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H_2O as the Hydrogen Donor: Stereo-Selective Synthesis of *E*- and *Z*-Alkenes by Palladium-Catalyzed Semihydrogenation of Alkynes

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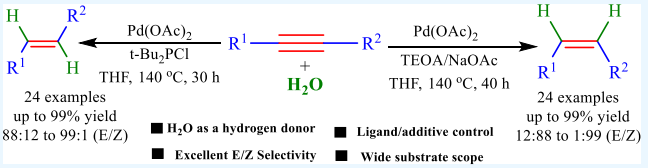
ABSTRACT: It is very desirable to develop a facile controllable method for selective semihydrogenation of alkynes to alkenes with a cheap and safe hydrogen donor but remains a big challenge. H_2O is one of the best choices of the transfer hydrogenation agent of the world, and the development of methods for synthesizing *E*- and *Z*-alkenes using H_2O as the hydrogen source is worthwhile. In this article, a palladium-catalyzed synthesis of *E*- and *Z*-alkenes from alkynes using H_2O as the hydrogenation agent was reported. The use of di-*tert*-butylphosphinous chloride (*t*-Bu_2PCl) and triethanolamine/sodium acetate (TEOA/NaOAc) was essential for the stereo-selective semihydrogenation of alkynes. The general applicability of this procedure was highlighted by the synthesis of more than 48 alkenes, with good yields and high stereoselectivities.

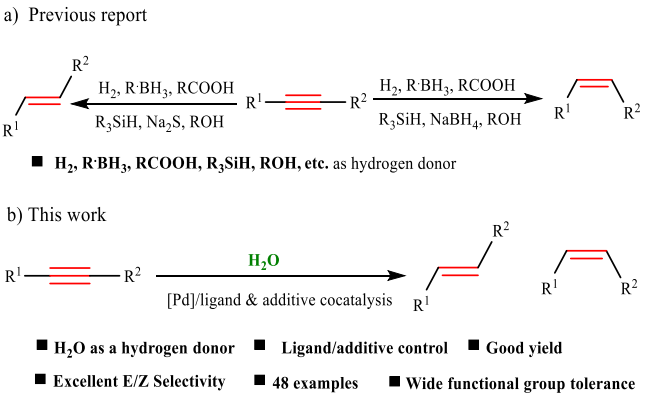


INTRODUCTION

Olefin structures are ubiquitous motifs in many synthetic organic chemistry, and the synthesis of alkenes is receiving considerable attention and extensively used in the manufacture of industrial materials, bioactive molecules, and organic intermediates.[1−7] At present, a series of reaction methods for alkene synthesis have been developed, including Julia olefination,[8−11] Wittig−Horner reaction,[12−15] Perkin condensation,[16−19] Wilkinson catalyst,[20,21] and Lindlar catalyst.[22] Among these reported synthesis systems, one of the important procedures to obtain alkenes is the catalytic semihydrogenation of internal alkynes in organic synthesis. A series of methods have been developed for the catalytic semihydrogenation of internal alkynes to *Z*-alkenes.[23−31] However, these reaction methods usually provide good *cis*-selectivity and poor *trans*-selectivity, which may be attributed to the fact that the hydrogenation is more difficult to form stereo-complementary *E*-alkenes than *Z*-alkenes.

Recently, various reaction systems have been developed to provide switchable selectivity for either the *Z*- or *E*-alkene isomer.[32−34] Moreover, these reaction methods usually require the use of flammable, explosive, corrosive, or expensive hydrogen sources, for example, hydrogen,[35−38] borane,[34,39−43] formic acid,[28,44−46] amine,[47] and alcohol,[48−52] to obtain good yields (Scheme 1a). Also, these methods may have disadvantages, such as poor stereo-selectivity,[5,15,53] their relatively high prices, and poor functional group tolerance.[54] It is very desirable to develop a facile controllable method for selective semihydrogenation of alkynes with a cheap and safe hydrogen donor but remains a big challenge. The use of H_2O as the hydrogen donor for synthesizing alkenes is worthwhile. To date, several reaction systems for the transformation of alkynes to alkenes using H_2O as the hydrogen source have been developed.[55−63] Herein, we report a palladium-catalyzed stereo-selective semihydrogenation of alkynes to *E*- and *Z*-alkenes employing H_2O as the hydrogenation donor, where *t*-Bu_2PCl and TEOA/NaOAc played an important role for the *trans*/*cis* stereo-selective semihydrogenation of alkynes (Scheme 1b).

Scheme 1. Various Strategies for Semihydrogenation of Alkynes



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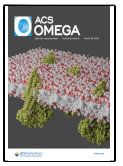
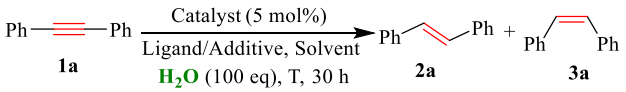


Table 1. Optimization of Reaction Conditions



entry	catalyst	ligand/additive	solvent	T (°C)	conv. **1a**[a] (%)	yield **2a** (%)	yield **3a** (%)
1	none	DPPE	THF	120	0	0	0
2	ZnI_2	DPPE	THF	120	0	0	0
3	FeI_2	DPPE	THF	120	0	0	0
4	CuI	DPPE	THF	120	0	0	0
5	$Mncl_2$	DPPE	THF	120	0	0	0
6	$BrMn(Co)_5$	DPPE	THF	120	0	0	0
7	$CoCl_2$	DPPE	THF	120	0	0	0
8	$Co(OAc)_2$	DPPE	THF	120	0	0	0
9	$Nicl_2$	DPPE	THF	120	0	0	0
10	$PdCl_2$	DPPE	THF	120	42	29	71
11	$Pd(OAc)_2$	DPPE	THF	120	56	25	75
12	$Pd(OAc)_2$	DPPE	THF	110	30	17	83
13	$Pd(OAc)_2$	DPPE	THF	130	88	23	77
14	$Pd(OAc)_2$	DPPE	THF	140	100	24	76
15	$Pd(OAc)_2$	DPPE	toluene	140	29	48	52
16	$Pd(OAc)_2$	DPPE	CH_3CN	140	60	42	48
17	$Pd(OAc)_2$	DPPE	DCE	140	trace	0	0
18	$Pd(OAc)_2$	DPPE	DMSO	140	trace	0	0
19	$Pd(OAc)_2$	DPPE	DMF	140	63	51	49
20	$Pd(OAc)_2$	DPPE	*P*-xylene	140	trace	0	0
21	$Pd(OAc)_2$	DPPE	*n*-Hexane	140	0	0	0
22	$Pd(OAc)_2$	none	THF	140	85	27	73
23[b]	$Pd(OAc)_2$	DPPEde	THF	140	100	25	75
24[c]	$Pd(OAc)_2$	BINAP	THF	140	100	24	76
25[d]	$Pd(OAc)_2$	Dppf	THF	140	100	40	60
26[e]	**$Pd(OAc)_2$**	***t*-Bu_2PCl**	**THF**	**140**	**100**	**98**	**2**
27[f]	$Pd(OAc)_2$	PPh_3	THF	140	100	22	78
28	$Pd(OAc)_2$	THOA	THF	140	100	17	83
29	$Pd(OAc)_2$	NaOAc	THF	140	9	11	89
30[g]	**$Pd(OAc)_2$**	**TEOA + NaOAc**	**THF**	**140**	**100**	**4**	**96**

[a]Isolated product and reaction conditions: substrate 1a (0.1 mmol, 1 equiv), ligand (0.2 equiv), and solvent (1.5 mL). [b]DPPBde = 2-diphenylphosphinobenzaldehyde. [c]BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene. [d]Dppf = 1,1′-bis(diphenylphosphino)ferrocene. [e]*t*-Bu_2PCl (0.2 equiv). [f]PPh_3 = triphenylphosphine. [g]TEOA(0.5 equiv), NaOAc (2 equiv), 40 h.

RESULTS AND DISCUSSION

Our study commences with the transfer hydrogenation reaction of internal alkynes 1,2-diphenylethyne **1a** with H_2O, 1,2-bis(diphenylphosphino)ethane (DPPE) as a ligand, and tetrahydrofuran (THF) as a solvent. The reaction cannot be carried out without a catalyst (Table 1, entry 1). First, we identified the best catalyst for this reaction. The control experiments indicated that most of the transition-metal catalysts such as Zn, Fe, Cu, Mn, Co, and Ni catalysts have no catalytic activity for this reaction, while the Pd catalyst gave catalytic activity. This may be attributed to the high activity and reaction characteristics of the Pd catalyst. $Pd(OAc)_2$ shows higher catalytic activity than $PdCl_2$ for the semihydrogenation of alkynes with H_2O (Table 1, entries 2−11). Then, we screened the range of reaction temperatures from 110 to 140 °C (Table 1, entries 12−14). In this temperature range, the reaction efficiency increased with the increase of reaction temperature, and alkynes were converted to alkenes completely at an optimum temperature of 140 °C with 24:76 *E*/*Z* selectivity (Table 1, entry 14). Next, we evaluated the influence of solvent factors on the reaction (Table 1, entries 15−21). Other solvents such as toluene, CH_3CN, dichloroethane (DCE), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), *p*-xylene, and *n*-hexane could not perform better than THF. Then, we further investigated the influence of different ligands on the reaction (Table 1, entries 22−30). An 85% conversion rate of alkyne with *E*/*Z* 27:73 selectivity without any ligand was observed in the reaction system (Table 1, entry 22). This result indicated that THF may be used not only as a solvent for the reaction but also as a reductant for the hydrogen transfer. Palladium catalysts and phosphine ligands are widely used in various reaction types due to their high catalytic activity and selectivity. The results showed that most of the ligands make the reaction tend to give the *Z*-selectivity. Fortunately, A 98% yield of *E*-alkene with *E*/*Z* 98:2 selectivity was obtained when *t*-Bu_2PCl (di-*tert*-butylphosphinous chloride) was used (Table 1, entry **26**), which may be due to the large steric hindrance of *t*-Bu_2PCl. According to our previous research, triethanolamine (TEOA) and NaOAc play important roles in catalytic transfer hydrogenation.[52] TEOA and NaOAc were used as ligands/additives to study the effect on the reaction. The use of TEOA provided a 100% conversion rate of alkyne with *E*/*Z* 17:83 selectivity (Table 1, entry 28). These results indicated that the selectivity of the reaction is regulated by ligands. In order to further improve stereo-selectivity to the *Z*-alkene, we screened a variety of reaction conditions. The

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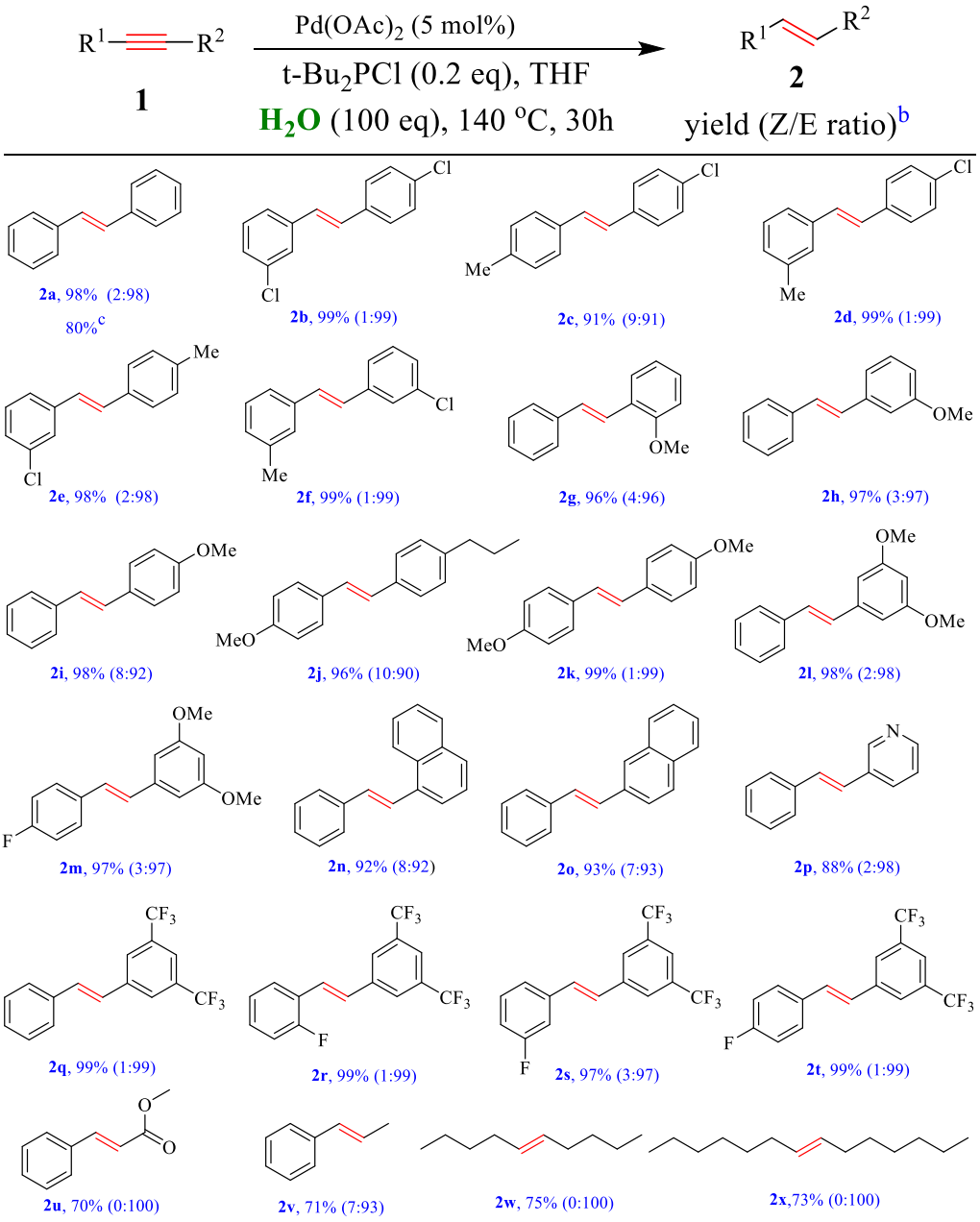
Scheme 2. Substrate Scope of *E*-Selective Alkyne Semihydrogenation[a]



[a]Isolated product yields and reaction conditions: substrate **1** (0.1 mmol), H_2O (10 mmol), $Pd(OAc)_2$ (5 μmol), *t*-Bu_2PCl (20 μmol), and THF (1.5 mL) at 140 °C for 30 h. The [b] *Z*/*E* ratio was determined by gas chromatography (GC) analysis. [c] Gram-scale synthesis.

results showed that the combined use of TEOA/NaOAc can increase stereo-selectivity of the *Z*-alkene effectively; a 96% yield of *Z*-alkene (*E*/*Z* 4:96) was obtained (Table 1, entry **30**). This result suggested that the use of base was helpful for improving *Z*-selectivity. Additional experiments were performed to investigate the H_2O amount of the reaction. Our results imply that when the amount of H_2O is small, the reaction is slow and the selectivity is poor (Table S1). The 100 equiv of H_2O provided a 100% conversion rate of alkyne with *E*/*Z* 24:76 selectivity.

We explored the generality of this reaction for different 1,2-disubstituted acetylene under the optimized reaction conditions. First, we tested the scope of *E*-selective alkyne semihydrogenation. As summarized in Scheme 2, the semihydrogenation of alkynes with H_2O as the hydrogen donor displayed good functional group tolerance (**2a**−**2x**). The diarylethynes with electron-withdrawing groups on the phenyl rings such as fluoro (**2m** and **2s**−**2t**), chloro (**2b**−**2f**), and trifluoromethyl (**2q**−**2t**) were compatible with high stereoselectivity in excellent yield. The reaction was also compatible with different diarylethynes with a wide scope of electron-donating groups such as alkyl (**2c**−**2f,** and **2j**), methoxy (**2g**−**2m**), naphthyl (**2n**−**2o**), and pyridyl (**2p**) and gave the corresponding *Z*-alkenes in good to excellent yields with high selectivity. Some monoaryacetylenes were also tolerated and afforded the corresponding groups (**2u** and **2v**). The reaction was also compatible with unactivated dialkyl-alkynes and gave the corresponding *Z*-alkenes (**2w**−**2x**). These results indicated that various substitutions including fluoro, chloro, trifluoromethyl, methoxy, alkyl, phenyl, naphthyl, and pyridyl were

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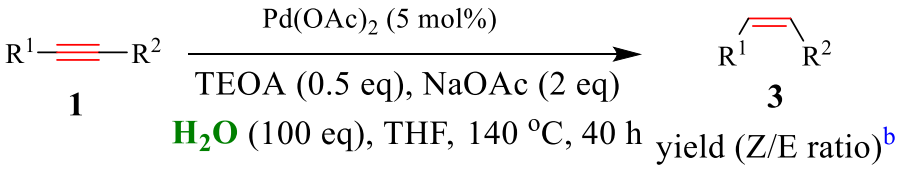
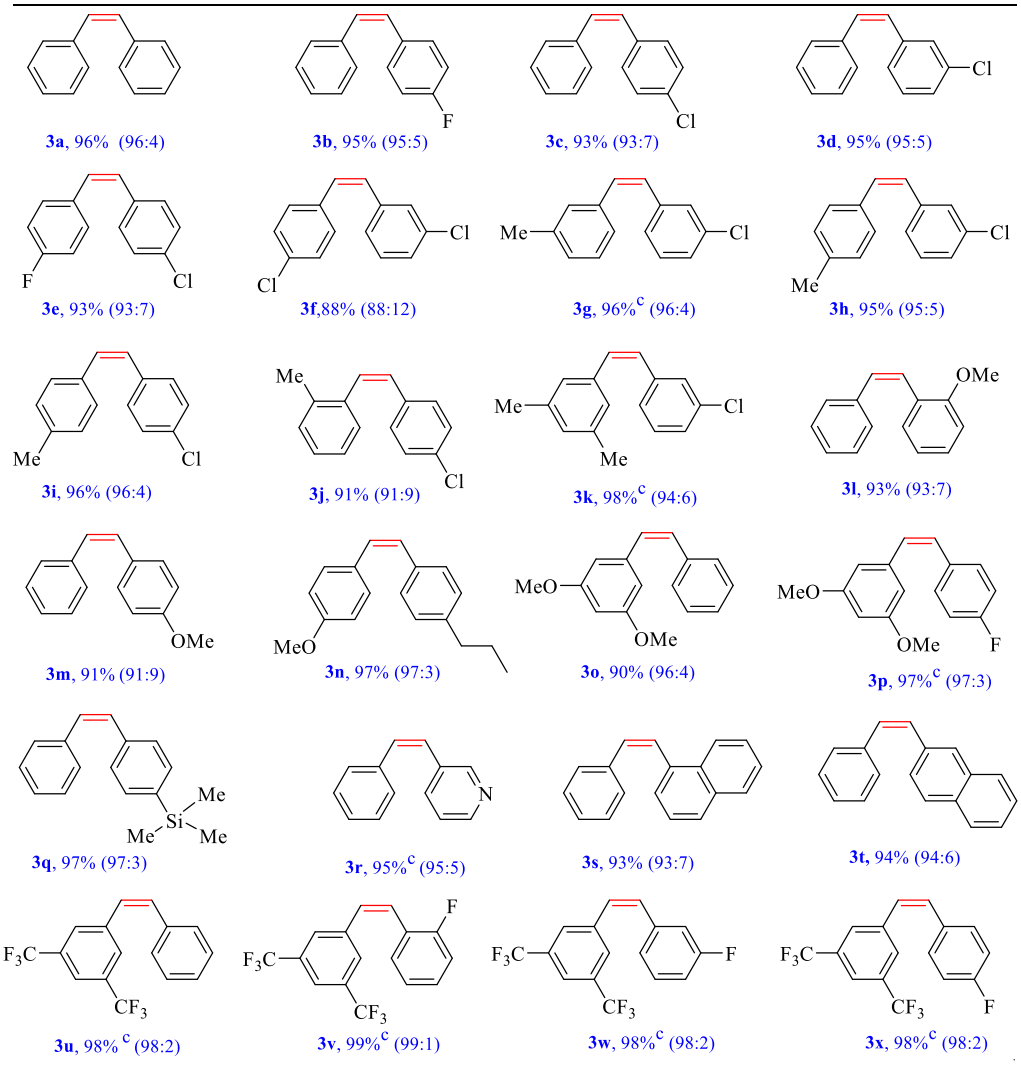
Scheme 3. Substrate Scope of *Z*-Selective Alkyne Semihydrogenation[a]





[a]Isolated product yields and reaction conditions: substrate **1** (0.1 mmol), H_2O (10 mmol), $Pd(OAc)_2$ (5 μmol), TEOA (0.05 mmol), NaOAc (0.2 mmol), and THF (1.5 mL) at 140 °C for 40 h. The [b] *Z*/*E* ratio was determined by GC analysis. [c] Reaction time for **3g, k, p, r, u, v, w,** and **x**: 48 h.

compatible under the optimum reaction conditions. A gram-scale (1 g) semihydrogenation of alkyne using H_2O as the hydrogen donor was performed to check the utility of our method. The target *E*-product in 80% yield was obtained (**2a**).

Subsequently, we examined the generality of alkynes for the synthesis of *Z*-alkenes with the use of a combination of TEOA/NaOAc as ligands/additives. The reaction was also compatible with various diarylethynes with different functional groups. As shown in Scheme 3 (**3a−3x**), the diarylethynes with fluoro (**3b, 3p,** and **3v−3x**), chloro (**3c−3k**), alkyl (**3g−3k** and **3n**), methoxyl (**3l−3p**), trimethylsilyl (**3q**), and trifluoromethyl (**3u−3x**) on the phenyl rings and the diarylethynes containing phenyl (**3a**), pyridyl (**3r**), and naphthyl (**3s−3t**) were all tolerated. It is noteworthy that trimethylsilyl alkynes do not get the corresponding trans-products [(*E*)-trimethyl(4-styrylphenyl)silane] under the optimal reaction conditions, but (*E*)-1,2-diphenylethene, indicating that the hydrolysis reaction may have occurred. All of these diarylethynes gave the corresponding *Z*-alkenes products in good to excellent yields with high *Z*/*E* stereo-selectivity under the optimum reaction conditions. These results displayed the semihydrogenation of alkynes containing electron-donating and electron-withdrawing groups using H_2O as the hydrogen donor which has broad applicability.

The control experiments indicate that the Pd(II) catalyst is crucial for this reaction (Table 1, entry 1), and the ligand/additive plays a regulatory role in the selectivity of reaction products (Table 1, entries 26 and 30). We performed additional experiments to explore the possible reaction mechanisms. As shown in Scheme 4, (*Z*)-1,2-diphenylethene is isomerized into (*E*)-1,2-diphenylethene with 100% yield in the presence of $Pd(OAc)_2$/*t*-Bu_2PCl. Also, the reaction is shut

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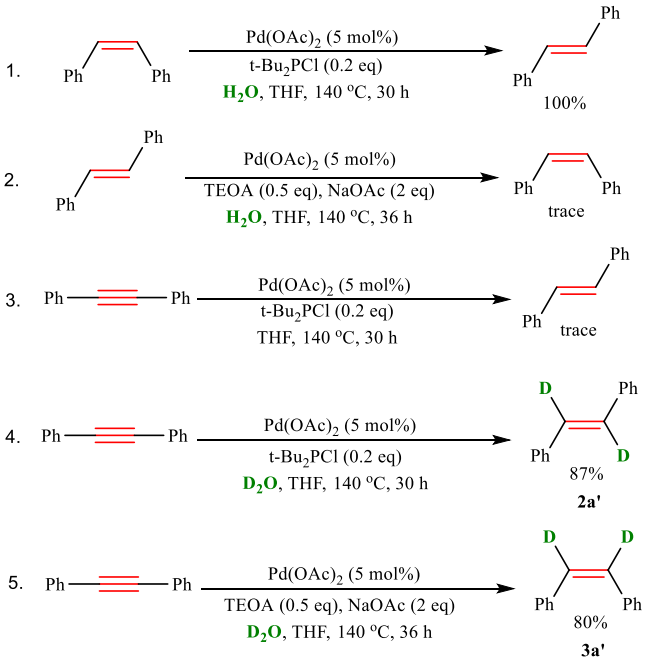
Scheme 4. Mechanism Experiments

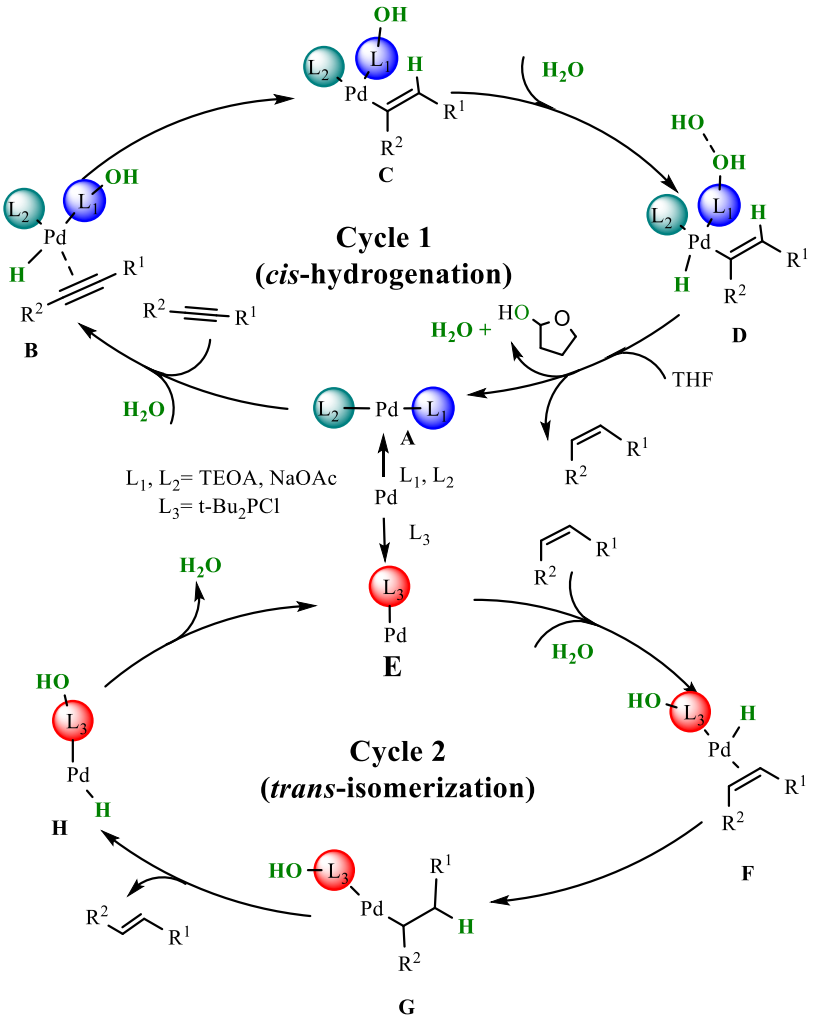


down in the absence of H_2O. Deuterated product **2a′/3a′** was obtained in 87/80% yield when D_2O was used. According to these observations and reported literature studies,[52,64] we proposed the following catalytic cycle including *cis*-hydrogenation and *trans*-isomerization, as shown in Scheme 5. Initially, an active Pd(II) catalyst **A** is generated by coordination of TEOA/NaOAc (L1/L2) to $Pd(OAc)_2$. Next, the oxidative addition with H_2O to catalyst **A** and then coordination of alkyne to provide Pd−H complex **B** were carried out. The subsequent insertion of alkene into the Pd−H bond affords species **C**. Then, the oxidative addition with H_2O to species **C** affords intermediate **D**. The reductive elimination of intermediate **D** gives *cis*-alkene product and Pd(II) catalyst **A** (cycle 1). The *cis*-alkene product undergoes the coordination of ***E*** and the oxidative addition with H_2O to form complex **F**, and then the subsequent insertion into the Pd−H bond affords intermediate **G.** The subsequent reductive elimination of **G** affords *trans*-alkene (cycle 2).

CONCLUSIONS

In summary, we have developed a method which is compatible with a wide range of substrates using H_2O as the hydrogen donor in palladium-catalyzed semihydrogenation of alkynes for synthesizing *E*- and *Z*-alkenes. THF may be used not only as a solvent for the reaction but also as a reductant for the

Scheme 5. Possible Reaction Mechanism



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hydrogen transfer. The stereo-selectivity of the reaction is controlled by ligands/additives with good yields and high stereo-selectivity. In addition, *t*-Bu_2PCl is essential for *trans*-selectivity and TEOA/NaOAc is essential for *cis*-selectivity. Finally, more work to develop more mild reaction conditions for this semihydrogenation of alkynes with H_2O as the hydrogen donor is underway in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in pressure tubes. Thin-layer chromatography was visualized using a combination of UV and potassium permanganate staining techniques. Silica gel (particle size 40−63 m) was used for flash column chromatography. The NMR spectrum was detected at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) on the Bruker AV 400 spectrometer. The carbon chemical shifts and proton are reported relative to the solvents used as the internal reference. The electrospray ionization (ESI) resource was used to detect high-resolution mass spectra on a Q Exactive Focus mass spectrometer (Thermo). The *Z*/*E* ratio was determined by GC (GCMS-QP2020, Shimadzu) analysis (chromatographic conditions: column oven temperature was 100 °C, injection temperature was 280 °C, injection mode was split, pressure was 88.5 kpa, total flow was 10.1 mL/min, column flow was 1.19 mL/min, linear velocity was 40.5 cm/min, purge flow was 3.0 mL/min, and split ratio was 5.0).

Typical Procedure for the Synthesis of (*E*)-1,2-Diphenylethene. Substrate **1** (0.10 mmol), *t*-Bu_2PCl (0.02 mmol, 3.8 μL), and $Pd(OAc)_2$ (5 μmol, 1.12 mg) were added to a 15 mL pressure tube, and then THF (1.5 mL) and H_2O (10 mmol, 180 μL) were added. The mixed solution was stirred at 140 °C for about 30 h. Then, the solution was cooled to room temperature and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. Product 2 was obtained after purification by column chromatography (*n*-hexane or *n*-Hex/EtOAc = 100:1 to 40:1).

Typical Procedure for the Synthesis of (*Z*)-1,2-Diphenylethene. Substrate **1** (0.10 mmol), NaOAc (0.2 mmol, 16.4 mg), and $Pd(OAc)_2$ (5 μmol, 1.12 mg) were added to a 15 mL pressure tube, and then THF (1.5 mL), TEOA (0.5 mmol, 66.5 μL), and H_2O (10 mmol, 180 μL) were added. The mixed solution was stirred at 140 °C for about 40 h. Then, the solution was cooled to room temperature and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. Product **3** was obtained after purification by column chromatography (*n*-hexane or *n*-Hex/EtOAc = 100:1 to 40:1).

Gram-Scale Synthesis. Diphenylacetylene **1** (5.62 mmol, 1.0 g), *t*-Bu_2PCl (1.124 mmol, 213.6 μL), and $Pd(OAc)_2$ (0.562 mmol, 126.2 mg) were added to a 250 mL pressure tube, and then H_2O (562 mmol, 10.12 mL) and THF (35 mL) were added. The mixed solution was stirred for 96 h at 140 °C. The coupling product (0.809 g, yield 80%) is obtained using column purification (*n*-hexane).

Deuterium-Labeling Experiments. (1) Diphenylacetylene **1** (0.10 mmol) and *t*-Bu_2PCl [0.02 mmol, $Pd(OAc)_2$ (5 mmol, 1.12 mg) 3.8 μL] were added to a 15 mL pressure tube, and then THF (1.5 mL) and D_2O (10 mmol, 180 μL) were added. The resulting solution was stirred at 140 °C for 30 h. Then, the solution was cooled to room temperature, and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine, and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The desired deuterated product **2a′** (87% yield) was obtained after purification by column chromatography (*n*-hexane). (2) Diphenylacetylene **1** (0.10 mmol), NaOAc (0.2 mmol, 16.4 mg), and $Pd(OAc)_2$ (5 mmol, 1.12 mg) were added to a 15 mL pressure tube, and then TEOA (0.5 mmol, 66.5 μL), THF (1.5 mL), and D_2O (10 mmol, 180 μL) were added. The mixed solution was stirred for 36 h at 140 °C. Then, the solution was cooled to room temperature and diluted with ethyl acetate (10 mL). The combined organic phases were washed with brine and the aqueous phase was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The desired deuterated product **3a′** (80% yield) was obtained after purification by column chromatography (*n*-hexane).

2a: (*E*)-1, 2-Diphenylethene,[34] white solid (17.6 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 4H), 7.34 (t, *J* = 8.0 Hz, 4H), 7.26−7.22 (m, 2H), 7.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.45, 128.82, 127.76, 126.65.

2b: (*E*)-2-(3-Chlorophenyl)-1-(4-chlorophenyl)ethene,[65] white solid (24.7 mg, 99% yield). 1H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 4H), 7.36−7.30 (m, 3H), 7.28−7.22 (m, 2H), 7.02 (dd, *J* = 28.0, 16.0 Hz, 2H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 139.03, 135.47, 134.86, 133.80, 130.07, 129.01, 127.93, 126.47, 124.93.

2c: (*E*)-1-(4-Chlorostyryl)-4-methylbenzene,[19] white solid (20.8 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (t, *J* = 8.9 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.03 (q, *J* = 16.3 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.97, 136.16, 134.32, 133.05, 129.60, 129.36, 128.94, 127.67, 126.55, 21.43.

2d: (*E*)-1-(4-Chlorostyryl)-3-methylbenzene,[66] white solid (22.6 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H), 7.32−7.29 (m, 4H), 7.24−7.22 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.43, 137.04, 136.06, 133.20, 129.54, 129.06, 128.96, 128.84, 128.66, 127.75, 127.32, 123.88, 21.57.

2e: (*E*)-1-(3-Chlorostyryl)-4-methylbenzene,[19] white solid (22.2 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.30−7.26 (m, 1H), 7.23−7.18 (m, 3H), 7.04 (dd, J = 44.0, 16.0 Hz, 2H), 2.37 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 139.57, 138.17, 134.75, 134.17, 130.18, 129.98, 129.61, 127.40, 126.71, 126.33, 124.77, 21.43.

2f: (*E*)-1-Chloro-3-(3-methylstyryl)benzene,[67] white solid (22.4 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.36 (d, J = 8 Hz, 1H), 7.30 (dd, J = 12.0, 8.0 Hz, 3H), 7.25−7.16 (m, 2H), 7.11−7.09 (m, 1H), 7.03 (t, J = 12 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.46, 138.46, 136.87, 134.76, 130.35, 130.00, 129.01, 128.78, 127.51, 127.12, 126.39, 124.84, 123.99, 21.57.

2g: (*E*)-1-Methoxy-2-styrylbenzene,[68] colorless liquid (20.2 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.59 (m, 1H), 7.55−7.47 (m, 3H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.27−7.22 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 1H), 6.97 (t, *J* = 8.0

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Hz,1H), 6.91 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.04, 138.08, 129.23, 128.76, 127.49, 126.70, 126.56, 126.53, 123.61, 120.87, 111.05, 55.66.

2h: (E)-1-Methoxy-3-styrylbenzene,[68] white solid (20.4 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.51 (m, 2H), 7.38−7.34 (m, 2H), 7.30−7.25 (m, 2H), 7.14−7.09 (m, 3H), 7.06−7.05 (m, 1H), 6.84−6.81 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.01, 138.92, 137.35, 129.79, 129.14, 128.83, 128.71, 127.83, 126.69, 119.38, 113.44, 111.85, 55.41.

2i: (E)-1-Methoxy-4-styrylbenzene,[68] white solid (20.6 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.45 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 3H), 7.02 (dd, J = 36.0, 16.0 Hz, 2H), 6.91−6.89 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.43, 130.28, 128.79, 128.34, 127.86, 127.36, 126.75, 126.39, 114.27, 55.48.

2j: (E)-1-(4-Propylstyryl)-4-methoxybenzene,[49] white solid (24.2 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.40 (m, 4H), 7.17 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 16.0 Hz, 1H), 6.95 (d, J = 16.0 Hz, 1H), 6.90−6.88 (m, 2H), 3.83 (s, 3H), 2.58 (t, J = 8.0 Hz, 2H), 1.69−1.60 (m, 2H), 0.95 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.27, 142.09, 135.25, 130.50, 128.92, 127.72, 127.40, 126.74, 126.28, 114.24, 55.47, 37.94, 24.67, 13.98.

2k: (E)-1, 2-Bis(4-methoxyphenyl)ethene,[49] yellow solid (23.8 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 4H), 6.93 (s, 2H), 6.90−6.88 (d, J = 8.0 Hz, 4H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.13, 130.61, 127.55, 126.30, 114.23, 55.47.

2l: (E)-1-(3, 5-Dimethoxystyryl)benzene,[69] yellow solid (23.5 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.28−7.25 (m, 1H), 7.03 (dd, J = 24.0, 16.0 Hz, 2H), 6.68 (d, J = 4.0 Hz, 2H), 6.40 (t, J = 4.0 Hz, 1H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 161.09, 139.47, 137.24, 129.33, 128.83, 128.78, 127.88, 126.71, 104.68, 100.09, 55.51.

2m: (E)-1-(3,5-Dimethoxystyryl)-4-fluorobenzene,[70] white solid (24.8 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.0, 4.0 Hz, 2H), 7.07−6.93 (m, 4H), 6.66 (d, J = 2.0 Hz, 2H), 6.40 (t, J = 2.0 Hz, 1H), 3.83 (s, 6H);^{13}C NMR (100 MHz, $CDCl_3$): δ 163.76, 161.21 161.21 (d, J_{C-F} = 17.9 Hz), 139.31, 133.44 (d, J_{C-F} = 3.4 Hz), 128.58 (d, J_{C-F} = 2.4 Hz), 128.24 128.16, 128.13, 115.89, 115.67, 104.65, 100.09, 55.52.

2n: (E)-1-Styrylnaphthalene,[19] white solid (21.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 1H), 7.92−7.87 (m, 2H), 7.83−7.75 (m, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.54−7.49 (m, 3H), 7.42 (t, J = 8.0 Hz, 2H), 7.32 (dd, J = 7.3, 3.9 Hz, 1H), 7.17 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.75, 135.15, 133.85, 131.90, 131.53, 128.83, 128.18, 127.93, 126.83, 126.24, 125.98, 125.94, 125.84,123.91, 123.76, 123.84.

2o: (E)-2-Styrylnaphthalene,[71] white solid (21.3 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.81 (m, 4H), 7.76−7.74 (m, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.50−7.43 (m, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.31−7.21 (m, 2H), 7.23 (d, J = 16 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.48, 134.95, 133.84, 133.17, 129.15, 128.89, 128.45, 128.14, 127.84, 126.65, 126.05, 123.63.

2p: (E)-3-Styrylpyridine,[72] white solid (15.9 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, J = 4.0 Hz, 1H), 8.50−8.49 (m, 1H), 7.86−7.83 (m, 1H), 7.54−7.52 (m, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.32−7.28 (m, 2H), 7.28 (d, J = 16.0 Hz, 1H), 7.08 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.69, 136.76, 132.85, 130.98, 128.94, 128.38, 126.81, 124.99, 123.72.

2q: (E)-1-Styryl-3, 5-bis(trifluoromethyl)benzene,[73] white solid (31.3 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.74 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34−7.32 (m, 1H), 7.25 (d, J = 16.0 Hz, 1H), 7.14 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.57, 136.13, 132.68, 132.33, 132.00, 128.99 (d, J_{C-F} = 12.9 Hz), 127.07, 126.28, 125.67, 124.85, 120.91.

2r: (E)-1-(2-Fluorostyryl)-3,5-bis(trifluoromethyl)benzene, white solid (33.1 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 2H), 7.76 (s, 1H), 7.60 (td, J = 8.0, 4.0 Hz, 1H), 7.39 (d, J = 16.0 Hz, 1H), 7.33−7.28 (m, 1H), 7.25−7.17 (m, 2H), 7.15−7.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.84 (d, J_{C-F} = 249.5 Hz), 139.46, 132.71, 132.37, 132.04, 130.20 (d, J_{C-F} = 8.6 Hz), 128.02 (d, J_{C-F} = 5.7 Hz), 127.69 (d, J_{C-F} = 3.3 Hz), 126.47, 125.15 (d, J_{C-F} = 3.3 Hz), 124.80, 124.58(d, J_{C-F} = 3.6 Hz), 124.07 (d, J_{C-F} = 11.8 Hz), 122.09, 121.23, 116.35, 116.13. High-resolution mass spectrometry (HRMS)(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0660.

2s: (E)-1-(3-Fluorostyryl)-3,5-bis(trifluoromethyl)benzene, white solid (32.4 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.77 (s, 1H), 7.40−7.34 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.26−7.23 (m, 1H), 7.15 (dd, J = 32.0, 16.0 Hz, 2H), 7.06−7.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.31 (d, J_{C-F} = 244.6 Hz), 139.06, 138.42 (d, J_{C-F} = 7.7 Hz), 132.42, 132.09, 131.43 (d, J_{C-F} = 2.8 Hz), 130.55 (d, J_{C-F} = 8.4 Hz), 126.98, 126.47, 124.78, 123.06 (d, J = 2.7 Hz) 122.06, 121.30, 115.86, 115.65, 113.45, 113.23. HRMS(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0659.

2t: (E)-1-(4-Fluorostyryl)-3,5-bis(trifluoromethyl)benzene, white solid (33.1 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 2H), 7.75 (s, 1H), 7.52 (dd, J = 8.0, 4.0 Hz, 2H), 7.21 (d, J = 16.4 Hz, 1H), 7.08 (dd, J = 20.0, 12.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.10 (d, J_{C-F} = 247.6 Hz), 139.40, 132.34 (d, J_{C-F} = 3.1 Hz), 132.02, 131.43, 128.68 (d, J_{C-F} = 8.2 Hz), 126.25, 125.45 (d, J_{C-F} = 2.3 Hz), 124.82, 122.10, 120.96, 116.21, 115.99. HRMS(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0663.

2u: Methyl cinnamate,[49] white solid (11.3 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 16.0 Hz, 1H), 7.53 (dd, J = 6.6, 3.0 Hz, 2H), 7.39 (m, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.04, 130.46, 129.05, 128.23, 117.92, 51.88.

2v: (E)-Prop-1-en-1-ylbenzene,[49] colorless liquid (8.4 mg, 71% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.18 (m, 5H), 6.42 (dd, J = 15.8, 1.2 Hz, 1H), 6.30−6.21 (m, 1H), 1.90 (dd, J = 6.5, 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.12, 131.21, 128.65, 126.91, 125.93, 18.66.

2w: (E)-Dec-5-ene(3o),[49] colorless liquid (11.3 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (m, 2H), 1.97 (m, 4H), 1.31 (dd, J = 7.1, 3.7 Hz, 8H), 0.88 (dd, J = 9.7, 4.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.47, 32.46, 32.01, 22.36, 14.12.

2x: (E)-Tetradec-7-ene(3p),[49] colorless liquid (11.0 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39−5.34 (m, 2H), 2.02−1.96 (m, 4H), 1.32−1.27 (m, 16H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 130.52, 130.05, 32.79, 31.94, 29.85, 29.09, 27.38, 22.82, 14.26.

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3a: (*Z*)-1,2-Diphenylethene,[34] colorless liquid (17.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.21 (m, 10H), 6.64−6.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.38, 130.39, 130.38, 129.02, 128.35, 127.23.

3b: (*Z*)-1-Fluoro-4-styrylbenzene,[74] colorless liquid (18.8 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.18 (m, 7H), 6.91 (t, J = 8.0 Hz, 2H), 6.57 (dd, J = 20.0, 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.15, 130.65 (d, J_{C-F} = 7.9 Hz), 130.38, 129.20, 128.95, 128.44, 127.32, 115.39, 115.18.

3c: (*Z*)-1-Chloro-4-styrylbenzene,[75] colorless liquid (19.9 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.15 (m, 9H), 6.58 (dd, J = 40.0, 12.0 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.98, 135.76, 132.86, 131.07, 130.35, 129.05, 128.94, 128.54, 128.47, 127.45.

3d: (*Z*)-1-Chloro-3-styrylbenzene,[54] colorless liquid (20.4 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.21 (m, 6H), 7.18−7.09 (m, 3H), 6.58 (dd, J = 52.0, 12.0 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.22, 136.73, 134.18, 131.69, 129.57, 128.96, 128.85, 128.47, 127.59, 127.27, 127.14.

3e: (*Z*)-1-(4-Chlorostyryl)-4-fluorobenzene,[76] colorless liquid (21.6 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21−7.13 (m, 6H), 6.92 (t, J = 8.0 Hz, 2H), 6.55(dd, J = 24.0, 12.0 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.05 (d, J_{C-F} = 245.5 Hz), 135.55, 132.99, 132.94, 130.63 (d, J_{C-F} = 7.9 Hz), 130.66, 130.30, 129.90, 129.08, 128.65, 115.56, 115.34.

3f: (*Z*)-2-(3-Chlorophenyl)-1-(4-chlorophenyl)ethene,[49] colorless liquid (21.9 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.13 (m, 7H), 7.09−7.07 (d, J = 8.0 Hz, 1H), 6.56 (dd, J = 16.0, 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.86, 135.13, 134.36, 133.28, 130.35, 130.32, 129.73, 129.53, 128.92, 128.68, 127.51, 127.05.

3g: (*Z*)-1-(3-Chlorostyryl)-3-methylbenzene,[67] colorless liquid (21.9 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.16−7.11 (m, 4H), 7.06−7.02 (m, 3H), 6.62 (dd, J = 52.0, 16.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.29, 138.06, 136.65, 134.12, 131.80, 129.67, 129.50, 128.97, 128.64, 128.32, 127.21, 127.15, 125.94, 21.47.

3h: (*Z*)-1-(3-Chlorostyryl)-4-methylbenzene,[49] colorless liquid (21.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.17−7.11 (m, 5H), 7.04 (d, J = 8.0 Hz, 2H), 6.54 (dd, J = 52.0, 16.0 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.52, 137.44, 134.18, 133.76, 131.64, 129.15, 128.94, 128.89, 128.12, 127.15, 127.11, 21.40.

3i: (*Z*)-1-(4-Chlorostyryl)-4-methylbenzene,[49] colorless liquid (21.9 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 4H), 7.12 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 12.0 Hz, 1H), 6.48 (d, J = 12.4 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.30, 136.02, 134.01, 132.71, 131.04, 130.33, 129.17, 128.86, 128.52, 128.37, 21.39.

3j: (*Z*)-1-(4-Chlorostyryl)-2-methylbenzene,[77] colorless liquid (20.7 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.02 (m, 8H), 6.62 (dd, J = 44.0, 12.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.77, 136.21, 135.58, 132.76, 130.31, 129.36, 128.91, 128.40, 127.57, 125.95, 20.00.

3k: (*Z*)-1-(3-Chlorostyryl)-3, 5-dimethylbenzene, colorless liquid (23.7 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 7.15−7 0.12 (m, 3H), 6.86 (s, 3H), 6.53 (dd, J = 48.0, 12.0 Hz, 2H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.39, 137.92, 136.63, 134.09, 131.93, 129.43, 129.26, 129.00, 128.45, 127.17, 126.69, 21.33. HRMS(ESI) m/z calcd for C16H15Cl $[M + H]^+$ 243.0935; found, 243.0931.

3l: (*Z*)-1-(2-Methoxystyryl)benzene,[54] colorless liquid (19.6 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.15 (m, 7H), 6.90 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.67 (dd, J = 28.0, 12.0 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.31, 137.43, 130.30, 128.98, 128.72, 128.16, 127.04, 126.32, 125.92, 120.34, 110.77, 55.58.

3m: (*Z*)-1-(4-Methoxystyryl)benzene,[54] colorless liquid (19.1 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.17 (m, 7H), 6.75 (d, J = 12.0 Hz, 2H), 6.52 (dd, J = 12.0, 12.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.78, 137.74, 130.28, 129.88, 129.77, 128.94, 128.88, 128.36, 127.03, 113.70, 55.33.

3n: (*Z*)-1-Methoxy-4-(4-propylstyryl)benzene,[49] colorless liquid (24.5 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 8.0 Hz, 4H), 7.04 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 6.48 (s, 2H), 3.79 (s, 3H), 2.55 (t, J = 8.0 Hz, 2H), 1.65−1.55 (m, 2H), 0.93 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.69, 141.64, 134.97, 130.23, 130.06, 129.20, 128.93, 128.80, 113.68, 77.48, 55.33, 37.94, 24.58, 14.01.

3o: (*Z*)-1-(3, 5-Dimethoxystyryl)benzene(2n),[78] yellow liquid (21.6 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.18 (m, 5H), 6.57 (dd, J = 36.0, 12.0 Hz, 2H), 6.40−6.39 (m, 2H), 6.32−6.31 (m, 1H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.66, 139.19, 137.40, 130.82, 130.36, 129.08, 128.31, 127.31, 106.87, 100.07, 55.31.

3p: (*Z*)-1, 2-Bis(4-methoxyphenyl)ethene,[79] colorless liquid (25.0 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.22 (m, 4H), 6.92 (t, J = 8.0 Hz, 2H), 6.57−6.50 (m, 2H), 6.38−6.37 (m, 2H), 6.33−6.32 (m, 1H), 3.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.20, 160.73, 138.99, 133.24 (d, J_{C-F} = 3.4 Hz), 130.78 (d, J_{C-F} = 7.9 Hz), 130.33 (d, J_{C-F} = 1.1 Hz), 129.58, 115.32 115.11, 106.77, 99.92, 55.34.

3q: (*Z*)-Trimethyl(4-styrylphenyl)silane,[51] colorless liquid (25.0 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H), 7.29−7.20 (m, 7H), 7.59 (dd, J = 20.0, 16.0 Hz, 2H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.50, 137.66, 137.49, 133.34, 130.51, 130.35, 128.97, 128.38, 128.25, 127.24, −0.99.

3r: (*Z*)-3-Styrylpyridine,[80] colorless liquid (16.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49−8.41 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.25−7.21 (m, 5H), 7.14−7.11 (m, 1H), 6.76 (d, J = 12.0 Hz, 1H), 6.55 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.31, 148.22, 136.02, 133.16, 132.86 128.83, 128.67, 127.74, 126.52, 123.17.

3s: (*Z*)-1-Styrylnaphthalene,[78] colorless liquid (21.4 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10−8.07 (m, 1H), 7.89−7.87 (m, 1H), 7.79−7.77 (m, 1H), 7.51−7.47 (m, 2H), 7.37−7.32 (m, 2H), 7.09−7.04 (m, 6H), 6.85 (d, J = 12.0 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.89, 135.42, 133.83, 132.17, 131.72, 129.20, 128.64, 128.58, 128.18, 127.66, 127.22, 126.60, 126.18, 126.09, 125.75, 125.06.

3t: (*Z*)-2-Styrylnaphthalene,[78] colorless liquid (21.6 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.71 (m, 3H), 7.66 (d, J = 6.0 Hz 1H), 7.46−7.42 (m, 2H), 7.37−7.35 (m, 1H), 7.31−7.28 (m, 2H), 7.25−7.21 (m, 3H), 6.74 (dd, J = 32.0, 16.0 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.35, 135.00, 133.58, 132.67, 130.74, 130.30, 129.11, 128.37, 128.12, 128.08, 127.62, 127.36, 127.07, 126.14, 126.02.

3u: (*Z*)-1-Styryl-3,5-bis(trifluoromethyl)benzene,[81] colorless liquid (31.0 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ

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7.67−7.64 (m, 3H), 7.28−7.26 (m, 3H), 7.19−7.17 (m, 2H), 6.84 (d, J = 12.0 Hz, 2H), 6.60 (d, J = 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.29, 135.82, 134.05, 131.75, 131.42, 129.14, 128.74 (d, J_{C-F} = 8.9 Hz), 128.27, 127.16, 124.69, 121.98, 120.73.

3v: (*Z*)-1-(2-Fluorostyryl)-3, 5-bis(trifluoromethyl)benzene, colorless liquid (33.1 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60 (s, 2H), 7.28−7.23 (m, 1H), 7.11−7.02 (m, 2H), 6.99−6.96 (m, 1H), 6.76 (dd, J = 44.0, 12.0 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.22 (d, J_{C-F} = 247.0 Hz), 139.00, 131.86, 131.53, 130.21, 129.28, 128.83, 126.74 (d, J_{C-F} = 2.6 Hz), 124.67, 124.19 (d, J_{C-F} = 3.6 Hz), 123.64 (d, J_{C-F} = 14.7 Hz), 121.96, 121.02, 116.32, 116.10. HRMS(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0661.

3w: (*Z*)-1-(3-Fluorostyryl)-3, 5-bis(trifluoromethyl)-benzene, colorless liquid (32.8 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.63 (s, 2H), 7.24−7.20 (m, 1H), 6.99−6.94 (m, 2H), 6.89−6.87 (m, 1H), 6.79 (d, J = 12.0 Hz 1H), 6.65 (d, J = 12.0 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.05 (d, J_{C-F} = 245.2 Hz), 138.76, 138.01 (d, J_{C-F} = 7.7 Hz), 132.69 (d, J_{C-F} = 2.2 Hz), 131.96, 131.62, 130.38 (d, J_{C-F} = 8.4 Hz), 129.12, 128.29, 124.52, 121.93, 121.07, 115.67, 115.37 (d, J_{C-F} = 17.7 Hz), 115.07. HRMS(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0667.

3x: (*Z*)-1-(4-Fluorostyryl)-3, 5-bis(trifluoromethyl)benzene, colorless liquid (32.8 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.64 (s, 2H), 7.17−7.14 (m, 2H), 6.96 (t, J = 8.0 Hz 2H), 6.78 (d, J = 12.0 Hz 1H), 6.60 (d, J = 16.0 Hz 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.52 (d, J_{C-F} = 246.9 Hz), 139.11, 132.80, 131.78 (dd, J_{C-F} = 18.4, 14.9 Hz), 130.55 (d, J_{C-F} = 8.1 Hz), 129.08, 127.19, 120.88, 115.94, 115.72. HRMS(ESI) m/z calcd for $C_{16}H_9F_7$ $[M + H]^+$ 335.0665; found, 335.0666.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00287.

Additional experimental details, ^{1}H NMR and ^{13}C NMR spectra, and GC−MS for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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