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Synthesis of cyclic dienamide using ruthenium-catalyzed ring-closing metathesis of ene–ynamide

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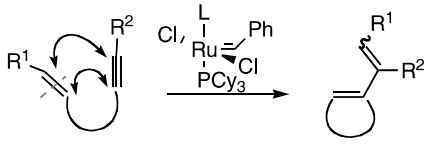
Abstract—Ring-closing metathesis of ene–ynamide, which has alkene and ynamide moieties in a molecule, using a second-generation ruthenium carbene complex produced nitrogen-containing heterocycles, which have a dienamide moiety, in high yields. Diels–Alder reaction of the cyclized product with dienophile proceeded smoothly to give an indole or quinoline derivative in high yield.

1. Introduction

A transition metal carbene complex-catalyzed olefin, enyne, and diyne metatheses are recognized as powerful and useful methodologies in synthetic organic chemistry.[1] Ring-closing metathesis (RCM), ring-opening metathesis (ROM), and cross-metathesis (CM) are now widely used for the synthesis of complex molecules, including natural products and biologically active substances. An intramolecular enyne metathesis is a particularly interesting reaction because carbon–carbon bond formation occurs between the double and triple bonds and the double bond of the enyne is cleaved, and the cleaved alkylidene part of the double bond migrates to the alkyne carbon to afford a cyclized compound having a diene moiety (Scheme 1).[2] We have recently developed enyne metathesis using a Grubbs' ruthenium carbene complex **1** and have reported some applications, including natural product synthesis.[3]



Scheme 1. Ring-closing enyne metathesis.

Ynamide is an interesting moiety because nitrogen is conjugated with an alkyne part.[4] Thus, the metathesis of ene–ynamide, which has an electron-rich ynamide moiety and an alkene moiety in a molecule, is interesting. If the reaction of ene–ynamide **I** with ruthenium carbene complex **1** proceeds, ruthenacyclobutene **III** would be formed and ring opening of **III** would give ruthenium carbene complex **IV**, whose ruthenium carbene would react with an alkene intramolecularly to give ruthenacyclobutane **V**. Ring opening of this would give cyclic dienamide **II**, which should be reactive toward an electron-deficient agent or a dienophile in the Diels–Alder reaction (Scheme 2).[5]

The starting ene–ynamides were synthesized according to the procedure shown in Scheme 3.[6] Coupling reaction of *N*-tosylformamide **2a** and alcohol **3** in the presence of DEAD and PPh_3 followed by treatment with CCl_4 and PPh_3 gave **4a** or **6a**, which was treated with BuLi to give desired ene–ynamides **5a** and **7a** in high yields, respectively. In a similar manner, ene–ynamide **7b** was synthesized from **2a** and alcohol **3c**. Ene–ynamides **5b**, **7c**, and **7d** having an aryl group on an alkyne were synthesized using Negishi-coupling reaction of the alkynylzinc of the terminal alkyne and ArX in the presence of palladium catalyst.[7] An ethoxycarbonyl group on the alkyne of ene–ynamide **5c** was introduced by treatment of **4a** with BuLi and then $ClCO_2Et$. Ene–ynamides *E*-**5d** and *Z*-**5d** having a substituent on the alkene were prepared from **2b** and alcohol *E*-**3d** or *Z*-**3d** by a procedure similar to that used for the synthesis of **5a**, **7a** and **7b**.[8]

Keywords: Ene–ynamide; Dienamide; Enyne metathesis; Indole; Quinoline; Ethylene.
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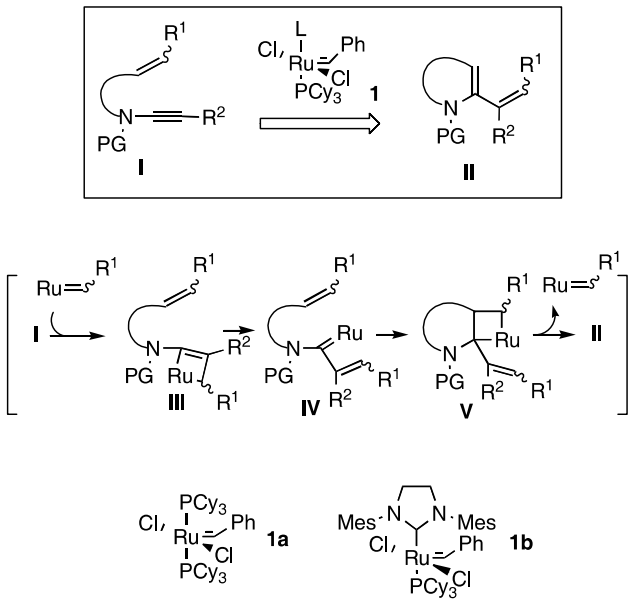


Scheme 2. Plan for synthesis of cyclic dienamide using RCM.

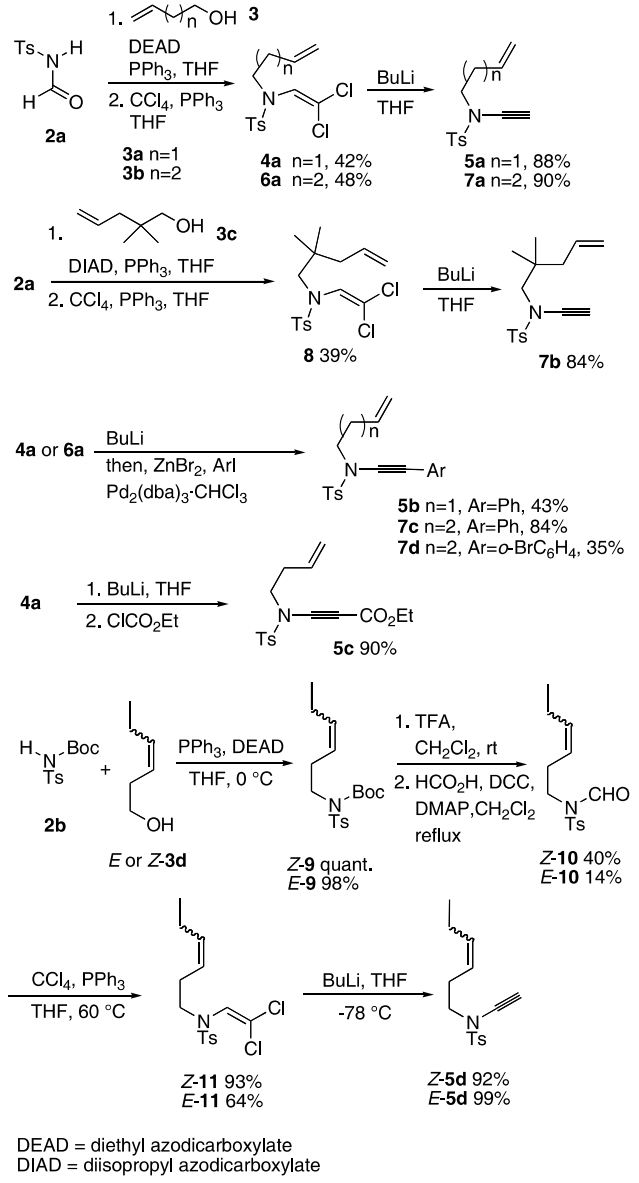
2. Results and discussion

2.1. Synthesis of dihydropyrrolidine derivatives using RCM of ene–ynamide

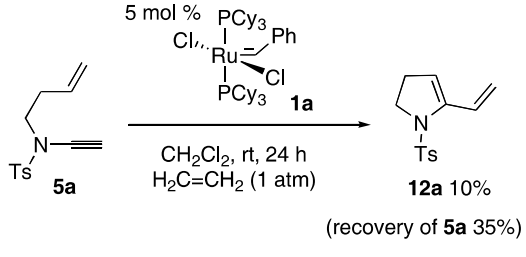
When a CH_2Cl_2 solution of ene–ynamide **5a** was stirred in the presence of 5 mol% of the first-generation ruthenium carbene complex **1a**[9a] under ethylene gas[3e] at rt for 24 h, desired cyclic compound **12a** having a dienamide moiety was obtained in 10% yield along with the starting material in 35% yield. Although the yield was low, it is clear that cyclic dienamide **12a** was obtained from **5a** using RCM (Scheme 4).

To improve the yield of the desired compound, the reaction was carried out under various conditions. The yield of **12a** was further decreased when the CH_2Cl_2 solution was refluxed overnight (entry 2). However, interestingly, the use of the second-generation ruthenium carbene complex **1b**[9b] instead of **1a** improved the yield of **12a** to 66% and the reaction time was shortened (entry 3). Toluene can be used as a solvent, and the reaction was carried out at 80 °C for only 15 min to give **12a** in 83% yield (entry 4).[10] The yield was slightly decreased when the reaction was carried out under argon gas (entry 5) (Table 1).[11]

The substituent effect on the enyne, especially that on the alkyne, was interesting. The substituent effect on the alkyne was first examined. Ene–ynamide **5b** having a phenyl group on the alkyne gave cyclic dienamide **12b** in 85% yield when the reaction was carried out using 10 mol% of **1b** at 80 °C in toluene under ethylene gas. (Table 2, entry 1). Even 5 mol% of the catalyst gave a good result (entry 2). In this case, ethylene gas was effective because the yield was decreased to 31% when the reaction was carried out under argon (entry 3). The electron-withdrawing group on the alkyne tolerates in this reaction and desired cyclic compound **12c** was obtained from **5c** having an ethoxycarbonyl group on the alkyne in 87% yield after only 30 min.



Scheme 3. Synthesis of various ene–ynamides.



Scheme 4. Synthesis of cyclic dienamide.

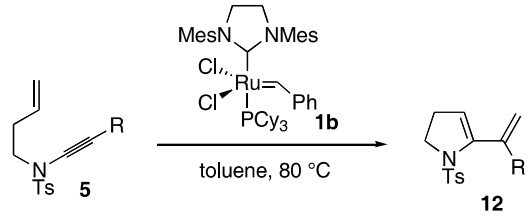
Next, the substituent effect on the alkene was examined. When a toluene solution of ene–ynamide *Z*-**5d** was warmed at 80 °C for 15 min under ethylene gas, surprisingly, cyclic dienamide **12a**, which was previously obtained from **5a**, was obtained in 66% yield. Presumably, the methylidene carbene complex generated from **1b** and ethylene reacts with an alkyne part of *Z*-**5d** to give ruthenacyclobutene **VI**,

Table 1. Ring-closing metathesis of **5a** using **1a** or **1b**[a]

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield of **12a** (%)
1	**1a**	CH_2Cl_2	rt	24	10[b]
2	**1a**	CH_2Cl_2	Reflux	24	7[b]
3	**1b**	CH_2Cl_2	Reflux	4	66
4	**1b**	Toluene	80	0.25	83
5[c]	**1b**	Toluene	80	0.5	76

[a] All reactions were carried out using 5 mol% of the catalyst under ethylene atmosphere except entry 5.
[b] Starting material **5a** was recovered in 35% (run 1) and 36% (run 2) yields, respectively.
[c] The reaction was carried out under Ar.

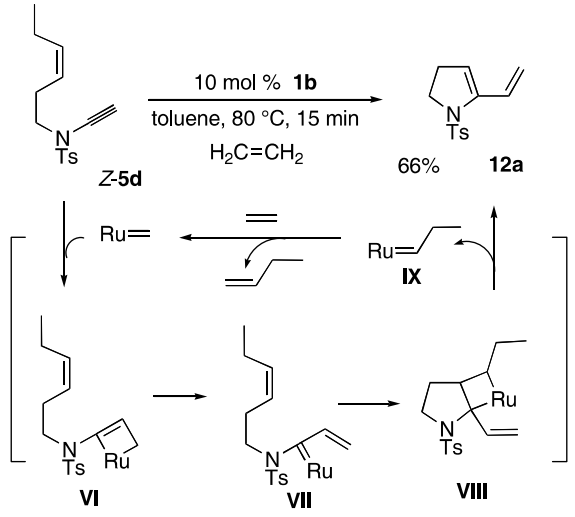
Table 2. Synthesis of various cyclic using **1b**



Entry	R		**1b** (mol%)	Atmosphere	Time (h)	Yield of **12** (%)
1	Ph	**5b**	10	$CH_2{=}CH_2$	0.25	85
2	Ph	**5b**	5	$CH_2{=}CH_2$	0.5	78
3	Ph	**5b**	5	Ar	22	31[a]
4	CO_2Et	**5c**	5	$CH_2{=}CH_2$	0.5	87

[a] Starting material was recovered in 47% yield.

which converts into ruthenium carbene complex **VII**. Then intramolecular reaction occurs to give ruthenacyclobutane **VIII**, whose ring opening gives **12a** and propylidene carbene complex **IX**. However, this complex **IX** would react with ethylene to form methylidene ruthenium carbene complex and propene. Thus, the real species in this reaction would be methylidene ruthenium carbene complex, not propylidene carbene complex **IX**, and **12a** would therefore be formed from *Z*-**5d** (Scheme 5).



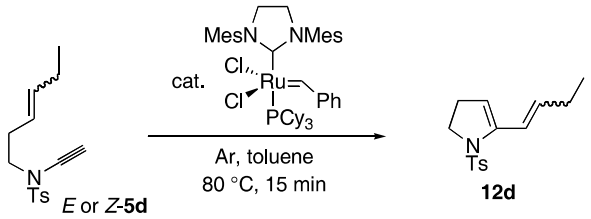
Scheme 5. Synthesis of cyclic dienamide from ene–ynamide having a substituent on alkene.

Thus, the reaction of *Z*-**5d** and **1b** was carried out under argon gas, and a mixture of desired cyclic dienamides *E*-**12d** and *Z*-**12d** was obtained in 39% yield in a ratio to 1 to 1 (Table 3, entry 1). The use of a smaller amount of the catalyst increased the yield of **12d**, and the ratio to *E*- to *Z*- was 1–4.1 (entry 2). However, a longer reaction time did not improve the yield of **12d** (entry 3). From *E*-**5d**, the same compound **12d** was obtained in 48% yield, and the isomeric ratio was 1.5–1. In this case, the use of 5 mol% of the catalyst also increased the yield of **12d** to 57% with a ratio to 1–2.6. These results indicated that a smaller amount of the catalyst improved the yield and that the ratio of the *Z*-isomer of the product was raised, but the reason for this is not clear.

2.2. Synthesis of piperidine derivatives using metathesis of ene–ynamide

Since the synthesis of dihydropyrrole derivative **12** from ene–ynamide **5** was achieved, the reaction of ene–ynamide **7**, which has a one-carbon elongated substituent on nitrogen, using **1b** was carried out. In this case, tetrahydropiperidine derivative **13** would be produced. When a toluene solution of **7a** was warmed in the presence of 5 mol% of **1b** under ethylene gas at 80 °C for 20 h, desired piperidine derivative **13a** was obtained, though the yield was low (entry 1). A lower reaction temperature decreased the yield of **13a** (entry 2). When the solvent was changed from toluene to CH_2Cl_2, the yield of desired compound **13a** was slightly improved (entry 3), and an increase of the amount of the catalyst **1b** to 10 mol% increased the yield of **13a** to 85% (entry 4). The same reaction was carried out under argon gas to afford **13a** in almost the same yield (entry 5). Cyclic dienamide **13b** was obtained from ene–ynamide **7b** using these reaction conditions under ethylene gas in 61% yield (entry 6). Ene–ynamide **7c** having a phenyl group on the alkyne was treated in a similar manner to give cyclic dienamide **13c** in 76% yield (entry 7). In this case, the use of toluene as a solvent improved the yield of **13c** (entry 8).

Table 3. Reaction of *E*-**5d** or *Z*-**5d** with **1b**



Entry	Substrate	cat. (mol%)	Yield (%)	Ratio of **12d** (*E*/*Z*)
1	*Z*-**5d**	10	39	1:1
2	*Z*-**5d**	5	48	1:4.1
3[a]	*Z*-**5d**	5	41	1:5.9
4	*E*-**5d**	10	48	1.5:1
5	*E*-**5d**	5	57	1:2.6

[a] Reaction time, 30 min.

However, ene–ynamide **7d** having an *ortho*-bromophenyl group on the alkyne did not give a good result even when 20 mol% of the catalyst was used due to the steric hindrance (entry 9) (Table 4).

Thus, a cyclic dienamide could be synthesized from ene–ynamide using ring-closing enyne metathesis.

2.3. Synthesis of indole and quinoline derivatives from cyclic dienamide by Diels–Alder reaction

Since the products obtained by the present RCM reaction have a dienamide moiety, they should be good Diels–Alder precursors. A toluene solution of **12a** was warmed at 60 °C in the presence of dimethyl but-2-ynedioate (DMAD) to give tetrahydroindole derivatives **14a** and **14b** in 52% yield in a ratio of 1.3–1. Compound **14b** is an isomerization product of the double bond of **14a**. Since the cyclic dienamide is unstable, a one-pot reaction from ene–ynamide **5a** was examined. A toluene solution of **5a** and 10 mol% of **1b** was stirred under ethylene gas at 80 °C for 15 min, and then DMAD was added after cooling. The toluene solution was warmed at 60 °C for 12 h under argon to give desired indole derivative **14a** in 80% yield. Furthermore, when 1-phenyl-1*H*-pyrrole-2,5-dione was used as a dienophile, tricyclic compound **15** was obtained in 68% yield. In a similar manner, *Z*-**5d** was stirred in the presence of **1b** in toluene, and then to the toluene solution was added DMAD and the whole solution was warmed at 100 °C for 3 h. The resultant product was treated with DDQ in toluene at 80 °C for 20 h to give indoline **16** and indole **17** derivatives in 20 and 12% yields, respectively, via three steps (Scheme 6).

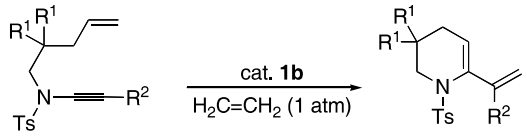
Furthermore, synthesis of quinoline derivatives was examined. A toluene solution of cyclic dienamide **13a** and DMAD was heated at 100 °C for 12 h to give quinoline derivative **18b** in 71% yield. On the other hand, to a toluene solution of the reaction product **13a**, obtained from **7a** using 10 mol% of **1b**, was added DMAD and the solution was heated at 100 °C for 12 h to give quinoline derivative **18a** in 57% yield (Scheme 7).

These results indicated that indole and quinoline derivatives, which are important skeletons in natural products or biologically active substances, could be synthesized from ene–ynamide using RCM followed by Diels–Alder reaction as a one-pot reaction. The reason why the reaction of the isolated product **12a** or **13a** gave isomerization product **14b** or **18b** of the double bond is not clear.

3. Conclusions

Since an alkyne part of ynamide is conjugated with nitrogen, the reactivity of ynamide is very interesting. It was expected that metathesis of enyne containing ynamide would give a cyclic dienamide, whose reactivity is also interesting. Thus, metathesis of enyne containing ynamide was examined. As a result, cyclic dienamides were obtained from ene–ynamide using the second-generation ruthenium carbene

Table 4. Ring-closing metathesis of **7** using catalyst **1b**



7a R^1=R^2=H
7b R^1=Me, R^2=H
7c R^1=H, R^2=Ph
7d R^1=H, R^2=*o*-BrC_6H_4

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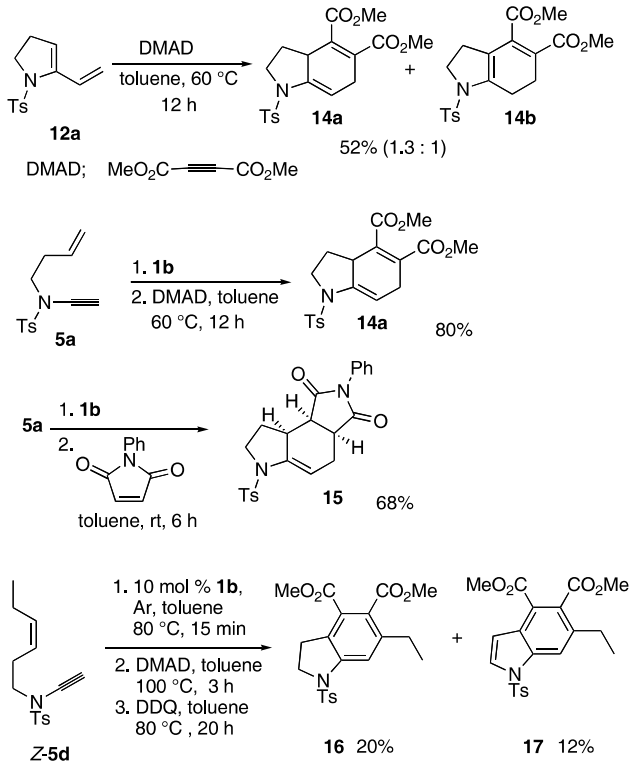
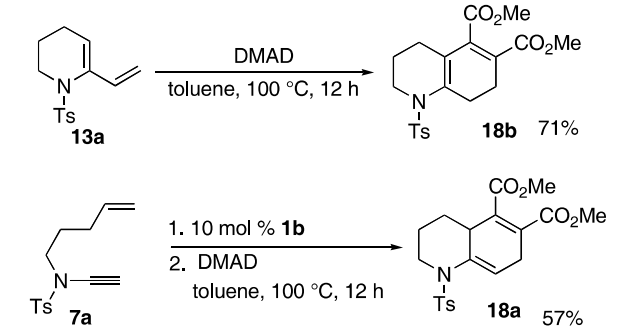
Entry	Substrate	**1b** (mol%)	Solvent	Temperature (°C)	Product	Time (h)	Yield (%)
1	**7a**	5	Toluene	80	**13a**	20	22
2	**7a**	5	Toluene	60	**13a**	20	19[a]
3	**7a**	5	CH_2Cl_2	Reflux	**13a**	27	36[a]
4	**7a**	10	CH_2Cl_2	Reflux	**13a**	6	85
5[b]	**7a**	10	CH_2Cl_2	Reflux	**13a**	5	82
6	**7b**	10	CH_2Cl_2	Reflux	**13b**	6	61
7	**7c**	10	CH_2Cl_2	Reflux	**13c**	70	76
8	**7c**	5	Toluene	80	**13c**	0.5	88
9	**7d**	20	Toluene	80	**13d**	41	34[a]

[a] Starting material was recovered in 20% (run 2), 38% (run 3) and 23% (run 9) yields, respectively.
[b] The reaction was carried out under Ar.



Scheme 6. Synthesis of indole derivatives.



Scheme 7. Synthesis of quinoline derivatives.

complex. The cyclic dienamide is good precursor toward the Diels–Alder reaction and afforded an indole or quinoline derivative under mild conditions in high yield. These compounds are important skeletons of natural products or biologically active substances. Further investigations of RCM of ene–ynamide should give various interesting compounds.

4. Experimental

4.1. General

The metathesis reactions were carried out under an atmosphere of ethylene (1 atm) unless otherwise mentioned. All other manipulations were carried out under an atmosphere of argon unless otherwise mentioned. Solvents were distilled under an atmosphere of argon from sodium–benzophenone (toluene) or CaH_2 (CH_2Cl_2). Ethylene gas was purified by passage through the aqueous CuCl solution (2 g of CuCl in 180 mL of saturated NH_4Cl solution) and concentrated H_2SO_4 and then KOH tubes. Ruthenium complexes were purchased from Strem Chemicals or Aldrich Chemical Company. All other solvents and reagents were purified when necessary using standard procedure.

4.2. Typical procedure for the metathesis reaction

A solution of **5a** (91.5 mg, 0.37 mmol) and **1b** (15.6 mg, 0.018 mmol) in toluene was stirred at 80 °C for 15 min under ethylene atmosphere (1 atm). After the solution was cooled to rt, a few drops of ethyl vinyl ether was added. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/Et_2O/Et_3N 100:5:1) to give **12a** (76.2 mg, 83%) as colorless oil.

4.3. Spectral data of metathesis products

4.3.1. 1-*p*-Toluenesulfonyl-5-vinyl-2,3-dihydro-1*H*-pyrrole (12a). IR (neat) ν 1647, 1589, 1343, 1147 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.10 (ddd, J=8.4, 8.4, 3.0 Hz, 2H), 2.40 (s, 3H), 3.77 (dd, J=8.4, 8.4 Hz, 2H), 5.20 (d, J=10.8 Hz, 1H), 5.35 (dd, J=3.0, 3.0 Hz, 1H), 5.53 (d, J=17.6 Hz, 1H), 6.60 (dd, J=17.6, 10.8 Hz, 1H), 7.26 (d, J=8.4 Hz, 2H), 7.64 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5, 27.5, 50.5, 103.9, 113.5, 117.0, 127.9, 128.8, 129.5, 133.9, 143.6; EI-LRMS m/z 249 (M^+), 184, 155, 91; EI-HRMS m/z calcd for $C_{13}H_{15}O_2NS$ (M^+) 249.0823, found 149.0831.

4.3.2. 5-(1-Phenyl-vinyl)-1-*p*-toluenesulfonyl-2,3-dihydro-1*H*-pyrrole (12b). IR (KBr) ν 1597 (w), 1350 (m), 1167 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.12 (dt, J=2.9, 8.3 Hz, 2H), 2.42 (s, 3H), 3.95 (t, J=8.3 Hz, 2H), 5.48 (t, J=2.9 Hz, 1H), 5.50 (s, 2H), 7.25–7.43 (m, 7H), 7.68 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5, 28.0, 51.2, 116.5, 119.8, 127.1, 127.7, 127.8, 128.1, 129.4, 134.6, 138.9, 142.2, 143.6, 144.5; EI-LRMS m/z 325 (M^+), 260, 246, 186, 168, 103, 91; EI-HRMS m/z calcd for $C_{19}H_{19}O_2NS$ (M^+) 325.1137, found 325.1147.

4.3.3. Ethyl 2-(1-*p*-toluenesulfonyl-4,5-dihydro-1*H*-pyrrol-2-yl)-acrylate (12c). IR (KBr) ν 1721 (s), 1598 (m), 1352 (s), 1164 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.36 (t, J=7.1 Hz, 3H), 2.18 (dt, J=2.8, 8.7 Hz, 2H), 2.43 (s, 3H), 3.85 (t, J=8.7 Hz, 2H), 4.31 (q, J=7.1 Hz, 2H), 5.44 (t, J=2.8 Hz, 1H), 5.88 (d, J=1.3 Hz, 1H), 6.29 (d, J=1.3 Hz, 1H), 7.30 (d, J=8.2 Hz, 2H), 7.66 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 21.5, 28.0, 50.2, 61.2, 118.4, 127.2, 127.8, 129.5, 133.9, 134.8, 140.6, 143.7, 165.2; EI-LRMS m/z 321 (M^+), 276, 182, 166, 155, 120, 92; EI-HRMS m/z calcd for $C_{16}H_{19}O_4NS$ (M^+) 321.1035, found 321.1010.

4.3.4. 5-But-1-enyl-1-*p*-toluenesulfonyl-2,3-dihydro-1*H*-pyrrole (12d). IR (neat) ν 2964, 1598, 1351, 1164 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.03 (t, J=7.4 Hz, 1.5H), 1.09 (t, J=7.4 Hz, 1.5H), 2.08–2.31 (m, 4H), 2.42 (s, 3H), 3.76 (t, J=8.2 Hz, 1H), 3.78 (t, J=7.8 Hz, 1H), 5.10 (t, J=2.8 Hz, 0.5H), 5.22 (t, J=2.8 Hz, 0.5H), 5.73 (dt, J=11.5, 7.1 Hz, 0.5H), 6.07 (dt, J=15.8, 6.3 Hz, 0.5H), 6.24

(m, 1H), 7.27 (m, 2H), 7.69 (m, 2H); EI-LRMS *m/z* 277 (M^+), 198, 184, 155, 122, 91; EI-HRMS *m/z* calcd for $C_{15}H_{19}O_2NS$ (M^+) 277.1136, found 277.1144.

4.3.5. 1-*p*-Toluenesulfonyl-6-vinyl-1,2,3,4-tetrahydropyridine (13a). IR (neat) ν 1654, 1343, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20–1.30 (m, 2H), 1.90–1.97 (m, 2H), 2.42 (s, 3H), 3.58–3.63 (m, 2H), 5.04 (d, J=10.7 Hz, 1H), 5.39 (d, J=17.2 Hz, 1H), 5.50 (dd, J=4.0, 4.0 Hz, 1H), 6.51 (dd, J=17.2, 10.7, 1 Hz), 7.27 (d, J=8.5 Hz, 2H), 7.63 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.6, 22.8, 46.4, 112.8, 116.0, 127.2, 129.4, 136.4, 136.5, 137.6, 143.3; EI-LRMS *m/z* 263 (M^+), 198, 155, 108, 91; EI-HRMS *m/z* calcd for $C_{14}H_{17}O_2NS$ (M^+) 263.0980, found 263.0965.

4.3.6. 3,3-Dimethyl-1-*p*-toluenesulfonyl-6-vinyl-1,2,3,4-tetrahydro-pyridine (13b). IR (neat) ν 1635, 1598, 1349, 1163 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 6H), 1.83 (d, J=3.8 Hz, 2H), 2.41 (s, 3H), 3.34 (s, 2H), 4.98 (d, J=10.6 Hz, 1H), 5.13 (t, J=3.8 Hz, 1H), 5.32 (d, J=16.9 Hz, 1H), 6.47 (dd, J=16.9, 10.6 Hz, 1H), 7.26 (d, J=8.0 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.4, 29.5, 37.5, 56.9, 110.0, 114.3, 127.0, 129.4, 134.3, 136.4, 138.2, 143.0; EI-LRMS *m/z* 291 (M^+), 276, 262, 248, 155, 136, 91; EI-HRMS *m/z* calcd for $C_{16}H_{21}O_2NS$ (M^+) 291.1293, found 291.1289.

4.3.7. 6-(1-Phenyl-vinyl)-1-*p*-toluenesulfonyl-1,2,3,4-tetrahydro-pyridine (13c). IR (KBr) ν 1599 (w), 1357 (m), 1166 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.52–1.62 (m, 2H), 2.12 (dt, J=3.8, 6.8 Hz, 2H), 2.37 (s, 3H), 3.48–3.53 (m, 2H), 5.30 (d, J=1.6 Hz, 1H), 5.35 (d, J=1.6 Hz, 1H), 5.61 (t, J=3.8 Hz, 1H), 7.14 (d, J=8.2 Hz, 2H), 7.27–7.33 (m, 5H), 7.40 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.5, 21.3, 22.8, 46.2, 113.8, 120.6, 127.2, 127.3, 127.3, 127.8, 129.2, 136.5, 138.5, 139.6, 143.1, 149.1; EI-LRMS *m/z* 339 (M^+), 274, 184, 170, 156, 142, 130, 103, 91; EI-HRMS *m/z* calcd for $C_{20}H_{21}O_2NS$ (M^+) 339.1293, found 339.1292.

4.3.8. 6-[1-(2-Bromo-phenyl)-vinyl]-1-*p*-toluenesulfonyl-1,2,3,4-tetrahydro-pyridine (13d). IR (neat) ν 1598 (m), 1348 (s), 1165 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.48–1.58 (m, 2H), 2.06 (dt, J=4.0, 6.9 Hz, 2H), 2.39 (s, 3H), 3.42–3.46 (m, 2H), 5.17 (d, J=1.3 Hz, 1H), 5.60 (d, J=1.3 Hz, 1H), 5.71 (t, J=4.0 Hz, 1H), 7.15 (ddd, J=1.8, 7.4, 7.9 Hz, 1H), 7.18 (d, J=8.2 Hz, 2H), 7.29 (ddd, J=1.3, 7.4, 7.5 Hz, 1H), 7.42 (d, J=8.2 Hz, 2H), 7.51 (dd, J=1.8, 7.5 Hz, 1H), 7.54 (dd, J=1.3, 7.9 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.3, 21.5, 22.8, 46.2, 117.1, 122.9, 123.4, 127.1, 127.6, 128.6, 129.4, 132.7, 133.6, 136.8, 138.6, 140.9, 143.4, 148.3; EI-LRMS *m/z* 419 (M^+, ^{81}Br), 417 (M^+, ^{79}Br), 338, 274, 262, 182, 91; EI-HRMS *m/z* calcd for $C_{20}H_{20}O_2NS^{81}Br$ (M^+) 419.0378, found 419.0361, *m/z* calcd for $C_{20}H_{20}O_2NS^{79}Br$ (M^+) 417.0398, found 419.0362.

4.4. Procedure for the synthesis of 5 and 7

4.4.1. *N*-But-3-enyl-*N*-(2,2-dichlorovinyl)-*p*-toluenesulfonamide (4a). To a solution of **2a** (2.9 g, 14 mmol) in THF (29 mL) were added PPh_3 (4.9 g, 19 mmol), **3a** (1.5 mL, 17 mmol) and DEAD (2.7 mL, 17 mmol) at 0 °C, and the mixture was stirred at rt for 14 h. After the solvent was evaporated, the residue was purified by short column chromatography on silica gel (hexane/AcOEt 10:1) to give an inseparable mixture of *N*-alkylated product and *O*-alkylated product (2.9 g, in the ratio of 1.3:1). To a solution of the above mixture (2.9 g) in THF (38 mL) were added PPh_3 (9.0 g, 35 mmol) and CCl_4 (11 mL, 115 mmol) at rt, and the mixture was stirred at 60 °C for 6 h. To the mixture was added saturated $NaHCO_3$ solution, and the aqueous layer was extracted with Et_2O. The organic layer was washed with saturated NaCl solution, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 20:1) to give **4a** (1.9 g, 42%, two steps) as a colorless crystal. Mp 53–55 °C; IR (Nujol) ν 1642, 1597, 1357, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (dt, J=6.8, 7.3 Hz, 2H), 2.44 (s, 3H), 3.41 (t, J=7.3 Hz, 2H), 5.05 (d, J=10.2 Hz, 1H), 5.08 (d, J=17.0 Hz, 1H), 5.70 (ddt, J=17.0, 10.2, 6.8 Hz, 1H), 6.31 (s, 1H), 7.32 (d, J=8.1 Hz, 2H), 7.68 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 32.9, 48.5, 117.4, 124.1, 124.7, 127.1, 129.7, 133.9, 135.3, 144.0; EI-LRMS *m/z* 319 (M^+), 278, 223, 164, 155, 91; EI-HRMS *m/z* calcd for $C_{13}H_{15}O_2NS^{35}Cl_2$ (M^+) 319.0200, found 319.0190.

4.4.2. *N*-But-3-enyl-*N*-ethynyl-*p*-toluenesulfonamide (5a). To a solution of **4a** (200 mg, 0.64 mmol) in THF (12 mL) was added BuLi (1.58 M solution in hexane, 0.87 mL, 1.37 mmol) at −78 °C, and the solution was stirred for 1 h. To the solution was added saturated NH_4Cl solution, and the aqueous solution was extracted with Et_2O. The organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 5:1) to give **5a** (137.1 mg, 88%) as colorless oil. IR (Nujol) ν 3260, 2150, 1374, 1167 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.40 (dt, J=7.3, 7.6 Hz, 2H), 2.46 (s, 3H), 2.75 (s, 1H), 3.38 (t, J=7.6 Hz, 2H), 5.05 (d, J=10.2 Hz, 1H), 5.10 (d, J=17.3 Hz, 1H), 5.71 (ddt, J=17.3, 10.2, 7.3 Hz, 1H), 7.35 (d, J=8.4 Hz, 2H), 7.81 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.6, 32.0, 50.5, 59.4, 75.9, 117.8, 127.6, 129.8, 133.4, 134.6, 144.7; EI-LRMS *m/z* 248 (M^+-H), 184, 155, 96, 55; EI-HRMS *m/z* calcd for $C_{13}H_{14}O_2NS$ (M^+-H) 248.0745, found 248.0736.

4.4.3. *N*-(2,2-Dichloro-vinyl)-*N*-pent-4-enyl-*p*-toluenesulfonamide (6a). A crude product, which was obtained from **2a** (3.44 g, 17 mmol), PPh_3 (6.34 g, 24 mmol), **3b** (2.4 mL, 23 mmol) and DEAD (10.2 mL, 22 mmol), was purified by short column chromatography on silica gel (hexane/AcOEt 5:1) to give an inseparable mixture of *N*-alkylated product and *O*-alkylated product (4.46 g, in the ratio of 1.8:1). To a solution of the above mixture (4.46 g) and PPh_3 (11.32 g, 43 mmol) in THF (38 mL) was added CCl_4 (14 mL, 142 mmol) at 60 °C for 3 h, and the mixture was stirred continuously at 60 °C for 12 h. To the mixture was added saturated $NaHCO_3$ solution, and the aqueous layer was extracted with Et_2O. The organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 10:1) to give

6a (2.79 g, 48%, two steps) as a colorless crystal. Mp 73–75 °C; IR (Nujol) ν 1638, 1597, 1351, 1161 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (tt, J=7.4, 7.4 Hz, 2H), 2.08 (dt, J=6.8, 7.4 Hz, 2H), 2.44 (s, 3H), 3.32 (t, J=7.4 Hz, 2H), 4.99 (d, J=10.2 Hz, 1H), 5.02 (d, J=16.9 Hz, 1H), 5.75 (ddt, J=16.9, 10.2, 6.8 Hz, 1H), 6.26 (s, 3H), 7.32 (d, J=8.1 Hz, 2H), 7.68 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.5, 30.5, 48.6, 115.3, 124.6, 124.7, 127.0, 129.7, 135.0, 136.9, 144.0; EI-LRMS m/z 333 (M^+), 318, 298, 278, 237, 178, 91; EI-HRMS m/z calcd for $C_{14}H_{17}O_2NS^{35}Cl_2$ (M^+) 333.0357, found 333.0354.

4.4.4. *N*-Ethynyl-*N*-pent-4-enyl-*p*-toluenesulfonamide (7a). In a similar manner to that for the synthesis of **5a** from **4a**, **7a** (262 mg, 99%) was synthesized from **6a** (347 mg, 1.0 mmol) and BuLi (1.66 M solution in hexane, 1.4 mL, 2.3 mmol). IR (neat) ν 3297, 2132, 1641, 1597, 1364, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.75 (tt, J=7.2, 7.2 Hz, 2H), 2.09 (dt, J=6.6, 7.2 Hz, 2H), 2.45 (s, 3H), 2.73 (s, 1H), 3.31 (*t*, J=7.2 Hz, 2H), 4.99 (d, J=10.1 Hz, 1H), 5.02 (d, J=16.9 Hz, 1H), 5.75 (ddt, J=16.9, 10.1, 6.6 Hz, 1H), 7.35 (d, J=8.3 Hz, 2H), 7.80 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 26.8, 30.2, 50.6, 59.1, 75.9, 115.5, 127.4, 129.6, 134.3, 136.8, 144.6; FAB-LRMS m/z 264 (M^++H), 237, 198, 155, 108, 91; FAB-HRMS m/z calcd for $C_{14}H_{18}O_2NS$ 264.1058 (M^++H), found 264.1034.

4.4.5. *N*-(2,2-Dichloro-vinyl)-*N*-(2,2-dimethyl-pent-4-enyl)-*p*-toluenesulfonamide (8). To a solution of **2a** (1.6 g, 8.0 mmol) in THF (26 mL) were added PPh_3 (2.5 g, 20 mmol), **3c** (1.1 g, 9.6 mmol) and DIAD (1.9 mL, 9.7 mmol) at 0 °C, and the mixture was stirred at 50 °C for 16 h. After the solvent was evaporated, the residue was purified by short column chromatography on silica gel (hexane/AcOEt 10:1) to give an inseparable mixture of *N*-alkylated product and *O*-alkylated product (1.5 g, in the ratio of 1:1.4). To a solution of the above mixture (1.5 g) in THF (17 mL) were added PPh_3 (1.0 g, 15 mmol) and CCl_4 (4.9 mL, 51 mmol) at rt, and the mixture was stirred at 60 °C for 24 h. To the mixture was added saturated $NaHCO_3$ solution, and the aqueous layer was extracted with Et_2O. The organic layer was washed with saturated NaCl solution, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 20:1) to give **8** (675 mg, 23%, two steps) as colorless oil. IR (Nujol) ν 1638, 1598, 1358, 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 6H), 2.03 (d, J=7.3 Hz, 2H), 2.44 (s, 3H), 3.02 (s, 2H), 5.02 (d, J=16.9 Hz, 1H), 5.05 (d, J=9.2 Hz, 1H), 5.77 (ddt, J=16.9, 9.2, 7.3 Hz, 1H), 7.32 (d, J=8.1 Hz, 2H), 7.65 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 25.3, 35.4, 44.6, 59.8, 117.7, 127.2, 127.3, 127.7, 129.7, 134.1, 135.1, 143.9.

4.4.6. *N*-(2,2-Dimethyl-pent-4-enyl)-*N*-ethynyl-*p*-toluenesulfonamide (7b). In a similar manner to that for the synthesis of **5a** from **4a**, **7b** (247 mg, 84%) was synthesized from **8** (366 mg, 1.0 mmol) and BuLi (1.66 M solution in hexane, 1.4 mL, 2.3 mmol). IR (neat) ν 3302, 2134, 1638, 1597, 1367, 1170 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 6H), 2.10 (d, J=7.5 Hz, 2H), 2.23 (s, 3H), 2.68 (s, 1H), 3.13 (s, 2H), 5.03 (d, J=10.3 Hz, 1H), 5.04 (d, J=16.9 Hz, 1H), 5.81 (ddt, J=16.9, 10.3, 7.5 Hz, 1H), 7.35 (d, J=8.2 Hz, 2H), 7.79 (d, J=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 25.1, 35.9, 44.4, 58.3, 61.6, 78.6, 117.9, 127.6, 129.5, 135.1, 134.2, 144.6; EI-LRMS m/z 291 (M^+), 290, 276, 262, 250, 155, 136, 91; EI-HRMS m/z calcd for $C_{16}H_{21}O_2NS$ (M^+) 291.1293, found 291.1287.

4.4.7. *N*-But-3-enyl-*N*-phenylethynyl-*p*-toluenesulfonamide (5b). To a solution of **4a** (300 mg, 0.94 mmol) in THF (6 mL) was added BuLi (1.58 M solution in hexane, 1.3 mL, 2.1 mmol) at −78 °C, and the mixture was stirred for 1 h. Then, a solution of $ZnBr_2$ (253 mg, 1.12 mmol) in THF (4 mL) was added via syringe and the solution was stirred at rt for 30 min. The whole mixture was transferred via cannula to a solution of $Pd_2dba_3\cdot CHCl_3$ (48.5 mg, 0.05 mmol), PPh_3 (49.1 mg, 0.19 mmol) and iodobenzene (0.13 mL, 1.12 mmol) in THF (5 mL), and the solution stirred at rt for 18 h. The volatiles were removed and the residue was dissolved in AcOEt (30 mL). The organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N 250:50:3) to give **5b** (130.4 mg, 43%). IR (neat) ν 2235 (s), 1598 (m), 1367 (s), 1171 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.41–2.50 (m, 2H), 2.45 (s, 3H), 3.47 (t, J=7.3 Hz, 2H), 5.06 (dd, J=1.4, 10.2 Hz, 1H), 5.11 (dd, J=1.4, 17.1 Hz, 1H), 5.75 (ddt, J=10.2, 17.1, 6.9 Hz, 1H), 7.27–7.39 (m, 7H), 7.84 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.6, 32.2, 50.9, 70.9, 82.1, 117.7, 122.8, 127.7, 127.8, 128.2, 129.7, 131.3, 133.6, 134.5, 144.6; EI-LRMS m/z 325 (M^+), 260, 233, 186, 170, 155, 128, 105, 91; EI-HRMS m/z calcd for $C_{19}H_{19}O_2NS$ (M^+) 325.1137, found 325.1138.

4.4.8. *N*-Pent-4-enyl-*N*-phenylethynyl-*p*-toluenesulfonamide (7c). In a similar manner to that for the synthesis of **5b** from **4a**, **7c** (260 mg, 84%) was synthesized from **6a** (303 mg, 0.91 mmol), BuLi (1.58 M solution in hexane, 1.3 mL, 2.0 mmol), $ZnBr_2$ (245 mg, 1.08 mmol), $Pd_2dba_3\cdot CHCl_3$ (46.9 mg, 0.05 mmol), PPh_3 (47.9 mg, 0.18 mmol) and iodobenzene (0.12 mL, 1.09 mmol). IR (neat) ν 2236 (s), 1598 (m), 1367 (s), 1171 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.75–1.87 (m, 2H), 2.08–2.18 (m, 2H), 2.45 (s, 3H), 3.41 (t, J=7.2 Hz, 2H), 4.97–5.09 (m, 2H), 5.78 (ddt, J=10.2, 16.8, 6.6 Hz, 1H), 7.26–7.39 (m, 7H), 7.84 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.6, 27.1, 30.2, 51.0, 70.6, 82.3, 115.6, 122.8, 127.6, 127.7, 128.2, 129.7, 131.3, 134.4, 137.0, 144.6; EI-LRMS m/z 339 (M^+), 274, 184, 170, 142, 130, 116, 105, 91; EI-HRMS m/z calcd for $C_{20}H_{21}O_2NS$ (M^+) 339.1293, found 339.1317.

4.4.9. *N*-(2-Bromo-phenylethynyl)-*N*-pent-4-enyl-*p*-toluenesulfonamide (7d). In a similar manner to that for the synthesis of **5b** from **4a**, **7d** (142.5 mg, 35%) was synthesized from **6a** (329.6 mg, 0.99 mmol), BuLi (1.60 M solution in hexane, 1.4 mL, 2.17 mmol), $ZnBr_2$ (266.5 mg, 1.18 mmol), $Pd_2dba_3\cdot CHCl_3$ (51.0 mg, 0.05 mmol), PPh_3 (51.7 mg, 0.20 mmol) and 2-bromo-iodobenzene (0.15 mL, 1.18 mmol). IR (neat) ν 2236 (s), 1597 (m), 1369 (s), 1172 (s) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.86 (tt, J=7.1, 7.3 Hz, 2H), 2.14 (dt, J=6.6, 7.3 Hz, 2H), 2.45 (s, 3H), 3.45 (t, J=7.1 Hz, 2H), 4.99 (d, J=10.2 Hz, 1H), 5.05

(d, J=16.8 Hz, 1H), 5.78 (ddt, J=10.2, 16.8, 6.6 Hz, 1H), 7.11 (dd, J=7.6, 7.9 Hz, 1H), 7.24 (dd, J=7.6, 7.6 Hz, 1H), 7.35 (d, J=8.2 Hz, 2H), 7.39 (d, J=7.6 Hz, 1H), 7.54 (d, J=7.9 Hz, 1H), 7.88 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.7, 27.0, 30.3, 51.1, 70.0, 86.8, 115.6, 124.6, 125.2, 126.9, 127.7, 128.6, 129.8, 132.3, 132.5, 134.6, 137.1, 144.7; EI-LRMS m/z 419 (M^+, ^{81}Br), 417 (M^+, ^{79}Br), 354, 338, 274, 262, 182, 91; EI-HRMS m/z calcd for $C_{20}H_{20}O_2NS^{81}Br$ (M^+) 419.0378, found 419.0367, m/z calcd for $C_{20}H_{20}O_2NS^{79}Br$ (M^+) 417.0398, found 419.0389.

4.4.10. Ethyl (but-3-enyl-*p*-toluenesulfonyl-amino)-propiolate (5c). To a solution of **4a** (220.4 mg, 0.69 mmol) in THF (14 mL) was added BuLi (1.58 M solution in hexane, 0.96 mL, 1.51 mmol) at −78 °C. After the stirring for 1 h, $ClCO_2Et$ (0.13 mL, 1.38 mmol) was added, and the mixture was stirred at −50 °C for 0.5 h. To the mixture was added saturated NH_4Cl solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N 80:20:1) to give **5c** (199.5 mg, 90%). IR (neat) ν 2218 (s), 1705 (s), 1597 (m), 1376 (s), 1175 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.31 (t, J=7.1 Hz, 3H), 2.41 (dt, J=6.8, 7.4 Hz, 2H), 2.47 (s, 3H), 3.49 (t, J=7.4 Hz, 2H), 4.23 (q, J=7.1 Hz, 2H), 5.05 (dd, J=1.4, 10.2 Hz, 1H), 5.09 (dd, J=1.4, 17.0 Hz, 1H), 5.67 (ddt, J=10.2, 17.0, 6.8 Hz, 1H), 7.38 (d, J=8.4 Hz, 2H), 7.82 (d, J=8.4 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 21.6, 32.1, 50.5, 61.4, 67.9, 82.1, 118.3, 127.7, 130.0, 132.8, 134.1, 145.5, 154.0; EI-LRMS m/z 321 (M^+), 276, 256, 242, 228, 184, 155, 91; EI-HRMS m/z calcd for $C_{16}H_{19}O_4NS$ (M^+) 321.1035, found 321.1059.

4.4.11. (*Z*)-*N*-Formyl-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*Z*)-10). To a solution of (*Z*)-**9** (1.98 g, 5.60 mmol) in CH_2Cl_2 (11 mL) was added TFA (2.1 mL, 27.7 mmol) at 0 °C, and the mixture was stirred at rt for 3 h. The mixture was extracted with AcOEt, and the organic layer was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 3:1) to give (*Z*)-*N*-hex-3-enyl-*p*-toluenesulfonamide (1.36 g, 96%) as colorless oil. To a solution of (*Z*)-*N*-hex-3-enyl-*p*-toluenesulfonamide (1.26 g, 4.97 mmol), DMAP (0.218 mg, 1.78 mmol) and formic acid (0.39 mL, 10.4 mmol) in CH_2Cl_2 (26 mL) was added DCC (2.66 g, 13.2 mL) at 0 °C, and the mixture was refluxed for 18 h. Undissolved materials were removed by filtration through the Celite pad, and filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 5:1) to give (*Z*)-**10** (0.59 g, 40%, two steps) as colorless oil along with recovered (*Z*)-*N*-hex-3-enyl-*p*-toluenesulfonamide (0.70 g, 56%). IR (neat) ν 2934, 1701, 1597, 1359, 1166 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J=7.5 Hz, 3H), 2.00 (dq, J=6.7, 7.5 Hz, 2H), 2.27 (dt, J=7.5, 7.9 Hz, 2H), 2.46 (s, 3H), 3.40 (t, J=7.9 Hz, 2H), 5.19 (dt, J=10.7, 6.7 Hz, 1H), 5.45 (dt, J=10.7, 7.5 Hz, 1H), 7.37 (d, J=8.2 Hz, 2H), 7.75 (d, J=8.2 Hz, 2H), 9.10 (s, 1H); EI-LRMS m/z 281 (M^+), 184, 155, 126, 91, 82; EI-HRMS m/z calcd for $C_{14}H_{19}O_3NS$ (M^+) 281.1086, found 281.1104.

4.4.12. (*E*)-*N*-Formyl-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*E*)-10). In a similar manner to that for the synthesis of (*Z*)-**10** from (*Z*)-**9**, (*E*)-**10** (0.21 g, 14%, two steps) was synthesized from (*E*)-**9** (2.51 g, 7.10 mmol), TFA (2.5 mL, 34.1 mmol), DMAP (0.12 g, 1.01 mmol), Formic acid (0.57 mL, 15.2 mmol) and DCC (3.09 g, 15.2 mmol), and (*E*)-*N*-hex-3-enyl-*p*-toluenesulfonamide (0.94 g, 73%) was recovered. Colorless oil; IR (neat) ν 2934, 1705, 1597, 1360, 1166 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J=7.5 Hz, 3H), 1.95 (dq, J=6.9, 7.5 Hz, 2H), 2.20 (dt, J=6.2, 7.7 Hz, 2H), 2.46 (s, 3H), 3.45 (t, J=7.7 Hz, 2H), 5.22 (dt, J=15.3, 6.9 Hz, 1H), 5.45 (dtt, J=15.3, 6.2 Hz, 1H), 7.37 (d, J=8.5 Hz, 2H), 7.74 (d, J=8.5 Hz, 2H), 9.08 (s, 1H); EI-LRMS m/z 281 (M^+), 184, 155, 126, 91, 82; EI-HRMS m/z calcd for $C_{14}H_{19}O_3NS$ (M^+) 281.1086, found 281.1106.

4.4.13. (*Z*)-*N*-(2,2-Dichloro-vinyl)-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*Z*)-11). To a solution of (*Z*)-**10** (0.59 g, 2.10 mmol) and PPh_3 (1.72 g, 6.57 mmol) in THF (18 mL) was added CCl_4 (2.11 mL, 21.9 mmol) at 60 °C for 6 h, and the mixture was stirred continuously at 60 °C for 18 h. To the mixture was added saturated $NaHCO_3$ solution, and the aqueous layer was extracted with Et_2O. The organic layer was washed with saturated NaCl solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt 7:1) to give (*Z*)-**11** (0.67 g, 93%) as a colorless needle. Mp 68–70 °C; IR (KBr) ν 2967, 1597, 1355, 1165 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H), 2.01 (dq, J=6.7, 7.4 Hz, 2H), 2.29 (dt, J=6.8, 7.4 Hz, 2H), 2.44 (s, 3H), 3.38 (t, J=7.4 Hz, 2H), 5.22 (dt, J=12.1, 6.7 Hz, 1H), 5.46 (dt, J=12.1, 6.8 Hz, 1H), 6.37 (s, 1H), 7.32 (d, J=8.2 Hz, 2H), 7.69 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.2, 20.6, 21.6, 26.6, 48.7, 123.5, 123.8, 124.8, 127.2, 129.8, 134.7, 135.7, 144.1; EI-LRMS m/z 347 (M^+), 319, 278, 155, 91; EI-HRMS m/z calcd for $C_{15}H_{19}O_2NS^{35}Cl_2$ (M^+) 347.0514, found 347.0483.

4.4.14. (*E*)-*N*-(2,2-Dichloro-vinyl)-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*E*)-11). In a similar manner to that for the synthesis of (*Z*)-**11** from (*Z*)-**10**, (*E*)-**11** (0.37 g, 64%) was synthesized from (*E*)-**10** (0.47 g, 1.67 mmol), PPh_3 (1.31 g, 5.01 mmol) and CCl_4 (1.61 mL, 16.7 mmol). A colorless needle; mp 60–65 °C; IR (KBr) ν 2969, 1598, 1357, 1161 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J=7.5 Hz, 3H), 1.98 (dq, J=6.6, 7.5 Hz, 2H), 2.21 (dt, J=6.5, 7.5 Hz, 2H), 2.44 (s, 3H), 3.38 (t, J=7.5 Hz, 2H), 5.26 (dt, J=15.3, 6.6 Hz, 1H), 5.52 (dt, J=15.3, 6.5 Hz, 1H), 6.32 (s, 1H), 7.32 (d, J=8.5 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.6, 21.6, 25.6, 31.9, 49.1, 123.8, 124.3, 124.9, 127.2, 129.8, 135.4, 135.7, 144.1; EI-LRMS m/z 347 (M^+), 319, 278, 155, 91; EI-HRMS m/z calcd for $C_{15}H_{19}O_2NS^{35}Cl_2$ (M^+) 347.0514, found 347.0517.

4.4.15. (*Z*)-*N*-Ethynyl-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*Z*)-5d). In a similar manner to that for the synthesis of **5a** from **4a**, (*Z*)-**5d** (0.46 g, 92%) was synthesized from (*Z*)-**11** (0.63 g, 1.81 mmol) and BuLi (1.58 M solution in hexane, 3.6 mL, 5.70 mmol). A pale yellow oil; IR (neat) ν 3301, 2964, 2137, 1597, 1370, 1171 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J=7.5 Hz, 3H), 2.01

(dq, J=7.2, 7.5 Hz, 2H), 2.38 (dt, J=7.7, 7.5 Hz, 2H), 2.45 (s, 3H), 2.75 (s, 1H), 3.31 (t, J=7.5 Hz, 2H), 5.22 (dt, J=12.1, 7.2 Hz, 1H), 5.46 (dt, J=12.1, 7.7 Hz, 1H), 7.35 (d, J=8.2 Hz, 2H), 7.80 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 20.6, 21.6, 25.7, 50.9, 59.2, 75.9, 123.3, 127.6, 129.8, 134.6, 135.1, 144.7; EI-LRMS *m/z* 276 (M^+), 198, 184, 155, 122, 91; EI-HRMS *m/z* calcd for $C_{15}H_{19}O_2NS$ (M^+) 277.1136, found 277.1122.

4.4.16. (*E*)-*N*-Ethynyl-*N*-hex-3-enyl-*p*-toluenesulfonamide ((*E*)-5d). In a similar manner to that for the synthesis of **5a** from **4a**, (*E*)-**5d** (0.21 g, 99%) was synthesized from (*E*)-**11** (0.27 g, 0.78 mmol) and BuLi (1.58 M solution in hexane, 1.3 mL, 2.10 mmol). Colorless oil; IR (neat) ν 3299, 2963, 2136, 1597, 1369, 1170 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, J=7.4 Hz, 3H), 1.96 (dq, J=6.8, 7.4 Hz, 2H), 2.33 (dt, J=7.0, 7.2 Hz, 2H), 2.45 (s, 3H), 2.75 (s, 1H), 3.33 (t, J=7.2 Hz, 2H), 5.26 (dt, J=15.2, 6.8 Hz, 1H), 5.53 (dt, J=15.2, 7.0 Hz, 1H), 7.35 (d, J=8.2 Hz, 2H), 7.80 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.5, 21.6, 25.5, 30.9, 51.1, 59.3, 75.9, 123.6, 127.6, 129.8, 134.7, 135.6, 144.6; EI-LRMS *m/z* 276 (M^+), 198, 184, 155, 91; EI-HRMS *m/z* calcd for $C_{15}H_{19}NO_2S$ (M^+) 277.1136, found 277.1147.

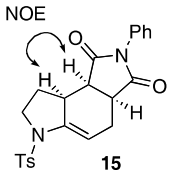
4.5. Typical procedure for the Diels–Alder reaction

A solution of **5a** (55 mg, 0.22 mmol) and **1b** (10 mg, 0.012 mmol) in toluene (7 mL) was refluxed for 30 min under ethylene gas (1 atm). After the reaction solution was cooled to rt, the atmosphere of ethylene gas was replaced by argon gas. To this solution was added DMAD (0.14 mL, 1.2 mmol), and the resulting mixture was stirred at 60 °C for 12 h. After the volatiles were removed under reduce pressure, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt 3:1) to give **14a** (69 mg, 80%, two steps) as colorless oil. (Scheme 6, Eq. 2).

4.6. Spectral data of Diels–Alder products

4.6.1. Dimethyl 1-*p*-toluenesulfonyl-2,3,3a,6-tetrahydro-1*H*-indole-4,5-dicarboxylate (14a). IR (neat) ν 1733, 1646, 1597, 1359, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (dddd, J=11.8, 11.8, 11.3, 8.2 Hz, 1H), 2.15 (ddd, J=11.8, 6.0, 6.0 Hz, 1H), 2.43 (s, 3H), 2.94 (m, 1H), 3.08 (ddd, J=22.5, 11.3, 2.2 Hz, 1H), 3.24 (ddd, J=22.5, 7.0, 5.6 Hz, 1H), 3.35 (ddd, J=10.0, 6.0, 6.0 Hz, 1H), 3.75 (s, 3H), 3.76 (s, 3H), 3.79 (dd, J=10.0, 8.2 Hz, 1H), 5.79 (dd, J=5.6, 2.2 Hz, 1H), 7.29 (d, J=8.2 Hz, 2H), 7.69 (d, J=8.2 Hz, 2H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 21.6, 27.3, 28.8, 39.5, 48.9, 52.3, 52.4, 101.4, 127.2, 133.4, 134.3, 134.7, 136.4, 144.1, 167.3, 167.4; EI-LRMS *m/z* 391 (M^+), 236, 159, 91; EI-HRMS *m/z* calcd for $C_{19}H_{21}O_6NS$ (M^+) 391.1080, found 391.1089.

4.6.2. (3a*S,8a*S**,8b*R**)-2-Phenyl-6-*p*-toluenesulfonyl-4,6,7,8,8a,8b-hexahydro-3a*H*−2,6-diaza-as-indacene-1,3-dione (15).** IR (Nujol) ν 1707, 1348, 1162 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (m, 1H), 2.26 (m, 1H), 2.35 (s, 3H), 2.60 (m, 1H), 2.82 (m, 1H), 2.89 (ddd, J=15.6, 7.8, 1.5 Hz, 1H), 3.20 (ddd, J=10.7, 7.3, 1.5 Hz, 1H), 3.29 (dd, J=9.3, 7.3 Hz, 1H), 3.61–3.71 (m, 2H), 5.65 (ddd, J=7.8, 2.0, 2.0 Hz, 1H), 6.95 (d, J=8.3 Hz, 2H), 7.21 (br d, J=8.3 Hz, 2H), 7.34–7.42 (m, 3H), 7.68 (br d, J=8.3 Hz, 2H); ^{13}C NMR (67.8 Hz, $CDCl_3$) δ 21.3, 21.5, 21.6, 29.4, 39.5, 42.1, 49.0, 115.1, 126.2, 127.3, 128.6, 129.1, 129.9, 131.6, 134.2, 138.8, 143.9, 174.5, 177.1; EI-LRMS *m/z* 422 (M^+), 267, 155, 120, 91; EI-HRMS *m/z* calcd for $C_{23}H_{22}O_4N_2S$ (M^+) 422.1300, found 422.1301. The stereochemistry of **15** was determined by NOE experiment.



15

4.6.3. Dimethyl 6-ethyl-1-*p*-toluenesulfonyl-2,3-dihydro-1*H*-indole-4,5-dicarboxylate (16) and dimethyl 6-ethyl-1-*p*-toluenesulfonyl-1*H*-indole-4,5-dicarboxlate (17). To a solution of diastereoisomeric mixture (22.7 mg, 54.1 μmol) in toluene (2 mL), which was prepared from (*Z*)-**5d**, **1b** and DMAD according to typical procedure, was added DDQ (113 mg, 0.497 mmol), and the mixture was stirred at 80 °C for 20 h. After the volatiles were removed under reduce pressure, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt 3:1) to give **16** (13.7 mg, 20%, three steps) as a colorless crystal and **17** (7.9 mg, 12%, three steps) as pale yellow oil. **16**: IR (KBr) ν 2967, 1729, 1598, 1364, 1167 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.24 (t, J=7.5 Hz, 3H), 2.39 (s, 3H), 2.68 (q, J=7.5 Hz, 2H), 3.15 (t, J=8.8 Hz, 2H), 3.81 (s, 3H), 3.87 (s, 3H), 3.93 (t, J=8.8 Hz, 2H), 7.26 (d, J=8.1 Hz, 2H), 7.67 (d, J=8.1 Hz, 2H), 7.68 (s, 1H); EI-LRMS *m/z* 417 (M^+), 385, 327, 262, 230, 198, 91; EI-HRMS *m/z* calcd for $C_{21}H_{23}O_6NS$ (M^+) 417.1246, found 417.1259. Compound **17**: IR (neat) ν 2953, 1732, 1597, 1378, 1168 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.27 (t, J=7.5 Hz, 3H), 2.35 (s, 3H), 2.76 (q, J=7.5 Hz, 2H), 3.92 (s, 6H), 7.13 (d, J=3.7 Hz, 1H), 7.23 (d, J=8.6 Hz, 2H), 7.65 (d, J=3.7 Hz, 1H), 7.70 (d, J=8.6 Hz, 2H), 8.07 (s, 1H); EI-LRMS *m/z* 415 (M^+), 383, 325, 228, 91; EI-HRMS *m/z* calcd for $C_{21}H_{21}O_6NS$ (M^+) 415.1090, found 415.1084.

4.6.4. Dimethyl 1-*p*-toluenesulfonyl-1,2,3,4,4a,7-hexahydro-quinoline-5,6-dicarboxylate (18a). Mp 129 °C (decomp.); IR (Nujol) ν 1724, 1594, 1346, 1156 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30–1.55 (m, 2H), 1.75 (br d, J=13.3 Hz, 1H), 1.87 (m, 1H), 2.43 (s, 3H), 2.77 (m, 1H), 3.03 (m, 1H), 3.05 (ddd, J=23.7, 8.3, 3.7 Hz, 1H), 3.20 (ddd, J=23.7, 8.1, 3.8 Hz, 1H), 3.75 (s, 6H), 4.17 (br d, J=13.4 Hz, 1H), 5.83 (ddd, J=3.6, 3.6, 1.4 Hz, 1H), 7.29 (d, J=8.4 Hz, 2H), 7.71 (d, J=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 24.0, 27.7, 30.5, 36.6, 47.8, 52.1, 52.3, 119.5, 126.9, 127.8, 129.6, 133.2, 137.8, 138.4, 143.4, 166.6, 168.0; EI-LRMS *m/z* 405 (M^+), 374, 282, 218, 131, 91; EI-HRMS *m/z* calcd for $C_{20}H_{23}O_6NS$ (M^+) 405.1246, found 405.1226.

4.6.5. Dimethyl 1-*p*-toluenesulfonyl-1,2,3,4,7,8-hexahydro-quinoline-5,6-dicarboxylate (18b). IR (neat) ν 1734, 1708, 1635, 1596, 1343, 1162 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 1.45–1.54 (m, 2H), 1.96–2.02 (m, 2H), 2.44 (s, 3H), 2.48–2.55 (m, 2H), 2.75–2.85 (m, 2H), 3.63–3.68 (m, 2H), 3.78 (s, 3H), 3.81 (s, 3H), 7.31 (d, $J=8.3$ Hz, 2H), 7.65 (d, $J=8.3$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 22.8 (2C), 26.6, 46.5, 52.0, 52.3, 115.3, 120.8, 128.9, 129.8, 136.7, 139.2, 142.0, 144.0, 166.0, 168.8; EI-LRMS *m/z* 405 (M^+), 374, 250, 218, 190, 158; EI-HRMS *m/z* calcd for $C_{20}H_{23}O_6NS$ (M^+) 405.1246, found 405.1234.

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