Stereoselective Synthesis of 1,2,3-Trisubstituted 1,3-Dienes through Novel [3,3]-Sigmatropic Rearrangements in α-Allenic Methanesulfonates: Application to the Preparation of Fused Tricyclic Systems by Tandem Rearrangement/Diels−Alder Reaction

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Dedicated to the memory of Dr. Juan C. del Amo[‡]

Keywords: Allenes / Cycloaddition / Dienes / Domino reactions / Sigmatropic rearrangement

An unprecedented stereoselective and general synthesis of 1,2,3-trisubstituted 1,3-dienes from α-allenols just by treatment with a methanesulfonyl chloride/tertiary amine system has been developed. This transformation might be tentatively explained in terms of a migration of the methanesulfonyl group in the initially formed α-allenic methanesulfonate to give the corresponding mesyloxy-diene through a [3,3]-sigmatropic rearrangement. This reactivity pattern was incorporated into a domino process, allowing the development of a novel one-pot synthetic strategy for the preparation of fused tricycles from monocyclic allenols, masked functionalized dienes, when subjected to a domino allenol transposition/intramolecular Diels–Alder reaction process.

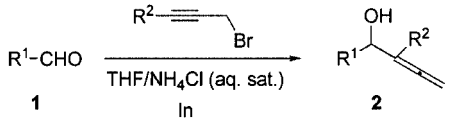
Introduction

Heteroatom-substituted 1,3-dienes are versatile reagents in chemical synthesis, playing a very important role in cycloadditions. Danishefsky and co-workers, for example, developed 1-methoxy-3-trimethylsiloxybuta-1,3-diene, which has had many creative applications in complex organic synthesis.[1] Trost and colleagues prepared another kind of heteroatomic 1,3-dienes, 2-alkoxy-3-alkyl(aryl)-thiobuta-1,3-dienes, which have been used as regiochemical control elements in cycloadditions.[2]

Allylic and propargylic alcohols react with metal complexes to form 1,3-transposition products. Surprisingly, the corresponding rearrangement of allenyl alcohols has been virtually ignored, only Trost, en route to aldol- or Mannich-type products, having recently postulated the formation of an intermediate involving the 1,3-transposition of α-allenic alcohols.[3] In our ongoing project directed toward the asymmetric synthesis of natural products and derivatives of biological interest[4] we initiated a study into the use of allene substrates in organic synthesis. Here we present full details of a novel, simple, stereoselective, and general synthesis of 1,2,3-trisubstituted 1,3-dienes from α-allenols,[5] together with its incorporation into a domino transposition/intramolecular Diels−Alder reaction scheme for the preparation of tricyclic compounds.[6]

Results and Discussion

The starting substrates, the α-allenic alcohols **2**, were prepared in aqueous media in a totally regioselective fashion[7] from propargyl bromides, through metal-mediated Barbier-type carbonyl allenylation of the appropriate aldehyde **1** (Scheme 1, Table 1).



Scheme 1. Regioselective preparation of α-allenic alcohols **2** in aqueous media

In an initial experiment, the α-allenol *syn*-(+)-**2a** (1.0 mmol) and methanesulfonyl chloride (1.1 mmol) were mixed in dichloromethane at room temperature. Next, tri-

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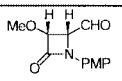
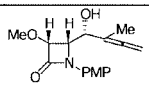
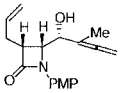
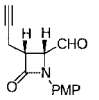
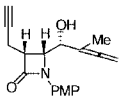
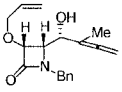
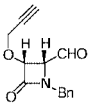
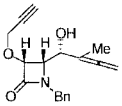
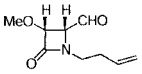
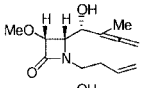
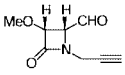
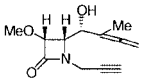
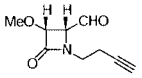
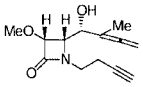
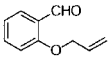
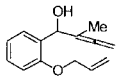
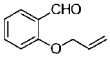
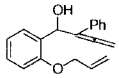
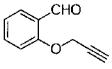
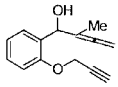
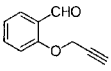
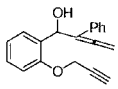
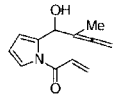
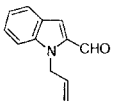
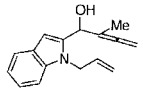
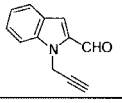
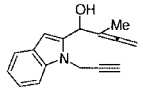
Table 1. Indium-mediated Barbier-type carbonyl allenylation of aldehydes **1**[a]

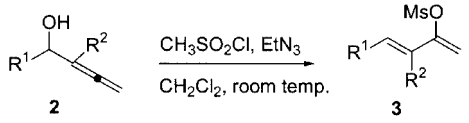
Entry	Substrate		R^2	Product		Yield (%)[b]
1		(+)-**1a**	Me		(+)-**2a**	70
2		(±)-**1b**	Me		(±)-**2b**	90
3		(±)-**1c**	Me		(±)-**2c**	81
4		(+)-**1d**	Me		(+)-**2d**	80
5		(+)-**1e**	Me		(+)-**2e**	58
6		(+)-**1f**	Me		(+)-**2f**	77
7		(+)-**1g**	Me		(+)-**2g**	75
8		(+)-**1h**	Me		(+)-**2h**	69
9		**1i**	Me		**2i**	60
10		**1i**	Ph		**2j**	65
11		**1j**	Me		**2k**	91
12		**1j**	Ph		**2l**	65
13		**1k**	Me		**2m**	62
14		**1l**	Me		**2n**	58
15		**1m**	Me		**2o**	73

[a] All reactions were carried out on 1 mmol scale. PMP = 4-$MeOC_6H_4$.[b] Yield of pure, isolated product with correct analytical and spectroscopic data.

ethylamine (1.2 mmol) was slowly added to the reaction mixture at 0 °C, and the reaction was then allowed to proceed for 30 minutes at room temperature. To our delight, this gave the 2,3-difunctionalized diene (+)-**3a** as the only product, in reasonable yield and with total stereoselectivity. The susceptibility of the reaction to stereochemically different β-lactam allenic alcohols was examined next, by exploring the potential for the use of the α-allenol *anti*-(+)-**2a**.[8] Gratifyingly, the enantiopure diene (+)-**3a** was obtained in similar yield and with similar selectivity.

We also performed a solvent screen for the one-pot allenol-diene transformation. The reaction worked well in polar aprotic solvents such as DMF, providing similar yields of the 1,3-diene (+)-**3a**. There was no significant solvent effect in the observed yield or stereoselectivity when a few other solvents (tetrahydrofuran or toluene) were also scre-

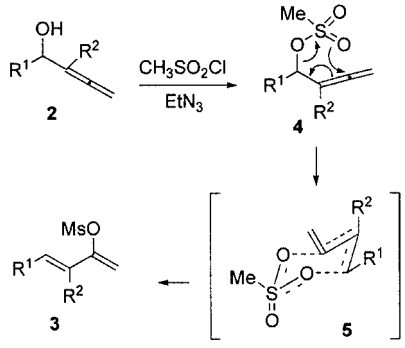
ened. We next investigated the range of potential allenol components. We found that β-lactam α-allenols bearing substituents of different natures at the N1 or C3 positions of the 2-azetidinone ring were excellent substrates for the conversion of the allene moiety into 1,3-dienes. Up to this point, we had established that reactions with β-lactam allenols provided excellent results. We were not certain, however, whether α-allenols with aromatic or heteroaromatic substituents might serve as precursors for the allene-conjugated diene conversion, so we treated different α-allenols derived from (hetero)aromatic aldehydes with methanesulfonyl chloride in the presence of triethylamine in dichloromethane. Interestingly, the sulfonyl chloride/tertiary amine system was able to induce the preparation of 1-aryl-2,3-trisubstituted 1,3-dienes in good yields and with full stereocontrol (Scheme 2, Table 2).[9]



Scheme 2. Stereoselective preparation of 1,2,3-trisubstituted 1,3-dienes **3** from α-allenols **2**

Total *E* stereoselectivity was observed for every single α-allenyl alcohol used as starting material. The stereochemistry at the double bond for dienes **3** was assigned by qualitative homonuclear NOE difference spectra. In most cases these 2,3-difunctionalized 1,3-dienes are reasonably stable, although they decompose after prolonged storage at 20 °C.

The mechanism of the one-pot allenol-diene transformation is depicted in Scheme 3. The extremely high selectivity observed in the formation of dienes **3** may indicate a pericyclic reaction pathway, the allenol component reacting with methanesulfonyl chloride, resulting in a methanesulfonate intermediate. Next, the α-allenic methanesulfonate **4** generated in situ undergoes a [3,3]-sigmatropic rearrangement, involving the chair-like six-membered cyclic transition structure **5**, to give the corresponding mesyloxy-diene counterpart **3**.



Scheme 3. Feasible reaction pathway for the transformation of α-allenic alcohols **2** into 1,3-dienes **3**

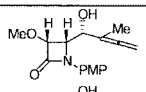
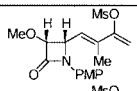
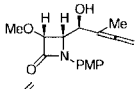
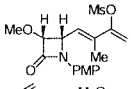
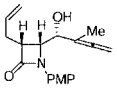
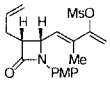
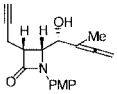
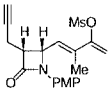
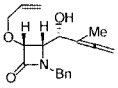
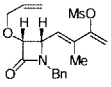
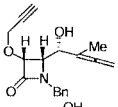
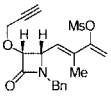
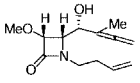
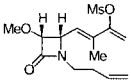
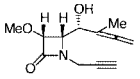
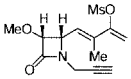
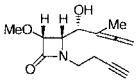
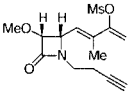
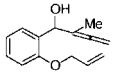
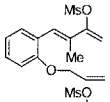
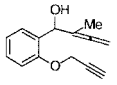
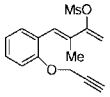
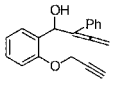
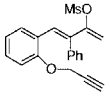
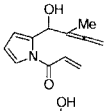
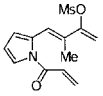
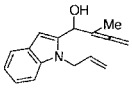
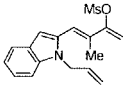
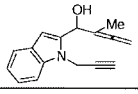
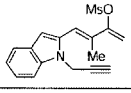
Tandem, cascade, or domino reactions are being increasingly widely applied to the construction of natural and designed molecules.[10] Such processes, in which (ideally) a single event triggers the conversion of a starting material into a product that then becomes a substrate for the next reaction until termination affords a stable final product, are highly desirable not only due to their elegance, but also because of their efficiency and economy in terms of reagent consumption and purification. Often, these multi-step, one-pot procedures are accompanied by dramatic increases in molecular complexity and impressive selectivity.

In view of the importance of ring structures in essentially all classes of natural products,[11] the constructions of rings represents a central theme in organic synthesis. Many synthetic routes devise a ring-closure reaction at some stage, since many synthetic targets possess at least one cycle in their core structure. The discovery of new molecular diversity from nature and the demand for more efficient and environmentally benign chemical processes dictates and invites the further development of sustainable methodologies. Domino reactions based on Diels−Alder chemistry are important examples of such synthetic strategies,[12] but the intricacy of routes to the appropriate functionalized 1,3-dienes is often a major drawback to practical use of these reactions. Because tandem reactions offer many advantages over stepwise processes, we decided to attempt a novel method for the straightforward synthesis of functionalized polycyclic compounds from monocyclic aldehydes. Our approach was based on regioselective condensation between aldehydes and propargyl bromides to give α-allenols, masked functionalized dienes, which then underwent a domino allenol transposition/intramolecular Diels−Alder reaction process upon treatment with methanesulfonyl chloride. Thus, we first thought that α-allenol-tethered alkenes **2** might be appropriate precursors for the construction of the tricyclic cores of some bioactive products. Treatment of α-allenyl alcohols **2** bearing alkenyl tethers with methanesulfonyl chloride/triethylamine in toluene at 190 °C in sealed tubes afforded the expected products, the fused tricycles **6**, in moderate yields (35−54%) and in most cases with good stereoselectivities (*dr*s up to 100:0) (Scheme 4).

The applicability of the tandem transposition/cycloaddition reaction approach for the synthesis of tricycles was still restricted to α-allenol-tethered alkenes (enallenes). We next turned our attention to the applicability of the domino reaction to α-allenyl alcohols **2** bearing alkynyl tethers (allenynes). The extra alkynyl moiety was indeed tolerated in this process, and the usefulness of this approach for the stereoselective synthesis of polycyclic β-lactams and chromenes is shown in Scheme 5. The hydroxybenzochromene **7d**, the result of further mesylate cleavage with concomitant aromatization, was the only product resulting from the thermally induced reaction of α-allenol **2k**. Tricycles **6d**−**6f**, as well as **7e**, were prepared as racemic mixtures.

Although this multibond formation reaction for the synthesis of tricycles appears complex, it is in fact simple: the methanesulfonyl chloride/triethylamine system promotes the formation of the corresponding 2-mesyloxy 1,3-diene

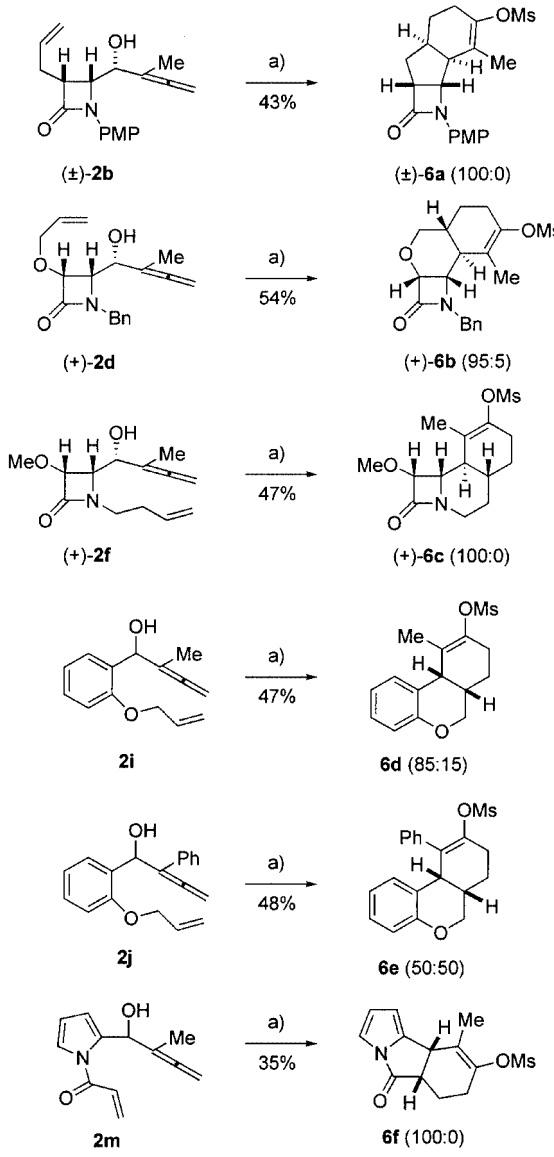
Table 2. Methanesulfonyl chloride/triethylamine-promoted synthesis of (*E*)-1,2,3-trifunctionalized 1,3-dienes **3** from α-allenols **2**[a]

Entry	Substrate		R^2	Product		Yield (%)[b]
1		(+)-**2a**	Me		(+)-**3a**	59
2		*anti*-(+)-**2a**	Me		(+)-**3a**	59
3		(±)-**2b**	Me		(±)-**3b**	73
4		(±)-**2c**	Me		(±)-**3c**	96
5		(+)-**2d**	Me		(+)-**3d**	46
6		(+)-**2e**	Me		(+)-**3e**	67
7		(+)-**2f**	Me		(+)-**3f**	90
8		(+)-**2g**	Me		(+)-**3g**	78
9		(+)-**2h**	Me		(+)-**3h**	73
10		**2i**	Me		**3i**	62
11		**2k**	Me		**3j**	64
12		**2l**	Ph		**3k**	61
13		**2m**	Me		**3l**	48
14		**2n**	Me		**3m**	43
15		**2o**	Me		**3n**	50

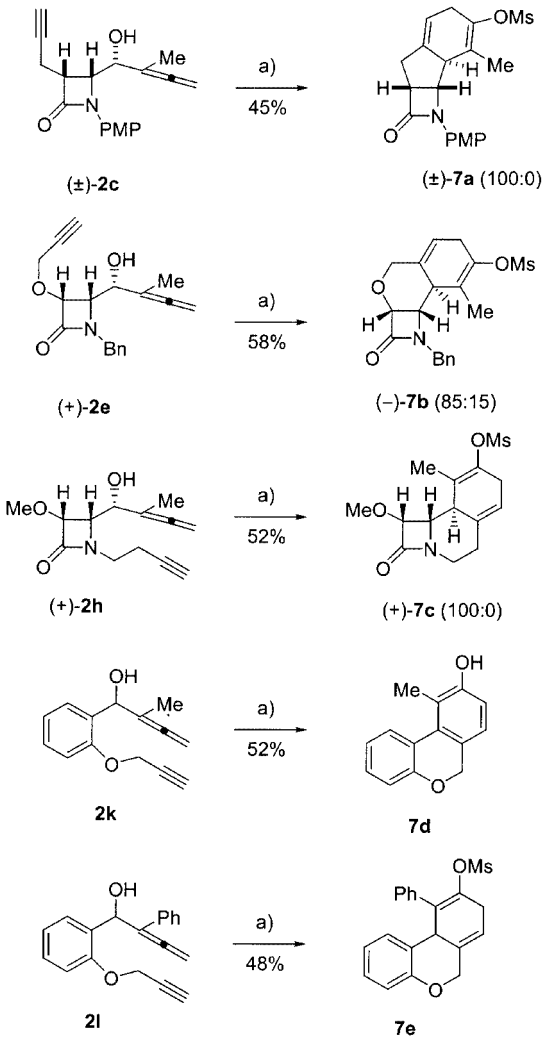
[a] All reactions were carried out on 1 mmol scale. PMP = 4-$MeOC_6H_4$. In all cases, compounds **2** refer to the *syn* isomers, except for Entry 2.[b] Yield of pure, isolated product with correct analytical and spectroscopic data.

from the appropriate α-allenol, and is followed by a subsequent intramolecular [4+2] cycloaddition reaction.

The stereochemical outcomes of the IMDA reactions producing tricycles **7** may be explained in terms of transition states similar to those depicted in Scheme 6. In the 2-azetidinone series the sense of diastereoselectivity seems to be controlled by the C4 stereogenic center in the β-lactam ring.



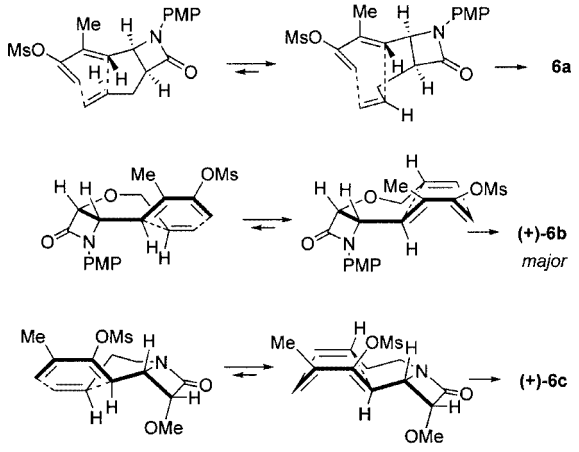
Scheme 4. Stereoselective synthesis of tricycles **6** from monocyclic enallenes; reagents and conditions: a) CH_3SO_2Cl, Et_3N, toluene, sealed tube, 190 °C



Scheme 5. Stereoselective synthesis of tricycles **7** from monocyclic allenynes; reagents and conditions: a) CH_3SO_2Cl, Et_3N, toluene, sealed tube, 190 °C

Conclusions

In conclusion, we have successfully developed a strategy for the one-step stereoselective synthesis of tricycles − found in many biologically active natural products, such as β-lactams, chromenes, and pyrrolizidines − from monocyclic α-allenic alcohols. These products contain mesylate functional groups, which might also be useful substrates for further functionalization through transition metal-catalyzed processes. The ready availability of allenols − through the Barbier-type reaction between aldehydes and propargyl bromides in aqueous media, for example − makes such a strategy very attractive. This unprecedented domino sequence represents a practical opportunity to connect the rapidly expanding fields of environmentally benign chemistry and multiple bond-forming processes.



Scheme 6

Experimental Section

General Methods: ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker Avance 300, Varian VRX 300S, or Bruker AC 200 instruments. NMR spectra were recorded in $CDCl_3$ solutions, except if stated otherwise. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm) or $CDCl_3$ (^{13}C, 76.9 ppm). Low- and high-resolution mass spectra were taken on a HP5989A spectrometer in the chemical ionization (CI) modes unless otherwise stated. Specific rotations: measured at 20 °C, concentration (*c*) is expressed in g per 100 mL. All commercially available compounds were used without further purification. The starting substrates, the 4-oxoazetidine-2-carbaldehydes **1a**−**h**, were prepared both in racemic and in optically pure forms by our previously described methodologies. Enantiopure 2-azetidinones (+)-**1a** and **1d**−**h** were obtained as single *cis* enantiomers from imines of (*R*)-2,3-*O*-(isopropylidene)glyceraldehyde, through Staudinger reactions with the corresponding acid chlorides in the presence of Et_3N, followed by sequential acidic acetonide hydrolysis and oxidative cleavage.[13] Racemic compounds (±)-**1b** and (±)-**1c** were obtained from *N*,*N*-bis(*p*-methoxyphenyl)glyoxal diimine in one-pot fashion as single *cis* diastereoisomers.[14] The aromatic aldehydes **1i** and **1j** were prepared from salicylaldehyde as described in the literature.[15] Heteroaromatic aldehyde **1k** was prepared from pyrrole-2-carboxaldehyde,[16] while aldehydes **1l** and **1m** were obtained from indole-2-carboxylic acid as previously reported.[16]

Indium-Promoted Reactions between 3-Substituted Prop-2-ynyl Bromides and Carbaldehydes 1. General Procedure for the Synthesis of α-Allenic Alcohols 2: 1-Bromo-2-butyne or 1-bromo-3-phenyl-2-propyne (3.0 mmol) was added at 0 °C to a well stirred suspension of the corresponding carbaldehyde **1** (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 5 mL). After disappearance of the starting material (TLC), the mixture was extracted with ethyl acetate (3 × 5 mL). The organic extract was washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue with ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of **2** follow.[17]

Preparation of α-Allenic Alcohols (±)-2c and *anti*-(±)-2c: The less polar *anti*-(±)-**2c** (17 mg, 9%) and the more polar (±)-**2c** (157 mg, 81%) were obtained from aldehyde (±)-**1c** (159 mg, 0.654 mmol) after chromatography of the residue with dichloromethane/ethyl acetate (9:1) as eluent.

(3*RS*,4*SR*)-4-[(*RS*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propynyl)-2-azetidinone [(±)-2c]: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.28 and 6.86 (dd, J = 6.6, 2.2 Hz, each 2 H), 4.70 (m, 3 H), 4.35 (dd, J = 5.4, 4.6 Hz, 1 H), 3.78 (s, 3 H), 3.58 (m, 1 H), 2.87 (td, J = 6.3, 2.7 Hz, 1 H), 2.40 (br. s, 1 H), 2.09 (t, J = 2.7 Hz, 1 H), 1.75 (t, J = 3.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.8, 166.2, 156.5, 130.2, 119.9, 114.3, 98.7, 81.9, 77.6, 69.7, 68.9, 57.1, 55.4, 50.7, 15.2, 14.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3422, 2990, 2120, 1940, 1749 cm^{-1}. MS (CI): *m*/*z* (%) = 298 (100) [M + H]$^+$, 297 (25) [M]$^+$. $C_{18}H_{19}NO_3$ (297.3): calcd. C 72.71, H 6.44, N 4.71; found C 72.78, H 6.46, N 4.70.

(3*RS*,4*SR*)-4-[(*SR*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propynyl)-2-azetidinone [*anti*-(±)-2c]: Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.39 and 6.85 (dd, J = 6.6, 2.2 Hz, each 2 H), 4.81 (m, 1 H), 4.53 (m, 1 H), 4.47 (m, 2 H), 3.79 (s, 3 H), 3.54 (dt, J = 9.0, 5.4 Hz, 1 H), 2.91 (ddd, J = 17.6, 9.0, 2.7 Hz, 1 H), 2.73 (dq, J = 17.6, 2.7 Hz, 1 H), 2.07 (t, J = 2.7 Hz, 1 H), 2.02 (br. s, 1 H), 1.85 (t, J = 3.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.0, 166.2, 156.4, 130.9, 120.6, 113.9, 100.1, 81.3, 78.8, 70.2, 56.8, 55.5, 49.9, 15.6, 14.5 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3420, 2990, 2121, 1941, 1745 cm^{-1}. MS (CI): *m*/*z* (%) = 298 (100) [M + H]$^+$, 297 (32) [M]$^+$. $C_{18}H_{19}NO_3$ (297.3): calcd. C 72.71, H 6.44, N 4.71; found C 72.77, H 6.43, N 4.73.

(3*R*,4*S*)-1-Benzyl-4-[(*R*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-(2-propenyloxy)-2-azetidinone [(+)-2d]: This compound was obtained from aldehyde (+)-**1d** (70 mg, 0.280 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**2d** (68 mg, 80%) as a colorless oil. $[\alpha]_D^{25}$ = +24.6 (*c* = 0.8 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (m, 5 H), 5.89 (m, 1 H), 5.25 (m, 2 H), 4.71 (m, 4 H), 4.28 (m, 4 H), 3.79 (d, J = 12.0 Hz, 1 H), 2.65 (d, J = 4.4 Hz, 1 H), 1.63 (t, J = 2.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.3, 167.7, 135.9, 133.2, 128.6, 128.1, 127.5, 118.1, 99.5, 81.4, 77.2, 72.4, 70.4, 58.7, 45.1, 15.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3428, 2994, 1939, 1741 cm^{-1}. MS (CI): *m*/*z* (%) = 300 (100) [M + H]$^+$, 299 (20) [M]$^+$. $C_{18}H_{21}NO_3$ (299.36): calcd. C 72.22, H 7.07, N 4.68; found C 72.12, H 7.10, N 4.66.

(3*R*,4*S*)-1-(3-Butenyl)-4-[(*R*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-methoxy-2-azetidinone [(+)-2f]: This compound was obtained from aldehyde (+)-**1f** (95 mg, 0.52 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**2f** (95 mg, 77%) as a colorless oil. $[\alpha]_D^{25}$ = +46.1 (*c* = 0.7 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.73 (m, 1 H), 5.06 (m, 2 H), 4.81 (q, J = 3.0 Hz, 1 H), 4.42 (d, J = 4.8 Hz, 1 H), 4.23 (m, 1 H), 3.94 (t, J = 4.6 Hz, 1 H), 3.55 (s, 3 H), 3.50 (m, 1 H), 3.20 (ddd, J = 13.6, 7.0, 6.0 Hz, 1 H), 2.67 (br. s, 1 H), 2.31 (m, 2 H), 1.79 (t, J = 3.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.4, 167.7, 135.0, 116.8, 99.8, 83.3, 77.2, 70.3, 59.5, 59.3, 40.7, 31.9, 16.0 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3421, 2992, 1942, 1747 cm^{-1}. MS (CI): *m*/*z* (%) = 238 (100) [M + H]$^+$, 237 (19) [M]$^+$. $C_{13}H_{19}NO_3$ (237.3): calcd. C 65.80, H 8.07, N 5.90; found C 65.87, H 8.09, N 5.88.

(3*R*,4*S*)-1-(3-Butynyl)-4-[(*R*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-methoxy-2-azetidinone [(+)-2h]: This compound was obtained from aldehyde (+)-**1h** (137 mg, 0.756 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**2h** (123 mg, 69%) as a colorless oil. $[\alpha]_D^{25}$ = +40.2 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.84 (td, J = 3.2, 1.0 Hz, 1 H), 4.48 (d, J = 4.8 Hz, 1 H), 4.25 (m, 1 H), 4.03 (t, J = 4.8 Hz, 1 H), 3.59 (m, 1 H), 3.58 (s, 3 H), 3.36 (dt, J = 13.7, 6.8 Hz, 1 H), 2.59 (d, J = 4.6 Hz, 1 H), 2.50 (td, J = 7.3, 2.7 Hz, 1 H), 1.99 (t, J = 2.7 Hz, 1 H), 1.81 (t, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.4, 167.6, 99.7, 83.5, 81.2, 77.3, 70.4, 70.0, 59.9, 59.6, 40.2, 17.9, 16.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3424, 2989, 2118, 1940, 1745 cm^{-1}. MS (CI): *m*/*z* (%) = 236 (100) [M + H]$^+$, 235 (17) [M]$^+$. $C_{13}H_{17}NO_3$ (235.3): calcd. C 66.36, H 7.28, N 5.95; found C 66.43, H 7.26, N 5.94.

1-(2-Allyloxyphenyl)-2-methylbuta-2,3-dien-1-ol (2i): This compound was obtained from aldehyde **1i** (207 mg, 1.27 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **2i** (167 mg, 60%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (m, 2 H), 6.93 (m, 2 H), 6.05 (m, 1 H), 5.36 (m, 3 H), 4.81 (td, J = 2.9, 0.9 Hz, 2 H), 5.47 (dt, J = 5.1, 1.5 Hz, 2 H), 2.93 (d, J = 6.8 Hz, 1 H), 1.64 (t, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.0, 156.1, 133.0, 130.1, 128.6, 128.0, 120.8, 117.5, 111.9, 102.2, 77.3, 70.9, 68.9, 15.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3416, 1223, 761 cm^{-1}. MS (CI):

m/*z* (%) = 217 (100) $[M + H]^+$, 216 (15) $[M]^+$. $C_{14}H_{16}O_2$ (216.3): calcd. C 77.75, H 7.46; found C 77.86, H 7.43.

1-(2-Propargyloxyphenyl)-2-methylbuta-2,3-dien-1-ol (2k): This compound was obtained from aldehyde **1j** (104 mg, 0.65 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **2k** (126 mg, 91%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (m, 3 H), 7.01 (m, 2 H), 5.35 (m, 1 H), 4.84 (m, 2 H), 4.37 (d, J = 2.2 Hz, 2 H), 2.72 (d, J = 6.6 Hz, 1 H), 2.51 (t, J = 2.4 Hz, 1 H), 1.64 (t, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.9, 155.1, 130.7, 128.6, 128.1, 121.6, 112.3, 102.2, 78.4, 77.5, 75.6, 70.3, 56.1, 15.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3381, 3314, 2124, 1245, 752 cm^{-1}. MS (CI): *m*/*z* (%) = 215 (100) $[M + H]^+$, 214 (11) $[M]^+$. $C_{14}H_{14}O_2$ (214.3): calcd. C 78.48, H 6.59; found C 78.37, H 6.62.

1-(1-Acryloyl-1*H*-pyrrol-2-yl)-2-methylbuta-2,3-dien-1-ol (2m): This compound was obtained from aldehyde **1k** (34 mg, 0.22 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **2m** (28 mg, 62%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.14 (dd, J = 3.4, 1.5 Hz, 1 H), 6.88 (dd, J = 16.8, 10.0 Hz, 1 H), 6.65 (dd, J = 16.6, 1.6 Hz, 1 H), 6.34 (m, 1 H), 6.24 (t, J = 3.4 Hz, 1 H), 6.08 (dd, J = 10.0, 1.5 Hz, 1 H), 5.26 (dt, J = 8.3, 2.3 Hz, 1 H), 4.67 (m, 3 H), 1.76 (t, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.6, 165.1, 136.6, 133.6, 127.8, 121.6, 115.4, 111.9, 100.6, 76.4, 68.5, 16.2 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3392, 1679 cm^{-1}. MS (CI): *m*/*z* (%) = 204 (100) $[M + H]^+$, 203 (16) $[M]^+$. $C_{12}H_{13}NO_2$ (203.2): calcd. C 70.92, H 6.45, N 6.89; found C 71.00, H 6.42, N 6.91.

1-(*N*-Propargylindol-2-yl)-2-methylbuta-2,3-dien-1-ol (2o): This compound was obtained from aldehyde **1m** (100 mg, 0.54 mmol); chromatography of the residue with hexanes/ethyl acetate (8:1) as eluent gave compound **2o** (94 mg, 73%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.61 (dm, J = 7.8 Hz, 1 H), 7.45 (dm, J = 8.3 Hz, 1 H), 7.28 (tm, J = 7.1 Hz, 1 H), 7.15 (m, 1 H), 6.41 (s, 1 H), 5.36 (br. s, 1 H), 5.28 (m, 4 H), 2.40 (br. s, 1 H), 2.27 (t, J = 2.4 Hz, 1 H), 1.71 (t, J = 3.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.7, 138.0, 137.6, 127.4, 122.3, 120.9, 120.1, 109.5, 102.5, 101.2,78.8, 78.5, 72.1, 68.4, 33.2, 15.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3396, 2126 cm^{-1}. MS (CI): *m*/*z* (%) = 238 (100) $[M + H]^+$, 237 (14) $[M]^+$. $C_{16}H_{15}NO$ (237.3): calcd. C 80.98, H 6.37, N 5.90; found C 80.84, H 6.39, N 5.91.

Methanesulfonyl Chloride/Tertiary Amine System: Induced Reactions of α-Allenic Alcohols 2. General Procedure for the Synthesis of 2,3-Difunctionalized 1,3-Dienes 3: Methanesulfonyl chloride (1.10 mmol) and triethylamine (1.20 mmol) were added sequentially and dropwise at 0 °C to a solution of the corresponding α-allenol **2** (1.0 mmol) in dichloromethane (10 mL). The resulting stirred mixture was warmed to room temperature until disappearance of the starting allenol. The reaction mixture was diluted with water (2 mL). The organic phase washed with brine (2 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue, with elution with dichloromethane/ethyl acetate or hexanes/ethyl acetate mixtures, gave analytically pure functionalized 1,3-dienes **3**.

(3*R*,4*S*)-3-Methoxy-1-(*p*-methoxyphenyl)-4-[(2-methyl-3-methylsulfonyloxy-1,3-butadienyl]-2-azetidinone [(+)-3a]: This compound was obtained from allenol (+)-**2a** (44 mg, 0.41 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**2a** (35 mg, 59%) as a colorless oil. $[\alpha]_D^{25}$ = +103.7 (c = 0.6 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.28 and 6.85 (d, J = 9.0 Hz, each 2 H), 6.08 (dd, J = 9.3, 0.5 Hz, 1 H), 5.31 (dd, J = 14.1, 2.9 Hz, 2 H), 4.94 (dd, J = 9.3, 4.9 Hz, 1 H), 4.74 (d, J = 4.9 Hz, 1 H), 3.78 (s, 3 H), 3.48 (s, 3 H), 3.06 (s, 3 H), 2.07 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 163.2, 156.5, 152.1, 133.7, 130.7, 124.8, 118.5, 114.5, 105.4, 84.9, 58.9, 56.2, 55.5, 38.0, 13.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1742, 1365, 1170 cm^{-1}. MS (CI): *m*/*z* (%) = 368 (100) $[M + H]^+$, 367 (12) $[M]^+$. $C_{17}H_{21}NO_6S$ (367.4): calcd. C 55.57, H 5.76, N 3.81; found C 55.66, H 5.73, N 3.79.

(3*RS*,4*SR*)-1-(*p*-Methoxyphenyl)-4-[(2-methyl-3-methylsulfonyloxy-1,3-butadienyl]-3-(2-propynyl)-2-azetidinone [(±)-3c]: This compound was obtained from allenol (±)-**2c** (47 mg, 0.16 mmol); chromatography of the residue with dichloromethane/ethyl acetate (9:1) as eluent gave compound (±)-**3c** (52 mg, 96%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 and 6.83 (d, J = 9.0 Hz, 2 H), 6.11 (d, J = 8.8 Hz, 1 H), 5.28 (dd, J = 11.2, 2.9 Hz, 1 H), 4.70 (m, 3 H), 4.93 (dd, J = 9.0, 5.8 Hz, 1 H), 3.76 (s, 3 H), 3.68 (m, 1 H), 3.04 (s, 3 H), 2.58 (m, 2 H), 2.01 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.2, 156.2, 152.2, 134.2, 131.0, 125.3, 118.0, 114.3, 104.8, 80.7, 70.2, 55.4, 52.9, 37.8, 31.5, 15.2, 14.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2120, 1740, 1362, 1172 cm^{-1}. MS (CI): *m*/*z* (%) = 376 (100) $[M + H]^+$, 375 (15) $[M]^+$. $C_{19}H_{21}NO_5S$ (375.4): calcd. C 60.78, H 5.64, N 3.73; found C 60.89, H 5.61, N 3.71.

(3*R*,4*S*)-1-Benzyl-4-[(2-methyl-3-methylsulfonyloxy-1,3-butadienyl]-3-(2-propenyloxy)-2-azetidinone [(+)-3d]: This compound was obtained from allenol (+)-**2d** (69 mg, 0.23 mmol); chromatography of the residue with dichloromethane/ethyl acetate (9:1) as eluent gave compound (+)-**3d** (37 mg, 46%) as a colorless oil. $[\alpha]_D^{25}$ = +64.6 (c = 0.4 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (m, 2 H), 7.23 (m, 3 H), 5.95 (dd, J = 9.8, 0.5 Hz, 1 H), 5.82 (m, 1 H), 5.22 (m, 4 H), 4.73 (d, J = 4.6 Hz, 1 H), 4.66 (d, J = 14.9 Hz, 1 H), 4.33 (dd, J = 9.5, 4.6 Hz, 1 H), 4.07 (m, 2 H), 3.97 (d, J = 14.9 Hz, 1 H), 3.07 (s, 3 H), 1.68 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.5, 152.3, 135.1, 133.9, 134.4, 128.8, 128.4, 127.9, 124.0, 118.2, 104.9, 83.5, 71.9, 55.0, 44.3, 38.1, 13.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1742, 1370, 1170 cm^{-1}. MS (CI): *m*/*z* (%) = 378 (100) $[M + H]^+$, 377 (23) $[M]^+$. $C_{19}H_{23}NO_5S$ (377.5): calcd. C 60.46, H 6.14, N 3.71; found C 60.57, H 6.10, N 3.73.

(3*R*,4*S*)-1-(3-Butenyl)-3-methoxy-4-[(2-methyl-3-methylsulfonyloxy-1,3-butadienyl]-2-azetidinone [(+)-3f]: This compound was obtained from allenol (+)-**2f** (70 mg, 0.29 mmol); chromatography of the residue with dichloromethane/ethyl acetate (9:1) as eluent gave compound (+)-**3f** (75 mg, 90%) as a colorless oil. $[\alpha]_D^{25}$ = +80.0 (c = 0.7 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.96 (d, J = 9.0 Hz, 1 H), 5.71 (m, 1 H), 5.25 (dd, J = 15.4, 2.9 Hz, 2 H), 5.07 (m, 2 H), 4.53 (m, 2 H), 3.37 (s, 3 H), 3.38 (m, 1 H), 3.12 (s, 3 H), 3.04 (m, 1 H), 2.26 (m, 2 H), 1.92 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.5, 152.2, 134.7, 133.6, 124.5, 117.1, 105.1, 85.4, 58.6, 55.8, 39.5, 37.9, 32.0, 13.6 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1734, 1368, 1174 cm^{-1}. MS (CI): *m*/*z* (%) = 316 (100) $[M + H]^+$, 315 (16) $[M]^+$. $C_{14}H_{21}NO_5S$ (315.4): calcd. C 53.32, H 6.71, N 4.44; found C 53.42, H 6.68, N 4.46.

(3*R*,4*S*)-1-(3-Butynyl)-3-methoxy-4-[(2-methyl-3-methylsulfonyloxy-1,3-butadienyl]-2-azetidinone [(+)-3h]: This compound was obtained from allenol (+)-**2h** (56 mg, 0.24 mmol); chromatography of the residue with dichloromethane/ethyl acetate (9:1) as eluent gave compound (+)-**3h** (49 mg, 73%) as a colorless oil. $[\alpha]_D^{25}$ = +54.3 (c = 0.7 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.32 and 5.24 (d, J = 2.9 Hz, each 1 H), 4.71 and 4.65 (t, J = 4.9 Hz, each 1 H), 3.49 (m, 1 H), 3.41 (s, 3 H), 3.16 (m, 1 H), 3.15 (s, 3 H), 2.42 (ddd, J = 13.6, 7.3, 2.7 Hz, 1 H), 2.03 (t, J = 2.7 Hz, 1

H), 1.96 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.6, 152.2, 133.9, 124.3, 105.2, 85.7, 81.0, 70.4, 58.7, 56.4, 39.1, 38.1, 18.3, 13.7 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2119, 1735, 1372, 1175 cm^{-1}. MS (CI): m/z (%) = 314 (100) $[M + H]^+$, 313 (12) $[M]^+$. $C_{14}H_{19}NO_5S$(313.4): calcd. C 53.66, H 6.11, N 4.47; found C 53.76, H 6.08, N 4.44.

3-[2-(Allyloxy)phenyl]-2-methyl-1-methyleneprop-2-enyl 4-Methanesulfonate (3i): This compound was obtained from allenol **2i** (29 mg, 0.13 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **3i** (24 mg, 62%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25 (m, 2 H), 6.90 (m, 2 H), 6.61 (s, 1 H), 6.05 (m, 1 H), 5.27 (m, 4 H), 4.55 (tt, J = 7.1, 1.5 Hz, 2 H), 3.17 (s, 3 H), 2.01 (d, J = 0.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 156.5, 153.9, 133.0, 130.4, 128.9, 128.6, 127.3, 120.3, 117.9, 111.7, 104.4, 69.0, 38.0, 14.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1360, 1175, 765 cm^{-1}. MS (EI): m/z (%) = 295 (7) $[M + H]^+$, 294 (100) $[M]^+$. $C_{15}H_{18}O_4S$ (294.4): calcd. C 61.20, H 6.16; found C 61.31, H 6.12.

1-Acryloyl-2-[2-methyl-3-(methylsulfonyloxy)buta-1,3-dienyl]-1*H*-pyrrole (3l): This compound was obtained from allenol **2m** (24 mg, 0.12 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **3l** (16 mg, 48%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.43 (dd, J = 4.0, 1.8 Hz, 1 H), 7.23 (dd, J = 3.8, 1.7 Hz, 1 H), 6.87 (dd, J = 16.8, 10.2 Hz, 1 H), 6.58 (dd, J = 16.8, 1.7 Hz, 1 H), 6.38 (m, 2 H), 6.03 (dd, J = 10.2, 1.7 Hz, 1 H), 5.31 (m, 2 H), 3.19 (s, 3 H), 2.02 (d, J = 1.2 Hz, 3 H) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1679, 1364, 1173 cm^{-1}. MS (CI): m/z (%) = 282 (100) $[M + H]^+$, 281 (11) $[M]^+$. $C_{13}H_{15}NO_4S$ (281.3): calcd. C 55.50, H 5.37, N 4.98; found C 55.40, H 5.33, N 5.00.

3-(1-Ethynyl-1*H*-indol-2-yl)-1-methyleneprop-2-enyl 4-Methanesulfonate (3n): This compound was obtained from allenol **2o** (51 mg, 0.21 mmol); chromatography of the residue with hexanes/ethyl acetate (5:1) as eluent gave compound **3n** (32 mg, 50%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.62 (d, J = 7.6 Hz, 1 H), 7.27 (m, 4 H), 6.56 (s, 1 H), 5.36 (m, 2 H), 4.89 (d, J = 2.4 Hz, 2 H), 3.15 (s, 3 H), 2.23 (t, J = 2.4 Hz, 1 H), 2.13 (d, J = 1.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.1, 135.1, 132.0, 128.5, 123.3, 121.4, 120.8, 119.9, 118.0, 109.6, 105.6, 105.5, 78.7, 73.1, 38.6, 33.2, 15.8 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2121, 1370, 1168 cm^{-1}. MS (CI): m/z (%) = 316 (100) $[M + H]^+$, 315 (14) $[M]^+$. $C_{17}H_{17}NO_3S$ (315.4): calcd. C 64.74, H 5.43, N 4.44; found C 64.84, H 5.40, N 4.42.

Domino Transposition/Intramolecular Diels−Alder Reaction in α-Allenol-tethered Alkenes/Alkynes. 2. General Procedure for the Synthesis of Tricycles 6 and 7: Methanesulfonyl chloride (1.10 mmol) and triethylamine (1.20 mmol) were sequentially added dropwise to a solution of the corresponding α-allenyl alcohol **2** (1.0 mmol) and hydroquinone (cat.) in toluene (10 mL). The resulting solution was heated in a sealed tube at 190 °C until disappearance of the starting material (TLC). The reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. Chromatography of the residue, with elution with dichloromethane/ethyl acetate or hexanes/ethyl acetate mixtures, gave analytically pure fused tricycles **6** and **7**.

Tricyclic β-Lactam (+)-6b: This compound was obtained from allenol (+)-**2d** (73 mg, 0.24 mmol); chromatography of the residue with hexanes/ethyl acetate (1:2) as eluent gave compound (+)-**6b** (50 mg, 54%) as a colorless oil. $[\alpha]_D^{25}$ = +10.0 (c = 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.27 (m, 5 H), 4.76 (d, J = 16.1 Hz, 1 H), 4.65 (d, J = 5.9 Hz, 1 H), 3.76 (dd, J = 16.1, 3.0 Hz, 1 H), 3.50 (dd, J = 10.5, 4.0 Hz, 1 H), 3.22 (t, J = 10.5 Hz, 1 H), 2.89 (dd, J = 6.9, 5.1 Hz, 1 H), 2.36 (s, 3 H), 2.23 (m, 1 H), 2.12 (m, 1 H), 1.93 (m, 1 H), 1.52 (s, 3 H), 1.09 (m, 2 H), 0.79 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.5, 142.9, 136.9, 128.9, 124.4, 116.5, 78.9, 69.2, 55.1, 45.9, 44.0, 38.5, 34.4, 28.0, 24.7, 14.4 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1740, 1370, 1171 cm^{-1}. MS (CI): m/z (%) = 378 (100) $[M + H]^+$, 377 (23) $[M]^+$. $C_{19}H_{23}NO_5S$ (377.5): calcd. C 60.46, H 6.14, N 3.71; found C 60.34, H 6.16, N 3.73.

Tricyclic β-Lactam (+)-6c: This compound was obtained from allenol (+)-**2f** (69 mg, 0.29 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**6c** (44 mg, 47%) as a colorless oil. $[\alpha]_D^{25}$ = +119.5 (c = 0.9 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.05 (dd, J = 4.4, 1.2 Hz, 1 H), 3.69 (dd, J = 12.9, 4.6 Hz, 1 H), 3.49 (s, 3 H), 2.76 (dd, J = 10.3, 4.4 Hz, 1 H), 2.38 (s, 3 H), 2.21 (m, 3 H), 1.78 (s, 3 H), 1.46 (m, 1 H), 1.21 (dd, J = 12.5, 7.0 Hz, 1 H), 1.02 (m, 1 H), 0.79 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.8, 143.3, 124.8, 84.7, 58.7, 56.9, 41.1, 39.1, 37.9, 35.8, 31.0, 29.4, 28.3, 13.3 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1741, 1372, 1168 cm^{-1}. MS (CI): m/z (%) = 316 (100) $[M + H]^+$, 315 (14) $[M]^+$. $C_{14}H_{21}NO_5S$ (315.4): calcd. C 53.32, H 6.71, N 4.44; found C 53.41, H 6.69, N 4.46.

Tricyclic Chromene 6d: This compound was obtained from allenol **2i** (58 mg, 0.26 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **6d** (37 mg, 47%), containing ca. 15% of its *anti* epimer, as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.97 (m, 3 H), 6.76 (m, 1 H), 3.87 (dd, J = 10.7, 8.1 Hz, 1 H), 3.72 (dd, J = 10.7, 3.7 Hz, 1 H), 2.94 (br. s, 1 H), 2.17 (s, 3 H), 2.11 (m, 2 H), 1.72 (td, J = 1.9, 0.7 Hz, 3 H), 1.61 (m, 1 H), 1.31 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.9, 142.2, 130.7, 128.2, 125.9, 124.5, 119.8, 116.9, 67.2, 40.1, 39.1, 30.7, 25.8, 23.0, 16.9 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1366, 1170, 758 cm^{-1}. MS (EI): m/z (%) = 295 (21) $[M + H]^+$, 294 (100) $[M]^+$. $C_{15}H_{18}O_4S$ (294.4): calcd. C 61.20, H 6.16; found C 61.32, H 6.12.

Tricyclic Pyrrolizidine 6f: This compound was obtained from allenol **2m** (48 mg, 0.23 mmol); chromatography of the residue with hexanes/ethyl acetate (3:1) as eluent gave compound **6f** (28 mg, 35%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.04 (d, J = 3.0 Hz, 1 H), 6.45 (t, J = 3.0 Hz, 1 H), 6.11 (m, 1 H), 3.92 (d, J = 7.6 Hz, 1 H), 3.41 (m, 1 H), 3.06 (s, 3 H), 2.39 (m, 2 H), 2.05 (m, 2 H), 1.97 (s, 3 H) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1734, 1370, 1166 cm^{-1}. MS (CI): m/z (%) = 282 (100) $[M + H]^+$, 281 (12) $[M]^+$. $C_{13}H_{15}NO_4S$ (281.3): calcd. C 55.50, H 5.37, N 4.98; found C 55.62, H 5.40, N 4.96.

Tricyclic β-Lactam (±)-7a: This compound was obtained from allenol (±)-**2c** (62 mg, 0.21 mmol); chromatography of the residue with hexanes/ethyl acetate (1:1) as eluent gave compound (±)-**6a** (35 mg, 45%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38 and 6.82 ppm (dd, J = 6.0, 2.0 Hz, each 2 H), 4.99 (br. s, 1 H), 3.71 (t, J = 3.4 Hz, 1 H), 3.38 (m, 1 H), 2.86 (m, 2 H), 2.57 (m, 2 H), 2.34 (s, 3 H), 2.13 (m, 1 H), 1.84 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 168.0, 157.3, 147.5, 141.6, 141.3, 129.6, 123.7, 122.1, 121.8, 116.1, 114.4, 61.5, 55.5, 52.7, 48.8, 39.1, 37.6, 29.9, 29.6, 16.1 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2120, 1743, 1366, 1170 cm^{-1}. MS (CI): m/z (%) = 376 (100) $[M + H]^+$, 375 (16) $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{21}NO_5S$ (377.5): calcd. C 60.78, H 5.64, N 3.73; found C 60.89, H 5.61, N 3.75.

Tricyclic β-Lactam (+)-7c: This compound was obtained from allenol (+)-**2h** (59 mg, 0.25 mmol); chromatography of the residue with hexanes/ethyl acetate (1:2) as eluent gave compound (+)-**7c**

(41 mg, 52%) as a colorless oil. $[\alpha]_D^{25} = +77.0$ ($c = 0.5$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 5.60$ (br. s, 1 H), 4.51 (dd, $J = 4.1$, 1.2 Hz, 1 H), 3.92 (m, 1 H), 3.64 (s, 3 H), 3.45 (m, 1 H), 3.41 (d, $J = 4.4$ Hz, 1 H), 3.14 (m, 3 H), 3.13 (s, 3 H), 2.69 (m, 1 H), 1.73 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 166.8, 141.1, 131.8, 122.8, 120.4, 81.1, 59.5, 58.8, 40.9, 39.7, 39.0, 33.9, 29.8, 14.2 ppm. IR ($CHCl_3$): $\tilde{\nu} = 1745$, 1375, 1170 cm^{-1}. MS(CI): *m/z* (%) =314 (100) $[M + H]^+$, 313 (20) $[M]^+$. $C_{14}H_{19}NO_5S$ (313.4): calcd. C 53.66, H 6.11, N 4.47; found C 53.78, H 6.08, N 4.49.

Tricyclic Chromene 7d: This compound was obtained from allenol **2k** (48 mg, 0.22 mmol); chromatography of the residue with hexanes/ethyl acetate (4:1) as eluent gave compound **7d** (25 mg, 52%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.74$ (m, 1 H), 7.27 (m, 1 H), 7.09 (m, 2 H), 6.96 and 6.75 (d, $J =$ 8.0 Hz, each 1 H), 5.01 (br. s, 1 H), 4.90 (s, 2 H), 2.53 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 156.6$, 154.4, 130.8, 128.6, 128.2, 127.2, 124.4, 122.6, 121.2, 120.4, 117.3, 113.5, 69.6, 14.3 ppm. IR ($CHCl_3$): $\tilde{\nu} = 1372$, 1166, 762 cm^{-1}. MS (EI): *m/z* (%) = 213 (6) $[M + H]^+$, 212 (100) $[M]^+$. $C_{14}H_{12}O_2$ (212.2): calcd. C 79.22, H 5.70; found C 79.36, H 5.75.

Supporting Information (see also footnote on the first page of this article): Compound characterization data and experimental procedures for compounds (+)-**2a**, (±)-**2b**, (+)-**2e**, (+)-**2g**, **2j**, **2l**, **2n**, (±)-**3b**, (+)-**3e**, (+)-**3g**, **3j**, **3k**, **3m**, (±)-**6a**, **6e**, (−)-**7b**, and **7e**.

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[17] Full spectroscopic and analytical data for compounds not included in this Exp. Sect. are described in the Supporting Information.

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