

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

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In the presence of BiCl₃, 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

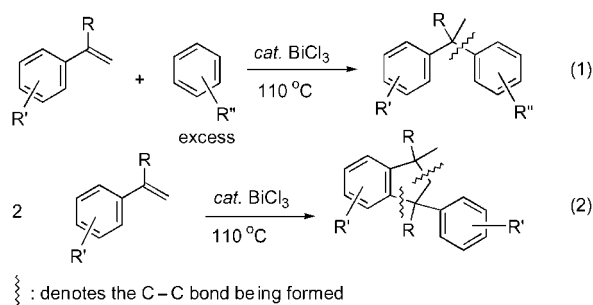
and subsequent intramolecular hydroarylation produced the cyclic dimers of α -substituted styrenes in good yields.

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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 BiCl₃,^[2] BiBr₃,^[3] Bi(NO₃)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 non-toxic, and inexpensive. In this paper, we report our new findings of BiCl₃-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 BiCl₃ 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 BiCl₃ 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

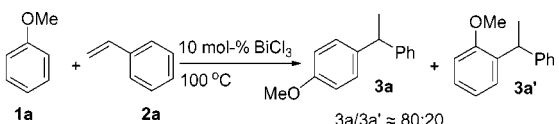
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of two Markovnikov addition products, **3a** and **3a'**, was in a ratio of ca. 80:20. However, other bismuth compounds such as $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $(\text{BiO})_2\text{CO}_3$, and Bi_2O_3 did not show this catalytic activity at all.

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

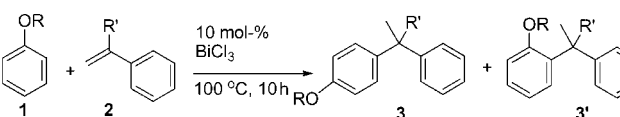


Entry	1a/2a [molar]	BiCl_3 [mol-%] ^[b]	Time [h]	GC yield [%] ^[b,c]
1	1:1	5	15	complicated
2	5:1	5	12	59
3	10:1	5	12	86
4	10:1	5	15	94
5	10:1	10	10	>99(92)

[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]



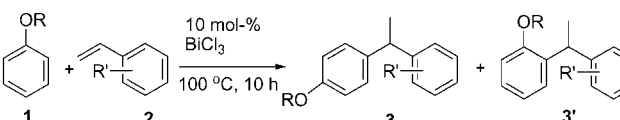
Entry	R	R'	GC yield [%] (isolated yield) ^[b]	3/3' ^[c]
1	Et	1b H 2a	94(93)	80:20(3b/3b')
2	Me	1a Me 2b	95(87)	98:2(3c/3c')
3	Me	1a Ph 2c	(61)	>99:1(3d/3d')
4	Et	1b Me 2b	95(80)	98:2(3e/3e')

[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]



Entry	Styrenes	Products
1	2d	3 + 3' R = Me >99, ^[b] 80, ^[c] 78:22(3f/3f') ^[d] Et 93, ^[c] 83:17(3g/3g') ^[d]
2	2e	3 + 3' R = Me 89, ^[b] 74, ^[c] 67:33(3h/3h') ^[d] Et 91, ^[b] 85, ^[c] 65:35(3i/3i') ^[d]
3	2f	3 + 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. BiCl₃-catalyzed hydroarylation of styrenes with arenes.^[a]

Entry	Arenes	Styrenes	Products
1		2a	+ 93; ^[b] 95:5(3l/3l') ^[c]
2	1c	2d	+ 83; ^[d] 76; ^[b] 77:23(3m/3m') ^[c]
3		2a	65 ^[b]
4	1d	2d	82 ^[b]
5		2a	34 ^[b]
6	1e	2d	64 ^[b]
7		2d	+ 58; ^[b] 94:6(3s/3s') ^[c]
8		2a	89 ^[b]
9	1g	2d	94 ^[b]

[a] Reactions were carried out at 100 °C for 10 h with **2** (2.0 mmol), 10 equiv. of **1**, and BiCl₃ (0.2 mmol). [b] Isolated yield based on the amount of employed **2**. [c] Determined by GC analysis. [d] GC yield [%].

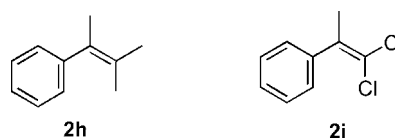
only the α -substituted styrenes underwent the dimerization selectively in *n*-octane to afford cyclic dimer **4** in good to high yields (Table 5). The use of other solvents such as THF, DMF, and 1,2-dichloroethane resulted in the formation of a mixture of dimers (non-cyclic dimers and cyclic dimers). The structures of **4** were confirmed by ¹H- and ¹³C 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. BiCl₃-catalyzed dimerization of α -substituted styrenes.^[a]

Entry	Styrenes	Dimer	Yield [%] ^[b]
1			73
2			56
3			65
4			92

[a] Reactions were carried out at 110 °C for 24 h with **2** (2.0 mmol) and BiCl₃ (0.1 mmol) in *n*-octane (2 mL). [b] Isolated yield.



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 BiCl₃. 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) BiCl₃ shows good catalytic activity in the hydroarylation of both electron-deficient and electron-rich styrenes; 2) BiCl₃ has a low toxicity, is readily available, has a low cost, and is easily handled.

Experimental Section

General Methods: ¹H- and ¹³C 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 (δ) 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 BiCl₃ (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 BiCl₃ (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 ¹H-, ¹³C NMR spectroscopy, GC–MS, and HRMS (for new compounds).

Characterization Data of Products **3** and **4**

4-(1-Phenylethyl)anisole (3a): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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'): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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'): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 7.35–6.85 (m, 9 H), 3.84 (s, 3 H), 1.74 (s, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 7.30–6.70 (m, 14 H), 3.76 (s, 3 H), 2.15 (s, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (600 MHz, CDCl₃): δ = 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. ¹³C NMR (125 MHz, CDCl₃): δ = 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 C₁₅H₁₅ClO 246.0811; found 246.0812.

1-(4-Chlorophenyl)-1-(2-methoxyphenyl)ethane (3f'): ¹H NMR (600 MHz, CDCl₃): δ = 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. ¹³C NMR (150 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₆H₁₇ClO 260.0968; found 260.0967.

1-(4-Chlorophenyl)-1-(2-ethoxyphenyl)ethane (3g'): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₅H₁₅ClO 246.0811; found 246.0814.

1-(2-Chlorophenyl)-1-(2-methoxyphenyl)ethane (3h'): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₆H₁₇ClO 260.0968; found 260.0957.

1-(2-Chlorophenyl)-1-(2-ethoxyphenyl)ethane (3i’): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₆H₁₈O 226.1358; found 226.1355.

1-(2-Methoxyphenyl)-1-(2-methylphenyl)ethane (3j’): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 157.0, 144.3, 138.2, 136.0, 130.4, 128.5 (2C), 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 C₁₇H₂₀O 240.1514; found 240.1509.

1-(2-Ethoxyphenyl)-1-(2-methylphenyl)ethane (3k’): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₇H₂₀O 240.1514; found 240.1511.

1-(4-Chlorophenyl)-1-(2-methoxy-4,6-dimethylphenyl)ethane (3m): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₇H₁₉ClO 274.1124; found 274.1129.

1-(4-Chlorophenyl)-1-(4-methoxy-2,6-dimethylphenyl)ethane (3m’): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₇H₁₉ClO 258.1175; found 258.1173.

1-(2,4-Dimethylphenyl)-1-phenylethane (3q): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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 C₁₆H₁₇Cl 244.1019; found 244.1020.

1-(4-Chlorophenyl)-1-(3,4-dimethylphenyl)ethane (3s): ¹H NMR (300 MHz, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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. ¹³C NMR (75 MHz, CDCl₃): δ = 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, CDCl₃): δ = 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) $[\text{M}]^+$, 261 (32), 245 (7), 207 (16), 165 (15), 139 (12), 125 (86), 91 (9).

4a: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.30\text{--}7.10$ (m, 9 H), 2.41, 2.19 (AB, $J_{\text{AB}} = 13.0$ 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) $[\text{M}]^+$, 221 (100), 178 (11), 165 (12), 143 (54), 115 (13), 91 (25).

4b: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.30\text{--}7.00$ (m, 19 H), 3.42, 3.12 (AB, $J_{\text{AB}} = 13.0$ 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) $[\text{M}]^+$, 345 (85), 267 (100), 252 (57), 205 (47), 191 (34), 165 (44), 91 (38).

4c: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.10\text{--}7.00$ (m, 6 H), 6.93 (s, 1 H), 2.40, 2.19 (AB, $J_{\text{AB}} = 13.0$ 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) $[\text{M}]^+$, 249 (100), 157 (50), 142 (19), 105 (18), 91 (10).

4d: ^1H NMR (300 MHz, CDCl_3): $\delta = 7.30\text{--}7.00$ (m, 7 H), 2.36, 2.19 (AB, $J_{\text{AB}} = 13.0$ 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) $[\text{M}]^+$, 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): ^1H -, ^{13}C NMR spectra for all products.

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