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TfOH- and HBF_4-Mediated Formal Cycloisomerizations and [4+3] Cycloadditions of Allene-alkynylbenzenes

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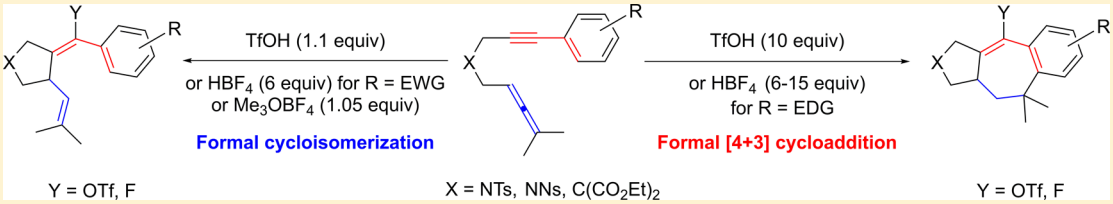
Supporting Information



ABSTRACT: A metal-free, TfOH (1.1 equiv)-mediated formal cycloisomerization of easily prepared allene-alkynylbenzenes to give pyrrolidines and cyclopentanes derivatives was developed. This reaction is initiated by the generation of allylic cation from allene, followed by alkyne's reaction with the allylic cation, to give a vinyl cation, which is finally intercepted by the triflate (TfO) anion. This cycloisomerization can be further tuned to become an acid-mediated intramolecular formal [4+3] cycloaddition by using 10 equiv of TfOH (The excess acid was used to promote the Friedel−Crafts reaction of the acid-mediated cycloisomerization products). The present system can also be applied to synthesized F-incorporated products by using HBF_4 or Me_3OBF_4 as the fluoro source.

INTRODUCTION

In 1985, the Trost[1] group pioneered the Pd-catalyzed cycloisomerization of 1,6-enynes for the synthesis of cyclopentane derivatives. Since then, many other transition-metal-catalyzed cyclizations of 1,6-enynes have been developed and these reactions are now becoming powerful methods for constructing cyclic molecules using relatively simply prepared linear substrates. Many other leading organic chemists have been further expanding enyne cycloisomerization by trapping the cycloisomerization intermediates using either reductive, oxidative, or nucleophilic reagents to get various products.[2] It has been known that allenes share many similar reactions with alkenes. In principle, 1,7-allene-ynes can also undergo various cycloisomerizations under different transition-metal catalysis. This has been proved by many pioneering works in this direction[3] (Scheme 1a). But to our surprise, trapping the intermediates in the cycloisomerization of 1,7-allene-ynes to generate further functionalized molecules had only a few reports (Scheme 1b).[4] The Bäckvall[4d−g] group has performed excellent work in this field. In their systematic work, Bäckvall and co-workers showed allenynes can undergo oxidative cyclization by using a Pd(II) catalyst, and the intermediates can be trapped by different pro-nucleophiles to give various functionalized five-membered rings. Another example was reported by Liu,[4b] who showed that a cationic gold complex-catalyzed cyclization/hydration of allene-ynes afforded acylcyclopentane derivatives. To the best of our knowledge, all activations of allene-ynes (including the trapping of the in situ generated intermediates) reported previously were catalyzed by transition metals.[3g]

Here we report a Brønsted acid-mediated[5] formal cycloisomerization of allene-alkynylbenzenes to give acid-mediated cycloisomerization products (Scheme 1c). The used acids can be trifluoromethanesulfonic acid (TfOH) or HF equivalents (Here we used HBF_4 and Me_3OBF_4). These reaction features used Brønsted acids to initiate cycloisomerization giving an allylic cation.[6] Then the in situ generated allylic cation reacts with an alkyne moiety of the substrate to give a vinyl cation.[7] Trapping the vinyl cations by the counteranion TfO^- or F^- generates a final cycloisomerization product.[8] Of the same importance, we found that the acid-mediated cycloisomerization can be carried out in tandem with an acid-catalyzed Friedel−Crafts reaction to give acid-mediated formal [4+3] cycloadducts[9] (allenes as the three-carbon synthon, while alkynylbenzenes as the four-carbon synthon). This acid-mediated [4+3] reaction can be carried out directly from the allene-alkynylbenzene substrates, without the need of isolating the cycloisomerization intermediates when more excess acids were used. For some allene-alkynylbenzene substrates, the reaction cannot stop at the cycloisomerization stage and can directly give the acid-mediated [4+3] cycloadducts. This acid-mediated [4+3] reaction of allene-alkynylbenzenes provides an efficient synthesis of seven-membered rings (here 5−7−6 skeletons),[10] which belong to the challenging medium-ring-sized skeletons in organic synthesis. Here we report our developments of these reactions.

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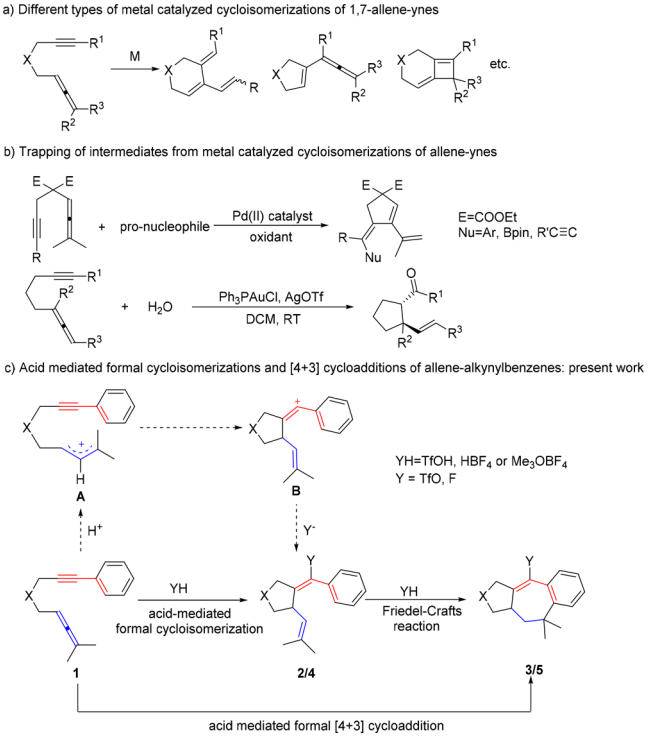
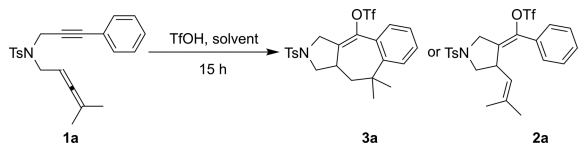
Scheme 1. Cycloisomerizations and [4+3] Reactions of 1,7-Allene-ynes Catalyzed/Mediated by Metal Catalysts/TfOH/HBF_4 Acid



RESULTS AND DISCUSSION

TfOH-Mediated Formal Cycloisomerization and [4+3] Reactions. These reactions were discovered unexpectedly. When we treated allene-alkynylbenzene **1a** with TfOH, the acid-mediated [4+3] cycloadduct **3a** was obtained (Table 1, entry 1). With the proposed mechanism shown in Scheme 1c, we hypothesized that adding less TfOH could intercept this reaction to get the acid-mediated cycloisomerization intermediate as the reaction product (This was later on truly realized through adding 1.1 equiv of TfOH to the reaction system; see Table 1, entry 6). It is known that the TfO group can be transformed to various functional groups, and we thought that this product could be used for further synthesis.[11] Considering that both acid-mediated cycloisomerization and [4+3] cycloaddition products are useful in synthesis, we decided to screen the reaction conditions. We planned to first concentrate our efforts on getting the optimized reaction conditions for the [4+3] reaction, considering that the cycloisomerization could then be achieved by adjusting the once-obtained [4+3] cycloaddition conditions, either by shortening the reaction time, lowering the reaction temperature, or reducing the amount of used Brønsted acid. For operational simplicity, all reactions were operated under open air conditions. Table 1 lists the reaction conditions we screened. We found that treatment of substrate **1a** with 10 equiv of TfOH in DCE at 60 °C for 15 h generated the [4+3] cycloadduct **3a** in 94% yield (Table 1, entry 1).

Table 1. Optimizations of Reaction Conditions for the Formal [4+3] and Cycloisomerization Reactions Using TfOH[a,b,c]



entry	solvent	equiv of acid[b]	T [°C]	yield of **3a** [%][c]
1	DCE	10	60	94
2	DCE	10	40	78
3	DCE	6	60	90
4	DCE	2	60	81
5	THF	10	60	trace
6[d]	DCE	1.1	rt	84(**2a**)[e]

[a]All of the reactions were carried out on a 0.046 mmol scale of **1a** in 2 mL of solvent. [b]40 μL (0.46 mmol, 10 equiv) of TfOH was added, unless specified. [c]Yield of isolated product. [d]1 h reaction time. [e]**2a** as the product.

Decreased yields were obtained when the temperature was decreased to 40 °C or TfOH was reduced from 10 equiv to 6 equiv or 2 equiv (entries 2−4). The reaction did not give the desired [4+3] product when it was carried out in THF instead of DCE (entry 5). Therefore, we chose the optimal reaction conditions for the [4+3] as those given in entry 1 of Table 1 (10 equiv of TfOH, SuperDry DCE as solvent, 60 °C). With the [4+3] reaction conditions in hand, we then tried to isolate the initial cyclization product. As depicted in Table 1, entry 6, **1a** can be transformed into **2a** in a yield of 85% when 1.1 equiv of TfOH was used (The reaction temperature was lowered to room temperature, and the reaction time was shorten to 1 h).

The reaction scope of both the acid-mediated formal cycloisomerization and [4+3] cycloaddition were then investigated (Tables 2 and 3). Substrates with a weak electron-withdrawing substituent such as a chlorine or bromine atom in the *para*- or *meta*-position of the aryl rings gave moderate to good yields for [4+3] cycloaddition and good yields for the cycloisomerization (Table 2, entries 2−5). Substrates with the substitution of a relatively stronger electron-withdrawing group such as a *para*-ester group or CF_3 group were found less reactive. For example, substrate **1f** with CF_3 at the *para*-position of the benzene ring gave cycloisomerization product **2f** in 85% yield and [4+3] product **3f** in 67% yield (Table 2, entry 6). Substrate **1g** with a CF_3 group at the *meta*-position of the benzene ring can only give the acid-mediated cycloisomerization product **2g** in 87% yield. No [4+3] product was obtained from **1g**, mainly due to the fact that the aromatic ring in **2g** is electron deficient and is not reactive enough for the required Friedel−Crafts reaction conditions. Entry 9 in Table 2 indicates that the fluorine substitution at the phenyl ring is detrimental because substrate **1i** gave moderate yields of both cycloisomerization and [4+3] cycloaddition reactions. Cl-Disubstituted substrate **1j** can undergo both cycloisomerization and [4+3] reaction to give the final products **2j** (91%) and **3j** (82%) (Table 2, entry 10), respectively. It was expected that substrates possessing an electron-donating group in the benzene ring could be difficult to be stopped at the cycloisomerization step because the followed Friedel−Crafts reaction with the electron-rich aromatic ring could be facile to give the [4+3] adduct directly. This hypothesis was proven to be correct, as demonstrated by the successful [4+3] reactions in Table 3. All efforts to isolate the acid-mediated cycloisomerization products for these substrates failed. It is interesting to note that substrates with electron-donating groups (Table 3) always give higher yields of [4+3] cycloadducts, compared with substrates with electron-

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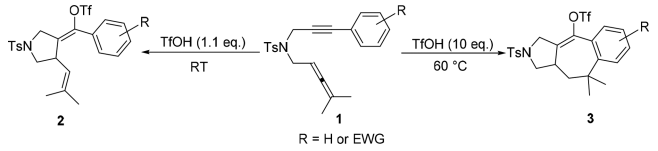
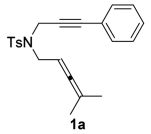
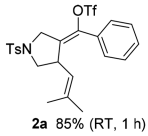
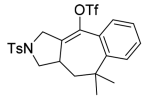
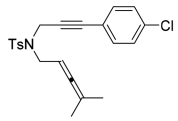
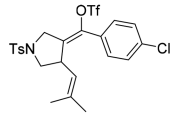
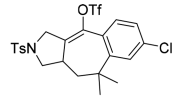
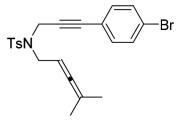
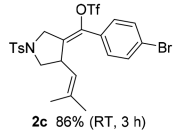
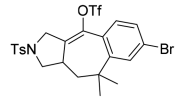
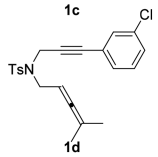
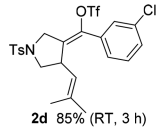
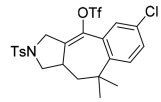
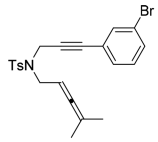
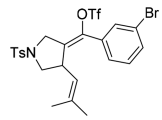
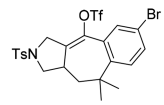
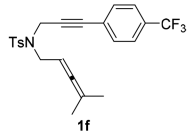
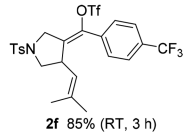
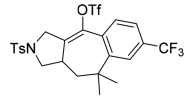
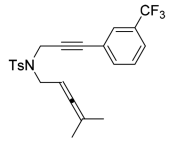
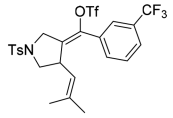
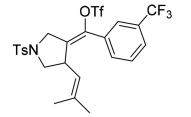
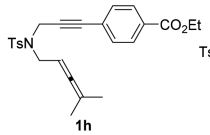
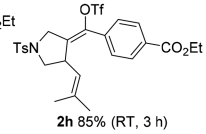
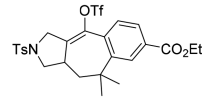
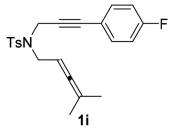
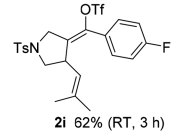
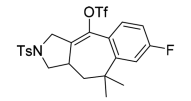
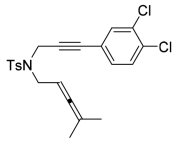
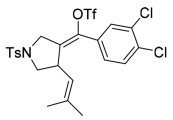
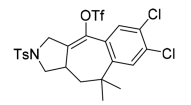
Table 2. Reaction Scopes of Formal Cycloisomerization and [4+3] Cycloaddition Mediated by TfOH[a,b,c,d]



Entry	1	2	3
1	 1a	 2a 85% (RT, 1 h)	 3a 94% (60 °C, 15 h)
2	 1b	 2b 81% (RT, 3 h)	 3b 71% (60 °C, 27 h)
3	 1c	 2c 86% (RT, 3 h)	 3c 89% (60 °C, 27 h)
4	 1d	 2d 85% (RT, 3 h)	 3d 84% (60 °C, 27 h)
5	 1e	 2e 82% (RT, 3 h)	 3e 76% (60 °C, 27 h)

Entry	1	2	3
6	 1f	 2f 85% (RT, 3 h)	 3f 67% (60 °C, 27 h)
7	 1g	 2g 87% (RT, 3 h)	 2g 40% (60 °C, 27 h)
8	 1h	 2h 85% (RT, 3 h)	 3h 67% (60 °C, 27 h)
9	 1i	 2i 62% (RT, 3 h)	 3i 49% (60 °C, 27 h)
10	 1j	 2j 91% (RT, 3 h)	 3j 82% (60 °C, 27 h)

[a]All of the reactions were carried out on a 0.046 mmol scale in 2 mL of SuperDry DCE solvent with TfOH. [b]For product **3**, about 40 μL (0.46 mmol, 10 equiv with respect to substrate) of TfOH was added; for product **2**, about 0.45 mL of TfOH solution (0.11 M) in DCE (0.05 mmol TfOH, 1.1 equiv with respect to substrate) was added. [c]Yield of isolated product was based on an average of two runs. [d]The determinations of structures of **3d**, **3e**, and **3j**; see the experimental part.

withdrawing groups shown in Table 2. For example, substrates **1k** and **1m**, which possess a methyl group and a methoxyl group, respectively, can give good to excellent yields of [4+3] adducts (Table 3, entries 1 and 3). Product **3n** from substrate **1n** with a naphthyl group can also be obtained in 91% yield (Table 3, entry 4). Substrate **1l** with a methoxy group at the *para*-position of the benzene ring in the allene-alkynylbenzene substrate decomposed under the standard reaction conditions (Table 3, entry 2). We were happy to see that the tether of the allene-ynes can be NsN, which was expected to be more easily removed than TsN, and the corresponding substrate **1o** gave [4+3] product in 75% yield (Table 3, entry 5). We were also pleased to observe that substrate **1p** with a carbon tether also gave the [4+3] cycloadduct in 73% yield (Table 3, entry 6). We must emphasize here that adding 4 Å MS was necessary to carry out the corresponding [4+3] reactions for both substrates **1o** and **1p**. Adding MS was presumed to scavenge adventitious water and prevent the easily hydrolyzable tethers here.

We also investigated the substitution effects of the allene moiety of allene-alkynylbenzenes in the [4+3] reaction (Table 3, entries 7−9). Substrate **1q** with a cyclohexylidene group in the allene produced the corresponding [4+3] product **3q** in a moderate yield of 68% (Table 3, entry 7). Substrate **1r** with a tetrasubstituted allene can undergo the [4+3] cycloaddition to give the desired product in 27% yield (Table 3, entry 8). Substrate **1s** with one methyl group in the allene moiety failed to give the desired product, possibly due to the difficulty in generating an allylic cation, which is the first step of the [4+3] reaction (Table 3, entry 9). According to the reported literature, all acid-mediated allylic cation generation from allene requires two methyl groups.[7a] The aryl moiety in allene-alkynylbenzenes is required because substrate **1t** without the benzene ring was also not appropriate for the present reactions (Table 3, entry 10).

HBF_4/Me_3OBF_4-Mediated Formal Cycloisomerization and [4+3] Cycloaddition. With the above results, we also tested several other acids such as acetic acid, trifluoroacetic acid, and benzoic acid, but all efforts did not succeed to give the desired compounds. Considering that vinyl fluorides[12] are useful in biology (such as enzyme inhibition mimics)[13] and materials science (such as fluorinated PPVs and PPEs),[14] and used as organic synthetic building blocks,[15] we decided to test whether these reactions can give their fluorinated counterparts if fluorine reagents were used.

We screened pyridine/HF, triethylamine/HF complexes, and fluoroboric acid to examine the reactions using allene-alkynylbenzene **1a**. We found that, under similar conditions as those used for TfOH-mediated processes, the HBF_4-mediated

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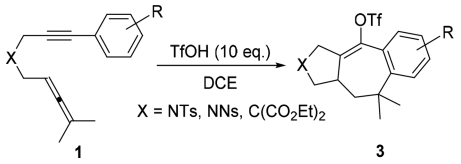
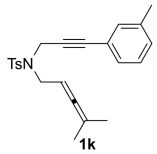
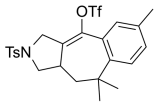
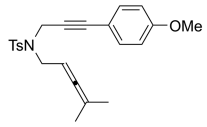
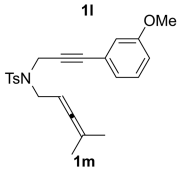
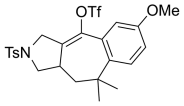
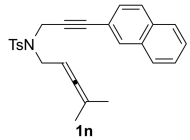
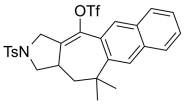
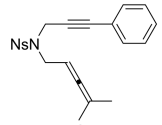
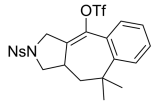
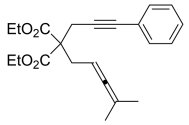
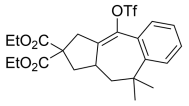
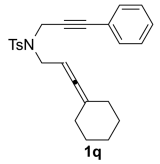
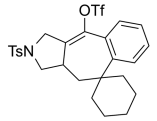
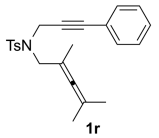
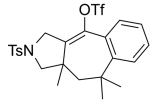
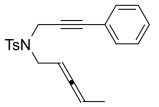
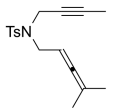
Table 3. Further Study of the Reaction Scope of Formal [4+3] Cycloaddition Mediated by TfOH[a,b,c,d]



Entry	1	3
1	 1k	 3k 93% (60 °C, 15 h)
2	 1l	decomposed (60 °C, 15 h)
3	 1m	 3m 80% (rt, 24 h)
4	 1n	 3n 91% (rt, 24 h)
5	 1o	 3o 75% (4Å MS, 60 °C, 15 h)
6	 1p	 3p 73% (4Å MS, 60 °C, 15 h)
7	 1q	 3q 68% (rt, 24 h)
8	 1r	 3r 27% (60 °C, 15 h)
9	 1s	decomposed (60 °C, 15 h)
10	 1t	mixture (60 °C, 15 h)

[a]All of the reactions were carried out on a 0.046 mmol scale in 2 mL of SuperDry DCE solvent. [b]40 μL of TfOH (0.46 mmol, 10 equiv with respect to substrate) was added. [c]Yield of isolated product was based on an average of two runs. [d]The determinations of structures of **3k**, **3m**, and **3n**; see the experimental part.

reaction gave [4+3] product **5a** in 91% yield (Table 4). **5a** was further confirmed by X-ray analysis (Supporting Information). When we screened the scope of the [4+3] reaction, we found that many substrates (details in the experimental part), which were suitable for the TfOH-mediated [4+3] reactions, did not give the desired product, except those substrates shown in Table 4. We could not find the rules to explain the success/failure of these [4+3] reactions. We reasoned that, for the failed substrates, either the trapping of intermediate B (which was not reactive) in Scheme 1 by the BF_4^- anion did not take place or their Friedel–Crafts reactions were sluggish. The latter hypothesis was supported by the experiments; these substrates in Table 5 indeed afforded cycloisomerization products using HBF_4, but no [4+3] reaction occured when even more HBF_4 was used. Product **4b** was further confirmed by X-ray analysis. (See the Supporting Information.)

We did not observe the formation of cycloisomerization product **4a** using HBF_4 when the amount of HBF_4 was reduced or the other reaction conditions were changed. The commercially available HBF_4 in Et_2O is a viscous liquid with an approximate concentration of 50% to 55%; the HF concentration could not be measured accurately. We speculated that using an easily weighted HF equivalent reagent could control the amount of HF and could then stop the reaction at the cycloisomerization step. It was reported that solid Me_3OBF_4 can deliver HBF_4 by moisture.[16] We speculated that using the easily weighted solid Me_3OBF_4 could give the exact HBF_4 equivalents to generate the desired cycloisomerization product. Fortunately, cycloisomerizations could be realized using solid Me_3OBF_4 as masked HBF_4; by using 1.05 equiv of Me_3OBF_4 in DCE (no need of using SuperDry solvent) in open air, intermediate **4a** was produced in a high yield of 88% (Table 6). Ester group-substituted allene-alkynylbenzene **1h** can also give **4h** in 90% yield. Using less or more than 1.05 equiv of Me_3OBF_4 gave poor results for substrates in Table 6. We proposed that Me_3OBF_4 first reacts with a trace amount of water in DCE to generate HBF_4 quantitatively. Then the quantitative HBF_4 can initiate the cycloisomerization. This is the first example of using Me_3OBF_4 as a convenient and high efficient fluorine reagent in fluorination chemistry. We were happy that **1d** and **1r** can also give cycloisomerization products with this new HF equivalent reagent. However, **1n**, which is electron rich, only could get trace cycloisomerization product.

Transformation Studies of the Formal Cycloisomerization and [4+3] Reaction Products. Finally, a few

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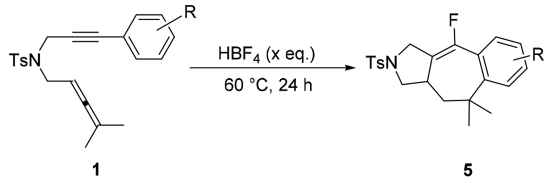
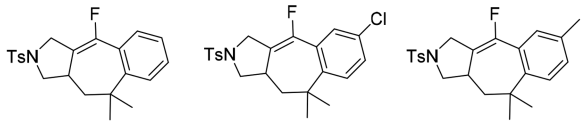
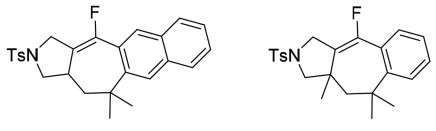
Table 4. Reaction Scope of the Formal [4+3] Reaction Mediated by HBF_4[a,b,c,d]

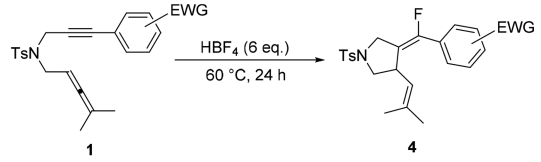


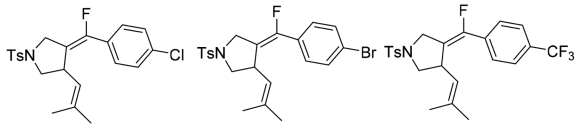


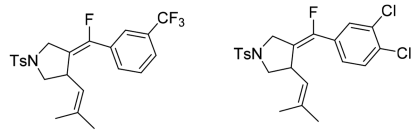


[a]All of the reactions were carried out on a 0.05 mmol scale in 2 mL of DCE solvent. [b]For **5a**, **5k**, and **5n**, 40 μL of HBF_4 (0.29 mmol) was added; for **5d** and **5r**, 100 μL of HBF_4 (0.73 mmol) was added. [c]Yield of isolated product was based on an average of two runs. [d]The determinations of structures of **5d**, **5k**, and **5n**; see the experimental part.

Table 5. Reaction Scope of Formal Cycloisomerization Mediated by HBF_4[a,b,c]



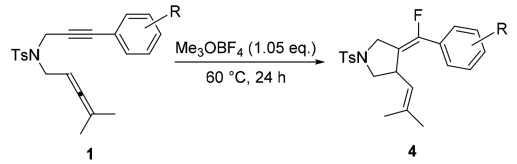


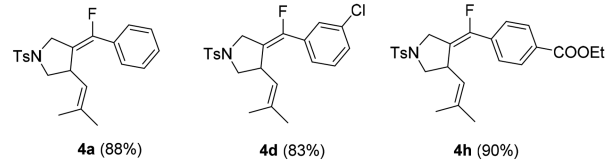


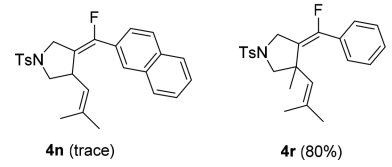
[a]All of the reactions were carried out on a 0.05 mmol scale in 2 mL of SuperDry DCE solvent. [b]40 μL of HBF_4 (0.29 mmol) was added. [c]Yield of isolated product was based on an average of two runs.

synthetic transformations of cycloisomerization and [4+3] products were performed to demonstrate the usefulness of these reactions in synthesis. We found that cycloisomerization product **2a** and [4+3] cycloadduct **3a** can be hydrolyzed to give ketones **6** and **7**[17] (reactions 1 and 2, Scheme 2). **3a** can undergo the Suzuki cross-coupling reaction[18] to give product **8** (reaction 3, Scheme 2). All of these reactions gave excellent yields (90%, 90%, and 93%, respectively).

Table 6. Reaction Scope of Formal [4+3] Cycloisomerization Mediated by Me_3OBF_4[a,b,c]

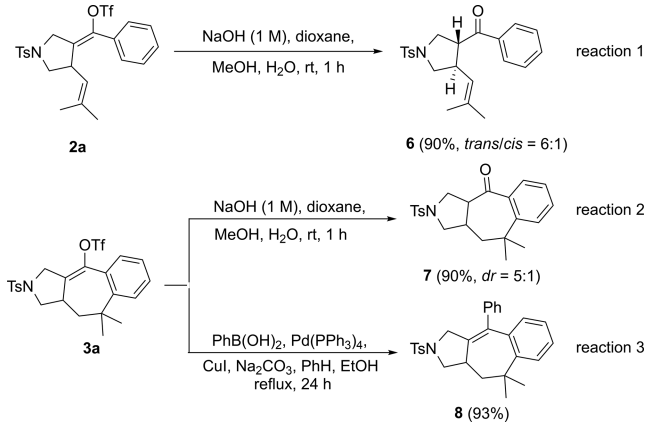






[a]All of the reactions were carried out on a 0.05 mmol scale in 2 mL of anhydrous DCE solvent. [b]1.05 equiv of Me_3OBF_4 (0.053 mmol) was added. [c]Yield of isolated product was based on an average of two runs.

Scheme 2. Transformations of Cycloisomerization and [4+3] Reaction Products



We point out that in HBF_4 initiated cycloisomerization, the vinyl cation intermediate can be intercepted by water. We found that, by just adding a drop of water in the reaction of **1a** with 1.5 equiv of HBF_4, hydrated ketones **6** were generated (confirmed by NMR), together with several compounds (not identified). In the previous work of the Liu group,[4b] the same transformation needed Au as a catalyst. Very recently, the Zhang[7j] group reported a similar process of catching a vinyl cation by water using enyne-ketone as substrates. We did not further investigate this hydration reaction, considering that our TfOH-mediated cycloisomerization products could be easily hydrolyzed to give the same product (reaction 1, Scheme 2).

CONCLUSION

In conclusion, we have developed a new metal-free, TfOH- or HBF_4/Me_3OBF_4-mediated formal cycloisomerization of readily available allene-alkynylbenzenes to give pyrrolidines and cyclopentanes derivatives. Many of the cycloisomerization intermediates could undergo further Friedel–Crafts reaction to

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give formal [4+3] cycloaddition products containing seven-membered carbocycles. The use of acid to initiate cycloisomerization and the interception of in situ generated cation by the counteranion of the used acid would inspire further development of metal-free cycloisomerization and cycloaddition chemistry.

EXPERIMENTAL SECTION

General Information. Tetrahydrofuran was distilled from sodium and benzophenone prior to use. 1,2-Dichloroethane (SuperDry, with molecular sieves) was commercially available and used without further purification, unless otherwise indicated. ^{1}H NMR (400, 500 MHz) and ^{13}C NMR (101, 126 MHz) spectra were recorded using tetramethylsilane (TMS) as an internal standard. HRMS were performed under the ESI ionization technique using a FT-ICR analyzer. ^{1}H NMR spectra are reported relative to Me_4Si (0.00 ppm); ^{13}C NMR are reported relative to the residual solvent peak ($CDCl_3$ 77.0 ppm). The following abbreviations are defined as DCE = 1,2-dichloroethane, DCM = dichloromethane, DIAD = diisopropyl azodicarboxylate, EA = ethyl acetate, MS = molecular sieves, Ns = *o*-nitrobenzenesulfonyl, PE = petroleum ether, THF = tetrahydrofuran, TLC = thin layer chromatography, Ts = *p*-toluenesulfonyl.

General Procedure A: Synthesis of Allene-alkynylbenzene Substrates ***1***. To a solution of benzenesulfonamide (1 equiv) and PPh_3 (2 equiv) in THF (5 mL) at room temperature was added alleneol (1 equiv), and the resulting solution was cooled with an ice−water bath and stirred for 10 min. Then DIAD (2 equiv) was added slowly, and the resulting solution was stirred for 3 h. The reaction was concentrated under reduced pressure and then was purified by flash column chromatography on silica gel (eluted with PE/EA = 20:1) to afford allene-alkynylbenzenes **1**. A general scheme for these syntheses is given in the Supporting Information.

Allene-alkynylbenzenes substrates **1a**,[19g] **1l**,[19i] **1m**,[19g] **1n**,[19g] **1p**,[19g] **1s**,[19h] and **1t**[19i] were synthesized according to the literature.

*N-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1b**).* Following the general procedure above, *N*-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S2**) (141.0 mg, 0.44 mmol), PPh_3 (230.9 mg, 0.88 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (43.2 mg, 0.44 mmol), and DIAD (178.0 mg, 0.88 mmol) were converted to the allene-alkynylbenzenes product **1b** (149.8 mg, 85%): white solid, mp = 84−85 °C, TLC R_f = 0.64 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 7.30−7.17 (m, 4H), 6.99 (d, J = 7.6 Hz, 2H), 4.89 (m, 1H), 4.36 (s, 2H), 3.83 (d, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.66 (d, J = 1.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.4, 136.0, 134.3, 132.6, 129.5, 128.4, 127.8, 120.8, 97.0, 84.2, 83.7, 82.9, 46.9, 36.4, 21.4, 20.3; HRMS (ESI) calcd for $C_{22}H_{23}ClNO_2S$ ([M + H]$^+$) 400.1133, found 400.1132.

*N-(3-(4-Bromophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1c**).* Following the general procedure above, *N*-(3-(4-bromophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S3**) (105.3 mg, 0.29 mmol), PPh_3 (151.6 mg, 0.58 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (28.3 mg, 0.29 mmol), and DIAD (116.9 mg, 0.58 mmol) were converted to the allene-alkynylbenzenes product **1c** (106.7 mg, 83%): white solid, mp = 85−86 °C, TLC R_f = 0.47 (PE/EA, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.5, 2H), 4.94−4.85 (m, 1H), 4.35 (s, 2H), 3.83 (d, J = 6.8 Hz, 2H), 2.35 (s, 4H), 1.66 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.4, 136.1, 132.9, 131.4, 129.5, 127.8, 122.5, 121.3, 97.0, 84.3, 83.8, 83.1, 47.0, 36.5, 21.4, 20.3; HRMS (ESI) calcd for $C_{22}H_{23}BrNO_2S$ ([M + H]$^+$) 444.0627, found 444.0625.

*N-(3-(3-Chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S4**).* $Pd(PPh_3)_2Cl_2$ (100 mg, 0.09 mmol), CuI (60 mg, 0.32 mmol), and 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.19 g, 5 mmol) were added to a solution of 1-chloro-3-iodobenzene (0.95 g, 4.5 mmol) in THF (20 mL) at rt, and the resulting solution was cooled with an ice−water bath. Then Et_3N (4 mL) was added to the mixture slowly, and the resulting solution was stirred for 2 h at rt. The reaction was quenched with a saturated NH_4Cl solution and extracted with ether three times. The combined organic phase was successively washed with a saturated NH_4Cl solution and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA = 5:1) to afford **S4** (1.03 g, 71%): white solid, mp = 135−137 °C, TLC R_f = 0.3 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.29−7.24 (m, 1H), 7.21−7.14 (dd, 1H), 7.05−7.00 (m, 2H), 4.65 (t, J = 6.0 Hz, 1H), 4.09 (d, J = 6.2 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.8, 133.9, 131.4, 129.7, 129.6, 129.4, 128.8, 127.5, 123.7, 84.5, 83.3, 33.5, 21.5; HRMS (ESI) calcd for $C_{16}H_{15}ClNO_2S$ ([M + H]$^+$) 320.0507, found 320.0511.

*N-(3-(3-Chlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1d**).* Following the general procedure above, *N*-(3-(3-chlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S4**) (932.6 mg, 3.90 mmol), PPh_3 (1.69 g, 6.45 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (287.9 mg, 2.93 mmol), and DIAD (1.24 g, 6.14 mmol) were converted to the allene-alkynylbenzenes product **1d** (968.9 mg, 83%): white solid, mp = 74−75 °C, TLC R_f = 0.64 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.29−7.23 (m, 3H), 7.16 (dd, J = 10.7, 5.0 Hz, 1H), 6.99−6.93 (m, 2H), 4.97−4.85 (m, 1H), 4.37 (s, 2H), 3.84 (d, J = 6.4 Hz, 2H), 2.37 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.6, 135.9, 133.9, 131.4, 129.5, 129.5, 129.3, 128.6, 127.8, 124.0, 97.1, 84.0, 83.7, 83.0, 47.0, 36.4, 21.4, 20.3; HRMS (ESI) calcd for $C_{22}H_{23}ClNO_2S$ ([M + H]$^+$) 400.1133, found 400.1136.

*N-(3-(3-Bromophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1e**).* Following the general procedure above, *N*-(3-(3-bromophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S5**) (113 mg, 0.31 mmol), PPh_3 (162.7 mg, 0.62 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (30.4 mg, 0.31 mmol), and DIAD (125.4 mg, 0.62 mmol) were converted to the allene-alkynylbenzenes product **1e** (117.1 mg, 85%): white solid, mp = 80−81 °C, TLC R_f = 0.64 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 8.3 Hz, 2H), 7.15−7.07 (m, 2H), 7.02 (d, J = 7.8 Hz, 1H), 4.96−4.86 (m, 1H), 4.37 (s, 2H), 3.83 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.6, 135.9, 134.3, 131.4, 129.9, 129.6, 129.5, 127.8, 124.3, 121.8, 97.1, 83.9, 83.7, 83.2, 47.0, 36.4, 21.5, 20.3; HRMS (ESI) calcd for $C_{22}H_{23}BrNO_2S$ ([M + H]$^+$) 444.0627, found 444.0639.

*4-Methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (**1f**).* Following the general procedure above, 4-methyl-*N*-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (**S6**) (106.2 mg, ca. 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 mg, 0.60 mmol) were converted to the allene-alkynylbenzenes product **1f** (114.6 mg, 88%): white solid, mp = 83−85 °C, TLC R_f = 0.62 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0, 2H), 4.96−4.86 (m, 1H), 4.39 (s, 2H), 3.85 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.67 (d, J = 2.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.5, 136.0, 131.7, 130.2, 129.9, 129.5, 127.8, 126.2 (d, J = 2.02), 125.0 (q, J = 3.8), 97.1, 84.5, 84.0, 83.7, 47.0, 36.4, 21.4, 20.3; HRMS (ESI) calcd for $C_{23}H_{23}F_3NO_2S$ ([M + H]$^+$) 434.1396, found 434.1386.

*4-Methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)-N-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (**1g**).* Following the general procedure above, 4-methyl-*N*-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide (**S7**) (105.7 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 mg, 0.60 mmol) were converted to the allene-alkynylbenzenes product **1g** (111.5 mg, 86%): colorless oil, TLC R_f = 0.53 (PE/EA, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.30−7.23 (m, 4H),

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4.95−4.89 (m, 1H), 4.39 (s, 2H), 3.85 (d, J = 7.1 Hz, 2H), 2.32 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.4, 136.0, 132.8, 131.3, 129.5, 127.8, 122.5, 121.3, 97.0, 84.3, 83.7, 83.0, 46.9, 36.4, 21.4, 20.3; HRMS (ESI) calcd for $C_{23}H_{23}F_3NO_2S$ ($[M + H]^+$) 434.1396, found 434.1401.

*Ethyl 4-(3-((4-Methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)-phenyl)sulfonamido)prop-1-yn-1-yl)benzoate (**1h**).* Following the general procedure above, ethyl 4-(3-((4-methylphenyl)sulfonamido)-prop-1-yn-1-yl)benzoate (**S8**) (106.2 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 mg, 0.6 mmol) were converted to the allene-alkynylbenzenes product **1h** (106.6 mg, 82%): yellow solid, mp = 80−81 °C, TLC R_f = 0.51 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.2, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.99−4.83 (m, 1H), 4.39 (s, 2H), 4.38 (q, J = 7.2 Hz, 2H), 3.85 (d, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.66 (d, J = 2.8 Hz, 6H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 165.9, 143.5, 135.9, 131.3, 129.9, 129.5, 129.2, 127.8, 126.9, 97.0, 84.8, 84.7, 83.7, 61.2, 47.0, 36.4, 21.4, 20.3, 14.3; HRMS (ESI) calcd for $C_{25}H_{28}NO_4S$ ($[M + H]^+$) 438.1734, found 438.1734.

*N-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1i**).* Following the general procedure above, *N*-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S9**) (93.4 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 mg, 0.60 mmol) were converted to the allene-alkynylbenzenes product **1i** (95.6 mg, 81%): white solid, mp = 83−84 °C, TLC R_f = 0.63 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.09−7.01 (m, 2H), 6.97−6.88 (m, 2H), 4.95−4.86 (m, 1H), 4.35 (s, 2H), 3.84 (d, J = 7.0 Hz, 2H), 2.34 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 162.4 (d, J = 251.5 Hz), 143.3, 136.1, 133.3 (d, J = 8.3 Hz), 129.5, 127.8, 118.5 (d, J = 3.5 Hz), 115.4 (d, J = 3.5 Hz), 97.0, 84.3, 83.8, 81.5, 46.9, 36.4, 21.4, 20.3; HRMS (ESI) calcd for $C_{22}H_{23}FNO_2S$ ($[M + H]^+$) 384.1428, found 384.1424.

*N-(3-(3,4-Dichlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)benzenesulfonamide (**1j**).* Following the general procedure above, *N*-(3-(3,4-dichlorophenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**S10**) (120.3 mg, 0.34 mmol), PPh_3 (178.1 mg, 0.68 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (33.3 mg, 0.34 mmol), and DIAD (137.3 mg, 0.68 mmol) were converted to the allene-alkynylbenzenes product **1j** (128.3 mg, 87%): white solid, mp = 84−85 °C, TLC R_f = 0.59 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 1.8 Hz, 1H), 6.92 (dd, J = 8.3 Hz, 1.9 Hz, 1H), 4.94−4.87 (m, 1H), 4.36 (s, 2H), 3.83 (d, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.6, 136.0, 133.2, 132.8, 132.3, 130.5, 130.2, 129.5, 127.8, 122.3, 97.1, 84.0, 83.7, 83.1, 47.0, 36.3, 21.4, 20.3; HRMS (ESI) calcd for $C_{22}H_{22}Cl_2NO_2S$ ($[M + H]^+$) 434.0743, found 434.0743.

*4-Methyl-N-(4-methyl-3λ^5-penta-2,3-dien-1-yl)-N-(3-(m-tolyl)-prop-2-yn-1-yl)benzenesulfonamide (**1k**).* Following the general procedure above, 4-methyl-*N*-(3-(*m*-tolyl)prop-2-yn-1-yl)-benzenesulfonamide (**S11**) (92.3 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 mg, 0.60 mmol) were converted to the allene-alkynylbenzenes product **1k** (93.6 mg, 80%): white solid, mp = 90−91 °C, TLC R_f = 0.57 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.16−7.05 (m, 2H), 6.91−6.82 (m, 2H), 4.98−4.86 (m, 1H), 4.37 (s, 2H), 3.84 (d, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 1.67 (d, J = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0, 143.3, 137.7, 135.1, 132.0, 129.5, 129.1, 128.5, 128.0, 127.8, 122.2, 97.0, 85.5, 83.8, 81.3, 46.8, 36.5, 21.4, 21.2, 20.3; HRMS (ESI) calcd for $C_{23}H_{26}NO_2S$ ($[M + H]^+$) 380.1679, found 380.1682.

*N-(4-Methyl-3λ^5-penta-2,3-dien-1-yl)-2-nitro-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1o**).* Following the general procedure above, 2-nitro-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**S12**) (96.8 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 4-methylpenta-2,3-dien-1-ol (**S13**) (29.4 mg, 0.30 mmol), and DIAD (121.2 g, 0.30 mmol) were converted to the allene-alkynylbenzenes product **1o** (87.3 mg, 72%): colorless oil, TLC R_f = 0.34 (PE/EA, 5:1); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.10−8.04 (m, 1H), 7.69−7.59 (m, 3H), 7.34−7.22 (m, 5H), 4.97−4.89 (m, 1H), 4.44 (s, 2H), 4.03 (d, J = 6.7 Hz, 2H), 1.68 (d, J = 2.8 Hz, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 204.3, 148.7, 134.1, 133.4, 132.1, 132.0, 131.1, 129.0, 128.7, 124.5, 122.6, 98.1, 85.7, 84.1, 82.6, 47.6, 37.1, 20.4; HRMS (ESI) calcd for $C_{21}H_{21}N_2O_4S$ ($[M + H]^+$) 397.1217, found 397.1209.

*N-(3-Cyclohexylidene-3λ^5-allyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1q**).* Following the general procedure above, 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**S1**) (87.4 mg, 0.30 mmol), PPh_3 (157.2 mg, 0.60 mmol), 3-cyclohexylideneprop-2-en-1-ol (**S14**) (41.4 mg, 0.30 mmol), and DIAD (121.2 g, 0.30 mmol) were converted to the allene-alkynylbenzenes product **1q** (103.1 mg, 83%): white solid, mp = 97−99 °C, TLC R_f = 0.66 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.29−7.21 (m, 5H), 7.05 (d, J = 6.8 Hz, 2H), 4.95−4.88 (m, 1H), 4.38 (s, 2H), 3.86 (d, J = 7.2 Hz, 2H), 2.32 (s, 3H), 2.12−2.05 (m, 4H), 1.61−1.41 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 143.4, 136.0, 131.4, 129.5, 128.2, 128.0, 127.7, 122.4, 104.2, 85.4, 83.5, 81.7, 47.0, 36.3, 31.2, 27.1, 25.9, 21.4; HRMS (ESI) calcd for $C_{25}H_{28}NO_2S$ ($[M + H]^+$) 406.1835, found 406.1831.

*N-(2,4-Dimethyl-3λ^5-penta-2,3-dien-1-yl)-4-methyl-N-(3-phenyl-prop-2-yn-1-yl)benzenesulfonamide (**1r**).* To a solution of ethyl 2,4-dimethyl-3λ^5-penta-2,3-dienoate (82.3 mg, 0.53 mmol) were added DCM (5 mL) and DIBAL-H (1.2 mL, 1 M in hexane) at 0 °C. Then the resulting solution was stirred at room temperature for 2 h. Then the reaction was quenched with water and filtered with a silica gel pad to afford crude 2,4-dimethyl-3λ^5-penta-2,3-dien-1-ol (**S15**) as a yellow oil, which was directly used for the next step. To 2,4-dimethyl-3λ^5-penta-2,3-dien-1-ol (**S15**) was added THF (5 mL), and the resulting solution was cooled with an ice−water bath. Then PPh_3 (277.7 mg, 1.06 mmol) and 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (**S1**) were added, and the mixture was stirred for 10 min. Then DIAD (214.1 mg, 1.06 mmol) was added slowly, and the resulting solution was stirred for 2 h at rt. The reaction was concentrated under reduced pressure and then purified by flash column chromatography on silica gel (eluted with PE/EA = 50:1 to 10:1) to afford **1r** (147.8 mg, 73% for two steps): white solid, mp = 119−121 °C, TLC R_f = 0.69 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.27−7.20 (m, 5H), 7.06−6.99 (m, 2H), 4.31 (s, 2H), 3.77 (s, 2H), 2.32 (s, 3H), 1.70 (s, 3H), 1.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 143.3, 136.1, 131.4, 129.4, 128.3, 128.0, 127.7, 122.4, 95.3, 91.3, 85.3, 81.7, 51.1, 36.2, 21.4, 20.6, 16.5; HRMS (ESI) calcd for $C_{23}H_{26}NO_2S$ ($[M + H]^+$) 380.1679, found 380.1670.

General Procedure B: TfOH-Mediated Formal Cycloisomerization. To 5 mL of SuperDry DCE was added 50 μL of TfOH (0.57 mmol) to form a TfOH solution (0.11 M in DCE). A solution of substrate **1** (0.046 mmol) in SuperDry DCE (1.55 mL) in a reaction bottle was cooled in an ice bath. Then 0.45 mL of the TfOH solution (0.05 mmol TfOH) was added. After that, the reaction mixture was stirred for 3 h at room temperature. Then the reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **2**. We point out here that running flash column chromatography to get the products should be fast, especially for **2a** and **2i**; otherwise, some of these compounds isomerized to their [4+3] products.

*(Z)-(4-(2-Methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)-(phenyl)methyl Trifluoromethanesulfonate (**2a**).* Following the general procedure above. Reaction time: 1 h. Eluted with PE/EA 20:1. Run 1: 16.9 mg of **1a** was converted to 19.8 mg of **2a**, yield 83%. Run 2: 16.5 mg of **1a** was converted to 20.3 mg of **2a**, yield 87%. So the average yield of two runs was 85%. **2a**: yellow oil, TLC R_f = 0.49 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.36−7.28 (m, 3H), 7.25−7.21 (m, 2H), 4.71 (d, J = 9.7 Hz, 1H), 4.23 (d, J = 15.7 Hz, 1H), 4.16 (dd, J = 15.7, 1.4 Hz, 1H), 3.57−3.48 (m, 1H), 3.43 (dd, J = 9.6, 6.9 Hz, 1H),

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3.04 (dd, J = 9.6, 4.9 Hz, 1H), 2.47 (s, 3H), 1.41 (d, J = 0.7 Hz, 3H), 1.26 (d, J = 0.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.1, 134.6, 134.5, 132.3, 131.3, 130.0, 129.9, 128.8, 128.2, 127.9, 121.9, 118.0 (q, J = 320.3 Hz), 54.7, 50.1, 40.4, 25.3, 21.6, 17.6; HRMS (ESI) calcd for $C_{23}H_{24}F_3NNaO_5S_2$ ([M + Na]$^+$) 538.0940, found 538.0937.

*(Z)-(4-Chlorophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2b**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 18.3 mg of **1b** was converted to 19.9 mg of **2b**, yield 79%. Run 2: 18.6 mg of **1b** was converted to 21.0 mg of **2b**, yield 82%. So the average yield of two runs was 81%. **2b**: yellow oil, TLC R_f = 0.51 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 4.70 (d, J = 9.6 Hz, 1H), 4.22 (d, J = 15.8 Hz, 1H), 4.14 (dd, J = 15.8, 1.2 Hz, 1H), 3.54−3.46 (m, 1H), 3.44 (dd, J = 9.5, 7.0 Hz, 1H), 3.03 (dd, J = 9.5, 4.8 Hz, 1H), 2.47 (s, 3H), 1.44 (d, J = 1.2 Hz, 3H), 1.30 (d, J = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.8, 136.2, 135.6, 134.8, 132.3, 130.1, 129.9, 129.8, 128.5, 127.9, 121.8, 118.0 (q, J = 320.3 Hz), 54.7, 50.1, 40.4, 25.3, 21.6, 17.7; HRMS (ESI) calcd for $C_{23}H_{24}ClF_3NO_5S_2$ ([M + H]$^+$) 550.0731, found 550.0728.

*(Z)-(4-Bromophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2c**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 19.9 mg of **1c** was converted to 23.4 mg of **2c**, yield 88%. Run 2: 20.4 mg of **1c** was converted to 22.9 mg of **2c**, yield 84%. So the average yield of two runs was 86%. **2c**: light yellow oil, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.69 (d, J = 9.6 Hz, 1H), 4.22 (d, J = 15.9 Hz, 1H), 4.13 (d, J = 15.9 Hz, 1H), 3.53−3.45 (m, 1H), 3.43 (dd, J = 9.2, 7.2 Hz, 1H), 3.03 (dd, J = 9.2, 4.8 Hz, 1H), 2.47 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.8, 135.7, 134.9, 132.3, 131.4, 130.29, 130.25, 129.9, 127.9, 124.5, 121.8, 118.0 (q, J = 320.4 Hz), 54.9, 50.1, 40.4, 25.3, 21.6, 17.7; HRMS (ESI) calcd for $C_{23}H_{24}BrF_3NO_5S_2$ ([M + H]$^+$) 594.0226, found 594.0244.

*(Z)-(3-Chlorophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2d**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 19.0 mg of **1d** was converted to 21.9 mg of **2d**, yield 84%. Run 2: 18.7 mg of **1d** was converted to 22.1 mg of **2d**, yield 86%. So the average yield of two runs was 85%. **2d**: yellow oil, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.19−7.12 (m, 2H), 4.68 (d, J = 8.4 Hz, 1H), 4.26 (d, J = 16.0 Hz, 1H), 4.15 (d, J = 16.0 Hz, 1H), 3.51−3.41 (m, 2H), 3.03 (dd, J = 13.6, 8.4 Hz, 1H), 2.48 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.3, 136.2, 135.2, 134.1, 133.0, 132.4, 130.1, 129.9, 129.5, 129.1, 127.9, 126.6, 121.4, 118.1 (q, J = 320.4 Hz), 54.7, 50.3, 40.4, 25.3, 21.6, 17.6; HRMS (ESI) calcd for $C_{23}H_{24}ClF_3NO_5S_2$ ([M + H]$^+$) 550.0731, found 550.0745.

*(Z)-(3-Bromophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2e**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 19.6 mg of **1e** was converted to 22.0 mg of **2e**, yield 84%. Run 2: 19.8 mg of **1e** was converted to 21.2 mg of **2e**, yield 80%. So the average yield of two runs was 82%. **2e**: light yellow oil, TLC R_f = 0.57 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.51−7.47 (m, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.35−7.32 (m, 1H), 7.22−7.18 (m, 2H), 4.68 (dd, J = 8.2, 1.2 Hz, 1H), 4.26 (d, J = 15.0 Hz, 1H), 4.15 (dd, J = 15.6, 1.2 Hz, 1H), 3.50−3.42 (m, 2H), 3.03 (dd, J = 13.2, 8.4 Hz, 1H), 2.48 (s, 3H), 1.46 (d, J = 1.2 Hz, 3H), 1.35 (d, J = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.2, 136.2, 135.3, 133.2, 133.0, 132.4, 132.0, 129.9, 129.7, 127.9, 127.0, 122.0, 121.4, 118.1 (q, J = 320.6 Hz), 54.7, 50.3, 40.4, 25.3, 21.6, 17.7; HRMS (ESI) calcd for $C_{23}H_{24}BrF_3NO_5S_2$ ([M + H]$^+$) 594.0226, found 594.0226.

*(Z)-(4-(2-Methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)(4-(trifluoromethyl)phenyl)methyl Trifluoromethanesulfonate (**2f**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 19.6 mg of **1f** was converted to 22.4 mg of **2f**, yield 85%. Run 2: 20.1 mg of **1f** was converted to 22.7 mg of **2f**, yield 84%. So the average yield of two runs was 85%. **2f**: light yellow oil, TLC R_f = 0.52 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 4.65 (d, J = 9.4 Hz, 1H), 4.28 (d, J = 16.0 Hz, 1H), 4.16 (dd, J = 16.0, 1.3 Hz, 1H), 3.58−3.50 (m, 1H), 3.47 (dd, J = 9.4, 7.1 Hz, 1H), 3.01 (dd, J = 9.5, 5.1 Hz, 1H), 2.47 (s, 3H), 1.39 (d, J = 0.7 Hz, 3H), 1.29 (d, J = 0.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 139.2, 136.9, 135.2, 134.9, 132.3, 131.9 (q, J = 32.9 Hz), 129.9, 129.3, 127.9, 125.1 (q, J = 3.7 Hz), 123.5 (q, J = 272.5 Hz), 121.5, 118.0 (q, J = 320.3 Hz), 54.6, 50.3, 40.5, 25.1, 21.6, 17.6; HRMS (ESI) calcd for $C_{24}H_{24}F_6NO_5S_2$ ([M + H]$^+$) 584.0995, found 584.0993.

*(Z)-(4-(2-Methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)(3-(trifluoromethyl)phenyl)methyl Trifluoromethanesulfonate (**2g**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 20.2 mg of **1g** was converted to 23.9 mg of **2g**, yield 88%. Run 2: 19.9 mg of **1g** was converted to 22.8 mg of **2g**, yield 85%. So the average yield of two runs was 87%. **2g**: light yellow oil, TLC R_f = 0.50 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 7.4 Hz, 1H), 7.52−7.43 (m, 3H), 7.40 (d, J = 8.1 Hz, 2H), 4.65 (d, J = 9.0 Hz, 1H), 4.30 (d, J = 16.1 Hz, 1H), 4.17 (d, J = 16.1 Hz, 1H), 3.53−3.43 (m, 2H), 3.09−2.95 (m, 1H), 2.47 (s, 3H), 1.40 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 139.1, 136.8, 135.5, 132.4, 132.2, 131.9, 130.8 (q, J = 32.7 Hz), 130.3, 128.9, 128.0, 126.7 (q, J = 3.6 Hz), 126.3 (q, J = 308.3 Hz), 125.8 (q, J = 3.9 Hz), 121.5, 118.0 (q, J = 320.3 Hz), 54.7, 50.4, 40.4, 25.1, 21.5, 17.4; HRMS (ESI) calcd for $C_{24}H_{24}F_6NO_5S_2$ ([M + H]$^+$) 584.0995, found 584.0994.

*Ethyl (Z)-4-((4-(2-Methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)(((trifluoromethyl)sulfonyl)oxy)methyl)benzoate (**2h**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 10:1. Run 1: 20.4 mg of **1h** was converted to 23.3 mg of **2h**, yield 85%. Run 2: 20.2 mg of **1h** was converted to 22.8 mg of **2h**, yield 84%. So the average yield of two runs was 85%. **2h**: light yellow oil, TLC R_f = 0.41 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.72 (d, J = 9.6 Hz, 1H), 4.38 (q, J = 8.0 Hz, 2H), 4.25 (d, J = 16.0 Hz, 1H), 4.18 (d, J = 16.0 Hz, 1H), 3.58−3.49 (m, 1H), 3.44 (dd, J = 9.7, 6.9 Hz, 1H), 3.07 (dd, J = 9.7, 4.8 Hz, 1H), 2.47 (s, 3H), 1.43 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 144.2, 139.8, 136.4, 135.5, 135.0, 132.3, 131.6, 129.9, 129.3, 128.6, 127.9, 121.8, 118.0 (q, J = 320.4 Hz), 61.4, 54.8, 50.2, 40.5, 25.3, 21.6, 17.8, 14.2; HRMS (ESI) calcd for $C_{26}H_{28}F_3NNaO_7S_2$ ([M + Na]$^+$) 610.1152, found 610.1137.

*(Z)-(4-Fluorophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2i**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 17.1 mg of **1i** was converted to 14.9 mg of **2i**, yield 61%. Run 2: 17.2 mg of **1i** was converted to 15.1 mg of **2i**, yield 62%. So the average yield of two runs was 62%. **2i**: yellow oil, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.25−7.20 (m, 2H), 7.05−6.96 (m, 2H), 4.69 (d, J = 9.2 Hz, 1H), 4.22 (d, J = 15.7 Hz, 1H), 4.13 (dd, J = 15.7, 1.5 Hz, 1H), 3.53−3.48 (m, 1H), 3.44 (dd, J = 9.3, 7.0 Hz, 1H), 3.01 (dd, J = 9.2, 4.8 Hz, 1H), 2.47 (s, 3H), 1.43 (d, J = 1.2 Hz, 3H), 1.27 (d, J = 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (d, J = 251.6 Hz), 144.2, 140.0, 135.2, 134.7, 132.2, 131.1 (d, J = 8.6 Hz), 129.9, 128.0, 127.4 (d, J = 3.3 Hz), 121.8, 118.0 (q, J = 320.3 Hz), 115.4 (d, J = 22.0 Hz), 54.6, 50.1, 40.4, 25.3, 21.6, 17.6; HRMS (ESI) calcd for $C_{23}H_{24}F_4NO_5S_2$ ([M + H]$^+$) 534.1027, found 534.1032.

*(Z)-(3,4-Dichlorophenyl)(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl Trifluoromethanesulfonate (**2j**).* Following the general procedure above. Reaction time: 3 h. Eluted with PE/EA 20:1. Run 1: 20.3 mg of **1j** was converted to 24.6 mg of **2j**, yield 90%. Run 2: 20.2 mg of **1j** was converted to 25.0 mg of **2j**, yield 92%. So the average yield of two runs was 91%. **2j**: yellow oil, TLC R_f = 0.44 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz,

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2H), 7.41 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 2.0 Hz, 1H), 7.11 (dd, J = 8.4, 2.0 Hz, 1H), 4.69 (d, J = 8.4 Hz, 1H), 4.25 (d, J = 16.1 Hz, 1H), 4.14 (d, J = 16.0 Hz, 1H), 3.51−3.41 (m, 2H), 3.05 (dd, J = 8.8, 4.8 Hz, 1H), 2.48 (s, 3H), 1.48 (d, J = 1.1 Hz, 3H), 1.38 (d, J = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 138.3, 136.8, 135.5, 134.4, 132.5, 132.4, 131.2, 130.9, 130.3, 129.9, 127.9, 127.6, 121.4, 118.1 (q, J = 320.4 Hz), 54.7, 50.3, 40.5, 25.3, 21.6, 17.7; HRMS (ESI) calcd for $C_{23}H_{23}Cl_2F_3NO_5S_2$ ([M + H]$^+$) 584.0341, found 584.0342.

General Procedure C: Formal [4+3] Cycloaddition. To a solution of substrate **1** (0.046 mmol) in SuperDry DCE (2.0 mL) in a reaction bottle was added TfOH (40 μL, 0.46 mmol). Then the reaction mixture was immersed into a 60 °C oil bath and stirred. When the reactions finished, the reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **3**. For substrates **1m**, **1n**, and **1q**, the reactions were conducted at room temperature. For substrates **1o** and **1p**, 4 Å MS were added to the reaction systems.

Here we want to point out that the determinations of the structures of **3d**, **3e**, **3k**, and **3m** were based on their ^{1}H NMR because their benzene ring hydrogen coupling constants followed the rules of 1,2,4- not 1,2,3-trisubstituted benzene rings.[19a−c] For **3n**, we assigned its structure based on the benzene ring hydrogen coupling patterns with two separate singlet peaks in ^{1}H NMR, 7.93 (s, 1H), 7.84 (s, 1H).[19d−f] The structure of **3j** was determined based on two singlet peaks at the aromatic region in ^{1}H NMR, 7.51 (s, 1H), 7.46 (s, 1H).[19]

*9,9-Dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3a**).* Following the general procedure above. Reaction time: 15 h. Eluted with PE/EA 20:1 to 5:1. Run 1: 16.5 mg of **1a** was converted to 22.1 mg of **3a**, yield 95%. Run 2: 16.8 mg of **1a** was converted to 21.8 mg of **3a**, yield 92%. So the average yield of two runs was 94%. **3a**: colorless oil, TLC R_f = 0.36 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.49−7.39 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.32−7.22 (m, 2H), 4.27 (d, J = 15.5 Hz, 1H), 4.17 (d, J = 15.5 Hz, 1H), 3.55 (dd, J = 9.8, 8.2 Hz, 1H), 2.93 (dd, J = 9.8, 7.0 Hz, 1H), 2.67−2.57 (m, 1H), 2.42 (s, 3H), 2.15 (dd, J = 13.7, 6.7 Hz, 1H), 1.93 (dd, J = 13.7, 12.4 Hz, 1H), 1.36 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 144.2, 138.7, 133.6, 132.2, 131.1, 129.8, 129.3, 127.9, 126.8, 126.3, 123.0, 118.3 (q, J = 320.3 Hz), 54.1, 51.0, 50.5, 39.3, 37.9, 31.5, 31.3, 21.5; HRMS (ESI) calcd for $C_{23}H_{24}F_3NNaO_5S_2$ ([M + Na]$^+$) 538.0940, found 538.0952.

*7-Chloro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3b**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 20:1. Run 1: 18.6 mg of **1b** was converted to 18.4 mg of **3b**, yield 72%. Run 2: 18.3 mg of **1b** was converted to 17.4 mg of **3b**, yield 69%. So the average yield of two runs was 71%. **3b**: light yellow oil, TLC R_f = 0.38 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 3H), 7.25 (dd, J = 8.6, 1.9 Hz, 1H), 4.26 (d, J = 15.6 Hz, 1H), 4.15 (dd, J = 15.6, 2.0 Hz, 1H), 3.55 (dd, J = 10.0, 7.9 Hz, 1H), 2.93 (dd, J = 10.0, 7.0 Hz, 1H), 2.68−2.55 (m, 1H), 2.43 (s, 3H), 2.15 (dd, J = 13.9, 6.8 Hz, 1H), 1.92 (dd, J = 13.9, 12.0 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 144.2, 137.7, 135.3, 134.3, 132.1, 129.9, 129.7, 128.1, 127.9, 127.3, 126.5, 118.2 (q, J = 320.3 Hz), 54.1, 50.5, 39.3, 38.0, 31.3, 31.1, 29.7, 21.6; HRMS (ESI) calcd for $C_{23}H_{24}ClF_3NO_5S_2$ ([M + H]$^+$) 550.0731, found 550.0730.

*7-Bromo-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3c**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 20.5 mg of **1c** was converted to 24.5 mg of **3c**, yield 89%. Run 2: 19.5 mg of **1c** was converted to 23.3 mg of **3c**, yield 89%. So the average yield of two runs was 89%. **3c**: light yellow solid, mp = 127−128 °C, TLC R_f = 0.33 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 1.9 Hz, 1H), 7.41 (dd, J = 8.5, 1.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 9.0 Hz, 1H), 4.25 (d, J = 15.6 Hz, 1H), 4.13 (dd, J = 15.6, 2.0 Hz, 1H), 3.55 (dd, J = 9.9, 7.9 Hz, 1H), 2.92 (dd, J = 9.9, 7.2 Hz, 1H), 2.68−2.53 (m, 1H), 2.43 (s, 3H), 2.15 (dd, J = 13.9, 6.8 Hz, 1H), 1.92 (dd, J = 13.9, 12.0 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 144.2, 137.8, 134.5, 132.2, 130.3, 130.20, 129.9, 129.5, 128.3, 127.9, 123.8, 118.2 (q, J = 315.0 Hz), 54.1, 50.6, 50.5, 39.4, 38.1, 31.4, 31.1, 21.6; HRMS (ESI) calcd for $C_{23}H_{24}BrF_3NO_5S_2$ ([M + H]$^+$) 594.0226, found 594.0234.

*6-Chloro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3d**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 18.1 mg of **1d** was converted to 20.0 mg of **3d**, yield 81%. Run 2: 18.1 mg of **1d** was converted to 21.6 mg of **3d**, yield 87%. So the average yield of two runs was 84%. **3d**: light yellow solid, mp = 160−164 °C, TLC R_f = 0.36 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.34 (d, J = 8.2, 2H), 7.26 (dd, J = 8.8, 2.0 Hz, 1H), 4.29 (d, J = 15.6 Hz, 1H), 4.16 (dd, J = 15.6, 2.0 Hz, 1H), 3.59 (dd, J = 10.0, 8.0 Hz, 1H), 2.93 (dd, J = 10.0, 7.2 Hz, 1H), 2.63−2.52 (m, 1H), 2.42 (s, 3H), 2.13 (dd, J = 14.0, 6.8 Hz, 1H), 1.90 (dd, J = 14.0, 12.0 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.3, 137.2, 135.4, 132.7, 132.4, 132.2, 129.9, 129.1, 128.4, 127.8, 126.6, 118.3 (q, J = 320.4 Hz), 54.1, 50.6, 50.5, 39.3, 37.7, 31.4, 31.3, 21.5; HRMS (ESI) calcd for $C_{23}H_{24}ClF_3NO_5S_2$ ([M + H]$^+$) 550.0731, found 550.0743.

*6-Bromo-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3e**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 20.4 mg of **1e** was converted to 20.4 mg of **3e**, yield 75%. Run 2: 20.5 mg of **1e** was converted to 21.2 mg of **3e**, yield 77%. So the average yield of two runs was 76%. **3e**: white solid, mp = 155−158 °C, TLC R_f = 0.37 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4, 1H), 4.29 (d, J = 15.6 Hz, 1H), 4.16 (dd, J = 15.6, 2.0 Hz, 1H), 3.58 (dd, J = 10.2, 8.0 Hz, 1H), 2.93 (dd, J = 10.2, 7.2 Hz, 1H), 2.63−2.52 (m, 1H), 2.43 (s, 3H), 2.13 (dd, J = 13.6, 6.8 Hz, 1H), 1.90 (dd, J = 13.6, 12.0 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 144.3, 137.1, 135.4, 133.0, 132.2, 132.1, 129.9, 129.5, 128.6, 127.8, 120.3, 118.2 (q, J = 320.5 Hz), 54.1, 50.6, 50.4, 39.3, 37.8, 31.3, 31.2, 21.5; HRMS (ESI) calcd for $C_{23}H_{24}BrF_3NO_5S_2$ ([M + H]$^+$) 594.0226, found 594.0226.

*9,9-Dimethyl-2-tosyl-7-(trifluoromethyl)-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3f**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 19.5 mg of **1f** was converted to 17.1 mg of **3f**, yield 65%. Run 2: 20.0 mg of **1f** was converted to 18.6 mg of **3f**, yield 69%. So the average yield of two runs was 67%. **3f**: yellow solid, mp = 107−110 °C, TLC R_f = 0.46 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.70 (s, 1H), 7.55−7.52 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.30 (d, J = 15.8 Hz, 1H), 4.18 (dd, J = 15.8, 1.9 Hz, 1H), 3.58 (dd, J = 10.0, 7.9 Hz, 1H), 2.94 (dd, J = 10.0, 7.1 Hz, 1H), 2.68−2.56 (m, 1H), 2.42 (s, 3H), 2.20 (dd, J = 13.9, 6.8 Hz, 1H), 1.96 (dd, J = 13.9, 12.0 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 144.3, 137.3, 136.2, 134.8, 132.1, 130.8 (q, J = 32.4 Hz), 129.9, 127.9, 127.2, 123.8 (q, J = 3.8 Hz), 123.7 (q, J = 272.6 Hz), 123.2 (q, J = 3.7 Hz), 118.2 (q, J = 320.5 Hz), 54.0, 50.6, 50.6, 39.4, 38.1, 31.3, 31.1, 21.5; HRMS (ESI) calcd for $C_{24}H_{24}F_6NO_5S_2$ ([M + H]$^+$) 584.0995, found 584.0990.

*Ethyl 9,9-Dimethyl-2-tosyl-4-(((trifluoromethyl)sulfonyl)oxy)-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrole-7-carboxylate (**3h**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 19.6 mg of **1h** was converted to 17.1 mg of **3h**, yield 65%. Run 2: 20.5 mg of **1h** was converted to 18.7 mg of **3h**, yield 68%. So the average yield of two runs was 67%. **3 h**: yellow oil, TLC R_f = 0.27 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 1.5 Hz, 1H), 7.93 (dd, J = 8.0, 1.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 4.30 (d, J = 15.8 Hz, 1H), 4.17 (dd, J = 15.8, 2.0 Hz, 1H), 3.55 (dd, J = 10.0, 8.0 Hz, 1H), 2.93 (dd, J = 10.0, 7.2 Hz, 1H), 2.69−2.57 (m, 1H), 2.42 (s, 3H), 2.18 (dd, J = 13.9, 6.7 Hz, 1H), 1.94 (dd, J = 13.9, 12.0 Hz, 1H), 1.43 (s,

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3H), 1.40 (t, J = 7.2 Hz, 3H), 1.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 147.0, 144.3, 137.9, 136.1, 135.3, 132.2, 130.7, 129.9, 128.1, 127.9, 127.3, 126.8, 118.3 (q, J = 321.3 Hz), 61.3, 54.1, 50.7, 50.5, 39.4, 38.1, 31.4, 31.2, 21.5, 14.3; HRMS (ESI) calcd for $C_{26}H_{29}F_3NO_7S_2$ ([M + H]$^+$) 588.1332, found 588.1330.

*7-Fluoro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3i**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 17.6 mg of **1i** was converted to 11.7 mg of **3i**, yield 48%. Run 2: 17.7 mg of **1i** was converted to 12.5 mg of **3i**, yield 51%. So the average yield of two runs was 49%. **3i**: yellow oil, TLC R_f = 0.34 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.40 (dd, J = 8.7, 6.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 11.3, 2.6 Hz, 1H), 6.97 (ddd, J = 8.8, 7.4, 2.6 Hz, 1H), 4.25 (d, J = 15.5 Hz, 1H), 4.16 (dd, J = 15.5, 1.8 Hz, 1H), 3.54 (dd, J = 9.9, 7.9 Hz, 1H), 2.93 (dd, J = 7.0, 5.3 Hz, 1H), 2.67−2.55 (m, 1H), 2.43 (s, 3H), 2.16 (dd, J = 13.9, 6.8 Hz, 1H), 1.93 (dd, J = 13.8, 12.0 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 162.6 (d, J = 250.6 Hz), 150.0 (d, J = 6.9 Hz), 144.2, 137.8, 133.4, 132.3, 129.9, 129.0 (d, J = 8.7 Hz), 127.9, 127.3 (d, J = 3.5 Hz), 118.3 (d, J = 320.9 Hz), 114.4 (d, J = 23.2 Hz), 113.3 (d, J = 21.8 Hz), 54.1, 50.7, 50.4, 39.3, 38.1, 31.4, 31.0, 21.6; HRMS (ESI) calcd for $C_{23}H_{23}F_4NNaO_5S_2$ ([M + Na]$^+$) 556.0842, found 556.0846.

*6,7-Dichloro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3j**).* Following the general procedure above. Reaction time: 27 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 19.5 mg of **1j** was converted to 22.1 mg of **3j**, yield 84%. Run 2: 20.3 mg of **1j** was converted to 21.8 mg of **3j**, yield 80%. So the average yield of two runs was 82%. **3j**: yellow solid, mp = 154−155 °C, TLC R_f = 0.33 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.51 (s, 1H), 7.46 (s, 1H), 7.35 (d, J = 8.1 Hz, 2H), 4.28 (d, J = 15.9 Hz, 1H), 4.15 (dd, J = 15.9, 2.0 Hz, 1H), 3.59 (dd, J = 10.1, 7.9 Hz, 1H), 2.93 (dd, J = 10.1, 7.3 Hz, 1H), 2.65−2.54 (m, 1H), 2.43 (s, 3H), 2.12 (dd, J = 13.9, 6.7 Hz, 1H), 1.89 (dd, J = 13.9, 12.0 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 144.4, 136.5, 135.9, 133.3, 132.2, 131.0, 130.8, 129.9, 129.2, 128.4, 127.8, 118.2 (q, J = 320.5 Hz), 54.0, 50.6, 49.8, 39.4, 37.8, 31.2, 31.1, 21.5; HRMS (ESI) calcd for $C_{23}H_{22}Cl_2F_3NNaO_5S_2$ ([M + Na]$^+$) 606.0161, found 606.0147.

*6,9,9-Trimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]-cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3k**).* Following the general procedure above. Reaction time: 15 h. Eluted with PE/EA 20:1 to 10:1. Run 1: 17.9 mg of **1k** was converted to 23.0 mg of **3k**, yield 92%. Run 2: 17.6 mg of **1k** was converted to 23.1 mg of **3k**, yield 94%. So the average yield of two runs was 93%. **3k**: light yellow solid, mp = 119−121 °C, TLC R_f = 0.38 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.22 (brs, 1H), 7.10 (dd, J = 8.0, 1.2 Hz, 1H), 4.27 (d, J = 15.5 Hz, 1H), 4.14 (dd, J = 15.5, 2.0 Hz, 1H), 3.55 (dd, J = 9.9, 7.9 Hz, 1H), 2.91 (dd, J = 9.9, 7.1 Hz, 1H), 2.73−2.53 (m, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.11 (dd, J = 13.8, 6.7, 1H), 1.89 (dd, J = 13.8, 11.9 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.8, 138.8, 135.9, 133.4, 132.1, 130.8, 130.0, 129.8, 127.9, 127.3, 126.8, 118.3 (q, J = 320.3 Hz), 54.2, 50.7, 50.5, 39.3, 37.5, 31.54, 31.46, 21.5, 20.7; HRMS (ESI) calcd for $C_{24}H_{27}F_3NO_5S_2$ ([M + H]$^+$) 530.1277, found 530.1270.

*6-Methoxy-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3m**).* Following the general procedure above. Reaction time: 24 h. Eluted with PE/EA 20:1 to 10:1. Run 1: 17.9 mg of **1m** was converted to 19.2 mg of **3m**, yield 78%. Run 2: 18.0 mg of **1m** was converted to 20.4 mg of **3m**, yield 82%. So the average yield of two runs was 80%. **3m**: colorless oil, TLC R_f = 0.42 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 2.8 Hz, 1H), 6.84 (dd, J = 9.0, 2.8 Hz, 1H), 4.27 (d, J = 15.6 Hz, 1H), 4.15 (dd, J = 15.6, 2.0 Hz, 1H), 3.78 (s, 3H), 3.55 (dd, J = 9.9, 7.8 Hz, 1H), 2.93 (dd, J = 9.9, 7.0 Hz, 1H), 2.69−2.56 (m, 1H), 2.42 (s, 3H), 2.12 (dd, J = 13.8, 6.7 Hz, 1H), 1.89 (dd, J = 13.8, 11.9 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 144.2, 138.9, 138.5, 134.1, 132.2, 132.0, 129.9, 128.1, 127.9, 118.3 (q, J = 320.4 Hz), 114.9, 112.0, 55.2, 54.2, 50.9, 50.5, 39.4, 37.2, 31.8, 31.6, 21.5; HRMS (ESI) calcd for $C_{24}H_{27}F_3NO_6S_2$ ([M + H]$^+$) 546.1226, found 546.1229.

*11,11-Dimethyl-2-tosyl-1,2,3,11,12,12a-hexahydronaphtho-[2′,3′:4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3n**).* Following the general procedure above. Reaction time: 24 h. Eluted with PE/EA 15:1 to 5:1 Run 1: 18.7 mg of **1n** was converted to 23.2 mg of **3n**, yield 90%. Run 2: 18.5 mg of **1n** was converted to 22.7 mg of **3n**, yield 91%. So the average yield of two runs was 91%. **3n**: yellow solid, mp = 186−188 °C, TLC R_f = 0.37 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.84 (s, 1H), 7.82−7.77 (m, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.55−7.46 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.31 (d, J = 15.6 Hz, 1H), 4.22 (dd, J = 15.6, 1.5 Hz, 1H), 3.55 (dd, J = 10.0, 7.9 Hz, 1H), 2.97 (dd, J = 10.0, 6.9 Hz, 1H), 2.69−2.55 (m, 1H), 2.36 (s, 3H), 2.18 (dd, J = 13.6, 6.9 Hz, 1H), 1.93 (dd, J = 13.6, 12.3 Hz, 1H), 1.48 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 144.2, 143.1, 138.9, 133.1, 132.8, 132.4, 131.0, 129.9, 129.7, 127.9, 127.8, 127.7, 127.5, 127.1, 126.7, 125.6, 118.4 (d, J = 320.9 Hz), 54.3, 50.6, 49.4, 39.4, 37.7, 31.60, 31.56, 21.5; HRMS (ESI) calcd for $C_{27}H_{27}F_3NO_5S_2$ ([M + H]$^+$) 566.1277, found 566.1285.

*9,9-Dimethyl-2-((2-nitrophenyl)sulfonyl)-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3o**).* Following the general procedure above. Reaction time: 15 h. Eluted with PE/EA 10:1 to 5:1. Run 1: 18.0 mg of **1o** was converted to 19.4 mg of **3o**, yield 78%. Run 2: 17.2 mg of **1o** was converted to 17.0 mg of **3o**, yield 72%. So the average yield of two runs was 75%. **3o**: yellow oil, TLC R_f = 0.24 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.02 (m, 1H), 7.77−7.72 (m, 2H), 7.67−7.62 (m, 1H), 7.52−7.46 (m, 2H), 7.36−7.27 (m, 2H), 4.49 (d, J = 15.5 Hz, 1H), 4.43 (dd, J = 15.5, 1.8 Hz, 1H), 3.84 (dd, J = 10.0, 8.0 Hz, 1H), 3.24 (dd, J = 10.0, 7.4 Hz, 1H), 2.96−2.87 (m, 1H), 2.21 (dd, J = 13.9, 6.8 Hz, 1H), 1.99 (dd, J = 13.9, 11.7 Hz, 1H), 1.39 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 146.8, 138.9, 134.0, 133.4, 131.7, 131.0, 130.9, 130.8, 129.5, 127.0, 126.7, 126.4, 124.2, 118.3 (q, J = 320.9 Hz), 54.1, 50.3, 49.6, 39.7, 37.9, 31.3, 31.0; HRMS (ESI) calcd for $C_{22}H_{25}F_3N_3O_7S_2$ ([M + NH_4]$^+$) 564.1080, found 564.1091.

*Diethyl 9,9-Dimethyl-4-(((trifluoromethyl)sulfonyl)oxy)-3,9,10,10a-tetrahydrobenzo[f]azulene-2,2(1H)-dicarboxylate (**3p**).* Following the general procedure above. Reaction time: 15 h. Eluted with PE/EA 100:1 to 25:1. Run 1: 16.8 mg of **1p** was converted to 16.7 mg of **3p**, yield 70%. Run 2: 16.2 mg of **1p** was converted to 17.3 mg of **3p**, yield 75%. So the average yield of two runs was 73%. **3p**: colorless oil, TLC R_f = 0.73 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.42 (m, 2H), 7.32−7.14 (m, 2H), 4.23 (q, J = 7.2 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.40 (d, J = 17.6 Hz, 1H), 3.31 (d, J = 17.6 Hz, 1H), 2.74−2.56 (m, 2H), 2.27 (dd, J = 13.9, 6.2 Hz, 1H), 2.05−1.86 (m, 2H), 1.39 (s, 6H), 1.28 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.6, 146.7, 139.5, 137.8, 131.9, 128.6, 126.7, 126.5, 126.1, 118.4 (q, J = 320.1 Hz), 61.9, 61.8, 59.6, 53.5, 41.2, 38.8, 38.3, 38.1, 31.8, 31.4, 14.0, 13.9; HRMS (ESI) calcd for $C_{23}H_{28}F_3O_7S$ ([M + H]$^+$) 505.1502, found 505.1498.

*N-(3-Cyclohexylidene-3l5-allyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**3q**).* Following the general procedure above. Reaction time: 24 h. Eluted with PE/EA 15:1 to 5:1. Run 1: 18.4 mg of **1q** was converted to 17.4 mg of **3q**, yield 69%. Run 2: 18.9 mg of **1q** was converted to 17.1 mg of **3q**, yield 66%. So the average yield of two runs was 68%. **3q**: yellow oil, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (dd, J = 7.6, 1.5 Hz, 1H), 7.33 (d, J = 8.2 Hz, 2H), 7.31−7.22 (m, 2H), 4.22−4.12 (m, 2H), 3.45 (dd, J = 10.1, 7.8 Hz, 1H), 3.00 (dd, J = 10.1, 6.0 Hz, 1H), 2.52−2.44 (m, 1H), 2.42 (s, 3H), 2.16−2.03 (m, 2H), 1.99−1.86 (m, 2H), 1.80−1.70 (m, 1H), 1.71−1.62 (m, 2H), 1.54−1.36 (m, 3H), 1.34−1.28 (m, 1H), 1.15−1.02 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 144.1, 138.8, 132.7, 132.3, 131.9, 129.8, 129.0, 128.0, 127.9, 126.8, 126.0, 118.3 (q,

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J = 320.9 Hz), 54.2, 50.2, 40.8, 39.5, 38.8, 38.4, 29.7, 25.9, 22.7, 22.5, 21.5; HRMS (ESI) calcd for $C_{26}H_{29}F_3NO_5S_2$ ([M + H]$^+$) 556.1434, found 556.1430.

*9,9,10a-Trimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]-cyclohepta[1,2-c]pyrrol-4-yl Trifluoromethanesulfonate (**3r**).* Following the general procedure above. Reaction time: 15 h. Eluted with PE/EA 20:1. Run 1: 17.8 mg of **1r** was converted to 6.9 mg of **3r**, yield 28%. Run 2: 17.6 mg of **1r** was converted to 6.4 mg of **3r**, yield 26%. So the average yield of two runs was 27%. **3r**: yellow oil, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.42 (dd, J = 5.0, 2.6 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.35−7.17 (m, 2H), 4.37 (d, J = 16.0 Hz, 1H), 4.08 (d, J = 16.0 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 2.94 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H), 2.11 (d, J = 14.6 Hz, 1H), 2.03 (d, J = 14.6 Hz, 1H), 1.37 (s, 3H), 1.28 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 144.2, 138.6, 137.1, 131.7, 130.7, 129.84, 129.80, 127.9, 127.6, 126.6, 126.0, 118.2 (q, J = 320.2 Hz), 63.3, 58.2, 51.0, 43.3, 37.6, 32.6, 27.2, 26.9, 21.6; HRMS (ESI) calcd for $C_{24}H_{26}F_3NNaO_5S_2$ ([M + Na]$^+$) 552.1097, found 552.1091.

General Procedure D: Me_3OBF_4-Mediated Formal Cycloisomerization. To a solution of Me_3OBF_4 (7.7 mg, 0.053 mmol, 1.05 equiv) in anhydrous DCE (2.0 mL) in a reaction bottle was added substrate **1** (0.05 mmol). Then the reaction mixture was immersed into a 60 °C oil bath and stirred for 24 h. Then the reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **4**.

General Procedure E: HBF_4-Mediated Formal Cycloisomerization and [4+3] Cycloaddition. To a solution of substrate **1** (0.05 mmol) in SuperDry DCE (2.0 mL) in a reaction bottle was added 50−55% HBF_4·Et_2O (40 μL, 0.29 mmol). Then the reaction mixture was immersed into a 60 °C oil bath and stirred for 24 h. When TLC analysis (by UV) indicated the disappearance of the starting material, the reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **4** or **5**. For substrates **1d** and **1r**, 100 μL of HBF_4·Et_2O (100 μL, 0.73 mmol) was added.

The substrates tested for these two transformations are **1a**−**1q**, except **1e**, **1i**, **1m**, and **1p**. The reactions of **1o** and **1q** gave mixtures.

Here we want to point out that the determinations of the structures of **5d** and **5k** were based on their ^{1}H NMR because their benzene ring hydrogen coupling constants followed the patterns of 1,2,4- not 1,2,3-trisubstituted benzene rings.[19a−c] For **5n**, we assigned its structure based on the benzene ring hydrogen coupling pattern with two separate singlet peaks in ^{1}H NMR, 8.14 (s, 1H), 7.83 (s, 1H).[19d−f]

*(Z)-3-(Fluoro(phenyl)methylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4a**).* Following the general procedure D. Eluted with PE/EA 25:1. Run 1: 18.2 mg of **1a** converted to 16.5 mg of **4a**, yield 86%. Run 2: 18.2 mg of **1a** was converted to 17.1 mg of **4a**, yield 89%. So the average yield of two runs was 88%. **4a**: colorless oil, TLC R_f = 0.44 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.33−7.27 (m, 5H), 4.86 (d, J = 9.3 Hz, 1H), 4.17 (dd, J = 15.0, 2.9 Hz, 1H), 4.09 (ddd, J = 15.0, 2.0, 2.0 Hz, 1H), 3.70−3.60 (m, 1H), 3.39 (dd, J = 9.2, 7.1 Hz, 1H), 3.07 (ddd, J = 9.2, 4.4, 1.8 Hz, 1H), 2.44 (s, 3H), 1.57 (d, J = 1.0 Hz, 3H), 1.53 (d, J = 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (d, J = 243.5 Hz), 143.8, 133.7, 132.3, 131.3 (d, J = 28.2 Hz), 129.7, 128.9, 128.0, 127.9, 126.9 (d, J = 5.9 Hz), 123.6 (d, J = 2.1 Hz), 118.5 (d, J = 20.0 Hz), 55.4, 49.4 (d, J = 8.6 Hz), 39.0 (d, J = 4.9 Hz), 25.4, 21.5, 18.0; HRMS (ESI) calcd for $C_{22}H_{25}FNO_2S$ ([M + H]$^+$) 386.1585, found 386.1596.

*(Z)-3-((4-Chlorophenyl)fluoromethylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4b**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 20.3 mg of **1b** was converted to 19.4 mg of **4b**, yield 91%. Run 2: 20.0 mg of **1b** was converted to 18.5 mg of **4b**, yield 88%. So the average yield of two runs was 90%. **4b**: yellow solid, mp = 114−115 °C, TLC R_f = 0.45 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 4.85 (d, J = 9.4 Hz, 1H), 4.15 (dd, J = 15.0, 3.2 Hz, 1H), 4.09 (ddd, J = 15.0, 2.0, 2.0 Hz, 1H), 3.66−3.57 (m, 1H), 3.41 (dd, J = 9.2, 7.2 Hz, 1H), 3.06 (ddd, J = 9.2, 4.6, 1.6 Hz, 1H), 2.44 (s, 3H), 1.59 (d, J = 1.0 Hz, 3H), 1.55 (d, J = 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4 (d, J = 243.4 Hz), 143.9, 134.9, 134.2, 132.4, 129.720, 129.717 (d, J = 29.0 Hz), 128.21 (d, J = 5.9 Hz), 128.17, 128.0, 123.4 (d, J = 2.1 Hz), 119.3 (d, J = 19.8 Hz), 55.4, 49.5 (d, J = 8.5 Hz), 39.1 (d, J = 4.8 Hz), 25.4, 21.5, 18.0; HRMS (ESI) calcd for $C_{22}H_{24}ClFNO_2S$ ([M + H]$^+$) 420.1195, found 420.1201.

*(Z)-3-((4-Bromophenyl)fluoromethylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4c**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 22.1 mg of **1c** was converted to 20.1 mg of **4c**, yield 89%. Run 2: 22.4 mg of **1a** was converted to 19.9 mg of **2a**, yield 85%. So the average yield of two runs was 87%. **4c**: yellow solide, mp = 119−121 °C, TLC R_f = 0.45 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 4.85 (d, J = 9.4 Hz, 1H), 4.14 (dd, J = 15.1, 3.0 Hz, 1H), 4.06 (d, J = 15.1 Hz, 1H), 3.65−3.56 (m, 1H), 3.40 (dd, J = 9.2, 6.8 Hz, 1H), 3.06 (ddd, J = 9.2, 4.4, 1.2 Hz, 1H), 2.44 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (d, J = 244.4 Hz), 143.8, 134.2, 132.2, 131.1, 130.1 (d, J = 28.8 Hz), 129.7, 128.4 (d, J = 5.9 Hz), 128.0, 123.3 (d, J = 2.1 Hz), 123.1, 119.4 (d, J = 19.8 Hz), 55.4, 49.5 (d, J = 8.5 Hz), 39.0 (d, J = 4.8 Hz), 25.4, 21.5, 18.0; HRMS (ESI) calcd for $C_{22}H_{24}BrFNO_2S$ ([M + H]$^+$) 464.0690, found 464.0684.

*(Z)-3-((3-Chlorophenyl)fluoromethylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4d**).* Following the general procedure D. Eluted with PE/EA 25:1. Run 1: 20.0 mg of **1d** was converted to 17.6 mg of **4d**, yield 84%. Run 2: 21.0 mg of **1a** was converted to 17.8 mg of **4d**, yield 81%. So the average yield of two runs was 83%. **4d**: yellow solid, mp = 113−115 °C, TLC R_f = 0.44 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.30−7.17 (m, 4H), 4.84 (d, J = 9.5 Hz, 1H), 4.17 (dd, J = 15.3, 3.1 Hz, 1H), 4.08 (d, J = 15.3 Hz, 1H), 3.67−3.58 (m, 1H), 3.42 (dd, J = 9.2, 7.6 Hz, 1H), 3.06 (ddd, J = 9.4, 4.7, 1.4 Hz, 1H), 2.44 (s, 3H), 1.63 (d, J = 0.8 Hz, 3H), 1.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (d, J = 243.2 Hz), 143.9, 134.5, 133.9 (d, J = 1.3 Hz), 132.9 (d, J = 28.9 Hz), 132.3, 129.7, 129.2, 128.9, 128.0, 127.3 (d, J = 6.5 Hz), 124.7 (d, J = 5.8 Hz), 123.0 (d, J = 2.1 Hz), 120.0 (d, J = 19.5 Hz), 55.4, 49.6 (d, J = 8.5 Hz), 39.0 (d, J = 4.7 Hz), 25.4, 21.5, 18.0; HRMS (ESI) calcd for $C_{22}H_{24}ClFNO_2S$ ([M + H]$^+$) 420.1195, found 420.1194.

*(Z)-3-(Fluoro(4-(trifluoromethyl)phenyl)methylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4f**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 21.4 mg of **1f** was converted to 20.6 mg of **4f**, yield 92%. Run 2: 21.6 mg of **1f** was converted to 19.9 mg of **4f**, yield 88%. So the average yield of two runs was 90%. **4f**: white solid, mp = 106−110 °C TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.84 (d, J = 9.6 Hz, 1H), 4.19 (dd, J = 15.5, 3.2 Hz, 1H), 4.10 (ddd, J = 15.5, 2.0, 2.0 Hz, 1H), 3.71−3.62 (m, 1H), 3.43 (dd, J = 9.2, 7.3 Hz, 1H), 3.08 (ddd, J = 9.2, 4.7, 1.7 Hz, 1H), 2.44 (s, 3H), 1.61 (d, J = 1.2 Hz, 3H), 1.54 (d, J = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9 (d, J = 243.2 Hz), 143.9, 134.56 (qd, J = 28.7, 1.2 Hz), 134.5, 132.2, 130.7 (d, J = 33.0 Hz), 129.7, 128.0, 127.1 (d, J = 6.1 Hz), 124.8 (q, J = 3.2 Hz), 123.7 (q, J = 272.2 Hz), 123.1 (d, J = 2.1 Hz), 121.1 (d, J = 19.4 Hz), 55.4, 49.6 (d, J = 8.5 Hz), 39.1 (d, J = 4.7 Hz), 25.3, 21.5, 18.0; HRMS (ESI) calcd for $C_{23}H_{24}F_4NO_2S$ ([M + H]$^+$) 454.1458, found 454.1459.

*(Z)-3-(Fluoro(3-(trifluoromethyl)phenyl)methylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4g**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 21.1 mg of **1g** was converted to 20.5 mg of **4g**, yield 93%. Run 2: 21.8 mg of **1g** was converted to 20.8 mg of **4g**, yield 91%. So the average yield of two runs was 92%. **4g**: light red solid, mp = 97−100 °C TLC R_f = 0.46 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.56−7.43 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 4.81 (d, J = 9.2 Hz, 1H), 4.20 (dd, J = 15.2, 3.2 Hz, 1H), 4.09 (d, J = 15.3 Hz, 1H), 3.70−3.60 (m, 1H), 3.47 (dd, J = 8.8, 7.2 Hz, 1H), 3.04 (ddd, J = 9.6, 5.1, 1.2 Hz, 1H), 2.44 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8 (d, J = 243.0 Hz), 143.9, 135.2, 132.3, 132.0 (d, J = 29.2 Hz), 130.4 (q, J = 32.5 Hz), 129.8 (d, J = 4.6 Hz),

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129.7, 128.5, 128.0, 125.5 (q, J = 3.6 Hz), 124.0 (q, J = 3.9 Hz), 123.8 (q, J = 273.0 Hz), 122.9 (d, J = 2.1 Hz), 120.6 (d, J = 19.5 Hz), 55.4, 49.7 (d, J = 8.5 Hz), 39.0 (d, J = 4.7 Hz), 25.2, 21.5, 17.8; HRMS (ESI) calcd for $C_{23}H_{24}F_4NO_2S$ ([M + H]$^+$) 454.1458, found 454.1461.

*Ethyl (Z)-4-(Fluoro(4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-ylidene)methyl)benzoate (**4h**).* Following the general procedure D. Eluted with PE/EA 15:1. Run 1: 21.6 mg of **1h** was converted to 19.9 mg of **4h**, yield 88%. Run 2: 21.7 mg of **1h** was converted to 20.9 mg of **4h**, yield 92%. So the average yield of two runs was 90%. **4h**: yellow oil, TLC R_f = 0.4 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H, 2H), 4.88 (d, J = 9.4 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 4.18 (dd, J = 15.4, 3.0 Hz, 1H), 4.11 (d, J = 14.2 Hz, 1H), 3.70−3.65 (m, 1H), 3.41 (dd, J = 9.2, 7.0 Hz, 1H), 3.10 (ddd, J = 9.2, 4.4, 1.7 Hz, 1H), 2.44 (s, 3H), 1.63 (s, 3H), 1.56 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 150.4 (d, J = 242.7 Hz), 143.9, 135.2 (d, J = 28.2 Hz), 134.4, 132.2, 130.5, 129.7, 129.1, 128.0, 126.6 (d, J = 6.2 Hz), 123.2 (d, J = 2.9 Hz), 121.0 (d, J = 19.6 Hz), 61.2, 55.5, 49.6 (d, J = 8.8 Hz), 39.1 (d, J = 4.8 Hz), 25.4, 21.5, 18.0, 14.3; HRMS (ESI) calcd for $C_{25}H_{29}FNO_4S$ ([M + H]$^+$) 458.1796, found 458.1792.

*(Z)-3-((3,4-Dichlorophenyl)fluoromethylene)-4-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4j**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 21.7 mg of **1j** was converted to 17.9 mg of **4j**, yield 79%. Run 2: 21.7 mg of **1j** was converted to 17.0 mg of **4j**, yield 75%. So the average yield of two runs was 77%. **4j**: yellow solid, mp = 110−112 °C, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.40−7.33 (m, 4H), 7.15 (dd, J = 8.5, 2.0 Hz, 1H), 4.84 (d, J = 9.5 Hz, 1H), 4.16 (dd, J = 15.4, 3.2 Hz, 1H), 4.07 (ddd, J = 15.5, 2.0, 2.0 Hz, 1H), 3.66−3.57 (m, 1H), 3.43 (dd, J = 9.0, 7.4 Hz, 1H), 3.06 (ddd, J = 9.5, 4.8, 1.5 Hz, 1H), 2.44 (s, 3H), 1.65 (d, J = 1.1 Hz, 3H), 1.59 (d, J = 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1 (d, J = 242.7 Hz), 144.0, 134.9, 133.0, 132.2, 131.0 (d, J = 29.6 Hz), 130.0, 129.7, 129.0 (d, J = 6.6 Hz), 128.0, 127.9, 125.7 (d, J = 5.9 Hz), 122.8 (d, J = 2.1 Hz), 120.7 (d, J = 19.3 Hz), 55.4, 49.6 (d, J = 8.5 Hz), 39.1 (d, J = 4.5 Hz), 25.4, 21.5, 18.0; HRMS (ESI) calcd for $C_{22}H_{23}Cl_2FNO_2S$ ([M + H]$^+$) 454.0805, found 454.0815.

*(Z)-4-(Fluoro(phenyl)methylene)-3-methyl-3-(2-methylprop-1-en-1-yl)-1-tosylpyrrolidine (**4r**).* Following the general procedure D. Eluted with PE/EA 25:1. Run 1: 19.1 mg of **1r** was converted to 15.7 mg of **4r**, yield 78%. Run 2: 18.8 mg of **1r** was converted to 16.0 mg of **4r**, yield 81%. So the average yield of two runs was 80%. **4r**: yellow oil, TLC R_f = 0.46 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.33−7.28 (m, 5H), 4.92 (s, 1H), 4.29 (dd, J = 15.0, 3.0 Hz, 1H), 4.08 (dd, J = 15.0, 3.3 Hz, 1H), 3.25 (dd, J = 9.2, 2.3 Hz, 1H), 3.14 (d, J = 9.2 Hz, 1H), 2.45 (s, 3H), 1.36 (s, 3H), 1.34 (d, J = 1.1 Hz, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1 (d, J = 242.8 Hz), 143.7, 134.9, 132.2, 131.5 (d, J = 28.3 Hz), 129.7, 129.1 (d, J = 1.7 Hz), 128.1(d, J = 5.3 Hz), 128.0, 127.61, 127.60, 122.9 (d, J = 19.6 Hz), 61.9, 50.2 (d, J = 10.9 Hz), 43.9 (d, J = 5.2 Hz), 28.1, 26.6, 21.6, 18.8; HRMS (ESI) calcd for $C_{23}H_{27}FNO_2S$ ([M + H]$^+$) 400.1741, found 400.1738.

*4-Fluoro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrole (**5a**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 18.0 mg of **1a** was converted to 16.9 mg of **5a**, yield 89%. Run 2: 18.2 mg of **1a** was converted to 17.7 mg of **5a**, yield 92%. So the average yield of two runs was 91%. **5a**: white solid, mp = 127−130 °C, TLC R_f = 0.38 (PE/EA, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.64 (dd, J = 6.7, 2.1 Hz, 1H), 7.44 (d, J = 7.4, Hz, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.27−7.19 (m, 2H), 4.27 (d, J = 15.1 Hz, 1H), 4.08 (ddd, J = 15.1, 2.7, 2.6 Hz, 1H), 3.75 (ddd, J = 8.8, 7.4, 3.5 Hz, 1H), 3.07−2.96 (m, 1H), 2.69 (dd, J = 10.1, 9.1 Hz, 1H), 2.42 (s, 3H), 1.79 (dd, J = 13.6, 4.4 Hz, 1H), 1.58 (dd, J = 13.6, 11.9 Hz, 1H), 1.43 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9 (d, J = 237.7 Hz), 146.3 (d, J = 6.9 Hz), 143.8, 132.7, 129.7, 128.43, 128.42 (d, J = 24.2 Hz), 127.8, 126.5 (d, J = 3.9 Hz), 126.2 (d, J = 3.2 Hz), 125.5 (d, J = 17.1 Hz), 120.0 (d, J = 22.2 Hz), 54.3, 49.9 (d, J = 9.8 Hz), 40.2, 37.9, 37.3 (d, J = 6.6 Hz), 32.4, 29.2, 21.5; HRMS (ESI) calcd for $C_{22}H_{25}FNO_2S$ ([M + H]$^+$) 386.1585, found 386.1584.

*6-Chloro-4-fluoro-9,9-dimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrole (**5d**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 21.6 mg of **1d** was converted to 17.2 mg of **5d**, yield 76%. Run 2: 21.9 mg of **1d** was converted to 18.1 mg of **5d**, yield 79%. So the average yield of two runs was 77%. **5d**: yellow solid, mp = 168−171 °C, TLC R_f = 0.37 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 2.2 Hz, 1H), 7.36 (dd, J = 8.6, 1.2 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.20 (dd, J = 8.6, 2.3 Hz, 1H), 4.29 (d, J = 15.4 Hz, 1H), 4.06 (ddd, J = 15.4, 2.6, 2.6 Hz, 1H), 3.76 (ddd, J = 8.8, 7.5, 3.6 Hz, 1H), 3.10−2.96 (m, 1H), 2.67 (dd, J = 10.2, 9.1 Hz, 1H), 2.43 (s, 3H), 1.78 (dd, J = 13.6, 4.3 Hz, 1H), 1.53 (dd, J = 13.6, 12.1 Hz, 1H), 1.42 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8 (d, J = 238.1 Hz), 144.6 (d, J = 6.7 Hz), 143.9, 132.4, 132.2 (d, J = 3.3 Hz), 130.1 (d, J = 24.4 Hz), 129.8, 128.14, 128.10, 127.8, 125.4 (d, J = 18.7 Hz), 121.6 (d, J = 21.9 Hz), 54.2, 49.9 (d, J = 9.7 Hz), 39.64, 37.63, 37.2 (d, J = 6.4 Hz), 32.3, 29.1, 21.5; HRMS (ESI) calcd for $C_{22}H_{24}ClFNO_2S$ ([M + H]$^+$) 420.1195, found 420.1201.

*4-Fluoro-6,9,9-trimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo-[4,5]cyclohepta[1,2-c]pyrrole (**5k**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 18.9 mg of **1k** was converted to 12.3 mg of **5k**, yield 62%. Run 2: 19.1 mg of **1k** was converted to 11.5 mg of **5k**, yield 57%. So the average yield of two runs was 60%. **5k**: white solid, mp = 134−137 °C, TLC R_f = 0.53 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.45 (s, 1H), 7.34 (d, J = 8.2 Hz, 2H), 7.32 (dd, J = 8.1, 1.3 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 4.27 (ddd, J = 15.1, 1.8, 1.7 Hz, 1H), 4.08 (ddd, J = 15.1, 2.9, 2.5 Hz, 1H), 3.74 (ddd, J = 8.8, 7.4, 3.5 Hz, 1H), 3.10−2.92 (m, 1H), 2.68 (dd, J = 10.2, 9.0 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.77 (dd, J = 13.6, 4.4 Hz, 1H), 1.55 (dd, J = 13.6, 11.9 Hz, 1H), 1.41 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0 (d, J = 237.6 Hz), 143.8, 143.4 (d, J = 6.8 Hz), 135.7 (d, J = 3.0 Hz), 132.6, 129.7, 129.1, 128.2 (d, J = 23.8 Hz), 127.8, 126.6 (d, J = 4.0 Hz), 126.1 (d, J = 16.7 Hz), 119.9 (d, J = 22.3 Hz), 54.4, 49.9 (d, J = 9.9 Hz), 40.4, 37.5, 37.2 (d, J = 6.6 Hz), 32.4, 29.4, 21.5, 20.8; HRMS (ESI) calcd for $C_{23}H_{27}FNO_2S$ ([M + H]$^+$) 400.1741, found 400.1737.

*4-Fluoro-11,11-dimethyl-2-tosyl-1,2,3,11,12,12a-hexahydronaphtho[2′,3′:4,5]cyclohepta[1,2-c]pyrrole (**5n**).* Following the general procedure E. Eluted with PE/EA 20:1. Run 1: 21.5 mg of **1n** was converted to 23.4 mg of **5n**, yield 80%. Run 2: 20.7 mg of **1n** was converted to 16.9 mg of **5n**, yield 79%. So the average yield of two runs was 80%. **5n**: yellow solid, mp = 187−190 °C, TLC R_f = 0.23 (PE/EA, 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.83 (s, 1H), 7.81−7.73 (m, 4H), 7.50−7.41 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.33 (ddd, J = 15.1, 1.7, 1.7 Hz, 1H), 4.16 (ddd, J = 15.1, 3.1, 2.4 Hz, 1H), 3.75 (ddd, J = 8.8, 7.2, 3.6 Hz, 1H), 3.16−3.03 (m, 1H), 2.72 (dd, J = 10.4, 8.9 Hz, 1H), 2.41 (s, 3H), 1.88 (dd, J = 13.7, 4.7 Hz, 1H), 1.63 (dd, J = 13.7, 12.0 Hz, 1H), 1.57 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (d, J = 237.5 Hz), 143.8, 143.4 (d, J = 6.8 Hz), 132.8, 131.3 (d, J = 3.0 Hz), 129.8, 127.9, 127.8, 127.4, 127.00 (d, J = 23.1 Hz), 126.97, 126.2, 125.7, 125.5, 124.9 (d, J = 3.7 Hz), 119.8 (d, J = 22.2 Hz), 54.2, 50.0 (d, J = 10.4 Hz), 39.5, 37.8 (d, J = 6.6 Hz), 37.6, 32.6, 28.6, 21.5; HRMS (ESI) calcd for $C_{26}H_{27}FNO_2S$ ([M + H]$^+$) 436.1741, found 436.1738.

*4-Fluoro-9,9,10a-trimethyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrole (**5r**).* Following the general procedure E. Eluted with PE/EA 25:1. Run 1: 19.3 mg of **1r** was converted to 14.0 mg of **5r**, yield 69%. Run 2: 19.5 mg of **1r** was converted to 14.7 mg of **5r**, yield 72%. So the average yield of two runs was 71%. **5r**: yellow oil, TLC R_f = 0.48 (PE/EA, 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.46−7.41 (m, 1H), 7.35 (d, J = 8.4 Hz, 3H), 7.28−7.23 (m, 2H), 4.22 (dd, J = 14.7, 3.2 Hz, 1H), 4.16 (dd, J = 14.7, 2.4 Hz, 1H), 3.16 (d, J = 1.5 Hz, 2H), 2.43 (s, 3H), 2.05 (d, J = 14.8 Hz, 1H), 1.95 (d, J = 14.8 Hz, 1H), 1.37 (s, 3H), 1.14 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3 (d, J = 244.7 Hz), 146.5 (d, J = 6.7 Hz), 143.7, 132.7, 130.2 (d, J = 25.8 Hz), 129.7, 129.0, 127.8, 127.3 (d, J = 6.2 Hz), 126.3, 125.3 (d, J = 2.4 Hz), 121.7 (d, J = 18.0 Hz), 62.1, 55.4, 49.2

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(d, J = 6.6 Hz), 41.5 (d, J = 5.7 Hz), 38.0, 32.5, 28.2 (d, J = 2.8 Hz), 26.6, 21.5; HRMS (ESI) calcd for $C_{23}H_{27}FNO_2S$ ([M + H]$^+$) 400.1741, found 400.1734.

Reaction 1, Scheme 2: trans-(4-(2-Methylprop-1-en-1-yl)-1-tosylpyrrolidin-3-yl)(phenyl)methanone (trans-6). To 0.5 mL of H_2O was added 360.2 mg of NaOH, and then 3 mL of MeOH and 6 mL of 1,6-dioxane were added to form a NaOH (1 M) solution. Substrate **2a** (25.4 mg, 0.049 mmol) in a reaction flask was added to 2 mL of the above prepared NaOH (1 M) solution. Then the reaction mixture was stirred for 1 h at room temperature. Then the reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding products **6** (17.0 mg, 90%) as diastereomers (6:1, with the *trans*-**6** as the major diastereomer). The two diastereomers can be separated and characterized. The structures of ketones *cis*-**6**[19g] and *trans*-**6**,[19g] which were confirmed by ^{1}H and ^{13}C NMR spectra, are consistent with those reported previously.

Reaction 2, Scheme 2: 9,9-Dimethyl-2-tosyl-2,3,3a,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrol-4(1H)-one (7). To 0.5 mL of H_2O was added 360.2 mg of NaOH, and then 3 mL of MeOH and 6 mL of 1,6-dioxane were added to form a NaOH (1 M) solution. Substrate **3a** (30.0 mg, 0.058 mmol) in a reaction bottle was added to 2 mL of the NaOH (1 M) solution. Then the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **7** (20.1 mg, 90%) as diastereomers (5:1, the ratio of two diastereomers was determined by the peak of 7.79 (major, d, J = 8.2 Hz, 2H) and 7.73 (minor, d, J = 8.4 Hz, 2H)): white solid, TLC R_f = 0.33 (PE/EA, 5:1). The major diastereomer could be separated partly and characterized: mp = 216−218 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 7.9 Hz, 1H), 7.41−7.37 (m, 3H), 7.23 (dd, J = 7.6, 1.5 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 3.81−3.75 (m, 1H), 3.68 (dd, J = 9.3, 6.8 Hz, 1H), 3.58−3.50 (m, 2H), 2.95−2.83 (m, 1H), 2.58 (dd, J = 9.8, 9.8 Hz, 1H), 2.46 (s, 3H), 1.74 (dd, J = 12.3, 4.4 Hz, 1H), 1.68 (dd, J = 14.7, 12.3 Hz, 1H), 1.46 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.2, 147.9, 143.6, 138.9, 133.1, 130.8, 129.7, 128.4, 127.9, 127.9, 126.3, 53.1, 52.6, 47.8, 42.0, 38.6, 37.4, 35.0, 27.8, 21.6. The major diastereomer HRMS (ESI) calcd for $C_{22}H_{26}NO_3S$ ([M + H]$^+$) 384.1628, found 384.1626.

Reaction 3, Scheme 2: 9,9-Dimethyl-4-phenyl-2-tosyl-1,2,3,9,10,10a-hexahydrobenzo[4,5]cyclohepta[1,2-c]pyrrole (8). **3a** (29.3 mg, 0.057 mmol) was dissolved in PhH under a glovebox environment. To the solution were added $PhB(OH)_2$ (27.0 mg, 0.22 mmol), $Pd(PPh_3)_4$ (3.3 mg, 0.0029 mmol), CuI (16.1 mg, 0.085 mmol), and Na_2CO_3 (41.6 mg, 7 equiv). Then more PhH and EtOH were added so that the final volumes of PhH and EtOH in the reaction were 1.8 and 0.6 mL. The mixture was immersed into an 86 °C oil bath and stirred for 24 h. When TLC analysis (by UV) indicated the disappearance of the starting material, the reaction mixture was purified by flash column chromatography on silica gel to afford corresponding products **8** (23.4 mg, 93%): white solid, mp = 167−169 °C, TLC R_f = 0.52 (PE/EA, 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.32 (dd, J = 7.6, 7.0 Hz, 2H), 7.30−7.24 (m, 1H), 7.17 (ddd, J = 12.0, 7.9, 1.3 Hz, 1H), 7.11−7.07 (m, 2H), 7.07−7.03 (m, 1H), 6.73 (dd, J = 7.7, 1.2 Hz, 1H), 4.13 (dd, J = 14.8, 1.0 Hz, 1H), 3.89 (d, J = 14.8 Hz, 1H), 3.21 (d, J = 9.2 Hz, 1H), 2.91 (dd, J = 9.1, 6.8 Hz, 1H), 2.64−2.54 (m, 1H), 2.45 (s, 3H), 2.29−2.17 (m, 2H), 1.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 143.8, 141.1, 140.8, 136.4, 134.9, 131.7, 130.7, 129.7, 128.8, 128.3, 128.1, 127.2, 126.8, 125.7, 125.4, 55.4, 53.6, 52.0, 40.6, 37.2, 32.1, 31.4, 21.5; HRMS (ESI) calcd for $C_{28}H_{30}NO_2S$ ([M + H]$^+$) 444.1992, found 444.1979.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00393.

Crystal data for **4b** (CIF)

Crystal data for **5a** (CIF)

Spectra for all new compounds, X-ray data, and preparation of substrates **1** (PDF)

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Notes

The authors declare no competing financial interest.

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