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Regioselective Hydronickelation of Allenes and Its Application to the Hydrocyanative Carbocyclization Reaction of Allene−Ynes and Bis-Allenes

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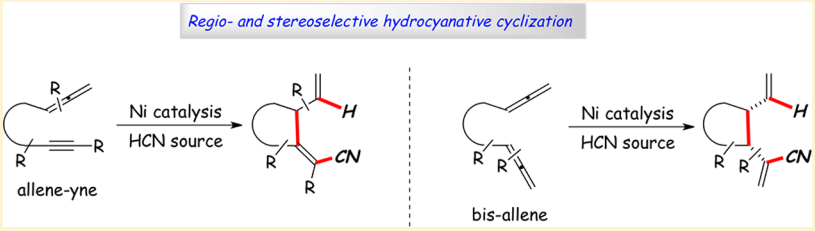
Supporting Information



ABSTRACT: The carbocyanative cyclization of allene−ynes and bis-allenes under nickel catalysis is described. The key steps are the regioselective hydronickelation of allenes and subsequent cyclization via carbometalation. The former step determines the reaction pathway, and the latter controls the stereochemistry of substituted olefins. The products are useful carbo- and heterocycles that include a cyano group, functionalized double bonds, and quaternary carbons.

INTRODUCTION

A cyano group is a masked carbonyl functionality, and its introduction, particularly by catalysis, has been an important issue in synthetic chemistry. Ever since the hydrocyanation of simple and nonactivated alkynes was developed,[1] C−C triple bonds have been recognized as versatile substrates for catalytic cyanation using X−CN (X = Si,[2] Ge,[3] B,[4] Sn,[5] S,[6] C,[7] Br[8]) under transition-metal catalysis. These protocols mainly offer electrophilic cyanation to form X−CN bonds via reductive elimination from X−M−CN (M = Ni, Pd). The carbocyanation (carbon−CN) of alkynes is a powerful and simple tool that provides facile access to functionalized olefins in one operation, and nickel complexes are key catalysts in these transformations.[7] On the other hand, we have developed a nucleophilic cyanation of nonactivated alkynes under palladium catalysis with molecular oxygen.[9] This unique carbocyanation provides 1,2-dicyanation products in a stereoselective manner, and the reaction is triggered by direct nucleophilic cyanation (cyanopalladation) onto C−C triple bonds activated by Pd(II).

When C−M−CN species are provided, not from C−CN bond cleavage but rather from C−H bond formation of allenes triggered by hydrometalation, a facile and alternative carbocyanation can be established through the sequential regio- and stereoselective connection among allenes, alkynes, and an HCN source in one operation (eq 3, Scheme 1).

Since allene−ynes are versatile substrates for preparing highly functionalized organic molecules via cyclization, cycloaddition, and cycloisomerization reactions under transition metal catalysis, their utility in synthetic organic chemistry has been widely studied[10,11] and the catalysts should be able to achieve the regio- and stereoselective functionalization of C−C multiple bonds through the above transformations. In general, allenes are more reactive[12] than alkynes and predominantly react with metal species to give the corresponding vinyl- and/or allylmetal intermediates.

In representative carbocyclizations using hydro-[13] and stannylsilanes[14] (eqs 1 and 2, Scheme 1), more nucleophilic silicon functionalities are predominantly installed onto allenes via silylmetalation (C−Si bond formation), as outlined in Scheme 2. On the other hand, we found that regio- and stereoselective exo-cyclization under nickel catalysis gives a cyclized product in a regio- and stereoselective manner with the use of hydrogen cyanide (eq 3). This transformation is triggered by hydronickelation to allenes (C−H bond formation) and a cyano group is always installed into C−C triple bonds through syn-carbometalation.[15] In this article, we report the details of a hydrocyanative carbocyclization under nickel catalysis and reveal a new aspect of the utility of allene−ynes as versatile cyclization precursors.

RESULTS AND DISCUSSION

To realize a significant difference in the reactivity of allene and alkyne, we initially started to investigate the hydrocyanation reaction in detail under nickel catalysis using **1a** and **2a** (Scheme 3). The reaction using equal amounts of both **1a** and **2a** in the presence of acetone cyanohydrin (AC) as an HCN source[16] with $Ni[P(OPh)_3]_4$ (10 mol %) under thermal conditions gave three products **3a−c** that all originated from **1a**, while **1b** was recovered quantitatively.[17] This result suggests that **1a** is

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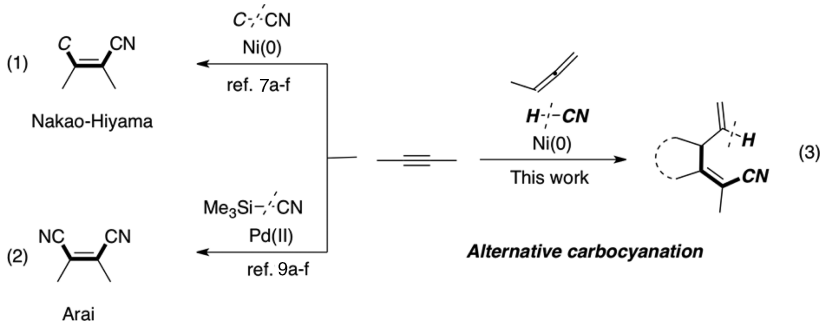
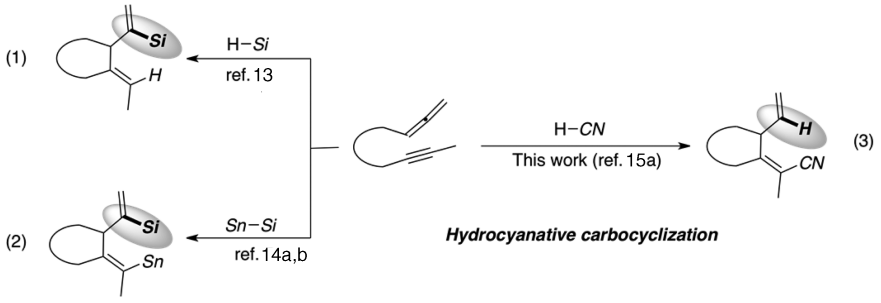
Scheme 1. Representative Strategies for Carbocyanation



Scheme 2. Allene−Yne Cyclization



Scheme 3. Reactivity of Allene and Alkyne

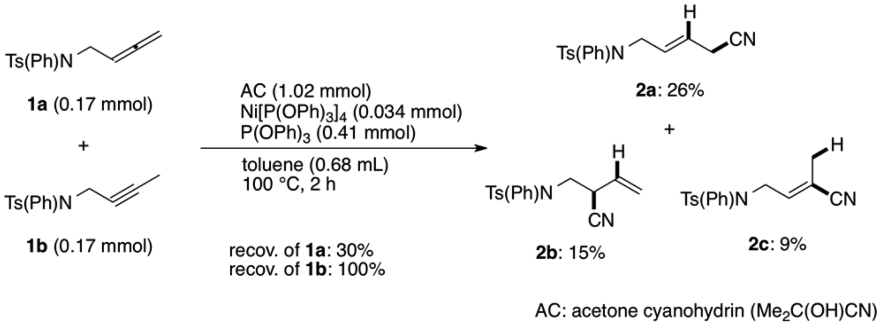
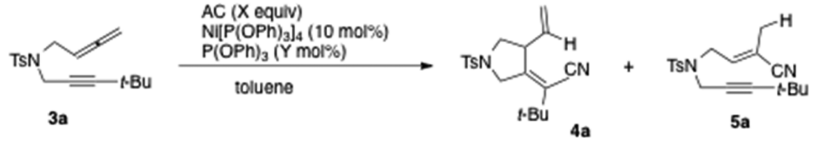


Table 1. Optimization of Hydrocyanative Allene-yne Cyclization using 3a



entry	X (equiv)	Y (mol%)	conditions	**4a** (%)	**5a** (%)
1	3	50	70 °C, 2.5 h	32	9
2	10	50	70 °C, 0.5 h	70	20
3	10	0	70 °C, 0.5 h	57	16
4	10	120	70 °C, 4 h	70	19
5	10	50	50 °C, 6 h	72	20


ORTEP of **4a**

sufficiently reactive to be discriminated from **1b** and C−H bond formation by hydrometalation is more likely to occur at a central allenyl carbon.

Encouraged by these results, we next turned to the use of allene−ynes for hydrocyanative cyclization (Table 1). Initially, **3a** was subjected to nickel catalysis in the presence of AC (3 equiv). The cyclized product **4a** was, as expected, obtained in 32% yield in a regio- and stereoselective manner, and its structure was confirmed by X-ray crystallographic analysis (entry 1).[18] On the other hand, the structure of the minor product was assigned to be **5a**, which could be obtained without cyclization. C−H bond formation at a terminal allenyl carbon in the hydronickelation step seems to be a key step for determining the reaction pathway. The reasonable agreement observed between the above structural information and the results in Scheme 3 indicate that hydrometalation predominantly occurred, not with

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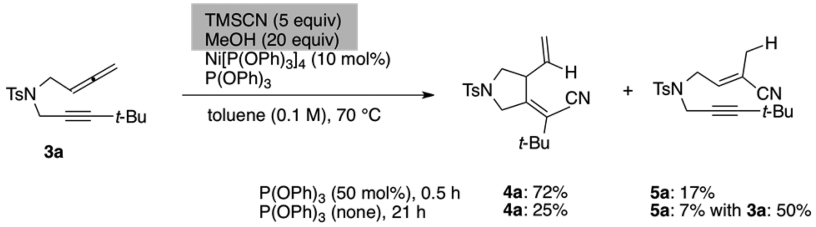
Scheme 4. Alternative Protocol for Hydrocyanative Cyclization

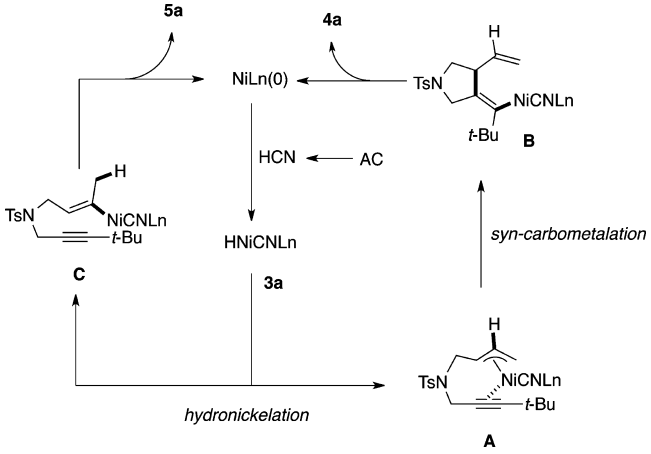


respect to an alkyne but rather with an allene. An increased amount of AC raised the yield of **4a** with a shorter reaction time, the absence of triphenyl phosphite prevented smooth conversion, and a greater amount of ligand did not affect the yield (entries 2−4). Finally, this reaction proceeded smoothly even at 50 °C to give **4a** in 72% yield (entry 5).

We also found that HCN generated in situ from TMSCN with MeOH[19] acts as an alternative cyano source and could be used in this cyclization protocol to give similar results; however, the presence of $P(OPh)_3$ was quite important for the reaction to proceed to completion (Scheme 4). For example, both a lack of ligand and a greater loading of HCN obviously prevented the reaction. These results suggest that Ni(0) could be poisoned to form $Ni(CN)_2$.

On the basis of the above results, a plausible reaction pathway is outlined in Scheme 5. Initially, HNiCNLn is formed by the

Scheme 5. Plausible Reaction Pathway



oxidative addition of HCN generated from AC to Ni^0Ln. A sequential hydrometalation to the allene in **3a** gives π-allyl intermediate **A**, which is smoothly converted to **B** via syn-carbometalation, and reductive elimination then gives **4a** together with Ni(0). The minor pathway is explained by the formation of vinylnickel species **C**, which gives **5a** by reductive elimination. These pathways suggest that the regioselectivity in hydrometalation determines the products and a cyano group is installed in **4** with perfect regio- and stereochemistry. In the case of $Ni(cod)_2$,[20] cyclization did not proceed effectively. This result indicates that oxidative cyclization between an allene−yne and Ni(0) might be much faster than the oxidative addition of HCN to Ni(0), so that the yield of **4a** decreased, unfortunately.

To investigate the scope and limitations of this hydrocyanative cyclization, we examined various substrates under the optimized conditions (Table 2). Trimethylsilyl and methyl groups on the C−C triple bond (**3b**,**c**) gave the corresponding cyclized products as major products in respective yields of 67% and 64% (entries 1 and 2).[18] Other products such as **6** and **7** originated from the simple hydrocyanation of allenes via noncyclization. Substrates bearing hydroxyl and alkoxy groups required a higher temperature for smooth conversion (entries 3 and 4), and disubstituted allene (**3f**) cyclized to **4f** through the construction of a quaternary carbon in 62% yield (entry 5). In the case of substituted pyrrolidine and the formation of carbocycles, **4g−i** were obtained in respective yields of 44%, 38%, and 71% (entries 6−8). The formation of a six-membered ring decreased the cyclization efficiency to give **4j** in 29% yield with a large amount of noncyclized products **6j−8j** (entry 9). Since the origin of the side products (**5**−**7**) would depend on the regiochemistry in the initial C−H bond-formation step, we next investigated 1,3-disubstituted allenes **3k−n** to evaluate the hydrometalation step (entries 10−12). As expected, the cyclization reaction using **3k**,**m** exclusively gave **4k**,**m** as sole products that included inseparable stereoisomers in respective yields of 53% and 60%. In the case of a trisubstituted allene such as **3n**, both **4n** and **6n** were obtained and the latter originated from simple hydrocyanation of the C−C triple bond before the regioselective hydrometalation of allene (entry 12). When a bulky substituent such as a *t*-Bu or TMS group on the C−C triple bond and an internal allenyl carbon were introduced, unique products were obtained. For example, the reaction of **3o**,**p** gave cyclized **4** and noncyclized **5** together with [3 + 2] cycloadducts **9**, which do not include a cyano group (entries 13 and 14). The reaction pathway that provides **9** will be discussed in Scheme 6. Finally, aryl substituents were examined and similar cyclization gave **4q−s** in moderate yield (entries 15−17).

As described above, a substrate bearing a 1,1-disubstitued allenyl moiety with a bulky substituent on the C−C triple bond showed unique reactivity. When the reaction was performed with **3o** under nickel catalysis, three products were obtained (Scheme 6). The major and minor products **4o** and **5o** were obtained in respective yields of 38 and 13%. The other product did not contain a cyano group and was assigned to be the bicyclic compound **9o**. On the basis of the reaction pathway described above, the intermediate **D** would be obtained after the hydrometalation−carbocyclization of **3o**. If a vinyl group in **D** prefers to coordinate to the Ni(II) center, a second cyclization would proceed before reductive elimination and conversion to **E** via 5-endo cyclization. The resulting alkylnickel species would be converted to Ni(0) through β-hydride elimination. A trans stereochemistry of the alkenyl−Ni−CN bonds in $\mathbf{D}_{trans}$ would be favored when a bulky substituent such as a *t*-Bu or TMS group on the C−C triple bond causes steric repulsion between CN groups. The reason that no bicyclic products were obtained from **3f**,**n** is that less bulky groups on the C−C triple bond would favor the formation of a $\mathbf{D}_{cis}$ intermediate that promotes rapid reductive elimination to **4f**,**n** before a second cyclization. A methyl group on the proximal C−C double bond of allene is also essential for

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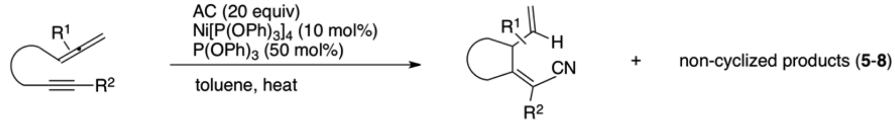
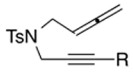
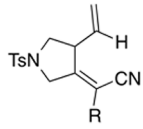
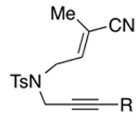
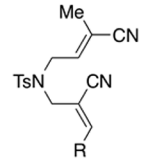
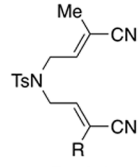
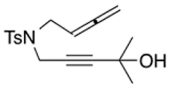
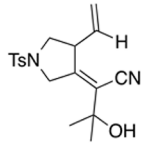
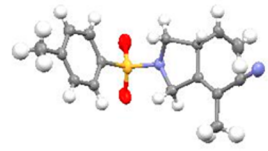
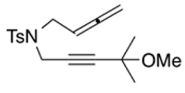
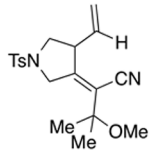
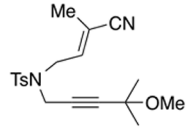
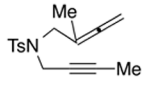
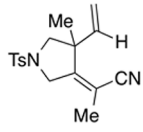
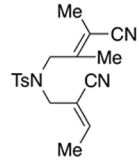
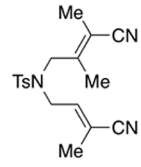
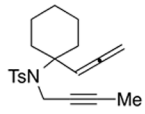
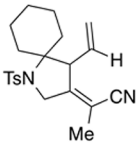
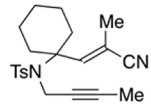
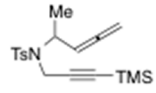
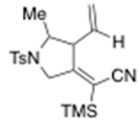
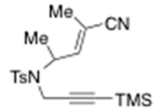
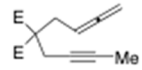
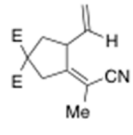
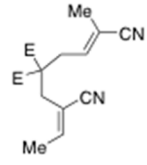
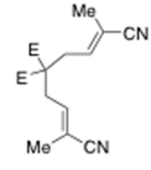
Table 2. Substrate Scope

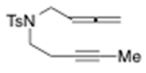
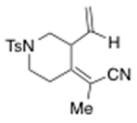
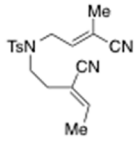
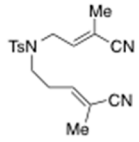
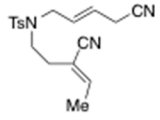
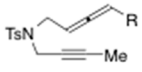
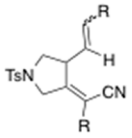
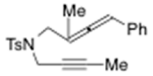
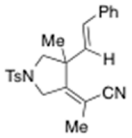
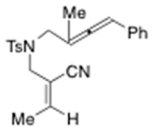
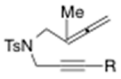
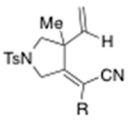
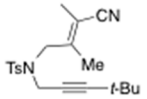
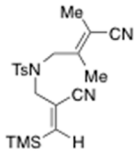
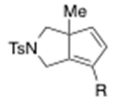
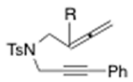
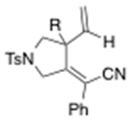
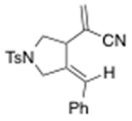


3 4

entry	substrate	conditions	products			
1	 **3b**: R = TMS	70 °C, 0.5 h	 **4b**: 67%	 **5b**: 2%	 **6b**: 19%	 **7b**: 0%
2	**3c**: R = Me	70 °C, 0.5 h	**4c**: 64%	**5c**: 0%	**6c**: 16%	**7c**: 6%
3	 **3d**	70-100 °C, 19 h	 **4d**: 52%		 ORTEP of **4c**	
4[1)]	 **3e**	100 °C, 0.5 h	 **4e**: 43%	 **5e**: 12%		
5	 **3f**	100 °C, 0.5 h	 **4f**: 62%	 **6f**: 9%	 **7f**: 5%	
6	 **3g**	100 °C, 0.5 h	 **4g**: 44%	 **5g**: 6%		
7[1)]	 **3h**	80 °C, 1 h	 **4h**: 38% (dr = 3.4:1)	 **5h**: 12%		
8	 **3l** (E = CO_2Et)	70 °C, 0.5 h	 **4l**: 71%	 **5l**: 10%	 **6l**: 7%	

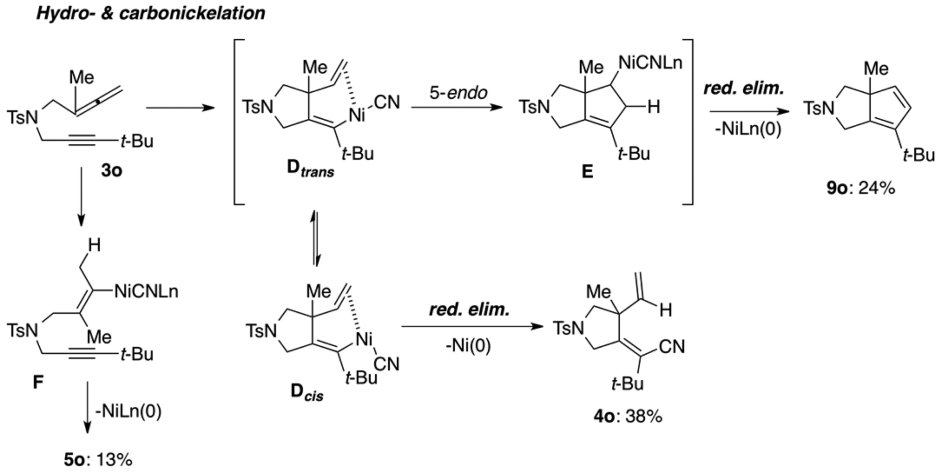
dx.doi.org/10.1021/jo401758v | J. Org. Chem. 2013, 78, 10763−10775

Table 2. continued

entry	substrate	conditions	products			
9	 **3j**	100 °C, 4 h	 **4j**: 29%	 **6j**: 17%	 **7j**: 5%	 **8j**: 4%
10	 **3k**: R = Ph	100 °C, 2 h	 **4k**: 53 (cis:trans = 2.7:1)			
11	**3m**: R = *n*-Bu	100 °C, 0.5 h	**4m**: 60 (cis:trans = 1:1.3)			
12	 **3n**	150 °C, neat, 2.5 h	 **4n**: 32%	 **6n**: 5%		
13	 **3o**: R = *t*-Bu	100 °C, 0.5 h	 **4o**: 38%	 **5o**: 13%	 **6p**: 7%	 **9o**: 24%
14	**3p**: R = TMS		**4p**: 50%			**9p**: 6%
15	 **3q**: R = H	100 °C, 0.5 h	 **4q**: 35%	 **4qq**: 12%		
16	**3r**: R = Me	100 °C, 7 h	**4r**: 45%			
17	**3s**: R = Et	100 °C, 5 h	**4s**: 34%			

1) AC (10 equiv) was used.

Scheme 6. Plausible Pathway to the [3 + 2] Cycloadduct



obtaining **9o,p** (**3a,b** vs **3o,p**). This substituent would promote the coordination of a vinyl group to the Ni(II) center and endo-cyclization to give **9o,p**.

An attempt to achieve the selective formation of [3 + 2] cycloadducts in the hydrometalation sequence using **3t,u** is shown in Scheme 7. Both substrates have Lewis basic

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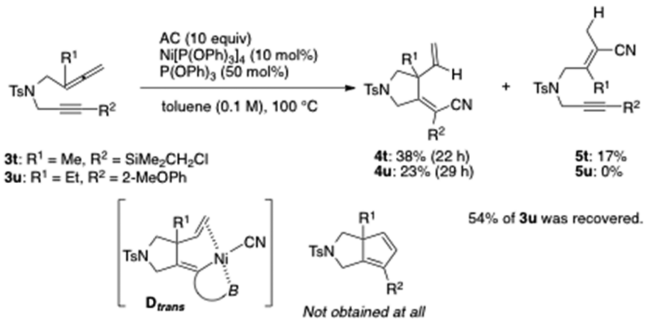
Scheme 7. Reactions of 3t,u



functionalities and were expected to form predominantly $\mathbf{D}_{trans}$ as an intermediate. If these proposed species are generated, the coordination from *B* to Ni(II) would prevent reductive elimination to **4** and promote the second cyclization to give the corresponding [3 + 2] cycloadducts as major products. However, these attempts all failed to give **4** and **5** in lower yields.

We next investigated bis-allenes as cyclization precursors. These substrates are useful because all four C−C double bonds can be discriminated in a single operation and independently functionalized through single catalysis to give **11**−**13**. Related studies under palladium catalysis[21a,b,d] and a radical protocol[21c] have been reported, and silyl-[21a] and germylstannanes[21b] have been key reagents in promoting silyl- and germylmetalation. In our strategy, the trigger is regioselective C−H bond formation to allenes via hydronickelation, and two possible reaction pathways are proposed: 5-exo cyclization to give **11** and the formation of a six-membered ring to give **12** and/or **13**. These products are provided by regioselective insertion to allenyl double bonds (**14a** vs **14b**) in a cyclization step (Scheme 8).

In fact, this cyclization proceeded as well as in an allene−yne system and the sole cyclized product was *cis*-**11a** when **10a** was used under nickel catalysis (Table 3, entry 1). A nonsymmetric bis-allene such as **10b** also gave the corresponding adduct **11b**[18] in 26% yield; however, the cyclization efficiency was significantly lower (entry 2). The stereochemistry of **11a** was determined by NOE observance after conversion to **17a** by hydrogenation to be cis. In the case of **11b**, the structural assignment was established on the basis of the results of an X-ray crystallographic analysis to be *cis*-(*E*). The latter result suggests that the initial hydrometalation in **10b** prefers a less substituted double bond, and a cyano group could be installed in the *E* form to avoid repulsion by a methyl group on the distal C−C double bond in **10b**. A methyl group on the proximal C−C double bond in **10c** completely prevented the reaction, and **11c** was isolated in only 3% yield (entry 3). The substituents on the pyrrolidine ring did not affect the cyclization efficiency or the diastereoselectivity and gave **11da**,**db** as a 3:2 mixture together with 3 noncyclized products (entry 4). A quaternary carbon in **10e** was obviously useful for the discrimination of the hydrometalation step, and the regioselectivity was improved to give a 5.5:1 ratio of **11ea**,**eb** in 52% yield (entry 5). In the case of a malonate derivative, the cyclization proceeded smoothly and **11a** was isolated in 60% yield as a single diastereomer together with **15f** and **6f** (entry 6). These results are summarized in Table 3.

Finally, the synthetic application of the cycloadduct was investigated (Scheme 9). Compound **4b** was effectively converted to **18** through a desilylation protocol.[22] Subsequent α-allylation by LiHMDS gave triene **19**, which could be transformed to the corresponding cyclic diene **20** by RCM in 55% yield without any aromatization.

CONCLUSION

We have shown that allene−ynes are versatile substrates for hydrocyanative cyclization under nickel catalysis. Various functionalities such as hydroxyl, ether, amide, and ester groups can be used in this hydrocyanative cyclization, and a cyano group is always installed in a regio- and stereoselective manner to give functionalized cyanoalkenes with perfect stereochemistry. Further studies are currently underway to establish more facile protocols and apply them to the synthesis of useful molecules.

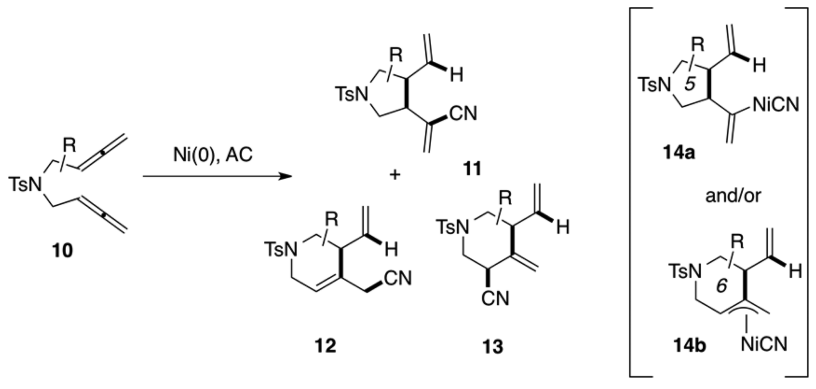
EXPERIMENTAL SECTION

General Procedure for Ni-Catalyzed Allene-yne Cyclization. A solution of allene−yne (0.15 mmol), $P(OPh)_3$ (20 μL, 0.096 mmol), $Ni[P(OPh)_3]_4$ (19.7 mg, 0.035 mmol, 10 mol %), and acetone cyanohydrin (139 μL, 1.5 mmol) in toluene (1.5 mL) was heated under an argon atmosphere. The reaction mixture was poured into silica gel to be purified by column chromatography (hexane/AcOEt), and the desired cyanocyclized product was given together with noncyclized products.

*(E)-N-(3-Cyanobut-2-en-1-yl)-N-(4,4-dimethylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (**5a**):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.00 (s, 9H), 1.95 (s, 3H), 2.44 (s, 3H), 3.97 (d, 2H, J = 7.2 Hz), 4.06 (s, 2H), 6.29 (t, 1H, J = 7.2 Hz), 7.32 (d, 2H, J = 7.2 Hz), 7.72 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 21.5, 27.2, 30.6, 37.4, 43.6, 70.5, 95.3, 113.6, 119.4, 127.7, 129.8, 135.8, 141.4, 143.9; IR (ATR) ν 2969, 2221, 1347, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_2NaO_2S$ $[M + Na]^+$ 367.1456, found 367.1444; yield 20%, 10.2 mg.

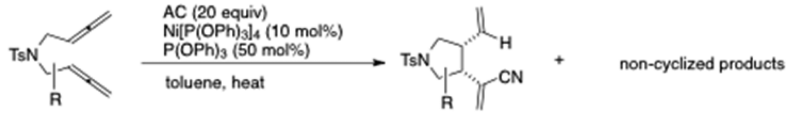
*N-((E)-2-Cyano-3-(trimethylsilyl)allyl)-N-((E)-3-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**6b**):* colorless solid; ^{1}H NMR

Scheme 8. Cyclization of Bis-Allenes

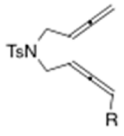
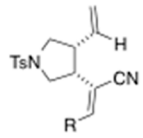
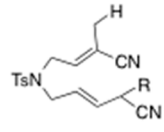
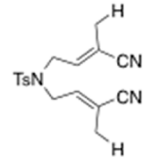
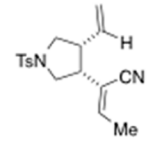
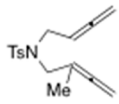
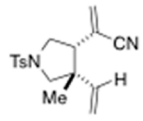
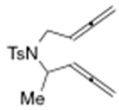
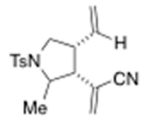
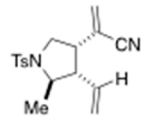
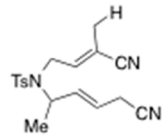
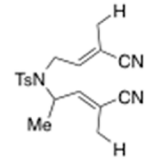
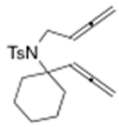
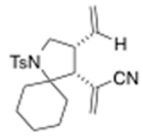
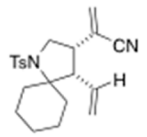
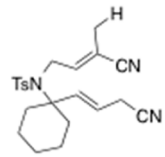
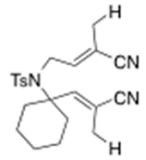
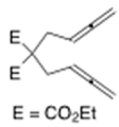
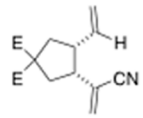
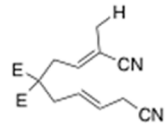
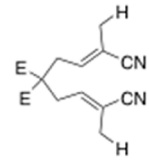


dx.doi.org/10.1021/jo401758v | J. Org. Chem. 2013, 78, 10763−10775

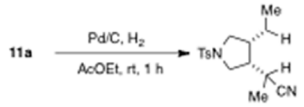
Table 3. Substrate Scope of Bis-Allene Cyclization



10 **11**

entry	substrate	conditions	products			
1 2	 **10a**: R = H **10b**: R = Me	70 °C, 0.5 h 100 °C, 0.5 h	 **11a**: 66%[2)] **11b**: 26%	 **15a**: 10% **15b**: 14%	 **7c**: 3%	 **17b**: 3%
3	 **10c**	100 °C, 0.5 h	 **11c**: 3%		 ORTEP of **11b**	
4	 **10d**	70 °C, 0.5 h	 **11da**: 35% (α:β = 3:2)	 **11db**: 15%	 **15d**: 7%	 **16d**: 4%
5	 **10e**	100 °C, 0.5 h	 **11ea**: 45%	 **11eb**: 8%	 **15e**: 5%	 **16e**: 6%
6	 E = CO_2Et **10f**	70 °C, 0.5 h	 **11f**: 60%	 **15f**: 12%	 **6i**: 5%	

1) Structual determination of **11a** is as follows.



17a: 82% (2.6:1)

($CDCl_3$, 400 MHz) δ 0.23 (s, 9H), 1.89 (d, 3H, J = 1.6 Hz), 2.45 (s, 3H), 4.01−4.02 (m, 4H), 6.21 (tq, 1H, J = 6.8, 1.6 Hz), 6.74 (s, 1H), 7.35 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.69, 15.3, 21.6, 45.1, 48.6, 113.4, 117.9, 119.1, 124.7, 127.6, 130.0, 135.7, 141.5, 44.6, 154.2; IR (ATR) ν 2958, 2926, 2215, 1346, 1161, 843 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{25}N_3NaO_2SSi$ $[M + Na]^+$ 410.1334, found 410.1347; mp 83 °C; yield 19%, 11.6 mg.

*N-((E)-2-Cyanobut-2-en-1-yl)-N-((E)-3-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**6c**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.91 (s, 3H), 1.95 (d, 3H, J = 7.2 Hz), 2.46 (s, 3H), 3.98 (s, 2H), 4.02 (d, 2H, J = 6.4 Hz), 6.17 (tq, 1H, J = 6.4, 1.6 Hz), 6.65 (q, 1H, J = 7.2 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.8, 15.3, 21.6, 44.4, 45.2, 111.2, 113.5, 118.6, 119.1, 127.4, 130.1, 135.7, 141.3, 144.6, 148.3; IR (ATR) ν 2925, 2220,

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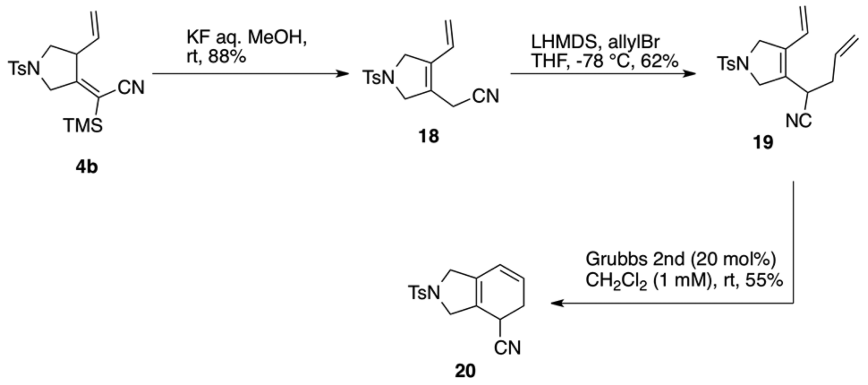
Scheme 9. Synthetic Application



1341, 1158 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{19}N_3NaO_2S$ $[M + Na]^+$ 352.1096, found 352.1106; yield 16%, 8.2 mg.

*N,N-Bis((E)-3-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**7c**):* colorless solid; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.90 (d, 6H, J = 1.2 Hz), 2.47 (s, 3H), 3.92 (d, 4H, J = 6.4 Hz), 6.11 (tq, 2H, J = 6.4, 1.2 Hz), 7.37 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.3, 21.6, 44.8, 113.7, 119.0, 127.2, 130.2, 135.9, 143.8, 144.7; IR (ATR) ν 2925, 2220, 1335, 1154 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{19}N_3NaO_2S$ $[M + Na]^+$ 352.1096, found 352.1100; mp 113 °C; yield 6%, 3.4 mg.

*(E)-N-(3-Cyanobut-2-en-1-yl)-N-(4-methoxy-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (**5e**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.23 (s, 6H), 1.95 (d, 3H, J = 1.2 Hz), 2.44 (s, 3H), 3.12 (s, 3H), 3.99 (d, 2H, J = 6.8 Hz), 4.14 (s, 2H), 6.28 (tq, 1H, J = 6.8, 1.2 Hz), 7.33 (d, 2H, J = 8.4 Hz), 7.72 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2, 21.5, 28.0, 37.1, 43.7, 51.5, 70.2, 76.2, 88.4, 113.9, 119.3, 127.6, 129.9, 135.7, 141.1, 144.1; IR (ATR) ν 2987, 2930, 2218, 1341 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{24}N_2NaO_3S$ $[M + Na]^+$ 383.1405, found 383.1414; yield 12%, 6.6 mg.

*N-((E)-3-Cyano-2-methylbut-2-en-1-yl)-N-((E)-2-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**6f**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.94 (d, 3H, J = 7.2 Hz), 1.95 (s, 3H), 2.07 (d, 3H, J = 1.6 Hz), 2.45 (s, 3H), 3.91 (s, 2H), 4.07 (s, 2H), 6.55 (q, 1H, J = 7.2 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.8, 16.1, 20.2, 21.6, 44.6, 49.1, 109.0, 111.1, 118.6, 118.7, 127.4, 129.9, 136.1, 144.4, 147.9, 149.2; IR (ATR) ν 2925, 2215, 1344, 1159 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1250; yield 9%, 5.0 mg.

*N-((E)-3-Cyano-2-methylbut-2-en-1-yl)-N-((E)-3-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**7f**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.87 (s, 3H), 1.89 (s, 3H), 2.05 (d, 3H, J = 1.6 Hz), 2.47 (s, 3H), 3.84 (d, 2H, J = 6.8 Hz), 3.87 (s, 2H), 5.98 (tq, 1H, J = 6.8, 1.6 Hz), 7.37 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 16.0, 20.3, 21.6, 44.8, 48.2, 109.0, 113.3, 118.5, 118.9, 127.2, 130.2, 136.0, 140.8, 144.7, 148.8; IR (ATR) ν 2925, 2219, 1340, 1158 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1259; yield 5%, 2.5 mg.

*(E)-N-(But-2-yn-1-yl)-N-(1-(2-cyanoprop-1-en-1-yl)cyclohexyl)-4-methylbenzenesulfonamide (**5g**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.10−1.17 (m, 1H), 1.33 (q, 2H, J = 13.2 Hz), 1.60−1.63 (m, 1H), 1.68 (s, 3H), 1.68−1.73 (m, 2H), 1.73 (s, 3H), 1.88 (dt, 2H, J = 7.2, 3.0 Hz), 2.34 (d, 2H, J = 12.0 Hz), 2.43 (s, 3H), 4.15 (d, 2H, J = 1.8 Hz), 6.53 (s, 1H), 7.29 (d, 2H, J = 7.2 Hz), 7.77 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 3.42, 16.3, 21.5, 23.2, 24.8, 35.4, 35.7, 64.3, 75.7, 80.6, 112.1, 120.9, 127.7, 129.3, 139.0, 143.2, 150.1; IR (ATR) ν 2928, 2862, 2217, 1330, 1153 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{26}N_2NaO_2S$ $[M + Na]^+$ 393.1613, found 393.1611; yield 6%, 3.4 mg.

*(E)-N-(4-Cyanopent-3-en-2-yl)-4-methyl-N-(3-(trimethylsilyl)-prop-2-yn-1-yl)benzenesulfonamide (**5h**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 0.09 (s, 9H), 1.31 (d, 3H, J = 7.2 Hz), 1.86 (d, 3H, J = 1.6 Hz), 2.43 (s, 3H), 4.04 (d, 1H, J = 18.8 Hz), 4.33 (d, 1H, J = 18.8 Hz), 4.85 (dq, 1H, J = 9.2, 6.8 Hz), 6.49 (dq, 1H, J = 9.2, 1.6 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.75 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ −0.54, 14.9, 18.3, 21.5, 33.8, 50.6, 91.0, 100.6, 111.2, 119.5, 127.6, 129.5, 137.2, 143.9, 145.4; IR (ATR) ν 2961, 2220, 1347, 1157, 844 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{26}N_2NaO_2SSi$ $[M + Na]^+$ 397.1382, found 397.1371; yield 12%, 3.3 mg.

*Diethyl 2-(but-2-yn-1-yl)-2-(buta-2,3-dien-1-yl)malonate (**3i**; CAS Registry No. 792950-32-4):* spectral data identical with the literature data;[14b] ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, 6H, J = 7.2 Hz), 1.75 (t, 3H, J = 2.8 Hz), 2.75 (dt, 2H, J = 8.0, 2.8 Hz), 2.78 (q, 2H, J = 2.8 Hz), 4.20 (q, 4H, J = 7.2 Hz), 4.66 (dt, 2H, J = 6.8 Hz), 4.97 (tt, 1H, J = 8.0, 6.8 Hz); yield 21%, 63.7 mg.

*(Z)-Diethyl 3-(1-cyanoethylidene)-4-vinylcyclopentane-1,1-dicarboxylate (**4i**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, 3H, J = 7.2 Hz), 1.27 (t, 3H, J = 7.2 Hz), 1.92 (dd, 3H, J = 3.2, 1.6 Hz), 2.26 (dd, 1H, J = 13.6, 6.8 Hz), 2.68 (ddd, 1H, J = 13.6, 8.4, 1.2 Hz), 3.02 (d, 1H, J = 18.4 Hz), 3.08 (dt, 1H, J = 18.4, 1.6 Hz), 3.55−3.60 (m, 1H), 4.21 (q, 4H, J = 7.2 Hz), 5.15 (dt, 1H, J = 10.0, 1.2 Hz), 5.16 (dt, 1H, J = 17.2, 1.2 Hz), 5.68 (ddd, 1H, J = 17.2, 10.0, 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9, 17.7, 39.1, 39.7, 47.7, 58.6, 61.9, 62.0, 103.5, 117.1, 118.2, 136.3, 160.2, 170.6, 170.7; IR (ATR) ν 2982, 2943, 2214, 1727, 1253, 1187 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}NNaO_4$ $[M + Na]^+$ 314.1368, found 314.1373; yield 71%, 33.0 mg.

*Diethyl 2-((E)-2-cyanobut-2-en-1-yl)-2-((E)-3-cyanobut-2-en-1-yl)malonate (**5i**), Diethyl 2,2-bis((E)-3-cyanobut-2-en-1-yl)malonate (**6i**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.277 (t, 0.74 × 6H, J = 7.2 Hz), 1.284 (t, 6H, J = 7.2 Hz), 1.84 (d, 3H, J = 7.8 Hz), 1.90 (s, 0.74 × 6 + 3H), 2.73 (d, 0.74 × 4H, J = 7.2 Hz), 2.85 (d, 2H, J = 7.8 Hz), 2.90 (s, 2H), 4.19−4.29 (m, 0.74 × 4 + 4H), 6.22 (t, 0.74 × 2H, J = 7.8 Hz), 6.27 (t, 1H, J = 7.8 Hz), 6.63 (q, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.9, 14.0, 15.0, 15.2, 15.3, 31.3, 31.6, 32.3, 56.2, 56.5, 62.4, 62.4, 109.8, 112.9, 113.1, 119.3, 119.8, 119.9, 141.0, 141.3, 148.3, 169.3, 169.4; IR (ATR) ν 2984, 2218, 1727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{22}N_2NaO_4$ $[M + Na]^+$ 341.1477, found 341.1490; yield 17%, 8.7 mg.

*N-(Buta-2,3-dien-1-yl)-4-methyl-N-(pent-3-yn-1-yl)-benzenesulfonamide (**3j**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.75 (t, 3H, J = 2.8 Hz), 2.38−2.43 (m, 2H), 2.42 (s, 3H), 3.30 (t, 2H, J = 7.6 Hz), 3.89 (dt, 2H, J = 6.8, 2.8 Hz), 4.73 (dt, 2H, J = 6.4, 2.8 Hz), 4.94 (tt, 1H, J = 6.4, 6.8 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 3.39, 19.3, 21.4, 46.2, 47.1, 75.7, 76.3, 77.4, 86.0, 127.1, 129.6, 137.1, 143.2, 209.3; IR (ATR) ν 2979, 2920, 1956, 1335, 1158 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{19}NNaO_2S$ $[M + Na]^+$ 312.1034, found 312.1031; mp 46−47 °C; yield 74%, 201.2 mg.

*(Z)-2-(1-Tosyl-3-vinylpiperidin-4-ylidene)propanenitrile (**4j**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.87 (d, 3H, J = 1.6 Hz), 2.18 (dt, 1H, J = 11.6, 3.6 Hz), 2.39−2.57 (m, 3H), 2.43 (s, 3H), 3.69−3.71 (m, 1H), 3.89−3.96 (m, 2H), 5.23 (ddd, 1H, J = 10.4, 1.2, 1.2 Hz), 5.31 (ddd, 1H, J = 17.6, 1.2, 1.2 Hz), 6.02 (ddd, 1H, J = 17.6, 10.4, 6.4 Hz), 7.33 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.6, 21.5, 25.9, 45.1, 46.1, 50.4, 104.3, 117.9, 118.6, 127.6, 129.8, 132.7, 135.8, 143.9, 153.5; IR (ATR) ν 2970, 2926, 2849, 2211,

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1337, 1161 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1133; yield 29%, 14.8 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-3-cyanopent-3-en-1-yl)-4-methylbenzenesulfonamide (**6j**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.90 (d, 3H, J = 7.2 Hz), 1.92 (s, 3H), 2.45 (s, 3H), 2.57 (t, 2H, J = 7.2 Hz), 3.23 (t, 2H, J = 7.2 Hz), 3.96 (d, 2H, J = 6.4 Hz), 6.07 (tq, 1H, J = 6.4, 1.6 Hz), 6.58 (q, 1H, J = 7.2 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.6, 15.2, 21.6, 29.1, 46.5, 46.9, 111.6, 113.1, 119.1, 119.3, 127.1, 130.1, 135.8, 141.6, 144.3, 146.1; IR (ATR) ν 2927, 2218, 1339, 1155 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1252; mp 43 °C; yield 17%, 9.2 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-4-cyanopent-3-en-1-yl)-4-methylbenzenesulfonamide (**7j**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.90 (d, 3H, J = 1.6 Hz), 1.91 (d, 3H, J = 1.6 Hz), 2.43−2.47 (m, 2H), 2.46 (s, 3H), 3.18 (t, 2H, J = 7.6 Hz), 3.95 (d, 2H, J = 6.8 Hz), 6.08 (tq, 1H, J = 6.8, 1.6 Hz), 6.21 (tq, 1H, J = 7.2, 1.6 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.67 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 15.3, 21.6, 28.5, 45.6, 46.7, 112.4, 113.0, 119.1, 119.8, 127.1, 130.1, 135.9, 141.6, 142.7, 144.4; IR (ATR) ν 2927, 2219, 1337, 1155 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1262; yield 5%, 2.6 mg.

*N-((E)-4-Cyanobut-2-en-1-yl)-N-((E)-3-cyanopent-3-en-1-yl)-4-methylbenzenesulfonamide (**8j**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.90 (d, 3H, J = 7.2 Hz), 2.45 (s, 3H), 2.56 (t, 2H, J = 7.2 Hz), 3.11 (d, 2H, J = 6.0 Hz), 3.19 (t, 2H, J = 7.2 Hz), 3.81 (d, 2H, J = 6.0 Hz), 5.57 (dt, 1H, J = 15.0, 6.0 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.7, 20.3, 21.5, 29.2, 45.8, 50.7, 111.9, 116.6, 119.6, 123.0, 127.2, 129.8, 130.0, 135.9, 144.0, 146.0; IR (ATR) ν 2925, 2251, 2214, 1337, 1156 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1253; yield 4%, 2.1 mg.

*(E)-N-(2-Cyanobut-2-en-1-yl)-4-methyl-N-(2-methyl-4-phenylbuta-2,3-dien-1-yl)benzenesulfonamide (**6n**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.63 (s, 3H), 1.85 (d, 3H, J = 7.2 Hz), 2.42 (s, 3H), 3.86 (dd, 1H, J = 15.2, 2.4 Hz), 3.96 (s, 2H), 4.10 (dd, 1H, J = 15.2, 2.4 Hz), 6.01 (tq, 1H, J = 2.4, 2.4 Hz), 6.50 (tq, 1H, J = 7.2, 0.8 Hz), 7.17−7.38 (m, 7H), 7.71 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.7, 16.5, 21.6, 44.0, 51.9, 95.8, 99.4, 111.9, 118.8, 126.9, 127.1, 127.4, 128.6, 129.7, 134.3, 136.6, 143.8, 147.1, 203.8; IR (ATR) ν 2921, 2219, 1954, 1343, 1157 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{24}N_2NaO_2S$ $[M + Na]^+$ 415.1456, found 415.1471; yield 5%, 2.5 mg.

*N-(4,4-Dimethylpent-2-yn-1-yl)-4-methyl-N-(2-methylbuta-2,3-dien-1-yl)benzenesulfonamide (**3o**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (s, 9H), 1.72 (t, 3H, J = 7.2 Hz), 2.41 (s, 3H), 3.77 (t, 2H, J = 2.4 Hz), 4.08 (s, 2H), 4.66 (tq, 2H, J = 3.2, 2.4 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 7.4 Hz) ; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.7, 21.4, 27.0, 30.5, 36.0, 49.6, 70.4, 74.8, 93.3, 94.6, 127.7, 129.4, 136.3, 143.1, 207.7; IR (ATR) ν 2964, 2925, 2865, 2236, 1955, 1346, 1161 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NNaO_2S$ $[M + Na]^+$ 354.1504, found 354.1498; mp 68−69 °C; yield 42%, 216.6 mg.

*(E)-3,3-Dimethyl-2-(4-methyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)-butanenitrile (**4o**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 9H), 1.50 (s, 3H), 2.47 (s, 3H), 2.96 (d, 1H, J = 9.6 Hz), 3.02 (d, 1H, J = 9.6 Hz), 3.95 (d, 1H, J = 16.0 Hz), 4.18 (d, 1H, J = 16.0 Hz), 5.20 (d, 1H, J = 17.2 Hz), 5.24 (d, 1H, J = 10.4 Hz), 5.80 (dd, 1H, J = 17.2, 10.4 Hz), 7.38 (d, 2H, J = 8.0 Hz), 7.70 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.5, 21.6, 29.6, 35.8, 50.5, 52.2, 59.7, 115.9, 116.2, 118.8, 128.1, 129.9, 131.2, 138.7, 144.3, 157.3; IR (ATR) ν 2970, 2867, 2213, 1335, 1151 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{29}NNaO_2S$ $[M + Na]^+$ 370.1812, found 370.1814; mp 142−143 °C; yield 38%, 22.8 mg.

*(E)-N-(3-cyano-2-methylbut-2-en-1-yl)-N-(4,4-dimethylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (**5o**):* colorless solid; ^1H NMR ($CDCl_3$, 600 MHz) δ 0.96 (s, 9H), 1.97 (s, 3H), 2.13 (d, 3H, J = 1.8 Hz), 2.43 (s, 3H), 3.92 (s, 2H), 3.96 (s, 2H), 7.32 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.9, 20.5, 21.5, 27.1, 30.5, 36.7, 46.7, 70.6, 95.2, 109.0, 118.9, 127.8, 129.7, 135.8, 143.8, 149.1; IR (ATR) ν 2970, 2236, 2211, 1328, 1161 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{26}N_2NaO_2S$ $[M + Na]^+$ 381.1613, found 381.1612; mp 132−133 °C; yield 13%, 7.7 mg.

*6-(tert-Butyl)-3a-methyl-2-tosyl-1,2,3,3a-tetrahydrocyclopenta-[c]pyrrole (**9o**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.02 (s, 9H), 1.08 (s, 3H), 2.41 (s, 3H), 3.39 (d, 1H, J = 8.4 Hz), 4.02 (d, 1H, J = 13.2 Hz), 4.10 (d, 1H, J = 13.2 Hz), 6.13 (d, 1H, J = 5.4 Hz), 6.24 (d, 1H, J = 5.4 Hz), 7.31 (d, 2H, J = 7.8 Hz), 7.70 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 19.3, 21.5, 29.6, 32.4, 44.6, 53.8, 60.8, 127.4, 129.6, 133.8, 134.1, 138.9, 143.3, 143.8, 145.2; IR (ATR) ν 2961, 2928, 2868, 1344, 1157 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{25}NNaO_2S$ $[M + Na]^+$ 354.1504, found 354.1518; yield 24%, 13.2 mg.

*4-Methyl-N-(2-methylbuta-2,3-dien-1-yl)-N-(3-(trimethylsilyl)-prop-2-yn-1-yl)benzenesulfonamide (**3p**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ −0.04 (s, 9H), 1.71 (t, 3H, J = 3.2 Hz), 2.41 (s, 3H), 3.77 (t, 2H, J = 2.0 Hz), 4.10 (s, 2H), 4.66 (tq, 2H, J = 3.2, 2.4 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.73 (d, 2H, J = 8.0 Hz); ^{13}C NMR (CDCl3, 100 MHz) δ −0.46, 15.7, 21.5, 36.6, 49.9, 75.0, 90.9, 93.2, 97.5, 127.7, 129.5, 136.1, 143.3, 207.7; IR (ATR) ν 2959, 2917, 2175, 1963, 1345, 1163, 840 cm-1; HRMS (ESI) *m/z* calcd for $C_{18}H_{25}NNaO_2SSi$ $[M + Na]^+$ 370.1273, found 370.1278; mp 77 °C; yield 85%, 325.9 mg.

*(Z)-2-(4-Methyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)-2-(trimethylsilyl)acetonitrile (**4p**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.26 (s, 9H), 1.49 (s, 3H), 2.46 (s, 3H), 3.04 (d, 1H, J = 9.6 Hz), 3.13 (d, 1H, J = 9.6 Hz), 3.85 (d, 1H, J = 16.4 Hz), 3.96 (d, 1H, J = 16.4 Hz), 5.22 (d, 1H, J = 17.2 Hz), 5.24 (d, 1H, J = 10.4 Hz), 5.84 (dd, 1H, J = 17.2, 10.4 Hz), 7.38 (d, 2H, J = 8.0 Hz), 7.69 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −1.24, 21.61, 21.62, 51.9, 53.4, 59.7, 107.4, 116.1, 117.0, 128.0, 129.9, 131.2, 138.2, 144.4, 173.9 ; IR (ATR) ν 2958, 2867, 2197, 1341, 1158, 841 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{26}N_2NaO_2SSi$ $[M + Na]^+$ 397.1382, found 397.1374; mp 90−92 °C; yield 50%, 24.6 mg.

*N-((E)-3-Cyano-2-methylbut-2-en-1-yl)-N-((E)-2-cyano-3-(trimethylsilyl)allyl)-4-methylbenzenesulfonamide (**6p**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 0.24 (s, 9H), 1.94 (s, 3H), 2.05 (s, 3H), 2.44 (s, 3H), 3.96 (s, 2H), 4.12 (s, 2H), 6.65 (s, 1H), 7.33 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ −0.69, 16.1, 20.3, 21.6, 48.4, 48.6, 109.2, 118.1, 118.7, 124.3, 127.5, 129.9, 136.3, 144.4, 149.1, 154.2; IR (ATR) ν 2956, 2214, 1345, 1159, 840 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{27}N_3NaO_2SSi$ $[M + Na]^+$ 424.1491, found 424.1497; yield 7%, 3.9 mg.

*3a-Methyl-2-tosyl-6-(trimethylsilyl)-1,2,3,3a-tetrahydrocyclopenta[c]pyrrole (**9p**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 0.04 (s, 9H), 1.12 (s, 3H), 2.36 (d, 1H, J = 9.0 Hz), 2.41 (s, 3H), 3.45 (d, 1H, J = 9.0 Hz), 3.82 (d, 1H, J = 13.2 Hz), 4.13 (d, 1H, J = 13.2 Hz), 6.16 (d, 1H, J = 4.8 Hz), 6.23 (d, 2H, J = 4.8 Hz), 7.30 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ −1.37, 18.7, 21.6, 44.8, 54.4, 62.6, 127.5, 129.7, 134.0, 136.0, 136.1, 139.0, 143.5, 163.7; IR (ATR) ν 2955, 1345, 1157, 835 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{25}NNaO_2SSi$ $[M + Na]^+$ 370.1273, found 370.1259; yield 6%, 2.9 mg.

*N-(Buta-2,3-dien-1-yl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)-benzenesulfonamide (**3q**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.33 (s, 3H), 3.93 (dt, 2H, J = 6.8, 2.4 Hz), 4.37 (s, 2H), 4.80 (dt, 2H, J = 6.8, 2.4 Hz), 5.11 (tt, 1H, J = 6.8, 6.8 Hz), 7.09 (dd, 2H, J = 8.0, 2.0 Hz), 7.21−7.30 (m, 5H), 7.77 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 21.4, 36.8, 45.9, 78.4, 77.2, 81.6, 85.6, 122.3, 127.8, 128.1, 128.4, 129.5, 131.5, 136.0, 143.5, 209.9; IR (ATR) ν 3063, 2916, 1953, 1324, 1164 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NNaO_2S$ $[M + Na]^+$ 360.1034, found 360.1032; mp 67 °C; yield 83%, 185.2 mg.

*(E)-2-Phenyl-2-(1-tosyl-4-vinylpyrrolidin-3-ylidene)acetonitrile (**4q**):* colorless solid; ^1H NMR ($CDCl_3$, 600 MHz) δ 2.44 (s, 3H), 3.38 (dd, 1H, J = 10.2, 6.0 Hz), 3.45 (dd, 1H, J = 10.2, 3.6 Hz), 3.92 (d, 1H, J = 16.8 Hz), 4.29 (d, 1H, J = 16.8 Hz), 5.23 (d, 1H, J = 10.2 Hz), 5.34 (d, 1H, J = 16.8 Hz), 5.76 (ddd, 1H, J = 16.8, 10.2, 7.2 Hz), 7.28−7.29 (m, 2H), 7.33 (d, 2H, J = 7.8 Hz), 7.39−7.45 (m, 3H), 7.67 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6, 48.9, 51.2, 52.2, 111.0, 116.5, 118.3, 127.7, 127.8, 129.1, 129.4, 130.0, 132.46, 143.53, 134.0, 144.3, 156.2; IR (ATR) ν 2993, 2851, 2815, 1348, 1158 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{20}N_2NaO_2S$ $[M + Na]^+$ 387.1143, found 387.1150; mp 136−137 °C; yield 35%, 18.7 mg.

*(Z)-2-(4-Benzylidene-1-tosylpyrrolidin-3-yl)acrylonitrile (**4qq**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 3.20 (dd, 1H, J =

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7.2, 5.6 Hz), 3.65−3.72 (m, 2H), 4.02 (d, 1H, J = 15.2 Hz), 4.32 (dd, 1H, J = 15.2, 2.8 Hz), 5.95 (s, 1H), 6.06 (s, 1H), 6.30 (d, 1H, J = 2.0 Hz), 7.17 (d, 2H, J = 8.4 Hz), 7.26−7.39 (m, 5H), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6, 49.4, 50.4, 50.8, 116.7, 122.1, 126.6, 127.8, 127.9, 128.3, 128.7, 130.0, 132.6, 133.1, 135.1, 135.5, 144.2; IR (ATR) ν 2925, 2223, 1344, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2NaO_2S$ [M + Na]$^+$ 387.1143, found 387.1128; yield 12%, 6.4 mg.

4-Methyl-N-(2-methylbuta-2,3-dien-1-yl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**3r**): colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.75−1.77 (dd, 3H, J = 3.2, 3.2 Hz), 2.32 (s, 3H), 3.84−3.85 (dd, 2H, J = 3.2, 3.2 Hz), 4.31 (s, 2H), 4.67−4.70 (m, 2H), 7.03−7.05 (dd, 2H, J = 8.0, 1.6 Hz), 7.21−7.31 (m, 5H), 7.75 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): 15.8, 21.3, 36.4, 50.2, 75.0, 81.4, 85.5, 93.3, 122.2, 127.7, 128.0, 128.2, 129.4, 131.4, 136.0, 143.4, 207.7; IR (ATR) ν 3060, 2982, 2921, 1961, 1347, 1159, 1092, 898, 755, 660 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{21}NNaO_2S$ [M + Na]$^+$ 374.1191, found 374.1201; mp 88−96 °C; yield 76%, 126.4 mg.

(E)-2-(4-Methyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)-2-phenylacetonitrile (**4r**): colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61 (s, 3H), 2.46 (s, 3H), 3.13 (d, 1H, J = 9.6 Hz), 3.19 (d, 1H, J = 9.6 Hz), 3.88 (d, 1H, J = 16.4 Hz), 3.99 (d, 1H, J = 16.4 Hz), 5.30 (d, 1H, J = 17.2 Hz), 5.31 (d, 1H, J = 10.4 Hz), 5.89 (dd, 1H, J = 17.2, 10.4 Hz), 7.22−7.25 (dd, 2H, J = 8.0, 2.0 Hz), 7.36−7.44 (m, 5H), 7.65 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 21.7, 49.7, 52.9, 60.4, 109.5, 116.1, 116.3, 127.7, 128.0, 129.1, 129.3, 129.9, 131.5, 133.8, 138.1, 144.4, 160.8; IR (ATR) ν 3853, 3750, 3649, 2925, 2852, 2215, 1597, 1445, 1347, 1160, 1091, 1046, 814, 698, 661 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{22}N_2NaO_2S$ [M + Na]$^+$ 401.1300, found 401.1301; mp 111−116 °C; yield 45%, 56.8 mg.

N-(2-Ethylbuta-2,3-dien-1-yl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**3s**): yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.06 (t, 3H, J = 7.2 Hz), 2.03−2.10 (m, 2H), 2.32 (s, 3H), 3.88 (br s, 2H), 4.30 (s, 2H), 4.77−4.80 (m, 2H), 7.03−7.05 (dd, 2H, J = 7.6, 1.2 Hz), 7.20−7.25 (m, 5H), 7.75 (d, 2H,J = 8.4 Hz) δ; ^{13}C NMR ($CDCl_3$, 100 MHz): 11.9, 21.4, 22.1, 36.5, 49.2, 76.9, 81.5, 85.5, 99.9, 122.3, 127.7, 128.0, 128.3, 129.5, 131.5, 136.1, 143.4, 207.1; IR (ATR) ν 3750, 3649, 3063, 2967, 2921, 2874, 2242, 1958, 1348, 1161, 1093, 897, 756, 661 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{23}NNaO_2S$ [M + Na]$^+$ 388.1347, found 388.1336; mp 78−82 °C; yield 78%, 82.5 mg.

(E)-2-(4-Ethyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)-2-phenylacetonitrile (**4s**): colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, 3H, J = 7.2 Hz), 2.03−2.17 (m, 2H), 2.46 (s, 3H), 3.19 (d, 1H, J = 9.6 Hz), 3.33 (d, 1H, J = 9.6 Hz), 3.86 (d, 1H, J = 16.0 Hz), 3.94 (d, 1H, J = 16.0 Hz), 5.22 (d, 1H, J = 17.6 Hz), 5.29 (d, 1H, J = 10.8 Hz), 6.03−6.10 (dd, 1H, J = 17.6, 10.8 Hz), 7.22−7.24 (m, 2H), 7.35−7.42 (m, 5H), 7.65 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.04, 21.6, 28.2, 53.2, 53.5, 56.8, 109.3, 116.2, 116.7, 127.8, 127.9, 129.1, 129.3, 129.9, 131.6, 133.9, 137.6, 144.3, 160.5; IR (ATR) ν 3853, 3649, 2969, 2927, 2879, 2214, 1347, 1159, 1091, 1047, 661 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{24}N_2NaO_2S$ [M + Na]$^+$ 415.1456, found 415.1463; mp 104−105 °C; yield 34%, 28.0 mg.

N-(3-((Chloromethyl)dimethylsilyl)prop-2-yn-1-yl)-4-methyl-N-(2-methylbuta-2,3-dien-1-yl)benzenesulfonamide (**3t**): colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.09 (s, 6H), 1.71−1.73 (dd, 3H, J = 3.2, 3.2 Hz), 2.43 (s, 3H), 2.59 (s, 2H), 3.77−3.78 (dd, 2H, J = 2.0, 2.0 Hz), 4.12 (s, 2H), 4.66- 4.68 (m, 2H), 7.29 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −3.6, 15.7, 21.5, 29.5, 36.5, 50.0, 75.0, 87.2, 93.1, 99.7, 127.7, 129.5, 136.0, 143.5, 207.8; IR (ATR) ν 3853, 3749, 3649, 3058, 2965, 2922, 2181, 1960, 1339, 1161, 1092, 842, 739 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{24}ClNNaO_2SSi$ [M + Na]$^+$ 404.0883, found 404.0883; mp 83−85 °C; yield 75%, 235.5 mg.

(Z)-2-((Chloromethyl)dimethylsilyl)-2-(4-methyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)acetonitrile (**4t**): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.41 (s, 6H), 1.51 (s, 3H), 2.47 (s, 3H), 2.92 (s, 2H), 3.06 (d, 1H, J = 9.6 Hz), 3.12 (d, 1H, J = 9.6 Hz), 3.88 (d, 1H, J = 16.4 Hz), 4.00 (d, 1H, J = 16.4 Hz), 5.22 (d, 1H, J = 17.6 Hz), 5.25 (d, 1H, J = 10.8 Hz), 5.79−5.86 (dd, 1H, J = 17.6, 10.8 Hz), 7.37 (d, 2H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.0, 21.5, 21.5, 28.3, 52.2, 53.7, 59.6, 103.9, 116.3, 116.4, 127.9, 129.9, 131.0, 137.8, 144.5, 176.7; IR (ATR) ν 2970, 2927, 2199, 1598, 1348, 1161, 1092, 816, 662 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{25}ClN_2NaO_2SSi$ [M + Na]$^+$ 431.0992, found 431.0982; yield 38%, 95.9 mg.

(E)-N-(3-((Chloromethyl)dimethylsilyl)prop-2-yn-1-yl)-N-(3-cyano-2-methylbut-2-en-1-yl)-4-methylbenzenesulfonamide (**5t**): yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.10 (s, 6H), 1.96 (br s, 3H), 2.12 (d, 3H, J = 1.6 Hz), 2.45 (s, 3H), 2.58 (s, 2H), 3.95 (s, 2H), 4.01 (s, 2H), 7.32 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −3.6, 16.0, 20.4, 21.6, 29.2, 37.0, 46.9, 88.2, 99.3, 109.4, 118.8, 127.8, 129.7, 135.4, 144.0, 148.5; IR (ATR) ν 3057, 2962, 2215, 2179, 1598, 1349, 1265, 1163, 734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{25}ClN_2NaO_2SSi$ [M + Na]$^+$ 431.0992, found 431.0981; mp 118−120 °C; yield 17%, 43.6 mg.

N-(2-Ethylbuta-2,3-dien-1-yl)-N-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (**3u**): orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.06 (t, 3H, J = 7.2 Hz), 2.02−2.10 (m, 2H), 2.29 (s, 3H), 3.80 (s, 3H), 3.89 (dd, 2H, J = 2.0, 2.0 Hz), 4.37 (s, 2H), 4.76−4.79 (m, 2H), 6.80 (d, 2H, J = 8.0 Hz), 6.87−6.89 (dd, 1H, J = 7.6, 1.2 Hz), 7.19 (d, 2H, J = 8.0 Hz), 7.22 (d, 1H, J = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9, 21.3, 22.1, 36.9, 48.9, 55.6, 76.9, 82.0, 85.6, 100.0, 110.5, 111.6, 120.0, 127.7, 129.3, 129.7, 133.4, 136.1, 143.2, 159.9, 206.9; IR (ATR) ν 2966, 2931, 2874, 2838, 2234, 1958, 1596, 1492, 1345, 1263, 1157, 1092, 896, 751, 660 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{25}NNaO_3S$ [M + Na]$^+$ 418.1453, found 418.1466; mp 70−73 °C; yield 54%, 85.2 mg.

(E)-2-(4-Ethyl-1-tosyl-4-vinylpyrrolidin-3-ylidene)-2-(2-methoxyphenyl)acetonitrile (**4u**): yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.95 (t, 3H, J = 7.2 Hz), 2.05 (q, 2H, J = 7.2 Hz), 2.46 (s, 3H), 3.20 (d, 1H, J = 10.0 Hz), 3.31 (d, 1H, J = 10.0 Hz), 3.70 (d, 1H, J = 16.4 Hz), 3,75 (d, 1H, J = 16.4 Hz), 3.81 (s, 3H), 5.24 (dd, 1H, J = 17.6, 1.6 Hz), 5.27 (dd, 1H, J = 10.4, 1.6 Hz), 6.00−6.08 (ddd, 1H, J = 17.6, 10.4, 1.6 Hz), 6.93−6.99 (dd, 2H, J = 16.0, 8.0 Hz), 7.06 (d, 1H, J = 8.0 Hz), 7.34−7.38(dd, 3H, J = 7.6, 7.6 Hz), 7.62 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.9, 21.6, 28.4, 53.2, 53.4, 55.6, 57.3, 105.6, 111.6, 115.9, 121.0, 122.4, 126.9, 127.9, 129.6, 129.8, 131.0, 135.8, 137.9, 144.1, 156.1, 161.4; IR (ATR) ν 2964, 2925, 2213, 1597, 1492, 1347, 1160, 1021, 661 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{26}N_2NaO_3S$ [M + Na]$^+$ 445.1562, found 445.1577; yield 23%, 21.5 mg.

N,N-Di(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide (**10a**; *CAS Registry No. 314730-91-1*): spectral data identical with the literature data;[21a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 3.90 (dt, 4H, J = 7.2, 2.4 Hz), 4.72 (dt, 4H, J = 6.8, 2.4 Hz), 4.93 (tt, 2H, J = 7.2, 6.8 Hz), 7.30 (d, 2H, J = 8.0 Hz), 7.70 (d, 2H, J = 8.0 Hz); yield 62%, 1.03 g)

2-((3R,4R*)-1-Tosyl-4-vinylpyrrolidin-3-yl)acrylonitrile* (**11a**): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 2.96−3.01 (m, 2H), 3.30−3.37 (m, 2H), 3.52 (dd, 1H, J = 10.0, 6.4 Hz), 3.60 (dd, 1H, J = 10.0, 7.6 Hz), 5.11 (d, 1H, J = 17.2 Hz), 5.13 (d, 1H, J = 10.8 Hz), 5.47 (ddd, 1H, J = 17.2, 10.8, 8.4 Hz), 5.66 (d, 1H, J = 1.2 Hz), 5.95 (s, 1H), 7.36 (d, 2H, J = 8.0 Hz), 7.74 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6, 45.8, 45.8, 49.4, 51.6, 117.7, 119.2, 121.0, 127.5, 129.9, 132.1, 132.8, 133.6, 144.0; IR (ATR) ν 2979, 2931, 2224, 1340, 1162 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{18}N_2NaO_2S$ [M + Na]$^+$ 325.0987, found 325.0984; yield 66%, 31.6 mg.

N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-4-cyanobut-2-en-1-yl)-4-methylbenzenesulfonamide (**15a**): colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.89 (d, 3H, J = 1.6 Hz), 2.45 (s, 3H), 3.09 (dd, 2H, J = 5.2, 1.2 Hz), 3.81 (d, 2H, J = 5.2 Hz), 3.92 (d, 2H, J = 6.4 Hz), 5.57 (dt, 1H, J = 15.2, 5.2 Hz), 5.68 (dt, 1H, J = 15.2, 5.2 Hz), 6.09 (tq, 1H, J = 6.4, 1.6 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.3, 20.2, 44.3, 48.9, 112.7, 116.6, 119.2, 122.6, 127.1, 129.8, 130.1, 136.3, 141.6, 144.3; IR (ATR) ν 2925, 2221, 1338, 1156 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{19}N_3NaO_2S$ [M + Na]$^+$ 352.1096, found 352.1099; yield 10%, 5.4 mg.

N-(Buta-2,3-dien-1-yl)-4-methyl-N-(penta-2,3-dien-1-yl)-benzenesulfonamide (**10b**): colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.62 (dd, 3H, J = 6.6, 3.2 Hz), 2.42 (s, 3H), 3.84 (ddd, 1H, J = 14.4, 7.2, 1.8 Hz), 3.88 (ddd, 1H, J = 14.4, 7.2, 1.8 Hz), 3.89−3.92 (m, 2H), 4.70−4.71 (m, 2H), 4.84−4.89 (m, 1H), 4.94 (tt, 1H, J = 6.6 Hz), 5.07−5.12 (m, 1H), 7.29 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); ^{13}C NMR

($CDCl_3$, 150 MHz) δ 14.1, 21.5, 45.4, 46.1, 76.1, 85.6, 85.7, 87.1, 127.2, 129.7, 137.7, 143.2, 206.3, 209.6; IR (ATR) ν 2925, 1955, 1340, 1155 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{19}NNaO_2S$ $[M + Na]^+$ 312.1034, found 312.1029; yield 24%, 123.5 mg.

(E)-2-((3R,4R*)-1-tosyl-4-vinylpyrrolidin-3-yl)but-2-enenitrile (**11b**):* colorless solid; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.79 (d, 3H, J = 6.6 Hz), 2.45 (s, 3H), 2.92−2.97 (m, 2H), 3.22 (dd, 1H, J = 10.2, 6.0 Hz), 3.26−3.29 (m, 1H), 3.33 (dd, 1H, J = 10.2, 10.2 Hz), 3.62 (dd, 1H, J = 10.2, 6.6 Hz), 3.70 (dd, 1H, J = 10.2, 7.2 Hz), 5.00 (d, 1H, J = 16.8 Hz), 5.06 (d, 1H, J = 16.8 Hz), 5.48 (ddd, 1H, J = 16.8, 10.2, 7.2 Hz), 6.52 (q, 1H, J = 6.6 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.8, 21.5, 40.0, 46.2, 50.1, 51.9, 113.6, 118.5, 118.7, 127.6, 129.8, 133.47, 133.50, 143.8, 146.0; IR (ATR) ν 2871, 2212, 1333, 1163 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1140; mp 119−120 °C; yield 26%, 13.9 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-4-cyanopent-2-en-1-yl)-4-methylbenzenesulfonamide (**15b**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.39 (d, 3H, J = 7.6 Hz), 1.89 (s, 3H), 2.45 (s, 3H), 3.31 (dq, 1H, J = 7.6, 5.6 Hz), 3.80 (d, 2H, J = 6.0 Hz), 3.92 (d, 2H, J = 6.4 Hz), 5.56 (dd, 1H, J = 15.6, 5.6 Hz), 5.68 (dt, 1H, J = 15.6, 6.0 Hz), 6.10 (tq, 1H, J = 6.4, 1.6 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2, 18.5, 21.5, 27.7, 344.3, 48.9, 112.8, 119.2, 120.2, 127.1, 127.5, 130.0, 130.1, 136.3, 141.6, 144.3; IR (ATR) ν 2925, 2220, 1339, 1157 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1244; yield 14%, 7.5 mg.

(Z)-2-((3R,4R*)-1-Tosyl-4-vinylpyrrolidin-3-yl)but-2-enenitrile (**17b**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.96 (d, 3H, J = 7.2 Hz), 2.45 (s, 3H), 2.90−2.95 (m, 2H), 3.27−3.33 (m, 2H), 3.51 (dd, 1H, J = 10.2, 6.6 Hz), 3.58 (dd, 1H, J = 10.2, 6.6 Hz), 5.07 (d, 1H, J = 18.6 Hz), 5.09 (d, 1H, J = 11.4 Hz), 5.47 (ddd, 1H, J = 18.6, 11.4, 6.6 Hz), 6.17 (q, 1H, J = 7.2 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.2, 21.6, 45.6, 46.1, 49.8, 51.7, 113.7, 116.6, 118.9, 127.5, 129.9, 133.3, 133.7, 143.9, 144.6; IR (ATR) ν 2925, 2216, 1342, 1160 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1143; yield 3%, 1.6 mg.

*N-(Buta-2,3-dien-1-yl)-4-methyl-N-(2-methylbuta-2,3-dien-1-yl)-benzenesulfonamide (**10c**; CAS Registry No. 1039513-84-2):* spectral data identical with the literature data;[23] ^1H NMR ($CDCl_3$, 400 MHz) δ 1.67 (t, 3H, J = 3.2 Hz), 2.42 (s, 3H), 3.81 (t, 2H, J = 2.4 Hz), 3.87 (dt, 2H, J = 6.8, 2.4 Hz), 4.61 (tq, 2H, J = 3.2, 2.4 Hz), 4.66 (dt, 2H, J = 6.8, 2.4 Hz), 4.83 (tt, 1H, J = 6.8, 6.8 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.4 Hz); yield 39%, 169.1 mg.

2-((3S,4S*)-4-Methyl-1-tosyl-4-vinylpyrrolidin-3-yl)acrylonitrile (**11c**):* colorless solid, ^1H NMR ($CDCl_3$, 400 MHz) δ 1.15 (s, 3H), 2.46 (s, 3H), 2.56 (t, 1H, J = 8.8 Hz), 3.14 (d, 1H, J = 10.0 Hz), 3.44 (dd, 1H, J = 10.0, 9.6 Hz), 3.4 (d, 1H, J = 10.0 Hz), 3.65 (dd, 1H, J = 10.0, 7.6 Hz), 4.99 (d, 1H, J = 17.2 Hz), 5.11 (d, 1H, J = 10.8 Hz), 5.60 (dd, 1H, J = 17.2, 10.8 Hz), 5.70 (d, 1H, J = 0.8 Hz), 5.97 (s, 1H), 7.36 (d, 2H, J = 8.0 Hz), 7.75 (d, 2H, J = 8.0 Hz).; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6, 22.2, 47.5, 49.5, 52.2, 57.8, 116.1, 117.4, 119.9, 127.4, 129.9, 133.5, 134.0, 137.4, 143.9; IR (ATR) ν 2918, 2849, 2223, 1335, 1152 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1137; mp 94−95 °C; yield 3%, 1.6 mg.

*N-(Buta-2,3-dien-1-yl)-4-methyl-N-(penta-3,4-dien-2-yl)-benzenesulfonamide (**10d**; CAS Registry No. 1039513-76-2):* spectral data identical with the literature data;[23] ^1H NMR ($CDCl_3$, 400 MHz) δ 1.23 (d, 3H, J = 6.8 Hz), 2.42 (s, 3H), 3.74 (ddt, 1H, J = 15.6, 7.2, 2.4 Hz), 3.89 (ddt, 1H, J = 15.6, 6.4, 3.2 Hz), 4.59−4.65 (m, 1H), 4.71−4.80 (m, 4H), 4.95 (dt, 1H, J = 6.4, 5.2 Hz), 5.20 (ddd, 1H, J = 7.2, 6.8, 6.4 Hz), 7.29 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); yield 54%, 357.3 mg.

2-((2S,3R*,4R*)-2-Methyl-1-tosyl-4-vinylpyrrolidin-3-yl)-acrylonitrile (**11da-α**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.41 (d, 3H, J = 6.4 Hz), 2.44 (s, 3H), 2.66−2.73 (m, 1H), 2.89 (dd, 1H, J = 6.8, 6.8 Hz), 3.70 (d, 2H, J = 9.6 Hz), 3.87 (dq, 1H, J = 6.8, 6.4 Hz), 5.10 (d, 1H, J = 17.6 Hz), 5.17 (d, 1H, J = 10.8 Hz), 5.70 (ddd, 1H, J = 17.6, 10.8, 7.6 Hz), 5.79 (s, 1H), 6.06 (s, 1H), 7.34 (d, 2H, J = 8.0 Hz), 7.77 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 18.0, 21.6, 44.6, 51.8, 54.1, 58.3, 118.6, 119.1, 119.4, 127.5, 129.8, 133.3, 135.2, 135.7, 143.7; IR (ATR) ν 2979, 2891, 2221, 1338, 1156 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1131; yield 21%, 5.2 mg.

2-((2R,3R*,4R*)-2-Methyl-1-tosyl-4-vinylpyrrolidin-3-yl)-acrylonitrile (**11da-β**) and 2-((3S*,4S*,5R*)-5-methyl-1-tosyl-4-vinylpyrrolidin-3-yl)acrylonitrile (**11db**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.40 (d, 1.1 × 3H, J = 6.6 Hz), 1.46 (d, 3H, J = 6.6 Hz), 2.45 (s, 3 + 1.1 × 3H), 2.59−2.62 (m, 1.1H), 2.70 (dd, 1H, J = 6.6 Hz), 2.97−3.01 (m, 1H), 3.19−3.25 (m, 1.1 × 2H), 3.30 (dd, 1H, J = 10.8, 7.2 Hz), 3.61−3.63 (m, 1 + 1.1 H), 3.68 (dd, 1.1 H, J = 8.4, 6.0 Hz), 3.73 (dq, 1H, J = 7.2, 6.6 Hz), 4.83 (dt, 1.1 × 1H, J = 16.8, 10.2, 10.2 Hz), 4.93 (d, 1.1 × 1H, J = 10.2 Hz), 4.95 (d, 1H, J = 16.8 Hz), 5.01 (d, 1H, J = 10.8 Hz), 5.05 (d, 1H, J = 15.6 Hz), 5.17 (ddd, 1H, J = 15.6, 10.8, 9.0 Hz), 5.51 (s, 1H), 5.62 (s, 1.1 × 1H), 5.88 (s, 1H), 5.93 (s, 1.1 × 1H), 7.35 (d, 2 + 1.1 × 2H, J = 8.4 Hz), 7.75 (d, 2 + 1.1 × 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): 21.6, 21.6, 21.9, 22.4, 43.5, 45.1, 49.3, 52.4, 53.7, 54.9, 58.3, 61.1, 117.6, 117.8, 119.0, 119.1, 120.9, 121.5, 127.58, 127.59, 129.87, 129.91, 131.7, 132.6, 132.88, 132.93, 134.2, 134.8, 143.9, 143.9; IR (ATR) ν 2977, 2930, 2223, 1340, 1163 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO_2S$ $[M + Na]^+$ 339.1143, found 339.1132; yield 29%, 7.2 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-5-cyanopent-3-en-2-yl)-4-methylbenzenesulfonamide (**15d**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (d, 1H, J = 6.8 Hz), 1.91 (s, 3H), 2.45 (s, 3H), 3.08 (dt, 2H, J = 5.6, 1.6 Hz), 3.73 (dd, 1H, J = 18.0, 6.4 Hz), 3.96 (dd, 1H, J = 18.0, 6.4 Hz), 4.60−4.66 (m, 1H), 5.48 (ddt, 1H, J = 15.6, 5.6, 2.0 Hz), 5.67 (ddt, 1H, J = 16.0, 4.4, 1.6 Hz), 6.19 (dt, 1H, J = 6.4, 1.6 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.68 (d, 2H, J = 8.4 Hz) ; ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 18.1, 20.3, 21.6, 40.8, 53.7, 111.0, 116.6, 119.5, 120.9, 127.0, 130.0, 134.7, 137.4, 144.1, 144.6 ; IR (ATR) ν 2970, 2926, 2251, 2219, 1335, 1151 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1251; yield 7%, 1.8 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-((E)-4-cyanopent-3-en-2-yl)-4-methylbenzenesulfonamide (**16d**):* colorless solid; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (d, 3H, J = 7.2 Hz), 1.92 (s, 3H), 1.94 (s, 3H), 2.45 (s, 3H), 3.82 (dd, 1H, J = 17.4, 6.6 Hz), 3.98 (dd, 1H, J = 17.4, 6.6 Hz), 4.86 (dq, 1H, J = 8.4, 7.2 Hz), 6.01 (d, 1H, J = 8.4 Hz), 6.20 (t, 1H, J = 6.6 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 15.4, 19.1, 21.6, 41.2, 50.5, 111.4, 112.8, 119.21, 119.24, 127.1, 130.0, 136.8, 143.97, 143.99, 144.5; IR (ATR) ν 2979, 2930, 2220, 1336, 1152 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1238; mp 108−110 °C; yield 4%, 1.0 mg.

*N-((E)-4-Cyanobut-2-en-1-yl)-N-((E)-4-cyanopent-3-en-2-yl)-4-methylbenzenesulfonamide (**17d**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (d, 3H, J = 7.2 Hz), 1.90 (d, 3H, J = 1.6 Hz), 2.44 (s, 3H), 3.11 (dd, 2H, J = 5.6, 1.6 Hz), 3.79 (ddd, 1H, J = 16.8, 6.0, 1.6 Hz), 3.87 (ddd, 1H, J = 16.8, 6.0, 1.6 Hz), 4.83 (dq, 1H, J = 9.2, 7.2 Hz), 5.61 (dt, 1H, J = 15.6, 5.6 Hz), 5.83 (dt, 1H, J = 15.6, 5.6 Hz), 6.05 (dd, 1H, J = 9.2, 1.6 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.65 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.3, 19.0, 20.2, 21.5, 45.0, 50.7, 111.9, 116.7, 119.5, 121.1, 127.2, 129.9, 132.5, 137.2, 144.2, 145.0; IR (ATR) ν 2970, 2925, 2220, 1335, 1153 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3NaO_2S$ $[M + Na]^+$ 366.1252, found 366.1251; yield 4%, 1.2 mg.

*N-(Buta-2,3-dien-1-yl)-4-methyl-N-(1-(propa-1,2-dien-1-yl)-cyclohexyl)benzenesulfonamide (**10e**):* colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.07−1.19 (m, 1H), 1.31−1.42 (m, 2H), 1.48−1.57 (m, 3H), 1.85 (dt, 2H, J = 12.4, 3.2 Hz), 2.01 (d, 2H, J = 12.4 Hz), 2.41 (s, 3H), 4.06 (dt, 2H, J = 6.8, 2.4 Hz), 4.75−4.78 (m, 4H), 5.14 (t, 1H, J = 6.4 Hz), 5.37 (dd, 1H, J = 6.8, 6.8 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 23.1, 25.2, 35.7, 44.8, 64.8, 76.0, 77.4, 90.5, 94.7, 127.0, 129.3, 141.1, 142.5, 208.4, 209.1; IR (ATR) ν 2033, 2859, 1953, 1315, 1151 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{25}NNaO_2S$ $[M + Na]^+$ 366.1504, found 366.1510; yield 30%, 103.2 mg.

2-((3R,4R*)-1-Tosyl-3-vinyl-1-azaspiro[4.5]decan-4-yl)-acrylonitrile (**11ea**):* colorless oil; ^1H NMR ($CDCl_3$, 600 MHz) δ 1.05−

1.09 (m, 1H), 1.26−1.31 (m, 2H), 1.63−1.65 (m, 2H), 1.76−1.80 (m, 2H), 1.92 (d, 1H, J = 13.2 Hz), 2.31−2.36 (m, 1H), 2.40 (s, 3H), 2.64 (dt, 1H, J = 13.2 Hz), 3.06 (d, 1H, J = 6.6 Hz), 3.24−3.30 (m, 1H), 3.47 (dd, 1H, J = 9.6, 9.6 Hz), 3.85 (dd, 1H, J = 9.6, 9.6 Hz), 5.15 (d, 1H, J = 18.0 Hz), 5.16 (d, 1H, J = 10.2 Hz), 5.64 (ddd, 1H, J = 18.0, 10.2, 7.2 Hz), 5.72 (bs, 1H), 5.99 (s, 1H), 7.28 (d, 2H, J = 8.4 Hz), 7.79 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.5, 23.7, 24.5, 24.9, 31.9, 36.7, 41.9, 50.8, 55.1, 71.7, 118.6, 118.8, 119.5, 127.3, 129.4, 133.8, 135.6, 138.4, 143.0; IR (ATR) ν 2931,2865, 2220, 1327, 1153 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{26}N_2NaO_2S$ [M + Na]$^+$ 393.1613, found 393.1599; yield 45%, 26.4 mg.

2-((3S,4S*)-1-Tosyl-4-vinyl-1-azaspiro[4.5]decan-3-yl)-acrylonitrile (**11eb**):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.12−1.39 (m, 3H), 1.52−1.54 (m, 2H), 1.60 (m, 1H), 1.71−1.76 (m, 1H), 1.80−1.82 (m, 1H), 2.19 (dt, 1H, J = 13.8, 4.2 Hz), 2.36−2.43 (m, 1H), 2.43 (s, 3H), 3.03 (dd, 1H, J = 10.2, 6.0 Hz), 3.20−3.24 (m, 1H), 3.40 (dd, 1H, J = 10.8, 9.6 Hz), 3.86 (dd, 1H, J = 9.6, 8.4 Hz), 5.19−5.32 (m, 3H), 5.61 (s, 1H), 5.93 (s, 1H), 7.30 (d, 2H, J = 7.8 Hz), 7.74 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.6, 23.1, 24.6, 24.9, 32.2, 36.3, 42.1, 48.9, 52.5, 72.2, 117.8, 120.8, 121.6, 126.9, 129.7, 130.7, 131.2, 139.1, 143.1; IR (ATR) ν 2929, 2866, 2224, 1330, 1155 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{26}N_2NaO_2S$ [M + Na]$^+$ 393.1613, found 393.1611; yield 8%, 4.6 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-(1-((E)-2-cyanoprop-1-en-1-yl)-cyclohexyl)-4-methylbenzenesulfonamide (**16e**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08−1.15 (m, 1H), 1.25−1.37 (m, 2H), 1.56−1.66 (m, 3H), 1.69−1.73 (m, 2H), 1.70 (d, 3H, J = 1.6 Hz), 1.91 (s, 3H), 2.28 (d, 2H, J = 10.8 Hz), 2.45 (s, 3H), 4.09 (d, 2H, J = 6.0 Hz), 6.33 (dt, 1H, J = 6.0, 1.6 Hz), 6.46 (s, 1H), 7.33 (d, 2H, J = 8.0 Hz), 7.66 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.2, 16.6, 21.6, 23.2, 24.7, 36.4, 43.8, 64.6, 110.6, 113.1, 119.5, 120.4, 127.4, 129.8, 138.6, 144.1, 145.4, 149.3; IR (ATR) ν 2931, 2864, 2219, 1333, 1153 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3NaO_2S$ [M + Na]$^+$ 420.1722, found 420.1728; yield 6%, 3.7 mg.

*N-((E)-3-Cyanobut-2-en-1-yl)-N-(1-((E)-3-cyanoprop-1-en-1-yl)-cyclohexyl)-4-methylbenzenesulfonamide (**15e**) and N-((E)-4-cyanobut-2-en-1-yl)-N-(1-((E)-2-cyanoprop-1-en-1-yl)cyclohexyl)-4-methylbenzenesulfonamide (**17e**):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.07−1.18 (m, 0.73 × 2H), 1.25−1.32 (m, 2 + 0.73 2H), 1.56−1.60 (m, 4H), 1.64 (s, 0.73 × 3H), 1.68−1.71 (m, 0.73 × 4H), 1.78 (dt, 2H, J = 12.6, 3.0 Hz), 1.92 (s, 3H), 2.03 (d, 2H, J = 12.6 Hz), 2.39 (d, 0.73 × 2H, J = 12.0 Hz), 2.435 (s, 0.73 × 3H), 2.439 (s, 3H), 3.10 (d, 2H, J = 6.0 Hz), 3.12 (d, 0.73 × 2H, J = 5.4 Hz), 4.00 (d, 0.73 × 2H, J = 6.0 Hz), 4.09 (d, 2H, J = 5.4 Hz), 5.50−5.57 (m, 1 + 0.73 × 1H), 5.70 (d, 1H, J = 16.2 Hz), 5.95 (dt, 0.73 × 1H, J = 15.6, 6.0 Hz), 6.38 (t, 1H, J = 5.4 Hz), 6.46 (s, 0.73 × 1H), 7.30−7.32 (m, 2 + 0.72 × 2H), 7.64 (d, 2H, J = 8.4 Hz), 7.68 (d, 0.73 + 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 15.3, 16.7, 20.3, 20.7, 21.6, 21.6, 23.0, 23.3, 24.9, 25.1, 35.5, 36.4, 43.3, 47.3, 64.6, 65.4, 110.1, 112.8, 116.9, 116.9, 119.9, 120.7, 120.9, 121.2, 127.0, 127.5, 129.7, 129.9, 134.0, 137.1, 139.0, 140.3, 143.67, 143.72, 146.6, 149.8; IR (ATR) ν 2932, 2862, 2218, 1330, 1151 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{27}N_3NaO_2S$ [M + Na]$^+$ 420.1722, found 420.1737; yield 5.0 mg, 8%.

*Diethyl 2,2-bis(buta-2,3-dien-1-yl)malonate (**10f**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, 6H, J = 7.2 Hz), 2.65 (dt, 4H, J = 8.0, 2.4 Hz), 4.19 (q, 4H, J = 7.2 Hz), 4.66 (dt, 4H, J = 6.8, 2.4 Hz), 4.95 (tt, 2H, J = 7.2, 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 31.7, 57.5, 61.2, 74.4, 84.0, 170.3, 210.0; IR (ATR) ν 2982, 1956, 1728 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{20}NaO_4$ [M + Na]$^+$ 287.1259, found 287.1248; yield 19%, 171.1 mg.

(3R,4R*)-Diethyl 3-(1-cyanovinyl)-4-vinylcyclopentane-1,1-dicarboxylate (**11f**):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.26 (t, 6H, J = 7.2 Hz), 2.32−2.37 (m, 2H), 2.50−2.60 (m, 2H), 2.95−2.98 (m, 1H), 5.10 (d, 1H, J = 10.4 Hz), 5.12 (d, 1H, J = 17.6 Hz), 5.64−5.73 (m, 1H), 5.70 (s, 1H), 5.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0, 36.2, 38.5, 46.2, 46.7, 58.7, 61.7, 61.8, 117.3, 118.3, 123.5, 130.7, 136.0, 171.3, 172.1; IR (ATR) ν 2982, 2223, 1725 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{21}NNaO_4$ [M + Na]$^+$ 314.1368, found 314.1374; yield 60%, 27.5 mg.

*Diethyl 2-((E)-3-cyanobut-2-en-1-yl)-2-((E)-4-cyanobut-2-en-1-yl)malonate (**15f**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (t, 6H, J = 7.2 Hz), 1.90 (s, 3H), 2.66, (d, 2H, J = 7.2 Hz), 2.71 (d, 2H, J = 8.0 Hz), 3.08 (d, 2H, J = 5.6, 0.8 Hz), 4.22 (q, 4H, J = 7.2 Hz), 5.48 (dt, 2H, J = 15.6, 5.6 Hz), 5.69 (dt, 2H, J = 15.2, 7.2 Hz), 6.25 (t, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.1, 15.2, 20.5, 31.9, 36.1, 56.6, 62.0, 112.5, 116.9, 120.0, 122.5, 129.3, 141.6, 169.8; IR (ATR) ν 2983, 2219, 1726 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{22}N_2NaO_4$ [M + Na]$^+$ 341.1477, found 341.1483; yield 12%, 5.9 mg.

*Diethyl 2,2-bis((E)-3-cyanobut-2-en-1-yl)malonate (**6i**):* colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, 6H, J = 7.2 Hz), 1.89 (d, 6H, J = 1.2 Hz), 2.73 (d, 4H, J = 7.6 Hz), 4.23 (q, 4H, J = 7.2 Hz), 6.22 (tq, 1H, J = 7.6, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.0, 15.2, 32.3, 56.2, 62.3, 113.1, 119.8, 140.9, 169.4; IR (ATR) ν 2983, 2918, 2219, 1744, 1715 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{22}N_2NaO_4$ [M + Na]$^+$ 341.1477, found 341.1484; mp 38 °C; yield 5%, 2.8 mg.

(R)-2-((3R*,4R*)-4-Ethyl-1-tosylpyrrolidin-3-yl)propanenitrile (**17a**-major):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.76−0.83 (m, 1H), 0.86 (t, 3H, J = 10.8 Hz), 1.28 (d, 3H, J = 10.8 Hz), 1.40−1.44 (m, 1H), 2.13−2.17 (m, 1H), 2.21−2.26 (m, 1H), 2.45 (s, 3H), 2.52 (dq, 1H, J = 10.8, 6.6 Hz), 2.90 (dd, 1H, J = 10.2, 10.2 Hz), 3.24 (dd, 1H, J = 10.2, 6.6 Hz), 3.38 (dd, 1H, J = 10.2, 2.4 Hz), 3.44 (dd, 1H, J = 10.2, 7.2 Hz), 7.34 (d, 2H, J = 8.8 Hz), 7.71 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 12.1, 17.0, 19.2, 21.5, 24.9, 42.2, 45.6, 49.1, 51.0, 121.2, 127.3, 129.8, 133.8, 143.7; IR (ATR) ν 2963, 2931, 2878, 2240, 1340, 1151 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{22}N_2NaO_2S$ [M + Na]$^+$ 329.1300, found 329.1303; yield 59%, 38.1 mg.

(R)-2-((3R*,4R*)-4-)Ethyl-1-tosylpyrrolidin-3-yl)propanenitrile (**17a**-minor):* colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.86 (t, 3H, J = 7.2 Hz), 0.92−0.97 (m, 1H), 1.21−1.28 (m, 1H), 1.28 (d, 3H, J = 7.2 Hz), 1.98−2.03 (m, 1H), 2.17−2.23 (m, 1H), 2.44 (s, 3H), 2.57 (dq, 1H, J = 7.2, 7.2 Hz), 3.09 (dd, 1H, J = 9.6, 9.6 Hz), 3.31 (dd, 1H, J = 10.2, 6.0 Hz), 3.35 (dd, 1H, J = 10.2, 3.6 Hz), 3.63 (dd, 1H, J = 9.6, 8.4 Hz), 7.34 (d, 2H, J = 7.8 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 12.2, 17.0, 18.8, 21.5, 24.4, 41.2, 45.0, 49.5, 51.3, 121.3, 127.4, 129.7, 133.8, 143.6; IR (ATR) ν 2892, 2221, 1338, 1156 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{22}N_2NaO_2S$ [M + Na]$^+$ 329.1300, found 329.1294; yield 23%, 14.5 mg.

*2-(1-Tosyl-4-vinyl-2,5-dihydro-1H-pyrrol-3-yl)acetonitrile (**18**):* colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 3.23 (s, 2H), 4.26−4.27 (m, 4H), 5.18 (d, 1H, J = 17.2 Hz), 5.34 (d, 1H, J = 10.8 Hz), 6.38 (dd, 1H, J = 17.2, 10.8 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.74 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.9, 21.5, 54.7, 56.9, 115.4, 119.4, 122.1, 125.6, 127.4, 129.9, 133.4, 134.1, 143.9; IR (ATR) ν 2918, 2847, 2251, 1596, 1346, 1162 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{24}KN_2O_2S$ [M + K]$^+$ 327.0570, found 325.0578; mp 111−112 °C; yield 88%, 48.0 mg.

*2-(1-Tosyl-4-vinyl-2,5-dihydro-1H-pyrrol-3-yl)pent-4-enenitrile (**19**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.35 (ddd, 1H, J = 14.0, 7.6, 7.2 Hz), 2.44 (s, 3H), 2.50 (ddd, 1H, J = 14.0, 7.6, 7.2 Hz), 3.64 (t, 1H, J = 7.6 Hz), 4.20−4.37 (m, 4H), 5.13−5.20 (m, 3H), 5.33 (d, 1H, J = 10.8 Hz), 5.66 (ddt, 1H, J = 17.6, 10.8, 7.6 Hz), 6.38 (dd, 1H, J = 17.2, 10.8 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.74 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 28.8, 36.2, 54.9, 55.5, 118.0, 119.5, 120.0, 125.7, 126.9, 127.5, 130.0, 131.7, 133.6, 133.9, 143.9; IR (ATR) ν 2979, 2922, 2858, 2251, 1733, 1598, 1345, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{20}N_2NaO_2S$ [M + Na]$^+$ 351.1143, found 351.1150; yield 62%, 32.3 mg.

*2-Tosyl-2,3,4,5-tetrahydro-1H-isoindole-4-carbonitrile (**20**):* colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 3H), 2.59−2.62 (m, 2H), 3.42 (t, 1H, J = 9.6 Hz), 4.14−4.22 (m, 3H), 4.27−4.31 (m, 1H), 5.86 (dt, 1H, J = 9.6, 4.0 Hz), 5.94 (d, 1H, J = 9.6 Hz), 7.36 (d, 1H, J = 8.0 Hz), 7.74 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 24.0, 27.2, 54.7, 54.9, 118.5, 120.3, 122.1, 125.6, 127.5, 130.0, 132.4, 134.0, 143.9; IR (ATR) ν 3057, 2921, 2858, 2243, 1597, 1457, 1342, 1161 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{16}N_2NaO_2S$ [M + Na]$^+$ 323.0830, found 323.0835; yield 55%, 9.8 mg.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra for all new compounds and CIF files giving X-ray analyses for **4a,c** and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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