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A Bidentate Ru(II)-NC Complex as a Catalyst for Semihydrogenation of Alkynes to (*E*)-Alkenes with Ethanol

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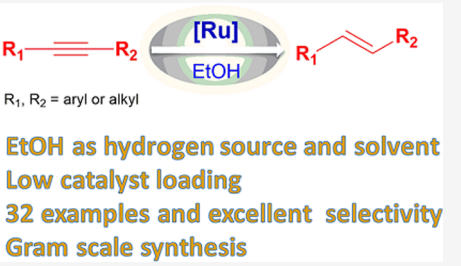
ABSTRACT: Four Ru(II)-NC complexes were tested as catalysts for semihydrogenation of internal alkynes to (*E*)-alkenes with ethanol, and the complex $\{(C_5H_4N)(C_6H_4)\}RuCl(CO)(PPh_3)_2$ (**1a**) showed the highest activity. The reactions proceeded well with 1 mol % catalyst loading and 0.1 equiv of *t*-BuONa at 110 °C for 1 h, and 32 alkenes were synthesized with excellent *E*:*Z* selectivity. This is the first ruthenium-catalyzed semihydrogenation of internal alkynes to (*E*)-alkenes using ethanol as the hydrogen donor.



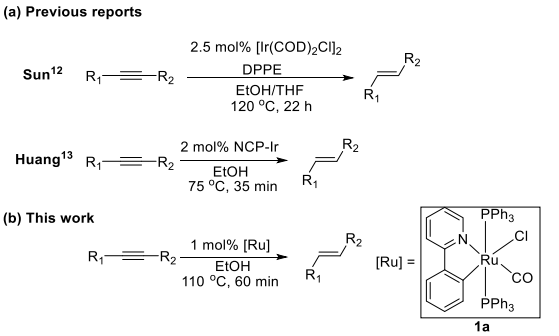
INTRODUCTION

Alkenes are versatile building blocks in organic chemistry, especially in medicinal chemistry and the total synthesis of natural products.[1] As one of the most fundamental processes for the preparation of alkenes, the semihydrogenation of alkynes remains challenging. There are two major issues that have to be addressed: one is the stereoselectivity control, and the other is the over-reduction to alkanes.[2] Thus, the exploration of suitable catalysts to solve these problems is important.

To obtain (*Z*)-alkenes, many catalytic systems have been developed, including the most commonly used Lindlar catalyst that has been presented in classical textbooks.[3−5] In contrast, the stereospecific synthesis of (*E*)-alkenes is more difficult to achieve, as a result of the intrinsic *syn*-addition pattern in most cases. Birch reduction using Na/K in NH_3 is an optional route, while its functional group tolerance is not satisfactory.[6] In this decade, transition-metal-catalyzed hydrogenation and transfer hydrogenation have emerged as alternative ways.[7−10] However, the hydrogen sources such as H_2,[8] HCOOH,[9] and NH_3BH_3[10] are explosive, corrosive, flammable, or expensive, which requires special facilities and limits their applications.

Ethanol is an attractive reagent for transfer hydrogenation due to its low toxicity and sustainability. Nevertheless, its utilization for the stereoselective semihydrogenation of alkynes to (*E*)-alkenes has rarely been investigated. Kumara Swamy and co-workers reported the transformation of ynamides to (*E*)-enamides catalyzed by $Pd(PPh_3)_4$ in ethanol, while unactivated internal alkynes are unsuitable.[11] In 2019, Sun et al. reported a $[Ir(COD)Cl]_2$/DPPE/EtOH (DPPE = 1,2-bis(diphenylphosphino)ethane) system in THF to synthesize (*E*)-alkenes (Scheme 1a).[12] For most of the unactivated internal alkynes, the *E*:*Z* selectivities are higher than 10:1. In the same year, the Huang group discovered an efficient pincer type NCP-Ir complex, and interestingly, after the full conversion of internal alkynes to (*E*)-alkenes, a clear color change from dark green to yellow could be observed (Scheme 1a).[13] In most cases, the *E*:*Z* ratios reach up to 98:2, and the over-reduced products (alkanes) are less than 2%. Notably, if the NCP ligand was replaced by BQ-NCOP that contains a rigid benzoquinoline skeleton, the formation of alkanes was dominant.[14]

Scheme 1. Examples of Semihydrogenation from Unactivated Alkynes to (*E*)-Alkenes with Ethanol



To our knowledge, other transition-metal-based catalysts for the semihydrogenation of internal alkynes to (*E*)-alkenes with ethanol have not been established. Herein, we present the first ruthenium catalyst for such a transformation, $\{(C_5H_4N)(C_6H_4)\}RuCl(CO)(PPh_3)_2$ (**1a**) (Scheme 1b). Ruthenium has

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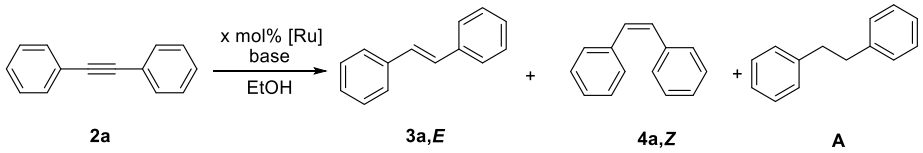
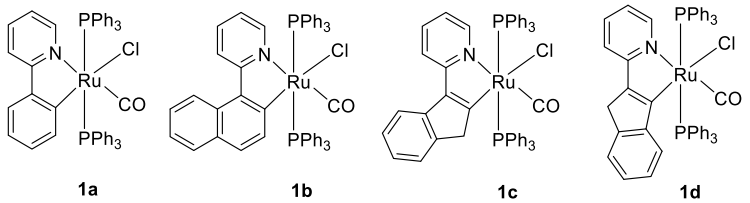
Table 1. Optimization of Reaction Conditions[a]





entry	cat. (mol %)	T (°C)	base (equiv)	t (h)	yield (%)[b]
1	**1a** (1)	110	*t*-BuONa (0.10)	1	>99 (*E*:*Z* > 99:1, **A** = 1%)
2	**1b** (1)	110	*t*-BuONa (0.10)	1	40 (*E*:*Z* = 13:32, **A** < 1%)
3	**1c** (1)	110	*t*-BuONa (0.10)	1	23 (*E*:*Z* = 14:9, **A** < 1%)
4	**1d** (1)	110	*t*-BuONa (0.10)	1	17 (*E*:*Z* = 5:4, **A** < 1%)
5	**1a** (1)	110	*t*-BuONa (0.10)	0.5	72 (*E*:*Z* = 1:4, **A** < 1%)
6	**1a** (0.5)	110	*t*-BuONa (0.10)	1	70 (*E*:*Z* = 57:43, **A** < 1%)
7	**1a** (0.5)	110	*t*-BuONa (0.10)	4	>99 (*E*:*Z* > 99:1, **A** < 1%)
8	**1a** (1)	100	*t*-BuONa (0.10)	2	44 (*E*:*Z* = 1:49, **A** < 1%)
9	**1a** (1)	110	*t*-BuOK (0.10)	1	>99 (*E*:*Z* > 99, **A** < 1%)
10	**1a** (1)	110	Cs_2CO_3 (0.20)	1	trace
11	**1a** (1)	110	*t*-BuONa (0.05)	1	98 (*E*:*Z* = 95:5, **A** < 1%)
12[c]	**1a** (1)	110		1	n.r.
13[c]		110	*t*-BuONa (0.10)	1	n.r.

[a]Reaction conditions: **2a** (1 mmol), base, EtOH (3 mL), Ru catalyst, Ar. The yield and ratio were determined by ^{1}H NMR using 1,3,5-methoxybenzene as the internal standard. [b]Yield of **3a** and **4a**. [c]n.r. = no reaction.

a relatively low cost in comparison to iridium, and complex **1a** can be easily synthesized by starting from $RuHCl(CO)(PPh_3)_3$ and 2-phenylpyridine.[15] Moreover, this bidentate complex has been reported as an efficient catalyst for the dehydrogenative reaction of primary alcohols and α-alkylation of unactivated amides and esters;[15] therefore, such a multifunctional complex is anticipated to be highly valuable because it can reduce the number of precious-metal catalysts that should be stored for future use in the limited space of laboratories.

RESULTS AND DISCUSSION

Catalysis. 1,2-Diphenylacetylene in ethanol (3 mL) was chosen as the model reaction (Table 1). From entries 1−4, **1a** was the most efficient catalyst among the four tested complexes **1a**−**d** (notably, the catalytic performances of **1a**−**d** are not related to their ν(CO) values[15a]), and after reacting at 110 °C for 1 h with 1 mol % catalyst loading, 1,2-diphenylethene was produced in high yield with excellent selectivity (>99%, *E*:*Z* > 99:1). Thus, **1a** was selected for further experiments. When the reaction time was shortened to 0.5 h, the yield was decreased to 72%, with a ratio of **3a** to **4a** of 1:4, indicating that the *E* isomer was converted from the *Z* isomer (entry 5). If the catalyst loading was decreased to 0.5 mol %, to obtain good conversion and selectivity, the reaction time should be prolonged to 4 h (entries 6 and 7). Lowering the temperature to 100 °C significantly decreased the yield (entry 8). *t*-BuOK was as good as *t*-BuONa, while Cs_2CO_3 was much worse (entries 9 and 10). When the amount of *t*-BuONa was decreased to 0.05 equiv, although the yield was still high, the stereoselectivity was lowered (entry 11). In the absence of base or catalyst, no conversion was discovered (entries 12 and 13).

With the optimum reaction conditions (Table 1, entry 1), a series of internal alkynes were investigated for testing the substrate scope and functional group tolerance. As shown in Table 2, diarylalkynes bearing an electron-withdrawing or electron-donating group at the *para* or *meta* position were converted to the corresponding (*E*)-alkenes in isolated yields of 94−97% (**3a**−**o**). Furthermore, the *E*:*Z* selectivities were all as high as 99:1, accompanied by over-reduced products (alkanes) in lower than 1% yields except for **3n**. Functional groups including alkyl, halogen, CF_3, ester, amino, alkoxy, and TMS are all tolerated under the catalytic conditions. When a Cl, Br, or methoxy group was introduced in the *ortho* position of 1,2-diphenylacetylene, the reactions also gave excellent selectivity, with the alkanes in less than 2% yields (**3p**−**r**). However, for *o*-methyl-1,2-diphenylacetylene, the *E*:*Z* selectivity was decreased to 92:8 (**3s**). For the derivatives with two functional groups in both *para* positions, the selectivities were excellent as well (**3t**−**w**). It should be noted that a longer reaction time (4 h) was needed for 1,2-bis(4-chlorophenyl)-ethyne and 1,2-bis(4-bromophenyl)ethyne, owing to their poor solubility in ethanol. Other functional groups such as ferrocenyl and naphthyl did not influence the reactivity (**3x**,**y**); however, lower isolated yields were obtained in the presence of 2-thienyl and 4-pyridyl groups (**3z**,**aa**). Especially for **3aa**, a 14% ratio of the corresponding alkane was mixed in with the final products. In addition to diarylalkynes, arylalkylalkynes were also suitable for the system (**3ab**,**ac**), while a dialkylalkyne (6-dodecyne) exhibited low stereoselectivity (**3ad**).

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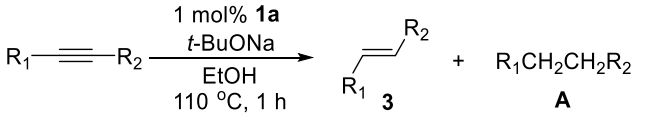
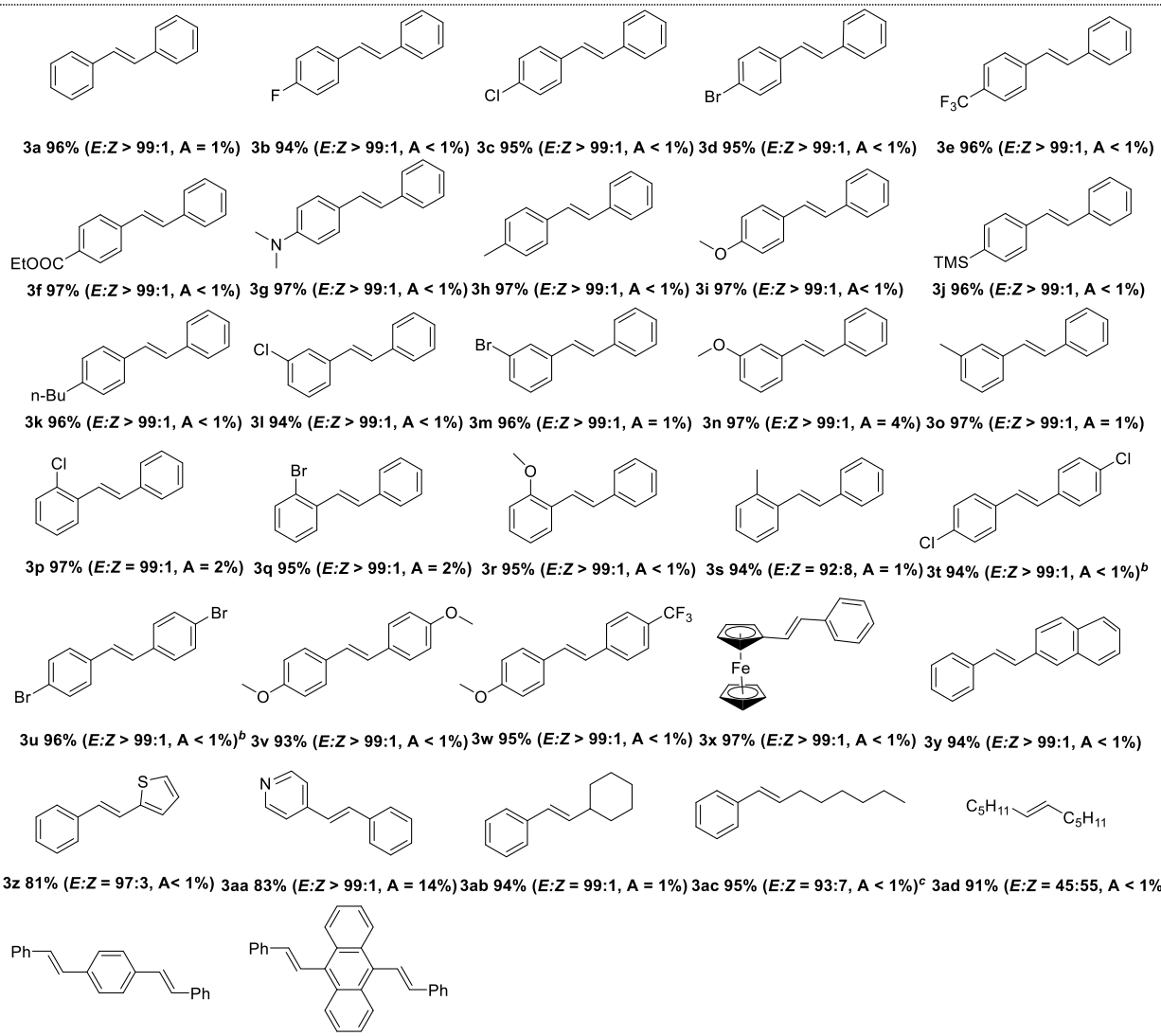
Table 2. Substrate Scope for Semihydrogenation of Alkynes using Precatalyst 1a[a]





[a]Reaction conditions unless specified otherwise: alkyne (1 mmol), *t*-BuONa (0.10 equiv), EtOH (3 mL), **1a** (1.0 mol %), Ar, 1 h. Isolated yields are given. The ratio was determined by GC. **A** represents the over-reduced product (alkane). [b]4 h. [c]0.5 mol % of **1a**. [d]45 min. [e]12 h.

In addition, this methodology has been extended to the synthesis of benzene-1,4-bis(phenylenevinylene) (OPPV) (**3ae**) and 9,10-distyrylanthracene (DSA) (**3af**), which have great potential in the area of organic light-emitting diodes (OLEDs), although 12 h was needed in both cases due to the poor solubility of the starting alkynes 1,4-bis(phenylethynyl)-benzene and 9,10-bis(phenylethynyl)anthracene.[16] In comparison to the Wittig reaction, this method is preferable because it does not generate as much waste and column chromatography is not necessary to remove the *cis*−*cis* and *cis*−*trans* isomers.[17]

It is noteworthy that, under standard conditions, even if the reaction time was prolonged to 24 h, only 11% of 1,2-diphenylethane was observed in the case of 1,2-diphenylacetylene. This demonstrates that, in such transfer hydrogenation reactions, **1a** is much more active for alkyne than for alkene, and this is the reason that, for most substrates, the over-reduced products were hardly detected. Furthermore, even in a gram-scale reaction, no more than a trace amount of 1,2-diphenylethane was observed (1.76 g of 1,2-diphenylethene, 98%, *E*:*Z* > 99:1).

Mechanism Study. In order to study the reaction mechanism, some control experiments were carried out (Scheme 2). When 1,2-diphenylacetylene was treated with ethanol, **1a**, and *t*-BuONa in C_6D_6 at 110 °C for 1 h, in addition to (*E*)-1,2-diphenylethene, the only byproduct identified by ^{1}H NMR was EtOAc (Scheme 2, eq 1). Furthermore, (*Z*)-1,2-diphenylethene was found to be transformed to (*E*)-1,2-diphenylethene completely under the standard conditions (Scheme 2, eq 2), and this reaction did not occur in the absence of catalyst (Scheme 2, eq 3). These results demonstrate that EtOAc is the byproduct during this

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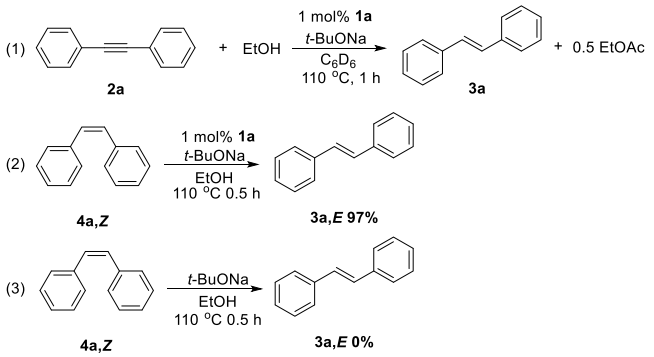
Scheme 2. Control Experiments



semihydrogenation of alkynes and further confirm that the *E* isomer originates from olefin isomerization catalyzed by **1a**.

Additional deuterium-labeling experiments were tested (Scheme 3). When CH_3CH_2OD was used as the solvent, the reaction proceeded more slowly under the standard conditions; thus, it was carried out in the presence of **1a** (2 mol %) and *t*-BuOK (0.3 equiv). In the final (*E*)-diphenylethene, the D-incorporation level in one of the alkenyl hydrogen atoms was 84% (Scheme 3, eq 1). When CD_3CD_2OD was used, the D-incorporation level in two alkenyl hydrogen atoms was 100% (Scheme 3, eq 2). The results suggest that, during the semihydrogenation process, each of the Et and hydroxyl groups donates one hydrogen, which is different from Sun's system.[12] If C_6D_6 was selected as the solvent and CH_3CH_2OD (3 equiv) was chosen as the hydrogen donor, not only the alkenyl grouo of (*E*)-diphenylethene but also the α-hydrogens of EtOAc were partially deuterated (Scheme 3, eq 3). This demonstrates that, under such basic conditions, D/H exchange between CH_3CH_2OD and the acetaldehyde intermediate (or EtOAc) would happen, which explains why the D-incorporation levels in both cases of eqs 1 and 3 of Scheme 3 were less than 100%.

On the basis of the above results, and according to the related literature,[10b,13] a possible mechanism is presented in Scheme 4. Initially, **1** reacts with *t*-BuONa and ethanol to form the Ru-OEt intermediate **B**. β-Hydride elimination of **B** generates **C** and acetaldehyde. Coordination of alkyne with **C** gives **D**, which then undergoes C≡C insertion into the Ru−H bond to afford **E**. The reaction of **E** with ethanol produces the (*Z*)-alkene, and **B** is regenerated, completing cycle I. Subsequently, the *Z*−*E* isomerization occurs, probably through the Ru-alkyl intermediate **G**, which is formed through alkene insertion into the Ru−H bond of **F**. In addition, the formation of EtOAc is attributed to the dehydrogenation of hemiacetal formed by the reaction of EtOH with acetaldehyde.

CONCLUSIONS

In summary, we have demonstrated a bidentate Ru(II)-NC complex (**1a**) catalyzed semihydrogenation of internal alkynes to (*E*)-alkenes with ethanol. The methodology showed good functional group tolerance, and 32 alkenes were prepared with a low catalyst loading (1 mol %). Furthermore, the reaction can be performed on a gram scale. More importantly, in most cases, *E*:*Z* ratios were as high as 99:1, and the over-reduced products were less than 1%, exhibiting excellent selectivity. Preliminary mechanistic studies suggest the hydrogen sources for (*E*)-alkenes as both of the Et and hydroxyl groups of EtOH, and reveal the byproduct as EtOAc. The results in this manuscript provide a new catalytic system for semihydrogenation of alkynes to (*E*)-alkenes, using a multifunctional Ru catalyst that can be easily synthesized.

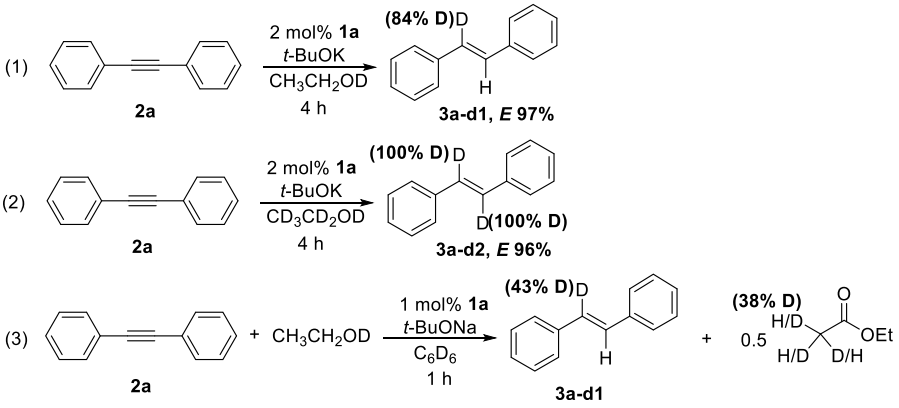
EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard high-vacuum-line, oven-dried standard Schlenk techniques or in an Vigor inert-atmosphere drybox containing an atmosphere of purified Ar. All solvents were distilled from the appropriate drying agents under N_2 before use. All reagents were obtained from commercial suppliers and used without further purification. Ru complexes **1a**−**d** were prepared as previously described, respectively.[15a] The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 or 600 spectrometer. The ^1H NMR chemical shifts were referenced to the residual solvent as determined relative to Me_4Si (δ 0 ppm). The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm). High-resolution mass spectra (HR-MS) were recorded on a Varian 7.0T FTICR-MS by the ESI technique.

General Procedure for Transfer Hydrogenation of Alkynes. In an argon-filled glovebox, EtOH (3 mL), base, catalyst (0.5−1 mol %), and alkyne (1 mmol) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for the appropriate time. The mixture was cooled to room temperature and reduced in vacuo. The residue was purified by chromatography on silica gel to give the alkene products.

Semihydrogenation of 1,2-Diphenylacetylene with Ethanol in C_6D_6. In an argon-filled glovebox, EtOH (3.0 mmol), *t*-BuONa (0.10 equiv), **1a** (1 mol %), 1,2-diphenylacetylene (1 mmol), and C_6D_6 (3 mL) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 1 h. The ^1H NMR spectrum showed that 0.27 mmol of EtOAc

Scheme 3. Deuterium-Labeling Experiments



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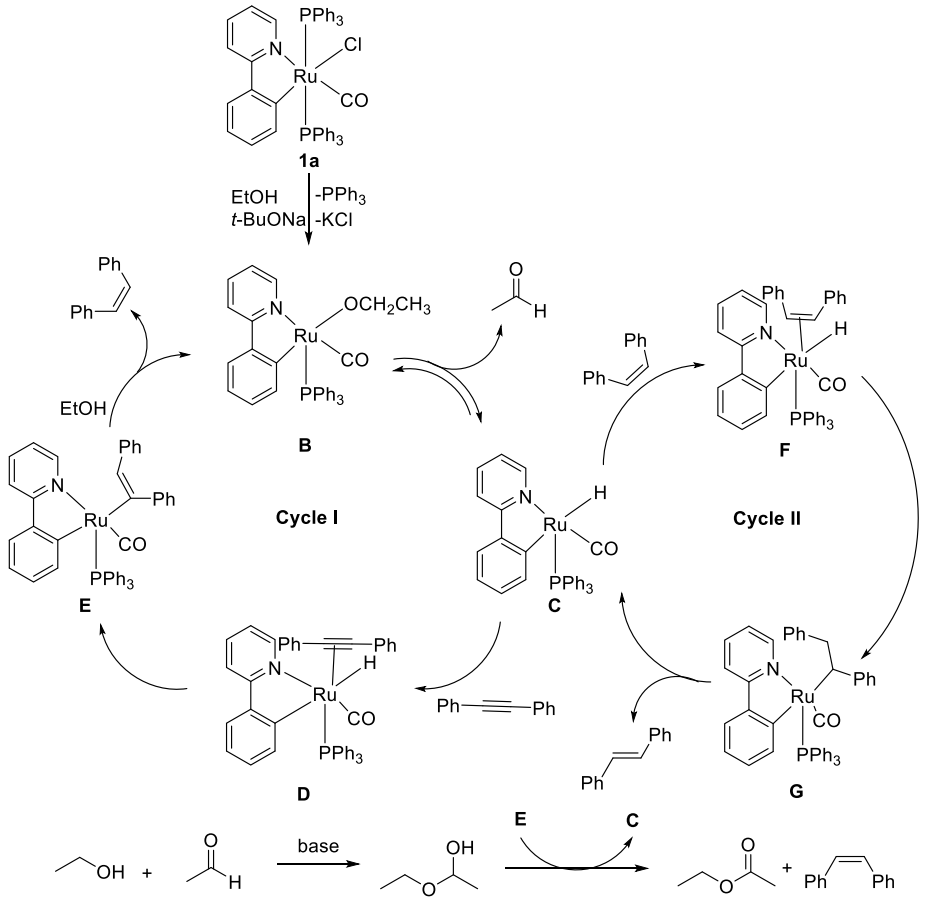
Scheme 4. Proposed Reaction Mechanism



was formed and 1,2-diphenylacetylene was transformed to (*E*)-1,2-diphenylethene completely (Figure S1).

Isomerization of (*Z*)-1,2-Diphenylethene to (*E*)-1,2-Diphenylethene. In an argon-filled glovebox, EtOH (3 mL), *t*-BuONa (0.10 equiv), **1a** (1 mol %), and **4a** (1 mmol) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 30 min. The mixture was cooled to room temperature and reduced in vacuo. The residue was purified by chromatography on silica gel to give **3a** as a white solid (175 mg, 97%).

Semihydrogenation of 1,2-Diphenylacetylene with CH_3CH_2OD. In an argon-filled glovebox, CH_3CH_2OD (3 mL), *t*-BuOK (0.30 equiv), **1a** (2 mol %), and **2a** (1 mmol) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 4 h. The mixture was cooled to room temperature and reduced in vacuo. The residue was purified by chromatography on silica gel to give **3a-d1** as a white solid (175 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.55 (d, J = 4.0 Hz, 4H), 7.39 (t, J = 8.0 Hz, 4H), 7.29 (t, J = 8.0 Hz, 2H), 7.15 (s, 1.16H) (Figure S2).

Semihydrogenation of 1,2-Diphenylacetylene with CD_3CD_2OD. In an argon-filled glovebox, CD_3CD_2OD (1.5 mL), *t*-BuOK (0.30 equiv), **1a** (2 mol %), and **2a** (0.5 mmol) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 4 h. The mixture was cooled to room temperature and reduced in vacuo. The residue was purified by chromatography on silica gel to give **3a-d2** as a white solid (86 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.55 (d, J = 4.0 Hz, 4H), 7.39 (t, J = 8.0 Hz, 4H), 7.29 (t, J = 8.0 Hz, 2H) (Figure S3).

Semihydrogenation of 1,2-Diphenylacetylene with CH_3CH_2OD in C_6D_6. In an argon-filled glovebox, EtOD (3.0 mmol), *t*-BuONa (0.10 equiv), **1a** (1 mol %), 1,2-diphenylacetylene (1 mmol), and C_6D_6 (3 mL) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 1 h. The mixture was cooled to room temperature and identified by ^{1}H NMR (Figure S4).

Procedure for Gram-Scale Reaction. In an argon-filled glovebox, EtOH (30 mL), *t*-BuONa (1 mmol, 96 mg), **1a** (1 mol %, 84 mg), and 1,2-diphenylacetylene (10 mmol, 1.78 g) were placed in a 100 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 1 h. The mixture was cooled to room temperature and reduced in vacuo. The residue was purified by chromatography on silica gel to give (*E*)-1,2-diphenylethene as a white solid (1.76 g, 98%, *E*:*Z* > 99:1).

Synthesis of OPPV (3ae) and DSA (3af). In an argon-filled glovebox, EtOH (3 mL), *t*-BuONa (0.10 equiv), catalyst (1 mol %), and alkyne (1 mmol) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 12 h. The mixture was cooled to room temperature and filtrated to give the corresponding alkene products.

Transfer Hydrogenation of 1,2-Diphenylacetylene for 24 h. In an argon-filled glovebox, EtOH (3 mL), *t*-BuONa (0.1 mmol, 9.6 mg), **1a** (1 mol %, 8.4 mg), and 1,2-diphenylacetylene (1 mmol, 178 mg) were placed in a 10 mL Schlenk tube. The tube was then moved out of the glovebox, and the contents were stirred at 110 °C for 24 h. The yield was determined by GC analysis.

*(E)-1,2-Diphenylethene (**3a**).*[13] White solid (173 mg, 96%, *E*:*Z* > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.55 (d, J = 4.0 Hz, 4H), 7.39 (t, J = 8.0 Hz, 4H), 7.29 (t, J = 8.0 Hz, 2H), 7.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.4, 128.7, 127.7, 126.5.

*(E)-1-Fluoro-4-styrylbenzene (**3b**).*[13] White solid (186 mg, 94%, *E*:*Z* > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.53−7.49 (m, 4H), 7.38 (t, J = 4.8 Hz, 2H), 7.31−7.27 (m, 1H), 7.12−7.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 162.4 (d, J = 245.0 Hz), 137.2, 133.5

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(d, J = 3.0 Hz), 128.7, 128.5 (d, J = 3.0 Hz), 128.0 (d, J = 8.0 Hz), 127.7, 127.5, 126.5, 115.6 (d, J = 22.0 Hz).

(E)-1-Chloro-4-styrylbenzene (**3c**).[13] White solid (204 mg, 95%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.50 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.38−7.24 (m, 5H), 7.10−7.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.0, 135.9, 133.2, 129.3, 128.9, 128.8, 127.9, 127.7, 127.4, 126.6.

(E)-1-Bromo-4-styrylbenzene (**3d**).[13] White solid (246 mg, 95%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.52−7.48 (m, 4H), 7.39−7.36 (m, 4H), 7.27 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 16.2 Hz, 1H), 7.04 (d, J = 16.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.0, 136.3, 131.8, 129.5, 128.8, 128.0, 127.9, 127.4, 126.6, 121.3.

(E)-1-Styryl-4-(trifluoromethyl)benzene (**3e**).[13] White solid (238 mg, 96%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.64−7.59 (m, 4H), 7.55 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 16.0 Hz, 1H), 7.13 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 140.8, 136.7, 131.2, 129.4 (q, J = 34.5 Hz), 128.8, 128.3, 127.1, 126.8, 126.6, 125.7 (q, J = 3.7 Hz), 124.2 (q, J = 271.6 Hz).

Ethyl (E)-4-Styrylbenzoate (**3f**).[13] White solid (244 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.04 (d, J = 12.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 4H), 7.38 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 16.0 Hz, 1H), 7.13 (d, J = 16.0 Hz, 1H), 4.39 (q, J = 8.0 Hz, 2H), 1.41 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 166.5, 141.8, 136.8, 131.2, 130.0, 129.3, 128.8, 128.2, 127.6, 126.8, 126.3, 61.0, 14.4.

(E)-N,N-Dimethyl-4-styrylaniline (**3g**).[13] White solid (217 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.49 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 16.0 Hz, 1H), 6.75 (d, J = 12.0 Hz, 2H), 2.99 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 150.0, 138.2, 128.8, 128.6, 127.6, 126.7, 126.1, 124.5, 112.6, 40.6.

(E)-1-Methyl-4-styrylbenzene (**3h**).[13] White solid (188 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.52 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.28−7.24 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.08−7.10 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.6, 134.6, 129.4, 128.7, 128.7, 127.72, 127.4, 126.5, 126.4, 21.3.

(E)-1-Methoxy-4-styrylbenzene (**3i**).[13] White solid (204 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.50−7.45 (m, 4H), 7.35 (t, J = 8.0 Hz, 2H), 7.26−7.24 (m, 1H), 7.07 (d, J = 16.0 Hz, 1H), 6.98 (d, J = 16.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 159.3, 137.7, 130.2, 128.7, 128.2, 127.7, 127.2, 126.6, 126.26, 114.2, 55.4.

(E)-Trimethyl(4-styrylphenyl)silane (**3j**).[13] White solid (242 mg, 96%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.54−7.50 (m, 6H), 7.37 (t, J = 8.0 Hz, 2H), 7.29−7.25 (m, 1H), 7.18−7.09 (m, 2H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 141.1, 138.9, 138.5, 134.8, 130.0, 129.8, 128.8, 127.7, 126.9, 0.

(E)-1-Butyl-4-styrylbenzene (**3k**). White solid (227 mg, 96%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.50 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.12−7.03 (m, 2H), 2.61 (t, J = 8.0 Hz, 2H), 1.64−1.57 (m, 2H), 1.41−1.32 (m, 2H), 0.93 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 142.7, 137.6, 134.8, 128.8, 128.7, 127.8, 127.4, 126.5, 126.4, 35.5, 33.6, 22.4, 14.0. HRMS for C18H20 + H, 237.1643. Found, 237.1636.

(E)-1-Chloro-3-styrylbenzene (**3l**).[12] White solid (202 mg, 94%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.52−7.51 (m, 3H), 7.39−7.36 (m, 3H), 7.31−7.22 (m, 3H), 7.12 (d, J = 16.0 Hz, 1H), 7.04 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 139.3, 136.9, 134.7, 130.2, 129.9, 128.8, 128.1, 127.5, 127.3, 126.7, 126.4, 124.8.

(E)-1-Bromo-3-styrylbenzene (**3m**).[12] White solid (249 mg, 96%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.64 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.40−7.33 (m, 4H), 7.28−7.17 (m, 2H), 7.08 (d, J = 16.0 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 139.6, 136.8, 130.4, 130.2, 129.3, 128.8, 128.1, 127.1, 126.7, 125.2, 122.9.

(E)-1-Methyl-3-styrylbenzene (**3n**).[10b] White solid (188 mg, 97%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.50 (d, J = 6.0 Hz, 2H), 7.41 (d, J = 6.0 Hz, 2H), 7.35 (t, J = 6.0 Hz, 2H), 7.26−7.23 (m, 1H), 7.16 (d, J = 6.0 Hz, 2H), 7.11−7.04 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 138.3, 137.5, 137.4, 128.9, 128.8, 128.7, 128.6, 127.6, 127.3, 126.6, 123.8, 21.5.

(E)-1-Methoxy-3-styrylbenzene (**3o**).[18] Colorless liquid (204 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.53 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.31−7.27 (m, 2H), 7.53 (d, J = 8.0 Hz, 4H), 6.84 (m, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.0, 138.8, 137.3, 129.7, 129.1, 128.7, 128.6, 127.7, 126.6, 119.3, 113.4, 111.8, 55.3.

(E)-1-Chloro-2-styrylbenzene (**3p**).[19] Colorless liquid (208 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.71 (d, J = 8.0 Hz, 1H), 7.59−7.53 (m, 3H), 7.40 (t, J = 8.0 Hz, 3H), 7.33−7.27 (m, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.1, 135.5, 133.5, 131.3, 129.9, 128.8, 128.6, 128.1, 127.0, 126.9, 126.5, 124.8.

(E)-1-Bromo-2-styrylbenzene (**3q**)..[19,20] Colorless liquid (246 mg, 95%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.79 (d, J = 8.0 Hz, 1H), 7.62−7.49 (m, 4H), 7.41 (t, J = 8.0 Hz, 2H), 7.35−7.30 (m, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.2, 137.1, 133.1, 131.5, 128.9, 128.8, 128.1, 127.6, 127.5, 126.9, 126.8, 124.2.

(E)-1-Methoxy-2-styrylbenzene (**3r**).[12] Colorless liquid (200 mg, 95%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.65 (d, J = 8.0 Hz, 1H), 7.60−7.54 (m, 3H), 7.40 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 16.0 Hz, 1H), 7.02 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 12.0 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.0, 138.0, 129.2, 128.7, 128.7, 127.4, 126.6, 126.5, 126.4, 123.6, 120.8, 111.0, 55.6.

(E)-1-Methyl-2-styrylbenzene (**3s**).[13] Colorless liquid (183 mg, 94%, E:Z = 92:8). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.67 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.46−7.39 (m, 3H), 7.36−7.20 (m, 4H), 7.08 (d, J = 16.0 Hz, 1H). 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.8, 136.5, 135.9, 130.5, 130.1, 128.8, 127.7, 126.7, 126.6, 126.4, 125.5, 20.1.

(E)-1,2-Bis(4-chlorophenyl)ethane (**3t**).[21] White solid (234 mg, 94%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.44−7.41 (m, 4H), 7.34−7.32 (m, 4H), 7.02 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): 135.6, 133.5, 128.9, 128.0, 127.7.

(E)-1,2-Bis(4-bromophenyl)ethane (**3u**).[21] White solid (324 mg, 96%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.48 (d, J = 8.4 Hz, 4H), 7.37 (d, J = 8.4 Hz, 4H), 7.02 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): 135.9, 131.9, 128.2, 128.0, 121.7.

(E)-1,2-Bis(4-methoxyphenyl)ethene (**3v**).[21] White solid (223 mg, 93%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.43 (d, J = 8.0 Hz, 4H), 6.93 (s, 2H), 6.89 (d, J = 8.0 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 130.5, 127.4, 126.2, 114.1, 55.3.

(E)-1-Methoxy-4-(4-(trifluoromethyl)styryl)benzene (**3w**).[22] White solid (264 mg, 95%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.61−7.55 (m, 4H), 7.48 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 16.0 Hz, 1H), 7.00 (d, J = 16.0 Hz, 1H), 6.93 (d, J = 12.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.8, 141.2, 130.7, 129.4, 128.8 (q, J = 32.5 Hz), 128.1, 126.3, 125.7 (q, J = 3.7 Hz), 125.0, 124.4 (q, J = 272.6 Hz), 114.3, 55.4.

(E)-1-Phenyl-1-enylferrocene (**3x**).[13] Red solid (280 mg, 97%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.45 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 16.0 Hz, 1H), 6.72 (d, J = 16.0 Hz, 1H), 4.47 (s, 2H), 4.29 (s, 2H), 4.15 (s, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 137.9, 128.7, 126.9, 126.8, 126.1, 125.8, 83.4, 69.2, 69.1, 66.9.

(E)-2-Styrylnaphthalene (**3y**).[13] White solid (216 mg, 94%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.89−7.83 (m, 4H), 7.77 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.59−7.52 (m, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34−7.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 137.4, 134.7, 133.7, 133.1, 129.1, 128.8, 128.8, 128.3, 128.0, 127.7, 126.7, 126.6, 126.4, 125.9, 123.5.

(E)-2-Styrylfuran (**3z**).[13] White solid (151 mg, 81%, E:Z = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.47 (d, J = 8.0 Hz, 2H), 7.35 (t,

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J = 4.0 Hz, 2H), 7.27−7.23 (m, 1H), 7.20 (t, J = 4.0 Hz, 1H), 7.07 (d, J = 4 Hz, 1H), 7.02−7.00 (m, 1H), 6.93 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.9, 137.0, 128.7, 128.4, 127.6, 126.3, 124.4, 121.8.

*(E)-4-Styrylpyridine (**3aa**).*[13] Pink solid (150 mg, 83%, E:Z > 99:1, with 14% alkane product). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.62 (br, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.44−7.29 (m, 6H), 7.05 (d, J = 16.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$):150.2, 144.6, 136.1, 133.2, 128.9, 128.9, 127.1, 126.0, 120.9.

*(E)-(2-Cyclohexylvinyl)benzene (**3ab**).*[13] Colorless liquid (175 mg, 94%, E:Z > 99:1). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.35 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.19 (t, J = 8.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.19 (dd, J = 16.0, 8.0 Hz, 1H), 2.10−1.83 (m, 1H), 1.80 (m, 4H), 1.70 (m, 1H), 1.37−1.29 (m, 2H), 1.23−1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):138.1, 136.9, 128.5, 127.3, 126.8, 126.0, 41.2, 33.0, 26.2, 26.1.

*(E)-Oct-1-en-1-ylbenzene (**3ac**).*[23] Colorless liquid (179 mg, 95%, E:Z = 96:4). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.35 (d, J = 7.8 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.24 (dt, J = 15.6, 7.8 Hz, 1H), 2.33 (q, J = 7.2 Hz, 2H), 1.49−1.45 (m, 2H), 1.38−1.27 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 138.0, 131.3, 129.7, 128.5, 126.8, 125.9, 33.1, 31.0, 29.4, 29.0, 22.7, 14.2.

*OPPV (**3ae**).*[17] Write solid (265 mg, 94%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 7.53−7.52 (m, 8H), 7.37 (t, J = 12.0 Hz, 4H), 7.27 (m, 4H), 7.12 (dd, J = 12.0, 6.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 137.3, 136.7, 128.7, 128.6, 128.3, 127.7, 126.9, 126.5.

*DSA (**3af**).*[16c] Yellow solid (320 mg, 84%, E:Z > 99:1). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): 8.27−8.24 (m, 4H), 7.30−7.25 (m, 4H), 7.30−7.25 (m, 2H), 7.16 (d, J = 12.0 Hz, 2H), 7.00−6.96 (m, 2H), 6.92 (t, J = 12.0 Hz, 4H), 6.86 (d, J = 12.0 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): 136.6, 134.1, 132.4, 128.8, 128.7, 128.6, 128.1, 128.0, 127.3, 126.9, 126.7, 126.6, 126.5, 125.6, 125.6.

■ ASSOCIATED CONTENT

Supporting Information

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NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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