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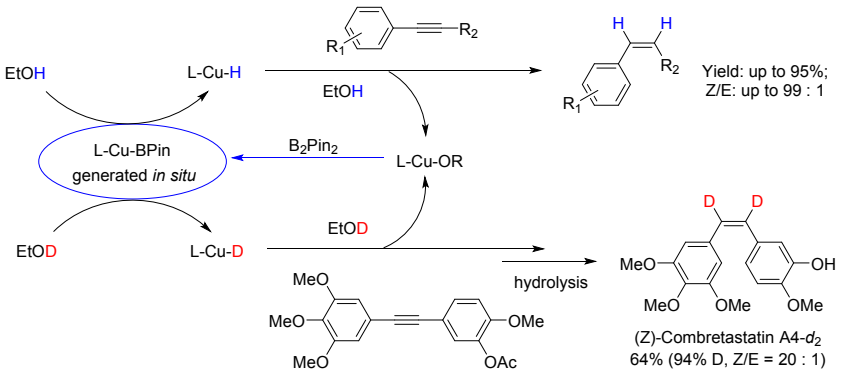
TOC graphic



ABSTRACT

We herein describe a B_2Pin_2-assisted copper-catalyzed semihydrogenation of alkynes. A variety of alkenes were obtained in good to excellent yields with Z-selectivity under mild reaction conditions. Mechanistic studies indicated that a transfer hydrogenation process was involved and ethanol acted as both a solvent and a hydrogen donor in this reaction. The present protocol enabled convenient synthesis of deuterium-substituted Z-alkenes such as Z-Combretastain A4-d_2 in high deuteration ratio by using readily available ethanol-d_1 as the deuterium source.

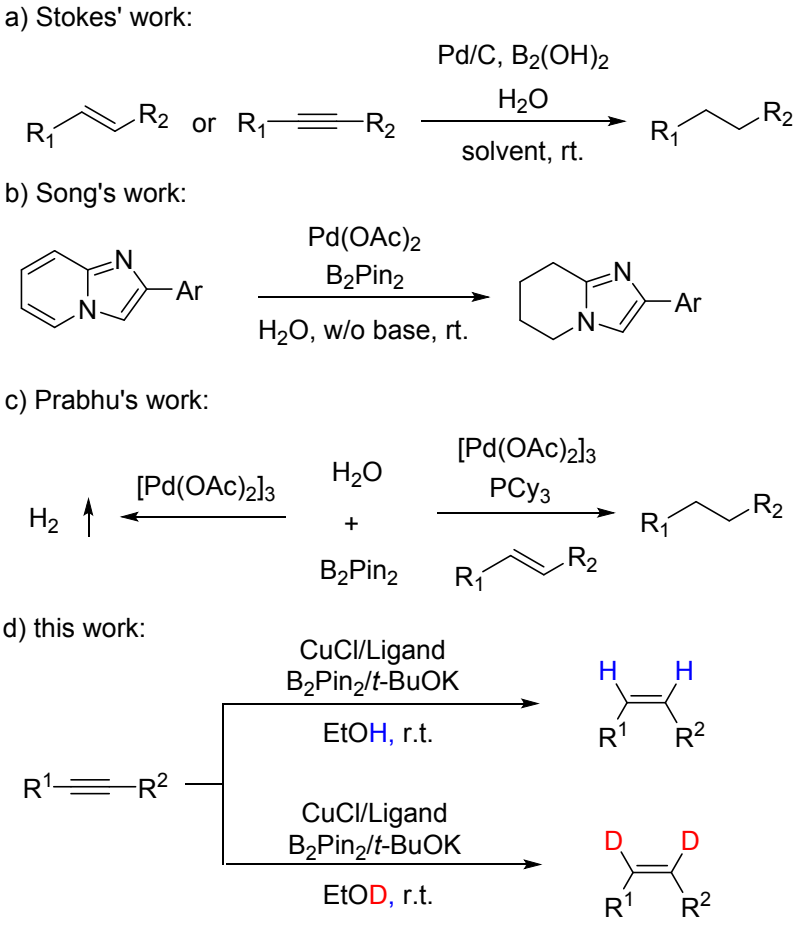
Introduction

Z-Alkene moieties are among the most important structural units in organic molecules due to their practical utilities in some advanced materials as well as their potential bioactivities in various drugs and natural products.[1] As such, a wide range of synthetically useful methods have been established, among which the transition metal-catalyzed (especially palladium) semihydrogenation of alkynes with hydrogen dominates this field for decades.[1d,2] However, the inevitable use of flammable hydrogen gas in those reactions[2d,3] prompts chemists to explore more safe and facile hydrogenation processes.[4-10] In this regard, catalytic transfer hydrogenation (TH) emerges as an alternative way to access Z-alkenes, which necessitates the development of various transfer hydrogenating reagents such as ammonia borane,[4] silane,[5] formic acid-triethylamine,[2f,6] isopropanol,[7] ethanol,[8] and even water.[9] Among them, ethanol and water have received considerable attention due to their intrinsic advantages of easy availability and non-toxicity. Thus, the exploration of TH reactions with water or ethanol as the economical hydrogen sources is still highly desirable.

Typically, diboron reagents served as efficient boron precursors in traditional cross-coupling reactions, C-H activations, and functionalizations of alkenes, etc.[11] In addition, diboron reagents could also serve as reductants for generating hydride from water as exemplified in the reduction of various unsaturated C-C bonds.[12-14] In 2016, Stokes group first described a palladium-catalyzed transfer hydrogenation of alkenes and alkynes with water under the assistance of $B_2(OH)_4$ (Scheme 1a).[12] Soon later, Song group independently reported a palladium-catalyzed transfer hydrogenation

of *N*-heteroaromatics using a combined H_2O/B_2Pin_2 system as the hydrogen source (Scheme 1b).[13] Similarly, Prabhu group conducted a palladium-catalyzed reduction of alkenes or alkynes by using the combined H_2O/B_2Pin_2 system to produce hydrogen (Scheme 1c).[14] Note that these diboron-assisted transfer hydrogenation reactions inevitably produce alkanes, while the selective reduction of alkynes to (Z)-alkenes remains challenging.[12-14] As part of our continued efforts to develop copper-catalyzed efficient transformations,[15] we herein disclose an efficient copper-catalyzed semihydrogenation of alkynes[5b-e,16] to access Z-alkenes with excellent stereoselectivity by using a combined ethanol/B_2pin_2 system as the hydrogen source.

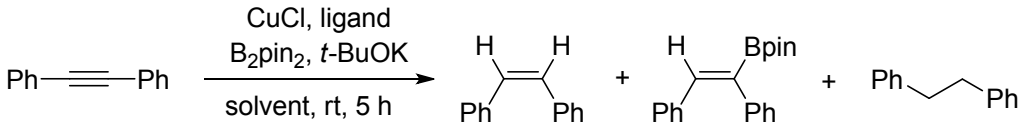
Scheme 1. Diboron-assisted transfer hydrogenation reactions



Results and Discussion

Initially, diphenylacetylene **1a** was selected as the model substrate to investigate the optimal reaction conditions (Table 1). Screening of various ligands revealed that the NHC **L5** gave a high conversion of alkyne in the presence of CuCl (10 mol %), B_2Pin_2 (1.2 equiv) and *t*-BuOK (1.0 equiv) in THF, but a considerable amount of hydroboronated product **3a** was detected (entries 1-5, Table 1). Unfortunately, no hydrogenation occurred when the reaction was carried out in water (entry 6).[12-14] We then chose ethanol as a hydrogen donor as well as a solvent. Gratifyingly, in this case **2a** was obtained in 94% yield with an excellent Z-selectivity (Z/E > 99/1, entry 7, Table 1). Several other alcohols were also surveyed and ethanol was proved to be the most suitable one (entries 8-10 vs 7, Table 1). The use of other NHC ligands in ethanol or in the absence of a ligand only resulted in lower yields of **2a** together with poor Z/E stereoselectivities (entries 11-14 vs 7, Table 1). Several other diboron reagents were also investigated for the reaction, it was found that $B_2(OH)_4$ and $B_2(nep)_2$ (bis(neopentyl glycolato)diboron) could also give good conversion as well as high stereoselectivity, while $B_2(cat)_2$ (biscatecholato)diboron) gave poor results (entries 15-17 vs 7, Table 1). Controlled experiments indicated that B_2Pin_2 and CuCl were indispensable for this semihydrogenation reaction (entries 18, 19, Table 1). Reducing the amount of copper salt, ligand, *t*-BuOK, and B_2Pin_2, respectively, would lower the yield of **2a** (entries 20-23 vs 7, Table 1). When *t*-BuONa was used as a base instead of *t*-BuOK, a comparable yield of **2a** was obtained in 94%, but in slightly lower conversion (entry 24, Table 1). The reaction failed to give **2a** when HBPin was used instead of B_2Pin_2 (entry 25, Table 1).

Table 1. Optimization of reaction conditions[a]



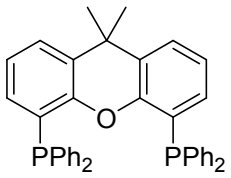
1a **2a** **3a** **4a**

entry	ligand	solvent	H_2O (equiv)	diboron (equiv)	conversion (%)	yield of **2a**/**3a**/**4a** (%)[b]	Z/E for **2a**[c]
1	L1	THF	7.5	B_2Pin_2 (1.2)	94	25/67/2	>99/1
2	L2	THF	7.5	B_2Pin_2 (1.2)	84	4/80/0	--
3	L3	THF	7.5	B_2Pin_2 (1.2)	95	40/54/1	>99/1
4	L4	THF	7.5	B_2Pin_2 (1.2)	92	45/46/1	>99/1
5	L5	THF	7.5	B_2Pin_2 (1.2)	90	28/61/1	>99/1
6	L5	H_2O	--	B_2Pin_2 (1.2)	23	0/23/0	--
7	**L5**	**EtOH**	**--**	**B_2Pin_2 (1.2)**	**99**	**94[d]/4/0**	**>99/1**
8	L5	MeOH	--	B_2Pin_2 (1.2)	89	32/13/0	>99/1
9	L5	*i*-PrOH	--	B_2Pin_2 (1.2)	90	20/68/0	>99/1
10	L5	*t*-BuOH	--	B_2Pin_2 (1.2)	89	0/86/0	--
11	L6	EtOH	--	B_2Pin_2 (1.2)	73	32/37/0	46/1
12	L7	EtOH	--	B_2Pin_2 (1.2)	92	70/22/0	56/1
13	L8	EtOH	--	B_2Pin_2 (1.2)	74	36/33/0	15/1
14	--	EtOH	--	B_2Pin_2 (1.2)	43	15/15/0	11/2
15	L5	EtOH	--	$B_2(OH)_4$ (1.2)	99	90/0/1	>99/1
16	L5	EtOH	--	$B_2(cat)_2$ (1.2)	4	3/0/0	--
17	L5	EtOH	--	$B_2(nep)_2$ (1.2)	97	92/0/0	>99/1
18	L5	EtOH	--	--	0	0/0/0	--
19[e]	L5	EtOH	--	B_2Pin_2 (1.2)	10	6/4/0	1/1
20[f]	L5	EtOH	--	B_2Pin_2 (1.2)	81	78/3/0	>99/1
21[g]	L5	EtOH	--	B_2Pin_2 (1.2)	99	89/9/0	>99/1
22[h]	L5	EtOH	--	B_2Pin_2 (1.2)	0	0/0/0	--
23	L5	EtOH	--	B_2Pin_2 (1.0)	91	86/4/0	>99/1
24[i]	L5	EtOH	--	B_2Pin_2 (1.2)	95	94/1/0	>99/1
25[j]	L5	EtOH	--	--	0	0/0/0	--

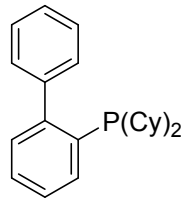
[a]Reaction conditions: **1a** (0.2 mmol), CuCl (10 mol %), ligand (15 mol %), B_2Pin_2 (0.24 mmol),

t-BuOK (0.2 mmol), solvent (3.0 mL), 25 ºC for 5 h under N_2 atmosphere unless otherwise noted. [b]Yield was determined by GC analysis using diphenyl as an internal standard. [c]Z/E ratio was determined by GC analysis. [d]Isolated yield: 92%. [e]Without CuCl. [f]CuCl (5 mol%) and **L5** (7.5 mol%). [g]*t*-BuOK (50 mol%). [h]*t*-BuOK (15 mol%). [i]*t*-BuONa (1.0 equiv.) was used instead of *t*-BuOK. [j]HBPin (1.2 equiv.) was used instead of B_2Pin_2.

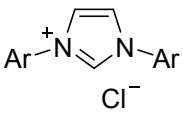
dppe (**L1**)



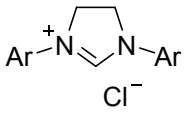
Xantphos (**L2**)



CyJohnPhos (**L4**)



IMes•HCl (**L5**): Ar = 2,4,6-trimethylphenyl
IPr•HCl (**L6**): Ar = 2,6-diisopropylphenyl

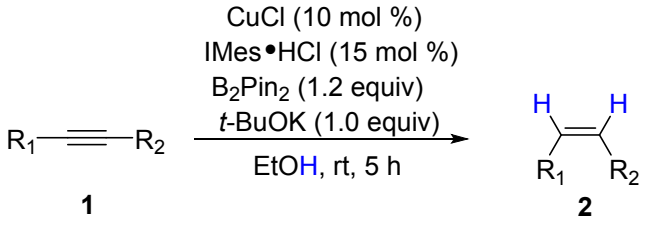


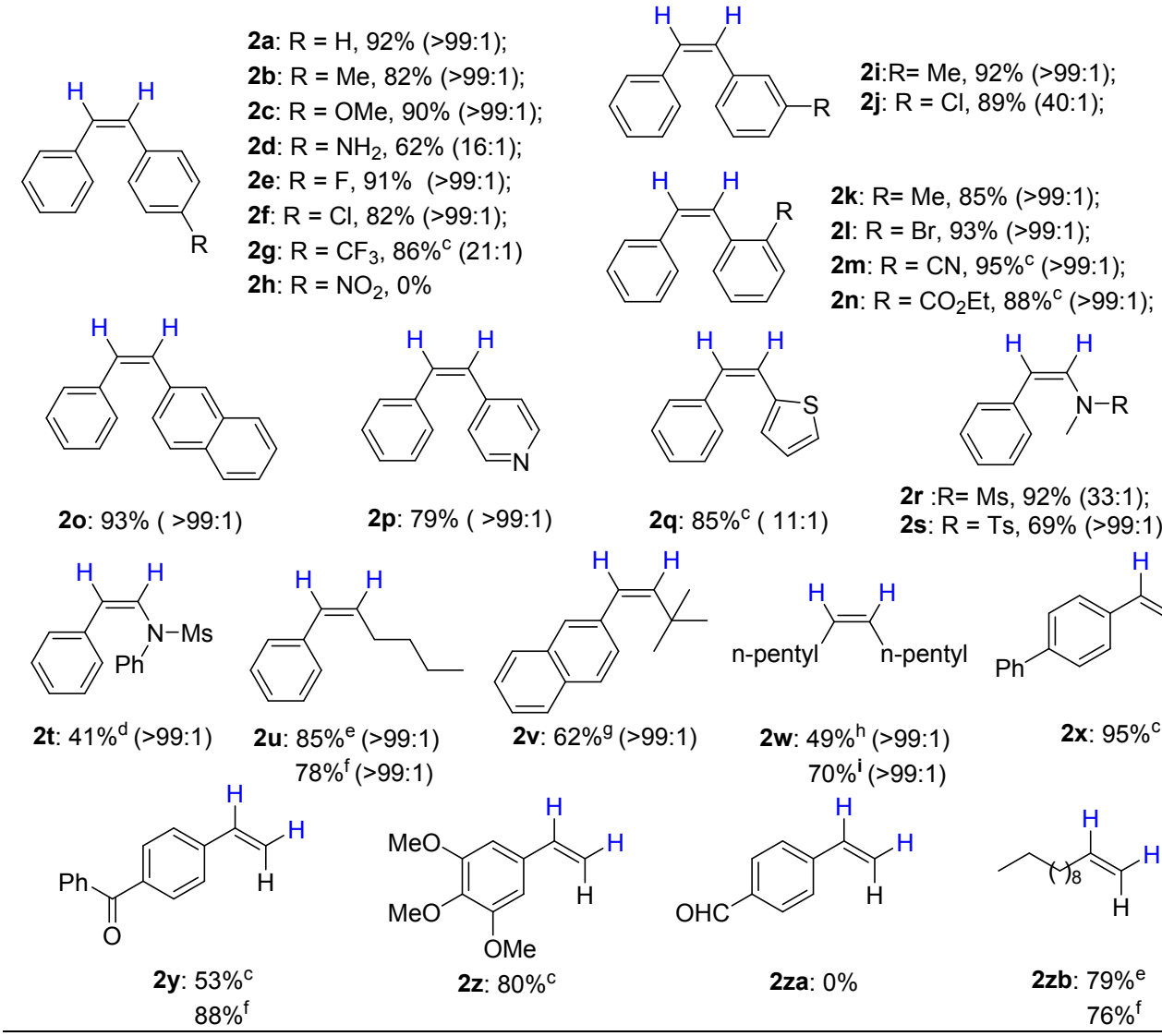
SIMes•HCl (**L7**): Ar = 2,4,6-trimethylphenyl
SIPr•HCl (**L8**): Ar = 2,6-diisopropylphenyl

With the optimized reaction conditions in hand, the substrate scope of alkynes **1** was first examined as shown in Table 2. Both electron-donating and electron-withdrawing substituents on the benzene ring of alkynes **1** were compatible with the reaction conditions and the desired Z-alkenes **2** were obtained in good yields (except **1h**) with excellent stereoselectivities (**2a-g**, **2k-o)**. Alkynes bearing a heteroarene such as 4-pyridinyl or 2-thienyl ring were also tolerable under the current reaction conditions to give Z-alkenes in good yields with high stereoselectivity (**2p**, **2q**). Notably, this transfer semihydrogenation process could be applied to ynamines leading to the formation of Z-enamines which could be used as versatile building blocks in organic synthesis (**2r-t**). Aryl alkyl acetylenes such as hex-1-yn-1-ylbenzene **1u** and 2-(3,3-dimethylbut-1-yn-1-yl)naphthalene **1v** were

also workable for the semihydrogenation to give highly selective Z-alkene albeit in moderate yields (**2u**, **2v**). An aliphatic internal alkyne **1w** could also be semihydrogenated to give the corresponding Z-alkene **2w** in excellent stereoselectivity (**2w**). As expected, the semihydrogenation of terminal alkynes also proceeded smoothly to give the corresponding alkenes in moderate to excellent yields (**2x-2z**, **2zb**) except in the case of **1za** as a substrate.

Table 2. Substrate scope of alkynes.[a,b]

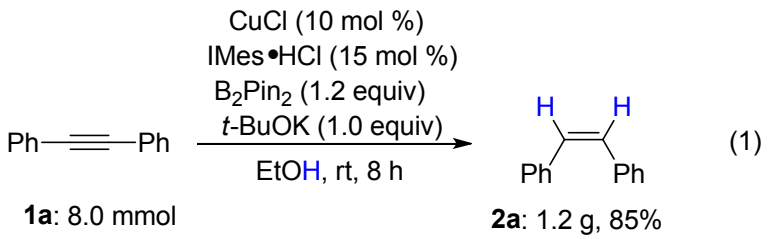




[a]Reaction conditions: **1** (0.2 mmol), CuCl (10 mol %), IMes·HCl (15 mol %), B_2Pin_2 (0.24 mmol), t-BuOK (0.2 mmol), ethanol (3.0 mL), 25 ºC for 5 h under N_2 atmosphere unless otherwise noted. [b]The Z/E ratios were determined by GC-MS. [c]The reaction time was prolonged to 12 h. [d]39% of **1s** was recovered. [e]The reaction temperature was increased to 80 ºC and the reaction time was prolonged to 12 h. [f]$B_2(OH)_4$ (0.24 mmol) was used instead of B_2Pin_2 at 25 ºC and the reaction time was prolonged to 12

h. [g]26% of **1t** was recovered. [h]Reaction condition: **1w** (0.2 mmol), CuCl (15 mol%), IMes·HCl (22.5 mol %), B_2Pin_2 (0.3 mol), *t*-BuOK (0.2 mmol), ethanol (3.0 mL), 80 °C for 36 h under N_2 atmosphere. [i]Reaction condition: **1w** (0.2 mmol), CuCl (15 mol %), IMes·HCl (22.5 mol%), B_2OH_4 (0.3 mol), *t*-BuOK (0.2 mmol), ethanol (3.0 mL), 25 ºC for 12 h under N_2 atmosphere.

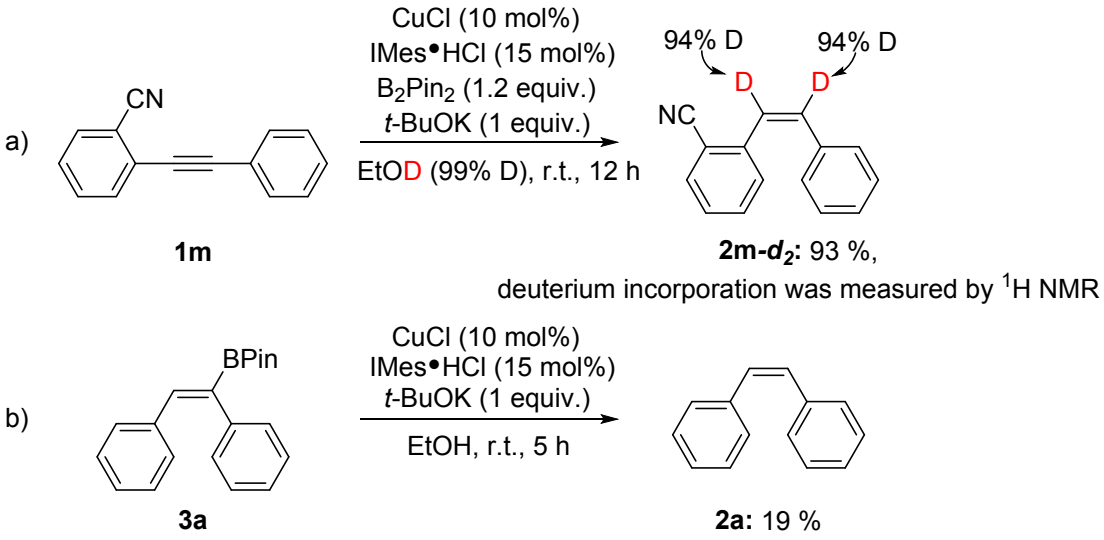
In addition, a gram-scale (8.0 mmol of **1a** used) synthesis of **2a** was also tried, and the target Z-alkene **2a** was obtained in 85% yield (eq. 1).



(1)

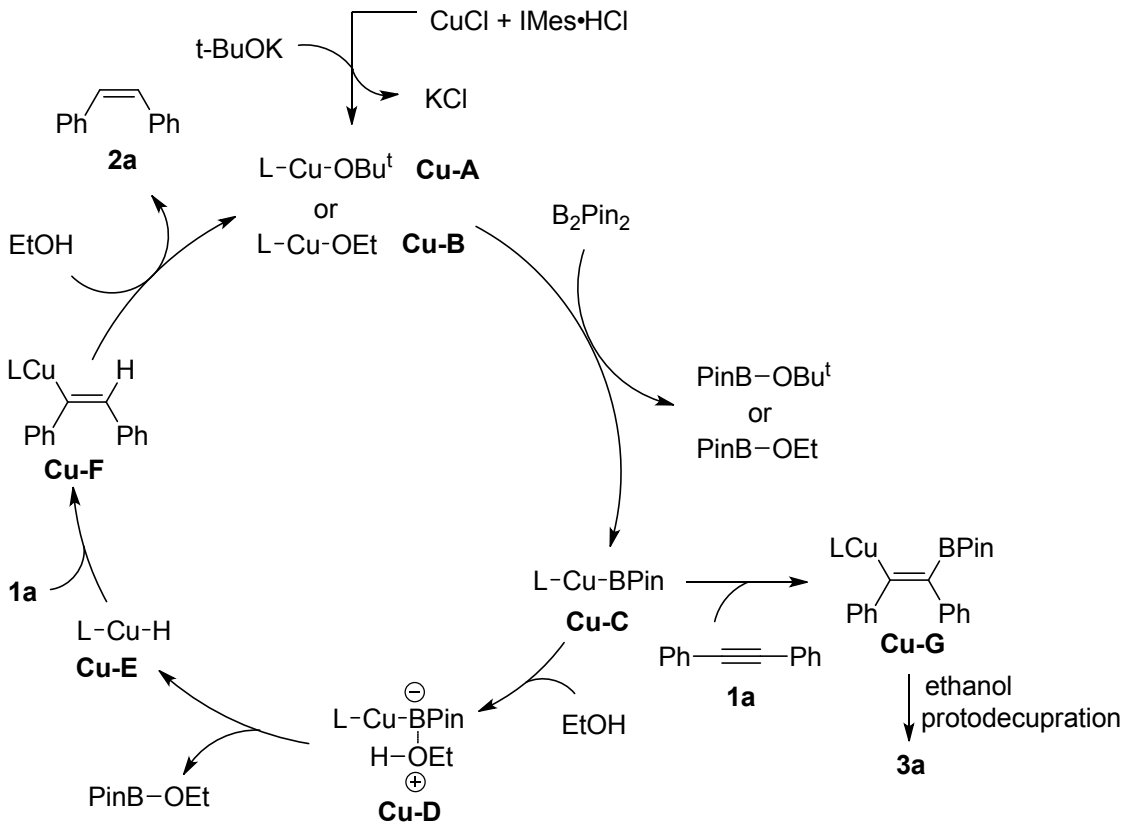
To gain insight into the mechanism of the reaction, a deuterium-labeled experiments was first carried out (Scheme 2a). When EtOD (99% D-enrichment of the hydroxyl proton) was used as the solvent, the deuterium was incorporated into both the 1,2-olefinic positions of **2m-*d*$_2$** (both 94% D-enrichment) (Scheme 2a). This result suggested that ethanol acted as a hydrogen donor in this reaction. To probe the possible intermediate,[17] the byproduct **3a** was subjected to the standard conditions without the extra addition of B_2Pin_2 (Scheme 2b). As a result, a low yield of **2a** (19%) was obtained which indicated that **3a** might not be the most likely intermediate in the catalytic cycle.

Scheme 2. Mechanistic experiments



On the basis of the above experiments and previous literature,[12-14,18] a plausible mechanism was described in Scheme 3. The alkoxocopper species **Cu-A** was first formed and it further reacted with B_2Pin_2 to produce the Cu-boron complex **Cu-C**. Ethanol could then coordinate to boron atom, followed by a hydrogen transfer to generate copper hydride species **Cu-E**. The *syn*-addition of **Cu-E** to the alkyne **1a** afforded the vinylcuprate intermediate **Cu-F**. The protonation of **Cu-F** by ethanol released the Z-alkene and regenerated the active catalyst.

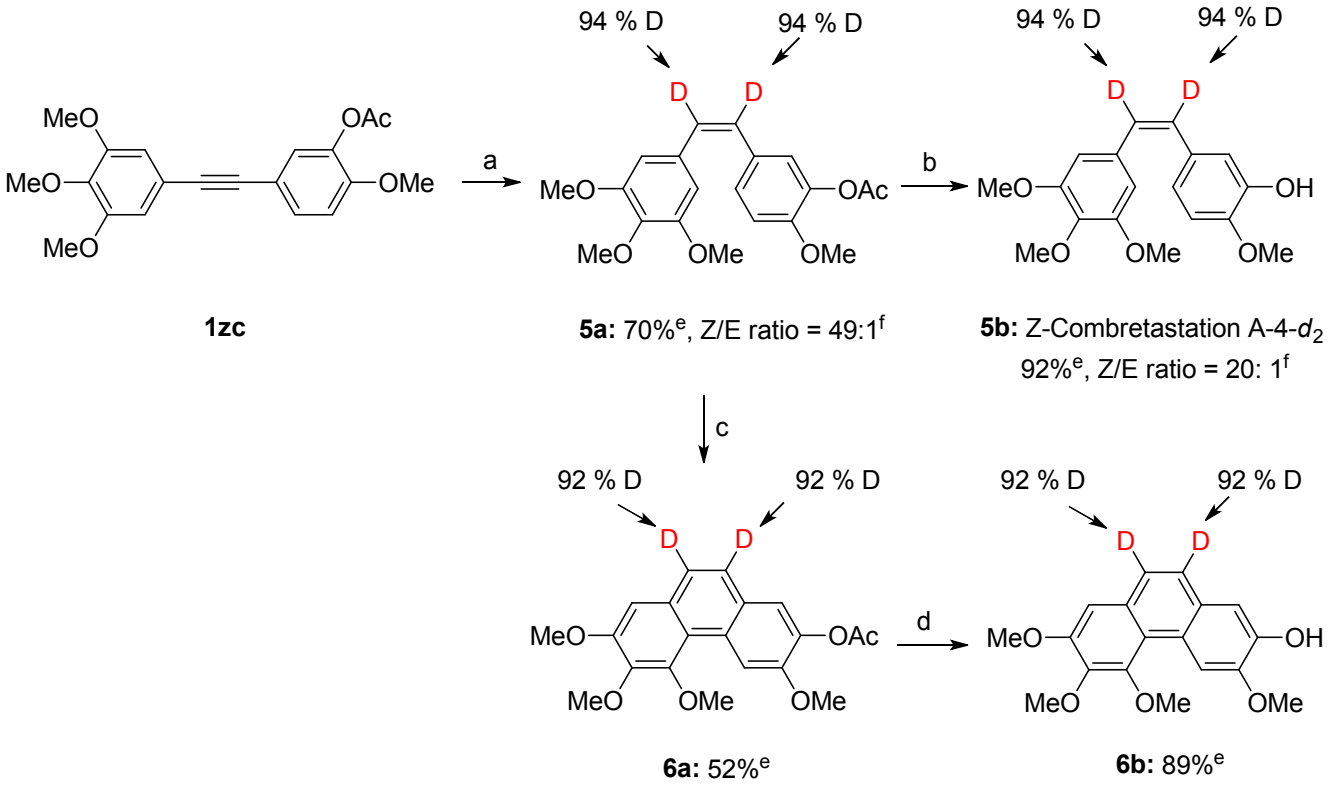
Scheme 3. Proposed mechanism



Recent researches indicated that the incorporation of deuterium into drugs or nature products would significantly improve their pharmacological and biological activities.[19] From the above mechanism illustration, we can expect that the present protocol enables an expedient way to access olefinic deuterium-incorporated Z-alkenes by using commercially available ethanol-d_1 as the deuterium source. To fully demonstrate the synthetic potential of the present protocol, the synthesis of deuterated Z-Combretastation A-4-d_2 **5b** from alkyne **1zc** was carried out under our catalytic system (Scheme 4).[4b,5d] Gratifyingly, a total 64% yield of **5b** with a 94% D-enrichment at both the 1,2-olefinic positions was obtained through a two-step process. Furthermore, the resulting intermediate **5a** from **1zc** could be easily converted to the corresponding phenanthrenes-d_2 **6a** and **6b** almost without a deuterium loss.[20]

Note that these deuterium-labeled compounds might exhibit unique bioactivities compared to the unlabeled ones.[1c,21,22]

Scheme 4. Synthesis of Z-Combretastation A-4-d_2 and Phenanthrenes-d_2



Reaction condition: (a) **1zc** (0.2 mmol), CuCl (10 mol %), IMes·HCl (15 mol %), B_2Pin_2 (0.24 mmol), t-BuOK (0.2 mmol), EtOD (3.0 mL, 99% D-enrichment), 25 ºC for 10 h under N_2 atmosphere. (b) **5a** (0.2 mmol), K_2CO_3 (0.6 mmol), MeOH (6 mL), 25 ºC for 5 h. (c) **5a** (0.2 mmol), I_2 (0.2 mmol), cyclohexane (100 mL), irradiated at a distance of 5 cm from 500 W high pressure mercury lamp for 5 h at room temperature. (d) **6a** (0.2 mmol), K_2CO_3 (0.6 mmol), MeOH (6 mL), 25 ºC for 5 h. (e) Isolated yields. (f) Z/E ratios were determined by GC analysis and deuterium incorporations were measured by ^{1}H NMR analysis.

Conclusion

In summary, we have developed an efficient copper-catalyzed transfer semihydrogenation of various alkynes to stereoselectively afford Z-alkenes in high yields with a combined ethanol/B_2Pin_2 system as the hydrogen source. The present protocol has advantages of mild reaction conditions, inexpensive catalyst, excellent stereoselectivity, and good functional group tolerance. Moreover, the present strategy enabled a convenient way to access deuterium-labeled molecules such as Z-Combretastation A-4-d_2 and Phenanthrenes-d_2 in highly selective manner using readily available ethanol-d_1 as the deuterium source which demonstrates the practically useful application of our protocol in organic synthesis.

Experimental Section

Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 500 MHz, 125 MHz, respectively, with TMS as internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. GC-MS experiments were performed with EI source; high resolution mass spectra (HRMS) were obtained on a TOF-MS instrument with EI or ESI source.

Preparation of the starting material 1 and 3a. Alkynes (**1a-1q, 1v**) were synthesized via a Sonogashira cross-coupling reaction according to the literature procedure.[4c] The ynamines (**1r-1t**) were synthesized according to the known literature procedure.[23] Alkynes (**1y-1za**) were synthesized via a

Sonogashira cross-coupling reaction of corresponding aryl iodide with trimethylsilylacetylene according to the literature procedure, subsequently hydrolysis of trimethysilylethynyl-substrates.[24] The **3a** was synthesized from **1a** under the standard reaction conditions by using *t*-BuOH as the solvent instead of EtOH.

Preparation of the starting material 1zc.[4b,5d] 5-ethynyl-1,2,3-trimethoxybenzene (1.77 g, 3 mmol), 5-iodo-2-methoxyphenol (0.75 g, 3 mmol), $Pd(PPh_3)_4$ (158 mg, 0.14 mmol) and CuI (23 mg, 0.12 mmol) were added to a 50 mL Schlenk flash with a stir bar under an atmosphere of nitrogen. Then pyrrolidine (20 mL) were added sequentially. The reaction mixture was stirred at 80 ºC overnight. Then a saturated NH_4Cl solution (20 mL) was added into it. The mixture was extracted with Et_2O (20 mL × 3), the combined organic fractions were washed with brine and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with the mixture of ethyl acetate (EA)/petroleum ether (PE) = 3/1 to give 2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (yellow solid, 740.0 mg, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10 (d, J = 2.0 Hz, 1H), 7.07 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 6.83 (d, J = 8.5 Hz, 1H), 6.79 (s, 2H), 5.70 (s, 1H), 3.92 (s, 3H), 3.88 (s, 6H), 3.87 (s, 3H).[5d] Then acetyl chloride (197 mg, 2.61 mmol) was added slowly to a solution of 2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenol (740 mg, 2.4 mmol), Et_3N (0.75 mL, 5.2 mmoL) and dry CH_2Cl_2 (3 mL) at 0 ºC under an atmosphere of nitrogen, the mixture was allowed to warm to room temperature and stirred for 6 h. Upon completion, quenching the reaction with water (5 mL). The mixture was extracted with CH_2Cl_2, the organic fractions were combined. Afterwards the solvent was

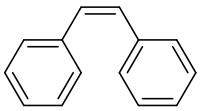
removed under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with the mixture of ethyl acetate (EA)/ petroleum ether (PE) = 3/1 to give pure **1zc** (white solid, 752.0 mg, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 7.23 (d, J = 2.5 Hz, 1H), 6.94 (d, J = 8.5 Hz, 1H), 6.75 (s, 2H), 3.88 (s, 6H), 3.87 (s, 3H), 3.86 (s, 3H), 2.33 (s, 3H).

General procedure for the synthesis of Z-alkenes 2. CuCl (2.0 mg, 0.02 mmol, 10 mol %), IMes·HCl (10.2 mg, 0.03 mmol, 15 mol %) and *t*-BuOK (22.4 mg, 0.2 mmol, 1 equiv) were placed in a dried 25 mL Schlenk tube. The tube was evacuated and refilled with N_2 three times. Ethanol (1.0 mL) was added and the resulting mixture was stirred at room temperature for 15 min. A solution of **1** (0.2 mmol), B_2Pin_2 (61.0 mg, 0.24 mmol, 1.2 equiv) and ethanol (2 mL) was then added and the mixture was stirred at room temperature for 5 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure Z-alkene **2**.

Gram-scale synthesis of 2a. CuCl (79.0 mg, 0.8 mmol, 10 mol %), IMes·HCl (409.0 mg, 1.2 mmol, 15 mol %) and *t*-BuOK (898.0 mg, 8.0 mmol, 1 equiv.) were placed in a dried 250 mL Schlenk flash. The flash was evacuated and refilled with N_2 three times. Ethanol (40 mL) was added and the resulting mixture was stirred at room temperature for 15 min. A solution of **1a** (1.4 g, 8.0 mmol), B_2Pin_2 (2.4 g, 9.6 mmol, 1.2 equiv) and ethanol (80 mL) was then added and the mixture was stirred at room temperature for 8 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with petroleum

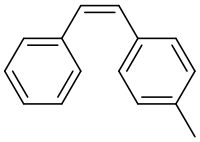
ether (PE) to give pure Z-alkene **2a** as colorless liquid (1.2 g, 85%).

(Z)-1,2-diphenylethene (2a)[4c]



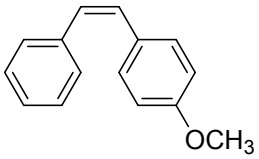
Product was isolated via column chromatography (PE) as colorless liquid (33.0 mg, 92%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25-7.15 (m, 10H), 6.59 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 137.3, 130.3, 128.9, 128.2, 127.1.

(Z)-1-methyl-4-styrylbenzene (2b)[4c]



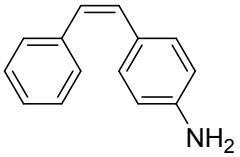
Product was isolated via column chromatography (PE) as colorless liquid (31.8 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27-7.13 (m, 7H), 7.01 (d, J = 8.0 Hz, 2H), 6.55 (s, 2H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 137.6, 136.9, 134.3, 130.3, 129.6, 128.9, 128.9, 128.8, 128.2, 127.0, 21.3.

(Z)-1-methoxy-4-styrylbenzene (2c)[4c]



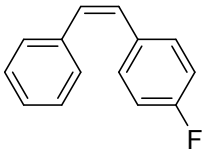
Product was isolated via column chromatography (PE/EA 100:1) as yellow liquid (37.9 mg, 90%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34-7.22 (m, 7H), 6.62-6.79 (m, 2H), 6.59 (d, J = 12.0 Hz, 1H), 6.56 (d, J = 12.0 Hz, 1H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 158.7, 137.6, 130.2, 129.8, 129.7, 128.82, 128.78, 128.2, 126.9, 113.6, 55.2.

(Z)-2-styrylaniline (2d)[4c]



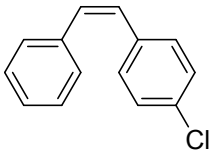
Product was isolated via column chromatography (PE/EA 20:1-5:1) as yellow liquid (24.3 mg, 62%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35-7.20 (m, 5H), 7.11 (d, J = 8.0 Hz, 2H), 6.57-6.55 (m, 2H), 6.52 (d, J = 12.0 Hz, 1H), 6.47 (d, J = 12.0 Hz, 1H), 3.68 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 145.5, 138.0, 130.2, 130.1, 128.8, 128.2, 127.6, 127.5, 126.7, 114.7.

(Z)-1-fluoro-4-styrylbenzene (2e)[4c]



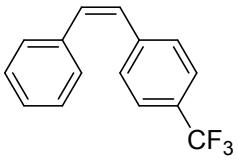
Product was isolated via column chromatography (PE) as colorless liquid (36 mg, 91%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.22 (m, 7H), 6.94 (t, J = 8.8 Hz, 2H), 6.63 (d, J = 12.2 Hz, 1H), 6.58 (d, J = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 161.8 (d, J =246.7 Hz), 137.1, 133.2 (d, J = 3.5 Hz), 130.5 (d, J = 7.9 Hz), 130.3 (d, J = 1.0 Hz), 129.1, 128.8, 128.3, 127.2, 115.2 (d, J = 21.4 Hz).

(Z)-1-chloro-4-styrylbenzene (2f)[4c]



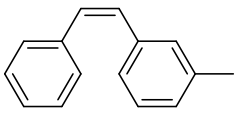
Product was isolated via column chromatography (PE) as colorless liquid (35 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.21 (m, 9H), 6.68 (d, J = 12.2 Hz, 1H), 6.58 (d, J = 12.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 136.9, 135.7, 132.8, 131.0, 130.2, 128.9, 128.8, 128.4, 128.3, 127.3.

(Z)-1-styryl-4-(trifluoromethyl)benzene (2g)[4c]



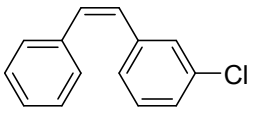
Product was isolated via column chromatography (PE) as colorless liquid (42.8 mg, 86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30-7.24 (m, 5H), 6.75 (d, *J* = 12.2 Hz, 1H), 6.62 (d, *J* = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 141.0, 136.6, 132.3, 129.1, 129.0 (q, *J* = 32.5 Hz), 128.8, 128.7, 128.4, 127.6, 125.1 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.1 Hz).

(Z)-1-methyl-3-styrylbenzene (2i)[4c]



Product was isolated via column chromatography (PE) as colorless liquid (35.8 mg, 92%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.21 (m, 5H), 7.17-7.05 (m, 4H), 6.62 (s, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 137.8, 137.4, 137.2, 130.4, 130.1, 129.6, 128.9, 128.2, 128.1, 127.9, 127.1, 125.9, 21.3.

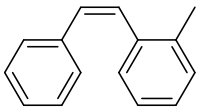
(Z)-1-chloro-3-styrylbenzene (2j)[4c]



Product was isolated via column chromatography (PE) as colorless liquid (38.3 mg, 89%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30-7.14 (m, 9H), 6.69 (d, *J* = 12.2 Hz, 1H), 6.56 (d, *J* = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 139.1, 136.6, 134.1, 131.6, 129.4, 128.9, 128.8, 128.7, 128.3, 127.5, 127.1,

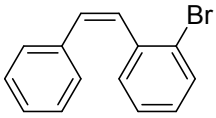
127.0.

(Z)-1-methyl-2-styrylbenzene (2k)[4c]



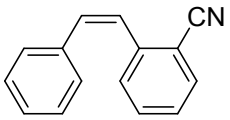
Product was isolated via column chromatography (PE) as colorless liquid (33 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25-7.08 (m, 9H), 6.70 (d, J = 12.2 Hz, 1H), 6.66 (d, J = 12.2 Hz, 1H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 137.13, 137.05, 136.1, 130.5, 130.1, 129.6, 128.93, 128.89, 128.1, 127.2, 127.0, 125.7, 19.9.

(Z)-1-bromo-2-styrylbenzene (2l)[25]



Product was isolated via column chromatography (PE) as colorless liquid (48.3 mg, 93%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67-7.62 (m, 1H), 7.24-7.17 (m, 6H), 7.14-7.10 (m, 2H), 6.73 (d, J = 12.1 Hz, 1H), 6.66 (d, J = 12.1 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 138.0, 136.4, 132.7, 131.4, 130.9, 129.5, 129.0, 128.7, 128.2, 127.3, 127.0, 123.9.

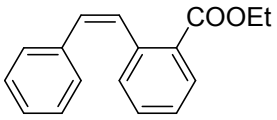
(Z)-2-styrylbenzonitrile (2m)



Product was isolated via column chromatography (PE/EA 100:1) as yellow liquid (39.0 mg, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, J = 8.3 Hz, 1H), 7.40-7.30 (m, 3H), 7.25-7.23 (m, 3H), 7.18-7.16 (m, 2H), 6.88 (d, J = 12.2 Hz, 1H), 6.80 (d, J = 12.2 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ

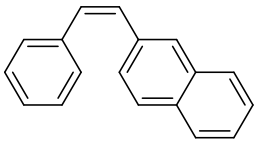
141.2, 135.9, 134.4, 132.9, 132.2, 129.7, 128.9, 128.4, 127.8, 127.5, 125.9, 117.9, 112.3; HRMS (ESI) for $C_{15}H_{11}NNa$ $[M + Na]^+$: calcd. 228.0784, found 228.0786.

ethyl (Z)-2-styrylbenzoate (2n)



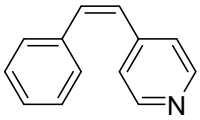
Product was isolated via column chromatography (PE/EA 100:1) as yellow liquid (44.4 mg, 88%). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.05-8.01 (m, 1H), 7.34-7.29 (m, 2H), 7.25-7.22 (m, 1H), 7.18-7.12 (m, 3H), 7.10-7.07 (m, 3H), 6.67 (d, J = 12.0 Hz, 1H), 4.38 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 167.1, 139.6, 136.8, 131.8 131.0, 130.5, 129.6, 129.5, 129.2, 128.0 (2C), 127.0, 126.9, 61.0, 14.3; HRMS (ESI) for $C_{17}H_{17}O_2$ $[M + H]^+$: calcd. 253.1223, found 253.1224.

(Z)-1-styrylnaphthalene (2o)[26]



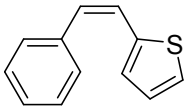
Product was isolated via column chromatography (PE) as colorless liquid (42.7 mg, 93%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.84-7.75 (m, 3H), 7.70 (d, J = 8.5 Hz, 1H), 7.50-7.47 (m, 2H), 7.41 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.36-7.34 (m, 2H), 7.30-7.24 (m, 3H), 6.82 (d, J = 12.0 Hz, 1H), 6.74 (d, J = 12.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 137.3, 134.9, 133.5, 132.6, 130.6, 130.2, 129.0, 128.3, 128.0, 128.0, 127.6, 127.5, 127.2, 127.0, 126.0, 125.9.

(Z)-4-styrylpyridine (2p)[4c]



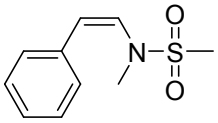
Product was isolated via column chromatography (PE/EA = 10:1-3:1) as colorless liquid (28.6 mg, 79%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.46 (d, J = 1.0 Hz, 2H), 7.28-7.21 (m, 5H), 7.12 (d, J = 5.5 Hz, 2H), 6.81 (d, J = 12.0 Hz, 1H), 6.51 (d, J = 12.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 149.8, 145.0, 136.2, 134.1, 128.8, 128.5, 127.9, 127.6, 123.5.

(Z)-2-styrylthiophene (2q)[26]



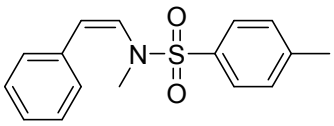
Product was isolated via column chromatography (PE) as colorless liquid (31.3 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.33 (m, 5H), 7.13 (d, J = 5.0 Hz, 1H), 7.02 (d, J = 3.5 Hz, 1H), 6.93 (dd, J_1 = 5.1 Hz, J_2 = 3.6 Hz, 1H), 6.75 (d, J = 12.0 Hz, 1H), 6.63 (d, J = 12.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 139.8, 137.4, 128.9, 128.8, 128.5, 128.1, 127.5, 126.4, 125.5, 123.4.

(Z)-N-methyl-N-styrylmethanesulfonamide (2r)



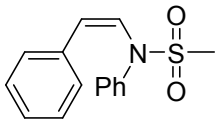
Product was isolated via column chromatography (PE/EA = 10:1) as colorless liquid (38.9 mg, 92%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42-7.41 (m, 2H), 7.36-7.33 (m, 2H), 7.28-7.26 (m, 1H), 6.35 (d, J = 9.0 Hz, 1H), 6.07 (d, J = 9.0 Hz, 1H), 2.94 (s, 3H), 2.90 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 134.6, 128.9, 128.2, 127.6, 126.9, 120.5, 36.4, 36.1; HRMS (ESI) for $C_{10}H_{13}NNaO_2S$ $[M + Na]^+$: calcd. 234.0559, found 234.0569.

(Z)-N,4-dimethyl-N-styrylbenzenesulfonamide (2s)[8]



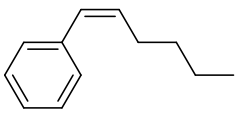
Product was isolated via column chromatography (PE/EA = 10:1) as colorless liquid (39.5 mg, 69%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78-7.76 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.29-7.21 (m, 5H), 6.27 (d, J = 9.0 Hz, 1H), 6.03 (d, J = 9.0 Hz, 1H), 2.77 (s, 3H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 144.0, 134.9, 134.2, 129.8, 129.0, 128.2, 127.6, 127.5, 127.3, 121.0, 36.6, 21.6.

(Z)-4-methyl-N-phenyl-N-styrylbenzenesulfonamide (2t)



Product was isolated via column chromatography (PE/EA = 10:1) as yellow solid (22.4 mg, 41%). m.p. 93.5-94.6 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.31 (m, 2H), 7.20-7.16 (m, 4H), 7.11-7.04 (m, 4H), 6.71 (d, J = 9.1 Hz, 1H), 6.15 (d, J = 9.1 Hz, 1H), 2.94 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 139.1, 133.8, 128.92, 128.90, 127.7, 127.3, 127.2, 126.9, 126.2, 121.8, 37.1; HRMS (ESI) for $C_{15}H_{15}NNaO_2S$ $[M + Na]^+$: calcd. 296.0716, found 296.0724.

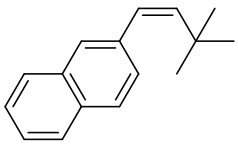
(Z)-hex-1-en-1-ylbenzene (2u)[26]



Product was isolated via column chromatography (PE) as colorless liquid (27.2 mg, 85%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.31 (m, 4H), 7.27-7.23 (m, 1H), 6.44 (d, J = 11.7 Hz, 1H), 5.71 (dt, J_1 = 11.7 Hz, J_2 = 7.3 Hz, 1H), 2.40-2.35 (m, 2H), 1.51-1.45 (m, 2H), 1.43-1.36 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 137.8, 133.2, 128.7, 128.7, 128.1, 126.4, 32.2, 28.3, 22.4,

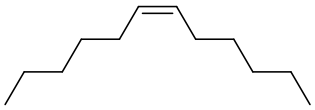
14.0.

(Z)-1-(3,3-dimethylbut-1-en-1-yl)naphthalene (2v)



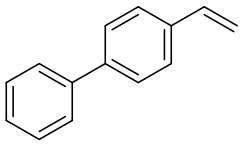
Product was isolated via column chromatography (PE/EA = 50:1) as colorless liquid (26.0 mg, 62%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.85-7.82 (m, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.51-7.45 (m, 2H), 7.67 (s, 1H), 7.37 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 6.58 (d, J = 12.5 Hz, 1H), 5.73 (d, J = 12.5 Hz, 1H), 1.04 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 143.1, 140.0, 133.0, 132.0, 127.8, 127.7, 127.6, 127.3, 127.1, 127.0, 126.0, 125.5, 34.3, 31.3. HRMS (EI) for $C_{16}H_{18}$ [M^+]: calcd. 210.1409, found 210.1415.

(Z)-dodec-6-ene (2w)[4c]



Product was isolated via column chromatography (PE) as colorless liquid (23.6 mg, 70%, conversion: 82%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.40-5.34 (m, 2H), 2.05-2.01 (m, 4H), 1.39-1.27 (m, 12H), 0.91 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 129.9, 31.6, 29.5, 27.2, 22.6, 14.1.

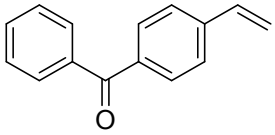
4-vinyl-1,1'-biphenyl (2x)[27]



Product was isolated via column chromatography (PE) as white solid (34.1 mg, 95%). m.p. 122.5-123.8 °C (lit.[27] m.p. 118-120 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.55 (m, 4H), 7.49-7.41 (m, 4H), 7.35-7.31 (m, 1H), 6.75 (dd, J_1 = 18.0 Hz, J_2 = 11.0 Hz, 1H), 5.79 (dd, J_1 = 17.5 Hz, J_2 = 1.0

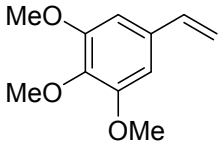
Hz, 1H), 5.27 (dd, J_1 = 11.0 Hz, J_2 = 1.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 140.8, 140.6, 136.7, 136.5, 128.8, 127.3, 127.3, 127.0, 126.7, 113.9.

phenyl(4-vinylphenyl)methanone (2y)[28]



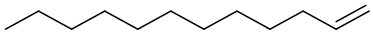
Product was isolated via column chromatography (PE/EA = 20:1) as colorless liquid (36.7 mg, 88%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.82-7.80 (m, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.53-7.49 (m, 4H), 6.80 (dd, J_1 = 17.6 Hz, J_2 = 10.9 Hz, 1H), 5.91 (d, J = 17.6 Hz, 1H), 5.43 (d, J = 10.9 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 196.2, 141.6, 137.8, 136.7, 136.0, 132.3, 130.6, 130.0, 128.3, 126.1, 116.6.

1,2,3-trimethoxy-5-vinylbenzene (2z)[29]



Product was isolated via column chromatography (PE/EA = 50:1) as colorless liquid (31.0 mg, 80%). ^1H NMR ($CDCl_3$, 500 MHz): δ 6.68-6.62 (m, 3H), 5.67 (d, J = 17.5 Hz, 1H), 5.23 (d, J = 10.8 Hz, 1H), 3.90 (s, 6H), 3.86 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 153.3, 138.1, 136.8, 133.3, 113.2, 103.3, 60.9, 56.1.

dodec-1-ene (2zb)[30]



Product was isolated via column chromatography (PE) as colorless liquid (26.7 mg, 79%). ^1H NMR ($CDCl_3$, 500 MHz): δ 5.88-5.79 (m, 1H), 5.03-4.99 (m, 1H), 5.96-5.93 (m, 1H), 2.08-2.04 (m, 2H),

1.41-1.28 (m, 16H), 0.90 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 139.3, 114.1, 33.9, 31.9, 29.7 (2C), 29.5, 29.4, 29.2, 29.0, 22.7, 14.1.

Mechanistic Studies.

Reaction of 1m in EtOD. CuCl (2.0 mg, 0.02 mmol, 10 mol %), IMes·HCl (10.2 mg, 0.03 mmol, 15 mol %) and *t*-BuOK (22.4 mg, 0.2 mmol, 1 equiv.) were placed in a dried 25 mL Schlenk flash. The tube was evacuated and refilled with N_2 three times. EtOD (1.0 mL) was added and the result mixture was stirred at room temperature for 15 min. Subsequently, a solution of **1l** (40.6 mg, 0.2 mmol), B_2Pin_2 (61 mg, 0.24 mmol, 1.2 equiv.) and EtOD (2.0 mL) was added, and the resulting mixture was stirred at room temperature for 12 h. Upon completion, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with the mixture of PE/EA = 50/1 to give pure products in 93% yield. The resulting product **2m-*d*$_2$** was sampled for ^1H NMR analysis (see Figure *S1* in Supporting Information).

Reaction of 3a under the standard reaction conditions in the absence of B_2Pin_2. CuCl (2.0 mg, 0.02 mmol, 10 mol%), IMes·HCl (10.2 mg, 0.03 mmol, 15 mol%) and *t*-BuOK (22.4 mg, 0.2 mmol, 1 equiv.) were placed in a dried 25 mL Schlenk flash. The tube was evacuated and refilled with N_2 three times. Then, ethanol (1.0 mL) was added, and the result mixture was stirred at room temperature for 15 min. Subsequently, a solvent of **3a** (61.2 mg, 0.2 mmol) and ethanol (2.0 mL) was added, and the resulting mixture was stirred at room temperature for 5 h. Upon completion, after evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with PE to give **2a** in 19% yield.

Synthesis of (Z)-2-methoxy-5-(2-(3,4,5-trimethoxyphenyl)vinyl-1,2-d2)phenyl acetate (5a) CuCl (2.0 mg, 0.02 mmol, 10 mol%), IMes·HCl (10.2 mg, 0.03 mmol, 15 mol%) and *t*-BuOK (22.4 mg, 0.2 mmol, 1 equiv.) were placed in a dried 25 mL Schlenk tube. The tube was evacuated and refilled with N_2 three times. EtOD (1.0 mL) was added and the resulting mixture was stirred at room temperature for 15 min. 2-methoxy-5-((3,4,5-trimethoxyphenyl)ethynyl)phenyl acetate **1zc** (0.2 mmol) and B_2Pin_2 (61.0 mg, 0.24 mmol, 1.2 equiv) was added under N_2 atmosphere. Then EtOD (2.0 mL) was added to wash **1zc** and B_2Pin_2 which might remain on the Schlenk tube wall. The reaction was stirred at room temperature for 10 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the mixture of ethyl acetate (EA)/petroleum ether (PE) = 6/1-3/1 to give pure **5a** (colorless liquid, 50.4 mg, 70 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 6.52 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.72 (s, 6H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 168.8, 152.9, 150.2, 139.3, 137.1, 132.3, 129.9, 129.0 (t, J = 23.4 Hz), 128.1 (t, J = 23.4 Hz), 127.7, 123.1, 111.9, 105.7, 60.8, 55.8, 20.6.

Synthesis of Z-Combretastation A-4-d_2 (5b). 5a (72.0 mg, 0.2 mmol), K_2CO_3 (83 mg, 0.6 mmol) and MeOH (6 mL) was added to a 15 mL reaction tube with a stir bar. The reaction mixture was stirred at room temperature for 5 h. Upon completion, extra water (15 mL) was added and the mixture was extract with CH_2Cl_2 (20 mL × 3). The organic phase was combined. Afterwards the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the mixture of ethyl acetate (EA)/ petroleum ether (PE) = 6/1-3/1 to give **5b**[21e]

(colorless liquid, 58.5 mg, 92%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.94 (d, J = 2.0 Hz, 1H), 6.82 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.55 (s, 2H), 5.58 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.71 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 152.7, 145.8, 145.2, 137.0, 132.5, 130.4, 128.9 (t, J = 23.4 Hz), 128.4 (t, J = 23.3 Hz), 121.0, 114.9, 110.3, 106.0, 60.8, 55.81, 55.79.

Synthesis of 3,5,6,7-tetramethoxyphenanthren-2-yl-9,10-d_2 acetate (6a).[20] Iodine (50.8 mg, 0.2 mmol) was added to a solution of **5a** (72 mg, 0.2 mmol) and cyclohexane (100 mL) with a stir bar. The reaction mixture was irradiated at a distance of 5 cm from 500 W high pressure mercury lamp and stirred for 5 h at room temperature. Then extra sat. $Na_2S_2O_8$ was added until the solution turn to colorless and the mixture was extract with CH_2Cl_2. The organic phase was combined. Afterwards the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh), eluting with the mixture of ethyl acetate (EA)/ petroleum ether (PE) = 10/1-3/1 to give **6a** (colorless liquid, 37 mg, 52%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.21 (s, 1H), 7.52 (s, 1H), 7.10 (s, 1H), 4.06 (s, 6H), 4.05 (s, 3H), 4.03 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (CDCl3, 125 MHz): δ 169.2, 152.5, 152.1, 150.2, 142.7, 138.9, 130.2, 128.9, 126.6, 125.8 (t, J = 24.6 Hz), 124.6 (t, J = 24.5 Hz), 120.9, 118.4, 108.9, 105.3, 61.3, 60.5, 55.86, 55.84, 20.7.

Synthesis of 3,5,6,7-tetramethoxyphenanthren-9,10-d2-2-ol (6b). 6a (71.7 mg, 0.2 mmol), K_2CO_3 (83 mg, 0.6 mmol) and MeOH (6 mL) was added to a 15 mL reaction tube with a stir bar. The reaction mixture was stirred at room temperature for 5 h. Upon completion, extra water (15 mL) was added and the mixture was extract with CH_2Cl_2 (20 mL × 3). The organic phase was combined. Afterwards the solvent was removed under vacuum and the residue was purified by column chromatography on silica

gel (200-300 mesh), eluting with the mixture of ethyl acetate (EA)/ petroleum ether (PE) = 6/1-3/1 to give **6b**[31] (white solid, 56.3 mg, 89%). m.p. 162.9-163.7 ºC. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.09 (s, 1H), 7.34 (s, 1H), 7.09 (s, 1H), 5.95 (s, 1H), 4.11 (s, 3H), 4.06 (s, 3H), 4.05 (s, 3H), 4.02 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 151.5, 146.7, 144.7, 142.5, 129.3, 127.6, 125.8 (t, J = 24.0 Hz), 124.4 (t, J = 24.0 Hz), 124.0, 118.7, 111.1, 107.1, 105.2, 61.4, 60.4, 55.9 (2C).

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Supporting Information

Charts for mechanistic studies as well as copies of ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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