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Transition-Metal-Free Carbofluorination of TBS-Protected Nitrogen-Containing Cyclic Enynols: Synthesis of Fluorinated Azabicycles

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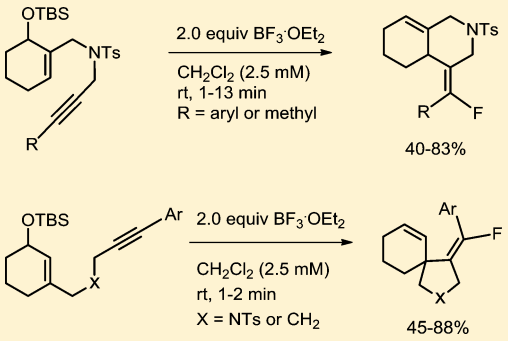
Supporting Information

ABSTRACT: The synthesis of fluorinated azabicycles from *tert*-butyldimethylsilyl-protected *N*-containing cyclic enynols using inexpensive $BF_3{\cdot}OEt_2$ is described. In this reaction, BF_3 reacts as both the Lewis acid and the fluoride source for cyclization/fluorination of the TBS-protected cyclic *N*-containing enynols. The method provides an easy access to fluorinated azabicycles where a new C(sp^2)−F bond and a new bicyclic skeleton are generated at ambient temperature within 1−13 min under metal-free reaction conditions.



INTRODUCTION

Fluorine-containing molecules play an important role in agrochemicals, pharmaceuticals, biomedical imaging agents, and chemical-resistant materials due to their unique physical and chemical properties.[1] Among them, monofluoroalkenes are of particular interest since they have potential applications in material sciences,[2] medicinal chemistry,[3] and synthetic organic chemistry[4] where they can be metalated and elaborated to other functionalities. Therefore, many synthetic methods have been developed for the efficient synthesis of these moieties, including Wittig-type olefination reactions via fluorine-containing diphenylphosphane oxides and aldehydes,[5] fluorination reactions of vinylstannanes and -silanes with electrophilic fluorine reagents,[6] the nucleophilic 1,4-addition of fluoride to ethyl prop-2-ynoate,[7] and the reaction of alkenylboronic acid with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor).[8] Recently, transition-metal-catalyzed fluorination of alkynes employing nucleophilic or electrophilic fluorinating reagents to generate alkenyl fluorides have been studied extensively, including attack of nucleophiles onto the gold-activated C−C triple bond followed by treatments of the resulting vinylgold intermediates with electrophilic fluorinating reagents,[9] the silver-catalyzed intramolecular oxidative aminofluorination of alkynes or allenes using *N*-fluorobenzenesulfonimide (NFSI) as an electrophilic fluorinating reagent,[10] the palladium-catalyzed carbofluorination of nitrogen-containing 1,6-enynes using NFSI as the fluorinating source,[11] and the (NHC)gold-catalyzed *trans*-hydrofluorination of alkynes using $Et_3N{\cdot}3HF$ as the nucleophilic fluorination reagent.[12] Despite the above-mentioned metal-catalyzed fluorination of alkynes affording alkenyl fluorides using various fluorine sources, a direct regio- and stereoselective fluorination of unactivated alkynes employing a simple, inexpensive Lewis acid to generate C(sp^2)−F bonds has yet to be developed. Inspired by our recent results on the $FeCl_3$-promoted carbochlorination of *N*-containing 2-en-7-yn-1-ols to give arylchloromethylene-substituted azaspirocycles[13] and the literature reports on the $BF_3{\cdot}OEt_2$-promoted Prins fluorination reactions of unsaturated alcohols and aldehydes to produce fluorinated heterocycles,[14] we envision an easy available fluorine-containing reagent that may act as both the Lewis acid and the nucleophilic fluorine source would greatly assist the synthesis of potential biologically active fluorinated azabicycles from *tert*-butyldimethylsilyl (TBS)-protected *N*-containing cyclic enynols. In this paper, we report a simple reaction that forms arylfluoromethylene-substituted azabicycles in a regio- and stereoselective fashion by the $BF_3{\cdot}OEt_2$-promoted carbofluorination of 3-arylpropagyltosylaminomethyl-tethered cyclohex-2-en-1-ols. In this transformation, detachment of the siloxy group of the enynol by $BF_3{\cdot}OEt_2$ generated an allylic carbonium ion. A subsequently *anti*-addition of the transient allylic carbonium ion and a fluoride ion across the alkyne led to the stereoselective formation of fluorinated-octahydroisoquinolines and 2-azaspiro[4.5]decenes. Furthermore, this process can be applied to the synthesis of fluorinated spirocarbocyclic analogous from 3-(5-arylpent-4-yn-1-yl)-cyclohex-2-en-1-ols.

RESULTS AND DISCUSSION

The required TBS-protected 3-phenylpropagyltosylamine-tethered 2-methylcyclohex-2-en-1-ol **1a** was prepared, according to the literature procedure, starting from treatments of cyclohex-2-en-1-one with formaldehyde under Baylis−Hillman reaction

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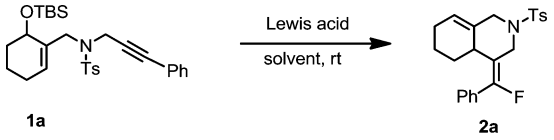
conditions.[15] Compound **1a** was used as the parent substrate for the survey of the optimal combination of solvent, concentration and fluorine-containing Lewis acids as revealed in Table 1. When $BF_3{\cdot}OEt_2$ (1.0 molar equiv) was subjected to

Table 1. Optimizing of Reaction Conditions in the Carbofluorination of 1a with $BF_3{\cdot}OEt_2$

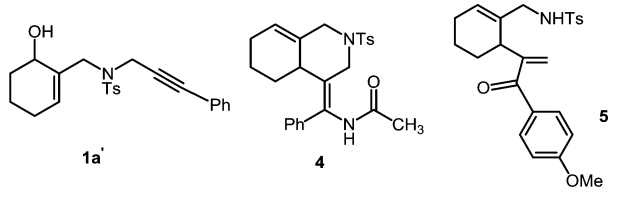


1a **2a**

entry	Lewis acid	loading (equiv)	solvent	time	yield[a] (%)
1	$BF_3{\cdot}OEt_2$	1	0.1 M CH_2Cl_2	1 min	25
2	$BF_3{\cdot}OEt_2$	2	0.1 M CH_2Cl_2	1 min	48
3	$BF_3{\cdot}OEt_2$	2	0.1 M DBE	1 min	34
4	$BF_3{\cdot}OEt_2$	2	0.1 M DCE	1 min	33
5	$BF_3{\cdot}OEt_2$	2	0.1 M $CHCl_3$	1 min	34
6	$BF_3{\cdot}OEt_2$	2	0.1 M toluene	1 min	6
7	$BF_3{\cdot}OEt_2$	2	0.01 M toluene	15 min	11
8	$BF_3{\cdot}OEt_2$	2	2.5 mM toluene	35 min	25
9	$BF_3{\cdot}OEt_2$	2	0.1 M CH_3CN	1 min	0[b]
10	$BF_3{\cdot}OEt_2$	10	0.1 M CH_2Cl_2	1 min	50
11	Ph_3CBF_4	2	0.1 M CH_2Cl_2	1 min	26
12	Ph_3CBF_4	5	0.1 M CH_2Cl_2	1 min	27
13	$BF_3{\cdot}OEt_2$	2	0.1 M THF	10 h	0[c]
14	*n*-Bu_4NF	2	0.1 M THF	0.5 h	0[c]
15	$BF_3{\cdot}OEt_2$	2	0.01 M THF	36 h	0[d]
16	$BF_3{\cdot}OEt_2$	2	0.01 M CH_2Cl_2	1 min	51
17	$BF_3{\cdot}OEt_2$	2	2.5 mM CH_2Cl_2	1 min	56

[a]Isolated yields by column chromatography. [b]Compound **4** was isolated in 79% yield. [c]Deprotection product **1a′** was isolated in good yields. [d]Compound **1a** was recovered quantitatively.

compound **1a** in 0.1 M of CH_2Cl_2 (DCM) at room temperature under an atmosphere of nitrogen, the reaction proceeded instantaneously to afford the phenyl(fluoro)-methylene-substituted octahydroisoquinolines **2a** with (*Z*)-configuration in 25% isolated yield (Table 1, entry 1), together with a trace amount of 4-benzoyloctahydroisoquinolines **3a** (Figure 1). None of the regioisomer resulting from addition of

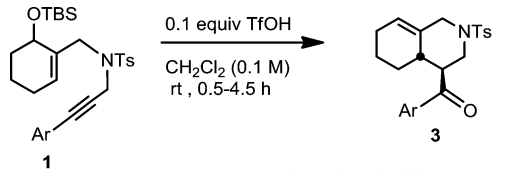


1a′ **4**

Figure 1. Structures of **1a′**, **4**, and **5**.

fluoride at the alkynyl carbon distal to the phenyl was detectable in the ^1H NMR spectrum of the crude mixture. The structure of **2a** was confirmed by X-ray diffraction analysis. Ketone **3a** may derive from $BF_3{\cdot}OEt_2$-assisted addition of water, presumably presenting in CH_2Cl_2, and the allylic moiety across the acetylene. To further clarify the structure of **3a**, compounds **1a–d** were treated with 0.1 molar equiv of TfOH at room temperature for 0.5–4.5 h,[16] ketones **3a–d** were obtained as the only diastereomer in each case, in 51–93% yields after aqueous workup and column chromatography on silica gel (Scheme 1). The relative configuration within **3a** was assigned as depicted on the basis of NOESY experiments and

Scheme 1. Synthesis of Ketones 3a–d



1 **3**

a : Ar = phenyl 72%
b : Ar = 4-methylphenyl 51%
c : Ar = 3-methylphenyl 88%
d : Ar = 1-naphthyl 93%

was further characterized by X-ray diffraction analysis of **3b** and **3d**. Moreover, the use of unprotected enynol **1a′** (Figure 1) and 1.0 equiv of $BF_3{\cdot}OEt_2$ significantly increased the yield of ketone **3a**. The desired **2a** and ketone **3a** was isolated in a ratio of 2:1 and in 20% overall yield. It was speculated that $HOBF_2$, detached by BF_3 from **1a′** may attack at the acetylene to produce ketone **3a** while $TBSOBF_2$ from **1a** does not add at the acetylene in the case of **1a**.

In order to eliminate the formation of the undesired ketone **3**, the following screening of the cyclization/fluorination reaction conditions was conducted using the TBS-protected substrate **1a**. Delightfully, the yield of **2a** increased up to 48% when **1a** (0.1 M in CH_2Cl_2) was treated with 2.0 equiv of $BF_3{\cdot}OEt_2$ at room temperature for 1 min (Table 1, entry 2). The use of dibromoethane (DBE), dichloroethane (DCE), chloroform, or toluene as solvents (substrates concentration 0.1 M) and 2.0 molar equiv of $BF_3{\cdot}OEt_2$ did not improve the yield of **2a** (Table 1, entries 3–6). Moreover, lowering concentration of **1a** in toluene to 0.01 M or 2.5 mM slightly increased the yield of **2a** to 11% and 25%, respectively (Table 1, entries 7 and 8). Changing the solvent to CH_3CN, a cyclization/amidation reaction occurred rapidly and generated the acetamido-(phenyl)methylene-substituted hexahydroisoquinoline **4** (Figure 1) as the major product in 79% yield, and no fluorinated compound was isolated (Table 1, entry 9). Moreover, increasing $BF_3{\cdot}OEt_2$ loading to 10 molar equiv did not improvement the yield of **2a** (Table 1, entry 10). The other fluoride source such as triphenylcarbenium tetrafluoroborate (Ph_3CBF_4) was also tested for the cyclization reaction. Reaction of Ph_3CBF_4 (2 or 5 equiv) with **1a** in CH_2Cl_2 at room temperature within 1 min produced **2a**, albeit in 26% and 27% yields, respectively (Table 1, entries 11 and 12). On the other hand, treatment of **1a** with 2.0 equiv of $BF_3{\cdot}OEt_2$ (0.1 M) or tetra-*n*-butylammonium fluoride (0.1 M) in THF at room temperature gave desilylation product **1a′** in good yields, and no fluorination reaction took place (Table 1, entries 13 and 14). When treated with $BF_3{\cdot}OEt_2$ in THF at lower concentration (0.01 M), **1a** was recovered quantitatively (Table 1, entry 15). Lowering concentration of **1a** in CH_2Cl_2 to 0.01 M gave **2a** in 51% yield (Table 1, entry 16). Finally, an increasing yield (56%) of **2a** was observed with decreasing concentration of **1a** to 2.5 mM in CH_2Cl_2 (Table 1, entry 17). Therefore, the use of $BF_3{\cdot}OEt_2$ (2.0 equiv) and **1a** in diluted CH_2Cl_2 (2.5 mM) at room temperature under nitrogen was found to be the most effective method and was selected as the standard reaction conditions. It is noteworthy that carbofluorination of **1a** under the optimal reaction conditions exclusively generated the fluorinated isoquinoline derivatives with the (*Z*)-

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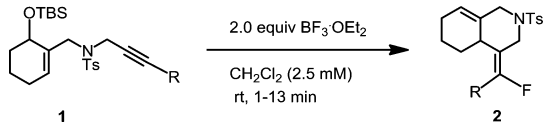
configuration. However, most transition-metal-catalyzed fluorination of alkynes required complex reaction conditions, elevated reaction temperatures or prolonged reaction times to give fluorinated olefins as a mixture of regio- or stereoisomers.[9,12b]

With these optimized reaction conditions, we next turned our effort to the scope of the substituent at the terminal position of the acetylene in this C(sp^2)−F-forming reaction using $BF_3 \cdot OEt_2$ in diluted CH_2Cl_2 at room temperature (Table 2). Substrates **1a−d** bearing electron-neutral aryl groups, within

Table 2. Substrate Scope



1 2

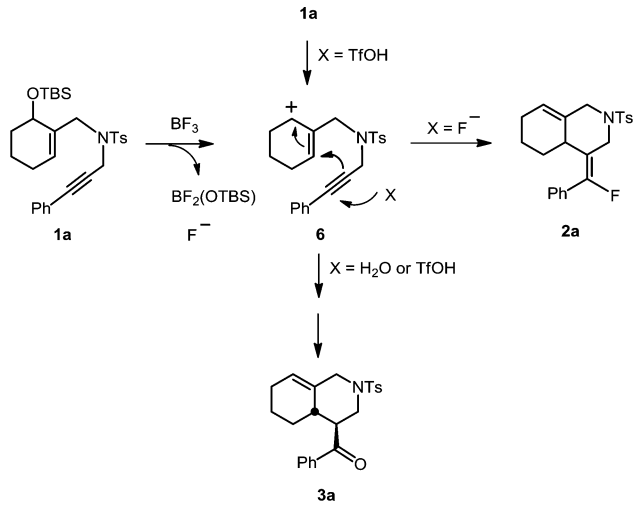
entry	enynol	R	product	yield[a] (%)
1	**1a**	phenyl	**2a**[c]	56
2	**1b**	4-methylphenyl	**2b**[c]	40
3	**1c**	3-methylphenyl	**2c**[c]	50
4	**1d**	1-naphthyl	**2d**	56
5	**1e**	4-nitrophenyl	**2e**[c]	74
6	**1f**	3-nitrophenyl	**2f**[c]	71
7	**1g**	4-carbethoxyphenyl	**2g**[c]	72
8	**1h**	3-carbethoxyphenyl	**2h**[c]	56
9	**1i**	4-methoxyphenyl	**2i**	0[b]
10	**1j**	4-bromophenyl	**2j**[c]	52
11	**1k**	hydrogen	**2k**	0
12	**1l**	methyl	**2l**	83

[a]Yields of isolated products. [b]Dienone **5** was isolated in 50% yield. [c]Structures were confirmed by X-ray diffraction analysis.

1−13 min, produced the corresponding fluorinated octahydroisoquinolines **2a−d** in 40−56% yields (Table 2, entries 1−4). The presence of electron-withdrawing nitro or ester groups on the phenyl ring, for example, **1e−h**, has been shown to be more efficient as evidenced by good yields (56−74%) of **2e−h** (Table 1, entries 5−8). Furthermore, treatment of the *p*-nitrophenyl alkyne **1e** with Ph_3CBF_4 in CH_2Cl_2 (2.5 mM) at room temperature for 1 min and triphenylcarbenium hexafluorophosphate (Ph_3CPF_6) in CH_2Cl_2 (2.5 mM) at room temperature for 1 h also produced **2e** in 60% and 59% yields, respectively. Compound **1i** with an electron-donating methoxy group at the C-4 position of the phenyl ring (Table 2, entry 9) did not afford any fluorinated isoquinoline derivatives. Instead, the dienone **5** (Figure 1) was obtained in 50% isolated yield. A bromine at the C-4 position of the phenyl ring, for example, **1j**, did not interfere with the activity of $BF_3 \cdot OEt_2$ and gave the corresponding fluorinated isoquinoline derivative **2j** in 52% yield (Table 2, entry 10). Unfortunately, the reaction of $BF_3 \cdot OEt_2$ with the terminal alkyne **1k** (Table 2, entry 11) resulted in decomposition of starting substrates. Finally, we were glad to find that the methyl terminal alkyne **1l** reacted efficiently with 2.0 molar equiv of $BF_3 \cdot OEt_2$ at room temperature for 5 min, leading to the desired fluorinated octahydroisoquinoline derivative **2l** in 83% isolated yield (Table 2, entry 12). It is important to mention that the palladium-catalyzed carbofluorination of nitrogen-containing 1,6-enynes with the *p*-nitrophenyl- or the methyl terminal-alkynes was inefficient and only produced trace amounts of the desired fluorinated lactams.[9d] The current approach to the synthesis of fluorinated octahydroisoquinolines **2e** and **2l** is accomplished without employing transition metal catalysts or complex reaction conditions, only requiring 2.0 equiv of $BF_3 \cdot OEt_2$ in diluted CH_2Cl_2 at room temperature for 1−5 min.

A concerted reaction path for the formation of **2** and **3** is suggested in Scheme 2. Detachment of the siloxy group of **1a**

Scheme 2. Postulated Reaction Paths for Formation of 1a and 3a



by $BF_3 \cdot OEt_2$ generated the allylic carbonium ion **6** and released a fluoride ion.[17] The acetylene was then simultaneously attacked by the allylic carbonium ion and an external fluoride (from the less congested side) in a *trans* manner to generate **2a** with (*Z*)-configuration. Addition of H_2O or TfOH to the allylic carbonium ion **6** afforded ketone **3a** after aqueous workup. This suggestion agreed with better yields obtained from substrates bearing an electron-withdrawing nitro- or ester groups on the phenyl ring (Table 2, entries 5−8). A similar cation-π cyclization of alkynes terminated by fluoride to give fluorinated bicyclo[4.4.0]decanes was observed when cyclodec-5-yn-1-ol was treated with $BF_3 \cdot OEt_2$ in CH_2Cl_2.[18]

However, given that 2.0 molar equiv of BF_3 was required for the carbofluorination, we suspect that tetrafluoroborate (BF_4^-), generated from fluoride and BF_3, may be the nucleophilic fluorine source. This suggestion is consistent with the success of Ph_3CBF_4 (Table 1, entries 11 and 12) acting as both the Lewis acid and the fluoride source in the cyclization/fluorination reactions. Examples of fluoride abstraction from tetrafluoroborates have been reported in the $AgBF_4$-assisted vinylation of aromatic compounds[19a] and photochemical decomposition of vinyl iodonium tetrafluoroborates.[19b] The formation of the dienone **5** is postulated in Scheme 3. The transient allylic carbonium ion **7** was attacked by the electron-rich (*p*-methoxyphenyl)alkynyl group to give the allenyl cation **8**. Upon aqueous quenching, attack of H_2O at the sp-hybridized carbon center of the allenyl moiety afforded **9**, which after the proton shuffle followed by the six-membered ring fragmentation gave dienone **5**.

This chemistry can be extended to the synthesis of (*Z*)-4-(arylfluoromethylene)-substituted azaspirocycles. As revealed in Scheme 4, the carbofluorination reaction of TBS-protected *N*-tosyl-3-arylpropagylamine-tethered 3-methylcyclohex-2-en-1-ol derivatives **10a−d**[13] proceeded within 1−2 min at room temperature to generate fluorinated azaspiro[4.5]dec-6-enes **11a−d** with (*Z*)-configuration in 45−77% yields. The structure

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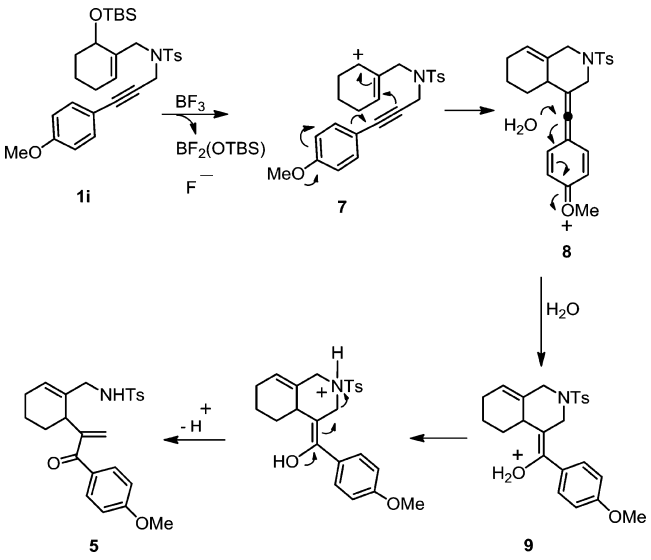
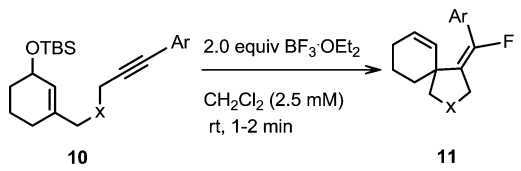
Scheme 3. Postulated Reaction Path Led to the Formation of Dienone 5 from 1i



Scheme 4. Synthesis of (*Z*)-4-(Arylfluoromethylene)-Substituted Aza- and Carbospirocycles



a : x = NTs, Ar = phenyl 73%
b : x = NTs, Ar = 4-methylphenyl 77%
c : x = NTs, Ar = 1-naphthyl 60%
d : x = NTs, Ar = 4-bromophenyl 45%
e : x = CH_2, Ar = phenyl 76%
f : x = CH_2, Ar = 4-bromophenyl 88%
g : x = CH_2, Ar = 4-methylphenyl 52%
h : x = CH_2, Ar = 4-phenylphenyl 76%

elucidation of **11a** was accomplished by X-ray diffraction analysis.[20] Moreover, this method can be applied to the synthesis of fluorinated carbospirocycles. Cyclic TBS-protected enynols **10e−h**[21] also underwent carbofluorination smoothly with 2.0 equiv of $BF_3{\cdot}OEt_2$ under the standard reaction conditions for 1−2 min to afford fluorinated carbospirocycles **11e−h** in 52−88% yields (Scheme 4).

In conclusion, we have developed a mild but highly efficient $BF_3{\cdot}OEt_2$-mediated carbofluorination of TBS-protected *N*-containing cyclic enynols. This reaction is operationally simple and proceeds to completion within 13 min at ambient temperature, providing a highly practical and economical method to the stereodefined fluorinated azabicycles.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Solvents were predried by molecular sieves and then by passing through an Al_2O_3 column. ^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 internal standard. ^{13}C NMR spectra were recorded with a 100 MHz spectrometer with $CDCl_3$ (77.0 ppm) as the internal standard. ^{19}F NMR spectra were recorded with a 376 MHz spectrometer. Mass spectra were acquired on a spectrometer at an ionization potential of 70 eV and were reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra were obtained with a double-focusing mass spectrometer.

Representative Procedure for Synthesis of Starting Compound 1. To a solution of cyclohex-2-en-1-one (7.69 g, 80.0 mmol) in MeOH (26.67 mL) and H_2O (133.33 mL) under nitrogen were added formaldehyde (37 wt % solution in water, 3.00 g, 100 mmol), $Ba(OH)_2$ (0.206 g, 1.2 mmol), and *N*-methyl-2-pyrrolidone (NMP, 0.34 g, 4.00 mmol). The reaction mixture was stirred at 29 °C for 4 h. The reaction mixture was extracted with CH_2Cl_2 (100 mL × 3). The combined extracts were washed with water (300 mL × 3) and brine (300 mL × 3), dried over anhydrous $MgSO_4$ (20 g), and concentrated to give a crude oil. The crude mixture was purified by flash column chromatography (silica gel, 1:3 ethyl acetate/hexanes) to afford 2-(hydroxymethyl)cyclohex-2-enol (4.33 g, 34.32 mmol, 43%). To the solution of 2-(hydroxymethyl)cyclohex-2-enol (4.33 g, 34.32 mmol) in CH_2Cl_2 (171.6 mL) were added triethylamine (4.55 g, 44.61 mmol) and acetic anhydride (4.20 g, 41.18 mmol). The reaction mixture was stirred at 30 °C for 6 h before quenching with 100 mL of saturated ammonium chloride solution. The solution was washed with water (300 mL × 3) and brine (300 mL × 3), dried over anhydrous $MgSO_4$ (15 g), and concentrated to give a crude oil. The crude mixture was purified by flash column chromatography (silica gel, 1:5 ethyl acetate/hexanes) to afford the corresponding acetate (3.23 g, 19.20 mmol, 56%). To the solution of the above acetate in 171 mL of CH_2Cl_2 was added $CeCl_3{\cdot}7H_2O$ (7.90 g, 21.12 mmol) followed by addition of $NaBH_4$ (0.73 g, 19.2 mmol) at 0 °C under nitrogen. The reaction was stirred at 0 °C for 30 min before quenching with 100 mL of saturated ammonium chloride solution. The resulting mixture was extracted with CH_2Cl_2 (200 mL × 3), and the combined extracts were washed with water and brine and dried over $MgSO_4$ (10 g). The filtrate was concentrated in vacuo to give (6-hydroxycyclohex-1-en-1-yl)methyl acetate (3.23 g, 19.01 mmol, 99%). To the above enol in 19.0 mL of CH_2Cl_2 were added triethylamine (3.88 g, 38.0 mmol), 4-dimethylaminopyridine (DMAP, 0.23 g, 1.90 mmol), and *tert*-butyldimethylsilyl chloride (4.30 g, 41.18 mmol). The reaction mixture was heated at reflux for 12 h, after which time the reaction mixture was filtered through a bed of Celite. The resulting solution was concentrated, and the residue was separated by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to afford (6-*tert*-butyldimethylsiloxycyclohex-1-en-1-yl)methyl acetate (3.95 g, 13.88 mmol, 73%). To the above crude mixture in MeOH (65.40 mL) in a 200 mL round-bottom flask was added K_2CO_3 (1.93 g, 13.88 mmol). The reaction was stirred at 30 °C for 1 h followed by quenching with 200 mL of saturated ammonium chloride. The resulting mixture was washed with water (200 mL × 3) and brine (200 mL × 3) and dried over $MgSO_4$ (10 g) to give (3-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methanol (3.30 g, 13.6 mmol, 98%). To the above crude product in 68 mL of THF at 0 °C under nitrogen were added diisopropyl azodicarboxylate (DIAD, 3.30 g, 16.3 mmol), triphenylphosphine (4.28 g, 16.3 mmol), and *N*-tosylprop-2-yn-1-amine (2.85 g, 13.6 mmol). The reaction was stirred at 0 °C for 2 h before quenching with 100 mL of water. The resulting mixture was extracted with CH_2Cl_2 (200 mL × 3), and the combined extracts were washed with water (200 mL × 3) and brine (200 mL × 3) and dried over $MgSO_4$ (10 g). The filtrate was concentrated in vacuo to give a crude oil. The crude mixture was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:20) to give *N*-((6-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)methyl)-4-methyl-*N*-(prop-2-yn-1-yl)-*p*-toluenesulfonamide (4.77 g, 11.0 mmol, 78%). To the above product in Et_3N (22.0 mL) were added $Pd(PPh_3)_4$ (25.40 mg, 0.022 mmol), CuI (0.084 g, 0.44 mmol), and iodobenzene (2.69 g, 13.2 mmol). The reaction mixture was stirred at 40 °C for 12 h before quenching with 100 mL of saturated aqueous ammonium chloride. The resulting solution was extracted with CH_2Cl_2 (100 mL × 3). The combined organic solution was washed with water (200 mL × 3) and brine (200 mL × 3) and dried over $MgSO_4$ (10 g). The filtrate was concentrated in vacuo to give a crude

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oil. The crude mixture was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:20) to produce *N*-((6-((tert-butyldimethylsilyl)oxy)cyclohex-1-en-1- yl)methyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-*p*-toluenesulfonamide (**1a**) (2.7 g, 5.30 mmol, 48%) as colorless crystals: mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.27−7.18 (m, 5H), 6.99 (d, J = 6.8 Hz, 2H), 5.84 (s, 1H), 4.41 (d, J = 18.5 Hz, 1H), 4.22 (s, 1H), 4.09 (d, J = 18.6 Hz, 1H), 4.04 (d, J = 15.7 Hz, 1H), 3.62 (d, J = 14 Hz, 1H), 2.30 (s, 3H), 2.12−1.97 (m, 2H), 1.78−1.74 (m, 2H), 1.67−1.52 (m, 2H), 0.89 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 135.9, 133.5, 131.4, 129.4, 129.3, 128.2, 128.0, 127.9, 122.3, 85.8, 81.9, 65.4, 49.5, 36.8, 32.3, 25.9, 25.4, 21.4, 18.1, 17.6, −4.4, −4.6; IR (CH_2Cl_2) 2929, 2851, 2356, 1351, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{39}NO_3NaSSi$ [M + Na]$^+$ 532.2318, found 532.2310.

To the solution of **1a** (0.62 g, 1.21 mmol) in 2.42 mL of THF was added tetra-*n*-butylammonium fluoride (TBAF, 0.379 g, 1.45 mmol) at 0 °C. The reaction was stirred at 0 °C for 30 min before filtering through a bed of Celite. The resulting solution was concentrated in vacuo to give a crude oil. The oil was purified by flash column chromatography (silica gel, ethyl acetate/hexanes 1:10) to give *N*-((6-hydroxycyclohex-1-en-1-yl)methyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-*p*-toluenesulfonamide (**1a′**) (0.44 g, 1.12 mmol, 93%) as colorless crystals: mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.2 Hz, 2H), 7.32−7.22 (m, 5H), 7.09−7.05 (m, 2H), 5.81 (t, J = 3.4 Hz, 1H), 4.54 (d, J = 18.5 Hz, 1H), 4.37−4.28 (m, 2H), 4.04 (d, J = 18.4 Hz, 1H), 3.45 (d, J = 14 Hz, 1H), 2.94 (d, J = 4.6 Hz, 1H), 2.34 (s, 3H), 2.14−1.95 (m, 2H), 1.94−1.84 (m, 1H), 1.80−1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 135.7, 134.1, 131.5, 130.8, 129.5, 128.4, 128.1, 127.8, 122.1, 85.7, 81.7, 64.3, 49.9, 36.4, 31.0, 25.5, 21.4, 19.0; IR (CH_2Cl_2) 3527, 2930, 1598, 1444, 1346, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{25}NO_3NaS$ [M + Na]$^+$ 418.1453, found 418.1451.

General Experimental Procedure for BF_3-Mediated Carbofluorination of TBS-Protected 3-Phenylpropagyltosylamine-Tethered 2-Methylcyclohex-2-en-1-ol 1a. To a solution of **1a** (0.1 g, 0.2 mmol) in 80.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.048 mL, 0.39 mmol). The reaction mixture was stirred at room temperature for 1 min, after which time no substrate **1a** was detected, as monitored by TLC. The reaction mixture was quenched with saturated aqueous sodium bicarbonate. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with brine (100 mL × 3), dried over anhydrous $MgSO_4$ (10 g), and concentrated to give the crude mixture.

*Data for (Z)-4-(Fluoro(phenyl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2a**).* In the typical procedure, to a solution of **1a** (0.1 g, 0.2 mmol) in 80.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.048 mL, 0.39 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **2a** (0.044 g, 0.11 mmol, 56%) as colorless crystals: mp 143−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.37−7.30 (m, 3H), 7.28−7.26 (m, 2H), 7.09−7.07 (m, 2H), 5.70 (s, 1H), 4.75 (d, J = 14.0 Hz, 1H), 3.94 (d, J = 11.9 Hz, 1H), 3.52−3.43 (m, 2H), 2.84 (s, 1H), 2.37 (s, 3H), 2.00−1.94 (m, 2H), 1.64−1.60 (m, 1H), 1.56−1.52 (m, 1H), 1.32−1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1 (d, J = 246 Hz), 143.2, 134.8, 131.2, 129.4, 129.3, 128.3, 128.2, 127.9, 127.8, 115.1 (d, J = 17 Hz), 50.8, 40.5 (d, J = 9 Hz), 36.1 (d, J = 3 Hz), 28.3 (d, J = 3 Hz), 24.9, 21.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −96.2; IR (CH_2Cl_2) 2923, 1676, 1598, 1447, 1344, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}FNO_2NaS$ [M + Na] $^+$ 420.1409, found 420.1399. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(Fluoro(p-tolyl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2b**).* In the typical procedure, to a solution of **1b** (0.15 g, 0.28 mmol) in 111.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.069 mL, 0.56 mmol). The reaction mixture was stirred for 13 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **2b** (0.046 g, 0.11 mmol, 40%) as colorless crystals: mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.97 (d, J = 7.9 Hz, 2H), 5.69 (s, 1H), 4.74 (d, J = 14.0 Hz, 1H), 3.93 (d, J = 11.9 Hz, 1H), 3.49 (d, J = 13.8 Hz, 1H), 3.44 (dd, J = 14.1, 4.8 Hz, 1H), 2.83 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.00−1.93 (m, 2H), 1.67−1.58 (m, 1H), 1.58−1.51 (m, 1H), 1.34−1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (d, J = 246 Hz), 143.1, 139.4, 134.9, 131.4, 129.4, 129.0, 128.6, 128.5, 128.1, 127.8, 114.6 (d, J = 18 Hz), 50.8 (d, J = 9 Hz), 36.2 (d, J = 4 Hz), 28.3 (d, J = 3 Hz), 25.0, 21.5, 21.4, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −95.9; IR (CH_2Cl_2) 2924, 2860, 2358, 1347, 1162 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}FNO_2NaS$ [M + Na]$^+$ 434.1566, found 434.1570. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(Fluoro(m-tolyl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2c**).* In the typical procedure, to a solution of **1c** (0.1 g, 0.19 mmol) in 74.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.046 mL, 0.37 mmol). The reaction mixture was stirred for 10 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **2c** (0.048 g, 0.093 mmol, 50%) as colorless crystals: mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.24−7.14 (m, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.70 (s, 1H), 4.74 (d, J = 14.0 Hz, 1H), 3.94 (d, J = 11.9 Hz, 1H), 3.49 (d, J = 13.3 Hz, 1H), 3.45 (dd, J = 14.1, 5 Hz, 1H), 2.81 (s, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.00−1.94 (m, 2H), 1.67−1.60 (m, 1H), 1.55−1.50 (m, 1H), 1.33−1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (d, J = 246 Hz), 143.1, 138.0, 134.9, 131.8, 131.5, 131.3, 130.1, 129.4, 128.6, 128.2, 127.9, 125.1 (d, J = 4 Hz), 114.8 (d, J = 18 Hz), 50.8, 40.5 (d, J = 8 Hz), 36.2 (d, J = 3 Hz), 28.4 (d, J = 3 Hz), 25.0, 21.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −95.5; IR (CH_2Cl_2) 2925, 2863, 2362, 1348, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}FNO_2NaS$ [M + Na]$^+$ 434.1566, found 434.1558. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(Fluoro(naphthalen-1-yl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2d**).* In the typical procedure, to a solution of **1d** (0.1 g, 0.18 mmol) in 72.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.044 mL, 0.36 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **2d** (0.045 g, 0.10 mmol, 56%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 3H), 7.84 (d, J = 8.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.36−7.31 (m, 3H), 7.19 (s, 1H), 7.07 (d, J = 4.9 Hz, 1H), 5.73 (s, 1H), 4.90 (d, J = 14.2 Hz, 1H), 4.00 (d, J = 11.4 Hz, 1H), 3.61 (dd, J = 14.2, 4.8 Hz, 1H), 3.49 (d, J = 11.4 Hz, 1H), 2.47 (s, 1H), 2.38 (s, 3H), 1.94−1.87 (m, 2H), 1.50−1.42 (m, 1H), 1.27−1.12 (m, 2H), 1.09−0.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3 (d, J = 251 Hz), 143.4, 134.8, 133.5, 131.1 (d, J = 6 Hz), 130.4 (d, J = 3 Hz), 129.6, 129.3, 128.6, 128.5, 128.3, 128.0, 127.0, 126.3, 124.9, 124.7, 117.2 (d, J = 16 Hz), 50.7, 40.1 (d, J = 6 Hz), 36.4 (d, J = 3 Hz), 29.7, 28.2 (d, J = 3 Hz), 24.9, 21.5, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −89.8; IR (CH_2Cl_2) 2926, 2858, 1459, 1345, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}FNO_2NaS$ [M + Na]$^+$ 470.1566, found 470.1574.

*Data for (Z)-4-(Fluoro(4-nitrophenyl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2e**).* In the typical procedure, to a solution of **1e** (0.1 g, 0.18 mmol) in 72.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.045 mL, 0.36 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **2e** (0.059 g, 0.133 mmol, 74%) as colorless crystals: mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 5.74 (s, 1H), 4.77 (d, J = 14.0 Hz, 1H), 3.97 (d, J = 12.1 Hz, 1H), 3.55 (d, J = 12.1 Hz, 1H), 3.47 (dd, J = 14.1, 5.0 Hz, 1H), 2.91 (s, 1H), 2.37 (s, 3H), 2.03−

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1.96 (m, 2H), 1.71−1.63 (m, 1H), 1.56−1.49 (m, 1H), 1.37−1.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5 (d, J = 244 Hz), 147.9, 143.4, 137.9, 137.6, 134.8, 130.3, 129.4, 128.8, 128.6, 128.5, 127.8, 123.7, 118.9 (d, J = 16 Hz), 50.7, 40.5 (d, J = 9 Hz), 36.1 (d, J = 3 Hz), 28.4, 24.8, 21.5, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −99.7; IR (CH_2Cl_2) 2930, 1599, 1520, 1347, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}FN_2O_4S$ [M − H]$^-$ 441.1284, found 441.1290. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(Fluoro(3-nitrophenyl)methylene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2f**).* In the typical procedure, to a solution of **1f** (0.1 g, 0.18 mmol) in 72.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.045 mL, 0.36 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **2f** (0.057 g, 0.128 mmol, 71%) as colorless crystals: mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 5.76 (s, 1H), 4.77 (d, J = 14.2 Hz, 1H), 3.98 (d, J = 12.0 Hz, 1H), 3.55 (d, J = 12.1 Hz, 1H), 3.47 (dd, J = 14.2, 5.0 Hz, 1H), 2.83 (s, 1H), 2.37 (s, 3H), 2.04−1.97 (m, 2H), 1.71−1.63 (m, 1H), 1.55−1.49 (m, 1H), 1.37−1.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3 (d, J = 245 Hz), 148.1, 143.6, 134.8, 133.6 (d, J = 4 Hz), 133.2 (d, J = 31 Hz), 130.4, 129.6, 129.5, 128.9, 127.8, 124.1, 122.9 (d, J = 4 Hz), 118.0 (d, J = 16 Hz), 50.8, 40.4 (d, J = 9 Hz), 36.1 (d, J = 3 Hz), 28.4 (d, J = 3 Hz), 24.9, 21.4, 21.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −98.4; IR (CH_2Cl_2) 2932, 1694, 1533, 1351, 1160 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}FN_2O_4S$ [M − H]$^-$ 441.1284, found 441.1291. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-Ethyl 4-(Fluoro(2-tosyl-2,3,4a,5,6,7-hexahydroisoquinolin-4(1H)- ylidene)methyl)benzoate (**2g**).* In the typical procedure, to a solution of **1g** (0.1 g, 0.17 mmol) in 68.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.042 mL, 0.34 mmol). The reaction mixture was stirred for 3 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **2g** (0.058 g, 0.12 mmol, 72%) as colorless crystals: mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 5.72 (s, 1H), 4.76 (d, J = 14.1 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.96 (d, J = 12.0 Hz, 1H), 3.53 (d, J = 12.0 Hz, 1H), 3.46 (dd, J = 14.2, 5.0 Hz, 1H), 2.87 (s, 1H), 2.37 (s, 3H), 2.01−1.95 (m, 2H), 1.67−1.60 (m, 1H), 1.55−1.48 (m, 1H), 1.40 (t, J = 7.1 Hz, 3H), 1.34−1.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 152.9 (d, J = 246 Hz), 143.3, 135.8 (d, J = 30 Hz), 134.8, 131.2, 130.8, 129.5, 129.4, 128.5, 127.8, 127.7, 117.0 (d, J = 17 Hz), 61.3, 50.8, 40.5 (d, J = 9 Hz), 36.1 (d, J = 3 Hz), 28.3 (d, J = 3 Hz), 24.9, 21.5, 21.4, 14.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −98.4; IR (CH_2Cl_2) 2923, 2856, 1716, 1277, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{29}FNO_4S$ [M + H]$^+$ 470.1801, found 470.1796. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-Ethyl 3-(Fluoro(2-tosyl-2,3,4a,5,6,7- hexahydroisoquinolin-4(1H)-ylidene)methyl)benzoate (**2h**).* In the typical procedure, to a solution of **1h** (0.155 g, 0.27 mmol) in 106.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.066 mL, 0.53 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **2h** (0.070 g, 0.150 mmol, 56%) as colorless crystals: mp 164−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.9 Hz, 1H), 7.80−7.76 (m, 3H), 7.42 (t, J = 7.8 Hz, 1H), 7.31−7.26 (m, 3H), 5.71 (s, 1H), 4.75 (d, J = 14.1 Hz, 1H), 4.39 (quart, J = 7.1 Hz, 2H), 3.96 (d, J = 12.0 Hz, 1H), 3.53 (d, J = 12.0 Hz, 1H), 3.47 (dd, J = 14.1, 5.0 Hz, 1H), 2.85 (s, 1H), 2.35 (s, 3H), 2.01−1.95 (m, 2H), 1.67−1.61 (m, 1H), 1.57−1.51 (m, 1H), 1.41 (t, J = 7.2 Hz, 3H), 1.33−1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 152.9 (d, J = 246 Hz), 143.4, 134.7, 132.0, 131.9, 131.9 (d, J = 30 Hz), 130.9, 130.8, 130.3, 129.4, 128.9 (d, J = 4 Hz), 128.5, 128.4, 127.7, 116.1 (d, J = 17 Hz), 61.3, 50.8, 40.5, (d, J = 9 Hz), 36.1 (d, J = 3 Hz), 28.3 (d, J = 3 Hz), 24.9, 21.4 (d, J = 3 Hz), 14.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −97.6; IR (CH_2Cl_2) 2934, 2867, 1721, 1255, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{28}FNO_4NaS$ [M + Na]$^+$ 492.1612, found 492.1621. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-((4-Bromophenyl)fluoromethylene)-2-tosyl-1,2,3,4,4a,5,6,7- octahydroisoquinoline (**2j**).* In the typical procedure, to a solution of **1j** (0.12 g, 0.204 mmol) in 82.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.051 mL, 0.41 mmol). The reaction mixture was stirred for 12 min and the crude mixture was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **2j** (0.051 g, 0.11 mmol, 52%) as colorless crystals: mp 164−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.3 Hz, 2H), 5.71 (s, 1H), 4.73 (d, J = 14.0 Hz, 1H), 3.94 (d, J = 12.0 Hz, 1H), 3.51 (d, J = 11.9 Hz, 1H), 3.44 (dd, J = 14.0, 4.8 Hz, 1H), 2.80 (s, 1H), 2.38 (s, 3H), 2.01−1.94 (m, 2H), 1.68−1.60 (m, 1H), 1.54−1.47 (m, 1H), 1.35−1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (d, J = 245 Hz), 143.2, 134.8, 131.7, 130.9, 130.5 (d, J = 30 Hz), 129.5, 129.4, 128.5, 127.8, 123.6, 116.0 (d, J = 17 Hz), 50.8, 40.4 (d, J = 8 Hz), 36.1, 28.3, 24.9, 21.5, 21.4; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −97.2; IR (CH_2Cl_2) 2925, 2361, 1685, 1347, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}BrFNO_2NaS$ [M + Na]$^+$ 500.0494, found 500.0497. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(1-Fluoroethylidene)-2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinoline (**2l**).* Compound **1l** was prepared from *N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide and (3-((*tert*-butyldimethylsilyl)oxy)cyclo-hex-1-en-1-yl)methanol under the Mitsunobu reaction condition. In the typical procedure, to a solution of **1l** (0.1 g, 0.224 mmol) in 89.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.055 mL, 0.45 mmol). The reaction mixture was stirred for 5 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:20 ethyl acetate/hexanes) to give **2l** (0.063 g, 0.186 mmol, 83%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 5.66 (s, 1H), 4.58 (d, J = 13.8 Hz, 1H), 3.88 (d, J = 11.9 Hz, 1H), 3.39 (d, J = 11.9 Hz, 1H), 3.23 (dd, J = 13.7, 1.9 Hz, 1H), 2.65 (d, J = 9.7 Hz, 1H), 2.42 (s, 3H), 2.03−1.95 (m, 2H), 1.79−1.69 (m, 5H), 1.51−1.38 (m, 1H), 1.281.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6 (d, J = 249 Hz), 143.0, 134.9, 131.4, 129.2, 128.0, 127.7, 112.0 (d, J = 14 Hz), 50.4, 39.6 (d, J = 9 Hz), 36.3 (d, J = 5 Hz), 28.1 (d, J = 3 Hz), 24.9, 21.5, 14.3 (d, J = 31 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ −98.2; IR (CH_2Cl_2) 2925, 2849, 2361, 1715, 1347, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}FNO_2NaS$ [M + Na]$^+$ 358.1253, found 358.1260.

*Data for Phenyl(2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinolin-4-yl)methanone (**3a**).* In the typical procedure, to a solution of **1a** (0.2 g, 0.39 mmol) in 3.9 mL of CH_2Cl_2 at room temperature under open system was added TfOH (0.0036 mL, 0.04 mmol). The reaction mixture was stirred for 4.5 h, and the crude mixture was purified by flash column chromatography (silica gel, 1:15 ethyl acetate/hexanes) to give **3a** (0.113 g, 0.282 mmol, 72%) as colorless crystals: mp 167−168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4 Hz, 2H), 7.64−7.60 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.80 (s, 1H), 4.17 (dd, J = 12.6, 1.44 Hz, 1H), 3.91 (ddd, J = 11.8, 3.3, 2.0 Hz, 1H), 3.50 (td, J = 11.1, 3.7 Hz, 1H), 2.94 (d, J = 12.5 Hz, 1H), 2.48−2.42 (m, 5H), 2.00 (m, 2H), 1.72−1.60 (m, 2H), 1.40−1.29 (m, 1H), 1.12−1.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 143.8, 136.7, 133.9, 133.1, 131.4, 129.7, 128.9, 128.4, 127.8, 126.1, 52.8, 49.2, 38.1, 28.0, 25.2, 21.5, 21.2; IR (CH_2Cl_2) 2926, 1677, 1597, 1587, 1348, 1167 cm^{-1}; (ESI) calcd for $C_{23}H_{25}NO_3NaS$ [M + Na]$^+$ 418.1453, found 418.1451.

*Data for p-Tolyl(2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinolin-4-yl)methanone (**3b**).* In the typical procedure, to a solution of **1b** (0.15 g, 0.28 mmol) in 2.8 mL of CH_2Cl_2 at room temperature under open system was added TfOH (0.0026 mL, 0.028 mmol). The reaction mixture was stirred for 18 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3b** (0.058 g, 0.14 mmol, 51%) as colorless crystals: mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.62 (d, J

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= 8.2 Hz, 2H), 7.35−7.27 (m, 4H), 5.80 (s, 1H), 4.16 (d, J = 12.5 Hz, 1H), 3.89 (dd, J = 11.6, 1.8 Hz, 1H), 3.47 (td, J = 11.1, 3.7 Hz, 1H), 2.93 (d, J = 12.5 Hz, 1H), 2.49−2.41 (m, 8H), 2.05−1.96 (s, 2H), 1.73−1.65 (m, 1H), 1.64−1.57 (m, 1H), 1.40−1.27 (m, 1H), 1.11−1.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 144.9, 143.7, 134.2, 133.1, 131.5, 129.7, 129.6, 128.5, 127.8, 126.1, 52.8, 49.3, 49.0, 38.1, 28.0, 25.2, 21.7, 21.5, 21.2; IR (CH_2Cl_2) 2925, 2360, 1673, 1348, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}NO_3NaS$ [M + Na]$^+$ 432.1609, found 432.1600. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for m-Tolyl(2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinolin-4-yl)methanone (**3c**).* In the typical procedure, to a solution of **1c** (0.1 g, 0.19 mmol) in 1.9 mL of CH_2Cl_2 at room temperature under open system was added TfOH (0.0017 mL, 0.019 mmol). The reaction mixture was stirred for 3.5 h, and the crude mixture was purified by flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3c** (0.067 g, 0.16 mmol, 88%) as colorless crystals: mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.45−7.36 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.80 (s, 1H), 4.17 (d, J = 12.5 Hz, 1H), 3.90 (d, J = 11.8 Hz, 1H), 3.49 (td, J = 11.1, 3.7 Hz, 1H), 2.94 (d, J = 12.5 Hz, 1H), 2.48−2.41 (m, 8H), 2.05−1.97 (s, 2H), 1.73−1.66 (m, 1H), 1.65−1.58 (m, 1H), 1.41−1.28 (m, 1H), 1.12−1.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 143.7, 138.7, 136.7, 134.6, 133.0, 131.4, 129.7, 128.8, 127.8, 126.1, 125.6, 52.7, 49.2, 38.0, 27.9, 25.1, 21.5, 21.3, 21.1; IR (CH_2Cl_2) 2926, 2360, 1676, 1349, 1162 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}NO_3NaS$ [M + Na]$^+$ 432.1609, found 432.1614.

*Data for Naphthalen-1-yl(2-tosyl-1,2,3,4,4a,5,6,7-octahydroisoquinolin-4-yl)methanone (**3d**).* In the typical procedure, to a solution of **1d** (0.1 g, 0.18 mmol) in 1.8 mL of CH_2Cl_2 at room temperature under open system was added TfOH (0.0016 mL, 0.018 mmol). The reaction mixture was stirred for 35 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:10 ethyl acetate/hexanes) to give **3d** (0.074 g, 0.17 mmol, 93%) as colorless crystals: mp 187−188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.63 (d, J = 8.2 Hz, 2H), 7.61−7.51 (m, 3H), 7.32 (d, J = 8 Hz, 2H), 5.79 (s, 1H), 4.18 (d, J = 12.6 Hz, 1H), 4.02 (dt, J = 11.8, 1.6 Hz, 1H), 3.48 (td, J = 11, 3.7 Hz, 1H), 2.99 (d, J = 12.5 Hz, 1H), 2.62 (t, J = 11.6 Hz, 1H), 2.56 (s, 1H), 2.44 (s, 3H), 2.02−1.95 (m, 2H), 1.83−1.75 (m, 1H), 1.62−1.55 (m, 1H), 1.42−1.30 (m, 1H), 1.16−1.03(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 143.7, 135.5, 134.0, 133.7, 133.2, 131.3, 130.0, 129.7, 128.6, 128.3, 127.8, 126.6, 126.1, 125.5, 124.4, 53.0, 52.7, 49.3, 38.6, 28.0, 25.1, 21.5, 21.2; IR (CH_2Cl_2) 2927, 2358, 1670, 1591, 1347, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{27}NO_3NaS$ [M + Na]$^+$ 468.1609, found 468.1604. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-N-(Phenyl(2-tosyl-2,3,4a,5,6,7-hexahydroisoquinolin-4(1H)ylid- ene)methyl)acetamide (**4**).* In the typical procedure, to a solution of **1a** (0.1 g, 0.2 mmol) in 2.0 mL of CH_3CN at room temperature under open system was added $BF_3{\cdot}OEt_2$ (0.048 mL, 0.39 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:1 ethyl acetate/hexanes) to give **4** (0.068 g, 0.155 mmol, 79%) as colorless crystals: mp 204−205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.33−7.30 (m, 5H), 7.10−7.08 (m, 2H), 6.75 (s, 1H), 5.59 (s, 1H), 4.21 (d, J = 13.9 Hz, 1H), 3.84 (d, J = 12.1 Hz, 1H), 3.75 (d, J = 12.1 Hz, 1H), 3.35 (d, J = 13.9 Hz, 1H), 2.98 (s, 1H), 2.42 (s, 3H), 2.09 (s, 3H), 1.90−1.88 (m, 2H), 1.56−1.48 (m, 2H), 1.26−1.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 143.4, 137.1, 135.5, 131.6, 131.1, 131.0, 129.5, 128.7, 128.3, 128.2, 127.8, 127.5, 50.8, 43.7, 38.0, 28.3, 24.9, 23.5, 21.5; IR (CH_2Cl_2) 3247, 2929, 1669, 1507, 1158 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}N_2O_3NaS$ [M + Na]$^+$ 459.1718, found 459.1715. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for N-((6-(3-(4-Methoxyphenyl)-3-oxoprop-1-en-2-yl)-cyclohex-1-en-1-yl)methyl)-4-methylbenzenesulfonamide (**5**).* In the typical procedure, to a solution of **1i** (0.1 g, 0.19 mmol) in 74.0 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.046 mL, 0.37 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, 1:5 ethyl acetate/hexanes) to give **5** (0.039 g, 0.093 mmol, 50%) as a pale-yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.84 (s, 1H), 5.53 (d, J = 17.1 Hz, 2H), 5.16 (t, J = 6.2 Hz, 1H), 3.88 (s, 3H), 3.58−3.44 (m, 2H), 3.28 (s, 1H), 2.38 (s, 3H), 2.08−1.99 (m, 1H), 1.95−1.84 (m, 1H), 1.53−1.45 (m, 3H), 1.42−1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 163.5, 149.3, 143.0, 137.6, 133.0, 132.2, 129.9, 129.4, 128.5, 127.2, 124.4, 113.6, 55.5, 47.6, 37.6, 27.8, 24.8, 21.4, 17.8; IR (CH_2Cl_2) 3278, 2931, 1945, 1599, 1160 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}NO_4NaS$ [M + Na]$^+$ 448.1559, found 448.1555.

*Data for (Z)-4-(Fluoro(phenyl)methylene)-2-tosyl-2-azaspiro-[4.5]dec-6-ene (**11a**).* In the typical procedure, to a solution of **10a** (0.13 g, 0.25 mmol) in 101 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.062 mL, 0.51 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to give **11a** (0.073 g, 0.18 mmol, 73%) as colorless crystals: mp 146−147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.37−7.33 (m, 4H), 7.31 (d, J = 6.7 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 5.50−5.47 (m, 1H), 5.03 (d, J = 11.1 Hz, 1H), 4.28 (dd, J = 14.7, 3.4 Hz, 1H), 3.96 (dd, J = 14.7, 3.4 Hz, 1H), 3.40 (dd, J = 9.4, 2.5 Hz, 1H), 2.78 (d, J = 9.4 Hz, 1H), 2.46 (s, 3H), 1.99−1.91 (m, 1H), 1.83−1.75 (m, 1H), 1.70 (dd, J = 13.5, 2.9 Hz, 1H), 1.61 (dd, J = 12.0, 1.3 Hz, 1H), 1.53−1.43 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9 (d, J = 242 Hz), 143.7, 132.3, 131.3 (d, J = 27 Hz), 129.7, 129.4, 129.3, 129.2, 128.8, 128.0, 127.5, 123.2 (d, J = 19 Hz), 59.4, 49.7 (d, J = 10 Hz), 44.6 (d, J = 5 Hz), 32.3 (d, J = 3 Hz), 24.4, 21.6, 20.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −90.4; IR (CH_2Cl_2) 2935, 1713, 1598, 1446, 1351, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}FNO_2S$ [M − H]$^-$ 396.1434, found 396.1439. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

*Data for (Z)-4-(Fluoro(p-tolyl)methylene)-2-tosyl-2-azaspiro[4.5]-dec-6-ene (**11b**).* In the typical procedure, to a solution of **10b** (0.13 g, 0.25 mmol) in 101 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.062 mL, 0.51 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to give **11b** (0.08 g, 0.20 mmol, 77%) as colorless crystals: mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 5.52−5.49 (m, 1H), 5.05 (dd, J = 10.0, 1.0, Hz, 1H), 4.26 (dd, J = 14.6, 2.8 Hz, 1H), 3.95 (dd, J = 14.7, 3.3 Hz, 1H), 3.39 (dd, J = 9.3, 2.44 Hz, 1H), 2.78 (d, J = 9.3 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 1.98−1.92 (m, 2H), 1.86−1.77 (m, 1H), 1.73−1.63 (m, 2H), 1.54−1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0 (d, J = 242 Hz), 143.7, 139.3, 132.2, 129.7, 129.3, 128.6, 128.5, 128.2, 128.1, 128.0, 122.5 (d, J = 20 Hz), 59.4, 49.8 (d, J = 11 Hz), 44.5 (d, J = 5 Hz), 32.1 (d, J = 2 Hz), 24.4, 21.4 (d, J = 22 Hz), 20.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −90.4; IR (CH_2Cl_2) 3027, 2935, 2865, 2361, 1712, 1598, 1451, 1350 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}FNO_2S$ [M − H]$^-$ 410.1590, found 410.1599.

*Data for (Z)-4-(Fluoro(naphthalen-1-yl)methylene)-2-tosyl-2-azaspiro[4.5]dec-6-ene (**11c**).* In the typical procedure, to a solution of **10c** (0.11 g, 0.25 mmol) in 101 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.062 mL, 0.51 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to give **11c** (0.068 g, 0.15 mmol, 60%) as colorless crystals: mp 193−194 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87−7.77 (m, 5H), 7.51−7.47 (m, 2H), 7.44−7.33 (m, 4H), 5.07 (dd, J = 9.8, 5.6 Hz, 1H), 4.85 (d, J = 9.6 Hz, 1H), 4.44 (dd, J = 14.5, 2.9 Hz, 1H), 4.09 (dd, J = 14.5, 3.3 Hz, 1H), 3.39 (dd, J = 9.4, 2.6 Hz, 1H), 2.79 (d, J = 9.4 Hz, 1H), 2.49 (s, 3H), 1.90−1.87 (m, 1H), 1.67 (dd, J = 12.2, 4.3 Hz, 1H), 1.49−1.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2 (d, J = 247 Hz), 143.7, 133.2, 132.7, 132.0, 130.4 (d, J = 2 Hz), 129.8, 129.6, 129.5 (d, J = 4 Hz), 128.8, 128.6, 128.2, 128.0, 126.7, 126.1, 125.3 (d, J = 18 Hz), 125.3, 124.2, 59.1, 49.2 (d, J = 7

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Hz), 44.8 (d, J = 4 Hz), 32.8, 24.3, 21.6, 20.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −84.2; IR (CH_2Cl_2) 2934, 2341, 1717, 1597, 1447, 1348, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{26}FNO_2S$ $[M - H]^-$ 446.1590, found 446.1594.

*Data for (Z)-4-((4-Bromophenyl)fluoromethylene)-2-tosyl-2-azaspiro[4.5]dec-6- ene (**11d**).* In the typical procedure, to a solution of **10d** (0.15 g, 0.25 mmol) in 101 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.062 mL, 0.51 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, 1:30 ethyl acetate/hexanes) to give **11d** (0.054 g, 0.11 mmol, 45%) as colorless crystals: mp 147−148 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 (d, J = 8.1 Hz, 2H), 7.39 (dd, J = 20.2, 8.1 Hz, 4H), 7.22 (d, J = 8.3 Hz, 2H), 5.57−5.54 (m, 1H), 5.01 (d, J = 10.1 Hz, 1H), 4.27 (dd, J = 14.9, 2.6 Hz, 1H), 3.92 (dd, J = 14.9, 3.3 Hz, 1H), 3.41 (dd, J = 9.3, 2.2 Hz, 1H), 2.77 (d, J = 2.2 Hz, 1H), 2.46 (s, 3H), 2.02−1.97 (m, 2H), 1.84−1.78 (m, 1H), 1.75−1.71 (m, 1H), 1.58−1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, J = 242 Hz), 143.8, 132.2, 130.7, 130.2, 130.1, 130.0, 129.7, 128.9, 128.0, 124.1 (d, J = 19 Hz), 123.6 (d, J = 2 Hz), 59.3, 49.8 (d, J = 10 Hz), 44.6 (d, J = 5 Hz), 32.1 (d, J = 2 Hz), 24.4, 21.5, 19.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −92.0; IR (CH_2Cl_2) 3024, 2936, 2864, 2257, 1916, 1711, 1595, 1488, 1394, 1350, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}BrFNO_2S$ $[M + H]^+$ 476.0695, found 476.0692.

*Data for (E)-1-(Fluoro(phenyl)methylene)spiro[4.5]dec-6-ene (**11e**).* In the typical procedure, to a solution of **10e** (0.177 g, 0.5 mmol) in 200 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.127 mL, 1.0 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, hexanes) to give **11e** (0.092 g, 0.38 mmol, 76%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 2H), 7.29−7.27 (m, 3H), 5.40−5.33 (m, 2H), 2.76−2.63 (m, 2H), 1.91−1.85 (m, 1H), 1.76−1.65 (m, 5H), 1.63−1.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7 (d, J = 236 Hz), 135.0, 133.3 (d, J = 30 Hz), 129.9 (d, J = 19 Hz), 129.1 (d, J = 4 Hz), 128.3 (d, J = 2 Hz), 127.3, 125.0, 45.3 (d, J = 5 Hz), 42.5, 32.6 (d, J = 2 Hz), 29.9 (d, J = 6 Hz), 24.6, 22.2, 20.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −90.8; IR (CH_2Cl_2) 3059, 3020, 2936, 2862, 1700, 1602, 1492, 1446, 1435, 1292, 1261 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{19}F$ $[M]^+$ 242.1471, found 242.1477.

*Data for (E)-1-((4-Bromophenyl)fluoromethylene)spiro[4.5]dec-6-ene (**11f**).* In the typical procedure, to a solution of **10f** (0.217 g, 0.5 mmol) in 200 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.127 mL, 1.0 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, hexanes) to give **11f** (0.141 g, 0.44 mmol, 88%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 5.43 (ddd, J = 9.8, 5.3, 2.0 Hz, 1H), 5.34 (dd, J = 2.5, 1.3 Hz, 1H), 2.78−2.59 (m, 2H), 1.94−1.89 (m, 1H), 1.77−1.65 (m, 5H),1.56−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5 (d, J = 235 Hz), 134.7, 132.1 (d, J = 31 Hz), 130.9 (d, J = 19 Hz), 130.5 (d, J = 5 Hz), 127.9, 125.5, 122.5 (d, J = 24 Hz), 45.3 (d, J = 5 Hz), 42.5, 32.4, 30.0 (d, J = 6 Hz), 24.6, 22.1, 20.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −92.4; IR (CH_2Cl_2) 3018, 2936, 2862, 1699, 1590, 1487, 1393, 1258 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{18}BrF$ $[M]^+$ 320.0576, found 320.0574.

*Data for (E)-1-(Fluoro(p-tolyl)methylene)spiro[4.5]dec-6-ene (**11g**).* In the typical procedure, to a solution of **10g** (0.184 g, 0.5 mmol) in 200 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.127 mL, 1.0 mmol). The reaction mixture was stirred for 1 min and the crude mixture was purified by flash column chromatography (silica gel, hexanes) to give **11g** (0.066 g, 0.26 mmol, 52%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.43−5.36 (m, 2H), 2.74−2.60 (m, 2H), 2.34 (s, 3H), 1.93−1.87 (m, 1H), 1.78−1.63 (m, 5H), 1.62−1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9 (d, J = 236 Hz), 138.2 (d, J = 21 Hz), 135.1, 130.5 (d, J = 30 Hz), 129.3 (d, J = 20 Hz), 128.9 (d, J = 5 Hz), 128.1, 124.9, 45.2 (d, J = 5 Hz), 42.6, 32.5 (d, J = 2 Hz), 29.9 (d, J = 6 Hz), 24.6, 22.2, 21.3, 20.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −90.6; IR (CH_2Cl_2) 3020, 2936, 2866, 1701, 1613, 1512, 1450, 1260 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{21}F$ $[M]^+$ 256.1627, found 256.1634.

*Data for (E)-4-(Fluoro(spiro[4.5]dec-6-en-1-ylidene)methyl)-1,1′-biphenyl (**11h**).* In the typical procedure, to a solution of **10h** (0.177 g, 0.41 mmol) in 164 mL of CH_2Cl_2 at room temperature under an atmosphere of nitrogen was added $BF_3{\cdot}OEt_2$ (0.104 mL, 0.82 mmol). The reaction mixture was stirred for 1 min, and the crude mixture was purified by flash column chromatography (silica gel, hexanes) to give **11h** (0.099 g, 0.31 mmol, 76%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.60 (m, 2H), 7.57−7.51 (m, 4H), 7.45−7.41 (m, 2H), 7.36−7.32 (m, 1H), 5.47−5.40 (m, 2H), 2.78−2.64 (m, 2H), 1.95−1.89 (m, 1H), 1.83−1.67 (m, 5H), 1.66−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4 (d, J = 235 Hz), 140.7 (d, J = 30 Hz), 135.0, 132.2 (d, J = 30 Hz), 130.3 (d, J = 19 Hz), 129.3 (d, J = 5 Hz), 128.8, 127.4, 126.0, 125.2, 45.4 (d, J = 5 Hz), 42.6, 32.5 (d, J = 2 Hz), 30.1 (d, J = 6 Hz), 24.7, 22.2, 20.3; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −92.0; IR (CH_2Cl_2) 3029, 2936, 2863, 1698, 1582, 1487, 1434, 1272 cm^{-1}; HRMS (FAB+) calcd for $C_{23}H_{23}F$ $[M]^+$ 318.1784, found 318.1790.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for compounds **1a−l**, **2a−h,j,l**, **3a−d**, **4**, **5**, **10a−h**, and **11a−h** and X-ray crystallographic information files for compounds **2a−c,e−h,j**, **3b,d**, **4**, and **11a**. 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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(20) CCDC 926589 (**2a**), 926590 (**2b**), 926591 (**2c**), 926592 (**2e**), 926593 (**2f**), 926594 (**2g**), 926595 (**2h**), 926596 (**2j**), 937158 (**3b**), 937170 (**3d**), 926597 (**4**), and 926598 (**11a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
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