H), 3.75 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 1.79–1.73 (m, 1 H, CH), 1.70–1.43 (m, 1 H, CH_2), 1.24–1.12 (m, 1 H, CH_2), 0.91 (t, *J* = 6.7 Hz, 3 H, CH_2-CH_3), 0.90 (d, *J* = 6.7 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4 (C-3′), 151.3 (C-4′′), 144.4 (C-1′), 141.9 (C-1′′), 129.0 (C-5′), 119.8 (C-6′), 114.7, 114.3 (4 × CH_{Ar}), 113.3, 111.6 (C-2′, C-4′), 63.4 (C-1), 55.7, 55.1 (2 × OCH_3), 41.5 (CH), 25.4 (CH_2), 16.0 (CH-CH_3), 11.7 (CH_2-CH_3) ppm. MS (EI): *m/z* (%) = 300 (2), 299 (12) $[M]^+$, 243 (16), 242 (100), 121 (3). HRMS: calcd. for $C_{19}H_{25}NO_2$ 299.1885; found 299.1883.

***N*-[1-(4-Fluorophenyl)pentyl]-*N*-(4-methoxyphenyl)amine (1v):** Yield 201 mg, 70%, colorless oil. R_f = 0.77 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3402, 3033, 2955, 2931, 2858, 1602, 1507, 1463, 1379 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 8.6, $J_{F,H}$ = 5.5 Hz, 2 H, 2′-H, 6′-H), 6.96 (t, *J* = 8.6 Hz, 2 H, 3′-H, 5′-H), 6.66 (d, *J* = 8.9 Hz, 2 H, 3′′-H, 5′′-H), 6.43 (d, *J* = 8.9 Hz, 2 H, 2′′-H, 6′′-H), 4.17 (t, *J* = 6.6 Hz, 1 H, 1-H), 3.67 (s, 3 H, OCH_3), 1.80–1.63 (m, 2 H, CH_2), 1.36–1.22 (m, 4 H, 2 × CH_2), 0.86 (t, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.7 (d, $^1J_{F,C}$ = 243.9 Hz, C-4′), 152.2 (C-4′′), 140.8, 139.7 (C-1′, C-1′′), 127.9 (d, $^3J_{F,C}$ = 7.5 Hz, C-2′, C-6′), 115.2 (d, $^2J_{F,C}$ = 21.4 Hz, C-3′, C-5′), 114.9, 114.7 (4 × CH_{Ar}), 58.9 (C-1), 55.6 (OCH_3), 38.5, 28.3, 22.5 (3 × CH_2), 13.9 (CH_3) ppm. MS (EI): *m/z* (%) = 288 (6), 287 (28) $[M]^+$, 231 (22), 230 (100), 109 (55). HRMS: calcd. for $C_{18}H_{22}FNO$ 287.1685; found 287.1687.

***N*-[1-(4-Fluorophenyl)-2-methylbutyl]-*N*-(4-methoxyphenyl)amine (1w)**

Isomer a: Yield 118 mg, 41%, colorless oil. R_f = 0.82 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3419, 3010, 2960,

2928, 1602, 1507, 1461, 1380, 1294 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 8.5, $J_{F,H}$ = 5.3 Hz, 2 H, 2′-H, 6′-H), 6.96 (t, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.64 (d, J = 8.8 Hz, 2 H, 3′′-H, 5′′-H), 6.40 (d, J = 8.8 Hz, 2 H, 2′′-H, 6′′-H), 4.17 (d, J = 4.5 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 1.81–1.70 (m, 1 H, CH), 1.58–1.42 (m, 1 H, CH_2), 1.23–1.12 (m, 1 H, CH_2), 0.90 (t, J = 7.5 Hz, 3 H, CH_2-CH_3), 0.88 (d, J = 7.5 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7 (d, $^1J_{F,C}$ = 215.0 Hz, C-4′), 151.7 (C-4′′), 141.7, 138.5 (C-1′, C-1′′), 128.4 (d, $^3J_{F,C}$ = 7.5 Hz, C-2′, C-6′), 115.1, 114.9 (4 × CH_{Ar}), 114.8 (d, $^2J_{F,C}$ = 20.2 Hz, C-3′, C-5′), 61.7 (C-1), 55.7 (OCH_3), 41.9 (CH), 26.6 (CH_2), 14.4 (CH-CH_3), 11.9 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 288 (2), 287 (8) [M]$^+$, 231 (14), 230 (100). HRMS: calcd. for $C_{18}H_{22}NOF$ 287.1685; found 287.1698.

Isomer b: Yield 118 mg, 41%, colorless oil. R_f = 0.78 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3409, 3015, 2960, 2931, 1602, 1508, 1461, 1380, 1292 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 8.5, $J_{F,H}$ = 5.4 Hz, 2 H, 2′-H, 6′-H), 6.95 (t, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.65 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.39 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.10 (d, J = 5.9 Hz, 1 H, 1-H), 3.66 (s, 3 H, OCH_3), 1.78–1.68 (m, 1 H, CH), 1.60–1.47 (m, 1 H, CH_2), 1.21–1.14 (m, 1 H, CH_2), 0.90 (t, J = 7.0 Hz, 3 H, CH_2-CH_3), 0.83 (d, J = 7.0 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.8 (d, $^1J_{F,C}$ = 215.0 Hz, C-4′), 151.8 (C-4′′), 141.8, 138.1 (C-1′′, C-1′), 128.7 (d, $^3J_{F,C}$ = 7.6 Hz, C-2′, C-6′), 114.9 (d, $^2J_{F,C}$ = 20.1 Hz, C-3′, C-5′), 114.7, 114.4 (4 × CH_{Ar}), 62.7 (C-1), 55.7 (OCH_3), 41.6 (CH), 25.4 (CH_2), 15.9 (CH-CH_3), 11.7 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 288 (2), 287 (9) [M]$^+$, 231 (15), 230 (100). HRMS: calcd. for $C_{18}H_{22}NOF$ 287.1685; found 287.1689.

***N*-[1-(4-Chlorophenyl)pentyl]-*N*-(4-methoxyphenyl)amine (1x):** Yield 218 mg, 72%, colorless oil. R_f = 0.77 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3402, 3025, 2954, 1617, 1592, 1509, 1463, 1378, 1233 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.24 (br. s, 4 H, CH_{Ar}), 6.65 (d, J = 8.7 Hz, 2 H, 3′′-H, 5′′-H), 6.41 (d, J = 8.7 Hz, 2 H, 2′′-H, 6′′-H), 4.15 (t, J = 6.8 Hz, 1 H, 1-H), 3.70 (s, 3 H, OCH_3), 1.79–1.63 (m, 2 H, CH_2), 1.37–1.19 (m, 4 H, 2 × CH_2), 0.85 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.9 (C-4′′), 143.1, 141.4 (C-1′′, C-4′), 132.3 (C-1′), 128.6, 127.8, 114.7, 114.4 (8 × CH_{Ar}), 58.4 (C-1), 55.7 (OCH_3), 38.7, 28.3, 22.5 (3 × CH_2), 13.9 (CH_3) ppm. MS (EI): m/z (%) = 305 (8), 303 (23) [M]$^+$, 249 (7), 248 (41), 247 (21), 246 (100), 127 (13), 125 (38). HRMS: calcd. for $C_{18}H_{22}ClNO$ 303.1390; found 303.1381.

***N*-[1-(4-Chlorophenyl)-2-methylbutyl]-*N*-(4-methoxyphenyl)amine (1y)**

Isomer a: Yield 127 mg, 42%, colorless oil. R_f = 0.84 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3414, 3025, 2960, 2930, 1591, 1577, 1509, 1460, 1381, 1295 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.20 (m, 4 H, CH_{Ar}), 6.65 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.40 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.17 (d, J = 4.8 Hz, 1 H, 1-H), 3.67 (s, 3 H, OCH_3), 1.84–1.69 (m, 1 H, CH), 1.53–1.43 (m, 1 H, CH_2), 1.24–1.14 (m, 1 H, CH_2), 0.90 (t, J = 7.5 Hz, 3 H, CH_2-CH_3), 0.87 (d, J = 7.5 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9 (C-4′′), 141.6, 141.5, 132.1 (3 × $C_{quat,Ar}$), 128.4, 128.3, 114.7, 114.3 (8 × CH_{Ar}), 61.8 (C-1), 55.6 (OCH_3), 41.7 (CH), 26.6 (CH_2), 14.5 (CH-CH_3), 11.9 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 305 (5), 303 (16) [M]$^+$, 249 (5), 248 (32), 247 (16), 246 (100). HRMS: calcd. for $C_{18}H_{22}NOCl$ 303.1390; found 303.1391.

Isomer b: Yield 127 mg, 42%, colorless oil. R_f = 0.80 (silica gel, 30% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3409, 3025, 2961, 2931, 1592, 1509, 1461, 1381, 1233 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.20 (m, 4 H, CH_{Ar}), 6.65 (d, J = 9.1 Hz, 2 H, 3′′-H, 5′′-H), 6.40 (d, J = 9.1 Hz, 2 H, 2′′-H, 6′′-H), 4.10 (d, J = 5.9 Hz, 1 H, 1-H), 3.67 (s, 3 H, OCH_3), 1.78–1.69 (m, 1 H, CH), 1.59–1.46 (m, 1 H, CH_2), 1.21–1.10 (m, 1 H, CH_2), 0.90 (t, J = 7.0 Hz, 3 H, CH_2-CH_3), 0.84 (d, J = 7.0 Hz, 3 H, CH-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.9 (C-4′′), 141.6, 141.1, 132.3 (3 × $C_{quat,Ar}$), 128.7, 128.3, 114.7, 114.4 (8 × CH_{Ar}), 62.8 (C-1), 55.7 (OCH_3), 41.5 (CH), 25.3 (CH_2), 15.9 (CH-CH_3), 11.7 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 305 (4), 303 (17) [M]$^+$, 249 (5), 248 (37), 247 (16), 246 (100). HRMS: calcd. for $C_{18}H_{22}NOCl$ 303.1390; found 303.1396.

***N*-[1-Ethyl-2-methylpropyl]-*N*-(4-methoxyphenyl)amine (2):** Yield 73 mg, 35% (one-pot procedure); 145 mg, 70% (from the preformed imine), colorless oil. R_f = 0.77 (silica gel, 12% methanol in chloroform). IR (neat): $\tilde{\nu}_{max}$ = 3399, 3057, 2958, 2931, 2830, 1616, 1579, 1509, 1462, 1380, 1240 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 6.52 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 3.71 (s, 3 H, OCH_3), 2.99 (dt, J = 8.6, J = 7.5 Hz, 1 H, 1-H), 1.89–1.80 (m, 1 H, 2-H), 1.59–1.51 (m, 1 H, CH_2), 1.38–1.28 (m, 1 H, CH_2), 0.90 (d, J = 7.5 Hz, 6 H, 2 × CH_3), 0.88 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.7 (C-4′), 136.8 (C-1′), 114.8 (4 × CH_{Ar}), 62.0 (C-1), 55.7 (OCH_3), 30.1 (C-2), 23.4 (CH_2), 18.6 (2 × CH_3), 10.9 (CH_3) ppm. MS (EI): m/z (%) = 207 (7) [M]$^+$, 178 (29), 164 (100), 121 (17). HRMS: calcd. for $C_{13}H_{21}NO$ 207.1623; found 207.1615.

***N*-(4-Methoxyphenyl)-*N*-[1-(tetrahydro-2-furanyl)propyl]amine (3)**

Isomer a: Yield 23 mg, 10%, colorless oil. R_f = 0.51 (silica gel, 20% ethyl acetate in hexane). Spectroscopic data for an enriched mixture of this isomer: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.6 (C-4′′), 142.6 (C-1′′), 114.9, 114.3 (4 × CH_{Ar}), 80.3 (C-2′), 68.6 (C-5′), 58.0 (C-1), 55.7 (OCH_3), 28.3, 26.1, 25.6 (3 × CH_2), 10.8 (CH_3) ppm.

Isomer b: Yield 164 mg, 70%, colorless oil. R_f = 0.44 (silica gel, 20% ethyl acetate in hexane). IR (neat): $\tilde{\nu}_{max}$ = 3408, 3068, 2965, 2937, 1605, 1509, 1460, 1380, 1253 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (d, J = 8.5 Hz, 2 H, 3′′-H, 5′′-H), 6.61 (d, J = 8.5 Hz, 2 H, 2′′-H, 6′′-H), 3.87 (dt, J = 7.5, J = 7.0 Hz, 1 H, 5′a-H), 3.82 (dt, J = 8.0, J = 7.0 Hz, 1 H, 5′b-H), 3.70–3.64 (m, 4 H, 2′-H, OCH_3), 3.24 (dt, J = 7.5, J = 5.0 Hz, 1 H, 1-H), 1.95–1.65 (m, 5 H, 2 × 3′-H, 2 × 4′-H, CH_2-CH_3), 1.48-1.37 (m, 1 H, CH_2-CH_3), 0.94 (t, J = 7.3 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1 (C-4′′), 141.9 (C-1′′), 114.8 (4 × CH_{Ar}), 81.1 (C-2′), 68.2 (C-5′), 59.6 (C-1), 55.7 (OCH_3), 27.9, 25.9, 24.3 (3 × CH_2), 10.4 (CH_3) ppm. MS (EI): m/z (%) = 235 (10) [M]$^+$, 164 (100), 122 (13). HRMS: calcd. for $C_{14}H_{21}NO_2$ 235.1572; found 235.1579.

Synthesis of Amines 4 and 5: Boron trifluoride–diethyl ether (250 μL, 2 mmol) was added to a solution of the corresponding amine (1 mmol) and *p*-methoxybenzaldehyde (0.12 mL, 1 mmol) in dichloromethane. The reaction mixture was stirred at room temperature for 2 h and then a 1 M solution of triethylborane in hexane (3 mL, 3 mmol) was added. Subsequently, an aqueous solution of hydrogen peroxide (0.1 mL, 33%) was added and the mixture stirred for 30 min. The crude mixture was concentrated to dryness under vacuum and purified by column chromatography (SiO_2, 10% ethyl acetate in hexane) to afford the alkylated amines in yields of 38–40%.

***N*-Methyl-*N*-[1-(4-methoxyphenyl)propyl]amine (4):** Yield 68 mg, 38% (one-pot procedure); 143 mg, 80% (from the preformed imine), colorless oil. R_f = 0.30 (silica gel, 12% methanol in chloroform). IR (neat): $\tilde{\nu}_{max}$ = 3291, 3064, 2932, 2873, 1610, 1585, 1509, 1462, 1421, 1376, 1241 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ =

7.15 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 6.86 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 3.78 (s, 3 H, OCH_3), 3.28 (dd, J = 8.2, J = 5.8 Hz, 1 H, 1-H), 2.23 (s, 3 H, NCH_3), 1.79–1.49 (m, 2 H, CH_2), 0.76 (t, J = 7.4 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.5 (C-4′), 135.7 (C-1′), 128.2 (C-2′, C-6′), 113.6 (C-3′, C-5′), 66.4 (C-1), 55.1 (OCH_3), 34.4 (NCH_3), 30.5 (CH_2), 10.7 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 151 (8), 150 (100), 121 (5). HRMS: calcd. for $C_{11}H_{18}NO$ $[MH]^+$ 180.1382; found 180.1386.

***N*-Butyl-*N*-[1-(4-methoxyphenyl)propyl]amine (5):** Yield 88 mg, 40% (one-pot procedure); 183 mg, 83% (from the preformed imine), colorless oil. R_f = 0.64 (silica gel, 12% methanol in chloroform). IR (neat): $\tilde{\nu}_{max}$ = 3400, 3061, 2956, 2928, 1610, 1585, 1509, 1460, 1376, 1244 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.16 (d, J = 8.5 Hz, 2 H, 2′-H, 6′-H), 6.83 (d, J = 8.5 Hz, 2 H, 3′-H, 5′-H), 3.77 (s, 3 H, OCH_3), 3.39 (dd, J = 7.9, J = 5.4 Hz, 1 H, 1-H), 2.39 (dt, J = 6.7, J = 2.4 Hz, 2 H, CH_2), 1.78–1.19 (m, 6 H, $3 \times CH_2$), 0.85 (t, J = 7.3 Hz, 3 H, CH_3), 0.83 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.4 (C-4′), 136.3 (C-1′), 128.2 (C-2′, C-6′), 113.5 (C-3′, C-5′), 64.5 (C-1), 55.2 (OCH_3), 47.4 (HN-CH_2), 32.4, 30.9, 20.5 ($3 \times CH_2$), 13.9, 10.8 ($2 \times CH_3$) ppm. MS (EI): m/z (%) = 221 (1) $[M]^+$, 193 (11), 192 (100), 164 (1), 149 (13), 136 (15), 121 (15). HRMS: calcd. for $C_{14}H_{23}NO$ 221.1779; found 221.1783.

1-Ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (6):[14] Boron trifluoride–diethyl ether (250 μL, 2 mmol) was added to a solution of 6,7-dimethoxy-3,4-dihydroisoquinoline[15] (191 mg, 1 mmol) in dichloromethane. The reaction mixture was stirred at room temperature for 10 min and then a 1 M solution of triethylborane in hexane (3 mL, 3 mmol) was added. Subsequently, an aqueous solution of hydrogen peroxide (0.1 mL, 33%) was added and the mixture stirred for 24 h. The crude mixture was concentrated to dryness under vacuum and purified by column chromatography (SiO_2, 10% ethyl acetate in hexane) to afford the alkylated amine **6** (32 mg, 60%) as a colorless oil. R_f = 0.44 (silica gel, 12% methanol in chloroform). IR (neat): $\tilde{\nu}_{max}$ = 3423, 3034, 2930, 1609, 1560, 1509, 1462, 1374, 1253 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.59, 6.54 (2 s, 1 H each, 5-H, 8-H), 3.88–3.87 (m, 1 H, 1-H), 3.82 (s, 6 H, $2 \times OCH_3$), 3.17, (ddd, J = 12.2, J = 4.9, J = 4.9 Hz, 1 H, 3_{eq}-H), 2.90 (ddd, J = 12.2, J = 7.3, J = 4.9 Hz, 1 H, 3_{ax}-H), 2.75–2.57 (m, 2 H, 4_{eq}-H, 4_{ax}-H), 1.93–1.59 (m, 2 H, CH_2-CH_3), 0.98 (t, J = 7.3 Hz, 3 H, CH_2-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.1, 147.0 (C-6, C-7), 132.2, 127.2 (C-4a, C-8a), 111.7, 109.2 (C-5, C-8), 56.6 (C-1), 55.9, 55.8 ($2 \times OCH_3$), 41.0 (C-3), 29.5, 29.0 (C-4, CH_2-CH_3), 10.5 (CH_2-CH_3) ppm. MS (EI): m/z (%) = 221 (2) $[M]^+$, 193 (63), 192 (100), 177 (43), 176 (72), 148 (31). HRMS: calcd. for $C_{13}H_{19}NO_2$ 221.1416; found 221.1411.

Supporting Information (see also the footnote on the first page of this article): ^1H NMR and ^{13}C NMR spectra for new compounds.

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