Synthesis S. E. Denmark, H. M. Chi PSP

Synthesis of 2-Alkenyl-Tethered Anilines

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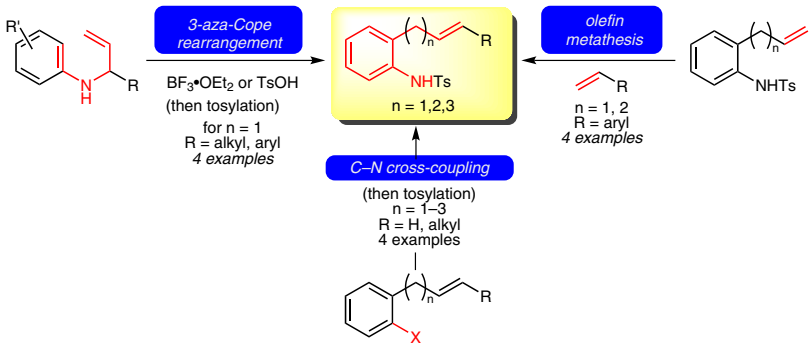

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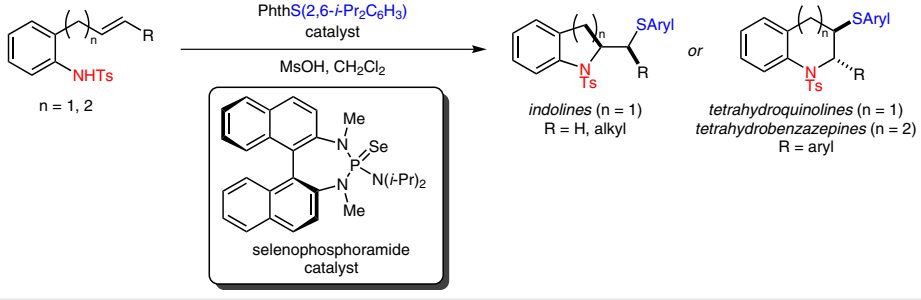
Abstract Three general routes for the synthesis of (*E*)-2-alkenyl-tethered anilines have been developed. The first route involves a 3-aza-Cope rearrangement of *N*-allylic anilines in the presence of a Lewis acid. The requisite *N*-allylic anilines were prepared by the addition of vinylmagnesium reagents to the corresponding aldimines. The second route details a direct cross-metathesis of 2-allylic or 2-homoallylic anilines with styrenes. The third route involves a palladium-catalyzed C–N cross-coupling of aryl halides. Taken together, these three strategies allowed access to the requisite aniline substrates with pendant alkenes at the 2-position with excellent *trans* selectivities.

Key words 2-alkenylanilines, 3-aza-Cope rearrangement, olefin metathesis, C–N cross-coupling, *trans* olefins

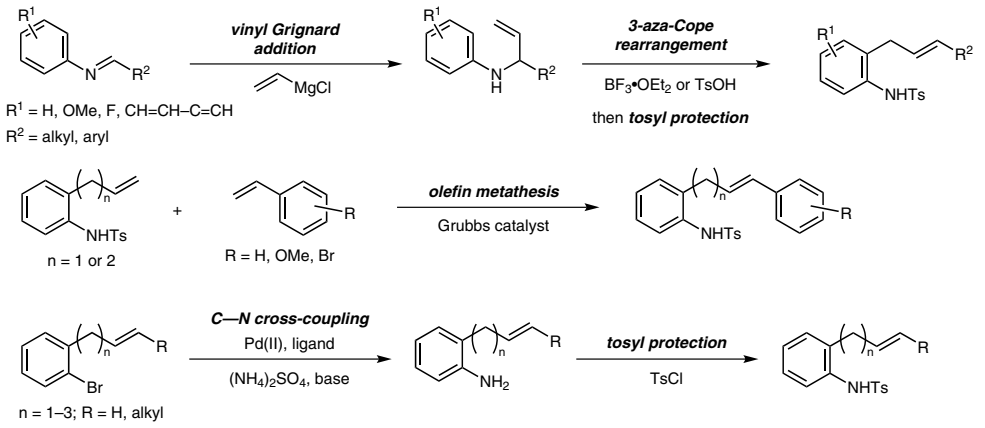
Recent studies in these laboratories have described the catalytic, enantioselective, intramolecular sulfenoamination of 2-alkenyl-tethered anilines[1] as a general method to access enantioenriched *N*-containing heterocycles (Scheme 1), such as indolines, tetrahydroquinolines, and tetrahydrobenzazepines, which represent important classes of compounds exhibiting a range of biological activities.[2]

In the course of the reaction development, *N*-tosyl-protected anilines with pendant olefins at the 2-position were identified as viable substrates for the sulfenoamination process. Specifically, these reactions were found to be highly enantioselective and site-selective with *E*-disubstituted and terminal alkenes.[1] Therefore, a rapid and versatile protocol for the preparation of these 2-alkenyl-substituted anilines was necessary. As no single method could provide all of the different substitution patterns and tether lengths, developing a number of different methods to arrive at the substrates was necessary. Specifically, three different routes were developed that control the geometry of the double bond in the tether and the introduction of the amino group by rather different means, namely: (1) vinylmagnesium chloride addition to imines followed by 3-aza-Cope rearrangement of the resulting *N*-allylic anilines, (2) cross-metathesis of 2-substituted anilines bearing a terminal alkene, and (3) palladium-catalyzed C–N coupling of 2-substituted halobenzenes (Scheme 2).

Through application of these three strategies, twelve 2-alkenylaniline compounds **1a–l** were prepared as substrates for the sulfenoamination reaction (Figure 1). 2-Allylic anilines **1a–d** were synthesized by the addition of vinylmagne-

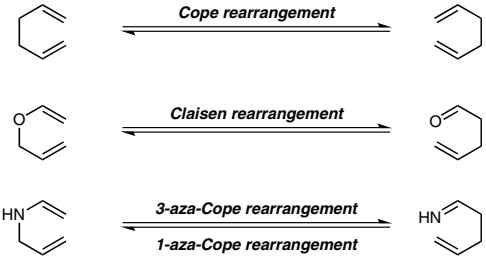


Scheme 1



Scheme 2

sium chloride followed by a tandem 3-aza-Cope rearrangement. While the preparations of **1e–g** were also viable through the first route, those compounds are also accessible by a more direct olefin cross-metathesis reaction that requires only a single step. 2-Homoallylic aniline **1h** was also prepared via the second route, showing its ability to derivatize alkenylanilines with longer chains. Compounds **1i–l** were made by C–N cross-coupling to demonstrate its complementary ability to access dialkyl-substituted alkene substrates with different tether lengths.



Scheme 3

3-Aza-Cope Rearrangement

The aza-Cope rearrangement is a heteroatom variant of the Cope rearrangement, replacing a carbon with a nitrogen atom in one of the allyl components (Scheme 3).[3] This reaction is often referred to as an amino-Claisen or an aza-Claisen rearrangement because of its structural similarity to the Claisen rearrangement.

The 3-aza-Cope rearrangement reactions have received less attention than Cope or Claisen rearrangements owing to the higher reaction temperatures needed, which inevitably leads to the formation of side products by thermal decomposition.[3] Much effort has been invested to lower the activation barrier for the rearrangement by employing Brønsted or Lewis acids.[4] Ward and co-workers were able to promote the rearrangement of 1,1-disubstituted *N*-allylic anilines at significantly reduced temperature (65 °C) through the addition of a catalytic amount of toluenesulfonic acid (Scheme 4).[4a]

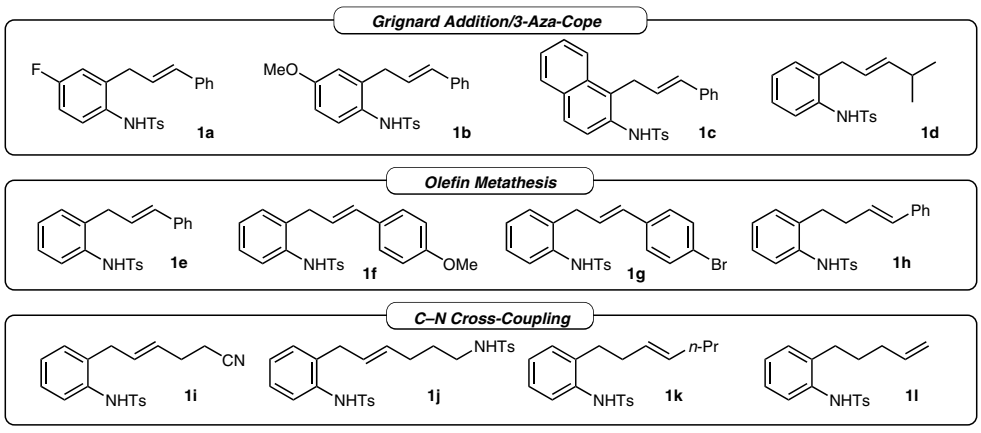
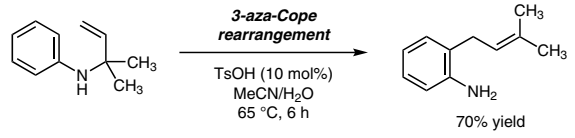


Figure 1 Three approaches for the preparation of 2-alkenylanilines

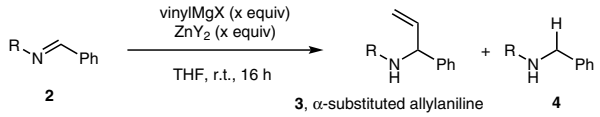


Scheme 4

In our case, the 2-cinnamylanilines **5** were synthesized by 3-aza-Cope rearrangement of α-substituted allylic anilines **3**, which were prepared by the addition of vinylmagnesium chloride to the corresponding imines **2**. This [3,3]-sigmatropic rearrangement was especially attractive due to its inherent high stereospecificity, furnishing *trans*-alkenes exclusively. This three-step sequence (imine formation/Grignard addition/rearrangement) was very effective for the synthesis of 2-cinnamylaniline derivatives.

The imines **2** were prepared by a straightforward condensation of the appropriate anilines and aldehydes,[5] which was followed by a subsequent addition of vinylmagnesium chloride in the presence of zinc chloride to afford α-substituted allylic anilines **3** (Table 1).[6] Initially, vinylmagnesium bromide was tested with zinc bromide as an additive, but no product formation was observed (entry 1). Interestingly, a slight excess (1.3 equiv) of the vinylmagnesium chloride was insufficient and resulted in production of only reduction product **4a** (entry 2).[6] However, successful addition of the vinyl moiety to the aldimines **2** was observed with 2 equivalents of the Grignard reagent (entries 3–5).

Table 1 Addition of Vinylmagnesium Reagents to Aldimines **2**

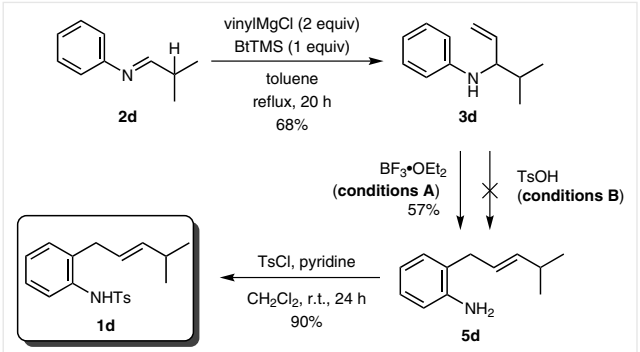


Entry	R	VinylMgX (equiv)	ZnY_2 (equiv)	Yield (%)[a]	
				3	**4**
1	4-FC_6H_4	X = Br (1.3)	Y = Br (0.1)	–	–
2	4-FC_6H_4	X = Cl (1.3)	Y = Cl (0.1)	–	**4a**, 79
3	4-FC_6H_4	X = Cl (2.0)	Y = Cl (0.2)	**3a**, 83	–
4	4-$MeOC_6H_4$	X = Cl (2.0)	Y = Cl (0.2)	**3b**, 82	–
5	2-naphthyl	X = Cl (2.0)	Y = Cl (0.2)	**3c**, 95	–

[a] Yield of isolated, purified products.

α-Substituted allylic anilines **3** were then subjected to aza-Cope rearrangement conditions (Table 2). When α-aryl-substituted allylic aniline **3a** was treated with boron trifluoride–diethyl ether complex, it rearranged to afford the desired *trans*-alkene **5a** upon heating (Conditions A, entry 1).[7] However, because of the unsatisfying yield of the rearrangement with generation of many side products, a simplified reaction protocol was employed. *p*-Toluenesulfonic acid catalyzed the 3-aza-Cope rearrangement of α-aryl-substituted allylic aniline **3a** under much milder reaction conditions (Conditions B, entry 2).[4a] Other allylic anilines **3b** and **3c** also successfully rearranged to **5b** and **5c**, respectively (entries 3 and 4). Protection of the resulting primary aniline with tosyl chloride afforded the desired substrates **1a**, **1b**, and **1c**.

A similar strategy was employed for the construction of the isopropyl-substituted allylic aniline (Scheme 5). Aniline and isobutyraldehyde were first condensed to afford aldimine **2d**, which was subsequently treated with vinylmagnesium chloride and 1-(trimethylsilyl)benzotriazole using Katritzky's 1,2-addition protocol for imines bearing acidic α-protons.[8] The resulting α-substituted allylic aniline **3d** was then treated with boron trifluoride–diethyl ether complex to generate the expected primary aniline **5d**, which was subsequently protected with tosyl chloride to furnish tosylamide **1d**. Interestingly, in this case *p*-toluenesulfonic acid failed to promote the rearrangement.



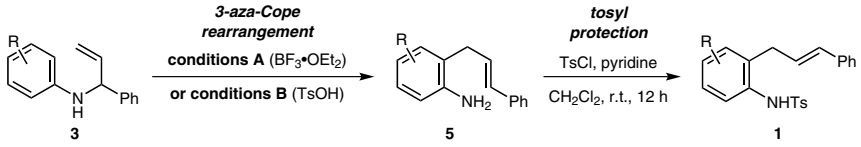
Scheme 5

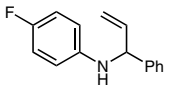
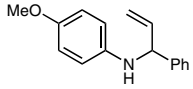
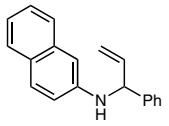
Olefin Cross-Metathesis

Olefin cross-metathesis is arguably one of the most powerful methods of olefin synthesis in modern organic chemistry.[9] This process redistributes the double bonds of olefins allowing the formation of more highly functionalized olefins from simple alkene precursors. Pronounced functional group compatibility and mild reaction conditions render these reactions highly valuable and contribute to their wide application in many fields including polymer chemistry and natural product synthesis.[10]

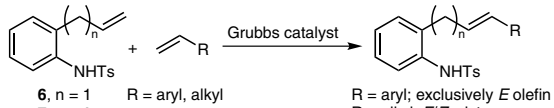
Cross-metathesis of precursors bearing terminal alkenes was attempted to access disubstituted substrates, which would allow a one-step synthesis of diverse alkene substitution patterns and tether lengths. *N*-Tosyl-2-(2-propenyl)aniline (**6**)[11] and *N*-tosyl-2-(3-butenyl)aniline (**7**)[12] were combined with several terminal olefins in the presence of a number of different ruthenium catalysts (Scheme 6). Although styrenyl products were formed with high *E*-selectivity, dialkyl-substituted products were formed as mixtures of geometrical isomers.

Table 2 Preparation of 2-Alkenylanilines by 3-Aza-Cope Rearrangement



Entry	Substrate		Conditions[a]	Yield (%)[b]	Yield (%)[b]
1 2		**3a**	A B	**5a**, 45 **5a**, 71	**1a**, 86
3		**3b**	B	**5b**, 81	**1b**, 83
4		**3c**	B	**5c**, 81	**1c**, 83

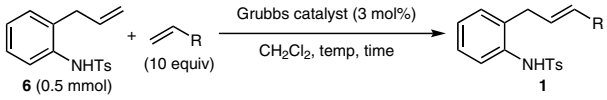
[a] Reaction conditions A: BF_3·OEt_2 (1.2 equiv), xylenes (0.5 M), 180 °C, 17 h; Reaction conditions B: TsOH (0.2 equiv), MeCN/H_2O (10:1, 0.1 M), 65 °C, 6–36 h.
[b] Yield of isolated, purified products.



Scheme 6

Next, the Grubbs–Hoveyda 2nd generation catalyst was examined for an initial survey of cross-metathesis, but a rapid homodimerization of styrenes was observed with no desired product (Table 3, entry 1). In contrast, Grubbs 1st generation indenylidene catalyst showed strong cross-metathesis by affording *trans*-olefin **1e** with excellent geometrical selectivity (entry 2). Despite the excess amount of styrene added, substrate olefin **6** still remained after 18 hours. Extended reaction times showed a slight increase in yield (entry 3). Whereas metathesis with styrene afforded *trans*-olefin exclusively, metathesis with 1-pentene gave approximately a 2:1 mixture of *trans*- and *cis*-disubstituted olefins (entry 4). Neohexene, which has significant steric bulk adjacent to the olefin, was stable under the metathesis conditions (entry 5). Interestingly, the reaction with 4-pentenenitrile failed to give any products (entry 6). This reaction was repeated with the more reactive Grubbs–Hoveyda 2nd generation catalyst to promote metathesis, and higher temperature was needed to initiate the reaction (entry 7). However, a complex mixture of *E*- and *Z*-olefins was obtained along with some olefin isomerization products.

Table 3 Optimization of Olefin Cross-Metathesis Conditions



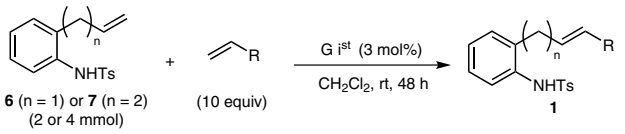
Entry	R	Catalyst[a]	Temp, time	Yield (%)[b]	*trans*/*cis*[c]
1	Ph	G–H 2nd	reflux, 12 h	–	–
2	Ph	G 1st	r.t., 18 h	**1e**, 43	>20:1
3	Ph	G 1st	r.t., 48 h	**1e**, 58	>20:1
4	*n*-Pr	G 1st	r.t., 18 h	**1m**, 62	2:1
5	*t*-Bu	G 1st	r.t., 18 h	–	–
6	$(CH_2)_2CN$	G 1st	r.t., 18 h	–	–
7	$(CH_2)_2CN$	G–H 2nd	reflux, 18 h	–[d]	–

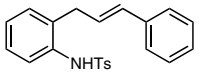
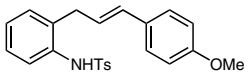
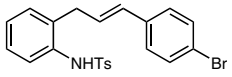
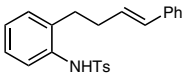
[a] G 1st: Grubbs 1st generation indenylidene catalyst; G–H 2nd: Grubbs–Hoveyda 2nd generation catalyst.
[b] Isolated yield.
[c] The *trans*/*cis* ratios were determined by ^{1}H NMR spectroscopy of the crude mixtures.
[d] A complex mixture was obtained.

Encouraged by the positive screening result with styrene, the reaction was repeated on a gram scale which afforded the desired 2-cinnamyl-*N*-tosylaniline (**1e**) with the expected *trans* selectivity (Table 4, entry 1). In a similar manner, other styrenes were also examined. Metathesis with 4-vinylanisole and 4-bromostyrene produced the 2-cinnamylaniline derivatives **1f** and **1g**, respectively, in excellent selectivities (entries 2 and 3). Since these aniline

compounds **1f**, **1g** can also be accessed through the aza-Cope rearrangement route, cross-metathesis of 2-homoallylaniline **7** was performed to demonstrate the advantage of this strategy (entry 4). Gratifyingly, the cross-metathesis of olefin **7** and styrene furnished longer-tethered compound **1h** in good yield with exclusive *trans* selectivity.

Table 4 Preparation of Substrates **1e–h** by Cross-Metathesis



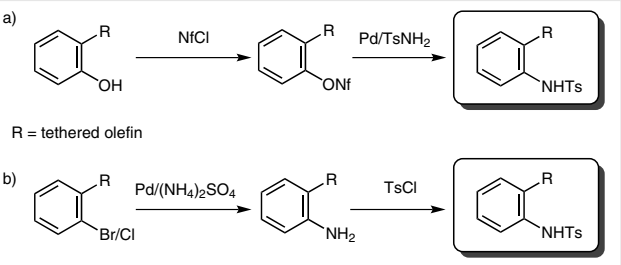
Entry	Substrate	Product		Yield (%)[a]	*trans*/*cis*[b]
1	**6** R = Ph		**1e**	47	>20:1
2	**6** R = 4-MeOC$_6$H$_4$		**1f**	54	>20:1
3	**6** R = 4-BrC$_6$H$_4$		**1g**	50	>20:1
4	**7** R = Ph		**1h**	49	>20:1

[a] Isolated yield.
[b] The *trans*/*cis* ratios were determined by ^{1}H NMR spectroscopy of the crude mixtures.

Palladium-Catalyzed Amination

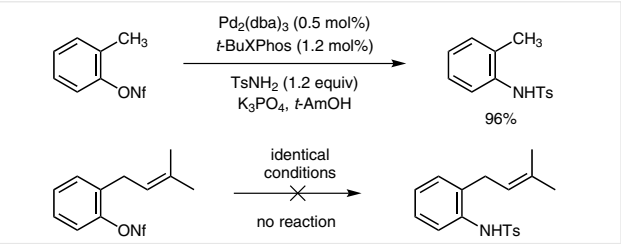
Although the aza-Cope rearrangement approach was successful for the preparation of aliphatic alkene tethers, the scope is limited to one-methylene-tethered substrates. For longer tethers, olefin metathesis is suitable for styrenes, but aliphatic alkenes were formed in poor geometrical selectivity. Accordingly, a different route was needed for the aliphatic substituents.

The synthesis of aniline derivatives has been tremendously facilitated by advances in transition-metal-catalyzed coupling of aryl halides with various nitrogen sources. The palladium-catalyzed C–N cross-coupling strategy was additionally appealing because the requisite, 2-substituted phenols were readily available with high geometrical purity.[13] The phenols could then be converted into anilines in two simple steps by either a direct installation of the tosylamide or by an amination followed by a tosyl protection (Scheme 7).[14]



Scheme 7

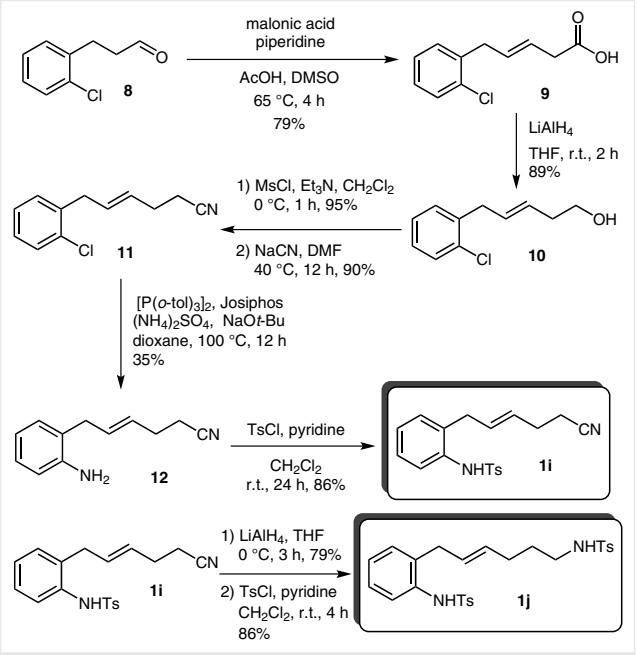
Between these two routes, the palladium-catalyzed C–N coupling of aryl nonaflates with tosylamide appeared more attractive because the starting phenols are readily available (Scheme 7, a).[14a] However, whereas the nonaflate derived from *o*-cresol could be converted into the tosylaniline in excellent yield, this approach failed to afford any product for substrates bearing an *ortho*-tethered olefin (Scheme 8). This failure suggested a possible inhibition through binding of the palladium catalyst by the alkene.



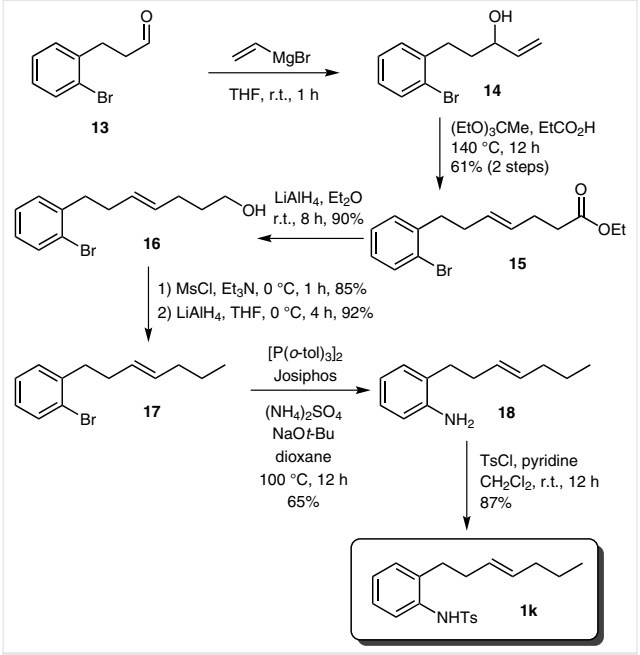
Scheme 8

In the alternative route, aryl halides are cross-coupled with ammonium sulfate under palladium catalysis to generate *N*-unsubstituted anilines, which can be subsequently tosylated (Scheme 7, b).[14b] This strategy was suitable for the synthesis of two- and three-methylene-tethered substrates.

The configuration of the double bond in the 2-substituted haloarene was established with a Knoevenagel–Doebner condensation of malonic acid with 3-(2-chlorophenyl)propanal (**8**) to afford the nonconjugated carboxylic acid **9** (Scheme 9).[15] Then, reduction of **9** to primary alcohol **10**,[15a] followed by mesylation and displacement with cyanide, furnished nitrile intermediate **11** for the aryl amination. Aryl chloride **11** was coupled with ammonium sulfate to form aniline **12** following the palladium-catalyzed C–N coupling developed by Hartwig and co-workers.[14b] The desired product was generated in modest yield along with isomerized side products. Tosylation of **12** afforded nitrile **1i** which was reduced with $LiAlH_4$ to the free amine. Subsequent tosyl protection of the amine furnished bistosylamide **1j**.



Scheme 9

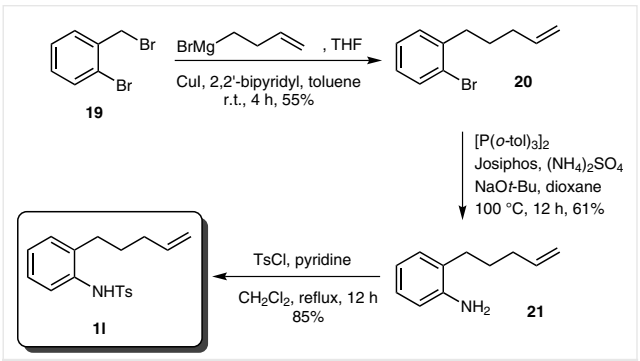


Scheme 10

As was observed previously with the shorter tether, synthesis of the alkyl-substituted olefin side chain by cross-metathesis was only modestly *trans*-selective. A more selective synthesis of the *trans*-dialkyl-substituted alkene with a two-methylene tether entailed a Johnson orthoester Claisen rearrangement to set the configuration of the double bond in **1k** (Scheme 10). Synthesis of the aniline substrate **1k** was accomplished in a few steps from the alcohol intermediate **16**, which was prepared by following a reported protocol by Wolfe and co-workers.[16] Addition of vinylmagnesium bromide to aldehyde **13** afforded allylic alcohol **14**, which was followed by heating with triethyl orthoacetate in the presence of a catalytic amount of acid to promote a [3,3]-sigmatropic rearrangement.[16] Reduction of the resulting ester **15** to alcohol **16**,[16] followed by a two-step sequence of mesylation and hydride reduction, afforded the aryl bromide **17**.[17] The aryl bromide **17** was then subjected to Hartwig's C–N coupling method.[14b] Gratifyingly, in contrast to the one-methylene-tethered system, the reaction proceeded cleanly with no olefin migration observed. Tosyl protection of the resulting primary aniline **18** furnished the target substrate **1k**.

Encouraged by the satisfying results, the palladium-catalyzed C–N coupling method was then applied to the preparation of even-longer-tethered substrates. 2-(4-Pentenyl)aniline was prepared from 2-bromobenzyl bromide (**19**) by initial addition of 3-butenylmagnesium bromide with catalytic assistance of copper(I) iodide to afford the 2-pentenylaryl bromide **20** (Scheme 11).[18] Hartwig's C–N coupling method was then employed to install the amine moiety,[14b] and the resulting primary aniline **21** was protected with a tosyl group to furnish the target sulfonamide **1l**.

In conclusion, three routes to accomplish the *trans*-selective preparation of 2-olefin-tethered anilines have been developed. The first method combines $ZnCl_2$-assisted Grignard addition to aldimines with 3-aza-Cope rearrangement to access single-methylene-tethered 2-olefinic anilines with high efficiency. The second method is a more direct olefin cross-metathesis approach, which is especially effective for styrenyl substrates. The third method involves a C–N cross-coupling reaction that is complementary to the other methods, and allows access to dialkyl olefinic anilines containing longer tethers. These *N*-tosylanilines are suitable substrates for general electrophilic addition reactions,



Scheme 11

specifically designed for the enantioselective, catalytic sulfenoamination reaction that has been recently developed.

All reactions were performed in oven-dried (140 °C) and/or flame-dried glassware under an atmosphere of dry argon, unless otherwise noted. Column chromatography was performed using Merck silica gel 60 (40–63 μm particle size) purchased from Aldrich. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. R_f values reported were measured using 10 × 2 cm TLC plates in a developing chamber containing the solvent system described. Visualization was accomplished with UV light (254 nm) and/or $KMnO_4$. Boiling points for Kugelrohr distillations correspond to corrected air bath temperatures. Melting points were determined in sealed tubes under vacuum on a Thomas Hoover capillary melting point apparatus, and are corrected. IR spectra were recorded on a Perkin-Elmer FT-IR system. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on an Inova spectrometer (500 MHz, ^1H; 126 MHz, ^{13}C; 470 MHz, ^{19}F). ^1H and ^{13}C NMR spectra were acquired in $CDCl_3$ referenced to residual $CHCl_3$ at 7.26 and 77.00 ppm, respectively. Assignments were obtained by reference to COSY, HSQC, and HMBC correlations; atom numbering is shown in the Supporting Information. Mass spectrometry was performed by the University of Illinois Mass Spectrometry Center. ESI mass spectra were performed on a Waters or Micromass Q-Tof Ultima instrument. EI mass spectra were performed on a 70-VSE instrument. Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory and Robertson Microlit Laboratories, Inc.

Reaction solvents THF (Fisher, HPLC grade), Et_2O (Fisher, BHT-stabilized ACS grade), and CH_2Cl_2 (Fisher, unstabilized HPLC grade) were dried by passage through two columns of neutral alumina in a solvent dispensing system. Reaction solvent toluene (Fischer, ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Reaction solvent DMF (Fisher, HPLC grade) was dried by percolation through a column packed with molecular sieves in a solvent dispensing system. Solvents for chromatography, filtration, and recrystallization [CH_2Cl_2 (Aldrich, ACS grade), EtOAc (Fisher, ACS grade), Et_2O (Fisher, ACS grade), hexanes (Fisher, Optima)] were used as received. Et_3N (Alfa Aesar) and pyridine (Fisher) were freshly distilled from CaH_2. 'Brine' refers to a saturated aqueous solution of sodium chloride.

Addition of Grignard Reagent to Aldimines (Table 1)

4-Fluoro-*N*-(1-phenylallyl)aniline (3a)[6]

To a flame-dried, 50-mL Schlenk flask was added a solution of vinylmagnesium chloride in THF (18.8 mL, 1.6 M, 30 mmol, 2 equiv) and a solution of $ZnCl_2$ in THF (3 mL, 1.0 M, 3 mmol, 0.2 equiv). After the solution was stirred for 20 min at r.t., imine **2a**[5a] (2.99 g, 15 mmol) was added under positive argon pressure. The solution was stirred at r.t. for 16 h. The reaction was quenched with sat. aqueous NH_4Cl solution (30 mL) and extracted with EtOAc (3 × 40 mL). The organic layers were combined, washed with brine (30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford 3.05 g of a dark brown oil. Purification by silica gel flash chromatography (16 × 5 cm; 800 mL of 93:5:2 hexane/EtOAc/Et_3N, 200 mL of 90:10 hexane/EtOAc, 200 mL of 85:15 hexane/EtOAc, 200 mL of 80:20 hexane/EtOAc) afforded 2.84 g (83%) of **3a** as a brown liquid; R_f = 0.54 (hexanes/EtOAc, 9:1) [UV]. The spectroscopic data matched those reported previously.[19]

IR (neat): 3413 (w), 3029 (w), 1612 (w), 1506 (s), 1452 (m), 1401 (w), 1312 (m), 1217 (s), 1156 (m), 1139 (w), 1108 (w), 1066 (w), 1028 (w), 991 (w), 817 (s), 779 (m), 748 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.38 (m, 4 H, HC(10,11)), 7.34 (tt, *J* = 6.5, 1.5 Hz, 1 H, HC(12)), 6.93–6.87 (m, 2 H, HC(7)), 6.61–6.55 (m, 2 H, HC(6)), 6.09 (ddd, *J* = 16.5, 10.0, 6.0 Hz, 1 H, HC(4)), 5.37–5.26 (m, 2 H, HC(5)), 4.93 (d, *J* = 6.0 Hz, 1 H, HC(3)), 3.99 (s, 1 H, HN(2)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.8 (d, *J* = 235.2 Hz, C8), 143.5 (C1), 141.7 (C9), 139.0 (C4), 128.7 (C10), 127.5 (C12), 127.0 (C11), 116.1 (C5), 115.5 (C7), 114.4 (C6), 61.5 (C3).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –128.2.

MS (ESI): *m*/*z* (%) = 117 (27), 145 (24), 183 (16), 200 (18), 228 (12) [M + H]$^+$, 280 (15), 290 (100), 291 (32), 317 (24), 342 (15), 370 (21), 404 (19).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}FN$: 228.1189; found: 228.1197.

4-Methoxy-*N*-(1-phenylallyl)aniline (3b)[6]

To a flame-dried, 100-mL Schlenk flask was added a solution of vinylmagnesium chloride in THF (18.8 mL, 1.6 M, 30 mmol, 2 equiv) and a solution of $ZnCl_2$ in THF (3 mL, 1.0 M, 3 mmol, 0.2 equiv). After the solution was stirred for 20 min at r.t., imine **2b**[5b] (3.17 g, 15 mmol) was added under positive argon pressure. The solution was stirred at r.t. for 16 h. The reaction was quenched with sat. aqueous NH_4Cl solution (30 mL) and extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with brine (30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a dark brown oil. Purification by silica gel flash chromatography (18 × 5 cm; 1000 mL of 93:5:2 hexane/EtOAc/Et_3N, 500 mL of 95:5 hexane/EtOAc, 300 mL of 93:7 hexane/EtOAc, 300 mL of 90:10 hexane/EtOAc) afforded 2.93 g (82%) of **3b** as a brown liquid; R_f = 0.44 (hexanes/EtOAc, 4:1) [UV]. The spectroscopic data matched those reported previously.[19]

IR (neat): 3394 (w), 3027 (w), 2831 (w), 1617 (w), 1508 (s), 1463 (m), 1451 (m), 1442 (w), 1406 (w), 1308 (w), 1290 (w), 1240 (s), 1229 (s), 1178 (m), 1156 (w), 1139 (w), 1114 (w), 1094 (w), 1034 (m), 991 (w), 923 (m), 817 (s), 764 (m), 746 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 4 H, HC(10,11), 7.31–7.24 (m, 1 H, HC(12)), 6.78–6.72 (m, 2 H, HC(7)), 6.61–6.54 (m, 2 H, HC(6)), 6.04 (ddd, *J* = 17.2, 10.2, 6.0 Hz, 1 H, HC(4)), 5.32–5.19 (m, 2 H, HC(5)), 4.87 (d, *J* = 6.1 Hz, 1 H, HC(3)), 3.82 (s, 1 H, HN(2)), 3.73 (s, 3 H, HC(13)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 152.4 (C8), 142.3 (C9), 141.7 (C1), 139.7 (C4), 128.9 (C11), 127.6 (C12), 127.4 (C10), 116.1 (C6), 115.1 (C5), 114.9 (C7), 61.0 (C3), 55.9 (C13).

MS (ESI): *m*/*z* (%) = 117 (33), 217 (25), 240 (75) [M + H]$^+$, 241 (13), 262 (22), 270 (21), 328 (100), 329 (29), 371 (96), 372 (31), 479 (23).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}NO$: 240.1388; found: 240.1393.

N-(1-Phenylallyl)naphthalen-2-amine (3c)[6]

To a flame-dried, 50-mL Schlenk flask was added a solution of vinylmagnesium chloride in THF (18.8 mL, 1.6 M, 30 mmol, 2 equiv) and a solution of $ZnCl_2$ in THF (3 mL, 1.0 M, 3 mmol, 0.2 equiv). After the solution was stirred for 20 min at r.t., imine **2c**[5c] (3.47 g, 15 mmol) was added under positive argon pressure. The solution was stirred at r.t. for 16 h. The reaction was quenched with sat. aqueous NH_4Cl solution (30 mL) and extracted with EtOAc (3 × 40 mL). The organic layers were combined, washed with brine (30 mL), dried over $MgSO_4$, and

filtered. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford 3.05 g of a dark brown oil. Purification by silica gel flash chromatography (16 × 5 cm; 800 mL of 93:5:2 hexane/EtOAc/Et_3N, 200 mL of 90:10 hexane/EtOAc, 200 mL of 85:15 hexane/EtOAc, 200 mL of 80:20 hexane/EtOAc) afforded 3.70 g (95%) of **3c** as a brown liquid; R_f = 0.35 (hexanes/EtOAc, 4:1) [UV]. The spectroscopic data matched those reported previously.[20]

IR (neat): 3409 (w), 3056 (w), 3026 (w), 2847 (w), 1627 (s), 1601 (m), 1519 (s), 1478 (m), 1451 (m), 1424 (w), 1396 (m), 1358 (m), 1301 (w), 1265 (w), 1223 (m), 1188 (m), 1157 (w), 1145 (w), 1125 (w), 1094 (w), 1066 (w), 1028 (w), 1018 (w), 990 (w), 967 (w), 954 (w), 924 (m), 909 (m), 865 (w), 827 (s), 806 (s), 743 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.1 Hz, 1 H, HC(11)), 7.62 (d, *J* = 8.8 Hz, 1 H, HC(13)), 7.54 (dd, *J* = 8.3, 1.1 Hz, 1 H, HC(8)), 7.54 (d, *J* = 8.2 Hz, 1 H, HC(16)), 7.43 (d, *J* = 7.5 Hz, 2 H, HC(16)), 7.45–7.41 (m, 2 H, HC(17)), 7.37 (t, *J* = 7.6 Hz, 1 H, HC(9)), 7.34–7.27 (m, 1 H, HC(18)), 7.18 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H, HC(10)), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1 H, HC(14)), 6.77 (d, *J* = 2.4 Hz, 1 H, HC(6)), 6.10 (ddd, *J* = 17.1, 10.2, 5.8 Hz, 1 H, HC(4)), 5.33 (dt, *J* = 17.1, 1.4 Hz, 1 H, HC(5)), 5.27 (dt, *J* = 10.2, 1.3 Hz, 1 H, HC(5)), 5.08 (t, *J* = 5.5 Hz, 1 H, HC(3)), 4.22 (d, *J* = 5.2 Hz, 1 H, HN(2)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.7 (C1), 141.6 (C15), 138.7 (C4), 134.9 (C7), 128.8 (C13,17), 127.6 (C11), 127.5 (C18), 127.5 (C12), 127.2 (C16), 126.2 (C9), 126.0 (C8), 122.1 (C10), 118.1 (C14), 116.2 (C5), 105.9 (C6), 60.8 (C3).

MS (ESI): *m*/*z* (%) = 117 (100), 156 (63), 234 (48), 260 (60) $[M + H]^+$, 274 (31), 400 (20), 415 (19), 517 (34).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}N$: 260.1439; found: 260.1445.

Preparation of 2-Alkenylanilines by 3-Aza-Cope Rearrangement (Table 2)

(*E*)-2-Cinnamyl-4-fluoroaniline (5a)[4a]

To a 500-mL Schlenk flask equipped with a magnetic stir bar were added 4-fluoro-*N*-(1-phenylallyl)aniline (**3a**) (2.05 g, 9.0 mmol), $TsOH·H_2O$ (352 mg, 1.8 mmol, 0.2 equiv), and a mixed solution of MeCN (90 mL) and H_2O (10 mL). The solution was heated to 65 °C in an oil bath while the reaction was monitored by NMR spectroscopy (the reaction stalled after 36 h). Volatiles were removed under reduced pressure and the residue was extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with 1 M NaOH (30 mL) and H_2O (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure (30 °C, 10 mmHg). Purification of the residue by silica gel flash chromatography (9.5 × 5 cm; 500 mL of 88:10:2 hexane/EtOAc/Et_3N, 200 mL of 90:10 hexane/EtOAc, 200 mL of 80:20 hexane/EtOAc, 250 mL of 50:50 hexane/EtOAc) afforded 1.45 g (71%) of **5a** as a brown liquid; R_f = 0.26 (hexanes/EtOAc, 4:1) [UV]. The spectroscopic data matched those reported previously.[20]

IR (neat): 3444 (w), 3367 (w), 3032 (w), 1624 (m), 1610 (w), 1596 (w), 1577 (w), 1494 (s), 1448 (w), 1436 (s), 1420 (m), 1352 (w), 1332 (w), 1277 (w), 1261 (m), 1197 (m), 1144 (m), 1081 (w), 1070 (w), 1055 (w), 1028 (w), 990 (m), 983 (m), 972 (w), 951 (s), 859 (s), 822 (m), 807 (s), 751 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 5 H, HC(11,12,13)), 6.88 (ddt, *J* = 19.9, 8.5, 2.7 Hz, 2 H, HC(2,6)), 6.65 (dd, *J* = 8.7, 4.9 Hz, 1 H, HC(3)), 6.50 (d, *J* = 15.9 Hz, 1 H, HC(9)), 6.35 (dtd, *J* = 15.8, 6.3, 1.8 Hz, 1 H, HC(8)), 3.59 (s, 2 H, HN(14)), 3.45 (d, *J* = 6.3 Hz, 2 H, HC(7)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.7 (d, *J* = 235.9 Hz, C1), 141.1 (C4), 137.3 (C10), 132.0 (C13), 128.9 (C12), 127.8 (C9 or C11), 127.0 (C9 or C11), 126.5 (C8), 126.2 (d, *J* = 6.6 Hz, C5), 116.9 (d, *J* = 5.7 Hz, C3), 116.7 (d, *J* = 20.4 Hz, C6), 114.1 (d, *J* = 22.1 Hz, C2), 35.6 (C7).

MS (ESI): *m*/*z* (%) = 124 (41), 228 (100) $[M + H]^+$, 229 (29).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{15}FN$: 228.1189; found: 228.1192.

(*E*)-*N*-(2-Cinnamyl-4-fluorophenyl)-4-methylbenzenesulfonamide (1a)[11]

To a flame-dried, 50-mL Schlenk flask equipped with a magnetic stir bar, purged with a positive pressure of argon, were added aniline **5a** (1.13 g, 5.0 mmol) and CH_2Cl_2 (15 mL, 0.3 M). The solution was cooled to 0 °C and pyridine (2.0 mL, 25.0 mmol, 5.0 equiv) and TsCl (1.43 g, 7.5 mmol, 1.5 equiv) were added. The reaction mixture was warmed to r.t. and stirred for 12 h. Then, brine (30 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg). The crude solid was purified by silica gel flash chromatography (8 × 5 cm; 500 mL of 90:10 hexane/EtOAc, 200 mL of 85:15 hexane/EtOAc, 200 mL of 80:20 hexane/EtOAc, 200 mL of 75:25 hexane/EtOAc, 200 mL of 50:50 hexane/EtOAc) to afford 1.88 g (98%) of a brown liquid. Crystallization of the brown liquid was achieved by dissolving in boiling EtOAc (10 mL) and cooling the solution to r.t. and then to –20 °C in a freezer. The 1st crop was collected by filtration, and the mother liquor was concentrated and recrystallized (boiling EtOAc, 5 mL). After cooling at –20 °C and filtration, a combined yield of 1.63 g (86%) of **1a** was obtained; fluffy solid; mp 128–129 °C (sealed tube); R_f = 0.32 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3270 (w), 3028 (w), 2924 (w), 1614 (w), 1598 (w), 1494 (m), 1448 (w), 1435 (w), 1392 (w), 1328 (w), 1305 (w), 1273 (w), 1200 (w), 1184 (w), 1157 (s), 1120 (w), 1092 (w), 1019 (w), 963 (w), 904 (w), 814 (w), 754 (w), 730 (w), 706 (w), 692 (w), 664 (m), 595 (w), 548 (m), 527 (m), 493 (w) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.3 Hz, 2 H, HC(16)), 7.31–7.26 (m, 6 H, HC(3,11,12,13)), 7.21 (d, *J* = 8.1 Hz, 2 H, HC(17)), 6.89 (ddd, *J* = 19.0, 8.6, 3.0 Hz, 2 H, HC(2,6)), 6.32 (s, 1 H, HN(14)), 6.27 (dt, *J* = 16.2, 0.9 Hz, 1 H, HC(9)), 6.04 (dt, *J* = 15.9, 6.5 Hz, 1 H, HC(8)), 3.18 (d, *J* = 6.01 Hz, 2 H, HC(7)), 2.39 (s, 3 H, HC(19).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.3 (C1), 144.2 (C18), 136.7 (C15), 136.6 (C4), 132.7 (C9), 130.6 (C5 or C10), 130.5 (C5 or C10), 129.9 (C17), 128.8 (C6), 128.0 (d, *J* = 6.0 Hz, C3), 127.9 (C12), 127.8 (C13), 127.4 (C16), 126.5 (C11), 126.4 (C8), 117.3 (d, *J* = 22.7 Hz, C6), 114.6 (d, *J* = 22.2 Hz, C2), 35.2 (C7), 21.8 (C19).

^{19}F NMR (470 MHz, $CDCl_3$): δ = –115.2.

MS (ESI): *m*/*z* (%) = 226 (21), 227 (100) $[M - Ts + H]^+$, 228 (18), 382 (72) $[M + H]^+$, 399 (36), 404 (17).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{21}FNO_2S$: 382.1271; found: 382.1273.

Anal. Calcd for $C_{22}H_{20}FNO_2S$ (381.46): C, 69.27; H, 5.28; N, 3.67. Found: C, 69.36; H, 5.20; N, 3.70.

(*E*)-2-Cinnamyl-4-methoxyaniline (5b)[4a]

To a 100-mL Schlenk flask equipped with a magnetic stir bar were added 4-methoxy-*N*-(1-phenylallyl)aniline (**3b**) (239 mg, 1 mmol), $TsOH·H_2O$ (39 mg, 0.2 mmol, 0.2 equiv), and a mixed solution of MeCN (10 mL) and H_2O (1 mL). The solution was heated to 65 °C in an oil bath while the reaction was monitored by NMR spectroscopy (the

reaction stalled after 36 h). Volatiles were removed under reduced pressure and the residue was extracted with Et_2O (3 × 10 mL). The combined organic layer was washed with 1 M NaOH (10 mL) and H_2O (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure (30 °C, 10 mmHg). Purification of the residue by silica gel flash chromatography (16 × 2 cm; 500 mL of 95:5 hexane/EtOAc with 10 mL of Et_3N, 200 mL of 90:10 hexane/EtOAc, 200 mL of 50:50 hexane/EtOAc) afforded 195 mg (81%) of a brown liquid. Crystallization of the brown liquid was achieved by dissolving in boiling Et_2O (0.5 mL), followed by slow addition of pentane (3 mL). The solution was cooled to r.t. and then to –20 °C in a freezer. Filtration over glass wool afforded 170 mg (71%) of **5b**; white needle-like crystals; mp 63–64 °C (sealed tube); R_f = 0.25 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3358 (w), 3024 (w), 2998 (w), 2936 (w), 2906 (w), 2831 (w), 1607 (w), 1500 (s), 1465 (m), 1448 (m), 1432 (m), 1323 (w), 1286 (w), 1242 (s), 1211 (w), 1189 (w), 1154 (m), 1075 (w), 1040 (m), 969 (m), 940 (w), 870 (w), 854 (w), 811 (m), 747 (m), 732 (m), 692 (s), 566 (m), 498 (w), 475 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 7.0 Hz, 2 H, HC(11)), 7.31–7.27 (m, 2 H, HC(12)), 7.24–7.17 (m, 1 H, HC(13)), 6.72 (d, *J* = 2.8 Hz, 1 H, HC(6)), 6.67 (dd, *J* = 8.4, 2.9 Hz, 1 H, HC(2)), 6.65 (d, *J* = 8.5 Hz, 1 H, HC(3)), 6.45 (dt, *J* = 16.0, 1.4 Hz, 1 H, HC(9)), 6.33 (dt, *J* = 15.8, 6.2 Hz, 1 H, HC(8)), 3.75 (s, 3 H, HC(14)), 3.45 (d, *J* = 7.3 Hz, 4 H, HC(7) and HN(15)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.2 (C1), 138.5 (C4), 137.4 (C5), 131.6 (C9), 128.8 (C12), 127.7 (C8), 127.5 (C13), 126.4 (C11), 126.2 (C10), 117.3 (C3), 116.3 (C6), 113.0 (C2), 56.0 (C14), 36.0 (C7).

MS (ESI): *m*/*z* (%) = 136 (51) [M – styrene + H]$^+$, 239 (12), 240 (100) [M + H]$^+$, 241 (17).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}NO$: 240.1388; found: 240.1391.

Anal. Calcd for $C_{16}H_{17}NO$ (239.31): C, 80.30; H, 7.16; N, 5.85. Found: C, 80.25; H, 7.05; N, 5.93.

(*E*)-*N*-(2-Cinnamyl-4-methoxyphenyl)-4-methylbenzenesulfonamide (1b)[11]

To a flame-dried, 25-mL Schlenk flask equipped with a magnetic stir bar, purged with a positive pressure of argon, were added aniline **5b** (1.17 g, 4.9 mmol) and CH_2Cl_2 (15 mL, 0.3 M). The solution was cooled to 0 °C and pyridine (1.97 mL, 24.5 mmol, 5.0 equiv) and TsCl (1.4 g, 7.35 mmol, 1.5 equiv) were added. The reaction mixture was warmed to r.t. and stirred for 12 h. Then, brine (30 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg). The crude solid was purified by recrystallization by dissolving in boiling EtOAc (10 mL) and cooling the solution to r.t. and then to –20 °C in a freezer. The 1st crop was collected by filtration, and the mother liquor was concentrated and recrystallized (boiling EtOAc, 5 mL). After cooling at –20 °C and filtration, a combined yield of 1.6 g (83%) of **1b** was obtained; white solid; mp 114–115 °C (sealed tube); R_f = 0.30 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3271 (w), 3027 (w), 2957 (w), 2837 (w), 1599 (m), 1581 (w), 1496 (s), 1464 (w), 1448 (w), 1433 (w), 1399 (m), 1327 (m), 1304 (m), 1290 (m), 1215 (m), 1185 (w), 1159 (s), 1092 (m), 1038 (m), 968 (m), 945 (w), 899 (m), 814 (m), 753 (m), 731 (m), 693 (m), 665 (m), 596 (w), 550 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.2 Hz, 2 H, HC(16)), 7.31–7.27 (m, 4 H, HC(11,12)), 7.24–7.20 (m, 3 H, HC(17,13)), 7.19 (d, *J* = 8.7 Hz, 1 H, HC(3)), 6.72 (dd, *J* = 8.7, 3.0 Hz, 1 H, HC(2)), 6.69 (d, *J* = 2.9 Hz, 1 H, HC(6)), 6.31 (s, 1 H, HN(14)), 6.22 (dt, *J* = 15.8, 1.7 Hz, 1 H, HC(9)), 6.06 (dt, *J* = 15.9, 6.5 Hz, 1 H, HC(8)), 3.77 (s, 3 H, HC(20)), 3.17 (dd, *J* = 6.5, 1.6 Hz, 2 H, HC(7)), 2.39 (s, 3 H, HC(19)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.7 (C1), 143.9 (C18), 137.02 (C4), 136.99 (C5), 132.0 (C9), 129.8 (C17), 128.8 (C12), 128.5 (C3), 127.73 (C13), 127.69 (C10 or C15), 127.5 (C16), 127.4 (C10 or C15), 127.3 (C8), 126.5 (C11), 116.0 (C6), 112.6 (C2), 55.6 (C20), 35.4 (C7), 21.8 (C19).

MS (ESI): *m*/*z* (%) = 239 (100) [M – Ts + H]$^+$, 240 (18), 394 (45) [M + H]$^+$, 395 (12), 411 (10).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{24}NO_3S$: 394.1471; found: 394.1479.

Anal. Calcd for $C_{23}H_{23}NO_3S$ (393.50): C, 70.20; H, 5.89; N, 3.56. Found: C, 69.85; H, 5.81; N, 3.59.

(*E*)-1-Cinnamylnaphthalen-2-amine (5c)[4a]

To a 50-mL Schlenk flask equipped with a magnetic stir bar were added *N*-(1-phenylallyl)naphthalen-2-amine (**3c**) (259 mg, 1.0 mmol), $TsOH·H_2O$ (39 mg, 0.2 mmol, 0.2 equiv), and a mixed solution of MeCN (10 mL) and H_2O (1 mL). The solution was heated to 65 °C in an oil bath for 6 h. The solution was cooled to r.t. at which point a solid started to form. To this suspension were added 2 M NaOH (10 mL) and Et_2O (20 mL). The organic layer was separated, washed with brine (10 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (30 °C, 10 mmHg). Purification of the residue by silica gel flash chromatography (16 × 2 cm; 300 mL of 95:5 hexane/EtOAc, 200 mL of 90:10 hexane/EtOAc, 250 mL of 50:50 hexane/EtOAc) afforded 210 mg (81%) of a brown liquid. Crystallization of the brown liquid was achieved by dissolving in boiling Et_2O (0.5 mL), followed by slow addition of pentane (2 mL). The solution was cooled to r.t. and then to –20 °C in a freezer. Filtration over glass wool afforded 192 mg (74%) of **5c**; white crystals; mp 66–68 °C (sealed tube); R_f = 0.40 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3023 (w), 1622 (s), 1600 (m), 1496 (m), 1473 (m), 1446 (m), 1435 (m), 1393 (m), 1356 (w), 1282 (m), 1259 (m), 1222 (w), 1164 (w), 964 (s), 908 (m), 857 (w), 811 (s), 782 (m), 731 (s), 691 (s), 672 (m), 648 (m), 617 (m), 599 (m), 586 (m), 545 (m), 518 (m), 500 (m), 477 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.6 Hz, 1 H, HC(10)), 7.75 (dt, *J* = 8.1, 0.7 Hz, 1 H, HC(13)), 7.64 (d, *J* = 8.7 Hz, 1 H, HC(2)), 7.45 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1 H, HC(11)), 7.28 (tt, *J* = 5.4, 1.5 Hz, 3 H, HC(12,15)), 7.26–7.22 (m, 2 H, HC(16)), 7.17 (tt, *J* = 7.2, 2.2 Hz, 1 H, HC(17)), 6.99 (d, *J* = 8.7 Hz, 1 H, HC(3)), 6.44–6.34 (m, 2 H, HC(8,9)), 3.86 (d, *J* = 4.5 Hz, 4 H, HC(7) and HN(18)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.3 (C4), 137.4 (C14), 133.6 (C6), 130.7 (C9), 128.9 (C13), 128.8 (C1), 128.7 (C16), 128.3 (C2), 127.4 (C17), 127.3 (C8), 126.8 (C11), 126.3 (C12), 122.5 (C10), 122.4 (C15), 119.1 (C3), 114.7 (C5), 29.9 (C7).

MS (ESI): *m*/*z* (%) = 156 (100) [M – styrene + H]$^+$, 157 (11), 260 (43) [M + H]$^+$, 261 (10).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}N$: 260.1439; found: 260.1441.

Anal. Calcd for $C_{19}H_{17}N$ (259.35): C, 87.99; H, 6.61; N, 5.40. Found: C, 87.76; H, 6.44; N, 5.50.

(*E*)-*N*-(1-Cinnamyl-2-naphthyl)-4-methylbenzenesulfonamide (1c)[11]

To a flame-dried, 50-mL Schlenk flask equipped with a magnetic stir bar, purged with a positive pressure of argon, were added aniline **5c** (1.43 g, 5.5 mmol) and CH_2Cl_2 (17 mL, 0.3 M). The solution was cooled to 0 °C and pyridine (2.2 mL, 27.5 mmol, 5.0 equiv) and TsCl (1.57 g, 8.25 mmol, 1.5 equiv) were added. The reaction mixture was warmed to r.t. and stirred for 12 h. Then, brine (30 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg) to afford a dark brown oil. The crude product was dissolved in Et_2O and a yellow solid precipitated immediately. Recrystallization was undertaken by dissolving the yellow solid in boiling EtOAc (10 mL) and then cooling the solution to r.t. and subsequently to –20 °C in a freezer. The 1st crop was collected by filtration, and the mother liquor was concentrated and recrystallized (boiling EtOAc, 5 mL). After cooling at –20 °C and filtration, a combined yield of 1.9 g (83%) of **1c** was obtained; yellow solid; mp 148–149 °C (sealed tube); R_f = 0.38 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3283 (w), 1598 (m), 1512 (w), 1496 (w), 1468 (w), 1447 (w), 1407 (m), 1367 (m), 1320 (m), 1304 (m), 1234 (w), 1185 (w), 1159 (s), 1092 (m), 1067 (w), 1019 (w), 966 (m), 907 (m), 864 (w), 847 (w), 813 (m), 763 (m), 733 (s), 706 (m), 691 (m), 669 (s), 598 (m), 552 (s), 532 (m), 494 (w) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.5 Hz, 1 H, HC(10)), 7.84 (d, *J* = 8.1 Hz, 1 H, HC(2)), 7.75 (d, *J* = 8.8 Hz, 1 H, HC(13)), 7.66 (d, *J* = 8.8 Hz, 1 H, HC(12)), 7.61 (d, *J* = 8.1 Hz, 2 H, HC(20)), 7.53–7.42 (m, 2 H, HC(11,3)), 7.24 (dd, *J* = 7.2, 1.2 Hz, 2 H, HC(16)), 7.22–7.17 (m, 3 H, HC(15,17)), 7.13 (d, *J* = 7.9 Hz, 2 H, HC(21)), 6.64 (s, 1 H, HN(18)), 6.19 (dtd, *J* = 16.1, 5.1, 1.1 Hz, 1 H, HC(8)), 6.13 (d, *J* = 16.1 Hz, 1 H, HC(9)), 3.65 (dd, *J* = 5.4, 1.3 Hz, 2 H, HC(7)), 2.31 (s, 3 H, HC(23)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.1 (C22), 136.9 (C14), 136.8 (C19), 132.7 (C6), 132.6 (C1), 132.4 (C5), 131.6 (C9), 129.9 (C21), 129.8 (C4), 128.9 (C2), 128.7 (C16), 128.4 (C13), 127.7 (C17), 127.4 (C20), 127.0 (C11), 126.8 (C8), 126.4 (C15), 125.8 (C3), 124.5 (C10), 123.6 (C12), 30.0 (C7), 21.8 (C23).

MS (ESI): *m*/*z* (%) = 258 (22), 259 (100) $[M - Ts + H]^+$, 260 (18), 436 (25) $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{26}H_{23}NO_2SNa$: 436.1342; found: 436.1347.

Anal. Calcd for $C_{26}H_{23}NO_2S$ (413.53): C, 75.52; H, 5.61; N, 3.39. Found: C, 75.19; H, 5.63; N, 3.51.

***N*-(1-Isopropyl-2-propenyl)aniline (3d) (Scheme 5)**

By adopting the described procedure,[8] to an oven-dried, 100-mL, round-bottomed flask equipped with a magnetic stir bar were added imine **2d**[5d] (736 mg, 5 mmol) and toluene (30 mL, 0.17 M). After a condenser was installed, the flask was purged with argon and 1-(trimethylsilyl)benzotriazole (BtTMS; 957 mg, 5 mmol, 1 equiv) was added by syringe. After the reaction mixture was stirred for 30 min at r.t., it was cooled to 0 °C in an ice bath and a solution of vinylmagnesium chloride in THF (6.25 mL, 1.6 M, 10 mmol, 2 equiv) was added by syringe. To the resulting yellow turbid mixture was added Et_2O (10 mL). The reaction mixture was refluxed under heat (bath temperature 90 °C) for 20 h. After the reaction mixture was cooled to r.t., it was quenched by pouring into ice–water (30 mL), and then the mixture was extracted with Et_2O (3 × 60 mL). The organic layers were combined and washed with aqueous 2 M NaOH solution (2 × 20 mL) and H_2O (2 × 30 mL). The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg). Purification by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 19:1) afforded 595 mg (68%) of **3d** as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation (60 °C/0.01 mmHg), affording 550 mg (63%) of **3d** as a colorless oil; bp 60 °C/0.01 mmHg; R_f = 0.58 (hexanes/EtOAc, 4:1) [UV]. The spectroscopic data matched those reported previously.[19]

^1H NMR (500 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 8.0 Hz, 2 H, HC(3)), 6.69 (t, *J* = 7.5 Hz, 1 H, HC(4)), 6.63 (d, *J* = 8.5 Hz, 2 H, HC(2)), 5.76 (ddd, *J* = 17.0, 10.5, 6.0 Hz, 1 H, HC(6)), 5.27–5.16 (m, 2 H, HC(7)), 3.75–3.63 (br s + m, 2 H, HN + HC(5)), 1.90 (dq, *J* = 13.5, 6.5 Hz, 1 H, HC(8)), 1.01 (dd, *J* = 15.0, 7.0 Hz, 6 H, HC(9)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.8 (C1), 137.9 (C6), 129.1 (C3), 117.0 (C4), 116.0 (C7), 113.3 (C2), 61.4 (C5), 32.4 (C8), 18.8 (C9), 18.5 (C9).

MS (ESI): *m*/*z* (%) = 94 (20), 97 (22), 98 (15), 106 (14), 114 (56), 118 (28), 138 (16), 140 (13), 142 (26), 148 (34), 150 (28), 176 (78) $[M + H]^+$, 188 (50), 202 (43), 219 (100), 220 (17), 230 (16), 235 (69), 248 (16), 251 (19), 258 (25), 262 (14), 274 (40).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}N$: 176.1439; found: 176.1440.

(*E*)-2-(4-Methyl-2-pentenyl)aniline (5d)

By adopting the described procedure,[7,11] to an oven-dried, 38-mL pressure tube with a side arm in the neck, equipped with a magnetic stir bar, were added allylaniline **3d** (350 mg, 2.0 mmol) and xylenes (4 mL, 0.5 M). The tube was capped with a septum and purged with a positive pressure of argon. The solution was cooled to –40 °C in a MeCN/dry ice bath under positive argon pressure. To the tube was added $BF_3{\cdot}OEt_2$ (48% solution, 0.62 mL, 2.4 mmol, 1.2 equiv). The reaction mixture was warmed to r.t. and the septum was replaced with a pressure screw cap under a positive stream of argon. Then, the mixture was heated to 180 °C and stirred for 17 h. After completion, the reaction mixture was cooled to 0 °C with continuous vigorous stirring and quenched with 2 M NaOH (15 mL) at 0 °C. The resulting biphasic layer was extracted with Et_2O (3 × 15 mL). The organic layers were combined, filtered over Celite, and concentrated under reduced pressure (30 °C, 10 mmHg). The crude solid was purified by silica gel flash chromatography (30 g, 20 mm ∅; hexanes to hexanes/EtOAc, 6:1) to afford 199 mg (57%) of **5d** as a yellow oil. An analytically pure sample was obtained by Kugelrohr distillation (80 °C/0.01 mmHg), affording 179 mg (51%) of **5d** as a colorless oil; bp 80 °C/0.01 mmHg; R_f = 0.43 (hexanes/EtOAc, 4:1) [UV].

^1H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.07 (m, 2 H, HC(3,5)), 6.80 (tt, *J* = 7.5, 1.5 Hz, 1 H, HC(4)), 6.72 (dd, *J* = 7.5, 1.5 Hz, 1 H, HC(6)), 5.63–5.50 (m, 2 H, HC(8,9)), 3.75 (br s, 2 H, H_2N), 3.30 (d, *J* = 5.5 Hz, 2 H, HC(7)), 2.35 (hept d, *J* = 6.5, 2.0 Hz, 1 H, HC(10)), 1.04 (dd, *J* = 7.0, 2.0 Hz, 6 H, HC(11)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.9 (C1), 139.5 (C9), 129.9 (C5), 127.3 (C3), 125.1 (C2), 124.3 (C8), 118.7 (C4), 115.7 (C6), 35.4 (C7), 31.0 (C10), 22.5 (C11).

MS (ESI): *m*/*z* (%) = 106 (100), 114 (27), 176 (13) $[M + H]^+$, 177 (13).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}N$: 176.1439; found: 176.1443.

Anal. Calcd for $C_{12}H_{17}N$ (175.27): C, 82.23; H, 9.78; N, 7.99. Found: C, 82.25; H, 10.00; N, 7.80.

(*E*)-4-Methyl-*N*-[2-(4-methyl-2-pentenyl)phenyl]benzenesulfonamide (1d)[11]

To an oven-dried, 50-mL, round-bottomed flask equipped with a magnetic stir bar were added aniline **5d** (876 mg, 5.0 mmol) and CH_2Cl_2 (10 mL, 0.5 M) under positive argon pressure. The solution was cooled to 0 °C and pyridine (1.21 mL, 15.0 mmol, 3.0 equiv) and TsCl (1.05 g, 5.5 mmol, 1.1 equiv) were added. The reaction mixture was warmed to r.t. and stirred for 24 h. To quench the reaction, H_2O (20 mL) was added and then the solution was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg). The crude solid was purified by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 6:1) to afford 1.48 g (90%) of **1d** as a yellow solid. An analytically pure sample was obtained by recrystallization (boiling pentane, 50 mL). The solution was cooled to r.t. and then to –20 °C in a freezer. The 1st crop was collected by filtration, and the mother liquor was concentrated and recrystallized (boiling pentane, 10 mL). After cooling at –20 °C and filtration, a combined yield of 1.34 g (82%) of **1d** was obtained; white crystalline solid; mp 128–129 °C (sealed tube); R_f = 0.32 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3286 (m), 2963 (w), 1489 (m), 1458 (w), 1391 (m), 1334 (s), 1307 (w), 1291 (w), 1275 (w), 1187 (w), 1166 (s), 1119 (w), 1090 (s), 1045 (w), 1021 (w), 969 (m), 901 (m), 834 (w), 810 (m), 762 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.0 Hz, 2 H, HC(8)), 7.43 (d, *J* = 8.0 Hz, 1 H, HC(6)), 7.22 (d, *J* = 8.0 Hz, 2 H, HC(9)), 7.19 (t, *J* = 7.5 Hz, 1 H, HC(5)), 7.09 (t, *J* = 7.5 Hz, 1 H, HC(4)), 7.04 (d, *J* = 7.5 Hz, 1 H, HC(3)), 6.69 (s, 1 H, HN), 5.44 (dd, *J* = 15.5, 6.5 Hz, 1 H, HC(14)), 5.31 (dt, *J* = 15.5, 6.0 Hz, 1 H, HC(13)), 2.93 (d, *J* = 6.0 Hz, 2 H, HC(12)), 2.39 (s, 3 H, HC(11)), 2.34–2.22 (m, 1 H, HC(15)), 0.99 (d, *J* = 7.0 Hz, 6 H, HC(16)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.7 (C10), 140.7 (C14), 136.9 (C7), 135.3 (C1), 132.2 (C2), 130.3 (C3), 129.6 (C9), 127.6 (C5), 127.0 (C8), 125.9 (C4), 124.0 (C13), 123.9 (C6), 35.5 (C12), 31.0 (C15), 22.3 (C16), 21.5 (C11).

MS (ESI): *m*/*z* (%) = 118 (52), 132 (22), 146 (13), 160 (39), 174 (17), 175 (100), 176 (14), 330 (36) $[M + H]^+$, 352 (42).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{24}NO_2S$: 330.1528; found: 330.1526.

Anal. Calcd for $C_{19}H_{23}NO_2S$ (329.46): C, 69.27; H, 7.04; N, 4.25. Found: C, 69.42; H, 7.23; N, 4.26.

Olefin Cross-Metathesis (Table 4)

(*E*)-4-Methyl-*N*-[2-(3-phenyl-2-propenyl)phenyl]benzenesulfonamide (1e)

By adopting the described procedure,[21] an oven-dried, 50-mL Schlenk flask equipped with a magnetic stir bar was introduced into a glovebox. Grubbs 1st generation indenylidene catalyst (CAS no. 250220-36-1; 111 mg, 0.12 mmol, 0.03 equiv) was loaded into the flask, which was sealed with a septum and removed from the glovebox. The Schlenk flask was hooked up to a Schlenk manifold and was purged thoroughly with argon. To a separate 50-mL, round-bottomed flask were added sulfonamide **6**[11] (1.15 g, 4.0 mmol, 1 equiv), styrene (4.60 mL, 40.0 mmol, 10 equiv), and CH_2Cl_2 (20 mL, 0.2 M, degassed with argon); then, the flask was sealed with a septum. The mixture turned into a solution while being degassed for an additional 30 min with argon (needle and a bubbler outlet attached). The premixed, degassed solution of the two olefin substrates was transferred to the Schlenk flask by syringe. The top area of the Schlenk flask, including the needle-punctured septum, was thoroughly sealed with Parafilm. The black mixture was stirred for 48 h at r.t. The mixture was filtered through a plug of silica gel, then rinsed with CH_2Cl_2 (2 × 25 mL) and EtOAc (2 × 25 mL) to afford a dark solution. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a black solid. Purification by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 6:1) afforded 685 mg (47%) of **1e** as a white solid. Recrystallization of the solid with hot pentane (36 °C, 30 mL) afforded 630 mg (43%) of **1e** as white crystals; mp 159–160 °C (sealed tube). The spectroscopic data matched those reported previously.[22]

IR (neat): 3280 (m), 1492 (m), 1448 (w), 1403 (m), 1333 (s), 1305 (w), 1291 (w), 1278 (w), 1184 (w), 1165 (s), 1119 (w), 1090 (s), 1053 (w), 1040 (w), 1019 (w), 969 (m), 954 (w), 907 (s), 810 (m), 756 (m) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.0 Hz, 2 H, HC(9)), 7.43 (d, *J* = 8.0 Hz, 1 H, HC(6)), 7.35–7.21 (m, 6 H, HC(aryl)), 7.21–7.13 (m, 4 H, HC(aryl)), 6.52 (br s, 1 H, HN), 6.29 (dt, *J* = 16.0, 1.5 Hz, 1 H, HC(14)), 6.11 (dt, *J* = 16.0, 6.5 Hz, 1 H, HC(13)), 3.25 (dd, *J* = 6.5, 1.5 Hz, 2 H, HC(12)), 2.39 (s, 3 H, HC(11)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.8 (C10), 136.6 (C7), 136.6 (C15), 134.9 (C1), 132.2 (C2), 131.9 (C14), 130.5 (C3), 129.6 (C9), 128.6 (C17), 127.8, 127.6, 127.2 (C8), 127.0 (C13), 126.2 (C16), 126.2, 124.2 (C6), 35.2 (C12), 21.5 (C11).

MS (ESI): *m*/*z* (%) = 208 (15), 209 (100), 210 (24), 364 (28) $[M + H]^+$, 381 (44), 382 (13), 386 (17).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{22}NO_2S$: 364.1371; found: 364.1373.

(*E*)-*N*-{2-[3-(4-Methoxyphenyl)-2-propenyl]phenyl}-4-methylbenzenesulfonamide (1f)

By adopting the described procedure,[21] an oven-dried, 25-mL Schlenk flask equipped with a magnetic stir bar was introduced into a glovebox. Grubbs 1st generation indenylidene catalyst (CAS no. 250220-36-1; 55 mg, 0.06 mmol, 0.03 equiv) was loaded into the flask, which was sealed with a septum and removed from the glovebox. The Schlenk flask was hooked up to a Schlenk manifold and was purged thoroughly with argon. To a separate 25-mL, round-bottomed flask were added sulfonamide **6**[11] (575 mg, 2.0 mmol, 1 equiv), 4-vinylanisole (2.66 mL, 20.0 mmol, 10 equiv), and CH_2Cl_2 (10 mL, 0.2 M, degassed with argon); then, the flask was sealed with a septum. The mixture turned into a solution while being degassed for an additional 30 min with argon (needle and a bubbler outlet attached). The premixed, degassed solution of the two olefin substrates was transferred to the Schlenk flask by syringe. The top area of the Schlenk flask, including the needle-punctured septum, was thoroughly sealed with Parafilm. The black mixture was stirred for 48 h at r.t. The mixture was filtered through a plug of silica gel, then rinsed with CH_2Cl_2 (2 × 15 mL) and EtOAc (2 × 15 mL) to afford a dark solution. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a black solid. Purification by silica gel flash chromatography (25 g, 20 mm ∅; hexanes to hexanes/EtOAc, 6:1) afforded 425 mg (54%) of **1f** as a white solid. Recrystallization of the solid with hot pentane (36 °C, 30 mL) afforded 396 mg (50%) of **1f** as white crystals; mp 117–118 °C (sealed tube); R_f = 0.20 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3271 (m), 3005 (w), 2965 (w), 1739 (w), 1606 (m), 1578 (w), 1510 (m), 1488 (m), 1469 (w), 1456 (w), 1437 (w), 1406 (m), 1332 (m), 1308 (w), 1292 (m), 1275 (w), 1251 (s), 1177 (w), 1160 (s), 1121 (w), 1109 (w), 1089 (m), 1066 (w), 1032 (m), 1018 (w), 969 (m), 908 (m), 862 (w), 820 (m), 812 (m), 778 (w), 761 (m), 754 (m) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.5 Hz, 2 H, HC(8)), 7.42 (d, *J* = 8.0 Hz, 1 H, HC(6)), 7.25–7.13 (m, 7 H), 6.84 (d, *J* = 8.5 Hz, 2 H, HC(17)), 6.56 (br s, 1 H, HN), 6.22 (d, *J* = 16.0 Hz, 1 H, HC(14)), 5.94 (dt, *J* = 16.0, 6.5 Hz, 1 H, HC(13)), 3.81 (s, 3 H, HC(19)), 3.19 (dd, *J* = 6.5, 2.0 Hz, 2 H, HC(12)), 2.37 (s, 3 H, HC(11)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.1 (C18), 143.7 (C10), 136.6 (C7), 134.9 (C1), 132.3 (C2), 131.3 (C14), 130.5 (C3), 129.6 (C9), 129.4, 127.6, 127.4 (C8), 127.1 (C16), 126.1, 124.7 (C13), 124.0 (C6), 113.9 (C17), 55.3 (C19), 35.1 (C12), 21.5 (C11).

MS (ESI): *m*/*z* (%) = 238 (17), 239 (100), 240 (37), 297 (34), 394 (52) $[M + H]^+$, 395 (16), 411 (79), 412 (25).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{24}NO_3S$: 394.1477; found: 394.1484.

Anal. Calcd for $C_{23}H_{23}NO_3S$ (393.50): C, 70.20; H, 5.89; N, 3.56. Found: C, 70.05; H, 5.81; N, 3.55.

(*E*)-*N*-{2-[3-(4-Bromophenyl)-2-propenyl]phenyl}-4-methylbenzenesulfonamide (1g)

By adopting the described procedure,[21] an oven-dried, 25-mL Schlenk flask equipped with a magnetic stir bar was introduced into a glovebox. Grubbs 1st generation indenylidene catalyst (CAS no. 250220-36-1; 55 mg, 0.06 mmol, 0.03 equiv) was loaded into the flask, which was sealed with a septum and removed from the glovebox. The Schlenk flask was hooked up to a Schlenk manifold and was purged thoroughly with argon. To a separate 25-mL, round-bottomed flask were added sulfonamide **6**[11] (575 mg, 2.0 mmol, 1 equiv), 4-bromostyrene (2.62 mL, 20.0 mmol, 10 equiv), and CH_2Cl_2 (10 mL, 0.2 M, degassed with argon); then, the flask was sealed with a septum. The mixture turned into a solution while being degassed for an additional 30 min with argon (needle and a bubbler outlet attached). The premixed, degassed solution of the two olefin substrates was transferred to the Schlenk flask by syringe. The top area of the Schlenk flask, including the needle-punctured septum, was thoroughly sealed with Parafilm. The black mixture was stirred for 48 h at r.t. The mixture was filtered through a plug of silica gel, then rinsed with CH_2Cl_2 (2 × 15 mL) and EtOAc (2 × 15 mL) to afford a dark solution. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a black solid. Purification by silica gel flash chromatography (25 g, 20 mm ∅; hexanes to hexanes/EtOAc, 6:1) afforded 440 mg (50%) of **1g** as a white solid. Recrystallization of the solid with hot pentane (36 °C, 30 mL) afforded 404 mg (46%) of **1g** as white crystals; mp 141–142 °C (sealed tube); R_f = 0.22 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.5 Hz, 2 H, HC(8)), 7.45 (d, *J* = 8.5 Hz, 2 H, HC(17)), 7.41 (dd, *J* = 8.0, 1.0 Hz, 1 H, HC(6)), 7.25 (ddd, *J* = 8.5, 6.0, 3.0 Hz, 1 H, HC(aryl)), 7.22 (dd, *J* = 8.0, 1.0 Hz, 2 H, HC(9)), 7.20–7.15 (m, 4 H, HC(aryl)), 6.5 (br s, 1 H, HN), 6.23 (d, *J* = 16.0 Hz, 1 H, HC(14)), 6.15 (dt, *J* = 16.0, 6.0 Hz, 1 H, HC(13)), 3.29 (dd, *J* = 6.0, 1.5 Hz, 2 H, HC(12)), 2.41 (s, 3 H, HC(11)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.1 (C10), 136.8 (C7), 135.8 (C15), 135.0 (C1), 132.5 (C2), 131.9 (C17), 130.9 (C14), 130.8 (C3), 129.9 (C9), 128.2 (C13), 128.1 (C5), 128.0 (C16), 127.4 (C8), 126.7 (C4), 124.6 (C6), 121.6 (C18), 35.3 (C12), 21.8 (C11).

MS (ESI): *m*/*z* (%) = 440 (95) $[M - H]^+$, 441 (22), 442 (100), 443 (23), 456 (13).

HRMS (ESI): *m*/*z* $[M - H]^+$ calcd for $C_{22}H_{19}BrNO_2S$: 440.0320; found: 440.0318.

Anal. Calcd for $C_{22}H_{20}BrNO_2S$ (442.37): C, 59.73; H, 4.56; N, 3.17. Found: C, 59.93; H, 4.39; N, 3.13.

(*E*)-4-Methyl-*N*-[2-(4-phenyl-3-butenyl)phenyl]benzenesulfonamide (1h)

By adopting the described procedure,[21] an oven-dried, 50-mL Schlenk flask equipped with a magnetic stir bar was introduced into a glovebox. Grubbs 1st generation indenylidene catalyst (CAS no. 250220-36-1; 110 mg, 0.12 mmol, 0.03 equiv) was loaded into the flask, which was sealed with a septum and removed from the glovebox. The Schlenk flask was hooked up to a Schlenk manifold and was purged thoroughly with argon. To a separate 25-mL, round-bottomed flask were added sulfonamide **7**[12] (1.21 g, 4.0 mmol, 1 equiv), styrene (4.60 mL, 40.0 mmol, 10 equiv), and CH_2Cl_2 (16 mL, 0.25 M, degassed with argon); then, the flask was sealed with a septum. The mixture turned into a solution while being degassed for an additional 30 min with argon (needle and a bubbler outlet attached). The premixed, degassed solution of the two olefin substrates was transferred to the Schlenk flask by syringe. The top area of the Schlenk flask, including the needle-punctured septum, was thoroughly sealed with Parafilm. The black mixture was stirred for 48 h at r.t. The mixture was filtered through a plug of silica gel, then rinsed with CH_2Cl_2 (2 × 30 mL) and EtOAc (2 × 30 mL) to afford a dark solution. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a black solid. Purification by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 6:1) afforded 740 mg (49%) of **1h** as a gray solid. Recrystallization of the solid (boiling EtOAc/pentane, 1:10; 20 mL) afforded 649 mg (43%) of **1h** as white crystals; mp 110–111 °C (sealed tube); R_f = 0.25 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3222 (m), 1597 (w), 1493 (w), 1456 (w), 1448 (w), 1411 (w), 1324 (s), 1305 (w), 1294 (w), 1269 (w), 1185 (w), 1155 (s), 1120 (w), 1090 (s), 985 (w), 964 (m), 913 (m), 812 (m), 795 (w), 766 (s) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.5 Hz, 2 H, HC(8)), 7.33–7.27 (m, 5 H, HC(17,18,aryl)), 7.25–7.19 (m, 3 H, HC(aryl,9)), 7.17–7.11 (m, 3 H, HC(aryl)), 6.30 (d + br s, *J* = 16.0 Hz, 2 H, HC(15) + HN), 6.10 (dt, *J* = 16.0, 7.0 Hz, 1 H, HC(14)), 2.54 (dd, *J* = 9.0, 6.5 Hz, 2 H, HC(12)), 2.37 (s, 3 H, HC(11)), 2.30 (qd, *J* = 7.5, 7.0 Hz, 2 H, HC(13)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.8 (C10), 137.3 (C16), 136.7 (C7), 135.1 (C2), 134.0 (C1), 131.0 (C14), 129.9 (C3), 129.6 (C9), 128.9 (C15), 128.5 (C18), 127.2 (C8), 127.2, 127.1, 126.5, 126.0 (C17), 124.8 (C6), 33.2 (C13), 30.7 (C12), 21.5 (C11).

MS (ESI): *m*/*z* (%) = 194 (13), 222 (22), 223 (100), 224 (16), 378 (49) $[M + H]^+$, 379 (13), 400 (32).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{24}NO_2S$: 378.1528; found: 378.1525.

Anal. Calcd for $C_{23}H_{23}NO_2S$ (377.50): C, 73.18; H, 6.14; N, 3.71. Found: C, 72.99; H, 6.29; N, 3.62.

(*E*)-6-(2-Chlorophenyl)-4-hexenenitrile (11) (Scheme 9)

To an oven-dried, 200-mL, round-bottomed flask equipped with a magnetic stir bar were added homoallylic alcohol **10**[15] (787 mg, 4.0 mmol) and CH_2Cl_2 (40 mL, 0.1 M), and then the flask was connected to an argon inlet. The solution was cooled to 0 °C in an ice bath, and Et_3N (1.95 mL, 14.0 mmol, 3.5 equiv) and MsCl (0.46 mL, 6.0 mmol, 1.5 equiv) were added by syringe. The reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched by adding H_2O (20 mL) and the resulting biphasic solution was separated. The aqueous layer was further extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was dried over Na_2SO_4 and filtered over glass wool. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a brown oil. Purification by silica gel plug filtration (10 g, 30 mm ∅; hexanes/EtOAc, 7:3) afforded 1.04 g (95%) of the mesylate as a pale yellow oil. (The mesylate intermediate slowly turned into a dark oil

upon standing.) To an oven-dried, 100-mL, round-bottomed flask with a magnetic stir bar were added the mesylate (1.04 g, 3.79 mmol), DMF (30 mL, 0.125 M), and NaCN (557 mg, 11.4 mmol, 3 equiv). A condenser was installed on the flask, and connected to an argon inlet. The flask was purged with argon and the solution was stirred for 12 h at 40 °C. Then, the flask was cooled to r.t. and the reaction was quenched by pouring into ice–water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), and each layer was washed with brine (2 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure (25 °C, 10 mmHg). Residual DMF was additionally removed by passage through a silica plug (10 g), rinsed with 4:1 hexanes/EtOAc. The collected organic layer was concentrated, and was purified by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 4:1) to afford 701 mg (90%) of **11** as a colorless oil; bp 80 °C/0.1 mmHg; R_f = 0.53 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 8.0, 1.5 Hz, 1 H, HC(9)), 7.28–7.16 (m, 3 H, HC(aryl)), 5.79 (dtd, *J* = 15.0, 6.5, 1.5 Hz, 1 H, HC(5)), 5.54 (dddt, *J* = 15.0, 6.5, 5.0, 1.5 Hz, 1 H, HC(4)), 3.52 (dd, *J* = 6.5, 1.5 Hz, 2 H, HC(6)), 2.47–2.36 (m, 4 H, HC(2,3)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 137.6 (C7), 133.9 (C8), 130.6 (C5), 130.3 (C12), 129.4 (C9), 127.8 (C4), 127.6 (C11), 126.9 (C10), 119.2 (C1), 36.3 (C6), 28.3 (C3), 17.5 (C2).

MS (EI): *m*/*z* (%) = 89 (11), 115 (30), 116 (25), 125 (30), 128 (25), 129 (100), 130 (26), 151 (64), 153 (20), 164 (14), 170 (50), 205 (45) $[M]^+$, 207 (15).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{12}NCl$: 205.0658; found: 205.0662.

Anal. Calcd for $C_{12}H_{12}NCl$ (205.68): C, 70.07; H, 5.88; N, 6.81. Found: C, 69.99; H, 5.81; N, 6.76.

(*E*)-6-(2-Aminophenyl)-4-hexenenitrile (12)

By adopting the described procedure,[14b] to an oven-dried, 38-mL pressure tube equipped with a magnetic stir bar were added aryl chloride **11** (737 mg, 3.6 mmol) and $(NH_4)_2SO_4$ (710 mg, 5.4 mmol, 1.5 equiv), and then the tube was introduced into a glovebox. In the glovebox, in a separate oven-dried, 20-mL vial with a magnetic stir bar were added $Pd[P(2\text{-}Tol)_3]_2$[23] (12.8 mg, 0.018 mmol, 0.005 equiv), Josiphos (CAS no. 158923-11-6; 9.9 mg, 0.018 mmol, 0.005 equiv), and dioxane (1 mL), and the mixture was stirred for 5 min. To the pressure tube were added NaO*t*-Bu (1.55 g, 16.1 mmol, 4.5 equiv), dioxane (18 mL, 0.2 M), and the Pd/Josiphos solution (1 mL). The pressure tube was tightly sealed with the screw cap and removed from the glovebox. The reaction mixture was heated to 100 °C and stirred for 12 h. Then, the mixture was cooled to r.t. and diluted with EtOAc (10 mL). The resulting dark mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to yield a brown oil. Purification by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 9:1) afforded 274 mg (41%) of **12** as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation (90 °C/0.01 mmHg), affording 236 mg (35%) of **12** as a colorless oil; bp 90 °C/0.01 mmHg; R_f = 0.41 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11–7.02 (m, 2 H, HC(10,12)), 6.77 (t, *J* = 7.5 Hz, 1 H, HC(11)), 6.69 (d, *J* = 7.5 Hz, 1 H, HC(9)), 5.71 (dtd, *J* = 15.0, 6.5, 1.5 Hz, 1 H, HC(5)), 5.53 (ddd, *J* = 15.0, 6.5, 4.5 Hz, 1 H, HC(4)), 3.63 (br s, 2 H, HN), 3.21 (dd, *J* = 6.5, 1.5 Hz, 2 H, HC(6)), 2.46–2.35 (m, 4 H, HC(2,3)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 139.5 (C7), 136.7 (C8), 130.4 (C5), 129.3 (C12), 128.1 (C4), 126.4 (C10), 119.1 (C11), 119.1 (C1), 115.1 (C9), 33.6 (C6), 28.4 (C3), 17.5 (C2).

MS (ESI): *m*/*z* (%) = 103 (17), 187 (100) $[M + H]^+$, 209 (26).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{15}N_2$: 187.1235; found: 187.1232.

Anal. Calcd for $C_{12}H_{14}N_2$ (186.12): C, 77.38; H, 7.58; N, 15.04. Found: C, 77.24; H, 7.41; N, 14.92.

(*E*)-*N*-[2-(5-Cyano-2-pentenyl)phenyl]-4-methylbenzenesulfonamide (1i)[11]

To an oven-dried, 25-mL, round-bottomed flask equipped with a magnetic stir bar were added aniline **12** (236 mg, 1.27 mmol), CH_2Cl_2 (2.5 mL, 0.5 M), pyridine (133 µL, 1.65 mmol, 1.3 equiv), and TsCl (266 mg, 1.39 mmol, 1.1 equiv) in order at r.t. The reaction mixture was stirred for 24 h, then washed with 1 M HCl solution (3 mL) and brine (2 × 3 mL). The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg) to yield a yellow oil. The crude product was purified by silica gel flash chromatography (25 g, 30 mm ∅; hexanes to hexanes/EtOAc, 4:1) to afford 372 mg (86%) of **1i** as a yellow solid. An analytically pure sample was obtained by recrystallization of the solid (boiling EtOAc/pentane, 1:10; 15 mL), affording 341 mg (79%) of **1i** as pale yellow crystals; mp 91–92 °C (sealed tube); R_f = 0.35 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.0 Hz, 2 H, HC(8)), 7.39 (d, *J* = 7.5 Hz, 1 H, HC(3)), 7.22 (d, *J* = 7.5 Hz, 2 H, HC(9)), 7.19–7.09 (m, 3 H, HC(aryl), 6.47 (br s, 1 H, HN), 5.75 (dt, *J* = 15.0, 6.0 Hz, 1 H, HC(13)), 5.59 (ddd, *J* = 15.0, 6.0, 4.5 Hz, 1 H, HC(14)), 3.23 (dd, *J* = 6.5, 1.5 Hz, 2 H, HC(12)), 2.42 (s, 3 H, HC(11)), 2.50–2.35 (m, 4 H, HC(15,16)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.6 (C10), 136.5 (C7), 135.9 (C2), 134.1 (C1), 131.6 (C14), 130.5 (C13), 129.8 (C6), 129.6 (C9), 127.1 (C4), 127.1 (C3), 127.0 (C8), 126.9 (C5), 119.0 (C17), 35.9 (C12), 28.4 (C15), 21.5 (C11), 17.4 (C16).

MS (EI): *m*/*z* (%) = 105 (23), 118 (67), 130 (20), 184 (27), 185 (40), 186 (100), 272 (15), 340 (52) $[M]^+$, 357 (10), 363 (11).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}N_2O_2S$: 340.1245; found: 340.1248.

Anal. Calcd for $C_{19}H_{20}N_2O_2S$ (340.44): C, 67.03; H, 5.92; N, 8.23. Found: C, 67.17; H, 6.10; N, 8.31.

(*E*)-4-Methyl-*N*-{2-[6-(4-methylphenylsulfonamido)-2-hexenyl]phenyl}benzenesulfonamide (1j)

An oven-dried, 100-mL Schlenk flask equipped with a magnetic stir bar was charged with $LiAlH_4$ (223 mg, 5.87 mmol, 2.0 equiv) and capped with a septum under argon. The flask was immersed in an ice bath and THF (10 mL) was added. To the resulting suspension was added a solution of nitrile **1i** (1.0 g, 2.94 mmol, 1 equiv) in THF (10 mL). The suspension was stirred for 2 h at 0 °C and gradually warmed to r.t. over 1 h. The reaction was cooled to 0 °C and slowly quenched with aqueous 1 M NaOH solution (0.4 mL) upon completion. The resulting emulsion was filtered through a short pad of Celite and rinsed with Et_2O (3 × 15 mL). Concentration of the filtrate under reduced pressure (25 °C, 10 mmHg) gave 799 mg (79%) of amine. Then, an oven-dried, 25-mL Schlenk flask equipped with a magnetic stir bar was charged with the crude amine (689 mg, approx. 2.0 mmol, 1 equiv), CH_2Cl_2 (4 mL), and pyridine (210 µL, 2.6 mmol, 1.3 equiv). To the solution was added TsCl (419 mg, 2.2 mmol, 1.1 equiv) portionwise at 0 °C under a positive stream of argon. The solution was warmed to r.t. and stirred for 4 h. The reaction mixture was washed with aqueous 1 M HCl (4 mL), then brine (2 × 4 mL). The resulting organic layer was dried over Na_2SO_4 and concentrated under reduced pressure (25 °C, 10 mmHg). Purification by silica gel flash chromatography (40 g, 25 mm ∅; hexanes to hexanes/EtOAc, 4:1) afforded 858

mg (86%) of the homologated tosylamine **1j** as a white solid. An analytically pure sample was obtained by recrystallization of the solid (boiling EtOAc/pentane, 1:10; 30 mL), affording 756 mg (76%) of **1j** as white crystals; mp 104–105 °C (sealed tube); R_f = 0.28 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2 H, HC(19)), 7.65 (d, *J* = 8.0 Hz, 2 H, HC(8)), 7.39 (d, *J* = 7.5 Hz, 1 H, HC(3)), 7.33 (d, *J* = 8.0 Hz, 2 H, HC(20)), 7.22 (d, *J* = 7.5 Hz, 2 H, HC(9)), 7.19–7.09 (m, 3 H, HC(aryl)), 6.47 (br s, 1 H, HN), 5.69 (dt, *J* = 15.0, 6.5 Hz, 1 H, HC(13)), 5.54 (dd, *J* = 15.0, 7.0 Hz, 1 H, HC(14)), 4.65 (br s, 1 H, HN), 3.24 (dd, *J* = 6.5, 1.5 Hz, 2 H, HC(12)), 2.92 (app q, *J* = 7.0 Hz, 2 H, HC(17)), 2.43 (s, 3 H, HC(22)), 2.41 (s, 3 H, HC(11)), 1.98 (app q, *J* = 7.0 Hz, 2 H, HC(15)), 1.52 (app p, *J* = 7.0 Hz, 2 H, HC(16)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.6 (C10), 143.3 (C21), 137.0 (C18), 136.5 (C7), 135.9 (C2), 134.1 (C1), 130.7 (C13), 129.9 (C14), 129.8 (C6), 129.7 (C20), 129.6 (C9), 127.1 (C4), 127.1 (C3), 127.1 (C19), 127.0 (C8), 126.9 (C5), 42.6 (C17), 35.8 (C12), 29.3 (C15), 29.2 (C16), 21.5 (C11), 21.5 (C22).

MS (ESI): *m*/*z* (%) = 118 (21), 273 (13), 344 (36), 499 (100) $[M + H]^+$, 521 (53), 537 (24).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{31}N_2O_4S_2$: 499.1725; found: 499.1728.

Anal. Calcd for $C_{26}H_{30}N_2O_4S_2$ (498.66): C, 62.62; H, 6.06; N, 5.62. Found: C, 62.85; H, 6.23; N, 5.69.

(*E*)-1-Bromo-2-(3-heptenyl)benzene (17) (Scheme 10)

To an oven-dried, 250-mL, round-bottomed flask equipped with a magnetic stir bar were added bromo alcohol **16**[24] (3.21 g, 11.9 mmol) and CH_2Cl_2 (120 mL, 0.1 M), and then the flask was connected to an argon inlet. The solution was cooled to 0 °C in an ice bath, and Et_3N (5.83 mL, 41.8 mmol, 3.5 equiv) and MsCl (1.38 mL, 17.9 mmol, 1.5 equiv) were added by syringe. The reaction mixture was stirred for 1 h at 0 °C. The reaction was quenched by adding H_2O (30 mL) and the resulting biphasic solution was separated. The aqueous layer was further extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was dried over Na_2SO_4 and filtered over glass wool. The filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a brown oil. Purification by silica gel plug filtration (10 g, 30 mm ∅; hexanes/EtOAc, 7:3) afforded 3.52 g (85%) of the mesylate as a pale yellow oil. (The mesylate intermediate slowly turned into a dark oil upon standing.) To an oven-dried, 200-mL, round-bottomed flask with a magnetic stir bar were added the mesylate (2.5 g, 7.2 mmol) and THF (80 mL, 0.09 M). The flask was connected to an argon inlet and capped with a septum. The solution was cooled to 0 °C in an ice bath and a suspension of $LiAlH_4$ (273 mg, 7.2 mmol, 1 equiv) in THF (10 mL) was added by cannula dropwise. The resulting reaction mixture was stirred for 4 h at 0 °C. The Fieser & Fieser workup method was used to quench the reaction, adding H_2O (0.3 mL), 15% NaOH (0.3 mL), and H_2O (0.9 mL) in order, dropwise by syringe at 0 °C. The resulting white slurry was filtered through Celite and rinsed with Et_2O (2 × 20 mL). The colorless filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to afford a colorless oil. Purification by silica gel flash chromatography (120 g, 35 mm ∅; hexanes to hexanes/EtOAc, 19:1) afforded 1.68 g (92%) of **17** as a colorless oil. An analytically pure sample was obtained by Kugelrohr distillation (80 °C/0.1 mmHg), affording 1.62 g (89%) of **17** as a colorless oil; bp 80 °C/0.1 mmHg; R_f = 0.67 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.0 Hz, 1 H, HC(6)), 7.25–7.17 (m, 2 H, HC(3,4)), 7.07–7.02 (m, 1 H, HC(5)), 5.46 (q, *J* = 5.0 Hz, 2 H, HC(9,10)), 2.83–2.76 (m, 2 H, HC(7)), 2.35–2.27 (m, 2 H, HC(8)), 1.97 (dt, *J* = 7.0, 6.5 Hz, 2 H, HC(11)), 1.36 (app sext, *J* = 7.5 Hz, 2 H, HC(12)), 0.88 (t, *J* = 7.5 Hz, 3 H, HC(13)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.3 (C1), 132.7 (C6), 131.2 (C10), 130.4 (C3), 129.0 (C9), 127.4 (C5), 127.2 (C4), 124.4 (C2), 36.4 (C7), 34.7 (C11), 32.8 (C8), 22.6 (C12), 12.7 (C13).

MS (EI): *m*/*z* (%) = 55 (92), 67 (15), 82 (48), 83 (70), 89 (20), 90 (33), 91 (17), 117 (34), 169 (100), 171 (98), 173 (43), 182 (18), 184 (17), 252 (20) $[M]^+$, 254 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{17}Br$: 252.0514; found: 252.0507.

Anal. Calcd for $C_{13}H_{17}Br$ (253.18): C, 61.67; H, 6.77. Found: C, 62.01; H, 6.69.

(*E*)-2-(3-Heptenyl)aniline (18)

By adopting the described procedure,[14b] to an oven-dried, 200-mL pressure tube equipped with a magnetic stir bar were added aryl bromide **17** (1.52 g, 6.0 mmol) and $(NH_4)_2SO_4$ (1.19 g, 9.0 mmol, 1.5 equiv), and then the tube was introduced into a glovebox. In the glovebox, in a separate oven-dried, 20-mL vial with a magnetic stir bar were added $Pd[P(2\text{-Tol})_3]_2$[23] (21.5 mg, 0.03 mmol, 0.005 equiv), Josiphos (CAS no. 158923-11-6; 16.6 mg, 0.03 mmol, 0.005 equiv), and dioxane (1 mL), and the mixture was stirred for 5 min. To the pressure tube were added NaO*t*-Bu (2.60 g, 27.0 mmol, 4.5 equiv), dioxane (60 mL), and the Pd/Josiphos solution (1 mL). The pressure tube was tightly sealed with the screw cap and removed from the glovebox. The reaction mixture was heated to 100 °C and stirred for 12 h. Then, the mixture was cooled to r.t. and diluted with EtOAc (30 mL). The resulting dark mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to yield a brown oil. Purification by silica gel flash chromatography (120 g, 35 mm ∅; hexanes to hexanes/EtOAc, 9:1) afforded 738 mg (65%) of **18** as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation (110 °C/0.1 mmHg), affording 701 mg (62%) of **18** as a colorless oil; bp 110 °C/0.1 mmHg; R_f = 0.43 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08–7.01 (m, 2 H, HC(3,5)), 6.74 (t, *J* = 7.5 Hz, 1 H, HC(4)), 6.68 (d, *J* = 8.0 Hz, 1 H, HC(6)), 5.50 (m, 2 H, HC(9,10)), 3.62 (br s, 2 H, NH_2), 2.55 (dd, *J* = 9.0, 6.5 Hz, 2 H, HC(7)), 2.32 (m, 2 H, HC(8)), 1.98 (m, 2 H, HC(11)), 1.38 (tq, *J* = 7.5, 7.5 Hz, 2 H, HC(12)), 0.89 (t, *J* = 7.5 Hz, 3 H, HC(13)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.1 (C1), 131.1 (C10), 129.5 (C9 or C3), 129.4 (C3 or C9), 126.9 (C5), 126.3 (C2), 118.7 (C4), 115.5 (C6), 34.7 (C11), 31.8 (C8), 31.5 (C7), 22.6 (C12), 13.7 (C13).

MS (ESI): *m*/*z* (%) = 106 (13), 190 (100) $[M + H]^+$, 191 (32).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{20}N$: 190.1596; found: 190.1595.

Anal. Calcd for $C_{13}H_{19}N$ (189.30): C, 82.48; H, 10.12; N, 7.40. Found: C, 82.48; H, 9.95; N, 7.69.

(*E*)-*N*-[2-(3-Heptenyl)phenyl]-4-methylbenzenesulfonamide (1k)[11]

To an oven-dried, 25-mL, round-bottomed flask equipped with a magnetic stir bar were added aniline **18** (568 mg, 3.0 mmol), CH_2Cl_2 (6 mL, 0.5 M), pyridine (315 µL, 3.9 mmol, 1.3 equiv), and TsCl (686 mg, 3.6 mmol, 1.2 equiv) in order at r.t. The reaction mixture was stirred for 12 h, then washed with 1 M HCl solution (5 mL) and brine (2 × 5 mL). The resulting organic layer was dried over Na_2SO_4, filtered,

and concentrated under reduced pressure (30 °C, 10 mmHg) to yield a yellow oil. The crude product was purified by silica gel flash chromatography (80 g, 30 mm ∅; hexanes to hexanes/EtOAc, 5:1) to afford 896 mg (87%) of **1k** as a yellow oil which crystallized upon standing. An analytically pure sample was obtained by recrystallization of the solid (boiling EtOAc/pentane, 1:10; 20 mL), affording 841 mg (82%) of **1k** as pale yellow crystals; mp 58–59 °C (sealed tube); R_f = 0.35 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.5 Hz, 2 H, HC(8)), 7.38 (d, *J* = 7.5 Hz, 1 H, HC(3)), 7.25 (d, *J* = 7.5 Hz, 2 H, HC(9)), 7.20–7.10 (m, 3 H, HC(aryl), 6.51 (br s, 1 H, HN), 5.41–5.29 (m, 2 H, HC(14,15)), 2.42 (s, 3 H, HC(11)), 2.41–2.35 (m, 2 H, HC(12)), 2.10 (q, *J* = 7.0 Hz, 2 H, HC(13)), 1.97 (q, *J* = 6.5 Hz, 2 H, HC(16)), 1.38 (sept d, *J* = 7.5, 1.0 Hz, 2 H, HC(17)), 0.90 (td, *J* = 7.5, 1.0 Hz, 3 H, HC(18)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.7 (C10), 136.6 (C7), 135.1 (C2), 134.0 (C1), 132.1 (C15), 129.9 (C6), 129.6 (C9), 128.5 (C14), 127.1 (C8), 126.9 (C5), 126.2 (C4), 124.5 (C3), 34.6 (C16), 32.8 (C13), 30.9 (C12), 22.5 (C17), 21.5 (C11), 13.7 (C18).

MS (ESI): *m*/*z* (%) = 118 (25), 130 (19), 132 (76), 146 (17), 187 (29), 188 (37), 189 (100), 190 (13), 205 (13), 286 (13), 342 (13), 344 (38) $[M + H]^+$, 360 (12), 366 (12).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{26}NO_2S$: 344.1684; found: 344.1680.

Anal. Calcd for $C_{20}H_{25}NO_2S$ (343.48): C, 69.93; H, 7.34; N, 4.08. Found: C, 69.89; H, 7.56; N, 4.05.

2-(4-Pentenyl)aniline (21) (Scheme 11)

By adopting the described procedure,[14b] to an oven-dried, 250-mL pressure tube equipped with a magnetic stir bar were added aryl bromide **20**[18] (2.45 g, 10.9 mmol) and $(NH_4)_2SO_4$ (2.16 g, 16.3 mmol, 1.5 equiv), and then the tube was introduced into a glovebox. In the glovebox, in a separate oven-dried, 20-mL vial with a magnetic stir bar were added $Pd[P(2\text{-}Tol)_3]_2$[23] (38.9 mg, 0.054 mmol, 0.005 equiv), Josiphos (CAS no. 158923-11-6; 30.2 mg, 0.054 mmol, 0.005 equiv), and dioxane (1 mL), and the mixture was stirred for 5 min. To the pressure tube were added NaO*t*-Bu (4.71 g, 49.0 mmol, 4.5 equiv), dioxane (110 mL), and the Pd/Josiphos solution (1 mL). The pressure tube was tightly sealed with the screw cap and removed from the glovebox. The reaction mixture was heated to 100 °C and stirred for 12 h. Then, the mixture was cooled to r.t. and diluted with EtOAc (50 mL). The resulting dark mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure (30 °C, 10 mmHg) to yield a brown oil. Purification by silica gel flash chromatography (120 g, 35 mm ∅; hexanes to hexanes/EtOAc, 6:1) afforded 1.07 g (61%) of **21** as a pale yellow oil. An analytically pure sample was obtained by Kugelrohr distillation (70 °C/0.1 mmHg), affording 1.01 g (57%) of **21** as a colorless oil; bp 70 °C/0.1 mmHg; R_f = 0.34 (hexanes/EtOAc, 4:1) [UV].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07 (td, *J* = 7.5, 1.5 Hz, 2 H, HC(3,5)), 6.76 (tt, *J* = 7.5, 1.5 Hz, 1 H, HC(4)), 6.70 (d, *J* = 8.0 Hz, 1 H, HC(6)), 5.89 (ddtd, *J* = 17.0, 10.0, 6.5, 1.5 Hz, 1 H, HC(10)), 5.09 (dp, *J* = 17.0, 1.5 Hz, 1 H, HC(11)), 5.04 (dt, *J* = 10.0, 1.5 Hz, 1 H, HC(11)), 3.62 (br s, 2 H, H_2N), 2.53 (t, *J* = 8.0 Hz, 2 H, HC(7)), 2.18 (dtd, *J* = 6.5, 6.5, 1.5 Hz, 2 H, HC(9)), 1.76 (qdd, *J* = 8.5, 7.0, 1.5 Hz, 2 H, HC(8)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.9 (C1), 138.4 (C10), 129.5 (C3), 126.9 (C5), 126.5 (C2), 118.8 (C4), 115.6 (C6), 114.9 (C11), 33.5 (C9), 30.5 (C7), 27.8 (C8).

MS (ESI): *m*/*z* (%) = 106 (10), 162 (100) $[M + H]^+$, 163 (15), 174 (10), 216 (25).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{16}N$: 162.1283; found: 162.1288.

Anal. Calcd for $C_{11}H_{15}N$ (161.24): C, 81.94; H, 9.38; N, 8.69. Found: C, 81.97; H, 9.13; N, 8.63.

4-Methyl-*N*-[2-(4-pentenyl)phenyl]benzenesulfonamide (1l)[11]

To an oven-dried, 25-mL, round-bottomed flask equipped with a magnetic stir bar were added aniline **21** (806 mg, 5.0 mmol), CH_2Cl_2 (10 mL, 0.5 M), pyridine (526 µL, 6.5 mmol, 1.3 equiv), and TsCl (1.14 g, 6.0 mmol, 1.2 equiv) in order at r.t. A condenser was installed on top of the flask and the reaction mixture was refluxed for 12 h, then cooled to r.t. and washed with 1 M HCl solution (10 mL) and brine (3 × 5 mL). The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure (30 °C, 10 mmHg) to yield a yellow oil. The crude product was purified by silica gel flash chromatography (120 g, 35 mm ∅; hexanes to hexanes/EtOAc, 5:1) to afford 1.34 g (85%) of **1l** as a white crystalline solid. An analytically pure sample was obtained by recrystallization of the solid (boiling pentane, 50 mL), affording 1.23 g (78%) of **1l** as white crystals; mp 70–71 °C (pentane); R_f = 0.30 (hexanes/EtOAc, 4:1) [UV].

IR (neat): 3280 (m), 1490 (m), 1392 (m), 1335 (s), 1305 (w), 1291 (w), 1274 (w), 1185 (w), 1160 (s), 1120 (m), 1092 (s), 1019 (w), 993 (w), 951 (w), 910 (s), 886 (w), 875 (w), 832 (w), 814 (m), 762 (m) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H, HC(8)), 7.40 (d, *J* = 8.0 Hz, 1 H, HC(6)), 7.25 (d, *J* = 8.0 Hz, 2 H, HC(9)), 7.21–7.11 (m, 3 H, HC(3,4,5)), 6.36 (br s, 1 H, HN), 5.78 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1 H, HC(15)), 5.09–5.01 (m, 2 H, HC(16)), 2.43 (s, 3 H, HC(11)), 2.34 (app t, *J* = 7.5 Hz, 2 H, HC(12)), 2.01 (app q, *J* = 7.0 Hz, 2 H, HC(14)), 1.49 (app p, *J* = 7.5 Hz, 2 H, HC(13)).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.8 (C10), 138.0 (C15), 136.6 (C7), 135.2 (C1), 134.0 (C2), 129.7 (C3), 129.6 (C9), 127.2 (C8), 126.9 (C4), 126.2 (C5), 124.5 (C6), 115.4 (C16), 33.1 (C14), 29.8 (C12), 29.0 (C13), 21.5 (C11).

MS (ESI): *m*/*z* (%) = 160 (15), 161 (93), 162 (16), 316 (100) $[M + H]^+$, 317 (20), 333 (34), 335 (38), 338 (95), 339 (22), 492 (72), 493 (47).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{22}NO_2S$: 316.1371; found: 316.1376.

Anal. Calcd for $C_{18}H_{21}NO_2S$ (315.43): C, 68.54; H, 6.71; N, 4.44. Found: C, 68.43; H, 6.92; N, 4.31.

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Supporting Information

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