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Ligand Control of *E*/*Z* Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction

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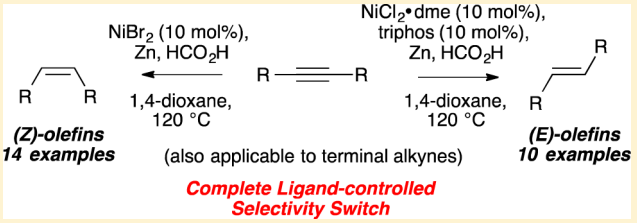
Supporting Information

ABSTRACT: A nickel-catalyzed transfer hydrogenative alkyne semireduction protocol that can be applied to both internal and terminal alkynes using formic acid and Zn as the terminal reductants has been developed. In the case of internal alkynes, the (*E*)- or (*Z*)-olefin isomer can be accessed selectively under the same reaction conditions by judicious inclusion of a triphos ligand.



The Lindlar semireduction of alkynes[1] is a long-standing synthetic transformation that has found widespread application in the preparation of pharmaceuticals, agrochemicals, natural products, and fine fragrance components.[2] It remains, more than 60 years after its inception, the de rigueur method for alkyne reduction, typically affording the (*Z*)-olefinic product. Nevertheless, this classic reduction method is not without its limitations; commercial samples of Lindlar's catalyst are notorious for their between-batch variability, and *E*/*Z* selectivities can often be modest because of isomerization of products under the reaction conditions.[3] Over-reduction of the alkenes to the fully saturated alkane is perhaps the most common drawback, particularly with terminal acetylene functionalities or highly polar substrates.[4] In recent years, a multitude of homogeneous and heterogeneous[5] catalytic methods primarily based on transition metals have been developed in an attempt to address these limitations.[6] Significant progress has been made in the area of *Z*-selective alkyne reductions, and a variety of catalytic systems have been developed employing transition metal precatalysts in combination with hydrogen gas[7] or in tandem with transfer hydrogenation agents such as silanes,[8] or HCO_2H.[9] Although less well-developed in comparison, catalytic systems that provide selective access to the (*E*)-olefin product have also been reported,[10,11] including Rh-, Ru-, Pd-, and Ir-catalyzed hydrogenations and transfer hydrogenations. Recently, *E*-selective semireductions catalyzed by base metals have been developed, including a Ni-catalyzed transfer hydrogenation from H_3PO_2[10g] and an Fe-catalyzed hydrogenation.[10h] Nevertheless, few catalytic systems allow switchable selectivity[11] for either the (*E*)- or (*Z*)-olefin isomer in a single transformation,[12] and to the best of our knowledge, none are switchable under ligand control. We report a nickel-catalyzed transfer hydrogenative semireduction of alkynes with zinc and formic acid whereby judicious inclusion of a commercially available triphosphine ligand allows for the generation of either the (*E*)- or (*Z*)-alkene isomer, typically with complete selectivity (>95/5). Importantly, the reaction does not require purified solvents, reagents, or an inert atmosphere, and no additional change to the reaction conditions is necessary to induce the switch in selectivity. Preliminary mechanistic experiments indicate that the reaction initially yields the (*Z*)-alkene isomer, which is rapidly isomerized under the reaction conditions by a nickel phosphine complex.

As a continuation of our previous investigations toward the accelerated discovery of metal-catalyzed reaction processes by screening and deconvoluting complex mixtures of catalyst components,[13] a new, unexpected product was isolated upon subjecting propargylic allylamine **1** to conditions originally intended to promote reductive cyclization-type reactivity[14] (Scheme 1). Rather, this compound, isolated in 65% yield, was assigned as the (*Z*)-alkene arising from selective alkyne semireduction. No over-reduction of the nascent internal olefin or of the pendant allyl group was observed under these reaction conditions, suggesting that such a catalytic system may be able to address some of the issues commonly encountered using Lindlar's catalyst. Deconvolution of the reaction components rapidly identified nickel(II) triflate as the active catalyst, with zinc, formaldehyde, and DABCO also necessary for reduction to occur. We hypothesized that the combination of DABCO and formaldehyde would function as a transfer hydrogenation agent akin to ammonium formate.[15] Indeed, upon replacement of these components with formic acid, both the rate and cleanliness of the reaction notably increased.[16] Slight optimization of the reaction conditions established a reliable protocol for the *Z*-selective semireduction of alkynes.[17]

Emboldened by this initial discovery, we sought to develop divergent reaction conditions that would allow selective access to either the (*Z*)- or (*E*)-alkene isomer. Using a model bis(aryl)alkyne, several nickel(II) precursors were shown to be effective catalysts for this transformation, yet addition of a variety of mono- or bidentate phosphines either proved detrimental to reactivity or had no effect on *E*/*Z* selectivity

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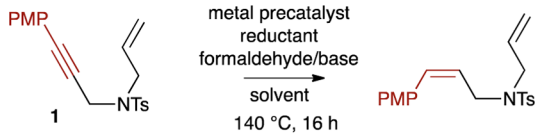
Scheme 1. Reaction Discovery and Deconvolution[a]



Metal Precatalysts - $Ni(OTf)_2$, $CoCl_2$, $Fe(acac)_3$, $NiCl_2(PCy_3)_2$, $Pd(OAc)_2$. **Reductants** - Zn, Mn.

Step 1: All metal precatalysts (20 mol%), reductants (1.0 mmol) and formaldehyde (1.0 mmol) screened against 5 bases (1.0 mmol) in 2 solvents (1.0 mL).
Step 2: Individual metal precatalyst (20 mol%) and individual reductant (1.0 mmol) screened with HCO_2H (5.0 mmol) in 1,4-dioxane (1.0 mL).

Step 1	Toluene	1,4-dioxane
CsF	<1%	<1%
K_3PO_4	<1%	<1%
Cs_2CO_3	<1%	<1%
DABCO	<1%	**65%**
Na_2CO_3	<1%	<1%

Step 2	Zn	Mn
$Ni(OTf)_2$	75%	<1%
$CoCl_2$	<1%	<1%
$Fe(acac)_3$	<1%	<1%
$NiCl_2(PCy_3)_2$	<10%	<1%
$Pd(OAc)_2$	<10%	<10%

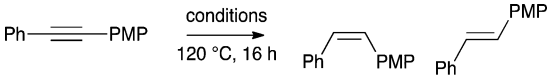
optimization: $NiBr_2$ (20 mol%) / Zn (5.0 eq); 1,4-dioxane (0.5 mL); HCO_2H (5.0 eq); 140 °C, 16 h; 80% conversion

(w/ HCO_2H replacing DABCO/formaldehyde)

[a]Combinatorial discovery and deconvolution of *in situ*-generated catalysts for semireduction of alkyne **1**. Conversion determined by ^1H NMR analysis of the crude mixtures in $CDCl_3$. Abbreviations: PMP, *p*-methoxyphenyl-; DABCO, 1,4-diazabicyclo[2.2.2]octane.

(see the Supporting Information for full optimization information). In contrast, the presence of tridentate ligand bis(diphenylphosphinoethyl)phenylphosphine (triphos) furnished a 1/1 mix of geometric isomers (Table 1, entry 3).

Table 1. Ligand Control of *E*/*Z* Selectivity



entry	nickel source (20 mol %)	ligand (20 mol %)	conversion (%)[a]	*E*/*Z* ratio
1	$NiBr_2$	–	>95	<5/95
2	$NiCl_2$·dme	–	>95	<5/95
3	$NiBr_2$	triphos	>95	50/50
4	$NiCl_2$·dme	triphos	>95	>95/5
5	$NiBr_2$ (10)	–	>95	<5/95
6	$NiCl_2$·dme (10)	triphos (10)	>95	>95/5

[a]Conversion determined by ^1H NMR analysis of the crude reaction mixtures in $CDCl_3$. Abbreviation: PMP, *p*-methoxyphenyl-.

Switching to $NiCl_2$·dme as a catalyst precursor resulted in complete selectivity for the (*E*)-isomer (entry 4). Finally, reducing the catalyst loadings to 10 mol % had no impact on either conversion levels or *E*/*Z* selectivities (entries 5 and 6).

With optimal reaction conditions in hand, an evaluation of the reaction generality was undertaken using the $NiBr_2$ system to allow the selective preparation of (*Z*)-alkenes. When the requisite acetylene derivatives were subjected to the reaction conditions, the corresponding alkenes were delivered in excellent yields and typically as a single geometric isomer (Table 2).[18] (*Z*)-Stilbene derivatives **2a**–**i** were all delivered in >90% isolated yield, with excellent *Z* selectivities. Additionally, substrates bearing reducible functionalities such as a nitrile and *O*-Bn, typically unsuitable substrates for related nickel-catalyzed reductions,[19] were smoothly reduced to the desired alkenes **2f** and **2g** with no competitive nitrile reduction or *O*-Bn deprotection observed. Similarly, a substrate bearing an aryl bromide was also cleanly reduced to (*Z*)-stilbene **2h** with no evidence of protodebromination.[20] A series of olefins **2j**–**n** was also prepared in excellent yields, with good selectivity for the (*Z*)-olefin isomer in all cases.

Not all substrates subjected to the reaction conditions proved to be amenable to reduction. Substrates bearing nitro-aryl groups exhibited no reduction of either alkyne or nitro functionality, even at elevated temperatures. Aldehydes also proved to be incompatible with the reaction conditions, yielding a complex mixture of products, presumably as a result of over-reduction.

To explore the ability of the developed catalytic method to selectively deliver (*E*)-olefins simply by inclusion of the triphos ligand, a further selection of substrates was examined (Table 3). Diarylacetylenes were amenable to the reaction conditions, furnishing the requisite (*E*)-stilbenes **3a**–**h** in excellent yields and with complete selectivity for the (*E*)-isomer. Once more, an *O*-Bn substituent was tolerated well by the reaction system (**3f**), as was an aryl bromide functionality (**3g**).

Acetylene derivatives bearing ester functional groups were also smoothly reduced to the corresponding (*E*)-alkenes **3h**–**j** in high yields. Bis-alkene **3k** was also generated via this catalytic methodology, albeit in more modest selectivity for the (*E*)-isomer. Unfortunately, when 4-octyne was subjected to the *E*-selective reaction conditions, only the (*Z*)-alkene isomer **3l** was detected with poor levels of conversion.

The $NiBr_2$-catalyzed semireduction system was next applied to a series of terminal alkynes, yielding the expected terminal olefins in excellent yields (Table 4). Relatively simple olefins **4a**–**d** were isolated as the sole reaction product, as was estradiol derivative **4e**, generated in 88% yield despite the adjacent quaternary carbon center. Additionally, propargylic allylamine **4f** was prepared from the requisite bis-alkyne starting material, demonstrating the ability to selectively reduce terminal alkynes in the presence of internal alkyne functionalities.

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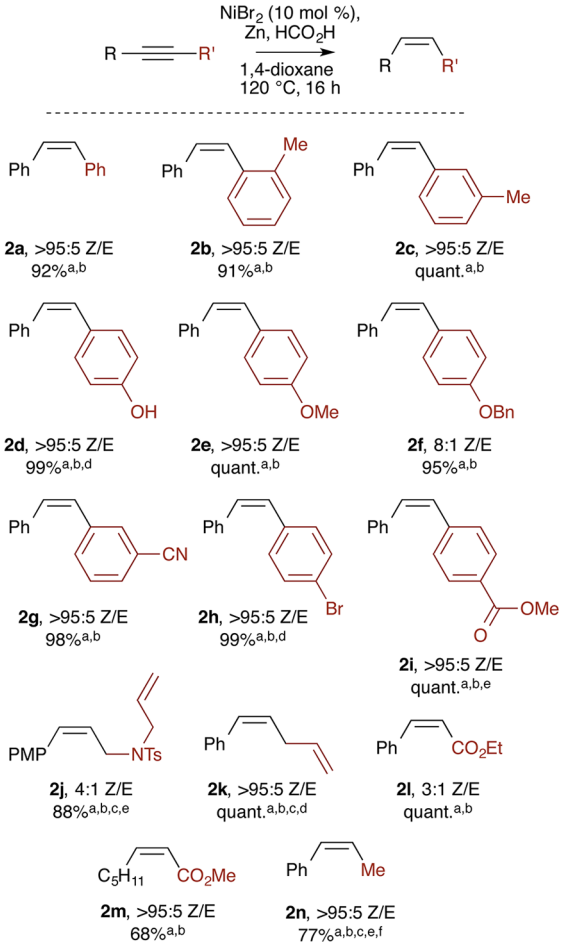
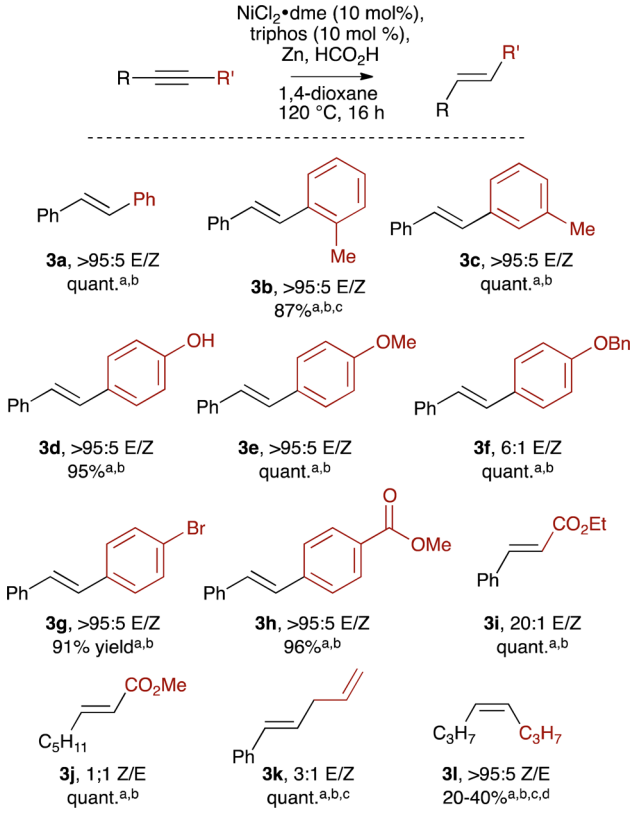
Table 2. *Z*-Selective Alkyne Semireduction



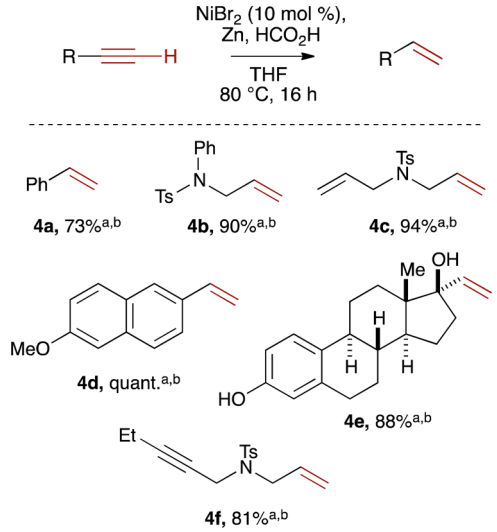
[a]A mixture of alkyne (0.2 mmol), $NiBr_2$ (10 mol %), zinc (1.0 mmol), and HCO_2H (1.0 mmol) in 1,4-dioxane (0.5 mL) was stirred at 120 °C for 16 h. [b]Isolated yield, from an average of two runs. [c]Reaction performed at 140 °C. [d]15 mol % $NiBr_2$ was used. [e]20 mol % $NiBr_2$ was used. [f]Yield determined by ^1H NMR in comparison to that of 1,3,5-trimethoxybenzene as an internal standard.

Table 3. *E*-Selective Alkyne Semireduction



[a]A mixture of alkyne (0.2 mmol), $NiCl_2$·dme (10 mol %), triphos (10 mol %), zinc (1.0 mmol), and HCO_2H (1.0 mmol) in 1,4-dioxane (0.5 mL) was stirred at 120 °C for 16 h. [b]Isolated yield, from an average of two runs. [c]Reaction performed at 140 °C. [d]Yield determined by ^1H NMR in comparison to 1,3,5-trimethoxybenzene as an internal standard.

Table 4. Terminal Alkyne Semireduction



[a]A mixture of alkyne (0.2 mmol), $NiBr_2$ (10 mol %), zinc (1.0 mmol), and HCO_2H (1.0 mmol) in THF (0.5 mL) was stirred at 80 °C for 16 h. [b]Isolated yield, from an average of two runs.

To gain insight into the role of the triphos ligand, an isolated sample of (*Z*)-stilbene was exposed to both sets of reaction conditions. Upon treatment with $NiBr_2$, zinc, and HCO_2H at 120 °C for 1 h, no alkene isomerization was observed. However, upon treatment of (*Z*)-stilbene with $NiCl_2$·dme and triphos under identical conditions, complete isomerization to the (*E*)-alkene was observed after only 1 h at 120 °C (Figure 1). Isomerization was not accomplished by any other phosphine ligands tested in our initial screen (see the Supporting Information for details). These observations are highly suggestive of an initial *Z*-selective alkene reduction followed by rapid Ni–triphos complex-catalyzed isomerization.[21]

In conclusion, a robust catalytic protocol for the selective semireduction of alkynes using inexpensive nickel precursors, zinc, and formic acid is reported. The ability of an *in situ*-generated Ni–triphos complex to isomerize (*Z*)-olefins to (*E*)-olefins under simple reaction conditions has also been discovered. The applicability of this catalytic protocol to a wide range of substrates has been demonstrated providing selective access to a range of terminal, (*Z*), and (*E*)-olefins. The inexpensive nature of the reaction components, the ability to perform the reactions without an inert atmosphere, and the tunable *E*/*Z* selectivity should render this an appealing addition to modern catalytic, chemoselective methodologies. Ongoing

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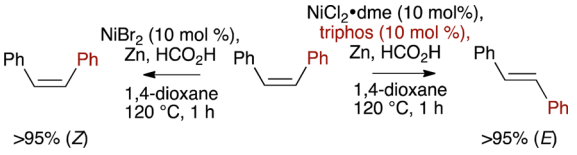

Figure 1. Evidence of the "(*Z*)-first" reduction mechanism.

investigations aim to ascertain the nature of the catalytic species involved in these transformations and to extend the utility of this selective catalyst system in synthesis.

EXPERIMENTAL SECTION

General Information. All reagents were used as received without purification. 1,4-Dioxane refers to ≥99.5% (GC) (33147-1L) and THF to ≥99.0% ReagentPlus (178810-1L) both purchased from Sigma-Aldrich. Formic acid refers to 98−100 grade and zinc to zinc dust (<10 μm, ≥98.0%) both purchased from Sigma-Aldrich. Triphos refers to bis(diphenylphosphinoethyl)phenylphosphine (CAS Registry No. 23582-02-7). $NiBr_2$ and $NiCl_2$·dme are both 98% grade (Aldrich).

General laboratory techniques were used throughout, and no special precautions were taken to exclude air or moisture from the reaction mixtures. Elevated temperatures were achieved by way of a stirrer-hot plate, heating block, and thermocouple. Where applicable, analytical thin layer chromatography was performed on precoated aluminum plates (Kieselgel 60 F254 silica). TLC visualization was conducted with ultraviolet light (254 nm), followed by staining with a 1% aqueous $KMnO_4$ solution. Flash column chromatography was performed on Kieselgel 60 silica eluting with the stated solvent system.

Nuclear magnetic resonance (NMR) spectra were acquired at 400 MHz (^{1}H), 100 MHz (^{13}C), and 376 MHz (^{19}F) at ambient temperature in the stated deuterated solvent. All chemical shifts are quoted in parts per million relative to that of the residual solvent as the internal standard. GC−MS analysis was performed on a GC System connected to a MSD block using a high-resolution gas chromatography column (30 m × 0.250 mm, 0.25 μm). High-resolution mass spectra were obtained using electrospray ionization (ESI).

General Procedure for Sonogashira Coupling Reaction. Starting material alkynes were prepared according to a reported literature procedure.[22] To an oven-dried Schlenk flask were added $PdCl_2(PPh_3)_2$ (10 mol %), CuI (10 mol %), and the desired aryl iodide (2.2 mmol). MeCN (3 mL) was then introduced by syringe, followed by phenylacetylene (2.0 mmol), and Et_3N (4.0 mmol). The reaction mixture was stirred for 16 h at room temperature before being concentrated *in vacuo*, directly onto silica gel, and purified by flash column chromatography on silica (petroleum ether/diethyl ether) to give the desired arylalkynes. 1-Methoxy-4-(phenylethynyl)benzene,[23] 1-methyl-3-(phenylethynyl)benzene,[23] 1-methyl-2-(phenylethynyl)-benzene,[23] 4-(phenylethynyl)phenol,[24] 1-nitro-4-(phenylethynyl)-benzene,[24] 1-nitro-3-(phenylethynyl)benzene,[24] 1-bromo-4-(phenylethynyl)benzene,[25] methyl 4-(phenylethynyl)benzoate,[26] 3-(phenylethynyl)benzonitrile,[27] and 4-(phenylethynyl)benzaldehyde[23] were all prepared with analytical data in agreement with the literature.

1-(Benzyloxy)-4-(phenylethynyl)benzene. The title compound was prepared from 4-(phenylethynyl)phenol (1.00 mmol, 0.194 g), K_2CO_3 (1.10 mmol, 0.152 g), and benzyl bromide (0.900 mmol, 0.107 mL). The reactants were dissolved in acetone and heated to reflux until TLC analysis indicated consumption of starting material (~4 h). The reaction mixture was then cooled, filtered, and diluted with EtOAc (30 mL). The organic layer was then washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give the title compound as an off-white solid (0.276 g, 97% yield) with analytical data in agreement with the literature:[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, dd, J = 7.5, 1.8 Hz), 7.47 (2H, d, J = 8.6 Hz), 7.45−7.38 (4H, m), 7.35−7.32 (4H, m), 6.95 (2H, d, J = 8.6 Hz), 5.09 (2H, s).

N-Allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide. To a stirred solution of *N*-(tosyl)allylamine (4.52 g, 21.4 mmol) and K_2CO_3 (4.44 g, 32.1 mmol) in acetone (50 mL) at ambient temperature was added dropwise propargyl bromide (3.46 mL, 32.1 mmol), and the reaction mixture was heated at reflux for 5 h. After being allowed to cool, the reaction mixture was quenched with H_2O (40 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an off-white semisolid. The crude material was dissolved in Et_2O (approximately 20 mL) and cooled in the refrigerator overnight to give the title compound as an off-white crystalline solid (3.36 g, 63% yield) that was collected by filtration. Analytical data were in agreement with the literature:[29] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, J = 8.3 Hz), 7.29 (2H, d, J = 8.3 Hz), 5.73 (1H, ddt, J = 17.0, 10.1, 6.6 Hz), 5.29 (1H, dt, J = 17.0, 1.3 Hz), 5.24 (1H, dd, J = 10.1, 1.3 Hz), 4.09 (2H, d, J = 2.4 Hz), 3.83 (2H, d, J = 6.6 Hz), 2.43 (3H, s), 2.00 (1H, t, J = 2.4 Hz).

N-Allyl-N-[3-(4-methoxyphenyl)prop-2-yn-1-yl]-4-methylbenzenesulfonamide. The title compound was prepared according to the general procedure described above from *N*-Allyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide and 4-iodoanisole as a pale yellow solid (0.429 g, 86% yield) with analytical data in agreement with the literature:[30] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, d, J = 8.2 Hz), 7.30 (2H, d, J = 7.6 Hz), 7.06 (2H, d, J = 8.7 Hz), 6.81 (2H, d, J = 8.7 Hz), 5.84 (1H, ddt, J = 17.0, 10.2, 6.6 Hz), 5.37 (1H, dd, J = 17.0, 1.1 Hz), 5.30 (1H, d, J = 10.2 Hz), 4.33 (2H, s), 3.92 (2H, d, J = 6.4 Hz), 3.84 (3H, s), 2.40 (3H, s).

4-Methyl-N-(pent-2-yn-1-yl)-N-(prop-2-yn-1-yl)-benzenesulfonamide. To a stirred solution of *N*-(tosyl)-propargylamine (1.00 g, 4.78 mmol) in DMF (30 mL) at 0 °C was added NaH (0.230 g, 5.74 mmol) in four portions. The reaction mixture was allowed to stir for 1 h at 0 °C, before 1-bromopent-2-yne (0.640 mL, 6.21 mmol) was added dropwise and the reaction mixture was stirred for 4 h, being allowed to warm to room temperature. The reaction was quenched carefully with brine (20 mL), and the mixture was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give an orange oil that was purified by column chromatography over silica (5% EtOAc in petrol) to give the title compound as a viscous, colorless oil (0.068 g, 52% yield) with analytical data in agreement with the literature:[31] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (2H, d, J = 8.2 Hz), 7.29 (2H, d, J = 8.2 Hz), 4.13 (4H, app t, J = 2.3 Hz), 2.42 (3H, s), 2.13 (1H, t, J = 2.4 Hz), 2.01 (2H, dddd, J = 9.9, 7.5, 5.1, 2.4 Hz), 0.97 (3H, t, J = 7.5 Hz).

4-Methyl-N-phenylbenzenesulfonamide. To a stirred solution of aniline (0.400 g, 4.30 mmol) and Et_3N (0.900 mL, 6.50 mmol) in CH_2Cl_2 (20 mL) at 0 °C was slowly added TsCl (1.00 g, 5.25 mmol), and the reaction mixture was stirred for 1 h at room temperature. The reaction was quenched with 0.1 M HCl (20 mL) and the mixture extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a white solid (1.02 g, 96% yield) used without further purification and with analytical data in agreement with the literature:[32] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.68 (2H, m), 7.30−7.25 (4H, m), 7.15 (1H, t, J = 7.5 Hz), 7.12−7.06 (2H, m), 6.68 (1H, br s), 2.42 (3H, s).

4-Methyl-N-phenyl-N-(prop-2-yn-1-yl)benzenesulfonamide. To a stirred solution of 4-methyl-*N*-phenylbenzenesulfonamide (1.00 g, 4.04 mmol) and K_2CO_3 (0.910 g, 8.08 mmol) in DMF (10 mL) at rt was added propargyl bromide (0.670 mL, 6.06 mmol) dropwise, and the reaction mixture was stirred for 16 h at room temperature. The reaction was quenched with 0.1 M HCl (10 mL) and the mixture extracted with Et_2O (3 × 30 mL). The combined organic layers were then washed with H_2O (3 × 15 mL) and brine (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give an off-white solid (1.07 g, 93% yield) that was used without further purification with analytical data in agreement with the literature:[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (2H, d, J = 8.2 Hz), 7.32−7.31 (2H, m), 7.26−7.22 (5H, m), 4.44 (2H, d, J = 2.4 Hz), 2.42 (3H, s), 2.16 (1H, t, J = 2.4 Hz).

General Procedure for *Z*-Selective Reduction. To an oven-dried 10 mL screw-top vial equipped with a magnetic stir bar were added the desired alkyne (0.20 mmol), zinc (1.0 mmol), $NiBr_2$ (10

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mol %), 1,4-dioxane (0.5 mL), and HCO_2H (1.0 mmol). The vial was then sealed and transferred to a heating block at 120 °C, and its contents were stirred rapidly (1200 rpm) at this temperature for 16 h. After being allowed to cool, the crude reaction mixture was filtered through a Celite plug; the filter cake was then washed with CH_2Cl_2, and the reaction mixture was concentrated *in vacuo* to give the desired (*Z*)-alkene.

(*Z*)-Stilbene (**2a**) was prepared according to the general procedure described above as a colorless oil with analytical data in agreement with the literature:[11b] run 1, 0.032 g, 89% yield; run 2, 0.034 g, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (10H, m), 6.65 (2H, s).

(*Z*)-1-Methyl-2-styrylbenzene (**2b**) was prepared according to the general procedure described above as a colorless oil with analytical data in agreement with the literature:[11b] run 1, 0.035 g, 92% yield; run 2, 0.034 g, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.04 (9H, m), 6.66 (1H, d, J = 12.2 Hz), 6.63 (1H, d, J = 12.2 Hz), 2.28 (3H, s).

(*Z*)-1-Methyl-3-styrylbenzene (**2c**) was prepared according to the general procedure described above as a yellow liquid with analytical data in agreement with the literature:[8d] run 1, 0.033 g, quantitative yield; run 2, 0.038 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (6H, m), 7.17−7.11 (2H, m), 7.07 (1H, t, J = 7.7 Hz), 6.62 (2H, s), 2.31 (3H, s).

(*Z*)-4-Styrylphenol (**2d**) was prepared according to the general procedure described above with 15 mol % $NiBr_2$ as a yellow solid with analytical data in agreement with the literature:[8e] run 1, 0.041 g, quantitative yield; run 2, 0.039 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.30 (4H, m), 7.28−7.23 (1H, m), 7.18 (2H, d, J = 8.6 Hz), 6.72 (2H, d, J = 8.6 Hz), 6.56 (2H, s), 4.80 (1H, br s).

(*Z*)-1-Methoxy-4-styrylbenzene (**2e**) was prepared according to the general procedure described above as an off-white solid with analytical data in agreement with the literature:[34] run 1, 0.046 g, quantitative yield; run 2, 0.044 g, 100% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.22 (7H, m), 6.80 (2H, d, J = 8.7 Hz), 6.60−6.53 (2H, m), 3.83 (3H, s).

(*Z*)-1-(Benzyloxy)-4-styrylbenzene (**2f**) was prepared according to the general procedure described above with analytical data in agreement with the literature:[9f] run 1, 0.058 g, quantitative yield; run 2, 0.051 g, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (5H, m), 7.33−7.22 (5H, m), 6.87 (2H, d, J = 8.5 Hz), 6.56 (2H, s), 5.08 (2H, s).

(*Z*)-3-Styrylbenzonitrile (**2g**) was prepared according to the general procedure described above as a yellow oil with analytical data in agreement with the literature:[35] run 1, 0.039 g, 98% yield; run 2, 0.042 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (1H, s), 7.50 (2H, t, J = 8.3 Hz), 7.35 (1H, t, J = 7.8 Hz), 7.30−7.28 (3H, m), 7.23−7.21 (2H, m), 6.78 (1H, d, J = 12.2 Hz), 6.59 (1H, d, J = 12.2 Hz).

(*Z*)-1-Bromo-4-styrylbenzene (**2h**) was prepared according to the general procedure described above with 15 mol % $NiBr_2$ as a yellow solid with analytical data in agreement with the literature:[34] run 1, 0.049 g, 98% yield; run 2, 0.050 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 8.5 Hz), 7.24−7.20 (5H, m), 7.11 (2H, d, J = 8.5 Hz), 6.63 (1H, d, J = 12.2 Hz), 6.51 (1H, d, J = 12.2 Hz).

(*Z*)-Methyl 4-styrylbenzoate (**2i**) was prepared according to the general procedure described above with 20 mol % $NiBr_2$ as an off-white solid with analytical data in agreement with the literature:[11e] run 1, 0.045 g, quantitative yield; run 2, 0.043 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (2H, d, J = 8.1 Hz), 7.30 (2H, d, J = 8.1 Hz), 7.22 (5H, br s), 6.71 (1H, d, J = 12.2 Hz), 6.61 (1H, d, J = 12.2 Hz), 3.90 (3H, s).

(*Z*)-*N*-Allyl-*N*-[3-(4-methoxyphenyl)allyl]-4-methylbenzenesulfonamide (**2j**) was prepared according to a slight modification of the general procedure described above on a 0.1 mmol scale at 140 °C with 20 mol % $NiBr_2$ as a 4/1 *Z*/*E* mixture: run 1, 0.031 g, 91% yield; run 2, 0.028 g, 85% yield; ^{1}H NMR [400 MHz, $CDCl_3$, only (*Z*)-isomer signals reported] δ 7.68 (2H, d, J = 8.2 Hz), 7.28 (2H, d, J = 8.0 Hz), 7.08 (2H, d, J = 8.6 Hz), 6.85 (2H, d, J = 8.6 Hz), 6.47 (1H, d, J = 11.7 Hz), 5.56 (1H, ddt, J = 16.9, 10.3, 6.5 Hz), 5.39 (1H, dt, J = 11.9, 6.2 Hz), 4.97 (1H, d, J = 10.5 Hz), 4.92 (1H, m), 4.09 (2H, d, J = 6.4 Hz), 3.81 (3H, s), 3.75 (2H, d, J = 6.3 Hz), 2.43 (3H, s); ^{13}C NMR [125 MHz, $CDCl_3$, only (*Z*)-isomer signals reported] δ 158.8, 143.2, 137.4, 132.5, 131.9, 130.0, 129.7, 128.8, 127.3, 125.5, 119.0, 113.7, 55.3, 49.8, 44.6, 21.5; HRMS (ESI+) $C_{20}H_{23}NO_3S$ ($[M + Na]^+$) found 380.1290, expected 380.1291 (+0.3 ppm).

(*Z*)-Penta-1,4-dien-1-ylbenzene (**2k**) was prepared according to the general procedure described above at 140 °C with 15 mol % $NiBr_2$ as a colorless oil with analytical data in agreement with the literature:[36] run 1, 0.025 g, 89% yield; run 2, 0.031 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.26 (5H, m), 6.58 (1H, d, J = 11.5 Hz), 5.97 (1H, ddt, J = 16.9, 10.4, 6.0 Hz), 5.76 (1H, dt, J = 11.5, 7.6 Hz), 5.18 (1H, dd, J = 17.2, 1.6 Hz), 5.11 (1H, d, J = 10.4 Hz), 3.12 (2H, t, J = 6.7 Hz).

(*Z*)-Ethyl 3-phenyl acrylate (**2l**) was prepared according to the general procedure described above as a colorless liquid with analytical data in agreement with the literature.[35] The title compound was isolated as a 3/1 *Z*/*E* isomer mixture: run 1, 0.045 g, quantitative yield; run 2, 0.042 g, quantitative yield; ^{1}H NMR [400 MHz, $CDCl_3$, only (*Z*)-isomer signals reported] δ 7.58 (2H, dd, J = 7.5, 1.7 Hz), 7.36−7.32 (3H, m), 6.95 (1H, d, J = 12.6 Hz), 5.95 (1H, d, J = 12.6 Hz), 4.18 (2H, q, J = 7.1 Hz), 1.24 (3H, t, J = 7.1 Hz).

(*Z*)-Methyl oct-2-enoate (**2m**) was prepared according to the general procedure described above as a colorless liquid with analytical data in agreement with the literature:[11c] run 1, 0.018 g, 53% yield; run 2, 0.028 g, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23 (1H, dt, J = 11.5, 7.5 Hz), 5.77 (1H, d, J = 11.5 Hz), 3.71 (3H, s), 2.65 (1H, qd, J = 7.4, 1.3 Hz), 1.45−1.42 (2H, m), 1.35−1.29 (5H, m), 0.88 (3H, t, J = 6.7 Hz).

(*Z*)-Prop-1-en-1-ylbenzene (**2n**) was prepared according to the general procedure described above at 140 °C with 20 mol % $NiBr_2$ with analytical data in agreement with the literature:[8e] run 1, 70% ^{1}H NMR yield relative to 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard; run 2, 84% ^{1}H NMR yield relative to 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.22 (5H, m), 6.47 (1H, dd, J = 11.6, 1.7 Hz), 5.82 (1H, dq, J = 11.6, 7.2 Hz), 1.93 (3H, dd, J = 7.2, 1.8 Hz).

General Procedure for *E*-Selective Reduction. To an oven-dried 10 mL screw-top vial equipped with a magnetic stirrer bar were added the desired alkyne (0.20 mmol), zinc (1.0 mmol), $NiCl_2$·dme (10 mol %), triphos (10 mol %), 1,4-dioxane (0.5 mL), and HCO_2H (1.0 mmol). The vial was then sealed and transferred to a heating block at 120 °C, and its contents were stirred rapidly (1200 rpm) at this temperature for 16 h. After being allowed to cool, the crude reaction mixture was filtered through a Celite plug; the filter cake was then washed with CH_2Cl_2 and the reaction mixture concentrated *in vacuo* to give the desired (*E*)-alkene.

(*E*)-Stilbene (**3a**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[11b] run 1, 0.042 g, quantitative yield; run 2, 0.047 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.56 (4H, m), 7.44−7.39 (4H, m), 7.34−7.29 (2H, m), 7.17 (2H, s).

(*E*)-1-Methyl-2-styrylbenzene (**3b**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[11b] run 1, 0.038 g, quantitative yield; run 2, 0.028 g, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, d, J = 7.0 Hz), 7.57 (2H, d, J = 7.4 Hz), 7.41 (1H, t, J = 7.6 Hz), 7.38 (1H, d, J = 16.2 Hz), 7.32 (1H, d, J = 7.4 Hz), 7.25−7.22 (4H, m), 7.05 (1H, d, J = 16.2 Hz), 2.44 (3H, s).

(*E*)-1-Methyl-3-styrylbenzene (**3c**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[37] run 1, 0.040 g, quantitative yield; run 2, 0.043 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 7.2 Hz), 7.43−7.37 (4H, m), 7.31 (2H, t, J = 7.7 Hz), 7.15 (2H, s), 7.13 (1H, m), 2.44 (3H, s).

(*E*)-4-Styrylphenol (**3d**) was prepared according to the general procedure described above as a yellow solid with analytical data in agreement with the literature:[38] run 1, 0.034 g, 89% yield; run 2, 0.039 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 8.1 Hz), 7.41 (2H, d, J = 8.1 Hz), 7.35 (2H, t, J = 7.4 Hz), 7.26−7.23

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(1H, m), 7.05 (1H, d, J = 16.3 Hz), 6.97 (1H, d, J = 16.3 Hz), 6.84 (2H, d, J = 8.0 Hz), 4.89 (1H, br s).

(*E*)-1-Methoxy-4-styrylbenzene (**3e**) was prepared according to the general procedure described above as an off-white white solid with analytical data in agreement with the literature:[11b] run 1, 0.049 g, quantitative yield; run 2, 0.043 g, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (4H, m), 7.35 (2H, t, J = 7.6 Hz), 7.24 (1H, t, J = 7.3 Hz), 7.07 (1H, d, J = 16.3 Hz), 6.99 (1H, d, J = 16.3 Hz), 6.93−6.89 (2H, m), 3.84 (3H, s).

(*E*)-1-(Benzyloxy)-4-styrylbenzene (**3f**) was prepared according to the general procedure described above as a yellow solid with analytical data in agreement with the literature:[39] run 1, 0.058 g, quantitative yield; run 2, 0.064 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.36 (14H, m), 6.95 (2H, m), 5.09 (2H, s).

(*E*)-1-Bromo-4-styrylbenzene (**3g**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[34] run 1, 0.042 g, 82% yield; run 2, 0.055 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.47 (4H, m), 7.39−7.35 (4H, m), 7.30−7.28 (1H, m), 7.10 (1H, d, J = 16.3 Hz), 7.04 (1H, d, J = 16.3 Hz).

(*E*)-Methyl 4-styrylbenzoate (**3h**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[34] run 1, 0.045 g, 94% yield; run 2, 0.047 g, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, d, J = 8.3 Hz), 7.60 (4H, app dd, J = 12.0, 8.0 Hz), 7.43 (2H, t, J = 7.5 Hz), 7.36−7.30 (1H, m), 7.26 (1H, d, J = 16.4 Hz), 7.18 (1H, d, J = 16.4 Hz), 3.97 (3H, s).

Ethyl cinnamate (**3i**) was prepared according to the general procedure described above as a colorless liquid with analytical data in agreement with the literature:[35] run 1, 0.040 g, quantitative yield; run 2, 0.042 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, d, J = 16.0 Hz), 7.54−7.52 (2H, m), 7.39−7.37 (3H, m), 6.45 (1H, d, J = 16.0 Hz), 4.27 (2H, q, J = 7.1 Hz), 1.34 (3H, t, J = 7.1 Hz).

(*E*)-Methyl oct-2-enoate (**3j**) was prepared according to the general procedure described above as a 1/1 *E*/*Z* mix with analytical data in agreement with the literature:[36] run 1, 0.047 g, quantitative yield; run 2, 0.047 g, quantitative yield; ^{1}H NMR [400 MHz, $CDCl_3$, a 1/1 *E*/*Z* mixture; only the characteristic (*E*)-olefinic protons are reported] δ 7.01 (1H, dt, J = 15.6, 7.0 Hz), 5.86 (1H, d, J = 15.6 Hz).

(*E*)-Penta-1,4-dien-1-ylbenzene (**3k**) was prepared according to the general procedure described above as a 3/1 *E*/*Z* mixture with analytical data in agreement with the literature:[40] run 1, 0.061 g, quantitative yield; run 2, 0.050 g, 87% yield; ^{1}H NMR [400 MHz, $CDCl_3$, a 3/1 *E*/*Z* mixture; only the characteristic (*E*)-olefinic protons are reported] δ 6.41 (1H, dt, J = 15.9, 1.4 Hz), 6.22 (1H, dt, J = 15.9, 6.7 Hz).

General Procedure for Terminal Alkyne Reduction. To an oven-dried 10 mL screw-top vial equipped with a magnetic stirrer bar were added the desired alkyne (0.20 mmol), zinc (1.0 mmol), $NiBr_2$ (10 mol %), THF (0.5 mL), and HCO_2H (1.0 mmol). The vial was then sealed and transferred to a heating block at 80 °C, and its contents were stirred rapidly (1200 rpm) at this temperature for 16 h. After being allowed to cool, the crude reaction mixture was filtered through a Celite plug; the filter cake was then washed with CH_2Cl_2 and the reaction mixture concentrated *in vacuo* to give the desired alkene.

Styrene (**4a**) was prepared from phenylacteylene according to the general procedure described above to give a colorless oil with analytical data in agreement with those of a commercially available sample: run 1, 0.009 g, 45% yield; run 2, 0.021 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, d, J = 7.5 Hz), 7.33 (2H, t, J = 7.4 Hz), 7.27−7.26 (1H, m), 6.72 (1H, dd, J = 17.6, 10.9 Hz), 5.75 (1H, d, J = 17.6 Hz), 5.25 (1H, d, J = 10.9 Hz).

N-Allyl-4-methyl-*N*-phenylbenzenesulfonamide (**4b**) was prepared according to the general procedure described above as an off-white solid with analytical data in agreement with the literature:[41] run 1, 0.050 g, 86% yield; run 2, 0.054 g, 93% yield; mp 65 °C (Lit.[41] 69 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, d, J = 8.1 Hz), 7.33−7.28 (5H, m), 7.08 (2H, app dd, J = 7.4, 1.8 Hz), 5.78 (1H, ddt, J = 16.8, 10.4, 6.4 Hz), 5.13−5.07 (2H, m), 4.22 (2H, d, J = 6.2 Hz), 2.47 (3H, s).

N,*N*-Diallyl-4-methylbenzenesulfonamide (**4c**) was prepared according to the general procedure described above to give a colorless oil with analytical data in agreement with the literature:[42] run 1, 0.052 g, quantitative yield; run 2, 0.044 g, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (2H, d, J = 8.1 Hz), 7.30 (2H, d, J = 8.1 Hz), 5.66−5.56 (2H, m), 5.15−5.12 (4H, m), 3.80 (4H, d, J = 6.1 Hz), 2.43 (3H, s).

2-Methoxy-6-vinylnaphthalene (**4d**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[43] run 1, 0.037 g, quantitative yield; run 2, 0.040 g, quantitative yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (3H, m), 7.61 (1H, dd, J = 8.8, 1.3 Hz), 7.15−7.12 (2H, m), 6.85 (1H, dd, J = 17.6, 10.9 Hz), 5.82 (1H, d, J = 17.6 Hz), 5.28 (1H, d, J = 10.9 Hz), 3.92 (3H, s).

(8*R*,9*S*,13*S*,14*S*,17*R*)-13-Methyl-17-vinyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (**4e**) was prepared according to the general procedure described above as a white solid with analytical data in agreement with the literature:[37] run 1, 0.046 g, 77% yield; run 2, 0.059 g, 98% yield; ^{1}H NMR (400 MHz, MeOD) δ 7.06 (1H, d, J = 8.3 Hz), 6.53 (1H, dd, J = 8.3, 2.6 Hz), 6.48 (1H, br s), 6.11 (1H, dd, J = 17.3, 10.9 Hz), 5.16 (1H, dd, J = 17.3, 1.5 Hz), 5.11 (1H, dd, J = 10.9, 1.5 Hz), 3.33−3.31 (2H, m), 2.80−1.30 (13H, m), 0.94 (3H, s).

N-Allyl-4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide **4f** was prepared according to the general procedure described above as a colorless oil with analytical data in agreement with the literature:[31] run 1, 0.057 g, quantitative yield; run 2, 0.034 g, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, J = 8.1 Hz), 7.29 (2H, d, J = 8.1 Hz), 5.74 (1H, ddt, J = 17.0, 10.2, 6.5 Hz), 5.27 (1H, d, J = 17.0 Hz), 5.22 (1H, d, J = 10.2 Hz), 4.05 (2H, s), 3.80 (2H, d, J = 6.4 Hz), 2.42 (3H, s), 1.92 (2H, q, J = 7.5 Hz), 0.90 (3H, t, J = 7.5 Hz).

■ ASSOCIATED CONTENT

Supporting Information

Reaction optimization details and spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01047.

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Notes

The authors declare no competing financial interest.

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