DOI: 10.1002/ejoc.200600390

# An Efficient and Selective Hydroarylation of Styrenes with Electron-Rich Arenes, Catalyzed by Bismuth(III) Chloride and Affording Markovnikov Adducts

**Hong-Bin Sun,[a,b] Biao Li,[a] Ruimao Hua,*[a] and Yingwu Yin[b]**

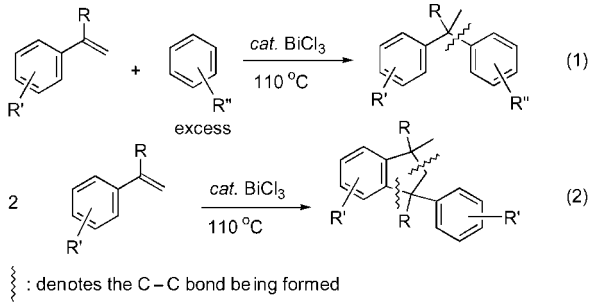
**Keywords:** Arenes / Bismuth trichloride / Dimerization / Hydroarylation / Markovnikov adduct

In the presence of $BiCl_3$, the hydroarylation of styrenes with electron-rich arenes afforded Markovnikov adducts selectively in good to high yields. Under arene-free conditions, the intermolecular hydroarylation of α-substituted styrenes and subsequent intramolecular hydroarylation produced the cyclic dimers of α-substituted styrenes in good yields.


## Introduction

Catalytic hydroarylation of alkenes is one of the current interesting and useful reactions to construct a new C–C bond. Therefore, in recent years, the transition-metal-catalyzed intramolecular and intermolecular hydroarylation of alkenes has been extensively explored.[1] Among the reported procedures, the use of either specific structures of aromatic compounds, activated alkenes (electron-deficient alkenes), or specific solvents were required for achieving the acceptable yields. Therefore, development of a simple, easily available, and efficient catalyst system for hydroarylation of alkenes is still one of the challenging subjects in organic and catalysis chemistry.

In recent years, bismuth(III) compounds such as $BiCl_3$,[2] $BiBr_3$,[3] $Bi(NO_3)_3$,[4] and $Bi(OTf)_3$[5] have attracted more attention because of their diverse applicability as catalysts in organic synthesis.[6] Compared with transition-metal complexes, bismuth(III) salts are stable in air, relatively nontoxic, and inexpensive. In this paper, we report our new findings of $BiCl_3$-catalyzed hydroarylation of styrenes with electron-rich arenes to afford Markovnikov adducts selectively and of the cyclic double hydroarylation of two molecules of α-substituted styrenes to produce the cyclic dimers [Equations (1) and (2)].




## Results and Discussion

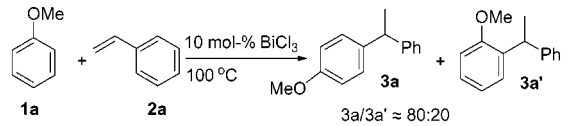
To determine the optimum reaction conditions, the reaction of anisole **1a** with styrene **2a** under several reaction conditions was first investigated, and the reaction progress and yield were monitored and determined by GC with the use of an internal standard. The obtained results are summarized in Table 1. The reaction of equimolar amounts of **1a** with **2a** at 100 °C for 15 h in the presence of 5 mol-% of $BiCl_3$ resulted in the conversion of **2a** completely. The GC and GC–MS analyses of the reaction mixture disclosed that the reaction produced a complicated mixture of products including **3a**, **3a′**, and the hydroarylated products of **2a** with **3a** or **3a′**, as well as the dimers of **2a** (vide infra) (Table 1, Entry 1). The use of an excess amount of **1a** could effectively suppress these side reactions, and the yields of **3** could be increased significantly. When a 10:1 ratio of **1a** and **2a** was used, the formation of by-products could be negligible (Table 1, Entries 2 and 3). Furthermore, the prolonged reaction time or the increase in the amount of $BiCl_3$ led to the formation of **3** in high to quantitative yields (Table 1, Entries 4 and 5). Note that in Entries 3 and 4, the formation

[a] Department of Chemistry, Tsinghua University, Key Laboratory of Organic Optoelectronics & Molecular Engineering of Ministry of Education,
Beijing 100084, China
Fax: + 86-10-62792596
E-mail: ruimao@mail.tsinghua.edu.cn
[b] Key Laboratory of Bioorganic Phosphorus Chemistry of Ministry of Education,
Beijing 100084, China.
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

of two Markovnikov addition products, **3a** and **3a′**, was in a ratio of ca. 80:20. However, other bismuth compounds such as $Bi(NO_3)_3{\cdot}5H_2O$, $(BiO)_2CO_3$, and $Bi_2O_3$ did not show this catalytic activity at all.

Table 1. $BiCl_3$-catalyzed hydroarylation of styrene with anisole.[a]

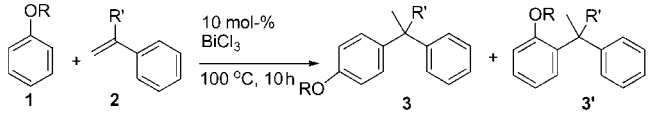



| Entry | **1a**/**2a** [molar] | $BiCl_3$ [mol-%][b] | Time [h] | GC yield [%][b,c] |
|---|---|---|---|---|
| 1 | 1:1 | 5 | 15 | complicated |
| 2 | 5:1 | 5 | 12 | 59 |
| 3 | 10:1 | 5 | 12 | 86 |
| 4 | 10:1 | 5 | 15 | 94 |
| 5 | 10:1 | 10 | 10 | >99(92) |

[a] Reactions were carried out at 100 °C with **2a** (2.0 mmol). [b] Based on the amount of employed **2a**. [c] The value in parenthesis is isolated yield.

Table 2 summarizes the results of the reactions of phenetole **1b** with **2a** and **1a** or **1b** with α-substituted styrenes. As expected, **1b** reacted with **2a** to give two corresponding hydroarylated products, **3b** and **3b′**, in a ratio of 80:20 as **1a** did (Table 2, Entry 1). The hydroarylation of α-substituted styrenes took place affording **3c**–**e** with very high selectivity (Table 2, Entries 2–4). The formation of **3d** in only a moderate yield might be a result of the lower reactivity of **2c** when compared with those of other styrenes.

Table 2. $BiCl_3$-catalyzed hydroarylation of styrenes with anisole or phenetole.[a]



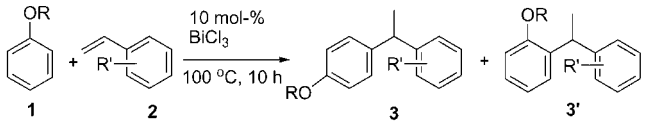

| Entry | R | | R' | | GC yield [%] (isolated yield)[b] | **3**/**3′**[c] |
|---|---|---|---|---|---|---|
| 1 | Et | **1b** | H | **2a** | 94(93) | 80:20(**3b**/**3b′**) |
| 2 | Me | **1a** | Me | **2b** | 95(87) | 98:2(**3c**/**3c′**) |
| 3 | Me | **1a** | Ph | **2c** | (61) | >99:1(**3d**/**3d′**) |
| 4 | Et | **1b** | Me | **2b** | 95(80) | 98:2(**3e**/**3e′**) |

[a] Reactions were carried out at 100 °C for 10 h with **2** (2.0 mmol), 10 equiv. of **1**, and $BiCl_3$ (0.2 mmol). [b] Based on the amount of employed **2**. [c] Determined by GC analysis.

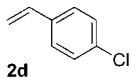
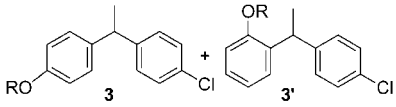
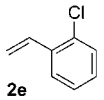
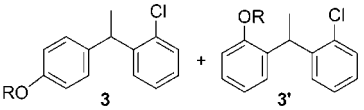
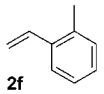
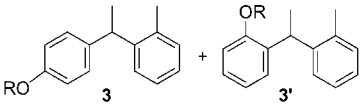
In order to explore the scope and limitations of the present catalytic procedure, a variety of functionalized aromatic compounds were treated with substituted styrenes, and the results examined (Table 3 and Table 4).

As shown in Table 3, electron-rich **1a** and **1b** reacted smoothly with both electron-rich and electron-deficient styrenes to give the corresponding adducts in good to high yields. In the case of 2-chlorostyrene (**2e**), the selectivity of the two adducts (**3h**/**3h′** and **3i**/**3i′**) were somewhat lower

Table 3. $BiCl_3$-catalyzed hydroarylation of styrenes with anisole or phenetole.[a]




R = Me, **1a**; Et, **1b**

| Entry | Styrenes | Products |
|---|---|---|
| 1 |  |  R = Me >99,[b] 80,[c] 78:22(**3f**/**3f′**)[d]; Et 93,[c] 83:17(**3g**/**3g′**)[d] |
| 2 |  |  R = Me 89,[b] 74;[c] 67:33(**3h**/**3h′**)[d]; Et 91,[b] 85;[c] 65:35(**3i**/**3i′**)[d] |
| 3 |  |  R = Me >99,[b] 92;[c] 86:14(**3j**/**3j′**)[d]; Et 88;[c] 86:14(**3k**/**3k′**)[d] |

[a] Reactions were carried out at 100 °C for 10 h with **2** (2.0 mmol), 10 equiv. of **1**, and $BiCl_3$ (0.2 mmol). [b] GC yield [%]. [c] Isolated yield based on the amount of employed **2**. [d] Determined by GC analysis.

than those observed in the reactions of **1a** or **1b** with either 4-chlorostyrene (**2d**) or 2-methylstyrene (**2f**).

It is clear from Table 4 that the $BiCl_3$-catalyzed hydroarylation of styrenes proceeded best with more electron-rich arenes. *m*-Xylene (**1e**) and *o*-xylene (**1f**) showed considerably lower reactivities compared to those of 3,5-dimethylanisole (**1c**) and mesitylene (**1d**).

It is worth noting that in the cases of **1e** and **1f**, the hydroarylation occurred with a high selectivity. The reactions of **2a** or **2d** with **1e** afforded **3q** or **3r**, respectively, as the exclusive adduct (Table 4, Entries 5 and 6), and reaction of **2d** with **1f** generated **3s** with a high selectivity (Table 4, Entry 7).

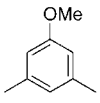
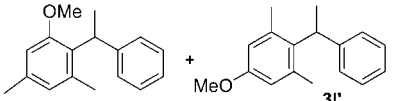
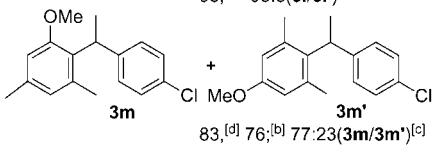
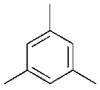
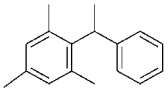
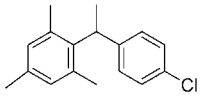
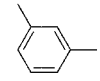
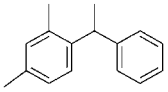
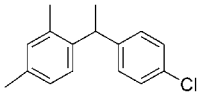
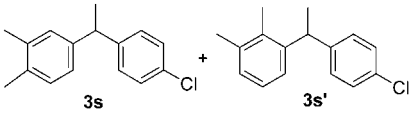
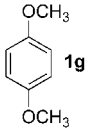
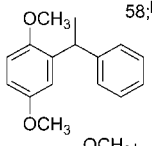
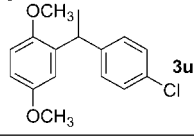
Again, the reaction of electron-rich 1,4-dimethoxybenzene (**1g**) with **2a** or **2d** furnished the corresponding adducts **3t** or **3u**, respectively, in high isolated yields (Table 4, Entries 8 and 9).

In addition, the reaction of electron-deficient chlorobenzene with **2a** produced a trace amount of adduct, and the hydroarylation of nitrobenzene with **2a** did not occur at all.

As previously mentioned, when the reaction of **1a** with **2a** was performed in a 1:1 ratio, a complicated mixture of products was formed. One of the side reactions was the dimerization of **2a**. Therefore, we investigated the $BiCl_3$-catalyzed dimerization of styrenes in detail. It was found that although $BiCl_3$ showed good catalytic activity for the dimerization of both electron-rich and electron-poor styrenes,

Table 4. $BiCl_3$-catalyzed hydroarylation of styrenes with arenes.[a]

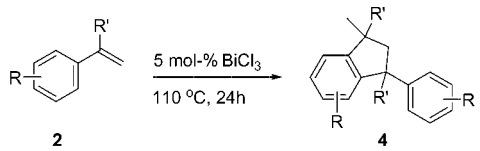
| Entry | Arenes | Styrenes | Products | | |
|---|---|---|---|---|---|
| 1 |  **1c** | **2a** |  **3l** + **3l'** | 93;[b] 95:5(**3l/3l'**)[c] | |
| 2 | **1c** | **2d** |  **3m** + **3m'** | 83,[d] 76;[b] 77:23(**3m/3m'**)[c] | |
| 3 |  **1d** | **2a** |  | **3n** | 65[b] |
| 4 | **1d** | **2d** |  | **3p** | 82[b] |
| 5 |  **1e** | **2a** |  | **3q** | 34[b] |
| 6 | **1e** | **2d** |  | **3r** | 64[b] |
| 7 |  **1f** | **2d** |  **3s** + **3s'** | 58;[b] 94:6(**3s/3s'**)[c] | |
| 8 |  **1g** | **2a** |  | **3t** | 89[b] |
| 9 | **1g** | **2d** |  | **3u** | 94[b] |

[a] Reactions were carried out at 100 °C for 10 h with **2** (2.0 mmol), 10 equiv. of **1**, and $BiCl_3$ (0.2 mmol). [b] Isolated yield based on the amount of employed **2**. [c] Determined by GC analysis. [d] GC yield [%].

only the α-substituted styrenes underwent the dimerization selectively in *n*-octane to afford cyclic dimer **4** in good to high yields (Table 5). The use of other solvents such as THF, DMF, and 1,2-dichloroethane resulted in the formation of a mixture of dimers (non-cyclic dimers and cyclic dimers). The structures of **4** were confirmed by $^1$H- and $^{13}$C NMR spectroscopy, MS data, and compared with the reported data.[7]

It should be noted that no results were obtained when α,β-trisubstituted styrenes **2h** and **2i** were employed (Scheme 1). The reaction of **2h** led to a complicated mixture of dimers, which was confirmed by GC and GC–MS. In the case of **2i** , no reaction occurred at all.

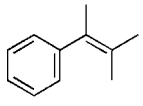
Table 5. $BiCl_3$-catalyzed dimerization of α-substituted styrenes.[a]

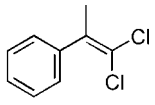



**2** **4**

| Entry | Styrenes | Dimer | Yield [%][b] |
|---|---|---|---|
| 1 | **2b** | **4a** | 73 |
| 2 | **2c** | **4b** | 56 |
| 3 | **2e** | **4c** | 65 |
| 4 | **2f** | **4d** | 92 |

[a] Reactions were carried out at 110 °C for 24 h with **2** (2.0 mmol) and $BiCl_3$ (0.1 mmol) in *n*-octane (2 mL). [b] Isolated yield.


**2h**


**2i**

Scheme 1.

## Conclusions

In this paper, we outline a general, mild, and simple method for the hydroarylation of styrenes with electron-rich arenes to give Markovnikov adducts in the presence of $BiCl_3$. α-Substituted styrenes have been shown to undergo inter- and intramolecular double hydroarylation, which affords dimers. This catalyst system has the following two remarkable advantages: 1) $BiCl_3$ shows good catalytic activity in the hydroarylation of both electron-deficient and electron-rich styrenes; 2) $BiCl_3$ has a low toxicity, is readily available, has a low cost, and is easily handled.

## Experimental Section

**General Methods:** $^1$H- and $^{13}$C NMR spectra were recorded with a JOEL JNM-ECA 300 or 600 spectrometer at 300 MHz or 600 MHz and 75 MHz or 125 MHz, respectively. The chemical shifts ($\delta$) were referenced to TMS or an internal solvent resonance. GC–MS was obtained with a HEWLETT 5890 PACKARD SERIES II GC–MS spectrometer. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer in the Department of Chemistry of Peking University. GC analyses were performed with an Agilent Technologies 1790 GC instrument. All re-

actions were carried out under air. Solvents and all reagents were used as received.

**Typical Experimental Procedure for Hydroarylation of Styrene 2a with Anisole 1a**

**Formation of 4-(1-Phenylethyl)anisole (3a) and 2-(1-Phenylethyl)-anisole (3a′):** A mixture of anisole (2.16 g, 20.0 mmol), styrene (208.0 mg, 2.0 mmol), and $BiCl_3$ (63.0 mg, 0.2 mmol) was stirred under air at 100 °C for 10 h. To this resulting reaction mixture were added cyclohexane (10.0 mL) as diluent and *n*-docosane (310.0 mg) as an internal standard for GC analysis. After removal of the precipitate by filtration, the filtrate was then subjected to GC and GC–MS analyses. A mixture of **3a** and **3a′** (390.0 mg, 92%) was isolated by column chromatography (silica gel, eluent: hexane, then diethyl ether/hexane = 1:20) after removal of the volatiles under vacuum. The results from GC analysis of the reaction mixture disclosed that **3a** and **3a′** were formed in quantitative yields (**3a**/**3a′** = 80:20) (Table 1, Entry 5).

Isomers **3** and **3′** could be separated by careful column chromatography of the obtained isomer mixtures. The major adducts **3a**, **3b**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, and **3m** were obtained with 94–98% isomeric purity, and the minor adducts were obtained with 83–96% isomeric purity.

**Typical Experimental Procedure for Cyclic Dimerization of 2b**

A mixture of α-methylstyrene (236.0 mg, 2.0 mmol) and $BiCl_3$ (32.0 mg, 0.1 mmol) in *n*-octane (2.0 mL) was stirred under air at 110 °C for 24 h. After cooling, the mixture was subjected to column chromatography separation (silica gel, eluent: hexane, then diethyl ether/hexane = 1:20) to give **4a** (172.3 mg, 73%) (Table 5, Entry 1).

The structures of products **3** and **4** were confirmed by $^1$H-, $^{13}$C NMR spectroscopy, GC–MS, and HRMS (for new compounds).

**Characterization Data of Products 3 and 4**

**4-(1-Phenylethyl)anisole (3a):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.29–7.15 (m, 5 H), 7.12 (d, $J$ = 8.6 Hz, 2 H), 6.82 (d, $J$ = 8.6 Hz, 2 H), 4.09 (q, $J$ = 7.2 Hz, 1 H), 3.75 (s, 3 H), 1.60 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.8, 146.8, 138.5, 128.5, 128.3, 127.5, 125.9, 113.7, 55.2, 43.9, 22.0 ppm. GC–MS: *m*/*z* (%) 212 (95) $[M]^+$, 197 (100), 182 (28), 165 (54), 153 (54), 91 (29), 77 (46).

**2-(1-Phenylethyl)anisole (3a′):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.80 (m, 9 H), 4.57 (q, $J$ = 7.2 Hz, 1 H), 3.77 (s, 3 H), 1.57 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 156.8, 146.4, 134.9, 128.1, 127.7, 127.6, 127.0, 125.7, 120.5, 110.6, 55.4, 37.3, 20.8 ppm. GC–MS: *m*/*z* (%) 212 (97) $[M]^+$, 197 (100), 181 (26), 165 (50), 152 (38), 91 (100) 77 (35).

**4-(1-Phenylethyl)phenetole (3b):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.16 (m, 5 H), 7.11 (d, $J$ = 8.6 Hz, 2 H), 6.81 (d, $J$ = 8.6 Hz, 2 H), 4.09 (q, $J$ = 7.2 Hz, 1 H), 3.98 (q, $J$ = 6.9 Hz, 2 H), 1.60 (d, $J$ = 7.2 Hz, 3 H), 1.38 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.2, 146.8, 138.4, 128.5, 128.3, 127.5, 125.9, 114.3, 63.3, 43.9, 22.0, 14.9 ppm. GC–MS: *m*/*z* (%) 226 (100) $[M]^+$, 211 (27), 183 (26), 165 (60), 152 (43), 91 (41), 77 (30).

**2-(1-Phenylethyl)phenetole (3b′):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.80 (m, 9 H), 4.55 (q, $J$ = 7.2 Hz, 1 H), 3.95 (q, $J$ = 6.9 Hz, 2 H), 1.58 (d, $J$ = 7.2 Hz, 3 H), 1.33 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 156.2, 146.6, 134.9, 128.0, 127.7, 127.5, 127.0, 125.6, 120.3, 111.4, 63.5, 37.7, 20.8, 14.8 ppm. GC–MS: *m*/*z* (%) 226 (100) $[M]^+$, 211 (26), 197 (91), 181 (40), 165 (66), 152 (53), 119 (40), 105 (78), 91 (46).

**4-(1-Methyl-1-phenylethyl)anisole (3c):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.35–6.85 (m, 9 H), 3.84 (s, 3 H), 1.74 (s, 6 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.4, 150.9, 142.8, 127.9, 127.7, 126.7, 125.5, 113.2, 55.1, 42.2, 30.9 (2 C) ppm. GC–MS: *m*/*z* (%) 226 (17) $[M]^+$, 211 (100), 165 (22), 152 (26), 103 (68), 91 (44), 77 (73).

**4-(1,1-Diphenylethyl)anisole (3d):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.70 (m, 14 H), 3.76 (s, 3 H), 2.15 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.6, 149.4, 141.2, 129.7, 128.7, 127.9, 125.9, 113.1, 55.2, 51.9, 30.65 ppm. GC–MS: *m*/*z* (%) 288 (24) $[M]^+$, 273 (100), 211 (17), 195 (16), 165 (34), 152 (16), 103 (16), 77 (15).

**2-(4-Ethoxyphenyl)-2-phenylpropane (3e):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.40–6.80 (m, 9 H), 4.05 (q, $J$ = 6.9 Hz, 2 H), 1.72 (s, 6 H), 1.44 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 156.8, 150.9, 142.7, 127.9, 127.7, 126.7, 125.5, 113.8, 63.3, 42.2, 30.9 (2 C), 14.9 ppm. GC–MS: *m*/*z* (%) 240 (26) $[M]^+$, 225 (100), 197 (27), 152 (12), 103 (16), 91 (16), 77 (12).

**1-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethane (3f):** $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.15 (d, $J$ = 8.9 Hz, 2 H), 7.04 (d, $J$ = 8.9 Hz, 2 H), 7.02 (d, $J$ = 8.9 Hz, 2 H), 6.75 (d, $J$ = 8.9 Hz, 2 H), 3.99 (q, $J$ = 6.8 Hz, 1 H), 3.68 (s, 3 H), 1.50 (d, $J$ = 6.8 Hz, 3 H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 158.1, 145.4, 138.1, 131.7, 129.0, 128.5 (2 C), 113.9, 55.3, 43.4, 22.1 ppm. GC–MS: *m*/*z* (%) 246 (73) $[M]^+$, 231 (100), 196 (31), 165 (30), 153 (50), 135 (13), 77 (23). HRMS: calcd. for $C_{15}H_{15}ClO$ 246.0811; found 246.0812.

**1-(4-Chlorophenyl)-1-(2-methoxyphenyl)ethane (3f′):** $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 7.12–6.74 (m, 8 H), 4.43 (q, $J$ = 7.6 Hz, 1 H), 3.66 (s, 3 H), 1.47 (d, $J$ = 7.6 Hz, 3 H) ppm. $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 156.9, 145.1, 134.3, 131.4, 129.1, 128.3, 127.5, 127.4, 120.6, 110.7, 55.5, 37.1, 20.9 ppm. GC–MS: *m*/*z* (%) 246 (44) $[M]^+$, 231 (74), 181 (16), 165 (37), 152 (27), 125 (100), 91 (19).

**1-(4-Chlorophenyl)-1-(4-ethoxyphenyl)ethane (3g):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.22 (d, $J$ = 8.6 Hz, 2 H), 7.11 (d, $J$ = 8.6 Hz, 2 H), 7.07 (d, $J$ = 8.6 Hz, 2 H), 6.81 (d, $J$ = 8.6 Hz, 2 H), 4.05 (q, $J$ = 7.2 Hz, 1 H), 3.98 (q, $J$ = 6.9 Hz, 2 H), 1.57 (d, $J$ = 7.2 Hz, 3 H), 1.38 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.3, 145.3, 137.8, 131.6, 128.9, 128.4 (2 C), 114.3, 63.4, 43.3, 22.0, 14.9 ppm. GC–MS: *m*/*z* (%) 260 (97) $[M]^+$, 245 (100), 217 (97), 181 (61), 165 (34), 152 (63), 91 (32), 77 (40). HRMS: calcd. for $C_{16}H_{17}ClO$ 260.0968; found 260.0967.

**1-(4-Chlorophenyl)-1-(2-ethoxyphenyl)ethane (3g′):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.80 (m, 8 H), 4.50 (q, $J$ = 7.2 Hz, 1 H), 3.94 (q, $J$ = 6.9 Hz, 2 H), 1.55 (d, $J$ = 7.2 Hz, 3 H), 1.32 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 156.2, 145.2, 134.2, 131.2, 129.1, 128.1 (2 C), 127.3, 120.3, 111.4, 63.5, 37.4, 20.7, 14.8 ppm. GC–MS: *m*/*z* (%) 260 (100) $[M]^+$, 245 (36), 231 (73), 181 (45), 152 (48), 139 (64), 107 (36), 91(27).

**1-(2-Chlorophenyl)-1-(4-methoxyphenyl)ethane (3h):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.40–7.20 (m, 6 H), 6.84 (d, $J$ = 8.6 Hz, 2 H), 4.62 (q, $J$ = 6.8 Hz, 1 H), 3.79 (s, 3 H), 1.60 (d, $J$ = 6.8 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 157.9, 144.0, 137.1, 133.8, 129.6, 128.7, 128.4, 127.2, 126.9, 113.7, 55.2, 40.1, 21.2 ppm. GC–MS: *m*/*z* (%) 246 (84) $[M]^+$, 231 (11), 196 (35), 165 (42), 152 (58), 135 (21), 91 (15), 77 (29). HRMS: calcd. for $C_{15}H_{15}ClO$ 246.0811; found 246.0814.

**1-(2-Chlorophenyl)-1-(2-methoxyphenyl)ethane (3h′):** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.80 (m, 8 H), 4.91 (q, $J$ = 6.9 Hz, 1

H), 3.74 (s, 3 H), 1.53 (d, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.1, 143.9, 134.0, 133.6, 129.4, 128.3, 127.4, 127.3, 127.0, 126.5, 120.3, 110.6, 55.5, 34.9, 19.9 ppm. GC–MS: *m/z* (%) 246 (100) $[M]^+$, 231 (80), 211 (56), 181 (30), 165 (71), 152 (39), 125 (91), 91 (20).

**1-(2-Chlorophenyl)-1-(4-ethoxyphenyl)ethane (3i):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.20–6.80 (m, 8 H), 4.59 (q, $J$ = 7.2 Hz, 1 H), 3.99 (q, $J$ = 6.9 Hz, 2 H), 1.57 (d, $J$ = 7.2 Hz, 3 H), 1.38 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.3, 144.1, 136.9, 133.7, 129.5, 128.6, 128.5, 127.2, 126.9, 114.2, 63.3, 40.1, 21.2, 14.9 ppm. GC–MS: *m/z* (%) 260 (42) $[M]^+$, 245 (100), 217 (61), 181 (33), 152 (38), 91 (7), 77 (13). HRMS: calcd. for $C_{16}H_{17}ClO$ 260.0968; found 260.0957.

**1-(2-Chlorophenyl)-1-(2-ethoxyphenyl)ethane (3i′):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.80 (m, 8 H), 4.91 (q, $J$ = 7.2 Hz, 1 H), 3.83 (q, $J$ = 6.9 Hz, 2 H), 1.53 (d, $J$ = 7.2 Hz, 3 H), 1.24 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 156.5, 144.5, 133.9, 133.6, 129.2, 128.3, 127.32, 127.27, 126.8, 126.5, 120.1, 111.4, 63.6, 35.0, 19.8, 14.7 ppm. GC–MS: *m/z* (%) 260 (87) $[M]^+$, 245 (12), 231 (48), 181 (100), 152 (76), 139 (63), 107 (76), 91 (33).

**1-(4-Methoxyphenyl)-1-(2-methylphenyl)ethane (3j):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.15 (m, 4 H), 7.05 (d, $J$ = 8.6 Hz, 2 H), 6.79 (d, $J$ = 8.6 Hz, 2 H), 4.26 (q, $J$ = 6.9 Hz, 1 H), 3.76 (s, 3 H), 2.23 (s, 3 H), 1.57 (d, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.7, 144.3, 138.4, 136.0, 130.4, 128.5 (2C), 126.5, 126.0, 113.7, 55.2, 40.1, 22.2, 19.7 ppm. GC–MS: *m/z* (%) 226 (96) $[M]^+$, 211 (100), 196 (32), 165 (41), 118 (33), 105 (35), 91 (41). HRMS: calcd. for $C_{16}H_{18}O$ 226.1358; found 226.1355.

**1-(2-Methoxyphenyl)-1-(2-methylphenyl)ethane (3j′):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.27– 6.82 (m, 8 H), 4.68 (q, $J$ = 6.9 Hz, 1 H), 3.80 (s, 3 H), 2.21 (s, 3 H), 1.52 (d, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 156.8, 144.7, 136.3, 134.8, 130.1, 127.5 (2C), 126.9, 126.5, 125.7, 120.5, 110.3, 55.5, 33.8, 20.6, 19.3 ppm. GC–MS: *m/z* (%) 226 (74) $[M]^+$, 211 (74), 178 (18), 165 (36), 135 (19), 105 (100), 91 (29).

**1-(4-Ethoxyphenyl)-1-(2-methylphenyl)ethane (3k):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.10 (m, 4 H), 7.03 (d, $J$ = 8.6 Hz, 2 H), 6.77 (d, $J$ = 8.6 Hz, 2 H), 4.26 (q, $J$ = 7.2 Hz, 1 H), 3.95 (q, $J$ = 6.9 Hz, 2 H), 2.22 (s, 3 H), 1.56 (d, $J$ = 7.2 Hz, 3 H), 1.36 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.0, 144.3, 138.2, 136.0, 130.4, 128.5 (2 C), 126.5, 126.0, 114.2, 63.3, 40.1, 22.2, 19.7, 14.9 ppm. GC–MS: *m/z* (%) 240 (39) $[M]^+$, 225 (100), 197 (33), 182 (12), 165 (17), 115 (11), 91 (14). HRMS: calcd. for $C_{17}H_{20}O$ 240.1514;, found 240.1509.

**1-(2-Ethoxyphenyl)-1-(2-methylphenyl)ethane (3k′):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.20–6.80 (m, 8 H), 4.68 (q, $J$ = 7.2 Hz, 1 H), 3.96 (q, $J$ = 6.9 Hz, 2 H), 2.26 (s, 3 H), 1.51 (d, $J$ = 7.2 Hz, 3 H), 1.32 (t, $J$ = 6.9 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 156.2, 144.7, 136.1, 134.8, 130.0, 127.5, 126.8, 126.5, 125.7, 125.6, 120.2, 111.1, 63.3, 33.9, 20.5, 19.3, 14.8 ppm. GC–MS: *m/z* (%) 240 (52) $[M]^+$, 225 (11), 211 (35), 165 (30), 119 (100), 107 (22), 91 (33).

**1-(4,6-Dimethyl-2-methoxyphenyl)-1-phenylethane (3l):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.10 (m, 5 H), 6.60 (s, 1 H), 6.55 (s, 1 H), 4.65 (q, $J$ = 7.2 Hz, 1 H), 3.59 (s, 3 H), 2.29 (s, 3 H), 2.18 (s, 3 H), 1.64 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 158.0, 146.0, 137.2, 136.5, 130.5, 127.7, 127.0, 125.0, 124.2, 110.7, 55.5, 35.8, 21.3, 20.6, 17.3 ppm. GC–MS: *m/z* (%) 240 (98) $[M]^+$, 225 (99), 178 (31), 165 (58), 115 (24), 91 (100), 77 (31). HRMS: calcd. for $C_{17}H_{20}O$ 240.1514; found 240.1511.

**1-(4-Chlorophenyl)-1-(2-methoxy-4,6-dimethylphenyl)ethane (3m):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.17 (d, $J$ = 8.6 Hz, 2 H), 7.11 (d, $J$ = 8.6 Hz, 2 H), 6.59 (s, 1 H), 6.53 (s, 1 H), 4.56 (q, $J$ = 7.2 Hz, 1 H), 3.57 (s, 3 H), 2.28 (s, 3 H), 2.18 (s, 3 H), 1.61 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.8, 144.6, 136.9, 136.8, 130.6, 129.9, 128.4, 127.7, 124.2, 110.6, 55.3, 35.5, 21.3, 20.5, 17.3 ppm. GC–MS: *m/z* (%) 274 (45) $[M]^+$, 259 (56), 179 (25), 165 (24), 125 (100), 91 (13), 77 (16). HRMS: calcd. for $C_{17}H_{19}ClO$ 274.1124; found 274.1129.

**1-(4-Chlorophenyl)-1-(4-methoxy-2,6-dimethylphenyl)ethane (3m′):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.21 (d, $J$ = 8.6 Hz, 2 H), 7.09 (d, $J$ = 8.6 Hz, 2 H), 6.55 (s, 2 H), 4.53 (q, $J$ = 7.2 Hz, 1 H), 3.77 (s, 3 H), 2.11 (s, 6 H), 1.62 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 157.4, 144.2, 137.8, 134.9, 131.0, 128.2, 114.4, 111.6, 55.0, 37.0, 21.4, 17.1 ppm. GC–MS: *m/z* (%) 274 (34) $[M]^+$, 259 (100), 209 (15), 165 (24), 103 (11), 91 (10), 77 (11).

**1-(2,4,6-Trimethylphenyl)-1-phenylethane (3n):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.10 (m, 5 H), 6.82 (s, 2 H), 4.63 (q, $J$ = 7.2 Hz, 1 H), 2.25 (s, 3 H), 2.10 (s, 6 H), 1.65 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 145.4, 140.0, 136.5, 135.4, 130.0, 128.1, 126.8, 125.2, 37.8, 21.0, 20.7, 16.8 ppm. GC–MS: *m/z* (%) 224 (100) $[M]^+$, 209 (100), 179 (33), 165 (14), 91 (6), 77 (7).

**1-(4-Chlorophenyl)-1-(2,4,6-trimethylphenyl)ethane (3p):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.16 (d, $J$ = 7.6 Hz, 2 H), 7.00 (d, $J$ = 7.6 Hz, 2 H), 6.74 (s, 2 H), 4.49 (q, $J$ = 7.2 Hz, 1 H), 2.18 (s, 3 H), 2.01 (s, 6 H), 1.55 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 144.1, 139.6, 136.5, 135.7, 131.1, 130.2, 128.8, 128.2, 37.5, 21.2, 20.8, 17.0 ppm. GC–MS: *m/z* (%) 274 (45) $[M]^+$, 259 (56), 179 (25), 165 (24), 125 (100), 91 (13), 77 (16). HRMS: calcd. for $C_{17}H_{19}ClO$ 258.1175; found 258.1173.

**1-(2,4-Dimethylphenyl)-1-phenylethane (3q):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.90 (m, 8 H), 4.27 (q, $J$ = 7.2 Hz, 1 H), 2.28 (s, 3 H), 2.19 (s, 3 H), 1.58 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 146.4, 140.9, 135.9, 135.4, 131.2, 128.5, 128.3, 127.6, 126.6, 125.7, 40.6, 22.2, 20.9, 19.6 ppm. GC–MS: *m/z* (%) 210 (98) $[M]^+$, 195 (100), 180 (78), 165 (77), 115 (27), 91 (27), 77 (40).

**1-(4-Chlorophenyl)-1-(2,4-dimethylphenyl)ethane (3r):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.20–6.98 (m, 6 H), 6.95 (s, 1 H), 4.22 (q, $J$ = 7.2 Hz, 1 H), 2.28 (s, 3 H), 2.16 (s, 3 H), 1.55 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 145.0, 140.3, 135.8, 135.7, 131.3, 128.9, 128.6, 128.4, 126.7, 126.4, 40.1, 22.1, 20.9, 19.6 ppm. GC–MS: *m/z* (%) 244 (34) $[M]^+$, 229 (100), 194 (28), 179 (41), 165 (14), 115 (11), 91 (8), 77 (14). HRMS: calcd. for $C_{16}H_{17}Cl$ 244.1019; found 244.1020.

**1-(4-Chlorophenyl)-1-(3,4-dimethylphenyl)ethane (3s):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–6.90 (m, 7 H), 4.04 (q, $J$ = 7.2 Hz, 1 H), 2.21 (s, 6 H), 1.58 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 145.2, 143.3, 136.5, 134.4, 131.6, 129.7, 128.9, 128.8, 128.4, 124.8, 43.8, 21.0, 19.8, 19.3 ppm. GC–MS *m/z* (%) 244 (34) $[M]^+$, 229 (100), 194 (27), 165 (15), 103 (12), 91 (11), 77 (14).

**1-(2,5-Dimethoxy)-1-phenylethane (3t):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.24–7.13 (m, 5 H), 6.76–6.64 (m, 3 H), 4.54 (q, $J$ = 7.2 Hz, 1 H), 3.70 (s, 3 H), 3,68 (s, 3 H), 1.55 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 153.6, 151.2, 126.1, 136.3, 128.1, 127.6, 125.7, 114.7, 110.6, 110.4, 56.1, 55.5, 37.5, 20.9 ppm. GC–MS: *m/z* (%) 242 (100) $[M]^+$, 227 (40), 211 (9), 165 (13), 103 (13), 91 (71).

**1-(4-Chlorophenyl)-1-(2,5-dimethoxyphenyl)ethane (3u):** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.19 (d, $J$ = 8.4 Hz, 2 H), 7.15 (d, $J$ = 8.4 Hz, 2 H), 6.76–6.66 (m, 3 H), 4.48 (q, $J$ = 7.2 Hz, 1 H), 3.72

(s, 3 H), 3,68 (s, 3 H), 1.53 (d, $J$ = 7.2 Hz, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 153.6, 151.1, 144.7, 135.6, 131.3, 129.0, 128.2, 114.6, 111.5, 110.6, 56.0, 55.6, 37.1, 20.7 ppm. GC–MS: *m/z* (%) 276 (100) $[M]^+$, 261 (32), 245 (7), 207 (16), 165 (15), 139 (12), 125 (86), 91 (9).

**4a:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.10 (m, 9 H), 2.41, 2.19 (AB, $J_{AB}$ = 13.0 Hz, 2 H), 1.69 (s, 3 H), 1.35 (s, 3 H), 1.03 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 152.2, 151.0, 148.7, 128.0, 127.2, 126.7, 126.6, 125.4, 125.0, 122.5, 59.2, 50.8, 42.8, 30.7, 30.6, 30.4 ppm. GC–MS: *m/z* (%) 236 (12) $[M]^+$, 221 (100), 178 (11), 165 (12), 143 (54), 115 (13), 91 (25).

**4b:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.00 (m, 19 H), 3.42, 3.12 (AB, $J_{AB}$ = 13.0 Hz, 2 H), 1.57 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 150.6, 149.4, 149.0, 148.6, 147.6, 128.9, 128.8, 128.1, 128.0, 127.7, 127.6, 127.5, 127.0, 126.9, 126.1, 125.8, 125.7, 125.1, 61.5, 61.0, 51.3, 28.9 ppm. GC–MS: *m/z* (%) 360 (41) $[M]^+$, 345 (85), 267 (100), 252 (57), 205 (47), 191 (34), 165 (44), 91 (38).

**4c:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.10–7.00 (m, 6 H), 6.93 (s, 1 H), 2.40, 2.19 (AB, $J_{AB}$ = 13.0 Hz, 2 H), 2.37 (s, 3 H), 2.32 (s, 3 H), 1.69 (s, 3 H), 1.35 (s, 3 H), 1.07 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 149.4, 149.3, 148.2, 136.2, 134.9, 128.8, 128.1, 126.7, 125.5, 122.3, 59.6, 50.5, 42.6, 31.0 (2 C), 30.6, 21.5, 21.0 ppm. GC–MS: *m/z* (%) 264 (18) $[M]^+$, 249 (100), 157 (50), 142 (19), 105 (18), 91 (10).

**4d:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.00 (m, 7 H), 2.36, 2.19 (AB, $J_{AB}$ = 13.0 Hz, 2 H), 1.64 (s, 3 H), 1.32 (s, 3 H), 1.03 (s, 3 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 150.6, 150.3, 148.8, 132.4, 131.5, 128.2, 128.0, 127.7, 124.9, 124.0, 59.2, 50.5, 42.6, 30.6, 30.6, 30.3 ppm. GC–MS: *m/z* (%) 304 (7) $[M]^+$, 289 (15), 269 (21), 203 (27), 139 (26), 125 (39), 77 (23), 28 (100).

**Supporting Information** (see footnote on the first page of this article): $^1$H-, $^{13}$C NMR spectra for all products.

## Acknowledgments

Financial supports from the National Natural Science Foundation of China (20573061) is gratefully acknowledged.

[1] a) T. Matsomoto, D. J. Taube, R. A. Periana, H. Taube, H. Yoshida, *J. Am. Chem. Soc.* **2000**, *122*, 7414–7415; b) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, *Science* **2000**, *287*, 1992–1995; c) R. K. Thalji, K. A. Ahrendt, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2001**, *123*, 9692–9693; d) K. B. Jensen, J. Thorhauge, R. G. Hazell, K. A. Jorgensen, *Angew. Chem. Int. Ed.* **2001**, *40*, 160–163; e) K. L. Tan, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2002**, *124*, 3202–3203; f) N. A. Paras, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2002**, *124*, 7894–7898; g) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1769; h) T. Matsumoto, R. A. Periana, D. J. Taube, H. Yoshida, *J. Mol. Catal. A* **2002**, *180*, 1–18; i) D. Drago, P. S. Pregosin, *Organometallics* **2002**, *21*, 1208–1215; j) K. A. Ahrendt, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2003**, *5*, 1301–1303; k) M. Lail, B. N. Arrowood, T. B. Gunnoe, *J. Am. Chem. Soc.* **2003**, *125*, 7506–7507; l) E. M. Ferreira, B. M. Stoltz, *J. Am. Chem. Soc.* **2003**, *125*, 9578–9579; m) E. M. Beccalli, G. Broggini, *Tetrahedron Lett.* **2003**, *44*, 1919–1920; n) R. Dorta, A. Togni, *Chem. Commun.* **2003**, 760–761; o) G. Dyker, E. Muth, A. S. K. Hashmi, L. Ding, *Adv. Synth. Catal.* **2003**, *345*, 1247–1252; p) S. W. Youn, S. J. Pastine, D. Sames, *Org. Lett.* **2004**, *6*, 581–584; q) J. Oxgaard, R. P. Muller, R. A. Periana, W. A. Goddard III, *J. Am. Chem. Soc.* **2004**, *126*, 352–363; r) J. Oxgaard, W. A. Goddard III, *J. Am. Chem. Soc.* **2004**, *126*, 442–443; s) J. Oxgaard, R. A. Periana, W. A. Goddard III, *J. Am. Chem. Soc.* **2004**, *126*, 11658–11665; t) D. Karshtedt, A. T. Bell, T. D. Tilley, *Organometallics* **2004**, *23*, 4169–4171; u) M. Lail, C. M. Bell, D. Conner, T. R. Gundari, T. B. Runnoe, J. L. Petersen, *Organometallics* **2004**, *23*, 5007–5020; v) G. Bhalla, J. Oxgaard, W. A. Goddart III, R. A. Periana, *Organometallics* **2005**, *24*, 3229–3232; w) J. Kischel, I. Jovel, K. Mertins, A. Zapf, M. Beller, *Org. Lett.* **2006**, *8*, 19–22.

[2] a) H. Robert, B. Garrigues, J. Dubac, *Tetrahedron Lett.* **1998**, *39*, 1161–1164; b) T. Ohe, S. Uemura, *Tetrahedron Lett.* **2002**, *43*, 1269–1271; c) G. Sabitha, E. V. Reddy, C. Maruthi, J. S. Yadav, *Tetrahedron Lett.* **2002**, *43*, 1573–1575; d) N. R. Swamy, Y. Venkateswarlu, *Tetrahedron Lett.* **2002**, *43*, 7549–7552; e) T. Ollevier, G. Lavie-Compin, *Tetrahedron Lett.* **2002**, *43*, 7891–7893; f) S. Repichet, C. Le Roux, N. Roques, J. Dubac, *Tetrahedron Lett.* **2003**, *44*, 2037–2040; g) G. Sabitha, E. V. Reddy, R. Swapna, N. M. Reddy, J. S. Yadav, *Synlett* **2004**, 1276–1278; h) S. K. De, R. A. Gibbs, *Tetrahedron Lett.* **2005**, *46*, 8345–8350 and references cited therein.

[3] a) E.-M. Keramane, B. Boyer, J. P. Roque, *Tetrahedron* **2001**, *57*, 1917–1921; b) J. N. Arnold, P. D. Hayes, R. L. Kohaus, R. S. Mohan, *Tetrahedron Lett.* **2003**, *44*, 9173–9175; c) P. A. Evans, J. Cui, S. J. Gharpure, R. J. Hinkle, *J. Am. Chem. Soc.* **2003**, *125*, 11456–11457.

[4] a) B. A. Nattier, K. J. Eash, R. S. Mohan, *Synthesis* **2001**, 1010–1012; b) N. Srivastava, S. K. Dasgupta, B. K. Banik, *Tetrahedron Lett.* **2003**, *44*, 1191–1193; c) N. Srivastava, B. K. Banik, *J. Org. Chem.* **2003**, *68*, 2109–2114; d) D. H. Aggen, J. N. Arnold, P. D. Hayes, N. J. Smoter, R. S. Mohan, *Tetrahedron* **2004**, *60*, 3675–3679; e) B. K. Banik, I. Banik, M. Renteria, S. K. Dasgupta, *Tetrahedron Lett.* **2005**, *46*, 2643–2645.

[5] a) M. D. Carrigan, D. Sarapa, R. C. Smith, L. C. Wieland, R. S. Mohan, *J. Org. Chem.* **2002**, *67*, 1027–1030; b) N. M. Leonard, M. C. Oswald, D. A. Freiberg, B. A. Nattier, R. C. Smith, R. S. Mohan, *J. Org. Chem.* **2002**, *67*, 5202–5207; c) L. C. Wieland, H. M. Zerth, R. S. Mohan, *Tetrahedron Lett.* **2002**, *43*, 4597–4600; d) J. R. Stephens, P. L. Butler, C. H. Clow, M. C. Oswald, R. C. Smith, R. S. Mohan, *Eur. J. Org. Chem.* **2003**, 3827–3831; e) A. V. Reddy, K. Ravinder, T. V. Goud, P. Krishnaiah, T. V. Raju, Y. Venkateswarlu, *Tetrahedron Lett.* **2003**, *44*, 6257–6260; f) T. Ollevier, T. Ba, *Tetrahedron Lett.* **2003**, *44*, 9003–9005; g) T. Ollevier, V. Desyroy, M. Asim, M.-C. Brochu, *Synlett* **2004**, 2794–2796; h) H. Gaspard-Iloughmane, C. Le Roux, *Eur. J. Org. Chem.* **2004**, 2517–2532; i) T. Ollevier, E. Nadeau, *J. Org. Chem.* **2004**, *69*, 9292–9295; j) M. P. Nguyen, J. N. Arnold, K. E. Peterson, R. S. Mohan, *Tetrahedron Lett.* **2004**, *45*, 9369–9371; k) J. S. Yadav, B. V. S. Reddy, T. Swamy, K. R. Rao, *Tetrahedron Lett.* **2004**, *45*, 6037–6039 and references cited therein; l) T. Ollevier, V. Desyroy, B. Debailleul, S. Vaur, *Eur. J. Org. Chem.* **2005**, 4971–4973; m) E. D. Anderson, J. J. Ernat, M. P. Nguyen, A. C. Palma, R. S. Mohan, *Tetrahedron Lett.* **2005**, *46*, 7747–7750; n) P. W. Anzalone, A. R. Baru, E. M. Danielson, P. D. Hayes, M. P. Nguyen, A. F. Panico, R. C. Smith, R. S. Mohan, *J. Org. Chem.* **2005**, *70*, 2091–2096; o) Y. Bonvin, E. Callens, I. Larrosa, D. A. Henderson, J. Oldham, A. J. Burton, A. G. M. Barrett, *Org. Lett.* **2005**, *7*, 4549–4552.

[6] Reviews, see: a) M. Postel, E. Dunach, *Coord. Chem. Rev.* **1996**, *155*, 127–144; b) N. M. Leonard, L. C. Wieland, R. S. Mohan, *Tetrahedron* **2002**, *58*, 8373–8397.

[7] Very recently, $InBr_3$- or $RuCl_3{\cdot}nH_2O$-catalyzed dimerization of vinylarenes has been reported: a) C. Peppe, E. S. Lang, F. Molinos de Andrade, L. Borges de Castro, *Synlett* **2004**, 1723–1726; b) M. Higashimura, K. Imamura, Y. Yokogawa, T. Sakakibara, *Chem. Lett.* **2004**, *33*, 728–729.

Received: May 3, 2006
Published Online: July 10, 2006