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Highly Chemo- and Stereoselective Palladium-Catalyzed Transfer Semihydrogenation of Internal Alkynes Affording *cis*-Alkenes

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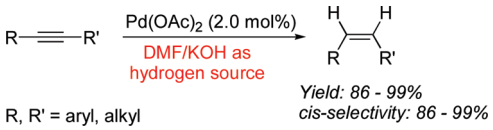

DMF (*N*,*N*-dimethylformamide)/KOH was found to be an efficient hydrogen source in the Pd(OAc)$_2$-catalyzed transfer semihydrogenation of various functionalized internal alkynes to afford *cis*-alkenes in good to high yields with excellent chemo- and stereoselectivity. This catalytic process was also applied to the synthesis of analogues of combretastatin A-4.

Introduction

The selective semihydrogenation of internal alkynes to *cis*-alkenes is an important transformation in organic synthesis, and there are two main classes of catalytic processes that accomplish this goal. One is hydrogenation with molecular hydrogen in the presence of Lindlar's catalyst.[1] The other is transfer hydrogenation with hydrogen donors. The latter has apparent advantages, including safer operation and better control of chemoselectivity of alkenes. However, although the transfer hydrogenation of the polar double bonds of molecules such as ketones and imines has been well documented,[2] the transfer semihydrogenation of internal alkynes to *cis*-alkenes is relatively undescribed in the literature.[3] In particular, the examples of transfer semihydrogenation of diarylacetylenes were very few and limited to diphenyl acetylene.[3a,c] Very recently, Elsevier and co-worker reported the transfer hydrogenation of internal alkynes by using palladium N-heterocyclic carbene complexes as catalysts and HCOOH/Et$_3$N as the hydrogen source.[3e] We noted that when two different diarylacetylenes were used, diphenylacetylene underwent transfer semihydrogenation smoothly to afford *cis*-stilbene in excellent chemoselectivity, but 4-acetylphenyl(phenyl)acetylene showed low chemoselectivity giving a mixture of the *cis*-stilbene derivative and alkane in a ratio of 69:31.

Since there are many important natural products containing the *cis*-stilbene skeleton that exhibit a variety of biological activities,[4] development of a general catalytic system for the transfer semihydrogenation of diarylacetylenes to afford *cis*-stilbenes with high stereo- and chemoselectivity is an important and challenging research topic. Therefore, in this paper, we wish to report our recent results on the efficient transfer semihydrogenation of various internal alkynes, focusing on diarylacetylenes bearing various functional groups catalyzed by Pd(OAc)$_2$ with the use of DMF/KOH as hydrogen source to give *cis*-alkenes.

Results and Discussion

We initially examined the Pd(OAc)$_2$-catalyzed hydrogenation of diphenylacetylene (**1a**) by using HCOOH/Et$_3$N as the

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(1) For representative examples, see: (a) Rajaram, J.; Narula, A. P. S.; Chawla, H. P. S.; Dev, S. *Tetrahedron* **1983**, *39*, 2315–2322. (b) Wovkulich, P. M.; Baggiolini, E. G.; Hennessy, B. M.; Uskokovic, M. R.; Mayer, E.; Norman, A. W. *J. Org. Chem.* **1983**, *48*, 4436–4438. (c) Hauser, F. M.; Ganguly, D. *J. Org. Chem.* **2000**, *65*, 1842–1849. (d) You, Z.-W.; Jiang, Z.-X.; Wang, B.-L.; Qing, F.-L. *J. Org. Chem.* **2006**, *71*, 7261–7267.

(2) For reviews, see: (a) Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567–580. (b) Johnstone, R. A. W.; Wilby, A. H. *Chem. Rev.* **1985**, *85*, 129–170. (c) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97–102. (d) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226–236. (e) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237–248.

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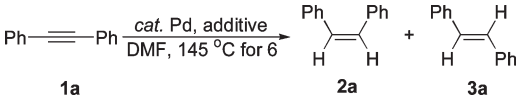
TABLE 1. Palladium-Catalyzed Semireduction of 1,2-Diphenylacetylene[a]



entry	catalyst (mol %)	additive (equiv)	GC yield (%)[b]	2a:3a[c]
1	$Pd(OAc)_2$ (2.0)		< 5	
2	$Pd(OAc)_2$ (2.0)	Cs_2CO_3 (1.5)	< 5	
3	$Pd(OAc)_2$ (0.7)	KOH (1.5)	16	> 99:1
4	$Pd(OAc)_2$ (2.0)	KOH (1.0)	80	98:2
5	$Pd(OAc)_2$ (2.0)	KOH (1.5)	> 99 (96)	97:3
6[d]	$Pd(OAc)_2$ (2.0)	KOH (1.5)	> 99	97:3
7[e]	$Pd(OAc)_2$ (2.0)	KOH (1.5)	> 99	86:14
8[f]	$Pd(OAc)_2$ (2.0)	KOH (1.5)	40	90:10
9[g]	$Pd(OAc)_2$ (2.0)	KOH (1.5)/DMF (1.5)	83	88:12
10	$Pd(OAc)_2$ (2.0)	KOH (1.5)/H_2O (3.0)	> 99	97:3
11	$PdCl_2$ (2.0)	KOH (1.5)	> 99	95:5
12	$PdCl_2(PPh_3)_2$(2.0)	KOH (1.5)	36	81:19
13		KOH (1.5)	0	

[a]Unless otherwise noted, the reactions were carried out with 0.5 mmol of **1a** in 1.0 mL of DMF in a sealed tube at 145 °C for 6 h under nitrogen. [b]The number in parentheses is isolated yield. [c]Determined by GC of reaction mixture. [d]The reaction time was 24 h. [e]The reaction was performed at 100 °C for 24 h. [f]The reaction was carried out under air. [g]Water was used as solvent.

hydrogen source, because HCOOH/Et_3N was used as the hydrogen source in the semihydrogenation of alkynes catalyzed by other palladium complexes.[3a,e] As shown in eq 1, $Pd(OAc)_2$ showed catalytic activity for the transfer hydrogenation of **1a** in toluene at 145 °C to give a 94% GC yield of stilbenes, but both stereo- and chemoselectivity remained to be improved. We then investigated the same reaction using DMF (undried, chemical pure) as the hydrogen source, because it was previously reported that DMF could be used as a hydrogen source via its decomposition catalyzed by Pd(II) complexes.[5]

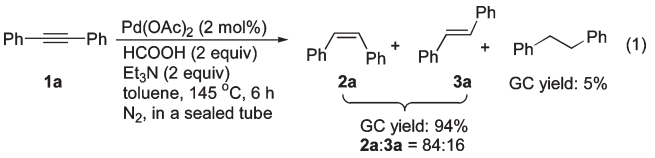
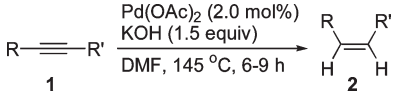


Table 1 shows the results of $Pd(OAc)_2$-catalyzed hydrogenation of **1a** with DMF as both solvent and hydrogen source under different conditions. When a mixture of **1a** and $Pd(OAc)_2$ (2 mol %) in DMF was heated at 145 °C for 6 h, the recovery yield of **1a** exceeded 95%, and only trace amounts of stilbenes were formed, which were confirmed by GC-MS (entry 1). Since it was reported that bases could promote the hydrolysis of DMF,[6] we then examined the reaction with the addition of Cs_2CO_3 and KOH. It was found that the addition of Cs_2CO_3 was ineffective (entry 2), but the addition of KOH could significantly accelerate the semihydrogenation of **1a** to afford *cis*-stilbene (**2a**) with excellent stereoselectivity (entries 3 and 4). In the case of 2 mol % of $Pd(OAc)_2$ and 1.5 equiv of KOH employed, stilbenes were formed in almost quantitative yield, with negligible amounts of 1,2-diphenylethane from the over-reduction of stilbenes. In addition, the stereoselectivity of **2a** was up to 97%, and

(5) Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6738–6742.
(6) (a) Buncel, E.; Zabel, A. W. *Can. J. Chem.* **1981**, 3177–3187. (b) Muccioli, G. G.; Poupaert, J. H.; Wouters, J.; Norberg, B.; Poppitz, W.; Scriba, G. K. E.; Lambert, D. *Tetrahedron* **2003**, *59*, 1301–1307.

TABLE 2. $Pd(OAc)_2$-Catalyzed Semireduction of Internal Alkynes[a]



entry	R	R'	*cis*-alkene		yield (%)	selectivity (%)[b]
1[c]	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	**1b**	**2b**	99	98:2
2[c]	*p*-$C_3H_7C_6H_4$	*p*-$EtOC_6H_4$	**1c**	**2c**	99	> 99:1
3[c]	Ph	BnO-	**1d**	**2d**	93	> 99:1
4	Ph	Ph-	**1e**	**2e**	99	> 99:1
5[c]	Ph	*p*-$CH_3OC_6H_4$	**1f**	**2f**	86	93:7
6[c]	Ph	*o*-$CH_3OC_6H_4$	**1g**	**2g**	93	95:5
7	Ph	*o*-FC_6H_4	**1h**	**2h**	98	97:3
8	Ph	O	**1i**	**2i**	92	96:4
9	Ph		**1j**	**2j**	99	> 99:1
10[c]	Ph		**1k**	**2k**	88	86:14
11	Ph	S	**1l**	**2l**	93	93:7
12	Ph	CH_3	**1m**	**2m**	88	98:2
13	Ph	*n*-C_4H_9	**1n**	**2n**	92	95:5
14	*n*-C_4H_9	*n*-C_4H_9	**1o**	**2o**	87	> 99:1

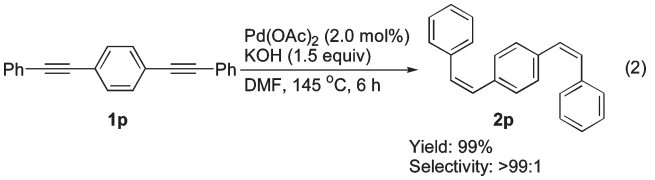
[a]Unless otherwise noted, the reactions were carried out with 0.5 mmol of **1**, 0.75 mmol of KOH, and 0.01 mmol of $Pd(OAc)_2$ in 1.0 mL of DMF in a sealed tube at 145 °C for 6 h under nitrogen. [b]Determined by GC of the reaction mixture. [c]For 9 h.

2a could be isolated in 96% yield from the reaction mixture by careful preparative TLC separation (entry 5). It should be noted that **2a** could not be isomerized into *trans*-stilbene (**3a**) even though the reaction time was prolonged to 24 h (entry 6). However, if the reaction was performed at a lower temperature (100 °C) for 24 h, or in an air atmosphere, either the stereoselectivty of **2a** or the total yield of stilbenes decreased (entries 7 and 8). Although the reaction in water with the use of 1.5 equiv of DMF resulted in a decrease of both total yield of stilbenes and stereoselectivity of **2a** (entry 9), the addition of a small amount of water (3.0 equiv) could not affect the outcome of the reaction (entry 10 vs entry 5). In addition, the catalytic activity of $PdCl_2$ and $Pd(PPh_3)_2Cl_2$ was also studied, and it was found that $PdCl_2$ showed almost the same catalytic activity and stereoselectivity as $Pd(OAc)_2$ (entry 11 vs entry 5). However, $Pd(PPh_3)_2Cl_2$ displayed not only low catalytic activity, but also low stereoselectivity to afford stilbenes in 36% GC yield with a ratio of cis- and trans isomers of 81:19 (entry 12). In the absence of $Pd(OAc)_2$, no reaction occurred at all (entry 13).

Table 2 summarizes the semihydrogenation of various internal alkynes in DMF catalyzed by $Pd(OAc)_2$ (2 mol %) in the presence of KOH (1.5 equiv) at 145 °C for 6−9 h. All the reactions afforded the *cis*-alkenes in good to high yields with excellent selectivity. One exception, however, was the semihydrogenation of 9-phenylethynylanthracene (**1k**), which showed relatively low stereoselectivity due to steric

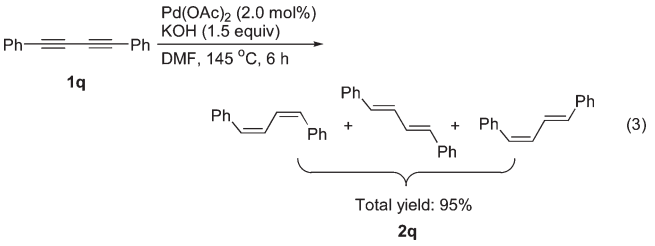
hindrance (Table 2, entry 10). On the basis of the results shown in Table 2, some other points need to be noted in the present semihydrogenation: (1) Both the C−O bond of benzyl ether and the C−F bond remained intact under the reaction conditions (entries 3 and 7). (2) The carbonyl group was not reduced at all (entry 8). (3) Alkyl-substituted internal alkynes also underwent the semihydrogenation with excellent stereoselectivity, and without the associated double-bond shift isomerization (entries 13 and 14).

Under the same reaction conditions, 1,4-bis(phenylethynyl)benzene (**1p**) also underwent the semihydrogenation to afford the *Z*,*Z*-isomer selectively in excellent yield (eq 2).



(2)

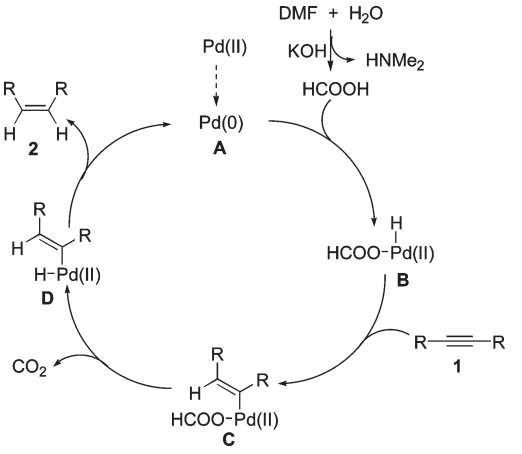
In addition, the transfer hydrogenation of 1,4-diphenylbuta-1,3-diyne (**1q**) was also examined. The reaction occurred smoothly under the same reaction conditions to afford a mixture of *Z*,*Z*-, *E*,*E*-, and *Z*,*E*-isomers in 95% total yield (eq 3). Attempts to separate these semihydrogenated products, however, were not successful.



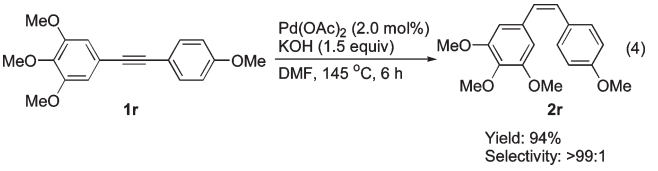
(3)

The synthesis of natural products of *cis*-combretastatin A-4 and analogues is an interesting research topic in organic and medicinal chemistry due to their important biological activities.[4a,7] The ease of the present semihydrogenation of internal alkynes provides a simple and efficient route for the synthesis of such compounds from the corresponding diarylated acetylene. For example, performing the semihydrogenation of 1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)acetylene (**1r**) resulted in the formation of the analogue of *cis*-combretastatin A-4 (**2r**) in 94% isolated yield, and the stereoselectivity of the reaction was up to 99% (eq 4). Compared to previously known procedures in which the synthesis of the analogues of *cis*-combretastatin A-4 required

SCHEME 1. Proposed Mechanism for $Pd(OAc)_2$-Catalyzed Semihydrogenation of Internal Alkynes

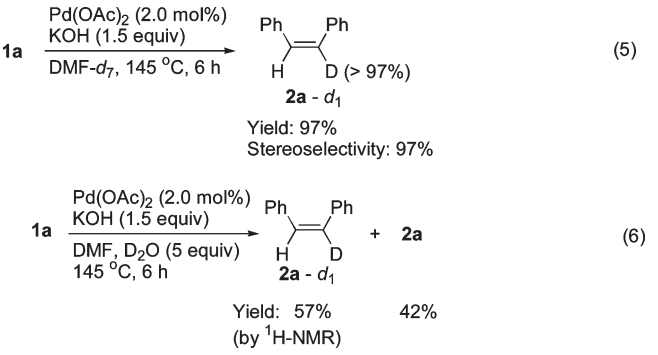


multiple steps,[8] the present procedure is more practical and cost-effective.



(4)

We consider that the success of this process relies on the hydrolysis of DMF in the presence of hydrated KOH to form in situ HCOOH as hydrogen source in the proper concentration range. To confirm the nature of the reducing agent, the semihydrogenation of **1a** in either DMF-d_7 or D_2O was examined. It was found that in the former case, as expected, a highly monodeuterated *cis*-stilbene (**2a**-d_1) was formed (eq 5), and in the latter case, the reaction gave 57% of **2a**-d_1 and 42% of **2a**, respectively (eq 6). The formation of **2a** was due to the existence of H_2O in undried DMF solvent and hydrated KOH. In addition, the formation of $HNMe_2$ and $HN(CD_3)_2$ in the reaction of entry 5 of Table 1 and eq 5 was confirmed by GC-MS analyses of the reaction mixtures.



(5)
(6)

On the basis of observed results and known palladium chemistry,[9] a proposed mechanism for the present semihydrogenation of internal alkynes is depicted in Scheme 1. It includes the formation of HCOOH and its oxidative

(7) For selected reports, see: (a) Pettit, G. R.; Rhodes, M. R.; Herald, D. L.; Hamel, E.; Schmidt, J. M.; Pettit, R. K. *J. Med. Chem.* **2005**, *48*, 4087–4099. (b) Gosslau, A.; Pabbaraja, S.; Knapp, S.; Chen, K. Y. *Eur. J. Pharmacol.* **2008**, *587*, 25–34. (c) Hall, J. J.; Sriram, M.; Strecker, T. E.; Tidmore, J. K.; Jelinek, C. J.; Kumar, G. D. K.; Hadimani, M. B.; Pettit, G. R.; Chaplin, D. J.; Trawick, M. L.; Pinney, K. G. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5146–5149. (d) Fürst, R.; Zupkó, I.; Berényi, A.; Ecker, G. F.; Rinner, U. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 6948–6951.

(8) For selected reports, see: (a) Lara-Ochoa, F.; Espinosa-Pérez, G. *Tetrahedron Lett.* **2007**, *48*, 7007–7010. (b) Giraud, A.; Provot, O.; Harnze, A.; Brion, J. D.; Alami, M. *Tetrahedron Lett.* **2008**, *49*, 1107–1110.

(9) (a) Trost, B. M.; Braslau, R. *Tetrahedron Lett.* **1989**, *30*, 4657–4660. (b) Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712–724. (c) Brunel, J. M. *Tetrahedron* **2007**, *63*, 3899–3906.

addition to Pd(0) species to give intermediate B, selective insertion of alkyne into Pd−H to give intermediate C, and subsequent decarboxylation and reductive elimination of the C−C bond to finally afford *cis*-alkenes and regenerate the Pd(0) species. The oxidative addition of HCOO−H to Pd(0)[9b,c] and the formation of vinyl−Pd by the insertion of alkynes to the Pd−H bond[9b] had been proposed as steps of the catalytic cycle in the palladium-catalyzed hydrocarboxylation of alkynes and reduction of alkenes with formic acid.

It should be noted that although $HCOOH/NEt_3$ can be used as the hydrogen source for the hydrogen transfer of **1a** in the presence of $Pd(OAc)_2$ as shown in eq 1, the use of HCOOH (2.0 equiv) or HCOOH (2.0 equiv)/KOH (1.5 equiv) resulted in the formation of **2a** in trace amounts only. These results indicated that the decomposition of HCOOH into H_2 and CO_2 was the predominant reaction under the reaction conditions, which limited the hydrogenation of **1a**. Therefore, the formation of HCOOH in a proper concentration in the reaction system is the crucial factor in the transfer semihydrogenation of internal alkynes.[10]

Conclusions

In summary, we have developed a practical and efficient $Pd(OAc)_2$-catalyzed transfer semihydrogenation of internal alkynes to afford *cis*-alkenes in good to high yields with excellent chemo- and stereoselectivity by using DMF/KOH as the hydrogen source system. The most significant advantages of the present catalytic system include the use of stable $Pd(OAc)_2$ as catalyst and the wide generality for semihydrogenation of diarylacetylenes bearing different functional groups, as well as dialkylacetyelenes to afford *cis*-alkenes without reduction to alkanes. The catalytic process was also found to be applicable to the synthesis of the analogues of combretastatin A-4.

Experimental Section

Typical Experimental Procedure for Transfer Semihydrogenation of Diphenylacetylene (1a) Affording *cis*-Stilbene (2a) (Table 1, entry 5). Diphenylacetylene (**1a**) (89.0 mg, 0.5 mmol), KOH (42.0 mg, 0.75 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), and DMF (1.0 mL) were placed in a thick-walled Pyrex screw-cap tube (25 mL) under a nitrogen atmosphere, and the tube was capped and the mixture heated in an oil bath at 145 °C with stirring for 6 h. After the reaction mixture was cooled to room temperature, the crude reaction mixture was diluted with CH_2Cl_2 (2.0 mL) and cyclohexane (2.0 mL), and *n*-octadecane (101.7 mg, 0.4 mmol) was then added as an internal standard for GC analysis. After GC and GC-MS analyses of the reaction mixture, volatiles were removed under reduced pressure, and the residue was subjected to silica gel column chromatography [eluting with cyclohexane] to afford **2a** as a colorless viscous oil (86.4 mg, 0.48 mmol, 96%). The GC analysis of the reaction mixture showed the formation of **2a** and **3a** in 99% GC yield, and the ratio of **2a**:**3a** was 97:3.

Characterization Data of Products. *cis*-Stilbene, 2a:[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.17 (m, 10H), 6.59 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 130.4, 129.0, 128.3, 127.2; GCMS *m*/*z* (% rel intensity) 180 (M^+, 100), 165 (52), 152 (14), 102 (10), 89 (29), 77 (22).

***cis*-1-Deuterio-1,2-diphenylethene, 2a-d_1:**[12] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24−7.15 (m, 10H), 6.58 (s, 1H); ^{2}D NMR (600 MHz, $CDCl_3$) δ 6.72 (s, 1D); GCMS *m*/*z* (% rel intensity) 181 (M^+, 90), 180 (100), 179 (68), 178 (32), 166 (32), 153 (11), 90 (24), 77 (21).

***cis*-4,4′-Dimethylstilbene, 2b:**[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, 4H, J = 7.9 Hz), 7.01 (d, 4H, J = 7.9 Hz), 6.50 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 134.6, 129.6, 129.0, 128.9, 21.4; GCMS *m*/*z* (% rel intensity) 208 (M^+, 100), 193 (76), 178 (70), 165 (11), 152 (6), 115 (18), 102 (14), 89 (13), 77 (5).

***cis*-4-Ethoxy-4′-propylstilbene, 2c:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, 4H, J = 7.9 Hz), 7.01 (d, 2H, J = 8.3 Hz), 6.73 (d, 2H, J = 8.6 Hz), 6.45 (s, 2H), 3.96 (q, 2H, J = 6.9 Hz), 2.53 (t, 2H, J = 7.5 Hz), 1.61 (m, 2H), 1.37 (t, 3H, J = 6.9 Hz), 0.92 (t, 3H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 141.5, 135.0, 130.2, 129.9, 129.3, 128.8, 128.4, 114.2, 63.4, 37.9, 24.5, 15.0, 14.0; GCMS *m*/*z* (% rel intensity) 266 (M^+, 100), 237 (81), 209 (54), 194 (8), 178 (13), 165 (26), 115 (9), 104 (8), 91 (8); HRMS *m*/*z* [M^+ + H] 267.1758, calcd for $C_{19}H_{23}O$ 267.1743.

***cis*-1-Phenyl-2-(4-benzyloxyphenyl)ethane, 2d:**[14] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−7.17 (m, 12H), 6.83 (d, 2H, J = 8.9 Hz), 6.52 (s, 2H), 5.03 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 137.7, 137.0, 130.3, 130.0, 129.8, 128.9, 128.7, 128.4, 128.1, 127.6, 127.0, 114.6, 70.1; GCMS *m*/*z* (% rel intensity) 286 (M^+, 22), 195 (19), 165 (10), 152 (7), 91 (100).

4-(*cis*-Styryl)biphenyl, 2e:[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.29 (m, 14H), 6.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 139.9, 137.4, 136.3, 130.5, 129.9, 129.5, 129.0, 128.9, 128.4, 127.4, 127.3, 127.0, 126.9; GCMS *m*/*z* (% rel intensity) 256 (M^+, 100), 239 (22), 178 (21), 165 (18), 152 (9), 91 (10), 77 (5).

***cis*-1-(4-Methoxyphenyl)-2-phenylethene, 2f:**[16] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.16 (m, 7H), 6.74 (d, 2H, J = 8.6 Hz), 6.51 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 137.7, 130.3, 129.9, 129.7, 128.9, 128.3, 127.0, 113.7, 55.3; GCMS *m*/*z* (% rel intensity) 210 (M^+, 100), 195 (21), 179 (18), 165 (39), 152 (30), 128 (4), 115 (8), 89 (12).

***cis*-1-(2-Methoxyphenyl)-2-phenylethene, 2g:**[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.16 (m, 7H), 6.90 (d, 1H, J = 8.2 Hz), 6.79−6.62 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 137.4, 130.4, 130.2, 129.0, 128.7, 128.2, 127.0, 126.3, 125.9, 120.3, 110.8, 55.6; GCMS *m*/*z* (% rel intensity) 210 (M^+, 100), 195 (7), 179 (17), 165 (54), 152 (31), 139 (6), 119 (36), 104 (32), 91 (37).

***cis*-1-(2-Fluorophenyl)-2-phenylethene, 2h:**[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.23 (m, 7H), 7.13−6.95 (m, 2H), 6.78 (d, 1H, J = 12.1 Hz), 6.68 (d, 1H, J = 12.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 (d, J = 247.3 Hz), 136.9, 132.3, 130.6 (d, J = 28.8 Hz), 129.0 (d, J = 86.6 Hz), 128.9, 128.3, 127.5, 125.1 (d, J = 151.3 Hz), 127.7 (d, J = 36.0 Hz), 122.7 (d, J = 28.8 Hz), 115.7 (d, J = 216.3 Hz); GCMS *m*/*z* (% rel intensity) 198 (M^+, 100), 183 (34), 177 (29), 165 (5), 120 (7), 98 (15), 77 (9).

***cis*-1-(4-Acetylphenyl)-2-phenylethene, 2i:**[19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.2 Hz), 7.31 (d, 2H, J = 8.2 Hz),

(10) One reviewer considered that the true reductant might be Me_2NH or Et_3N, and suggested authors to perform the semihydrogenation using amine/KOH as a possible reductant. However, under similar reaction conditions, the use of Et_3N or Bu_2NH instead of DMF resulted in only a trace amount of stilbenes formation in the reaction of **1a**.

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7.22 (s_{br}, 5H), 6.71 (d, 1H, J = 12.2 Hz), 6.59 (d, 1H, J = 12.2 Hz), 2.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 142.4, 136.7, 135.7, 132.5, 129.2, 129.1, 128.9, 128.8, 128.4, 127.6, 26.7; GCMS m/z (% rel intensity) 222 (M^+, 62), 207 (100), 178 (64), 152 (15), 103 (6), 89 (16), 77 (11).

***cis*-1-(2-Naphthyl)-1-phenylethene, 2j:**[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78−7.60 (m, 4H), 7.41−7.16 (m, 8H), 6.73 (d, 1H, J = 12.0 Hz), 6.65 (d, 1H, J = 12.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 135.0, 133.6, 132.7, 130.7, 130.3, 129.1, 128.4, 128.1, 128.1, 127.7, 127.6, 127.3, 127.1, 126.1, 126.0; GCMS m/z (% rel intensity) 230 (M^+, 100), 215 (27), 202 (12), 152 (7), 128 (6), 114 (23), 101 (18), 77 (4).

9-(*cis*-Styryl)anthracene and 9-(*trans*-styryl)anthracene (a mixture of two isomers), 2k:[21] ^{1}H NMR of cis isomer (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.18 (d, 2H, J = 8.3 Hz), 7.93 (d, 2H, J = 7.9 Hz), 7.39−7.29 (m), 7.10 (d, 2H, J = 6.5 Hz), 6.95−6.78 (m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 134.1, 132.6, 131.8, 131.6, 131.3, 128.8, 128.6, 128.2, 127.9, 127.3, 126.9, 126.7, 126.6, 126.5, 126.2, 125.7, 125.4; GCMS m/z (% rel intensity) cis isomer 280 (M^+, 100), 202 (39), 138 (12), 113 (5), 77 (1), trans isomer 280 (M^+, 100), 202 (37), 138 (9), 126 (12), 77 (3).

***cis*-2-Styrylthiophene, 2l:**[22] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.34 (m, 5H), 7.14 (d, 1H, J = 4.8 Hz), 7.03 (d, 1H, J = 2.7 Hz), 6.94 (m, 1H), 6.77 (d, 1H, J = 11.7 Hz), 6.64 (d, 1H, J = 11.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 137.5, 129.1, 129.0, 128.7, 128.4, 127.7, 126.6, 125.7, 123.6; GCMS m/z (% rel intensity) 186 (M^+, 100), 171 (18), 152 (31), 141 (21), 115 (15), 92 (9), 77 (7).

***cis*-1-Methyl-2-phenylethene, 2m:**[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.20 (m, 5H), 6.43 (d, 1H, J = 10.3 Hz), 5.78 (m, 1H), 1.90 (d, 3H, J = 8.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 130.0, 129.0, 128.2, 126.9, 126.5, 14.8; GCMS m/z (% rel intensity) 118 (M^+, 76), 117 (100), 103 (7), 91 (27), 77 (8), 65 (8), 51 (14).

***cis*-1-Phenyl-1-hexene, 2n:**[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32−7.24 (m, 5H), 6.39 (d, 1H, J = 11.7 Hz), 5.65 (m, 1H), 2.32 (m, 2H), 1.44−1.26 (m, 4H), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 133.3, 128.9, 128.8, 128.2, 126.5, 32.3, 28.5, 22.6, 14.1; GCMS m/z (% rel intensity) 160 (M^+, 28), 131 (6), 117 (100), 104 (76), 91 (33), 77 (7), 65 (8), 51 (7).

***cis*-5-Decene, 2o:**[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36−5.33 (t, 2H, J = 4.8 Hz), 2.10−1.95 (m, 4H), 1.38−1.21 (m, 8H), 0.89 (t, 6H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.0, 32.1, 27.1, 22.5, 14.1; GCMS m/z (% rel intensity) 140 (M^+, 18), 112 (2), 97 (11), 83 (12), 69 (51), 55 (100).

1,4-*cis*,*cis*-Distyrylbenzene, 2p:[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−7.02 (m, 14H), 6.57−6.48 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 136.2, 130.4, 130.1, 129.0, 128.9, 128.3, 127.3; GCMS m/z (% rel intensity) 282 (M^+, 100), 265 (11), 207 (23), 191 (17), 178 (30), 103 (9), 91 (5), 77 (9).

1,4-Diphenyl-1,3-butadiene (a mixture of three isomers), 2q:[27] ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.4, 135.0, 132.9, 132.2, 130.5, 130.4, 129.4, 129.3, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 127.4, 127.2, 126.7, 126.6, 126.5, 126.1, 125.3; GCMS m/z (% rel intensity) 206 (M^+, 100), 191 (38), 165 (15), 128 (55), 91 (99), 77 (18), 51 (17); 206 (M^+, 92), 191 (37), 165 (12), 128 (51), 91 (100), 77 (17), 51 (16); 206 (M^+, 100), 191 (35), 165 (12), 128 (48), 91 (93), 77 (14), 51 (14).

***cis*-1-(4-Methoxyphenyl)-1-(3,4,5-trimethoxyphenyl)ethene, 2r:**[28] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 2H, J = 8.6 Hz), 6.78 (d, 2H, J = 8.6 Hz), 6.50 (d, 1H, J = 12.0 Hz), 6.50 (s, 2H), 6.42 (d, 1H, J = 12.0 Hz), 3.83 (s, 3H), 3.77 (s, 3H), 3.68 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 153.0, 137.2, 133.0, 130.3, 129.8, 129.6, 128.8, 113.7, 106.1, 61.0, 56.0, 55.3; GCMS m/z (% rel intensity) 300 (M^+, 100), 285 (98), 225 (14), 171 (11), 128 (15), 91 (4).

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Supporting Information Available: General method, characterization data, copies of ^{1}H and ^{13}C NMR charts of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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