Synthesis H. Wakamatsu et al. Paper

Synthesis of Various Heterocycles Having a Dienamide Moiety by Ring-Closing Metathesis of Ene-ynamides

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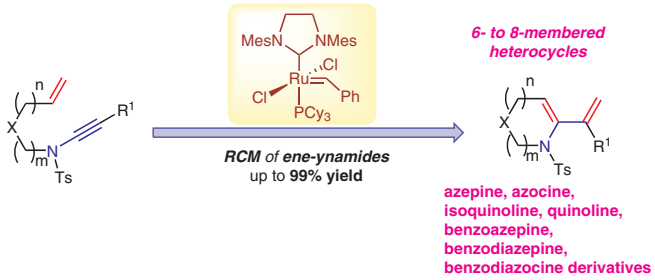

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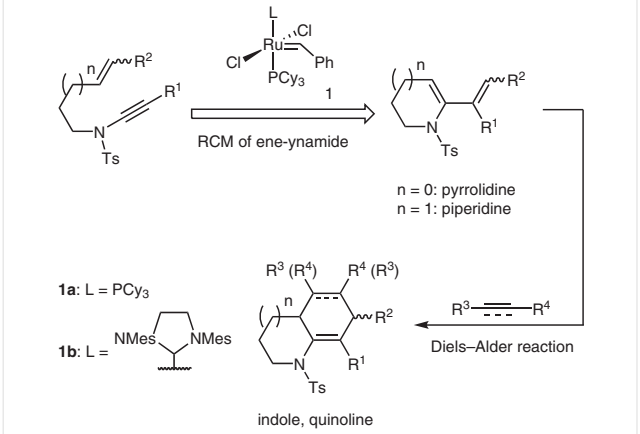
Abstract Ring-closing metathesis (RCM) of ynamides, having alkene substituents of various lengths on the side chain, was demonstrated using the second-generation Grubbs catalyst. When the reaction of ene-ynamides was carried out in the presence of 5 mol% of the catalyst, RCM proceeded smoothly to give quinoline or isoquinoline derivatives having a dienamide unit in good yields. Furthermore, RCM of ene-ynamides, having one more carbon on the side chain, proceeded smoothly to provide seven-membered heterocycles having a dienamide component. Similarly, eight-membered heterocycles, diazocine and benzodiazocine, were also synthesized by RCM of ene-ynamides in good yields.

Key words ruthenium carbene complex, ynamide, ring-closing metathesis, heterocycles, medium-sized ring

Carbon–carbon double bonds have been shown to be useful building blocks in synthetic organic chemistry.[1] Olefin metathesis, which is catalyzed by transition metal complexes, is one of the most powerful tools for the construction of the C=C bonds.[2] Ring-closing metathesis (RCM) is used as a key reaction for the synthesis of various natural products, and is the essential method for the construction of the carbon framework at this moment. Likewise, ring-closing enyne metathesis (RCEYM) has attracted much interest because various cyclic products having a conjugated diene moiety can be obtained in a single step.[3] The distinctive reactivity of ynamides, which have an electron-deficient π-orbital and higher stability relative to ynamines, is attractive for organic chemists.[4] As useful synthetic methods for the preparation of ynamides have already been reported by Kitamura,[5] Brückner[4i,6] and Hsung,[7] a variety of ynamides can be synthesized at present.

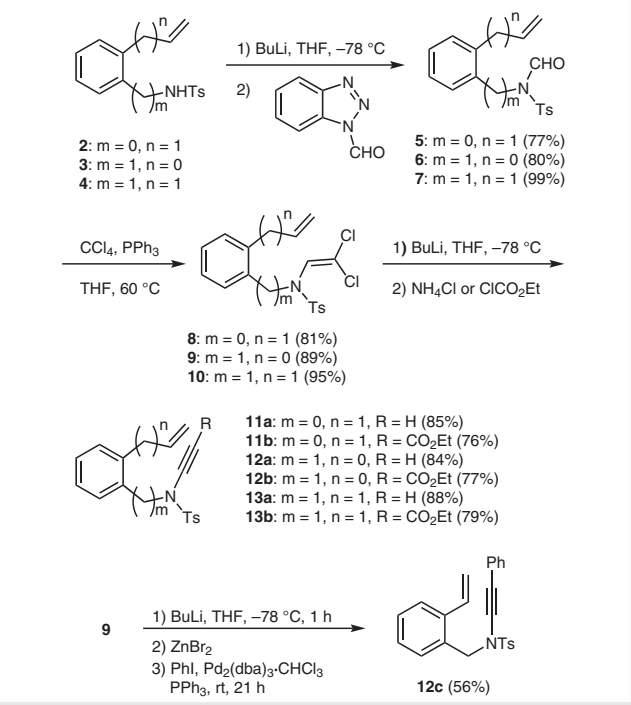
Several kinds of transition-metal-catalyzed reactions of ynamides, including [2+2+1] cycloaddition,[8g] Pauson–Khand reaction,[8h] cycloisomerization,[8i] triazole synthesis,[8j] [4+2] cycloaddition,[8k] [2+2] cycloaddition,[8l] and Sonogashira cross-coupling,[8m,n] have been reported in recent years.[8] We have studied RCM of ene-ynamides, which can be applied for the synthesis of pyrrolizidine and piperidine derivatives. Furthermore, the diene derivative, which was obtained by RCM of ene-ynamide, can afford indole and quinoline derivatives by Diels–Alder reaction (Scheme 1).[9]



Scheme 1 Synthesis of pyrrolidine and piperidine derivatives using RCM of ene-ynamide

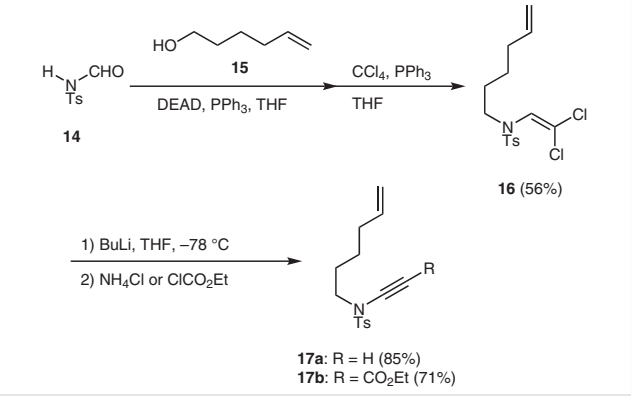
On the basis of the above discussion, we decided to explore the further expansion of the RCM of ene-ynamides. Herein, we wish to report the synthesis of various heterocyclic compounds having a dienamide moiety, especially to establish the efficient synthesis of seven- and eight-membered heterocycles.[10] Ene-ynamide derivatives were prepared by the several synthetic methods, as shown in Schemes 2 through 5.

Tosyl amides **2**–**4**, which were synthesized by the literature procedure,[11–13] were treated with butyllithium, followed by treatment with formylbenzotriazole, to provide *N*-formyl derivatives **5**–**7**. The ynamide unit was constructed by the modified Corey–Fuchs alkyne synthesis[6,14] to obtain ene-ynamides **11**–**13**. Ene-ynamide **12c**, having a phenyl group on the alkyne, was obtained from compound **9** by Negishi coupling (Scheme 2).[15]



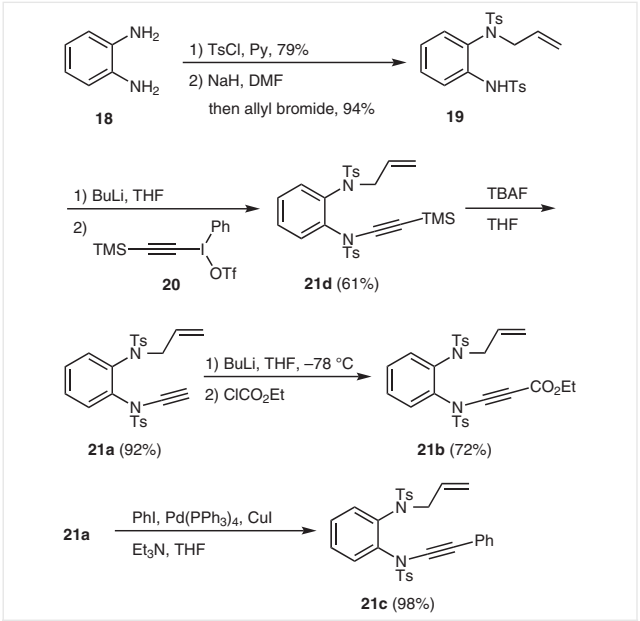
Scheme 2 Preparation of substrate for the synthesis of quinoline, isoquinoline, and benzazepine derivatives

Mitsunobu reaction[16] of **14** and **15**, followed by dichloroolefination, provided **16**, which could be converted into **17** in good yield by treatment with butyllithium (Scheme 3).



Scheme 3 Preparation of substrate for the synthesis of azepine derivative

Allyl tosyl amide **19**, whose synthesis was reported by Stetter,[17] was reacted with butyllithium and iodonium salt **20** to provide **21d** in 61% yield. Ene-ynamide **21a** was obtained from **21d** by the removal of the TMS group on the alkyne. The synthesis of ene-ynamide **21b** and **21c** from **21a** was accomplished by lithiation on the terminal alkyne or Sonogashira cross-coupling[18] (Scheme 4).



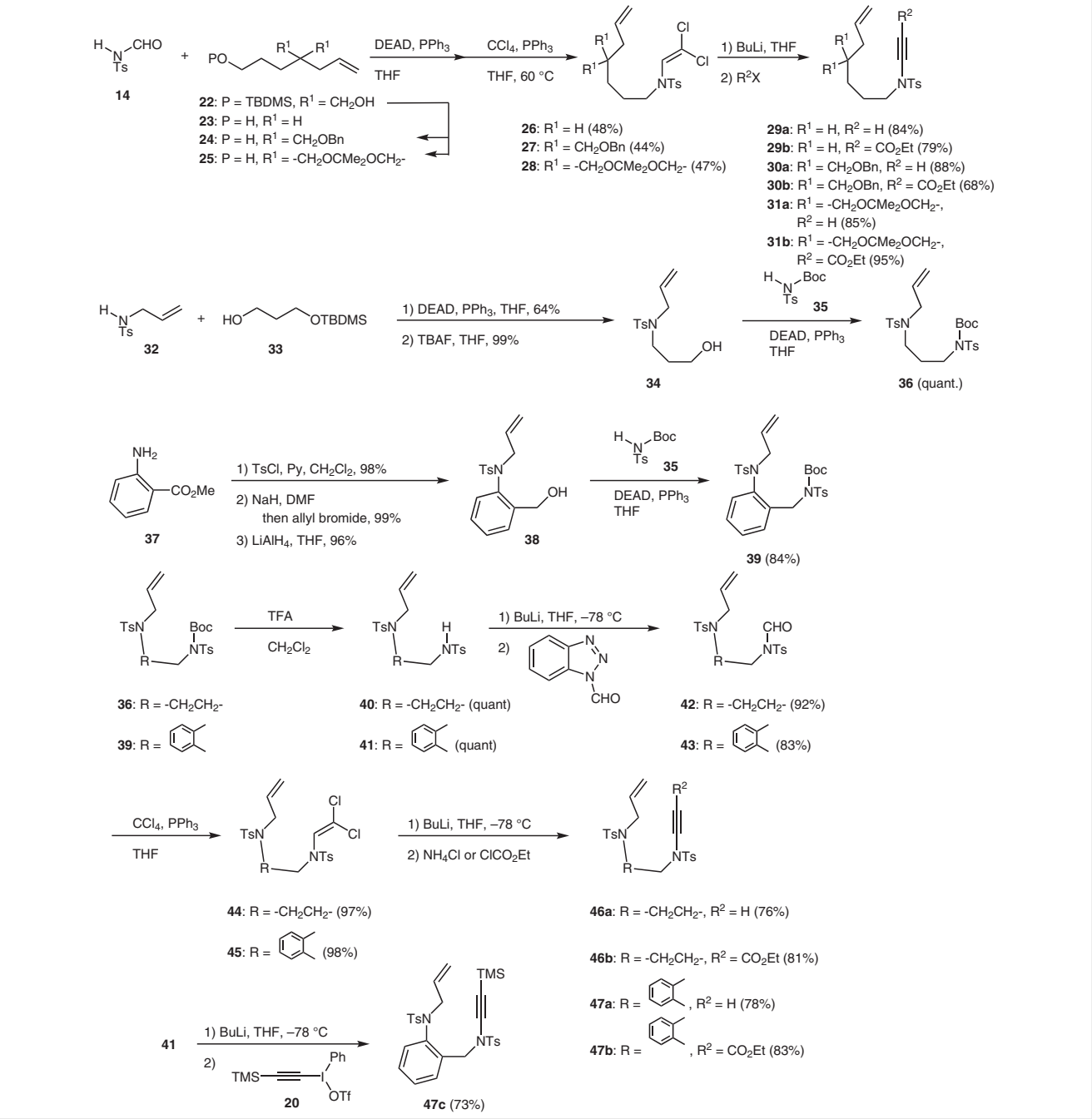
Scheme 4 Preparation of substrate for the synthesis of benzodiazepine derivatives

Alcohols **24** and **25** were prepared from **22**[19] by the easy exchange of its protecting group. Mitsunobu reaction of *N*-tosylformamide **14** and alcohol **23**–**25**, followed by treatment with carbon tetrachloride and triphenylphosphine, provided dichloroolefins **26**–**28**, which were treated with butyllithium and ammonium chloride or ethyl chlorocarbonate to obtain ene-ynamides **29**–**31** in good yields (Scheme 5).

The synthetic route for the preparation of compounds **46** and **47** is shown in Scheme 5. *N*-Boc-protected tosylamide derivative **36** was obtained through a stepwise Mitsunobu reaction of propanediol derivative **33** with allyl tosyl amide **32** and *N*-Boc tosylamide **35**, in good yield. On the other hand, the synthesis of an another *N*-Boc tosylamide derivative **39** having a phenyl group on the alkyl chain was accomplished by Mitsunobu reaction of **38**, which was synthesized by a literature procedure.[20] *N*-Boc deprotection of the compounds **36** and **39** by treatment with trifluoroacetic acid afforded tosylamide derivatives **40** and **41**, which upon formylation, dichloroolefination, and alkynylation provided ene-ynamides **46a**, **46b**, and **47a**, **47b**, respectively. TMS-protected ene-ynamide **47c**, on the other hand, was obtained by the reaction of tosylamide **41** with butyllithium and iodonium salt **20**.

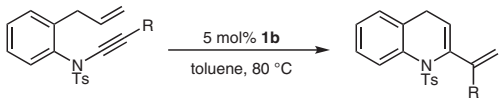
The synthesis of quinoline derivative **48** is shown in Table 1. The reaction of **11a** in the presence of 5 mol% of the second-generation Grubbs catalyst **1b** in toluene at 80 °C for 0.5 hour under ethylene atmosphere furnished quinoline derivative **48a** in 93% yield (Table 1, entry 1). The reaction of ene-ynamide having an ethoxycarbonyl group on the alkyne did not give good results (entry 2). However, this problem was solved by replacing ethylene by argon, leading to the formation of the cyclized product **48b** in 79% yield (entry 3).

Next, Diels–Alder reaction of **48a** with dimethyl acetylenedicarboxylate (DMAD) was examined. It was found that the construction of acridine skeleton was possible, and compound **49** was obtained in 45% yield (Scheme 6).



Scheme 5 Preparation of substrate for the synthesis of azocine derivatives

Table 1 Construction of Quinoline Ring

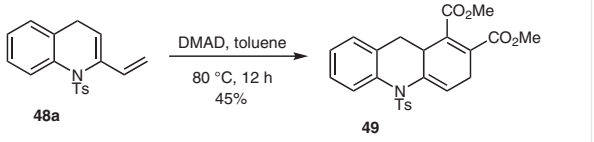


11a: R = H
11b: R = CO_2Et

48a: R = H
48b: R = CO_2Et

Entry	Substrate	Atmosphere	Time (h)	48	Yield (%)
1	**11a**	CH_2=CH_2	0.5	**48a**	93
2	**11b**	CH_2=CH_2	12	**48b**	49[a]
3	**11b**	Ar	1	**48b**	79

[a] Starting material **11b** was recovered in 11% yield.

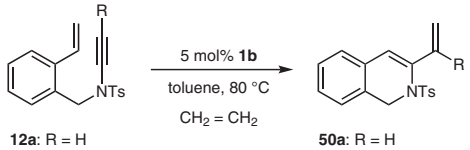


48a **49**

Scheme 6 Synthesis of acridine derivative by Diels–Alder reaction of cyclic dienamides

The synthesis of isoquinoline derivatives was examined as further application of the construction of 6+6 ring system. The reaction of ene-ynamide **12a** with 5 mol% of catalyst **1b** under an identical reaction conditions proceeded smoothly to furnish the cyclized product **50a** in 70% yield, in only 30 minutes (Table 2, entry 1). Substituted alkynes can be used in this isoquinoline synthesis, in contrast to the quinolone synthesis. The cyclized product **50b** was obtained in 78% yield, when the ethoxycarbonyl group was substituted on the alkyne (entry 2). Although a slightly longer reaction time was required in the case of the phenyl-substituted alkyne, the resulting isoquinoline derivative **50c** was obtained in almost identical yield (entry 3).

Table 2 Construction of Isoquinoline Ring

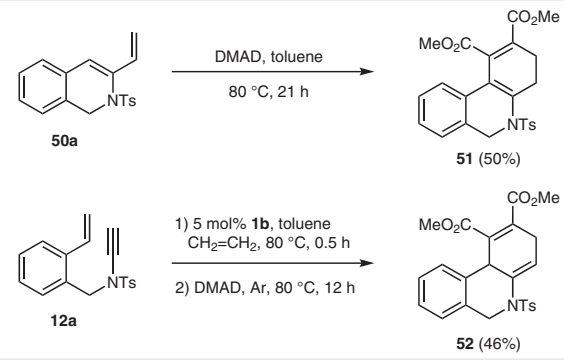


12a: R = H
12b: R = CO_2Et
12c: R = Ph

50a: R = H
50b: R = CO_2Et
50c: R = Ph

Entry	Substrate	Time (h)	50	Yield (%)
1	**12a**	0.5	**50a**	70
2	**12b**	1	**50b**	78
3	**12c**	1.5	**50c**	77

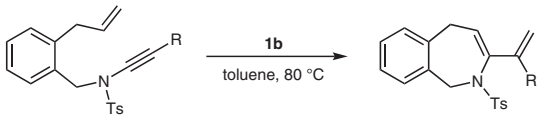
When a toluene solution of **50a** and DMAD was stirred at 80 °C for 21 hours, the Diels–Alder reaction proceeded smoothly to provide phenanthridine derivative **51** in 50% yield. However, the double bond of **51** was isomerized to a conjugated position, which was different from the expected position. On the other hand, tricyclic compound **52** was obtained without isomerization of the double bond when the metathesis reaction of **12a** was carried out under identical conditions, followed by the treatment with DMAD under argon atmosphere (Scheme 7).[21] It is not clear at this stage why the double bond of **52** is not isomerized to a conjugated position. If the lone pair of nitrogen or π electrons is associated to ruthenium center, the double bond isomerization is suppressed.



Scheme 7 Synthesis of phenanthridine derivatives

The construction of a benzazepine ring was examined next. When a toluene solution of **13a** was stirred with 10 mol% of the catalysts **1b** at 80 °C for 1.5 hours under an ethylene atmosphere, the cyclized product **53a** was obtained in 22% yield (Table 3, entry 1). A corresponding reaction carried out under an argon atmosphere led to an improved yield of **53a** at 49% (entry 2). RCM of **13b**, which was prepared by the introduction of an ethoxycarbonyl group on the alkyne, was attempted next. When the reaction of **13b** was carried out in a manner similar as that used for the synthesis of **53a**, benzazepine derivative **53b** was obtained in 69% yield (entry 3). This yield could be enhanced to 84%

Table 3 Construction of Benzazepine Ring



13a: R = H
13b: R = CO_2Et

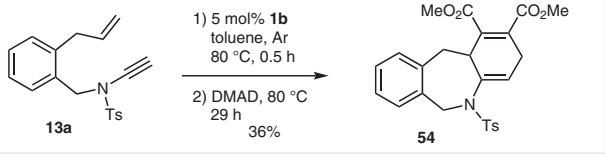
53a: R = H
53b: R = CO_2Et

Entry	Substrate	Atmosphere	1b (mol%)	Time (h)	53	Yield (%)[a]
1	**13a**	CH_2=CH_2	10	1.5	**53a**	22
2	**13a**	Ar	5	0.5	**53a**	49
3	**13b**	CH_2=CH_2	10	3.5	**53b**	69
4	**13b**	Ar	5	0.5	**53b**	84

[a] Isolated yield.

by performing the reaction under an argon atmosphere (entry 4).

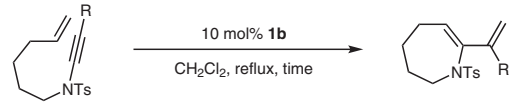
Furthermore, the synthesis of **54** was examined with the aim of constructing the dibenzoazepine skeleton (Scheme 8). Tricyclic heterocycle **54** was obtained in 36% yield when **13a** was exposed to a catalytic amount of **1b** in toluene at 80 °C for 0.5 hour under argon atmosphere, followed by treatment with DMAD at the same temperature.



Scheme 8 Synthesis of dibenzoazepine derivative

Next, RCM of linear α,ω-ene-ynamides was examined. When the reaction of **17a** was carried out in the presence of the catalyst **1b** in toluene at 80 °C for 1 hour, starting material **17a** was recovered in 53% yield (Table 4, entry 1). Replacement of toluene by CH_2Cl_2 led to a better result, and **55a** was obtained in 36% yield after heating for 15 hours, together with 38% of **17a** (entry 2). A similar result was achieved when the reaction was conducted under an argon atmosphere or upon prolonging the reaction time (entries 3 and 4). In the case of **17b**, a substrate having an ethoxycarbonyl group on the alkyne, the yield of the cyclized product **55b** was only 5% when the reaction was carried out in toluene with heating (entry 5). However, a higher yield of **55b** was obtained when the reaction was carried out in CH_2Cl_2 (entry 6).

Table 4 Construction of Azepine Ring



17a: R = H
17b: R = CO_2Et

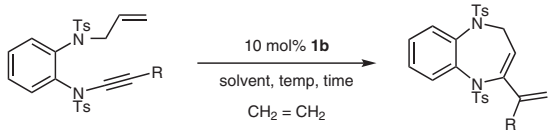
55a: R = H
55b: R = CO_2Et

Entry	Substrate	Atmosphere	Time (h)	55	Yield (%)[a]	17	Recovery of 17 (%)[a]
1[b]	**17a**	CH_2=CH_2	1	–	–	**17a**	53
2	**17a**	CH_2=CH_2	15	**55a**	36	**17a**	38
3	**17a**	Ar	26	**55a**	37	**17a**	33
4	**17a**	Ar	48	**55a**	33	**17a**	31
5[b]	**17b**	CH_2=CH_2	3	**55b**	5	**17b**	74
6	**17b**	CH_2=CH_2	1.5	**55b**	74[c]	**17b**	–

[a] Yields were determined by ^{1}H NMR spectroscopy using (*E*)-stilbene as an internal standard.
[b] Reaction was carried out in the presence of 5 mol% **1b** in toluene at 80 °C.
[c] Isolated yield.

Subsequently, the synthesis of 1,5-benzodiazepine derivatives was also examined. When a solution of **21a** in toluene was exposed to a catalytic amount of **1b** at 80 °C for 1 hour, the starting material **21a** was not consumed, and an inseparable complex mixture consisting of **21a**, cyclized product **56a**, an intermolecular metathesis product with ethylene, and undefined products was obtained (Table 5, entry 1). Replacement of the solvent and a longer reaction time gave a similar result (entry 2). The reaction of the TMS-substituted ene-ynamide **21d** did not proceed and the starting material was recovered (entry 3). Surprisingly, when **21b** was used as the substrate instead of **21a**, benzodiazepine **56b** was obtained in quantitative yield (entry 4). Reduction of the catalyst amount did not affect the yield of **56b** (entry 5). The RCM also proceeded smoothly in CH_2Cl_2 as the solvent, although a longer reaction time was required (entry 6). An excellent yield of **56b** was also observed when the reaction was carried out under an argon atmosphere (entry 7). Likewise, when the phenyl-substituted ene-ynamide **21c** was used as the substrate, benzodiazepine **56c** was obtained in quantitative yield (entry 8).

Table 5 Construction of Benzodiazepine Ring



21a: R = H
21b: R = CO_2Et
21c: R = Ph
21d: R = TMS

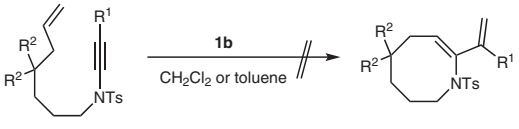
56a: R = H
56b: R = CO_2Et
56c: R = Ph
56d: R = TMS

Entry	Substrate	Solvent	Temp (°C)	Time (h)	56	Yield (%)[a]
1	**21a**	toluene	80	1	–	–
2	**21a**	CH_2=CH_2	reflux	28	–	–
3	**21d**	toluene	80	5	–	–[b]
4	**21b**	toluene	80	0.5	**56b**	99
5[c]	**21b**	toluene	80	0.5	**56b**	99
6	**21b**	CH_2Cl_2	reflux	15	**56b**	97
7[d]	**21b**	CH_2Cl_2	reflux	20	**56b**	95
8	**21c**	toluene	80	1	**56c**	97

[a] Isolated yield.
[b] Recovered **21d**: 87%.
[c] Catalyst **1b** used: 5 mol%.
[d] Reaction was carried out under an argon atmosphere.

Encouraged by the successful construction of the six-membered rings and a seven-membered ring, we became interested in the synthesis of eight-membered heterocycles. Initially, various linear ene-ynamides were examined for the synthesis of azocine derivative **57**. However, the desired cyclized product **57** was not obtained in any case, and the

only a trace amount of alkene dimer, formed by the intermolecular reaction of the ene-ynamides was observed in NMR experiment (Scheme 9).

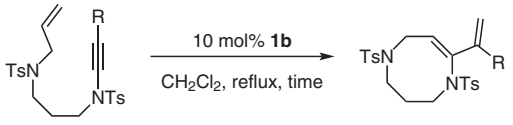


R^1 = H or CO_2Et
29: R^2 = H
30: R^2 = CH_2OBn
31: R^2 = -$CH_2OCMe_2OCH_2$-

Scheme 9 Construction of azocine ring

Furthermore, RCM of linear ene-ynamide **46**, which contains two tosylamide groups in the chain, was examined. When a CH_2Cl_2 solution of **46a** was heated for 21 hours in the presence of 10 mol% of **1b**, starting material **46a** was recovered in 33% yield (Table 6, entry 1). The introduction of an ethoxycarbonyl group on the alkyne promoted the formation of an eight-membered ring, and diazocine **58b** was obtained in 15% yield (entry 2). Improved yield was achieved when the reaction was performed under an argon atmosphere (entry 3). Higher recovery of starting material **46b** was observed when toluene was used as the solvent (entry 4). However, an encouraging result was observed in the construction of an eight-membered ring, and **58b** was obtained in 78% yield when the reaction was conducted under high-dilution conditions (entry 5).

Table 6 Construction of Diazocine Ring



46a: R = H
46b: R = CO_2Et

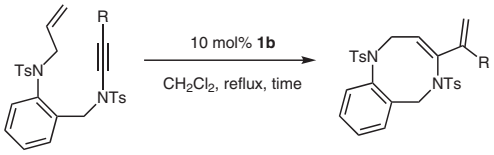
58a: R = H
58b: R = CO_2Et

Entry	Substrate	Atmosphere	Time (h)	58	Yield (%)[a]	46	Recovery of 46 (%)[a]
1	**46a**	CH_2=CH_2	21	–	–	**46a**	33
2	**46b**	CH_2=CH_2	21	**58b**	15	**46b**	49
3	**46b**	Ar	21	**58b**	33	**46b**	25
4[b]	**46b**	CH_2=CH_2	6	**58b**	–	**46b**	68
5[c]	**46b**	Ar	24	**58b**	78[d]	–	–

[a] Yields were determined by ^{1}H NMR spectrum using (*E*)-stilbene as an internal standard.
[b] Reaction was carried out in the presence of 5 mol% **1b** in toluene at 80 °C.
[c] Reaction was carried out under low concentration (0.002 M).
[d] Isolated yield.

Next, the synthesis of benzodiazocine was examined. The reaction of **47a** with the catalyst **1b** did not proceed, and starting material was recovered (Table 7, entry 1); shortening of the reaction time did not affect the result (entry 2). Then, a solution of **47b** in CH_2Cl_2 was heated in the presence of **1b** for 21 hours, and the reaction was monitered by TLC (entry 3). A new spot appeared on the TLC plate, suggesting the formation of **59b**. However, it was difficult to deduce the correct structure of **59b** due to the broad peaks in its ^{1}H NMR spectrum. This was probably due to the rapid interconversion of several stable confomers under the influence of the benzene ring, at room temperature. The peaks were clearly separated when the ^{1}H NMR spectrum was recorded at low temperature of –50 °C (Figure 1). We have reported that the dimeric compound was obtained, because the largest *m*/*z* value of FAB-MS spectra was observed at 1133 (M^+ + H).[10] However, the structure of the metathesis product was conclusively established by X-ray crystallography (Figure 2), and it was found that the desired eight-membered ring **59b** was obtained in 14% yield.

Table 7 Construction of Benzodiazocine Ring



47a: R = H
47b: R = CO_2Et
47c: R = Ph

59a: R = H
59b: R = CO_2Et
59c: R = Ph

Entry	Substrate	Atmosphere	Time (h)	59	Yield (%)[a]	47	Recovery of 47 (%)[a]
1	**47a**	CH_2=CH_2	21	–	–	**47a**	58
2[b]	**47a**	CH_2=CH_2	0.5	–	–	**47a**	53
3	**47b**	CH_2=CH_2	21	**59b**	14	**47b**	63
4	**47b**	Ar	21	**59b**	52	**47b**	44
5[b]	**47b**	CH_2=CH_2	6	–	–	**47b**	86
6[b]	**47b**	Ar	2	**59b**	77	–	–
7[b]	**47c**	Ar	17	–	–	**47c**	83
8	**47c**	Ar	6	–	–	**47c**	99

[a] Isolated yield.
[b] Reactions were carried out in the presence of 5 mol% **1b** in toluene at 80 °C.

An argon atmosphere was effective for the cyclization of **47b**, and the yield of **59b** was increased to 52% (Table 7, entry 4). Appropriate combination of the solvent and the atmosphere was important for the formation of **59b**. Upon changing the solvent to toluene from CH_2Cl_2, high recovery of **47b** was observed under an ethylene atmosphere (entry 5) and a higher yield of **59b** was observed under an argon atmosphere (entry 6). Unfortunately, in the case of the phenyl-substituted ene-ynamide **47c**, the formation of the eight-membered heterocycle **59c** was not observed, and the starting material was recovered in high yield (entries 7, 8).

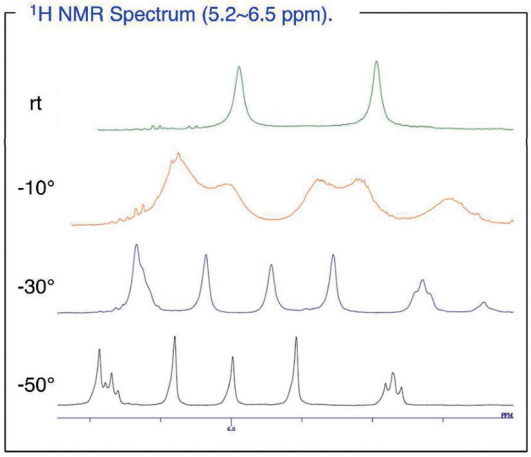


Figure 1 ^{1}H NMR spectrum of **59b**

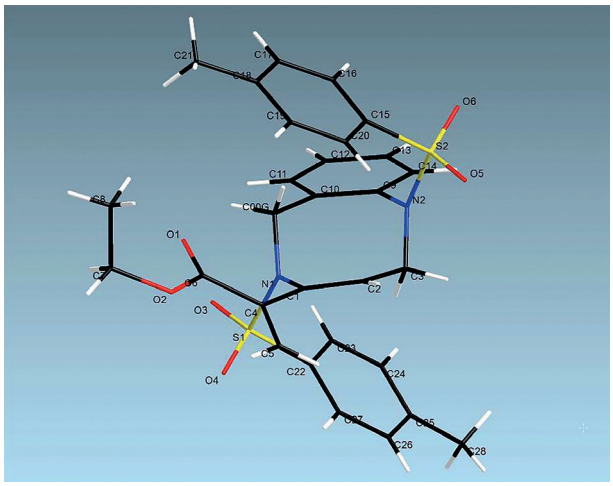
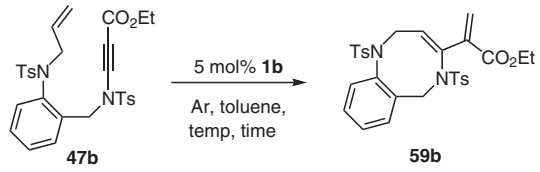


Figure 2 X-ray crystal structure of **59b**

Furthermore, the effect of temperature on the construction of the eight-membered-ring compounds was examined (Table 8). A lower reaction rate was observed with the decreasing reaction temperature, and **59b** was obtained in 45% yield at room temperature with the recovery of the starting material **47b** in 16% yield (entry 3).

It is thought that this reaction progresses via one of the two pathways described in Scheme 10. In the yne-then-ene pathway (cycle a), the carbene complex **1** first reacts with substrate **A** or ethylene to provide ruthenium carbene complex **I**, which is the active species for the metathesis reaction. Carbene complex **I** then reacts with the alkyne part of **A** to provide ruthenacyclobutene **II**, which is converted to complex **III**. If the ruthenium carbene part of **III** reacts with the alkene part intramolecularly, ruthenacyclobutane **IV** would be obtained, which then converts to product **B**, regenerating ruthenium carbene complex **I**. On the other hand, ruthenium carbene **V** is thought to be formed, when

Table 8 Temperature Effect for the Construction of Eight-Membered Ring



47b **59b**

Entry	Temp (°C)	Time (h)	Yield of **59b** (%)[a]	Recovery of **47b** (%)[a]
1	80	2	77	–
2	50	10	57	4
3	r.t.	42	45	16

[a] Isolated yield.

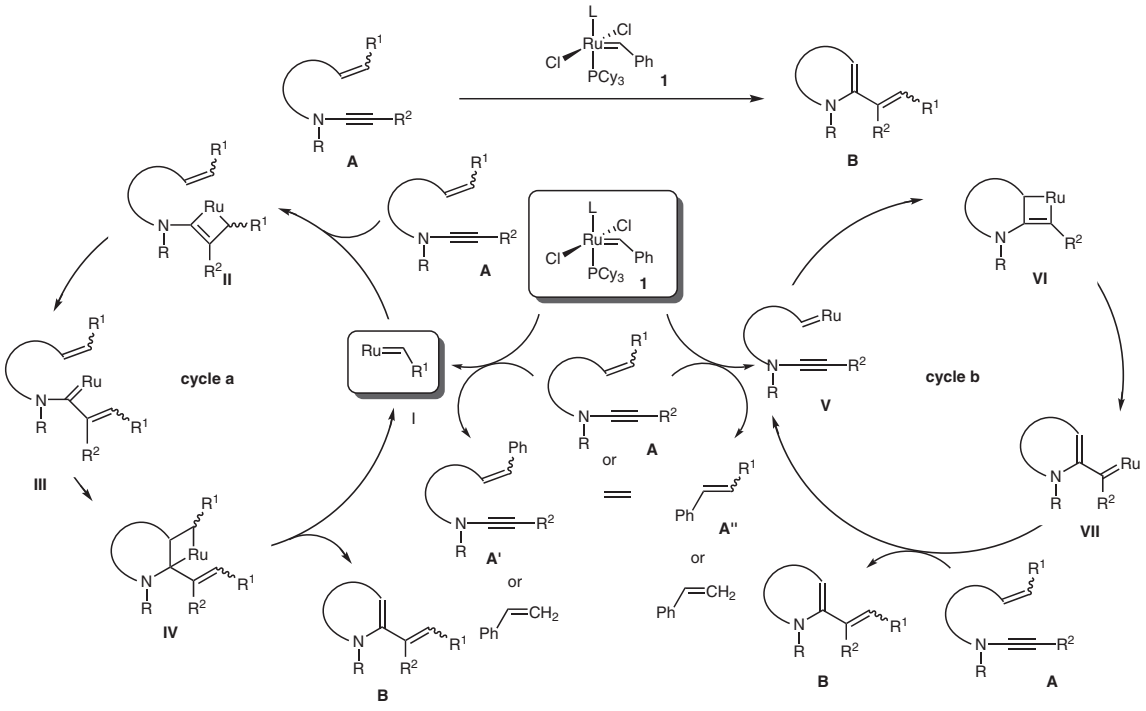
1 reacts with the alkene part of **A** (cycle b, ene-then-yne pathway). The carbene part of complex **V** then reacts with the alkyne part of **V** intramolecularly to provide ruthenacyclobutene **VI**, which converts into complex **VII**. If the carbene part of **VII** reacts with **A** intermolecularly, the desired product **B** would be obtained together with **V**. Two intriguing results were observed in the construction of the seven- and eight-membered ring:

1) The desired product was obtained in high yield when substituents were present on the terminal alkyne, while the yield of the cyclized product was decreased in the case of unsubstituted ene-ynamides.

2) The reaction proceeded under an argon atmosphere to provide the cyclized product in a yield similar to that obtained under an ethylene atmosphere.

The reactivity of the ruthenium complex with the C≡C bond should increase because of the higher electron density of ynamides. As a result, the yne-then-ene mechanism would predominate (cycle a). On the other hand, it is thought that the reaction of the ruthenium complex and the double bond have an advantage when a substituent exists on the terminal alkyne. The ruthenium carbene should react with the double bond instead of the triple bond, by the introduction of the ethoxycarbonyl group on the alkyne. These effects, which decrease the electron density of ynamides, would favor the predominance of the ene-then-yne mechanism (cycle b).

Taking into consideration the ring-closure factor, it is proposed that the rate of ring closure for medium-sized rings is lower than that for five- or six-membered rings. If the conversion rate from **III** to **IV** decreases, complex **III** would react with the substrate or the other alkene species to provide a variety of alkene compounds. On the other hand, if the conversion rate from **V** to **VI** decreases, complex **V** would react intermolecularly with the alkene part of an another substrate to form the alkene dimer. In addition, complex **V** would react only with ethylene in the case of the reaction of **47b** under ethylene atmosphere.



Scheme 10 Proposed reaction mechanism

It is more than evident from the current study that the reaction can proceed by both mechanisms, depending on the substituent on the terminal alkyne, although a recent study strongly supports the predominance of the initial cyclometalation on an alkene over an alkyne.[22] It is presumed that the reaction progresses via cycle b in the substrate with the ethoxycarbonyl group on the alkyne. In other words, the construction of medium-sized rings, which is a challenging task in organic chemistry, is achieved by the modification of the substrates suitable for cycle b.

In conclusion, the synthesis of various heterocycles having a dienamide unit was attempted by RCM of ene-ynamides. The reaction proceeded smoothly to provide the products in high yields in the synthesis of quinoline and isoquinoline derivatives, and the argon atmosphere was acceptable for the synthesis of quinoline derivatives. The introduction of an ethoxycarbonyl group on the terminal alkyne of the ene-ynamide was conducive for the construction of the seven-membered ring, although the synthesis of benzodiazepine derivatives from non-substituted ene-ynamides was difficult. Further, the presence of an ethoxycarbonyl group on the terminal alkyne of the ene-ynamides and an argon atmosphere under the given reaction conditions were necessary for the formation of the eight-membered ring. In particular, an eight-membered ring could be constructed under these reaction conditions; thus, this method would serve as a useful strategy for the construction of eight-membered rings, which is a challenging task in organic chemistry.

The metathesis reactions were carried out under an atmosphere of ethylene (1 atm) or an argon atmosphere (1 atm). All other manipulations were carried out under an atmosphere of argon, unless otherwise mentioned. Ru complexes were purchased from Aldrich Chemical Company. All other solvents and reagents were purified when necessary using standard procedure. Column chromatography was performed on silica gel 60 N (spherical, neutral, 40–60 µm, Kanto Chemical Co.). IR spectra were recorded on PerkinElmer FT-IR 1725X spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer. Chemical shift values were reported in ppm (δ) downfield from TMS as an internal standard, or residual solvent peak [^{1}H NMR, $CHCl_3$ (7.24): ^{13}C NMR, $CHCl_3$ (77.0)]. Coupling constants (*J*) are reported in hertz (Hz). EI mass spectra were recorded on a Jeol JMN-DX 303/JMA-DA 5000 mass spectrometer.

N-(2-Allylphenyl)-*N*-formyl-*p*-toluenesulfonamide (5)

To a solution of **2** (1.37 g, 4.77 mmol) in THF (25 mL) was added BuLi (3.6 mL, 5.72 mmol, 1.58 M hexane solution) slowly at –78 °C, and stirred at the same temperature for 1 h. To the resulting mixture was added 1-formylbenzotriazole (1.40 g, 9.53 mmol), and warmed to –30 °C for 1 h. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/Et_2O 3:1) to provide **5** (1.15 g, 77%) as a colorless oil.

IR (neat): 1715 (s), 1597 (m), 1361 (s), 1172 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (br, 1 H), 7.61 (d, *J* = 8.2 Hz, 2 H), 7.40–7.29 (m, 4 H), 7.16 (dt, *J* = 1.5, 7.7 Hz, 1 H), 6.66 (d, *J* = 7.7 Hz, 1 H), 5.68 (dddd, *J* = 6.3, 7.3, 10.1, 16.9 Hz, 1 H), 5.08–5.00 (m, 2 H), 3.19 (dd, *J* = 7.3, 15.9 Hz, 1 H), 2.99 (dd, *J* = 6.3, 15.9 Hz, 1 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 145.8, 140.4, 135.3, 134.5, 130.4, 130.2, 130.1, 130.1, 129.9, 128.2, 127.1, 117.2, 35.1, 21.7.

MS (EI): *m*/*z* = 315 (M^+), 287, 160, 132, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}NO_3S$ (M^+): 315.0929; found: 315.0926.

N-Formyl-*N*-(2-vinylbenzyl)-*p*-toluenesulfonamide (6)

According to the procedure for the synthesis of **5**, a solution of **3** (1.76 g, 6.12 mmol), BuLi (4.7 mL, 7.35 mmol, 1.58 M hexane solution) and 1-formylbenzotriazole (1.80 g, 12.25 mmol) in THF (30 mL) was stirred at 0 °C for 1 h to afford **6** (1.54 g, 80%) after purification by column chromatography on silica gel (hexane/EtOAc 5:1) as a colorless oil.

IR (neat): 1699 (s), 1597 (m), 1361 (s), 1166 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (s, 1 H), 7.40 (d, *J* = 8.2 Hz, 2 H), 7.26–7.09 (m, 6 H), 6.85 (dd, *J* = 11.1, 17.4 Hz, 1 H), 5.36 (dd, *J* = 1.5, 17.4 Hz, 1 H), 5.25 (dd, *J* = 1.5, 11.1 Hz, 1 H), 4.87 (s, 2 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 144.9, 137.1, 135.2, 133.9, 131.0, 129.7, 128.9, 128.0, 127.7, 127.1, 126.2, 117.1, 42.9, 21.5.

MS (EI): *m*/*z* = 315 (M^+), 160, 133, 115, 91.

HRMS (EI): *m*/*z* calcd for $C_{17}H_{17}NO_3S$ (M^+): 315.0929; found: 315.0922.

N-(2-Allylbenzyl)-*N*-formyl-*p*-toluenesulfonamide (7)

According to the procedure for the synthesis of **5**, a solution of **4** (2.95 g, 9.78 mmol), BuLi (7.4 mL, 11.74 mmol, 1.58 M hexane solution) and 1-formylbenzotriazole (2.88 g, 19.57 mmol) in THF (50 mL) was stirred at 0 °C for 40 min to afford **7** (3.18 g, 99%) after purification by column chromatography on silica gel (hexane/Et_2O 2:1) as a colorless oil.

IR (neat): 1699 (s), 1597 (m), 1361 (s), 1166 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 1 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.14 (d, *J* = 7.7 Hz, 1 H), 7.06–6.99 (m, 3 H), 5.86 (ddt, *J* = 10.3, 16.9, 6.0 Hz, 1 H), 5.05 (dd, *J* = 1.5, 10.3 Hz, 1 H), 4.88 (dd, *J* = 1.5, 16.9 Hz, 1 H), 4.77 (s, 2 H), 3.35 (d, *J* = 6.0 Hz, 2 H), 2.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 144.8, 136.9, 135.9, 134.7, 132.0, 129.5, 129.2, 127.3, 127.2, 126.8, 126.1, 115.7, 42.2, 36.4, 21.0.

MS (EI): *m*/*z* = 329 (M^+), 174, 130, 115, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{19}NO_3S$ (M^+): 329.1086; found: 329.1082.

N-(2-Allylphenyl)-*N*-(2,2-dichlorovinyl)-*p*-toluenesulfonamide (8)

To a solution of **5** (1.15 g, 3.65 mmol) and PPh_3 (2.39 g, 9.12 mmol) in THF (24 mL) was added CCl_4 (2.9 mL, 29.90 mmol) in THF (12 mL, total 0.1 M) at 60 °C over 3 h, and stirred at the same temperature for 1 h. After cooling the reaction mixture to r.t., sat. aq $NaHCO_3$ was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to provide **8** (1.12 g, 81%) as a pale red oil.

IR (neat): 1598 (w), 1367 (s), 1170 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.3 Hz, 2 H), 7.33–7.28 (m, 4 H), 7.10 (s, 1 H), 7.08 (m, 1 H), 6.71 (d, *J* = 7.8 Hz, 1 H), 5.83 (m, 1 H), 5.15–5.10 (m, 2 H), 3.35 (d, *J* = 4.9 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 140.7, 135.6, 135.2, 134.4, 130.0, 129.7, 129.7, 129.0, 127.8, 126.4, 125.9, 116.9, 112.8, 35.4, 21.5.

MS(EI): *m*/*z* = 381 (M^+), 285, 226, 191, 150, 130, 115, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}{}^{35}Cl_2NO_2S$ (M^+): 381.0357; found: 381.0360.

N-(2,2-Dichlorovinyl)-*N*-(2-vinylbenzyl)-*p*-toluenesulfonamide (9)

According to the procedure for the synthesis of **8**, a solution of **6** (1.42 g, 4.50 mmol), PPh_3 (2.95 g, 11.26 mmol) and CCl_4 (3.6 mL, 36.92 mmol) in THF (45 mL) was stirred at 60 °C for 12 h to afford **9** (1.53 g, 89%) as a pale yellow solid after purification by column chromatography on silica gel (hexane/EtOAc 10:1); mp 93 °C.

IR (KBr): 1596 (w), 1356 (m), 1164 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 7.7 Hz, 1 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.29 (dd, *J* = 7.2, 7.7 Hz, 1 H), 7.21 (dd, *J* = 7.2, 7.7 Hz, 1 H), 7.17 (d, *J* = 7.7 Hz, 1 H), 7.07 (dd, *J* = 11.1, 17.4 Hz, 1 H), 6.04 (s, 1 H), 5.63 (dd, *J* = 1.5, 17.4 Hz, 1 H), 5.35 (dd, *J* = 1.5, 11.1 Hz, 1 H), 4.53 (s, 2 H), 2.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 137.7, 135.0, 133.7, 131.4, 130.0, 129.9, 128.6, 128.0, 127.7, 127.5, 126.2, 124.5, 116.9, 50.8, 21.6.

MS (EI): *m*/*z* = 381 (M^+), 285, 226, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}N^{35}Cl_2O_2S$ (M^+): 381.0357; found: 381.0385.

N-(2-Allyl-benzyl)-*N*-(2,2-dichloro-vinyl)-*p*-toluenesulfonamide (10)

According to the procedure for the synthesis of **8**, a solution of **7** (2.65 g, 8.05 mmol), PPh_3 (5.28 g, 20.13 mmol) and CCl_4 (6.4 mL, 66.02 mmol) in THF (40 mL) was stirred at 60 °C for 9 h to afford **10** (3.03 g, 95%) as a white solid after purification by column chromatography on silica gel (hexane/Et_2O 2:1); mp 72–73 °C.

IR (KBr): 1598 (w), 1356 (m), 1165 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.27–7.15 (m, 4 H), 6.05 (s, 1 H), 5.94 (ddt, *J* = 10.1, 16.9, 6.3 Hz, 1 H), 5.08 (ddt, *J* = 1.9, 10.1, 1.5 Hz, 1 H), 4.97 (ddt, *J* = 1.9, 16.9, 1.5 Hz, 1 H), 4.46 (s, 2 H), 3.50 (dt, *J* = 6.3, 1.5 Hz, 2 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 138.6, 136.5, 134.7, 132.4, 130.0, 129.9, 129.8, 128.4, 127.7, 127.4, 126.3, 124.7, 116.0, 50.8, 36.4, 21.5.

MS (EI): *m*/*z* = 395 (M^+), 299, 155, 131, 105, 91.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}{}^{35}Cl_2NO_2S$ (M^+): 395.0514; found: 395.0492.

N-(2-Allylphenyl)-*N*-ethynyl-*p*-toluenesulfonamide (11a)

To a solution of **8** (228.1 mg, 0.60 mmol) in THF (10 mL) was added BuLi (0.85 mL, 1.31 mmol, 1.55 M hexane solution) at –78 °C, and stirred at the same temperature for 0.5 h. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to provide **11a** (157.5 mg, 85%) as a white solid; mp 87–88 °C.

IR (KBr): 2131 (m), 1597 (w), 1369 (s), 1168 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.32–7.29 (m, 2 H), 7.12 (m, 1 H), 6.82 (d, *J* = 7.7 Hz, 1 H), 5.91 (ddt, *J* = 10.6, 16.9, 6.8 Hz, 1 H), 5.15–5.09 (m, 2 H), 3.49 (br, 2 H), 2.76 (s, 1 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 139.6, 136.4, 135.6, 133.6, 130.4, 129.5, 129.5, 128.2, 127.6, 127.0, 116.7, 76.9, 57.7, 35.2, 21.5.

MS (EI): *m*/*z* = 311 (M^+), 263, 246, 156, 128, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}NO_2S$ (M^+): 311.0980; found: 311.0979.

Ethyl [(2-Allylphenyl)-(*p*-toluenesulfonyl)amino]propynoate (11b)

To a solution of **8** (0.33 g, 0.86 mmol) in THF (17 mL) was added BuLi (1.2 mL, 1.90 mmol, 1.58 M hexane solution) at –78 °C, and stirred at the same temperature for 0.5 h. To the resulting mixture was added ethyl chlorocarbonate (0.17 mL, 1.73 mmol) and warmed to –50 °C over 0.5 h. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to provide **11b** (0.25 g, 76%) as a pale yellow oil.

IR (neat): 2220 (s), 1706 (s), 1597 (w), 1375 (s), 1177 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.2 Hz, 2 H), 7.40–7.30 (m, 4 H), 7.16 (ddd, *J* = 1.9, 6.8, 8.2 Hz, 1 H), 6.83 (dd, *J* = 1.0, 7.7 Hz, 1 H), 5.87 (ddt, *J* = 10.6, 17.4, 6.8 Hz, 1 H), 5.14–5.07 (m, 2 H), 4.22 (q, *J* = 7.3 Hz, 2 H), 3.40 (br, 2 H), 2.49 (s, 3 H), 1.30 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 145.9, 139.4, 135.3, 135.2, 133.2, 130.6, 130.1, 129.9, 128.4, 127.8, 127.2, 117.1, 82.6, 65.9, 61.4, 35.1, 21.6, 14.0.

MS (EI): *m*/*z* = 383 (M^+), 338, 319, 290, 272, 244, 228, 154, 128, 115, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_4S$ (M^+): 383.1191; found: 383.1185.

N-Ethynyl-*N*-(2-vinylbenzyl)-*p*-toluenesulfonamide (12a)

According to the procedure for the synthesis of **11a**, a solution of **9** (305.9 mg, 0.80 mmol) and BuLi (1.1 mL, 1.76 mmol, 1.58 M hexane solution) in THF (16 mL) was stirred at –78 °C for 1 h to afford **12a** (209.6 mg, 84%) as a white solid after purification by column chromatography on silica gel (hexane/EtOAc 10:1); mp 88–89 °C.

IR (KBr): 2141 (m), 1596 (w), 1360 (s), 1174 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.2 Hz, 2 H), 7.49 (d, *J* = 7.7 Hz, 1 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.29 (ddd, *J* = 1.9, 7.3, 7.7 Hz, 1 H), 7.24–7.17 (m, 2 H), 7.01 (dd, *J* = 11.1, 17.4 Hz, 1 H), 5.62 (dd, *J* = 1.5, 17.4 Hz, 1 H), 5.32 (dd, *J* = 1.5, 11.1 Hz, 1 H), 4.52 (s, 2 H), 2.59 (s, 1 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 137.5, 133.9, 133.3, 130.5, 130.3, 129.7, 128.7, 127.6, 127.5, 125.9, 117.0, 75.8, 59.8, 52.4, 21.5.

MS (EI): *m*/*z* = 310 (M^+ – 1), 156, 129, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}NO_2S$ (M^+): 311.0980; found: 311.0992.

Ethyl [(*p*-Toluenesulfonyl)-(2-vinylbenzyl)amino]propynoate (12b)

According to the procedure for the synthesis of **11b**, a solution of **9** (313.3 mg, 0.82 mmol), BuLi (1.2 mL, 1.97 mmol, 1.58 M hexane solution), and ethyl chlorocarbonate (0.16 mL, 1.64 mmol) in THF (16 mL) was stirred at –50 °C for 0.5 h to afford **12b** (240.7 mg, 77%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/benzene 2:3).

IR (neat): 2219 (s), 1702 (s), 1375 (m), 1172 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.7 Hz, 2 H), 7.47 (d, *J* = 7.2 Hz, 1 H), 7.34–7.29 (m, 3 H), 7.24–7.21 (m, 2 H), 6.94 (dd, *J* = 10.9, 17.2 Hz, 1 H), 5.59 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.33 (dd, *J* = 1.2, 10.9 Hz, 1 H), 4.67 (s, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 2.46 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 145.4, 137.7, 133.9, 133.2, 130.3, 130.3, 129.9, 129.1, 127.8, 127.8, 126.3, 117.6, 82.5, 68.1, 61.4, 52.7, 21.6, 14.0.

MS (EI): *m*/*z* = 383 (M^+), 228, 182, 154, 129, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_4S$ (M^+): 383.1191; found: 383.1194.

N-Phenylethynyl-*N*-(2-vinylbenzyl)-*p*-toluenesulfonamide (12c)

To a solution of **9** (239.0 mg, 0.63 mmol) in THF (8 mL) was added BuLi (0.87 mL, 1.38 mmol, 1.58 M hexane solution) at –78 °C, and stirred at the same temperature for 0.5 h. To the resulting mixture was added $ZnBr_2$ (168.9 mg, 0.75 mmol) in THF (2 mL), and stirred at r.t. for 0.5 h to provide the crude alkynylzinc solution. This alkynylzinc solution was transferred with THF (3 mL) to the alkylpalladium complex in THF solution (5 mL), which was prepared from PhI (0.08 mL, 0.75 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (32.4 mg, 31.26 μmol) and PPh_3 (32.8 mg, 0.13 mmol). The resulting mixture was stirred at r.t. for 21 h. After the volatiles were removed under reduced pressure, brine was added and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to provide **12c** (134.9 mg, 56%) as a pale yellow oil.

IR (neat): 2238 (s), 1598 (m), 1366 (s), 1170 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.2 Hz, 2 H), 7.52 (d, *J* = 7.7 Hz, 1 H), 7.38–7.27 (m, 5 H), 7.25–7.14 (m, 5 H), 7.07 (dd, *J* = 11.1, 17.4 Hz, 1 H), 5.65 (dd, *J* = 1.0, 17.4 Hz, 1 H), 5.33 (dd, *J* = 1.0, 11.1 Hz, 1 H), 4.61 (s, 2 H), 2.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 137.8, 134.0, 133.4, 130.8, 130.7, 129.7, 128.8, 128.0, 127.7, 127.6, 127.4, 126.8, 126.0, 122.7, 117.0, 82.4, 71.5, 52.8, 21.6.

MS (EI): *m*/*z* = 387 (M^+), 248, 232, 217, 155, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}NO_2S$ (M^+): 387.1293; found: 387.1291.

N-(2-Allylbenzyl)-*N*-ethynyl-*p*-toluenesulfonamide (13a)

According to the procedure for the synthesis of **11a**, a solution of **10** (182.5 mg, 0.46 mmol) and BuLi (0.64 mL, 1.01 mmol, 1.58 M hexane solution) in THF (9 mL) was stirred at –78 °C for 1 h to afford **13a** (131.5 mg, 88%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 2132 (w), 1597 (w), 1369 (m), 1173 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.30–7.14 (m, 4 H), 5.93 (ddt, *J* = 10.1, 16.9, 6.0 Hz, 1 H), 5.06 (dd, *J* = 1.5, 10.1 Hz, 1 H), 4.96 (dd, *J* = 1.5, 16.9 Hz, 1 H), 4.47 (s, 2 H), 3.45 (d, *J* = 6.0 Hz, 2 H), 2.60 (s, 1 H), 2.47 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 138.7, 136.4, 133.9, 131.7, 130.3, 129.9, 129.7, 128.7, 127.6, 126.3, 116.0, 76.0, 59.7, 52.4, 36.5, 21.5.

MS (EI): *m*/*z* = 324 (M^+ – 1), 260, 170, 143, 131, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO_2S$ (M^+): 325.1136; found: 325.1143.

Ethyl [(2-Allylbenzyl)-(*p*-toluenesulfonyl)amino]propynoate (13b)

According to the procedure for the synthesis of **11b**, a solution of **10** (179.5 mg, 0.45 mmol), BuLi (0.69 mL, 1.09 mmol, 1.58 M hexane solution), and ethyl chlorocarbonate (0.09 mL, 0.91 mmol) in THF (9 mL) was stirred at –10 °C for 2 h to afford **13b** (142.7 mg, 79%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 2218 (s), 1705 (s), 1597 (w), 1375 (s), 1172 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.28 (dt, *J* = 1.9, 7.2 Hz, 1 H), 7.25–7.14 (m, 3 H), 5.91 (ddt, *J* = 10.1, 16.9, 5.8 Hz, 1 H), 5.06 (dd, *J* = 1.5, 10.1 Hz, 1 H), 4.94 (dd, *J* = 1.5, 16.9 Hz, 1 H), 4.60 (s, 2 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 3.41 (d, *J* = 5.8 Hz, 2 H), 2.46 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 21.6, 36.6, 52.5, 61.4, 68.0, 82.6, 116.2, 126.6, 127.8, 129.0, 129.9, 130.1, 130.2, 131.1, 133.9, 136.3, 138.6, 145.5, 153.9.

MS (EI): *m*/*z* = 398 (M^+ + 1), 242, 196, 155, 131, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{23}NO_4S$ (M^+): 397.1348; found: 397.1344.

***N*-(2,2-Dichlorovinyl)-*N*-hex-5-enyl-*p*-toluenesulfonamide (16)**

To a solution of **14** (2.99 g, 15.00 mmol), **15** (2.5 mL, 20.41 mmol), and PPh_3 (5.51 g, 21.01 mmol) in THF (30 mL) was added DEAD (8.9 mL, 19.51 mmol) at 0 °C, and the mixture was stirred at r.t. for 4 h. The volatiles were removed under reduced pressure, and the residue passed through a short column of silica gel (eluent: hexane/EtOAc 5:1) to provide the crude alkylated formyltosylamide. To a solution of this crude product and PPh_3 (9.84 g, 37.50 mmol) in THF (30 mL) was added CCl_4 (12 mL, 123.00 mmol) in THF (10 mL) at 60 °C over 3 h, and the resulting mixture was stirred at the same temperature for 12 h. Sat. aq $NaHCO_3$ was added after cooling to r.t., and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to provide **16** (2.91 g, 56%) as a white solid; mp 90 °C.

IR (KBr): 1599 (w), 1356 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 6.28 (s, 1 H), 5.76 (ddt, *J* = 10.2, 16.9, 6.8 Hz, 1 H), 5.02–4.94 (m, 2 H), 3.33 (t, *J* = 7.2 Hz, 2 H), 2.44 (s, 3 H), 2.05 (dt, *J* = 6.8, 7.2 Hz, 2 H), 1.56–1.48 (m, 2 H), 1.42–1.36 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 138.1, 135.5, 129.8, 127.2, 124.9, 124.3, 114.9, 48.9, 33.1, 27.8, 25.7, 21.6.

MS (EI): *m*/*z* = 347 (M^+), 264, 251, 192, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{19}{}^{35}Cl_2NO_2S$ (M^+): 347.0514; found: 347.0522.

***N*-Ethynyl-*N*-hex-5-enyl-*p*-toluenesulfonamide (17a)**

According to the procedure for the synthesis of **11a**, a solution of **16** (206.2 mg, 0.59 mmol) and BuLi (0.82 mL, 1.30 mmol, 1.58 M hexane solution) in THF (10 mL) was stirred at –78 °C for 1 h to afford **17a** (140.0 mg, 85%) as a white solid after purification by column chromatography on silica gel (hexane/EtOAc 10:1); mp 43 °C.

IR (KBr): 2133 (m), 1598 (w), 1359 (s), 1169 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 5.75 (ddt, *J* = 10.1, 16.9, 6.3 Hz, 1 H), 5.02–4.93 (m, 2 H), 3.31 (t, *J* = 7.3 Hz, 2 H), 2.73 (s, 1 H), 2.45 (s, 3 H), 2.05 (dt, *J* = 6.3, 7.3 Hz, 2 H), 1.66 (tt, *J* = 7.3, 7.7 Hz, 2 H), 1.41 (tt, *J* = 7.3, 7.7 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 138.0, 134.4, 129.7, 127.5, 114.8, 75.9, 59.0, 50.8, 32.9, 26.9, 25.2, 21.5.

MS (EI): *m*/*z* = 276 (M^+ – 1), 212, 155, 122, 91.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{19}O_2NS$ (M^+): 277.1136; found: 277.1122.

Ethyl [Hex-5-enyl-(*p*-toluenesulfonyl)amino]propynoate (17b)

According to the procedure for the synthesis of **11b**, a solution of **16** (313.0 mg, 0.90 mmol), BuLi (1.3 mL, 2.16 mmol, 1.63 M hexane solution), and ethyl chlorocarbonate (0.17 mL, 1.80 mmol) in THF (18 mL) was stirred at –20 °C for 1.5 h to afford **17b** (223.3 mg, 71%) as a colorless oil after purification by column chromatography on silica gel (hexane/Et_2O 3:1).

IR (neat): 2219 (s), 1705 (s), 1597 (w), 1376 (s), 1174 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 5.73 (ddt, *J* = 10.1, 16.9, 6.3 Hz, 1 H), 5.02–4.93 (m, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 3.42 (t, *J* = 7.3 Hz, 2 H), 2.46 (s, 3 H), 2.08–2.01 (m, 2 H), 1.72–1.63 (m, 2 H), 1.42–1.33 (m, 2 H), 1.31 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 145.4, 137.8, 134.2, 130.0, 127.7, 115.1, 82.4, 67.7, 61.5, 51.2, 32.9, 27.3, 25.2, 21.7, 14.1.

MS (EI): *m*/*z* = 348 (M^+ – 1), 304, 194, 166, 148, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{23}O_4NS$ (M^+): 349.1348; found: 349.1339.

***N*-[2-(*N*-Allyl-*N*-*p*-toluenesulfonylamino)phenyl]-*N*-ethynyl-*p*-toluenesulfonamide (21a)**

To a solution of **21d** (243.1 mg, 0.44 mmol) in THF (4 mL) was added TBAF (1.3 mL, 1.32 mmol, 1 M THF solution) at 0 °C, and stirred at the same temperature for 5 min. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **21a** (194.1 mg, 92%) as a white solid; mp 146 °C.

IR (KBr): 2130 (w), 1596 (m), 1372 (m), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 7.7 Hz, 2 H), 7.41–7.25 (m, 6 H), 7.20 (dd, *J* = 1.5, 7.7 Hz, 1 H), 6.99 (dd, *J* = 1.5, 7.7 Hz, 1 H), 5.95 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.09–5.02 (m, 2 H), 4.22 (d, *J* = 6.8 Hz, 2 H), 2.72 (s, 1 H), 2.49 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3, 143.8, 138.3, 137.6, 136.1, 133.5, 133.2, 131.4, 129.8, 129.6, 129.5, 129.1, 129.0, 128.7, 128.5, 119.3, 77.2, 58.1, 54.4, 21.8, 21.6.

MS (EI): *m*/*z* = 480 (M^+), 325, 262, 171, 139, 91.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{24}N_2O_4S_2$ (M^+): 480.1177; found: 480.1180.

Ethyl {[2-(Allyl-*p*-toluenesulfonylamino)phenyl]-*p*-toluenesulfonylamino}propynoate (21b)

To a solution of **21a** (305.9 mg, 0.64 mmol) in THF (13 mL) was added BuLi (0.42 mL, 0.70 mmol, 1.65 M hexane solution) at –78 °C, and stirred at the same temperature for 0.5 h. To the resulting mixture was added ethyl chlorocarbonate (0.07 mL, 0.76 mmol), and warmed to –15 °C for 1.5 h. Sat. aq NH_4Cl solution was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were

washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/Et_2O Ac 2:1) to provide **21b** (252.2 mg, 72%) as a white solid; mp 48 °C.

IR (KBr): 2221 (s), 1706 (s), 1597 (w), 1374 (m), 1176 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.7 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.41 (d, *J* = 8.7 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.39–7.28 (m, 2 H), 7.13 (dd, *J* = 1.5, 7.7 Hz, 1 H), 7.05 (dd, *J* = 1.9, 7.7 Hz, 1 H), 5.93 (ddt, *J* = 9.7, 16.9, 7.2 Hz, 1 H), 5.09–5.02 (m, 2 H), 4.21–4.15 (m, 4 H), 2.49 (s, 3 H), 2.44 (s, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 146.0, 143.9, 137.8, 136.6, 135.6, 133.0, 132.9, 131.3, 130.0, 129.8, 129.5, 129.2, 129.2, 128.6, 128.6, 119.6, 83.1, 66.5, 61.5, 54.6, 21.8, 21.6, 14.1.

MS (EI): *m*/*z* = 552 (M^+), 507, 397, 334, 259, 243, 169, 139, 91.

HRMS(EI): *m*/*z* calcd for $C_{28}H_{28}N_2O_6S_2$ (M^+): 552.1389; found: 552.1385.

N-[2-(*N*-Allyl-*N*-*p*-toluenesulfonylamino)phenyl]-*N*-(2-phenylethynyl)-*p*-toluenesulfonamide (21c)

To a mixture of $Pd(PPh_3)_4$ (13.4 mg, 11.59 μmol), CuI (2.2 mg, 11.59 μmol), and PhI (0.05 mL, 0.46 mmol) in Et_3N (2 mL) and benzene (1 mL) was added **21a** (111.4 mg, 0.23 mmol) at r.t., and the mixture was stirred at the same temperature for 48 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc, 2:1) to provide **21c** (126.4 mg, 98%) as a white solid; mp 53 °C.

IR (KBr): 2241 (w), 1597 (w), 1356 (m), 1168 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.86 (m, 4 H), 7.41–7.24 (m, 12 H), 7.05 (d, *J* = 8.3 Hz, 1 H), 5.97 (ddt, *J* = 9.8, 16.6, 6.8 Hz, 1 H), 5.10–5.02 (m, 2 H), 4.27 (d, *J* = 6.8 Hz, 2 H), 2.49 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 143.7, 138.1, 138.0, 136.5, 133.8, 133.3, 131.9, 131.4, 129.6, 129.6, 129.5, 129.1, 128.9, 128.7, 128.6, 128.2, 127.8, 122.7, 119.4, 83.8, 69.8, 54.4, 21.7, 21.6.

MS (EI): *m*/*z* = 556 (M^+), 456, 417, 401, 301, 245, 139, 119, 91.

HRMS (EI): *m*/*z* calcd for $C_{31}H_{28}O_4N_2S_2$ (M^+): 556.1490; found: 556.1497.

N-[2-(*N*-Allyl-*N*-*p*-toluenesulfonylamino)phenyl]-*N*-(2-trimethylsilyl)ethynyl-*p*-toluenesulfonamide (21d)

To a solution of **19** (811.2 mg, 1.78 mmol) in THF (27 mL) was added BuLi (1.3 mL, 1.95 mmol, 1.55 M hexane solution) at –78 °C, and stirred at the same temperature for 1 h. To the resulting mixture was added phenyl(trimethylsilylethynyl)iodonium triflate (960.0 mg, 2.13 mmol). The mixture was warmed to r.t. over 1 h, and stirred at the same temperature for 18 h. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **21d** (595.4 mg, 61%) as a white solid; mp 35–36 °C.

IR (KBr): 2165 (m), 1597 (w), 1359 (m), 1173 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.3 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H), 7.39–7.24 (m, 7 H), 7.01 (dd, *J* = 1.0, 7.3 Hz, 1 H), 5.93 (ddt, *J* = 9.8, 16.6, 6.8 Hz, 1 H), 5.05–4.99 (m, 2 H), 4.17 (d, *J* = 6.8 Hz, 2 H), 2.49 (s, 3 H), 2.45 (s, 3 H), 0.12 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 143.7, 137.9, 137.4, 136.4, 133.6, 133.2, 131.7, 129.5, 129.4, 129.4, 129.1, 129.0, 128.9, 128.4, 119.4, 95.9, 72.6, 54.1, 21.7, 21.6, –0.1.

MS (EI): *m*/*z* = 552 (M^+), 537, 397, 241, 169, 91.

HRMS (EI): *m*/*z* calcd for $C_{28}H_{32}N_2O_4S_2Si$ (M^+): 552.1573; found: 552.1567.

N-(2,2-Dichlorovinyl)-*N*-hept-6-enyl-*p*-toluenesulfonamide (26)

To a solution of **14** (3.00 g, 15.06 mmol), **23** (2.7 mL, 20.33 mmol), and PPh_3 (5.53 g, 21.08 mmol) in THF (30 mL) was added DEAD (8.9 mL, 19.58 mmol) at 0 °C, and the mixture was stirred at r.t. for 4 h. The volatiles were removed under reduced pressure, and the residue was passed through a short column of silica gel (eluent: hexane/EtOAc 5:1) to provide the crude alkylated formyltosylamide. To a solution of this crude product and PPh_3 (9.87 g, 37.64 mmol) in THF (30 mL) was added CCl_4 (12 mL, 123.48 mmol) in THF (10 mL) at 60 °C for 3 h, and the resulting mixture was stirred at the same temperature for 7 h. Sat. aq $NaHCO_3$ was added after cooling to r.t., and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/Et_2O 10:1) to provide **26** (2.59 g, 48%) as a white solid; mp 69 °C.

IR (KBr): 1599 (w), 1354 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.5 Hz, 2 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 6.27 (s, 1 H), 5.78 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.02–4.92 (m, 2 H), 3.31 (t, *J* = 7.5 Hz, 2 H), 2.44 (s, 3 H), 2.03 (dt, *J* = 6.8, 7.2 Hz, 2 H), 1.56–1.47 (m, 2 H), 1.42–1.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 138.6, 135.5, 129.8, 127.2, 124.9, 124.3, 114.6, 49.0, 33.5, 28.3, 28.2, 26.0, 21.6.

MS (EI): *m*/*z* = 361 (M^+), 278, 265, 206, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{21}{}^{35}Cl_2NO_2S$ (M^+): 361.0607; found: 361.0667.

N-[4,4-Bis(benzyloxymethyl)hept-6-enyl]-*N*-(2,2-dichlorovinyl)-*p*-toluenesulfonamide (27)

According to the procedure for the synthesis of **26**, a solution of **14** (0.799 g, 4.01 mmol), **24** (1.09 g, 3.09 mmol), PPh_3 (1.01 g, 3.86 mmol), and DEAD (1.7 mL, 3.70 mmol) in THF (6 mL) was stirred at r.t. for 1 h and then a solution of the crude product obtained, an additional amount of PPh_3 (2.02 g, 7.72 mmol), and CCl_4 (2.4 mL, 25.31 mmol) in THF (9 mL) were stirred at 60 °C for 24 h to afford **27** (811.2 mg, 44%) as a colorless oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 1639 (w), 1598 (w), 1360 (s), 1167 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.7 Hz, 2 H), 7.36–7.25 (m, 12 H), 6.29 (s, 1 H), 5.77–5.65 (m, 1 H), 5.04–4.98 (m, 2 H), 4.45 (s, 4 H), 3.30–3.23 (m, 6 H), 2.42 (s, 3 H), 2.07 (d, *J* = 7.7 Hz, 2 H), 1.54–1.44 (m, 2 H), 1.28–1.22 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 138.6, 135.3, 133.9, 129.7, 128.1, 128.1, 127.2, 127.0, 124.8, 123.0, 117.5, 73.0, 72.4, 49.5, 41.2, 36.4, 28.9, 22.0, 21.4.

MS (EI): *m*/*z* = 601 (M^+), 510, 446, 355, 340, 249, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{32}H_{37}{}^{35}Cl_2NO_4S$ (M^+): 601.1820; found: 601.1814.

N-[3-(5-Allyl-2,2-dimethyl[1,3]dioxan-5-yl)-propyl]-*N*-(2,2-dichlorovinyl)-*p*-toluenesulfonamide (28)

According to the procedure for the synthesis of **26**, a solution of **14** (784.3 mg, 3.94 mmol), **25** (703.0 mg, 3.28 mmol), PPh_3 (1.205 g, 4.59 mmol), and DEAD (1.9 mL, 4.26 mmol) in THF (15 mL) was stirred at

r.t. for 4 h and then a solution of the crude product obtained, an additional amount of PPh_3 (2.15 g, 8.20 mmol), and CCl_4 (2.6 mL, 26.90 mmol) in THF (15 mL) were stirred at 60 °C for 17 h to afford **28** (707.1 mg, 47%) as a white solid after purification by column chromatography on silica gel (hexane/EtOAc 5:1); 54 °C.

IR (KBr): 1598 (w), 1354 (s), 1167 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 6.31 (s, 1 H), 5.70 (ddt, *J* = 10.1, 17.9, 7.2 Hz, 1 H), 5.12–5.05 (m, 2 H), 3.56 (d, *J* = 11.6 Hz, 2 H), 3.50 (d, *J* = 11.6 Hz, 2 H), 3.31 (t, *J* = 7.2 Hz, 2 H), 2.44 (s, 3 H), 2.11 (d, *J* = 7.2 Hz, 2 H), 1.53–1.43 (m, 2 H), 1.40 (s, 3 H), 1.39 (s, 3 H), 1.34–1.28 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 135.5, 133.0, 129.9, 127.3, 124.8, 123.9, 118.4, 98.1, 67.5, 49.6, 36.6, 35.0, 29.2, 23.9, 23.6, 21.9, 21.6.

MS (EI): *m*/*z* = 461 (M^+), 446, 306, 277, 248, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{29}{}^{35}Cl_2NO_4S$ (M^+): 461.1194; found: 461.1175.

N-Ethynyl-*N*-hept-6-enyl-*p*-toluenesulfonamide (29a)

According to the procedure for the synthesis of **11a**, a solution of **26** (235.7 mg, 0.65 mmol) and BuLi (0.88 mL, 1.43 mmol, 1.63 M hexane solution) in THF (13 mL) was stirred at –78 °C for 20 min to afford **29a** (158.8 mg, 84%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 2133 (m), 1597 (w), 1366 (s), 1169 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 5.78 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.02–4.91 (m, 2 H), 3.29 (t, *J* = 7.3 Hz, 2 H), 2.73 (s, 1 H), 2.45 (s, 3 H), 2.02 (dt, *J* = 6.8, 7.2 Hz, 2 H), 1.69–1.60 (m, 2 H), 1.42–1.27 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 138.5, 134.5, 129.7, 127.5, 114.5, 75.9, 59.0, 51.0, 33.4, 28.2, 27.4, 25.5, 21.6.

MS (EI): *m*/*z* = 290 (M^+ – 1), 227, 155, 136, 91.

HRMS (EI): *m*/*z* calcd for $C_{16}H_{21}NO_2S$ (M^+): 291.1293; found: 291.1298.

Ethyl [Hept-6-enyl-(*p*-toluenesulfonyl)amino]propynoate (29b)

According to the procedure for the synthesis of **11b**, a solution of **26** (287.3 mg, 0.79 mmol), BuLi (1.1 mL, 1.74 mmol, 1.63 M hexane solution), and ethyl chlorocarbonate (0.11 mL, 1.19 mmol) in THF (16 mL) was stirred at –30 °C for 1 h to afford **29b** (228.6 mg, 79%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 2218 (s), 1705 (s), 1597 (w), 1376 (s), 1174 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 5.76 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.02–4.91 (m, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 3.41 (t, *J* = 7.3 Hz, 2 H), 2.46 (s, 3 H), 2.05–1.98 (m, 2 H), 1.71–1.62 (m, 2 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.42–1.24 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 145.4, 138.3, 134.1, 129.9, 127.5, 114.5, 82.3, 67.6, 61.4, 51.2, 33.3, 28.0, 27.6, 25.3, 21.5, 14.0.

MS (EI): *m*/*z* = 363 (M^+), 318, 208, 162, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{25}NO_4S$ (M^+): 363.1504; found: 363.1489.

N-[4,4-Bis(benzyloxymethyl)hept-6-enyl]-*N*-ethynyl-*p*-toluenesulfonamide (30a)

According to the procedure for the synthesis of **11a**, a solution of **27** (305.5 mg, 0.51 mmol) and BuLi (0.68 mL, 1.12 mmol, 1.63 M hexane solution) in THF (10 mL) was stirred at –78 °C for 10 min to afford **30a** (237.3 mg, 88%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 2135 (m), 1639 (w), 1597 (w), 1367 (s), 1169 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.2 Hz, 2 H), 7.35–7.25 (m, 12 H), 5.71 (m, 1 H), 5.04–4.97 (m, 2 H), 4.44 (s, 4 H), 3.28–3.21 (m, 6 H), 2.68 (s, 1 H), 2.42 (s, 3 H), 2.06 (d, *J* = 7.7 Hz, 2 H), 1.68–1.58 (m, 2 H), 1.30–1.23 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 138.6, 134.4, 133.9, 129.6, 128.1, 127.4, 127.2, 127.2, 117.6, 75.9, 73.0, 72.4, 59.0, 51.7, 41.3, 36.3, 28.5, 21.4, 21.4.

MS (EI): *m*/*z* = 530 (M^+ – 1), 440, 376, 270, 91.

HRMS (EI): *m*/*z* calcd for $C_{32}H_{37}O_4NS$ (M^+): 531.2443; found: 531.2467.

Ethyl {[4,4-Bis(benzyloxymethyl)hept-6-enyl](*p*-toluenesulfonyl)amino}propynoate (30b)

According to the procedure for the synthesis of **11b**, a solution of **27** (444.4 mg, 0.74 mmol), BuLi (1.0 mL, 1.62 mmol, 1.63 M hexane solution), and ethyl chlorocarbonate (0.08 mL, 0.88 mmol) in THF (15 mL) was stirred at –30 °C for 1 h to afford **30b** (302.7 mg, 68%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 5:1).

IR (neat): 2218 (s), 1704 (s), 1598 (w), 1376 (s), 1174 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.7 Hz, 2 H), 7.35–7.25 (m, 12 H), 5.68 (m, 1 H), 5.04–4.97 (m, 2 H), 4.44 (s, 4 H), 4.19 (q, *J* = 7.3 Hz, 2 H), 3.35 (t, *J* = 7.3 Hz, 2 H), 3.25 (s, 2 H), 3.24 (s, 2 H), 2.43 (s, 3 H), 2.05 (d, *J* = 6.8 Hz, 2 H), 1.68–1.59 (m, 2 H), 1.27 (t, *J* = 7.3 Hz, 3 H), 1.26–1.20 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 145.2, 138.5, 134.0, 133.7, 129.8, 128.1, 127.5, 127.2, 127.2, 117.6, 82.3, 73.0, 72.2, 67.7, 61.3, 51.9, 41.2, 36.3, 28.5, 21.7, 21.5, 14.0.

MS (EI): *m*/*z* = 603 (M^+), 448, 342, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{35}H_{41}NO_6S$ (M^+): 603.2655; found: 603.2673.

N-[3-(5-Allyl-2,2-dimethyl[1,3]dioxan-5-yl)propyl]-*N*-ethynyl-*p*-toluenesulfonamide (31a)

According to the procedure for the synthesis of **11a**, a solution of **28** (225.5 mg, 0.49 mmol) and BuLi (0.69 mL, 1.07 mmol, 1.55 M hexane solution) in THF (10 mL) was stirred at –78 °C for 0.5 h to afford **31a** (161.8 mg, 85%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 2134 (m), 1597 (w), 1372(s), 1170 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 5.70 (ddt, *J* = 11.6, 16.9, 7.7 Hz, 1 H), 5.11–5.05 (m, 2 H), 3.55 (d, *J* = 11.6 Hz, 2 H), 3.50 (d, *J* = 11.6 Hz, 2 H), 3.29 (t, *J* = 7.0 Hz, 2 H), 2.75 (s, 1 H), 2.45 (s, 3 H), 2.12 (d, *J* = 7.7 Hz, 2 H), 1.66–1.54 (m, 2 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.33–1.25 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 134.5, 132.9, 129.8, 127.6, 118.4, 98.1, 75.8, 67.4, 59.3, 51.6, 36.4, 35.0, 28.9, 24.1, 23.4, 21.6, 21.1.

MS (EI): *m*/*z* = 390 (M^+ – 1), 376, 304, 236, 178, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{29}NO_4S$ (M^+): 391.1817; found: 391.1815.

Ethyl {[3-(5-Allyl-2,2-dimethyl[1,3]dioxan-5-yl)propyl]-(*p*-toluenesulfonyl)amino}propynoate (31b)

According to the procedure for the synthesis of **11b**, a solution of **28** (212.8 mg, 0.46 mmol), BuLi (0.65 mL, 1.01 mmol, 1.55 M hexane solution), and ethyl chlorocarbonate (0.05 mL, 0.55 mmol) in THF (9 mL) was stirred at –30 °C for 1 h to afford **31b** (203.3 mg, 95%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 2218 (s), 1705 (s), 1598 (w), 1374 (s), 1175 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 5.67 (m, 1 H), 5.12–5.05 (m, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.55 (d, *J* = 11.6 Hz, 2 H), 3.48 (d, *J* = 11.6 Hz, 2 H), 3.40 (t, *J* = 7.0 Hz, 2 H), 2.46 (s, 3 H), 2.10 (d, *J* = 7.3 Hz, 2 H), 1.68–1.59 (m, 2 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.30–1.24 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 145.6, 134.2, 132.7, 130.1, 127.8, 118.5, 98.1, 82.1, 67.9, 67.4, 61.6, 51.8, 36.5, 35.0, 28.8, 23.8, 23.7, 21.7, 21.5, 14.2.

MS (EI): *m*/*z* = 462 (M^+ – 1), 448, 308, 250, 220, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{33}NO_6S$ (M^+): 463.2029; found: 463.2026.

***N*-Allyl-*N*-(3-hydroxypropyl)-*p*-toluenesulfonamide (34)**

To a solution of **32** (1.81 g, 8.57 mmol), **33** (1.63 g, 8.57 mmol), and PPh_3 (2.81 g, 10.71 mmol) in THF (20 mL) was added DEAD (4.7 mL, 10.29 mmol) at 0 °C, and the mixture was stirred at r.t. for 2 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1) to provide *N*-allyl-*N*-[3-(*tert*-butyldimethylsilanyloxy)propyl]-*p*-toluenesulfonamide (2.10 g, 64%) as a pale yellow oil.

IR (neat): 1644 (w), 1599 (m), 1345 (s), 1162 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 5.65 (ddt, *J* = 10.2, 16.6, 6.3 Hz, 1 H), 5.20–5.10 (m, 2 H), 3.81 (d, *J* = 6.3 Hz, 2 H), 3.58 (dd, *J* = 5.9, 6.3 Hz, 2 H), 3.23–3.18 (m, 2 H), 2.42 (s, 3 H), 1.76–1.68 (m, 2 H), 0.87 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 136.9, 133.1, 129.4, 127.0, 118.5, 60.1, 50.7, 44.4, 31.4, 25.7, 21.3, 18.0, –5.6.

MS (EI): *m*/*z* = 382 (M^+ – 1), 368, 326, 228, 91.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{33}NO_3SSi$ (M^+): 383.1950; found: 383.1946.

To a solution of the above coupling product (665.1 mg, 1.73 mmol) in THF (3.5 mL) was added TBAF (5.2 mL, 5.20 mmol, 1 M THF solution) at 0 °C, and the resulting mixture was stirred at r.t. for 40 min. Sat. aq NH_4Cl was added, and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine and dried ($MgSO_4$). The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to provide **34** (463.5 mg, 99%) as a colorless oil.

IR (neat): 3534 (m), 1644 (w), 1598 (m), 1337 (s), 1159 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 5.62 (ddt, *J* = 10.1, 16.4, 6.3 Hz, 1 H), 5.20–5.11 (m, 2 H), 3.82 (d, *J* = 6.3 Hz, 2 H), 3.74 (dd, *J* = 5.3, 5.8 Hz, 2 H), 3.25 (dd, *J* = 6.3, 6.8 Hz, 2 H), 2.44 (s, 3 H), 2.35 (br, 1 H), 1.76–1.69 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 136.3, 132.8, 129.6, 126.8, 118.8, 58.6, 50.8, 43.9, 30.6, 21.3.

MS (EI): *m*/*z* = 269 (M^+), 224 155, 114, 91.

HRMS (EI): *m*/*z* calcd for $C_{13}H_{19}NO_3S$ (M^+): 269.1086; found: 269.1104.

***N*-[3-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminopropyl]-*N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide (36)**

To a solution of **34** (304.5 mg, 1.13 mmol), **35** (337.4 mg, 1.24 mmol), and PPh_3 (370.6 mg, 1.41 mmol) in THF (6 mL) was added DEAD (0.62 mL, 1.36 mmol) at 0 °C, and the mixture was stirred at r.t. for 20 min. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 3:1) to provide **36** (590.9 mg, quant) as a colorless oil.

IR (neat): 1728 (s), 1644 (w), 1598 (m), 1350 (s), 1157 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H), 7.33–7.28 (m, 4 H), 5.63 (ddt, *J* = 10.1, 16.9, 6.3 Hz, 1 H), 5.20 (d, *J* = 16.9 Hz, 1 H), 5.15 (d, *J* = 10.1 Hz, 1 H), 3.85 (d, *J* = 6.3 Hz, 2 H), 3.83 (t, *J* = 7.2 Hz, 2 H), 3.22 (t, *J* = 7.2 Hz, 2 H), 2.44 (s, 3 H), 2.42 (s, 3 H), 2.05–1.96 (m, 2 H), 1.34 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 144.1, 143.2, 137.1, 136.7, 132.7, 129.6, 129.2, 127.6, 127.0, 119.2, 84.2, 50.4, 44.8, 44.6, 28.6, 27.7, 21.5, 21.4.

MS (EI): *m*/*z* = 522 (M^+), 465, 449, 421, 267, 224, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{34}N_2O_6S_2$ (M^+): 522.1858; found: 522.1843.

***N*-[2-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminobenzyl]-*N*-*tert*-butoxycarbonyl-*p*-toluenesulfonamide (39)**

To a solution of **38** (2.97 g, 9.36 mmol), **35** (2.79 g, 10.29 mmol), and PPh_3 (3.07 mg, 11.70 mmol) in THF (50 mL) was added DEAD (5.1 mL, 11.23 mmol) at 0 °C, and the mixture was stirred at r.t. for 0.5 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 4:1) to provide **39** (4.50 g, 84%) as a white solid; mp 65 °C.

IR (KBr): 1732 (s), 1598 (w), 1354 (s), 1167 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 7.2 Hz, 1 H), 7.34–7.28 (m, 5 H), 7.10 (ddd, *J* = 1.0, 7.2, 7.7 Hz, 1 H), 6.49 (dd, *J* = 1.0, 7.2 Hz, 1 H), 5.87 (m, 1 H), 5.42 (d, *J* = 17.6 Hz, 1 H), 5.26 (d, *J* = 17.6 Hz, 1 H), 5.07–5.01 (m, 2 H), 4.43 (dd, *J* = 5.8, 14.0 Hz, 1 H), 3.91 (dd, *J* = 7.7, 14.0 Hz, 1 H), 2.46 (s, 6 H), 1.35 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 144.2, 143.7, 139.5, 137.1, 136.6, 135.1, 132.4, 129.5, 129.2, 128.7, 128.2, 128.1, 127.8, 127.0, 126.9, 119.6, 84.3, 54.9, 47.9, 27.8, 21.6, 21.6.

MS (EI): *m*/*z* = 570 (M^+), 497, 415, 315, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{29}H_{34}N_2O_6S_2$ (M^+): 570.1858; found: 570.1854.

***N*-Allyl-*N*-[3-(*N*-*p*-toluenesulfonyl)aminopropyl]-*p*-toluenesulfonamide (40)**

To a solution of **36** (590.9 mg, 1.13 mmol) in CH_2Cl_2 (5 mL) was added TFA (1 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **40** (477.7 mg, quant) as a colorless oil.

IR (neat): 3283 (m), 1644 (w), 1598 (m), 1331 (s), 1159 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 8.2 Hz, 2 H), 7.34–7.29 (m, 4 H), 5.53 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.21 (t, *J* = 6.8 Hz, 1 H), 5.16–5.08 (m, 2 H), 3.73 (d, *J* = 6.8 Hz, 2 H), 3.15 (t, *J* = 6.3 Hz, 2 H), 3.04 (ddd, *J* = 5.3, 6.8, 6.8 Hz, 2 H), 2.44 (s, 3 H), 2.43 (s, 3 H), 1.76–1.68 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 142.9, 136.7, 135.9, 132.4, 129.5, 129.4, 126.7, 126.6, 118.9, 50.7, 44.2, 39.6, 27.8, 21.1, 21.1.

MS (EI): *m*/*z* = 422 (M^+), 267, 224, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{26}N_2O_4S_2$ (M^+): 422.1334; found: 422.1316.

N-Allyl-*N*-[2-(*N*-*p*-toluenesulfonyl)aminomethylphenyl]-*p*-toluenesulfonamide (41)

To a solution of **39** (4.43 g, 7.76 mmol) in CH_2Cl_2 (40 mL) was added TFA (8 mL) at 0 °C, and the mixture was stirred at r.t. for 1 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **41** (3.65 g, quant) as a white solid; mp 121 °C.

IR (KBr): 1597 (w), 1344 (s), 1160 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.2 Hz, 2 H), 7.53 (d, *J* = 7.7 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.7 Hz, 2 H), 7.31–7.25 (m, 3 H), 7.09 (dt, *J* = 1.0, 7.7 Hz, 1 H), 6.35 (d, *J* = 7.7 Hz, 1 H), 5.63 (dd, *J* = 3.9, 8.7 Hz, 1 H), 5.50 (dddd, *J* = 5.8, 8.2, 10.2, 16.9 Hz, 1 H), 4.95 (d, *J* = 10.2 Hz, 1 H), 4.88 (d, *J* = 16.9 Hz, 1 H), 4.39 (dd, *J* = 5.8, 14.0 Hz, 1 H), 4.23–4.15 (m, 2 H), 3.58 (dd, *J* = 8.2, 14.0 Hz, 1 H), 2.46 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 143.2, 138.1, 137.5, 137.0, 134.3, 131.7, 131.6, 129.7, 129.6, 129.0, 128.4, 128.1, 127.4, 127.2, 120.1, 55.0, 43.0, 21.6, 21.5.

MS (EI): *m*/*z* = 470 (M^+), 315, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{26}N_2O_4S_2$ (M^+): 470.1334; found: 470.1329.

N-[3-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminopropyl]-*N*-formyl-*p*-toluenesulfonamide (42)

According to the procedure for the synthesis of **5**, a solution of **40** (2.04 g, 4.84 mmol), BuLi (3.6 mL, 5.80 mmol, 1.63 M hexane solution), and 1-formylbenzotriazole (1.42 g, 9.67 mmol) in THF (25 mL) was stirred at –50 °C for 0.5 h to afford **42** (2.01 g, 92%) as a colorless oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 1699 (s), 1643 (w), 1597 (m), 1357 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 1 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 5.55 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.19–5.09 (m, 2 H), 3.79 (d, *J* = 6.8 Hz, 2 H), 3.49–3.43 (m, 2 H), 3.13 (t, *J* = 6.8 Hz, 2 H), 2.45 (s, 3 H), 2.41 (s, 3 H), 1.85–1.75 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 145.5, 143.3, 136.5, 134.5, 132.5, 130.3, 129.6, 127.3, 127.0, 119.3, 50.3, 44.5, 40.2, 26.5, 21.5, 21.4.

MS (EI): *m*/*z* = 450 (M^+), 295, 224, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{26}N_2O_5S_2$ (M^+): 450.1283; found: 450.1287.

N-[2-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminobenzyl]-*N*-formyl-*p*-toluenesulfonamide (43)

According to the procedure for the synthesis of **5**, a solution of **41** (3.55 g, 7.65 mmol), BuLi (5.8 mL, 9.05 mmol, 1.55 M hexane solution), and 1-formylbenzotriazole (2.22 g, 15.09 mmol) in THF (40 mL) was stirred at –30 °C for 1 h to afford **43** (3.12 g, 83%) as a white solid after purification by column chromatography on silica gel (hexane/EtOAc 4:1); mp 63 °C.

IR (KBr): 1702 (s), 1598 (w), 1349 (s), 1166 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 1 H), 7.77 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.17–7.26 (m, 2 H), 7.05 (ddd, *J* = 1.9, 6.8, 8.2 Hz, 1 H), 6.41 (d, *J* = 7.7 Hz, 1 H), 5.85 (dddd, *J* = 6.3, 7.7, 10.2, 16.9 Hz, 1 H), 5.02–5.10 (m, 2 H), 5.00 (d, *J* = 16.9 Hz, 1 H), 4.93 (d, *J* = 16.9 Hz, 1 H), 4.45 (dd, *J* = 6.3, 14.0 Hz, 1 H), 3.83 (dd, *J* = 7.7, 14.0 Hz, 1 H), 2.46 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 145.6, 143.9, 137.0, 136.9, 134.8, 134.4, 132.3, 130.3, 129.4, 128.5, 128.2, 127.5, 127.4, 127.3, 127.2, 119.7, 54.8, 42.6, 21.6, 21.6.

MS (EI): *m*/*z* = 498 (M^+), 343, 315, 159, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{26}N_2O_5S_2$ (M^+): 498.1283; found: 498.1273.

N-[3-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminopropyl]-*N*-(2,2-dichloroethenyl)-*p*-toluenesulfonamide (44)

According to the procedure for the synthesis of **8**, a solution of **42** (2.01 g, 4.45 mmol), PPh_3 (2.92 g, 11.13 mmol), and CCl_4 (3.5 mL, 36.51 mmol) in THF (15 mL) was stirred at 60 °C for 4.5 h to afford **44** (2.24 g, 97%) as a colorless oil after purification by silica gel column chromatography (hexane/EtOAc 3:1).

IR (neat): 1598 (m), 1345 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.65 (m, 2 H), 7.36–7.29 (m, 4 H), 6.20 (s, 1 H), 5.60 (ddt, *J* = 10.1, 16.9, 6.8 Hz, 1 H), 5.22–5.13 (m, 2 H), 3.79 (d, *J* = 6.8 Hz, 2 H), 3.33 (t, *J* = 7.3 Hz, 2 H), 3.15 (t, *J* = 7.2 Hz, 2 H), 2.45 (s, 3 H), 2.43 (s, 3 H), 1.85–1.76 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 143.0, 136.1, 134.4, 132.7, 129.6, 129.4, 126.9, 126.7, 124.8, 124.5, 118.7, 50.8, 46.6, 44.7, 27.0, 21.1, 21.1.

MS (EI): *m*/*z* = 516 (M^+), 481, 393, 361, 224, 155, 91.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{26}{}^{35}Cl_2N_2O_4S_2$ (M^+): 516.0711; found: 516.0704.

N-[2-(*N*-Allyl-*N*-*p*-toluenesulfonyl)aminobenzyl]-*N*-(2,2-dichlorovinyl)-*p*-toluenesulfonamide (45)

According to the procedure for the synthesis of **8**, a solution of **43** (2.93 g, 5.88 mmol), PPh_3 (3.85 g, 14.69 mmol), and CCl_4 (4.6 mL, 48.19 mmol) in THF (20 mL) was stirred at 60 °C for 4 h to afford **45** (3.27 g, 98%) as a white solid after purification by column chromatography on silica gel (hexane/EtOAc 4:1); mp 137 °C.

IR (KBr): 1736 (w), 1598 (m), 1351 (s), 1166 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.78 (m, 3 H), 7.46 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.33 (ddd, *J* = 1.0, 7.2, 7.7 Hz, 1 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.10 (ddd, *J* = 1.4, 7.7, 7.7 Hz, 1 H), 6.40 (dd, *J* = 1.0, 8.2 Hz, 1 H), 6.22 (s, 1 H), 5.63 (dddd, *J* = 5.8, 7.7, 10.1, 16.9 Hz, 1 H), 5.03 (dd, *J* = 1.5, 10.1 Hz, 1 H), 4.96 (dd, *J* = 1.5, 16.9 Hz, 1 H), 4.82 (d, *J* = 16.4 Hz, 1 H), 4.70 (d, *J* = 16.4 Hz, 1 H), 4.41 (dd, *J* = 5.8, 13.5 Hz, 1 H), 3.69 (dd, *J* = 7.7, 13.5 Hz, 1 H), 2.48 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 143.9, 138.0, 137.0, 135.3, 134.4, 131.7, 130.0, 129.5, 129.5, 128.6, 128.1, 127.7, 127.4, 127.1, 126.5, 125.7, 120.1, 54.8, 49.5, 21.6, 21.6.

MS (EI): *m*/*z* = 564 (M^+), 529, 441, 409, 300, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{26}{}^{35}Cl_2N_2O_4S_2$ (M^+): 564.0711; found: 564.0712.

N-[3-(N-Allyl-N-p-toluenesulfonyl)aminopropyl]-N-ethynyl-p-toluenesulfonamide (46a)

According to the procedure for the synthesis of **11a**, a solution of **44** (269.6 mg, 0.52 mmol) and BuLi (0.70 mL, 1.15 mmol, 1.63 M hexane solution) in THF (10 mL) was stirred at –78 °C for 10 min to afford **46a** (176.2 mg, 76%) as a colorless oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 2134 (m), 1644 (w), 1598 (m), 1364 (s), 1167 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.2 Hz, 2 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 5.60 (ddt, *J* = 10.1, 16.4, 6.3 Hz, 1 H), 5.22–5.12 (m, 2 H), 3.77 (d, *J* = 6.3 Hz, 2 H), 3.32 (dd, *J* = 6.8, 7.3 Hz, 2 H), 3.14 (dd, *J* = 6.8, 7.7 Hz, 2 H), 2.73 (s, 1 H), 2.46 (s, 3 H), 2.43 (s, 3 H), 1.99–1.91 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 143.2, 136.2, 133.8, 132.5, 129.7, 129.6, 127.4, 126.9, 119.2, 75.4, 59.3, 51.0, 48.7, 44.5, 26.6, 21.4, 21.3.

MS (EI): *m*/*z* = 445 (M^+ – 1), 381, 317, 291, 224, 155, 135, 91.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{26}N_2O_4S_2$ (M^+): 446.1334; found: 446.1353.

Ethyl {[3-(Allyl-p-toluenesulfonylamino)propyl]-(p-toluenesulfonyl)amino}propynoate (46b)

According to the procedure for the synthesis of **11b**, a solution of **44** (508.8 mg, 0.98 mmol), BuLi (1.3 mL, 2.16 mmol, 1.63 M hexane solution), and ethyl chlorocarbonate (0.11 mL, 1.18 mmol) in THF (20 mL) was stirred at –20 °C for 2 h to afford **46b** (415.2 mg, 81%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 2:1).

IR (neat): 2219 (s), 1705 (s), 1598 (w), 1372 (s), 1174 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 7.7 Hz, 2 H), 7.31 (d, *J* = 7.7 Hz, 2 H), 5.60 (ddt, *J* = 9.7, 16.4, 6.7 Hz, 1 H), 5.22–5.12 (m, 2 H), 4.23 (q, *J* = 7.3 Hz, 2 H), 3.76 (d, *J* = 6.7 Hz, 2 H), 3.45 (dd, *J* = 6.8, 7.7 Hz, 2 H), 3.13 (dd, *J* = 6.8, 7.3 Hz, 2 H), 2.47 (s, 3 H), 2.43 (s, 3 H), 2.00–1.91 (m, 2 H), 1.31 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 145.6, 143.4, 136.2, 133.7, 132.6, 130.1, 129.7, 127.6, 127.0, 119.4, 81.8, 67.7, 61.5, 51.2, 49.0, 44.5, 26.9, 21.6, 21.4, 14.0.

MS (EI): *m*/*z* = 518 (M^+), 473, 454, 363, 339, 317, 299, 267, 252, 224, 207, 155.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{30}N_2O_6S_2$ (M^+): 518.1545; found: 518.1538.

N-[2-(N-Allyl-N-p-toluenesulfonyl)aminobenzyl]-N-ethynyl-p-toluenesulfonamide (47a)

According to the procedure for the synthesis of **11a**, a solution of **45** (303.8 mg, 0.54 mmol) and BuLi (0.76 mL, 1.18 mmol, 1.55 M hexane solution) in THF (10 mL) was stirred at –78 °C for 0.5 h to afford **47a** (208.4 mg, 78%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 2136 (s), 1645 (w), 1597 (s), 1348 (s), 1171 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.7 Hz, 2 H), 7.62 (d, *J* = 6.8 Hz, 1 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.34–7.26 (m, 3 H), 7.12 (dt, *J* = 1.5, 7.7 Hz, 1 H), 6.46 (dd, *J* = 1.0, 8.2 Hz, 1 H), 5.71 (dddd, *J* = 5.8, 7.7, 10.6, 16.4 Hz, 1 H), 5.01–4.94 (m, 2 H), 4.86 (d, *J* = 15.9 Hz, 1 H), 4.72 (d, *J* = 15.9 Hz, 1 H), 4.38 (dd, *J* = 5.8, 14.0 Hz, 1 H), 3.77 (dd, *J* = 7.7, 14.0 Hz, 1 H), 2.63 (s, 1 H), 2.49 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 143.9, 137.1, 137.0, 134.6, 134.5, 131.9, 129.9, 129.5, 129.1, 128.7, 128.1, 127.9, 127.8, 127.5, 119.9, 60.4, 58.8, 54.8, 51.5, 21.7, 21.6.

MS (EI): *m*/*z* = 494 (M^+), 339, 183, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{26}H_{26}N_2O_4S_2$ (M^+): 494.1334; found: 494.1321.

Ethyl {[2-(Allyl-p-toluenesulfonylamino)benzyl](p-toluenesulfonyl)amino}propynoate (47b)

According to the procedure for the synthesis of **11b**, a solution of **45** (382.3 mg, 0.68 mmol), BuLi (0.96 mL, 1.49 mmol, 1.55 M hexane solution), and ethyl chlorocarbonate (0.08 mL, 0.81 mmol) in THF (10 mL) was stirred at –30 °C for 1 h to afford **47b** (318.8 mg, 83%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 2220 (s), 1706 (s), 1598 (m), 1348 (s), 1172 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.2 Hz, 2 H), 7.53 (d, *J* = 8.2 Hz, 1 H), 7.47 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 7.7 Hz, 2 H), 7.34–7.26 (m, 3 H), 7.13 (dt, *J* = 1.5, 7.7 Hz, 1 H), 6.45 (dd, *J* = 1.0, 8.2 Hz, 1 H), 5.73 (dddd, *J* = 5.8, 7.7, 10.2, 16.9 Hz, 1 H), 5.09–4.96 (m, 3 H), 4.81 (d, *J* = 15.9 Hz, 1 H), 4.41 (dd, *J* = 5.8, 13.5 Hz, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.76 (dd, *J* = 7.7, 13.5 Hz, 1 H), 2.49 (s, 3 H), 2.45 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 145.6, 144.0, 137.2, 136.4, 134.4, 134.1, 131.7, 130.2, 129.5, 129.0, 128.8, 128.2, 128.1, 127.9, 127.5, 120.4, 83.1, 67.3, 61.4, 54.7, 51.5, 21.7, 21.6, 14.1.

MS (EI): *m*/*z* = 566 (M^+), 521, 411, 365, 255, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{29}H_{30}N_2O_6S_2$ (M^+): 566.1545; found: 566.1533.

N-[2-(N-Allyl-N-p-toluenesulfonyl)aminobenzyl]-N-(2-trimethylsilylethynyl)-p-toluenesulfonamide (47c)

According to the procedure for the synthesis of **21d**, a solution of **41** (511.7 mg, 1.09 mmol), BuLi (0.80 mL, 1.20 mmol, 1.55 M hexane solution), and phenyl(trimethylsilylethynyl)iodonium triflate (587.5 mg, 1.30 mmol) in toluene (10 mL) was stirred at r.t. for 18 h to afford **47c** (452.1 mg, 73%) as a pale brownish solid after purification by column chromatography on silica gel (hexane/EtOAc 3:1); mp 105 °C.

IR (KBr): 2173 (s), 1647 (w), 1597 (m), 1368 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.2 Hz, 2 H), 7.60 (dd, *J* = 1.0, 7.7 Hz, 1 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 8.2 Hz, 2 H), 7.32–7.26 (m, 3 H), 7.12 (dt, *J* = 1.0, 7.7 Hz, 1 H), 6.46 (dd, *J* = 1.0, 8.2 Hz, 1 H), 5.70 (m, 1 H), 5.01–4.95 (m, 2 H), 4.87 (d, *J* = 15.7 Hz, 1 H), 4.65 (d, *J* = 15.7 Hz, 1 H), 4.35 (dd, *J* = 5.8, 14.0 Hz, 1 H), 3.82 (dd, *J* = 7.7, 14.0 Hz, 1 H), 2.48 (s, 3 H), 2.45 (s, 3 H), 0.08 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 143.8, 137.2, 137.1, 134.7, 134.4, 132.1, 129.7, 129.5, 129.5, 128.6, 128.1, 127.9, 127.8, 127.6, 119.7, 96.1, 72.8, 54.8, 51.8, 21.7, 21.6, –0.0.

MS (EI): *m*/*z* = 566 (M^+), 551, 411, 255, 144, 91.

HRMS (EI): *m*/*z* calcd for $C_{29}H_{34}N_2O_4S_2Si_2$ (M^+): 566.1729; found: 566.1717.

Metathesis Reaction of 11a; 1-(p-Toluenesulfonyl)-2-vinyl-1,4-dihydroquinoline (48a); Typical Procedure (Table 1, entry 1)

To a solution of the ruthenium carbene complex **1b** (17.2 mg, 20.22 μmol, 5 mol%) in toluene (15 mL) was added **11a** (125.9 mg, 0.40 mmol) in toluene (5 mL) at 0 °C, and the solution was stirred at 80 °C for 0.5 h under an ethylene atmosphere. A few drops of ethyl vinyl

ether was added to the mixture, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to afford **48a** (116.8 mg, 93%) as a pale yellow oil.

IR (neat): 1597 (w), 1354 (s), 1172 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 1.0, 8.2 Hz, 1 H), 7.30 (ddd, *J* = 1.0, 7.3, 8.2 Hz, 1 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.18 (ddd, *J* = 1.0, 7.3, 7.7 Hz, 1 H), 7.10 (d, *J* = 8.2 Hz, 2 H), 6.87 (dd, *J* = 1.0, 7.7 Hz, 1 H), 6.46 (dd, *J* = 10.6, 17.4 Hz, 1 H), 5.91 (t, *J* = 4.8 Hz, 1 H), 5.78 (d, *J* = 17.4 Hz, 1 H), 5.26 (d, *J* = 10.6 Hz, 1 H), 2.38 (s, 3 H), 2.43–2.02 (br, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.0, 140.1, 137.5, 134.7, 133.8, 133.8, 129.2, 128.0, 127.8, 127.2, 126.9, 126.6, 123.2, 115.5, 27.6, 21.6.

MS (EI): *m*/*z* = 311 (M^+), 156, 128.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}NO_2S$ (M^+): 311.0980; found: 311.0981.

Ethyl 2-[1-(*p*-Toluenesulfonyl)-1,4-dihydroquinolin-2-yl]acrylate (48b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **11b** (40.3 mg, 0.11 mmol) and **1b** (4.5 mg, 5.25 µmol) in toluene (5.5 mL) was stirred at 80 °C for 1 h under an argon atmosphere to afford **48b** (31.8 mg, 79%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 1719 (s), 1597 (w), 1351 (m), 1170 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.7 Hz, 1 H), 7.34–7.28 (m, 3 H), 7.19 (dd, *J* = 7.2, 7.7 Hz, 1 H), 7.14 (d, *J* = 7.7 Hz, 2 H), 6.89 (d, *J* = 7.3 Hz, 1 H), 6.31 (s, 1 H), 6.12 (s, 1 H), 6.11 (t, *J* = 4.8 Hz, 1 H), 4.29 (q, *J* = 7.3 Hz, 2 H), 2.39 (s, 3 H), 2.29 (br, 2 H), 1.34 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 144.1, 138.5, 137.3, 136.7, 134.1, 133.9, 129.2, 127.9, 127.4, 127.2, 127.0, 126.7, 125.9, 125.4, 61.0, 27.7, 21.6, 14.2.

MS (EI): *m*/*z* = 383 (M^+), 338, 318, 228, 182, 154, 128, 91.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_4S$ (M^+): 383.1191; found: 383.1194.

Dimethyl 10-(*p*-Toluenesulfonyl)-3,9,9a,10-tetrahydroacridine-1,2-dicarboxylate (49)

To a solution of **48a** (30.6 mg, 0.10 mmol) in toluene (5 mL) was added DMAD (0.06 mL, 0.49 mmol), and the solution was stirred at 80 °C for 12 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **49** (19.9 mg, 45%) as a pale yellow oil.

IR (neat): 1728 (s), 1361 (m), 1171 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.3 Hz, 1 H), 7.45 (d, *J* = 8.3 Hz, 2 H), 7.27–7.18 (m, 3 H), 7.10 (dd, *J* = 7.3, 7.8 Hz, 1 H), 6.96 (d, *J* = 7.8 Hz, 1 H), 6.17 (m, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.32–3.15 (m, 2 H), 2.80 (dd, *J* = 5.9, 15.6 Hz, 1 H), 2.67 (m, 1 H), 2.39 (s, 3 H), 2.37 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 167.0, 144.2, 137.0, 136.7, 135.4, 132.2, 129.8, 129.6, 129.0, 127.6, 127.6, 127.0, 125.4, 124.9, 121.4, 52.4, 52.3, 33.6, 33.1, 28.2, 21.5.

MS (EI): *m*/*z* = 453 (M^+), 422, 389, 330, 266, 238, 194, 179.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{23}NO_6S$ (M^+): 453.1246; found: 453.1263.

2-(*p*-Toluenesulfonyl)-3-vinyl-1,2-dihydroisoquinoline (50a)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **12a** (48.9 mg, 0.16 mmol) and **1b** (6.7 mg, 7.85 µmol) in toluene (8.0 mL) was stirred at 80 °C for 0.5 h under an ethylene atmosphere to afford **50a** (34.4 mg, 70%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 1598 (w), 1349 (s), 1164 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.2 Hz, 2 H), 7.04 (ddd, *J* = 1.0, 7.0, 7.2 Hz, 1 H), 6.99–6.92 (m, 2 H), 6.83 (d, *J* = 8.2 Hz, 2 H), 6.68 (d, *J* = 7.2 Hz, 1 H), 6.54 (dd, *J* = 11.1, 17.4 Hz, 1 H), 6.44 (s, 1 H), 5.84 (d, *J* = 17.4 Hz, 1 H), 5.37 (d, *J* = 11.1 Hz, 1 H), 4.75 (s, 2 H), 2.18 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 138.4, 134.3, 133.9, 131.1, 130.0, 128.3, 127.8, 127.5, 127.2, 125.2, 124.9, 120.4, 117.3, 50.4, 21.2.

MS (EI): *m*/*z* = 311 (M^+), 156, 128.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{17}NO_2S$ (M^+): 311.0980; found: 311.0979.

Ethyl 2-[2-(*p*-Toluenesulfonyl)-1,2-dihydroisoquinolin-3-yl]acrylate (50b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **12b** (45.4 mg, 0.12 mmol) and **1b** (5.0 mg, 5.92 µmol) in toluene (6.0 mL) was stirred at 80 °C for 1 h under an ethylene atmosphere to afford **50b** (35.2 mg, 78%) as a pale yellow oil after purification by column chromatography on silica gel (benzene/EtOAc 30:1).

IR (neat): 1721 (s), 1352 (s), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.5 Hz, 2 H), 7.09 (dd, *J* = 7.2, 7.7 Hz, 1 H), 7.03–6.98 (m, 2 H), 6.87 (d, *J* = 8.5 Hz, 2 H), 6.76 (d, *J* = 7.7 Hz, 1 H), 6.58 (s, 1 H), 6.34 (d, *J* = 1.0 Hz, 1 H), 6.08 (d, *J* = 1.0 Hz, 1 H), 4.85 (s, 2 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 2.19 (s, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 143.1, 138.9, 135.5, 134.6, 130.7, 130.0, 128.4, 128.2, 127.3, 127.3, 127.0, 125.2, 125.1, 122.9, 61.1, 50.1, 21.3, 14.1.

MS (EI): *m*/*z* = 383 (M^+), 228, 182, 154, 128.

HRMS (EI): *m*/*z* calcd for $C_{21}H_{21}NO_4S$ (M^+): 383.1191; found: 383.1194.

3-(1-Phenylvinyl)-2-(*p*-toluenesulfonyl)-1,2-dihydroisoquinoline (50c)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **12c** (40.2 mg, 0.10 mmol) and **1b** (4.4 mg, 5.19 µmol) in toluene (5.0 mL) was stirred at 80 °C for 1.5 h under an ethylene atmosphere to afford **50c** (30.8 mg, 77%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 1598 (w), 1354 (s), 1166 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.28 (m, 7 H), 7.07 (ddd, *J* = 1.0, 7.3, 7.8 Hz, 1 H), 7.02–6.95 (m, 2 H), 6.89 (d, *J* = 8.3 Hz, 2 H), 6.73 (d, *J* = 7.3 Hz, 1 H), 6.41 (s, 1 H), 5.75 (d, *J* = 1.0 Hz, 1 H), 5.47 (d, *J* = 1.0 Hz, 1 H), 4.80 (s, 2 H), 2.21 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 143.1, 140.0, 140.0, 135.3, 131.2, 130.3, 128.4, 128.2, 128.1, 128.0, 127.8, 127.5, 127.3, 125.2, 125.1, 122.6, 117.5, 50.5, 21.3.

MS (EI): *m*/*z* = 387 (M^+), 230, 217, 202, 154, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}NO_2S$ (M^+): 387.1293; found: 387.1293.

Dimethyl 5-(*p*-Toluenesulfonyl)-3,4,5,6-tetrahydrophenanthridine-1,2-dicarboxylate (51)

To a solution of **50a** (48.2 mg, 0.15 mmol) in toluene (3 mL) was added DMAD (0.06 mL, 0.46 mmol) at r.t., and the mixture was stirred at 80 °C for 21 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc, 2:1) to provide **51** (34.8 mg, 50%) as a pale yellow oil.

IR (neat): 1732 (s), 1354 (m), 1165 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2 H), 7.07 (ddd, *J* = 1.0, 6.8, 7.3 Hz, 1 H), 7.02–6.97 (m, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 7.3 Hz, 1 H), 4.72 (s, 2 H), 3.80 (s, 3 H), 3.66 (s, 3 H), 3.00 (t, *J* = 8.9 Hz, 2 H), 2.61 (t, *J* = 8.9 Hz, 2 H), 2.22 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 166.7, 143.7, 142.0, 136.8, 135.1, 130.2, 129.5, 128.8, 127.4, 127.4, 126.7, 126.6, 125.6, 123.4, 122.1, 52.3, 52.3, 50.8, 27.0, 23.9, 21.3.

MS (EI): *m*/*z* = 453 (M^+), 422, 298, 266, 238, 180.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{23}NO_6S$ (M^+): 453.1246; found: 453.1244.

Dimethyl 5-(*p*-Toluenesulfonyl)-3,5,6,10b-tetrahydrophenanthridine-1,2-dicarboxylate (52)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **12a** (43.5 mg, 0.14 mmol) and **1b** (5.9 mg, 6.98 µmol) in toluene (7.0 mL) was stirred at 80 °C for 0.5 h under an ethylene atmosphere. After cooling to r.t., DMAD (0.09 mL, 0.70 mmol) was added and the mixture was stirred at 80 °C for 12 h under an argon atmosphere. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **52** (29.1 mg, 46%) as a pale yellow oil.

IR (neat): 1732 (s), 1354 (m), 1168 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.2 Hz, 2 H), 7.24–7.21 (m, 3 H), 6.93 (m, 1 H), 5.93 (t, *J* = 3.6 Hz, 1 H), 4.89 (d, *J* = 13.8 Hz, 1 H), 4.34 (d, *J* = 13.8 Hz, 1 H), 3.86 (s, 3 H), 3.77 (t, *J* = 6.3 Hz, 1 H), 3.69 (s, 3 H), 3.22–3.16 (m, 2 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.6, 144.2, 138.9, 138.6, 134.8, 132.1, 131.6, 129.8, 128.3, 127.7, 127.4, 126.9, 126.9, 123.3, 110.7, 52.5, 52.4, 49.5, 39.2, 29.5, 21.6.

MS (EI): *m*/*z* = 453 (M^+), 422, 389, 330, 298, 266, 238, 180.

HRMS (EI): *m*/*z* calcd for $C_{24}H_{23}NO_6S$ (M^+): 453.1246; found: 453.1244.

2-(*p*-Toluenesulfonyl)-3-vinyl-2,5-dihydro-1*H*-benzo[*c*]azepine (53a)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **13a** (33.4 mg, 0.10 mmol) and **1b** (4.4 mg, 5.13 µmol) in toluene (5.1 mL) was stirred at 80 °C for 0.5 h under an argon atmosphere to afford **53a** (16.2 mg, 49%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 10:1).

IR (neat): 1597 (w), 1338 (s), 1159 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.2 Hz, 2 H), 7.19–7.11 (m, 2 H), 7.06 (ddd, *J* = 1.9, 7.3, 7.3 Hz, 1 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 6.73 (d, *J* = 7.7 Hz, 1 H), 6.38 (dd, *J* = 10.6, 16.9 Hz, 1 H), 5.77 (t, *J* = 5.8 Hz, 1 H), 5.43 (d, *J* = 16.9 Hz, 1 H), 5.13 (d, *J* = 10.6 Hz, 1 H), 4.81 (s, 2 H), 3.30 (d, *J* = 5.8 Hz, 2 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 141.1, 137.0, 135.3, 135.2, 129.8, 129.6, 129.0, 128.8, 127.4, 127.3, 126.3, 125.0, 115.1, 53.5, 33.9, 21.4.

MS (EI): *m*/*z* = 325 (M^+), 260, 170, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{19}H_{19}NO_2S$ (M^+): 325.1136; found: 325.1121.

Ethyl 2-[2-(*p*-Toluenesulfonyl)-2,5-dihydro-1*H*-benzo[*c*]azepin-3-yl]acrylate (53b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **13b** (35.7 mg, 0.09 mmol) and **1b** (3.8 mg, 4.49 µmol) in toluene (4.5 mL) was stirred at 80 °C for 0.5 h under an argon atmosphere to afford **53b** (29.9 mg, 84%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:1).

IR (neat): 1722 (s), 1599 (w), 1349 (s), 1162 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 7.7 Hz, 1 H), 7.11 (d, *J* = 7.7 Hz, 2 H), 7.20–7.09 (m, 2 H), 6.95 (d, *J* = 7.7 Hz, 2 H), 6.80 (d, *J* = 7.2 Hz, 1 H), 6.12 (d, *J* = 1.4 Hz, 1 H), 5.69 (d, *J* = 1.4 Hz, 1 H), 5.63 (t, *J* = 5.3 Hz, 1 H), 4.95 (s, 2H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.48 (d, *J* = 5.3 Hz, 2 H), 2.30 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.5, 141.4, 138.4, 136.5, 136.1, 135.9, 129.4, 129.2, 128.7, 127.6, 127.2, 126.5, 125.9, 124.4, 60.9, 54.4, 34.7, 21.4, 14.1.

MS (EI): *m*/*z* = 397 (M^+), 352, 242, 196, 168, 117, 91.

HRMS (EI): *m*/*z* calcd for $C_{22}H_{23}NO_4S$ (M^+): 397.1348; found: 397.1364.

Dimethyl 5-(*p*-Toluenesulfonyl)-5,6,11,11a-tetrahydro-3*H*-dibenzo[*b*,*e*]azepine-1,2-dicarboxylate (54)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **13a** (33.4 mg, 0.10 mmol) and **1b** (4.4 mg, 5.13 µmol) in toluene (5.1 mL) was stirred at 80 °C for 0.5 h under an argon atmosphere. After cooling to r.t., DMAD (0.04 mL, 0.31 mmol) was added and the mixture was stirred at 80 °C for 29 h under an argon atmosphere. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to provide **54** (17.1 mg, 36%) as a pale yellow oil.

IR (neat): 1732 (s), 1339 (m), 1160 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.2 Hz, 2 H), 7.32 (m, 1 H), 7.24–7.18 (m, 2 H), 7.09 (d, *J* = 8.2 Hz, 2 H), 7.00 (m, 1 H), 5.85 (dd, *J* = 3.4, 3.9 Hz, 1 H), 5.00 (d, *J* = 15.2 Hz, 1 H), 4.36 (d, *J* = 15.2 Hz, 1 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.18–3.00 (m, 2 H), 2.92–2.83 (m, 2 H), 2.70 (dd, *J* = 9.2, 15.0 Hz, 1 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 167.4, 143.2, 139.0, 137.0, 136.6, 136.6, 136.2, 130.9, 129.5, 129.3, 129.3, 128.3, 127.3, 126.9, 124.4, 53.9, 52.4, 52.3, 39.7, 39.5, 28.4, 21.4.

MS (EI): *m*/*z* = 467 (M^+), 436, 403, 371, 344, 280, 252, 213, 104.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{25}NO_6S$ (M^+): 467.1403; found: 467.1378.

1-(*p*-Toluenesulfonyl)-7-vinyl-2,3,4,5-tetrahydro-1*H*-azepine (55a)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **17a** (20.7 mg, 0.07 mmol) and **1b** (6.3 mg, 7.46 µmol) in CH_2Cl_2 (4.0 mL) was stirred at reflux for 26 h under an argon atmosphere to afford **55a** (7.7 mg, 37%) as a pale yellow oil together with **17a** (6.8 mg, 33%).

IR (neat): 1599 (w), 1343 (s), 1158 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 6.25 (dd, *J* = 10.6, 17.2 Hz, 1 H), 5.94 (dd, *J* = 6.8, 7.3 Hz, 1 H), 5.29 (d, *J* = 17.2 Hz, 1 H), 5.05 (d, *J* = 10.6 Hz, 1 H), 3.49 (br, 2 H), 2.42 (s, 3 H), 1.90–1.84 (m, 2 H), 1.73–1.66 (m, 2 H), 1.36–1.29 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 142.4, 139.1, 134.6, 131.9, 129.4, 127.5, 114.6, 49.1, 29.2, 26.0, 23.6, 21.5.

MS (EI): *m*/*z* = 277 (M^+), 212, 155, 122, 91.

HRMS (EI): *m*/*z* calcd for $C_{15}H_{19}NO_2S$ (M^+): 277.1136; found: 277.1134.

Ethyl 2-[1-(*p*-Toluenesulfonyl)-4,5,6,7-tetrahydro-1*H*-azepin-2-yl]acrylinoate (55b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **17b** (21.2 mg, 0.06 mmol) and **1b** (5.2 mg, 6.07 μmol) in CH_2Cl_2 (3.0 mL) was stirred at reflux for 1.5 h under an ethylene atmosphere to afford **55b** (15.6 mg, 74%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/Et_2O 3:2).

IR (neat): 1715 (s), 1599 (w), 1344 (s), 1161 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 6.14 (d, *J* = 1.7 Hz, 1 H), 5.87 (t, *J* = 6.8 Hz, 1 H), 5.86 (d, *J* = 1.7 Hz, 1 H), 3.92 (q, *J* = 7.3 Hz, 2 H), 3.69–3.63 (m, 2 H), 2.40 (s, 3 H), 2.11–2.04 (m, 2 H), 1.88–1.81 (m, 2 H), 1.50–1.42 (m, 2 H), 1.16 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.8, 139.8, 139.5, 138.4, 131.4, 129.3, 128.0, 127.2, 60.7, 50.7, 30.5, 27.0, 23.4, 21.5, 14.0.

MS (EI): *m*/*z* = 349 (M^+), 304, 194, 166, 148, 120, 91.

HRMS (EI): *m*/*z* calcd for $C_{18}H_{23}NO_4S$ (M^+): 349.1348; found: 349.1339.

Ethyl 2-[1,5-Bis-(*p*-toluenesulfonyl)-4,5-dihydro-1*H*-benzo[*b*][1,4]diazepin-2-yl]acrylate (56b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **21b** (33.3 mg, 0.06 mmol) and **1b** (5.1 mg, 6.03 μmol) in toluene (3.0 mL) was stirred at 80 °C for 0.5 h under an ethylene atmosphere to afford **56b** (33.2 mg, 99%) as a white solid after the purification by column chromatography on silica gel (hexane/EtOAc 2:1); mp 187–188 °C.

IR (KBr): 1720 (m), 1598 (w), 1355 (s), 1164 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.2 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.46 (m, 1 H), 7.36–7.26 (m, 7 H), 6.25 (s, 1 H), 5.88 (s, 1 H), 5.30 (dd, *J* = 2.9, 3.9 Hz, 1 H), 4.57 (dd, *J* = 3.9, 18.4 Hz, 1 H), 4.15–4.06 (m, 2 H), 3.73 (dd, *J* = 2.9, 18.4 Hz, 1 H), 2.44 (s, 3 H), 2.42 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 144.0, 143.7, 140.3, 139.4, 137.8, 137.0, 136.9, 136.3, 130.4, 129.9, 129.5, 129.1, 128.4, 128.3, 128.1, 127.5, 125.7, 121.4, 61.0, 49.1, 21.6, 21.6, 14.1.

MS (EI): *m*/*z* = 552 (M^+), 507, 397, 242, 169, 139, 91.

HRMS (EI): *m*/*z* calcd for $C_{28}H_{28}N_2O_6S_2$ (M^+): 552.1389; found: 552.1399.

4-(1-Phenylvinyl)-1,5-bis-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-benzo[*b*][1,4]diazepine (56c)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **21c** (41.9 mg, 0.08 mmol) and **1b** (6.4 mg, 7.53 μmol) in toluene (3.8 mL) was stirred at 80 °C for 1 h under an ethylene atmosphere to afford **56c** (40.7 mg, 97%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 2:1).

IR (neat): 1597 (m), 1356 (s), 1166 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.7 Hz, 2 H), 7.61–7.56 (m, 3 H), 7.38–7.32 (m, 3 H), 7.18 (d, *J* = 8.2 Hz, 2 H), 7.28–7.17 (m, 6 H), 7.10 (dd, *J* = 1.5, 7.7 Hz, 1 H), 5.39 (s, 1 H), 5.32 (dd, *J* = 3.4, 3.9 Hz, 1 H), 5.28 (s, 1 H), 4.54 (dd, *J* = 3.9, 18.4 Hz, 1 H), 3.79 (dd, *J* = 3.4, 18.4 Hz, 1 H), 2.44 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 144.2, 143.6, 140.4, 139.2, 138.7, 138.7, 137.3, 136.1, 129.7, 129.6, 129.3, 129.2, 128.6, 128.3, 128.2, 128.0, 127.9, 127.2, 126.5, 122.0, 116.4, 48.8, 21.6, 21.5.

MS (EI): *m*/*z* = 556 (M^+), 401, 301, 245, 145, 119, 91.

HRMS (EI): *m*/*z* calcd for $C_{31}H_{28}N_2O_4S_2$ (M^+): 556.1490; found: 556.1481.

Ethyl 2-[1,5-Bis(toluene-4-sulfonyl)-1,4,5,6,7,8-hexahydro[1,5]diazocin-2-yl]acrylate (58b)

According to the typical procedure for the metathesis reaction of **11a**, a solution of **46b** (34.4 mg, 0.07 mmol) and **1b** (5.6 mg, 6.63 μmol) in CH_2Cl_2 (33 mL) was stirred at reflux for 24 h under an argon atmosphere to afford **58b** (26.8 mg, 78%) as a pale yellow oil after purification by column chromatography on silica gel (hexane/EtOAc 3:2).

IR (neat): 1717 (s), 1598 (w), 1343 (s), 1161 (s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.2 Hz, 2 H), 7.58 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 7.7 Hz, 2 H), 7.23 (d, *J* = 7.7 Hz, 2 H), 6.18 (t, *J* = 8.2 Hz, 1 H), 6.16 (s, 1 H), 5.81 (s, 1 H), 3.90 (q, *J* = 7.3 Hz, 2 H), 3.85 (d, *J* = 8.2 Hz, 2 H), 3.63 (t, *J* = 5.3 Hz, 2 H), 3.47–3.41 (m, 2 H), 2.44 (s, 3 H), 2.40 (s, 3 H), 1.93–1.86 (m, 2 H), 1.15 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 143.4, 143.4, 139.3, 137.8, 136.7, 136.2, 131.0, 130.5, 129.8, 129.4, 127.4, 127.0, 60.9, 51.8, 48.5, 44.1, 27.9, 21.5, 21.5, 13.9.

MS (EI): *m*/*z* = 518 (M^+), 473, 397, 363, 335, 317, 267, 238, 207, 180, 155, 134, 91.

HRMS (EI): *m*/*z* calcd for $C_{25}H_{30}N_2O_6S_2$ (M^+): 518.1545; found: 518.1538.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609857.

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