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Introduction

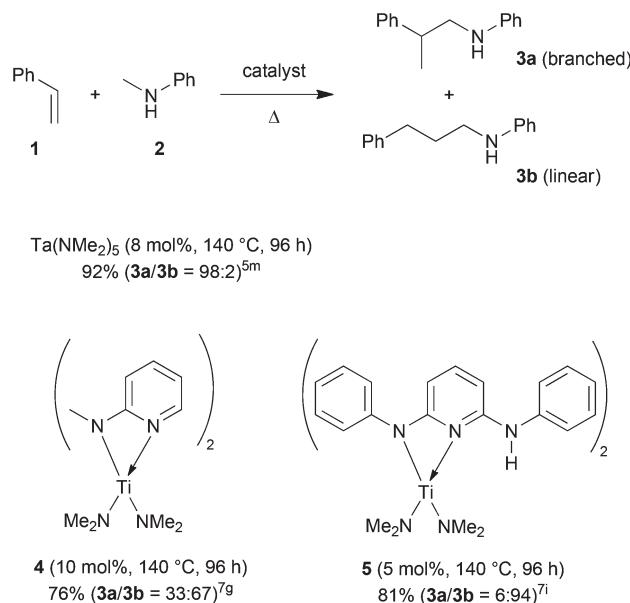
The direct addition of α -C(sp³)-H bonds of primary or secondary amines across C-C double bonds, the so-called hydroaminoalkylation of alkenes, represents a very promising and atom-efficient approach towards the synthesis of various nitrogen-containing molecules.¹ Due to the fact that the formed α -alkylated amines are of great importance in the agrochemical, fine chemical and pharmaceutical industries² a plethora of suitable hydroaminoalkylation catalysts has already been identified in recent years.^{3–7} Although hydroaminoalkylation reactions can be achieved in the presence of ruthenium,³ iridium,⁴ group 5 metal,⁵ zirconium,⁶ or titanium catalysts⁷ a number of limitations in scope still exists. For example, ruthenium and iridium catalysts can only be used for hydroaminoalkylation reactions of amine substrates bearing a directing 2-pyridinyl substituent bound to the nitrogen atom of the amine.^{3,4} Furthermore, zirconium complexes only catalyze intramolecular hydroaminoalkylation reactions of primary aminoalkenes.⁶ On the other hand, group 5 metal⁵ and titanium catalysts⁷ have successfully been applied for the intermolecular hydroaminoalkylation of alkenes, styrenes and 1,3-butadienes. For example, the conversion of styrene (**1**) into the corresponding hydroaminoalkylation products **3a** and **3b** (Scheme 1) could be achieved in the presence of tantalum or titanium catalysts.^{5m,7d,g,i}

In this context, it is worth mentioning that the regioselectivity of hydroaminoalkylation reactions of styrenes can simply

Intermolecular hydroaminoalkylation of alkenes and dienes using a titanium mono(formamidinate) catalyst†

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An easily accessible formamidinate ligand-bearing titanium complex initially synthesized by Eisen *et al.* is used as catalyst for intermolecular hydroaminoalkylation reactions of unactivated, sterically demanding 1,1- and 1,2-disubstituted alkenes and styrenes with secondary amines. The corresponding reactions, which have never been achieved with titanium catalysts before, take place with excellent regioselectivity (up to 99 : 1) and in addition, corresponding reactions of 1,3-butadienes with *N*-methylbenzylamine are also described for the first time.



Scheme 1 Intermolecular hydroaminoalkylation of styrene (**1**) with *N*-methylaniline (**2**) catalyzed by group 4 and group 5 metal catalysts.

be controlled by the nature of the catalyst. Whereas in the presence of $\text{Ta}(\text{NMe}_2)_5$, the branched product **3a** is formed almost exclusively,^{5m} the aminopyridinato titanium catalysts **4** and **5** favor the formation of the corresponding linear hydroaminoalkylation product **3b**.^{7g,i} However, so far, the use of titanium catalysts is limited to hydroaminoalkylation reactions of sterically less demanding mono-substituted alkenes, styrenes, or 1,3-butadienes with *N*-alkylanilines or dialkylamines. Among the class of sterically more demanding disubstituted alkenes, only norbornene^{7b–d,g} and methylenecyclohexane^{7c,g} were found to undergo hydroaminoalkylation reactions in the

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† Electronic supplementary information (ESI) available: Copies of the ¹H and ¹³C NMR spectra of all products. See DOI: 10.1039/c4dt03916e



presence of selected titanium catalysts. On the other hand, hydroaminoalkylation reactions of sterically demanding 1,1- and 1,2-disubstituted alkenes are well known for group 5 metal catalysts.^{5c,e-g,i,k,l,n} Most impressively, very recently, Schafer *et al.* reported a 2-pyridonate tantalum catalyst that is able to catalyze high-yielding hydroaminoalkylation reactions of sterically demanding *E*- and *Z*-internal alkenes like cyclohexene, (*E*)- and (*Z*)-3-hexene, (*Z*)- β -methylstyrene or (*E*)-1-(*para*-methoxyphenyl)propene.⁵ⁿ In the latter two cases, hydroaminoalkylation at the β -carbon of the β -substituted styrene derivatives is favored but only modest regioselectivities (up to 4.4 : 1) could be achieved.

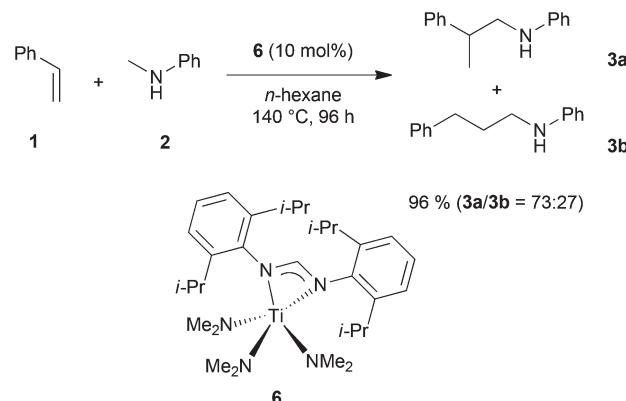
The mechanism of group 4 and 5 metal-catalyzed hydroaminoalkylation reactions has already been studied^{1,5c,d,i,6,7e} and it is generally accepted that the amine substrate undergoes N–H and C–H bond activation in the presence of the catalyst precursor to give a strained metallaaziridine as the catalytically active species. Subsequent alkene insertion into the M–C bond of the metallaaziridine which determines the regioselectivity of the over-all transformation then results in the formation of a 2-metallapyrrolidine. Finally, aminolysis of the M–C bond of the five membered intermediate and product-forming C–H bond activation regenerate the catalytically active metallaaziridine.

Herein, we present the first example of a titanium-based catalyst for intermolecular hydroaminoalkylation reactions of unactivated, sterically demanding 1,1- and 1,2-disubstituted alkenes and styrenes with secondary amines. The corresponding reactions take place with excellent regioselectivity (up to 99 : 1) and the formamidinate ligand-bearing catalyst is also capable of catalyzing reactions of 1,3-butadienes with *N*-methylbenzylamine.

Results and discussion

In order to develop a more efficient catalyst system that is able to expand the substrate scope of the titanium-catalyzed intermolecular hydroaminoalkylation of alkenes, we recently focused on ligand motifs which are structurally similar to the aminopyridinato ligands of the second-generation hydroaminoalkylation catalysts 4 and 5 (Scheme 1). In this context, it must be mentioned that the chelating heteroallylic N–C–N unit of the aminopyridinato ligands that binds to the titanium center can also be found in the well-known class of amidinate ligands $[R^1-C(NR^2)_2]^-$. A variety of corresponding group 4 amidinate complexes has already been used as catalysts in the polymerization of olefins by Eisen *et al.*⁸ and a particular advantage of this class of catalysts is that the ligands are easily prepared and modified.^{8a} On the other hand, corresponding catalysts have never been used for hydroaminoalkylation reactions of alkenes.

During an investigation of various titanium formamidinate catalysts we found that complex 6 (Scheme 2) which bears 2,6-diisopropylphenyl groups as the amidinate N-substituents^{8a} is a highly active catalyst for the hydroaminoalkylation of styrene (1) with *N*-methylaniline (2). Under usually applied conditions



Scheme 2 Intermolecular hydroaminoalkylation of styrene (1) with *N*-methylaniline (2) catalyzed by titanium mono(formamidinate) complex 6.

(10 mol% 6, *n*-hexane, 140 °C, 96 h, sealed Schlenk tube),^{7g,i} the reaction took place smoothly to give a mixture of the two regioisomeric hydroaminoalkylation products 3a and 3b in an excellent total yield of 96%. Unfortunately, the regioselectivity of the reaction which in this case, favors the formation of the branched product 3a was only modest ($3a/3b = 73:27$). However, an interesting finding is the fact that in comparison to the structurally related aminopyridinato catalysts 4 and 5, the regioselectivity is reversed with the formamidinate catalyst 6.

Impressed by the high catalytic activity of complex 6 and the clean formation of the desired hydroaminoalkylation products 3a and 3b, we further investigated whether complex 6 is also able to catalyze intermolecular hydroaminoalkylation reactions of sterically more demanding disubstituted alkenes with *N*-methylaniline (2, Table 1).

As can be seen from Table 1, a number of successful hydroaminoalkylation reactions of 1,1- and 1,2-disubstituted alkenes and styrenes with *N*-methylaniline (2) can be achieved at elevated temperatures (140–180 °C) in the presence of 10 mol% of catalyst 6. For example, methylenecyclohexane (7, Table 1, entries 1 and 2) regioselectively reacted to the corresponding branched amine 21a which could be isolated in excellent yield of 90%. Even though bulky 1,1-diphenylethylene (8) did not react at all under the applied conditions (Table 1, entries 3 and 4), α -methylstyrene (9) and *para*- α -dimethylstyrene (10) could be converted regioselectively to the corresponding branched hydroaminoalkylation products 22a and 23a, respectively (Table 1, entries 5–8). In these cases, the yields of the reactions were significantly improved by increasing the reaction temperature from 140 °C to 180 °C. Finally, it was possible to isolate the branched products 22a and 23a in 86% and 91% yield, respectively. Although a corresponding dependence on the reaction temperature had not been observed during the initially performed reactions of methylenecyclohexane (7, Table 1, entries 1 and 2) we performed most additional reactions presented in Table 1 at 180 °C. A similar observation was made when reactions of 7 or 9 were conducted with reduced reaction times of 24 h or 48 h. While the reduced reac-



Table 1 Hydroaminoalkylation of disubstituted alkenes with *N*-methylaniline (2)

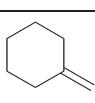
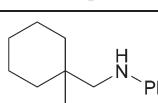
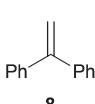
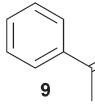
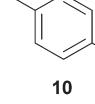
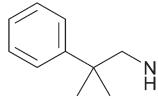
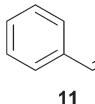
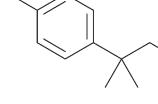
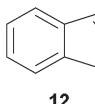
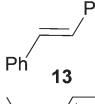
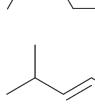
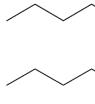
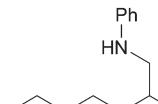
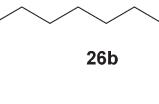
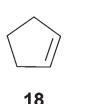
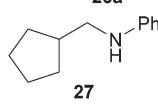
Entry	Alkene	<i>T</i> (°C)	Isolated product(s)	Yield ^a (%)	Selectivity a/b ^b
					a
1		140		90	99:1
2					
3		180	—	90 ^c	99:1
4		140	—	—	—
5		180	—	43	99:1
6		140	—	—	—
7		180		86 ^d	99:1
8		140	—	38	99:1
9		180		91	99:1
10		140	—	17	1:99
11		180	—	64	1:99
12		180	—	97 ^e	34:66
13		180	—	—	—
14		180	—	—	—
15		180	—	—	—
16		180		16 ^e	35:65
17				—	—
18		180		75	—



Table 1 (Contd.)

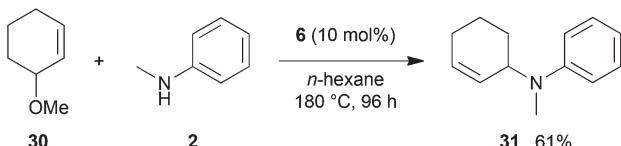
Entry	Alkene	T (°C)	Isolated product(s)	Yield ^a (%)	Selectivity a/b ^b
					a b
18		180		72 ^f	—
19		180		93	—

^a Reaction conditions: *N*-methylaniline (2, 2.0 mmol, 214 mg), alkene (3.0 mmol), **6** (109 mg, 0.2 mmol, 10 mol%), *n*-hexane (1 mL), 140 °C or 180 °C, 96 h, sealed Schlenk tube. Yields refer to the yield of the isolated product (a or b). ^b GC analysis prior to chromatography. ^c A yield of 89% was obtained after a reaction time of 24 h. ^d Yields of 76% and 67% were obtained after reaction times of 48 h and 24 h, respectively. ^e The yield refers to the total yield of isolated products (a + b). ^f A comparable yield of 69% was obtained after a reaction time of 192 h.

tion times did not affect the conversion of methylenecyclohexane (7, 89% yield of product **21a** after 24 h), corresponding reactions of α -methylstyrene (9) gave product **22a** in significantly reduced yields (76% after 48 h and 67% after 24 h). As a consequence, we performed all additional experiments with a reaction time of 96 h. To the best of our knowledge, the results obtained with styrenes **9** and **10** represent the first successful examples of group 4 metal-catalyzed hydroaminoalkylation reactions of α -substituted styrene derivatives. In addition, it is worth to mention that only two examples of a corresponding reaction catalyzed by a group 5 metal catalyst have been described in the literature^{5k,m} and in this case, the yield was only modest (61%). An additional finding that underlines the high catalytic activity of **6** is the fact that with this catalyst, it was even possible to react the 1,2-disubstituted substrate (*E*)- β -methylstyrene (**11**) with *N*-methylaniline (2, Table 1, entries 9 and 10). Interestingly and in contrast to the reaction of α -methylstyrene, the hydroaminoalkylation took place regioselectively at the sterically less shielded β -carbon of the double bond and correspondingly, the regioisomer **24b** could be isolated as the sole product of the reaction in 64% yield. Most impressively, the regioselectivity of the reaction was found to be **24a/24b** = 1 : 99. Previously, only two successful hydroaminoalkylations of β -substituted styrene derivatives had been achieved with a tantalum catalyst⁵ⁿ and in these cases, the regioselectivities were only modest (1 : 2.0 and 1 : 4.4). The well-established fact that hydroaminoalkylation product **24b** can be obtained from allylbenzene under much milder conditions^{5e} is strongly underlined by a hydroaminoalkylation reaction between allylbenzene and *N*-methylaniline (2) performed at 140 °C in the presence of 10 mol% of catalyst **6**. While under these conditions, (*E*)- β -methylstyrene (**11**) gave **24b** only in 17% yield (Table 1, entry 9), **24b** was obtained in 87% yield from allylbenzene. Interestingly, isomerization of (*E*)- β -methyl-

styrene (**11**) to allylbenzene during the reactions of **11** could not be observed by GC analysis. Additional experiments with indene (**12**, Table 1, entry 11) then revealed that even this challenging substrate undergoes successful hydroaminoalkylation with **2**. Although the reaction delivered the two regioisomers **25a** and **25b** in 97% combined yield, the regioselectivity was found to be surprisingly low (**25a/25b** = 34 : 66). However, as can be seen from Table 1, entries 12–15, sterically more demanding internal alkenes like **13–16** failed to react in the presence of catalyst **6**. On the other hand, it was possible to convert (*E*)-2-octene (**17**) to a mixture of the corresponding hydroaminoalkylation products **26a** and **26b** (Table 1, entry 16) but in this case, the yield and the regioselectivity of the reaction turned out to be poor. In contrast to the disappointing behavior of the 1,2-dialkyl-substituted (*E*)-alkenes **15–17**, the (*Z*)-double bond-containing substrates cyclopentene (**18**) and cyclohexene (**19**) gave access to the corresponding hydroaminoalkylation products **27** and **28** in reasonable yields of 75% and 72%, respectively (Table 1, entries 17 and 18). In this context, it can be noted that additional alkyl-substituted cyclohexenes like 4-methyl- or 3-methylcyclohexene also underwent high-yielding hydroaminoalkylation reactions with **2** but unfortunately, formation of four inseparable regio- and diastereomers was observed in both reactions. As the result, all attempts on a precise structure assignment of the isomers failed so far. With regard to catalyst stability it can be stated that longer reaction times do not necessarily lead to improved yields. For example, reactions of cyclohexene (**19**) with *N*-methylaniline (2) gave comparable yields of product **28** after 96 h (72%, Table 1, entry 18) and 192 h (69%). Interestingly, the additional double bond present in 1,4-cyclohexadiene (**20**) seems to facilitate the hydroaminoalkylation reaction and as a consequence, an excellent yield of 93% of product **29** was obtained in this case (Table 1, entry 19). The remarkable fact





Scheme 3 Intermolecular reaction of 3-methoxycyclohexene (**30**) with *N*-methylaniline (**2**) catalyzed by titanium mono(formamidinate) complex **6**.

that only the monoalkylated product **29** could be isolated from the reaction mixture is in good agreement with results from Schafer *et al.*⁵ⁿ and the remaining double bond offers a promising chance for further functionalization. Finally, 3-bromocyclohexene turned out to be unreactive under the reaction conditions while 3-methoxycyclohexene (**30**) underwent a nucleophilic substitution reaction that delivered the tertiary amine **31** in 61% yield (Scheme 3). The assumption that the latter process does not require the presence of a titanium catalyst is strongly supported by the fact that product **31** could also be isolated in comparable yield (58%) from a control experiment performed in the absence of **6**.

Encouraged by the promising results obtained with *N*-methylaniline (**2**) we next turned our attention towards hydroaminoalkylation reactions of α - and (*E*)- β -methylstyrene with various other secondary amines (Table 2). The unsymmetrically substituted styrenes were chosen as substrates to get further information about the regioselectivity of the hydroaminoalkylation. Initial reactions of α -methylstyrene (**9**) with the donor- and acceptor-substituted *N*-methylanilines **32–34** (Table 2, entries 1–3) performed at 180 °C in the presence of 10 mol% **6** showed that both classes of substituents are generally tolerated and the *para*-substituents do not affect the regioselectivity of the hydroaminoalkylation. In all cases, the regioselectivity was determined to be 99:1 in favor of the branched product **a** which is formed by hydroaminoalkylation at the sterically more hindered α -carbon of **9**. On the other hand, the nature of the substituent on the benzene ring of the *N*-methylaniline seems to influence the efficiency of the reaction significantly. For example, *N*-methylaniline **33** bearing an electron-withdrawing *para*-fluoro substituent on the benzene ring gave the hydroaminoalkylation product **40a** in 98% yield (Table 2, entry 2) while the corresponding donor-substituted substrate *para*-phenoxy-*N*-methylaniline (**34**) delivered the corresponding product **41a** only in significantly reduced yield of 67% (Table 2, entry 3). This trend in reactivity is further supported by the observation that *para*-methyl-*N*-methylaniline (**32**) with its weak electron-donating methyl substituent gave the hydroaminoalkylation product **39a** in 88% yield (Table 2, entry 1) which is comparable to the result obtained with *N*-methylaniline (2, 86%, Table 1, entry 6). The well-established fact that the efficiency of titanium-catalyzed hydroaminoalkylation reactions of alkenes is strongly influenced by the steric bulk of the amine^{7b,d,i} is in good agreement with our observation that the sterically more demanding amines *N*-benzylamine (**35**, Table 2, entry 4), *N*-ethylamine, *N*-propylamine,

N-2,3,4-tetrahydroquinoline, and *ortho*-methyl-*N*-methylaniline failed to react with α -methylstyrene (**9**) in the presence of catalyst **6**. On the other hand, the dialkylamines *N*-methylcyclohexylamine (**36**) and *N*-methylhexylamine (**37**) (Table 2, entries 5 and 6) were found to undergo highly regioselective hydroaminoalkylation with **9** under identical reaction conditions. Unfortunately, the branched products which were always formed with excellent regioselectivity (**a/b** = 99:1) could only be obtained in modest to poor yields (14–49%) after derivatization as the corresponding *para*-toluenesulfonamides **42a** and **43a**. The observation that both reactions took place at the methyl group of the amines exclusively is in good agreement with results obtained before with *N*-methylcyclohexylamine (**36**) and *N*-methylhexylamine (**37**).^{5e,j,k,n,7f,g,i} Finally, it must be noted that no successful alkylation of *N*-methylbenzylamine (**38**, Table 2, entry 7) could be achieved with α -methylstyrene (**9**). Additional hydroaminoalkylation reactions performed with (*E*)- β -methylstyrene (**11**, Table 2, entries 8–14) then revealed that **11** is significantly less reactive than α -methylstyrene (**9**) and as a result, the corresponding hydroaminoalkylation products could only be obtained in modest to poor yields (14–65%). However, the trend in reactivity observed with the *N*-methylanilines **32–34** (Table 2, entries 8–10) is in good agreement with the results obtained with α -methylstyrene (**9**, Table 2, entries 1–3). Again, the *para*-fluoro-substituted aniline **33** gave the best result (65% yield) while the electron-donating *para*-phenoxy substituent present in **34** caused a severe drop in yield (14%). Among the dialkylamines **36–38** (Table 2, entries 12–14), again only *N*-methylcyclohexylamine (**36**) and *N*-methylhexylamine (**37**) reacted successfully with **11** and in these cases, the products could be isolated after derivatization as the corresponding *para*-toluenesulfonamides **47b** and **48b** in 38% and 41% yield, respectively. On the other hand, no reaction could be achieved with *N*-methylbenzylamine (**38**) and the sterically more demanding substrate *N*-benzylamine (**35**, Table 2, entries 11 and 14). However, as described above (Table 1, entry 9), all successful hydroaminoalkylation reactions of (*E*)- β -methylstyrene (**11**) took place with excellent regioselectivities ($\geq 98:2$) at the sterically less hindered β -carbon of **11** giving access to 3-phenylpropylamine derivatives.

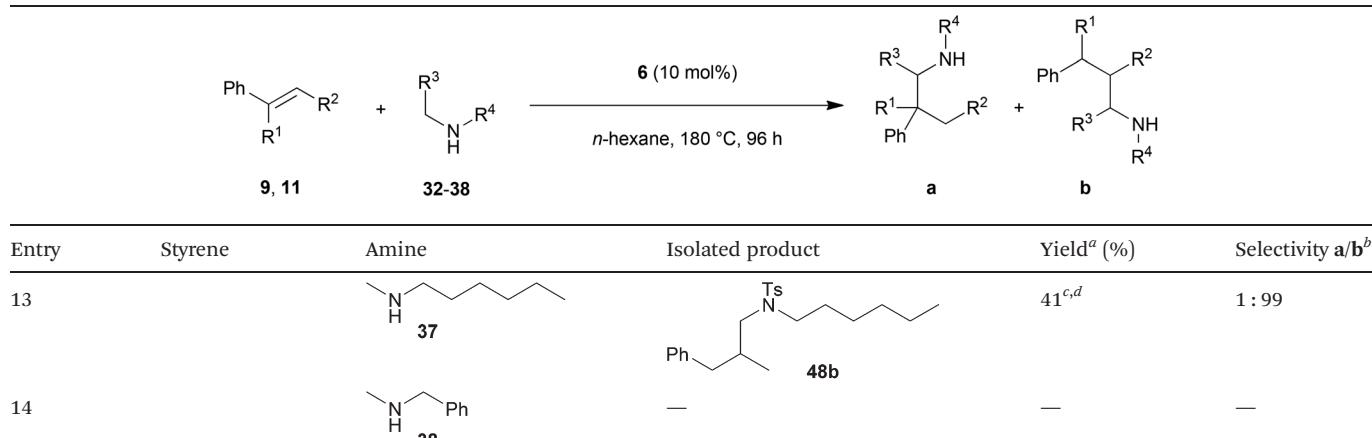
Owing to the electronic similarities between styrenes and conjugated dienes, we next turned our attention towards hydroaminoalkylation reactions of substituted 1,3-butadienes. Corresponding reactions are extremely rare in the literature^{4,7h,i} and so far, $\text{Ind}_2\text{TiMe}_2$ ($\text{Ind} = \eta^5\text{-indenyl}$)^{7h} and aminopyridinato titanium complex **5⁷ⁱ** represent the only suitable early transition metal catalysts for the intermolecular hydroaminoalkylation of 1-aryl- and 1-alkyl-substituted 1,3-butadienes. Unfortunately, the titanium-catalyzed reaction is limited to selected *N*-methylanilines and the efficiency of the reaction strongly depends on the substituents bound to the 1,3-diene or the benzene ring of the *N*-methylaniline. For example, reactions performed with the chloro-substituted substrates *para*-chloro-*N*-methylaniline or (*E*)-1-(*para*-chlorophenyl)-1,3-butadiene gave the corresponding hydroaminoalkylation products only in poor yields ($\leq 37\%$) and in addition, dialkylamines or

Table 2 Hydroaminoalkylation of α - and (*E*)- β -methylstyrene (**9**, **11**) with various amines

Entry	Styrene	Amine	Isolated product	Yield ^a (%)	Selectivity a/b ^b
					a
1				88	99:1
2				98	99:1
3				67	99:1
4			—	—	—
5				14 ^{c,d}	99:1
6				49 ^{c,d}	99:1
7			—	—	—
8				31	1:99
9				65	2:98
10				14	1:99
11			—	—	—
12				38 ^{c,d}	1:99



Table 2 (Contd.)

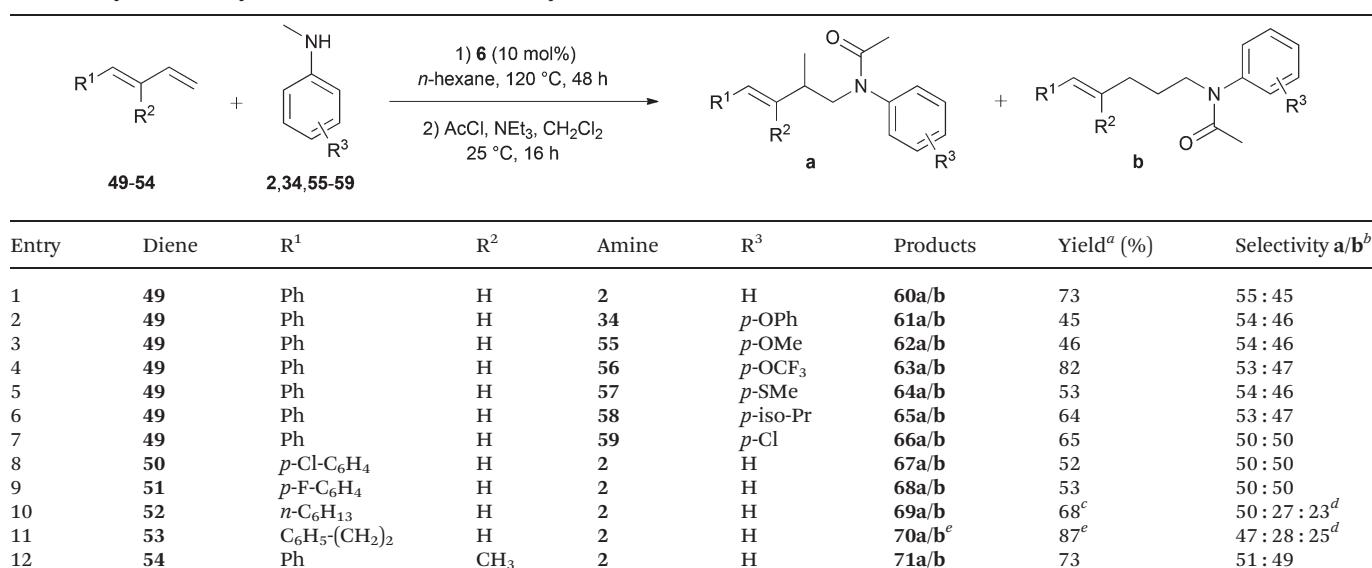


^a Reaction conditions: amine (2.0 mmol), alkene (3.0 mmol), **6** (109 mg, 0.2 mmol, 10 mol%), *n*-hexane (1 mL), 180 °C, 96 h, sealed Schlenk tube. Yields refer to the yield of the isolated product (**a** or **b**). ^b GC analysis prior to chromatography. ^c The product was isolated after derivatization as the corresponding *para*-toluenesulfonamide. ^d The reaction took place at the methyl group of the amine exclusively.

N-alkylanilines bearing alkyl groups larger than a methyl group did not react at all in the presence of $\text{Ind}_2\text{TiMe}_2$. Initial hydroaminoalkylation reactions of (*E*)-1-phenyl-1,3-butadiene (**49**) with various *para*-substituted *N*-methylanilines were performed in the presence of 10 mol% **6** at 120 °C. The relatively low reaction temperature was chosen because it has already been observed that dimerization of the 1,3-butadiene by Diels-Alder cycloaddition becomes a yield-reducing side reaction at temperatures above 130 °C.^{7h} As can be seen from Table 3, entries 1–7, successful hydroaminoalkylation could be achieved with electron donor-^(34, 55–58) and electron accep-

tor-substituted *N*-methylanilines (**59**) and in all cases, only the terminal double bond of the diene reacted. Owing to their better separation from other nitrogen-containing molecules in the reaction mixture, the hydroaminoalkylation products were isolated after conversion into their corresponding acetamides (AcCl, NET_3 , CH_2Cl_2 , rt). Although the products **60–66a/b** could be obtained with good to modest yields (45–82%), the regioselectivity of the hydroaminoalkylation was always close to 1 : 1 which is worse compared to typical regioselectivities obtained with the catalysts **5** or $\text{Ind}_2\text{TiMe}_2$. With the latter catalyst, formation of the branched regioisomer was usually favored and

Table 3 Hydroaminoalkylation of 1,3-dienes with *N*-methylanilines



^a Reaction conditions: (1) amine (2.0 mmol), diene (3.0 mmol), **6** (109 mg, 0.2 mmol, 10 mol%), *n*-hexane (1 mL), 120 °C, 48 h, sealed Schlenk tube; (2) acetyl chloride (1 M in CH₂Cl₂, 4.0 mmol), NEt₃ (4.0 mmol), CH₂Cl₂ (30 mL), 25 °C, 16 h. Yields refer to the total yield of isolated products (**a** + **b**). ^b GC analysis prior to acetylation and chromatography. ^c The reaction was carried out on a 4 mmol scale. ^d Formation of an additional branched product with an isomerized double bond was observed. The selectivity is given as branched (**a**)/branched isomerized/linear (**b**). For details, see the experimental section. ^e Directly isolated as the corresponding amine (without acetylation).

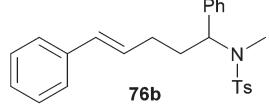
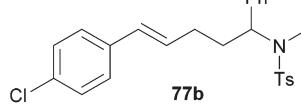
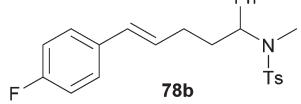
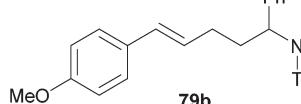
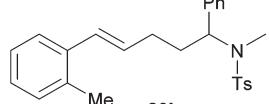
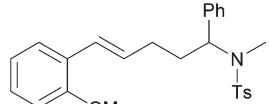
selectivities between 2 : 1 and 3 : 1^{7h} could be achieved while 5 produced linear regioisomers almost exclusively.⁷ⁱ In this context, it should be noted that separation of the regioisomers is possible by chromatography. On the other hand, it is worth mentioning that with several substrates significantly improved yields were obtained with the new catalyst 6. For example, *para*-chloro-*N*-methylaniline (59) gave a mixture of the corresponding products 66a and 66b in 65% combined yield (Table 3, entry 7) while the corresponding reaction performed with Ind₂TiMe₂ gave the same products only in 6% yield.^{7h} In addition, a significantly improved yield (46% *versus* 23%^{7h}) was obtained with *para*-methoxy-*N*-methylaniline (55) and it was also possible to perform the hydroaminoalkylation with *para*-trifluoromethoxy-*N*-methylaniline (56, Table 3, entry 4). Amine 56 represents a highly promising substrate because the *para*-trifluoromethoxy group is often present in synthetic agrochemicals and pharmaceuticals.⁹ Impressively, even *para*-thiomethyl-*N*-methylaniline (57) which does not undergo hydroaminoalkylation with 49 in the presence of Ind₂TiMe₂ did react in the presence of catalyst 6 (Table 3, entry 5). Additional reactions between *N*-methylaniline (2) and 1,3-butadienes 50–54 (Table 3, entries 8–12) delivered mixtures of the branched and the linear hydroaminoalkylation products 67–71a/b in good to modest yields but again, only with poor regioselectivities. In this context, it must be mentioned that a third product was formed during reactions of the 1-alkyl-substituted dienes (*E*)-1,3-decadiene (52) and (*E*)-6-phenyl-1,3-hexadiene (53, Table 3, entries 10 and 11). These additionally formed products were identified to be branched hydroaminoalkylation products with an isomerized double bond. The formation of two branched isomeric olefins from 2 and 52 was confirmed by hydrogenation of a mixture of 69a and its isomer with Pd/C which gave the corresponding saturated compound *N*-phenyl-*N*-(2-methyldecyl)acetamide (72) as the sole hydrogenation product in 85% yield. On the other hand, formation of additional linear hydroaminoalkylation products with isomerized double bond was not observed in the presence of catalyst 6. This is in sharp contrast to the finding that linear products with isomerized double bond are formed during hydroaminoalkylation reactions of 1,3-butadienes catalyzed by aminopyridinato titanium catalyst 5.⁷ⁱ Finally, it was found that even the 1,2-disubstituted 1,3-diene 54 undergoes successful hydroaminoalkylation with 2. The corresponding products 71a and 71b were obtained in 73% combined yield and the regioselectivity was determined to be 51 : 49 (Table 3, entry 12). In this context, it is worth mentioning that 54 and 2 are exclusively converted into the branched hydroaminoalkylation product with the catalyst Ind₂TiMe₂.

Because hydroaminoalkylation reactions of styrenes with *N*-alkylanilines catalyzed by aminopyridinato complex 4 have already revealed that the regioselectivity in favor of the linear product increases with increasing size of the *N*-alkyl substituent,^{7g} we additionally tried to react (*E*)-1-phenyl-1,3-butadiene (49) with the sterically more demanding amines *N*-benzylaniline (35), *N*-methylcyclohexylamine (36), *N*-methylhexylamine (37), and *N*-methylbenzylamine (38). All reactions were

performed with 10 mol% 6 in *n*-hexane at 120 °C in sealed Schlenk tubes and after 48 h, the reaction mixtures were analyzed by GC. During this study, it was found that among the four amines, only *N*-methylbenzylamine (38) underwent successful hydroaminoalkylation with 49 in the presence of catalyst 6 (Table 4, entry 1). Interestingly and in good agreement with the behavior of aminopyridinato catalyst 4, a high regioselectivity of 93 : 7 in favor of the linear hydroaminoalkylation product was observed and after conversion into the corresponding *para*-toluenesulfonamide and purification by chromatography, the linear product 76b was isolated in 58% yield. Due to the high regioselectivity of the reaction, the branched product could not be isolated but the NMR spectra of 76b showed very weak signal sets, which could be assigned to trace impurities of the branched product. In this context, it must also be mentioned that the isolated material additionally contained minor amounts of tosylated *N*-methylbenzylamine formed from unreacted amine 38. Interestingly and in contrast to the reactions of *N*-methylcyclohexylamine (36) and *N*-methylhexylamine (37) with α - and (*E*)- β -methylstyrene (9 and 11, Table 2, entries 5, 6, 12 and 13), alkylation of 38 occurred at the benzyl position of the amine exclusively. However, this observation is in good agreement with the fact that group 4^{7g,i} and 5^{5e} metal-catalyzed hydroaminoalkylation reactions of sterically less demanding mono-substituted alkenes and styrenes performed with 38 usually take place selectively at the benzyl position of 38. Selective alkylation at the methyl group of *N*-methylbenzylamine (38) has only been achieved with vinylcyclohexane in the presence of tantalum and niobium binaphtholate catalysts developed by the Hultsch group.^{5h,i} With these results in hand, we finally used the *para*-substituted 1-phenyl-1,3-butadienes 50, 51, and 73 as well as the *ortho*-substituted dienes 74 and 75 for hydroaminoalkylation reactions with amine 38 (Table 4, entries 2–6). The results obtained with these substrates clearly prove that electron-withdrawing chloro or fluoro substituents (Table 4, entries 2 and 3) and electron-donating methyl or methoxy groups (Table 4, entries 4–6) as well as *ortho*-substitution of the phenyl ring (Table 4, entries 5 and 6) are tolerated with no significant impact on the yield (60–71%) and the regioselectivity (13 : 87–8 : 92) of the reaction. The latter finding is in good agreement with the remote position of the phenyl substituent relative to the reacting double bond of the diene.^{7h} However, in all cases, again only the linear hydroaminoalkylation products 77–81b could be isolated from the reaction mixtures and the branched products were only detected by GC or as trace impurities in the NMR spectra of the isolated linear products. In this context, it is worth mentioning that corresponding δ -alkenylamine derivatives are promising substrates for the synthesis of *cis*-*N*-methyl-2,5-disubstituted pyrrolidines.¹⁰ Although Table 4 summarizes the first successful examples of hydroaminoalkylation reactions of conjugated dienes with *N*-methylbenzylamine (38), complex 6 unfortunately failed to catalyze a number of closely related reactions. For example, 1-phenyl-substituted 1,3-butadienes bearing additional methyl or chloro substituents in the 2-position of the diene system



Table 4 Hydroaminoalkylation of 1,3-dienes with *N*-methylbenzylamine (38)

Entry	Diene	R	Isolated linear product ^a	Yield ^b (%)	Selectivity a/b ^c
1	49	H		58	7 : 93
2	50	p-Cl		67	8 : 92
3	51	p-F		71	9 : 91
4	73	p-MeO		60	10 : 90
5	74	<i>o</i> -Me		69	13 : 87
6	75	<i>o</i> -MeO		66	11 : 89

^a Only the isolated, linear product is presented. ^b Reaction conditions: (1) *N*-methylbenzylamine (38, 242 mg, 2.0 mmol), diene (3.0 mmol), **6** (109 mg, 0.2 mmol, 10 mol%), *n*-hexane (1 mL), 120 °C, 48 h, sealed Schlenk tube; (2) *para*-toluenesulfonyl chloride (763 mg, 4.0 mmol), pyridine (10 mL), 25 °C, 16 h. Yields refer to the yield of the isolated linear product (**b**). ^c GC analysis prior to tosylation and chromatography.

did not undergo the reaction and the 1-alkyl-substituted 1,3-butadiene **52** delivered only trace amounts of the expected hydroaminoalkylation products which could only be detected and characterized by GC/MS analysis. In addition, even a small variation of the *N*-methylbenzylamine motif resulted in a lack of reactivity. Neither *N*-ethyl-, *N*-iso-propyl-, *N*-cyclohexyl-, *N*-benzyl-, nor *N*-(2-phenylethyl)-substituted benzylamines underwent successful hydroaminoalkylation with (*E*)-1-phenyl-1,3-butadiene (**49**) in the presence of catalyst **6**.

Conclusions

In summary, we have shown that the easily accessible titanium mono(formamidinate) complex **6**^{8a} which bears 2,6-diisopropylphenyl groups as the amidinate *N*-substituents is a highly active catalyst for the regioselective intermolecular hydroaminoalkylation of 1,3-dienes with *N*-methylbenzylamine (38).

noalkylation of unactivated, sterically demanding 1,1- and 1,2-disubstituted alkenes and styrenes with secondary amines. While corresponding reactions of 1,1-disubstituted alkenes and styrenes give access to the branched hydroaminoalkylation products exclusively, (*E*)- β -methylstyrene selectively reacts at the sterically less hindered β -carbon. In addition, with catalyst **6**, it is also possible for the first time to convert 1-phenyl-substituted (*E*)-1,3-butadienes and *N*-methylbenzylamine into δ -alkenylamine derivatives.

Experimental

General information

All reactions were performed under an inert atmosphere of nitrogen in oven-dried Schlenk tubes (Duran glassware, 100 mL, \varnothing = 30 mm) equipped with Teflon stopcocks and mag-



netic stirring bars (15 × 4.5 mm). Prior to use, all alkenes, styrenes, and amines were distilled and degassed. *n*-Hexane was purified by distillation from sodium wire and degassed. The alkenes, styrenes, amines, and *n*-hexane were stored in a nitrogen-filled glove box. Catalyst **6**^{8a} and the dienes^{7h,i} were synthesized according to literature procedures and stored in a nitrogen-filled glove box. All other chemicals were purchased from commercial sources and were used without further purification. Unless otherwise noted, the ratio of regiosomers was determined by gas chromatography prior to flash column chromatography. For thin layer chromatography, silica on TLC aluminium foils with fluorescent indicator 254 nm was used. The substances were detected with UV light and/or iodine. For flash column chromatography, silica gel (particle size 0.037–0.063 mm) was used. Light petroleum ether (b.p. 40–60 °C, PE), *tert*-butyl methyl ether (MTBE) and ethyl acetate (EtOAc) used for chromatography were distilled *via* Raschig columns at ambient pressure. Other solvents used for chromatography were distilled prior to use. All products that have already been reported in the literature were identified by comparison of the obtained ¹H NMR and ¹³C NMR spectra with those reported in the literature. New compounds were additionally characterized by infrared spectroscopy, mass spectrometry, and high resolution mass spectrometry (HRMS). ¹H, ¹³C and ¹⁹F NMR spectra were recorded at 500, 470, 300, 125 and 75 MHz. All ¹H NMR spectra are reported in δ units (ppm) relative to the signal of TMS at 0.00 ppm or relative to the residual solvent signal of CDCl₃ at 7.26 ppm. All ¹³C NMR spectra are reported in δ units (ppm) relative to the central line of the triplet for CDCl₃ at 77.0 ppm. All ¹⁹F NMR spectra are reported in δ units (ppm) relative to the signal of CFCl₃ at 0.00 ppm. Infrared spectra were recorded either *via* KBr pellets or on an ATR spectrometer. Mass spectra and high resolution mass spectra (HRMS) were recorded either in EI (with an ionization potential of 70 eV) or in ESI mode (ESI, TOF).

General procedure A for the hydroaminoalkylation of disubstituted alkenes and styrenes with N-substituted arylamines (Tables 1 and 2)

An oven dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with complex **6** (109 mg, 0.2 mmol, 10 mol%) and *n*-hexane (0.5 mL). Afterwards the N-substituted arylamine (2.0 mmol), the alkene or styrene (3.0 mmol), and *n*-hexane (0.5 mL) were added. After heating the mixture to 180 °C for 96 h, the mixture was cooled to room temperature and dichloromethane (40 mL) was added. Then the regioselectivity of the reaction was determined by GC (if applicable) and finally, the crude product was purified by flash column chromatography (SiO₂).

General procedure B for the hydroaminoalkylation of disubstituted styrenes with dialkylamines (Table 2)

An oven dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with complex **6** (109 mg,

0.2 mmol, 10 mol%) and *n*-hexane (0.5 mL). Afterwards the dialkylamine (2.0 mmol), the styrene (3.0 mmol), and *n*-hexane (0.5 mL) were added. After heating the mixture to 180 °C for 96 h, the crude product was transferred to a 100 mL round-bottomed flask and the Schlenk tube was rinsed with dichloromethane (4 × 10 mL). The regioselectivity of the reaction was determined by GC and subsequently, the combined solutions were concentrated under vacuum to a total volume of 10 mL. The resulting mixture was then treated with 2 N aqueous NaOH (5 mL, 10.0 mmol) and *para*-toluenesulfonyl chloride (572 mg, 3.0 mmol). The resulting biphasic mixture was stirred vigorously at room temperature for 20 h before the solution was partitioned between dichloromethane (50 mL) and water (20 mL). The formed layers were separated, the aqueous one was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were dried with MgSO₄. After concentration under vacuum, the product was isolated by flash column chromatography (SiO₂).

General procedure C for the hydroaminoalkylation of 1,3-dienes with N-methylanilines (Table 3)

An oven dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with **6** (109 mg, 0.20 mmol, 10 mol%), the diene (3.0 mmol), the amine (2.0 mmol), and *n*-hexane (1 mL). Then the tube was sealed and the resulting mixture was heated to 120 °C for 48 h. After the mixture had been cooled to room temperature, *tert*-butyl methyl ether (30 mL) was added and the regioselectivity of the reaction was determined by GC. To achieve a better separation of the products from remaining *N*-methylanilines, acetyl chloride (1 M in CH₂Cl₂, 4 mL, 4 mmol), and triethylamine (405 mg, 4 mmol) were added and the reaction mixture was stirred at room temperature for 16 h. Finally, the solvent was removed in the presence of Celite® and the residue was purified by flash column chromatography (SiO₂).

General procedure D for the hydroaminoalkylation of 1,3-dienes with *N*-methylbenzylamine (38, Table 4)

An oven dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with **6** (109 mg, 0.20 mmol, 10 mol%), the diene (3.0 mmol), *N*-methylbenzylamine (38, 242 mg, 2.0 mmol), and *n*-hexane (1 mL). Then the tube was sealed and the resulting mixture was heated to 120 °C for 48 h. After the mixture had been cooled to room temperature, *tert*-butyl methyl ether (30 mL) was added and the regioselectivity of the reaction was determined by GC. Then the solvent was removed under reduced pressure and pyridine (10 mL) and *para*-toluenesulfonyl chloride (763 mg, 4.0 mmol) were added. After the resulting mixture had been stirred overnight at room temperature, dichloromethane (50 mL) was added and the organic mixture was extracted with aqueous HCl (4 M, 50 mL). Then the aqueous layer was extracted with dichloromethane (3 × 15 mL) and the combined organic layers were dried with MgSO₄ and concentrated under reduced pressure in the



presence of silica gel. (Note: The use of Celite® instead of silica gel leads to significantly reduced yields.) Finally, the product was purified by flash column chromatography (SiO₂). Due to the viscosity of the products, removal of remaining solvents required storage of the products under high vacuum for several hours.

Amines 3a^{5m} and 3b.⁷ⁱ General procedure A was used to synthesize **3a** and **3b** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and styrene (**1**, 313 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 40 : 1), a mixture of **3a** and **3b** (406 mg, 1.92 mmol, 96%) was isolated as a yellow oil. Prior to chromatography, the ratio **3a**/**3b** was determined to be 73 : 27. For characterization, it was possible to separate the regioisomers by chromatography (PE-EtOAc, 40 : 1). **3a**: ¹H NMR (300 MHz, CDCl₃, TMS) δ = 7.25 (t, *J* = 7.3 Hz, 2H), 7.19–7.13 (m, 3H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 3.26 (dd, *J* = 12.4, 6.2 Hz, 1H), 3.16 (dd, *J* = 12.3, 8.3 Hz, 1H), 2.99 (sext, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 147.8 (C), 144.4 (C), 129.2 (CH), 128.6 (CH), 127.2 (CH), 126.6 (CH), 117.5 (CH), 113.1 (CH), 51.0 (CH₂), 39.1 (CH), 19.7 (CH₃) ppm. **3b**: ¹H NMR (300 MHz, TMS) δ = 7.34–7.24 (m, 2H), 7.24–7.09 (m, 5H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 2H), 3.59 (br. s, 1H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.94 (quin, *J* = 7.3 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.1 (C), 141.6 (C), 129.2 (CH), 128.4 (CH), 128.4 (CH), 125.9 (CH), 117.4 (CH), 112.9 (CH), 43.5 (CH₂), 33.4 (CH₂), 31.0 (CH₂) ppm.

Amine 21a.^{7g} General procedure A was used to synthesize **21a** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and methylenecyclohexane (**7**, 289 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 100 : 1), **21a** (364 mg, 1.79 mmol, 90%) was isolated as a yellow oil. Prior to chromatography, the ratio **21a**/**21b** was determined to be 99 : 1. **21a**: ¹H NMR (300 MHz, CDCl₃, TMS) δ = 7.15 (t, *J* = 7.4 Hz, 2H), 6.70–6.56 (m, 3H), 3.59 (br. s, 1H), 2.92 (s, 2H), 1.59–1.18 (m, 11H), 0.97 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 149.1 (C), 129.1 (CH), 116.7 (CH), 112.6 (CH), 54.6 (CH₂), 35.8 (CH₂), 34.2 (C), 26.4 (CH₂), 23.5 (CH₃), 22.0 (CH₂) ppm.

Amine 22a.^{5k} General procedure A was used to synthesize **22a** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 100 : 1), **22a** (387 mg, 1.72 mmol, 86%) was isolated as a yellow oil. Prior to chromatography, the ratio **22a**/**22b** was determined to be 99 : 1. **22a**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.42–7.38 (m, 2H), 7.35 (t, *J* = 7.0 Hz, 2H), 7.25–7.21 (m, 1H), 7.13 (br. t, *J* = 7.3 Hz, 2H), 6.66 (br. t, *J* = 7.3 Hz, 1H), 6.53 (br. d, *J* = 8.5 Hz, 2H), 3.28 (s, 2H), 1.41 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.7 (C), 146.7 (C), 129.1 (CH), 128.5 (CH), 126.2 (CH), 126.1 (CH), 117.1 (CH), 112.7 (CH), 55.7 (CH₂), 38.9 (C), 27.4 (CH₃) ppm.

Amine 23a.^{5m} General procedure A was used to synthesize **23a** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and *para*- α -dimethylstyrene (**10**, 397 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 100 : 1), **23a** (435 mg, 1.82 mmol, 91%) was isolated as a yellow oil. Prior to chromatography, the ratio **23a**/**23b** was determined to be 99 : 1. **23a**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.28 (br. d, *J* = 8.2 Hz, 2H), 7.22–7.09 (m, 4H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 3.32 (br. s, 1H), 3.25 (s, 2H), 2.33 (s, 3H), 1.39 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.7 (C), 143.6 (C), 135.7 (C), 129.2 (CH), 129.1 (CH), 126.0 (CH), 117.0 (CH), 112.7 (CH), 55.6 (CH₂), 38.5 (C), 27.5 (CH₃), 20.9 (CH₃) ppm.

Amine 24b.^{7g} General procedure A was used to synthesize **24b** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 95 : 1), **24b** (288 mg, 1.28 mmol, 64%) was isolated as a yellow oil. Prior to chromatography, the ratio **24a**/**24b** was determined to be 1 : 99. **24b**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.28 (t, *J* = 7.4 Hz, 2H), 7.22–7.11 (m, 5H), 6.67 (br. t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 2H), 3.66 (br. s, 1H), 3.08 (dd, *J* = 12.5, 6.1 Hz, 1H), 2.93 (dd, *J* = 12.5, 7.0 Hz, 1H), 2.74 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.49 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.06 (octet, *J* = 6.8 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.3 (C), 140.5 (C), 129.2 (CH), 129.1 (CH), 128.3 (CH), 125.9 (CH), 117.0 (CH), 112.7 (CH), 49.8 (CH₂), 41.3 (CH₂), 35.0 (CH), 18.1 (CH₃) ppm.

Amines 25a and 25b. General procedure A was used to synthesize **25a** and **25b** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and indene (**12**, 348 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 80 : 1) gave three fractions as oils. Fraction 1 contained pure compound **25a** (30 mg, 0.13 mmol, 7%), fraction 2 contained a mixture of **25a** and **25b** (203 mg, 0.91 mmol, 45%) and fraction 3 contained pure compound **25b** (200 mg, 0.90 mmol, 45%) as yellow oils. Prior to chromatography, the ratio **25a**/**25b** was determined to be 34 : 66. **25a**: R_f = 0.13 (PE-MTBE, 80 : 1). ¹H NMR (500 MHz, CDCl₃) δ = 7.33–7.27 (m, 2H), 7.25–7.18 (m, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 3.75 (br. s, 1H), 3.54–3.44 (m, 2H), 3.29 (dd, *J* = 11.8, 7.3 Hz, 1H), 3.06–2.98 (m, 1H), 2.98–2.89 (m, 1H), 2.39–2.30 (m, 1H), 1.99–1.91 (m, 1H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.4 (C), 144.7 (C), 144.4 (C), 129.3 (CH), 126.9 (CH), 126.3 (CH), 124.7 (CH), 124.0 (CH), 117.4 (CH), 112.8 (CH), 48.0 (CH₂), 44.6 (CH), 31.3 (CH₂), 30.0 (CH₂) ppm. IR (ATR) ν_{max} = 3417 (w), 3047 (w), 3019 (w), 2939 (w), 2847 (w), 1601 (s), 1504 (s), 1319 (m), 1260 (m), 744 (vs), 691 (s) cm⁻¹. GC/MS *m/z* = 223 ([M]⁺), 106 ([C₇H₈N]⁺), 77 ([C₆H₅]⁺). HRMS (ESI⁺) *m/z* calcd for C₁₆H₁₈N 224.1439 ([M + H]⁺), found 224.1438. **25b**: R_f = 0.10 (PE-MTBE, 80 : 1). ¹H NMR (500 MHz, CDCl₃) δ = 7.25–7.15 (m, 6H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 2H), 3.74 (br. s, 1H), 3.22 (d, *J* = 6.7 Hz, 2H), 3.19–3.11 (m, 2H), 2.87–2.75 (m, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.4 (C), 142.6 (C), 129.2 (CH), 126.3 (CH), 124.6 (CH), 117.3 (CH), 112.7 (CH), 48.8 (CH₂), 39.1 (CH), 37.2 (CH₂) ppm. IR (ATR) ν_{max} = 3414 (w), 3048 (w), 3020 (w), 2929 (w), 2900 (w), 2841 (w), 1601 (s), 1505 (s), 1316 (m), 1256 (m), 740 (vs), 690 (s) cm⁻¹. GC/MS *m/z* = 223 ([M]⁺), 106 ([C₇H₈N]⁺), 93 ([C₆H₇N]⁺), 77 ([C₆H₅]⁺). HRMS (ESI⁺) *m/z* calcd for C₁₆H₁₈N 224.1439 ([M + H]⁺), found 224.1436.

Amines 26a and 26b.^{7g} General procedure A was used to synthesize **26a** and **26b** from *N*-methylaniline (**2**, 214 mg,



2.0 mmol) and (*E*)-2-octene (**17**, 337 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 100 : 1), a mixture of **26a** and **26b** (69 mg, 0.32 mmol, 16%) was isolated as a yellow oil. Prior to chromatography, the ratio **26a/26b** was determined to be 35 : 65. ¹H NMR (500 MHz, CDCl₃, TMS, mixture of two regioisomers) signals of the major regioisomer **26b**: δ = 7.09 (t, J = 8.4 Hz, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.6 Hz, 2H), 3.59 (br. s, 1H), 3.01–2.92 (m, 1H), 2.80 (dd, J = 12.2, 7.3 Hz, 1H), 1.66 (octet, J = 6.6 Hz, 1H), 1.41–1.05 (m, 13H), 0.89 (d, J = 6.7 Hz, 3H), 0.81 (t, J = 6.8 Hz, 3H) ppm; important signals of the minor regioisomer **26a**: δ = 3.01–2.92 (m, 2H), 1.49 (sept, J = 6.1 Hz, 1H), 0.84 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 6.8 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃, mixture of two regioisomers) signals of the major regioisomer **26b**: δ = 148.7 (C), 129.2 (CH), 116.9 (CH), 112.6 (CH), 50.3 (CH₂), 34.8 (CH₂), 32.9 (CH), 31.9 (CH₂), 29.6 (CH₂), 26.9 (CH₂), 22.7 (CH₂), 18.1 (CH₃), 14.1 (CH₃) ppm; signals of the minor regioisomer **26a**: δ = 148.6 (C), 129.2 (CH), 116.9 (CH), 112.6 (CH), 47.0 (CH₂), 39.1 (CH), 32.3 (CH₂), 31.6 (CH₂), 26.4 (CH₂), 24.5 (CH₂), 22.7 (CH₂), 14.1 (CH₃), 10.9 (CH₃) ppm. IR (neat, mixture of two regioisomers) ν_{max} = 3421 (s), 3052 (w), 3021 (w), 2957 (s), 2926 (s), 2856 (s), 1603 (s), 1506 (s), 1465 (m), 1320 (m), 1260 (m), 747 (s), 691 (s) cm⁻¹. GC/MS m/z = 219 ([M]⁺), 106 ([C₇H₈N]⁺), 77 ([C₆H₅]⁺).

Amine 27.¹¹ General procedure A was used to synthesize **27** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and cyclopentene (**18**, 204 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1), **27** (262 mg, 1.49 mmol, 75%) was isolated as a yellow oil. **27**: ¹H NMR (300 MHz, CDCl₃, TMS) δ = 7.17 (br. t, J = 7.9 Hz, 2H), 6.68 (br. t, J = 7.3 Hz, 1H), 6.61 (br. d, J = 8.1 Hz, 2H), 3.64 (br. s, 1H), 3.02 (d, J = 7.2 Hz, 2H), 2.15 (sept, J = 7.5 Hz, 1H), 1.91–1.72 (m, 2H), 1.67–1.47 (m, 4H), 1.37–1.17 (m, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 148.6 (C), 129.2 (CH), 117.0 (CH), 112.6 (CH), 49.5 (CH₂), 39.4 (CH), 30.7 (CH₂), 25.3 (CH₂) ppm.

Amine 28.^{5k} General procedure A was used to synthesize **28** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and cyclohexene (**19**, 246 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 100 : 1), **28** (272 mg, 1.44 mmol, 72%) was isolated as a yellow oil. **28**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.18–7.13 (m, 2H), 6.67 (tt, J = 7.3, 1.0 Hz, 1H), 6.61–6.56 (m, 2H), 3.71 (br. s, 1H), 2.95 (d, J = 6.7 Hz, 2H), 1.85–1.78 (m, 2H), 1.78–1.71 (m, 2H), 1.70–1.65 (m, 1H), 1.64–1.52 (m, 1H), 1.31–1.13 (m, 3H), 0.98 (qd, J = 12.1, 3.1 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.6 (C), 129.2 (CH), 116.9 (CH), 112.7 (CH), 50.6 (CH₂), 37.6 (CH), 31.3 (CH₂), 26.6 (CH₂), 26.0 (CH₂) ppm.

Amine 29. General procedure A was used to synthesize **29** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and 1,4-cyclohexadiene (**20**, 240 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 90 : 1), **29** (348 mg, 1.86 mmol, 93%) was isolated as a yellow oil. **29**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.17 (br. t, J = 6.9 Hz, 2H), 6.68 (br. t, J = 7.3 Hz, 1H), 6.61 (br. d, J = 8.5 Hz, 2H), 5.73–5.63 (m, 2H), 3.73 (br. s, 1H), 3.10–3.01 (m, 2H), 2.24–2.15 (m, 1H), 2.13–2.03 (m, 2H), 1.96–1.83 (m, 2H), 1.83–1.74 (m, 1H), 1.39–1.28 (m, 1H)

ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 148.5 (C), 129.2 (CH), 127.2 (CH), 125.8 (CH), 117.0 (CH), 112.6 (CH), 49.7 (CH₂), 33.5 (CH), 29.7 (CH₂), 26.8 (CH₂), 24.7 (CH₂) ppm. IR (neat) ν_{max} = 3418 (m), 3051 (w), 3021 (m), 2916 (s), 2837 (m), 1603 (s), 1507 (s), 1433 (m), 1323 (s), 1254 (s), 1179 (w), 748 (s), 692 (s) cm⁻¹. GC/MS m/z = 187 ([M]⁺), 106 ([C₇H₈N]⁺), 77 ([C₆H₅]⁺). HRMS (ESI⁺) m/z calcd for C₁₃H₁₈N 188.1439 ([M + H]⁺), found 188.1435.

Amine 31.¹² General procedure A was used to synthesize **31** from *N*-methylaniline (**2**, 214 mg, 2.0 mmol) and 3-methoxyxycyclohexene (**30**, 337 mg, 3.0 mmol). After purification by flash chromatography (PE-Et₂O, 80 : 1 → PE-Et₂O, 40 : 1), **31** (228 mg, 1.22 mmol, 61%) was isolated as a yellow oil. **31**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.27–7.18 (m, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 5.94–5.88 (m, 1H), 5.63 (br. d, J = 10.2 Hz, 1H), 4.48–4.41 (m, 1H), 2.78 (s, 3H), 2.12–1.95 (m, 2H), 1.91–1.77 (m, 2H), 1.71–1.52 (m, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 149.7 (C), 130.6 (CH), 129.9 (CH), 129.1 (CH), 116.2 (CH), 112.8 (CH), 54.9 (CH), 32.4 (CH₃), 25.3 (CH₂), 24.9 (CH₂), 21.5 (CH₂) ppm.

Amine 39a. General procedure A was used to synthesize **39a** from *para*-methyl-*N*-methylaniline (**32**, 242 mg, 2.0 mmol) and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 95 : 1), **39a** (422 mg, 1.76 mmol, 88%) was isolated as a yellow oil. Prior to chromatography, the ratio **39a/39b** was determined to be 99 : 1. **39a**: ¹H NMR (500 MHz, CDCl₃, TMS) δ = 7.39 (br. d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 7.22 (br. t, J = 7.3 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 8.4 Hz, 2H), 3.25 (s, 2H), 3.17 (br. s, 1H), 2.21 (s, 3H), 1.40 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 146.8 (C), 146.5 (C), 129.6 (CH), 128.5 (CH), 126.2 (C), 126.1 (CH), 126.1 (CH), 112.8 (CH), 56.1 (CH₂), 38.9 (C), 27.4 (CH₃), 20.3 (CH₃) ppm. IR (neat) ν_{max} = 3413 (m), 3021 (m), 2964 (m), 2920 (m), 1619 (s), 1521 (s), 1480 (m), 1317 (m), 1294 (m), 1251 (m), 806 (s), 764 (m), 700 (s) cm⁻¹. GC/MS m/z = 239 ([M]⁺), 120 ([C₈H₁₀N]⁺), 91 ([C₇H₇]⁺). HRMS (ESI⁺) m/z calcd for C₁₇H₂₁NNa 262.1572 ([M + Na]⁺), found 262.1567.

Amine 40a. General procedure A was used to synthesize **40a** from *para*-fluoro-*N*-methylaniline (**33**, 250 mg, 2.0 mmol) and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1), **40a** (475 mg, 1.95 mmol, 98%) was isolated as a yellow oil. Prior to chromatography, the ratio **40a/40b** was determined to be 99 : 1. **40a**: ¹H NMR (300 MHz, CDCl₃, TMS) δ = 7.43–7.30 (m, 4H), 7.23 (tt, J = 6.8, 1.7 Hz, 1H), 6.87–6.77 (m, 2H), 6.49–6.39 (m, 2H), 3.22 (s, 2H), 3.21 (br. s, 1H), 1.41 (s, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ = 155.6 (d, $J_{\text{C},\text{F}}$ = 234.5 Hz, C), 146.6 (C), 145.1 (C), 128.5 (CH), 126.2 (CH), 126.0 (CH), 115.5 (d, $J_{\text{C},\text{F}}$ = 22.2 Hz, CH), 113.5 (d, $J_{\text{C},\text{F}}$ = 7.4 Hz, CH), 56.5 (CH₂), 38.8 (C), 27.4 (CH₃) ppm. IR (neat) ν_{max} = 3412 (w), 3059 (w), 2965 (m), 1612 (w), 1511 (s), 1481 (m), 1221 (s), 819 (s), 765 (s), 701 (s) cm⁻¹. GC/MS m/z = 243 ([M]⁺), 124 ([C₇H₇-NF]⁺), 91 ([C₇H₇]⁺). HRMS (ESI⁺) m/z calcd for C₁₆H₁₉NF 244.1502 ([M + H]⁺), found 244.1503.

Amine 41a. General procedure A was used to synthesize **41a** from *para*-phenoxy-*N*-methylaniline (**34**, 399 mg, 2.0 mmol)



and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 60 : 1), **41a** (424 mg, 1.34 mmol, 67%) was isolated as a yellow solid. Prior to chromatography, the ratio **41a/41b** was determined to be 99 : 1. **41a**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.40 (br. d, J = 8.3 Hz, 2H), 7.37–7.32 (m, 2H), 7.27–7.21 (m, 3H), 6.98 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 6.85 (br. d, J = 8.8 Hz, 2H), 6.51 (br. d, J = 8.8 Hz, 2H), 3.26 (br. s, 3H), 1.42 (s, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 159.1 (C), 147.3 (C), 146.6 (C), 145.4 (C), 129.4 (CH), 128.5 (CH), 126.2 (CH), 126.0 (CH), 121.8 (CH), 121.2 (CH), 116.9 (CH), 113.7 (CH), 56.4 (CH₂), 38.8 (C), 27.4 (CH₃) ppm. IR (neat) ν_{max} = 3412 (s), 3053 (w), 3034 (w), 2965 (m), 2924 (w), 2854 (w), 1613 (s), 1517 (s), 1489 (m), 1233 (s), 1163 (m), 832 (m), 752 (m), 704 (m), 692 (m) cm^{-1} . GC/MS m/z = 317 ([M⁺]), 198 ([C₁₃H₁₂NO⁺]), 91 ([C₇H₇]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{NONa}$ 340.1677 ([M + Na]⁺), found 340.1681.

para-Toluenesulfonamide 42a. General procedure B was used to synthesize **42a** from *N*-methylcyclohexylamine (**36**, 226 mg, 2.0 mmol) and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1 \rightarrow PE-EtOAc, 40 : 1 \rightarrow PE-EtOAc, 20 : 1), **42a** (107 mg, 0.28 mmol, 14%) was isolated as a colorless solid. Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 99 : 1. **42a**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.68 (d, J = 8.3 Hz, 2H), 7.40–7.35 (m, 2H), 7.32 (br. t, J = 7.8 Hz, 2H), 7.26–7.24 (m, 2H), 7.21 (br. t, J = 7.3 Hz, 1H), 3.44 (s, 2H), 2.53–2.45 (m, 1H), 2.41 (s, 3H), 1.39 (s, 6H), 1.35–1.12 (m, 7H), 0.74–0.59 (m, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ 147.9 (C), 142.7 (C), 139.2 (C), 129.4 (CH), 128.2 (CH), 127.3 (CH), 126.3 (CH), 126.1 (CH), 60.9 (CH), 59.4 (CH₂), 39.0 (C), 31.4 (CH₂), 27.3 (CH₃), 26.6 (CH₂), 25.1 (CH₂), 21.5 (CH₃) ppm. IR (neat) ν_{max} = 3029 (w), 2940 (m), 2859 (m), 1601 (s), 1494 (m), 1371 (s), 1161 (s), 1045 (w), 816 (m), 761 (s), 705 (s) cm^{-1} . MS (ESI⁺) m/z = 408 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_2\text{SNa}$ 408.1973 ([M + Na]⁺), found 408.1980.

para-Toluenesulfonamide 43a. General procedure B was used to synthesize **43a** from *N*-methylhexylamine (**37**, 230 mg, 2.0 mmol) and α -methylstyrene (**9**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1 \rightarrow PE-EtOAc, 40 : 1 \rightarrow PE-EtOAc, 30 : 1), a mixture of **43a** and tosylated *N*-methylhexylamine (421 mg) was isolated as a colorless oil. According to ^1H NMR spectroscopy, the mixture contained 380 mg of **43a** (0.98 mmol, 49%) and 41 mg of tosylated *N*-methylhexylamine (0.15 mmol). Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 99 : 1. **43a**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.65 (d, J = 8.3 Hz, 2H), 7.37 (br. d, J = 8.1 Hz, 2H), 7.33–7.24 (m, 4 H), 7.19 (br. t, J = 7.3 Hz, 1H), 3.39 (s, 2H), 2.54–2.47 (m, 2H), 2.41 (s, 3H), 1.41 (s, 6H), 1.12–0.98 (m, 3H), 0.95–0.85 (m, 3H), 0.78 (t, J = 7.3 Hz, 3H), 0.62 (pent, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 147.4 (C), 142.9 (C), 137.3 (C), 129.5 (CH), 128.2 (CH), 127.2 (CH), 126.1 (CH), 126.0 (CH), 59.7 (CH₂), 49.3 (CH₂), 39.0 (C), 31.1 (CH₂), 27.1 (CH₃), 27.1 (CH₂), 26.3 (CH₂), 22.4 (CH₂), 21.5 (CH₃), 13.9

(CH₃) ppm. IR (neat) ν_{max} = 2958 (s), 2929 (s), 2858 (m), 1599 (m), 1495 (m), 1465 (m), 1340 (s), 1160 (s), 1091 (m), 815 (m), 757 (m), 702 (s), 655 (s) cm^{-1} . MS (ESI⁺) m/z = 410 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_2\text{SNa}$ 410.2130 ([M + Na]⁺), found 410.2123.

Amine 44b.^{7b} General procedure A was used to synthesize **44b** from *para*-methyl-*N*-methylaniline (**32**, 242 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 95 : 1), **44b** (150 mg, 0.63 mmol, 31%) was isolated as a yellow oil. Prior to chromatography, the ratio **44a/44b** was determined to be 1 : 99. **44b**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.28 (t, J = 7.4 Hz, 2H), 7.22–7.13 (m, 3H), 6.96 (d, J = 8.1 Hz, 2 H), 6.47 (br. d, J = 8.4 Hz, 2 H), 3.53 (br. s, 1H), 3.06 (dd, J = 12.4, 6.0 Hz, 1H), 2.92 (dd, J = 12.4, 6.9 Hz, 1H), 2.74 (dd, J = 13.4, 6.4 Hz, 1H), 2.49 (dd, J = 13.5, 7.9 Hz, 1H), 2.22 (s, 3H), 2.06 (oct, J = 6.7 Hz, 1H), 0.96 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 146.1 (C), 140.6 (C), 129.7 (CH), 129.1 (CH), 128.2 (CH), 126.3 (C), 125.9 (CH), 112.9 (CH), 50.2 (CH₂), 41.4 (CH₂), 35.0 (CH), 20.3 (CH₃), 18.1 (CH₃) ppm.

Amine 45b. General procedure A was used to synthesize **45b** from *para*-fluoro-*N*-methylaniline (**33**, 250 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1), **45b** (316 mg, 1.30 mmol, 65%) was isolated as a red oil. Prior to chromatography, the ratio **45a/45b** was determined to be 2 : 98. **45b**: ^1H NMR (300 MHz, CDCl_3 , TMS) δ = 7.37–7.11 (m, 5H), 6.91–6.79 (m, 2H), 6.50–6.38 (m, 2H), 3.52 (br. s, 1H), 3.03 (dd, J = 12.3, 6.1 Hz, 1H), 2.90 (dd, J = 12.3, 6.9 Hz, 1H), 2.73 (dd, J = 13.5, 6.5 Hz, 1H), 2.51 (dd, J = 13.5, 7.7 Hz, 1H), 2.05 (oct, J = 6.7 Hz, 1H), 0.97 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 155.6 (d, $J_{\text{C},\text{F}}$ = 234.4 Hz, C), 144.7 (C), 140.4 (C), 129.1 (CH), 128.3 (CH), 126.0 (CH), 115.6 (d, $J_{\text{C},\text{F}}$ = 22.2 Hz, CH), 113.4 (d, $J_{\text{C},\text{F}}$ = 7.4 Hz, CH), 50.5 (CH₂), 41.4 (CH₂), 35.0 (CH), 18.1 (CH₃) ppm. IR (neat) ν_{max} = 3422 (m), 3061 (w), 3027 (m), 2958 (m), 2925 (m), 1612 (m), 1511 (s), 1454 (m), 1319 (w), 1256 (m), 1221 (s), 819 (s), 741 (s), 701 (s) cm^{-1} . GC/MS m/z = 243 ([M⁺]), 124 ([C₇H₇NF]⁺), 91 ([C₇H₇]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{FN}$ 244.1502 ([M + H]⁺), found 244.1496.

Amine 46b. General procedure A was used to synthesize **46b** from *para*-phenoxy-*N*-methylaniline (**34**, 399 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80 : 1 \rightarrow PE-EtOAc, 20 : 1), **46b** (88 mg, 0.28 mmol, 14%) was isolated as a dark yellow solid. Prior to chromatography, the ratio **46a/46b** was determined to be 1 : 99. **46b**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.31–7.24 (m, 4H), 7.23–7.14 (m, 3H), 6.99 (br. t, J = 7.4 Hz, 1H), 6.92 (br. d, J = 7.7 Hz, 2H), 6.87 (br. d, J = 8.8 Hz, 2H), 6.54 (br. d, J = 8.9 Hz, 2H), 3.58 (br. s, 1H), 3.08 (dd, J = 12.3, 6.0 Hz, 1H), 2.94 (dd, J = 12.3, 7.0 Hz, 1H), 2.75 (dd, J = 13.5, 6.5 Hz, 1H), 2.52 (dd, J = 13.5, 7.7 Hz, 1H), 2.08 (oct, J = 6.7 Hz, 1H), 0.99 (d, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 159.2 (C), 147.4 (C), 145.1 (C), 140.5 (C), 129.5 (CH), 129.1 (CH), 128.3 (CH), 126.0 (CH), 121.9 (CH), 121.2 (CH), 117.1 (CH), 113.7 (CH), 50.5 (CH₂), 41.4 (CH₂), 35.1 (CH), 18.1 (CH₃) ppm. IR (neat) ν_{max} = 3026 (m), 2957 (m), 2925 (m), 2870 (m),



1613 (m), 1589 (m), 1512 (s), 1488 (s), 1232 (s), 869 (s), 832 (s), 745 (s), 700 (s), 692 (s) cm^{-1} . GC/MS m/z = 317 ($[\text{M}]^+$), 198 ($[\text{C}_{13}\text{H}_{12}\text{NO}]^+$), 91 ($[\text{C}_7\text{H}_7]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{22}\text{H}_{24}\text{NO}$ 318.1858 ($[\text{M} + \text{H}]^+$), found 318.1854.

para-Toluenesulfonamide 47b. General procedure B was used to synthesize **47b** from *N*-methylcyclohexylamine (**36**, 226 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80:1 \rightarrow PE-EtOAc, 40:1 \rightarrow PE-EtOAc, 20:1), **47b** (294 mg, 0.76 mmol, 38%) was isolated as a colorless solid. Prior to tosylation and chromatography, the ratio of the α - and the β -alkylated product was determined to be 1:99. **47b**: ^1H NMR (300 MHz, CDCl_3 , TMS) δ = 7.64 (d, J = 8.3 Hz, 2H), 7.35–7.10 (m, 7H), 3.66–3.53 (m, 1H), 3.06 (dd, J = 14.4, 6.9, 1H), 2.97 (dd, J = 14.4, 7.7, 1H), 2.82 (dd, J = 13.0, 5.0 Hz, 1H), 2.40 (s, 3H), 2.36–2.11 (m, 2H), 1.77–1.49 (m, 5H), 1.38–1.12 (m, 5H), 0.90 (d, J = 6.4 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 142.7 (C), 140.8 (C), 138.0 (C), 129.5 (CH), 129.0 (CH), 128.2 (CH), 126.9 (CH), 125.8 (CH), 58.5 (CH), 50.2 (CH₂), 41.0 (CH₂), 35.8 (CH), 31.9 (CH₂), 31.8 (CH₂), 26.2 (CH₂), 26.2 (CH₂), 25.4 (CH₂), 21.4 (CH₃), 17.5 (CH₃) ppm. IR (neat) ν_{max} = 3027 (m), 2935 (s), 2856 (s), 1599 (s), 1494 (s), 1453 (s), 1334 (s), 1155 (s), 1090 (m), 1005 (m), 988 (m), 849 (m), 814 (m), 742 (m), 702 (s), 661 (s) cm^{-1} . MS (ESI $^+$) m/z = 408 ($[\text{M} + \text{Na}]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_2\text{NaS}$ 408.1973 ($[\text{M} + \text{Na}]^+$), found 408.1967.

para-Toluenesulfonamide 48b. General procedure B was used to synthesize **48b** from *N*-methylhexylamine (37, 230 mg, 2.0 mmol) and (*E*)- β -methylstyrene (**11**, 355 mg, 3.0 mmol). After purification by flash chromatography (PE-EtOAc, 80:1 \rightarrow PE-EtOAc, 40:1 \rightarrow PE-EtOAc, 20:1), **48b** (322 mg, 0.83 mmol, 41%) was isolated as a colorless oil. Prior to tosylation and chromatography, the ratio of the α - and the β -alkylated product was determined to be 1:99. **48b**: ^1H NMR (500 MHz, CDCl_3 , TMS) δ = 7.64 (d, J = 8.3 Hz, 2H), 7.30–7.25 (m, 4H), 7.19 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 7.1 Hz, 2H), 3.12–2.96 (m, 3H), 2.92 (dd, J = 13.7, 8.0 Hz, 1H), 2.77 (dd, J = 13.6, 5.7 Hz, 1H), 2.41 (s, 3H), 2.34 (dd, J = 13.6, 8.8 Hz, 1H), 2.12–2.01 (m, 1H), 1.51–1.40 (m, 2H), 1.30–1.15 (m, 6H), 0.89 (d, J = 6.6 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 142.9 (C), 140.4 (C), 136.7 (C), 129.5 (CH), 129.0 (CH), 128.2 (CH), 127.2 (CH), 125.9 (CH), 54.6 (CH₂), 49.2 (CH₂), 40.9 (CH₂), 34.3 (CH), 31.3 (CH₂), 28.4 (CH₂), 26.5 (CH₂), 22.5 (CH₂), 21.5 (CH₃), 17.5 (CH₃), 14.0 (CH₃) ppm. IR (neat) ν_{max} = 3027 (m), 2928 (s), 2870 (s), 1599 (m), 1495 (m), 1455 (s), 1340 (s), 1161 (s), 1191 (m), 981 (m), 815 (m), 741 (s), 701 (m), 655 (s) cm^{-1} . MS (ESI $^+$) m/z = 410 ($[\text{M} + \text{Na}]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_2\text{Na}$ 410.2130 ($[\text{M} + \text{Na}]^+$), found 410.2126.

(E)-N-(2-Methyl-4-phenylbut-3-en-1-yl)-N-phenylacetamide (60a) and (E)-N-phenyl-N-(5-phenylpent-4-en-1-yl)acetamide (60b). General procedure C was used to synthesize **60a** and **60b** from *N*-methylaniline (2, 214 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (**49**, 391 mg, 3.0 mmol). Purification by flash column chromatography gave three fractions as oils. Fraction 1 contained pure compound **60a** (151 mg, 0.54 mmol, 27%) and fraction 2 contained a mixture of **60a** and **60b**

(115 mg, 0.41 mg, 21%). Fraction 3 contained pure compound **60b** (140 mg, 0.50 mmol, 25%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 55:45. **60a**: R_f = 0.16 (PE-MTBE, 2:1).

^1H NMR (500 MHz, CDCl_3) δ = 7.39 (t, J = 7.5 Hz, 2H), 7.35–7.27 (m, 5H), 7.22–7.20 (m, 1H), 7.17 (d, J = 7.4 Hz, 2H), 6.37 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 15.8, 8.5 Hz, 1H), 3.80 (dd, J = 13.5, 8.8 Hz, 1H), 3.73 (dd, J = 13.5, 6.5 Hz, 1H), 2.62 (hept, J = 6.9 Hz, 1H), 1.81 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.6 (C), 143.4 (C), 137.5 (C), 133.9 (CH), 129.9 (CH), 129.6 (CH), 128.5 (CH), 128.3 (CH), 127.7 (CH), 127.0 (CH), 126.1 (CH), 54.5 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.4 (CH₃) ppm. IR (ATR) ν_{max} = 3057 (w), 3025 (w), 2967 (w), 2927 (w), 2871 (w), 1656 (vs), 1594 (m), 1494 (s), 1394 (s), 1292 (m), 1277 (m), 966 (m), 749 (s), 695 (vs) cm^{-1} . MS (ESI $^+$) m/z = 302 ($[\text{M} + \text{Na}]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{Na}$ 302.1521 ($[\text{M} + \text{Na}]^+$), found 302.1514. **60b**: R_f = 0.11 (PE-MTBE, 2:1). ^1H NMR (500 MHz, CDCl_3) δ = 7.43 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.31–7.25 (m, 4H), 7.19–7.15 (m, 3H), 6.33 (d, J = 15.8 Hz, 1H), 6.16 (dt, J = 15.8, 6.8 Hz, 1H), 3.78–3.73 (m, 2H), 2.25–2.18 (m, 2H), 1.84 (s, 3H), 1.70 (pent, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.3 (C), 143.1 (C), 137.6 (C), 130.3 (CH), 129.7 (CH), 129.6 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 126.9 (CH), 125.9 (CH), 48.7 (CH₂), 30.3 (CH₂), 27.4 (CH₂), 22.8 (CH₃). IR (ATR) ν_{max} = 3060 (w), 3027 (w), 2931 (w), 2860 (w), 1655 (vs), 1596 (m), 1496 (s), 1397 (s), 1296 (m), 1280 (m), 968 (m), 744 (m), 698 (vs) cm^{-1} . MS (ESI $^+$) m/z = 302 ($[\text{M} + \text{Na}]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{Na}$ 302.1521 ($[\text{M} + \text{Na}]^+$), found 302.1511.

(E)-N-(2-Methyl-4-phenylbut-3-en-1-yl)-N-(4-phenoxyphenyl)-acetamide (61a) and (E)-N-(4-phenoxyphenyl)-N-(5-phenylpent-4-en-1-yl)acetamide (61b). General procedure C was used to synthesize **61a** and **61b** from *para*-phenoxy-*N*-methylaniline (**34**, 399 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (**49**, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2:1) gave three fractions as oils. Fraction 1 contained pure compound **61a** (62 mg, 0.17 mmol, 8%) and fraction 2 contained a mixture of **61a** and **61b** (198 mg, 0.53 mmol, 27%). Fraction 3 contained pure compound **61b** (74 mg, 0.20 mmol, 10%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 54:46. **61a**: R_f = 0.22 (PE-MTBE, 2:1). ^1H NMR (500 MHz, CDCl_3) δ = 7.40–7.35 (m, 2H), 7.33–7.27 (m, 4H), 7.22–7.14 (m, 2H), 7.11 (br. d, J = 8.8 Hz, 2H), 7.05 (br. d, J = 7.7 Hz, 2H), 6.99 (br. d, J = 8.8 Hz, 2H), 6.38 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9, 8.5 Hz, 1H), 3.78 (dd, J = 13.4, 8.9 Hz, 1H), 3.72 (dd, J = 13.4, 6.4 Hz, 1H), 2.70–2.60 (m, 1H), 1.84 (s, 3H), 1.10 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.7 (C), 156.8 (C), 156.3 (C), 138.1 (C), 137.4 (C), 133.9 (CH), 129.9 (CH), 129.9 (CH), 129.5 (CH), 128.5 (CH), 127.0 (CH), 126.1 (CH), 124.0 (CH), 119.4 (CH), 119.0 (CH), 54.5 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.4 (CH₃) ppm. IR (ATR) ν_{max} = 3059 (w), 3025 (w), 2964 (w), 2926 (w), 2869 (w), 1656 (vs), 1588 (m), 1504 (s), 1488 (vs), 1393 (m), 1234 (vs), 967 (m), 870 (m), 844 (m), 749 (s), 692 (s) cm^{-1} . MS (ESI $^+$) m/z = 372 ($[\text{M} + \text{H}]^+$). HRMS (ESI $^+$) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{Na}$ 394.1783 ($[\text{M} + \text{Na}]^+$),



found 394.1787. **61b**: $R_f = 0.14$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.41\text{--}7.36$ (m, 2H), 7.34–7.26 (m, 4H), 7.21–7.15 (m, 2H), 7.12 (br. d, $J = 8.8$ Hz, 2H), 7.07 (br. d, $J = 7.7$ Hz, 2H), 7.02 (br. d, $J = 8.8$ Hz, 2H), 6.36 (d, $J = 15.9$ Hz, 1H), 6.19 (dt, $J = 15.9, 6.9$ Hz, 1H), 3.76–3.71 (m, 2H), 2.24 (q, $J = 7.4$ Hz, 2H), 1.87 (s, 3H), 1.72 (pent, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.3$ (C), 157.0 (C), 156.2 (C), 137.8 (C), 137.5 (C), 130.3 (CH), 129.9 (CH), 129.6 (CH), 129.3 (CH), 128.4 (CH), 126.8 (CH), 125.9 (CH), 124.0 (CH), 119.4 (CH), 119.1 (CH), 48.7 (CH₂), 30.2 (CH₂), 27.4 (CH₂), 22.8 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3062$ (w), 3028 (w), 2926 (w), 2851 (w), 1658 (s), 1506 (s), 1489 (s), 1397 (m), 1294 (m), 1233 (vs), 968 (m), 750 (m), 693 (s) cm^{-1} . MS (ESI⁺) $m/z = 372$ ([M + H]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_2\text{Na}$ 394.1783 ([M + Na]⁺), found 394.1778.

(E)-N-(4-Methoxyphenyl)-N-(2-methyl-4-phenylbut-3-en-1-yl)-acetamide (62a) and **(E)-N-(4-methoxyphenyl)-N-(5-phenyl-pent-4-en-1-yl)acetamide (62b)**.^{7h} General procedure C was used to synthesize **62a** and **62b** from *para*-methoxy-*N*-methyl-aniline (55, 274 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (49, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2 : 1) gave three fractions as oils. Fraction 1 contained pure compound **62a** (82 mg, 0.27 mmol, 13%) and fraction 2 contained a mixture of **62a** and **62b** (142 mg, 0.46 mmol, 23%). Fraction 3 contained pure compound **62b** (59 mg, 0.19 mmol, 10%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 54 : 46. **62a**: $R_f = 0.24$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.30\text{--}7.24$ (m, 4H), 7.19–7.15 (m, 1H), 7.05 (br. d, $J = 8.8$ Hz, 2H), 6.86 (br. d, $J = 8.8$ Hz, 2H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.04 (dd, $J = 15.8, 8.4$ Hz, 1H), 3.79 (s, 3H), 3.73 (dd, $J = 13.4, 8.4$ Hz, 1H), 3.66 (dd, $J = 13.4, 6.5$ Hz, 1H), 2.62–2.54 (m, 1H), 1.77 (s, 3H), 1.05 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.9$ (C), 158.7 (C), 137.5 (C), 136.1 (C), 133.9 (CH), 129.8 (CH), 129.2 (CH), 128.4 (CH), 127.0 (CH), 126.1 (CH), 114.6 (CH), 55.4 (CH₃), 54.5 (CH₂), 36.5 (CH), 22.7 (CH₃), 18.3 (CH₃) ppm. **62b**: $R_f = 0.21$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.32\text{--}7.24$ (m, 4H), 7.19–7.15 (m, 1H), 7.08 (br. d, $J = 8.9$ Hz, 2H), 6.92 (br. d, $J = 8.9$ Hz, 2H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.16 (dt, $J = 15.8, 6.9$ Hz, 1H), 3.83 (s, 3H), 3.73–3.69 (m, 2H), 2.21 (q, $J = 7.6$ Hz, 2H), 1.82 (s, 3H), 1.68 (pent, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.6$ (C), 158.9 (C), 137.6 (C), 135.8 (C), 130.2 (CH), 129.7 (CH), 129.1 (CH), 128.4 (CH), 126.9 (CH), 125.9 (CH), 114.7 (CH), 55.4 (CH₃), 48.7 (CH₂), 30.3 (CH₂), 27.4 (CH₂), 22.8 (CH₃) ppm.

(E)-N-(2-Methyl-4-phenylbut-3-en-1-yl)-N-(4-(trifluoromethoxy)-phenyl)acetamide (63a) and **(E)-N-(5-phenylpent-4-en-1-yl)-N-(4-(trifluoromethoxy)phenyl)acetamide (63b)**. General procedure C was used to synthesize **63a** and **63b** from *para*-trifluoromethoxy-*N*-methylaniline (56, 382 mg, 2.0 mmol), and (*E*)-1-phenyl-1,3-butadiene (49, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 1 : 1) gave three fractions as oils. Fraction 1 contained pure compound **63a** (76 mg, 0.21 mmol, 11%) and fraction 2 contained a mixture of **63a** and **63b** (412 mg, 1.14 mmol, 57%). Fraction 3 contained pure

compound **63b** (107 mg, 0.30 mmol, 14%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 53 : 47. **63a**: $R_f = 0.28$ (PE-MTBE, 1 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.31\text{--}7.27$ (m, 4H), 7.24–7.17 (m, 5H), 6.36 (d, $J = 15.9$ Hz, 1H), 6.01 (dd, $J = 15.8, 8.6$ Hz, 1H), 3.79–3.70 (m, 2H), 2.68–2.58 (m, 1H), 1.82 (s, 3H), 1.08 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.4$ (C), 148.2 (C), 142.0 (C), 137.3 (C), 133.7 (CH), 130.2 (CH), 129.8 (CH), 128.5 (CH), 127.2 (CH), 126.1 (CH), 122.0 (CH), 120.4 (q, $J_{\text{C},\text{F}} = 258.0$ Hz, CF₃), 154.7 (CH₂), 36.7 (CH), 22.8 (CH₃), 18.4 (CH₃) ppm. ^{19}F NMR (500 MHz, CDCl_3) $\delta = -58.0$ ppm. IR (ATR) $\nu_{\text{max}} = 3061$ (w), 3026 (w), 2965 (w), 2929 (w), 2872 (w), 1662 (s), 1506 (s), 1392 (m), 1252 (vs), 1198 (vs), 1160 (vs), 967 (m), 858 (m), 749 (s), 694 (s) cm^{-1} . MS (EI) $m/z = 363$ ([M]⁺). HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{NF}_3$ 363.1441 ([M]⁺), found 363.1441. **63b**: $R_f = 0.20$ (PE-MTBE, 1 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.30\text{--}7.26$ (m, 5H), 7.23–7.17 (m, 4H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.15 (dt, $J = 15.7, 6.8$ Hz, 1H), 3.78–3.71 (m, 2H), 2.25–2.18 (m, 2H), 1.84 (s, 3H), 1.70 (pent, $J = 7.5$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.0$ (C), 148.4 (C), 141.7 (C), 137.5 (C), 130.5 (CH), 129.6 (CH), 129.4 (CH), 128.5 (CH), 127.0 (CH), 126.0 (CH), 122.1 (CH), 120.4 (q, $J_{\text{C},\text{F}} = 258.0$ Hz, CF₃), 48.8 (CH₂), 30.3 (CH₂), 27.5 (CH₂), 22.8 (CH₃) ppm. ^{19}F NMR (500 MHz, CDCl_3) $\delta = -58.0$ ppm. IR (ATR) $\nu_{\text{max}} = 3063$ (w), 3027 (w), 2931 (w), 2866 (w), 1660 (s), 1506 (s), 1448 (m), 1396 (m), 1252 (vs), 1203 (vs), 1161 (vs), 967 (m), 857 (m), 747 (m), 695 (m) cm^{-1} . MS (EI) $m/z = 363$ ([M]⁺). HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{O}_2\text{NF}_3$ 363.1441 ([M]⁺), found 363.1444.

(E)-N-(2-Methyl-4-phenylbut-3-en-1-yl)-N-(4-(methylthio)-phenyl)-acetamide (64a) and **(E)-N-(4-(methylthio)phenyl)-N-(5-phenyl-pent-4-en-1-yl)acetamide (64b)**. General procedure C was used to synthesize **64a** and **64b** from *para*-thiomethyl-*N*-methylaniline (57, 306 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (49, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 1.5 : 1) gave three fractions as oils. Fraction 1 contained pure compound **64a** (123 mg, 0.38 mmol, 19%) and fraction 2 contained a mixture of **64a** and **64b** (149 mg, 0.46 mmol, 23%). Fraction 3 contained pure compound **64b** (73 mg, 0.23 mmol, 11%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 54 : 46. **64a**: $R_f = 0.24$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.31\text{--}7.28$ (m, 4H), 7.23 (br. d, $J = 8.5$ Hz, 2H), 7.21–7.18 (m, 1H), 7.07 (br. d, $J = 8.5$ Hz, 2H), 6.35 (d, $J = 15.8$ Hz, 1H), 6.04 (dd, $J = 15.9, 8.5$ Hz, 1H), 3.76 (dd, $J = 13.4, 8.8$ Hz, 1H), 3.70 (dd, $J = 13.4, 6.5$ Hz, 1H), 2.64–2.57 (m, 1H), 2.49 (s, 3H), 1.81 (s, 3H), 1.07 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.6$ (C), 140.2 (C), 138.4 (C), 137.4 (C), 133.8 (CH), 129.9 (CH), 128.6 (CH), 128.5 (CH), 127.1 (CH), 126.1 (CH), 54.4 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.4 (CH₃), 15.6 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3025$ (w), 2963 (w), 2921 (m), 2851 (w), 1656 (vs), 1492 (vs), 1391 (s), 1286 (m), 1098 (m), 966 (s), 829 (m), 747 (s), 694 (s) cm^{-1} . MS (ESI⁺) $m/z = 348$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NOSNa}$ 348.1398 ([M + Na]⁺), found 348.1401. **64b**: $R_f = 0.20$ (PE-MTBE, 1 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.24\text{--}7.18$ (m, 6H), 7.13–7.09 (m, 1H), 7.01 (br. d, $J = 8.4$ Hz, 2H), 6.25 (s, 3H), 1.81 (s, 3H), 1.07 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.6$ (C), 140.2 (C), 138.4 (C), 137.4 (C), 133.8 (CH), 129.9 (CH), 128.6 (CH), 128.5 (CH), 127.1 (CH), 126.1 (CH), 54.4 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.4 (CH₃), 15.6 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3025$ (w), 2963 (w), 2921 (m), 2851 (w), 1656 (vs), 1492 (vs), 1391 (s), 1286 (m), 1098 (m), 966 (s), 829 (m), 747 (s), 694 (s) cm^{-1} . MS (ESI⁺) $m/z = 348$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NOSNa}$ 348.1398 ([M + Na]⁺), found 348.1401.



(d, $J = 15.7$ Hz, 1H), 6.08 (dt, $J = 15.8, 6.9$ Hz, 1H), 3.68–3.62 (m, 2H), 2.43 (s, 3H), 2.17–2.11 (m, 2H), 1.77 (s, 3H), 1.61 (pent, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.3$ (C), 139.9 (C), 138.6 (C), 137.5 (C), 130.3 (CH), 129.6 (CH), 128.5 (CH), 128.4 (CH), 127.2 (CH), 126.9 (CH), 125.9 (CH), 48.6 (CH₂), 30.3 (CH₂), 27.4 (CH₂), 22.8 (CH₃), 15.6 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3024$ (w), 2920 (m), 2851 (w), 1654 (vs), 1492 (s), 1438 (m), 1392 (s), 1291 (m), 1098 (m), 966 (s), 828 (m), 747 (m), 693 (s) cm^{-1} . MS (ESI⁺) $m/z = 348$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NOSNa}$ 348.1398 ([M + Na]⁺), found 348.1397.

(E)-N-(4-Isopropylphenyl)-N-(2-methyl-4-phenylbut-3-en-1-yl)-acetamide (65a) and (E)-N-(4-isopropylphenyl)-N-(5-phenylpent-4-en-1-yl)acetamide (65b). General procedure C was used to synthesize **65a** and **65b** from *para*-isopropyl-*N*-methylaniline (**58**, 299 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (**49**, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 1.5 : 1) gave three fractions as oils. Fraction 1 contained pure compound **65a** (74 mg, 0.23 mmol, 12%) and fraction 2 contained a mixture of **65a** and **65b** (278 mg, 0.87 mmol, 43%). Fraction 3 contained pure compound **65b** (61 mg, 0.19 mmol, 9%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 53 : 47. **65a:** ^1H NMR (500 MHz, CDCl_3) $\delta = 7.31$ –7.27 (m, 4H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.21–7.18 (m, 1H), 7.07 (d, $J = 8.3$ Hz, 2H), 6.36 (d, $J = 15.9$ Hz, 1H), 6.06 (dd, $J = 15.8, 8.4$ Hz, 1H), 3.77 (dd, $J = 13.4, 8.7$ Hz, 1H), 3.71 (dd, $J = 13.4, 6.5$ Hz, 1H), 2.93 (hept, $J = 6.9$ Hz, 1H), 2.67–2.58 (m, 1H), 1.81 (s, 3H), 1.26 (d, $J = 6.9$ Hz, 6H), 1.08 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.8$ (C), 148.4 (C), 140.9 (C), 137.6 (C), 134.0 (CH), 129.7 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 127.0 (CH), 126.1 (CH), 54.4 (CH₂), 36.5 (CH), 33.7 (CH), 23.9 (CH₃), 22.9 (CH₃), 18.3 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3027$ (w), 2963 (m), 2929 (w), 2872 (w), 1658 (vs), 1511 (s), 1395 (s), 1289 (m), 1215 (w), 968 (m), 845 (m), 749 (s), 696 (s) cm^{-1} . MS (ESI⁺) $m/z = 344$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{22}\text{H}_{27}\text{NONa}$ 344.1990 ([M + Na]⁺), found 344.1982. **65b:** ^1H NMR (500 MHz, CDCl_3) $\delta = 7.31$ –7.24 (m, 7H), 7.07 (d, $J = 8.3$ Hz, 2H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.16 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.75–3.71 (m, 2H), 2.94 (hept, $J = 7.0$ Hz, 1H), 2.24–2.18 (m, 2H), 1.83 (s, 3H), 1.70 (pent, $J = 7.6$ Hz, 2H), 1.27 (d, $J = 6.9$ Hz, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.5$ (C), 148.6 (C), 140.7 (C), 137.6 (C), 130.2 (CH), 129.8 (CH), 128.4 (CH), 127.8 (CH), 127.6 (CH), 126.9 (CH), 125.9 (CH), 48.7 (CH₂), 33.7 (CH), 30.3 (CH₂), 27.4 (CH₂), 23.9 (CH₃), 22.8 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3028$ (w), 2962 (m), 2930 (w), 2872 (w), 1658 (vs), 1511 (s), 1397 (s), 1294 (m), 968 (m), 845 (m), 749 (m), 696 (s) cm^{-1} . MS (ESI⁺) $m/z = 344$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{22}\text{H}_{28}\text{NO}$ 322.2165 ([M + H]⁺), found 322.2168.

(E)-N-(4-Chlorophenyl)-N-(2-methyl-4-phenylbut-3-en-1-yl)-acetamide (66a)^{7h} and (E)-N-(4-chlorophenyl)-N-(5-phenylpent-4-en-1-yl)acetamide (66b). General procedure C was used to synthesize **66a** and **66b** from *para*-chloro-*N*-methylaniline (**59**, 283 mg, 2.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (**49**, 391 mg, 3.0 mmol). Purification by flash column chromatography

(PE-MTBE, 1 : 1) gave three fractions as oils. Fraction 1 contained pure compound **66a** (111 mg, 0.36 mmol, 18%) and fraction 2 contained a mixture of **66a** and **66b** (206 mg, 0.66 mmol, 33%). Fraction 3 contained compound **66b** (88 mg, 0.28 mmol, 14%) with trace impurities of **66a**. Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 50 : 50. **66a:** $R_f = 0.23$ (PE-MTBE, 1 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.36$ (d, $J = 8.6$ Hz, 2H), 7.32–7.28 (m, 4H), 7.24–7.19 (m, 1H), 7.10 (d, $J = 8.5$ Hz, 2H), 6.35 (d, $J = 15.9$ Hz, 1H), 6.02 (dd, $J = 15.8, 8.6$ Hz, 1H), 3.76 (dd, $J = 13.5, 9.0$ Hz, 1H), 3.70 (dd, $J = 13.5, 6.4$ Hz, 1H), 2.65–2.56 (m, 1H), 1.81 (s, 3H), 1.07 (d, $J = 6.7$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.3$ (C), 141.9 (C), 137.3 (C), 133.6 (CH), 133.5 (C), 130.1 (CH), 129.8 (CH), 129.6 (CH), 128.5 (CH), 127.2 (CH), 126.1 (CH), 54.5 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.4 (CH₃) ppm. **66b:** $R_f = 0.19$ (PE-MTBE, 1 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.36$ (d, $J = 8.6$ Hz, 2H), 7.28–7.21 (m, 4H), 7.16–7.12 (m, 1H), 7.07 (d, $J = 8.6$ Hz, 2H), 6.29 (d, $J = 15.8$ Hz, 1H), 6.10 (dt, $J = 15.7, 6.9$ Hz, 1H), 3.71–3.66 (m, 2H), 2.20–2.14 (m, 2H), 1.80 (s, 3H), 1.63 (pent, $J = 7.6$ Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.0$ (C), 141.6 (C), 137.5 (C), 133.7 (C), 130.4 (CH), 129.9 (CH), 129.4 (CH), 128.4 (CH), 126.9 (CH), 125.9 (CH), 48.7 (CH₂), 30.2 (CH₂), 27.4 (CH₂), 22.8 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3059$ (w), 3025 (w), 2929 (m), 2864 (w), 1657 (vs), 1489 (vs), 1446 (m), 1392 (s), 1289 (m), 1091 (s), 1014 (m), 966 (s), 838 (m), 746 (s) 693 (s) cm^{-1} . MS (ESI⁺) $m/z = 336$ ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NOClNa}$ 336.1131 ([M + Na]⁺), found 336.1130.

(E)-N-(4-Chlorophenyl)-2-methylbut-3-en-1-yl)-N-phenylacetamide (67a) and (E)-N-(5-(4-chlorophenyl)pent-4-en-1-yl)-N-phenylacetamide (67b).^{7h} General procedure C was used to synthesize **67a** and **67b** from *N*-methylaniline (2, 214 mg, 2.0 mmol) and (*E*)-1-(*para*-chlorophenyl)-1,3-butadiene (**50**, 494 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2 : 1) gave three fractions as oils. Fraction 1 contained pure compound **67a** (65 mg, 0.21 mmol, 10%) and fraction 2 contained a mixture of **67a** and **67b** (150 mg, 0.48 mmol, 25%). Fraction 3 contained pure compound **67b** (109 mg, 0.35 mmol, 17%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 50 : 50. **67a:** $R_f = 0.19$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.38$ (t, $J = 7.6$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.25–7.19 (m, 4H), 7.14 (d, $J = 7.7$ Hz, 2H), 6.31 (d, $J = 15.9$ Hz, 1H), 6.03 (dd, $J = 15.8, 8.4$ Hz, 1H), 3.79 (dd, $J = 13.5, 8.8$ Hz, 1H), 3.70 (dd, $J = 13.4, 6.4$ Hz, 1H), 2.66–2.56 (m, 1H), 1.80 (s, 3H), 1.07 (d, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) $\delta = 170.6$ (C), 143.3 (C), 135.9 (C), 134.6 (CH), 132.6 (C), 129.6 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 127.7 (CH), 127.3 (CH), 54.4 (CH₂), 36.6 (CH), 22.8 (CH₃), 18.3 (CH₃) ppm. IR (ATR) $\nu_{\text{max}} = 3028$ (w), 2965 (w), 2926 (m), 2871 (w), 1655 (vs), 1594 (s), 1491 (s), 1394 (s), 1291 (s), 1276 (s), 1089 (s), 967 (m), 806 (m), 776 (m), 700 (s) cm^{-1} . MS (ESI⁺) $m/z = 314$ ([M + H]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NOClNa}$ 336.1131 ([M + Na]⁺), found 336.1122. **67b:** $R_f = 0.10$ (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) $\delta = 7.42$ (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.23–7.19 (m, 4H), 7.16 (d, $J =$



7.5 Hz, 2H), 6.27 (d, J = 15.9 Hz, 1H), 6.13 (dt, J = 15.8, 6.8 Hz, 1H), 3.77–3.72 (m, 2H), 2.20 (q, J = 7.0 Hz, 2H), 1.83 (s, 3H), 1.68 (pent, J = 7.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.3 (C), 143.0 (C), 136.0 (C), 132.3 (C), 130.4 (CH), 129.7 (CH), 129.1 (CH), 128.5 (CH), 128.0 (CH), 127.8 (CH), 127.1 (CH), 48.6 (CH₂), 30.2 (CH₂), 27.3 (CH₂), 22.7 (CH₃) ppm. IR (ATR) ν_{max} = 3026 (w), 2924 (m), 2850 (w), 1652 (vs), 1595 (m), 1491 (s), 1396 (s), 1294 (m), 1089 (m), 967 (m), 775 (m), 700 (vs) cm^{-1} . MS (ESI⁺) m/z = 336 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NOClNa}$ 336.1131 ([M + Na]⁺), found 336.1124.

(E)-N-(4-(4-Fluorophenyl)-2-methylbut-3-en-1-yl)-N-phenylacetamide (68a) and (E)-N-(5-(4-fluorophenyl)pent-4-en-1-yl)-N-phenylacetamide (68b). General procedure C was used to synthesize **68a** and **68b** from *N*-methylaniline (2, 214 mg, 2.0 mmol) and (E)-1-(*para*-fluorophenyl)-1,3-butadiene (**51**, 445 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2 : 1) gave three fractions as oils. Fraction 1 contained pure compound **68a** (100 mg, 0.34 mmol, 18%) and fraction 2 contained a mixture of **68a** and **68b** (151 mg, 0.51 mmol, 25%). Fraction 3 contained pure compound **68b** (62 mg, 0.21 mmol, 10%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 50 : 50. **68a:** R_f = 0.19 (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.31 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.19–7.15 (m, 2H), 7.08 (d, J = 7.4 Hz, 2H), 6.89 (t, J = 8.7 Hz, 2H), 6.25 (d, J = 15.9 Hz, 1H), 5.89 (dd, J = 15.9, 8.5 Hz, 1H), 3.72 (dd, J = 13.4, 8.9 Hz, 1H), 3.63 (dd, J = 13.4, 6.4 Hz, 1H), 2.57–2.49 (m, 1H), 1.73 (s, 3H), 0.99 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.6 (C), 161.9 (d, $^1\text{J}_{\text{C},\text{F}}$ = 246.0 Hz, C), 143.3 (C), 133.6 (CH), 129.5 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 127.5 (d, $^3\text{J}_{\text{C},\text{F}}$ = 7.9 Hz, CH), 115.3 (d, $^2\text{J}_{\text{C},\text{F}}$ = 21.4 Hz, CH), 54.4 (CH₂), 36.5 (CH), 22.8 (CH₃), 18.3 (CH₃) ppm. ^{19}F NMR (500 MHz, CDCl_3) δ = -115.4 ppm. IR (ATR) ν_{max} = 3038 (w), 2967 (w), 2927 (w), 2871 (w), 1655 (vs), 1594 (m), 1507 (m), 1495 (m), 1395 (m), 1293 (m), 1277 (m), 1224 (s), 1158 (m), 967 (m), 849 (m), 813 (m), 772 (m), 700 (s) cm^{-1} . MS (ESI⁺) m/z = 298 ([M + H]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{FNO}$ 298.1607 ([M + H]⁺), found 298.1606. **68b:** R_f = 0.12 (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.34 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.19–7.14 (m, 2H), 7.09 (d, J = 7.9 Hz, 2H), 6.87 (t, J = 8.7 Hz, 2H), 6.21 (d, J = 15.9 Hz, 1H), 5.99 (dt, J = 15.9, 6.9 Hz, 1H), 3.69–3.64 (m, 2H), 2.12 (q, J = 7.4 Hz, 2H), 1.76 (s, 3H), 1.61 (pent, J = 7.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.2 (C), 161.8 (d, $^1\text{J}_{\text{C},\text{F}}$ = 245.7 Hz, C), 143.1 (C), 133.7 (d, $^4\text{J}_{\text{C},\text{F}}$ = 3.3 Hz, C), 129.7 (CH), 129.4 (CH), 129.1 (CH), 128.1 (CH), 127.8 (CH), 127.3 (d, $^3\text{J}_{\text{C},\text{F}}$ = 7.9 Hz, CH), 115.2 (d, $^2\text{J}_{\text{C},\text{F}}$ = 21.4 Hz, CH), 48.6 (CH₂), 30.2 (CH₂), 27.4 (CH₂), 22.8 (CH₃) ppm. ^{19}F NMR (500 MHz, CDCl_3) δ = -115.7 ppm. IR (ATR) ν_{max} = 3038 (w), 2926 (m), 2853 (w), 1652 (vs), 1595 (s), 1506 (s), 1495 (s), 1395 (s), 1224 (s), 967 (m), 838 (m), 770 (m), 700 (vs) cm^{-1} . MS (ESI⁺) m/z = 298 ([M + H]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NOF}$ 298.1607 ([M + H]⁺), found 298.1602.

(E)-N-(2-Methyldec-3-en-1-yl)-N-phenylacetamide (69a) and (E)-N-phenyl-N-(undec-4-en-1-yl)acetamide (69b). General procedure C was used to synthesize **69a** and **69b** from *N*-methyl-

aniline (2, 214 mg, 2.0 mmol) and (E)-1,3-decadiene (**52**, 415 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2 : 1) gave three fractions as oils. Fraction 1 contained compound **69a** and a derivative with isomerized double bond (526 mg, 1.83 mmol, 46%). Fraction 2 contained compound **69a**, its isomerized derivative as well as compound **69b** (143 mg, 0.50 mmol, 12%). Fraction 3 contained compound **69b** (112 mg, 0.39 mmol, 10%) with trace impurities of **69a**. Prior to acetylation and chromatography, the ratio of the branched, the branched isomerized, and the linear product was determined to be 50 : 27 : 23. **69a:** ^1H NMR (500 MHz, CDCl_3) δ = 7.44–7.37 (m, 2H), 7.35–7.29 (m, 1H), 7.16 (d, J = 7.5 Hz, 2H), 5.43–5.33 (m, 1H), 5.26 (dd, J = 15.4, 8.0 Hz, 1H), 3.66 (dd, J = 13.5, 8.4 Hz, 1H), 3.59 (dd, J = 13.3, 6.9 Hz, 1H), 2.33 (hept, J = 7.3 Hz, 1H), 2.95 (q, J = 7.0 Hz, 2H), 1.81 (s, 3H), 1.35–2.26 (m, 8H), 0.95 (d, J = 6.8 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.5 (C), 143.4 (C), 133.2 (CH), 130.7 (CH), 129.5 (CH), 128.2 (CH), 127.6 (CH), 54.4 (CH₂), 35.7 (CH), 32.5 (CH₂), 31.7 (CH₂), 29.5 (CH₂), 28.8 (CH₂), 22.9 (CH₃), 22.6 (CH₂), 14.1 (CH₃) ppm. IR (ATR) ν_{max} = 2957 (m), 2925 (m), 2855 (m), 1661 (vs), 1595 (m), 1495 (m), 1393 (s), 1276 (m), 1217 (w), 1073 (w), 968 (m), 776 (w), 700 (vs). MS (ESI⁺) m/z = 310 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{NONa}$ 310.2147 ([M + Na]⁺), found 310.2145. **69b:** ^1H NMR (500 MHz, CDCl_3) δ = 7.39 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 5.36–5.26 (m, 2H), 3.69–3.64 (m, 2H), 1.95 (q, J = 7.0 Hz, 2H), 1.91 (q, J = 6.2 Hz, 2H), 1.80 (s, 3H), 1.55 (pent, J = 7.5 Hz, 2H), 1.30–1.19 (m, 8H), 0.85 (t, J = 6.7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.1 (C), 143.2 (C), 131.1 (CH), 129.6 (CH), 128.9 (CH), 128.1 (CH), 127.7 (CH), 48.7 (CH₂), 32.5 (CH₂), 31.7 (CH₂), 29.8 (CH₂), 29.4 (CH₂), 28.7 (CH₂), 27.6 (CH₂), 22.8 (CH₃), 22.6 (CH₂), 14.0 (CH₃) ppm. IR (ATR) ν_{max} = 2955 (w), 2924 (m), 2854 (m), 1659 (vs), 1596 (m), 1405 (m), 1394 (s), 1294 (m), 967 (m), 774 (w), 700 (vs). MS (ESI⁺) m/z = 310 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{NONa}$ 310.2147 ([M + Na]⁺), found 310.2143.

(E)-N-(2-Methyl-6-phenylhex-3-en-1-yl)aniline (70a)^{7h} and (E)-N-(7-phenylhept-4-en-1-yl)aniline (70b). General procedure C was used without the acetylation step to synthesize **70a** and **70b** from *N*-methylaniline (2, 214 mg, 2.0 mmol) and (E)-6-phenylhexa-1,3-diene (**53**, 475 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 70 : 1) gave three fractions as oils. Fraction 1 contained compound **70a** and its double bond isomer (E)-N-(2-methyl-6-phenylhex-4-en-1-yl)aniline (301 mg, 1.13 mmol, 57%) in a ratio of 2 : 1 and fraction 2 contained a mixture of **70a** and **70b** (88 mg, 0.33 mmol, 17%). Fraction 3 contained pure compound **70b** (72 mg, 0.27 mmol, 13%). Prior to chromatography, the ratio of the branched (**70a**), the branched isomerized, and the linear product (**70b**) was determined to be 47 : 28 : 25. **70a:** R_f = 0.24 (PE-MTBE, 70 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.31–7.26 (m, 2H), 7.23–7.15 (m, 5H), 6.70 (t, J = 7.3 Hz, 1H), 6.62–6.55 (m, 2H), 5.57–5.50 (m, 1H), 5.30 (dd, J = 15.4, 8.0 Hz, 1H), 3.66 (br. s, 1H), 3.06 (dd, J = 11.9, 5.4 Hz, 1H), 2.84 (dd, J = 11.8, 8.5 Hz, 1H), 2.71 (t, J = 7.5 Hz, 2H), 2.37 (m, 2H), 1.05 (d, J = 6.8 Hz,



3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 148.3 (C), 141.8 (C), 134.3 (CH), 130.3 (CH), 129.2 (CH), 128.5 (CH), 128.3 (CH), 125.8 (CH), 117.1 (CH), 112.9 (CH), 49.6 (CH₂), 36.7 (CH), 35.9 (CH₂), 34.3 (CH₂), 18.1 (CH₃) ppm. **70b**: R_f = 0.23 (PE-MTBE, 70 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.29 (t, J = 7.5 Hz, 2H), 7.23–7.16 (m, 5H), 6.71 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 5.56–5.42 (m, 2H), 3.63 (br. s, 1H), 3.10 (t, J = 7.1 Hz, 2H), 2.73–2.66 (m, 2H), 2.34 (q, J = 7.4 Hz, 2H), 2.11 (q, J = 7.0 Hz, 2H), 1.68 (pent, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 148.4 (C), 142.0 (C), 130.2 (CH), 130.0 (CH), 129.2 (CH), 128.4 (CH), 128.2 (CH), 125.7 (CH), 117.1 (CH), 112.7 (CH), 43.3 (CH₂), 36.0 (CH₂), 34.4 (CH₂), 30.0 (CH₂), 29.2 (CH₂) ppm. IR (ATR) ν_{max} = 3412 (w), 3052 (w), 3024 (w), 2925 (m), 2852 (w), 1602 (vs), 1505 (vs), 1453 (m), 1319 (m), 1257 (m), 1179 (w), 968 (m), 867 (w), 745 (s), 691 (s) cm^{-1} . MS (ESI⁺) m/z = 266 ([M + H]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{24}\text{N}$ 266.1909 ([M + H]⁺), found 266.1901.

(E)-N-(2,3-Dimethyl-4-phenylbut-3-en-1-yl)-N-phenylacetamide (71a) and (E)-N-(4-methyl-5-phenylpent-4-en-1-yl)-N-phenylacetamide (71b). General procedure C was used to synthesize **71a** and **71b** from *N*-methylaniline (2, 214 mg, 2.0 mmol) and (*E*-2-methyl-1-phenyl-1,3-butadiene (**54**, 433 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 2 : 1) gave three fractions as oils. Fraction 1 contained pure compound **71a** (159 mg, 0.54 mmol, 27%) and fraction 2 contained a mixture of **71a** and **71b** (236 mg, 0.81 mmol, 41%). Fraction 3 contained pure compound **71b** (30 mg, 0.10 mmol, 5%). Prior to acetylation and chromatography, the ratio of the branched and the linear product was determined to be 51 : 49. **71a**: R_f = 0.26 (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.40–7.36 (m, 2H), 7.33–7.28 (m, 3H), 7.23–7.16 (m, 5H), 6.30 (s, 1H), 3.87 (dd, J = 13.6, 9.1 Hz, 1H), 3.79 (dd, J = 13.6, 6.1 Hz, 1H), 2.66–2.57 (m, 1H), 1.83 (s, 3H), 1.68 (s, 3H), 1.08 (d, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.3 (C), 143.1 (C), 140.4 (C), 138.0 (C), 129.3 (CH), 128.7 (CH), 128.1 (CH), 127.9 (CH), 127.5 (CH), 126.0 (CH), 125.9 (CH), 52.7 (CH₂), 42.1 (CH), 22.7 (CH₃), 17.1 (CH₃), 13.7 (CH₃) ppm. IR (ATR) ν_{max} = 3057 (w), 3025 (w), 2967 (w), 2933 (w), 2874 (w), 1658 (vs), 1596 (m), 1496 (s), 1395 (s), 1295 (m), 1277 (m), 779 (m), 745 (m), 700 (vs) cm^{-1} . MS (ESI⁺) m/z = 316 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NONa}$ 316.1677 ([M + Na]⁺), found 316.1682. **71b**: R_f = 0.17 (PE-MTBE, 2 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.43 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.21–7.15 (m, 5H), 6.21 (s, 1H), 3.77–3.71 (m, 2H), 2.20–2.14 (m, 2H), 1.85 (s, 3H), 1.80 (d, J = 1.3 Hz, 3H), 1.79–1.73 (m, 2H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.2 (C), 143.2 (C), 138.4 (C), 138.1 (C), 129.7 (CH), 128.8 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 125.8 (CH), 125.2 (CH), 48.9 (CH₂), 37.8 (CH₂), 26.1 (CH₂), 22.8 (CH₃), 17.6 (CH₃) ppm. IR (ATR) ν_{max} = 3057 (w), 3025 (w), 2932 (w), 2859 (w), 1656 (s), 1597 (s), 1496 (s), 1397 (s), 1298 (m), 1076 (w), 743 (m), 700 (vs) cm^{-1} . MS (ESI⁺) m/z = 316 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NONa}$ 316.1677 ([M + Na]⁺), found 316.1682.

N-Phenyl-N-(2-methyldecyl)acetamide (72). Under an inert atmosphere of argon, a flask was charged with a mixture of

69a and the derivative with isomerized double bond (350 mg, 1.22 mmol), Pd/C (17 mg, 5 wt%) and dry methanol (20 mL). Then the argon atmosphere was purged with hydrogen gas and the reaction mixture was stirred for 2 h at room temperature. After the starting materials had been completely consumed (monitored by TLC), the solvent was removed under reduced pressure in the presence of Celite®. After purification by flash column chromatography (SiO_2 , PE-MTBE, 5 : 1), compound **72** (301 mg, 1.04 mmol, 85%) was isolated as a colorless oil. **72**: ^1H NMR (500 MHz, CDCl_3) δ = 7.41 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.16 (d, J = 7.5 Hz, 2H), 3.65 (dd, J = 13.2, 8.2 Hz, 1H), 3.54 (dd, J = 13.4, 6.7 Hz, 1H), 1.83 (s, 3H), 1.60–1.51 (m, 1H), 1.32–1.11 (m, 14 H), 0.89–0.84 (m, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 170.6 (C), 143.4 (C), 129.6 (CH), 128.0 (CH), 127.6 (CH), 54.7 (CH₂), 34.2 (CH₂), 31.9 (CH₂), 31.5 (CH), 29.8 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 26.8 (CH₂), 22.9 (CH₃), 22.6 (CH₂), 17.3 (CH₃), 14.1 (CH₃) ppm. IR (ATR) ν_{max} = 2956 (m), 2924 (s), 2854 (m), 1662 (vs), 1595 (m), 1495 (m), 1455 (m), 1395 (s), 1290 (m), 1276 (m), 776 (w), 700 (s) cm^{-1} . MS (ESI⁺) m/z = 312 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{19}\text{H}_{31}\text{NONa}$ 312.2303 ([M + Na]⁺), found 312.2294.

para-Toluenesulfonamide 76b. General procedure D was used to synthesize **76b** from *N*-methylbenzylamine (38, 242 mg, 2.0 mmol) and (*E*-1-phenyl-1,3-butadiene (**49**, 391 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 12 : 1) gave one fraction (504 mg) as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained a mixture of **76b** (466 mg, 1.15 mmol, 58%) and tosylated *N*-methylbenzylamine (35 mg, 0.13 mmol). Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 7 : 93. **76b**: R_f = 0.25 (PE-MTBE, 12 : 1). ^1H NMR (300 MHz, CDCl_3) δ = 7.62 (d, J = 8.3 Hz, 2H), 7.31–7.16 (m, 12H), 6.27 (d, J = 15.8 Hz, 1H), 6.13 (dt, J = 15.8, 6.4 Hz, 1H), 5.11 (t, J = 7.3 Hz, 1H), 2.62 (s, 3H), 2.37 (s, 3H), 2.18–1.99 (m, 3H), 1.88–1.75 (m, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ = 143.0 (C), 138.0 (C), 137.5 (C), 137.2 (C), 130.7 (CH), 129.5 (CH), 129.1 (CH), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.2 (CH), 127.0 (CH), 125.9 (CH), 59.5 (CH), 30.3 (CH₂), 29.9 (CH₂), 28.8 (CH₃), 21.5 (CH₃) ppm. IR (ATR) ν_{max} = 3062 (w), 3028 (w), 2941 (w), 2872 (w), 1598 (m), 1494 (m), 1452 (m), 1333 (s), 1131 (vs), 1088 (s), 933 (s), 813 (m), 736 (s), 712 (vs) cm^{-1} . MS (ESI⁺) m/z = 428 ([M + Na]⁺). HRMS (ESI⁺) m/z calcd for $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{SNa}$ 428.1660 ([M + Na]⁺), found 428.1666.

para-Toluenesulfonamide 77b. General procedure D was used to synthesize **77b** from *N*-methylbenzylamine (38, 242 mg, 2.0 mmol) and (*E*-1-(*para*-chlorophenyl)-1,3-butadiene (**50**, 494 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 12 : 1) gave one fraction (615 mg) as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained a mixture of **77b** (590 mg, 1.34 mmol, 67%) and tosylated *N*-methylbenzylamine (25 mg, 0.09 mmol). Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 8 : 92. **77b**: R_f = 0.22 (PE-MTBE, 12 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.62 (d, J = 8.4 Hz, 2H), 7.30–7.17 (m, 11H), 6.28 (d, J = 15.8



Hz, 1H), 6.14 (dt, J = 15.8, 6.7 Hz, 1H), 5.13 (t, J = 7.6 Hz, 1H), 2.63 (s, 3H), 2.38 (s, 3H), 2.22–2.03 (m, 3H), 1.90–1.82 (m, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 143.0 (C), 138.0 (C), 137.2 (C), 136.0 (C), 132.5 (C), 129.9 (CH), 129.5 (CH), 129.4 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.1 (CH), 59.4 (CH), 30.2 (CH₂), 29.8 (CH₂), 28.7 (CH₃), 21.4 (CH₃) ppm. IR (ATR) ν_{max} = 3064 (w), 3032 (w), 2939 (w), 1599 (m), 1493 (m), 1455 (m), 1335 (s), 1157 (vs), 1090 (s), 935 (s), 812 (s), 701 (s), 659 (vs) cm^{-1} . MS (ESI+) m/z = 462 ([M + Na]⁺). HRMS (ESI+) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_2\text{SClNa}$ 462.1270 ([M + Na]⁺), found 462.1267.

para-Toluenesulfonamide 78b. General procedure D was used to synthesize **78b** from *N*-methylbenzylamine (**38**, 242 mg, 2.0 mmol) and (*E*)-1-(*para*-fluorophenyl)-1,3-butadiene (**51**, 445 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 12 : 1) gave one fraction (661 mg) as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained a mixture of **78b** (597 mg, 1.41 mmol, 71%) and tosylated *N*-methylbenzylamine (64 mg, 0.23 mmol). Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 9 : 91. **78b**: R_f = 0.24 (PE-MTBE, 12 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.64 (d, J = 8.3 Hz, 2H), 7.33–7.25 (m, 6H), 7.24–7.19 (m, 3H), 6.99 (br. t, J = 8.7 Hz, 2H), 6.30 (d, J = 15.9 Hz, 1H), 6.08 (dt, J = 15.9, 6.8 Hz, 1H), 5.15 (t, J = 7.6 Hz, 1H), 2.65 (s, 3H), 2.40 (s, 3H), 2.23–2.14 (m, 2H), 2.12–2.04 (m, 1H), 1.90–1.83 (m, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 161.9 (d, $^1\text{J}_{\text{C},\text{F}}$ = 245.9 Hz, CF), 143.0 (C), 138.0 (C), 137.2 (C), 133.6 (d, $^4\text{J}_{\text{C},\text{F}}$ = 3.2 Hz, C), 129.4 (CH), 128.4 (CH), 128.0 (CH), 127.3 (d, $^3\text{J}_{\text{C},\text{F}}$ = 7.8 Hz, CH), 127.1 (CH), 115.3 (d, $^2\text{J}_{\text{C},\text{F}}$ = 21.5 Hz, CH), 59.4 (CH), 30.3 (CH₂), 29.8 (CH₂), 28.7 (CH₃), 21.4 (CH₃) ppm. ^{19}F NMR (500 MHz, CDCl_3) δ = -115.5 ppm. IR (ATR) ν_{max} = 3059 (w), 3031 (w), 2948 (w), 2920 (w), 1598 (m), 1508 (m), 1452 (m), 1336 (s), 1228 (m), 1154 (s), 1088 (m), 972 (m), 927 (s), 820 (m), 699 (s), 656 (s) cm^{-1} . MS (ESI+) m/z = 446 ([M + Na]⁺). HRMS (ESI+) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_2\text{SFNa}$ 446.1566 ([M + Na]⁺), found 446.1560.

para-Toluenesulfonamide 79b. General procedure D was used to synthesize **79b** from *N*-methylbenzylamine (**38**, 242 mg, 2.0 mmol) and (*E*)-1-(*para*-methoxyphenyl)-1,3-butadiene (**73**, 481 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 6 : 1) gave one fraction as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained **79b** (524 mg, 1.20 mmol, 60%) and trace amounts of the corresponding branched product. Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 10 : 90. **79b**: R_f = 0.30 (PE-MTBE, 6 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.65 (d, J = 8.3 Hz, 2H), 7.29–7.24 (m, 5H), 7.24–7.21 (m, 4H), 6.85 (d, J = 8.7 Hz, 2H), 6.27 (d, J = 15.9 Hz, 1H), 6.02 (dt, J = 15.8, 6.6 Hz, 1H), 5.14 (t, J = 7.4 Hz, 1H), 3.81 (s, 3H), 2.65 (s, 3H), 2.40 (s, 3H), 2.22–2.04 (m, 3H), 1.87–1.79 (m, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 158.8 (C), 143.0 (C), 138.1 (C), 137.3 (C), 130.3 (C), 130.1 (CH), 129.4 (CH), 128.4 (CH), 128.0 (CH), 127.7 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 59.5 (CH), 55.3 (CH₃), 30.4 (CH₂), 29.9 (CH₂), 28.8 (CH₃), 21.5 (CH₃) ppm. IR (ATR) ν_{max} =

3062 (w), 3032 (w), 2956 (w), 2923 (m), 2853 (m), 1608 (m), 1512 (s), 1457 (m), 1335 (m), 1248 (s), 1156 (vs), 1089 (m), 1033 (m), 934 (m), 809 (s), 701 (s), 660 (vs) cm^{-1} . MS (ESI+) m/z = 458 ([M + Na]⁺). HRMS (ESI+) m/z calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3\text{SNa}$ 458.1766 ([M + Na]⁺), found 458.1758.

para-Toluenesulfonamide 80b. General procedure D was used to synthesize **80b** from *N*-methylbenzylamine (**38**, 242 mg, 2.0 mmol) and (*E*)-1-(*ortho*-methylphenyl)-1,3-butadiene (**74**, 433 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 9 : 1) gave one fraction (605 mg) as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained a mixture of **80b** (575 mg, 1.37 mmol, 69%), tosylated *N*-methylbenzylamine (30 mg, 0.11 mmol), and trace amounts of the corresponding branched product. Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 13 : 87. **80b**: R_f = 0.18 (PE-MTBE, 9 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.65 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 6.6 Hz, 1H), 7.30–7.26 (m 3H), 7.25–7.20 (m, 4H), 7.19–7.12 (m, 3H), 6.53 (d, J = 15.9 Hz, 1H), 6.01 (dt, J = 15.8, 6.8 Hz, 1H), 5.16 (t, J = 7.5 Hz, 1H), 2.67 (s, 3H), 2.40 (s, 3H), 2.32 (s, 2H), 2.29–2.08 (m, 3H), 1.90–1.80 (m, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 143.0 (C), 138.0 (C), 137.3 (C), 136.6 (C), 135.0 (C), 130.5 (CH), 130.1 (CH), 129.4 (CH), 128.7 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.2 (CH), 127.0 (CH), 126.0 (CH), 125.4 (CH), 59.4 (CH), 30.3 (CH₂), 30.2 (CH₂), 28.8 (CH₃), 21.5 (CH₃), 19.8 (CH₃) ppm. IR (ATR) ν_{max} = 3064 (w), 3031 (w), 2928 (w), 2868 (w), 1600 (w), 1496 (w), 1456 (m), 1336 (s), 1157 (vs), 1090 (m), 936 (s), 815 (m), 736 (s), 701 (vs), 660 (vs) cm^{-1} . MS (ESI+) m/z = 442 ([M + Na]⁺). HRMS (ESI+) m/z calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_2\text{SNa}$ 442.1817 ([M + Na]⁺), found 442.1814.

para-Toluenesulfonamide 81b. General procedure D was used to synthesize **81b** from *N*-methylbenzylamine (**38**, 242 mg, 2.0 mmol) and (*E*)-1-(*ortho*-methoxyphenyl)-1,3-butadiene (**75**, 481 mg, 3.0 mmol). Purification by flash column chromatography (PE-MTBE, 1 : 1) gave one fraction as an oil of high viscosity. According to ^1H NMR spectroscopy, the fraction contained **81b** (574 mg, 1.32 mmol, 66%) and trace amounts of the corresponding branched product. Prior to tosylation and chromatography, the ratio of the branched and the linear product was determined to be 11 : 89. **81b**: R_f = 0.44 (PE-MTBE, 9 : 1). ^1H NMR (500 MHz, CDCl_3) δ = 7.63 (d, J = 8.3 Hz, 2H), 7.36 (dd, J = 7.6, 1.4 Hz, 1H), 7.28–7.15 (m, 8H), 6.89 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 8.2, 1H), 6.62 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 15.9, 6.7 Hz, 1H), 5.13 (t, J = 7.4 Hz, 1H), 3.82 (s, 3H), 2.63 (s, 3H), 2.37 (s, 3H), 2.20–2.03 (m, 3H), 1.85–1.76 (m, 1H) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ = 156.3 (C), 142.9 (C), 138.2 (C), 137.3 (C), 129.9 (CH), 129.5 (CH), 128.4 (CH), 128.1 (CH), 127.7 (CH), 127.2 (CH), 126.5 (C), 126.5 (CH), 125.4 (CH), 120.6 (CH), 110.8 (CH), 59.6 (CH), 55.4 (CH₃), 30.4 (CH₂), 28.8 (CH₃), 21.5 (CH₃) ppm. IR (ATR) ν_{max} = 3063 (w), 3031 (w), 2924 (w), 2851 (w), 1597 (m), 1489 (m), 1455 (m), 1333 (s), 1242 (s), 1155 (vs), 1088 (m), 1027 (m), 933 (s), 813 (m), 751 (s), 700 (vs), 658 (vs) cm^{-1} . MS (ESI+) m/z = 458 ([M + Na]⁺). HRMS (ESI+) m/z calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3\text{SNa}$ 458.1766 ([M + Na]⁺), found 458.1778.



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Notes and references

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