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Synthesis of 2-Azaspiro[4.6]undec-7-enes from *N*-Tosyl-*N*-(3-arylpropargyl)-Tethered 3-Methylcyclohex-2-en-1-ols

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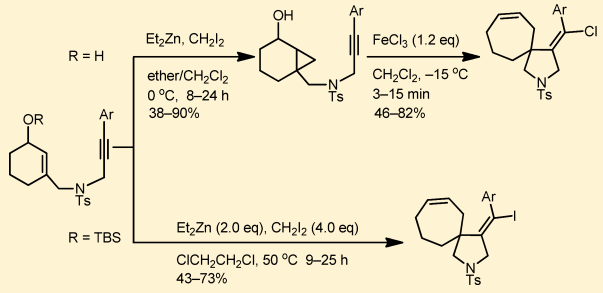
Supporting Information

ABSTRACT: The $FeCl_3$-promoted synthesis of 2-azaspiro[4.6]-undec-7-ene rings proceeds via ring expansion/cyclization/chlorination of *N*-tosyl-*N*-(3-arylpropargyl)-tethered 6-methylbicyclo[4.1.0]heptan-2-ols. This azaspirocyclic ring skeleton can also be obtained in one pot from the *tert*-butyldimethylsilyl-protected *N*-tosyl-*N*-(3-arylpropargyl)-tethered 3-methylcyclohex-2-en-1-ols and diethylzinc/diiodomethane.



INTRODUCTION

The development of facile and practical synthetic strategies for the construction of azaspirocyclic building blocks is of great importance because such ring skeletons are present in numerous natural products with a range of biological interest.[1] Therefore, many studies have been devoted to construct these structural motifs, including the ruthenium-catalyzed ring-closing metathesis reaction of nitrogen heterocycles possessing geminal olefinic side chains,[2a−d] the rhodium-catalyzed cycloaddition of *N*-tosyl-linked 1,6-dien-10-ynes followed by oxidative cleavage of the carbon−carbon double bond of the resulting azatricycles,[3] the thermolysis of *N*-unsaturated alkyl-*N*-alkyl-*β*-ketoamides,[4] the platinum(II)-catalyzed reaction of cyclic *N*-sulfonyl enamines with the terminal alkyne,[5] the cationic palladium-catalyzed ene-type cyclization of *N*-tosyl-linked cyclic 1,7-enynes,[6] the thiourea-catalyzed Michael addition of *β*-ketoamides to methyl vinyl ketone followed by spirolactamization,[7] the cationic gold(I)-catalyzed addition of silyl enol ethers to the terminal alkyne,[8] and the gold-catalyzed addition of five-membered-ring *β*-ketoamides to the tethered unactivated alkene.[9] While most of these approaches focused on synthesis of azaspiro[4.4]nonane and -[4.5]decane ring skeletons, methods for the construction of the azaspiro[4.6]-undecene scaffold were limited.[2b,6b] Herein, we report a simple and mild synthesis of (*Z*)-4-(arylchloromethylene)-substituted azaspiro[4.6]undec-7-enes from (3-arylpropargyl)tosylamide-tethered 6-methylbicyclo[4.1.0]heptan-2-ols and $FeCl_3$. In this reaction, the iron salt acts as the Lewis acid to remove the hydroxyl group of the bicyclic ynols, affording a bicyclo[4.1.0]-hept-2-yl cationic intermediate. *anti*-Addition of the cyclopropylcarbinyl cation and a chloride ion across the alkyne provides the azaspiro[4.6]undec-7-ene derivatives. Moreover, this azaspirocyclic skeleton can also be constructed in one pot by reaction of *tert*-butyldimethylsilyl-protected *N*-tosyl-*N*-propargyl-tethered 3-methylcyclohex-2-en-1-ols with diethylzinc/diiodomethane.

RESULTS AND DISCUSSION

The starting *N*-tosyl-*N*-(3-arylpropargyl)-tethered 6-methylbicyclo[4.1.0]heptan-2-ols **1** were prepared from cyclopropanation of the known *N*-tosyl-*N*-propargyl-tethered 3-methylcyclohex-2-en-1-ols[10] with the Furukawa-modified Simmons−Smith reagent derived in situ from diethylzinc and diiodomethane[11] in CH_2Cl_2 and ether at 0 °C in 68−90% yields. Compound **1a** was used as the model substrate to search optimal reaction conditions for the ring expansion/cyclization/chlorination reaction, as revealed in Table 1. A moderate yield (66%) of the desired (*Z*)-4-(chlorophenylmethylene)-2-tosyl-2-azaspiro[4.6]undec-7-ene (**2a**) was obtained when **1a** was mixed with 1.2 equiv of $FeCl_3$ in CH_2Cl_2 at 30 °C under nitrogen for 1 min (Table 1, entry 1). The *Z*-configuration of **2a** was confirmed by NMR spectroscopies and was further secured by X-ray diffraction analysis (Figure 1). A comparable yield (63%) of **2a** was achieved when the reaction was run in open air for 1 min at 30 °C (Table 1, entry 1). Therefore, the following optimization experiments were carried out under an ambient atmosphere. At 0 °C, **1a** gave **2a** in 73% yield upon treatment with 1.2 molar equiv of $FeCl_3$ for 3 min (Table 1, entry 2). Lowering the reaction temperature to −15 °C for 3 min and −78 °C for 4 h provided **2a** in 82% and 75% yields, respectively (Table 1, entries 3 and 4). The use of 1.2 equiv of $FeBr_3$ in CH_2Cl_2 at −15 °C resulted in the formation of the brominated azaspiro[4.6]undecene derivative **3**[12] (Figure 2) in 81% yield, whereas the use of $FeCl_3{\cdot}6H_2O$ was less effective and gave **2a** in 70% yield after 50 min at 30 °C (Table 1, entry

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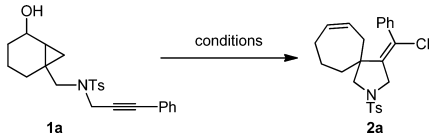
Table 1. Optimization of the Ring Expansion/Cyclization/Chlorination of 1a to 2a



1a 2a

entry	acid	solvent	temp (°C)	time	yield (%)[a]
1	$FeCl_3$	CH_2Cl_2	30	1 min	63
2	$FeCl_3$	CH_2Cl_2	0	3 min	73
3	$FeCl_3$	CH_2Cl_2	−15	3 min	82
4	$FeCl_3$	CH_2Cl_2	−78	4 h	75
5	$FeCl_3{\cdot}6H_2O$	CH_2Cl_2	30	50 min	70
6	$TiCl_4$	CH_2Cl_2	−15	1 min	67
7	$InCl_3$	CH_2Cl_2	30	25 min	54
8	$ZnCl_2$	CH_2Cl_2	30	1 h	49
9	(TMS)Cl	CH_2Cl_2	30	24 h	0
10	$Fe(OTf)_3$[b]	MeOH	30	24 h	0
11	HCl(aq)[c]	CH_2Cl_2	−15	10 min	10
12	$FeCl_3$	DCE	−15	1 min	35
13	$FeCl_3$	DBE	30	1 min	52
14	$FeCl_3$	DBM	−15	1.5 h	80
15	$FeCl_3$	CH_3CN	30	24 h	0

[a]All reactions were conducted using 0.1 M **1a** and 1.2 molar equiv of acids in the air, and yields were obtained by flash column chromatography. [b]A catalytic amount (10 mol %) of $Fe(OTf)_3$ was used. [c]An excess amount of HCl(aq) was used.

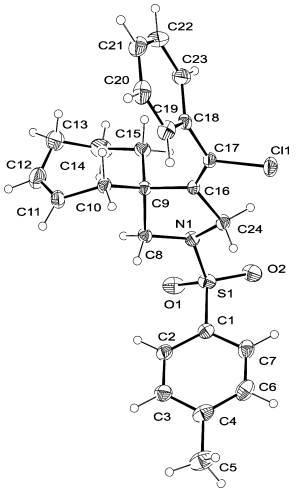


Figure 1. X-ray crystallographic structure of **2a**.

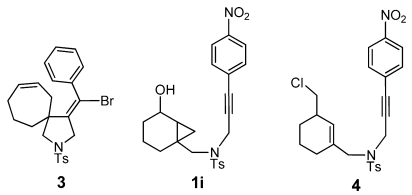


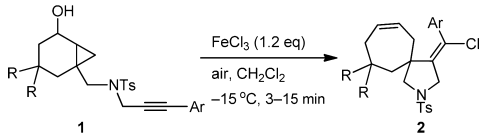
Figure 2. Compounds **3**, **1i**, and **4**.

5). The reaction of **1a** with 1.2 equiv of $TiCl_4$ in CH_2Cl_2 at −15 °C took place instantaneously and afforded **2a** in 67% yield (Table 1, entry 6), while other Lewis acids, such as $InCl_3$ and $ZnCl_2$, were much less reactive and generated **2a** in 54% and 49% yields (Table 1, entries 7 and 8), respectively. On the other hand, (TMS)Cl did not give any desired product **2a** (Table 1, entry 9), and the use of a catalytic amount of $Fe(OTf)_3$ at 30 °C for 24 h with an external source of nucleophile (MeOH, 2.0 molar equiv) did not give any cyclized products (Table 1, entry 10). Moreover, treatment of **1a** with an excess amount of concentrated HCl(aq) at −15 °C for 10 min in CH_2Cl_2 produced only a 10% yield of **2a** (Table 1, entry 11), while HBr(aq) caused the decomposition of **1a** under the same reaction conditions.

The investigation of various reaction media showed that the use of 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE) decreased the isolated yields of **2a** to 35% and 52% (Table 1, entries 12 and 13), respectively, whereas the use of dibromomethane (DBM) required an extended reaction time (1.5 h) at −15 °C and the desired **2a** was isolated in 80% yield (Table 1, entry 14). In contrast, no reaction took place in CH_3CN even after prolonged reaction at 30 °C for 24 h (Table 1, entry 15). Thus, the optimal reaction procedure follows: a mixture of **1a** and $FeCl_3$ (1.2 molar equiv) was stirred in CH_2Cl_2 at −15 °C in the air (Table 1, entry 3) until no starting substrate **1a** was detected by TLC (3 min). Although ruthenium[2b] and palladium[6b] were used to construct the azaspiro[4.6]undecane ring scaffold from unsaturated *N*-containing compounds, these protocols required complex catalyst systems and higher reaction temperatures (40−100 °C). Furthermore, the palladium-catalyzed cycloisomerization of 1,6-enynes produced the azaspiro[4.6]undecane ring skeleton needing seven-membered-ring starting substrates.[6b] The present method to the synthesis of the azaspiro[4.6]-undecenes is operated without removal of air and moisture, requiring only *N*-tosyl-linked six-membered cyclic 8-aryl-2-en-7-yn-1-ols, Et_2Zn/CH_2I_2, and $FeCl_3$ at −15 °C in the air for 3−15 min.

With a satisfactory protocol we next examined the substrate scope of this reaction. Results of the ring expansion/cyclization/chlorination of substrates **1a−h** to produce azaspiro[4.6]undecenes **2a−h** are listed in Scheme 1. It was

Scheme 1. Iron Trichloride-Promoted Synthesis of Azaspiro[4.6]undecene Derivatives 2



1 2

a : Ar = phenyl, R = H 82%
b : Ar = 4-methylphenyl, R = H 58%
c : Ar = phenyl, R = CH_3 80%
d : Ar = 4-methylphenyl, R = CH_3 63%
e : Ar = 4-bromophenyl, R = H 77%
f : Ar = 4-bromophenyl, R = CH_3 70%
g : Ar = 3-carbethoxyphenyl, R = H 46%
h : Ar = 3-methoxyphenyl, R = H 77%

observed that the reaction was quite general with a phenyl or tolyl group at the alkyne terminus, for example, **1a−d**, as the yields of desired products **2a−d** ranged from 58% to 82%. Only the *Z*-isomers of the chloro-containing azacycles **2a−d** were noticed in 400 MHz ^{1}H NMR spectra of crude mixtures (vide infra). It was found that a bromine atom at the C-4 position of the phenyl ring, for example, **1e** and **1f**, had little influence on product yields, as azaspirocycles **2e**[12] and **2f** were isolated in 77% and 70% yields, respectively. However, substrate **1g**, bearing a carbethoxy group at the C-3 position of the phenyl ring, reacted less efficiently with $FeCl_3$ to produce the desired product **2g**[12] in 46% yield. The electron-donating methoxy

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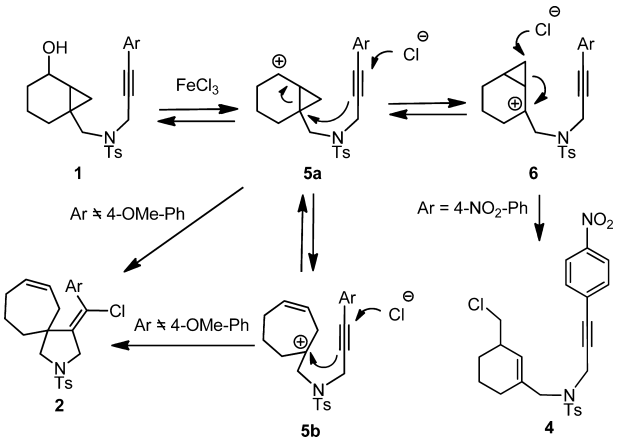
group at the C-3 position of the phenyl ring, for example, **1h**, did not affect the activity of $FeCl_3$ and afforded the corresponding azaspirocycle **2h** in 77% isolated yield. Unfortunately, the reaction of the substrate with the stronger electron-withdrawing nitro group at the C-4 position of the phenyl ring, for example, **1i** (Figure 2), failed to give any cyclized products. The homoallylic chloride **4**[12] was isolated in 64% yield (Figure 2). It must be mentioned that compounds bearing a methyl substituent at the alkynyl terminus or with a terminal alkyne led to decomposition of starting substrates upon treatment with $FeCl_3$.

A reaction pathway is speculated in Scheme 2. Detachment of the hydroxyl group of **1** by $FeCl_3$ led to the bicyclo[4.1.0]-

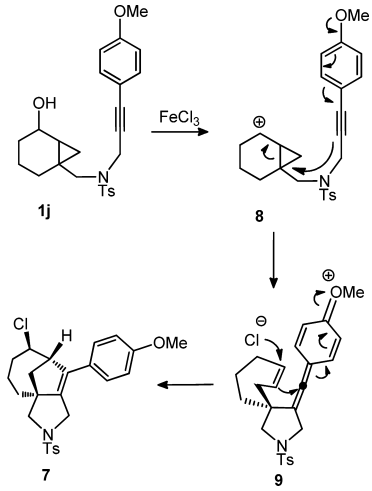
Scheme 2. Plausible Mechanism for Formation of 2 and 4



hept-2-yl cation **5a**, which may rearrange to the seven-membered tertiary cation **5b** and the bicyclic tertiary cation **6**.[13] A subsequent *anti*-addition of the cyclopropylcarbinyl cation and a chloride ion across the alkyne of **5a** gave the azaspiro[4.6]undecene derivative **2** with *Z*-selectivity. Alternatively, *anti*-addition of the tertiary cation and a chloride ion across the alkyne of **5b** also led to the formation of **2**. A similar reaction path involving a bicyclo[4.1.0]hept-2-yl cation for the synthesis of bicyclo[5.3.0]decane derivatives was reported in the literature.[14] However, cyclization/chlorination of **1i**, with a *p*-nitrophenyl group at the alkyne, did not occur, but instead attack of a chloride ion at the cyclopropyl ring of intermediate **6** took place, generating the homoallylic chloride **4** (Scheme 2).

Interestingly, compound **1j** with the electron-releasing methoxy group at the C-4 position of the phenyl ring gave the azatricyclic compound **7**[12] as the only stereoisomer isolated in 57% yield (Scheme 3). It is worth noting that three stereogenic centers of azatricycle **7** are created in a single step and only one diastereomer is isolated. The formation of **7** is suggested in Scheme 3. The initial formed bicyclo[4.1.0]hept-2-yl cation **8** was attacked by the electron-rich (*p*-methoxyphenyl)alkynyl group to give the allenyl intermediate **9**. *anti*-Addition of a chloride anion and the sp-hybridized carbon center of the allenyl moiety across the double bond led to azatricycle **7** as a single diastereomer. The stereochemistry of **7** was confirmed by a single-crystal X-ray analysis (Figure 3). A similar azatricyclic ring obtained by the platinum-catalyzed cycloisomerization of the propargyltosylamide-tethered cycloheptatriene in toluene at 90 °C for 10 h was reported in the literature.[15]

Scheme 3. Plausible Mechanism for the Formation of Compound 7



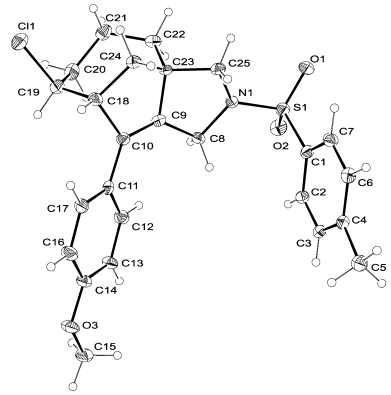
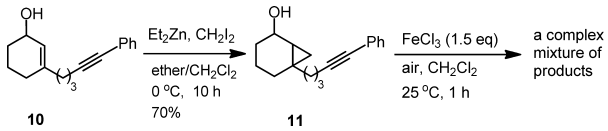


Figure 3. X-ray crystallographic structure of **7**.

Unfortunately, treatment of 5-phenyl-4-pentynyl-tethered bicyclo[4.1.0]heptan-1-ol **11**, readily accessible by cyclopropanation of the known cyclic enynol **10**,[16] gave a complex mixture of products when treated with 1.2 molar equiv of $FeCl_3$ in CH_2Cl_2 at 25 °C in the air for 3 min (Scheme 4). Much to our

Scheme 4. Reaction of Compound 11 with Iron Trichloride



delight, bicyclo[4.1.0]heptan-2-one **12a** afforded, upon reaction with 1.5 molar equiv of $FeCl_3$ in DBE at 50 °C for 1 h, a 50% yield of (*E*)-1-(chlorophenylmethylene)spiro[4.6]undecan-8-one (**13a**).[12] Several examples of the $FeCl_3$-promoted ring expansion/cyclization/chlorination of the bicyclic phenylalkynones **12a–f** to afford the C-4-substituted spiro[4.6]-undecan-8-ones **13a–f** are summarized in Scheme 5. The structure elucidation of **13** was achieved by X-ray diffraction analysis of **13a** and **13c**. In general, the $FeCl_3$-promoted synthesis of the spiro[4.6]undecan-8-one derivatives required longer reaction times (1–6 h) at 50 °C in DBE and in moderate yields (45–62%).

Surprisingly, when the cyclopropanation was performed through treatment of the *tert*-butyldimethylsilyl-protected (3-

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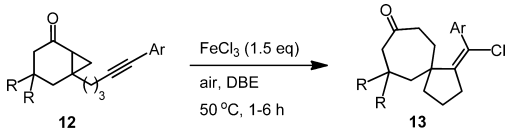
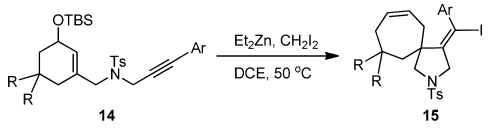
Scheme 5. Iron Trichloride-Promoted Synthesis of Spiro[4.6]undecan-8-ones 13



a : Ar = phenyl, R = H 50%
b : Ar = 4-methylphenyl, R = H 46%
c : Ar = 3-methoxyphenyl, R = H 45%
d : Ar = phenyl, R = CH_3 62%
e : Ar = 4-methylphenyl, R = CH_3 53%
f : Ar = 3-methoxyphenyl, R = CH_3 60%

arylpropargyl)sulfonamide-tethered 3-methylcyclohex-2-en-1-ol with diethylzinc and diiodomethane in DCE, the azaspiro[4.6]-undecene ring skeleton was afforded directly. Thus, the reaction of the TBS-protected *N*-tosyl-linked six-membered 8-phenyl-2-en-7-yn-1-ol **14a** with Et_2Zn and CH_2I_2 in DCE at 50 °C under 1 atm of nitrogen for 9 h resulted in the direct formation of the iodine-incorporated 2-azaspiro[4.6]undec-7-ene derivative **15a**[12] in 43% isolated yield (Table 2, entry 1). The

Table 2. One-Pot Process for the Construction of Azaspiro[4.6]undecene Derivatives 15[a]

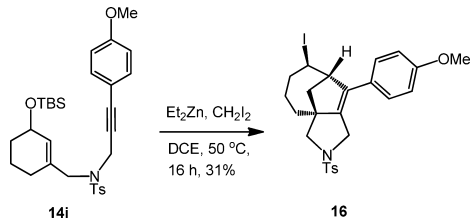


entry	substrate	R	Ar	time (h)	yield (%)
1	**14a**	H	phenyl	9	43 (**15a**)
2	**14b**	H	4-methylphenyl	25	46 (**15b**)
3	**14c**	H	4-bromophenyl	20	56 (**15c**)
4	**14d**	CH_3	phenyl	12	73 (**15d**)
5	**14e**	CH_3	4-methylphenyl	11	48 (**15e**)
6	**14f**	CH_3	4-bromophenyl	12	57 (**15f**)
7	**14g**	CH_3	3-methoxyphenyl	9	59 (**15g**)
8	**14h**	CH_3	4-phenylphenyl	9	47 (**15h**)

[a]All reactions were run in dried DCE under nitrogen, and yields were obtained after flash column chromatography.

advantageous feature of this procedure is that it is a one-pot process in which the cyclopropanation of the olefin, the ring expansion of the resulting bicyclo[4.1.0]heptane ring, and cyclization/iodination of the newly formed *N*-propargyl-tethered cyclopropylcarbinyl cation proceeded successively to provide azaspirocycle **15a**. It was suggested that the initial formed ZnI_2, generated from Et_2Zn and CH_2I_2, may trigger the desiloxylation of **14a** to form a bicyclo[4.1.0]hept-2-yl cation which then undergoes the same ring expansion/cyclization/halogenation as that found for intermediate **5**, affording **15a** as a single stereoisomer. Several examples of (*Z*)-4-(iodoaryl-methylene)-2-tosyl-2-azaspiro[4.6]undec-7-enes in a multistep, one-pot synthesis from TBS-protected *N*-tosyl-linked six-membered cyclic 8-aryl-2-en-7-yn-1-ols **14** and Et_2Zn/CH_2I_2 are listed in Table 2. In general, the one-pot process required a higher reaction temperature (50 °C) and longer reaction times (9−25 h) in DCE under nitrogen. As illustrated in Table 2, substrate **14d** with two methyl groups at the C-5 position of the six-membered ring obtained the best result (73%, Table 2, entry 4). Moreover, substrate **14i** with the C-4 methoxyphenyl group at the alkyne terminus underwent a reaction with Et_2Zn/CH_2I_2 analogous to that observed for **1j**, generating the iodine-containing azatricycle **16**[12] as the only diastereomer in 31% yield (Scheme 6).

Scheme 6. Diethylzinc/Diiodomethane-Promoted Synthesis of Azatricycle 16



In conclusion, this work showed simple and mild methods for the construction of (*Z*)-4-(arylchloromethylene)-substituted azaspiro[4.6]undecene ring skeletons from *N*-tosyl-*N*-(3-arylpropargyl)-tethered 3-methylcyclohex-2-en-1-ol, diethylzinc/diiodomethane, and the economic and environmentally friendly iron trichloride. This azaspirocyclic ring skeleton can be obtained directly from treatment of TBS-protected *N*-tosyl-*N*-(3-arylpropargyl)-tethered 3-methylcyclohex-2-en-1-ol with diethylzinc/diiodomethane. Further studies on the one-pot synthesis of other heterocycles using the Furukawa reagent are currently under way in our laboratory.

EXPERIMENTAL SECTION

General Considerations. All Lewis acids, dichloromethane (DCM), and dibromoethane (DBE) were purchased from commercial sources and were used without further purification. Dichloroethane (DCE) used for general procedure V was dried by passage through Al_2O_3. Flash column chromatography was carried out with silica gel (230−400 mesh) using the indicated solvents. All melting points were determined in open capillaries and are uncorrected. ^1H nuclear magnetic resonance (NMR) spectra were obtained with 400 and 500 MHz spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm) as the internal standard. ^{13}C NMR spectra were recorded with 100 and 125 MHz spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded as neat solutions. High-resolution mass spectra were obtained with a double-focusing mass spectrometer.

General Procedure I for the Synthesis of Starting Substrates 1. To a solution of 1,3-cyclohexanedione (3.360 g, 30 mmol) and isobutanol (10 mL, 108 mol) in toluene (20 mL) was added *p*-toluenesulfonic acid (0.260 g, 1.50 mmol). The reaction mixture was heated to reflux to remove water using a Dean−Stark apparatus. After 10 h, the mixture was cooled to room temperature followed by addition of triethylamine (0.50 mL, 3.73 mmol), and the mixture was concentrated under reduced pressure. The crude mixture was purified via flash chromatography (silica gel, 50% ethyl acetate/hexanes) to give 3-isobutoxycyclohex-2-en-1-one (4.45 g, 26.4 mmol, 88%). To a stirred solution of tetramethylethylenediamine (9.06 mL, 60 mmol) at 0 °C was added *n*-BuLi (1.6 M, 37.5 mL, 60 mmol) dropwise, and the mixture was stirred at 0 °C for 0.5 h followed by addition of dimethyl sulfide (4.43 mL, 60 mmol). The resulting mixture was stirred at room temperature for 4 h. The mixture was cooled to −78 °C, and then 3-isobutoxy-2-cyclohexen-1-one (5.040 g, 30 mmol) in THF (30 mL) was added. The reaction mixture was further stirred for 2 h at room temperature followed by addition of 2.5 N HCl(aq) (40 mL) at 0 °C. The reaction mixture was extracted with ether (30 mL × 4). The mixture was concentrated under reduced pressure. The crude mixture was purified via flash chromatography (silica gel, 10% ethyl acetate/hexanes) to give 3-((methylthio)methyl)cyclohex-2-en-1-one (3.840 g, 24.6 mmol, 82%). To a stirred solution of 3-((methylthio)methyl)-cyclohex-2-en-1-one (3.50 g, 22.4 mmol) in 25 mL of CH_2Cl_2 was

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added methyl iodide (12.710 g, 89.6 mmol) at room temperature. The mixture was heated at 45 °C for 3 days in a sealed tube. The reaction mixture was poured into $Na_2S_2O_3$(aq) (20 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic extracts were dried to give the crude 3-(iodomethyl)cyclohex-2-en-1-one. The crude product was used for the following step without further purification. To the crude 3-(iodomethyl)cyclohex-2-en-1-one (0.98 g, 4.15 mmol) and K_2CO_3 in 6 mL of acetone was added 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (0.91g, 3.190 mmol) in 6.0 mL of acetone via syringe. The mixture was reacted at room temperature for 10 h. The reaction mixture was concentrated, poured into saturated NH_4Cl(aq), and extracted with CH_2Cl_2 (10 mL × 3). The combined organic extracts were dried. The crude mixture was purified via flash chromatography (silica gel, 30% ethyl acetate/hexanes) to give of the crude 4-methyl-*N*-((3-oxocyclohex-1-en-1-yl)methyl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1.01 g, 2.57 mmol, 81%). To a solution of the crude 4-methyl-*N*-((3-oxocyclohex-1-en-1-yl)methyl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (2.10 g, 5.34 mmol) and $CeCl_3{\cdot}7H_2O$ (1.99 g, 5.34 mol) in MeOH (25 mL) at 0 °C was added $NaBH_4$ (0.240 g, 6.41 mmol), and the mixture was stirred for 1 h. The mixture was concentrated under reduced pressure, poured into saturated NH_4Cl(aq), and extracted with CH_2Cl_2 (10 mL × 3). The combined organic extracts were dried to give *N*-((3-hydroxycyclohex-1-en-1-yl)methyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide. To the above crude enynol was added Et_2Zn (1.5 M, 10.68 mL, 16.02 mmol) in ether/CH_2Cl_2 (20 mL/5 mL) followed by slow addition of CH_2I_2 (5.72 g, 21.36 mmol) at 0 °C, and the reaction mixture was allowed to stir at 30 °C for 10 h. The reaction mixture was poured into saturated NH_4Cl(aq) (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The crude mixture was purified via flash chromatography (silica gel, 30% ethyl acetate/hexanes) to give **1a**.

*Data for (±)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)-methyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1a**):* yield 1.99 g (4.59 mmol, 86%); white solid; mp 131−132 °C; IR (CH_2Cl_2) 3383, 2935, 1599, 1443, 1347, 1162, 1116, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2 H), 7.31−7.17 (m, 5 H), 7.04−6.95 (m, 2 H), 4.50 (d, *J* = 18.6 Hz, 1 H), 4.39 (d, *J* = 18.6 Hz, 1 H), 4.28−4.17 (m, 1 H), 3.14 (d, *J* = 13.0 Hz, 1 H), 3.04 (d, *J* = 13.0 Hz, 1 H), 2.32 (s, 3 H), 2.09−2.00 (m, 1 H), 1.68−1.63 (m, 1 H), 1.55−1.37 (m, 3 H), 1.29−1.15 (m, 2 H), 1.11−0.97 (m, 1 H), 0.66−0.60 (m, 1 H), 0.60−0.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 135.9, 131.4, 129.5, 128.4, 128.1, 127.7, 122.0, 86.2, 81.4, 66.5, 54.8, 36.7, 29.8, 25.1, 23.6, 21.4, 20.4, 20.1, 12.1; HRMS (ESI) *m/e* 432.1603, calcd for $C_{24}H_{27}NO_3NaS$ $[M + Na]^+$ 432.1603.

*Data for (±)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)-methyl)-4-methyl-N-(3-p-tolylprop-2-yn-1-yl)benzenesulfonamide (**1b**):* yield 0.60 g (1.35 mmol, 90%) from the corresponding enone (0.61 g, 1.50 mmol); white solid; mp 130−131 °C; IR (CH_2Cl_2) 3375, 2935, 1598, 1347, 1161, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 4.49 (d, *J* = 18.6 Hz, 1 H), 4.38 (d, *J* = 18.6 Hz, 1H), 4.28−4.20 (m, 1 H), 3.14 (d, *J* = 13.0 Hz, 1 H), 3.03 (d, *J* = 13.0 Hz, 1 H), 2.33 (s, 3H), 2.32 (s, 3 H), 2.09−1.99 (m, 1 H), 1.69−1.60 (m, 1 H), 1.57−1.43 (m, 1 H), 1.43−1.38 (br, 1 H), 1.30−1.16 (m, 2 H), 1.11−0.98 (m, 1 H), 0.68−0.60 (m, 1 H), 0.60−0.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.4, 135.7, 131.1, 129.3, 128.6, 127.5, 118.7, 86.1, 80.5, 66.1, 54.6, 36.5, 29.5, 25.0, 23.4, 21.2, 20.1, 20.0, 12.0; HRMS (ESI) *m/e* 446.1761, calcd for $C_{25}H_{29}NO_3NaS$ $[M + Na]^+$ 446.1766.

*Data for (±)-N-(((1R,5R,6S)-5-hydroxy-3,3-dimethylbicyclo[4.1.0]-heptan-1-yl)methyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (**1c**):* yield 0.30 g (0.64 mmol, 64%) from the corresponding enone (0.42 g, 1.00 mmol); white solid; mp 143−144 °C; IR (CH_2Cl_2) 3380, 2953, 1490, 1347, 1162, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2 H), 7.29−7.20 (m, 5 H), 7.00 (d, *J* = 7.2 Hz, 2 H), 4.59 (d, *J* = 18.7 Hz, 1 H), 4.39 (d, *J* = 18.6 Hz, 1 H), 4.39−4.31 (m, 2 H), 3.47 (d, *J* = 13.0 Hz, 1 H), 2.73 (d, *J* = 13.0 Hz, 1 H), 2.33 (s, 3 H), 1.89 (d, *J* = 14.4 Hz, 1 H), 1.57−1.50 (m, 1 H), 1.33 (br s, 1 H), 1.23−1.15 (m, 2 H), 0.93 (s, 3 H), 0.90 (s, 3 H), 0.83−0.71 (m, 2 H), 0.46 (t, *J* = 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.0, 131.4, 129.4, 128.4, 128.1, 127.7, 122.0, 86.2, 81.4, 65.3, 55.3, 41.8, 39.3, 36.9, 32.0, 31.5, 25.6, 22.0, 21.3, 20.6, 14.4; HRMS (ESI) *m/e* 460.1913, calcd for $C_{26}H_{31}NO_3SNa$ $[M + Na]^+$ 460.1913.

*Data for (±)-N-(((1R,5R,6S)-5-hydroxy-3,3-dimethylbicyclo[4.1.0]-heptan-1-yl)methyl)-4-methyl-N-(3-p-tolylprop-2-yn-1-yl)-benzenesulfonamide (**1d**).* yield 0.31 g (0.65 mmol, 65%) from the corresponding enone (0.44 g, 1.00 mmol); white solid; mp 134−135 °C; IR (CH_2Cl_2) 3379, 2952, 1449, 1347, 1161, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2 H), 7.26−7.22 (m, 2 H), 7.02 (d, *J* = 7.9 Hz, 2 H), 6.89 (d, *J* = 8.0 Hz, 2 H), 4.57 (d, *J* = 18.4 Hz, 1 H), 4.35 (d, *J* = 18.4 Hz, 1 H) 4.37−4.29 (m, 1 H), 3.44 (d, *J* = 13.0 Hz, 1 H), 2.72 (d, *J* = 13.0 Hz, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 1.88 (d, *J* = 14.2 Hz, 1 H), 1.56−1.49 (m, 1 H), 1.20−1.14 (m, 2 H), 1.41 (s, 1 H), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.82−0.70 (m, 1 H), 0.44 (t, *J* = 5.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.6, 136.1, 131.4, 129.5, 128.9, 127.8, 119.0, 86.3, 80.7, 65.4, 55.3, 41.8, 39.3, 37.0, 32.0, 31.5, 25.6, 22.0, 21.4, 20.6, 14.4; HRMS (ESI) *m/e* 474.2072, calcd for $C_{27}H_{33}NO_3SNa$ $[M + Na]^+$ 474.2079.

*Data for (±)-N-(3-(4-bromophenyl)prop-2-yn-1-yl)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)methyl)-4-methyl-benzenesulfonamide (**1e**):* yield 0.67 g (1.32 mmol, 88%) from the corresponding enone (0.71 g, 1.50 mmol); white solid; mp 130−132 °C; IR (CH_2Cl_2) 3393, 2928, 1598, 1346, 1161, 1115, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 4.49 (d, *J* = 18.7 Hz, 1 H), 4.38 (d, *J* = 18.7 Hz, 1 H), 4.23 (br s, 1 H), 3.14 (d, *J* = 13.0 Hz, 1 H), 3.04 (d, *J* = 13.0 Hz, 1 H), 2.35 (s, 3 H), 2.10−1.98 (m, 1 H), 1.73−1.62 (m, 1 H), 1.57−1.44 (m, 2 H), 1.42−1.34 (m, 1 H), 1.30−1.16 (m, 2 H), 1.11−1.00 (m, 1 H), 0.67−0.61 (m, 1 H), 0.61−0.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 135.5, 132.6, 131.0, 129.2, 127.4, 122.3, 120.6, 84.7, 82.5, 65.9, 54.6, 36.3, 29.3, 24.8, 23.3, 21.1, 19.9, 12.0; HRMS (ESI) *m/e* 510.0718, calcd for $C_{24}H_{26}BrNO_3NaS$ $[M + Na]^+$ 510.0714.

*Data for (±)-N-(3-(4-bromophenyl)prop-2-yn-1-yl)-N-(((1R,5R,6S)-5-hydroxy-3,3-dimethylbicyclo[4.1.0]heptan-1-yl)-methyl)-4-methylbenzenesulfonamide (**1f**):* yield 0.37 g (0.68 mmol, 68%) from the corresponding enone (0.50 g, 1.00 mmol); white solid; mp 121−122 °C; IR (CH_2Cl_2) 3394, 2952, 1485, 1347, 1161, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1 H), 7.39−7.34 (m, 1 H), 7.27−7.22 (m, 1 H), 6.90−6.82 (m, 1 H), 4.56 (d, *J* = 18.4 Hz, 1 H), 4.41−4.30 (m, 2 H) 3.45 (d, *J* = 13.1 Hz, 1 H), 2.71 (d, *J* = 13.1 Hz, 1 H), 2.34 (s, 3 H), 1.89−1.83 (m, 1 H), 1.57−1.50 (m, 1 H), 1.37−1.28 (m, 1 H), 1.22−1.13 (m, 1 H), 0.92 (s, 3 H), 0.90 (s, 3 H), 0.83−0.75 (m, 1 H), 0.73−0.67 (m, 1 H), 0.46 (t, *J* = 5.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 135.5, 132.6, 131.0, 129.2, 127.4, 122.3, 120.6, 84.7, 82.5, 65.9, 54.6, 36.3, 29.3, 24.8, 23.3, 21.1, 19.9, 12.0; HRMS (ESI) *m/e* 538.1027, calcd for $C_{26}H_{30}BrNO_3SNa$ $[M + Na]^+$ 538.1036.

*Data for (±)-ethyl 3-(3-(N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]-heptan-1-yl)methyl)-4-methylbenzenesulfonamido)prop-1-yn-1-yl)-benzoate (**1g**):* yield 0.51 g (1.02 mmol, 68%) from the corresponding enone (0.70 g, 1.50 mmol); colorless oil; IR (CH_2Cl_2) 3412, 2937, 1719, 1599, 1347, 1229, 1161, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.90 (m, 1 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.70−7.68 (m, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.20−7.16 (m, 1 H), 4.50 (d, *J* = 18.7 Hz, 1 H), 4.43−4.35 (m, 3 H), 4.26−4.18 (m, 1 H), 3.14 (d, *J* = 13.0 Hz, 1 H), 3.05 (d, *J* = 13.0 Hz, 1 H), 2.29 (s, 3 H), 2.07−1.97 (m, 1 H), 1.70−1.57 (m, 2 H), 1.56−1.44 (m, 2 H), 1.41(t, *J* = 7.1 Hz, 3 H), 1.28−1.17 (m, 2 H), 1.11−1.01 (m, 1 H), 0.67−0.61 (m, 1 H), 0.60−0.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 143.6, 135.7, 135.4, 132.4, 130.6, 129.4, 129.3, 128.2, 127.7, 122.3, 85.1, 82.4, 66.4, 61.2, 54.8, 36.5, 29.7, 25.1, 23.6, 21.3, 20.4, 20.1, 14.3, 12.1; HRMS (ESI) *m/z* = 504.1812, calcd for $C_{27}H_{31}NO_5NaS$ $[M + Na]^+$ 504.1821.

*Data for (±)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)-methyl)-N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzene-sulfonamide (**1h**):* yield 0.41 g (0.89 mmol, 82%) from the corresponding enone (0.46 g, 1.08 mmol); white solid; mp 122−123 °C; IR (CH_2Cl_2) 3403, 2936, 1598, 1347, 1290, 1162, 1116, 1092, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2 H),

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7.24 (d, J = 8.0 Hz, 2 H), 7.13 (t, J = 8.0 Hz, 1 H), 6.85−6.79 (m, 2 H), 6.58 (d, J = 7.6 Hz, 1 H), 6.53 (s, 1 H), 4.49 (d, J = 18.6 Hz, 1 H), 4.39 (d, J = 18.8 Hz, 1 H), 3.77 (s, 3 H), 3.13 (d, J = 13.0 Hz, 1 H), 3.03 (d, J = 13.0 Hz, 1 H), 2.33 (s, 3 H), 2.08−1.98 (m, 1 H), 1.72−1.60 (m, 1 H), 1.54−1.42 (m, 3 H), 1.28−1.17 (m, 2 H), 1.11−0.99 (m, 1 H), 0.63 (t, J = 5.4 Hz, 1 H), 0.60−0.53 (m, 1 H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 143.4, 135.5, 132.0, 129.3, 128.5, 127.5, 123.1, 87.0, 84.0, 66.0, 54.9, 36.3, 29.3, 24.9, 23.3, 21.1, 20.0, 19.9, 12.6; HRMS (ESI) m/e 462.1719, calcd for $C_{25}H_{29}NO_4SNa$ [M + Na]$^+$ 462.1715.

*Data for (±)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)methyl)-4-methyl-N-(3-(4-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (**1i**):* yield 0.36 g (0.79 mmol, 38%) from the corresponding enone (0.91 g, 2.08 mmol); white solid; mp 101−103 °C; IR (CH_2Cl_2) 3393, 2937, 1594, 1519, 1344, 1161, 1092, 854 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dt, J = 8.8, 2.0 Hz, 2 H), 7.74 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.14 (dt, J = 8.8, 2.0 Hz, 2 H), 4.52 (d, J = 18.8 Hz, 1 H), 4.43 (d, J = 18.8 Hz, 1 H), 4.26−4.18 (m, 1 H), 3.14 (d, J = 13.1 Hz, 1 H), 3.06 (d, J = 13.1 Hz, 1 H), 2.34 (s, 3 H), 2.06−1.97 (m, 1 H), 1.70−1.59 (m, 1 H), 1.55−1.40 (m, 3 H), 1.29−1.15 (m, 2 H), 1.12−1.00 (m, 1 H), 0.66 (t, J = 5.4 Hz, 1 H), 0.58−0.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 134.4, 135.5, 132.0, 129.3, 128.5, 127.5, 123.1, 87.0, 84.0, 66.0, 54.9, 36.3, 29.3, 24.9, 23.3, 21.1, 20.0, 19.9, 12.1; HRMS (ESI$^-$) m/e 453.1476, calcd for $C_{24}H_{25}N_2O_5S$ [M + H]$^-$ 453.1484.

*Data for (±)-N-(((1S,5R,6S)-5-hydroxybicyclo[4.1.0]heptan-1-yl)methyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**1j**):* yield 0.47 g (1.02 mmol, 79%) from the corresponding enone (0.55 g, 1.29 mmol); white solid; mp 124−125 °C; IR (CH_2Cl_2) 3386, 2936, 1606, 1346, 1249, 1161,1092, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 6.95 (d, J = 8.4 Hz, 2 H), 6.75 (d, J = 8.4 Hz, 2 H), 4.50 (d, J = 18.6 Hz, 1 H), 4.38 (d, J = 18.6 Hz, 1 H), 4.27−4.18 (m, 1 H), 3.79 (s, 3 H), 3.14 (d, J = 13.2 Hz, 1 H), 3.03 (d, J = 13.2 Hz, 1 H), 2.35 (s, 3 H), 2.10−1.98 (m, 1 H), 1.72−1.60 (m, 1 H), 1.51−1.41 (m, 3 H), 1.30−1.15 (m, 2 H), 1.12−0.98 (m, 1 H), 0.62−0.57 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 143.3, 135.5, 132.0, 129.3, 128.5, 127.5, 123.1, 87.0, 84.0, 66.0, 54.9, 36.3, 29.3, 24.9, 23.3, 21.1, 20.0, 19.9, 12.0; HRMS (ESI) m/e 462.1706, calcd for $C_{25}H_{29}NO_4NaS$ [M + Na]$^+$ 462.1715.

General Procedure II for Formation of Compounds 2a−h, 3, 4, and 7. To a 25 mL oven-dried round-bottom flask equipped with a stir bar were added compound **1a** (0.10 g, 0.25 mmol), CH_2Cl_2 (2.5 mL), and $FeCl_3$ (0.049 g, 0.30 mmol) at −15 °C under air. The reaction mixture was stirred at −15 °C for 3 min. The solvent was concentrated, and the residue was added to 10 mL of water. The resulting mixture was extracted with diethyl ether (10 × 3 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a bed of Celite, and concentrated to give the crude mixture. The crude mixture was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2a**.

*(Z)-4-(Chlorophenylmethylene)-2-tosyl-2-azaspiro[4.6]-undec-7-ene (**2a**).* The crude mixture from general procedure II (**1a**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2a** (0.088 g, 0.21 mmol, 82%) as a pale yellow solid: mp 191−193 °C; IR (CH_2Cl_2) 2930, 1598, 1450, 1349, 1162, 1094 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2 H), 7.38 (d, J = 8.5 Hz, 2 H), 7.34−7.33 (m, 3 H), 7.26−7.24 (m, 2 H), 5.79−5.74 (m, 1 H), 5.51−5.45 (m, 1 H), 4.08 (d, J = 15.5 Hz, 1 H), 4.03 (d, J = 15.5 Hz, 1 H), 3.17 (d, J = 9.5 Hz, 1 H), 3.11 (d, J = 9.5 Hz, 1 H), 2.47 (s, 3 H), 2.05−2.00 (m, 1 H), 1.95 (d, J = 6.6 Hz, 2 H), 1.85−1.81 (m, 1 H), 1.74−1.68 (m, 1 H), 1.46−1.36 (m, 2 H), 1.20−1.13 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.4, 138.1, 134.0, 132.4, 129.8, 129.3, 128.9, 128.3, 128.0, 127.6, 125.3, 57.0, 53.7, 48.5, 39.8, 36.2, 28.4, 22.8, 21.6; HRMS (ESI) m/e calcd for $C_{24}H_{27}ClNO_2S$ (M + H)$^+$ 428.1451, found 428.1446. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*(Z)-4-(Chloro-p-tolylmethylene)-2-tosyl-2-azaspiro[4.6]-undec-7-ene (**2b**).* The crude mixture from general procedure II (**1b**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2b** (0.064 g, 0.15 mmol, 58%) as a white solid: mp 191−192 °C; IR (CH_2Cl_2) 2925, 1598, 1350, 1162, 1094 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.13 (s, 4 H), 5.81−5.72 (m, 1 H), 5.53−5.44 (m, 1 H), 4.07 (d, J = 15.4 Hz, 1 H), 4.01 (d, J = 15.4 Hz, 1 H), 3.18 (d, J = 9.5 Hz, 1 H), 3.09 (d, J = 9.6 Hz, 1 H), 2.46 (s, 3 H), 2.35 (s, 3 H), 2.08−1.98 (m, 1 H), 1.98−1.88 (m, 2 H), 1.88−1.79 (m, 1 H), 1.79−1.68 (m, 1 H), 1.50−1.36 (m, 2 H), 1.24−1.11 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.1, 138.8, 133.9, 132.4, 129.7, 129.1, 128.9, 127.9, 127.6, 125.5, 56.9, 53.7, 48.4, 39.7, 36.2, 28.3, 22.7, 21.5, 21.3; HRMS (ESI) m/e 442.1611, calcd for $C_{25}H_{29}ClNO_2S$ [M + H]$^+$ 442.1608.

*(Z)-4-(Chlorophenylmethylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]-undec-7-ene (**2c**).* The crude mixture from general procedure II (**1c**, 0.12 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2c** (0.091 g, 0.20 mmol, 80%) as a white solid: mp 134−135 °C; IR (CH_2Cl_2) 2953, 1482, 1350, 1162, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8 Hz, 2 H), 7.39 (d, J = 8 Hz, 2 H), 7.32−7.22 (m, 3 H), 7.17 (d, J = 8.0 Hz, 2 H), 5.73−5.58 (m, 2 H), 4.01 (d, J = 15.2 Hz, 1 H), 3.75 (d, J = 15.2 Hz, 1 H), 3.50 (d, J = 9.2 Hz, 1 H), 3.09 (d, J = 9.2 Hz, 1 H), 2.48 (s, 3 H), 2.11 (d, J = 7.6 Hz, 2 H), 1.74−1.68 (m, 2 H), 1.37 (s, 2 H), 0.80 (s, 3 H), 0.59 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.7, 132.3, 132.2, 129.7, 128.5, 128.2, 128.0, 92.8, 61.1, 58.8, 51.6, 51.1, 40.0, 35.3, 34.6, 33.3, 26.4, 21.6. HRMS (ESI) m/e $C_{26}H_{31}ClNO_2S$ [M + H]$^+$ calcd 456.1764, found 456.1760.

*(Z)-4-(Chloro-p-tolylmethylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]undec-7-ene (**2d**).* The crude mixture from general procedure II (**1d**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2d** (0.074 g, 0.16 mmol, 63%) as a white solid: mp 138−139 °C; IR (CH_2Cl_2) 2952, 1482, 1351, 1162, 1094 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 16 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.16−7.08 (m, 4 H), 5.54−5.72 (m, 2 H), 3.96 (d, J = 15 Hz, 1 H), 3.75 (d, J = 15 Hz, 1 H), 3.44 (d, J = 9.5 Hz, 1 H), 3.12 (d, J = 9.5 Hz, 1 H), 2.48 (s, 3 H), 2.33 (s, 3 H), 2.14−2.04 (m, 2 H), 1.77−1.66 (m, 2 H), 1.77−1.66 (m, 2 H), 0.82 (s, 3 H), 0.62 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 143.7, 141.0, 138.2, 132.3, 129.8, 128.7, 128.6, 128.1, 128.0, 93.3, 61.2, 58.8, 51.6, 51.1, 40.1, 35.4, 34.7, 33.4, 26.5, 21.6, 21.3. HRMS (ESI) m/e $C_{27}H_{33}ClNO_2S$ [M + H]$^+$ calcd 470.1921, found 470.1924.

*(Z)-4-((4-Bromophenyl)chloromethylene)-2-tosyl-2-azaspiro[4.6]-undec-7-ene (**2e**).* The crude mixture from general procedure II (**1e**, 0.12 g, 0.24 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2e** (0.10 g, 0.20 mmol, 82%) as a white solid: mp 205−206 °C; IR (CH_2Cl_2) 2930, 1598, 1351, 1159, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8 Hz, 2 H), 7.13 (d, J = 8.4 Hz, 2 H), 5.84−5.75 (m, 1 H), 5.54−5.44 (m, 1 H), 4.07 (d, J = 15.8 Hz, 1 H), 4.00 (d, J = 15.5 Hz, 1 H), 3.18 (d, J = 9.6 Hz, 1 H), 3.10 (d, J = 9.6 Hz, 1H), 2.47 (s, 3 H), 2.12−2.00 (m, 1 H), 1.94 (d, J = 6.8 Hz, 2 H), 1.89−1.80 (m, 1 H), 1.80−1.70 (m, 1 H), 1.51−1.43 (m, 1 H), 1.42−1.30 (m, 1 H), 1.25−1.12 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 143.8, 137.0, 134.1, 132.3, 131.6, 130.9, 129.7, 127.9, 127.3, 123.9, 123.2, 56.8, 53.7, 48.5, 39.9, 36.3, 28.3, 22.7, 21.6; HRMS (FAB$^+$) m/e 506.0547, calcd for $C_{24}H_{26}BrClNO_2S$ [M + H]$^+$ 506.0556. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*(Z)-4-((4-Bromophenyl)chloromethylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]undec-7-ene (**2f**).* The crude mixture from general procedure II (**1f**, 0.14 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2f** (0.093 g, 0.18 mmol, 70%) as a white solid: mp 140−143 °C; IR (CH_2Cl_2) 2954, 1598, 1482, 1349, 1162, 1095 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 9.5 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.0 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 5.75−5.67 (m, 1 H), 5.66−5.62 (m, 1 H), 3.97 (d, J = 15.0 Hz, 1 H), 3.87 (d, J = 15.0 Hz, 1 H), 3.46 (d, J = 9.0 Hz, 1 H), 3.16 (d, J = 9.0 Hz, 1 H), 2.50 (s, 3

H), 2.10 (d, J = 6.5 Hz, 2 H), 1.81−1.72 (m, 2 H), 1.45 (d, J = 14.5 Hz, 1 H), 1.39 (d, J = 14.5 Hz, 1 H), 0.85 (s, 3 H), 0.68 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 143.9, 142.7, 132.5, 131.3, 129.9, 129.8, 128.3, 128.0, 122.3, 90.9, 61.2, 58.7, 51.9, 51.3, 40.1, 35.5, 34.7, 33.5, 26.4, 21.6. HRMS (FAB) m/e $C_{26}H_{30}BrClNO_2S$ $[M + H]^+$ calcd 534.0869, found 534.0864.

*(Z)-Ethyl 3-(chloro(2-tosyl-2-azaspiro[4.6]undec-7-en-4-ylidene)-methyl)benzoate (**2g**).* The crude mixture from general procedure II (**1g**, 0.13 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2g** (0.058 g, 0.12 mmol, 46%) as a pale yellow solid: mp 213-214 °C; IR (CH_2Cl_2) 2933, 1721, 1599, 1350, 1214, 1162 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.01 (m, 1 H), 7.94 (s, 1 H), 7.75 (d, J = 8.0 Hz, 2 H), 7.45−7.40 (m, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 5.82−5.74 (m, 1 H), 5.46−5.48 (m, 1 H), 4.38 (q, J = 14.4, J = 7.2 Hz, 2 H), 4.10 (d, J = 15.6 Hz, 1 H), 4.03 (d, J = 15.6 Hz, 1 H), 3.19 (d, J = 9.6 Hz, 1 H), 3.10 (d, J = 9.6 Hz, 1 H), 2.48 (s, 3 H), 2.10−1.98 (m, 1 H), 1.98−1.84 (m, 3 H), 1.77−1.65 (m, 1 H), 1.51−1.32 (m, 5 H), 1.25−1.15 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.3, 143.8, 138.3, 134.0, 133.5, 132.3, 130.7, 130.4, 130.0, 129.8, 128.4, 128.0, 127.3, 124.1, 61.3, 56.9, 53.7, 48.5, 39.9, 36.2, 28.3, 22.7, 21.6, 14.3; HRMS (ESI) m/e 500.1657, calcd for $C_{27}H_{31}ClNO_4S$ $[M + H]^+$ 500.1662. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*(Z)-4-(Chloro(3-methoxyphenyl)methylene)-2-tosyl-2-azaspiro-[4.6]undec-7-ene (**2h**).* The crude mixture from general procedure II (**1h**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **2h** (0.087 g, 0.19 mmol, 77%) as a pale yellow solid: mp 212−213 °C; IR (CH_2Cl_2) 2931, 1597, 1450, 1348, 1162, 1094, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8 Hz, 2 H), 7.38 (d, J = 8 Hz, 2 H), 7.25 (t, J = 8 Hz, 1 H), 6.89−6.83 (m, 2 H), 6.78 (t, J = 2 Hz, 1 H), 5.83−5.72 (m, 1 H), 5.55−5.43 (m, 1 H), 4.07 (d, J = 14.6 Hz, 1 H), 4.01 (d, J = 14.9 Hz, 1 H), 3.79 (s, 3 H), 3.18 (d, J = 9.5 Hz, 1 H), 3.11 (d, J = 9.5 Hz, 1 H), 2.47 (s, 3 H), 2.10−1.91 (m, 3 H), 1.90−1.81 (m, 1 H), 1.81−1.68 (m, 1 H), 1.52−1.39 (m, 2 H), 1.27−1.14 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.7, 143.2, 139.2, 134.0, 132.4, 129.7, 129.3, 128.0, 127.6, 125.0, 121.7, 114.9, 114.5, 57.0, 55.3, 53.6, 48.5, 39.7, 36.1, 28.4, 22.7, 21.6. HRMS (ESI) m/e 458.1558, calcd for $C_{25}H_{29}ClNO_3S$ $[M + H]^+$ 458.1557.

*(Z)-4-(Bromophenylmethylene)-2-tosyl-2-azaspiro[4.6]-undec-7-ene (**3**).* The crude mixture from general procedure II (**1a**, 0.11 g, 0.25 mmol, and $FeBr_3$, 0.089 g, 0.30 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **3** (0.097 g, 0.21 mmol, 82%) as a white solid: mp 214.0−214.5 °C; IR (CH_2Cl_2) 2931, 1605, 1444, 1349, 1161, 1094 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2 H), 7.40 (d, J = 8 Hz, 2 H), 7.35−7.30 (m, 3 H), 7.25−7.21 (m, 2 H), 5.80−5.71 (m, 1 H), 5.52−5.44 (m, 1 H), 4.04 (d, J = 15.4 Hz, 1 H), 3.97 (d, J = 15.4 Hz, 1 H), 3.21 (d, J = 9.5 Hz, 1 H), 3.13 (d, J = 9.5 Hz, 1 H), 2.47 (s, 3 H), 2.07−1.97 (m, 1 H), 1.97−1.91 (m, 2 H), 1.90−1.81 (m, 1 H), 1.75−1.64 (m, 1 H), 1.49−1.33 (m, 2 H), 1.23−1.13 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.7, 139.9, 134.0, 132.4, 129.8, 129.1, 128.8, 128.2, 128.0, 127.5, 116.0, 57.1, 56.3, 49.4, 39.7, 36.2, 28.3, 22.7, 21.6; HRMS (ESI) m/e 472.0947, calcd for $C_{24}H_{27}BrNO_2S$ $[M + H]^+$ 472.0946. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*N-((3-(Chloromethyl)cyclohex-1-enyl)methyl)-4-methyl-N-(3-(4-nitrophenyl)prop-2-yn-1-yl)benzenesulfonamide (**4**).* The crude mixture from general procedure II (**1i**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **4** (0.079 g, 0.16 mmol, 64%) as a pale yellow solid: mp 123−125 °C; IR (CH_2Cl_2) 2923, 1594, 1519, 1343, 1162 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.8 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.28−7.25 (m, 2 H), 7.19 (d, J = 8.8 Hz, 2 H), 5.66 (s, 1 H), 4.29 (d, J = 18.6 Hz, 1 H), 4.23 (d, J = 18.6 Hz, 1 H), 3.80 (d, J = 13.3 Hz, 1 H), 3.75 (d, J = 13.4 Hz, 1 H), 3.45 (dq, J = 25.5, J = 6.3 Hz, 2 H), 2.58−2.48 (m, 1 H), 2.36 (s, 3 H), 2.16−1.96 (m, 2 H), 1.88−1.77 (m, 2 H), 1.47−1.36 (m, 1 H), 1.35−1.21 (m, 1 H), 0.92−0.80 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.1, 134.7, 132.3, 129.5, 129.0, 128.1, 127.9, 123.4, 87.6, 83.8, 53.1, 49.1, 38.1, 36.3, 26.4, 26.2, 21.5, 20.9; HRMS (ESI) m/e 495.1120, calcd for $C_{24}H_{25}ClN_2O_4NaS$ $[M + Na]^+$ 495.1121. Crystals suitable for X-ray diffraction analysis were grown from diethyl ether.

*(±)-(1S,7S,8R)-8-Chloro-6-(4-methoxyphenyl)-3-tosyl-3-azatricyclo[5.4.1.0^{1,5}]dodec-5-ene (**7**).* The crude mixture from general procedure II (**1j**, 0.11 g, 0.25 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **7** (0.065 g, 0.14 mmol, 57%) as a pale yellow solid: mp 212−213 °C; IR (CH_2Cl_2) 2930, 1606, 1341, 1252, 1158, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 7.14 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 4.23 (d, J = 14.8 Hz, 1 H), 4.20−4.13 (m, 1 H), 3.88−3.77 (m, 5 H), 3.51 (d, J = 8.8 Hz, 1 H), 2.76 (d, J = 8.8 Hz, 1 H), 2.40 (s, 3 H), 2.34 (d, J = 12.7 Hz, 1 H), 2.23−2.11 (m, 1 H), 1.93−1.75 (m, 4 H), 1.69−1.60 (m, 1 H), 1.47−1.35 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.4, 141.5, 134.0, 133.6, 129.7, 128.5, 127.4, 125.5, 114.5, 61.6, 59.0, 58.7, 58.3, 55.3, 46.2, 36.6, 35.2, 35.2, 21.5, 21.4; HRMS (FAB$^+$) m/e 458.1548, calcd for $C_{25}H_{29}ClNO_3S$ $[M + H]^+$ 458.1557. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

Typical Experimental Procedure for Synthesis of Starting Substrates 12a−c. To a stirred solution of *t*-BuLi (1.6 M, 12.6 mL, 20.2 mmol) at −78 °C was added 1-phenyl-5-iodo-1-pentyne (4.0 g, 14.8 mmol) in ether (10 mL) dropwise over 0.5 h, and the mixture was stirred at −78 °C for 0.5 h followed by addition of 3-methoxycyclohex-2-en-1-one (1.5 g, 11.9 mmol) in 10 mL of ether. The resulting mixture was stirred at room temperature for 12 h followed by addition of 2.5 N HCl(aq) (15 mL) at 0 °C. The reaction mixture was extracted with ether (50 mL × 3). The mixture was concentrated, and the residue was purified via flash chromatography (silica gel, 5% ethyl acetate/hexanes) to give 3-(5-phenylpent-4-yn-1-yl)cyclohex-2-en-1-one (2.83 g, 8.6 mmol, 82%). To an oven-dried 100 mL round-bottom flask equipped with a stir bar was added NaH (0.67 g, 16.8 mmol). The apparatus was evacuated (oil pump) and filled with nitrogen three times, and then Me_3SOI (3.69 g, 16.78 mmol) and via syringe DMSO (16 mL) were added. The reaction mixture was stirred at room temperature for 0.5 h followed by addition of 3-(5-phenylpent-4-yn-1-yl)cyclohex-2-en-1-one in DMSO (2 mL), and the mixture was stirred at room temperature for 16 h. The reaction mixture was poured into water (30 mL) and extracted with ether (50 mL × 3). The crude mixture was purified via flash chromatography (silica gel, 5% ethyl acetate/hexanes) to give **12a**.

*Data for 6-(5-phenylpent-4-yn-1-yl)bicyclo[4.1.0]heptan-2-one (**12a**):* yield 1.164 g (4.61 mmol, 55%); pale yellow oil; IR (CH_2Cl_2) 3019, 2938, 2860, 2229, 1686, 1598, 1490, 1442, 1324, 1246, 758, 693, 523 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.28 (m, 3 H), 7.36−7.38 (m, 2 H), 2.39−2.43 (t, J = 6.8 Hz, 2 H), 2.25−2.31 (m, 1 H), 1.95−2.06 (m, 2 H), 1.47−1.79 (m, 8 H), 1.39−1.42 (t, J = 4.8 Hz, 1 H), 0.96−1.00 (dd, J = 10.0, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 131.4, 128.2, 127.6, 123.7, 89.5, 81.1, 38.0, 36.1, 33.5, 27.8, 25.6, 25.5, 19.3, 18.2, 17.1; HRMS (ESI) $[M + Na]^+$ m/e 275.1416, calcd for $C_{18}H_{20}ONa$ 275.1412.

*Data for (±)-(1S,6R)-6-(5-p-tolylpent-4-yn-1-yl)bicyclo[4.1.0]-heptan-2-one (**12b**):* yield 1.05 g (4.0 mmol, 46%) from the corresponding enone (2.17 g, 8.6 mmol); pale yellow oil; IR (CH_2Cl_2) 3026, 2938, 2861, 2200, 1686, 1510, 1444, 1326, 1247, 819, 526 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.28 (d, J = 8.0 Hz, 2 H), 7.07−7.09 (d, J = 8.0 Hz, 2 H), 2.39−2.42 (t, J = 6.8 Hz, 2 H), 2.26−2.33 (m, 4 H), 1.96−2.06 (m, 2 H), 1.58−1.79 (m, 7 H), 1.48−1.53 (m, 1 H), 1.39−1.41 (t, J = 4.8 Hz, 1 H), 0.96−1.00 (dd, J = 10.0, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 137.6, 131.3, 128.9, 120.7, 88.7, 81.1, 38.1, 36.2, 33.5, 27.8, 25.7, 25.6, 21.3, 19.3, 18.3, 17.1; HRMS (ESI) $[M + Na]^+$ m/e 289.1568, calcd for $C_{19}H_{22}ONa$ 289.1571.

*Data for (±)-(1S,6R)-6-(5-(3-methoxyphenyl)pent-4-yn-1-yl)-bicyclo[4.1.0]heptan-2-one (**12c**):* yield 0.53 g (1.88 mmol, 43%) from the corresponding enone (1.17 g, 4.36 mmol); pale yellow oil; IR (CH_2Cl_2) 3008, 2940, 2232, 1686, 1604, 1575, 1288, 1205, 1045, 785, 689, 479 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.21 (t, J = 8.0 Hz, 1 H), 6.96−6.98 (d, J = 7.6 Hz, 1 H), 6.91−6.92 (d, J = 2.0 Hz, 1

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H), 6.82−6.85 (dd, J = 8.3, 2.5 Hz, 1 H), 3.79 (s, 3 H), 2.40−2.43 (t, J = 7.0 Hz, 2 H), 2.26−2.32 (m, 1 H), 1.97−2.04 (m, 2 H), 1.58−1.80 (m, 7 H), 1.48−1.54 (m, 1 H), 1.40−1.42 (t, J = 4.8 Hz, 1 H), 0.97−1.01 (dd, J = 10.1, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 159.3, 129.2, 124.8, 124.0, 116.4, 114.1, 89.4, 81.0, 55.2, 38.1, 36.2, 33.5, 27.8, 25.6, 25.5, 19.3, 18.3, 17.1; HRMS (ESI) $[M + Na]^+$ m/e = 305.1518, calcd for $C_{19}H_{22}O_2Na$ 305.1517.

Typical Experimental Procedure for Synthesis of Starting Substrates 12d−f. To a stirred solution of *t*-BuLi (1.6 M, 6.52 mL, 10.4 mmol) at −78 °C was added 1-phenyl-5-iodo-1-pentyne (2.06 g, 7.64 mmol) in ether (10 mL) dropwise over 0.5 h, and the mixture was stirred at −78 °C for 0.5 h followed by addition of 3-methoxy-5,5-dimethylcyclohex-2-en-1-one (0.94 g, 6.1 mmol) in 10 mL of ether. The resulting mixture was stirred at room temperature for 12 h followed by addition of 2.5 N HCl(aq) (15 mL) at 0 °C. The reaction mixture was extracted with ether (50 mL × 3). The mixture was concentrated under reduced pressure and purified via flash chromatography (silica gel, 5% ethyl acetate/hexanes) to give 5,5-dimethyl-3-(5-phenylpent-4-yn-1-yl)cyclohex-2-en-1-one (1.26 g, 4.73 mmol, 68%). To an oven-dried 100 mL round-bottom flask equipped with a stir bar at 0 °C were added the crude enone (1.25 g, 4.7 mmol), $NaBH_4$ (0.23 g, 6.11 mmol), and $CeCl_3{\cdot}7H_2O$ (1.75 g, 4.7 mmol) in 10 mL of methanol at 0 °C for 20 min. The reaction mixture was poured into 50 mL of water and extracted with CH_2Cl_2 (3 × 30 mL). The combined orgainc solution was dried and concentrated to give the crude 5,5-dimethyl-3-(5-phenylpent-4-yn-1-yl)cyclohex-2-en-1-ol (1.24 g, 4.6 mmol, 98%). The crude enynol was used in the next step without further purification. To the above crude enynol in 10 mL of ether at 0 °C was added Et_2Zn (1.5 M, 9.4 mL, 14.1 mmol) followed by slow addition of CH_2I_2 (5.03 g, 18.8 mmol) at 0 °C, and the mixture was then stirred at 30 °C for 10 h. The reaction mixture was poured into saturated NH_4Cl(aq) (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The crude mixture was purified via flash chromatography (silica gel, 10% ethyl acetate/hexanes) to give the crude 4,4-dimethyl-6-(5-phenylpent-4-yn-1-yl)bicyclo[4.1.0]heptan-2-ol (0.64 g, 2.3 mmol, 58%). To the above crude ynol in 20 mL of acetone was added 2-iodoxybenzoic acid (1.27 g, 4.54 mmol). The reaction mixture was heated at reflux for 3 h. The solvent was concentrated under reduced pressure and purified via flash chromatography (silica gel, 10% ethyl acetate/hexanes) to give **12d**.

*Data for (±)-(1S,6R)-4,4-dimethyl-6-(5-phenylpent-4-yn-1-yl)-bicyclo[4.1.0]heptan-2-one (**12d**):* yield 0.38 g (1.35 mmol, 60%); pale yellow oil; IR (CH_2Cl_2) 3064, 2957, 2868, 2203, 1686, 1599, 1443, 1282, 1253, 758, 693, 525 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.38 (m, 2 H), 7.26−7.28 (m, 3 H), 2.40−2.43 (t, J = 6.5 Hz, 2 H), 2.02−2.06 (d, J = 14.3 Hz, 1 H), 1.80−1.83 (d, J = 14.3 Hz, 1 H), 1.67−1.74 (m, 4 H), 1.51−1.61 (m, 2 H), 1.35−1.42 (m, 1 H), 1.19−1.23 (dd, J = 9.6, 4.5 Hz, 1 H), 1.01−1.03 (t, J = 4.6 Hz, 1 H), 0.97 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 131.5, 128.2, 127.6, 123.8, 89.5, 81.1, 48.7, 42.4, 39.9, 37.0, 32.7, 30.8, 29.3, 26.5, 26.3, 26.0, 19.3; HRMS (ESI) $[M + Na]^+$ m/e 303.1723, calcd for $C_{20}H_{24}ONa$ 303.1725.

*Data for (±)-(1S,6R)-4,4-dimethyl-6-(5-p-tolylpent-4-yn-1-yl)-bicyclo[4.1.0]heptan-2-one (**12e**):* yield 0.14 g (0.48 mmol, 72%) from the corresponding bicyclic ynol (0.22 g, 0.75 mmol); yellow oil; IR (CH_2Cl_2) 3028, 2954, 2868, 2214, 1689, 1510, 1458, 1282, 818, 526 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.27 (d, J = 8.0 Hz, 2 H), 7.07−7.09 (d, J = 8.0 Hz, 2 H), 2.38−2.42 (t, J = 6.9 Hz, 2 H), 2.32 (s, 3 H), 2.02−2.06 (d, J = 14.3 Hz, 1 H), 1.80−1.83 (d, J = 14.3 Hz, 1 H), 1.66−1.73 (m, 4 H), 1.51−1.61 (m, 2 H), 1.34−1.41 (m, 1 H), 1.19−1.22 (dd, J = 9.7, 4.7 Hz, 1 H), 1.00−1.02 (t, J = 4.8 Hz, 1 H), 0.97 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 137.5, 131.3, 128.9, 120.6, 88.6, 81.1, 48.7, 42.3, 39.8, 37.0, 32.7, 30.8, 29.3, 26.5, 26.3, 26.0, 21.3, 19.3; HRMS (ESI) m/e 317.1888, calcd for $C_{21}H_{26}ONa$ $[M + Na]^+$ 317.1881.

*Data for 6-(5-(4-methoxyphenyl)pent-4-yn-1-yl)-4,4-dimethylbicyclo[4.1.0]heptan-2-one (**12f**):* yield 1.01 g (3.25 mmol, 91%) from the corresponding bicyclic ynol (1.12 g, 3.59 mmol); yellow oil; IR (CH_2Cl_2) 3000, 2953, 2867, 2049, 1688, 1607, 1509, 1289, 1247, 1173, 1034, 833, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.32 (d, J = 8.8 Hz, 2 H), 6.80−6.82 (d, J = 8.8 Hz, 2 H), 3.79 (s, 3H), 2.37−2.41 (t, J = 6.9 Hz, 2 H), 2.03−2.06 (d, J = 14.3 Hz, 1 H), 1.79−1.83 (d, J = 14.3 Hz, 1 H), 1.65−1.74 (m, 4 H), 1.50−1.61 (m, 2 H), 1.34−1.42 (m, 1 H), 1.19−1.23 (dd, J = 9.7, 4.6 Hz, 1 H), 1.01−1.03 (t, J = 4.7 Hz, 1 H), 0.97 (s, 3 H), 0.94 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 159.0, 132.7, 115.8, 113.7, 87.8, 80.8, 55.1, 48.7, 42.2, 39.8, 37.0, 32.6, 30.8, 29.3, 26.4, 26.3, 26.0, 19.3; HRMS (ESI) $[M + Na]^+$ m/e 333.1822, calcd for $C_{21}H_{26}O_2Na$ 333.1831.

General Procedure III for Formation of Spiro[4.6]undecan-8-ones 13. To a stirred solution of **12a** (0.13 g, 0.5 mmol) in DBE (5 mL) was added $FeCl_3$ (0.12 g, 0.75 mmol), and the mixture was stirred at 50 °C for 1 h. The solvent was concentrated under reduced pressure, and the crude mixture was poured into water (30 mL) and extracted with ether (30 mL × 3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a bed of Celite, and concentrated to give the crude mixture.

*(E)-1-(Chlorophenylmethylene)spiro[4.6]undecan-8-one (**13a**).* The crude mixture from general procedure III (**12a**, 0.14 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 3% ethyl acetate/hexanes) to give **13a** (0.078 g, 0.25 mmol, 50%) as a colorless solid: mp 85−87 °C; IR (CH_2Cl_2) 3057, 2949, 2868, 1704, 1454, 1444, 1342, 881, 834, 771, 732, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.35 (m, 5 H), 2.70−2.72 (m, 2 H), 2.34−2.43 (m, 1 H), 2.27−2.32 (dd, 12.0, 6.0 Hz, 1 H), 2.17−2.23 (m, 1 H), 2.05−2.12 (m, 1 H), 1.60−1.72 (m, 7 H), 1.42−1.50 (m, 2 H), 1.30−1.37 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.3, 149.7, 139.5, 129.6, 128.4, 128.1, 124.8, 50.6, 43.6, 39.7, 39.1, 36.2, 35.2, 32.9, 21.2, 20.7; HRMS (ESI) $[M + Na]^+$ m/e = 311.1185, calcd for $C_{18}H_{21}OClNa$ 311.1179. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2.

*(E)-1-(Chloro-p-tolylmethylene)spiro[4.6]undecan-8-one (**13b**).* The crude mixture from general procedure III (**12b**, 0.15 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 3% ethyl acetate/hexanes) to give **13b** (0.075 g, 0.23 mmol, 46%) as a pale yellow oil: IR (CH_2Cl_2) 3026, 2947, 2869, 1702, 1607, 1453, 885, 810, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13−7.19 (m, 4 H), 2.68−2.70 (m, 2 H), 2.28−2.41 (m, 5 H), 2.09−2.24 (m, 2 H), 1.31−1.74 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.5, 149.6, 138.3, 136.7, 129.5, 128.9, 125.1, 50.6, 43.6, 39.8, 39.0, 36.2, 35.3, 32.8, 21.3, 21.2, 20.8; HRMS (ESI) $[M + Na]^+$ m/e 325.1332, calcd for $C_{19}H_{23}OClNa$ 325.1335.

*(E)-1-(Chloro(3-methoxyphenyl)methylene)spiro[4.6]undecan-8-one (**13c**).* The crude mixture from general procedure III (**12c**, 0.15 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 3% ethyl acetate/hexanes) to give **13c** (0.077 g, 0.23 mmol, 45%) as a colorless solid: mp 137−140 °C; IR (CH_2Cl_2) 3026, 2950, 2863, 1700, 1593, 1457, 1317, 1262, 1165, 1042, 784, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.26 (m, 1 H), 6.86−6.89 (m, 2 H), 6.83−6.84 (m, 1 H), 3.82 (s, 3 H), 2.67−2.70 (m, 2 H), 2.29−2.42 (m, 2 H), 2.10−2.26 (m, 2 H), 1.62−1.75 (m, 6 H), 1.37−1.59 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 159.2, 149.6, 140.7, 129.2, 124.5, 122.0, 115.4, 113.8, 55.3, 50.7, 43.6, 39.8, 39.0, 36.2, 35.2, 32.7, 21.2, 20.8; HRMS (EI) $[M + Na]^+$ m/e 341.1293, calcd for $C_{19}H_{23}O_2ClNa$ 341.1284. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*(E)-1-(Chlorophenylmethylene)-10,10-dimethylspiro[4.6]-undecan-8-one (**13d**).* The crude mixture from general procedure III (**12d**, 0.15 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 3% ethyl acetate/hexanes) to give **13d** (0.098 g, 0.31 mmol, 62%) as a pale yellow oil: IR (CH_2Cl_2) 3048, 2958, 1698, 1594, 1450, 1238, 734, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.37 (m, 3 H), 7.27−7.31 (m, 2 H), 2.63−2.69 (m, 2 H), 2.24−2.38 (m, 3 H), 1.96−2.21 (d, J = 12.0 Hz, 1 H), 1.61−1.76 (m, 6 H), 1.45 (s, 2 H), 0.91 (s, 3 H), 0.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 150.7, 139.7, 129.6, 128.3, 128.1, 124.5, 54.9, 51.9, 51.1, 40.2, 37.3, 35.8, 34.6, 33.7, 32.3, 26.6, 21.6; HRMS (EI) $[M]^+$ m/e 316.1591, calcd for $C_{20}H_{25}OCl$ 316.1594.

*(E)-1-(Chloro-p-tolylmethylene)-10,10-dimethylspiro[4.6]-undecan-8-one (**13e**).* The crude mixture from general procedure III

(**12e**, 0.16 g, 0.5 mmol) was purified by flash column chromatography (silica gel, 2% ethyl acetate/hexanes) to give **13f** (0.10 g, 0.29 mmol, 55%) as a pale yellow oil: IR (CH_2Cl_2) 3026, 2957, 1701, 1606, 1458, 1237, 816, 783, 748, 526 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15−7.20 (m, 4 H), 2.63−2.68 (m, 2 H), 2.20−2.40 (m, 6 H), 1.97−2.00 (d, J = 12.0 Hz, 1 H), 1.58−1.78 (m, 6 H), 1.51−1.54 (d, J = 14.6 Hz, 1 H), 1.45−1.48 (d, J = 14.6 Hz, 1 H), 0.92 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 150.6, 138.2, 136.9, 129.6, 128.8, 124.8, 55.0, 51.8, 51.2, 40.3, 37.4, 36.0, 34.7, 33.8, 32.5, 26.7, 21.7, 21.3; HRMS (EI) $[M]^+$ m/e 330.1748, calcd for $C_{21}H_{27}OCl$ 330.1750.

*(E)-1-(Chloro(3-methoxyphenyl)methylene)-10,10-dimethylspiro-[4.6]undecan-8-one (**13f**).* The crude mixture from general procedure III (**12f**, 0.16 g, 0.5 mmol) was purified by flash column chromatography (silica gel, 2% ethyl acetate/hexanes) to give **13f** (0.10 g, 0.29 mmol, 55%) as a white solid: mp 119−120 °C; IR (CH_2Cl_2) 3055, 2955, 1701, 1596, 1457, 1428, 1286, 1261, 1043, 782, 748, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−7.29 (m, 1 H), 6.87−6.90 (m, 2 H), 6.84 (s, 1 H), 3.81 (s, 3 H), 2.62−2.67 (m, 2 H), 2.38−2.41 (d, J = 12.0 Hz, 1 H), 2.30−2.34 (dd, J = 12.2, 4.6 Hz, 1 H), 2.21−2.28 (dt, J = 18.6, 4.4 Hz, 1 H), 1.97−2.00 (d, J = 12.0 Hz, 1 H), 1.61−1.79 (m, 6 H), 1.53−1.57 (d, J = 14.4 Hz, 1 H), 1.45−1.49 (d, J = 14.4 Hz, 1 H), 0.92 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 159.1, 150.5, 140.7, 129.0, 124.1, 122.0, 115.2, 114.0, 55.2, 54.8, 51.7, 51.1, 40.2, 37.2, 35.9, 34.5, 34.5, 33.7, 32.2, 26.5, 21.5; HRMS (ESI) $[M + Na]^+$ m/e 369.1595, calcd for $C_{21}H_{27}O_2ClNa$ 369.1597.

General Procedure IV for Synthesis of Starting Compounds 14a−f. To a stirred solution of *N*-((3-hydroxycyclohex-1-en-1-yl)methyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulf-onamide (1.05 g, 2.65 mmol) in 5.0 mL of CH_2Cl_2 was added 0.032 g (0.27 mmol) of (dimethylamino)pyridine, 0.60 g (3.98 mmol) of *tert*-butyldimethylsilyl chloride, and 1.18 g (2.31 mmol) of triethylamine. The reaction mixture was stirred at 30 °C for 12 h. The reaction mixture was added to 10 mL of water and extracted with CH_2Cl_2 (10 × 3 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a bed of Celite, and concentrated to give the crude mixture.

*N-((3-((tert-Butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**14a**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14a** (1.33 g, 2.60 mmol, 98%) as a white solid: mp 66−67 °C; IR (CH_2Cl_2) 3057, 2930, 1598, 1491, 1349, 1163, 1092, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2 H), 7.28−7.18 (m, 5 H), 7.06−7.01 (m, 2 H), 5.67 (s, 1 H), 4.30 (d, J = 18.4 Hz, 1 H), 4.24 (br s, 1 H), 4.17 (d, J = 18.4 Hz, 1 H), 3.82 (d, J = 13.4 Hz, 1 H), 3.70 (d, J = 13.4 Hz, 1 H), 2.32 (s, 3 H), 2.08−2.00 (m, 2 H), 1.78−1.75 (m, 2 H), 1.58−1.49 (m, 2 H), 0.87 (s, 9 H), 0.07−0.03 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.0, 134.0, 131.4, 131.1, 129.4, 129.3, 128.2, 128.0, 127.7, 122.2, 85.6, 81.6, 66.7, 52.4, 36.3, 32.2, 25.9, 25.8, 21.3, 19.4, 18.1, −4.7; HRMS (ESI^+) m/z 532.2325, $C_{29}H_{39}NO_3SSiNa$ $[M + Na]^+$ calcd 532.2318.

*N-((3-((tert-Butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methyl)-4-methyl-N-(3-p-tolylprop-2-yn-1-yl)benzenesulfonamide (**14b**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14b** (0.52 g, 0.96 mmol, 66%) from the corresponding enol (0.60 g, 1.45 mmol) as a yellow oil: IR (CH_2Cl_2) 2929, 2857, 1661, 1447, 1349, 1163, 1092, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 8.2 Hz, 2 H), 7.03 (d, J = 8.0 Hz, 2 H), 6.93 (d, J = 8.0 Hz, 2 H), 5.66 (s, 1 H), 4.29 (d, J = 18.4 Hz, 1 H), 4.24 (br s, 1 H), 4.15 (d, J = 18.4 Hz, 1 H), 3.81 (d, J = 13.4 Hz, 1 H), 3.69 (d, J = 13.4 Hz, 1 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.09−1.98 (m, 2 H), 1.87−1.74 (m, 2 H), 1.61−1.46 (m, 2 H), 0.87 (s, 9 H), 0.07−0.03 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 136.0, 134.1, 131.3, 131.1, 129.4, 128.8, 127.7, 119.1, 85.8, 80.9, 66.7, 52.4, 36.4, 32.3, 25.9, 25.8, 21.3, 19.5, 18.1, −4.6, −4.7; HRMS (ESI^+) m/e 546.2477, $C_{30}H_{41}NO_3SSiNa$ $[M + Na]^+$ calcd 546.2474.

*N-(3-(4-Bromophenyl)prop-2-yn-1-yl)-N-((3-((tert-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methyl)-4-methylbenzenesulfonamide (**14c**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14c** (0.31 g, 0.50 mmol, 32%) from the corresponding enol (0.74 g, 1.56 mmol) as a colorless oil: IR (CH_2Cl_2) 2930, 2857, 1634, 1486, 1351, 1255, 1164, 1071, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2 H), 7.38−7.32 (m, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 6.9−6.88 (m, 2 H), 5.63 (m, 1 H), 4.26 (d, J = 18.5 Hz, 2 H), 4.22 (br s, 1 H) 4.14 (d, J = 18.4 Hz, 1 H), 3.79 (d, J = 13.2 Hz, 1 H), 3.68 (d, J = 13.2 Hz, 1 H), 2.33 (s, 3 H), 2.06−1.97 (m, 2 H), 1.85−1.74 (m, 2 H), 1.59−1.45 (m, 2 H), 0.86 (s, 9 H), 0.04 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.0, 134.0, 132.8, 131.3, 129.4, 127.8, 122.5, 121.1, 84.5, 83.0, 66.7, 52.5, 36.3, 32.2, 25.9, 25.8, 21.4, 19.5, 18.1, −4.6, −4.7; HRMS (ESI^+) m/z 610.1430, $C_{29}H_{38}BrNO_3SSiNa$ $[M + Na]^+$ calcd 610.1423.

*N-((3-((tert-Butyldimethylsilyl)oxy)-5,5-dimethylcyclohex-1-en-1-yl)methyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (**14d**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14d** (0.93 g, 1.66 mmol, 75%) from the corresponding enol (0.94 g, 2.21 mmol) as a white solid: mp 99−100 °C; IR (CH_2Cl_2) 2954, 2929, 1459, 1351, 1165, 1071, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2 H), 7.27−7.20 (m, 5 H), 7.03 (d, J = 6.8 Hz, 2 H), 5.64 (s, 1 H), 4.35 (d, J = 18.4 Hz, 1 H), 4.29 (br s, 1 H), 4.11 (d, J = 18.4 Hz, 1 H), 3.84 (d, J = 13.2 Hz, 1 H), 3.67 (d, J = 13.2 Hz, 1 H), 2.32 (s, 3 H), 1.89−1.87 (m, 2 H), 1.68−1.63 (m, 1 H), 1.39−1.34 (m, 1 H), 1.01 (s, 3 H), 0.90 (s, 3 H), 0.87 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.0, 132.2, 131.4, 131.4, 130.2, 129.4, 129.4, 128.2, 128.0, 127.7, 122.1, 85.8, 81.3, 66.9, 52.4, 45.1, 39.6, 36.2, 31.0, 30.8, 26.3, 25.8, 21.3, 18.1, −4.6, −4.8; HRMS (ESI^+) m/e 560.2632, $C_{31}H_{43}NO_3SSiNa$ $[M + Na]^+$ calcd 560.2631.

*N-((3-((tert-Butyldimethylsilyl)oxy)-5,5-dimethylcyclohex-1-en-1-yl)methyl)-4-methyl-N-(3-p-tolylprop-2-yn-1-yl)-benzenesulfonamide (**14e**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14e** (0.94 g, 1.63 mmol, 71%) from the corresponding enol (1.00 g, 2.30 mmol) as a yellow oil: IR (CH_2Cl_2) 2952, 1669, 1510, 1348, 1093, 905, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 6.98 (d, J = 8.0 Hz, 2 H), 6.89 (d, J = 8.0 Hz, 2 H), 5.62 (m, 1 H), 4.32−4.28 (m, 2 H), 4.07 (d, J = 18.4 Hz, 1 H), 3.80 (d, J = 13.2 Hz, 1 H), 3.66 (d, J = 13.2 Hz, 1 H), 2.28 (s, 3 H), 2.26 (s, 3 H), 1.90−1.79 (m, 2 H), 1.64−1.60 (m, 1 H), 1.36−1.31 (m, 1 H), 0.97 (s, 3 H), 0.87 (s, 3 H), 0.84 (s, 9 H), 0.02 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.2, 135.8, 132.1, 131.2, 130.0, 129.3, 128.6, 127.6, 119.0, 85.8, 80.5, 66.8, 52.1, 45.0, 39.5, 36.2, 30.9, 30.7, 26.3, 25.7, 21.2, 18.0, − 4.7, −4.8; HRMS (ESI^+) m/e 574.2783, $C_{32}H_{45}NO_3SSiNa$ $[M + Na]^+$ calcd 574.2787.

*N-(3-(4-Bromophenyl)prop-2-yn-1-yl)-N-((3-((tert-butyldimethylsilyl)oxy)-5,5-dimethylcyclohex-1-en-1-yl)methyl)-4-methylbenzenesulfonamide (**14f**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14f** (0.32 g, 0.50 mmol, 17%) from the corresponding enol (1.51 g, 3.00 mmol) as a yellow solid: mp 84−85 °C; IR (CH_2Cl_2) 2956, 1665, 1486, 1347, 1162, 905, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2 H), 7.37−7.35 (m, 2 H), 7.27−7.23 (m, 2 H), 6.90−6.88 (m, 2 H), 5.62 (m, 1 H), 4.34−4.29 (m, 2H), 4.10 (d, J = 18.5 Hz, 1H), 3.82 (d, J = 13.2 Hz, 1 H), 3.68 (d, J = 13.2 Hz, 1 H), 2.34 (s, 3 H), 1.88−1.86 (m, 2 H), 1.67−1.63 (m, 1 H), 1.38−1.33 (m, 1 H), 1.01 (s, 3 H), 0.91 (s, 3 H), 0.87 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 135.8, 132.8, 132.2, 131.3, 130.3, 129.4, 127.8, 122.5, 121.1, 84.6, 82.7, 66.9, 52.4, 45.1, 39.6, 36.2, 31.0, 30.8, 26.4, 25.8, 21.3, 18.1, −4.6, −4.8; HRMS (ESI^+) m/e 638.1735, $C_{31}H_{42}BrNO_3SSiNa$ $[M + Na]^+$ calcd 638.1736.

*N-((3-((tert-Butyldimethylsilyl)oxy)-5,5-dimethylcyclohex-1-en-1-yl)methyl)-N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**14g**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14g** (0.73 g, 1.23 mmol, 71%) from the corresponding enol (0.78 g, 1.73 mmol) as a white solid: mp 90−91 °C; IR (CH_2Cl_2) 2952, 1424, 1164, 1071, 877 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 8.1 Hz, 2 H), 7.16 (t, J = 8.0 Hz, 1 H), 6.86−6.83 (m, 1 H), 6.65 (d, J = 7.6 Hz, 1 H), 6.59−6.58 (m, 1 H), 5.65 (m, 1 H),

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4.39−4.31 (m, 2 H), 4.12 (d, J = 18.5 Hz, 1 H), 3.86 (d, J = 13.2 Hz, 1 H), 3.79 (s, 3H), 3.69 (d, J = 13.2 Hz, 1 H), 2.36 (s, 3 H), 1.90−1.89 (m, 2 H), 1.70−1.65 (m, 1 H), 1.40−1.35 (m, 1 H), 1.03 (s, 3 H), 0.91 (s, 3 H), 0.86 (s, 9 H), 0.04 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 143.5, 135.9, 132.3, 130.2, 129.5, 129.1, 127.8, 124.0, 123.2, 116.9, 114.3, 85.7, 81.3, 66.9, 55.2, 52.3, 45.2, 39.6, 36.2, 31.0, 30.9, 26.4, 25.8, 21.3, 18.1, −4.6, −4.7; HRMS (ESI) m/e 590.2740, $C_{32}H_{45}NO_4SSiNa$ $[M + Na]^+$ calcd 590.2736.

*N-(3-([1,1′-Biphenyl]-4-yl)prop-2-yn-1-yl)-N-((3-((tert-butyldimethylsilyl)oxy)-5,5-dimethylcyclohex-1-en-1-yl)methyl)-4-methylbenzenesulfonamide (**14h**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14h** (0.72 g, 1.14 mmol, 71%) from the corresponding enol (0.80 g, 1.60 mmol) as a white oil: IR (CH_2Cl_2) 2953, 2928, 1486, 1349, 1162, 1071, 840 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.5 Hz, 2 H), 7.55 (d, J = 7.5 Hz, 2 H), 7.46 (d, J = 8.5 Hz, 2 H), 7.43 (d, J = 7.8 Hz, 2 H), 7.35 (t, J = 7.3 Hz, 1 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.2 Hz, 2 H), 5.66 (m, 1 H), 4.37 (d, J = 18.5 Hz, 1 H), 4.34−4.26 (m, 1 H), 4.13 (d, J = 18.5 Hz, 1 H), 3.86 (d, J = 13.2 Hz, 1 H), 3.70 (d, J = 13.2 Hz, 1 H), 2.33 (s, 3 H), 1.95−1.83 (m, 2 H), 1.70−1.62 (m, 1 H), 1.41−1.33 (m, 1 H), 1.02 (s, 3 H), 0.91 (s, 3 H), 0.88 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 141.1, 140.0, 135.8, 132.3, 131.8, 130.2, 129.4, 128.8, 127.8, 127.7, 126.9, 126.6, 121.0, 85.6, 82.0, 66.9, 52.3, 45.1, 39.5, 36.3, 31.0, 30.9, 26.3, 25.8, 21.4, 18.1, −4.6, −4.7; HRMS (ESI$^+$) m/e 636.2942, $C_{37}H_{47}NO_3SSiNa$ $[M + Na]^+$ calcd 636.2944.

*N-((3-((tert-Butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**14i**).* The crude mixture was purified by flash column chromatography (silica gel, 10% ethyl acetate/hexanes) to give **14i** (0.95 g, 1.70 mmol, 95%) from the corresponding enol (0.76 g, 1.79 mmol) as a yellow oil: IR (CH_2Cl_2) 2931, 2858, 1607, 1463, 1350, 1250, 1163, 1075, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.8 Hz, 2 H), 6.99 (d, J = 8.8 Hz, 2 H), 6.75 (d, J = 8.8 Hz, 2 H), 5.65 (s, 1 H), 4.28 (d, J = 18.4 Hz, 1 H), 4.24 (br s, 1 H), 4.14 (d, J = 18.4 Hz, 1 H), 3.82−3.79 (m, 4 H), 3.68 (d, J = 13.4 Hz, 1 H), 2.35 (s, 3 H), 2.03 (m, 2 H), 1.82−1.80 (m, 2 H), 1.55−1.53 (m, 2 H), 0.87 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 143.2, 136.2, 134.2, 132.9, 131.1, 129.4, 127.8, 114.2, 113.7, 85.6, 80.2, 66.8, 55.3, 52.4, 36.5, 32.3, 26.0, 25.9, 21.4, 19.6, 18.2, −4.6; HRMS (ESI$^+$) m/e 562.2428, $C_{30}H_{41}NO_4SSiNa$ $[M + Na]^+$ calcd 562.2423.

General Procedure V for Formation of Compounds 15a−f and 16. To a dried DCE solution (5.0 mL) of compound **14a** (0.27 g, 0.50 mmol) were added Et_2Zn (0.66 mL, 1.0 mmol) and CH_2I_2 (0.54 g, 2.0 mmol) at 0 °C under 1 atm of nitrogen for 1 h. The resulting mixture was then stirred at 50 °C until no starting compound **14a** was detected on TLC (ca. 9−12 h). The reaction mixture was added to 10 mL of water and extracted with diethyl ether (10 × 3 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered through a bed of Celite, and concentrated to give the crude mixture.

*(Z)-4-(Iodophenylmethylene)-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15a**).* The crude mixture from general procedure V (**14a**, 0.27 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15a** (0.12 g, 0.22 mmol, 43%) as a colorless solid: mp 101−102 °C; IR (CH_2Cl_2) 2922, 2841, 1638, 1347, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 7.9 Hz, 2 H), 7.30−7.17 (m, 5 H), 5.74 (m, 1 H), 5.47−5.45 (m, 1 H), 3.98 (d, J = 15.2 Hz, 1 H), 3.90 (d, J = 15.2 Hz, 1 H), 3.28 (d, J = 9.4 Hz, 1 H), 3.17 (d, J = 9.5 Hz, 1 H), 2.47 (s, 3 H), 2.03−1.83 (m, 4 H), 1.71−1.67 (m, 1 H), 1.43−1.37 (m, 2 H), 1.19−1.13 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.7, 143.4, 133.9, 132.3, 129.7, 128.2, 128.0, 127.9, 127.4, 92.4, 61.5, 57.5, 50.0, 39.7, 36.1, 28.2, 22.6, 21.6; HRMS (ESI) m/z calcd for $C_{24}H_{26}INO_2SNa$ $(M + Na)^+$ 542.0627, found 542.0632. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*(Z)-4-(Iodo-p-tolylmethylene)-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15b**).* The crude mixture from general procedure V (**14b**, 0.27 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15b** (0.12 g, 0.23 mmol, 46%) as a yellow solid: mp 163−164 °C; IR (CH_2Cl_2) 2915, 1640, 1349, 1160 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.09 (s, 4 H), 5.77−5.75 (m, 1 H), 5.50−5.47 (m, 1 H), 3.98 (d, J = 14.8 Hz, 1 H), 3.88 (d, J = 14.8 Hz, 1 H), 3.31 (d, J = 9.5 Hz, 1 H), 3.16 (d, J = 9.5 Hz, 1 H), 2.49 (s, 3 H), 2.34 (s, 3 H), 2.05−2.01 (m,1 H), 1.95 (d, J = 6.6 Hz, 2 H), 1.87−1.85 (m, 1 H), 1.75−1.69 (m, 1 H), 1.48−1.19 (m, 2 H), 1.17 (q, J = 12.4 Hz,1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.7, 143.4, 133.9, 132.3, 129.7, 128.2, 128.0, 127.9, 127.4, 92.4, 61.5, 57.5, 50.0, 39.7, 36.1, 28.2, 22.6, 21.6; HRMS (ESI) m/e 534.0966, $C_{25}H_{29}INO_2S$ $[M + H]^+$ calcd 534.0964.

*(Z)-4-((4-Bromophenyl)iodomethylene)-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15c**).* The crude mixture from general procedure V (**14c**, 0.31 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15c** (0.17 g, 0.28 mmol, 56%) as a white solid: mp 212−214 °C; IR (CH_2Cl_2) 2934, 1482, 1346, 1158, 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.44 (d, J = 8.8 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.4 Hz, 2 H), 5.78−5.75 (m, 1 H), 5.48−5.46 (m, 1 H), 3.96 (d, J = 15.2 Hz, 1 H), 3.87 (d, J = 15.2 Hz, 1 H), 3.29 (d, J = 9.6 Hz, 1 H), 3.17 (d, J = 9.5 Hz, 1 H), 2.48 (s, 3 H), 2.08−2.02 (m, 1 H), 1.96−1.92 (m, 2 H), 1.88−1.84 (m, 1 H), 1.77−1.70 (m, 1 H), 1.45−1.34 (m, 2 H), 1.25−1.15 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 143.8, 142.4, 134.1, 132.3, 131.4,129.9, 129.8, 128.0, 127.2, 122.3, 90.5, 61.6, 57.5, 50.2, 39.9, 36.3, 28.3, 22.7, 21.6; HRMS (FAB$^+$) m/e 597.9902, $C_{24}H_{26}BrINO_2S$ $[M + H]^+$ calcd 597.9912.

*(Z)-4-(Iodophenylmethylene)-10,10-dimethyl-2-tosyl-2-azaspiro-[4.6]undec-7-ene (**15d**).* The crude mixture from general procedure V (**14d**, 0.28 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15d** (0.21 g, 0.37 mmol, 73%) as a white solid: mp 124−126 °C; IR (CH_2Cl_2) 2952, 1635, 1347, 1162 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.33−7.26 (m, 3H), 7.17 (d, J = 8.0 Hz, 2 H), 5.71−5.59 (m, 2 H), 4.01 (d, J = 15.2 Hz, 1H), 3.75 (d, J = 15.2 Hz, 1 H), 3.50 (d, J = 9.2 Hz, 1 H), 3.09 (d, J = 9.2 Hz, 1 H), 2.48 (s, 3 H), 2.12−2.10 (m, 2 H), 1.71−1.68 (m, 2 H), 1.37 (s, 2 H), 0.80 (s, 3 H), 0.59 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.8, 143.7, 132.3, 132.2, 129.7, 128.5, 128.2, 128.0, 92.8, 61.1, 58.8, 51.6, 51.1, 40.0, 35.3, 34.6, 33.3, 26.4, 21.6; HRMS (ESI$^+$) m/e 570.0946, $C_{26}H_{30}INO_2SNa$ $[M + Na]^+$ calcd 570.0940.

*(Z)-4-(Iodo-p-tolylmethylene)-10,10-dimethyl-2-tosyl-2-azaspiro-[4.6]undec-7-ene (**15e**).* The crude mixture from general procedure V (**14e**, 0.29 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15e** (0.14 g, 0.24 mmol, 48%) as a white solid: mp 157−158 °C; IR (CH_2Cl_2) 2949, 1349, 1160, 1093 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 5.71−5.59 (m, 2 H), 3.96 (d, J = 15.0 Hz, 1 H), 3.75 (d, J = 15.0 Hz, 1 H), 3.44 (d, J = 9.5 Hz, 1 H), 3.12 (d, J = 9.5 Hz, 1 H), 2.48 (s, 3 H), 2.33 (s, 3 H), 2.14−2.04 (m, 2 H), 1.78−1.66 (m, 2 H), 1.44 (d, J = 14.3 Hz, 1 H), 1.40 (d, J = 14.5 Hz, 1 H), 0.81 (s, 3 H), 0.62 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 143.7, 141.0, 138.2, 132.3, 129.8, 128.7, 128.6, 128.1, 128.0, 93.3, 61.2, 58.8, 51.6, 51.1, 40.1, 35.4, 34.7, 33.4, 26.5, 21.6, 21.3; HRMS (ESI$^+$) m/e 562.1286, $C_{27}H_{33}INO_2S$ $[M + H]^+$ calcd 562.1277.

*(Z)-4-((4-Bromophenyl)iodomethylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15f**).* The crude mixture from general procedure V (**14f**, 0.32 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15f** (0.18 g, 0.29 mmol, 57%) as a yellow solid: mp 176−178 °C; IR (CH_2Cl_2) 2923, 1598, 1348, 1159, 1012 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.0 Hz, 2 H), 7.08 (d, J = 8.0 Hz, 2 H), 5.75−5.70 (m, 1 H), 5.67−5.62 (m, 1 H), 3.98 (d, J = 15.0 Hz, 1 H), 3.78 (d, J = 15.0 Hz, 1 H), 3.46 (d, J = 9.0 Hz, 1 H), 3.16 (d, J = 9.0 Hz, 1 H), 2.50 (s, 3 H), 2.10 (d, J = 6.5 Hz, 2 H), 1.81−1.72 (m, 2 H), 1.46 (d, J = 14.5 Hz, 1 H), 1.39 (d, J = 14.5 Hz, 1 H), 0.85 (s, 3 H), 0.67 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 143.9, 142.7, 132.5, 131.3, 130.0, 129.9, 128.3, 128.0, 128.0, 122.3, 90.9, 61.2, 58.7, 51.9, 51.3, 40.1, 35.5, 34.7, 33.5,

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26.4, 21.6; HRMS (ESI$^+$) *m/e* 626.0217, $C_{26}H_{30}BrINO_2S$ $[M + H]^+$ calcd 626.0225.

*(Z)-4-(Iodo(3-methoxyphenyl)methylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15g**).* The crude mixture from general procedure V (**14g**, 0.30 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15g** (0.17 g, 0.30 mmol, 59%) as a yellow solid: mp 157−158 °C; IR (CH_2Cl_2) 2952, 1595, 1348, 1160, 1093 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.20 (t, J = 8.0 Hz, 1 H), 6.81−6.76 (m, 2 H), 6.71 (s, 1 H), 5.69−5.62 (m, 2 H), 3.98 (d, J = 14.8 Hz, 1 H), 3.78−3.74 (m, 4 H), 3.46 (d, J = 9.2 Hz, 1 H), 3.12 (d, J = 9.2 Hz, 1 H), 2.47 (s, 3 H), 2.16−2.09 (m, 2 H), 1.76−1.70 (m, 2 H), 1.47 (d, J = 14.3 Hz, 1 H), 1.40 (d, J = 14.5 Hz, 1 H), 0.82 (s, 3 H), 0.63 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 150.9, 144.7, 143.8, 132.3, 132.2, 129.7, 129.0, 128.5, 128.0, 120.7, 92.4, 61.0, 58.8, 55.3, 51.6, 51.1, 40.0, 35.2, 34.6, 33.3, 26.4, 21.6; HRMS (ESI$^+$) *m/e* 578.1230, $C_{27}H_{33}INO_3S$ $[M + H]^+$ calcd 578.1226.

*(Z)-4-([1,1′-Biphenyl]-4-yliodomethylene)-10,10-dimethyl-2-tosyl-2-azaspiro[4.6]undec-7-ene (**15h**).* The crude mixture from general procedure V (**14h**, 0.32 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **15h** (0.15 g, 0.24 mmol, 47%) as a white solid: mp 201−202 °C; IR (CH_2Cl_2) 2937, 1348, 1160, 1086 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2 H), 7.58 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2 H), 7.48−7.38 (m, 4 H), 7.38−7.34 (m, 1 H), 7.25 (d, J = 8.0 Hz, 2H), 5.69−5.63 (m, 2 H), 4.02 (d, J = 15.2 Hz, 1 H), 3.78 (d, J = 15.0 Hz, 1 H), 3.51 (d, J = 9.0 Hz, 1 H), 3.11 (d, J = 9.5 Hz, 1 H), 2.48 (s, 3 H), 2.21−2.11 (m, 2 H), 1.76−1.66 (m, 2 H), 1.47 (d, J = 14.4 Hz, 1 H), 1.40 (d, J = 14.3 Hz, 1 H), 0.81 (s, 3 H), 0.60 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 143.8, 142.7, 141.1, 140.2, 132.4, 132.3, 129.8, 128.9, 128.8, 128.5, 128.1, 127.7, 127.1, 126.7, 92.5, 61.2, 58.9, 51.8, 51.2, 40.1, 35.5, 34.7, 33.4, 26.4, 21.6; HRMS (ESI$^+$) *m/e* 624.1431, $C_{32}H_{35}INO_2S$ $[M + H]^+$ calcd 624.1433.

*(±)-(1S,7S,8R)-8-Iodo-6-(4-methoxyphenyl)-3-tosyl-3-azatricyclo-[5.4.1.0^{1,5}]dodec-5-ene (**16**).* The crude mixture from general procedure V (**14i**, 0.27 g, 0.50 mmol) was purified by flash column chromatography (silica gel, 5% ethyl acetate/hexanes) to give **16** (0.09 g, 0.16 mmol, 31%) as a white solid: mp 196−198 °C; IR (CH_2Cl_2) 2915, 1513, 1336, 1247, 1098 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 8.5 Hz, 2 H), 7.11 (d, J = 8.5 Hz, 2 H), 6.92 (d, J = 8.5 Hz, 2 H), 4.49−4.47 (m, 1 H), 4.18 (d, J = 15.0 Hz, 1 H), 4.05 (d, J = 6.5 Hz, 1 H), 3.83 (s, 3 H), 3.75 (d, J = 15.0 Hz, 1 H), 3.51 (d, J = 8.5 Hz, 1 H), 2.75 (d, J = 8.5 Hz, 1 H), 2.40 (s, 3 H), 2.34 (d, J = 12.5 Hz, 1 H), 2.24−2.17 (m, 1 H), 2.14−2.05 (m, 1 H), 1.89−1.81 (m, 2 H), 1.69−1.65 (m, 2 H), 1.41−1.38 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 143.5, 141.3, 134.5, 134.1, 129.8 128.5, 127.4, 125.4, 114.5, 60.7, 59.0, 58.4, 55.4, 46.3, 38.2, 36.5, 36.3, 35.5, 24.9, 21.5; HRMS (ESI$^+$) *m/e* 550.0905, $C_{25}H_{29}INO_3S$ $[M + H]^+$ calcd 550.0913.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for compounds **1a−j**, **2a−d**, **2f−h**, **3**, **4**, **7**, **12a−f**, **13a−f**, **14a−i**, **15a,b,d−h**, and **16** and X-ray structure data and crystallographic information files for compounds **2a,c−e,g**, **3**, **4**, **7**, **13a,c**, **15a**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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