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Palladium-catalyzed reduction of alkynes employing $HSiEt_3$: stereoselective synthesis of *trans*- and *cis*-alkenes

Fang Luo [a], Changduo Pan [b], Wenhui Wang [a], Zhishi Ye [a], Jiang Cheng [a,*]

[a] College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou, 325027, PR China
[b] Wenzhou Institute of Industry & Science, Wenzhou 325000, PR China

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ABSTRACT

The palladium-catalyzed semi-hydrogenation of alkynes to *trans*- or *cis*-alkenes employing $HSiEt_3$ as the reductant is developed. The $CuSO_4$ played a significant role for the *trans*/*cis* stereoselectivity. The labeling study revealed that the two olefinic hydrogen atoms came from $HSiEt_3$ and H_2O, respectively.

1. Introduction

The stereoselective semi-hydrogenation of alkynes to alkenes is an important process, which has been extensively used in the construction of bioactive molecules, natural products, and industrial materials.[1] Among the reported examples,[2] the Lindlar catalyst-catalyzed hydrogenation,[3] is probably the most facile procedure to obtain *cis*-alkenes. Recently, organosilicons have been reported as reductants for the aforementioned transformations. For example, Trost and Braslav reported reduction of alkynes to *cis*-alkenes using tetramethyldihydrosiloxane (TMDHS) as the reductant.[4] Kini and co-workers described the reduction of alkynes employing hydrosilane immobilized on silica gel, providing the *cis*-alkenes in good yields.[5] Very recently, Giraud and co-workers demonstrated synthesis of *cis*-alkenes via a new hydrosilylation–protodesilylation process.[6] However, examples of semi-hydrogenation of alkynes to *trans*-alkenes were rarely studied or reported before. The reduction of alkynes by alkali metals (Li, Na) in liquid ammonia is the traditional and powerful method for the synthesis of *trans*-alkenes,[7] but the harsh reaction condition diminished the functional group tolerance. In 1999, Tani and co-workers reported an efficient iridium-catalyzed selective hydrogenation of alkynes to *trans*-alkenes using methanol as the hydrogen donor.[8] In 2005, Shirakawa described reduction of alkynes with hexamethyldisilane and deuterium oxide to *trans*-1,2-dideuterioalkenes.[9] From the synthetic point of view, it is a high desired goal to stereoselectively provide *trans*/*cis* alkenes in a simple way. Herein, we wish to report the stereoselective semi-hydrogenation of alkynes to *trans*- or *cis*-alkenes employing $HSiEt_3$ as the reductant, where $CuSO_4$ played an important role for the *trans*/*cis* stereoselective.

2. Result and discussion

Initial studies were performed by using diphenylacetylene as a model substrate (Table 1). Only 20% yield of *trans*-stilbene was obtained with the combination of $PdCl_2$(dppf)/dppf in toluene/H_2O after 72 h (Table 1, entry 1). Interestingly, the yield was sharply increased to 99% within 24 h when 15 mol % of $CuSO_4$ was used as an additive (Table 1, entry 2). The ligands used had dramatic effects on the reaction (Table 1, entries 2–7). Dppf was better than dppb, dppe, dppp, and PPh_3. In addition, a profound solvent effect was observed and the co-solvent (toluene/H_2O) was tested to be superior to others (Table 1, entries 8–11). Water was essential in the reaction and dry toluene inhibited the reaction (Table 1, entry 2). Among the palladium sources tested, $PdCl_2$(dppf) was the best, while the use of $Pd(OAc)_2$ or $PdCl_2(CH_3CN)_2$ produced only trace amount of product (Table 1, entries 6–11). No product was detected without Pd source. Moreover, the replacement of $CuSO_4$ with $Cu(OAc)_2$, $Cu(OTf)_2$, CuI, or Ag_2O resulted in no reaction or lower yields.

* Corresponding author. Tel./fax: +86 577 88156826.
E-mail address: jiangcheng@wzu.edu.cn (J. Cheng).

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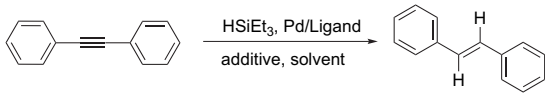
Table 1
Selected results of Pd sources, ligands, additives and solvents screening[a]



Entry	Pd source	Ligand	Additive	Solvent	Yield[b] (%)
1	$PdCl_2$(dppf)	dppf		Toluene/H_2O	20[c]
2	$PdCl_2$(dppf)	dppf	$CuSO_4$	Toluene/H_2O	99 (<5)[d]
3	$PdCl_2$(dppf)	dppe	$CUSO_4$	Toluene/H_2O	<5
4	$PdCl_2$(dppf)	P(1-nap)$_3$	$CuSO_4$	Toluene/H_2O	88
5	$PdCl_2$(dppf)	PPh_3	$CuSO_4$	Toluene/H_2O	<5
6	$PdCl_2$(dppf)	dppp	$CuSO_4$	Toluene/H_2O	10
7	$PdCl_2$(dppf)	dppb	$CuSO_4$	Toluene/H_2O	10
8	$PdCl_2(PPh_3)_2$	dppf	$CuSO_4$	Toluene/H_2O	86
9	$PdCl_2(CH_3CN)_2$	dppf	$CuSO_4$	Toluene/H_2O	<5
10	$PdCl_2$	dppf	$CuSO_4$	Toluene/H_2O	28
11	$Pd(OAc)_2$	dppf	$CuSO_4$	Toluene/H_2O	<5
12	$PdCl_2$(dppf)	dppf	$CuSO_4$	CH_3CN/H_2O	30
13	$PdCl_2$(dppf)	dppf	$CuSO_4$	DCE/H_2O	70
14	$PdCl_2$(dppf)	dppf	$CuSO_4$	DME/H_2O	40
15	$PdCl_2$(dppf)	dppf	$CuSO_4$	DMAc/H_2O	<5
16	$PdCl_2$(dppf)	dppf	$Cu(OAc)_2$	Toluene/H_2O	<5
17	$PdCl_2$(dppf)	dppf	$Cu(OTf)_2$	Toluene/H_2O	72
18	$PdCl_2$(dppf)	dppf	CuI	Toluene/H_2O	<5
19	$PdCl_2$(dppf)	dppf	Ag_2O	Toluene/H_2O	<5
20		dppf	$CuSO_4$	Toluene/H_2O	<5

[a] All of the reactions were run with diphenylacetylene (35.6 mg, 0.2 mmol), $HSiEt_3$ (46.5 mg, 0.4 mmol), Pd source (1.5 mol %), ligand (5 mol %), additive (15 mol %), solvent (1 mL), and H_2O (0.1 mL), reflux, under air, 24 h.
[b] Isolated yield.
[c] 72 h.
[d] Dry toluene.

Finally, the optimized reaction condition to obtain *trans*-alkenes was as follows: $PdCl_2$(dppf) (1.5 mol %), dppf (5.0 mol %), $HSiEt_3$ (2 equiv), and $CuSO_4$ (15 mol %) in toluene/H_2O (1/0.1 mL), under reflux condition. With the optimized reaction conditions in hand, a series of alkynes were tested. The results are summarized in Table 2.

As expected, the semi-hydrogenation with $HSiEt_3$–H_2O was applied to various internal alkynes, providing the *trans*-alkenes in good to excellent yields. Aromatic alkynes possessing both electron-withdrawing and electron-donating groups on the phenyl rings worked well under the reaction condition. A range of functional groups, such as chloro, fluoro, methoxy, hydroxyl, acetyl, carbethoxy, cyano and nitro groups were tolerated in this procedure. The alkyne having one hetero aromatic ring also ran smoothly in the procedure (Table 2, entry 15). Moreover, alkyl(aryl)acetylenes was subjected to the procedure and produced the semi-hydrogenation product in 75% yield (Table 2, entry 16). Particularly, the nitro group of **1k** survived under these conditions while this group may transform to amine in hydrogenation reaction (Table 2, entry 11).[10] It is worth noting that semi-hydrogenation of 1,4-diphenylbuta-1,3-diyne to (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene was obtained with 66% yield (Table 2, entry 17). Importantly, the rigorous exclusion of air/moisture was not required in any of these transformations. As such, this represents an exceedingly practical alternative method for the synthesis of *trans*-alkenes.

Next, labeling studies were conducted. Interestingly, under the co-solvent (toluene/D_2O), *trans*-1-deuterio-1,2-diphenylethene was formed in 92% yield (Scheme 1). We could conclude that two olefinic hydrogen atoms came from $HSiEt_3$ and H_2O, respectively, which was different from the previous report of Shirakawa's.[7] Moreover, it provided a simple method for the synthesis of *trans*-1-deuterio-1,2-diaryl ethene.

Importantly, $CuSO_4$ had a significant effect on the stereoselectivity. In the absence of $CuSO_4$, *cis*-alkenes were obtained in a slightly modified procedure. The results are shown in Table 3.

A controlling experiment was run to understand the role of $CuSO_4$. *cis*-Stilbene was transformed completely to *trans*-stilbene in the presence of $CuSO_4$ in two hours, while the reaction was transformed incompletely without $CuSO_4$ (Scheme 2). It revealed $CuSO_4$ could accelerate the transformation of *cis*-alkenes to the *trans*-analogues.

A working mechanism was proposed as outlined in Scheme 3 on the basis of the previously reported mechanism.[3a,6] It included reduction of $PdCl_2$(dppf) to Pd(0) in the presence of dppf and $HSiEt_3$, releasing a molecular of HCl in the presence of H_2O.[11,12] Then, hydropalladation of an alkyne with chloropalladium hydride, which was generated by the oxidative addition of hydrochloric acid to a Pd(0) species, occurred to form alkenylpalladium chloride intermediate **A**. The intermediate **A** exchanged the chloro group to hydride with $HSiEt_3$, producing alkenylpalladium chloride intermediate **B**. The following reductive elimination of the alkenylpalladium hydride **B** afforded *cis*-alkene and regenerated the Pd(0) species. Finally, *cis*-alkenes were converted to *trans*-alkenes in the presence of $CuSO_4$.

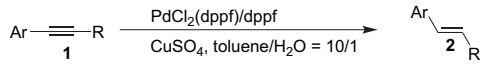
In summary, we have successfully developed the stereoselective semi-hydrogenation of alkynes to *trans*-alkenes or *cis*-alkenes employing $HSiEt_3$ as the reductant. $CuSO_4$ played an important role for the stereoselectivity. The rigorous exclusion of air/moisture was not required in any of these transformations, as such, it represents a simple and facile way for the synthesis of *trans*- or *cis*-alkenes.

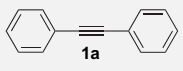
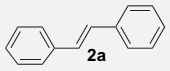
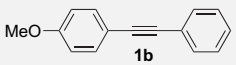
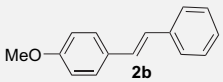
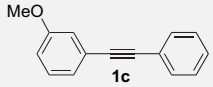
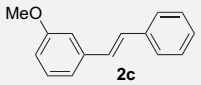
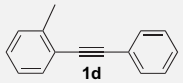
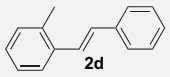
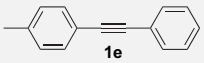
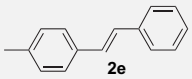
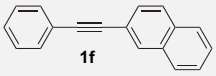
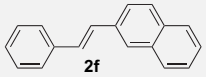
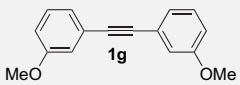
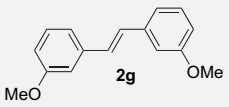
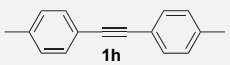
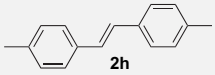
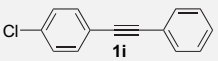
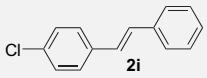
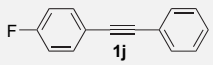
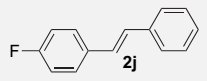
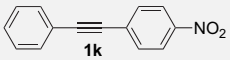
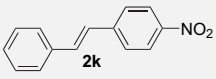
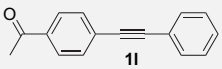
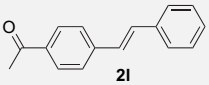
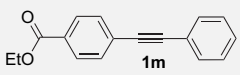
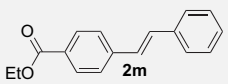
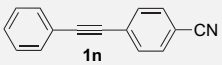
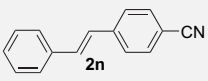
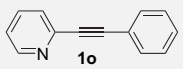
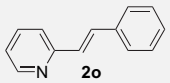
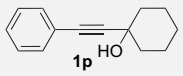
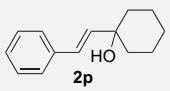
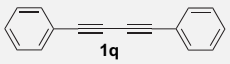
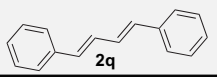
3. Experimental section

3.1. General procedure

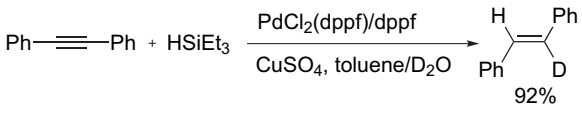
Chemicals were either purchased or purified by standard techniques without special instructions. ^1H NMR and ^{13}C NMR spectra were measured on a 300 MHz Bruker spectrometer (^1H 300 MHz, ^{13}C 75 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are

Table 2
Palladium-catalyzed reduction of alkynes to *trans*-alkenes[a]



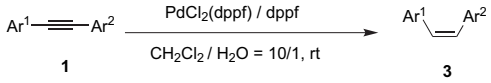
Entry	Substrate **1**	Product **2**	Yield[b] (%)
1			99
2			90
3			92
4			98
5			88
6			99
7			90
8			87
9			99
10			80
11			80
12			79
13			83
14			86
15			78
16			75
17			66[c]

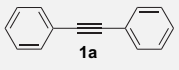
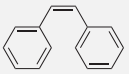
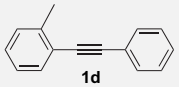
[a] The reactions were run with internal alkynes (0.2 mmol), $HSiEt_3$ (0.4 mmol), $PdCl_2(dppf)$ (1.5 mol %), dppf (5 mol %), $CuSO_4$ (15 mol %), toluene (1 mL), and H_2O (0.1 mL), reflux, under air, 24 h.
[b] Isolated yield.
[c] 1q (0.2 mmol), $HSiEt_3$ (0.8 mmol), $PdCl_2(dppf)$(3 mol %), dppf (10 mol %), $CuSO_4$ (30 mol %).



Scheme 1. Labeling study using D_2O.

Table 3
Palladium-catalyzed reduction of alkynes to *cis*-alkenes[a]



Entry	Substrate **1**	Product **3**	Yield[b] (%)
1			75
2			85
3			74
4			73
5			70
6			61

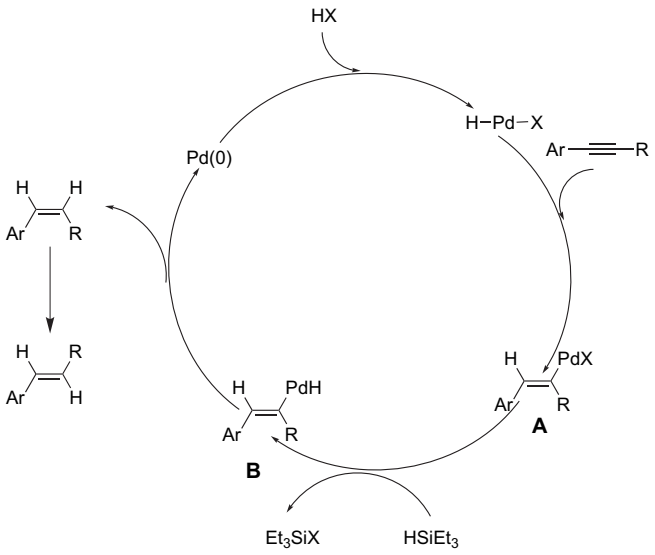
[a] All of the reactions were run with internal alkynes (0.2 mmol), $HSiEt_3$ (0.4 mmol), $PdCl_2(dppf)$ (1.5 mol %), dppf (5 mol %), CH_2Cl_2 (1 mL), and H_2O (0.1 mL), rt, under air, 36 h.
[b] Isolated yield.

given in Hertz. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

3.2. Typical experimental procedure for palladium-catalyzed reduction of alkynes into *trans*-alkenes

Under air atmosphere, a reaction tube was charged with internal alkynes (0.2 mmol), $HSiEt_3$ (46.5 mg, 0.4 mmol), $PdCl_2(dppf)$ (2.2 mg, 1.5 mol %), dppf (5.5 mg, 5 mol %), $CuSO_4$ (4.8 mg, 15 mol %), toluene/H_2O (1/0.1 mL). After the mixture was refluxed for 24 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the product.

Scheme 2. The role of $CuSO_4$.



Scheme 3. Possible mechanism.

3.3. Typical experimental procedure for palladium-catalyzed reduction of alkynes into *cis*-alkenes

Under air atmosphere, a reaction tube was charged with internal alkynes (0.2 mmol), $HSiEt_3$ (46.5 mg, 0.4 mmol), $PdCl_2$(dppf) (2.2 mg, 1.5 mol %), dppf (5.5 mg, 5 mol %), CH_2Cl_2/H_2O (1/0.1 mL). After the mixture was stirred at rt for 36 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel to give the product.

*3.3.1. (E)-1,2-Diphenylethene (**2a**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56–7.53 (m, 4H), 7.41–7.36 (m, 4H), 7.31–7.28 (m, 2H,), 7.14 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3, 128.7, 127.6, 126.5.

*3.3.2. (E)-1-(4-Methoxystyryl)benzene (**2b**)*[14]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51–7.45 (m, 4H), 7.38–7.33(m, 2H), 7.24–7.22 (m, 1H), 7.08 (d, J=16.3 Hz, 1H), 6.94 (d, J=16.3 Hz, 1H), 6.90 (d, J=7.5 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.3, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.1, 55.30.

*3.3.3. (E)-1-Methoxy-3-styrylbenzene (**2c**)*[15]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55–7.52 (m, 2H), 7.40–7.35 (m, 2H), 7.30–7.27 (m, 2H), 7.15–7.07 (m, 4H), 6.86–6.84 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.9, 138.8, 137.2, 129.6, 129.0, 128.7, 128.6, 127.7, 126.5, 119.2, 113.3, 111.8, 55.2.

*3.3.4. (E)-1-Methyl-2-styrylbenzene (**2d**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.60 (m, 1H), 7.56–7.53 (m, 2H), 7.41–7.19 (m, 7H), 7.01 (d, J=16.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.7, 136.4, 135.8, 130.4, 129.9, 128.7, 127.6, 127.5, 126.5, 126.2, 125.4, 19.9.

*3.3.5. (E)-1-Methyl-4-styrylbenzene (**2e**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54 (d, J=7.5 Hz, 2H), 7.45–7.36 (m, 4H), 7.30–7.28 (m, 1H), 7.20 (d, J=7.9 Hz, 2H), 7.12 (s, 2H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.5, 134.5, 129.4, 128.7, 128.6, 127.7, 127.4, 126.43, 126.40, 21.3.

*3.3.6. (E)-2-Styrylnaphthalene (**2f**)*[16]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.25 (d, J=7.5 Hz, 1H), 7.95–7.76 (m, 4H), 7.65–7.63 (m, 2H), 7.57–7.52 (m, 3), 7.44–7.41 (m, 1H), 7.19 (d, J=16.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.6, 135.0, 133.7, 131.7, 131.4, 128.8, 128.6, 128.0, 127.8, 126.7, 126.1, 125.8, 125.79, 125.70, 123.8, 123.6.

*3.3.7. (E)-1,2-Bis(3-methoxyphenyl)ethene (**2g**)*[17]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31–7.28 (m, 2H), 7.15–7.08 (m, 6H), 6.85 (d, J=8.1 Hz, 2H), 3.87 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.9, 138.7, 129.7, 128.9, 119.3, 113.4, 111.7, 55.2.

*3.3.8. (E)-1,2-Dip-tolylethene (**2h**)*[18]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43 (d, J=8.1 Hz, 4H), 7.18 (d, J=8.0 Hz, 4H), 7.07 (s, 2H), 2.38 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3, 134.7, 129.4, 127.6, 126.3, 21.2.

*3.3.9. (E)-1-Chloro-4-styrylbenzene (**2i**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51 (m, 2H), 7.45 (m 2H), 7.40–7.30 (m, 5H), 7.07 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.9, 135.8, 133.1, 129.3, 128.8, 128.7, 127.8, 127.6, 127.3, 126.5.

*3.3.10. (E)-1-Fluoro-4-styrylbenzene (**2j**)*[14]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50–7.44 (m, 4H), 7.37–7.32 (m, 2H), 7.27–7.24 (m, 1H), 7.07–6.97 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.4, 137.1, 133.5, 128.7, 128.5 (d, J=2.4 Hz), 127.9 (d, J=7.8 Hz), 127.6, 127.5, 126.4, 115.6 (d, J=21.4 Hz).

*3.3.11. (E)-1-Nitro-4-styrylbenzene (**2k**)*[19]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (d, J=8.8 Hz, 2H), 7.64 (d, J=8.8 Hz, 2H), 7.56 (d, J=8.3 Hz, 2H), 7.44–7.26 (m, 4H), 7.15 (d, J=16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 136.2, 133.3, 128.9, 128.85, 128.84, 127.0, 126.8, 126.3, 124.1.

*3.3.12. (E)-1-(4-Styrylphenyl)ethanone (**2l**)*[20]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95 (d, J=8.4 Hz, 2H), 7.59–7.53 (m, 4H), 7.41–7.30 (m, 3H), 7.22 (d, J=16.4 Hz, 1H), 7.13 (d, J=16.3 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.5, 141.9, 136.7, 135.9, 131.4, 128.8, 128.7, 128.3, 127.4, 126.8, 126.5, 26.5.

*3.3.13. (E)-Ethyl 4-styrylbenzoate (**2m**)*[21]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, J=8.4 Hz, 2H), 7.55 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.22 (d, J=16.3 Hz, 1H), 7.12 (d, J=16.3 Hz, 1H), 4.39 (q, J=7.1 Hz, 2H), 1.41 (t, J=7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.4, 141.7, 136.7, 131.1, 129.9, 129.2, 128.7, 128.2, 127.6, 126.7, 126.2, 60.9, 14.3.

*3.3.14. (E)-4-Styrylbenzonitrile (**2n**)*[22]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65–7.52 (m, 6H), 7.42–7.32 (m, 3H), 7.22 (d, J=16.3 Hz, 1H), 7.08 (d, J=16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.8, 136.3, 132.5, 132.4, 128.8, 128.6, 126.9, 126.8, 126.7, 118.9, 110.5.

*3.3.15. (E)-2-Styrylpyridine (**2o**)*[14]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.62 (s, 1H), 7.72–7.58 (m, 4H), 7.44–7.18 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.4, 149.1, 136.9, 136.5, 133.3, 128.7, 128.6, 128.4, 127.3, 127.2, 122.1.

*3.3.16. (E)-1-(4-Methoxystyryl)cyclohexanol (**2p**)*[23]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.33 (d, J=8.5 Hz, 2H), 6.84 (d, J=8.5 Hz, 2H), 6.64 (d, J=16.0 Hz, 1H), 6.39 (d, J=16.1 Hz, 1H), 5.84 (s, 1H), 3.8 (s, 3H), 2.25–2.17 (m, 4H), 1.74–1.61 (m, 4H), 0.87–0.83 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.7, 135.9, 130.8, 130.7, 129.7, 127.2, 124.1, 114.0, 55.3, 26.1, 24.5, 22.6, 22.5.

*3.3.17. (1E,3E)-1,4-Diphenylbuta-1,3-diene (**2q**)*[24]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47–7.45 (m, 4H), 7.37–32 (m, 4H), 7.28–7.24 (m, 2H), 7.01–6.95 (dd, 2H, J=14.6 Hz, J=12.0 Hz), 6.71–6.66 (dd, 2H, J=14.6 Hz, J=11.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3, 132.8, 129.2, 128.6, 127.5, 126.4.

*3.3.18. (Z)-1,2-Diphenylethene (**3a**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28–7.21 (m, 10H), 6.63 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.2, 130.2, 128.9, 128.2, 127.1.

*3.3.19. (Z)-1-Methyl-2-styrylbenzene (**3d**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23–7.06 (m, 9H), 6.66–6.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.1, 136.9, 136.1, 130.5, 130.0, 129.5, 128.9, 128.8, 128.0, 127.2, 127.0, 125.7, 19.8.

*3.3.20. (Z)-1-Methyl-4-styrylbenzene (**3e**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.27–7.20 (m, 5H), 7.16 (d, J=8.0 Hz, 2H), 7.05 (d, J=7.9 Hz, 2H), 6.58 (s, 2H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.5, 136.9, 134.3, 130.2, 129.5, 128.89, 128.87, 128.83, 128.77, 128.2, 127.0, 21.2.

*3.3.21. (Z)-2-Styrylnaphthalene (**3f**)*[25]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11–8.08 (m, 1H), 7.90–7.87 (m, 1H), 7.78–7.76 (m, 1H), 7.52–7.48 (m, 2H), 7.37–7.35 (m, 2H), 7.11–7.04 (m, 6H), 6.85 (d, J=12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.7, 135.3, 133.7, 132.0, 131.6, 129.0, 128.5, 128.4, 128.0, 127.5, 127.0, 126.4, 126.0, 125.9, 125.6, 124.9.

*3.3.22. (Z)-1-Chloro-4-styrylbenzene (**3i**)*[13]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.16 (m, 9H), 6.64 (d, J=12.2 Hz, 1H), 6.54 (d, J=12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.9, 135.6, 132.7, 130.9, 130.2, 128.9, 128.8, 128.4, 128.3, 127.3.

*3.3.23. (Z)-1-Fluoro-4-styrylbenzene (**3j**)*[26]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.19 (m, 7H), 6.92 (t, J=8.7 Hz, 2H), 6.61 (d, J=12.2 Hz, 1H), 6.54 (d, J=12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.4, 160.2, 137.0, 133.2, 133.1, 130.5, 130.4, 130.2, 129.0, 128.8, 128.3, 127.2, 115.2, 115.0.

3.3.24. (E)-1-Deuterio-1,2-diphenylethene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–7.54 (m, 3H), 7.42–7.37 (m, 4H), 7.32–7.27 (m, 2H), 7.15 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.3, 137.2, 128.7, 128.6, 128.4, 127.6, 126.5.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.11.098.

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