Regio- and Diastereoselective Ene Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with Chiral Allylic Alcohols and Their Derivatives

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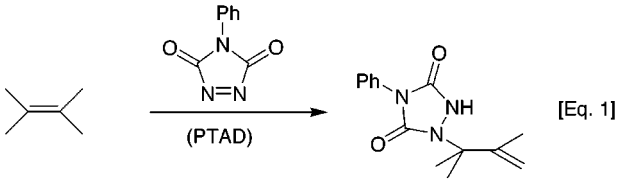
Chiral allylic alcohols **1a**−**e** reacted with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in CH_2Cl_2 to produce 3-amino-1-alken-4-ols **2** and **3** in 78−89% yields, with 68−90% diastereomeric excess (de) in favor of the threo isomer. Chiral allylic ethers **1f**,**g** and acetates **1h**,**i** gave similar yields but lower de (34−66%). Reaction of allylic alcohols **6a**−**e** with PTAD in CH_2Cl_2 produced 1,3-regioisomers **7** and **8** exclusively in 33−65% yields without apparent diastereoselectivity, except when R_1 was a Bu^t group, in which case only syn product **7** was formed. However, when **6a** or **6c** was subjected to reaction with PTAD in a polar solvent, up to 88% de was observed. Reaction of allylic ethers **6f**,**g** and acetates **6h**,**i** with PTAD in CH_2Cl_2 also produced **7** and **8** exclusively with improved yields (56−96%) and diastereoselectivity (50−100% de in favor of the syn isomer).

Introduction

The 1,2-amino alcohol and 1,3-amino alcohol moieties are found as unit(s) in various biologically active substances such as antifungal peptidyl nucleoside antibiotics,[1] enzyme inhibitors,[2] amino sugar antibiotics,[3] and sympathomimetic amines.[1,4] The ene reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) with alkenes bearing allylic hydrogens has attracted considerable attention and remains an active field of study for both synthetic and mechanistic studies (eq 1).[5] The regioselective ene



[Eq. 1]

reaction of triazolinedione with alkyl-substituted alkenes is known to give geminal selectivity.[6] This reaction constitutes a convenient method for the synthesis of an allylic amine from an olefinic compound; thus, 1,2-amino alcohols and 1,3-amino alcohols may be prepared from appropriate precursors. Herein we report our findings on a series of ene reactions of PTAD with chiral allylic alcohols and their derivatives that proceeded with high diastereoselectivity and complete regioselectivity. This type of reaction is potentially useful for the preparation of 1,2-amino alcohols and 1,3-amino alcohols (Scheme 1).

Results and Discussion

Ene reaction of **1a** with PTAD in chloroform at 25 °C gave the expected ene products *threo*-**2a** and *erythro*-**3a** in a ratio of 3:1. When the reaction was performed at 0 °C the diastereoselectivity increased to 4:1. The diastereoselectivity of the ene reaction was further improved to 19:1 when the reaction was carried out over a temperature range of −78 to +25 °C in dichloromethane. Under similar reaction conditions, **1b**−**e** gave the corresponding ene products in 78−89% yields with 68−90% diastereoselectivity. These results are summarized in Table 1. Stereoisomers were assigned according to the vicinal proton coupling constants between the protons on the hydroxy-bearing and amino-bearing carbons of the corresponding isopropylidene derivatives of threo and erythro isomers **4** and **5**, prepared from **2** and **3** respectively by treatment with 2,2-dimethoxypropane in the presence of an acid catalyst (Scheme 2). The vicinal coupling constants of H_a and H_b in compounds **4** and **5** are summarized in Table 2. The H_a and H_b protons in threo isomers were assigned to have vicinal coupling constants 9.2−9.7 Hz due to a trans-diaxial coupling. The H_a and H_b protons in erythro isomers were assigned to have vicinal coupling constants 3.2−3.9 Hz due to an axial−equatorial coupling. When the hydroxy group was methylated (**1f**,**g**) or acetylated (**1h**,**i**), the diastereoselectivities was found to decrease (entries 6−9). The stereochemistry of **2f**−**i** and **3f**−**i** was assigned by

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(1) (a) Griengli, H.; Singer, M.; Pucker, R.; Marschner, C.; Baumgartner, H. *Tetrahedron Lett.* **1992**, *33*, 6443. (b) Isono, K.; Kobinate, K.; Uramoto, M. *Tetrahedron* **1981**, *37*, 1599.

(2) (a) Pohland, A.; Sullivan, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 4458; (b) **1955**, *77*, 3400. (c) Reetz, M. T.; Binder, J. *Tetrahedron Lett.* **1989**, *30*, 5425.

(3) Po, S. Y.; Uang, B. J. *Tetrahedron: Asymmetry* **1994**, *5*, 8169 and references therein.

(4) (a) Umezawa, H.; Aoyagi, T.; Suda, H.; Hamada, M.; Takeuchi, T. *J. Antibiot.* **1976**, 29, 97. (b) Aoyagi, T.; Tobe, H.; Kojima, F.; Hamada, M.; Takeuchi, T. J. Umezawa, H. *Ibid*. **1978**, 31, 636. (c) Jung, M. E.; Shaw, T. *J. Am. Chem. Soc.* **1980**, *102*, 6304.

(5) (a) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910. (b) Nelsen, S. F.; Kapp, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 5548. (c) Clennan, E. L.; Koola, J. J.; Oolman, K. A. *Tetrahedron Lett.* **1990**, *31*, 6759. (d) Squillacote, M.; Mooney, M.; De Felippis, J. *J. Am. Chem. Soc.* **1990**, *112*, 5364. (e) Elemes, Y.; Foote C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6044 and references therein. (f) Clennan, E. L.; Koola, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 3802.

(6) (a) Orfanopoulos, M.; Elemes, Y.; Stratakis, M. *Tetrahedron Lett.* **1990**, *31*, 5775. (b) Orfanopoulos, M.; Stratakis, M.; Elemes, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6417. (c) Orfanopoulos, M.; Stratakis, M.; Elemes, Y.; Jensen, F. *J. Am. Chem. Soc.* **1991**, *113*, 3180. (d) Elemes, Y.; Stratakis, M.; Orfanopoulos, M. *Tetrahedron Lett.* **1989**, *30*, 6903.

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Scheme 1

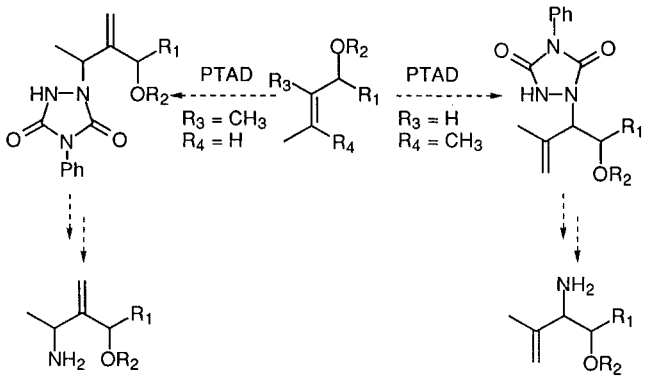
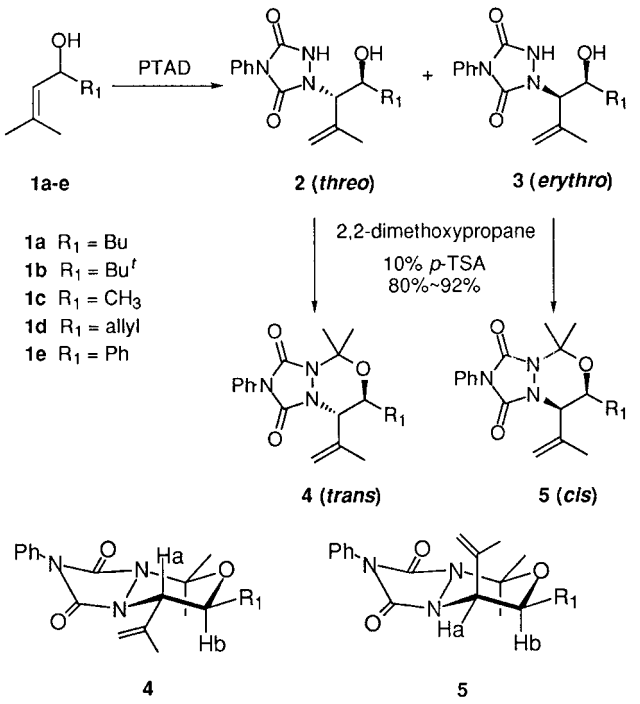


Table 1. Diastereoselectivity of Reaction of 1 with PTAD[a]

entry		R_1	R_2	**2** (threo):**3** (erythro)	yield (%)
1	**1a**	Bu^n	H	95:5	89
2	**1b**	Bu^t	H	84:16	80
3	**1c**	CH_3	H	92:8	82
4	**1d**	allyl	H	89:11	78
5	**1e**	phenyl	H	90:10	84
6	**1f**	Bu^n	CH_3	67:33	81
7	**1g**	Bu^t	CH_3	83:17	78
8	**1h**	Bu^n	Ac	73:27	82
9	**1i**	Bu^t	Ac	70:30	86

[a] Reaction was performed in dichloromethane at a temperature range from −78 to +25 °C for 3−5 h.

Scheme 2



comparison of their ^{1}H NMR spectra with those of the methylated and acetylated products of **2a**,**b** and **3a**,**b**.

The above results suggest that the hydroxy group might be involved in the ene reaction. To examine further this possibility, the reaction of **1a** with PTAD was carried out in more polar solvents, as shown by the results summarized in Table 3. In these experiments, the degree of diastereoselectivity was inversely proportional to the polarity of the solvent. It appears, therefore, that the hydroxy group plays a positive role in enhancing the diastereoselectivity via hydrogen bonding.

Table 2. Selected ^{1}H NMR Spectral Data of Acetonides 4 and 5

compd	R_1	H_a (δ)	H_b (δ)	J_{ab} (Hz)
4a	Bu^n	3.99	3.85	9.5
4b	Bu^t	4.51	3.74	9.2
4c	Me	3.87	4.05	9.5
4d	allyl	4.06	3.96	9.6
4e	phenyl	4.22	4.91	9.7
5a	Bu^n	4.43	4.13	3.7
5b	Bu^t	4.62	3.81	3.2
5c	Me	4.39	4.36	3.8
5d	allyl	4.47	4.20	3.7
5e	phenyl	4.77	5.41	3.9

Table 3. Solvent Effect on Reaction of Chiral Allylic Alcohols 1a with PTAD[a]

entry	solvent	**2** (threo):**3** (erythro)
1	CH_2Cl_2	95:5
2	$CHCl_3$	91:9
3	CH_3CN	85:15
4	acetone	72:28

[a] Reaction was performed at a temperature range from −78 to +25 °C for 3−5 h.

According to the experimental data in Tables 1 and 3, chiral allylic alcohols **1a**−**e** presumably react with PTAD through a transition structure $\mathbf{B}^{\ddagger}$ of lower energy, in which the hydroxy group of **1** forms an intermolecular hydrogen bond with PTAD, to give the threo isomer as the preferred product. Although transition structure $\mathbf{A}^{\ddagger}$ had an intermolecular hydrogen bond between two reacting molecules, the 1,3-allylic strain[7] between R_1 and the *cis*-methyl group in **1** raised its energy above that of $\mathbf{B}^{\ddagger}$ (Scheme 3). There is no intermolecular hydrogen bond between PTAD and chiral allylic ether or acetate when they react. Chiral allylic ether and acetate presumably reacted with PTAD through a transition structure $\mathbf{D}^{\ddagger}$ of lower energy, in which the PTAD molecule approaching the chiral allylic ether or acetate would experience less steric strain, to give the threo isomer as the preferred product. Thus, chiral allylic alcohols, ethers, and esters possibly reacted with PTAD through a conformation of a similar type in the transition structure. The "inside alkoxy" effect proposed by Houk and co-workers,[8] which has been successfully used to predict the stereoselectivities of many electrophilic reactions with chiral allylic ethers, is unable to explain our results. The model of Kozikowski and Ghosh[9] is also unable to explain these results, as it would predict the erythro isomer to be the major product for chiral allylic ethers and esters. Although the directing effect of the hydroxy functionality is well recognized for organic reactions of many types[8a,10] including the Diels−Alder reaction of PTAD with electron-rich dienes,[11] it is novel for PTAD in an ene reaction with chiral allylic alcohols.[12]

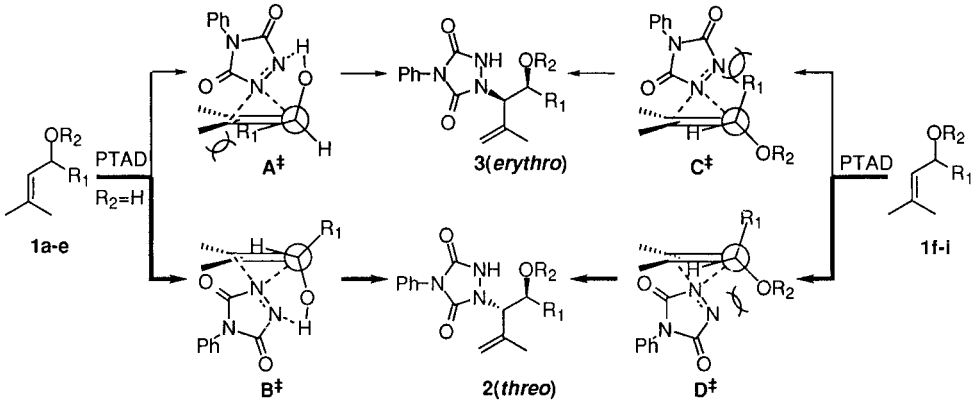
Reaction of **6a**−**e** with PTAD in dichloromethane over a temperature range of −78 to +25 °C produced the corresponding ene products **7** and **8** with complete regioselectivity. However, there was no diastereoselectivity detected except for **6d**, from which **7d** was isolated

(7) (a) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841. (b) Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006.

(8) (a) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jager, V.; Schohe, R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1984**, *106*, 3880. (b) Houk, K. N.; Rondan, N. G.; Wu, Y.-D.; Metz, J. T.; Paddon-Row, M. N. *Tetrahedron* **1984**, *40*, 2257.

(9) Kozikowski, A. P.; Ghosh, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 5788.

Scheme 3



1a $R_1 = Bu^n$
1b $R_1 = Bu^t$
1c $R_1 = CH_3$
1d R_1 = allyl
1e R_1 = phenyl

1f $R_1 = Bu^n$, $R_2 = CH_3$
1g $R_1 = Bu^t$, $R_2 = CH_3$
1h $R_1 = Bu^n$, R_2 = Ac
1i $R_1 = Bu^t$, R_2 = Ac

Table 4. Diastereoselectivity of Reaction of 6 with PTAD[a]

compounds	R_1	R_2	yield (%)	**7** (syn):**8** (anti)
6a	Ph	H	43	1:1
6b	allyl	H	33	1:1
6c	Bu^n	H	60	1:1
6d	Bu^t	H	65	1:0
6e	CH_3	H	50	1:1
6f	Bu^n	CH_3	61	10:1
6g	Bu^t	CH_3	82	~1:0
6h	Bu^n	Ac	96	5:1
6i	Bu^t	Ac	68	23:1

[a] Reaction was performed in dichloromethane at a temperature range from −78 to +25 °C for 3−5 h.

Table 5. Proton Chemical Shifts of the Methine Proton at the Amino-Bearing Carbon Atom

		N−C−H	
		7	**8**
a	R = Ph	4.64	4.81
b	R = allyl	4.76	4.95
c	R = *n*-Bu	4.76	4.93
d	R = *t*-Bu	4.74	5.08
e	R = Me	4.76	5.02

Table 6. Solvent Effect on Reaction of Chiral Allylic Alcohols 6a and 6c with PTAD[a]

solvent	substrate	**7**: **8**	yield (%)
acetone	**6a**	6:1	59
ethyl acetate	**6a**	5:1	58
acetonitrile	**6a**	6:1	58
THF	**6a**	15:1	31
DMF	**6a**	10:1	21
$CHCl_3$	**6a**	3:2	38
acetone	**6c**	10:1	50
ethyl acetate	**6c**	5:1	28
acetonitrile	**6c**	5:1	42
THF	**6c**	5:1	55
DMF	**6c**	16:1	41
$CHCl_3$	**6c**	2:3	64

[a] Reaction was performed at a temperature range from −78 to +25 °C for 3−5 h.

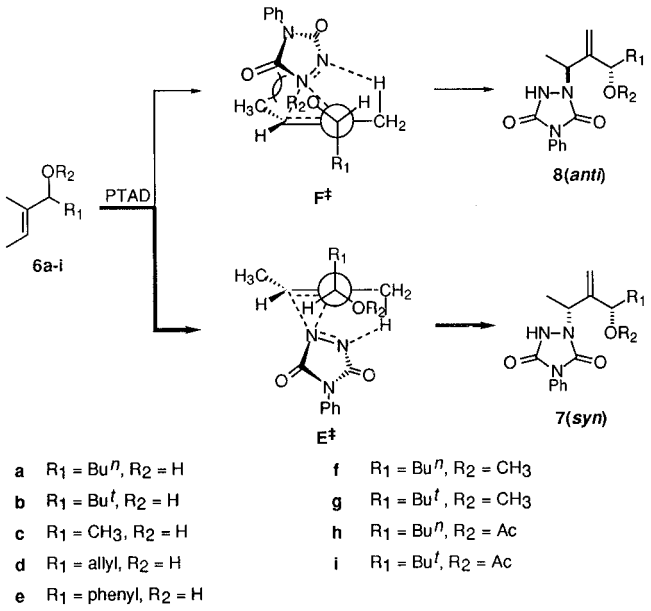
as the sole product. In contrast, under similar reaction conditions **6f**−**i** reacted with PTAD with high diastereoselectivity in favor of the syn isomer and with complete regioselectivity (Table 4). Assignments of stereochemistry for 1,3-amino alcohols were confirmed by an X-ray analysis of **7g**, by correlation of the ^{1}H NMR chemical shifts of the methine proton at the amino-bearing carbon atom (Table 5), and by comparison of the spectral data with those of the corresponding O-methylated or O-acetylated compounds prepared from 1,3-amino alcohols **7c**,**d** and **8c**,**d**. When **6a** or **6c** was reacted with PTAD in a more polar solvent such as tetrahydrofuran, acetone, or *N*,*N*-dimethylformamide, enhancement of diastereoselectivity was observed (Table 6). In these reactions, the directing effect of the hydroxy functionality on the two reacting molecules is expected to reduce. The second nitrogen atom, which forms an intermolecular hydrogen bond with the hydroxy group of **6a** or **6c** in dichloromethane, must now locate in an orientation anti to the solvated hydroxy group to avoid severe steric strain (as shown by transition structure **F**‡ in Scheme 4). The effect of 1,2-allylic strain during the formation of aziridinium ion from chiral allylic alcohols is proposed to be determined by the transition structure.[10h] Thus, the reaction presumably proceeds through a transition structure **E**‡ of lower energy, in which PTAD experienced less torsional and steric strain, to give the syn isomer as the preferred product. Here again, neither the "inside alkoxy" effect nor the model of Kozikowski and Ghosh can explain our observations satisfactorily, as they predict the anti

(10) (a) Chautemps, P.; Pierre, J. L. *Tetrahedron* **1976**, *32*, 549. (b) Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S. *J. Am. Chem. Soc.* **1979**, *101*, 159. (c) Rossiter, B. E.; Verhoeven, T. R.; Sharpless, K. B. *Tetrahedron Lett.* **1979**, *20*, 4733. (d) Narula, A. S. *Ibid*. **1981**, *22*, 2017. (e) Narula, A. S. *Ibid*. **1982**, *23*, 5579. (f) Narula, A. S. *Ibid*. **1983**, *24*, 5421. (g) Finn, G. M.; Sharpless K. B. *Asymmetric Synthesis*; Academic Press: Orlando, FL, 1985; Vol. V, p 247. (h) Kocovsky, P.; Turecek, F.; Hajicek, J. *Synthesis of Natural Products: Problems of Stereoselectivity*; CRC Press: Boca Raton, FL, 1986; Vol. II, p 138 and references therein. (i) Adam, W.; Nestler, B. *J. Am. Chem. Soc.* **1992**, *114*, 6549. (j) Adam, W.; Brunker, H.-G.. *J. Am. Chem. Soc.* **1993**, *115*, 3008. (k) Adam, W.; Prein, M. *J. Am. Chem. Soc.* **1993**, *115*, 3766. (l) Adam, W.; Nestler, B. *J. Am. Chem. Soc.* **1993**, *115*, 5041. (m) Lu, W. F. Ph.D. Thesis, Department of Chemistry, National Tsing Hua University, 1993.

(11) Kerrigan, J. E.; McDougal, P. G.; VanDerveer, D. *Tetrahedron Lett.* **1993**, *34*, 8055.

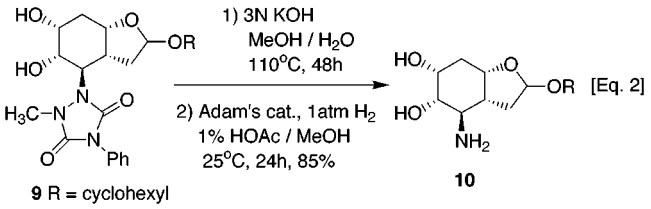
(12) While this manuscript was in preparation two works dealing with 1,2-diastereoselctivity on the ene reaction of triazolindione with allylic alcohols appeared in the literature: (a) Stratakis, M.; Vassilikogiannakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **1998**, *39*, 2393. (b) Adam, W.; Nestler, B.; Pastor, A.; Wirth. T. *Ibid*. 2625.

Scheme 4



isomer to be the major product for chiral allylic ethers and esters.

Conversion of an urazole moiety to an amino group had been demonstrated by Corey and Snider in high yield (eq 2).[13] It is conceivable that one should be able to convert



the urazole moiety of compounds **2**, **3**, **7**, and **8** to an amino group by Corey's procedure. In principle, compounds **2** and **3** could be converted to the corresponding 1,2-amino alcohols, whereas compounds **7** and **8** could be converted to the corresponding 1,3-amino alcohols.

In conclusion, the ene reaction of PTAD with chiral allylic alcohols or their derivatives were found to be highly diastereoselective and completely regioselective. The formation of 1,2- or 1,3-amino alcohols can be tuned by structural modification of chiral allylic alcohols. The results reported herein provide a potential synthetic method for the preparation of 1,2- and 1,3-amino alcohols. In addition, these results provide valuable information for mechanistic consideration on the ene reactions of chiral allylic alcohols.

Experimental Section

Unless otherwise noted, infrared spectra were run as neat films. The NMR spectra were run at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR in $CDCl_3$ solution and are referenced to internal standard tetramethylsilane (TMS) in ppm units except a few that were run in DMSO-d_6, C_6D_6, or CD_3OD or at a higher field. Mass spectra and high-resolution mass spectra (HRMS) were measured using the electron-impact (EI, 12 eV) technique.

Typical Procedure for the Preparation of Chiral Allylic Alcohols. To a 250 mL round-bottomed flask charged with *trans*-3-methyl-2-butenal (4.41 g, 52.4 mmol) and tetrahydrofuran (100 mL) was slowly added butyllithium (25.0 mL, 2.5 M, 62.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 4 h, and then the reaction was quenched with saturated ammonium chloride solution (50 mL). The aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with brine (3 × 25 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with ethyl acetate−hexane (1:8) to give **1a** (5.92 g, 41.7 mmol, 80%).

2-Methyl-2-octen-4-ol (1a): IR 3353, 1676 cm^{-1}; ^{1}H NMR δ 5.13 (d, J = 8.8 Hz, 1H), 4.31 (dt, J = 8.8, 6.6 Hz, 1H), 1.70 (s, 3H), 1.66 (s, 3H), 1.60−1.25 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 134.27 (s), 128.37 (d), 68.45 (d), 37.30 (t), 27.49 (t), 25.57 (q), 22.55 (t), 17.99 (q), 13.88 (q); MS (*m*/*z*, rel intensity) 142 (M$^+$, 31), 127 (19), 100 (46), 85 (100), 67 (41), 57 (47), 43 (37); HRMS calcd for $C_9H_{18}O$: 142.1358, found 142.1353.

2,2,5-Trimethyl-4-hexen-3-ol (1b): yield 58%; IR 3401, 1673 cm^{-1}; ^{1}H NMR δ 5.19 (d, J = 9.3 Hz, 1H), 3.95 (d, J = 9.3 Hz, 1H), 1.71 (s, 3H), 1.65 (s, 3H), 0.85 (s, 9H); ^{13}C NMR δ 135.43 (s), 124.95 (d), 75.82 (d), 35.22 (s), 25.90 (q), 25.39 (q), 18.25 (q); MS (*m*/*z*, rel intensity) 142 (M$^+$, 3), 125 (10), 109 (25), 85 (100), 67 (17), 57 (41), 43 (41); HRMS calcd for $C_9H_{18}O$ 142.1358, found 142.1364.

4-Methyl-3-penten-2-ol (1c): yield 86%; IR 3347, 1676 cm^{-1}; ^{1}H NMR δ 5.17(d, J = 8.4 Hz, 1H), 4.51 (dq, J = 8.4, 6.1 Hz, 1H), 1.67 (s, 3H), 1.65 (s, 3H), 1.19 (d, J = 6.1 Hz, 3H); ^{13}C NMR δ 133.44 (s), 129.39 (d), 64.48 (d), 25,45 (q), 23.41 (q), 17.79 (q); MS (*m*/*z*, rel intensity) 100 (M$^+$, 8), 85 (100), 82 (43), 67 (37), 58 (14), 43 (16); HRMS calcd for $C_6H_{12}O$ 100.0888, found 100.0886.

6-Methyl-1,5-heptadien-4-ol (1d): yield 78%; IR 3354, 3076, 1676 cm^{-1}; ^{1}H NMR δ 5.86−5.71 (m, 1H), 5.20−5.07 (m, 3H), 4.41−4.33 (m, 1H), 2.25 (t, J = 6.7 Hz, 2H), 1.71 (s, 3H), 1.67 (s, 3H); ^{13}C NMR δ 135.01 (s), 134.50 (d), 127.25 (d), 117.50 (t), 67.65 (d), 42.07 (t), 25.59 (q), 18.10 (q); MS (*m*/*z*, rel intensity) 126 (M$^+$, 0.1), 108 (10), 93 (16), 85 (100), 67 (17), 57 (20), 41 (27); HRMS calcd for $C_8H_{13}O$ (M$^+$ − 1) 125.0966, found 125.0971.

3-Methyl-1-phenyl-2-buten-1-ol (1e): yield 93%; IR 3344, 3028, 1673, 1599 cm^{-1}; ^{1}H NMR δ 7.45−7.23 (m, 5H), 5.43 (d, J = 8.9 Hz, 1H), 5.40 (d, J = 8.9 Hz, 1H), 1.95 (br, 1H), 1.79 (s, 3H), 1.74 (s, 3H); ^{13}C NMR δ 144.20 (s), 134.80 (s), 128.30 (d), 127.67 (d), 127.08 (d), 125.73 (d), 70.56 (d), 25.69 (q), 18.16 (q); MS (*m*/*z*, rel intensity) 162 (M$^+$, 65), 147 (100), 129 (69), 120 (61), 105 (70), 91 (57), 69 (70); HRMS calcd for $C_{11}H_{14}O$ 162.1046, found 162.1038.

(*E*)-2-Methyl-1-phenyl-2-buten-1-ol (6a): yield 96%; IR 3369, 3028 cm^{-1}; ^{1}H NMR δ 7.22−7.36 (m, 5H), 5.69 (q, J = 6.6 Hz, 1H), 5.13 (s, 1H), 1.85 (s, 1H), 1.65 (d, J = 6.6 Hz, 3H), 1.48 (s, 3H); ^{13}C NMR δ 142.46 (s), 137.53 (s), 128.02 (d), 127.02 (d), 126.09 (d), 121.04 (d), 79.14 (d), 13.02 (q), 11.53 (q); MS (*m*/*z*, rel intensity) 162 (M$^+$, 100), 129 (38), 105 (67), 91 (25), 77 (68); HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1053; mp 39 °C. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.41; H, 8.70.

(*E*)-5-Methyl-1,5-heptadien-4-ol (6b): yield 82%; IR 3373, 1641 cm^{-1}; ^{1}H NMR δ 5.69−5.80 (m, 1H), 5.46 (q, J = 5.0 Hz, 1H), 5.11 (d, J = 17.0 Hz, 1H), 5.07 (d, J = 9.3 Hz, 1H), 4.03 (t, J = 6.8 Hz, 1H), 2.29 (t, J = 6.8 Hz, 2H), 1.74 (br, 1H), 1.61 (s, 3H), 1.60 (d, J = 5.0 Hz, 3H); ^{13}C NMR δ 137.22 (s), 134.94 (d), 120.65 (d), 117.39 (t), 76.53 (d), 39.85 (t), 12.93 (q), 11.25 (q); MS (*m*/*z*, rel intensity) 126 (M$^+$,1), 108 (10), 93 (15), 85 (100), 57 (17); HRMS calcd for $C_8H_{14}O$ 126.1045, found 126.1035.

(*E*)-3-Methyl-2-octen-4-ol (6c): yield 77%; IR 3363 cm^{-1}; ^{1}H NMR δ 5.38 (q, J = 6.3 Hz, 1H), 3.90 (t, J = 6.6 Hz, 1H), 1.83 (br, 1H), 1.54 (d, J = 6.2 Hz, 3H), 1.53 (s, 3H), 1.43−1.50 (m, 2H), 1.01−1.26 (m, 4H), 0.837 (t, J = 6.6 Hz, 3H); ^{13}C NMR δ 138.01 (s), 120.47 (d), 77.92 (d), 34.43 (t), 27.96 (t), 22.55 (t), 13.93 (q), 12.87 (q), 10.62 (q); MS (*m*/*z*, rel intensity) 142 (M$^+$, 59), 127 (43), 85 (100), 57 (52); HRMS calcd for $C_9H_{18}O$ 142.1358, found 142.1355.

(13) Corey, E. J.; Snider, B. B. *Tetrahedron Lett.* **1973**, *14*, 3091.

(*E*)-2,2-Dimethyl-4-methyl-4-hexen-3-ol (6d): yield 25%; IR 3426, 1646 cm^{-1}; ^1H NMR (400 MHz) δ 5.41 (q, $J = 6.8$ Hz, 1H), 3.7 (s, 1H), 1.63 (s, 3H), 1.59 (d, $J = 6.8$ Hz, 3H), 0.885 (s, 9H); ^{13}C NMR δ 136.88 (s), 122.51 (d), 85.11 (d), 35.46 (s), 26.63 (q), 13.94 (q), 13.00 (q); MS (*m*/*z*, rel intensity) 142 (M^+, 4), 109 (11), 85 (100), 71 (31), 57 (40); HRMS calcd for $C_9H_{18}O$ 142.1358, found 142.1370.

(*E*)-3-Methyl-3-penten-2-ol (6e): yield 72%; IR 3359 cm^{-1}; ^1H NMR δ 5.45 (q, $J = 6.9$ Hz, 1H), 4.17 (q, $J = 6.4$ Hz, 1H), 1.58 (s, 3H), 1.57. (d, $J = 6.9$ Hz, 3H), 1.21 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR δ 139.18 (s), 118.95 (d), 73.18 (d), 21.36 (q), 12.81 (q), 10.92 (q); MS (*m*/*z*, rel intensity) 100 (M^+, 74), 99 (12), 85 (20), 67 (31), 57 (100), 56 (95); HRMS calcd for $C_6H_{12}O$ 100.0888, found 100.0892.

Typical Procedure for the Preparation of Chiral Allylic Methyl Ethers. A 100 mL round-bottomed flask was charged with NaH (60% in mineral oil, 1.05 g, 26.3 mmol) and prewashed with hexanes (3 × 15 mL) and tetrahydrofuran (30 mL). The flask was cooled on an ice−water bath with stirring, and allylic alcohol **1a** (2.92 g, 20.6 mmol) in tetrahydrofuran (20 mL) was slowly added. The mixture was stirred at 25 °C for 10 min, and then methyl iodide (1.6 mL, 25.5 mmol) was added. The resulting mixture was stirred at 25 °C for 5 h and quenched with the addition of water (15 mL) at 0 °C. The aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with ethyl acetate−hexane (1:30) to give **1f** (2.85 g, 18.3 mmol, 89%).

4-Methoxy-2-methyl-2-octene (1f): IR 1676 cm^{-1}; ^1H NMR δ 4.97 (d, $J = 9.3$ Hz, 1H), 3.79 (dt, $J = 9.3$, 6.7 Hz, 1H), 3.18 (s, 3H), 1.73 (s, 3H), 1.65 (s, 3H), 1.60−1.52 (m, 1H), 1.45−1.20 (m, 5H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 135.62 (s), 126.33 (d), 77.44 (d), 55.49 (q), 35.35 (t), 27.53 (t), 25.81 (q), 22.74 (t), 18.24 (q), 14.01 (q); MS (*m*/*z*, rel intensity) 156 (M^+, 3), 141 (14), 99 (100), 95 (11), 72 (11), 69 (25), 67 (16); HRMS calcd for $C_{10}H_{20}O$ 156.1514, found 156.1510.

4-Methoxy-2,5,5-trimethyl-2-hexene (1g): yield 65%; IR 1673 cm^{-1}; ^1H NMR δ 5.03 (d, $J = 9.7$ Hz, 1H), 3.40 (d, $J = 9.7$ Hz, 1H), 3.18 (s, 3H), 1.76 (s, 3H), 1.65 (s, 3H) 0.84 (s, 9H); ^{13}C NMR δ 136.49 (s), 123.32 (d), 85.25 (d), 56.30 (q), 35.28 (s), 26.09 (q), 25.94 (q), 18.41 (q); MS (*m*/*z*, rel intensity) 155 ($M^+ - 1$), 109 (23), 99 (100), 83 (20), 67 (43), 55 (36); HRMS calcd for $C_{10}H_{19}O$ ($M^+ - 1$) 155.1436, found 155.1438.

(*E*)-3-Methyl-4-methoxy-2-octene (6f): yield 67%; IR 1670 cm^{-1}; ^1H NMR δ 5.38 (q, $J = 6.6$ Hz, 1H), 3.36 (t, $J = 6.9$ Hz, 1H), 3.13 (s, 3H), 1.61 (d, $J = 6.6$ Hz, 3H), 1.58∼1.04 (m, 6H), 1.48 (s, 3H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 135.16 (s), 122.68 (d), 87.64 (d), 55.56 (q), 33.21 (t), 28.10 (t), 22.64 (t), 14.01 (q), 12.94 (q), 9.92 (q); MS (*m*/*z*, rel intensity) 156 (M^+, 3), 124 (2), 99 (100), 69 (4); HRMS calcd for $C_{10}H_{20}O$ 156.1514, found 156.1517.

(*E*)-2,2-Dimethyl-3-methoxy-4-methyl-4-hexene (6g): yield 69%; IR 1655 cm^{-1}; ^1H NMR (400 MHz) δ 5.34 (q, $J = 6.8$ Hz, 1H), 3.13 (s, 3H), 3.05 (s, 1H), 1.61 (d, $J = 6.8$ Hz, 3H), 1.54 (s, 3H), 0.85 (s, 9H); ^{13}C NMR (400 MHz) δ 134.15 (s), 124.35 (d), 95.14 (d), 56.57 (q), 35.22 (s), 27.17 (q), 13.08 (q), 12.89 (q); HRMS calcd for $C_{10}H_{20}O$ 156.1515, found 156.1523.

Typical Procedure for the Preparation of Chiral Allylic Acetates. To a 25 mL round-bottomed flask charged with **1a** (0.80 g, 5.63 mmol), 4-(*N*,*N*-dimethylamino)pyridine (80 mg), and dichloromethane (10 mL) were added triethylamine (1.2 mL, 8.66 mmol) and acetic anhydride (0.85 mL, 9.0 mmol). The mixture was stirred at 25 °C for 12 h, and then the mixture was quenched with the addition of 1 N HCl (10 mL) at 0 °C. The aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with 1 N HCl (2 × 5 mL) and brine (3 × 5 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with ethyl acetate−hexane (1:30) to give **1h** (0.88 g, 4.82 mmol, 86%).

4-Acetoxy-2-methyl-2-octene (1h): IR 1735, 1676 cm^{-1}; ^1H NMR δ 5.44 (dt, $J = 8.0$, 6.8 Hz, 1H), 5.07 (d, $J = 8.0$ Hz, 1H), 1.99 (s, 3H), 1.70 (s, 6H), 1.66∼1.57 (m, 1H), 1.51∼1.41 (m, 1H), 1.33∼1.17 (m, 4H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 170.26 (s), 136.76 (s), 123.91 (d), 71.52 (d), 34.59 (t), 27.19 (t), 25.60 (q), 22.43 (t), 21.18 (q), 18.28 (q), 13.85 (q); MS (*m*/*z*, rel intensity %) 184 (M^+, 7), 142(74), 127 (82), 109 (56), 95 (79), 85 (100), 69 (64); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1471.

4-Acetoxy-2,5,5-trimethyl-2-hexene (1i): yield 90%; IR 1735 cm^{-1}; ^1H NMR δ 5.22 (d, $J = 9.9$ Hz, 1H), 5.10 (d, $J = 9.9$ Hz, 1H), 2.00 (s, 3H), 1.72 (s, 3H), 1.71 (s, 3H), 0.86 (s, 9H); ^{13}C NMR δ 170.25 (s), 137.60 (s), 120.74 (d), 77.85 (d), 34.80 (s), 25.87 (q), 25.61 (q), 21.02 (q), 18.43 (q); MS (*m*/*z*, rel intensity) 184 (M^+, 3), 127 (90), 109 (38), 85 (100), 68 (30), 57 (8), 43 (11); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1475.

(*E*)-4-Acetoxy-3-methyl-2-octene (6h): yield 77%; IR 1738 cm^{-1}; ^1H NMR δ 5.48 (q, $J = 6.6$ Hz, 1H), 5.08 (t, $J = 7.0$ Hz, 1H), 1.99 (s, 3H), 1.50∼1.61 (m, 2H), 1.59 (d, $J = 6.6$ Hz. 3H), 1.56 (s, 3H), 1.16−1.31 (m, 4H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR δ 170.42 (s), 133.70 (s), 122.77 (d), 79.61 (d), 32.18 (t), 27.65 (t), 22.41 (t), 21.30 (q), 13.93 (q), 12.99 (q), 11.26 (q); MS (*m*/*z*, rel intensity) 184 (M^+, 3), 142 (93), 124 (87), 109 (42), 85 (100), 67 (45); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1456.

(*E*)-3-Acetoxy-2,2-dimethyl-4-methyl-4-hexene (6i): yield 78%; IR 1740 cm^{-1}; ^1H NMR δ 5.42 (q, $J = 6.4$ Hz, 1H), 4.70 (s, 1H), 2.02 (s, 3H), 1.59 (s, 3H), 1.57 (d, $J = 6.4$ Hz, 3H), 0.87 (s, 9H); ^{13}C NMR δ 170.26 (s), 132.79 (s), 123.86 (d), 85.50 (d), 34.03 (s), 26.55 (q), 21.03 (q), 14.31 (q), 13.02 (q); MS (*m*/*z*, rel intensity) 184 (M^+, 3), 142 (10), 127 (82), 109 (24), 85 (100), 57 (16); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1472.

Representative Experimental Procedure for the Reaction of PTAD with Chiral Allylic Alcohols, Ethers, and Acetates. At −78 °C, to a flask (25 mL) containing allylic alcohol **1a** (0.42 g, 2.96 mmol) in dichloromethane (6 mL) was slowly added a dichloromethane solution (11 mL) of PTAD (0.483 g, 2.76 mmol). After being stirred at −78 °C for 1 h, the reaction mixture was allowed to warm to 25 °C until the red color of PTAD faded. The mixture was concentrated in vacuo, and an ^1H NMR spectrum of the residue was taken to determine the diastereomeric ratio. The residue was purified on silica gel eluting with ethanol and chloroform (1:40) to give **2a** and **3a**.

Under similar reaction conditions, compounds **1** gave compounds **2** and **3** as the reaction products and compounds **6** gave compounds **7** and **8** as the reaction products. Their yields and ratios are summarized in the text.

(3*S,4*S**)-2-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-octen-4-ol (2a):** IR 3485, 1771, 1696 cm^{-1}; ^1H NMR δ 8.25 (br, 1H), 7.52−7.30 (m, 5H), 5.10 (s, 1H), 5.08 (s, 1H), 4.48 (d, $J = 4.5$ Hz, 1H), 4.17−4.10 (m, 1H), 2.61 (br, 1H), 1.77 (s, 3H), 1.58−1.25 (m, 6H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR δ 152.91 (s), 152.60 (s), 139.80 (s), 131.25 (s), 128.96 (d), 128.11 (d), 125.61 (d), 115.77 (t), 70.13 (d), 64.29 (d), 34.00 (t), 27.61 (t), 22.40 (t), 21.12 (q), 13.89 (q); MS (*m*/*z*, rel intensity) 317 (M^+, 1), 231 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1739, found 317.1753. Anal. Calcd for $C_{17}H_{23}N_3O_3$: C, 64.33; H, 7.30; N, 13.24. Found: C, 64.31; H, 7.36; N, 13.21.

(3*R,4*S**)-2-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-octen-4-ol (3a):** IR 3440, 1766, 1697 cm^{-1}; ^1H NMR δ 7.50−7.32 (m, 5H), 5.13 (s, 2H), 4.44 (d, $J = 4.8$ Hz, 1H), 4.12 (td, $J = 5.1$, 4.8 Hz, 1H), 1.86 (s, 3H), 1.55−1.23 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR δ 152.62 (s), 151.61 (s), 139.21 (s), 131.23 (s), 29.12 (d), 128.28 (d), 125.62 (d), 117.86 (t), 72.37 (d), 64.63 (d), 33.72 (t), 27.89 (t), 22.52 (t), 22.11 (q), 13.93 (q); MS (*m*/*z*, rel intensity) 317 (M^+, 0.4), 231 (100).

(3*S,4*S**)-2,5,5-Trimethyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexen-4-ol (2b):** IR 3374, 1768, 1698 cm^{-1}; ^1H NMR δ 8.20 (br, 1H), 7.55−7.30 (m, 5H), 5.16 (s, 1H), 5.10 (s, 1H), 4.88 (s, 1H), 3.82 (s, 1H), 1.76 (s, 3H), 0.99 (s, 9H); ^{13}C NMR δ 152.42 (s), 151.42 (s), 141.40 (s), 131.45 (s), 129.08 (d), 128.10 (d), 125.54 (d), 115.26 (t), 78.82 (d), 57.30 (d), 35.37 (s), 25.91 (q), 21.33 (q); MS (*m*/*z*, rel intensity) 317

(M^+, 3), 231 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1739, found 317.1745. Anal. Calcd for $C_{17}H_{23}N_3O_3$: C, 64.33; H, 7.30; N, 13.24. Found: C, 64.45; H, 7.29; N, 13.06.

(3*R,4*S**)-2,5,5-Trimethyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexen-4-ol (3b):** IR 3464, 1763, 1694 cm^{-1}; ^1H NMR δ 8.55 (br, 1H), 7.52−7.28 (m, 5H), 5.21 (s, 1H), 5.08 (s, 1H), 4.75 (d, J = 4.1 Hz, 1H), 3.83 (d, J = 4.1 Hz, 1H), 2.54 (br, 1H), 1.96 (s, 3H), 1.00 (s, 9H); ^{13}C NMR δ 152.34 (s), 150.67 (s), 140.70 (s), 131.20 (s), 129.03 (d), 128.16 (d), 125.52 (d), 118.87 (t), 80.00 (d), 61.62 (d), 35.14 (s), 26.17 (q), 23.30 (q); MS (*m*/*z*, rel intensity) 318 ($M^+ + 1$, 2), 230 (91), 119 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1739, found 317.1732.

(2*S,3*S**)-4-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-4-penten-2-ol (2c):** IR 3239, 1766, 1696 cm^{-1}; ^1H NMR δ 8.70 (br, 1H), 7.50−7.31 (m, 5H), 5.04 (s, 1H), 5.02 (s, 1H), 4.34 (d, J = 6.0 Hz, 1H), 4.25 (qd, J = 6.1, 6.0 Hz, 1H), 3.19 (br, 1H), 1.72 (s, 3H), 1.22 (d, J = 6.1 Hz, 3H); ^{13}C NMR δ 153.05 (s), 152.85 (s), 193.84 (s), 131.29 (s), 129,07 (d), 128.23 (d), 125.70 (d), 116.01 (t), 66.30 (d), 65.90 (d), 21.11 (q), 20.83 (q); MS (*m*/*z*, rel intensity) 275 (M^+, 2), 231 (100); HRMS calcd for $C_{14}H_{17}N_3O_3$ 275.1270, found 275.1254. Anal. Calcd for $C_{14}H_{17}N_3O_3$: C, 61.08; H, 6.22; N, 15.26. Found: C, 61.07; H, 6.29; N, 15.24.

(2*S,3*R**)-4-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-4-penten-2-ol (3c):** IR 3440, 1766, 1697 cm^{-1}; ^1H NMR δ 8.62 (br, 1H), 7.50−7.34 (m, 5H), 5.15 (s, 1H), 5.12 (s, 1H), 4.40−4.30 (m, 2H), 2.60 (br, 1H), 1.86 (s, 3H), 1.26 (d, J = 5.9 Hz, 3H); ^{13}C NMR δ 152.68 (s), 151.71 (s), 139.03 (s), 131.11 (s), 129.14 (d), 128.36 (d), 125.25 (d), 117.70 (t), 67.74 (d), 65.87 (d), 21.87 (q), 20.15 (q); MS (*m*/*z*, rel intensity) 275 (M^+, 2), 231 (100).

(3*S,4*S**)-2-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1,6-heptadien-4-ol (2d):** IR 3462, 1768, 1697 cm^{-1}; ^1H NMR δ 8.15 (br, 1H), 7.55−7.30 (m, 5H), 5.87−5.73 (m, 1H), 5.20 (s, 1H), 5.16−5.15 (m, 1H), 5.12 (s, 2H), 4.53 (d, J = 4.1 Hz, 1H), 4.23−4.16 (m, 1H), 2.64 (br, 1H), 2.44−2.22 (m, 2H), 1.76 (s, 3H); ^{13}C NMR δ 152.94 (s), 152.74 (s), 139.63 (s), 133.19 (d), 131.29 (s), 129.03 (d), 128.17 (d), 125.62 (d), 119.21 (t), 115.99 (t), 69.59 (d), 63.22 (d), 38.97 (t), 21.18 (q); MS (*m*/*z*, rel intensity) 301 (M^+, 2), 231 (44), 41(100); HRMS calcd for $C_{16}H_{19}N_3O_3$ 301.1426, found 301.1418. Anal. Calcd for $C_{16}H_{19}N_3O_3$: C, 13.94; H, 63.70; N, 6.36. Found: C, 13.92; H, 63.70; N, 6.42.

(3*R,4*S**)-2-Methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1,6-heptadien-4-ol (3d):** IR 3440, 1765, 1657 cm^{-1}; ^1H NMR δ 8.05 (br, 1H), 7.55−7.30 (m, 5H), 5.87−5.72 (m, 1H), 5.24 (s, 1H), 5.22 (s, 1H), 5.20 (s, 1H), 5.16 (s, 1H), 4.53 (d, J = 4.3 Hz, 1H), 4.24−4.17 (m, 1H), 2.42−2.24 (m, 2H), 1.90 (s, 3H); ^{13}C NMR δ 152.65 (s), 151.53 (s), 138.84 (s), 133.55 (d), 131.14 (s), 129.10 (d), 128.28 (d), 125.59 (d), 119.01 (t), 118.14 (t), 71.01 (d), 64.00 (d), 38.49 (t), 21.81 (q); MS (*m*/*z*, rel intensity) 301 (M^+, 11), 231 (100).

(1*S,2*S**)-3-Methyl-1-phenyl-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-3-buten-1-ol (2e):** IR 3440, 1766, 1697 cm^{-1}; ^1H NMR δ 7.45−7.25 (m, 10H), 5.28 (d, J = 5.5 Hz, 1H), 5.17 (s, 1H), 5.27 (s, 1H), 4.81 (d, J = 5.5 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.51 (s), 152.56 (s), 141.99 (s), 139.48 (s), 131.97 (s), 128.66 (d), 127.89 (d), 127.53 (d), 127.34 (d), 127.14 (d), 125.80 (d), 116.19 (t), 70.92 (d), 66.41 (d), 21.45 (q); MS (*m*/*z*, rel intensity) 337 (M^+, 4), 320 (46), 231 (100); HRMS calcd for $C_{19}H_{19}N_3O_3$ 337.1426, found 337.1418. Anal. Calcd for $C_{19}H_{19}N_3O_3$: C, 67.64; H, 5.68; N, 12.45. Found: C, 67.12; H, 5.93; N, 12.12.

(1*S,2*R**)-3-Methyl-1-phenyl-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-3-buten-1-ol (3e):** IR 3477, 1769, 1692 cm^{-1}; ^1H NMR (CD_3OD) δ 7.48−7.42 (m, 2H), 7.42−7.30 (m, 6H), 7.05−6.95 (m, 2H), 5.40 (s, 1H), 5.28 (s, 1H), 5.16 (d, J = 9.8 Hz, 1H), 4.75 (d, J = 9.8 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR-(100 MHz, DMSO-d_6) δ 151.43 (s), 151.25 (s), 142.32 (s), 140.21 (s), 131.42 (s), 128.53 (d), 127.61 (d), 127.54 (d), 127.36 (d), 127.05 (d), 125.65 (d), 116.14 (t), 70.54 (d), 64.92 (d), 20.75 (q); MS (FAB, *m*/*z*, rel intensity) 338 [$(M + 1)^+$, 37], 320 (78), 230 (85), 178 (100).

(3*S,4*S**)-2-Methyl-4-methoxy-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-2-octene (2f):** IR 3200, 1771, 1704 cm^{-1}; ^1H NMR δ 7.55−7.28 (m, 5H), 5.09 (s, 1H), 5.02 (s, 1H), 4.64 (d, J = 2.1 Hz, 1H), 3.73−3.68 (m, 1H), 3.39 (s, 3H), 1.82 (s, 3H), 1.80−1.23 (m, 6H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 152.26 (s), 152.20 (s), 140.17 (s), 131.57 (s), 129.00 (d), 127.96 (d), 125.50 (d), 115.04 (t), 80.74 (d), 60.30 (d), 57.47 (q), 30.09 (t), 27.38 (t), 22.73 (t), 21.33 (q), 13.89 (q); MS (*m*/*z*, rel intensity) 331 (M^+, 40), 231 (87), 101 (100); HRMS calcd for $C_{18}H_{25}N_3O_3$ 331.1896, found 331.1904.

(3*R,4*S**)-2-Methyl-4-methoxy-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-2-octene (3f):** IR 3184, 1770, 1700 cm^{-1}; ^1H NMR δ 7.88 (br, 1H), 7.55−7.26 (m, 5H), 5.19 (s, 1H), 5.11 (s, 1H), 4.76 (d, J = 4.5 Hz, 1H), 3.67−3.60 (m, 1H), 3.39 (s, 3H), 1.84 (s, 3H), 1.74−1.68 (m, 1H), 1.57−1.49 (m, 1H), 1.37−1.29 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 152.63 (s), 151.68 (s), 138.70 (s), 131.41 (s), 128.93 (d), 127.97 (d), 125.44 (d), 117.91 (t), 82.60 (d), 61.24 (d), 57.23 (q), 29.68 (t), 27.74 (t), 22.73 (t), 22.05 (q), 13.86 (q); MS (*m*/*z*, rel intensity) 331 (M^+, 16), 231 (89), 101 (100).

(3*S,4*S**)-2,5,5-Trimethyl-4-methoxy-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexene (2g):** IR 3226, 1770, 1703 cm^{-1}; ^1H NMR δ 8.31 (br, 1H), 7.54−7.30 (m, 5H), 5.14 (s, 1H), 5.09 (s, 1H), 4.89 (d, J = 1.0 Hz, 1H), 3.58 (s, 3H), 3.39 (d, J = 1.0 Hz, 1H), 1.85 (s, 3H), 0.99 (s, 9H); ^{13}C NMR δ 151.85 (s), 150.58 (s), 141.64 (s), 131.45 (s), 128.81 (d), 127.76 (d), 125.36 (d), 114.08 (t), 88.98 (d), 62.50 (q), 56.84 (d), 36.32 (s), 26.36 (q), 21.56 (q); MS (*m*/*z*, rel intensity) 331 (M^+, 8), 231 (41), 101 (100); HRMS calcd for $C_{18}H_{25}N_3O_3$ 331.1896, found 331.1884. Anal. Calcd for $C_{18}H_{25}N_3O_3$: C, 65.23; H, 7.30; N, 12.68. Found: C, 65.32; H, 7.64; N, 12.69.

(3*R,4*S**)-2,5,5-Trimethyl-4-methoxy-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexene (3g):** IR 3121, 1768, 1698 cm^{-1}; ^1H NMR δ 7.55−7.30 (m, 5H), 5.24 (s, 1H), 5.07 (s, 1H), 4.74 (d, J = 5.5 Hz, 1H), 3.45 (s, 3H), 3.34 (d, J = 5.5 Hz, 1H), 1.89 (s, 3H), 0.98 (s, 9H); ^{13}C NMR δ 152.74 (s), 150.98 (s), 140.88 (s), 131.34 (s), 129.02 (d), 128.12 (d), 125.39 (d), 117.44 (t), 90.63 (d), 62.19 (q), 60.79 (d), 36.46 (s), 26.77 (q), 23.46 (q); MS (*m*/*z*, rel intensity) 331 (M^+, 4), 230 (3), 101 (100).

(3*S,4*S**)-4-Acetoxy-2-methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-octene (2h):** IR 3216, 1776, 1716, 1696 cm^{-1}; ^1H NMR δ 7.85 (br, 1H), 7.50−7.30 (m, 5H), 5.28−5.20 (m, 1H), 5.08 (s, 2H), 4.60 (d, J = 8.2 Hz, 1H), 2.07 (s, 3H), 1.81 (s, 3H), 1.65−1.57 (m, 2H), 1.34−1.27 (m, 4H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 171.54 (s), 153.58 (s), 153.45 (s), 138.76 (s), 131.23 (s), 128.98 (d), 128.12 (d), 125.39 (d), 117.20 (t), 71.52 (d), 62.91 (d), 31.22 (t), 27.25 (t), 22.23 (t), 21.43 (q), 20.90 (q), 13.79 (q); MS (*m*/*z*, rel intensity) 359 (M^+, 4), 299 (19), 230 (39), 119 (100); HRMS calcd for $C_{19}H_{25}N_3O_4$ 359.1845, found 359.1842. Anal. Calcd for $C_{19}H_{25}N_3O_4$: C, 63.49; H, 7.01; N, 11.69. Found: C, 63.42; H, 7.06; N, 11.62.

(3*R,4*S**)-4-Acetoxy-2-methyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-octene (3h):** IR 3145, 1776, 1712, 1696 cm^{-1}; ^1H NMR δ 7.51−7.33 (m, 5H), 5.46−5.38 (m, 1H), 5.15 (s, 1H), 5.13 (s, 1H), 4.68 (d, J = 6.8 Hz, 1H), 2.04 (s, 3H), 1.83 (s, 3H), 1.68−1.50 (m, 2H), 1.45−1.20 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ 170.77 (s), 153.40 (s), 152.39 (s), 138.39 (s), 131.17 (s), 129.06 (d), 128.22 (d), 125.50 (d), 117.02 (t), 71.60 (d), 62.35 (d), 31.19 (t), 27.25 (t), 22.40 (t), 21.60 (q), 20.96 (q), 13.84 (q); MS (*m*/*z*, rel intensity) 359 (M^+, 5), 299 (41), 230 (100).

(3*S,4*S**)-4-Acetoxy-2,5,5-trimethyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexene (2i):** IR 3232, 1768, 1745, 1705 cm^{-1}; ^1H NMR δ 8.38 (br, 1H), 7.50−7.28 (m, 5H), 5.20 (d, J = 3.9 Hz, 1H), 5.15 (s, 1H), 5.04 (s, 1H), 4.95 (d, J = 3.9 Hz, 1H), 1.99 (s, 3H), 1.76 (s, 3H), 0.97 (s, 9H); ^{13}C NMR δ 170.49 (s), 152.96 (s), 152.14 (s), 140.17 (s), 131.25 (s), 128.99 (d), 128.16 (d), 125.44 (d), 115.90 (t), 77.27 (d), 58.56 (d), 35.31 (s), 26.36 (q), 21.65 (q), 20.67 (q); MS (*m*/*z*, rel intensity) 359 (M^+, 8), 299 (37), 230 (100); HRMS calcd for $C_{19}H_{25}N_3O_4$ 359.1845, found 359.1846. Anal. Calcd for $C_{19}H_{25}N_3O_4$: C, 63.49; H, 7.01; N, 11.69. Found: C, 63.30; H, 7.09; N, 11.69.

(3*R,4*S**)-4-Acetoxy-2,5,5-trimethyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-1-hexene (3i):** IR 3168, 1768, 1711, 1688 cm^{-1}; ^1H NMR δ 7.53−7.30 (m, 5H), 5.16 (s, 1H), 5.08 (s, 1H), 5.06 (d, J = 5.5 Hz, 1H), 4.93 (d, J = 5.5 Hz, 1H),

2.09 (s, 3H), 1.84 (s, 3H), 1.01 (s, 9H); ^{13}C NMR δ 171.43 (s), 152.38 (s), 151.12 (s), 139.65 (s), 131.24 (s), 128.94 (d), 128.00 (d), 125.45 (d), 116.90 (t), 77.60 (d), 59.07 (d), 34.96 (s), 26.15 (q), 22.62 (q), 20.84 (q); MS (*m*/*z*, rel intensity) 359 (M^+, 6), 299 (34), 230 (100).

(1*R,3*R**)-2-Methylene-1-phenyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-butan-1-ol (7a):** IR 3460, 1764, 1697 cm^{-1}; ^{1}H NMR δ 1.28 (d, J = 6.7 Hz, 3H), 4.64 (q, J = 6.7 Hz, 1H), 5.15 (s, 1H), 5.31 (s, 1H), 5.61 (s, 1H), 7.24−7.47 (m, 10H); ^{13}C NMR δ 14.59 (q), 51.84 (d), 74.22 (d), 114.52 (t), 125.29 (d), 126.53 (d), 127.98 (d), 128.20 (d), 128.45 (d), 129.04 (d), 130.89 (s), 140.85 (s), 147.78 (s), 151.80 (s), 153.70 (s); MS (FAB$^+$, *m*/*z*, rel intensity) 338 (M^+ + 1, 19), 320 (100), 143 (80).

(1*R,3*S**)-2-Methylene-1-phenyl-3-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-butan-1-ol (8a):** ^{1}H NMR (DMSO-d_6) δ 1.29 (d, J = 6.8 Hz, 3H), 3.34 (br, 1H), 4.81 (q, J = 6.8 Hz, 1H), 5.12 (s, 2H), 5.22 (s, 1H), 7.20−7.50 (m 10H); ^{13}C NMR (DMSO-d_6) δ 16.50 (q), 50.97 (d), 73.75 (d), 114.26 (t), 125.96 (d), 126.81 (d), 126.98 (d), 127.63 (d), 127.79 (d), 128.76 (d), 131.90 (s), 142.85 (s), 149.17 (s), 151.57 (s), 152.23 (s); MS (FAB$^+$, *m*/*z*, rel intensity) 338 (M^+ + 1), 320 (7), 143 (100); HRMS calcd for $C_{19}H_{19}N_3O_3$ 337.1426, found 337.143; mp 183 °C.

(2*S,4*R**)-3-Methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-6-hepten-4-ol (7b):** IR 3450, 1765, 1697 cm^{-1}; ^{1}H NMR δ 1.37 (d, J = 6.4 Hz, 3H), 2.22−2.32 (m, 1H), 2.37−2.45 (m, 1H), 4.18 (dd, J = 7.7, 4.5 Hz, 1H), 4.76 (q, J = 6.4 Hz, 1H), 5.10 (d, J = 15.7 Hz, 1H), 5.09 (d, J = 12.4 Hz, 1H), 5.30 (s, 1H), 5.48 (s, 1H),0.6.69−5.82 (m, 1H), 7.33−7.46 (m, 5H); ^{13}C NMR δ 14.55 (q), 40.78 (t), 53.00 (d), 70.61 (d), 114.84 (t), 118.39 (t), 125.38 (d), 128.31 (d), 129.13 (d), 130.98 (s), 133.94 (d), 148.09 (s), 152.49 (s), 154.02 (s); MS (*m*/*z*, rel intensity) 301 (M^+, 10), 177 (100); HRMS calcd for $C_{16}H_{19}O_3N_3$ 301.1426, found 301.1398.

(2*S,4*S**)-3-Methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-6-hepten-4-ol (8b):** IR 3429, 1763, 1691 cm^{-1}; ^{1}H NMR δ 1.43 (d, J = 6.7 Hz, 3H), 1.61 (br, 1H), 2.40−2.49 (m, 2H), 4.26 (t, J = 6.6 Hz, 1H), 4.97 (q, J = 6.7 Hz, 1H), 5.17 (d, J = 16.7 Hz, 1H), 5.16 (d, J = 10.7 Hz, 1H) 5.34 (s, 1H), 5.35 (s, 1H), 5.71−5.80 (m, 1H), 7.33−7.51 (m, 5H); ^{13}C NMR δ 15.71 (q), 39.35 (t), 52.32 (d), 72.70 (d), 117.34 (t), 118.66 (t), 125.49 (d), 128.19 (d), 129.08 (d), 131.19 (s), 133.94 (d), 146.83 (s), 152.41 (s), 153.85 (s); MS (*m*/*z*, rel intensity) 301 (M^+, 100), 177 (67); HRMS calcd for $C_{16}H_{19}N_3O_3$ 301.1426, found 301.1420.

(2*S,4*R**)-3-Methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)octan-4-ol (7c):** IR 3442, 1765, 1697 cm^{-1}; ^{1}H NMR δ 0.87 (t, J = 6.9 Hz, 3H), 1.40 (d, J = 6.5 Hz, 3H), 1.23−1.64 (m, 6H), 4.12 (dd, J = 4.4, 7.7 Hz, 1H), 4.76 (q, J = 6.5 Hz, 1H), 5.27 (s, 1H), 5.49 (s, 1H), 7.35−7.47 (m, 5H); ^{13}C NMR δ 13.93 (q), 14.64 (q), 22.51 (t), 27.83 (t), 36.09 (t), 53.18 (d), 71.65 (d), 114.34 (t), 125.38 (d), 128.37 (d), 129.18 (d), 130.98 (s), 149.20 (s), 152.35 (s), 154.20 (s); MS (*m*/*z*, rel intensity) 317 (M^+, 4), 299 (71), 177 (62), 123 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1739, found 317.1720; mp 147−148 °C. Anal. Calcd for $C_{17}H_{23}N_3O_3$: C, 64.33; H, 7.30; N, 13.24. Found: C, 64.35; H, 7.30; N, 13.26.

(2*S,4*S**)-3-Methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)octan-4-ol (8c):** IR 3443, 1753, 1687 cm^{-1}; ^{1}H NMR δ 0.87 (t, J = 6.9 Hz, 3H), 1.17−1.36 (m, 4H), 1.40 (d, J = 6.9 Hz, 3H), 1.58−1.66 (m, 2H), 4.11 (t, J = 6.9 Hz, 1H), 4.93 (q, J = 6.7 Hz, 1H), 5.25 (s, 2H), 7.33−7.49 (m, 5H); ^{13}C NMR δ 13.96 (q), 16.02 (q), 22.45 (t), 28.05 (t), 34.36 (t), 51.78 (d), 74.35 (d), 116.86 (t), 125.51 (d), 128.14 (d), 129.04 (d), 131.23 (s), 147.44 (s), 152.36 (s), 153.88 (s); MS (*m*/*z*, rel intensity) 317 (M^+, 3), 299 (72), 177 (51), 123 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1739, found 317.1758; mp 130−131 °C.

(2*R,4*S**)-5,5-Dimethyl-3-methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)-hexan-4-ol (7d):** IR 3423, 1767, 1697 cm^{-1}; ^{1}H NMR δ 0.93 (s, 9H), 1.35 (d, J = 6.7 Hz, 3H), 3.88 (s, 1H), 4.74 (q, J = 6.7 Hz, 1H), 5.46 (s, 1H), 5.53 (s, 1H), 7.36−7.49 (m, 5H); ^{13}C NMR δ 13.71 (q), 25.74 (q), 35.84 (s), 55.07 (d), 77.95 (d), 117.22 (t), 125.34 (d), 128.26 (d), 129.09 (d), 130.94 (s), 147.59 (s), 152.54 (s), 154.23 (s); MS (*m*/*z*, rel intensity) 317 (M^+, 6), 299 (63), 178 (90), 123 (100); HRMS calcd for $C_{17}H_{23}N_3O_3$ 317.1740, found 317.1741; mp 173−174 °C. Anal. Calcd for $C_{17}H_{23}N_3O_3$: C, 64.33; H, 7.30; N, 13.24. Found: C, 64.45; H, 7.25; N, 13.01.

(2*S,4*R**)-3-Methylene-4-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)pentan-2-ol (7e):** IR 3425, 1754, 1682 cm^{-1}; ^{1}H NMR δ 1.27 (d, J = 6.4 Hz, 3H), 1.38 (d, J = 6.6 Hz, 3H), 4.26 (q, J = 6.4 Hz, 1H), 4.76 (q, J = 6.6 Hz, 1H), 5.22 (s, 1H), 5.48 (s, 1H), 7.34−7.49 (m, 5H); ^{13}C NMR δ 14.87 (q), 22.63 (q), 53.00 (d), 67.68 (d), 113.49 (t), 125.42 (d), 128.37 (d), 129.16 (d), 130.96 (s), 150.16 (s), 152.35 (s), 154.10 (s); MS (*m*/*z*, rel intensity) 275 (M^+, 8), 257 (100), 177 (65); HRMS calcd for $C_{14}H_{17}N_3O_3$ 275.1270, found 275.1274.

(2*S,4*S**)-3-Methylene-4-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)pentan-2-ol (8e):** ^{1}H NMR δ 1.37 (d, J = 6.5 Hz, 3H), 1.43 (d, J = 6.8 Hz, 3H), 4.39 (q, J = 6.5 Hz, 1H), 5.02 (q, J = 6.8 Hz, 1H), 5.26 (s, 1H), 5.30 (s, 1H), 7.33−7.50 (m, 5H), 8.40 (br, 1H); ^{13}C NMR δ 15.80 (q), 21.19 (q), 52.11 (d), 68.90 (d), 115.95 (t), 125.53 (d), 128.20 (d), 129.08 (d), 131.18 (s), 148.55 (s), 152.23 (s), 153.72 (s); MS (FAB$^+$, *m*/*z*, rel intensity) 276 (M^+ + 1, 90), 258 (100); HRMS calcd for $C_{14}H_{17}N_3O_3$ 275.1270, found 275.1272.

(2*R,4*S**)-3-Methylene-4-methoxy-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)octane (7f):** IR 3412, 1720, 1672 cm^{-1}; ^{1}H NMR δ 0.87 (t, J = 6.4 Hz, 3H), 1.19−1.37 (m, 4H), 1.41 (d, J = 6.8 Hz, 3H), 1.56−1.65 (m, 2H), 3.22 (s, 3H), 3.62 (t, J = 6.5 Hz, 1H), 4.82 (q, J = 6.8 Hz, 1H), 5.36 (s, 1H). 5.37 (s, 1H), 7.33−7.51 (m, 5H); ^{13}C NMR δ 13.81 (q), 15.69 (q), 22.36 (t), 27.68 (t), 33.83 (t), 51.28 (d), 56.30 (q), 83.03 (d), 115.16 (t), 125.18 (d), 127.92 (d), 128.81 (d), 131.13 (s), 145.35 (s), 151.84 (s), 153.50 (s); MS (*m*/*z*, rel intensity) 331 (M^+, 5), 299 (100); HRMS calcd for $C_{18}H_{25}N_3O_3$ 331.1896, found 331.1893.

(2*R,4*S**)-5,5-Dimethyl-3-methylene-4-methoxy-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)hexane (7g):** IR 3139, 1769, 1698 cm^{-1}; ^{1}H NMR δ 0.90 (s, 9H), 1.39 (d, J = 6.8 Hz, 3H), 3.09 (s, 3H), 3.28 (s, 1H), 4.78 (q, J = 6.9 Hz, 1H), 5.36 (s, 1H), 5.47 (s, 1H), 7.34−7.50 (m, 5H), 8.80 (br, 1H); ^{13}C NMR δ 14.76 (q), 25.94 (q), 35.92 (s), 53.71 (d), 56.83 (q), 89.53 (d), 116.46 (t), 125.24 (d), 128.14 (d), 129.02 (d), 131.19 (s), 144.03 (s), 152.17 (s), 153.47 (s); MS (*m*/*z*, rel intensity) 331 (M^+, 4), 299 (65), 123 (100); HRMS calcd for $C_{18}H_{25}N_3O_3$ 331.1896, found 331.1907; mp 134−135 °C. Anal. Calcd for $C_{18}H_{25}N_3O_3$: C, 65.23; H, 7.60; N, 12.68. Found: C, 65.32; H, 7.68; N, 12.67.

(2*S,4*S**)-4-Acetoxy-3-methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)octane (7h):** IR 3390, 1773, 1724 cm^{-1}; ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 3H), 1.44−1.26 (m, 4H), 1.36 (d, J = 6.4 Hz, 3H), 1.58−1.72 (m, 2H), 2.08 (s, 3H), 4.68 (q, J = 6.4 Hz, 1H), 5.03 (dd, J = 3.5, 8.5 Hz, 1H), 5.20 (s, 1H), 5.27 (s, 1H), 7.30−7.52 (m, 5H), 8.19 (br, 1H); ^{13}C NMR δ 13.33 (q), 13.39 (q), 20.52 (q), 21.81 (t), 27.16 (t), 33.35 (t), 52.01 (d), 73.68 (d), 113.07 (t), 124.97 (d), 127.44 (d), 128.44 (d), 131.03 (s), 145.44 (s), 153.08 (s), 153.36 (s), 170.97 (s); MS (*m*/*z*, rel intensity) 359 (M^+, 2), 299 (100); HRMS calcd for $C_{19}H_{25}N_3O_4$ 359.1845, found 359.1841.

(2*S,4*S**)-4-Acetoxy-3-methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)octane (8h):** IR 3412, 1768, 1696, 1648 cm^{-1}; ^{1}H NMR(400 MHz) δ 0.92 (t, J = 7.0 Hz, 3H), 1.40 (d, J = 6.5 Hz, 3H), 1.31−1.48 (m, 4H), 1.63−1.74 (m, 2H), 2.14 (s, 3H), 4.72 (q, J = 6.5 Hz, 1H), 5.06 (dd, J = 2.8, 8.8 Hz, 1H), 5.25 (s, 1H), 5.31 (s, 1H), 7.27−7.54 (m, 5H), 8.16, (br, 1H); ^{13}C NMR δ 13.88 (q), 15.52 (q), 21.05 (q), 22.27 (t), 27.66 (t), 33.34 (t), 51.99 (d), 75.57 (d), 117.43 (t), 125.34 (d), 128.08 (d), 129.04 (d), 131.26 (s), 144.89 (s), 152.11 (s), 153.73 (s), 171.04 (s); MS (*m*/*z*, rel intensity) 359 (M^+, 2), 299 (100), 123 (33); HRMS calcd for $C_{19}H_{25}N_3O_4$ 359.1845, found 359.1845; mp 73−74 °C. Anal. Calcd for $C_{19}H_{25}N_3O_4$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.13; H, 6.75; N, 10.35.

(2*R,4*S**)-4-Acetoxy-5,5-dimethyl-3-methylene-2-(4′-phenyl-1′,2′,4′-triazolidine-3′,5′-dion-1′-yl)hexane (7i):** IR 3362, 1773, 1752 cm^{-1}; ^{1}H NMR δ 1.00 (s, 9H), 1.36 (d, J = 6.6 Hz 3H), 2.09 (s, 3H), 4.87 (s, 1H), 4.89 (q, J = 6.6 Hz, 1H), 5.36 (br s, 1H), 5.45 (s, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.45 (dd, J = 7.8, 8.0 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 8.27 (br s, 1H);

^{13}C NMR(C_6D_6) δ 13.75 (q), 20.47 (q), 26.01 (q), 34.83 (s), 54.64 (d), 80.01 (d), 116.32 (t), 125.71 (d), 127.65 (d), 128.88 (d), 132.72 (s), 145.04 (s), 154.37 (s), 154.63 (s), 171.19 (s); MS (*m*/*z*, rel intensity) 359 (M^+, 13), 299 (62), 123 (100); HRMS calcd for $C_{19}H_{25}N_3O_4$ 359.1845, found 359.1845; mp 140−141 °C. Anal. Calcd for $C_{19}H_{25}N_3O_4$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.15; H, 6.73; N, 10.38.

General Procedure for the Preparation of Acetonides 4 and 5. In a 10 mL round-bottomed flask were charged 2,2-dimethoxypropane (2.0 mL, 12.6 mmol) and *p*-toluenesulfonic acid(16 mg, 0.1 mmol) with compound **2** or compound **3** (1.01 mmol). The mixture was stirred at 25 °C for 18 h and then quenched with saturated sodium carbonate solution (2 mL). The aqueous layer was extracted with ether (2 × 3 mL). The combined organic layers were washed with brine (2 × 3 mL), dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with ethyl acetate−hexane (1:7) to give **4** or **5** in good yield.

(7*S,8*S**)-7-Butyl-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (4a):** yield 92%; IR 2941, 1772, 1717 cm^{-1}; ^{1}H NMR δ 7.48−7.28 (m, 5H), 5.10 (s, 2H), 3.99 (d, J = 9.5 Hz, 1H), 3.90−3.82 (m, 1H), 1.82 (s, 3H), 1.75 (s, 3H), 1.69 (s, 3H), 1.60−1.23 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 151.14 (s), 150.64 (s), 138.72 (s), 131.18 (s), 128.89 (d), 127.93 (d), 125.48 (d), 117.66 (t), 90.49 (s), 70.47 (d), 67.60 (d), 30.51 (t), 27.32 (t), 25.47 (q), 22.35 (t), 21.84 (q), 18.56 (q), 13.90 (q); MS (*m*/*z*, rel intensity) 357 (M^+, 8), 271 (100); HRMS calcd for $C_{20}H_{27}N_3O_3$ 357.2052, found 357.2059; mp 127−128 °C. Anal. Calcd for $C_{20}H_{27}N_3O_3$: C, 67.20; H, 7.61; N, 11.76. Found: C, 67.18; H, 7.54; N, 11.75.

(7*S,8*S**)-7-(1,1-Dimethyethyl)-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]-oxadiazine-1,3-dione (4b):** yield 90%; IR 2952, 1772, 1717, 1595 cm^{-1}; ^{1}H NMR δ 7.47−7.28 (m, 5H), 5.20 (s, 1H), 5.08 (s, 1H), 4.51 (d, J = 9.2 Hz, 1H), 3.74 (d, J = 9.2 Hz, 1H), 1.85 (s, 3H), 1.74 (s, 3H), 1.55 (s, 3H), 0.98 (s, 9H); ^{13}C NMR δ 152.08 (s), 151.13 (s), 140.44 (s), 131.21 (s), 128.85 (d), 127.83 (d), 125.26 (d), 118.01 (t), 92.14 (s), 76.58 (d), 63.40 (d), 34.17 (s), 26.15 (q), 23.20 (q), 22.69 (q), 20.31 (q); MS (*m*/*z*, rel intensity) 357 (M^+, 3), 242 (100), 119 (92); HRMS calcd for $C_{20}H_{27}N_3O_3$ 357.2052, found 357.2059; mp 81−82 °C. Anal. Calcd for $C_{20}H_{27}N_3O_3$: C, 67.20; H, 7.61; N, 11.76. Found: C, 67.22; H, 7.64; N, 11.72.

(7*S,8*S**)-8-(1-Methylethenyl)-5,5,7-trimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (4c):** yield 90%; IR 2987, 1772, 1718, 1600 cm^{-1}; ^{1}H NMR δ 7.50−7.27 (m, 5H), 5.10 (s, 2H), 4.05 (dt, J = 9.5, 6.1 Hz, 1H), 3.87 (d, J = 9.5 Hz, 1H), 1.86 (s, 3H), 1.57 (s, 3H), 1.11 (d, J = 6.1 Hz, 3H); ^{13}C NMR δ 151.11 (s), 150.22 (s), 138.60 (s), 131.08 (s), 128.82 (d), 127.88 (d), 125.45 (d), 117.49 (t), 89.73 (s), 69.02 (d), 66.88 (d), 26.05 (q), 21.38 (q), 18.40 (q), 17.13 (q); MS (*m*/*z*, rel intensity) 315 (M^+, 1), 119 (100); HRMS calcd for $C_{17}H_{21}N_3O_3$ 315.1583, found 315.1581; mp 91−92 °C. Anal. Calcd for $C_{17}H_{21}N_3O_3$: C, 64.74; H, 6.71; N, 13.32. Found: C, 64.73; H, 6.75; N, 13.36.

(7*S,8*S**)-7-(2-Propenyl)-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]-oxadiazine-1,3-dione (4d):** yield 82%; IR 2987, 1772, 1718, 1645, 1600 cm^{-1}; ^{1}H NMR δ 7.48−7.28 (m, 1H), 5.92−5.78 (m, 1H), 5.15−5.07 (m, 4H), 4.06 (d, J = 9.6 Hz, 1H), 4.00−3.93 (m, 1H), 2.44−2.35 (m, 1H), 2.27−2.14 (m, 1H), 1.84 (s, 3H), 1.77 (s, 3H), 1.69 (s, 3H); ^{13}C NMR δ 151.24 (s), 150.57 (s), 138.49 (s), 133.15 (d), 131.16 (s), 128.91 (d), 127.97 (d), 125.50 (d), 117.95 (t), 90.38 (s), 70.15 (d), 66.76 (d), 35.02 (t), 25.57 (q), 21.71 (q), 18.54 (q); MS (*m*/*z*, rel intensity) 341 (M^+, 8), 242 (100), 119 (87); HRMS calcd for $C_{19}H_{23}N_3O_3$ 341.1739, found 341.1732; mp 84−85 °C. Anal. Calcd for $C_{19}H_{23}N_3O_3$: C, 66.84; H, 6.79; N, 12.31. Found: C, 66.84; H, 6.74; N, 12.29.

(7*S,8*S**)-8-(1-Methylethenyl)-5,5-dimethyl-2,7-diphenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (4e):** yield 82%; IR 2992, 1773, 1718, 1599 cm^{-1}; ^{1}H NMR δ 7.52−7.28 (m, 10H), 4.92 (s, 1H), 4.91 (d, J = 9.7 Hz, 1H), 4.71 (s, 1H), 4.22 (d, J = 9.7 Hz, 1H), 1.91 (s, 3H), 1.81 (s, 6H); ^{13}C NMR δ 151.33 (s), 150.39 (s), 137.64 (s), 136.37 (s), 131.07 (s), 128.89 (d), 128.34 (d), 128.00 (d), 127.59 (d), 125.51 (d), 117.59 (t), 90.25 (s), 74.38 (d), 68.49 (d), 26.00 (q), 21.44 (q), 19.22 (q); MS (*m*/*z*, rel intensity) 377 (M^+, 0.4), 319 (100); mp 119−120 °C. Anal. Calcd for $C_{22}H_{23}N_3O_3$: C, 70.01; H, 6.14; N, 11.13. Found: C, 70.04; H, 6.16; N, 11.09.

(7*S,8*R**)-7-Butyl-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (5a):** yield 86%; IR 2831, 1769, 1714, 1643, 1599 cm^{-1}; ^{1}H NMR δ 7.50−7.28 (m, 5H), 5.11 (s, 1H), 5.07 (s, 1H), 4.43 (d, J = 3.7 Hz, 1H), 4.16−4.10 (m, 1H), 1.90 (s, 6H), 1.60 (s, 3H), 1.55−1.29 (m, 6H), 0.90 (d, J = 7.0 Hz, 3H); ^{13}C NMR δ 150.16 (s), 138.42 (s), 131.21 (s), 128.88 (d), 127.87 (d), 125.38 (d), 118.65 (t), 89.64 (s), 70.87 (d), 59.58 (d), 30.86 (t), 27.55 (t), 27.02 (q), 22.36 (t), 21.83 (q), 19.66 (q), 13.87 (q); MS (*m*/*z*, rel intensity) 357 (M^+, 6), 118 (90), 84 (100); HRMS calcd for $C_{20}H_{27}N_3O_3$ 357.2052, found 357.2057; mp 82−83 °C.

(7*S,8*R**)-7-(1,1-Dimethyethyl)-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]-oxadiazine-1,3-dione (5b):** yield 85%; IR 2951, 1768, 1714, 1599 cm^{-1}; ^{1}H NMR δ 7.50−7.28 (m, 5H), 5.16 (s, 5H), 5.04 (s, 1H), 4.62 (d, J = 3.2 Hz, 1H), 3.81 (d, J = 3.2 Hz, 1H), 1.95 (s, 3H), 1.94 (s, 3H), 1.57 (s, 3H), 1.01 (s, 9H); ^{13}C NMR δ 149.97 (s), 149.75 (s), 139.64 (s), 131.28 (s), 128.93 (d), 127.89 (d), 125.42 (d), 119.72 (t), 89.84 (s). 78.99 (d), 58.92 (d), 33.64 (s), 27.14 (q), 25.88 (q), 21.87 (q), 19.27 (q); MS (*m*/*z*, rel intensity) 357 (M^+, 2), 118 (100); HRMS calcd for $C_{20}H_{27}N_3O_3$ 357.2052, found 357.2043; mp 86−87 °C.

(7*S,8*R**)-8-(1-Methylethenyl)-5,5,7-trimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (5c):** yield 85%; IR 2986, 1768, 1714 cm^{-1}; ^{1}H NMR δ 7.50−7.28 (m, 5H), 5.09 (s, 1H), 5.09 (d, J = 1.3 Hz, 1H), 4.40−4.33 (m, 2H), 1.91 (s, 3H), 1.89 (s, 3H), 1.62 (s, 3H), 1.22 (d, J = 6.1 Hz, 3H); ^{13}C NMR δ 150.33 (s), 150.27 (s), 138.35 (s), 131.29 (s), 128.97 (d), 127.97 (d), 125.47 (d), 118.73 (t), 89.67 (s), 66.77 (d), 60.29 (d), 27.14 (q), 21.98 (q), 19.72 (q), 17.30 (q); MS (*m*/*z*, rel intensity) 315 (M^+, 11), 119 (100); HRMS calcd for $C_{17}H_{21}N_3O_3$ 315.1583, found 315.1599; mp 122−123 °C.

(7*S,8*R**)-7-(2-Propenyl)-8-(1-methylethenyl)-5,5-dimethyl-2-phenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (5d):** yield 83%; IR 2961, 1769, 1714, 1642, 1599 cm^{-1}; ^{1}H NMR δ 7.50−7.29 (m, 5H), 5.84−5.70 (m, 1H), 5.17−5.09 (m, 4H), 4.47 (d, J = 3.7 Hz, 1H), 4.20 (td, J = 6.8, 3.7 Hz, 1H), 2.38−2.18 (m, 2H), 1.91 (s, 6H), 1.61 (s, 3H); ^{13}C NMR-(C_6D_6) δ 150.28 (s), 150.25 (s), 138.14 (s), 132.98 (d), 131.23 (s), 128.96 (d), 127.97 (d), 125.44 (d), 119.15 (t), 118.26 (t), 89.80 (s), 70.71 (d), 59.18 (d), 35.63 (t), 27.04 (q), 22.01 (q), 19.66 (q); MS (*m*/*z*, rel intensity) 341 (M^+, 13), 119 (100); HRMS calcd for $C_{19}H_{23}N_3O_3$ 341.1739, found 341.1742; mp 95−96 °C.

(7*S,8*R**)-8-(1-Methylethenyl)-5,5-dimethyl-2,7-diphenylperhydro[1,2,4]triazolo[1,2-*c*][1,3,4]oxadiazine-1,3-dione (5e):** yield 80%; IR 2997, 1769, 1714 cm^{-1}; ^{1}H NMR δ 7.52−7.25 (m, 10H), 5.41 (d, J = 3.9 Hz, 1H), 4.98 (s, 1H), 4.85 (s, 1H), 4.77 (d, J = 3.9 Hz, 1H), 2.07 (s, 3H), 1.72 (s, 3H), 1.55 (s, 3H); ^{13}C NMR δ 150.54 (s), 150.27 (s), 138.32 (s), 136.31 (s), 131.17 (s), 129.03 (d), 128.28 (d), 125.80 (d), 128.09 (d), 128.03 (d), 125.51 (d), 118.27 (t), 90.02 (s), 72.39 (d), 60.21 (q), 27.20 (q), 22.77 (q), 19.57 (q); MS (*m*/*z*, rel intensity) 377 (M^+, 0.7), 319 (58), 128 (100); mp 169−170 °C.

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Supporting Information Available: ^{1}H NMR of new compounds and X-ray crystallographic data of compound **7g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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