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Synthesis of α-Substituted Enoximes with Nucleophiles via Nitrosoallenes

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Supporting Information

ABSTRACT: This paper reports nitrosoallene-mediated synthesis of α-substituted enoximes. Nucleophilic substitution of nitrosoallenes, a novel chemical species prepared from allenyl *N*-hydroxysulfonamides, afforded α-functionalized enoximes. Introduction of various nucleophiles proceeded smoothly to form C−N, C−O, C−S, C−F, and C−C bonds in the presence of azodicarboxylates.

INTRODUCTION

α,β-Unsaturated carbonyl compounds, and especially their imine derivatives (i.e., enimines and enoximes), have found recent attention as highly useful synthons serving as Michael acceptors, Diels−Alder dienophiles, and heterocycle precursors toward bioactive molecules (Figure 1).[1] Moreover, enimine structures are

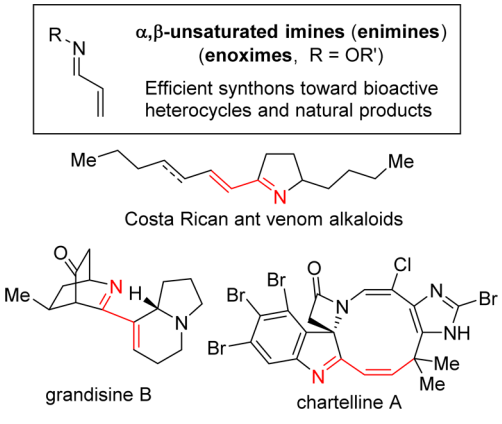
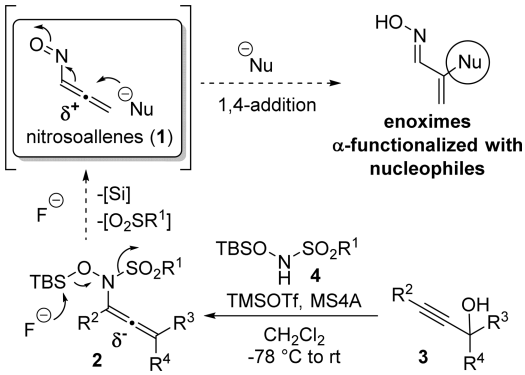


Figure 1. Unsaturated imines.

also found in bioactive natural products.[2] In this context, developing new functionalized enimine and enoxime syntheses is required. Among these syntheses, introducing methods of polar substituents like amines and sulfones to the α-positions of enimines or enoximes could provide the basis for achievement of highly efficient organic syntheses while β-functionalization can be achieved by 1,4-addition.

It is apparent in previous studies that allenamine derivatives could produce enamines substituted with nucleophiles at α-positions in low yields.[3,4] Inspired by these umpolung reactions, we envisioned that nitrosoallenes **1** could be efficient intermediates producing α-functionalized enoximes in a similar manner (Scheme 1).[5] Thus, we anticipated that 1,4-additions of

Scheme 1. New Approach to α-Functionalized Enoximes Using Nitrosoallenes



nucleophiles to **1** would proceed to afford α-functionalized enoximes. The nitroso group is a well-known strong electron-withdrawing substituent, and applications of nitrosoalkenes have been extensively documented.[6,7] However, to the best of our knowledge, no synthetic report of compounds **1** is found, and their chemical reactivity should be explored.[8,9] Additionally, enoximes are efficient precursors for construction of various amino compounds through cascade reactions and for the assembly of functionalized heterocycle cores like pyridines and isoxazolines in agrochemicals and anticancer agents.[10] We herein describe the study of novel chemical species nitrosoallenes and the nucleophilic addition reaction affording α-functionalized enoximes.

RESULTS AND DISCUSSION

Because of the instability of nitroso groups, we selected N-sulfonyl hydroxylamines, which easily dissociate to generate

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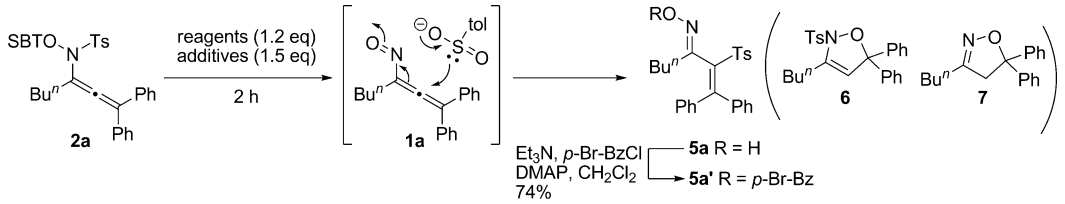
Table 1. Optimization of Reaction Conditions



entry	conditions	yield [%][a]
1	CsF, CH_3CN, rt	73
2	CsF, THF, rt	0
3	TBAF, CH_3CN, rt	42
4	TBAF, THF, rt	72
5	TBAF, THF, 0 °C	64
6	TBAF, AcOH, THF, 0 °C	94
7	TBAF, AcOH, THF, rt	88
8	TBAF, AcOH, CH_3CN, 0 °C	88
9	TBAF, AcOH, Et_2O, 0 °C	81
10	TBAF, AcOH, CPME, 0 °C	85
11	TBAF, AcOH, 4-MTHP, 0 °C	89
12	TBAF, AcOH, 1,4-dioxane, rt	74
13	TBAF, AcOH, DMF, 0 °C	77
14[b]	TBAF (2.5 equiv), AcOH, $CHCl_3$, 0 °C	88
15[b]	TBAF, AcOH, toluene, 0 °C to rt	54 (**6**: 11%)
16	AgF, CH_3CN, rt	0 (**6**: 48%)
17[c,16]	TfOH (2 equiv), CH_2Cl_2–CH_3CN (1:1), 0 °C	0 (**7**: 63%)

[a]Isolated yield. [b]Performed in 3 h. [c]Performed in 1 h. CPME: cyclopentyl methyl ether. 4-MTHP: 4-methyltetrahydropyran.

the corresponding nitroso compounds.[11] Thus, *N*-allenyl-*N*-siloxysulfonamides **2**, which have not been reported as well as nitrosoallenes, were prepared from propargyl alcohols **3** and Fukuyama's reagent[12] or its analogues **4** by applying a modified procedure of Lu's and Wang's protocol (Scheme 1).[3,13a] At this point, although other procedures (isomerization of *N*-siloxyl propargylamides with base or S_N2'-type additions)[13d] were unsuccessful and R^{3-4} positions (Scheme 1) are limited to aromatic rings, it was clear that the unknown reactivity of nitrosoallenes should be revealed. From the outset, we examined the transfer of the sulfone moiety of **2a** to afford α-sulfonyl enoxime **5a**, a series of useful vinyl sulfones,[14] via 1,4-addition of sulfinates[15] to nitrosoallene **1a** (Table 1).

Cesium fluoride[12] in acetonitrile successfully gave the desired **5a** in good yield, whereas the reaction in THF did not because of the insolubility in THF (entries 1–2). Tetrabutylammonium fluoride (TBAF) in acetonitrile afforded **5a** in moderate yield (entry 3). Use of TBAF in THF improved the product yield (entries 4–5), and the conversion to **5a** was significantly improved using acetic acid (AcOH) as an additive (entries 6–7). This finding can be attributed to the reactivity of the sulfinic acids under acidic conditions. TBAF with a large excess of AcOH gave exclusively desilylated product. Reactions in other solvents afforded **5a** in similar yields, whereas dioxane and dimethylformamide gave **5a** in slightly lower yields (entries 8–13). Although chloroform was applicable in this reaction, it required 2.5 equiv of TBAF and longer reaction time (entry 14). Reaction in toluene yielded **5a** in 54% along with 11% of isoxazoline **6** (entry 15). Silver fluoride gave cyclocondensation product **6** exclusively (entry 16).[13b] Trifluoromethanesulfonic acid[16] afforded 2-isoxazoline **7**, probably derived from **6** after the removal of the toluenesulfonyl group. It is noteworthy that the reaction (entry 6) was completed within 10 min. The rapid conversions of nitrosoallenes compared to that of nitrosoalkenes[7,8] and nitrosoketenes[9] showcase the unique reactivity of these novel chemical species. The structures of **5a′**, prepared from **5a**, and **6**, were determined by X-ray crystallographic analyses (see the Supporting Information).

With reaction conditions optimized (Table 1, entry 6), and before examination of the various nucleophiles to be installed, the focus was shifted to the exploration of the substrate scope (Table 2). Electron-donating as well as electron-withdrawing groups on the sulfone moiety were well-tolerated, and the sulfones were successfully transferred to the α-position of the enoximes in excellent yields (entries 1–5). The sterically hindered mesitylenesulfonyl group also afforded **5g** in moderate yield (entry 6). When all substituents on the allenylamides were aryl groups, the 2-isoxazolines **8h–i** were afforded as major products derived from the cyclocondensation of initially generated vinylsulfones **5h–i** probably due to their steric bulkiness. Thus, overall yields of the sulfone-transfer reactions (entries 7–8) were nearly 80%. Moreover, aldoxime **5j** and functionalized alkyl ketoximes **5k–m** were successfully accessed (entries 9–12). Electron-withdrawing as well as electron-rich aromatic substituents of R^3 and R^4 gave **5n–o** in excellent yields (entries 13–14). Unsymmetrical allene **2p** delivered **5p** in excellent yield (entry 15). Since no isomerization of (*E*)- or (*Z*)-**5p** under the same reaction conditions occurred, the excellent (*Z*)-selectivity is presumably attributed to the steric repulsion between the *o*-tolyl group and the BuC(NO) moiety at the late transition state of 1,4-addition. The structure of (*Z*)-**5p** was unambiguously determined by X-ray crystallographic analysis (see the Supporting Information).

Following our mechanistic rationale (Table 1), we speculated that other nucleophiles could be installed and thus examined the α-functionalizations of enoximes with various nucleophilic reagents. However, because of the strong nucleophilicity of the in situ generated sulfinates,[17] formation of undesired vinyl sulfones was inevitable even in the presence of a large excess of

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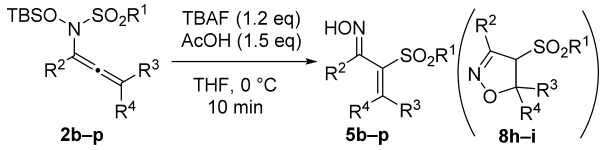
Table 2. Scope of Substrates and Sulfones

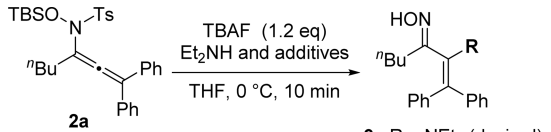


entry	R^1	R^2	R^3	R^4	yield [%][a,b]
1	Ph	*n*-Bu	Ph	Ph	94 (**5b**)
2	4-Cl-C_6H_4	*n*-Bu	Ph	Ph	96 (**5c**)
3	4-F-C_6H_4	*n*-Bu	Ph	Ph	96 (**5d**)
4	4-MeO-C_6H_4	*n*-Bu	Ph	Ph	88 (**5e**)
5	Me	*n*-Bu	Ph	Ph	91 (**5f**)
6[c]	Mes	*n*-Bu	Ph	Ph	63 (**5g**)
7	4-tol	Ph	Ph	Ph	26 (**5h**)
					51 (**8h**)
8	4-tol	4-Br-C_6H_4	Ph	Ph	22 (**5i**)
					53 (**8i**)
9	4-tol	H	Ph	Ph	60 (**5j**)
10	4-tol	*c*-Hex	Ph	Ph	96 (**5k**)
11	4-tol	$PhOCH_2$	Ph	Ph	85 (**5l**)
12	4-tol	TIPSCC-$(CH_2)_5$	Ph	Ph	84 (**5m**)
13	4-tol	*n*-Bu	4-Cl-C_6H_4	4-Cl-C_6H_4	98 (**5n**)
14	4-tol	*n*-Bu	4-MeO-C_6H_4	4-MeO-C_6H_4	91 (**5o**)
15	4-tol	*n*-Bu	2-Me-C_6H_5	Ph	92 (**5p**)[d]

[a]Isolated yield. [b]Obtained as a single isomer on oxime. [c]Performed at rt. [d]*E*/*Z* ratio = 1:19 determined by ^{1}H NMR.

the additional nucleophiles. After extensive examination of trapping reagents[18] of sulfinates and oxidizers to sulfonates[19] (MeI, acrylates, propiolates, DCC, NBS, iodine, oxone, etc.), we were pleased to discover azodicarboxylates[20] as powerful and selective scavenging reagents. In the absence of azodicarboxylates, 1.5 equiv of diethylamine did not give the adduct **9a** (Scheme 2). Excess use of amine could afford the

Scheme 2. Addition of Azodicarboxylate as a Scavenger of Sulfinates



Conditions

A) Et_2NH (1.5 eq), **9a** (0%), **5a** (68%)
B) Et_2NH (5.0 eq), AcOH (6.2 eq), **9a** (49%), **5a** (36%)
C) Et_2NH (as a solvent), **9a** (72%), **5a** (3%)
D) Et_2NH (1.5 eq), DIAD (1.5 eq), **9a** (98%), **5a** (0%)

desired compound, but only in moderate to fair yields even with diethylamine as a solvent. However, in the presence of the discovered scavenger, the desired **9a** was successfully afforded in excellent yield without the undesired tosyl adduct **5a**. The poorly electrophilic 1,1′-(azodicarbonyl)dipiperidine[21] was not successful, whereas the reaction in the presence of diethyl (DEAD), diisopropyl (DIAD), or dimethoxyethyl azodicarboxylate (DMEAD) as sulfinate traps could be performed at 0 °C as well as at lower temperature. At −60 to −78 °C, the peppermint green color of the solution, analogous to that of nitrosoalkynes[6a,22] (see the Supporting Information) and probably emitted by the nitrosoallenes, was maintained for more than 3 h, and the following substitution with additional nucleophiles proceeded successfully. No greenish color could be detected in the absence of the scavenger because of rapid sulfonylation.

We next turned to the α-substitution reaction with additional nucleophiles (Scheme 3).[23] When reactive nucleophiles with the scavengers were used, the trapping step was performed at low temperature prior to the addition of the nucleophile. Under these conditions and nucleophiles, addition of acetic acid was unnecessary. Acyclic as well as cyclic amino groups were successfully introduced to obtain α-amino enoximes **9a**−**e** in good to excellent yields. $TsNH_2$ could be introduced in moderate yield, whereas vinyl imides **9g**−**h** and nitroolefin **9i** were obtained in high yields. Efficient synthon vinyl azide **9j**[24] was afforded in excellent yield as an inseparable mixture with 2*H*-azirine **9j′**. Vinyl azide **9j** was an unstable compound and was slowly converted to azirine **9j′** even under refrigeration. **9j′** could also be selectively prepared in a one-pot reaction in 62% yield. The crystalline **9i** and **9j′** were subjected to X-ray crystallographic analysis (see the Supporting Information). Nitrosoallenes allowed nucleophilic fluorination to give **9k** simply using commercially available weak fluorinating agent TBAF. Although methanol gave **9l** in low yield, the acetoxy moiety was efficiently installed, and a thiol nucleophile produced **9n** in 86% yield. Moreover, introduction of the scavenger facilitates complete transfer of the additional sulfinate to afford **5b** from tosylamide **2a**. The carbon nucleophile cyanide was also successfully installed in excellent yield to give **9o**, which could be applicable in the synthetic derivatives of entacapone for Parkinson's disease and antitumor CC-5079.[25] The absence of isonitriles is probably due to the same as 1,4-addition to enones.[26] Upon completion of the reactions in the presence of azodicarboxylates, formation of sulfonylhydrazides **10a**−**b**[27] was observed. It should be noted that **9d**, **9f**, and **9k**−**m** could not be obtained without the addition of scavengers.

After identification of a suitable sulfinate scavenger allowing reactive nitrosoallenes to remain in the flask, low temperature IR spectra of reaction mixtures were tested for spectroscopic

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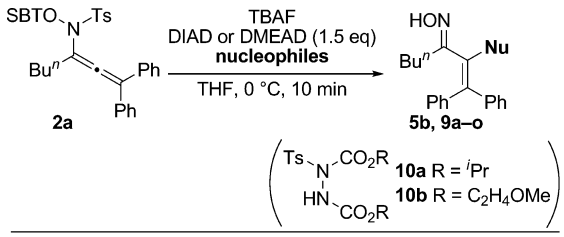
Scheme 3. α-Functionalizations with Additional Nucleophiles



nucleophiles	products	nucleophiles	products
pyrrolidine (2.0 eq)	**9b** (99%)[a]	dicyclohexylammonium nitrite (3.0 eq)	**9i** (90%)[a]
piperidine (1.5 eq)	**9c** (92%)	$TMSN_3$ (1.5 eq)[c]	**9j** (83%)[a,b] (0%)[d]; **9j'** (12%)[a,b] (62%)[d]
morpholine (1.5 eq)	**9d** (70%)	TBAF (10 eq)	**9k** (43%)[a]
L-proline methyl ester HCl salt (3.0 eq)	**9e** (74%)[a]	MeOH (5.0 eq)	**9l** (15%)
$TsNH_2$ (3.0 eq)	**9f** (49%)	AcOH (5.0 eq)[e]	**9m** (52%)
phthalimide (3.0 eq)	**9g** (73%)[a]	2-naphthalenethiol (1.5 eq)	**9n** (83%)[a]
succinimide (3.0 eq)	**9h** (79%)[a]	$NaSO_2Ph$ (3.0 eq)	**5b** (99%)[a]
		TMSCN (1.5 eq)[c]	**9o** (94%)

[a] −78 or −60 °C for 5 min; then the nucleophile was added and the mixture was stirred at 0 °C for 10 min. [b] Determined by ^{1}H NMR. [c] 2.7 equiv of TBAF was used. [d] 0 °C for 10 min, then reflux for 15 min. [e] 4.0 equiv of TBAF was used.

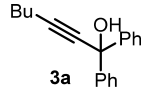
evidence of nitrosoallenes (see the Supporting Information). The spectra showed a new absorption at 1925 cm^{-1}, probably derived from allene stretch (1940 cm^{-1} for **2a**). Unfortunately, the absorption from a nitroso group of **1a** is not clear because of overlap with the absorption peaks from THF, substituents of nitrosoallene, and other reagents at the expected region (1500−1400 cm^{-1}).[6a,9c,28]

In conclusion, we have developed a synthesis of α-functionalized enoximes via novel nitrosoallenes. Various nucleophiles, including carbon nucleophiles, were successfully attached to the α-position of enoximes. We believe that the field of synthetic organic chemistry will find utility for these novel reactive species.[29] Further investigations on developing preparation methods of allenylsulfonamides, the reactivity and physical properties of nitrosoallenes under modified conditions, and their applications are currently in progress.

EXPERIMENTAL SECTION

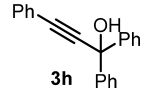
General Information. NMR spectra were recorded at 500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR, and 471 MHz for ^{19}F NMR. Chemical shifts are reported as δ values in ppm and calibrated by residual solvent peaks ($CDCl_3$, δ 7.26 for ^{1}H NMR, δ 77.00 for ^{13}C NMR; DMSO-*d6*, δ 2.50 for ^{1}H NMR, δ 39.52 for ^{13}C NMR), tetramethylsilane (δ 0 for ^{1}H NMR), or hexafluorobenzene (δ −162.0 for ^{19}F NMR). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), br (broad peak), m (complex multiplet). Mass spectra were by EI (70 eV), CI, FAB, or ESI using a double-focusing mass spectrometer. Low temperature IR spectra were measured with a cryostat (CaF_2 windows). The purification of materials which were hard to purify with silica gel was performed using a preparative high-performance liquid chromatography (HPLC) or recycling gel-permeation chromatography (GPC).

Preparation of Propargyl Alcohols (3a, 3h−p). *1,1-Diphenyl-2-hexyn-1-ol (**3a**).*



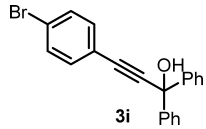
Prepared in accordance with our previous report.[3a,b]

*1,1,2-Triphenyl-2-propyn-1-ol (**3h**).*



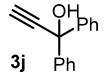
Prepared in accordance with our previous report.[3a,b]

*3-(4-Bromophenyl)-1,1-diphenylprop-2-yn-1-ol (**3i**).*



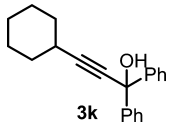
To a stirred solution of 1-bromo-4-ethynylbenzene (481 mg, 2.66 mmol) in THF (25 mL) was added lithium hexamethyldisilazide (1.0 M in THF, 3.8 mL, 3.8 mmol) at 0 °C under a nitrogen atmosphere. After 1 h, benzophenone (456 mg, 2.50 mmol) was added to the mixture in one portion, and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with saturated ammonium chloride aqueous solution. The mixture was extracted with ethyl acetate and was washed with water and brine. The combined organic layers were dried over sodium sulfate and were concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 50/1 to 20/1 to 10/1) to afford propargyl alcohol **3i** (902.1 mg, 99%). Pale yellow oil; R_f value 0.15 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3428, 3059, 3028, 1486, 1449, 1334, 1011, 823, 751, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, 4H, J = 7.5 Hz), 7.45 (d, 2H, J = 8.5 Hz), 7.36−7.33 (m, 6H), 7.27 (t, 2H, J = 7.5 Hz), 2.92 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 133.2, 131.6, 128.3, 127.8, 126.0, 122.9, 121.2, 92.7, 86.1, 74.8; HRMS (ESI) calcd for $C_{21}H_{15}{}^{79}BrNaO$ $[M + Na]^+$ 385.02040, found 385.02063.

*1,1-Diphenyl-2-propyn-1-ol (**3j**).*



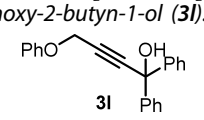
Prepared in accordance with our previous report.[3a,b]

*1,1-Diphenyl-2-cyclohexyl-2-propyn-1-ol (**3k**).*



Prepared in accordance with our previous report.[3a,b]

*1,1-Diphenyl-4-phenoxy-2-butyn-1-ol (**3l**).*



Prepared in accordance with our previous report.[3a,b]

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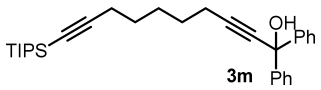
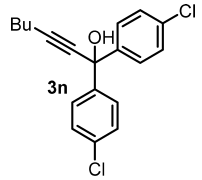
*1,1-Diphenyl-10-(triisopropylsilyl)deca-2,9-diyn-1-ol (**3m**).*



3m

To a stirred solution of 1,8-nonadiyne (602.7 mg, 5.00 mmol) in THF (65 mL) under a nitrogen atmosphere was added *n*-butyllithium (1.63 M in hexane, 5.1 mL, 8.3 mmol) at −78 °C, and the mixture was stirred for 1 h. After warming up to 0 °C, benzophenone (911 mg, 5.00 mmol) was added, and the mixture was stirred at ambient temperature for 3 h. After cooling back to −78 °C, additional *n*-butyllithium (1.63 M in hexane, 5.1 mL, 8.3 mmol) was added and triisopropylsilyl chloride (1.18 mL, 5.50 mmol) was added at 0 °C. Stirred overnight at ambient temperature, reaction mixture was extracted with ether, and the organic layer was washed with water and brine. The combined organic layers were dried over sodium sulfate and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 99/1 to 90/10), followed by recycling HPLC separation to afford propargyl alcohol **3m** (817.0 mg, 35%). Colorless oil; R_f = 0.32 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3462, 3060, 2940, 2864, 2170, 1449, 1329, 1204, 1139, 996 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, 4H, J = 7.0 Hz), 7.31 (dd, 4H, J = 7.5 Hz, J = 7.0 Hz), 7.24 (t, 2H, J = 7.5 Hz), 2.71 (s, 1H), 2.34 (t, 2H, J = 7.0 Hz), 2.25 (t, 2H, J = 7.0 Hz), 1.62 (tt, 2H, J = 7.0, 6.5 Hz), 1.58−1.52 (m, 4H), 1.11−0.98 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 128.1, 127.5, 126.0, 108.9, 88.1, 83.1, 80.2, 74.4, 28.3, 28.13, 28.11, 19.7, 18.9, 18.6, 11.3; HRMS (ESI) calcd for $C_{31}H_{42}OSiNa$ $[M + Na]^+$ 481.29026, found 481.29001.

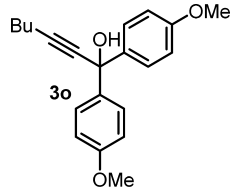
*1,1-Di(4-chlorophenyl)-2-hexyn-1-ol (**3n**).*



3n

Prepared in accordance with our previous report.[3a,b]

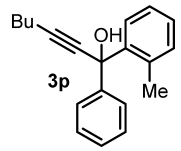
*1,1-Di(4-methoxyphenyl)-2-hexyn-1-ol (**3o**).*



3o

Prepared in accordance with our previous report.[3a,b]

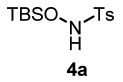
*1-Phenyl-1-(o-tolyl)hept-2-yn-1-ol (**3p**).*



3p

To a stirred solution of 1-hexyne (1.48 mL, 13.0 mmol) in THF (20 mL) a under nitrogen atmosphere was added *n*-butyllithium (1.63 M in hexane, 7.36 mL, 12.0 mmol) at 0 °C. After 1 h, 2-methylbenzophenone (1.81 mL, 10.0 mmol) was added to the mixture, which was stirred overnight at room temperature. The reaction mixture was extracted with ether and was washed with water and brine. The combined organic layers were dried over sodium sulfate and concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 100/1 to 50/1 to 20/1) to afford propargyl alcohol **3p** (2.68 g, 97%). Pale yellow oil; R_f = 0.35 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3545, 3458, 3060, 2957, 2931, 2871, 2228, 1601, 1484, 1448, 1328, 999 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, 1H, J = 8.0 Hz), 7.49 (d, 2H, J = 6.5 Hz), 7.32−7.21 (m, 5H), 7.10 (d, 1H, J = 7.0 Hz), 2.61 (s, 1H), 2.32 (t, 2H, J = 7.0 Hz), 2.08 (s, 3H), 1.56 (tt, 2H, J = 7.5, 7.0 Hz), 1.43 (tq, 2H, J = 7.5, 7.5 Hz), 0.92 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 142.1, 136.2, 131.9, 128.1, 127.7, 127.6, 126.4, 125.8, 125.3, 88.4, 81.9, 73.9, 30.6, 22.0, 20.9, 18.6, 13.6; HRMS (ESI) calcd for $C_{20}H_{22}ONa$ $[M + Na]^+$ 301.15683, found 301.15625.

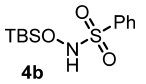
Preparation of Siloxysulfonamides (4a−g). *N-((tert-Butyldimethylsilyl)oxy)-4-toluenesulfonamide (**4a**).*



4a

Prepared in accordance with Fukuyama's report.[12]

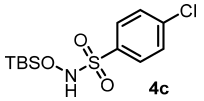
*N-((tert-Butyldimethylsilyl)oxy) Benzenesulfonamide (**4b**).*



4b

To a stirred solution of *O-tert*-butyldimethylsilylhydroxylamine (362.5 mg, 2.46 mmol)[30] in THF (8.5 mL) were added pyridine (0.4 mL, 4.92 mmol) and benzenesulfonyl chloride (0.31 mL, 2.46 mmol) at room temperature. After 24 h, the reaction was quenched with saturated ammonium chloride aqueous solution. The reaction mixture was extracted with ether and was washed with water and brine. The combined organic layers were dried over sodium sulfate and were concentrated *in vacuo*. The resulting residual solid was purified by silica gel column chromatography (hexane/ethyl acetate = 8/1 to 6/1) to afford benzenesulfonamide **4b** (464.2 mg, 66%). White solid; R_f value 0.30 (hexane/ethyl acetate = 7/1); mp 58−60 °C; IR (NaCl, neat) ν_{max} 3188, 2929, 1254, 1167, 834, 787, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, 2H, J = 7.5, 1.0 Hz), 7.65 (dd, 1H, J = 7.5, 1.0 Hz), 7.55 (dd, 2H, J = 7.5, 7.5 Hz), 6.55 (s, 1H), 0.88 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 133.8, 128.8, 25.8, 17.9, −5.5; HRMS (FAB) calcd for $C_{12}H_{22}NO_3SSi$ $[M + H]^+$ 288.1089, found 288.1090.

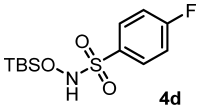
*N-((tert-Butyldimethylsilyl)oxy)-4-chlorobenzenesulfonamide (**4c**).*



4c

4c (685.5 mg, 63%) was obtained from *O-tert*-butyldimethylsilylhydroxylamine (500 mg, 3.39 mmol), pyridine (0.5 mL, 6.78 mmol), and 4-chlorobenzenesulfonyl chloride (716.5 mg, 3.39 mmol) after silica gel column chromatography (hexane/ethyl acetate = 8/1 to 6/1). White solid; R_f value 0.28 (hexane/ethyl acetate = 7/1); mp 98−99 °C; IR (NaCl, neat) ν_{max} 3199, 2929, 1337, 1169, 1092, 831, 767 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, 2H, J = 8.5 Hz), 7.53 (d, 2H, J = 8.5 Hz), 6.50 (s, 1H), 0.89 (s, 9H), 0.19 (s, 6H); ^{13}C NMR(125 MHz, $CDCl_3$) δ 140.5 134.5, 130.3, 129.2, 25.8, 17.9, −5.5; HRMS (FAB) calcd for $C_{12}H_{21}ClNO_3SSi$ $[M + H]^+$ 322.0700, found 322.0694.

*N-((tert-Butyldimethylsilyl)oxy)-4-fluorobenzenesulfonamide (**4d**).*



4d

4d (1.38 g, 65%) was obtained from *O-tert*-butyldimethylsilylhydroxylamine (1.03 g, 6.99 mmol), pyridine (1.1 mL, 14 mmol), and 4-fluorobenzenesulfonyl chloride (1.36 g, 6.99 mmol) after silica gel column chromatography (hexane/ethyl acetate = 5/1) to afford sulfonamide. White solid; R_f value 0.73 (hexane/ethyl acetate = 2/1); mp 106−107 °C; IR (NaCl, neat) ν_{max} 3189, 2929, 1590, 1337, 1166, 837, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95−7.92 (m, 2H), 7.26−7.21 (m, 2H), 6.52 (s, 1H), 0.88 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ; 165.9 (d, $J_{C\text{-}F}$ = 256 Hz), 132.0 (d, $J_{C\text{-}F}$ = 2.5 Hz), 131.7 (d, $J_{C\text{-}F}$ = 9.7 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 25.8, 17.9, −5.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ −103.6; HRMS (ESI) calcd for $C_{12}H_{20}FNO_3SSiNa$ $[M + Na]^+$ 328.08149, found 328.08029.

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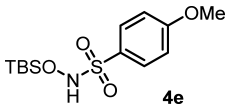
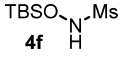
*N-((tert-Butyldimethylsilyl)oxy)-4-methoxybenzenesulfonamide (**4e**).*



4e

To a stirred solution of hydroxylamine hydrochloride (69.5 mg, 1.00 mmol) and *tert*-butyldimethylsilyl chloride (151 mg, 1.00 mmol) in dimethylformamide was added triethylamine (0.65 mL, 4.5 mmol) dropwise at 0 °C. The mixture was warmed up to room temperature and was stirred for 30 min. After cooling the mixture again to 0 °C, 4-methoxybenzenesulfonyl chloride (198 mg, 0.95 mmol) was added; then the mixture was stirred overnight at room temperature. The mixture was extracted with ether and was washed with water, 20% citric acid aqueous solution, and brine. The combined organic layers were dried over sodium sulfate and were concentrated *in vacuo*. The resulting residual solid was purified by recrystallization (hexane/ethyl acetate = 10/1) to afford methoxybenzenesulfonamide **4e** (229.8 mg, 75%). White solid; R_f value 0.22 (hexane/ethyl acetate = 4/1); mp 101−103 °C; IR (NaCl, neat) ν_{max} 3193, 2930, 2859, 1598, 1499, 1329, 1259, 1160, 1093, 1018 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, 2H, J = 8.5 Hz), 7.00 (d, 2H, J = 8.5 Hz), 6.47 (br, 1H), 3.89 (s, 3H), 0.88 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 131.0, 127.5, 114.0, 55.7, 25.8, 17.9, −5.5; HRMS (ESI) calcd for $C_{13}H_{23}NNaO_4SSi$ $[M + Na]^+$ 340.10147, found 340.10054.

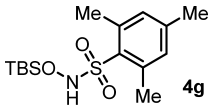
*N-((tert-Butyldimethylsilyl)oxy)methanesulfonamide (**4f**).*



4f

4f (892.9 mg, 66%) was obtained from hydroxylamine hydrochloride (417.1 mg, 6.0 mmol), *tert*-butyldimethylsilyl chloride (904.3 mg, 6.0 mmol), triethylamine (4.2 mL, 30 mmol), and methanesulfonyl chloride (0.47 mL, 6.0 mmol) after silica gel column chromatography (hexane/ethyl acetate = 3/1). White solid; R_f value 0.40 (hexane/ethyl acetate = 3/1); mp 31−32 °C; IR (NaCl, neat) ν_{max} 3210, 2931, 1330, 1254, 1168, 833, 788 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.85 (s, 1H), 3.03 (s, 3H), 0.93 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 35.6, 25.8, 17.9, −5.5; Anal. Calcd for $C_7H_{19}NOSSi$: C. 37.30%; H. 8.50%; N: 6.21%, found: C. 37.31%; H. 8.79%; N: 6.22%.

*N-((tert-Butyldimethylsilyl)oxy)-2,4,6-trimethylbenzenesulfonamide (**4g**).*

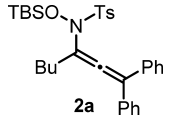


4g

4g (800.6 mg, 49%) was obtained from *O-tert*-butyldimethylsilylhydroxylamine (736.5 mg, 5.0 mmol), pyridine (0.8 mL, 10 mmol), and mesitylsulfonyl chloride (1.09 g, 5.0 mmol) after silica gel column chromatography (hexane/ethyl acetate = 15/1 to 10/1). White solid; R_f value 0.43 (hexane/ethyl acetate = 7/1); mp 99−101 °C; IR (NaCl, neat) ν_{max} 3168, 2930, 1603, 1333, 1254, 1165, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 2H), 6.51 (s, 1H), 2.65 (s, 6H), 2.32 (s, 3H), 0.84 (s, 9H), −0.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 141.2, 131.9, 130.0, 25.8, 23.2, 21.0, 17.9, −5.8; HRMS (ESI) calcd for $C_{15}H_{27}NO_3SSiNa$ $[M + Na]^+$ 352.13786, found 352.13748.

Preparation of Allenamides (2a−p). Allenamides were prepared by modified conditions of Lu and Wang's procedure.[13] To a stirred solution of propargyl alcohol, sulfonamide (1 equiv), and activated molecular sieves 4A (400 g/mol to propargyl alcohol) in dichloromethane (0.1 M) was added trimethylsilyl trifluoromethanesulfonate (0.1 equiv) slowly at −78 °C. The mixture was stirred overnight with gradual warming up to room temperature. The mixture was filtrated by short plug silica gel column chromatography,followed by concentration *in vacuo*. The obtained residue was purified by silica gel column chromatography to afford allenamides.

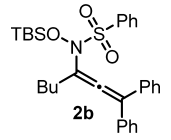
*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-4-methylbenzenesulfonamide (**2a**).*



2a

1067 mg (65%) of product **2a** was obtained from propargyl alcohol **3a** (3.0 mmol, 793.1 mg) with sulfonamide **4a** (904.4 mg, 3.0 mmol), activated molecular sieves 4A (1200 mg), and trimethylsilyl trifluoromethanesulfonate (54 μL, 0.3 mmol) (silica gel column chromatography: hexane/diethyl ether = 40/1 to 20/1), followed by recrystallization (hexane). Pale yellow solid; R_f value 0.45 (hexane/ethyl acetate = 9/1); mp 94−96 °C; IR (NaCl, neat) ν_{max} 3058, 3030, 2956, 2929, 2858, 1940, 1598, 1363, 1173, 829 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.5 Hz), 7.27−7.17 (m, 8H), 6.97 (br, 4H), 2.58 (dd, 2H, J = 8.0 Hz), 2.45 (s, 3H), 1.62 (tt, 2H, J = 8.0, 7.0 Hz), 1.38 (tq, 2H, J = 7.5, 7.0 Hz), 0.91 (t, 3H, J = 7.0 Hz), 0.79 (s, 9H), 0.07 (br, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 144.3, 136.7, 130.1, 130.0, 129.2, 128.8, 127.9, 127.5, 119.4, 117.9, 32.3, 29.8, 25.8, 22.6, 21.8, 17.8, 13.9, −4.8; HRMS (ESI) calcd for $C_{32}H_{41}NO_3SSiNa$ $[M + Na]^+$ 570.24741, found 570.24791.

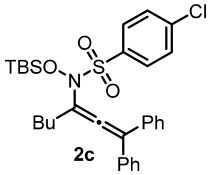
*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-benzenesulfonamide (**2b**).*



2b

238.8 mg (40%) of product **2b** was obtained from propargyl alcohol **3a** (295 mg, 1.11 mmol), sulfonamide **4b** (319.1 mg, 1.11 mmol), activated molecular sieves 4A (350 mg), and trimethylsilyl trifluoromethanesulfonate (20 μL, 0.111 mmol) (silica gel column chromatography: hexane/diethyl ether = 25/1). Pale yellow oil; R_f value 0.53 (hexane/ethyl acetate = 8/1); IR (NaCl, neat) ν_{max} 2957, 1937, 1447, 1362, 1253, 1183, 830, 578 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, 2H, J = 7.0, 1.5 Hz), 7.64 (td, 1H, J = 7.5, 1.5 Hz), 7.42 (t, 1H, J = 7.5 Hz), 7.28−7.22 (m, 7H), 6.97 (br, 4H), 2.59 (t, 2H, J = 7.5 Hz), 1.65 (tt, 2H, J = 7.5, 7.5 Hz), 1.40 (tq, 2H, J = 7.5, 7.5 Hz), 0.93 (t, 3H, J = 7.5 Hz), 0.81 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 136.6, 133.6, 133.2, 130.0, 128.8, 128.5, 128.0, 127.6, 119.2, 118.1, 32.2, 29.7, 25.8, 22.6, 17.8, 13.9, −4.9; HRMS (ESI) calcd for $C_{31}H_{39}NO_3SSiNa$ $[M + Na]^+$ 556.23176, found 556.23184.

*N-((tert-Butyldimethylsilyl)oxy)-4-chloro-N-(1,1-diphenylhepta-1,2-dien-3-yl)benzenesulfonamide (**2c**).*



2c

199.4 mg (40%) of product **2c** was obtained from propargyl alcohol **3a** (227.4 mg, 0.86 mmol), sulfonamide **4c** (277.9 mg, 0.86 mmol), activated molecular sieves 4A (344 mg), and trimethylsilyl trifluoromethanesulfonate (16 μL, 0.086 mmol) (silica gel column chromatography: hexane/diethyl ether = 25/1). Pale yellow oil; R_f value 0.44 (hexane/ethyl acetate = 7/1); IR (NaCl, neat) ν_{max} 2956, 2929, 1938, 1367, 1182, 1091, 829, 756 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.5 Hz), 7.24−7.29 (m, 8H), 6.96 (br, 4H), 2.61 (t, 2H, J = 8.0 Hz), 1.63 (tt, 2H, J = 8.0, 7.5 Hz), 1.39 (qt, 2H, J = 7.5, 7.5 Hz), 0.93 (t, 3H, J = 7.5 Hz), 0.81 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 140.3, 136.5, 131.33, 131.28, 128.8, 128.7, 128.1, 127.8, 119.2, 118.4, 32.7, 29.7, 25.8, 22.6, 17.8, 13.9, −4.74; HRMS (FAB) calcd for $C_{31}H_{39}ClNO_3SSi$ $[M + H]^+$ 568.2108, found 568.2107.

DOI: 10.1021/acs.joc.5b02364
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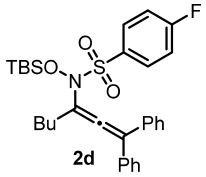
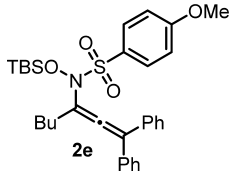
*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-4-fluorobenzenesulfonamide (**2d**).*



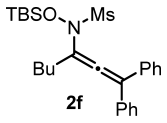
153.9 mg (28%) of product **2d** was obtained from propargyl alcohol **3a** (264 mg, 1.00 mmol), sulfonamide **4d** (305 mg, 1.00 mmol), activated molecular sieves 4A (400 mg), and trimethylsilyl trifluoromethanesulfonate (18 μL, 0.10 mmol) (silica gel column chromatography: hexane/ethyl acetate = 99/1 to 95/5, followed by recycling HPLC separation). Colorless oil; R_f = 0.59 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3060, 3027, 2957, 2930, 2859, 1937, 1592, 1493, 1367, 1253, 1238, 1181, 1155, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, 2H, J = 9.0, 5.0 Hz), 7.28−7.22 (m, 6H), 7.00−6.95 (m, 6H), 2.59 (t, 2H, J = 7.5 Hz), 1.62 (tt, 2H, J = 7.5, 7.5 Hz), 1.38 (tq, 2H, J = 7.5, 7.5 Hz), 0.91 (t, 3H, J = 7.5 Hz), 0.79 (s, 9H), 0.10 (br, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 165.8 (d, $J_{C\text{-}F}$ = 256 Hz), 136.5, 132.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 128.8, 128.7, 128.0, 127.8, 119.3, 118.3, 115.8 (d, $J_{C\text{-}F}$ = 22.8 Hz), 32.6, 29.7, 25.8, 22.6, 17.8, 13.9, −4.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ −103.9; HRMS (ESI) calcd for $C_{31}H_{38}FNNaO_3SSi$ $[M + Na]^+$ 574.22234, found 574.22245.

*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-4-methoxybenzenesulfonamide (**2e**).*



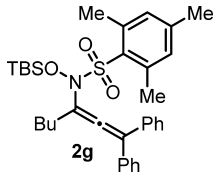
374.4 mg (65%) of product **2e** was obtained from propargyl alcohol **3a** (264 mg, 1.00 mmol), sulfonamide **4e** (317 mg, 1.00 mmol), activated molecular sieves 4A (400 mg), and trimethylsilyl trifluoromethanesulfonate (18 μL, 0.10 mmol) (silica gel column chromatography: hexane/ethyl acetate = 99/1 to 4/1). Pale yellow oil; R_f = 0.35 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3060, 2954, 2928, 2854, 1937, 1596, 1496, 1362, 1260, 1167, 1092, 1027 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, 2H, J = 8.5 Hz), 7.26−7.19 (m, 6H), 6.93 (br, 4H), 6.85 (d, 2H, J = 8.5 Hz), 3.86 (s, 3H), 2.60 (t, 2H, J = 8.0 Hz), 1.63 (tt, 2H, J = 8.0, 7.5 Hz), 1.39 (tq, 2H, J = 7.5, 7.0 Hz), 0.92 (t, 3H, J = 7.0 Hz), 0.77 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 163.7, 136.8, 132.1, 128.8, 127.9, 127.5, 124.4, 119.6, 117.9, 113.8, 55.5, 32.4, 29.8, 25.8, 22.6, 17.8, 13.9, −4.8; HRMS (ESI) calcd for $C_{32}H_{41}NO_4SSiNa$ $[M + Na]^+$ 586.2423, found 586.2412.

*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-methanesulfonamide (**2f**).*



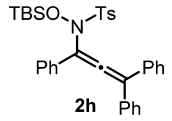
62.2 mg (13%) of product **2f** was obtained from propargyl alcohol **3a** (396.6 mg, 1.5 mmol), sulfonamide **4f** (338.1 mg, 1.5 mmol), activated molecular sieves 4A (600 mg), and trimethylsilyl trifluoromethanesulfonate (27 μL, 0.15 mmol) (silica gel column chromatography: hexane/diethyl ether = 25/1). Pale yellow oil; R_f value 0.58 (hexane/ethyl acetate = 8/1); IR (NaCl, neat) ν_{max} 2956, 2929, 1939, 1358, 1171, 954, 830, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−7.32 (m, 10H), 2.79 (s, 3H), 2.58 (t, 2H, J = 8.0 Hz), 1.59 (tt, 2H, J = 8.0, 7.0 Hz), 1.37 (qt, 2H, J = 8.0, 7.0 Hz), 1.80 (t, 3H, J = 7.0 Hz), 0.90 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.6, 135.8, 128.6, 128.4, 128.1, 120.3, 119.0, 33.0, 31.0, 29.3, 25.8, 22.4, 17.8, 13.9, −4.7; HRMS (ESI) calcd for $C_{26}H_{37}NO_3SSiNa$ $[M + Na]^+$ 494.21611, found 494.21589.

*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenylhepta-1,2-dien-3-yl)-2,4,6-trimethylbenzenesulfonamide (**2g**).*



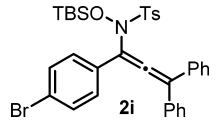
53.7 mg (16%) of product **2g** was obtained from propargyl alcohol **3a** (152.5 mg, 0.576 mmol), sulfonamide **4g** (190.1 mg, 0.576 mmol), molecular sieves 4A (230 mg), and trimethylsilyl trifluoromethanesulfonate (10 μL, 0.0576 mmol) (silica gel column chromatography: hexane/diethyl ether = 25/1). pale yellow oil; R_f value 0.52 (hexane/ethyl acetate = 8/1); IR (NaCl, neat) ν_{max} 2956, 2929, 1942, 1341, 1256, 1166, 830, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, 4H, J = 7.0 Hz), 7.36−7.29 (m, 6H), 6.92 (s, 2H), 2.69 (s, 6H), 2.67 (t, 2H, J = 8.0 Hz), 2.30 (s, 3H), 1.60 (tt, 2H, J = 8.0, 7.5 Hz), 1.41 (tq, 2H, J = 7.5, 7.5 Hz), 0.91 (t, 3H, J = 7.5 Hz), 0.65 (s, 9H), −0.44 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6, 143.4, 142.1, 136.1, 131.8, 130.7, 129.0, 128.2, 127.7, 117.1, 116.9, 30.0, 29.3, 25.6, 23.3, 22.5, 21.0, 17.6, 14.0, −5.8; HRMS (ESI) calcd for $C_{34}H_{45}NO_3SSiNa$ $[M + Na]^+$ 598.27871, found 598.27887.

*N-((tert-Butyldimethylsilyl)oxy)-4-methyl-N-(1,3,3-triphenylpropa-1,2-dien-1-yl)benzenesulfonamide (**2h**).*



129.9 mg (46%) of product **2h** was obtained from propargyl alcohol **3h** (142 mg, 0.500 mmol), sulfonamide **4a** (151 mg, 0.500 mmol), activated molecular sieves 4A (201 mg), and trimethylsilyl trifluoromethanesulfonate (9 μL, 0.05 mmol) (silica gel column chromatography: hexane/ethyl acetate = 200/1 to 100/1 to 50/1). Pale yellow solid; R_f value 0.46 (hexane/ethyl acetate = 10/1); mp 54−57 °C; IR (NaCl, neat) ν_{max} 3057, 2928, 2857, 1912, 1362, 1172 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 7.0 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.42 (t, 2H, J = 8.5 Hz), 7.30−7.36 (m, 3H), 7.25 (dd, 4H, J = 8.5, 8.5 Hz), 7.08 (d, 2H, J = 8.0 Hz), 7.00 (d, 4H, J = 7.5 Hz), 2.42 (s, 3H), 0.89 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 144.3, 135.7, 134.3, 130.2, 129.7, 129.0, 128.9, 128.4, 128.1, 128.0, 126.3, 120.7, 120.2, 25.8, 21.8, 17.8, −4.7; HRMS (ESI) calcd for $C_{34}H_{37}NNaO_3SSi$ $[M + Na]^+$ 590.2161, found 590.2153.

*N-(1-(4-Bromophenyl)-3,3-diphenylpropa-1,2-dien-1-yl)-N-((tert-butyldimethylsilyl)oxy)-4-methylbenzenesulfonamide (**2i**).*



95.7 mg (29%) of product **2i** was obtained from propargyl alcohol **3i** (182 mg, 0.500 mmol), sulfonamide **4a**, activated molecular sieves 4A (203 mg), and trimethylsilyl trifluoromethanesulfonate (9 μL, 0.05 mmol) (silica gel column chromatography: hexane/ethyl acetate = 100/1 to 50/1 to 20/1). Pale yellow solid; R_f value 0.46 (hexane/ethyl acetate = 10/1); mp 56−58 °C; IR (NaCl, neat) ν_{max} 3058, 2955, 2928, 1910, 1597, 1485, 1362, 1254, 1171 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, 2H, J = 8.0 Hz), 7.51 (d, 2H, J = 8.5 Hz), 7.48 (d, 2H, J = 8.5 Hz), 7.30 (t, 2H, J = 7.5 Hz), 7.22 (dd, 4H, J = 7.5, 7.5 Hz), 7.06 (d, 2H, J = 8.0 Hz), 6.92 (d, 4H, J = 7.5 Hz), 2.40 (s, 3H), 0.83 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.0, 144.5, 135.5, 133.5, 131.6, 130.2, 129.6, 129.1, 128.9, 128.3, 128.2, 127.8, 122.0, 121.2, 119.6, 25.8, 21.8, 17.8, −4.7; HRMS (ESI) calcd for $C_{34}H_{36}{}^{79}BrNaNO_3SSi$ $[M + Na]^+$ 668.1266, found 668.1268.

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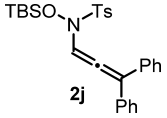
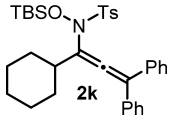
*N-((tert-Butyldimethylsilyl)oxy)-N-(3,3-diphenylpropa-1,2-dien-1-yl)-4-methylbenzenesulfonamide (**2j**).*



2j

61.0 mg (12%) of product **2j** was obtained from propargyl alcohol **3j** (208 mg, 1.00 mmol), sulfonamide **4a** (301 mg, 1.00 mmol), activated molecular sieves 4A (400 mg), and trimethylsilyl trifluoromethanesulfonate (18 μL, 0.10 mmol) (silica gel column chromatography: hexane/ethyl acetate = 98/2 to 85/15). Yellow oil; R_f value 0.35 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3031, 2955, 2928, 2857, 1950, 1365, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, 2H, J = 8.0 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.26 (t, 2H, J = 7.5 Hz), 7.17 (br, 4H), 7.11 (s, 1H), 6.96 (br, 4H), 2.56 (s, 3H), 0.74 (s, 9H), −0.03 (br, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 144.7, 135.7, 130.2, 129.3, 129.2, 128.8, 128.0, 127.8, 120.6, 106.6, 25.7, 21.9, 17.7, −5.3; HRMS (ESI) calcd for $C_{28}H_{33}NNaO_3SSi$ $[M + Na]^+$ 514.1848, found 514.1847.

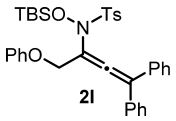
*N-((tert-Butyldimethylsilyl)oxy)-N-(1-cyclohexyl-3,3-diphenylpropa-1,2-dien-1-yl)-4-methylbenzenesulfonamide (**2k**).*



2k

64.9 mg (14%) of product **2k** was obtained from propargyl alcohol **3k** (232 mg, 0.800 mmol), sulfonamide **4a** (241 mg, 0.800 mmol), activated molecular sieves 4A (320 mg), and trimethylsilyl trifluoromethanesulfonate (15 μL, 0.080 mmol) (silica gel column chromatography: hexane elution to hexane/ethyl acetate = 95/5). White solid; R_f = 0.33 (hexane/ethyl acetate = 20/1); mp 41−42 °C; IR (NaCl, neat) ν_{max} 3058, 2928, 2854, 1935, 1598, 1492, 1448, 1362, 1258, 1173, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, 2H, J = 8.5 Hz), 7.22 (t, 2H, J = 7.5 Hz), 7.17 (dd, 4H, J = 7.5, 7.0 Hz), 7.12 (d, 2H, J = 8.5 Hz), 6.91 (d, 4H, J = 7.0 Hz), 2.88 (tt, 1H, J = 11.5, 3.0 Hz), 2.42 (s, 3H), 2.13 (br, 2H), 1.80 (br, 2H), 1.73 (br, 1H), 1.39(qt, 4H, J = 12.5, 3.0 Hz), 1.28−1.17 (m, 3H), 0.75(s, 9H), 0.07 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 144.2, 136.8, 130.1, 130.0, 129.2, 128.6, 127.9, 127.3, 125.1, 118.7, 40.9, 32.6, 26.43, 26.38, 25.6, 21.8, 17.8, −4.6; HRMS (ESI) calcd for $C_{34}H_{43}NNaO_3SSi$ $[M + Na]^+$ 596.2631, found 596.2634.

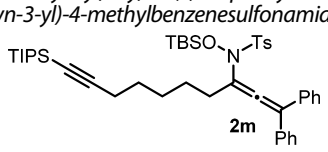
*N-((tert-Butyldimethylsilyl)oxy)-4-methyl-N-(1-phenoxy-4,4-diphenylbuta-2,3-dien-2-yl)benzenesulfonamide (**2l**).*



2l

66.3 mg (6%) of product **2l** was obtained from propargyl alcohol **3l** (629 mg, 2.00 mmol) and sulfonamide **4a** (603 mg, 2.00 mmol), activated molecular sieves 4A (800 mg), and trimethylsilyl trifluoromethanesulfonate (36 μL, 0.20 mmol) (silica gel column chromatography: hexane/ethyl acetate = 98/2 to 90/10, followed by recycling HPLC). Colorless sticky oil; R_f = 0.44 (hexane/ethyl acetate = 1/10); IR (NaCl, neat) ν_{max} 3060, 2927, 2856, 1943, 1599, 1493, 1461, 1362, 1253, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.0 Hz), 7.25 (t, 2H, J = 7.5 Hz), 7.20−7.14 (m, 8H), 6.95−6.87 (m, 7H), 4.97 (s, 2H), 2.44 (s, 3H), 0.78 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.6, 158.2, 144.7, 135.8, 130.3, 129.5, 129.34, 129.29, 129.1, 127.94, 127.92, 121.0, 120.9, 115.4, 114.7, 66.6, 25.8, 21.8, 17.8, −4.9; HRMS (ESI) calcd for $C_{35}H_{39}NO_4SSiNa$ $[M + Na]^+$ 620.2267, found 620.2262.

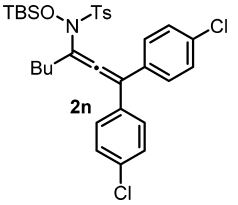
*N-((tert-Butyldimethylsilyl)oxy)-N-(1,1-diphenyl-10-(triisopropylsilyl)-deca-1,2-dien-9-yn-3-yl)-4-methylbenzenesulfonamide (**2m**).*



2m

86.8 mg (24%) of product **2m** was obtained from propargyl alcohol **3m** (226 mg, 0.492 mmol), sulfonamide **4a** (148 mg, 0.492 mmol), activated molecular sieves 4A (197 mg), and trimethylsilyl trifluoromethanesulfonate (9 μL, 0.049 mmol) (silica gel column chromatography: hexane/ethyl acetate = 19/1). Colorless oil; R_f = 0.52 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3060, 2939, 2862, 2170, 1936, 1598, 1462, 1364, 1253, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 8.0 Hz), 7.25 (t, 2H, J = 7.5 Hz), 7.20 (dd, 4H, J = 7.5, 7.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 6.96 (br, 4H), 2.56 (t, 2H, J = 7.5 Hz), 2.44 (s, 3H), 2.17 (t, 2H, J = 7.0 Hz), 1.63 (tt, 2H, J = 7.5, 7.5 Hz), 1.53−1.41 (m, 4H), 1.09−0.98 (m, 21H), 0.79 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 144.3, 136.6, 130.2, 130.0, 129.2, 128.8, 128.0, 127.6, 119.2, 118.0, 109.0, 80.0, 32.4, 28.7, 28.6, 27.0, 25.9, 21.8, 19.7, 18.6, 17.8, 11.3, −4.8; HRMS (ESI) calcd for $C_{44}H_{63}NO_3SSi_2Na$ $[M + Na]^+$ 764.39649, found 764.39688.

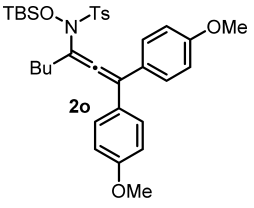
*N-(1,1-Bis(4-chlorophenyl)hepta-1,2-dien-3-yl)-N-((tert-butyldimethylsilyl)oxy)-4-methylbenzenesulfonamide (**2n**).*



2n

187.3 mg (61%) of product **2n** was obtained from propargyl alcohol **3n** (167 mg, 0.500 mmol), sulfonamide **4a** (151 mg, 0.500 mmol), activated molecular sieves 4A (200 mg), and trimethylsilyl trifluoromethanesulfonate (9 μL, 0.05 mmol) (silica gel column chromatography: hexane/ethyl acetate = 200/1 to 100/1). Pale yellow solid; R_f value 0.51 (hexane/ethyl acetate = 10/1); mp 106−109 °C; IR (NaCl, neat) ν_{max} 3032, 2929, 1934, 1489, 1363, 1174, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.0 Hz), 7.18 (d, 4H, J = 9.0 Hz), 6.88 (br, 4H), 2.58 (t, 2H, J = 7.5 Hz), 2.48 (s, 3H), 1.60 (tt, 2H, J = 7.5, 7.5 Hz), 1.38 (tq, 2H, J = 7.5, 7.5 Hz), 0.91 (t, 3H, J = 7.5 Hz), 0.80 (s, 9H), 0.09 (s, 6H); ^{13}C NMR(126 MHz, $CDCl_3$) δ 200.7, 144.6, 134.8, 133.5, 130.1, 129.94, 129.88, 129.2, 128.3, 120.3, 115.8, 31.9, 29.8, 25.8, 22.5, 21.7, 17.7, 13.9, −4.8; HRMS (ESI) calcd for $C_{32}H_{39}Cl_2NaNO_3SSi$ $[M + Na]^+$ 638.1695, found 638.1693.

*N-(1,1-Bis(4-methoxyphenyl)hepta-1,2-dien-3-yl)-N-((tert-butyldimethylsilyl)oxy)-4-methylbenzenesulfonamide (**2o**).*



2o

100.1 mg (33%) of product **2o** was obtained from propargyl alcohol **3o** (121.3 mg, 0.50 mmol), sulfonamide **4a** (151.1 mg, 0.500 mmol), activated molecular sieves 4A (200 mg), and trimethylsilyl trifluoromethanesulfonate (9 μL, 0.05 mmol) (silica gel column chromatography: hexane/ethyl acetate = 100/1 to 50/1 to 25/1). Pale yellow oil; R_f value 0.43 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3036, 2929, 1931, 1605, 1509, 1248, 1173 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, 2H, J = 8.0 Hz), 7.21 (d, 2H, J = 8.0 Hz), 6.90 (br, 4H), 6.75 (d, 4H, J = 8.5 Hz), 3.82 (s, 6H), 2.54 (t, 2H, J = 8.0 Hz), 2.47 (s, 3H), 1.60 (tt, 2H, J = 8.0, 7.5 Hz), 1.37 (tq, 2H, J = 7.5, 7.5 Hz), 0.90 (t, 2H, J = 7.5 Hz), 0.82 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.7, 159.0, 144.2, 130.4, 130.0, 129.9, 129.2, 129.1, 118.6, 117.1, 113.3, 55.2, 32.2, 29.8, 25.8, 22.5, 21.8, 17.8, 13.9, −4.8; HRMS (ESI) calcd for $C_{34}H_{45}NaNO_5SSi$ $[M + Na]^+$ 630.2685, found 630.2684.

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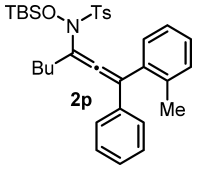
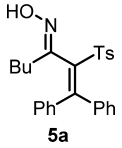
*N-((tert-Butyldimethylsilyl)oxy)-4-methyl-N-(1-phenyl-1-(o-tolyl)-hepta-1,2-dien-3-yl)benzenesulfonamide (**2p**).*



235.8 mg (17%) of product **2p** was obtained from propargyl alcohol **3p** (696 mg, 2.50 mmol), sulfonamide **4a** (754 mg, 250 mmol), activated molecular sieves 4A (1.0 g), and trimethylsilyl trifluoromethanesulfonate (45 μL, 0.25 mmol) (silica gel column chromatography: hexane/ethyl acetate = 99/1 to 91/9, followed by recycling HPLC). Pale yellow oil; R_f = 0.47 (hexane/ethyl acetate = 10/1); IR (NaCl, neat) ν_{max} 3060, 2928, 1943, 1598, 1462, 1362, 1252, 1173, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, 2H, J = 8.0 Hz), 7.24−7.15 (m, 4H), 7.10−7.07 (m, 2H), 6.97−6.94 (m, 4H), 6.87 (d, 1H, J = 7.5 Hz), 2.59−2.48 (m, 2H), 2.33 (s, 3H), 1.82 (s, 3H), 1.65−1.54 (m, 2H), 1.38 (tq, 2H, J = 7.5, 7.5 Hz), 0.91 (t, 3H, J = 7.5 Hz), 0.80 (s, 9H), 0.20 (br, 3H), 0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 144.1, 136.5, 136.0, 135.7, 130.0, 129.91, 129.85, 129.6, 128.9, 128.1, 127.4, 127.2, 125.6, 118.8, 116.6, 32.2, 29.8, 25.8, 22.6, 21.7, 19.9, 17.8, 13.9, −4.5, −4.8; HRMS (ESI) calcd for $C_{33}H_{43}NNaO_3SSi$ $[M + Na]^+$ 584.26306, found 584.26241.

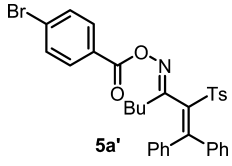
General Procedure of α-Sulfonyl Enoxime (Vinyl Sulfones) Synthesis. To a stirred solution of allenylsulfonamide (1 equiv) and acetic acid (1.5 equiv) in THF (0.1 M) was added tetrabutylammonium fluoride (1.2 equiv) at 0 °C. After 10 min, the reaction was quenched with saturated sodium bicarbonate aqueous solution. The reaction mixture was extracted with ethyl acetate and was washed with water and brine. The combined organic layers were dried over sodium sulfate or magnesium sulfate and were concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography to afford α-sulfonyl enoximes. *E*/*Z* chemistry of oximes is not determined except for **5a**, but all were obtained as single isomers.

*(E)-1,1-Diphenyl-2-tosylhept-1-en-3-one Oxime (**5a**).*



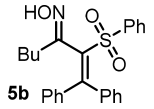
30.6 mg (94%) of product **5a** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), acetic acid (6.5 μL, 0.113 mmol), and tetrabutylammonium fluoride (90 μL, 1.0 M in THF, 0.09 mmol) (silica gel column chromatography: hexane/ethyl acetate = 10/1 to 3/1). Colorless solid; R_f value 0.25 (hexane/ethyl acetate = 3/1); mp 144−145 °C; IR (NaCl, neat) ν_{max} 3424, 3192, 2958, 2929, 2871, 1596, 1444, 1315, 1146, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.40 (d, 2H, J = 8.0 Hz), 7.31−7.20 (m, 8H), 7.12−7.07 (m, 4H), 2.35 (s, 3H), 2.32 (t, 2H, J = 8.0 Hz), 1.39 (tt, 2H, J = 8.0, 7.0 Hz), 1.22 (tq, 2H, J = 7.5, 7.0 Hz), 0.83 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 154.8, 143.6, 139.7, 138.6, 138.1, 138.0, 129.09, 129.07, 129.01, 128.7, 128.20, 128.16, 128.0, 127.6, 29.8, 26.9, 22.8, 21.5, 13.7; HRMS (ESI) calcd for $C_{26}H_{27}NO_3SNa$ $[M + Na]^+$ 456.16093, found 456.16097.

*(E)-1,1-Diphenyl-2-tosylhept-1-en-3-one O-(4-Bromobenzoyl) Oxime (**5a′**, CCDC 1056831).*



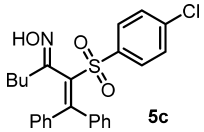
To a stirred solution of oxime **5a** (31.6 mg, 0.073 mmol) in dichloromethane (2.0 mL) were added triethylamine (30 μL, 0.219 mmol), *N*,*N*-dimethyl-4-aminopyridine (1.8 mg, 0.015 mmol), and *p*-bromobenzoyl chloride (19.2 mg, 0.089 mmol) at room temperature under a nitrogen atmosphere, and the mixture was stirred for 15 h. After quenching the reaction with saturated sodium bicarbonate aqueous solution, the mixture was extracted with ethyl acetate and was washed with water and brine. The combined organic layers were dried over magnesium sulfate and were concentrated *in vacuo*. The resulting residual solid was purified by decantation (hexane/ethyl acetate = 6:1) to afford bromobenzoate **5a′** (33.5 mg, 74%). White solid; R_f value 0.50 (hexane/ethyl acetate = 3/1); mp 168−169 °C (recrystallized from ether); IR (NaCl, neat) ν_{max} 2959, 1749, 1590, 1320, 1251, 1149, 1059, 748, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, 2H, J = 9.0 Hz), 7.64 (d, 2H, J = 9.0 Hz), 7.43 (d, 2H, J = 8.5 Hz), 7.35−7.30 (m, 3H), 7.22−7.27 (m, 5H), 7.14 (d, 2H, J = 8.0 Hz), 7.09 (d, 2H, J = 6.5 Hz), 2.54 (t, 2H, J = 7.5 Hz), 2.37 (s, 3H), 1.43 (tt, 2H, J = 7.5, 7.5 Hz), 1.19 (tq, 2H, J = 7.5, 7.5 Hz), 0.80 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 162.6, 155.8, 144.2, 138.9, 138.0, 137.7, 137.3, 132.0, 131.1, 129.5, 129.11, 129.08, 129.04, 128.62, 128.56, 128.4, 128.1, 127.8, 127.6, 32.0, 27.2, 22.7, 21.6, 13.7; HRMS (ESI) calcd for $C_{33}H_{30}BrNO_4SNa$ $[M + Na]^+$ 638.09766, found 638.09757.

*1,1-Diphenyl-2-(phenylsulfonyl)hept-1-en-3-one Oxime (**5b**).*



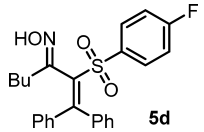
30.6 mg (94%) of product **5b** was obtained from allenamide **2b** (40.0 mg, 0.075 mmol), acetic acid (6.5 μL, 0.113 mmol), and tetrabutylammonium fluoride (90 μL, 1.0 M in THF, 0.09 mmol) (silica gel column chromatography: hexane/ethyl acetate = 7/1 to 3/1). Colorless oil; R_f value 0.20 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3492, 2958, 1445, 1307, 1147, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.88 (br, 1H), 7.54 (dd, 2H, J = 7.0, 1.0 Hz), 7.46 (td, 1H, J = 7.5, 1.0 Hz), 7.30−7.19 (m, 10H), 7.09 (d, 2H, J = 7.5 Hz), 2.32 (t, 2H, J = 8.5 Hz), 1.40 (tt, H, J = 8.5, 7.5 Hz), 1.22 (tq, 2H, J = 7.5, 7.5 Hz), 0.83 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 155.1, 141.2, 139.6, 138.6, 137.8, 132.7, 129.2, 129.1, 128.8, 128.3, 128.2, 128.1, 128.0, 127.6, 29.7, 27.0, 22.8, 13.7; HRMS (ESI) calcd for $C_{25}H_{25}NO_3SNa$ $[M + Na]^+$ 442.14528, found 442.14592.

*2-((4-Chlorophenyl)sulfonyl)-1,1-diphenylhept-1-en-3-one Oxime (**5c**).*



32.1 mg (96%) of product **5c** was obtained from allenamide **2c** (42.0 mg, 0.074 mmol), acetic acid (6.3 μL, 0.11 mmol), and tetrabutylammonium fluoride (89 μL, 1.0 M in THF, 0.089 mmol) (hexane/ethyl acetate = 10/1 to 3/1). Colorless oil; R_f value 0.42 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3442, 3194, 2959, 1579, 1317, 1148, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.43 (d, 2H, J = 9.0 Hz), 7.32−7.19 (m, 10H), 7.08 (d, 2H, J = 7.5 Hz), 2.33 (t, 2H, J = 8.0 Hz), 1.42 (tt, 2H, J = 8.0, 7.5 Hz), 1.24 (tq, 2H, J = 7.5, 7.5 Hz), 0.84 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 155.5, 139.6, 139.43, 139.35, 138.3, 137.7, 129.5, 129.2, 129.1, 129.0, 128.6, 128.5, 128.1, 127.7, 29.7, 27.0, 22.8, 13.7; HRMS (ESI) calcd for $C_{25}H_{24}ClNO_3SNa$ $[M + Na]^+$ 476.10631, found 476.10649.

*2-((4-Fluorophenyl)sulfonyl)-1,1-diphenylhept-1-en-3-one Oxime (**5d**).*



41.9 mg (96%) of product **5d** was obtained from allenamide **2d** (55.2 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 95/5 to 70/30). White solid; R_f = 0.39 (hexane/ethyl acetate = 2/1); mp 37−39 °C; IR (NaCl, neat) ν_{max} 3427, 3188, 3056, 2959, 2931, 2871, 1590, 1492, 1317, 1290, 1236, 1146 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.94 (br, 1H),

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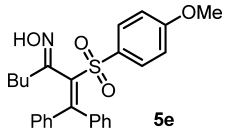
7.50 (dd, 2H, J = 8.5, 5.0 Hz), 7.29 (m, 1H), 7.26−7.19 (m, 7H), 7.08 (d, 2H, J = 6.5 Hz), 6.93 (dd, 2H, J = 8.5, 8.5 Hz), 2.32 (t, 2H, J = 8.0 Hz), 1.41 (tt, 2H, J = 8.0, 7.5 Hz), 1.23 (tq, 2H, J = 7.5, 7.0 Hz), 0.83 (t, 3H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (d, $J_{C\text{-}F}$ = 256 Hz), 156.5, 155.3, 139.5, 138.5, 137.7, 137.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 130.9 (d, $J_{C\text{-}F}$ = 9.6 Hz), 129.2, 129.1, 129.0, 128.4, 128.1, 127.7, 115.6 (d, $J_{C\text{-}F}$ = 22.8 Hz), 29.7, 27.0, 22.8, 13.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ −105.0; HRMS (ESI) calcd for $C_{25}H_{24}FNNaO_3S$ $[M + Na]^+$ 460.13586, found 460.13584.

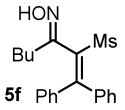
*2-((4-Methoxyphenyl)sulfonyl)-1,1-diphenylhept-1-en-3-one Oxime (**5e**).*



5e

39.4 mg (88%) of product **5e** was obtained from allenamide **2e** (56.4 mg, 0.1 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 92/8 to 1/1). White solid; R_f = 0.21 (hexane/ethyl acetate = 2/1); mp 40−42 °C; IR (NaCl, neat) ν_{max} 3427, 3192, 3058, 2959, 2871, 1594, 1496, 1444, 1317, 1298, 1261, 1144 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (br, 1H), 7.43 (d, 2H, J = 9.5 Hz), 7.30−7.19 (m, 8H), 7.12 (d, 2H, J = 6.5 Hz), 6.75 (d, 2H, J = 9.5 Hz), 3.79 (s, 3H), 2.32 (t, 2H, J = 8.0 Hz), 1.39 (tt, 2H, J = 8.0, 7.5 Hz), 1.21 (tq, 2H, J = 7.5, 7.0 Hz), 0.82 (t, 3H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 156.5, 154.4, 139.8, 138.9, 138.0, 132.6, 130.4, 129.09, 129.06, 128.7, 128.2, 128.0, 127.6, 113.6, 55.5, 29.8, 26.9, 22.9, 13.7; HRMS (ESI) calcd for $C_{26}H_{27}NO_4SNa$ $[M + Na]^+$ 472.15585, found 472.15593.

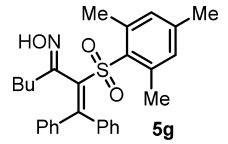
*2-(Methylsulfonyl)-1,1-diphenylhept-1-en-3-one Oxime (**5f**).*



5f

22.4 mg (91%) of product **5f** was obtained from allenamide **2f** (32.4 mg, 0.069 mmol), acetic acid (5.9 μL, 0.103 mmol), and tetrabutylammonium fluoride (83 μL, 1.0 M in THF, 0.083 mmol) (silica gel column chromatography: hexane/ethyl acetate = 10/1 to 3/1). Colorless oil; R_f value 0.10 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3407, 2959, 1309, 1139, 964, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.34 (m, 5H), 7.30−7.25 (m, 5H), 2.88 (s, 3H), 2.24 (t, 2H, J = 8.0 Hz), 1.37 (m, 2H), 1.19 (tq, 2H, J = 7.5, 7.5 Hz), 0.80 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 155.0, 139.5, 138.1, 136.9, 129.3, 129.1, 129.0, 128.8, 128.2, 127.9, 43.7, 29.6, 26.9, 22.8, 13.7; HRMS (ESI) calcd for $C_{20}H_{23}NO_3SNa$ $[M + Na]^+$ 380.12963, found 380.12953.

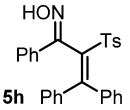
*2-(Mesitylsulfonyl)-1,1-diphenylhept-1-en-3-one Oxime (**5g**).*



5g

At room temperature, 17.0 mg (63%) of product **5g** was obtained from allenamide **2g** (33.9 mg, 0.059 mmol), acetic acid (5.0 μL, 0.088 mmol), and tetrabutylammonium fluoride (70 μL, 1.0 M in THF, 0.070 mmol) (silica gel column chromatography: hexane/ethyl acetate = 10/1 to 3/1). Pale yellow oil; R_f value 0.31 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3419, 2958, 1603, 1444, 1303, 1138, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (br, 1H), 7.25−7.12 (m, 10H), 6.72 (s, 2H), 2.52 (s, 6H), 2.35 (t, 2H, J = 8.0 Hz), 2.20 (s, 3H), 1.34 (m, 2H), 1.14 (qt, 2H, J = 7.5, 7.5 Hz), 0.78 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 151.7, 142.4, 140.0, 139.7, 138.6, 138.2, 134.6, 131.6, 129.7, 128.80, 128.76, 128.2, 127.9, 127.5, 30.1, 26.9, 22.8, 22.5, 20.9, 13.7; HRMS (ESI) calcd for $C_{28}H_{31}NO_3SNa$ $[M + Na]^+$ 484.19223, found 484.19215.

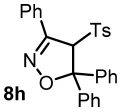
*1,3,3-Triphenyl-2-tosylprop-2-en-1-one Oxime (**5h**).*



5h

11.2 mg (25%) of oxime **5h**, and 25.5 mg (57%) of dihydroisoxazole **8h** were obtained from allenamide **2h** (56.7 mg, 0.1 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.120 mmol) (silica gel column chromatography: hexane/ethyl acetate = 50/1 to 10/1 to 5/1). Colorless oil; R_f value 0.29 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 3404, 3156, 3057, 3025, 2854, 1595, 1443, 1314, 1146, 1081, 763, 702 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (br, 1H), 7.49−7.47 (m, 2H), 7.43 (d, 2H, J = 9.0 Hz), 7.30−7.21 (m, 6H), 7.18−7.11 (m, 5H), 7.08 (t, 4H, J = 8.0 Hz), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 151.9, 143.7, 139.8, 139.4, 138.2, 137.9, 132.4, 129.2, 129.1, 129.03, 128.96, 128.8, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 21.6; HRMS (ESI) calcd for $C_{28}H_{23}NNaO_3S$ $[M + Na]^+$ 476.12963, found 476.12940.

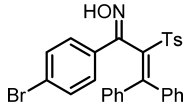
*3,5,5-Triphenyl-4-tosyl-4,5-dihydroisoxazole (**8h**).*



8h

White solid; R_f = 0.37 (hexane/ethyl acetate = 4/1); mp 234−235 °C; IR (NaCl, neat) ν_{max} 3060, 3029, 2978, 2920, 2596, 1494, 1447, 1326, 1149, 1085 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, 2H, J = 7.0 Hz), 7.59 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.0 Hz), 7.38−7.20 (m, 9H), 7.07 (d, 2H, J = 7.5 Hz), 7.01 (d, 2H, J = 7.5 Hz), 5.77 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 145.1, 143.5, 135.5, 134.4, 130.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.7, 127.5, 124.8, 94.0, 76.4, 21.6; HRMS (ESI) calcd for $C_{28}H_{23}NO_3SNa$ $[M + Na]^+$ 476.12963, found 476.13009.

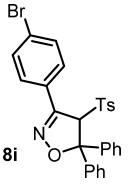
*1-(4-Bromophenyl)-3,3-diphenyl-2-tosylprop-2-en-1-one Oxime (**5i**).*



5i

11.6 mg (22%) of oxime **5i** and 28.3 mg (53%) of dihydroisoxazole **8i** were obtained from allenamide **2i** (64.7 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 10/1 to 5/1 to 2/1). Colorless oil; R_f value 0.24 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 3398, 3160, 3028, 2864, 1587, 1487, 1314, 1146 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (br, 1H), 7.43 (d, 2H, J = 8.5 Hz), 7.37 (d, 2H, J = 8.5 Hz), 7.32 (d, 2H, J = 8.5 Hz), 7.29 (t, 1H, J = 7.0 Hz), 7.23 (dd, 2H, J = 7.5, 7.0 Hz), 7.17 (t, 1H, J = 7.5 Hz), 7.14 (dd, 2H, J = 7.5, 6.5 Hz), 7.10−7.09 (m, 4H), 7.04 (d, 2H, J = 6.5 Hz), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 151.1, 143.9, 139.6, 138.9, 138.0, 137.7, 131.3, 130.9, 130.6, 129.1, 128.9, 128.8, 128.7, 128.4, 128.0, 127.6, 123.5, 21.6; HRMS (ESI) calcd for $C_{28}H_{22}{}^{79}BrNaNO_3S$ $[M + Na]^+$ 554.0402, found 554.0418.

*3-(4-Bromophenyl)-5,5-diphenyl-4-tosyl-4,5-dihydroisoxazole (**8i**).*



8i

White solid; R_f = 0.41 (hexane/ethyl acetate = 2/1); mp 90−91 °C; IR (NaCl, neat) ν_{max} 3060, 2981, 1593, 1492, 1448, 1397, 1329, 1149 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, 4H, J = 8.5, 7.5 Hz), 7.39 (d, 2H, J = 8.5 Hz), 7.35 (d, 2H, J = 7.0 Hz), 7.24−7.14 (m, 7H), 6.97 (br, 4H), 5.64 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$)

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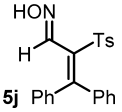
δ 155.0, 145.4, 143.3, 135.2, 134.2, 131.7, 129.2, 129.1, 128.7, 128.5, 128.2, 128.1, 127.6, 124.9, 124.8, 94.3, 76.3, 21.7; HRMS (ESI) calcd for $C_{28}H_{22}{}^{79}BrNNaO_3S$ $[M + Na]^+$ 554.04015, found 554.03949.

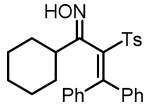
*3,3-Diphenyl-2-tosylacrylaldehyde Oxime (**5j**).*



5j

23.1 mg (60%) of product **5j** was obtained from allenamide **2j** (49.2 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 92/8 to 50/50). White solid; R_f = 0.32 (hexane/ethyl acetate = 2/1); mp 234–235 °C; IR (NaCl, neat) ν_{max} 3312, 3055, 3027, 1598, 1563, 1489, 1444, 1312, 1137, 993 cm^{-1}; ^1H NMR (500 MHz, DMSO-*d6*) δ 11.44 (s, 1H), 7.81 (s, 1H), 7.51 (d, 2H, *J* = 8.0 Hz), 7.34–7.26 (m, 8H), 7.10 (d, 2H, *J* = 7.5 Hz), 7.01 (d, 2H, *J* = 7.0 Hz), 2.36 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d6*) δ 156.0, 144.0, 143.8, 140.4, 138.8, 138.2, 134.1, 129.4, 129.3, 128.93, 128.90, 128.6, 128.5, 127.7, 127.5, 21.1; HRMS (ESI) calcd for $C_{22}H_{19}NNaO_3S$ $[M + Na]^+$ 400.09833, found 400.09826.

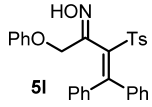
*1-Cyclohexyl-3,3-diphenyl-2-tosylprop-2-en-1-one Oxime (**5k**).*



5k

43.3 mg (96%) of product **5k** was obtained from allenamide **2k** (57.4 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 95/5 to 70/30). White solid; R_f = 0.40 (hexane/ethyl acetate = 2/1); mp 72–75 °C; IR (NaCl, neat) ν_{max} 3435, 3185, 3028, 2927, 2852, 1596, 1445, 1302, 1146, 1086 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.93 (br, 1H), 7.33 (d, 2H, *J* = 8.5 Hz), 7.28–7.21 (m, 6H), 7.18 (dd, 2H, *J* = 8.0, 7.5 Hz), 7.05–7.01 (m, 4H), 2.95 (tt, 1H, *J* = 12.0, 3.0 Hz), 2.32 (s, 3H), 1.65 (br, 7H), 1.27–1.20 (m, 2H), 1.11–1.03 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 154.9, 143.3, 140.2, 138.6, 138.3, 138.0, 129.9, 129.6, 128.9, 128.8, 128.2, 128.1, 127.9, 127.5, 39.7, 28.5, 26.3, 25.9, 21.5; HRMS (ESI) calcd for $C_{28}H_{29}NNaO_3S$ $[M + Na]^+$ 482.17658, found 482.17700.

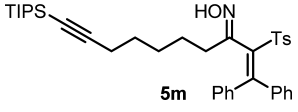
*1-Phenoxy-4,4-diphenyl-3-tosylbut-3-en-2-one Oxime (**5l**).*



5l

41.2 mg (85%) of product **5l** was obtained from allenamide **2l** (59.8 mg, 0.1 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 20/1 to 10/1 to 4/1 to 2/1). White solid; R_f = 0.29 (hexane/ethyl acetate = 2/1); mp 47–48 °C; IR (NaCl, neat) ν_{max} 3400, 3193, 3060, 2876, 1597, 1495, 1444, 1303, 1242, 1146, 1086 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.18 (br, 1H), 7.40–7.35 (m, 4H), 7.27 (t, 1H, *J* = 7.5 Hz), 7.21–7.16 (m, 7H), 7.08 (d, 2H, *J* = 7.0 Hz), 7.05 (t, 1H, *J* = 7.0 Hz), 7.01–6.99 (m, 4H), 4.91 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 157.0, 154.4, 143.6, 140.1, 138.0, 137.6, 136.5, 129.6, 129.2, 128.8, 128.7, 128.4, 128.27, 128.25, 128.18, 127.7, 121.5, 114.7, 64.4, 21.5; HRMS (ESI) calcd for $C_{29}H_{25}NNaO_4S$ 506.14020 $[M + Na]^+$, found 506.14008.

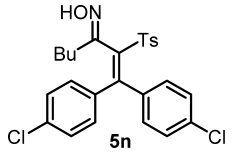
*1,1-Diphenyl-2-tosyl-10-(triisopropylsilyl)dec-1-en-9-yn-3-one Oxime (**5m**).*



5m

52.8 mg (84%) of product **5m** was obtained from allenamide **2m** (74.2 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 98/2 to 70/30). colorless oil; R_f = 0.47 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 3431, 3190, 3058, 2940, 2864, 2170, 1596, 1463, 1317, 1148 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 (br, 1H), 7.39 (d, 2H, *J* = 8.0 Hz), 7.29 (t, 1H, *J* = 7.0 Hz), 7.26–7.18 (m, 7H), 7.10–7.08 (m, 4H), 2.35 (s, 3H), 2.29 (t, 2H, *J* = 7.5 Hz), 2.16 (t, 2H, *J* = 7.5 Hz), 1.44 (tt, 2H, *J* = 7.5, 7.0 Hz), 1.40–1.28 (m, 4H), 1.08–0.98 (m, 21H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 154.8, 143.7, 139.7, 138.6, 138.1, 137.9, 129.1, 129.0, 128.8, 128.24, 128.20, 128.1, 127.6, 109.0, 80.0, 29.9, 28.7, 28.4, 24.2, 21.6, 19.6, 18.6, 11.2; HRMS (ESI) calcd for $C_{38}H_{49}NO_3SSiNa$ $[M + Na]^+$ 650.31001, found 650.31007.

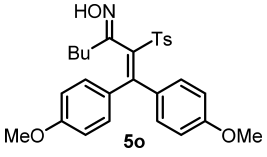
*1,1-Bis(4-chlorophenyl)-2-tosylhept-1-en-3-one Oxime (**5n**).*



5n

49.2 mg (98%) of product **5n** was obtained from allenamide **2n** (61.8, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.12 mmol) (silica gel column chromatography: hexane/ethyl acetate = 50/1 to 10/1 to 5/1). White solid; R_f value 0.13 (hexane/ethyl acetate = 4/1); mp 62–66 °C; IR (NaCl, neat) ν_{max} 3423, 2958, 1594, 1489, 1146, 1090, 1014, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (br, 1H, OH), 7.40 (d, 2H, *J* = 8.0 Hz), 7.213 (d, 2H, *J* = 9.0 Hz), 7.211 (d, 2H, *J* = 8.5 Hz), 7.13 (d, 2H, *J* = 9.0 Hz), 7.11 (d, 2H, *J* = 8.5 Hz), 7.01 (d, 2H, *J* = 8.0 Hz), 2.38 (s, 2H), 2.32 (t, 3H, *J* = 8.0 Hz), 1.36 (tt, 2H, *J* = 8.0, 7.0 Hz), 1.22 (tq, 2H, *J* = 7.5, 7.0 Hz), 0.83 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 151.9, 144.2, 139.8, 137.8, 137.7, 135.9, 135.3, 134.8, 130.7, 129.1, 128.4, 128.2, 128.0, 29.7, 27.0, 22.8, 21.6, 13.7; HRMS (ESI) calcd for $C_{26}H_{25}Cl_2NaNO_3S$ $[M + Na]^+$ 524.0830, found 524.0823.

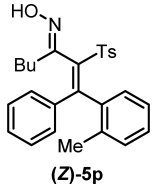
*1,1-Bis(4-methoxyphenyl)-2-tosylhept-1-en-3-one Oxime (**5o**).*



5o

44.8 mg (91%) of product **5o** was obtained from allenamide **2o** (60.8 mg, 0.100 mmol), acetic acid (9 μL, 0.15 mmol), and tetrabutylammonium fluoride (120 μL, 1.0 M in THF, 0.120 mmol) (silica gel column chromatography: hexane/ethyl acetate = 50/1 to 10/1 to 5/1). Pale yellow oil; R_f value 0.32 (hexane/ethyl acetate = 2/1); IR (NaCl, neat) ν_{max} 3502, 2929, 1603, 1509, 1254, 1175 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.05 (br, 1H), 7.43 (d, 2H, *J* = 8.5 Hz), 7.12 (d, 2H, *J* = 9.0 Hz), 7.08 (d, 2H, *J* = 8.5 Hz), 7.01 (d, 2H, *J* = 9.0 Hz), 6.76–6.73 (m, 4H), 3.82 (s, 3H), 3.72 (s, 3H), 2.34 (s, 3H), 2.31 (t, 2H, *J* = 8.0 Hz), 1.40 (tt, 2H, *J* = 8.0, 7.5 Hz), 1.23 (tq, 2H, *J* = 7.5, 7.5 Hz), 0.83 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 159.7, 156.7, 154.4, 143.3, 138.5, 136.8, 132.6, 131.34, 131.30, 130.7, 128.9, 128.1, 113.3, 112.8, 55.2, 55.1, 29.7, 27.0, 22.8, 21.5, 13.7; HRMS (ESI) calcd for $C_{28}H_{31}NNaO_5S$ $[M + Na]^+$ 516.18206, found 516.18142.

*(1Z,3E)-1-Phenyl-1-(o-tolyl)-2-tosylhept-1-en-3-one Oxime ((Z)-**5p**, CCDC 1056832).*



(*Z*)-5p

155.0 mg (87%, (*Z*)-**5p**/(*E*)-**5p** = 19/1 determined by ^1H NMR) of products as a mixture was obtained from allenamide **2p** (225 mg, 0.400 mmol), acetic acid (34 μL, 0.60 mmol), and tetrabutylammonium fluoride (480 μL, 1.0 M in THF, 0.480 mmol) (silica gel column chromatography: hexane/ethyl acetate = 95/5 to 60/40).

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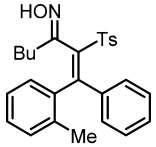
Separation of (*Z*)-**5p** and (*E*)-**5p** was performed with HPLC (Column: Kaseisorb LC ODS 2000) (methanol/water = 75/25) to afford purified (*Z*)-**5p** (132.0 mg) and (*E*)-**5p** (4.3 mg). White solid; R_f = 0.41 (hexane/ethyl acetate = 2/1); mp 122−124 °C; IR (NaCl, neat) ν_{max} 3433, 3178, 3061, 3023, 2958, 2929, 2871, 1596, 1455, 1316, 1147, 1085 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.27 (br, 1H), 7.39−7.21 (m, 10H), 7.09 (d, 2H, *J* = 8.0 Hz), 6.95 (br, 1H), 2.50 (ddd, 1H, *J* = 14.5, 10.5, 5.5 Hz), 2.36 (s, 3H), 2.19 (br, 1H), 1.69 (br, 3H), 1.39 (br, 2H), 1.30−1.14 (m, 2H), 0.81 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 154.2, 143.8, 139.1, 138.2, 137.9, 136.8, 135.9, 130.1, 129.9, 129.4, 128.9, 128.8, 128.6, 128.5, 127.9, 124.9, 30.0, 27.0, 22.9, 21.5, 19.6, 13.7; HRMS (ESI) calcd for $C_{27}H_{29}NNaO_3S$ $[M + Na]^+$ 470.17658, found 470.17690.

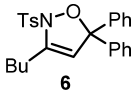
*(1E)-1-Phenyl-1-(o-tolyl)-2-tosylhept-1-en-3-one Oxime ((E)-**5p**).*



(*E*)-5p

White solid; R_f value 0.41 (hexane/ethyl acetate = 2/1); mp 152−154 °C; IR (NaCl, neat) ν_{max} 3433, 3060, 2958, 2927, 2871, 1596, 1456, 1315, 1146, 1085 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, 2H, *J* = 8.5 Hz), 7.26−7.06 (m, 11H), 2.36 (s, 3H), 2.23 (t, 2H, *J* = 8.0 Hz), 2.17 (s, 3H), 1.43 (br, 2H), 1.26 (m, 2H), 0.87 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 155.0, 143.5, 140.3, 139.1, 138.3, 136.7, 135.2, 130.6, 129.3, 128.9, 128.6, 128.4, 128.3, 128.1, 127.4, 125.2, 30.0, 26.9, 23.1, 21.6, 20.2, 13.8; HRMS (ESI) calcd for $C_{27}H_{29}NNaO_3S$ $[M + Na]^+$ 470.17658, found 470.17659.

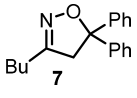
Synthesis of Isoxazoline Byproducts. *3-Butyl-5,5-diphenyl-2-tosyl-2,5-dihydroisoxazole (**6**, CCDC 1056830).*



6

To a stirred solution of allenamide **2a** (110 mg, 0.20 mmol) in acetonitrile (4.0 mL) was added silver fluoride (30.6 mg, 0.241 mmol) at room temperature, and the reaction mixture was stirred overnight. Concentration of the mixture *in vacuo*, followed by silica gel column chromatography (hexane/ethyl acetate = 98/2 to 85/15), gave dihydroisoxazole **6** (42.1, mg, 48%). White solid; R_f = 0.23 (hexane/ethyl acetate = 10/1); mp 126−127 °C; IR (NaCl, neat) ν_{max} 3059, 2957, 2871, 1664, 1596, 1362, 1172 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, 2H, *J* = 8.0 Hz), 7.21−7.14 (m, 6H), 7.96 (dd, 4H, *J* = 6.5, 2.0 Hz), 7.83 (d, 2H, *J* = 8.0 Hz), 5.36 (s, 1H), 2.60 (t, 2H, *J* = 8.0 Hz), 2.30 (s, 3H), 1.64 (tt, 2H, *J* = 8.0, 7.0 Hz), 1.37 (tq, 2H, *J* = 7.0, 7.5 Hz), 0.92 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 144.2, 141.1, 129.5, 128.95, 128.88, 127.9, 127.2, 126.5. 114.6, 94.5, 29.8, 27.5, 22.2, 21.6, 13.8; LRMS (EI) *m*/*z* 433 (9%, M^+), 278 (35), 167 (43), 105 (100); HRMS (EI) calcd for $C_{26}H_{27}NO_3S$ (M^+) 433.1712, found 433.1717.

*3-Butyl-5,5-diphenyl-4,5-dihydroisoxazole (**7**).*

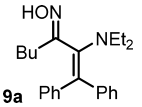


7

To a stirred solution of allenamide **2a** (0.075 mmol, 41.1 mg) in dichloromethane (0.7 mL) was added trifluoromethanesulfonic acid (13 μL, 0.15 mmol) at 0 °C. After 1 h, the reaction was quenched with saturated sodium bicarbonate aqueous solution. The mixture was extracted with ether and was washed with water and brine. The combined organic layers were dried over sodium sulfate and were concentrated *in vacuo*. The resulting residue was purified by flash silica gel column chromatography (hexane/diethyl ether = 10/1) to afford isoxazoline **7** (25.8 mg, 63%). White solid; R_f value 0.60 (hexane/ethyl acetate = 3/1); mp 55−56 °C; IR (NaCl, neat) ν_{max} 2957, 1492, 1447, 889, 754, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.40 (m, 4H), 7.34−7.31 (m, 4H), 7.27−7.24 (m, 2H), 3.54 (s, 2H), 2.35 (t, 2H, *J* = 8.0 Hz), 1.54 (tt, 2H, *J* = 8.0, 7.5 Hz), 1.29 (tq, 2H, *J* = 7.5, 7.5 Hz), 0.88 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 144.3, 128.3, 127.4, 126.0, 90.6, 50.1, 28.3, 27.6, 22.2, 13.7; HRMS (ESI) calcd for $C_{19}H_{21}NONa$ $[M + Na]^+$ 302.15208, found 302.15242.

General Experimental Procedure of Sulfinate-Trapping Substitutions To Afford α-Sulfonyl Enoximes. (**Procedure A**) To a stirred solution of allenamide, azodicarboxylate (1.5 equiv), and nucleophile reagent (1.5 equiv in general) in THF (0.05 M) was added tetrabutylammonium fluoride THF solution (1.2 equiv in general) at 0 °C under a nitrogen atmosphere. After 10 min, the mixture was extracted with ether and was washed with water and brine. The combined organic layers were dried over magnesium sulfate and were concentrated *in vacuo*. The resulting residual solid was purified by silica gel column chromatography to afford the desired α-substituted enoxime. (**Procedure B**) To a stirred solution of allenamide and azodicarboxylate (1.5 equiv) was added tetrabutylammonium fluoride THF solution (2 equiv in general) at −78 or −60 °C under a nitrogen atmosphere. After 5 min, nucleophile reagent (equivalent depending on used reagent; see below) was added at the same temperature, and the mixture was warmed up to 0 °C. After 10 min, the reaction mixture was treated in the same manner of procedure A to obtain the desired α-substituted enoxime. When the R_f values of the products on TLC were equal or similar to that of DIAD or tosylhydorazides, we used DMEAD instead of DIAD for purifications. *E*/*Z* chemistry of oximes is not determined except for **9g** and **9h′**, but all were obtained as single isomers.

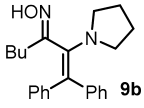
*2-(Diethylamino)-1,1-diphenylhept-1-en-3-one Oxime (**9a**).*



9a

(**Procedure A**) 25.8 mg (98%) of product **9a** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (0.113 mmol, 22 μL), diethylamine (12 μL, 0.113 mmol), and tetrabutylammonium fluoride (90 μL, 1.0 M in THF, 0.09 mmol) (silica gel column chromatography: hexane/diethyl ether = 35/1 to 10/1). Yellow oil; R_f value 0.57 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3175, 2962, 2929, 1550, 1442, 1071, 765, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, 2H, *J* = 7.0 Hz), 7.15 (m, 5H), 7.09 (tt, 1H, *J* = 7.5, 2.0 Hz), 7.03 (d, 2H, *J* = 7.0 Hz), 2.72 (q, 4H, *J* = 7.0 Hz), 2.09 (t, 2H, *J* = 8.0 Hz), 1.47 (tt, 2H, *J* = 8.0, 7.0 Hz), 1.26 (qt, 2H, *J* = 7.0, 7.5 Hz), 0.98 (t, 6H, *J* = 7.0 Hz), 0.85 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 143.8, 143.7, 141.7, 130.8, 130.5, 127.7, 127.6, 125.7, 125.5, 123.2, 45.0, 28.9, 27.7, 23.3, 13.8, 13.3; HRMS (ESI) calcd for $C_{23}H_{31}N_2O$ $[M + H]^+$ 351.24364, found 351.24321.

*1,1-Diphenyl-2-(pyrrolidin-1-yl)hept-1-en-3-one Oxime (**9b**).*



9b

(**Procedure B**) 25.9 mg (99%) of product **9b** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), bis(2-methoxyethyl) azodicarboxylate (26.3 mg, 0.113 mmol), tetrabutylammonium fluoride (150 μL, 1.0 M in THF, 0.15 mmol), and then pyrrolidine (12.5 μL, 0.15 mmol) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/diethyl ether = 13:1). Yellow oil; R_f value 0.48 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3168, 2959, 2858, 1554, 1442, 1377, 764, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (br, 1H), 7.27−7.24(m, 2H), 7.18−7.08 (m, 8H), 2.86 (s, 4H), 2.06 (br, 2H), 1.70 (dd, 4H, *J* = 10.0, 3.0 Hz), 1.44 (tt, 2H, *J* = 8.5, 7.0 Hz), 1.27 (qt, 2H, *J* = 7.5, 7.0 Hz), 0.85 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 143.6, 143.4, 140.2, 131.0, 130.9, 127.6, 127.5, 125.3, 125.2, 119.3, 50.0, 28.5, 27.8, 25.1, 23.1, 13.8; HRMS (ESI) calcd for $C_{23}H_{29}N_2O$ $[M + H]^+$ 349.22799, found 349.22641.

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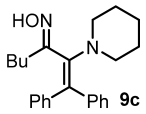
J. Org. Chem. 2016, 81, 559−574

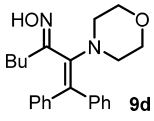
*1,1-Diphenyl-2-(piperidin-1-yl)hept-1-en-3-one Oxime (**9c**).*



9c

(**Procedure A**) 25.1 mg (92%) of product **9c** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (22 μL, 0.113 mmol), piperidine (11 μL, 0.113 mmol), and tetrabutylammonium fluoride (90 μL, 1.0 M in THF, 0.09 mmol) (silica gel column chromatography: hexane/diethyl ether = 35/1 to 10/1). Yellow oil; R_f value 0.48 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3171, 2931, 1442, 1386, 978, 765, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.50 (br, 1H), 7.29 (t, 2H, J = 7.5 Hz), 7.19−7.15 (m, 3H), 7.12−7.09 (m, 1H), 7.05 (d, 4H, J = 7.5 Hz), 2.59 (br, 4H), 2.10 (t, 2H, J = 7.0 Hz), 1.50−1.43 (m, 8H, J = 7.0, 7.5 Hz), 1.27 (qt, 2H, J = 7.0, 7.5 Hz), 0.85 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 144.6, 143.64, 143.62, 130.7, 130.6, 127.7, 127.6, 125.8, 125.7, 123.5, 52.0, 28.4, 27.8, 26.3, 24.2, 23.2, 13.8; HRMS (ESI) calcd for $C_{24}H_{31}N_2O$ $[M + H]^+$ 363.24364, found 363.24339.

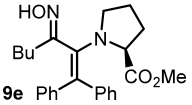
*2-Morpholino-1,1-diphenylhept-1-en-3-one Oxime (**9d**).*



9d

(**Procedure A**) 19.2 mg (70%) of product **9d** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (22 μL, 0.113 mmol), morpholine (10 μL, 0.113 mmol), and tetrabutylammonium fluoride (90 μL, 1.0 M in THF, 0.09 mmol) (silica gel column chromatography: toluene/ethyl acetate = 20/1). Yellow solid; R_f value 0.28 (hexane/ethyl acetate = 3/1); mp 158−160 °C; IR (NaCl, neat) ν_{max} 3172, 2958, 1442, 1263, 1116, 983, 757, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.55 (br, 1H), 7.32−7.29 (m, 2H), 7.23−7.05 (m, 8H), 3.55 (t, 4H, J = 4.5 Hz), 2.68 (t, 4H, J = 4.5 Hz), 2.10 (t, 2H, J = 8.0 Hz), 1.45 (tt, 2H, J = 8.5, 8.0 Hz), 1.27 (tq, 2H, J = 7.5, 7.0 Hz), 0.86 (t, 3H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 143.3, 143.1, 142.9, 130.7, 130.6, 128.0, 127.8, 126.4, 126.2, 125.3, 67.1, 50.9, 28.5, 27.9, 23.2, 13.8; HRMS (ESI) calcd for $C_{23}H_{28}N_2O_2Na$ $[M + Na]^+$ 387.20485, found 387.20477.

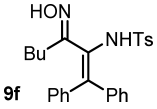
*Methyl (3-(Hydroxyimino)-1,1-diphenylhept-1-en-2-yl)-L-prolinate (**9e**).*



9e

(**Procedure B**) 22.6 mg (74%) of product **9e** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), bis(2-methoxyethyl) azodicarboxylate (26.3 mg, 0.113 mmol), tetrabutylammonium fluoride (1.0 M in THF, 150 μL, 0.15 mmol), and then methyl L-prolinate hydrochloride (37.3 mg, 0.225 mmol) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/diethyl ether = 5/1). Yellow oil ; R_f value 0.37 (hexane/ethyl acetate = 3/1); $[\alpha]_D^{20}$ + 841.7 ($CHCl_3$, c = 1.0); IR (NaCl, neat) ν_{max} 3187, 2956, 1745, 1560, 1442, 1372, 1172, 763, 700 cm^{-1}; ^1H NMR(500 MHz, $CDCl_3$) δ 9.42 (br, 1H), 7.31−7.08 (m, 10H), 3.99 (t, 1H, J = 6.5 Hz), 3.69 (s, 3H), 3.07 (q, 1H, J = 8.5 Hz), 2.79−2.75 (m, 1H), 2.41−2.35 (m, 1H), 2.12−2.05 (m, 1H), 1.83−1.64 (m, 4H), 1.34−1.14 (m, 4H), 0.81 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 158.8, 143.1, 143.0, 139.0, 131.1, 130.8, 127.7, 127.6, 125.9, 125.8, 122.8, 60.2, 52.2, 51.8, 30.4, 28.9, 27.5, 24.6, 23.1, 13.8; HRMS (ESI) calcd for $C_{25}H_{30}N_2O_3Na$ $[M + Na]^+$ 429.21541, found 429.21467.

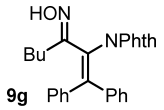
*N-(3-(Hydroxyimino)-1,1-diphenylhept-1-en-2-yl)-4-methylbenzenesulfonamide (**9f**).*



9f

(**Procedure A**) 21.9 mg (49%) of product **9f** was obtained from allenamide **2a** (54.8 mg, 0.10 mmol), bis(2-methoxyethyl) azodicarboxylate (35.0 mg, 0.15 mmol), *p*-toluenesulfonamide (0.30 mmol, 51.0 μL), and tetrabutylammonium fluoride (200 μL, 1.0 M in THF, 0.20 mmol) (silica gel column chromatography: hexane/diethyl ether = 2/1). White solid; R_f value 0.12 (hexane/ethyl acetate = 2/1); mp 158−159 °C; IR (NaCl, neat) ν_{max} 3270, 3059, 2958, 1738, 1598, 1322, 1167, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.64 (d, 2H, J = 8.0 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.26−7.13 (m, 6H), 7.00 (dd, 2H, J = 7.0, 1.0 Hz), 6.58 (dd, 2H, J = 7.0, 1.0 Hz), 5.95 (s, 1H), 2.52 (m, 5H), 1.63 (m, 2H), 1.37 (tq, 2H, J = 7.5, 7.5 Hz), 0.95 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 144.1, 139.5, 138.3, 135.6, 134.9, 129.7, 129.2, 129.0, 128.8, 128.6, 128.1, 127.9, 127.8, 127.2, 28.5, 27.2, 23.3, 21.7, 13.9; HRMS (ESI) calcd for $C_{26}H_{28}N_2O_3SNa$ $[M + Na]^+$ 471.17183, found 471.17138.

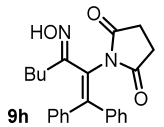
*2-(3-(Hydroxyimino)-1,1-diphenylhept-1-en-2-yl)isoindoline-1,3-dione (**9g**).*



9g

(**Procedure B**) 33.1 mg (73%) of product **9g** was obtained from allenamide **2a** (54.8 mg, 0.10 mmol), bis(2-methoxy ethyl)-azodicarboxylate (35.1 mg, 0.15 mmol), tetrabutylammonium fluoride (420 μL, 0.42 mmol, 1.0 M in THF), and then phthalimide (44.1 mg, 0.30 mmol) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/ethyl acetate = 4/1 with 1% MeOH, followed by GPC purification). White solid; R_f value 0.48 (hexane/ethyl acetate = 2/1); mp 189−190 °C; IR (NaCl, neat) ν_{max} 3404, 2958, 1720, 1377, 1115, 887 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.74−7.72 (m, 2H), 7.64−7.62 (m, 2H), 7.36−7.28 (m, 5H), 7.16−7.12 (m, 5H), 1.99−1.96 (m, 2H), 1.50−1.44 (m, 2H), 1.11 (tq, 2H, J = 7.5, 7.5 Hz), 0.76 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 159.4, 148.3, 140.7, 139.6, 133.9, 131.8, 130.2, 128.8, 128.7, 128.3, 128.2, 128.0, 123.5, 122.8, 28.0, 27.4, 23.0, 13.6; HRMS (ESI) calcd for $C_{27}H_{24}N_2O_3Na$ $[M + Na]^+$ 447.16846, found 447.16805.

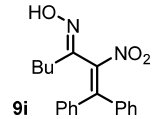
*1-(3-(Hydroxyimino)-1,1-diphenylhept-1-en-2-yl)pyrrolidine-2,5-dione (**9h**).*



9h

(**Procedure B**) 29.7 mg (79%) of product **9h** was obtained from allenamide **2a** (54.8 mg, 0.10 mmol), bis(2-methoxy ethyl)-azodicarboxylate (35.1 mg, 0.15 mmol), tetrabutylammonium fluoride (420 μL, 0.42 mmol, 1.0 M in THF), and then succinimide (29.7 mg, 0.30 mmol) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/ethyl acetate = 3/2 to 1/1, followed by GPC purification). White solid; R_f value 0.40 (hexane/ethyl acetate = 1/1); mp 130−131 °C; IR (NaCl, neat) ν_{max} 3366, 2957, 1714, 1380, 1189, 988 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.78 (br-s, 1H), 7.37−7.31 (m, 3H), 7.28−7.24 (m, 5H), 7.15−7.12 (m, 2H), 2.63 (m, 2H), 2.34 (m, 2H), 1.99 (m, 2H), 1.46 (m, 2H), 1.11 (tq, 2H, J = 7.5, 7.5 Hz), 0.75 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 158.8, 148.2 140.4, 139.1, 130.1, 128.9, 128.35, 128.32, 128.29, 128.1, 123.3, 28.2, 27.9, 27.5, 22.9, 13.6,; HRMS (ESI) calcd for $C_{23}H_{24}N_2O_3Na$ $[M + Na]^+$ 399.16846, found 399.16808.

*(E)-2-Nitro-1,1-diphenylhept-1-en-3-one Oxime (**9i**, CCDC 1056829).*



9i

(**Procedure B**) 21.8 mg (90%) of product **9i** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (22 μL, 0.113 mmol), tetrabutylammonium fluoride (150 μL, 1.0 M in THF, 0.15 mmol), and then dicyclohexylamine nitrite (51 mg, 0.225 mmol) by a reaction at −78 to 0 °C (silica gel column chromatography: hexane/diethyl ether = 20/1 to 13/1). Yellow solid; R_f value 0.42 (hexane/ethyl acetate = 3/1); mp 110−111 °C; IR (NaCl, neat)

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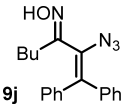
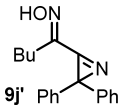
ν_{max} 3303, 2958, 1528, 1342, 976, 759, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.41−7.33 (m, 6H), 7.23−7.19 (m, 4H), 4.26 (t, 2H, J = 8.0 Hz), 1.50 (m, 2H), 1.27 (tq, 2H, J = 7.5, 7.5 Hz), 0.84 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 144.6, 143.5, 137.6, 137.1, 130.1, 129.8, 129.6, 128.7, 128.6, 128.5, 27.6, 27.0, 22.6, 13.6; HRMS (ESI) calcd for $C_{19}H_{20}N_2O_3Na$ $[M + Na]^+$ 347.13716, found 347.13687.

*2-Azido-1,1-diphenylhept-1-en-3-one Oxime (**9j**) (as an Inseparable Mixture with Azirine **9j′**).*



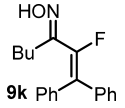
(**Procedure B**) 45.2 mg (6.7:1 determined by ^1H NMR; azide **9j** 83%, azirine **9j′** 12%) of product **9j** as an inseparable mixture with azirine **9j′** was obtained from allenamide **2a** (82.2 mg, 0.15 mmol), bis(2-methoxyethyl) azodicarboxylate (52.7 mg, 0.225 mmol), tetrabutylammonium fluoride (480 μL, 1.0 M in THF, 0.48 mmol), and then azidotrimethylsilane (40 μL, 0.30 mmol) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/ethyl acetate = 10/1). **9j** was an unstable compound, and it was gradually converted to **9j′** even in a refrigerator. Pale yellow oil; R_f value 0.55 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3263, 2959, 2105, 1444, 1298, 751, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.36−7.24 (m, 8H), 7.16−7.14 (m, 2H), 2.08 (t, 2H, J = 8.0 Hz), 1.46−1.38 (m, 2H), 1.25 (tq, 2H, J = 7.5, 7.5 Hz), 0.85 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 139.6, 139.3, 132.3, 130.3, 130.2, 129.1, 128.2, 128.0, 127.8, 127.7, 27.7, 27.6, 22.6, 13.7; LRMS (EI) m/z 320 (M^+, 0.2%), 275 (26), 182 (76), 165 (60); HRMS (EI) calcd for $C_{19}H_{20}N_4O$ (M^+) 320.1637, found 320.1620.

*One-Pot Conversion from Allenamide **2a** to Pure 1-(2,2-Diphenyl-2H-azirin-3-yl)pentan-1-one Oxime (**9j′**, CCDC 1056828) via Vinyl Azide **9j**.*



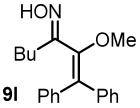
To stirred mixture of allenamide **2a** (54.8 mg, 0.10 mmol), diisopropyl azodicarboxylate (29 μL, 0.15 mmol), and azidotrimethylsilane (20 μL, 0.15 mmol) in THF (2.0 mL) was added tetrabutylammonium fluoride (270 μL, 1.0 M in THF, 0.15 mmol) at 0 °C. After 10 min, the mixture was heated under reflux condition for 15 min. The reaction mixture was extracted with ether and washed with water and brine. The combined organic layers were dried over sodium sulfate and were concentrated *in vacuo*. The resulting residual solid was purified by silica gel column chromatography (hexane/ethyl acetate = 13/1) to afford azirine **9j′** (18.1 mg, 62%). White solid; R_f value 0.55 (hexane/ethyl acetate = 3/1); mp 105−106 °C; IR (NaCl, neat) ν_{max} 3244, 2959, 1731, 1447, 1003, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.31−7.25 (m, 10H), 2.80 (t, 2H, J = 8.0 Hz), 1.68 (tt, 2H, J = 8.0, 7.5 Hz), 1.37 (tq, 2H, J = 7.5, 7.5 Hz), 0.92 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 151.2, 140.8, 128.3, 128.1, 127.4, 46.4, 27.7, 25.5, 22.7, 13.7; LRMS (EI) m/z 292 (M^+, 23%), 275 (53), 166 (47), 165 (100); HRMS (EI) calcd for $C_{19}H_{20}N_2O$ (M^+) 292.1576, found 292.1563.

*2-Fluoro-1,1-diphenylhept-1-en-3-one Oxime (**9k**).*



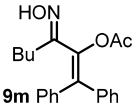
(**Procedure B**) 25.6 mg (43%) of product **9k** was obtained from allenamide **2a** (109.6 mg, 0.20 mmol), bis(2-methoxyethyl) azodicarboxylate (70.3 mg, 0.30 mmol), and tetrabutylammonium fluoride (2.0 mL, 1.0 M in THF, 2.0 mmol, used without dehydration) by a reaction at −78 to 0 °C (silica gel column chromatography: hexane/ethyl acetate = 10/1). Colorless oil; R_f value 0.57 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3232, 2958, 1444, 1186, 963, 367, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.80 (br, 1H), 7.33−7.25 (m, 8H), 7.16−7.14 (m, 2H), 2.25 (t, 2H, J = 8.0 Hz), 1.48 (tt, 2H, J = 8.0, 7.5 Hz), 1.27 (tq, 2H, J = 7.5, 7.5 Hz), 0.87 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9 (d, J_{C-F} = 29 Hz), 149.9 (d, J_{C-F} = 255 Hz), 137.7 (d, J_{C-F} = 6.0 Hz), 137.2, 130.2 (d, J_{C-F} = 4.0 Hz), 129.9 (d, J_{C-F} = 5.0 Hz), 128.3, 128.0, 127.8, 127.7, 125.6 (d, J_{C-F} = 16 Hz), 27.8, 25.9, 22.7, 13.7; ^{19}F NMR (471 MHz, $CDCl_3$, hexafluorobenzene δ −162.0) δ −109.9; HRMS (CI) calcd for $C_{19}H_{21}FNO$ $[M + H]^+$ 298.1607, found 298.1603.

*2-Methoxy-1,1-diphenylhept-1-en-3-one Oxime (**9l**).*



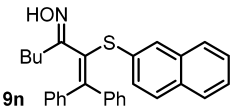
(**Procedure A**) 3.5 mg (15%) of product **9l** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (29 μL, 0.15 mmol), methanol (15 μL, 0.375 mmol), and tetrabutylammonium fluoride (150 μL, 1.0 M in THF, 0.15 mmol) (silica gel column chromatography: hexane/ethyl acetate = 35/1 to 10/1). Colorless oil; R_f value 0.46 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3195, 2957, 1596, 1443, 1211, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31−7.12 (m, 10H), 3.57 (s, 3H), 2.28 (t, 2H, J = 8.0 Hz), 1.54 (m, 2H), 1.31 (qt, 2H, J = 7.5, 7.5 Hz), 0.89 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 140.2, 139.8, 130.3, 129.7, 128.1, 127.91, 127.89, 126.9, 126.8, 58.0, 27.6, 27.4, 23.1, 13.8; HRMS (ESI) calcd for $C_{20}H_{23}NO_2Na$ $[M + Na]^+$ 332.16265, found 332.16272.

*3-(Hydroxyimino)-1,1-diphenylhept-1-en-2-yl Acetate (**9m**).*



(**Procedure A**) 17.6 mg (52%) of product **9m** was obtained from allenamide **2a** (54.8 mg, 0.10 mmol), bis(2-methoxyethyl) azodicarboxylate (35 mg, 0.15 mmol), acetic acid (29 μL, 0.50 mmol), and tetrabutylammonium fluoride (1.0 M in THF, 400 μL, 0.40 mmol) (silica gel column chromatography: hexane/ethyl acetate = 10/1 to 3/1). Colorless oil; R_f value 0.31 (hexane/ethyl acetate = 3/1); IR (NaCl, neat) ν_{max} 3255, 2958, 1764, 1444, 1212, 766, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (br, 1H), 7.32−7.16 (m, 10H), 2.05 (t, 2H, J = 8.0 Hz), 2.04 (s, 3H), 1.44 (tt, 2H, J = 8.0, 7.5 Hz), 1.14 (tq, 2H, J = 7.5, 7.0 Hz), 0.78 (t, 3H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 157.9, 139.5, 139.2, 138.7, 135.4, 130.2, 129.1, 128.3, 128.10, 128.07, 127.7, 27.7, 27.3, 22.9, 20.7, 13.6; HRMS (ESI) calcd for $C_{21}H_{23}NO_3Na$ $[M + Na]^+$ 360.15756, found 360.15721.

*2-(Naphthalen-2-ylthio)-1,1-diphenylhept-1-en-3-one Oxime (**9n**).*



(**Procedure B**) 27.4 mg (83%) of product **9n** was obtained from allenamide **2a** (0.075 mmol, 41.1 mg), diisopropyl azodicarboxylate (22 μL, 0.113 mmol), tetrabutylammonium fluoride (150 μL, 1.0 M in THF, 0.15 mmol), and then 2-naphthalenethiol (0.113 mmol, 18 mg) by a reaction at −78 to 0 °C (silica gel column chromatography: hexane/toluene = 1/1 to 1/3). Pale yellow solid; R_f value 0.43 (hexane/ethyl acetate = 3/1); mp 90−91 °C; IR (NaCl, neat) ν_{max} 3191, 2957, 1442, 944, 758, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (br, 1H), 7.73−7.63 (m, 4H), 7.42−7.37 (m, 3H), 7.32−7.14 (m, 10H), 2.29 (t, 2H, J = 8.0 Hz), 1.37 (tt, 2H, J = 8.0, 7.5 Hz), 1.21 (qt, 2H, J = 7.5, 7.0 Hz), 0.80 (t, 3H, J = 7.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 150.2, 142.1, 141.7, 133.6, 132.6, 131.8, 129.5, 129.4, 129.0, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 126.3, 125.7, 28.9, 27.7, 23.1, 13.7; LRMS (EI) m/z 437 (M^+, 53%), 420 (53), 210 (100); HRMS (EI) calcd for $C_{29}H_{27}NOS$ (M^+) 437.1813, found 437.1815.

*1,1-Diphenyl-2-(phenylsulfonyl)hept-1-en-3-one Oxime (**5b**) from Allenyl Tosylamide (**2a**).* (**Procedure B**) 41.4 mg (99%) of product **5b** was obtained from tosyl allenamide **2a** (54.8 mg, 0.10 mmol), bis(2-methoxyethyl) azodicarboxylate (35 mg, 0.15 mmol),

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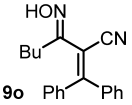
tetrabutylammonium fluoride (200 μL, 1.0 M in THF, 0.20 mmol), and then sodium benzenesulfinate (60 mg, 0.30 mmol) dissolved in methanol (1.0 mL) by a reaction at −60 to 0 °C (silica gel column chromatography: hexane/ethyl acetate = 7/1 to 3/1).

*2-(Diphenylmethylene)-3-(hydroxyimino)heptanenitrile (**9o**).*

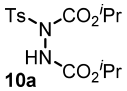


9o

(**Procedure A**) 22.1 mg (94%) of product **9o** was obtained from allenamide **2a** (41.1 mg, 0.075 mmol), diisopropyl azodicarboxylate (22 μL, 0.113 mmol), trimethylsilyl cyanide (14 μL, 0.113 mmol), and tetrabutylammonium fluoride (200 μL, 1.0 M in THF, 0.20 mmol) (silica gel column chromatography: hexane/diethyl ether = 35/1 to 10/1). No-odor white solid; R_f value 0.33 (hexane/ethyl acetate = 3/1); mp 170−172 °C; IR (NaCl, neat) ν_{max} 3278, 2954, 2208, 1555, 1444, 966, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (br, 1H), 7.46−7.34 (m, 8H), 7.18−7.16 (m, 2H), 2.13 (t, 2H, J = 8.0 Hz), 1.45 (tt, 2H, J = 8.0, 7.5 Hz), 1.25 (qt, 2H, J = 7.5, 7.5 Hz), 0.84 (t, 3H, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 157.4, 139.2, 138.6, 130.3, 130.04, 129.96, 128.5, 118.5, 107.3, 27.9, 27.2, 22.6, 13.7; HRMS (ESI) calcd for $C_{20}H_{20}N_2ONa$ $[M + Na]^+$ 327.14733, found 327.14716.

Analytical Data of 1-Tosylhydrazine-1,2-dicarboxylates. Yields of obtained hydrazides **10a−b** were not calculated, but **10a−b** was easily obtained by a general procedure of sulfinate-trapping substitutions.

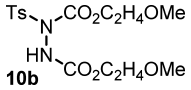
*Diisopropyl 1-Tosylhydrazine-1,2-dicarboxylate (**10a**).*



10a

Colorless crystal; R_f value 0.31 (hexane/ethyl acetate = 3/1); mp 93−95 °C; IR (NaCl, neat) ν_{max} 3331, 2984, 1743, 1375, 1241, 1175, 1103 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, 2H, J = 8.5 Hz), 7.33 (d, 2H, J = 8.5 Hz), 7.00 (s, 1H), 5.00−4.90 (m, 2H), 2.44 (s, 3H), 1.33−1.14 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 150.9,145.2, 135.0, 129.5, 129.2, 72.9, 70.9, 21.9, 21.7, 21.6; HRMS (ESI) calcd for $C_{15}H_{22}N_2NaO_6S$ $[M + Na]^+$ 381.10963, found 381.11054.

*Bis(methoxyethyl) 1-Tosylhydrazine-1,2-dicarboxylate (**10b**).*



10b

White solid; R_f value 0.25 (hexane/ethyl acetate = 1/1); mp 93 °C; IR (NaCl, neat) ν_{max} 3675, 3331, 2929, 1746, 1523, 1377, 1233, 1068 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, 2H, J = 8.0 Hz), 7.66 (s, 1H), 7.32 (d, 2H, J = 8.0 Hz), 4.34−4.20 (m, 4H), 3.63 (t, 2H, J = 4.0 Hz), 3.51 (t, 2H, J = 4.0 Hz), 3.40 (s, 3H), 3.31 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 151.4, 145.3, 134.7, 129.6, 129.2, 70.4, 69.8, 66.8, 65.5, 59.0, 58.8, 21.7; HRMS (ESI) calcd for $C_{15}H_{22}N_2NaO_8S$ $[M + Na]^+$ 413.09946, found 413.09919.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02364.

The results of low temperature IR, and ^1H and ^{13}C NMR spectra (PDF)

Crystallographic data of new compound (CCDC number 1056828) **9j′** (CIF)

Crystallographic data of new compound (CCDC number 1056829) **9i** (CIF)

Crystallographic data of new compound (CCDC number 1056830) **6** (CIF)

Crystallographic data of new compound (CCDC number 1056831) **5a′** (CIF)

Crystallographic data of new compound (CCDC number 1056832) (*Z*)-**5p** (CIF)

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Notes

The authors declare no competing financial interest.

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